CATALYTIC APPLICATIONS OF SOLID ACID/BASE CATALYST FOR THE BENIGN SYNTHESIS OF FINE CHEMICALS

A THESIS

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BY

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UNDER THE GUIDANCE OF

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CERTIFICATE

       This is to certify that, the work incorporated in the thesis entitled **"CATALYTIC APPLICATIONS OF SOLID ACID/BASE CATALYST FOR THE BENIGN SYNTHESIS OF FINE CHEMICALS"** submitted by Ms. Lalita B. Kunde, for the degree of **Doctor of Philosophy**, was carried out by the candidate under my supervision, in the Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune-411008, India. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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Declaration by the candidate

I hereby declare that the thesis entitled **"Catalytic Applications of Solid Acid/Base Catalyst for the Benign Synthesis of Fine Chemicals''** submitted by me for the degree of Doctor of Philosophy, to the University of Pune, is the record of work carried out by me under the guidance of Dr. S. P. Gupte and has not formed the basis for the award of any degree, diploma, associateship, fellowship, titles in this or any other University or other institution of higher learning.

I further declare that the material obtained from other sources has been duly acknowledged in this thesis.

Lalita B. Kunde

September 2011   (Candidate)

Pune

Dedicated

to

My Parents

Acknowledgement

List of Contents

Chapter 2. Synthesis and Characterization of Immobilized Catalyst

Chapter 3. Organic transformations using immobilized/organic-inorganic hybrid catalyst

Section A: Immobilized Ionic Liquid: Efficient Catalyst for Cycloaddition of CO_2 to Epoxides under mild conditions

Section B: Catalytic synthesis of chalcone and flavanone using Zn-Al hydrotalcite adhere ionic liquid

Section C: Dibutyltin oxide catalyzed aminolysis of oxalate to carbamate, oxamat and derivatives of imidazolidine trione

Section D: Immobilized Ionic Liquid Catalyzed O-alkylation of Phenol by DMC

Abbreviations

A^*_{CO2}	Solubility of CO_2,(mol/cc)
P_{CO2}	CO_2 pressure, (atm)
Ro	Initial rate of CO_2 absorption, (mol/cc/s)
[BMim]Cl	Butyl methyl imidazolium chloride
BET	Brunauer-Emmett-Teller
$[C_2Mim]BF_4$	Propyl methyl imidazolium tetra fluro borate
CHTlc	Calcined Hydrotalcite
DMC	Dimethyl carbonate
G-L-S	Gas-Liquid-Solid
HTlc	Hydrotalcite
IL	Ionic liqiud
PO	Propylene Oxide
PC	Propylene Carbonate
scCO2	supercritical CO_2
SO	Styrene Oxide
SC	Styrene Carbonate
SS NMR	Solid State NMR
SEM	Scanning electron microscopy
TEM	Transmission Electron Microscopy
TBAB	Tetra butyl ammonium bromide
TBHP	*tert*-butyl hydroperoxide
TESPMimCl	Triethoxy silyl propyl methyl imidazolium chloride
TOF	Turn over frequency
XRD	X-ray diffraction

Abstract of the Thesis

During recent years, the entire arsenal of catalytic methodologies-homogeneous, heterogeneous and enzymatic catalysis have motivated towards use of cleaner methodologies for production of chemical compounds like fine and bulk chemicals. This conscious effort is a result of increasingly demanding legislation as well as public and economic pressure for environmental protection.[1] Fine chemicals are complex and multifunctional molecules which have invaded our daily life through various chemical substances such as pharmaceuticals, flavors, agro-chemicals, personal-care chemicals and essences etc.[2] The manufacture of these essential fine chemicals involve multistep synthesis performed in the liquid phase and utilize to a great extent stoichiometric traditional chemistry or homogeneous acid and base catalysts. At present catalysis-based chemical synthesis accounts for 95% of bulk chemicals and only 3–5% accounts for synthesis of fine chemicals. This low fraction contributes for approximately 20% of the profit in industrial segment.[3] This implies that even though bulk chemicals are usually produced in highly efficient processes with low amounts of by-products and waste, many of the intermediates still use synthesis routes that follow stoichiometric traditional chemistry accompanied by unavoidable side products and inorganic salts which pose threat to the environment. This crisis provided an important stimulus for the development of heterogeneous catalysts. The field of heterogeneous catalyst was first applied in bulk chemistry with particular interest to petrochemical industry. Later on its use was extended to synthetic organic chemistry for production of fine chemicals and pharmaceuticals.

Heterogeneous catalysts are preferred for fine chemical synthesis by virtue of its properties like easy separation from reactants and products by simple filtration and good recyclability. These properties make preparation of sophisticated fine chemicals less expensive and also help in circumventing the contamination of the products by trace amounts of metals. As the science of preparation of heterogeneous catalyst evolved through years, new synthesis methodologies such as grafting, tethering, anchoring etc.

opened up new avenues for organic-inorganic hybrid catalyst. These catalysts are laced with combined properties of homogeneous counterpart i.e. organic metal complexes/(chiral) organic catalysts combined along with the properties of inorganic support. Significant properties shown by these types of catalysts are increased thermal stability along with enhanced catalytic activity. The applications of this family of heterogeneous catalyst have already paved its way into new industrial processes which have been developed to replace traditional problematic synthetic methods.[4]

Indeed the solution for the challenges faced for fine chemical synthesis resides in the use of this new class of heterogeneous catalyst so as to replace conventional catalysts and reagents based route which are corrosive, toxic, and produce inorganic salts that causes environmental problems. Keeping in view the state of the art for current fine chemical synthesis this thesis was aimed at developing greener routes along with more efficient and more selective catalyst systems. Synthesis of a variety of fine chemicals like cyclic carbonates, chalcones, flavanones, aryl alkyl ethers, carbamates, oxamates and imidazolidine trione derivatives was attempted using organic-inorganic hybrid catalyst systems.

Cyclic carbonates find wide applications such as solvents, selective reagents, fuel additives and monomers for polymers, herbicides, disinfectants, preparation of cosmetics personal care products, and dyeing of textiles. Cyclic carbonates are conventionally manufactured using poisonous and hazardous routes using phosgene and glycol. Often epoxides based routesare used as starting material for the synthesis of cyclic carbonate. With the advent of CO_2 chemistry and ionic liquid (IL) the synthesis methods are becoming more green chemistry oriented. Similarly these days the synthesis of chalcones, flavanones, aryl alkyl ethers, carbamates, oxamates and imidazolidine trione derivatives which have wide range of applications in pharmaceuticals, agriculture and polymer industries is attempted through greener routes pertaining to green chemistry goals.

This thesis was planned taking into account above described green chemistry requirement in fine chemical synthesis. With this objective various organic inorganic hybrid catalysts with acid/base properties were synthesized for following industrially important reactions

- ✓ CO_2 cycloaddition to epoxides,
- ✓ *O*-alkylation of phenol,
- ✓ Claisen Schmidth condensation and
- ✓ Synthesis of carbamates, oxamates and heterocyclic compounds (imidazolidine trione derivatives).

This thesis is presented in three chapters, a brief summary of which is outlined below.

CHAPTER.1: GENERAL INTRODUCTION

Chapter 1 presents general introduction on catalysis, solid acid/base catalysts in the synthesis of fine chemicals, green chemistry, ionic liquids, activation and utilization of CO_2 as C_1 feedstock for synthesis of industrially important chemicals. This is followed by objectives and scope of the thesis and abstract of thesis. Important literature references are discussed to generate an overview on the following subject areas that forms the theme of this thesis. The topics discussed are

1. Synthesis and characterization of immobilized/organic-inorganic hybrid catalyst.

   Organic transformations using immobilized/organic-inorganic hybrid catalyst. The organic transformations of the interest were

   i)   Catalytic conversion of CO_2 to cyclic carbonate from epoxides using ionic liquid immobilized on silica as highly efficient catalyst.

   ii)   Catalytic synthesis of chalcone and flavanone via Claisen Schmidth condensation using Zn-Al hydrotalcite adhere ionic liquid.

   iii)   Aminolysis of oxalate to carbamate, oxamate and derivatives of imidazolidine trione catalyzed by Dibutyltin oxide (DBTO).

   iv)   *O*-methylation of phenols with dimethyl carbonate to aryl methyl ethers catalyzed by ionic liquid immobilized on silica.

CHAPTER.2: SYNTHESIS AND CHARACTERIZATION OF IMMOBILIZED CATALYST

This chapter presents a detailed literature survey on preparation of various heterogeneous catalysts and their industrial application. The evolution of heterogeneous catalyst to immobilized/organic-inorganic hybrid catalyst is described along with its various preparation methods. Since these catalysts are comprised of inorganic component which forms the support for heterogenization of organic part (ionic liquid), some supports were synthesized and used whereas some of them used were commercially available. Various methods of immobilization described in the literature were experimented like capillary impregnation, diffusional impregnation and grafting for the synthesis of immobilized IL catalyst. Inorganic supports used for immobilization of IL were selected based on their inherent acid/base properties. Supports like SiO_2, MCM-41, hydrotalcites, montmorillonite clays were examined for their synergistic effect on immobilized catalyst thus formed. These catalysts were thoroughly characterized by various characterization techniques such as XRD, IR, DRIFT, surface area and pore volume measurements, SEM, TEM, ^{29}Si, ^{27}Al and ^{13}C CP Mass NMR. All the physicochemical characterizations are interpreted meticulously for catalyst structure, activity and stability. Synthesized organic-inorganic hybrid catalysts were then employed for various organic transformation of industrial importance.

CHAPTER.3: ORGANIC TRANSFORMATIONS USING IMMOBILIZED/ORGANIC-INORGANIC HYBRID CATALYST

This chapter is divided in four sections based upon type of reaction investigated for making process green and sustainable.

SECTION A: IMMOBILIZED IONIC LIQUID: EFFICIENT CATALYST FOR CYCLOADDITION OF CO$_2$ TO EPOXIDES UNDER MILD CONDITIONS

This chapter deals with catalytic conversion of CO_2 to cyclic carbonate from epoxides using IL immobilized on silica as highly efficient catalyst. Chemical fixation of CO_2 is gaining importance due to its rising level in the atmosphere which is responsible for the green house effect and is great cause of concern.[5] Carbon dioxide has been used as a building block in the industrial synthesis of organics such as urea and salicylic acid. Such applications of CO_2 are in accordance with principles of sustainable chemistry for

chemical industry, as they are based on clean reactions that reduce carbon dioxide emission into the atmosphere. Among the many ways of CO_2 fixation to chemicals one of the underdeveloped areas is cycloaddition of CO_2 to epoxides to give cyclic carbonate. Styrene oxide is taken as model substrate to test the activity of immobilized catalyst. 1-(tri-ethoxy-silyl-propyl)-3-methyl imidazolium chloride immobilized on various support is used as catalyst for styrene carbonate synthesis from styrene oxide under mild pressure and temperature conditions. Reaction parameters like solvent, temperature, pressure, catalyst loading and recycle are investigated for synthesis of styrene carbonate. The activities of immobilized ionic liquids are compared with that of unsupported ionic liquids. It was observed that IL 1-(tri-ethoxy-silyl-propyl)-3-methyl imidazolium chloride immobilized on SiO_2 efficiently catalyzed the reaction with 99.5% conversion and 100% selectivity under mild conditions. Activity of MCM-41 as support for carboxylation of styrene oxide is encouraging (98.5% yield of styrene carbonate in 2h) as compared to SiO_2, hydrotalcite (68.83% yield of styrene carbonate in 6h) and montmorillonite (inactive). But stability and economy of MCM-41 is of concern. Whereas SiO_2 was chosen as preferred support for immobilization of modified IL (TESP-MImCl) owing to its green parameters like cheap and stable. Also the activity shown for this reaction is comparable to the catalyst immobilized on MCM support. This work demonstrates the effects of various methods for heterogenization of IL on SiO_2 for carboxylation of epoxides to cyclic carbonate. The catalyst prepared by impregnation or incipient wetness method, involves physical coating of IL on support and can be used in presence of aromatic solvents to avoid leaching of IL. The silica supported 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride catalyst system exhibits synergistic effect of silica gel support and grafted IL in enhancing carbonate yield. The CO_2 pressure effect shows that this catalyst system helps in absorption and activation of CO_2 and gives near comparable results to $scCO_2$ systems for carboxylation of epoxides. The n-hexane solvent facilitates separation of carbonate from heterogeneous catalyst by forming multi phase system which allows easy separation of styrene carbonate a high boiler avoiding costly distillation. Further this catalyst effectively catalyzed carboxylation of various epoxides. Finally a plausible reaction mechanism has been predicted which explains the activity

behavior observed for the grafted ionic liquid catalyst. Synthesized cyclic carbonates were characterized by IR, NMR and GC-MS analysis.

SECTION B: CATALYTIC SYNTHESIS OF CHALCONE AND FLAVANONE USING Zn-Al HYDROTALCITE ADHERE IONIC LIQUID

This chapter deals with catalytic synthesis of chalcone and flavanone via Claisen Schmidt condensation using Zn-Al hydrotalcite adhere ionic liquid. In the recent year's synthesis of chalcones and flavanones using heterogeneous base catalyst have attracted interest of many researchers.[67] The work presented in this chapter deals with synthesis of chalcones and flavanones using hydrotalcite like material. These solid base catalysts derived from hydrotalcite possess novel physical and catalytic properties that are tunable due to the wide variety of possible combinations of M^{2+}/M^{3+} ions.[8] The optimized hydrotalcite is then used as support for immobilization of modified IL (TESP-MImCl). The Claisen-Schmidt condensation of 2`-hydroxy acetophenone and benzaldehyde to chalcone and flavanone show that calcined Zn-Al (6) hydrotalcite is active for this synthesis. The activity of this catalyst can be further increased by about 1.5 times by coating ionic liquid triethoxysilane-3-methyl imidazolium chloride on calcined hydrotalcite.

The comparison of catalytic activities of these virgin hydrotalcites and IL impregnated hydrotalcites show that 35% loading of modified IL on calcined Zn/Al HT (x=6) gives 99.2% conversion of O-hydroxy acetophenone with 69% selectivity for flavanone. It was observed that as the % loading of IL decreases the selectivity for chalcone increases. Under optimized conditions among various catalysts screened, IL on NaX, NaY, SiO_2 and montmorillonite gave poor conversions (22-30%). Whereas IL on calcined Zn/Al HT (x=3) gave 53% conversion with ~50% selectivity for chalcone and flavanone. Another important aspect that is investigated here is changes in Al geometry due to interaction of IL with Al^{3+} ion using ^{27}Al CPMAS NMR and ^{13}C CPMAS NMR. It was observed that due to interaction of IL with Al^{3+} ion original active sites on the oxide catalysts are modified (reconstructed site) and are believed to be more active. Increase in IL loading increases the tetra and penta coordinated Al^{3+} species at the expense of octahedral aluminum (~50 % amount) present in calcined HTlc. At maximum loading of

35 % IL the amount of octahedral aluminum drops to almost 30 % while tetra and penta coordinate aluminum increase up to ~70 %. Thus from this study it was concluded that this change in geometry of aluminum and hence structure of Zn-Al (6) CHTlc might be responsible for enhanced activity due to loading of IL. An additional feature of this catalyst is the adaptation of selectivity towards chalcone and flavanone synthesis depending upon loading of IL on hydrotalcite.

SECTION C: DIBUTYLTIN OXIDE CATALYZED AMINOLYSIS OF OXALATE TO CARBAMATE, OXAMATE AND DERIVATIVES OF IMIDAZOLIDINE TRIONE

This chapter deals with aminolysis of oxalate to carbamate, oxamate and derivatives of imidazolidine trione catalyzed by Dibutyltin oxide(DBTO). This chapter focuses on the development of replacing reagent based approach for the synthesis of carbamate, oxamate and derivatives of imidazolidine trione from ureas and oxalates in presence of dibutyltin oxide (DBTO) catalyst. A cross-coupling reaction between urea and oxalate to carbamate and oxamate in presence of a catalyst further undergo in-situ condensation of products to produce imidazolidine trione derivatives via a low energy path compared to direct condensation between urea and oxalate. An important observation made was that, DBTO produce selectively 1,3 imidazolidine trione when DEO is used as a solvent (90% yield and selectivity) with small amount of carbamate and oxamate ~9% remaining unconverted at this stage). While when polar solvents are used, 1,3 imidazolidine trione is almost absent and selectively carbamate and oxamate are obtained (~ 75% yield for DMF and ~65% yield for NMP). In presence of solid base catalysts such as MgO, PbO and PbZrO3 (leadzirconate) and silica gel, high to moderate conversions of urea was realized (60-80%) with good selectivity corresponding to carbamate and oxamate were obtained (24-77% yield), with concurrent formation of parabanic acid (~ 5% yield).

It has been shown that by controlling deactivation of acid-base sites of DBTO, the selectivity and yield of both carbamate and oxamate or imidazolidine trione derivatives can be manipulated, e.g. by blocking the acidic sites of tin catalyst in a basic solvent media such as DMF and NMP higher selectivity of carbamate and oxamate could be achieved, while in absence of basic media higher selectivity of imidazolidine trione derivatives could be obtained. Various catalysts were screened and role of catalysis in

product selectivity and catalyst activity has been discussed. It has been shown that product selectivity pattern depends on acidobasic properties of tin catalyst. It was observed that simple urea does not yield imidazolidine trione under experimental condition employed and in this case carbamate and oxamate are produced along with diethylimino dicarbonate as a side product. Derivative of imidazolidine trione is produced when methyl and phenyl urea are used as substrates, and other substituted ureas give rise to mainly carbamate and oxamate.

The role of DBTO as catalyst seems to activate and stabilize the $^{\ominus}$OR moiety of activated oxalate, thus making it prone to nucleophilic attack of urea and at the same time facilitates alkoxide attack to carbonyl carbon of urea. The possibility of producing important organic intermediates such as dialkyl carbonate, oxomalonate and imino dicarbonate is an interesting outcome of the work. Synthesized oxamates, carbamtes and imidazolidine trione derivatives were isolated by flash chromatography and were characterized by IR, NMR and GC-MS analysis.

SECTION D: IMMOBILIZED IONIC LIQUID CATALYZED *O*-ALKYLATION OF PHENOL BY DMC

In this chapter benign synthesis of aryl methyl ethers by *O*-methylation of phenol with dimethyl carbonate is studied using immobilized catalyst. Alkylation of phenol is carried out employing stoichiometric reagents like DMS and alkyl halides which are toxic.[9] Aryl methyl ethers obtained by Friedel craft alkylation of phenol are valuable intermediates and find application in preparation of dyes, pesticides, agrochemicals, fragrances, as a raw material for manufacture of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, surface active agents, rubber chemicals, antioxidants, fungicides, petroleum additives, UV absorbers and heat stabilizers for polymeric materials. In this chapter selective *O*-methylation of phenol is attempted with dimethyl carbonate using IL (TESP-MImCl) heterogenized over silica. Under optimized reaction conditions immobilized catalyst i.e. ionic liquid immobilized on silica was found to give anisole with 100% selectivity and 99.9% yield and no *C*-methylated products were obtained. This catalyst efficiently catalyzed O-methylation of various substituted phenols to their corresponding aryl methyl ethers in high selectivities and yields. Various

alkylating agents were also screened for alkylation using ionic liquid immobilized on silica as catalyst. Among the various alkylating agents like diethyl carbonate, dibutyl carbonate, ethylene carbonate and methanol this catalyst was found effective only for dimethyl carbonate. This catalyst system shows remarkable environmentally benign features like: economic use of costly IL by heterogenization (0.739mmoles IL is efficiently used to catalyze *O*-alkylation of phenol using DMC giving 100% yield of anisole), use of cheap and non toxic DMC, selective *O*-methylation of phenol and various phenol derivatives, efficient recycling ability without decrease in catalytic activity for five recycles, easy catalyst-product separation just by filtration and byproduct methanol can be recycled for DMC synthesis. Plausible mechanism is proposed for this Friedel Craft alkylation of phenol with immobilized IL catalyst showing simultaneous activation of DMC and phenol. This suggests that the synergistic actions of immobilized catalyst is playing important role in activation of substrates. Phenol attacks DMC by BAL2 mechanism.

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Chapter 1

General Introduction

1.1. INTRODUCTION

In the 20th century, chemistry has changed our lives. It has shaped our modern technological society by supplying us with energy, medicines, crop protection, foodstuffs, and new materials worldwide. The field of catalysis existed way back at the dawn of civilization when mankind began to produce alcohol by fermentation. The science and the art of catalysis has become an important factor in almost all facets of human life and civilization itself. Catalysis plays a critical role in the development of efficient production methods for a wide range of materials, from fuels to polymers, and in the development of more effective and safer pharmaceuticals. Catalysis is perhaps one of the most important technologies available today to chemists and chemical industries due to its intrinsic features of energy and time efficient alternative pathways. The chemical industry of the 20th century could not have developed to its present status on the basis of non-catalytic, stoichiometric reactions alone. The importance of catalysis in the chemical industry is shown by the fact that 75 % of all chemicals are produced with the aid of catalysts; in newly developed processes, the figure is over 90 %. Numerous organic intermediate products, required for the production of plastics, synthetic fibers, pharmaceuticals, dyes, crop-protection agents, resins, and pigments, can only be produced by catalytic processes. For more than 100 years, catalysts have been successfully used in the chemical industry in synthesis of sulfuric acid, conversion of ammonia to nitric acid, and catalytic hydrogenation. Later developments include new highly selective multicomponent oxide and metallic catalysts, zeolites, and the introduction of homogeneous transition metal complexes in the chemical industry. This development of field of catalysis was supplemented by new high-performance techniques for probing catalysts and elucidating the mechanisms of heterogeneous and homogenous catalysis.

In 1836 famous Swedish chemist J. J. Brezelius first introduced the concept of catalysis. In the Edinburgh New Philosophical Journal, he stated "I hence will name it the catalytic force of the substances, and I will name decomposition by this force catalysis. The catalytic force is reflected in the capacity that some substances have, by their mere presence and not by their own reactivity, to awaken activities that are

slumbering in molecules at a given temperature".[1] Later on W. Ostwald defined catalysis which helped in understanding of the phenomenon of the catalysis. He defined catalyst as a species which increases the rate of a chemical reaction through the formation of intermediate compounds and which is restored at the end of the reaction. In 1909, Ostwald was awarded the Nobel Prize in Chemistry for his work on catalysis, chemical equilibrium and reaction velocities.[2] The industrial production of bulk chemicals was at an all time high during nineteenth century. The beginning of the 1970's was strongly characterized by the petrochemical industry and various catalytic processes for the manufacturing of synthetic polymers. The most significant new process innovation of this period was the FCC (Fluid Catalytic Cracking) process. It was the early 70's, which saw the rise of new discipline of environmental catalysis. At this point of rapid industrial development, world started to become aware of the negative impacts that chemical industry had on the environment. Thus environmental catalysis was considered as first step towards the modern chemical industry where catalysis is applied to almost every process, including the production of fine chemicals for pharmaceutical applications to the production of bulk chemicals and exhaust gas catalysts. This was followed by continuous invention of new catalytic processes. Nowadays frequent use of enzymatic bio-catalysis could possibly be the start of a new catalytic era.

Catalysis is the occurrence by which certain chemicals (catalysts) can promote a chemical reaction without undergoing any permanent chemical transformation themselves. Thus, theoretically, recovery of the catalyst is possible after the reaction is completed, enabling it to be recycled. Without the proper catalyst, many reactions proceed infinitely slowly or not at all. Moreover, because of its effects on the kinetics of the reaction, which can lead to different chemical entities, the chemical nature of the catalyst can have decisive impact on the selection of reaction manifolds. Catalysts accelerate reactions by orders of magnitude, enabling them to be carried out under the most favorable thermodynamic regime, and at much lower temperatures and pressures. In this way efficient catalysts, in combination with optimized reactor and total plant design, are the key factor in reducing both the investment and operation costs of a chemical processes.

Table. 1.1 summarises the relation between development of catalyst and history of industrial processes.

Table.1.1: The relation between development of catalyst and history of industrial processes.		
Catalytic reaction	**Catalyst**	**Discoverer or company/year**
Sulfuric acid (lead-chamber process)	NO_x	Désormes, Clement, 1806
Chlorine production by HCl oxidation	$CuSO_4$	Deacon, 1867
Sulfuric acid (contact process)	Pt, V_2O_5	Winkler, 1875; Knietsch, 1888 (BASF)
Nitric acid by NH_3 oxidation	Pt/Rh nets	Ostwald, 1906
Fat hardening	Ni	Normann, 1907
Ammonia synthesis from N_2, H_2	Fe	Mittasch, Haber, Bosch, 1908 Production, 1913 (BASF)
Hydrogenation of coal to hydrocarbons	Fe, Mo, Sn	Bergius, 1913; Pier, 1927
Oxidation of benzene, naphthalene to MSA or PSA	V_2O_5	Weiss, Downs, 1920
Methanol synthesis from CO/H_2	ZnO/Cr_2O_3	Mittasch, 1923
Hydrocarbons from CO/H_2 (motor fuels)	Fe, Co, Ni	Fischer, Tropsch, 1925
Oxidation of ethylene to ethylene oxide	Ag	Lefort, 1930
Alkylation of olefins with isobutene to gasoline	$AlCl_3$	Ipatieff, Pines, 1932
Cracking of hydrocarbons	Al_2O_3/SiO_2	Houdry, 1937
Hydroformylation of ethylene to propanal	Co	Roelen, 1938 (Ruhrchemie)
Cracking in a fluidized bed	aluminosilicates	Lewis, Gilliland, 1939 (Standard Oil)
Ethylene polymerization, low-pressure	Pd/Cu chlorides	Ziegler, Natta, 1954
Oxidation of ethylene to acetaldehyde	Rh-, Ru complexes	Hafner, Smidt (Wacker)

Catalytic reaction	Catalyst	Discoverer or company/year
Hydrogenation, isomerization, hydroformylation	Rh/chiral phosphine	Wilkinson, 1964
Asymmetric hydrogenation	Pt, Rh/monolith	Knowles, 1974; l-Dopa (Monsanto)
Three-way catalyst	Zeolites	General Motors, Ford, 1974
Methanol conversion to hydrocarbons	Ni/chelate phosphine	Mobil Chemical Co., 1975
α−olefines from ethylene	Ti/ROOH/tartrate	Shell (SHOP process) 1977
Sharpless oxidation, epoxidation	titanium zeolite(TS-1)	May & Baker, Upjohn, ARCO, 1981
Selective oxidations with H_2O_2	Rh/phosphine/ aqueous	Enichem, 1983
Hydroformylation	zirconocene/MAO	Rhône-Poulenc/Ruhrchemie,1984
Polymerization of olefines	V, W, Ti oxides/ monolith	Sinn, Kaminsky, 1985
Selective catalytic reduction SCR (power plants)	Ir/I–/Ru	~1986
Acetic acid		"Cativa"- process, BP Chemicals,1996

Irrespective of the constitution of the catalyst, the suitability of a catalyst for an industrial process depends mainly on three properties viz; *activity, selectivity* and *stability* (deactivation behavior)

Activity is a measure of how fast one or more reactions proceed in the presence of the catalyst. Activity is defined in terms of kinetics by rate of reaction 'r'.

Another measure of catalyst activity is the turnover number TON, which originates from the field of enzymatic catalysis. Since, in the case of heterogeneous catalysts the activity depends on the size of the catalyst, TON could not be used directly due to its non-uniform structure. Whereas in case of homogeneous catalysis the TON can be directly determined owing to homogeneity of it with solution resulting in definite number of catalyst molecules present in solution. Therefore for heterogeneous

catalysis turn over frequency TOF, can be safely used to define its activity. Most of heterogeneous catalysts contain so-called 'active sites' in their structures. Interactions at the active site permit the reacting molecules to perform a certain chemical reaction at much lower activation energy than would be possible in the absence of such sites. The total number of active sites and their accessibility control the turnover frequency of the process.

Turn over frequency is a measure of the specific activity of a catalytic center for a special reaction under defined reaction conditions by the number of molecular reactions or catalytic cycles occurring at the center per unit time. For industrial applications the TON is in the range 10^6–10^7.

The selectivity gives information about the course of the reaction.

Selectivity is the fraction of the starting material that is converted to the desired product. It is expressed by the ratio of the amount of desired product to the reacted quantity of a reaction partner.

Catalyst stability is governed by various factors like decomposition, cocking and poisoning. In industrial reactors, lifetime of a catalyst is determined by chemical, thermal and mechanical stability and is of crucial importance for the economics of a process. Today the efficient use of raw materials and energy is of major importance, and it is preferable to optimize existing processes than to develop new ones.

Catalysts can be roughly divided into two main categories depending on their physical nature: *heterogeneous and homogeneous*. There are also intermediate forms such as homogeneous catalysts attached to solids (supported catalysts), also known as *immobilized catalysts*.

In *homogeneous catalysis*, both the catalyst and the reactants are in the same phase, i.e. all molecules are in gas phase, or, more commonly, in the liquid phase. Due to their high degree of dispersion, homogeneous catalysts exhibit a high activity per unit mass of metal than heterogeneous catalysts. Homogeneously catalyzed reactions are controlled mainly by kinetics and less by material transport, because diffusion of the reactants to the catalyst can occur more readily. .

In *heterogeneous catalysis*, solids catalyze reactions of molecules in gas or solution. In case of nonporous solids since they are impenetrable, catalytic reactions occur at

the surface. By far the most important catalysts are the heterogeneous catalysts. Approximately 80% of all catalytic processes require heterogeneous catalysts, 15% homogeneous catalysts and 5% biocatalysts.[3] The total commercial value of all catalysts worldwide is over 12 billion EUR. Another major topic for the 21st century, the production, storage, and conversion of energy, will also be promoted by catalysts.[4] Table 1.2 sums up the strong and weak points of homogeneous and heterogeneous catalyst.

Table.1.2: The strong and weak points of homogeneous and heterogeneous catalyst.

	Homogeneous	Heterogeneous
Strong points	Structure/stoichiometry defined. Modification possibilities high. Active centers all metal atoms. Selectivity high. Diffusion problems are practically absent. Reaction conditions are mild (323–473K).	Wide applicability. Seperation, recovery and recycling easy. Easy handling due to good stability. Cost of catalyst low and several catalysts are commercially available.
Weak points	Seperation, sensitivity (less stable), high cost of catalyst thus losses during separation not economic.	Structure/stoichiometry undefined. Modification possibilities low. Active centers only surface atoms. Selectivity lower. Diffusion problems present (mass-transfer-controlled reaction). Reaction conditions severe (often >523K). Preparation needs special know how.

Currently there are more than 15 international companies that are engaged in production of about 100 fundamental types of solid catalysts.

- Engelhard Corp. (inclusive Harshaw Catalyst)

- Synetix (ICI Catalysts and ICI Catalco)

- Davison Chemicals and Grace

- SÜD-CHEMIE Catalyst Group (inclusive UCI, Houdry, Prototec/USA, NGC,CCIFE/Japan, UCIL/India, AFCAT and SYNCAT/South Africa)

- UOP and Katalytiks

- Shell and Criterion Catalysts inclusive Zeolyst International

- Johnson Matthey

- Calsicat

- Degussa

- BASF

- Haldor Topsoe

- Nippon Shokubai

- Nikki Chemicals

For the next few decades heterogeneous catalyst will continue to demonstrate tremendous development potential due to lack of scientific knowledge of individual steps and mechanisms therein and also due to increasing necessity to produce chemicals in an economic and environmentally friendly manner.

On the other hand the third type of catalyst; *immobilized catalyst* is gaining significance owing to its higher potential to develop cleaner industrial technologies. Economic considerations and green chemistry approach lead to designing of immobilized catalyst using range of novel materials like silica and mesoporous solids like MCM, SBA 15, and clays functionalized at their surfaces so as to replace homogeneous (soluble) catalyst by heterogeneous (solid) catalyst with useful catalytic properties. These organic functionalized mesoporous materials can be used as environmentally friendly replacements for traditional acids, bases, metal compounds and other useful but environmentally unacceptable reagents and catalysts.

These catalytic materials can be prepared by heterogenization or immobilization of soluble active ingredients on the surface of appropriate solids. These systems combine both the properties of the parent homogeneous catalyst (wide scope of reaction, homogeneously distributed active sites) and the advantage of the heterogeneous systems (easy handling and efficient recovery). The fine chemical industry, in particular, can benefit from processes of high atom efficiency performed with these organic functionalized heterogeneous catalysts of high activity and selectivity in the present environmental conscious time.

1.2. Fine chemicals

Chemicals are broadly classified in three main categories as bulk (commodity), fine, and specialty (performance) chemicals. Bulk chemicals include petrochemicals, basic chemicals, organic chemicals (large-volume), monomers, commodity fibers and plastics, while advanced intermediates, building blocks, bulk drugs and bulk pesticides, active ingredients, bulk vitamins and flavor and fragrance chemicals are listed under fine chemicals. Performance chemicals comprise adhesives, diagnostics, disinfectants, electrochemicals, food additives, mining chemicals, pesticides, pharmaceuticals, photographic chemicals, specialty polymers and water treatment chemicals.

There are no universally accepted definitions of bulk, fine, and specialty chemicals, nor are these classifications based on any intrinsic properties. A useful working definition of a fine chemical is one with a price of more than 10 US dollars/kg and a volume of less than 10000 tons per annum on a worldwide basis. The type of technology used to manufacture these products is dictated more by volume than by product application. From a chemical viewpoint fine chemicals are generally complex, multifunctional molecules and, consequently, are often of low volatility and limited thermal stability. This means that processes are generally performed in the liquid phase. Fine chemicals manufacture often involves multistep syntheses and is generally performed in multipurpose equipment. This contrasts with the manufacture of bulk chemicals which usually involves continuous processing in dedicated plants.

Hence, the emphasis in fine chemicals manufacture is on the development of processes that have broad scope and can be implemented in standard multipurpose equipment.

Fine and speciality chemicals have shorter life cycles in comparison to bulk chemicals, therefore product innovation requires enormous resources those are highly knowledge based. These chemicals need to be manufactured to high and well-defined standards of purity compatible to the desired performance as opposed to bulk chemicals that are made in large amounts to technical levels of purity.

The growth of the fine chemicals business is mainly advanced by the introduction of new pharmaceuticals, agrochemicals, engineering plastics and other specialties

requiring high value organic intermediates. This growth impelled fine chemical industry to utilize catalytic processes thus cutting down the expenditure significantly, while keeping pace with the environmental regulations laid out so as to surmount 15–20 kg waste generated per kg of product in multistep process causing pollution. Majority of the chemical processes in fine chemical industry are known to be catalyzed by solid acids/bases.

1.2.1. Solid acid/base catalysts in fine chemical synthesis

Processes catalyzed by acids and bases play a key role from economical and ecological point of view in chemical and petrochemical industry as well as refinery technology in the oil refining and in the manufacture of a wide variety of specialty chemicals such as pharmaceuticals, agrochemicals, flavors and fragrances. Few examples are hydrocracking, alkylation, catalytic cracking, isomerization, oligomerization, hydration/dehydration, esterification and hydrolysis and a variety of condensation reactions, to name but a few.[5] In most of these processes, traditional Brønsted acids (H_2SO_4, HF, HCl, *p*-toluenesulfonic acid) or Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3) in liquid-phase homogeneous systems or on inorganic supports in vapor phase systems are employed. Similarly, typical bases include NaOH, KOH, NaOMe and KOBut. Oil refining and petrochemical industries, use only catalytic amounts of these acids or bases, but not always, and the absolute quantities of waste generated are considerable owing to the enormous production volumes involved. Their subsequent neutralization leads to the generation of inorganic salts which ultimately end up in aqueous waste streams. Whereas in fine and specialty chemical industries acids and bases are often used in stoichiometric quantities despite the fact that production volumes are much smaller, for e.g. Friedel-Crafts acylations, aldol and related condensations.[6] Rising environmental concerns and stringent regulations have led to the widespread replacement of traditional Brønsted and Lewis acids with recyclable solid acids and bases.[7,7,8]

The use of solid acids and bases as catalysts provides additional benefits:

- Separation and recycling is facilitated, resulting in a simpler process, which translates in lower production costs.

- Solid acids are safer and easier to handle than their liquid counterparts, e.g.H_2SO_4, HF, which are highly corrosive and require expensive construction materials.

- Contamination of the product by trace amounts of (neutralized) catalyst is generally avoided when the latter is a solid.

1.2.2. Solid acid catalysis

Solid acids have been the subject of the most extensive and detailed studies of all heterogeneous catalysts

Definition[9]: Solid acid may be understood to be a solid on which the color of a basic indicator changes or a solid on which a base is chemically adsorbed or a solid acid shows a tendency to donate a proton or to accept an electron pair.

The number of these sites determines the total surface acidity while their structure (coordination, partial charge) is responsible for the acid strength.

A wide variety of solid acids include mixed oxides such as silica–alumina and sulfated zirconia, acidic clays, zeolites, supported heteropoly acids, organic ion exchange resins and hybrid organic–inorganic materials such as mesoporous oxides containing pendant organic sulfonic acid moieties and Nafion.

Some of the processes employing solid acids are, catalytic Cracking (X and Y zeolites), paraffin Isomerization (chlorinated Pt-Ag), reforming (silica-alumina, noble metal support), alcohol from olefin formation (SiO_2-H_3PO_4), alkylation (SiO_2-H_3PO_4).

1.2.3. Solid base catalysis

In comparison to catalysis by solid acids, the applications of recyclable solid base catalysts are far fewer.[6] This is probably because acid-catalyzed reactions are much more common in the production of commodity chemicals.

The main features of the reactions catalyzed by solid bases in contrast to solid acids are high activity and high selectivity; suppress undesired reactions, when used as supports, or as additives and high possibility of transforming the molecules resulting in new products.

Definition[10]: Solid base is defined as a solid on which the color of an acidic indicator changes or a solid on which an acid is chemically adsorbed or a solid base shows a tendency to accept a proton or to donate an electron pair.

Examples include anionic clays,[10] alkali or alkaline earth metal occluded large pore zeolites and mesoporous silicas grafted with pendant organic bases[11] are effective catalysts for isomerization, Aldol, Knoevengel, and related condensations those are widely used in fine chemical synthesis.

More than three hundreds of solid acids and bases have been developed during the last 40 years. Their surface properties and the structures have been clarified by newly developed measurement methods using modern instruments and sophisticated techniques. The characterized solid acids/bases have been applied as catalysts for various reactions, and role of their acid-base properties in catalytic activities and selectivities are being studied extensively. Now, solid acid-base catalysis is one of the economically and ecologically important fields in catalysis. They have many advantages over liquid Bronsted- and Lewis-acid and base catalysts. They are non-corrosive and environmentally benign, presenting fewer disposal problems. Their repeated use and recovery from liquid products become much easier. Therefore, the replacement of the homogeneous catalyst with heterogeneous catalyst is becoming even more important in chemical and life science. Large number of industrial processes use solid acid/base catalysts such as zeolites (40 % of all collected processes), complex oxides, ion-exchange resins, phosphates, clay immobilized enzymes, sulfates plus carbonates and sulfonated polysiloxane (see table 1.3).
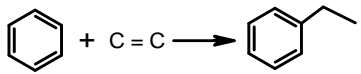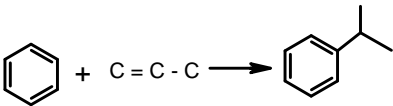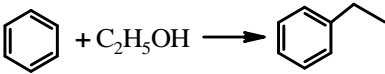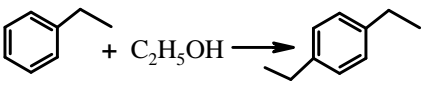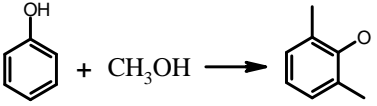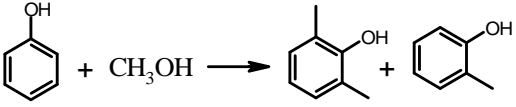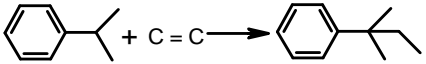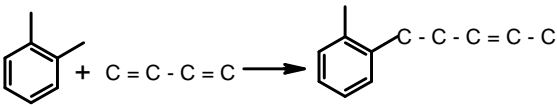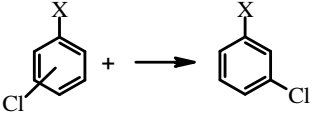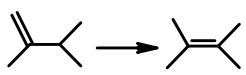
Table.1.3. **Types of catalysts used in Industrial processes[12]**		
Sr.No.	**Catalyst**	**No. of processes**
1	Zeolites	74
2	Oxides, complex oxides	54
3	Ion-exchange resins	16
4	Solid acids (not specified)	7
5	Phosphates	16
6	Immobilized enzymes	3
7	Sulfate, carbonate	3
8	Clays	4
9	Sulfonated polysiloxanes	3

Based on above catalysts, industrial processes namely alkylation, isomerization, dehydration and condensation, amination, cracking and etherification, and the smaller

ones for aromatization, hydration, hydrocracking, MTG/MTO, oligomerization, polymerization and esterification are carried out (see table 1.4a and 1.4b).

Table.1.4a. Industrial processes using solid acid-base catalysts.[13]		
Sr.No.	**Type of reaction**	**No. of processes**
1	Dehydration and condensation	18
2	Isomerization	15
3	Alkylation	13
4	Etherification	10
5	Amination	9
6	Cracking	8
7	Aromatization	7
8	Hydration	7
9	Oligomerization & polymerization	6
10	MTG/MTO-processes	5
11	Hydrocracking	4
12	Hydrogenation	4
13	Esterification	3
14	Disproportionation	2
16	MTBE-iC_4	1
17	Other	15
	Total	127

Table.1.4b. Industrial processes using Solid acid-base catalyst[13]

Sr.No	Process	Catalyst	Company
	Alkylation reaction		
1		H-ZSM-5	Mobil-Badger
2		High silica zeolite β-zeolite	Mobil-Badger /Raytheon Enichem
3		Pentasil zeolite Encilite 2	Hinduston Polymers
4		Pore size regulated ZSM-5	Paschim/IPCL
5		MgO	General Electric BASF AG
6		Fe-V-O/SiO$_2$	Asahi Chem.
7		K/KOH/Al$_2$O$_3$	Sumitomo Chemical
8		Na/K$_2$CO$_3$ basic catalyst	AMOCO Chemical, Teijin
	isomerization reaction		
9	Xylene isomerization ⟶ *p*-xylene	H-ZSM-5	Mobil Oil
10		High silica zeolite	Toray
11		H. ion-exchange resin	Exxon
12		Na/NaOH/g-Al2O3	Sumitomo Chemical
13	n-C$_4$ ⟶ *i*-C$_4$	Fe/Mn/sulfated ZrO2	Sun Zeolite BP-Chemicals,

14

		Zeolite	Huntsman
		Zeolite	Shell

Table.1.4b. Continued
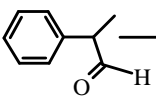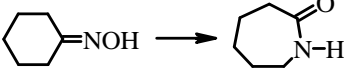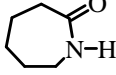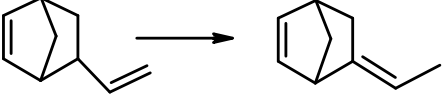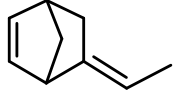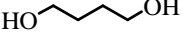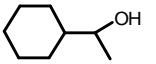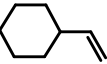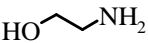
Sr.No	Process	Catalyst	Company
14	$n\text{-}C'_4 \longrightarrow i\text{-}C'_4$	SiO_2 modified Al_2O_3 Ferrierite B_2O_3/Al_2O_3	IFP Shell SNAM
15	$CH_2 = C = CH_2 \longrightarrow CH_3 - C \equiv CH$	K_2O/Al_2O_3	Shell
16	→ allyl alcohol	Li_3PO_4	ARCO
17	→ $Ph\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$	Pentasil zeolite	BASF AG
18		SAPO 11 High silicious Pentasil zeolite Ta-alkoxide/SiO_2	UCC Sumitomo Chemical Mitsubishi chem..
19		$Na/NaOH/Al_2O_3$	Sumitomo Chemical
Dehydration and Condensation process			
20	$EtOH \xrightarrow{-\,H_2O} C_2H_4$	Al_2O_3	Petrobrass
21	$t\text{-BuOH} \xrightarrow{-\,H_2O} i\text{-}C'_4$	Sulfonic acid resin	UOP
22		Ion exchange resin	Davy-Mckee
23		$ZrO_2\text{-}NaOH$	Sumitomo
24		$Nb_2O_5.nH_2O$	Sumitomo
25		$ZrO_2\text{-}KOH$	Koei Chem.
26		$Cs\text{-}Ba\text{-}P\text{-}O/SiO_2$	Nippon Shokubai

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Table.1.4b. Continued
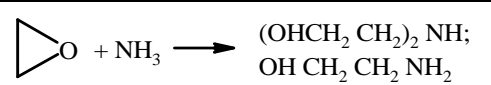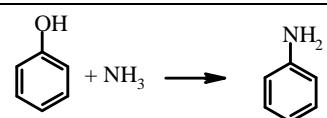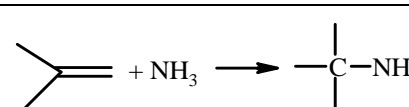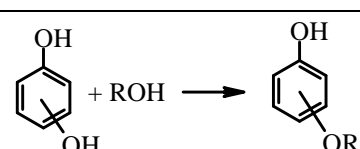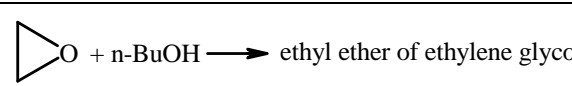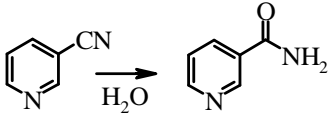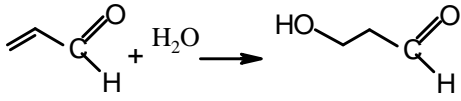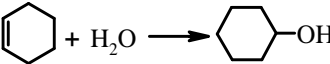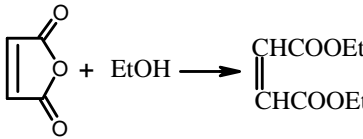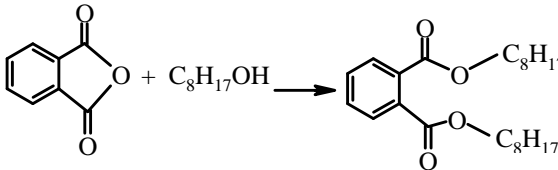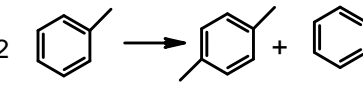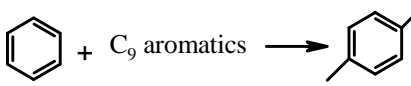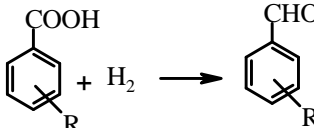
Sr. No	Process	Catalyst	Company
	Amination process		
27	$2MeOH + NH_3 \longrightarrow Me_2NH , MeNH_2$	RHO-ZK5 zeolite	Du pont
28	$O + NH_3 \longrightarrow$ $(OHCH_2 CH_2)_2 NH;$ $OH CH_2 CH_2 NH_2$	Al-Si zeolite	Berol/Nobel
29	$+ NH_3 \longrightarrow$	Mgo, B_2O_3, Al_2O_3 or TiO_2/SiO_2 or Al_2O_3	USS
30	$+ NH_3 \longrightarrow$ $-C-NH_2$	Pentasil zeolite	BASF AG
	Cracking process		
31	FCC-processes	Novel Y/ SiO_2-Al_2O_3	Cosmo
32	Heavy oil	Mgo-Al_2O_3 -zeolite	Nippon oil
33	Deep cracking of vacuum gas oil	Pentasil zeolite	China petro
34	Selective cracking of straight chain paraffins and olefins to C_3' and c_4'	H-ZSM-5	Mobil
	Etherification processes		
35	i-$C'_{4;} + MeOH \longrightarrow$ MTBE	Ion exchange resin	IFP, ACRO
36	i-$C'_{4;} + EtOH \longrightarrow$ ETBE	Ion exchange resin	SNAM
37	$Olefinss + MeOH \longrightarrow$ MTBE / TAME	Ion exchange resin	Erdoelchemi
38	$+ ROH \longrightarrow$	Al-B-P-O	Ube
39	$O + n$-$BuOH \longrightarrow$ ethyl ether of ethylene glycol	Pillared clay or smectite	BP
	Aromatization process		
40	C_3' C_4' to alkyl aromatics paraffins	ZSM-5	Mobil
41	LPG (mainly C_3, C_4) to BTX	Zeolite + promoter	UOP
42	LPG to aromatics	Metallosilicate	Mitsubishi oil
	Hydrocracking process		
43	Lub dewaxing; Wax+ H_2 tolower mol.wt. hydrocarbon	ZSM-5	Mobil
44	Hydrocracking of gas oils; Wax+ H_2 to gasoline	ZSM-5	BASF

Table1.4b. *Continued*

Sr.No	Process	Catalyst	Company
	Hydration process		
45	$C=C + H_2O \longrightarrow EtOH$	Solid phosphoric acid	Shell, BP
46		MgO MnO$_2$	Distillers Reynolds Tobaco
47		Acid base catalyst on TiO$_2$/H$_3$PO$_4$	Degussa
48		Highly silicious H-ZSM-5	Ashi Chem.
	Esterification process		
49		Ion exchange resin	Davy-McKee
50		Mercapto functionalized sulfonated polysiloxane	Degussa AG
	Oligomerization & polymerization processes		
51	i-C$_4$ + butane to codimer	High SiO$_2$ mordenie	Tonen
52	C$_3$ to polypropylene	TiO$_2$ – MgO	China Petro
53	C$_4$ to linear octanes	H$_3$PO$_4$ / SiO$_2$	UOP
	Disproportionation process		
54		Zeolite ZSM-5	UOP Mobil
55		Zeolite	UOP
	Hydrogenation process		
56	CO + H$_2$ to gasoline	Zeolite	BP
57		ZrO$_3$-Cr$_2$O$_3$ Zeolite	Mitsubishi chem.. Crossfield

1.3. Green Chemistry

Over the past century industries utilizing chemistry and chemical engineering have been major contributors to worldwide economic development yet the chemical industry is often taken to task for many serious environmental problems. This has resulted in bad public image of modern chemistry. There is an urgent need to raise public awareness towards the chemical community's positive and invaluable contributions to the continuous improvement of the quality of everyday life. It was in the early seventies when world started to become aware of environmental pollution caused by chemical industries. This period saw the rise of environmental catalysis. In the early 90's the concept of environmental catalysis was conceived as Green Chemistry to overcome the issue of pollution. Since its inception Green Chemistry has grown significantly.

Worldwide demand for environmentally friendly chemical processes and products requires the development of novel and cost-effective approaches to pollution prevention. One of the most attractive concepts for pollution prevention is green chemistry since its main focus is on the fundamentals of chemical research.

Definition[13]: the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and applications of chemical products.

Industries have realized, environmentally friendly products and processes are economical in the long term. In this aspect Green Chemistry plays a vital role by advancing in key research areas, such as catalysis, design of safer chemicals and environmentally benign solvents, and development of renewable feedstocks. Advances in green chemistry address both obvious hazards and those associated with such global issues as climate change, energy production, availability of a safe and adequate water supply, food production, and the presence of toxic substances in the environment.

The design of environmentally benign products and processes may be guided by the 12 Principles of Green Chemistry.[14]

1. It is better to prevent waste than to treat or clean up waste after it is formed.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Energy requirements should be recognized for their environmental and economic impacts and should be conducted at ambient temperature and pressure.

7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.

8. Unnecessary derivatization (blocking group, protection/deprotection, and temporary modification of physical/chemical process) should be avoided whenever possible.

9. Catalytic regents (as selective as possible) are superior to stoichiometric reagents.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11. Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Substances and form of substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Tang et al have produced a simpler statement of the principles of green chemistry that is understandable to wide range of audience.[14]   Principles of green chemistry = productively.

P- Prevent wastes

r- Renewable materials

o- Omit derivatization steps

d- Degradable chemical products

u- Use safe synthetic methods

c- Catalytic reagents

t- Temperature, pressure ambient

i- In-process monitoring

v- Very few auxiliary substances

e- E-factor, maximize feed in product

l- Low toxicity of chemical products

y- Yes, it is safe

1.3.1. Goal of green chemistry

The goal of green chemistry is to reduce the hazards associated with the product and processes and also maintain the quality of life. Risk can be summarized in simple term as the product of hazard of particular substance and the exposure to that substance.

$$\text{Risk} = \text{Hazard} \times \text{Exposure}$$

Green chemistry seeks to reduce the risk associated with the activity by reducing the hazard side of the risk if substance posses no significant hazard, there is no limit to the exposure to substance. Hazard is not simply defined as toxicity but it includes acute and chronic toxicity, carcinogenicity, flammability, direct ecological impact and atmospheric damage.

1.3.2. Catalysis and green chemistry

The area of catalysis is often referred to as a "foundational pillar" of green chemistry.[15] Catalytic reactions often reduce energy requirements and decrease separations due to increased selectivity; they may permit the use of renewable feedstocks or minimize the quantities of reagents needed. No doubt the 2001 Nobel Prize-winning work of Sharpless, Noyori, and Knowles met many green chemistry goals.[16]Their research on catalytic asymmetric synthesis has been crucial in producing single enantiomer compounds, particularly for the pharmaceutical industry. Catalysis has played a pivotal role in implementation of green chemistry principles by minimizing the use of toxic reagents, for e.g. in oxidation reactions hydrogen peroxide is used in place of traditional heavy metal catalysts,[17]use of renewable resources, such as soya sterols and glucose[18] as feedstocks, use of photocatalyst that absorbs light in the visible range that split water into oxygen and hydrogen.[19] This technology is still in preliminary stage but has potential to provide an efficient source of hydrogen for use in fuel cells. Hydrogen fuel cells in cars would greatly reduce air pollution, as the oxidation product (water) is environmentally benign.[20]

Of course, no chemical activity is ever completely innocuous or totally benign to human health and environment. Many companies have adopted goals of 'zero accidents' or 'zero defects', it is recognized that any goal of perfection is not fully attainable. It is also recognized that in setting goal, the value lies not in the actual goal but in the process of striving toward that goal. Striving toward nothing less than perfection ensures that improvement will always be sought in each step of process.

1.3.3. E factor and green chemistry[21]

Green chemistry or sustainable chemistry marked a paradigm shift from traditional concepts of product innovation and chemical yield to economic value, eliminating waste and avoiding the use of toxic and/or hazardous substances. Environmental acceptability of any chemical processes depends mainly on E factor and atom efficiency.

E factor can be defined as the mass ratio of waste to desired product. It is the actual amount of waste produced in the process taking into account chemical yield, reagents

solvents losses, all process aids and, in principle, even fuel (although this is often difficult to quantify), exception: water. In case of aqueous waste only the inorganic salts and organic compounds contained in the water are counted to avoid exceptionally high E factors. A higher E factor means more waste and, consequently, greater negative environmental impact.

In comparison to bulk, fine chemicals and pharmaceuticals E factor increases dramatically since later involves multistep syntheses and partly because of the use of stoichiometric (inorganic) reagents rather than catalytic methodologies. Even though the absolute quantities are much smaller than in the synthesis of bulk chemicals, the need for greener, low-salt technologies is clearly more urgent in fine chemicals manufacture.

The sheer magnitude of the waste management problem in the manufacture of chemicals is readily apparent from a consideration of the amount of waste produced per kg product, in different segments of the chemical industry (Table 1.5).

Table.1.5: E factor in various chemical industries.[22]

Industry segment	Product tonnage [a]	kg waste [b]/kg product
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–>50
Pharmaceuticals	10–10^3	25–>100

a) Typically represents annual production volume of a product at one site (lower end of range) or world- wide (upper end of range). b) Defined as everything produced except the desired product (including all inorganic salts, solvent losses, etc.)

Atom efficiency is another extremely useful tool for rapid evaluation of the amounts of waste that will be generated by alternative processes. It was introduced by Trost and can be calculated by dividing the molecular weight of the product by the sum total of the molecular weights of all substances formed in the stoichiometric equation for the reaction involved. In another words it is a theoretical number, i.e. it assumes a

yield of 100% and exactly stoichiometric amounts and disregards substances which do not appear in the stoichiometric equation.

E factor and atom efficiency account only for mass of waste generated but it is essential to consider the environmental impact of this waste.

In accordance with green chemistry principles a new concept is shaping incorporating a novel class of catalysts in fine chemical synthesis. These novel catalyst systems are referred as organic inorganic hybrid catalysts and are contributing towards development of benign routes for catalytic synthesis of fine chemicals. The work incorporated in this thesis focuses on designing of organic inorganic hybrid catalyst system by heterogenizing IL on various supports. Further aim was to check the applicability of these catalysts for various organic transformations.

1.4. Organic Inorganic Hybrid Catalysts for Sustainable chemistry.

It is evident from the overview of the literature for synthesis of cyclic carbonate, alkylation of phenol, claisen schmidth condensation and synthesis of carbamates, oxamates and heterocycles viz; imidazolidine trione derivatives that, the key issue is concerning to the development of *efficient* heterogeneous catalyst. This activity is mainly driven by economic and environmental considerations to replace existing homogeneous as well as heterogeneous catalysts. Practical applications of homogeneous catalysts in industrial process are hindered due to the difficulty in recovery and reuse of the expensive catalyst, as well as product contamination caused by metal leaching. On the other hand traditional heterogeneous catalysts suffer from lowered catalytic activity as their catalytic sites are randomly oriented among the supports and microenvironment around the active sites is usually not clear.

To overcome these problems, a practical strategy is to immobilize homogeneous catalyst onto solid support to create organic inorganic hybrid catalyst. These catalysts provide avenues to recovery, recyclability, improved activity due to high dispersion and high density of active sites of support in addition to active sites of organic moiety.

In the last decade applications of ionic liquids as alternative solvents for homogeneous catalysis[23] as well as a green catalyst have increased significantly.

Their ionic nature, non-volatility, and thermal stability make them highly suitable for catalysis. Moreover, appropriate ionic liquids can enhance substrate solubility while possessing low product solubility, and thus facilitate simple product separation and complete catalyst recovery. A plethora of tailor-made ionic liquids can be synthesized with unlimited combinations of cation and anion available of the shelf.

1.4.1. Immobilized Ionic Liquids.

Recently, the use of room temperature ionic liquids as environmentally benign media and/or catalysts for clean catalytic transformations is gaining importance from green chemistry point of view. The first report of the use of an IL as a catalyst in Friedel-Crafts acylations was reported in 1986.[24] Room temperature ionic liquids exhibit certain properties which make them attractive media for performing green catalytic reactions. They have essentially no vapor pressure and are thermally robust with liquid ranges of e.g. 573K, compared to 373K for water. Polarity and hydrophilicity/hydrophobicity can be tuned by a suitable combination of cation and anion, which has earned them the accolade, 'designer solvents'. They are generally salts of organic cations, e.g. tetraalkylammonium, alkylpyridinium, 1,3-dialkylimidazolium, tetraalkylphosphonium (scheme 15). Ionic liquids have been successfully used for hydrogenation, oxidation, alkylation, hydroformylation, Heck and Suzuki coupling reactions showing profound effects on the reaction rate and product selectivity.[25,26,27,28,29] Owing to significant solubility of CO_2 in ionic liquids,[30,31] they are by now widely established to be attractive media/catalysts for cyclic carbonate synthesis.[32, 33] A variety of IL's have been employed for cyclic carbonate synthesis (scheme 1.14.). A detailed literature survey applications of ionic liquids for cyclic carbonate synthesis is presented in chapter 3, section A.

Scheme.1.14. Ionic liquids used in the synthesis of cyclic carbonates
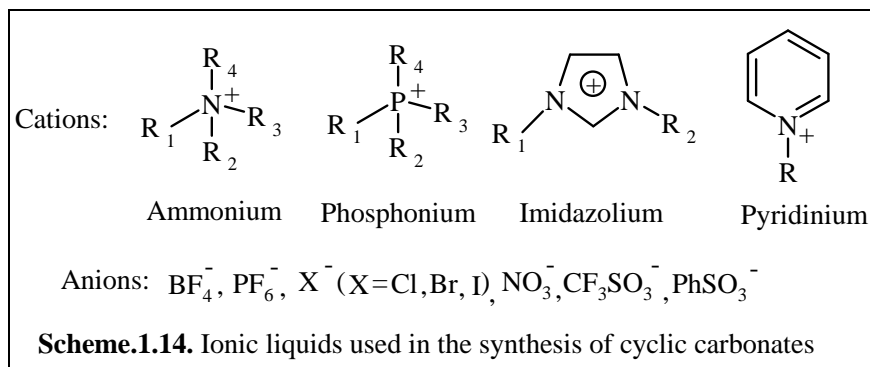
Ionic liquids hitherto termed green are expensive thus making it as unattractive option even though they are now commercially available.[34] Besides the high viscosity of ionic liquids can induce mass transfer limitations if the chemical reaction is fast, causing only a minor part of the ionic liquid and precious transition metal catalyst dissolved therein if any to contribute in the reaction. Growing amount of research in this direction has resulted in design of organic-inorganic hybrid catalyst incorporating the benefits of both the ionic liquid and the support material.

Various organic inorganic hybrid catalysts can be tailor made according to the requirement of reaction environment. Numbers of methods for immobilization are well documented in the literature like physisorption, immobilization by ionic bonds[35,36,37] or encapsulation. The methods in practice are based upon the following approaches

(i) Adsorption of the organic species into the pores of the support;

(ii) Construction of the organic molecule piece by piece within the confines

of cavities of the support (the "ship-in-bottle" technique);

(iii) Attachment of the desired functionality to the support by covalent bond

formation;

(iv) Direct synthesis into the final composite material.

The types of supports used can be organic (e.g, polymer) or inorganic (e.g, silica, mesoporous materials, alumina etc.). Heterogeneous catalysts with fine tuning of acid base bifunctional pairs can be envisaged for various organic reactions with judicious use of diverse synthesis methods reported in the literature. Recent impetus is on the use of ionic liquid as catalyst and/or solvent owing to green chemistry considerations.

But the major hindrance is the economics of ionic liquid that makes recovery a costly issue as discussed above.

General understanding of the present state of art of various immobilization methods along with advantages/disadvantages and significant improvements therein are presented in chapter 2. Thus a "heterogenized" type of homogeneous ionic liquid catalyst system can serve as better alternative for virgin ionic liquid.

Chapter 2 addresses the issue of designing of sustainable catalysts by immobilization and/ or impregnation and/ or encapsulation of a variety of ionic liquids and their applications in synthesis of fine chemicals pertaining/exploiting green chemistry principle. Another significant aspect investigated here is characterization of these catalysts to get the in-depth knowledge of the mechanism involved in catalytic cycles so as to develop "green catalysts" with better activity and selectivity.

1.5. CO_2 and global warming

The 20th century has experienced explosive growth in energy consumption and rapid increase in population worldwide along with unprecedented pace of inventions of new technologies and ever-increasing expansion of manmade materials. Electrical power plants, electric home appliances, personal computers, and mobile cell phones increasingly rely on electricity generated largely from carbon-based resources such as coal and natural gas. Another factor that has worsened the environmental issue is population explosion. High-pressure ammonia synthesis and development of the chemical fertilizers with nitrogen, phosphorus, and potassium and the engine-based machinery for crop production were fueled by the rapid growth in global population. This resulted in emission of pollutants such as NOx, SOx, and particulate matter and also the greenhouse gases (GHG) such as carbon dioxide (CO_2) and methane (CH_4).

Since early 1980s witnessed globalization of manufacturing led by the industrialized nations and economical developments in the developing countries greatly accelerated the growth in energy consumption along with worldwide CO_2 emissions per capita. According to a recent study, about 290 billion tons of carbon have been released to the atmosphere from the consumption of fossil fuels and cement production since 1751, but half of these emissions have occurred since the mid 1970s.[38] Energy

consumption and GHG emissions has shown parallel growth. Thus fundamental problem is that we consume more resources than needed. As a consequence consumption of the carbon-based energy has projected largely in GHG problems.

In fact, CO_2 a GHG; plays an important role in the earth's carbon cycle, and is a necessary ingredient in the life cycle of animals and plants.[39] Carbon dioxide whether in free or chemically combined form is a considerable natural source of carbon. It is present in atmosphere with a volumetric concentration of 0.038 % (387 parts per million by volume, ppmv) as of March 2009. [40] In terms of chemical throughput, therefore, photosynthesis is by far the most important synthetic process. Here Carbon dioxide and water are converted into carbohydrates and oxygen in plant chloroplasts, this photosynthetic process forms organic compounds from low energy carbon dioxide by utilizing sunlight (equation 1.).

$$n\,CO_2 + nH_2O \rightleftharpoons (CH_2O)_n + nO_2 \uparrow \quad .... \text{(eqn 1)}$$
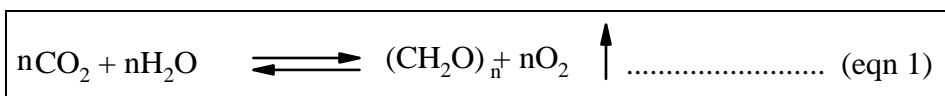
The respiration of man and animals and the decomposition of organic substances return carbon dioxide to atmosphere in considerable quantities establishing equilibrium. This equilibrium has however been considerably shifted in recent years by human activities. A reduction of these negative effects could be achieved by a change in energy policy by reduction of CO_2 emission by exploiting alternative energy sources and also by chemically converting CO_2 into useful products in those places where it is formed in large concentrations rather than releasing it into atmosphere. Thus there is an urgent need to design the strategies that address the global challenges for control, conversion and utilization of CO_2 (GHG) to cope with global warming.

1.5.1. Carbon Dioxide as an alternative C_1 Synthetic unit

A large amount of CO_2 is being released in atmosphere which needs to be exploited for industrial applications. Beyond fossil fuel-based electric power plants, other sources of CO_2 are independent power producers, vehicles & devices, volcano, earthquake, other human and natural sources. Major concentrated industrial CO_2 sources include plants for manufacturing hydrogen, ammonia, cement, limestone,

soda ash, fermentation processes, as well as number of processes using carbon monoxide and chemical oxidation processes.

One of the ways for utilization of CO_2 to overcome the issue of global warming is to incorporate CO_2 as C_1 synthetic unit in the production of useful chemicals. A large numbers of industrial processes are well established on CO_2 chemistry. The four major large scale industrial processes that utilize carbon dioxide for organic synthesis[41] are synthesis of urea (commercialized in 1992), synthesis of cyclic carbonates (first commercialized by Hüls, West Germany), synthesis of salicylic acid (Kolbe-Schmitt process, commercialized in 1890), and synthesis of methanol (scheme 1.1).

Scheme 1.1: Industrial processes for organic synthesis using CO_2 as feedstock.
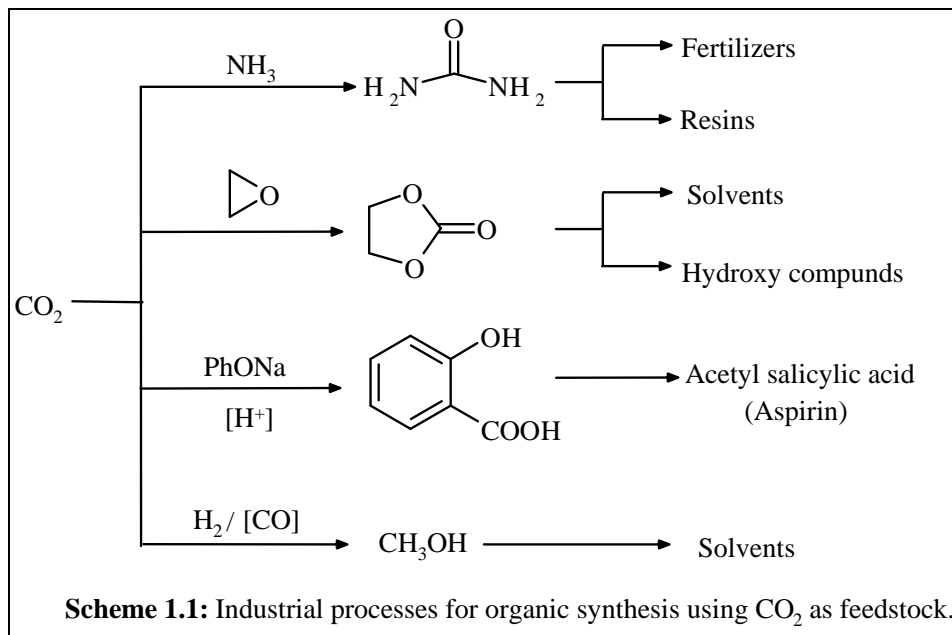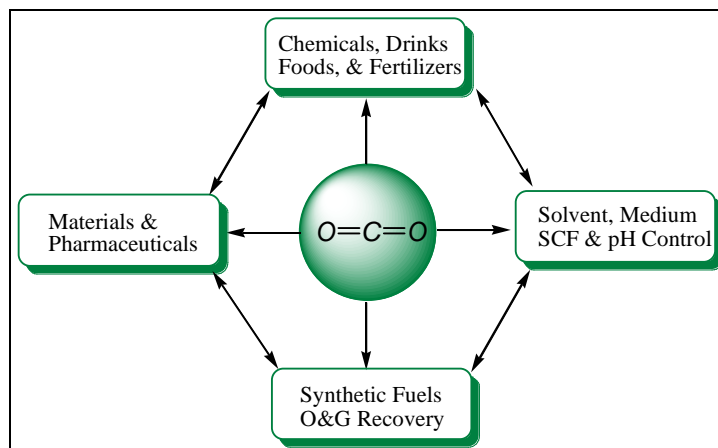
Figure.1. Existing and emerging applications of CO_2

The current global market for industrial transformations utilizing CO_2 as a synthetic building block is 128 Mt/year. This amounts to CO_2 fixation of less than 1% of global CO_2 emissions. Among the industrial transformations major application of CO_2 is towards synthesis of urea amounting to 90 Mt/year.

Utilization of CO_2 in industry is broadly based on its use (Figure 1);

(i) As reagent and solvent for synthesis of molecular chemicals, Co-monomer for polymers, as sc-fluid in solventless reactions. This application amounts to 128 Mt/y fixation of CO2 in chemical industry.

(ii) Technological use of CO2 as additive to beverages, food packaging, antibacterial, extraction of essences, caffeine, chemicals, antiflame, cleaning solvent, water treatment, enhanced oil recovery, fire extinguisher amount to 18 Mt/y.

1.5.2. Thermodynamics of CO_2 conversion and utilization

The carbon dioxide molecule has a linear structure. It is a thermodynamically stable molecule with bond strength measured at D=532 kJ/mol.[42] The heat of formation at 298K (ΔH^o) is -393.5 kJ/mol, and Gibbs free energy of formation at 298K (ΔG^o) is -394.3 kJ/mol. Since CO_2 is thermodynamically highly stable and kinetically often inert, the problem of CO_2 activation is a permanent challenge to the chemists to force this substrate into selective reactions under mild conditions as far as possible. Therefore the reactions involving CO_2 conversions are endothermic i.e. these reactions show positive change in enthalpy. Accordingly active catalysts, effective reaction conditions and substantial input of energy are required to accomplish CO_2

fixation. Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon atom, which result in the bending of the O–C–O angle to about 120°. [43]Apparently CO_2 conversion would be so endothermic that its conversion would not be feasible. However there are many large scale industrial processes that are operated based on endothermic reactions but are economic owing to certain applications of the products (e.g. pyrolysis (thermal cracking) of hydrocarbons for manufacture of ethylene and propylene, dehydrogenation reaction for manufacture of petrochemicals such as styrene from ethylbenzene, and steam reforming of hydrocarbons for producing synthesis gas and hydrogen).

1.5.3. Challenges for CO_2 utilization

Since CO_2 itself is not a high end product for chemical industry; the endothermic CO_2 fixation is viewed as non economic. Although endothermic reactions consume energy they are useful for certain applications in view of the fact that chemical reactions that are endothermic are driven by the difference in Gibbs free energy between the products and reactants at certain conditions. Accordingly challenges involved in the processes for CO2 utilization are;

- Costs of CO_2 capture separation, purification, and transportation to user site.
- Energy requirements of CO_2 chemical conversion (plus source and cost of H_2 and/or other co-reactants if involved).
- Market size limitations, little investment-incentives and lack of industrial commitments for enhancing CO_2-based chemicals.
- Lack of socio-economical driving forces for enhanced CO_2 utilization.

1.5.4. Strategies for CO_2 conversion and utilization

The research on CO_2 conversion and utilization will help us to achieve the challenge of sustainability with the help of new technologies and proper strategies. Strategies that need to be considered are;

- Select concentrated CO_2 sources for CO_2 capture and/or utilization; aim for on-site/nearby uses if possible.

- Use CO_2 to replace a hazardous or less-effective substance in existing chemical processes for making products with significant volumes.

- Take value-added approaches for CO_2 sequestration coupled with utilization.

- For applications that do not require pure CO_2, develop effective processes for using the CO_2-concentrated flue gas from industrial plants or CO_2-rich resources such as CO_2-rich natural gases without CO_2 separation.

- For applications that need pure CO_2, develop more efficient and less-energy intensive processes for separation of CO_2 selectively without the negative impacts of co-existing gases such as H_2O, O_2, and N_2.

- Replace a hazardous or less-effective substance in existing processes with CO_2 as an alternate medium or solvent or co reactant or a combination of them

- Make use of CO_2 based on the unique physical properties as supercritical fluid or as either solvent or anti-solvent

- Make use of CO_2 based on the unique chemical properties for CO_2 to be incorporated with high 'atom efficiency' such as carboxylation and carbonate synthesis

- Produce useful chemicals and materials using CO_2 as a reactant or feedstock

- Use CO_2 for energy recovery while reducing its emissions to the atmosphere by sequestration

- Recycle CO_2 as C-source for chemicals and fuels using renewable sources of energy.

- Convert CO_2 under either bio-chemical or geologic-formation conditions into ''new fossil'' energies.

1.5.5. Application of CO_2 for synthesis of organic carbonates

Organic carbonates stands on the verge of becoming an extremely valuable tool to the organic chemist. Mainly, organic carbonates are used as carboxylating or alkylating agent in organic synthesis and have applications in medicine and polymer chemistry. The industrially important organic carbonates are dimethyl carbonate (DMC), diphenyl carbonate (DPC), ethylene carbonate (EC) and propylene carbonate (PC). The use of DPC as an intermediate in plastic manufacturing accounts to 2 Mtons/yr,

whereas annual production of cyclic carbonates contributes to a lesser amount of 0.1 Mtons/yr.[44] Applications of organic carbonates in organic synthesis are summarized in scheme 1.2.

Scheme.1.2. Applications of organic carbonates
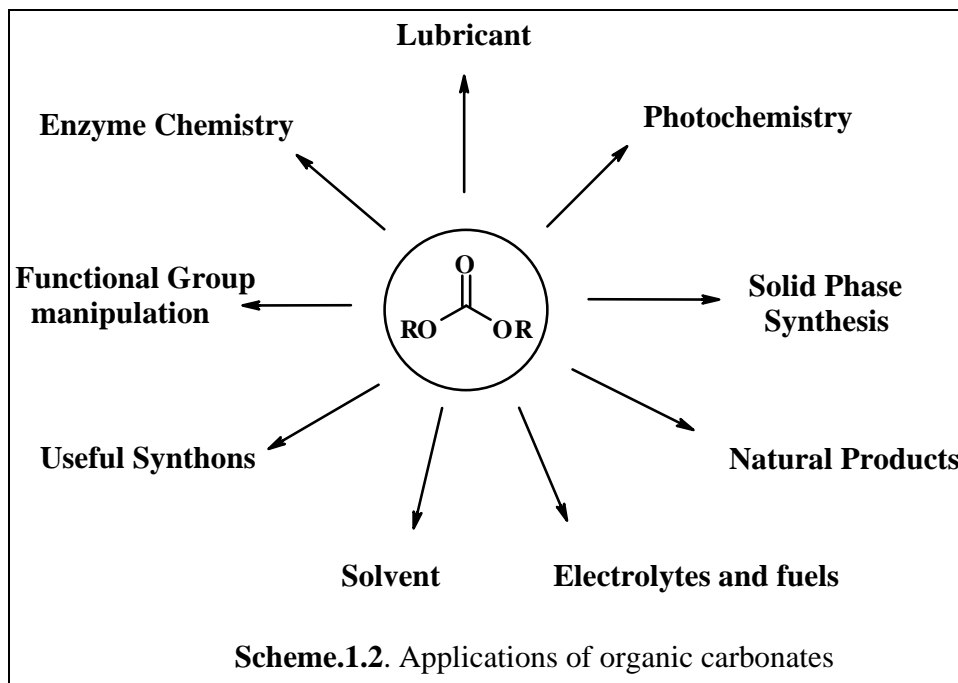
Organic carbonates are classified mainly in two groups as saturated and unsaturated carbonates. Saturated carbonates are further classified as aliphatic, aliphatic - aromatic, aromatic and others. Aromatic carbonates are further classified into simple, activated and cyclic. In the present work more stress is given on the research related to synthesis of cyclic carbonates and application of DMC (aliphatic symmetrical linear carbonate) as alkylating agent. These works will be discussed in detail in section A and section D respectively.

1.5.6. Methods for preparation of organic carbonates[45]

Broadly these methods are discussed here based on phosgene chemistry (non CO_2 route) and non phosgene chemistry (utilizing CO_2).

1.5.6.1. *Phosgenation method* (non CO_2 route)

This conventional synthesis of acyclic carbonates involves phosgenation of alcohols. (Scheme 1.3). Practically all the organic carbonates can be prepared by this method

except ortho-and pyro- carbonates. In this method aliphatic/aromatic hydroxy compounds are dissolved in large excess amount of anhydrous, inert solvent or mixture of solvent (dichloromethane, benzene, chloroform, and toluene). This is followed by reaction with phosgene ($COCl_2$) in the presence of excess pyridine at or below room temperature. Pyridine acts as an acid acceptor and reacts with phosgene forming an ionic adduct. Symmetrical carbonates can be prepared in one step, whereas unsymmetrical (alkyl aryl or substituted alkyl aryl) carbonates are obtained in two-steps. The reactivity of hydroxy compounds with phosgene follows the order; aliphatic hydroxy compounds > Aromatic hydroxy compounds > acidic hydroxy compounds.[46]

Scheme.1.3. Synthesis of organic carbonates by phosgenation method
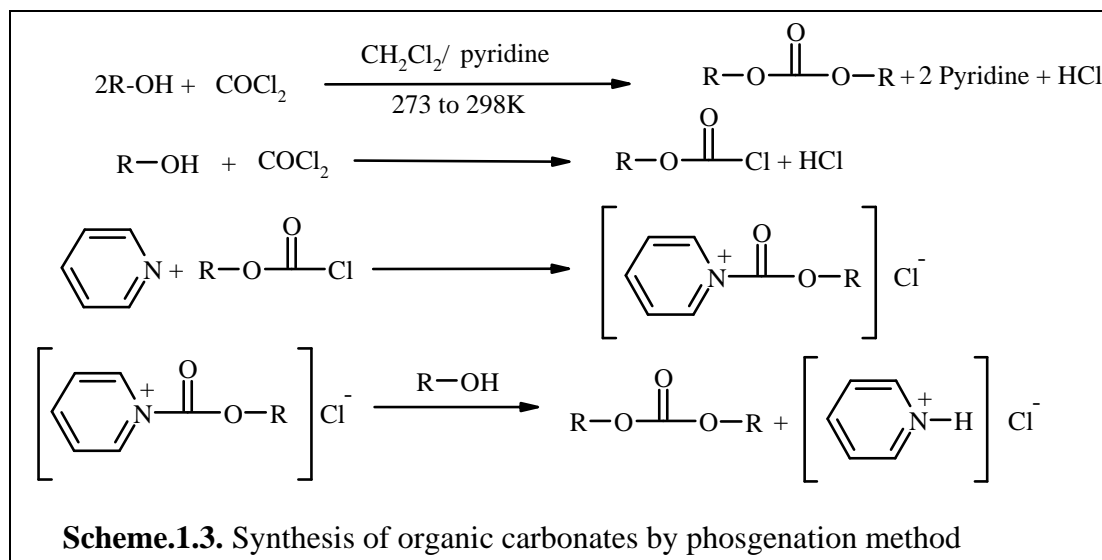
Another approach for cyclic carbonate synthesis from diol involves substitution of phosgene by compounds such as chloroformic acid, trichloromethyl ester (diphosgene) and bis(trichloromethyl) carbonate (Scheme 1.4). For example, 1, 2- and 1, 3-diols are easily converted to cyclic carbonates with triphosgene in dichloromethane and pyridine at 343 K.[47]

Scheme.1.4. Synthesis of cyclic carbonate by phosgenation method

.
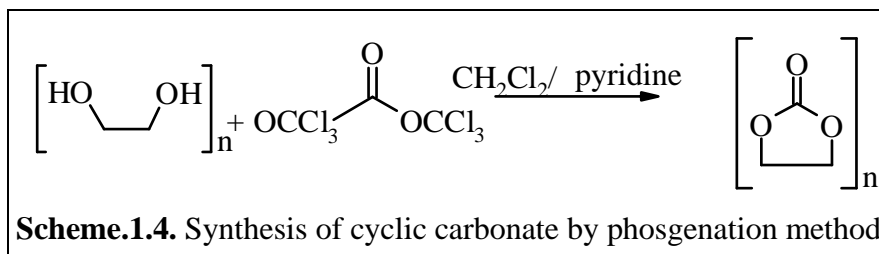
Bisphenol-A is selectively converted to corresponding carbonates under pseudo-high-dilution conditions employing triethylamine catalyst.[48] Phosgenation method is advantageous for the preparation of variety of carbonates in a short period of time in a continuous process with very high yields. But, the major disadvantage of this method of carbonates synthesis is that the process involves use of stoichiometric amount of highly toxic and hazardous chemicals like phosgene and pyridine. At the end of the reaction pyridine has to be neutralized generating byproduct salt (1kg of phosgene generates 1.17 kg of salt waste).

1.5.6.2. Oxidative Carbonylation of Alcohols/Phenols.

Dialkyl carbonates can be synthesized by oxidative carbonylation of alcohols/phenols. In 1990, ENIChem Synthesis commercialized the process for dimethyl carbonate synthesis based on oxidative carbonylation of methanol over CuCl catalyst.[49] This plant has the capacity to produce 8800 tons/year dimethyl carbonate.[50] Simultaneously UBE Industries Ltd. commercialized similar process using Pd-nitric oxide system.[51] This methodology is also followed by Dow Chemicals for the synthesis of dimethyl carbonate.[52]

Alcohols/phenols undergo oxidative carbonylation in the presence of transition metal compounds of viz; palladium, mercury, and copper and post-transition metal compounds. [53] In the case of palladium and mercury, however, the reaction does not seem to be selective and involves reduction of the metal, which cannot be reoxidized directly. The reactivity of copper is of greater interest. Romano et al. [54] explored the synthesis of dimethyl carbonate by oxidative carbonylation of methanol using a copper salt such as copper chloride as catalyst. The reaction takes place in two steps, in which cuprous chloride is oxidized to cupric methoxy chloride and this is reduced

with carbon monoxide to form dimethyl carbonate; cuprous chloride is regenerated (Scheme 1.5).

$$2\ CuCl + 2CH_3OH + 1/2\ O_2 \longrightarrow 2Cu(OCH_3)Cl + H_2O$$

$$2Cu(OCH_3)Cl + CO \longrightarrow (CH_3O)_2CO + 2\ CuCl$$
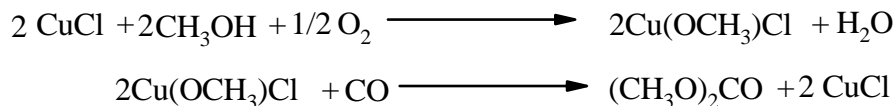
Scheme.1.5. Oxidative carbonylation of alcohols catalysed by copper salt

An alternative route for the synthesis of dimethyl carbonate is by continuous gas phase reaction of alkyl nitrites (RONO) with CO in the presence of a catalyst consist of platinum halide or a complex with alkali metal or alkaline earth metal halides.[55] By this method dimethyl carbonate was obtained in 70-80% yield with selectivity in the range of 80-90%. Similarly synthesis of diphenyl carbonate can carried out by oxidative carbonylation of phenols but with poor yields. This reaction is carried out in the presence of catalysts containing palladium compounds, alkyl ammonium halide, and an organic or inorganic base under a pressure of 4 - 30 MPa, at $373 - 473$ K, for 1 - 13 h (Scheme 1.6). Diphenyl carbonate is obtained in 4 - 30% yield with 90 - 96% selectivity.[56]Use of molecular sieves is also found to have favorable effect on yield and selectivity.[57]Diphenyl carbonate, in 39.5% yield, with 99% selectivity, is produced by a continuous process, in a multistage distillation column, in which water formed in the reaction is removed as steam by distillation.[58]
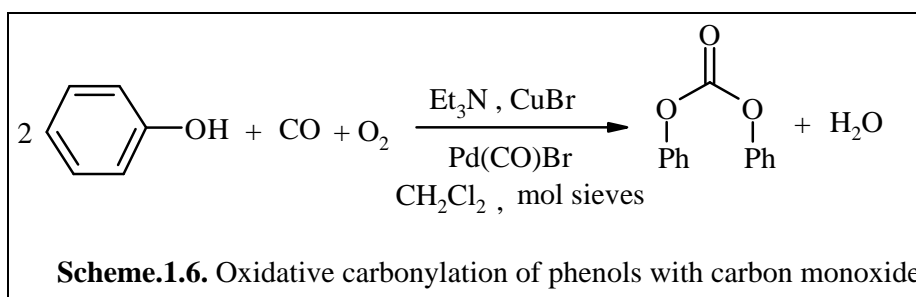
Scheme.1.6. Oxidative carbonylation of phenols with carbon monoxide

The major drawback of this method is the potential explosion hazard due to use of CO and O_2. This method was not commercialized due to lower basicity of phenols,

expensive catalysts, use of dichloromethane as solvent, low yields, and low catalyst turnover efficiencies.

1.5.6.3. Reaction of urea with alcohols/phenols

Paquin[59] reported the reaction of urea and alcohol using metal salts like zinc acetate and lead acetate to produce carbamates. Prolongation of the reaction or the addition of triphenylphosphine as cocatalyst results in the formation of carbonate with isocyanuric acid as major byproduct. To overcome the formation of isocyanuric acid titanium, aluminium, or zirconium alkoxides with suitable cocatalyst are employed.[60] Other effective catalyst systems giving high yields of carbonates for this reactions are dibutyltin oxide, dibutyltin dimethoxide and triphenyltin chloride. Heterogeneous catalysts such as antimony trioxide and aluminium trioxide have also been reported. This reaction is carried out at 423-468K for 4.5h and at 468-493K for 14h depending upon the catalyst system with >99% yield of carbonates.[61] Primary, secondary, and low boiling alcohols can be converted to carbonates. The ammonia liberated can be recycled for urea synthesis (Scheme 1.7).

Scheme.1.7. Organic carbonate synthesis from urea and alcohol
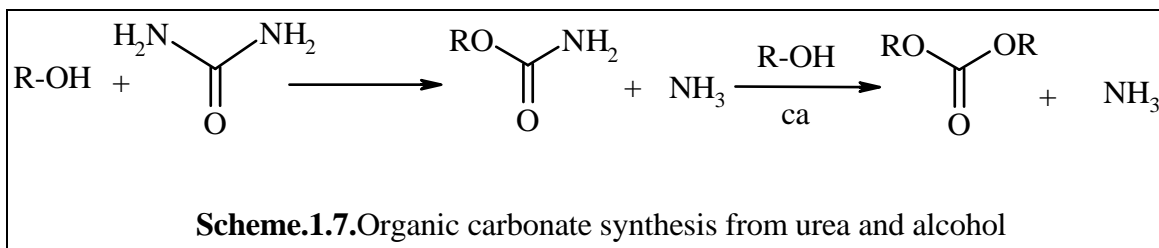
Other methods practiced for preparation of organic carbonates are carbonate interchange reactions and use of metal carbonates.[62,63] Rockicki et al. have reported a number of organic carbonates by reaction of alkali metal carbonates with alkyl halide in the presence of activating agents such as crown ethers, polyglymes, polyamines and triethylbenzylammonium chloride and various solvents. More than 90% yield were obtained by reaction of K_2CO_3 (Group I and II alkali metal carbonates) with benzyl bromide (primary alkyl halides) using 0.1 mol % 18-crown-6-ether and triethylbenzylammonium chloride as activating agent at 343-353K for 24 h. The major disadvantages of this reaction are low yield, high reaction temperature and time, formation of dialkyl ethers as side products. This reaction works satisfactorily

for alkyl bromide and K_2CO_3 system due to low basicity and nucleophilicity of bromide anion as compared to chloride anion. This method is not applicable for diaryl carbonates.

Carbonate interchange reactions can be carried out by reacting appropriate aliphatic/aromatic hydroxy compound with organic carbonate in the presence of suitable catalyst. This reaction follows the general rule: the more nucleophilic hydroxy compound displaces the less nucleophilic compound and if both hydroxy compounds have similar nucleophilicity then the less volatile compound displaces the more volatile one.[64]

From these literature reported methods it is evident that these methods suffers from one or other drawback like low yield, high operating temperatures, use of stoichiometric and/or toxic reagents. In the wake of current stringent environmental legislation on chemical industry, emphasis is given on those methods which abide by green chemistry principles. In this context fixation of CO_2 as C_1 building block for synthesis of organic carbonates is looked upon as potent methodology that encompass the limitations of above discussed routes.

1.5.6.4. Preparation of organic carbonates from CO_2 (Non-phosgene route)

Both dialkyl and cyclic carbonates can be obtained using CO_2 as C_1 synthetic unit. Symmetrical and unsymmetrical dialkyl carbonates can be prepared in good yields by reaction of alcohol with alkyl halide and CO_2 using K_2CO_3 as catalyst (Scheme 1.8).[65]

Scheme.1.8. Synthesis of organic carbonates from CO_2, alcohols and alkyl halide
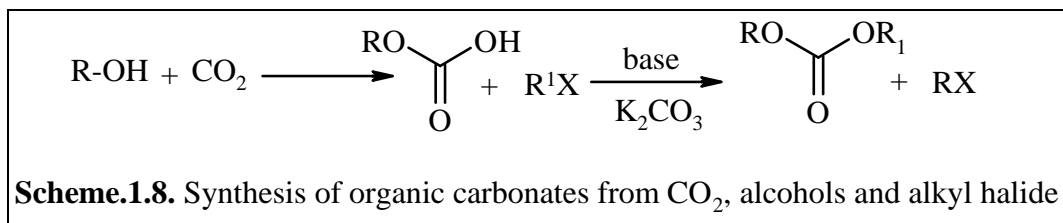
Another method for preparation of organic carbonates involves reaction of alcohol with CO_2 in presence of triphenyl phosphine and diethyl azodicarboxylate. This reaction gives dialkyl carbonates in good yields under ambient temperature (Scheme 1.9).[66]

$$\text{R-OH} + \text{CO}_2 + \text{Ph}_3\text{P:} + \text{EtO}_2\text{CN} = \text{NC O}_2\text{Et} \xrightarrow[\text{RT}]{\text{THF, 453K}} \text{EtO}_2\text{CNHNHC O}_2\text{Et} + \text{PH}_3\text{P} = \text{O} +$$
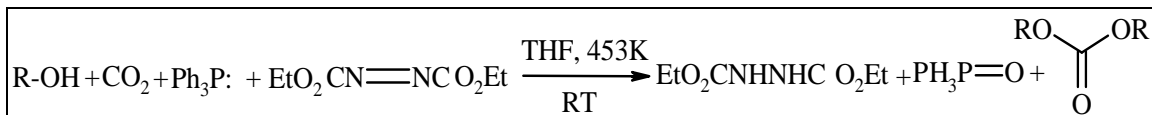
Scheme.1.9. Dialkyl carbonate synthesis from alcohol, carbondioxide and triphenylphosphine

Cyclic carbonates can be synthesized in high yield from reaction of vicinal halohydrins with tetramethyl ammonium hydrogen carbonate in acetonitrile solvent at 293K for 10-75 min (Scheme 1.10).[67]
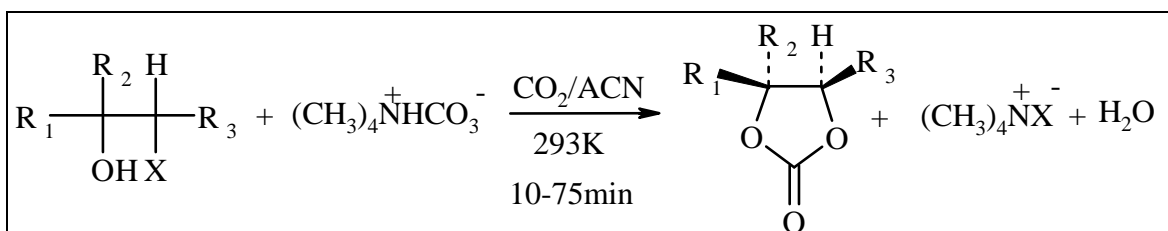
Scheme.1.10. Cyclic carbonate synthesis from vicinal halohydrins and tetramethyl-ammonium hydrogencarbonate.

Cyclic as well as acyclic carbonate can be prepared by carbonylation of alcohol in the presence using elemental sulphur in the presence of triethyl amine or 1-methylpyrolidine (Scheme 1.11).[68]
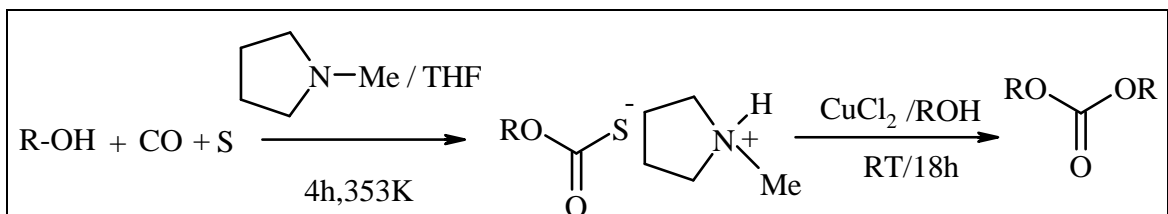
Scheme.1.11. Synthesis of carbonates by carbonylation of alcohol using elemental sulfur

Cyclic carbonates were obtained in 90% yield by heating mono or dihalogenated alkyl carbonates at 453-473K for 1-4 h with/without mercuric acetate as catalyst(Scheme 1.12).[69,70]

Scheme.1.12. Cyclic carbonate synthesis from mono or dihalogenated alkyl carbonates
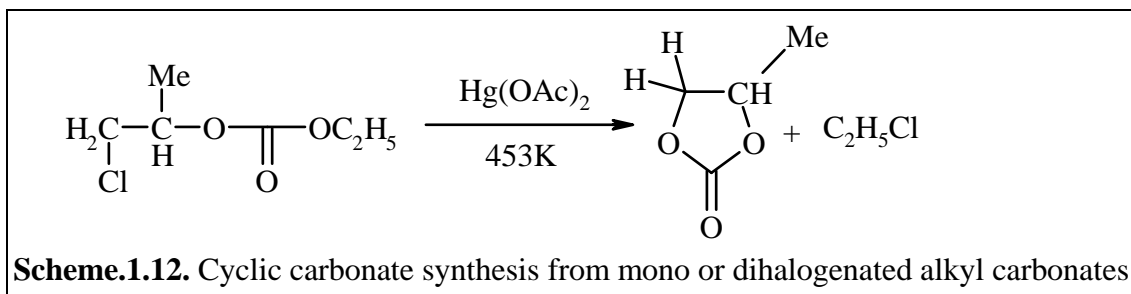
Similar to linear dialkyl carbonates, cyclic carbonates are useful as intermediates for polycarbonates, electrolytes in lithium ion batteries, or green solvents. Apart from above mentioned methodologies for synthesis of cyclic carbonate a new efficient, phosgene-free and eco-friendly synthetic route involves cycloaddition of CO_2 to epoxides (Scheme 1.13).

Scheme.1.13. Cycloaddition of CO2 to epoxides
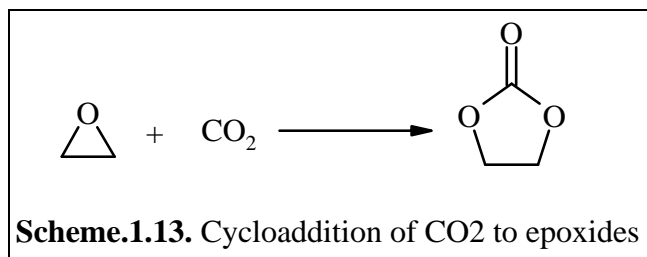
1.6. Cycloaddition of CO_2 to Epoxides

The production of five-membered cyclic carbonates from CO_2 and epoxides has been industrialized since the 1950's.[71] This reaction is highly atom efficient. There are several homogeneous and heterogeneous catalyst systems, which catalyze this cycloaddition reaction.[26] Researchers have investigated efficacy of several quaternary ammonium salt[72], phosphonium salt[73] and group I metal salts-based catalysts[74,75,76,] for this reaction. Besides these catalysts other catalytic systems reported were M(II) Alkoxide and carboxalate catalysts comprising of Zn(II) complexes, schiff base complexes comprising of metal salen complexes,[77,78,79] porphyrine and phthalocyanine complexes.[80,81] But most of these systems give good yield of cyclic carbonate in the presence of organic bases. Various heterogeneous catalysts like Mg-Al mixed oxides (with Mg/Al = 5) obtained by calcination of hydrotalcites[82], were found to give excellent yield of cyclic carbonates. Nowadays ionic liquids[83,84,85,86]
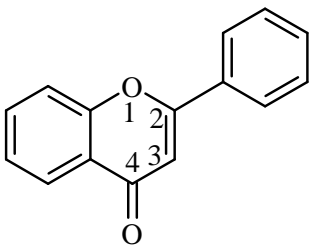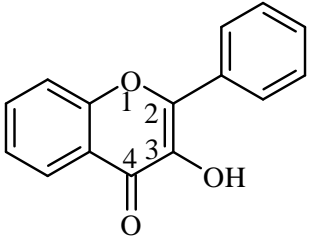
are employed extensively as catalyst for synthesis cyclic carbonates to make this process more benign. Though ionic liquids have proved their niche as efficient and ecofriendly catalyst they are costly and recycling of these catalysts involves energy intensive steps. Next generation of the catalyst reported for this transformation belongs to immobilized class of catalyst. Various immobilized catalysts like guanidine anchored to MCM-41[87] and ionic liquids anchored on MCM-41[88]/silica[89] were found to give excellent activity for cyclic carbonate synthesis along with good recyclability. A detailed literature survey on cycloaddition of CO_2 to epoxides is reported in chapter 3; section A. In this section of chapter 3, cycloaddition of CO2 to epoxides is explored using immobilized IL catalyst. Emphasis is given on studying the various parameters like methods of heterogenization, effect of various inorganic supports on final activity of these catalyst, optimum temperature and pressure conditions so as to avoid use of CO_2 under supercritical conditions.
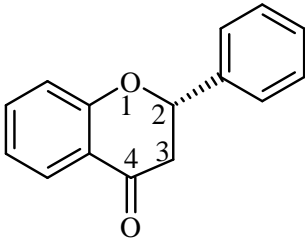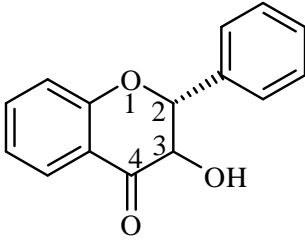
1.7. Efficient synthesis of chalcone and flavanone catalysed by immobilized IL

Chalcone and flavanones are poly phenolic compounds that form important class of plant pigment having wide range of biological activity. Chalcones are main precursors for the biosynthesis of flavonoids. Chalcone is aromatic ketone that forms the central core for the variety of biological molecules with significant activity. They belong to class of flavanoids having the basic C_6–C_3–C_6 arrangement but in which the middle three carbon atoms do not form a closed ring, in contrast to other flavonoids (structure A Scheme 1.15). In plants chalcones and flavanones are synthesized by enzyme chalcone synthase and from isomerisation of chalcone mediated by chalcone isomerase respectively. Flavanoids also known as Vitamin P is classified (IUPAC nomenclature) into flavanoids, isoflavanoids and neoflavanoids. The basic flavanoid structure is a flavone nucleus, which consists of 15 carbon atom, arranged in 2 rings labeled as A, B, C.(structure B scheme 1.15).

Scheme.1.15. Chalcone and Flavanone synthesis from condensation of o-hydroxy acetophenone and benzaldehyde
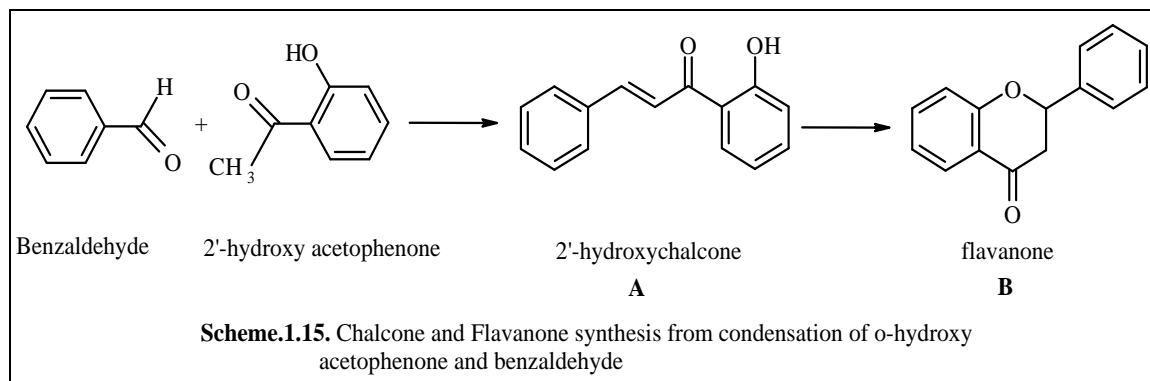
Much of the current research is focused on natural and synthetic flavanoids and flavanones because of their interesting biological activity, including, antioxidant, antifungal, antibacterial, anti-inflammatory, antiasthmatic, antihypertensive, antiviral, estrogenic and diuretic activity. Table 1.7 summarizes the four main classes of flavones (class of flavanoids) with their structural backbone and examples.

Table 1.7. Main classes of flavones				
Group	**Structure (name)**	**Functional groups**		**Examples**
Flavone	2-phenylchromen-4-one	nil	nil	Luteolin, Apigenin, Tangeritin
Flavonol	3-hydroxy-2- phenylchromen-4-one	3-hydroxyl	nil	Quercetin, Kaempferol, Myricetin, Fisetin, Isorhamnetin, Pachypodol, Rhamnazin

Flavanone	 2,3-dihydro-2-phenylchromen-4-one	nil	2,3-dihydro	Hesperetin, Naringenin, Eriodictyol, Homoeriodictyol
Flavanonol	 3-hydroxy-2,3-dihydro-2-phenylchromen-4-one	3-hydroxyl	2,3-dihydro	Taxifolin(or Dihydroquercetin), Dihydrokaempferol

Chalcones too have attracted considerable attention due to numerous applications such as attractants of pollinators, UV protectors, and insect repellents, pesticides, photoprotectors in plastic, solar creams, food additives, and significant biological activities like antimalarial,[90] anti-inflammatory,[91] cytotoxic,[92] anticancer,[93] diuretic, and choleretic.[94,95]

The most commonly used method for chalcone synthesis is Claisen–Schmidt (CS) condensation between acetophenone and benzaldehyde derivatives. This method is a valuable C–C bond-forming reaction that allows α,β-unsaturated ketones called chalcones to be obtained in good yield. This method is traditionally carried out at 323 K using 10–60% of alkaline hydroxides or sodium ethoxide over a period of 12–15 h.[96]This method uses harmful alkaline hydroxides as catalyst generating inorganic salt wastes.

 Recently solid bases are looked upon as green alternative for replacement of soluble bases. A variety of heterogeneous basic catalysts, such as alumina,[97] Ba(OH)$_2$ either dehydrated[98] or activated by ultrasound,[99] hydrotalcites,[100] MgO, and natural phosphates modified with sodium nitrate,[101] have been reported to efficiently catalyze Claisen–Schmidt condensation for chalcone synthesis. Other synthetic methods for

chalcone synthesis employed acid catalysts viz; AlCl₃,[102] BF₃,[103] Al₂O₃,[104] and zeolites.[105] Recently Dong et al. reported chalcones with 95% yield at 413K in 1.2h using SO₃H-functionalized ionic liquids as catalysts.[106]

There are number of methods available for the synthesis of flavanoids and flavanones like Kostanecki method,[107,108] Allan–Robinson method,[109] Mahal–Venkataraman method,[110] the Chalcone method, the Wheeler method and others. Almost all the methods of synthesis of flavanones and flavanoids required more amount of heating during the reaction and the yields of the products obtained are less (50—60% yield).[111,112,113] In 1904 Kostanecki realized the cyclization of chalcone to flavanone for the first time with a mineral acid catalyst.[114]Other strategies for flavanone synthesis involve the isomerization of appropriately substituted 2'-hydroxy chalcones. These cyclizations have been reported under numerous conditions using acids,[115] bases,[116] silica gel,[117] heat,[118] and Ni/Zn/K halides.[119]

The increasing requirement for the sustainability of large scale processes and the need for continuously enhanced environmental compatibility have created new momentum for development of clean and economical processes. Most of the methods for chalcone and flavanone synthesis results in generating inorganic salt waste such as sodium chloride, sodium sulfate, and ammonium sulfate formed during the reaction or in subsequent neutralization steps that can be major concern in the synthesis of fine chemicals and pharmaceuticals. Also most of these catalyst systems still require expensive toxic solvents to facilitate the heat and mass transfer of the liquid phase in reaction systems Thus, replacement of liquid catalyst by solid-base catalysts for the production of fine chemicals not only allows easy separation and recycling of the catalyst from the reaction mixture, but for many bimolecular reactions heterogeneous catalysts can give better selectivity than homogeneous catalysts.

As part of an exploration of the possibility of utilizing heterogeneous catalysts for Claisen–Schmidt (CS) condensation and subsequent intramolecular Michael addition, hydrotalcites and ionic liquid grafted on hydrotalcites as solid acid/base catalyst are probed for their activity in chapter 3, section B. One of the significant objectives was to study the selectivity behavior of this catalyst system towards synthesis of chalcone / flavanone. In this chapter ²⁷Al MAS NMR spectroscopy was used to investigate

valuable information on the structural geometry of Al^{3+} ions and its environment in hydrotalcites and ionic liquid grafted on hydrotalcite for their activity towards chalcone and flavanone synthesis.

1.8. DBTO catalyzed synthesis of 1,3,5 imidazolidine trione, carbamates and oxamates.

Trans-functionalization is an efficient way to generate organic intermediates considering the fact that value added products can be synthesized using this methodology. For the first time efficient one pot cross-coupling reaction between urea and oxalate in presence of organometallic catalyst is probed in detail for synthesis of industrially important chemicals 1,3 dimethylimidazolidine 2,4,5 trione, ethyl *N* – Aryl (or *N*-Alkyl) oxamates and carbamates by condensation of urea with diethyl oxalate using catalytic amount of   DBTO (scheme.1.16). This protocol furnished carbamate and oxamate selectively depending upon the catalyst used. Further in-situ condensation of carbamate and oxamate produce imidazolidine trione derivative via a low energy path compared to direct condensation between urea and oxalate. This reaction is explored under pot as well as autoclave condition. Interestingly the reaction under autoclave condition was found to give diethyl iminodicarbonate and alloxan along with carbamate, oxamate and imidazolidine trione derivative. As a part of this study the formation of iminodicarbonate and alloxan is investigated and reported here for the first time.

Scheme 1.16. Transfunctionalization and cyclization of urea and oxalate
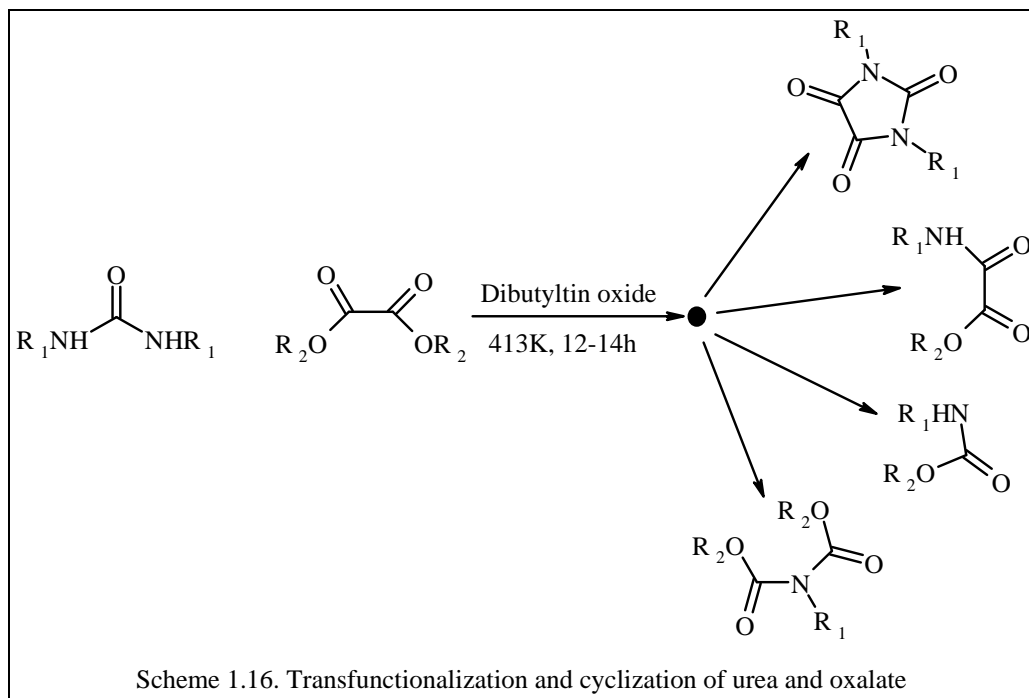
1,3 dimethylimidazolidine 2,4,5 trione is related to two biological molecule alloxan and barbituric acid. Its derivatives are reported to exhibit excellent activity as a drug for the treatment or complications of diabetes.[120] Hydroxyl derivatives of imidazolidine trione are used to produce polyester resin[121] of high thermal stability and heat resistance.[122] Other applications include preparation of crease proof cotton fabrics[123,124] and electrically conducting CuS-polyparabanic acid films.[125]

Most of the cases for 1,3 dimethylimidazolidine 2,4,5 trione synthesis involve generation of stoichiometric amount of salt and acid wastes. The protocol studied here is environmentally benign. Diethyl oxalate is well documented as 1, 2-dielectrophiles[126] and DBTO has been employed as a highly effective intermolecular transesterification and esterification catalyst.[127]There are ample reports on Biginili[128] reaction which is also a three component condensation reaction of an aldehyde, a beta ketoester and urea under strongly acidic condition to produce dihydropyrimidine- 2-ones but very scanty literature is available on the synthesis of 1,3 dimethylimidazolidine 2,4,5 trione.

 Murray[129] has reported synthesis of 1,3 dimethylimidazolidine 2,4,5 trione starting from diethyl oxalate and urea catalyzed by *insitu* generation of Na ethoxide. Recently

1,3 dimethylimidazolidine 2,4,5 trione was synthesized from 2-(Dinitromethylene) 4,5imidazolidinedione and methanol[130]and also from hydantoin by oxidation with bromine.[131] Larson et. al.[132] reported 1,3 dimethylimidazolidine 2,4,5 trione from equimolar quantities of appropriately N-substituted urea with oxalyl chloride in anhydrous ether in the presence of sodium carbonate. But this methodology generates stoichiometric amount of salt waste.

Another important products obtained during this course of reaction were Ethyl *N –* Aryl (or *N*-Alkyl) oxamates (EAO) and carbamates. The potential of EAO lay in their use as intermediate in pharmaceutical industry for the synthesis of drugs with neuritogenic activity[133] as well as synthetic intermediate; synthesis of ligands for Pd catalysed asymmetric alkylation. [134] Although oxamates are conveniently synthesized from ethyl oxalylchloride and aromatic or aliphatic amines in presence of TEA at 278 K,[135] but they generate stoichiometric amount of acid waste posing environmental hazard.

The other product formed is carbamate which holds applications in the field of pharmaceuticals,[136] agriculture,[137] in synthetic organic chemistry, particularly as synthesis intermediates,[138] protection of amino groups in peptide chemistry. [139]

Carbamates are conventionally synthesized from phosgene.[140] Other synthesis methodologies involve use of phosgene derivatives[141] and carbon monoxide[142], carbonylation of nitro compounds, [143] oxidative carbonylation of amines,[144] and carboxylation of amines using organic carbonates[145] or carbon dioxide[146] and alcoholysis of substituted urea.[147] .

The study incorporated in Section C of Chapter3, is aimed to explore the role of catalyst and solvent towards selectivity for synthesis of imidazolidine trione derivative and/or carbamate and oxamate. In this section effect of controlling deactivation of acid base sites of DBTO, towards the selectivity of both carbamate and oxamate or 1,3 dimethylimidazolidine 2,4,5 trione is studied using basic solvent media such as DMF and NMP.

1.9. Alkylation of phenol by Dimethyl carbonates using organic inorganic hybrid catalyst/ immobilized IL

The Friedel–Crafts alkylation is one of the oldest and most intensively studied organic reactions. The Friedel–Crafts alkylation of phenol gives both C- and *O*-alkylated phenols depending upon reaction conditions such as temperature, source of reagent and type of catalyst. C-alkylated phenols, in particular, tertbutyl-, iso-octyl-, and iso-decyl phenols, are widely used in the chemical industry as drilling oil additives, antioxidants, and polymer stabilizers. The isomeric O-alkylated phenol products are used as raw materials for the manufacture of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, surface-active agents, rubber chemicals, antioxidants, fungicides, petroleum additives, ultraviolet absorbers, and heat stabilizers for polymeric materials. [148,149,150,151,152]

C-alkylation of phenol is carried out using liquid acid catalyst resulting in wide product distribution. Recently heterogeneous solid acids like anion exchange resins, NaX and Y zeolites, heteropoly acids, acid-treated clays, and titania-supported $AlPO_4$ have replaced use of highly corrosive and polluting liquid acids which pose a major environmental problem. O-/C-Alkylation of phenol, substituted phenols and napthol are well reviewed by Viswanathan et al.[153]

O-alkylation of phenol to anisole is reported widely by both academic and industrial sources using alkylating agents such as methyl iodide, dimethyl sulfate (Williamson reaction), non toxic dimethyl carbonate and with methanol (Scheme 1.17, eqn (1), (2) and (3) (4), and (5)).).[154] *O*-methylation of the phenols with methyl halides or dimethyl sulfate requires not only harmful reagents but also a stoichiometic amount of a strong base to neutralize acid by-product. Whereas with methanol as methylating agent failed to give total conversion of phenols and the C-methylation always occurred in competition with the *O*-methylation.[155,156] In view of environmental impact of methyl halides and dimethyl sulfate and the poor atom economy of methanol, dimethyl carbonate (DMC) a green reagent have been looked as a potential substitute for these reagents.[157,158]

O-methylation of phenols with DMC employing continuous-flow process under gas/liquid phase transfer catalysis (GL-PTC) conditions is reported using K_2CO_3 and

polyethylene glycol (PEG) as catalysts.[159] This methodology gives anisole in good yields but poses a serious concern for high boiling point substrate. This reaction is also reported under liquid/solid PTC conditions in the presence of K_2CO_3 and crown ether at 373K,[160] or with K_2CO_3 and tetrabutylammonium bromide at reflux temperature of DMC.[161] But the yield of anisole was not too encouraging. The *O*-methylation of phenols with DMC is also reported using alkali base,[162,163] a tertiary amine and an iodide,[164] a nitrogen containing heterocyclic such as [4-dimethlylamino]-pyridine,[165] or a pentaalkylguanidine.[166] Eventhough reactions were carried out under autoclave conditions, still the kinetics of the reactions were slow. Shieh et al. have reported good yield of anisole from phenol and DMC employing microwave irradiation technique.

Scheme.1.17. Various methods for alkylation of phenol
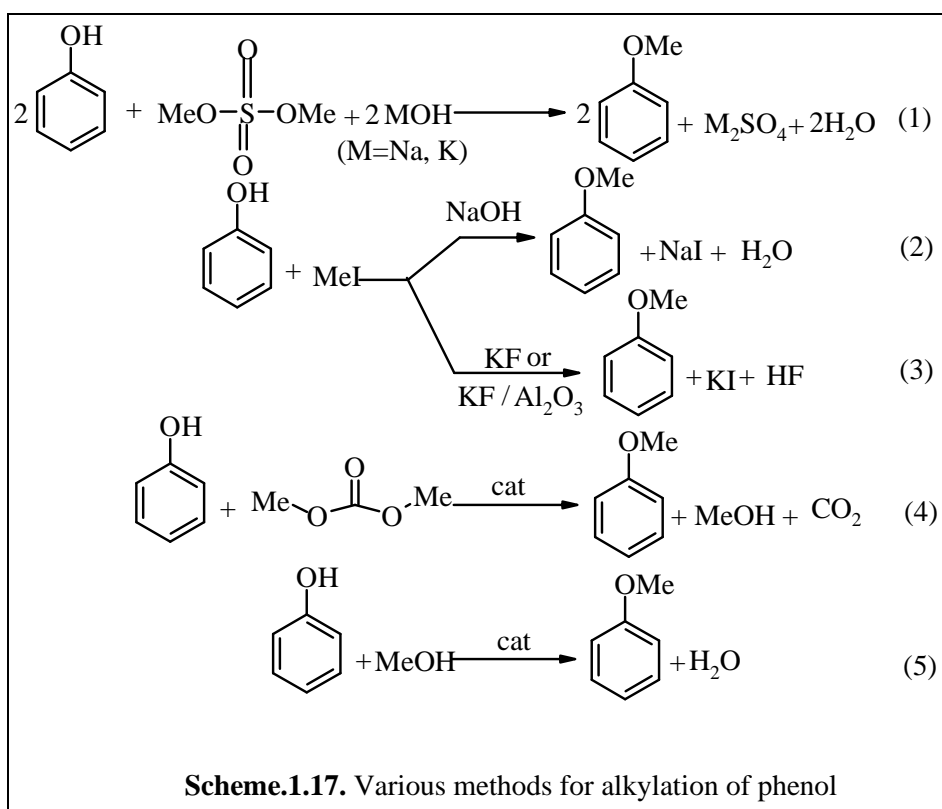
They achieved good phenol conversion using 1, 8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst at 433K in 20bar.[167] Later on Ouk et al. reported *O*-methylation of phenols as well as the highly hindered phenols with DMC in a semi-continuous

process using tetrabutylammonium bromide as catalyst. The reaction was carried out at 403K for 4h however complete conversion of substrates cannot be achieved.

Recently Shen et al. reported quantitative phenol conversion with 100% selectivity for O-methylation using 1-n-butyl-3-methylimidazolium chloride.[168] The reaction is carried out in batch reactor at 393K for 1.5h. In this method residual DMC has to be distilled from the reaction mixture, the products obtained by distillation under reduced pressure.

The traditional methods for synthesis of phenyl ethers suffer a rigorous condition such as the strong base and high temperature via Williamson reaction[169] whereas DMC and methanol is looked upon as very promising greener methylating agents with no waste (mass indexes in the range of 3-6).[170] Section D of Chapter 3 is intended for establishing a heterogeneous, eco-friendly catalyst for *O*-alkylation of phenol keeping in view atom economy. This work along with literature on *O*-alkylation of phenol is reported in this chapter.

1.10. Scope and objective of thesis

In view of the literature discussed in earlier sections for various organic transformations like synthesis of cyclic carbonate, Claisen Schmidth condensation for chalcone and flavanone synthesis, synthesis of alkyl phenyl ethers by *O*-methylation of phenols with DMC and synthesis of carbamates, oxamates and imidazolidine trione derivatives it is evident that there is need to replace conventional reagent/homogeneous/heterogeneous catalyst based systems with new class of hybrid catalyst pertaining to green chemistry principles. These types of catalysts show better activity even at low catalyst loading, good recyclability, with minimal use of solvent and increased product yield and selectivity. Recently use of IL as a catalyst or solvent has been reported widely. Though IL acts as a good solvent and gives improved activity when used as a catalyst for range of organic transformation including those mentioned above, still the cost, viscosity and recovery remains to be the major drawbacks from industrial application point of view. Thus a new class of catalyst system termed as organic-inorganic hybrid catalysts prepared by immobilizing IL on inorganic support has been reported widely as efficient catalyst for these reactions.

These catalysts can be prepared employing methods like co-condensation, grafting/anchoring and encapsulation. Various inorganic supports are already being used as catalyst in industry to accomplish fine chemical synthesis by virtue of their large surface areas, acid/base properties, shape selectivity and cost effective factors. Taking advantage of these properties of support, immobilized catalysts is prepared which showed the synergetic effect imparted due to organic moiety and inorganic support resulting in alteration of acid/base property of final immobilized catalyst. The understanding of this type of catalyst structure is important from activity point of view. Thus various characterization techniques can be explored to understand the changes occurred in final catalyst structure and can be used for explaining the activity imparted for various organic transformations.

Chemical fixation of CO_2 is gaining importance from environmental and economical point of view as value added products like carbonates and carbamates can be synthesized using non hazardous chemicals. These organic carbonates and carbamates can ultimately be used for production of polycarbonates and polyurethane. The synthesis of cyclic carbonates via cycloaddition of CO_2 to epoxides is one of the industrially important routes and also an effective routes for chemical fixation of CO_2. Current methods used for synthesis of cyclic carbonates require the use additional of co-catalysts, solvents, high temperatures and high pressures, along with the use of highly purified CO_2. By now it is well established that the catalyst with Lewis-acid and a Lewis- or Brønsted-base sites are required for activation of epoxides and CO_2. However, there is ample scope for exploiting the use of immobilized catalysts with both Lewis-acid and Lewis-base for this reaction which can utilize waste CO_2 efficiently from a power station or other major fixed site producer and also alters the reaction conditions at or near room temperature and pressure.

Claisen-Schmidt condensation of ketone and benzaldehyde for the synthesis of chalcones, and flavanones is studied widely using acid or base catalysts. Chalcones and flavanones are extensively used in cosmetic and pharmaceutical industry due to its wide range of biological activity. Besides homogeneous catalyst like alkaline hydroxides, sodium ethoxide, liquid acids/bases, ILs, a variety of other solid

acid/base catalysts including hydrotalcites, metal oxides, zeolites are also been reported for this industrially important condensation reaction.

However, the high cost and viscosity makes separation of IL difficult from a high boiling product. Instead the supported ILs as catalyst has been found to be an attractive alternate making this transformation more economical.

Aryl methyl ethers obtained by *O*-methylation of phenols find wide industrial applications in resins, coatings, fragrances, agrochemicals etc. Alkylation of phenol is reported using toxic reagents like DMS and alkyl halides as alkylating agents in liquid phase. Literature survey on this reaction shows use of DMC as an attractive alternative to replace these conventional alkylating agents due to its environmentally benign nature. The catalysts reported for this reaction using DMC as alkylating agent either lack selectivity for O-alkylated product or gives poor phenol conversions. Moreover many of these catalysts are either not suitable for high boiling phenols or showed poor recycling due to lack of appropriate catalyst-product separation methodology. Thus the major challenge for this reaction is to develop efficient heterogeneous catalyst which selectively gives O-alkylated product, with good recycling ability and which can further be used in continuous flow reactor for economical production of aryl methyl ethers.

Carbamates, oxamates and imidazolidine trione derivatives are another class of industrially important compounds. Fewer reports were found in the literature for synthesis of oxamates and imidazolidine trione derivatives. The present route for synthesis of carbamates, oxamates and imidazolidine trione derivatives are not based on green approach. Though now a days carbamate synthesis are reported using CO_2 based routes but there is always scope for exploring new catalyst for its synthesis. While almost all the routes for synthesis of oxamates and imidazolidine trione derivatives use corrosive reagents there is a need to develop efficient catalyst as well as new route that uses milder reagents like urea and oxalate for this reaction. DBTO is explored extensively for transesterification reactions. However there is scope for exploring DBTO for transfunctionalization and cyclization reaction occurring in one pot for selective synthesis of either carbamates and oxamates or imidazolidine trione derivatives.

Accordingly the objective of the present thesis was to synthesize efficient solid catalysts with acid/base properties for application in fine chemical synthesis. Further aim is to synthesize immobilized IL using various immobilization techniques as well as to explore diverse supports like MCM-41, SiO_2, hydrotalcites and montmorillonite clays for immobilization. These synthesized catalysts are aimed to screen various organic transformations like

 1) CO_2 cycloaddition to epoxides,

2) Claisen Schmidth condensation for chalcone and flavanone synthesis,

3) *O*-methylation of phenols with DMC and

4) Synthesis of carbamates, oxamates and imidazolidine trione derivatives.

It was also an objective of this work to use characterization tools to elucidate the catalyst structure and correlate it to the activity shown for these reactions. The work presented in this thesis is intended to develop greener and sustainable methodologies for organic transformations exploiting greener catalytic systems.

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Chapter 2

Synthesis and Characterization of Immobilized Catalyst

2.1. INTRODUCTION

Chemical industry employs both homogeneous and heterogeneous catalysts to make process green. Most of the industrial processes employ heterogeneous catalysts compared to homogeneous counterparts to overcome shortfalls like catalyst separation, recycling, recovery of the often valuable metal and short catalyst lifetimes.

A heterogeneous catalyst needs to meet many requirements to be employed as industrial catalyst like activity, selectivity, lifetime, optimal geometric form and chemical and mechanical stability. Therefore, in the last twenty years or so, attempts are made towards the development of heterogenized homogeneous catalysts (supported catalyst), which are intended to combine the advantages of homogeneous catalysts, in particular high selectivity and activity, with those of heterogeneous catalysts (ease of separation, metal recovery and high surface area).Supported catalysts represent the largest group of heterogeneous catalysts and are of major economic importance, especially in refinery technology and the chemical industry. These catalysts are composed of small amounts of catalytically active materials (viz; metals or homogeneous organic catalyst) supported on the surface of porous, mostly inert solids – the supports. The supports can have special forms such as pellets, rings, extrudates, and granules. These catalysts are also identified as fixed or organic-inorganic hybrid catalyst. Table 2.1 summarizes the important catalyst supports and their industrial applications.[1] Chemical industry prefers use of supported catalysts over heterogeneous catalyst due cost, activity, selectivity and regenerability factors.

Recently a new class of supported catalysts comprising of quaternary ammonium and phosphonium salts, various salen complexes and ionic liquids immobilized on inorganic as well as polymeric supports is gaining importance in view to make industrial processes economical and sustainable. These immobilized catalysts have established their niche beyond doubt. Binding catalytically active species (ionic liquid/ homogeneous catalyst/ metal complex) to supports can be achieved by wide range of methods. This catalyst basically is comprised of organic moiety immobilized/ trapped onto the inorganic component termed as "carrier"/ support. The inorganic components can provide mechanical, thermal, or structural stability, whereas the organic ingredient besides its catalytic activity can introduce flexibility into the framework. In the preceding section a

brief overview of the various methods of immobilization and the properties of various supports are described. These properties can be used to synthesize tailor made immobilized catalysts.

Support	Specific surface area, m^2/g	Applications
Table 2.1. Catalyst supports and their industrial applications		
Alumina		cracking, hydrogenation, dehydrogenation,
γ - Al_2O_3	160–300	metathesis
α- Al_2O_3	5 –10	selective hydrogenation of acetylene; selective oxidation (ethylene oxide)
Aluminosilicates	up to 180	cracking reactions, dehydrations, isomerizations, ammoxidation
Silica SiO_2	200–1000	polymerization, hydrogenation, oxidation, NOx reduction (SCR process)
Titania TiO_2	40–200	TiO_2 on SiO_2: oxidation of o-xylene to phthalic anhydride; V_2O_5/TiO_2 selective oxidation
Activated carbon	600–1200	vinylation with acetylene, selective hydrogenation with noble metal catalysts (fine chemicals)
Corundum ceramic	0.5– 1	selective oxidation (ethylene oxide, benzene to maleic anhydride, o-xylene to phthalic anhydride)
Diatomaceous earth	up to 200	hydrogenation
Clays	50–300	hydrogenation, condensation
Zeolites	300–600	refinery processing, bifunctional catalysis, organic syntheses
Cordierite monoliths		mechanical supports: automotive exhaust gascleaning

2.1.1. Support Materials

Another equally important aspect in the synthesis of immobilized catalyst is the choice of support materials or "carriers". These support materials are expected to show properties like thermal and chemical resistance, a large surface area, a high amount of centers for chemisorption of the catalyst[2] and usually catalytically inactive surface.[3] Since the immobilized/supported catalysts exhibits combine effect of a high dispersion–amount of active surface with enhanced stability; highly porous materials with surface areas of 100

m^2 g^{-1} or more and good availability are preferred as supports. For example γ-Al$_2$O$_3$, SiO$_2$, charcoal, and to a lesser extent TiO$_2$, ZrO$_2$, and Nb$_2$O$_5$.[4]

Among these supports silica is often used as a carrier as it offer good thermal and mechanical stability along with a large number of silanol functionalities that allow bonding of organic molecules. At the same time it usually lacks strongly Lewis-acidic properties that could influence organic reactions[5] (however even the weak Brønsted acidity of a pure silica can catalyze side-reactions).

One of the favored carriers for homogeneous catalyst belongs to MS41 family of mesoporous materials fabricated by micelle templated synthesis (MTS) because of its highly ordered structure. Since its inception in 1992 mesoporous materials has opened up new avenues to varied applications including excellent catalysts for a wide range of reactions themselves.[6,7,8] Distinctively these materials have large surface areas ranging from 500-1500 m^2g^{-1} with well defined pore shapes (hexagonal/cylindrical/cross-linked/zigzag), narrow pore size distribution and large number of silanol (-OH) groups. Prominent examples of these mesoporous silicas are MCM-41 (Mobil Composition of Matter, No. 41), HMS (Hexagonal Mesoporous Silica) and SBA-15 (made at university of California and Santa Barbara).

Some of the unique features of the materials most used as catalyst/ support are illustrated below

I. MCM-41[9,10]- contains a long-range hexagonal framework with uniform pore structure. These need to be synthesized under basic conditions with use of cationic surfactants.

II. HMS[11,12, 13]- is characterized by hexagonal disordered structure. Synthesis is carried out under acidic condition with neutral templates such as amine.

III. SBA-15[14,15]- Neutral polyether tempelating affords other families of mesoporous materials with disordered sponge-like or wormhole-like channel structure with uniform diameters. SBA-15 often used as support is prepared under acidic condition with neutral polyether template like poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block-copolymer and has a two-dimensional hexagonal structure. Other SBA materials include SBA-1 (cubic, acidic conditions, cationic surfactants),[16,17] SBA-3 (2D hexagonal, acidic conditions, cationic surfactants).

IV. MCM-48[18]- having cubic structure with three-dimensional pore system is fabricated with surfactant/silica ratio higher than unity.

V. FSM-16[19]-(Folded Sheet Materials) is a highly ordered mesoporous material with hexagonal array of uniform channels prepared by ion exchange of interlayer Na^+ ions of a layered polysilicate kanemite with alkyltrimethylammonium ions, followed by calcinations.

Further supports that can be functionalized include polysilsesquioxane[20, 21] frames. These are unique family of silicate-like materials with organic rigid-rod spacers inserted at regular intervals into the silicate network. The presence of the bridging organic spacer within the framework is expected to impart the catalytic properties.

The type of assembly in these mesoporous material plays a vital role in their selection as support and its catalytic behavior. These mesoporous materials surely have rich advantages which overdo other supports in performance.

Advantages-

✓ The tunable mesoporosity of these materials facilitates access of substrates to the catalytically active centers thereby minimizing diffusion problems.

✓ Medium sized pores of dimensions ranging from 20 to 100Å in contrast to microporous materials makes them preferred candidate for immobilization approach.

✓ Their main advantage as supports lies in the fact that even when organic groups are grafted onto the inner surface, the pores are still wide enough to allow diffusion of the reactants and products. Amorphous materials on the other hand, always contain a certain amount of micropores that will be blocked by grafted functionalities. [22]

Disadvantages-

✓ The synthesis methodology involves many steps that needs to be followed crucially and is not economic. Once dried some of these materials are moisture sensitive so extra care required for long term storage.

2.1.2. Advantages and Disadvantages of (Organic-inorganic hybrid catalysts) immobilized catalyst

Advantages

✓ Seperation and recovery of the catalyst from the product stream is straight-forward

✓ Multifunctional catalysts can be obtained in which more than one activecomponent

is bound to a carrier.

✓ Stabilization of highly reactive, coordinatively unsaturated species that cannot
exist in solution.

Disadvantages

✓ Insufficient stability of the immobilized homogeneous catalysts due to leaching of
the metal and/or ligand.

✓ Problematic features of homogeneous catalysts, such as corrosion, catalyst recovery,
and catalyst recycling, have so far not been overcome satisfactorily.

✓ Lower catalytic activity than with homogeneous catalyst due to:

- Poor accessibility of the active sites for the substrate.

- Steric effects of the matrix.

- Incompatibility of the solvent and support (in particular polymers).

- Deactivation of the active centers.

- Inhomogeneity due to different linkages between support matrix and complex

Despite the above disadvantages heterogeneous catalysts/ immobilized catalysts are
preferred in the industry taking into account their application for particular process they
are sought for with desired outcome.

2.1.3. Immobilization techniques

A variety of approaches are in practice to obtain a desired immobilized catalyst. With this
tool one can obtain grafted, anchored and impregnated catalysts. The classification of
these methods is based upon the interaction between phases of catalytically active
component and support material. These interactions are mainly classified in two groups
as:

- Liquid-Liquid phase differentiation and

- Solid – liquid phase differentiation

2.1.3.1. Liquid-Liquid phase differentiation (The active component is physisorbed on the support)

*2.1.3.1.1. Biphasic catalysis –*this system represents liquid-liquid systems containing two
immiscible liquids (aqueous, non- aqueous, flourous) governed by solvation forces
without any additional additive. The catalyst can exist in either of the phases facilitating

catalyst product separation. This methodology is employed mostly for exotic homogeneous transition metal catalysts.

2.1.3.1.2. Phase transfer catalysis–This system is not much differentiated from reverse biphasic. Phase-transfer catalysts accelerate reactions of two immiscible reactants. Here in catalyst exist at the boundary of two immiscible phases. Reactants and products have solubility in either of the layers. Vigorous stirring causes droplets and helps catalyst in shuttling of anion or neutral compound from aqueous or solid phase into organic reaction phase or interfacial region. Reaction of anion or neutral compound with the organic reactant occurs in organic phase. After the reaction an anionic leaving group is generated and is brought to the aqueous (or solid) phase by the shuttling catalyst thus facilitating the separation of the waste material from the product. Catalysts with highly lipophilic cation(i. e. have strong affinity for an organic solvent) are appropriate for PTC e.g. quaternary ammonium or phosphonium salts (quats). Neutral complexing agents for organic cations, e. g. crown ethers, polyethylene glycols (PEGs), cryptands, etc., are also suitable catalysts. Open chain PEGs (e. g. PEG 400) are the least expensive catalysts and may be preferable to quats in some processes. In both the above methods stirring speed is the deciding factor for enhanced reaction rate which is also a major drawback.

2.1.3.1.3. Supported liquid phase catalysis (SLPC) – This methodology is a special case of adsorption wherein catalyst is dissolved in suitable solvent of low vapor pressure. This thin film gets adsorbed on hydrophobic ends of the inner surfaces of the support

2.1.3.1.4. Supported aqueous phase catalysis (SAPC) - Here water soluble catalyst is dissolved in a very polar solvent and is adsorbed on a hydrophilic support forming a water film on the inner surface of the support.

The reaction occurs at the interface of supported liquid film or in the supported liquid, or in gas phase or organic phase. These catalysts can be employed only for the synthesis of low – boiling compounds.

2.1.3.2. Solid – liquid phase differentiation

2.1.3.2.1. Impregnation

Several excellent reviews have been published on the impregnation of support catalysts. Extensive studies have been performed by Ertl et al.[23] and Campanati et al.[24] in this area.

During impregnation, the precursor is deposited on the support (typically of high surface area) from a liquid solution, which in most cases is water-based. If the support surface is hydrophobic or if hydrolysis of the support must be avoided, a nonaqueous solution is used.[25]

Impregnation can be sub classified in two types[26]

I. *Capillary Impregnation*

This method is typified by use of previously dried support that is immersed in a solution that is to be impregnated. Typically the operation consists of putting into contact approximately equal amount of the support of a pore volume Vp and the impregnating liquid of volume Vimp (Vp ~ Vimp) so that at the end of the operation no excess solution remains outside of the pore space. This method is therefore also termed as Dry or incipient wetness. The dominant driving force for pore filling is capillary pressure (i.e., fluid mechanical), thus rendering the quality of impregnation insensitive to surface interactions between support and surface precursor that might otherwise limit the overall loading by other methods (e.g., equilibrium adsorption)[27]

This method represents the most widely cited method for synthesis of supported metal oxides.

II. *Diffusional Impregnation*

In case of equilibrium adsorption, diffusional, or ion exchange the support bodies are immersed in a solution of the active precursor and subsequently drained. When a liquid volume larger than the pore volume contacts the support bodies, the dissolved precursor present in the liquid phase out of the support bodies diffuses into the pores of the support, because flow does not proceed by capillary action (Vimp > Vp)

The precursor salt migrates progressively from the solution into the heart of the grains of the support. The driving force at all times is the concentration gradient between the extragranular solution and the advancement front of the soluble precursor in the intragranular solution. The migration time is obviously much longer than for capillary impregnation

2.1.3.2.2. Encapsulation/ Encapsulated catalyst

The term ship-in-a-bottle complex[28] is widely used for these encapsulated catalysts. Herein active component is encapsulated or encaged within the structure of the support.

This method is generally used for the immobilization of metal complexes into zeolites. The first ship-in-a-bottle type of catalyst was synthesized by Romanovsky, and Zakharov and colleagues in 1977.[29] Encapsulation of different metal phthalocyanines and the reactivity of these catalysts were studied by this[30,31] and other research groups. [32,33,34] This technique is further classified into,

I. *Intercalated catalyst* - here a metal complex is introduced between the layers of clay. [35,36,37]

II. *Physical entrapment of catalysts*- in this method the active molecule is added during the synthesis of the solid support.

III. *"Ship in the bottle"-method*- The metal macrocycles is assembeled in the zeolite or modified zeolite cages topologically rather than chemically. The distinct advantage of this method is the trapped metal complexes cannot leave the pores due to steric constraints. In case of the large cages, the metal complexes are free to move about within the confines of the cavities. Reactants can diffuse through these small pore channels that are too narrow to allow leaching of the catalyst. Since these complexes may retain their solution-like activity due to freedom of movement they resemble much to their homogeneous counterpart[38]. The zeolite is also expected to impart shape selectivity to the catalyst. However the high experimental expenditure for catalyst synthesis and steric hindrance due to limited pore sizes limits the use of this catalyst in an industrial process. Yet these catalyst show enhanced stability[39] in comparison to other supported catalysts due to stabilizing effect of zeolite through blocking of bimolecular deactivation pathways (site *isolation effect)*.

2.1.3.2.3. Anchoring /Anchored Catalyst

Anchored catalysts are not much distinguished from grafted ones. A marginal difference exists in the treatment of the catalyst. Campbell [40] has distinguished anchoring from grafting as;

"An anchored catalyst is created by the binding of a species, without substantial change in its structure, to a solid surface. A grafted catalyst is produced when an initial structure bound to the surface is altered considerably by subsequent treatments. Here, the initially bound species is not usually an active catalyst."

Above definition imply that anchoring will necessarily occur before grafting can take place. Anchoring is achieved through deposition involving the formation of a strong (e.g. a covalent) bond between the functional groups (e.g. hydroxyl groups) on the surface of the support and an appropriately selected inorganic or organometallic compound of the active element.[41]

Two different approaches are practiced to effect the anchoring of metal complexes.

I. *The direct reaction of surface hydroxyl groups or functional groups of carrier with reactive ligands.*

This approach, consists of synthesizing first the complex with the desired metal-functionalized ligand ratio which is then directly anchored by covalent bond on support matrices like silica or functional organic polymers,

Functional organic polymers used are like polystyrene, styrenedivinylbenzene co-polymer, polyvinyls,[42] polyacrylates,[43] cellulose[44] modified with $-PPh_2$ & $-NRR'$[45], - CH_3CN[46], $-SH$[47], etc. groups which can bind to the complex.

 To be useful as a catalyst support, the gelular polymers must be swellable, the propensity of which can be controlled by the degree of cross-linking. Polymers can be tailor-made to swell in a particular solvent by appropriate selection of monomer and cross-linking agent. Use of cross linking in the polymer support also afforded flexibility of polymer backbone. Exploiting this technique a series of Rh and Ir complexes anchored on cross-linked polymer support was reported by Grubbs[48] and Collman[49]. Various other groups have studied the effect of crosslinking on the activity of the catalyst. But this subject is out of the scope of this work.

A frequently investigated approach is based on Merrifield's resin, which is a polystyrene polymer.[50] This technique is conveniently applied to commercially available underivatized beaded resins of various types and many polymers (such as polyethylene, polystyrene, polyacrylates, polysaccharides, and many others). The multiplicity of ways in which to functionalize these resins is shown in Scheme 2.1.

Scheme 2.1. Functionalization of Merrifield's resins
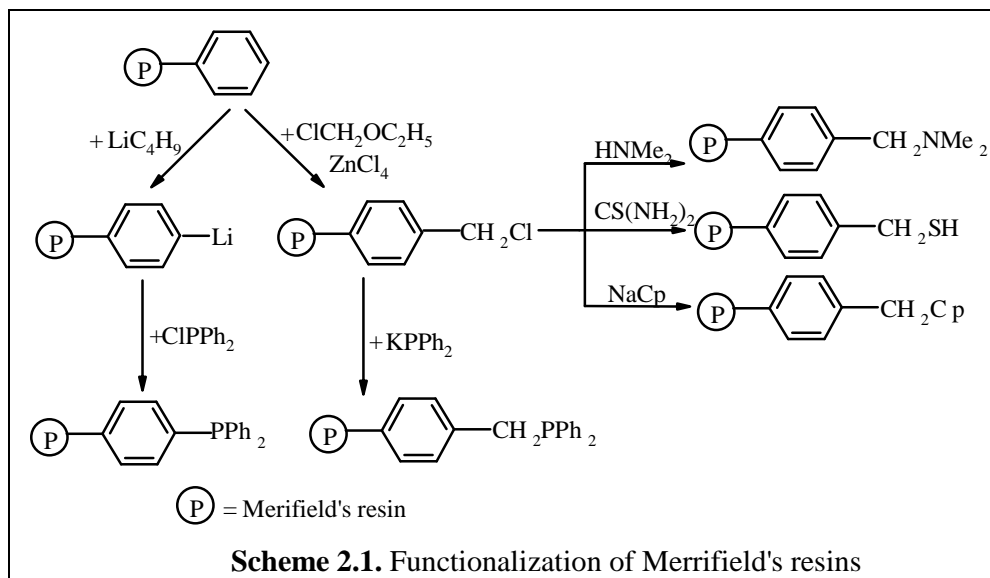
Another approach is the use of ion-exchanged resins. Scheme 2.2 illustrates the principle

Scheme 2.2. Functionalization of ion exchange resin.
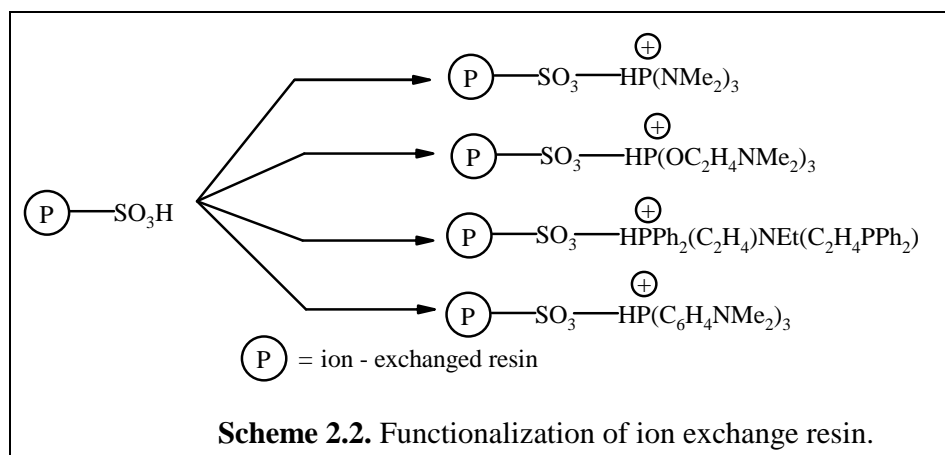
Polymer-supported catalysts often have lower activities than the soluble catalysts because of the intraparticle diffusion resistance.

II. *Functionalizing the surface of support (e.g silica) by reaction between a molecular linker and surface silanol (-OH) that holds the complex.*

The molecular linker chosen is a bifunctional molecule with group X that react easily with hydroxyls by permanent covalent bond; it is generally Cl, $SiCl_3$, $Si(OEt)_3$, OH or $SiR'_2(OR)$ and group Y capable of holding the complex . This methodology has been implied mainly for anchoring of organic complexes to mesoporous supports and silica

since it has been established that unlike polymers, they prevent the intermolecular aggregations of the active surface species because of their rigid structures. This route generates physically heterogeneous catalysts with active sites identical to those of homogeneous systems.[51]

The alkyl chain $(CH_2)_n$ acts as a spacer between the support and the complex. Its length allows for a certain mobility of the complex and a partial release of the steric hindrance induced by the support, but may not exceed a certain length to avoid reactions with neighboring complexes.[52]

From the above discussed methods the catalysts of interest for present study are those prepared by grafting/immobilization of organic functionality on siliceous support.

2.1.4. Immobilization on siliceous support

These classes of organic inorganic hybrid materials are very much sought after by chemist for the tunability factor that can provide tailor-made catalyst assigned for particular application. Noteworthy are the reviews by Valkenberg et al. and Hölderich et al.,[53] Weitkamp et al,[54] Stein et al[55] wherein advances in this field along with application of this class of hybrid catalyst have been surveyed comprehensively. In the case of synthesis of hybrid materials from organic complexes immobilized onto/into inorganic support diverse approaches are followed like

- Grafting method/ Post-synthesis grafting method
- Coating method
- Co-condensation method

Besides organic functionality other essential component of this type of catalyst is silylating agents.

A variety of silylating agents have been employed for derivatization of surface silanols to form Si-O-C, Si-C, Si-O-Si bonds applying grafting technique. This method was developed in 1970s for the chromatography applications by surface modification of silica gels by reacting silanol groups with aliphatic alcohols to form Si-O-C bond. [56,57] But this type of bond is unstable at higher temperature. Alternatively surface silanols can be derivatised using chlorination tool by reacting with thionyl chloride or carbontetrachloride and subsequently reacting with grignards reagent. The Si-C bond

formed by this method is highly stable but this route is not preferred due to hazardous nature of reagents. A new approach involved use of chlorosilanes, alkoxysilanes, and disilylazanes for silylation of silica. In 1970's Kirkland and DeStefano used chlorosilanes for the silylation of silica gels. [58] Even though this method resulted in stable Si-O-Si bond, this approach was not preferred for large scale catalyst preparation due to formation of highly corrosive HCl. On the other hand silylation with alkoxysilanes[59] is getting wide acceptance in developing "cleaner" catalyst due to its ready availability and low toxicity of by-products (see Scheme 2.3).[60]

Scheme 2.3. Silylating agents for surface silylation
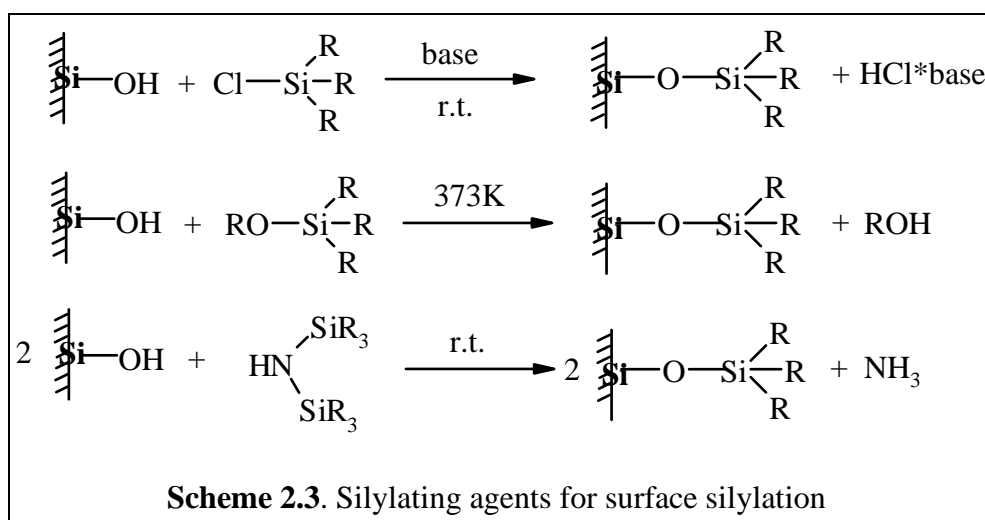
Alkoxysilanes can be bound to surface silanols via one, two or three siloxane bridges. In most of the references a graphical representation of three bridges is reported but NMR studies indicate the preferential formation of two bridges (scheme 2.4). Yet possibility of three siloxane bridges is not ruled out. This finding can be attributed for stearic hinderance caused by silylation procedure. Distribution of number of bridges is influenced by silica microporosity and on details of grafting process like amount of trace water, reaction time, reaction temperature.

Scheme 2.4. Possible siloxane bridge after surface silylation
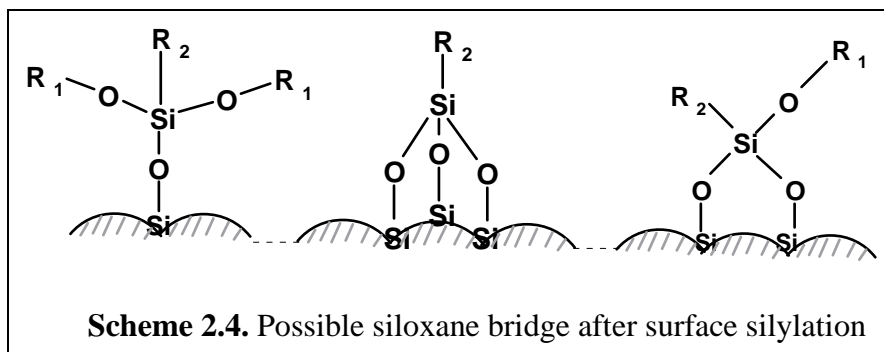
2.1.4.1. Grafting method

Grafting term in context to siliceous support matrices essentially comprise of post-synthesis grafting method. This method is most important method to achieve the formation of a stable covalent bond between an organic molecule and the surface of an inorganic support material by "grafting" of the functional group to the support. Very often the practice is to use organic groups containing alkyl chains as "spacers" between surface of the carrier and the catalytically active group. This allows the active sites to flutter with reactant molecules. Frequently the term anchored catalyst is used synonymously to the grafted and/or tethered catalyst. To avoid confusion some authors[61,62, 63] use the term "grafted catalysts" for metal complexes only when the complex is bound to the surface via the metal itself.

If the complex is bound via the ligand, the term "tethered" is used. Other authors[64,65] use the term grafting also for the immobilization of organic groups by covalent bonds.

2.1.4.1.1 Post synthesis grafting method

In this method a prefabricated mesoporous support/ silica free from surfactant is functionalized at surface silanols by organic molecule through covalent bond. One of the benefits of this method is original structure of the mesoporous support is generally maintained after grafting. Degree of silylation depends upon concentration of free silanols and geminal silanol groups. Whereas hydrogen bonded silanols are less accessible for silylation due to formation of hydrophilic network among themselves.

Post synthesis grafting can be realized by three different routes based upon the nature of organic group.

2.1.4.1.2. Grafting with passive surface groups

This method was developed for tailoring the surfaces of mesoporous solids for the properties like surface hydrophobicity, passivation of surface silanol groups for protection of framework from hydrolysis. This involves grafting of surface silanols with less reactive organic groups such as alkyl chains or phenyl groups. Reduction of pore sizes of MCM-41,[66,67] FSM ,[68,69] type mesoporous silicas was accomplished by this technique using trimethylsilane. Use of varying amount of grafted long-chain silylating agent resulted in tailoring the pore size of ordered mesoporous materials according to the requirement. In comparison to MCM-41, FSM types of material comprise of fewer geminal silanols therefore the amount of silylation in MCM-41 is significant. A systematic study by Zhao and Lu revealed that maximum degree of surface coverage

in MCM-41 employing trimethylchlorosilane was ~ 85 %.[70] From the studies of Tatsumi et al. and Anwander et al. it was observed that sterically less demanding silyl groups resulted in efficient silylation and the concurrent surface hydroxyl consumption. This reflected in improved stability of the material towards moisture and mechanical compression.[71] Multiple functionalization experiments revealed that the grafting rate depended on the steric bulkiness of the silyl groups of the silylamine, with preferential grafting of smaller groups.

2.1.4.1.3. Grafting with Reactive Surface Groups

This method was envisaged for grafting of mesoporous matrices with reactive organic groups wherein further alteration in functionalization was aimed at. A number of reactive silane coupling agents like olefins, nitriles, alkylthiols, alkyl amines, alkyl halides, epoxides, are used depending upon the nature of derivatization required like coordination to metal complexes/metal ions or further transformation of it. A brief description of each group with the functionalization intended is given below.

- Olefins with vinyl groups can be modified by bromination[72] or hydroboration.[73]

- Nitriles can be hydrolyzed to form carboxylic acids, and alkylthiols are oxidized to sulfonic acids,[74,75] which function as electrostatic anchoring points for amino acids.

- Amines can be functionalized by alkylation, nucleophilic aromatic substitution, or by formation of amides or imines.[76]

- Alkyl halides can be functionalized by nucleophilic displacement of the halogen atom.[77]

✓ Where the functionalisation with metal complex is desired, the functional groups like oxiranes, 3-chloropropylsilane, or certain chelating agents are used.

- 3-chloropropylsilane grafted on MCM-41 was used for obtaining MnIII Schiff-base complex known as (Mn-salen) complex.

- 3-trimethoxylsilylpropoxymethyloxirane was reacted with amines for attachment of basic surface group.[78]

- Amine functionalized ligands like ethylenediamine, diethylenetriamine, and ethylenediaminetriacetic acid (EDT) proved to be efficient for complexing of ligands with cobalt centre. [79]

- Amide complexes like yttrium bis(dimethylsilyl) amide was used as anchoring group for chelating complexes .[80]

2.1.4.1.4. Site selective grafting

This technique is usually applied for multiple grafting wherein uncovered areas are left after silylation procedure. Such passivation is done with trimethyl silane which changes the hydrophobicity of the surface. [81,82] In course of grafting it is observed that exterior surface is more accessible for passivation than interior. During reaction exterior functional groups are more easily accessible and can alter the selectivity. Thus strategic blocking by re-silylation can lead to the improved selectivity wherein benefits of pore confinement are reaped.

Shephard et al[83] demonstrated controlled twofold passivation of the external surface of surfactant free MCM-41, using Ph_2SiCl_2 followed by the functionalization of the internal surface using 3-aminopropyltrimethoxysilane (APTS) to anchor redox-active Ru-cluster. Exactly opposite approach was followed by Juan et al[84] by grafting of the external surface of as-synthesized MCM-41 followed by removal of the template. The surfactant filled internal channels of as-synthesized material prevented internal grafting due to stearic hindrance. This externally passivated mesoporous material was then subjected to functionalisation of internal surface forming diverse-functionalized material for desired catalytic application.

2.1.4.2. Coating Method

When a monolayer distribution of surface silanols on the pore surface is desired then the mesopore surface is hydrated with just enough water to regenerate more silanols so as to obtain continuous coats of organosilanes after silylation procedure. The main advantage of this method is creation of high concentration of organics in the product. Excess amount of water can lead to uncontrolled polymerization of the silylation reagents within the channels or external to the mesoporous sieve. Typically anhydrous conditions are needed during silylation to avoid hydrolysis and self condensation and also to preserve hydrophilic portion of the silica surface ensuing even silylation. Feng et al.[85] and van Rhijn et al.[86] reported water controlled coating using mercaptopropyl functions on MCM-41 and HMS materials. In another attractive method known as imprint coating reported by Dai et al. wherein MCM-41 surface was coated with metal complexes followed by removal of metal ions.[87] This leaves the surface grafted with *metal imprinted ligand* ready for complexation with similar metal ions. This methodology is applicable to mesoporous silicas only.

2.1.4.3. Co-condensation method

Co-condensation method or better known as 'one-pot' synthesis is one of the elegant and convenient approach for the synthesis of organic-inorganic hybrid materials in a single step. By using sol-gel technique, a co-condensation involving tetra-alkoxy silane precursor of siliceous framework with organo-alkoxy silane from functional group leads to the formation of organically modified silicas.[88] This in-situ incorporation of organofunctional group in the solid matrix of silica during preparation has also been applied for preparation of ordered mesoporous materials and the process is called micelle templated sol-gel synthesis. This method was developed with the aim to avoid phase separation of the precursors so as to achieve uniform distributions of functional groups and also for preventing Si-C bond cleavage during sol-gel process and during surfactant removal. The most important component of the synthesis mixture is alkoxy-organosilane imparting catalytic properties as it is or by further functionalisation.

Many research groups,[89,90,91,92,93]have attempted co-condensation reactions to prepare hybrid mesoporous silicates under a wide range of reaction conditions. Approaches are classified depending upon the reaction pathway based on the varied nature of surfactant and silica source (ionic/non polar).

- S^+I^- pathway

- $S^+X^-\ I^+$ pathway

- S^0I^0 pathway

- N^0I^0 pathway

- Random multifunctional surfaces

The present work emphasizes on synthesis immobilized catalysts using ionic liquids grafted on various siliceous supports like silica, MCM-41, hydrotalcites and montmorillonite clay. Ionic liquids are widely used as green solvent as well as catalyst to catalyze a number of organic reactions.

2.1.5. Ionic liquid (IL)

The chemical industry is under considerable pressure to replace many of the volatile organic compounds (VOCs) that are currently used as solvents in organic synthesis. The important driving force in the quest for novel reaction media is motivated by need for efficient methods for recycling homogeneous catalysts, waste minimization in chemicals manufacture by substitution of classical 'stoichiometric' syntheses by atom efficient, catalytic alternatives and replacing toxic and/or hazardous solvents, particularly chlorinated hydrocarbons posing serious environmental hazards due to atmospheric emissions and contamination of aqueous effluents. These issues were dealt with by practicing   homogeneous catalysis in aqueous biphasic[94,95] and fluorous biphasic[96] systems as well as in supercritical carbon dioxide.[97] The introduction of ionic liquids as novel reaction media has opened up new avenues as convenient solution to both the solvent emission and the catalyst recycling problem.[98,99] Ionic liquids may be viewed as a new and remarkable class of "green solvents", for its recent applications as solvent for reactions and materials processing, as extraction media or as working fluids in mechanical applications. The rationale for calling them green is generally based on its properties viz;

- Their vapor pressure is generally negligible, and thus inhalative exposure of workers is reduced as compared to conventional molecular solvents.

- They have been shown to be non-flammable, and thus the risk of fast, exothermic oxidations in the case of an accident is strongly reduced; and

- They are claimed to be relatively nontoxic

2.1.5.1. Constitution of ionic liquids [100]

They are commonly known as liquids that are composed entirely of ions with a melting point lower than 373 K (100 °C). The much smaller group of room-temperature ionic liquids (RTILs) exhibit melting points up to 298 K. Often the term ionic liquid and RTILs is used synonymously. The term "neoteric solvent" has been used in recent years to mean new types of solvents, or older materials that are finding new applications as solvents. Supercritical fluids and ionic liquids are good examples of neoteric solvents that have been known for a long time, but are being considered as process solvent.

Room temperature ionic liquids are generally salts of organic cations, *e.g.* tetraalkylammonium, tetraalkylphosphonium, *N*-alkylpyridinium, 1,3-dialkylimidazolium and trialkylsulfonium cations (Scheme 2.5).

First-generation ionic liquids consist of bulky cations such as 1,3-dialkylimidazolium (or N,N'-dialkylimidazolium) or 1-alkylpyridinium (or N-alkylpyridinium), and anions based mostly on haloaluminate(III). The merit of these ionic liquids is their tuneable Lewis acidity depending on the molar ratio of cation to anion. The drawback of these systems is their great sensitivity towards water, which forms hydroxoaluminate(III) species with the aluminium(III) chloride and therefore decomposes the ionic liquid.[101]

Second-generation ionic liquids are usually air-stable and water-stable and can be used on the bench-top. They are composed of 1,3-dialkylimidazolium salts containing a wide variety of anions *e.g.* PF_6, CF_3SO_3, $[CF_3SO_2]_2N$, CF_3CO_2, CH_3CO_2, $PhSO_3$ etc. Recently, a third generation of ''task-specific'' ionic liquids has emerged. Various ammonium cations have been prepared bearing side-chain functionalities (''task-specific ionic liquids'') such as alkene-, [102] alkyne-,[103] ester-, hydroxyl- or chloro-, [104,105] fluoro- [106,107] ether-, [108] sulfonate-, [108] carbonyl-, [109] thiourea-, thioether- and urea-substituents.[110,111] Other anions have also been used, including tricyanomethanide ,[112]

$[Co(CO)_4]^-$,[113], isocyanates and cyanates,[114] $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$,[115] $[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, $[IrCl_6]^{2-}$, [116] $[PdCl_4]^{2-}$,[117], $[AuX_4]^-$,[118] and chiral anions, such as lactate and tartrate.[119] The pioneering work of Seddon,[120] Chauvin and Olivier-Bourbigou[121] and more recently the groups of Welton,[122] Keim and Wasserscheid,[123] made the use of IL popular. They have been employed as novel media for catalytic hydrogenations, hydroformylations, isomerisations, olefin dimerisations, oligomerisations and polymerisations and Heck couplings. Recent reviews by Paˆrvulescu and Hardacre et al., [124] Dyson et al.,[125] Muzart et al.,[126] gives the vivid description and their application for various organic transformations (Figure 2.1).
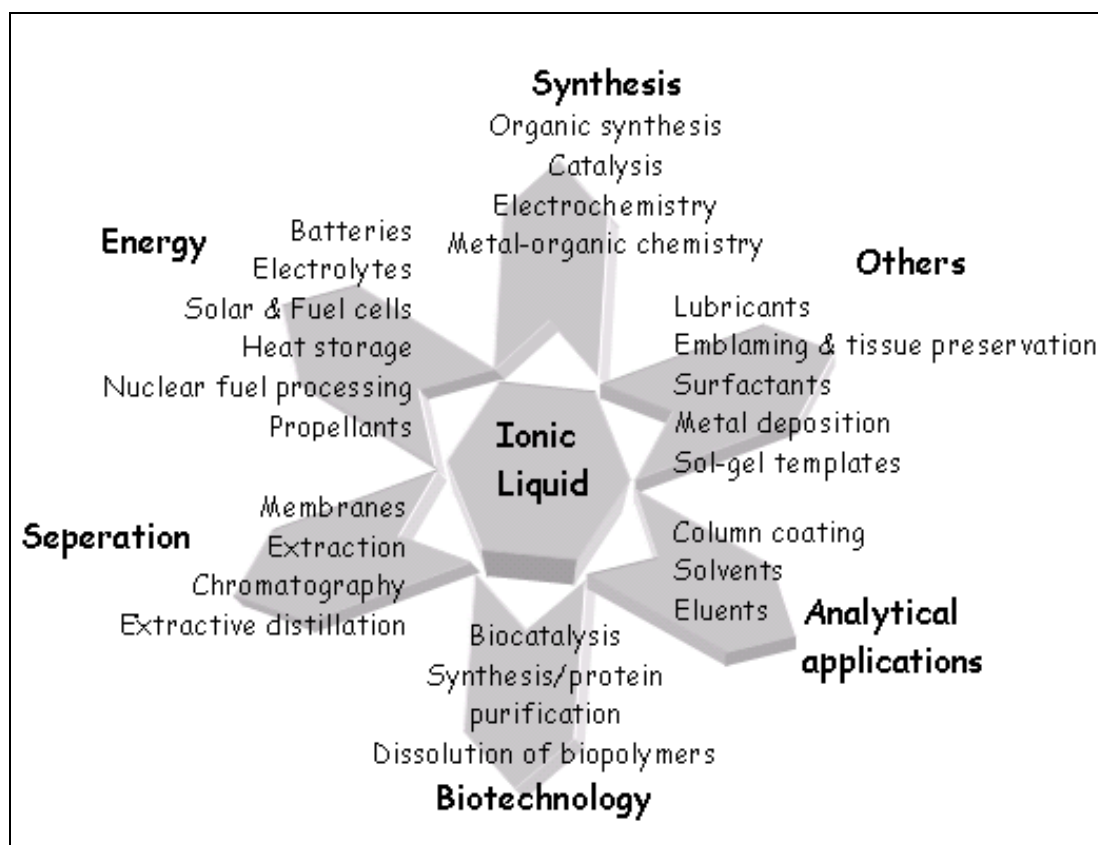
Figure 2.1. Applications of ILs in various fields.

2.1.5.2. History of IL

Formerly IL's were used only for specialized electrochemical applications. Ethylammonium nitrate, which is liquid at room temperature (but usually contains 200–600 ppm water), was first described in 1914.[127] In the late 1940s, *N*-alkylpyridinium chloroaluminates were studied as electrolytes for electroplating aluminium. These systems were further improvised by the groups of Hussey,[128] Osteryoung[129] and Wilkes[130] in the late 1970s. The pioneering work by Wilkes and coworkers resulted in first example of ionic liquids based on dialkylimidazolium cations in the early 1980s. They were composed of chloroaluminate anions ($AlCl_4^-$ or $Al_2Cl_7^-$) and were applied as catalysts/solvents for Friedel–Crafts acylations.[131] But these chloroaluminate ionic liquids are highly water sensitive. Wilkes *et al.* in 1992 reported ethylmethylimidazolium tetrafluoroborate(emimBF$_4$), the first example of IL that created impact in the field of homogeneous catalysis.[132] This was followed by series of 1,3-dialkylimidazolium salts containing a wide variety of anions *e.g.* PF_6, $CF_3SO_3^-$, $[CF_3SO_2]_2N^-$, $CF_3CO_2^-$, $CH_3CO_2^-$, $PhSO_3^-$. These series of IL proved to be much stable than chloroaluminate counterpart.

2.1.5.3. Properties of IL

1. They have essentially no vapour pressure, *i.e.* they do not evaporate and are easy to contain.

2. They generally have reasonable thermal stability. While tetraalkylammonium salts have limited thermal stability, owing to decomposition *via* the Hoffmann elimination, emimBF$_4$ is reportedly stable up to 573K and emim-$(CF_3SO_2)_2N$ up to 673K. [133] In other words many ionic liquids have liquid ranges of more than 573K, compared to the 373K liquid range of water.

3. They are able to dissolve a wide range of organic, inorganic and organometallic compounds.

4. The solubility of gases, *e.g.* H_2, CO and O_2, is generally good which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations, and aerobic oxidations.

5. They are immiscible with some organic solvents, *e.g.* alkanes, and, hence, can be used in two-phase systems. Similarly, lipophilic ionic liquids can be used in aqueous biphasic systems.

6. Polarity and hydrophilicity/lipophilicity can be readily adjusted by a suitable choice of cation/anion (see earlier) and ionic liquids have been referred to as 'designer solvents'.[134]

7. They are often composed of weakly coordinating anions, *e.g.* BF_4^- and PF_6^- and, hence, have the potential to be highly polar yet non-coordinating solvents. They can be expected, therefore, to have a strong rate-enhancing effect on reactions involving cationic intermediates.

8. Ionic liquids containing chloroaluminate ions are strong Lewis, Franklin and Brønsted acids. Protons present in emimAlCl₄ have been shown to be superacidic with Hammett acidities up to 218.23. Such highly acidic ionic liquids are, nonetheless, easily handled and offer potential as non-volatile replacements for hazardous acids such as HF in several acid-catalyzed reactions.

Different types of interactions are present in imidazolium based ILs rendering it with properties like a good catalyst and as a good solvent. These interactions are shown in Figure 2.2[135]
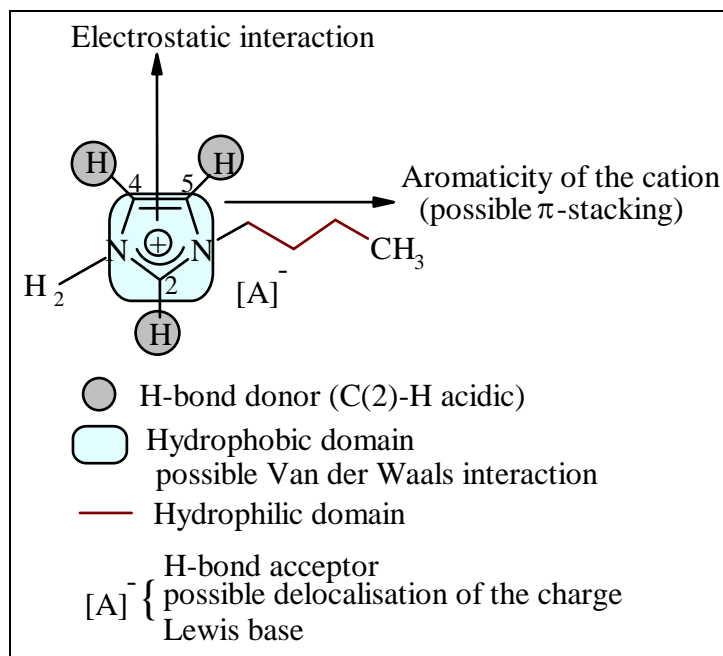
Figure. 2.2. Types of interactions in IL

2.1.5.4. ILs are liquid at room temperature[136]

The negative $\Delta_{fus}G°$ values obtained by calculating the free energies of solvation ($\Delta_{sol}G°$) of each ion in the bulk molten salt using the COSMO solvation model and experimentally determined dielectric constants for all ILs indicate that these salts are liquid at ambient temperatures because the liquid state is thermodynamically favorable under these conditions. This is due to the large size and conformational flexibility of the ions, which leads to small lattice enthalpies and large entropy changes that favor the liquid state.

2.1.5.5. Synthesis of IL

A generalized procedure for synthesis of IL's includes alkylation of 1-methylimidazole by halo alkane. If the chloroalkane is gaseous at room temperature, eg, chloroethane, the alkylation is usually carried out in an autoclave, at autogenous pressures and 363K, without addition of solvent. Higher homologues can be prepared under reflux at atmospheric pressure. The preparation of the 1-alkylpyridinium or 1-alkyl-2,3-dimethylimidazolium derivatives follows the same method, starting from pyridine or 1,2-dimethylimidazole, respectively. This intermediate salt is then either used in a metathetic reaction (ion exchange), where the 1-alkyl-3-methylimidazolium halide (in most cases the chloride) is exchanged with the anion of a Group 1 metal or silver (I) salt. Otherwise, it is treated with an acid, HY. Thus depending on the anion and the cation of choice, a variety of IL can be synthesized ranging from water soluble to water insoluble ones (scheme.2.5.)[137].

2.1.5.6. Commercial availability

The first commercial supply of ILs was started in 1999 by Solvent Innovation.[138] Today, all of the major suppliers of fine chemicals like inter alia, Merck KGaA/EMD Chemicals Inc., Cytec, DuPont, SACHEM, BASF Solvent Innovation, and Acros [139] have entered the market. But still, ILs can be quite expensive, when used as solvent and as task specific ILs requires them to be in pure form.

Most commonly used cations

1 Alkyl-3-methyl imidazolium   *N*-Alkyl pyridinium   *N,N*-Dialkyl piperidinium   Tetraalkyl ammonium   Tetraalkyl phosphonium

N,N-Dialkyl-pyrrolidinium   1,2-Dialkyl-pyrazolium   *N*-Alkyl-thiazolium   Trialkyl-sulfonium

R $_{1,2,3,4}$ = CH$_3$(CH$_2$)$_n$ (n=0, 1, 3, 5, 7, 9); aryl, etc.

Possible anions

water-immiscible ———————————→ water-miscible

[PF$_6$]$^-$ [BF$_4$]$^-$ [CH$_3$COO]$^-$

[NTf$_2$]$^-$ [OTf]$^-$ [CF$_3$COO]$^-$ [NO$_3$]$^-$

[N(CN)$_2$]$^-$ Br$^-$ Cl$^-$ I$^-$

[Al$_2$Cl$_7$]$^-$ [AlCl$_4$]$^-$ (decomp.)

Scheme 2.5. Commonly used cations and anioins for synthesis of ionic liquids.

2.1.5.7. Immobilized IL

In most of the reactions IL is used as reaction media with the purpose of isolation of soluble reaction products. But ironically, for separation of volatile and non- volatile products distillation and solvent extraction respectively are used rendering a few economical and environmental benefits from IL. In this context current focus is on use of supercritical carbon dioxide to extract products from ionic liquids. Another solution for recovery of these costly but catalytically active IL lies in immobilization of these species on inorganic support. Recent advances in this area have resulted in immobilization of IL on various supports with wide application area.[140] In this context the concept referred as "supported IL catalysis", is gaining significance. Mehnert et al. [141, 142] have demonstrated covalently bound imidazolium cations of ILs to the solid phase; catalyze reactions including hydroformylations and hydrogenations.[143] The similar approach was used for

synthesis of supported IL-phase (SILP) catalyst by dissolving a catalyst in a thin IL film that is held on a porous solid by physisorption.[144] These catalysts are preferred for industrial purposes especially for traditional fixed-bed technology. These immobilized IL catalysts employed for this type of technology uses expensive IL/expensive transition metal catalyst dissolved in IL in significantly less amount making their use economical. These approaches bring in synergistic effects of support as well as ILs and also make the removal and recycling of the IL straightforward. Another aspect explored in this work was investigation of altered acid/base sites developed by immobilization of IL on basic support like hydrotalcite and acidic support like montmorillonite clay K5. Hydrotalcites and montmorillonites are already employed as solid base and solid acid catalysts for various organic transformations respectively. Their catalytic properties arise due to their peculiar structural arrangement.

2.2. Hydrotalcite

In recent years hydrotalcites (HT) have received increasing attention in the search for environmentally benign catalysts for base-catalyzed reactions. Replacement of the traditional homogeneous catalysts, such as aqueous KOH, by heterogeneous catalysts could result in the reduction of waste streams, facile separation of the catalyst, and reusability of the catalyst. The catalytic activity of LDHs as well as mixed metal oxides formed by calcination of LDHs have been exploited as basic catalysts in many chemical processes including aldol and Knoevenagel condensation[145,146] Michael addition[147] alkylation[148] and transesterfication[149] at ambient temperature with appreciable rates and selectivity.

Hydrotalcite-like layered double hydroxides (LDHs), belong to a general class called anionic clay minerals. They have synthetic as well as natural origin. The most commonly known naturally occurring hydrotalcite Mg-Al-LDH have chemical formula $Mg_6Al_2(OH)_{16}CO_30.4H_2O$. LDHs are represented by general formula $[M^{2+}_{(1-x)}M^{3+}_{(x)}(OH)_2][A^n]x/n \cdot yH_2O$ where M^{2+} represent divalent cation such as Mg^{2+}, Ca^{2+}, Zn^{2+}, etc and M^{3+} is trivalent cation such as Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, etc in the octahedral sites within the hydroxyl layers and x is equal to the ratio $M^{3+}/(M^{2+} + M^{3+})$ with a value varying in the range of 0.17-0.50. *"A"* is an exchangeable interlayer anion such as Cl^-, CO_3^{2-},

NO_3^-, etc. It is very important that M^{2+} and M^{3+} cations should have ionic radii not too different from 0.65 Å (characteristic of Mg^{2+}) to form a stable structure of hydrotalcite.[150,151,152] The structure of hydrotalcite is analogous to the structure of brucite, $Mg(OH)_2$. A brucite crystal is comprised of a hexagonal close packing of hydroxyl ions with alternate octahedral sites occupied by Mg^{2+} ions. These metal hydroxide sheets are neutral in charge and stacked one upon another with interlayer distance/ basal spacing of about 0.48 nm. Each metal hydroxide sheet is bound to another by Van der Waal's interaction. Whereas in LDH, some of the divalent Mg^{2+} cations of these brucite-like sheets are isomorphously substituted by a trivalent cation such as Al^{3+} and the mixed metal hydroxide layers thus formed acquire a net positive charge. This excess charge on the metal hydroxide layers is compensated by the anions and water molecules accumulated in the interlayer region. Carbonate is the interlayer anion in naturally occurring LDH's. Incorporation of anions and water molecules in the interlayer result in enlargement of the basal spacing from 0.48 nm in brucite to about 0.77 nm in Mg-Al–LDH (figure 2.3).

One of the remarkable property exhibited by LDH is their high reactivity towards various organic anions, which can exchange as much as 80 – 100% of the interlayer anions in LDHs.[153] Many LDH materials show unique phenomenon called 'memory effect', which involves the regeneration of the layered crystalline structure from their calcined form, when the later is dispersed in an aqueous solution containing suitable anion.[154] Mg(Al)O exhibits a unique reconstruction ability provided that the calcination temperature must be low so as to avoid appearance of the spinel phase $MgAl_2O_4$. This reconstructed material is known as "meixnerite" and behaves as Brønsted type catalyst. This reconstruction is realized when calcined hydrotalcites are rehydrated in water or in flowing nitrogen saturated with water (to avoid contamination by CO_3^{2-}). The reconstructed material is more basic than the original hydrotalcite as it contains OH^- ions in the interlayer in contrast to CO_3^{2-} ions in the interlayers of the original hydrotalcite (Figure.2.3).
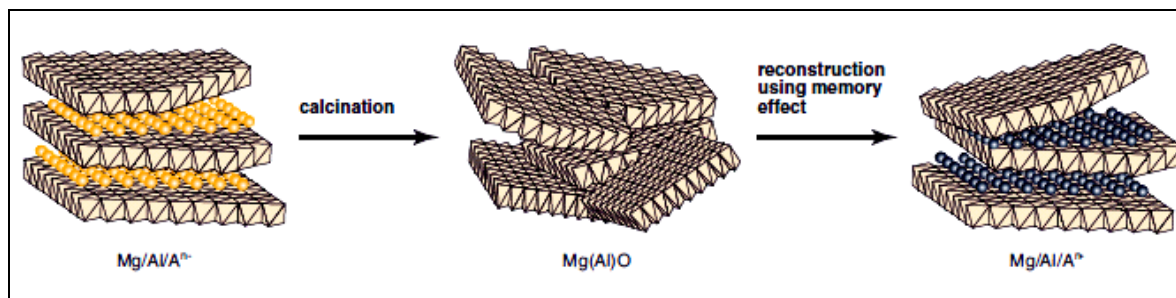
Figure.2.3. Schematic representation of memory effect in Mg/Al HT.[155]

Different methods are well documented in literature for the synthesis of LDHs. Some of these are *co-precipitation method*, *homogeneous precipitation method, ion exchange method* and *hydrothermal crystallization method.*

- In co-precipitation method[156,157,158,159] selected pairs of metal ions are co-precipitated from their aqueous solution by a dilute NaOH or $NaHCO_3$ or Na_2CO_3 or NH_4OH solution. The pH of the reaction medium is maintained in the range of 8 to 10 depending on the nature of the metal ions. The final suspension is subjected to hydrothermal treatment for a long period to obtain well crystallized material.

- Homogeneous precipitation method[160,161,162] provides LDH with a high degree of crystallinity and a narrow distribution of particle size. This method involves hydrolysis of urea. Usually, an aqueous solution of desired metal ions and urea in calculated molar ratio is heated in the temperature range 90ºC to reflux condition for 24 – 36 hours. The urea molecules undergo decomposition producing ammonium carbonate, which finally causes the precipitation of LDH containing CO_3^{2-} as intercalating anion.

- The ion exchange method[163],[164],[165] is formulated on the basis of exchange of interlayer anions present in LDHs by other anionic species. Based on this property, the LDHs containing one type of intercalating anionic species can be synthesized from the LDHs containing another type of intercalating anion. Typically the original LDH is dispersed in an aqueous solution of the desired anionic species and the dispersion is stirred at room temperature for several hours. This exchange is governed by enhanced affinity of some anionic species to the inter gallery region of LDH than the other.

- In Hydrothermal crystallization method the aqueous suspension of $M^{3+}_2O_3$ precursor in presence of a suitable $M^{2+}O$, is pressurized in a vessel at elevated temperature for several days. $M^{2+}O$ function as a crystallizing agent.[166] The precursor $M^{3+}_2O_3$ is an

amorphous hydrated oxide of the trivalent metal component of LDH whereas the crystallizing agent. $M^{2+}O$ are a reactive and basic oxide of the divalent metal component.

2.3. Clay Minerals

In recent years, there has been an increasing interest in utilizing clays such as bentonite, kaolinite, diatomite and fullers earth for their capacity to adsorb not only inorganic but also organic molecules. These clays have emerged as excellent substitute for heterogeneous solid acid catalysts considering their environmentally benign nature.

These clays have substituted the conventional Brønsted acids such as H_2SO_4, HF and HCl which suffer from serious drawbacks such as harmful and highly corrosive nature, difficulty in handling and work up procedure and their disposal. In particular, the clay catalysts have received considerable attention in different organic syntheses because of their environmental compatibility, low cost, high selectivity, reusability and operational simplicity. Among smectite clays, montmorillonite, in natural and exchanged forms, possesses both Lewis and Brønsted acidity that enables it to function as an efficient catalyst in organic transformations.

Many interesting reviews have appeared in the literature on the use of clays in organic synthesis and/or industrial applications.[167,168,169,170,171,172,173]Clay materials show a layered structure that is composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalies and alkali earths. Clays or sheet silicates are hydrous layer silicates composed of basic building blocks of $Si(O,OH)_4$ tetrahedra and $M(O,OH)$, octahedral (M = Al^{3+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, etc), which polymerize to form two-dimensional sheets. Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygens and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygens or hydroxyls. The second unit is built of silica tetrahedrons. The silica tetrahedrons are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition, $Si_4O_6(OH)_4$ (Ralph 1968).[174] Montmorillonite possess alumino-silicate structure consists of two tetrahedral layers sandwiching an octahedral layer and Na^{+1} or Ca^{+2} ions residing in the interlayer. Also other important characteristics shown by montmorillonite clay are largest surface area

and highest cation exchange capacity. Its current market price (about US\$ $0 \cdot 04$–$0 \cdot 12$/kg) is considered to be 20 times cheaper than that of activated carbon.[175]

Clays belong to phyllosilicate family. Depending on the number of available octahedral sites in the structure occupied by cations, and type of cation present (for example Al^{3+} or Mg^{2+}) in the octahedral sheets, clays can be classified into two main groups, viz; two-layered silicates and three-layered silicates.

Two layered silicates such as kaolinite are formed by condensation of $Al(OH)_6$ octahedral sheets with tetrahedral sheets of $Si_2O_3(OH)_2$ i.e 1:1 mineral. In three layered silicates, an octahedral layer is sandwiched between two tetrahedral layers. These clays are industrially important from catalysis point of view. These are further divided into dioctahedral structure and trioctahedral structure. The dioctahedral structure have general formula $Al_2(Si_4O_{10})(OH)_2$ and is electrically neutral structure, wherein only two-third of all the octahedral sites are occupied by Al^{3+}. Whereas in trioctahedral structure Mg^{2+} ions occupy all three such sites in a unit cell and can be represented by general formula $Mg_3(Si_4O_{10})(OH)_2$. When the incoming cation has a lower valence than the outgoing cation the lattice becomes negatively charged and neutrality is maintained by the exchangeable cations. There are several classes of clays classified by the difference in their layered structure such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite.[176] The main electroneutral structures and those obtained by isomorphous substitution of Si^{4+} in the tetrahedral sheet or Al^{3+} or Mg^{2+} in the octahedral sheets (which occur most often) are summarized in Table 2.2.

Table 2.2 Classification of clays [177]				
Group	**Layer type**	**Octahedral occupancy**	**Subgroup**	**Examples**
Serpenite	1:1	tri-	Serpentines	Chrysolite
Kaolinite		di-	Kaolinites	Kaolinite, dickite
Talc	2:1	tri-	Talcs	Talc
Pyrophyllite		di-	Pyrophyllites	Pyrophyllite
Smectite	2:1	tri-	Saponites	Saponite, hectorite
		di-	Montmorillonites	Montmorillonite, Beidellite
Vermiculite	2:1	tri-	Trioctahedral Vermiculite	Trioctahedral Vermiculite
		di-	Dioctahedral Vermiculite	Dioctahedral Vermiculite
Mica	2:1	tri-	Trioctahedral micas	Phlogopite, Biotite
		di-	Dioctahedral micas	Muscovite, Paragonite
Brittle mica	2:1	tri-	Trioctahedral brittle micas	Clintonite
		di-	Dioctahedral brittle micas	Margarite
Sepiolitie	——	tri-	Sepiolities	Sepiolities
Palygorskite		di-	Palygorskites	Palygorskites

In view of the key references discussed in Chapter 1 giving general idea on improvements required for reactions like CO_2 cycloaddition, alkylation of phenol and Claisen-Schmidth condensation it is evident that there is need for developing an efficient, cheaper and corrosion free catalyst system showing enhanced overall catalyst activity and

selectivity of desired product enduring green chemistry goals. With this objective variety of catalyst systems were developed taking into consideration broad applicability of ionic liquids as catalyst. Emphasis was given on economics and recyclability of ionic liquid accordingly heterogenization was conceived as key to this problem.

2.4. Synthesis and characterization of Immobilized IL catalysts

From the various methods of immobilization discussed in previous section post synthesis grafting approach was used herein for synthesis of immobilized IL on various supports. For the heterogenization of pendant IL modified with silylating arm the support material was chosen depending on the desired characteristics in the resulting heterogenized catalyst. Diverse supports like silica, MCM-41, hydrotalcite, and montmorillonite clay were selected for immobilization of modified ionic liquid as representative of their class. Silica was used by virtue of its distinctive properties like thermal stability and availability of large number of free surface silanol groups, whereas MCM-41 was selected due to its surface areas ranging from 500-1500 m^2 g^{-1} with well defined pore shapes, narrow pore size distribution and large number of silanol (-OH) groups. Hydrotalcites and montmorillonite clay was chosen on the basic and acidic properties shown by these materials respectively keeping in view to generate acido-basic nature in the resultant immobilized catalyst. With this aim and the insight gained from literature methods of immobilization, *post-synthesis grafting methodology* was preferred over *co-condensation method* to avoid intricate procedure and for maximum utilization of the silanol groups.

2.4.1 EXPERIMENTAL

2.4.1.1. Materials

1-chlorobutane, N-methyl imidazole, 1-chlorohexane, 1-chlorooctane, 3-chloropropyl-triethoxy-silane, fumed silica, CTAB, TMAOH, were purchased from Aldrich in 99% purity. Montmorillonite clay K5 was purchased from Fluka. Aluminum nitrate, Zinc nitrate and other reagents were purchased from S.D. Fine ltd.

2.4.2.2. Analytical

All the catalysts (homogeneous and immobilized/supported catalyst) synthesized above were characterized by various characterization techniques such as XRD, IR, DRIFT

(Diffuse reflectance infra red Fourier transform spectroscopy), surface area and pore volume measurements, SEM, TEM, TG-DTA, TPR, TPD, ^{29}Si and ^{27}Al and ^{13}C CP Mass NMR. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku Dmax 2500 diffractrometer equipped with graphite monochromatized CuKα radiation (λ=1.5406Å) employing a scanning rate of 2°/min in the 2θ range from 10 to 80°. Nitrogen adsorption–desorption isotherms were measured on Quantachrome Autochem II Chemisorption analyzer. Samples were degassed at 373K for 4 h before the measurements. The specific surface areas were evaluated using Brunauer–Emmett– Teller (BET) method in the P/P0 range of 0.05–0.3. Pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method based on the adsorption branch of the isotherms, and the pore size was reported from the peak position of the distribution curve. The scanning electron microscopy was carried out on a SEM-Leica-440 Electron Microscope. FT-IR spectra were recorded on Perkin-Elmer System 2000 Infrared Spectroscope. The samples were scanned through DRIFT mode in the range between 400 and 4000 cm-1. ^{27}Al and ^{13}C cross polarization magic angle spinning (CPMAS) NMR experiments were carried out on a Bruker Avance 300 wide bore spectrometer equipped with a superconducting magnet with a field of 7.1 Tesla with $Al(NO_3)_3$ and adamantine as internal standards respectively. Similarly ^{29}Si cross polarization magic angle spinning (CPMAS) NMR experiments were carried out on a Bruker Avance 500 wide bore spectrometer with 2,2-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) as internal standard. The operating frequencies for ^{13}C and ^{27}Al were 75.4MHz and 78.17MHz respectively. The samples were packed into a 4mm zirconia rotor and loaded into a 4mm BL MAS probe and spun about the magic angle (54.74) at 10kHz using a standard ramp-CP pulse sequence was used for both the experiments. Typically 10000 scans with a recycle delay of 3s were collected depending on the sensitivity of the sample.

From fundamental point of view, the ultimate goal of catalyst characterization is to examine the surface of the catalyst atom by atom (possibly under reaction conditions). The many aspects that we need to study in order to properly understand catalyst/supported catalysts on a fundamental level include structural properties and kinetic effects. Structural properties of supported catalyst can be studied by physicochemical characterization that aid to reveal structure/morphology of support

surface and support defects, type and site of catalyst promoters (if promoter present), type and site of catalyst poisons, structure of particle-support interface, particle shape and structure of active particle (immobilized catalyst), particle orientation and size. Physicochemical characterizations of catalyst include various characterization methods like spectroscopy, microscopy, diffraction and methods based on adsorption and desorption or reduction or oxidation. The information gathered from these tools help in establishing of empirical relationships between the factors that govern catalyst composition, particle size and shape and pore dimensions on the one hand, and catalytic performance on the other hand. Consequently catalyst characterization is extremely useful in the process of developing an active, selective, stable and mechanically robust catalyst.

Subsequent discussion includes a brief description of theory and principle of various characterization techniques used for catalyst characterization. This is followed by comprehensive interpretation contributing towards the catalyst structure and its role in activity and selectivity displayed for a particular product in the respective chapters.

2.4.2.3. Theory and experimental procedures

2.4.2.3.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) is one of the oldest and most frequently applied techniques in catalyst characterization. It is used to identify crystalline phases inside catalysts by means of lattice structural parameters, and to obtain an indication of particle size. Principle of X-ray diffraction depends on the elastic scattering of X-ray photons by atoms in a periodic lattice. The scattered monochromatic X-rays that are in phase produce constructive interference. The XRD pattern of a powdered sample is measured with a stationary monochromatic X-ray source (usually Cu Kα) and a movable detector, which scans the intensity of the diffracted radiation as a function of the angle 2θ between the incoming and the diffracted beams.

Bragg relationship is used to obtain lattice spacings from the spectra generated by diffraction of X-rays from crystal planes. If the distance between two periodic lattice planes is 'd' and the angle between the incoming X-rays and the normal to the reflecting lattice plane is 'θ' then Bragg's equation is

nλ = 2d sinθ ; n = 1, 2, 3, ... (1)

where λ is the wavelength of the X-rays and *n* is an integer called the order of the reflection. By measuring the angle, 2θ, under which constructively interfering X-rays leave the crystal, the Bragg's equation (1) gives the corresponding lattice spacings, which are characteristic for a particular compound.

The width (shape) of diffraction peaks signifies the dimensions of the reflecting planes. Diffraction lines from perfect crystals are very narrow whereas for crystallite sizes below 100 nm, line broadening occurs due to incomplete destructive interference in scattering directions where the X-rays are out of phase.

The Scherrer formula relates crystal size to line width:

$$\langle L \rangle = \frac{K\,\lambda}{\beta\,cos\,\theta} \qquad ....(2)$$

where < L > is a measure of the dimension of the crystal in the direction perpendicular to the reflecting plane, λ is the X-ray wavelength, β is the peak full width at half maximum (FWHM), θ is the angle between the beam and the normal to the reflecting plane and *K* is a constant (often taken as 1).

2.4.2.3.2. Vibrational spectroscopy (IR and DRIFT)

Infrared spectroscopy is the most common form of vibrational spectroscopy and is the first modern spectroscopic technique to have found general acceptance in catalysis. This technique is applied in catalysis to identify adsorbed species and to study the way in which these species are chemisorbed onto the surface of the catalyst. Probe molecules such as CO and NO are employed to generate the infrared spectra that provide valuable information with regards to the adsorption sites that are present on a catalyst.

Basic principle of vibrational spectroscopy is; molecules possess discrete levels of rotational and vibrational energy. Transitions between vibrational levels occur by absorption of photons with frequency ν in the mid-infrared range. A general selection rule for the absorption of a photon is that the dipole moment of the molecule must change

during the vibration. Not all vibrations can be observed this implies that the absorption of an infrared photon occurs only if a dipole moment changes during the vibration.

Currently, several forms of infrared spectroscopy are in general use in order to get information on the surface chemistry of different solid catalysts. With respect to the characterization of heterogeneous/supported catalysts two techniques largely predominate, namely, the transmission/absorption and the diffuse reflectance techniques. Transmission infrared spectroscopy can be applied if the bulk of the catalyst absorbs weakly. This is usually the case with typical oxide supports for wavenumbers above about 1000 cm^{-1}, whereas carbon-supported catalysts cannot be measured in transmission mode.

In recent years, the use of FT-IR spectroscopy in the diffuse reflectance mode is grown strongly for characterization of strongly scattering materials employed in heterogeneous catalysis. A major advantage of this technique is that the sample can be used as loose powders and the tedious preparation of wafers can be avoided. Kubelka and Munk [178] developed the theory of diffuse reflectance spectra and extended by Kortum et al.[179] According to this theory:

$$f\left(R\infty\right)=\frac{\left(1-R\infty\right)^{2}}{2R\infty}=\frac{K}{S}\ldots\ldots\ldots(3)$$

where R∞ is the reflectivity of a sample of infinite thickness, measured as function of frequency ν, K is the absorption coefficient, a function of ν and S is the scattering coefficient. If the scattering coefficient does not depend on the infrared frequency, the Kubelka-Munk function transforms the measured spectrum R∞ into the absorption spectrum (K). A great advantage of infrared spectroscopy is that the technique can be used to study catalysts under working conditions in the real world or conditions close to that. Several cells for *in situ* investigations have been described in the literature.[180]

2.4.2.3.3. Transition Electron Microscopy[181]

For studying supported catalysts, TEM is the commonly applied form of electron microscopy. Electron microscopy is a technique used to determine the composition and internal structure and size and shape of supported particles. Thus information on morphology, crystallography, and chemical composition is collected by detecting the

characteristic X-rays that are produced by the interaction of the electrons with matter, or by analyzing how the electrons are diffracted.

In TEM, a primary electron beam of high energy between 100 and 400 keV and high intensity passes through a condenser to produce parallel rays, which impinge on the sample. As the attenuation of the beam depends on the density and the thickness, the transmitted electrons form a two-dimensional projection of the sample mass, which is subsequently magnified by the electron optics to produce a so-called bright-field image. The dark-field image is obtained from the diffracted electron beams, which are slightly off-angle from the transmitted beam. Typical operating conditions of a TEM instrument are 100 to 200 keV electrons, 10^{-6} mbar vacuum, 0.3 nm resolutions, and a magnification of 3.10^5 to 10^6.

2.4.2.3.4 Scanning Electron Microscopy

In Scanning electron microscopy (SEM) a narrow electron beam is projected over the surface to give image generated by secondary or backscattered electrons as a function of the position of the primary beam.[181] The secondary electrons have mostly low energies (A5 to 50 eV), and originate from the surface region of the sample. Backscattered electrons come from deeper and carry information on the composition of the sample, because heavy elements are more efficient scatterers and appear brighter in the image. Contrast in the SEM image is caused by orientation of the sample. Parts of the surface facing the detector appear brighter than parts of the surface pointing away from the detector. The main difference between SEM and TEM is that SEM sees contrast due to the topology and composition of a surface, whereas the electron beam in TEM projects all information on the mass it encounters in a two-dimensional image which, however, is of subnanometer resolution.

2.4.2.3.5. Nuclear Magnetic Resonance Spectroscopy

• *Nuclear magnetic resonance (NMR)*

NMR has been recognized for many years as a remarkably powerful technique for investigating the structure and dynamic behaviour of molecules and its value for studying systems of catalytic interest has become increasingly evident It is fully multi-elemental in

its scope since the only requirement for its application is that the element under study has at least one isotope whose nucleus has a magnetic moment.

Nuclear magnetic resonance spectroscopy involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field. When these nuclei with small magnetic field are placed in an external strong magnetic field *Ho*, their magnetic moments tend either to align with field or against the field. When a nucleus is under the influence of the right combination of magnetic field and electromagnetic radiation to flip its spin it is said to be in resonance. The greater the operating frequency of the NMR spectrometer and stronger the magnet the better is the resolution of the spectrum. Commonly, nuclei those exhibiting the NMR phenomenon (have spin quantum numbers greater than zero) are ^{13}C, ^{19}F, ^{31}P, ^{15}N, ^{1}H etc. Two types of NMR spectroscopy are commonly practiced namely ^{1}H NMR and ^{13}C NMR. With ^{1}H NMR technique one can know the number of types of protons and different kinds of environments of the hydrogen atoms in the molecule. Whereas ^{13}C NMR spectroscopy gives the information about the number and nature of carbon atoms present in an organic molecule.

A newer technique called DEPT-NMR *(distortionless enhancement by polarization transfer)* is used to determine the number of hydrogens attached to each carbon.

- *Solid-state NMR (SSNMR)*

Solid-state NMR is another weapon in the arsenal for studying catalysts. In media with no or little mobility (e.g. crystals, powders, large membrane vesicles, molecular aggregates), anisotropic interactions have a substantial influence on the behavior of a system of nuclear spins.In a classical liquid-state NMR experiment, Brownian motion leads to an averaging of anisotropic interactions (directionally dependent). In such cases, these interactions can be neglected on the time-scale of the NMR experiment. On the contrary solid-state NMR (SSNMR) spectroscopy is characterized by the presence of anisotropic interactions.

Chemical shift- is the most important parameter of solid-state NMR spectroscopy; it gives information on the chemical nature of the atoms under study. Chemical shift is caused by the shielding effect of the electron shell and is given by, $\delta = 10^{6} (\gamma - \gamma_{ref})/ \gamma_{0}$; where γ and

γ_{ref} are the resonance frequencies of the sample under observation and of the reference material, respectively, and γ_0 is the spectrometer operating frequency. The anisotropic interactions in solids results in broadening of signal rendered the SSNMR spectra analysis very difficult or even impossible. Introduction of *Magic-angle Spinning* in SSNMR helps to overcome line broadening in the spectra. The line broadening due to chemical shift anisotropy contains the angular term $3\cos\theta$-1, which becomes zero at magic angle ($\theta = 54.7^o$).[182]

Magic-angle Spinning- It has already been mentioned that rapid molecular motion, as in liquids, causes line narrowing by averaging out the dipolar broadening and the chemical shift anisotropy. Magic-angle spinning (MAS) is a technique which, in effect, provides a substitute for this molecular motion in solids and thereby allows direct observation of the isotropic chemical shift. *MAS* removes dipolar interactions by introducing motion of the spin vectors around the magnetic field. In order to obtain a true high-resolution spectrum, therefore, *MAS* must also be applied. While the latter allows decoupling of interactions in spin space

Cross-polarization (CP)-This concept was first reported by Waugh and co-workers[183], in that it allows transfer of magnetization from the abundant species I, to the rare species S. The benefits of this are an intensity enhancement of the S signal by a factor of γ_I / γ_S *(ie.,* a factor 4 for ^{1}H-^{13}C) and a reduction in the waiting time between experiments since the rate-determining relaxation time is now that of the *I* species, rather than the *S* species which tends to be very much longer than that of the *I.* Advantage of *CP* studies is that it provides motional information and is employed to improve the sensitivity (the signal to noise ratio) of the spectra of nuclei with low natural abundance (for instance ^{13}C, ^{29}Si).[184] Solid-state ^{13}C NMR in combination with MAS and CP techniques gives high quality resolved spectra. The combination of ^{29}Si and ^{13}C NMR can be used as a means to examine ^{29}Si nuclei at the surface relative to those in the bulk material and to identify chemically bound species on SiO_2, respectively. An obvious area of application of this technique lies in the chemistry of SiO_2-supported catalysts. The results reported in this thesis on ^{29}Si, ^{27}Al and ^{13}C CPMAS (cross polarization magic angle spinning) NMR measurements were carried out with MSL Bruker spectrometer operating at 75.15 MHz on solid catalysts.

2.4.2.3.6. Surface area determination by BET Method

The BET (Brunauer-Emmett-Teller) method is the most widely employed procedure to determine the surface area of the solid materials. During the thirties Brunauer, Emmett, and Teller[185] presented a theory dealing with the multilayer adsorption of gases on solids. They assumed that the first layer of gas molecules is adsorbed more strongly than subsequent layers, and that the heat of adsorption of subsequent layers is constant. The total surface area is calculated from the amount of physical adsorption of nitrogen at 77 K. With physical adsorption the amount of gas adsorbed is usually plotted as a function of the relative pressure that is the pressure divided by the saturation pressure at the same temperature. From the surface area of one molecule adsorbed in the monolayer the total surface area can be calculated; this has become known as the BET surface area after Brunauer, Emmett and Teller. Nitrogen is usually employed as adsorbate, but measurements have also been obtained with argon and xenon.

By using the BET equation (4):

$$\frac{P}{V_a(P_0-P)} = \frac{1}{V_0\chi} + \frac{(x-1)P}{\chi V_0 P_0} \equiv \eta + \alpha\frac{P}{P_0} \quad\ldots\ldots\ldots\ldots\ldots(4)$$

Where,

P = adsorption equilibrium pressure,

P_0 = standard vapor pressure of the adsorbate,

V_a = volume at STP occupied by molecules adsorbed at pressure P,

V_0 = volume of adsorbate required for a monolayer coverage,

χ = constant related to heat of adsorption.

Plotting $P/[V_a(P-P_0)]$ versus P/P_0 yields a straight line with a slope $\alpha = (\chi-1)/\chi V_0$, crossing the y-axis at $\eta = 1/\chi V_0$. The volume adsorbed in the first monolayer is found as $Vo=1/(\alpha+\eta)$. The volume V_0 can be converted into the number of molecules adsorbed by $N_0= PV_0/RT$ and if we know how big an area occupies by each molecule (A_0) then the total area, $A = N_0A_0$, can be found. For N_2 molecule $A_0 = 0.16nm^2$.

The t-plot analysis was developed by Lippens and de Boer to differentiate pore shapes (micro, meso, macro). This was further developed by De Boer in five different hysteresis loops and related the different loops to more detailed pore shapes.

By plotting the volume of the adsorbate as a function of the statistical film thickness, t of the adsorbed layer leads to a straight line, the t-plot. The slope of the t-plot represents the surface area of the material. The pore size distribution is obtained from the analysis of the desorption isotherms by applying the BJH model[186] which involves the area of the pore walls and uses the Kelvin equation to correlate the partial pressure of nitrogen in equilibrium with the porous solid to the size of the pores where the capillary condensation takes place.

2.4.2.4. Preparation of Catalysts

2.4.2.4.1. Synthesis of Ionic liquids

2.4.2.4.1.1. Synthesis of (1-butyl-3-methyl imidazolium) chloride (IL1) (scheme2.6)

Various ionic liquids reported here were prepared according to literature procedure.[187] In a typical synthesis a solution of 1-chlorobutane (108 mmol) and N-methyl imidazole (108 mmol) was refluxed in round bottom flask at 343K for 24 h under inert atmosphere. After 24 h the reaction mixture showed two distinct layers. The upper layer containing unreacted starting material was decanted and bottom layer was extracted with ethyl acetate (a volume approximately equal to half that of bottom layer). This procedure was repeated thrice. Washing with ethyl acetate should suffice to remove any untreated starting material from bottom phase. The remaining solvent from crude ionic liquid was distilled off on rotavacc and the product was dried under high vacuum. Dried IL1 showed slightly yellow appearance and crystallizes at room temperature.

N-methyl imidazole   1-chlorobutane   1-butyl-3-methyl imidazolium chloride

Scheme 2.6. Synthesis of imidazoliun based IL
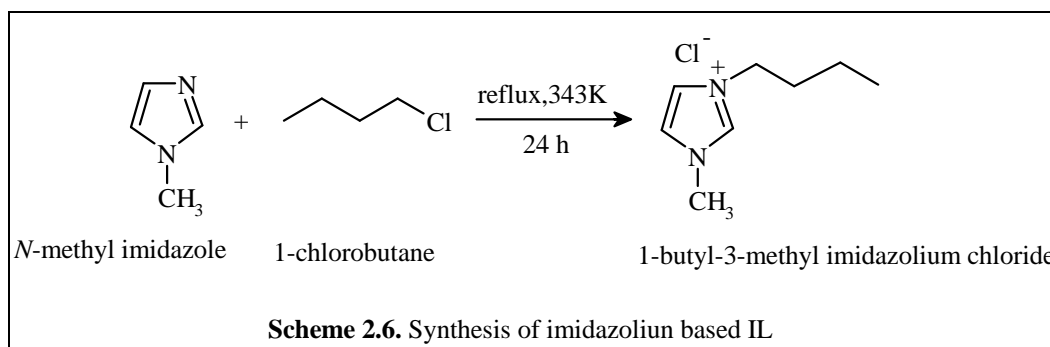
2.4.2.4.1.2. Synthesis of (1-hexyl-3-methyl imidazolium) chloride (IL 2)

A similar procedure described in section 2.8.2.1a was applied for the synthesis of *(1-hexyl-3-methyl imidazolium) chloride* by replacing 1-chlorobutane with 108 mmol of 1-chlorohexane.

2.4.2.4.1.3. Synthesis of (1-octyl-3-methyl imidazolium) chloride (IL 3)

For synthesis of *(1-octyl-3-methyl imidazolium) chloride a* solution of 1-chlorooctane (108 mmol) and N-methyl imidazole (108 mol) was refluxed in round bottom flask under the conditions described in section 2.8.2.1a.

2.4.2.4.2. Synthesis of IL Immobilized catalyst by various methods of immobilization

Ionic liquid immobilized catalysts were prepared by each of grafting[188] and impregnation[189] methods on flash chromatography silica support.

2.4.2.2.2.1. Synthesis of immobilized catalyst by diffusional Impregnation method (^{Imb}CAT-1)

In this method 1.7 g i.e. 9.7 mmoles(1-butyl-3-methyl imidazolium) chloride (IL1) was dissolved in 15 ml deionised water. 10 g of flash chromatography silica which was degassed prior at 573K in vacuum for 6 h was added to clear solution of IL1 and stirred. Excess of water was evaporated on rotavacc and the resulting solid was further dried under vacuum (10^{-2} torr) at 323K for 12 h. This free flowing catalyst is designated as ^{Imb}CAT-1.

2.4.2.4.2.2. Synthesis of immobilized catalyst by capillary impregnation method (^{Imb}CAT-2)

In the second method 10g (57 moles) IL1 was added to 5 g of flash chromatography silica which was degassed at 573K in vacuum for 6 h prior to use, till it lost the appearance of dry powder.

2.4.2.4.2.3. *Grafting method*

2.4.2.4.2.3.1 *Synthesis of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium* chloride (TESPMimCl)(CAT 3)

In a round bottomed flask equipped with a reflux condenser mixture of 1-methyl imidazole (250 mmol) and 3-chloropropyl-triethoxy-silane (250 mmol) were stirred at 373K for 30 h under inert atmosphere. The dense yellowish product was extracted twice with diethyl ether and dried under high vacuum at 353K **(step-1, scheme 2.7)**

Scheme 2.7. Synthesis and grafting of TESPMimCl on silica.
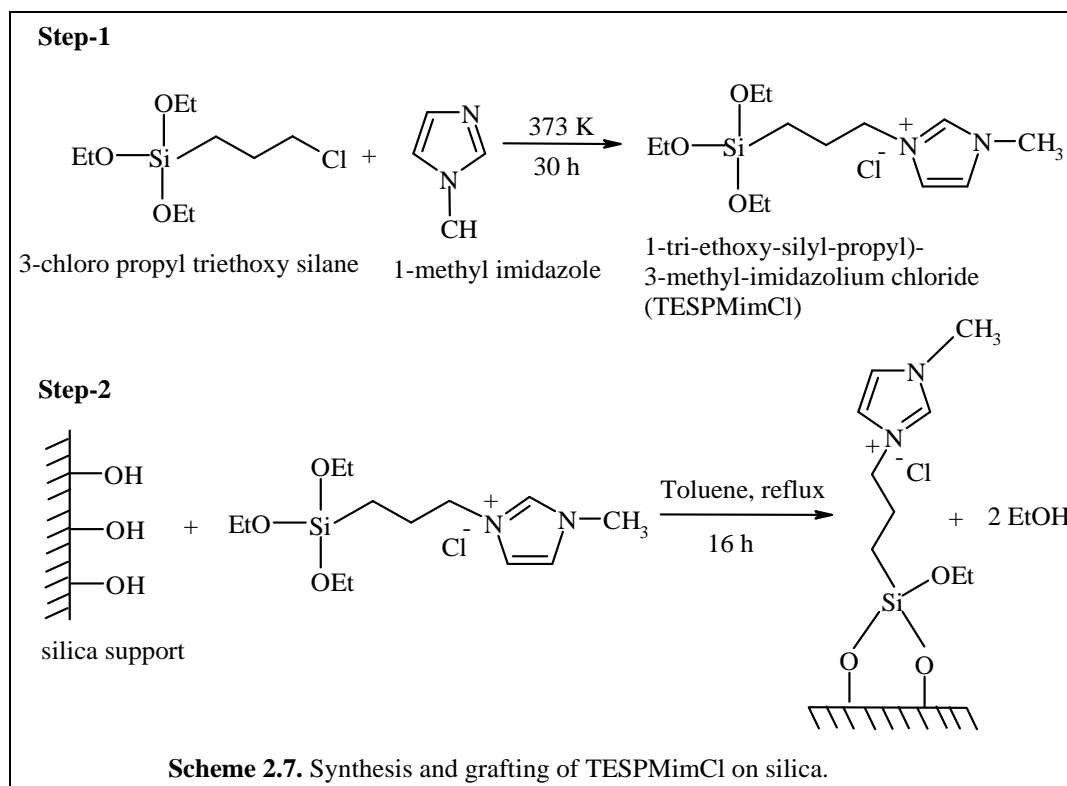
2.4.2.4.2.3.2. Immobilization of CAT 3 on various supports

2.4.2.4.2.3.2.1.   *Immobilization   of   1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride* (TESPMimCl) *on silica support:* ([Imb]35%CAT-3a)

Flash chromatographic silica support 6g; calcined at 823K for 3 h was dispersed in dry toluene   in   a   distillation   apparatus.   3.23g   1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (CAT 3) was added to this mixture and stirred at reflux temperature for 16 h. The solvent and ethanol formed during grafting step were distilled off, solid catalyst dried under high vacuum. Solid catalyst was then subjected to soxhlet extraction in boiling dichloromethane so as to remove excess of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride **(step-2, scheme 2.7).**

Similarly **[Imb]15%CAT-3a** and **[Imb]75%CAT-3a** were synthesized by taking into consideration proper weights corresponding to their percentages (see Table 2.3). A visual presentation of grafting of CAT 3 on silica support is given in scheme 2.8.

Table 2.3. Details of % loading of CAT-3 on 6g silica

Entry	CAT-3 loading, %	CAT-3, g
1	15	1.05
2	35	3.23
3	75	18

Scheme 2.8. Schematic representation of grafting of TESPMimCl on silica
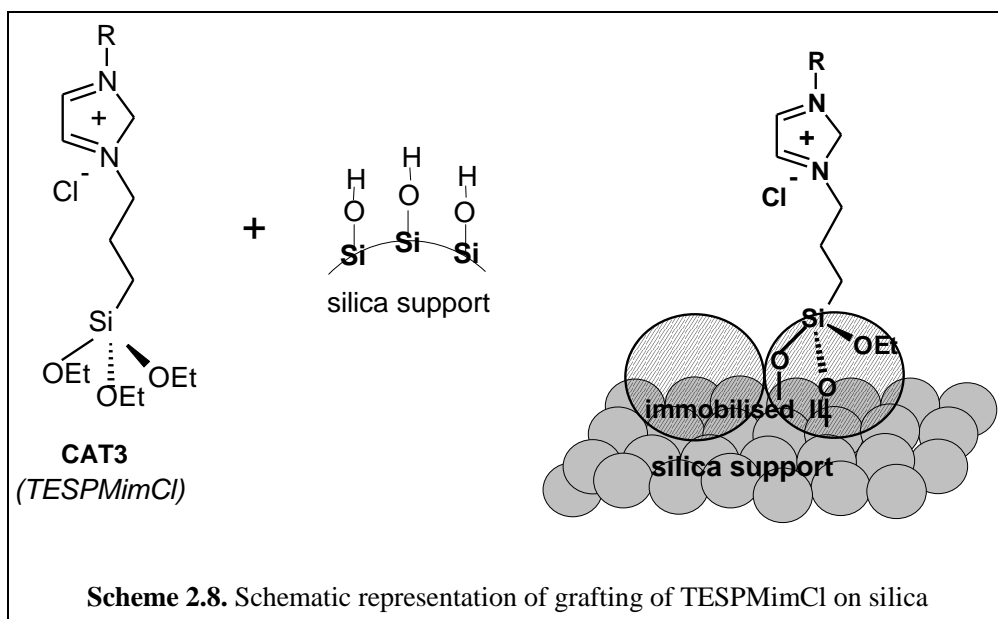
2.4.2.4.2.3.2.2. Synthesis of MCM-41 (CAT-4)

A MCM-41 sample was prepared from fumed silica by using the procedure outlined by Klinowski et al.[29] A solution containing 11.7 g of TMAOH (25% in H_2O) and 16.40 g of CTABr was added to 125 ml of deionized H_2O with stirring at 318K until the surfactant dissolved. To this solution was added 10.0 g of fumed silica (99.8%, Aldrich) to bring the reaction stoichiometry to the following molar ratios: 1.00 SiO_2: 0.19 TMAOH: 0.28 CTAB: 53 H_2O. The mixture was stirred for 2 h, aged statically at 293K for 24 h, and then heated statically in a teflon-lined stainless steel autoclave at 423K under autogenous pressure for 48 h. The solid product was recovered by filtration, washed with copious amounts of H_2O, air-dried at 298K for 24 h, and calcined at 813K for 8 h in air to remove the surfactant and cross-link the framework.

2.4.2.4.2.3.2.3. Immobilization of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESPMimCl) on MCM-41 support: ([Imb]35%CAT-3b)

6g MCM-41 synthesized according to above procedure (2.8.4.2b) was dispersed in dry toluene in a distillation apparatus.3.23g 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (CAT 3) was added to this mixture and stirred at reflux temperature for 16 h. The solvent and ethanol formed during grafting step were distilled off, solid catalyst dried under high vacuum. Solid catalyst was then subjected to soxhlet extraction in boiling dichloromethane so as to remove excess of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride.

2.4.2.4.2.3.2.4. Immobilization of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESPMimCl) on montmorillonite clay support: ([Imb]35%CAT-3c)

6 g Montmorillonite clay K 5; dried at 393K for 12 h under vaccum was dispersed in dry toluene in a distillation apparatus.3.23g 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (CAT 3) was added to this mixture and stirred at reflux temperature for 16 h. The solvent was distilled off, solid catalyst dried under high vacuum. Solid catalyst was then subjected to soxhlet extraction in boiling dichloromethane so as to remove excess of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride.

2.4.2.4.2.3.2.5. Preparation of Zn-Al hydrotalcite (Zn to Al ratio 6): (CAT 5)

Solution-A, containing aluminum nitrate nonahydrate 7.50g (20 mmol) and Zinc nitrate 35.696g (120mmol) dissolved in 100 ml of distilled water and solution-B, containing sodium hydroxide 6.44g (161 mmol) and sodium carbonate 1.58g (15 mmol) dissolved in 100 ml of distilled water were prepared. Both the solutions were added simultaneously drop wise into a 500ml beaker containing 100ml of distilled water with vigorous stirring for 0.5-0.75h and pH of the solution was maintained in the range of 10-11. After completion of addition, the mixture was kept for ageing at 338K without stirring for 18h. The solid mass was filtered and more washings of distilled water was given until washings were free of alkali. The white solid was dried at 383K for 12h. This white solid was calcined at 873K in air for 6h to obtain Zn-Al calcined hydrotalcite denoted by Zn-

Al (6) CHTlc. Similarly Zn-Al hydrotalcites of ratio x=3 was synthesized. These catalysts will be referred as CAT 6.

2.4.2.4.2.3.2.6. Immobilization of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESPMimCl) on Zn-Al (6) CHTlc support: ([Imb]35%CAT-5a (cal))

Functionalized CHTlc materials were then prepared by one-pot impregnation method. For this purpose Zn-Al (6) CHTlc support 0.305gm; was taken in a round bottom flask equipped with a reflux condenser and provision for argon flushing. To this flask, CAT 3; 0.106 gm was added followed by addition of dry toluene and the content were stirred at reflux temperature for 16h under argon atmosphere. The solvent was then distilled off on a rotary evaporator in order to evenly coat CAT 3 on CHTlc. The solid catalyst thus obtained was dried under high vacuum and kept in oven overnight at about 373K to give [Imb]*35% CAT 5a*. In a similar manner various amounts of CAT-3 2.06 %, 4.2 %, 8.5 %, 17.5 % on Zn-Al (6) CHTlc were immobilized (see Table 2.4). Various immobilized catalysts were synthesized by immobilizing CAT 3 on different supports e.g. 35% CAT 3 on Na-X, 35 % CAT 3 on Na-Y, 35 % CAT 3 on Zn-Al (3) CHTlc. These catalysts are denoted as **[Imb]35% *CAT NaX*,** **[Imb]35% *CAT NaY*** and **[Imb]35% *CAT-5c (cal)*** respectively. Employing above procedure 35 % of CAT 3 was loaded on Zn-Al (6) HTlc (**[Imb]35%CAT-5b).**

Table 2.4. Details of % loading of CAT-3 on 100g HTlc

Catalyst	CAT-3 loading, %	CAT-3, g
[Imb]2% CAT 5a	2.06	2.0
[Imb]4% CAT 5a	4.2	4.4
[Imb]8% CAT 5a	8.5	9.4
[Imb]17.5% CAT 5a	17.5	21
[Imb]35% CAT 5a	35	53
[Imb]35% CAT NaX	35	53
[Imb]35% CAT NaY	35	53
[Imb]35% *CAT-5b*	35	53

2.4.2.4.2.3.2.7. Synthesis of 1-(tri-ethoxy-silyl-propyl)-pyridinium chloride (TESPPyCl):
(CAT 6)

In a round bottomed flask equipped with a reflux condenser mixture of pyridine
(0.25mol) and 3-chloropropyl-triethoxy-silane (0.25mol) were stirred at 373K for 30 h
under inert atmosphere. The dense yellowish red product was extracted twice with ethyl
acetate and dried under high vacuum at 353K temperature. **(scheme 2.8.)**

2.4.2.4.2.3.2.8. Immobilization of 1-(tri-ethoxy-silyl-propyl)-pyridinium chloride on silica
  (^{Imb}35%CAT-6a)

Flash chromatographic silica support 6g; calcined at 823K for 3h was dispersed in dry
toluene in a distillation apparatus. 3.23g 1-(tri-ethoxy-silyl-propyl)-pyridinium chloride
(CAT 6) was added to this mixture and stirred at reflux temperature for 16 h. The solvent
and ethanol formed during grafting step were distilled off, solid catalyst dried under high
vacuum. Solid catalyst was then subjected to soxhlet extraction in boiling
dichloromethane so as to remove excess of 1-(tri-ethoxy-silyl-propyl)-pyridinium
chloride (scheme 2.9.).

Scheme 2.9. Synthesis and grafting of TESPPyCl on silica
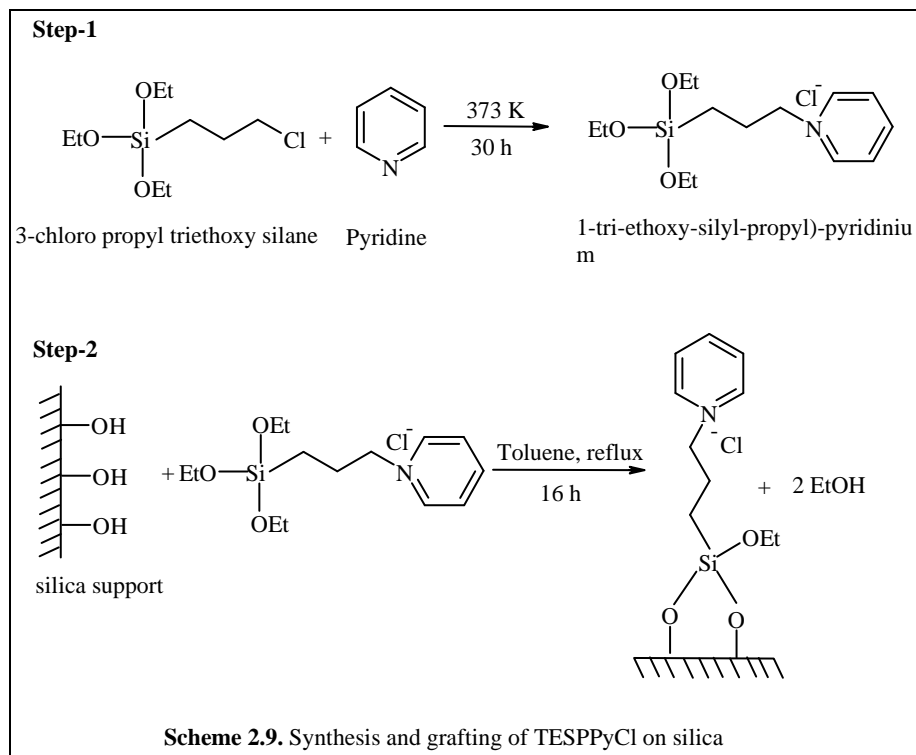
2.4.2.4.2.3.2.9. Quaternization of 3-(1-Imidazol-1-yl) propyl-functionalised silica gel with n-butyl chloride ([Imb]22%CAT-7)

5 g of 3-(1-Imidazol-1-yl) propyl-functionalised silica gel Aldrich make was dispersed in 25cc round bottom flask containing 10 g (108 mmoles) of n-butyl chloride. This heterogeneous mixture was refluxed at 350K under argon atmosphere for 24 h. After 24 h the reaction mixture was filtered on gooch crucible no.2 and washed with dry toluene. This catalyst was dried in oven at 398K prior to use (Scheme 2.10).

Scheme 2.10. Synthesis and grafting of 3-(1-Imidazol-1-yl) propyl functionalised silica gel quaternized with n-butyl chloride on silica
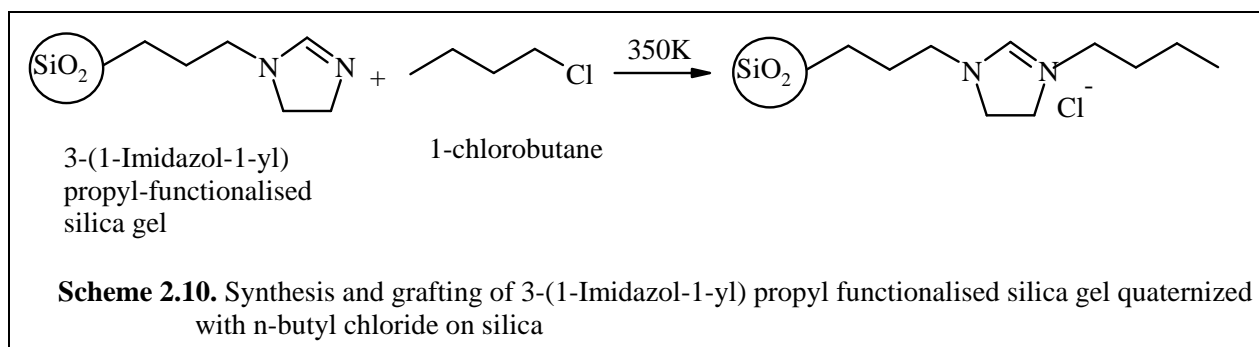
2.4.2.4.2.4. BSTFA treatment of CAT 3 immobilised on silica

N,O-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) is known to quench acidic H from the substrate.[190] It was observed that support plays important role in enhancing the activity of catalyst. Therefore to verify the role of silanol groups of silica the preformed catalyst were treated with BSTFA. In a typical procedure 3 g of preformed catalyst (i.e. **[Imb]15%CAT-3a)** was stirred for 6 h at ambient temperature with 5-7ml of BSTFA in a round bottom flask equipped with a cooling condenser. This procedure was carried out under inert atmosphere to avoid atmospheric moisture from deactivating BSTFA. The unreacted BSTFA was recovered and catalyst thus formed was then filtered through sartorius 393-grade filter paper and washed with copious amount of dry toluene to remove excess of BSTFA adhered to catalyst. These catalysts were then subjected to soxhlet extraction in dry toluene for 12 h and dried in oven at 398K prior to use. Similar procedure was followed for modifying **[Imb]35%CAT-3a** and **[Imb]75%CAT-3a** with BSTFA. These catalysts are designated for differentiation from virgin catalysts as BSTFA **[Imb]15%CAT-3a**, BSTFA **[Imb]35%CAT-3a** and BSTFA **[Imb]75%CAT-3a.**

2.4.2.5. Physicochemical characterization of catalysts

2.4.2.5.1. Characterization of (1-butyl-3-methyl imidazolium) chloride (IL1)
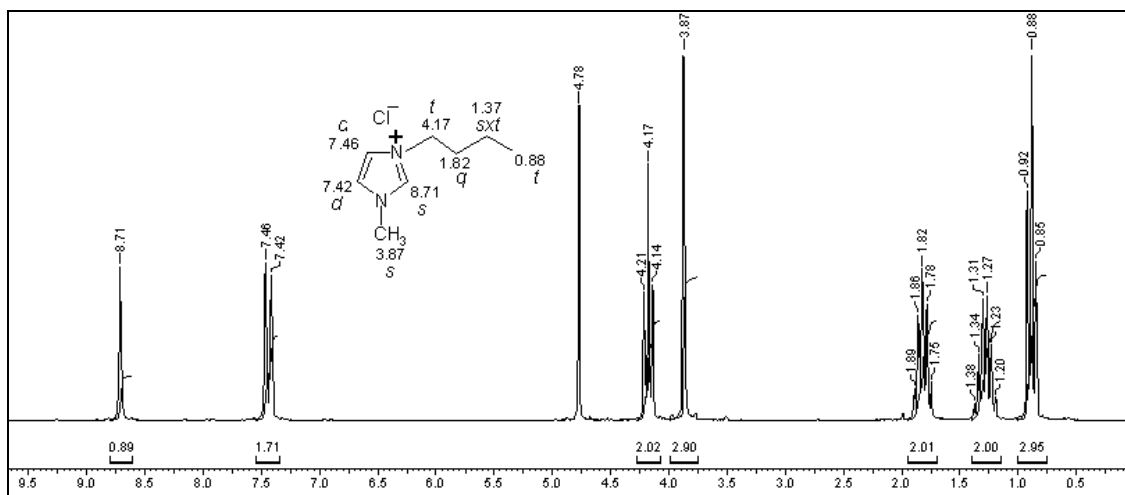
Spectra 2.1. ^{1}H NMR spectra of [C$_4$mim][Cl] (D$_2$O, ppm) consisting of the following peaks: δ 0.88 (t, 3H, J=7.07Hz, CH$_3$), 1.37 (sextet, 2H, J=7.08Hz, CH$_2$), 1.82 (q, 2H, J=7.08Hz, CH$_2$), 3.87 (s, 3H, CH$_3$), 4.17 (t, 2H, J=7.08Hz, CH$_2$), 8.71 (s, 1H, Ar-CH), 7.46 (d, 1H, J= 9.2 Hz, Ar-CH), 7.42 (d, 1H, J= 9.2 Hz, Ar-CH).

2.4.2.5.2. Characterization of(1-hexyl-3-methyl imidazolium) chloride (IL2)
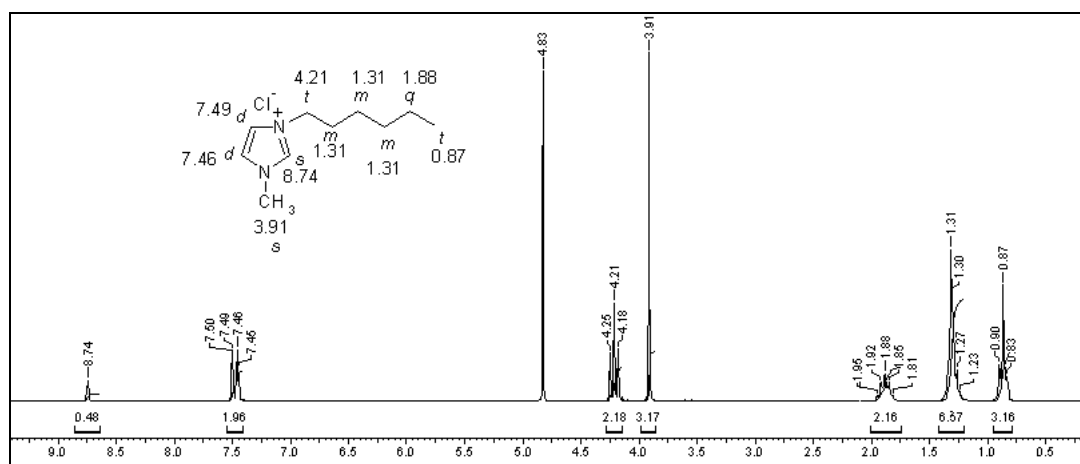
Spectra 2.2. ^{1}H NMR spectra of [C$_6$mim][Cl] (D$_2$O, ppm) consisting of the following peaks: δ 0.87 (t, 3H, J=6.95 Hz, CH$_3$), 1.31 (m, 6H, J=7.08Hz, CH$_2$), 1.88 (q, 2H, J=6.95 Hz, CH$_2$), 3.91 (s, 3H, CH$_3$), 4.21 (t, 2H, J=7.08Hz, CH$_2$), 8.74 (s, 1H, Ar-CH), 7.46 (d, 1H, J= 9.2 Hz, Ar-CH), 7.42 (d, 1H, J= 9.2 Hz, Ar-CH).

2.4.2.5.3. Characterization of (1-octyl-3-methyl imidazolium) chloride (IL3)
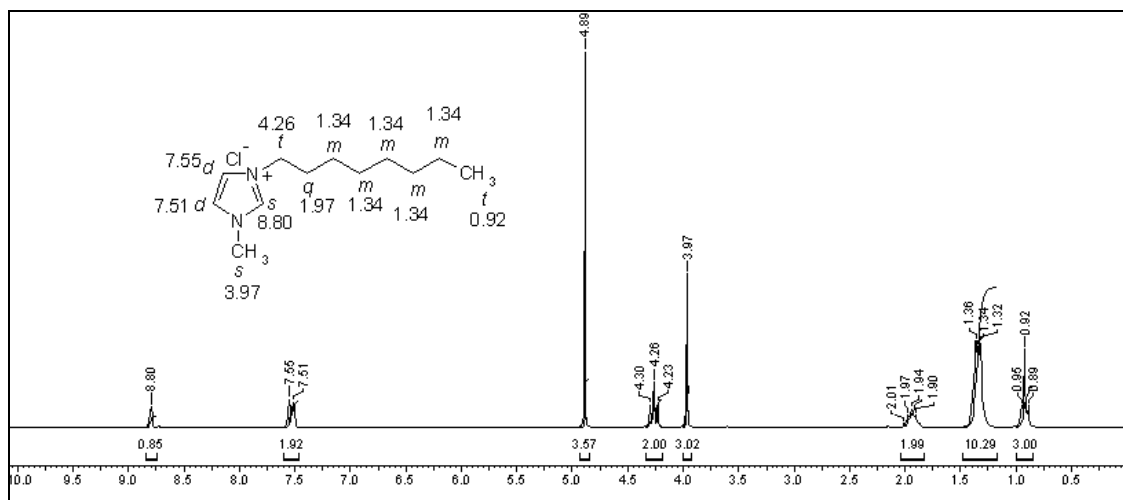
Spectra 2.3. ^{1}H NMR spectra of [C_8mim][Cl] (D_2O, ppm) consisting of the following peaks: δ 0.92 (t, 3H, J=6.8 Hz, CH_3), 1.34 (m, 10H, J=3.9 Hz, CH_2), 1.97 (q, 2H, J=7.07 Hz, CH_2), 3.97 (s, 3H, CH_3), 4.26 (t, 2H, J=7.08Hz, CH_2), 8.80 (s, 1H, Ar-CH), 7.51 (d, 1H, J= 9.48 Hz, Ar-CH), 7.55 (d, 1H, J= 9.48 Hz, Ar-CH).

2.4.2.5.4. Characterisation of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESPMimCl) immobilized on silica support:

2.4.2.5.4.1. DRIFT IR

Curve **a**, the Drift IR spectrum of neat silica shows broad peak at position 3433 cm^{-1} characteristic of Si–OH stretching (intermolecular hydrogen bonding results in intense broad peak). Other characteristic peaks observed in this spectrum are corresponding to Si-O-Si stretching, Si-H symmetric and asymmetric bending at positions 1133 and 950, 801 cm^{-1} respectively.

 The IR peaks in curve **b, c** and **d** show the prominent indication of immobilization of CAT 3 on silica support. The appearance of peaks at 3101 cm^{-1} and 3149 cm^{-1} are ascribed to aromatic C-H stretching in the imidazolium ring in particular of C(2)-H, and C(4)/C(5)-H (figure 2.5). Another indication is the emergence of the peaks in the region 2800-3000 cm^{-1} and sharp peak at 1456 cm^{-1} responsible for aliphatic C-H stretching frequency and C=N stretching frequency respectively. Aromatic C=C stretching vibration

can be distinguished by sharp peak at 1572 cm^{-1} which can be seen prominently at higher loading (35 and 75%). These peaks are absent in the spectra for neat silica confirming the immobilization of CAT 3. Also it can be noted that as the loading of CAT 3 on silica increases there is consistent increase in the intensity of these characteristic peaks for CAT-3. It is worth noting that imidazole ring is comprised of 3° nitrogen's ensuing lack of N-H absorption (sharp) in the region 3200-3500 cm^{-1}.

Dieter et al.[191] have suggested that -Cl interacts with imidazolium cation to induce H-bonds. This fact was also observed by[192] in a similar fashion by inclusion of InCl$_4$ in [C$_4$Mim][Cl] to confirm the occurrence of hydrogen bonding of C(2), C(4), and C(5) hydrogen's. From their results the outcome of this effect was enhanced activity for propylene oxide conversion to propylene carbonate. Thus it is expected to have H-bonding between grafted IL (intramolecular) and SiO$_2$ support (intermolecular). By taking into account these facts we attribute the enhanced activity observed for CO$_2$ insertion to epoxides by 35% loading of CAT 3 on silica to the hydrogen bonding effect in CAT 3 (detail discussed in chapter 3, Section B) in addition to synergistic effect of support and grafted IL (CAT 3). At higher loading (75%) there is no significant improvement in activity; owing to steric constraint (the moles of CAT 3 accommodated are restricted). Therefore a considerable difference in enhancement of hydrogen bonding may not be occurring at both intramolecular and intermolecular level.
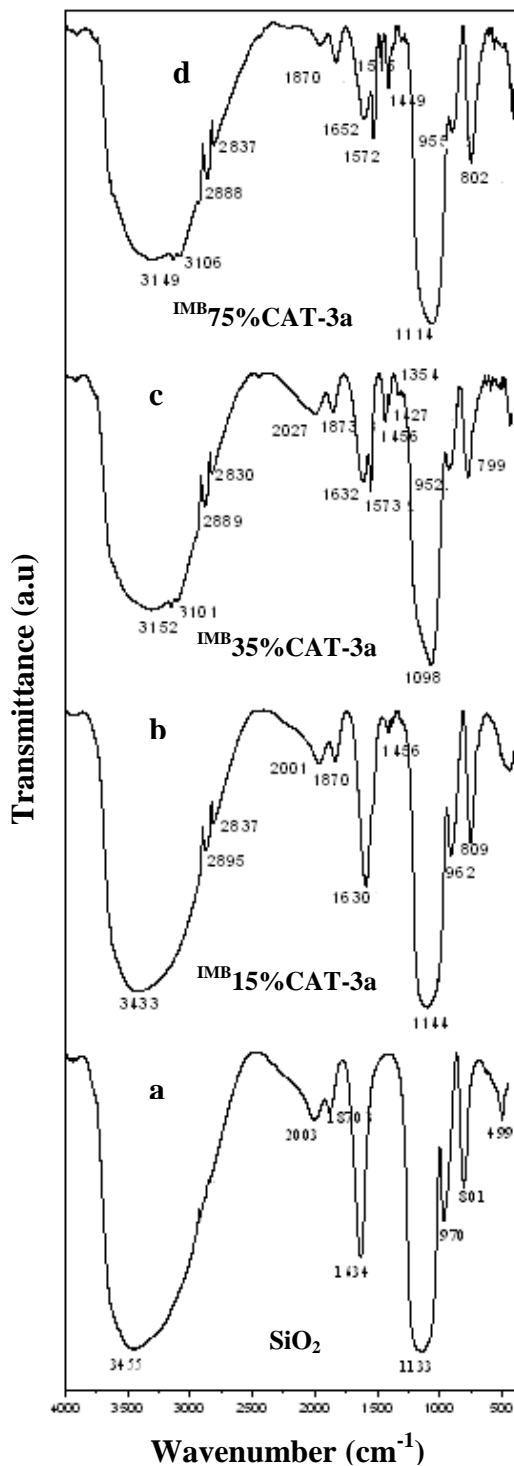
Figure. 2.4. DRIFT IR spectra of 15, 35 and 75 % grafting of CAT 3 (TESPMimCl) on silica support
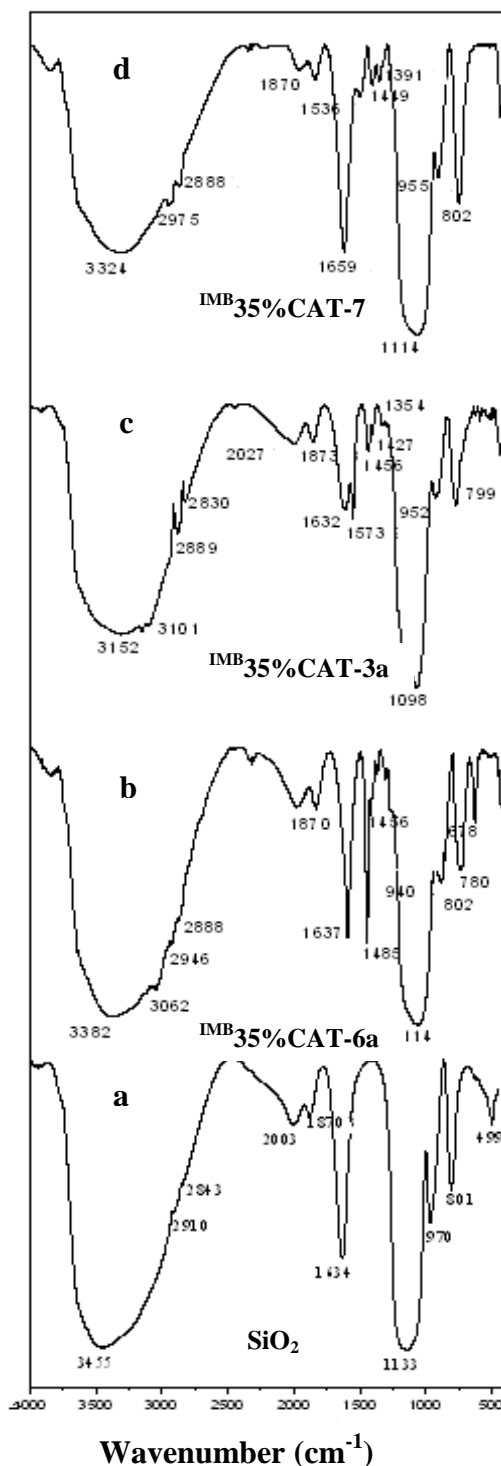
Figure. 2.5 .DRIFT IR spectra of 35% grafting of TESPMimCl, TESPPyCl and imidazolyl IL on silica support

2.4.2.5.4.2. Characterization of pyridinium and imidazolyl IL supported on silica by DRIFT IR

Variation of cation in IL was carried out before immobilization onto silica to explore the effect of cation on catalyst activity. Cations screened were selected on their basicity behavior viz; pyridine and imidazolyl. Figure 2.6 shows cumulative IR peaks for each cation variant under investigation. For the purpose to illustrate the immobilization of modified IL on silica curve **a**, is included corresponding to the Drift IR spectrum of neat silica (IR peaks are described in previous section 3.2.1a.) as reference.

The IR peaks in curve **b** show the 35% loading of *1-(tri-ethoxy-silyl-propyl)-pyridinium chloride* on silica support (**^{IMB}35% CAT-6a**). In this curve the appearance of peaks at 3062 cm^{-1} and 1456 cm^{-1} are ascribed to aromatic C-H stretching and C=N stretching frequency in the pyridine ring respectively. The peaks in the region 2800-3000 cm^{-1} are ascribed to aliphatic C-H stretching frequency of propyl chain.

Curve **c**, refer to 35% loading of *1-(tri-ethoxy-silyl-propyl)-imidazolium chloride* on silica support (**^{IMB}35% CAT-3a**). This spectra also shows the similar characteristic peaks corresponding to C-H, C=N and C=C stretching frequencies in the imidazole ring and also the aliphatic C-H stretching frequency of propyl chain.

Curve **d**, represents *3-(1-Imidazol-1-yl) propyl-functionalised silica gel quaternized with n- butyl chloride* (**^{Imb}35%CAT-7**)**. This curve is also dominated by frequencies corresponding to C-H, C=N and C=C stretching frequencies of imidazolyl ring and aliphatic C-H stretching frequency of propyl and butyl chain.

Comparison of DRIFT IR of neat silica (curve a) before and after immobilization (curves b, c and d) confirms the immobilization owing to emergence of prominent peaks for C-H, C=N and C=C stretching frequencies and aliphatic C-H stretching frequencies corresponding to organic moieties in addition to peaks characteristic of silica

2.4.2.5.4.3. Characterization of BSTFA treated 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride immobilized on silica support:
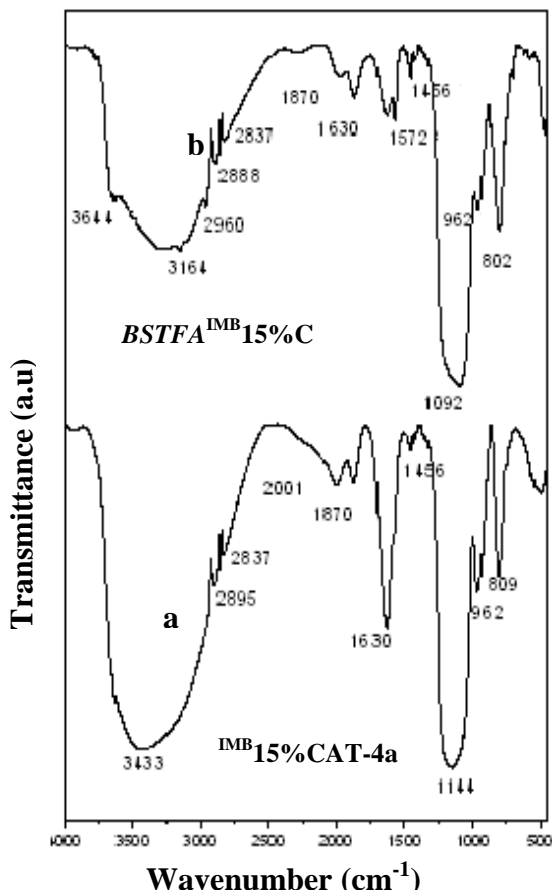
Figure.2.6a. DRIFT IR spectra of BSTFA treated 15% CAT-3 loaded on silica (**BSTFA ^{IMB}15% CAT-3a)** and neat 15% CAT-3 loaded on silica (**^{IMB}15% CAT-3a).**

The preformed catalyst were treated with BSTFA [N,O-Bis(trimethylslyl) trifluoroacetamide] to quench surface silanols. Drift IR of various amount of loading of CAT 3 on silica is compared with their BSTFA treated sample to realize the modification occurred in the catalyst. Figure 2.7a shows IR spectra for ^{IMB}15% CAT-3a and its BSTFA treated sample. From the curve b the effect of BSTFA treatment is evident due to appearance of peaks at 2960 cm^{-1} and 3164cm^{-1} ascribed to aromatic C-H stretching in the imidazolium ring in particular of C(2)-H, and C(4)/C(5)-H which are inconspicuous in curve a and merged with peak for hydroxyl group at 3433 cm^{-1}. This hydroxyl peak is seen shifted to 3644 cm^{-1} in curve b. An additional important peak that have appeared after BSTFA treatment is at 1572 cm^{-1} (sharp) signifying the aromatic C=C stretching. For 15% loading of CAT 3 on silica (curve a) most of the surface silanol groups remain unutilized, this is reflected in broad peak at 3433 cm^{-1} for –OH

stretching. Also since the spectrum loading of CAT 3 is in a lesser amount hence the peaks for organic moiety are undeveloped. Other characteristic peaks seen spectrum are corresponding to Si-O-Si stretching, Si-H symmetric and asymmetric bending at positions 1133 and 950, 801 cm^{-1} respectively. A similar trend is observed for 35% (**^{IMB}35% CAT-3a)** and 75% (**^{IMB}75% CAT-3a)** catalyst loading confirming the utilization of free surface silanols by BSTFA treatment (figures 2.6 b and 2.6c).

Figure 2.6b. DRIFT IR spectra of BSTFA treated 35% CAT-3 loaded on silica (BSTFA ^{IMB}35% CAT-3a) and neat 15% CAT-3 loaded on silica (^{IMB}35% CAT-3a).

Figure 2.6c. DRIFT IR spectra of BSTFA treated 75% CAT-3 loaded on silica (BSTFA ^{IMB}75% CAT-3a) and neat 75% CAT-3 loaded on silica (^{IMB}75% CAT-3a).

2.4.2.5.4.4. ^{29}Si CP MAS NMR spectra of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESPMimCl) immobilized on silica support:

Figure 2.7 shows ^{29}Si CP MAS NMR spectra of neat SiO_2 and 15, 35 and 75% loading of CAT-3 on silica. The spectrum's showed well resolved peaks for T-sites along with signals for Q^3 and Q^4 site between -56 and -66 ppm, -95 to -101 ppm and -103 to -180 ppm respectively. In the spectra "a" for neat SiO_2 the signals at ca. -99 ppm and -101

ppm corresponds to Q^3 sites indicating the presence of silanol in $(SiO)_3Si-OH$ form. Whereas in the spectra's b, c, d in addition to Q^3 signal, the signals at -106 ppm and -109 ppm could be attributed to $Si(SiO)_4$ linkage (Q^4 site). The signal at -58 and -67 ppm were assigned to $Si-O-SiR-(OEt)_2$ (T^2) and $(SiO)_2-SiR-OEt$ (T^3). As seen from fig 2.7 a comparison of ^{29}Si CPMAS NMR of 15, 35 and 75% grafting of CAT-3 on silica shows that with increase in loading of CAT-3 on silica a gradual increase in peaks corresponding to Q^4 sites is observed. 15% loading of CAT-3 on silica shows remarkable difference in characteristic signal for Q^3 site. The majority of the signals correspond to Q^3 site indicating the presence of $(SiO)_3-Si-OH$ linkage. Whereas Q^4 site $(SiO)_4Si$ linkage are more intense in case of 35 and 75% loading of CAT 3. This implies that with increase in loading of IL CAT 3 the utilization of surface silanol group increases. Other significant difference in signal for T-site can be observed. 15% loading of CAT-3 on silica shows weak signal for T^3 and T^2 sites due to less loading of CAT-3. As the loading increases from 35 to 75% a fair increase in signal for T^3 and T^2 site can be observed asserting the grafting of higher percentage.

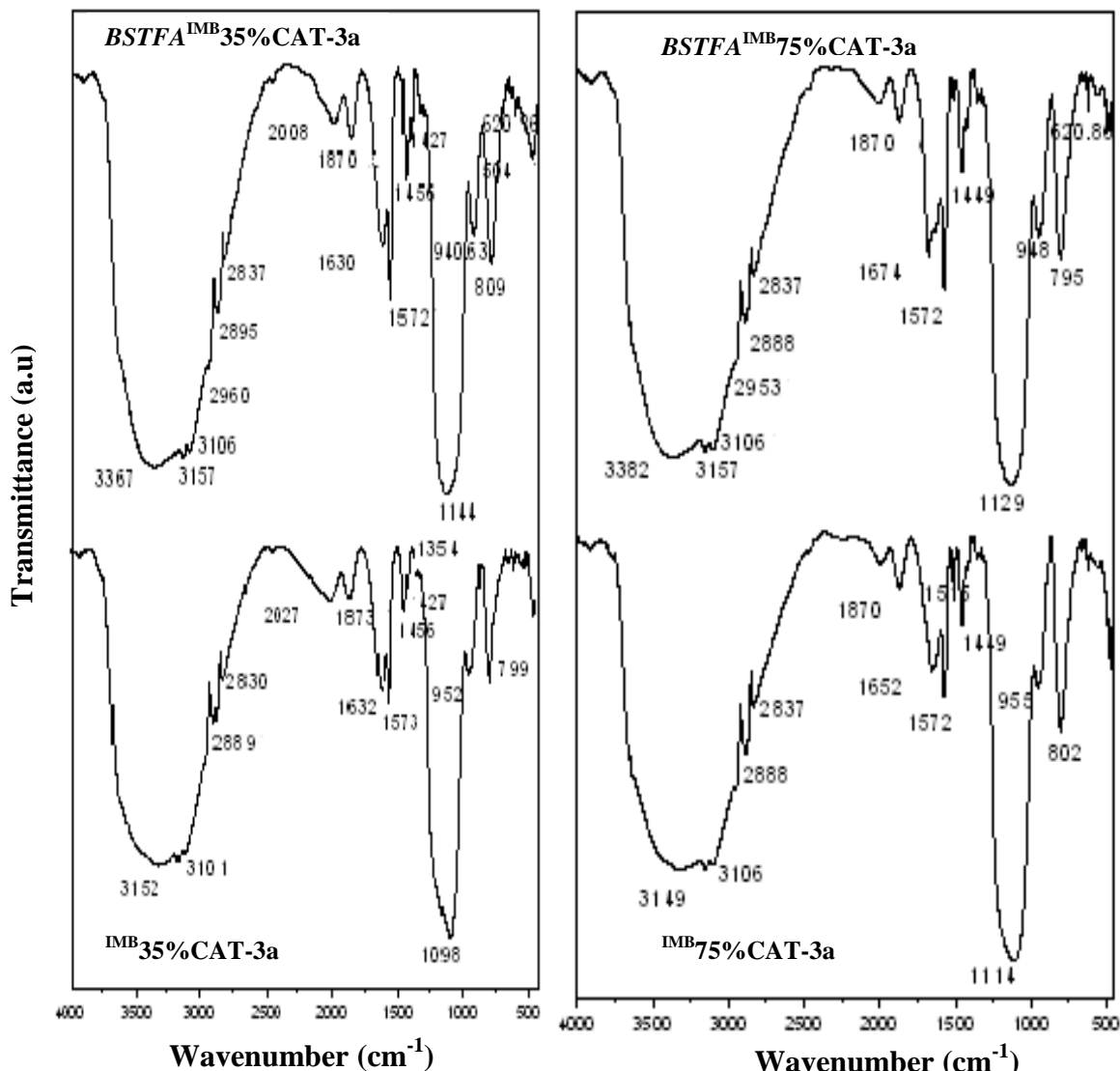*2.4.2.5.4.5. ^{29}Si CP MAS NMR spectra of BSTFA treated 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride immobilized on silica support:*

Figure 2.8 shows crosspolarised ^{29}Si MAS-NMR spectra for BSTFA treated ^{Imb} 15, ^{Imb} 35, and ^{Imb} 75% CAT-3a. BSTFA treatment of the above catalysts results in the resolved peaks corresponding to Q^4 site and Q^3 site. Spectra's a, b and c shows the characteristic signals corresponding to Q^3, Q^4, T^2 and T^3 sites. BSTFA treatment was carried out with the aim to quench the surface silanol Q^3 sites if any in order to study the role of these sites in catalysis of the reactions under investigation. This is reflected in the spectra with the dominant signals corresponding to Q^4 sites whereas signals corresponding to Q^3 site are found to be feeble. The signals for T^3 sites are found to be intact even after BSTFA treatment.
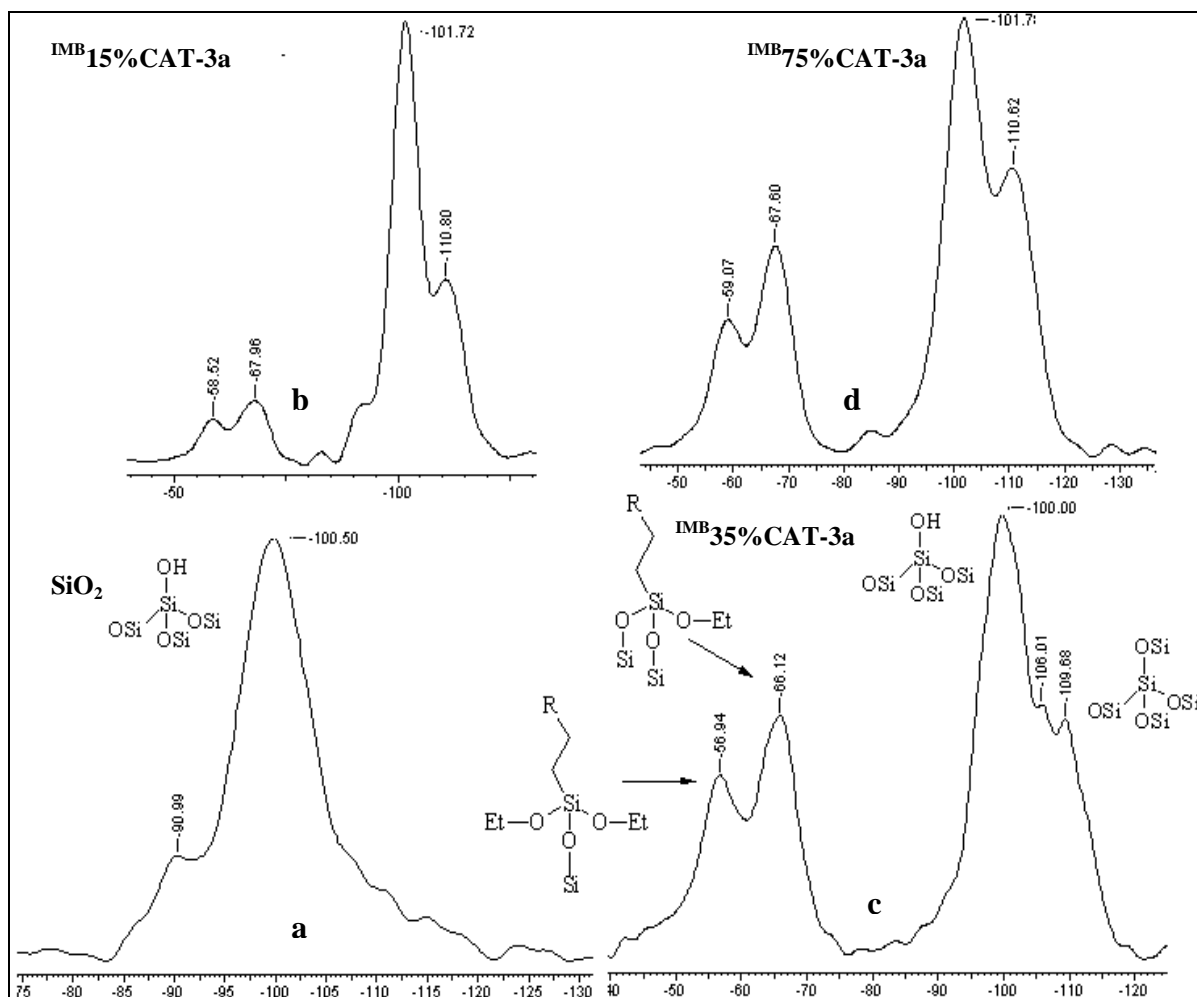
Figure 2.7 ^{29}Si CP MAS NMR spectra of CAT-3 (TESPMimCl) immobilized on silica support at 15,35 and 75% loading.

2.4.2.5.4.6. ^{13}C CPMAS NMR spectra of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESPMimCl) immobilized on silica support:

^{13}C MAS NMR of above catalysts is shown below in figure 2.9. The spectrum shows signals in two regions viz., aliphatic from 0-55 ppm and aromatic from 120-170 ppm. The signals appearing in aliphatic region are due to silica bound ethoxy moiety (Si-OC$_2$H$_5$), silica bound propyl moiety (Si-C(1)H$_2$-C(2)H$_2$-C(3)H$_2$-N-) and N- CH$_3$. The signal at δ=9.01 ppm is due to CH$_3$ of ethoxy moiety attached to Si while other methyl group attached to N of imidazoline ring (NCH$_3$) resonate at δ=36.32 ppm (See inset scheme in Figure 2.9). The signal at δ=23.27 ppm is due to carbon of propyl group that is attached to Si-CH$_2$-. The other two carbons of propyl group -C-CH$_2$-C- and CH$_2$-N are

undeveloped. The signal appearing at δ=51.58 ppm can be assigned to CH_2 of ethoxy group attached to Si. In the aromatic region three prominent signals are present. The N*CH*C*H*N are resolved at δ=123.64 ppm and δ=122.35 ppm and are assigned to NCH*C*HN and N*C*HCHN respectively while signal at δ=136.14 ppm is due to N*C*H-N. It can be clearly seen from Figure 2.9 that, at higher IL loadings (75%) clear interactions of IL with support can be visible (splitting of NMR signals) while at lower loadings (15 & 35%) NMR signals are indistinguishable since they appear to be fused. These results indicate that ionic liquid TESP-MImCl is immobilised on silica support.

δ **ppm**
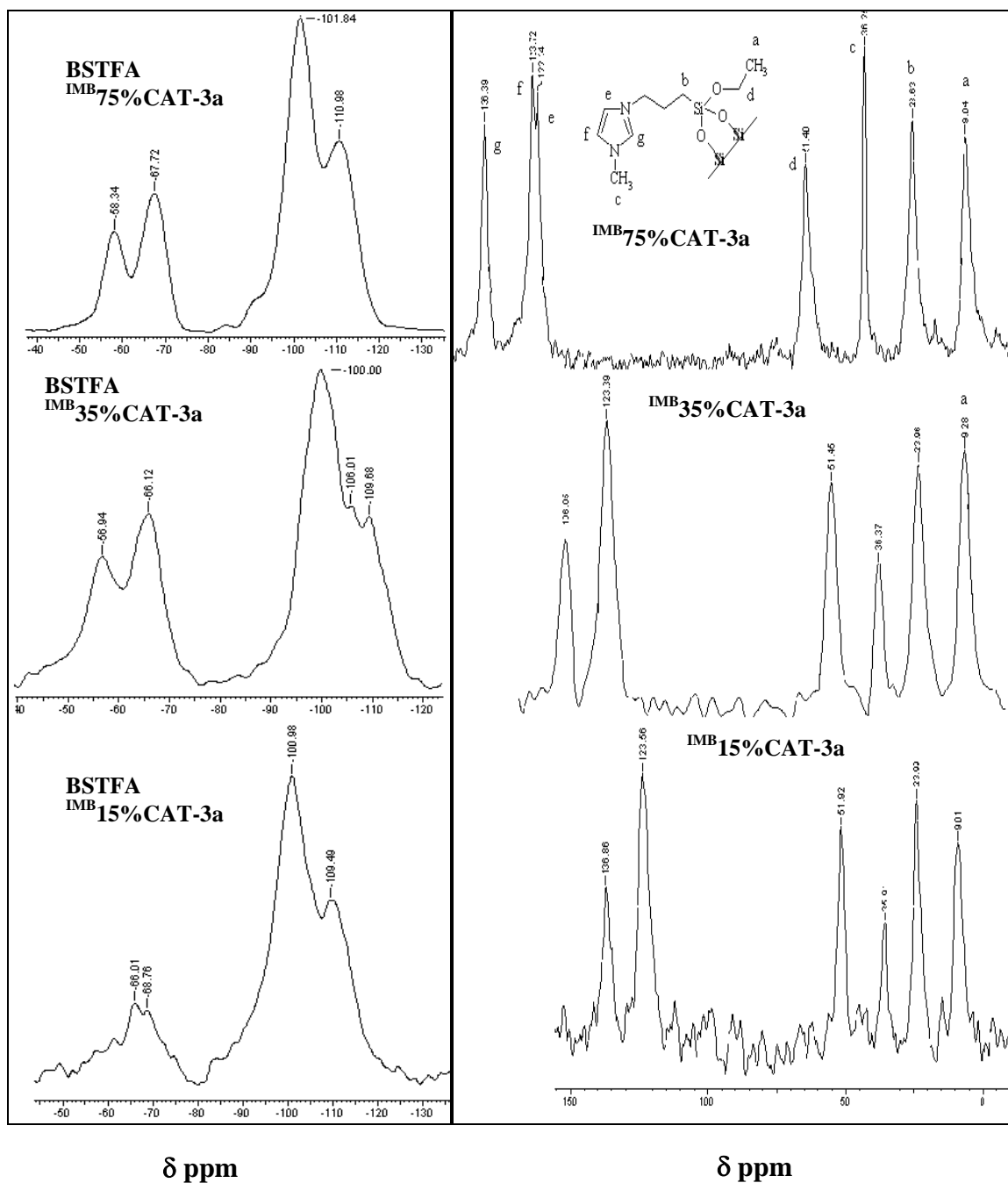
Figure. 2.8. ^{29}Si CP MAS NMR of 15%, 35% and 75% CAT-3 loaded on silica treated with BSTFA

δ **ppm**

Figure. 2.9. ^{13}C CP MAS NMR of 15%, 35% and 75% CAT-3 loaded on silica

2.4.2.5.4.7. ^{13}C CPMAS NMR spectra of BSTFA treated 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride immobilized on silica support:

BSTFA treatment of the same does not show any remarkable difference in ^{13}C CPMAS NMR as only the alteration in the unutilized surface –OH groups occur resulting in Si-O-

Si linkage after the treatment. Some of the signals associated with N-CH3 (δ=37ppm) and

NCHN (δ=137ppm) are observed to be weak in contrast to ^{13}C CPMAS NMR of BSTFA

untreated catalyst. Otherwise the signals corresponding to aliphatic and aromatic carbons

appear at same δ as discussed in section 4.2.2c.

δ **ppm**
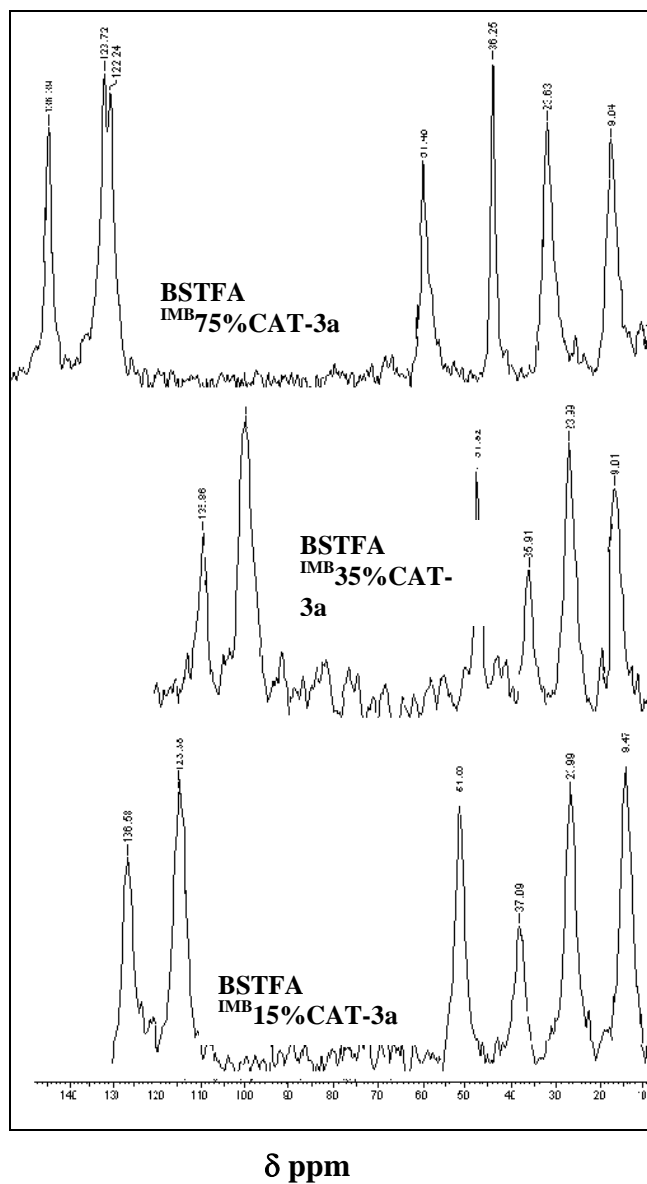
Figure.2.10 ^{13}C CP MAS NMR of 15%, 35% and 75% CAT 3 loaded on silica treated
with BSTFA.

2.4.2.5.4.8. ^{13}C CP MAS NMR and ^{29}Si CP MAS NMR spectra of pyridinium and imidazolyl IL supported on silica

^{13}C CP MAS NMR spectra of pyridinium and imidazolyl IL supported on silica

Figure 2.11 shows ^{13}C CP MAS NMR of ^{IMB}35% CAT-6a and ^{IMB}35% CAT-7 respectively. Spectra a shows resonances corresponding to aliphatic carbons in the region -1 ppm to 50ppm. The signal at δ=-1.32 ppm indicates the deshielded carbon of propyl group that is attached to Si. Whereas aliphatic carbon of propyl group $CH_2CH_2CH_2$ and CH_2CH_2NH appears at 41 and 43 ppm respectively. The butyl group carbons can be located at 8.99, 19.67, 29.02, 47.79 ppm corresponding to CH_3, $CH_2CH_2CH_3$, $CH_2CH_2CH_3$ and CH_2NH respectively. The ring carbons NCH_2 and $CHNCH_2$ are found at 57.70 and 59.23ppm respectively. The signal at 163.77 ppm can be ascribed to ring carbon of NCHN group.

Spectra b shows the resonances typical of IL comprising pyridinium cation. The resonance at 9.23 and 25.17 ppm are due to $CH_2CH_2CH_2$ and $CH_2CH_2CH_2$ carbons of propyl chain respectively. The resonance at 63.70 ppm is due to NCH_2 carbon. The signals for ethoxy group are found to merge with the signals for $CH_2CH_2CH_2$ and NCH_2 carbons of propyl chain. While aromatic carbons of pyridine ring appear at 144.88 and 128.89 ppm equivalent to NCHCH and NCHCH groups. The signal for CHCHCH carbon of pyridine ring is found to be merged with the signal at 128.89 ppm.

^{29}Si CP MAS NMR spectra of pyridinium and imidazolyl IL supported on silica

^{29}Si CP MAS NMR of ^{IMB}35% CAT-6a and ^{IMB}35% CAT-7 (figure 2.12) shows signal at -102.82 ppm indicating Q^3 silanol. The signals in spectra b signifying the presence of organosiloxane groups surface at -59.76 and -68.61 ppm corresponding to T^2 and T^3 respectively assigned to Si–O–**Si**R–(OEt)$_2$ and (Si-O)$_2$–**Si**R–OEt groups. While in spectra a broad signal at -67.77ppm indicates the organosiloxane group assigned to (Si-O)$_2$–**Si**R–OEt groups. This suggests that in ^{IMB}35% CAT-6a the condensation of majority of the ethoxy groups of organic labile arm has taken place. Whereas in ^{IMB}35% CAT-7 both the possible condensation modes of ethoxy groups of organosiloxane are found to be taking place i.e. bidentate and tridentate.

δ ppm
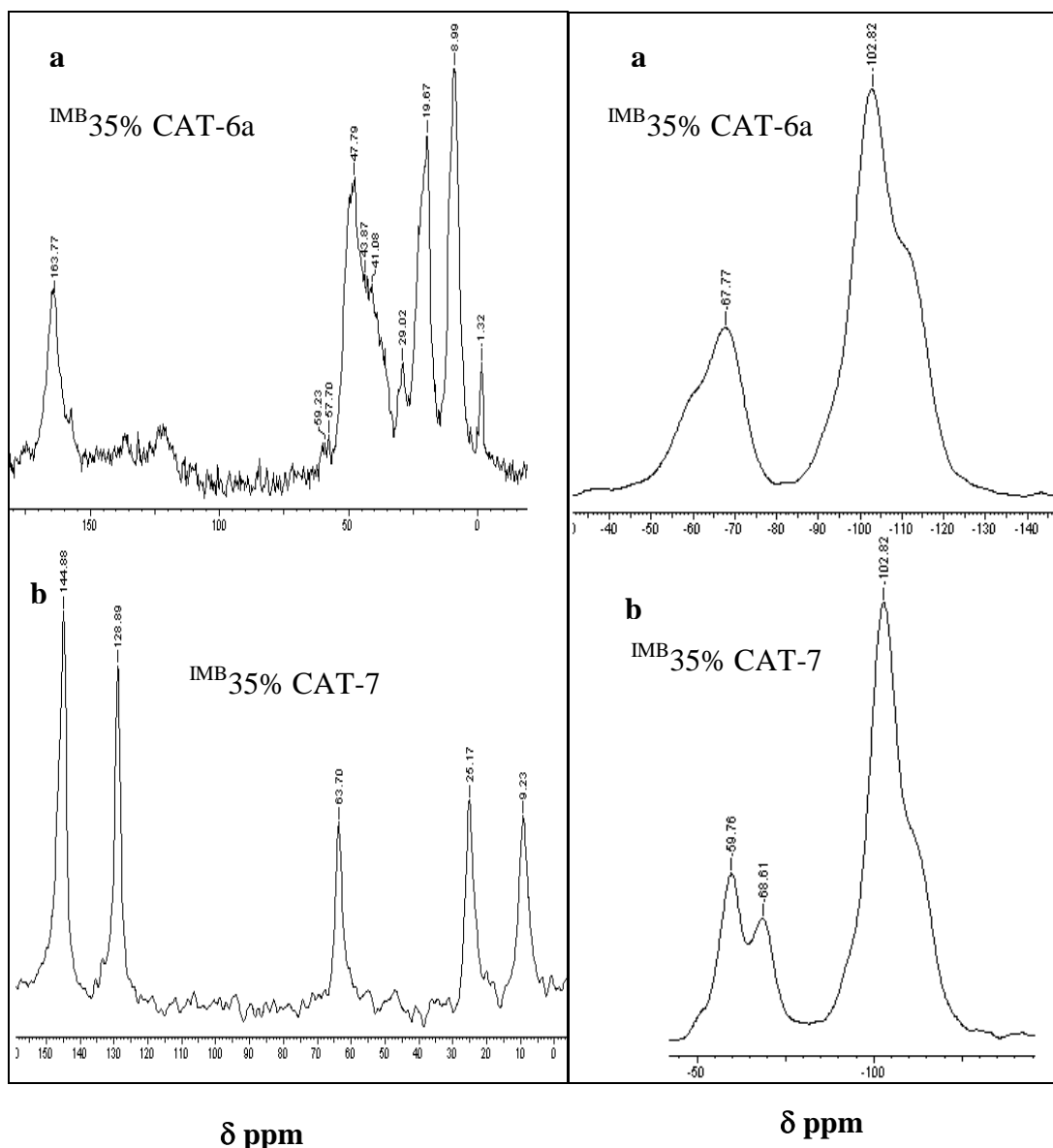
Figure. 2.11. ^{13}C CP MAS NMR of pyridinium and imidazolyl IL supported on silica.

δ ppm

Figure. 2.12. ^{29}Si CP MAS NMR of pyridinium and imidazolyl IL supported on silica.

2.4.2.5.4.9. Surface area determination by BET method

The nitrogen isotherms of flash silica are shown in figure 2.13. The isotherm can be classified as type IV isotherm as defined by IUPAC.[193] The isotherm of neat silica exhibits a steep increase at relative pressure (P/Po) around 1.5 to 0.4. A distinct hysteresis loop is observed from P/Po ~ 0.4 to 0.9. This hysteresis loop is classified as type H2 characteristic of ink bottle type of pores. The BJH pore size distribution based on desorption branches indicate that silica is mesoporous with pore diameter 49.77 Å and

surface area 477.94 m^2g^{-1}. The nitrogen adsorption isotherms for 15, 35 and 75% IL loading on silica as well shows type IV isotherm (figure 2.13) typical of mesoporous solids which are associated with capillary condensation taking place in mesopores. The nitrogen adsorption isotherms show a significant decrease in maximum adsorbed amount of nitrogen, however, the shape of the isotherms and hysteresis loops doesn't change. Thus with increase in loading of IL on SiO_2 there is significant drop in the amount of nitrogen adsorbed (figure 2.13) along with BET surface area and pore diameter (table 2.3). BJH pore size distribution curve support this observation (figure 2.14). This confirms that these grafted silicas retained their mesoporosity even after functionalisation.
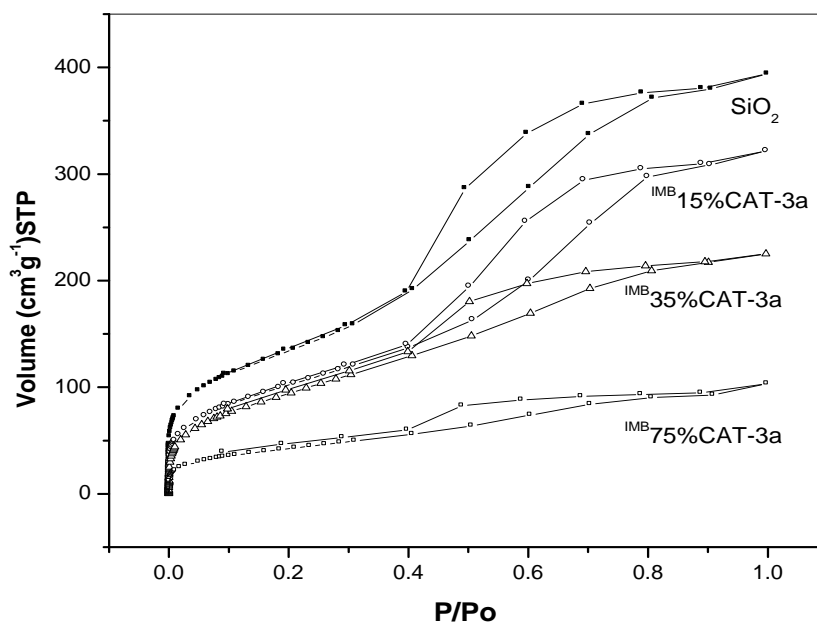
Figure 2.13. Nitrogen adsorption-desorption isotherms for neat silica and CAT-3 loaded on silica at 15, 35 and 75% loading

Some of the important physical properties of neat silica and IL grafted silica are given in table 2.5.

Table 2.5. Physical properties of neat silica and IL grafted silica.			
Entry	**Sample**	**Surface area** $(\mathbf{m^2/g})$	**Pore volume** $(\mathbf{cm^3/g})$	**Pore diameter** $(\mathbf{\AA})$
1	SiO2	477.94	0.6111	49.77
2	15	362.02	0.498	52.67
3	35	338.75	0.3490	39.1
4	75	148.86	0.1603	41.67
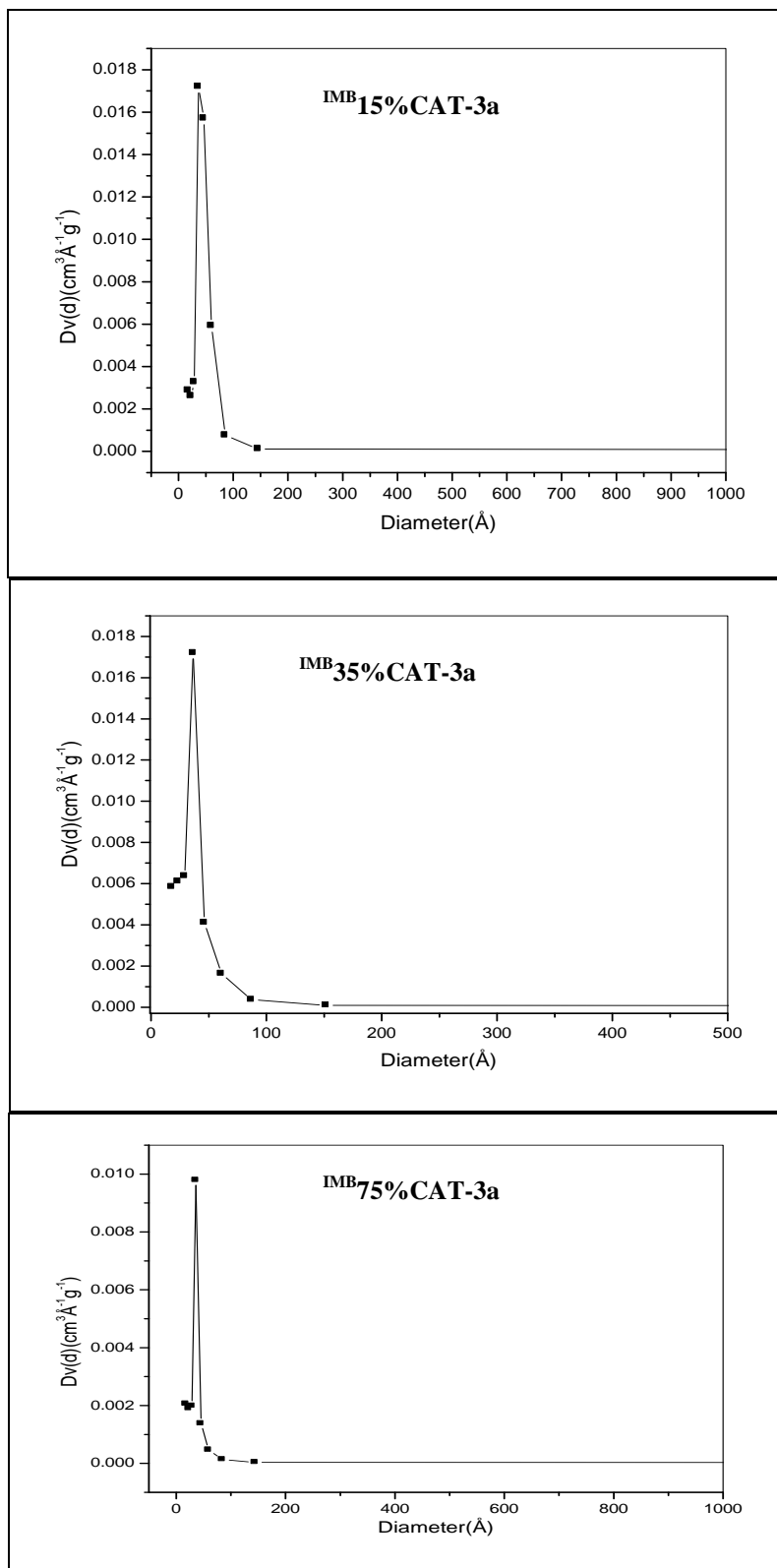
Figure 2.14. Pore size distribution curve for neat silica and CAT-3 loaded on silica at 15, 35 and 75% loading

2.4.2.5.5.0. Characterisation of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride on MCM-41 support: (^{Imb}35%CAT-3b)

2.4.2.5.5.1. DRIFT IR

Fig 2.15 shows Drift IR spectra of parent MCM-41 (calcined) and modified MCM-41 confirming immobilization of CAT-3 on parent MCM-41. Curve *a* exhibit IR spectra for MCM-41 (calcined) displaying the characteristic absorption peaks for ν_{as} (Si-O-Si) and ν_s (Si-O-Si) at 1200 cm^{-1} and 1090 cm^{-1} respectively along with the band at 966 cm^{-1} related to modifiable silanols. The broad band at 460 cm^{-1} is characteristic of amorphous material. The IR absorptions of C-H stretching and rocking vibrations in the region 2800-2900 cm^{-1} and 1450-1500 cm^{-1} are vanished implying removal of template.

After immobilization of CAT-3 on MCM-41 support (curve **b**) the peaks at 3092 cm^{-1} and 3150 cm^{-1} appear that are ascribed to aromatic C-H stretching in the imidazolium ring in particular of C(2)-H, and C(4)/C(5)-H (see figure 2.15). Another indication is the emergence of the peaks in the region 2850-3000 cm^{-1} and sharp peak at 1456 cm^{-1} responsible for aliphatic C-H stretching frequency and C=N stretching frequency respectively. Aromatic C=C stretching vibration can be distinguished by sharp peak at 1572 cm^{-1}. Noticeably the peak intensity at ca. 966 cm^{-1} characteristic of modifiable silanols was found decreased owing to immobilization of CAT-3 on MCM-41 support.

Figure 2.15. DRIFT IR spectra of neat MCM and 35% CAT-3 loaded on MCM (^{IMB}35% CAT-3b).

2.4.2.5.5.2. XRD

Wide angle powdered XRD of the calcined MCM-41 (Figure 2.16a and 2.16b) sample shows three resolved peaks at low angle indexed as strong (100), and weak (110 and 200) reflections related with hexagonal (*p6mm*) symmetry corresponding to 2θ values of 2.25º, 3.95º and 4.6º respectively. The XRD pattern shows that MCM-41 has highly ordered long-range mesoporosity. The characteristic strong (100) peak shows d spacing of 3.92 nm. Spectra b shows the XRD pattern for CAT-3 immobilized on calcined MCM-41. All the three peaks at (100, 110 and 200) at 2θ values of 2.20º, 3.90º and 4.5º respectively with the d spacing of 4.01 nm for (100) peak were observed to be intact.

Figure 2.16a. PXRD spectra of neat MCM-41
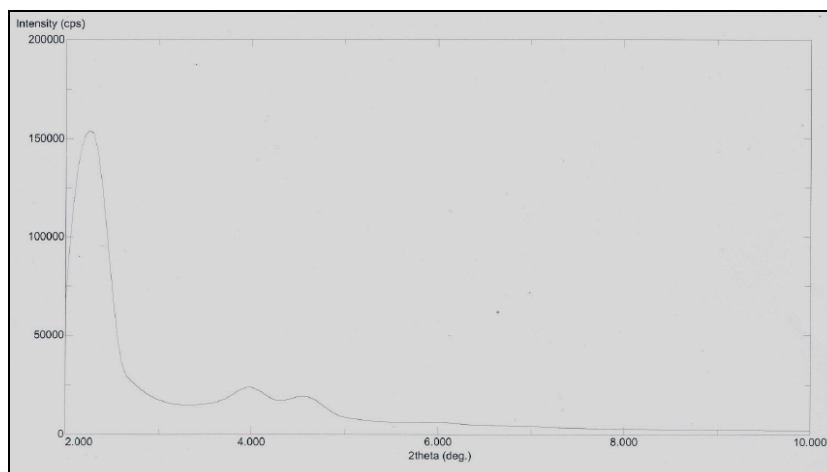
Figure 2.16b. PXRD spectra of ^{IMB}35%CAT-3b
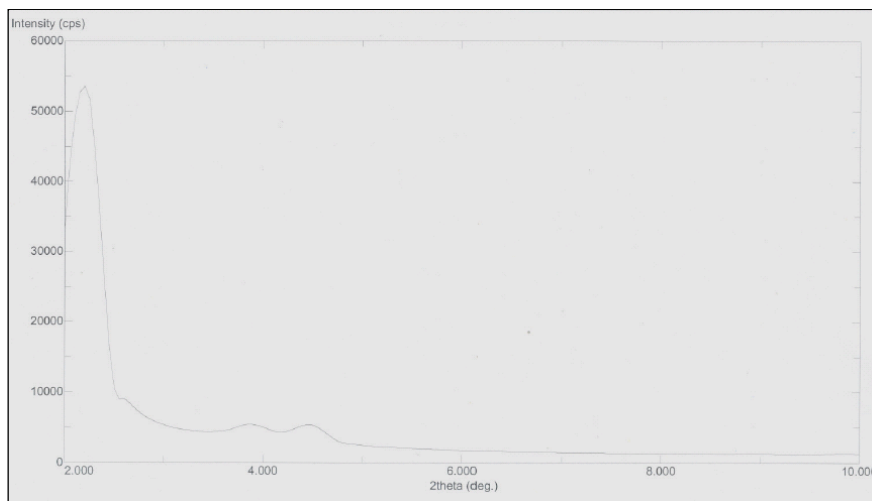
2.4.2.5.5.3. Solid State NMR

2.4.2.5.5.3.1. ^{29}Si CP MAS-NMR

Crosspolarised ^{29}Si MAS-NMR spectra of virgin MCM-41 (spectra a) show single signal at −101 ppm, assigned to (Q^3) i.e. (SiO)$_3$Si–OH groups. After the reaction of organic cation with hydroxyl groups on the surface of the support (spectra a) signal at −101 ppm, assigned to Q^3 groups is seen diminished whereas distinct resonances can be clearly observed for Q^4 i.e. (SiO)$_4$Si linkage. Two new peaks appearing at -60 ppm (T^2) and -68 ppm (T^3) corresponding to organosiloxane groups are assigned to Si–O–**Si**R–(OEt)$_2$ and (Si-O)$_2$–**Si**R–OEt respectively.[194] This proves that the grafting of the organic cation to the surface is either via one or two Si–O–Si bonds. (figure 2.17)

δ **ppm**
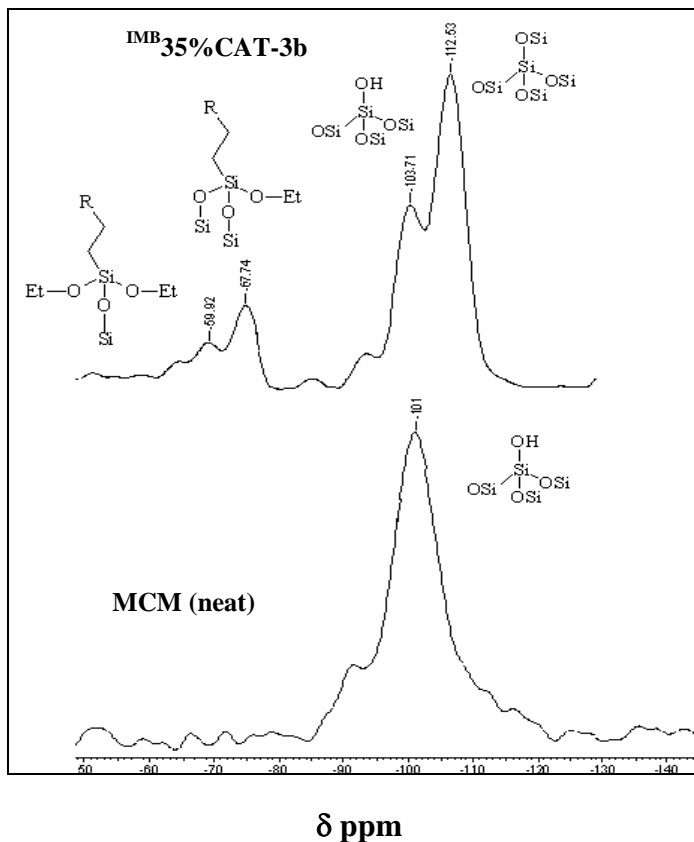
Figure 2.17. ^{29}Si CP MAS-NMR spectra of virgin MCM-41 and 35% CAT-3 loaded on MCM (^{IMB}35% CAT-3b).

2.4.2.5.5.3.2 ^{13}C CP MAS-NMR

CP ^{13}C MAS NMR spectra of 35% CAT 3 grafted on MCM support shows the signals at δ=8.74 ppm is due to CH$_3$ of ethoxy moiety attached to Si while other assigned to methyl group attached to N of imidazoline ring (NCH$_3$) resonate at δ=36.32ppm (See Figure2.18). The signal at δ=23.27ppm is due to carbon of propyl group that is attached to Si-CH$_2$-. The signals for other two carbons of propyl group -C-CH$_2$-C- and CH$_2$-N are found to be merged with neighboring signals. The signal appearing at δ=51.58ppm can be assigned to CH$_2$ of ethoxy group attached to Si. In the aromatic region three prominent signals are present The NCHCHN are resolved at δ=123.82 ppm and δ=122.35 ppm and are assigned to NCHCHN and NCHCHN respectively while signal at δ=136.14 ppm is due to NCH-N. (See Figure 2.18)

δ ppm
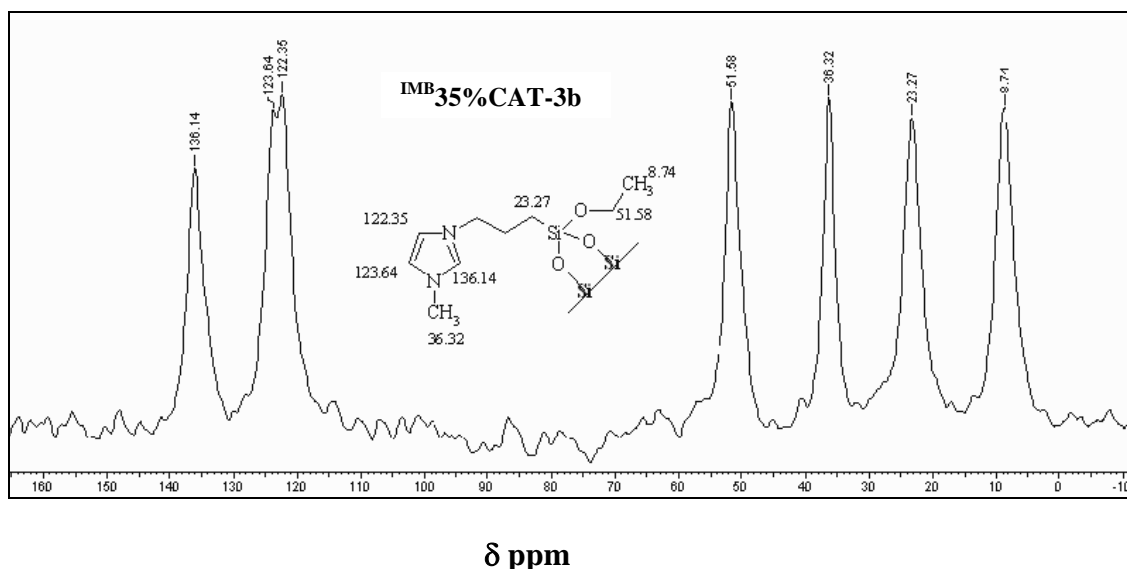
Figure 2.18. ^{13}C CP MAS-NMR spectra of 35% CAT-3 loaded on MCM (^{IMB}35% CAT-3b).

2.4.2.5.5.4.. SEM

The SEM images of pure siliceous MCM-41 (calcined) and 35% CAT-3 grafted on MCM-41 support are shown in Fig 2.19a and 2.19b. Images clearly reveal the size of the particles. Although the particles appear to be of uniform size in the range of 1μm for pure siliceous MCM-41 (calcined) they are seen to be deposited together. The SEM image of ^{IMB}35%CAT-3b shows agglomerated particles appearing to be covered with IL

(TESPMimCl) CAT-3 where shape of the particles is found to be indistinguishable in the 1 μm image of the same.
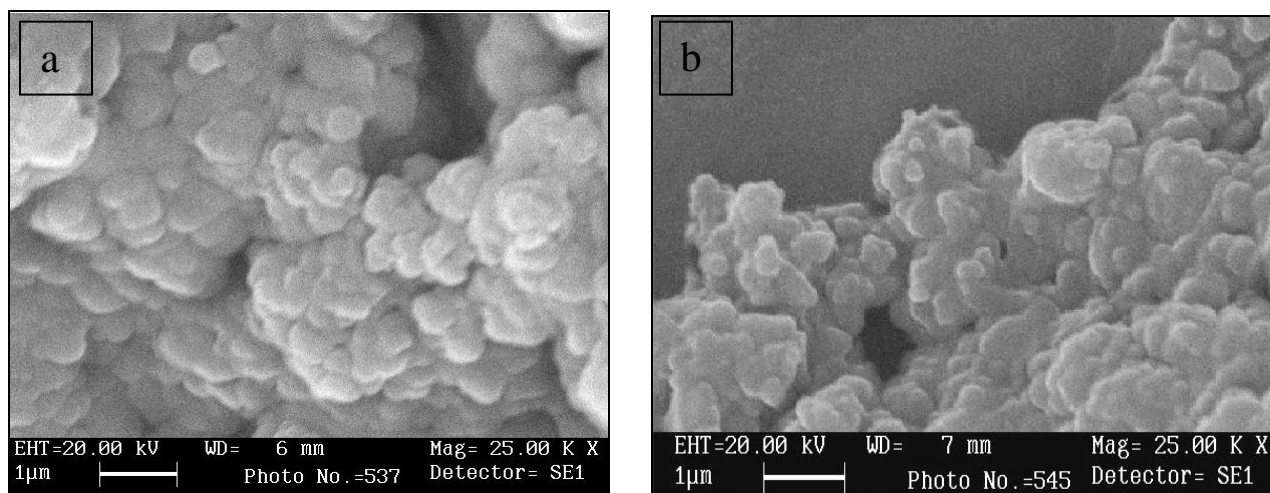
Figure 2.19. SEM micrographs of a) pure siliceous MCM-41 (calcined) and b) 35% CAT-3 grafted on MCM-41

2.4.2.5.5.5. TEM

The corresponding TEM image shown in Fig. 2.20a, 2.20b, 2.20c demonstrates that pure siliceous MCM-41 (calcined) shows clearly the uniform hexagonal mesoporous structure in the 1 0 0 direction. The TEM image of 35% CAT-3 grafted on MCM-41 support shows the particles with the same morphology as that of pure MCM-41 but without hexagonal mesoporous structure. This change in morphology of hexagonal structure may be attributed to the filling of mesopores by IL (TESPMimCl) CAT-3 owing to grafting procedure. Remarkably no wear and tear in the structure was observed in the image of MCM-41 before and after the grafting procedure.
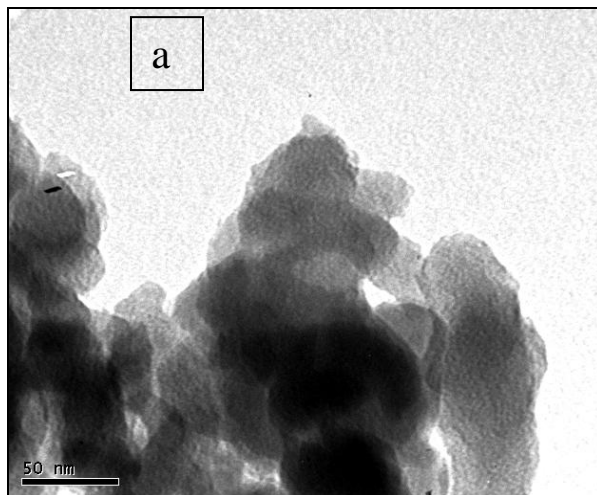
Calcined MCM-41 (50nm image)   **Calcined MCM-41 (20nm image)**
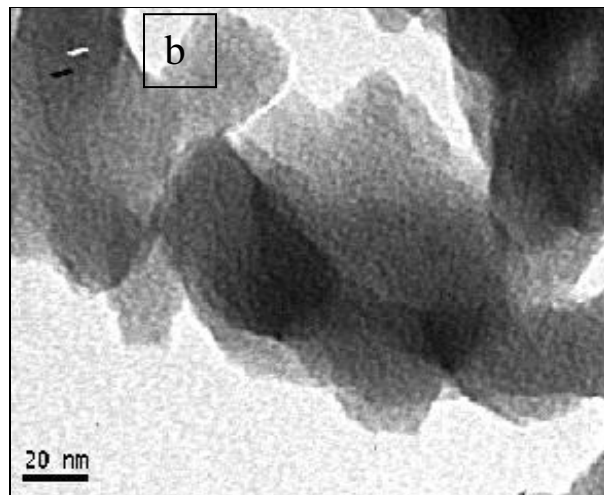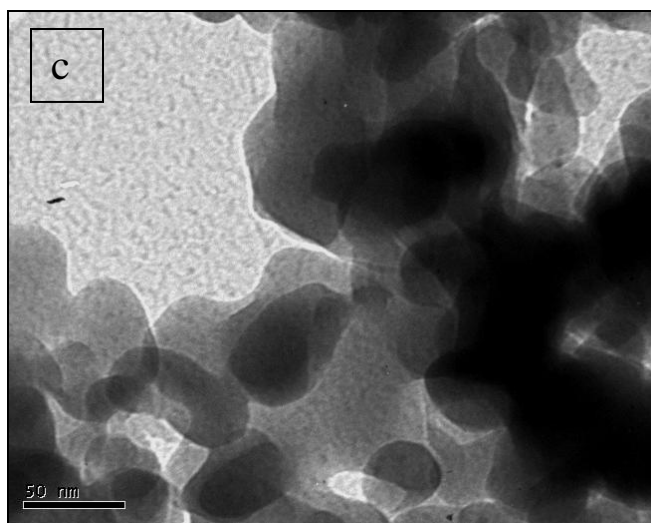
Calcined MCM-41 grafted with 35% of IL CAT-3

Figure 2.20. TEM images of different MCM-41 catalysts.

2.4.2.5.5.6. Nitrogen adsorption-desorption isotherms

The nitrogen adsorption-desorption isotherms along with pore size distribution shown in figure 2.21 confirm the MCM-41 with very narrow pore size distribution and high surface area. Virgin MCM-41 shows a type IV isotherm as defined by IUPAC[195], typical of mesoporous solids which are associated with capillary condensation taking place in mesopores. The adsorption and desorption regions of isotherms almost overlap each other except for a very small hysterisis loop along multilayer range of physisorption around P/Po ~ 0.25 to 0.4. Adsorption at lower pressure is accounted for thin layer adsorption of

gas on the walls of mesopores. The hysteresis loop exhibited here is classified as type H1 showing sharp inflection point near P/Po ~ 0.3 to 0.4. The P/Po position of the inflection point is related to the pore diameter. The sharpness in this step is a characteristic of sharp capillary condensation indicating a very uniform pore diameter. This MCM-41 assembled from fumed silica shows pore diameter 47.22 Å and high surface area 1417 m^2g^{-1}. Cheng et al. has pointed out the effect of sources of silica on final MCM-41 structure.[196] From ^{29}Si MAS NMR study of Sigma fumed silica and Cab-O-Sil silica he observed lower Q^4 units in former silica. This indicate that Sigma fumed silica is partially dissolved during aging due to lower degree of silica polymerization giving high quality MCM-41. The nitrogen adsorption desorption isotherm for 35% IL CAT-3 on MCM showed significant decrease in maximum adsorbed amount of nitrogen, but the shape of the isotherm is unaffected. This indicated that the mesoporous structure and uniform pore diameter is retained along with the decrease in BET surface area and pore diameter after functionalisation by post synthesis grafting method. Similar observations were reported by *D. M´ehn et al.* [197] for pore expansion and pore narrowing of MCM-41. The BET surface area and average pore diameter for ^{IMB}35% CAT-3b obtained were 465.48m^2g^{-1} and 50.04 Å respectively.
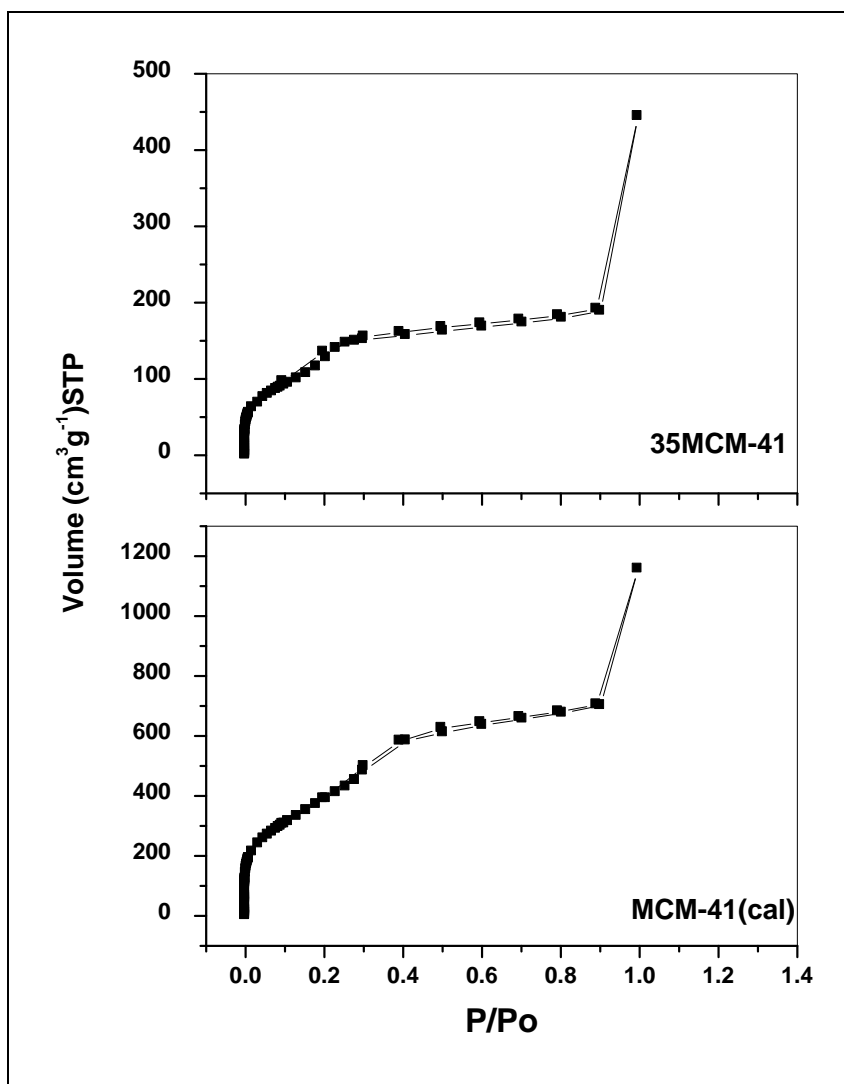
Figure 2.21. Nitrogen adsorption-desorption isotherms for neat MCM and 35% CAT-3 loaded on MCM.

Some of the important physical properties of neat MCM-41 and IL grafted MCM-41 are given in table 2.6.

Table 2.6. Physical properties of neat MCM-41silica and IL grafted on MCM-41.			
Entry	Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter $(\mathring{A})$
1	MCM-41	1417.27	1.794	47.22
2	35MCM-41	465.48	0.6884	50.04

2.4.2.5.6. Characterisation of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride immobilized on Zn/Al Hydrotalcite: (^{Imb}35%CAT-5a)

2.4.2.5.6.1. DRIFT IR

DRIFT IR spectra for CHTlc 3 (calcined Zn/Al x=3) show broad absorption peak between 3600-3300 cm^{-1} due to metal-OH stretching vibrations from brucite-like layers (figure 2.22 spectra a). Effect of higher calcination temperature (873K) is reflected in disappearance of carbonate-water bridging vibrations at 2900-2850 cm^{-1} due to loss of water. The peak at 1360 cm^{-1} is ascribed to $[CO_3]^{2-}$ vibration which is weak in intensity resulting from absorption of atmospheric CO_2 during synthesis. Another weak absorption peak is observed between 500-450 cm^{-1} ascribed to translation of Zn/Al-OH bonds.

Immobilization of CAT-3 on CHTlc 3 can be confirmed from spectra b in figure 2.22. In addition to the peaks for CHTlc 3 appearance of peaks at 3142 cm^{-1} and 2900-3000 cm^{-1} can be noticed indicating the C-H stretching of imidazolium and C-H stretching of aliphatic chain respectively. Aromatic C=N and C=C stretching vibrations can be observed at 1456 cm^{-1} and 1572 cm^{-1} correspondingly. The broad peak at 3400 cm^{-1}, less in intensity as compared to CHTlc 3 is seen merged with C-H stretching vibrations of imidazolium moiety. This implies that upon calcination the brucite-like layered structure collapses (see section 2.1.9, Chapter 2) to an extent but still appreciable amount of metal-OH interactions are present indicating partial loss of structural water which is expected to show substantial decrease at higher calcination temperature of above 973K.
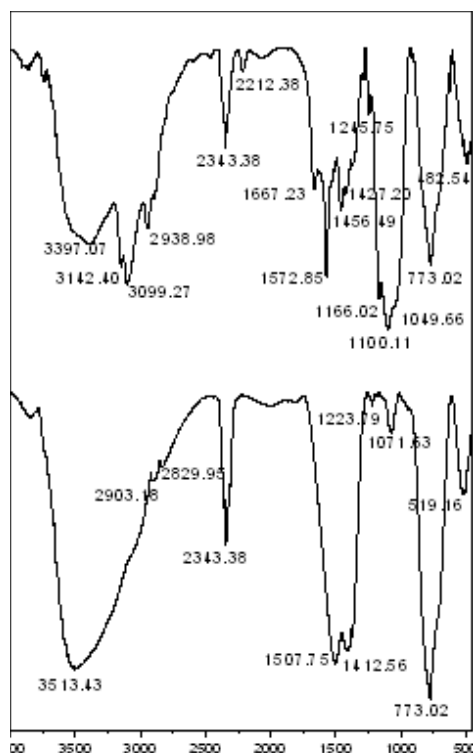
Figure 2.22. DRIFT IR spectra of CHTlc and 35% IL CAT-3 grafted CHTlc (Zn/Al x=3)

2.4.2.5.6.2. XRD

Figure 2.23 and 2.24 shows powder XRD patterns of the as-synthesized hydrotalcite samples with Zn/Al molar ratios of 3 and 6. The samples exhibit the typical hydrotalcite structure, with (003), (006), (101), (012), (104), (015) and (018) diffraction peaks, at 0.757, 0.382, 0.280, 0.259, 0.247, 0.229 and 0.194 nm respectively, typical of the LDH phase, zincite type ZnO and composite Zn-Al phases. Figure 2.23 spectra corresponding to HT X=3 shows the diffraction peaks at (003), (006), (015) and (01 8) typical of the LDH structure, at 0.759, 0.378, 0.229 and 0.194 nm respectively along with less resolved peaks corresponding to zincite phase. The XRD pattern shows increase in crystallinity with the increases in Zn content. This is reflected in increase in sharpness of the peaks along with emergence of the other major peaks (figure 2.23) observed at d-values 0.281, 0.259, 0.247, 0.190, 0.162, 0.148 and 0.138 nm, coinciding with the ZnO phase. The main peak with d (003) spacing for HT with Zn/Al molar ratios of 3, 6 shows the value of 0.76 nm attributed to the diffraction for the space between the adjacent layers in the hydrotalcites.[198] The d (003) spacing of the nitrate absorbed hydrotalcite is 0.76 nm. The

Zn-Al hydrotalcites have a rhombohedral R-3m symmetry, in which the Zn^{2+} and Al^{2+} cations are incorporated in brucite type layers and the excessive positive charges on the layers are compensated by carbonate anions in the interlayers.
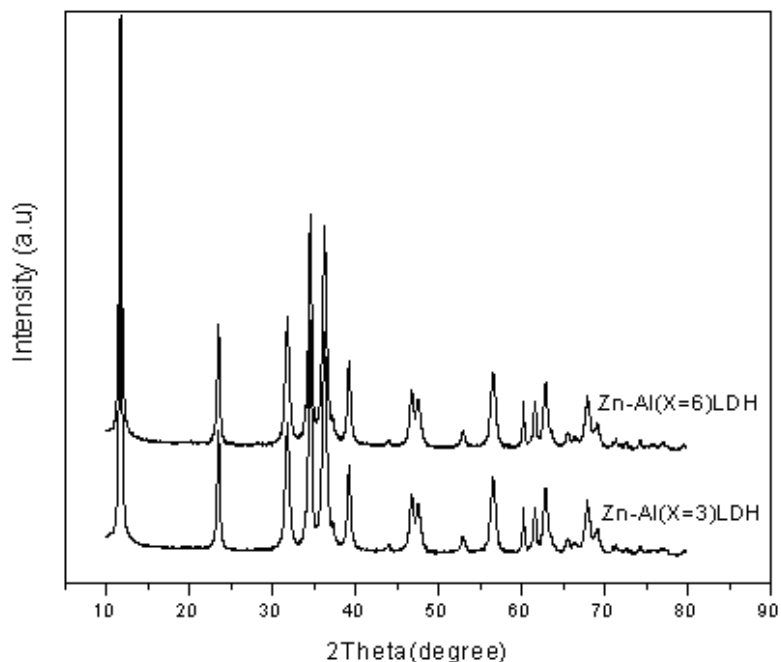
Figure 2.23. Powder XRD pattern of uncalcined Zn-Al HT (x=3, 6).

The XRD pattern of Zn-Al (6) CHTlc calcined at 873K and Zn-Al (6) CHTlc loaded with different amounts of TESP-MImCl IL is shown in Figure 2.24. The CHTlc shows the diffraction peaks corresponding to zincite-type ZnO phase at (100), (002), (101), (102), (110), (103) and (112) appearing at *d* space (nm) 0.279, 0.258, 0.246, 0.190, 0.162, 0.147, and 0.137 respectively. The absence of (003), (006), (101), (012), (104), (015) and (018) diffraction peaks, typical of the LDH structure, at *d* space (nm) 0.757, 0.382, 0.280, 0.259, 0.247, 0.229 and 0.194, respectively, indicates the formation of mixed oxide phase. This data is in accordance with ASTM data for ZnO zincitetype phase (ASTM 5-664). The XRD profiles of TESP-MImCl IL loaded on calcined HT for various loading viz, 2.06, 4.2, 8.26, 17.5 and 35 % does not show significant change in diffraction pattern indicating retention of zinc oxide phase after IL loading. This supports our assumption that IL is coated on mixed oxide support by ionic interactions.
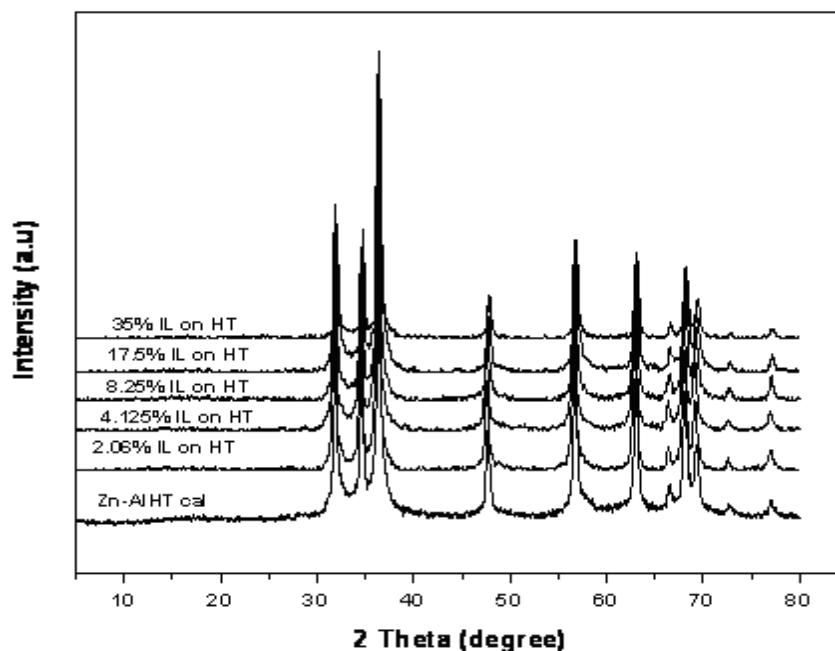
Figure 2.24. Powder XRD pattern of calcined Zn-Al HT (x= 6) and grafted with different amount IL CAT-3.

2.4.2.5.6.3. SEM

SEM images of uncalcined Zn-Al (6) HT showed (Figure 2.25) evenly dispersed thin plates with hexagonal morphology of average diameter of 100nm. Calcined samples showed (Figure 2.25b) disordered thin plates with hexagonal morphology. The SEM observations were in good agreement with XRD results and surface area measurements. Hexagonal plates embedded in IL are clearly visible in SEM image of 35% IL loading on CHTlc with amorphous morphology (Figure 2.25c).
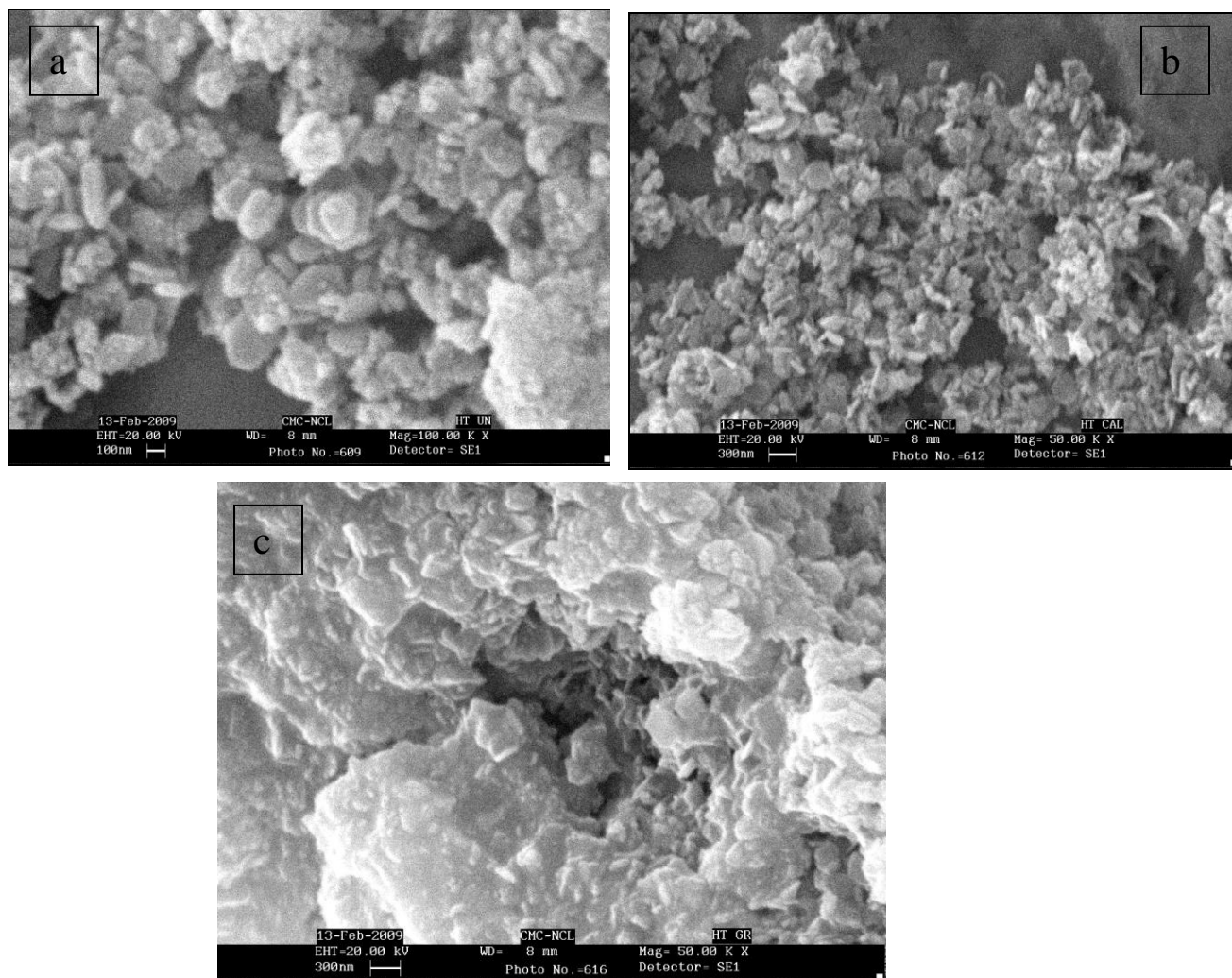
Figure 2.25. SEM micrographs of a) HTlc (Zn/Al x=6) b) CHTlc (Zn/Al x=6) and c) 35% CAT-3 loaded CHTlc (Zn/Al x=6).

2.4.2.5.6.4. SSNMR

2.4.2.5.6.4.1. ^{13}C CP MAS NMR.

Usually mixed metal oxides obtained by calcinations of hydrotalcites do not have enough active OH groups, the conventional anchoring methodology does not work here, however coating by incipient wetness can be of significant interest in this case. Figure 2.24 shows the ^{13}C CP MAS spectra of varied degree of TESP-MImCl loading on CHTlcs support. The characterization of ionic liquid TESP-MImCl immobilized on silica by ^{13}C CP MAS has been earlier reported.[199] The spectrum shows (Figure 2.26) signals in two regions viz., aliphatic from 0-55 ppm and aromatic from 120-170 ppm. The signals

appearing in aliphatic region are due to silica bound ethoxy moiety (Si-OC$_2$H$_5$), silica bound propyl moiety (Si-C(1)H$_2$-C(2)H$_2$-C(3)H$_2$-N-) and N-CH$_3$. The signal at δ=12.6 ppm is due to CH$_3$ of ethoxy moiety attached to Si while other methyl group attached to N of imidazoline ring (NCH$_3$) resonate at δ=37.6 ppm (See Figure 2.26a). The signal at δ=25.84 ppm is due to carbon of propyl group that is attached to Si-CH$_2$-. The other two carbons of propyl group give signals at δ=33.4 ppm (-C-CH$_2$-C-) and CH$_2$-N at δ=49.2 ppm. The signal appearing at δ=53.05 ppm can be assigned to CH$_2$ of ethoxy group attached to Si. In the aromatic region three prominent signals are present (Figure 2.26a), The N*CH*C*H*N are resolved at δ=123.82 ppm and 138.71 ppm and are assigned to NCH*C*HN and N*C*HCHN respectively while signal at δ=167.94 ppm is due to N*C*H- N. It can be clearly seen from Figure 2.26 (a-e) that, at lower IL loadings (≤ 8.5%) clear interactions of IL with support can be visible (splitting of NMR signals) while at higher loadings (17.5 & 35% Figure 2.26, d-e) NMR signals due to neat IL are observed. These results indicate that ionic liquid TESP-MImCl is remaining intact on hydrotalcite support and may be stabilized by acid-base sites on CHTlc as shown in (Scheme 3.2 Chapter 4). In Figure 2.28, spectra c shows ^{13}C MAS NMR spectra for Zn-Al (6) LDH phase with single prominent peak corresponding to carbon of carbonate anion in the interlayers.

2.4.2.5.6.4.2. ^{27}Al CP MAS NMR

^{27}Al CP MAS NMR spectroscopy of hydrotalcites and hydrotalcite like materials provide useful information on the structural geometry of Al^{3+} ions and it`s environment. Figure 2.26 shows ^{27}Al CP MAS NMR spectras for calcined hydrotalcite and TESPMimCl (CAT-3) IL impregnated on calcined hydrotalcite. ^{27}Al CP MAS NMR spectrum of calcined hydrotalcite show that transition of Al^{3+} ion from octahedral (Al$_O$) to tetrahedral (Al$_T$) sites occurred during calcinations of LDH. [200,201,202]Figure 2.27a shows the ^{27}Al MAS NMR spectra of Zn-Al(6)CHTlc calcined at 873K and that of Zn-Al (6) CHTlc loaded with TESP-MImCl IL (Figure 2.26, b-f). ^{27}Al CP MAS NMR spectrum of Zn-Al (6) CHTlc shows peaks at 5.38, 75.47 and one new peak at 48ppm (Figure 2.26a) the first two peaks corresponding to Al^{3+} in Al$_O$ and Al$_T$ sites respectively, while resonance at 48 ppm is attributed to penta coordinated Al^{3+} ion.[203] It may be noted that ^{27}Al CP MAS NMR of uncalcined Zn-Al(6) HTlc showed signal at 14.6 ppm with spinning side bands indicating that before calcinations Al$_O$ geometry was predominant (figure 2.27

spectra a). After calcination peaks at 5.38, 75.47 and one new peak at 48ppm are developed indicating transition of Al^{3+} in Al_O, Al_T and in penta coordinated form (figure 2.27 spectra b). The formation of penta coordinated Al^{3+} ion (Al_P) is not generally observed for Mg-Al HTlcs, however, for Zn-Al HTlc it has been observed earlier.[204] The ^{27}Al MAS NMR spectra of samples with lower loading 2.6 and 4.12 % of IL on Zn-Al(6) CHTlc shows Al_T and Al_P peaks contributing weakly whereas peak corresponding to Al_O coordination is enhanced suggesting a high probability of ionic interaction between IL and Al^{3+} in octahedral coordination. As the IL loading was increased from 8.2 to 14% a gradual increase in Al_T and Al_P peaks was observed with concomitant decrease in Al_O coordination peak (Figure 2.27d,e) whereas at 35% loading showed diminished peaks for Al_T and Al_O coordination and peak corresponding to Al_P coordination was enhanced (Figure 2.27f). This suggests that at lower IL loading ionic interactions between metal and oxygen species of CHTlc and IL might be prominent with Al_O sites and at higher loadings (> 4.26% IL) interactions with Al_T and Al_P sites predominantly are dominating. Such variation in Al_T and Al_O sites could modify morphology of the mixed oxides formed. These results are indicative of changes in the structure of CHTlc upon increase in loading of IL. The results obtained from ^{27}Al MAS NMR spectroscopy are important particularly since XRD data of the samples did not showed any phase changes in CHTlc structure. NMR is a more sensitive tool to phase transition and less affected by particle size and degree of crystallinity of samples.[205,206] And that it can probe the change in environment of Al^{3+} cations more efficiently than do XRD. The physical properties of above synthesized hydrotalcites used for catalytic investigation are reported in Table 4.1 in Chapter 3, Section B.

δ ppm
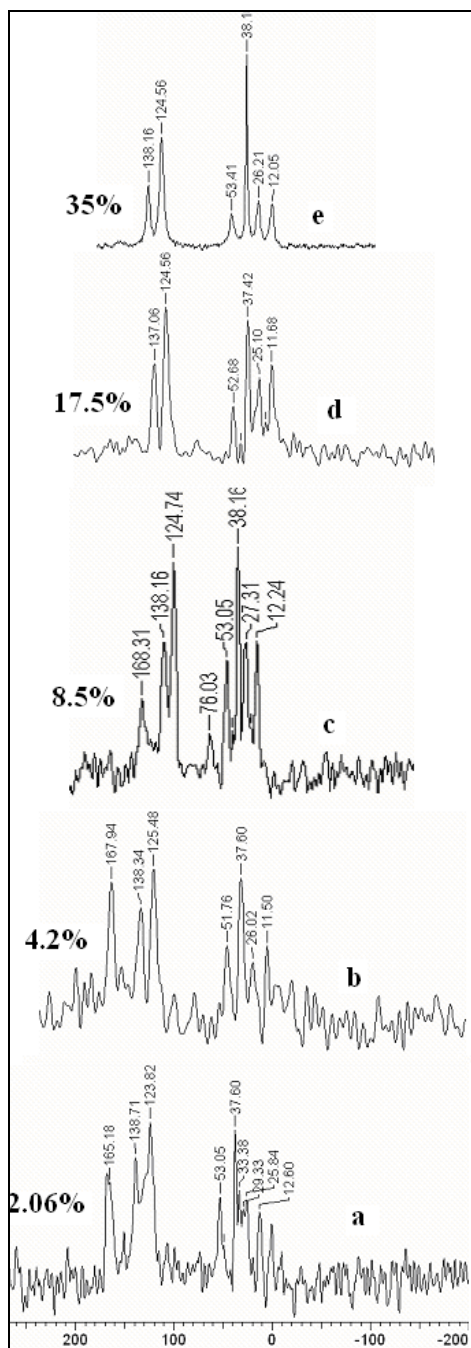
Figure. 2.26. ^{13}C CP MAS NMR of different loading of CAT-3 IL supported on CHTlc (Zn/A/ x=6)

δ ppm
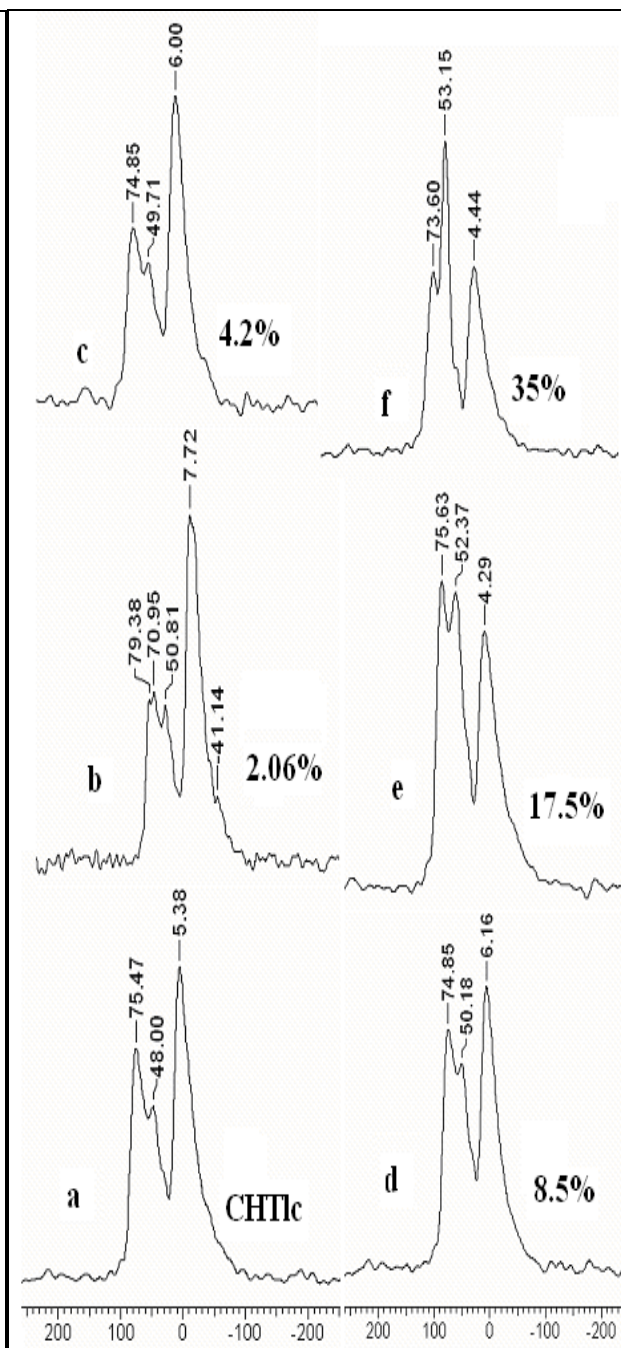
Figure. 2.27. ^{27}Al CP MAS NMR of different loading of CAT-3 IL supported on CHTlc (Zn/A/ x=6)
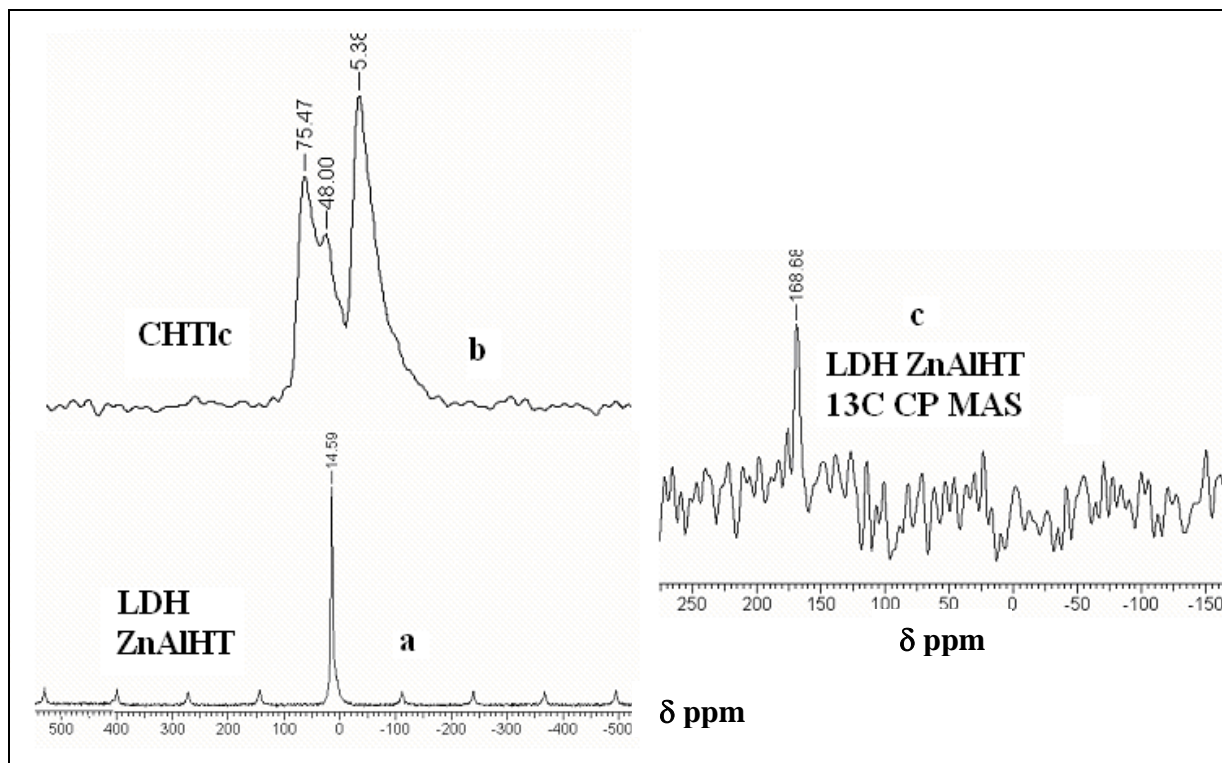
Figure 2.28 a) [27] Al CP MAS NMR of HTLc (Zn/Al x=6), b) [27] Al CP MAS NMR of
CHTLc(Zn/Al x=6) and c) [13] C CP MAS NMR of HTLc (Zn/Al x=6)

2.4.2.5.7. Characterisation of 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride immobilized on Montmorillonite

2.4.2.5.7.1. DRIFT IR

The DRIFT IR spectra for MK5 and 35%MK5 are shown in Figure 2.25. Both samples were characterized by absorptions at 1089, 1024, and 461 cm^{-1} related to Si-O-Si groups and absorptions at 517 cm^{-1} related to Al-O-Al groups. Other absorptions at about 3411 and 1630 cm^{-1}, related to the adsorbed water, were also observed. Weak bands at 779 and 630 cm^{-1} were associated with quartz and cristoballite, respectively. In the spectrum of 35%MK5, absorptions related to C-H stretching of imidazolium and C-H stretching of aliphatic chain is observed at 3157 cm^{-1} and 2850-3000 cm^{-1} respectively. Aromatic C=N and C=C stretching vibrations can be observed at 1464 cm^{-1}and 1573 cm^{-1} correspondingly. This substantiates the presence of organic moiety on MK5.
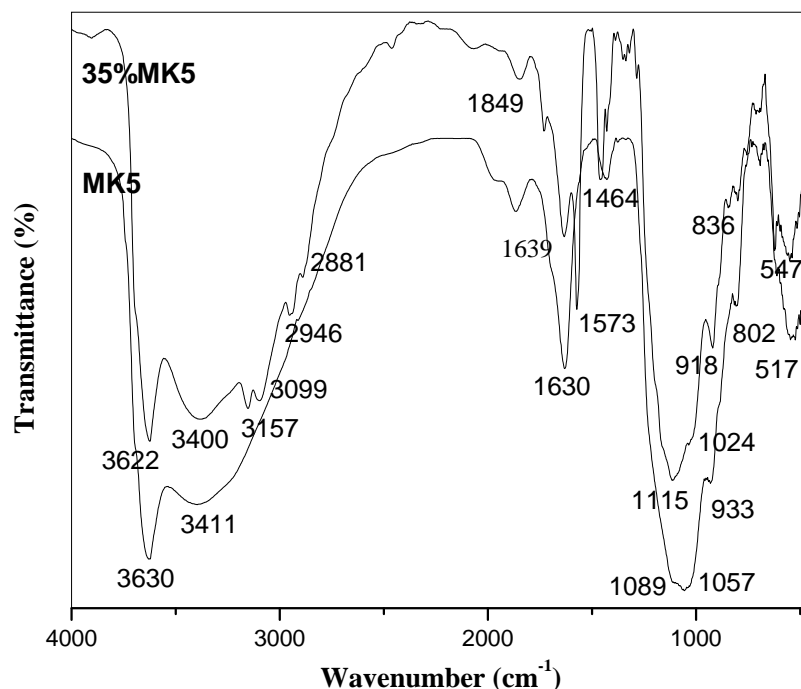
Figure 2.29. DRIFT IR spectra of MK5 and 35% IL CAT-3 grafted on MK5

2.4.2.5.7.2. SSNMR

2.4.2.5.7.2.1. ^{29}Si MAS NMR Spectra

Figure 2.28 shows the ^{29}Si spectra for montmorrillonite K5 and 35% loaded CAT 3 on montmorrillonite K5. Both the spectra show a prominent signal at δ=-91-99 ppm attributable to one ^{29}Si coordinated with three tetrahedral silica, Q^3(OAl), as reported in the literature[207],[208] for the bidimensional framework of sheet silicates. The signal between δ=−108-109 ppm is attributable to one ^{29}Si coordinated with four silica, Q^4(OAl). It comes from the feldspar/silica impurities already present in the initial montmorillonite sample. In addition to above signals the signals in spectra (figure 2.28) at 60 ppm and 69 ppm referred as T^2 and T^3 respectively indicates presence of organosiloxane groups assigned to Si–O–**Si**R–(OEt)$_2$ and (Si-O)$_2$–**Si**R–OEt groups.

2.4.2.5.7.2.2. ^{27}Al MAS NMR Spectra

In the case of the ^{27}Al MAS NMR spectra Al atom in Al[(H$_2$O)$_6$]$^{3+}$, Al resonances in the range 50 ± 20 ppm indicates the presence of tetrahedral coordinated Al while the octahedrally coordinated Al resonates at 0 ± 20 ppm. [209],[210] The ^{27}Al spectra of the montmorrillonite K5 and 35% loaded CAT 3 on montmorillonite K5 (figure 2.29) show a central line close to -1.24 ppm, assigned to Al (VI) of the octahedral layer of sheet silicates. A very weak signal around 50 ppm and 64 ppm, attributable to Al (IV) due to the replacement of Si by Al in the tetrahedral layer or to impurities in the starting materials. The small resonances on either side of the principal resonance are spinning sidebands (SSBs) which are due to chemical-shift anisotropy.[211] The fact that the signals in ^{27}Al and ^{29}Si CP MAS NMR of montmorrillonite K5 and 35% loaded CAT-3 on montmorrillonite K5 does not show shift indicates that the original layered structure is preserved during immobilization step.

δ ppm
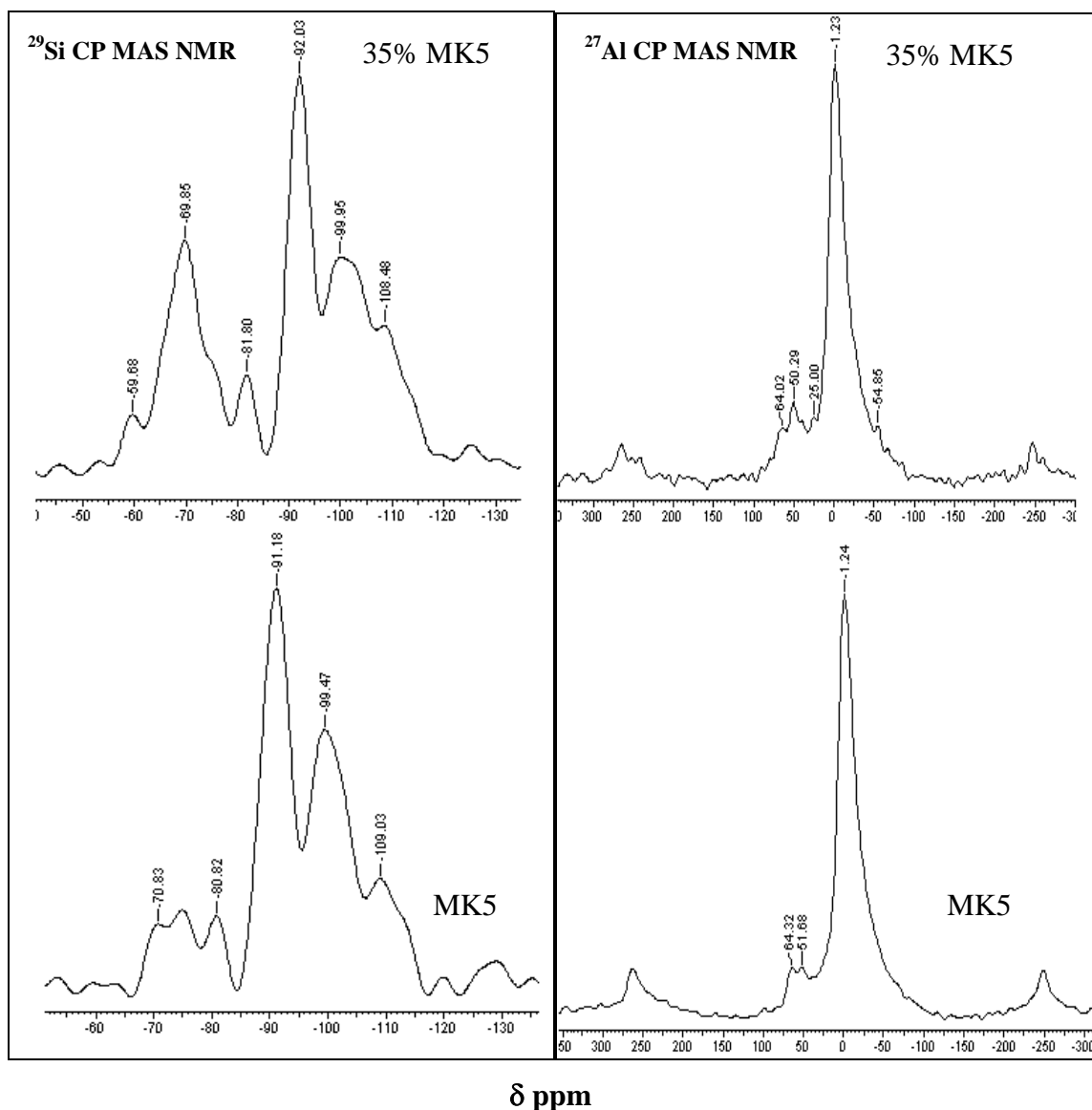
Figure. 2.30. ^{29}Si and ^{27}Al CP MAS NMR of MK5 and CAT-3 IL supported on MK5

2.4.2.5.7.2.3. Surface area determination by BET Method

The nitrogen adsorption desorption isotherm for montmorilloniote clay K5 show characteristics of isotherm types I and IV corresponding to microporous and mesoporous solids according to IUPAC classification.[212],[213] Initial part of isotherm is steep (P/Po ~ 0.0 to 0.4) typical of microporous solids with a distinct hysteresis loop from P/Po ~ 0.4 to 1.0. The shape of hysteresis loop is H3 type indicating slit shaped pores.[214] The surface area of MK5 was found to be 140.79m^{2}g^{-1} with average pore diameter 92.59Å. The nitrogen adsorption desorption isotherm for CAT3 IL immobilized on montmorilloniote

clay K5 show similar nature of isotherm as that for MK5. But the shape of hysteresis loop seems to be compressed indicating filling of pores by IL maintaining original structure of MK5. This is supported by sharp decrease in surface area ($31.58m^2g^{-1}$). Other physical properties are given in table 2.7.
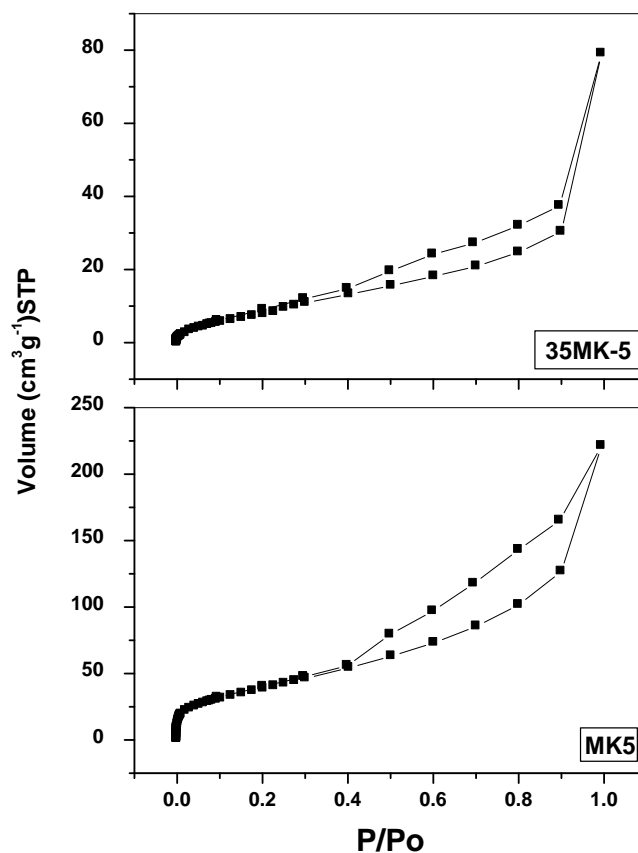
Figure 2.31. Nitrogen adsorption-desorption isotherms for neat MK5 and 35% CAT-3 loaded on MK5.

Table 2.7. Physical properties of neat MK5 and IL grafted on MK5.			
Entry	Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter ($\mathring{A}$)
1	MK5	140.79	3.432×10^{-1}	92.59
2	35MK5	31.58	1.227×10^{-1}	127.4

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Chapter 3

Organic transformations using immobilized/organic-inorganic hybrid catalyst

Section A

Immobilized Ionic Liquid:
Efficient Catalyst for Cycloaddition of CO$_2$ to Epoxides under mild conditions
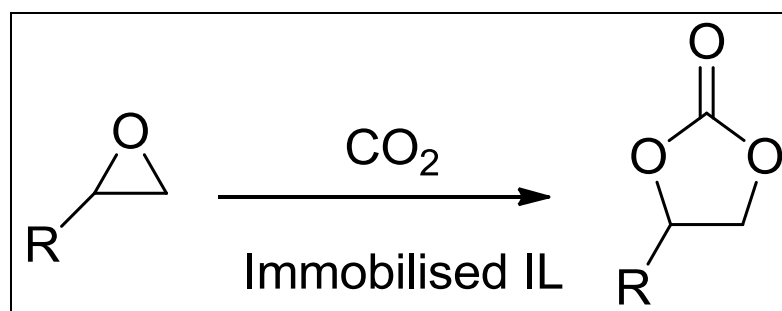
3.1. INTRODUCTION

The subject of cycloaddition of carbon dioxide to epoxide in the synthesis of carbonate has been the focus of chemical industry for last two decades or more for being a benign alternative route for carbonate synthesis. The ultimate goal of carbonate synthesis from epoxides and CO_2 is to produce polycarbonate. In the development of CO_2 based route, two approaches have been adopted by researchers, the first being the direct synthesis of polycarbonate, while in the second approach which is based on the synthesis of monomer (cyclic carbonate) from epoxide and CO_2, followed by transesterification of monomer with methanol to dimethyl carbonate and further to polycarbonate using established process.[1] Cyclic carbonates find wide applications as polar aprotic solvents, electrolytes for lithium-ion batteries, and as intermediates in the manufacture of fine chemicals.[2,3,4] They are also used as constituents of oils and paints and as raw materials in the synthesis of polycarbonates and polyurethanes.[2,5] They are also employed in polymer modification, pre-polymer synthesis and the production of super-absorbent polymers.[3,6] Cyclic carbonates are useful alkylating agents for aromatic amines, phenols and thiols, though high temperaturesare required.[2] A number of methods are in practise for the synthesis of cyclic carbonates. Besides cycloaddition of CO_2 to epoxides, cyclic carbonates can be accomplished via alternate routes viz;

a) Oxidative carboxylation of olefin

b) Carboxylative cyclization of propargyl alcohol with CO_2

c) From CO_2 and 1,2-diols

d) Electrochemical synthesis of cyclic carbonates

The details of these methods are;

a)Oxidative carboxylation of olefin

This method couples two sequential reactions; epoxidation of olefin and CO_2 cycloaddition to epoxide. This reaction was reported to be catalyzed by Niobium oxide catalysts in the presence of molecular oxygen and DMF as the solvent. With this catalyst styrene carbonate was obtained in poor conversion (27%) and selectivity and under high pressures (50 atmospheres) and temperature (398K) conditions.[7] Later on Arai et al reported use of ionic liquid in the presence of TBAB and *tert*-butyl-hydroperoxide (TBHP) as the oxidizing agent, as catalyst for this reaction. With this

catalyst system improved yield of styrene carbonate were achieved though high pressure and temperature conditions were still required (10 atmospheres, 353K, 6 h, 38% yield).[8] Arai et al. reported further improvement in terms of one-pot catalytic system consisting of 2.5 mol% of ZnBr$_2$ and 5mol% of TBAB using 1–8 weight% loading of gold on silica and TBHP or cumene hydroperoxide as oxidant under 80 atmospheres pressure of CO$_2$ at 353K yielding 31–37% of styrene carbonate in 4 h. Besides low conversion another significant drawback of this system was formation of benzaldehyde during course of reaction.[9] From the study of various parametric effects of pressure and temperature they concluded that the limiting process is the oxidation of the alkene to the epoxides (Scheme 3.2)[10].

Scheme 3.2 Oxidative carboxylation of olefin
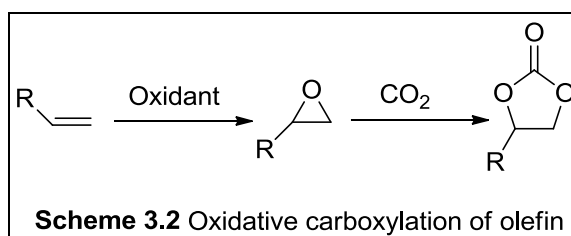
b) Carboxylative cyclization of propargyl alcohol with CO$_2$

Cyclic carbonate synthesis was also reported by carboxylative cyclization of propargylic alcohols in supercritical CO$_2$ (Scheme 3.3)[11] using(CuI-[(dimethylamino)methylpolystyrene;DMAM-PS) as catalyst giving cyclic carbonate in 99% yield at 313K and 14 atmospheres.[12] Even though this catalyst showed good recycling ability for five recycles the only drawback of this system was a high pressure condition.

Scheme 3.3. Carboxylative cyclization of propargyl alcohol with CO$_2$
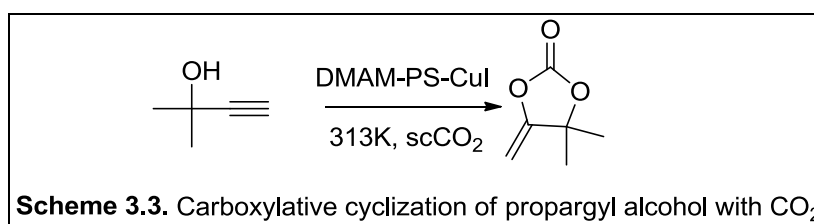
c) From CO$_2$ and 1,2-diols

In this method synthesis of cyclic carbonates was reported by reacting diols and urea using metal oxide catalyst. Ethylene carbonate was reported using zinc oxide[13] as catalyst and propylene carbonate was reported using anhydrous zinc acetate[14]or dibutyltin oxide or dibutyltin dimethoxide[15] as catalysts (Scheme 3.4).

Scheme 3.4. Cyclic carbonate synthesis from CO$_2$ and diols
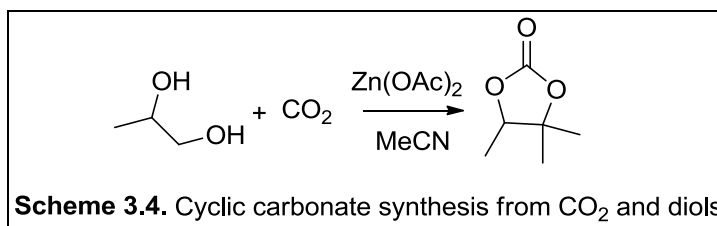
d) Electrochemical synthesis of cyclic carbonates

Cyclic carbonate synthesis was also explored by electrochemical route from CO$_2$ with epoxides, alcohols and glycols.[16,17,18] A number of catalyst investigated for this system include ionic liquid[19] Ni(cyclam)Br$_2$ catalyst,[20] [Ni(bipy)$_3$]2-(BF$_4$)$_2$ complex[21] In these methods, harmful organic solvents, supporting electrolytes and/or catalysts were necessarily used and owing to reaction conditions employed, this method is less explored from industrial application point of view.

Recently, several excellent reviews[9, 10] have appeared on cyclic carbonate synthesis which mentions the use of various catalysts to catalyze this transformation effectively. These reviews stress the fact that both acido-basic nature of catalyst is necessary (cooperative catalysis) for efficient operation of catalyst for this system. Since the work presented here focuses on cycloaddition of CO$_2$ to epoxides for carbonate synthesis (Scheme 3.5) using immobilized IL, literature corresponding to IL and various immobilized catalysts will be discussed in detail in following section.

Scheme 3.5. Cycloaddition of CO2 toepoxide
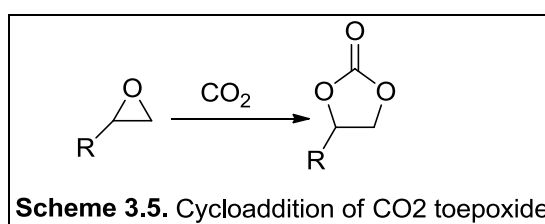
3.1.1. Cyclic carbonate synthesis using various catalysts

Synthesis of cyclic is reported employing variety of catalysts. A brief literature survey on activity shown by these catalysts and mechanism is presented below.

3.1.1.1. Ionic liquids

Use of Ionic liquids, as catalyst for cyclic carbonate synthesis was reported for first time by Peng and Deng.[22] They reported quantitative yield of propylene carbonate in the presence of 2.5 mol% of [BMIm]BF$_4$, at 25 atmospheres pressure and 383K for

six hours with a TOF of 6.6 h-1. Ionic liquids or their combination with Lewis acids like metal salts as co-catalyst have been explored extensively as catalysts for the synthesis of cyclic carbonates.[8,10] Kim et al.[23] have reported better yields with Lewis acid $ZnBr_2$ as co-catalyst along with ([BMIm]BF_4 although high-pressure conditions were still necessary. Later on Xia *et al.* reported detailed screening of ILs [BMIm]X (X = Cl, Br, BF_4, PF_6) and zinc salts as catalyst for addition of CO_2 to propylene oxide.[24] $ZnBr_2$ and [BMIm]Br as a catalyst system was found to be highly effective because 98% yield of propylene carbonate were obtained using mild operating conditions at 373K for one hour using a CO_2 pressure of 15 atmospheres. $ZnCl_2$/[BMIm]Br as catalyst system gave comparable results of 95% yield. This catalyst system was effective for other epoxides like epichlorohydrin, 1,2-epoxybutane and styrene oxide except cyclohexene oxide which gave poor yield (34%). Soon after he reported use of immobilized catalytic system prepared from silica supported covalently bonded ionic liquid via a sol–gel method and used as a catalyst along with $ZnCl_2$.[25] After detailed parametric study of catalyst loading, CO_2 pressure and temperature, 96% yield of propylene carbonate was realised using 1.2 g of the immobilized ionic liquid at 15 atmospheres pressure and a temperature of 383K in one hour. A similar solvent less catalytic system, comprising of [BMIm]BF_4 adsorbed onto amorphous silica to form supported ionic liquid catalysts was reported to give excellent yields of 96% with >99% selectivity for cyclic carbonate synthesis.[26] The optimal conditions were found to be 433K for 4 h using 1.8 mmol% in the presence of supercritical CO_2 at 80 atmospheres pressure. Even though a minor drop in activity was observed using silica supported [BMIm]BF_4 against the neat [BMIm]BF_4, the supported catalyst showed obvious advantage of catalyst separation and recycling. Similar to Xia et al they also observed retarded reaction rates for these catalyst systems above and below optimised temperature and pressure conditions. In 2008 Udaykumar et al.[27] reported synthesis of allyl-glycidol carbonate using immobilized ammonium salt based system. These immobilized catalysts were prepared from covalently binding quaternary ammonium salts *via* an organic linker to MCM-41. With 1.0 g of catalyst tri ethyl ammonium chloride (-NR₃Cl) immobilized on MCM-41 gave 70% conversion, with 89% selectivity under solvent-free conditions at 7.5 atmospheres pressure of CO_2 for 10 h at 383K. On varying alkyl group of ammonium salt i.e. with (-NHex₃Cl) and with pyridinium chloride gave poor

conversions. Later on Udaykumar and co-workers reported synthesis of allylglycidyl carbonate using immobilized imidazolium-based ionic liquids{ [BMIm]X; X=I,Br and [BPrIm]Br }.[28] He investigated the effect of various forms of silica as support towards formation of cyclic carbonate. He reported low TOFs ranging from 4.4 h-1 to 5.3 h-1 with [BMIm]Br, [B*n*-PrIm]Br and [B*i*-PrIm]Br supported on MCM-41 at 16.5 atmospheres pressure and 383K. By increasing CO_2 pressure to 17.7 atmospheres and using amorphous silica as the support better TOFs of 13.0 h-1 for ILs [BMIm]I, [B*n*-PrIm]Br and 16.2 h-1 for [BMIm]Br were achieved. Further increasing the pressure to 35 atmospheres increased the rate of reaction with TOF ranging from 13.5-19.9 h-1. Best result was accomplished with [BMIm]Br supported on mesoporous silica giving TOF of 32.6 h-1 at 35 atmospheres CO_2 pressure. A similar catalyst [BMIm]Br supported on silica was used by Park *et al.* for allylglycidyl carbonate synthesis which gave only 77% conversions at 383K under 7.5 atmospheres of CO_2 pressure. Lee *et al* investigated [OMIm]Cl as catalyst for CO_2 addition to 4-vinyl-cyclohexene oxide.[29] This catalyst furnished 62% cyclic carbonate yield at 413K, and 10 atmospheres pressure. Electrochemical synthesis of cyclic carbonates from CO_2 and epoxides using Ionic liquids is also reported extensively.[30] A new series of hydroxyl-functionalized imidazolium-based ionic liquids [HeMIm]Br are reported as active catalyst for propylene carbonate in 99% yield at 398K and 20 atmospheres CO_2 pressure. The immobilized form of the same catalyst (1.6 mol%) was also explored by immobilizing as a copolymer with styrene with moderate enhancement in activity. [31]This immobilized form of IL was effective for cyclohexene carbonate (80% yield in 20 h at 398K). The results of neat and immobilized catalyst were comparable and immobilized version had the added advantage of catalyst recyclability, with no apparent loss of activity after six reactions. Qiao and Yokoyama reported one-pot synthesis of styrene carbonate in 83% yield from styrene in a multi-step process under a 30 atmospheres pressure of CO_2 at 383K using zinc based cocatalyst ($Zn[EMIm]_2Br_4$) with urea hydrogen peroxide as oxidant and 2 mol% methyltrioxorhenium as oxidation catalyst.[32]

3.1.1.2. Quaternary ammonium and phosphonium salts

Various quaternary ammonium and phosphonium salts have been screened as catalyst for cyclic carbonate synthesis. Amongst tetrabutylammonium bromide,[33]

tetraalkylammonium salts, tetrahexylammonium chloride, the best result of 81% cyclic carbonate was obtained at 373K and 9 atmospheres pressure using tetrahexylammonium chloride as a catalyst for CO$_2$ insertion to epoxides.[34] Baba *et al.* reported 100% propylene carbonates yield using tetraalkylammonium or phosphonium halides combined with n-Bu$_3$SnI at 313K under 49 atmospheres of CO$_2$ pressure in 1h.[35] Pentavalent organoantimony halides such as Ph$_4$SbBr, Ph$_3$SbBr$_2$ and Me$_3$SbBr$_2$ were also found to be active catalysts for cyclic carbonate synthesis.[36] Later on He *et al.* reported a range of silica-supported quaternary ammonium salt catalyst for the synthesis of cyclic carbonates in excellent yields ($\geq$96%) and selectivity ($\geq$97%) from terminal epoxides under supercritical conditions and at 423K for 10 h.[37] Though catalyst recovery was easy by filtration but these catalysts showed slight reduction in activity after four recycles. Sakay *et al. reported* 3-(Triethoxysilyl)propyltriphenylphosphonium bromide supported on mesoporous silica to be a highly active catalyst for the addition of CO$_2$ to 1,2-epoxyhexane under solvent-free conditions.[38] The cyclic carbonate product was obtained with 99% conversion at 363K and 10 atmospheres pressure. Catalyst recycle study showed that this catalyst could be reused over 10 runs, without a significant loss in activity. With a range of quaternary ammonium or phosphonium salts supported on a polystyrene support, moderate results were obtained for cyclic carbonate synthesis.[39] A quaternary trimethylammonium iodide supported on chitosan (chitosan-NMe$_3$I) was found to catalyse the synthesis of propylene carbonate in 100% yield with high selectivity.[40] Other supported catalysts reported for this transformation include silica-supported ammonium and aminopyridinium halides.[41]

3.1.1.3. Metal porphyrin, polyoxometallate Phthalocyanine Complexes.

Aluminium porphyrinate complex with *N*-methylimidazole as cocatalyst activates CO$_2$ at room temperature, and atmospheric pressure in a dichloromethane solution affording propylene carbonate in moderate yields (8–40%) with poor selectivity for propylene carbonate against poly propylene carbonate.[42] Similarly, Kasuga *et al.* reported the aluminium(III) phthalocyanine complexes in presence of *N*-methylimidazole for the addition of CO$_2$ to propylene oxide at room temperature and atmospheric pressure, giving selectively propylene carbonate but in poor yield.[43] In addition to these complexes a variety of other metal complexes has been reported for

cyclic carbonate synthesis. These include chromium(III) and chromium(IV) derivatives[44] with NMI or DMAP as co catalyst resulted in quantitative cyclic carbonate yield at 343–373K and 26 atmospheres pressure. Another striking feature of this system was the introduction of methyl substituents onto the phenyl rings improved the solubility of complex. Cobalt porphyrin/DMAP system was reported by Nguyen *et al.* for CO$_2$ cycloaddition to epoxides.[45] Co(III)TPP(Cl) and Co(II)TPPCl were prepared from tetraphenylporphyrin (TPP) as a ligand to chelate cobalt. The best result was obtained using Co(III)TPP(Cl) with two equivalents of DMAP showed 50 times higher activity than Co(II)TPPCl at 17 atmospheres of CO$_2$ at 393K. Jing et al. reported cobalt TPP complexes with other counterions and phenyltrimethylammonium tribromide (PTAT) as cocatalyst for the addition of CO$_2$ to propylene oxide. [46]Other metal complexes explored were manganese iron and ruthenium (TPP)Cl, but none of these were particularly effective with poor TOFs of 33 to 90 h-1 as compared to Cobalt(III) acetate/TPP complex (TOF of 620 h^{-1}). Copper phthalocyanine complex with DMAP as cocatalyst in dichloromethane as solvent was reported by Srinivas *et al.* for the addition of CO$_2$ to epichlorohydrin. A series of copper and manganese macrocycles and Schiff base complexes were also investigated for cyclic carbonate synthesis by the same group.[47] Copper tetraphenylporphyrin gave a TOF of 489 h-1 against Copper phthalocyanine complex (TOF 502 h-1).

Manikandan *et al. reported the* use of the zinc-substituted polyoxometalate system Na$_{12}$[WZn$_3$(H$_2$O)$_2$(ZnW$_9$O$_{34}$)$_2$]·46H$_2$O in dichloromethane with DMAP as co catalyst for cyclic carbonate synthesis with 84-97% epoxides conversion at four atmospheres CO$_2$ pressure and 413–433K temperature.[48] Other metal substituted polyoxometalate systems explored by Sakakura *et al.* for the synthesis of cyclic carbonates were [(X)$_6$(a-SiW$_{11}$O$_{39}$M)] type complexes where X is a tetraalkylammonium salt and M as metal(M= Co, Mn, Ni, Fe, Cu).[49] Cobalt and manganese were found to be the most effective as catalysts with cyclic carbonate yield of 73-83%. Polyoxometallate [(*n*-Bu$_4$N)$_9$(P$_2$W$_{17}$O$_{61}$Co(II)Br)] /TBAB / PEG-400 as catalyst at 2.5 atmospheres of CO2 pressure and at 393K was found to give 98% yields of propylene carbonate.[50]

Along with these metal complexes other metal complexes screened for this reaction include palladium(0) complexes[51,52] [Pd(0)BINAP] complex.[53] Re complexes[54,55] Aluminium 8-hydroxyquinolate complex,[56] Organobismuth

complex[57,58] cobalt (III) isophthaldehyde complex,[59] Ruthenium complex,[60] and heterobimetallic complexes prepared by the combination of ruthenium complex and manganese complex.[61] But most of these complexes gave good activity in presence of co catalyst like quaternary salts or strong bases like DMAP.

3.1.1.4. Metal salen complexes and Schiffs bases

In the past decades a variety of salen complexes have been developed from salen ligands and metals from both transition and main-group viz; Chromium, Aluminium, Cobalt, Ruthenium (II) and (III), Manganese (III), Tin (IV), as catalysts for the coupling reaction of epoxides and CO_2. Amongst these complexes, salen complexes of those metals with +3 oxidation state have been found to give best activity for this reaction.

Cr(III)(salen)Cl complex with DMAP as cocatalyst[62] gave cyclic carbonate in near quantitative yield at 373K and 4 atmospheres pressure. Later on Darensbourg's group reported Cr(III)(salen)Cl complex with trans $-(CH_2)_4$ groups on salen ligand to give cyclic carbonate in good yield under 25 atmospheres CO_2 pressure at 313K and with toluene as solvent.[63] Further reports on chromium salen complexes were on solid supported Cr(III)(salen)Cl complex with tributylamine or NMI as co catalyst, for styrene carbonate synthesis.[64] The process was carried out at 353K and 100 atmospheres pressure, and exhibited a moderate epoxides conversion of 74%. Cr(III)(pyrrolidine-salen)Cl complex,[65] (prepared from salen ligand with a nucleophilic unit i.e. strong organic base corresponding to 1,5,7-triazabicyclo-[4.4.0]-dec-5-ene and an electrophilic site the metal centre) gave excellent yield (>95%) of propylene carbonate under 20 atmospheres pressure at 353K. Cr(III)(salophen)NO_3 complex with DMAP[66] have also been reported to give moderate activity for this transformation.

Aluminium salen complexes are reported to catalyzed most of the copolymerization reactions. The pioneering work in 1969 by Inoue et al. in copolymerization of propylene oxide and CO_2 showed that 1:1 Et_2Zn/H_2O mixture as effective catalyst for this reaction at 50–60 atmospheres pressure and 353K. Motivated by work reported by Inoue et al., Darensbourg showed aluminium (III) (salen) complexes effectively catalyzed polymerization of cyclohexene oxide and CO_2 but under supercritical conditions.[67,68] Further reports on aluminium salen complexes

include Aluminium(III)(salen)Cl complex along with TBAB as cocatalyst for quantitative synthesis of ethylene carbonate[69] under 160 atmospheres pressure and at 383K. But this system gave poor results in absence of TBAB cocatalyst. Al(III)(salen)Et complex and 18-crown-6/KI as catalyst exhibited a moderate activity for the synthesis of propylene carbonate, under 6 atmospheres pressure and at room temperature.[70] Cyclic carbonate yields were found to be increased using TBAI instead of 18-crown-6/KI at 308K and 6 atmospheres pressure.[71] *N-N'*-Disubstituted imidazol(in)ium-2-carboxylates and a binary system composed of *N-N'*-Disubstituted imidazol(in)ium-2-carboxylates and Al(III)(salen)Et complex have been reported for propylene carbonate synthesis.[72,73] Later on Garcia et al reported solid supported Al(III)(salen)Cl complex to give styrene carbonate in near quantitative yield under supercritical CO_2 at 353K. Dimeric aluminium(salen) complexes with TBAB as a cocatalyst were found to give 98% conversion of styrene oxide in 24 h using CO_2 at ambient temperature, pressure and under solvent-free conditions. Dimeric aluminium (salen) complexes with covalently bonded quaternary ammonium bromides to the salen ligand[74] and its immobilized form on Merrifield resin and aluminium (salen) complexes immobilized on amorphous silica, MCM-41 were also reported by the same group in batch and/or continuos flow reactor system.[75]

Other family of metal salen complexes found to be effective for cyclic carbonate synthesis were cobalt salen complexes. These complexes are effective for monomeric cyclic carbonate though few reports include stereo-controlled synthesis of polycarbonates from epoxides and CO_2.[76] Chiral [Co(III)(salen)]O_2CCCl_3 and [Co(III)(salen)]OTs with quaternary salts like TBAB, TBACl, and PTAT as a cocatalyst were reported by Lu *et al. and* Jing *et al.* respectively for enantioselective synthesis of propylene carbonate with 50-70% enantiomeric excess at 273K-room temperature and 15 atmospheres pressure.[77,78] Co(II)(salen) complex supported on MCM-41 was also investigated for ethylene carbonate synthesis but under supercritical CO_2 conditions and 383K with 86% of epoxides conversion.[79]

The combination of [Co(III)(salen)]Cl and DMAP was found to be highly active for the synthesis of propylene carbonate at 373K and 10 atmospheres pressure in dichloromethane with 100% selectivity and 99% conversion of epoxides.[80] An additional cocatalyst comprising of chiral DMAP catalyst ((*R*)-(+)-4-dimethylaminopyridinyl-pentaphenylcyclopentadienyl)iron) was also found to give

improved selectivity but low TOF at 276K. Other chiral complexes reported for asymmetric addition of CO_2 to propylene oxide include [Co(III)(salen)]OTs/TBACl[81] and [Co(III)(binad)]OAc[82] in 83-87% enantiomeric excess at 273 and 258K under atmospheric CO_2 pressure. Polymers of chiral BINOL-Co(III)(salen) salts in polymeric form with PTAT/ TBAF were investigated for the synthesis of enantiomeric propylene carbonate at room temperature and 12 atmospheres pressure.[83] A modified bifunctional Co(II)(salen) complex with covalently bonded quaternary phosphonium halides/acetates to the salen ligand were reported to give propylene carbonate in 94% yield at 373K and 40 atmospheres pressure.[84] Acetate as anion gave poor yield. Bimetallic Co(II)(salen) complex containing Lewis-acidic $AlCl_3$ group,[85] along with ionic-liquid [EMIm]OH/TBAI/K_2CO_3 as co catalyst were explored for synthesis of propylene carbonate in enantiomeric excess up to 83%. Other catalyst systems reported for enantiomeric pure propylene carbonate include cobalt salen complexes with cinchona alkaloids as cocatalysts[86] and cobalt (III) salen complexes with various quaternary phosphonium and ammonium salts substituted onto the phenyl rings.[87]

Ruthenium(II) and (III)(salen) complexes were also found effective for the asymmetric synthesis of cyclic carbonates. These include [Ru(III)(salen)]Cl and [Ru(II)(salen)](PPh₃)₂ complex with PTAT as co catalyst at 343K and 8 atmospheres pressure in dichloromethane with 42% yield in 4.5h.[88] Recently a series of diimine Ru(II) complexes were reported for the synthesis of cyclic carbonates from CO_2, and epoxides.[89] Best result was obtained when these complexes were used with DMAP as cocatalyst at 373K and 16 atmospheres pressure and 67% yield of cyclic carbonate.

Baiker et al [90]has thoroughly investigated various homogeneous and immobilized form of [Mn(III)salen]X complexes as catalysts for the addition of CO_2 to epoxides along with mechanistic studies to understand the kinetics and catalytic cycles of the reaction using *in situ* FTIR and X-ray absorption spectroscopy. [Mn(III)salen]I complex gave propylene carbonate and styrene carbonate in 91% and 31% yield respectively, at 413K and 200 atmospheres pressure. While [Mn(III)salen]Br gave propylene carbonate and styrene carbonate in 34% and 67% yield respectively. The silica immobilized form of [Mn(III)salen]Br complex under identical conditions gave styrene carbonate in 96% yield and catalyst showed constant activity for three recycles. [Sn(IV)(salen)]I2 complex with DMAP as a cocatalyst,[91] was used to obtain

propylene carbonate in quantitative yield at 393K, and 7 atmospheres pressure in dichloromethane as solvent.[92]

The use of Schiff base as catalyst for cyclic carbonate synthesis was first reported by Shen *et al.*[93] Employing Schiffs base in the presence of a DMAP as cocatalyst gave propylene carbonate in quantitative yield at 393K and 35 atmospheres pressure in dichloromethane solvent. The work reported by Yamada *et al.* used chiral *C$_2$*-symmetric cobalt(acen) complexes to catalyse the addition of CO$_2$ to epoxides with 2 mol% of catalyst and 1 mol% of an amine cocatalyst under 20 atmospheres pressure of CO$_2$.[94] This catalyst with a number of other nucleophilic amine cocatalysts like *N* trimethylsilyldiethylamine was used to screen number of glycidol based epoxides for cycloaddition of CO$_2$. Other Schiffs bases reported for CO$_2$ addition to propylene oxide and 2-ethylhexylglycidol as epoxides substrate include Cobalt Schiff base complexes with TBAB or DMAP as cocatalyst under 10 atmospheres of CO$_2$ at 418K.[95]

3.1.1.4. Metal halides and metal oxides

A variety of metal salts like K$_2$CO$_3$, KCl, KI, LiBr and NaOH were reported to give cyclic carbonate in quantitative yield when used with crown ethers at 50 atmospheres pressure and 393K. [96] Sakakura *et al.*[97] reported samarium oxychloride as a catalyst in DMF for synthesis of propylene carbonate in quantitative yields at 473K under supercritical conditions. Other metal salts such as NaI/PPh$_3$/PhOH, CaCl$_2$/octyl$_3$(Me)NCl and NiCl$_2$/PPh$_3$/TBAB with zinc powder as a reducing agent were reported to catalyze this reaction with moderate to good yield of cyclic carbonate. [98] Solid supported RuCl$_3$ on SiO$_2$, or tetraethylammonium bromide as the support demonstrated high catalytic activity for cyclic carbonate formation at 353K and under supercritical conditions. However with polyphosphotungstinic acid as support polycarbonate products were obtained.[99]

Based on the requirement of Lewis acid sites for activation of epoxide and Lewis base sites for CO$_2$ activation, metal oxides have emerged as efficient catalyst due to its inherent acidic and basic properties which allow them to interact with polarizable species such as CO$_2$. A range of metal oxides like MgO, CaO, TiO$_2$, ZnO and BeO have been studied for activation of CO$_2$.[100,101] These catalysts showed an added advantage of catalyst recovery and product separation due to their heterogeneous
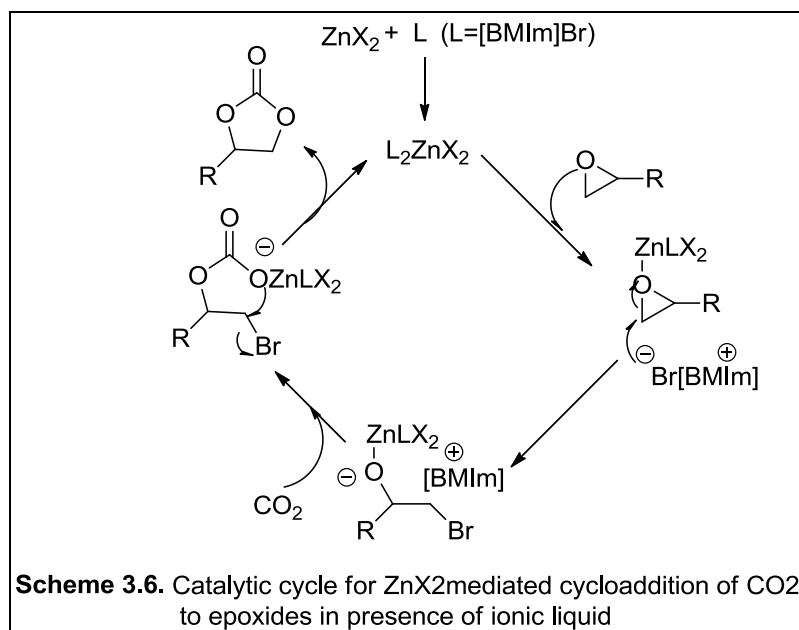
nature. MgO and Mg–Al mixed oxides gave propylene carbonate in 41% yield at 408K and 20 atmospheres pressure and 88% yield at 393K and 3 atmospheres pressure respectively. With styrene oxide as substrate both these catalyst gave poor conversions under identical conditions.[102,103] A heterogenized type of magnesium catalyst comprising of magnesium hydroxychloride [Mg(OH)Cl] and potassium iodide gave propylene carbonate in 98% yield at 403K and 60 atmospheres pressure and styrene carbonate in 75% yield.[104] When smectite (mixtures of Mg–Ni and alkali metals, such as Na, K and Li) was used as catalyst propylene carbonate was obtained in 81% yield at 423K and 80 atmospheres pressure. [105] Other solid metal oxide catalysts investigated for this reaction include zeolites, modified form of zeolites, molecular sieves, SBA-15, MCM-41 to name a few. Davis *et al*.[106] reported use of Cs-zeolite at 423K and 100 atmospheres pressure to obtain 33% yield of ethylene carbonate while Sakakura et al reported caesium-phosphorous-silicon mixed oxide (Cs–P–Si) for synthesis of propylene carbonate in quantitative yields at 80 atmospheres pressure and 473K.[107] Titanosilicate molecular sieves with TBAB or DMAP as cocatalyst,[108] metal-alkali derivatized titanosilicate (ETS-10),[109] titanium-MCM-41[110] have been reported to catalyze the cycloaddition of CO_2 to epoxides. Amongst the Titanium catalyst studied Titanosilicate molecular sieves with cocatalyst and titanium-MCM-41 gave epichlorohydrin carbonate and propylene carbonate in 85% and 90% yield at 393K and 7 atmospheres pressure.[111,112] The same group have reported titanium incorporated in adenine modified SBA-15 silica support as catalyst for the synthesis of cyclic carbonates at 393K and 7 atmospheres CO_2 pressure with cyclic carbonates in 94-95% yield in 4-8 h time.[113] Another modified metal oxide catalyst was reported by Bhanage et al. He found that silica supported-poly(4-vinylpyridine) catalyst to be active for synthesis of propylene carbonate in 93% yield and styrene carbonate as well as epichlorohydrin carbonate in 84% yield at 423K and 54 atmospheres pressure.[114] Zinc-based metal oxides reported for cyclic carbonate synthesis include zinc containing hydroxyapatite with DMAP as a cocatalyst,[115] zinc-based catalysts supported on silica with TBAB as cocatalyst . The former catalyst gave styrene carbonate in 89% yield at 373K and 100 atmosphere CO_2 pressure while the later one gave 15-20 % yields of carbonate at 373K and 45 atmospheres pressure. These catalysts were prepared by combining a zinc source with a silica precursor either *via* a sol–gel route or by flame spray pyrolysis.[116] These zinc supported on

silica doped with barium or strontium were also tested for cyclic carbonate synthesis but gave poor conversions. A composite oxide material composed of zinc, aluminium and a third metal like Zn–Mg–Al–O with triethylamine as an additive were reported to give propylene carbonate in 89% yield in 12 h at 393K and 25 atmospheres pressure of CO_2.[117]

3.1.1.5. Mechanism of activation of CO_2 and epoxides for cyclic carbonate synthesis

Activation of epoxides and CO_2 is reported to take place differently based upon the active sites present on the catalyst. As reported in earlier section, cooperative catalysis i.e. both acido-basic nature of catalyst is necessary for activation of epoxides and CO_2. In this section activation of epoxides and CO_2 is discussed using IL and metal salen complex as model systems to get an understanding of mechanism operational with this type of catalysts.

With [BMim]Br and $ZnBr_2$[118] as catalyst reaction mechanism proposed for styrene carbonate synthesis showed catalytic activity arising from the cooperative actions of both the acidic site (Zn) for epoxide activation and basic site Br$^-$ in [BMim]Br and/or Br$^-$ in $ZnBr_2$ for CO_2 activation. Activation of the epoxide is done by zinc followed by ring-opening with bromide. CO_2 could then insert into the Zn–O bond with ring-closure giving the cyclic carbonate. Based on above mechanism the role of types of metal halides and ionic liquids and the requirement of the optimum ratio of 2 for [BMim]Cl/$ZnBr_2$ is evident (Scheme 3.6).

Scheme 3.6. Catalytic cycle for ZnX2mediated cycloaddition of CO2 to epoxides in presence of ionic liquid

Whereas in aluminium salen complex type of catalysts a catalytic cycle was proposed in which the epoxide was first activated by one of the aluminium atoms within the dimeric catalyst followed by ring opening by bromide ion. The CO_2 interacts with tributylamine and can form a carbamate salt. This salt then coordinates to the other aluminium atom of the activated epoxide-aluminium complex, thus allowing the key reaction between the ring-opened epoxide and CO_2 to occur intra molecularly. Ring-closure and elimination of bromide then forms the cyclic carbonate and regenerates the catalyst (Scheme. 3.7).[119]

Scheme 3.6 Catalytic cycle for CO2 inserttion to epoxides catalyzed by Al salen complex
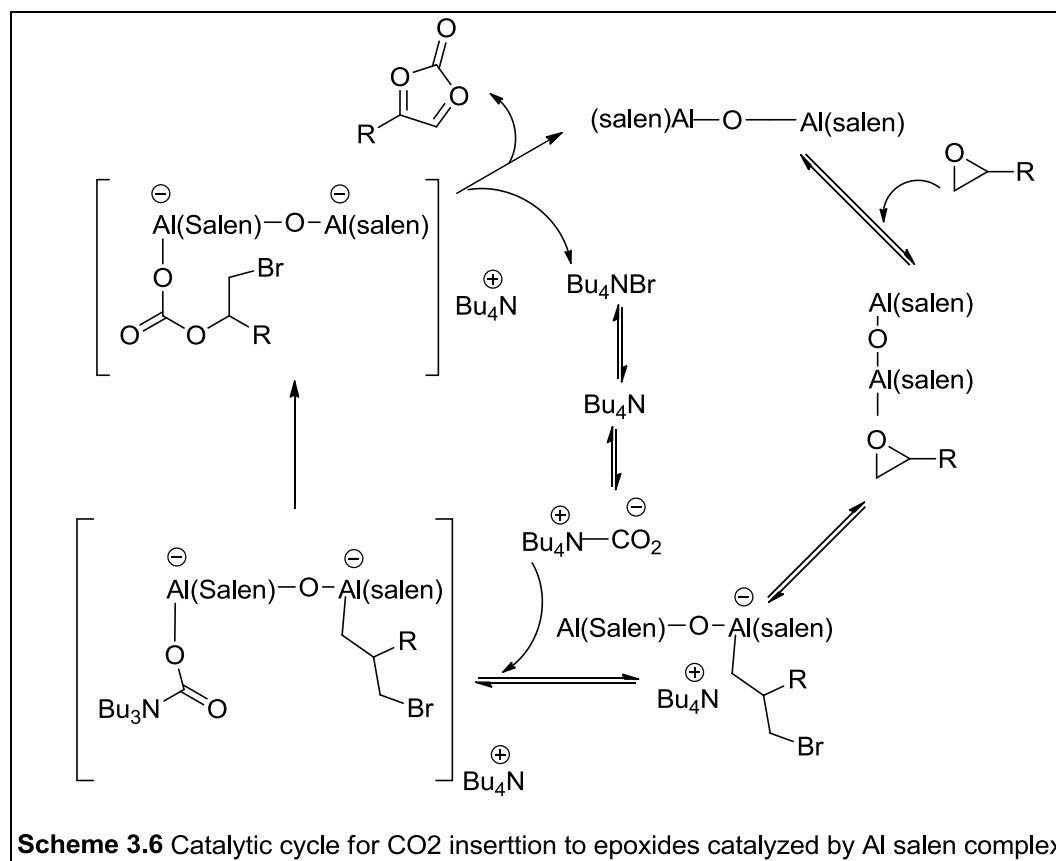
From the literature reports discussed in above section several catalytic systems have shown promising results for the feasibility of CO_2 cycloaddition to epoxides; however heterogeznised catalysts have been preferred over some promising homogeneous catalysts due to obvious reason of their ability of recycling and catalyst product separation ease. It was also observed that the activity of IL grafted on silicagel-$ZnCl_2$ is promising for industrial application point of view; much work is still required to be done on catalyst stability, recycling ability and recovery aspects. As addition of $ZnCl_2$ catalyst limits the scope of heterogenized catalyst as well as the reactants and products needs to be distilled off prior to recycling of catalyst and cyclic carbonates of low boiling points only can be used. In this regard ethylene and propylene oxides only are feasible for carboxylation reactions. Also most of these catalysts needs to be tested on styrene oxide as substrate since the reactivity of SO is known to be poor compared to ethylene and propylene oxide due to lesser reactivity of β-carbon atom of SO making cycloaddition of CO_2 difficult in comparison with ethylene oxide and propylene oxide. [120,121] This severely limits the applicability of protocol.

In view of the facts established from literature presented above, objective of the present study was to investigate grafted IL as catalysts for addition of CO_2 to oxiranes under non $scCO_2$ condition. In this chapter, experimental results on carboxylation of epoxide using grafted catalyst prepared by various methods of immobilization and various IL immobilized on silica are demonstrated. Various aspects such as process parameters and effect of CO_2 pressure on product yield and selectivity are explored here for heterogeneous catalysts which held greater promise from industrial application compared to homogeneous catalysts below $scCO_2$ pressures. The another aspect investigated was role of support such as silica, MCM-41, hydrotalcites and montmorillonite clays which are expected to show synergistic effect resulting in increased yield of cyclic carbonate under mild reaction condition. Hence, diverse methods of catalyst preparations reported in literature weree adopted here for catalyst preparation and catalytic activities shown by these cataysts are evaluated to minimize drawbacks mentioned with other homogeneous as well as heterogeneous catalysts reported so far.

3.2. EXPERIMENTAL SECTION

3.2.1. MATERIALS

 Propylene oxide, epichlorohydrin, 1,2-epoxy-3- phenoxy propane and styrene oxide, were purchased from M/S Sigma Aldrich, USA. A.R grade solvents used were supplied by Merck. Transition metal chlorides were purchased from S.D. Fine-CHEM India. All the chemicals were used without further purification unless specified in the text. Carbon dioxide was purchased form local source; M/s. deluxe industrial gases, Pune (99.9% pure). Various ionic liquids reported here were prepared according to reported procedure in Chapter 2.

3.2.2. GENERAL PROCEDURE FOR CARBOXYLATION OF EPOXIDES

The coupling reactions were carried out in a 50 cc Parr SS-316 autoclave. Typical conditions and procedures are; Styrene oxide (25 mmol), immobilized catalyst [Imb]35%CAT-3a (2 g), and n-hexanene (17g) were charged into the reactor. Reactor was flushed and then pressurized with CO_2 at 6.8 atm. The reactor was heated with stirring up to 373K for 6h. After the reaction the reactor was cooled to 298K and depressurized. The liquid reaction mixture was analyzed quantitatively on a gas

chromatography (M/s Agilent, USA, model 6890) equipped with a HP-1 capillary column of 30m length and auto-sampler. Products were confirmed by GC-MS (M/s Agilent, USA, model 6890) (EI, 70 eV) and characterized by ^{1}H NMR spectra. Styrene carbonate was isolated by flash chromatography using Combiflash Companion instrument (Teledyne ISCO, USA) on a 4g normal phase RediSep silica column using n-hexane-ethyl acetate as eluent and gradient programming. After completion of the experiment, catalyst was separated by filtration through Sartorius 393-grade filter paper. Separated catalyst was washed several times with acetonitrile to remove adhered organic impurities. The catalyst was dried under vacuum at 398 K for 6 h and reused for the next experiment. Appropriate charge of reactant was taken accounting for the handling loss of the catalyst during each recycle.

3.2.3. GENERAL PROCEDURE FOR CO₂ SOLUBILITY MEASUREMENT

The gas solubility measurement under experimental conditions was performed based on the apparatus and the methodology reported earlier.[122] The principle of the constant-volume method is to bring a measured quantity of a solute gas into contact with a measured quantity of gas-free solution, agitate until equilibrium is established, and then measure the quantity of the remaining gas. The gas solubility in the solvent is then calculated from the material balance.

In a typical solubility experiment, the autoclave which was previously checked for gas leakage was charged with 17 g of degassed n- hexane solvent and to this exact weighed quantity of grafted IL on silica gel was added. The autoclave was then closed and gas phase was flushed with nitrogen without disturbing the liquid. The contents of the autoclave were brought to the desired temperature under gentle stirring, and then the stirring was stop and carbon dioxide was introduced to the autoclave up-to desired pressure in the space above liquid. The system was left to equilibrate for more than 1 h, the pressure and temperature of the autoclave were recorded, and this pressure was used as the saturated vapor pressure of the system at the equilibrium temperature (it is assumed that under static conditions the CO_2 dissolution to liquid surface is negligible compared to total solubility in liquid phase). The magnetic stirring apparatus was turned on and set at a constant rotation speed. After 10 minutes, the temperature and pressure of the autoclave were recorded again and monitored for further 2h ensuring that during this time the pressure of the autoclave did not change, the system was considered to be at equilibrium, and then final temperature and pressure of autoclave

were recorded. Then the gas solubility at this carbon dioxide partial pressure was calculated according to the material balance as per the details given elsewhere.[122] The CO_2 capture capacity of the system (absorption + adsorption) is then calculated from the CO_2 solubility in n-hexane and enhancement in solubility due to solid. The density of n-hexane at 373K was obtained from the published literature.[123]

3.2.4. ANALYTICAL METHODS

Liquid samples were diluted by acetonitrile and analyzed on a Hewlett Packard 6890 Series GC equipped with auto sampler instrument, controlled by the HP Chemstation software, by using an HP- 5capillary column (30 m×0.32 mm×0.25 μm) with FID detector. Identification of products was done using GC-Mass spectrometry of Agilent, USA make, model 6890 GC with 5973N mass selective detector using HP-5 MS capillary column of 30m×0.32mmx 0.25μm dimension. Immobilised catalysts were characterized by XRD, ^{27}Al CP MAS NMR, ^{13}C CP MAS NMR, IR, surface area, pore volume and SEM. X-ray powder diffraction The standard conditions for GC analysis are given in Table 3.1.

Table 3.1. Standard GC conditions for GC analysis	
Parameters	**Conditions**
Injector (split) temperature	473K
Flame ionization detector (FID) temperature	523 K
Column temperature (HP-1 capillary column)	343 K–563 K (programmed)
Inlet Pressure (He)	5 psig
Carrier gas (He) pressure (ramped)	5-10 psig
Split ratio	100:1

The conversion, selectivity, yield, were calculated as follows.

$$\% \ Conversion \ = \frac{Initial \ moles \ of \ epoxide \ - \ Final \ moles \ of \ epoxide}{Initial \ moles \ of \ epoxide} \ X \ 100$$

$$\% \ Selectivity \ = \frac{No. \ of \ moles \ of \ product \ formed}{No. \ of \ moles \ of \ epoxide \ converted} \ X \ 100$$

$$\% \ Yield \ = \frac{No. \ of \ moles \ of \ product \ formed}{No. \ of \ moles \ of \ epoxide \ charged} \ X \ 100$$

3.3. RESULTS AND DISCUSSION

In this work attempt has been made to critically evaluate the advantages of operating the reaction of cycloaddition of carbon dioxide to epoxide for cyclic carbonate synthesis under non scCO₂ conditions. The role of CO₂ solubility and CO₂ capture capacity of heterogenised catalyst system in enhancement of activity of catalyst under non scCO₂ conditions has been explained. It has been demonstrated that, tuning of physical properties such as CO₂ solubility, CO₂ adsorption capacity of support can help to improve the performance of immobilized catalyst under non scCO₂ conditions avoiding the use of scCO₂.

3.3.1. SYNTHESIS OF CYCLIC CARBONATE VIA CYCLOADDITION OF CO₂ TO EPOXIDES USING IMMOBILIZED CATALYSTS

3.3.1.1. Preliminary experiments for catalyst screening

Various catalysts like metal salts, quaternary ammonium halides and IL were screened for synthesis of cyclic carbonate from epoxide and CO₂ and results are tabulated in Table 3.2. One of the aspect investigated here is the role of metal chloride as promoter and for this purpose several promoters such as ZnCl₂, FeCl₃, MnCl₂ and AlCl₃ were examined along with IL and onium salts as catalyst (See Table 3.2). Since, quaternary salts and ILs are efficient catalyst for carboxylation of epoxides to carbonates[124,125,126] two experiments with already known catalyst were repeated for establishing the activity of quaternary ammonium salt and IL under our operating conditions. It was observed that n-butyl methyl imidazolium chloride and tetra ethyl ammonium bromide gave SC yield of ~29 and 12% respectively (entry 4 and 5). While, addition

of metal chloride to TEAB increased the activity of resulting catalyst system (except $MnCl_2$), addition of these metal chlorides to [BMIm]Cl decreased the activity of resulting catalyst system except $ZnCl_2$ (See entry 6-13). These results indicate that use of $ZnCl_2$ as promoter was most effective among these metal salts and IL as a catalyst is more active compared to TEAB (entry 6 and 10). Recently[127] have examined the effect of IL and Zn for this reaction and found that Zn-IL adduct formation is active compared to its physical mixture. The role of $ZnCl_2$ as promoters was earlier explained by several investigators.[128,129,130] The enhancement of activity observed by earlier researchers on addition of $ZnCl_2$ to quaternary salt is due to the in-situ formation of adduct acting as a catalyst, forming cation and anion ion pair. It has been shown that two dimethylimidazolium cations were paired with a dibromo dichloro zincate dianion which is probably responsible for enhanced activity of the system.[127] Thus quaternary ammonium salt and transition metal atom plays an important role in deciding the overall activity of the catalyst. The results on screening of catalyst shows that Mn, Fe, Al are less effective compared to Zn and [BMim] [Cl] i.e. IL1 is more active than TEAB.

Table3.2. Screening of catalyst and metal halide[a]			
Entry	Catalyst(mmol)	SO Conversion (%)	SC Yield (%)
1	MgO (nano)	0	0
2	N-methyl Imidazole	0	0
3	18-crown-6	0	0
4	[BMIm]Cl, IL1	30	29
5	TEAB(1.04)	12	11.9
6	TEAB+ZnCl₂	51	50
7	TEAB+MnCl₂	9	9
8	TEAB+FeCl₃	38	37
9	TEAB+AlCl₃	40	39
10	[BMIm]Cl +ZnCl₂	80	78
11	[BMIm]Cl +MnCl₂	12	11
12	[BMIm]Cl +FeCl₃	28	27
13	[BMIm]Cl +AlCl₃	21	20

Reaction Conditions: [a]Catalyst: 5 mmol, (MgO:200 mg); Styrene oxide: 25 mmol; Temperature: 373 K; Contact time: 6h; CO_2 pressure: 14.3 atm; Solvent: Toluene (17 g)

3.3.1.2. Solvent effect

Solvents are known to enhance the reaction performance in many instances.[131] The carboxylation of epoxide by quaternary salts is known to proceed via ion pair cooperative catalysis. Therefore, it is likely that solvents which stabilize ionic intermediates would enhance the catalysis. The concept of superelectrophilic solvation in addition to conventional electrophilic solvation has been reported to enhance the electrophilic reactivity. The systems containing nonbonding electron pair donors as well as π-donor readily react with Brønsted or Lewis acids enhancing the reaction rates and product yields.[132] Carbon dioxide solubility is greatly enhanced in polar solvents, especially solvents having oxygen atom for example ketones, acetates and carbonates.[133] The polar nature of oxygen helps enhance the CO_2 solubility. As shown by Kawanami et al. use of DMF as a solvent for CO_2 cycloaddition to epoxides overcomes the low solubility of reactants as well as liquid-liquid mass transfer effect. The accelerated reaction rates were due to combination of $ScCO_2$ and DMF that increases the diffusion rate due to decrease in viscosity.[134] Tomishige et al. have also reported effect of CO_2 solubility in acetonitrile solvents to give propylene carbonate in very good yield.[135] In the present study the high SC yields obtained when polar solvents such as *N*-methyl pyrrolidone, acetonitrile and ethyl acetate is used is associated with high initial CO_2 solubility in the medium enhancing the SC yield (this was qualitatively observed by the pressure drop in initial 5 min of reaction). Toluene and *m*-xylene showed poor activity while aliphatic solvents such as n-hexane and cyclohexane showed good activity that is comparable to polar solvents even though they had nearly same initial CO_2 solubility. Tomishige et al. have also reported effect of CO_2 solubility in acetonitrile solvents to give propylene carbonate.[135] Here an attempt is made to correlate catalyst activity with physical properties of solute such as relative polarity but the results could not be explained based on polarity. Therefore, at present the exact role of solvent is not clear but the high boiling styrene carbonate could be phase separated in n-hexane and cyclohexane solvents (see Figure.3.1) and hence further reactions were undertaken using n-hexane as solvent.
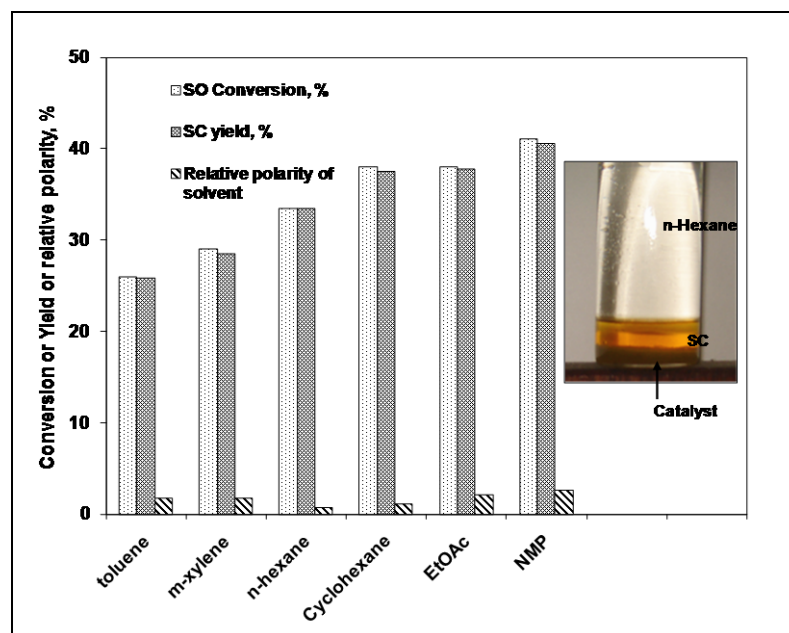
Figure. 3.1. Effect of various solvent on SO conversion.

Reaction Conditions: Styrene oxide: 25mmoles, Catalyst: 1g cat, Temperature: 373K, CO_2 :13.6 atm, 1000rpm, Time: 6h.

### 3.3.1.3. Effect of Silica Gel Coated and Grafted IL

Use of IL as solvent as well as catalyst is beneficial in many ways as it serves both the purpose which has been demonstrated by several researchers earlier for carbonate synthesis.[136] The major disadvantage of using IL as solvent arise due to their extremely high cost or when liquid products and reactants are high boilers (> 423K) as in this case product separation becomes energy intensive step. Therefore, the supported IL is the choice in this case, since both the purpose e.g. solvation of reactants and phase separation of catalyst can be accomplished. However, comparison of activity of heterogeneous catalyst prepared by different methods for carboxylation of epoxides to carbonate is not reported in literature. Several heterogenised forms of IL catalysts were prepared for this purpose and the results are depicted in Figure3.2. The Figure shows that catalyst prepared by impregnating IL1 i.e. {[BMIm]Cl} on silica gel, gives SO conversion of 24.5 % and yield of SC is 23.2% (See Figure3.2 Run A) which is similar to that obtained when IL1 is tested in absence of silica gel (Table 3.2, entry 4, SC yield ~ 29%). Thus the activity shown by these two catalysts are almost comparable, indicating that the activity of IL1 is mainly due to the fine dispersion of IL1 in reaction solution where as in the case of impregnation of IL1 on

silica gel, since IL1 is insoluble in toluene it adheres onto silica gel forming a fine coating (or spreading) of IL on SiO$_2$, and this is believed to give good activity to the catalyst. Next the recycling of catalyst of run A (separating solution by decantation and fresh charge was added to settled catalyst in autoclave) was tested to see if leaching of coated IL on silica gel occurs. The recycle run `A (See Figure3.2) showed that the activity of recycled catalyst is comparable to original catalyst (run A) indicating that there is almost no leaching in this case. Run B was then carried out with coating of IL1 on SiO$_2$ (^{IMB}CAT-1) until dryness (by incipient wetness i.e. diffusional impregnation method), in this case higher activity of catalyst is observed (SO conversion of 34% and SC yield of 32.7%, Run B) compared to Run A. Since the catalyst used in run B was prepared by dissolving IL1 in deionized water and then coating IL on silica gel by incipient wetness method. In this case the IL probably has more chance to penetrate deep into the pores of silica gel giving rise to higher coverage of IL on silica surface with better uniformity resulting in high activity. The recovered catalyst of run B was recharged without washing (Run `B), the results indicate that in this case about 10% loss in activity was observed (See Run `B, conversion of SO ~31 % and SC yield ~ 30%).
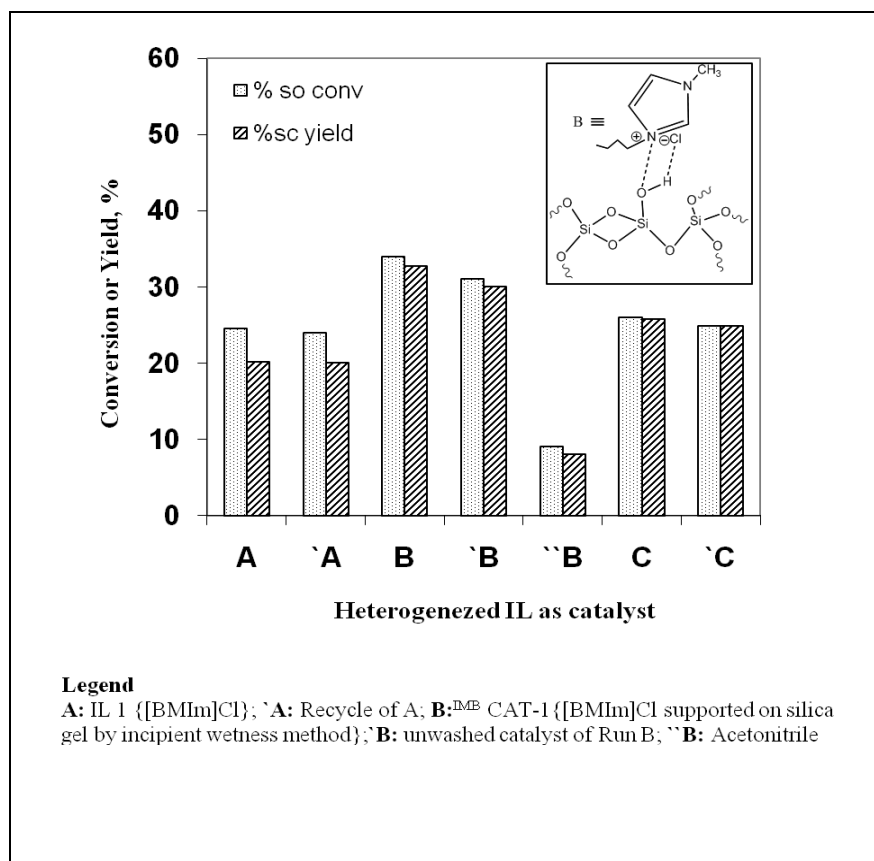
Figure.3.2 Effect of method of IL heterogenization on catalyst activity.

Reaction Conditions: Styrene oxide: 25 mmole, CO2:13.6 atm, Catalyst equivalent to 1.08 mmol of A, Time: 6h, Solvent: Toluene 17g, 600.
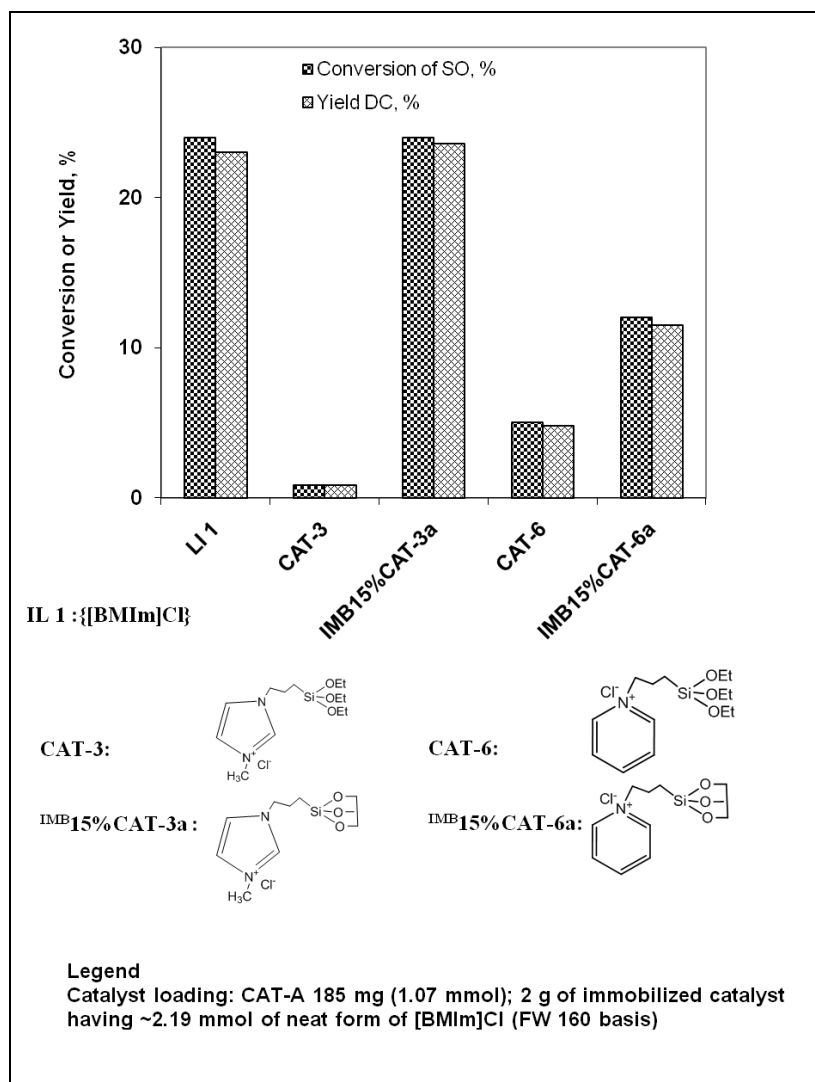
Figure.3.3. Effect of grafting on catalyst activity

Reaction Conditions: Styrene oxide: 25 mmole, CO_2:13.6 atm, Time: 6h, Solvent: Toluene 17g, 600 rpm.

To see the effect of washing with polar solvent, run B was repeated under identical conditions and recovered catalyst was washed with a portion of acetonitrile (~ 50ml) dried in oven at 393K over night and reused (Run ``B). In this case, drastic loss in activity was observed (Run ``B, ~9% SO conversion, ~8% SC yield). When catalyst was washed with acetonitrile prior to recycle (Run ``B), the polar nature of solvent washed away ionic liquid, decreasing the catalyst activity. The better recycling ability observed in Run `A and `B might be due to fact that in a physically supported catalyst, leaching of catalyst from support depends on affinity towards solvent phase to that of support. Since ionic liquid coated is not lipophilic and hence has least

affinity for aromatic solvent in comparison to support. In fact it adheres to the surface due to hydrogen bonding with the most acidic C^2-H of the imidazolium cation[137,138] and also due to silanol groups of silica gel thus adhere to the support rather than going into solution (See inset scheme in Figure3.2 relevant to run B and run B`). The $3^{rd}$ category of heterogenized catalyst tested was prepared by chemically anchoring IL on silica gel supports. The result of catalyst prepared by grafted IL on silica is shown in run C (33.5% SO conversion and 33% SC yield) and the recycled catalyst of run C is shown in Run `C, which gave almost similar conversion and yield (33 % and 32.5% respectively). It may be noted that catalyst used in run `C was washed thoroughly with acetonitrile prior to recycling.

For the purpose of evaluating the efficiency of grafted IL over ungrafted IL (silane functionalized IL before grafting), two different kind of IL`s were examined in their ungrafted as well as in their grafted form and their activity was compared with 1-butyl-3-methyl imadazolium chloride chosen as a model catalyst (IL1). Figure.3.3 shows the results obtained with CAT-3 (1-(triethoxysilylpropyl)-3-methy limidazolium chloride prior to grafting onto SiO_2 support) and ^{IMB}15%CAT-3a (ILs in their grafted form). The loading of quaternized nitrogen atom was kept constant in all IL based catalyst (1.08 mmol). The ungrafted ILs as catalysts (CAT-3) showed very poor activity towards SO conversion and scanty yield of SC were realized. Rather it was found that the catalyst being very viscous was not dispersed under the reaction conditions, resulting in formation of lumps that were sticking to the internal parts of the autoclave (walls, stirrer etc.). The sticky and insoluble nature of IL greatly decreases the activity due to very poor dispersion in reaction phase. Figure. 3.3 shows about 0.8 % yields of styrene carbonate was realized for CAT-3, with the selectivity being almost close to 100%. However, when neat CAT-3 was immobilized onto SiO_2, the activity of grafted IL catalysts (^{IMB}15%CAT-3a) was greatly improved (31.6% SC yield) compared to it`s counter part (See Figure. 3.3). The other ILs tested also showed a similar trend, e.g. pyridinium based ILs viz. CAT-6 and ^{IMB}15%CAT-6a gave ~ 5% and 12% yields of SC respecively but comparitively poor yields than to imidazolium ones. These results indicate that grafting the ILs on silica gel support evenly spread IL over the surface of silica gel, their by increasing the catalyst activity and enhancing the efficiency of ILs as catalyst.

The results on effect of catalyst preparation methods showed that impregnation or

incipient wetness method that essentially physically coat IL can be used when solvents are aromatic in nature. However, grafted IL is the choice of catalysts when polar solvents such as acetone, acetonitrile, THF etc. are used as reaction media. Finally it can be seen that grafted ILs are better catalysts compared to conventional ILs (IL1) because they are evenly distributed on heterogeneous support also due to synergistic effect imparted by silanol groups of silica in catalyzing the carboxylation reaction (also discussed later).

3.3.1.4. Activity of various immobilised IL catalysts

From the study of effect of impregnated catalyst Vs immobilized catalyst (see section 3.3.1.3) it was found that 15% imidazolium and pyridinium based immobilized catalyst gave better activity than impregnated IL catalyst. Further studies were carried out on amount of loading of imidazolium (CAT-3) and pyridinium (CAT-6) based IL on silica to obtain maximum SO conversion. For this purpose IL loading effect was studied in the range of 15-75% and results are tabulated in Table 3.2. It was observed that for CAT-3 and CAT-4 increase in % catalyst loading on silica increased SO conversion. (Table 3.3, entry1-6). But overall activity shown by catalyst IMB75%CAT-3a was high with 65% SO conversion and 100% selectivity for SC (entry 3). The catalyst prepared from Aldrich functionalised silica (entry 7) gave poor performance than pyridinium based immobilized IL catalyst. Thus the order of reactivity of these catalyst based on their cation in decreasing order is imidazolium > pyridinium > imidazolyl.

Table 3.3. Screening of immobilized catalyst for carboxylation of styrene oxide

Entry	Catalyst	CAT-3 loading (%)	SO Conversion (%)	SC Yield (%)
1	IMB15%CAT-3a	15	24	23.5
2	IMB35%CAT-3a	35	35.5	35
3	IMB75%CAT-3a	75	65	64.85
4	IMB15%CAT-6a	15	12	11.25
5	IMB35%CAT-6a	35	23	22.8
6	IMB75%CAT-6a	75	45	44.5
7	IMB22%CAT-7	22	12	11.5

Reaction Conditions: styrene oxide: 25mmoles, Catalyst: 1g cat, Temperature: 373K, CO_2 :13.6 atm, 1000rpm, time: 6h,

3.3.1.5. Effect of SO concentration

Study of SO concentration effect showed that with increase in SO concencentration SC yield increased linearly. It was observed that 1g of catalyst (IMB35%CAT-3a) was active for 25 mmoles and 50 mmoles of SO. But for 75 mmoles of SO catalyst loading of 2g was required to obtain 99% SO conversion (Figure 3.4).
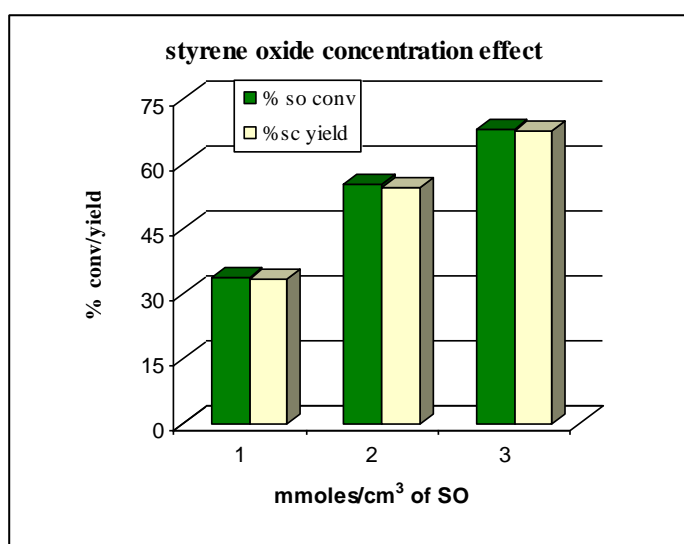

Figure 3.4 . Effect of SO concentration on SC yield

Reaction Conditions: Catalyst: 1g catalyst for 25mmole and 50mmole SO, 2g catalyst for 75mmole SO, Solvent: n-hexane(adjusted accordingly to make volume of total charge to 20g, Temperature: 373K, CO_2 :13.6 atm, 1000rpm, Time: 6h,

3.3.1.6. Temperature screening

The effect of temperature was investigated using 1g of catalyst ^{IMB}35%CAT-3a in the range of 373-423K and the results are shown in Figure 3.5 as a plot of SO conversion and SC yield at different temperatures. The conversion of SO increased sharply with increase in temperature. This indicates that reaction is not operating in solid to liquid mass transfer regime. At lower temperature (373K) poor SO conversion (33%) were obtained whereas at higher temperature 398K, SO conversion increased exponentially to 70% with 100% selectivity for SC. But at higher temperature 423K, even though 97% SO conversion was obtained SC was obtained in 62%yield. This decrease in SC yield was due to formation of some amount of polymeric compound which could not be detected on GC. Thus optimised reaction temperature found for this reaction was 398K.
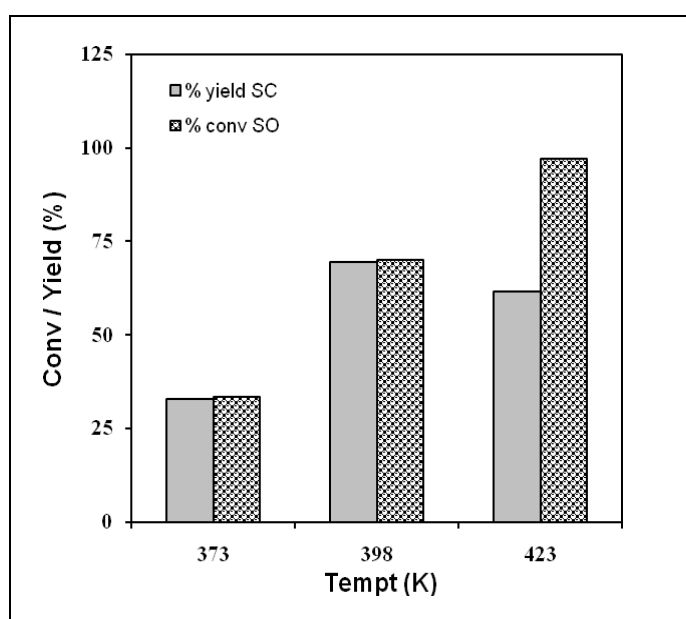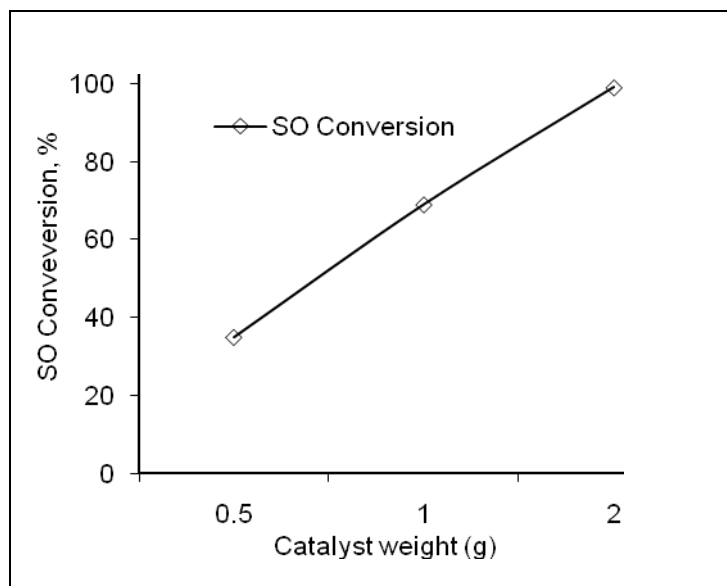

Figure 3.5. Effect of temperature on SO conversion.

Reaction Conditions: Reaction Conditions: Styrene oxide: 3g, Solvent:17g n-hexane, CO_2:13.6atm, Time: 6h,1000RPM, Catalyst:1g ^{IMB}35%CAT-3a

3.3.1.7. Effect of catalyst loading

The effect of ^{IMB}35%CAT-3a catalyst loading on SO conversion is shown in Figure 3.6. The figure showed linear dependency of SO conversion with catalyst loading. This indicates that sufficient active sites are available to obtain 99% SO conversion and SC yield when catalyst loading of 2g is taken at 398K.

Figure 3.6. Effect of catalyst loading on SO conversion

Reaction Conditions: Styrene oxide: 3g, Solvent:17g n-hexane, Temperature:398K, CO_2:13.6atm, Time: 6h,1000RPM, ^{IMB}35%CAT-3a.

From SO concentration effect, temperature screening and catalyst loading effect, maximum SO conversion and SC yields were obtained at optimised reaction conditions of catalyst loading of 2g for 25 mmoles of SO at 398K. Further parametric effects were carried out under these optimised reaction conditions.

3.3.1.8a. Effect of CO_2 capture capacity of grafted IL catalyst on catalyst activity

In heterogeneous catalysis, the optimum activity of the catalyst is attained when the diffusional resistance offered by the pore structure of the support to reactant diffusing towards active sites is negligible. In the present case, wherein IL is grafted onto silica support, the bulky silylated IL can also offer diffusional resistance due to it`s steric hindrance. However, since the silica gel is a mesoporous material (pore diameter ~50 Å) and molecular layers of grafted silica is only few molecular layers thick (pore diameter of SiO_2 upon grafting of IL ~ 45 Å, see characterization details) the pore diffusional resistances can
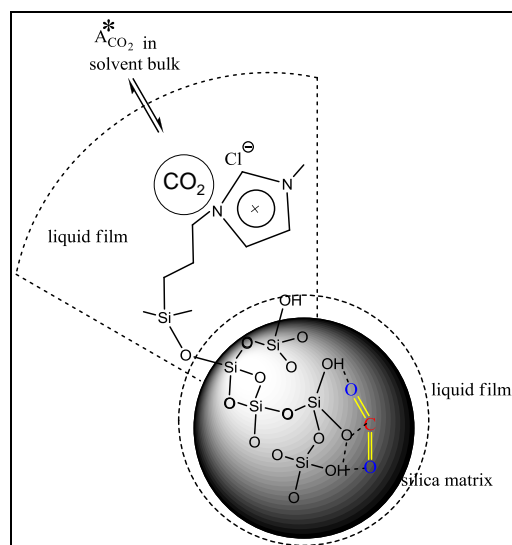
Figure 3.7. Interaction of CO_2 with grafted IL and silanol groups of silica gel support

be assumed to be negligible.[139] Therefore in the present study, the efficiency of the catalyst will depend on the local concentration of CO_2 and epoxide prevailing near the active site of the catalyst in the pores of support (See Figure 3.7). The enhanced solubility of CO_2 in IL compared to common organic solvents such as hexane, cyclohexane, benzene etc. is due to the CO_2 interaction with anionic part of IL.[140] Further improvement of CO_2 solubility in IL was demonstrated using task specific ILs, which have CO_2 philic functionality such as amine incorporated in structure of IL. These task specific ILs dissolve almost mole to mole quantity of CO_2 to IL e.g. tetrabutylphosphonium 2-aminoacetate.[141] It has been reported in the literature that, primary amine functionalized task specific IL are much more efficient in their CO_2 capture capacity (73.5mg CO_2/g IL at ambient conditions) compared to simple IL.[142] However, they tend to get deactivated when used as a catalyst for cycloaddition of CO_2 to epoxide[8]. Therefore, silica gel support functionalized with 1-(triethoxysilylpropyl)-3-methy limidazolium chloride type IL (^{IMB}15-75%CAT-3) were examined for their CO_2 capture capacity in order to correlate them based on their CO_2 adsorption capacity and catalyst activity. Table 3.43 shows the CO_2 capture capacity of typical grafted IL catalyst system and their activity under standard reaction conditions. It may be noted here that, the literature reported CO_2 capture capacity is invariably for adsorption of gas on solid supports, while the CO_2 capture capacities reported herein is for adsorption as well as absorption in a G-L-S system prevailing under the reaction conditions, except in absence of SO (reactant). This

means that, one has to consider the absorption as well as adsorption phenomenon to understand the catalyst activity. For CO_2 gas to be adsorbed (or absorbed by grafted IL moiety) by the silica surface it has to first diffuse from gas phase to liquid phase where it saturates the liquid phase (n-hexane in the present case). The dissolved CO_2 is then adsorbed on the liquid saturated surface of silica gel via hydrogen bonding with silanol groups, while imidazoline ionic liquid functionality grafted to silica surface tend to dissolve CO_2 in it's ionic environment much like IL dissolves CO_2 (See Figure 3.7). Under the kinetically controlled reaction conditions all these steps are in equilibrium and in presence of active sites of catalyst, adsorbed (and dissolved) CO_2 and SO on surface bring about the reaction forming SC. Mass trasfer free conditions for the data were determined by evaluating the values of k_laA^* for the maximum physical CO_2 absorption rates. Reactions carried out under highest temperature, catalyst loading, SO concentration were monitored for mass transfer limitations. It was found that initial rate of reactions were at least ten times less than the k_laA^* (maximum physical absorption rate). k_laA^* of 0.175 s^{-1} was adopted from data reported by Chaudhari et. al. for a similar kind of reactor used in this work. It may be noted that CO_2 dissolves readily in SC[40] and hence as the reaction proceeds, SC in liquid phase increases and thus CO_2 concentration in L-S film is expected to increase compared to initial conditions (See Figure 3.7). Table 3.4 shows the CO_2 capture capacity of catalytic system and catalyst activity obtained at 373K.

The activity of the catalyst depends on the catalyst system used. The CO_2 capture capacity indicates the degree of CO_2 available near the reaction zone (Figure 3.7). Thus the factors such as activation of substrate by IL (here C_4MImCl) and role played by the support in activation of substrate and CO_2 capture capacity greatly affects the catalyst activity (expressed in terms of initial reaction rate of CO_2 absorption) besides reaction parameters such as temperature, epoxide concentration, P_{CO2} pressure and stirrer speed. The Table shows that catalyst IL grafted on MCM-41 as support enhance the activity of the catalyst as compared to when IL is grafted on SiO_2 (See entry 1 and 2). This is reflected in increase in the CO_2 capture capacity of catalyst system and increase in the reaction rates (entry 1 and 2). The yield of carbonate increases more than two fold by loading of IL on MCM-41. However, CO_2 capture capacity of the CO_2-n-hexane-IL-MCM-41 is not very high compared to CO_2-n-hexane-IL-SiO_2 (entry 1 and 2). This shows that CO_2 capture capacity is very high

compared to initial rates. Increasing the SO concentration increases the rates (entry 1, 3 and 4) and for pure SO (no hexane) the maximum rate obtained is 45.58×10^{-8}, mol/cc/s with 50% yield of SC (See Table 3.4). PO was found to be more reactive compared to SO and initial rate of reaction was more than almost 2.5 times higher than that observed for SO (entry 4,5 compared to 6,7). In presence of $ZnCl_2$ in the system the catalyst activity was found to increase slightly (entry 5 and 7). The high activity in presence of $ZnCl_2$ is due to the higher concentration of dissolved CO_2 available in the reaction medium in presence of $ZnCl_2$ (the interaction of CO_2 and $ZnCl_2$ bring about the enhancement of CO_2 solubility). For example, activity of catalyst system CO_2-n hexane-[bmim][Cl] can be increased by using IL grafted on SiO_2 catalyst (See Figure 3.7, catalyst system CO_2-n-hexane-MImCl 35% SiO_2). Here, spreading of IL over large surface of SiO_2 has effect (compared to same amount of IL dissolved in medium) on activity. The heterogeneous nature of support, which appears to assists in activation of substrates as well as in increasing the CO_2 availability in the vicinity of reaction centers (i.e. IL acid-base pairs) play an important role in increasing the activity (it may be noted here that dissolution of CO_2 is concomitant to the activation of CO_2 as these two phenomenon are often inseparable with each other). The IL-SiO_2 catalyst system has been also reviewed by Ma et al., however, the CO_2 capture capacity and the activity of the catalyst system has not been reported.[143] Thus it may be worth exploring and analyzing systems that enhance CO_2 capture capacity under non-scCO_2 conditions for enhancing catalyst activity.

Table 3.4. Effect of CO2 capture capacity of catalyst system and activity[a]

Sr. No.	System[b] (%,w/w)	Epoxide mmol	CO_2 capture capacity of system (at 373K), CO_2 mole/cm^3/atm[c]	Yield of carbonate, %	Initial rate of CO_2 absorption, (mol/cm^3/s)[d]
Styrene oxide					
1	CO_2-n-hexane ^{IMB}35%CAT-3a-(on SiO$_2$) (7)	25	6.10E^{-05}	94	3.94x10^{-8}
2	CO_2-n-hexane-^{IMB}35%CAT-3b-(on MCM) (7)	25	6.47E^{-05}	99[d]	6.29x10^{-8}
3	CO_2-n-hexane-^{IMB}35%CAT-3a - (7)	50	6.61E^{-05}	49	13.56x10^{-8}
4	CO_2-n-hexane-^{IMB}35%CAT-3a - (7)	258	6.84E^{-05}	50	45.80x10^{-8}
5	CO_2-n-hexane-^{IMB}35%CAT-3a (7) + ZnCl$_2$	31	7.07E^{-05}	99	47.80x10^{-8}
Propylene oxide					
6	CO_2-n-hexane-^{IMB}35%CAT-3a (7)	PO 19.7g	7.61E^{-05}	91	117x10^{-8}
7	CO_2-n-hexane-^{IMB}35%CAT-3a (7) + ZnCl$_2$	PO 19.7g	7.84E^{-05}	91	116x10^{-8}

[a]Reaction conditions: P_{CO2} : 13.6atm, Time 6h, n-hexane 17 g, Temperature 373 K, Catalyst: 2g

[b] Percent loading of IL grafted catalyst for solubility measurement.

[c]CO_2 capture capacity is presented in terms of amount of CO_2 dissolved in unit volume of n-hexane at one atmosphere.

[d]Initial rates were calculated from the plot of CO_2 Vs. time data and for discussion on mass transfer effect see text.

[e] Time 4h

3.3.1.8b. Effect of CO_2 Pressure

The effect of carbon dioxide pressure on cycloaddition of epoxide for the synthesis of cyclic carbonate was investigated in the pressure range of 3.4-55.8 atm. The initial rate data (R_o) when plotted against P_{CO2} or A^*_{CO2} clearly indicates that beyond ~ 22 atm, initial reaction rate has a mild effect on pressure (Figure. 3.8) although, CO_2 solubility increases with increase in pressure. The reaction has been earlier explored under non $scCO_2$ conditions and $scCO_2$ conditions have been shown to be highly beneficial.[144] However, in an independent study by Sun et al. and Darensbourg et al., on pressure effect, they reported that several factors are responsible for the negative effect of pressure on catalyst activity e.g. volume of phase in which the reaction take place and hence the concentration of reactant beyond pressure of P_{CO2} ~ 70 atm and catalyst in that phase, the reaction mechanism (i.e. factors contributing towards active species formation) and kinetics.[145, 146] Moreover, literature result shows that yields of cyclic carbonate are either decreased or has little effect beyond ~ 70 bar,[147] which means that increase in pressure is beneficial but not necessarily efficient. The poor efficiency of catalyst system at higher pressures can be clearly realized from Figure.3.9 wherein a plot of catalyst activity (R_o/P_{CO2}) and P_{CO2} shows a bell shape nature with maximum activity at ~22 atm pressure. The P_{CO2} pressure effect especially under $scCO_2$ conditions is more complex due to complex phase behavior of the system, which depends on the type of catalyst system employed. Therefore, one can find completely contradicting behavior of catalyst activity to pressure relationship under certain regions. For an example Kawanami et al. found that for $[C_8\text{-mim}][BF_4]$ and $[C_2\text{-mim}][BF_4]$ system, the yield of carbonate depends on the chain length of alkyl group of imidazoline in IL, $[C_8\text{-mim}][BF_4]$ having bigger chain length, dissolves more CO_2 and hence yield of carbonate in this case is higher compared to $[C_2\text{-mim}][BF_4]$-IL[42]. However, in both these cases P_{CO2} pressure effect shows that yields does not improve beyond 80 bar (in fact for C_2-mim system yield actually drops). Lu et al. found that for Al(salen)Cl-n-Bu₄NI system at supercritical pressures also the P_{CO2} effect is not linear, beyond ~4 bar CO_2 pressure, TOF remains independent of P_{CO2} (up-to ~ 20 bar).[148] Thus, it can be seen that increase in pressure is beneficial only in limited and narrow range. Several investigators have highlighted the possible inefficiency of catalytic system associated with operating the system under $scCO_2$ conditions for cycloaddition of CO_2 to epoxide and observed that increase in pressure

does not necessarily lead to advantageous situations.[149] The uses of scCO$_2$ for carbonate synthesis from epoxide needs to be reviewed critically as enhancement of CO$_2$ pressure is often counter productive. Only for few systems it is observed that pressure beyond 80 bar are beneficial, e.g. Polyfluroalkyl iodides does help in slightly increasing the rates[19]. Baiker et al. have discussed effect of pressure on rate enhancement of mass and heat transfer when supper critical fluids are used as solvents.[150] Wei et al. highlight poor solubility of metal complex catalyst under scCO$_2$ as the cause of decreased catalyst activity for auto oxidation of dibutylphenol.[151] These investigators show that beneficial use of CO$_2$-exapanded solvent phase (acetonitrile and methylene chloride) over scCO$_2$ phase. Thus it is clear that scCO$_2$ condition is not always beneficial for the reaction.
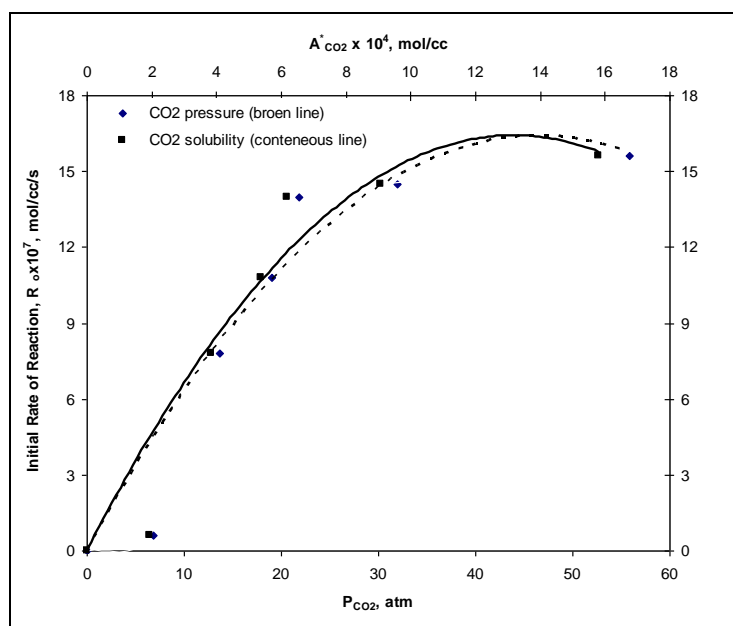

Figure.3.8 Effect of CO$_2$ pressure and solubility on initial rate of reaction
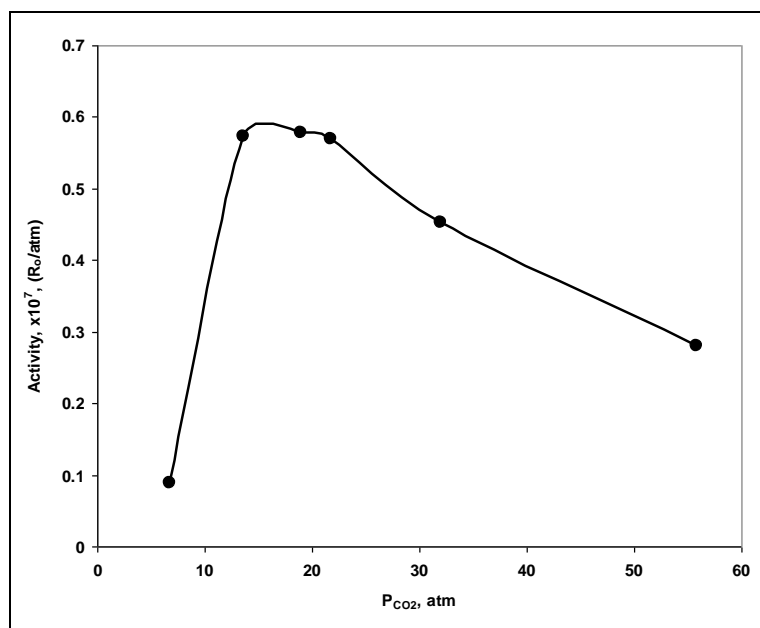
Figure.3.9 Effect of pressure on catalyst activity

Reaction Conditions: Styrene oxide: 3g, Solvent:17g n-hexane, Temperature:398K, Time: 6h,1000RPM, [IMB]35% CAT-3a.

Figure.3.10. shows a plot of catalyst activity obtained under non-scCO$_2$ conditions and that obtained at scCO$_2$ condition. The current data at non scCO$_2$ conditions are compared with typical literature data obtained at non scCO$_2$ and also at scCO$_2$ conditions. It can be seen that by manipulation of reaction conditions such as carrying out the reaction in neat epoxide with $ZnCl_2$ as promoter, it is even possible to obtained catalyst activity almost closed to that obtained under scCO$_2$ pressures (See Figure. 3.10, activity: 4 mol/mol/h/atm)
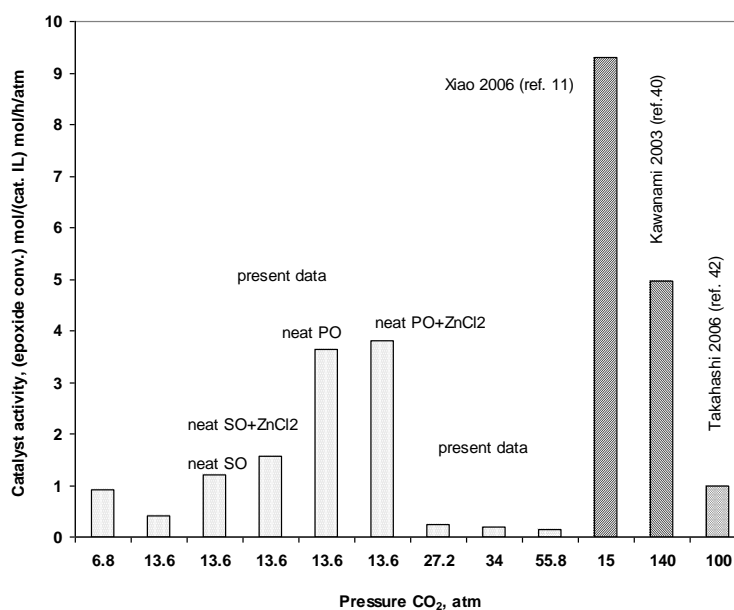
Figure. 3.10. Catalyst activity and pressure effect comparison with typical literature data

3.3.1.9. Effect of support

Various immobilized catalysts were screened at optimised reaction conditions to study the effect imparted by inorganic support on SC yield. It was found that neat SiO_2 failed to give any activity whereas it's immobilized counterpart [IMB]35%CAT-3a (CAT-3 immobilized on SiO_2) showed remarkable difference in activity by giving 99% SC yield in same 6h time. This showed that with immobilization of CAT-3 on silica acido-basic sites may possibly be created which showed enhanced rates as compared to neat SiO_2 (Table 3.54, entry 1)and neat IL CAT-3 (see Figure 3.3 effect of heterogenization of IL). As mentioned by many authors promoters like metal halides have significant enhancement in activity of of IL catalyst (see section 3.1.1.1). To study the effect of promoter on activity of catalyst [IMB]35%CAT-3a, $ZnCl_2$ was selected as promoter based on best performance reported in literature for immobilized catalyst system. It was observed that 99% SC yield with 100% selectivity was achieved in 4h. This enhanced activity of [IMB]35%CAT-3a and [IMB]35%CAT-3a+$ZnCl_2$ ascertains role of $ZnCl_2$ in assisting catalyst [IMB]35%CAT-3a for activation epoxide giving SC in quantitative yield in reduced time (Table 3.5, entry 2,3) . Further investigation on effect of support showed that when MCM was used as support catalyst [IMB]35%CAT-3b gave ~ 99% SC yield in reduced time, indicating role of

surface silanol and IL (CAT-3) in generating acid base sites on final catalyst (Table 3.5 entry 5). With basic support like Zn/Al hydrotalcite([IMB]35%CAT-5a) and acidic support like montmorillonite clay K-5 ([IMB]35%CAT-3c) 60% and nil SO conversion were obtained respectively (Table 3.5 entry 7,8.). These two results indicate requirement of balanced acido basic nature of catalyst for activation of epoxides as shown by IL+ZnCl$_2$ or other metal complexes with cocatalyst (see section3.1.1.1). From these results it can be concluded that benign nature and cost effective factors of silica as better option for catalyst support for this transformation.

Table 3.5. Effect of support used for immobilizing CAT-3 on carboxylation of styrene oxide to styrene carbonate.

| Entry	Support	CAT-3 loading (%)	ZnCl$_2$ co-catalyst (mg)	SO Conversion (%)	SC (%)	Yield Time (h)
1	SiO$_2$	0	0	0	0	6
2	SiO$_2$	35	0	99.5	99	4
3	SiO$_2$	35	13.6	99.5	99	2
4	MCM	0	0	0	0	6
5	MCM	35	0	99	98.88	2
6	HT (Zn/Al x=3)	0	0	5	4.8	6
7	HT (Zn/Al x=3)	35	0	69	68.53	6
8	MK5	0	0	0	0	6
9	MK5	35	0	0	0	6

Reaction Conditions: Temperature: 398K, Catalyst: 2g, Styrene oxide: 25mmoles (3g), CO$_2$:14.3atm, n-hexane:17g, 1000rpm

### 3.3.2.0. Role of surface hydroxy group of silica gel

It has been postulated that surface hydroxy groups (silanol) on silica gel can assist in activation of epoxide via acid-base interaction of mildly acidic silanol groups and mildly basic nature of epoxide oxygen however; it is not confirmed by any

experimental evidence.[152] The indirect evidence obtained by this study support the above mention proposition. For this purpose, we have used silylation technique for deactivating the surface silanol groups present on silica gel after grafting of IL in order to establish its role silanol groups in catalysis (See Scheme 3.9). *N,O*-bis(trimethylsilyl) trifluoro-acetamide (BSTFA) was used as silylating agent due to it`s selective reactivity towards silanol groups present on the surface compared to commonly used agent e.g. trimethyl silylchloride.[153] The Figure 3.11 shows the activity of catalyst and yields of SC obtained before and after BSTFA treatment to the catalyst [CAT-3(MImCl) and CAT-6 (PyCl) type grafted IL on SiO_2). Two types of trends can be clearly seen from the plot, firstly, increase in CAT-3 loading on silica increases catalyst activity and yield of SC (See bar chart for 15 and 35% loading respectively) and secondly, treatment of BSTFA to catalyst decreases the activity and SC yield in all catalyst samples. It may be noted that surface silanol alone do not show good activity (SiO_2 as catalyst). The amount of BSTFA used was in good excess to quench all the surface silanol groups. In-spite of this the catalyst is not completely deactivated; this indicates that IL alone can catalyze the reaction but the presence of OH on the surface has a synergistic effect. It is tempting to view the role of surface OH groups from surface hydrophilicity and hydrophobicity point of view. BSTFA treatment to the catalyst is believed to increases the surface hydrophobicity, similar to that is known for treatment of silica gel surface with tetraethoxysilane (TEOS). This might cause the surface of silica gel behave like a hydrophobic one,[154] which might repel the approaching epoxide molecules that usually prefers nucleophilic environment on the surface.[155] Thus removal of silanol groups from silica surface results in reduction in the activity of catalyst. The plateau observed for activity of BSTFA treated catalyst beyond 35% loading of CAT-3 (with and without BSTFA treatment) might indicate that, at high loading of IL (75% CAT-3) the catalyst activity then becomes limited by availability of OH groups on the catalyst surface. However, the ^{29}Si and ^{13}C CP NMR spectra of BSTFA treated IL anchored catalyst do not show any appreciable change in the nature of spectra form that of untreated ones. The DRIFT IR spectra of BSTFA treated and untreated ^{IMB}75%CAT-3 catalyst (see chapter 2,section 2.4.3.4.3) showed broad and strong absorption peaks in the region 3360-3100 cm^{-1} indicating the presence of silanols. Therefore, from nmr and IR spectra it may be concluded that silanol groups on silica surface is not completely

removed by BSTFA treatment, but the decrease in catalyst activity upon BSTFA treatment observed in the present case indicates that the treatment either modifies active sites by reducing the availability of OH groups in

Scheme 3.7. IMB35%CAT-3a upon BSTFA treatment
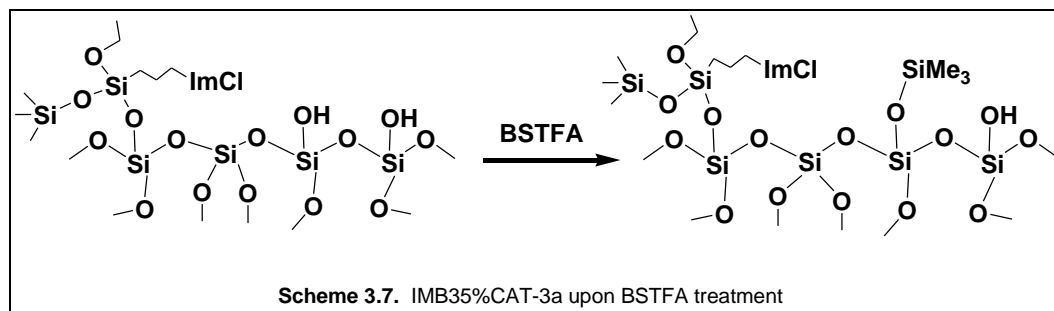
the neighborhood of imidazolium ion (which is the active sites contributing to catalysis by forming acid-base pairs), or the surface modification caused by BSTFA treatment tends to increase hydrophobic character of silica surface reducing affinity towards polar reactant molecules. It is also likely that both these parameters may contribute simultaneously to observed deactivation.
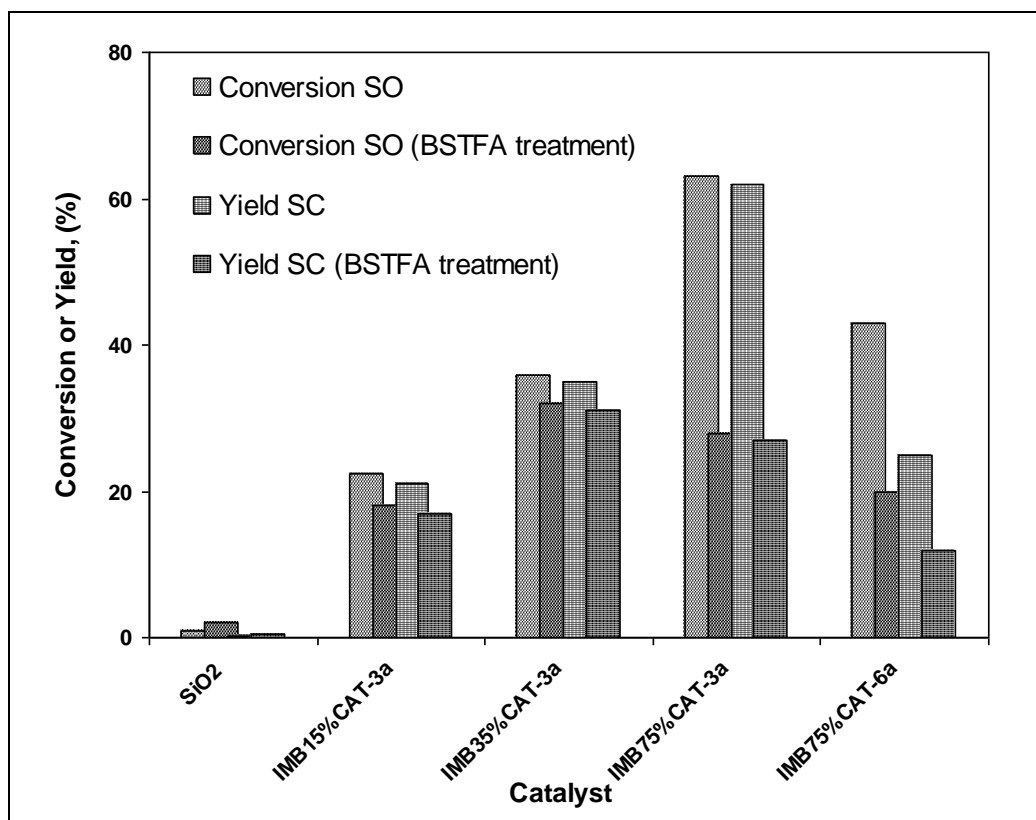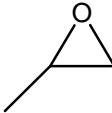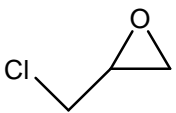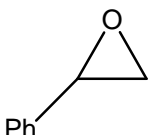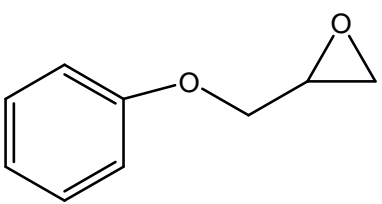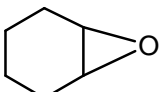

Figure.3.11. Effect of BSTFA treatment on catalyst activity

Reaction Conditions: Styrene oxide: 3g, Solvent:17g n-hexane, Temperature:398K, CO_2:13.6atm, Time: 6h,1000RPM.

3.3.2.1 Effect of Substrate

The applicability of catalyst [IMB]35%CAT-3a was established by screening various epoxides under optimised reaction conditions mentioned in Table 3.6. It was observed that reactive epoxides like propylene oxide and epichlorohydrin were converted to their corresponding carbonates with ~99% yield in 3h and 1h time respectively (Table 3.6, entry 1,2). Where as substrates like styrene oxide and 1,2-epoxy-3-phenoxy propane which are difficult to activate gave corresponding carbonates in 99% and 98% yield respectively in 4-5h reaction time (Table 3.6, entry 3,4). Stearically hindered cyclohexene epoxide failed to give any conversion (entry 5). Thus order of reactivity of epoxides decreased in order epichlorohydrin>propylene oxide>styrene oxide>1,2-epoxy-3-phenoxy propane.

**Table 3.6. Synthesis of cyclic carbonates using [IMB]35%CAT-3a catalyst**

Entry	Epoxides	Epoxide Conversion (%)	Cyclic Carbonate Yield (%)	Time (h)
1		99	98.65	3
2		98.50	98	1
3		99.5	99	4
4		98	97.66	5
5		0	0	6

Reaction Conditions: Temperature: 398K, Catalyst: [IMB]35%CAT-3a 2g, Epoxide: 25mmoles, CO_2:14.3atm, n-hexane:17g, 1000rpm

3.3.2.2. Catalyst recycle study

From the industrial point of view, one of the most intriguing aspects is the reusability of catalyst. The catalyst recycle experiments were carried out at two different temperatures to find out if the catalyst gets deactivated faster at higher temperature. The results of the catalyst reusability studies are given in Figure.3.12. The catalyst was recycled six times and it was observed that there was ~ 20% loss in its catalytic activity at 398K at the end of sixth recycle. There were losses of catalyst during handling of catalyst, typically about 15-20% catalyst was lost during five recycles and these losses were accounted for activity calculations.
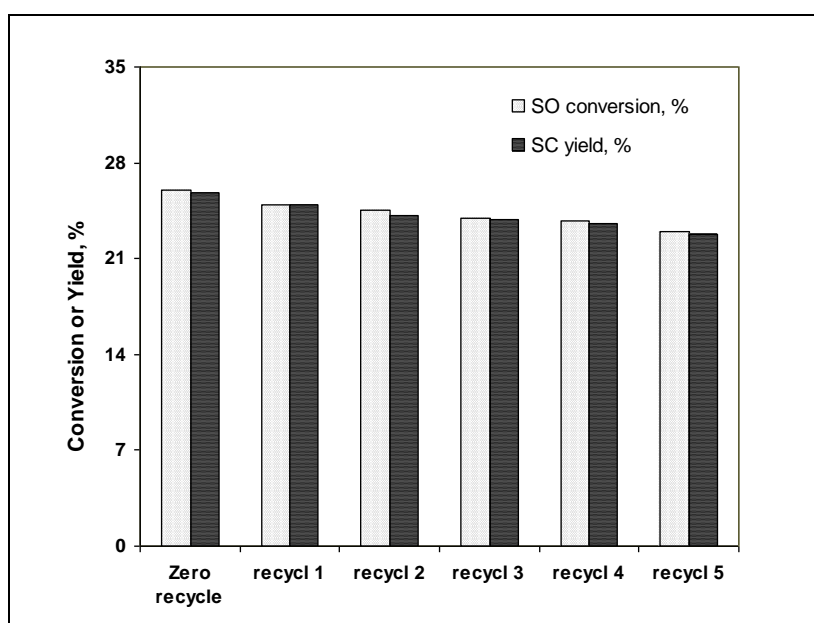

Figure. 3.12. Catalyst recycle study

Reaction Conditions :SO: 25 mmol; Temperature 373 K, P CO_2: 13.6 atm; Catalyst: ^{IMB}35%CAT-3a 2g; IL loading: equivalent to 1.08 mmol of IL grafted on silica catalyst; Contact time: 6h; Solvent: toluene 17 ml; rpm 600

3.3.2.3. Mechanism

Based on the literature work and the results of this study presented herein, a plausible reaction mechanism is depicted in Scheme 3.10. It is well known that simple

quaternary salts such as alkyl ammonium or phosphonium halides are extremely effective for high yield conversions of many epoxides with CO_2 to form corresponding cyclic carbonates. As reported by Darensbourg,[156] the onium salts having no interaction from the cation are expected to have highly reactive anions capable of nucleophilic attack. However the reduced nucleophilicity of the anion in the metal salts may be compensated by the electrophilic interaction of the metal ion with an epoxide. Thus the mechanism involves the nucleophilic attack of the anion at the least hindered carbon on the epoxide as a first step resulting in opening of epoxide ring followed by CO_2 addition (See Scheme 3.8. interaction A). The linear carbonate intermediate thus formed (Scheme 3.8., Step 1) converts into cyclic carbonate via intramolecular cyclization, followed by product elimination and regenerating quaternary salt catalyst (Scheme 3.8., Step 2). As suggested by Endo et al., under high pressures of CO_2 condition a different mechanism may be at work. CO_2 may be first activated by nucleophile which in turn interacts with the epoxide.[157] Therefore, in the present catalyst system bearing both acidic and basic sites (CAT-3 immobilized on silica) a cooperative mechanism has been postulated.[158] The organic part of catalyst i.e immobilized IL CAT-3 helps in CO_2 absorption and activation. Whereas the epoxide activation may occur by acidic H of silanol groups of the support. This activated epoxide is now facile for nucleophilic attack by halide ion on least hindered carbon of the epoxide facilitating the ring opening. This is followed by CO_2 insertion into the C-O bond of epoxide (step 1) followed by intramolecular substitution giving cyclic carbonate (step 2). Cyclization has been proposed to be preferred rather than polymer formation, owing to the thermodynamic stability of five membered cyclic carbonates. This mechanism suggests the synergistic effect of silanol group and halide part of ionic liquid for epoxide activation and CO_2 insertion.

Scheme 3.8. Plausible mechanism of epoxide activation and CO_2 insertion
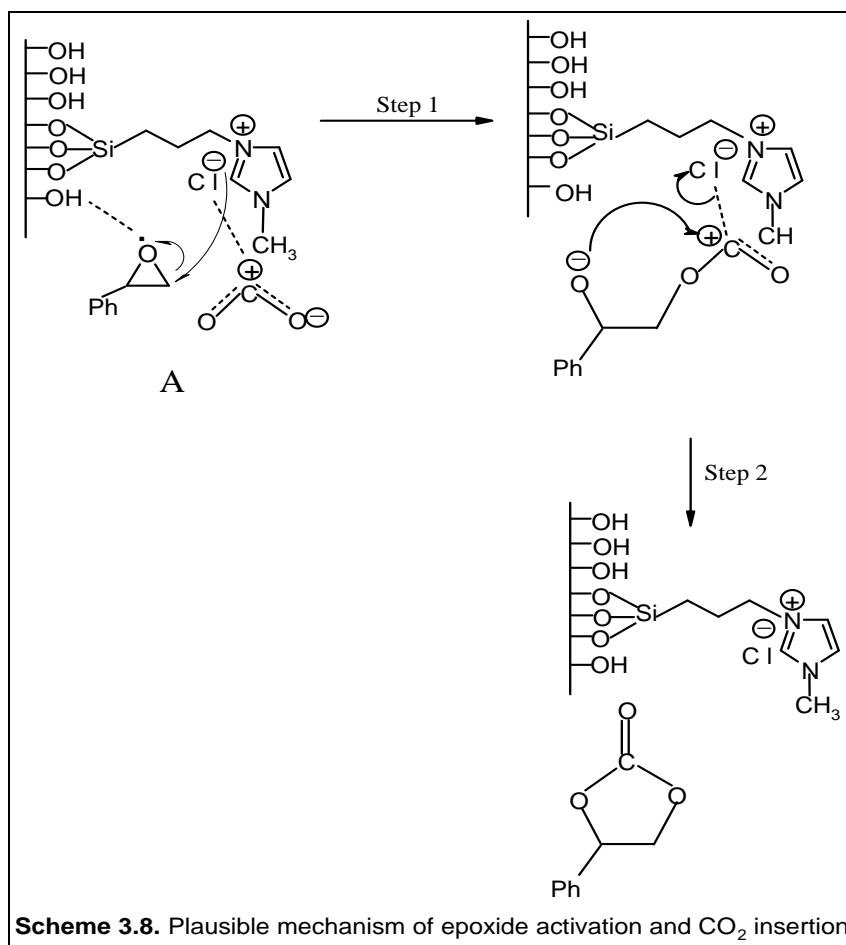
3.4. CONCLUSIONS

Attempt has been made to critically evaluate the advantages of operating the reaction of cycloaddition of carbon dioxide to epoxide for carbonate synthesis under non scCO₂ conditions. The role of CO_2 solubility and CO_2 capture capacity of heterogenised catalyst system in enhancement of activity of catalyst under non scCO₂ conditions has been explained. It has been demonstrated that, tuning of physical properties such as CO_2 solubility, CO_2 adsorption capacity of support can help to improve the catalyst performance under non scCO₂ conditions avoiding the use of scCO₂ which is a much less understood system from reaction engineering point of view. The catalyst prepared by impregnation or incipient wetness method, involves physical coating of IL on support and can be used in presence of aromatic solvents to avoid leaching of IL. The silica supported 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride catalyst ([IMB]35%CAT-3a) exhibits synergistic effect of silica gel support and grafted IL in enhancing carbonate yield. The n-hexane solvent

facilitates separation of carbonate from heterogeneous catalyst by forming multi phase system which allows easy separation of styrene carbonate a high boiler avoiding costly distillation. Finally a plausible reaction mechanism has been predicted which explains the activity behaviour observed for the grafted ionic liquid catalyst.

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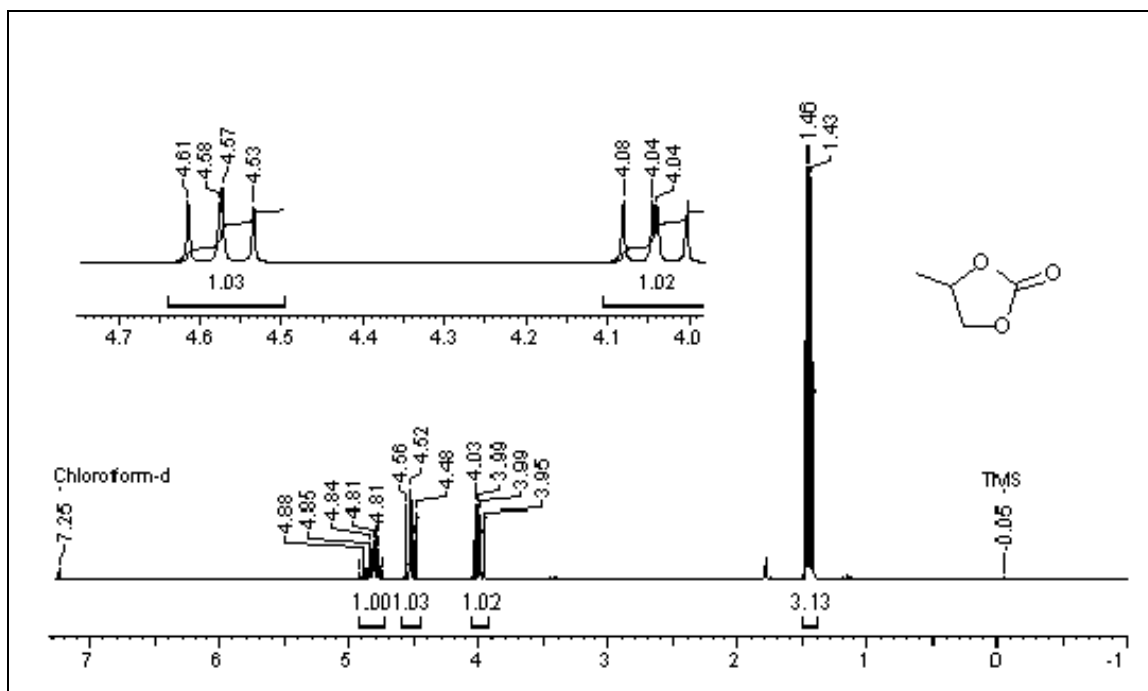120.Yano T., Matsui H., Koike T., ishiguro H., Fujihara H., Yoshihara M., Maeshima

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Spectra

¹H NMR (200MHz, CDCl₃): Propylene Carbonate
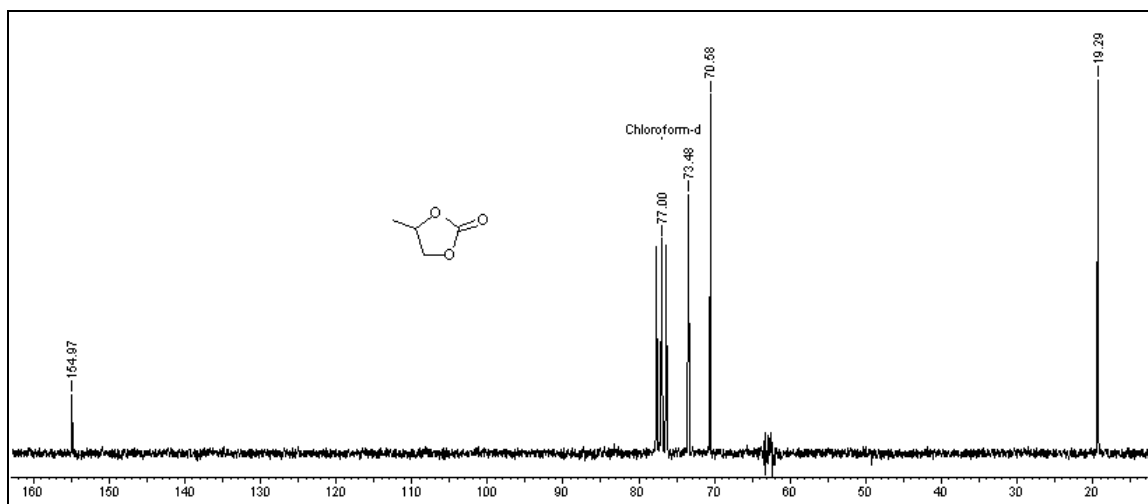
^{1}H NMR (200MHz, CDCl$_3$): Propylene Carbonate

^{13}C NMR (200MHz, CDCl$_3$): Propylene Carbonate

GC-MS: Propylene Carbonate

^{1}H NMR (200MHz, CDCl$_3$): Styrene Carbonate
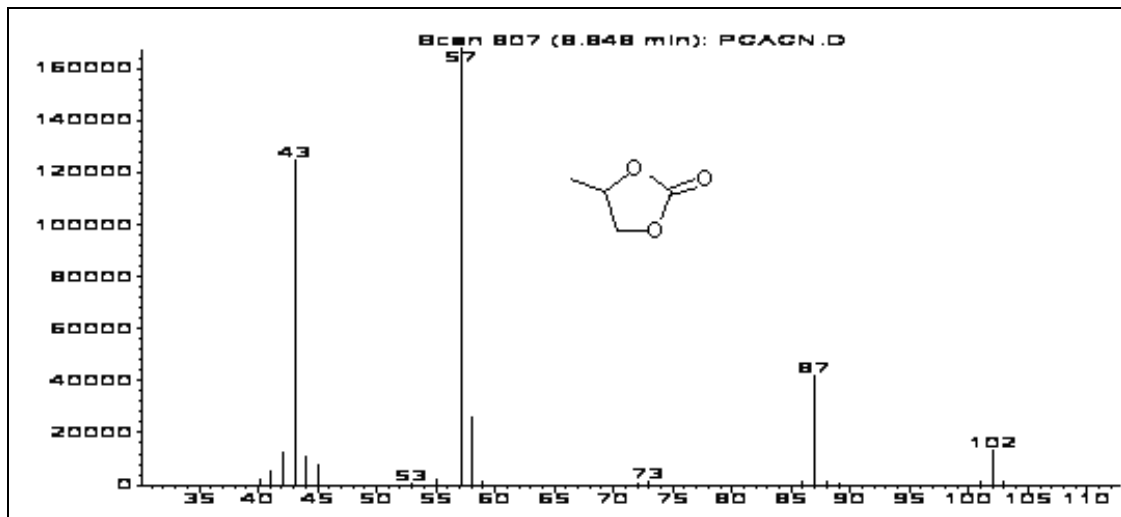
¹³C NMR (200MHz, CDCl₃): Styrene Carbonate
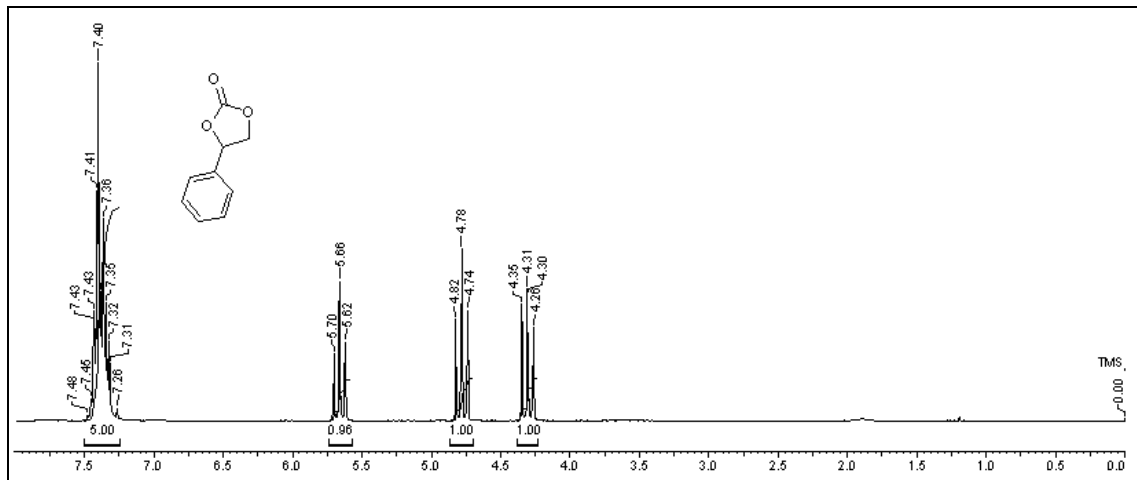
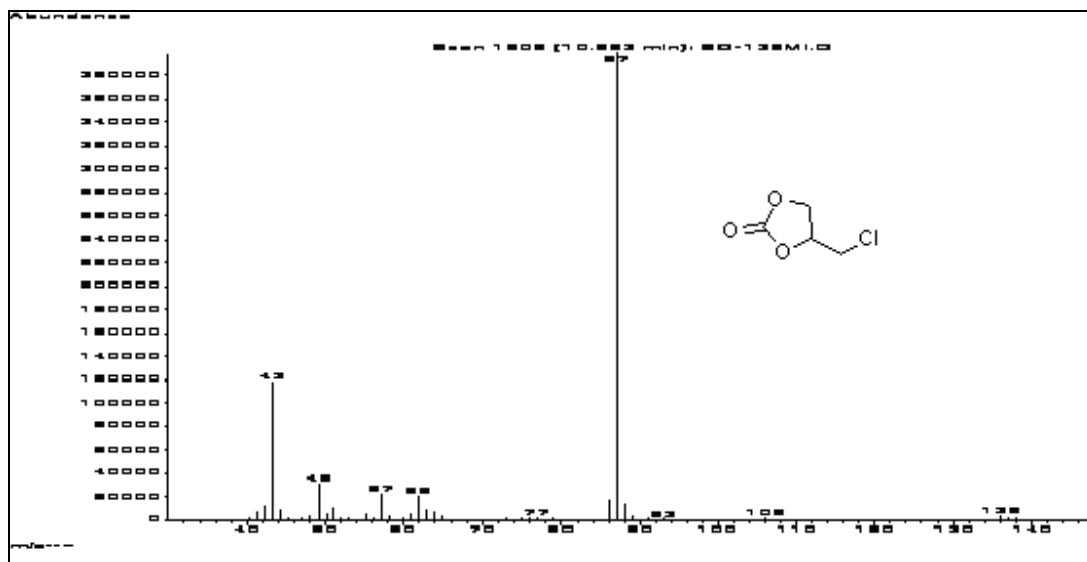^{13}C NMR (200MHz, CDCl$_3$): Styrene Carbonate
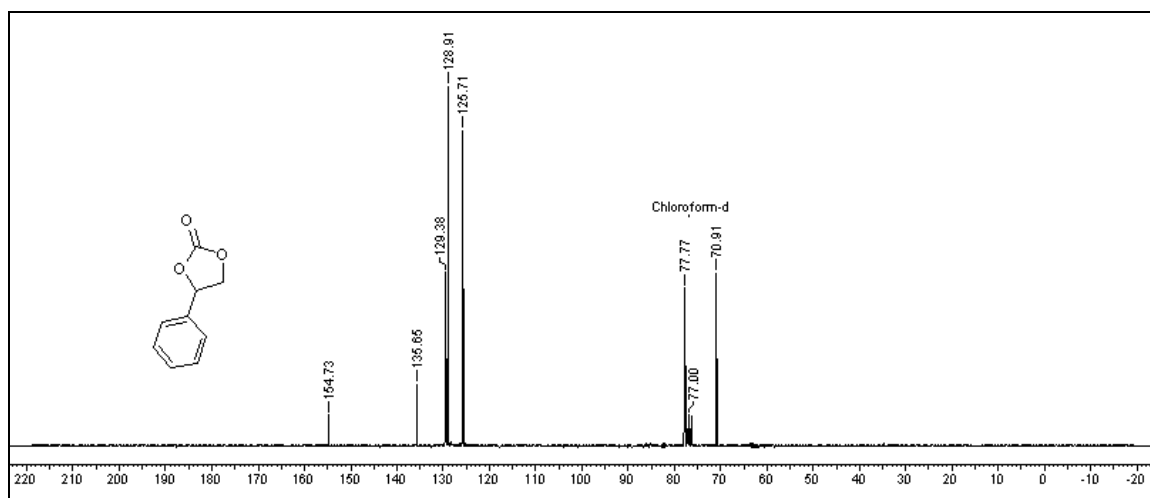
GC-MS: Styrene Carbonate
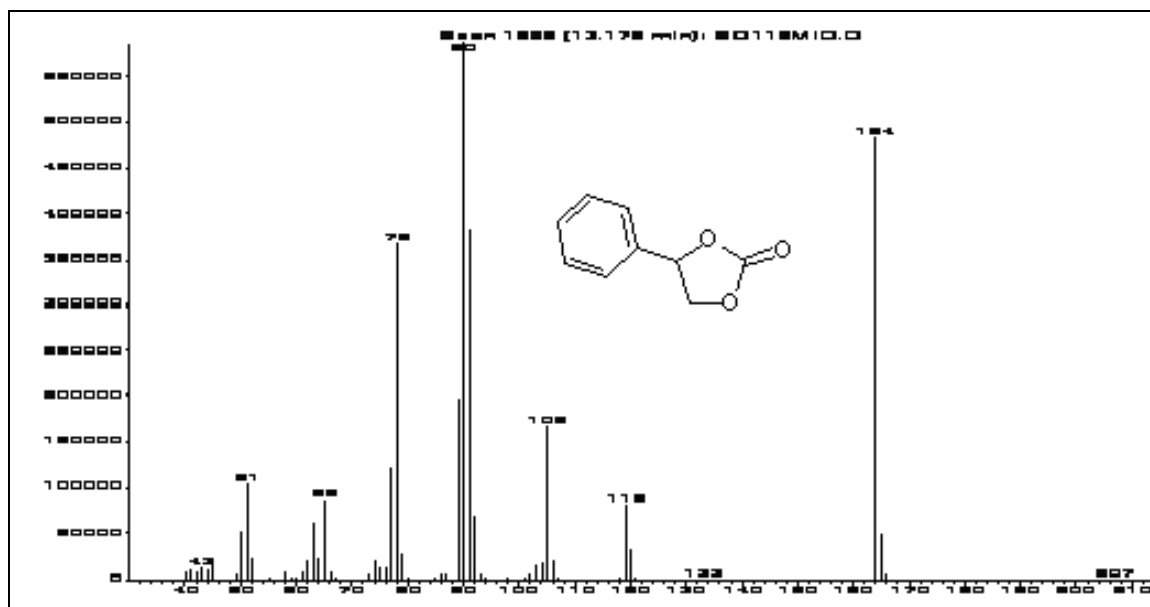
^{1}H NMR (200MHz, CDCl$_3$): 1,2-epoxy-3-phenoxy propane carbonate
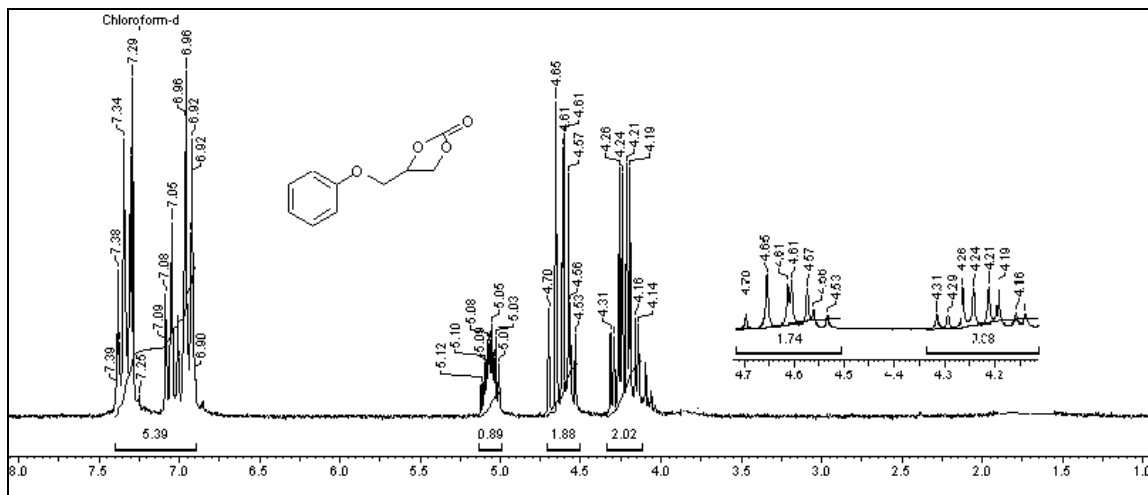
GC-MS: 1,2-epoxy-3-phenoxy propane carbonate
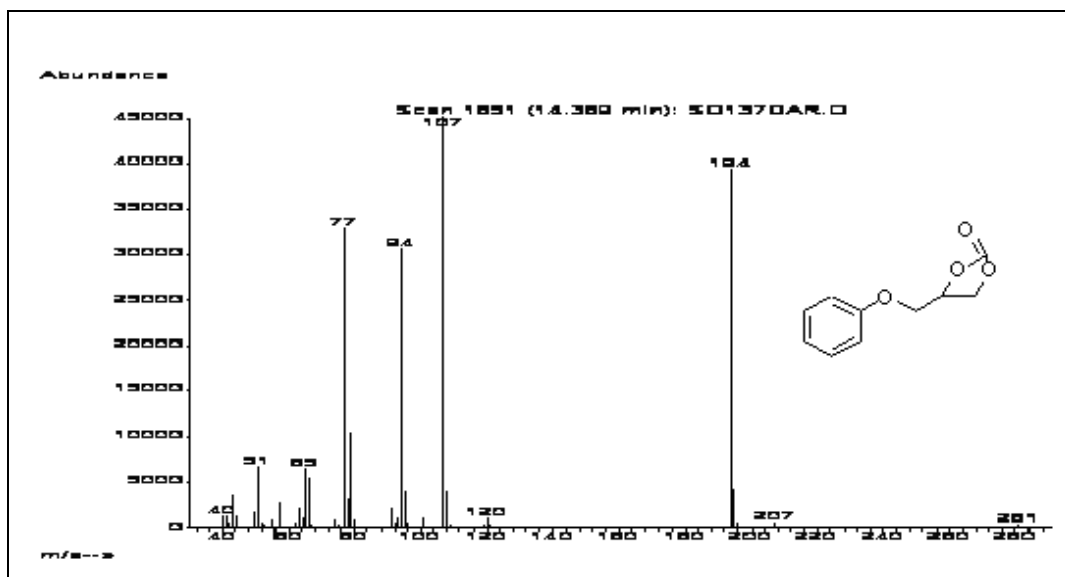
GC-MS: Epichlorohydrin carbonate

Section B

Catalytic synthesis of chalcone and flavanone using Zn-Al hydrotalcite adhere ionic liquid
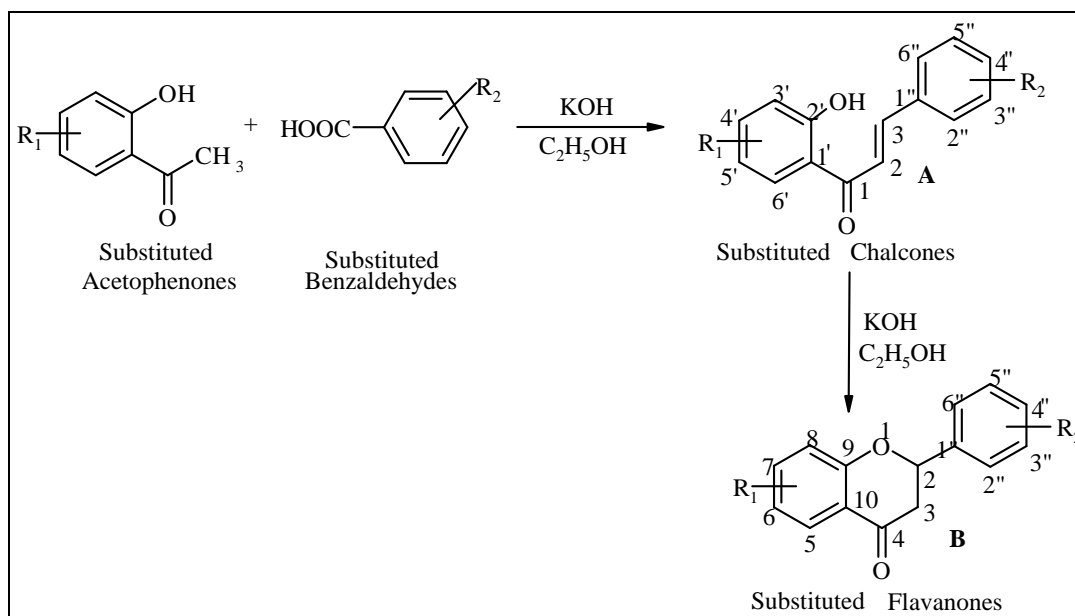
4.1. INTRODUCTION

 Claisen-Schmidt condensation of ketone and benzaldehyde leads to chalcones, which on isomerization produce flavanones (Scheme 4.1). Chalcones and flavanones have wide range of applications ranging from biological activity to cosmetic uses. [1,2,3] Flavanones are subclass of flavonoid family of substances and are commonly found in plants (especially in yellow color plant pigments), fruits, vegetables etc. Besides the wide range of application, flavanones possess at least one chiral carbon atom in position 2, which is a unique structural feature of these compounds (Scheme 4.1).[1] Conventionally, alkaline hydroxides or sodium ethoxide is used as a homogeneous catalyst for their synthesis,[3] but recently due to the development of increasing awareness about adopting greener technologies for making chemicals, solid acid/base catalysts are preferred over homogeneous ones due to their ease of handling, storage and disposal, besides their higher through puts. The synthesis of chalcones is reported using acid catalysts such as HCl[4], AlCl$_3$[5], BF$_3$[6], POCl$_3$[7], borax[8], Al$_2$O$_3$[9], titanium (IV) chloride[10], and zeolites[11]. The mechanism for chalcone formation using acid[12] or base[13] catalyst is presented in scheme 5.2a and 5.2b. On the other hand flavanone synthesis has been achieved by cyclization of 2-hydroxychalcone, a oxa-Michael type cyclization (obtained by aldol condensation between 2-hydroxyacetophenone and an aldehyde) using acids,[14] bases,[15] silica gel,[16] heat,[17] photoirradiation,[18] electrolysis,[19] Ni/Zn/K halides,[20] aqueous buffers at variable pH,[21] acidic ion-exchange resin,[22] acetic acid,[23] alkali metal hydroxide[24] (sometimes combined with phase-transfer catalysts),[25] sodium acetate,[26] potassium fluoride,[27] amine bases,[28] amino acids,[28] thermal reaction at 333K in the solid state[29] or in the melt at 503K,[30] catalysis by CoIII-salen complexes,[31] Lewis acids,[32] and others.[33] Other alternative procedures to synthesize flavanones include oxidation of flavan-4-ol.[34] Reacting benzaldehydes with 1-(2-hydroxyphenyl)-3-phenyl propane- 1,3-diones in basic medium [35] and transformation of 3-bromo-1-phenylprop-2-ynyl aryl ethers in the presence of mercury(II) trifluoroacetate. [36] Fride´n-Saxin et al reported a base-promoted condensation between 2-hydroxyacetophenones and aliphatic aldehydes. The reaction afforded 2-alkyl-substituted 4-chromanones in an efficient manner using microwave heating. Performing the reaction using diisopropylamine in EtOH at 443K for 1 h gave

moderate to high yields of flavanone (43-88%).[37] A combined yield of 70% of chalcone and flavanone was reported by Chandrasekhar et al. using L-proline (30 mol %) in DMF (0.02 M) at 353K for 18 h.[38] Solid bases such as K_2CO_3,[39] MgO, [40,41] LiNO$_3$/natural phosphate,[42] organic resins[43] calcined hydrotalcites (CHTlcs) and alkali exchanged zeolites have been shown to be efficient catalysts for Claisen-Schmidt condensation reaction.[44,45] The activity of calcined Mg-Al hydrotalcite for Claisen-Schmidt condensation can be markedly improved by rehydrating it with optimum amount of water[46,47,48] . Recently, the use of acidic IL as catalyst for chalcone synthesis has been reported [49] because of their benign nature as solvents and ability to dissolve wide range of compounds. However, the high cost, viscosity and issues related to their separation especially when product is a high boiling liquid or is a solid limit their use. Instead the supported ILs as catalyst has been found to be an attractive alternate.

Recent literature indicate that HTlcs are particularly promising catalyst in the synthesis of fine chemicals due to their unique catalytic feature besides easy preparation methodology involving low cost chemicals.[50,51] Many a times due to this advantages they are preferred over zeolite catalysts that are much costlier. The mixed oxides derived from calcination of HTlcs are often found to be more active than as prepared HTlcs due to presence of acido-basic pairs in their structure. In fine chemical synthesis usually substrates and products involved are polar in nature hence proper acid-base strength of active sites is necessary to match polarity of reactants and products for optimum utilization of catalyst.[52] The acido-basic properties of these mixed oxides can be easily tunable depending upon the nature of the condensation reaction e.g. structurally demanding condensation reactions such as flavanone synthesis from aldehyde and ketone can be complicated depending on the nature of reactants. Catalyst synthesis parameters such as calcination temperature[53] nature and ratio of divalent to trivalent cations[54] and the crystalline size[55] control the nature of acidic and basic sites in mixed oxides derived from HTlcs. The literature on this topic shows that most of the study on the synthesis of chalcone and flavanone using HTlcs and HTlcs derived mixed oxide, as catalyst is limited to mostly Mg-Al containing HT catalysts. While Zn-Al type of HTlcs and related compounds are largely overlooked in-spite of their versatility as acid-base catalyst.

Catalytic synthesis of chalcone and flavanone
using Zn-Al hydrotalcite adhere ionic liquid
                                                    SECTION-B

Scheme 4.1 Synthesis of chalcones by Claisen-Schmidt condensation and flavanones by subsequent intramolecular michael addition.
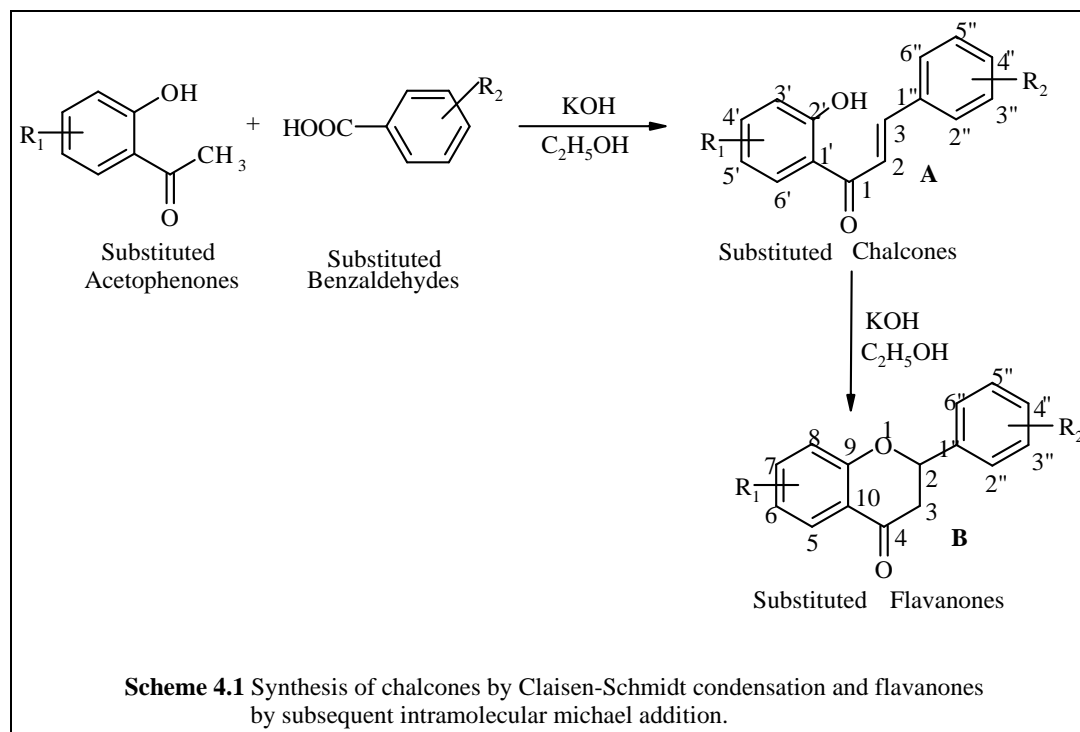
Saravanamurugan et al. found that using various metal oxides supported on ZnO as catalyst, the activity of the catalyst (in terms of conversion of 2′-hydroxy acetophenone) varies in the range of 80-45% and ZnO alone as the catalyst shows ~40% activity,[56] however, no report on the use of Zn-Al HTlcs and related compounds as catalyst was found in the literature. It has also been pointed out by researchers that Mg-Al CHTlcs are prone to deactivation by excessive water (although small quantities are beneficial[54]) and atmospheric pollutants like carbon dioxide, sulfur dioxide etc.

From above literature study the aim of this chapter was to develop efficient heterogeneous catalyst for this transformation to make the process sustainable. Also it can be noted that literature lacks report on use of Zn/Al HT as catalyst for this organic transformation.Since the use of Zn-Al HTls seems promising in this context, the objective of the present work therefore was to investigate the activity of Zn-Al HTlc and their oxide as catalyst for the synthesis of chalcone and flavanone.
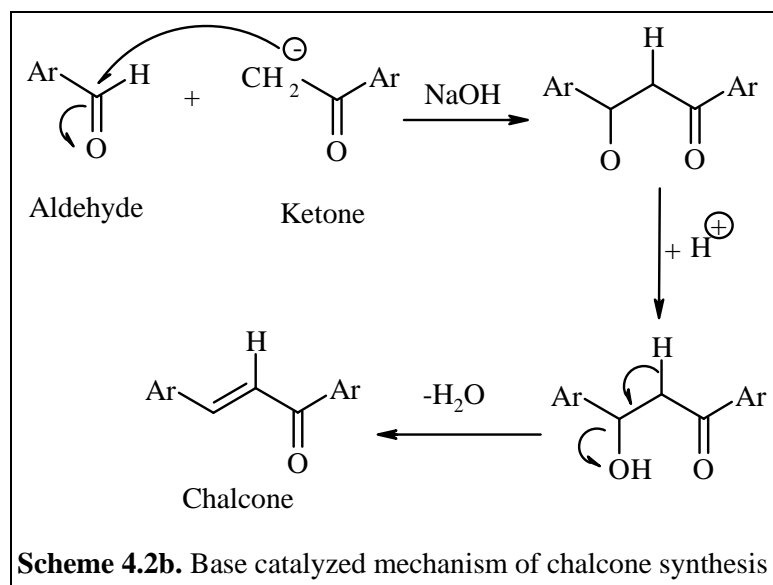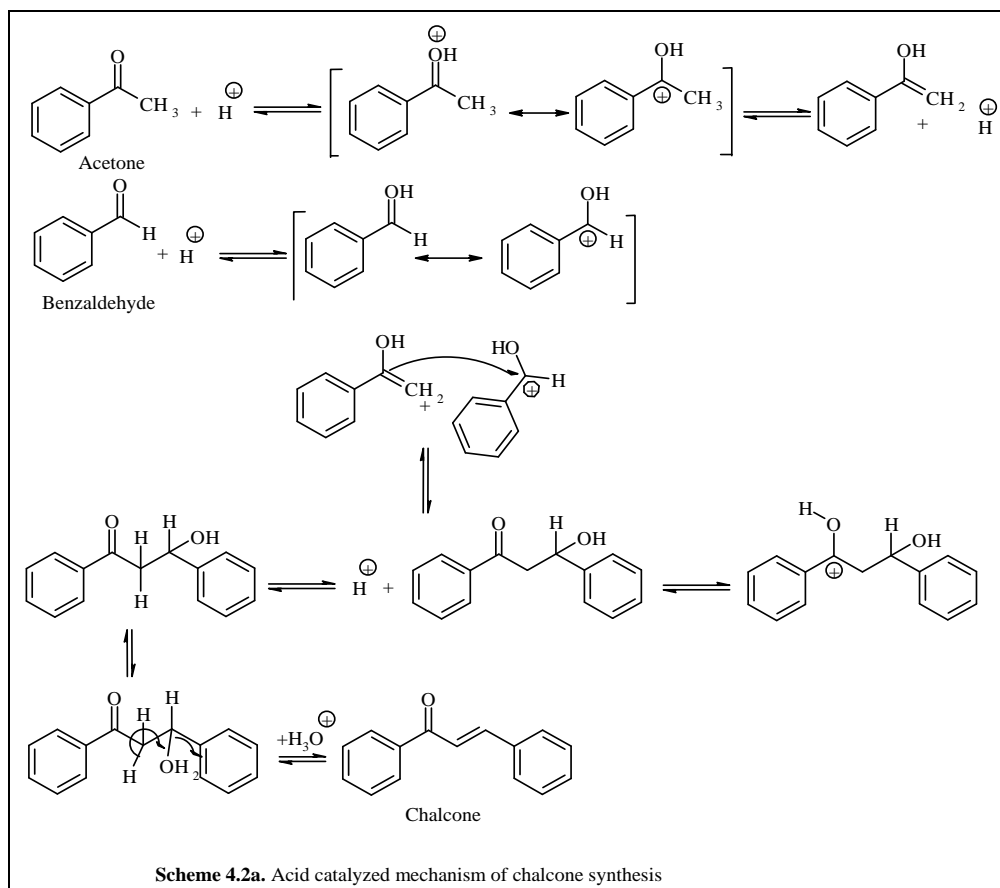
Scheme 4.2a. Acid catalyzed mechanism of chalcone synthesis

Scheme 4.2b. Base catalyzed mechanism of chalcone synthesis

Table 4.1. Literature on Chalcone and Flavanone synthesis.

Sr. No	Aldehyde	Ketone	Catalyst	Time; h	Temp. K	Conv. %	Chalcone sel.;%	Flavanone sel.,%	Reference
1	PhCHO	2'OH PhCOCH$_3$	Ba(OH)$_2$	1	333	90	100	0	Sathyanarayana et al. [57]
2	PhCHO	PhCOCH$_3$	Ba(OH)$_2$	10 min	333	98	100	0	Aguilera et al.[58]
3	PhCHO	PhCOCH$_3$	Ba(OH)$_2$	10min, (sonochem.)	298	36	100	0	Fuentes et al. [59]
4	PhCHO	PhCOCH$_3$	Al$_2$O$_3$	2.5	298	83	100	0	Varma [60]
5	PhCHO	2'OH PhCOCH$_3$	MgO	1.5	393-433	78	30	70	Drexler et al[61]
6	PhCHO	2'OH PhCOCH$_3$	Hydrotalcite	1	423	78	64	36	Climent et al.[62]
7	PhCHO	PhCOCH$_3$	NaNO$_3$/NP	18	298	98	100		Sebti et al.[63a,b]
8	PhCHO	2'OH PhCOCH$_3$	KF$_6$/NP	2	453	90	34	65	Macquarrie et al.[64] (44)
9	PhCHO	NCCH$_2$COOEt	Alkali exchange zeolite	2.5	413	68	100 (RCH=CCNCOOEt)		Corma et al.[65]
10	PhCHO	NCCH$_2$COOEt	Sepiolite (Cs)	2	363	68	100 (RCH=CCNCOOEt)		Corma et al.[66]
11	PhCHO	NCCH$_2$COOEt	Mg-Al HTlc (calcined)	2	393	82	100		Corma et al [67a,b]
12	PhCHO	NCCH$_2$COOEt	Aluminophoshate oxinitrides	15min	333	77	100		Climent et al [68]

Table 4.1. Literature on Chalcone and Flavanone synthesis.

Sr. No	Aldehyde	Ketone	Catalyst	Time; h	Temp. K	Conv. %	Chalcone sel.;%	Flavanone sel.,%	Reference
			(ALPON-4)						
13	PhCHO	PhCOCH$_3$	Mg-Al-O^{t}Bu	3.5	383	98		98	Kantam et al.[69]
14	PhCHO	2'OH PhCOCH$_3$	10%NH$_2$-SBA-15	8	413	92	23	69	Wang et al. [70]
15	PhCHO	PhCOCH$_3$	[(HSO$_3$)BMIm] HSO$_4$	6	413	99		98.8	Shen et al.[71]

4.2. EXPERIMENTAL SECTION

4.2.1. MATERIALS

Benzaldehyde, 2`-Hydroxyacetophenone and substituted 2`-Hydroxyacetophenone, were purchased from S.D. fine chemical ltd. India. IL CAT-3 1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride (TESP-MImCl) and various Zn-Al hydrotalcite (Zn/Al=6 and Zn/Al=3) were prepared according to literature procedure (see Chapter 2) and well characterized before use.

4.2.2. GENERAL PROCEDURE FOR SYNTHESIS OF CHALCONES AND FLAVANONES

Reactions were carried out in 25 cc two-neck round bottom flask equipped with reflux condenser and magnetic bar for stirring. The flask was previously dried and flushed with argon. The solid catalyst (222 mg); 2`-Hydroxyacetophenone, 1.26 g (9.25 mmol) and benzaldehyde, 2.41 g (22.72 mmol) were charged to the flask under atmosphere of argon and then immersed in the oil bath preheated to 413K. The temperature of the flask as well as that of oil bath was maintained using temperature controller. Standard reaction was carried out for 6h and time sampling was done at every one hour time intervals using a syringe having attachment for filtering solid catalyst particles. Dilutions of these samples were done by acetonitrile and liquid phase was quantitatively analyzed using gas chromatography. Details of the liquid phase analysis are given in the following section. The products were confirmed by GC-MS analysis.

Conversion and yield were calculated from GC analysis of reactants and products respectively. Activity of catalyst was based on conversion of *o*-hydroxy acetophenone measured under standard conditions of reaction. For recycle study after completion of the experiment, catalyst was separated by filtration through Sartorius 393 grade filter paper. Separated catalyst was Soxhlet extracted with dichloromethane to remove adhered organic impurities. The catalyst was dried at 398 K under vacuum for 6 h and reused. The catalyst was recycled five times and it was observed that there was minor loss in catalyst weight during each recycle (total loss < 10 %), this was taken into consideration and each recycle was carried out so that catalyst and reactant concentration do not deviate much from zero recycle experiment.

4.2.3. GENERAL PROCEDURE FOR SYNTHESIS OF HYDROTALCITES

A detailed procedure for synthesis of Zn-Al HTlc, IL CAT-3 adhere on HTlc and Mg-Al HTlc supplemented by thorough characterization is mentioned in Chapter 2. The physical properties of some of the hydrotalcites used as catalyst for this reaction are presented in table 4.2.

Table 4.2. Physical properties of some important catalysts used in this study

Entry	Sample	Surface area (m^2/g)	Pore volume (cm^2/g)	Pore diameter (Å)
1	Zn-Al(6) HTlc	70.57	6.054 x 10^{-1}	3.121 x 10^2
2	Zn-Al (6) CHTlc	105.43	8.48 x 10^{-1}	2.799 x 10^2
3	17.5% CAT-3 on Zn-Al (6) CHTlc	98.90	8.26 x 10^{-1}	3.00 x 10^2
4	35% CAT-3 on Zn-Al (6) CHTlc	19.75	7.48 x 10^{-2}	7.76 x 10^2

4.2.4. ANALYTICAL METHODS

Liquid samples were diluted by acetonitrile and analyzed on a Hewlett Packard 6890 Series GC equipped with auto sampler instrument, controlled by the HP Chemstation software, by using an BPX5 (30 m×0.32 mm×0.25 μm) capillary column with FID detector. Identification of products was done using GC-Mass spectrometry of Agilent, USA make, model 6890 GC with 5973N mass selective detector using HP-5 MS capillary column of 30m×0.32mmx 0.25μm dimension.

Calcined hydrotalcite and functionalized CHTls catalysts were characterized by XRD, ^{27}Al CP MAS NMR, ^{13}C CP MAS NMR, IR, surface area, pore volume, ammonia TPD and SEM, while other solid catalysts were characterized by IR. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku Dmax 2500 diffractometer equipped with graphite monochromatized CuKα radiation (λ=1.5406Å) employing a scanning rate of 2^0/min in the 2θ range from 10 to 80^0. Nitrogen adsorption–desorption isotherms were measured on Quantachrome Autochem II Chemisorption analyzer The scanning electron microscopy was carried out on a SEM-Leica-440 Electron Microscope. IR spectra were recorded on Perkin-Elmer System 2000 Infrared Spectroscope. [27]Al and

[13]C cross polarization magic angle spinning (CPMAS) NMR experiments were carried out on a Bruker Avance 300 wide bore spectrometer equipped with a superconducting magnet with a field of 7.1 Tesla. The operating frequencies for ^{13}C and [27]Al were 75.4MHz and 78.17MHz respectively.

The standard conditions for GC analysis are given in Table 4.3.

Table 4.3. Standard conditions for GC analysis

Parameters	Conditions
Injector (split) temperature	523 K
Flame ionization detector (FID) temperature	523 K
Column temperature (HP-5 capillary column)	343 K–493 K (programmed)
Inlet Pressure (He)	10 psig
Carrier gas (He) pressure	10 psig
Split ratio	50:1

The conversion, selectivity, yield, were calculated as follows.

$$\% \text{ Conversion} = \frac{\text{Initial moles of ketone} - \text{Final moles of ketone}}{\text{Initial moles of ketone}} \times 100$$

$$\% \text{ Selectivity} = \frac{\text{No. of moles of product formed}}{\text{No. of moles of ketone converted}} \times 100$$

$$\% \text{ Yield} = \frac{\text{No. of moles of product formed}}{\text{No. of moles of ketone charged}} \times 100$$

4.3. RESULTS AND DISCUSSION

In this work, solid base catalyzed synthesis of chalcones through the Claisen–Schmidt condensation and subsequent intramolecular Michael addition to flavanones of substituted acetophenones and benzaldehyde derivatives in the absence of solvent was investigated. The selectivities for chalcone and flavanone synthesis by Claisen-Schmidt condensation of 2`-hydroxy acetophenone and benzaldehyde were found to be governed by acid-base sites on the catalyst. Thus role of acid base sites formed after the interaction of impregnated IL on hydrotalcite towards selective synthesis of chalcone and/or flavanone was investigated using ^{27}Al CP MAS NMR technique.

4.3.1. Preliminary experiments for catalyst screening

Before attempting a detailed catalytic screening work, a non-catalytic reaction between hydroxy acetophenone and benzaldehyde was examined and it was observed that under the experimental conditions, trace formation of chalcone and flavanone was detected; indicating that from practical point of view the reaction is not taking place in the absence of any catalyst (Table 4.4, entry1). It is well known that Claisen-Schmidt condensation of 2`-hydroxy acetophenone and benzaldehyde is catalyzed by solid base catalysts, however some of these catalysts were re-examined here in order to establish the bench-mark under our experimental conditions. Thus condensation using SiO_2, hydrotalcites (Zn-Al=3), montmorillonite (MK-5) and zeolites NaX and NaY as a solid base catalyst was also examined (see table 2), the results indicated that except hydrotalcite as catalysts (43% total yield, entry 3) other solid bases showed poor activity for chalcone and derivative flavanone (< 21% combined yield). Zeolites NaX and NaY have pore diameter of 7.4 Å pose hindrance to the diffusion of reactants and products resulting in poor catalyst activity (entry 5 and 6). Since hydrotalcites, showed a significant enhancement in yields over other catalysts, further exploration of this reaction was carried out using hydrotalcites as catalysts.

Table 4.4. Screening of solid base catalysts[a]

Entry	Catalyst	Conversion,**1a**[b] (%)	Yield[b] (%) Chalcone, **3**	Flavanone, **4**
1	Nil	1	Trace	Trace
2	SiO_2 (230-280 mesh)	6	2.6	3.1
3	Zn-Al (3) HT	43	24	19
4	MK-5	21	11	9.8
5	NaX	12	6.5	5.2
6	NaY	4	2.8	1.2

[a]*Reaction conditions: 22.72 mmol benzaldehyde, 9.27 mmol o-hydroxy acetophenone, 222 mg catalyst, 140°C,6h.*

[b] *Conversion and yield based on GC analysis of reactants and products.*

4.3.2. Screening of catalysts prepared by impregnation of CAT-3 IL on various support towards selectivity for chalcone and flavanone synthesis

The results of activity of catalysts functionalized by CAT-3 IL on various support is shown in Table 4.5. The results indicate that IL functionalized supports are more active than non-functionalized supports screened earlier (See Table 4.4). The activity of neat CAT-3 was found to be very poor (~ 2 % conversion of 2`-hydroxy acetophenone, entry1). It was observed that neat CAT-3 was not soluble in organic medium and was found to stick at the bottom of the flask under reaction conditions resulting in poor activity. To check this, another IL viz. 1-butyl-3-methylimidazolium chloride which was soluble under reaction conditions was tested for it`s activity, however it was also found to be inactive for the reaction (entry 2). Thus confirming that IL with chloride as anion is not active for the reaction. The highest activity of 53 % conversion of *o*-hydroxy acetophenone was obtained when IL, CAT-3 was coated on Zn-Al (3) CHTlcs as support (Table 4.5, entry 5), while CAT-3 supported on SiO_2 (entry 3,4) montmorillonite (MK-5) and zeolite (entry 6-8) did not show promising results. The loading of IL on the hydrotalcite derived support enhances the activity due to evenly spreading of IL by

surface coating[72] which allows IL to efficiently interact with surface acid-base sites, there by increasing the activity (See Table 4.4 and 4.5 for comparison of activity).

Table 4.5. Activity of 35% immobilized CAT-3 catalyst.[a]

| Entry	Catalyst	Conversion[b] % (phenol)	Yield [b] (%)	
			Chalcone 3	**Flavanone 4**
1	CAT-3	2	0.6	0.8
2	[BMIm]Cl	Nil	Nil	Nil
3	[IMB]35%CAT-3a	23	11	12
4	[IMB]75%CAT-3a	30	17	12
5	[IMB]35%CAT-5a (Zn/Al x=3)	53	26	24
6	[IMB]35%CAT-3c (MK 5)	21.5	8	13
7	[IMB]35%CAT-NaX	17	7	10
8	[IMB]35%CAT-NaY	22	6	16

[a]*Reaction conditions: 22.72 mmol benzaldehyde, 9.27 mmol o-hydroxy acetophenone, 222 mg catalyst, 140°C,6h.*

[b] *Conversion and yield based on GC analysis of reactants and products.*

4.3.3. Effect of loading of CAT-3 on calcined Zn-Al (6) hydrotalcite

The activity of impregnated CAT-3 on calcined Zn-Al (6) hydrotalcite was investigated systematically by loading IL in the range 2.06-35 % and 35 % loading on uncalcined HT and these results are shown in Table 4.6. It can be seen from the table that supporting 35 % IL on calcined or uncalcined HT increases the activity by nearly 1.5 times compared to unsupported ones (Table 4.6, entry 1,2 and 7,8). And compared to Zn-Al (3) CAT-3 (Table 4.5, entry5) it is almost two times. Another striking difference that is observed here is the good activity exhibited by uncalcined Zn-Al(6) HTlc. This is in contrast to the poorer activity of Mg-Al HTlcs reported earlier. It is known that solution decomposition of Zn-Al hydrotalcite under hydrothermal conditions begins at as low as 423K forming Zn-Al mixed oxide.[73] Under the experimental conditions mentioned here, it would

facilitate formation of mixed oxide phase during the course of reaction, enhancing the catalyst activity. This argument is also supported by the fact that Zn-Al HTlc is unstable compared to Mg-Al.[74] The loading of IL results indicate that increasing IL loading from 2.06% increases the catalyst activity of Claisen-Schmidt condensation but further increase of IL up-to 8.5 %, the activity decreases slightly (See entry 3 and 4,5) and levels off with Zn-Al (6) CHTlcs activity (entry 1). Catalyst activity increases again beyond 17.5 % IL and at 35 % IL loading a maximum of ~ 99.2 % activity is observed (entry 6 and 7). A maximum yield of ~ 68% flavanone was achieved when IL loading was 35 % (entry 7). The loading of IL decreases the surface area from 105.43 m^2/g for calcined Zn-Al(6) HTlc to 98.90 m^2/g for 17.5 % IL. Thus covering the active sites of CHTlcs and since the activity increase due to IL is marginal under these conditions the effective rise in activity was not observed. However, for catalyst with 35 % IL, even though the surface area is decreased to 19.75 m^2/g (See Table 4.2, entry 4) highest activity (99.2 % conversion, Table 4.6, entry 7) is realized. This intriguing result warrants some explanation. It is true that increase in surface area exposes large number of active sites on the surface to reactant molecules enhancing the reaction rate, provided that the nature of active sites is not altered. Most of the time this is the cases and one might be able to correlate the activity of the catalyst with the surface area,[75] however, in complex cases, instead of surface area; the number and nature of active sites on the surface represents a realistic picture.[76] In the present case wherein, due to interaction of IL with Al^{3+} ion, original active sites on the oxide catalysts are modified (reconstructed site) and are believed to be more active. For example, it can be seen from Figure 4.1 that increase in IL loading increases the tetra and penta coordinated Al^{3+} species at the expense of octahedral aluminum (~ 50 % amount) present in calcined HTlc (Figure 4.1a). At maximum loading of 35 % IL the amount of octahedral aluminum drops to almost 30 % (Figure 4.1f) while tetra and penta coordinate aluminum increase up to ~ 70 %. It can be concluded that this change in geometry of aluminum and hence structure of Zn-Al (6) CHTlc might be responsible for enhanced activity due to loading of IL. The stability of [IMB]35%CAT-5a (Zn-Al (6)) CHTlc was investigated by recycling the catalyst.
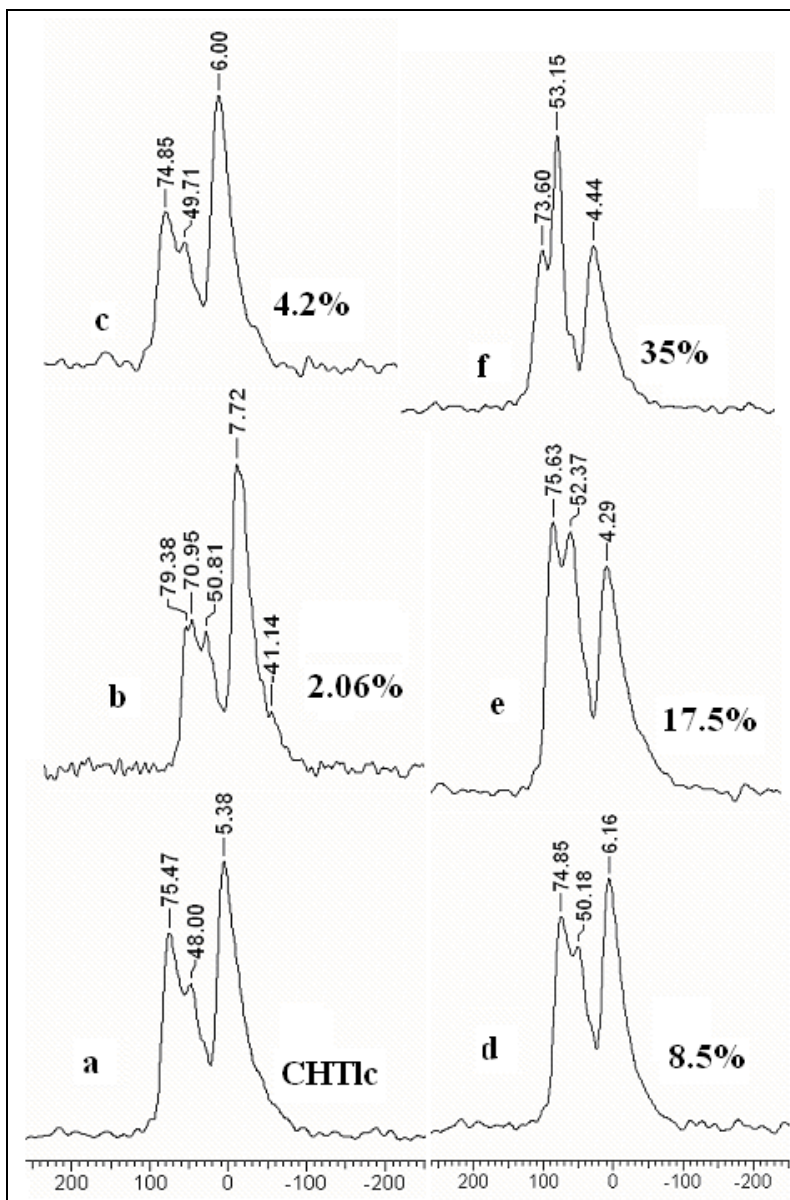
Figure:4.1. ^{27}Al CP MAS NMR spectra of CAT-3 loaded on Zn–Al (6) CHTlc.

Table 4.6. Effect of CAT-3 IL loading on Zn-Al (6) CHTlc catalyst.[a]

Entry	Catalyst	Conversion[b],**1a** (%)	Yield [b] (%)	
			Chalcone **3**	Flavanone **4**
1	0% Loading	66.4	38.1	28.2
2	Zn-Al HTlc	62.2	41.1	20.0
3	2.06% Loading	76.6	46.6	30
4	4.2% Loading	59.0	33	26
5	8.5% Loading	60.6	35.8	24.8
6	17.5% Loading	72.2	46.1	26.1
7	35% Loading	99.2	30.7	68.5
8	35% Loading Zn-Al on HTlc	86.3	38.5	47.5

[a]*Reaction conditions: 22.72 mmol benzaldehyde, 9.27 mmol o-hydroxy acetophenone, 222 mg catalyst, 140°C,6h.*

[b] *Conversion and yield based on GC analysis of reactants and products.*

4.3.4. Catalyst recovery and recycling

From the industrial point of view, one of the important aspects is the reusability of catalyst. The results of the catalyst reusability studies are given in Figure 4.2. After completion of the experiment, catalyst was separated by filtration through Sartorius 393-grade filter paper. Separated catalyst was washed several times with acetonitrile to remove adhered organic impurities. The catalyst was dried at 398 K for 6 h and reused. It was observed that at the end of fifth recycle, catalyst retained almost 98 % of it`s original activity and selectivity confirming that the catalyst is stable as well as selective for synthesis of chalcone and flavanone. There were losses during handling since the particle size was very small and typically about 15-20% catalyst was lost during five recycles and these losses were accounted for activity calculations.
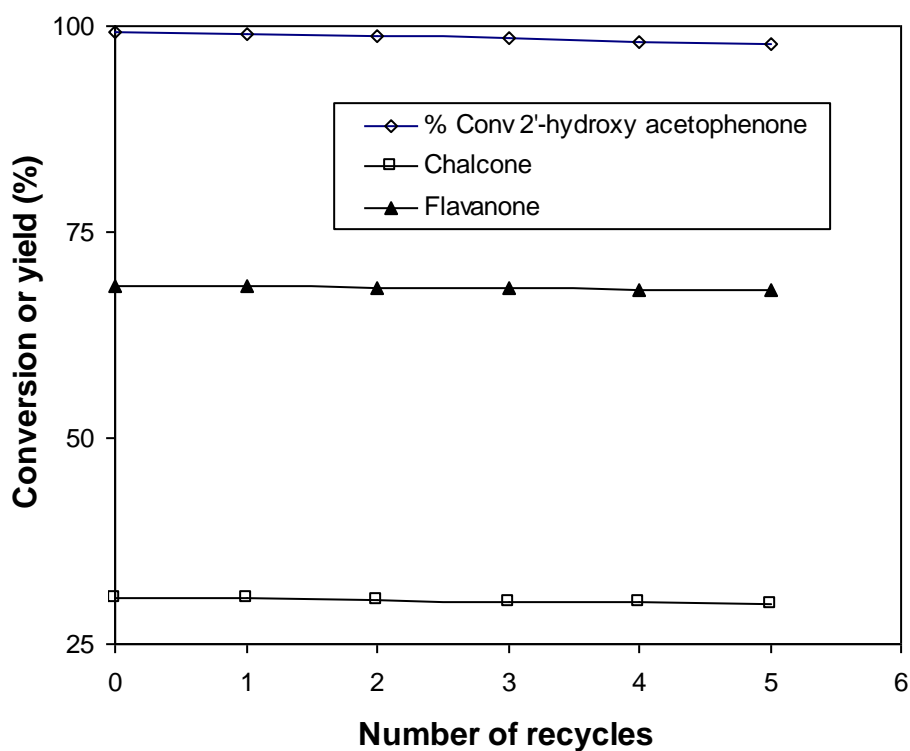
Figure:4.2. Catalyst recycles study.

Reaction conditions: 22.72 mmol benzaldehyde, 9.27 mmol o-hydroxy acetophenone, 222 mg catalyst, 140°C,6h. Yields were determined by GC and are based on conversion of reactants

4.3.5. Role of acid base sites created after impregnation of CAT-3 IL on calcined Zn-Al (6) hydrotalcite

The Claisen Schmidt condensation reaction catalyzed by MgAl(O) mixed oxides derived from HT like material are known to be excellent catalysts for this reaction. It has been shown that in the base catalyzed reaction stabilization of enolate anion by Lewis acidic sites is critical. While for initial activation of acetophenone basic sites play a key role. Thus Mg-Al HTls and related materials having M^{2+} ion and oxygen in their structure function as acidic and basic sites respectively are good catalysts for this reaction. Further fine tuning of these acido-basic properties of catalyst is possible for improving the

activity of the catalyst derived from HT. In the present work, IL loaded on Zn-Al (6) CHTlcs is shown to alter the environment around Al^{3+} ion depending on amount of IL loaded on the catalyst (scheme 4.4). A comprehensive description on the variation observed after supporting CAT-3 IL on calcined Zn-Al (6) hydrotalcite based on XRD, SEM, ^{27}Al CP MAS NMR, and ^{13}C CP MAS NMR is discussed in Chapter 2.

Scheme 4.4. Schematic view of TESPMimCl IL interaction with calcined Zn-Al (6) HTlc.
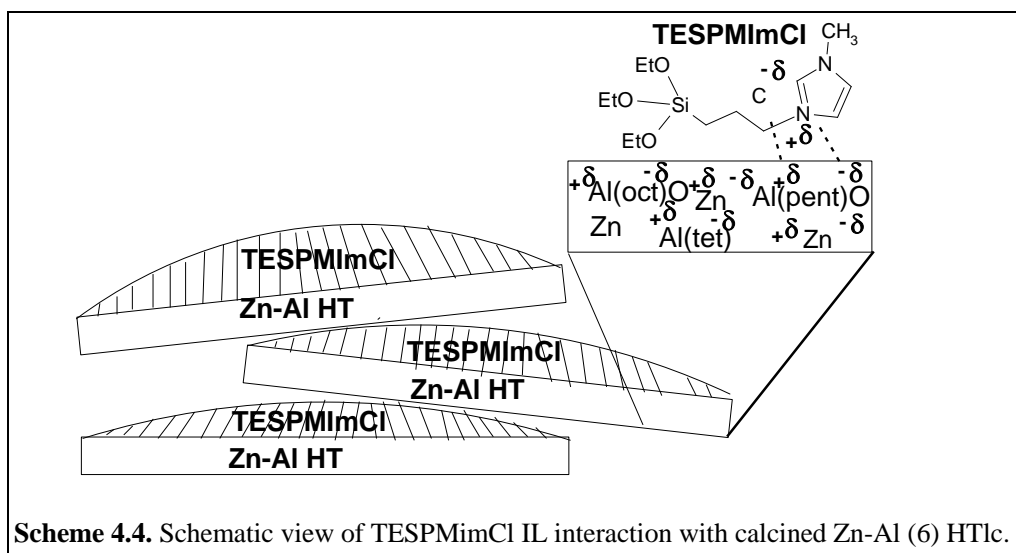
The question is what is the effect of acid-base properties of active sites upon modification of Al^{3+} environment from octahedral to tetra and pentahedral? The information about this in published literature is scanty. Tichit and co-workers[77] has reported that in Ni-Al mixed oxide, both Ni^{2+} and Al^{3+} provide Lewis acid sites. And since Zn-Al mixed oxide is more acidic than Mg-Al mixed oxide, it is reasonable to believe that Al^{3+} in tetra and penta environment can contribute to development of Lewis acidic sites in hydrotalcite derived materials. While migration of Al_T^{3+}, away from adjacent Mg^{2+} in the structure leaves more O_2^{2-} anions in the neighborhood of Mg^{2+} giving rise to increase in the basicity.[78] Our results of IL interaction with Al^{3+} in generating tetra and penta coordination environment around Al^{3+} thus has specific relevance to modifying acid-base properties of these materials. The results are in agreement with observed catalyst activity which is low at low loading of IL and is high for 35% loading of IL.

There is only scanty information available in literature on acid-base properties of Zn-Al hydrotalcite type materials that are having Al^{3+} ions in tetra, penta and octahedral coordination environment. It can only be acknowledged from the present results that IL do interact with aluminum ion of Zn-Al HT to create Al^{3+} ions in tetra and penta coordinated environment which are supposedly more active compared to unloaded calcined HT having almost 60% Al^{3+} in octahedral geometry. The preliminary results of ammonia TPD of 17.5 and 35 % IL loaded on Zn-Al (6) CHTlc sample, do show ammonia desorption at 618K indicating the presence of acidic sites for 35% loaded sample, while such sites are completely absent for 17 % sample (See TPD graph figure 4.3). Thus, the interaction of IL seems to generate modified sites on our catalyst (mixed oxide derived from hydrotalcite). However, we need to confirm the kind of interaction that take place with IL and NH_3 at this temperature in order to comment on nature of acidic site. Therefore, at this stage we do not exactly know the nature of reconstructed acid-base pairs due to interaction with IL we can not predict the mechanism of reaction. Obviously more work is needed in this direction to arrive at a definitive conclusion. Since the calcined sample of Zn-Al (6) LDH possess appreciable amount of Al^{3+} in tetra and penta coordination (~56.4%), interaction of IL liquid with Zn-Al CHT further increase the amount of Al^{3+} in tetra and penta coordination. This is also expected to distort the structural geometry of Al^{3+} in order to preserve the stability of structure. This situation creates more Al^{3+} surrounded by fewer than six oxygen atoms, making large number of Al^{3+} having vacant coordination site that are then susceptible to reactant attack. The Lewis acidic sites of Zn-Al mixed oxides derived from calcination of HT depends on amount of aluminum.
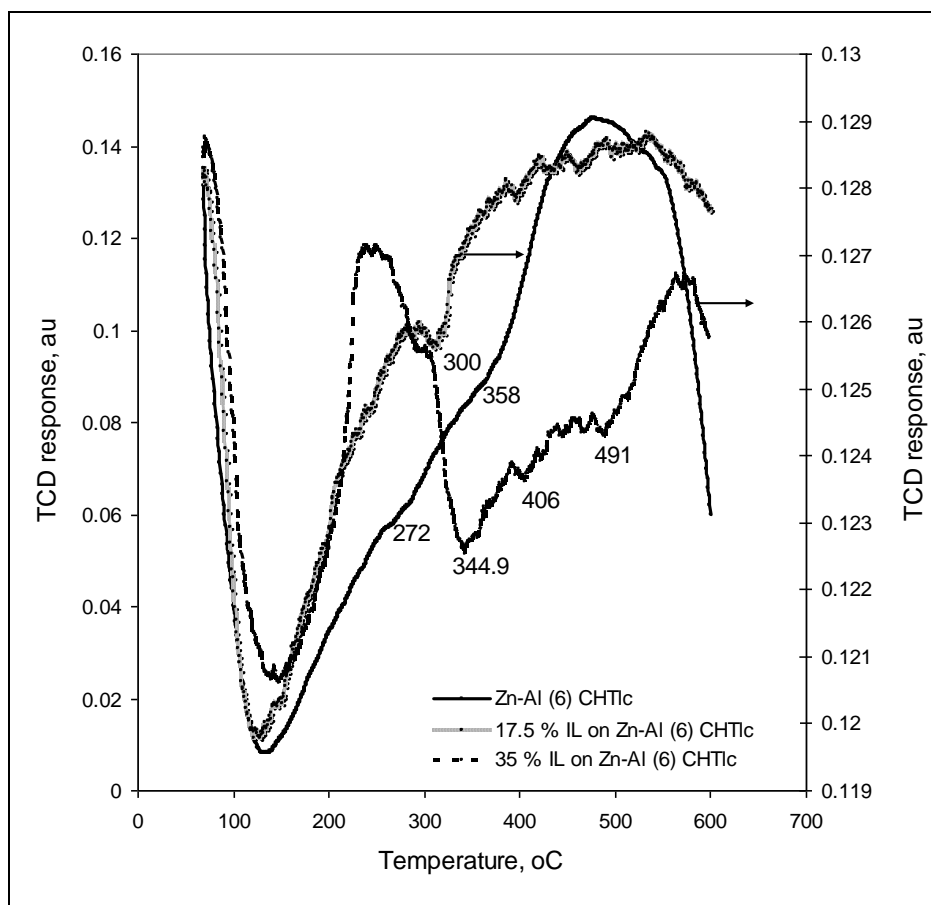
Figure 4.3. NH$_3$ TPD of A) Zn-Al (6) CHTlc, B) 17.5% TESPMimcl on Zn-Al (6) CHTlc and C) 35% TESPMimcl on Zn-Al (6) CHTlc

While the acid-base pairs are formed due to Zn-O and Al-O linkages having net charges on their atoms due to defects that exist in the structure. Several other parameters such as Zn^{2+}/Al^{3+} ratio, synthesis method, calcination conditions control the property of active sites. In other words, parameters that alter the bonding characteristics of Metal-Oxygen, change the acid-base property. Therefore, since IL alters the Al^{3+} geometry, it is expected also to change the acid-base property of the catalyst.

4.3.6. Effect of substrate

The synthesis of various chalcones and flavanones from substituted benzaldehyde is shown in Table 4.7 for Zn-Al (6) CHTlc as catalyst. The data indicate that *p*-tolyl benzaldehyde is least active towards condensation and almost 41h is required for conversion of ~ 90% of 2`-hydroxy acetophenone (Table 4.7, entry 2). The activity of other aldehydes investigated is not too much different in comparison to each other for 6h

reaction time (4.7, entry 1,3-5). It may be noted here that catalyst is active for extended period of reaction (12-41h) and almost 90% conversion is realized for higher contact times. The yield of chalcone and flavanone are in agreement with the conversion indicating that no major side products are formed.

Table 4.7. Synthesis of chalcones and flavanones using Zn-Al (6) CHTlc as catalysts.[a]

Entry	R	1	2	Conversion,**1a**[b] (%)	Yield [b] (%)	
					3	**4**
1	H	1a	2a	66.4	38.1 (3a)	28.2 (4a)
2	4-CH$_3$	1a	2b	21.0 96.0[c]	15 (3b) 50	6 (4b) 46
3	4-Cl	1a	2c	64.0	34 (3c)	30 (4c)
4	4-F	1a	2d	55.0 87.0[d]	24 26.8 (3d)	31 (4d) 60
5	3-OH	1a	2e	56.0 91.0[d]	31.0 (3e) 40.0	25 (4e) 50

[a]Reaction conditions: 22.72 mmol aldehyde, 9.27 mmol *o*-hydroxy acetophenone, 222 mg catalyst, 140°C,6h.

[b]Conversion and yield based on GC analysis of reactants and products.

[c]41h.

[d]12h, reaction time.

4.4. Conclusions

The Claisen-Schmidt condensation of 2`-hydroxy acetophenone and benzaldehyde to chalcone and flavanone show that calcined Zn-Al (6) hydrotalcite is active for this synthesis. The activity of this catalyst can be further increased by about 1.5 times by coating ionic liquid triethoxysilane-3-methyl imidazolium chloride on calcined hydrotalcite. Coating 35% IL on calcined and uncalcined Zn-Al (6) hydrotalcite showed selectivity for flavanone synthesis as compared to lower loading of IL on hydrotalcite. It has been shown by ^{13}C and ^{27}Al NMR spectroscopic study that IL is coated without degradation and that structural changes in calcined hydrotalcite take place when IL in amount greater than 17.5 % is coated on to CHTlc. At 35 % loading of IL it was observed

that almost 50 % alumina gets converted into pentacooardination which seems to be the reason for enhancement in the catalytic activity at higher loading of IL.

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Spectra

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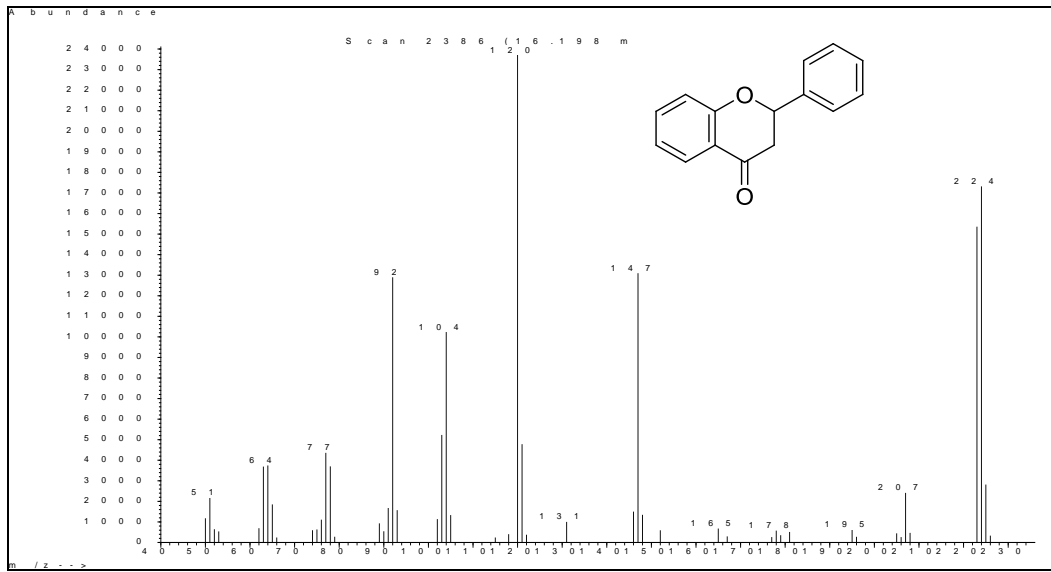
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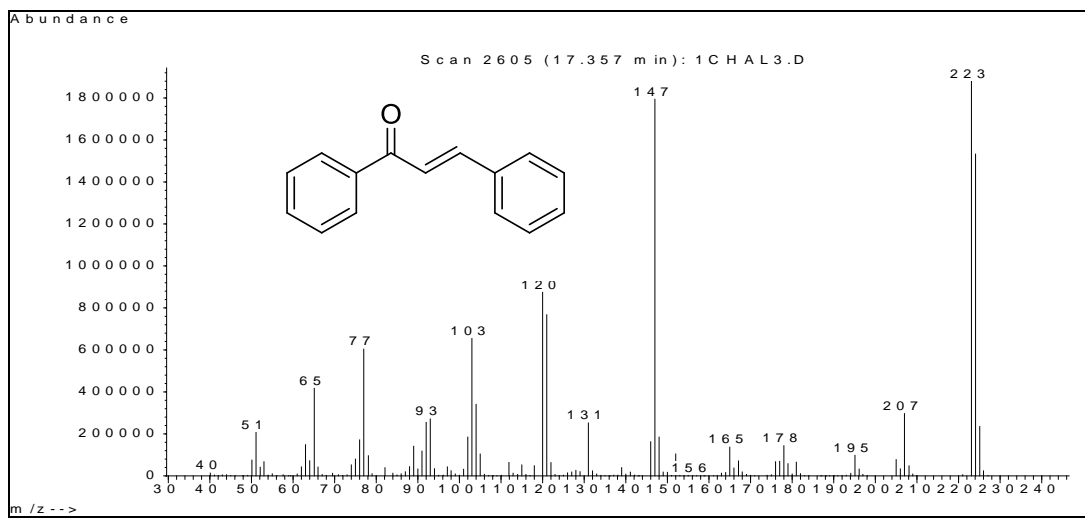
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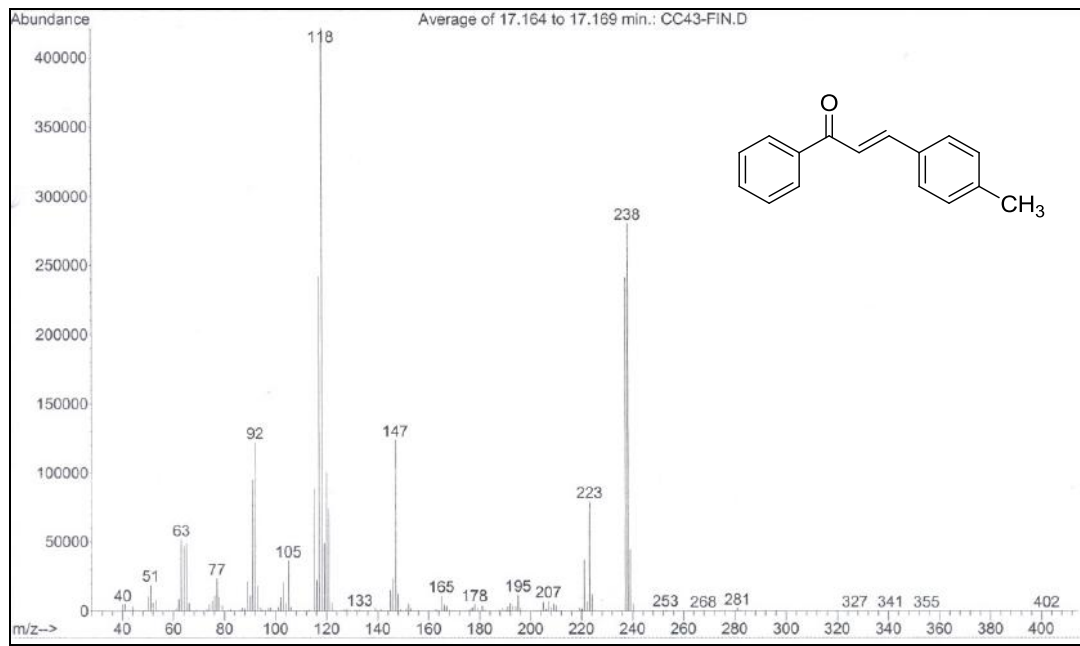
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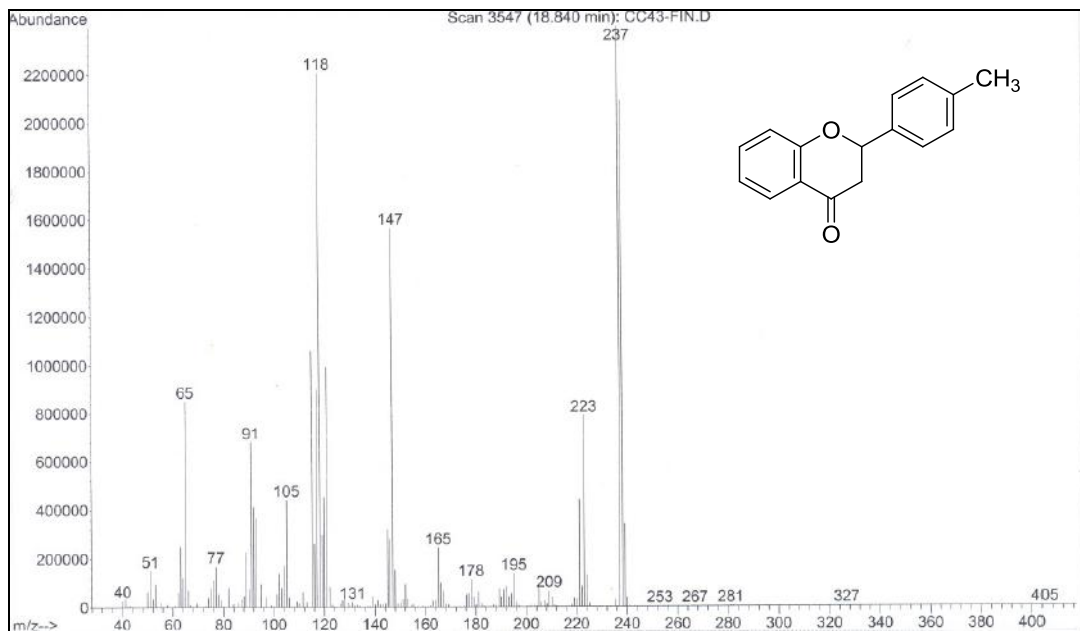
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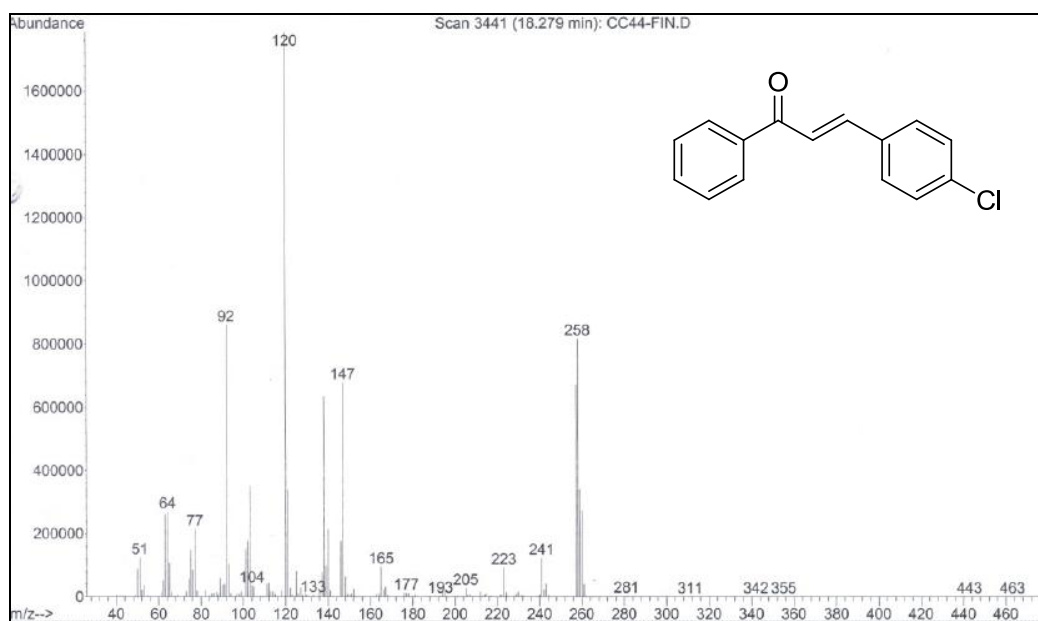
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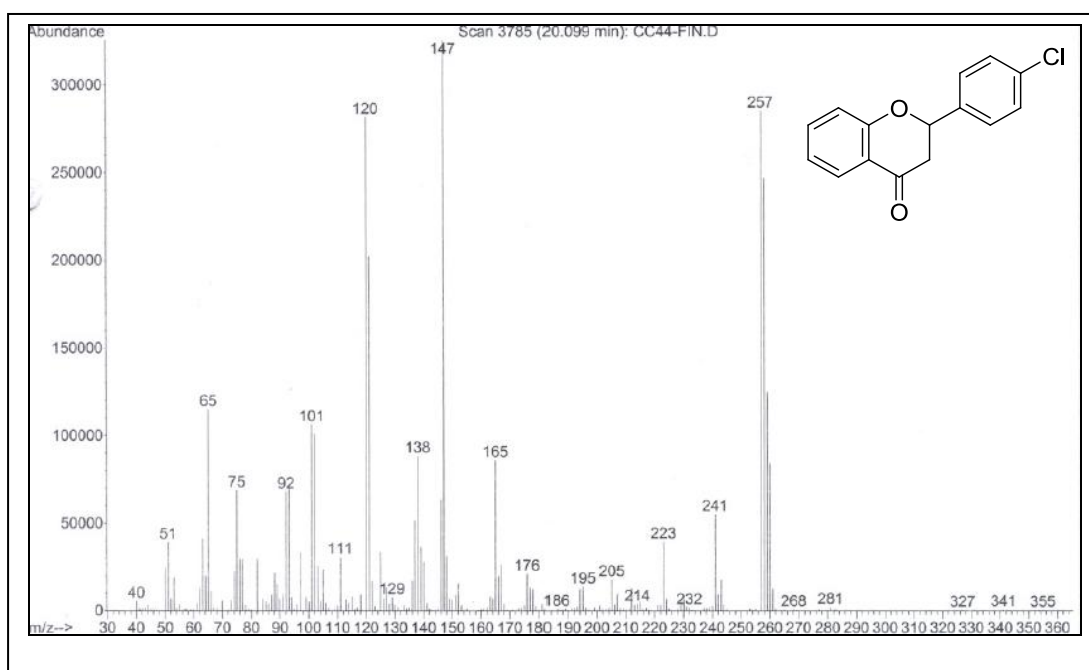
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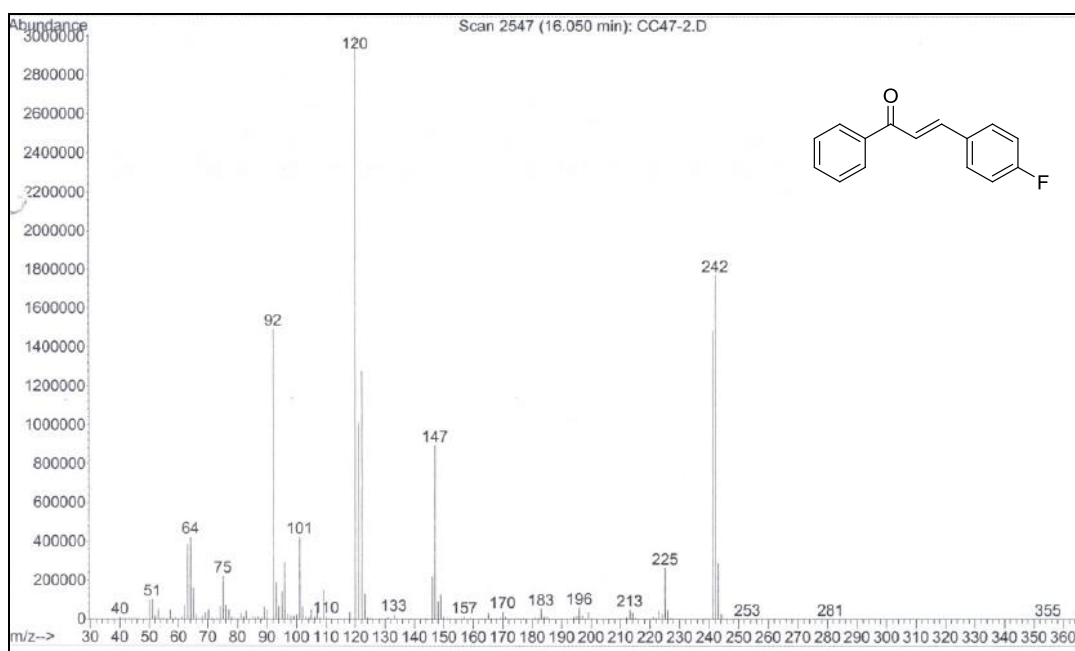
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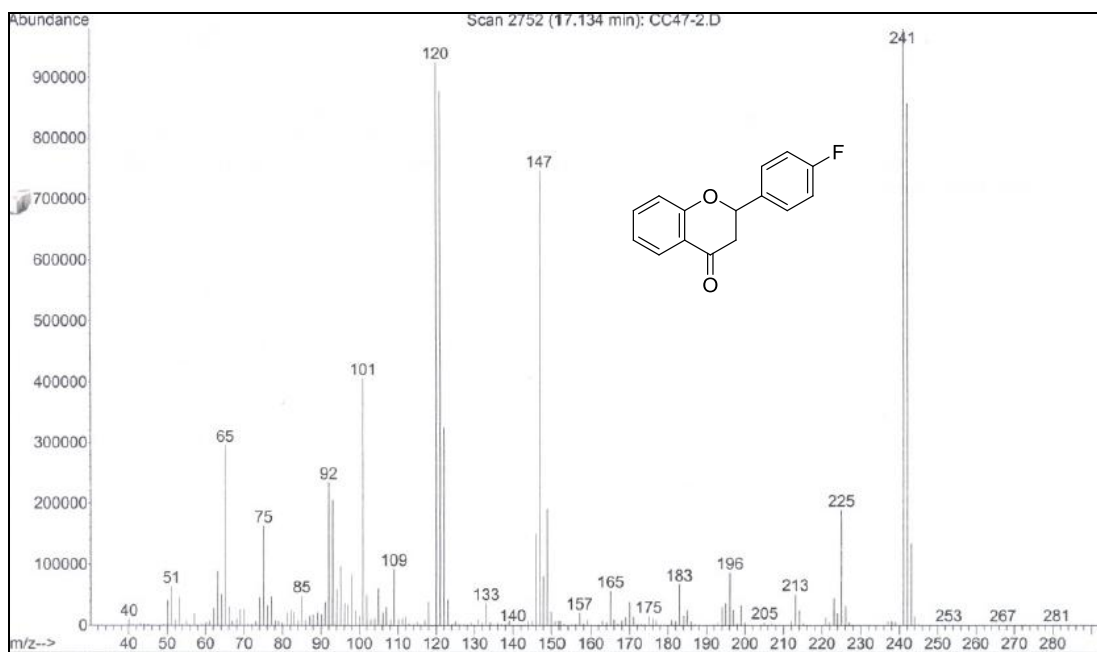
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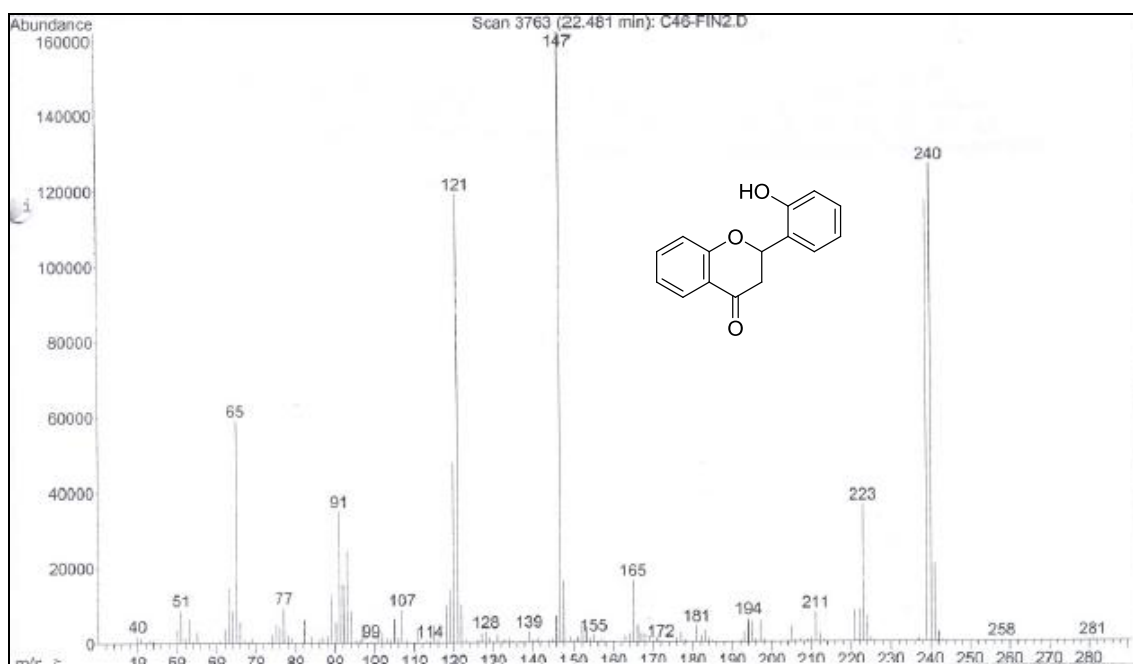
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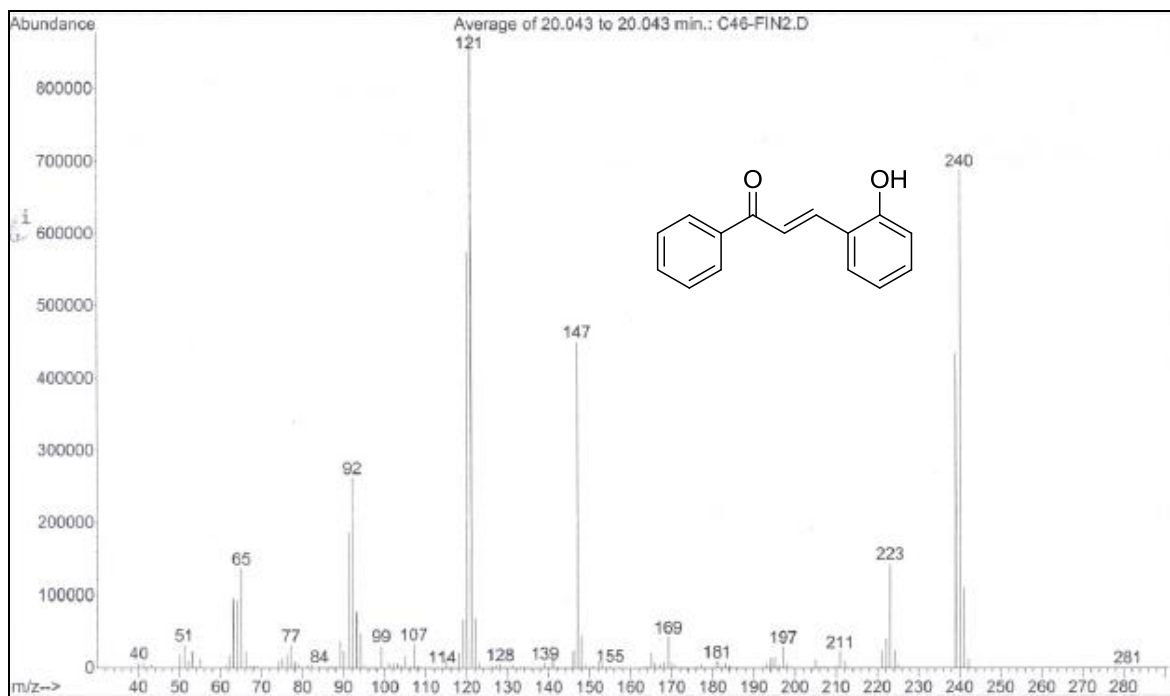
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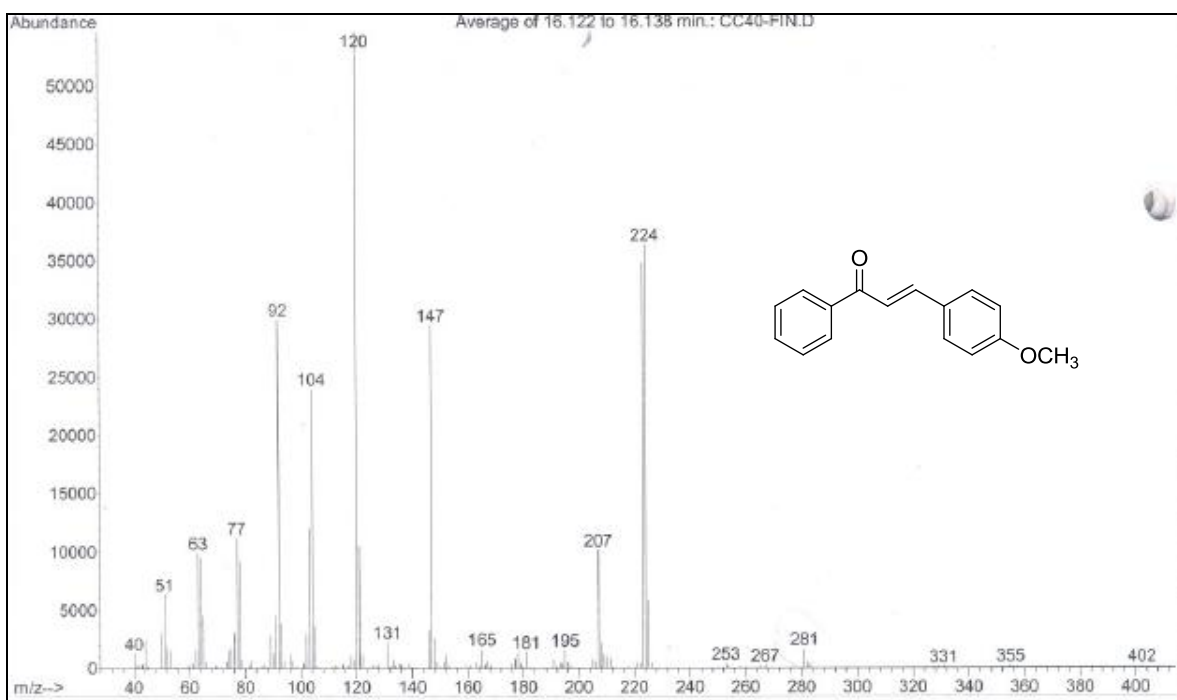
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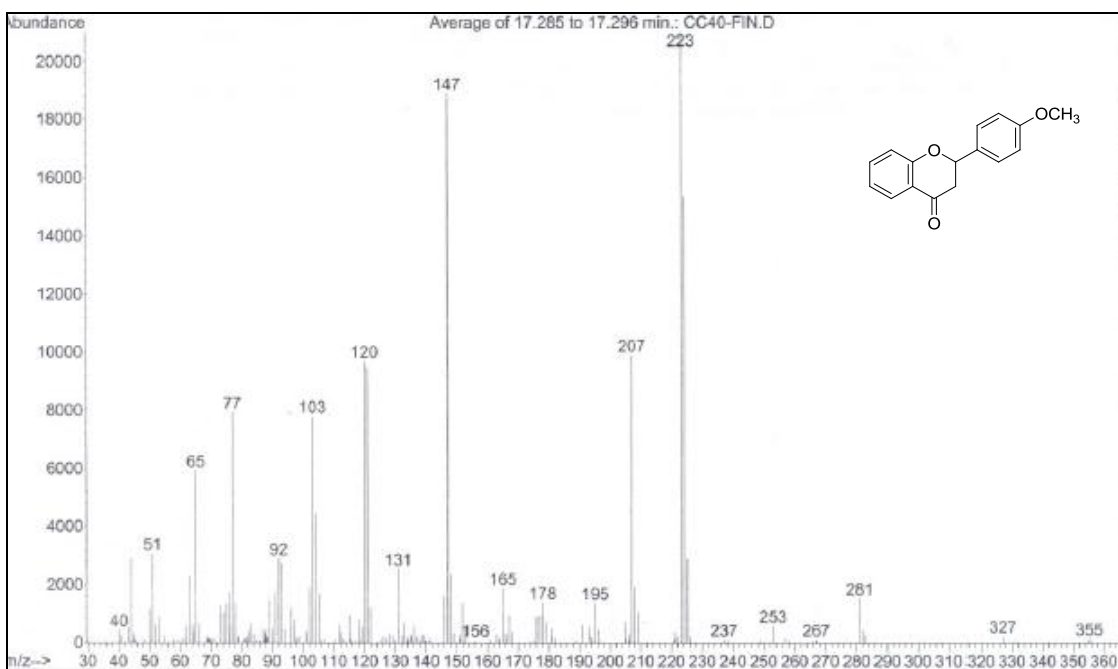
Section C

Dibutyltin oxide catalyzed aminolysis of oxalate to carbamate, oxamate.

and derivatives of imidazolidine trione
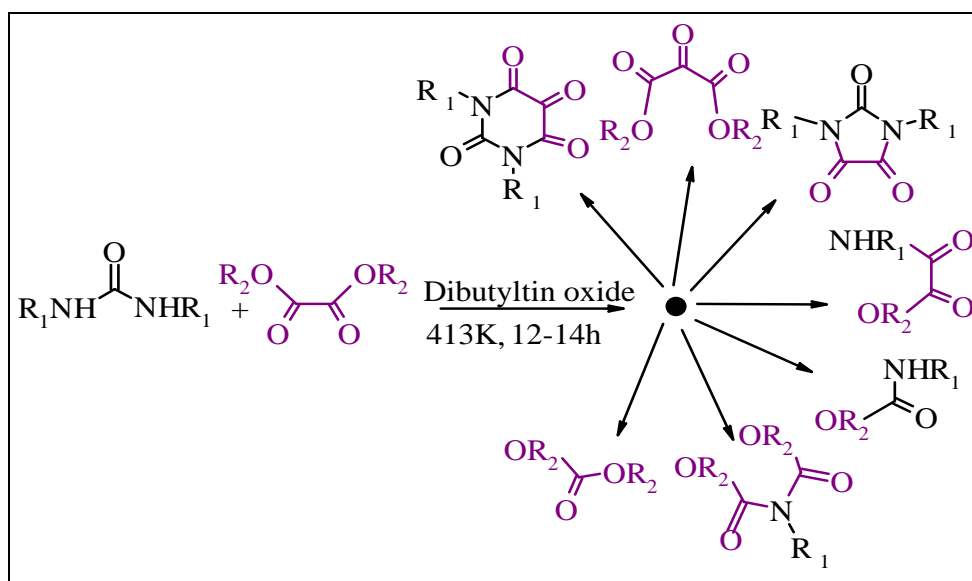
5.1 INTRODUCTION

Organic molecules containing amide (peptide bond) and heterocyclic *N* containing functionality are important in the synthesis of drug intermediates as these organics have some proximity to peptide structure which works as a blueprint for the synthesis of drug molecules.[1] The popular approach of `scaffold hopping' in the discovery of novel drugs[2], requires that varied functionality be present in a single molecule. This is often been achieved by reagent based approach mainly because this approach is convenient and affordable. However, many a times in such an approach, protection and deprotection strategy is required as reagents are having harsh nature which gives rise to unwanted transformations. Instead, a catalytic step can be an alternate solution as it may avoid necessity of protecting/deprotecting step. One such example is in the synthesis of amide from amine which involves insertion of carbonyl functionality in amines which is a key step.

Trans-functionalization is an efficient way to generate organic intermediates considering the fact that value added products can be synthesized using this methodology, for example Shivarkar et al. have earlier shown the efficiency of this protocol wherein carbamates were synthesized with atom economy from substituted ureas and carbonates.[3] The present work is intended to investigate the trans-functionalization reaction between urea and oxalate. This reaction can be viewed as an addition of two reactions, viz. aminolysis of oxalate and alcoholysis of urea. Here oxalate and urea functionality is converted into oxamate and carbamate functionality without generating amine and alcohol usually expected in aminolysis of oxalate[4] and alcoholysis of urea respectively.[5] Formation of oxamate and carbamate by trans-functionalization of substituted urea and oxalate is a simple reaction which has not been probed earlier in detail. This reaction takes place in-situ in two steps; the first step involves trans-functionalization of urea and oxalate forming carbamate and oxamate (Scheme 5.5). In the second step, cyclization of carbamate and oxamate yield 1,3-dimethylimidazolidine-2,4,5-trione with a loss of alcohol. Further reaction of carbamate and oxalate produce oxomalonate and iminodicarbonate with a loss of alcohol when simple urea is used as a substrate (Scheme 5.6). In spite of the fact that this simple reaction can yield versatile products such as carbamate, oxamate and 1,3-dimethylimidazolidine-2,4,5-trione (which

can be viewed as multi functional compounds having Cis-glyoxal, Cis- urea, oxamide, carbonyl, formamide, imide and amide functionalities)[6] from point of view of making organic drug-intermediates, the reaction is however largely overlooked. What is more, urea is an amide and it`s alcoholysis is of particular interest from point of view of protein analysis in analytical biochemistry [7] (The amide bond in urea is extremely unreactive and ~600 years of half life is estimated for it`s nonenzymatic hydrolysis by water [8] and therefore, catalytic alkoxy carbonylation of urea is of great interest particularly to biochemists. [9]

Oxamate functionality has been found to play a vital role in many drugs. e.g. a potent antimalarial drug having oxamate functionality has been reported recently.[10] The drug has been shown to inhibit the activity of plasmodium falciparum lactate dehydrogenase (pfLDH) a key enzyme responsible for metabolizing glucose in malarial parasite. *N*-substituted 3- pyrrolines exhibit neuritogenic activity, are reported to be synthesized from oxamate as one of the starting materials.[11] Oligonucleotides having different functionality can be easily synthesized by functionalizing oligonucleotide with oxamate and carbamate. The highly electrophilic nature of ester carbonyl carbon of methoxyoxalyl moiety of oxamate can interact with strong nucleophiles giving rise to functionalized oligonucleotides.[12]

Carbamates are conventionally prepared from amines employing hazardous reagents such as phosgene/acetyl chloride derivatives.[13] It is evident from the use of phosgenation process in the chemical industry (~2 $\times$ 10^6 tone/year of phosgene worldwide[14]) that in spite of the hazards involved in phosgenation process economy still favors its use. This fact can be justified as phosgene technology is cheaper, simple and convenient hence seemingly over rides the danger of handling phosgene and isocyanates,[15] which is unavoidable in phosgenation of amines. Apparently this quantity of phosgene in chemical industry is low since it is a captive consumption but still it results in significant amount of waste formation (use of 1 kg phosgene gives 1.17 kg of salt waste[16]) and air pollution.

R-NH$_2$ + ClCOCl $\longrightarrow$ R-N $=$ C $=$ O + 2 HCl

R-N $=$ C $=$ O + R'OH $\longrightarrow$ R-NHCOOR'
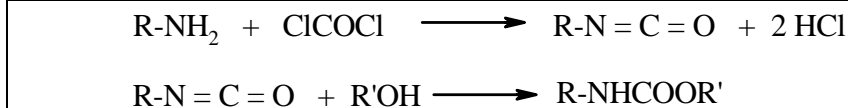
Scheme 5.**1.** Synthesis of carbamtes from amines using phosgene technology

Synthesis of carbamates is also reported by using reagent based chemistry and rearrangements (scheme 5.2.).[17]

1. R-N $=$ C $=$ O + R'OH $\longrightarrow$ R-NHCOOR'

2. R-NH$_2$ + ClCOOR' $\longrightarrow$ R-NHCOOR'

3. ClCN + RCl + FeCl$_3$ $\longrightarrow$ (RN $=$ CCl$_2$)n (FeCl$_3$)$_m$

   (RN $=$ CCl$_2$)n (FeCl$_3$)$_m$+ R'OH $\longrightarrow$ R-NHCOOR'

4. RCONH$_2$ + NaOBr $\xrightarrow{\text{Hoffman}}{\text{rearrangement}}$ R-N $=$ C $=$ O $\xrightarrow{\text{R'OH}}$ R-NHCOOR'

5. RCON$_3$ $\xrightarrow[\text{rearrangement}]{\text{Curtious}}$ R-N $=$ C $=$ O $\xrightarrow{\text{R'OH}}$ R-NHCOOR'
   Pyrolysis

6. RCONHOCOR $\xrightarrow[\text{rearrangement}]{\text{Lossen}}$ R-N $=$ C $=$ O $\xrightarrow{\text{R'OH}}$ R-NHCOOR'
   Base

7. RCOOH + HN$_3$ $\xrightarrow[\text{rearrangement}]{\text{Schmidt}}$ R-N $=$ C $=$ O $\xrightarrow{\text{R'OH}}$ R-NHCOOR'
   H$_2$SO$_4$

8. RNHCOCl$_3$ $\xrightarrow{\text{Na}_2\text{CO}_3}$ R-N $=$ C $=$ O $\xrightarrow{\text{R'OH}}$ R-NHCOOR'

Scheme 5.2. Various routes for carbamate preparation

The routes mentioned above for carbamate synthesis either deals with handling of potentially hazardous chemicals or requires acid and bases in stoichiometric amount

which produces inorganic salts that ends up with aqueous effluent. Recent developments in the preparation of carbamates employ non-toxic reagents and use of novel environmentally friendly methodologies.

Major routes for carbamate synthesis using green chemistry are,

1. Carbonylation of nitro aromatic compounds to carbamates

2. Oxidative carbonylation of amines to carbamates

3. Carboxylation of amines using CO_2

4. Carboxylation of amine using organic carbonates

5. Alcoholysis of urea

The use of carbon monoxide (CO) for reduction of nitrogen-oxygen aromatic bonds was initially reported in 1949 by Buckeley and Ray who converted nitrobenzene in azo benzene.[18] This discovery initiated the research on various reduction processes of the nitroso aromatic linkage assisted by transition metal complexes using CO.[19]Subsequently, in 1967, Hardy and Bennet reported the catalytic generation of isocyanates from nitro compounds using rhodium, palladium or other metal salts in the presence of a Lewis acid promoter.[20] Catalytic systems comprising of a variety of catalyst reported for this reaction typically consists of various transition metal salts, catalyst precursor used in conjunction with various promoters such as ligands or co-catalyst (mostly Lewis acid) or both, Ir or Pt complexes performed as precursors like $PtCl_2(PPh_3)_2/SnCl_4$,[21] carbonyl clusters of rhodium or ruthenium ruthenium complexes of Schiff bases[22] or Pd salts with Keggin-type heteropolyanions $(PdCl_2/HPA)$,[23] were also effective.

Oxidative carbonylation of aromatic amines for the synthesis of carbamates is reported to be effectively carried out using variety of noble metal catalyst (viz. Pd, Pt, Rh, Ir, Ru etc.) and other catalysts and promoters such as iodide ion and α.-benzoinoxim etc. Carbon dioxide mediated carboxylation of amine to carbamate have been reported using various catalyst systems like transition metal complexes of *N,N* dimethyl amide $M(Me_2N)_n$, aluminum porpohyrine, Ruthenium etc.

Alcoholysis of urea is the preferred commercial route to methyl or ethyl carbamate synthesis.[24] Hofmann[24] and later workers studied the preparation of ethyl carbamate by heating urea and ethanol under pressure at 423 K. Higher temperature is necessary for the

optimum dissociation of urea to the reactive intermediates, cynic acid and ammonia, only those alcohols boiling above 413-423 K gave good yields of carbamates.

R = H, alkyl or aryl; R' = alkyl or aryl

Scheme 5.3. Alcoholysis of urea
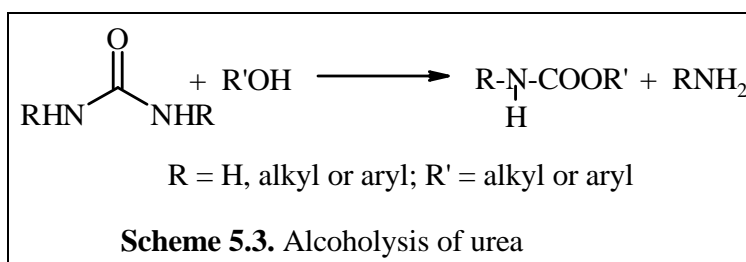
In 1946, Paquin reported the catalytic effect of various metal salts upon the rate of reaction of an alcohol with urea. By using heavy metal salts of weak organic acids, or zinc and cobalt chlorides, alkyl carbamates were obtained in high yields (90 % >) with shorter heating cycles.

There is only scanty information available on alcoholysis of substituted urea and the patented literature in this field mainly discloses the process and yield of carbamate. [25] Ball et al has studied the reaction between aromatic or aliphatic alcohols and urea. The reaction of urea with aliphatic alcohols leads to carbamate formation using tin complexes as catalyst while, aromatic alcohols lead to side product formation such as isocynic acid, which decreases yield of carbamate.[26]

A detailed literature survey of above methods for preparation of carbamates is given in table 5.1.

Table 5.1. Literature on carbamate synthesis								
Sr. No.	Catalytic system	Solvent	Time, min	Temp.^{0}C	Pressure: CO atm	Conv. %	Sel. of carbamate%	Reference
Mono nitro aromatic substrates								
1	Ru$_3$ (CO)$_{12}$-Net$_4$Cl	Toluene –MeOH	300	170	60	100	93	Cenini et al.[27]
2	Ru(PPh$_3$)$_2$(CO)$_3$-Net$_4$Cl	Toluene –MeOH	420	170	60	100	85	Cenini et al.[27]
4	Ru (py)$_3$Cl$_3$/Al$_2$O$_3$-FeCl$_3$	MeOH	300	165	100	99	98	Rode et al.[28]
5	(PPN)$_2$RuRh$_4$(CO)$_{16}$	THF-MeOH	90	170	60	82	66	Ragaini et al.[29]
7	PdO-2Py-FeCl$_3$	EtOH	120	200	120	73	57	Lapidus et al.[28c]
9	(Phen)Pd(OAc)-CuCl$_2$	MeOH	600	200	30	45	100	Halligudi et al[30]
10	Pd(tmphen)$_2$ (PF$_6$)$_2$	EtOH	120	180	40	100	95	Bontempi et al[31]
11	Pd/bipy/Clay-FeCl$_3$-	Toluene –MeOH	330	170	60	98	78	Choudary et

	Py						al.[28d]
12	Pt(PPh$_3$)$_2$Cl$_2$-SnCl$_4$-NEt$_3$	EtOH	240	180	60	97	86	Watanabe et al.[32]

Di nitro aromatic substrates

14	Ru$_3$(CO)$_{12}$-Net$_4$Cl	Toluene –MeOH	420	170	60	100	50	Cenini et al.[27]
15	Pd(tmphen)$_2$(OAc)$_2$-TrMBA	EtOH	120	180	40	100	90	Alessio et al.[33]

Oxidative carbonylation of amines in alcohol to carbamates

$$R\text{-}NH_2 \ + \ CO \ + \ 1/2\ O_2 \ \xrightarrow[\text{R'OH}]{\text{Catalyst}} \ RNHCOOR' \ + \ H_2O$$

Sr. No.	Substrate	Catalyst	Temp., ^{0}C	Pressure: CO : O$_2$, atm	Conv., %	Sel. % (I)	Sel. % (II)	Reference
1	C$_6$H$_5$-NH$_2$; EtOH	Pd / KIO$_4$	160	80 : 6	-	85	-	Ashi Chem.Ind [34a]
3	C$_6$H$_5$-NH$_2$; EtOH	Pd / NaI	160	80 : 6	92	93	1.5	Fukuoka et al [34c]
5	C$_6$H$_5$-NH$_2$; MeOH	PdCl$_2$ / CuCl$_2$/HCl	25	Bubbling	100	99	-	Alper &

Sr. No.	Substrate	Catalyst	Temp.	Ratio	Amine Conv. %	Carbamate Yield %	Reference
							Hartstock[35]
7	C_6H_5-NH_2; EtOH	5%Pd/C / NaI	170	55 : 11	80	100	-	Gupte & Chaudhari [34e]
8	CH_3-NH_2; MeOH	$PdCl_2(PPh_3)_2$/ NaI	170	56 : 5	88	80	20	Kelkar et al.[34f]
9	C_6H_5-NH_2; EtOH	SeO_2 / K_2CO_3/ KI	130	55 : 13	67	80.4	9.5	Kim et al.[36]
12	C_6H_5-NH_2; MeOH	$Au(PPh_3)_2Cl_2$ / PPh_3	200	4 0 : 10	98.5	86	-	Shi & Deng[37]
13	C_6H_5-NH_2; MeOH	$CuCl_2$ / NaI	165	30 : 10	-	43.5	-	Chen et al.[38]
14	C_6H_5-NH_2; MeOH	$Pd(Phen)Cl_2$/$BMImBF_4$	175	45 : 5	99	98		Shi et al.[39]

Carbon dioxide mediated Carboxylation of amine to carbamate

$$RNH_2 + CO_2 + R'\text{-}X \longrightarrow RNHCOOR' + H\text{-}X$$

Sr. No.	Substrate	Catalyst	Time, h	Temp., ^0C	CO_2 Pressure, atm	Amine Conv. %	Carbamate Yield, %	Reference
1	C_6H_5-CH_2-NH_2; allyl bromide	18-crown-6 ether	40	10	1	-	57	Aresta & Quaranta[40]
3	C_6H_5-NH_2; C_6H_5-CH_2-Cl	CyTMG	-	55	5-10	100	90	McGhee et al[41]
5	n-C_4H_9-NH_2; C_6H_5-	MTDB	-	55	5	100	86	McGhee et al

	CH$_2$-Cl							41
9	C$_6$H$_5$-NH$_2$; BuCl	Bu$_4$NBr/ K$_2$CO$_3$	4	100	80	-	75	Yoshida et al[42]
11	Pyrrolidine; BuCl	But$_4$NHSO$_4$/ K$_2$CO$_3$	2	100	80	-	69	Yoshida et al [42a]
13	C$_6$H$_5$-(CH$_2$)$_2$-NH$_2$; C$_6$H$_5$-CH$_2$-Cl	Bu$_4$NI/ Cs$_2$CO$_3$	5	23	Bubbling	-	96	Salvatore et al [42b]
7	C$_6$H$_{11}$-NH$_2$; EtBr	Et$_4$NHCO$_3$	-	25	1	-	90	Inesi et al [42]

Carboxylation of amine to carbamate using organic carbonate

$$RR'NH + R''OCOOR'' \longrightarrow RR'NHCOOR'' + R''OH$$

R, R' = H, alkyl or aryl; R'' = alkyl or aryl

Sr. No.	Substrate	Organic carbonate	Catalyst	Time; h	Temp.^{0}C	Amine Conv. %	CarbamateYield, %	Reference
1	C$_6$H$_5$-NH$_2$	DMC	PbO (red)	1	160	98	97	Fu & Ono[43a]
4	*m*-Cl-C$_6$H$_4$-NH$_2$	DEC	NaH	1.5	25	-	93	Angeles et al[44]
Sr.	Substrate	Organic carbonate	Catalyst	Time;	Temp.^{0}C	Amine	CarbamateYield,	Reference

No.					h		Conv. %	%	
5	$C_6H_{13}-NH_2$	DMC	$Pb(NO_3)_2$	2	120		99	99	Baba et al.[43b]
7	$C_6H_5-NH_2$	DMC	γ-Al_2O_3	48	90		100	95	Vauthey et al.[45]
9	$C_{10}H_{21}-NH_2$	DMC	$scCO_2$	17	130		96	83	Tundo et al.[46]
11	n-$C_4H_9-NH_2$	DMC	$Yb(OTf)_3$	8	80		-	93	Curini et al.[47]
14	$C_6H_5-CH_2-NH_2$	DEC	MCM-41-TBD	24	125		99	98	Carloni et al.[48]
16	$C_6H_{11}-NH_2$	DMC	BMImCl	1	170		100	83	Sima et al.46

Oxamates are conventionally prepared from amines employing hazardous reagents such as oxalylchloride [49] respectively. A method of preparation of oxamate from diisopropyl oxalate has been reported, however, synthesis of this reagent involves costly ruthenium catalyst.[50] *N*-substituted oxamates can be synthesized from *N*-Boc ethyl oxamate via Mitsunobu couplings. Aminolysis of oxalate by amine produce oxamate, e.g. refluxing a mixture of aniline and diethyloxalate in toluene for 45 minutes, oxamates are obtained in 75-90 % yield, however alcohol is produced as a unwanted side product. Less reactive anilines such as fluro, chloro, nitro and cyano anilines however, required ethoxycarbonyl ethanoyl chloride for conversion to oxamate. The catalytic synthesis of oxamates has also been reported in the recent literature. One such route employs Pd(II) catalyzed carbonylation of *N*-methyl amino ethanol, yield morpholinedione.[51] The reaction is feasible under mild conditions with *N*-methyl and butyl amino ethanols only. In an another approach, oxidative alkoxycarbonylation of amine has been shown to yield cyclic oxamate, however linear oxamates are not synthesized by this methodology and costly Pd catalyst is required in stoichiometric amount.[52] One pot cerium based catalytic synthesis by air oxidation of acetoacetamide has also been reported to yield oxamates in over 70% yields. However, the synthesis of catalyst is cumbersome in this case.[53] From above discussion on literature on oxamate synthesis it is clear that this topic is studied inadequately.

Another important product that can be synthesized under certain conditions from urea and oxalate employing the present protocol is 1,3-dimethylimidazolidine-2,4,5-trione. Synthesis of 1,3-dimethylimidazolidine-2,4,5-trione and its derivatives is not studied in specific up till now and reports on this topic are found to be addressed scantily in literature. 1,3-dimethylimidazolidine-2,4,5-trione derivatives are reported to exhibit excellent activity as a drug.[54] Because of their high decomposition temperature, mechanical and thermal resistant properties, 1,3-dimethylimidazolidine-2,4,5-trione and its derivatives find numerous applications in the synthesis of polyester resin polyurethanes, polyacrylates, polymethylacrylates,[55] increase crease proof property of cotton fabrics,[56] and electrically conducting CuS-polyparabanic acid films.[57] [($\acute{\eta}^5C_5H_5$) fe (CO)$_2$] (FP) complex of 1,3-dimethylimidazolidine-2,4,5-trione finds application

as potential metallocarbonyl labelling reagents of proteins.[58] Synthesis of 1,3-dimethylimidazolidine-2,4,5-trione was reported first time by Murray[59] and later by others [59] starting from diethyl oxalate and urea in presence of stoichiometric quantities of sodium methoxide (relative to urea) and requires copious amount of dil HCl to obtained desired acid, these reactions are not atom efficient and generate stoichiometric quantities of salt. Recently Cai [60] has reported synthesis of 1,3-dimethylimidazolidine-2,4,5-trione   from   2-(Dinitromethylene)   4,5 imidazolidinedione and methanol. 1,3-dimethylimidazolidine-2,4,5-trione can be readily formed from hydantoin by oxidation with bromine.[61] A detailed electronic and spectroscopic study of 1,3-dimethylimidazolidine-2,4,5-trione and its derivatives is reported by Larson et al.[62] wherein 1,3-dimethylimidazolidine-2,4,5-trione were prepared by the reaction in anhydrous ether of equimolar quantities of the appropriately N-substituted urea with oxalyl chloride in the presence of sodium carbonate. But these methodologies generates stoichiometric amount of salt or acid waste or uses corrosive oxalyl chloride as substrate.

In view of the literature discussed for imidazolidine trione derivatives, carbamates and oxamates the objective of the present work was to develop, a greener approach for the synthesis of several important amide derivatives (carbamate, oxamate, 1,3-dimethylimidazolidine-2,4,5-trione and iminocarbonate) from urea and oxalate in presence of dibuty tin oxide (DBTO) catalyst.

5.2. EXPERIMENTAL SECTION

5.2.1. MATERIALS

Substituted ureas were synthesized by reported procedure (37). DMO, NMP, tetraglyme, PbO, PbZrO$_3$ were procured from Aldrich USA. DEO, DMF were purchased from s.d. fine. chem. ltd. MgO and DBTO used was purchased from Merck.

5.2.2. GENERAL PROCEDURE FOR SYNTHESIS OF CARBAMATE, OXAMATE AND DERIVATIVES OF IMIDAZOLIDINE TRIONE

5g (34.2 mmoles) of DEO was taken in 2-neck 25ml round bottom flask equipped with reflux condenser and magnetic bar for stirring under argon atmosphere. To this

0.5g (5.68 mmoles) dimethyl urea and 0.2g (0.806 mmoles) of DBTO were added. System was flushed with argon and then immersed in the oil bath preheated to 413K temperature. Internal reaction temperature as well as was oil bath temperature was maintained by temperature controller. Standard reaction was carried out for 12h and time sampling was done at every four hours time intervals. For reaction under autogenous pressure, similar procedure as mentioned for atmospheric pressure condition was followed except instead of glass reactor a 50 cc Par autoclave (USA make) was used with urea charge of 66.7 mmoles, DEO charge of 154.8 mmoles and DBTO charge of 5.64 mmoles were used. Contents of the autoclave were flushed with 50 psig of nitrogen pressure, 2-3 times before starting the reaction under autogenous condition. Liquid phase was quantitatively analyzed on Hewlett Packard 6890 series gas chromatograph equipped with BP10, 30m x 0.32 μm ID capillary column. The products were separated from organic phase by flash chromatography on a 4 g normal phase silica RediSep column employing n-hexane-ethyl acetate as the eluent with gradient programming. Liquid chromatography was performed using CombiFlash Companion, supplied by Teledyne ISCO, USA. The yields of products were based on GC analysis and calculated using stoichiometry Grid tool of ChemDraw Ultra 11 software. Carbamates, oxamates, 1,3-dimethylimidazolidine-2,4,5-trione and imidazolidine trione derivatives reported herein were fully characterized by ^{1}H NMR, ^{13}C NMR, IR, GC–MS (EI, 70 eV) and compared with authentic samples whenever possible (For spectral characterization refer to spectra section). The ^{1}H NMR and ^{13}C NMR spectra in CDCl$_3$ were recorded on a 200 and 500MHz Brucker instrument, respectively. Infrared (IR) spectra were recorded on a Perkin-Elmer system 2000 Infrared spectroscope. Samples for IR spectroscopy were prepared employing a potassium bromide under normal mode. GC-MS was done on Agilent 6890 GC with 5973 N mass selective detector using HP-5 MS capillary column. The synthesized hydrotalcites were characterized by XRD using Rigaku Dmax 2500 diffractometer equipped with graphite monochromatized CuKα radiation (λ= 1.5406 Å) employing a scanning rate of 2°/min in the 2θ range from 10 to 80°.

5.2.3. ANALYTICAL METHODS

Liquid samples were diluted by acetonitrile and analyzed on a Hewlett Packard 6890 Series GC equipped with auto sampler instrument, controlled by the HP Chemstation software, by using an BPX10 (30 m×0.32 mm×0.25 μm) capillary column with FID detector. Identification of products was done using GC-Mass spectrometry of Agilent, USA make, model 6890 GC with 5973N mass selective detector using HP-5 MS capillary column of 30m×0.32mmx 0.25μm dimension.

The standard conditions for GC analysis are given in Table 5.2.

Table 5.2. Standard conditions for GC analysis

Parameters	Conditions
Injector (split) temperature	523 K
Flame ionization detector (FID) temperature	573 K
Column temperature (BP-10 capillary column)	343K–563 K (programmed)
Inlet Pressure (He)	10 psig
Carrier gas (He) pressure	10 psig
Split ratio	50:1

5.3. RESULTS AND DISCUSSION

The reaction considered here is exceptional and falls in the category, aminolysis of oxalate or oxalatolysis of urea by transfunctionalization. The reaction takes place in-situ in two steps; in the first step transfunctionalization of urea and oxalate yield *N –* Aryl (or *N*-Alkyl) carbamate and *N –* Aryl (or *N*-Alkyl) oxamate, in the second step cyclization of carbamate and oxamate yield 1,3-dimethylimidazolidine-2,4,5-trione with loss of alcohol (see scheme 5.4). Diethyl oxalate is well documented as 1,2-dielectrophiles [63] while DBTO is known to be a highly effective intermolecular transesterification catalyst.[64] These types of reactions are similar to aminolysis of carbonates[65] or esters[66] or benzoates[67] and alcoholysis (viz. methanolysis, ethanolysis, butanolysis and so on) of urea[68] commonly encountered in literature.

Scheme 5.4. DBTO catalyzed aminolysis of oxalate
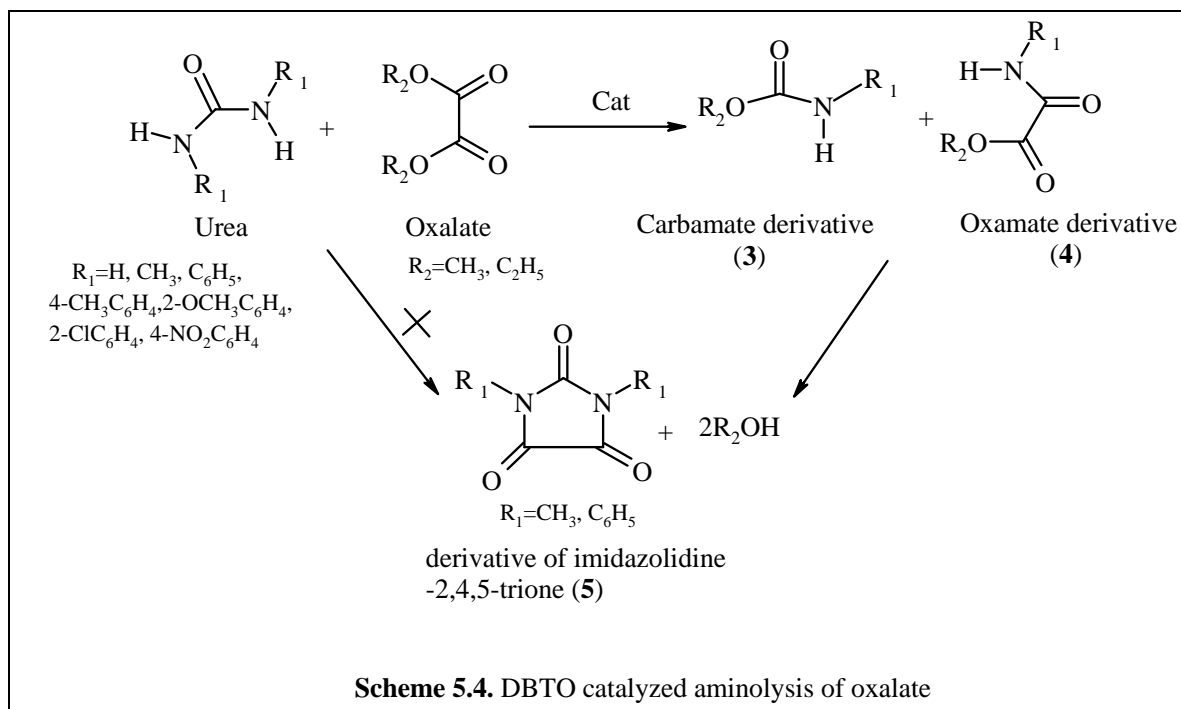
5.3.1. Effect of Process Parameters under pot conditions

5.3.1.1. Catalysts Screening

A non catalytic reaction between *N,N`* dimethyl urea (DMU) and diethyloxalate (DEO) was examined initially for understanding of their interactions. It was observed that at 413K and under non catalytic conditions with oxalate as solvent, ~25% of methyl urea was found to beat the end of 12h reaction time forming 24% yield of *N*-methyl ethyl carbamate, 24.5% yield of *N*-methyl ethyl oxamate and 1.1% yield of 1,3-dimethylimidazolidine-2,4,5-trione according to stoichiometry shown in Scheme 4.3 (See Table 5.3, entry 1). Dimethyl urea is weakly basic in nature (pKa =18.3)[69] and can catalyze base assisted aminolysis of acetate functionality in oxalate giving rise to carbamate and oxamate, which further cyclize in presence of unreacted urea acting as a catalyst forming 1,3-dimethylimidazolidine-2,4,5-trione (also discussed later). Such a base catalyzed aminolysis of carbonate by dimethyl urea has earlier been observed.[70] In presence of solid base catalysts such as MgO, PbO and PbZrO$_3$ (leadzirconate) and silica gel, high to moderate conversions of urea was realized (Table 5.3, entry 2-5, 60-80%) with good selectivity corresponding to carbamate and oxamate were obtained (24-77% yield), with concurrent formation of 1,3-

dimethylimidazolidine-2,4,5-trione (~ 5% yield). Basic catalyst, dibutyl tin oxide (DBTO) was found to give excellent yield of 1,3-dimethylimidazolidine-2,4,5-trione (See Table 5.3, entry 6, ~90%) with small amount of carbamate and oxamate (~ 9% yield) remaining unconverted at this stage. Time sampling of DBTO catalyzed reaction revealed that carbamate and oxamate are formed as intermediates and their condensation give rise to 1,3-dimethylimidazolidine-2,4,5-trione with elimination of alcohol. It also eliminates the possibility of urea and oxalate condensation directly giving rise to1,3-dimethylimidazolidine-2,4,5-trione (See Scheme 5.5). Tin(IV) compounds have often been used as catalysts in esterifications and transesterifications reactions in organic synthesis.[71] Tin has ability to easily form hybridisation orbital with ligands, and making tin centre Lewis acidic depending on the electronegative nature of ligands. Generally, the acidity of tin in organotin compounds is not enough to catalyze organic reactions of general interest, however, the acidity of tin can be increased by attaching electron withdrawing groups on tin.[72]DBTO catalyst in this case show amphoteric nature[73] due to the presence of butyl groups on tin and has been known to react with methanol forming methoxy compound.[74] The amphoteric nature of DBTO seems to be playing important role in activating DEO and also in cyclization of carbamate and oxamate producing 1,3-dimethylimidazolidine-2,4,5-trione with elimination of ethanol. Next, Mg-Al and Zn-Al hydrotalcites known to be good condensation reaction catalysts were examined for their activity for the reaction and it was observed that excellent yields of carbamate and oxamate were realized (See Table 5.5 entry 7 and 8; ~ 97 % yield) with only ~ 2.8% yield of1,3-dimethylimidazolidine-2,4,5-trione, however, Mg-Al hydrotalcite was found to be much more active compared to Zn-Al. The presence of Mg^{2+} or Zn^{2+} cations behave as Lewis acid site and O^{2-} Lewis base site forming an acid-base pairs in hydrotalcites and are responsible for excellent activity obtained in this case. Thus screening of catalysts shows that Lewis acid/base sites in hydrotalcite favor carbamate and oxamate formation, while moderately basic DBTO catalyze further condensation of carbamate and oxamate to1,3-dimethylimidazolidine-2,4,5-trione. Thus, depending on the choice of catalyst, both carbamate and oxamate or imidazolidine trione derivatives can be selectively synthesized, however, the exact role of catalyst in

selectivity behavior is not known and hence the objective of this work is also to understand the role of catalyst in aminolysis of oxalate.

Table 5.3. Catalyst Screening[a]

Entry	Catalyst	Urea Conversion [b] (%)	Yield [b] (%)		
			(3b)	**(4b)**	**(5b)**
1	nil	25	24	24.5	1.1
2	MgO	83	77.4	77.2	5.4
3	PbO	66	59	58	7
4	PbZrO3	48	43.2	43.5	4.3
5	WR Grace silica	63	59.5	60	2.7
6	DBTO	100	9	9.5	90
7	Mg-Al hydrotalcite (Mg/Al =3)	100[c]	97.1	97	2.8
8	Zn-Al hydrotalcite (Zn/Al =3)	100[d]	96.9	97	2.8

[a]**Reaction conditions**: DMU: 5.68 mmol; DEO: 34.2 mmol; catalyst: 0.806 mmol; Time: 14h; solvent: DEO, 10ml; temperature: 413K.

[b] Conversion and yield based on GC analysis by comparing with isolated standards of carbamates and oxamates.

[c] Mg-Al hydrotalcite 220mg; time: 4h

[d] Zn-Al hydrotalcite 220mg; time: 8h

5.3.1.2. Temperature

Reaction temperature was found to have a pronounced effect on the activity of the catalyst and selectivity of products and these results are shown in Table 5.4. Interestingly, increase in temperature from 403 to 413K increased the yield of 1,3-dimethylimidazolidine-2,4,5-trione, due to increased condensation of intermediate products viz. carbamate and oxamate to 1,3-dimethylimidazolidine-2,4,5-trione (entry 2). However, further increase in temperature from 403 to 423 K increase the yield of intermediate (carbamate and oxamate, entry 3) and decrease the formation of 1,3-dimethylimidazolidine-2,4,5-trione presumably due to deactivation of acidic sites of

tin by oxalate at higher temperature rendering the catalyst inactive towards cyclization of carbamate and oxamate (also discussed under solvent screening).

Table 5.4. Temperature effect[a]					
Entry	Temperature	Urea Conversion [b]	Yield [b] (%)		
	(K)	(%)	**(3**b)	**(4**b)	**(5**b)
1	403	60	38	40	20
2	413	100	9	9.5	90
3	423	100	88	89	10
[a]**Reaction conditions:** DMU: 5.68 mmol; DEO: 34.2 mmol; DBTO: 0.806 mmol; Time: 14h; Temperature: 413K.					
[b] Conversion and yield based on GC analysis of reactants and products.					

5.3.1.3. Solvent Screening

Polar solvents such as tetra-glyme, *N*-methyl pyrrolidin (NMP) and dimethyl formamide (DMF) were screened. Reactions were also run in absence of catalyst using DMF as solvents to check their catalytic activity arising from their polar and basic nature. Table 5.5; represent the results of solvent screening experiments. Activity of DBTO as catalyst was found to be highest in DEO, which was used as solvent and as one of the reactants in this case (Table 5.5, entry 1). The other solvents used are arranged in the decreasing order of DBTO activity and follows the sequence DMF>NMP>Tetra-glyme (Table 5.5, entry 2-4). In absence of DBTO, DMF seems to assist methyl urea in catalysis, as can be seen by 58% (Table 5.5, entry 5) conversion of urea as against only 25% when DEO is used as solvent (Table 5.3, entry 1). The non catalytic reaction was found to be selective towards carbamate and oxamate. An important observation made was that, DBTO produce selectively 1,3-dimethylimidazolidine-2,4,5-trione when DEO is used as a solvent, while when polar solvents are used, 1,3-dimethylimidazolidine-2,4,5-trione is almost absent and selectively carbamate and oxamate are obtained (Table 5.5, entry 2-4). Thus, it may be reasoned that acidic tin sites of DBTO might be responsible for cyclization

reaction of carbamate and oxamate to 1,3-dimethylimidazolidine-2,4,5-trione, which might be deactivated by the basic nature of polar solvents. And further, acidic sites of DBTO viz. tin seem to be playing a vital role in 1,3-dimethylimidazolidine-2,4,5-trione synthesis along with basic sites. This probably explains, why at higher temperature (~ 423K), 1,3-dimethylimidazolidine-2,4,5-trione yields are decreased (See also section on temperature effect).

Table 5.5. Solvent effect[a]

Entry	Solvent	Urea Conversion [b] (%)	Yield [b] (%)		
			(**3**b)	(**4**b)	(**5**b)
1	DEO	100	2.7	3.2	94.1
2	DMF	75.5	74	74	1
3	NMP	67	64	66	1
4	Tetraglyme	48.5	44	44.6	3
5[c]	DEO	26	24	24.5	1.1
6[c]	DMF	58	55.3	54	2.5

[a]Reaction conditions: DMU: 5.68 mmol; DEO: 34.2 mmol; DBTO: 0.806 mmol; Time: 14h; solvent: 10ml; Temperature: 413K.

[b] Conversion and yield based on GC analysis of reactants and products.

[c]In the absence of DBTO.

5.3.1.4. Catalyst loading

Catalyst loading experiments were carried out to understand the role of DBTO as catalyst compared to non catalytic reaction. Figure 5.1 depicts the time-conversion profiles of dimethyl urea conversion for various loadings of DBTO and Figure 5.2 represents the effect of DBTO loading on urea conversion (activity) at contact times of 2h. Both these plots show that noncatalytic reaction is very slow compared to catalytic one, and contribute significantly only at higher reaction times (>12h, Figure 5.1). These figures show that conversion of urea is highly sensitive to DBTO loading, a higher catalyst loading (~1.6 mmol) is necessary for achieving complete conversion of urea in reasonable time (~2 h). Similar results were earlier obtained for dimethyl

carbonate synthesis from carbamate using $Bu_2Sn(OMe)_2$.[75] These researchers showed that a catalyst loading of 7.5 mmol significantly enhances the rate of reaction and reaction which otherwise requires 12h for completion is almost finishes in 2h. In the present investigation visual observations indicated that at higher loading (> 0.45 mmole of DBTO) certain amount of DBTO always remains insoluble in reaction medium and still dependency of DBTO loading on urea conversion is observed which indicate that the reaction is taking place with insoluble DBTO as well. A truly homogeneous nature of catalyst would have resulted in tapering of urea conversion beyond the saturation point of DBTO solubility in reaction medium, and since catalyst activity increases linearly with loading proves that partly the heterogeneous behavior of DBTO is also responsible for catalyst activity in this case.[76] It may be noted here that relatively high loading of DBTO is required to obtain complete conversion when contact time is low (~2h, Figure 5.1).
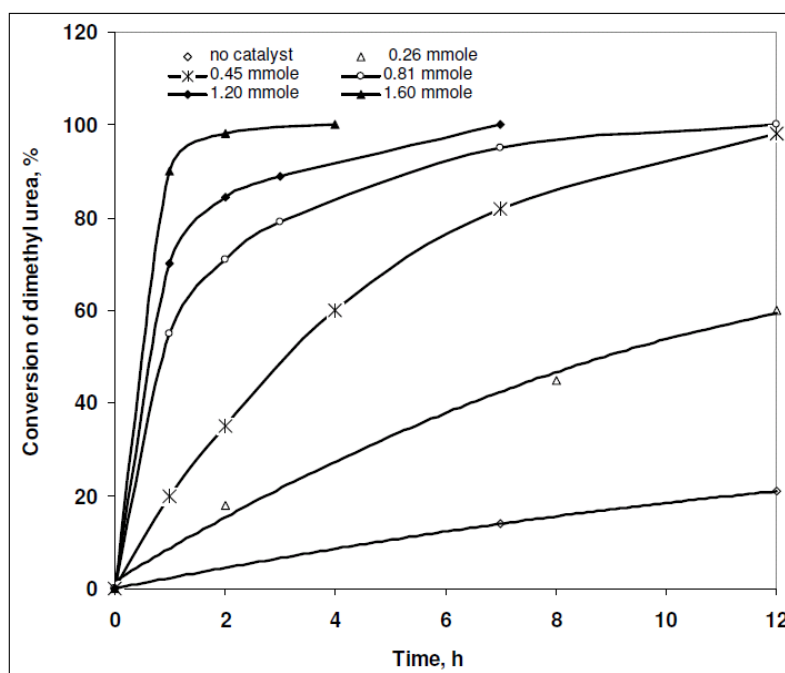
Figure 5.1. Effect of DBTO loading on catalyst activity.

Reaction conditions: DMU: 5.68 mmol; DEO: 34.2 mmol; Time: 14h;Temperature: 413K.
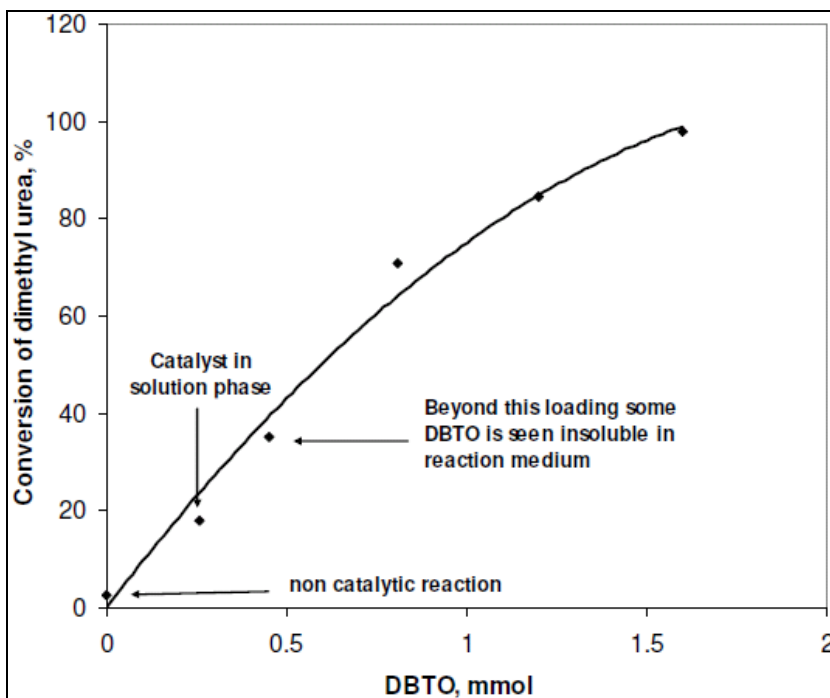
Figure 5.2. Effect of DBTO loading on urea conversion at contact times of 2h.

Reaction conditions: DMU: 5.68 mmol; DEO: 34.2 mmol; Time: 2h; Temperature: 413K

5.3.1.5. Reactivity of urea and oxalate

The reaction between urea and oxalate giving rise to carbamate and oxamate is a complex one as both aminolysis and alcoholysis of ester (or oxalate) and urea respectively is taking place at the same time in a single molecule. The reactivity pattern of urea and oxalate can be understood if one realizes the nature of two separate reactions viz, aminolysis and alcoholysis (as mentioned earlier) which are well documented in literature. The knowledge on reactivity pattern of amine and ester as well as urea and alcohol is expected to serve as a guide line for understanding of reaction under consideration. The aminolysis of ester and carbonate has been investigated in great details due to their relevance to chemistry and biochemistry.[77] The aminolysis of carbonate has been shown to take place via two routes, one with formation of tetrahedral intermediate which is referred to as, `stepwise mechanism', and one without the formation of intermediate termed as, `concerted mechanism'.[78] It has been shown that the possibility of mechanism taking path via concerted route is

highest when one deals with aminolysis catalyzed by very weak base as catalyst. In such a case an extremely unstable intermediate is formed (life time $\sim 10^{-10}$s) and for all practical purposes it ceased to exist.[79] While in stepwise mechanism, formation of intermediate or it`s breakdown will control the rate of reaction depending on the pKa value of attacking amine or leaving group of substrate (-OR or -OAr in ester and carbonate). Usually, for any step to be controlling (i.e. formation of intermediate or breakdown of it) difference in pKa of 4-5 pKa units is necessary between attacking amine and leaving group of substrate.[80] It follows that; nucleophilic attack of amine would be accelerated by an electron donating substituent and retarded by an electron withdrawing one on attacking amine. Similarly, an electron withdrawing nature of substituent on acyl group of ester would retard leaving group departure from addition intermediate and electron donating nature would enhance leaving group departure, thus accelerating the reaction.[81] However, the final reactivity will depend on the difference in the pKa values of attacking amine as mentioned earlier. The information on reactivity of ureas and alcohols during alcoholysis of urea is scanty, the published information shows that, alcoholysis of substituted urea is accelerated by electron-donating group on alcohol and slowed by electronwithdrawing groups, provided that hindrance factor is not coming into play. On the other hand, electron donating substituents on phenyl urea increase reactivity of urea, while decreased by electron-attracting substituents on aryl group.[82]

5.3.1.6. Substrate effect

The reactivity pattern of aliphatic and aromatic urea towards aminolysis of oxalate under pot conditions is investigated and the results are presented in Table 5.6. Aliphatic urea such as simple urea and *N*-methyl urea showed completely different reactivity pattern both under pot conditions and under autogenous pressure (discussed later). The results are presented in Table 5.6 (the first entry under each substrate heading represent the result obtained at 2h contact time). It was observed that, simple urea as substrate give rise to diethyl iminodicarbonate (~ 15 wt. % yield, Table 5.6 entry 1, see foot note in Table 5.6), along with expected carbamate and oxamate (~84 yield). The plausible formation iminodicarbonate is shown in box of scheme 5.6, and

the key step in this scheme is the catalytic decarbonylation DEO by DBTO to diethyl carbonate and CO. In order to confirm this step (See Step Ib in Scheme 5.5) the reaction was monitored for liberation of CO, which was qualitatively detected by exposing the gas phase to $PdCl_2$ soaked strip, which turned black indicating the CO in gas phase. The scheme shows diethyl carbonate (DEC) to react with urea according to a known route to yield ethyl carbamate[83] which in turn react with DEC giving rise to diethyl iminodicarbonate (Scheme 5.5, compound 6). The data shows that, methyl urea is more reactive as compared to simple urea (Table 5.6, entry 1 & 2), while for aromatic urea, it was found that, electron donating substituents enhances the reactivity of diphenyl urea, while electron withdrawing substituents reduce its reactivity. *o*-chloro diphenyl urea giving rise to N^1,N^2-bis(2- chlorophenyl)oxalamide (10) as a side product (~5%) along with expected carbamate and oxamate (entry 6). *p*-nitro diphenyl urea was found to be extremely unreactive towards aminolysis of oxalate due to the electron withdrawing nature of *p-NO$_2$*, which reduces the nucleophilicity of attacking urea. As expected dimethyl oxalate is less reactive compared to diethyl oxalate towards aminolysis by methyl urea (entry 2 and 8), due to poor leaving group ability of OCH_3 compared to OC_2H_5. Further condensation of carbamate and oxamate to 1,3-dimethylimidazolidine-2,4,5-trione is facilitated by higher basicity of -OC_2H_5 compared to -OCH_3. Thus, carboxylation of methyl urea by diethyl oxalate results in almost quantitative formation of 1,3-dimethylimidazolidine-2,4,5-trione (See entry 2 and 8) compared to dimethyl oxalate. The reactivity pattern of aromatic carbamate and oxamate towards condensation show that, substituents on amines have pronounced hindrance effect, which decreases the reactivity towards condensation. Thus, condensation of phenyl carbamate and phenyl oxamate yields ~ 68 % 1,3-diphenylimidazolidine-2,4,5-trione (entry 3), while substituted derivative of aromatic carbamate and oxamate were found completely unreactive towards condensation reaction (entry 4-7).

Table 5.6. Substrate effect[a]

Sr. No.	Substrate	Urea Conversion[b] (%)	Yield[b] (%) (3)	(4)	(5)
1	H₂N—C(=O)—NH₂	65 / 100	63.5 / 84.3; 80* (3a)	63 / 84; 80* (4a)	00[c]
2	CH₃NH—C(=O)—NHCH₃	80 / 100	2.8 / 9 (3b)	2.5 / 9.5 (4b)	77 / 90; 85* (5b)
3	PhNH—C(=O)—NHPh	55 / 100	30.8 / 31.9 (3c)	30 / 32 (4c)	24 / 68;63* (5c)
4	(4-Me-C₆H₄)NH—C(=O)—NH(C₆H₄-4-Me)	80 / 100	79 / 99.5;95* (3d)	79.5 / 99;93* (4d)	00
5	(2-OMe-C₆H₄)NH—C(=O)—NH(C₆H₄-2-OMe)	71 / 100	69 / 99.2;90* (3e)	70 / 99;94* (4e)	00
6	(2-Cl-C₆H₄)NH—C(=O)—NH(C₆H₄-2-Cl)	38 / 80	36 / 74.5; 70* (3f)	36 / 74;69* (4f)	00[d]
7	(4-O₂N-C₆H₄)NH—C(=O)—NH(C₆H₄-4-NO₂)	0	0	0	0
8	CH₃O—C(=O)—C(=O)—OCH₃	60[f] / 100	47 / 77; 72* (3i)	48 / 77; 73* (4f)	12 / 22; 18* (5b)

[a]**Reaction conditions:** Urea:5.68 mmol; DEO:34.2 mmol; DBTO:0.806 mmol; Time:14h; solvent: 10ml; Temperature: 413K. [b] Conversion and yield based on GC analysis; yields are based on urea conversions. The first entry shows conversion for 2h reaction time. [c]~ 15% yield of $H_5C_2OCONHOCOC_2H_5$(diethyl iminodicarbonate (**6**) as a side product was realised in this case. [d]~ 5% yield of $ClC_6H_4NHCOCONHC_6H_4Cl$ (N^1,N^2-bis(2-chlorophenyl) oxalamide (**10**) as a side product was detected. [e] Dimethyl urea : 5.68 mmoles and dimethyl oxalate:34.2 mmoles as reactants. [f]Conversion of methyl urea; * indicates isolated yield.

5.4. Reaction under autoclave conditions

The reaction between urea and oxalate was explored under autogenous pressure conditions in presence of DBTO as catalyst. Initially simple urea and diethyl oxalate were made to react in presence of catalytic amount of DBTO at 413K and for 12h. The GC and GC-MS analysis of reaction mixture indicated the presence of ethanol, diethyl oxomalonate, diethyl carbonate, alloxan and diethyl iminodicarbonate (Table5.7, entry 1 and for spectral analysis of compounds refer to supplementary information provided separately) along with ethyl carbamate and ethyl oxamate. It can be seen from Table 5.7 (entry 1), that appreciable amount of ethyl carbamate and ethanol is produced in this reaction as compared to the same reaction under pot conditions (See Table 5.6, entry 1). The plausible path way for the formation of four additional products (viz. diethyl carbonate, diethyl oxomalonate, alloxan and diethyl iminodicarbonate) along with usual carbamate and oxamate is depicted in scheme 5.5 (the box shows reaction taking place under pot in addition to autogenous condition).

Scheme 5.5. DBTO catalyszed urea and oxalate reaction under autogeneous pressure
the box shows the reaction taking place also under pot condition.
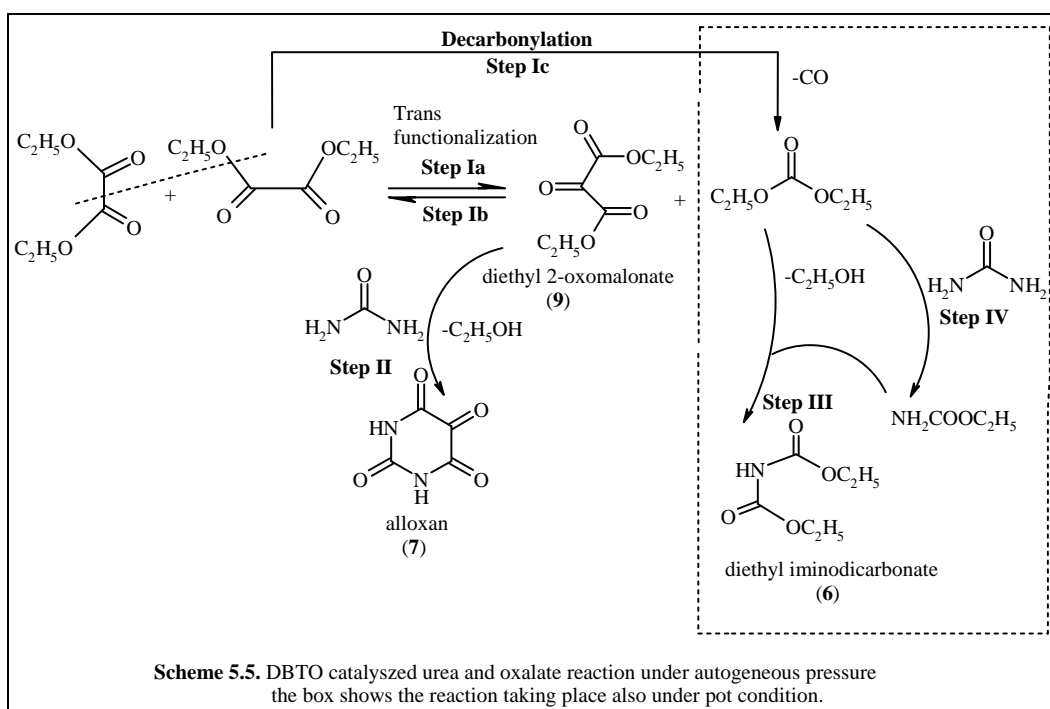
It is shown in this scheme that, intermolecular transfunctionalization of DEO results in diethyl 2-oxomalonate and diethyl carbonate formation (See step Ia, Scheme 5.5).

We have not been able to find any report on this reaction and hence carried out a separate reaction to confirm the feasibility. It was observed that in presence of DBTO as catalyst and under autogenous pressure (See Table 5.7, entry 2 for details) small quantities (~5%) of diethyl 2-oxomalonate was indeed detected along with DEC, while ethanol was formed as the major product. DEC is also formed by decarbonylation of DEO (Step Ib, Scheme 5.5). The formation of CO under autogenous condition has been confirmed by PdCl2 test described in earlier section. At this stage it is interesting to note that dialkyl carbonate can be produced from dialkyl oxalate via energy intensive decarbonylation step. Usually, expensive Pd catalyst [84] or highly reactive and unstable phosphonium salts have been employed for decarbonylation of DEO to DEC. [85]We believed that, simple urea causes aminolysis of diethyl 2-oxomalonate followed by condensation to yield alloxan (~ 2%, See Table 5.7, entry 1 and Step II in Scheme 5.5). The other reaction between diethyl carbonate and urea to yield carbamate is known (Step IV), and accordingly more ethyl carbamate is produced, which seems to be the reason for formation of substantial quantities of ethyl carbamate in this case. It is shown that aminolysis of DEC by ethyl carbamate produce diethyl iminodicarbonate (**6**, See Step III, Scheme 5.5). This reaction is also unknown in literature. It may be noted here that diethyliminodicarbonate is formed in pot as well as under autoclave conditions, however, since under pot conditions either diethyl 2-oxomalonate or alloxan are not detected, we presume that diethyl carbonate (which is the precursor to diethyl iminodocarbonate formation) is produced by two different routes (step 1a and 1b) as shown in Scheme 5.5.
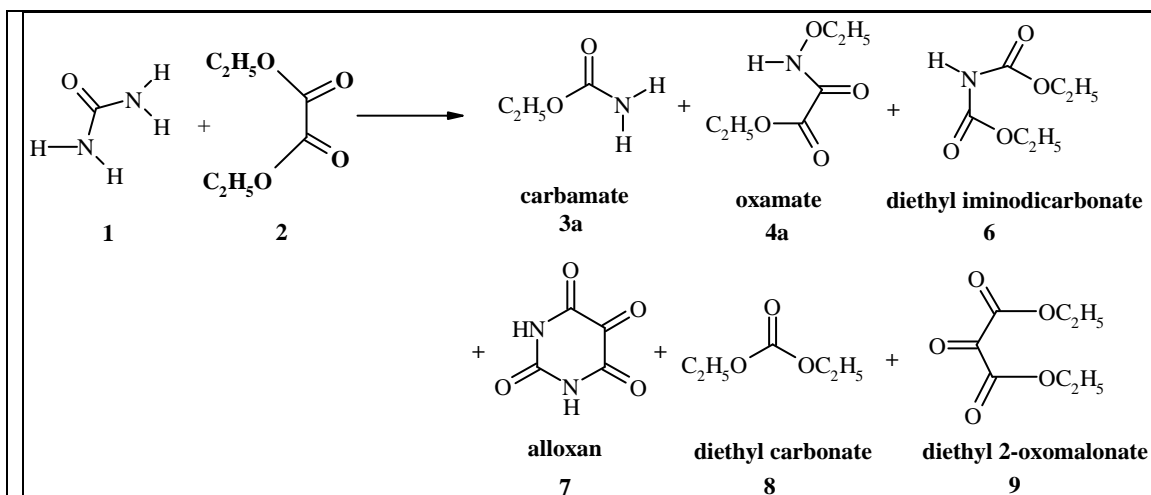
Table 5.7. Urea and oxalate reaction under autogenous pressure

Sr. No.	Substrate		Urea conversion (%)	Product, Yield[a] (%)					
	Urea 1	Oxalate 2		3	4	6	7	8	9
1	H	C_2H_5	100	60	30	2.5	2	~3	2.5
2	-	C_2H_5	-	-	-	-	-	5	5

Reaction conditions: Urea: 66.7 mmoles, DEO: 154.8 mmoles, DBTO: 5.64 mmoles, Time: 14h, Temp : 413K, autogenous pressure.

[a] Conversions and yields were calculated from gas chromatography analysis (for details see supporting information), ethanol is also formed ~ 24 % yield but is excluded from percentile calculations for the sake of convenience.

5.5. Mechanism

The reaction between N,N` dimethyl urea and diethyl oxalate to carbamate and oxamate shows non catalytic as well as catalytic behavior. The uncatalyzed reaction gives urea conversion up-to 25 % with ~24% yield of carbamate and oxamate and ~ 1% yield of 1,3-dimethylimidazolidine-2,4,5-trione in 12h (discussed earlier). This result indicates that, milder basicity of urea might be responsible for the uncatalyzed reaction, although it is not efficient as uncatalyzed reaction was found to be quite sluggish. (~2% conversion of urea in 2h, as against 100% with DBTO, See Figure 4.2). One of the reasons why dimethyl urea does not work as an efficient aminolysis catalyst for oxalate lie in the fact that, dimethyl urea can be considered as having

intermediate softness between harder methylamine and softer diphenylurea, while oxalate posses hard carbonyl carbon centre, making methyl urea as a poor nucleophile according to HSAB concept.[86] However, presence of mild basic catalyst such as DBTO is expected to increase the hardness of methyl urea, facilitating the nucleophilic attack on harder carbon of carbonyl in accordance with HSAB theory. The DBTO catalyst can be considered as having Lewis acidic Sn centers and oxygen which represent hard basicity centers.[87] And accordingly DBTO is expected to activate oxalate ester via hard-hard interaction between tin and alkoxy oxygen of oxalate as well as between oxygen of DBTO and carbonyl carbon of oxalate as shown in scheme 5.6. The activated oxalate is thus more prone to be attacked by urea giving rise to carbamate and oxamate as shown in scheme 5.7. Conversely, it can be argued that, urea can also be perturbed by mild acidic nature of Sn in DBTO and thus can react with activated oxalate via a lower energy pathway to produce products viz. carbamate and oxamate.

Scheme 5.6. Hard-hard interaction of DBTO and oxalate
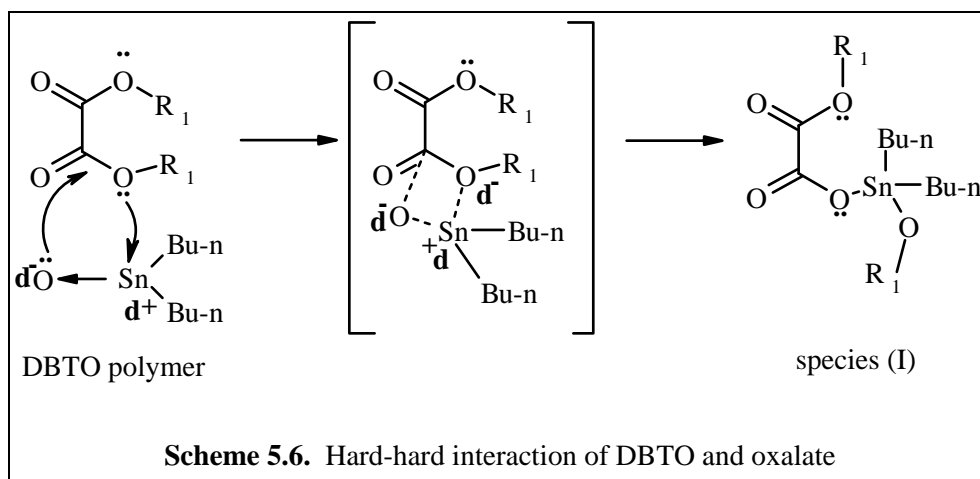
The activation of urea and diethyl oxalate by DBTO was examined in order to understand the role of catalyst. In order to check the activation of urea and DEO by DBTO, urea and DEO were made to react with DBTO separately under otherwise similar experimental conditions (i.e. 413K and 12h, See experimental for details). The recovered DBTO was washed off for excess reactants (or solvents) and recovered solid was examined by IR spectroscopy for any change in DBTO structure. Treatment with urea leaves DBTO unchanged while DEO treated DBTO shows marked changes

in the IR spectrum of pure DBTO, probably (See Figure 5.3, trace B) due to highly electrophilic nature of dicarbonyl carbons of DEO which preferably makes DEO susceptible towards interaction with DBTO.

Scheme 5.7. Plausible mechanism showing formation of carbamate and oxamate
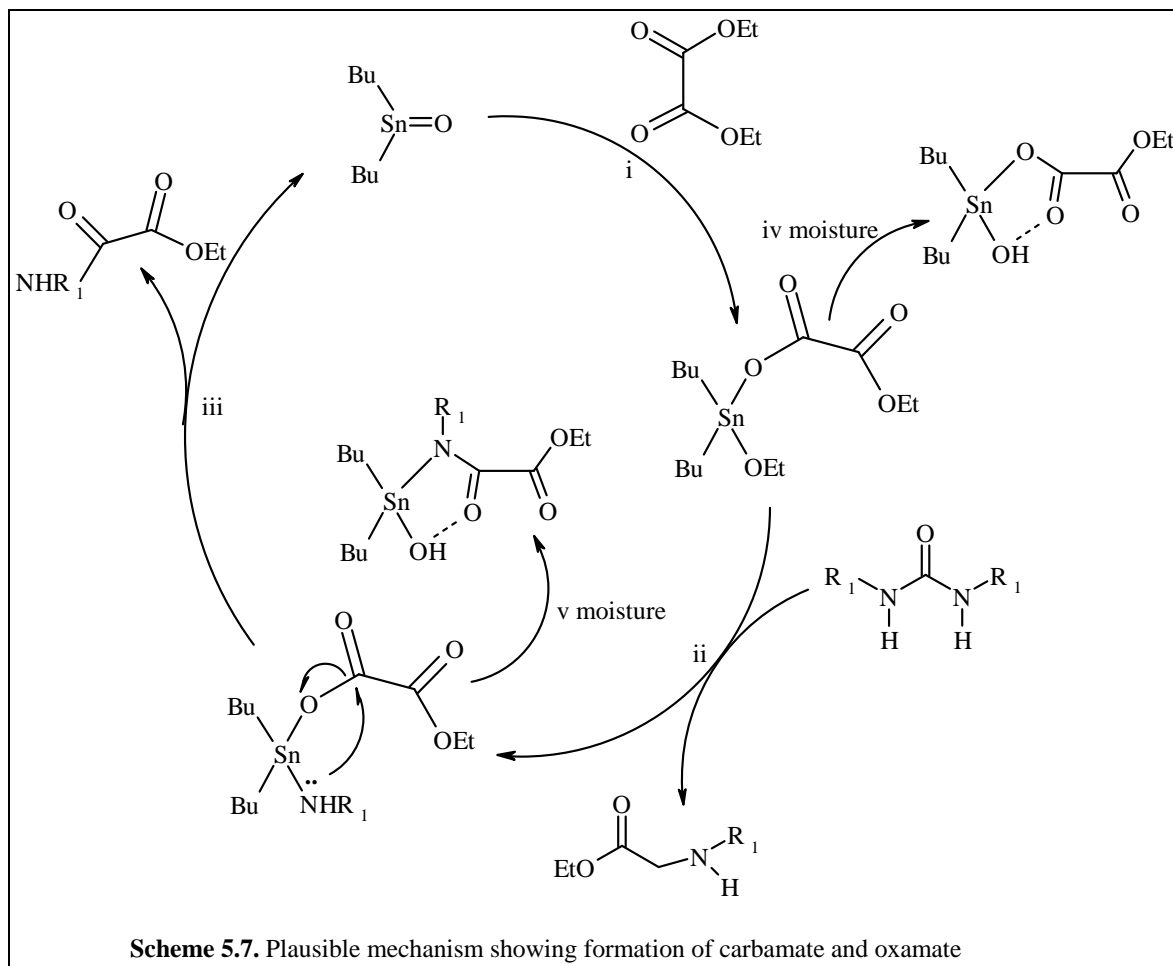
Comparison of DBTO and DEO treated catalyst in 4000-2000 cm^{-1} region shows in addition to aliphatic group absorption in 2930-2866 cm^{-1}. A strong absorption at 3374 cm^{-1} which is most likely due to coordinated OH to tin. The possibility of hydroxide moiety in tin coordination is most likely due to the atmospheric moisture interacting with highly reactive species (I) postulated in scheme 5.6 and 5.7, forming tin hydroxo species II as shown in scheme 5.8. The OH deformation frequency of coordinated water can be seen at 3374 cm^{-1} as a broad absorption, while bending mode of OH which absorbs at ~ 1640 cm^{-1} masked by carbonyl region of oxalate. The occurrence of OH absorption at 3374 cm^{-1} is much lower than expected, showing the possibility

of hydrogen bonding interactions between hydrogen of hydroxyl group and oxygen of carbonyls in coordinated oxalate which results in weakening the OH bond (See species II, in Scheme 5.7). Such interactions are commonly observed in zeolites when zeolitic protons interact with probe molecules such as carbon monoxide.[88] Presence of butyl group which shows a blue shift by 10-15 cm^{-1} compared to pure DBTO[89] (See trace B, Figure 5.3) at 2954 cm^{-1} (CH$_3$ asymmetrical stretching), 2925 cm^{-1} (CH$_2$ symmetrical), 2858 cm^{-1} (CH$_2$ symmetrical stretching), the absorption of ethyl group due to oxalate coordination have been overlapped due to butyl group absorption. CH$_3$ bending mode is seen at 1463 cm^{-1} and CH$_3$ rocking mode at 794 cm^{-1}. However, the presence of oxalate moiety attached to tin can be ascertained by the characteristics of υCO asymmetric absorption at 1686 and 1607 cm^{-1} and symmetric υCO absorption at 1347 and 1308 cm^{-1}, also a sharp intense absorption at 794 cm^{-1} due to υO-C=O deformation in complex (species II) (See Figure 4.3, trace B and C).[90] These additional bands due to oxalate ligand were absent in DBTO. Signals at 678 cm^{-1} is tentatively assigned to υSn-C, while weak doublet at 510 cm^{-1} and 482 cm^{-1} is due to υSn-O stretching and shows the presence of non identical groups coordinated to tin via oxygen.[91] The ab initio generated IR spectrum of species I agrees well with the IR spectrum of species isolated after DBTO and oxalate interaction.[§]The IR spectrum of recovered tin complex from aminolysis reaction is shown in Figure 5.3 (See trace C), and is almost similar to the one obtained by DBTO and DEO interaction (trace B) except, the IR peak at 1715 cm^{-1} which probably shows the presence of oxamate functionality coordinated to tin (species III in scheme 5.8). Thus from IR spectroscopy one can conclude that oxalate do react with DBTO forming Sn-oxalate species which further react with urea forming oxamate species however, true catalytic species are much more reactive and difficult to isolate. The species that are isolated are stable precursors of these active species present under reaction conditions as recycle experiments employing the isolated solid gave up to ~80% yield of carbamate and oxamate respectively. The formation of 1,3-dimethylimidazolidine-2,4,5-trione

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[§] The ab initio (DFT) calculations required for the generation of IR spectrum were carried out using program, `demon', using method PW91 with basis set DZVP (for all atoms).

from urea and oxalate requires strong base catalyst such as CH_3ONa in order to eliminate alcohol.[92] The mechanism depicted here shows an alternate pathway for 1,3-dimethylimidazolidine-2,4,5-trione synthesis using milder catalytic system such as DBTO via carbamate and oxamate.
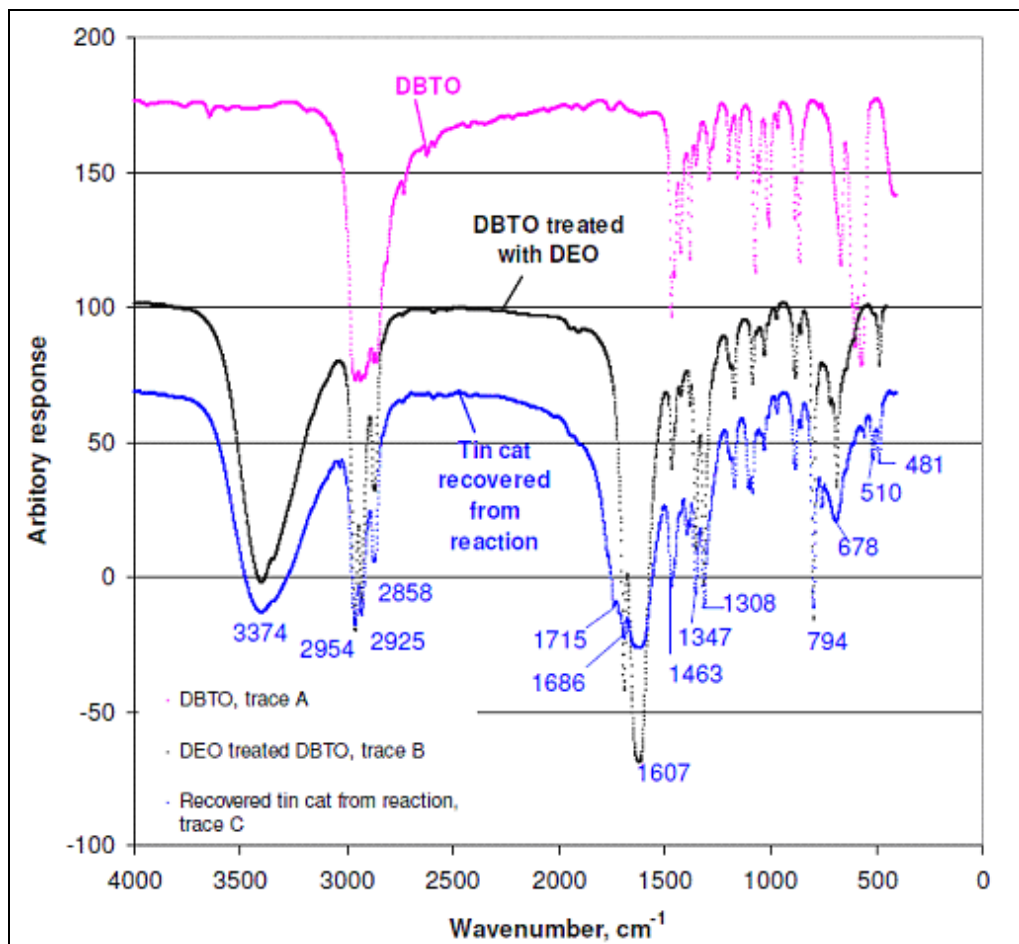
Figure 5.3. IR spectrum of A) neat DBTO, B) DEO treated DBTO and C) DBTO recovered after reaction

Elimination of alcohol from condensation of carbamate and oxamate is facile for 1,3-dimethylimidazolidine-2,4,5-trione synthesis (See Scheme 5.8). The initial activation of carbamate by DBTO instead of oxamate (See Scheme 5.8, step 1) is consistent with the higher reactivity of carbamate usually observed as compared to oxamate.[93] The other steps shown in the mechanism are based on HSAB concept of catalysis discussed earlier.

Scheme 5.8. Plausible mechanism showing formation of 1,3-dimethyl imidazolidine-2,4,5-trione
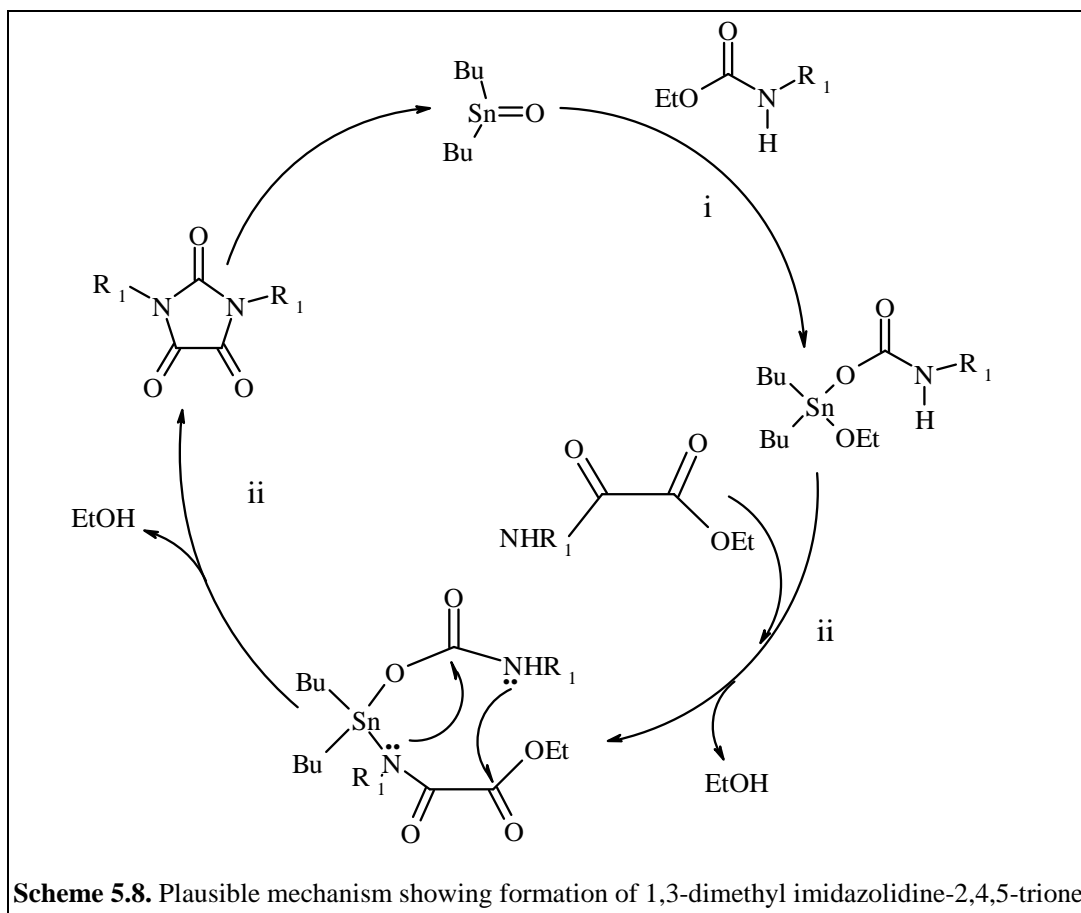
5.6. CONCLUSIONS

Here an efficient but simple catalytic route is reported, that can replace the toxic reagent based route employed in the transformation of amines to carbamates and oxamates. It has been shown that by controlling deactivation of acid-base sites of DBTO, the selectivity of both carbamate and oxamate or 1,3-dimethylimidazolidine-2,4,5-trione can be manipulated, e.g. by blocking the acidic sites of tin catalyst in a basic solvent media such as DMF and NMP higher selectivity of carbamate and oxamate could be achieved, while in absence of basic media higher selectivity of 1,3-dimethylimidazolidine-2,4,5-trione could be obtained. Hydrotalcite as catalyst selectively gives carbamate and oxamate. The nature of activation of urea and oxalate was investigated by IR spectroscopy, which indicated that urea is not directly activated by DBTO but oxalate first coordinates followed by urea. The plausible reaction scheme has been suggested for the aminolysis of oxalate by urea. The role of

DBTO as catalyst seems to activate and stabilize the OR moiety of activated oxalate, thus making it prone to nucleophilic attack of urea and at the same time facilitates alkoxide attack to carbonylcarbon of urea. The possibility of producing important organic intermediates such as dialkyl carbonate, oxomalonate and imino dicarbonate is an interesting spillover of the work.

5.7. IDENTIFICATION OF PRODUCTS

Carbamates, oxamates and imidazolidine trione derivatives were isolated in pure frm and fully characterized by elemental analysis, ^{1}HNMR, ^{13}CNMR and GC-MS.

Ethyl carbamate (3a)

^{1}H NMR (200MHz, CDCl$_3$): δ=1.24 (t, 3H, *J*=7.08Hz, CH$_3$), 4.08 (q, 2H, *J*=7.07Hz, CH$_2$),4.71 (br s, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=14.55 (CH$_3$), 61.16 (OCH$_2$), 157.19 (CO); IR(CHCl$_3$): υmax/cm^{-1} 3434 (N-H stretching), 1721 (C=O Amide I),

GC-MS (EI, 70eV): m/z (%): 89 (3) [M]$^+$, 74 (18) [NH$_2$COOCH$_2$]$^+$, 62 (97) [NH$_2$COOH$_2$]$^+$, 44 (100) [NH$_2$CO]$^+$;

elemental analysis calcd (%) for C$_3$H$_7$NO$_2$: C 40.44, H 7.92, N 15.72; found: C 40.28, H 7.80, N 15.60.

Ethyl oxamate (4a)

^{1}H NMR (200MHz, CDCl$_3$): δ=1.38 (t, 3H, *J*=7.07Hz, CH$_3$), 4.33 (q, 2H, *J*=7.07Hz, CH$_2$);

^{13}C NMR (50MHz, CDCl$_3$): δ=14.00 (CH$_3$), 63.48 (OCH$_2$), 158.75 (CON), 160.13 (CO); IR(KBr): υmax (cm^{-1}) 3375 (N-H stretching), 1685 (C=O Amide I) and 1718(C=O);

GC-MS (EI, 70eV): m/z (%) : 17 (2) [M]$^+$, 89 (11) [NH$_2$COOH]$^+$, 72 (7.6) [NH$_2$COCO]$^+$, 44 (100) [NH$_2$CO]$^+$;

elemental analysis calcd (%) for C$_4$H$_7$NO$_3$: C 41.04, H 6.03, N 11.96; found: C 40.98, H 6.00, N 11.88.

Ethyl N-methylcarbamate (3b):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.16 (t, 3H, *J*=7.08Hz, CH$_3$, 2.70 (d, 3H, *J*=5.18Hz, CH$_3$), 4.01 (q, 2H, *J*=7.07Hz, CH$_2$), 4.95 (br s, 1H, NH);

^{13}C NMR (125MHz, CDCl$_3$): δ=14.42 (CH$_3$), 27.17 (CH$_3$NH), 60.47 (OCH$_2$), 157.33 (COO); IR(KBr): υmax/cm^{-1} 3349 (N-H stretching),1704 (C=O);

GC-MS (EI, 70eV): m/z (%): 104 (2) [M+1], 103 (36) [M]$^+$, 88 (5) [CH$_3$NHCOOCH$_2$]$^+$, 75 (52) [CH$_3$NHCOOH]$^+$, 58 (100)[CH$_3$NHCO]$^+$,45(12)[C$_2$H$_5$O]$^+$;

elemental analysis calcd (%) for C$_4$H$_9$NO$_2$: C 46.59, H 8.80 N 13.58; found: C 46.62, H 8.88, N 13.64.

Ethyl N-methyloxamate (4b):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.39 (t, 3H, *J*=7.08Hz, CH$_3$), 2.92 (d, 3H, *J*=5.18Hz, NCH$_3$), 4.34 (q, 2H, *J*=7.07Hz, CH$_2$), 7.25 (br s, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=13.95 (CH$_3$), 26.44 (CH$_3$NH), 63.15 (OCH$_2$), 157.23 (CON), 160.62 (COO);

IR(CHCl$_3$): υmax/cm^{-1} 3430 (N-H stretching),1706 (C=O);

GC-MS (EI, 70eV): m/z (%):131 (1) [M]$^+$, 103 (10) [CH$_3$NHCOOCH$_2$CH$_3$]$^+$, 60 (11) , 58 (100) [CH$_3$NHCO]$^+$, 45 (12) [C$_2$H$_5$O]$^+$;

elemental analysis calcd (%) for C$_5$H$_9$NO$_3$**:** C 45.80, H 6.92, N 10.68; found: C 45.84, H 6.90, N 10.70.

1,3- dimethylimidazolidine-2,4,5- trione (5b):

^{1}H NMR (200MHz, CDCl$_3$): δ=3.17 (s, 6H, 2CH$_3$);

^{13}C NMR (100MHz, CDCl$_3$): δ=24.91 (CH$_3$), 154.23 (CON), 156.83 (CO); IR (KBr): νmax/cm^{-1} 3422 (N-H), 1709 and 1759 (C=O);

GC-MS (EI, 70eV): m/z (%) :143 (6.6) [M+1], 142 (100) [M]$^+$, 58 (62) [CH$_3$NHCO]$^+$, 57 (33) [CH$_3$NCO]$^+$;

 elemental analysis calcd (%) for C$_5$H$_6$N$_2$O$_3$: C 42.26, H 4.26, N 19.71; found: C 42.20, H 4.30, N 19.76.

Ethyl N-(phenyl)carbamate (3c):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.32 (t, 3H, *J*=7.08Hz, CH$_3$), 4.22 (q, 2H, *J*=7.08Hz, CH$_2$), 6.66 (br s, 1H, NH), 7.03-7.42 (m, 5H, Ar-CH);

^{13}C NMR (125 MHz, CDCl$_3$): δ=14.45 (CH$_3$), 61.10 (OCH$_2$), 118.71 (Ar-C), 123.25 (Ar-C), 128.91 (Ar-C), 137.99 (Ar-C), 153.70 (COO);

IR(KBr): υmax/cm^{-1} 3330 (N-H, S), 1703 (C=O Amide I);

GC-MS (EI, 70eV): m/z (%): 166 (8.5) [M+1], 165 (80) [M]$^+$, 137 (5.7) [C$_6$H$_5$NHCOOH]$^+$, 119 (17) [C$_6$H$_5$NCO]$^+$, 106 (71) [C$_6$H$_5$CH$_2$CH$_3$]$^+$, 93 (100) [C$_6$H$_5$NH$_2$]$^+$, 77 (18) [C$_6$H$_5$]$^+$; elemental analysis calcd (%) for C$_9$H$_{11}$NO$_2$: C 65.44, H 6.71, N 8.48; found: C 65.50, H 6.72, N 8.50.

Ethyl N-(phenyl)oxamate (4c):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.26 (t, 3H, J=7.07Hz, CH$_3$), 4.16 (q, 2H, J=7.07Hz, CH$_2$), 6.96-7.35 (m, 5H, Ar-CH), 6.64 (br s, 1H, NH);

^{13}C NMR (500 MHz,CDCl$_3$): δ= 14.24 (CH$_3$), 62.37 (OCH$_2$), 119.74 (Ar-C), 125.53 (Ar-C), 129.28 (Ar-C), 136.17 (Ar-C), 156.70 (CON), 162.08 (COO);

IR(CHCl$_3$): υmax/cm^{-1} 3018.99 (Ar C-H stretching), 1726.27(C=O) and 1650.08 (C=O Amide I);

GC-MS (EI, 70eV):m/z (%): 194 (8.5) [M+1], 193 (70) [M]$^+$, 120 (100) [C$_6$H$_5$NHCO]$^+$, 119 (28) [C$_6$H$_5$NCO]$^+$, 92 (42) [C$_6$H$_5$NH]$^+$, 77 (49) [C$_6$H$_5$]$^+$; elemental analysis calcd (%) for C$_{10}$H$_{11}$NO$_3$: C 62.17, H 5.74, N 7.25; found: C 62.15, H 5.80, N 7.28.

1,3- diphenylimidazolidine-2,4,5- trione (5c):

^{1}H NMR (200MHz, CDCl$_3$): δ= 7.18-7.61 (m, 10H, Ar-CH);

^{13}C NMR (50MHz, CDCl$_3$): δ= 125.83 (Ar-C), 129.57 (Ar-C),129.72 (Ar-C), 151.74 (CON),   155.01 (CO);

IR(KBr): υmax/cm^{-1} 3066 (CN), 1736 and 1785 (C=O);

GC-MS (EI, 70eV):m/z (%): 267 (10) [M+1], 265.6 (58) [M]$^+$, 118.8 (100) [C$_6$H$_5$NCO]$^+$, 90.9 (18) [C$_6$H$_5$N]$^+$; elemental analysis calcd (%) for C$_{15}$H$_{10}$N$_2$O$_3$: C 67.67, H 3.79, N 10.52; found: C 67.65, H 3.75, N 10.50.

Ethyl N-(4-methylphenyl) carbamate (3d):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.29 (t, 3H, J=7.07Hz, CH$_3$), 2.29 (s, 3H, CH$_3$), 4.18 (q, 2H, J=7.07Hz, CH$_2$), 7.07-7.11 (d, 2H, J=8.21Hz, Ar-CH), 7.22-7.27 (d, 2H, J =8.47 Hz, Ar-CH); ^{13}C NMR (500 MHz, CDCl$_3$): δ= 14.56 (CH$_3$), 20.71 (Ar-C), 61.20 (OCH$_2$), 119.02 (Ar-C), 129.54 (Ar-C), 133.04 (Ar-CN), 135.33 (Ar-C), 159.49 (-CON);

IR(CHCl$_3$): υmax/cm^{-1} 3438 (N-H stretching), 1729 (C=O Amide I);

GC-MS (EI, 70eV): m/z (%): 180 (9.5) [M+1], 179 (88) [M]$^+$, 151 (9.5) [CH$_3$C$_6$H$_4$NHCOOH] $^+$, 120 (63), 106 (100) [CH$_3$C$_6$H$_4$NH] $^+$, 91 (12) [C$_6$H$_4$NH] $^+$, 77 (28) [C$_6$H$_5$] $^+$;

elemental analysis calcd (%) for C$_{10}$H$_{13}$NO$_2$: C 67.02, H 7.31, N 7.82; found: C 67.01, H 7.30, N 7.80.

Ethyl N-(4-methylphenyl)oxamate (4d):

^{1}H NMR (500MHz, CDCl$_3$): δ=1.42 (t, 3H, J=7.15Hz, CH$_3$), 2.33 (s, 3H, CH$_3$), 4.40 (q, 2H, J=7.15Hz, CH$_2$), 7.16-7.17 (d, 2H, J=8.21Hz, Ar-CH), 7.50-7.52 (d, 2H, J=8.25 Hz, Ar-CH), 8.81 (br s, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=13.97 (CH$_3$), 20.94 (Ar-CH$_3$), 63.67 (OCH$_2$), 119.71 (Ar-CH), 129.68 (Ar-CH), 133.73 (Ar-CN), 135.26 (Ar-C), 153.69 (-CON), 161.05 (-COO);

IR(KBr): υmax/cm^{-1} 3344 (N-H), 1698 (C=O Amide I) and 1729 (C=O);

GC-MS (EI, 70eV): m/z (%) : 208 (12) [M+1], 207 (97) [M]$^+$, 134 (88.5) [CH$_3$C$_6$H$_4$NHCO]$^+$, 106 (100) [CH$_3$C$_6$H$_4$NH] $^+$, 91 (33) [CH$_3$C$_6$H$_4$] $^+$;

elemental analysis calcd (%) for C$_{11}$H$_{13}$NO$_3$: C 63.76, H 6.32, N 6.76; found: C 63.72, H 6.29, N 6.73.

Ethyl N-(2-methoxyphenyl)carbamate (3e):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.32 (t, 3H, J=7.08Hz, CH$_3$), 3.86 (s, 3H, OCH$_3$), 4.25 (q, 2H, J=7.08Hz, CH$_2$), 6.83-7.0 (m, 4H, Ar-CH), 8.06-8.1 (br, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=14.54 (CH$_3$), 55.58 (OCH$_3$), 61.05 (OCH$_2$), 109.88 (Ar-C), 118.06 (Ar-C), 121.06 (Ar-C), 122.58 (Ar-C), 127.67 (Ar-C-O), 147.48 (ArC-N), 153.51 (CO);

IR(KBr): υmax/cm^{-1} 3433 (N-H stretching), 1727.94 (C=O Amide I stretching);

GC-MS (EI, 70eV): m/z (%): 196 (11) [M+1], 195 (100) [M]$^+$, 149 (14) [CH$_3$OC$_6$H$_4$NCO] $^+$, 136 (32) [CH$_3$OC$_6$H$_4$NCH$_3$] $^+$, 108 (71) [CH$_3$OC$_6$H$_5$] $^+$,77 (40) [C$_6$H$_5$]$^+$;

elemental analysis calcd (%) for C$_{10}$H$_{13}$NO$_3$**:** C 61.53, H 6.71, N 7.18; found: C 61.55, H 6.73, N 7.20.

Ethyl N-(2-methoxyphenyl)oxamate (4e):

^{1}H NMR (500MHz, CDCl$_3$): δ=1.41 (t, 3H, *J*=7.15Hz, CH$_3$), 3.90 (s, 3H, OCH$_3$), 4.39 (q, 2H, *J*=7.16Hz, CH$_2$), 6.88-8.40 (m, 4H, Ar-CH), 9.48 (br s, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=13.91 (CH$_3$), 55.66 (OCH$_3$), 63.47 (CH$_2$), 109.96 (Ar-C), 119.71 (Ar-C), 120.94 (Ar-C), 125.16 (Ar-C-N)), 125.95 (Ar-C), 148.30 (Ar-C-O), 153.58 (CON), 160.75 (COO);

 IR(KBr): υmax/cm^{-1} 3378 (N-H), 1698 (C=O Amide I) and 1700 (C=O);GC-MS (EI, 70eV): m/z (%): 224 (9.5) [M+1], 223 (88.5) [M]$^+$, 150 (100) [CH$_3$OC$_6$H$_4$NHCO] $^+$, 149 (38) [CH$_3$OC$_6$H$_4$NCO] $^+$, 135 (42.85) [OHC$_6$H$_4$NCO] $^+$, 122 (25.7) [CH$_3$OC$_6$H$_4$NH] $^+$; elemental analysis calcd (%) for C$_{11}$H$_{13}$NO$_4$: C 59.19, H 5.87, N 6.27; found: C 59.15, H 5.85, N 6.25.

Ethyl N-(2-chlorophenyl)carbamate (3f):

 ^{1}H NMR (200MHz, CDCl$_3$): δ=1.26 (t, 3H, *J*=7.20Hz, CH$_3$), 4.16 (q, 2H, *J*=7.06Hz, CH$_2$), 6.88-8.12 (m, 4H, Ar-CH), 7.06 (br s, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=14.53 (CH$_3$), 61.59 (OCH$_2$), 119.85 (Ar-C), 121.98 (Ar-CCl), 123.62 (Ar-C), 127.77 (Ar-C), 129.06 (Ar-C), 134.83 (Ar-CN), 153.26 (CO); IR(KBr): υmax/cm^{-1} 3421 (N-H), 1741 (C=O Amide I stretching);

GC-MS (EI, 70eV):m/z (%): 201 (24) [M+2], 200 (7.6) [M+1], 199 (71) [M]$^+$, 153 (14) [ClC$_6$H$_4$NCO]$^+$, 140 [ClC$_6$H$_4$NHCH$_2$]$^+$, 127 (100) [ClC$_6$H$_4$NH2]$^+$;

elemental analysis calcd (%) for $C_9H_{10}ClNO_2$: C 54.15, H 5.05, Cl 17.76, N 7.02; found: C 54.13, H 5.01, Cl 17.77, N 7.00.

Ethyl N-(2-chlorophenyl)oxamate (4f):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.42 (t, 3H, *J*=7.20Hz, CH$_3$), 4.39 (q, 2H, *J*=7.16Hz, CH$_2$), 7.14-7.74 (m, 4H, Ar-CH), 8.89 (br s, 1H, NH);

^{13}C NMR (50MHz, CDCl$_3$): δ=14.01 (CH$_3$), 63.99 (OCH$_2$), 117.88 (Ar-CH), 119.96 (Ar-CCl), 125.66 (Ar-CH), 130.29 (Ar-CH), 134.95 (Ar-CH), 137.43 (Ar-CN), 153.95 (CONH), 160.73 (COO);

IR(KBr): υmax/cm^{-1} 3333 (N-H, Stretching), 1702(C=O Amide I stretching) and 1716 (C=O);GC-MS (EI, 70eV): m/z (%) :229 (24) [M+2], 228 (8.5) [M+1], 227 (71) [M]$^+$, 192 (45) [M$^+$- Cl], 154 (100) [ClC$_6$H$_4$NHCO] $^+$, 126 (43) [ClC$_6$H$_4$NH] $^+$, 111 (33) [ClC$_6$H$_5$] $^+$;

elemental analysis calcd (%) for $C_{10}H_{10}ClNO_3$: C 52.76, H 4.43, Cl 15.57, N 6.15; found: C 52.74, H 4.44, Cl 15.55, N 6.14.

Methyl N-methylcarbamate (3i):

^{1}H NMR (200MHz, CDCl$_3$): δ=2.78 (d, 3H, *J*=4.88Hz, CH$_3$), 3.67 (s, 3H, CH$_3$), 4.93 (br s, 1H, NH);

^{13}C NMR (125MHz, CDCl$_3$): δ=27.36 (CH$_3$), 51.91 (OCH$_3$), 157.77 (CO);

IR(KBr): υmax/cm^{-1} 3366 (N-H), 1710 (C=O), 1570 (N-H bending);

GC-MS (EI, 70eV):m/z (%): 89 (63) [M] $^+$, 74 (57) [CH$_3$NHCOO] $^+$, 58 (100) [NCO] $^+$, 44 (19) [CO] $^+$;

elemental analysis calcd (%) for $C_3H_7NO_2$: C 40.44, H 7.92, N 15.72; found: C 40.41, H 7.90, N 15.69.

Methyl N-methyloxamate (4i):

^{1}H NMR (200MHz, CDCl$_3$): δ=2.87-2.96 (q, 1H, NH), 2.9 (d, 3H, CH$_3$), 3.87 (s, 3H, OCH$_3$);

^{13}C NMR (50MHz, CDCl$_3$): δ=26.55 (CH$_3$), 53.68 (OCH$_3$), 157.05 (CON), 161.14 (CO); IR(KBr): υmax/cm^{-1} 3428 (N-H), 1704 (C=O Amide I)and 1741 (C=O);

GC-MS (EI, 70eV): m/z (%) : 117 (6) [M] $^+$, 89 (28) [NH$_2$COCOOH] $^+$, 58 (100) [NCO] $^+$, 44 (3) [CO] $^+$;

elemental analysis calcd (%) for C$_4$H$_7$NO$_3$: C 41.03, H 6.03, N 11.96; found: C 41.00, H 6.01, N 11.94.

Diethyl iminodicarbonate (6):

^{1}H NMR (200MHz, CDCl$_3$): δ=1.20 (t, 3H, *J*=7.07Hz, CH$_3$), 1.25 (t, 3H, *J*=7.07Hz, CH$_3$), 4.05 (q, 2H, *J*=7.07Hz, CH$_2$), 4.17 (q, 2H, *J*=7.08Hz, CH$_2$);

^{13}C NMR (50MHz, CDCl$_3$): δ=14.21 (CH$_3$), 14.49 (CH$_3$), 61.11 (OCH$_2$), 62.28 (OCH$_2$), 151.19 (COO), 157.54 (COO),

IR(CHCl$_3$): υmax/cm^{-1} 3432.17(N-H stretching), 3023.79 (C-H aliphatic stretching), 1801.65, 1722.13 (C=O Amide I);

GC-MS (EI, 70eV): m/z (%) :162 (.01) [M+1], 134 (100) [C$_2$H$_5$OOCNHCOOH$_2$]$^+$, 117 (28.5) [C$_2$H$_5$OOCNHCOH]$^+$,106 (28.5) [HOOCNH$_2$COOH], 88 (29.5) [C$_2$H$_5$ONHCO]$^+$, 45 (46) [C$_2$H$_5$O]$^+$;

elemental analysis calcd (%) for C$_6$H$_{11}$NO$_4$: C 44.72, H 6.88, N 8.69; found: C 44.70, H 6.85, N 8.66.

Alloxan (7): GC-MS (EI, 70eV): m/z (%):142 (90) M$^+$, 114 (10) [M$^+$-CO], 99 (8) [NHCOCOCO]$^+$, 86 (6) [CONHCONH]$^+$,71 (45) [NHCOCO]$^+$, 56 (100) [COCO]$^+$.

Diethyl carbonate (8): GC-MS (EI, 70eV): m/z (%) = 91 (60) [C$_2$H$_5$CO(OH)$_2$]$^+$, 63 (20) [H$_3$CO$_3$]$^+$, 45 (100) [C$_2$H$_5$O]$^+$, 29 (80) [C$_2$H$_5$]$^+$.

N1,N2-bis(2-chlorophenyl)oxalamide (10): GC-MS (EI, 70eV): m/z (%) :310 (4) [M++2], 308 (5) [M] $^+$, 275 (25) [(M++2)-Cl], 274 (8) [(M++1)-Cl], 273 (100) [(M$^+$)-Cl], 154 (12) [ClC$_6$H$_4$NHCO]$^+$, 127 (60) [ClC$_6$H$_4$NH$_2$]$^+$.

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Spectra

Ethyl carbamate (3a)

^{1}H NMR (200MHz, CDCl$_3$): Ethyl carbamate (3a)
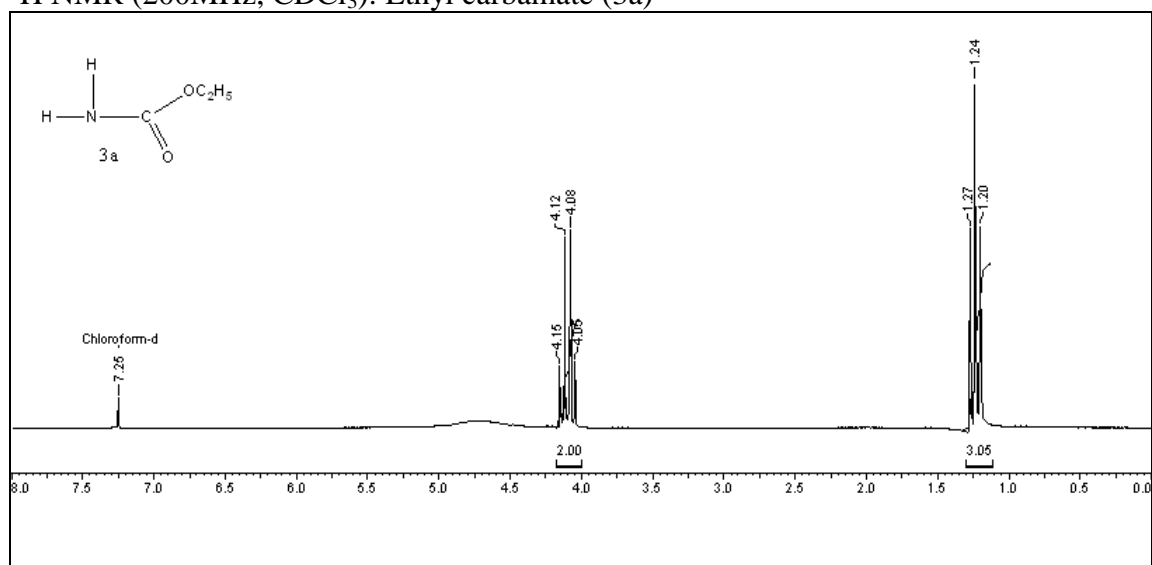
^{13}C NMR (50MHz, CDCl$_3$): Ethyl carbamate (3a)
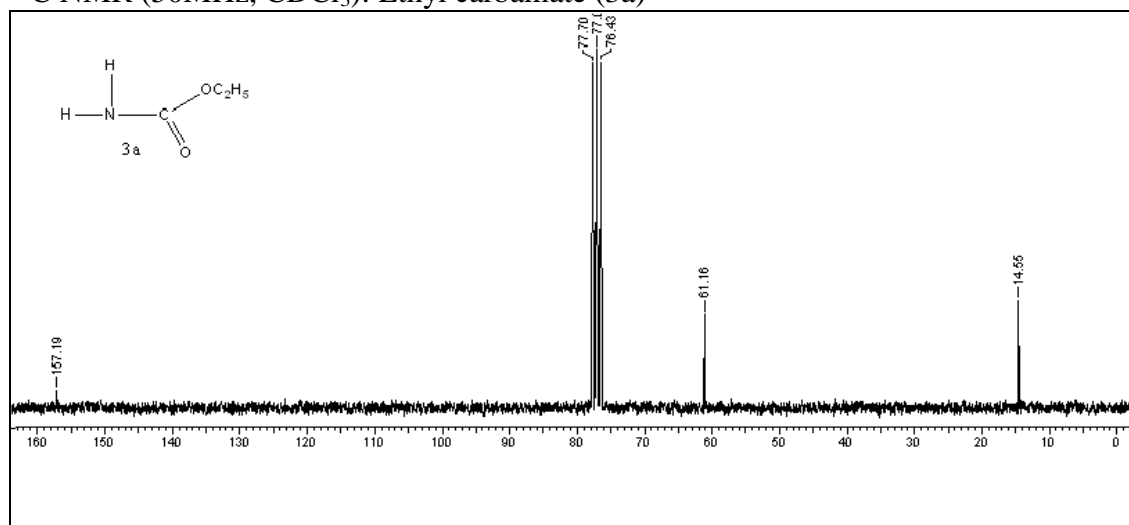
IR(CHCl₃): Ethyl carbamate (3a)
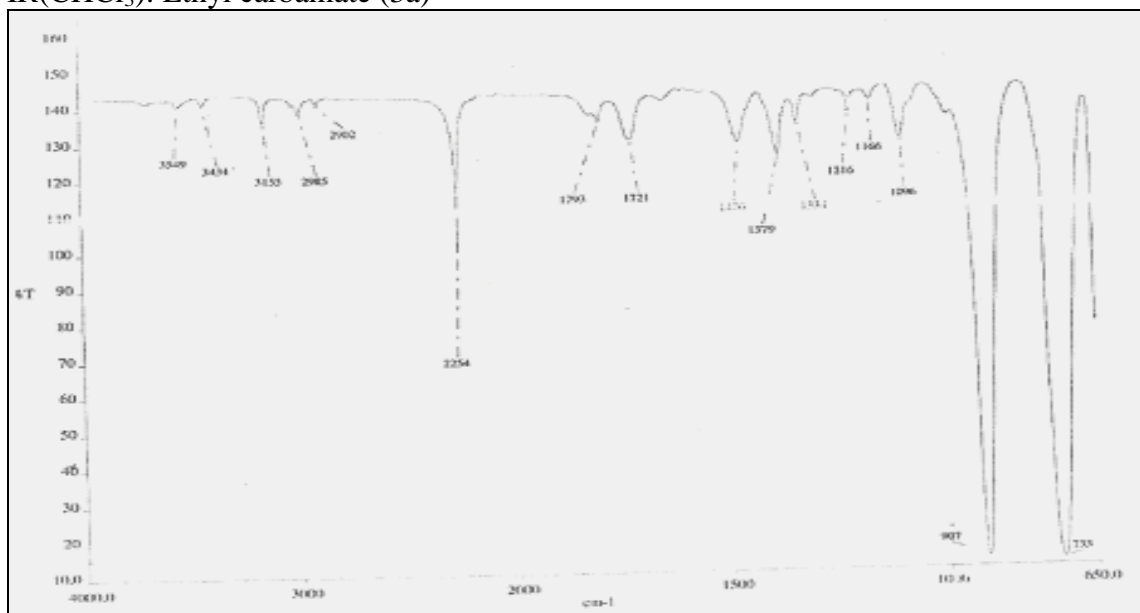
GC-MS (EI, 70eV): Ethyl carbamate (3a)

Scan 290 (5.114 min): MEC-48.D
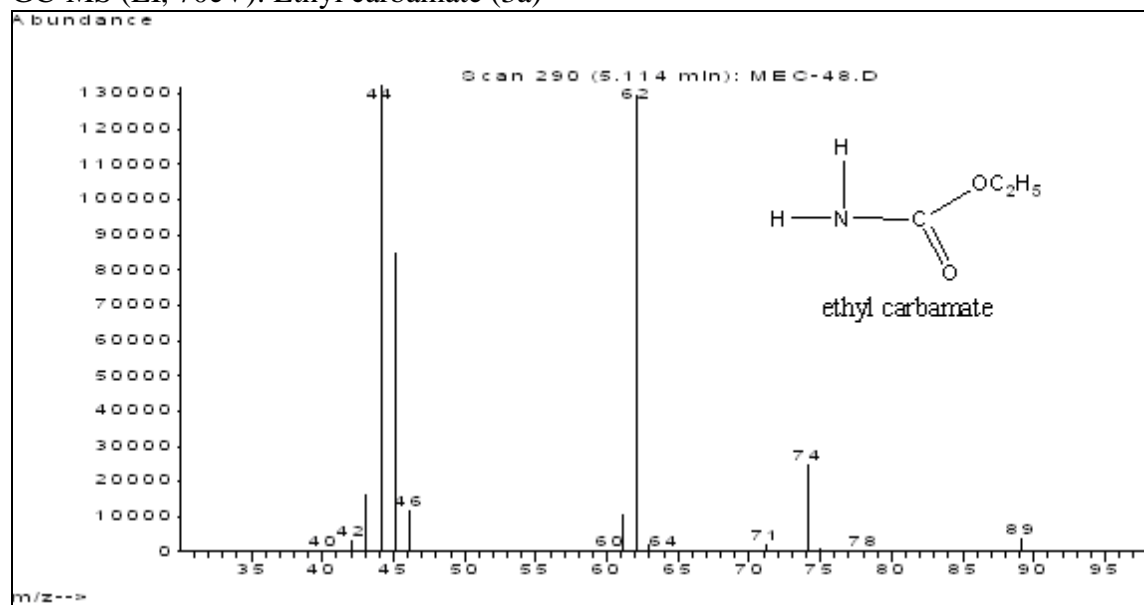
ethyl carbamate

Ethyl oxamate (4a)

^{1}H NMR (200MHz, CDCl$_3$): Ethyl oxamate (4a)
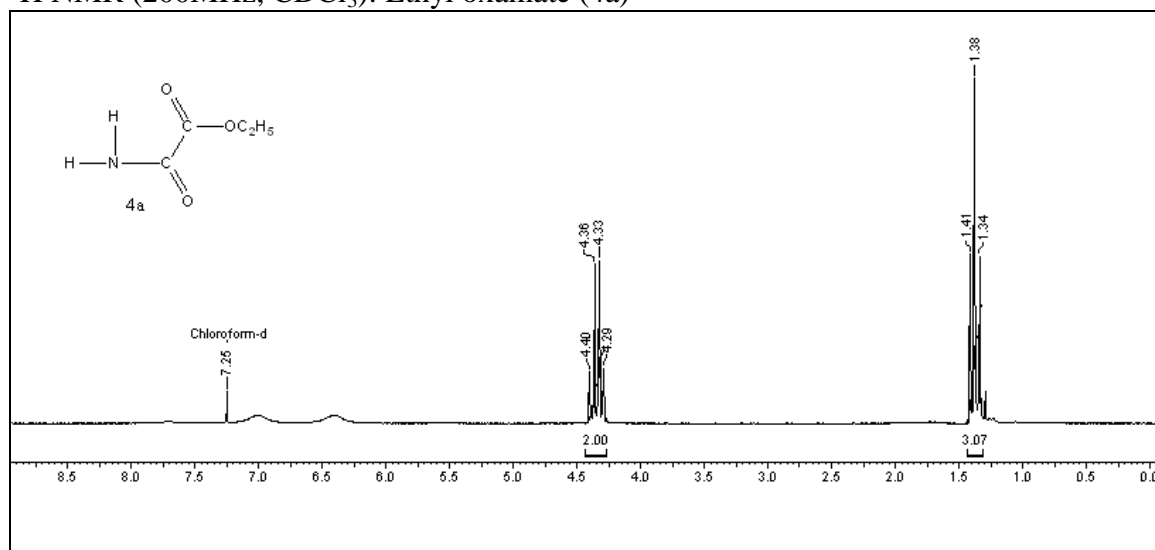
^{13}C NMR (50MHz, CDCl$_3$): Ethyl oxamate (4a)
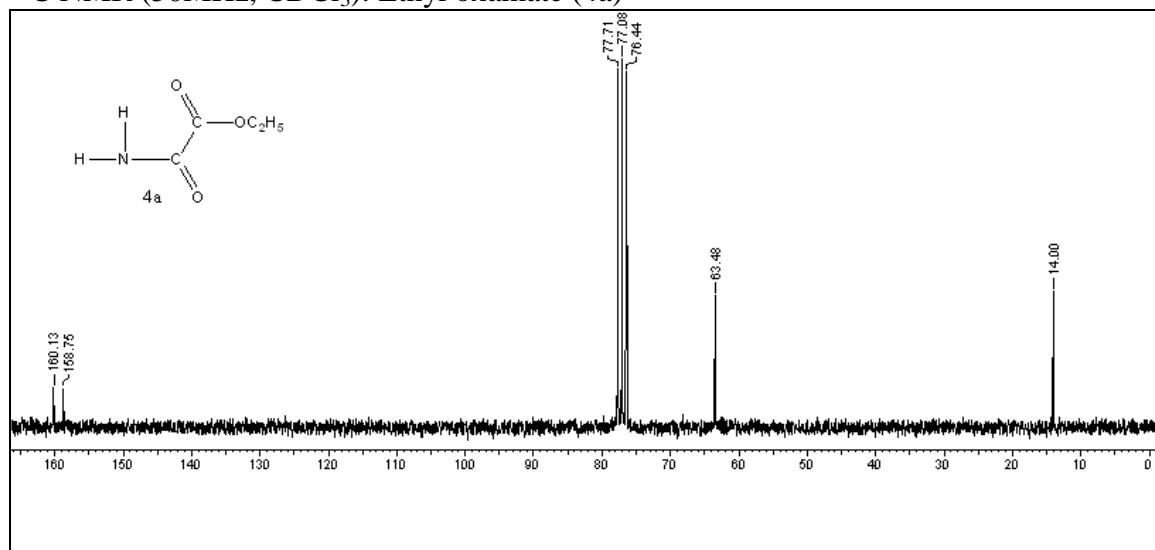
IR(KBr): υ_{max}/cm^{-1} Ethyl oxamate (4a)
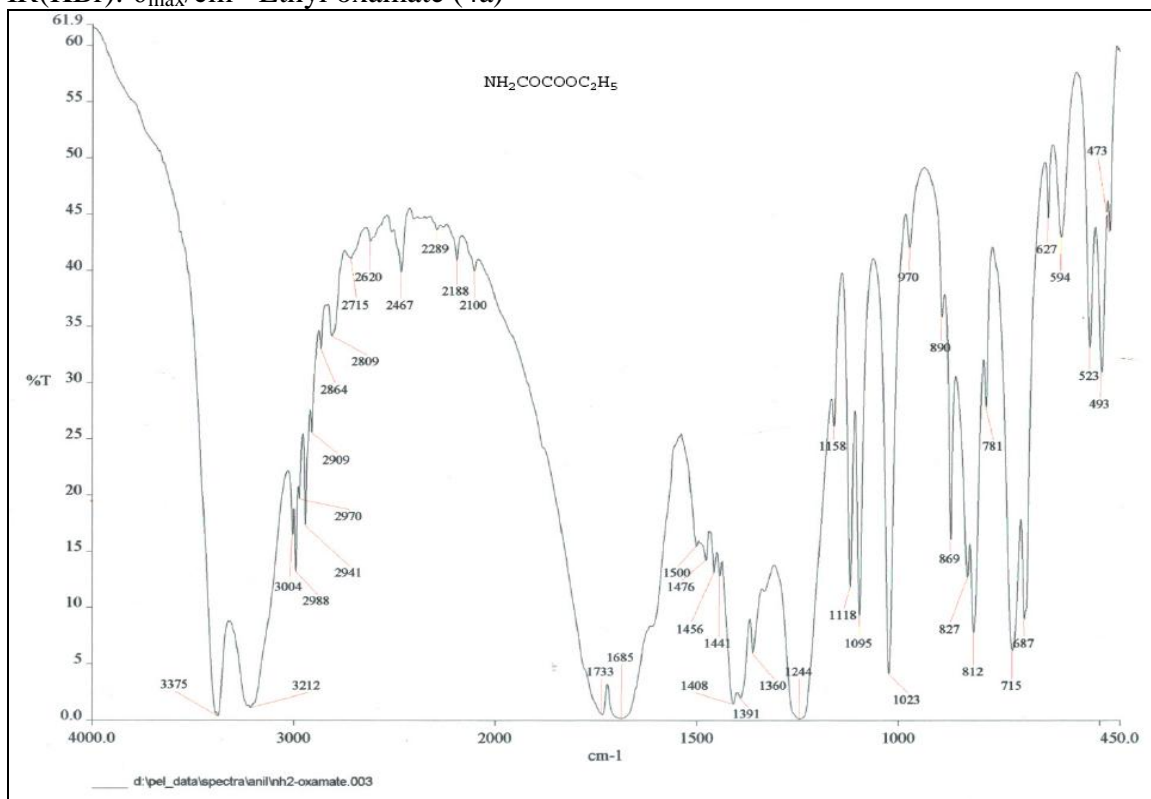
GC-MS (EI, 70eV): Ethyl oxamate(4a)
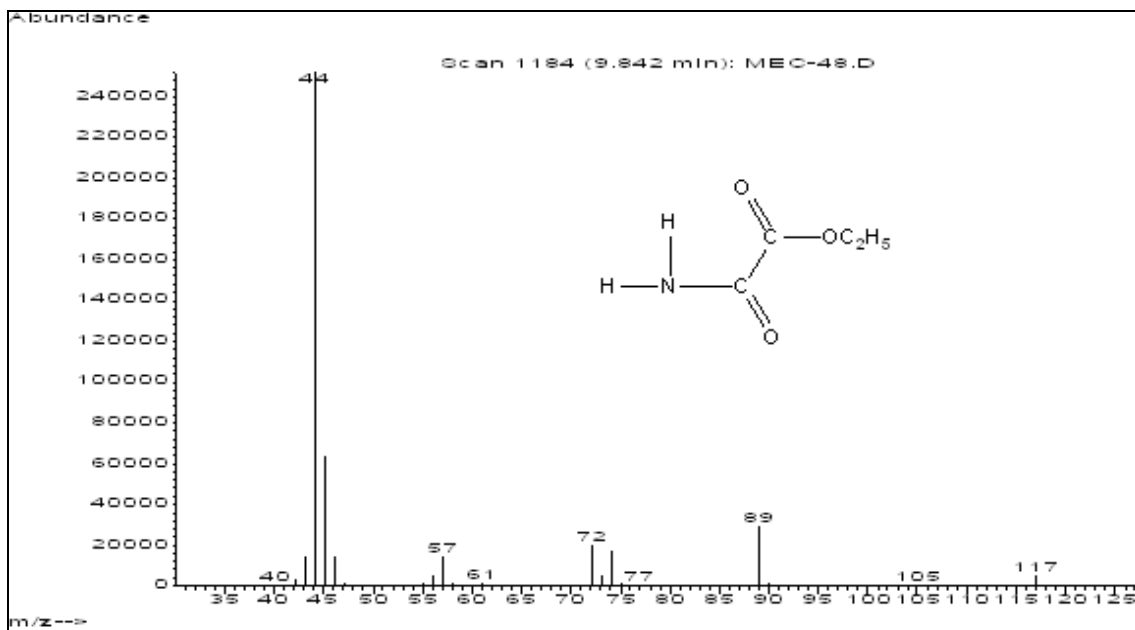
Ethyl N-methylcarbamate (3b)

¹H NMR (200MHz, CDCl₃): Ethyl *N*-methylcarbamate(3b)
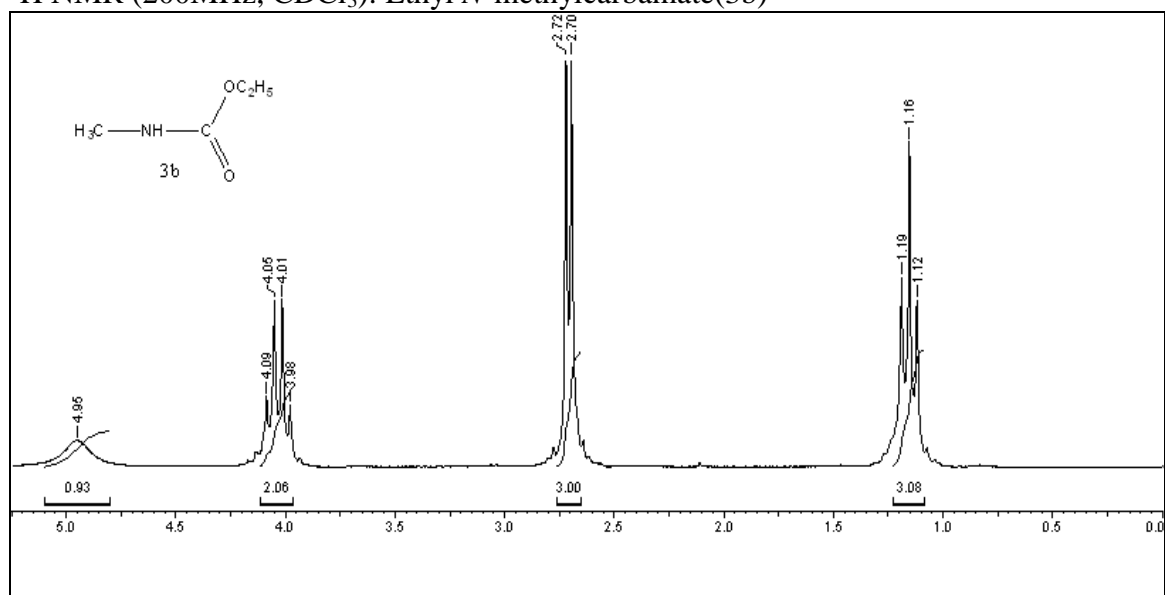
¹³C NMR (125MHz, CDCl₃): Ethyl *N*-methylcarbamate (3b)

295
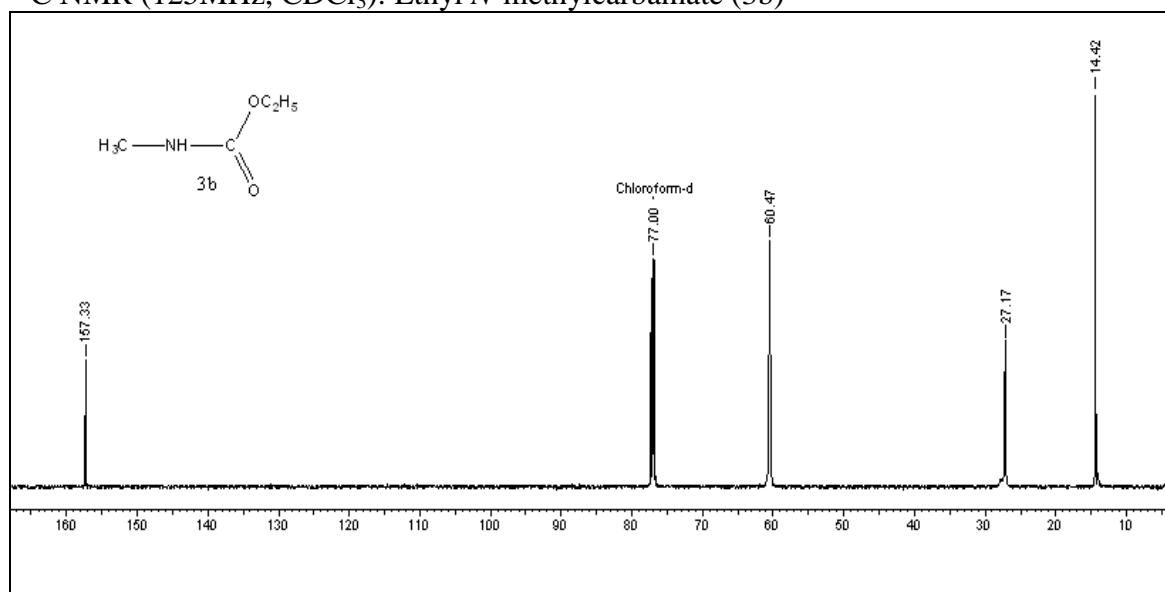
IR(KBr): υ_{max}/cm^{-1} :Ethyl *N*-methylcarbamate (3b)[1]
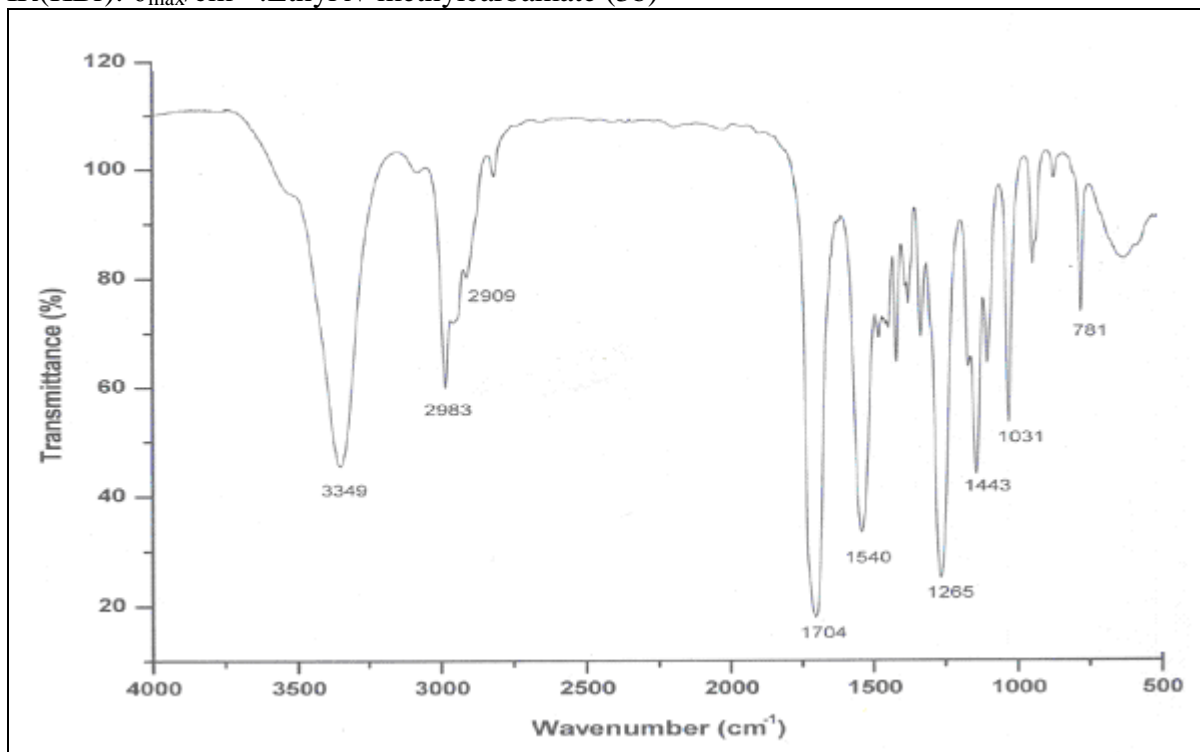
GC-MS (EI, 70eV): Ethyl *N*-methylcarbamate (3b)
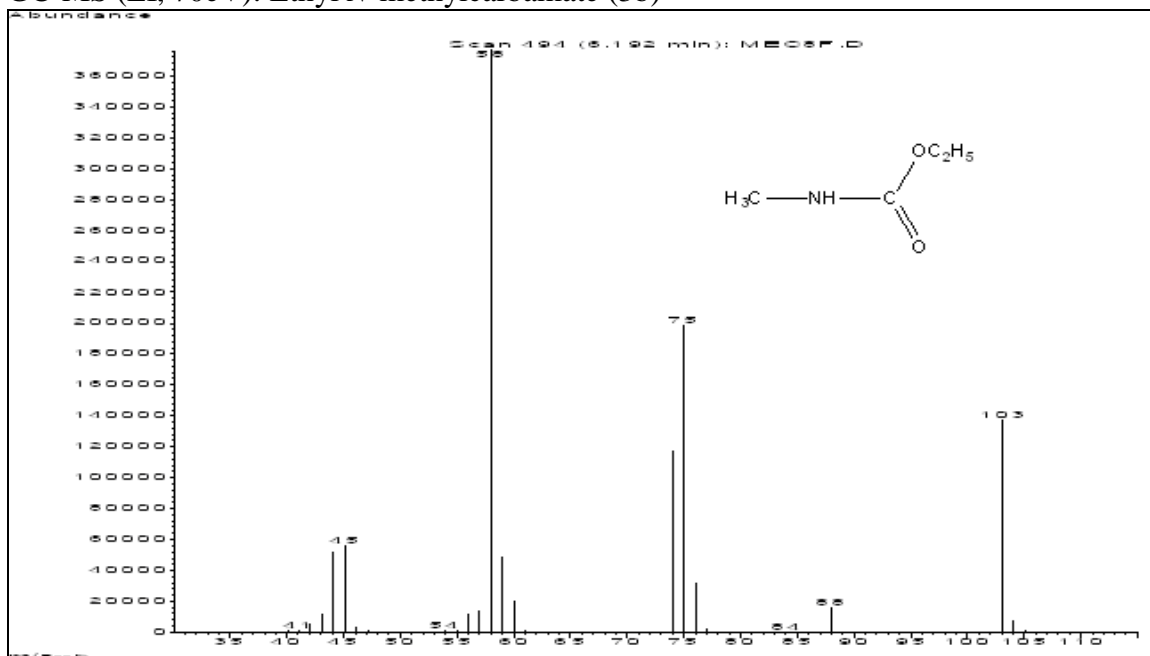
Ethyl N-methyloxamate (4b):

^{1}H NMR (200MHz, CDCl$_3$): Ethyl *N*-methyloxamate (4b)
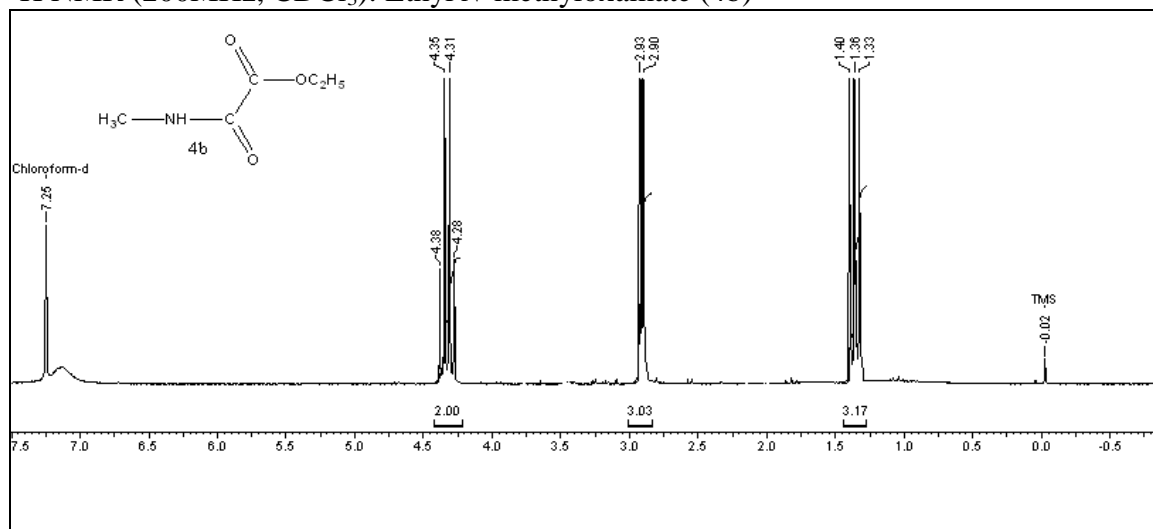
^{13}C NMR (50MHz, CDCl$_3$): Ethyl *N*-methyloxamate (4b)
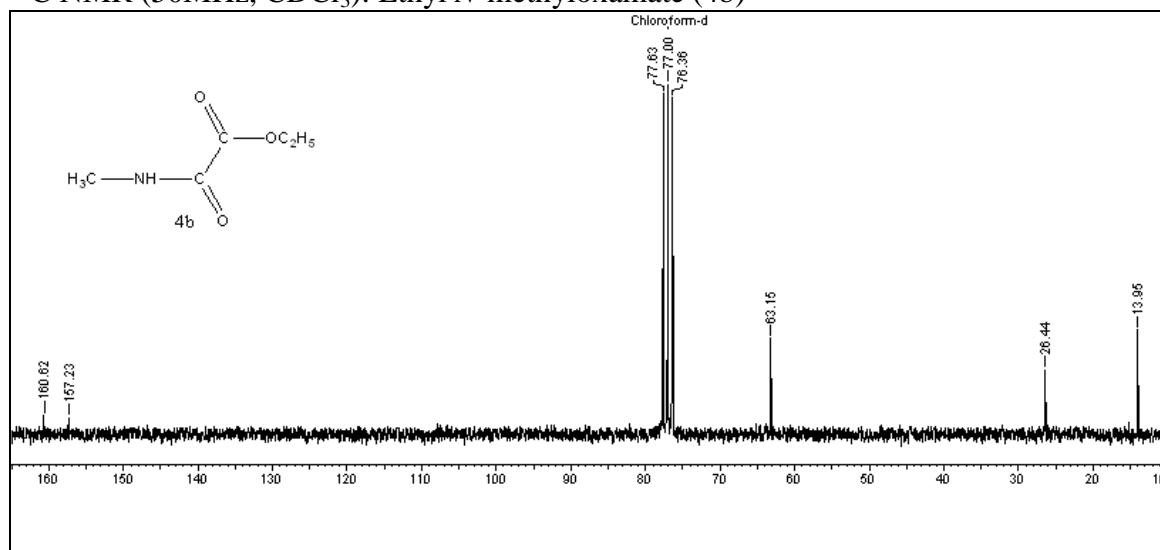
IR(CHCl₃): Ethyl *N*-methyloxamate (4b)[2]
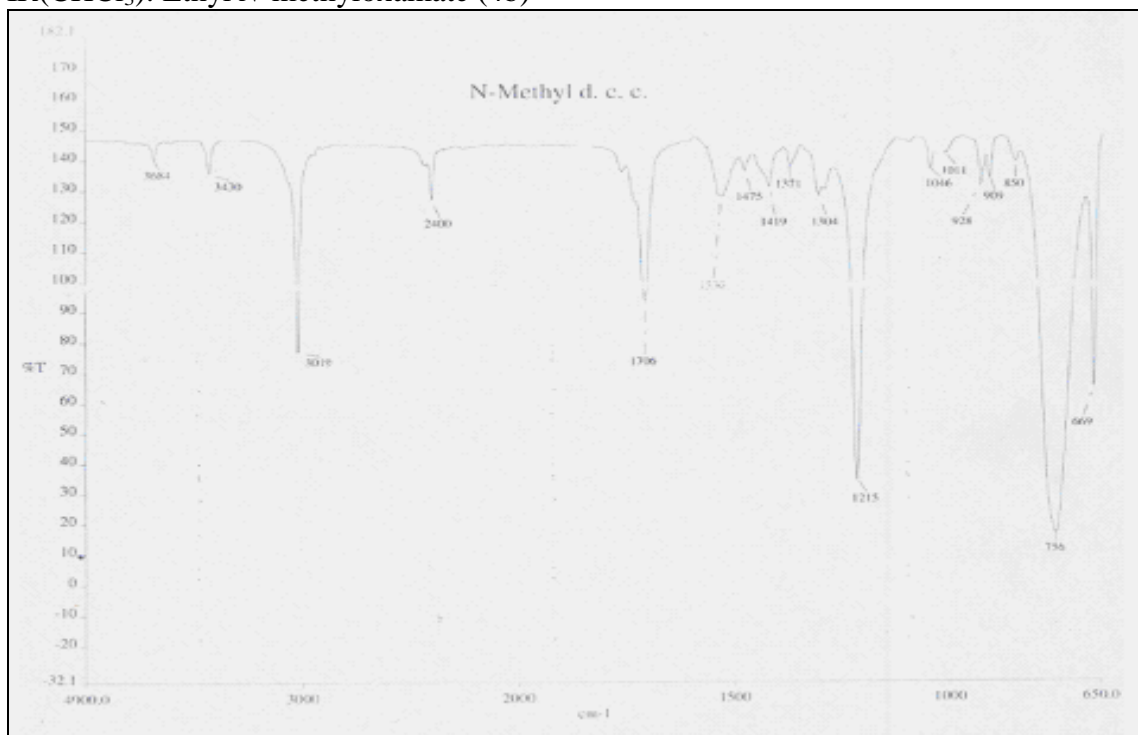
GC-MS (EI, 70eV): Ethyl *N*-methyloxamate (4b)
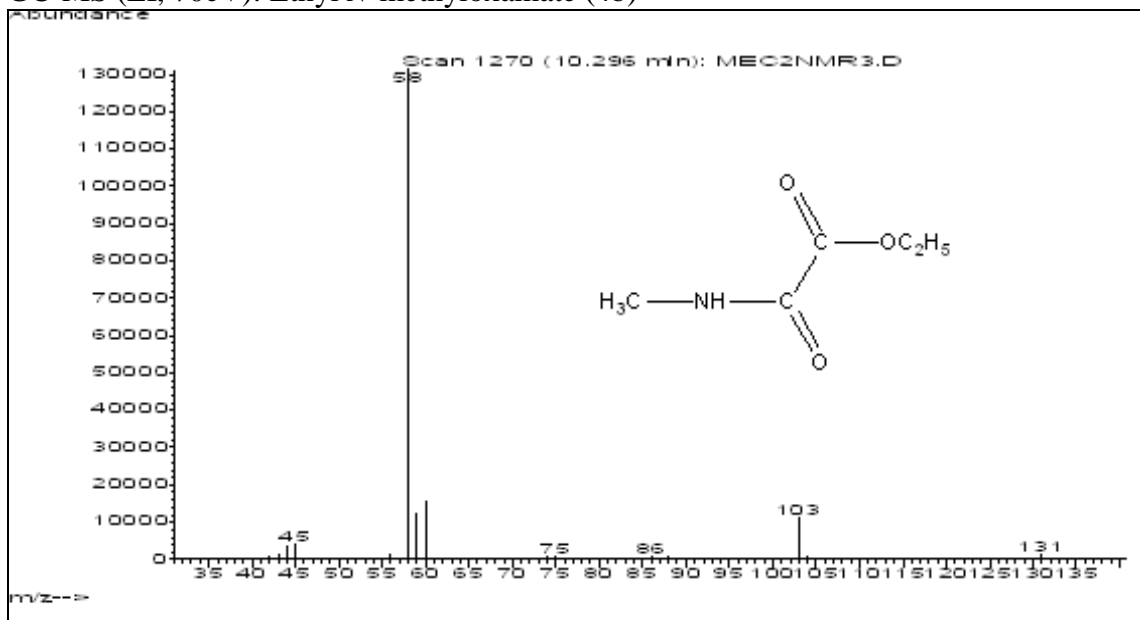
1,3 dimethyl-2,3,5-imidazolidine trione (5b):

^{1}H NMR (200MHz, CDCl$_3$): 1,3 dimethyl-2,4,5-imidazolidine trione (5b):
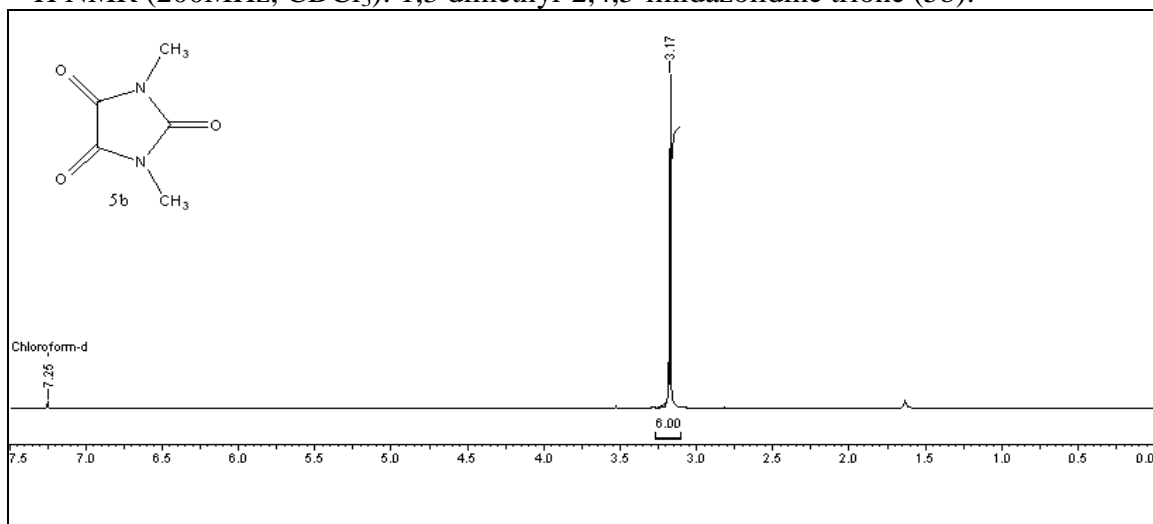
^{13}C NMR (100MHz, CDCl$_3$): 1,3 dimethyl-2,4,5-imidazolidine trione (5b):

299
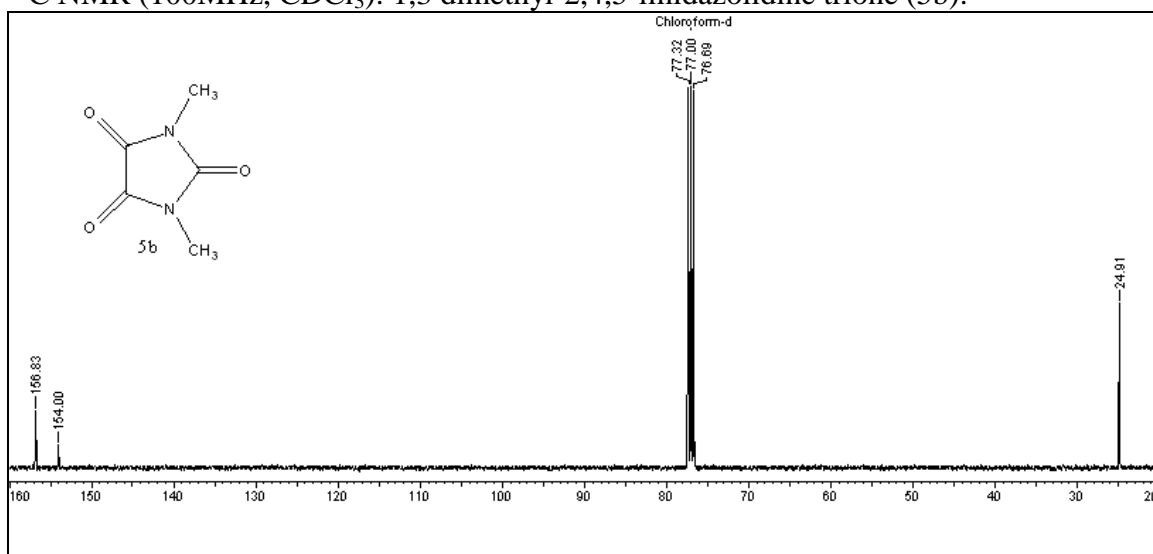
IR (KBr): 1,3 dimethyl-2,4 ,5-imidazolidine trione (5b):
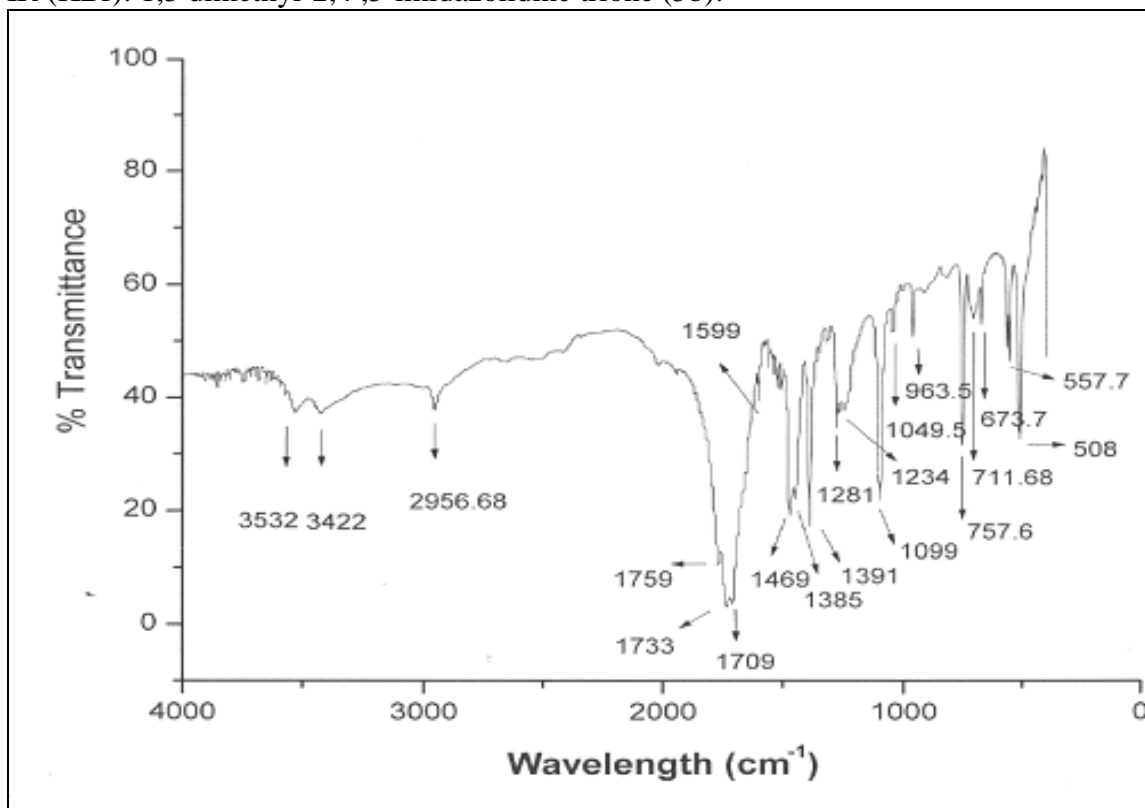
GC-MS (EI, 70eV): 1,3 dimethyl-2,4 ,5-imidazolidine trione (5b):
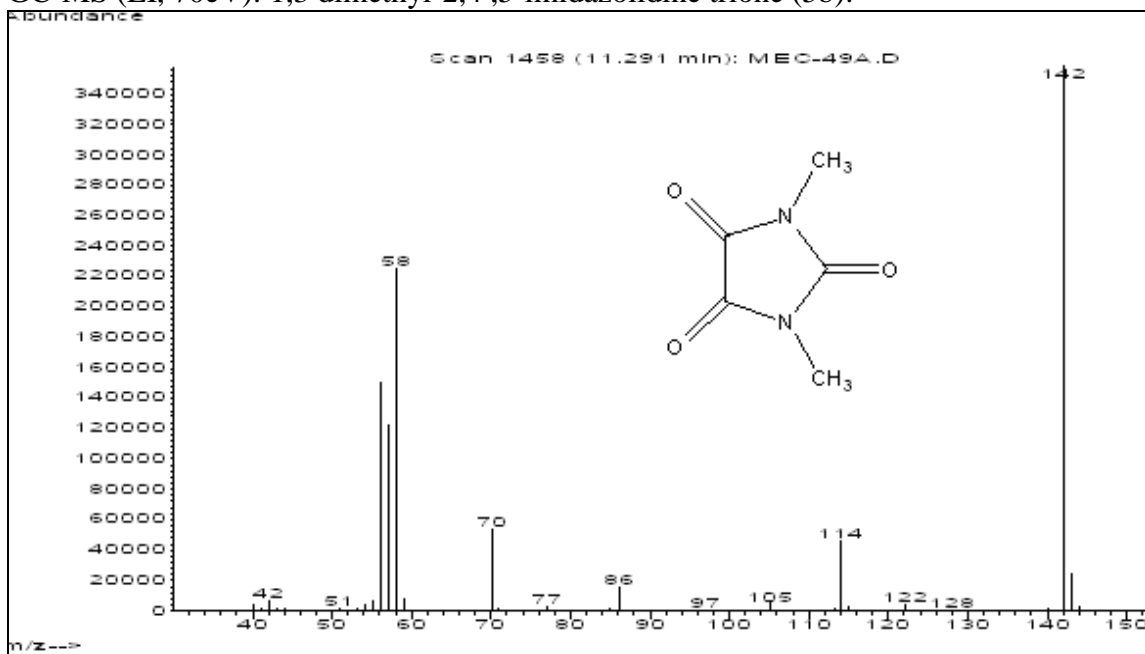
Ethyl N-(phenyl)carbamate (3c):

^{1}H NMR (200MHz,CDCl$_3$): Ethyl*N*-(phenyl)carbamate(3c)
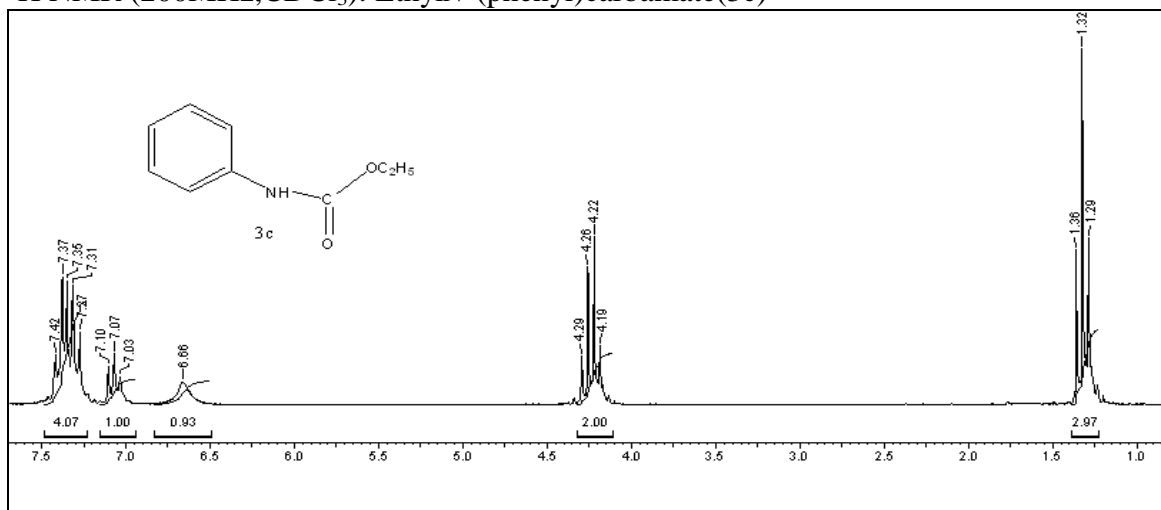
^{13}C NMR (125 MHz, CDCl$_3$): Ethyl *N*-(phenyl) carbamate (3c)
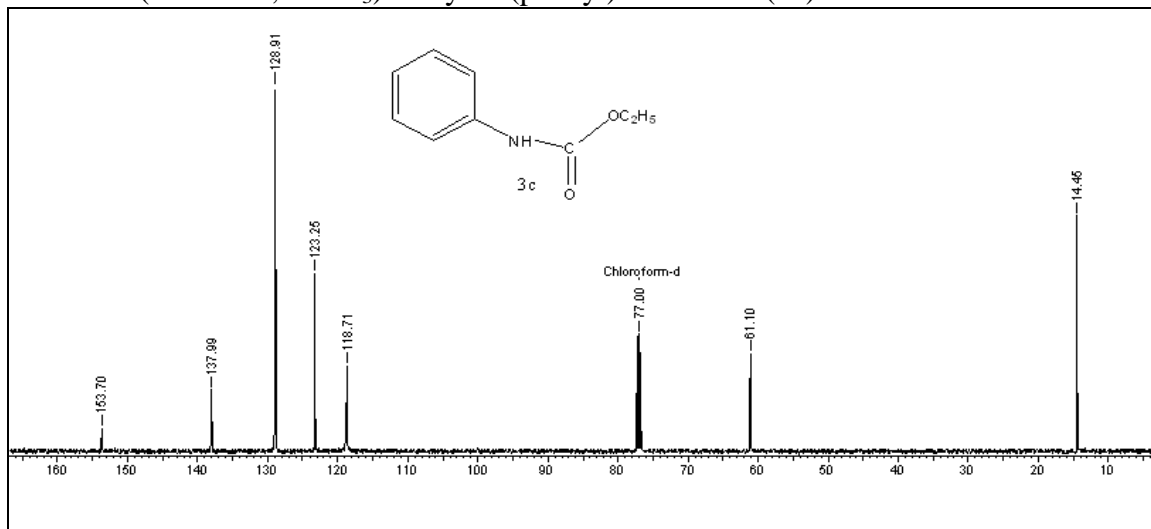
IR(KBr): Ethyl *N*-(phenyl)carbamate (3c)[1]
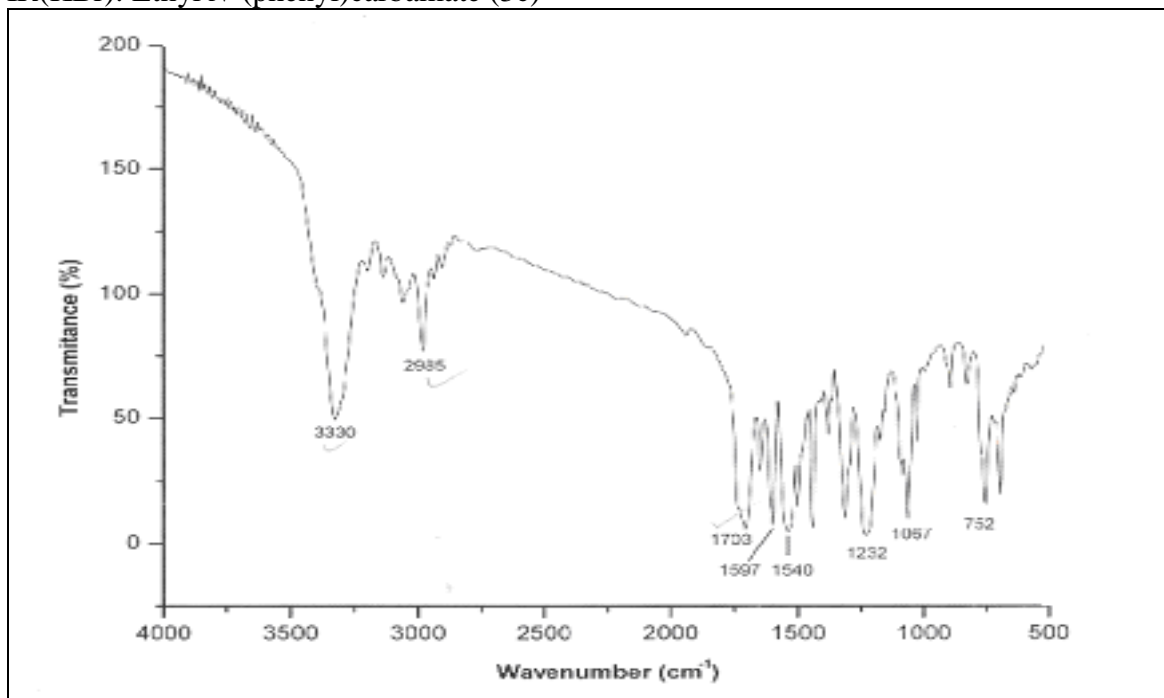
GC-MS (EI, 70eV) : m/z (% intensity) : Ethyl *N*-(phenyl)carbamate (3c)
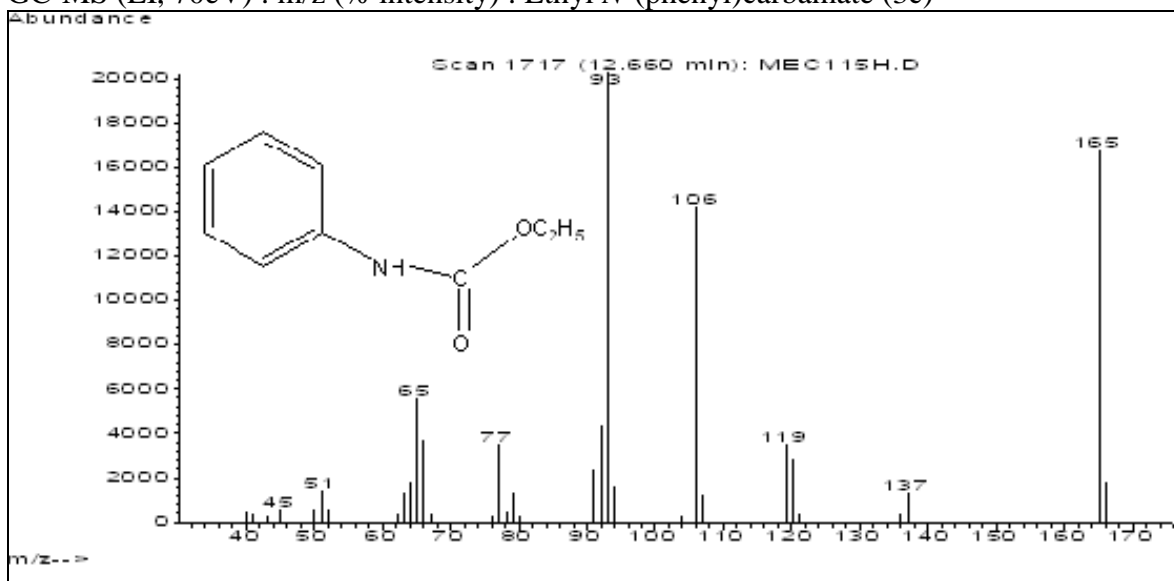
Ethyl N-(phenyl)oxamate (4c):

^{1}H NMR (200MHz, CDCl$_3$): Ethyl *N*-(phenyl)oxamate (4c)
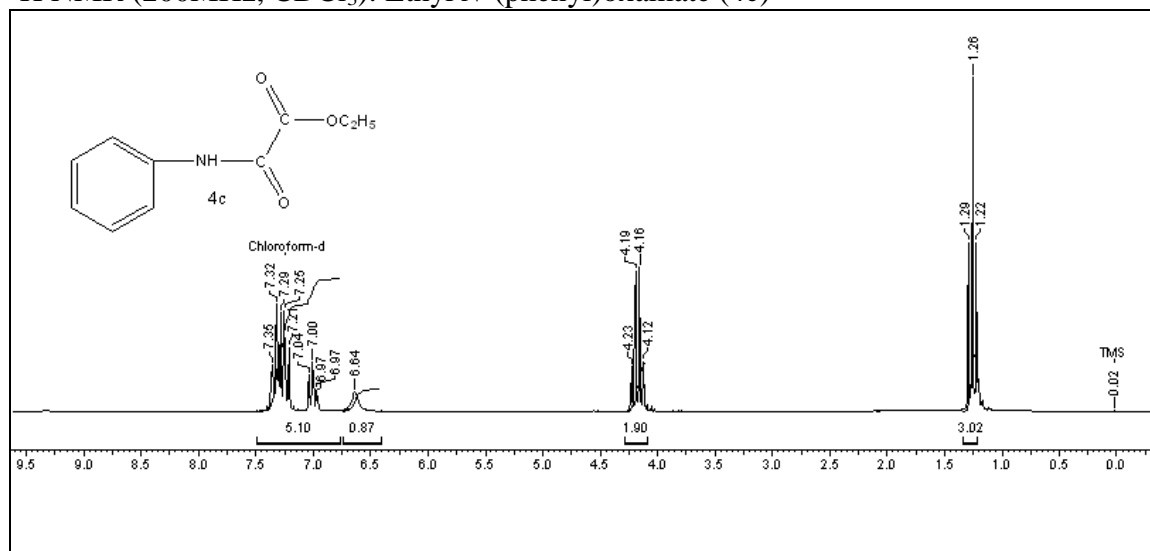
^{13}C NMR (500 MHz,CDCl$_3$): Ethyl *N*-(phenyl)oxamate (4c)
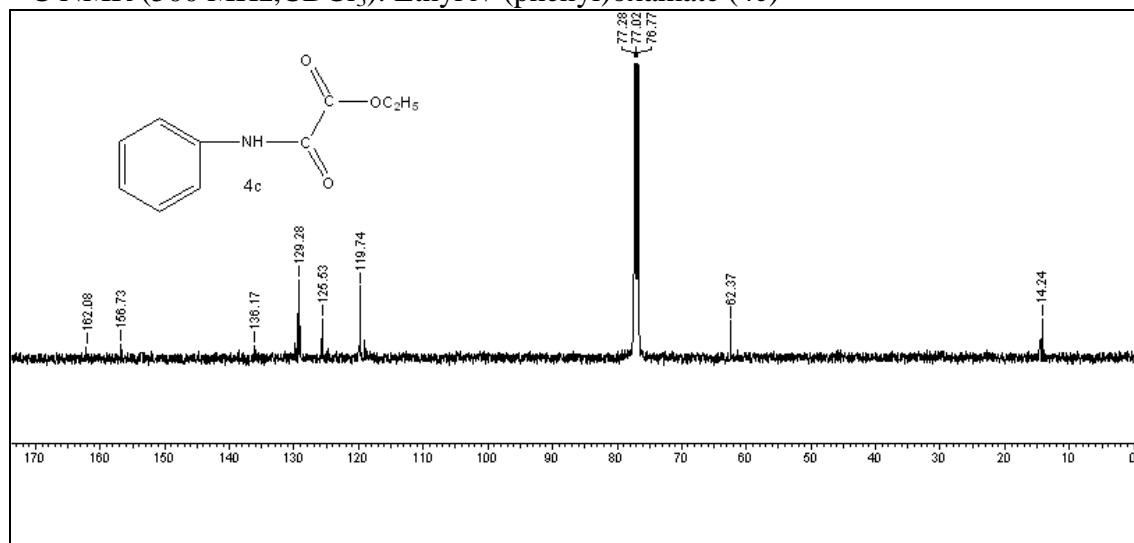
GC-MS (EI, 70eV): Ethyl *N*-(phenyl)oxamate (4c)
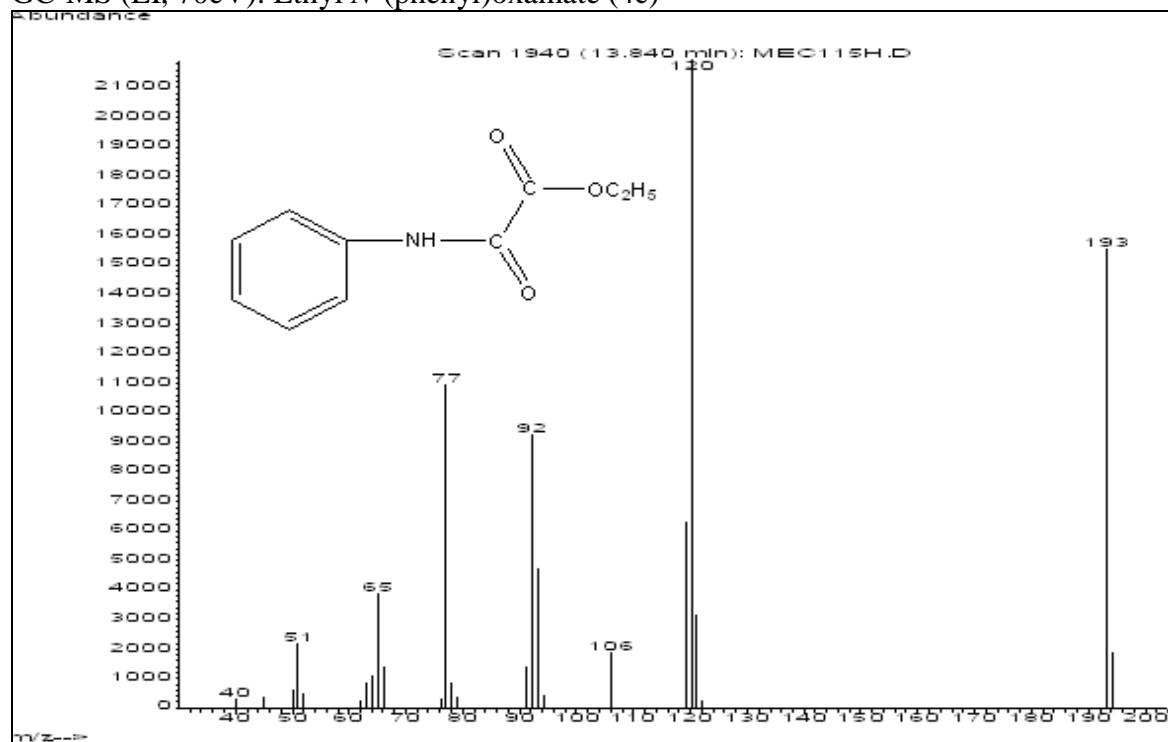
IR(CHCl$_3$): Ethyl *N*-(phenyl)oxamate (4c)[3]
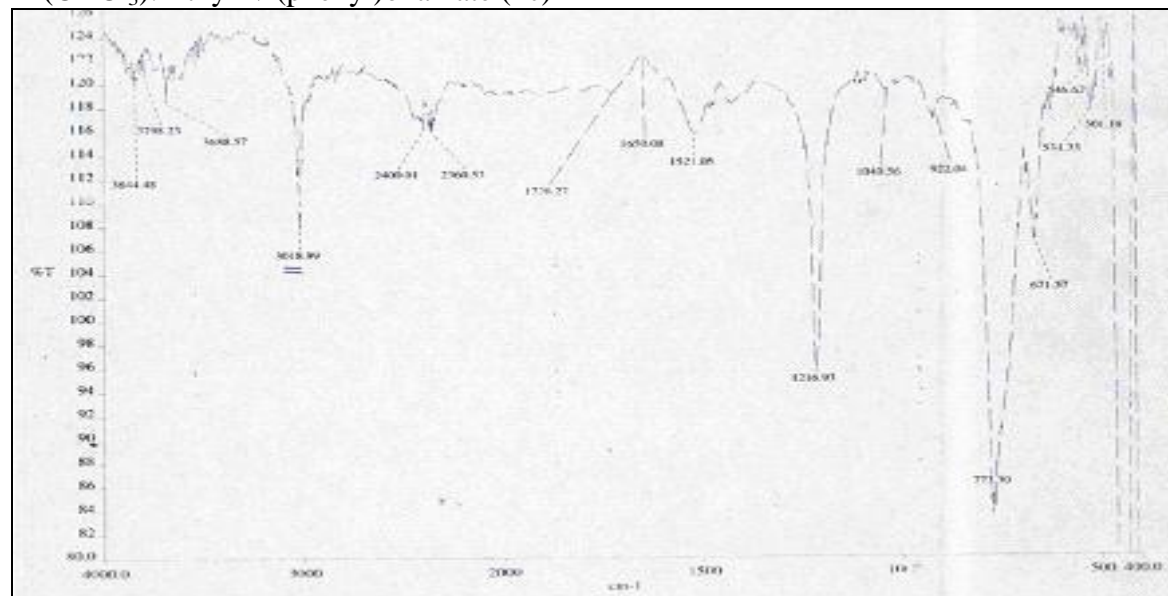
1,3 diphenyl-2,4,5-imidazolidine trione (5c):

¹H NMR (200MHz, CDCl₃): 1,3 diphenyl-2,4,5-imidazolidine trione (5c):
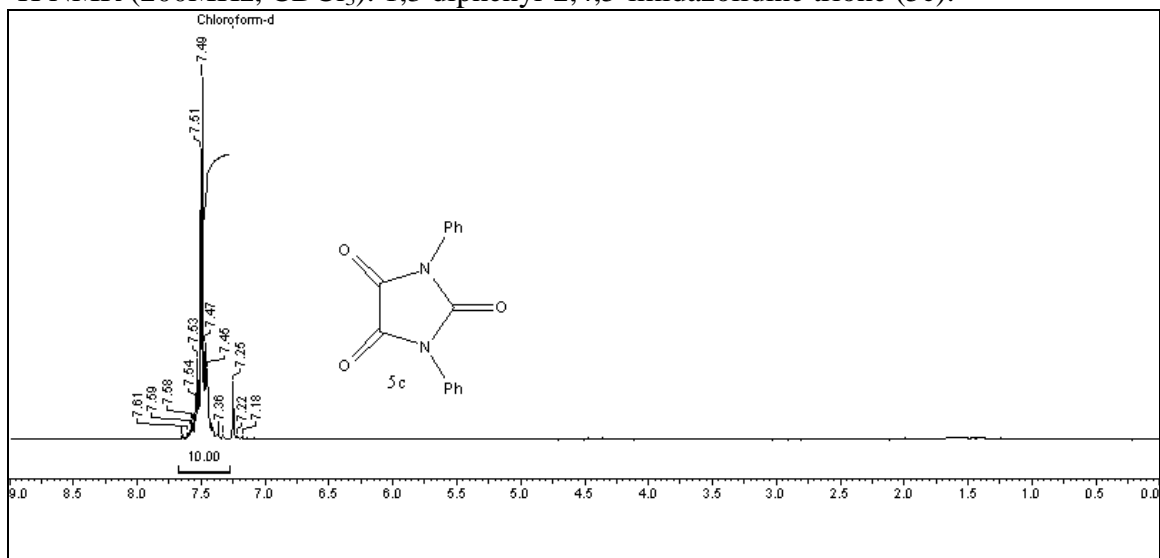
¹³C NMR (50MHz, CDCl₃): 1,3 diphenyl-2,4,5-imidazolidine trione (5c):
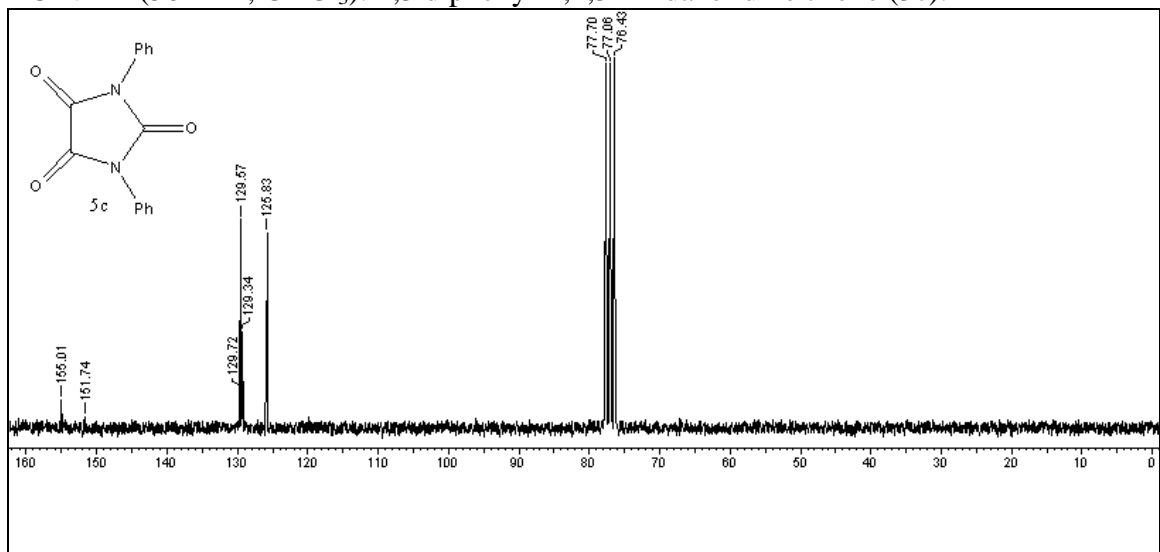
IR(KBr): 1,3 diphenyl-2,4,5-imidazolidine trione (5c):
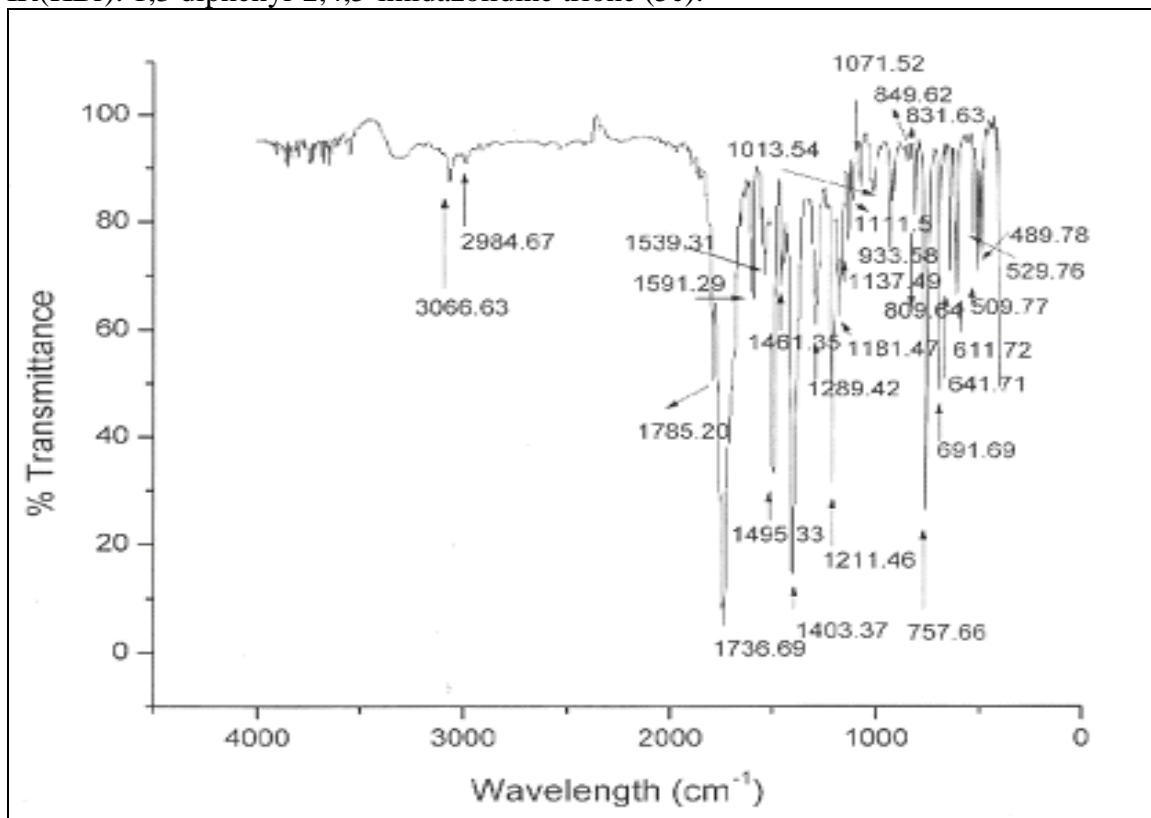
HRMS (EI, 70eV): 1,3 diphenyl-2,4,5-imidazolidine trione (5c):
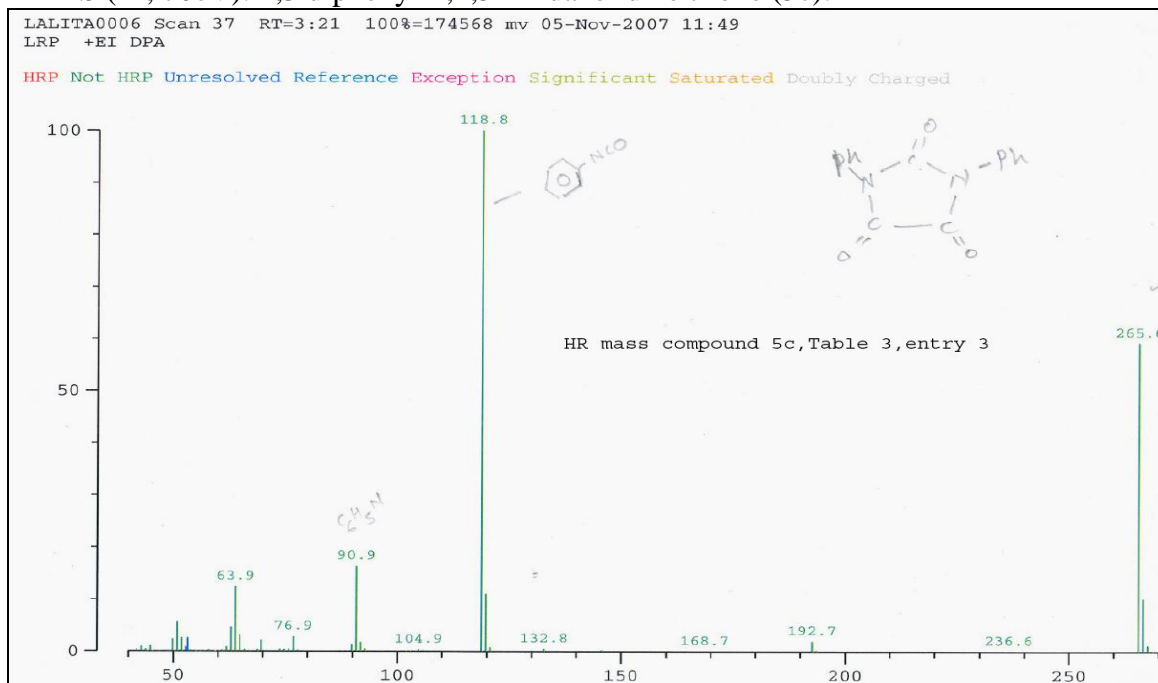
Ethyl N-(4-methylphenyl) carbamate (3d):

¹H NMR (200MHz, CDCl₃): Ethyl *N*-(4-methylphenyl) carbamate (3d)
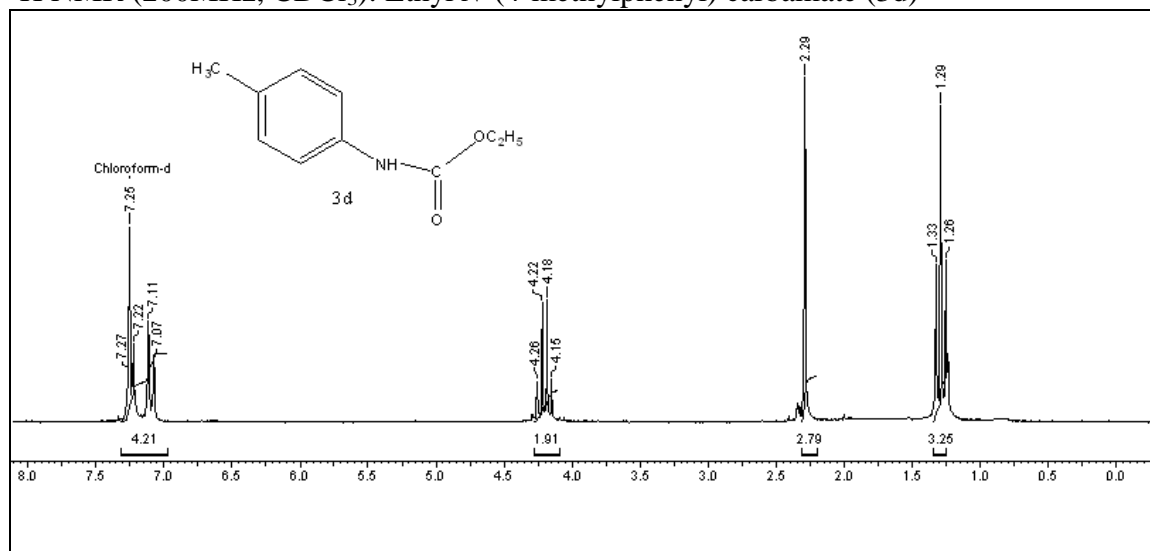
¹³C NMR (500 MHz, CDCl₃): Ethyl *N*-(4-methylphenyl) carbamate (3d)
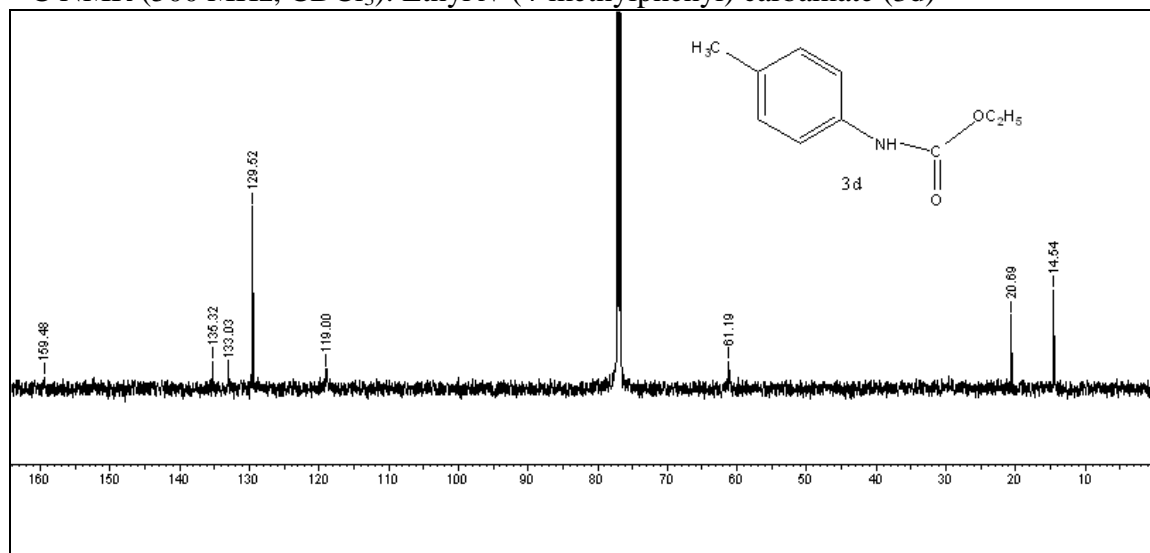
IR(CHCl₃): Ethyl *N*-(4-methylphenyl) carbamate (3d)
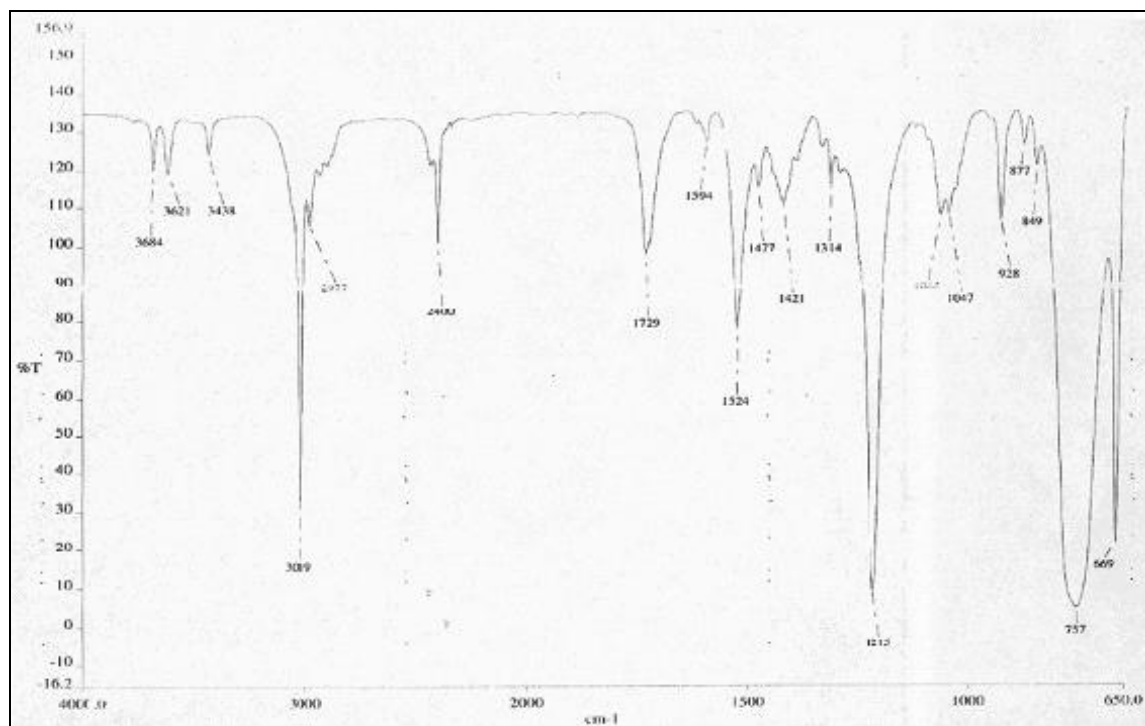
GC-MS (EI, 70eV): Ethyl *N*-(4-methylphenyl) carbamate (3d)
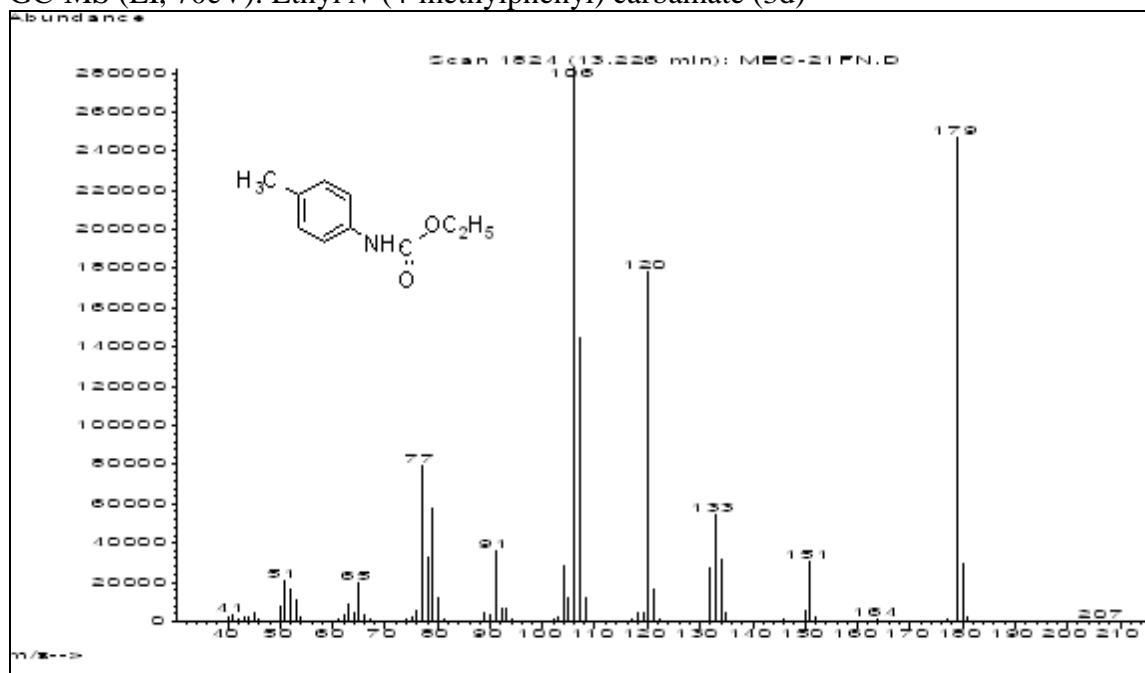
Ethyl N-(4-methylphenyl)oxamate (4d):

^{1}H NMR (500MHz,CDCl$_3$): Ethyl$N$-(4-methylphenyl)oxamate(4d)
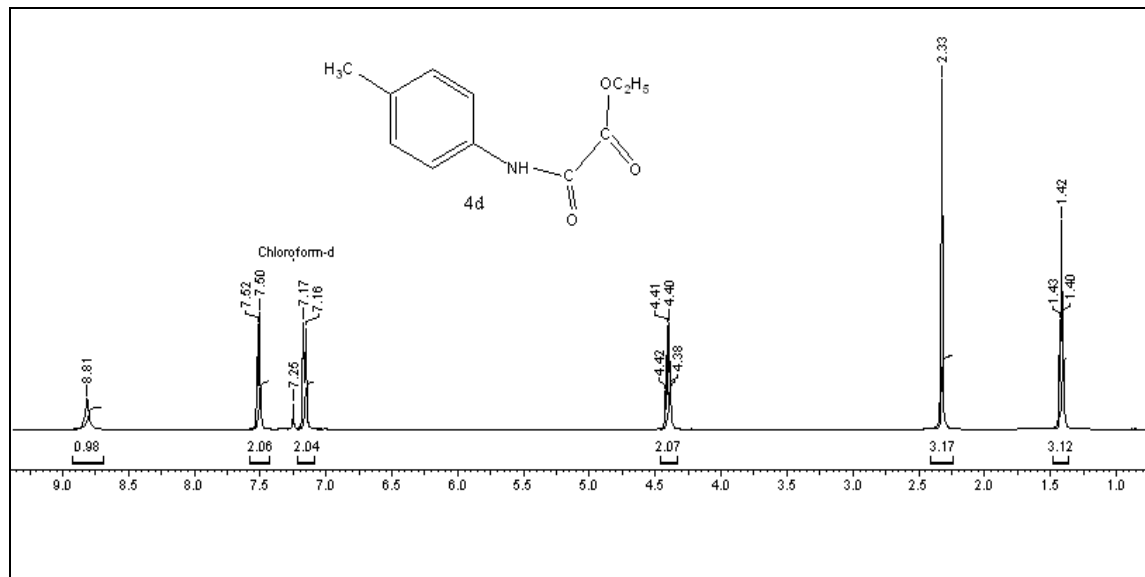
^{13}C NMR (50MHz, CDCl$_3$): Ethyl N-(4-methylphenyl) oxamate (4d)
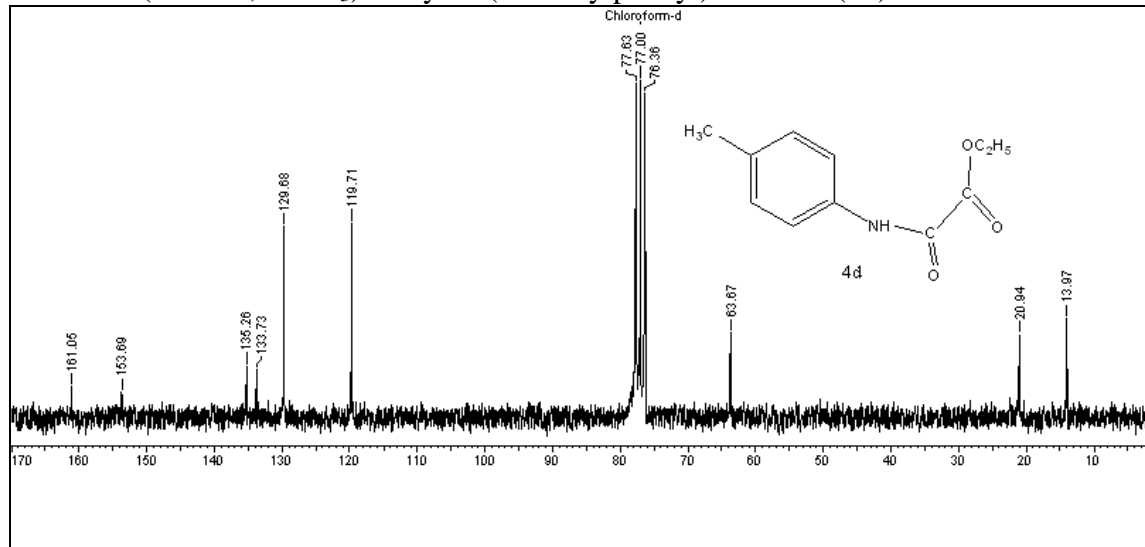
IR(KBr): Ethyl *N*-(4-methylphenyl)oxamate (4d)[3]
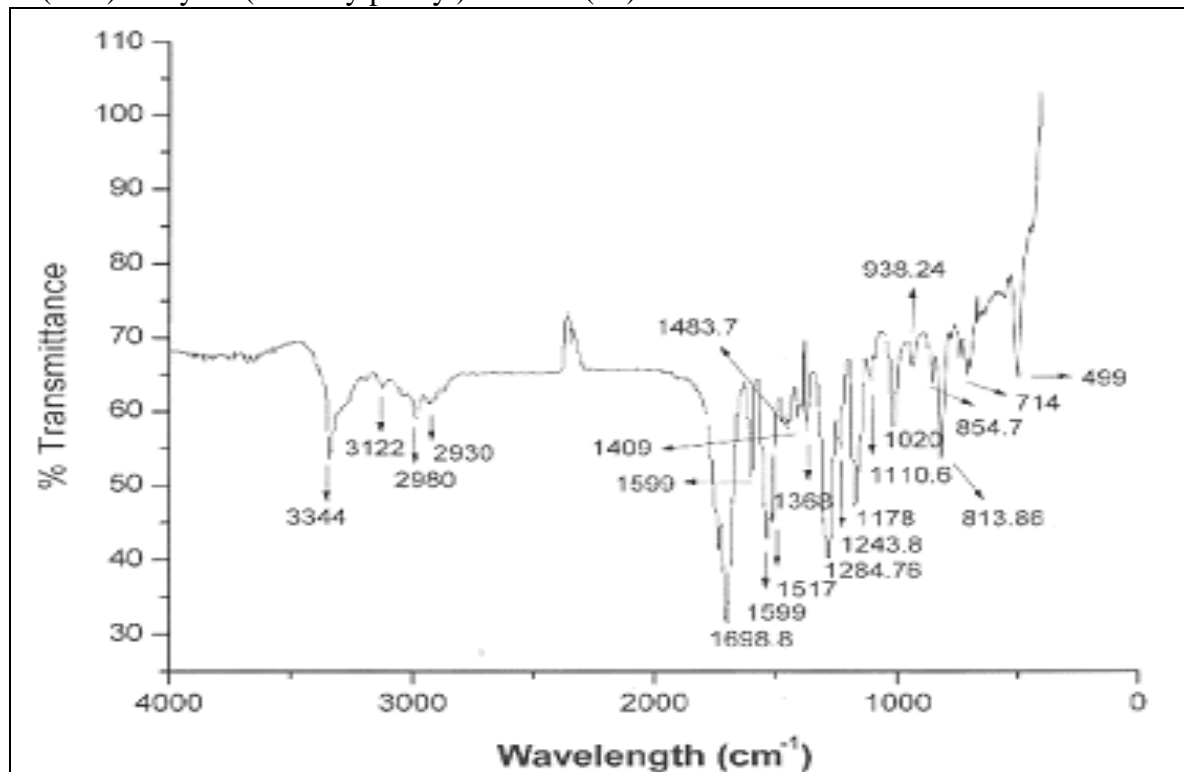
GC-MS (EI, 70eV): Ethyl *N*-(4-methylphenyl)oxamate (4d)
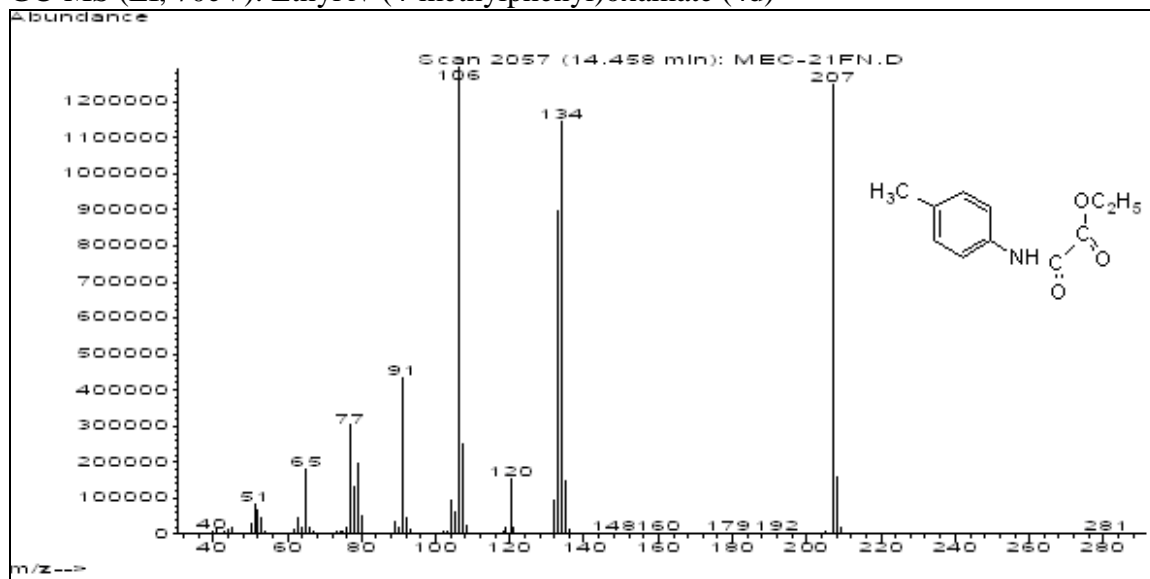
Ethyl N-(2-methoxyphenyl)carbamate (3e):

¹H NMR (200MHz, CDCl₃):Ethyl *N*-(2-methoxyphenyl)carbamate (3e)
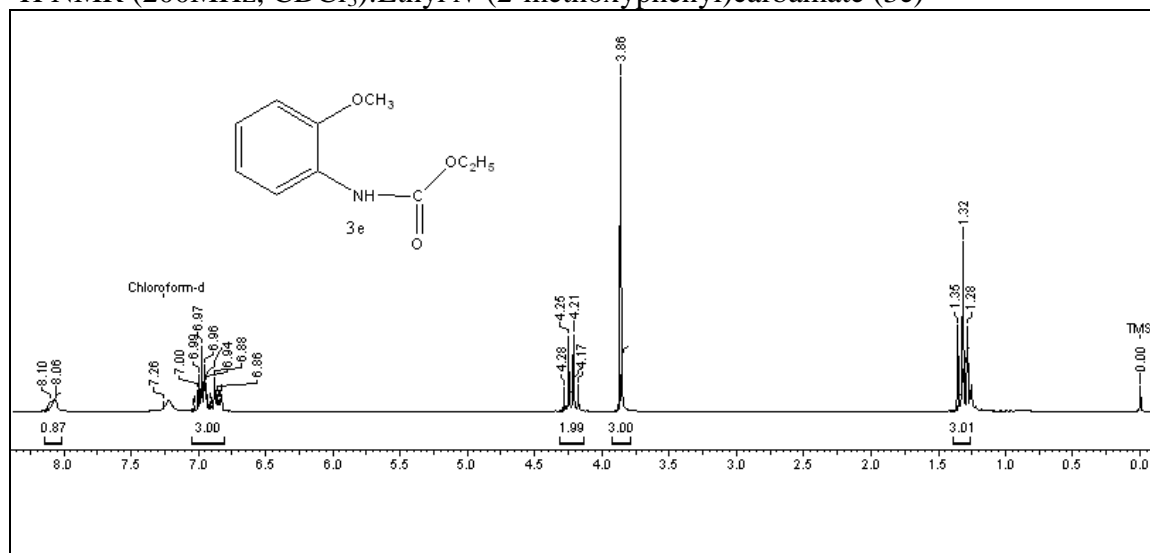
¹³C NMR (50MHz, CDCl₃): Ethyl *N*-(2-methoxyphenyl)carbamate (3e)
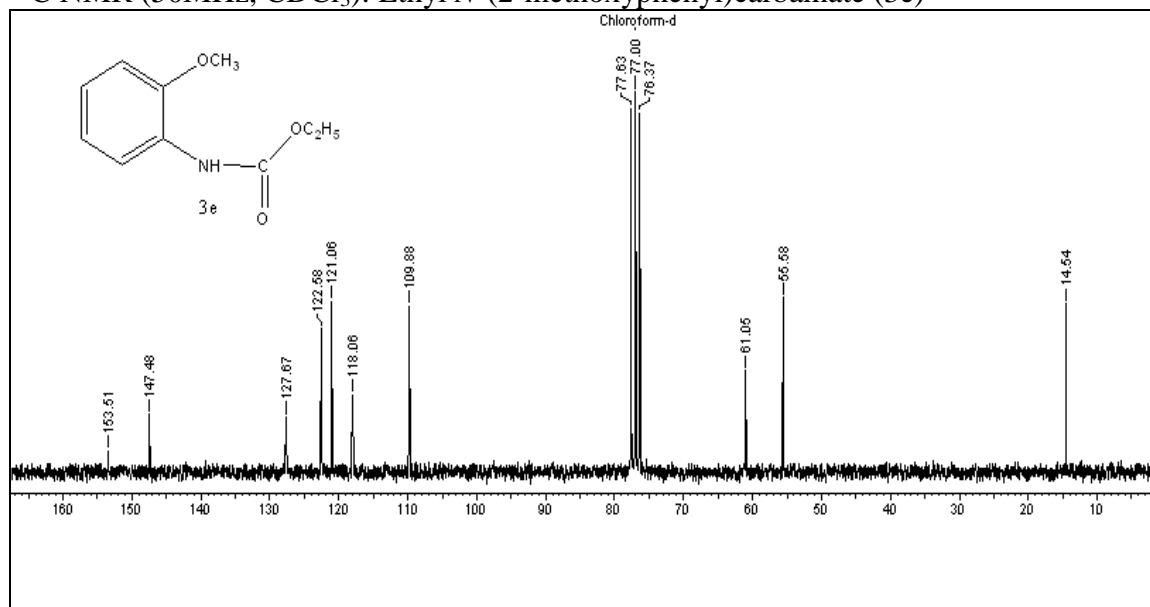
IR(KBr): Ethyl *N*-(2-methoxyphenyl)carbamate (3e)
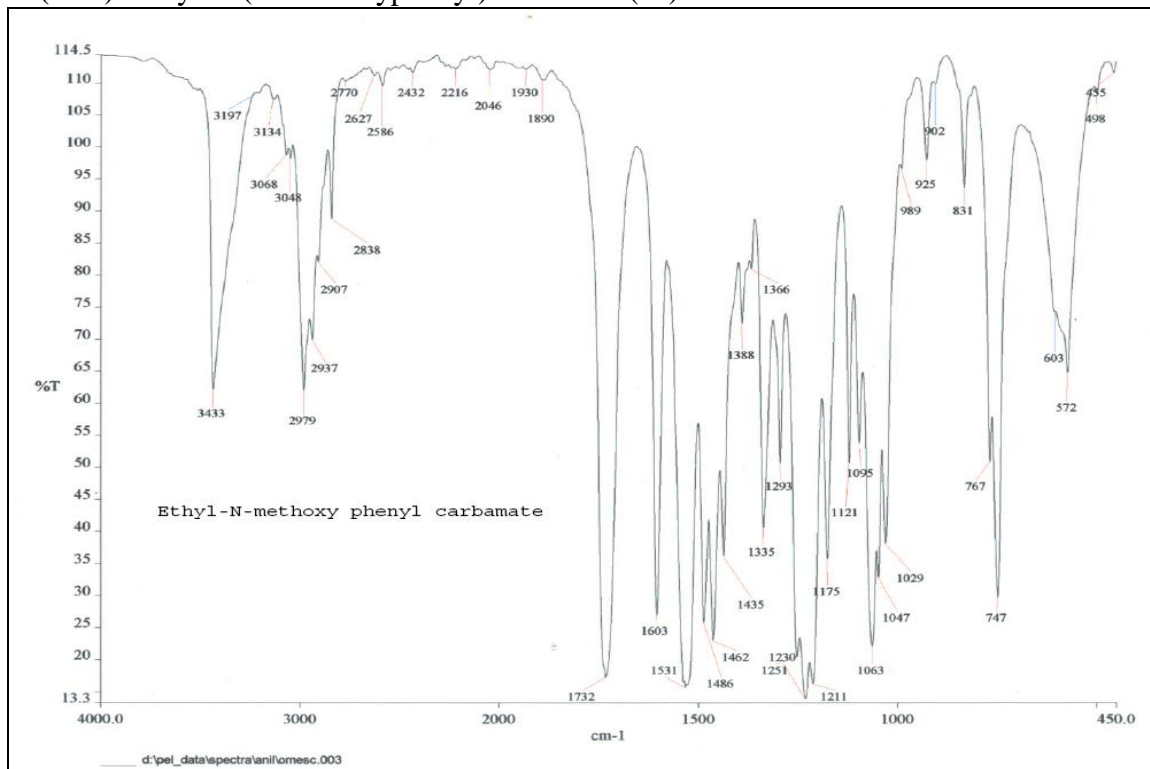
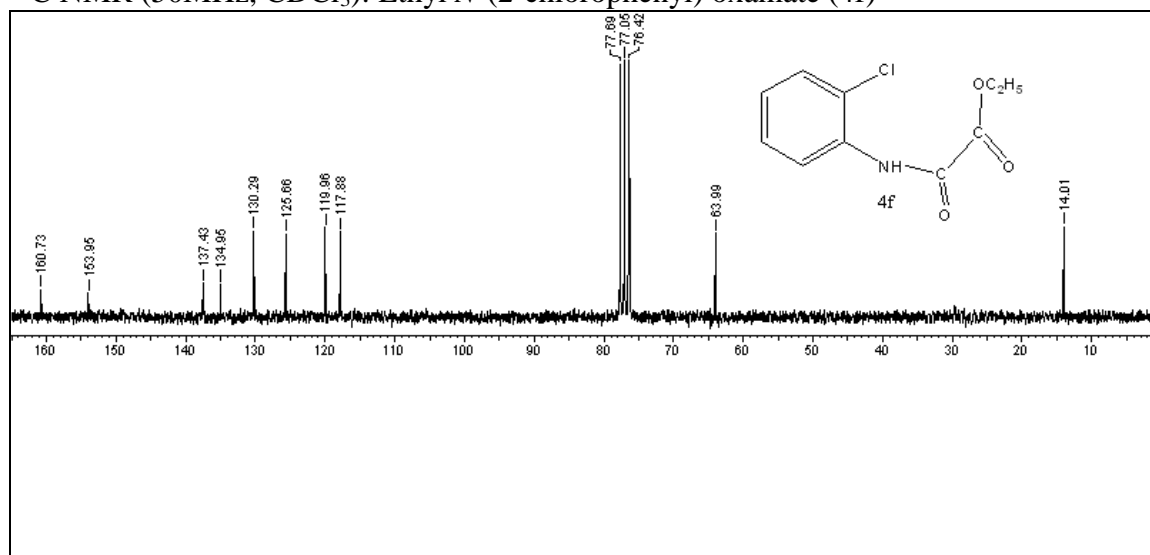GC-MS (EI, 70eV): Ethyl *N*-(2-methoxyphenyl) carbamate (3e)
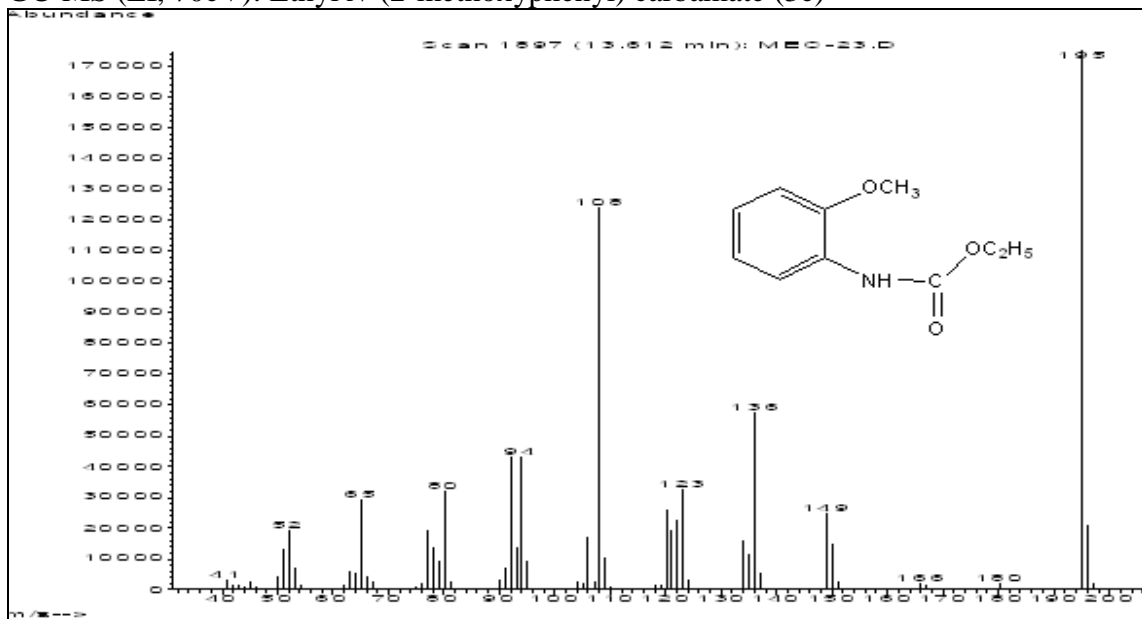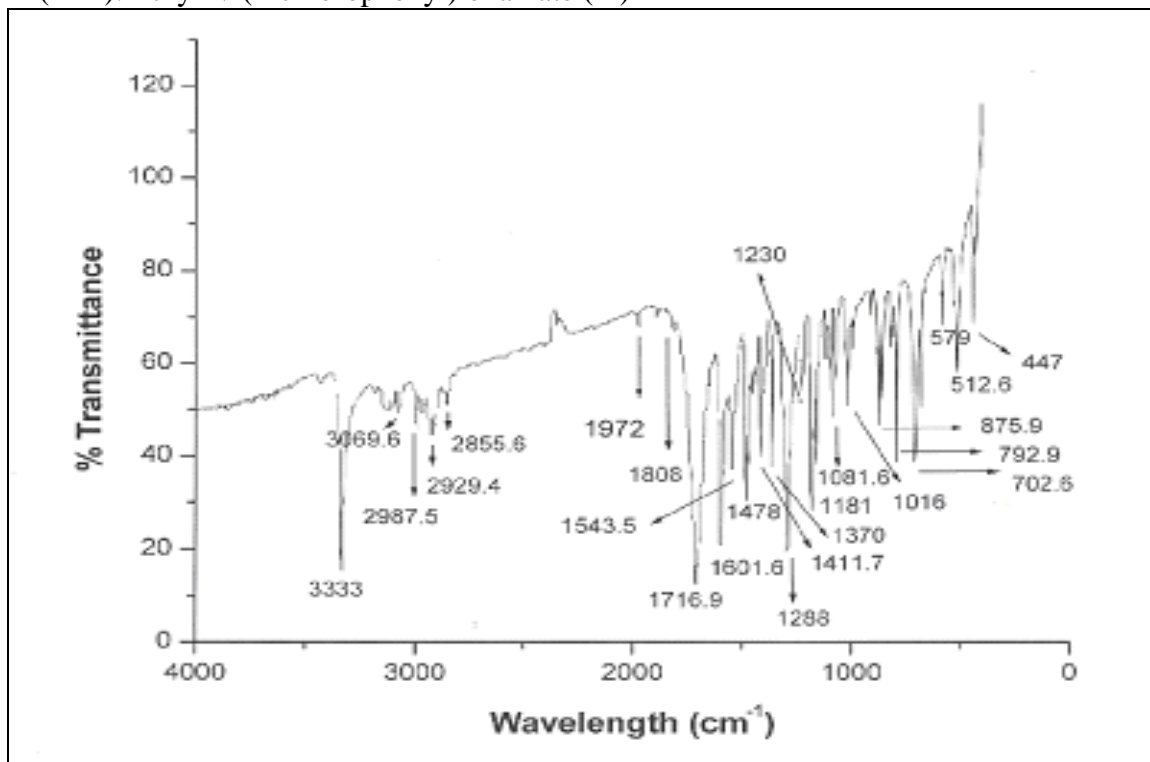
Ethyl N-(2-methoxyphenyl)oxamate (4e):
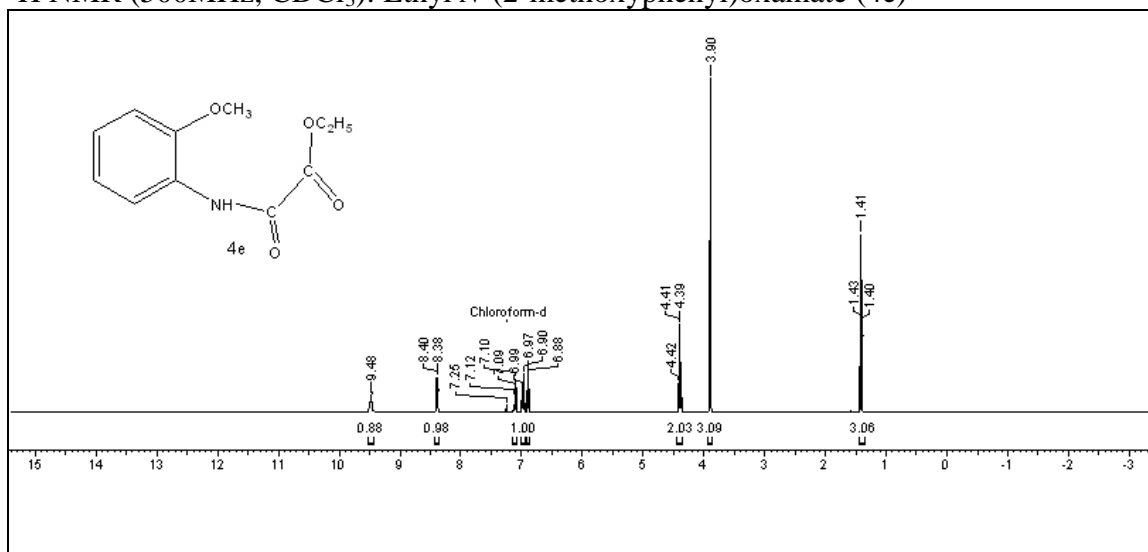
^{1}H NMR (500MHz, CDCl$_3$): Ethyl *N*-(2-methoxyphenyl)oxamate (4e)

^{13}C NMR (50MHz, CDCl$_3$): Ethyl *N*-(2-methoxyphenyl)oxamate (4e)

313
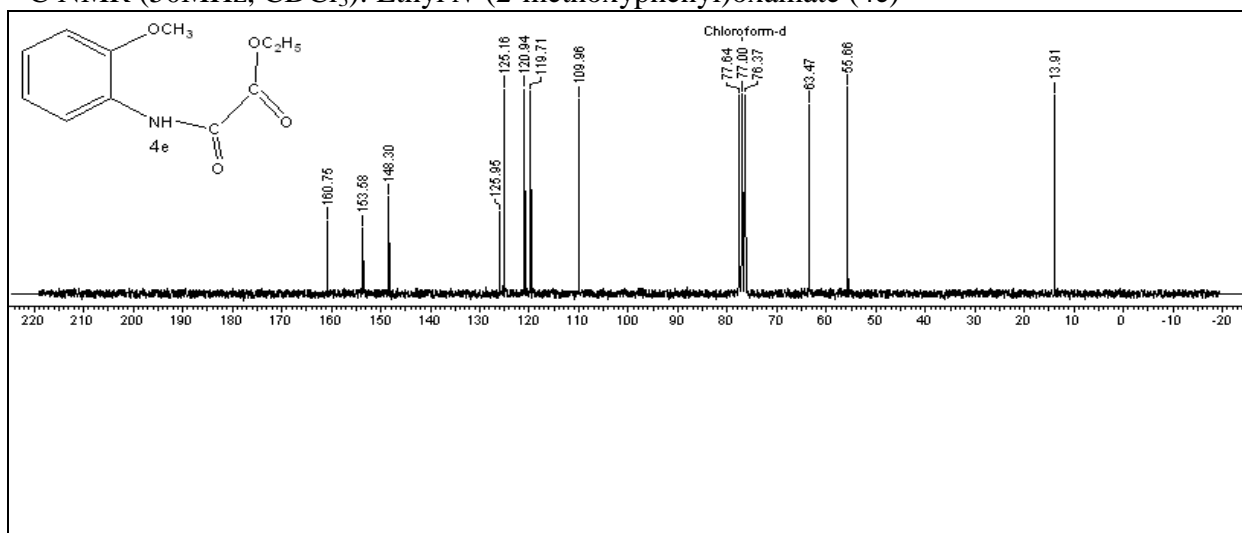
IR(KBr): Ethyl *N*-(2-methoxyphenyl)oxamate (4e)
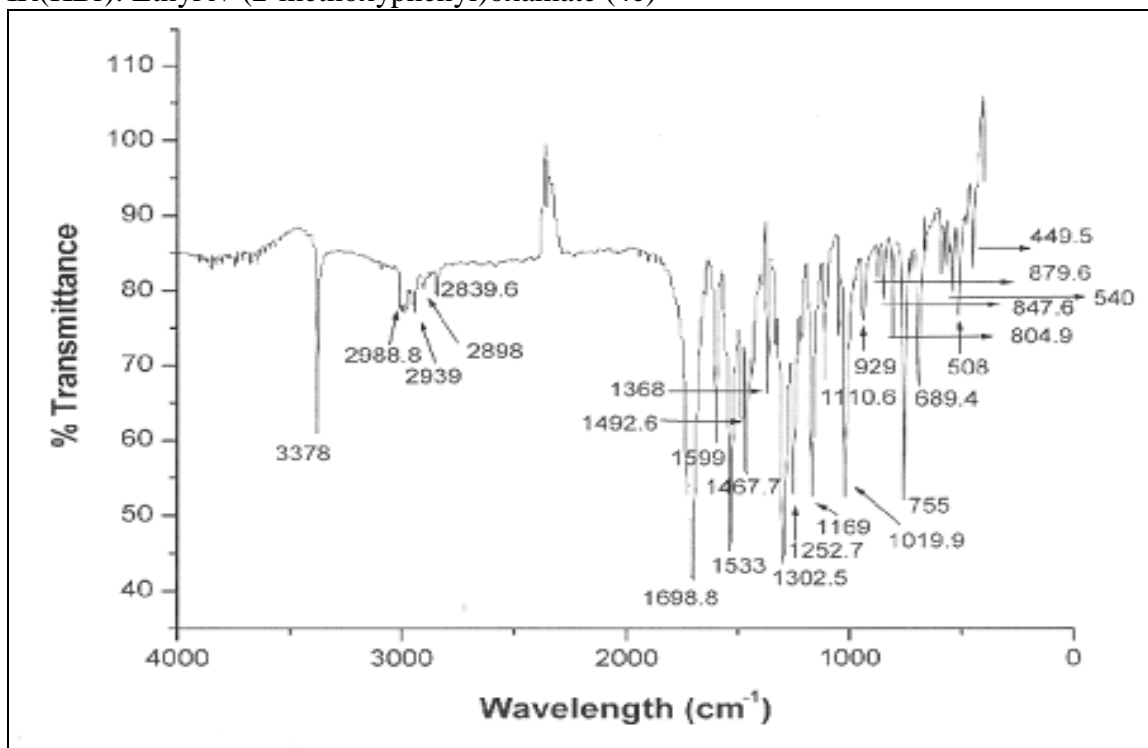
GC-MS (EI, 70eV): Ethyl *N*-(2-methoxyphenyl)oxamate (4e)
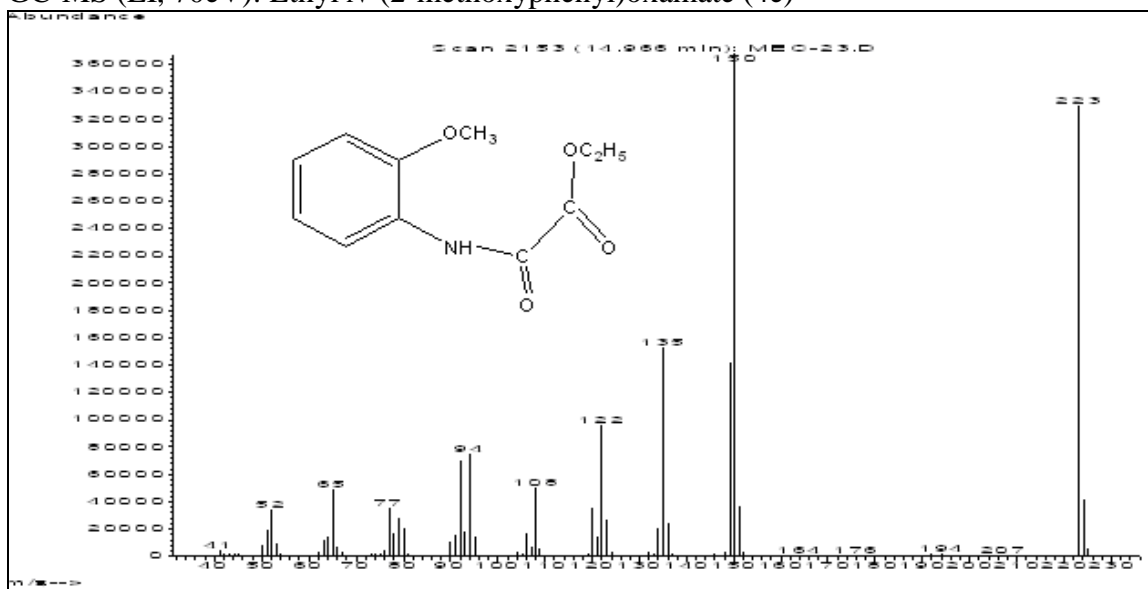
Ethyl N-(2-chlorophenyl)carbamate (3f):

^{1}H NMR (200MHz, CDCl$_3$): Ethyl *N*-(2-chlorophenyl) carbamate (3f)
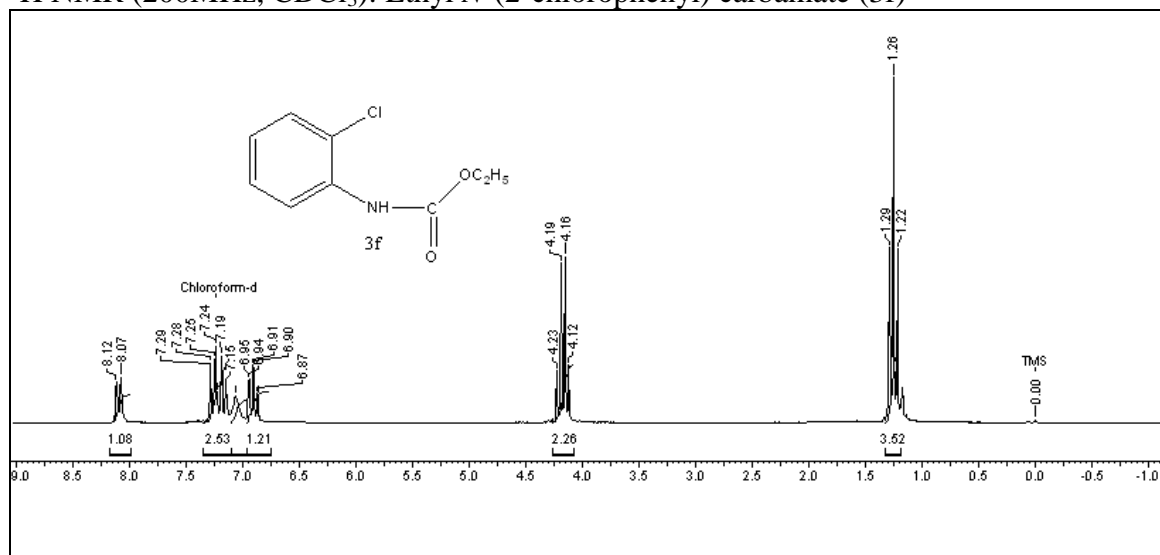
^{13}C NMR (50MHz, CDCl$_3$): Ethyl *N*-(2-chlorophenyl) carbamate (3f)
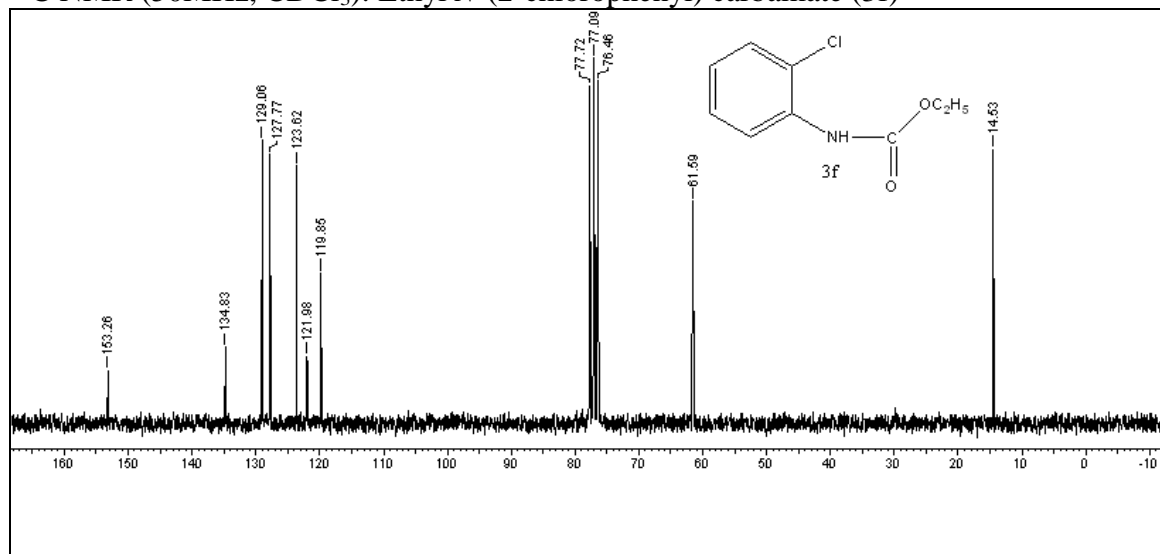
IR(KBr): Ethyl *N*-(2-chlorophenyl) carbamate (3f)
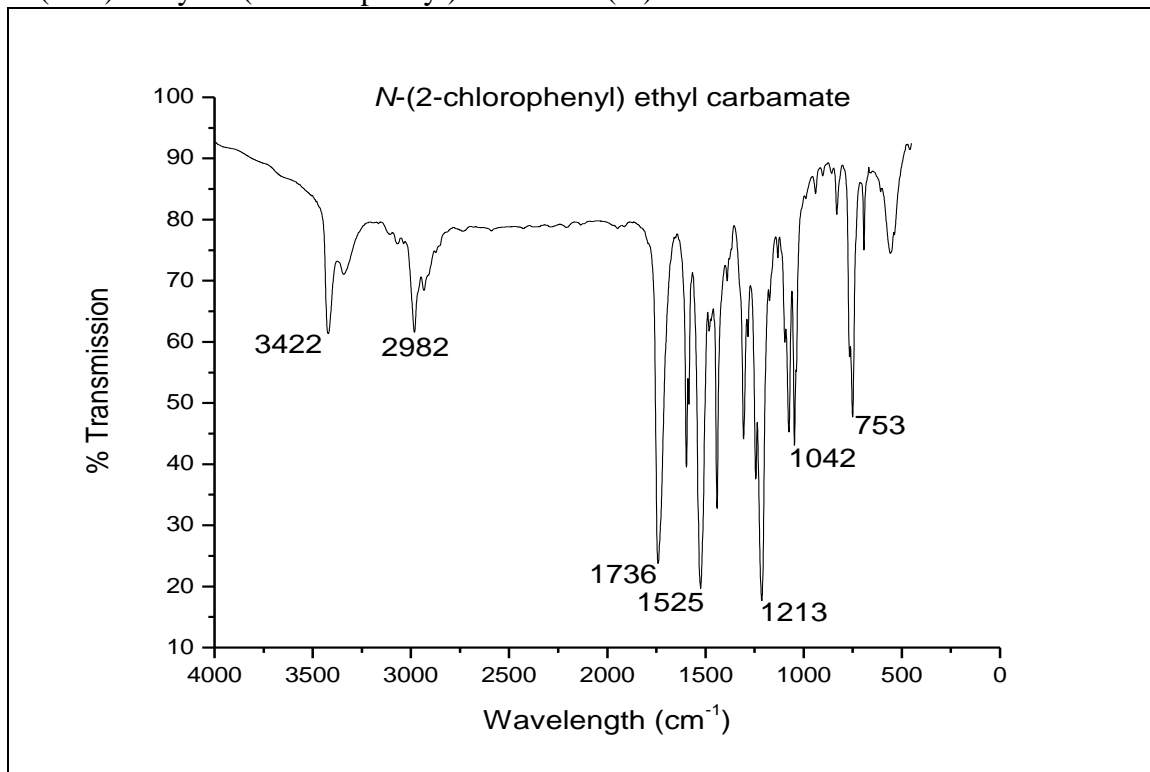
GC-MS (EI, 70eV): Ethyl *N*-(2-chlorophenyl) carbamate (3f)
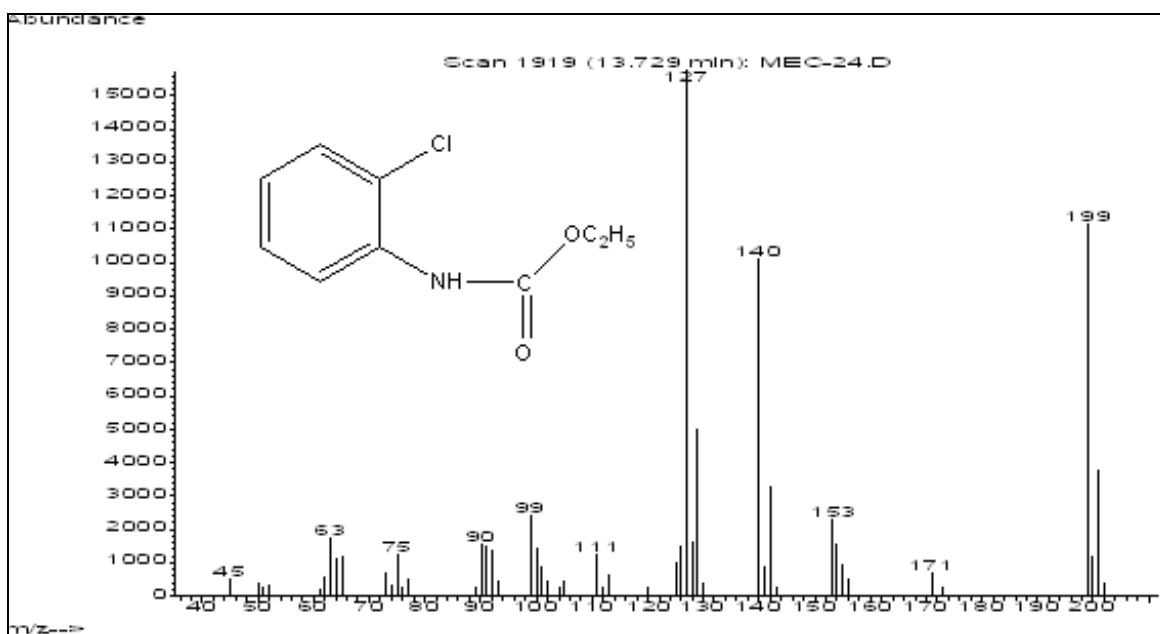
Ethyl N-(2-chlorophenyl)oxamate (4f):

^{1}H NMR (200MHz, CDCl$_3$): Ethyl *N*-(2-chlorophenyl) oxamate (4f)
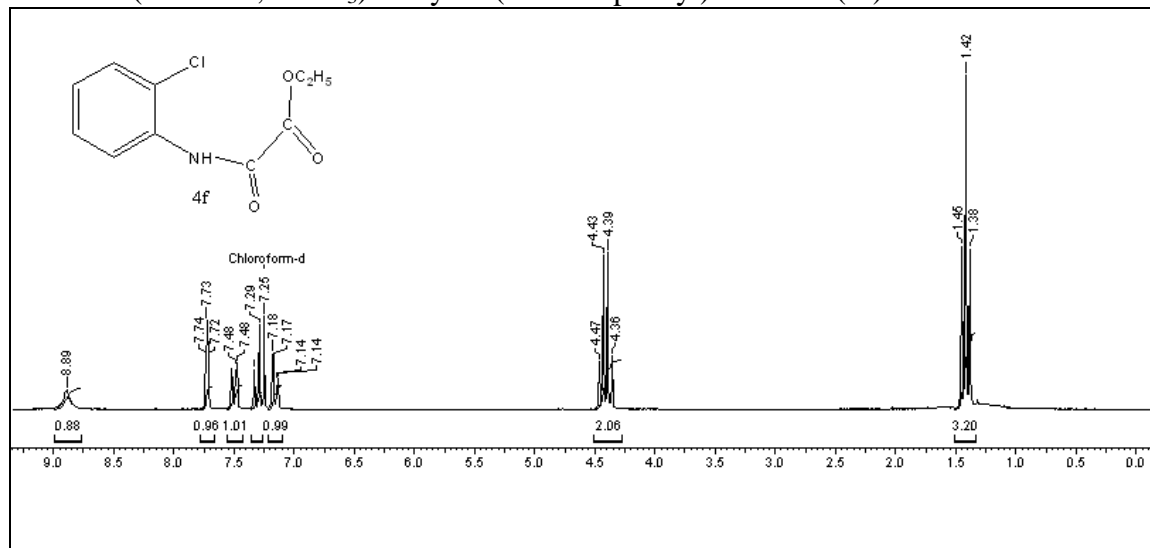
^{13}C NMR (50MHz, CDCl$_3$): Ethyl *N*-(2-chlorophenyl) oxamate (4f)

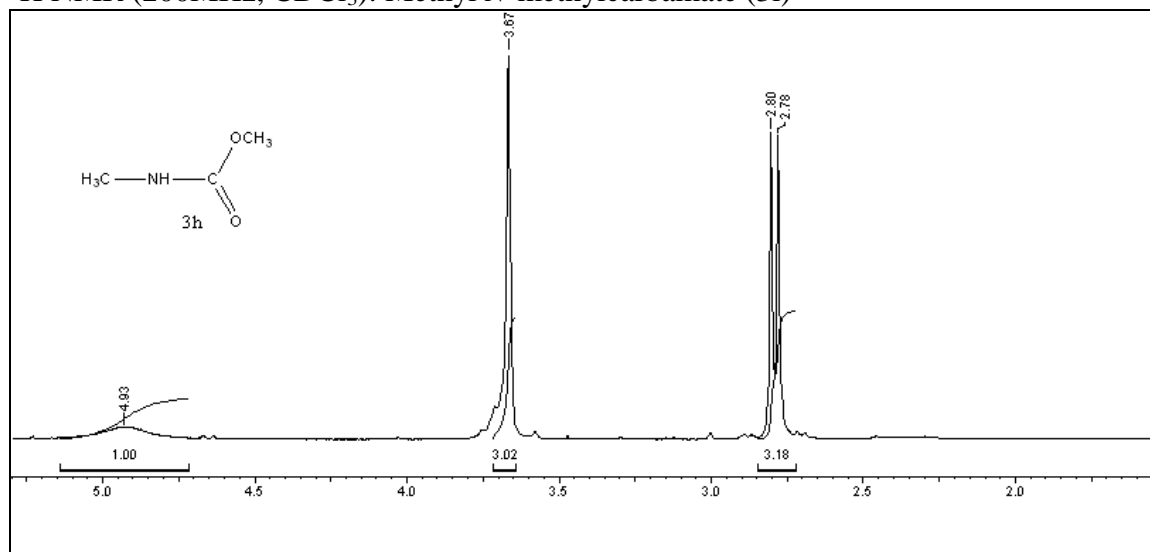IR(KBr): Ethyl *N*-(2-chlorophenyl) oxamate (4f)

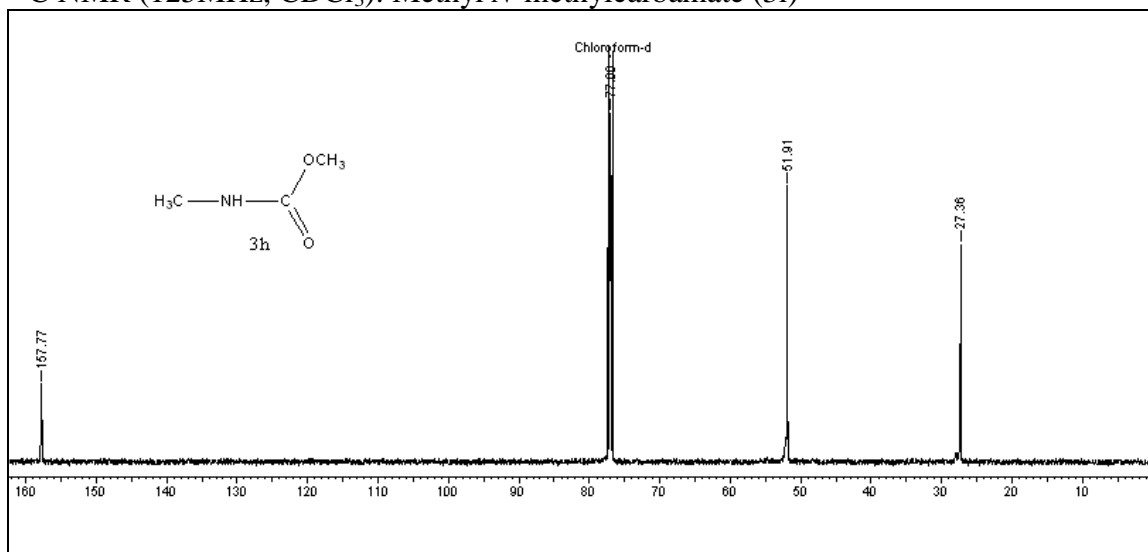GC-MS (EI, 70eV): Ethyl *N*-(2-chlorophenyl) oxamate (4f)
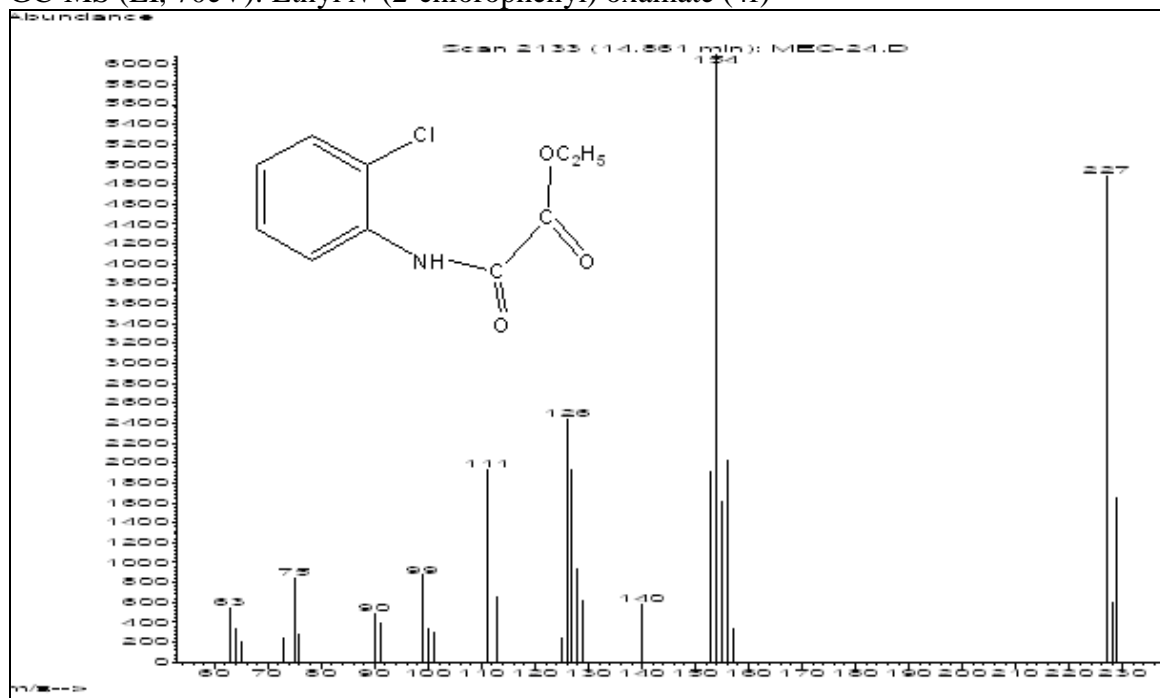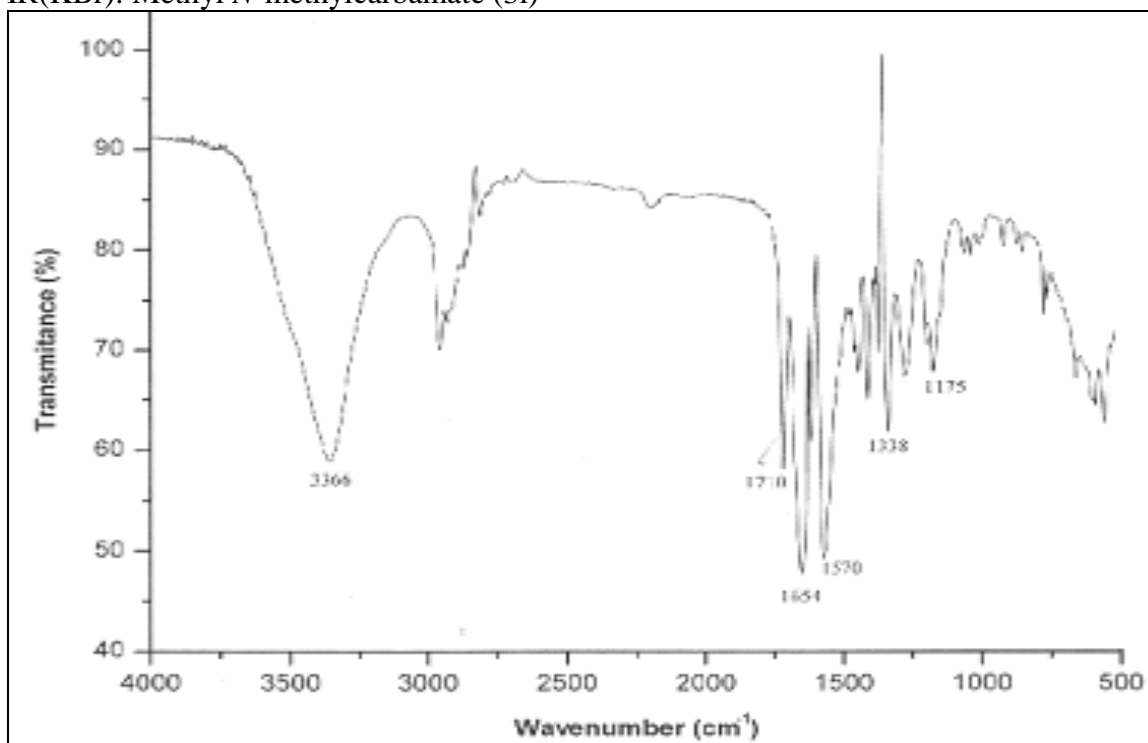

Methyl N-methylcarbamate (3i):

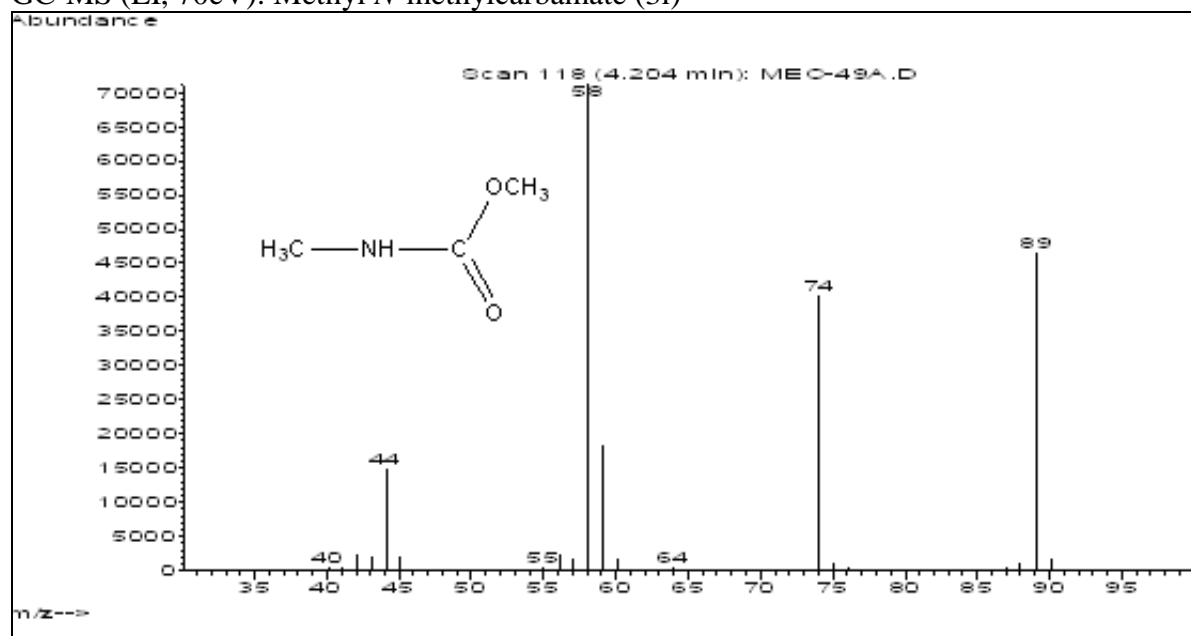^{1}H NMR (200MHz, CDCl$_3$): Methyl *N*-methylcarbamate (3i)

¹³C NMR (125MHz, CDCl₃): Methyl *N*-methylcarbamate (3i)

IR(KBr): Methyl *N*-methylcarbamate (3i)[1]
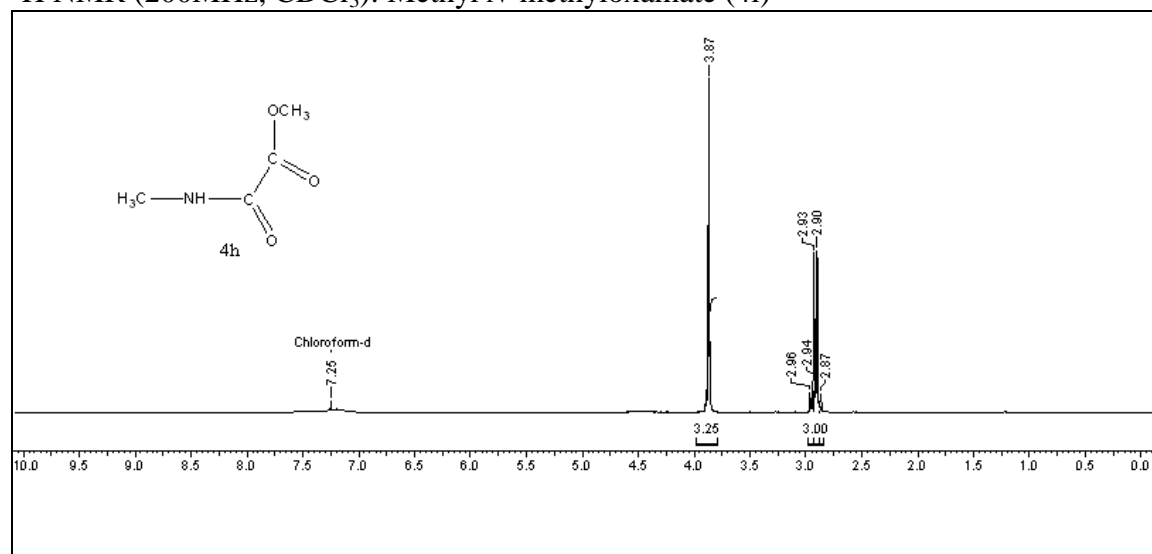
GC-MS (EI, 70eV): Methyl *N*-methylcarbamate (3i)

Scan 118 (4.204 min): MEC-49A.D
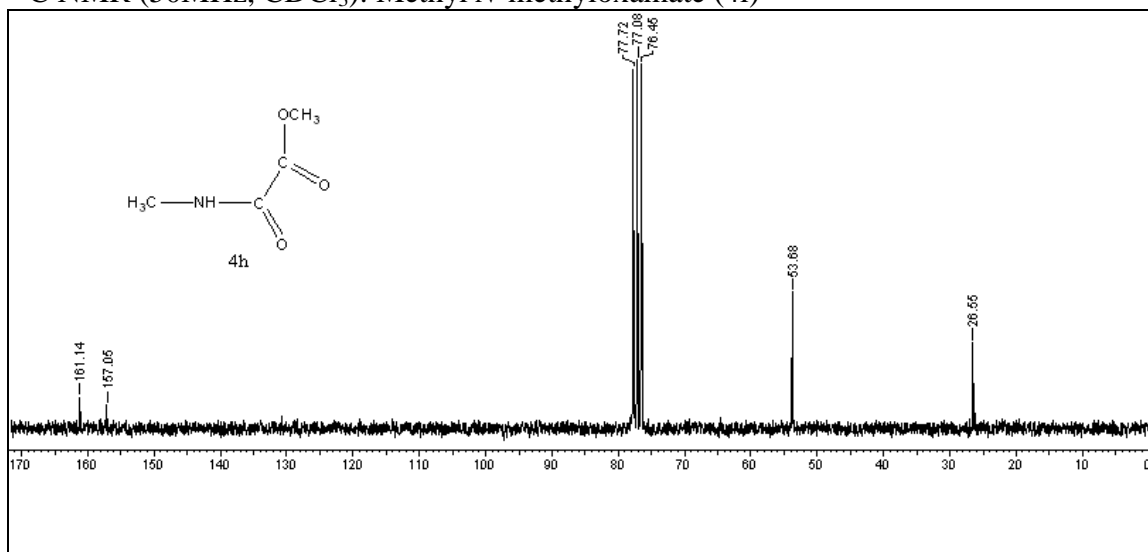
Methyl N-methyloxamate (4i):

^{1}H NMR (200MHz, CDCl$_3$): Methyl *N*-methyloxamate (4i)

¹³C NMR (50MHz, CDCl₃): Methyl *N*-methyloxamate (4i)

IR(CHCl₃): Methyl *N*-methyloxamate (4i)
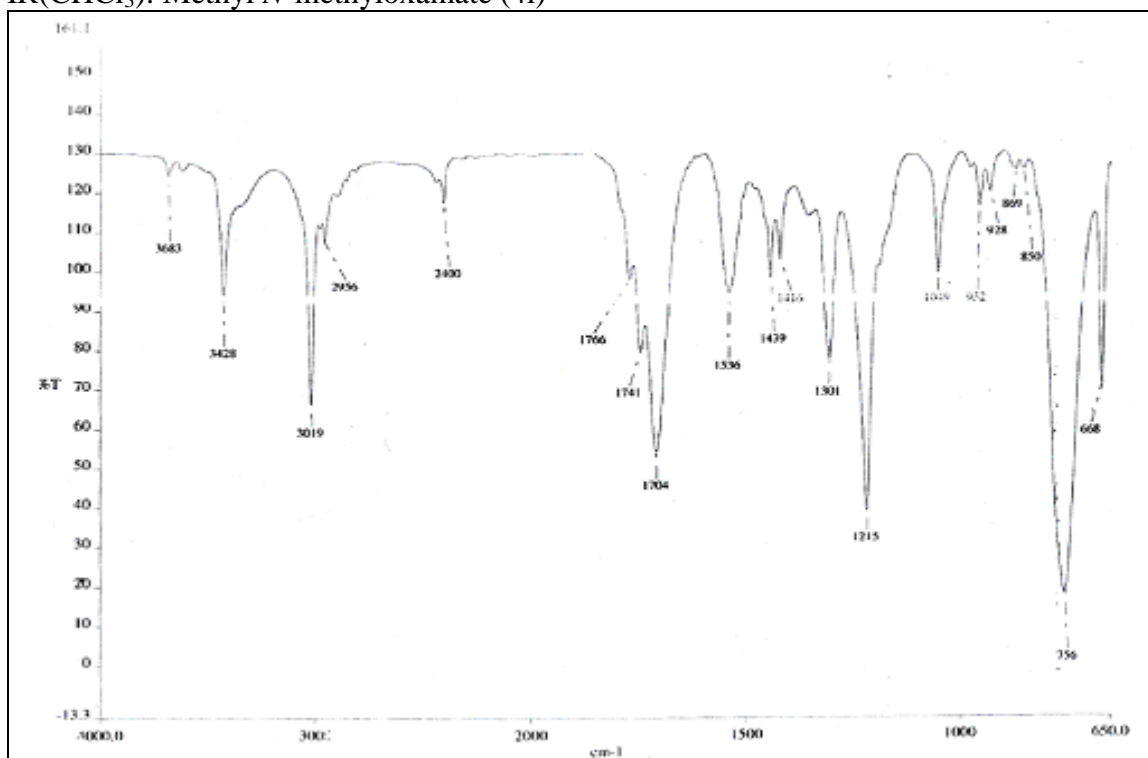
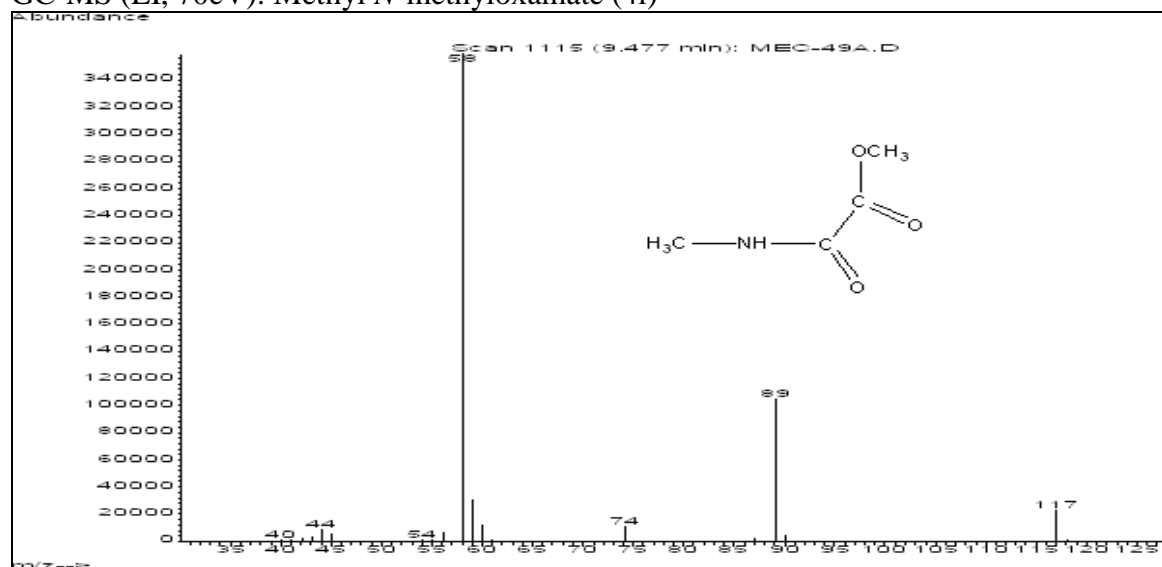GC-MS (EI, 70eV): Methyl *N*-methyloxamate (4i)

Diethyl iminodicarbonate (6):

^{1}H NMR (200MHz, CDCl$_3$): Diethyl iminodicarbonate (6)
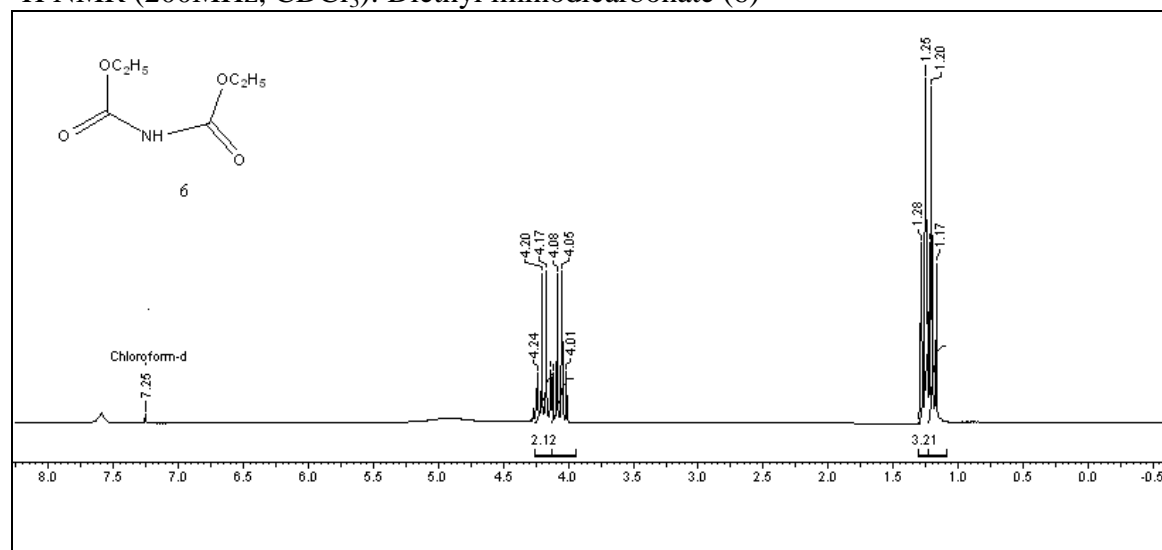
^{13}C NMR (50MHz, CDCl$_3$): Diethyl iminodicarbonate (6)
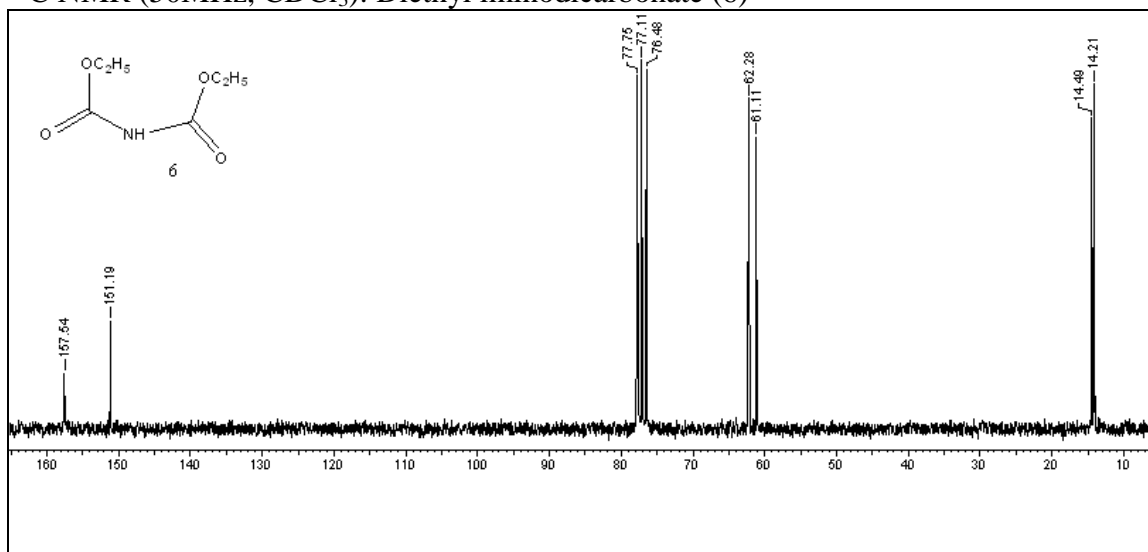
IR(KBr): Diethyl iminodicarbonate (6)
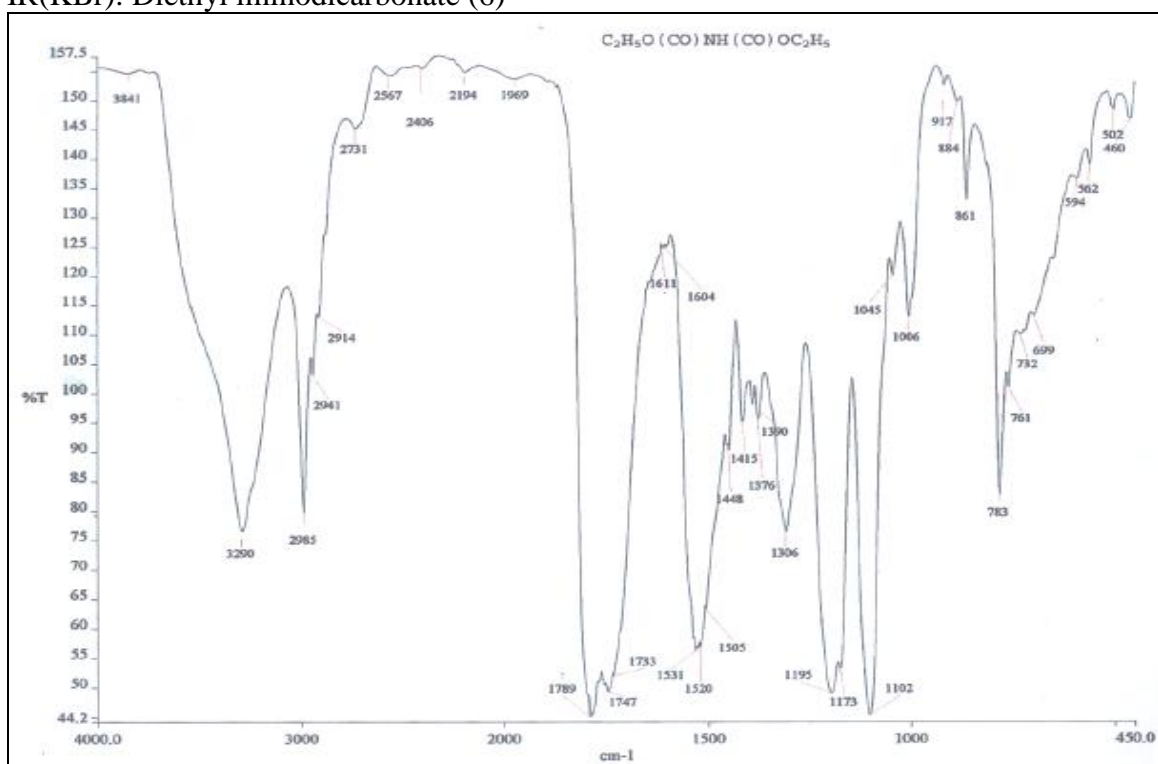
GC-MS (EI, 70eV): Diethyl iminodicarbonate (6)

File   : C:\MSDCHEM\1\DATA\SAMPLE\NIMT\MEC51F.D
Operator : savita
Acquired : 11 Apr 2008 15:18   using AcqMethod LALITA
Instrument :   Instrumen
Sample Name: lalita
Misc Info :
Vial Number: 22
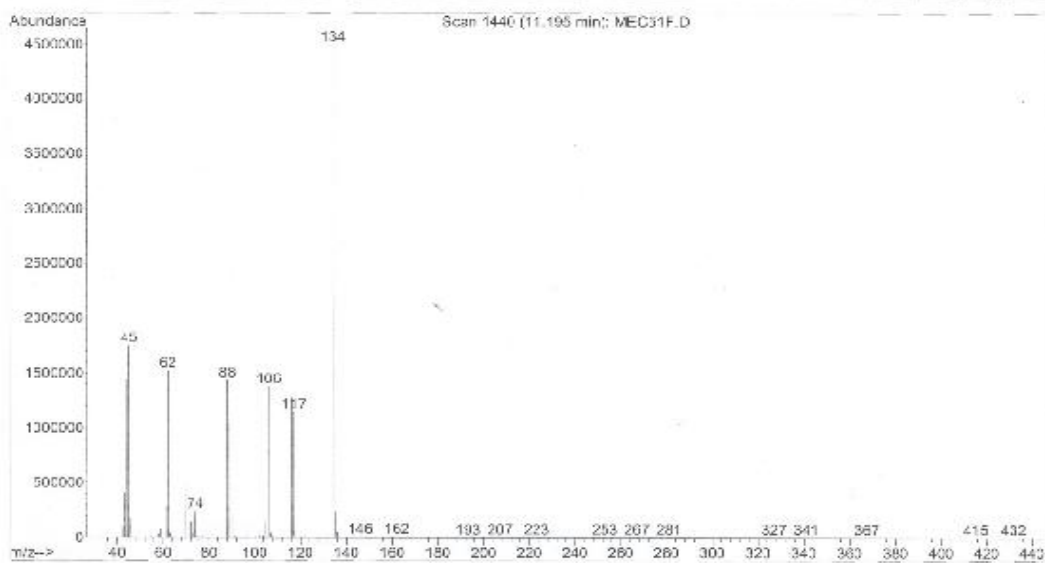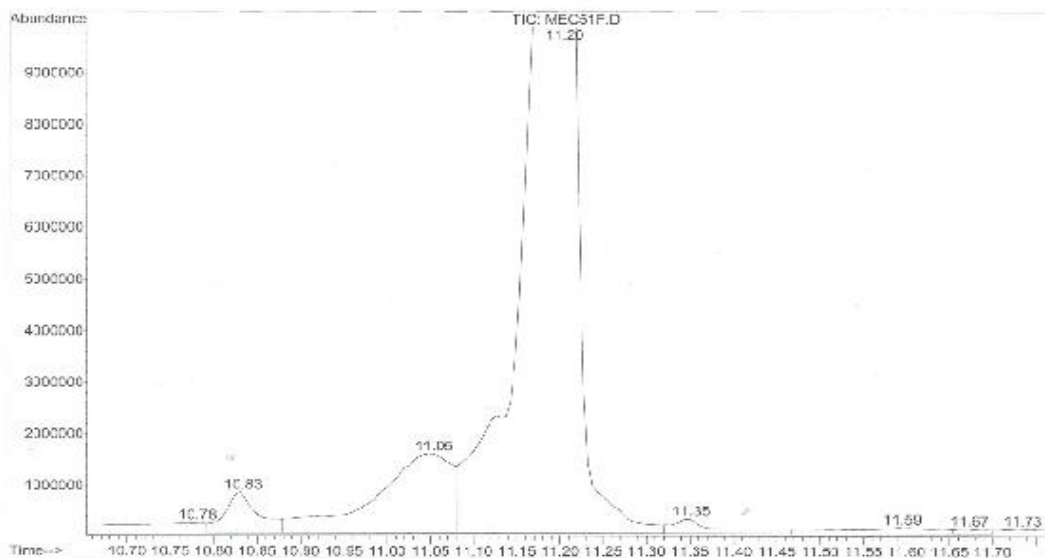
Alloxan (7):
GC-MS (EI, 70eV): Alloxan (7)
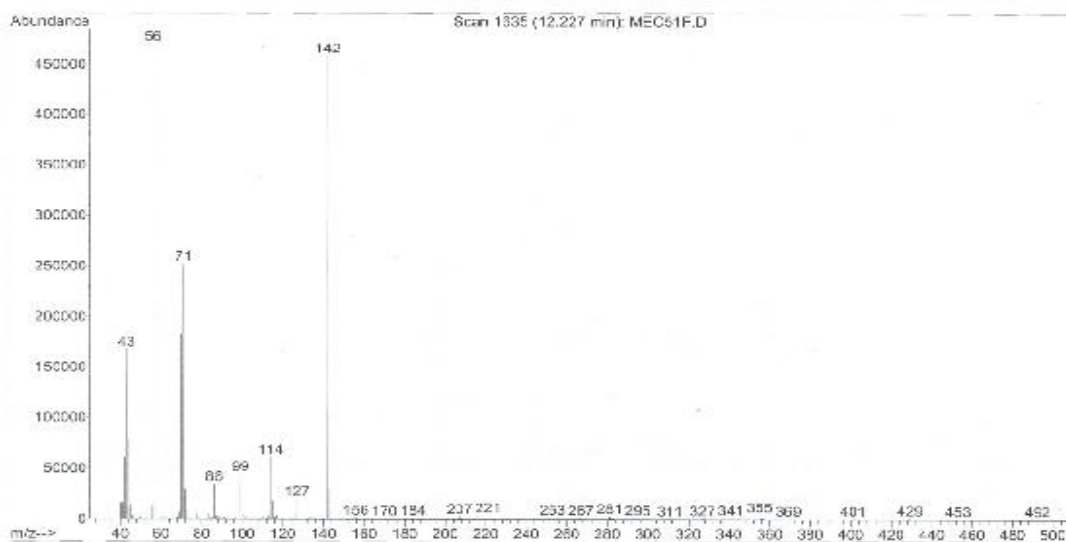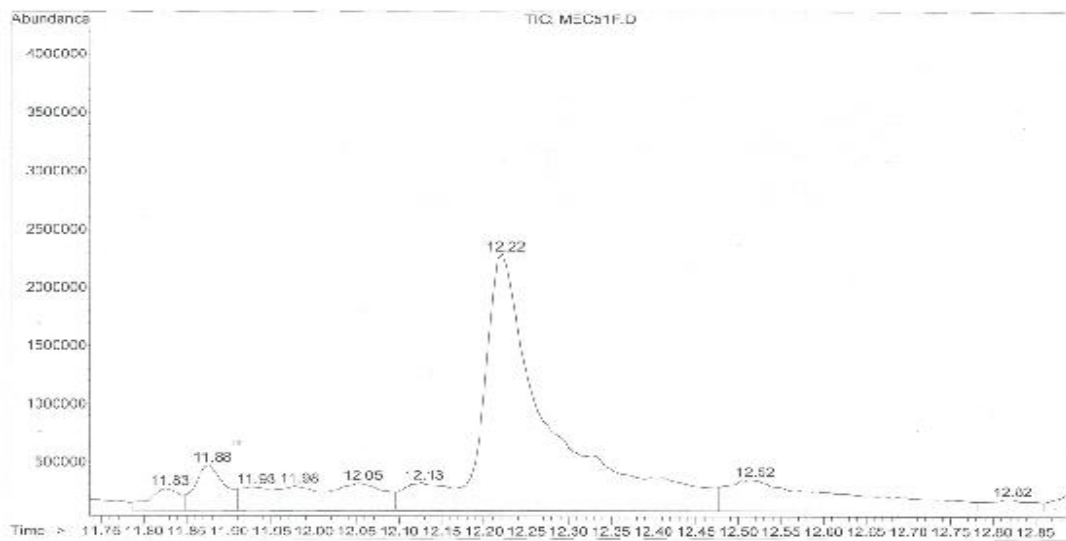
Diethyl carbonate (8):
GC-MS (EI, 70eV): Diethyl carbonate (8)
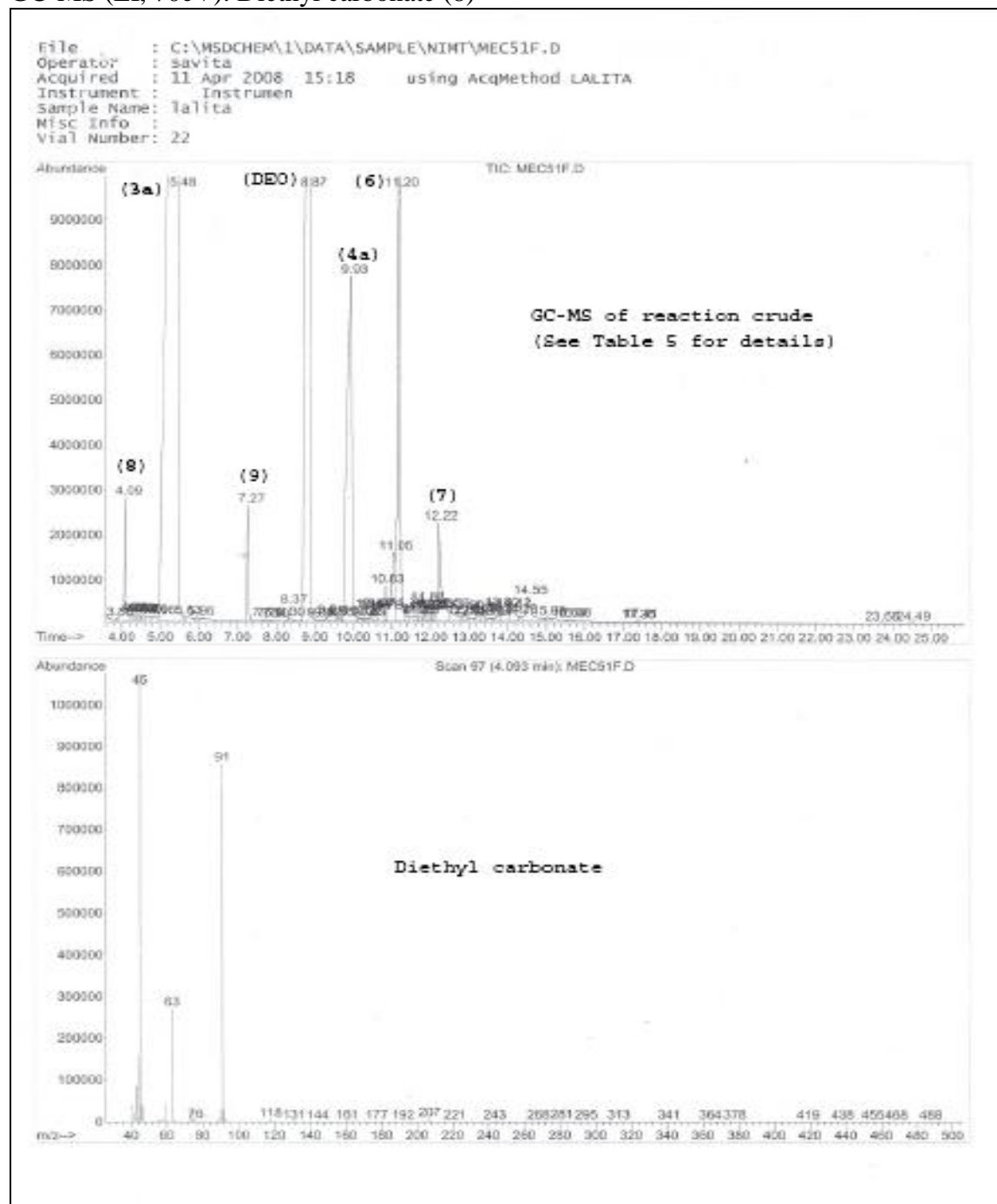
N1,N2-bis(2-chlorophenyl)oxalamide (10)

GC-MS (EI, 70eV): N^1,N^2-bis(2-chlorophenyl)oxalamide (10)
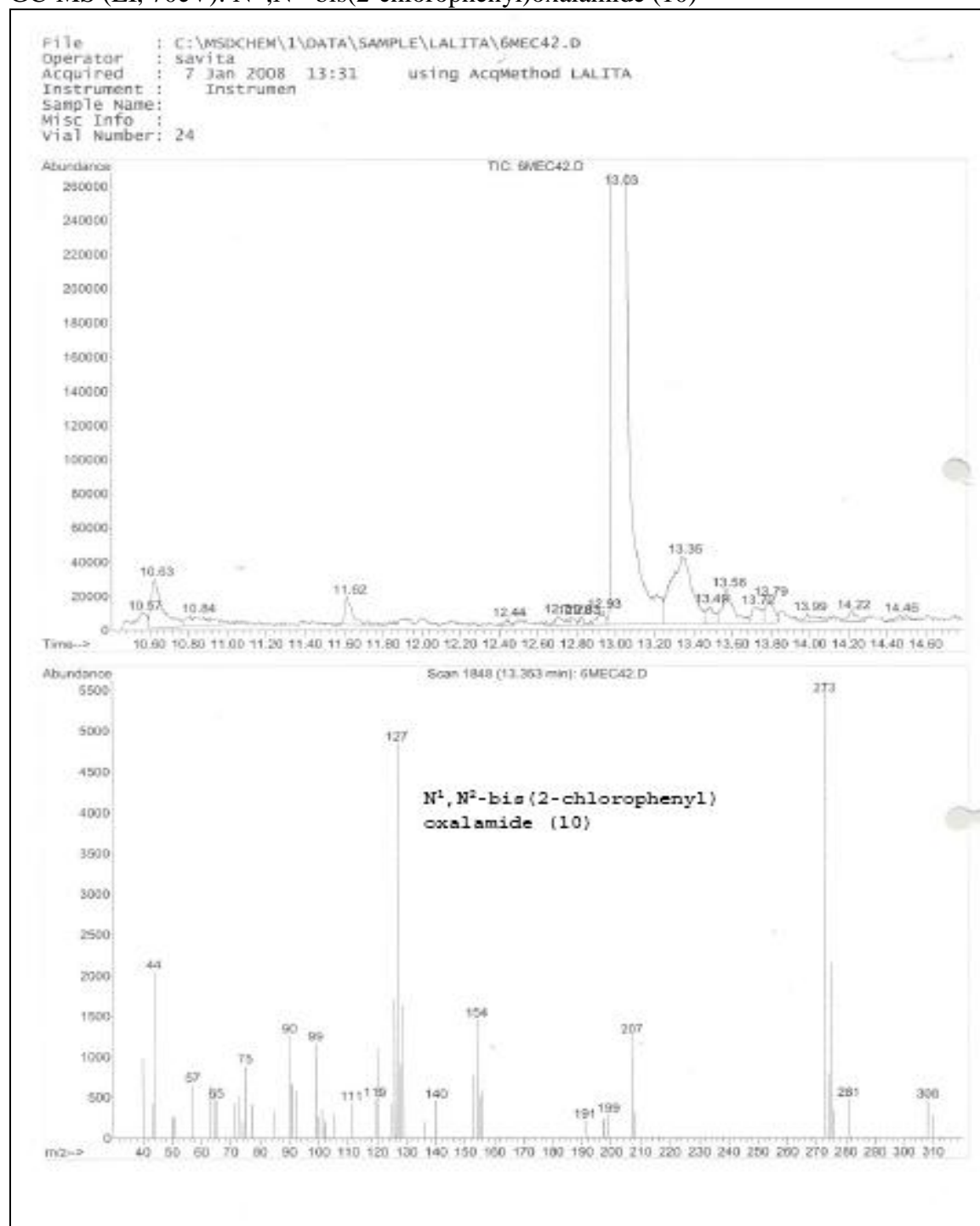
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[1] A. B. Shivarkar, S. P. Gupte, R. V. Chaudhari, J. Mol. Catal. A: Chemical, 2004, *22,* 385–
  92.
[2] I. Yavari, M. Bayat, Syn. Commun. 2002, 32, 2527 – 2534.
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Section D

Immobilized Ionic Liquid Catalyzed O-alkylation

of Phenol by DMC
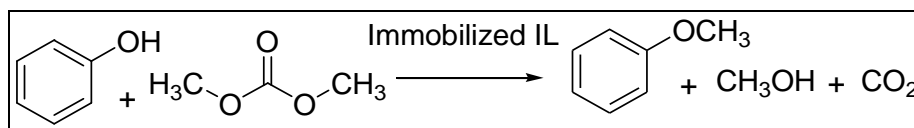
6.1. INTRODUCTION

Friedel Craft reactions are important from both industrial and academic point of view. Aryl methyl ethers obtained by Friedel Craft alkylation of phenol are valuable intermediates and find application in preparation of dyes, pesticides, agrochemicals, fragrances[1], as a raw material for manufacture of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, surface active agents, rubber chemicals, antioxidants, fungicides, petroleum additives, UV absorbers and heat stabilizers for polymeric materials.[2-5]

In majority of the processes the common practice is to use stoichiometric reagents for the alkylation procedure. Alkylation of phenol is carried out employing DMS[6-9,] alkyl halides[10-15] as alkylating agent in liquid phase. These reagents are toxic, needs stoichiometric amounts of base, generate salt waste along with cumbersome recovery and separation procedure. In the past decade chemical industry has experienced emphasis on the replacement of chemical processes generating undesirable inorganic salt wastes by those processes that are reagent based, clean / green with innovative technology that utilizes environmentally benign reagents. So there is need to replace these stoichiometric reagents with catalytic ones wherein heterogeneous catalyst is favored to achieve these conversions. Research in this area has revealed DMC as a versatile compound that replaces methyl halides/ Dimethyl sulphate/ phosgene for methylation and carbonylation reactions respectively. DMC is viewed as potent candidate for the replacement of such toxic reagents. Table 6.2[16] gives a comparison of major environmental benefits between DMC and phosgene/DMS based reactions.

Taking into account the tunable reactivity of DMC with variety of nucleophiles[17]; DMC was chosen as methylating agent for alkylation of phenol. Another fact that makes DMC as a choice for methylating agent is that the DMC mediated methylations are catalytic and irreversible as CO_2 and methanol formed as by product during the course of reaction are in gaseous phase . DMC is environmentally benign due to non toxic nature, behaves as selective and efficient methylating agent and generates methanol as co product which can be recycled for DMC synthesis. Alkylation of

various nucleophilic substrates such as phenols, 1° amines, thiols, sulfones and methylene active derivatives were accomplished readily with DMC.

Table 6.1. Comparision of DMC and phosgene/DMS based reactions.

Phosgene or DMS	DMC
Dangerous reagent (toxic, corrosive)	Harmless reagent (non-toxic, non-corrosive)
Use of solvent	No solvent
Waste water treatment	No waste water
Base consumption (e.g.NaOH)	The base is catalytic
By-products: NaCl, Na_2SO_4	By-product: MeOH, CO_2
Exothermic	Slightly or not exothermic

DMC is a unique molecule having versatile reactivity.[18] It has two carbon centers at which a nucleophile can attack: the carbonyl and methyl group. DMC can replace phosgene as a source for carbonic acid derivative by affording methoxycarbonyl product via nucleophilic attack at carbonyl carbon of DMC. Further DMC can replace DMS and MeX as methylating agent by nucleophilic attack at methyl carbon of DMC to form methylated product. DMC is an archetype example of green solvent by virtue of its properties like nontoxicity, synthesized by clean process, easily biodegradable, easily activated by catalytic amount of base.

As mentioned above DMC exhibits tunable chemical reactivity depending on reaction temperature either as methoxycarbonylating agent or as a methylating agent. This property of DMC is by the virtue of its double electrophilic character (Scheme 6.2).[19] The possibility of alcohol nucleophile attacking on either carbon (or both) can be understood on the basis of HSAB theory.[20] Scheme 6.2 shows dialkyl carbonate reaction with aromatic or aliphatic alcohol. The electrophilicity of carbons in dialkyl carbonate depends on the hybridization of carbon atom, CH_3 carbon having sp^3 hybridization is soft, and while carbonyl carbon having sp^2 hybridization is considered as a hard carbon.[21] The reactivity of these carbons however, depends on number of other factors besides electrophilicity[22] under our experimental conditions; comparison of reactivity of these two carbons based on electrophilicity of carbon may be justifiable. Thus, in dimethyl carbonate, there are two reactive carbon centers within the same molecule with alkyl carbon being slightly softer than the carbonyl carbon.[23] And according to HSAB theory, phenol being the softer nucleophile, will preferably react with soft alkyl carbon centre of carbonate producing anisole (Scheme 6.1), while usually aliphatic alcohol reacts with

hard carbon atom of carbonyl giving rise to predominantly transesterification products such as dialkyl carbonate. Thus, as shown in the Scheme 6.1, *O*-alkylation of phenol is favored at CH_3 carbon centre of carbonate and transesterification of aliphatic alcohol dominates at carbonyl carbon atom of carbonate. However, if a softer phenoxide ion to attack on harder carbonyl carbon, the reaction would be very sluggish. In practice, the synthesis of diphenyl carbonate (DPC) from dimethyl carbonate (DMC) is usually accomplished in two steps. In the first step, phenol is converted into methyl phenyl carbonate (MPC), and in the second step, MPC is converted into DPC by the reaction with phenol or by disproportion (Scheme 6.1).

Scheme 6.1. Synthesis of diphenyl carbonate from dimethyl carbonate
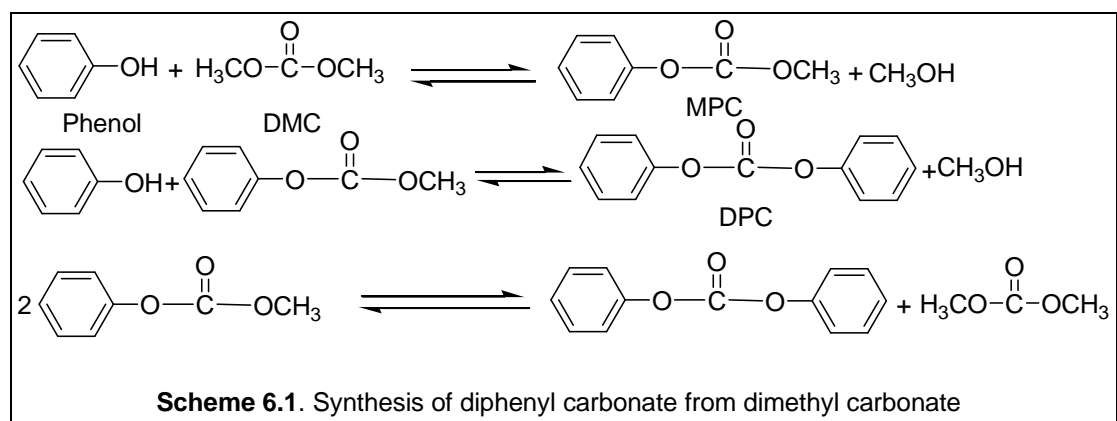
But the reaction suffers from low yield and selectivity even at elevated temperature due to a critical thermodynamic limitation in the formation of MPC (3×10^{-4} at 453 K) and the reaction rate is somewhat slow.[24] Such types of dual reactivity centers within the molecule are not uncommon in organic reactions.[25] The ambident character of dimethyl carbonate as an electrophile in reactions with amine, resulting in formation of carbamate and N-alkylated amines as products has been demonstrated earlier.[26]

O-alkylation

* soft electrophilic carbon

Transesterification

dialkyl carbonate

● hard electrophilic carbon

Scheme 6.2: Dialkyl carbonate reactivity towards phenol and methanol
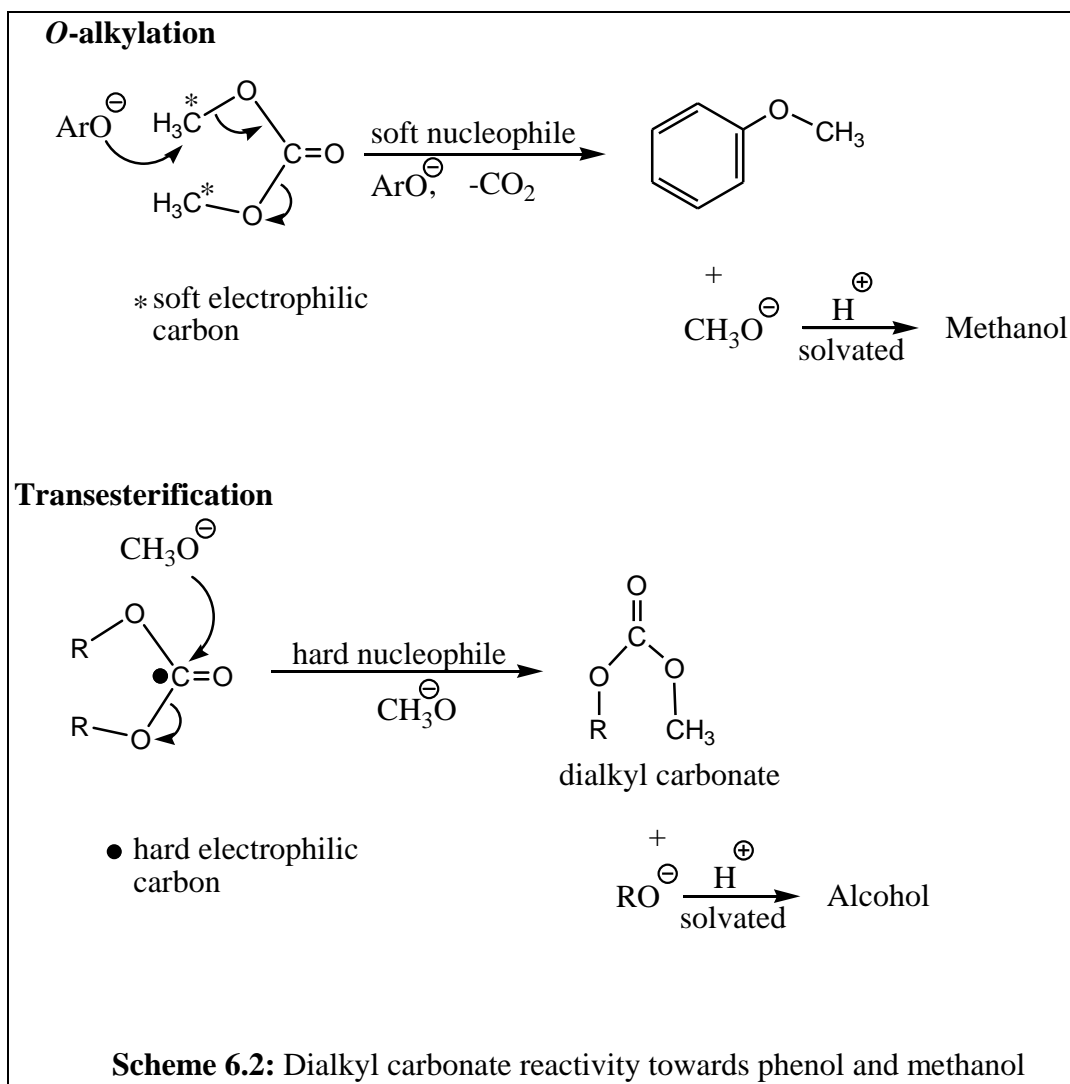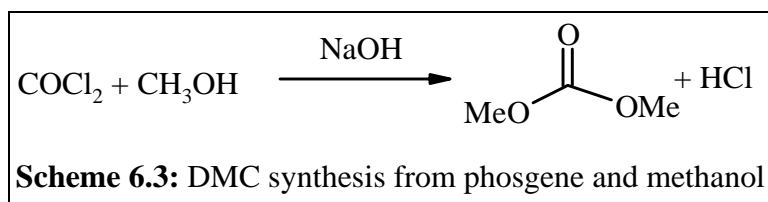
6.1.1. DMC synthesis

Synthesis of DMC is possible by a number of methods. Only a few important methods from literature are cited here to give an overview.

i) From phosgene and methanol

DMC has been prepared by reaction of methanol and phosgene in the presence of concentrated NaOH solution (Scheme 6.3).

Scheme 6.3: DMC synthesis from phosgene and methanol

ii) Oxycarbonylation of methanol

In 1983 Enichem synthesis patented a production technology for DMC synthesis based on oxycarbonylation of methanol in the presence of Cu salts as catalyst. This process afforded operational (phosgene free) and environmental (water co-product, no corrosive reagents) advantages (Scheme 6.4).

$$CH_3OH + CO_2 + 1/2\ O_2 \xrightarrow{\text{Cu salt}} \underset{\underset{MeO \qquad OMe}{}}{\overset{O}{\|}} + H_2O$$

Scheme 6.4: Oxycarbonylation of methanol for DMC synthesis
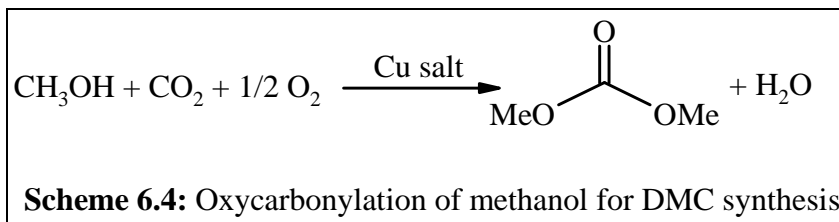
iii) Ube process

Ube industry has developed a process for synthesis of DMC from carbonylation of methyl nitrite using Pd catalyst (Scheme6.5) This route involves the formation of methyl nitrite from methanol, nitric oxide, and oxygen. Methyl nitrite is subsequently reacted with carbon monoxide to give DMC and releases nitric oxide for recycles. This approach overcomes the shortfalls like the handling of solids/slurries as in the Enichem process.

$$2NO + 2CH_3OH + 1/2\ O_2 \longrightarrow 2CH_3ONO + H_2O$$

$$CO + CH_3ONO \longrightarrow \underset{\underset{MeO \qquad OMe}{}}{\overset{O}{\|}} + 2NO$$

Scheme.6.5: DMC synthesis for carbonylation of methyl nitrite
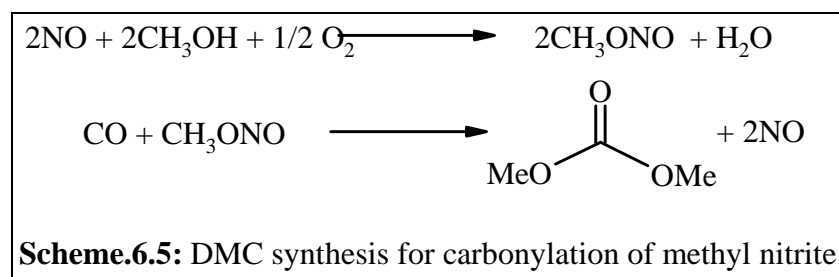
iv) DMC is also formed by the transesterification reaction between ethylene carbonate and methanol, giving ethylene glycol as a co-product (Scheme 6.6). The DMC reactor is assumed to be a boiling pot, operating at 423 K, surmounted by a trayed or packed section from the top of which DMC is distilled as the

methanol/DMC azeotrope. Extractive distillation with water and a second column to remove water from DMC provides a pure product.

Scheme. 6.6: DMC synthesis from carboxylation of epoxides
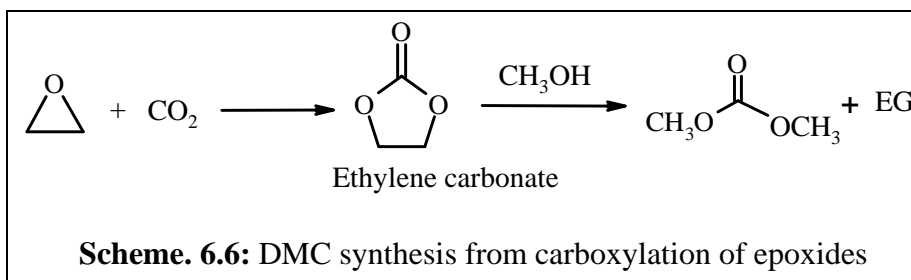
v)   DMC is also formed by transfunctionalization reaction of methanol with urea using tin catalyst; however, yields are typically low because intermediate methyl carbamate is prone to decompose to isocyanic acid or isocyanuric acid. Catalytic Distillation Technologies has developed technology using high-boiling organic electron donor solvents, such as triethylene glycol dimethyl ether using tin-based catalysts, and continuous distillation of product dimethyl carbonate as it is made (Scheme 6.7)

Scheme.6.7: Transfunctionalization of urea and methanol for DMC synthesis.
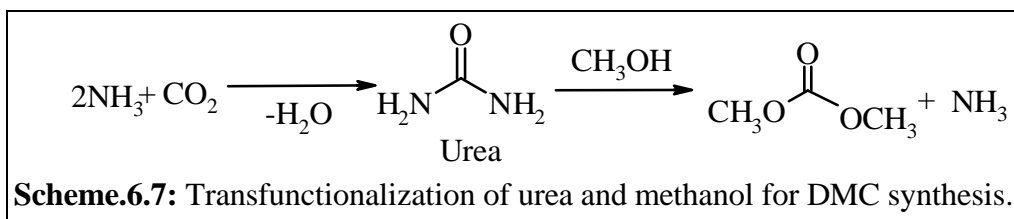
6.1.2. Applications of DMC in organic reactions

DMC has been effectively used as an environmentally benign building block for   various organic reactions such as, green oxidant for oxidation, carbamate synthesis, alkylation reaction such as, *C-* alkylation, *N*-alkyaltion, *O*-alkylation and *S*-alkylation and transesterification reaction for the synthesis of higher molecular alkyl carbonate and aromatic carbonates (Scheme 6.8). [27]

Scheme. 6.8: DMC for environmentally benign organic reactions
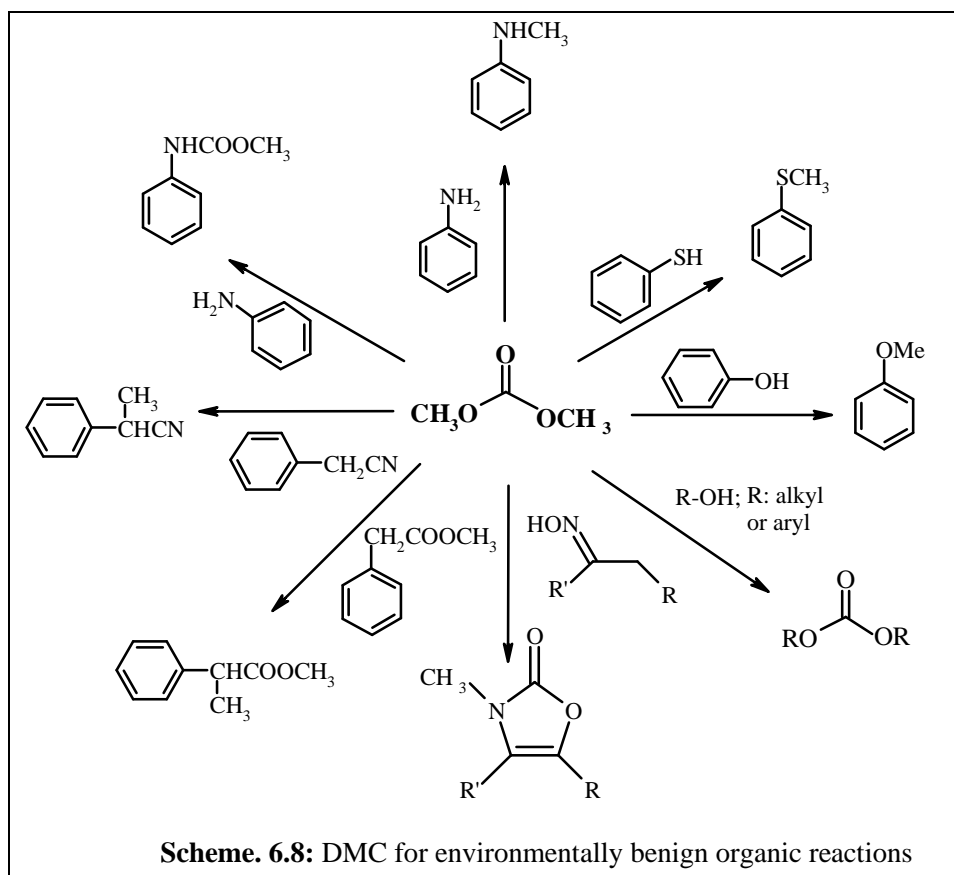
In the present work *O*-alkylation of phenol with DMC is explored using heterogeneous catalyst. The traditional Williamson ether synthesis[28] is largely employed for commercial productions of anisoles through a number of relatively old processes.[29]The *O*-alkylation/arylation of phenols with various alkylating/arylating agents such as methanol, alkyl bromide,[30] allyl bromide,[31] epoxides[32] and cyclohexane[33] has been studied extensively. Other methods that have been reported for phenyl ethers include the use of crown ethers,[34] phase-transfer catalysis,[35] ionic liquids,[36] microwave method,[37] and solid-state reaction.[38]

In case of methanol as methylating agent strong acid catalyst[39-41] as well as high operating temperatures are required with zeolite as catalyst.[42-47]This methodology suffers from poor phenol conversions and selectivities towards *O*-alkylated product. The vapour phase methylation of phenol using methanol is reported to be catalyzed by metal oxide, sulphate, phosphate zeolite and alkali loaded silica catalysts.[48(a-m)] The products obtained were usually mixtures of anisole (product of *O*-methylation) and cresols and xylenols (products of ring methylation), the selectivity being strongly dependent on the catalyst.

The chemistry and catalysis of other alkylating agents mentioned above are beyond the scope of this thesis. Reports on selective *O*-alkylation, however, are limited.

The phenolic –OH group kinetically favors *O*-alkylation whereas thermodynamically *C*-alkylation is favoured due to stearic hinderance. Strong acid catalyst gives *C*-alkylation at 2, 4 positions on phenol ring as a major product along with m-isomer in small amounts due to isomerisation of o- and p-isomers. Whereas basic sites of a catalyst behave as active centre for *O*-alkylation.

Many alternative methods are reported in the literature for methylation of phenol with DMC under gas-liquid phase-transfer catalysis (GL-PTC) conditions in a continuous-flow process by using K_2CO_3 and polyethylene glycol as catalyst.[49] The continuous-flow transformation of phenol to anisole by using DMC as methylating agent was first time reported by Tundo and co-workers under GL-PTC conditions at a temperature of 433-453K.[50] They achieved 100% phenol conversion with 100% selectivity for anisole in about 1h. Fu and Ono reported a substantially quantitative phenol conversion with a very high selectivity for anisole with sodium exchanged zeolite (NaX) as catalyst at 553K. But with this system *C*-methylated products are always formed.

Different authors have illustrated a continuous-flow methylation of phenol with DMC using number of basic catalytic beds.[51] Besides the excellent aryl methyl ether yield with high selectivity most of these procedures are not suitable for high boiling phenols. Other catalyst systems explored for this system are, $CrPO_4$,[52] $CrPO_4$-$AlPO_4$,[53] $AlPO_4$ –Al_2O_3 and $AlPO_4$. These catalysts furnished both C- and *O*-alkylated products.

Catalysts used for alkylation of phenol with DMC in autoclave include $CsCO_3$,[54] pentaalkylguanidines,[55] 4-(dimethylaminopyridine),[56] tertiary amines or phosphines,[57] organic bases with iodide.[58] These catalysts require high reaction temperature. Batch synthesis of *O*-methylated phenols has also been reported using calcined Mg-Al hydrotalcite,[59,60] K_2CO_3,[61] K_2CO_3-crown ether,[62] K_2CO_3-Bu_4NBr[63] or DBU.[64] A semi-continuous process was used by Ouk et al for *O*-methylation of phenol by DMC in the presence of Bu_4NBr at 403K or with K_2CO_3 at 433K.[65,66] Both the above methods suffer from obvious disadvantage of catalyst-product separation and recycling of homogeneous catalyst. Another disadvantage was incomplete conversion of substrate. Recently Shen et al. reported [BMIm]Cl as efficient catalyst for *O*-alkylation of phenol and various

substituted phenols with DMC.[67] He obtained *O*-methylated product in 99% yield with 100% selectivity at 393K under atmospheric pressure.

Ionic liquids are green solvents but are expensive. Alkylation using basic zeolites, aluminas is reported at temperature 453-573K in vapour phase. These catalysts furnished good yield of alkylated phenol but along with C-alkylated products.[68,69] A detailed literature study on *O*-alylation of phenol with DMC using various catalyst is tabulated in Table 6.2.

All these catalyst suffers from one or another drawback. Solid acid deactivates due to coke formation where as liquid acids cause equipment corrosion and environmental pollution and homogeneous catalyst suffers from catalyst product separation and poor recycling ability. On the other hand IL even though is a green alternative is not economical and suffer loss during handling. The activities obtained with these catalysts are not too encouraging.

From the above literature study significant improvement necessary for this reaction system was to design greener catalyst systems based on blend of ionic liquid with silica replacing other homogeneous catalyst as well as neat IL. This type of catalyst system was proposed taking into account economy of the reaction for industrial application. These immobilized catalysts illustrate dual activity due to Lewis acid and Lewis base sites generated after grafting that resulted in formation of anisole selectively. In the discussion hereafter catalyst [IMB]35%CAT-3a will be representing 35% [TESPMim] [Cl] immobilized on SiO_2.

Sr. No	Substrate	Alkylating agent	Catalyst	Time; h	Temp K	Conv. %	*O*-alkylation selectivity;%	C-alkylation selectivity ;%	Reference
1	PhOH	DMC	BMimCl	1.5	393	99.8	100	-	Shen et.al.[70]
2	PhOH/p-cresol	DMC	K$_2$CO$_3$	30	433	90	100	-	Sophie et al.[71]
3	PhOH	t-butyl alcohol	[OMim]BF$_4$/ [HMim]BF$_4$	4	333	43	99.5	-	Hao et al.[72]
4	PhOH	CH3I	CsCO$_3$	5	353	39	100	-	J.C.Lee[73]
5	PhOH	Allyl bromide	CsCO$_3$	5	353	84	100	-	J.C.Lee[74]
6	PhOH	PhBr	CsCO$_3$	5	353	92	100	-	J.C.Lee[75]
7	Substituted PhOH	DMS	LiOH	0.5-1.5	273-343	100	100	-	Basak[76]
8	PhOH	MeI	KOH	30min	273	85	100	-	R.A.W johnstone[77]
9	*peri*-hydroxylated 9,10-Anthracenediones	DMS	CsCO$_3$	15	Acetone reflux	94	100		R.T. Winters[78]
10	PhOH	MeI	NaH	24	353	80	100		B.A.Stoochnoff[79]
12	aryl borates (PhO)$_3$B	Styrene oxide	-	2	R.T	100	80 20		F. Bertolini[80]
13	PhOH	epichlorohydrin	NaOH(aq)	5	373	83	69(yield)	14	B.K. Pchelka[81]

Table 6.2. Literature on *O*-methylation of phenol

340

Sr. No	Substrate	Alkylating agent	Catalyst	Time; h	Temp K	Conv. %	*O*-alkylation selectivity;%	C-alkylation selectivity ;%	Reference
14	PhOH	epichlorohydrin	NaOH/ TBAB	6min	MW	99	100	-	B.K. Pchelka[81]
15	2-hydroxy-4-methylacetophenone	DMS	NaOH	1min	MW	97.6	100		M.L.sharma [82]
16	p-methoxy phenol	CH$_2$=CH-CH$_2$Br	NaOH/ TBAB	3	300 (L-PTC)	100	98.494 0.4		G.D.Yadav [83]
17	PhOH	PhCH$_2$Br	DABCO/ K$_2$CO$_3$	8 min	S.S, r.t. grinding	100	100		X Bu.[84]
18	PhOH	DMS	KOH	1.5	338	100	100		D. Achet[85]
19	p-Cyano phenol	2-chloro ethyl methyl ether	K$_2$CO$_3$	30	413 M.W	96	100		J. Sarju [86]
20	Guaiacol	Cyclohexene	Sulphated zirconia	2	353	78	68	27	G. D. Yadav [87]
21	PhOH	CH$_3$OH	CsNaX zeolite	2	503	2.6	100		S.C. Lee [88]
22	catechol	CH$_3$OH	10wt% Cs$_2$O/SiO$_2$	1	623	100	75 (guaiacol) 16(veratrole)	4(c-lkylated)	V.Vishwanathan[89]
23	PhOH	tert-butyl alcohol	SO$_3$H functionalize imidazolium IL	8	343	80	- 60.2		J. Gui [90]
24	PhOH	CH$_3$OH	HY zeolite	2.5	523	50	8.3	38.6	s. balsama[91]
25	PhOH	C$_2$H$_5$OH	CoAl-MCM-41	1	673	40	20	80	A. Vinu[92]

| Sr. No	Substrate	Alkylating agent	Catalyst	Time; h	Temp K	Conv. %	*O*-alkylation selectivity;%	C-alkylation selectivity ;%	Reference
26	PhOH	CH$_3$OH	Al-MCM-41	2	698	44	20	55	K. Bhattacharyya [93]
27	PhOH	tert-butyl alcohol	20%PW/ Al-MCM-41	5	463	88.7		100	K. Usha Nandini [94]
28	PhOH	CH$_3$OH	Mg/Al=2 CHTlc	6	573	12.9	81.7 17.6		M. Bolognini [95]
29	p-cresol	CH$_3$OH DMC	Cu0.5Co0.5 Fe$_2$O$_4$	3	623	97 96	- 100		T. Mathew [96]
30	m-cresol	tert-butyl alcohol	15%WO$_3$/ZrO$_2$	2	403	69.8	1.3	92.4(mono-alkylated) 6.3 (di - alkylated)	S.Sarish [97]
31	PhOH	tert-butyl alcohol	Sulphated zirconia	2	393	80	-	100	G. D. Yadav [98]
32	PhOH	DMC	TBAB	4	403	100	100		S. Ouk [99]
33	Catechol	DMC	K2CO3	2.5	473	97	100		P. Tundo [100]
34	PhOH	DMC	Amorphous 15% AlPO4-Al2O3(pyridine treated)	4	573	11.2	100		R. Luque [101]
35	2-napthol	DMC	PEG 1000 and K$_2$CO$_3$,	5	423	70	100		S. Ouk
36	catechol	DMC MeOH	Hβ, HY zeolite		473	75 73	80 70	20 30	S. R. Kirumakki [102]
37	catechol	DMC	Mg/Al=4 CHTlc	2	523	40	86 12.6(di*O*-alk)		M. B. Talwar [103]

6.1.3. Reaction mechanism for alkylation of phenol/phenolic substrate with DMC/CH₃OH on solid acid/base catalyst:

Alkylation of aromatics (phenol/2-napthol) over solid catalysts is known to occur either by Langmuir–Hinshelwood (LH) mechanism wherein the adsorption of both the aromatic and the alkylating agent molecules followed by the reaction occurs on the surface or by a Eley–Rideal (ER) mechanism where the reaction of the adsorbed alkylating agent occurs with aromatic molecules in gas phase. The kinetic study by Kirumakki et al.[104] of 2-naphthol alkylation with DMC/MeOH over zeolites β and Y catalyst supports reaction follows a Langmuir–Hinshelwood mechanistic pathway. He proposed simultaneous activation of 2-napthol and DMC/MeOH on protonic acid sites of zeolite by adsorption mechanism (Scheme 6.9 and 6.10). He deduced from their study that the active sites for *O*-alkylation and *C*-alkylation are not necessarily the same. But *O*-alkylation is more facile with zeolites catalyst and sites for *O*-alklation get deactivated faster than sites for *C*-alkylation. From the variation in selectivity and yield of products obtained viz; 2-methoxy naphthalene(*O*-alkylated product), 1-methly-2-napthalene(C-alkylated product) and 1-methly-2-methoxynapthalene (*O*- and C- alkylated product) he noted that 1- methyl – 2-methoxy naphthalene is formed from C-alkylation of *O*-alkalytated product as well as *O*-alkylation of *C*-alkylated product.

He also observed that yield of *O*-alkalyated product i.e., 2-methoxy naphthalene is always higher than *C*-alkylated product. This confirms the fact that contribution of 2-methoxynapthalene (*O*-alkylated product) towards the formation of 1-methly-2-methoxynapthane is more than (C-alklyated product).

Santacesaria et al.[105] have tried to establish the types of sites responsible for the *O*- and C-alkylation of phenol. Studies on O & C alkylation of phenol revealed that the activation of alkylating agent on acid site forms carbon cation which reacts with both *O*- & C- centres of phenol. The simultaneous adsorption followed by activation of phenol molecule on another adjacent site facilitates attack of alkylating agent on *O*- & C- centres of phenol. Thus the key factors contributing towards the selectivity of *O*- & C- alkylated products are energy of activiation of the molecules, orientation of the reacting molecules and the proximity of the active sites. The mechanism based on in

situ spectroscopic studies by Beutel et al [106] on the alkylation of phenol with DMC, shows that the DMC is activated on the Lewis acid site by its carbonyl oxygen and phenol on an adjacent Lewis base site by H-bonding. This type of mechanism, making use of both the acid and the basic sites on the catalyst is also supported by Jyothi et al. for the alkylation reaction using DMC (Scheme 6.11).[107]
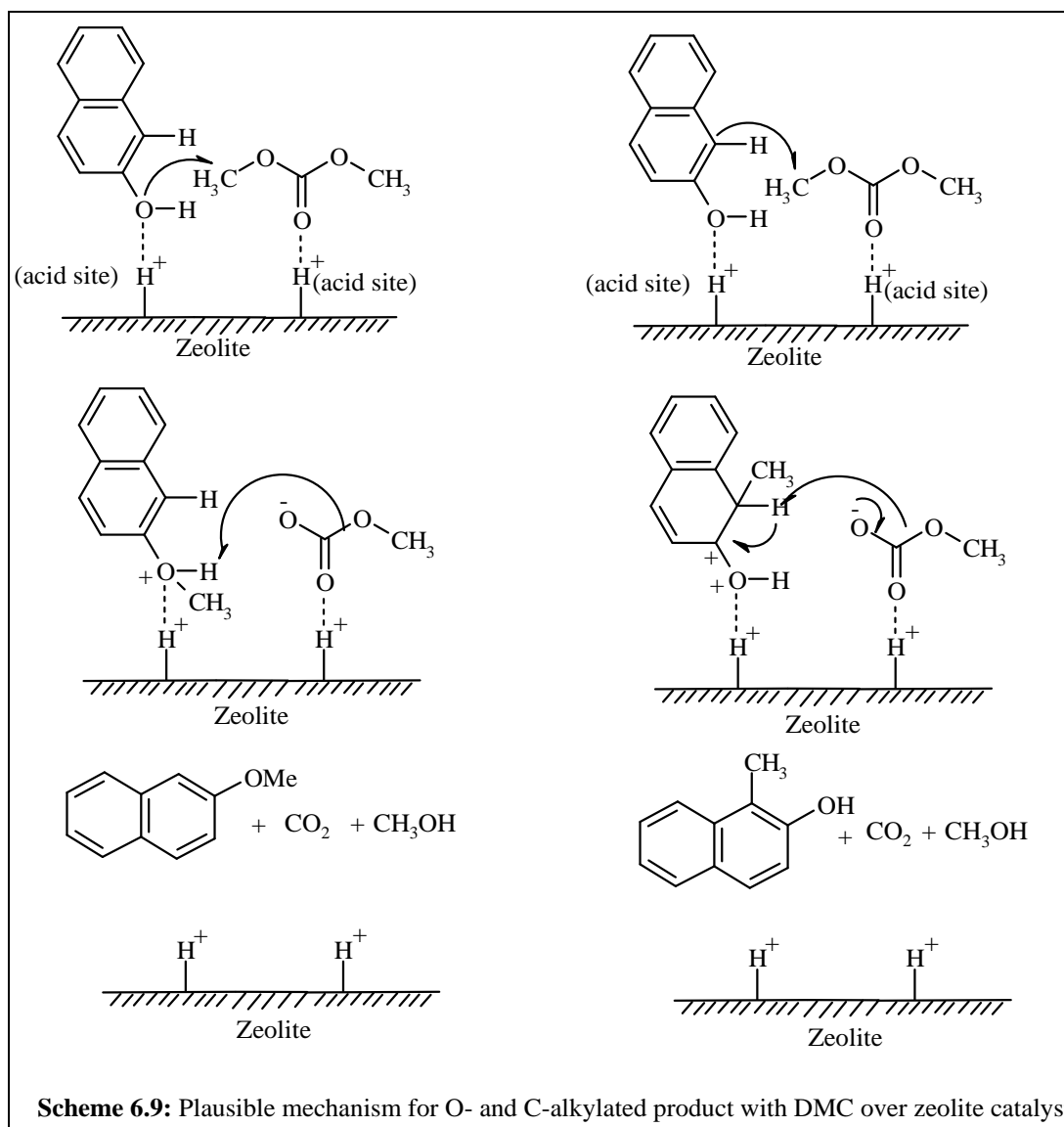
Scheme 6.9: Plausible mechanism for O- and C-alkylated product with DMC over zeolite catalyst

Scheme 6.10: Plausible mechanism for O- and C-alkylated product with methanol over zeolite catalyst

Scheme 6.11: Plausible mechanism for O- alkylation of phenol with DMC over MgO catalyst
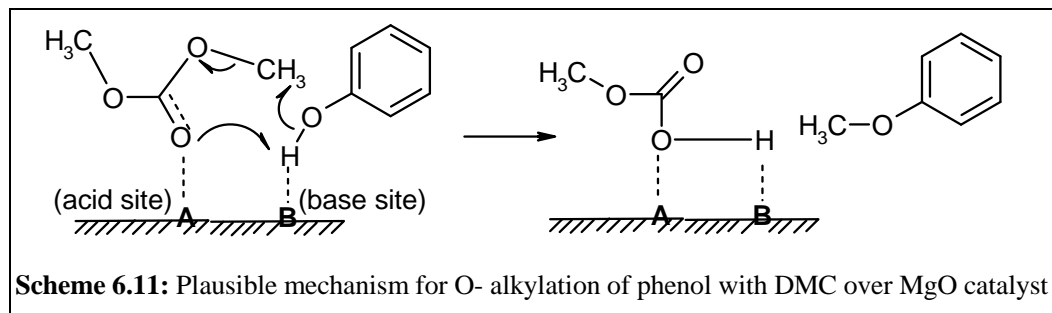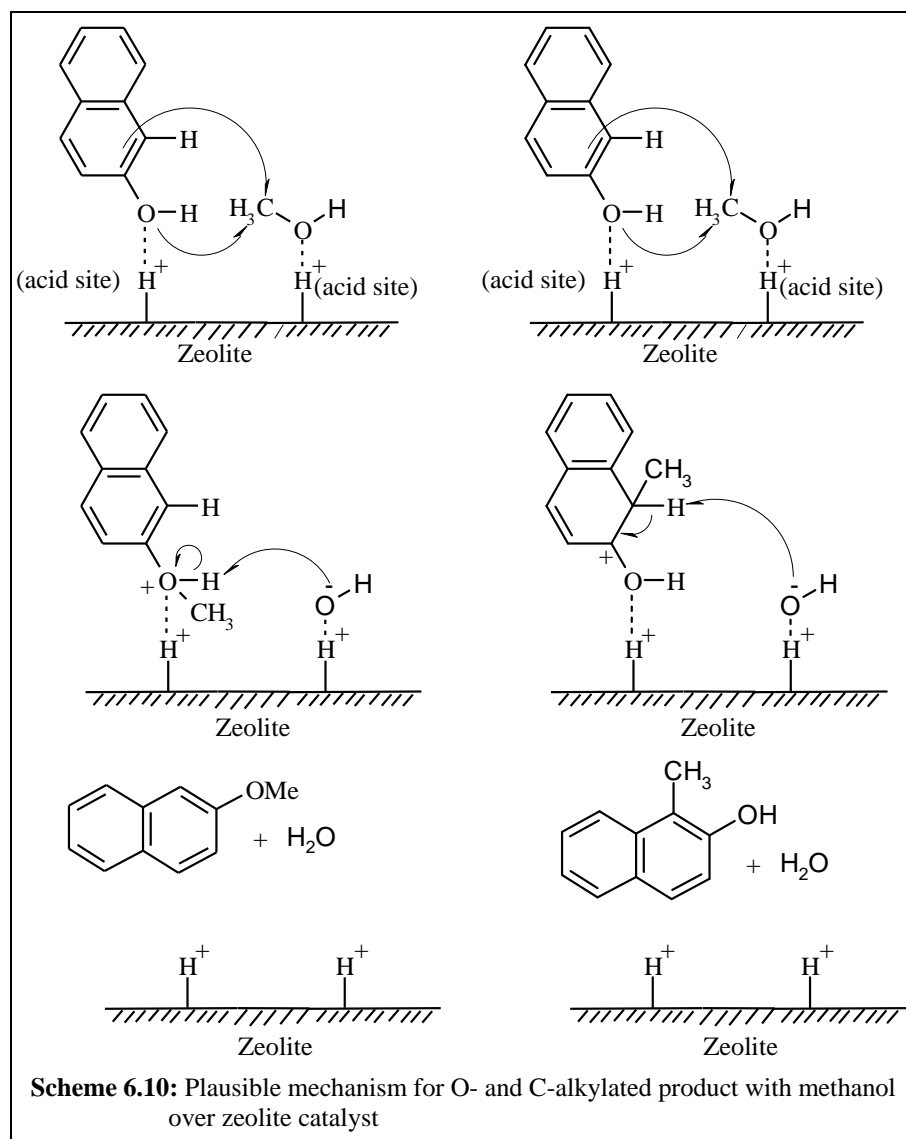
6.2. EXPERIMENTAL

6.2.1. MATERIALS

Phenol (99% pure) and DMC were purchased from Sigma Aldrich. Various substituted phenols, were purchased from S.D. fine chemical ltd. India. CAT 3 [1-(tri-ethoxy-silyl-propyl)-3-methyl-imidazolium chloride] and catalyst [IMB]35%CAT-3a (35% TESPMimCl immobilized on silica) were prepared according to literature procedure section and well characterized before use (see Chapter 2).

6.2.2. GENERAL PROCEDURE FOR SYNTHESIS OF PHENYL METHYL ETHERS

Alkylation reactions with DMC were carried out in a 50 cc Parr reactor at 423K operating temperature. The reaction mixture consisting of phenol (5.54 mmoles) and DMC (226 mmoles) was charged into reactor containing 0.5g of immobilized catalyst. Autoclave was purged with nitrogen to ensure inert atmosphere. The reaction was carried out for 2.5h and conversions were monitored by time sampling. Liquid phase was quantitatively analyzed on GC; and products were confirmed by GC–MS. For recycle study after completion of the experiment, catalyst was separated by filtration through Sartorius 393 grade filter paper. Separated catalyst was Soxhlet extracted with dichloromethane to remove adhered organic impurities. The catalyst was dried at 398 K under vacuum for 6 h and reused. The catalyst was recycled five times and it was observed that there was minor loss in catalyst weight during each recycle (total loss < 10 %), this was taken into consideration and each recycle was carried out so that catalyst and reactant concentration do not deviate much from zero recycle experiment.

6.2.3. ANALYTICAL METHODS

Liquid samples were diluted by acetonitrile and analyzed on a Hewlett Packard 6890 Series GC equipped with auto sampler instrument, controlled by the HP Chemstation software, by using an HP5 (30 m×0.32 mm×0.25 μm) capillary column with FID detector. Identification of products was done using GC-Mass spectrometry of Agilent, USA make, model 6890 GC with 5973N mass selective detector using HP-5 MS capillary column of 30m×0.32mmx 0.25μm dimension. Conversions and yields were

calculated based on phenol conversion and by injecting authentic samples available of products respectively. The synthesized immobilized catalysts were characterized by ^{29}Si and ^{13}C cross polarization magic angle spinning (CPMAS) NMR experiments that were carried out on a Bruker Avance 300 wide bore spectrometer equipped with a superconducting magnet with a field of 7.1 Tesla. The operating frequencies for ^{13}C and ^{29}Si were 75.47MHz and 59.63 MHz respectively.

Table 6.3. Standard conditions for GC analysis

Parameters	Conditions
Injector (split) temperature	523 K
Flame ionization detector (FID) temperature	573 K
Column temperature (HP-5 capillary column)	353 K–563 K (programmed)
Inlet Pressure (He)	10 psig
Carrier gas (He) pressure	5-10 psig
Split ratio	50:1

The conversion, selectivity, yield, were calculated as follows.

$$\% \; Conversion \; = \frac{Initial \; moles \; of \; phenol \; - \; Final \; moles \; of \; phenol}{Initial \; moles \; of \; phenol} \; X \; 100$$

$$\% \; Selectivity \; = \frac{No. \; of \; moles \; of \; product \; formed}{No. \; of \; moles \; of \; phenol \; converted} \; X \; 100$$

$$\% \; Yield \; = \frac{No. \; of \; moles \; of \; product \; formed}{No. \; of \; moles \; of \; phenol \; charged} \; X \; 100$$

6.3. RESULT AND DISCUSSION

6.3.1. Effect of reaction temperature

Reflux temperature favours transesterification and higher temperature favours *O*-alkylation. The variation of phenol conversion and product selectivity as a function of temperature was investigated in temperature range 403-443K for 2.5h reaction time using catalyst [IMB]35%CAT-3a. Results are tabulated in Table 6.4. At 403K poor phenol conversion was achieved (27%) but no transesterification product was seen. Remarkable increase in phenol conversion with 100% selectivity for anisole was observed with rise in temperature (entry 2-3, Table 6.4, 99% conv). This indicates that at lower temperature even with 0.5g loading of catalyst [IMB]35%CAT-3a sufficient catalytic sites are not activated thereby failing to activate phenol. This results in poor phenoxide ion concentration thus affecting DMC activation leading to poor anisole yield.

Table 6.4. Temperature screening

Entry	Temperature (K)	Phenol Conversion, (%)	Anisole Yield (%)
1	403	27	0.7
2	413	61	60.87
3	423	99.9	99.9

Reaction Conditions: PhOH: 0.522g (5.54 mmoles), DMC: 20.346g (226mmoles), [IMB]35%CAT-3a: 0.501g, 2.5H, N_2 atm, 1000rpm

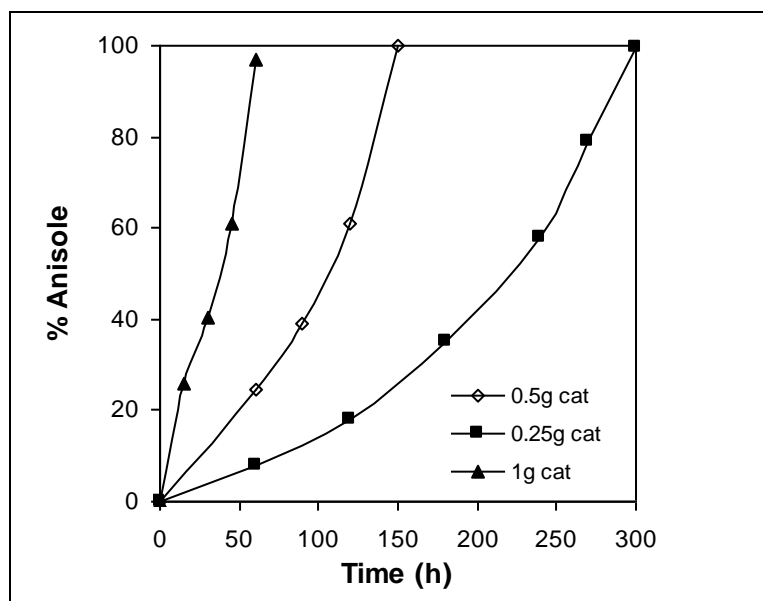### 6.3.2. Effect of catalyst loading:

Catalyst activity of [IMB]35%CAT-3a was tested for various loadings, 0.25 g (0.369 mmoles), 0.5 g (0.739 mmoles) and 1.0 g (1.47 mmoles), at 423K. It was observed that 99% phenol conversion and 99% anisole yield were obtained for catalyst loading ranging from 0.25g-1.0g (Table 6.5., entries 1-3) but with significant difference in time. For 5h contact time 0.25g catalysts resulted in 99% conversion whereas for 1.0 g catalyst same conversion was achieved within 1h contact time indicating reaction is not operating in liquid to solid mass transfer regime. Time sampling against catalyst loading is plotted in Figure 6.1. Rates of reaction are slow for lower catalyst loading and higher as catalyst loading was increased from 0.5g to 1g (Figure 6.1). This effect

can be attributed to number of active sites available for each catalyst loading from 0.25g-1g that is accountable for phenol as well as DMC activation. For lower catalyst loading of 0.25g population of these active sites is low as compared to moles of phenol and DMC available in reaction mixture. From the mechanism suggested in section 6.7; simultaneous activation of phenol as well as DMC on the Lewis acid/base sites of catalyst occurs resulting in formation of phenoxide ion which in turn attacks DMC giving anisole, CO_2 and CH_3OH. This low activity for lower catalyst loading can be explained using proposed mechanism wherein after activation of each mole of phenol and DMC followed by departure of anisole activation of each new fresh mole of phenol and DMC is possible only after certain time interval due to limited available active sites (Table 6.5., entry 1). Similarly this rationale is true for higher activity at higher catalyst loading. Thus from reaction temperature and catalyst loading data, optimum catalyst loading was 0.5g catalyst for 99% phenol conversion at 423K in 2.5h contact time.

Table 6.5. Catalyst loading effect on phenol conversion.

Entry	Catalyst loading (g)	Phenol Conversion, (%)	Anisole Yield (%)
1	0.25[a]	99.9	99.9
2	0.50	99.9	99.9
3	1.0[b]	99.9	99.9

Reaction Conditions: PhOH: 5.54 mmoles (0.522g), DMC: 226mmoles (20.346g), Catalyst: [IMB]35%CAT-3a Reaction time: [a] 5H, [b] 1H. 2.5H, N_2 atm, 1000rpm

Figure 6.1: Catalyst loading effect on phenol conversion for 0.25g, 0.5g and 1g loading of ^{IMB}35%CAT-3a.

6.3.3. Effect of molar ratio of phenol to DMC:

The effect of molar ratio of phenol to DMC on *O*-alkylation of phenol is shown in Table 6.6. Results indicate that 0.5g ^{IMB}35%CAT-3a (35% loading of IL CAT-3 on silica) gives better activity for 5.54 mmoles phenol: 226 mmoles DMC ratio. Higher phenol to DMC ratio (entry 2 Table 6.6) resulted in 60% conversion at 4h contact time. This indicates that a concerted mechanism is operational for this reaction wherein phenol, DMC and catalyst play vital role in activation process. Phenol and DMC both gets activated on catalyst surface and nucleophilic attack of phenolate ion on methyl carbon atom of DMC results in *O*-alkylated product by BAL^2 mechanism.

At higher phenol concentration DMC moles are not sufficient for alkylating phenol over 0.5g catalyst loading. Therefore optimum molar concentration for 0.5g catalyst is 5.54 mmoles of phenol: 226 mmoles of DMC. This is evident from catalyst loading experiments when DMC: phenol was taken in molar ratio of 226 mmoles: 5.54 mmoles, 0.25g catalyst resulted in 99% conversion in 5h whereas same DMC: phenol ratio yielded 99% product in exactly the half time i.e. 2.5h on doubling the catalyst loading. As discussed in section 6.6.2. lower catalyst loading makes fewer sites available for activation of phenol and DMC. This supports the mechanism speculated

by us that simultaneous formation of phenoxide ion and its attack on DMC is occurring on catalyst surface. Phenoxides are softer nucleophile therefore it attacks softer electrophile i.e (CH_3) methyl group, according to HSBA principle. Thus weak Lewis acid/base sites are required for activation of phenol and DMC. This reaction is advantageous from green aspect that the products formed are anisole, methanol and CO_2. Methanol and CO_2 can be recycled for DMC synthesis (Enichem process)[108].

Table 6.6. Effect of phenol concentration on Anisole yield.

Entry	Phenol Concentration (mmoles)	Phenol Conversion, (%)	Anisole Yield (%)	Time (h)
1	5.54[a]	99.9	99.9	2.5
2	11.13[b]	99.9	99.9	4

Reaction Conditions: DMC: [a]226mmoles (20.122g) and [b] 210mmoles (18.9800g), [IMB]35%CAT-3a: 0.501g, temperature: 423K , N_2 atm, 1000rpm.
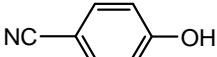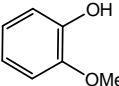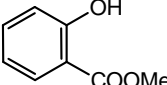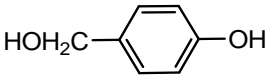
6.3.4. Substrate screening:
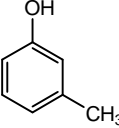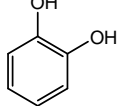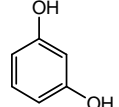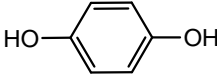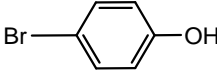
Activity of [IMB]35%CAT-3a was tested on various substituted phenols for *O*-alkylation with DMC. Results are tabulated in Table 6.6. Among the functional groups hydroxyl, methoxy, and methyl are electron donating groups and halogen, cyano group's fall under electron withdrawing groups. The former groups tend to lower the acidity while the later ones tend to increase the acidity of corresponding phenol if present at ortho and/or para position on phenol. Thus the acidity of reactant affects significantly its activation on basic sites of catalyst. Since [IMB]35%CAT-3a is proposed to demonstrate mild basic and acidic sites (discussed in mech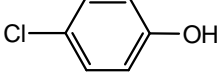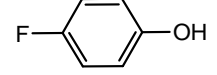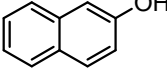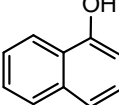anism section), therefore weak acidic substrates like those with –CN, -OME, -COOMe, -CH_2OH and –OH groups at 2 and 3 positions (Table 6.6., entry 1, 2,3,4,6 and 7) show poor phenol conversions. On the contrary strong acidic substrates with –Cl, -Br, and -F at para position resulted in good phenol conversion (Table 6.6., entry 10, 9 and11). Electronegativity of halogens follows the order F> Cl> Br. This effect dominated the conversions of *p*-halogenated phenols to *O*-alkylated products. Flourine being the most electronegative in the halogen series resulted in near quantitative yield of *O*-alkylated product (Table 6.6., entry11).Among *p*-halogenated phenols (Table 6.6.,

entry 9, 10, and 11) *p*-fluoro anisole yield of 99.5% was realized in 2.5h whereas *p*-chloro phenol and p-bromo phenol did not show much difference in reactivity yielding 66.51% and 66.15% of *O*-alkylated product in same time. More stable the phenoxide ion; more is the %yield of *O*-alkylated products. Fluorine being more electronegative than chlorine and bromine it stabilizes phenoxide ion efficiently resulting in higher conversions and yield. [IMB]35%CAT-3a efficiently gave mono-alkylated products in 2.5h time for 2-napthol, 3-napthol, *m*-cresol in comparison to [BMim] Cl[109] which required 2.8h and 3.0h respectively. Methyl group at meta position (*m*-cresol) exerts very mild electron donating effect. This reflect in acidic nature of phenolic substrate unaffected behaving similar to phenol. Thus 99.5% yield of 3MA can be attributed to acidic -H of phenol assisting for its activation on basic sites of catalyst [IMB]35%CAT-3a. Napthol and phenol both posses strong acidic hydrogen resulting in 99.5% conversion (entry 12, 13) using this catalyst. The methylation of 2-naphthol assumes importance as *O*-alkylated product namely 2-methoxy naphthalene is a starting material in the production of naproxen, a widely used nonsteroidal anti-inflammatory drug.[110]Hydroquinone as substrate resulted in mono methylated and di methylated product. 4-methoxy phenol (mono methylated product) is a valuable intermediate for perfume and flavor industry especially in food additives like vanilline. At the optimized reaction conditions hydroquinone showed 60% conversion with 66% selectivity for mono methylated product.

Dihydroxy benzenes showed poor conversions and yield with [IMB]35%CAT-3a. Catechol showed poor conversions (1%) owing to stearic hinderance whereas for resorcinol and hydroquinone 29% and 60% yield were recognized respectively with 40% monoalkylated and 15% dialkylated product in case of hydroquinone see entry 6,7,8 Table 6.6). This result suggest that –OH group at meta and para position in resorcinol and hydroquinone exert weak electron donating effect and less steric hinderance for its activation and methylation on basic sites of solid catalyst.

Except for catechol, reaction selectively yielded monoalkylated product with 60-99% conversions depending on various substrates. [IMB]35%CAT-3a could efficiently convert various phenolic substrates to *O*-alkylated product with DMC as alkylating agent in short time.

Table 6.7. Substrate screening for *O*-alkylation with DMC on different phenolic substrates

Entry	Substrate	Phenol Conversion (%)	Yield O-alkylated product (%)
1	NC—⬡—OH	24.36	24.36
2	OH, OMe	16	16
3	OH, COOMe	18.42	18.42
4	HOH$_2$C—⬡—OH	0	0
5	OH, CH$_3$	99.5	99.5
6	OH, OH	1	1
7	OH, OH	29	29
8	HO—⬡—OH	60	40[a] 15[b]
9	Br—⬡—OH	66.15	66.15
10	Cl—⬡—OH	66.51	66.51
11	F—⬡—OH	99.5	99.5
12	⬡⬡—OH	99.5	99.5
13	OH (naphthalene)	99.5	99.5

Reaction Conditions: DMC: 226mmoles (20.122g), ^{IMB}35%CAT-3a: 0.501g, temperature: 423K , 2.5h,N$_2$ atm, 1000rpm. [a]monoalkylated, [b]dialkylated
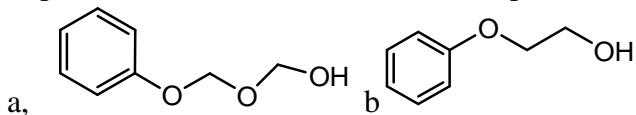
6.3.5. Alkylating agent:

Various alkylating agents were tested for their efficiency as *O*-alkylating agent under our reaction conditions. With Cat1 as heterogeneous catalyst only DMC could yield 99.5% anisole (Table6.8 entry 1, 2, 3 and 5), whereas methanol, DEC and DBC were inactive. Ethylene carbonate resulted in 77.5% conversion but gave phenoxy methoxy methanol in 67% yield along with 10.5% yield of mono-ethylene glycol phenyl ether. Gupte et al. reported mono-ethylene glycol phenyl ethers in good yield with KL zeolite without any 2-(2-phenoxyethoxy) ethanol[111].

Table 6.8. Efficacy of various alkylating agent for *O*-alkylation of phenol

Entry	Alkylating agent	Phenol Conversion (%)	Anisole yield (%)
1	H_3CO-C with OCH_3 and O	99.5	99.5
2	C_2H_5O-C with OC_2H_5 and O	0	0
3	C_4H_9O-C with OC_4H_9 and O	0	0
4	(cyclic carbonate)	77.51	67[a] 10.5[b]
5	CH_3OH	0	0

Reaction Conditions: Organic Carbonates : 216mmoles, ^{IMB}35%CAT-3a: 0.501g, temperature: 423K , 2.5h, N_2 atm, 1000rpm.

a, (phenoxy methoxy methanol structure)   b, (mono-ethylene glycol phenyl ether structure)

6.3.6. Catalyst Recycle Study:

The recycling ability of catalyst was tested for 5 recycles. Catalyst could be recycled for 5 recycles with minor loss in activity owing to handling loss (see Figure 6.2).
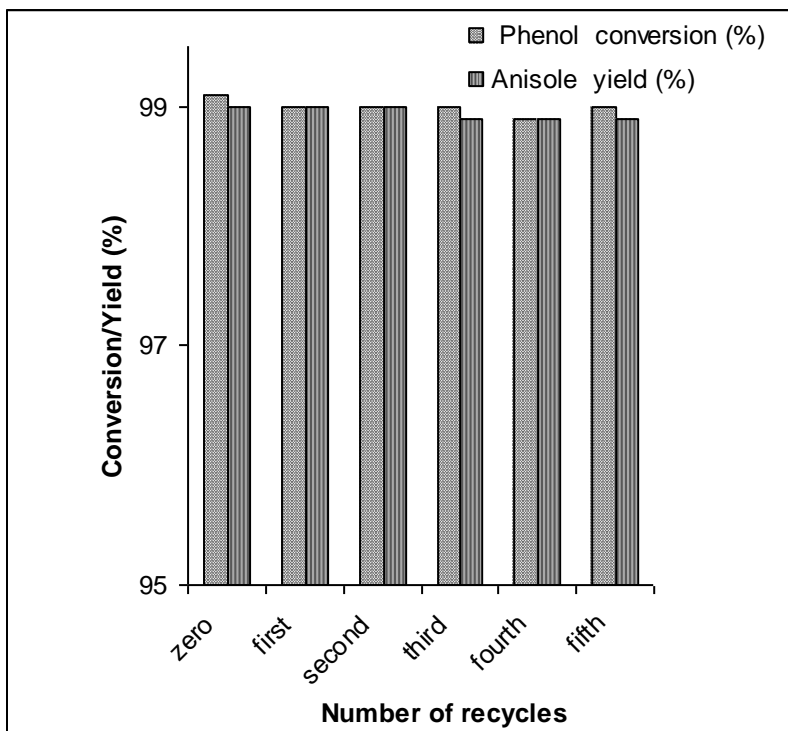
**Figure 6.2:** Catalyst recycle study of catalyst [IMB]35%CAT-3a for *O*-alkylation of phenol with DMC.
Reaction Conditions: DMC: 226mmoles (20.122g), [IMB]35%CAT-3a: 0.501g, temperature: 423K , 2.5h, N_2 atm, 1000rpm.

6.3.7. Mechanism

According to HSBA principle, weak nucleophile attacks weak electrophile. Phenoxide ions are weak nucleophile therefore it preferably attacks weak electrophile i.e CH_3 carbon. Based on in situ spectroscopic studies for the alkylation of phenol with dimethyl carbonate, Beutel et al. [112] have proposed a mechanism that supports the attack of phenoxide ion at methyl carbon of DMC. This mechanistic study was done at 423K and they found that DMC was activated on the Lewis acid sites by its carbonyl oxygen and phenol by H-bonding with Lewis base sites of Na-Y zeolite. Thus weak acid/base sites are required for phenol and DMC activation. Based on this report a concerted mechanism is speculated for the present system in which DMC is activated on IL site (Lewis acid) through carbonyl oxygen and phenol on –OH of silica support (Lewis base sites) of catalyst [IMB]35%CAT-3a forming phenoxide ion which in turn attacks methyl carbon of DMC by BAL^2 mechanism forming anisole, CO_2 and CH_3OH (scheme 6.12). Formation of coke in this case is ruled out for the

reason that phenol inhibits the formation of chelating DMC which is responsible for decomposition of DMC.

Scheme 6.12: Plausible mechanism of Phenol and DMC activation on ^IMB35%CAT-3b catalyst for anisole synthesis.
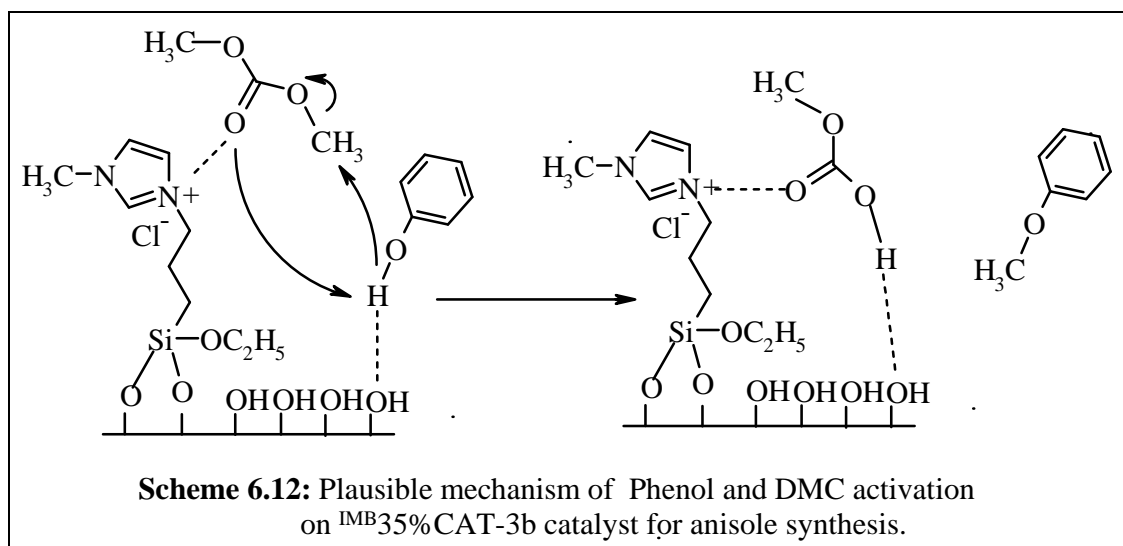
6.4. CONCLUSION

0.739mmoles IL is efficiently used to catalyze *O*-alkylation of phenol using DMC giving 100% yield of anisole. This catalyst is totally *O*-selective except for hydroquinone. 2-napthol, 3- napthol, *p*-fluro phenol and *m*-cresol furnished corresponding *O*-alkylated product with 100% selectivity and yield. Among various alkylating agents screened, DMC was found to be efficient. We proposed the plausible mechanism for this Friedel Craft alkylation with immobilized catalyst CAT 1 showing simultaneous activation of DMC and phenol. This suggests that the synergistic actions of immobilized catalyst is playing important role in activation of substrates. Phenol attacks DMC by BAL2 mechanism. Catalyst was recycled 5 times with minor loss in activity owing to handling loss.

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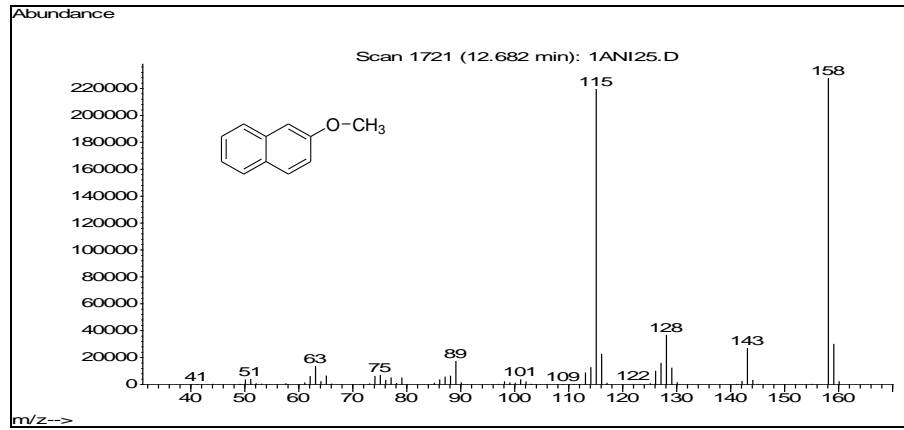
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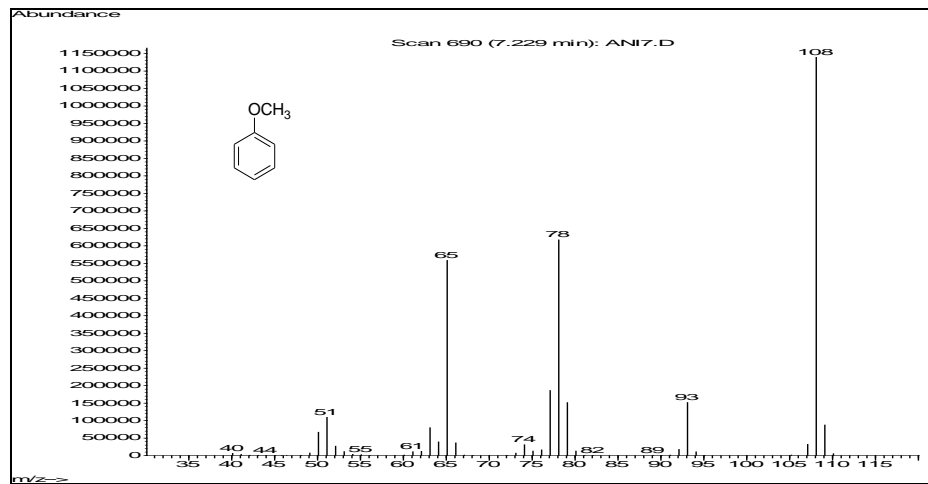98. Yadav G. D., Pathre G. S., *Microporous and Mesoporous Materials*, **2006**, 89, 16.

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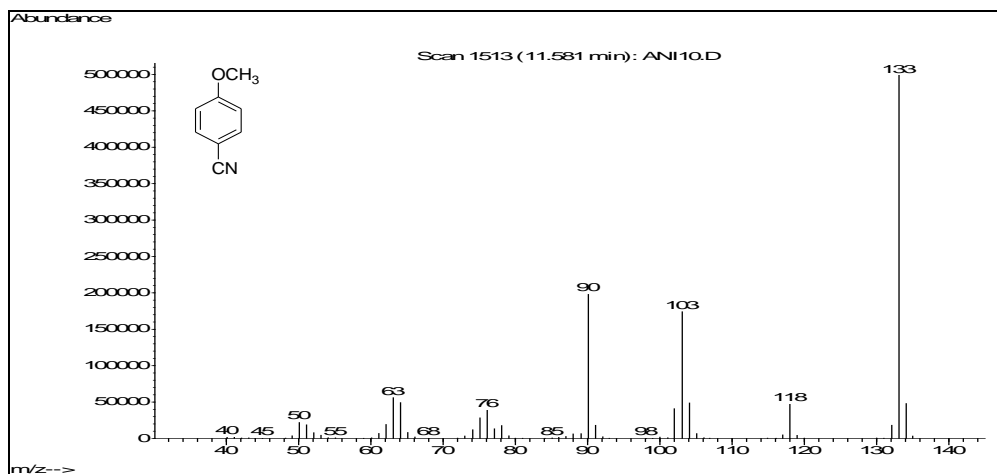
Spectra

GC-MS:2-methoxynaphthalene

Abundance
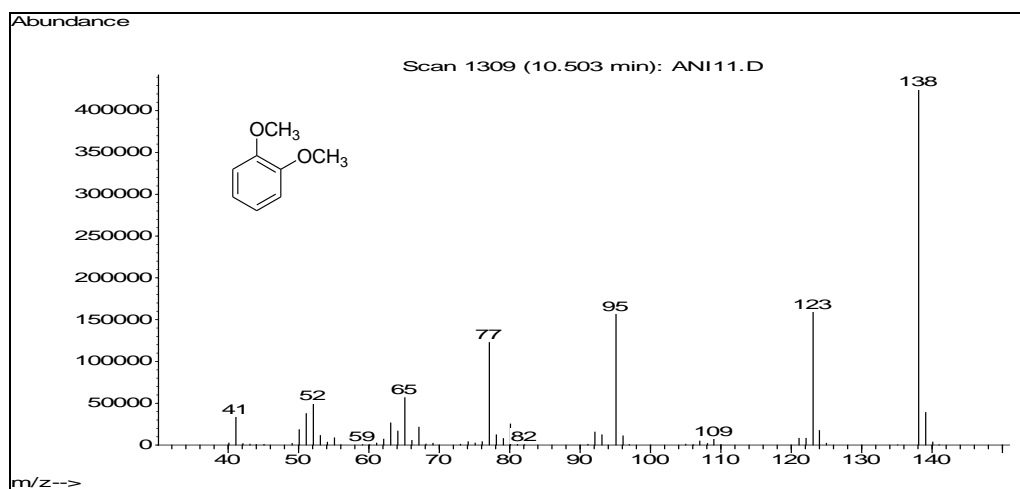
Scan 1721 (12.682 min): 1ANI25.D

O−CH₃

(Mass spectrum with peaks at m/z: 41, 51, 63, 75, 89, 101, 109, 115, 122, 128, 143, 158)

m/z-->

GC-MS:Anisole

Abundance

Scan 690 (7.229 min): ANI7.D

OCH₃

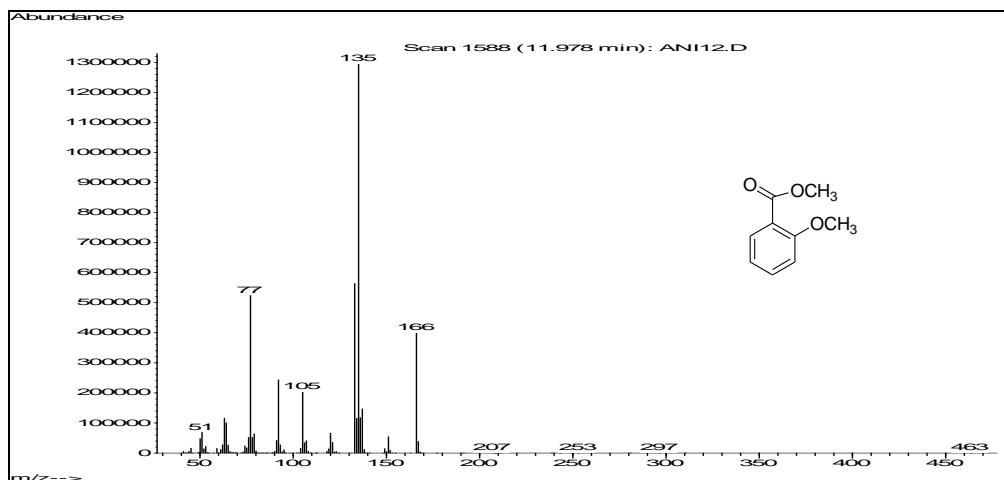(Mass spectrum with peaks at m/z: 40, 44, 51, 55, 61, 65, 74, 78, 82, 89, 93, 108)
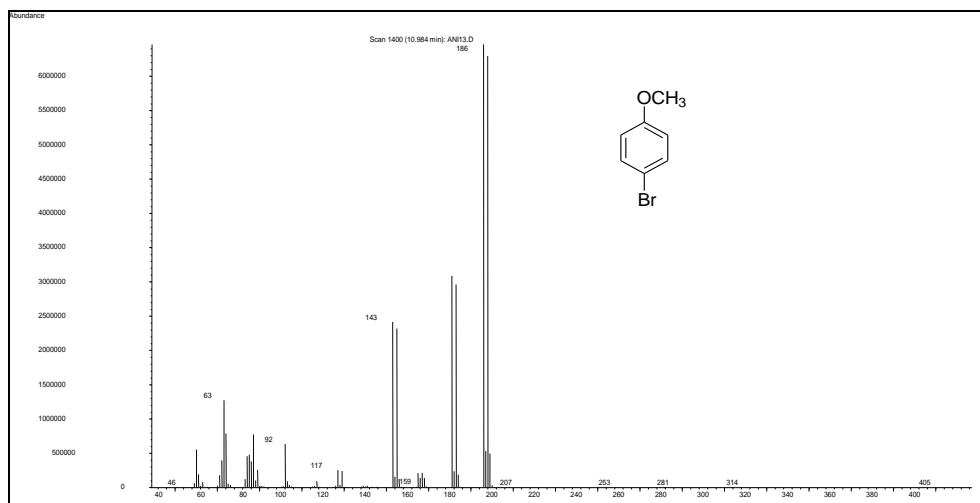
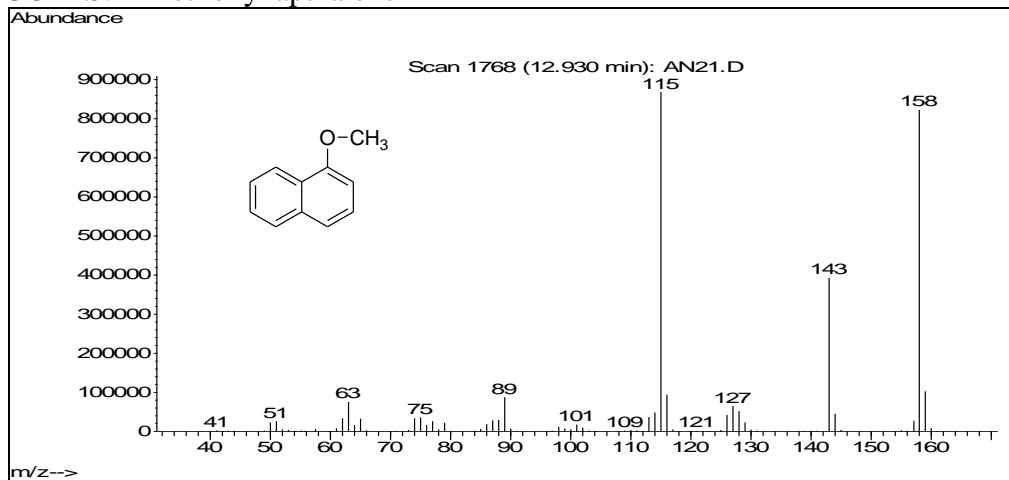m/z-->

GC-MS: 4-methoxybenzonitrile

GC-MS:1,2-dimethoxybenzene

GC-MS: methyl 2-methoxybenzoate

GC-MS:1-bromo-4-methoxybenzene

GC-MS: 1-methoxynapthalene

Scan 1768 (12.930 min): AN21.D

GC-MS:3-methoxyphenol

Scan 1469 (11.349 min): AN22.D
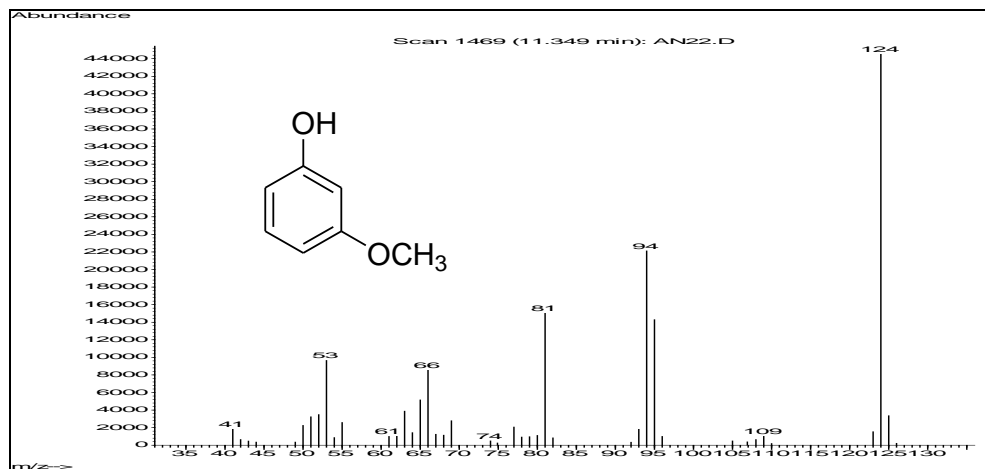
GC-MS:1-methoxy-3-methylbenzene

Scan 1075 (9.265 min): AN24.D
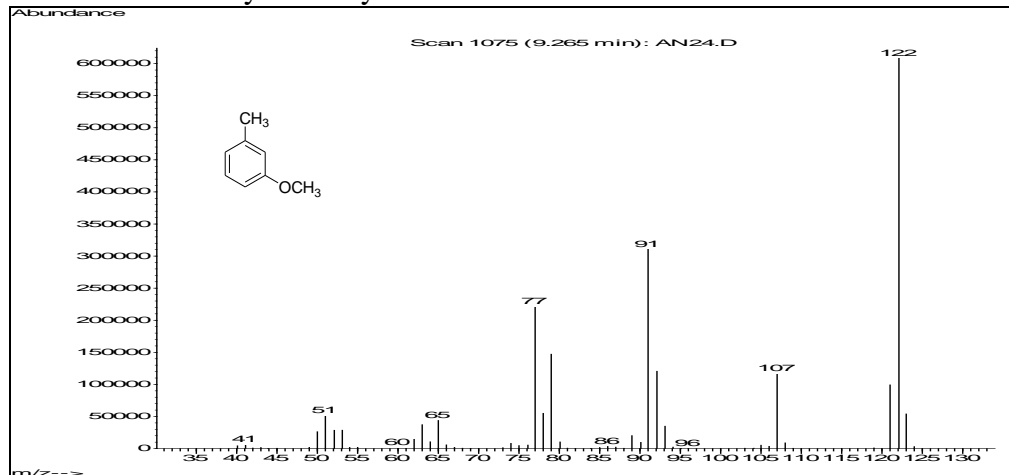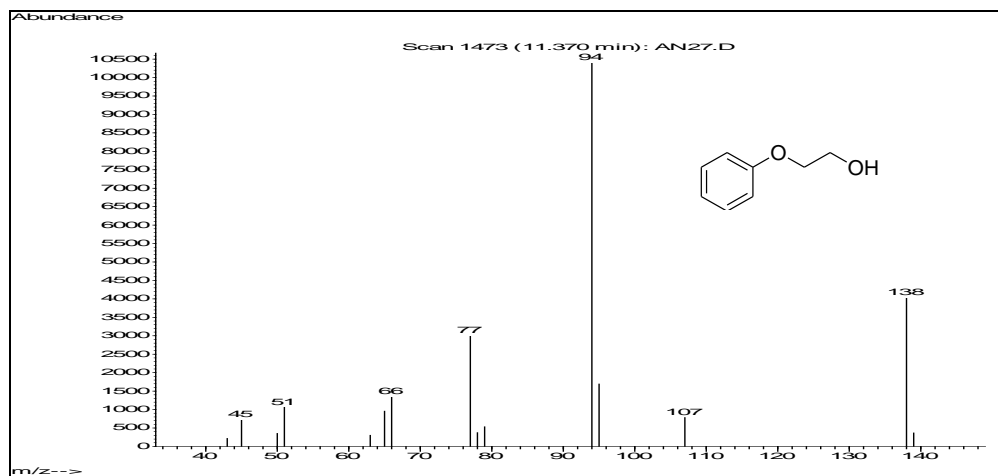
GC-MS:2-methoxynapthalene
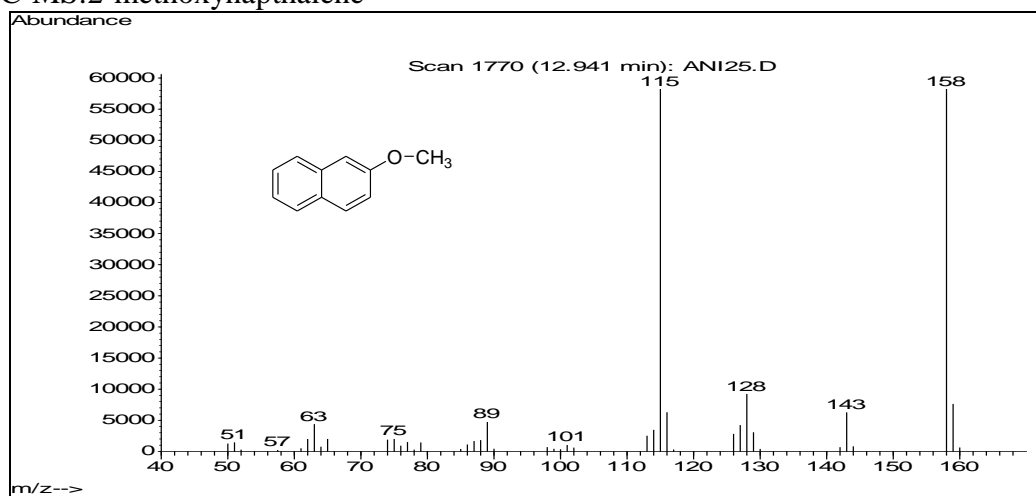
GC-MS: 2-(2-phenoxyethoxy)ethanol
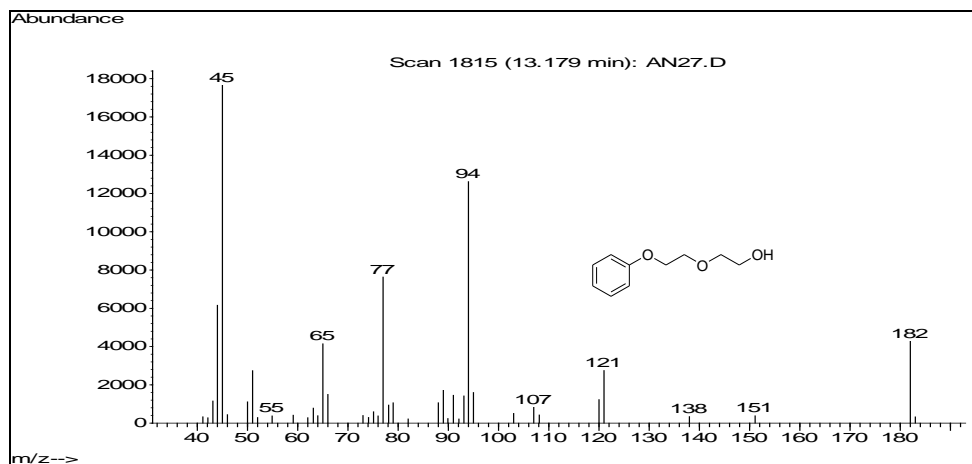
GC-MS:2-phenoxyethanol

List of publications

1. Dibutyltin oxide catalysed aminolysis of oxalate to carbamate, oxamate and derivatives of imidazolidine trione, Lalita B. Kunde, Vishwanath S. Kalyani and Sunil P. Gupte, **Apllied Organometallic Chemistry, 2010, 24, 402-407.**

2. Catalytic synthesis of chalcone and flavanone using Zn-Al hydrotalcite adhere ionic liquid, Lalita B. Kunde, Swapana M. Gade, Vishwanath S. Kalyani and Sunil P. Gupte, **Catalysis Communication, 2009, 10, 1881-1888.**

3. Synthesis of styrene carbonate from carbondioxide and styrene oxide: Evaluation of process and catalyst parameters, Lalita B. Kunde and Sunil P. Gupte, **Catalysis Science and Technology, Communicated.**

List of symposia participation

1. Poster entitled, "Investigation of role of catalysts in the synthesis of Chalcones and Flavanones "presented at 19th National Symposium on Catalysis, in NCL, January 18-21 2009.

2. Oral presentation of paper entitled, "Immobilized ionic liquid as a catalyst for carboxylation of styrene oxide under mild reaction conditions: *a greener approach*" at '18th National Symposium On Catalysis and Indo-US Seminar on Catalysis' at Indian Institute of Petroleum, Dehra Dun, India, April 16-18, 2007.