ORGANIC REACTIONS USING NOVEL REUSABLE SOLID CATALYSTS FOR THE SYNTHESIS OF FINE/SPECIALTY CHEMICALS

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By

RANI JHA, M.Sc.

CHEMICAL ENGINEERING AND PROCESS DEVELOPMENT DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE?411008, INDIA

APRIL, 2005

CERTIFICATE AS PER FORM 'A'

Certified that the work incorporated in the thesis "**ORGANIC REACTIONS USING NOVEL REUSABLE SOLID CATALYSTS FOR THE SYNTHESIS OF FINE/SPECIALTY CHEMICALS**' submitted by Ms. Rani Jha was carried out by the candidate under my guidance. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. Vasant R. Choudhary)

Research Guide

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PUNE   **Rani Jha**

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SUMMARY AND CONCLUSIONS

Synthesis of fine chemicals using conventional homogeneous catalysts poses several problems, such as difficulty it its separation and recovery, disposal of spent catalyst, formation of undesirable and/or toxic wastes, etc. Worldwide efforts have been made for replacing homogeneous catalysts by easily separable and reusable heterogeneous catalysts.

Liquid phase benzylation and acylation of aromatic compounds, using homogeneous Lewis acid catalysts, is commonly practiced Friedel?Crafts type reaction in organic synthesis. However, the commonly used homogeneous acid catalyst, $AlCl_3$ poses several problems, such as requirement of more than stoichiometric amount, difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. moreover, it is highly moisture sensitive and hence demands moisture?free solvent and reactants and anhydrous catalyst, and also dry atmosphere for catalyst handling. Development of reusable solid catalysts having high activity, with little or no moisture sensitivity for the liquid phase Friedel?Crafts reactions is, therefore, of great practical importance. The benzylation or acylation of aromatic compounds containing electron- donating groups (e.g. alkyl, alkoxy, hydroxy, etc) can be accomplished with ease but it is difficult in the absence of such aromatic ring?activating group (e.g. benzene and naphthalene). Hence, worldwide efforts have been made for the benzylation or acylation of benzene and other aromatic compounds, using a number of solid acid catalysts, such as heteropolyacids, sulphated zirconia or Fe_2O_3, Nafion?H, Fe?containing MCM?41, ion?exchanged clays and clayzic for benzylation of benzene, HY, H?beta and H?ZSM?5 zeolites for benzylation of toluene, and heteropolyacids, H?beta, H?ZSM?5 and sulphated zirconia for benzoylation of aromatic compounds. However, these catalysts show low or moderate activity and/or poor selectivity in these reactions. It would be interesting to develop novel metal chloride grafted solid catalysts for their use in the Friedal?Crafts type reactions.

Synthesis by the Friedel?Crafts reactions of benzylated and acylated aromatic compounds containing strong electron withdrawing groups, such as nitro groups, is believed to be not possible. This is because of an electron deficient aromatic ring resulting due to the presence of nitro group(s). Till today no report on the direct Friedel ?Crafts type alkylation and/or acylation of a nitro aromatic compound is known. Hence, the development of a reusable solid catalyst(s) having high activity for the benzylation and/or acylation of nitro aromatic compounds is of both scientific and practical importance.

Aromatic ketones, such as acetophenone and benzophenone are important intermediates for perfumes, drugs and pharmaceuticals. In the past, efforts have been made to produce aromatic ketones by oxidizing the methylene group attached to aromatic ring using stiochiometric quantities of oxidizing agents e.g. oxidation of ethyl benzene to acetophenone by $KMnO_4$, oxidation of diphenylmethane to benzophenone by $KMnO_4$, SeO_2 or CrO_3-SiO_2 and oxidation of alkyl arenes by $KMnO_4$ supported on Mont-K10. However, in these stiochiometric oxidation reactions, the waste produced is very large and, moreover, the separation of reactants and products from the reaction mixture is difficult. Acetophenone can also be produced by the liquid phase oxidation of ethyl benzene by oxygen or air using homogeneous transition metal (viz. Co, Mn, Cu, or Fe) compounds as catalyst. For developing an environ-friendly/green process for the production of aromatic ketones, it is necessary to have a non-toxic and reusable solid catalyst, which shows high activity and selectivity in the oxidation of ethyl benzene to acetophenone and diphenyl methane to benzophenone by molecular oxygen in the absence of any solvent and also without significant leaching of its components in the liquid reaction mixture. It is therefore, interesting to explore the possibility of using $MnO4^{-1}$-exchanged Mg-Al-hydrotalcite catalyst for the selective oxidation of ethyl benzene to acetophenone and diphenylmethane to benzophenone, using O_2 as an oxidizing agent.

Styrene oxide is an important organic intermediate in the synthesis of fine chemicals and pharmaceuticals. It is traditionally produced by epoxidation of styrene using stiochiometric amounts of per acids as an oxidising agent. However, per acids are very expensive, hazardous to handle, non‑selective for the epoxide formation and also lead to formation of undesirable products creating a lot of waste. In order to overcome these limitations, a few studies have been reported on the epoxidation of styrene over environ‑friendly solid catalysts (viz. Ti/SiO_2, TS-1, Ti-MCM-41, Fe or V/SiO_2, TBS-2, TS-2 and ?? Al_2O_3 catalysts, using TBHP, H_2O_2 or urea- H_2O_2 adduct, as an oxidizing agents. With H_2O_2 as an oxidizing agent, although the styrene conversion was very high, the selectivity for styrene oxide was very poor. On the other hand, with TBHP and urea-H_2O_2 adduct as oxidizing agents, high styrene oxide selectivity (> 80%) was observed but only at a low styrene conversion (9.8 and 17.7%, respectively). It is, therefore, important to develop a novel reusable solid catalyst, to achieve high styrene conversion particularly at high styrene oxide selectivity in the epoxidation of styrene.

Oxidation reactions using molecular oxygen as an oxidizing agent, particularly using reusable solid catalyst, are also very important in modern organic synthesis. It is interesting

to explore the possibility of using supported nano‑gold catalysts for the selective oxidation of benzyl alcohol to benzaldehyde, a model oxidation reaction, using O_2 as an oxidizing agent.

The present work for thesis was undertaken as a part of the comprehensive R and D programme in our laboratory for replacing conventional homogeneous catalysts by novel, reusable and highly active/selective heterogeneous catalysts for the synthesis of fine chemicals by green environmentally benign/green processes.

The thesis has been divided into eight chapters, as follows:

CHAPTER‑1 INTRODUCTION ‑ LITERATURE SURVEY, OBJECTIVES AND SCOPE

In this chapter, a brief literature survey on the reactions:

‑ Friedel‑Crafts type benzylation of aromatic compounds,

‑ Friedel‑Crafts type acylation of aromatic compounds,

‑ oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone,

‑ epoxidation of styrene to styrene oxide,

‑ oxidation of benzyl alcohols to aldehydes, using solid catalysts,

has been covered, indicating the objective/scope of the Ph.D. work.

CHAPTER‑2 EXPERIMENTAL

In this chapter, preparation of the following catalysts,

‑ metal chloride grafted zeolites and zeolite‑like micro‑ and mesoporous solid catalysts,

‑ $AlCl_3$ and/or $GaCl_3$ grafted Si‑MCM‑41 and Montmorillonite‑K10 catalysts,

‑ preparation of hydrotalcite and metal exchanged hydrotalcite‑like solid catalysts,

‑ preparation of metal oxide supported catalysts,

‑ supported nano‑size gold catalysts.

characterization of the catalysts for their;

‑ crystalline phases (by XRD),

‑ surface area (using surface area analyzer BET instrument),

‑ crystal size and morphology (by SEM or TEM),

‑ surface hydroxyl groups (by FT‑IR),

? surface composition (by XPS),

? TGA analysis, and also the

procedures for carrying out the catalytic reactions,

? benzylation of aromatic compounds,

? acylation of aromatic compounds,

? oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone,

? epoxidation of styrene to styrene oxide, and

? oxidation of substituted benzyl alcohols to corresponding aldehydes,

have been described.

CHAPTER?3 NOVEL METAL CHLORIDE GRAFTED MICROPOROUS AND MESOPOROUS ZEOLITE?LIKE SOLID CATALYSTS FOR FRIEDAL?CRAFTS REACTIONS

Liquid phase benzylation of benzene by benzyl chloride to diphenylmethane and also acylation of p-Xylene by benzoyl chloride over the thermally activated supported $InCl_3$, $FeCl_3$ and $GaCl_3$ on Si-MCM-41, Mont.K-10 clay and H-beta zeolite have been investigated. The metal chlorides were heterogenized on the supports by reacting the impregnated anhydrous metal chlorides with surface hydroxyl of the support at an elevated temperature (95-800 ^{o}C), resulting in the evolution of HCl gas (which was measured quantitatively) with the formation of oxy-metal chloride species chemically bonded to the support surface. All the catalysts showed high activity for both the benzylation and acylation reactions. The benzylation and acylation using different aromatic substrates have also been investigated. A plausible reaction mechanism for the benzylation and acylation reactions over the grafted metal chloride catalysts is proposed. Among the thermally activated supported metal chloride catalysts $FeCl_3$/H-beta, $InCl_3$/Mont.K-10 or H-beta and $GaCl_3$/H-beta show relatively better performance in both the benzylation and benzoylation reaction.

CHAPTER?4 NOVEL TRANSITION METAL CONTAINING LAYERED DOUBLE HYDROXIDES AND/OR MIXED HYDROXIDES?LIKE SOLID CATALYSTS FOR FRIEDEL?CRAFTS REACTIONS

This chapter deals with the investigating the performance of In-Mg-hydrotalcite (In-Mg-HT) and Fe-Mg-hydrotalcite (Fe-Mg-HT) catalysts in the Friedel-Crafts type benzylation of benzene and substituted benzene by benzyl chloride with or without HCl gas

pretreatment or catalyst calcination. The benzylation reactions of different aromatic substrates have also been investigated. Both the In-Mg-hydrotalcite and Fe-Mg-hydrotalcite catalyst showed high activity in the benzylation of benzene and substituted benzene; the later however is more active.For the catalyst (hydrotalcite or derived from hydrotalcite) in its most active form, the catalytically active species for the benzylation are finely dispersed $InCl_3$ and In_2O_3 on MgO or finely dispersed $FeCl_3$ and Fe_2O_3 on MgO.

CHAPTER?5 BENZYLATION AND ACYLATION OF AROMATIC COMPOUNDS, WITH OR WITHOUT CONTAINING NITRO GROUP, USING $GaCl_x$- AND $GaAlCl_x$- GRAFTED Si?MCM?41 AND MONT. K-10 CATALYSTS

This chapter deals with the use of $GaCl_x$? and $GaAlCl_x$?grafted Si?MCM?41 or Mont.K-10 as a highly active catalyst for Friedal?Crafts type benzylation and acylation of aromatic compounds with or without containing nitro groups. These catalysts were found to be highly active even for the benzylation and acylation of nitrobenzene and other nitro aromatic compounds. The catalysts were prepared by reacting anhydrous $AlCl_3$ and/or $GaCl_3$ with the supports in non?aqueous solvent (viz. CCl_4), leading to the grafting of metal chlorides by their reaction with the surface hydroxyls of the supports. Also, the catalysts showed high activity for the nitrobenzene benzoylation even in the presence of moisture in the catalyst or in the substrate. The active catalytic species are partially chlorided Al and Ga species, $(-SiO)_2Ga(or Al)$, or $(-SiO)_3Ga(or Al)$.

CHAPTER?6: SELECTIVE OXIDATION OF ETHYLBENZENE TO ACETOPHENONE AND DIPHENYLMETHANE TO BENZOPHENONE BY O_2 OVER MnO_4^{-1}-EXCHANGED Mg-Al-HT

Among a number of polyoxo metallate anion exchanged hydrotalcite catalysts, $MnO4^{?1}$?exchanged Mg?Al hydrotalcite is found to be highly active, selective, stable and reusable catalyst for the liquid phase oxidation of ethyl benzene to acetophenone and diphenyl methane to benzophenone by molecular oxygen in the absence of solvent. The performance of the catalyst is markedly improved in its subsequent reuse in the oxidation reactions probably due to the removal of moisture from the catalyst. The oxidation reaction catalyzed by this catalyst is truly heterogeneous one, without leaching of the exchanged $MnO_4^{?1}$ anions. The oxidation activity, H_2O_2 decomposition activity and basicity of the catalyst are increased with increasing the Mg/Al ratio in the hydrotalcite, indicating a good

correlation among them. The thermal stability of the hydrotalcite is increased after the $MnO_4^{?1}$? exchange.

CHAPTER?7: EPOXIDATION OF STYRENE TO STYRENE OXIDE USING METAL OXIDES AND SUPPORTED METAL OXIDE CATALYSTS

This chapter deals with the use of different metal oxides (viz. Alkaline earth metal oxides, transition metal oxides, rare earth metal oxides and Gr. IIIa metal oxides) for the epoxidation of styrene-to-styrene oxide. Among these metal oxides MoO_3, CuO, CoO, NiO and Tl_2O_3 showed very good activity and selectivity for the epoxidation reaction. Some of these metal oxides were used for detailed investigation on the epoxidation of styrene to styrene oxide. Supported CuO, particularly, CuO/Si-MCM-41, CuO/SiO_2 and CuO/Ga_2O_3 are highly promising catalysts, showing high activity and selectivity in the epoxidation of styrene by aqueous TBHP

CHAPTER?8 OXIDATION OF BENZYLIC ALCOHOLS TO AROMATIC ALDEHYDES BY O_2 USING NANO-SIZE GOLD SUPPORTED OVER DIFFERENT METAL OXIDES

This chapter deals with the oxidation of different benzyl alcohols to their corresponding aldehydes using nano-gold catalyst supported on different metal oxide supports. Molecular oxygen is the most desirable oxidizing agent in the synthesis of fine chemicals, both from the environmental and economic considerations. A number of supported nano-gold catalysts (viz. Au supported on MgO, ZrO_2, BaO, CaO, Al_2O_3, TiO_2, MnO_2, Ga_2O_3, In_2O_3, Fe_2O_3 or U_3O_8) were evaluated for their performance in the oxidation of benzyl alcohol by O_2 to benzaldehyde at $130\ ^oC$ in a mechanically stirred reactor. Among the gold catalysts, the $Au(8\ wt.\%)/U_3O_8$ (HDP) catalyst showed the best performance (53% conversion and 95 % selectivity). This catalyst was further used for a detailed investigation on the oxidation of different substituted benzyl alcohols to corresponding aldehydes.

CHAPTER-1

INTRODUCTION - LITERATURE SURVEY, OBJECTIVES AND SCOPE

Chapter-1

INTRODUCTION – LITERATURE SURVEY, OBJECTIVES AND SCOPE

1.1   FINE CHEMICALS

Till to date there are no universal definition of bulk, fine and specialty chemicals. Fine chemicals may often include the intermediates and specialty chemicals such as pharmaceuticals, pesticides, flavors and fragrances, classified as the chemicals, which have prices ranging from 10 US Dollars.Kg^{-1} and above and have a volume of less than 10,000 tons per annum on a worldwide basis. A substance that comes under bulk chemicals might have been classified as a fine chemical in the initial stages of its development. There is almost no difference between the above two grades of chemicals classified as fine chemicals and the one under specialty chemicals.

From the chemical point of view, fine chemicals are generally complex molecules having multifunctional groups attached to it having low volatility and limited thermal stability and hence its formation requires mild reaction conditions. The synthesis of fine chemicals involves multiple steps carried out in a multipurpose apparatus. In contrast bulk chemicals are manufactured in continuous processor in plants. Hence the development of fine chemical synthesis needs processes, which may be used on a broader scale with a scope of implementation in multipurpose equipment.

1.2   ENVIRONMENTAL FACTOR

In the current era there is a serious concern over developing processes, which are eco-friendly, generally termed as "Green Chemistry" [1,2], or sustainable technology necessitates a shift from the traditional concepts of process efficiency, that focus exclusively on chemical yield, to one that assigns economic value to eliminating waste and avoiding the use of toxic and/or hazardous substances and are more environmentally acceptable processes [3].

The magnitude of the waste problem in the manufacture of chemicals measured as 'E-Factor' [4,5], in terms of the amount of waste produced per Kg of product, depicted in Table 1.1. The waste mainly consists of inorganic salts used or formed during or after the reaction during the workup process. The data in the above table clearly indicates the need for greener, environ-friendly technologies for the fine chemicals.

Table 1.1 E factors in the chemical industry.

Industry segment	Product tonnage [a]	E factor (Kg waste/Kg product
Bulk Chemicals	$< 10^4$-10^6	$< 1 \longrightarrow 5$
Fine Chemicals	10^2-10^4	$5 \longrightarrow > 50$
Pharmaceuticals	10-10^3	$25 \longrightarrow > 100$

[a]Depending on the product this could be the capacity of a single plant or the world-wide production.

1.3 DEVELOPMENT OF ORGANIC SYNTHESIS AND CATALYSIS

The main cause of waste production in the fine chemical industry is the widespread use of stiochiometric reagents for example Friedel-Crafts type alkylation and acylation reactions with more than stiochiometric use of $AlCl_3$.

In the past the need for the reduction of waste in the fine chemical industry was not fully appreciated, because of its requirement in small quantities. However, environmental legislation forced the fine chemical industry to focus its attention on waste minimization, avoiding the use of hazardous and/or toxic reagents. Hence, there is a growing interest towards the application of suitable catalytic methodologies in the synthetic organic chemistry.

1.4 HOMOGENEOUS VERSUS HETEROGENEOUS CATALYSIS

Catalytic reactions are mainly classified into two broad categories – homogeneous and heterogeneous catalysis. The major limitations of homogeneously catalyzed reactions are no possible reuse, troublesome work-up, disposal of spent catalyst, and/or high toxicity.

Heterogeneous solid catalysts have the advantages of easy separation of the catalyst from the reactants and products involving simple filtration or centrifugation, ease of recovery and recycling of the catalyst and are therefore environmentally friendly. Hence, efforts are being made to replace homogeneous catalysts by heterogeneous ones in the organic synthesis.

1.5 HETEROGENEOUSLY CATALYZED REACTIONS FOR THE SYNTHESIS OF FINE CHEMICALS

1.5.1 Friedel-Crafts Type Alkylation and Acylation Reactions

Freidel-Crafts reactions as described by Nobel Prize laureate G. A. Olah in the classical series 'FC Related Reactions' [6] in which he defines these reactions 'to be any substitution, isomerisation, elimination, cracking, polymerization or addition reaction taking place under the catalytic effect of Lewis acidic type acid halides or protonic acids'. These reactions are electrophilic in nature and can be divided into two main categories – alkylations and acylations. The reaction occurs by the replacement of a hydrogen atom of an aromatic compound by an alkyl or acyl group derived from an alkylating or an acylating agent in the presence of Lewis acids (e.g. $AlCl_3$, BF_3, $FeCl_3$, $ZnCl_2$, etc) or protonic acids (e.g. H_2SO_4, HF, etc). Among all the catalysts, $AlCl_3$ is commonly used for the Friedel-Crafts type reactions. The overall reaction scheme for the aromatic alkylations or acylations is written as follows:

$$ArH + RX \xrightarrow{\text{Catalyst}} ArR + HX$$
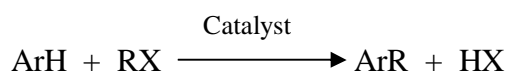
[Where, ArH = aromatic compound; RX = alkylating or acylating agent, X = OH, COCl, COBr, COI, COOH, $O(CO)_2R$].

The primary function of the catalysts is to generate an alkyl or acyl carbocation. A disadvantage of classical Freidel-Crafts chemistry with Lewis acid (metal halides) is that the catalyst coordinates strongly to the basic compounds and eventually becomes exhausted and cannot readily be regenerated. Other drawbacks are during alkylations several reactions can take place concurrently, (e.g. polymerization, polyalkylation, isomerisation, trans alkylation, cracking, etc.) which reduces selectivity for the desired compound.

Friedel-Crafts type alkylation reactions

Friedel-Crafts alkylation of aromatic compounds is widely used in the large-scale production of petrochemicals, fine chemicals and intermediates. Benzylation is an important class of Freidel-crafts type alkylation reaction used for the synthesis of cosmetics, dyes, pharmaceuticals and a variety of fine chemicals. Benzene and other aromatic compounds can be benzylated by different benzyl derivatives (e.g. benzyl chloride, bromide, iodide or alcohol), however benzyl chloride is a commonly used benzylating agent for the benzylation reaction. A number of solid acid catalysts (such as heteropolyacids and their salts [7-13,109], super acids [14-19], zeolites [20-26,111-112], mesoporous MCM-41 type catalysts [27-31,107], metal chloride and clay based catalysts [32-60], metal oxides [61-63], spinel

[64], metal sulfates [65], alumina or silica-alumina [66-68], carbon [69] and hydrotalcite [70]) for the benzylation of benzene and other aromatic compounds by benzyl chloride are reported earlier. The benzylation of aromatic compounds containing electron-donating group (e.g. alkyl, alkoxy, OH) can be accomplished with ease, but in the absence of such groups (e.g. benzene), the benzylation is relatively difficult [6]. The literature studies show that still there is a lot of scope in developing a good catalytic system for the Freidel-Crafts type benzylation reactions. The studies for the benzylation of benzene and other aromatic compounds by benzyl chloride, reported so far, are summarized in Table 1.2.

Friedel-Crafts type acylation reactions

Friedel-Crafts type acylation of aromatic compounds to aromatic ketones (important intermediates for the production of fine chemicals) is one of the most important synthesis methods in organic chemistry. Benzene and other aromatic compounds can be acylated by different carboxylic acid derivatives (e.g. acid halide, acid anhydride, and carboxylic acid as such); acid halide is, however, a commonly used acylating agent for the acylation reaction. In the last 15 to 20 years, worldwide efforts have been made to replace homogeneous acid catalysts by heterogeneous solid acid catalysts, such as heteropolyacids and salts [7-8,12-13], resins [72], modified ZrO_2 [73-77], zeolites [78-93], metal chloride and clay based catalysts [59,94-101], metal oxides [31,63], hydrotalcite [70], metal sulfate [65] and graphite [102] for the acylation of benzene and other aromatic compounds by different acyl halides. The studies for the acylation of aromatic compounds by different acid halides, reported so far, are summarized in Table 1.3.

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Table 1.2 Summary of work on the benzylation by benzyl chloride (BnCl)

Catalyst	Reaction conditions		Conversion of benzyl chloride (%)/Reaction period (min)	Remarks, if any
	Temp.	Reaction mixture		
I	II	III	IV	V
Heteropoly acids and their salts:				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Rb_{2.5}H_{0.5}PW_{12}O_{40}$, $(NH_4)_{2.5}PW_{12}O_{40}$, $Cs_2H_2SiW_{12}O_{40}$, $Rb_2H_2SiW_{12}O_{40}$, $(NH_4)_2H_2SiW_{12}O_{40}$, $K_2H_2SiW_{12}O_{40}$	Reflux	Benzene (100 mmol) + BnCl (5 mmol) + Catalyst (0.02 mmol)	75 (120) 49 (120) 53 (120) 75 (120) 99 (120) 43 (120) 26 (120) 72 (120)	The selectivity for the major mono -alk diphenyl methane (DPM) was 63 %. D active catalyst species from $Cs_{2.5}H_{0.5}$l observed, since, the alkyaltion did no solid catalyst was removed from the re of the reaction.
$H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, HY, LaY, Nafion H, Zn-Mont.-K10	Reflux	Benzene (100 mmol) + BnCl (5 mmol) + Catalyst (65 mg)	41 (120) 93 (120) 36 (120) 50 (120) 24 (120) 100 (120)	The salt catalyst was much more acti acid for the benzylation with benzyl salt catalysts could be repeatedly deactivation.
$Cs_xH_{3-x}(PW_{12}O_{40})$ (x = 2.0, 2.5 and 2.9)	-	Benzene + BnCl + Catalyst	-	Immobilization of heteropoly acid or (especially SiO_2 and Si-MCM-41) redu of dissolution into an aqueous phase.
$H_4SiMo_{12}O_{40}$	-	Anisole + BnCl + Catalyst	-	The reaction proceeds via carboca mechanism brought about by the strong
Tetra-butyl ammonium cation exchanged H_4SiMoO_{40}	-	Toluene + BnCl + Catalyst	-	Only tri-protonated forms of tetra-b cation-exchanged H_4SiMoO_{40} sh comparable with that of the parent cata
$H_0PMo_{12}O_{40}$ (15 wt %)/Silica B, $H_0PW_{12}O_{40}$ (15 wt %)/Silica B	80 ℃	Benzene (100 mmol) + BnCl (5 mmol) + Catalyst (acid = 0.02 mmol, loading 15 wt%)	72.2 (120) 27.2 (120)	Supported heteropoly acids are hig reusable catalysts for the benzylation re
Super acid catalysts:				
SO_4^{2-}/ZrO_2, SO_4^{2-}/heteropoly acids	80 ℃, 100 ℃	Toluene + BnCl + Catalyst	-	Alkylation of toluene with benzyl chlo alcohol in the presence of different sol has been studied.

Table 1.2: (continued)

I	II	III	IV	V
SO_4^{2-}/ZrO_2, Filtro-24, Dodeca-tungsto phosphoric acid	-	Toluene + BnCl + Catalyst	-	Benzyl chloride is more reactive than b the mixture benzyl alcohol reacts firs completely consumed, BnCl begins to to preferential adsorption of benzyl alc
SO_4^{2-}/ZrO_2, SO_4^{2-}/ Fe_2O_3, SO_4^{2-}/ZrO_2-Fe_2O_3	80 °C	Benzene + BnCl + Catalyst	-	Among the catalysts, SO_4^{2-}/ Fe_2O_3 activity; however, SO_4^{2-}/ZrO_2-Fe_2O reusability
Ion –exchange resins (Lewatit & Amberlist-15)	80 °C	Benzene (10 mmol) + BnCl (1 mmol) + Catalyst	-	The yield of DPM was low when Br benxylating agent instead of benzyl the ion-exchange resin Amberlyst-1! catalyst
Zeolites:				
H-ZSM-5 (Si/Al = 6.0) H-Beta (Si/Al = 27.5) $HY_{2.5}$ (Si/Al = 2.5) HY_{10} (Si/Al = 10) HY_{20} (Si/Al = 20)	110 °C	Toluene (2 5 g) + BnCl (5 g) + Catalyst (0.5 g)	50 (>1200) 50 (370) 50 (1100) 50 (370) 50 (42)	Protonic zeolites are active and catalysts for the benzylation reaction
HY	50-100 °C	Biphenyl + BnCl + Catalyst	-	Solvent effect stud ied. Mono-benzy appreciable quantity of di-benzyl obtained. Within the mono-benzylated p-product is observed.
H-Beta, HY	40-70 °C	Naphthalene + BnCl + Catalyst	-	H-Beta shows high activity and selec benzyl naphthalene
H-Beta	93 °C	O-Xylene + BnCl + Catalyst	33.5 (60)	H-Beta is recycled 4 times and a d conversion is observed after each related to the minor dealumination of by HCl formed during the reaction.
Mordenite	60-100 °C			The Freidel-Crafts hydroxyalkylation of supercritical CO_2 was studied.
Na-Y, ZSM-5 and ZSM-?	358 K	Benzene: Benzyl chloride = 3:1 molar ratio, Catalyst (0.5 g)	89.1 (360) 64.8 (360) 2.8 (360)	The catalysts were found to give compared with $AlCl_3$.
H-AlMFI H-FeMFI H-FeAlMFI H-GaMFI H-GaAlMFI	80 °C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	0 (90) 90 (25) 90 (104) 90 (82.5) 90 (56.2)	H-AlMFI zeolite (having high acidity) activity in the benzylation of be benzylation activity id decreased drasti partial or complete subs titution of its f Fe or Ga.

Table 1.2: (continued)

I	II	III	IV	V
ZnO/H-ZSM-5 Fe$_2$O$_3$/H-ZSM-5 Ga$_2$O$_3$/H-ZSM-5 In$_2$O$_3$/H-ZSM-5	80 ºC	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	50 (183) 90 (8.5) 90 (17.6) 90 (17.0)	The impregnation of the zeolite by Fe and In$_2$O$_3$ makes the zeolite highly benzylation reaction. The redox functio the modification of the H -ZSM-5 by seems to play important role in the ben
Mesoporous MCM-41 type catalysts:				
MCM-41	-	Biphenyl + BnCl + Catalyst	-	The mesoporous MCM -41 are only sl than amorphous silica -alumina and H' more active than them and about a s are.
Fe-MCM-41, Zn-MCM-41, Cr-MCM-41, Ni-MCM-41, Al-MCM-41	-	Benzene + BnCl + Catalyst	-	Fe-containing molecular sieve shows h no relationship between activity and ac metal containing (e.g. Zn, Cr, Ni, Al a was found.
AlSiMCM-41, LaSiMCM-41, Si-MCM-41, Fe(6.2)/Si-MCM-41, Fe-Si-MCM-41 (7.7), FeUSY (13), FEKL (6.5)	60 ºC	Benzene + BnCl + Catalyst	-	Both Fe-Si-MCM-41 and Fe/Si-MCl high activity with 100% selectiv Temperature greatly influences the containing zeolite samples. After H$^+$ Na$^+$, the conversion of BnCl on Fe decreased, indicating H$^+$ may enhanc the Fe(III) species deposited sample reaction.
Fe-HMS, Fe-MCM-41	333-363 K	Benzene (25 ml) + benzyl chloride (6.48 or 2.16 ml) + Catalyst (0.1 g)	100 (135) 95 (60) 73.6 (30)	Fe-MCM is an active catalyst for the F show lower sensitivity to water can easily by calcination.
Ga$_2$O$_3$/Si-MCM-41, In$_2$O$_3$/Si-MCM-41	60 ºC	Benzene (20 mmol) + BnCl (1 mmol) + Catalyst (60 mg)	3 (120) 1 (120) 91 (120) 99 (120) ?1 (120)	Fe-containing mesopo rous materials ar selective catalyst. Pore size is (influences activity of catalyst. Fe/KL a only pore size of 0.7 nm and a super diameter, respectively, exhibit little acti
ZnCl$_2$ (or NiCl$_2$)/Mont.-K10	-	Benzene (1.6 mol) + BnCl (1 mmol) + Catalyst (60 mg)	80 (15)	Mont.K-10 clay supported on Si-MC active catalyst for Friedel -Crafts alkyal
Zn, Ni, Al, Cu, Cd, Co or Mg deposited on clay or hydrous silicate	-	Benzene (140 ml) + BnCl (10 ml) + Catalyst (8 g)	99 (15)	-

Table 1.2: (continued)

I	II	III	IV	V
Metal chlorides and clay based catalysts:				
$ZnCl_2$ (or $CuCl_2$ or $MgCl_2$)/Mont.-K10	-	Benzene (or chlorobenzene) + BnCl + Catalyst	-	The alkylation of benzene with $ZnCl_2$/Mont.K10 gave 80% DPM and using $CuCl_2$/Mont.K-10 gave 2-diphenylmethane (30: 70) in 70% yield.
Zn(II) substituted Smectite clay	-	Benzene + BnCl + Catalyst	-	Maximum catalytic activity in the benzene was achieved after 150 ℃ acti
Fe-Pillared clay	-	-	-	The high activity of the catalyst is a higher Fe3+ contents in the catalyst a effect.
Acid treated Kaolinite	-	Benzene + BnCl + Catalyst	-	Natural Kaolinitic clays having trans their lattice posses disorder structure, results in the generation of larger amou cations, higher surface area and compared to the ideal Kaolinites. Th Kaolinites show high catalytic activity for the conversion of BnCl to DPM.
$FeCl_3$/Mont.K-10	-	-	100 (15) in case of benzene	Complete conversion of BnCl within 5 and toluene
H_2SO_4/Kaolinite, HNO_3/Kaolinite, H_2ClO_4/Kaolinite	80 ℃	Benzene (0.25 mol) + BnCl (0.025 mol) + Catalyst (1 g)	86.1 (45) 87 (30) 86.5 (240)	The acid treated clay was prepare calcined clay (calcined at 550 ℃ for 5 in the solid/liquid wt. ratio 1 : 4 fo samples were then washed thoroughl water and then dried in air oven at 110 then calcined at 400 ℃ for 3 h.
Fe(III) exchanged Kaolinites	80 ℃	Benzene (2 mol) + BnCl (0.1 mol) + Catalyst (2 g)	-	Modified Kaolinites containing Fe(III) for the interstial cations are efficie Friedel-Crafts benzene benzylation u 80% conversion with 100% selectivity.
$ZnCl_2$-Aluminosilicate	Room temp.	Benzene (22 ml) + BnCl (5.8 ml) + Catalyst (0.5 g)	97 (15)	Zn-aluminosilicate is an effective catalyst.
$FeCl_3$/Mont.K-10	80 ℃	Benzene (10 ml) + BnCl (0.23 ml) + Catalyst (0.1 g)	100 (5)	The maximum catalytic activity was Mont.K-10 modified by $FeCl_3$ in ace and activated at 120 ℃.
H_2SO_4 (30%) treated clay supported $ZnCl_2$	Room temp.	Benzene(0.2mmol), BnCl (0.01mmol), Catalyst(0.25mmo)	92 (30)	Optimum activity for the clay supp achieved after 20 h acid treatment.

Table 1.2: (continued)

I	II	III	IV	V
ZnCl$_2$/Al$_2$O$_3$	Room temp.	Benzene (22 ml) + BnCl (5.8 ml) + Catalyst (0.5 g)	98 (15)	Alumina was synthesized by a sol-g... modifying agent such as 2,4-pentanedio... benzophenone and dibenzoyl methane. T... and benzophenone modified alumina supp... found to be effective catalyst for Friedel-C...
Graphite-AlCl$_3$ intercalation compound	-	Aromatics +BnCl + Catalyst	-	Graphite-AlCl$_3$ intercalated compound is ... for the benzylation reaction.
Clayzic	-	Toluene (or mesitylene) + BnCl + Catalyst	-	Toluene is more reactive than mesitylen... benzylated separately but one-pot ... mesitylene, with high intermolecular select...
Clayzic	-	Toluene + BnCl + Catalyst	-	In the benzylation of toluene with clayzic, ... benzyl alcohol taking place preceden... chloride.
AlCl$_3$, FeCl$_3$ and ZnCl$_2$ doped Bentonite clay	-	Activated arenes + BnCl + Catalyst	-	The doping of bentonite K10 with lewis a... and ZnCl$_2$ has been found to enhance the ... of clay remarkably.
CuCl$_2$/Alumina	-	Aromatics + BnCl + Catalyst	-	Alumina supported CuCl$_2$ effectively c... Crafts benzylation of aromatics wit B... condition.
Envirocrat EPZ 10	90 ℃	Biphenyl + BnCl + Catalyst	> 99 (60)	Ortho/para selectivity = 1/3
GaCl$_3$/Mont.K-10, InCl$_3$/Mont.K-10, GaCl$_3$/ Si-MCM-41, InCl$_3$/Si-MCM-41,	80 ℃	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	90 (14.9) 90 (6.2) 90 (26.8) 90 (8.9)	Mont.K-10 and Si-MCM-41 shows little ... the benzylation of benzene; Mont.K -10 ... supported GaCl$_3$ and InCl$_3$ catalysts ... benzylation activity. The supported A... catalytic activity.
M(OTf)$_2$ (M = Sc, Cu, Zn and Sn) in ionic liquid	80 ?C	Anisole (5 mmol) + Benzoyl chloride (1mmol) + Catalyst (0.1 mmol) + ionic liquid (2 ml)	100 87 74 10 64 80 82	Metal triflates are a promising catalyst for ... Cu(OTf)$_2$ proved to be the best catalyst.
Aluminosilica SBA-15 meso / macroporous monoliths and mesoporous powders	-	-	>90%	Studies on the effects of framework cry... size, pore size, and pore structure on the c... was done.

Table 1.2: (continued)

I	II	III	IV	V
Metal oxide catalysts:				
H_2SO_4 treated SnO_2	-	Aromatics + BnCl + Catalyst	-	The alkylation activity of SnO_2 treatment.
TlO_x/silica-alumina (HS) TlO_x/silica-alumina (LS) TlO_x/SI-MCM-41 (HS) TlO_x/silica (HS) TlO_x/zircoina (HS) TlO_x/zircoina (LS)	80 °C	Benzene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	0 (150) 90 (10) 0 (150) 90 (19) 0 (150) 90 (8.2)	The supported TlO_x prepared us supports are inactive in the benzy contrast, the TlO_x supported c sintered macro porous supports benzylation activity.
Spinel:				
$CuCr_{2-x}Fe_xO4$	-	Benzene + BnCl + Catalyst	-	$CuFe_2O_4$ gives the high benzen The Lewis surface acidity of the responsible for the good catalytic
Metal sulphates:				
$FeSO_4$, $Fe_2(SO_4)_3$	45 °C	Toluene + BnCl + Catalyst	-	Both the catalysts calcined a maximum catalytic activity. The 700 °C contains 0.15% sulphur.
Amorphous silica -alumina	80 °C	Biphenyl + BnCl + Catalyst	-	Amorphous silica -alumna cataly less active than zeolites, ho advantage of being stable and a some cases it could be more catalyst in a long reaction time.
silica-alumina	160 °C	Biphenyl + BnCl + Catalyst	15 to 16 (-)	Silica-alumina shows hig h activi reaction.
$KF-Al_2O_3$	160 °C	$PhNH_2$ + BnCl + DMF+ Catalyst	88.4 (840)	$KF-Al_2O_3$ is an active catalyst f aniline.
Carbon catalyst:				
Carbon	170 °C	Naphthalene (1 mol) + BnCl (1 mol) + Catalyst	11.6 (30)	Selectivity of mono -benzyl na naphthalene and tri -benzyl naph 29.4% and 6.8%, respectively.
Hydrotalcite catalysts:				
Fresh Ga-Mg-Ht HCl pretreated GA-Mg-HT Used Ga-Mg-HT	110 °C	Toluene (13 ml) + BnCl (1 ml) + Catalyst (0.1 g)	90 (44) 90 (5.75) 90 (3.0)	Ga-Mg-HT (calcined at 200 °C) shows very large induction peri of toluene. But after its use in pretreatment, the hydrotalcite der very high activity in the benzylat a drastic reduction in the inductio presence of moisture in the reacti

Table 1.3 Summary of work on the acylation of aromatic compounds by acyl halides (AcCl)

Catalyst	Reaction conditions		Conversion of acyl chloride (%)/Reaction period (min)	Remarks, if any
	Temp.	Reaction mixture		
I	**II**	**III**	**IV**	**V**
Heteropoly acids and their salts:				
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Rb_{2.5}H_{0.5}PW_{12}O_{40}$, $(NH_4)_{2.5}PW_{12}O_{40}$, $Cs_2H_2SiW_{12}O_{40}$, $Rb_2H_2SiW_{12}O_{40}$, $(NH_4)_2H_2SiW_{12}O_{40}$, $K_2H_2SiW_{12}O_{40}$	Reflux	P-Xylene (100 mmol) + BzCl (5 mmol) + Catalyst (0.01 mmol)	57 (120) 64 (120) 46 (120) 18 (120) 12 (120)	Dissolution of any ac from $Cs_{2.5}H_{0.5}PW_{12}O_{40}$
$H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, HY, LaY, Nafion H, Zn-Mont.-K10 (140 mg)	Reflux	p-Xylene (100 mmol) + BnCl (5 mmol) + Catalyst (35 mg)	39 (120) 9 (120) 9 (120) 48 (120) 35 (120)	The salt catalyst was m the free acid.
Tunstosilicic acid/Silica B, Tunstophosphoric acid/Silica B	138 ℃	p-Xylene (30 mmol) + BnCl (3 mmol) + Catalyst (loading = 15 wt%, net amount of heteropolyacid = 0.01 mmol, calcined at 300 ℃)	46 (60) 33.2 (60)	Supported acid prove catalyze the Acylation insoluble catalysts calcined at 200 -500 ℃
$H_{0.5}Cs_{2.5}PW_{12}O_{40}$	463 K	Benzene (1.17 mol) + Benzoic anhydride (6.6 mol) + n -tetradecane (2.53 mmol) + catalyst (0.33 mmol)	52 98 >1 67	The heteropolyacid pro catalytic system for th detailed studies on the were also done.
Resin based catalysts:				
Silane modified perfluorosulphonic acid, Nafion resin	140 ℃	m-Xylene (21.2 g) + BzCl (14 g) + Catalyst (1 g)	99 (360) 99 (360)	Surface modified catal are very effective het for Friedel-Crafts acyla
ZrO$_2$ based catalysts:				
WO_3/ZrO_2, WO_3/TiO_2 WO_3/SnO_2, WO_3/Fe_2O_3 MoO_3/ZrO_2, SiO_2-Al_2O_3 Acidic zeolite, Mordenite	100 ℃	Toluene (15 ml) + BzCl (0.281 g) + Catalyst (0.5 g)	19 (180) 20 (180) 74 (180) 18 (180) 0 (180) 1 (180)	These catalysts show s the benzoylation of t difficulties in the intermediate acyl ca chloride.

Table 1.3 (Continued)

I	II	III	IV	V
ZrO$_2$ based catalysts:				
Zr/c1 [(ZrO$_2$ (from ZrOCl$_2$, 500 ºC)] Zr/amSO$_4$[Zr/1, (NH$_4$)$_2$SO$_4$] Zr/SOCl$_2$ [Zr/1, SOCl$_2$] Zr/SF$_4$ [Zr/1, SF$_4$] A/c [ZrO$_2$ aero gel, 300 ºC], A/c-SO$_4$ [A/c-H$_2$SO$_4$] A/c-PO$_4$ [A/c-H$_3$PO$_4$] Zr/com [SO$_4^{2-}$/ZrO$_2$, comer] ? AlF$_3$, ? Al$_2$O$_3$	140 ºC	Anisole (12 ml) + BzCl (0.00265 mol) + Catalyst (0.2 g)	0 (420) 76 (420) 1 (420) 12 (420) 0 (420) 86 (420) 57 (420) 57 (420) 0 (420) 2 (420)	Acylation of anisole over sulfated different methods has been s tudied.
Zeolite based catalysts:				
?-alumina Modified zeolite Y Nafion	130 ºC	m-Xylene (0.1 mol) + BzCl (0.05 mol) + solvent (sulfolane = 20 ml) + Catalyst (1 g)	96 (360) 94 (360) 80 (360)	Non-framework alumina in the zeoli catalyst in the acylation of m -Xylene wi
HY	-	Thiophene + BzCl (or acetyl chloride) + Catalyst	-	Thiophene is slightly more adsorbed tha catalyst. Kinetic follows La machanism .
H-Al-Beta H-Ga-Beta H-Fe-Beta	80 ºC	Benzene (0.1 mol) + BzCl (0.02 mol) + Catalyst (0.93 g)	54 (1080) 32.8 (1080) 19 (1080)	Higher yield of benzophenone was obt the reaction temp., catalyst conc. a benzene/BzCl. Isomorphous substitution significantly decreased yield of benzoph to decrease in acid strength order: H -A > H-Fe-Beta.
H-RE-Y H-Beta	85 ºC	Naphthalene (0.039 mol) + BzCl (0.0195 mol) + Catalyst (1.01 g) + Dichloroethane	7.2 (1080) 17.6 (1080)	H-Beta catalyzes the benzoylation of BzCl efficiently, which leads to the form naphthalene in high selectivity.
H-Beta In-H-Beta	70 ºC	Naphthalene (0.023 mol) + BzCl (0.011 mol) + Catalyst (1 g)	30.3 (-) 25.4 (-)	The yield of benzyl naphthalene is decre H-Beta as compared to H-Beta.
USY, ZSM-5	-	Anisole, Phenyl acet yl chloride + Catalyst	-	Zeolite catalysts are active in the acylati phenyl acetyl chloride.

Table 1.3 (Continued)

I	II	III	IV	V
H-ZSM-5	120 ℃ (bath temp.)	Activated arenas (0.01 mol) + BzCl (0.01 mol) + Cat. (0.1 g) + solvent (EDC = 25 ml)	50 (300) in case of anisole	Activated arenes underwent benzoyl the reaction is essentially regiospec benzenes and naphthalene failed to u under the reaction cond itions.
H-ZSM-5 H-ZSM-12 H-Beta H-Mordenite HY NaY NaREY HREY SiO$_2$-Al$_2$O$_3$	115 ℃	Toluene (0.1 mol) + BzCl (0.022 mol) + Catalyst (0.93 g)	4.2 (1080) 41 (1080) 83.4 (1080) 19.5 (1080) 18.8 (1080) 3.8 (1080) 31.6 (1080) 61.7 (1080) 3.2 (1080)	Acidic zeolites are active in th ben with BzCl. H-Beta shows high ac among the zeolite catalysts.
H-Beta	Reflux	Veratrole + propionyl chloride + Catalyst	67.8 (240) (isolated yield)	H-Beta shows high activity in the Ac
Arene sulphonic acid containing SBA -15 material		Anisole (185 mmol) + acetic anhydride (196 mmol) + Catalyst (0.5 g) + Solvent (40 g)	24 (180) 35.0 (180) 57.8 (180)	Arene sulpho nic acid modified SBA a highly active FC Acylation catalyst
H-Beta	270 ℃	Chlorobenzene + Propionyl chloride + Catalyst	5.6 (240) (isolated yield)	H-Beta is an active catalyst for the A
HBEA, HMFI and HFAU	90 ?C	-	-	It has been demonstrated that the co of the reactants is affected by the reactants, nature of the zeolite. T mechanism is also proposed.
Al-ITQ-7	573 K	2-methoxynaphthalene (4 mmol) + Acetic anhydride (2 mmol) + chlorobenzene (3 ml) + catalyst (100-200 mg)	10-80 %	Al-ITQ-7 zeolite is a highly active/ the Friedel -Crafts Acylation reaction
Metal chloride and clay based catalyst:				
EPZG	130℃-140 ℃	Benzene + BzCl + Catalyst	66 (1800)	EPZG is a supported active cataly reaction.
FeCl$_3$/silica gel	Reflux	Benzene (20 mmol) + benzotrichloride (40 mmol) + Catalyst (6 g) + Dichloroethane	72 (240)	Catalyst was prepared by co-grinding in an agate mortar and activating it a

Table 1.3 (Continued)

I	II	III	IV	V
Acid treated Mont.-FeCl$_3$	-	Aromatics + Acyl chloride + Catalyst	-	Acid treated Mont.-FeCl$_3$ is an a Acylation of aromatics with acyl
K-10, KSF	-	Alcohol + Acylating agent + Catalyst	-	Mont.K-10 and KSF are good a alcohols, phenols, thiols and chloride and BzCl.
In$_2$O$_3$/Si-MCM-41 Ga$_2$O$_3$/Si-MCM-41 ZnO/Si-MCM-41	80 ℃	Benzene (13 ml) + BzCl (1 ml) + Catalyst (0.4 g)	54 86 <3	Among the catalysts In$_2$O$_3$/Si-M results, redox function and act substrates play a major role.
Metal oxide catalysts:				
Ga$_2$O$_3$/Si-MCM-41 In$_2$O$_3$/Si-MCM-41	110 ℃	Toluene (13 ml) + BzCl (1 ml) + Catalyst (0.4 g)	80 (182) 80 (130)	Supported Ga$_2$O$_3$ and In$_2$O$_3$ are h for the benzoylation reactions.
TlO$_x$ (20)/zirconia (LS) TlO$_x$ (20)/zirconia (HS) TlO$_x$ (40)/zirconia (HS)	80 ℃	Benzene (13 ml) + BzCl (1 ml) + Catalyst (0.4 g)	50 (158) 0 (150) 50 (196)	TlO$_x$ supported catalyst carriers for the Acylation reaction.
Hydrotalcite catalyst:				
Fresh Ga-Mg-HT HCl treated Ga-Mg-HT Used Ga-Mg-HT	110 ℃	Toluene (13 ml) + BzCl (1 ml) + Catalyst (0.4 g)	0 (120) 0 (208) 90 (165)	Ga-Mg-HT is inactive in the Ac after its use in the toluene b pretreatment, the Ht derived ca activity in the Acylation reaction.
Metal sulfate catalyst:				
FeSO$_4$ (700 ℃) Fe(SO$_4$)$_3$ (700 ℃)	110 ℃	50 ml of 0.5 M BzCl in Toluene + Catalyst	7.7 (-) 10.1 (-)	Conversion of BzCl is calculat initial rate x 10^3 (mol/l.min.g)
Graphite	120 ℃	Anisole (2 mmol) + BzCl (3 mmol) + Catalyst (1 g) + Chlorobenzene	85 (480) isolated yield	Graphite was shown to hav Acylation activity, without disadvantages of using toxic ho such as AlCl$_3$.

1.5.2 OXIDATION OF BENZYLIC CARBON TO CARBONYLS

Aromatic ketones, such as acetophenone and benzophenone are important intermediates for perfumes, drugs and pharmaceuticals. Production of these aromatic ketones by Friedel-Crafts type acylation of aromatic compound by acid halide or acid anhydride, using stiochiometric amount of anhydrous $AlCl_3$, $KMnO_4$, SeO_2, CrO_3-SiO_2 and $KMnO_4$ supported on Mont-K10, leads to the formation of a large volume of highly toxic and corrosive waste [115]. A number of studies on the oxidation of ethylbenzene and diphenylmethane to acetophenone and benzophenone, respectively, using various oxidizing agents over a variety of solid catalysts have been reported in the literature. A detailed literature survey of these studies is presented in Table 1.4.

Although the metal compound used in most of the cases is in catalytic amounts, the reaction conditions are harsh, the product selectivity is poor, often corrosive promoters like bromide anions are used along with the catalyst, the separation of catalyst from the reaction mixture is difficult, the catalyst can't be reused and also a lot of tarry waste is produced. It is, therefore, of great practical interest to develop more efficient easily separable, reusable and environ-friendly catalyst for the production of aromatic ketones. Recently, Choudhary et al [137b] have reported MnO_4^{-1}-exchanged Mg-Al-hydrotalcite as a stable and reusable/environ-friendly catalyst for selective oxidation by oxygen of ethylbenzene to acetophenone and diphenylmethane to benzophenone. The oxidation reaction is expected to involve a mechanism similar to that described by Bukharkina and Digurov [137a] for manganese catalyzed ethylbenzene oxidation by molecular oxygen in non-polar media.

The above literature clearly indicates that the liquid phase oxidation of ethylbenzene and diphenylmethane (methylinic carbon) remains a challenge to an organic chemist using reusable solid catalysts. Hence, there is a need to develop novel heterogeneous catalytic system that can efficiently and selectively oxidize benzylic carbon atom to corresponding carbonyl group.

Table 1.4: Summary of the work on the oxidation of ethylbenzene to acetophenone and diphenylmetha

Catalyst	Oxidizing agent	Yield (%)	Remarks, if any
I	**II**	**III**	**IV**
Nitrous acid in acidic medium	-	-	EW groups retard the rate and ED groups and acid the rate; the oxidations have ionic character.
Electrochemical oxidation	-	-	Aromatic ketones are prepared by electrolysis compounds in the presence of a nucleophile.
KMnO$_4$	-	-	Pharmaceutically pure compounds were obtained in h
K-Peroxydisulfate and copper ions	-	86	The mechanism of the free radical-initiated reaction i
Fe (III) catalyst	H$_2$O$_2$	-	This reaction has been carried out at room temperatur
Transition metal-containing catalyst	Molecular O$_2$	20	Ketones are prepared by the catalytic oxidation/hydr the substrate in the presence of (O), an aldehyde, and proton donor and solvent, using a transition metal Fe catalyst.
Potassium dichromate supported on neutral alumina	Air	3.8% h^{-1}	Catalyst was highly selectivity, reusable and is truly the metal.
Co/Mn/Cl Co/Mn/Br Co/Mn/Cl/Br	-		A kinetic model was developed which explains activity of the Co/Mn/Cl/Br catalyst vs. that of th catalysts.
Silica-supported [g-(di-2-pyridylamino)propyl]siloxane-methyltrioxorhenium complex	-	70.8 84.1	The complex with a Re content of 0.45 mmol/g was catalyst for the oxygenation of diphe decahydronaphthalene (co-reductant) was used as sol
Ce-molybdovanadophosphate heteropoly complex	H$_2$O$_2$	-	The effects of solvent, temperature, H$_2$O$_2$: ethylber ratio) on the catalytic activity was discussed.
N-hydroxy-N-phenyl-2-pyridinecarboxamide cobalt complex	Molecular O$_2$	64	The conversion/selectivity of ethylbenzene increase rise of the reaction temperature or pressure, but cha with the catalyst concentration and Reaction time.
Silica supported transition metal ions (Co, Cu, Cr, Ni or Mn)	-	5.5% h^{-1}	Active transition metal species (Co, Cu, Cr, Ni or Mi on a chemically modified silica gel are used as he catalysts in a range of liquid phase oxidation of alk side chain reaction.
La-molybdovanadophoshate heteropoly complex	Air	-	The quaternary heteropoly complex was synthes precipitation and its structure was ide (NH$_4$)$_{15}$[La(PMo$_9$V$_2$O$_{39}$)$_2$] 6H$_2$O.
Mn-catalysts	Molecular O$_2$	-	Probable reaction mechanism in non-polar medi proposed.
Supported Co(III) complex	Air	70	Solvent-free aerial oxidation of alkyl aromatics efficient fashion is demonstrated.

Table 1.4: (continued)

I	II	III	IV
Cr(III) Schiff's base	Air	50	A highly stable clean process for the oxida aromatics.
Carboxylate bridged dimanganese(III) complex	Molecular O_2	16.9 37.3	Structure of the catalyst was confirmed by single 100% selectivity of the product was obtained.
Cr-supported on hydrophilic catalyst supports, i.e., alumina or silica (EPAD or CHRISS)	Air	43.1 48.7 54.2	Application of dehydration unit in the catalytic ethylbenzene in a batch reactor was studied usin Sieves/SiO_2 as dehydrants. Rate of reaction temperature of the oxidation process.
Fe(III) assisted by 2-picolinic acid	TBHP	84 92	Ketonisation occurs smoothly and shows excel relatively short duration.
Co(acac)$_2$	Molecular O_2	34.6 55.6	The oxidation of ethylbenzene to acetopheno smoothly in the presence of ionic liquids. The was much faster when compared with the reactic ionic liquid.
Co/Mn/Br (MC-type) catalyst	-	-	The promotional effect of CO_2 in the liquid phas ethylbenzene to acetophenone with the Co/Mn/l catalyst system was investigated.
Transition Metal Complexes Encapsulated in Zeolites	-	-	Biomimetic oxidations by metal phthalocyani tetra-aza macrocycles, Schiff bases (salen and sa Cu-acetate and Co-Mn-acetate complexes er zeolite-Y and mol. sieves is reported
Al_2O_3-supported V_2O_5	Molecular O_2	-	Ethylbenzene oxidation results reveal that 1 5% more active than higher vanadia loading catalysts
Cobalt(III) N-phenyl-2-pyridinecarboxamide complexes	-	-	Complexes were found to have high catalytic excellent selectivity in the solvent-free ethylbenzene. XRD of the complexes were also d
Fe/MgO	Molecular O_2	99 71	Activation of C-H bond is possible even at heterogeneous Fe/MgO catalyst. Mechanistic proposed to initiate the radical reaction..
Mn-containing MCM-41	Air	17.6 67.8 25.6	Oxidation of ethylbenzene was achieved at 350 free air over Mn-impregnated and Si- and M(
MnO_4^{-1}-exchanged-Mg-Al-hydrotalcite	Molecular O_2	22.7 32.5 34.6	Solvent-free oxidation of methylene group to carbonyl group without leaching of active compo is highly reusable. Selectivity in all the cases is >

1.5.3 EPOXIDATION

Epoxidation of olefins (to produce epoxides) is an important chemical reaction. Epoxides are intermediates used in the production of pharmaceuticals, agrochemicals, food additives, sweeteners, perfumes, epoxy resins, plasticizers, etc. Of the epoxidation of various olefinic compounds, epoxidation of styrene is of considerable interest because the styrene oxide formed is a valuable intermediate for production of UV-absorbers, perfumes, pharmaceuticals, sweeteners and epoxy resins. This makes the search for a new environmentally friendly, effective epoxidation catalytic system, which is demanding and also challenging one.

A number of studies on the epoxidation of different olefinic compounds (e.g. styrene, cyclohexene, allyl chloride, etc.) using various epoxidizing agents over a variety of solid catalysts have been reported in the literature. A detailed literature survey of these studies is presented in Table 1.5. A number of solid catalysts such as Ti-MCM-41 and Ti-HMS [188], TiZSM-5, -11 [191], Ti-beta, Ti-mordenite [192], Ti-substituted heteropolyanions [194], Cu-HMS [185], Ti-SiO$_2$ [181], V-Silicalite [199], Ti and B containing zeolites [189], transition metal supported on SiO$_2$, Al$_2$O$_3$, zeolite, ZrO$_2$, MgO and activated carbon [203], Fe or V-SiO$_2$ [195], Fe-MCM-41 [207], Cu$_2$(OH)PO$_4$ [208], ?-Al$_2$O$_3$ [222], TS-1 [176,182,222-224], have been used to catalyze the epoxidation of styrene in the liquid phase. Ti-supported on SBA-15 mesoporous silica [197] has been reported for epoxidation of styrene with good selectivity but with the leaching of Ti species during the reaction.

Recently, Choudhary et. al [247-251] has reported Gold nanoparticles deposited on different metal oxides as a highly active/selective and reusable catalyst for the epoxidation of styrene-to-styrene oxide. The literature reviewed clearly indicates that the liquid phase epoxidation of styrene (terminal olefins) remains a challenge using solid heterogeneous catalysts. Hence, there is a need to develop novel heterogeneous catalytic systems for the liquid phase epoxidation of styrene and other terminal olefins.

Table 1.5: Literature Survey for Epoxidation of Olefinic Compounds

Catalyst	Epoxidizing agent	Substrate	Remarks, if any
I	II	III	IV
As-containing catalyst As$_2$O$_3$	H$_2$O$_2$	Cyclohexene	Reaction was carried out with continuou (German Patent)
V$_2$O$_5$-Cr$_2$O$_3$	-	Cyclohexene	Influence of method of catalyst epoxidation/oxidation reaction was studi
B-containing catalyst B$_2$O$_3$	H$_2$O$_2$	Cyclohexene	Reaction is carried out with continuous German Patent
B-containing catalysts	H$_2$O$_2$	Cyclohexene	French Patent
Binary oxide systems V$_2$O$_5$-metal oxides (M = Cr, Mn, Fe, Bi, Mo)	-	Cyclohexene	Kinetic data was obtained.
B$_2$O$_3$ or H$_3$BO$_3$ esters	H$_2$O$_2$	Styrene, Cyclooctene, 1-doddecane	Japanese Patent.
B oxides or H$_3$BO$_3$ esters	H$_2$O$_2$	Cyclooctene Styrene 1-dodecene	Styrene oxide with 38% conversion of F selectivity was obtained.
Mo (V)/Silica	PhC(Me)$_2$OOH	Allyl chloride	-
Mo supported on NaY, ?-Al$_2$O$_3$ and SiO$_2$-Al$_2$O$_3$	Molecular oxygen	Cyclohexene	Low selectivity for epoxide is observed pros\ducts formed in the reaction.
Mo oxide acetylacetonate and N-nitrosodiethylamine	Cumene hydroperoxide	Styrene	Styrene oxide in 72% conversion and was obtained in this reaction.
Ti on silanol group containing silica	Alkylhydroperoxide	Allyl chloride	-
MoY zeolite	-	Cyclohexene	-
Mo-diboride	Cumene hydroperoxide	Styrene	USSR Patent
Mo oxide acetylacetonate and AcONa	Cumene hydroperoxide	Styrene	Styrene oxide in 65.3% conversion and was obtained in the reaction.
Ti-deposited on silica	Cumene hydroperoxide	Allyl chloride	-
Ti deposited on silica or MgO	Cumene hydroperoxide	Allyl chloride	-

Table 1.5: (continued)

I	II	III	IV
diperoxomolybdenum(VI) and HMPT	-	Styrene	The epoxidation of styrene by MoO autocatalytic process. Noncatalytic epoxidation and STO oxidation paths a
Pt-SiO$_2$	H$_2$ + O$_2$	Cyclohexene	1:1 O$_2$-H$_2$ mixture is used.
Chromium trioxide	TBHP	Cyclohexene Cyclopentene Cyclooctene Cycloheptene	Presence of Sodium bicarbonate inc epoxide.
bis(tri-n-alkylstannyloxy)molybdic acids and NR$_1$R$_2$R$_3$ (R$_1$-R$_3$ = H, Me, Et, C$_3$H$_7$, C$_4$H$_9$, CH$_2$CH$_2$OH)	H$_2$O$_2$	Styrene	Styrene 96% conversion and selectivi 82, vs. conversion of styrene and se oxide 10%, respectively, for a contr addition of Me3N.
MoSe$_2$, MoSi, MoS$_2$, Wse$_2$	Cumyl hydroperoxide Cyclohexyl hydroperoxide	Styrene Cyclohexene	-
MoSe$_2$	Cumyl hydroperoxide	Cyclohexene	--
W-containing heteropolyacid supported on different support	Aqueous H$_2$O$_2$ TBHP	Allyl chloride Allyl alcohol	Alumina, silica, basic resins are used catalysts (WO Patent)
Ti-ZSM-11	-	Allyl chloride	Different catalysts are prepared by hy and used in the epoxidation reaction .
TS-1	H$_2$O$_2$ in water or alcohol		High rate of reaction in methanol as of oxirane ring and oxidation of sol reactions.
TS-1	Aqueous H$_2$O$_2$	Allyl chloride	Different parameters affecting the e chloride are described.
TS-1	Aqueous H$_2$O$_2$	Styrene	The influence of polar and non -pol time, temperature and ratio of styrene
TS-1	Aqueous H$_2$O$_2$	Allyl chloride	Adsorption of allyl chloride and H $_2$ surface is investigated it shows high y less catalytic efficiency than Ti -ZSM-
Ti-MCM-41, Ti-HMS	Aqueous H$_2$O$_2$	Styrene, Methyl methacrylate, 2,6-di-t-butylphenol	All catalysts exhibited catalytic activit of Ti-silicalite for liquid -phase oxidati
Fe$_2$O$_3$	Molecular oxygen	Cyclohexene	Aldehydes are used in the presence of

Table 1.5: (continued)

I	II	III	IV
Ti-MCM-41	TBHP, 2-methyl-1-phenyl-2-pr-hydroperoxide (MPPH)	Cyclohexene	Surface grafted catalysts are more framework-embedded Ti-MCM-41 and epoxidizing agent than TBHP for alkene
Molybdenum diboride	Cumene hydroperoxide	Styrene	Molybdenum diboride showed good act the radical polymerization in the epoxida
Ti-containing Y Zeolites	-	Cyclohexene	Ti modifies hexagonal NaY and deallu zeolites and activity of these catalysts epoxidation reaction.
TiO$_2$-SiO$_2$	Me$_3$COOH	Allyl chloride	-
TS-1	Aqueous H$_2$O$_2$	Allyl chloride Methallyl chloride	Solvent effect of methanol and blocking catalyst was studied.
Ti-MCM-41	TBHP, 2-methyl-1-phenyl-2-pr-hydroperoxide (MPPH)	Cyclohexene	Reaction is carried out under argon a and high selectivity for epoxide is obser used as an oxidizing agent.
TiO$_2$-SiO$_2$ mixed oxides	TBHP Aqueous H$_2$O$_2$	Cyclohexene	Use of TBHP as an oxidant gives high epoxide.
TiO$_2$-SiO$_2$ mixed oxides	TBHP	Cyclohexene	Effect of water in reaction medium was i
Ti-ZSM-5 Ti-ZSM-11	Aqueous H$_2$O$_2$	Styrene,Propylene epoxidation	Catalysts was prepared by two methods compared in the reaction (Chinese paper
Ti-Silica	Cyclohexyl hydroperoxide	Cyclohexene	Ti-Silica was prepared by reacting TiF$_4$ phase. Maximum selectivity was o catalysts containing less than 2 wt% of 7
Ti substituted heteropoly anions	Air	Styrene Cyclohexene	Reaction is studied over the Ti sub anions in the presence of isobutyraldeh
Heteroployoxometallate as pillars in LDH	Molecular oxygen	Cyclohexene	Aldehyde is used with O$_2$ in the reaction
Co$_2$O$_3$	Molecular oxygen	Cyclohexene	Valeraldehyde is used with the oxygen. (
Hydrotalcite like compounds containing Co, Mn, Ni, Cr, V, etc.	Molecular oxygen	Cyclohexene oxidation and epoxidation	Both oxidation and epoxidation of cycl The main products are 2-cyclohex cyclohexene-1-ol.
Silica suppoted transition metal ions (Co, Cu, Cr, Ni and Mn)	Air or Molecular oxygen	Cyclohexene	Oxidation, epoxidation and Bayer-reactions are studied over these catalysts

Table 1.5: (continued)

I	II	III	IV
Ti and B co-substituted silicalite zeolite TBS-2	Aqueous H_2O_2	Styrene	The epoxidation of styrene and rearra oxide were studied to check the ox properties of the catalyst.
TS-1, Ti-ZSM-5, Ti-ZSM-11, Ti-?, Ti-mordenite	Aqueous H_2O_2	Styrene Propylene	Catalysts were prepared by isomor (Ti4+, Si4+) and hydrothermal crystall
Mn and Co-containing molecular sieves	Air	Cyclohexene, pinene, limonene and styrene	Mn and Co containing molecular siev replacing Al in the ALPO-36.
Ti(Al)-beta Ti-MCM-41	Aqueous H_2O_2	Cyclohexene	Low Al-containing Ti-b was foun production of epoxide and suppress the
Mesoporous TS-1	Aqueous H_2O_2	Cyclohexene Oct-1-ene	Novel mesoporous TS-1 catalyst is fo epoxidation of cyclohexene than the co
M-SiO$_2$ (M = Ti, Fe and V)	Aqueous H_2O_2	Styrene	Ti-SiO$_2$ shows selectivity for the styre
Mn (II) Salen immobilized materials	PhIO and m-CPBA	Cyclic olefins	-
Ti-ZSM-5	Aqueous H_2O_2	Allyl chloride	Effect of temperature, solvent, cata H_2O_2/allyl chloride molar ratio is inves
Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Mo, Ru, Rh, Pd and Ag are dispersed on the carrier such as SiO$_2$, Al$_2$O$_3$, zeolite, ZrO$_2$, MgO or activated carbon	-	Styrene, cyclohexene and higher olefins	Chinese patent.
Transition metals on HMS (mesoporous silica), Cu-HMS, Ti-HMS, Co-HMs and Fe-Silica	TBHP Aqueous H_2O_2	Styrene	Ti-HMS is found effective cataly epoxidation with TBHP. (Chinese Pap
Tungstate and molybdate exchanged LDH	Aqueous H_2O_2	Cyclohexene and allyl alcohol	Mo-exchanged LDH catalyst is activ cyclohexene.
Titanium treated dealuminated aluminosilicate	Aqueous H_2O_2 Cumene hydroperoxide	Propylene Cyclohexene	This material is found useful in t olefins.
TS-1 Ti-beta Ti-MCM-41	Aqueous H_2O_2	n-Hexene Cyclohexene	Large amount of byproduct was foun Ti-MCM-41 catalysts. Silylated Ti-M formation of byproducts in the reaction
Cu(OH)(PO$_4$)	Molecular oxygen	Styrene	-
Ti-MCM-41	Aqueous H_2O_2	Cyclohexene	-
ReO$_4$-Al$_2$O	Anhydrous H_2O_2 in ethyl acetate	Cyclohexene Cyclooctene	Catalyst is prepared by impregnation t

Table 1.5: (continued)

I	II	III	IV
Dodecatungstophosphoric acid (HPA) and cetyldimethylbenzylammonium chloride (PTC)	H_2O_2	Styrene	Kinetics of epoxidation wa s studie converted quantitatively to styren 100% selectivity in $(CH_2Cl)_2$ as s The effects of various parameters w the rate of reaction.
TS-1	Aqueous H_2O_2	Allyl chloride	-
TS-1	Aqueous H_2O_2	Allyl chloride	Reaction was carried out in presenc
Ti-silica	TBHP	Cyclohexene	Catalyst prepared by deposition dichloride on amorphous activity/selectivity to epoxide incr content.
Ti-tartarate complex over calcined mesoporous carriers (HMS, MCM)	-	Styrene	Ti catalysts with calcined mesop showed highest activity whereas, untreated support showed b selectivity.
TS-1 ?-Al_2O_3	Aqueous and Anhydrous H_2O_2	Styrene	Effect of presence of base, react poisoning of acid sites with continu reaction water is studied.
Nb-MCM-41, Nb-SM-2	H_2O_2	Cyclohexene	Both are highly active in the styrene
Al_2O_3	H_2O_2	Cyclooctene	Alumina is a versatile and reusable epoxidation of olefins. A very sm water is essential in the reaction.
M-MCM-41 (M = Fe, V, Mo amd Mn)	TBHP	Styrene Stilbene	Mn-MCM is prepared by direct method and template ion exch Activity and selectivity of these studied in the epoxidation reaction.
TiO_2 nanoparticles dispersed on the silica	Molecular oxygen	Styrene	Photocatalytic epoxidation of styr under mild conditions.
Au/MgO and other alkaline earth oxides	Anhy. TBHP	Styrene	First report on the epoxidation o Gold nanoparticles deposited on N alkaline earth oxides as highly activ reusable catalyst.
Au/TiO_2	Anhy. TBHP	Styrene	Au/TiO_2 was found to be a highly and reusable epoxidation catalyst. exist in both the metallic (Au°) (Au3+) forms.

Table 1.5: (continued)

I	II	III	IV
Au over Gr.IIIa metal oxides	Anhy. TBHP	Styrene	The activity/selectivity of the catalyst order: $Au/Al_2O_3 < Au/Ga_2O_3 < Au/In_2$
Au over transition metal oxides	Anhy. TBHP	Styrene	Among all, Au/TiO_2 and Au/CuO pre method are the promising catalysts.
Au over Yb_2O_3 and rare earth metal oxides	Aq./anhy. TBHP	Styrene	Gold nanoparticles deposited on Yb_2O metal oxides were found to be highly a epoxidation catalyst.
((Cetyl Py)$_{10}$[$H_2W_{12}O_{42}$]) on fluorapatite	Urea-H_2O_2	Cyclic alkenes	The catalyst is an efficient and reusa and solvent-free, catalytic system, catalyst, harmless.
Mn(III) Salen complex exchanged Mont.-K10	NaOCl	Styrene	Enantioselective epoxidation of styrene in high yields with this heterogeneous ee = 69-70%, higher than its heterogene
Manganese oxide octahedral molecular sieves	TBHP	Cyclic olefins	The effects of time, reaction tempera and amount of catalyst were investi reaction conditions and conversion c were maximized at 60 °C using acet solvent.
Potassium chromate and dichromate	TBHP	Styrene	Biphasic epoxidation of styrene by presence of water.

1.5.4 OXIDATION OF BENZYL ALCOHOL

The oxidation of alcohols into aldehydes is a ubiquitous transformation in organic chemistry, and numerous oxidizing agents (viz. organic peroxides, H_2O_2 and molecular oxygen) are available to effect this key reaction. Among the aforementioned oxidizing agents, molecular O_2 is the most attractive option. Selective oxidation of benzyl alcohol to benzaldehyde is a practically important reaction for the production of chlorine–free benzaldehyde required in perfumery and pharmaceutical Industries. A number of studies on the oxidation of benzyl alcohol to benzaldehyde using various oxidizing agents over a variety of solid catalysts have been reported in the literature. A detailed literature survey of these studies is presented in Table 1.6.

Vapor-phase oxidation of benzyl alcohol [253-259] suffers from the drawback of formation of carbon oxides leading to very significantly carbon loss. Liquid-phase oxidation of benzyl alcohol to benzaldehyde is therefore preferable. A number of catalysts viz. PTC [63-65], catalyst containing different metals as Pd [269-278], Pt [280], Ru [281-288], are reported in literature for benzyl alcohol oxidation. Recently, Choudhary et al [298-301] has reported different hydrotalcite and MnO_4^{-1} exchanged hydrotalcite as active and highly selective catalysts for the benzyl alcohol oxidation using aqueous TBHP.

The above literature review clearly tells us that though several studies have been performed on the liquid phase oxidation of benzyl alcohol to benzaldehyde, still there is enough scope for developing a novel solid catalyst for the selective oxidation of benzyl alcohol to benzaldehyde using molecular oxygen as the choice of oxidant.

Table 1.6 Summary of work on the liquid -phase oxidation of benzyl alcohol to benzaldehyde

Catalyst	Oxidizing agent	Reaction condition		Conversion (%) (Selectivity (%))	Remarks, if any
		Temp.	Reaction mixture		
I	II	III	IV	V	VI
PtO_2	Air	RT	Alcohol, Pt (by the reduction of PtO_2 by H_2)	72 (100)	Benzaldehyde was obtained yield.
Phase transfer catalysts with catalytic amounts of aqueous hypochlorite.	-	RT	Alcohol (0.01 mol), 2-chloronaphthalene (0.87 g, used as internal GC standard),tetrabutyla-mmonium bisulphate (5.4 x 10^{-4} mol), 25 ml CH_2Cl_2, sodium hypochlorite (0.04 mol)	77 (76) 49 (47) 89 (79) 82 (78) 100 (100) 99 (92) 98 (94)	PTC with aqueous Na effective, inexpensive an reagent equal or even sup oxidants for the oxidation o
Phase transfer catalyst (TOMA)- Electron transfer catalyst (TPPMn)	-	RT	Alcohol (2 mmol), TPP.Mn(III)Cl (0.007mmol), TOMA (0.12 mmol), NaOCl (0.36 mmol), CH_2Cl_2-H_2O (3 ml/2 ml)	88 (-) 94 (-) 57 (-)	Direct oxidation of benzyl was very slow, greatly transfer catalyst, TOMA transfer catalyst, TPPMn.
$CuCl_2$ and Nitroxyl radical ion (or its hydroxy analogue)	Molecular O_2		Alcohol (10 mmol), nitroxyl ion (1 mmol), CuCl (1 mmol), DMF (25 ml)	96 97 92 91 80	This catalytic system pr method for the oxidation of as the sole product in high y
Hypochlorite	-	30 ℃	Alcohol (0.926Kmmol/m^3,PT C(0.01Kmmol/m^3), Toluene	90 (100)	The optimum conditions CTMAB as PTC and toluen
Ru-Al-Mg-Hydrotalcite	Molecular O_2	60 ℃	Alcohol (2 mmol), Catalyst (0.3 g), Toluene (5 ml)	100 (91) 100 (100) 95 (91)	Catalyst has a carbonate catalyst is easily separab without appreciable loss of

Table 1.6 (continued)

I	II	III	IV	V	VI
5% CuCl, 5% Phenanthroline, 5% DBADH$_2$	Molecular O$_2$	80-90 ?C	CuCl (20 mmol), 1,10-phenanthroline (20 mmol), Toluene (800 ml), K$_2$CO$_3$ (0.8 mmol), DBAD$_2$ (20 mmol), Alcohol (0.4 mmol).	83 (100) 92 (95) 73 (87)	This process is not only eco applicable to large-scale re environmentally friendly.
TPAP and MS4A	Molecular O$_2$	60-70 ?C	Alcohol (2.5 mmol) TPAP (6.125 mol), powdered activated 4A MS (200 mg), Toluene (12 ml),	100 (100)	TPAP was used as an effi oxidation of alcohols to aldehydes.
Pd(OAc)$_2$/pyridine /MS 3A	Molecular O$_2$		Alcohol (1 mmol), base (0.1 mmol), Pd(OAc)$_2$ (0.05 mmol), MS 3A (0.5 g)	100 (100)	A novel combination of Pd 3A catalyzed the oxidation corresponding aldehydes in
Pd(OAc)$_2$	Molecular O$_2$	80 ?C	Alcohol (1 mmol), Pd(OAc)$_2$ (0.05 mmol), Pyridine (0.2 mmol), MS3A (500 mg), Toluene (10 ml)	100 (100) 100 (98) 97 (95) 100 (96) 100 (96) 100 (95) 94 (92) 97 (92)	A simple combination of co reagents Pd(OAc)$_2$/pyridine high catalytic activity for benzylic alcohols to corre The reaction was found to various substituents and pro
Pd-Ag (or monometallic Pd, Ag) supported on Pumice	Molecular O$_2$	60 ?C	Alcohol (0.05 ml), alcohol/Pd molar ratio = 100	-	For all the catalysts 10 observed. Monometallic showed the highest activity.
Ruthenium-TEMPO	Molecular O$_2$	100 ?C	15 mmol alcohol, Ru:TEMPO = 1:3, 13 ml PhCl, 10 mlmin -1 O2-N2 (8:92; v/v)	91 (100) 100 (100) 100 (100) 100 (100) 100 (100) 68 (100)	The combination of RuCl$_2$ affords an efficient catal aerobic oxidation of alcoh the corresponding aldeh selectivity in all the cases.
Perruthenate immobilized with MCM-41	Molecular O$_2$	80 ?C	Benzyl alcohol, Toluene, Catalyst (6 wt%)	100 (100)	A new, highly active, reco heterogeneous catalytic oxid of alcohols to carbonyl deri oxygen has been developed.

Table 1.6 (continued)

I	II	III	IV	V	VI
Ru-Co-Al-hydrotalcite	Molecular O_2	60 ?C	Alcohol (2 mmol), Catalyst (0.3 g), Toluene (5 ml)	100 (96) 100 (100) 100 (95) 100 (92)	The ruthenium hydrotalcite was found to an efficient he for the oxidation of alcoho molecular oxygen. The cata highly reusable.
Pd(II)supported Hydrotalcite	Molecular O_2	80 ºC	Alcohol (1 mmol), Pyridine, toluene (10 ml), Catalyst (1.56 mmolg^{-1} Pd)	74 (62) 100 (100) 98 (91) 94 (87)	Pd (II) supported hydrota efficient catalyst for the giving the aldehydes in high
Ru^{3+}-exchanged-hydroxypatite (RuHAP)	Molecular O_2	80 ºC	Alcohol (2 mmol), RuHAP (0.2 g), Toluene (5 ml)	100 (>99) 100 (95) 100 (99) 100 (92)	RuHAP is an effective he for the oxidation of a dominated by the formation species as the phosphat RuHAP-surface. No leachi the Ru catalyst was found t
Nitrosyl)Ru(salen) complex	-	RT	Alcohol (0.1 mmol), Catalyst (2 ?mol), Toluene (1 ml)	100 (100)	(Nitrosyl)Ru(salen) comple alcohol selectively in the p alcohol.
Polymer supported hypervalent Iodine (V) Resin	-	RT	Alcohol (1 equiv), DCM (15 ml), resin (1.75 equiv)	>95 (84) >95 (100) >95 (100) >95 (100)	First reported polymer su resin reagent capable of collection of alcohols aldehydes with sensitive stru
Ruthenium/TEMPO	Molecular O_2	100 ºC	Alcohol(15mmol),Ru :TEMPO =1:3, PhCl (30 ml)	>99 (90) 97 (100) >99 (93)	The combination of RuCl$_2$ affords an efficient catal oxidation of benzyl al corresponding aldehyde in >
Heteropolyacids and Phase transfer catalyst	H_2O_2	RT	Alcohol, CCL$_4$, heteropolyacid, 1 ml H_2O	-	A detailed investigation has the use of heteropolyacids PTC in the oxidation of Benzaldehyde. Dodeca-tu (WPA) and cetyl trimethyl was found to be the most and the best phase transfer exhibiting highest catalytic a
TEMPO and a polyoxometallate ($H_5PV_2Mo_{10}O_{40}$)	Molecular O_2	100 ?C	Alcohol (1 mmol), Polyoxomettalate (0.01mmol), TEMPO (0.15 ml in acetone)	99.6 (100) 98.3 (100) >99.9 (100) 98.7 (100)	It describes highly selectiv oxidation of alcohols in the as oxidant and polyoxometa

Table 1.6 (continued)

I	II	III	IV	V	VI
Octahedral molecular sieves K-OMS-2 H-K-OMS-2	Air	110 ?C	Alcohol (1 mmol), Toluene (10 ml), Catalyst (0.05 g)	90 (100) 97 (100) 95 (100) 99 (100)	First example of acic oxidation. Octahedral mc OMS-2 and H-K-OMS-: additives gave high convers
cobalt ion-exchanged X and Y zeolite	Molecular O_2		-	-	The catalytic activity in the correlated with the amt. c alkali metal/Co-NaX and -N
Pd(II)hydrotalcite	Molecular O_2	80 ?C	Alcohol (1.0 mmol), Pyridine (0.2 mmol), toluene (10 ml), Catalyst (0.05 mmol)	100 (100) 98 (91) 94 (87) 98 (94) 98 (92) 100 (97) 96 (95) 97 (90)	The catalyst is purely heterc shape selective, can be e prepared and reusable for se
Au/Fe$_2$O$_3$	Molecular O_2	-	-	-	The presence of gold str catalytic activity of iror practically inactive under conditions.
Pd-HAP-0 Pd-HAP-1	Molecular O_2		Alcohol (1mmol), trifluorotoluene (5 ml), Catalyst (0.1-0.3 g)	99 (100) 99 (100) 99 (100)	The PdHAP catalyst is su reactions, is a recyclable w metal.
Pd(OAc)$_2$	Molecular O_2		Alcohol (1.2 mmol), Pd(OAc)$_2$ (0.036 mmol), THF (0.6 ml), Toluene (3.4 ml), Et$_3$N (0.072 mmol), 3A MS (200 mg)	97 93 84	First report on the P oxidation of alcohol at Earlier mechanistic studie active catalyst might containing a single TEA lig:
Mn-Cu and Mn-Co-TEMPO	Molecular O_2	RT	Alcohol (12.5 mmol), TEMPO (1.25 mmol), Mn(NO$_3$)$_2$ (0.25 mmol), Co(NO$_3$)$_2$/Cu(NO$_3$)$_2$ (0.25 mmol), AcOH (12.5 ml)	98 (100) 99 (100) 98 (100) 97 (100) 98 (100)	The oxidation reaction takes condition, with the advan carried out even at large sc:
Aryl substituted NHPI/Co(acac)$_2$	Molecular O_2		-	>95%	Introduction of an aryl increases the activity of the

Table 1.6 (continued)

I	II	III	IV	V	VI
Mn(II), Co(II) or Cu(II) in combination with N-hydroxypthalimide	Molecular O_2	RT	Alcohol (3 mmol), NHPI (0.3 mmol), $Co(OAc)_2$ (0.015 mmol)	100 (92) 75 (94) 100 (98) 100 (95) 100 (95)	The polar effects play a ke the selectivity making the a than aldehyde.
PS-PEG resin/palladium-phosphane	Molecular O_2		Alcohol (0.17 mmol), K_2CO_3 (0.17 mmol), Catalyst (106 mg)	97	By using novel amphiphilic palladium nanoparticles ca alcohols was achieved in wa
$Na_2WO_4.2H_2O$ with acidic ligands	Aq. H_2O_2	-	-	-	The acidic ligands employ acids, heteropoly acid and F In all the cases Benzyl alc selectivity to benzaldeh increasing acidity of the liga
$Cu_2(OH)PO_4$ and $Cu_4O(PO_4)_2$	Molecular O_2	-	-	-	The catalysts are very ac oxidation of olefins and alc molecular oxygen on $Cu_4O(PO_4)_2$ catalysts show in infrared (IR) spectroscop
MnO_4^{-1}-exchanged Mg-Al-hydrotalcite	TBHP	Reflux	Alcohol (52 mmol), TBHP (78 mmol) (70% TBHP in water), catalyst (0.5 g)	28.5 (84.4) 35.2 (99.8) 45.3 (98.4) 50.2 (99.7)	Higher the Mg/Al ratio, hi activity and basicity of the It also shows high activi benzaldehyde to benzoic aci
Non-noble transition metal containing hydrotalcite-like solid	Molecular O_2	Reflux	Benzyl alcohol (96.6 mmol), Catalyst (0.5 g)	11.8 (97.3) 41.0 (70.8) 34.8 (83.7) 18.7 (99.5) 50.9 (70.1)	Among the transition meta Zn, Fe, Mn and Cr) contair solid materials, the Cu or are promising catalysts 1 oxidation of benzyl alcohol.
Pd^{II}-M oxides (M = Co, Cu, Fe and Mn)	Molecular O_2		Alcohol (2 mmol), Pd catalyst, toluene (10 ml)	53-95 (85-100%)	The reaction is purely hete It was suggested that the mostly by dehydrogenation
Pd/MgO	Molecular O_2	70-80 ?C	Alcohol (1 mmol), Catalyst (0.0094 mmol Pd), TFT (1.5 ml)	64 (100) 5 (100) 11 (100) 32 (100)	1% Pd/MgO was found to for the alcohol oxidation w or excess organic solvent.
Transition metal containing LDH and/or mixed hydroxides	TBHP	94 ?C	Alcohol (52 mmol), Catalyst (0.5 g), TBHP (68 mmol)	56.7 (77.4) 46.7 (91.3) 53.9 (70.6)	Out of all, the Mn, Cu hydrotalcite like solid cataly performance.

1.6   OBJECTIVES AND SCOPE

The present work for the Ph.D. thesis was undertaken as a part of the comprehensive R & D programme in our laboratory for replacing homogeneous catalysts by reusable heterogeneous solid catalysts for the synthesis of fine chemicals, with the following objectives.

1. To study the benzylation (by benzyl chloride) and acylation (by benzoyl chloride) of benzene and other aromatic compounds over
   - $FeCl_3$, $InCl_3$ and $GaCl_3$ grafted on microporous and mesoporous zeolite‑like solid catalysts,
   - Novel transition metal containing layered double hydroxides and/or mixed metal hydroxides‑like solid catalysts,

2. To study acylation of aromatic compounds, with or without containing nitro group, using $AlCl_3$ and/or $GaCl_3$ grafted Si‑MCM‑41 and Montmorillonite‑K10 catalysts.

3. To study oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone by molecular oxygen over "MnO_4^{-1}-exchanged Mg-Al-hydrotalcite catalysts.

4. To study selective epoxidation of styrene-to-styrene oxide by anhydrous or aqueous TBHP over metal oxides and supported metal oxide catalysts.

5. To study solvent-free oxidation of benzyl alcohol to benzaldehyde and other benzylic alcohols by molecular oxygen over nano-gold supported on U_3O_8 and other metal oxide catalysts.

1.7   REFERENCES

[1]   C Christ, Ed. Production-Integrated Enviornmental Protection and Waste Management in the chemical Industry, Wiley-VCH, Weinheim, (1999).

[2]   P. T. Anastase and J. C. Warner, Eds., Green Chemistry: Theory and Practice, Oxford Univ. Press, Oxford, (1998).

[3]   P. T. Anatase and T. C. Williamson, Eds., Green Chemistry: Frontiers in Chemical Synthesis and Processes, Oxford Univ. Press, Oxford, (1998).

[4]   R. A. Sheldon, Chemtech, March (1994) 38.

[5]   R. A. Sheldon, Chem. Ind. (London) (1992) 903 and (1997) 12.

[6]   G. A. Olah, Ed., " Friedel-Crafts and Related Reactions" Wiley-Interscience Publ., New York, Vol. 1-4 (1963-1965).

[7]   Y. Izumi, M. Ogawa, W. Nohara, and K. Urabe, Chem. Lett., 10 (1992) 1987.

[8]   Y. Izumi, M. Ogawa, and K. Urabe, Appl. Catal., A, 132 (1995) 127.

[9]   A. Molnar, T. Beregszaszi, A. Fudula, b. Torok, m. Rozsa-Tarjani and I. Kiricsi, Spec. Publ.-R. Eoc. Chem., 216 (1998) 25.

[10]   K. Nomiya, H. Saijo and M. Miwa, Bull. Chem. Soc. Jpn., 53 (1980) 3719.

[11]   K. Nomiya, s. Sasa and M. Miwa, Chem. Lett., 9 (1980) 1075.

[12]   Y. Izumi, N. Natsume, H. Takamine, I. Tamaoki and K. Urabe, Bull. Chem. Soc. Jpn., 62 (1987) 2159.

[13]   Y. Izumi and K. Urabe, Stud. Surf. Sci. Catal., 90 (1994) 1.

[14]   G. D. Yadav, T. S. Thorat and P. S. Kumbhar, Tetrahedron Lett., 34 (1993) 529.

[15]   G. D. Yadav, Adv. Chem. Eng. Nucl. Process Ind., Bhabha At. Res. Cent.: Bombay, India, (1994) 300.

[16]   G. D. Yadav and T. S. Thorat, Tetrahedron Lett., 37 (1996) 5405.

[17]   G. D. Yadav and T. S. Thorat, Catal., [Pap. Natl. Symp.], 12th Meeting Date 1994, 267, Edited by N. M. Gupta, D. K. Chakrabarty, Narosa, New Delhi, India (1996).

[18]   S. N. Koyande, R. G. Jaiswal and R. V. Jayaram, Ind. Eng. Chem. Res., 37 (1998) 908.

[19]   M. Marques da Silva, C. Lucas da Costa, M. Miriam da Magdala and E. R. Lachter, React. Ploym., 25 (1995) 55.

[20]   M. Akatsu, H. Takayama and M. Matsuoka, Eur. Pat. Appl. EP 428081 (1991).

[21]   B. Coq, V. Gourves and F. Fiqueras, Appl. Catal. A: 100 (1993) 69.

[22]   P. Beltrame and G. Zuretti, Ind. Eng. Chem. Res., 36 (1997) 3427.

[23]   D. Bhattacharya, A. K. Pandey and A. P. Singh, Stud. Surf. Sci. Catal., 113 (1998) 737.

[24]   A. P. Singh, B. Jacob and S. Sugunan, Appl. Catal. A: 174 (1998) 51.

[25]   V. R. Choudhary, S. K. Jana and B. P. Kiran, Catal. Lett., 59 (1999) 217.

[26]   V. R. Choudhary, S. K. Jana, Appl. Catal. A: Gen. 224 (2002) 51.

[27]   P. Beltrame, G. Zuretti and F. Demartin, Ind. Eng. Chem. Res., 39 (2000) 1209.

[28]   J. Cao, N. He, C. Li, J. Dong and Q. Xu, Stud. Surf. Sci. Catal., 117 (1998) 461.

[29]   N. He, J. Cao, S. Bao and Q. Xu, Cuihua Xuebao, 19 (1998) 273.

[30]   N. He, S. Bao and Q. Xu, Appl. Catal., A, 169 (1998) 29.

[31]   V. R. Choudhary, S. K. Jana and B. P. Kiran, J. Catal., 192 (2000) 257.

[32]   E. P. Mikheev and L. P. Fedorova, Zh. Prikl. Khim., 56 (1983) 232.

[33]   J. H. Clark, A. P. Kybett, D. J. Macquarrie, S. J. Barlow and P. Landon, J. Chem. Soc., Chem. Commun., (1989) 1353.

[34]   C. M. Brown, S. J. Barlow, D. J. Macquarrie, J. H. Clark and A. P. Kybett, Eur. Pat. Appl. EP 352878 (1990).

[35] S. J. Barlow, J. H. Clark, M. R. Darby, A. P. Kybett, P. Landon, and K. Martin, J. Chem. Res. Synop., 3 (1991) 74.

[36] V. Luca, L. Kevan, C. N. Rhodes and D. R. Brown, Clay Miner., 27 (1992) 515.

[37] C. N. Rhodes and D. R. Brown, J. Chem. Soc., Farady Trans., 88 (1992) 2269.

[38] K. R. Sabu, R. Sukumar and M. Lalithambika, Bull. Chem. Soc. Jpn., 66 (1993) 3535.

[39] S. J. Barlow, T. W. Bastock, J. H. Clark and S. R. Cullen, J. Chem. Soc., Perkin Trans., 2 (1994) 411.

[40] B. M. Choudhary, M. L. Kantam, M. Sateesh, K. K. Rao and P. L. Santhi, Appl. Catal., A., 149 (1997) 257.

[41] S. G. Pai, A. R. Bajpai, A. B. Deshpande and S. D. Samant, Synth. Commun., 27 (1997) 2267.

[42] R. Sukumar, K. R. Sabu, L. V. Bindu and M. Lalithambika, Stud. Surf. Sci. Catal., 113 (1998) 557.

[43] J. M. Miller, D. Wails, J. S. Hartmen, K. Schebesh and J. L. Belelie, Can. J. Chem., 113 (1998) 382.

[44] K. R. Sabu, R. Sukumar, R. Rekha and M. Lalithambika, Catal. Today, 49 (1999) 321.

[45] R. Sukumar, O. K. Shinamma, K. R. Sabu, M. Lalithambika and A. D. Damodaran, Catal. [Pap. Natl. Symp.], 12th Meeting Date 1994, 486, Edited by N. M. Gupta, D. K. Chakrabarty, Narosa, New Delhi, India (1996)

[46] J. M. Miller, M. Goodchild, J. L. Lakshmi, D. Wails and J. S. Hartman, Catal. Lett., 63 (1999) 199.

[47] S. G. Pai, A. R. Bajpai, A. B. Deshpande and S. D. Samant, J. Mol. Catal. A: Chem., 156 (2000) 233.

[48] J. M. Miller, M. Goodchild, J. L. Lakshmi, D. Wails and J. S. Hartman, Mater. Lett., 44 (2000) 164.

[49] A. G. Freeman and S. E. Goh, Pap.-London Int. Conf. Carbon Graphite, 4th, Meeting Date (1974) 329.

[50] C. N. Rhodes, M. Franks, G. M. B. Parkes and D. R. Brown, J. Chem. Soc., chem. Commun., (1991) 804.

[51] A. Cornelis, D. Dony, P. Laszlo and K. M. Nsunda, Tetrahedron Lett., 32 (1991) 2901.

[52] M. Davister and P. Laszlo, Tetrahedron Lett., 34 (1993) 533.

[53] J. H. Clark, S. R. Cullen, S. J. Barlow and T. W. Bastock, J. Chem. Soc., Perkin Trans., 2 (1994) 1117.

[54] P. D. Clark, A. Kirk and K.R. A. Kydd, Catal. Lett., 25 (1994) 163.

[55] T. Cseri, S. Bekassy, F. Figueras, E. Cseke, L-C. de. Menorval and D. Dutartre, Appl. Catal, A: 132 (1995) 141.

[56] R. S. Natekar and S. D. Samant, Indian J. Chem. Sexct. B: Org. chem. Ind. Med. Chem., 34B (1995) 257.

[57] M. Kodamari, G. Shimada and K. Mogi, Nippon Kagaku Kaishi, 12 (1994) 1137.

[58] J. M. Miller, D. Wails, J. S. Hartman and J. L. Balelai, J. Chem. Soc., Farady Trans., 93 (1997) 2939.

[59] C. Calvert, symp. Pap-Inst. Chem. Eng., North West Branch, 3 (3, Integr. Pollut. Control, Clean Technol.) 4.1-4.16 (1992).

[60] V. R. Choudhary, S. K. Jana and B. P. Kiran, Catal. Lett., 64 (2000) 223.

[61] A. Y. Jogalekar, R. G. Jaiswal and R. V. Jayaram, J. chem. Technol. Biotechnol., 71 (1998) 234.

[62] Nippon Steel Corp., Japan, Jpn. Kokai tokyo Koho JP 59181227 (1984).

[63] V. R. Choudhary and S. K. Jana, J. Catal.., 201 (2001) 225.

[64] S. P. Ghorpade, V. S. Dashane and S. G. Dixit, Appl. Catal. A: 166 (1998) 135.

[65] K. Arata, Y. Yabe and I. Toyoshima, J. Catal., 44 (1976) 385.

[66] P. Beltramme and G. Zuretti, Ind. Eng. Chem. Res., 37 (1998) 3540.

[67] K. Sakura, T. Takeuchi and M. Furumoto, Jpn. Kokai Tokyo Koho JP 0.170442 (1991).

[68] W. wang, C. Ma, Y. Yang and S. Hao, Yingyong Huaxue, 9 (1992) 100.

[69] P. Staeglich and n. Volkmann, Ger. Offen. DE 4038933 (1992).

[70] V. R. Choudhary, S. K. Jana and V. S. Narkhede, Catal. Lett., 74 (2001) 95.

[71] J. Chengguo, H. Meiyh and Y. Yiugyan, Chiu. J. Chem., 11 (1993) 452.

[72] M. A. Hrmer, Q. sun, M. J. Michael and Z. Yang, chem. Commun., (1997) 1803.

[73] V. Quashching, J. Deutsch, P. Druska, H. J. Nichlas and E. Kemnitz, J. Catal., 177 (1998) 164.

[74] Y. Xia, W. Hua and Z. Gao, Chem. Res. Chiu. Univ., 15 (1999) 188.

[75] Y. Xia, W. Hua and Z. Gao, Huazue Xuebao., 58 (2000) 86.

[76] K. Arata, H. Nakamura and M. Shouji, Appl. Catal. A: 197 (2000) 213.

[77] G. D. Yadav, M. S. Krishnan, N. S. Doshi, A. A. Pujari and M. S. M. M. Rahuman, Ger. Offen, DE 19857314 (2000).

[78] R. Fang, G. Harvey, H. W. Kuowenhoven and R. Prins, Appl. Catal. A: 130 (1995) 67.

[79] A. P. Singh and D. Bhatacharya, Catal. Lett., 32 (1995) 327.

[80] A. Finels, A. Calmettes, P. Geneste and P. Moreau, Atud. Surf. Sci. Catal., 78 (1993) 595.

[81]   R. Fang, H. W. Kuowenhoven and R. Prins, Surf. Sci. Catal., 84 (1994) 144.

[82]   V. Paul, A. Sudalai, T. Daniel and K. V. rinivasan, Tetrahedron Lett., 35 (1995) 2601.

[83]   A. P. Singh, D. Bhatacharya, and S. Sharma, J. Mol. Catal. A: Chem., 102 (1995) 139.

[84]   A. Myata, K. Matsunaga and M. Ichikawa, Jpn. Kakai Tokyo Koho JP 07089894 (1995).

[85]   D. Y. Ma, Q. L. Wang, W. Jiang, J. Be and Q. Qiu, chiu. Chem. Lett., 7 (1996) 841.

[86]   D. Bhattacharya, S. Sharma and A. P. Singh, Appl. Catal. A., 150 (1997) 53.

[87]   M. Chatterjee, D. Bhattacharya, H. Hayashi, T. Ebina, Y. Onodera, T. Nagashe, S. Sivashaker and T. Iwasaki, Micro. Meso. Mater., 20 (1998) 87.

[88]   A. Chatterjee, D. Bhattacharya, T. Iwasaki and T. Ebina, J. Catal., 185 (1999) 23.

[89]   A. Myata, K. Matsunaga and M. Mamoru, Jpn. Kokai Tokyo Koho, JP 07173096 (1992).

[90]   G. Harvey, A. Vogt, H. W. Kouwenhoven and R. Prins, Proc. Int. Zeolite Conf., 9th Meeting, 2 (1992) 363.

[91]   H. W. Kouwenhoven, E. A. Gunnewegh and H. Van. Bekkum, Ber. Otsch. Wiss. Ges. Erdoel, Erdgas Kphle, Tagunsber, 9601 (1996) 9.

[92]   M. Moromota, K. Akamoto and A. Miyata, Jpn. Kakoi Tokyo Koho, JP 09151156 (1997).

[93]   L. Gilbert and M. Spagnol, PCT Int. Appl. WO 9717324 (1997).

[94]   T. W. Bastock, J. H. clark, P. Landon and K. Martin, J. Chem. Res., Synop., (1994) 104.

[95]   A. Cornelis, P. Laszlo and S. F. Wang, Catal. Lett., 17 (1993) 63.

[96]   B. M. Khadilkar and S. D. Borkar, Tetrahedron Lett., 38 (1997) 1641.

[97]   B. D. Baudry, A. Dormond, F. Montagne and J. R. Desmurs, Fr. Demande FR 2745287 (1997).

[98]   T. S. Li and A. X. Li, J. Chem. Soc., Perkin Trans. 1 (1998) 1913.

[99]   M. Campanati, F. Fazzini, G. Fornasari, a. Tagliani, A. Vaccari and O. Picclo, chem. Ind. (Dekker), 75 (1998) 307.

[100] B. M. Baudry, A. Dormond, S. Richard, a. Bonazza and J. R. Desmurs, Fr. Demande FR 2768728 (1999).

[101] (a) V. R. Choudhary and S. K. Jana, J. Mol. Catal., A: Chemical 184 (2002) 247. (b) V. R. Choudhary and S. K. Jana, J. Mol. Catal., A: Chemical 180 (2002) 267. (c) V. R. Choudhary, S. K. Jana and N. S. Patil, Micropor. Mesopor. Mater., 3 (2003) 21.

[102] M. Kodamari, Y. Suzuki and Y. Yoshida, Chem. Commun., 16 (1997) 1567.

[103] K. Arata, A. Fukai and T. Toyoshima, J. Chem. Soc., Chem. Commun., (1978) 121.

[104] M. Hino and K. Arata, Chem. Lett., (1979) 1141.

[105] Mercedes Álvaro, Debasish Das, Monica Cano and Hermenegildo García, J. Catal., 217 (2003) 406.

[106] V. D. Choube, Catal. Commun., 5 (2004) 321.

[107] K. Bachari, J. M. M. Millet, B. Beniachouba, O. Cherifi and F. Figueras, J. Catal., 221 (2004) 55.

[108] J. J. Chiua, D. J. Pinea, b, S. T. Bishopa and B. F. Chmelka, J. Catal., 219 (2003) 464.

[109] T. Tagawa, J. Amemiya and S. Goto, Appl. Catal., A: General, 257 (2004) 19.

[110] J. A. Melero, R. v. Grieken, G. Morales and V. Nuno, Catal. Commun., 5 (2004) 131.

[111] E. G. Derouane, G. Crehan, C. J. Dillon, H. He and S. B. Derouane-Abd Hamid, J. Catal., 194 (2000) 410.

[112] M. J. Climent, A. Corma, A. Velty and M. Susarte, J. Catal., 196 (2000) 345.

[113] J. Ross and J. Xiao, Green chem., 4 (1979) 129.

[113] D. S. Ross and G. P. Hum, Gov. Rep. Announce. Index (U. S.)., 80 (1980) 335.

[114] M. V. Bhatt and P. T. Perumal, Tetrahedron Lett., 22 (1981) 2605.

[115] (a) P.H. Groggins and R. H. Nagel, Ind. Eng. Chem. 26 (1934) 1313. (b) H. J. Sanders, H. F. Keag and H. S. McCullough, Ind. Eng. Chem. 45 (1953) 2. (c) C. F. Cullis and J. W. Ladbury, J. Chem. Soc. (1955) 2850. (d) R. Gopalan and R. W. Sugumar, Indian J. Chem. 16A (1978) 198. (e) N. D. Valechha and A. Pradhan, J. Indian Chem. Soc. 61 (1984) 909. (f) S. D. Borkar and B. M. Khadilkar, Syn. Commun., 29 (1999) 4295. (g) A. Shaabani, A. Bazgir, F. Teimouri and D. G. Lee, Tet. Lett., 43 (2002) 5165.

[116] A. Brantner and J. Vamos, Gyogyszereszet (Hungarian), 24 (1980) 377.

[117] T. P. Malloy, M. A. Halter and D. W. House, U.S. Patent US 4459186 A (1984).

[118] W. A. Carvalho, U. Schuchardt and C. E. Z. Krahembuhl, Quim. Nova. (Portuguese)., 16 (1993) 242.

[119] S. Murahashi and Y. Oda, Eur. Pat. Appl. EP 531715 A1 (1993).

[120] I. C. Chisem, K. Martin, M. T. Shieh, J. Chisem, J. H. Clark, R. Jachuck, D. J. Macquarrie, J. Rafelt, C. Ramshaw and K. Scott, Org. Process Res. Dev., 1 (1997) 365.

[121] W. Partenheimer, Chem. Ind. (Dekker), 75 (1998) 357.

[122] S.-J. Su, J.-H. Bai, T.-J. Wang, M.-Y. Huang, and Y.-Y. Jiang, Polym. Adv. Technol., 10 (1999) 99.

[123] X. Li, Y. Yu, and S. Lin, Ziran Kexuebanv (Chinese), 15 (1999) 49.

[124] J. Qi, J. Hu, and X. Li, Cuihua Xuebao (Chinese), 20 (1999) 463.

[125] I. C. Chisem, J. Chisem, J. S. Rafelt, D. J. Macquarrie, J. H. Clark and K. A. Utting, J. Chem. Technol. Biotechnol., 74 (1999) 923.

[126] S. T. Man, C. Ramshaw, K. Scott, J. Clark, D. J. Macquarrie and R. Jachuck, Organic Process Research & Development, 5 (2001) 204.

[127] Y. Yu, X. Li and S. Lin, Huaxue Yanjiu Yu Yingyong (Chinese), 12 (2000) 654.

[128] J.-Y. Qi, H.-X. Ma, X.-J. Li, Z.-Y. Zhou, M. C. K. Choi, A. S. C. Chan, Q.-Y. Yang, Chem. Commun., (2003) 1294.

[129] S.-C. Baek, H.-S. Roh, S. A. Chavan, M.-H. Choi, K.-W. Jun, S.-E. Park, J. S. Yoo and K.-J. Kim, Applied Catalysis, A: General, 244 (2003) 19.

[130] D. Srinivas and S. Sivasanker, Catalysis Surveys from Asia, 7 (2003) 121.

[131] E. P. Reddy and R. S. Varma, J. Catal., 221 (2004) 93.

[132] O. Kneimeyer and J. Heider, J. Biol. Chem., 276 (2001) 21381.

[133] I. C. Chisem, K. Martin, M. K. Shieh, J. Chisem, J. H. Clark, R. Achuck, D.J. Macquarrie, J. Rafelt, C. Ramshaw and K. Scott, Org. Process Res. Develop., 1 (1997) 365.

[134] S. S. Kim, S. K. Sar and P. Tamrakar, Bull. Korean Chem. Soc., 23 (2002) 937.

[135] B. K. Das and J. H. Clark, Chem. Commun., (2000) 605.

[136] J. S. Rafelt and J. H. Clark, Catal. Today, 57 (2000) 33.

[137] (a) T. V. Bukharina and N. G. Digurov, Org. Proc. Res. Dev., 8 (2004) 320 (b) V. R. Choudhary, J. R. Indurkar, V. S. Narkhede and R. Jha, J. Catal., 227 (2004) 257 (c) Y. Ishii, S. Sakaguchi and T. Iwahama, Adv. Syn. Catal., 343 (2001) 393 and references cited therein.

[138] D. Srinivas, and S. Sivasanker, Catalysis Surveys from Asia, 7 (2003) 121.

[139] G. Blay, I. Fernandez, T. Gimenez, J. R. Pedro, R. Ruiz, E. Pardo, F. Lloret and M. C. Munoz, Chem. Commun., (2001) 2102.

[140] S.-H. Cho, M.-S. Cheong, K.-D. Jung, C.-S. Kim and S.-H. Han, Appl. Catal., A: General, (2004) in press.

[141] S. Vetrivel and S. Pandurangan, Appl. Catal., 264 (2004) 243.

[142] K. R. Seddon and A. Stark, Green Chem., 4 (2002) 119.

[143] M. Spadlo, H. Olkowski, Chem. Stosow., 26(3-4) (1982) 357-61 (Polish).

[144] C. Christophe, A. Hans and K. B. Sharpless, chem. Commun., (1997) 1565.

[145] J. P. Schirmann, M. Pralus and S. Y. Delavarene, Ger. Offen. (1978) DE 2803757.

[146] J. P. Schirmann, M. Pralus and S. Y. Delavarene, Ger. Offen. (1978) DE 2803791.

[147] J. P. Schirmann, M. Pralus and S. Y. Delavarene, Ger. Offen. (1978) DE 2407209.

[148] P. E. Dai and J. H. Lunsford, J. Catal., 64 (1980) 173.

[149] K. Takehira, T. Hayakawa and T. Ishikawa, Bull. Chem. Soc. Jpn., 51 (1978) 1685.

[150]   K. Takehira and T. Ishikawa, Bull. Chem. Soc. Jpn., 49 (1976) 2351.

[151]   P. E. Dai and J. H. Lunsford, J. Catal., 64 (1980) 184.

[152]   J. R. John and J. H. Lunsford, J. Mol. Catal., 32 (1985) 325.

[153]   D. D. Agarwal, S. Shrivastava and P. Chadha, Polygedron., 9 (1990) 487.

[154]   N. I. Kuznetsova, A. S. Lisitsyn and V. A. Likholobov, React. Kinet. Catal. Lett., 38 (1989) 205.

[155]   A. Tuel, Zeolites., 15 (1995) 236.

[156]   E. Jorda, A. Tuel, R. Teisser and J. Kelvennal, J. Chem. Soc. Chem. Commun., 17 (1995) 1775.

[157]   S. W. Brown, A. Hackett, A. Johnston and R. W. Johnston, PCT Int. Appl., (1993) WO 9300338.

[158]   A. Tuel, Zeolites., 15 (1995) 228.

[159]   S. V. Timofeev, A. L. Smirnova, T. V. Filpova and E. A. Blyumberg, Kinet. Katal., 33 (1992) 105.

[160]   T. V. Filppova, S. V. Timofeev, A. L. Smirnova and E. A. Blyumberg, Kinet. Katal., 33 (1992) 114.

[161]   R. D. Oldroyd, J. M. Thomas, T. Maschmeyer, P. A. MacFaul, D. W. Ingold and D. M. Wayner, Angew. Chem. Int. Ed. Engl., 35 (1997) 2787.

[162]   H. Kochkar and F. J. Figueras, J. Catal., 171 (1997) 420.

[163]   D. W. Ingold, D. W. Snelgrove, P. A. MacFaul, R. D. Oldroyd and J. M. Thomas, Catal. Lett., 48 (1997) 21.

[164]   K. J. Jr. Balkus, A. K. Khanmamedova and J. Shi, Stud. Surf. Sci. Catal., 110 (1997) 999.

[165]   L. Y. Chen, G. K. Chuah and S. Jaenicke, Catal. Lett., 50 (1998)107.

[166]   E. Jorda, A. Tuel, R. Teisser and J. Kevennal, J. Catal., 175 (1998) 93.

[167]   L. Nemeth, B. McCulloh, R. Jensen, S. Wilson and J. Moscoso, Stud. Surf. Sci. Catal., 125 (1999) 473.

[168]   M. H. Zahedi-Niaki, M. P. Kapoor and S. Kaliaguine, Proc. Int. Zeolite Conf., 2 (1998) 1221.

[169]   F. Figueras and H. Kochkar, Catal. Lett., 59 (1999) 79.

[170]   R. Raja, G. Sankar and J. M. Thomas, Chem. Commun., 9 (1999) 829.

[171]   B. F. Sels, D. E. De Vos and P. A. Jakob, Stud. Surf. Sci. Catal., 129 (2000) 845.

[172]   I. C. Chisem, J. Chisem, J. S. Rafelt, D. J. Macquarrie, J. H. Clark and K. A. Utting, J. Chem. Tech. Biotechnol., 74 (1999) 923.

[173] M. A. Holland, D. M. Pickup, G. Mountjoy, S. C. Tsang, G. W. Wallidge, R. J. Newport and M. E. Smith, Mater. Res. Soc. Symp. Proc., 590 (2000) 77.

[174] Y. Wantanabe, K. Yamamoto and T. Tatsumi, J. Mol. Catal. A: Chem., 145 (1999) 281.

[175] D. Levin, C. D. Chang, S. Luo, J. G. Satiesteban and J. C. Vartuli, US Patent., (2000) US 6114551.

[176] J. Bu, S. Yun, H. Ree and J. Karean, J. Chem. Eng., 17 (2000) 76.

[177] P. Dinka, Z. Cvengrosova and M. Hronec, Pet. Coal, 41 (1999) 57.

[178] G. Song, F. Wang, X. Lu and L. Zhang, Jiangsu Shiyou Huagong Xueyuan Xuebao., 11 (1999) 13 (CHINESE).

[179] I. Schmidt, A. Krogh, K. Wienberg, A. Carlsson, M. Brorson and C. J. H. Jacobsen, Chem. Commun., 21 (2000) 157.

[180] J. Bu and H. Ree, Stud. Surf. Sci. Catal., 129 (2000) 179.

[181] S. Yun, J. Bu and H. Ree, eact. Kinet. Catal. Lett., 72 (2001) 343.

[182] J. Yu, Z. Feng, L. Xu, M. Li, Q. Xin, Z. Liu and C. Li, Chem. Mater., 13 (2001) 994.

[183] D. Mandelli, M. C. A. van Vilet, U. Arnold, R. A. Sheldon and U. Schuchardt, J. Mol. Catal. A: Chem., 168 (2001) 165.

[184] S. Uemura, S. Hamamoto and N. Sanda, Jpn. Kokai Tokkyo Koho JP (1979) JP 54160310.

[185] E. A. Blyumberg, S. Yu. Zasedatelev, T. V. Filippova, E. S. Smirnov, A. G. Merzhanov, I. P. Borovinskaya and I. E. Pokrovskaya., U.S.S.R. Patent, (1981) U.S.S.R. SU 810691.

[186] S. B. Kumar, S. P. Marajkar, G. C. G. Pais, P. Kumar and R. Kumar, J. Catal., 156 (1995) 163.

[187] E. A. Blyumberg, B. N. Bobylev, T. V. Filippova, E. S. Smirnov, V. N. Leonov ans A. L. Smirniva, U.S.S.R. Patent, (1992) U.S.S.R. SU 1761754 A1.

[188] W. Zhang, M. Froeba, J. Wang, P. T. Tanev, J. Wong and T. J. Pinnavaia, J. Am. Chem. Soc., 118 (1996) 9164.

[189] X. Li, F. Wang, X. Lu, G. Song and L. Zhang, Synth. Commun., 27 (1997) 2075.

[190] T. V. Fillipova and E. A. Blyumberg, Oxid. Commun., 19 (1996) 516.

[191] X. Wang, X. Guo and J. Liu, Dalian Ligong Daxue Xuebao, 38 (1998) 348.

[192] X. Wang and X. Guo, Catal. Today, 51 (1999) 177.

[193] Z. Fu, D. Yin, Q. Li and Y. Zhang, Micro. Mesop. Mater., 29 (1999) 351.

[194] N. A. Alekar, C. Gopinathan and S. Gopinathan, Ind. J. Chem. Sect. A: Inorg., Bio-inorg., Phy. Theor. Anal. Chem., 38 A (1999) 1051.

[195] Z. Fu, J. Chen, Y. Xiang, L. Zhabg and D. Yin, Wuli Huaxue Xuebao, 16 (2000) 410.

[196] R. V. Grieken, J. L. Sotelo, C. Martos, J. L. G. Fierro, M. Lopez-Granados and R. Mariscal., Catal. Today, 61 (2000) 49.

[197] L. Zhang, Z. Fu, W. Zhao, D. Yin, Y. Chen and Y. Zhang, Fenzi Cuihua, 14 (2000) 55.

[198] J. Qi, Q. Yang, Z. Liu and X. Li, Fenzi Cuihua, 14 (2000) 294.

[199] R. Anand, S. S. Shevade, R. K. Ahedi, S. P. Mirajkar and B. S. Rao, Catal. Lett., 62 (1999) 209.

[200] Q. Yang, S. Wang, J. Lu, G. Xiong, X. Feng, Q. Xin and C. Li, Appl. Catal. A., 194-195 (2000) 507.

[201] L. Stoica, S. Serban, D. Bombos, C. Constantin, V. I. Constantin, M. Istrate, P. Enache and E. Apostu, Rom. Patent, (1998) RO 112867.

[202] B. M. Choudary, M. L. Kantum, B. Bharathi, P. Shreekanth and F. Figeras, J. Mo. Catal., 159 (2000) 417.

[203] C. Li, Q. Yang, P. Ying and Q. Xin, Faming Zhuanli Shenquing Gongkai Shuomingshu CN Patent (2000) CN 1253033.

[204] C. Xu, S. Lu, G. Deng and F. Qui, Xinshiji De Cuihau

[205] G. Calleja, R. van Grieken, R. Garcia, J. A. Melero and J. Iglesias, J. Mol. Catal. A, 182 (2002) 215.

[206] F. Xiao, Y. Han, Y. Yu, X. Meng, M. Yang and S. Wu, J. Am. Chem. Soc., 124 (2002) 888.

[207] Y. Wang, Q. Zhang, T. Shishido and K. Takehira, J. Catal., 209 (2002) 186.

[208] X. Meng, Z. Sun, R. Wang, S. Lin, J. Sun, M. Yang, K. Lin, D. Jiang and F. Xiao, Catal. Lett., 76 (2001) 105.

[209] H. P. Wuff and F. Wattimena, US patent, (1977) US 40214543.

[210] J. Sobczak and J. J. Ziolkowski, React. Kinet. Catal. Lett., 11 (1979) 359.

[211] T. K. Nakanishi and E. Koga, Jpn. Kokai Tokkyo Koho JP, (1980) JP 63044573.

[212] T. K. Nakanishi, Koga and I Fukada, Eur. Pat. Appl., (1998) EP 287347 A2.

[213] T. K. Nakanishi and E. Koga, Jpn. Kokai Tokkyo Koho JP, (198) JP 63044574 A2.

[214] M. G. Clerici and P. Ingallina, J. Catal., 140 (1993) 71.

[215] Q. Xia, G. Wang, M. Ying and L. Zheng, Shiyou Huagong, 22 (1993) 781.

[216] Q. Xia, G. Wang, M. Ying, G. Cao and L. Zheng, Shiyou Huagong, 23 (1994) 716.

[217] G. Cao, H. Li, Q. Xia, J. Huang and Y. Xu, Cuihua Xuebao, 16 (1995) 217.

[218] H. Gao, G. Lu, S. Suo and S. Li, Appl. Catal. A, 138 (1996) 27.

[219] V. Anghel, D. Stanescu, D. Plesu and S. Doru, Rom. Patent, (1994) RO 104334 B1.

[220] J. Catinat and M. Strebelle, PCT Int. Appl., (1999) WO 9928035.

[221] M. Strebelle, P. Gilbeau and J. Catinat, J. Eur. Pat. Appl., (1999) EP 919551 A1.

[222] T. Kitano and Y. Kituzono, Stud. Surf. Sci. Catal., 121 (1999) 355.

[223] C. Xu, S. Lu, G. Deng, F. Qui and J. Chin, J. Chem., 18 (2000) 576.

[224] J. Schoebrechts, Eur. Pat. Appl., (2001) EP 1125891.

[225] J. Schoebrechts, M. Strebelle and J. Cabinet, PCT Int. Appl., (2001) WO 2001068623.

[226] I. Nowak, B. Kilos, M. Ziolek and A. Lewandowska, Catal. Today, 78 (2003) 487.

[227] X. Li and C. Kuntal, J. Mater. Sci. Lett., 21 (2002) 1525.

[228] Q. Zhang, Y. Wang, S. Itsuki, T. Shishido and K. Takehira, J. Mol. Catal. A: Chem., 188 (2002) 189.

[229] D. Yin, Z. Fu, W. Wang, H. Wang and L. Zhang, Hunan Shifan Dexue Ziran Kexue Xuebao, 25 (2002) 45.

[230] V. R. Choudhary, N. S. Patil and S. K. Bhargava, Catal. Lett., 89 (2003) 55.

[231] C. V. Rode, U. N. Nehete and M. K. Dongre., Catal. Commun., 4 (2003) 365.

[232] S. C. Laha and R. Kumar, J. Catal., 204 (2001) 64.

[233] J. L. Sotelo, R. van Grieken and C. Martos., Chem. Commun., (1999) 549.

[234] M. Imanari, H. Iwane, S. Otaka, Mitsubishi Petrochemical Co., Ltd., Japan Jpn. Kokai Tokkyo Koho JP 61007263 A2 (1986).

[235] M. Imanari, H. Iwane, S. Otaka, Mitsubishi Petrochemical Co., Ltd., Japan Jpn. Kokai Tokkyo Koho JP 61007264 A2 (1986).

[236] Daicel Chemical Industries, Ltd., Japan Jpn. Kokai Tokkyo Koho JP 57077641 A2 (1982).

[237] S. Umemura, S., S. Hamamoto, N. Sanada, Ube Industries, Ltd., Japan Jpn. Kokai Tokkyo Koho JP 54160310 (1979).

[238] S. Enomoto, M. Inoe, T. Kamyama, O. Oora and H. Nito, Tokai Rika Co., Ltd., Japan Jpn. Kokai Tokkyo Koho JP 02202882 A2 (1990).

[239] E. Z-Budo, L. I. Simandi, Stud. Org. Chem., 33 (1988) 219-26 (English).

[240] G. D. Yadav, A. A. Pujari, A. A., Org. Process Res. Dev., 4 (2000) 88-9.

[241] R. I. Kureshy, N.-U. H. Khan, S. H. R. Abdi, S. Singh, I. Ahmad, R. V. Jasra and A. P. Vyas, J. Catal. (in press).

[242] R. Ghosh, Y.-C. Son, V. D. Makwana and S. L. Suib, J. Catal., 2004 (in press).

[243] R. I. Kureshy, N.-U. H. Khan, S. H. R. Abdi, I. Ahmad, S. Singh and R. V. Jasra, J. Catal., 221 (2004) 234.

[244] J. M. R. Gallo, I. S. Paulino and U. Schuchardt, J. Catal., 2004 (in press).

[245] M. C. A. van Vliet, D. Mandelli, I. W. C. E. Arends, U. Schuchardt and R. A. Sheldon, Green Chem., 3 (2001) 243.

[246] J. Ichihara, A. Kambara, K. Iteya, E. Sugimoto, T. Shinkawa, A. Takaoka, S. Yamaguchi and Y. Sasaki, Green Chem., 5 (2003) 491.

[247] N. S. Patil, B. S. Uphade, P. Jana, S. K. Bhargava and V. R. Choudhary, J. Catal., 223 (2004) 236.

[248] N. S. Patil, B. S. Uphade, P. Jana, R. S. Sonawane, S. K. Bhargava and V. R. Choudhary, Catal. Lett., 94 (2004) 89.

[249] N. S. Patil, R. Jha, S. K. Bhargava and V. R. Choudhary, Appl. Catal. A: General, 275 (2004) 87.

[250] N.S. Patil, B.S. Uphade, D.G. McCulloh, S.K. Bhargava and V.R. Choudhary, Catal. Commun. 5 (2004) 681.

[251] N. S. Patil, B. S. Uphade, P. Jana, S. K. Bhargava and V. R. Choudhary, Chem. Lett., 33 (2004) 400.

[252] V. R. Choudhary, N. S. Patil, N. K. Chaudhari and S. K. Bhargava, Catal. Commun., 5 (2004) 205.

[253] J. I. Kroshwitz, Kirk Othmer Encyclopedia of Chemical Technology, vol. 4, fourth ed., Wiley-Interscience Publications, New York, 1992, pp. 64-72.

[254] S. Tsuruya, Y. Okamoto and T. Kuwada, J. Catal., 56 (1979) 52.

[255] S. Tsuruya, H. Miyamoto, T. Sakae and M. Masai, J. Catal., 64 (1980) 260.

[256] M. Arai, S. Nishiyama, S. Tsuruya and M. Masai, J. Chem. Soc. Faraday Trans., 92 (1996) 2631.

[257] H. Hayashibara, S. Nishiyama, M. Tsuruya and M. Masai, J. Catal., 153 (1995) 254.

[258] S. Sueto, S. Nishiyama, T. Tsuruya and M. Masai, J. Chem. Soc. Faraday Trans., 93 (1997) 659.

[259] R. Sumathi, K. Johnson, B. Vishwanathan and T. K. Varadarajan, Appl. Catal., A: General, 172 (1998) 15.

[260] N. Idaka, S. Nishiyama and T. Tsuruya, Phys. Chem. Chem. Phys., 3 (2001) 1918.

[261] C. Annuziatini, M. F. Gerini, O. Lanzalunga and M. Lucarini, J. Org. Chem., 69 (2004) 3431.

[262] G. Sorg, A. Mengel, G. Jung and J. Rademann, Angew. Chem. Int. Ed., 40 (2001) 4395.

[263] G. A. Lee and H. H. Freedman, Tetrahedron Lett., 20 (1976) 1641.

[264] I. Tabushi and N. Koga, Tetrahedron Lett., 38 (1979) 3681.

[265] G. D. Yadav and C. K. Mistry, J. Mol. Catal. A: 172 (2001) 135.

[266] F. Minisci, C. Punta, F. Rcupero, F. Fontana and G. F. Pedulli, Chem. Commun., (2002) 688.

[267] R. B.-Daniel, P. Alsters and R. Newmann, J. Org. Chem., 66 (2001) 8650.

[268] T. Nishimura, N. Kakiuchi, M. I. Inoue and S. Uemura, Chem. Commun., (2000), 1245.

[269] N. Kakiuchi, T. Nishimura, M. Inoue and S. Uemura, Bull. Chem. Soc. Jpn., 74 (2001) 165.

[270] T. Nishimura, T. Onoue, K. Ohe and S. Uemura, J. Org. Chem., 64 (1999) 6750.

[271] N. Kakiuchi, Y. Maeda, T. Nishimura and S. Uemura, J. Org. Chem., 66 (2001) 6620.

[272] Y. Uozumi and R. Nakao, Angew. Chem. Int. Ed., 42 (2003) 194.

[273] M. J. Schultz, C. C. Park and M. S. Sigman, Chem. Commun., (2002) 3034.

[274] T. Nishimura, T. Onoue, K. Ohe and S. Uemura, Tetrahedron Lett., 39 (1998) 6011.

[275] K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, 124 (2002) 11572.

[276] U. R. Pillai and E. S.-Demessie, Green Chem., 6 (2004) 161.

[277] T. L. Stuchinskaya and I. V. Kozhenikov, Catal. Commun., 4 (2003) 417.

[278] L. F. Liotta, A. M. Venezia, G. Deganello, A. Longo, A. Martoana, Z. Schay and L. Guczi, Catal. Today, 66 (2001) 271.

[279] V. R. Choudhary, B. S. Uphade and D. K. Dumbre, Catal. Commun., (Accepted).

[280] R. P. A. Sneeden and R. B. Turner, J. Am. Chem. Soc., 77 (1954) 190.

[281] T. Matsushita, K. Ebitani and K. Kaneda, Chem. Commun., (1999) 265.

[282] I. E. Marko, P. R. Giles, M. Tsukazaki, I. C-Regnaut, S. M. Brown and C. J. Urch, J. Am. Chem. Soc., 119 (1997) 12661.

[283] K. Kaneda, T. Yamashita, T. Matsushita and K. Ebitani, J. Org. Chem., 63 (1998) 1750.

[284] A. Bleloch, B. F. G. Johnson, S. V. Ley, A. J. Price, D. J. Shephard and A. W.. Thomas, Chem. Commun., (1999) 1907.

[285] K. Yamaguchi, K. Mori, T. Mizigaki, K. Ebitani and K. Kaneda, J. Am. Chem. Soc., 122 (2000) 7144.

[286] A. Miyata, M. Murakami, R. Irie and T. Katsuki, Tetrahedron Lett., 42 (2000) 7067.

[287] A. Dijksman, A. M. Gonzalez, A. M. I Payeras, I. W. C. E. Arends and R. A. Sheldon, J. Am. Chem. Soc., 123 (2001) 6826.

[288] A. Dijksman, I. W. C. E. Arends and R. A. Sheldon, Chem. Commun., (1999) 1591.

[289] S. Asai, H. Nakamura and T. Sumita, AICHE Journal, 40 (1994) 2028.

[290] T. Seiki, A. Nakato, S. Nishiyama, S. Tsuruya, Physical Chemistry Chemical Physics, 5 (2003) 3818.

[291] Y.-C. Son, Y. D. Makwana, A. R. Howell and S. V. Suib, Angew. Chem. Int. Ed., 40 (2001) 4280.

[292] A. Cecchetto, F. Fontana, F. Minisci and F. Recupero, Tetrahedron Lett., 42 (2001) 6651.

[293] C. Milone, R. Ingoglia, G. Neri, A. Pistone and S. Galvagno, Appl. Catal., A: General, 211 (2001) 251.

[294] X. Meng, K. Lin, X. Yang, Z. Sun, D. Jiang and F.-S. Xiao, J. Catal., 218 (2003) 460.

[295] M. J. Schultz, C. C. Park and M S. Sigman, J. Catal., 126 (2000) 125.

[296] M. F. Semmelhack, C. R. Schmid, D. A. Cortes and C. S. Chou, J. Am. Chem. Soc., 106 (1984) 3374.

[297] H.-y. Wang, X.-d. Wang, S.-g. Zhang, H. Jiang, T.-t. Su, Hong Gong, Gongye Cuihua (Chinese), 11 (2003) 21.

[298] V. R. Choudhary, D. K. Dumbre, V. S. Narkhede and S. K. Jana, Catal. Lett., 86 (2003) 229.

[299] I. E. Marko, P. R. Giles, M. Tsukazaki, S. M. Brown and C. J. Urch, Science, 274 (1996) 2044.

[300] V. R. Choudhary, P. A. Choudhari and V. S. Narkhede, Catal. Commun., 4 (2003) 171.

[301] V. R. Choudhary, D. K. Dumbre, B. S. Uphade and V. S. Narkhede, J. Mol. Catal., A: General, 215 (2004) 129.

CHAPTER-2

EXPERIMENTAL

Chapter-2

EXPERIMENTAL

2.1: GASES AND CHEMICALS

The following gases and chemicals have been used.

Helium	? IOLAR-II Grade, Indian Oxygen Ltd., Mumbai.
Hydrogen	? IOLAR-II Grade, Indian Oxygen Ltd., Mumbai.
Nitrogen	? IOLAR-II Grade, Indian Oxygen Ltd., Mumbai.
Air	? IOLAR-II Grade, Indian Oxygen Ltd., Mumbai.
Oxygen	? IOLAR-II Grade, Indian Oxygen Ltd., Mumbai.
Tetra-ethyl ortho silicate	98+% Aldrich, USA.
Cetyltrimethylammoniumbromide (CTAB)	Lancaster, UK.
Ferric chloride	97% Aldrich, USA
Aluminium chloride	(Anhydrous) Lancaster, UK.
Indium chloride	(Anhydrous, 99.99%) Aldrich, USA.
Gallium Chloride	(Anhydrous, 99.99%) Aldrich, USA.
Aluminium nitrate	98.5 % Loba Chem., Mumbai.
Magnesium nitrate	99 % S. D. Fine Chemicals, Mumbai.
Ferric nitrate	98 % Qualigens, Mumbai, India.
Gallium oxide	99.99 % Aldrich, USA.
Indium nitrate	99.99 % Aldrich, USA.
Thallium nitrate	99.99 % Aldrich, USA.
Calcium oxide	Loba Chem., Mumbai.
Barium oxide	Loba Chem., Mumbai.
Strontium oxide	99 % S. D. Fine Chemicals, Mumbai.
Magnesium oxide	Loba Chem., Mumbai.
Sodium carbonate	Qualigens, Mumbai.
Silica	Fuji Davison ? ?type (white)
Ferric nitrate	Qualigens, Mumbai.
Cobalt oxide	Loba Chem., Mumbai.
Nickel oxide	SD Fine chem., Mumbai.
Copper oxide	Robert Johnson

Lanthanum oxide	99.99 % Aldrich, USA.
Cerium nitrate	99.9 % Loba Chem., Mumbai.
Neodymium acetate	Lancaster, UK.
Gadolinium oxide	99.99 % Aldrich, USA.
Samarium oxide	Loba Chem., Mumbai.
Antimony oxide	Loba Chem., Mumbai.
Europium oxide	99.99 % Aldrich, USA.
Terbium oxide	99.99 % Aldrich, USA.
Erbium oxide	99.99 % Aldrich, USA.
Ytterbium oxide	99.99 % Aldrich, USA.
Uranyl nitrate	BDH, Mumbai.
Hydrochloric acid	35 % Merck, Mumbai.
Nitric acid	69.02?72.0 % Thomas Baker, Mumbai,
Sulphuric acid	98 % Merck, Mumbai.
Urea	99.5 % Loba Chem., Mumbai.
t-butyl hydroperoxide	70 % Lancaster, UK.
Styrene	99 % Lancaster, UK.
Styrene oxide	97 % Aldrich, USA.
Phenyl acetaldehyde	80 % Lancaster, Germany.
Benzaldehyde	98.5 % S. D. Fine Chemicals, Mumbai.
Benzoic acid	99.0 % Reanal, Hungary.
Phenyl acetic acid	Loba Chem., Mumbai.
Benzene	(AR Grade) S. D Fine, Chemicals, Mumbai.
Toluene	(AR Grade) S. D Fine, Chemicals, Mumbai.
p-Xylene	(>99%) Fluka, Switzerland.
Anisole	(EP Grade) S. D Fine, Chemicals, Mumbai.
Silica gel (60-120 mesh)	Sisco Research Laboratory Pvt. Ltd., Mumbai.
Mesitylene	(>99%) Fluka, Switzerland.
Phenolphthalein	Merck (India) Pvt. Ltd., Mumbai.
Naphthalene	Loba Chem., Mumbai.
Benzyl chloride	(AR Grade) S. D Fine Chem., Mumbai.
Benzoyl chloride	(AR Grade) S. D Fine Chem., Mumbai.
Phenyl acetyl chloride	Aldrich, USA.
Acetyl chloride	Aldrich, USA.

Gold chloride	99.9% Thomas Baker.
Nitrobenzene	Merck, India.
3-Chloro Nitrobenzene	Aldrich, USA.
4-Chloro Nitrobenzene	Aldrich, USA.
3-Bromo Nitrobenzene	Aldrich, USA.
4 -Nitro Benzaldehyde	Aldrich, USA.
4 –Nitro Acetophenone	Aldrich, USA.
o-Nitro toluene	Aldrich, USA.
m-Nitro toluene	Lancaster, UK.
p-Nitro toluene	Lancaster, UK.
Benzyl alcohol	99.99% SD Fine Chem., Mumbai.
2-phenyl ethyl alcohol	Aldrich, USA.
p-Methoxy phenyl ethyl alcohol	Lancaster, UK.
p-Nitro benzyl alcohol	Aldrich, USA.
p-methoxy benzyl alcohol	Lancaster, UK.
Dichloroethane	(AR Grade) S. D Fine Chem., Mumbai.
Acetonitrile	(AR Grade) S. D Fine Chem., Mumbai.
Carbon tetrachloride	(AR Grade) S. D Fine Chem., Mumbai.
Potassium hydroxide	S. D Fine Chemicals, Mumbai.
Potassium carbonate	S. D Fine Chemicals, Mumbai.
Petroleum ether	(AR Grade) S. D Fine Chem., Mumbai.
Ethyl acetate	(AR Grade) S. D Fine Chem., Mumbai.

2.2 CATALYST PREPARATION

2.2.1 Si-MCM-41

It was prepared by the procedure given elsewhere [1]. A mixture of sodium hydroxide (1.7 g in 30 g of water) and tetramethyl ammonium hydroxide (2 ml of 25% TMAOH) solution was added to an aqueous solution of CTAB (14.6 g in 100 g of water) with continuous stirring. 210 g of water was added to the solution. After allowing the solution to stir for 10 min, tetra -ethylorthosilicate (TEOS, silica source) was added to the resulting solution at room temperature under s tirring, and kept for 24 h. The final gel composition of the mixture was 0.17 TEOS: 0.04 NaOH: 0.02 TMAOH: 0.04 CTAB: 18.9

H_2O. The solid product was obtained by filtration, washed with distilled water, dried in air at room temperature and finally calcined at 550 ℃ for 16 h.

2.2.2   Supported Metal Chloride Catalysts

Supported metal chloride (e.g.$FeCl_3$, $InCl_3$ and $GaCl_3$) catalysts with different metal chloride loadings were prepared by impregnating, Mont.-K10 (Montmorillonite-K10, Aldrich), Si-MCM-41 (high silica mesoporous MCM-41 having surface area of 1140 $m^2.g^{-1}$) and H-? with corresponding anhydrous metal chloride from their acetonitrile solution and evaporating the solvent in vacuum oven at 120 ℃ for 8 h.

The supported catalysts thus obtained were then calcined in an atmosphere of flowing N_2 and/or air at different temperatures (ranging from 100-900 ℃ for Si-MCM-41, 100-500 ℃ for Mont.-K10 and 100-600 ℃ for H-? catalysts at the rate of 10 ℃ min^{-1}.

2.2.3   Preparation of Mg-Al-hydrotalcite and other Hydrotalcite-like Catalysts

The hydrotalcite-like solid catalysts containing different divalent [M(II)] and trivalent [M(III)] metals with M(II)/M(III) mole ratio of 2.0, 3.0, 5.0 and 10.0 were prepared as follows: two aqueous solutions, one containing mixed nitrates of the divalent and the trivalent metals [with a M(II)/M(III) ratio of 2.0, 3.0, 5.0 and 10.0] and the second containing potassium hydroxide and potassium carbonate, are added drop wise into a flask containing deionized water under vigorous stirring at 40 ℃, while maintaining a constant pH of 11-12, following the procedure similar to that described earlier [2]. The resulting gel-like material was aged for 0.5 h and then filtered, thoroughly washed and dried at 80 ℃ in vacuum oven and then heated further in an air oven at 200 ℃ for 12 h.

MnO_4^{-1}-exchanged Mg-Al-hydrotalcite catalysts

The MnO_4^{-1} - exchanged Mg-Al-hydrotalcite catalysts [with Mg/Al ratio of 2, 3, 5 and 10 but same MnO_4^{-1} loading (0.42 $\pm$ 0.01mmol g^{-1})] were prepared as follows: Mg-Al-hydrotalcite was powered and calcined at 600 ℃ for 4h. The calcined mass (13 g) was then treated under stirring with an aqueous solution of $KMnO_4$ (1.58 g in 100 ml water), at 80 ℃. The resulting solid was filtered and washed with hot deionised water and then dried at 80 ℃ in vacuum oven.

2.2.4   Grafted Metal Chloride Catalysts

2.2.4.1 Al-Ga-Grafted-Si-MCM-41

8.3 g of crystalline mesoporous high silica MCM‒41, i.e. Si‒MCM‒41 having surface area of 1100 $m^2.g^{-1}$, was taken in 100-cm^3 dry carbon tetrachloride. To this was added 6 mmol anhydrous $AlCl_3$ dissolved in 6 ml dry acetonitrile and 4 mmol anhydrous $GaCl_3$ dissolved in 4 ml dry carbon tetrachloride. The resulting reaction mixture was refluxed for 4 h under moisture‒free N_2 (flow rate = 60 ml/min). The gaseous hydrogen chloride evolved during the reaction between the Si‒MCM‒41 and chlorides of Al and Ga was measured quantitatively by absorbing it in aqueous NaOH solution by a simple acid‒base titration using phenolphthalein indicator. The amount of HCl evolved in the reaction was 1.5 $mmol.g^{-1}$. The reaction mixture was cooled and the solid catalyst was separated by filtration and washed by dry carbon tetrachloride, under moisture‒free N_2 gas and dried under vacuum. The dried catalyst was stored in a desiccator.

2.2.4.2 Ga-grafted-Si-MCM-41

It was prepared by the procedure similar to that described earlier for Al-Ga-grafted-Si-MCM-41 except that 10 mmol of anhydrous $GaCl_3$ was used instead of 6 mmol of anhydrous $AlCl_3$ and 4 mmol of anhydrous $GaCl_3$. The amount of HCl evolved in the reaction was 1.2 $mmol.g^{-1}$.

2.2.4.3 Al-Ga-Grafted-Mont.-K10

It was prepared by the procedure similar to that described earlier for Al-Ga-grafted-Si-MCM-41 except that, montmorillonite K‒10 was used instead of Si‒MCM‒41 as the support. The amount of HCl evolved in the reaction was 1.65 $mmol.g^{-1}$.

2.2.5   Preparation of Supported Gold Catalyst

The supported gold catalysts were prepared by four different methods as follows:

2.2.5.1 Impregnation technique

In this method the catalyst was prepared by contacting the metal oxide support (2.0 g) with concentrated aqueous solution of $HAuCl_4.3H_2O$, evaporating the extra liquid on water bath, drying at 100 ºC for 12 hours and finally calcining the solid in air at 400 ºC for 2 h.

2.2.5.2 Deposition-Precipitation Method (DP)

In this method of catalyst preparation, a known amount of an aqueous solution of $HAuCl_4.3H_2O$ was added to distilled water and heated under constant stirring at a fixed temperature, 70 ℃. The pH of the solution was adjusted (except when alkaline earth oxides were used) using alkali hydroxide (NaOH) to about 7.0 [3]. The support was then added to the stirring solution and the pH was again adjusted to 7.0. The slurry was aged for 1.0 h, after that it was washed with 4 liters of distilled water (500 ml x 8 times) to remove chlorides and free $Au(OH)_3$. The resulting material was then dried at 90 ℃ overnight and calcined in air at 400 ℃ for 2 h.

2.2.5.3 Homogeneous Deposition Precipitation Method (HDP)

In this method, an aqueous solution of urea $(NH_2)_2CO$ can be utilized to generate ammonium hydroxide as a precipitating agent at elevated temperatures. This involve the following reaction,

<div align="center">upto 95 ℃</div>

$$(NH_2)_2CO + 3H_2O \ ? \ ? \ ? \ ? \ ? \ ? \ ? \quad 2NH_4^+ + 2OH^- + CO_2$$
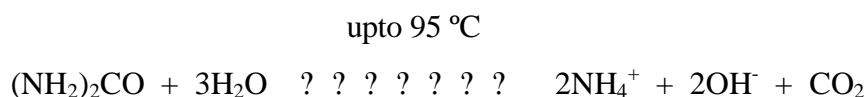
Urea was used as a precursor for the hydrolyzing agent [4]. In a typical procedure, a known amount of an aqueous gold chloride $(HAuCl_4)$ solution was added to 300 ml of distilled water. A known quantity of urea (normally 50 times more on a molar basis than gold chloride) was then added to the solution. To this clear solution a catalyst support (metal oxide) was added. The temperature was gradually increased and the pH was continuously monitored using a pH electrode. The initial pH of the reaction mixture (normally 2.0 to 2.5) at the initial temperature of 25 ℃ gradually increased with an increase in the temperature. The final temperature was set to 98.2 ℃. The observed final pH was 8.0. The colored solution at room temperature became almost colorless upon an increase in temperature and pH, indicating the metal chloride was converted into its hydroxide and homogeneously deposited on the metal oxide support. The solid mass was then filtered, washed thoroughly with distilled water (500 ml x 8 times), air dried at 90 ℃ for 12 h and then finally calcined at 400 ℃ for 2 h in static air.

2.2.5.4 Co-precipitation

In the present study, the co-precipitation method using Na_2CO_3 as a hydrolyzing agent was used for the preparation of several catalysts. The method was first developed by Haruta and co-workers for the preparation of highly active Au/Fe_2O_3, Au/Co_3O_4 and Au/NiO catalysts [5]. In this method, the metal nitrate precursor(s) and gold chloride solution were placed in a three necked round bottom flask and diluted with 200 ml of

distilled water. This solution was then heated to 60 ℃. The pH and temperature of the solution was monitored continuously. An aqueous solution of Na_2CO_3 (0.5 N) was added drop wise using a burette to the heated solution until the pH of the solution reached 8.0. The stirring was continued for a further 4h at 60 ℃. The solution was aged overnight at room temperature, filtered, washed thoroughly with distilled water (500 ml x 8 times), dried at 90 ℃ for 12 h and finally calcined in air at 400 ℃ for 2 h.

2.2.6 Preparation of Metal Oxides and Supported Metal Oxide Catalysts

Al_2O_3 was prepared by calcining bohemite at 500 ℃ for 4h in air oven. TlO_x, CeO_2, MoO_3 and U_3O_8 were prepared by decomposing thallium nitrate, cerium nitrate, ammonium molybdate and uranyl nitrate, respectively in muffle furnace at 500 ℃ for 2h. All the other metal oxides were procured from the different sources, as given in section 2.1. These metal oxides were heated in air at 400 ℃ before use. Supported metal oxide (e.g. NiO, CuO, TlO_x and BaO) catalysts with different metal oxide loadings were prepared by impregnating fine particles of support with corresponding metal nitrates aqueous solution by incipient wetness technique. A weighed quantity of corresponding metal nitrate (2 mmolg^{-1}) was first dissolved in minimum amount of deionized water. This was then added to the 2 g support (freshly dried and kept in a desiccator). The mixture was then heated on a water bath to remove the excess of water by evaporation with continuous stirring through out the process of drying. After complete dryness, the catalyst was calcined at 500 ℃ for 3 h under static air. Calcined material was then stored in a desiccator.

2.3 CATALYST CHARACTERISATION

2.3.1 X-Ray Diffraction (XRD)

XRD measurement of the selected catalysts was performed by the X-ray powder diffraction method using a Holland Philips, PW/1730 X-ray generator with CuK? radiation scintillation counter. The samples were prepared as a thin layer on a glass slide. XRD analysis was performed to identify the crystal phases of the metal oxide and gold. The identification of the catalysts crystalline phase was performed by, comparing the 2? values of XRD peaks with those of standard XRD values. In order to determine the particle size of the gold using XRD, a 100% peak of Au (111) at 38.2 ℃ was considered and Scherrer's equation was used as follows:

$$D = \frac{0.9\lambda}{\pi \cdot \beta/180 \cdot \cos\theta}$$

Where, λ = wavelength of the X-ray used (for Cu K$_\alpha$ radiation, λ = 1.5406 Å), β = Full width at half maximum, θ = Bragg's diffraction angle and D = particle size in Å. The corrected β value was determined by the following relation: $\beta = \surd [\beta^2_{(experimental)} - \beta^2_{(instrumental)}]$

2.3.2 Surface Area

The surface area of catalysts was measured by a single point BET method by measuring the adsorption of nitrogen at a concentration of 30 mol.% N$_2$ in He, using a Monosorb Surface Area Analyzer (Quantachrome Corp., USA) based on the dynamic adsorption/desorption technique.

Before carrying out surface area measurements, the catalyst was pretreated in-situ in the sample cell at 200 °C for 1 h in a flow (30 cm^3.min^{-1}) of N$_2$-He mixture (30 mol.% N$_2$) to remove the traces of moisture and the analyzer was calibrated by injecting a known amount of air. The surface area was calculated from the observed desorption counts.

Surface area (m^2.g^{-1}) = (Desorption counts x 2.84) / (Wt. of catalyst x Counts of 1 ml of air).

2.3.3 Induced Coupling Plasma (ICP) Analysis

ICP-OES (Perkin Elmer Analyzer) was used for bulk elemental chemical analysis. ICP analysis of gold containing catalysts was performed as followed: 50 mg of catalyst was dissolved in 5 ml of aqua regia. The solution was left for 30 min to dissolve all solids and filtered. Distilled water was used to wash the filter assembly and glassware in order to remove all gold from the glassware. The filtrate was then collected in a 25 ml volumetric flask and diluted with distilled water.

2.3.4 Energy Dispersive X-ray Analysis (EDX)

Bulk concentration of the different components present in the sample catalysts was detected by EDX analysis, using a Leico Cambridge model 440 instrument.

2.3.5 Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra of samples were recorded with a Shimadzu FT-IR Spectrometer (Model 8300). FTIR spectra of the catalysts in the framework region (450-4000 cm^{-1}) were obtained in KBr disc or in nujol film.

2.3.6 X-Ray Photoelectron Spectroscopy (XPS)

Surface chemical analysis of the catalyst was done by X-ray photoelectron spectroscopy (XPS) using a VG-Scientific ESCA-3 MK-II electron spectrometer (C1s with binding energy = 285.0 eV) was used as internal standard. The electron binding energies (with accuracy of 0.2 eV) were determined from the observed kinetic energies using the relation,

Binding energy (B.E.) = h? - kinetic energy (K. E.).

The X-ray radiation (h?) used in the XPS was Mg K? (1253.6 eV).

The atom ratio of two elements (say, A and B) on the catalyst surface was determined from the XPS peaks as follows:

A/B atom ratio = [peak area of A/photo ionization cross section of A]/[peak area of B/photo ionization cross section of B].

2.3.7 Transmission Electron Microscopy (TEM)

TEM analysis was done using a JEOL (Model No. JEM 1200 EX). The sample was prepared from an acetone suspension of solid sample by placing a drop of the sample solution on a carbon coated copper grid. It gives structure, size, shape and the distribution of phases that make up a material.

2.3.8 Thermal Gravimetric Analysis (TG/DTG/DTA)

Thermogravimetric analysis (TGA) also termed as dynamic thermogravimetry is based on the measurement of the weight loss of the material as a function of temperature, using TGA 320 Seiko model instrument (made in Japan). Evaluation of materials was done up to 1000 ºC.

2.4 CATALYTIC REACTIONS

2.4.1 Benzylation and Acylation Reactions

The benzylation and acylation reactions over the catalysts were carried out in a magnetically stirred glass reactor (capacity = 25 cm^3) fitted with a reflux condenser, having a low dead volume, mercury thermometer and arrangement for continuously bubbling moisture-free N_2 (30 ml.min^{-1}) through the liquid reaction mixture as shown in Figure 2.4.1. The reaction was started by injecting benzyl chloride or acyl chloride in the reaction mixture, containing the aromatic substrate, with or without solvent and the catalyst at the reaction temperature.

The course of the reaction was followed by measuring quantitatively the HCl evolved in the reaction by an acid-base titration (by absorbing the HCl carried by N_2 in a 0.1 M NaOH solution containing phenolphthalein indicator) as a function of time and also by analyzing the reaction mixture for the unconverted benzyl chloride or acyl chloride and benzylation or acylation product at the end of the experiment by gas chromatography. The conversion data were corrected for a small time lag between the evolution of HCl in the reaction and the analysis of the evolved HCl by the titration. In all the cases, the product formed was mainly mono benzylated or acylated and there was little or no formation of polybenzyl chloride or polyacyl chloride. The amount of benzylated or acylated product formed was equivalent (within 2-5% error) to the amount of benzylating or acylating agent consumed in the reaction.

A - Rotameter
B - Magnetic stirrer
C - Heating bath
D - 2-neck flask
E - Thermometer
F - Reflux condenser
G - Burette
H - Conical flask
I - Trap
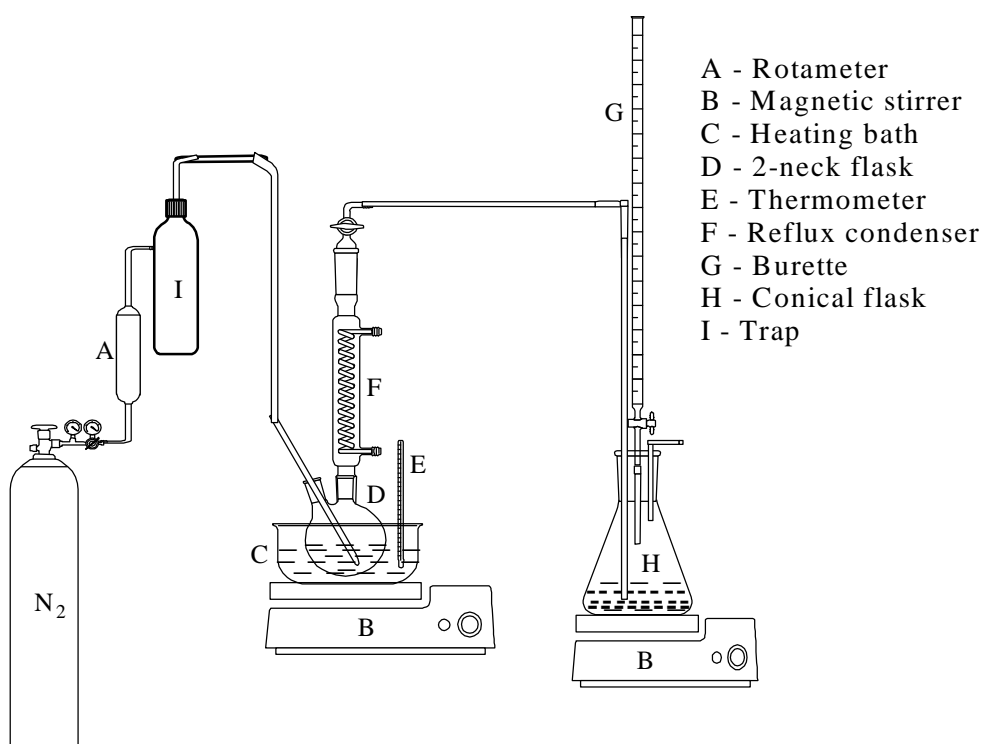
Figure 2.4.1 Setup for the liquid phase benzylation and acylation of aromatic compounds

The product of the acylation was isolated as follows: After the reaction, the catalyst was separated from the reaction mixture by filtration. The product from the filtrate was recovered by washing the filtrate with 0.1 M NaOH solution and removing the solvent and unconverted aromatic substrate by vacuum distillation and then it was purified by column chromatography. The structure of the product was determined by ^{1}H NMR spectroscopy. The isolated product yield was defined as follows: Yield (%) = [(moles of isolated product)/(moles of acyl chloride used)] x 100.

In order to study the effect of moisture present in the reaction mixture, the catalyst was stored over water at room temperature for 15-48 h and the aromatic substrate or solvent saturated with water at room temperature, respectively, were used for the benzylation and acylation reactions.

For studying the effect of HCl gas pretreatment to the catalyst, on its performance in the benzylation or acylation reaction, HCl (gas)-N_2 mixture (20 mol% HCl) was bubbled through a mixture of aromatic substrate and catalyst under stirring at the desired temperature for a period of 0.1-60 min, followed by flushing the mixture with pure N_2 (30 ml.min^{-1}) for 30 min to remove physically adsorbed or absorbed HCl gas in the reaction mixture and then the reaction was started by injecting benzyl or acyl chloride in the reaction mixture.

In order to study the reuse of the catalyst for the reaction, two different experiments were carried out. In the first experiment the catalyst was reused after removing the supernatant liquid from the reaction mixture, while retaining the catalyst in the reaction flask and avoiding as far as possible, the removal of the catalyst fine particles. In the second experiment, after completion of the reaction on a fresh catalyst, a period of 10 min was allowed to lapse and then 1.0 ml benzyl chloride (or acyl chloride) was injected in the reaction mixture already containing excess of aromatic substrate at the reaction temperature to start the reaction.

2.4.2 Epoxidation Reaction

Catalytic epoxidation reaction of styrene over the catalysts (viz. metal oxides and supported metal oxides) was carried out in a magnetically stirred glass reactor (capacity = 25 cm^3) under reflux (bath temperature = 107 ºC), using anhydrous TBHP [prepared from commercially available aqueous TBHP (70%) by solvent extraction with an organic solvent such as ethyl acetate or benzene and drying over $MgSO_4$] as oxidizing agent with continuous removal of the water formed in the reaction using a Dean-Stark trap between the reactor and the reflux condenser. The Dean-Stark trap was removed when aqueous TBHP (70%) was used as an oxidizing agent.

The unconverted styrene and reaction products (viz. styrene oxide, phenyl acetaldehyde, benzaldehyde, phenyl acetic acid and benzoic acid) were analyzed by gas chromatography, using a SE-30 (on chromosorb-W) column and a flame ionization detector.

The conversion, product selectivity and product yield in both the cases were calculated as follows: conversion (%) = [(moles of products formed) x 100] ? [moles of

reactant in feed], product selectivity (%) = [(moles of a particular product formed) x 100] ? [moles of reactant converted] and product yield (%) = (percentage of reactant converted to a particular product) or [conversion (%) x product selectivity (%)] ? 100.
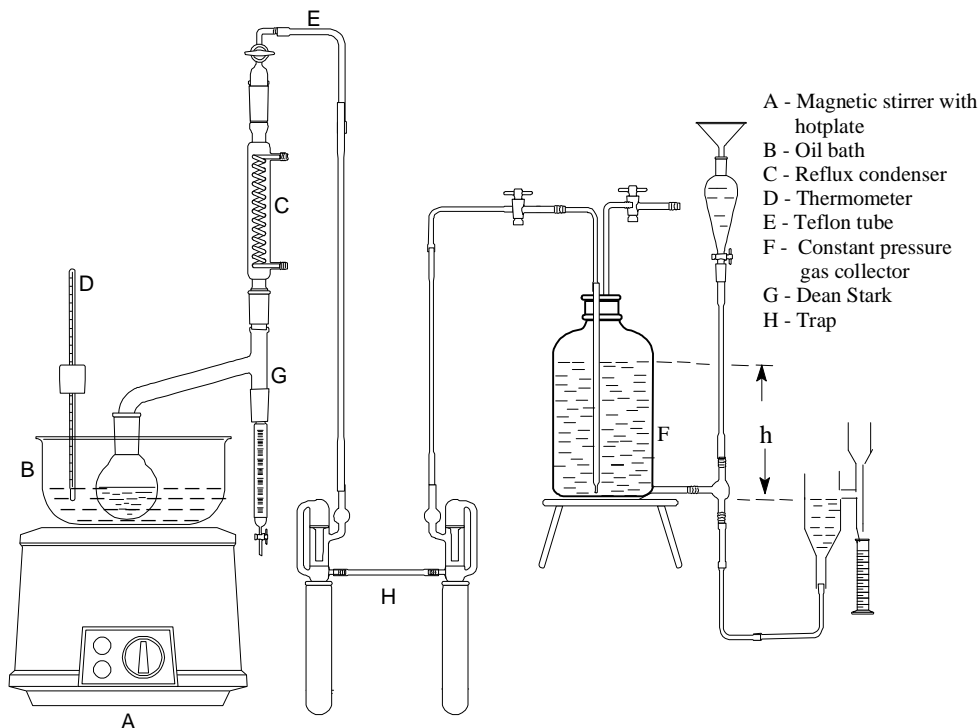
Figure 2.4.2   Experimental setup for the epoxidation of styrene

2.4.3   Oxidation of Benzylic C-H Bond to Carbonyls

The oxidation of aromatic compound containing methylene group attached to aromatic ring (viz. ethylbenzene, diphenylmethane and propylbenzene) by pure O_2 in the absence of solvent was carried out in a magnetically stirred glass reactor (capacity=25 cm^3), provided with a mercury thermometer for measuring the reaction temperature and reflux condenser as shown in Figure 2.4.3, at the following reaction conditions: 6ml aromatic substrate, 0.6 g catalyst, total pressure = 148 kPa, temperature = 130 °C and reaction time = 1-20 h. The reaction products were analyzed by gas chromatography with thermal conductivity detector, using a SE-30 column and hydrogen as carrier gas.

2.4.4   Oxidation of benzylic Alcohols

The catalytic oxidation of benzyl alcohol by pure O_2 in the absence (or in the presence) of solvent was carried out in a magnetically stirred round bottom flask (capacity = 25 cm^3), provided with a mercury thermometer for measuring the reaction temperature and

reflux condenser as shown in Fig. 2.4.3, at the following reaction conditions: reaction mixture = 29.0 mmol benzyl alcohol + 0.1 g catalyst, temperature = 130 ?C, total pressure= 148 kPa, reaction time = 1-10 h. The reaction products were analyzed by gas chromatograph with flame ionization detector, using a SE-30 column and N_2 as a carrier gas.

A - Ball valve
B - Oxygen reservoir (500 cm^3 capacity)
C - Digital pressure gauge (30 Psi capacity)
D - Flow control
E - Ultra torr connector
F - Heating bath
G - Magnetic stirrer
H - Water inlet
I - Water outlet
J - Reflux condensor
K - Thermometer
L - U-Tube manometer
M - Tube filled with mercury
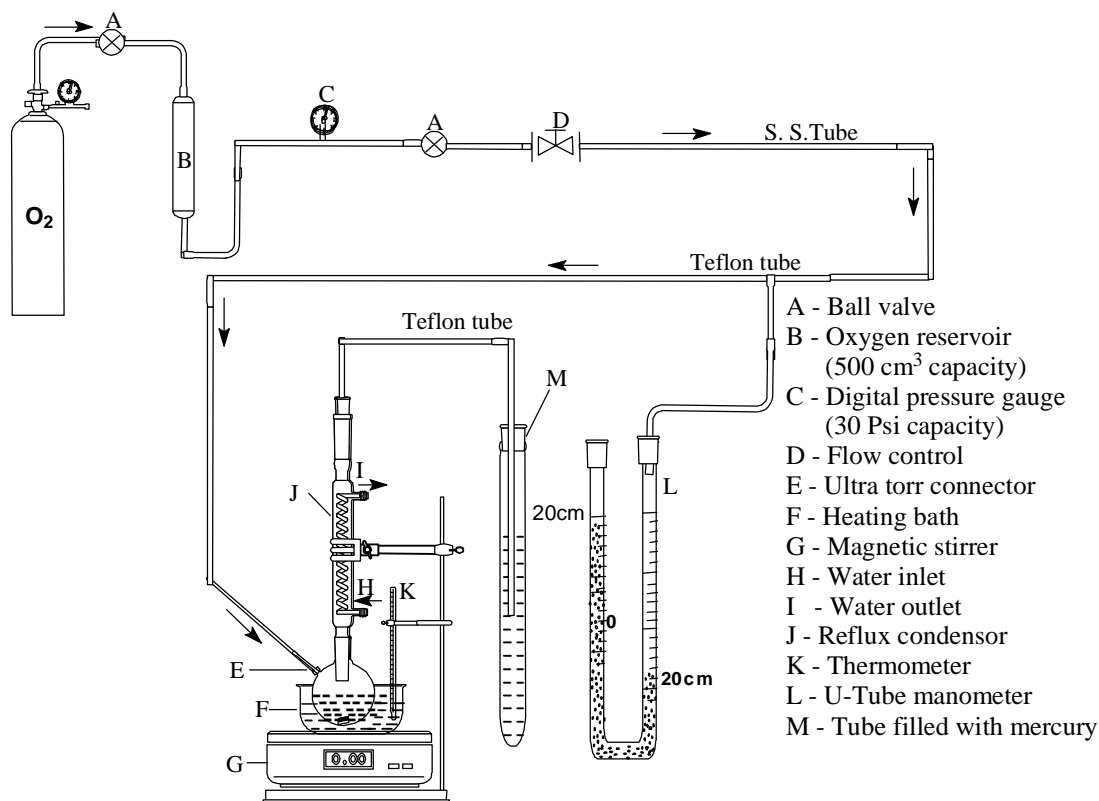
Figure 2.4.3   Experimental setup for the oxidation of Benzylic CH_2 to carbonyl

2.5   REFERENCE

[1]   R. Mokaya and W. Jones, Chem. Commun., (1997) 2187.

[2]   E. Lopez-Salinas, M. Garcia-Sanchez, M. L. Ramon-Garcia and I. Shifter, J. Porous Mater., 3 (1996) 169.

[3]   S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda and Y. Nakahara, Stud. Surf. Sci. Catal., 72 (1991) 695.

[4]   R. Zanella, S. Giorgio, C. R. Henry and C. J. Louis, J. Phys. Chem. B., 106 (1989) 7634.

[5]   M. Haruta, N. Yamada, T. Kobayashi and S. Lijima, J. Catal., 115 (1989) 301.

[6]   V. R. Choudhary, M. G. Parande and P. H. Brahme, Ind. Eng. Chem. Fundam., 21 (1982) 472.

CHAPTER-3
BENZYLATION AND ACYLATION OF AROMATIC COMPOUNDS OVER THERMALLY ACTIVATED Si-MCM-41, MONT.K-10 CLAY OR H-BETA SUPPORTED $FeCl_3$, $GaCl_3$ OR $InCl_3$ CATALYSTS

CHAPTER-3

BENZYLATION AND ACYLATION OF AROMATIC COMPOUNDS OVER THERMALLY ACTIVATED Si-MCM-41, MONT.K-10 CLAY OR H-BETA SUPPORTED FeCl₃, GaCl₃ OR InCl₃ CATALYSTS

3.1   INTRODUCTION AND OBJECTIVE OF PRESENT WORK

In order to make the Friedel-Crafts type benzylation and acylation reactions environmentally benign, use of a number of heterogeneous solid catalysts (having redox and/or acidic properties), listed in Tables 1.1 and 1.2, has been suggested earlier. In the earlier studies in our group [1], we have observed that a complete or partial substitution of Al in H-ZSM-5 zeolite by Fe or Ga or an impregnation of the zeolite by Fe_2O_3, ZnO, Ga_2O_3 or In_2O_3 makes the zeolite highly active in the benzylation process. The high catalytic activity of these zeolites is attributed to the presence of non-framework Fe, Zn, Ga or In oxide species, having redox function, in combination with the zeolitic protons. Recently, Choudhary et al have shown the high activity of clayzic ($ZnCl_2$/Mont.K-10) catalyst in the Freidel-Crafts reactions [2] is attributed to the formation of novel active sites –O-Zn-Cl by the reaction of $ZnCl_2$ with surface hydroxyls (-OH + $ZnCl_2$? ?   -O-Zn-Al + HCl) during the calcination of the mont.K-10 supported $ZnCl_2$. They have observed the evolution of an appreciable amount of HCl during the calcination of $ZnCl_2$/Mont.K-10. Earlier studies in our group also indicated a very good performance of other metal chlorides viz. $FeCl_3$, $GaCl_3$ and $InCl_3$ impregnated on Si-MCM-41, Mont.K-10 clay and H-beta zeolite [3-11]. Like Mont.K-10, the other supports (Si-MCM-41 and H-beta), also contains surface hydroxyls. Hence, it will be interesting to study the influence of calcination/thermal activation temperature of the anhydrous metal chlorides impregnated over the different supports (Si-MCM-41, Mont.K-10 and H-beta) on the extent of HCl evolved during the calcination and also on the activity (in Friedel-Crafts reactions) of the catalysts resulting after the calcination/thermal activation under an inert gas (N₂) or air.

The present investigation was undertaken for the purpose of investigating the benzylation and acylation of aromatic compounds over different supported metal chloride catalysts having redox functions, such as $FeCl_3$, $GaCl_3$ and $InCl_3$ supported on montmorilloniteK-10 clay, Si-MCM-41 and H-beta. Thermal activation of the supported metal chloride catalysts under different conditions and their catalytic activity in the Friedel-Crafts type benzylation and acylation reaction have been thoroughly investigated.

3.2   PREPARATION AND THERMAL ACTIVATION OF Si-MCM-41, MONT.K-10 OR H-BETA SUPPORTED FeCl₃, GaCl₃ AND InCl₃ CATALYSTS AND EVALUATION OF THEIR CATALYTIC PERFORMANCE

The metal chloride was deposited on the support (Si-MCM-41, Mont.K-10 and H-beta zeolite) by impregnating the metal chloride in its anhydrous form from its acetonitrile solution, followed by removing the solvent by evaporation at room temperature under vacuum (section 2.2.4). A number of supported metal chloride catalysts containing different metal chlorides with different metal chloride loadings (0.2, 0.5, 1.0 and 2.0 mmolg^{-1}) were prepared. The composition and/or surface properties of the supports are given in Table 3.1.

Table 3.1:   **Composition and/or surface properties of supports used in the supported metal chloride catalysts.**

Si-MCM-41 Si/Al ratio > 1000 Surface area = 1140 m^2.g^{-1} Average pore diameter = 2.5 nm Pore volume = 0.95 cm^3.g^{-1}
Mont.K-10: MontmorilloniteK-10 clay was obtained from Aldrich, USA Ammonia chemisorbed = 0.41 (at 50 °C) and 0.3 (at 200 °C) mmol.g^{-1}
H-beta Si/Al ratio = 27.1 Degree of H+ exchange ? 99 % Crystal size = 1 ? 0.5 ?m Surface area = 685 m^2.g^{-1} Ammonia chemisorbed = 2.15 (at 50 °C) and 1.1 (at 250 °C) mmol.g^{-1}

The supported metal chloride was thermally activated by calcining it at higher temperature (95-600 °C) in a tubular quartz reactor (containing about 1.0 g catalyst) in a flow of N$_2$ or air (30 ml.min^{-1}) for a period of 3 h. The HCl gas evolved during the thermal

activation is measured quantitatively by the simple acid-base titration described earlier. The evaluation of HCl gas in the thermal activation is attributed to the following solid-solid reaction(s) between the surface hydroxyl groups from the support and the supported metal chloride (MCl_3):

-OH + MCl_3 ? ? -O-MCl_2 + HCl? …………………………………………………….(1)

-OH + -O-MCl_2 ? ? $(-O)_2MCl$ + HCl? ……………………………………………….(2)
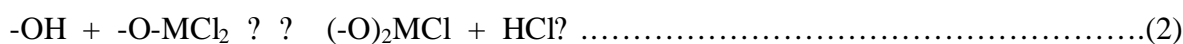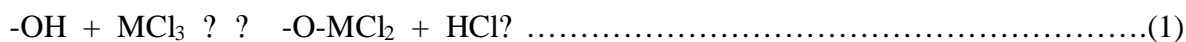
similar to that observed in case of the thermal activation of $ZnCl_2$/Mont.K-10 (clayzic) catalyst [2]. The performance of the different thermally activated Si-MCM-41, Mont.K-10 and H-beta supported $FeCl_3$, $GaCl_3$ and $InCl_3$ catalysts in the benzene benzylation,

C_6H_6 + $C_6H_5CH_2Cl$? ? $C_6H_5CH_2C_6H_5$ + HCl? ……………………………………(3)

and, p-xylene benzoylation,

$(CH_3)_2C_6H_4$ + C_6H_5COCl ? ? $(CH_3)_2C_6H_3COC_6H_5$ + HCl? ………………………(4)
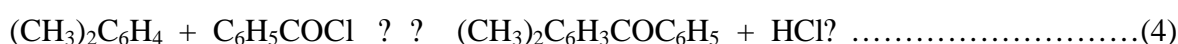
was evaluated at the following reaction conditions:

Benzene benzylation

Reaction mixture = 13 ml dry benzene + 1.0 ml benzyl chloride + 0.1 g catalyst

Reaction temperature = under reflux (80 ºC)

(HCl evolved in the reaction was measured as a function of time).

p-Xylene benzoylation

Reaction mixture = 13 ml dry p-xylene + 1.0 ml benzoyl chloride + 0.4 g catalyst

Reaction temperature = 110 ºC

(HCl evolved in the reaction was measured as a function of time).

Results of the benzene benzylation over the different supports are presented in Table 3.2. The Si-MCM-41 and Mont.K-10 supports showed very little or no activity in the benzene benzylation. The H-beta, however, showed a small benzene benzylation activity.

Table 3.2: Catalytic activity in the benzene benzylation of the different supports

Support	Time required for benzyl chloride conversion (min)	
	50 %	90 %
Si-MCM-41	No reaction for 2 h	
Mont.K-10	Only 4 % conversion in 2 h	
H-beta	Only 10 % conversion in 1.5 h	

3.3 PERFORMANCE OF SUPPORTED FeCl₃ CATALYSTS (THERMALLY ACTIVATED AT DIFFERENT CONDITIONS) IN BENZENE BENZYLATION AND P-XYLENE BENZOYLATION REACTIONS

FeCl$_3$/Si-MCM-41, FeCl$_3$/Mont.K-10 and FeCl$_3$/H-beta catalysts with different metal chloride loadings (0.5-2.0 mmol.g^{-1}) were thermally activated by their calcination at different temperatures (95-800 ºC) under different gas atmospheres (flowing N$_2$ or air) for 3 h. After their thermal activation, all the thermally activated supported FeCl$_3$ catalysts were evaluated for their performance in the benzene benzylation and/or p-xylene benzoylation reactions.
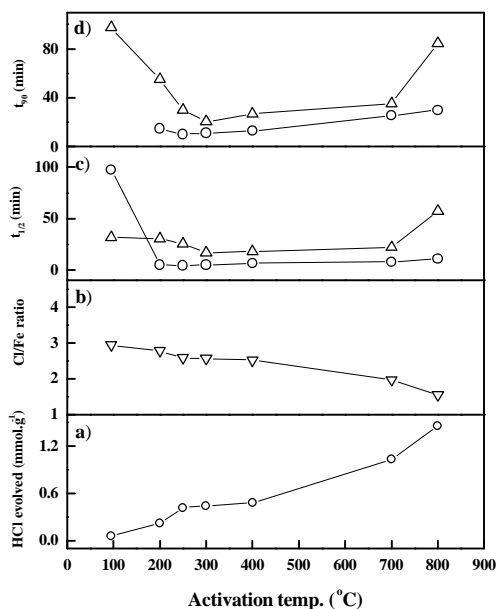
Figure 3.1: Effect of temperature of calcination/activation (in N$_2$) of FeCl$_3$(1.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in the activation in presence of N$_2$, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?).
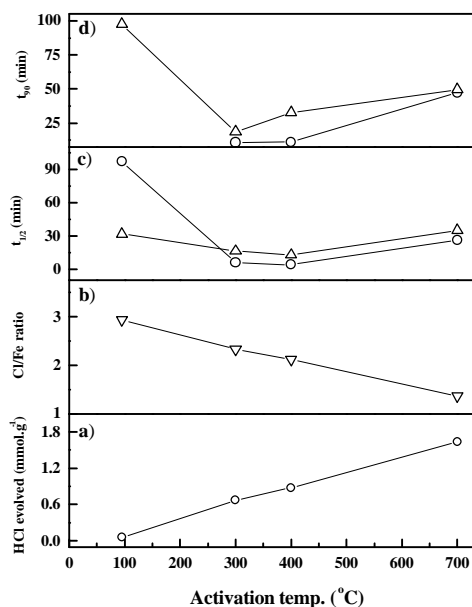
Figure 3.2: Effect of temperature of calcination/activation (in air) of FeCl$_3$(1.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in the activation in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?).
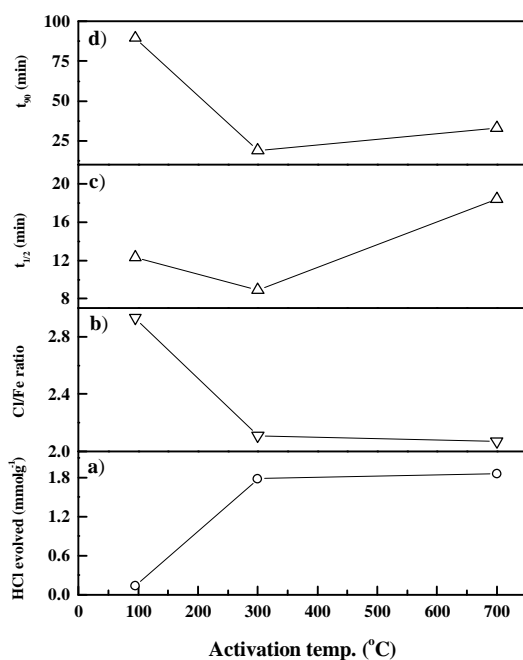
Figure 3.3: Effect of temperature of calcination/activation (in N_2) of $FeCl_3$(2.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?).
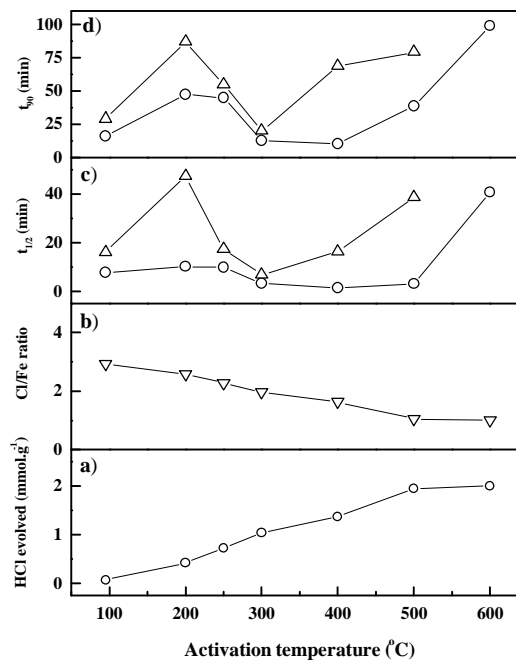
Figure 3.4: Effect of temperature of calcination/activation (in N_2) of $FeCl_3$(1.0 mmolg^{-1})/Mont.K-10 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?).

Results showing influence of the thermal activation temperature, the metal chloride loading in the supported FeCl$_3$ catalysts, the gas atmosphere employed during the thermal activation and the support used in the catalyst on the amount of HCl evolved, on the Cl/Fe ratio of the physically/chemically bound iron chloride species on the support surface, and also on the catalytic activity (in the benzene benzylation and p-xylene benzoylation reactions) of the supported FeCl$_3$ catalysts are presented in Figures 3.1-3.18. The catalytic activity is measured in terms of the time required for half the reaction (i.e. 50 % conversion

of benzyl chloride or benzoyl chloride). Data on the time required for 90 % conversion of benzyl chloride or benzoyl chloride are also included in the figures.
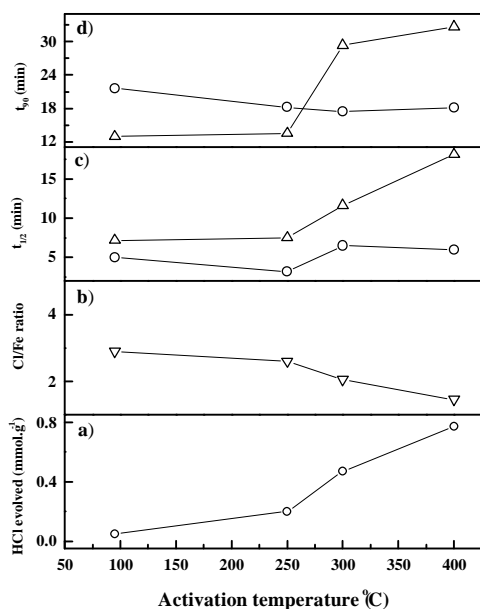
Figure 3.5: Effect of temperature of calcination/activation (in N_2) of $FeCl_3(0.5$ $mmolg^{-1}$)/Mont.K-10 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or
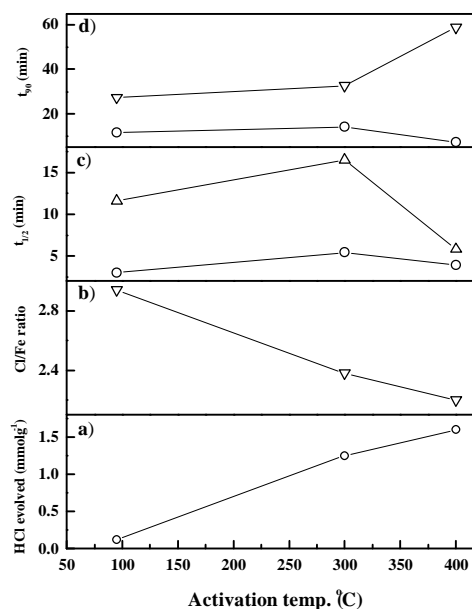
Figure 3.6: Effect of temperature of calcination/activation (in N_2) of $FeCl_3(2.0$ $mmolg^{-1}$)/Mont.K-10 on a) HCl evolved in its activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl

3.3.1 Influence of the Catalyst Thermal Activation Temperature

From the Results in Figures 3.1-3.12, following important observations can be made: For all the supported $FeCl_3$ catalysts, the amount of HCl evolved during the thermal activation is increased with increasing the activation temperature and consequently the Cl/Fe ratio is decreased accordingly. The amount of HCl evolved is larger when the $FeCl_3$ loading in the catalyst is higher. The HCl evolution is expected to be according to reaction-1 at the lower temperatures. However, at the higher temperatures, it is expected due to

reaction-2. Thus depending upon the $FeCl_3$ loading and gas atmosphere used in the thermal activation, the relative concentration of the different metal chloride species in the catalyst [viz. physically held $FeCl_3$ and chemically bonded $-O-FeCl_2$ and $(-O)_2FeCl$] is expected to vary with the activation temperature. In general, the species present in the catalyst after its activation at lower temperatures are mainly $FeCl_3$ with smaller concentration of $-O-FeCl_2$, those at the intermediate temperature (250-400 °C) are mainly $-O-FeCl_2$ and those at the high temperatures are $-O-FeCl_2$ and $(-O)_2FeCl$.
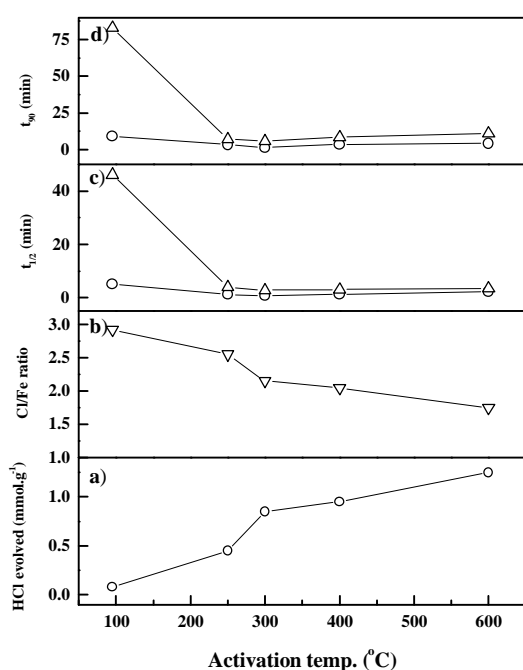
Figure 3.7: Effect of temperature of calcination/activation (in N_2) of $FeCl_3$ (1.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride
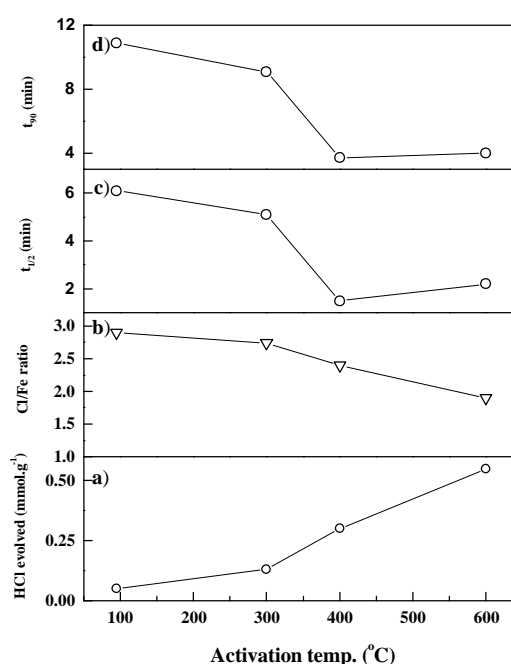
Figure 3.8: Effect of temperature of calcination/activation (in N_2) of $FeCl_3$ (0.5 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride in the benzylation of benzene.
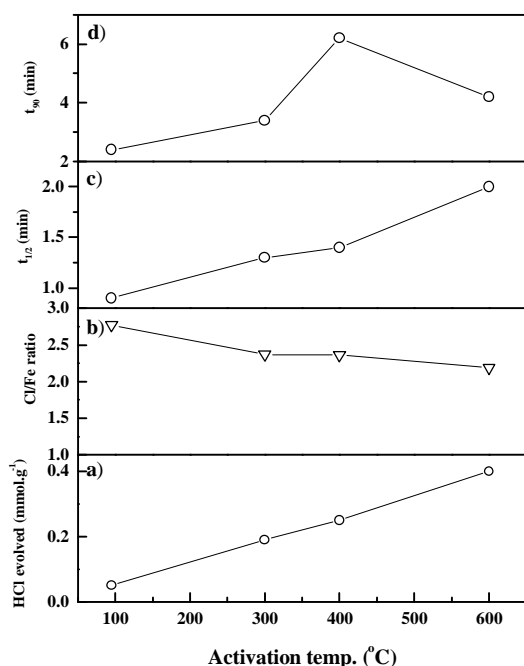
Figure 3.9: Effect of temperature of calcination/activation (in N_2) of $FeCl_3$ (2.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride in the benzylation of benzene.
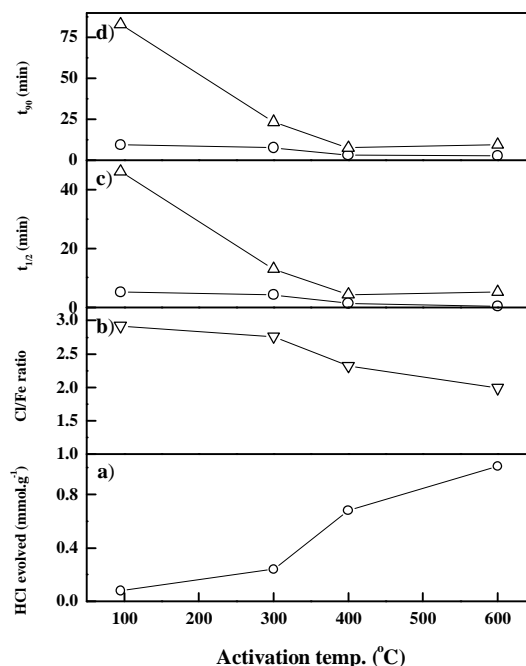
Figure 3.10: Effect of temperature of calcination/activation (in air) of $FeCl_3$ (1.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride

1) Both the benzene benzylation and p-xylene benzoylation activities are also strongly influenced by the catalyst activation temperature, depending upon the $FeCl_3$ loading and the gas atmosphere (N_2 or air) used in the thermal activation as follows:

   - In general for all the supported $FeCl_3$ catalysts with $FeCl_3$ loading of 1.0 or 0.5 mmol.g^{-1}, the catalytic activity for both the benzylation and benzoylation reactions passed through a maximum ($t_{1/2}$ or t_{90} is passed through a minimum) with increasing the catalyst activation temperature (Figures 3.1-3.5, 3.7, 3.8, 3.10 and 3.11). However, for the high $FeCl_3$ loading (2.0 mmol.g^{-1}), the catalytic activity is either decreased ($t_{1/2}$ or t_{90} is increased) continuously or it is passed

through a minimum (i.e. $t_{1/2}$ or t_{90} is passed through a maximum) with increasing the activation temperature (Figures 3.6, 3.9 and 3.12).

There is an optimum thermal activation temperature for all the supported $FeCl_3$ catalysts for their best performance in the benzylation and benzoylation reactions, depending upon the $FeCl_3$ loading and the gas atmosphere used in the activation, as shown in Table 3.3.
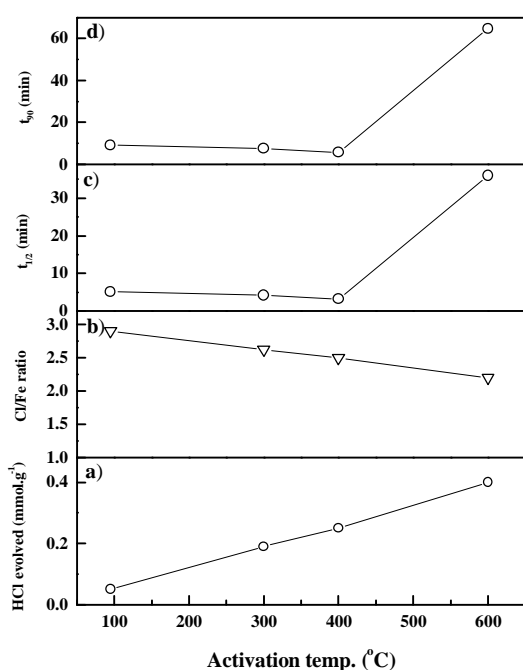
Figure 3.11: Effect of temperature of calcination/activation (in air) of $FeCl_3$ (0.5 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride in the benzylation of benzene.

Figure 3.12: Effect of temperature of calcination/activation (in air) of $FeCl_3$ (2.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride in the benzylation of benzene.

Table 3.3: Optimum catalyst activation temperature for the different supported $FeCl_3$ catalysts for their best performance in the benzene benzylation and p-xylene benzoylation reactions and surface metal chloride species present in the thermally activated catalysts at their optimum activation temperature.

Catalyst	$FeCl_3$ loading (mmol.g^{-1})	Gas atmosphere used in the activation (N_2 or air)	Optimum catalyst activation temperature (ºC)		Surface metal chloride species
			Benzylation	Benzoylation	
FeCl$_3$/Si-MCM-41	1.0	N_2	250 (2.58)[a]	300(2.58)[a]	FeCl$_3$ and –O-FeCl$_2$
	1.0	Air	300 (2.33)	300 (2.33)	Mainly – O-FeCl$_2$
	2.0	Air	-	300 (2.11)	Mainly – O-FeCl$_2$
FeCl$_3$/Mont.K-10	0.5	N_2	250 (2.60)	250 (2.60)	FeCl$_3$ and –O-FeCl$_2$
	1.0	N_2	300-400 (1.96-1.63)	300 (1.96)	Mainly – O-FeCl$_2$
	2.0	N_2	? 400 (2.20)	? 400 (2.20)	Mainly – O-FeCl$_2$
FeCl$_3$/H-beta	0.5	N_2 or air	400 (2.40)	-	FeCl$_3$ and –O-FeCl$_2$
	1.0	N_2	300 (2.15)	300 (2.15)	Mainly – O-FeCl$_2$
	1.0	Air	? 600 (1.99)	400 (2.30)	Mainly – O-FeCl$_2$
	2.0	N_2 or air	? 95 (2.77)	-	FeCl$_3$ and –O-FeCl$_2$

[a]values of Cl/Fe ratio of the surface metal chloride species are given in round brackets

- The most probable surface metal chloride species present in the supported FeCl$_3$ catalysts after the thermal activation at the optimal activation temperature are – O-FeCl$_2$ and FeCl$_3$ (Table 3.3).

The observed high catalytic activity in both the benzylation and benzoylation reactions is mostly attributed to the –O-FeCl$_2$ species formed during the thermal activation of the supported FeCl$_3$ catalysts.
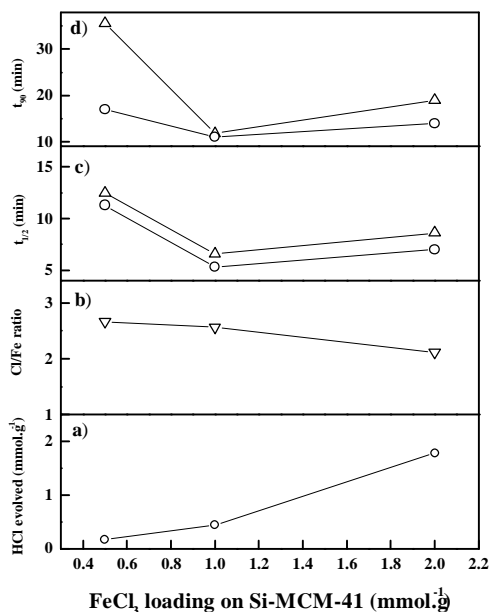
Figure 3.13: Effect of FeCl$_3$ loading in FeCl$_3$/Si-MCM-41 on a) HCl evolved in its thermal activation at 300 ^{o}C in presence of N$_2$, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?)
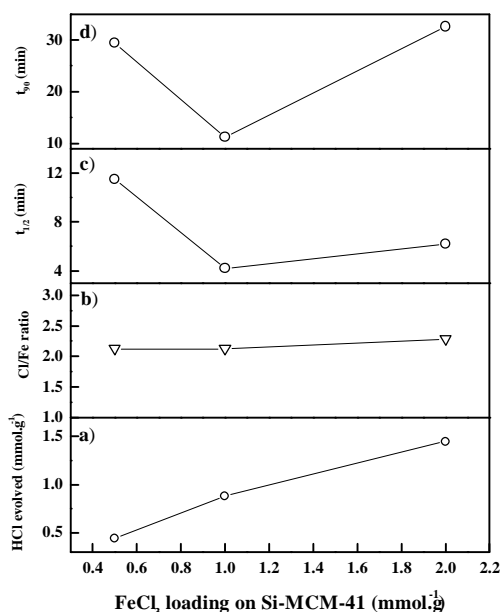
Figure 3.14: Effect of FeCl$_3$ loading in FeCl$_3$/Si-MCM-41 on a) HCl evolved in its thermal activation at 400 ^{o}C in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride in the benzylation of

3.3.2 Influence of Metal Chloride Loading in Supported FeCl$_3$ Catalysts

The results in Figures 3.13-3.18 reveal a strong influence of the FeCl$_3$ loading in the supported FeCl$_3$ catalysts (thermally activated at 300 or 400 °C for 3 h in N$_2$ or air atmosphere) on the HCl evolved in the thermal activation, Cl/Fe ratio of surface metal chloride species present in the catalyst after its thermal activation, and the catalytic activity in both the benzene benzylation and p-xylene benzoylation reactions, as follows:

In all the cases, the amount of HCl evolved is increased with increasing the FeCl$_3$ loading.
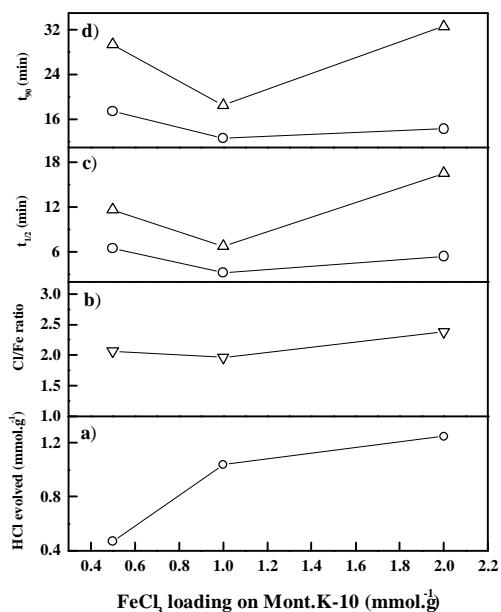
Figure 3.15: Effect of FeCl$_3$ loading in FeCl$_3$/Mont.K-10 on a) HCl evolved in its thermal activation at 300 °C in presence of N$_2$, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride
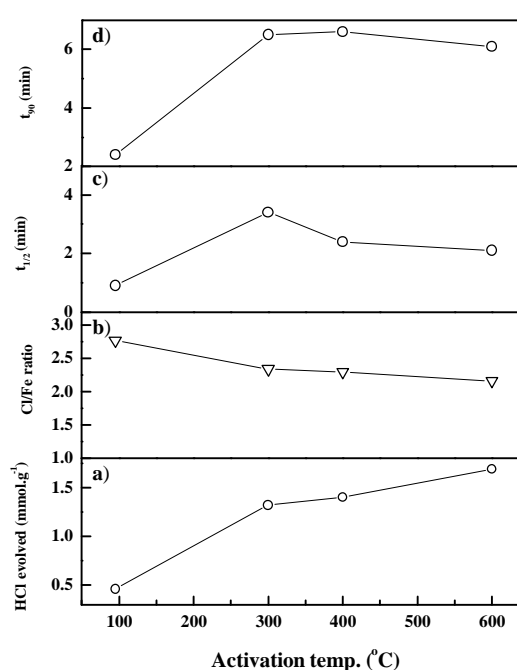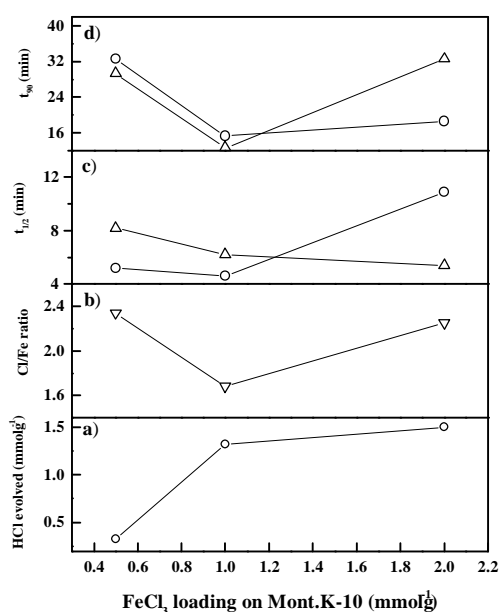
Figure 3.16: Effect of FeCl$_3$ loading in FeCl$_3$/Mont.K-10 on a) HCl evolved in its thermal activation at 300 °C in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or of benzoyl chloride (?).

- The effect of FeCl$_3$ loading however, differ from case to case; it depends not only on the support used in the supported FeCl$_3$ catalysts but also on the conditions (temperature and gas atmosphere) employed in the catalyst thermal activation, as shown in Figures 3.13b, 3.14b, 3.15b, 3.16b, 3.17b and 3.18b.

With increasing the FeCl$_3$ loading, the catalytic activity in both the benzylation and benzoylation reactions is passed through a maximum at the FeCl$_3$ loading of about 1.0 mmol.g^{-1} for all the supported FeCl$_3$ catalysts (Table 3.4). The most probable surface metal chloride species present in the thermally activated catalysts at their optimum FeCl$_3$ loading are listed in Table 3.4.

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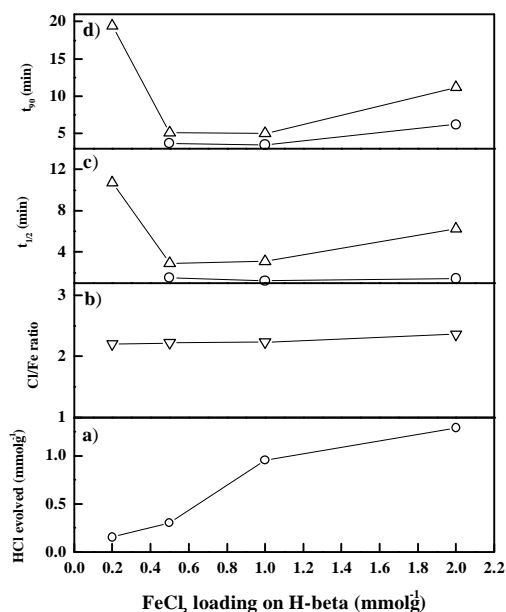
Figure 3.17: Effect of FeCl$_3$ loading in FeCl$_3$/H-beta on a) HCl evolved in its thermal activation at 400 ^{o}C in presence of N$_2$, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?).
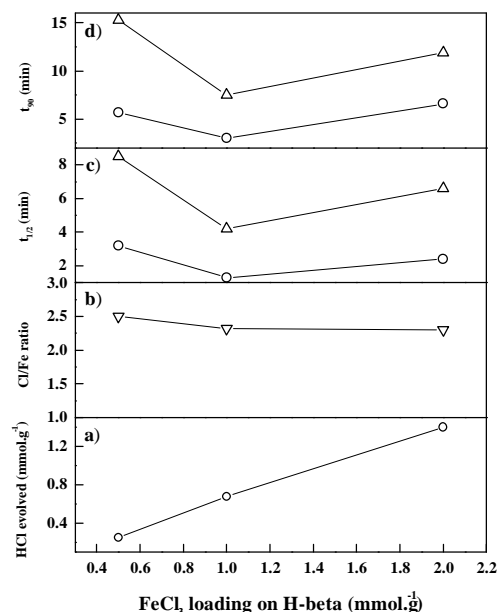
Figure 3.18: Effect of FeCl$_3$ loading in FeCl$_3$/H-beta on a) HCl evolved in its thermal activation at 400 ^{o}C in presence of air, b) Cl/Fe atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or of benzoyl chloride

The high benzylation or benzoylation activity of the thermally activated catalysts at their optimum FeCl$_3$ loading is attributed to the formation of –O-FeCl$_2$ species during the thermal activation. For the best catalytic performance in the benzylation and/or benzoylation, the observed optimum FeCl$_3$ loading (about 1.0 mmol.g^{-1}) is expected because of the presence of limited amount of surface hydroxyls (on the catalyst supports) for their reaction with the loaded FeCl$_3$ (reaction-1). The observed fact that, the catalyst with the FeCl$_3$ loading of 2.0 mmol.g^{-1} shows appreciably lower activity in both the reactions than that observed for the catalysts with lower FeCl$_3$ loadings, indicates that the –O-FeCl$_2$ species and not the physically held FeCl$_3$ are responsible for the catalytic activity. This is expected mostly due to the sintering of FeCl$_3$ present at the high concentrations on the support surface during the thermal treatment to the catalyst, resulting in a poor dispersion of the supported FeCl$_3$. This is consistent with the fact

that, for the high FeCl$_3$ loading (2.0 mmol.g^{-1}), the catalytic activity is decreased with increasing the catalyst activation temperature (Figures 3.6, 3.9 and 3.12).

Table 3.4: Optimum loading of FeCl$_3$ in the supported FeCl$_3$ catalysts for their best performance in the benzene benzylation and p-xylene benzoylation reactions and surface metal chloride species present in the thermally activates catalysts at their optimum FeCl$_3$ loadings.

Supported FeCl$_3$ catalyst	Thermal activation		Optimum FeCl$_3$ loading (mmol.g^{-1})		Cl/Fe ratio (at the optimum FeCl$_3$ loading)	Surface metal chloride species
	Temp. (^{o}C)	Gas atmosphere	Benzylation	benzoylation		
FeCl$_3$/Si-MCM-41	300	N$_2$	1.0	1.0	2.56	FeCl$_3$ and –O-FeCl$_2$
	400	Air	1.0	1.0	2.12	Mainly –O-FeCl$_2$
FeCl$_3$/Mont.K-10	300	N$_2$	1.0	1.0	1.96	Mainly –O-FeCl$_2$
	300	Air	1.0	1.0	1.68	-O-FeCl$_2$ and (-O)$_2$FeCl
FeCl$_3$/H-beta	400	N$_2$	1.0	1.0	2.05	FeCl$_3$ and –O-FeCl$_2$
	400	Air	1.0	1.0	2.32	FeCl$_3$ and –O-FeCl$_2$

3.3.3   Influence of gas Atmosphere Used in the Thermal Activation

A comparison of the results in Figures 3.1-3.18 and Tables 3.3 and 3.4, indicates that the HCl evolved and surface metal chloride species formed in the thermal activation of the supported FeCl$_3$ catalysts and consequently the catalytic activity in the benzene benzylation and p-xylene benzoylation reactions are influenced appreciably by the gas atmosphere (N$_2$ or air) used in the thermal activation of the catalyst. However, further detailed investigation is necessary for understanding the role of oxidizing atmosphere on the reaction between the metal chloride and surface hydroxyls from the different supports.

3.3.4 Influence of Catalyst Support

The results for the thermally activated metal chloride deposited on the different supports (viz. Si-MCM-41, Mont.K-10 and H-beta) (Figures 3.1-3.18) show that, the support plays an important role in the formation of catalytically active surface metal chloride species (viz. –O-FeCl$_2$) by the reaction of its surface hydroxyl groups, the nature (acidic, weekly acidic and non-acidic) and concentration of which varies from support to support, with the supported FeCl$_3$ during the thermal activation of the supported FeCl$_3$ catalysts. To a smaller extent the observed support effect is also expected to arise from the surface properties (viz. surface area pore diameter and acidity), which vary from support to support (Table 3.1). For example, the very high surface area (1140 m^2.g^{-1}) and larger pore diameter (2.5 nm) might have lead to a better dispersion of FeCl$_3$ on the support during the impregnation of FeCl$_3$ on the support. Whereas, the high acidity of the H-beta zeolite support is expected to provide both strong protonic sites (from H -beta) and Lewis acid sites and redox sites (surface –O-FeCl$_2$ species) in the thermally activated particularly for the benzoylation reaction.
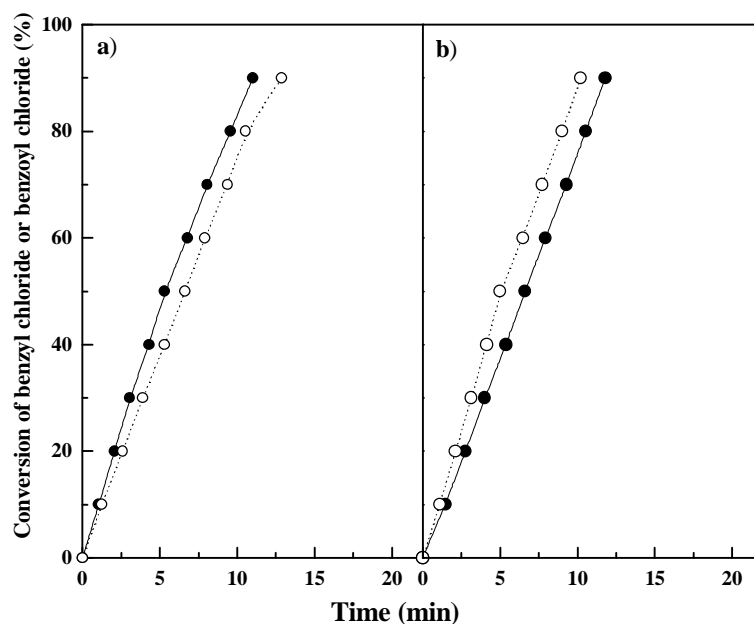
Figure 3.19: Performance of the FeCl$_3$(1.0 mmol.g^{-1})/Si-MCM-41 (activated at 300 ^{o}C under N$_2$) atmosphere in benzene benzylation (a) and p-xylene benzoylation (b) reactions (-?- fresh catalyst and -?- reuse of the catalyst).
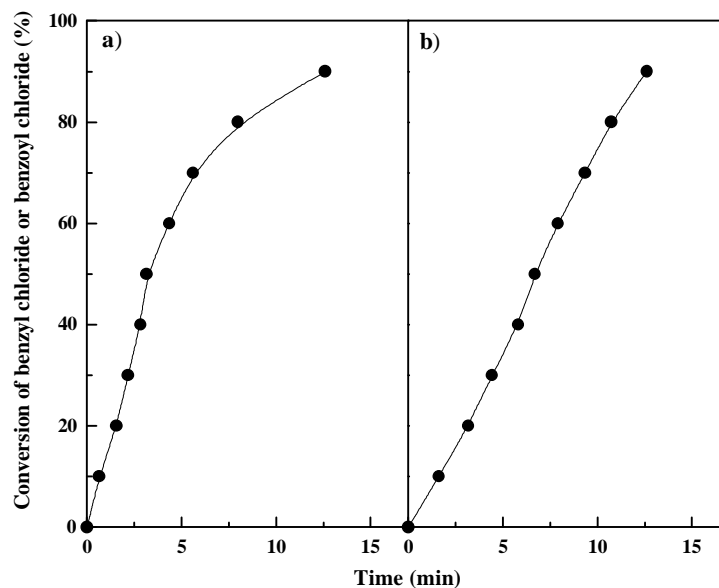
Figure 3.20: Performance of $FeCl_3$(1.0 mmol.g^{-1})/Mont.K-10 (activated at 300 ^{o}C under N_2) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions
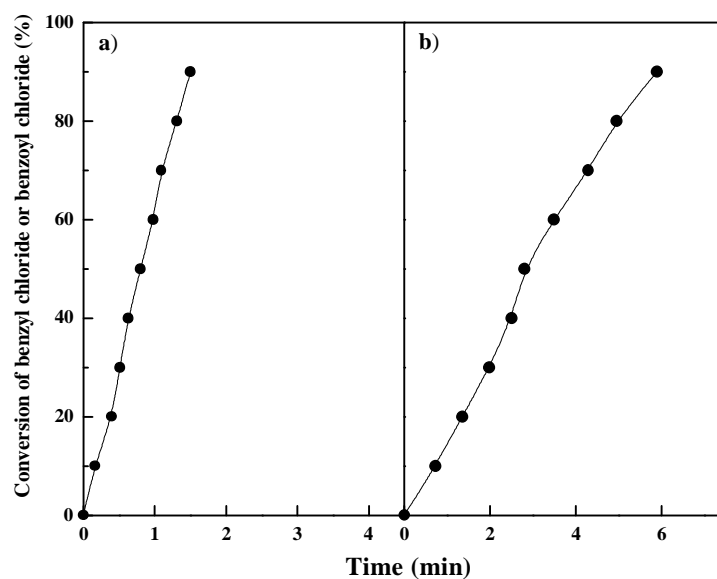
Figure 3.21: Performance of $FeCl_3$(1.0 mmol.g^{-1})/H-beta (activated at 300 ^{o}C under N_2) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions

For a purpose of comparison, data showing the catalytic performance (conversion of benzyl chloride or benzoyl chloride as a function of reaction time) of the $FeCl_3$/Si-MCM-41, $FeCl_3$/Mont.K-10 and $FeCl_3$/H-beta catalysts, having the optimum $FeCl_3$ loading (1.0 mmol.g^{-1}) and thermally activated at or close to optimum condition (at 300 ^{o}C under N_2

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atmosphere) are presented in Figures 3.19-3.21. A comparison of the results shows that the catalytic activity of the different supported $FeCl_3$ catalysts is in the following order:

For the benzylation reaction: $FeCl_3$/Mont.K-10 < $FeCl_3$/Si-MCM-41 < $FeCl_3$/H-beta

For the benzylation reaction: $FeCl_3$/Si-MCM-41 < $FeCl_3$/Mont.K-10 < $FeCl_3$/H-beta

3.4 PERFORMANCE OF SUPPORTED GaCl$_3$ CATALYSTS (THERMALLY ACTIVATED AT DIFFERENT CONDITIONS) IN BENZENE BENZYLATION AND P-XYLENE BENZOYLATION REACTIONS

GaCl$_3$/Si-MCM-41, GaCl$_3$/Mont.K-10 and GaCl$_3$/H-beta catalysts with different metal chloride loadings (0.5-2.0 mmol.g^{-1}) were thermally activated by their calcination at different temperatures (95-600 ºC) under different gas atmospheres (flowing N_2 or air) for 3 h.
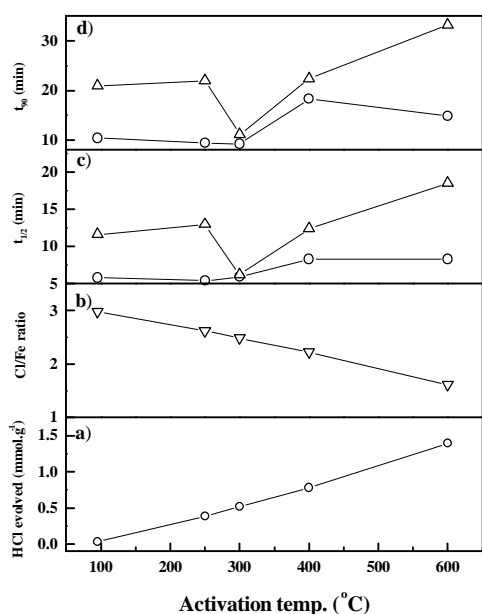
Figure 3.22: Effect of temperature of calcination/activation (in N_2) of GaCl$_3$(1.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride (?)
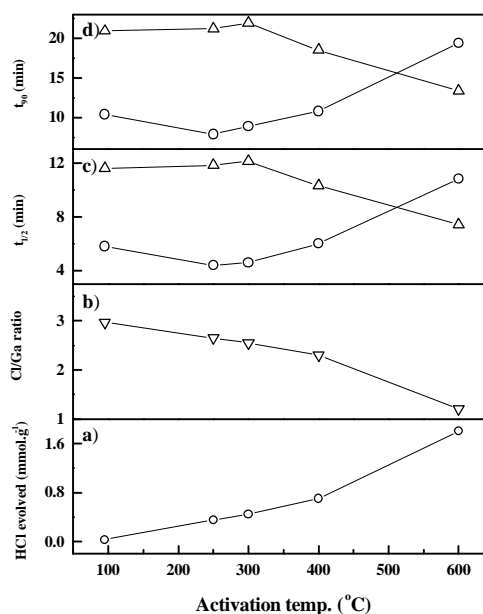
Figure 3.23: Effect of temperature of calcination/activation (in air) of GaCl$_3$(1.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in its thermal activation in presence of air, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride (?)
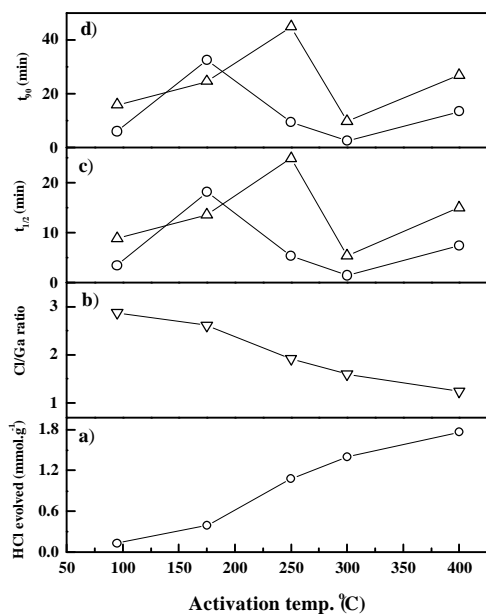
Figure 3.24: Effect of temperature of calcination/activation (in N_2) of $GaCl_3$(1.0 mmolg^{-1})/Mont.K-10 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride (?)

Figure 3.25: Effect of temperature of calcination/activation (in N_2) of $GaCl_3$(0.5 mmolg^{-1})/Mont.K-10 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or of benzoyl chloride (?)

After their thermal activation, all the thermally activated supported $GaCl_3$ catalysts were evaluated for their performance in the benzene benzylation and/or p-xylene benzoylation reactions. Results showing influence of the thermal activation temperature, the metal chloride loading in the supported $GaCl_3$ catalysts, the gas atmosphere employed during the thermal activation and the support used in the catalyst on the amount of HCl evolved, on the Cl/Ga ratio of the physically/chemically bound gallium chloride species on the support surface, and also on the catalytic activity (in the benzene benzylation and p-xylene benzoylation reactions) of the supported $GaCl_3$ catalysts are presented in Figures 3.22-3.33. The catalytic activity is measured in terms of the time required for half the reaction (i.e. 50

% conversion of benzyl chloride or benzoyl chloride). Data on the time required for 90 %
conversion of benzyl chloride or benzoyl chloride are also included in the figures.

Figure 3.26: Effect of temperature of calcination/activation (in N_2) of $GaCl_3$ (1.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or

Figure 3.27: Effect of temperature of calcination/activation (in air) of $GaCl_3$ (1.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of air, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride in the benzylation of benzene

3.4.1 Influence of the Catalyst Thermal Activation Temperature

The results in Figures 3.22-3.27 reveal that the influence of the activation temperature for the different supported $GaCl_3$ catalysts are more or less similar to that observed for the supported $FeCl_3$ catalysts (Section 3.3.1). Like for the supported $FeCl_3$ catalysts, there is an optimum thermal activation temperature for all the supported $GaCl_3$ catalysts for their best performance in the benzylation and benzoylation reactions, depending upon the $GaCl_3$ loading and the gas atmosphere used in the activation, as shown in Table 3.5. The most probable surface metal chloride species present in the supported $GaCl_3$ catalysts after the thermal activation at the optimal activation temperature are $GaCl_3$, $-O-GaCl_2$ and/or $(-O)_2GaCl$ (Table 3.5). The observed high catalytic

activity in both the benzylation and benzoylation reactions is mostly attributed to the $-O-GaCl_2$ and $(-O)_2GaCl$ species formed during the thermal activation of the supported $GaCl_3$ catalysts.

Table 3.5: Optimum catalyst activation temperature for the different supported $GaCl_3$ catalysts for their best performance in the benzene benzylation and p-xylene benzoylation reactions and surface metal chloride species present in the thermally activated catalysts at their optimum activation temperature.

Catalyst	$GaCl_3$ loading (mmol. g^{-1})	Gas atmosphere used in the activation (N_2 or air)	Optimum catalyst activation temperature (°C)		Surface Metal chloride species
			Benzylation	Benzoylation	
$GaCl_3$/Si-MCM-41	1.0	N_2	250-300 $(2.62-2.48)^a$	$300(2.48)^a$	$GaCl_3$ and $-O-GaCl_2$
	1.0	Air	250 (2.65)	? 600 (1.2)	$GaCl_3$ and $-O-GaCl_2$
$GaCl_3$/Mont.K-10	0.5	N_2	? 95 (2.8)	250 (2.56)	$-O-FeCl_2$ and $(-O)_2GaCl$
	1.0	N_2	300 (1.6)	300 (1.6)	$-O-FeCl_2$ and $(-O)_2GaCl$
$GaCl_3$/H-beta	1.0	N_2	300 (2.48)	400 (1.98)	$GaCl_3$ and/or $-O-GaCl_2$
	1.0	Air	400-500 (2.07-1.89)	-	Mainly $-O-GaCl_2$

[a]Values of Cl/Ga ratio of the surface metal chloride species are given in round brackets. [b]At the optimum catalyst activation temperature of 250 °C for the benzylation. [c]At the catalyst

activation temperature of 600 ^{o}C the surface metal chloride species are $(-O)_2GaCl$ with smaller amounts of $-O-GaCl_2$.

3.4.2 Influence of Metal Chloride Loading in Supported GaCl$_3$ Catalysts

The results in Figures 3.28-3.33 reveal a strong influence of the GaCl$_3$ loading in the supported GaCl$_3$ catalysts (thermally activated at 300 or 400 ºC for 3 h in N$_2$ or air atmosphere) on the HCl evolved in the thermal activation, Cl/Ga ratio of surface metal chloride species present in the catalyst after its thermal activation, and the catalytic activity in both the benzene benzylation and p-xylene benzoylation reactions.
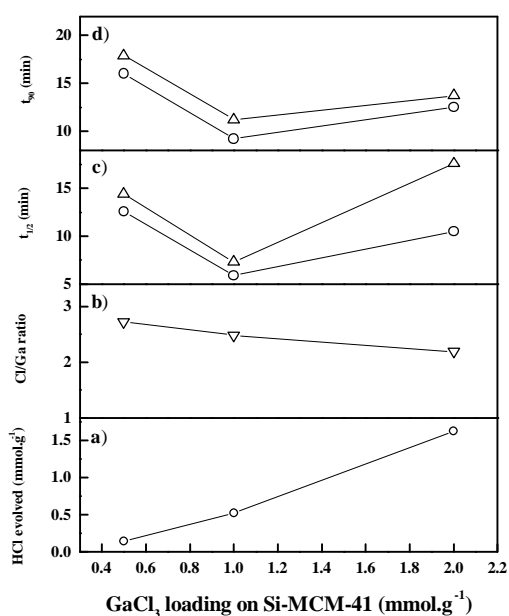
Figure 3.28: Effect of GaCl$_3$ loading in GaCl$_3$/Si-MCM-41 on a) HCl evolved in its thermal activation at 300 ^{o}C in presence of N$_2$, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?)
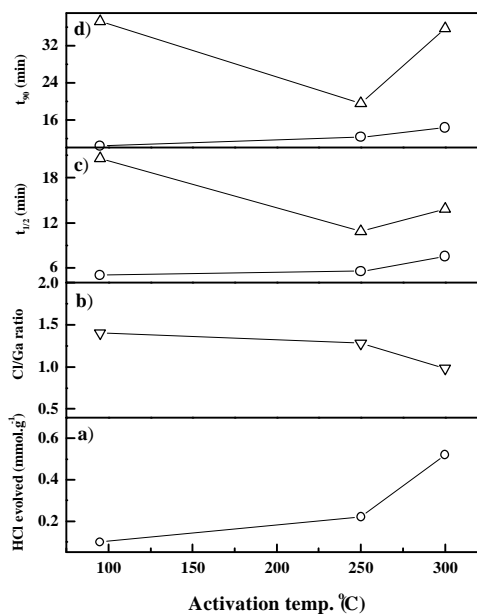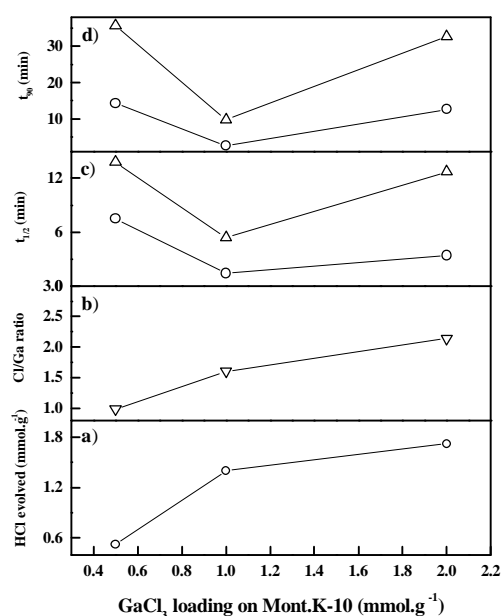
Figure 3.29: Effect of GaCl$_3$ loading in GaCl$_3$/Mont.K-10 on a) HCl evolved in its thermal activation at 300 ^{o}C in presence of N$_2$, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or of benzoyl chloride (?)
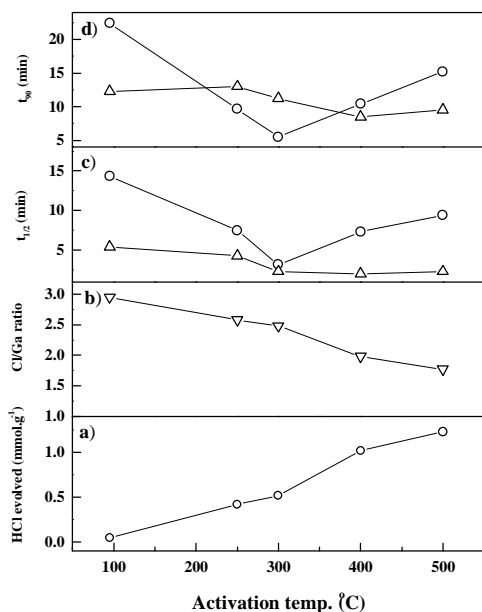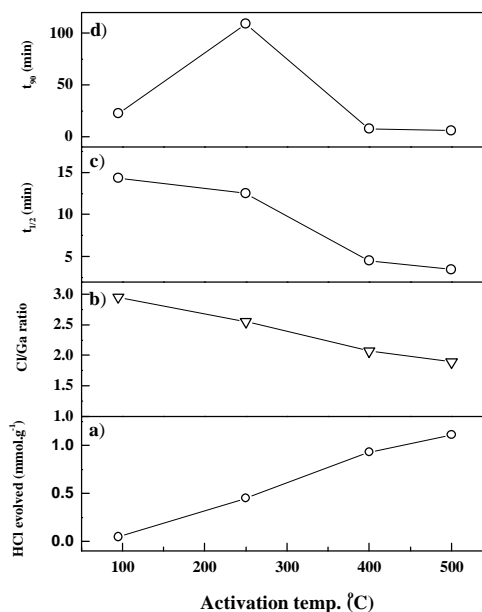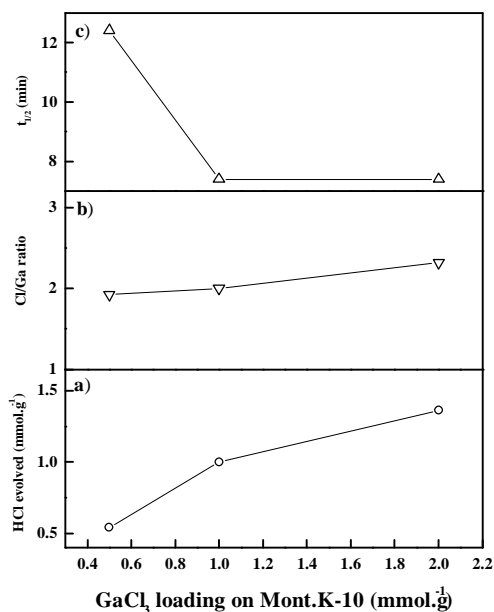
Figure 3.30: Effect of GaCl$_3$ loading in GaCl$_3$/Mont.K-10 on a) HCl evolved in its thermal activation at 300 $^{\circ}$C in presence of air, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the p-xylene benzoylation reaction (t$_{1/2}$)
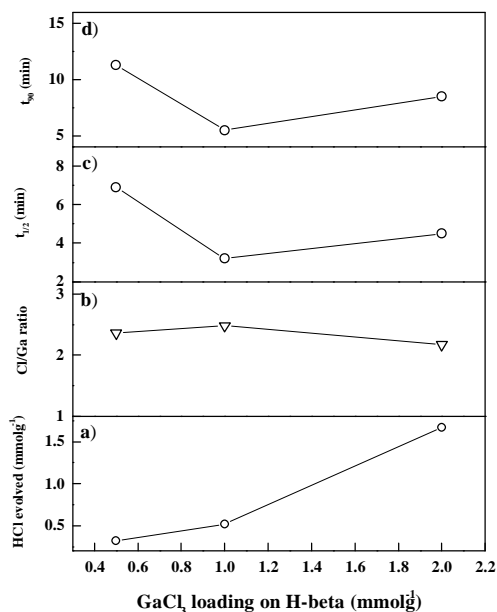
Figure 3.31: Effect of GaCl$_3$ loading in GaCl$_3$/H-beta on a) HCl evolved in its thermal activation at 300 $^{\circ}$C in presence of N$_2$, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride in the benzylation of benzene

The observed influence is almost similar to that observed in case of the supported FeCl$_3$ catalysts (Section 3.3.2). The most probable surface metal chloride species present in the thermally activated catalysts at their optimum GaCl$_3$ loading are listed in Table 3.6.

The high benzylation or benzoylation activity of the thermally activated catalysts at their optimum GaCl$_3$ loading is attributed to the formation of –O-GaCl$_2$ and/or (-O)$_2$GaCl species during the thermal activation. For the best catalytic performance in the benzylation and/or benzoylation, the observed optimum GaCl$_3$ loading (about 1.0 mmol.g^{-1}) is expected because of the presence of limited amount of surface hydroxyls (on the catalyst supports) for their reaction with the loaded GaCl$_3$ (reaction-1).
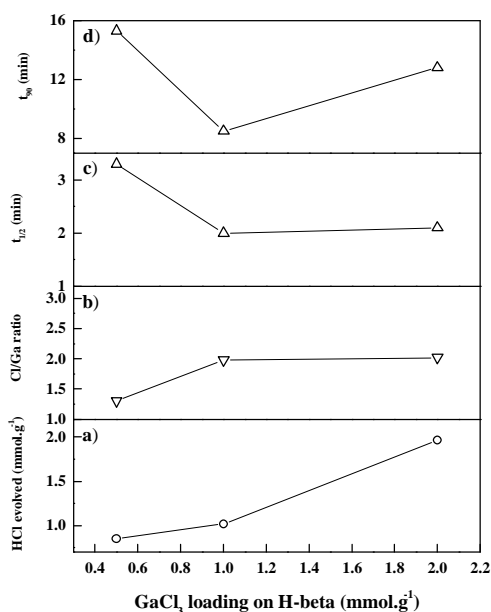
Figure 3.32: Effect of GaCl$_3$ loading in GaCl$_3$/H-beta on a) HCl evolved in its thermal activation at 400 $^{\circ}$C in presence of N$_2$, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the p-Xylene benzoylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzoyl chloride in the benzoylation of p-Xylene

Figure 3.33: Effect of GaCl$_3$ loading in GaCl$_3$/H-beta on a) HCl evolved in its thermal activation at 400 $^{\circ}$C in presence of air, b) Cl/Ga atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride in the benzylation of benzene

3.4.3 Influence of gas Atmosphere Used in the Thermal Activation

A comparison of the results in Figures 3.22-3.33 and Tables 3.5 and 3.6, indicates that the HCl evolved and surface metal chloride species formed in the thermal activation of the supported GaCl$_3$ catalysts and consequently the catalytic activity in the benzene benzylation and p-xylene benzoylation reactions are influenced appreciably by the gas atmosphere (N$_2$ or air) used in the thermal activation of the catalyst. However, further detailed investigation is necessary for understanding the role of oxidizing atmosphere on the reaction between the metal chloride and surface hydroxyls from the different supports.

Table 3.6: Optimum loading of GaCl$_3$ in the supported GaCl$_3$ catalysts for their best performance in the benzene benzylation and p-xylene benzoylation reactions and surface metal chloride species present in the thermally activates catalysts at their optimum GaCl$_3$ loadings.

| Supported GaCl$_3$ catalyst | Thermal activation | | Optimum GaCl$_3$ loading (mmol.g^{-1}) | | Cl/Ga ratio (at the optimum GaCl$_3$ loading) | Surface Metal chloride species |
	Temp. (^{o}C)	Gas atmosphere	Benzylation	Benzoylation		
GaCl$_3$/Si-MCM-41	300	N$_2$	1.0	1.0	2.48	GaCl$_3$ and –O-GaCl$_2$
	400	Air	1.0	1.0	2.30	Mainly –O-GaCl$_2$
GaCl$_3$/Mont.K-10	300	N$_2$	1.0	1.0	1.6	–O-FeCl$_2$ and (-O)$_2$GaCl
	300	Air	1.0	1.0	2.0	GaCl$_3$ and -O-GaCl$_2$
GaCl$_3$/H-beta	300	N$_2$	1.0	1.0	2.48	–O-GaCl$_2$
	400	N$_2$	1.0	1.0	1.98	Mainly –O-GaCl$_2$
	400	Air	1.0	1.0	2.07	GaCl$_3$ and –O-GaCl$_2$

3.4.4 Influence of Catalyst Support

The results for the thermally activated gallium chloride deposited on the different supports (viz. Si-MCM-41, Mont.K-10 and H-beta) (Figures 3.22-3.33) show that, the support plays an important role in the formation of catalytically active surface metal chloride species (viz. –O-GaCl$_2$) by the reaction of its surface hydroxyl groups, the nature (acidic, weekly acidic and non-acidic) and concentration of which varies from support to support, with the supported GaCl$_3$ during the thermal activation of the supported GaCl$_3$ catalysts. To a smaller extent the observed support effect is also expected to arise from the surface properties (viz. surface area pore diameter and acidity), which vary from support to support (Table 3.1).

For a purpose of comparison, data showing the catalytic performance (conversion of benzyl chloride or benzoyl chloride as a function of reaction time) of the $GaCl_3$/Si-MCM-41, $GaCl_3$/Mont.K-10 and $GaCl_3$/H-beta catalysts, having the optimum $GaCl_3$ loading (1.0 mmol.g^{-1}) and thermally activated at or close to optimum condition (at 300 ^{o}C under N_2 atmosphere) are presented in Figures 3.34-3.36.
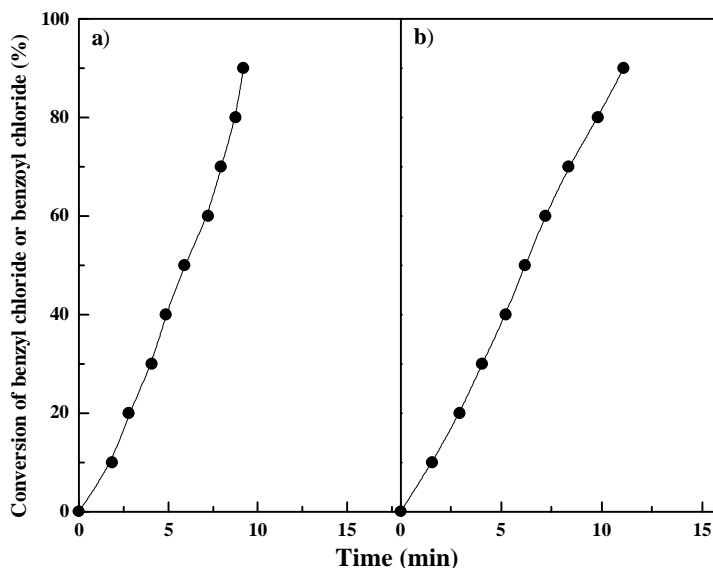
Figure 3.34: Performance of $GaCl_3$(1.0 mmol.g^{-1})/Si-MCM-41 (activated at 300 ^{o}C under N_2) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions
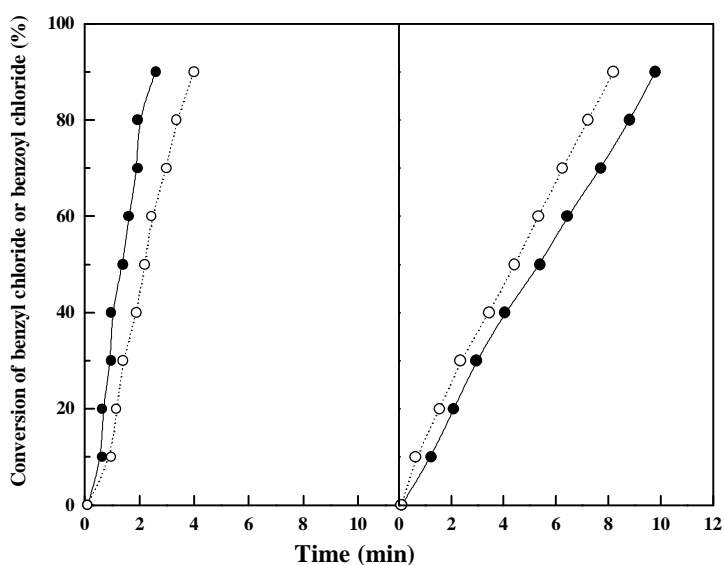
Figure 3.35: Performance of $GaCl_3$(1.0 mmol.g^{-1})/Mont.K-10 (activated at 300 ^{o}C under N_2) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions (-?- fresh catalyst and -?- reuse of the catalyst)
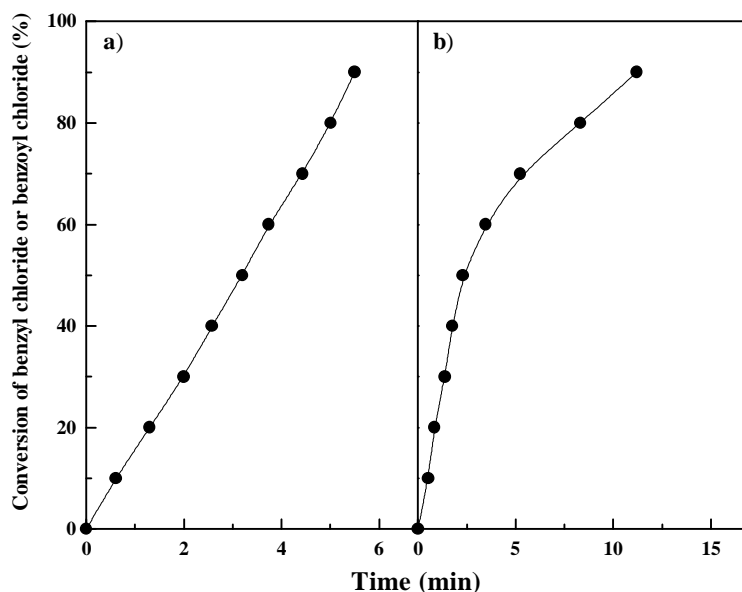
Figure 3.36: Performance of GaCl$_3$(1.0 mmol.g^{-1})/H-beta (activated at 300 ^{o}C under N$_2$) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions

A comparison of the results shows that the catalytic activity of the different supported GaCl$_3$ catalysts is in the following order:

For the benzylation reaction: GaCl$_3$/Si-MCM-41 < GaCl$_3$/H-beta < GaCl$_3$/Mont.K-10

For the benzoylation reaction: GaCl$_3$/Si-MCM-41 < GaCl$_3$/Mont.K-10 < GaCl$_3$/H-beta

3.5 PERFORMANCE OF SUPPORTED InCl$_3$ CATALYSTS (THERMALLY ACTIVATED AT DIFFERENT CONDITIONS) IN BENZENE BENZYLATION AND p-XYLENE BENZOYLATION REACTIONS

InCl$_3$/Si-MCM-41, InCl$_3$/Mont.K-10 and InCl$_3$/H-beta catalysts with different metal chloride loadings (0.5-2.0 mmol.g^{-1}) were thermally activated by their calcination at different temperatures (95-600 ℃) under different gas atmospheres (flowing N$_2$ or air) for 3 h. After their thermal activation, all the thermally activated supported InCl$_3$ catalysts were evaluated for their performance in the benzene benzylation and/or p-xylene benzoylation reactions.

Results showing influence of the thermal activation temperature, the metal chloride loading in the supported InCl$_3$ catalysts, the gas atmosphere employed during the thermal activation and the support used in the catalyst on the amount of HCl evolved, on the Cl/In ratio of the physically/chemically bound iron chloride species on the support surface, and

also on the catalytic activity (in the benzene benzylation and p-xylene benzoylation reactions) of the supported $InCl_3$ catalysts are presented in Figures 3.37-3.49.
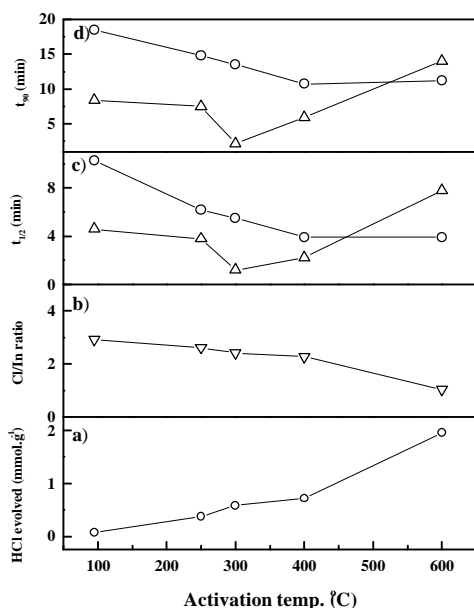
Figure 3.37: Effect of temperature of calcination/activation (in N_2) of $InCl_3$(1.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/In atomic ratio of surface metal chloride spe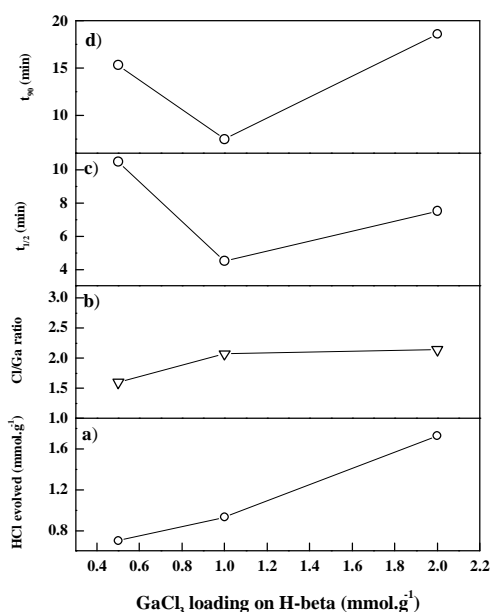cies, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride
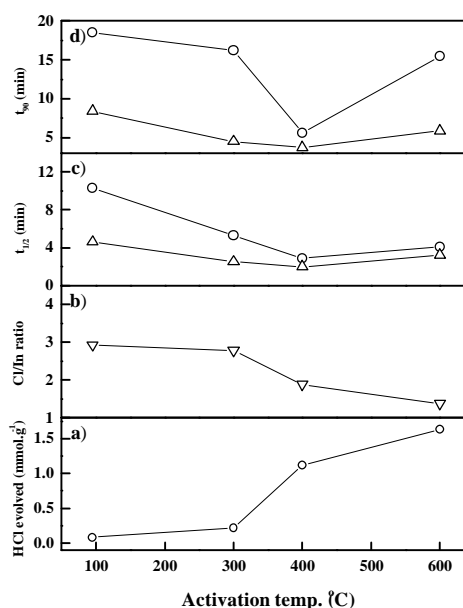
Figure 3.38: Effect of temperature of calcination/activation (in air) of $InCl_3$(1.0 mmolg^{-1})/Si-MCM-41 on a) HCl evolved in its thermal activation in presence of air, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride (?)

The catalytic activity is measured in terms of the time required for half the reaction (i.e. 50 % conversion of benzyl chloride or benzoyl chloride). Data on the time required for 90 % conversion of benzyl chloride or benzoyl chloride are also included in the figures.

3.5.1 Influence of the Catalyst Thermal Activation Temperature

The results in Figures 3.37-3.44 reveal that the influence of the activation temperature for the different supported $InCl_3$ catalysts are more or less similar to that observed for the supported $FeCl_3$ catalysts (Section 3.3.1). Like for the supported $FeCl_3$ catalysts, there is an optimum thermal activation temperature for all the supported $InCl_3$

catalysts for their best performance in the benzylation and benzoylation reactions, depending upon the InCl$_3$ loading and the gas atmosphere used in the activation, as shown in Table 3.7.

Figure 3.39: Effect of temperature of calcination/activation (in N$_2$) of InCl$_3$(1.0 mmolg^{-1})/Mont.K-10 on a) HCl evolved in its thermal activation in presence of N$_2$, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or benzoyl chloride
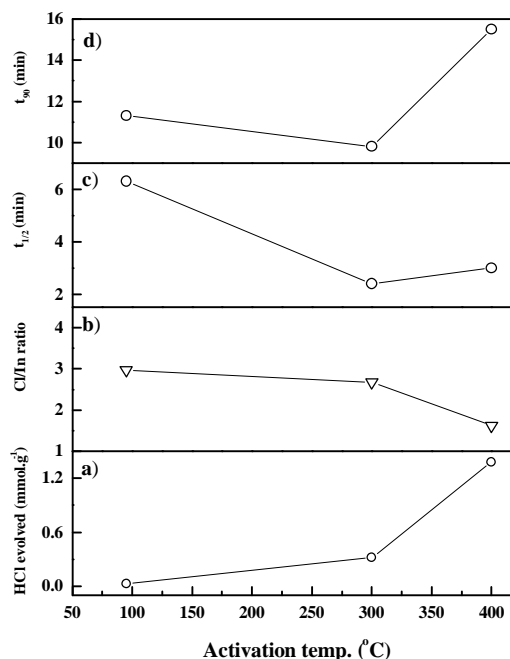
Figure 3.40: Effect of temperature of calcination/activation (in N$_2$) of InCl$_3$(1.0 mmolg^{-1})/Mont.K-10 on a) HCl evolved in its thermal activation in presence of N$_2$, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?)

The most probable surface metal chloride species present in the supported InCl$_3$ catalysts after the thermal activation at the optimal activation temperature are InCl$_3$, –O-InCl$_2$ and/or (-O)$_2$InCl (Table 3.7).
The observed high catalytic activity in both the benzylation and benzoylation reactions is mostly attributed to the –O-InCl$_2$ and (-O)$_2$InCl species formed during the thermal activation of the supported InCl$_3$ catalysts.
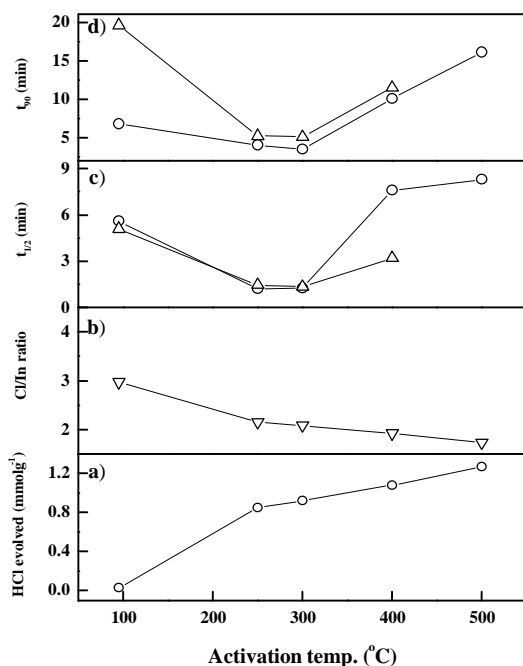
Figure 3.41: Effect of temperature of calcination/activation (in N_2) of $InCl_3$ (1.0 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride (?)
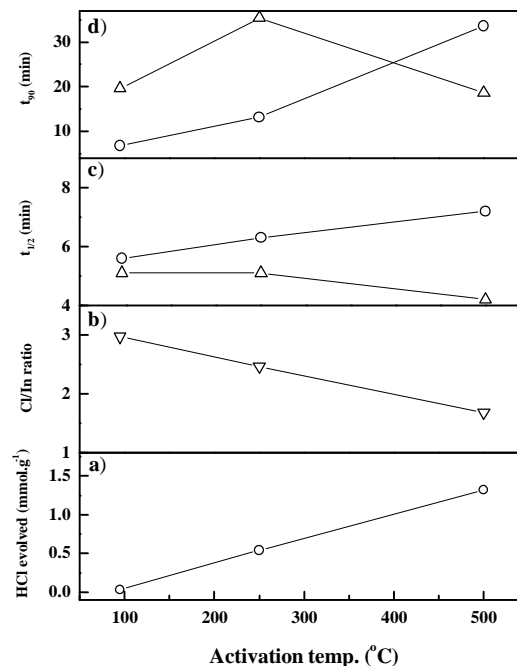
Figure 3.42: Effect of temperature of calcination/activation (in air) of $InCl_3$ (1.0 mmolg^{-1})/H-beta on a) HCl evolved in .its thermal activation in presence of air, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?) or benzoyl chloride (?)
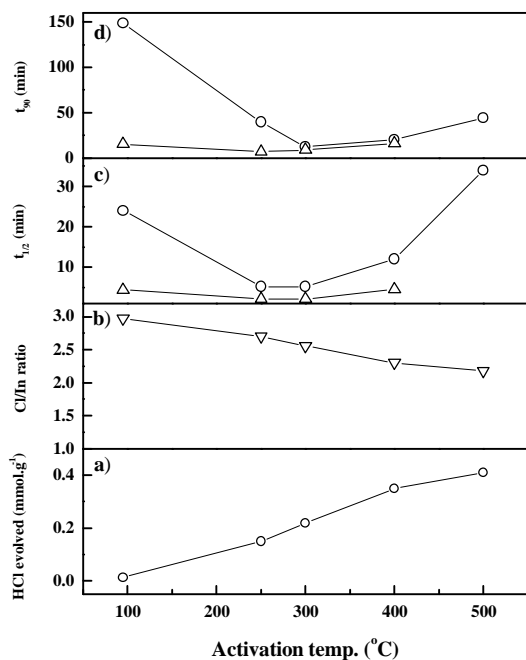
Figure 3.43: Effect of temperature of calcination/activation (in N_2) of $InCl_3$ (0.5 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of N_2, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride (?)
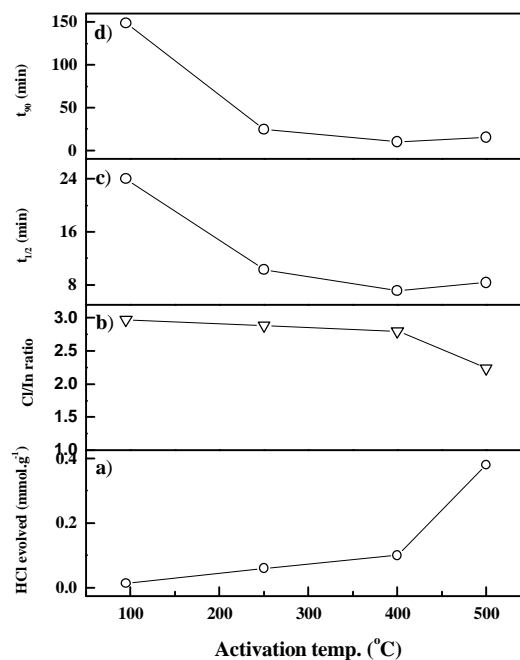
Figure 3.44: Effect of temperature of calcination/activation (in air) of $InCl_3$ (0.5 mmolg^{-1})/H-beta on a) HCl evolved in its thermal activation in presence of air, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride in the benzylation of benzene

Table 3.7: Optimum catalyst activation temperature for the different supported $InCl_3$ catalysts for their best performance in the benzene benzylation and p-xylene benzoylation reactions and surface metal chloride species present in the thermally activated catalysts at their optimum activation temperature.

Catalyst	$InCl_3$ loading (mmol.g^{-1})	Gas atmosphere used in the activation (N_2 or air)	Optimum catalyst activation temperature (°C)		Surface metal chloride species
			Benzylation	Benzoylation	
$InCl_3$/Si-MCM-41	1.0	N_2	300 (2.48)[a]	400 (2.28)[a]	$-O-InCl_2$ withsmaller amounts of $InCl_3$
	1.0	Air	400 (1.88)	400 (1.88)	$-O-InCl_2$ with smaller amounts of $(-O)_2InCl$
$InCl_3$/Mont.K-10	1.0	N_2	300 (2.25)	300 (2.25)	Mainly $-O-InCl_2$
	1.0	N_2	300 (2.68)	-	$-O-InCl_2$ and $InCl_3$
$InCl_3$/H-beta	1.0	N_2	300 (2.08)	300 (2.08)	Mainly $-O-InCl_2$
	1.0	Air	? 95 (2.97)	? 500 (1.68)	$InCl_3$ (for OCAT[b] ? 95°C) and $-O-InCl_2$ and $(-O)_2InCl$ (for OCAT ? 500°C)
	0.5	N_2	250-300 (2.7-2.56)	250-300 (2.7-2.56)	$-O-InCl_2$ and $InCl_3$
	0.5	Air	400 (2.8)	-	$-O-InCl_2$ and $InCl_3$

[a]values of Cl/Ga ratio of the surface metal chloride species are given in round brackets, [b]Optimum catalyst activation temperature.

3.5.2 Influence of Metal Chloride Loading in Supported InCl$_3$ Catalysts

The results in Figures 3.46-3.49 reveal a strong influence of the InCl$_3$ loading in the supported InCl$_3$ catalysts (thermally activated at 250, 300 or 400 °C for 3 h in N$_2$ or air atmosphere) on the HCl evolved in the thermal activation, Cl/In ratio of surface metal chloride species present in the catalyst after its thermal activation, and the catalytic activity in both the benzene benzylation and p-xylene benzoylation reactions. The observed influence is almost similar to that observed in case of the supported FeCl$_3$ catalysts (Section 3.3.2). The most probable surface metal chloride species present in the thermally activated catalysts at their optimum InCl$_3$ loading are listed in Table 3.8.
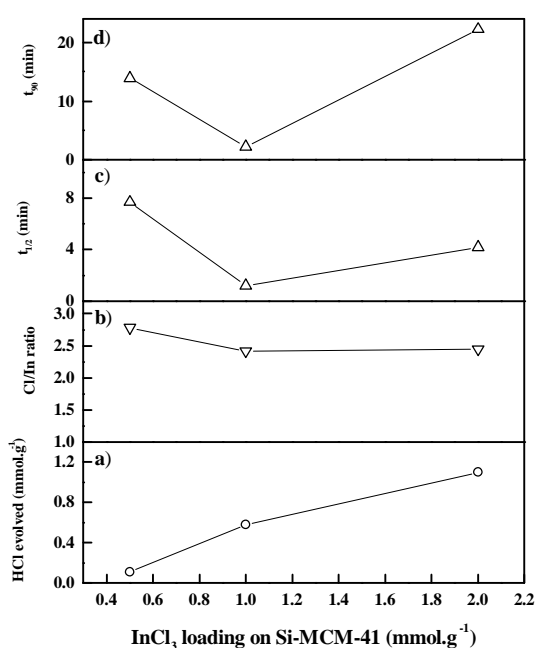
Figure 3.45: Effect of InCl$_3$ loading in InCl$_3$/Si-MCM-41 on a) HCl evolved in its thermal activation at 300 °C in presence of N$_2$, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the p-Xylene benzoylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzoyl chloride in the benzoylation of p-Xylene
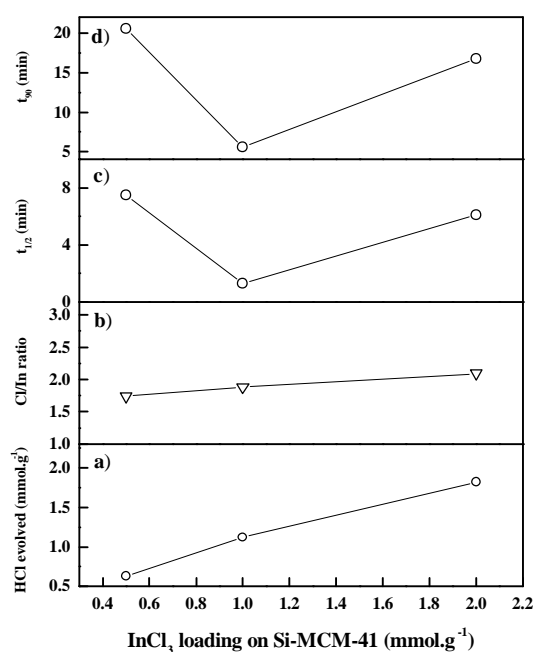
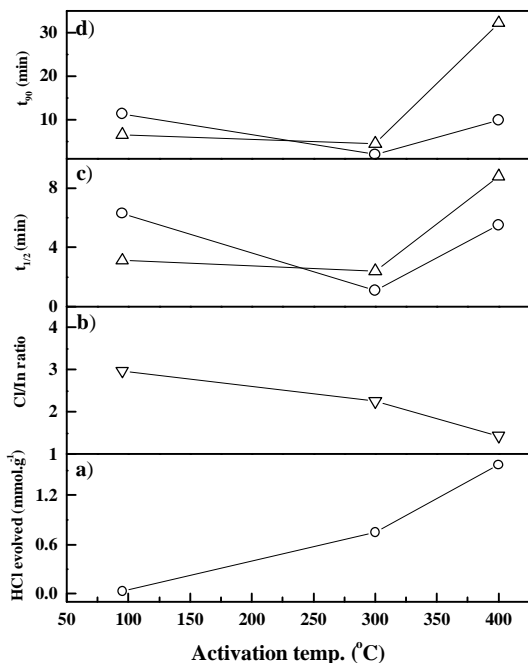**Figure 3.46:** Effect of InCl$_3$ loading in InCl$_3$/Si-MCM-41 on a) HCl evolved in its thermal activation at 400 °C in presence of air, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction ($t_{1/2}$), and d) time required for 90 % conversion (t_{90}) of benzyl chloride in the benzylation of benzene

The high benzylation or benzoylation activity of the thermally activated catalysts at their optimum InCl$_3$ loading is attributed to the formation of –O-InCl$_2$ and/or (-O)$_2$InCl

species during the thermal activation. For the best catalytic performance in the benzylation and/or benzoylation, the observed optimum InCl$_3$ loading (about 1.0 mmol.g^{-1}) is expected because of the presence of limited amount of surface hydroxyls (on the catalyst supports) for their reaction with the loaded InCl$_3$ (reaction-1).
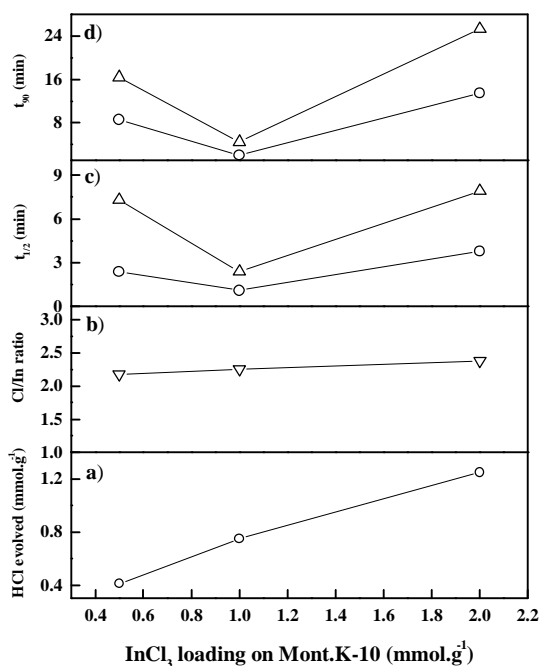
Figure 3.47: Effect of InCl$_3$ loading in InCl$_3$/Mont.K-10 on a) HCl evolved in its thermal activation at 300 ^{o}C in presence of N$_2$, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation (?) or p-Xylene benzoylation (?) reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride (?) or of benzoyl chloride (?)
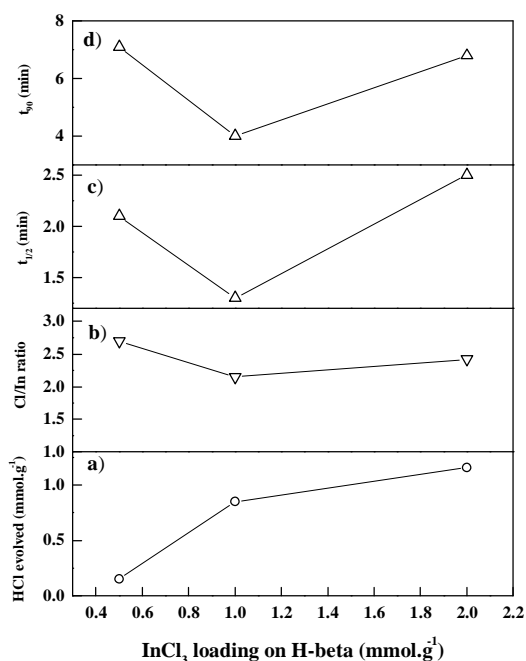
Figure 3.48: Effect of InCl$_3$ loading in InCl$_3$/H-beta on a) HCl evolved in its thermal activation at 250 ^{o}C in presence of N$_2$, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the p-Xylene benzoylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzoyl chloride in the benzoylation of p-Xylene
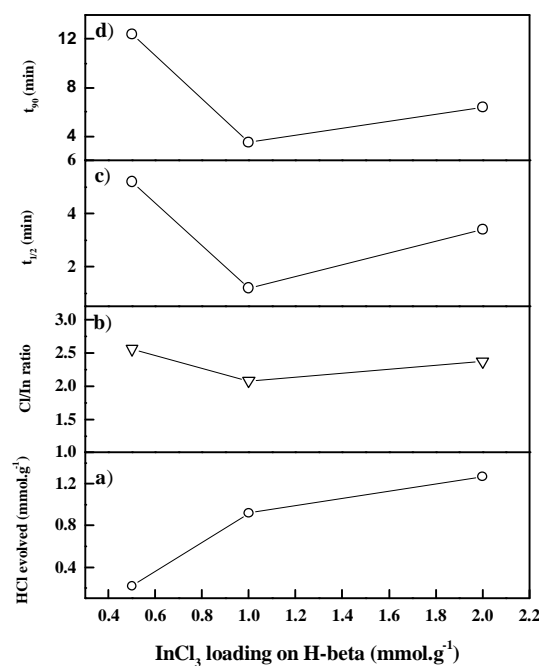
Figure 3.49: Effect of InCl$_3$ loading in InCl$_3$/H-beta on a) HCl evolved in its thermal activation at 300 ^{o}C in presence of N$_2$, b) Cl/In atomic ratio of surface metal chloride species, c) time required for half the benzene benzylation reaction (t$_{1/2}$), and d) time required for 90 % conversion (t$_{90}$) of benzyl chloride in the benzylation of benzene

3.5.3 Influence of gas Atmosphere Used in the Thermal Activation

A comparison of the results in Figures 3.37-3.50 and Tables 3.7 and 3.8, indicates that the HCl evolved and surface metal chloride species formed in the thermal activation of the supported InCl$_3$ catalysts and consequently the catalytic activity in the benzene benzylation and p-xylene benzoylation reactions are influenced appreciably by the gas atmosphere (N$_2$ or air) used in the thermal activation of the catalyst. However, further detailed investigation is necessary for understanding the role of oxidizing atmosphere on the reaction between the metal chloride and surface hydroxyls from the different supports.

3.4.4 Influence of Catalyst Support

The results for the thermally activated gallium chloride deposited on the different upports (viz. Si-MCM-41, Mont.K-10 and H-beta) (Figures 3.37-3.49) show that, the support plays an important role in the formation of catalytically active surface metal chloride species (viz. –O-InCl$_2$) by the reaction of its surface hydroxyl groups, the nature (acidic, weekly acidic and non-acidic) and concentration of which varies from support to support, with the supported InCl$_3$ during the thermal activation of the supported InCl$_3$ catalysts. To a smaller

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extent the observed support effect is also expected to arise from the surface properties (viz. surface area pore diameter and acidity), which vary from support to support (Table 3.1).

Table 3.8: Optimum loading of $InCl_3$ in the supported $InCl_3$ catalysts for their best performance in the benzene benzylation and p-xylene benzoylation reactions and surface metal chloride species present in the thermally activates catalysts at their optimum $InCl_3$ loadings.

| Supported $InCl_3$ catalyst	Thermal activation		Optimum $InCl_3$ loading (mmol.g^{-1})		Cl/In ratio (at the optimum $InCl_3$ loading)	Surface metal chloride species
	Temp. (^{o}C)	Gas atmosphere	Benzylation	benzoylation		
$InCl_3$/Si-MCM-41	300	N_2	1.0	1.0	2.42	$-O-InCl_2$ and $InCl_3$
	400	Air	1.0	1.0	1.88	$-O-InCl_2$ and $(-O)_2InCl$
$InCl_3$/ Mont.K-10	300	N_2	1.0	1.0	2.25	$-O-InCl_2$ and $InCl_3$
$InCl_3$/H-beta	250	N_2	1.0	1.0	2.15	mainly $-O-InCl_2$
	300	N_2	1.0	1.0	2.08	mainly $-O-InCl_2$

For a purpose of comparison, data showing the catalytic performance (conversion of benzyl chloride or benzoyl chloride as a function of reaction time) of the $InCl_3$/Si-MCM-41, $InCl_3$/Mont.K-10 and $InCl_3$/H-beta catalysts, having the optimum $InCl_3$ loading (1.0 mmol.g^{-1}) and thermally activated at or close to optimum condition (at 300 ^{o}C under N_2 atmosphere) are presented in Figures 3.50-3.52. A comparison of the results shows that the catalytic activity of the different supported $InCl_3$ catalysts is in the following order:

For the benzylation reaction: InCl$_3$/Si-MCM-41 < InCl$_3$/H-beta < InCl$_3$/ Mont.K-10

For the benzylation reaction: InCl$_3$/Si-MCM-41 < InCl$_3$/Mont.K-10 < InCl$_3$/H-beta
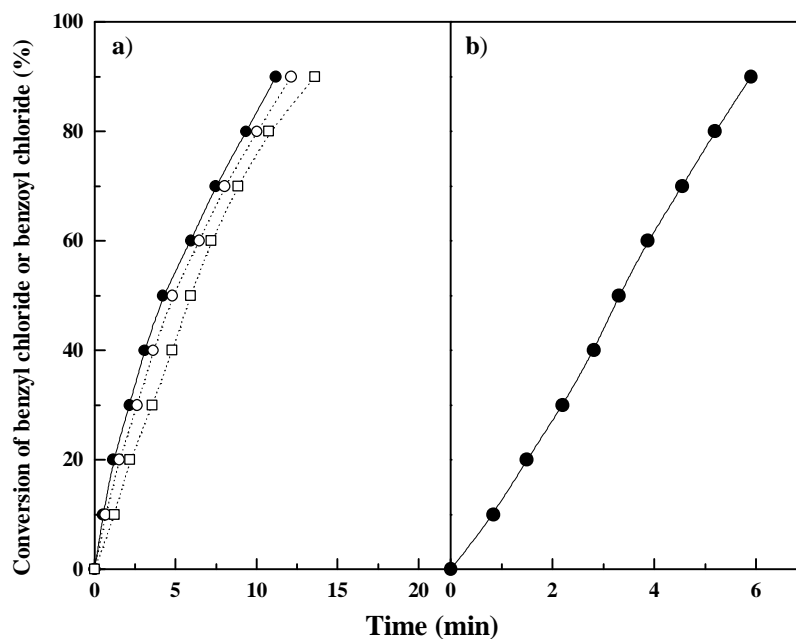
Figure 3.50: Performance of InCl$_3$(1.0 mmol.g^{-1})/Si-MCM-41 (activated at 400 ^{o}C under air) in the benzene benzylation (a) and p-xylene benzoylation (activated at 300 ^{o}C under N$_2$) (b) reactions (-?- fresh catalyst, -?- first reuse of the catalyst and -?- third reuse of the catalyst)
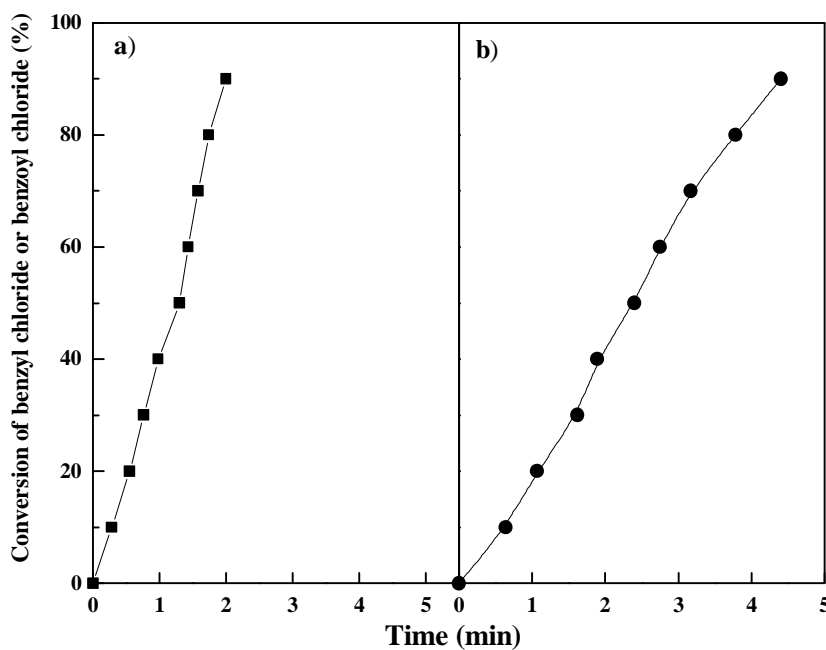
Figure 3.51: Performance of InCl$_3$(1.0 mmol.g^{-1})/Si-MCM-41 (activated at 300 ^{o}C under N$_2$) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions

Figure 3.52: Performance of InCl$_3$(1.0 mmol.g^{-1})/Si-MCM-41 (activated at 300 $^{\circ}$C under N$_2$) in the benzene benzylation (a) and p-xylene benzoylation (b) reactions

3.6 COMPARISON OF DIFFERENT SUPPORTED FeCl$_3$, GaCl$_3$ AND InCl$_3$ (THERMALLY ACTIVATED AT OPTIMUM CONDITIONS) CATALYSTS FOR THE PERFORMANCE IN THE BENZENE BENZYLATION AND P-XYLENE BENZOYLATION REACTIONS

The supported FeCl$_3$, GaCl$_3$ and InCl$_3$ catalysts (with the optimum metal chloride loading of 1.0 mml.g^{-1}) thermally activated at the optimum temperature (300 $^{\circ}$C) in N$_2$ for their catalytic activity (measured in terms of the time required for half the reaction/Turn over frequency determined at half the reaction) in the benzene benzylation and p-xylene benzoylation reactions are compared in Table 3.9.

In general for all the catalysts the reaction induction period for the benzoylation reaction is higher than that for the benzylation reaction. The induction period (t$_o$) for both reactions over all the supported metal chloride catalysts is influenced by the thermal activation temperature and the metal chloride loading in the catalyst. In a more or less similar way as that observed for t$_{1/2}$, the time required for half the corresponding reaction.

The comparison of t$_{1/2}$ or TOF values for the benzene benzylation and p-xylene benzoylation reactions, the catalytic activity of the supported metal chloride catalysts for the two reactions is in the following order:

For the benzene benzylation: FeCl$_3$/H-beta > InCl$_3$/Mont.K-10 ? InCl$_3$/H-beta > GaCl$_3$/Mont.K-10 > or InCl$_3$/Si-MCM-41 > GaCl$_3$/H-beta or FeCl$_3$/Mont.K-10 > FeCl$_3$/Si-MCM-41 > GaCl$_3$/Si-MCM-41

For the p-xylene benzoylation: InCl$_3$/H-beta > GaCl$_3$/H-beta > InCl$_3$/Mont.K-10 > FeCl$_3$/H-beta > InCl$_3$/Si-MCM-41 > GaCl$_3$/Mont.K-10 > GaCl$_3$/Si-MCM-41 > FeCl$_3$/Si-MCM-41 ? FeCl$_3$/Mont,K-10

Table 3.9: Comparison of the different supported FeCl$_3$, GaCl$_3$ and InCl$_3$ catalysts (with the optimum metal chloride loading of 1.0 mml.g^{-1}) thermally activated at 300 $^{\circ}$C in N$_2$ for their catalytic activity in the benzene benzylation and p-xylene benzoylation reactions [t_0 = reaction induction period, $t_{1/2}$ = time required for half the reaction (i.e. 50 % conversion of benzyl chloride or benzoyl chloride, and TOF = turn-over-frequency measured at half the reaction]

Catalyst	Benzene benzylation			P-xylene benzoylation		
	t_0	$t_{1/2}$	TOF	t_0	$t_{1/2}$	TOF
	(min)	(min)	(mmol.g^{-1}.h^{-1})	(min)	(min)	(mol.g^{-1}.h^{-1})
FeCl$_3$/Si-MCM-41	0.1	5.0	1.05	1.0	6.6	0.19
FeCl$_3$/Mont.K-10	0.1	3.2	1.64	0.8	6.7	0.19
FeCl$_3$/H-beta	0.0	0.8	6.54	0.1	2.8	0.45
GaCl$_3$/Si-MCM-41	0.4	5.9	0.89	0.6	6.2	0.21
GaCl$_3$/Mont.K-10	0.1	1.4	3.74	0.2	5.4	0.24
GaCl$_3$/H-beta	0.1	3.2	1.64	0.0	2.3	0.56
InCl$_3$/Si-MCM-41[a]	0.1	3.2	1.64	0.3	3.3	0.39
InCl$_3$/Mont.K-10	0.0	1.1	4.75	0.1	2.4	0.53
InCl$_3$/H-beta	0.1	1.2	4.35	0.1	1.3	0.97

[a]Thermally activated at 400 $^{\circ}$C which is the optimum activation temperature for this catalyst

For a purpose of comparison, the $t_{1/2}$ and/or TOF values for the benzene benzylation and p-xylene benzoylation reactions over the important/promising solid catalysts reported earlier are presented in Table 3.10.

A comparison of the results in Table 3.9 with that in Table 3.10 reveals that the thermally activated supported metal chloride catalysts, particularly the thermally activated FeCl$_3$/H-beta, InCl$_3$/Mont.K-10 or H-beta and GaCl$_3$/H-beta, which show much more activity in both the benzylation and benzoylation reactions than that sowed by the earlier reported catalysts are highly promising catalysts for both the benzylation and benzoylation reactions.

Table 3.10: Performance in benzene benzylation and p-xylene benzoylation of earlier reported important/promising solid catalysts

Catalyst	Time for half reaction, $t_{1/2}$ (min)	TOF (mol.g^{-1}.h^{-1})	Ref.
Benzylation of benzene (at 80 ^{o}C)			
Clayzic (ZnCl$_2$/Mont.K-10, activated at 270 ^{o}C for 5 h in N$_2$)[a]	7.9	0.66	[2]
InCl$_3$/Mont.K-10 (120 ^{o}C for 8 h)	1.3	3.96	[11]
FeCl$_3$/Mont.K-10 (120 ^{o}C for 8 h)	1.2	4.35	[11]
InCl$_3$/Mont.KSF (120 ^{o}C for 8 h)	1.8	2.90	[11]
InCl$_3$/Si-MCM-41 (120 ^{o}C for 8 h)	1.6	3.22	[11]
FeCl$_3$/Si-MCM-41 (120 ^{o}C for 8 h)	1.5	3.48	[11]
FeCl$_3$/Mont.K-10 (80 ^{o}C for 12 h)	1.8	2.90	[7]
FeCl$_3$/silica gel (450 ^{o}C for 4 h)	4.2	1.24	[7]
FeCl$_3$/Kaolin (80 ^{o}C for 12 h)	3.8	1.38	[7]
GaCl$_3$/Mont.K-10 (120 ^{o}C for 8 h)	4.7	1.11	[3]
InCl$_3$/Mont.K-10 (120 ^{o}C for 8 h)	2.0	2.61	[3]
H-FeAlMFI	30.3	0.17	[7]
Fe$_2$O$_3$/H-ZSM-5	2.5	2.07	[7]
Fe$_2$O$_3$/H-beta	3.3	1.58	[7]
Fe$_2$O$_3$/Si-MCM-41	4.4	1.19	[7]
InCl$_3$/Si-MCM-41 (120 ^{o}C for 8 h)	2.9	1.80	[3]
H-FeMFI	6.7	0.78	[7]
InCl$_3$(20%)/H-beta (120 ^{o}C for 8 h)	3.0	1.74	[9]
In$_2$O$_3$(20%)/H-beta	1.1	4.75	[9]
Ga$_2$O$_3$(20%)/H-beta	2.0	2.64	[9]
GaCl$_3$(20%)/H-beta (120 ^{o}C for 8 h)	4.0	1.30	[9]
Benzoylation of p-xylene (110 ^{o}C)			
InCl$_3$(20%)/H-beta (activated at 120 ^{o}C for 8 h in N$_2$)	225	0.006	[9]
In$_2$O$_3$(20%)/H-beta	30.0	0.04	[9]
Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$[b]	120	0.01	[12]
In$_2$O$_3$/Si-MCM-41[b]	6.6	0.19	[12]

[a]In round brackets, the conditions of thermal treatment given to the catalyst are provided.

[b]Reaction temperature = 140 ^{o}C.

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3.7 BENZYLATION AND BENZOYLATION OF OTHER AROMATIC COMPOUNDS OVER THERMALLY ACTIVATED SUPPORTED $FeCl_3$, $GaCl_3$ AND $InCl_3$ CATALYSTS

Results of the benzylation and benzoylation of different aromatic compounds (viz. benzene, toluene, p-xylene, mesitylene, anisole, cumene and/or naphthalene) over the different thermally activated (at optimum conditions) supported $FeCl_3$, $GaCl_3$ and $InCl_3$ catalysts (metal chloride loading = 1.0 mmol.g^{-1}), in the form of the conversion of benzyl or benzoyl chloride as a function of time, are presented in Figures 3.53-3.68. The benzylation and benzoylation activities of the different aromatic compounds, measured in terms of the time required for half the reaction, $t_{1/2}$ and Turn-over-frequency (TOF) determined at half the reaction are given in Tables 3.11-3.13.

The results reveal that the catalysts also show high activity for both the benzylation and benzoylation reactions of the other aromatic compounds. A comparison of the catalytic activity (i.e. $t_{1/2}$ or TOF) in both the benzylation and benzoylation reactions for the different aromatic substrates (with or without containing electron donating groups) indicate that, for all the catalysts, both the reactions does not follow the classical Friedel-Crafts mechanism for the acid catalyzed benzylation or benzoylation reactions. As observed earlier [8-11], because of their low redox potential [($E^o_{(Fe3+/Fe2+)}$ = + 0.77 V) and ($E^o_{(Ga3+/Ga1+)}$ = ($E^o_{(In3+/In1+)}$ = - 0.44 V)], redox properties of the catalysts therefore seems to play an important role in both the reactions over the thermally activated supported $FeCl_3$, $GaCl_3$ and $InCl_3$ catalysts. Also, the aromatic substrates might have been activated by the surface metal chloride, -OMCl$_2$ and/or (-O)$_2$MCl species, as follows:

$$R'—Ph—H \quad \xrightarrow{} \quad R'—Ph—H \quad \text{--------------------------------------}(5)$$
$$M^{3+}—X^{n-} \qquad\qquad\qquad M^{3+}—X^{n-}$$
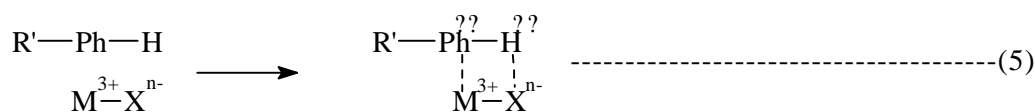
[X = Cl or O, n = 1 or 2, R = substituent group(s)]

A similar redox mechanism described earlier for the benzylation and benzoylation reactions over the supported chlorides or oxides of gallium, indium or iron [5-7,9-11] may also involve in the present cases. The presence of strong protonic acidity in the H-beta zeolite is expected to enhance the catalytic activity of the H-beta supported metal chloride catalysts, particularly for the benzoylation reaction. In the presence of redox and protonic acid, benzoyl chloride is activated as follows:

$$PhCOCl + H^+ \rightleftharpoons RCO^+ + HCl \quad \text{---}(6)$$

$$2PhCOCl + Ga^{3+} \rightleftharpoons 2PhCOCl^+ + Ga^{1+} \quad \text{---}(7)$$

$$PhCOCl^+ \ ? \ ? \ \ PhCO^+ + Cl? \text{--} (8)$$

$$Ga^{1+} + 2Cl? \ ? \ ? \ \ Ga^{3+} + 2Cl^- \text{---} (9)$$

$$R'\text{-}Ph^{-?}\text{----}H^{+?} + RCO^+ \ ? \ ? \ \ R'\text{-}Ph\text{-}CO\text{-}R + H+ \text{---} (10)$$

$$H^+ + Cl^- \ ? \ ? \ \ HCl? \text{------------------------------------} \quad \text{---} (11)$$
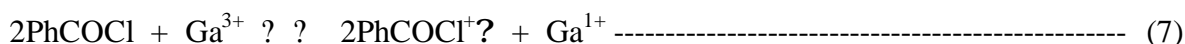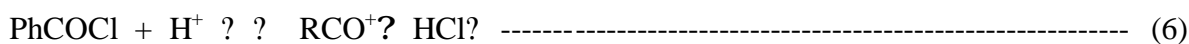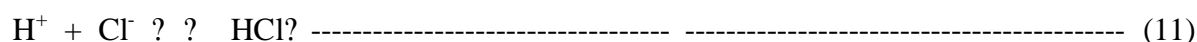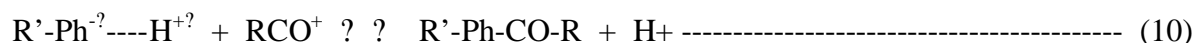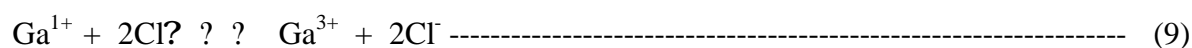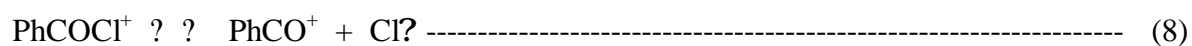
Table 3.11: Results of the benzylation and benzoylation of different aromatic compounds over the different supported FeCl$_3$ catalysts (reaction mixture = 13 ml aromatic substrate + 1 ml benzyl or benzoyl chloride + 0.1 (for benzylation) or 0.4 g (for benzoylation) catalyst, temperature = 110 ^{o}C (except for benzene benzylation and benzoylation reactions), t$_0$ = reaction induction period, t$_{1/2}$ = time required for half the reaction, TOF = Turn-over-frequency measured at 50 % conversion of the benzylating or acylating agent

Aromatic substrate	Benzene benzylation			P-Xylene benzoylation		
	t$_0$ (min)	t$_{1/2}$ (min)	TOF (mmol.g^{-1}.h^{-1})	t$_0$ (min)	t$_{1/2}$ (min)	TOF (mol.g^{-1}.h^{-1})
A] Catalyst: FeCl$_3$/Si-MCM-41 (thermally activated at 300 ^{o}C in N$_2$)						
Benzene	0.1	5.0	1.04	4.3	17.1	0.08
Toluene	1.6	2.7	1.93	6.1	36.2	0.04
p-Xylene	1.1	2.5	2.09	1.0	6.6	0.19
Mesitylene	0.7	2.3	2.27	4.2	5.1	0.25
Anisole	3.1	5.1	1.02	0.4	2.4	0.53
B] Catalyst: FeCl$_3$/Mont.K-10 (thermally activated at 300 ^{o}C in N$_2$)						
Benzene	0.1	3.2	1.63	7.3	28.1	0.05
Toluene	2.3	3.1	1.68	3.1	9.3	0.14
p-Xylene	2.0	2.4	2.18	0.8	6.7	0.19
Mesitylene	1.8	2.2	2.35	0.5	3.9	0.33
Anisole	2.1	2.5	2.09	0.5	3.1	0.41
C] Catalyst: FeCl$_3$/H-beta (thermally activated at 300 ^{o}C in N$_2$)						
Benzene	0.0	0.8	6.53	4.4	20.8	0.06
Toluene	3.0	5.5	0.95	3.6	14.5	0.09
p-Xylene	2.3	3.6	1.45	0.1	2.8	0.45
Mesitylene	1.1	2.3	2.27	1.1	3.3	0.39
Anisole	0.2	1.5	3.48	-	-	-
Cumene	-	-		0.2	1.6	0.79

Table 3.12: Results of the benzylation and benzoylation of different aromatic compounds over the different supported $GaCl_3$ catalysts (reaction mixture = 13 ml aromatic substrate + 1 ml benzyl or benzoyl chloride + 0.1 (for benzylation) or 0.4 g (for benzoylation) catalyst, temperature = 110 ^{o}C (except for benzene benzylation and benzoylation reactions), t_0 = reaction induction period, $t_{1/2}$ = time required for half the reaction, TOF = Turn-over-frequency measured at 50 % conversion of the benzylating or acylating agent

Aromatic substrate	Benzene benzylation			P-Xylene benzoylation		
	t_0 (min)	$t_{1/2}$ (min)	TOF (mmol.g^{-1}.h^{-1})	t_0 (min)	$t_{1/2}$ (min)	TOF (mol.g^{-1}.h^{-1})
A] Catalyst: GaCl$_3$/Si-MCM-41 (thermally activated at 300 ^{o}C in N$_2$)						
Benzene	0.4	5.9	0.89	10.2	48.8	0.03
Toluene	1.8	3.2	1.64	1.5	15.5	0.08
p-Xylene	1.2	1.8	2.90	0.6	6.2	0.21
Mesitylene	0.3	1.1	4.75	0.0	2.0	0.64
Anisole	1.6	3.1	1.68	0.0	3.2	0.40
B] Catalyst: GaCl$_3$/H-beta (thermally activated at 300 ^{o}C in N$_2$)						
Benzene	0.1	3.2	1.64	4.3	24.5	0.05
Toluene	1.6	2.4	2.18	3.2	20.3	0.06
p-Xylene	1.2	1.6	3.22	0.0	2.3	0.56
Mesitylene	0.3	1.5	3.48	0.4	3.2	0.40
Anisole	1.8	2.5	2.07	1.4	3.4	0.37

Table 3.13: Results of the benzylation and benzoylation of different aromatic compounds over the different supported $InCl_3$ catalysts (reaction mixture = 13 ml aromatic substrate + 1 ml benzyl or benzoyl chloride + 0.1 (for benzylation) or 0.4 g (for benzoylation) catalyst, temperature = 110 ^{o}C (except for benzene benzylation and benzoylation reactions), t_0 = reaction induction period, $t_{1/2}$ = time required for half the reaction, TOF = Turn-over-frequency measured at 50 % conversion of the benzylating or acylating agent

Aromatic substrate	Benzene benzylation			p-Xylene benzoylation		
	t_0 (min)	$t_{1/2}$ (min)	TOF (mmol.g^{-1}.h^{-1})	t_0 (min)	$t_{1/2}$ (min)	TOF (mol.g^{-1}.h^{-1})
A] Catalyst: $InCl_3$/Si-MCM-41 (thermally activated at 400 ^{o}C in N_2)						
Benzene	0.1	3.2	1.64	5.5	20.1	0.06
Toluene	5.1	6.4	0.81	3.2	13.0	1.00
p-Xylene	10.0	11.1	0.47	0.3	3.3	0.39
Mesitylene	-	-	-	0.3	1.0	1.27
Anisole	0.9	1.9	2.72	-	-	-
Cumene	3.3	4.2	1.24	1.4	2.6	0.49
Naphthalene	-	-	-	4.5	17.2	0.07
B] Catalyst: $InCl_3$/Mont.K-10 (thermally activated at 300 ^{o}C in N_2)						
Benzene	0.0	1.1	4.75	12.5	43.3	0.03
Toluene	8.5	12.4	0.42	6.1	21.4	0.06
p-Xylene	2.3	4.8	1.09	0.1	2.4	0.53
Mesitylene	-	-	-	1.6	2.8	0.45
Anisole	0.4	2.1	2.49	-	-	-
Cumene	0.6	3.4	1.53	0.8	2.0	0.64
Naphthalene	-	-	-	8.0	31.8	0.04
C] Catalyst: $InCl_3$/H-beta (thermally activated at 300 ^{o}C in N_2)						
Benzene	0.1	1.2	4.35	8.6	33.1	0.04
Toluene	1.7	3.1	1.67	3.5	13.4	0.10
p-Xylene	1.4	2.2	2.35	0.1	1.3	0.97
Mesitylene	1.5	2.3	2.27	1.9	3.6	0.35
Anisole	0.2	1.8	2.90	0.1	1.6	0.79
Naphthalene	-	-	-	4.6	25.6	0.05

[a] Reaction mixture: 2.0 g Naphthalene + 13 ml EDC + 1.0 ml benzoyl chloride + 0.4 g catalyst
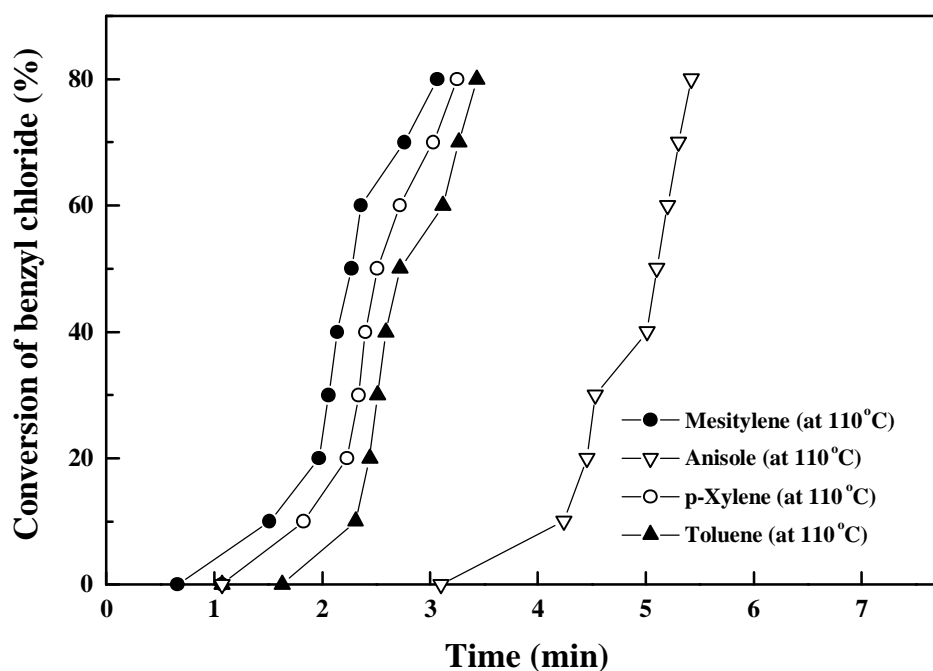
Figure 3.53: Benzylation of other aromatic compounds over FeCl$_3$/Si-MCM-41, activated at 300 $^{\circ}$C under N$_2$ atmosphere
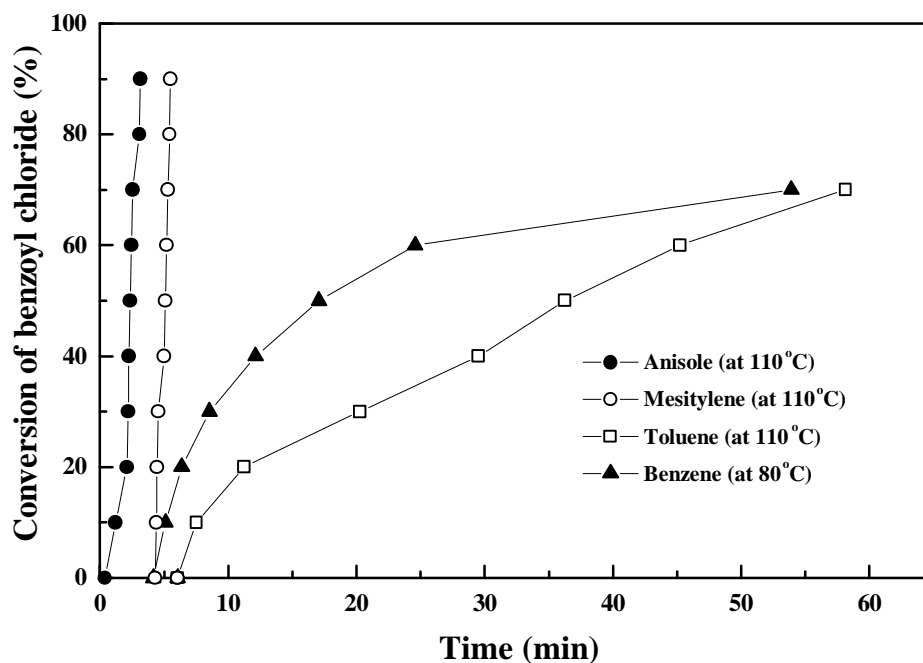
Figure 3.54: Benzoylation of other aromatic compounds over FeCl$_3$/Si-MCM-41, activated at 300 $^{\circ}$C under N$_2$ atmosphere
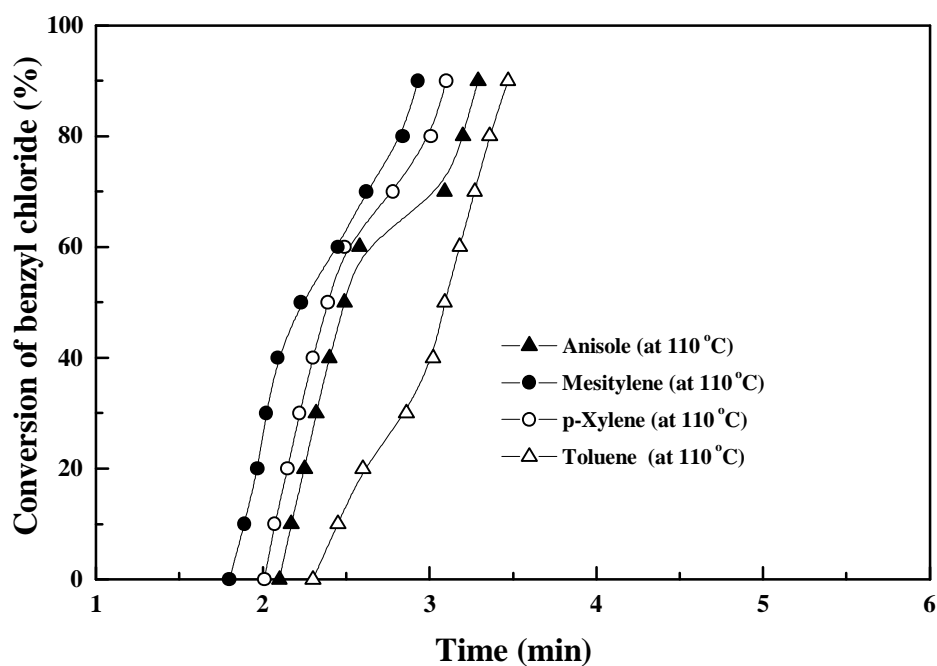
Figure 3.55: Benzylation of other aromatic compounds over FeCl$_3$/Mont.K-10, activated at 300 ^{o}C under N$_2$ atmosphere
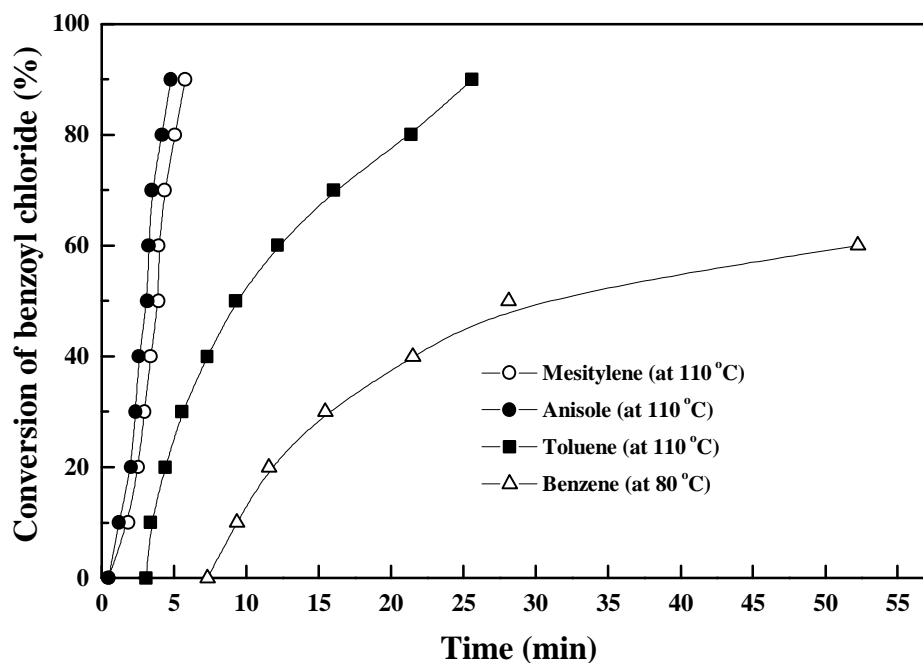
Figure 3.56: Benzoylation of other aromatic compounds over FeCl$_3$/Mont.K-10, activated at 300 ^{o}C under N$_2$ atmosphere
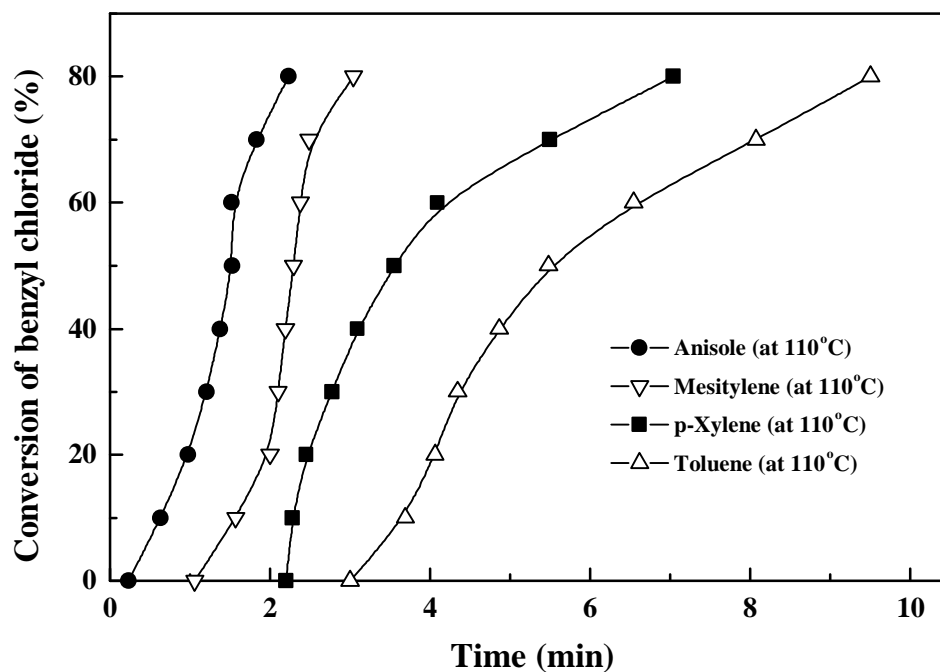
Figure 3.57: Benzylation of other aromatic compounds over FeCl$_3$/H-beta, activated at 300 $^{\circ}$C under N$_2$ atmosphere
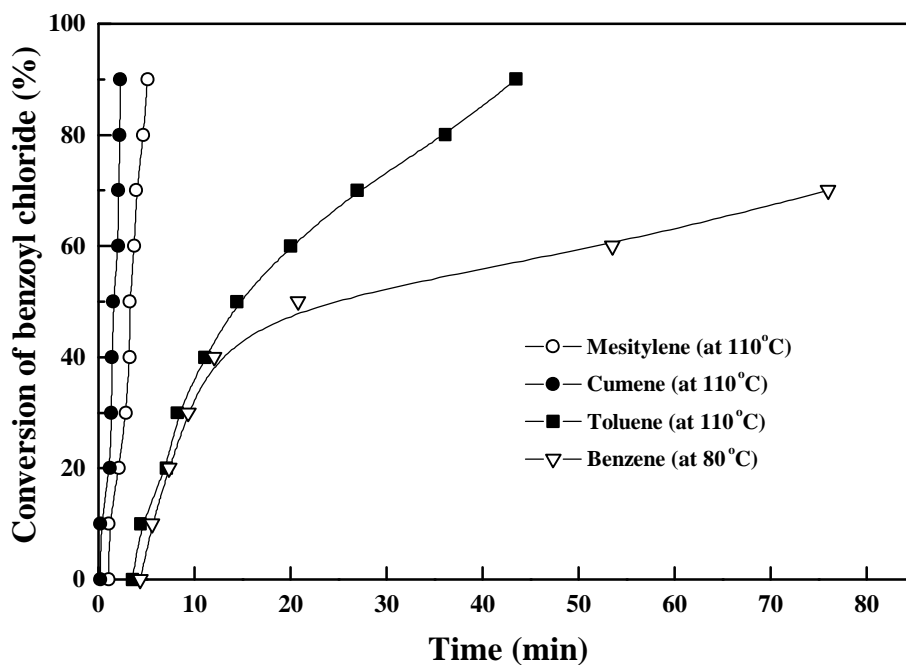
Figure 3.58: Benzoylation of other aromatic compounds over FeCl$_3$/H-beta, activated at 300 $^{\circ}$C under N$_2$ atmosphere
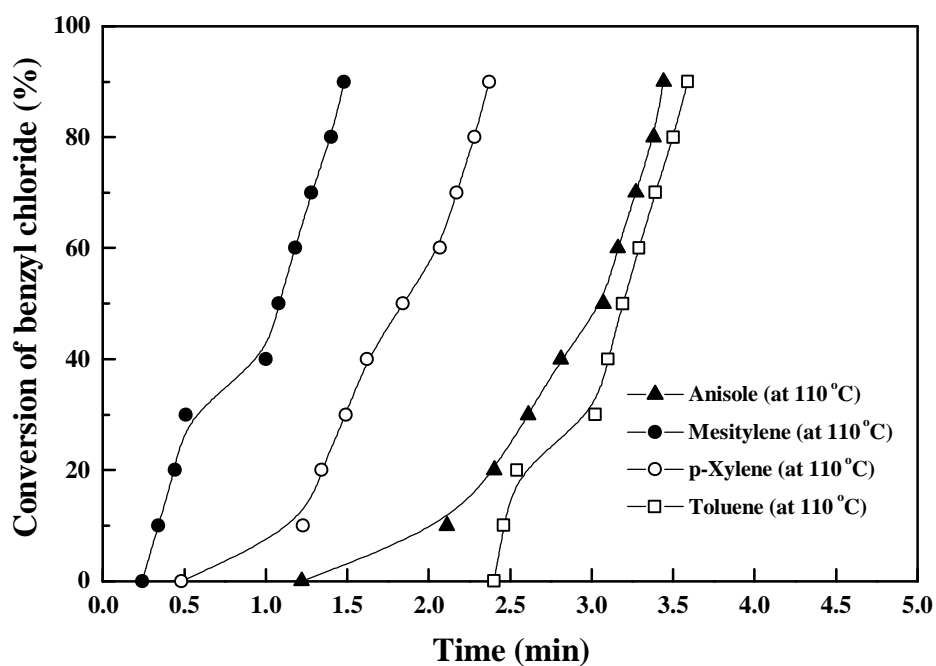
Figure 3.59: Benzylation of other aromatic compounds over GaCl$_3$/Si-MCM-41, activated at 300 $^{\circ}$C under N$_2$ atmosphere
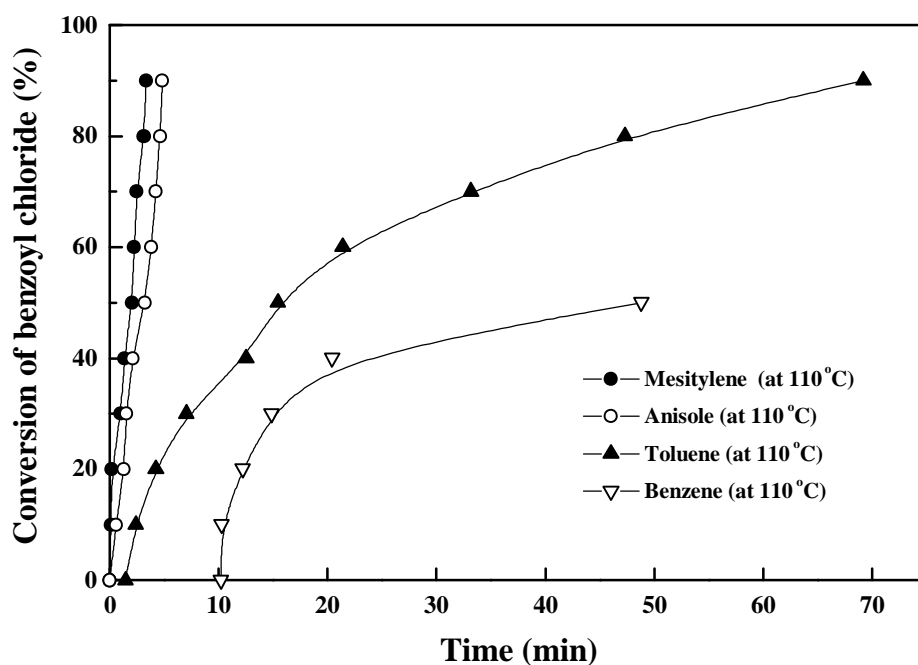
Figure 3.60: Benzoylation of other aromatic compounds over GaCl$_3$/Si-MCM-41, activated at 300 $^{\circ}$C under N$_2$ atmosphere
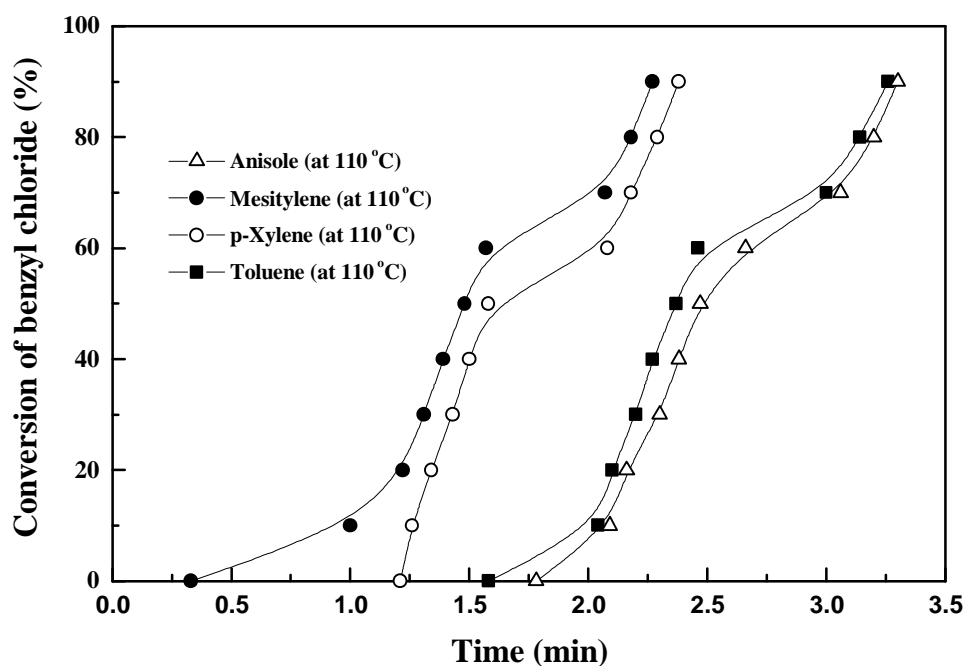
Figure 3.61: Benzylation of other aromatic compounds over $GaCl_3$/H-beta, activated at 300 $^\circ$C under N_2 atmosphere
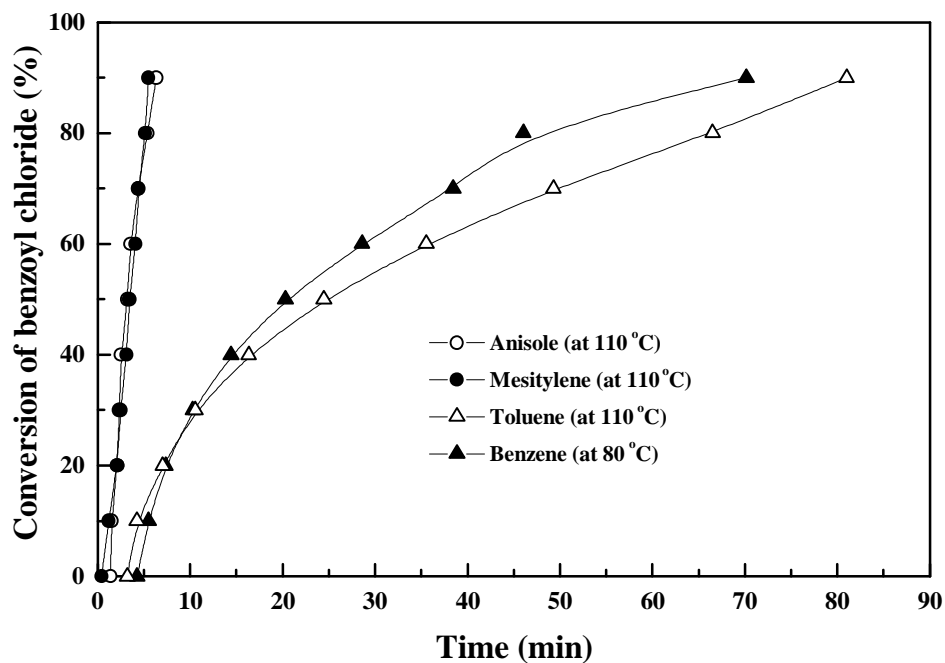
Figure 3.62: Benzoylation of other aromatic compounds over $GaCl_3$/H-beta, activated at 300 $^\circ$C under N_2 atmosphere
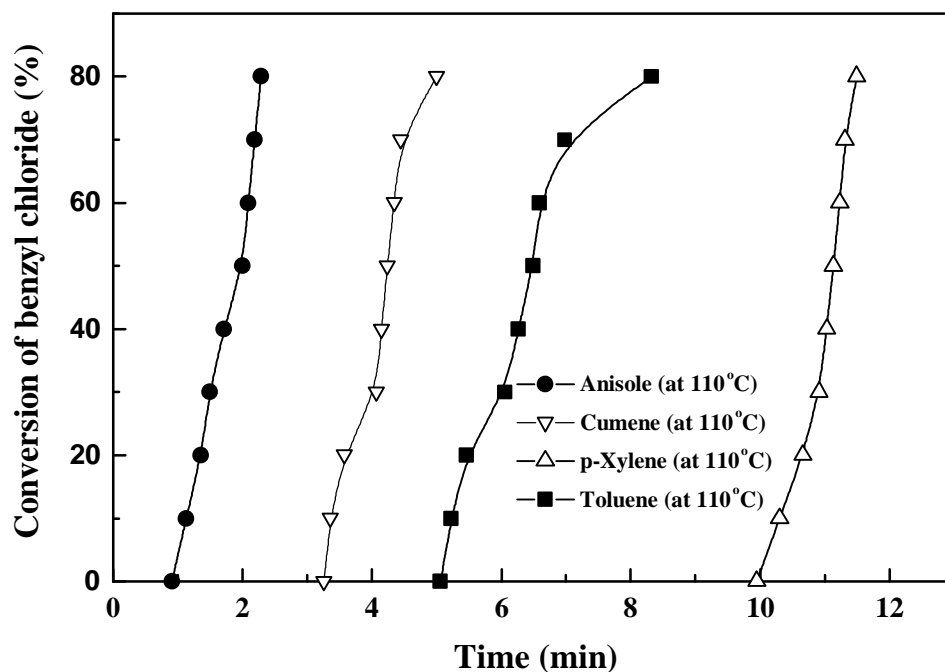
Figure 3.63: Benzylation of other aromatic compounds over InCl$_3$/Si-MCM-41, activated at 400 ^{o}C under N$_2$ atmosphere
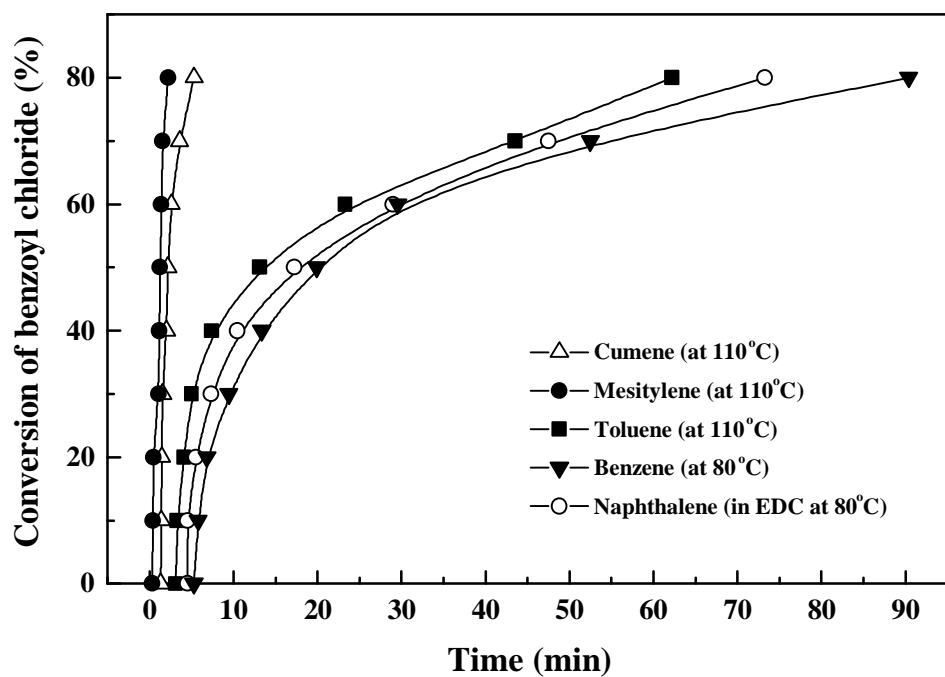
Figure 3.64: Benzoylation of other aromatic compounds over InCl$_3$/Si-MCM-41, activated at 400 ^{o}C under N$_2$ atmosphere
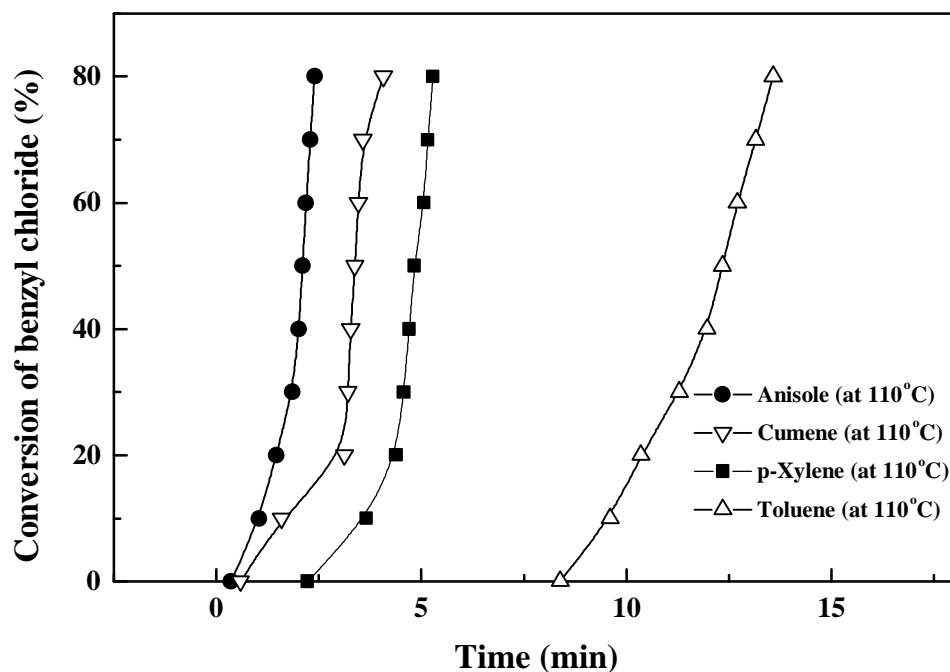
Figure 3.65: Benzylation of other aromatic compounds over InCl$_3$/Mont.K-10, activated at 300 ^{o}C under N$_2$ atmosphere
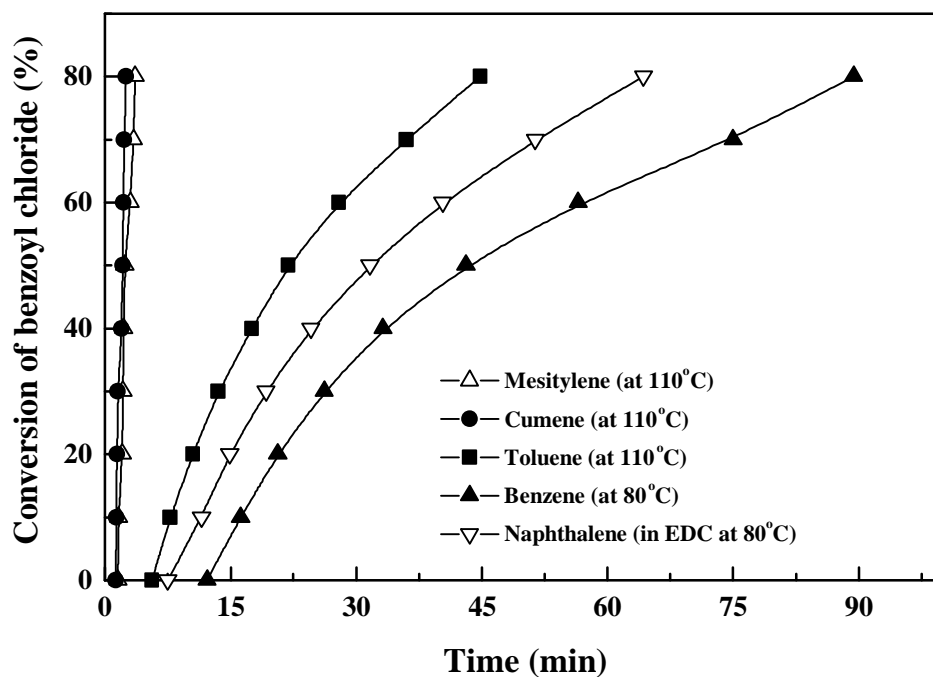
Figure 3.66: Benzoylation of other aromatic compounds over InCl$_3$/Mont.K-10, activated at 300 ^{o}C under N$_2$ atmosphere
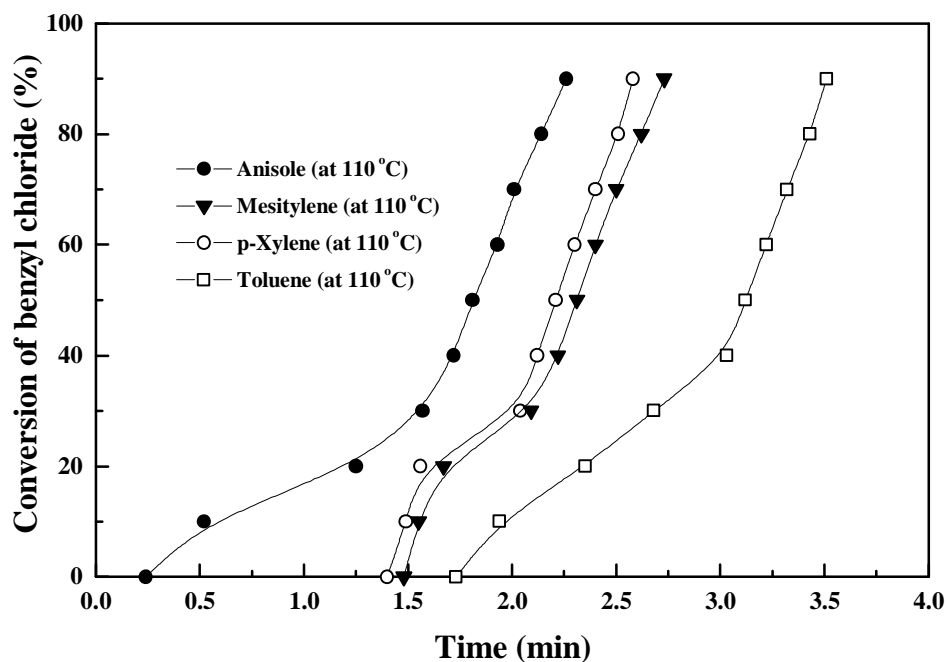
Figure 3.67: Benzylation of other aromatic compounds over InCl$_3$/H-beta, activated at 300 $^\circ$C under N$_2$ atmosphere
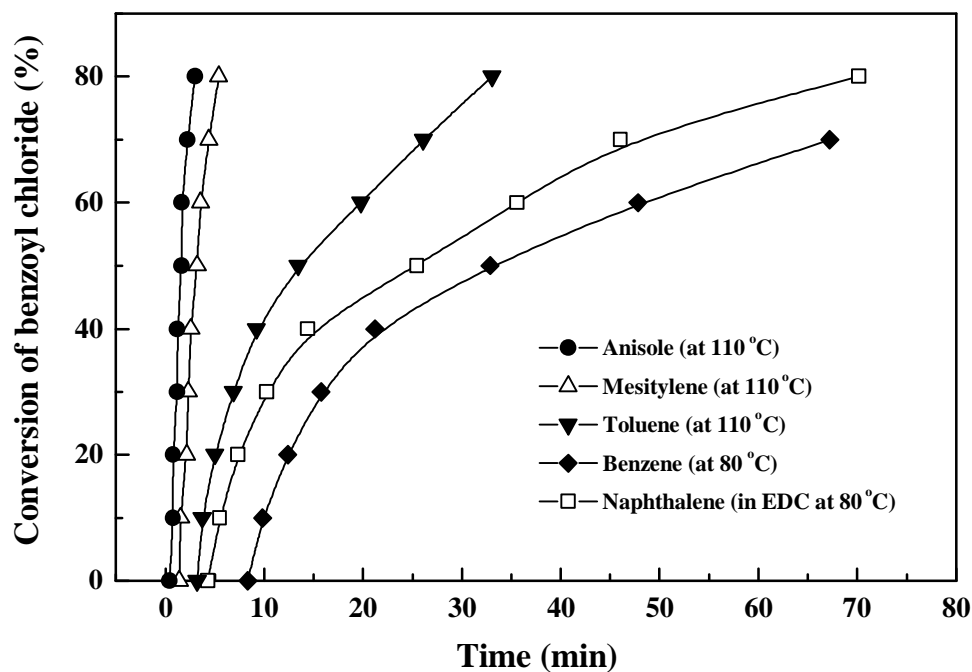
Figure 3.68: Benzoylation of other aromatic compounds over InCl$_3$/H-beta, activated at 300 $^\circ$C under N$_2$ atmosphere

3.8   CONCLUSIONS

From the above exhaustive/thorough investigation, following important conclusions have been drawn for the thermal activation under different conditions and catalytic activity in both the benzylation and benzoylation reactions of the thermally activated Si-MCM-41, mont,K-10 and H-beta zeolite supported $FeCl_3$, $GaCl_3$ and $InCl_3$ catalysts (with the metal chloride loading of 0.5, 1.0 and 2.0 $mmol.g^{-1}$).

1. For all the supported metal chloride catalysts, an appreciable amount of HCl is evolved during their thermal activation, depending upon the metal chloride loading and/or the thermal activation temperature and also upon the gas atmosphere used in the thermal activation, due to the solid-solid reaction between the supported metal chloride and surface hydroxyls of the catalyst support, catalytically active new surface species, such as $-O-MCl_2$ and/or $(-O)_2MCl$. These surface species are chemically bound to the support through $-O-$ linkage and are responsible for the high catalytic activity of the thermally activated supported metal chloride catalysts.

2. All the supported metal chloride catalysts show high activity in both the benzene benzylation and p-xylene benzoylation reactions and also in the benzylation and benzoylation of other aromatic compounds.

3. The thermally activated supported metal chloride catalysts showed their best performance at their optimum metal chloride loading of about 1.0 $mmol.g^{-1}$.

4. Among the thermally activated supported metal chloride catalysts $FeCl_3$/H-beta, $InCl_3$/Mont.K-10 or H-beta and $GaCl_3$/H-beta show relatively better performance in both the benzylation and benzoylation reaction. These catalysts are much more active in the benzylation and benzoylation reactions than the earlier reported highly promising catalysts, having redox and acidic properties, such as clayzic and supported oxides and chlorides of iron, gallium and indium and Ga or Fe containing zeolites.

5. The benzylation and benzoylation reactions over the thermally activated supported metal chloride catalysts do not follow the classical Friedel-Crafts mechanism. However, both the redox and acid properties of the catalysts are expected to play role in both the reactions and also the aromatic substrate seems to be activated on the catalyst.

6. For their performance in the benzene benzylation and p-xylene benzoylation reactions, the supported metal chloride catalysts (with the optimum metal loading of

1.0 mmol.g^{-1}) thermally activated at the optimum condition have the following order:

For the benzene benzylation: FeCl$_3$/H-beta > InCl$_3$/Mont.K-10 ? InCl$_3$/H-beta > GaCl$_3$/Mont.K-10 > or InCl$_3$/Si-MCM-41 > GaCl$_3$/H-beta or FeCl$_3$/Mont.K-10 > FeCl$_3$/Si-MCM-41 > GaCl$_3$/Si-MCM-41

For p-xylene benzoylation: InCl$_3$/H-beta > GaCl$_3$/H-beta > InCl$_3$/Mont.K-10 > FeCl$_3$/H-beta > InCl$_3$/Si-MCM-41 > GaCl$_3$/Mont.K-10 > GaCl$_3$/Si-MCM-41 > FeCl$_3$/Si-MCM-41 ? FeCl$_3$/Mont,K-10

3.9   REFERENCES

[1]   V. R. Choudhary, S. K. Jana and B. P. Kiran, Catal. Lett., 59 (1999) 217.

[2]   V. R. Choudhary and K. Mantri, Catal. Lett., 81 (2002) 163.

[3]   V. R. Choudhary, S. K. Jana and B. P. Kiran, Catal. Lett., 64 (2000) 223.

[4]   V. R. Choudhary, S. K. Jana and M. K. Chaudhari, J. Mol. Catal., A, 170 (2001) 251.

[5]   V. R. Choudhary, S. K. Jana and N. S. Patil, Catal. Lett., 76 (2001) 235.

[6]   V. R. Choudhary, S. K. Jana and N. S. Patil, Tetrahedron Lett., 43 (2002) 1105.

[7]   V. R. Choudhary, S. K. Jana and A. S. Mamman, Micropor. Mesopor. Mater., 56 (2002) 65.

[8]   V. R. Choudhary, S. K. Jana and B. P. Kiran, J. Catal., 192 (2000) 257.

[9]   V. R. Choudhary, S. K. Jana, N. S. Patil and S. K. Bhargava, Micropor. Mesopor. Mater., 57 (2003) 21.

[10]   V. R. Choudhary and S. K. Jana, J. Mol. Catal., A, 184 (2002) 247.

[11]   V. R. Choudhary and S. K. Jana, J. Mol. Catal., A, 180 (2002) 267.

[12]   N. Mizuno and M. Misono, Chem. Rev., 98 (1998) 199.

CHAPTER-4
NOVEL TRANSITION METAL CONTAINING LAYERED DOUBLE HYDROXIDES AND/OR MIXED HYDROXIDES LIKE SOLID CATALYSTS FOR FRIEDEL?CRAFTS REACTIONS

CHAPTER?4

NOVEL TRANSITION METAL CONTAINING LAYERED DOUBLE HYDROXIDES AND/OR MIXED HYDROXIDES LIKE SOLID CATALYSTS FOR FRIEDEL?CRAFTS REACTIONS

4.1   INTRODUCTION AND OBJECTIVE OF PRESENT WORK

Liquid phase Friedel-Crafts type benzylation of aromatic compounds, using homogeneous catalysts [1] and highly acidic solid catalysts (e.g. heteropolyacids [2], sulphated ZrO_2 or Fe_2O_3 [3], Nafion-H [2] and Fe- and Ga-substituted H-ZSM-5 [4] for benzylation of benzene, HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene [5]), has been reported in the literature. However, the reports on the use of basic catalysts for the benzylation reactions are scarce [6]. Recently, Choudhary et al [7] have observed high activity of supported basic In_2O_3 in the benzylation reactions. Hydrotalcite anionic clays are known to be highly basic solids [8]. Very recently, Choudhary et al [9,10]] have found that Ga-Mg-hydrotalcite anionic clay, after its first use in the reaction or HCl gas pretreatment, shows very high activity in the benzylation of toluene and benzene, even in the presence of moisture in the reaction mixture.

The present study was undertaken with the objective of investigating the performance of In-Mg-hydrotalcite (In-Mg-HT) and Fe-Mg-hydrotalcite (Fe-Mg-HT) catalysts in the Friedel-Crafts type benzylation of benzene and substituted benzene by benzyl chloride with or without HCl gas pretreatment to the catalysts. Procedures for the HCl pretreatment of the hydrotalcite catalysts have been described earlier (Chapter 2). Influence of the catalyst calcination temperature and HCl pretreatment conditions on the catalytic performance and reusability of the hydrotalcite catalysts in the benzylation reaction have also been thoroughly investigated.

4.2   FRIEDEL-CRAFTS TYPE BENZYLATION OVER In-Mg-HYDROTALCITE

4.2.1   Characterization of In-Mg-Hydrotalcite

The hydrotalcite structure of the In-Mg-HT anionic clay material, synthesis of which is described earlier (Chapter 2), was confirmed by its X-ray analysis (Figure 4.1); the XRD spectra of the material correspond to that of hydrotalcite [8]. In-Mg-HT-80 and In-Mg-HT-800 are In-Mg-HT heated at 80 ºC and 800 ºC, respectively.

The hydrotalcite and its solid products of calcination (in air at 800 ℃) have been characterized for their surface area and basicity (in terms of the pH of catalyst-water slurry) and crystalline phases (Table 4.1). After the HCl pretreatment and/or use in the reaction of the hydrotalcite catalysts,

- The color and crystalline phases of the hydrotalcite catalyst are changed.
- Its surface area and basicity are reduced.

All the above reveal that the catalyst undergoes an appreciable change in its properties by the HCl pretreatment and a structural collapse after its use in the reaction. The catalyst in its most active form seems to consist of the chlorides and oxides of indium on the catalyst surface.

Table 4.1: Physico-chemical properties of the fresh, calcined, HCl pretreated and used In-Mg-hydrotalcite (Mg/In = 3) catalysts.

Catalyst	Color	Surface area $m^2.g^{-1}$	PH of catalyst[a]	XRD phase(s)
Fresh In-Mg-HT-80	White	106	9.45	HT
Fresh In-Mg-HT-800	Yellowish	71	10.2	In_2O_3, $MgIn_2O_4$ and MgO
In-Mg-HT-800 pretreated by HCl at 80 ℃ for 0.1 h	Off-white	17.6	8.75	$MgCl_2$, $InCl_3$, In_2O_3, MgO and $MgIn_2O_4$
In-Mg-HT-800 pretreated by HCl at 80 ℃ for 1.0 h	Off-white	1.8	7.8	$MgCl_2$, $InCl_3$, In_2O_3, MgO and $MgIn_2O_4$
Used In-Mg-HT-80[b]	Off-white	35.6	7.68	$MgCl_2$, $InCl_3$, In_2O_3 and MgO

[a] 0.15 g catalyst in 10 ml distilled water, [b] the catalyst after its use in the benzylation of benzene.

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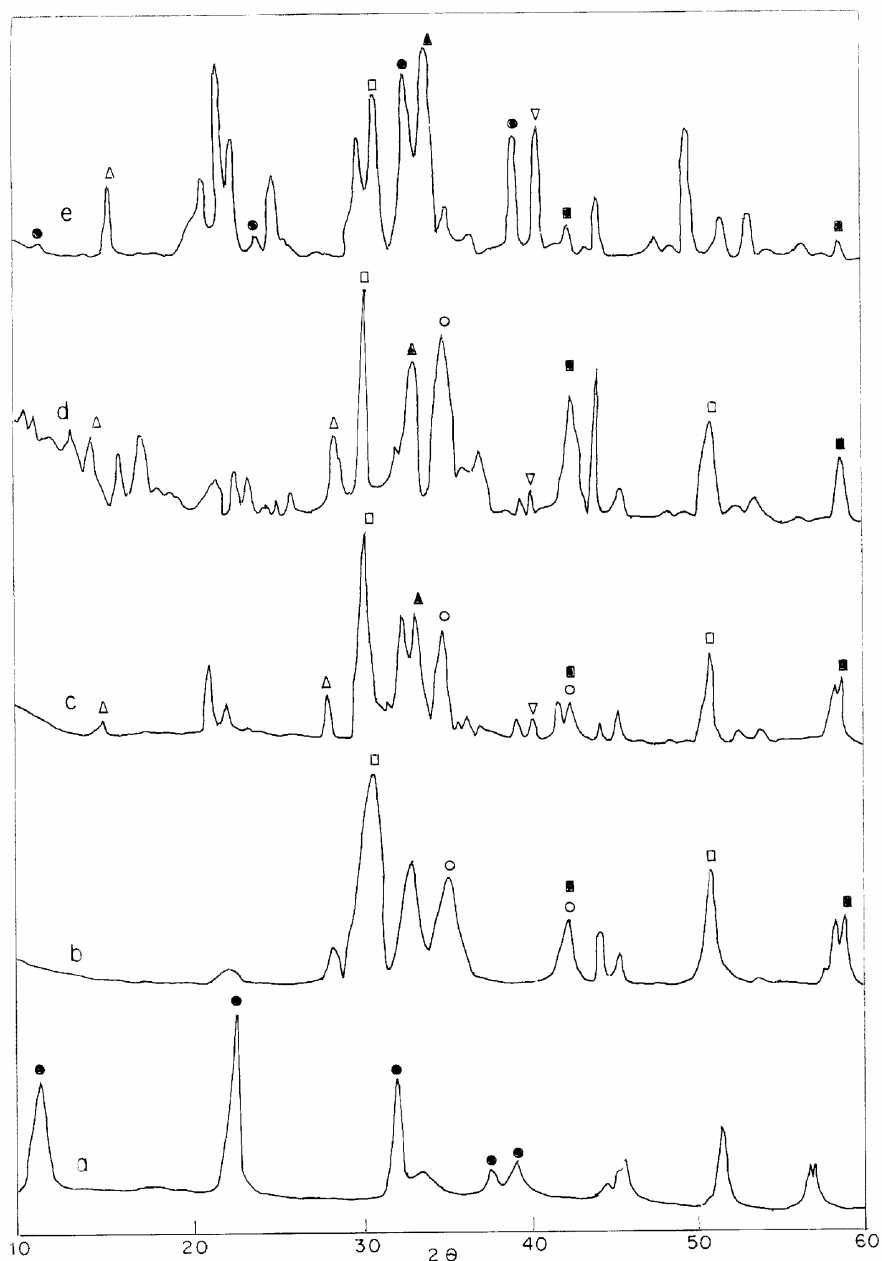
Figure 4.1: XRD spectra of (a) Fresh In-Mg-HT-80, (b) Fresh In-Mg-HT-800, (c) In-Mg-HT-800 pretreated by HCl at 80 °C for 0.1 h, (d) In-Mg-HT-800 pretreated by HCl at 80 °C for 1.0 h and (e) Used In-Mg-HT-80. [Crystalline phases: Pure HT ( ), $MgIn_2O_4$ spinel (o), MgO ($\clubsuit$), In_2O_3 (?), $MgCl_2$ (?) and $InCl_3$ (?)].

The In-Mg-hydrotalcite was also characterized by its thermal gravimetric (TG) analysis and differential thermal gravimetric (DTG) and differential thermal analysis (DTA) from 25° to 1000 °C; the TG, DTG and DTA curves are shown in Figure 4.2. The thermal decomposition of the hydrotalcite occurs in four steps: 1) 9.7% wt. loss from 25° to 192 °C, 2)

3.2% wt. loss from 192º to 282 ºC, 3) 12.5% wt. loss from 282º to 405 ºC, and 4) 3.6% wt. loss from 405º to 1000 ºC. The peak maximum temperatures for the observed DTG/DTA peaks are 178º, 271º and 370 ºC. The DTA peaks indicate that the decomposition in all the steps is endothermic.
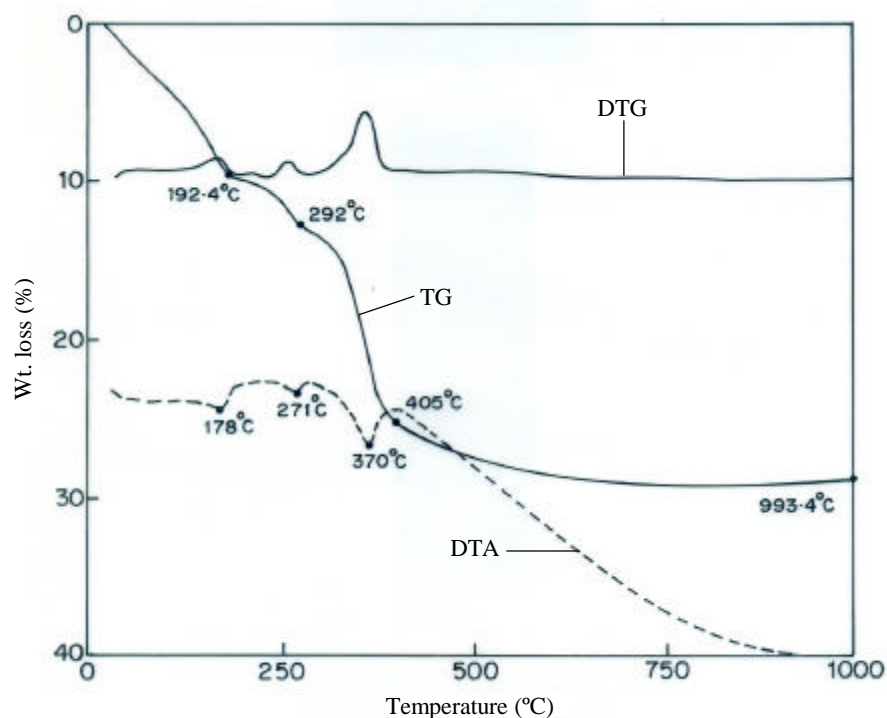
Figure 4.2: Thermal gravimetric (TG) analysis and differential thermal gravimetric (DTG) and differential thermal analysis (DTA) from 25º to 1000 ºC for In-Mg-HT.

The wt. loss in the first step is expected due to desorption of adsorbed water, whereas that in the second step may be due to the removal of the water of hydration from the hydrotalcite. However, the wt. loss in the third step is expected because of the dehydroxylation and decarbonation of the hydrotalcite with the destruction of its structure. In the fourth step, a small weight loss is expected to result from the decomposition of metal carbonate, particularly $MgCO_3$ formed during the third step of the decomposition.

4.2.2 Benzylation over In-Mg-HT-80

Results of the benzylation of benzene and substituted benzenes by benzyl chloride over the fresh and used (in respective reactions at 80º or 110 ºC) In-Mg-HT-80 catalysts are presented in Figures 4.3 and Figure 4.4, respectively. The results lead to the following important observations:

- In case of the benzylation reaction over the fresh catalyst (Figure 4.3), the reaction induction period for the different aromatic substrates is different and is found to depend strongly on the reactivity of the aromatic substrates with benzyl chloride on the catalyst.

- The induction period for the benzylation of different aromatic compound is as follows: mesitylene (9.1 min) < toluene (9.4 min) < p-xylene (46.0 min) < anisole (48.53 min) < naphthalene (52.15 min) < benzene (67.0 min).

- Interestingly, the hydrotalcite after its use in the benzylation reaction showed very high activity (Figure 4.4) for the benzylation reactions.

- The induction period for the benzylation of all the aromatic substrate is reduced drastically (Figure 4.3 and 4.4).
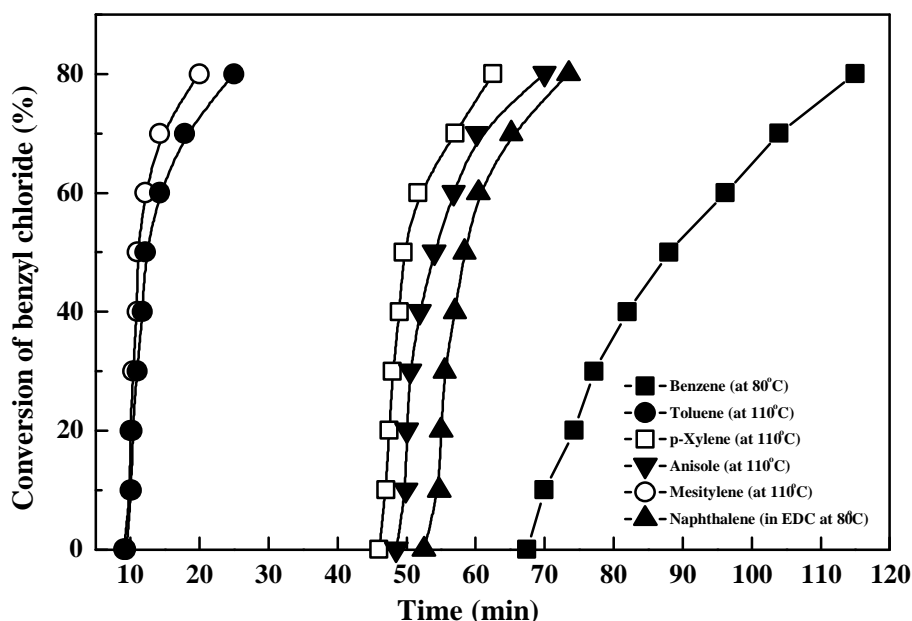
Figure 4.3: Activity of fresh In-Mg-HT-80 catalyst in the benzylation of benzene and substituted benzenes (at 80° or 110 °C) by benzyl chloride.

- The benzylation activity of the used catalyst for the different aromatic substrates (measured in terms of time required for half the reaction, $t_{1/2}$) is found to be in the following order: toluene ($t_{1/2} = 1.2$ min) < p-xylene (8.5 min) < anisole (9.5 min) < naphthalene (12.3 min) < benzene (32.4 min).

The XRD of the used catalyst (Figure 4.1e) showed the presence of crystalline phases (viz. $MgCl_2$, $InCl_3$, In_2O_3 and MgO) different from that observed for the fresh In-Mg-HT-80. This clearly shows a phase transformation/structural breakdown of the

hydrotalcite during its use in the reaction, mainly by the HCl produced in the reaction. The basicity of the hydrotalcite is also decreased after its use in the reaction (Table 4.1). The observed high benzylation activity of the hydrotalcite after the induction period is therefore attributed to the formation of catalytically active species (viz. $InCl_3$ and In_2O_3 as detected by the XRD), which are strongly adsorbed on the catalyst, during the induction period by the interactions of benzyl chloride and HCl (formed in the initial reaction) with the basic hydrotalcite. The HCl formed in the benzylation reaction is responsible for the structural breakdown of the hydrotalcite.
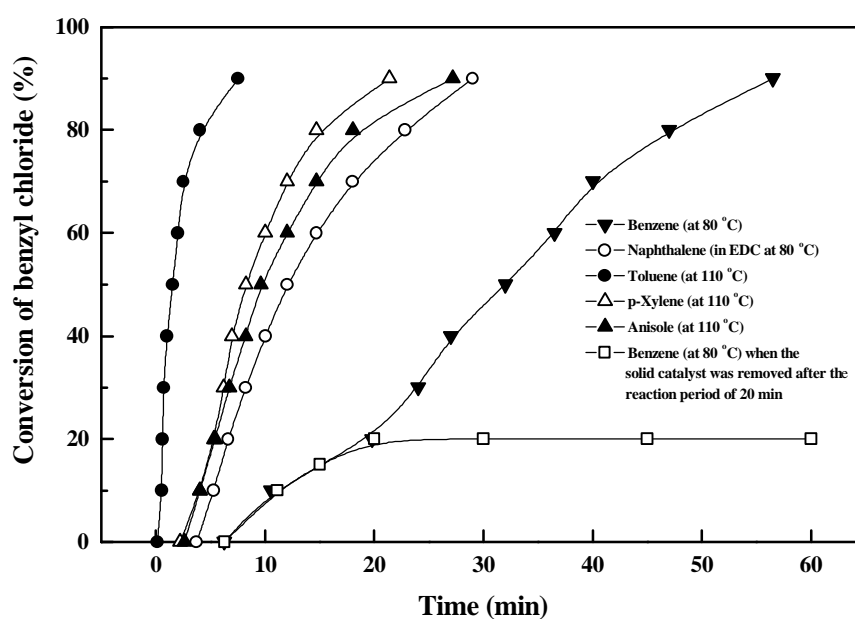
Figure 4.4: Activity of used In-Mg-HT-80 catalyst in the benzylation of benzene and substituted benzenes (at 80° or 110 °C) by benzyl chloride.

From the results in Fig. 4.4, it is interesting to note that, when the catalyst was removed after carrying out the benzene benzylation reaction for 20 min, by filtration, there was almost no further conversion of benzyl chloride. This indicates that the benzylation reaction is mainly catalyzed by the solid catalyst; the leached out metal chloride species; if any, from the catalyst play a little or no role in the catalytic reaction. Also the rate of benzylation showed no expected (by the Friedel-Crafts mechanism) dependence on the presence of different electron donating group(s) in the aromatic substrate; the rate of toluene benzylation is much higher than that of the anisole or p-Xylene benzylation. Thus, the

classical Friedel-Crafts mechanism does not simply hold good in the present catalytic system. This is consistent with that observed earlier in case of the benzylation of substituted benzenes over supported In_2O_3, Ga_2O_3, $GaCl_3$ and $InCl_3$ catalysts [7,12-14].

4.2.3 Effect of Calcination Temperature of In-Mg-HT

Results showing the influence of calcination temperature of the In-Mg-HT catalyst on its performance in the benzylation of benzene at 80 ℃ are presented in Figure 4.5. The increase in the calcination temperature from 80° to 200 ℃ causes a large decrease in the induction period, mostly because of the desorption of adsorbed water from the hydrotalcite [7].
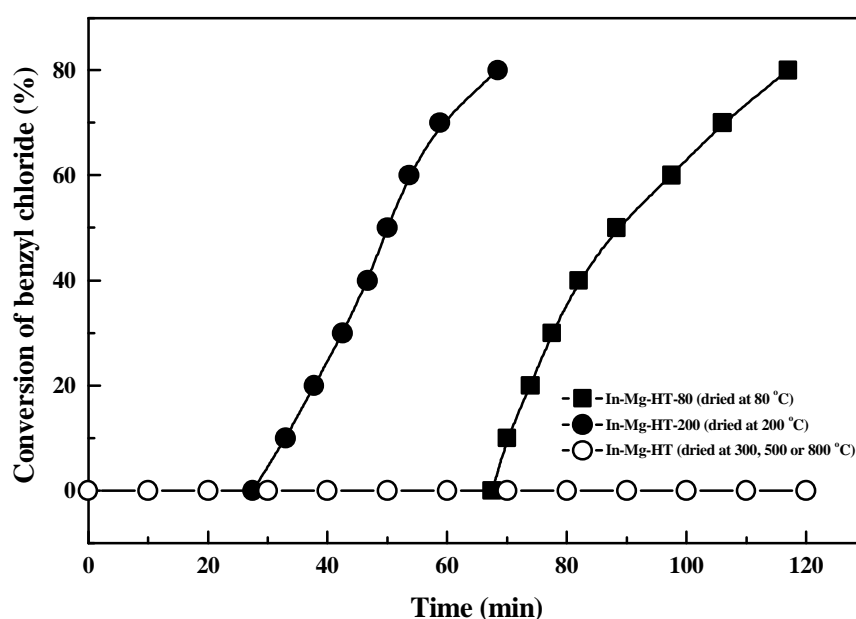
Figure 4.5:   Influence of calcination temperature (T_c) of In-Mg-HT on its activity in the benzylation of benzene (at 80 ℃) by benzyl chloride.

However, a further increase in the calcination temperature upto 300 ℃ or above (up to 800 ℃) results in a drastic increase in the reaction induction period; the calcined hydrotalcite showed no benzene benzylation activity for the reaction period of 2 h. This is expected because of the dehydration and/or structural breakdown of the hydrotalcite at ? 300 ℃. After its calcination at 800 ℃, the hydrotalcite is transformed into a mixture of MgO and $MgIn_2O_4$ spinel with smaller amounts of In_2O_3 (Fig. 4.1b and Table 4.1).

4.2.4 Effect of HCl Pretreatment to In-Mg-HT-800

Results showing the influence of HCl pretreatment to the In-Mg-HT-800 (at different temperatures and periods) on the benzylation of benzene at 80 ℃ are presented in Figure 4.6. The results can be summarized as follows:

- The fresh In-Mg-HT-800 catalyst showed no benzylation activity for the reaction period of 3 h. However, after the HCl gas pretreatment, the reaction proceeds at a high rate.
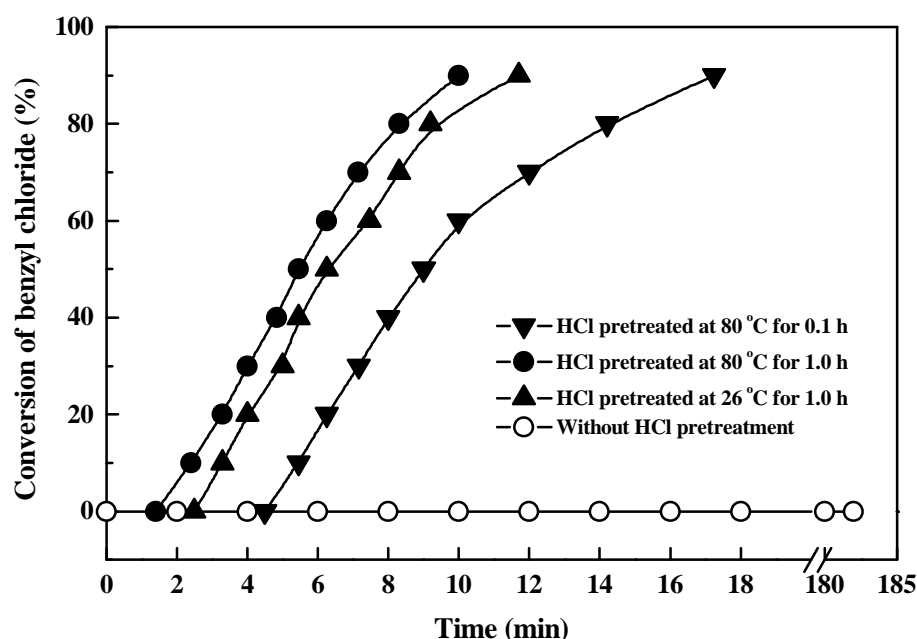
Figure 4.6: Influence of HCl pretreatment to In-Mg-HT-800 catalyst on its activity in the benzylation of benzene (at 80 ℃) by benzyl chloride.

- The HCl pretreatment caused a change in the reaction induction period, depending upon the pretreatment temperature and period. The In-Mg-HT-800 pretreated with HCl at 80 ℃ for 1.0 h showed the best performance for the benzene benzylation. The reaction induction period for the In-Mg-HT-800 pretreated by HCl at 80 ℃ for 0.1 h, 26 ℃ for 1.0 h, and 80 ℃ for 1.0 h is 4.5, 2.5 and 1.4 min, respectively.

- The XRD of the HCl pretreated In-Mg-HT-800 catalyst clearly indicated the chloridation of the catalyst, causing the destruction of its spinel structure (Figure 4.1b, c, d and Table 4.1). After the HCl pretreatment, the basicity and surface area of the catalyst are decreased markedly, depending upon the severity of the HCl treatment (Table 4.1).

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All the above results clearly indicate that the active catalytic species involved in the benzylation reactions over the activated (by HCl treatment before the reaction or during the reaction) catalyst are mainly the $InCl_3$ and In_2O_3 species on the catalyst surface. Unlike the classical Freidel-Crafts Lewis acid catalysts (e.g. $AlCl_3$), these catalytically active species show little or no sensitivity to the small amount moisture present in the reaction mixture (7,12-14]. The redox properties of the activated catalyst ($InCl_3$ and In_2O_3) seem to play important role in deciding the catalytic activity in the present case, involving a redox mechanism similar to that suggested earlier for the benzylation reactions over cation exchanged clays [15], supported thallium oxide [16] and oxides and chlorides of gallium and indium [12-17].

4.3   FRIEDEL-CRAFTS TYPE BENZYLATION OVER Fe-Mg-HT

4.3.1   Characterization of Fe-Mg-HT

The hydrotalcite structure of the synthesized Fe-Mg-HT anionic clay material (synthesis of which is described earlier in Chapter 2) was confirmed by its X-ray analysis (Figure 4.7).

Table 4.2: Physico-chemical properties of the fresh, calcined and used 3Fe-Mg-HT catalysts

Catalyst	Color	Surface area $m^2.g^{-1}$	PH of catalyst[a]	XRD phases
Fresh Fe-Mg-HT-80	Light brown	58	9.6	HT
Fresh Mg-Fe-HT-200	Light brown	70	8.7	HT
Fresh Fe-Mg-HT-500	Pale yellow	78	7.8	MgO and Fe_2O_3
Fresh Fe-Mg-HT-800	Pale yellow	95	7.6	MgO, Fe_2O_3 and $MgFe_2O_4$
Used Fe-Mg-HT-80[b]	Pale yellow	32.3	7.2	$MgCl_2$, $FeCl_3$, Fe_2O_3 and MgO

[a]0.15 g catalyst in 10 ml distilled water, [b]the catalyst after its use in the benzylation of toluene.

The XRD spectra of the material correspond to that of hydrotalcite [8]. Results of the characterization of the fresh, calcined and used (in the toluene benzylation at 110 °C) Fe-Mg-HT catalysts are presented in Table 4.2.

After the calcination and/or reuse (in the reaction) of the hydrotalcite catalysts, the color and crystalline phases of the hydrotalcite catalyst are changed. The surface area of the catalyst is increased and its basicity is decreased with the increase in the calcination temperature. However, after its use in the reaction, its surface area and basicity are reduced.
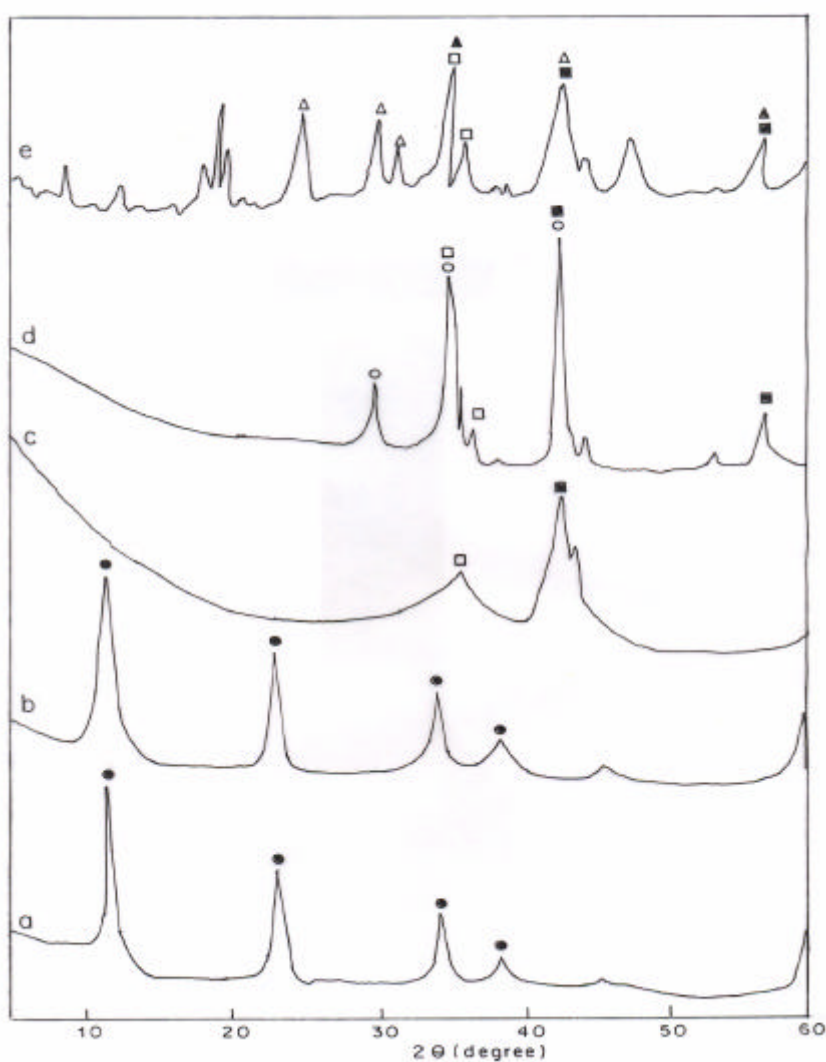
Figure 4.7: XRD spectra of (a) Fresh Fe-Mg-HT-80, (b) Fresh Fe-Mg-HT-200, (c) Fresh Fe-Mg-HT-500, (d) Fresh Fe-Mg-HT-800 and (e) Used Fe-Mg-HT-80 in the toluene benzylation [Crystalline phases: Pure HT ( ), $MgFe_2O_4$ spinel (o), MgO (♣), Fe_2O_3 (?), $MgCl_2$ (?) and $FeCl_3$ (?)].

4.3.2 Benzylation over Fe-Mg-HT-80

Results of the benzylation of toluene and other aromatic compounds over the fresh and used (in the respective benzylation reactions at 80º or 110 ºC) Fe-Mg-HT-80 are presented in Figure 4.8 and Figure 4.9, respectively. The results can be summarized as follows:

- For the fresh Fe-Mg-HT-80, the reaction induction period is large. However, after the induction period, the reaction proceeds at a high rate.

- The reaction induction period is found to depend strongly on the aromatic substrate. The induction period for the benzylation of different aromatic compounds was as follows: anisole (17.5 min) < mesitylene (22.0 min) < p-Xylene (32.0 min) < toluene (43.0 min) < naphthalene (62.5 min).

- Interestingly, the hydrotalcite after it use in the benzylation reaction showed very high benzylation activity (Figure 4.9); the induction period for the benzylation of all the aromatic substrates is reduced drastically.

- The benzylation activity of the used catalyst for the different aromatic substrate (measured in terms of time required for half the reaction, $t_{1/2}$) is found to be in the following order: anisole ($t_{1/2}$ = 1.1 min) < toluene (1.3 min) < mesitylene (1.6 min) < p-Xylene (2.2 min) < naphthalene (2.6 min).
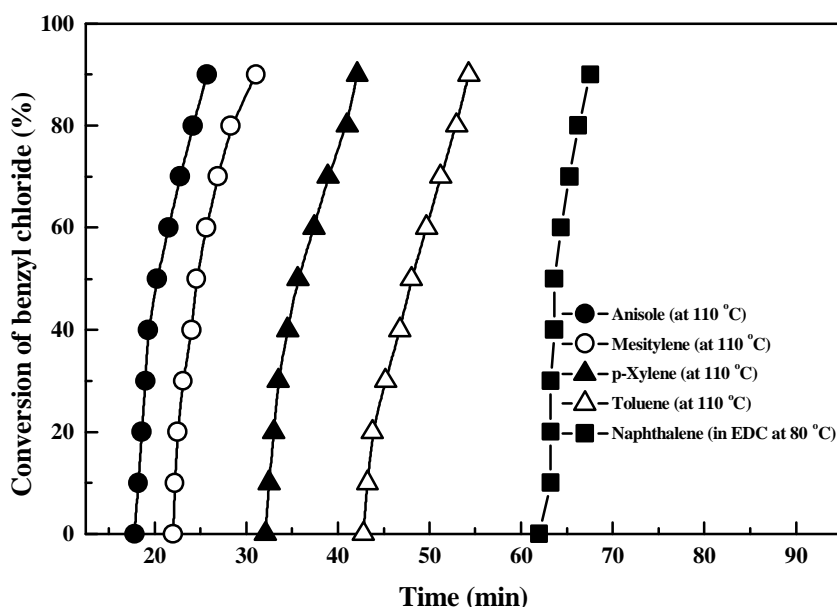
Figure 4.8: Activity of fresh Fe-Mg-HT-80 catalyst in the benzylation of toluene and other aromatic compounds (at 80º or 110 ºC) by benzyl chloride.

These results are consistent with that observed for the In-Mg-HT catalyst. The XRD of the used catalyst (Table 4.2) showed the presence of crystalline phases (viz. Fe_2O_3, MgO, $MgCl_2$ and $FeCl_3$) different from that observed for the fresh Fe-Mg-HT-80. This clearly shows a phase transformation and/or structural breakdown for the hydrotalcite during its use in the reaction, mainly by the HCl produced in the reaction. The basicity of the hydrotalcite is also decreased after its use in the reaction (Table 4.2).

The observed high benzylation activity of the hydrotalcite after the induction period is therefore attributed to the formation of catalytically active species (viz. Fe_2O_3 and $FeCl_3$) on the surface of the hydrotalcite during the induction period by the interaction of benzyl chloride and HCl (formed in the initial reaction) with the basic hydrotalcite. The HCl formed in the benzylation reaction is responsible for the structural breakdown of the hydrotalcite.
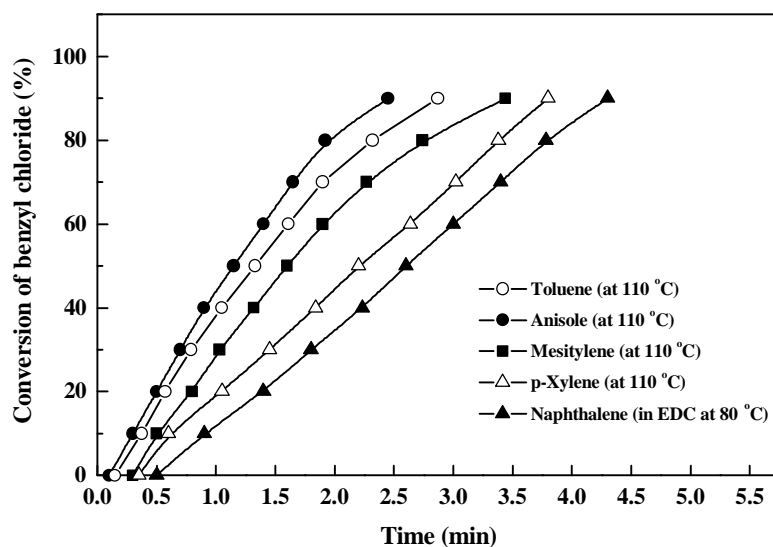
Figure 4.9: Activity of used Fe-Mg-HT-80 catalyst in the benzylation of toluene and other aromatic compounds (at 80° or 110 °C) by benzyl chloride.

The induction period for the different aromatic substrates is different (Figure 4.8). This is attributed to a difference in the reactivity of the aromatic substrates with benzyl chloride on the catalyst. It is interesting to note from the results in Figure 4.9 that the rate of benzylation showed no expected (by the classical Friedel-Crafts mechanism) dependence on the presence of different electron donating group(s) in the aromatic substrate; the rate of toluene benzylation is much higher than that of the mesitylene or p-Xylene benzylation. Thus, the classical Friedel-Crafts mechanism does not simply hold good in the present

catalytic system. This is consistent with that observed earlier in case of the benzylation of substituted benzenes over supported In_2O_3, Ga_2O_3, $GaCl_3$ and $InCl_3$ catalysts [7, 12-14].

4.3.3 Effect of Calcination Temperature of Fe-Mg-HT

Results showing the influence of calcination temperature of the Fe-Mg-HT catalyst on its performance in the benzylation of toluene at 110 °C are presented in Figure 4.10. The results can be summarized as follows:

- The increase in the calcination temperature causes a large decrease in the reaction induction period, depending upon the temperature; higher the calcination temperature, lower the induction period (43.0, 11.5, 4.3 and 1.5 min for the catalyst calcined at 80, 200, 500 and 800 °C, respectively.

- The benzylation activity of the catalyst is increased markedly with increasing its calcination temperature; the time for half the reaction (measured in terms of $t_{1/2}$) is 48.1, 13.0, 6.0 and 2.5 min for the catalyst calcined at 80, 200, 500 and 800 °C, respectively. Unlike the In-Mg-HT, the Fe-Mg-HT catalyst however shows high activity even after its calcination at high temperature (? 500 °C).
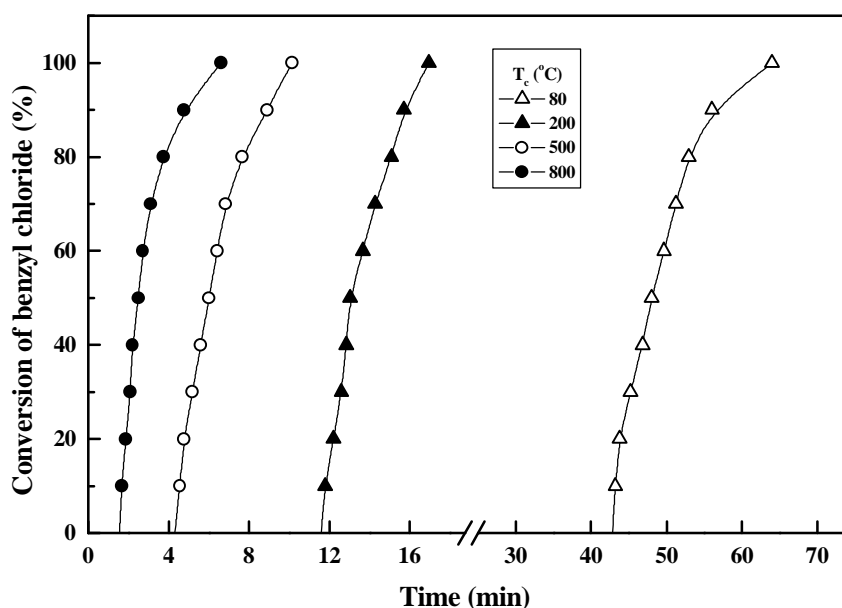
Figure 4.10: Influence of calcination temperature (T_c) of Fe-Mg-HT on its activity in the benzylation of toluene (at 110 °C) by benzyl chloride.

The results clearly show that the activation of the hydrotalcite catalyst for the benzylation reaction depend strongly upon the calcination temperature. The catalyst activation is expected because of the dehydration and/or decomposition of the Fe-Mg-HT-80 followed by the formation of single and/or mixed metal oxide phases, as shown by the

XRD spectra of the hydrotalcite calcined at different temperatures (Table 4.2). The surface area of the catalyst is also increased with increasing its calcination temperature. However, the very large increase in the benzylation activity of the catalyst with the increase in its calcination temperature cannot be attributed merely to the observed increase in the catalyst surface area. It is attributed mainly to the dehydration (at 200 ℃) and/or formation of catalytically active metal oxide species during the calcination (at? 500 ℃).

After the calcination at 200 ℃, the hydrotalcite structure is retained but the XRD peaks are broadened. However, after the calcination at 500 ℃, the hydrotalcite structure is destroyed with the formation of metal oxide (MgO and Fe_2O_3) phases. In the calcination at 800 ℃, two distinct phases, MgO and $MgFe_2O_4$ (spinel), are formed. This is consistent with that observed earlier [18]. The activation of the Fe-Mg-HT-80 by its calcination at 200 ℃ is expected because of the removal of the water of hydration present in the parent hydrotalcite, resulting in an increase in the surface area (from 58 to 70 $m^2.g^{-1}$). The activation of the hydrotalcite by its calcination at the higher temperature is attributed to both the removal of the water of hydration from the catalysts and the formation of single and/or mixed metal oxide phases such as finely dispersed Fe_2O_3 on MgO (formed at 500 ℃) or finely dispersed $MgFe_2O_4$ on MgO (formed at 800 ℃), with an increase in the surface area.

4.4   CONCLUSIONS

1. Both the In-Mg-hydrotalcite and Fe-Mg-hydrotalcite catalyst show high activity in the benzylation of benzene and substituted benzene; the later however is more active. After its use in the benzylation, the reaction induction period for both the catalyst is drastically reduced and consequently their benzylation activity is also drastically increased.

2. During the benzylation reaction both the hydrotalcite catalyst are structurally collapsed with the formation of metal chlorides and oxides.

3. The In-Mg-HT calcined at ? 300 ℃ is structurally collapsed with the formation of new phases, such as MgO, In_2O_3 and/or $MgIn_2O_4$, and it shows no benzylation activity for a long period. However, the Fe-Mg-HT [which is also structurally collapsed after calcination at high temperature (? 300 ℃)] shows high benzylation activity even when calcined at 500 or 800 ℃; its benzylation activity is increased with increase in the calcination temperature.

4. The In-Mg-HT calcined at high temperature (at 800 °C) can be highly activated by their HCl gas pretreatment; the HCl pretreated catalyst show very high benzylation activity.

5. For the catalyst (hydrotalcite or derived from hydrotalcite) in its most active form, the catalytically active species for the benzylation are finely dispersed $InCl_3$ and In_2O_3 on MgO or finely dispersed $FeCl_3$ and Fe_2O_3 on MgO.

4.5   REFERENCES

[1]   G. A. Olah. in Friedel-Crafts and related reactions" Wiley-Interscience Publ., New York, 1 (1963) 32.

[2]   I. Yusuke, O. Mayumi and U. Kazuo, Appl. Catal., A, 132 (1995) 127.

[3]   S. N. Koyande, R. G. Jaiswal and R. V. Jayaram, Ind. Eng. Chem. Res., 37 (1998) 908.

[4]   V. R. Choudhary, S. K. Jana and B. P. Kiran, Catal. Lett., 59 (1999) 217.

[5]   B. Coq, V. Gourves and F. Figueras, Appl. Catal., A, 100 (1993) 69.

[6]   Y. Ono and T. Baba, Catal. Today, 38 (1997) 321.

[7]   V. R. Choudhary, S. K. Jana and B. P. Kiran, J. Catal., 192 (2000) 257.

[8]   F. Cavani, F. Trifiro and A. Vaccari, Catal. Today, 11 (1991) 173.

[9]   V. R. Choudhary, S. K. Jana and A. B. Mandale, Catal. Lett., 74 (2001) 95.

[10]   V. R. Choudhary, S. K. Jana and V. S. Narkhede, Appl. Catal., A, 235 (2002) 207.

[11]   E. Lopez-Salinas, M. Garcia-Sanchez, M. L. Ramon-Garcia and I. Scifter, J. Porous Mater., 3 (1996) 169.

[12]   V. R. Choudhary, S. K. Jana, N. S. Patil and S. K. Bhargava, Micropor. Mesopor. Mater., 57 (2003) 21.

[13]   V. R. Choudhary and S. K. Jana, J. Mol. Catal., A, 184 (2002) 247.

[14]   V. R. Choudhary and S. K. Jana, J. Mol. Catal., A, 180 (2002) 267.

[15]   T. Cseri, S. Bekassay, F. Figueras, S. Rizner, J. Mol. Catal, A, 98 (1995) 101.

[16]   V. R. Choudhary and S. K. Jana, J. Catal., 201 (2001) 225.

[17]   V. R. Choudhary, S. K. Jana and V. S. Narkhede, Catal. Commun., 2 (2001) 331.

[18]   E. Lopez-Salinas, E. Torres-Garcia and M. Garcia-Sanchez, J. Phys. Chem. Solids, 58 (1997) 919.

CHAPTER – 5

BENZYLATION AND ACYLATION OF AROMATIC COMPOUNDS, WITH OR WITHOUT CONTAINING NITRO GROUP, USING GaCl$_x$- AND GaAlCl$_x$-GRAFTED Si?MCM?41 AND MONTMORILLONITE?K10 CATALYSTS

5.1 INTRODUCTION AND OBJECTIVE OF PRESENT WORK

The benzylation or acylation of aromatic compounds containing electron-donating groups (e.g. alkyl, alkoxy, hydroxy, etc) can be accomplished with ease but it is difficult in the absence of such aromatic ring-activating group (e.g. benzene and naphthalene). Friedel?Crafts benzylation or acylation of aromatic compounds containing strong electron withdrawing groups, such as nitro group, is very difficult to accomplish, because of the electron deficient aromatic ring system [1]. Till today no report on the direct Friedel?Crafts type benzylation and/or acylation of a nitro aromatic compound is known. Therefore, development of a reusable solid catalyst particulary for the acylation of nitro aromatic compounds is of both scientific and practical importance.

The present study was undertaken with the objective of investigating the performance of AlCl$_x$? and/or GaCl$_x$? grafted on high silica MCM?41 (viz. Si-MCM-41) or montmorillonite?K10, as solid catalysts, in the Friedel-Crafts type benzylation and acylation of aromatic compounds and also in the acylation of aromatic compounds containing strong electron withdrawing group such as nitro group. Influence of moisture (present in the reaction mixture or the catalyst) and acylating agent on the catalyst performance in the acylation has also been studied.

5.2 BENZYLATION AND ACYLATION OVER GaCl$_x$-GRAFTED Si-MCM-41 CATALYST

5.2.1 Preparation and Characterization of the Catalyst

A GaCl$_x$-grafted Si-MCM-41 catalyst was prepared as follows: 10 g of crystalline mesoporous high silica MCM?41, i.e. Si?MCM?41, having surface area of 1100 m^2.g^{-1} and pore size of 2.5 nm, was taken in 100-cm^3 dry carbon tetrachloride. To this was added 10 mmol anhydrous GaCl$_3$ dissolved in 10 ml dry CCl$_4$. The resulting reaction mixture was refluxed for 4 h under moisture?free N$_2$ (flow rate = 60 ml/min). The gaseous hydrogen chloride evolved during the reaction between the surface hydroxyls of the Si?MCM?41 and GaCl$_3$ (-OH + GaCl$_3$? ? -O-GaCl$_2$ + HCl) was measured quantitatively by absorbing it

in aqueous NaOH solution by a simple acid‑base titration using a phenolphthalein indicator. The total amount of HCl evolved in the reaction was 1.2 mmol.g^{-1}, as shown in Figure 5.1. The reaction mixture was cooled and the solid catalyst is separated by filtration and washed by dry carbon tetrachloride, under moisture‑free N$_2$ gas and dried under vacuum. The dried catalyst was then stored in a desiccator.
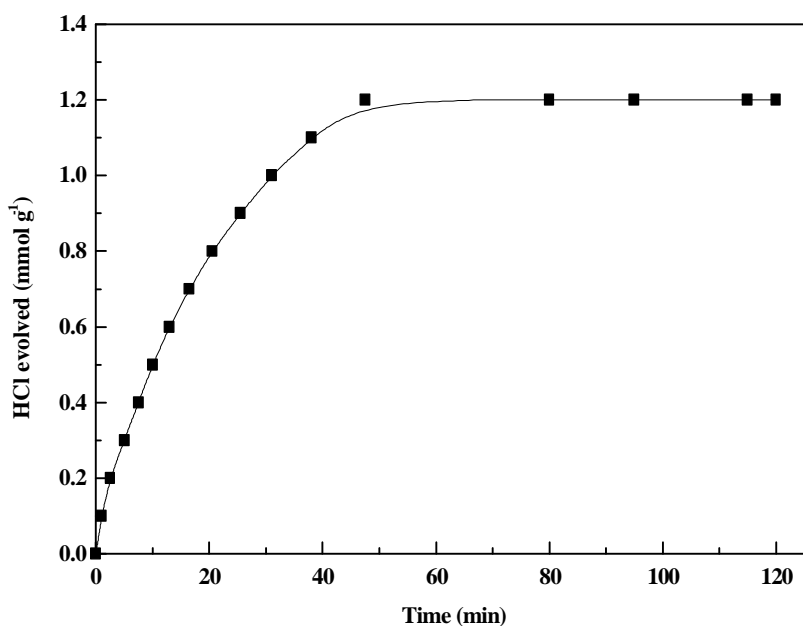
Figure 5.1:   HCl evolved during the grafting of GaCl$_3$ on Si-MCM-41

The catalysts characterization data (chemical composition: concentration of Ga and Cl, HCl evolved during the grafting, Cl/Ga atom ratio and the surface GaCl$_x$ species) for the GaCl$_x$-grafted-Si-MCM-41 are given in Table 5.1. The Cl/Ga ratio obtained from EDX analysis is 1.01, which is same as that obtained from the chemical analysis (Cl/Ga = 1.0) and also by the amount of HCl evolved (Cl/Ga = 1.01). Based on the observed Cl/Ga ratio for the catalyst, the expected surface species are (-SiO)$_2$GaCl,. The grafting of GaCl$_3$ on Si-MCM-41 is thus expected to involve the following reaction (with the evolution of 2 moles of HCl per mole of GaCl$_3$ grafted):

$$2(\text{-SiOH}) + \text{GaCl}_3 \ \ ? \ ? \ \ \ (\text{-SiO})_2\text{GaCl} + 2\text{HCl}? \ \text{- - - - - - - - - - - - - - - - (1)}$$

Table 5.1: Characterization of GaCl$_x$- and GaAlCl$_x$-grafted-Si-MCM-41 catalysts

Catalyst characteristics	GaCl$_x$-grafted Si-MCM-41	GaAlCl$_x$-grafted Si-MCM-41
Concentration of Ga (mmolg^{-1})	0.61	-
Concentration of Ga+Al (mmolg^{-1})	-	0.67
HCl evolved during grafting (mmolg^{-1})	1.2	1.5
Concentration of Cl (mmolg^{-1})[a]	0.61	0.45
Cl/(Al and/or Ga) atom ratio[b]	1.01	0.71
Surface Ga and Al species	(-SiO)$_2$GaCl	(-SiO)$_3$Ga(or Al) and (-SiO)$_2$Ga(or Al)Cl

[a] Estimated by potentiometric titration. [b] Estimated from EDX analysis

5.2.2 Benzylation over GaCl$_x$-grafted Si-MCM-41

Results showing the benzylation of benzene and other aromatic compounds by benzyl chloride over GaCl$_x$-grafted Si-MCM-41 (at 80 or 110 ºC) are presented in Figure 5.2. The reaction induction period for the different aromatic substrates is different and is found to depend strongly on the nature of the aromatic substrate used. The induction period for the benzylation of different aromatic compounds is in the following order: anisole (1.6 min) < cumene (2.1 min) < mesitylene (2.8 min) < p-Xylene (4.0 min) < toluene (5.5 min) < benzene (7.2 min) < naphthalene (10.2 min). The catalytic benzylation activity for the different aromatic substrates (measured in terms of the time required for half the reaction, $t_{1/2}$) is found to be in the following order: anisole ($t_{1/2}$ = 5.1 min) > cumene (6.3 min) > mesitylene (7.3 min) > p-Xylene (8.5 min) > toluene (10.1 min) > benzene (11.7 min) > naphthalene (14.5 min). However, after the induction period the benzylation of all the substrates proceeds with a high rate.
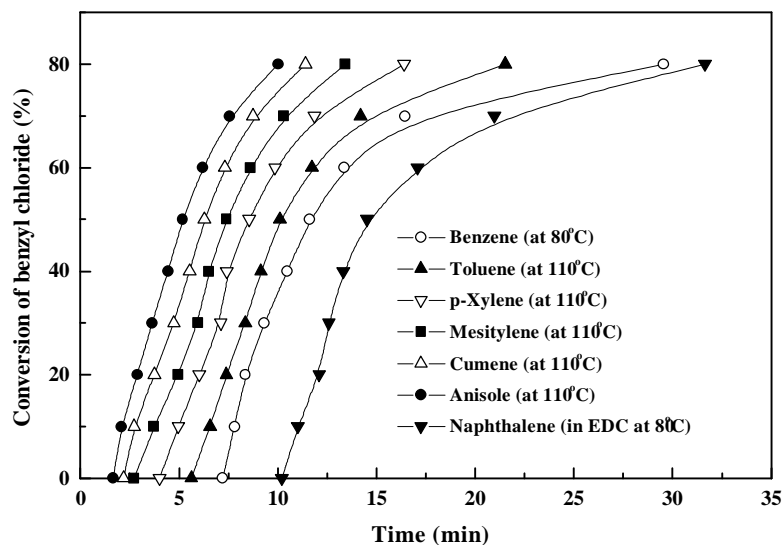
Figure 5.2: Conversion vs reaction time plots for the benzylation of aromatic compounds by benzyl chloride (at 80 or 110 °C) over GaCl$_x$-grafted Si-MCM-41 (reaction mixture: 13 ml aromatic substrate + 0.1 g catalyst).

5.2.3 Acylation of Aromatic Nitro Compound

Results showing the benzoylation of nitrobenzene by benzoyl chloride (at 150 °C) over GaCl$_x$-grafted Si-MCM-41 are presented in Table 5.2. The results lead to the following important conclusions:

- The catalyst shows high activity for the benzoylation of nitrobenzene even in the presence of moisture.

- A very low induction period (0.2 min) is seen for the benzoylation reaction.

- The rate of the benzoylation reaction is greatly enhanced in the presence of moisture in the catalyst or in the substrate.

- In the absence of nitrobenzene substrate, the conversion of benzoyl chloride was very slow (21.5 % conversion in about 4 h), indicating a very poor benzoyl chloride polycondensation activity of the catalyst as compared to its benzoylation.

The drastic increase in the catalytic activity in the benzoylation reaction after saturation with moisture of either catalyst or the substrate may be attributed to the modification of the active sites of the catalyst by the adsorbed/absorbed water.

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Table 5.2: Acylation of nitrobenzene by benzoyl chloride over the $GaCl_x$- or $GaAlCl_x$-grafted Si MCM-41 (at 150 ºC).

Entry no.	Substrate	Reaction induction period (min)	Time required for conversion of acylating agent (min)	
			50 %	90 %
Catalyst: $GaCl_x$-grafted Si-MCM-41				
1	Nitrobenzene	0.2	23.5	63.8(75 %)
2[a]	Nitrobenzene	0.0	1.2	12.7
3[b]	Nitrobenzene	0.0	1.4	16.2
4[c]	None (only benzoyl chloride)	1.0	224.4(21.5 %)	-
Catalyst: $GaAlCl_x$-grafted Si-MCM-41				
4	Nitrobenzene	1.0	15.9	98.9
5[a]	Nitrobenzene	0.0	3.2	39.9
6[b]	Nitrobenzene	0.8	6.2	42.4
7[d]	Nitrobenzene	1.2	13.1	60.4
8[e]	Nitrobenzene	0.5	2.2	14.5
9[c]	None (only benzoyl chloride)	1.3	222.4(18 %)	-
10[f]	Nitrobenzene	0.8	13.2	90.3
11[g]	Nitrobenzene	0.7	10.6	85.6
12[h]	Nitrobenzene	0.5	9.4	78.7

[a]Moist catalyst (the catalyst was saturated with water vapor by storing it over water at 28 ºC for 48 h. [b]Moist substrate (the substrate was saturated with water by stirring it with water at 28 ºC for 3 h. [c]Polycondensation of benzoyl chloride. [d]The catalyst was exposed to atmosphere at room temperature for 24 h. [e]Using $PhCH_2COCl$ as the acylating agent. [f,g,h]The first, third and fifth reuse of the catalyst, respectively.

5.2.4 Benzoylation of Other Aromatic Compounds

Results showing the benzoylation of benzene and other aromatic compounds by benzoyl chloride over GaCl$_x$-grafted Si-MCM-41 (at 80 or 110 ºC) are presented in Figure 5.3. From the results following important observations can be made:

- The reaction induction period for the different aromatic substrates depends strongly on the nature of the aromatic substrate used.
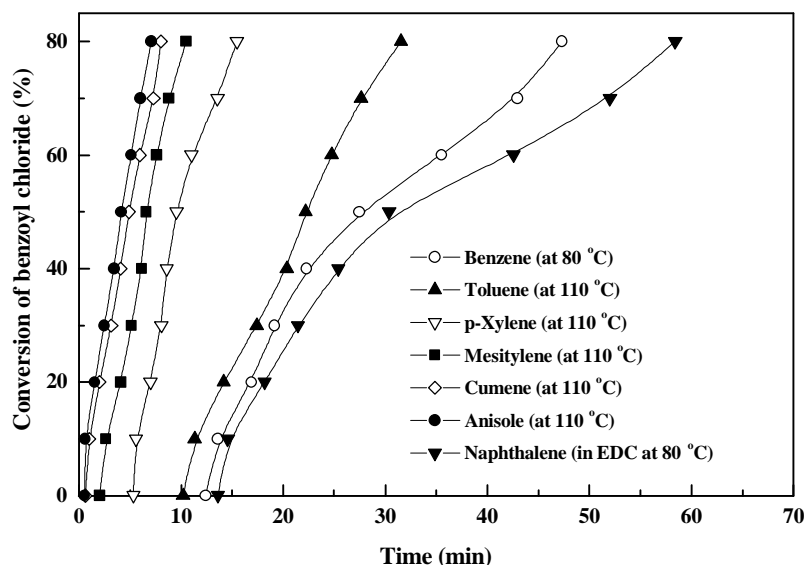
Figure 5.3: Conversion vs reaction time plots for the benzoylation of aromatic compounds by benzoyl chloride (at 80 or 110 ºC) over GaCl$_x$-grafted Si-MCM-41 (reaction mixture: 13 ml aromatic substrate + 0.4 g catalyst).

- The induction period for the benzoylation of different aromatic compound is in the following order: anisole = cumene (induction period = 0.7 min) < mesitylene (1.9 min) < p-Xylene (5.4 min) < toluene (10.4 min) < benzene (12.7 min) < naphthalene (14.0 min).

- The catalytic benzoylation activity for the different aromatic substrates (measured in terms of the time required for half the reaction, $t_{1/2}$) is found to be in the following order: anisole ($t_{1/2}$ = 4.0 min) > cumene (5.0 min) > mesitylene (6.6 min) > p-Xylene (9.5 min) > toluene (22.3 min) > benzene (27.3 min) > naphthalene (30.7 min).

- After the induction period, the benzoylation of anisole, cumene, mesitylene and p-Xylene proceeds with a high rate, while that of toluene, benzene and naphthalene proceeds at a somewhat slower rate.

5.3 BENZYLATION AND ACYLATION OVER GaAlCl$_x$-GRAFTED Si-MCM-41 CATALYST

5.3.1 PREPARATION AND CHARACTERIZATION OF THE CATALYST

GaAlCl$_x$-grafted Si-MCM-41 was prepared by a similar procedure used for the preparation of GaCl$_x$-grafted Si-MCM-41 (section 5.2.1) except that, instead of 10 mmol anhydrous GaCl$_3$, 6 mmol of AlCl$_3$ dissolved in 6 ml of dry acetonitrile and 4 mmol of GaCl$_3$ dissolved in 4 ml dry CCl$_4$ was used for the reaction. The amount of HCl evolved in the reaction (for 4 h) was 1.5 mmol.g$^{?1}$ (Figure 5.4).
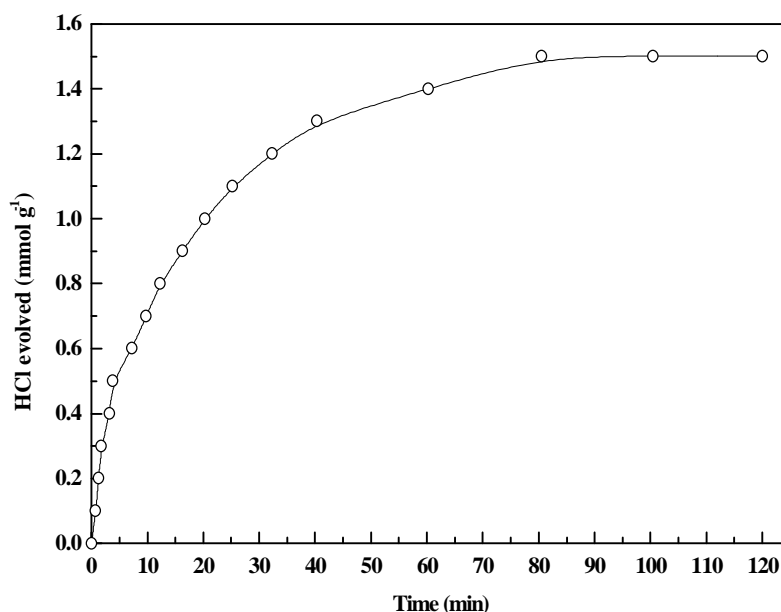
Figure 5.4: HCl evolved during the grafting of GaCl$_3$ and AlCl$_3$ on Si-MCM-41

The catalysts characterization data (chemical composition: concentration of Ga, Al and Cl, HCl evolved during the grafting, Cl/(Ga+Al) atom ratio and the surface GaAlCl$_x$ species) for the GaAlCl$_x$-grafted-Si-MCM-41 are given in Table 5.1. The Cl/(Ga+Al) ratio obtained from EDX analysis is 0.71, which is more or less the same as that obtained from the chemical analysis (Cl/(Ga+Al) = 0.67) and also by the amount of HCl evolved (Cl/(Ga+Al) = 0.72 ? 0.05). Based on the observed Cl/(Ga+Al) ratio for the catalyst, the expected surface species are (-SiO)$_2$Ga(or Al)Cl and (-SiO)$_3$Ga(or Al). The grafting of GaAlCl$_3$ on Si-MCM-41 is thus expected to involve the following reactions (with the evolution of 2 moles or 3 moles of HCl per mole of GaCl$_3$ and AlCl$_3$ grafted):

2(-SiOH) + Ga(or Al)Cl$_3$? ?   (-SiO)$_2$Ga(or Al)Cl + 2HCl? - - - - - - - - - - - - - (2)

3(-SiOH) + Ga(or Al)Cl$_3$? ?   (-SiO)$_3$Ga(or Al) + 3HCl? - - - - - - - - - - - - -- (3)

5.3.2 Benzylation of Aromatic Compounds

Results of the benzylation of benzene and other aromatic compounds by benzyl chloride over GaAlCl$_x$-grafted Si-MCM-41 (at 80 or 110 ℃) are presented in Figure 5.5.

The reaction induction period for the different aromatic substrates depends strongly on the nature of the aromatic substrate used.
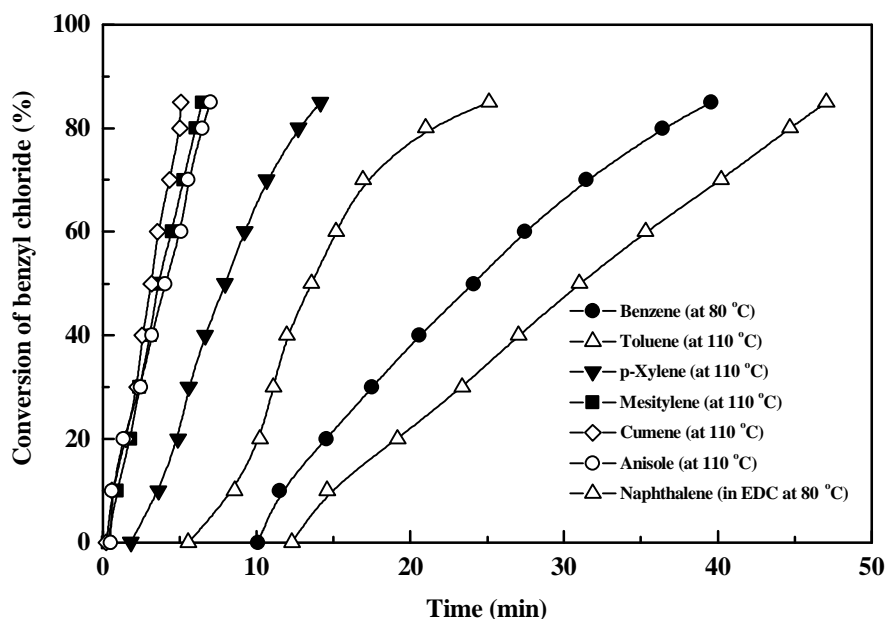
Figure 5.5: Conversion vs reaction time plots for the benzylation of aromatic compounds by benzyl chloride (at 80 or 110 ℃) over GaAlCl$_x$-grafted Si-MCM-41 (reaction mixture: 13 ml aromatic substrate + 0.1 g catalyst).

The induction period for the benzylation of different aromatic compounds is in the following order: anisole (induction period = 0.3 min) < cumene (0.4 min) < mesitylene (0.7 min) < p-Xylene (2.0 min) < toluene (5.8 min) < benzene (10.1 min) < naphthalene (12.4 min). The catalytic benzylation activity for the different aromatic substrates (measured in terms of the time required for half the reaction, t$_{1/2}$) is found to be in the following order: anisole (t$_{1/2}$ = 3.1 min) > cumene (3.5 min) > mesitylene (4.1 min) > p-Xylene (8.0 min) > toluene (13.7 min) > benzene (24.0 min) > naphthalene (31.1 min). However, after the induction period, the benzylation of all the substrates proceeds with a high rate. The rate of the benzylation reaction was found to be somewhat lower than that of the benzylation reaction catalyzed by the GaCl$_x$-grafted-Si-MCM-41 catalyst.

5.3.3 Acylation of Aromatic Nitro Compounds

Results of the benzoylation of nitrobenzene and substituted nitrobenzenes by benzoyl chloride over GaAlCl$_x$-grafted Si-MCM-41 are presented in Figure 5.6 and Tables 5.2 and 5.3.

Table 5.3: Yield of isolated product in the benzoylation of nitroaromatics over the GaAlCl$_x$-grafted Si-MCM-41 (reaction period = 3h)

Entry no.	Substrate	Temp. (^{o}C)	Time for half benzoyl chloride conversion,$t_{1/2}$ (min)	Yield of isolated product (%)
1	Nitrobenzene	150	15.9	56.2[Ref2]
2	o-Nitrotoluene	150	39.2	n.d.
3	m-Nitrotoluene	150	27.3	n.d.
4	p-Nitrotoluene	150	53.3	n.d.
5	3-Bromo-1-nitrobenzene	140	26.1	46.4[Ref2]
6	4-Chloro-1-nitrobenzene	140	24.2	n.d.
7	3-Chloro-1-nitrobenzene	140	48.2	n.d.
8	4-Nitroacetophenone	130	77.6	n.d.
9	4-Nitrobenzaldehyde	130	72.2	36.2[Ref2]

n.d. = not determined

The catalyst shows high activity for the benzoylation of nitrobenzene and substituted nitrobenzenes by benzoyl chloride. It even shows good activity in the presence of moisture either in the substrate (viz. nitrobenzene) or in the catalyst (Table 5.2, entry no. 5 and 6). Also the catalyst shows high activity even when it is exposed to the atmosphere for 24 h (Table 5.2, entry no. 7).

In a few cases (viz. for the benzoylation of nitrobenzene, 1-bromo-3-nitrobenzene and 4-nitrobenzaldehyde), the benzoylation reaction was carried out for 5 h and the reaction products (benzoylated nitrobenzene or substituted nitrobenzene), was isolated by the

column chromatography [8]. The isolated products were characterized by ^{1}H NMR and IR (the spectras are provided in Appendix 5.1-5.3). The melting point, ^{1}H NMR and IR data for the isolated products are provided in ref. [8].
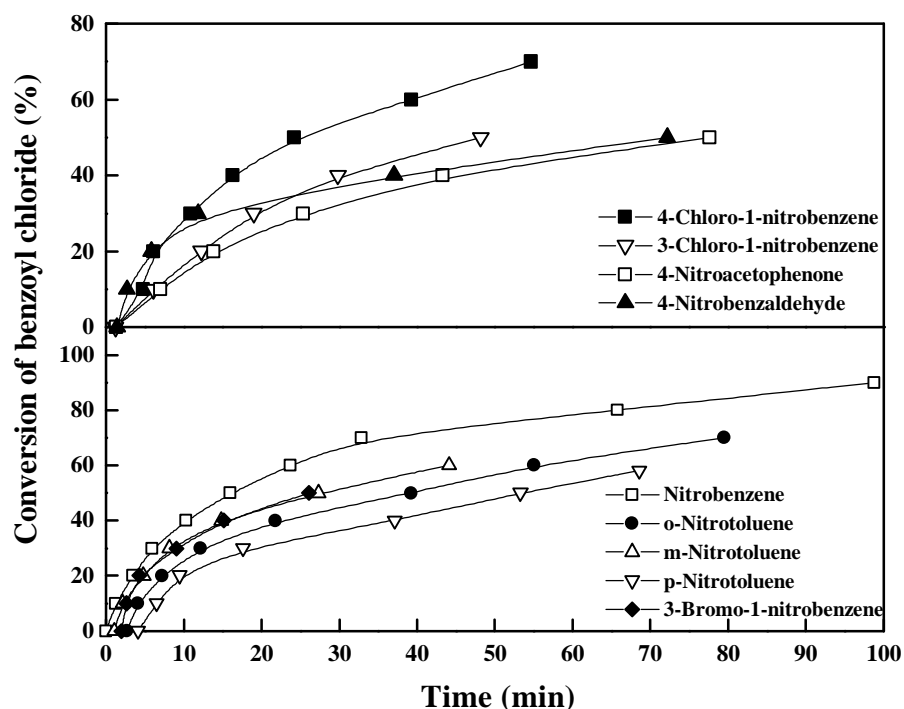
5.3.4 Benzoylation of other Aromatic Compounds

Results of the benzoylation of benzene and other aromatic compounds by benzoyl chloride over GaAlCl$_x$-grafted Si-MCM-41 (at 80 or 110 °C) are presented in Figure 5.7.
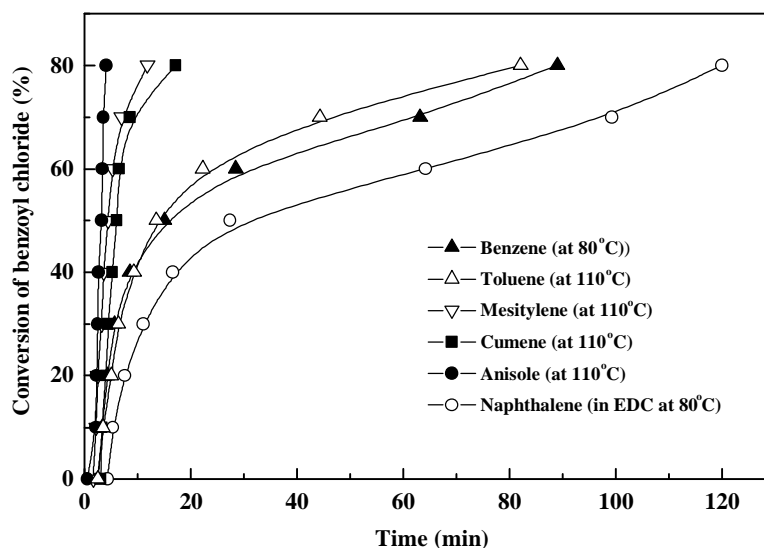

Figure 5.7: Conversion vs reaction time plots for the benzoylation of aromatic compounds by benzoyl chloride (at 80 or 110 °C) over GaAlCl$_x$-grafted Si-MCM-41 (reaction mixture: 13 ml aromatic substrate + 0.4 g catalyst)

The induction period for the benzoylation of different aromatic substrates is in the following order: anisole (induction period = 0.6 min) < cumene (0.7 min) < mesitylene (1.9 min) < p-Xylene (5.4 min) < toluene (10.4 min) < benzene (12.7 min) < naphthalene (14.0 min). The benzoylation activity for the different aromatic substrates (measured in terms of the time required for half the reaction, $t_{1/2}$) is found to be in the following order: anisole ($t_{1/2}$ = 4.0 min) > cumene (5.0 min) > mesitylene (6.6 min) > p-Xylene (9.5 min) > toluene (22.3 min) > benzene (27.3 min) > naphthalene (30.7 min). After the induction period, the benzoylation of anisole, cumene and mesitylene proceeds with a high rate, while that of toluene, benzene and naphthalene proceeds at a somewhat slower rate.

5.4 BENZYLATION AND ACYLATION OVER GaAlCl$_x$-Grafted-Mont.K-10 CATALYST

5.4.1 Preparation and Characterization of the Catalyst

A GaAlCl$_x$-grafted Mont.K-10 catalyst was prepared in a similar way as that for the GaAlCl$_x$-grafted-Si-MCM-41 (section 5.2.1) except that; Mont.K-10 was used as the catalyst support instead of Si-MCM-41. The amount of HCl evolved in the grafting reaction was 1.65 mmol.g$^{?1}$ (Figure 5.8).
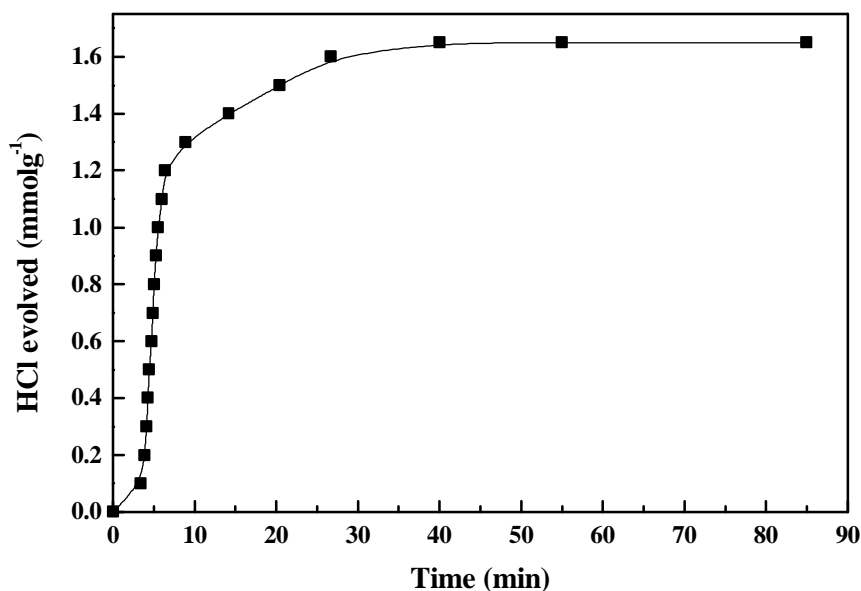
Figure 5.8: HCl evolved (mmolg^{-1}) during the simultaneous grafting of GaCl$_3$ and AlCl$_3$ on Mont.-K10

From the chemical analysis of GaCl₃ and AlCl₃ remaining in the grafting reaction mixture after the grafting, the total amount of Al and Ga grafted on the clay was found to be 0.81mmol.g^{-1}. From the amount of HCl evolved during the grafting (1.65 mmol.g^{-1}), the grafted Al and/or Ga chloride species are expected to be (–O)$_2$Ga(or Al)Cl.

5.4.2 Benzylation over GaAlCl$_x$-grafted Mont.K-10

Results of the benzylation of benzene and substituted benzenes by benzyl chloride (at 80 or 110 ºC) over GaAlCl$_x$-grafted Mont.K-10 are presented in Figure 5.9. From the results following important observations can be made:

- The induction period for the benzylation of different aromatic compounds is in the following order: cumene (induction period = 0.5 min) < p-Xylene (0.7 min) < toluene (3.3 min) < benzene (10.8 min) < naphthalene (15.7 min).
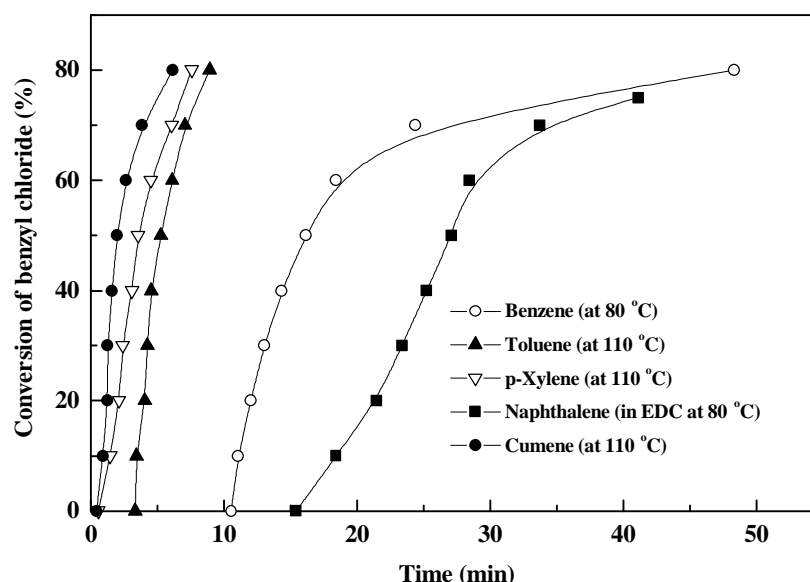
Figure 5.9: Conversion vs reaction time plots for the benzylation of aromatic compounds by benzyl chloride (at 80 or 110 ºC) over GaAlCl$_x$-grafted Mont.-K10 (reaction mixture: 13 ml aromatic substrate + 0.1 g catalyst)

- The benzylation activity for the different aromatic substrates (measured in terms of the time required for half the reaction, t$_{1/2}$) is in the following order: cumene (t$_{1/2}$ = 1.8 min) > p-Xylene (3.4 min) > toluene (5.4 min) > benzene (16.1 min) > naphthalene (27.2 min).
- After the induction period, the benzoylation of cumene, p-Xylene and toluene proceeds with a high rate, while that of benzene and naphthalene proceeds at a somewhat slower rate.

5.4.3 Benzoylation of Nitrobenzene

Results showing the benzoylation of nitrobenzene by benzoyl chloride (at 150 ℃) over GaAlCl$_x$-grafted Mont.-K10 are presented in Figure 5.10. The catalyst shows good conversion of benzoyl chloride (80 % in 56.5 min) in the benzoylation of nitrobenzene by benzoyl chloride. However, in the absence of nitrobenzene substrate, the conversion of benzoyl chloride was very slow (28.5 % conversion in about 4 h), indicating a low benzoyl chloride polycondensation activity of the catalyst as compared to its benzoylation.
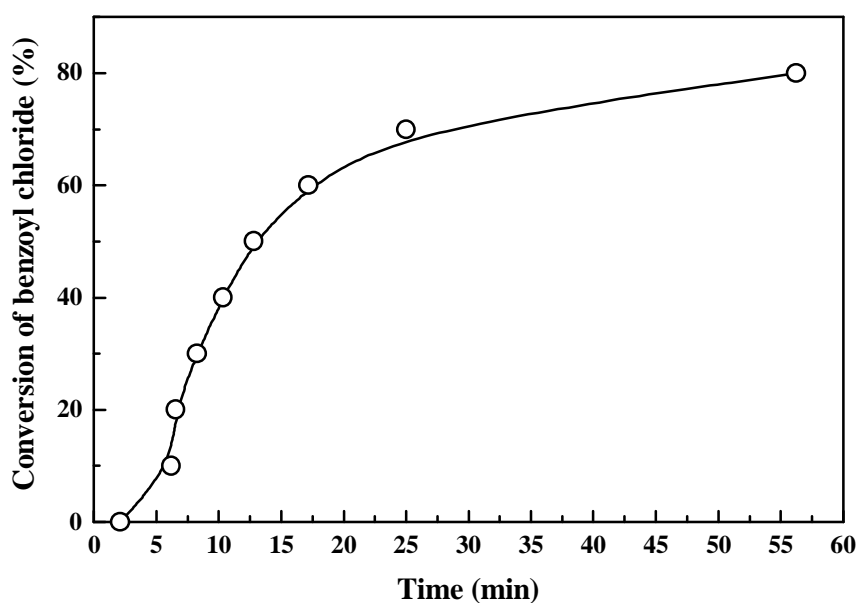
Figure 5.10: Conversion vs reaction time plots for the benzoylation of nitrobenzene by benzoyl chloride (at 150 ℃) over GaAlCl$_x$-grafted Mont.-K10

5.4.4 Benzoylation of other Aromatic Compounds

Results of the benzoylation of benzene and substituted benzenes by benzoyl chloride (at 80° or 110 ℃) over GaAlCl$_x$-grafted Mont.K-10 are presented in Figure 5.11.

The induction period for the benzoylation of different aromatic compounds is in the following order: cumene (induction period = 0.0 min) < p-Xylene (0.6 min) < toluene (0.7 min) < benzene (0.8 min) < naphthalene (3.9 min). The benzoylation activity for the different aromatic substrates (measured in terms of the time required for half the reaction, $t_{1/2}$) is found to be in the following order: cumene ($t_{1/2}$ = 1.3 min) > p-Xylene (3.1 min) > toluene (5.3 min) > benzene (7.8 min) > naphthalene (21.9 min). After the induction period, the benzoylation of cumene, p-Xylene, toluene and benzene proceeds with a high rate, while that of naphthalene proceeds at a somewhat slower rate.
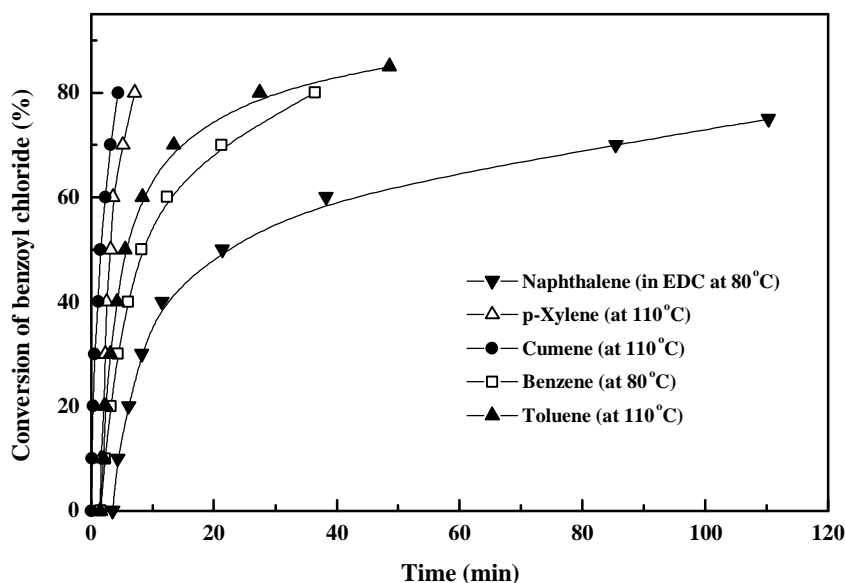
Figure 5.11: Conversion vs reaction time plots for the benzoylation of aromatic compounds by benzoyl chloride (at 80° or 110 °C) over GaAlCl$_x$-grafted Mont.K-10 (reaction mixture: 13 ml aromatic substrate + 0.4 g catalyst).

5.5   CONCLUSIONS

GaCl$_x$- and/or AlCl$_x$-grafted Si-MCM-41 and Mont.K-10 are highly active catalysts for the Friedel-Crafts type benzylation and acylation of aromatic compounds in the absence of electron donating group or even in the presence of strong electron withdrawing group like nitro group. Also, the catalysts showed high activity for the nitrobenzene benzoylation even in the presence of moisture in the catalyst or in the substrate. The active catalytic species are partially chlorided Al and Ga species (-SiO)$_2$Ga(or Al), or (-SiO)$_3$Ga(or Al).

5.6   REFERENCES

[1]   G. A. Olah, Ed., "Friedel-Crafts and Related Reactions" Wiley-Interscience Publ., New York, Vol. 1-4 (1963-1965).

[2]   Characterization data for a) C$_{13}$H$_9$NO$_3$ (mp. 96 °C) ^{1}H NMR (CDCl$_3$, 200 MHz) = 7.35-8.35 ? (m, 9H); IR = 665.4, 703.97, 810.05, 997.13, 1377.35, 1454.23, 1583.45, 1693.38, 2557.43, 2954.74. b) C$_{13}$H$_8$BrNO$_3$ (mp. 92 °C) ^{1}H NMR (CDCl$_3$, 200 MHz) = 7.35-7.75 ? (m, 5H), 8.05-8.2 ? (m, 3H); IR = 667.32, 738.69, 933.48, 1461.94, 1569.95, 2673.16, 2945.1. c) C$_{14}$H$_9$NO$_4$ (mp. 75 °C) ^{1}H NMR (CDCl$_3$, 200 MHz) 7.1-8.5 ? (m, 9H), 10.05 ? (s, 1H); IR = 738.69, 850.55, 1461.94, 1695.31, 2727.16, 2923.88.
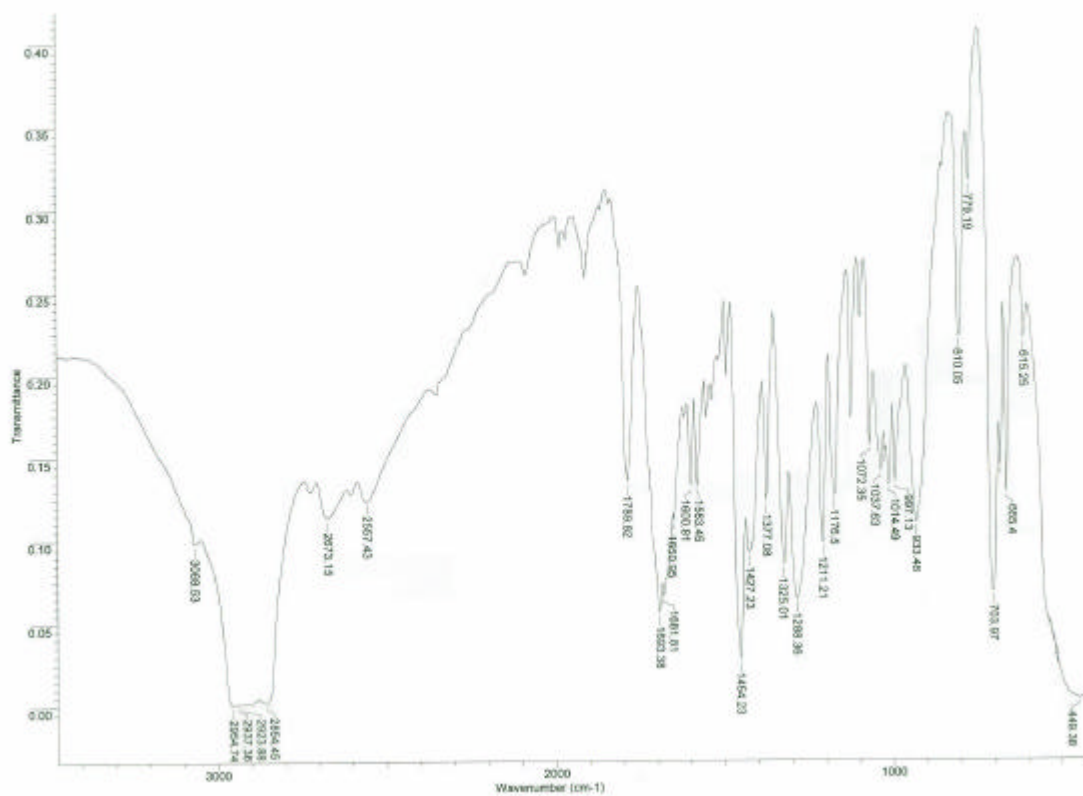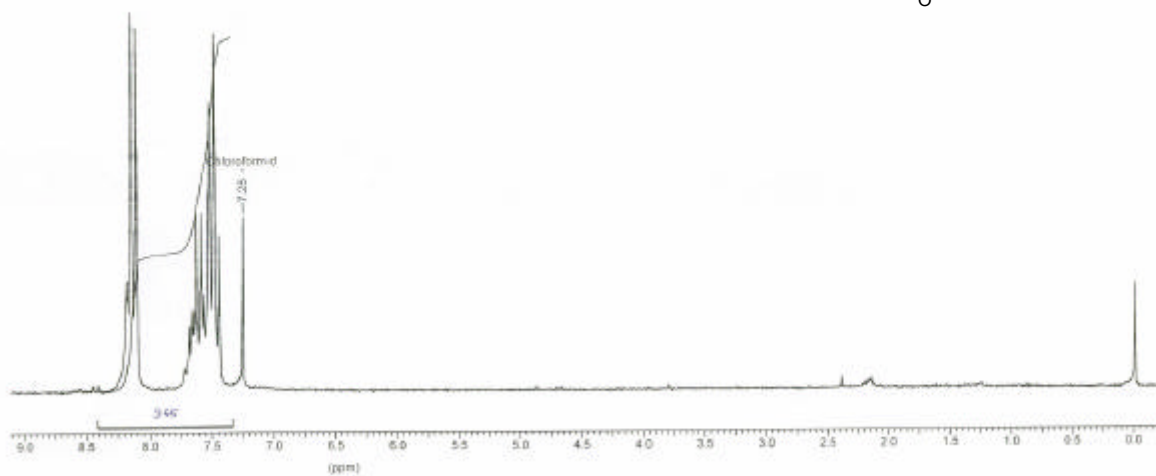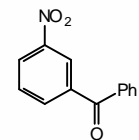
Appendix 5.1 ^{1}H NMR and IR spectra for 3-nitrobenzophenone

Chloroform-d
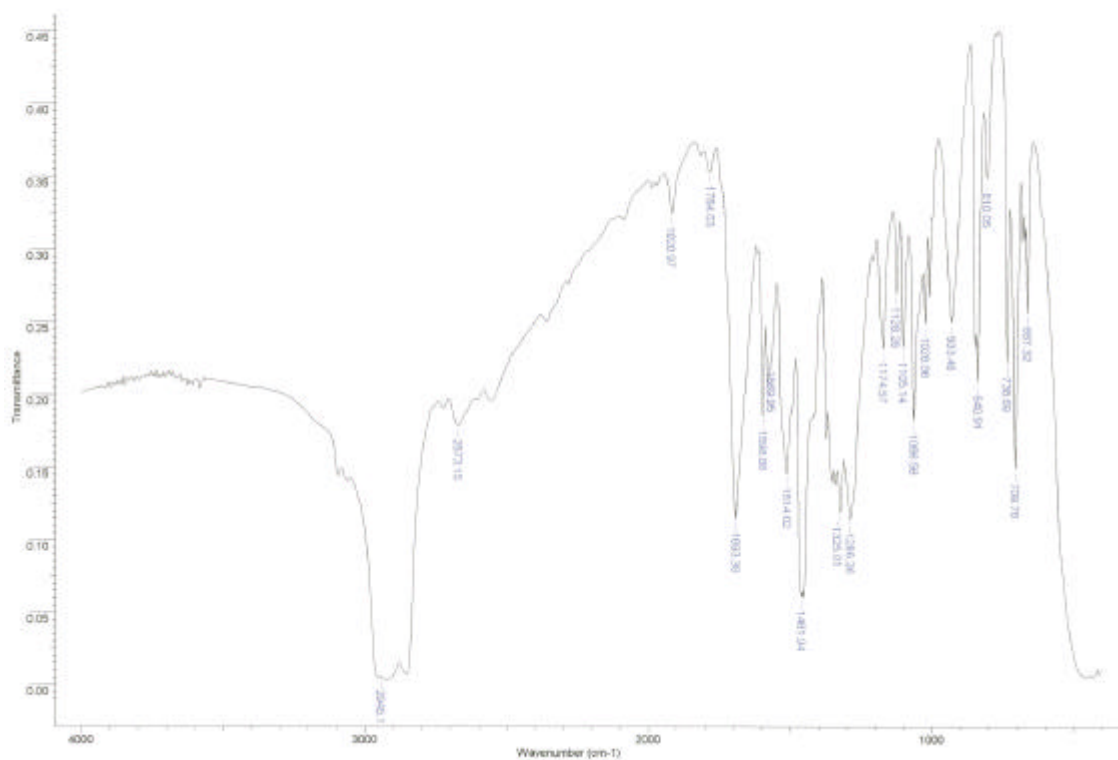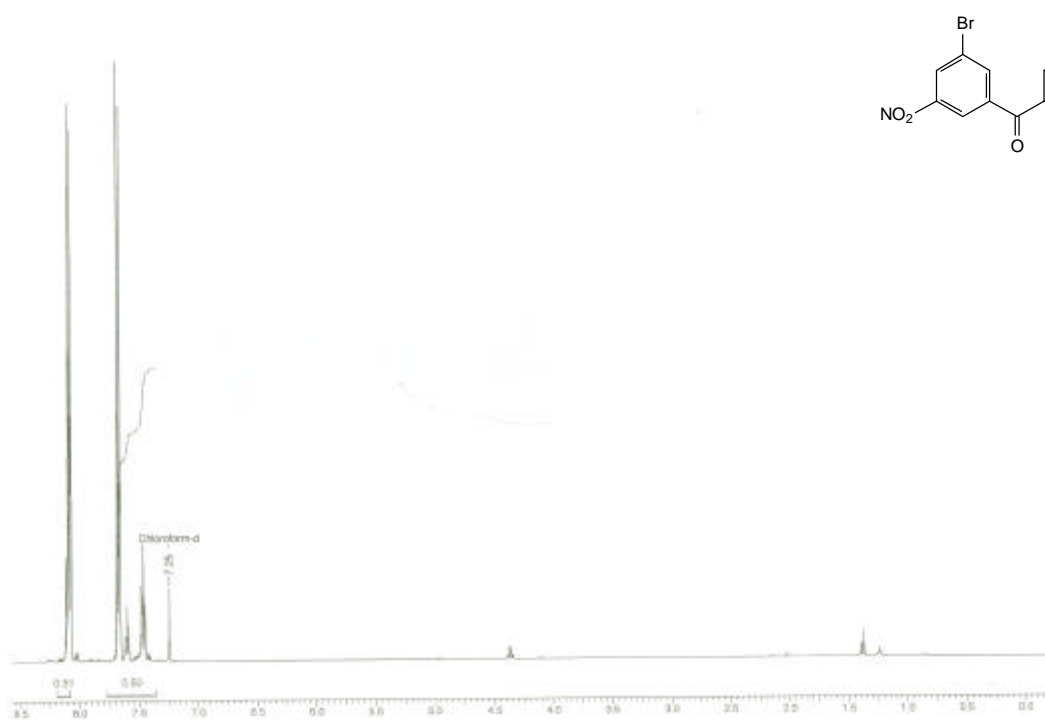
Appendix 5.2 1H NMR and IR spectra for 3-bromo-5-nitrobenzophenone
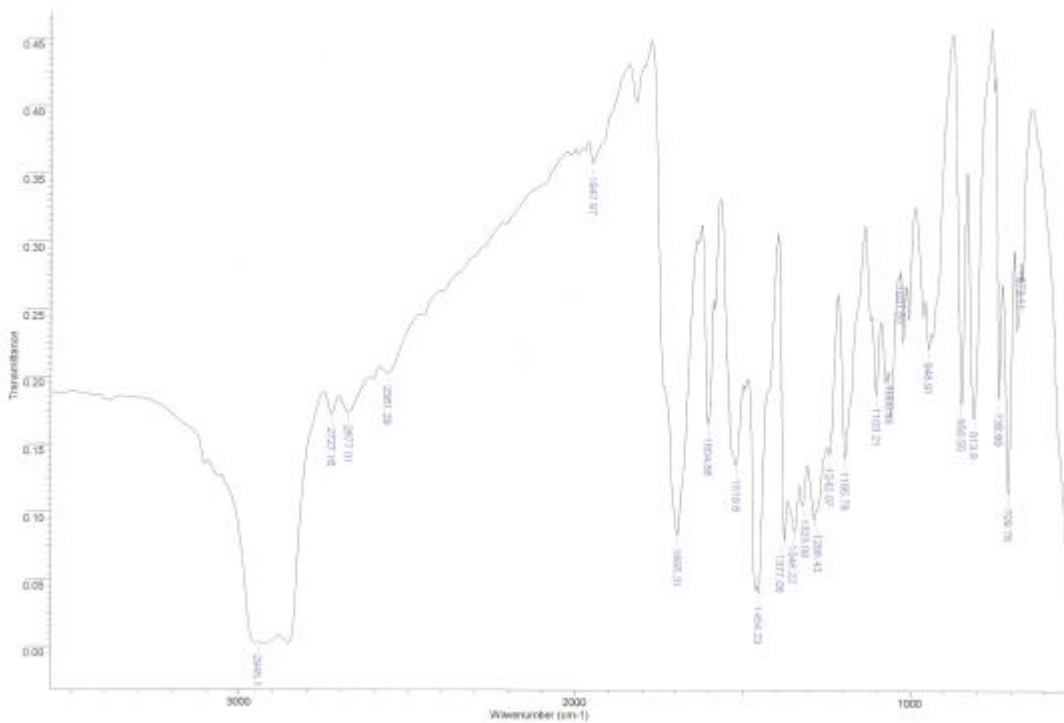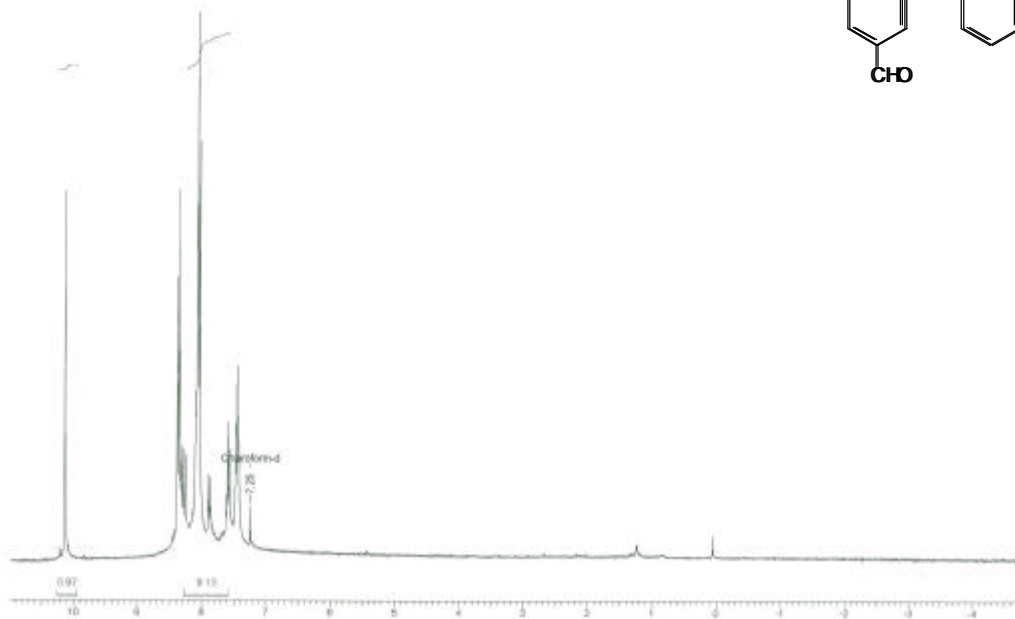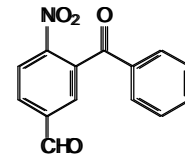
Appendix 5.3 ^{1}H NMR and IR spectra for 3-formyl-6-nitrobenzophenone

CHAPTER-6
SELECTIVE OXIDATION OF ETHYLBENZENE TO ACETOPHENONE AND DIPHENYLMETHANE TO BENZOPHENONE BY O_2 OVER MnO_4^{-1}-EXCHANGED Mg-Al-HT

CHAPTER‑6

SELECTIVE OXIDATION OF ETHYLBENZENE TO ACETOPHENONE AND DIPHENYLMETHANE TO BENZOPHENONE BY O$_2$ OVER MnO$_4^{-1}$-EXCHANGED Mg-Al-HT

6.1   INTRODUCTION AND OBJECTIVE OF PRESENT WORK

Aromatic ketones viz. acetophenone and benzophenone are important intermediates for perfumes, drugs and pharmaceuticals. These are produced by Friedel-Crafts type acylation of aromatic compound by acid halide or acid anhydride using stoichiometric amount of anhydrous aluminium chloride or other homogeneous acid catalyst. These can also be produced by oxidizing the methylene group attached to aromatic ring by oxidizing agents in stoichiometric amounts (viz. oxidation of ethyl benzene to acetophenone by KMnO$_4$ [4] transition metal (viz. Co, Mn, Cu or Fe) compounds [2,9], oxidation of diphenylmethane to benzophenone by KMnO$_4$ [5], SeO$_2$ [6] or CrO$_3$-SiO$_2$ [7] and oxidation of alkylarenes by KMnO$_4$ supported on Mont-K10 [8]) leading to the formation of a large volume of highly toxic and corrosive waste [1-3]. The major limitation of the homogeneous oxidation process are as follows: reaction conditions are harsh, the product selectivity is poor, often corrosive promoters like bromide anions are used along with the catalyst, the separation of catalyst from the reaction mixture is difficult, the catalyst can't be reused and also a lot of tarry waste is produced. It is, therefore, of great practical interest to develop more efficient easily separable, reusable and environ-friendly catalyst for the production of aromatic ketones. Processes based on hydrocarbon oxidation, particularly using molecular oxygen as an oxidizing agent, are desirable [10].

Recently, K$_2$Cr$_2$O$_7$ supported on alumina [11] and Cr-MCM-41 or 48 [11] have been employed as heterogeneous catalysts for the oxidation by oxygen of ethylbenzene to acetophenone [12-14] and diphenylmethane to benzophenone [11]. However, the leaching of chromium from the catalyst during the reaction, the lengthy induction periods and the rapid deactivation of the reused catalyst are serious problems [14-16]. For developing an environmental-friendly/green process for the production of aromatic ketones, it is necessary to have a non-toxic and reusable solid catalyst, which shows high activity and selectivity in the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone by molecular oxygen in the absence of any solvent and also without significant leaching of its components in the liquid reaction mixture.

The present study was undertaken with the objective of investigating the performance of MnO_4^{-1}-exchanged Mg–Al-hydrotalcites and other hydrotalcite-like catalysts in the solvent-free liquid phase oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone by molecular oxygen. Influence of the Mg/Al ratio of the catalyst and time on their activity/selectivity in the oxidation reaction has also been studied.

6.2 CHARACTERIZATION OF MnO_4^{-1}-EXCHANGED Mg-Al-HT

The hydrotalcite structure of the catalyst was confirmed by XRD (Figure 6.1). The XRD spectra of the Mg–Al–hydrotalcite catalyst, before and after the MnO_4^{-1}–exchange, and also of the MnO_4^{-1}–exchanged Mg–Al–HT catalyst after the oxidation reactions are given in Figure 6.1. The catalysts were also characterized by Infrared spectroscopy. From the results following important observations can be drawn:

- After the MnO_4^{-1}–exchange, the hydrotalcite structure remained intact (Figure 6.1a,b). It even remained intact after the oxidation reaction (Figure 6.1b–d).

- The appearance of an IR band in the region 890–920 cm^{-1} after exchanging the hydrotalcite with aqueous $KMnO_4$ indicated the presence of MnO_4^{-1} anions in the MnO_4^{-1}–exchanged hydrotalcite catalysts [19].

- When the MnO_4^{-1}–exchanged hydrotalcites were treated with an aqueous sodium carbonate solution, a quantitative replacement of the exchanged MnO_4^{-1} anions by carbonate anions was observed.

These observations clearly show that, in the MnO_4^{-1}–exchanged hydrotalcite catalysts, the MnO_4^{-1} anions are located at the anion-exchange positions in the hydrotalcite catalysts. A comparison of the XRD spectra of the catalyst before and after its use in the oxidation reaction (Figure 1b-d) reveals that the hydrotalcite structure of the catalyst is not changed during reaction. The surface area of the catalyst was also not changed significantly after the reaction.
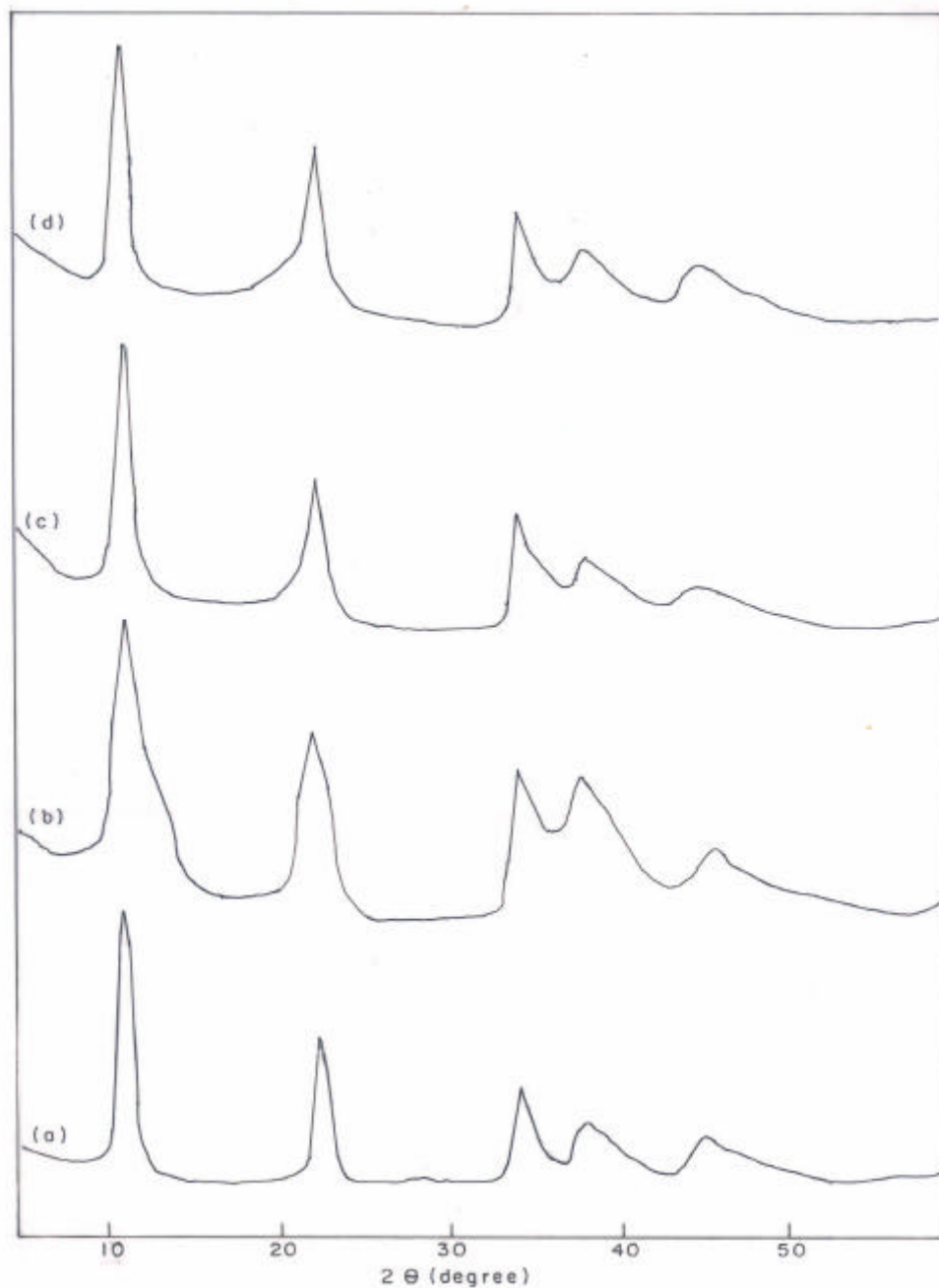
Figure 6.1: XRD spectra of a) 3Mg-Al-hydrotalcite, b) MnO_4^{-1}-3Mg-Al-HT (before the oxidation reaction), c) MnO_4^{-1}-3Mg-Al-HT after the ethylbenzene oxidation, and d) MnO_4^{-1}-3Mg-Al-HT after the diphenylmethane oxidation (MnO_4^{-1} exchange = 0.42 mmol.g^{-1}).

The hydrotalcites (Mg/Al=2?10), before and after $MnO_4^{?1}$?exchange, were also characterized by thermal analysis (Figure 6.2). After the exchange, the DTG / DTA peak for all the Mg-Al-hydrotalcites is shifted towards higher temperature (from 400 to 416 ºC, 395 to 447 ºC, 367 to 422 ºC and 366 to 392 ºC, for the hydrotalcites with a Mg/Al ratio of 2, 3, 5 and 10, respectively), indicating an increase in the thermal stability of the hydrotalcite due to the presence of MnO_4^{-1} anions at anion-exchange sites.
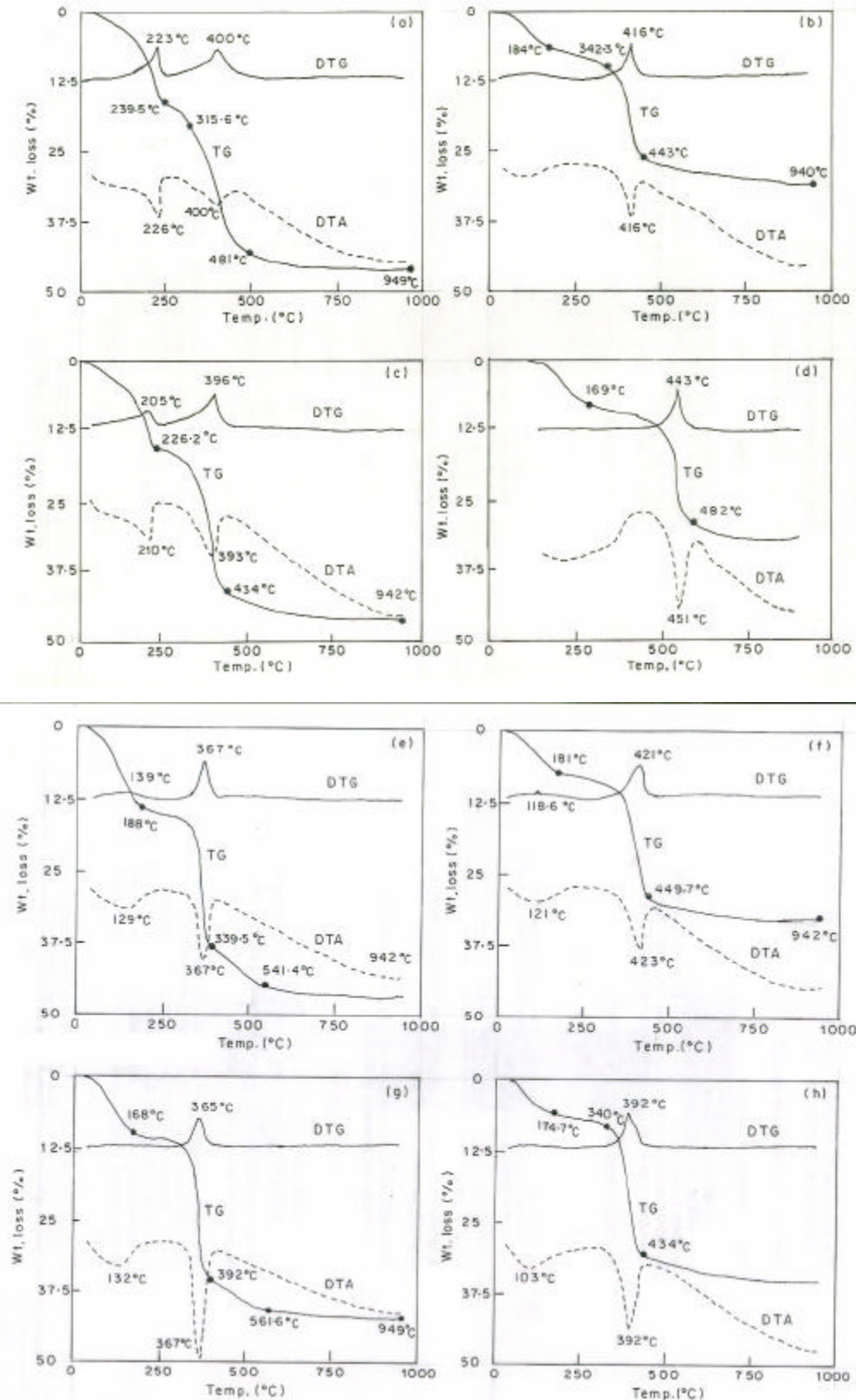
Figure 6.2: TG, DTG and DTA of (a) 2Mg-Al-HT, (b) MnO_4^{-1}-exchanged 2Mg-Al-HT, (c) 3Mg-Al-HT, (d) MnO_4^{-1}-exchanged 3Mg-Al-HT, (e) 5Mg-Al-HT, (f) MnO_4^{-1}-exchanged 5Mg-Al-HT, (g) 10Mg-Al-HT and (h) MnO_4^{-1}-exchanged 10Mg-Al-HT, (heating rate = 10 °C/min).

The surface areas of the MnO_4^{-1}-exchanged Mg-Al-hydrotalcites with Mg/Al ratios of 2, 3, 5 and 10 was 36.3, 31.5, 29.1 and 25.9 $m^2.g^{-1}$ respectively. In all the cases, the thermal stability of the hydrotalcite is increased after the MnO_4^{-1}-exchange.

The hydrotalcite catalysts were also characterized for their basicity and H_2O_2 decomposition activity. The basicity of the catalysts and hydrotalcite was studied by titrating them with non-aqueous benzoic acid using a phenolphthalein indicator (pKa=9.3) [18] and/or by measuring the pH of their suspension in water (0.15 g solid particles in 10 ml deionised water at 27 °C). The H_2O_2 decomposition over the catalysts was studied in a magnetically stirred glass reactor (25 cm^3 capacity) at 27 °C by introducing 1 ml of 30% aqueous H_2O_2 solution in the reactor containing 0.1 g catalyst and 10 ml deionised water and measuring quantitatively the amount of O_2 evolved in the H_2O_2 decomposition reaction ($2H_2O_2 \longrightarrow 2H_2O + O_2$), as a function of time. Results showing the influence of the Mg/Al ratio on the number of basic sites of the hydrotalcite (without MnO_4^{-1}-exchange), on the basicity of the hydrotalcite before and after the MnO_4^{-1}-exchange (measured in terms of the pH of the hydrotalcite or MnO_4^{-1}-exchanged hydrotalcite-water slurry) and also on the H_2O_2 decomposition activity (at 27 °C) of the MnO_4^{-1}-exchanged hydrotalcite are presented in Figure 6.3. The results lead to the following important observations:

- The hydrotalcites without MnO_4^{-1}-exchange showed no H_2O_2 decomposition activity under the same conditions.
- The H_2O_2 decomposition activity and basicity of the hydrotalcite catalyst increased with increasing Mg/Al ratio.
- The pH of the aqueous slurry of Mg-Al-hydrotalcite is increased after the MnO_4^{-1}–exchange of the hydrotalcite.

The above results clearly indicate that the hydrotalcite undergoes an appreciable change in its properties by its MnO_4^{-1} exchange.
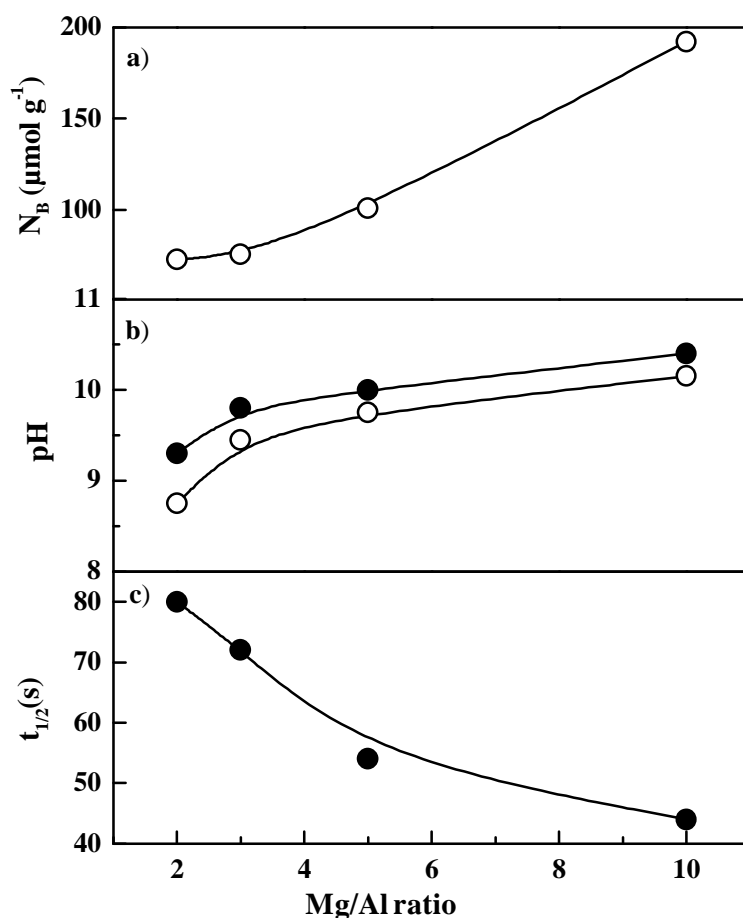
Figure 6.3: Variation with the Mg/Al ratio of a) number of basic sites of Mg-Al-hydrotalcite (N_B), b) pH of aqueous slurry of Mg-Al-hydrotalcite before (?) and after (?) the MnO_4^{-1}–exchange of the hydrotalcite and c) time required for half the H_2O_2 decomposition reaction at 27 °C ($t_{1/2}$). [MnO_4^{-1} exchange = 0.42 mmol.g^{-1}]

6.3 OXIDATION OF METHYLENE GROUP OF AROMATIC COMPOUND OVER MnO_4^{-1}-EXCHANGED HYDROTALCITES

6.3.1 Activity of Different MnO_4^{-1}-Exchanged Hydrotalcites

Results showing the performance of MnO_4^{-1}-exchanged hydrotalcite catalysts are presented in Table 6.1. Plane hydrotalcite catalysts without $KMnO_4$ exchange show very little or no activity for the ethylbenzene-to-acetophenone oxidation. Highest activity was shown by the 3Cu-Cr-HT with a conversion of 3.4 %. Except 3Zn-Cr-HT, 3Cu-Al-HT and 3Cu-Zn-Al-HT having a conversion of 2.2, 0.4 and 0.3 %, no other hydrotalcite showed any catalytic activity for the oxidation reaction. Among all the MnO_4^{-1}-exchanged HT catalysts, Mg-Al-HT showed the best result for the ethylbenzene-to acetophenone oxidation.

Whereas, in the case of diphenylmethane-to-benzophenone oxidation, Mg-Al-HT, Ni-Al-HT, Mg-Fe-HT and Mg-Cr-HT catalysts showed the best results. Also, the other MnO_4^{-1}-exchanged HT catalysts showed good activity for the diphenylmethane oxidation and very little or no activity towards the ethylbenzene oxidation. All the catalysts showed good selectivity (above 97 %) for the oxidation reactions.

Table 6.1: Results on the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone by molecular O_2 using different MnO_4^{-1}-exchanged hydrotalcite catalysts [reaction conditions: substrate = 6 ml, catalyst = 0.6 g, O_2 pressure = 148 kPa, temperature = 130 ºC, time = 5 h].

Catalyst	Amount of MnO_4^{-1} exchanged (mmolg^{-1})	pH of water slurry[a]	Conversion (%)	
			Ethylbenzene	Diphenylmethane
3Mg-Al-HT	0.42	9.8	18.1	26.8
3Ni-Al-HT	0.45	9.3	5.5	27.8
3Mg-Fe-HT	0.40	10	0.0	21.1
3Cu-Al-HT	0.25	7.9	0.8	12.3
3Mn-Al-HT	0.43	8.7	0.0	14.3
3Co-Al-HT	0.13	9.0	0.2	12.3
3Mg-Cr-HT	1.25	10.3	0.2	25.5

[a] 0.15 g catalyst in 10 ml distilled water

6.3.2   Performance of MnO_4^{-1}-Exchanged Mg-Al-HT

6.3.2.1 Oxidation of Methylene Group of Aromatic Compounds

Results showing the solvent-free oxidation of different aromatic hydrocarbons containing a methylene group (viz. ethylbenzene, diphenylmethane and n‑propylbenzene) by molecular oxygen over MnO_4^{-1}-exchanged-10Mg-Al-hydrotalcite are presented in Table 6.4. In the oxidation, the reactivity of the methylene group attached to the aromatic ring depends strongly on the other group (viz. methyl, ethyl and phenyl) attached to the

methylene group. The order for TOF in the oxidation of different aromatic compounds is ethylbenzene > diphenylmethane > n‑propylbenzene.

Table 6.2: Solvent‑free oxidation by O_2 of different aromatic compounds containing a methylene group over MnO_4^{-1}(MnO_4^{-1} exchange = 0.42 mmol.g^{-1})‑exchanged Mg‑Al hydrotalcite (Mg/Al=10) (reaction time: 5 h)

Aromatic compound	Conversion (%)	Selectivity for carbonyl compound (%)	TOF[a] (h^{-1})
Ethylbenzene	22.6	98.4	9.0
Diphenylmethane	27.4	100	8.0
n‑Propylbenzene	10.3	90.5	3.6

[a] Turn over frequency (number of substrate molecules converted per permagnate anion per hour)

6.3.2.2 Effect of Mg/Al ratio

Results showing the influence of Mg/Al ratio of the MnO_4^{-1}–exchanged Mg-Al-HT (MnO_4^{-1} exchange = 0.42 mmol.g^{-1}) on its performance in the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone are presented in Figure 6.4 and Figure 6.5, respectively. The results lead to the following important observations:

- The MnO_4^{-1}–exchanged Mg-Al-hydrotalcite catalyst with an Mg/Al ratio of 10 shows high activity and selectivity (above 95%) in the oxidation by O_2 of ethylbenzene to acetophenone and diphenylmethane to benzophenone (Figure 6.4a and Figure 6.5a).
- In both cases, the catalytic activity increases with increasing Mg/Al ratio in the catalyst (Figure 6.4b and Figure 6.5b) and there is no induction period. This is consistent with earlier observations in the oxidation of benzyl alcohol and benzaldehyde [20].

A comparison of the results in Figure 6.4b and Figure 6.5b with those in Figure 6.3 indicates a good correlation of the catalytic activity for both the ethylbenzene and diphenylmethane oxidation reactions with the H_2O_2 decomposition activity of the catalyst (Figure 6.3a), with the pH of the catalyst (when it is slurred in pure water) (Figure 6.3b) or with the basicity of the hydrotalcite used for the catalyst. Like the catalytic oxidation

activity, the H_2O_2 decomposition activity and pH of the catalyst and the basicity are increased with increasing Mg/Al ratio (Figure 6.3). However, the basicity has little or no effect on the product selectivity.
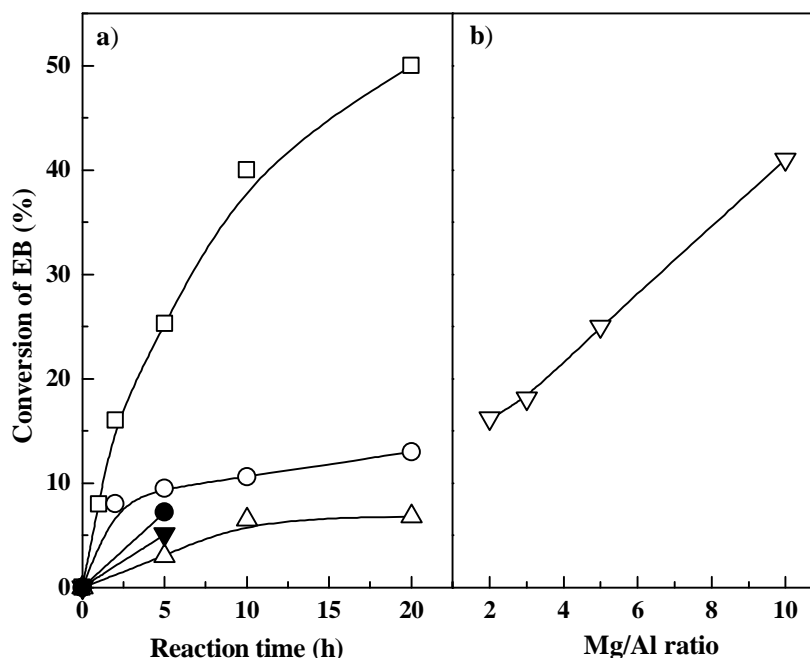
Figure 6.4:   Results showing the oxidation of ethylbenzene to acetophenone over MnO_4^- ^{1}(MnO_4^{-1} exchange = 0.42 mmol.g^{-1})-exchanged Mg-Al-hydrotalcite. a) Effect of the reaction time on the conversion of ethylbenzene (EB) for the catalyst with Mg/Al=10 (?), when the catalyst was removed after 1.0 h (?), in the absence of catalyst (**?**), the hydrotalcite without MnO_4^{-1} anions (**?**), and in the presence of equivalent amount of $KMnO_4$ (?). b) Effect of the Mg/Al ratio of the catalyst on the conversion (reaction time=10h) (**?**). Selectivity for acetophenone for all the catalysts= $97 \pm 2\%$.

        Results showing the influence of reaction time in the oxidation of ethyl benzene to acetophenone and diphenylmethane to benzophenone over MnO_4^{-1} -exchanged Mg-Al-hydrotalcite catalyst with Mg/Al=10 are presented in Figure 6.4a and 6.5a, respectively. The results lead to the following important observations:

- The oxidation reactions occur even in the absence of catalyst, but very slowly (Figure 6.4a). In the presence of an amount of $KMnO_4$, equivalent to the MnO_4^{-1}

anions present in the catalyst, the reaction also occurs but at a much slower rate than in the presence of the catalyst (Figure 6. 4a).

- After the removal by filtration of the catalyst from the reaction mixture while hot, the reaction rate is drastically reduced and the reaction proceeds at a very slow rate (Figure 6.4a).

These observations reveal that the catalytic activity of $KMnO_4$ is drastically increased by the immobilization of MnO_4^{-1} anions at anionic exchange sites in the hydrotalcite and that the oxidation reaction catalyzed by the solid catalyst is truly heterogeneous. No leaching of permanganate from the catalyst was observed in both the oxidation reactions.
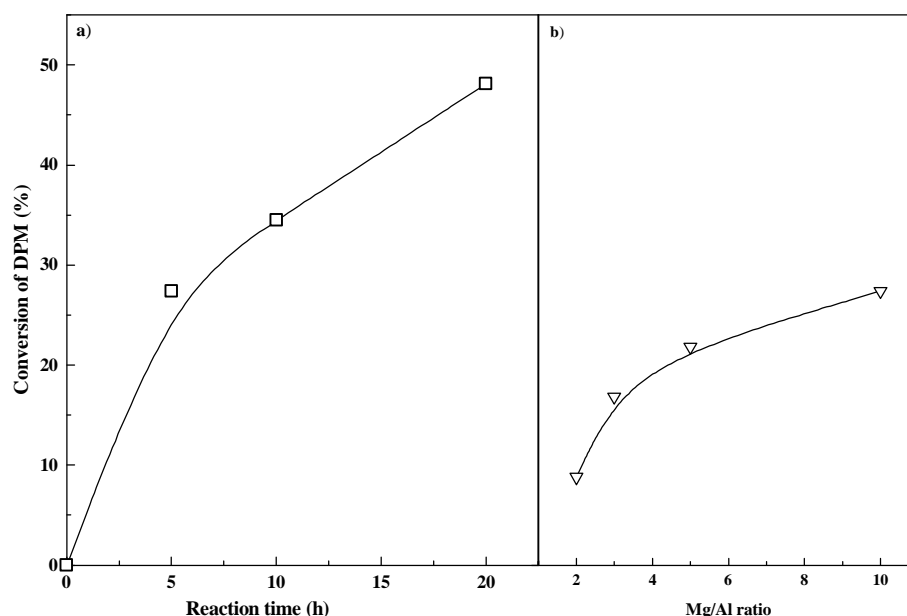
Figure 6.5: Oxidation of diphenylmethane to benzophenone over MnO_4^{-1}(MnO_4^{-1} exchange = 0.42 mmol.g^{-1})-exchanged Mg-Al-hydrotalcite. a) Effect of the reaction time on the conversion of diphenylmethane (DPM) for the catalyst with Mg/Al=10. b) Effect of the Mg/Al ratio of the catalyst on the conversion (reaction time=5h). Selectivity for benzophenone for all the catalysts= $99 \pm 1\%$.

6.3.2.3 Reusability of MnO_4^{-1}-Exchanged 10Mg-Al-HT

Results showing the reusability of the MnO_4^{-1}(MnO_4^{-1} exchange = 0.42 mmolg^{-1})-Exchanged Mg-Al-hydrotalcite (Mg/Al=10) in the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone (reaction time = 5 h) are presented in Table 6.3. The oxidation reaction catalyzed by this catalyst is truly heterogeneous one. No

leaching of MnO_4^{-1} anions was observed during the number of reuses of the catalyst. The performance of the catalyst is markedly improved in its subsequent reuse in the oxidation reactions probably due to the removal of moisture from the catalyst.

Table 6.3: Results showing reusability of the MnO_4^{-1}-exchanged Mg-Al-HT (Mg/Al=10) in the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone (reaction time = 5 h).

No. of uses of the catalyst	Ethylbenzene oxidation		Diphenylmethane oxidation	
	Conversion (%)	Selectivity for acetophenone (%)	Conversion (%)	Selectivity for benzophenone (%)
First	22.7	98.0	26.1	98.2
Second	32.5	98.0	32.3	98.4
Third	34.6	97.7	38.2	98.1
Fourth	34.6	98.0	38.0	98.3

The above results clearly tell us that the catalyst is highly active, selective and reusable towards the oxidation of ethylbenzene to acetophenone and diphenylmethane to benzophenone.

The oxidation reaction is expected to involve a mechanism similar to that described by Bukharkina and Digurov [21] for manganese catalyzed ethylbenzene oxidation by molecular oxygen in non-polar media. It is initiated by the direct interaction of the hydrocarbon with oxygen, leading to the formation of an intermediate hydroperoxide species, which is subsequently decomposed to the corresponding carbonyl compound and water. The presence of hydroperoxide in the reaction products was however not observed, most probably because of its fast catalytic decomposition; the catalyst has very high peroxide decomposition activity (Figure 2c).

6.3 CONCLUSIONS

From this investigation, following important conclusions have been drawn:

1. A stoichiometric $KMnO_4$ reagent, commonly employed for oxidations, can be transformed into a highly active, stable, easily separable and reusable

environmental-friendly catalyst for the oxidation of ethylbenzene to acetophenone, diphenylmethane to benzophenone or similar reactions by immobilizing MnO_4^{-1} anions in highly basic Mg-Al-hydrotalcite at its anion-exchange sites.

2. The oxidation activity, H_2O_2 decomposition activity and basicity of the catalyst are increased with increasing the Mg/Al ratio in the hydrotalcite, indicating a good correlation among them.

3. The oxidation reaction catalyzed by this catalyst is truly heterogeneous one, without leaching of the exchanged $MnO_4^{?1}$ anions.

4. The thermal stability of the hydrotalcite is increased after the $MnO_4^{?1}$? exchange.

6.4   REFERENCES

[1]   P.H. Groggins and R. H. Nagel, Ind. Eng. Chem. 26 (1934) 1313.

[2]   H. J. Sanders, H. F. Keag and H. S. McCullough, Ind. Eng. Chem. 45 (1953) 2.

[3]   G. A. Olah Friedel-Crafts and Related Reactions, Wiley-Interscience, New York 1963.

[4]   C. F. Cullis and J. W. Ladbury, J. Chem. Soc. (1955) 2850.

[5]   R. Gopalan and R. W. Sugumar, Indian J. Chem. 16A (1978) 198.

[6]   N. D. Valechha and A. Pradhan, J. Indian Chem. Soc. 61 (1984) 909.

[7]   S. D. Borkar and B. M. Khadilkar, Syn. Commun., 29 (1999) 4295.

[8]   A. Shaabani, A. Bazgir, F. Teimouri and D. G. Lee, Tet. Lett., 43 (2002) 5165.

[9]   (a) B. B. Wentzel, M. P. J. Donners, P. L. Alsters, M. C. Feiters and R. J. M. Nolte, Tetrahedron, 56 (2000) 7797. (b) V. F. Gaevskii and N. P. Evmenenko, Ukr. Khim. Zh. (Russ. Ed.), 48 (1982) 160. (c) S. N. Vyas, S. R. Patwardhan and T. N. Pal, Indian Chem. Engr., 28 (1986) 44. (d) G. B. Shul'pin and M. M. Kats, React. Kinet. Catal. Lett., 41 (1990) 239. (e) J. H. Clark, S. Evans and J. R. L. Smith, Spec. Publ. –R. Soc. Chem., 216 (1998) 187.

[10]   Y. Ishii, S. Sakaguchi and T. Iwahama, Adv. Syn. Catal., 343 (2001) 393 and references cited therein.

[11]   J. H. Clark, A. P. Kybett, P. London, D. J. Macquarrie and K. Martin, J. Chem. Soc. Chem. Commun. (1989) 1355.

[12]   A. Sakthivel, S. E. Dapurkar and P. Selvam, Catal. Lett., 77 (2001) 155.

[13]   J. H. Clark, P. London, S. J. Barlow, C. V. A. Duke and K. Martin, Chemistry & Industry, (1991) 800.

[14] I. C. Chisem, K. Martin, M. T. Shieh, J. Chisen, J. H. Clark, R. Jachuck, D. J. Macquarrie, J. Rafelt, C. Ramshaw and K. Scott, Org. Process Res. Dev. 1 (1997) 365.

[15] H. E. B. Lempers and R. A. Sheldon, J. Catal. 175 (1998) 62.

[16] I. W. C. E. Arends and R. A. Sheldon, Appl. Catal. A: 212 (2001) 175.

[17] E. Lopez-Salinas, M. Garcia-Sanchez, M. L. Ramon-Garcia and I. Schiffer, J. Porous Mater. 3 (1996) 169.

[18] F. M. P. R. Van Laar, D. E. de Vos, F. Pierard, A. Kirsch-De Mesmaeker, L. Fiermans and P. A. Jacobs, J. Catal. 197 (2001) 139.

[19] C. N. R. Rao in Chemical Application of Infrared Spectroscopy Academic Press Inc., New York, (1963) 337.

[20] V. R. Choudhary, D. K. Dumbre, V. S. Narkhede, S. K. Jana, Catal. Lett., 86 (2003) 229.

[21] T. V. Bukharina and N. G. Digurov, Org. Proc. Res. Dev., 8 (2004) 320.

CHAPTER-7

EPOXIDATION OF STYRENE TO STYRENE OXIDE USING METAL OXIDES AND SUPPORTED METAL OXIDE CATALYSTS

CHAPTER-7

EPOXIDATION OF STYRENE TO STYRENE OXIDE USING METAL OXIDES AND SUPPORTED METAL OXIDE CATALYSTS

7.1   INTRODUCTION AND OBJECTIVE OF PRESENT WORK

Styrene oxide is an important organic intermediate in the synthesis of fine chemicals and pharmaceuticals. It is traditionally produced by epoxidation of styrene using stoichiometric amounts of peracids as an oxidizing agent [1]. However, peracids are very expensive, hazardous to handle, non?selective for the epoxide formation and also lead to formation of undesirable products, creating a lot of waste. In order to overcome these limitations, a number of studies have been reported on the epoxidation of styrene over solid catalysts viz. Ti/SiO$_2$ [2-4], TS-1 [4-7], Ti-MCM-41 [7], Fe or V/SiO$_2$ [4], TBS-2 and TS-2 [8] catalysts, using TBHP [2], H$_2$O$_2$ [3-5, 7,8] or urea- H$_2$O$_2$ adduct [6], as an oxidizing agent. With H$_2$O$_2$ as an oxidizing agent, although the styrene conversion was very high, the selectivity for styrene oxide was very poor. On the other hand, with TBHP [2] and urea-H$_2$O$_2$ adduct [6] as oxidizing agents, high styrene oxide selectivity (> 80%) was observed, but only at a low styrene conversion (9.8 and 17.7%, respectively). Recently Choudhary and coworkers [9,10] used bohemite or alumina as a catalyst for the selective epoxidation of styrene by anhydrous H$_2$O$_2$ with a continuous removal of the reaction water. Very recently, they have also reported a number of highly active supported nano-gold catalysts for the selective epoxidation of styrene by TBHP [11-15].

Earlier, water-soluble compounds of transition metal (viz. sodium tunstate, molybdate and vanadate) have been used as homogeneous catalysts in the epoxidation of olefinic compounds [16]. It is interesting to know whether transition metal oxides can be used as active/selective heterogeneous catalysts for the epoxidation of styrene and other olefins. This investigation was undertaken for screening different transition and other metal oxides for ascertaining a possibility of their use in the epoxidation of styrene to styrene oxide. In the present investigation, performance of various metal oxides (alkaline and rare earth metal oxides, Group IIIa and transition metal oxides and supported BaO, TlO$_x$, NiO and CuO catalysts for the epoxidation of styrene to styrene oxide by TBHP has been studied. A detailed investigation on the performance of CuO/Ga$_2$O$_3$ catalyst in the epoxidation of styrene has also been carried out. The preparation or source of the metal

oxides and procedure for their evaluation in the epoxidation has been given earlier (Chapter 2).

7.2 EPOXIDATION OF STYRENE OVER ALKALINE EARTH METAL OXIDES

Results showing the performance of alkaline earth metal oxides in the epoxidation of styrene to styrene oxide by anhydrous TBHP is presented in Table 7.1. The results lead to the following important conclusions:

- Among the alkaline earth metal oxides, the BaO catalyst showed the best performance, the highest styrene oxide yield (32 %) in the epoxidation.

- The CaO catalyst showed the lowest performance (the highest conversion of TBHP but less than <1% conversion of styrene). The observed high TBHP conversion is due to the decomposition of TBHP over the catalyst (with the evolution of oxygen) according to the reaction:

$$(CH_3)_3COOH \quad ? \quad (CH_3)_3COH + 0.5O_2$$
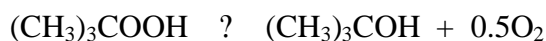
Table 7.1: Results of the epoxidation of styrene-to-styrene oxide by anhydrous TBHP over alkaline earth metal oxides (reaction conditions: styrene = 10 mmol, TBHP = 15 mmol, catalyst = 0.1 g, bath temp. = 107 ?C, time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
Without catalyst	16.5	7.5	11.0	7.7	1.7	81.7	0.8	1.3
MgO	28.0	15.9	19.8	7.0	4.9	68.2	3.2	4.3
CaO	45.3	0.9	-	-	-	100	? 0.0	? 0.0
SrO	24.2	15.2	60.2	8.0	0	31.8	9.2	10.4
BaO	32.1	40.7	78.7	8.9	1.1	11.2	32.0	35.7

This catalyst in fact inhibits the styrene oxidation; even in the absence of any catalyst the styrene conversion is much higher than obtained in the presence of the CaO catalyst.

- The SrO catalyst also showed a good styrene oxide selectivity (60.2 %) but at a low conversion of styrene (15.2 %).

For their styrene epoxidation performance, the alkaline earth metal oxide catalysts show the following order: BaO > SrO > MgO > without any catalyst > CaO.

7.3   EPOXIDATION OF STYRENE OVER Gr.IIIa METAL OXIDES

Results showing the performance of Gr.IIIa metal oxides in the epoxidation of styrene to styrene oxide by anhydrous TBHP are presented in Table 7.2. The results lead to the following important conclusions:

- Among the Gr.IIIa metal oxides, Tl_2O_3 showed the best activity (styrene conversion of 56.5 %) and epoxide selectivity (53.9 %) in the epoxidation.

- The Al_2O_3, Ga_2O_3 and In_2O_3 catalysts show very low activity for the styrene conversion in the epoxidation reaction. These catalysts showed even lower styrene conversion activity and/or epoxide selectivity than that obtained in the absence of any catalyst (Table 7.1); the products formed are mainly the secondary oxidation products-benzoic acid and phenylacetic acid. However the conversion of TBHP over these catalysts is quite high.

Table 7.2:   Results of the epoxidation of styrene-to-styrene oxide by anhydrous TBHP over Gr.IIIa metal oxides as catalyst (reaction conditions: styrene = 10 mmol, TBHP = 15 mmol, catalyst = 0.1 g, bath temp. = 107 ?C, time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
Al_2O_3	20.0	9.2	8.0	6.5	0	95.5	0.7	1.3
Ga_2O_3	30.4	7.0	3.1	2.4	0	94.5	0.2	0.4
In_2O_3	41.8	8.6	4.5	3.0	0	92.5	0.4	0.7
TlO_x	44.7	56.5	53.9	28.6	7.5	9.9	30.5	46.6

The high epoxidation activity of Tl_2O_3 catalyst seems to be attributed to both its very high basicity and reducibility (i.e. high value of standard reduction potential, E (Tl^{3+}/Tl^{+1}) = +1.25 V and E (Tl^{3+}/Tl^o) = +0.72 V). The epoxidation over Tl_2O_3 may involve a redox mechanism. However, further detailed work is necessary to understand the reaction mechanism. Nevertheless, thallium oxide is highly toxic and hence its use as a catalyst or in the catalyst for the epoxidation is very much limited because of its high toxicity.

7.4 EPOXIDATION OF STYRENE OVER RARE EARTH METAL OXIDES

Results showing the performance of rare earth metal oxides in the epoxidation of styrene to styrene oxide by anhydrous TBHP are presented in Table 7.3.

Table 7.3: Results of the epoxidation of styrene-to-styrene oxide by anhydrous TBHP over rare earth metal oxides (reaction conditions: styrene = 10 mmol, TBHP = 15 mmol, catalyst = 0.1 g, bath temp. = 107 ºC, time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
CeO_2	52.4	28.7	38.9	6.0	4.2	50.7	11.2	12.9
Tb_2O_3	10.5	9.8	48.3	8.2	0	43.5	4.7	5.5
Nd_2O_3	23.2	20.0	62.8	8.0	1.1	28.0	12.6	14.2
Gd_2O_3	16.0	15.7	60.0	10.8	0	29.0	9.4	11.1
Sm_2O_3	14.2	9.8	48.6	5.2	0	46.1	4.8	5.3
Er_2O_3	13.0	7.4	60.0	3.6	0.5	35.8	4.4	4.7
Eu_2O_3	12.1	9.8	50.2	5.3	0	44.4	4.9	5.4
Yb_2O_3	21.7	10.9	4.1	2.9	0	88.3	0.4	0.7
La_2O_3	19.5	3.2	69.0	4.7	0	26.3	2.2	2.4

From the results following important observations can be made:

- Among the rare earth metal oxides, the CeO_2, Nd_2O_3 and Gd_2O_3 catalysts showed a good performance in the epoxidation of styrene. When compared for the styrene oxide yield, the three catalysts showed a somewhat comparable performance. However, they differ in their styrene conversion activity and epoxide selectivity; the CeO_2 catalyst is more active but less selective for the epoxidation. Also, the Nd_2O_3 and Gd_2O_3 showed higher styrene oxide selectivity (62.8 and 60 %, respectively) but at a low styrene conversion (20 and 15.7 %, respectively).

- The Er_2O_3 and La_2O_3 also showed high epoxide selectivity (60 and 69 %, respectively) but at a very low conversion of styrene (7.4 and 3.2 %, respectively). The Yb_2O_3 showed very poor epoxide selectivity and also low styrene conversion activity. The other rare earth oxides Tb_2O_3, Sm_2O_3 and Eu_2O_3 catalysts showed good epoxide selectivity (about 50 %) but low atyrene conversion activity (below <10 % conversion).

The rare earth oxide catalysts show following order for their performance (styrene oxide yield) in the epoxidation : $Nd_2O_3 > CeO_2 > Gd_2O_3 > Eu_2O_3 > Sm_2O_3 > Tb_2O_3 > Er_2O_3 > La_2O_3 > Yb_2O_3$.

7.5 EPOXIDATION OF STYRENE OVER OTHER TRANSITION METAL OXIDES

Results showing the performance of other transition metal oxides in the epoxidation of styrene to styrene oxide by anhydrous TBHP are presented in Table 7.4. The results can be summarized as follows:

- Among the transition metal oxide catalysts, the NiO, CuO, CoO and MoO_3 showed both high activity and high selectivity in the epoxidation. For the styrene oxide yield obtained, the catalysts shows the following order: NiO (46.6 %) > CuO (35.9 %) > CoO (34.6 %) > MoO_3 (32.0 %).

- The Cr_2O_3 catalyst also showed good activity (44.4 % styrene conversion and selectivity (47.6 % epoxide selectivity) in the epoxidation; it showed much better performance than any of the rare earth oxides described earlier. It also showed high selectivity for the formation of phenylacetaldehyde (25.3 %).

- The Fe_2O_3, ZnO and U_3O_8 catalysts showed low activity and/or selectivity in the epoxidation. The TiO_2 catalyst showed very low activity and also poor

selectivity in the epoxidation. Whereas, the MnO$_2$ catalyst showed no selectivity for both the epoxide and the phenylacetaldehyde; it catalyze only the formation of benzaldehyde and benzoic acid from styrene.

Table 7.4: Results of the epoxidation of styrene-to-styrene oxide by anhydrous TBHP over transition metal oxides as catalyst (reaction conditions: styrene = 10 mmol, TBHP = 15 mmol, catalyst = 0.1 g, temperature = 107 ?C, time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
TiO$_2$	12.3	5.4	25.5	5.5	4.0	65.0	1.4	1.7
Cr$_2$O$_3$	83.6	44.4	47.6	25.3	11.9	15.1	21.1	32.4
MnO$_2$	100	27.3	0	0	43.0	57.0	0	0
Fe$_2$O$_3$	48.1	17.9	60.6	5.0	2.5	31.8	10.8	11.7
CoO	38.2	47.3	73.1	5.5	0.1	21.2	34.6	37.2
NiO	75.8	51.7	86.2	3.8	1.7	8.3	44.6	46.5
CuO	81.0	56.9	63.1	18.3	1.8	16.7	35.9	46.3
ZnO	20.7	17.2	45.0	7.1	0	47.8	7.7	9.0
MoO$_3$	35.1	42.0	76.2	10.9	0	9.6	32.0	36.6
U$_3$O$_8$	28.2	20.2	35.0	5.7	9.8	49.5	7.1	8.2

7.6   EPOXIDATION OVER SUPPORTED METAL OXIDE CATALYSTS

Since the BaO, TlO$_x$, CuO and NiO showed highly promising performance in the epoxidation, it was interesting to evaluate the performance of these metal oxide catalysts after supporting them on commonly used catalyst supports (e.g. SiO$_2$, Al$_2$O$_3$, Si-MCM-41, etc.). All the supported metal oxide catalysts were prepared by the impregnation technique described earlier (Chapter 2). The loading of metal oxide on the support in all the supported metal oxide catalysts was kept the same (2.0 mmolg^{-1}). Results showing the performance of

different supported metal oxide catalysts on the activity/selectivity for the epoxidation of styrene-to-styrene oxide by anhydrous TBHP are presented in Table 7.5-7.8.

7.6.1 Performance of Supported TlO$_x$ Catalyst

The supported TlO$_x$ catalyst also shows good performance in the epoxidation. The styrene oxide yield obtained with the TlO$_x$ supported on Si-MCM-41, Al$_2$O$_3$ and Ga$_2$O$_3$ is even higher than that of the unsupported TlO$_x$ (Table 7.5). The best performance is however shown by the Ga$_2$O$_3$ supported TlO$_x$ catalyst for anhydrous TBHP as an oxidizing agent. However, when aqueous TBHP is used, the Al$_2$O$_3$ and Si-MCM-41 supported TlO$_x$ catalysts showed much better performance in the epoxidation (Table 7.6).

Table 7.5: Performance of supported TlO$_x$ and BaO catalysts for the epoxidation of styrene by anhydrous TBHP (reaction conditions: styrene = 1.2 ml (10 mmol), TBHP = 15 mmol, catalyst = 0.1 g, temp. = under reflux, reaction time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
TlO$_x$/SiO$_2$	24.1	39.7	74.5	1.6	1.8	22.0	29.6	30.2
TlO$_x$/In$_2$O$_3$	23.7	36.3	69.8	1.5	0.8	27.8	25.3	25.9
TlO$_x$/Ga$_2$O$_3$	46.2	64.6	68.0	2.1	0	29.8	43.9	45.3
TlO$_x$/Al$_2$O$_3$	34.0	56.0	68.3	1.9	0	29.7	38.2	39.3
TlO$_x$/ Si-MCM-41	31.8	53.8	62.6	2.2	15.6	22.0	33.7	34.9
BaO/SiO$_2$	29.0	25.0	18.0	0.2	0.6	79.2	4.5	5.1
BaO/In$_2$O$_3$	28.6	23.6	36.2	3.8	2.0	58.0	8.5	9.4
BaO/Ga$_2$O$_3$	45.3	49.3	58.0	1.2	6.0	34.9	28.6	29.2
BaO/Al$_2$O$_3$	40.2	25.5	30.0	8.7	1.3	60.0	7.7	9.7
BaO/ Si-MCM-41	45.6	27.4	30.0	5.6	4.4	60.0	8.2	9.8

7.6.2 Performance of Supported BaO Catalyst

A comparison of the results in Tables 7.1, 7.5 and 7.6 indicates that the unsupported BaO catalyst shows better performance as compared to the supported BaO catalysts.

Table 7.6: Comparison of the performance of supported TlO_x and BaO catalysts for the epoxidation of styrene by aqueous TBHP (reaction conditions: styrene = 1.2 ml (10 mmol), TBHP = 15 mmol, catalyst = 0.1 g, temp. = reflux, reaction time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
TlO_x/SiO_2	27.3	26.9	68.0	1.9	6.1	23.9	18.2	18.8
TlO_x/In_2O_3	23.4	31.5	77.6	1.7	5.6	14.9	24.4	25.0
TlO_x/Ga_2O_3	23.1	38.3	73.1	3.4	7.6	15.9	28.0	29.3
TlO_x/Al_2O_3	30.6	60.2	67.1	2.1	4.9	25.9	40.4	41.6
$TlO_x/$ Si-MCM-41	100	62.2	64.0	1.6	2.2	32.2	40.0	40.8
BaO/SiO_2	45.0	41.8	57.2	0.7	5.6	36.5	23.9	24.2
BaO/In_2O_3	18.3	31.0	40.2	6.8	0.3	52.7	12.5	14.6
BaO/Ga_2O_3	58.6	40.1	56.1	0.6	2.3	41.1	22.5	22.7
BaO/Al_2O_3	32.4	20.4	41.0	6.5	2.5	50.0	8.4	9.5
$BaO/$ Si-MCM-41	48.0	30.8	36.2	3.1	2.7	58.0	11.1	12.1

7.6.3 Performance of Supported NiO Catalyst

The supported NiO catalysts particularly, the SiO_2 and In_2O_3 supported NiO catalysts showed good performance in the epoxidation even when aqueous TBHP is used as an oxidizing agent (Table 7.8).

Table 7.7: Comparison of the performance of supported CuO and NiO catalysts for the epoxidation of styrene by anhydrous TBHP (reaction conditions: styrene = 1.2 ml (10 mmol), TBHP = 15 mmol, catalyst = 0.1 g, temp. = reflux, reaction time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
CuO/SiO$_2$	29.3	58.2	77.1	1.4	0.8	20.6	44.9	45.7
CuO/In$_2$O$_3$	31.0	65.2	73.7	10.6	2.0	13.6	48.1	55.0
CuO/Ga$_2$O$_3$	26.5	48.5	63.9	17.9	1.5	16.5	31.0	39.7
CuO/Al$_2$O$_3$	35.1	26.6	45.0	9.0	17.6	28.3	12.0	14.4
CuO/ Si-MCM-41	92.7	61.4	53.3	13.1	7.6	26.0	32.7	40.8
NiO/SiO$_2$	38.2	49.8	61.9	1.3	1.0	35.8	30.8	31.5
NiO/Ga$_2$O$_3$	25.8	31.8	28.0	6.4	0.3	65.3	8.9	10.9
NiO/Al$_2$O$_3$	45.2	30.7	28.9	5.0	0.4	65.7	8.9	10.4
NiO/ Si-MCM-41	26.7	22.5	30.0	7.9	0	62.1	6.8	8.5

7.6.4 Performance of Supported CuO Catalyst

A comparison of the supported and unsupported CuO catalysts (Table 7.4, 7.7 and 7.8) shows that the In$_2$O$_3$ and Ga$_2$O$_3$ supported CuO catalysts show very good performance when the TBHP used in the epoxidation was anhydrous and aqueous, respectively. However, the SiO$_2$ supported CuO catalyst showed very good performance for both the aqueous and anhydrous TBHP.

Among all the unsupported and the supported metal oxide catalysts, the CuO/Ga$_2$O$_3$ showed the best performance (57.5 % styrene oxide yield) in the epoxidation of styrene by aqueous TBHP. However, the same catalyst showed a lower performance (31.0 % styrene oxide yield) when anhydrous TBHP was used instead of aqueous TBHP.

Table 7.8: Comparison of the performance of supported CuO and NiO catalysts for the epoxidation of styrene by aqueous TBHP (reaction conditions: styrene = 1.2 ml (10 mmol), TBHP = 15 mmol, catalyst = 0.1 g, temp. = reflux, reaction time = 3 h).

Catalyst	Conversion (%)		Selectivity (%)				Yield (%)	
	TBHP	Styrene	SO	PA	Bzh	Other products	SO	SO+PA
CuO/SiO$_2$	31.0	61.7	73.1	1.3	10.8	14.7	45.1	45.9
CuO/In$_2$O$_3$	35.5	70.2	35.0	5.7	12.9	46.3	24.6	28.6
CuO/Ga$_2$O$_3$	27.8	73.6	78.1	3.1	1.2	17.4	57.5	59.8
CuO/Al$_2$O$_3$	32.0	43.0	68.8	7.0	5.3	18.8	29.6	32.6
CuO/ Si-MCM-41	51.5	32.9	15.0	3.6	8.2	76.1	49.4	61.2
NiO/SiO$_2$	34.2	48.8	77.7	0.8	4.3	17.2	37.9	38.3
NiO/In$_2$O$_3$	48.6	61.9	60.1	1.1	13.5	25.3	37.2	37.9
NiO/Ga$_2$O$_3$	25.0	55.8	51.3	0.6	7.0	41.1	28.6	29.0
NiO/Al$_2$O$_3$	32.6	55.2	52.2	0.7	5.9	41.2	28.8	29.2
NiO/ Si-MCM-41	56.5	44.0	62.7	1.0	7.5	28.8	27.6	28.0

7.7   COMPARISON OF THE SUPPORTED/UNSUPPORTED METAL OXIDE CATALYSTS WITH THE EARLIER REPORTED ONES

The promising supported and unsupported metal oxide (TlO$_x$, BaO, CuO and NiO) catalysts are compared with the earlier reported catalysts for their turn-over-frequency (TOF) in the epoxidation of styrene in Table 7.9. The TOF values are estimated as the rate of styrene oxide produced per gram of the catalyst per hour.

It is interesting to note from the comparison in Table 7.9 that the metal oxides and supported metal oxide catalysts show the performance comparable or even better than the earlier reported costly solid catalysts. The CuO/Ga$_2$O$_3$ showed the highest TOF in the epoxidation using aqueous TBHP.

Table 7.9: Comparison of different solid catalysts used in the epoxidation of styrene to styrene oxide

Catalyst	Oxidizing agent used	TOF[a] $(mmol.g^{-1}.h^{-1})$	Ref.
Ti/SiO$_2$	TBHP	12.9	[3]
Si/Ti/SiO$_2$	TBHP	6.9	[3]
TS-1	H$_2$O$_2$ (Aq.)	0.09	[5]
TS-1	Urea-H$_2$O$_2$ adduct	0.62	[6]
?-Al$_2$O$_3$	Anhy. H$_2$O$_2$	2.6	[9]
Ti-HMS	TBHP (Aq.)	11.7	[17]
Au/MgO	TBHP (Unhy.)	11.3	[11]
Au/CaO	TBHP (Unhy.)	10.8	[11]
Au/TiO$_2$	TBHP (Unhy.)	11.2	[12]
Au/Yb$_2$O$_3$	TBHP (Unhy.)	11.6	[15]
Au/Yb$_2$O$_3$	TBHP (Aq.)	18.0	[15]
Au/Tl$_2$O$_3$	TBHP (Unhy.)	12.0	[13]
BaO	TBHP (Unhy.)	10.7	Present work
TlO$_x$	TBHP (Unhy.)	10.2	Present work
TlO$_x$/Ga$_2$O$_3$	TBHP (Unhy.)	14.6	Present work
TlO$_x$/Al$_2$O$_3$ or Si-MCM-41	TBHP (Aq.)	13.5	Present work
CoO	TBHP (Unhy.)	11.5	Present work
NiO	TBHP (Unhy.)	14.9	Present work
CuO	TBHP (Unhy.)	12.0	Present work
CuO/SiO$_2$	TBHP (Aq.)	15.0	Present work
CuO/In$_2$O$_3$	TBHP (Unhy.)	16.0	Present work
CuO/Ga$_2$O$_3$	TBHP (Aq.)	19.2	Present work

[a]Defined as the mmols of styrene oxide formed per gram of the catalyst per hour.

7.8   EPOXIDATION   OVER   CuO/Ga$_2$O$_3$ AT   DIFFERENT   PROCESS CONDITIONS

Since the CuO/Ga$_2$O$_3$ catalyst showed the best performance in the epoxidation of styrene by aqueous TBHP, further investigation were carried out to study the influence of reaction time, temperature and TBHP/styrene mole ratio on the conversion and selectivity in the epoxidation.

Results showing the influence of reaction time, temperature and TBHP/styrene mole ratio on the styrene conversion and product selectivity in the epoxidation are presented in Figures 7.1-7.3.

7.8.1   Effect of Reaction Time

When the reaction period is increased from 1 to 5 h, the conversion and the selectivity are influenced as follows:
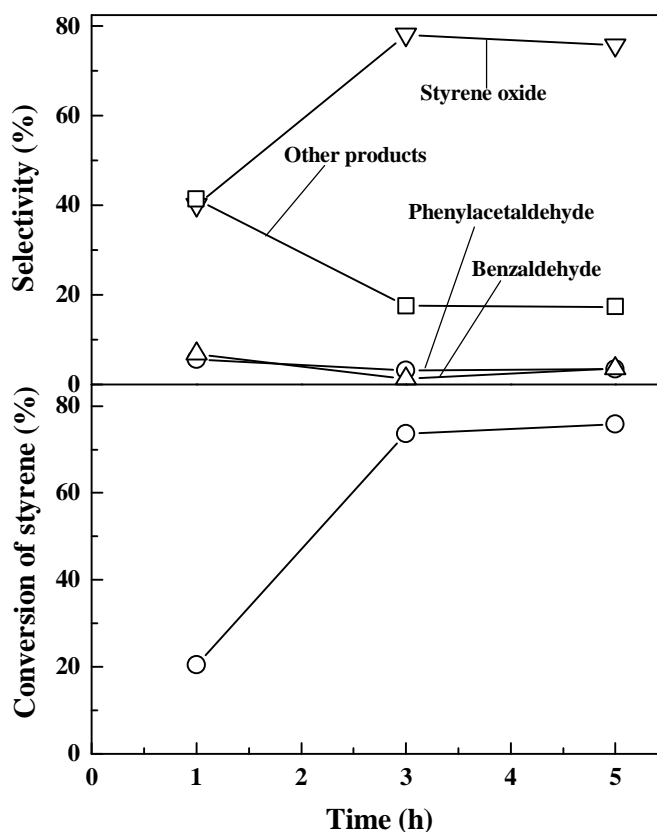
Figure 7.1:   Influence of reaction time on the epoxidation of styrene by aqueous TBHP over supported CuO/Ga$_2$O$_3$ catalyst (reaction conditions: styrene = 1.2 ml (10 mmol), TBHP = 15 mmol, catalyst = 0.1 g, temp. = under reflux).

- the styrene conversion is increased in the first 3 h and then almost leveled off.
- the selectivity for styrene oxide is passed through a maximum (at about 3 h). The selectivity of benzaldehyde and phenylacetaldehyde is passed through a minimum and that of the other products is decreased.

7.8.2   Effect of Reaction Temperature

With the increase in the reaction temperature, the conversion of both the reactants (styrene and TBHP) is increased almost linearly and the selectivity for styrene oxide is increased. The selectivity for phenylacetaldehyde, benzaldehyde and other products is however decreased with increasing the temperature.
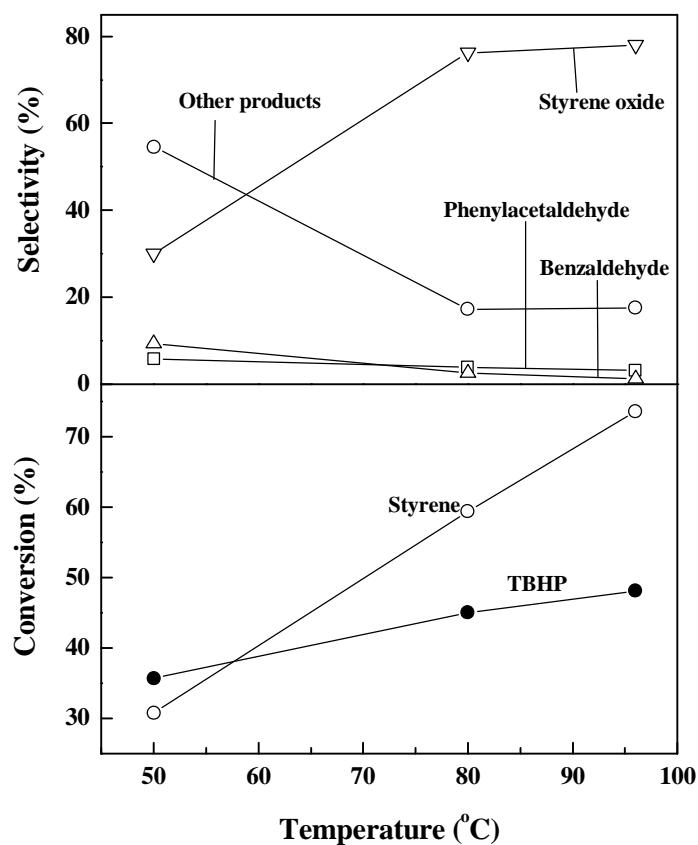
Figure 7.2:   Influence of reaction temperature on the epoxidation of styrene by aqueous TBHP over supported CuO/Ga_2O_3 catalyst (reaction conditions: styrene = 1.2 ml (10 mmol), TBHP = 15 mmol, catalyst = 0.1 g, reaction time = 3 h).

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7.8.3 Effect of TBHP/Styrene mole ratio

When the TBHP/styrene mole ratio in the epoxidation is increased (from 0.5 to 4.0), the styrene conversion is increased but the styrene oxide selectivity is decreased; the selectivity for benzaldehyde, phenylacetaldehyde and other products is however increased.
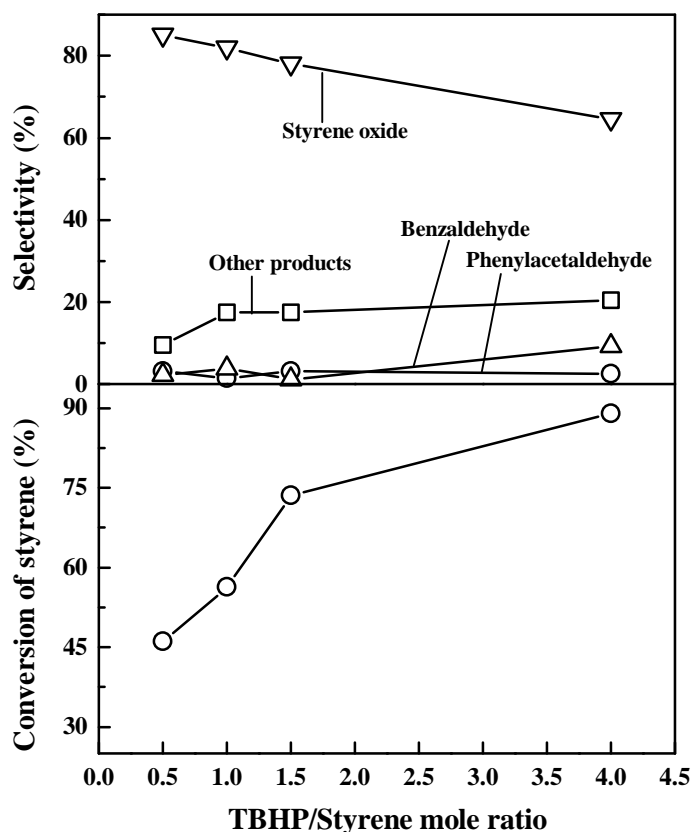
Figure 7.3: Influence of TBHP/styrene mole ratio on the epoxidation of styrene by aqueous TBHP over supported CuO/Ga$_2$O$_3$ catalyst (reaction conditions: styrene = 1.2 ml (10 mmol), catalyst = 0.1 g, temperature = under reflux, time = 3h).

7.9 CONCLUSIONS

From the present studies on the epoxidation of styrene to styrene oxide by aqueous/anhydrous TBHP over metal oxides and supported metal oxide catalysts, the following important conclusions can be drawn:

1. Among the alkaline earth metal oxides, BaO is a promising catalyst for the epoxidation of styrene to styrene oxide. Other alkaline earth metal oxides show poor activity and/or selectivity in the epoxidation.

2. The Al_2O_3, Ga_2O_3 and In_2O_3 catalysts show very low activity in the epoxidation reaction. However, TlO_x catalyst shows very high epoxidation activity and selectivity in the epoxidation.

3. Among the rare earth metal oxides, Nd_2O_3 showed the best performance in the epoxidation (62.8 % epoxide selectivity with 20 % styrene conversion). The CeO_2 and Gd_2O_3 also showed good performance in the epoxidation but with lower activity and/or selectivity. Their performance was however inferior to that of the BaO and TlO_x catalysts.

4. Among the different transition metal oxides, the NiO, CuO, CoO and MoO_3 catalysts showed very good activity and selectivity for the epoxidation; their performance in the epoxidation was in the following order: NiO > CuO > CoO > MoO_3.

5. Catalyst support plays important role in deciding the performance of the metal oxides in the epoxidation, using anhydrous or aqueous TBHP.

6. Supported CuO, particularly, CuO/Si-MCM-41, CuO/SiO_2 and CuO/Ga_2O_3 are highly promising catalysts, showing high activity and selectivity in the epoxidation of styrene by aqueous TBHP.

7. The styrene oxide selectivity in the epoxidation is increased with increasing the reaction time and temperature but it is decreased with increasing the TBHP/styrene ratio.

7.10   REFERENCES

[1]   D. Swern, in D. Swern (Ed), Organic Peroxide, Vol. 2, Wiley Interscience, New York, 1971.

[2]   V.R. Grieken, J.L. Sotelo, C. Martos, J.L.G. Fierro, M. Lopez-Granados, R. Mariscal, Catal. Today 61 (2000) 49.

[3]   Q. Yang, S. Wang, J. Lu, G. Xiong, Z. Feng, X. Xin, C. Li, Appl. Catal. A: Gen. 507 (2000) 194.

[4]   Q. Yang, C. Li, J.L. Wang, P. Ying, X. Xin, W. Shi, Stud. Surf. Sci. Catal. 130 (2000) 221.

[5]   S.B. Kumar, S.P. Mirajkar, G.C.G. Pais, P. Kumar, R. Kumar, J. Catal. 156 (1995) 163.

[6]   S.C. Laha, R. Kumar, J. Catal. 204 (2001) 64.

[7]   W. Zhang, M. Froba, J. Wang, P. Tanev, J. Wong, T.J. Pinnavaia, J. Am. Chem. Soc. 118 (1996) 9164.

[8]   J. Fu, D. Yin, Q. LI, L. Zhang, Y. Zhang, Micro. Mesopor. Mater. 29 (1999) 351.

[9]   V. R. Choudhary, N. S. Patil, S. K. Bhargava, Catal. Lett. 89 (2003) 55.

[10] V. R. Choudhary, N. S. Patil, N. K. Chaudhari and S. K. Bhargava, J. Mol. Catal. A: Chemical, 227 (2005) 217.

[11] N. S. Patil, B. S. Uphade, P. Jana, S. K. Bhargava and V. R. Choudhary, J. Catal., 223 (2004) 236.

[12] N. S. Patil, B. S. Uphade, P. Jana, R. S. Sonawane, S. K. Bhargava and V. R. Choudhary, Catal. Lett., 94 (2004) 89.

[13] N. S. Patil, R. Jha, S. K. Bhargava and V. R. Choudhary, Appl. Catal. A: General, 275 (2004) 87.

[14] N.S. Patil, B.S. Uphade, D.G. McCulloh, S.K. Bhargava and V.R. Choudhary, Catal. Commun. 5 (2004) 681.

[15] N. S. Patil, B. S. Uphade, P. Jana, S. K. Bhargava and V. R. Choudhary, Chem. Lett., 33 (2004) 400.

[16] H. Freidrich, W. Heim, A. Kleemann, H. Kolb and G. Schreyer, US Patent, 4 197,161 (April 8, 1980).

[17] J.L. Sotelo, R.Van Grieken and C. Martos, Chem. Commun., (1999) 549.

CHAPTER-8
OXIDATION OF BENZYLIC ALCOHOLS TO AROMATIC ALDEHYDES BY O_2 USING NANO-SIZE GOLD SUPPORTED OVER DIFFERENT METAL OXIDES

CHAPTER-8

OXIDATION OF BENZYLIC ALCOHOLS TO AROMATIC ALDEHYDES BY O$_2$ USING NANO-SIZE GOLD SUPPORTED OVER DIFFERENT METAL OXIDES

8.1   INTRODUCTION AND OBJECTIVE OF PRESENT WORK

Selective oxidation of benzyl alcohol to benzaldehyde is a practically important reaction for the production of chlorine-free benzaldehyde required in the perfumery and pharmaceutical industries. Several studies have been reported on the catalytic vapor-phase oxidation of benzyl alcohol to benzaldehyde [1]. However, in the vapor-phase oxidation, carbon oxides are also formed, leading to very significantly carbon loss. Liquid-phase oxidation of benzyl alcohol to benzaldehyde by oxygen or aqueous H$_2$O$_2$ in the presence of different solvents using Pd/C [2], Pd-Ag/pumice [3], heteropolyacid [4], Ni-Al-hydrotalcite [5], MnO$_4^-$ exchanged Mg-Al hydrotalcite [6] and transition metal containing double layered hydroxides and/or mixed hydroxides [7,8] as active and highly selective catalysts for the benzyl alcohol oxidation using aqueous TBHP have been reported in the literature.

The interest in studying supported gold catalysts has increased substantially since Haruta and coworkers [9] discovered that these catalysts are exceptionally active for low temperature CO oxidation. Supported Au catalysts have been shown to be active in various gas-phase reactions such as of NO decomposition [10,11], oxidation of CO [12,13], oxidation of hydrocarbons [14], epoxidation of propene [15] and selective hydrogenation [16,17]. Recently, Galvagno and coworkers [18,19] and Rossi and coworkers [20,21] have successfully used gold supported on Fe$_2$O$_3$, Co$_3$O$_4$, NiO, TiO$_2$ and SiO$_2$ catalysts in the liquid-phase oxidation of benzylic alcohols to aldehydes or ketones. Few studies have been reported on the uranium oxide as a catalyst viz. oxidation of CO by O$_2$ [22], oxidation of VOCs [23], catalytic reduction of NO$_x$ [24], and oxidative destruction of short chain alkanes [25,26]. U$_3$O$_8$ is also reported as an effective promoter for noble metals, viz. Rh and Pt in three-way catalysts in the presence of high sulfur levels [27].

It is therefore, of both practical and scientific interest to explore the use of Au supported on U$_3$O$_8$ and other metal oxides (viz. Fe$_2$O$_3$, CuO, CoO, NiO, MnO$_2$, ZnO, MgO, CaO, BaO, ZrO$_2$, Al$_2$O$_3$, La$_2$O$_3$, Sm$_2$O$_3$, and Eu$_2$O$_3$) for the selective oxidation of benzylic alcohols to the corresponding aromatic aldehydes by molecular oxygen, under solvent-free conditions, to make the processes environmentally more benign. The present work was

undertaken with this objective. Influence of Au loading in Au/U_3O_8 catalyst, method of Au loading and catalyst calcination temperature and reaction conditions on the catalyst performance in the benzyl alcohol-to-benzaldehyde oxidation has also been studied.

8.2 PERFORMANCE OF SUPPORTED GOLD CATALYSTS IN BENZYL ALCOHOL-TO-BENZALDEHYDE OXIDATION

8.2.1 Characterization of Supported Gold Catalysts

The catalysts were characterized for their Au loading by ICP‑OES (using Perkin‑Elmer Analyser), by XRD using a Phillips Diffractometer (1730 series) and CuK‑radiations, and for their Au particle size by TEM (at 200 kV in a JEOL 1200 EX using CCD camera). The surface area of the metal oxide supports and supported gold catalysts was measured by single point N_2 adsorption method (using a Surface Area Analyzer; Quanta Chrome, USA). The results for the catalyst characterization are presented in Table 8.1.

Although the same amount of gold was available for the different metal oxides for gold deposition by the HDP method, the gold loading varies from catalyst to catalyst, depending upon the metal oxide used in the catalyst. The HDP method provided the Au/TiO_2 catalyst with much higher Au loading than that could be achieved using the deposition-precipitation (DP) method [25,26]. Hence, in the present work, the HDP method was preferred for depositing gold on the different metal oxides. However, the gold loading in all the cases is quite high (4.1-8.0 wt.%), even though the supports vary widely in their surface area and acid-base properties. The acid-base properties of the metal oxide supports, was evaluated in terms of the pH of the metal- oxide-water slurry (0.1 g finely ground metal oxide in 10 ml deionised water). No direct correlation between the gold loading and the support surface properties is observed (Table 8.1). But when the gold particle size of he different supported gold catalyst is plotted against the surface area of the support used in the catalysts. The gold particle size shows a decreasing trend with increasing the surface area (Figure 8.1). This is expected because of a better dispersion of gold on the support having larger surface area. The Au particle size, however, shows no direct dependence upon the acid-base properties of the support used in the catalyst.

Table 8.1: Au loading and surface properties of supported gold catalysts.

Support used	pH of support-water slurry[a]	Au loading (wt.%)	Surface area of catalyst (m^2g^{-1})	Au particle size (nm)
MgO	10.5	7.5	24.5	8.9 ± 0.7
CaO	12.2	4.7	4.2	9.6 ± 1.2
BaO	13.5	5.3	14.0	7.1[a]
Al_2O_3	5.2	6.4	147	3.6 ± 1.1
ZrO_2	7.4	3.0	100	4.5 ± 1.2
La_2O_3	7.6	6.5	8.1	n.d.
Sm_2O_3	6.1	4.2	17.9	7.9 ± 0.5
Eu_2O_3	5.7	6.6	23.0	n.d.
U_3O_8	7.6	8.0	23.5	9.4 ? 3.2
MnO_2	7.4	4.1	13.3	6.1 ? 1.7
Fe_2O_3	7.5	6.1	32.4	5.8 ± 0.3
CoO	7.6	7.1	62.0	5.7 ± 1.3
NiO	7.9	6.2	9.2	23.1 ? 3.7
CuO	8.1	6.8	5.4	11.7 ? 2.6
ZnO	9.1	6.6	6.1	5.9[a]

[a] 0.1 g support in 10 ml deionised water, n.d. = not determined, a? by XRD using Scherrer equation
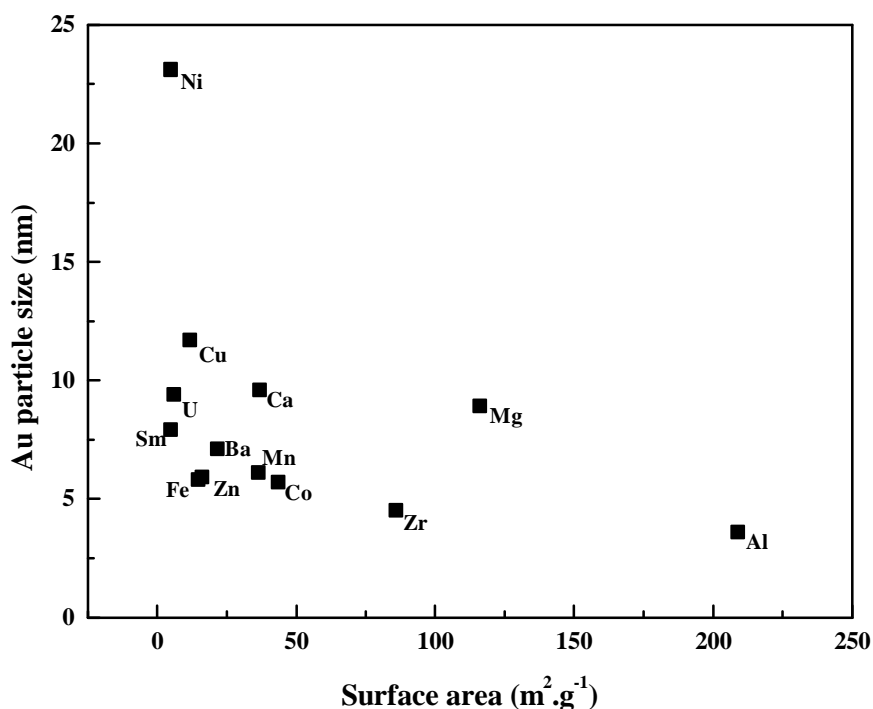
Figure 8.1: Dependence of Au particle size on surface area of support used for depositing gold in the preparation of different supported gold catalysts

8.2.2 Benzyl Alcohol Oxidation

Results showing the solvent-free liquid phase oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over nano-size gold supported over different metal oxides are presented in Table 8.2. In the absence of any catalyst, the benzyl alcohol conversion was 4 % with 96 % and 5 % selectivity for benzaldehyde and benzylbenzoate, respectively. From the results following important observations can be made:

- Among the gold catalysts, the Au/U_3O_8 catalyst showed the best performance [both high activity (53 % conversion) and selectivity (95 %)] in the oxidation of benzyl alcohol to benzaldehyde. The other supported gold catalysts, particularly Au/MgO, Au/Al_2O_3 and Au/ZrO_2 also showed good activity in the oxidation of benzyl alcohol-to-benzaldehyde oxidation.

- The highest activity (benzyl alcohol conversion of 68.9 %) was shown by the Au/Al_2O_3 catalyst. However, this catalyst showed somewhat lower benzaldehyde selectivity (65 %).

- The Au/Fe_2O_3 catalyst showed very high selectivity (100 %) for benzaldehyde but low activity (16.2 % conversion) in the oxidation

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- The order of the catalysts for the benzaldehyde formation (benzaldehyde yield) is Au/U$_3$O$_8$ (50.4 %) > Au/Al$_2$O$_3$ (44.8 %) > Au/ZrO$_2$ (44.1 %) > Au/MgO (43.9 %) > Au/BaO or Au/La$_2$O$_3$ (35.5 %) > Au/MnO$_2$ (34.5 %) > Au/Sm$_2$O$_3$ (33.3 %) > Au/ Eu$_2$O$_3$ (32.4 %) > Au/ CaO (30.4 %) > Au/CoO (26.7 %) > Au/NiO (25.0 %) > Au/CuO (18.6 %) > Au/Fe$_2$O$_3$ or Au/ZnO (16.2 %).

The results reveal a strong influence of metal oxide support on the catalytic performance (both the benzyl alcohol conversion activity and product selectivity in the oxidation of benzyl alcohol to benzaldehyde) of the supported gold catalysts. However, since the supported gold catalysts do not have the same gold loading, their comparison may not be valid. It is however, interesting to note that the Au/ZrO$_2$ catalyst shows high activity (much higher than many of the supported Au catalysts) inspite of the fact that its Au loading is the lowest. This may be because of the lower Au particle size of the Au/ZrO$_2$. A comparison of the data in Tables 8.1 and 8.2 also indicates that there is no direct relationship between the Au loading and the performance (in the benzyl alcohol-to-benzaldehyde oxidation) of the supported Au catalysts.

When the supported Au catalysts were compared for their turn-over-frequency (TOF), measured in terms of the rate of benzaldehyde forming per unit mass of gold deposited on the different metal oxide support, the supported Au catalysts show the following order: Au/ZrO$_2$ > Au/MnO$_2$ > Au/Sm$_2$O$_3$ > Au/Al$_2$O$_3$ > Au/BaO > Au/CaO > Au/U$_3$O$_8$ > Au/MgO > Au/ La$_2$O$_3$ > Au/Eu$_2$O$_3$ > Au/NiO > Au/CoO > Au/CuO > Au/Fe$_2$O$_3$ > Au/ZnO.

From both the comparisons (one based on the benzaldehyde yield and the second based on the TOF), following general observation can be made:

- The gold catalysts supported on the reducible metal oxides (e.g. NiO, CuO, CoO, Fe$_2$O$_3$ and ZnO), shows poor activity in the benzyl alcohol-to-benzaldehyde oxidation.
- The gold catalysts supported on non-reducible or difficult to reduce metal oxides (e.g. ZrO$_2$, Al$_2$O$_3$, U$_3$O$_8$, MgO, CaO, BaO, La$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, etc.) shows a good performance in the oxidation.

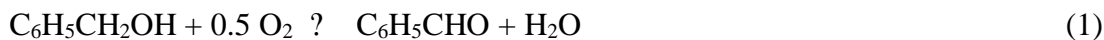The interaction between the supported gold and the support is expected to play an important role in deciding both the gold particle size and catalytic performance of the supported gold catalysts. Further detailed studies are essential for understanding the important role played by the support for controlling the deposition of gold (i.e. gold loading) gold particle size and catalytic performance of supported gold catalysts.

Table 8.2: Performance of the supported nano-gold catalysts in the oxidation of benzyl alcohol-to-benzaldehyde by molecular oxygen in absence of any solvent (reaction conditions: benzyl alcohol = 29 mmol, catalyst = 0.1 g, temperature = 130 ?C, time = 5 h).

Catalyst	Conversion of benzyl alcohol (%)	Selectivity (%)		Benzaldehyde yield (%)	TOF[a] (mmol. $g^{-1}_{(Au)}.h^{-1}$)
		Benzalehyde	Benzylbenzoate		
Au/MgO	51.0	86.0	14.0	43.9	339
Au/CaO	33.3	91.3	8.6	30.4	375
Au/BaO	43.5	81.5	18.5	35.5	388
Au/Al$_2$O$_3$	68.9	65.0	35.0	44.8	406
Au/ZrO$_2$	50.7	87.0	13.0	44.1	853
Au/La$_2$O$_3$	51.6	68.8	31.3	35.5	317
Au/Sm$_2$O$_3$	44.4	75.0	25.0	33.3	460
Au/Eu$_2$O$_3$	37.5	87.5	12.5	32.4	285
Au/U$_3$O$_8$	53.0	95.0	5.0	50.4	365
Au/MnO$_2$	39.7	88.8	11.1	34.5	488
Au/Fe$_2$O$_3$	16.2	100	-	16.2	154
Au/CoO	28.3	95.2	4.8	26.7	218
Au/NiO	32.0	78.0	22.0	25.0	234
Au/CuO	27.0	69.0	31.0	18.6	159
Au/ZnO	40.5	92.8	7.2	16.2	142

[a]rate of the formation of benzaldehyde per unit mass of the deposited gold.

It is interesting to note that benzyl benzoate is the only other product formed apart from benzaldehyde and the formation of benzoic acid was not at all detected in GC and/or in GC-MS analysis. The formation of benzyl benzoate involves following reaction in the presence and/or absence of catalyst:

$$C_6H_5CH_2OH + 0.5 \; O_2 \; ? \quad C_6H_5CHO + H_2O \tag{1}$$

$$C_6H_5CHO + 0.5 \; O_2 \; ? \quad C_6H_5COOH \tag{2}$$

$$C_6H_5COOH + C_6H_5CH_2OH \; ? \quad C_6H_5COOCH_2C_6H_5 \tag{3}$$

The absence of benzoic acid in the GC and GC-MS analysis indicates that, as soon as benzoic acid is formed (reaction –2), it reacts immediately with benzyl alcohol, which is available in much higher concentration, forming benzyl benzoate (reaction 3).

8.3 OXIDATION OF BENZYL ALCOHOL OVER Au/U$_3$O$_8$ CATALYST

Since the Au/U$_3$O$_8$ catalyst showed highly promising performance in the benzyl alcohol-to-benzaldehyde oxidation, it was interesting to carry out further detailed investigation on this catalyst by studying the influence of various Au deposition methods for the preparation of Au/U$_3$O$_8$, Au loading of the catalyst prepared by HDP method, catalyst calcination temperature, on the catalyst surface properties and performance in the benzyl alcohol-to-benzaldehyde oxidation. Influence of the different reaction conditions (reaction time, temperature and solvent) on the catalytic performance of the Au/U$_3$O$_8$ catalyst has also been investigated.

Unless otherwise mentioned, the reaction conditions employed for the oxidation of benzyl alcohol or other benzylic alcohols are as follows:

Amount of alcohol: 29 mmol, Amount of catalyst: 0.1 g,

Solvent: nil, Temperature: 130 ºC,

Reaction time: 5 h.

8.3.1 Influence of Au Deposition Method Used in Catalyst Preparation

The Au loading (measured by ICP-OES), surface area and Au particle size (measured by TEM and/or XRD) of the Au/U$_3$O$_8$ catalysts prepared by different methods are given in Table 8.3. Results of the catalytic performance (in the benzyl alcohol-to-benzaldehyde oxidation) of the Au/U$_3$O$_8$ catalysts prepared by the different methods are presented in Figure 8.2.

Table 8.3: Properties of Au/U$_3$O$_8$ catalysts prepared by different methods (Au available for loading: 8.0 wt.% of U$_3$O$_8$)

Method of preparation	Au loading (wt %) by ICP	Calcination temp. (°C)	Surface area (m^2.g^{-1})	Particle size of Au (nm) by	
				TEM	XRD
HDP	8.0	400	6.5	9.4	n.d.
DP	5.1	400	8.0	7.0	6.2
Co-precipitation	4.7	400	5.2	7.6	5.9
Impregnation	8.0	400	6.2	n.d.	8.4
HDP	8.0	900	5.7	34.3	n.d.

HDP = Homogeneous-Deposition Precipitation, DP = Deposition Precipitation, n.d. = not determined
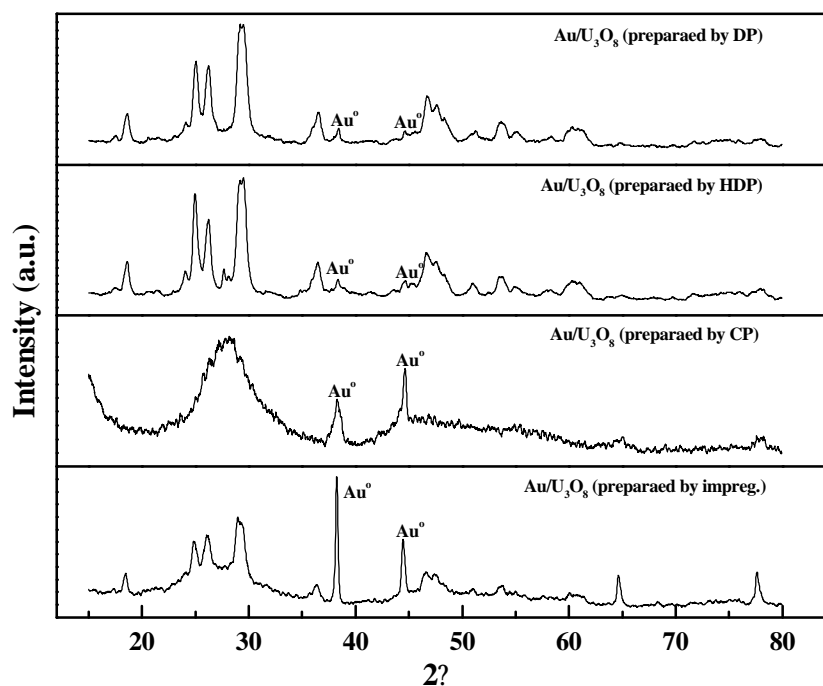
Figure 8.3: XRD of Au/U$_3$O$_8$ catalysts prepared by a) Impregnation b) Co-Precipitation, c) Homogeneous Deposition Precipitation and d) Deposition Precipitation, methods, calcined at 400 °C for 2 h.

The XRD, TEM photographs and Au particle size distribution for the Au/U$_3$O$_8$ catalyst prepared by the different methods are presented in Figures 8.3-8.7.

b) 5.1 wt% Au/U$_3$O$_8$(DP)
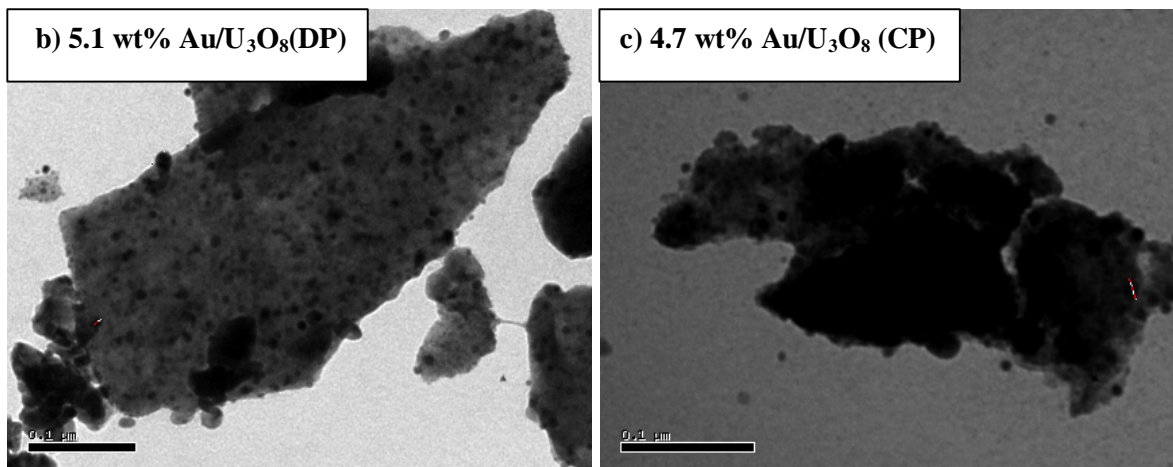
c) 4.7 wt% Au/U$_3$O$_8$ (CP)

Figure 8.4: TEM photographs of Au/U$_3$O$_8$ catalysts prepared by DP and CP methods catalysts calcined at 400 ℃ for 2h.

a) 400 ^{o}C

a) 700 ^{o}C

a) 900 ^{o}C
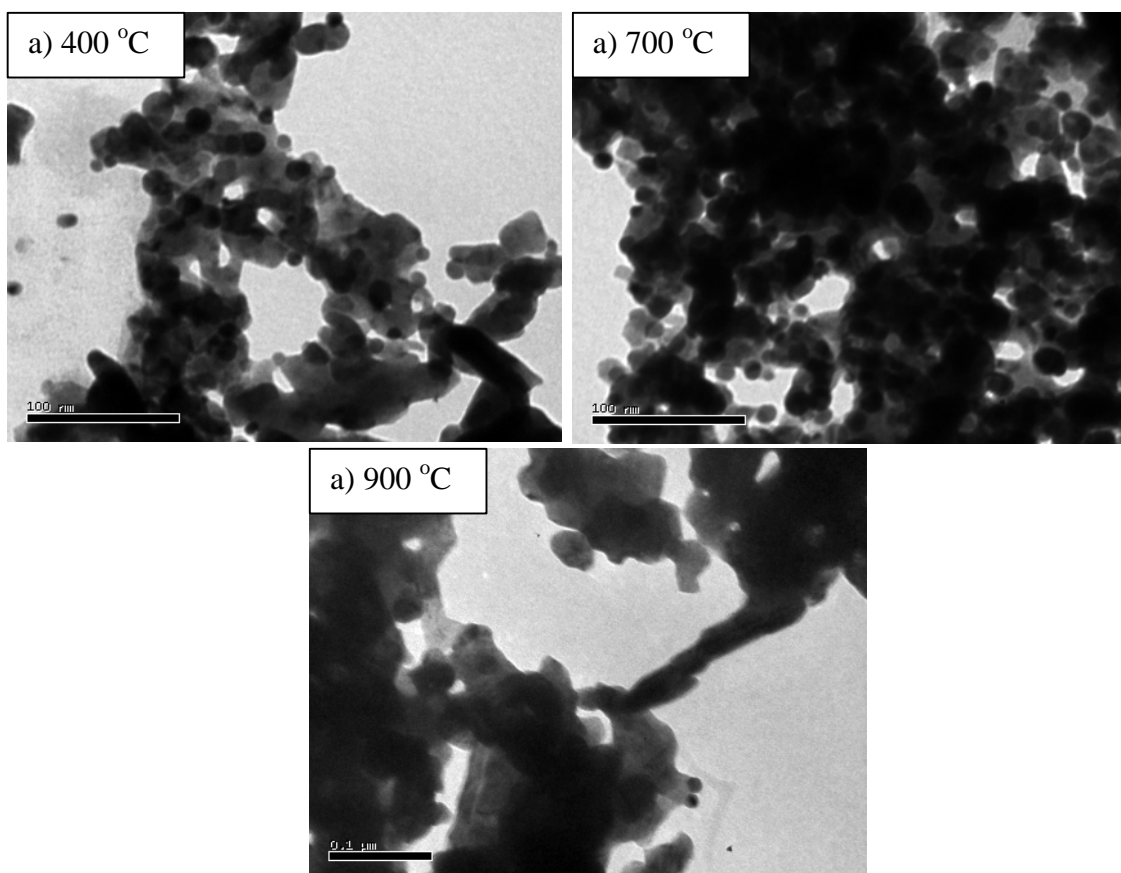
Figure 8.5: TEM photographs of 8 wt.% Au/U$_3$O$_8$ (HDP) catalysts calcined at (400, 700 and 900 ?C).

In the impregnation method, the gold compound was deposited on the support by the incipient wetness technique and hence the gold loading in the resulting catalyst was the same as that available for the deposition. There was a complete deposition of the available gold on the support when HDP method was used. However, in case of the DP and CP methods, the gold deposition on 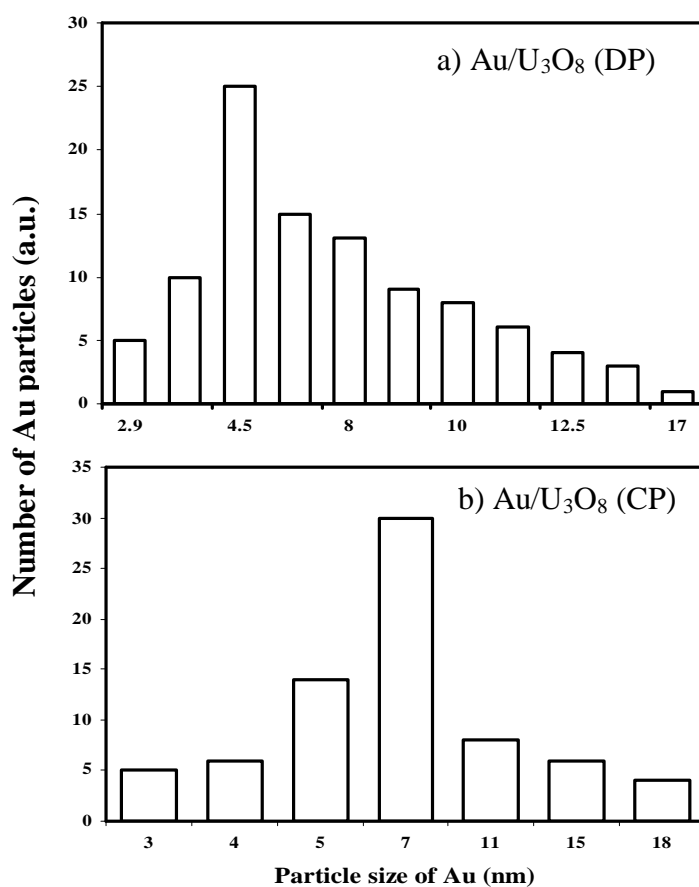the support was found to be about 60 % of that available. The Au particle size for the catalyst (calcined at 400 ºC) prepared by the different methods is found to be more or less the same (8.4 ? 1.0 nm).

Figure 8.6: Au particle size distribution of a) Au/U$_3$O$_8$ (DP) and b) Au/U$_3$O$_8$ (CP) catalysts calcined at 400 ºC for 2 h.

The Au/U$_3$O$_8$ catalysts prepared by the different methods are compared for their performance in the oxidation of benzyl alcohol in Figure 8.2. Their performance for the benzyl alcohol conversion or benzaldehyde yield is in the following order: Au/U$_3$O$_8$ (HDP) > Au/U$_3$O$_8$ (DP) ? Au/U$_3$O$_8$ (CP) > Au/U$_3$O$_8$ (Impregnation). The benzaldehyde selectivity for all the four catalysts is found to be very high (? 95 %).
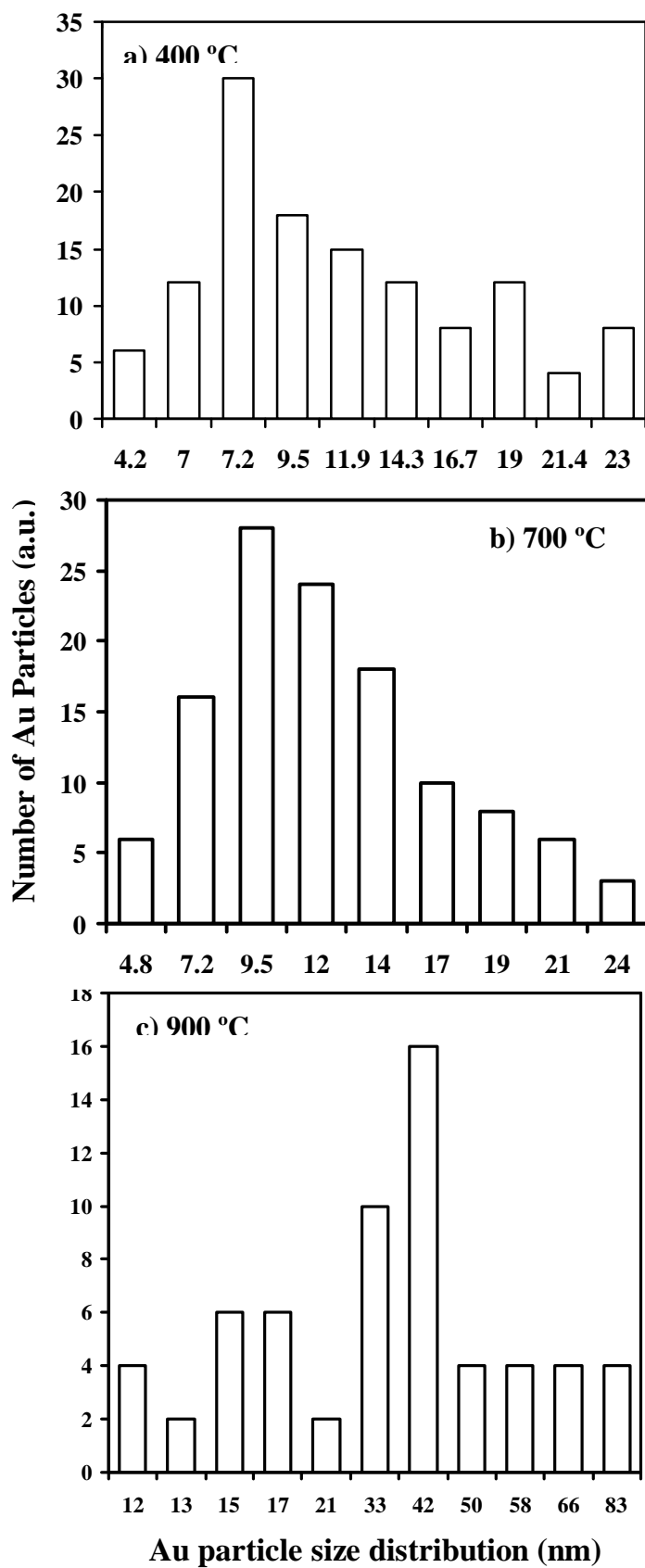
Figure 8.7: Au particle size distribution of 8% Au/U_3O_8 (HDP) catalysts calcined at a) 400 ℃, b) 700 ℃ and c) 900 ℃
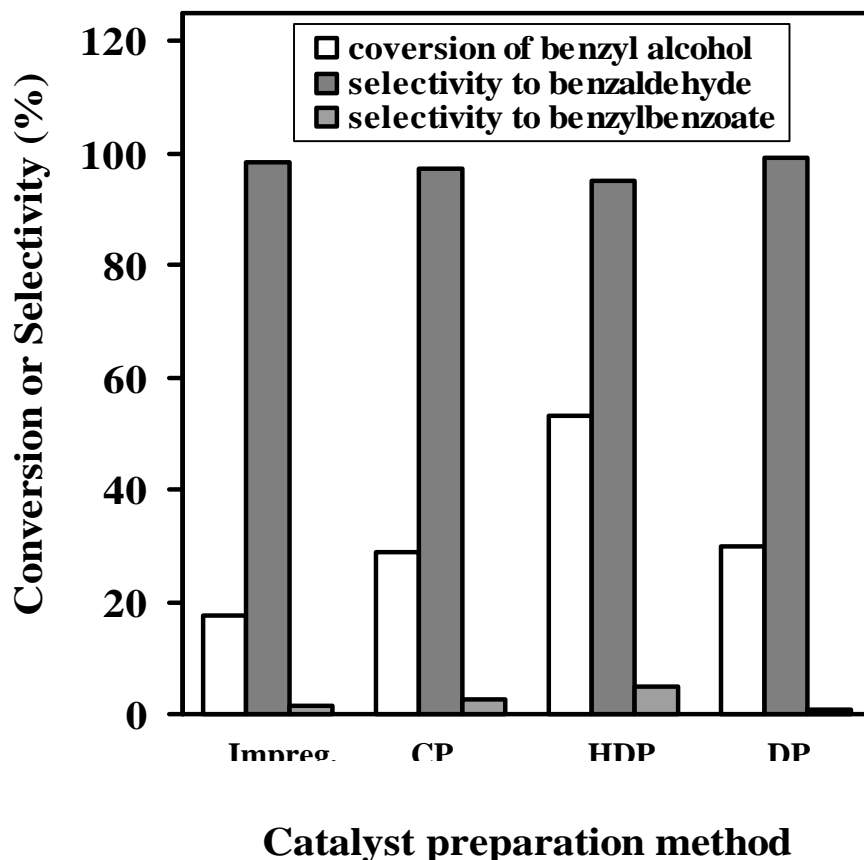
The Au/U_3O_8 catalysts prepared by the different methods are compared for their TOF (measured in terms of the rate of benzaldehyde formation per gram of deposited gold) as follows:

Catalyst preparation method:	HDP	DP	CP	Impregnation
TOF (mmol.g^{-1}.h^{-1}):	365	339	344	125

Figure 8.2: Performance of Au/U_3O_8 catalysts (calcined at 400 ?C) prepared by the different methods in the oxidation of benzyl alcohol to benzaldehyde by molecular oxygen at 130 ?C

Thus, when compared for their TOF, the performance of the catalysts prepared by the CP and DP methods is comparable to that of the catalyst prepared by the HDP method. However, the TOF for the catalyst prepared by the impregnation method is much lower inspite of the fact that the Au particle size of this catalyst is also comparable to that of the catalysts prepared by the other methods. The much lower catalytic activity may be due to the modification of the support surface by chloride anions during the impregnation of the U_3O_8 support with chloroauric acid and calcination of the impregnated catalytic mass. The chloride anions (particularly at high concentration) incorporated in the catalyst may also act as an inhibitor to the catalyst in the oxidation.

8.3.2 Influence of Au Loading in Au/U$_3$O$_8$ (HDP) Catalyst

Results showing the dependence of Au loading and surface area of Au/U$_3$O$_8$ (HDP) catalyst on the Au available for its deposition on the support during the Au deposition by the HDP method are shown in Figure 8.8.
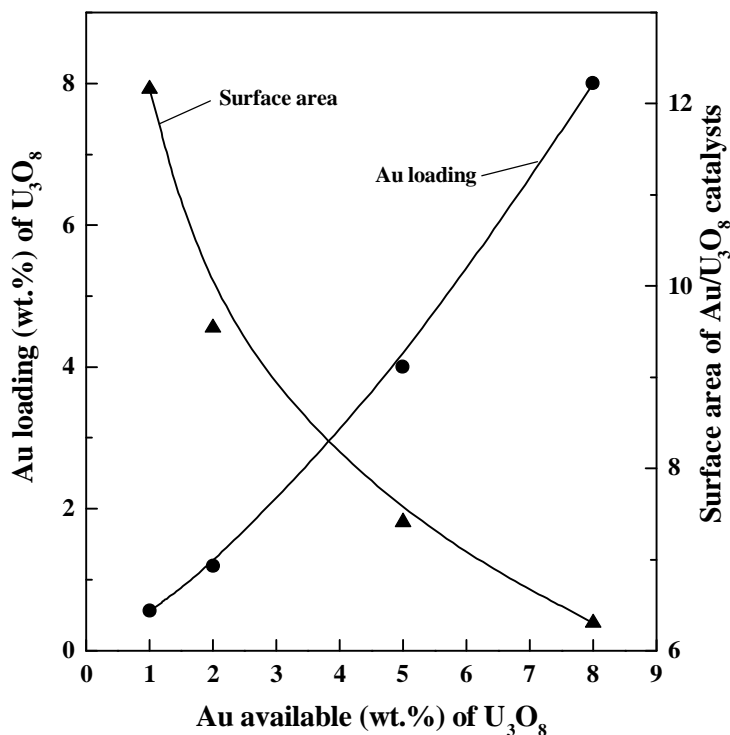
Figure 8.8 Correlation of Au loading available (wt.%) with the actual loading in the catalyst and its surface area.

The Au loading is increased, whereas, the surface area is decreased markedly with increasing the Au available for its deposition on the support. The catalyst surface area is decreased with increasing the Au loading. This may be because of the modification of the support surface during the gold deposition and calcination (at 400 ℃).

The influence of the Au loading in the Au/U$_3$O$_8$ catalyst prepared by the HDP method on its catalytic performance in the benzyl alcohol oxidation by molecular O$_2$ (at 130 ℃) is shown in Figure 8.9. As expected, an increase in the benzyl alcohol conversion was observed with an increase in the Au loading. However, higher gold loading on the support also resulted in the small decrease in the benzaldehyde selectivity resulting in the formation of benzyl benzoate as the byproduct.
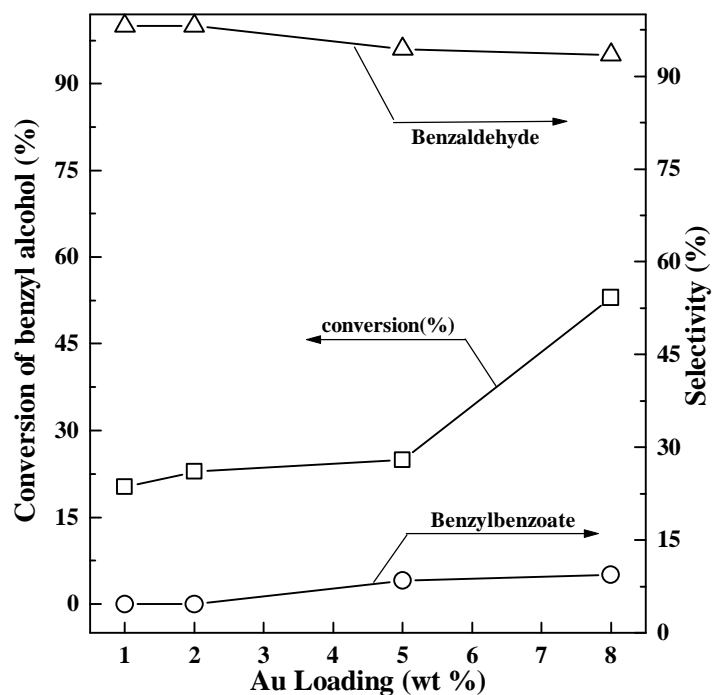
Figure 8.9 Influence of Au loading (wt.%) on the oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over Au/U₃O₈ (HDP) catalyst at 130 ℃.

8.3.3 Influence of Calcination Temperature of Au/U₃O₈ (HDP)

XRD spectra of the Au(8 wt.%)/U₃O₈ dried at 100 °C and calcined at different temperatures (400-900 °C) are presented in Figure 8.10.
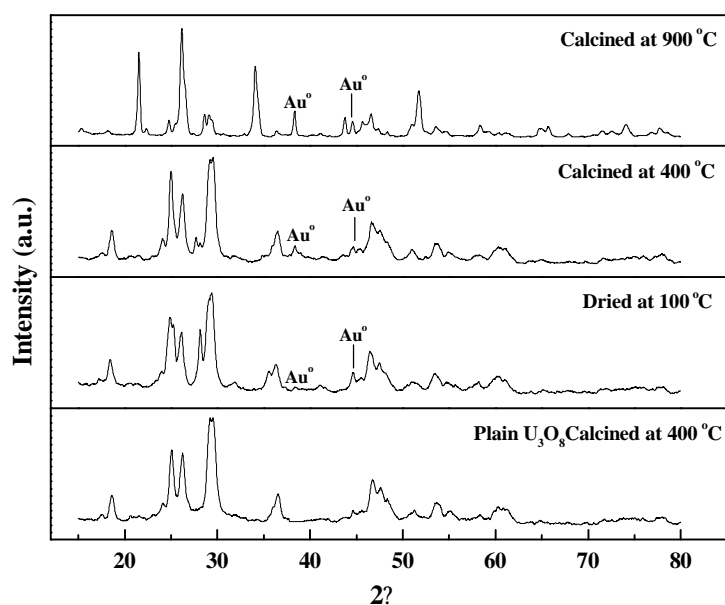
Figure 8.10: XRD of a) U₃O₈ calcined at 400 °C and 8 wt.% Au/U₃O₈ (HDP) catalysts calcined at b) 100 °C, c) 400 °C and d) 900 °C.

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TEM photographs and Au particle size distribution for the Au(8 wt.%)/U$_3$O$_8$ (HDP) catalysts calcined at different temperatures (400-900 °C) are already shown in Figures 8.5-8.7, respectively. The average Au particle size is increased from about 9.4 nm to 34.3 nm with the increase in the catalyst calcination temperature led to a small decrease in the surface area of the catalyst (Table 8.3).

Figure 8.11 Influence of catalyst calcination temperature on the oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over the Au(8 wt.%)/U$_3$O$_8$ (HDP) catalyst (at 130 °C).
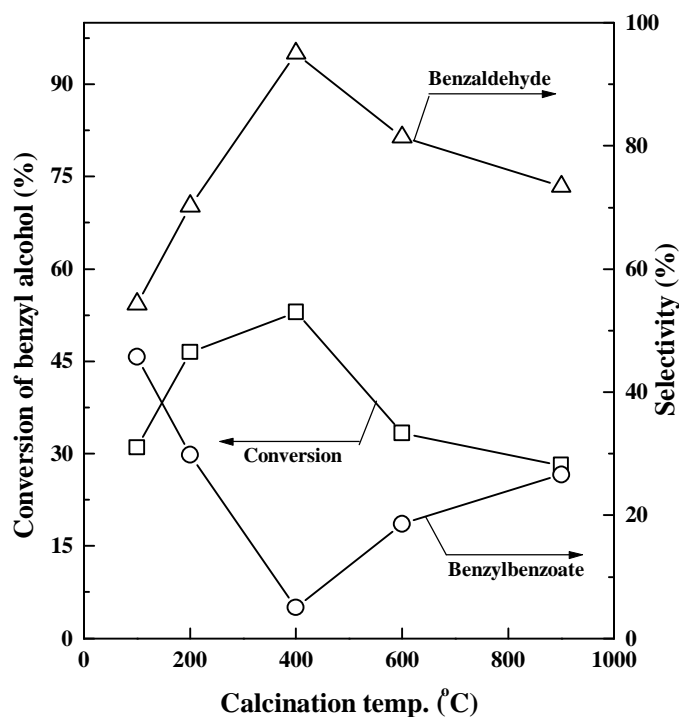
Results showing the influence of calcination temperature of the Au/U$_3$O$_8$ (HDP) catalyst on its performance in the benzyl alcohol-to-benzaldehyde oxidation by O$_2$ are presented in Figure 8.11. The increase in the catalyst calcination temperature from 100 to 900 °C has following influence on the conversion and product selectivity:

- The benzyl alcohol conversion is passed through a maximum.
- The selectivity for the benzaldehyde is also passed through a maximum.
- The selectivity for benzylbenzoate is passed through a minimum.

The maximum or minimum is observed for the catalyst calcination temperature of 400 °C. This indicates that 400 °C is an optimum catalyst calcination temperature for obtaining the best performance (i.e. highest benzyl alcohol conversion and benzaldehyde selectivity) in the benzyl alcohol-to-benzaldehyde oxidation. The poor catalyst performance

at the lower catalyst calcination temperature (100 or 200 ℃) is expected because of the presence of water and/or incomplete decomposition of the gold precursor compound deposited on the support during the homogeneous deposition precipitation. However, the increasingly poor performance at the higher catalyst calcination temperature (600-900 ℃) is mainly due to the growth of gold particles during the high temperature calcination (Table 8.3 and Figures 8.5 and 8.7).

8.3.4 Influence of Reaction Conditions

Results showing the influence of reaction time, temperature and solvent used in the reaction on the conversion and product selectivity in the oxidation of benzyl alcohol to benzaldehyde by O_2 over the Au(8 wt.%)/U_3O_8 (HDP), calcined at 400 ℃, is presented in Figures 8.12, 8.13 and Table 8.4, respectively.
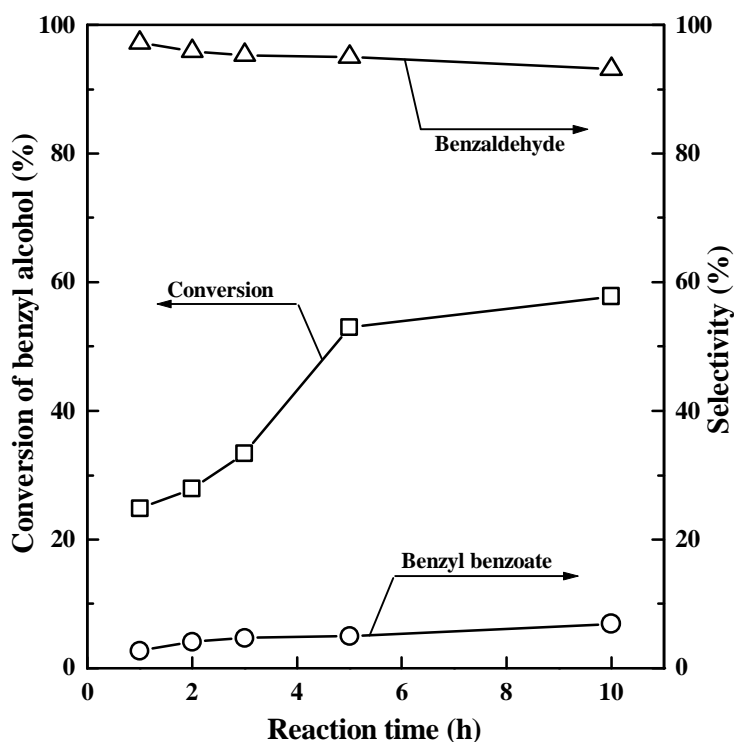
Figure 8.12 Influence of reaction time on the oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over the Au(8 wt.%)/U_3O_8 (HDP) catalyst at 130 ?C.

From the results, following important observations can be made:

- The benzyl alcohol conversion and selectivity for benzylbenzoate are increased and the selectivity for benzaldehyde is decreased with increasing the reaction period; the change in the product selectivities is however small.

- As expected, the benzyl alcohol conversion is increased very markedly with increasing the temperature. The selectivity is decreased and consequently the selectivity for benzylbenzoate is increased particularly when the temperature is increased above 130 °C.
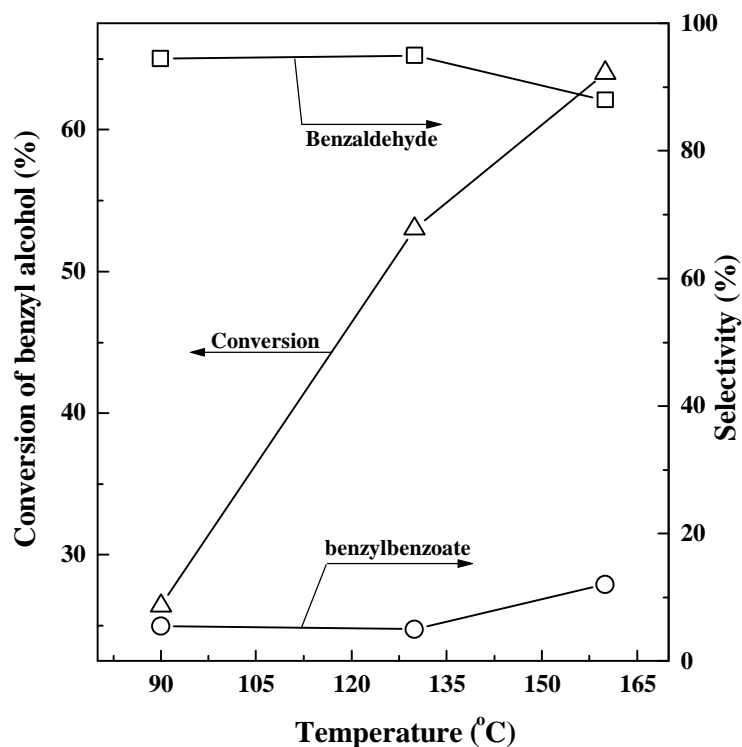
Figure 8.13 Influence of reaction temperature on the oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over the Au(8 wt.%)/U_3O_8 (HDP) catalyst calcined at 400 °C (reaction time = 5 h).

- The catalyst shows best performance (both high conversion and selectivity or highest yield in the benzyl alcohol-to-benzaldehyde oxidation in the absence of any solvent.

In the presence of dimethylformamide (DMF) and dimethylsulfoxide (DMSO), the conversion is lower even though the reaction is carried out at higher temperature. The observed lower conversion for the use of DMF, DMSO and p-xylene as solvent in the reaction is expected because of a competitive absorption on the catalyst between the solvent molecules and the reactants (benzyl alcohol and oxygen).

Table 8.4: Results for the oxidation of benzyl alcohol by molecular oxygen over Au (8 wt.%)/U$_3$O$_8$ (HDP), calcined at 400 ºC in the absence and presence of different solvents

Solvent used	Temp. (ºC)	Conversion (%)	Selectivity (%)		Benzaldehyde yield (%)
			Benzaldehyde	Benzylbenzoate	
Nil	130	53.0	95.0	5.0	50.4
Toluene	110	27.0	86.6	13.4	23.4
p-Xylene	110	45.0	82.5	17.5	37.1
DMF	135	49.6	72.0	28.1	35.7
DMSO	180	24.3	99.1	0.9	24.2

8.4 Oxidation of Other Aromatic Alcohols

Results of the oxidation of benzylic alcohols with or without substituent (nitro, methoxy or phenoxy group) in the benzene ring and also of the phenethylalcohol over the Au(8 %)/U$_3$O$_8$ (HDP) catalyst, in the absence of any solvent are presented in Table 8.5. The performance of the catalyst for the oxidation of different alcohols to their corresponding aldehydes is in the following order: 4-MeOPhCH$_2$OH > PhCH$_2$OH > 4-PhOPhCH$_2$OH > 4-NO$_2$PhCH$_2$OH > PhCH$_2$CH$_2$OH.

Table 8.5: Results for the oxidation of different alcohols by molecular oxygen over the Au(8 wt.%)/U$_3$O$_8$ (HDP), calcined at 400 ºC under solvent free condition

Substrate	Conversion (%)	Selectivity (%)		Aldehyde yield (%)
		Aldehyde	Ester	
PhCH$_2$OH	53.0	95.0	5.0	50.4
3-NO$_2$PhCH$_2$OH	40.8	98.5	1.5	40.2
3-PhOPhCH$_2$OH	42.5	98.0	2.0	41.7
4?MeOPhCH$_2$OH	67.0	92.5	7.5	62.0
PhCH$_2$CH$_2$OH	42.1	43.0	57.0	18.0

A comparison of the results in Table 8.5 shows a strong influence of the substituent in the benzene ring or the length of the hydrocarbon chain between the phenyl and the methylene group. The presence of electron donating (-OMe) group seems to enhance the reactivity of the $-CH_2OH$ grouping its oxidation to $-CHO$. However, in the presence of electron withdrawing group (attached to the benzene ring) or $-CH_2-$ group between the phenyl and CH_2OH group groups, the reactivity of the alcohol in the oxidation is reduced.

The above results indicate that the catalyst is in general useful for the oxidation of benzylic alcohols to corresponding aldehydes with high selectivity/yield.

8.5 CONCLUSIONS

From the investigations, following important conclusions have been made:

1. Among the supported gold catalysts (prepared by the HDP method), the Au/MgO, Au/Al_2O_3, Au/ZrO_2, Au/La_2O_3 and Au/U_3O_8 catalysts showed high activity (benzyl alcohol conversion >50%) in the oxidation of benzyl alcohol by O_2. The reaction products formed in the oxidation are benzaldehyde and benzylbenzoate. The benzoic acid formed in the oxidation is instantly reacted with benzyl alcohol over all the supported Au catalysts leading to the formation of benzylbenzoate.

2. Among the above promising supported gold catalysts, the Au/U_3O_8 shows the best performance (highest benzaldehyde yield) in the benzyl alcohol-to-benzaldehyde oxidation and it also has the highest gold loading..

3. Among the Au/U_3O_8 catalysts prepared by the different methods of gold deposition/incorporation on U_3O_8 support (is mainly impregnation, DP, HDP and CP), the catalyst prepared by the HDP method shows the best performance in the benzyl alcohol-to-benzaldehyde oxidation.

4. No direct relationship exists between the surface properties of the metal oxide supports and the gold loading in the supported metal oxide catalysts prepared by the HDP method. However, the particle size of the gold deposited on the metal oxides is found to be decreased with increasing the surface area of the support used in the catalyst.

5. The catalytic performance of Au(8 %)/U_3O_8 (HDP) in the oxidation of benzyl alcohol is strongly influenced by both the catalyst (viz. gold loading, method of preparation and catalyst calcination temperature) and reaction (viz. reaction time, temperature and solvent) parameters.

6. The Au/U_3O_8 catalyst also shows good performance in the oxidation of other benzylic alcohols to corresponding aldehydes and its performance is however, influenced by the substituent attached to the benzene ring.

8.6 REFERENCES

[1]   (a) S. Tsuruya, Y. Okamoto and T. Kuwada, J. Catal. 56 (1979) 52; (b) S. Tsuruya, H. Miyamoto, T. Sakae, M. Masai, J. Catal. 64 (1980) 260; (c) S. J. Kulkarni, R. R. Rao, M. Subramanyam, A. V. Rama Rao, A. Sarkarny, L. Guczi, Appl. Catal. A. 139 (1996) 59; (d) M. Arai, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc., Faraday Trans. 92 (1996) 2631; (e) H. Hayashibara, S. Nishiyama, S. Tsuruya, M. Masai, J. Catal. 152 (1995) 254; (f) S. Sueto, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc., Faraday Trans. 93 (1997) 659; (g) R. Sumathi, K. Johnso, B. Vishwanathan, T. K. Varadrajan. Appl. Catal. A. 172 (1998) 15; (h) N. Idaka, S. Nishiyama, T. Tsuruya, Phys. Chem. Chem. Phys. 3 (2001) 1918.

[2]   N. S. Bijlani, S. B. Chandalia, Indian Chem. Eng. 23 (1981) 44.

[3]   L. F. Liotta, A. M. Venezia, G. Deganello, A. Longo, A. Martorana, Z. Schay, L. Guczi, Catal. Today, 66 (2001) 271.

[4]   G. D. Yadav, C. K. Mistry, J. Mol. Catal. A. 172 (2001) 135.

[5]   B. M. Choudhary, M. Lashmi Kantam, A. Rahman, Ch. V Reddy, K. Koteshwara Rao, Angew. Chem. Int. Ed. Engl. 40 (2001) 304.

[6]   V. R. Choudhary, D. K. Dumbre, V. S. Narkhede, S. K. Jana, Catal. Lett. 86 (2003) 229.

[7]   V. R. Choudhary, Pankaj A. Choudhari, V. S. Narkhede, Catal. Commun., 4 (2003) 171.

[8]   V. R. Choudhary, D. K. Dumbre, B. S. Uphade, V. S. Narkhede, J. Mol. Catal. A. (in press).

[9]   M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.

[10]   M. C. Kung, J-H. Lee, A. Chu-Kung, H. H. Kung, Stud. Surf. Sci. Catal. 101 (1996) 701.

[11]   A. Ueda, T. Oshima, M. Haruta, Appl. Catal. B. 12 (1997) 81.

[12]   R. M. T. Sanchez, A. Ueda, T. Tanaka, M. Haruta, J. Catal. 168 (1997) 125.

[13]   G. K. Bethke, H. H. Kung, Appl. Catal. A. 194 (2000) 43.

[14]   Y. A. Kalvachev, T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 186 (1997) 125.

[15]   T. Hayashi, K. Tanaka, M. Haruta, J. Catal. 178 (1998) 566.

[16] J. F. Jia, K. Haraki, J. N. Kondo, K. Domen, K. Tamaru, J. Phys. Chem. B. 104 (2000) 11153.

[17] M. Okumura, T. Akita, M. Haruta, Catal. Today, 74 (2002) 265.

[18] C. Milone, R. Ingoglia, G. Neri, A. Pistone, S. Galvagno, Appl. Catal. A: Gen. 211 (2001) 251.

[19] C. Milone, R. Ingoglia, G. Neri, A. Pistone, S. Galvagno, Catal. Lett. 87 (2003) 201.

[20] S. Biela, L. Prati, M. Rossi, IV World Congress on Oxidation Catalysis, Berlin, (2001) 371.

[21] S. Biela, M. Rossi, Chem. Commun. (2003) 378.

[22] F. Nozaki, K. Ohki, Bull. Chem. Soc. Jpn. 45 (1972) 3473.

[23] R. H. Harris, V. J. Boyd, G. J. Hutchings, S. H. Taylor, Catal. Lett. 78 (2002) 369.

[24] S. D. Pollington, A. F. Lee, T. L. Overtone, P. J. Sears, P. B. Wells, S. E. Hawley, L. D. Hudson, D. F. Lee, V. Ruddock, Chem. Commun. (1999) 725.

[25] G. H. Hutchings, S. H. Taylor, I. D. Hudson, Stud. Surf. Sci. Catal. 121 (1999) 85.

[26] S. H. Taylor, S. R. O'Leary, Appl. Catal. B. 25 (2000) 137-149.

[27] G. Mobilon, D. Durand, P. Courty, M. Priget, US Patent 5051392 (1991).

Suggestions For Further Work

In this investigation for the Ph.D. thesis, a very large number of solid catalysts have been prepared and used for the different reactions (viz. benzylation and acylation of aromatic compounds, oxidation of benzyl alcohol to benzaldehyde, oxidation of ethylbenzene and diphenylmethane to acetophenone and benzophenone, respectively and epoxidation of styrene). Because of the limited facilities, funds and time, it was not possible to thorough ly characterize all the catalysts for their surface properties. Also their reactions have been carried out at close to the atmospheric pressure and/or at the temperature close to or below the boiling point of the reactant/solvent having the lowest boiling point. Following further work on the topics covered in this thesis may therefore be carried out in the future:

- Characterization of the different supported gold catalysts by XPS and other surface analysis tools for understanding the gold-support surface interactions causing change in electronic properties, if any, of gold depending upon the catalyst surface.

- Characterization of the surface properties of thermally activated different supported $FeCl_3$, $GaCl_3$ and $InCl_3$ catalysts for knowing the catalytically active surface metal chloride species formed in the thermal activation under different thermal activation conditions. Also to study the acidity of the different thermally activated supported metal chloride catalysts.

- To study the acylation of aromatic compounds by carboxylic acids at higher temperatures in high pressure autoclave using the highly promising catalysts in the thesis.

- To study the oxidation of ethylbenzene or diphenylmethane and of other benzyl alcohol by molecular oxygen in stirred autoclaves at much higher pressures and/or temperatures.

LIST OF PUBLICATIONS AND PATENTS

PUBLICATIONS BASED ON THESIS WORK

1. MnO_4^{-1}-exchanged Mg-Al-hydrotalcite: a stable and reusable/environmetal-friendly catalyst for selective oxidation by oxygen of ethylbenzene to acetophenone and dipheylmethane to benzophenone.

    V. R. Choudhary, J. R. Indurkar, V. S. Narkhede and **R. Jha,** J. Catal., 227 (2004) 257.

2. In-Mg-hydrotalcite anionic clay as catalyst or catalyst precursor for Friedel-Crafts type benzylation reactions.

    V. R. Choudhary, **R. Jha** and V. S. Narkhede, Catal. Commun., (communicated)

3. Highly active and reusable catalyst obtained from Mg-Fe-hydrotalcite anionic clay for Friedel-Crafts type benzylation reactions

    V. R. Choudhary, **R. Jha** and P. A. Choudhary, J. Chem.. Sci. (To be communicated shortly)

4. Solvent-free liquid phase oxidation of benzyl alcohol to benzaldehyde by O_2 over nano-size gold supported on U_3O_8 and other metal oxides.

    V. R. Choudhary, **R. Jha**, A. Dhar, B. S. Uphade and P. Jana, Catal. Commun. (To be communicated shortly)

5. Selective oxidation of benzylic alcohols to corresponding aldehydes by molecular oxygen over Au/U_3O_8 catalyst.

    V. R. Choudhary, **R. Jha** and B. S. Uphade, Catal. Lett., (To be communicated shortly)

6. Benzylation and acylation of aromatic compounds over $GaCl_x$- and $GaAlCl_x$-grafted on Si-MCM-41 or Mont.K-10 clay.

    V. R. Choudhary and **R. Jha**, Appl. Catal. A, (To be communicated shortly)

7. First report on the acylation of nitrobenzene and substituted nitrobenzenes by acyl chlorides over $GaAlCl_x$-grafted-Si-MCM-41 catalyst.

    V. R. Choudhary and **R. Jha**, Chem. Commun. (To be communicated shortly)

8.   Thermally activated FeCl$_3$ impregnated Si-MCM-41, Mont.K-10 and H-beta catalysts for Friedel-Crafts type benzylation and acylation reactions.

V. R. Choudhary, A. G. Gaikwad, P. S. Patil and **R. Jha**, J. Mol. Catal. A, (To be communicated shortly)

9.   Thermally activated GaCl$_3$ impregnated Si-MCM-41, Mont.K-10 and H-beta catalysts for Friedel-Crafts type benzylation and acylation reactions.

V. R. Choudhary, **R. Jha** and P. S. Patil, Appl. Catal.,   (To be communicated shortly)

10. Thermally activated InCl$_3$ impregnated Si-MCM-41, Mont.K-10 and H-beta catalysts for Friedel-Crafts type benzylation and acylation reactions.

V. R. Choudhary and **R. Jha**, Microporo. Mesopor. Mater., (To be communicated shortly)

11. Benzylation and benzoylation of aromatic compounds over thermally activated Si-MCM-41, Mont.K-10 and H-beta supported FeCl$_3$, GaCl$_3$ and InCl$_3$ catalysts

V. R. Choudhary and **R. Jha**, Chem. Lett., (To be communicated shortly)

12. Selective epoxidation of styrene by TBHP over metal oxide catalysts.

V. R. Choudhary, **R. Jha** and N. K. Choudhari, Appl. Catal. A, (To be communicated shortly)

PUBLICATIONS OTHER THAN THESIS WORK

1.   Gold supported on Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$ and Tl$_2$O$_3$ for epoxidation of styrene using anhydrous TBHP.

N.S. Patil, **R. Jha**, B. S. Uphade, S. K. Bhargava, V. R. Choudhary.; *Appl. Catal. A: General 275 (**2004**) 87-93.*

US AND INDIAN PATENT APPLICATIONS FILLED

1. Partially halogenated solid catalyst useful for Friedal?crafts reactions and its method of preparation.
    V.R. Choudhary and **Rani Jha**
    (Filed both US and Indian patent application, July 2003)

2. A process for the aryl?aryl carbon to carbon bond formation by the arylation with aryl halide of aromatic compound using a solid catalyst containing non?noble metallic elements.
    V.R. Choudhary and **Rani Jha**
    (Filed both US and Indian patent application, December 2003)

3. A process for the acylation of aromatic compounds with or without containing nitro group(s) using a reusable solid catalyst.
    V.R. Choudhary and **Rani Jha**
    (Filed both US and Indian patent application, December 2003)