# SYNTHESIS OF ORGANIC CARBONATES USING CARBON DIOXIDE: AN ENVIRONMENTALLY BENIGN ROUTE

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IN CHEMISTRY

BY
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# CERTIFICATE

This is to certify that the work discussed in the thesis entitled **"SYNTHESIS OF ORGANIC CARBONATES USING CARBON DIOXIDE: AN ENVIRONMENTALLY BENIGN ROUTE"** by **M. SANKAR**, submitted for the degree of ***Doctor of Philosophy in Chemistry*** was carried out under my supervision at the Catalysis Division of the National Chemical Laboratory, Pune, India. Such materials as have been obtained by other sources have been duly acknowledged in this thesis. To the best of my knowledge, the present work or any part thereof has not been submitted to any other University for the award of any other degree or diploma.

Date: **Dr. P. Manikandan**

Place: Pune (Research Guide)

# DECLARATION

I hereby declare that the work described in this thesis entitled **"SYNTHESIS OF ORGANIC CARBONATES USING CARBON DIOXIDE: AN ENVIRONMENTALLY BENIGN ROUTE"** submitted for the degree of ***Doctor of Philosophy in Chemistry*** has been carried out by me at the Catalysis Division of the National Chemical Laboratory, Pune, India under the supervision of Dr. P. Manikandan. Such materials as have been obtained by other sources have been duly acknowledged in this thesis. The work is original and has not been submitted in part or full by me for award of any other degree or diploma in any other University.

Date: **M.Sankar**

Place: Pune (Research Student)

***Dedicated to my***

***Teachers***
***&***
***Parents***

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# Chapter – I

## Introduction

# 1. Introduction:

## *1.1. Carbon dioxide –Environmental Issues*

Green house effect is defined as the effect of an increase in the absorption of radiation energy from sun caused by the existence of gases in the atmosphere. Because of this absorption the global atmospheric temperature is increasing which is termed as “global warming”. Many gases such as $CO_2$, $CH_4$, $O_3$, CFCs and $H_2O$ vapour, called as “greenhouse gases”, are responsible for this absorption. $CO_2$ being an important member of these gases, is responsible for many climatic changes demonstrating the importance of $CO_2$ content in the atmosphere. $CO_2$ content in the atmosphere is increasing at a rate of 1% per annum; from 250 ppm of the pre-industrial period to a present level of 400 ppm (315 ppm in 1958, 340 ppm in 1984) [1]. The reason for this increase in $CO_2$ load in the atmosphere is combustion of fossil fuels and deforestation. Among the industrial sectors, energy sector contributes about 25 % of the total global $CO_2$ emission. In addition to this industrial $CO_2$ emission, deforestation of the tropic forests contributes up to 10-30 % enhancement of $CO_2$ level. Other sources which contribute to the increase in $CO_2$ level in atmosphere to a significant level are (a) Volcanic gases, (b) Diluted $CO_2$ in flue gases from industries, (c) Exhaled air which contains 4% $CO_2$, (d) Petrol engine exhaust contains about 13 % and (e) Exhaust gases from several chemical processes [2].

Many research groups are exhaustively investigating for several years the possible connection between anthropogenic $CO_2$ emission, the increasing $CO_2$ content of the atmosphere and the global climate [3-7]. Last 15 years contain the 10 warmest years of the 20th century. Of these, 1998 was the warmest year on record. Because of this increase in global temperature the snow cover in the northern hemisphere and floating ice in the Artic Ocean has decreased considerably. Moreover, globally sea level increased up to 8 inches in the last century. There is an increase in worldwide precipitation by one percent. There is frequent extreme rainfall throughout the world. Unfortunately, green house gases are likely to increase the rate of climate changes [1].

Scientists expect in the next fifty years, the global temperature could increase by 1 - 4.5 $^{o}$F (0.6 - 2.5 $^{o}$C) and in the next century the increase may be 2.2 – 10 $^{o}$F (1.4 – 5.8$^{o}$C). These numbers may vary with regions. As a result of warmer climate there will be an increase in global precipitation. This may result in decline in soil moisture and intense rainstorms are likely to become more frequent. Scientists expect that sea level is likely to rise by two feet along the U.S. coast. Therefore, it is very important to estimate the risk that would follow from a global warming and then developing strategies for the prevention of further increase in the atmospheric $CO_2$ concentration [8].

### *1.2.Reduction in carbon dioxide load:*

The above mentioned environmental effects clearly demonstrate the pressing need for reduction of $CO_2$ load in the atmosphere. This can be achieved by three strategies viz., Reduction of the amount of $CO_2$ produced, Capture and Storage of $CO_2$ ($CO_2$ sequestration) and Utilization of $CO_2$. Among the above mentioned three possible ways reduction in $CO_2$ production is unlikely a viable option as there is always an increase in demand for the consumption of power and consumption of fossil fuels and other energy sources. The energy demand cannot be reduced in future and hence the other two ways should be looked into in an elaborate manner.

### *1.2.1. $CO_2$ capture and storage:*

#### *1.2.1.1. $CO_2$ separation:*

For any process aimed at reducing the emission to the atmosphere of $CO_2$ produced, $CO_2$ has to be separated and captured or at least the exhaust gases have to be enriched. This adds to the cost of the process considerably. For instance, in the case of flue gas from coal-fired plants, due to the relatively low $CO_2$ concentration, the separation will be expensive. In addition to this, there are various sulfur and nitrogen compounds in the coal. During combustion, they will be converted into $SO_x$ and $NO_x$ compounds, which are usually catalyst poisons in the downstream chemical processes and it adds up to the cost. But there are methods by which $CO_2$ can be separated.

Several separation technologies are available [9]. They are

A) Gas/Liquid scrubbing systems

B) Gas/Solid adsorption systems.

C) Cryogenic (fractionation) techniques and

D) Membrane separation technology.

Among the above listed technologies, separation by solvent absorption systems using monoethanolamine (MEA) or by membrane technology appears to be more viable technology [11]. An interested alternate method was proposed for concentrating $CO_2$ in flue gas instead of separating [12]. It is the combustion of fossil fuels in an atmosphere of pure oxygen and recycled $CO_2$ and by this way 90 % $CO_2$ can be produced. The cost of such process was estimated to be in the range of $15-100/t of $CO_2$ [12]. This air separation / flue gas recycling process is reported to be the most energy efficient process. It is estimated that this process cost around 26-31 % of the coal heating value, and at the same time the $CO_2$ recovery is close to 100 %. For other processes it requires 50 % of the coal heating value, and the resulting cost of electricity production increases by over 80 % [13]. But for practical purposes, these numbers are very high. Membrane technology is at the early stage of development. If a breakthrough occurs in the near future, this might well be the basis for feasible $CO_2$ separation processes.

### *1.2.1.2.$CO_2$ storage in aquifers:*

After separating the $CO_2$ the next step would be storing the separated $CO_2$. Important $CO_2$ sink and buffer are aquifers, especially seas and oceans [13 - 15]. Here the amount of $CO_2$ that can be stored is vast. This can be achieved by increasing micro algae biomass or by fixing $CO_2$ as $CaCO_3$ like coral reefs. It was estimated that treatment of Antarctic oceans with iron might allow the phytoplankton to convert all the available nutrients into new organic matter, this would amount to 0.3 - 1.7 Gt of Carbon. An estimate has also been made that Antarctic Ocean, equatorial Pacific and sub artic Pacific have a potential extra uptake of 2.8 Gt of C/y. $CO_2$ as liquid $CO_2$ can be injected into 700 – 1000 m or even to 3000 m, deep ocean water. It was estimated that 3 % of the $CO_2$ emitted by Japan, are used to for carbonates as coral reefs in the shallow sea banks near that country. In addition to carbonates $CO_2$ may form bi-carbonates also or it may dissolve in water. Some researchers feel that storage of $CO_2$ deep inside the ocean is an important method to combat the $CO_2$ problem [2, 14]. But the ecological impact of injecting large amount of $CO_2$ into sea and ocean water is still not certain. Another very important unanswered question is how the cations, e.g., iron or calcium can be provided in a sensible way.

### *1.2.1.3. Underground $CO_2$ storage:*

Another way by which $CO_2$ can be stored is by underground storage. Depleted oil or gas fields are porous and large amount of $CO_2$ can be stored in to those underground reservoirs [16]. It is estimated that in exhausted gas wells around 80 – 300 Gt of C can be stored and exhausted oil wells can accommodate 40-200 Gt of C. Although, these numbers are very high, it is still uncertain whether these kinds of storages can provide long term solution to this problem. Another less practical approach was also suggested where the large quantity of under ground brine deposits can be used to store $CO_2$. A practical problem in this approach is the non-availability of large amount of Ca source.

### *1.2.2. Utilization of $CO_2$ in chemical synthesis:*

The other option to reduce the $CO_2$ level in the atmosphere is to utilize the produced $CO_2$ in the synthesis of value added chemicals. Although this will have a minimum impact in reducing the $CO_2$ level it has its own advantages. The advantages of using $CO_2$ are

1) $CO_2$ is a cheap and renewable feedstock compared to oil and / or charcoal.
2) $CO_2$ is non-toxic and can replace many toxic chemicals such as phosgene and isocyanates.
3) The production of chemicals from $CO_2$ can lead to totally new materials with new properties.
4) The processes using $CO_2$ could be more efficient and economical than current methods.
5) The production of chemicals from $CO_2$ could have a small but some positive impact on the global carbon balance.

Carbon dioxide is being used in beverage industry, fire extinguisher technology, refrigeration, enhanced oil recovery and supercritical $CO_2$ extraction and cleaning. Solvay process for the synthesis of $NaHCO_3$ and manufacture of $Na_2CO_3$ and other carbonates are the other processes which use $CO_2$. Nearly 0.7-1.0 % of the produced $CO_2$ is used, and the consumption of chemical industries is about 0.1 %. The industrial usage of $CO_2$ is approximately 11 megatons of $CO_2$ for the production of chemicals. The main processes which use carbon dioxide are

1) Synthesis of urea
2) Synthesis of salicylic acid
3) Synthesis of cyclic carbonate and polycarbonate
4) Synthesis of methanol.

Synthesis of urea is the biggest user of $CO_2$ which is approximately 90 million metric tons per annum as per 1997 statistics. Other two reactions synthesis of methanol and synthesis of cyclic carbonate and polycarbonates are in pilot plant scale. In addition to these reactions there are many reactions which utilize $CO_2$ which is show in Fig. 1.1. All these reactions are currently being investigated in many of the research laboratories around the world.

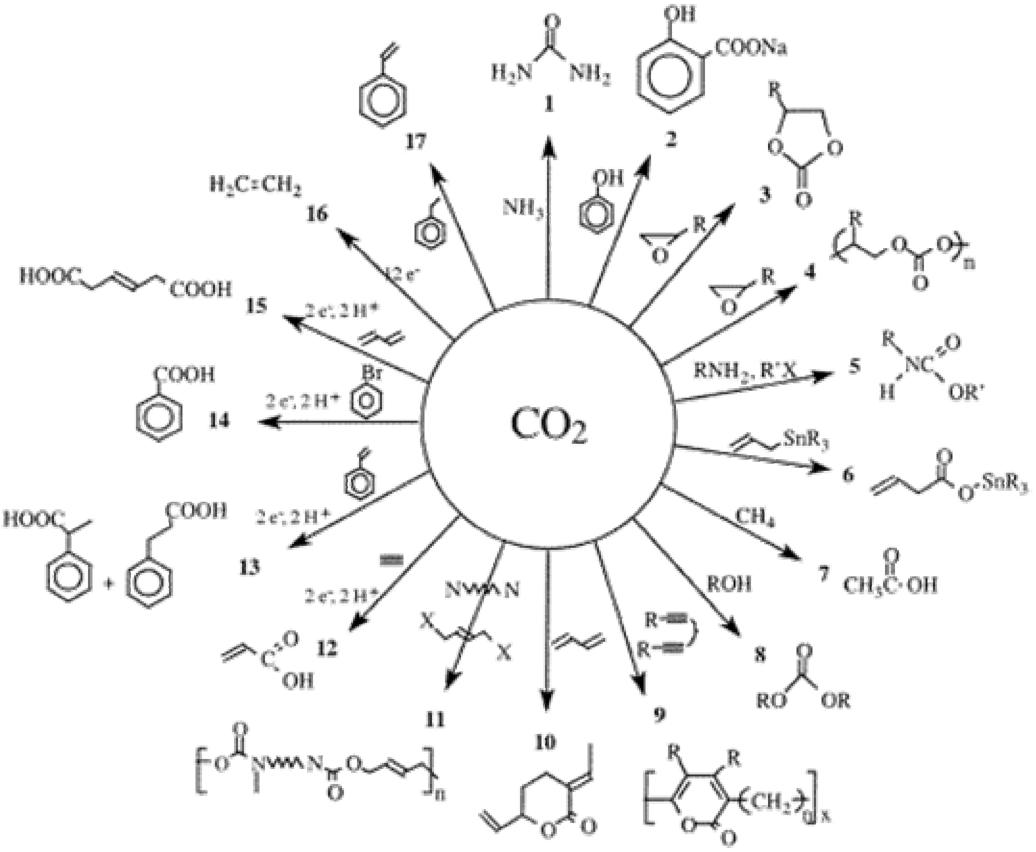


*Fig. 1.1: Various possible organic synthetic schemes which uses $CO_2$*

These reactions differ in the extent to which $CO_2$ is reduced during chemical transformation [8].

### *1.2.2.1. Supercritical $CO_2$ as solvent:*

In addition to these industrial processes, recently researchers are exploring the possibility of using supercritical $CO_2$ as a green and environmentally benign solvent. It is a hydrophobic solvent that can replace conventional organic solvents in number of applications. The main advantage of supercritical $CO_2$ is its critical point ($T_c = 31.0\ ^oC$ and $P_c = 73.8$ bar). The properties which are considered to be superior when supercritical $CO_2$ is used as a solvent are listed below.

1) $CO_2$ cannot be oxidized.
2) $CO_2$ is benign and hence contamination during liquid-liquid extraction is not a real contamination.
3) $CO_2$ is an aprotic solvent
4) $CO_2$ is generally immune to free radical chemistry
5) $CO_2$ is miscible with gases in all proportions above 304K
6) $CO_2$ exhibits solvent properties that allow miscibility with both fluorous and organic materials.
7) $CO_2$ exhibits a liquid viscosity only $1/10^{th}$ that of water.
8) Solvent costs and emission of toxic organics can be reduced.
9) Further separation of products and catalysts can be controlled easily by changing the $CO_2$ pressure.

Currently, supercritical $CO_2$ finds its application in extraction of caffeine, dry cleaning, and parts degreasing. These processes involve high-capacity plants of more than $22.5 \text{ X } 10^6$ Kg per year in the case of decaffeination processes. Other developing technologies include food processing, pharmaceutical processing, polymerizations, emulsion polymerization of water – soluble monomers, enhanced oil recovery and homogeneous and phase separable catalysis, which includes that based on ionic liquid solvents [18-22].

Although $CO_2$ has number of advantages as solvent, due to the inherent nature it has some disadvantages where chemistry is concerned; some of these disadvantages are unique to $CO_2$ while others are common to any solvent. $CO_2$ exhibits a relatively high critical pressure and vapor pressure. It exhibits a low dielectric constant and in a specific case $CO_2$ poisons Ziegler – type polymerization catalysts.

### *1.2.2.2. $CO_2$ as reactant:*

Before exploring the reactivity of $CO_2$, it is necessary to understand some basic physical and chemical properties of $CO_2$. Table 1.1 [23 - 28] lists some of the important properties of $CO_2$. $CO_2$ is a very stable molecule, as illustrated by its standard free energy of formation ($\Delta G^o = -394.359$ kJ/mol) [29]. $CO_2$ is the most oxidized form of carbon, and therefore the only chemical transformation at “normal” energies would be to reduce it.

*Table 1.1: Selected properties of $CO_2$*

| | |
|---|---|
| Point Group | $D_{\alpha}h$ |
| Ground State | $1\Sigma_g^+$ |
| Boiling point ($^oC$) | -78.5 |
| LUMO | $2\pi_u$ |
| HOMO | $1\pi_g$ |
| Bond length ($A^o$) | 1.16 (C-O) |
| Bond energy (eV) | 5.453 |
| Ionization potential (eV) | 13.78 |
| Electron affinity (eV) | -0.6 |
| IR data ($cm^{-1}$) | 1320, 235, 668 |

$CO_2$ is a linear molecule where the oxygen atoms are weak Lewis (and Brönsted) bases and the carbon is electrophilic [8]. The qualitative molecular orbital diagram of $CO_2$ is given below (Fig. 1.2.) [30].

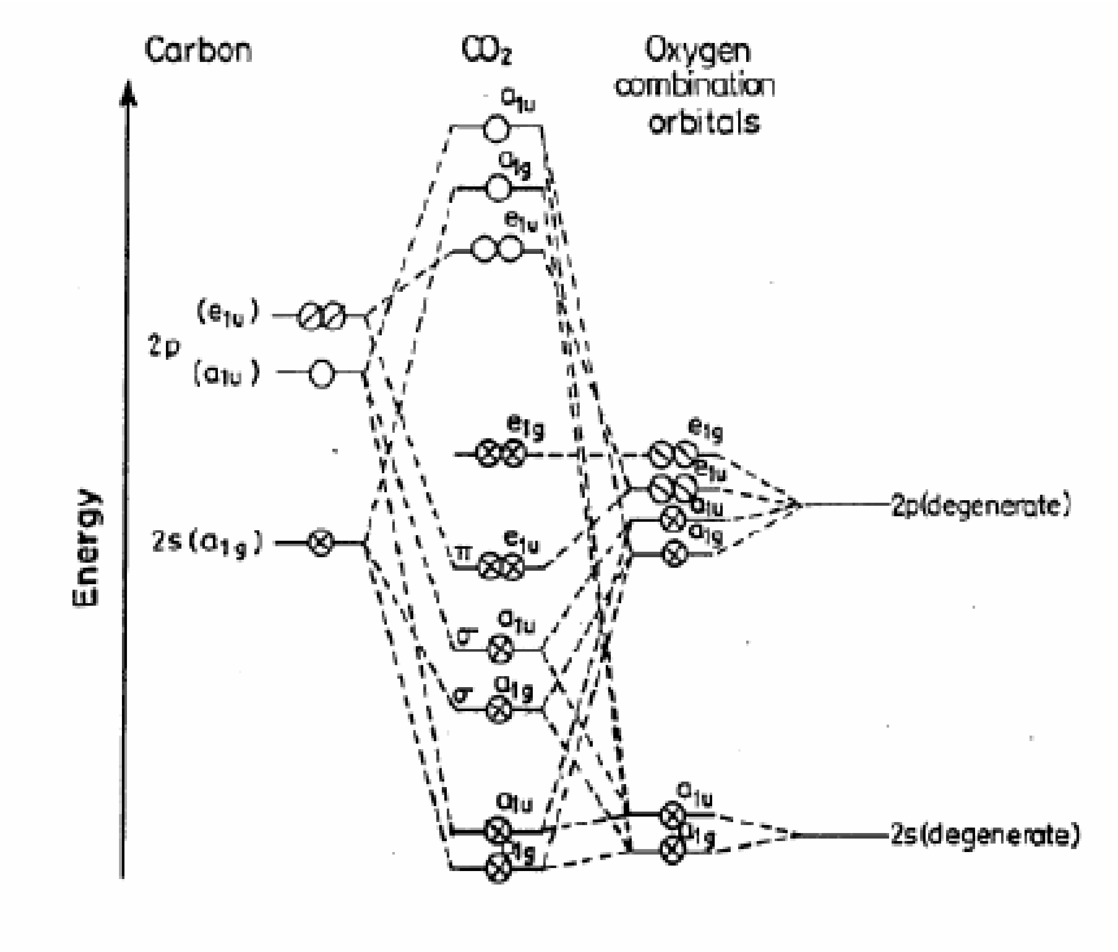


*Fig. 1.2: Qualitative molecular orbital diagram of $CO_2$.*

The central carbon atom is *sp* hybridized and the C-O distance is 1.16 Å. This is shorter than that of the normal C-O double bond where the C is $sp^2$ hybridized. The difference in electro negativities between C (2.5) and O (3.5) lead to a negative polarization on the oxygen atom and a partial positive charge on the C atom. Reactions of carbon dioxide are mostly dominated by nucleophilic attacks at the carbon, which result in bending of the C-O-C angle to about 120 $^{o}$ [31]. This is illustrated in Fig. 1.3.

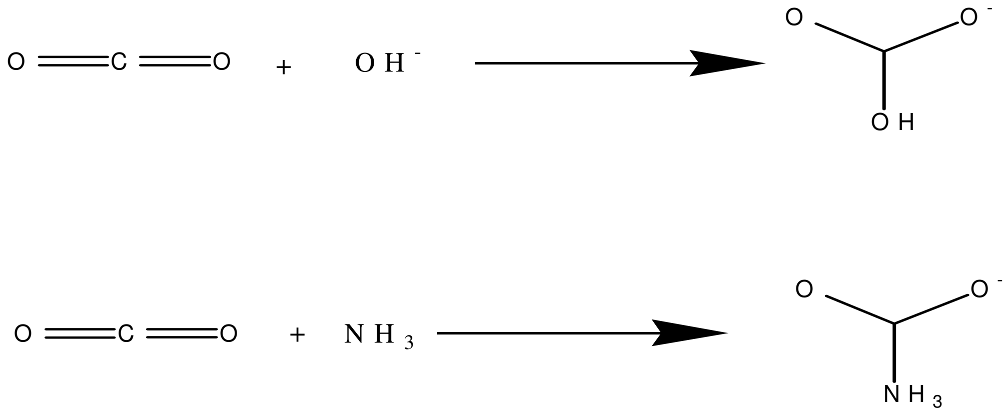
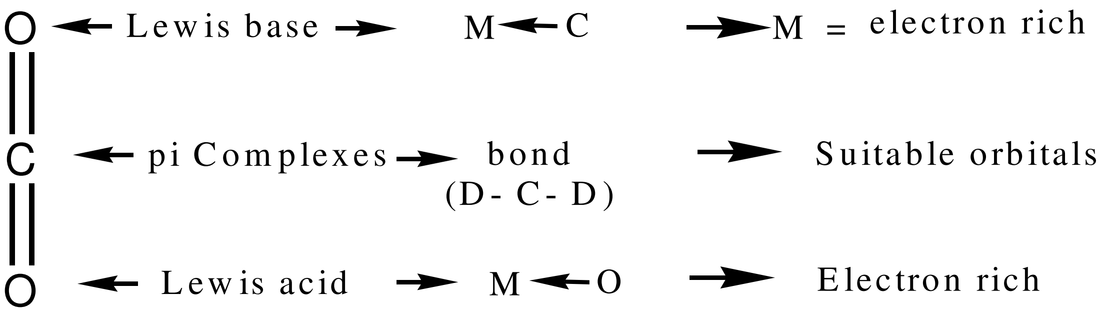


*Fig. 1.3: Nucleophilic attack at the carbon centre*

Although, nucleophilic attack on C is a common occurrence wherever $CO_2$ is involved in the reaction $CO_2$ is a molecule with multiple reactive sites: the carbon is a Lewis acid center (or electrophilic center) and oxygens are weak Lewis bases (or nuclephilic centers). These different centers and their specific electronic requirement for coordination are shown in Fig. 1.4.

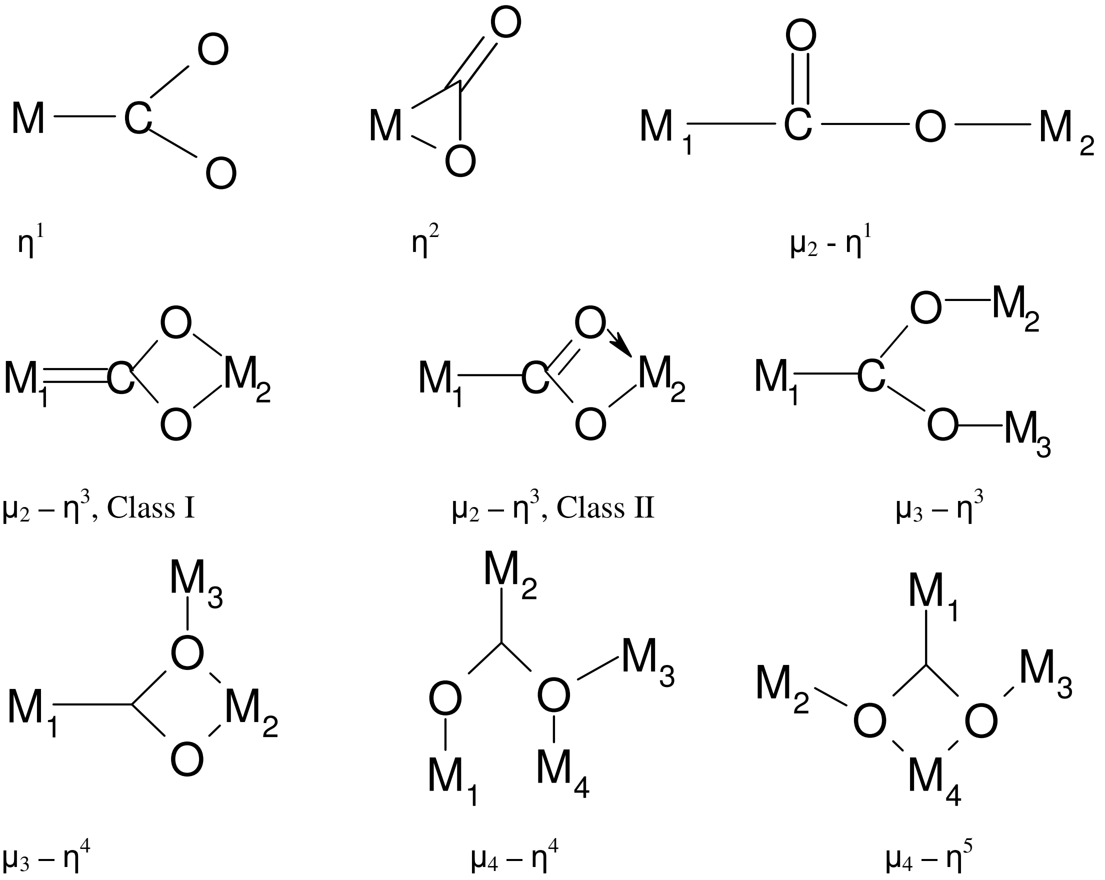


D-C-D = Dewar - Chatt - Duncanson

*Fig. 1.4 Reactive positions of the $CO_2$ molecule and the electronic properties of a transition metal centre required for complexation.*

For a clear understanding of the catalytic conversions using $CO_2$ their complexes with transition metal provides a structural and functional model. In recent past many metal–$CO_2$ complexes have been identified. Although initially thought to be a poor ligand [32] $CO_2$ has demonstrated surprising versatility by exhibiting a great variety of coordination modes in metal complexes. Vol'pin *et al* [33] reported the various possibility of coordinating $CO_2$ to transition metal centers in 1969 and then Jolly *et al*,

[34] in 1971. But the information provided at that time was limited. Recently, Gibson reviewed the synthesis, characterization and reactions of various types of $CO_2$ complexes in detail [35]. Different coordination modes of $CO_2$ to transition metal centers have been described in that paper (Fig. 1.5.).



$\eta^1$ $\eta^2$ $\mu_2 - \eta^1$

$\mu_2 - \eta^3$, Class I $\mu_2 - \eta^3$, Class II $\mu_3 - \eta^3$

$\mu_3 - \eta^4$ $\mu_4 - \eta^4$ $\mu_4 - \eta^5$

*Fig. 1.5: Various modes of coordination in metal $CO_2$ complexes.*

$CO_2$ molecule also gets inserted into M-H bond, M-C bond, M-N bond, M-O bond, M-Si bond and M-P bond. Pandey *et al,* recently reviewed the insertion reactions of $CO_2$ [36]. Other reactions which use $CO_2$ for the synthesis of various compounds are shown in Fig. 1.1. Among these reactions, many reactions utilize $CO_2$ as the C-1 source. Although there are other C-1 sources, $CO_2$ is having a few advantages, from green chemistry point of view. Comparison of properties of various C-1 sources is given in Table-1.2. From this table it can be clearly understood that $CO_2$ is more environment friendly and benign.

*Table 1.2: Properties of Various C1 building blocks.*

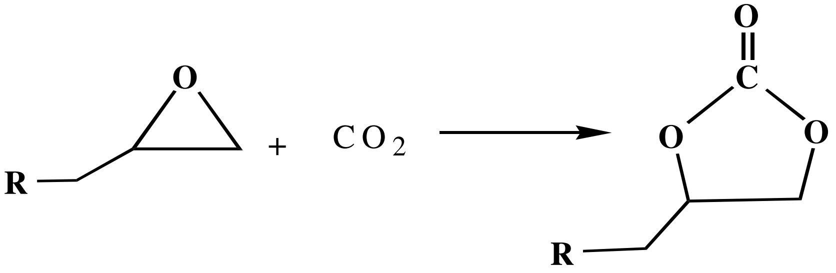
| **Factors** | **CO** | **$COCl_2$** | **$CO_2$** |
|---|---|---|---|
| MAK Value | 30 ppm | 0.1 ppm | 5000 ppm |
| Toxicology | Affinity for Hemoglobin 210 times that of $O_2$ | War gas | Danger of asphysiation at 10 vol% in air |
| Environmental Hazard | Yes | High | Negative |
| Flammability | 12-74% | No | No |
| Boiling point | 81 K | 291 K | 195 K |
| Storage | Only at < 3.5 MPa | Very difficult | No problem |
| Transport | Gas bottles or tanks kg quantities | Possible | Gas bottles or tanks |

### *1.2.2.2.1. Synthesis of cyclic carbonate using $CO_2$:*

Many possibilities are available in the recent literature where $CO_2$ can be used as a C-1 source. Among the various possibilities of utilizing $CO_2$ as a C-1 source, syntheses of organic carbonates are very important because of the applications of the resultant organic carbonates. Organic carbonates may be divided into two groups cyclic carbonates and linear carbonates. They have a large market value (1.8 Mt /year) because they find application as solvents, selective reagents, pharmaceutical intermediates, fuel additives and monomers for polymers [37]. First synthesis of cyclic carbonates will be discussed and then linear carbonates.

Traditionally cyclic carbonates are prepared from diol using phosgene, but it can be substituted by compounds like chloroformic acid, tricholoromethyl ester (diphosgene) and bis (trichloromethyl) carbonate. For example 1,2 and 1,3-diols react with triphosgene in $CH_2Cl_2$ and pyridine at 343 K to form cyclic carbonate [38, 39]. But the major drawback in this method of synthesis is that this process uses highly toxic and hazardous chemicals like phosgene and pyridine. In addition to that, after the completion of the reaction pyridine has to be neutralized and disposal of the byproduct salt is another big issue.

An alternate route which overcomes all the above mentioned shortcomings, which is efficient and environmentally benign for the synthesis of cyclic carbonates is the reaction of $CO_2$ with epoxides (Scheme 1. 1). This reaction is attractive in many ways and the most important one is, it is atom efficient; all the reactant molecules are converted into the desired product without any other product.



*Scheme 1.1: Reaction of epoxide and carbon dioxide to form cyclic carbonate.*

Several homogenous as well as heterogeneous catalysts are known for this conversion. A few of them are discussed below.

*(a) Quaternary ammonium salt, phosphonium salt and group I metal salts based catalysts:*

Simple quaternary salts such as alkyl ammonium and phosphonium halides are reported to be very efficient for the synthesis of cyclic carbonates from epoxides and $CO_2$ [40,41]. But these catalysts are homogeneous in nature, for heterogenizing this catalyst they were immobilized on resins and used as catalysts. BASF [42] and Chimei-Asahi Corporation (Taiwan) have recently started producing cyclic carbonates using these kinds of catalysts in a pilot plant scale [43]. But this process requires very high temperature and high pressure of $CO_2$ (30 - 80 bar) to get reasonably high cyclic carbonate yield. Rokicki *et al,* [44] reported a variety of alkali metal salts alone and in conjunction with crown ether to catalyze the reaction of epoxides and $CO_2$ to form cyclic carbonates in very high yield. There is no formation of polycarbonate at 393 K and 40 bar of $CO_2$ even after 24 h.

### *(b) M(II) alkoxide and carboxalate catalysts.*

Zn(II) complexes were studied to a maximum extent among the group 12 metal complexes for the conversion of epoxides to cyclic carbonates [45]. Because of this initial success a variety of Zn(II) complexes were synthesized and screened for their catalytic activity. A variety of metal carboxylates or alkoxides were reported to catalyze carbonate synthesis at relatively mild condition [46, 47]. Coates *et al* reported that zinc methoxide complexes which is active at a milder condition [48, 49] for the synthesis of polycarbonate from epoxide and $CO_2$.

### *(c) Schiff Base Complexes:*

Several metal Salen complexes are found to catalyze the reaction of epoxide with $CO_2$ in the presence of organic bases like N-methyl imidazole, Dimethyl aminopyridine etc. Among the various complexes reported Cr(III)(salen)Cl showed the highest activity for the synthesis of cyclic carbonate as well as polycarbonate. By manipulating the reaction condition either cyclic carbonate or polycarbonate could be obtained by the reaction of epoxide and $CO_2$. High temperature and low $CO_2$ pressure yielded cyclic carbonate at the same time, lower temperature and higher $CO_2$ pressure yielded polycarbonates [50,51]. IR spectroscopy can be used to differentiate between cyclic carbonate and polycarbonate. Cyclic carbonate has a characteristic IR peak at 1800 $cm^{-1}$ and polycarbonate has a peak at 1745 $cm^{-1}$.

### *(d) Porphyrine and Phthalocyanine Complexes:*

Tetraphenylporphinato aluminum methoxide, (TPP)AlOMe, in conjunction with a co catalyst like 1-methyl imidazole is very active for the conversion of epoxide to cyclic carbonate at relatively lower temperature and $CO_2$ pressure [52]. Other metals have also been investigated, but to a lesser extent as a potential catalysts for the coupling reaction of $CO_2$ with epoxide [53,54]. Kasuga *et al,* reported an interesting result where Co(III)TPP(Cl) showed 50 times higher activity than Co(II)TPP [55,56]. Structural analogues of metalloporphyrins, metallophthalocyanines also showed very high catalytic activity in conjunction with Lewis bases like tributylamine, 1-methylimidazole and triphenylphosphine.

### *(e) Heterogeneous Catalyst System:*

Although many of the reported catalysts are homogeneous in nature, there are some purely heterogeneous catalysts available in literature for the conversion of epoxide to cyclic carbonate. Few of them are listed below with their performance. Yamaguchi *et al* reported a purely heterogeneous catalytic system for this cyclo addition reaction. It is based on Mg-Al mixed metal oxides (Mg/Al = 5) and it was synthesized by the calcination of hydrotalcites. This particular catalytic system was found to be catalytically active at 373 K with a $CO_2$ pressure of 5 atm [57]. Here Al and Mg sites act as acidic and basic site respectively and this catalytic system can be recovered and reused. However, this reaction requires huge amount of catalyst and a reasonable conversion was obtained only after a very long reaction time. MgO alone was reported to be an effective catalyst for the conversion of epoxide to cyclic carbonate (with 99% *ee*) up to 70% but in the presence of DMF (N,N-Dimethylformamide) [58]. Another heterogeneous catalyst reported by Kim *et al* was zinc halides supported in poly(4-vinylpyridine) but cyclic carbonate yield was only a moderate 30-60 % to ethylene carbonate and 8-10 % to propylene carbonate [59]. Other catalyst reported for this reaction is Al phthalocyanine covalently bound to silica by He *et al*, [60], polymer supported chromium porphyrin [61], and guanidine anchored in MCM-41 [62]. Although these catalysts are heterogeneous in nature they exhibited lesser activity compared to their homogeneous analogues [63 - 65].

### *(f) Ionic Liquids:*

Room temperature ionic liquids find application as environmentally benign media for catalytic processes. They have negligible vapor pressure; they are thermally stable and special characteristics which are not found in conventional organic and inorganic solvents. Many reports are available where they have utilized room temperature ionic liquids for cyclic carbonate synthesis [66, 67].

### *1.2.2.2.2. Synthesis of dimethyl carbonate (DMC):*

Before reviewing the literature on the synthesis of dimethyl carbonate, the importance of dimethyl carbonate in industries and as “green” alternative is outlined below.

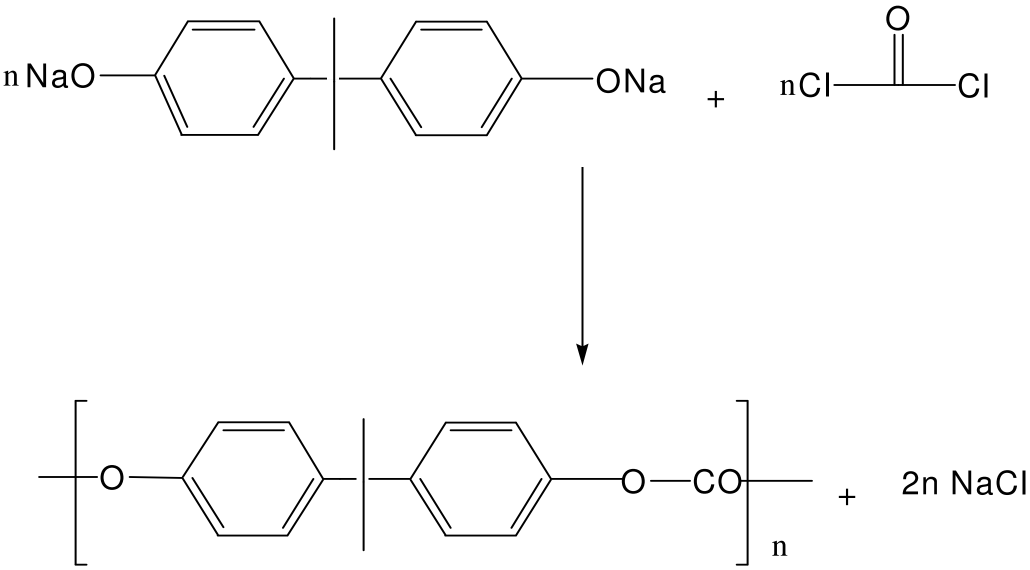
### *(a) DMC and fuels:*

Due to its very high oxygen content (53 %), dimethyl carbonate (DMC) is a strong contender to help the refining industry to meet the Clean Air Act specifications. It has about 3 times the oxygen content as methyl *tert*-butyl ether. It also has a good blending octane. Besides its blending properties, there is one physical property of DMC which is of paramount importance; it is the distribution of DMC in gasoline/water. This is much more favorable than for the $C_1$-$C_3$ alcohols. Another important property is that it freezes at 1 $^oC$ (34 $^oF$). But, at 3-4 % in gasoline, it remains in solution without becoming hazy or cloudy below -40 $^oC$ (-40 $^oF$). Apart from these properties, DMC is low in toxicity and degrades quickly. Recently scientists have shown that usage of DMC in reformulated gasoline is much more economical than MTBE produced from butane [68].

In addition to these interesting physical properties, DMC has interesting chemistry too. DMC is having two carbon centers, one the carbonyl carbon and the other one is the methyl carbon. Both these carbon centers are susceptible for nucleophilic attack. When a nucleophile attacks the carbonyl carbon of DMC, acyl-oxygen bond cleaves which results in a methoxycarbonyl product. Because of this chemical property DMC can replace the hazardous phosgene as a safe source for carbonic acid derivatives. Although phosgene has a very high reactivity, it is highly hazardous and very difficult to dispose of. In addition to that, by products like HCl and other chlorides present a serious disposal and corrosion problems. Thus, DMC is used as an environmentally benign substitute for phosgene. When a nucleophile attacks the methyl carbon of DMC, the alkyl-oxygen bond cleaves which result in a methylated product. Thus, DMC is a useful methylating agent and can be a safe substitute for dimethyl sulfate. A few representative examples for the use of DMC as an environmentally benign substitute for phosgene and dimethyl sulfate are given below in detail.

*(b) DMC in polycarbonate synthesis:*

Polycarbonates have been commercially produced using sodium salt of bisphenol-A and phosgene as follows:



*Scheme 1.2: Commercial synthesis of polycarbonates*

The main disadvantages of this phosgene process are

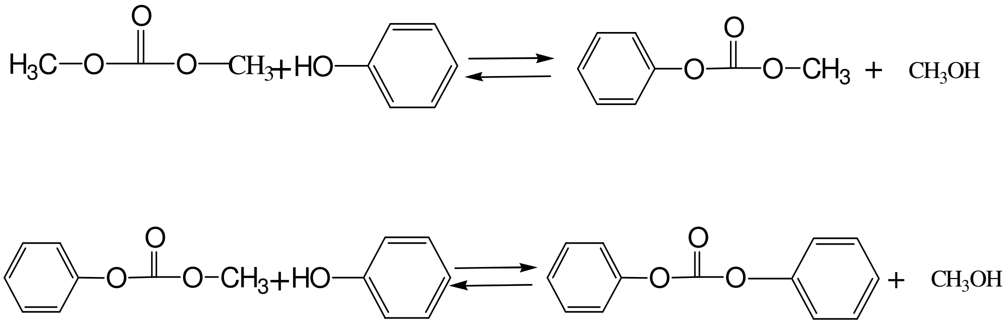
(a) Use of the high toxicity and corrosiveness of phosgene.

(b) Use of copious amounts of methylene chloride solvent (10 times the weight of the product). This solvent is water soluble, so it contaminates the wash water.

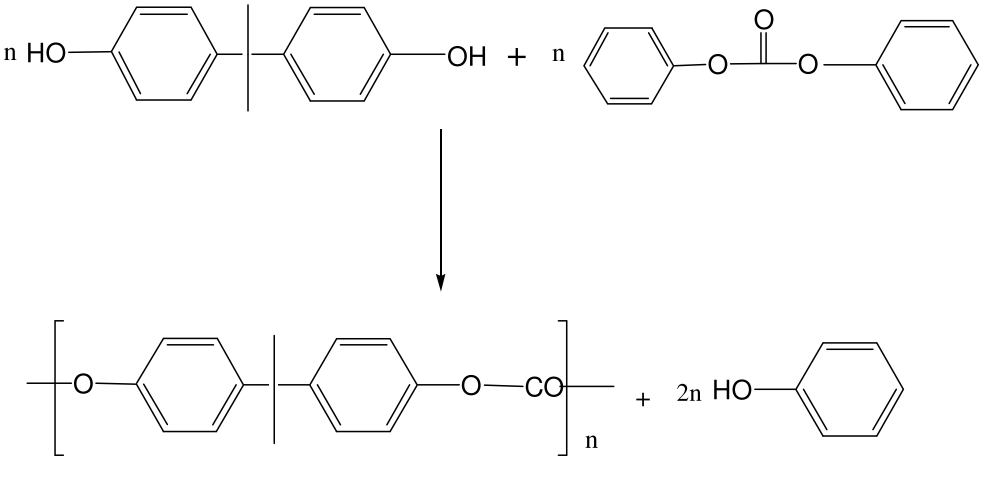
(c) The complex clean-up to remove ionic materials.

To overcome these disadvantages, a more practical non-phosgene process was proposed which uses DMC. The process is given below (Scheme 1.3.)

*Step – 1: Synthesis of Diphenyl Carbonate*



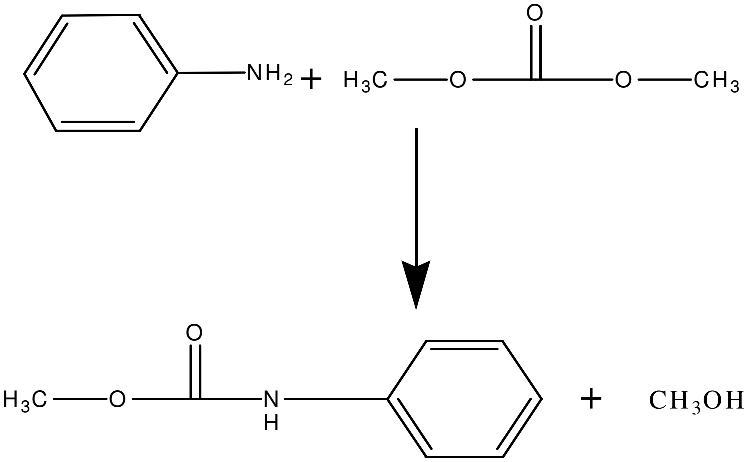
*Step 2: Synthesis of Polycarbonate from DPC and Bisphenol-A:*



*Scheme 1.3: Alternate route for the synthesis of polycarbonate using DMC.*

*(c) DMC in carbamate and isocyanate synthesis.*

DMC replaces phosgene in the synthesis of isocyanage for polyurethane by the following process. In this method, alkyl carbamates (precursor for isocyanate) is prepared by the following scheme (Scheme 1.4.).



*Scheme 1.4: Synthesis of carbamates using DMC*

(d) DMC as methylating agent:

Alkylation reactions are synthetically very important reactions. Conventionally, for methylations, methyl chloride or dimethyl sulfate is used as methylating agent. Both methyl chloride and dimethyl sulfate are toxic and corrosive and they require a stoichiometric amount of NaCl. It is always preferable to use catalytic amount rather than using stoichiometric amount of base. Besides, it requires rigorous work up procedures to separate the products in liquid phase reactions. But scientists have proved that these disadvantages can be over come by using DMC as methylating agent in the vapor phase methylation of phenyl acetonitrile, aniline and phenol with zeolite catalysts.

The above examples clearly indicate the importance of dimethyl carbonate in industrial chemistry point of view. Now after reviewing the uses of DMC, different methods of synthesizing DMC are discussed below.

### *(e) Synthesis of DMC by phosgenation of methanol:*

Conventionally, DMC was produced by the phosgenation of methanol in 1980s [69]. This process involves a methylchloroformate intermediate. This is shown in scheme 1.5.

$$COCl_2 + CH_3OH \longrightarrow ClCOOCH_3 + HCl \qquad (a)$$

$$ClCOOCH_3 + CH_3OH \longrightarrow (CH_3O)_2CO + HCl \qquad (b)$$

*Scheme 1.5: Synthesis of DMC by phosgenation of methanol.*

In this reaction the first step (formation of methylchloroformate) is faster compared to the second step but the second step can be also be accelerated using an acid scavenger like tertiary amine or any bases like NaOH etc. [70]

### *(e) Synthesis of DMC by oxy carbonylation of methanol:*

In the liquid phase synthesis, methanol is reacted with carbon monoxide and oxygen in the presence of a catalyst according to the reaction given below.

$$CH_3OH + CO + 1/2\ O_2 \longrightarrow (CH_3O)_2CO + H_2O$$

Enichem Co invented a copper chloride based catalyst for the liquid phase synthesis of DMC using this oxidative carbonylation of methanol [71]. This was found to be an effective catalytic system. This reaction was performed as follows, methanol, carbon monoxide and oxygen was fed at the same time to a suspension of catalyst in a mixture of methanol and DMC [72], the produced DMC was recovered by distillation after catalyst separation. The main advantage of this process is that this process is not influenced by the purity of carbon monoxide and other diluents like hydrogen did not interfere with the catalytic system [73]. The first plant based on this technology was started on 1983 and till now around 70 kt/year is produced world wide using this process.

In the gas-phase synthesis, again Enichem came up with a process which uses CuCl dispersed on alumina as catalyst [74]. Dow chemical used $CuCl_2$ alone or in combination with alkali and alkaline earth halides and the pyridine complex of $Cu(OCH_3)Cl$ all supported on active carbon as catalysts [75]. CuCl supported on Y-type gave a high productivity of DMC by a high temperature anhydrous reaction [76]. Both catalyst life as well as activity could be improved by adding tetra-alkyl ammonium chlorides to copper chlorides on zeolites or alumina [77]. Despite of the large amount of work on the catalytic systems, no process based on gas-phase direct methanol oxy-carbonylation to DMC has been established.

*(f) Synthesis of DMC by the direct reaction of $CO_2$ and methanol:*

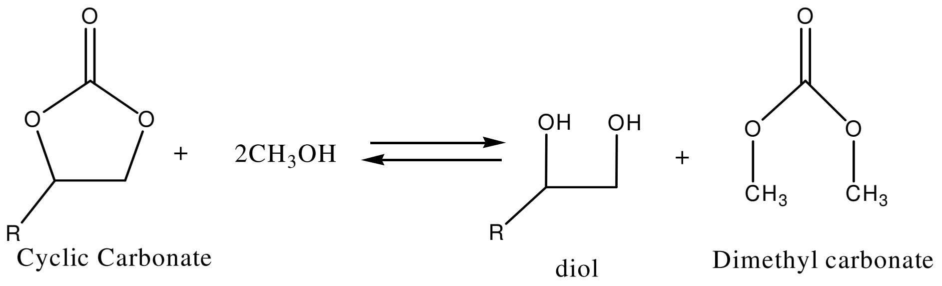
Hoffman studied the direct synthesis of organic carbonates directly from alcohols and $CO_2$ [78]. But currently, only the synthesis of dimethyl carbonate from methanol and carbon dioxide is studied intensively. This reaction occurs at around 140-190 $^{o}$C with a $CO_2$ pressure of about 5 MPa using $ZrO_2$ catalysts [79]. Unfortunately this method suffers a serious drawback; the methanol conversion is very low because of thermodynamics.

$$CO_2 + {}_2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O$$

But the equilibrium can be shifted towards right by removing the water formed or by using dehydrated derivatives of methanol, such as acetals. Further efforts in this very promising area are necessary to discover more efficient catalytic systems.

*(g) Synthesis of DMC by transesterification of cyclic carbonates:*

Another alternative method for the synthesis of DMC is the transesterification of ethylene carbonate (EC) with methanol. Here, DMC is co-generated with ethylene glycol (EG), according to the following scheme:



*Scheme 1.5: Transesterification of cyclic carbonate to form DMC and diol.*

Ethylene carbonate can be prepared by a well known process from ethylene oxide and carbon dioxide with a catalyst such as a quaternary ammonium halide at 150–175 °C [80]. Other catalysts for the synthesis of cyclic carbonates from epoxide and $CO_2$ are given in the previous section of this chapter. Both homogeneous and heterogeneous basic or acid catalysts can be used for the transesterification reaction; however, the base catalyzed reaction appears to be the most effective for the synthesis of DMC [81]. Recently, a new heterogeneous catalyst based on potassium carbonate treated titanium silicate (TS-1) molecular sieve was reported [82]. Unfortunately, the transesterification reaction of EC with methanol is an equilibrium reaction and the formation of DMC is thermodynamically not favored. Several methods have been suggested to improve the low yield of DMC, for example, by removal of the reaction product as DMC/$CH_3OH$ azeotrope from the reaction mixture by distillation [83] or by selective solvent extraction of the DMC produced [84]. In this reaction EC and methanol conversion are typically in the range 50–60 % and 15–20 %, respectively, whereas the DMC selectivity, based on both converted EC and methanol, is about 98 %.

## 1.3. Scope and Objective of the Present Work:

As mentioned above, utilization of $CO_2$ in the synthesis of organic compounds as a C-1 source is of great importance in the area of green chemistry and catalysis. Synthesis of organic carbonates is particularly very interesting because of the potential application of these carbonates. In addition to this, $CO_2$ can replace environmentally hazardous phosgene in these processes. Thus synthesis based on $CO_2$ is not only environmentally benign, but also it leads to the most efficient way of utilizing $CO_2$. Although, many catalysts are reported so far for this kind of synthesis, they have one or other short coming mentioned below, large amount of catalyst, need for co-catalyst, solvents, high temperature, high pressure and longer reaction time. Because of these facts, there is a pressing need for the development of single site active catalyst for the synthesis of cyclic carbonate using $CO_2$. A detailed understanding of the mechanism of carbon dioxide activation is also very important.

Dimethyl carbonate (DMC) can be synthesized by one pot synthesis directly from $CO_2$ and methanol, but the synthesis of DMC by the transesteification of cyclic carbonates (ethylene carbonate or propylene carbonate) is considered to be more efficient. Again this method is eco-friendly, and phosgene-free. But an efficient, reusable, very active catalyst for this transesterification reaction is still missing. Moreover very few catalysts are reported which are active for the continuous synthesis of DMC from cyclic carbonates.

Accordingly, the objective of the present study is to develop an efficient single site catalyst for

1) The synthesis of cyclic carbonate from epoxides and CO2
2) The transesterification of cyclic carbonate for the synthesis of DMC at ambient condition
3) The continuous production of DMC from cyclic cabonates at ambient condition.

The work conducted in this thesis is aimed at contributing significantly to green chemistry and sustainable chemical processes.

## 1.4. Organization of the thesis:

The thesis is divided into six chapters which includes a general introduction (Chapter-1).

*Chapter 2:*

This chapter deals with synthesize of Zn-W polyoxometalate and its application as an effective catalyst in conjunction with an organic bases for $CO_2$ insertion into an epoxide ring to form cyclic carbonates (see the above scheme). This catalytic system has been found to be efficient even at low $CO_2$ pressure range, 60-100 psig and at a moderate temperature range, 120 to 140 $^{o}$C. Zn-W polyoxometalate part of the catalytic system could be recovered and reused without losing its activity. A very high turnover number of more than 40,000 based on the Zn-W-polyoxometalate could be achieved with this catalytic system. The catalyst system is active for a variety of epoxides including epochlorohydrin, propylene oxide, butylene oxide etc. More importantly this reaction could be carried out without any organic solvent. We have found that there is a cooperative mechanism working between Zn-W-polyoxometalate part and the Lewis base and a reaction mechanism has also been proposed accordingly.

*Chapter 3:*

This chapter deals with yet another catalyst system for the $CO_2$ insertion reaction with epoxides for cyclic carbonates formation. The catalyst systems contain N-heterocyclic compounds anchored on silica support through a propyl group. Unlike the Zn-W-polyoxometalate catalyst system, the present catalytic systems do not need an additional base. This single solid catalyst has been found to be as efficient as Zn-W-polyoxometalate system though the turn over number is slightly low. This heterogeneous catalytic material could be recovered and reused for several cycles without lose in its activity. This material was characterized using physico-chemical methods like elemental analysis, IR and multi nuclear solid state NMR. The stability of the catalyst has been demonstrated by solid state NMR studies before and after the reaction.

*Chapter 4:*

Having achieved the synthesis of cyclic carbonate with near quantitative yield from $CO_2$ and epoxide using a single heterogeneous catalyst, our next objective was to synthesize another important organic carbonate namely dimethyl carbonate by transesterification of cyclic carbonates with methanol. We have discovered sodium tungsate as an efficient catalyst for the above transesterification reaction. This reaction could be carried out at ambient condition in a simple RB flask. We could achieve DMC yield of more than 80 mol % in 5 h of reaction time. In this chapter, we have tried to elucidate the mechanism of this reaction using *in-situ* Raman and IR spectroscopic techniques. A controlled experiments reveals that methoxide ion was an intermediate species that leads to the transesterification production and a reaction mechanism has been proposed based on this insitu studies. This catalyst could be recovered and reused for 3 runs without lose in activity. However, the activity decreases slightly during the further runs.

*Chapter 5:*

Although sodium tungstate catalyst was efficient for above transesterification reaction, use of this catalyst for the continuous mode operation needs addition of binder like silica to the catalyst to make pellets which leads to certain amount of cleaved products. In an effort to develop a highly stable robust catalyst with better activity, we found CaO-ZnO based catalysts better and suitable for both batch and continuous mode operations. The catalyst is highly active even at ambient conditions and DMC yield of more than 85 mol % was achieved within 2 h of reaction time. Experimental conditions for both batch and continuous mode operations have been optimized. The catalyst works effectively even at LHSV of more than 16 $h^{-1}$. Time on stream studies with the present catalyst upto 60 h showed no appreciable amount of loss in its activity. Both ethylene and propylene carbonates have been tested.

*Chapter 6:*

This chapter summarizes the overall conclusion from the work presented in this thesis.

In short, this thesis reports novel, single site, reusable, active catalyst for the synthesis of cyclic carbonate from epoxide and $CO_2$. Again for the synthesis of DMC a very efficient simple catalyst which is active at ambient condition. A continuous process is also reported for the synthesis of DMC at ambient condition using a mixed metal oxide catalyst.

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# Chapter – II

## Synthesis of cyclic carbonates using polyoxometalate based catalytic system

Part of the work described in this chapter has been published/patented:

(a) M. Sankar, N. H. Tarte, P. Manikandan, *Applied Catalysis A: General* 276 (2004), 21.

(b Palanichamy Manikandan, Meenakshisundaram Sankar *US Patent:* 6,924,379

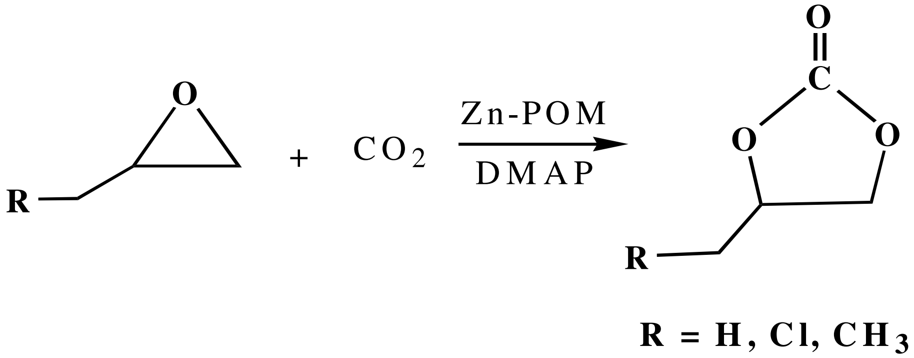
## 2.1. Introduction:

Research activities in the area of utilization of carbon dioxide, a global-warming gas, have gained great momentum in the recent years. These studies are important not only from green chemistry and environmental points of view but also from industrial application points of view. As a non-flammable, inexpensive and ubiquitous gas, $CO_2$ can be used as a C1 feed stock for the synthesis of cyclic carbonates, polycarbonates and for many other organic transformations [1–3]. High abundance of $CO_2$ in the nature can be added advantage. The above environmentally benign transformations are attractive processes, as $CO_2$ can be incorporated into selective organic groups like epoxides without any side products [4].

Organic cyclic carbonates have been widely used as precursors for the synthesis of polycarbonates, aprotic organic solvents, and fine chemical intermediates [5–7]. Several catalytic materials including amines, phosphines, alkali metal salts, metal oxides, coordination metal complexes, have been reported in the recent years for the synthesis of cyclic carbonates by cyclo-addition of $CO_2$ with epoxides [7–17]. Transition metal ion-based catalysts in conjunction with a Lewis base have also been reported to be efficient for the $CO_2$ cycloaddition reactions [1, 14–17]. Though good conversion and selectivity have been achieved, most of the reported catalytic systems carry at least one of the following disadvantages: the need for the high concentration of catalyst, instability of the catalyst, need for a co-solvent, requirement of higher temperature and pressure experimental conditions, longer duration for the completion of reaction, or difficulty in separating the catalyst after the reaction for reuse. For example, Cr-salen-based homogeneous catalyst was found to be efficient, but reusability of the catalyst was not reported [1]. Among the heterogeneous catalysts known, only a few are reported to be separable and reusable [16–26]. Yasuda *et al.* have used SmOCl as a catalyst to obtain higher selectivity without any additive under super critical $CO_2$ ($scCO_2$), but the yield to the cyclic carbonate was poor without an additive like DMF [24]. Yamaguchi *et al.* [20] reported an active mixed metal oxide catalyst for the cycloaddition reaction, but the reaction needs a higher catalyst/substrate ratio.

Tungsten based transition metal ions substituted sandwich type-polyoxometalates have attracted a great attention in recent years as they are oxidatively and solvolytically stable. These polyoxometalates are more stable than the conventional Keggin type polyoxometalates and metalloporphyrins and are easy to synthesize as compared to zeolites or molecular sieves [25, 26, 31]. In addition, the acid-base and oxidation properties of the polyoxometalate based catalysts can be modified using appropriate transition metal ions. Among the reported transition metal ion substituted polyoxometalates, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$, is reported to be highly stable and active for several catalytic reactions. In the present work, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$, is exploited for the $CO_2$ insertion reactions.

This chapter describes the cycloaddition of $CO_2$ with different epoxides using a zinc-substituted sandwich-type polyoxometalate, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$ hereafter will be referred as Zn-POM [29], in conjunction with dimethyl amino pyridine (DMAP) for cyclic carbonate synthesis (Scheme 2.1) with or without any organic solvent. To the best of our knowledge, this is the first report on polyoxometalate-based catalyst usage for the $CO_2$ cycloaddition reaction. It is gratifying to note that the present catalyst system could circumvent many of the above disadvantages. We have also found that Zn-POM in conjunction with DMAP efficiently promotes the cycloaddition reaction with a quantitative conversion and high selectivity. Also, the Zn-POM part of the catalyst can be recovered and reused for many cycles. The integrity of the structure of Zn-POM is not altered during the reaction as proven by IR, UV-Vis and powder XRD studies.



*Scheme - 1.1: Cycloaddition of epoxide with $CO_2$* using Zn-POM based catalyst

## 2.2. Experimental:

### *2.2.1. Chemicals:*

All the solvents of high-purity were locally purchased and used without further purification. Epichlorohydrin, propylene oxide, butylene oxide and dimethylamino pyridine were purchased from Merck Co. $CO_2$ with > 99.5 % purity was procured from De-lux Trading Co.

### *2.2.2. Synthesis and characterization of catalyst (Zn-POM):*

The zinc (II)-substituted polyoxometalate, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$, was synthesized by adopting a reported procedure [29]. In a typical synthesis, an aqueous solution of $Na_2WO_4.2H_2O$ (12.7 g, 38 mmol in 35 ml $H_2O$) was treated with concentrated nitric acid (14 M, 2.5 ml) at 358 K with vigorous stirring to obtain a clear solution. An aqueous solution of $Zn(NO_3)_2.6H_2O$ (2.98 g, 10 mmol in 10 ml of $H_2O$) was added to the above solution slowly at 363 K. A white precipitate readily soluble in the solution was formed under these conditions. The addition was carried out slowly to prevent the formation of any amorphous material. The hot solution was stirred for an hour, filtered and allowed to cool. On cooling, white needle shaped crystals started appearing. After separating the crystals, the liquid was evaporated to half the volume on a water bath and kept covered without disturbing. Needle-like crystals were allowed to grow for 3-4 days. The resulting cold filtrate was shaken with an equal volume of acetone and the dense lower layer was diluted and heated to 323 K and kept at this temperature. After the recovery of the product, the process was repeated with the filtrate till no more product separated out. All the different fractions of the product were recrystallized together from water to form a homogeneously hydrated product.

The prepared zinc containing polyoxometalate was characterized by elemental analysis, IR and UV spectroscopic methods. Elemental analysis was done using both ICP-AES (Perkin Elmer Plasma 1000 Emission Spectrometer). The results are found to be in accordance with the theoretically calculated values Elemental analysis: observed (expected), Na, 4.56 (4.60), Zn, 5.42 (5.45), W, 57.89 (58.1) %. IR spectrum of the sample was recorded as a KBr film using Shimadzu FT-IR 8201 PC instrument with a resolution of 4 $cm^{-1}$ and 100 scans were taken. The IR spectrum of the material is show**n** below, Fig. 2.1. The IR bands at 939, 881, 785 and 700 cm$^{-1}$ are characteristic of sandwich polyoxometalate structure and matches very well with the reported values [30-32]. Diffuse reflectance UV-Vis spectrum of this material showed absorption at 260 nm as shown in Fig. 2.6.

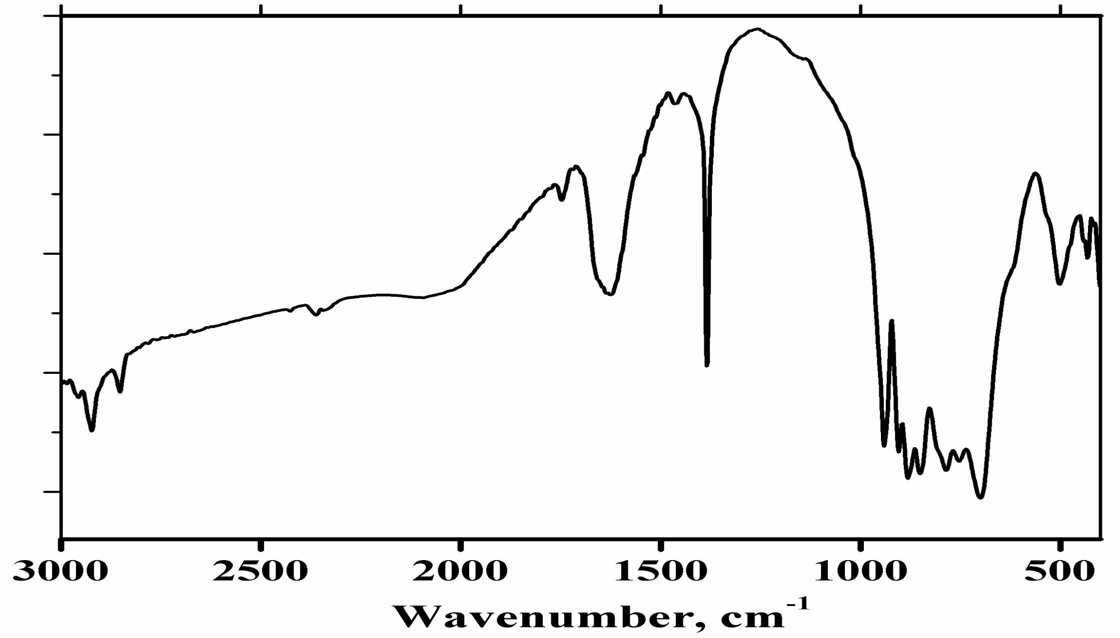


*Fig. 2.1: IR spectrum of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$*

### 2.2.3. Catalytic reaction and analyses:

In a typical reaction, a stainless steel autoclave (100 ml capacity) was charged with 0.0027 mmol of Zn-POM, 3 moles equivalent (to Zn-POM) of dimethyl amino pyridine (DMAP), an accurately weighed quantity of *n*-hexadecane (internal standard for GC analysis), the required amount of epoxide and 0 - 10 ml of $CH_2Cl_2$. After purging with $CO_2$, the autoclave was pressurized to the required level and the reaction mixture was heated to the required temperature. The reaction mixture was stirred (using a leak-proof mechanical overhead stirrer) at 400 rpm. For kinetic experiments, small amounts of sample were withdrawn periodically after quenching the reactor with ice cold water and after venting the excess gas. The samples were then subjected to GC analysis (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 30 m X 0.25 mm 5 % phenyl methyl silicone capillary column and nitrogen as the carrier gas). The conversion of the epoxide was estimated with reference to the internal standard. The products were identified by GC–MS (Shimadzu Gas Chromatography, GC-17A fitted with QP- 500MS Mass Spectrometer), IR (Shimadzu FTIR 8201 PC instrument), NMR (BRUKER, DRX500) and compared with the authentic samples. The reaction mixture was also subjected to mass balance and it was always found that the value was 2 –5 % less than expected; the reduction in the value may be due to the reaction mixture stuck to the reactor wall. In the present study three epoxides namely epichlorohydrin, propylene oxide and butylene oxide were chosen as the representative substrates and also to demonstrate the tolerance of the catalyst for the range of epoxides.

The products were purified after separating with the catalysts and solvent and characterized by NMR and IR spectroscopic techniques. The results match well with the reported literature values [9,34].

*(a) Chloropropylene carbonate,* IR: $\gamma$ C=O 1798 $cm^{-1}$, $^1H$ NMR ($CDCl_3$): $\delta$ 3.7–3.8 (m, 1H), 4.3– 4.5 (q, 1H), 4.5–4.7 (q, 1H), 4.9–5.1 (m, 1H).

*(b) Propylene carbonate,* IR: $\gamma$ C=O 1793 $cm^{-1}$, $^1H$ NMR ($CDCl_3$): $\delta$ 1.5 (d, 3H), 3.9–4.1 (t, 1H), 4.4–4.6 (q, 1H), 4.7–4.9 (m, 1H).

*(c) Butylene carbonate,* IR: $\gamma$ C=O 1793 $cm^{-1}$, $^1H$ NMR ($CDCl_3$): $\delta$ 0.99 (t, 3H), 1.68–1.82 (m, 2H), 4.05 (t, 1H), 4.64 (d, 1H), 4.5 (t, 1H).

## 2.3. Results and Discussion

### *2.3.1. Structural property of the catalyst*

Tourné *et al.* reported the synthesis and structural characterization of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$. The structure of this catalyst can be envisaged like the structure shown in Fig. 2.2 D This compound contains the *α-β-* $[ZnW_9O_{34}]^{12-}$ fragments represented by Fig 2.2 A and C of the Keggin-type polyanion $[ZnW_{12}O_{40}]^{6-}$ from which the triad of edge-sharing octahedral is removed (except for six oxygens, shared with the three adjacent triads). Two $[ZnW_9O_{34}]^{12-}$ units are also linked through a system of four coplanar metal atoms (Fig 2.2 B) in such a way that the latter are

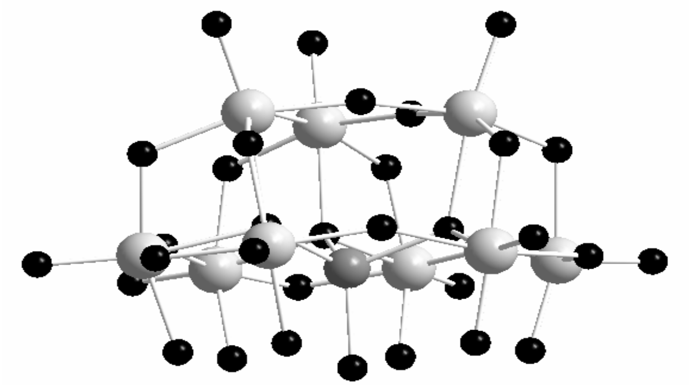


*Fig. 2.2 – A. Structural representation of* $[ZnW_9O_{34}]^{12-}$ *(Top).This structure is reproduced from Ref. No. 29.*

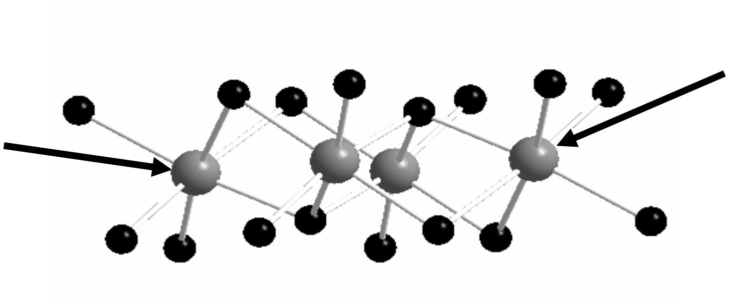


*Fig. 2.2 –B. Structural representation of four coplanar metal atoms in the middle. Two* $Zn^{2+}$ *ions bound to water molecules are marked by arrow. This structure is reproduced from Ref. No. 29*

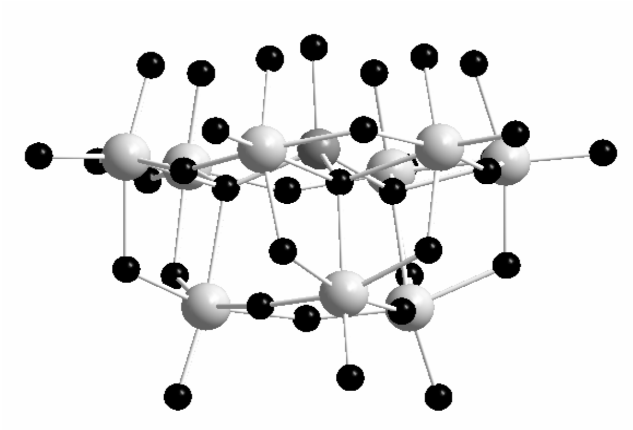


*Fig. 2.2 – C. Structural representation of* $[ZnW_9O_{34}]^{12-}$ *(Bottom). This structure is reproduced from Ref. No. 29.*

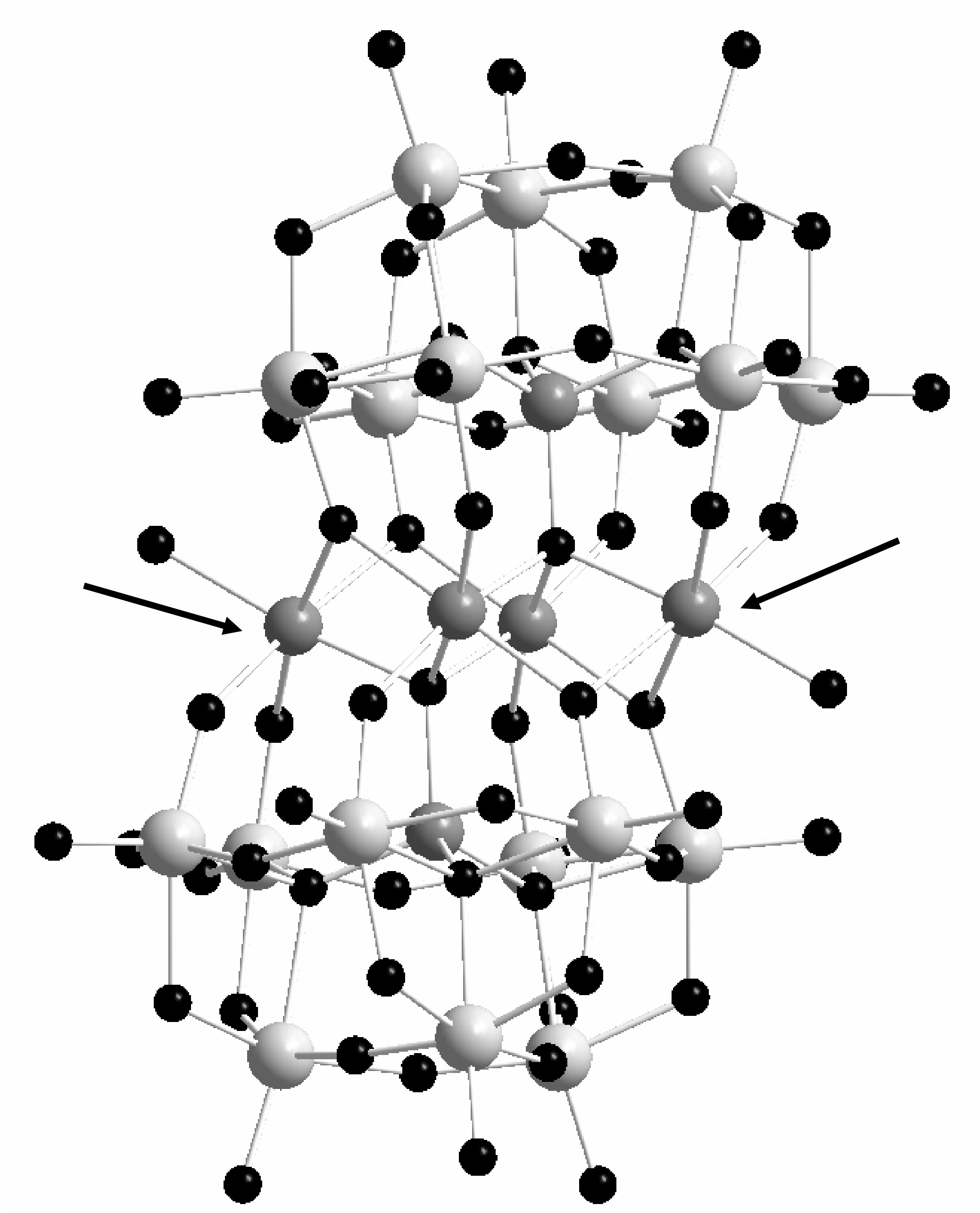


Fig. 2.2 - D. Structural representation of $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2].46H_2O$ . Two $Zn^{2+}$ ions bound to water molecules are marked by arrow. This structure is reproduced from Ref. No. 29.

octahedrally co-ordinated in a close-packed arrangement. These four sites, however, differ in their connectivities. Two M(1) (either W or Zn) sites, related by an inversion symmetry, are each surrounded by six oxygens belonging to $[ZnW_9O_{34}]^{12-}$ units. Here, each is found randomly occupied either by a tungsten atom or by another one, the Zn atom. The two other Zn sites remain equivalent and contain Zn. For these atoms, five surrounding oxygens belong to $[ZnW_9O_{34}]^{12-}$ units, the sixth one being the "free or labile" ligand, an aqua ligand and these Zn sites are believed to be catalytically active because a coordinatively unsaturated position can be created by "knocking-off" the labile aqua ligand. These two Zn sites are marked by arrow in Fig 2.2 B and in Fig. 2.2 D. The $Na^+$ cations of compounds are surrounded by five to seven neighboring oxygens (usually six) belonging chiefly to water molecules. They associate by means of two or three bridging water oxygens. In addition, a sixth $Na^+$ is linked to another $Na^+$ through two water molecules at the middle of the cationic chain.

Many reports are available in literature where they have exploited the catalytic property of this polyoxometalate [30-32]. Also, Zn ions in different matrices are being used extensively for the cycloaddition reaction of epoxide and $CO_2$. Keeping these things in mind, we decided to use this compound as catalyst for this cyclo addition reaction. It is noteworthy, here that the polyoxometalates are easy to synthesize from commonly available chemicals and are highly stable molecules. The polyoxometalate was recrystallized in water twice before being used as the catalyst.

### *2.3.2. Catalytic reaction and parameter optimization*

The reaction using Zn-POM as catalyst has been carried out with a few representative epoxides, and various experimental conditions were adopted to obtain optimum conditions and better yields. For all the catalytic reactions, dimethyl aminopyridine (DMAP) was used as a Lewis base and the mole ratio of DMAP/Zn-POM was kept at 3 unless otherwise stated in the text. Blank reactions were carried out in order to ascertain that the reaction did not take place without DMAP and the catalyst to an appreciable extent.

In the first experiment, at 0.4 MPa $CO_2$ pressure and 373 K, epichlorohydrin/Zn-POM mole ratio was varied from 4,000 to 50,000 and the reactions were monitored for 24 h at regular intervals. A representative plot is given in Fig. 2.3. Though conversion rates vary a bit for different mole ratios of epichlorohydrin / Zn-POM, the completion of reaction required nearly 24 h. However, it is interesting to note that conversion and selectivity are not altered and remained very high for epoxide / Zn-POM mole ratio up to 50,000 [22,23]. It is noteworthy here that selectivity was more than 96 % during the entire course of the reaction. The only by-product formed here was identified as 1,3-dichloropropane-2-ol using GC–MS. A trace amount of HCl present in $CH_2Cl_2$ solvent might have led to the formation of this by-product.

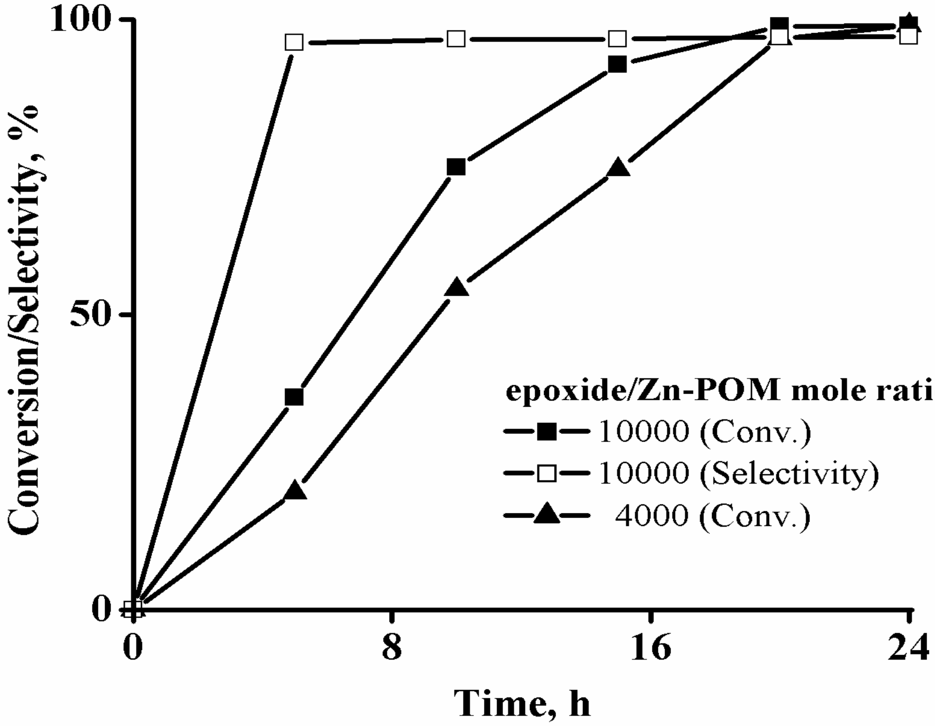


*Fig. 2.3: Effects of peroxide / Zn-POM mole ratio on the cycloaddition reaction of $CO_2$ with epichlorohydrin using Zn-POM / DMAP catalytic system (0.4 MPa $CO_2$, temperature 373K). Selectivity plot is given only for epoxide/Zn-POM ratio of 10,000 for clarity.*

In an effort to reduce the reaction time, temperature dependence (373-413 K) experiments have been carried out with epichlorohydrin / Zn-POM mole ratio 10,000 and at 0.4 MPa $CO_2$ pressure. The reactions were monitored till the complete conversion of the substrate to the product was achieved. The results are plotted in Fig. 2.4. The time required for the complete epoxide conversion decreases with increasing temperature. At 413 K, quantitative conversion with selectivity > 97 % could be reached within 3 h (Table 2.1.) even for different epichlorohydrin/Zn- POM mole ratios.

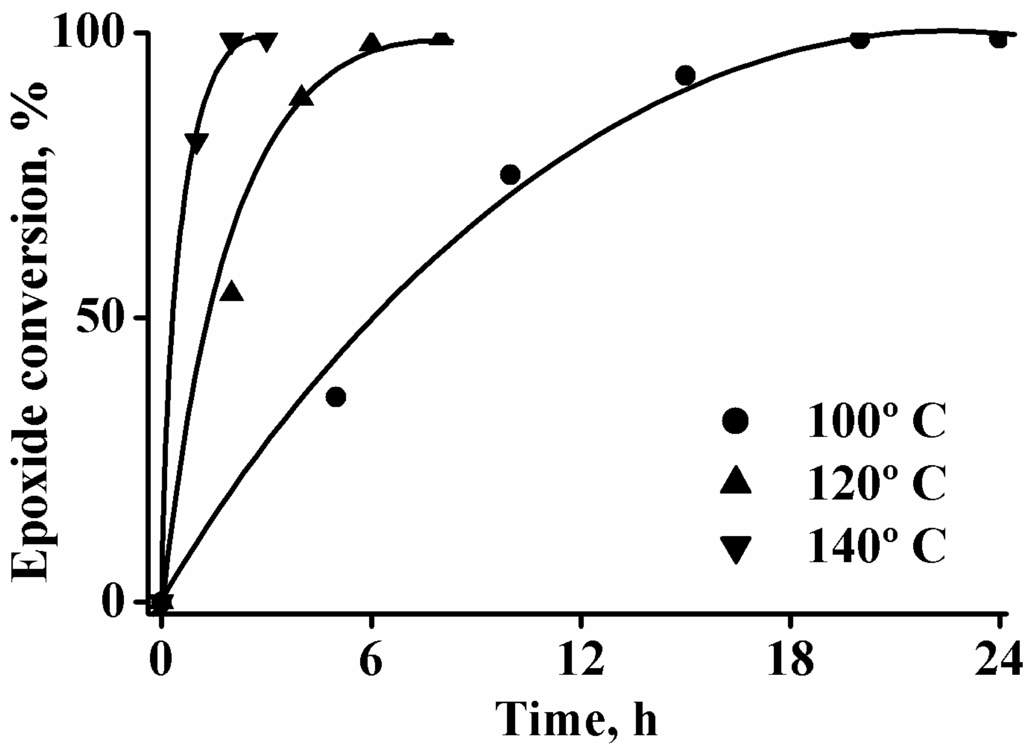


*Fig. 2.4 Kinetic plots for cycloaddition of $CO_2$ with epoxide using Zn-POM / DMAP system at different reaction temperatures. Experimental conditions: epoxide / Zn-POM mole ratio: 10,000, $CO_2$ pressure: 0.4 MPa.*

Experiments with varying $CO_2$ pressure indicate that the conversion and selectivity of cyclic carbonates were independent of the $CO_2$ pressure range 0.4 – 1.4 MPa at 413 K [13]. The catalytic activity was also tested with other epoxides like propylene oxide and butylene oxide at 433 K at 0.4 MPa $CO_2$ pressure. The present catalyst system was active for these epoxides as well. The results are given in Table 2.1

These epoxides require more time for the completion of reaction than the time required for epichlorohydrin; however, selectivity for cyclic carbonates remained very high throughout the reaction period.

*Table 2. 1: Cycloaddition reaction of carbon dioxide with different epoxides; effects of different mole ratios of epoxide/Zn-POM, solvent effect and reusability of Zn-POM.*

| Entry | Substrate | Epoxide/ Zn-POM ratio | Temp. (K) | Time, h | Conversion (%) | Selectivity (%) |
|---|---|---|---|---|---|---|
| 1 | Epichlorohydrin | 10000 | 413 | 3 | 97 | 98 |
| 2 | Propylene oxide | 25000 | 433 | 12 | 99 | 97 |
| 3 | Butylene oxide | 25000 | 433 | 9 | 96 | 97 |
| 4 | Epichlorohydrin | 25000 | 413 | 3 | 98 | 98 |
| 5 | Epichlorohydrin | 50000 | 413 | 3 | 84 | 98 |
| 6[a] | Epichlorohydrin | 10000 | 413 | 3 | 99 | 98 |
| 7[£] | Epichlorohydrin | 10000 | 413 | 3 | 99 | 98 |
| 8[$] | Epichlorohydrin | 10000 | 413 | 3 | 95 | 98 |

*Experimental conditions: 0.4 MPa $CO_2$, 10 ml $CH_2Cl_2$, 0.0026 mmol of Zn-POM, DMAP = 3 mole equivalent to epoxides, a = without organic solvent; £= reaction with once-recovered Zn-POM, $ = reaction with twice-recovered Zn-POM.*

An experiment has also been carried out in the absence of any organic solvent (Table 2.1, entry 6), and it was interesting to observe that the conversion and selectivity were similar to those of the reaction with solvent, indicating that the solvent does not play any role in the cycloaddition reaction with the present catalytic system. A few such catalytic systems are known in literature [1, 33].

### *2.3.3. Recycle study of the catalyst*

The reusability of Zn-POM was studied by carrying out the $CO_2$ cycloaddition reaction with epichlorohydrin using the recovered Zn-POM but with fresh addition of DMAP. Interestingly, the results were similar to those of the fresh Zn- POM (Table 2.1, cf. entries 1 and 7) indicating that the Zn- POM part of the catalyst system can be reused without losing its catalytic activity. Similar experiments were carried out for twice-recovered Zn-POM (Table 2.1, entry 8) and only a small reduction in the conversion was noticed; however, selectivity remained very high. To examine the integrity of Zn-POM and the possible leaching of Zn and W into the solution, we have carried out the following experiments: after completion of the reaction, the mixture was centrifuged and the solid (Zn-POM) part was separated out and washed thrice with dichloromethane. The resulting filtrate was analyzed by ICP and we found that Zn and W contents were below the detectable limit (< 0.01 ppm) indicating that Zn-W-POM catalyst is not disintegrated.

### *2.3.4. Structural Integrity of the Zn-W-POM Catalyst:*

IR and diffuse reflectance UV-Vis spectroscopic techniques were used to investigate the integrity of the structure of Zn-W-POM catalyst. The IR spectroscopy has been widely used as an effective spectroscopic tool to identify and to characterize W=O and W–O–W (corner and edge shared) units of POM [30]. IR spectroscopy is also used as one of the major tools to prove the integrity of the catalysts based on the retention of the characteristic IR band. The IR spectrum of the fresh Zn-polyoxometalate showed characteristic bands of Zn-polyoxometalate (peaks at 939, 881, 785, 700 $cm^{-1}$) that are in agreement with the reported literature (Fig. 2.5.). The IR spectrum of the recovered Zn-POM was identical to that of the fresh Zn-POM indicating that the integrity of Zn-POM has not been altered during the course of the reaction (Fig. 2.5.). Additional proof for the integrity of Zn-POM has also been imparted by measuring the W→O charge transfer band of polyoxotungstate anion that appears at 260 nm [31]. The UV spectra of both the fresh and the recovered catalysts showed the presence of a band at 260 nm (Fig. 2.6.), indicating that the structure of Zn-POM is intact. It may be recalled here that the recovered Zn-POM part of the catalytic system could be reused for at least two runs, reinforcing the point that the structure does not collapse under the current experimental conditions used.

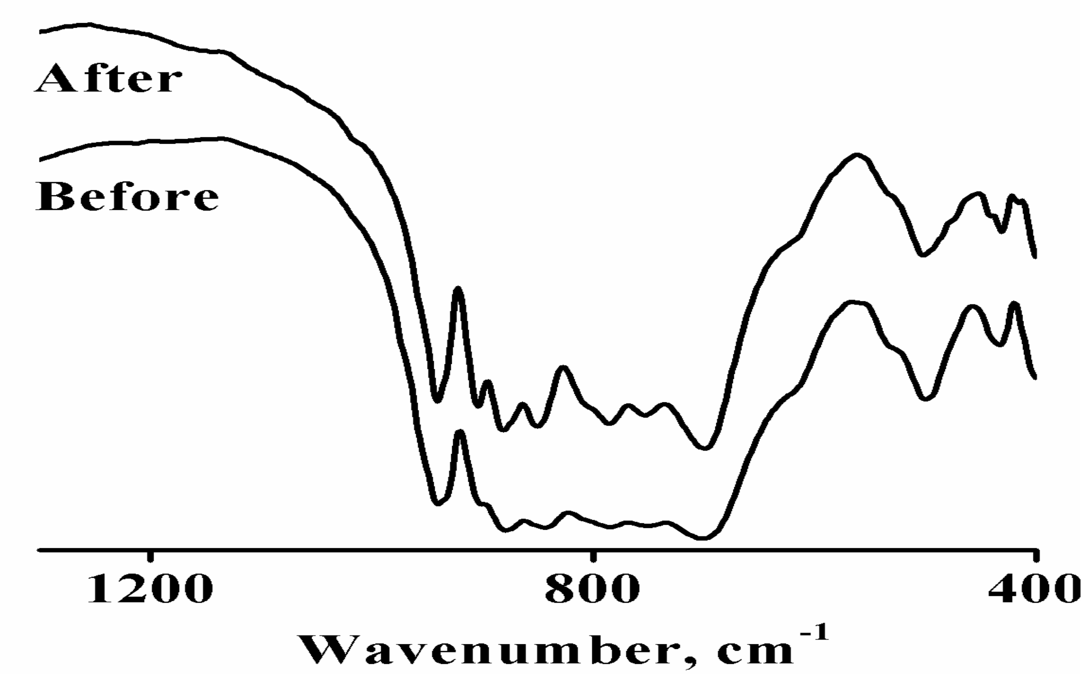


*Fig. 2.5: FT-IR spectra of Zn-POM before (a) and after (b) the $CO_2$ cycloaddition with epichlorohydrin.*

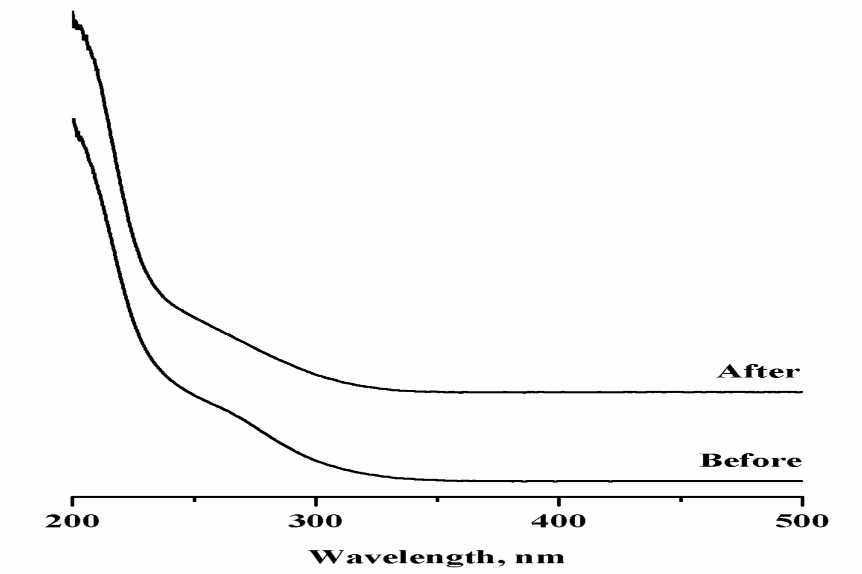


*Fig. 2.6: DRS-UV-Vis spectra of Zn-POM before (a) and after (b) the $CO_2$ cycloaddition with epichlorohydrin.*

### *2.3.5. Mechanistic study:*

To understand the role of the Zn-POM and DMAP in the present reaction, we conducted experiments (i) only with Zn-POM as a catalyst and (ii) only with DMAP as a catalyst. The results have been compared with the values obtained from the experiment where both Zn-POM and DMAP were utilized. Experiment (i) gave 49 % conversion; experiment (ii) gave 65% after 3 h reaction time (Table 2. 2, entries 2 and 3), whereas under the same experimental conditions, a reaction in the presence of both Zn-POM and DMAP gave 97 % conversion. The above results indicate that both Zn-POM and DMAP are themselves individually active for $CO_2$ cycloaddition reaction with epoxide to form cyclic carbonates.

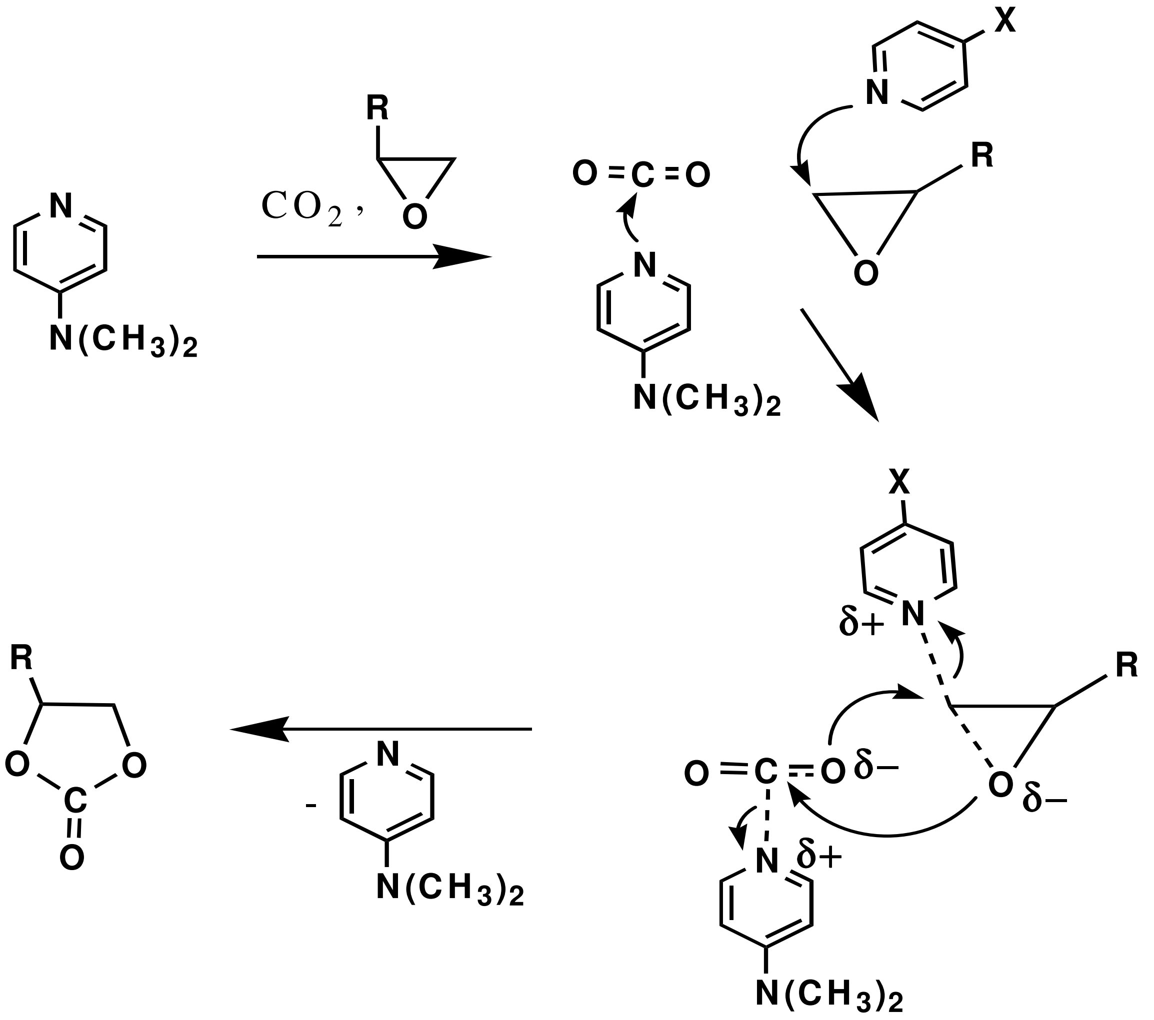
*Table 2.2: Effect of reaction parameters on $CO_2$ reaction with epichlorohydrin.*

| Entry | Zn-POM (mmol) | DMAP (mmol) | Temp. (K) | Time, h | Conversion (%) | Selectivity (%) |
|---|---|---|---|---|---|---|
| 1 | 0.0026 | 0.0078 | 413 | 3 | 97 | 98 |
| 2 | 0.0026 | 0 | 413 | 3 | 49 | 91 |
| 3 | 0 | 0.0078 | 413 | 3 | 65 | 98 |
| 4 | 0.0026 | 0.0078 | 393 | 2 | 54 | 98 |
| 5 | 0.0026 | 0 | 393 | 2 | 4 | 92 |
| 6 | 0 | 0.0078 | 393 | 2 | 42 | 96 |
| 7 | 0 | 0 | 393 | 2 | trace | - |

*Experimental conditions: 0.4 MPa $CO_2$, 10 ml $CH_2Cl_2$, 67.24 mmol of epichlorohydrin.*

### *2. 3. 5. 1. DMAP alone as catalyst:*

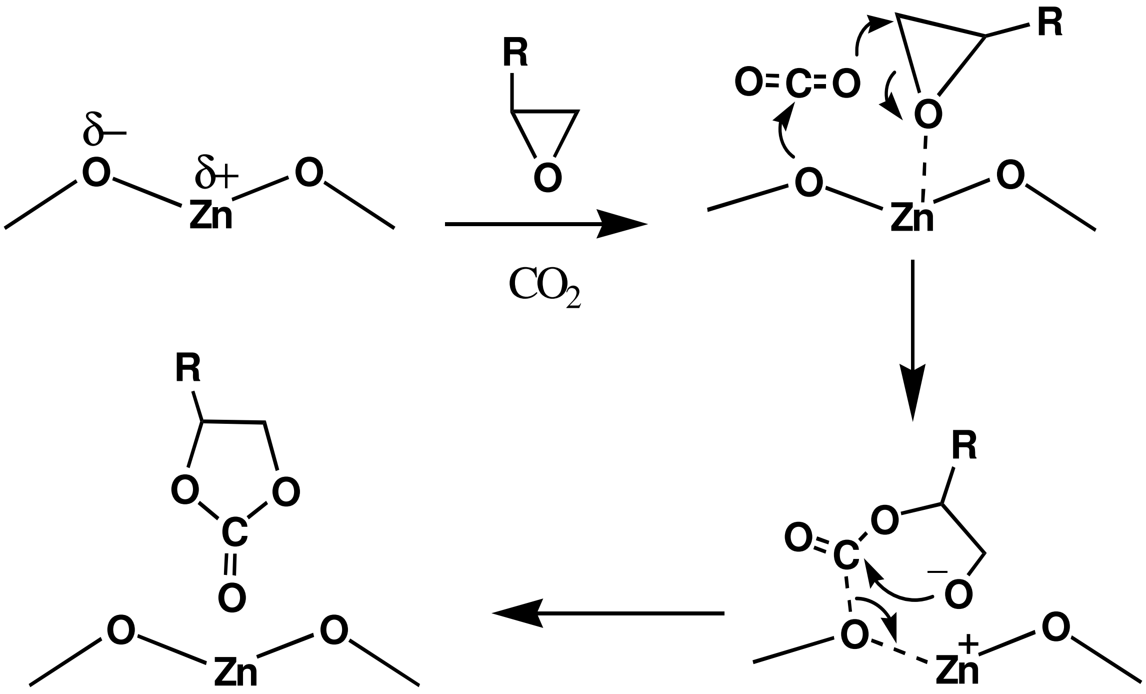
The higher activity of DMAP than that of Zn-POM may be attributed to the stronger Lewis basic property of DMAP, which can activate both $CO_2$ and epoxide (as shown in Scheme 2.2) effectively for the $CO_2$ cycloaddition reaction with epoxide. Here, it is believed that the epoxide is activated by nucleophilic interaction of DMAP on one of the carbons of the epoxide ring to polarize the C–O bond, and in parallel $CO_2$ is activated by another DMAP. Nucleophilic attack on the oxygen atom of the activated $CO_2$ on the epoxide carbon opens up the ring which leads to the formation of cyclic carbonate.



*Scheme 2.2: Postulated reaction mechanism for cycloaddition of $CO_2$ to an epoxide during the synthesis of cyclic carbonate over DMAP alone as catalyst.*

### *2. 3. 5. 2. Zn-POM alone as catalyst:*

In the case of Zn-POM, the epoxide is activated by a Lewis acidic site ($Zn^{2+}$) and in parallel $CO_2$ is activated by the neighboring weak Lewis basic site ($O^{2-}$) of Zn-POM to form cyclic carbonates as shown in Scheme 2. 3. Due to very poor Lewis basic property of bridged oxygens of POM the activity is much less than that of the DMAP [13, 23].



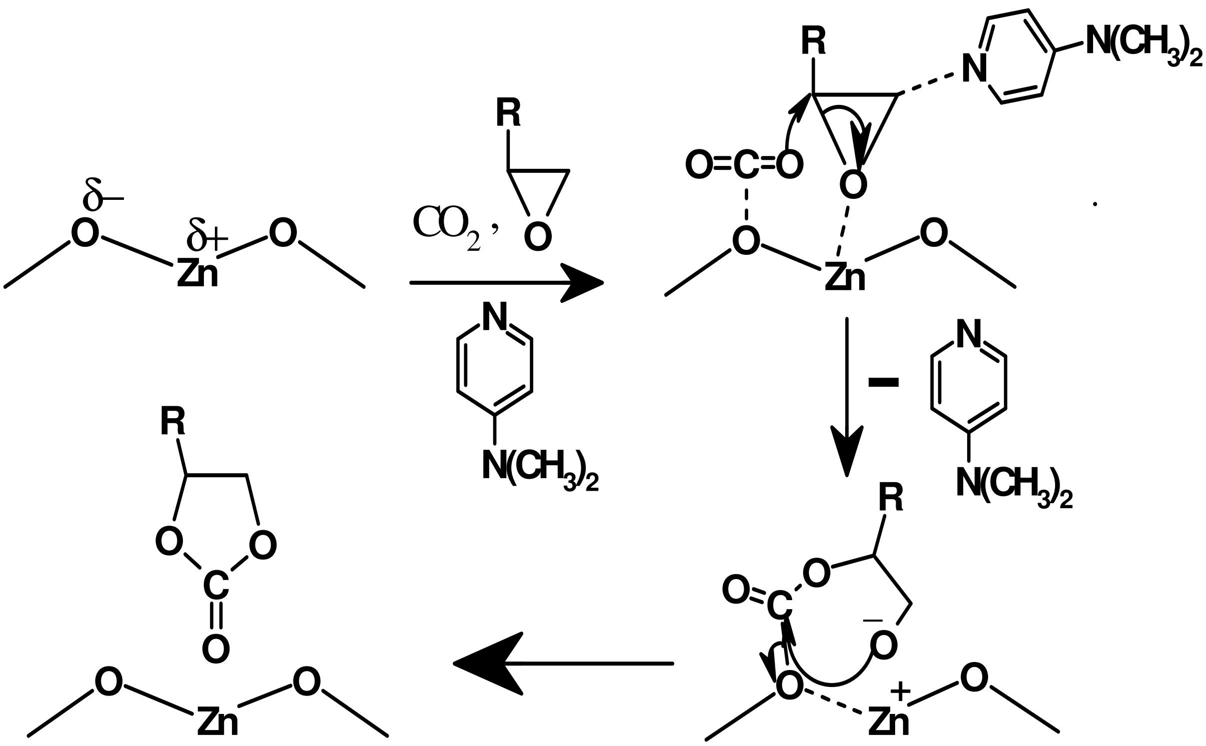
*Scheme 2.3: Postulated reaction mechanism for cycloaddition of $CO_2$ to an epoxide during the synthesis of cyclic carbonate over Zn-POM alone as catalyst.*

### *2. 3. 5. 3. Zn-POM and DMAP as catalyst:*

In this case when both POM and DMAP were present, we believe that the epoxide is activated simultaneously by Lewis acidic site ($Zn^{2+}$) from the POM as well as by nucleophilic interaction of DMAP, and in parallel $CO_2$ is activated mostly by DMAP, as shown in Scheme 2.4, leading to the formation of cyclic carbonate [13,18,23,24].

### *2. 3. 5. 4. Cooperative effect in the catalytic system:*

In order to understand the possible cooperative effect of the catalytic components in the current reaction, experiments (i) and (ii) were performed under 'lean' conditions (i.e. lower than 413K and less than 3 h duration). Accordingly, experiments have been carried out 393K and 0.4 MPa $CO_2$ for 2 h over (i) Zn-POM alone and (ii) DMAP alone. The results are given in Table 2.2 (entries 5 and 6); the corresponding conversions are 4 % and 42 %, respectively. Under the same condition, the experiment in the presence of



*Scheme 2.4: Postulated reaction mechanism for cycloaddition of $CO_2$ to an epoxide during the synthesis of cyclic carbonate over Zn-POM and DMAP as catalyst.*

both Zn-POM and DMAP (Table 2.2 , entry 4) gave 54 % conversion, which is more than the arithmetic summation of conversions of individual contributions (by Zn-POM and DMAP, respectively). The results from another set of experiments at 393 K, 0.4 MPa $CO_2$ with 1 h of reaction time shows a similar trend, i.e. the arithmetic summation of conversions of individual contributions is less than the conversion of the experiment where both Zn-POM and DMAP are involved. The higher activity in the presence of both Zn-POM and DMAP may be due to a cooperative effect.

Here, apart from the possibility of individual contributions as shown in Schemes 2.3 and 2.4, a possibility of the partial inhibition of the catalytic system due to the possible interaction of DMAP ring nitrogen with Zn ion of Zn-POM cannot, however, be ruled out. It may be noted that, in the absence of both Zn-POM and DMAP, no appreciable activity was observed. In the zinc-substituted polyoxometalate part of the catalytic system, two zinc ions are bonded with five $WO_6$ octrahedra and a water molecule, while three other zinc ions are bonded to six $WO_6$ octrahedra. The two zinc ions with water coordination are believed to be active for $CO_2$ cycloaddition reaction. Since the water coordination is labile the sixth coordination of the $Zn^{2+}$ ion may be available for epoxide oxygen coordination in the present experimental conditions and thus available for activation of epoxide.

## 2.4. Conclusion

In conclusion, a zinc-substituted sandwich-type polyoxometalate in conjunction with a Lewis base is found to be an efficient catalyst system for the cycloaddition of $CO_2$ with epoxides. The quantitative conversion and selectivity data for three representative epoxides indicate that the present catalytic system is active for a wide range of epoxides. The $CO_2$ cycloaddition reaction works even with a small amount of Zn-POM, for example, up to epoxide / Zn-POM ratio 50,000, with a high conversion and selectivity. Importantly, the zinc-substituted polyoxometalate part of the catalytic system can be separated and reused with high conversion and selectivity, and is active even in the absence of any organic solvent. In spite of many advantages, there are few disadvantages in the present catalytic system, the dimethyl aminopyridine part of the catalytic system is soluble in the reaction mixture so it cannot be recovered and reused. Since this catalytic system is having two components it becomes difficult to probe the mechanistic aspects using *in-situ* spectroscopic techniques. Thus a single site heterogeneous catalyst can solve the above mentioned shortcomings.

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# Chapter – III

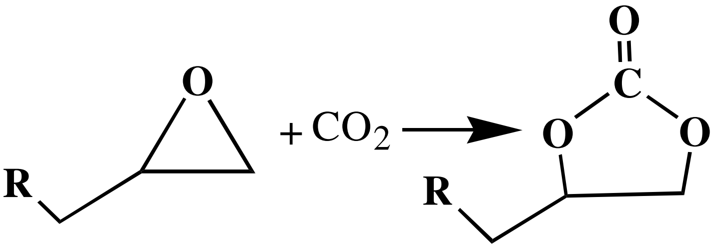
## *Synthesis of cyclic carbonate using inorganic-organic hybrid catalyst*

Part of the work described in this chapter has been communicated / under preparation:

*M. Sankar, T. Ajit Kumar, G. Sankar and P. Manikandan (Manuscript under preparation)*

## 3. 1. Introduction:

$CO_2$ chemical fixation is a challenging and important topic as $CO_2$ is an inexpensive and abundant feedstock [1-3]. $CO_2$ can be used as a safe and cheap C1 building block for various reactions and among them reaction involving the insertion of $CO_2$ into the epoxide ring for the formation of cyclic carbonate have of great interest in the recent time (Scheme 3.1.).



*Scheme 3.1: Reaction between epoxide and $CO_2$ to form cyclic carbonate.*

Cyclic carbonates are used for variety of applications including as precursors in fine chemical and pharmaceutical syntheses due to their cyclic and chiral nature, polar solvents, precursors for 1,2 diols, electrolytic applications [3-7]. Although numerous catalyst systems have been reported for this transformation, they normally suffer from drawbacks such as the low catalyst stability, complicated synthesis procedure, the need for co-solvent or co-catalyst, harsh reaction condition like high temperature and / or high pressure and homogeneous nature. In the case of homogeneous catalyst it becomes difficult to recover and reuse the catalyst [8 - 18]. To overcome this difficulty of separation, a large number of solid catalysts have been developed, for e.g. Yasuda *et al* used SmOCl as a catalyst to obtain higher selectivity without any additive under *sc*$CO_2$, but the yield was poor without an additive like DMF [19]. Yamaguchi *et al* reported an active mixed metal oxide catalyst, but a higher catalyst/substrate ratio was needed for the cycloaddition reaction [20]. More recently, Niobium ion catalysts, Ti-SBA and other heterogeneous catalysts have been found efficient for the $CO_2$ cycloaddition reactions with epoxides [21, 22]. Unfortunately, these solid catalysts need either solvent, higher temperature/pressure, longer duration for the completion of reaction or high cost involved in the materials synthesis.

Therefore development of a more efficient and environmentally benign catalyst for cyclic carbonate synthesis under mild conditions still remains a challenging task.

Recently, we have reported the use of a Zn-W polyoxometalate based catalyst in conjunction with an organic base like 4-(N,N-dialkylamino)pyridine as an effective catalytic system for the synthesis of cyclic carbonate [23] where we found there is a cooperative mechanism between the organic amine and the solid catalyst. Though the above catalytic system showed very high turn-over number and Zn-W-polyoxometalate part of the system could be recovered and reused many times, fresh addition of Lewis base part was needed in every reuse. Being a homogeneous catalyst, Lewis base itself can activate $CO_2$ and epoxide leading a moderate cyclic carbonate yield [24].

In the present work, we have overcome the above drawback by functionalizing imidazole on $SiO_2$ coupled through 3-chloropropyltriethoxysilane [25, 26]. The present catalyst is found to efficient as a single site solid catalyst for the coupling of epoxides with $CO_2$ for the formation of cyclic carbonates. The imidazole anchored $SiO_2$ catalyst catalyzes the $CO_2$ insertion reaction at moderate temperature and $CO_2$ pressure and most importantly it does not require any co-catalyst and any organic solvent.

## 3.2. Experimental:

### *3.2.1. Reagents:*

Fumed silica (specific surface area: 400 $m^2/g$), aminopropyl triethoxsilane and chloropropyltriethoxysilane were purchased from Aldrich Co. Imidazole was purchased from Spectrochem pvt. Ltd, Epichlorohydrin, propylene oxide, butylene oxide, styrene oxide, and (3-chloropropyl) triethoxysilane were purchased from Merck Co. 1-methyl - 2,3,4,6,7,8 hexahydro-1H-pyrimido[1,2-∝]pyrimidine was purchased from loba chemie, $CO_2$ with > 99.5 % purity was procured from De-lux Trading Co. Solvents were distilled and dried before use and reactions were carried at inert atmosphere.

### *3.2.2. Material characterization:*

The C, H and N composition was estimated by a Carlo-Erba 1106 analyzer. Solid state $^{13}C$ and $^{29}Si$ CP-MAS NMR spectra were recorded at 298 K on a Bruker MSL 300 spectrometer equipped with a 7.05 T wide bore superconducting magnet, resonating at 59.6 MHz and 75.4 MHz respectively, using a double bearing Bruker 4 mm CP-MAS probe. The samples were packed in a 4 mm zirconia rotor and were spun at 10 kHz. The magic angle was set-up by the standard procedure using KBr, monitoring the side-band patterns of the $^{81}$Br signal. The $^{13}$C CP-MAS experiment was first set-up on a Glycine sample and $^{29}$Si CP-MAS experiment was set-up on a standard sample of DSS. 5000 scans were acquired for the $^{13}$C CP-MAS experiment and 8000 for $^{29}$Si CP-MAS. The FT-IR spectra (KBr disc) were recorded from 4000 – 400 cm$^{-1}$ using Perkin Elmer instrument. The DRS UV-Vis spectra were recorded using Perkin-Elmer instrument (lambda 690).

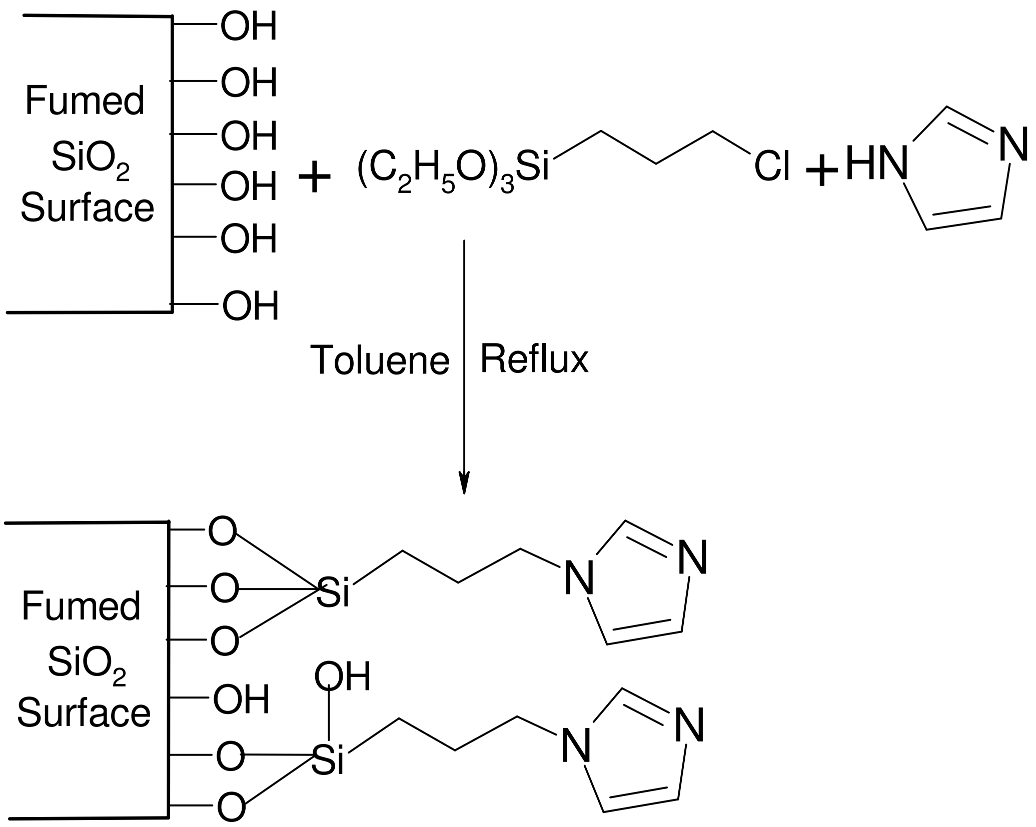
### *3.2.3. Catalytic reaction:*

A typical catalytic reaction was conducted taking 5 g of epoxide (epichlorohydrin, propylene oxide, butylene oxide or styrene oxide), 0.5 g of *p*-xylene (internal standard for GC analysis) and 0.500 g of solid catalyst in a 100 ml stainless steel PARR reactor. The reactor was pressurized with $CO_2$ (0.6 MPa), the temperature was raised to 403 K and the reaction was carried out for a specific period of time. Finally, the reactor was cooled using ice cold water, unreacted $CO_2$ was vented out, the catalyst was separated and products were analyzed by gas chromatography (Hewlett- Packard 5890 gas chromatograph with a flame ionization detector and 30 m X 0.25 mm 5 % phenyl methylsilicone capillary column and nitrogen as carrier gas). The conversion of epoxides was estimated with reference to the internal standard. The products were identified by GC–MS (Shimadzu Gas Chromatography, GC-17A fitted with QP- 500MS Mass Spectrometer), IR (Shimadzu FTIR 8201 PC instrument), NMR (BRUKER, DRX500) and compared with the authentic samples. The reaction mixture was also subjected to mass balance and it was always found that the value was 5–10 % less than expected and the reduction in the value may be due to the reaction mixture sticking to the reactor wall.

### *3.2.4. Preparation of imidazole anchored Si:*

Imidazole anchored in $SiO_2$ was synthesized using two different methods as described below:

### *3.2.4.1. One pot synthesis method:*



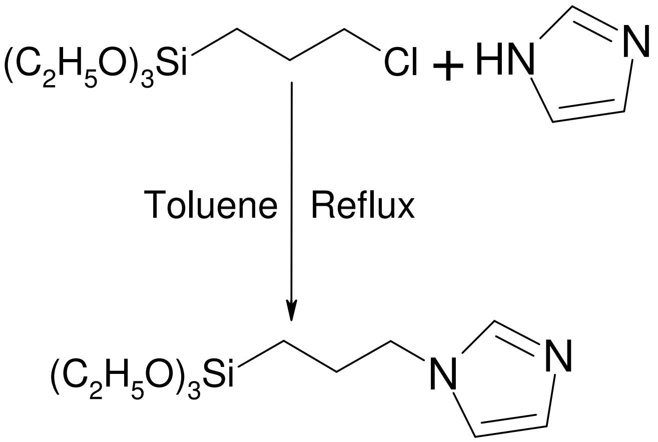
*Scheme 3.2: Schematic representation of the reaction for one pot synthesis (Method -1)*

The method is represented by Scheme 3.2. Silica (5 g, 0.08 mol), 3-triethoxychloropropylsilane (2.232 g, 0.01 mol) and imidazole (0.633 g, 0.01 mol) were mixed in a dry round bottom flask and to this 175 ml of dry toluene was added [25]. The solution was refluxed for 24 h. After cooling, the reaction mixture was filtered & washed with toluene. The material was then subjected to soxhlet extraction with toluene for 24 h and finally washed with propylene oxide, filtered and dried.

### *3.2.4.2. Two step synthesis method:*

The method is represented by the Schemes 3.3. and 3.4. The final material was prepared in two steps: the synthesis of 3-(2-imidazolin-1-yl) propyltriethoxysilane and then coupled with silica to form silica-3-(2-imidazolin-1-yl)propyltriethoxysilane. The detailed experimental procedures are explained below.

*Step – 1: Synthesis of 3-(2-imidazolin-1-yl) propyltriethoxysilane:*



*Scheme 3.3: Schematic representation of the synthesis of 3-(2-imidazolin-1-yl) propyltriethoxysilane (Step 1 in Method II)*

Imidazole (1.7 g, 0.025 mol) and 3-triethoxychloropropylsilane (2 g, 0.008 mol) were taken in a dry round bottom flask. The solution was refluxed under nitrogen atmosphere for 24 h. After refluxing, the reaction mixture was cooled to room temperature and the volatile impurities were removed by evaporation under reduced pressure. The product obtained was an orange colored viscous liquid. Yield: 62.5 %.

The structure and the purity of the final product were confirmed by the $^1$H and $^{13}$C NMR and IR spectra. NMR data: H$^1$-NMR (δ, ppm)**:** NCHN, 7.8; $CH_2NC\underline{H}CHN$, $CH_2NCHC\underline{H}N$, 7; $SiCH_2CH_2C\underline{H_2}N$, 3.8; $CH_3C\underline{H_2}O$, 3.5; $SiCH_2C\underline{H_2}CH_2$, 1.7; $C\underline{H_3}CH_2O$, 1; $SiC\underline{H_2}CH_2CH_2$, 0.4. C$^{13}$-NMR (δ, ppm)**:** $N\underline{C}HN$, 134; $CH_2N\underline{C}HCHN$, $CH_2NCH\underline{C}HN$, 121; $CH_3CH_2O$, 54; $SiCH_2CH_2\underline{C}H_2N$, 49; $SiCH_2\underline{C}H_2CH_2N$, 25; $\underline{C}H_3CH_2O$, 18; $Si\underline{C}H_2CH_2CH_2N$, 9. IR-data (KBr disk): 2959, 2929, 2858 (C-H), 1660 (C=N) cm$^{-1}$. The IR peak appeared around 2950 cm$^{-1}$ are characteristics of aliphatic C-H group and the band at 1660 cm$^{-1}$ is typical for imidazole ring C-N bond. Elemental analysis: Anal. Calc for $C_{12}H_{23}O_3N_2Si$: C, 58.14; H, 8.5; N, 10.3. Found C, 58.5; H, 9.0; N, 10.3. Elemental analysis data matches fairly with the experimental C-H-N values within the error limit.

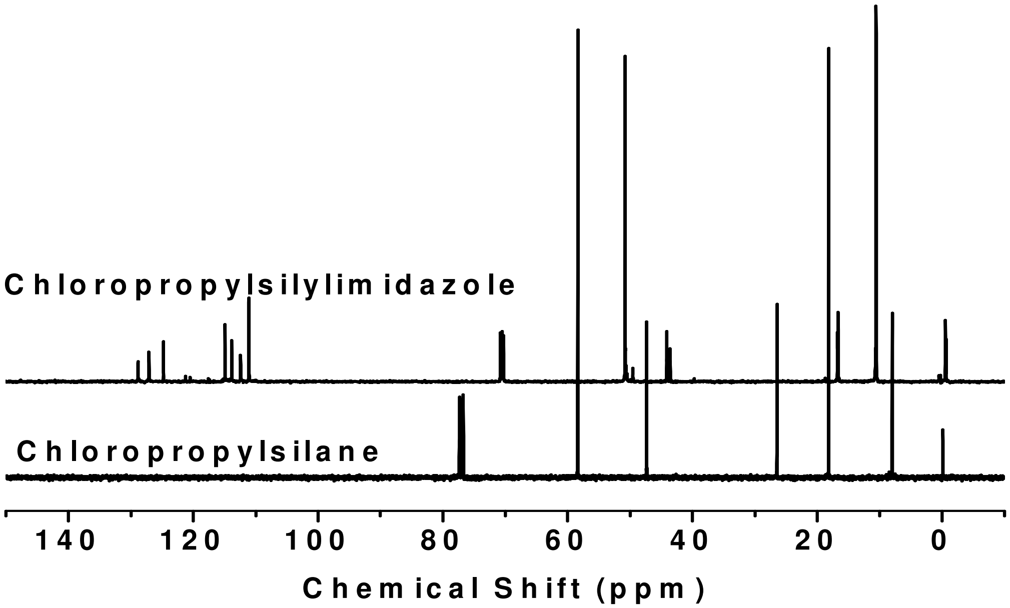


*Fig.3.1: $^{13}$C-NMR spectra of (a) 3-triethoxychloropropylsilane and (b) 3-(2-imidazolin-1-yl) propyltriethoxysilane in $CDCl_3$*

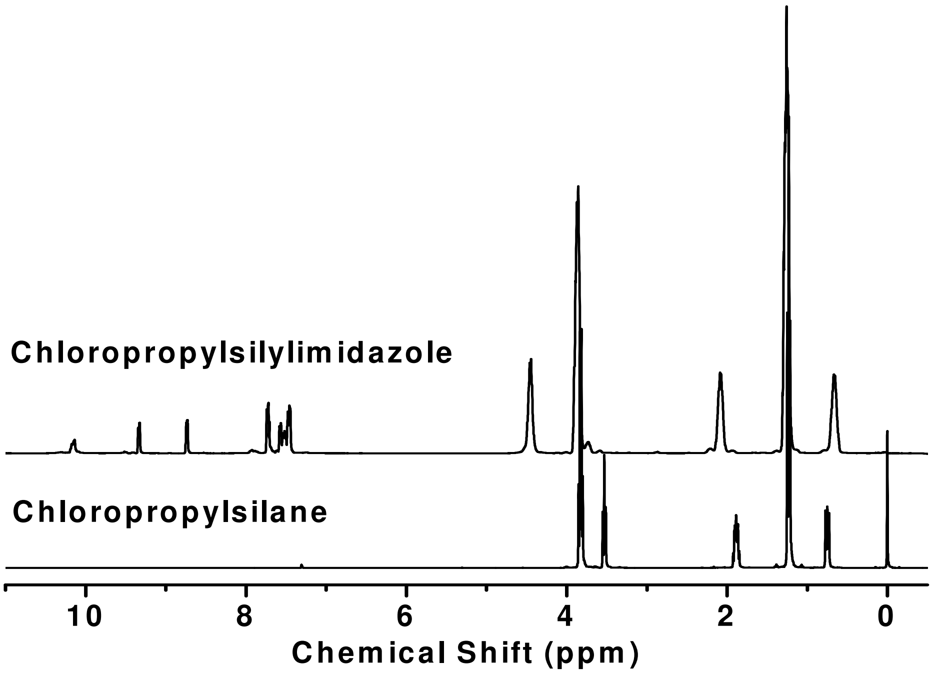
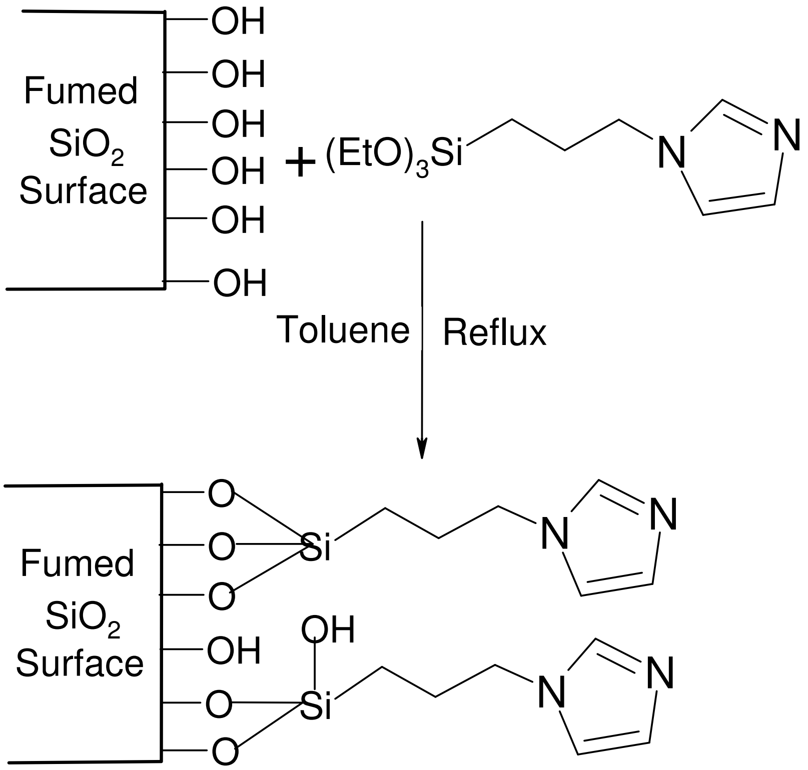


*Fig.3.2: $^1$H-NMR spectra of (a) 3-triethoxychloropropylsilane and (b) 3-(2-imidazolin-1-yl) propyltriethoxysilane in $CDCl_3$.*

*Step – 2: Synthesis of silica-3-(2-imidazolin-1-yl)propyltriethoxysilane:*



*Scheme 3.4: Schematic representation of the synthesis of silica-3-(2-imidazolin-1-yl)propyltriethoxysilane ( Step-2 in method II)*

3-(2-imidazolin-1-yl) propyltriethoxysilane (1.36 g, 0.005 mol) was anchored with silica support using fumed silica (5 g, 0.08 mol). These two precursors were taken in a dry round bottom flask and 125 ml of dry toluene was added and refluxed for 24 h. After cooling, the reaction mixture was filtered, washed with dichloromethane and dried. The final product obtained was a white powder.

With both ‘one step’ and ‘two steps’ synthesis methods, the yield for the final materials was around 60 % and elemental analysis and the data from IR and NMR spectroscopic measurements were more or less similar. Typical IR spectrum recorded as a KBr disk shows the following characteristic bands: 2960, 2931, 2860 (C-H), 1654 (C=N) cm$^{-1}$, elemental analysis (%): C: 9.57, H: 1.6 and N: 2.77. The final material was also characterized by $^{1}$H and $^{13}$C solid state NMR and the data is described in the results and discussion section. The final catalyst, silica-3-(2-imidazolin-1-yl)propyltriethoxysilane, is referred as Si-Imid in this chapter.

## 3.3. Results and Discussion:

### *3.3.1. Synthesis and structural elucidation:*

The present catalytic system, silica-3-(2-imidazolin-1-yl) propyltriethoxysilane, was prepared in two steps as described in the experimental section. The advantage with the two step method is that it was easy to elucidate the structure of the intermediate namely, 3-(2-imidazolin-1-yl) propyltriethoxysilane as it is a liquid product, before coupling with the silica support. However, the elemental analysis and other spectroscopic data clearly demonstrated that final structure and loading of 3-(2-imidazolin-1-yl) propyltriethoxysilane on silica support is more or less the same for the samples prepared by either method.

*Solid State NMR:* The structure of the imidazole functionalized silica was confirmed by $^{29}$Si and $^{13}$C solid-state NMR spectra and the results indicate that the imidazole moiety has been anchored to the $SiO_2$ surface through covalent bonding. $^{29}$Si CP MAS NMR spectrum show at least two sets of peaks, the first set of peaks at -110 ppm and -101 ppm correspond to the $Q^4$ (four Si-O-Si linkages) and $Q^3$ (three Si-O-Si linkages and one -OH linkage) of the silica support respectively [27]. This assignment has been supported by the $^{29}$Si CP MAS NMR spectrum of pure fumed silica which clearly shows two resonances one at -112 ppm and -101 ppm [28]. Second set of peaks in the imidazole anchored silica appeared at -68 ppm and -58 ppm assigned to the Si nuclei of the linker (triethoxychloropropylsilane). The peak appeared at -68 ppm is assigned to the Si nuclei attached to three –O-Si linkages along with a propyl imidazole group [27]. The peak appeared at -58 ppm is assigned to the Si attached two –O-Si, one ethoxy and one propyl imidazole moieties. Thus, from $^{29}$Si NMR studies we can conclude that the final product has both types of linkages.

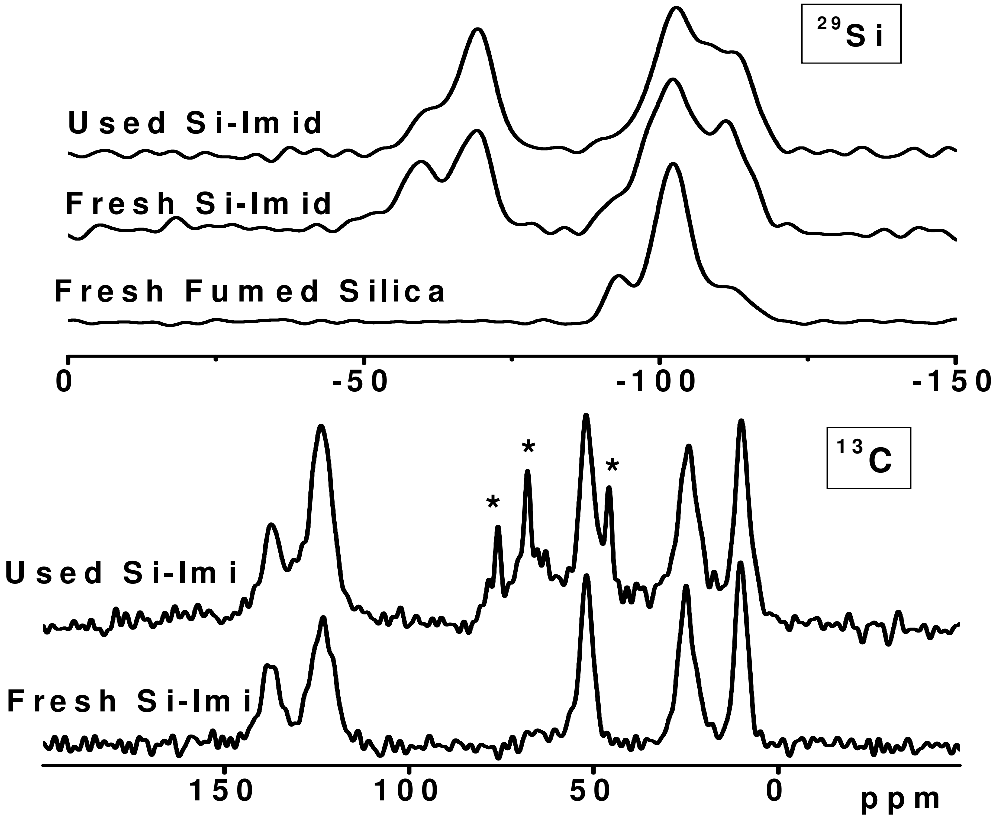


*Fig.3. 3: $^{13}$C and $^{29}$Si CP- MAS NMR spectra of the fresh and used catalysts (silica-3-(2-imidazolin-1-yl) propyltriethoxysilane catalyst) and $^{29}$Si CP-MAS NMR spectrum of the neat silica support. The spectra were recorded at room temperature.*

In addition, $^{13}$C CP-MAS NMR spectra of the imidazole anchored material were also recorded which show two sets of peaks. First set contains two peaks (123 ppm and 139 ppm) that correspond to the two types of C nuclei of the imidazole ring. Second set contains three peaks (100, 24 and 54 ppm) which are assigned to the three C nuclei of the propyl group [27].

*IR and UV Vis spectral studies:* IR and UV-Vis spectra were recorded for the imidazole functionalized silica material to provide additional support on the functionalized material and are given in Fig. 3.4 and Fig. 3.5 respectively. The C=N stretching frequency for the imidazole group appeared at 1654 cm$^{-1}$ whereas 1452 cm$^{-1}$

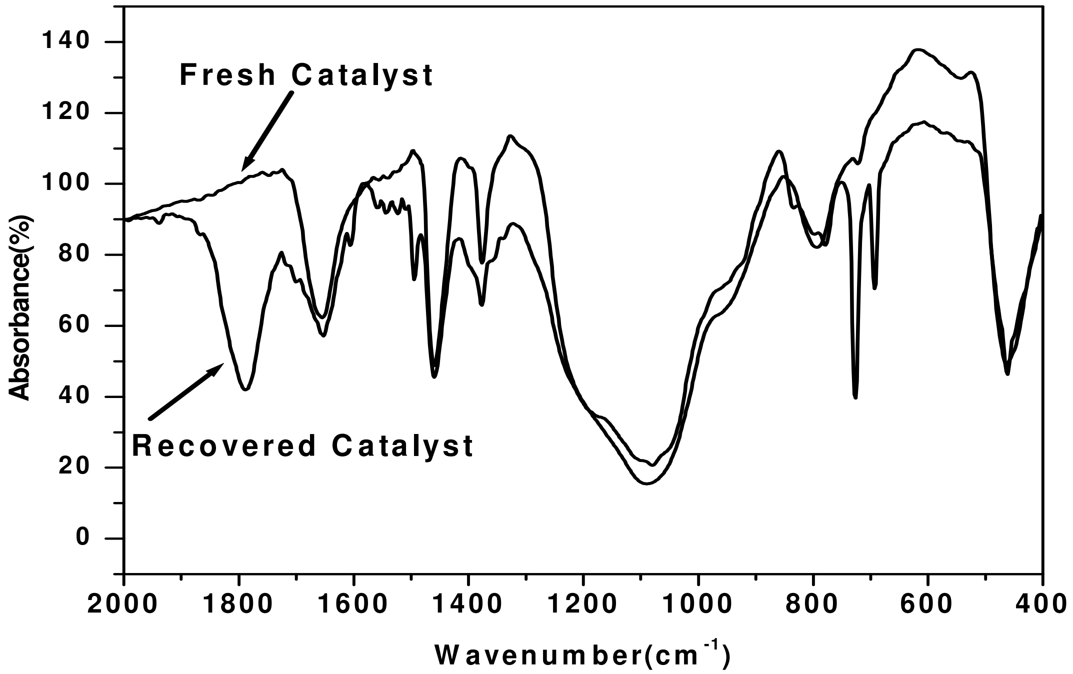


*Fig 3.4: FT-Infra Red spectra of the Imidazole anchored in Silica before and after the reaction.*

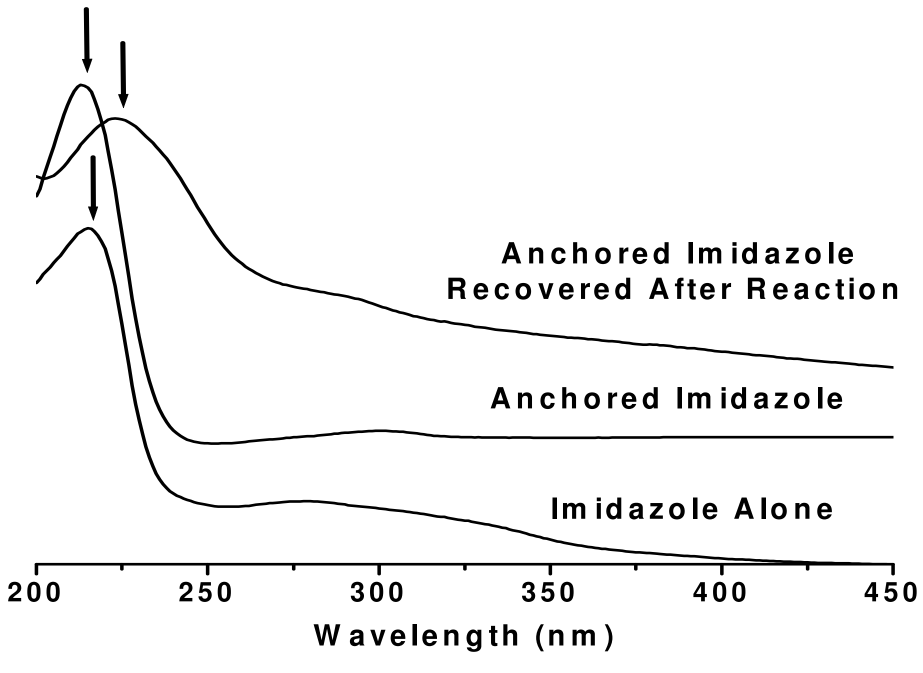


*Fig. 3.5: DRS-UV spectra of the Imidazole alone, Imidazole anchored in silica and Imidazole anchored in silica after reaction.*

stretching frequency assigned to C-H backbone [29]. Solid state UV-Vis spectra of pure imidazole moiety gave a band around 204 nm which correspond to the π-σ* transition of C=N group in the imidazole ring [30]. Presence of a 204 nm for the anchored material clearly showed unambiguously the presence of the imidazole group in the silica surface.

From the above studies and on comparing the NMR data of the neat of silica-3-(2-imidazolin-1-yl)propyltriethoxysilane, it is unambiguous that the imidazole molecule is anchored to the $SiO_2$ surface covalently.

### *3.3.2. Catalytic studies:*

The catalyst was tested for $CO_2$ insertion reaction with epoxide for the formation of cyclic carbonate at experimental parameters such as different reaction temperature, pressure and catalyst loading. The above reaction was carried with the catalysts prepared by both methods using epichlorohydrin as a representative substrate (epoxide) at 403 K and 0.4 MPa $CO_2$ and the results are given in Table 3.1. As seen in the table, at the end of 4 h of reaction time, the epoxide conversion was more than 97 mol % and the selectivity was more than 95 mol %.

*Table 3.1: Cycloaddition reaction of $CO_2$ with different epoxides and effect of catalyst.*

| Entry | Catalyst | Epoxide | Temp(K) /Time, h | Conversion Mol % | CC Selectivity, mol % |
|---|---|---|---|---|---|
| 1 | Si-Imid | ECH | 403/4 | 98 | 98 |
| 2 | Si-Imid (Method-2) | ECH | 403/4 | 97 | 95 |
| 2 | No Catalyst | ECH | 403/4 | < 5 | 0 |
| 3 | Si-Imid | PO | 403/10 | 99 | 99 |
| 4 | Si-Imid | BO | 403/10 | 99 | 95 |
| 5 | Si-Imid | SO | 403/10 | 79 | 97 |

*CC: Cyclic carbonate, ECH: Epichlorohydrin, PO: Propylene oxide, BO: Butylene oxide, SO: styrene oxide. Experimental conditions: 0.4 MPa $CO_2$, Si-Imid catalyst: 0.5 g.*

As the reaction results are more or less the same with both catalysts, henceforth, all the other experimental data are derived using the catalyst prepared from single step method. A temperature dependence experiment has been carried out with epichlorohydrin) using Si-Imid catalyst (0.5 g) at 0.4 MPa $CO_2$ pressure at different temperature in the range 343 - 403 K and the resultant kinetic plot is given in Fig. 3.6. The reactions were monitored till the complete conversion of the substrate to the product was achieved or up to 20 h. As seen in the figure, at low temperature (343 K) the conversion rate was slow and gradual and at higher temperatures the conversion rate was steep in the beginning and reached a quantitative conversion.

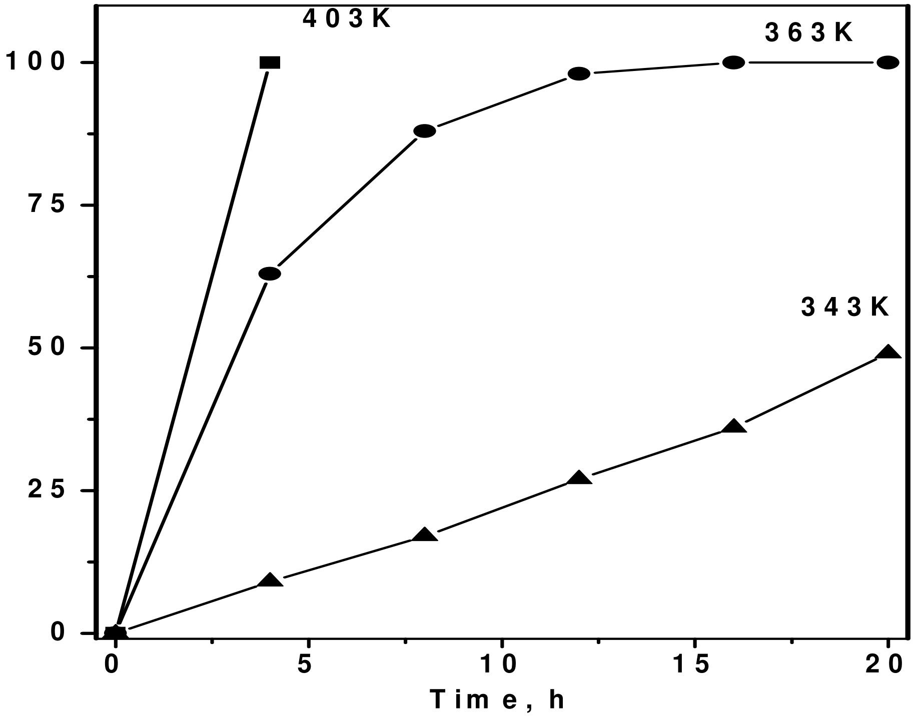


*Fig. 3.6: Profiles of cyclic carbonate yield with time. epichlorohydrin: 5 g, catalyst: 0.5gms, p-xylene (internal standard): 1gm.*

For example, the epichlorohdrin conversion was around 50 % at 343 K after 20 h whereas at 353 K a near quantitative conversion was achieved at 15 h of reaction. Interestingly, it took only around 3 h for the complete consumption of epoxide at elevated temperature, 403 K. Thus, the time required for the complete epoxide conversion decreases drastically with increasing temperature. In all the above experiments the selectivity to the required product, cyclic carbonate, was always more than 96 mol %. The data clearly demonstrates that the present catalyst system is highly effective for the conversion of epoxide to cyclic carbonate using $CO_2$. An experiment without the catalyst indicates no trace of cyclic carbonate formation indicating that the present reaction is indeed catalyzed by the Si-Imid catalyst.

The efficiency of the present catalyst system was demonstrated by testing the similar reaction with other epoxides like butylene oxide, propylene oxide and styrene oxide and the data are given in Table 3.1. A near quantitative conversion with a very high selectivity was achieved with propylene oxide and butylene oxide in 10 h at 403 K with more than 95 % selectivity to cyclic carbonate. It may be noticed that, being bulky, these epoxides require longer reaction time for the complete conversion to its products. The trend is common with most of the reported catalyst systems and the longer duration is explained based on the steric constrains involved with the propylene and butylene oxides. For example, Zhang *et al* reported a conversion of 99.5 mol % for propylene oxide at 423 K with a high $CO_2$ pressure of 2.0 MPa in 20 h using similar but with amine functionalized catalyst [25] where the experimental conditions are severe compared with the present systems apart from the longer reaction time of 20 h. The present catalyst system was also tested for aromatic ring bearing epoxide like styrene oxide and the results showed about 80 mol % to styrene carbonate at the end of 10 h at 0.4 MPa $CO_2$ and 343 K.

### *3.3.3. Reusability and integrity of the catalyst*

In order to reuse the catalyst further, the catalyst was recovered at the end of the reaction and washed with dichloromethane to remove any adsorbed materials and dried in oven. The recovered catalyst was tested for the present $CO_2$ insertion reaction with epichlorohydrin at identical conditions as that of the fresh catalyst reaction and the results are given in Table 3.2. The epoxide conversion with the recovered catalyst was slightly less than (around 90 mol %) that of the fresh catalyst and the selectivity to the cyclic carbonate was around 95 %. The cycle was repeated for at least thrice and as seen in

Table 3.2. The results are more or less similar indicating that Si-Imid system in indeed a good heterogeneous catalyst system.

*Table 3.2: Recycle Studies using the catalyst.*

| Catalyst | Epoxide | Temp/Time | Epoxide Conv, mol % | CC Selectivity, mol % |
|---|---|---|---|---|
| Si-Imid (Fresh) | ECH | 403/4 h | 98 | 98 |
| Si-Imid (I Recov) | ECH | 403/4 h | 90 | 95 |
| Si-Imid (II Recov) | ECH | 403/4 h | 87 | 95 |
| Si-Imid (III Recov) | ECH | 403/4 h | 89 | 95 |

*CC: Cyclic carbonate, ECH: epichlorohydrin, experimental conditions:*
*0.4 MPa $CO_2$, Si-Imid catalyst: 0.5 g, substrate: 5 g*

To prove further the integrity of the catalyst structure during the experiment, the catalyst was filtered off after performing the reaction and the reaction mixture was analyzed for N content by elemental analysis and it was found that the N was well below detectable limit. This clearly proves that imidazole is not leached into the reaction mixture and thereby the possibility for homogeneous reaction can be ruled out.

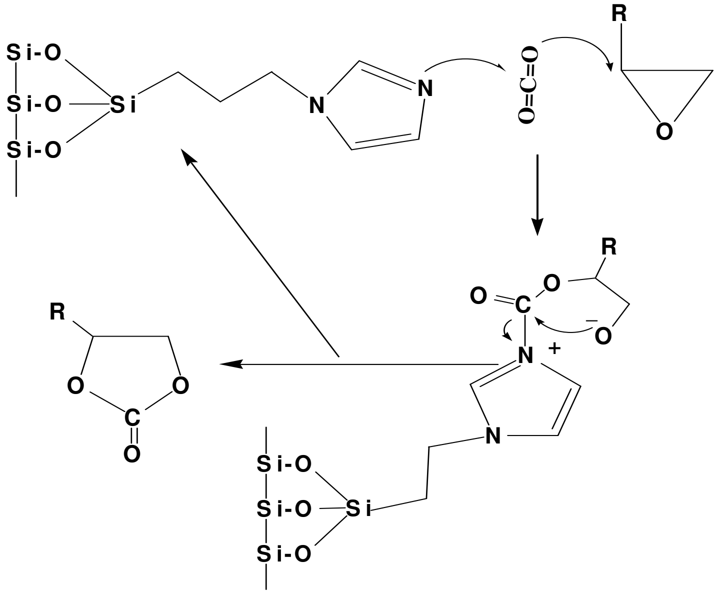
The recovered catalyst was washed and dried carefully and then it was characterized using $^{29}$Si and $^{13}$C solid state NMR (Fig 3.3.), IR (Fig 3.4.) and UV-Vis spectroscopy (Fig 3.5.). It was found that all the spectra matched exactly with the fresh catalyst clearly demonstrating that the structure of the catalyst is intact during the reaction. The extra peaks marked by * in the $^{13}$C NMR spectra of the recovered catalyst correspond to the adsorbed product molecules (cyclic carbonate) to the catalyst. Similarly the extra band at 1800 cm$^{-1}$ in the IR spectra of the recovered catalyst is due to the

–O-C (O)-O- stretching of the cyclic carbonates molecule. The above experiments also clearly demonstrate the heterogeneous nature of the catalyst.

The present catalyst system has many advantages over similar catalytic systems reported earlier by different groups. It is easy to synthesize, cost effective and highly efficient even for many cycles compared to most of the reported ones. Zang *et al* reported an anchored 1,5,7-triazabicyclo[4,4,0]dec-5-ene in fumed silica matrix [25] where the performance of the recovered catalysts were found to be poor as the conversion remained constant the selectivity towards cyclic carbonate kept on decreasing for the second, third and subsequent recycle experiments.. Imidazole anchored on an expensive Ti-MCM-41 matrix as reported by Srivastava *et al* gave an epoxide conversion of only around 32 mol % though the selectivity was 94 mol % cyclic carbonate at 393 K in 4 h [22].

### *3.3.4. Possible mechanism:*

For $CO_2$ insertion reactions bifunctional catalysts have been used mostly to achieve high yield of cyclic carbonates. It has been proposed both Lewis acid site as well as Lewis basic site is necessary and the proposed mechanism is a cooperative mechanism which involves both Lewis acidic site as well as basic site [18, 22, 25]. Generally it has



*Scheme3. 5: Proposed mechanism for the reaction of epoxide with $CO_2$.*

been proposed that epoxides are activated by a Lewis acid metal center and a nucleophilic ring-opening by the Lewis basic site and this is synergistic in nature [22]. But in our earlier report we have reported that a Lewis base (N,N-dimethylaminopyridine) alone can act as a catalyst for this cycloaddition reaction [23]. This may be due to activation of $CO_2$ by the Lewis base and that activated $CO_2$ interacts with the epoxide ring to form cyclic carbonate and at the same time the Lewis base facilitates the ring opening by the nucleophilic attack. This report prompted Jones *et al* to design a catalyst by anchoring dimethylaminopyridine in SBA-15 matrix and they found that its effective for the conversion of epoxide to cyclic carbonate using $CO_2$ [24]. Here also we have anchored a Lewis base imidazole in a very simple inorganic matrix, fumed $SiO_2$. We propose a mechanism where the N in the imidazole ring activates both $CO_2$ as well as the ring (Scheme-3.5.).

## 3. 4. Conclusion:

Silica functionalized with propyl imidazolyl silyl group synthesized and used as an efficient single solid catalyze for cycloaddition of $CO_2$ with epoxides at moderate reaction condition. The quantitative conversion and selectivity data for four different epoxides indicate that the present catalytic system is active for a wide range of epoxides. Importantly, the catalyst can be separated and reused with high conversion and selectivity for many cycles without any lose in the activity and is active even in the absence of any organic solvent.

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# Chapter – IV

## *Synthesis of dimethyl carbonate from cyclic carbonates using tungstate based catalytic system*

Part of the work described in this chapter has been published/patented:

(a) M.Sankar, C.M.Nair, K.V.G.K.Murty and P.Manikandan, *Applied Catalysis A: General* 312 (2006) 108.

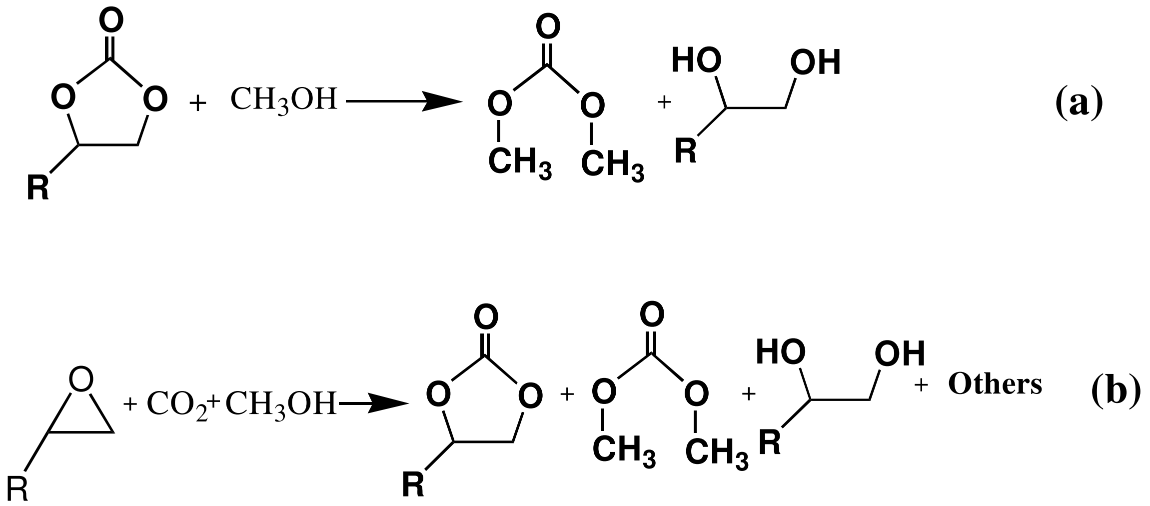
(b) Palanichamy Manikandan, Meenakshisundaram Sankar, *US Patent*: Filed (2006)

## 4.1. Introduction:

Dimethyl carbonate (DMC) is a non-toxic and environmentally benign carbonylating and methylating agent that can replace hazardous chemicals like phosgene and dimethyl sulphate and is also a raw material in the manufacture of polycarbonate resins [1,2]. DMC is an attractive chemical with many other potential applications, including, its use as a gasoline octane enhancer, due to its favorable properties like high oxygen content, negligible toxicity, and good biodegradability [2]. DMC is traditionally produced from phosgene and CO routes that are known to be environmentally hazardous, and rigorous safety measures are needed when these routes are practiced. Thus, the synthesis of DMC through non-toxic and environmentally clean routes has received considerable attention in recent years [2 - 7].

One of the alternative and cleaner routes for the production of DMC is by direct reaction of methanol and $CO_2$, however, the DMC yield by this method is restricted by thermodynamics [2, 8]. A more promising approach is the transesterification of cyclic carbonates (for example, ethylene carbonate and propylene carbonate) with methanol (Scheme 4.1) where the cyclic carbonates can be synthesized with a quantitative yield by the cycloaddition of $CO_2$ to epoxides [9, 10]. There are reports on the synthesis of DMC directly from epoxide in the presence of $CO_2$ and methanol, possibly via a cyclic carbonate as an intermediate, however, the selectivity is generally poor with heterogeneous catalysts when one uses this one-pot synthesis [11 - 13].

Having developed two successful catalyst systems for the quantitative yield of cyclic carbonate through the $CO_2$ addition route as discussed in the last two chapters, efforts were made to produce dimethyl carbonate from these cyclic carbonates by the transesterification route using methanol. Many homogeneous and heterogeneous catalytic systems have been reported for the transesterification of cyclic carbonates using methanol with high selectivity to DMC. While homogeneous catalyst systems have their own drawbacks of catalyst separation after the reaction for reuse, most of the reported heterogeneous catalysts need severe experimental conditions like high temperature and/or high pressure to obtain even a moderate DMC yield [14 – 16].



*Scheme 4.1: (a) Transesterification of cyclic carbonate with methanol to yield dimethyl carbonate and ethylene glycol (b) Possible products from one-pot synthesis.*

Even with strong bases like KOH, NaOH and LiOH, the maximum DMC yield reported was only around 62 % at RT under 0.3 MPa of $N_2$ pressure [7]. Moreover, these are homogeneous catalysts under the experimental conditions. Bhanage *et al.* reported around 32.4 mol % DMC yield by transesterification of propylene carbonate with methanol and 66 mol % DMC yield with ethylene carbonate using MgO catalyst but at 423 K and 3.5 MPa $CO_2$ pressure [11,12]. Feng *et al* used amino-functionalized MCM-41 as a catalyst to obtain 44 mol % DMC yield at 433 K [17]. Knifton and Duranleau reported organic phosphines/amine supported on partially cross-linked polymers as catalysts for DMC synthesis, but typically at around 373 K and at 0.7 MPa $CO_2$ pressure [18]. Tatsumi *et al* reported K-TS-1 as an effective catalyst with DMC yield of 57 % at reflux condition [19]. However, only a few solid heterogeneous catalysts were reported so far for the transesterification of ethylene carbonate with methanol at low temperatures at atmospheric pressure with a moderate DMC yield [6]. Hence, there is a need to identify catalyst systems for the transesterification reactions which are efficient at ambient conditions but with high DMC yield. As base catalysts have been known to be more effective than acids [18], we have screened many base catalysts for the transesterification reaction, we found alkali and alkaline-earth tungstates as efficient heterogeneous catalysts for the transesterification of ethylene carbonate with methanol at

RT (298 K) and at atmospheric pressure. DMC yield of 80 mol % has been obtained with the present catalysts. To the best of our knowledge this is the highest DMC yield obtained at ambient conditions using a heterogeneous catalyst system. An attempt to understand the effect of $CO_2$ pressure on the conversion of ethylene carbonate and DMC yield was also made.

## 4. 2. Experimental:

Sodium tungstate ($Na_2WO_4.2H_2O$), *p*-xylene and methanol were purchased from Loba Chemie, India. Ethylene carbonate, calcium tungstate, potassium tungstate and MgO were procured from Aldrich Co. The epoxides (epichlorohydrin, propylene oxide and butylenes oxide) were purchased from Merck and $CO_2$ with > 99.5 % purity from the De-lux Trading Co., India. All the chemicals were used without further purification. The IR spectra were recorded on a Shimadzu FT-IR 8201 PC instrument. *In situ* FT-IR spectra were recorded in the diffuse reflectance infrared Fourier transform (DRIFT) mode. In a typical measurement, the tungstate sample was placed in a DRIFT cell which is made up of a Zn–Se window and was heated to the required temperature; 10 μl methanol was sprayed into the cell at 50 ml/min $N_2$. The spectra were then measured at different time intervals and only with $N_2$ flow. Raman spectra were recorded at room temperature on a Ranishaw 2000 Raman Microscope excited with 633 nm laser. The powder X-ray diffraction (powder XRD) profiles were obtained on a Rigaku D Max III VC instrument using Ni-filtered Cu K∝ radiation. Typically, batch reactions at an atmospheric pressure were carried out in a round bottom flask where the flask was charged with 50 mmol of cyclic carbonate, 500 mmol of $CH_3OH$, 1 g of $Na_2WO_4.2H_2O$ and 1 g of *p*-xylene (internal standard). The reaction mixture was stirred with a magnetic bar and the reaction temperature was adjusted using a cryo-bath. Reactions with $CO_2$ pressure were typically carried out in a 100 ml S.S. reactor (parr reactor), which was charged with 50 mmol of cyclic carbonate, 500 mmol of methanol, 1 g of $Na_2WO_4.2H_2O$ and 1 g of *p*-xylene (internal standard), under a $CO_2$ pressure of 3.4 MPa, and the reaction mixture was heated to the required temperature. The above reaction mixture was stirred using a magnetically driven stirrer. In both the cases, the progress of the reaction was monitored by drawing small amounts of aliquots of the reaction mixture at regular time intervals and subjecting them to GC analysis (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m 0.32 mm 5% phenyl methylsilicone capillary column. The cyclic carbonate conversion and DMC yield were calculated based on the internal standard (*p*-xylene) and a calibration curve. The products were identified by GC–MS (Shimadzu-GC-17A fitted with a QP-500MS mass spectrometer). The yield of each product was calculated as the number of mol of the product formed per mol of the cyclic carbonate.

## 4. 3. Results and Discussion:

### *4. 3. 1. Transesterification of ethylene carbonate at atmospheric pressure:*

The transesterification reaction of ethylene carbonate with methanol was carried out at room temperature and at atmospheric pressure with 50 mmol of ethylene carbonate and 500 mmol of methanol over different loadings of $Na_2WO_4.2H_2O$ catalyst in the range 0 - 1 g. The reaction mixture was analyzed at the end of five hours of reaction time for each catalyst loading. The data of dimethyl carbonate yield are plotted in Fig. 4. 1. The DMC yield increases with increasing amount of catalyst; at 1 g of $Na_2WO_4.2H_2O$ loading maximum DMC yield of 80 mol % was obtained, as shown in the figure. Although higher catalyst loadings lower the turn over number, 1 g of $Na_2WO_4.2H_2O$ catalyst loading per 50 mmol of cyclic carbonate was used for all other experiments by considering DMC yield [11, 16, 20]. Similar experiments with different [methanol]/[ethylene carbonate] mol ratios were carried out in order to optimize the [methanol]/[ethylene carbonate] mol ratio, where the methanol amount was varied for fixed amounts of catalyst and ethylene carbonate. The results are shown in Fig. 4.1. As it is clear from the figure, the DMC yield increases with increase in the [methanol]/[ethylene carbonate] mol ratio; however, a [methanol]/[ethylene carbonate] mol ratio of 10:1was fixed for all other experiments by taking account of the yield and concentration (dilution) of DMC in the product mixture [12,20]. It may be noted here that DMC and ethylene glycol were the only products for the above transesterification reaction.

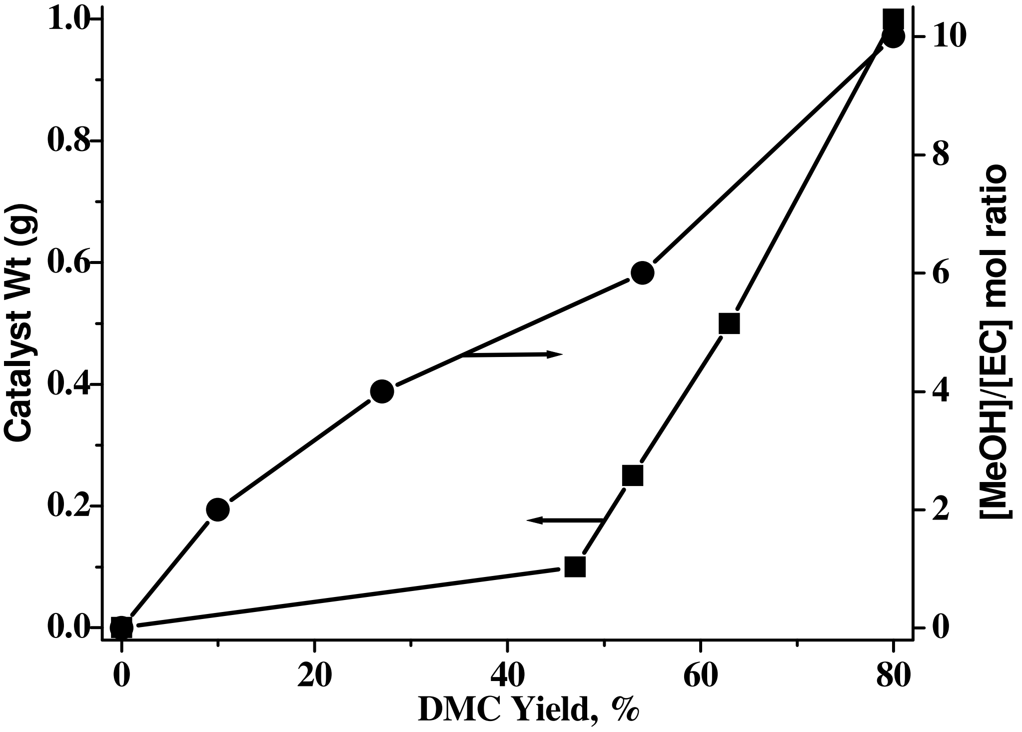


*Fig. 4.1: DMC yield as function of catalyst loading as well as [MeOH]/[Ethylene carbonate] mole ratio. Experimental condition: ethylene carbonate: 50 mmol, $CH_3OH$: 500 mmol (for catalyst loading experiments), $Na_2WO_4.2H_2O$: 3 mmol, atmospheric pressure, time: 5 h.*

The transesterification of ethylene carbonate with methanol was carried out at different temperatures in the range 278 - 373 K; here the reactor was charged with 50 mmol of ethylene carbonate, 500 mmol of $CH_3OH$ and 1 g of $Na_2WO_4.2H_2O$. The reactions at temperatures below 323 K were carried out in a 50 ml round-bottom flask attached to a condenser with the cold-water circulation; the reactions at temperatures above 323 K were carried out in a 100 ml capacity S.S. reactor. A slight autogeneous pressure was developed due to methanol vaporization (0.14 - 0.20 MPa at 373 K).

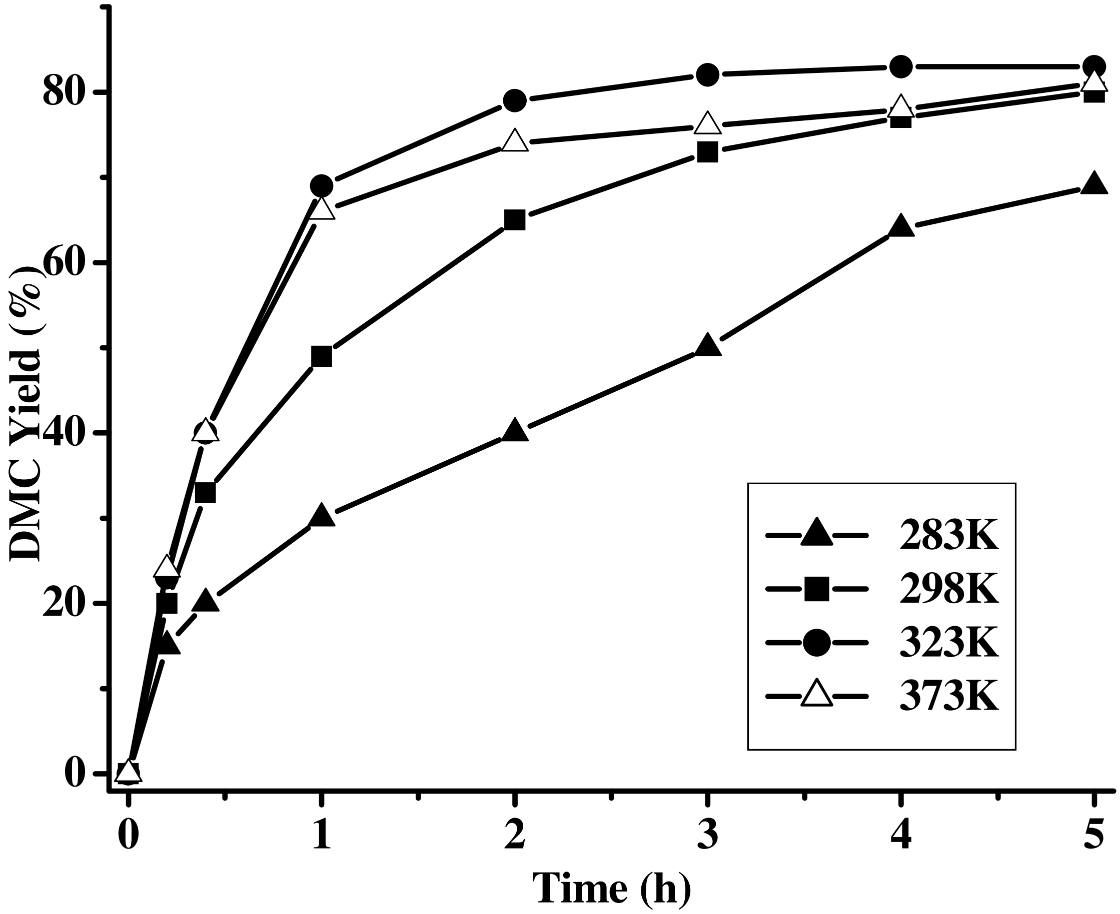


*Fig. 4. 2: Effect of reaction temperature on the DMC yield. Experimental condition: ethylene carbonate: 50 mmol, $CH_3OH$: 500 mmol, $Na_2WO_4.2H_2O$: 3 mmol, time: 5 h.*

The kinetic plots showing DMC yield with time are given in Fig. 4. 2 for different temperatures. As seen in the figure, the rate of DMC production was faster in the beginning especially for the reaction temperatures above RT, and thereafter the progress was gradual till reaching the chemical equilibrium.

At an ambient condition (298 K and atmospheric pressure), the DMC yield was 80 mol % at the end of 5 h of reaction time. To the best of our knowledge, this is the highest DMC yield obtained at ambient conditions using a heterogeneous catalyst system. Interestingly, the present catalyst was active even at sub-ambient temperatures.

***Table 4. 1:*** *Transesterification of ethylene carbonate with methanol over different catalysts and experimental conditions.*

| **Entry** | **Catalyst** | **Temp (K)** | **Pressure** | **EC Conv Mol %** | **DMC Yield Mol %** |
|---|---|---|---|---|---|
| 1 | $Na_2WO_4.2H_2O$ | 278 | Atmospheric | 52 | 51 |
| 2 | $Na_2WO_4.2H_2O$ | 283 | Atmospheric | 71 | 69 |
| 3 | $Na_2WO_4.2H_2O$ | RT | Atmospheric | 80 | 80 |
| 4 | $Na_2WO_4.2H_2O$ | 323 | Atmospheric | 83 | 83 |
| 5[a] | $Na_2WO_4.2H_2O$ | RT | Atmospheric | 80 | 79 |
| 6[b] | $Na_2WO_4.2H_2O$ | RT | Atmospheric | 79 | 78 |
| 7 | $K_2WO_4$ | RT | Atmospheric | 78 | 77 |
| 8 | $CaWO_4$ | RT | Atmospheric | 79 | 79 |
| 9 | MgO | RT | Atmospheric | 2 | 2 |
| 10[c] | KOH | RT | Atmospheric | 43 | 41 |
| 11[c] | LiOH | RT | Atmospheric | 62 | 62 |
| 12[c] | NaOH | RT | Atmospheric | 57 | 55 |
| 13 | - | RT | Atmospheric | 0 | 0 |
| 14 | - | 423 | 3.4 MPa $CO_2$ | 5 | 0 |
| 15 | $Na_2WO_4.2H_2O$ | 423 | 3.4 MPa $CO_2$ | 82 | 71 |

*Experimental condition: ethylene carbonate: 50 mmol, $CH_3OH$: 500 mmol, catalyst: 3 mmol, 5 h, atmospheric pressure. a,b: first and second recovered catalysts. c: pressure, 0.3 MPa by $N_2$, catalyst weight, 0.1 g, $CH_3OH$/ethylene carbonate, 4, 1 h (ref. [7]).*

For example, at the end of 5 h of reaction time, the DMC yield was 51 mol % at 278 K and 69 mol % at 283 K (Table 4. 1). At 323 K, the DMC yield was only slightly better (83 mol % DMC yield) than that at 298 K experiment (Fig. 4. 2 and Table 4. 1). The reaction temperature was increased to see the effect of temperature on the DMC yield. Due to the low boiling point of methanol, the reactions at the higher temperature were carried out in a closed and leak-tight S.S. pressure reactor (Parr reactor) as mentioned above; however, no appreciable improvement in the DMC yield was seen at higher temperatures. For example, the DMC yield was 81 mol % at 373 K which is nearly the same as that at ambient conditions (Fig. 4. 2). It may be noted here that the DMC yields at ambient conditions were nearly the same whether the reactions were carried out in an open glass reactor or in a closed reactor. There were no products other than the transesterified products, DMC and ethylene glycol (EG), in the temperature range employed. The transesterification reaction was also carried out over other tungstates like $K_2WO_4$ and $CaWO_4$ at ambient conditions and the results were similar to those of a $Na_2WO_4$-based reaction (Table 4. 1). For a comparison, the transesterification reactions were carried out with a MgO-based catalyst, one of the well known heterogeneous catalysts for this reaction; this catalyst was reported to be effective at high pressure and high temperature with 66 mol % DMC yield (at 423 K, 8 MPa $CO_2$ pressure) [11]. However, at ambient conditions, MgO produced only $< 2$ % DMC yield for the same reaction. It may also be noted here that even with strong bases like KOH, NaOH and LiOH, the maximum DMC yield reported was only 62 % at RT under 0.3 MPa of $N_2$ pressure (Table4. 1) [7].

### *4.3.2. Transesterification of ethylene carbonate under $CO_2$ pressure:*

Reports are available in the open literature on the improvement of DMC yield as well as on the mass balance for the transesterification reactions in the presence of $CO_2$, especially for experiments at higher temperatures, though $CO_2$ is not required for the above reaction [11,12,15]. We have carried out few transesterification experiments under $CO_2$ pressure in order to explore the possibility to obtain better DMC yield. Our experiments were carried out at different temperatures in the range 298 - 423 K for 4 h at a fixed $CO_2$ pressure of 3.4 MPa. The results at the end of the 4 h of reaction time for different temperatures are plotted in Fig. 4.3. Surprisingly, the conversion of ethylene carbonate and thus the DMC yields were nearly negligible up to 363 K under the 3.4 MPa $CO_2$ pressure, and the conversion of ethylene carbonate increases thereafter with increasing temperature. The dimethyl carbonate yield was around 12 % at 383 K and the maximum yield of 71 mol % was obtained at 423 K after 4 h (Table 4. 1). Compared with the reaction at ambient conditions where the DMC and ethylene glycol yields were nearly equal, the yield of EG was slightly higher than that of DMC for the reaction under $CO_2$ pressure at 423 K [11,20].

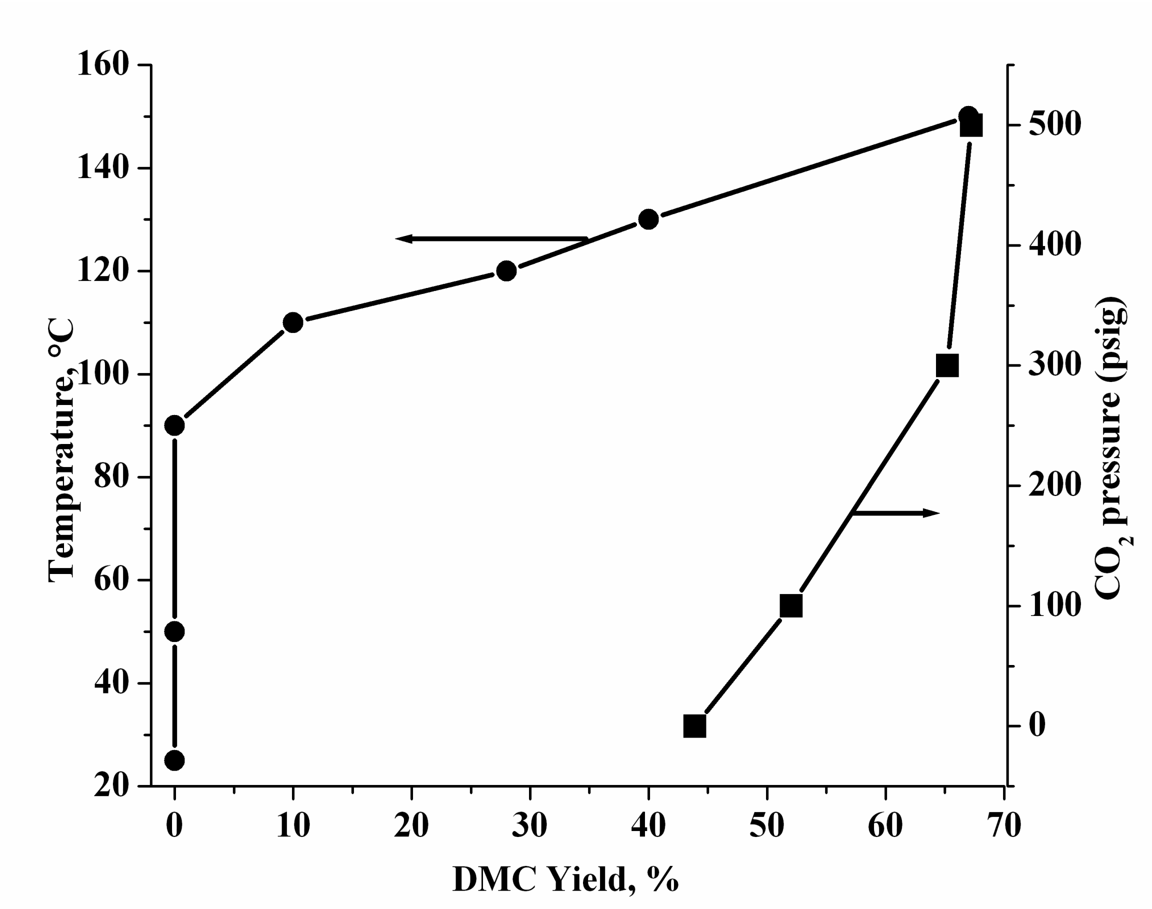


*Fig. 4. 3: Effect of reaction temperatures on DMC yield at 3.4 MPa $CO_2$ pressure (left axis) and effect of $CO_2$ pressure on DMC yield at 423 K. as function of catalyst loading as well as [MeOH]/[Ethylene carbonate] mole ratio. Experimental condition: ethylene carbonate: 50 mmol, $CH_3OH$: 500 mmol, $Na_2WO_4.2H_2O$: 3 mmol, time: 4 h.*

Similar experiments to optimize the DMC yield were carried at 423 K under different $CO_2$ pressures in the range 0 - 3.4 MPa and the results are shown in Fig. 4. 3. At 423 K in the absence of $CO_2$ pressure, the conversion of ethylene carbonate was nearly quantitative, where the DMC yield was only 50 mol %. GC analysis of the gaseous product mixture indicates the formation of $CO_2$ as a by-product under the above experimental conditions. The formation of $CO_2$ indicates possible ethylene carbonate decomposition at this high temperature in the absence of external $CO_2$ atmosphere

[11,21]. At the same temperature, the ethylene carbonate conversion decreases and the DMC yield increases on increasing the $CO_2$ pressure, the values reached a plateau in the range 2 - 3.4 MPa. Decrease in ethylene carbonate conversion and increase in the DMC yield under $CO_2$ pressure indicates that there is a reduction of ethylene carbonate decomposition. Thus, the above results substantiate the point that a $CO_2$ pressure of more than 3.4 MPa is necessary to avoid the decomposition of ethylene carbonate at these higher temperatures though there is no direct involvement of $CO_2$ in the transesterification reaction [11,18]. Maximum DMC yield was 71 mol % at 423 K and at 3.4 MPa $CO_2$ pressure (Table 4. 1).

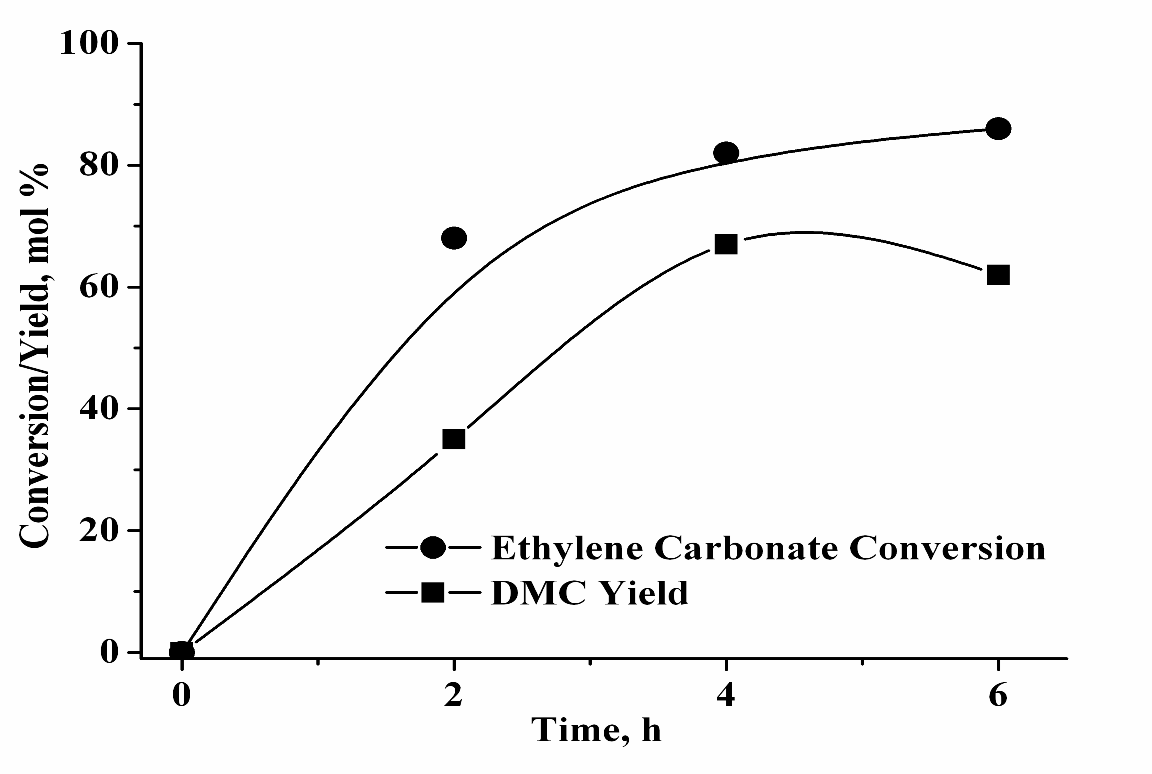


*Fig. 4.4: Kinetic profiles of ethylene carbonate conversion and DMC yield. Ethylene carbonate: 50 mmol, methanol: 500 mmol, $Na_2WO_4.2H_2O$: 1 g, p-xylene: 1 g, $pCO_2$: 3.4 MPa, temp.: 423K.*

The reaction kinetics of the transesterification reaction was monitored at 423 K at 3.4 MPa $CO_2$ pressure (Fig. 4. 4). The ethylene carbonate conversion and the DMC yield increase gradually with time and came close to a plateau after 4 h of reaction time. The maximum DMC yield was 71 mol % after 4 h.

### *4.3.3. Heterogeneous nature, recycling and stability of catalyst:*

The possibility of a homogeneous catalytic reaction in the present catalytic system was ruled out based on the following experiment. The kinetic plot of the transesterification reaction of ethylene carbonate with methanol over sodium tungstate catalyst at ambient condition (5 h of reaction time) was compared with the kinetic plot of another reaction where the transesterification reaction was stopped after 1 h, and the reaction was continued further after filtering out the solid catalyst. The results are reproduced in Fig. 4. 5. There was no further increase in the DMC yield after the solid catalyst was separated out. Also, the sodium content in the filtrate was estimated to be negligible (less than 0.5 ppm).

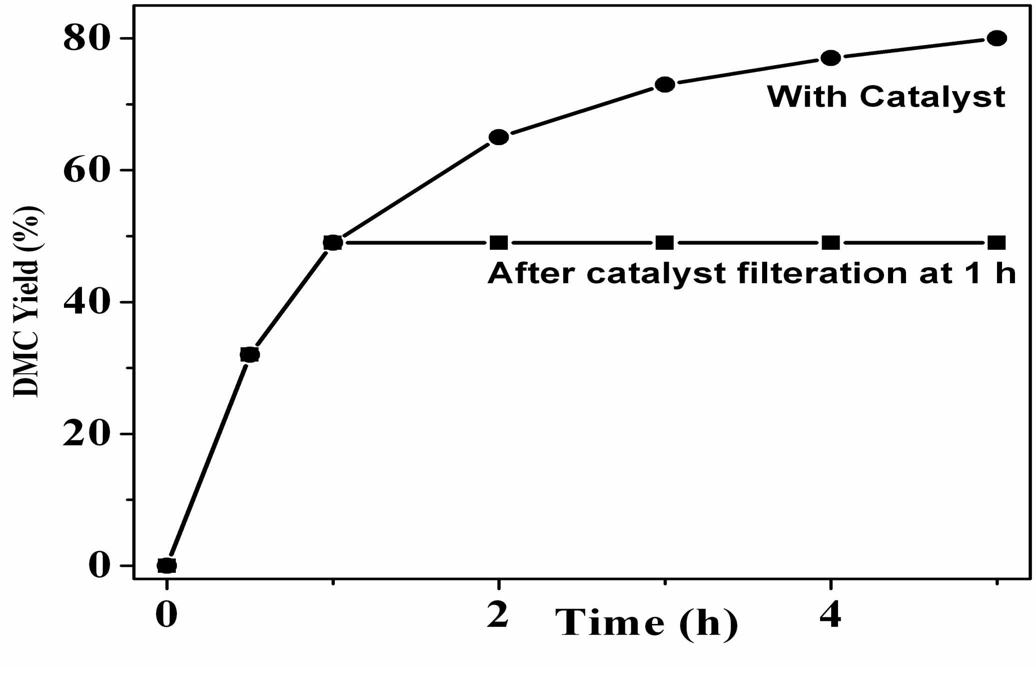


*Fig. 4.5: Profile of dimethyl carbonate formation from transesterification of ethylene carbonate with methanol without filtration of the catalyst, and after filtration of the catalyst at 1 h of reaction.*

This observation unambiguously demonstrates that sodium tungstate is a perfect heterogeneous catalyst for the present transesterification reaction. Also, there were no transesterified products in the absence of catalyst (Table 4.1). An attempt was made to recover the catalyst after the completion of a reaction at ambient conditions and to reuse it for subsequent runs. Accordingly, after 5 h of reaction time at RT (298 K), the solid catalyst was filtered, washed with methanol, dried, and recrystallized from water (recovered catalyst). The transesterification reaction over the recovered catalyst gave nearly the same result as that of the fresh catalyst with no loss in its activity. The cycle was repeated twice and the results were similar to those of the fresh reaction result (Table 4.1). Similar attempts were also made to reuse the catalyst recovered from the reaction mixture where the reaction was carried out under $CO_2$ pressure. Accordingly, after 4 h reaction at 423 K and at 3.4 MPa $CO_2$ pressure, the solid catalyst was isolated, washed with methanol, dried, and re-used for the transesterification of ethylene carbonate with methanol.

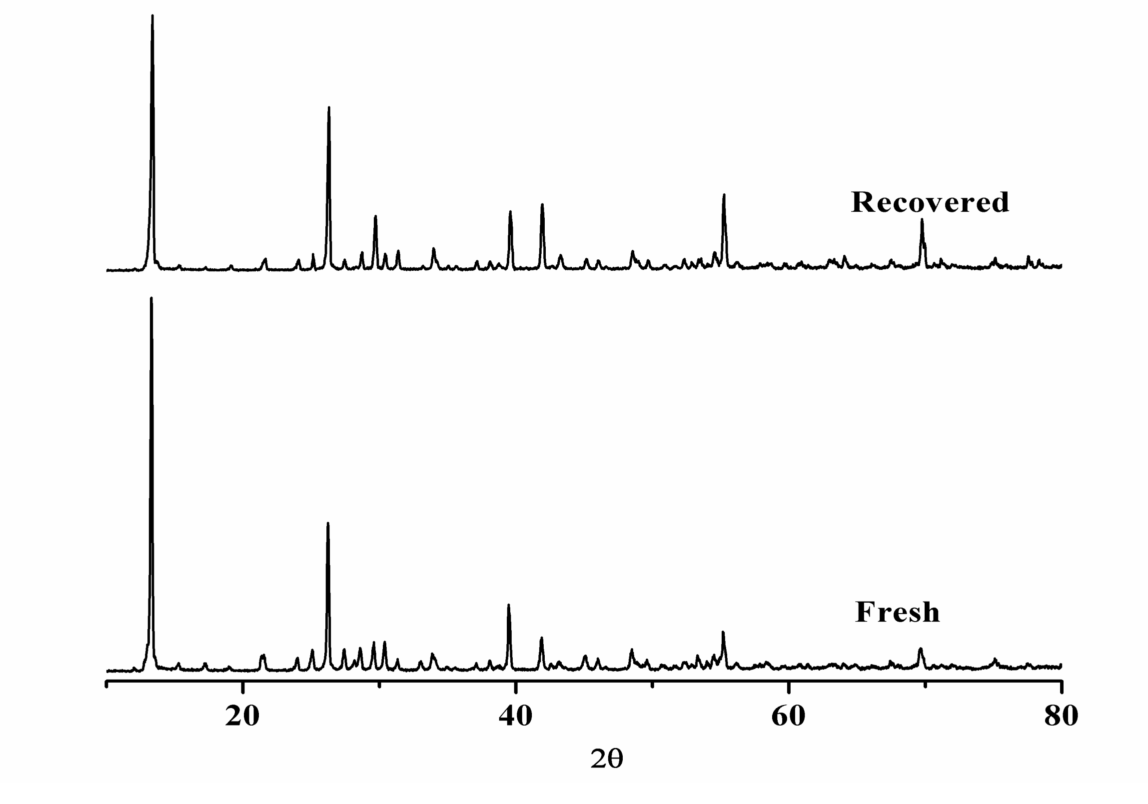


*Fig. 4.6: Powder XRD patterns of fresh and recovered sodium tungstate catalysts.*

The cycle was repeated twice and the results were nearly the same as those of the fresh catalyst with no loss in activity. The integrity of the catalyst under the present experimental conditions was analyzed by powder XRD and IR. The XRD patterns of sodium tungstate with orthorhombic system with the cell parameters of a = 10.592, b = 13.858, c = 8.479, $\alpha = \beta = \gamma = 90^o$ and with a space group of *Pbca* (JCPDS: 47-0064) match well for both fresh and recovered samples as shown in Fig. 4. 6.

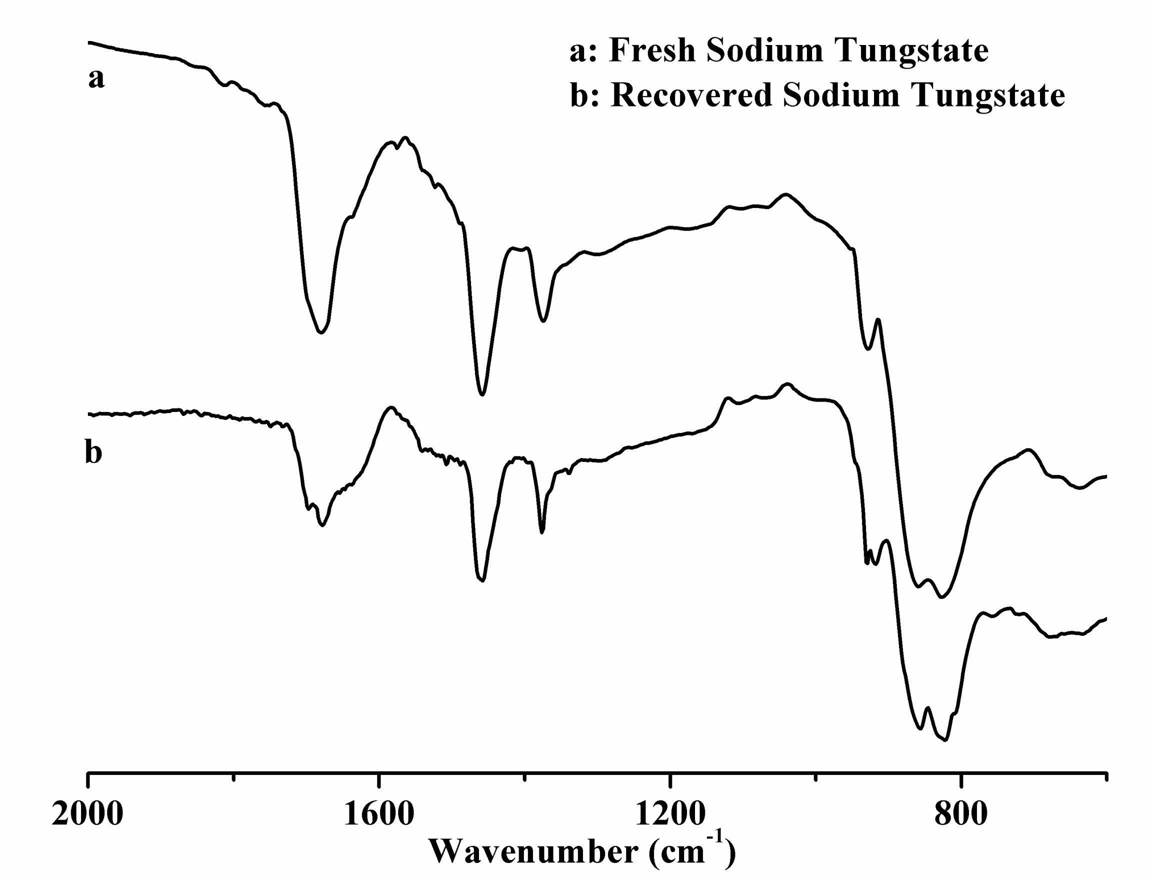


*Fig. 4. 7: FT-IR spectra of fresh and recovered sodium tungstate catalysts*

IR bands of recovered catalyst agree well with the characteristic IR bands of the fresh sodium tungstate catalyst (810 (w, sh), 823 (vs, b), 852 (vs, b), 926 (w), 1070 (w) and 3310 (s)) as shown in Fig. 4. 7 [22]. The above data clearly indicate that the structure of the catalyst did not change under the present experimental conditions.

### *4.3.4. Transesterification of propylene carbonate with methanol:*

The transesterification of propylene carbonate using $Na_2WO_4$ catalyst was also tested both at ambient conditions as well as under $CO_2$ atmosphere. The DMC yield was 23 mol % at ambient conditions after 5 h and 40 mol % at 423 K and 3.4 MPa $CO_2$ pressure after 4 h (Table 4. 2). Such a low reactivity with propylene carbonate compared to that with ethylene carbonate is the case with most of the reported catalyst systems apparently due to the steric hindrance associated with the bulky methyl group in propylene carbonate, as compared with symmetrical ethylene carbonate [6, 11].

**Table 4. 2.** *Transesterification of propylene carbonate (PC) with methanol over sodium tungstate catalyst.*

| Entry | Temp. K | Time, H | Pressure | Conv mol % | DMC Yield, mol % |
|---|---|---|---|---|---|
| 1 | 298 | 5 | Atmospheric | 25 | 23 |
| 2 | 423 | 4 | 3.4 MPa $CO_2$ | 54 | 40 |

*Experimental conditions:* Propylene carbonate: 50 mmol, methanol: 500 mmol, $Na_2WO_4.2H_2O$: 1 g, *p*-xylene (internal standard): 1 g.

### *4.3.5. Spectroscopic studies and reaction mechanism:*

While the exact reaction mechanism associated with the present catalytic system is not yet clear, Raman and IR spectroscopic techniques were explored to probe the possible reaction intermediates of the above transesterification reaction. In a controlled experiment, Raman spectra were recorded for sodium tungstate–methanol and sodium tungstate-ethylene carbonate mixtures at different time intervals. No new bands were found with the sodium tungstate-ethylene carbonate mixture apart from bands associated with pure sodium tungstate and ethylene carbonate. However, methanol soaked sodium tungstate showed new bands characteristic of methoxide ion adsorbed at the catalyst surface [23 - 25].

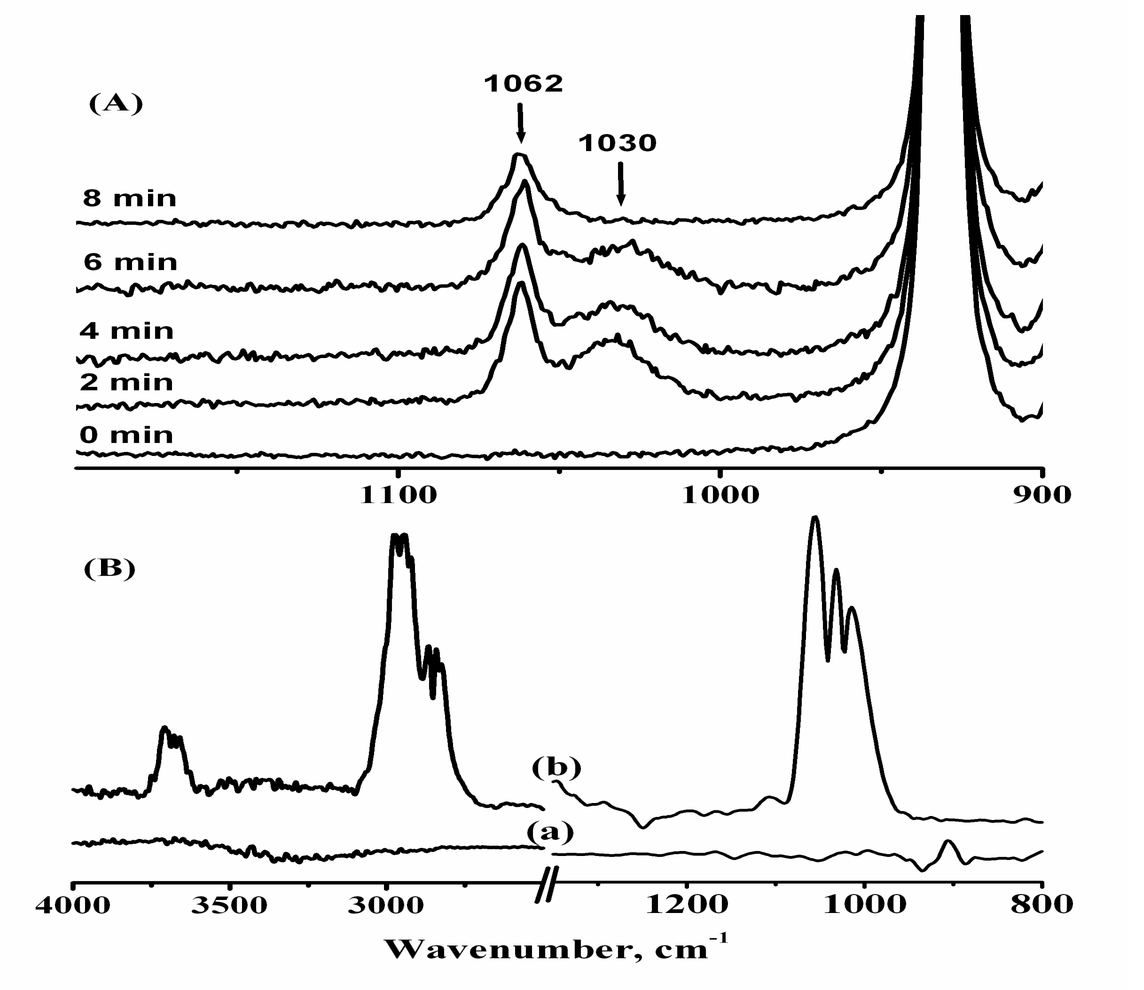


*Fig. 4. 8: (A) Raman spectra of methanol interacted sodium tungstate at RT and spectra were recorded at different time intervals after methanol exposure. Spectrum at 0 min corresponds to $Na_2WO_4$ before methanol exposure. Only C-O stretching frequency region is shown for clarity.(B) Infrared spectra taken during exposure of sodium tungstate catalyst to 10 $\mu$l of methanol in nitrogen flow at 50 ml/min at temperature of 423 K. (a) 2 min after the methanol exposure and (b) 30 min after the methanol exposure. The spectra referenced to sodium tungstate under atmospheric pressure $N_2$ flow at 423 K*

Raman spectra that were recorded every 2 min after $Na_2WO_4$ was soaked with methanol at RT are shown in Fig. 4.8 (A). The band at 1030 cm$^{-1}$ corresponds to the bending vibrational mode for the methoxide ion species adsorbed at the catalyst surface and that at 1062 cm$^{-1}$ has been ascribed to physisorbed methanol. Similar measurements using infrared spectroscopy were also carried out. The room temperature IR measurements showed heavy overlap of peaks corresponding to molecularly adsorbed methanol with that of the adsorbed methoxide ion. However, measurements at 423 K clearly exhibits peaks corresponding to formation of methoxide ion adsorbed at the catalyst surface. Fig. 4.8 (B) shows representative IR spectra taken during the exposure of the sodium tungstate catalyst to a pulse of methanol (10 ml in $N_2$ flowing at 50 ml/min) right after the exposure and 30 min after the exposure; the measurements were carried out at 423 K. Characteristic bands at 2921, 2825 and 1057 $cm^{-1}$ are assigned to methoxide groups adsorbed at the tungstate catalyst surface. The band at 2921 $cm^{-1}$ corresponds to the C–H stretching vibration of the methoxide species [6, 18, 19]. Bands at 1057 $cm^{-1}$ and at 1035 $cm^{-1}$ are assigned to the bending vibration of methoxide group adsorbed at the tungstate catalyst surface and molecularly adsorbed methanol, respectively. The absence of any new vibrational bands for the ethylene carbonate - sodium tungstate mixture and the presence of methoxide ion species adsorbed at the catalyst surface for the methanol–sodium tungstate indicate that the transesterification reactions are driven by activation of methanol (nucleophile) by the sodium tungstate catalyst rather than activation of the electrophile (Lewis acid complexation of the carbonyl group of ethylene carbonate with the catalyst). Alkali hydroxides which can deprotonate the methanol to form the methoxide ion showed a moderate activity for the present transesterification reaction (Table 4.1) which probably indicates that the methoxide ion is partially responsible for driving the transesterification reaction. However, much better performance of the tungstate-based catalysts for the present transesterification reaction with high DMC yield indicates that a new adduct or complex formed between sodium tungstate and methanol might be responsible for the improved performance of the present catalyst system. The new adduct or complex is likely to be a methoxide ion adsorbed dissociatively on the tungstate catalyst. In the absence of any concrete experimental proof for any reaction intermediates, but based on the above data, we propose a model reaction mechanism, where the above tungstate–methoxide ion adduct initiates the transesterification reaction as shown Scheme 4. 2. However, further in-depth investigation is needed to understand the exact nature of reaction intermediates responsible for improved performance of the present catalyst system at ambient conditions.

### *4.3.6. DMC synthesis from one-pot reaction:*

A reaction integrating the reactions of $CO_2$ insertion into epoxides to form cyclic carbonates and subsequent transesterification of cyclic carbonates with methanol was also carried for the synthesis of DMC by a one-pot method directly from epoxide, methanol, and $CO_2$. Typically the reaction was carried out at 3.4 MPa $CO_2$ and 423 K for 15 h where the reactor was charged with epoxide, methanol and sodium tungstate catalyst. Three epoxides: namely, propylene oxide, epichlorohydrin, and butylene oxide, were chosen as representative epoxides for the one-pot synthesis and the end results are given in Table 4. 3.

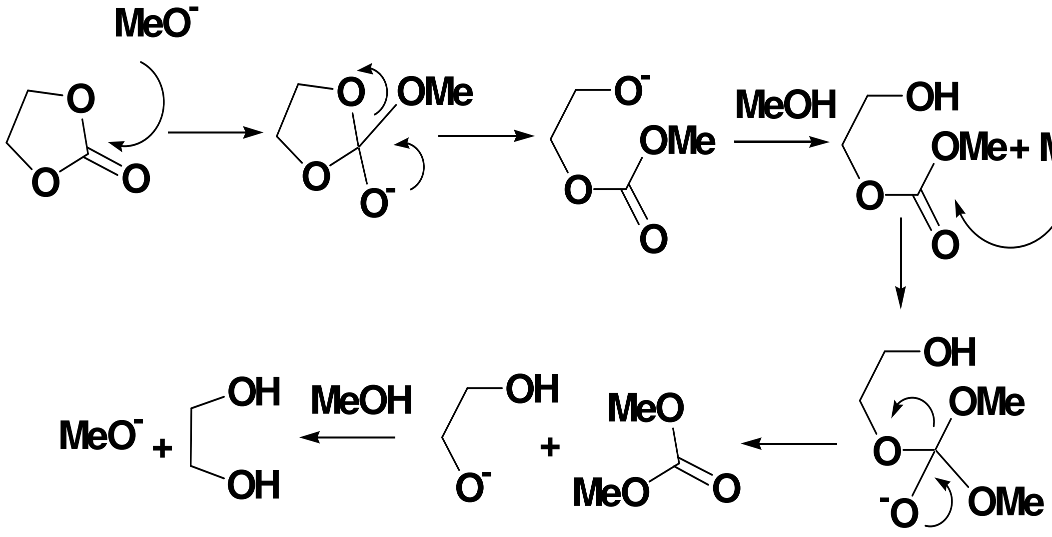
***Table 4. 3:*** *One pot synthesis of DMC from epoxide, $CO_2$, and methanol*

| Entry | Substrate | Conversion, mol % | Product yield, mol %[a] | |
|---|---|---|---|---|
| | | | CC | DMC |
| 1 | Propylene oxide | 92 | 17 | 24 |
| 2 | Epichlorohydrin | > 99 | 10 | 11 |
| 3 | Butylene oxide | > 99 | 5 | 23 |

*Experimental conditions: epoxide: 50 mmol, methanol: 500 mmol, $Na_2WO_4.2H_2O$: 1 g, p-xylene (internal standard): 0.2 g, $pCO_2$: 3.4 MPa, 423 K, 15 h,*

[a] *: other products are diol and its methylated products.*

Although conversion was nearly quantitative with all the epoxides, DMC yield was only moderate in all the cases. DMC yield was around 24 % with propylene oxide and butylenes oxide, it was only 11% with epichlorohydrin. Apart from DMC, cyclic carbonate and glycol, mono-, and di-methylated diol products were also found in the product mixture (Scheme 4. 1. (b)) [12,13]. Thus, the DMC yield in the one-pot synthesis was much lower compared to that from the transesterification of cyclic carbonates with methanol.



*Scheme 4. : Proposed reaction mechanism for the transesterification of ethylene carbonate with methanol over sodium tungstate catalyst to yield DMC and ethylene glycol.*

Though DMC synthesis from one-pot synthesis is attractive, but is not effective using the present catalytic system, similar to the cases with most of the reported heterogeneous catalyst systems [11, 12, 16].

## 4. 4. Conclusion:

In summary, tungstate-based heterogeneous catalysts ($Na_2WO_4.2H_2O$, $K_2WO_4$ and $CaWO_4$) are efficient for the transesterification of ethylene carbonate with methanol to produce DMC yield of 80 mol % at ambient conditions which is the highest DMC yield obtained so far at ambient conditions. The tungstate-based catalysts are totally heterogeneous and could be recovered and reused. Reactions under $CO_2$ pressure indicated that $CO_2$ atmosphere totally retards the reaction at temperatures less than 373 K, however, a DMC yield of 71 % was obtained at 423 K but this is still lower than that obtained at ambient conditions. A methoxide ion species adsorbed at the catalyst surface was identified as a possible reaction intermediate using IR and Raman spectroscopic techniques. DMC yield from one-pot synthesis using the present catalyst was only moderate and much lower than that from the transesterification of cyclic carbonate routes.

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# Chapter – V

## Transesterification of cyclic carbonates using solid oxide catalyst

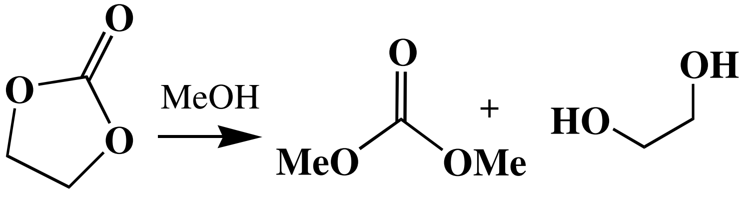
Part of the work described in this chapter has been communicated:

M. Sankar, S. Satav, P. Manikandan *Applied Catalysis A: General* (communicated)

## 5. 1. Introduction:

Dimethyl carbonate (DMC) is used for a variety of applications in the chemical industries owing to its low toxicity and versatile chemical nature. DMC is a safe and environmentally acceptable carbonylating, carboxylating and methylating agent which can substitute toxic phosgene, dimethyl sulphate [5-9]. In addition, DMC is an attractive chemical with many other potential applications, including its use as a gasoline octane enhancer, due to its favorable properties like high oxygen content, negligible toxicity, and good biodegradability [10].

DMC is traditionally produced from phosgene and CO routes that are known to be environmentally hazardous and rigorous safety measures are involved with these processes [4,10]. Thus, the synthesis of DMC through non-toxic and environmentally clean routes has received considerable attention in recent years [3,4,9-11]. There are two alternate "green" routes available now for the synthesis of DMC. One is the direct reaction of methanol with $CO_2$; however, it suffers a major disadvantage as the DMC yield in this process is restricted by thermodynamics [10,11]. The other route is the transesterification of cyclic carbonates using methanol [12-14] where the cyclic carbonates can be produced quantitatively from $CO_2$ insertion to epoxides method [15,16]. The latter method, as an environmentally benign process, has gained considerable attention in recent years as $CO_2$ is cheap, non-toxic, non-flammable and inexpensive C-1source [1-4].



*Scheme 5.1: Transesterification of cyclic carbonate*

A schematic diagram for the transesterification reaction is shown in Scheme – 5.1. This route is advantageous as it is an atom economic process without any waste material formation. Many homogeneous and heterogeneous catalytic systems have been reported for the transesterification of cyclic carbonates with methanol with high selectivity to DMC [12,14,17]. Although homogeneous catalyst systems are more active, they have their own drawbacks of catalyst separation after the reaction. In case of heterogeneous catalysts both acidic and basic catalysts have been used for the transesterification of cyclic carbonate, however~~,~~ the basic catalysts are found to be better in general with better selectivity for the transesterified product [12,18]. Many basic metal oxides as heterogeneous catalysts were reported for the synthesis of DMC from cyclic carbonates [12] but in most of the cases the reaction need severe reaction condition like high temperature and high $CO_2$ pressure [12,23]. Only very few catalysts are available in literature which are found to be active at lower temperatures, for example, at ambient conditions [13,14,19]. In addition, all of them are batch reactions and not a continuous reaction. A continuous process for the synthesis of DMC from EC at room temperature is important from the industrial point of view. Thus, the objective of the present chapter is to develop a heterogeneous catalytic system which is efficient for the above transformation at ambient conditions for both batch and for continuous operations.

Among the various basic metal oxides screened, we found CaO based catalysts are very efficient for the transesterificaton reaction. Practical difficulties were encountered when pure CaO was used as the catalyst for the above transformation, thus, CaO with various supports were investigated. Recently, CaO supported on $ZrO_2$ was reported as an effective catalyst for the transesterification of propylene carbonate using methanol in a continuous reaction but at higher temperature [20,21]. However, this system is not efficient for the transesterification of ethylene carbonate with methanol at ambient conditions. Among various supported CaO catalysts, we found CaO-ZnO based catalysts with varying Ca/Ca+Zn ratio were efficient for the transesterification of ethylene carbonate using methanol at ambient conditions with more than 80 mol % DMC yield. To the best of our knowledge this is the highest DMC yield obtained at the ambient conditions. Importantly, the efficiency of the present catalyst system has also been demonstrated with both batch as well as continuous reactors.

## 5. 2. Experimental:

### *5. 2. 1. Synthesis & Characterization of catalyst:*

$Ca(NO_3)_2.4H_2O$ and ZnO were purchased from Loba Chemie, ethylene carbonate was purchased from Aldrich Co. and methanol from Merck Co. All the chemicals were used without further purification. CaO-ZnO catalysts were prepared by wet-impregnation method [20]. In a typical procedure $Ca(NO_3)_2.4H_2O$ was dissolved in required amount of water and then ZnO was added to the $Ca(NO_3)_2$ solution slowly and the mixture was stirred vigorously at room temperature for 12 h. The final sample was dried at 363 K and then calcined at 1123 K. The calcined material was characterized using powder XRD (Rigaku D Max III VC instrument using Ni-filtered Cu Kα radiation). CaO in other supports were synthesized using the same procedure as described above. In a typical synthesis $Ca(NO_3)_2$ was dissolved in required amount of water and then the support was added slowly to the $Ca(NO_3)_2$ solution with vigorous stirring at room temperature. The resultant sample was dried at 373K and then calcined at 1123K for 12h.

### *5. 2. 2. Catalytic performance – Batch reaction:*

The batch reaction at ambient conditions was carried out in a 50 ml round bottom flask where the flask was, typically, charged with 50 mmol of cyclic carbonate, 500 mmol of $CH_3OH$, 0.25 g of CaO-ZnO and 1 g of *p*-xylene (internal standard). The reaction mixture was stirred with a magnetic bar and the reaction temperature (298 K) was maintained using a cryo-bath. The progress of the reaction was monitored by drawing small amount of aliquots of the reaction mixture at regular time intervals and subjecting them to GC analysis (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m X 0.32 mm 5 % phenyl methylsilicone capillary column). DMC Yield was calculated based on the internal standard (*p*-xylene). The products were identified by GC-MS (Shimadzu-GC-17A fitted with a QP-500MS mass spectrometer). Yield of the products was calculated as number of mols of the product formed per mol of the ethylene carbonate.

### *5. 2. 3. Catalytic performance – Continuous reaction:*

The continuous reaction for the synthesis of DMC from EC was performed using a glass reactor. A schematic representation of the reactor is shown in Fig.5.1 where A represents a reservoir for the reactants, EC and MeOH and from the reservoir the reactants were pumped into the reactor (upward flow) using a HPLC pump B at a desired flow rate. The granulated catalyst sample (typically 6 g, 20-30 mesh) in the reactor was packed in between porcelain beeds. The product mixture was collected at regular intervals, after condensing, in a round bottomed flask D. The temperature of the catalyst bed was maintained at the required temperature using a cryobath. The product mixture was analyzed using a GC (Hewlett-Packard 5890 gas chromatograph with a flame ionization detector and 50 m X 0.32 mm 5 % phenyl methylsilicone capillary column). EC conversion was calculated using standard calibration curves

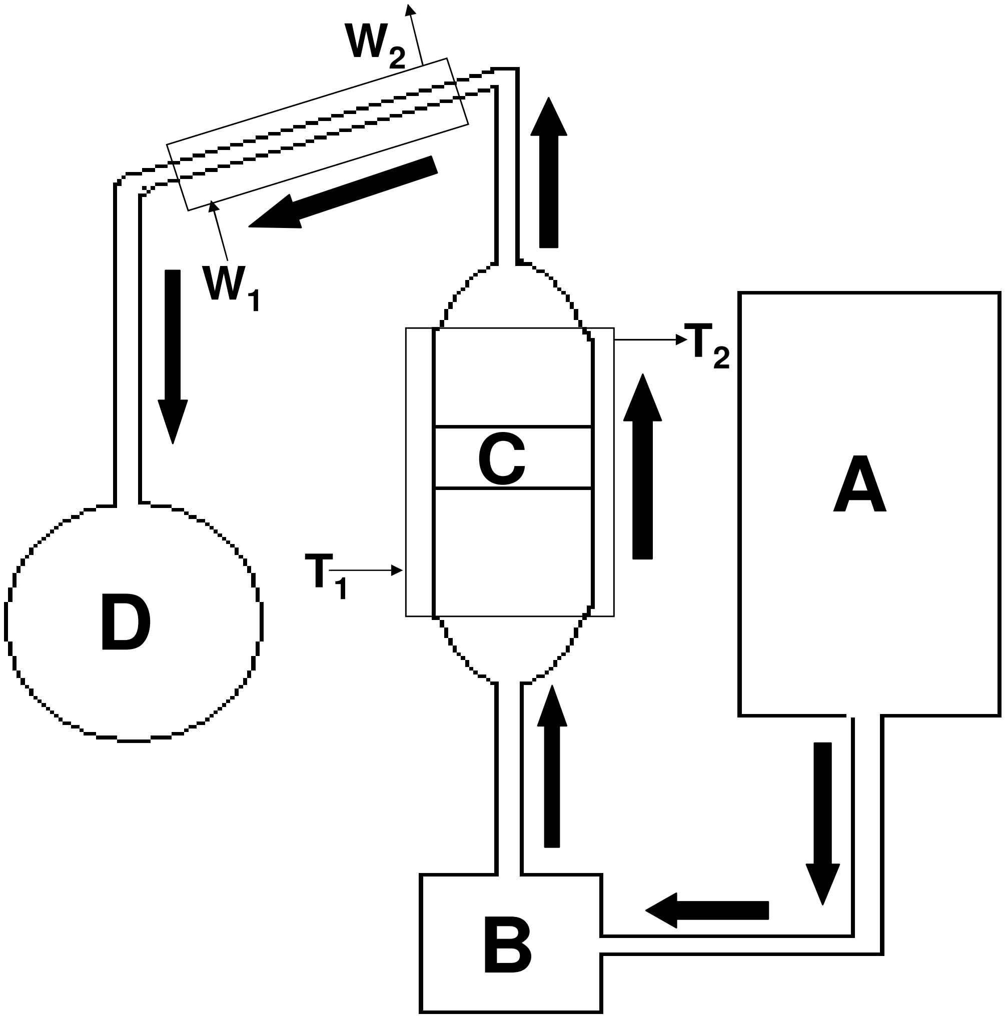


*Fig.5.1: Schematic representation of the reactor used for the continuous synthesis of DMC. A: Reservoir for reactants; B – Liquid feed pump; C- Catalyst bed; D – Product collection point; $T_1$- Water inlet from thermostat to maintain reactor temperature; $T_2$- Water outlet; $W_1$&$W_2$- Cooling water circulation for condensing the products; Solid arrows indicate the flow of reactants and products (upward flow).*

## 5. 3. Result and Discussion:

### *5. 3. 1. Catalytic performance – Batch reaction:*

The catalytic activity of CaO-ZnO catalysts was tested in the batch reactor first and the reaction conditions were optimized systematically. In order to optimize the catalyst loading, the transesterification reaction was carried at ambient conditions with varying catalyst weight in the range 0.05 - 0.5 g and 0.05 mol of EC where Ca/Ca+Zn ratio of the catalyst was 0.5 and EC: MeOH ratio was 10. The products at the end of the 1h of reaction time were analyzed and the results are shown in Fig. 5. 2. As seen in the figure, the DMC yield increases steeply up to 0.25 g catalyst loading and the reached near plateau thereafter. Thus, the optimum weight of catalyst needed to obtain maximum DMC was 0.25 g to obtain maximum DMC yield of ~ 84 mol %. It is interesting to note that even at the lowest catalyst loading of 0.05 g, the DMC yield was 55 mol % indicating the efficiency of the catalyst. In the absence of the catalyst, the DMC yield was negligible even after 10 h.

In order to understand the effect of the reaction temperature on the DMC yield, the reactions were carried out at different temperatures in the range 283 to 313 K and resultant kinetic data are shown in Fig. 5.3. The experiments were carried out using the CaO-ZnO catalyst with low Ca/(Ca+Zn) ratio of 0.2 in order to collect sufficient data points even at higher temperature. As seen in the figure, the catalyst is active and efficient for the entire temperature range employed. In general, DMC yield increases steeply in the beginning and then reached the chemical equilibrium. The rate of the DMC formation was low at sub-ambient conditions as anticipated. At near room temperature (300 K), the DMC yield reached around 80 % within 4 h of reaction time at an equilibrium stage. Though the rise in temperature up to 313 K improved the DMC yield slightly, temperature higher than that did not benefit in improving the DMC yield further where the reaction reaches equilibrium faster. It is interesting to note that the catalyst is active even at the sub-ambient conditions.

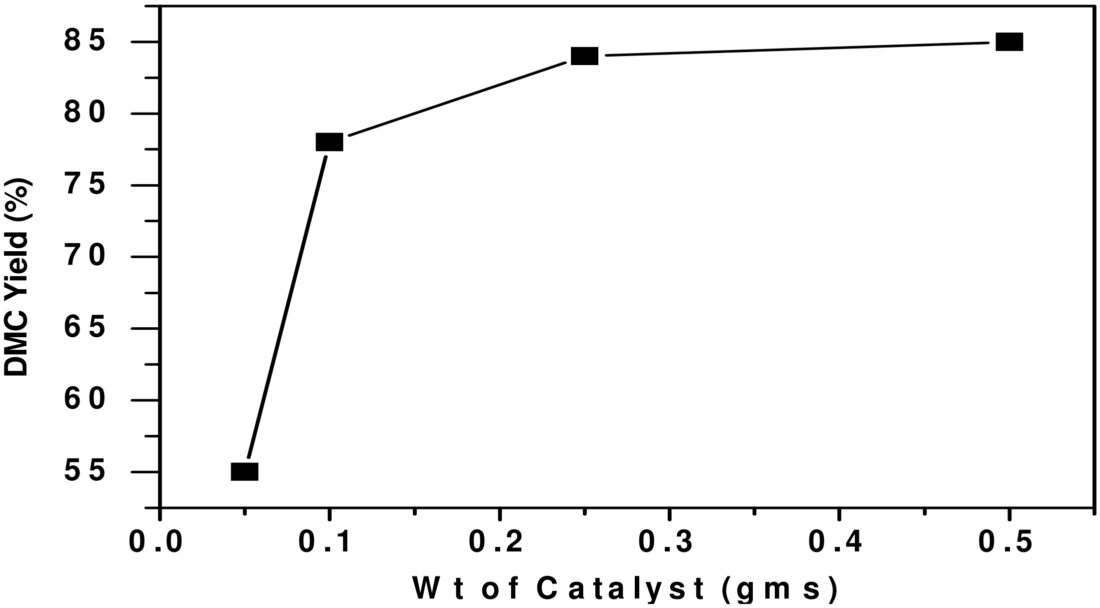


*Fig.5. 2: Batch reaction: Effect of catalyst weight on DMC Yield, EC= 0.05 mol ; Ca/Ca+Zn ratio = 0.5; MeOH = 0.5 mol; Time = 1 h; Temp = RT (300K).*

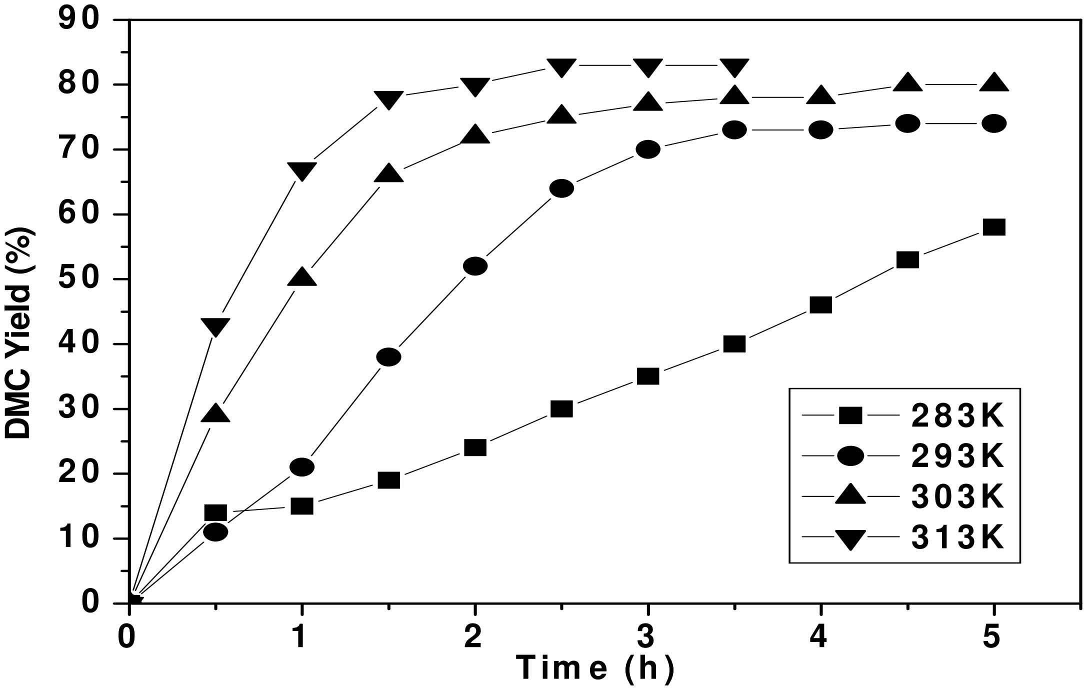


*Fig.5. 3: Kinetic Plots for various temperatures (T= 283K, 293K, 303K, 313K & 323K); Batch Reaction; EC= 0.05 mol.; Ca/Ca+Zn ratio = 0.2; MeOH = 0.5mol.*

Catalysts with different (Ca/Ca+Zn) loadings were tested for their catalytic activity at room temperature for a fixed amount of time and the results are given in Table 5.1. As seen in the table, the catalytic activity increased nearly in a linear fashion with Ca content, indicating that CaO is the active component for the present reaction. A reaction with pure ZnO showed (data is not shown here) no trace of DMC indicating ZnO does not play any catalytic role, however, it gives a good binding effect such that it allows easy separation of the catalyst after the reaction for the re-use. The reusability of the catalyst was demonstrated as follows: the catalyst after the reaction was recovered by simple filtration, washed with methanol to remove other organic reactant and products, dried at 373 K for 5 h and then reused for a fresh batch of reactants. The cycle was repeated few times and the activity of the catalyst was retained without loss in activity (entries 7 and 8, Table 5. 1).

***Table 5. 1:*** *Catalytic performance of the present catalytic systems with different CaO loadings, catalyst reusability and efficiency for different substrates*

| Entry | Catalyst | Substrate | Time, h | DMC Yield (%) |
|---|---|---|---|---|
| 1 | CaO-ZnO(0.05) | EC | 0.5 | 14 |
| 2 | CaO-ZnO(0.1) | EC | 0.5 | 20 |
| 3 | CaO-ZnO(0.2) | EC | 0.5 | 34 |
| 4 | CaO-ZnO(0.4) | EC | 0.5 | 48 |
| 5 | CaO-ZnO(0.5) | EC | 0.5 | 84 |
| 6 | CaO-ZnO (0.4) | EC | 4.0 | 83 |
| 7 | CaO-ZnO (0.4) (I Recovered) | EC | 4.0 | 82 |
| 8 | CaO-ZnO (0.4) (II Recovered) | EC | 4.0 | 83 |
| 9 | CaO-ZnO (0.4) | PC | 4.0 | 47 |

*EC= 4.4 g; p-xylene = 1 g; MeOH= 16 g; Temp= 298 K, Catalyst wt.= 0.25 g.*

To prove the tolerance of the present catalyst system for higher homologous of ethylene carbonate, transesterification of propylene carbonate with methanol was also tested at ambient conditions. With the CaO-ZnO(0.4) catalyst, the transesterification reaction of propylene carbonate at room temperature yielded 47 mol % DMC in 4 h of reaction time (Table 5. 1). DMC yield from the propylene carbonate based reaction was lesser than that from ethylene carbonate based reaction (Table 5. 1). This may be due to the steric hindrance associated with the propylene carbonate that leads to lesser reactivity, as proposed in the earlier reports [12].

***Table 5. 2:*** *Comparison of catalytic activities of the present catalytic systems for batch with a few selected reported systems.*

| Catalyst | Substrate | Temp (K) | Time (h) | DMC (%) | Ref |
|---|---|---|---|---|---|
| $CaO-SiO_2$ | EC | 298 | 4.0 | 0 | Present work* |
| $CaO-CeO_2-ZrO_2$ | EC | 298 | 4.0 | 0 | Present work* |
| $CaO-ZrO_2$[20] | EC | 298 | 4.0 | 0 | Present work* |
| CaO-ZnO (0.4) | EC | 298 | 3.0 | 70 | Present work* |
| CaO-ZnO (0.4) | EC | 313 | 3.0 | 83 | Present work* |
| Mg-Na Smectite | EC | 423 | 4 | 74 | [23] |
| $Mg_2-Al-NO_3$ LDH | EC | Reflux | 3 | 54 | [24] |
| Sodium Tungstate | EC | 300 | 4 | 78 | [14] |
| LiOH (homogeneous) | EC | 298 | 1 | 62 | [25] |

*EC = 4.4g; *p*-xylene = 1 g; MeOH = 16g Time = 0.5 h, Catalyst = 0.5 g

Superiority of the present catalytic system is demonstrated by comparing with few selected reported catalytic systems for the cyclic carbonate transesterification reaction (Table 5. 2). For example, Wang *et al* reported [20, 21] a similar catalytic system, $CaO-ZrO_2$, that is active for the synthesis of DMC from propylene carbonate but only at temperature more than 410 K. However, at ambient conditions, $CaO-ZrO_2$ catalyst system was inactive even after 4 h of reaction time unlike the present catalytic systems. In the case of $CaO-ZrO_2$ system, it was reported that it forms either a homogeneous solid solution or $CaZrO_3$ [21]. However, in the present system, CaO phase was seen as a distinct phase without any phase change with ZnO support as seen in the powder XRD of the material. The observation of the phases against activity data reveals that CaO phase supported on an inert support is needed for the effective transesterification reaction at ambient conditions. To substantiate the above conclusion and to understand the effect of support on the activity of the catalyst, CaO was supported on $SiO_2$, $CeO_2$-$ZrO_2$ (1:1) and $ZrO_2$ and their activity were examined at ambient condition. As seen in the table 5.2, these catalyst systems are inactive at the ambient conditions. The CaO phase was not seen distinctly in all the above three cases which probably indicates that CaO is not available freely for the reactants to interact unlike in ZnO case. The reason for the non-availability of free CaO may be these supports ($SiO_2$, $ZrO_2$, $CeO_2$-$ZrO_2$) tend to form new phases with CaO [21] so they may be in an intermediate stage where CaO is surrounded by support molecules and thereby the access to CaO is restricted. A comparison has also been made with the catalytic activity data of few reported catalysts in Table 5. 2, for the synthesis of DMC from cyclic carbonate and methanol. Mg-Na-Smectite based catalyst has been reported to give more than 74 % DMC yield but at 423 K and $Mg_2$-Al-$NO_3$ based LDH catalyst gave only 54 % DMC yield. Even for the alkali based homogeneous catalyst like LiOH, the DMC yield was only around 62 mol %. The sodium tungstate based catalyst, however, was the only heterogeneous catalyst reported to be efficient close to the present catalyst system at ambient conditions (Table 2) as reported by the present authors.

### *5. 3. 2. Catalytic performance - Continuous reaction:*

As the present catalyst system was found to be active for the transesterification reaction at ambient conditions with the batch reactor system, we attempted to test this catalyst for the continuous DMC production from EC using a simple reactor set up explained in Fig.5. 1. The reactants, MeOH and EC, were taken in the reservoir with a required molar ratio and were pumped by a feed pump in an up-flow manner as described in the experimental section. The downstream product mixture was collected and was analyzed by GC. The results showed that the catalyst is active and efficient even at the ambient conditions even for the continuous mode of operation. Experiments to study the effect of MeOH: EC molar ratio on the DMC yield Was carried out at ambient conditions at LHSV of 2 $h^{-1}$ by MeOH: EC molar ratio from 2 to 10 and the results are shown in Fig. 5.4. Ethylene carbonate conversion increases with increase in the MeOH: EC molar ratio. DMC yield of 70 mol % was obtained at the MeOH: EC ratio of 2 and the DMC yield increased gradually on increasing the MeOH: EC ratio and reached 88 % mole when MeOH: EC ratio was 10. The shift of higher DMC yield at the higher MeOH: EC was expected for the equilibrium controlled reaction, MeOH: EC ratio might have shifted the equilibrium towards the right hand side i.e. towards DMC yield [ 22].

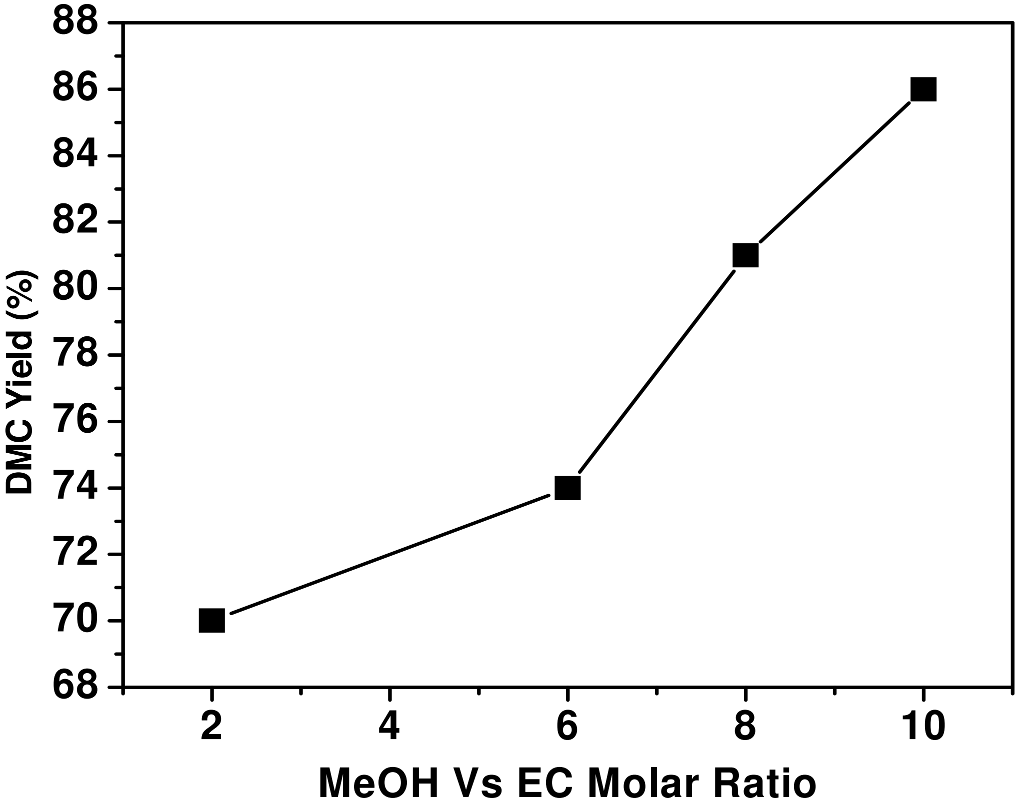


*Fig.5. 4: Effect of MeOH Vs EC molar ratio on EC Conversion in the continuous reaction. Ca/Ca+Zn = 0.4; LHSV = 2 $h^{-1}$ Temp = RT (300K).*

Higher the LHSV, more the productivity of the required product for the given amount of the catalyst. Hence, experiments were carried out to monitor the DMC yield at 6 g catalyst loading at different LHSV and the results are plotted in Fig.5.5. It is interesting to find that the DMC yield was more or less the same up to LHSV of 16 $h^{-1}$.

To the best of our knowledge this is the highest space velocity reported for this cyclic carbonate transesterification reaction for the production of DMC at ambient conditions. A comparison has also been made with few reported catalytic systems as shown in Table 5.3. As seen in the table, the reported catalyst systems $CaO\text{-}ZrO_2$, Amberlite IRA-68 and $NH_2$-MCM-41 were active and efficient only at elevated temperature for the cyclic carbonate transesterification reaction; however, these catalysts are inactive at ambient conditions unlike the present catalyst system. This comparison clearly demonstrates the superiority of this catalytic system over other reported catalytic systems.

***Table 5.3:*** *Comparison of catalytic activities of the present catalytic system for continuous reaction with a few reported systems.*

| Catalyst | Substrate | LHSV ($h^{-1}$) | Temp (K) | DMC (%) | Ref |
|---|---|---|---|---|---|
| $CaO\text{-}ZrO_2$ | PC | 0.03 | 410 | 55 | [20] |
| Amberlite IRA-68 | EC | 4.0 | 373 | 24 | [14] |
| $NH_2$-MCM-41 | EC | 3.0 | 433 | 43 | [26] |
| CaO-ZnO(0.4) | EC | 16.0 | 300 | 84 | Present work* |

* Ca/Ca+Zn = 0.4; LHSV = 2 $h^{-1}$ Temp = 300 K. Catalyst wt. = 6 g

Time on stream study for the system with 6 g catalyst loading was carried out at ambient conditions at LHSV of 2 $h^{-1}$ for several hours and the results are shown in Fig. 5. 6. The catalyst was found to retain its activity up to 60 h and after that the activity started decreasing. This observation could be due the disintegration of the catalyst into finer particles of $Ca(OH)_2$ and leaching out along with the product stream. A physical observation of a clear down stream products turned into a milky-like solution at the end of 60 h of time on stream experiments confirms such disintegration. The reason for the reduced activity of the catalyst after 60 h of continuous reaction was also analyzed by powder XRD

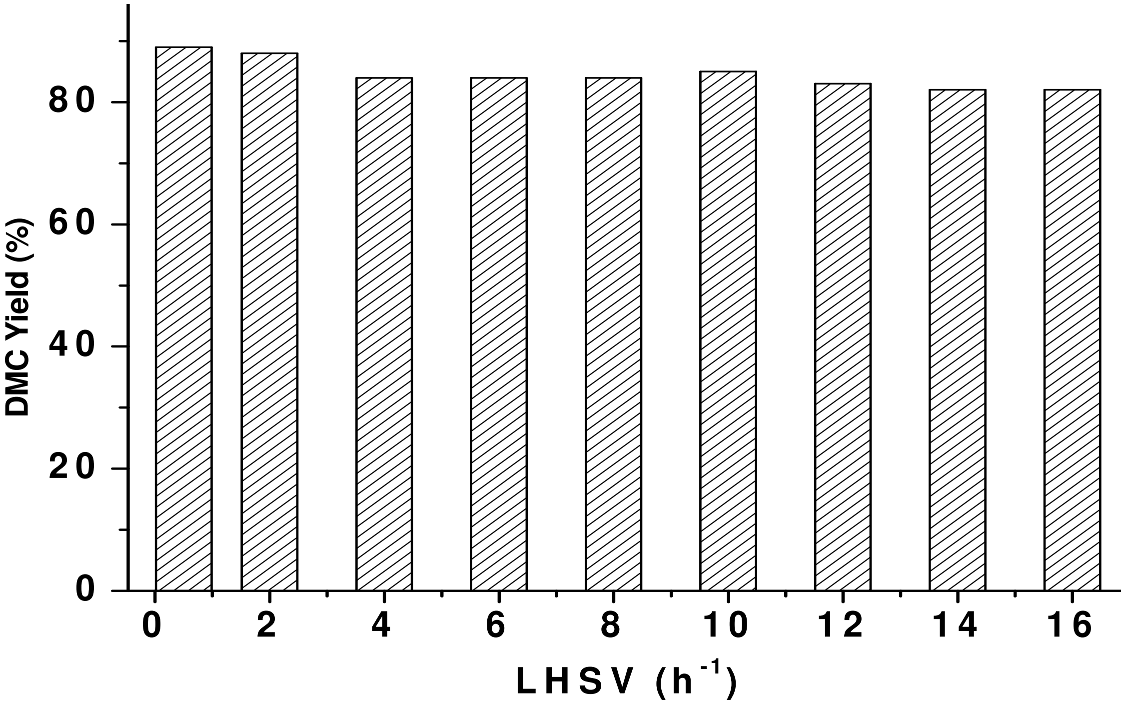


*Fig.5. 5: Catalytic Performance of Ca/Ca+Zn = 0.4 catalyst at 300K in the continuous reaction for various LHSV (2 $h^{-1}$ to 16 $h^{-1}$); MeOH Vs EC molar ratio = 10; Catalyst wt.= 6g.*

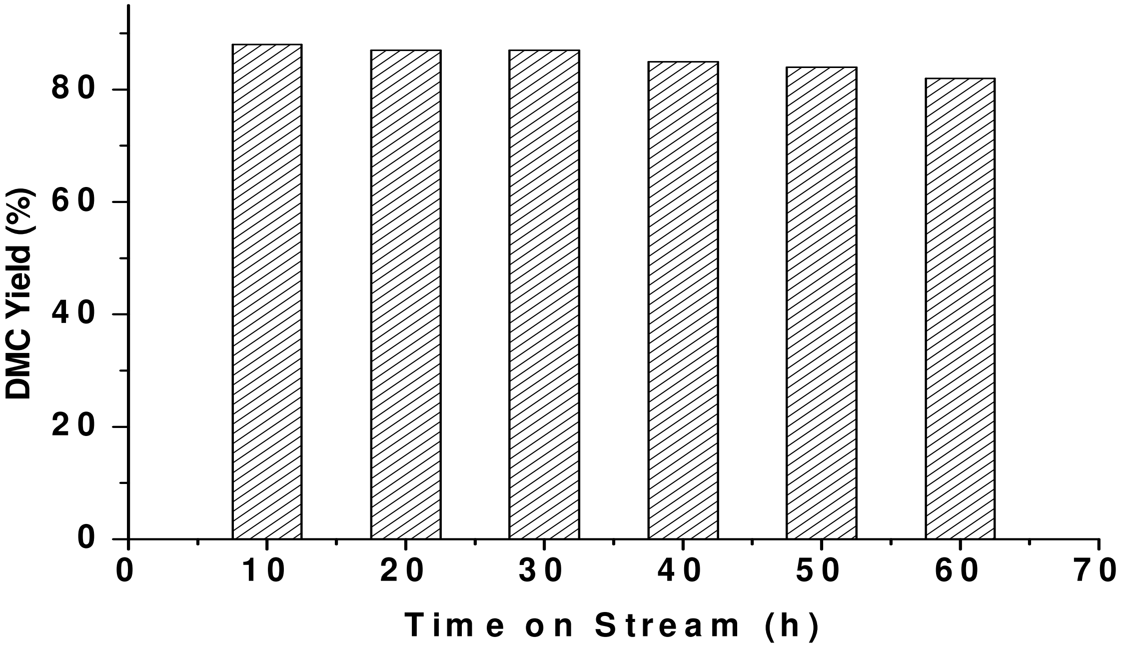


*Fig.5.6: Stability of catalyst in the continuous reaction for Ca/Ca+Zn = 0.4 catalyst at RT (300K) for LHSV 2$h^{-1}$; MeOH Vs EC molar ratio = 10; Catalyst wt. =6g*

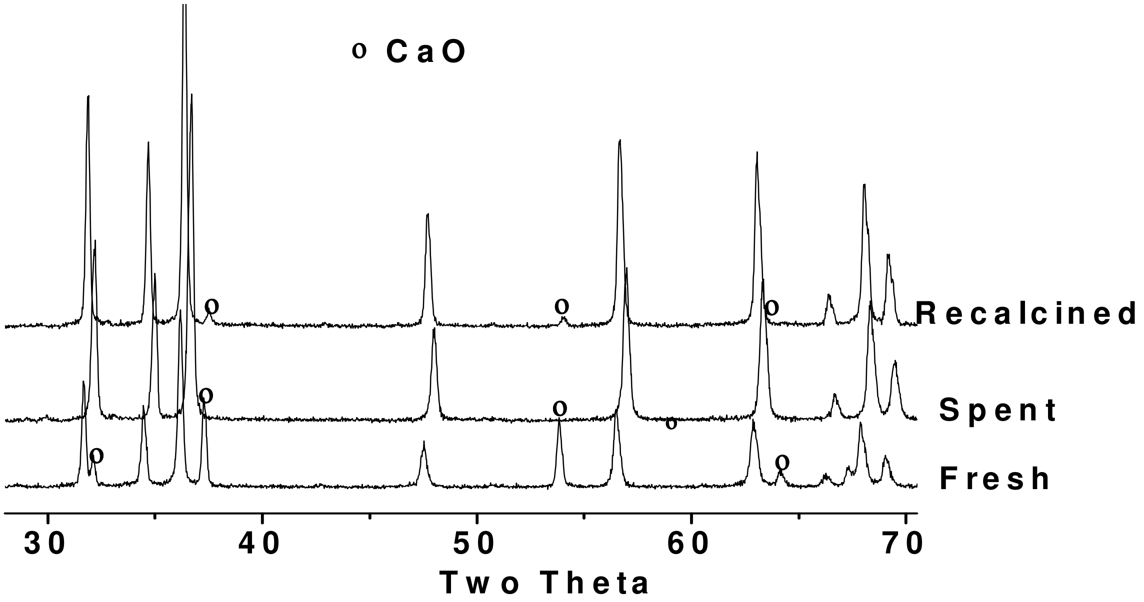


*Fig. 5.7: XRD pattern of Ca/Ca+Zn=0.4 catalyst (Fresh, Spent (Deactivated) and calcined at 1173K for 5h (Active).*

The powder XRD patterns for the fresh and spent catalysts (recovered after 60 h of reaction) are reproduced in Fig.5. 7. As seen in the figure, the fresh catalyst showed the presence of characteristic CaO peaks which was totally absent in the spent catalyst. This deactivated catalyst was calcined at 1173 K for 5 h and XRD of this recalcined sample showed CaO peaks but with a much lesser intensity (Fig. 5. 7). This indicates that part of CaO has been transformed into another amorphous phase (as it is seen in the XRD pattern) over the reaction time of 60 h. The Ca content of the catalysts were estimated using atomic absorption spectroscopy, deactivated catalyst showed lesser amount of Ca compared to the fresh catalyst. Thus, it is concluded that the deactivation process may be due to the combination of two phenomena i.e leaching and formation of dispersed $CaCO_3$ or $Ca(OH)_2$. Further detailed investigation is needed to understand the mechanism of deactivation.

## 5. 4. Conclusion

CaO-ZnO based catalysts are highly efficient for the synthesis of dimethyl carbonate from ethylene carbonate and propylene carbonate and methanol at ambient and sub-ambient conditions. The superiority of the present catalyst systems was demonstrated by both batch and continuous reactors with more than 84 mol % DMC yield at ambient conditions. With the continuous reactor system, the catalyst was found to be active for more than 60 h and the reaction could be carried out upto LHSV of more than 16 $h^{-1}$. The activity is directly proportional to the Ca content of the catalyst and CaO is the active phase for this transesterification reaction. The studies with different supports indicate that CaO phase supported on an inert support where CaO retains its phase is must for the effective transesterification reaction at ambient conditions.

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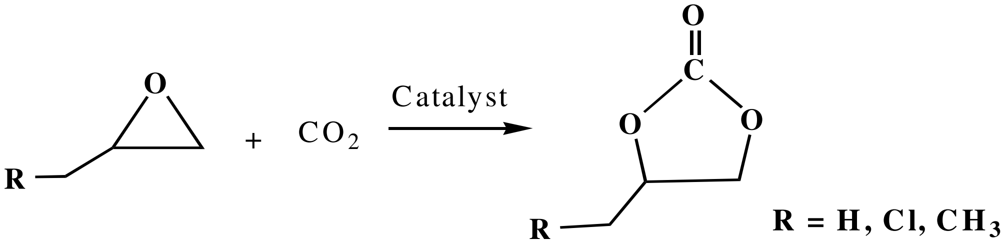
# Chapter -VI

# Summary and conclusion

Small molecule activation is an interesting and challenging area both from academic as well as industrial points of view. Among various small molecules, utilization of $CO_2$ is very important because it is an environmentally benign substitute for various hazardous C-1 sources like phosgene, CO etc., and also there is a pressing need for the utilization of $CO_2$ because of its negative effects in the atmosphere due to the increase in $CO_2$ load. Moreover, $CO_2$ is an inexpensive reagent, environmentally benign, non-flammable and easily separable from the reaction mixture. Hence, the activation and utilization of $CO_2$ in the synthesis of organic compounds is of considerable importance. Cyclo addition of $CO_2$ to an epoxide ring to form a five membered cyclic carbonate is a potential method for $CO_2$ fixation because of the versatility in the application of these cyclic carbonates. These cyclic carbonates find applications as aprotic solvent, pharmaceutical intermediates, production of agrochemicals such as pesticides and herbicides and in some fine chemicals. Another important organic compound, which can be prepared using $CO_{2,}$ is dialkyl carbonates like dimethyl carbonate. Conventionally dimethyl carbonate is prepared either by methanolysis of phosgene or by the oxycarbonylation of methanol. Both these methods use either phosgene or CO. Both these compounds are hazardous and rigorous safety measures have to be taken for the process involving these compounds. Dimethyl carbonate can also be prepared from $CO_2$ and methanol directly, but this reaction is restricted by thermodynamics. Another method which uses carbon dioxide for the synthesis of dimethyl carbonate from cyclic carbonates using methanol. These cyclic carbonates can be prepared from epoxides and carbon dioxide. This method of preparing dimethyl carbonate is advantageous as there is no other product other than dimethyl carbonate and glycols. This thesis deals with the synthesis of both cyclic carbonates and dimethyl carbonate. A detailed summary and conclusion derived from each chapter are explained below.

### *6.2. Chapter-II:*

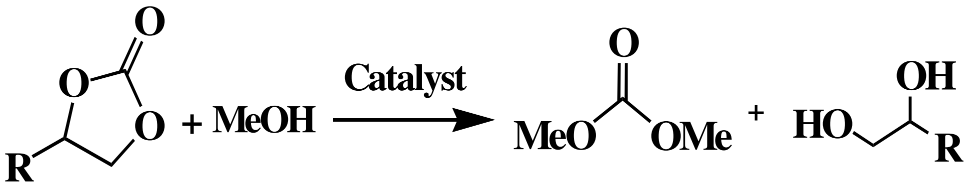


This chapter deals with synthesize of Zn-W polyoxometalate and its application as an effective catalyst in conjunction with an organic base for $CO_2$ insertion into an epoxide ring to form cyclic carbonates (see the above Scheme). This catalytic system has been found to be efficient even at low $CO_2$ pressure range, 60-100 psig and at a moderate temperature range, 393K to 413K. Zn-W polyoxometalate part of the catalytic system could be recovered and reused without losing its activity. A very high turnover number of more than 40,000 based on the Zn-W-polyoxometalate could be achieved with this catalytic system. The catalyst system is active for variety of epoxides including epichlorohydrin, propylene oxide, butylene oxide etc. More importantly this reaction could be carried out without any organic solvent. We found there is a cooperative mechanism working between Zn-W-polyoxometalate part and the Lewis base and a reaction mechanism has also been proposed accordingly.

### *6. 3. Chapter-III:*

This chapter deals with yet another catalyst system for the $CO_2$ insertion reaction with epoxides for cyclic carbonates formation. The catalyst systems contain N-containing heterocyclic compounds anchored on silica support through a propyl group. Unlike the Zn-W-polyoxometalate catalyst system, the present catalytic systems do not need an additional base. This single solid catalyst has been found to be as efficient as Zn-W-polyoxometalate system though the turn over number is slightly low. This heterogeneous catalytic material could be recovered and reused for several cycles without lose in its activity. This material was characterized using physico-chemical methods like elemental analysis, IR and multi nuclear solid state NMR. The stability of the catalyst has been demonstrated by solid state NMR studies before and after the reaction.

### 6. 4. Chapter – IV:



Having achieved the synthesis of cyclic carbonate with near quantitative yield from $CO_2$ and epoxide using a single heterogeneous catalyst, our next objective was to synthesize another important organic carbonate namely dimethyl carbonate by transesterification of cyclic carbonates with methanol. We have discovered sodium tungstate as an efficient catalyst for the above transesterification reaction. This reaction could be carried out at ambient condition in a simple RB flask. We could achieve DMC yield of more than 80 mol % in 5 h of reaction time. In this chapter, we have tried to elucidate the mechanism of this reaction using *in-situ* Raman and IR spectroscopic techniques. A controlled experiment reveals that methoxide ion was an intermediate species that leads to the transesterification production and a reaction mechanism has been proposed based on this *in situ* studies. This catalyst could be recovered and reused for 3 runs without loss in activity. However, the activity decreases slightly during the further runs.

### 6. 5. Chapter – V:

Although sodium tungstate catalyst was efficient for the above transesterification reaction, use of this catalyst for the continuous mode operation needs addition of binder like silica to the catalyst to make pellets which leads to certain amount of cleaved products. In an effort to develop a highly stable robust catalyst with better activity, we found CaO-ZnO based catalysts better and suitable for both batch and continuous mode operations. The catalyst is highly active even at ambient conditions and DMC yield of more than 85 mol % was achieved within 2 h of reaction time. Experimental conditions for both batch and continuous mode operations have been optimized. The catalyst works effectively even at LHSV of more than 16 $h^{-1}$. Time on stream studies with the present catalyst up to 60 h showed no appreciable amount of loss in its activity. Both ethylene and propylene carbonates have been tested.

### *6. 6. Overall conclusion and Future outlook:*

In this thesis, a Na Zn-W polyoxometalate based catalyst in conjunction with Lewis base like dimethyl aminopyridine (DMAP) is reported for the synthesis of cyclic carbonate from epoxide and $CO_2$. This system works even without solvent. Main advantage of this catalytic system was it works at a very high substrate vs catalyst ratio. The polyoxometalate part of the catalytic system can be recovered and reused without loss in activity. But this system suffers a big disadvantage of having two components.

Next part of this thesis reports a single component catalyst for the synthesis of cyclic carbonate; this catalyst was prepared by anchoring organic bases like imidazole to an inorganic solid matrix like fumed silica. This catalyst was found to be active for a variety of epoxides and this could be recovered and reused without much loss in activity for several runs.

After reporting a single site effective catalyst for the synthesis of cyclic carbonate this thesis reports a tungstate based catalyst for the transesterification of cyclic carbonates (ethylene carbonate and propylene carbonate) using methanol to form dimethyl carbonate and glycols at ambient conditions (room temperature and atmospheric pressure). This catalyst could be recovered and reused without loss in activity. It is active even at sub ambient temperatures. But this catalyst was found to be effective for the batch reaction, not for the continuous production of dimethyl carbonate.

To overcome this difficulty, in the final part of the thesis, CaO-ZnO based mixed metal oxide was reported to be effective for the synthesis of dimethyl carbonate again at ambient condition. Here the advantage is this catalyst can be used for both batch reaction as well as continuous reaction. It is found that CaO phase is responsible for the catalytic activity. But a structure-activity correlation is yet to be derived. There is lot of room in studying the effect of structure and activity using various characterization techniques.

# List of Publications / Patents

## Papers:

1. Effective catalytic system of zinc-substituted polyoxometalate for cycloaddition of $CO_2$ to epoxides.
   **M. Sankar**, N.H. Tarte, P. Manikandan*
   Applied Catalysis A: General 276 (2004) 217–222.

2. Transesterification of cyclic carbonates with methanol at ambient conditions over ungstate based solid catalysts
   **M. Sankar**, C. Madhavan Nair, K. V. G. K. Murty, P. Manikandan*
   Applied Catalysis A: General 312 (2006) 108-114.

3. A robust inorganic - organic hybrid heterogeneous catalyst for cyclic carbonate synthesis with no solvent and co-catalyst
   **M. Sankar**, T. G. Ajithkumar, G. Sankar, P. Manikandan* (Manuscript under preparation)

4. Synthesis of dimethyl carbonate by transesterification of cyclic carbonates using solid oxide catalyst at ambient conditions
   **M. Sankar*,** S. Satav, and P. Manikandan* (Communicated to Applied Catalysis A: General )

## Patents:

1. Process for preparation of cyclic carbonate by cycloaddition of carbon dioxide to epoxide.
   Palanichamy Manikandan , Meenakshisundaram Sankar
   US Patent Number: 6,924,379
   Indian Patent Granted.

2. Improved process for the production of dialkyl carbonate
   Palanichamy Manikandan, Meenakshisundaram Sankar, Rajiv Kumar
   US Patent (Applied)
   Indian Patent (Applied)