SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF MCM-41 IMIDAZOLIUM HALIDE CATALYSTS FOR THE REACTION BETWEEN EPOXIDES AND CARBON DIOXIDE

JIMMY NELSON A/L APPATURI

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JIMMY NELSON A/L APPATURI

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LIST OF SYMBOLS AND ABBREVIATIONS

1,3-DCP	1,3-dichloropropan-2-ol
^{13}C CP/MAS NMR	Carbon-13 Cross Polarisation/Magic Angle Spinning Nuclear Magnetic Resonance
^{1}H NMR	Proton Nuclear Magnetic Resonance
^{29}Si CP/MAS NMR	Silicon -29 Cross Polarisation/Magic Angle Spinning Nuclear Magnetic Resonance
3-AP	3-(allyloxy)propane-1,2-diol
3-BP	3-bromo-1,2-propanediol
3-CP	3-chloropropane-1,2-diol
3-MMP	3-methoxypropanoate
4-BD	4-butyl-1-3-dioxolan-2-one
a_0	Lattice value or hexagonal unit cell parameter
Ade	Adenine
AGC	Allyl Glycidyl Carbonate
AGE	Allyl Glycidyl Ether
BET	Barret-Joyner-Halenda
BJH	Brunauer-Emmett-Teller
CC	Chloropropene Carbonate
CHN	Carbon, Hydrogen, Nitrogen
CNT	Carbon NanoTubes
CPTES	3-(chloropropyl)triethoxysilane
CTAB	Cetyltrimethylammonium bromide
CTAC	Cetyltrimethylammonium chloride

d_{100}	Diffraction plane-100
DMA	Dimethyl acetamide
DMF	*N,N*-dimethylformamide
DMSO	Dimethyl sulfoxide
EDS	Energy Dispersive X-ray spectroscopy
EH	1,2-epoxyhexane
EPCH	Epichlorohydrin
FT-IR	Fourier Transform Infra-Red spectrometry
GC	Gas chromatograph
GC	Glycerol Carbonate
GC-MS	Gas chromatograph interfaced to a mass spectrometer
Gly	Glycerol
GOH	Glycidol
Gua	Guanine
hkl	Miller indices
IC	Ion Chromatograph
IL	Ionic-Liquid
Imi	Imidazole
IUPAC	International Union of Pure and Applied Chemistry
M	Molar amount of grafted organic phase
$M^{+\bullet}$	The molecular ion
m/z	The mass of ion divided by its charge
MCM	Mobil Crystalline Material
MWCNT	Multi Wall Carbon Nanotubes

N	Surface coverage
n	Number of carbon atoms per organic molecule
NMR	Nuclear Magnetic Resonance
P/P_0	Relative pressure
P_c	Percentage of carbon
PC	Propylene carbonate
PGC	Phenyl Glycidyl Carbonate
PGE	Phenyl Glycidyl Ether
PMO	Periodic Mesoporous Organosilane
PO	Propylene Oxide
POM	Partial Oxidation of Methanol
PSD	Pore Size Distribution
P_w	Weight Percentage (amount of organic ligand grafted)
R	Alkyl or aryl group
RH	Rice Husk
RHA	Rice Husk Ash
rpm	rotations per minute
RT	Retention Time
S	Specific surface area
SBA	Santa Barbara Amorphous
sc	Super critical
SC	Styrene Carbonate
SDA	Structure Directing Agent
SEM	Scanning Electron Microscope

SG	Styrene Glycol
SO	Styrene Oxide
TEM	Transmission Electron Microscope
TEOS	Tetraethylorthosilicate
TG-DTG	Thermogravimetry- Derivative Thermogram
TOF	Turnover frequency
TON	Turnover number
USY	Ultrastable Y-type Zeolite
W_t	wall thickness
wt.%	weight percentage
XRD	X-ray Diffraction
ZIF-8	Zeolitic imidazolate frameworks
ZSM-5	Zeolite Socony Mobil–5

SINTESIS, PENCIRIAN DAN AKTIVITI PEMANGKINAN MCM-41 IMIDAZOLIUM HALIDA MANGKIN BAGI TINDAK BALAS ANTARA EPOKSIDA DAN KARBON DIOKSIDA

ABSTRAK

Penetapan kimia karbon dioksida (CO_2) telah mendapat perhatian yang semakin meningkat sebagai sumber karbon yang berpotensi dalam proses kimia perindustrian berikutan kebimbangan yang semakin meningkat daripada kesan rumah hijau. Salah satu cara yang paling menjanjikan untuk penggunaan berharga CO_2 adalah melalui sintesis karbonat siklik. Dalam karya ini, sintesis karbonat siklik dan kajian mekanistik tindak balas penambahan siklik antara epoksida dan CO_2 menggunakan mangkin MCM-41-Imidazolium halida telah diteroka. MCM-41 telah disediakan daripada abu sekam padi (RHA) dengan menggunakan cetiltrimetilammonium bromida (CTAB) melalui kaedah sol-gel. MCM-41 telah dimodifikasikan dengan imidazol menggunakan 3-(kloropropil)trietoksisilana (CPTES) diikuti oleh pengalkilan dengan 1,2-dihaloethana. Pencirian spektroskopi membuktikan pencantuman ligan organik pada rangka silika. Tindak balas penambahan siklik telah dijalankan menggunakan autoklaf makmal tekanan tinggi di bawah keadaan tanpa pelarut. Hasil karbonat siklik masing-masing menggunakan MCM-41-Imi/Br ialah: 98.8 % bagi stirena oksida, 97.0 % bagi epiklorohidrina, 98.3 % bagi glisidol, 97.5 % bagi alil glisidil eter, 96.7 % bagi fenil glisidil eter dan 100 % untuk 1,2-epoksiheksana. Untuk semua mangkin yang lain, analisis produk menunjukkan pembentukan karbonat siklik masing-masing pada hasil yang tinggi melebihi 97.0%. Pembukaan gelang stirena oksida dan eksperimen pengaktifan CO_2 telah dijalankan. Pembukaan gelang stirena oksida berlaku pada atom

karbon yang kurang dihalang (β-karbon) melalui serangan nukleofilik ion bromida. Analisis GC-MS menunjukkan kehadiran dua produk iaitu 2-bromo-1-feniletanol (produk perantaraan) dan stirena glikol sebagai hasil sampingan. Molekul CO_2 diaktifkan oleh kumpulan beralkali nitrogen daripada imidazol yang telah disahkan oleh analisis FT-IR. Dua mekanisma yang munasabah telah dicadangkan bagi tindak balas pemangkinan. Pembukaan gelang epoksida yang berlaku melalui serangan nukleofilik oleh ion halida membentuk spesies haloalkoksi. Pada masa yang sama, CO_2 diaktifkan oleh amina tersier melalui ikatan koordinat hidrogen berasid daripada imidazol membentuk ikatan hidrogen dengan salah satu daripada oksigen karbon dioksida. Begitu juga, CO_2 juga boleh diaktifkan melalui oksigen daripada karbon dioksida dengan cara ikatan koordinat ion ammonium kuarternari daripada mangkin. Ion ammonium kuarternari atau amina tersier dan anion halida menunjukkan kesan sinergi untuk mempromosikan tindak balas, yang bertanggungjawab untuk aktiviti pemangkinan yang tinggi dan berselektif.

SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF MCM-41 IMIDAZOLIUM HALIDE CATALYSTS FOR THE REACTION BETWEEN EPOXIDES AND CARBON DIOXIDE

ABSTRACT

The chemical fixation of carbon dioxide (CO_2) has received increasing attention as a potential carbon source in industrial chemical processes due to the growing concern of the greenhouse effect. One of the most promising ways for valuable utilization of CO_2 is the synthesis of cyclic carbonates. In this work, the synthesis of cyclic carbonates and mechanistic study of cycloaddition reaction between epoxides and CO_2 using MCM-41-Imidazolium halide catalysts were explored. MCM-41 was prepared from rice husk ash (RHA) using cetyltrimethylammonium bromide (CTAB) via sol-gel method. MCM-41 was functionalized with imidazole using 3-(chloropropyl)triethoxysilane (CPTES) followed by alkylation with 1,2-dihaloethane. Spectroscopic characterization confirmed the successful immobilization of organic ligand on the silica framework. The cycloaddition reactions were carried out in high pressure laboratory autoclave under solvent less condition. The yields of the respective cyclic carbonates using MCM-41-Imi/Br were: 98.8 % for styrene oxide, 97.0 % for epichlorohydrin, 98.3 % for glycidol, 97.5 % for allyl glycidyl ether, 96.7 % for phenyl glycidyl ether and 100 % for 1,2-epoxyhexane. For all the other catalysts, the product analysis revealed the formation of the respective cyclic carbonates at high yield of more than 97.0 %. The ring opening of styrene oxide and the activation of CO_2 experiments were carried out. The ring opening of styrene oxide occurred at the less hindered carbon atom (β-carbon) via the nucleophilic attack of the bromide ion. The GC-MS analysis

showed the presence of two products which corresponds to 2-bromo-1-phenylethanol (intermediate product) and styrene glycol as a by-product. CO_2 molecules are activated at the basic nitrogen group of imidazole which was confirmed by FT-IR analysis. Two plausible reaction mechanisms were proposed for the catalytic reaction. The ring opening of the epoxide was shown to take place by means of a nucleophilic attack by the halide ion forming the haloalkoxy species. Simultaneously, the CO_2 was activated by the tertiary amine through the coordinate bond of the acidic hydrogen from the imidazole forming a hydrogen bond with one of the oxygen of the carbon dioxide. Similarly, the CO_2 can also be activated through the oxygen of the CO_2 by way of a coordinate bond to the quaternary ammonium ion of the catalyst. The quaternary ammonium ion or tertiary amine and the halide anion are shown to exhibit a synergistic effect to promote the reaction, which is responsible for the high catalytic activity and selectivity.

CHAPTER 1

INTRODUCTION

1.1 Global warming

Naturally, the presence of carbon dioxide (CO_2) in the atmosphere is to help in the photosynthesis of plants for their food. Although this gas plays a pivotal role for all the living things in the world, it is also the main constituent among the greenhouse gases and it circulates in the environment through a carbon cycle (Srivastava et al., 2005a). About 32 % of CO_2 is produced due to hydrocarbon combustion and gasification which are released into the atmosphere. The use of fossil fuel in transportation releases ~30 % of the total CO_2. Natural phenomena such as volcanic eruption and decay of plants and animals too release CO_2 into the atmosphere.

As a consequence, the CO_2 concentration increases in the atmosphere and results in climate change due to the greenhouse effect (Alvaro et al., 2005). Figure 1.1 shows the changes in the global atmospheric CO_2 concentration for 55 years since 1958 which was based on continuous measurement recorded at the Mauna Loa Observatory in Hawaii. The concentration of atmospheric CO_2 was 399.89 ppm till May 2013, and it is estimated to reach 550 ppm by the year 2020 (McGee, 2013). The continuous rise in atmospheric CO_2 concentration resulted in global warming leading to serious environmental issues including melting of glacier, drought, flood, rising of sea level and damage of habitat and living species.

Increasing concern in global climate changes has necessitated various forums, debates and international programs to brainstorm ways of reducing the rate of emission of CO_2 into the atmosphere. In recent years, various utilization of this naturally abundant CO_2 has gained considerable attention as part of an effort to reduce the concentration of CO_2 in the atmosphere.

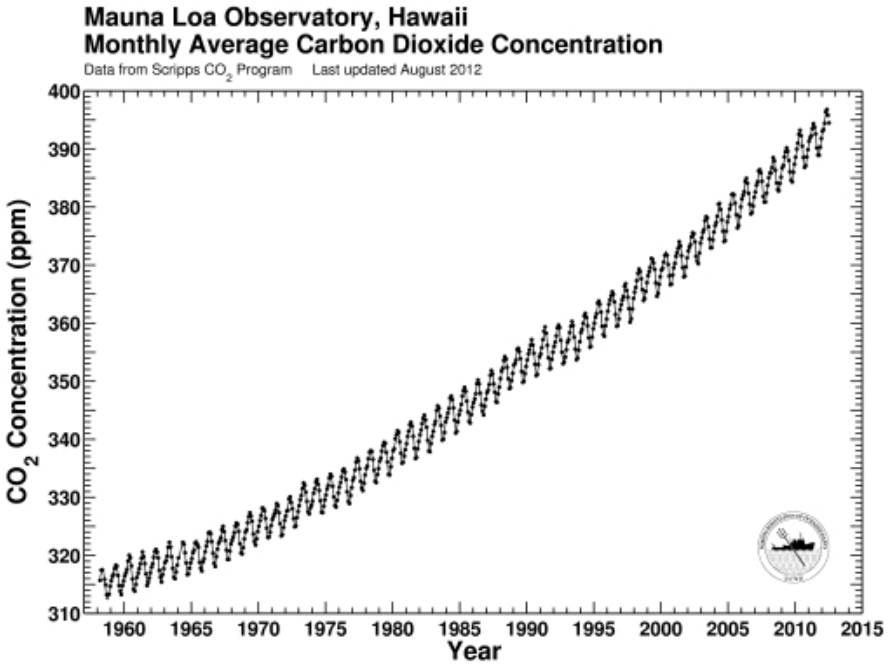


Figure 1.1: The Keeling Curve: Atmospheric CO_2 concentration for the period of 1958 to 2012 (McGee, 2013).

1.2 Carbon dioxide

Carbon dioxide is a colourless and odourless gas. It is a linear molecule with double bonds between the carbon and oxygen atoms (O=C=O). The central carbon atom is sp hybridized and the C–O bond length is 1.16 Å. This bond length is shorter than a C=O double bond involving a sp^2 hybridized carbon atom.

Carbon dioxide is recognized as a non-flammable, non-toxic (Liu et al., 2014), inexpensive reagent and environmentally benign molecule (Barbarini et al., 2003). It is a safe, renewable carbon source (Zhou et al., 2008) and thermodynamically stable compound (Alvaro et al., 2004). It is kinetically inert (Dai et al., 2010, Alvaro et al., 2004), and is used as C1 building block in organic synthesis (Dai et al., 2010). More importantly it can be substituted in chemical reactions for carbonyl dichloride known as phosgene ($COCl_2$), carbon monoxide (CO) and isocyanides (R-NCO) as these compounds are poisonous and toxic (Srivastava et al., 2005a).

Carbon dioxide can be utilized as an oxygen source or a mild oxidant (Noh et al., 2000). It can be used as an alternate medium or solvent (Song, 2006), as a supercritical (sc) fluid (Hutchings, 2009) and as a carbon source. It can be used based on its unique chemical properties to be incorporated with high 'atom efficiency' such as in carboxylation synthesis or in catalyst synthesis (Song, 2006). Hutchings (2009) used supercritical CO_2 as an anti-solvent for the preparation of Au/scCO_2 and sc-VPO catalysts. The catalysts were tested in many applications, which have resulted in high activity.

1.2.1 The use of CO_2 as C1 building block

The growing concern about the environmental impact of CO_2 emission, have triggered industrialist, researchers and academicians to synthesize organic molecules from CO_2. Currently, CO_2 has been used in various industrial applications such as chemical, pharmaceutical, foodstuff, beverage, healthcare, environment, pulp and paper, electronics, metal industry, laboratories and analysis, safety and others (Song, 2006).

Among these industries, the application of CO_2 as C1 raw material in the chemical industry has created much attention lately. It has been reported that approximately 110 million metric tonnes of CO_2 is currently used on a yearly base (Peters et al., 2011) in the chemical industry.

Carbon dioxide plays a versatile role in the process of various chemical transformations such as in the production of urea, methanol (Huo et al., 2012), salicylic acid (Iijima and Yamaguchi, 2008), formic acid (Leitner, 1995), cyclic carbonates (Darensbourg et al., 1998), copolymers, polymer building blocks and fine chemicals. Figure 1.2 shows an overview of some of the possible chemical transformation that can be carried out using CO_2 as the C1 source.

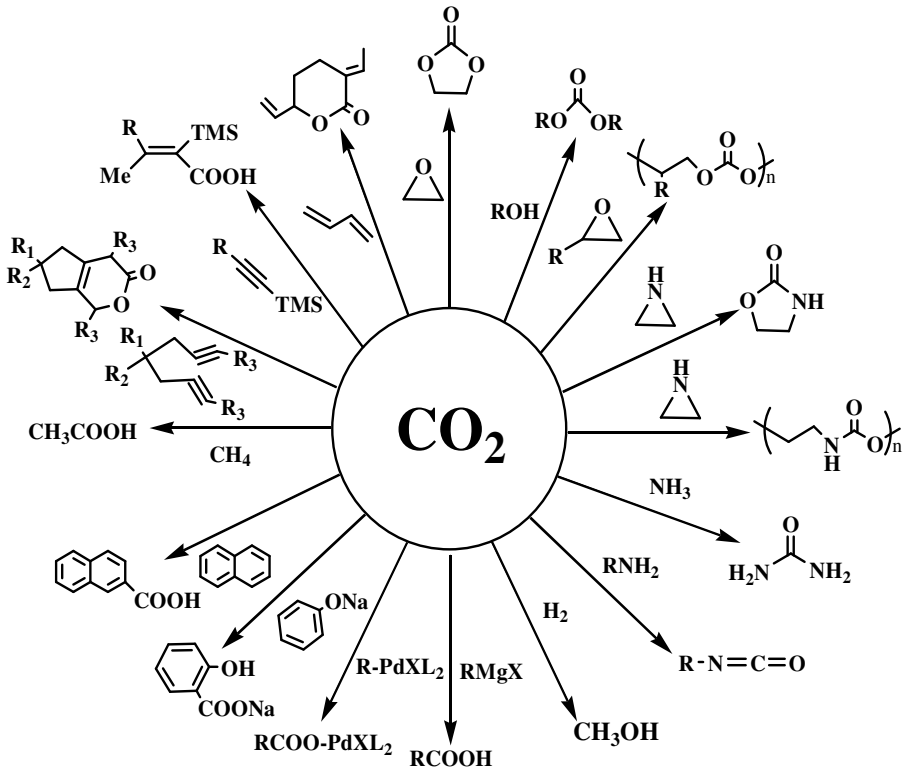


Figure 1.2: A summary of organic transformations using CO_2.

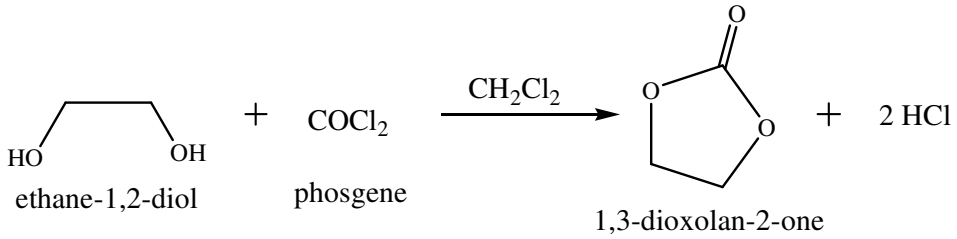
Among the chemicals produced, urea is one of the largest-volume industrial example of converting CO_2 into value-added products. More than 100 million tonnes (Mt) of urea are produced worldwide yearly (Aresta and Dibenedetto, 2007). The urea is synthesized from ammonia and CO_2 and used as fertilizer and also in producing various types of polymers, such as melamine and urea-formaldehyde resin. Salicylic acid is produced from phenol and CO_2 via the Kolbe-Schmitt reaction (Kosugi et al., 2003). The product is used to produce acetyl salicylic acid which is known as aspirin, a commonly used medicine to thin the blood.

1.2.2 Synthesis of cyclic carbonate

The production of cyclic carbonate from the cycloaddition reaction has been well established since 1950s (Metcalfe et al., 2013). The cyclic carbonates are colourless, odourless and biodegradable (Ghosh et al., 2010). The cyclic carbonates are used industrially as aprotic polar solvents (Khoshro et al., 2013), additives and as monomers for polymer synthesis too (Dharman et al., 2010). In addition, it has been used in electrolytic materials such as secondary batteries (lithium batteries) (Zalomaeva et al., 2013), resins, cleaning, cosmetics and personal care products (Jutz et al., 2008).

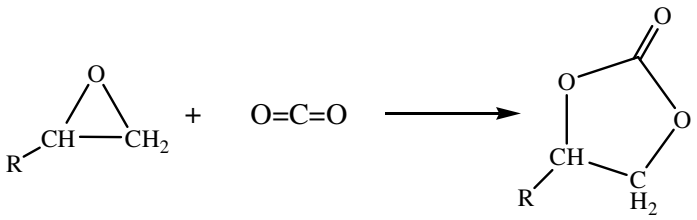
Cyclic carbonates are used as intermediates for pharmaceutical and biomedical fine chemical synthesis too (Zhou et al., 2008). In the agricultural industry, cyclic carbonates are used in the synthesis of herbicides and disinfectants (Aresta et al., 2003). In addition, cyclic carbonates play an important role as an intermediate for the synthesis of fuel additives (Sibaouih et al., 2009).

Traditionally, cyclic carbonates were synthesized by reacting phosgene with ethane-1,2-diol in the presence of excess amounts of dichloromethane as a solvent. At the end of the reaction, hydrochloric acid was produced as a by-product which is harmful to human being (Aresta et al., 2003) and the environment. The conventional synthesis method of organic carbonates is shown in Scheme 1.1.



Scheme 1.1: Synthesis of organic carbonate through conventional method.

By considering the economic value and possible toxicity due to the use of phosgene and with the rising demand of the cyclic carbonates in the chemical industry, CO_2 seems to be a natural choice to replace phosgene. Cyclic carbonates can be synthesized via cycloaddition of CO_2 with epoxides. The CO_2 can be incorporated into the epoxides without formation of by-products (Du et al., 2005). However, due to the inert nature of CO_2, its activation and incorporation into epoxide still remains ambitious (Barbarini et al., 2003) and has stimulated the study of various types of catalysts for the activation of CO_2. The cycloaddition of CO_2 to epoxide is shown in Scheme 1.2.



Scheme 1.2: Cycloaddition of CO_2 to epoxide forming cyclic carbonate.

1.3 Role of catalysts in the production of cyclic carbonates

Catalyst contains “active sites”, which are able to affect the kinetics of chemical reactions and make reactions go faster by reducing the activation energy. Thus, the main recipe to increase the yield of cyclic carbonates from cycloaddition between CO_2 and epoxides is by using catalyst. A wide range of homogeneous and heterogeneous catalysts have been developed to catalyze the so-called CO_2 fixation process. Homogeneous catalysts, such as $CoCl_2$/onium salt (Sibaouih et al., 2009), diimine Ru(II) complex (Ulusoy et al., 2009), Al-salen-PEA (Alvaro et al., 2005), betaine-based quaternary ammonium ion and carboxylic acid (Zhou et al., 2008), DMF (Kawanami and Ikushima, 2000, Jiang and Hua, 2006), $SnCl_4$-organic base (Jing and Nguyen 2007), Au/$Fe(OH)_3$-$ZnBr_2$/Bu_4NBr (Wang et al., 2009), ionic liquid-highly cross linked polymer (Xie et al., 2007), $BrBu_3PPEG_{600}PBU_3Br$ (He et al., 2009), cellulose/KI (Liang et al., 2011) and Au/R201 (Xiang et al., 2009) have been studied.

Several heterogeneous catalysts, such as metal oxides; MgO (Bhanage et al., 2001, Yano et al., 1997), Nb_2O_5 (Aresta et al., 2003), Mg-Al oxide (Yamaguchi et al., 1999), guanidine-MCM-41 (Barbarini et al., 2003), Adeine-Pr-Al-SBA-15 (Srivastava et al., 2006a), Cr-salen-SiO_2 (Alvaro et al., 2004), Mn-salen- SiO_2 (Jutz et al., 2008), ClAlPC-MCM-41 (Lu et al., 2002), as-synthesized MCM-41 (Srivastava et al., 2006b), Ti-SBA-15-Pre-Ade (Srivastava et al., 2005a), 3-(2-hydroxyl-ethyl)-1-propyl imidazolium bromide-SBA-15 (Dai et al., 2010) and zeolite based organic-inorganic hybrid catalysts (Srivastava et al., 2005b) have also been investigated.

Both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. Homogeneous catalyst usually gives higher catalytic activity and selectivity in comparison to heterogeneous catalyst. In heterogeneous catalyst the selectivity is a major problem. In heterogeneous processes mixture of products are obtained due to the nature of the solid support as well as the active site. In some cases, heterogeneous catalysts have requires the use of co-catalyst to enhance its catalytic activity (Srivastava et al., 2005b).

Homogeneous catalysts are less preferred in the industry due to the catalyst-product separation difficulty (Bhanage et al., 2001), which may require more energy and time, but this results in decomposition of the catalysts (Zhou et al., 2008). Therefore, heterogeneous catalysts are far more suitable for large scale industrial synthesis. It can be easily separated from the reaction products and regenerated for subsequent reuse (Alvaro et al., 2005). However, it is important to design and synthesize more efficient heterogeneous catalysts due to the demand for environmentally friendly technologies (Adam et al., 2011b, Adam et al., 2012b).

1.3.1 Heterogeneous ionic liquid catalyst

The development of environmentally benign catalyst for chemical transformation of CO_2 into useful compounds is of vital importance from a green chemistry standpoint. Ionic liquid (IL) is known to be a good reaction media which contributes to its growing importance over the past century (Jutz et al., 2010). In 2003, ILs were widely used in the industry as a solvent as well as a catalyst for the production of useful chemicals (Yang et al., 2011).

In general, the ILs are very useful due to the nature of the anion and cation (X^- Y^+) in the compound with melting point less than 100 °C. In comparison to homogeneous IL catalysts, heterogeneous IL catalysts has important physical and chemical features such as non-volatility, non-flammability, good thermal stability, wide liquid temperature ranges and high solvation interaction with both polar and non-polar compounds (Han et al., 2011, Kim et al., 2014).

Several chemical reactions have been catalyzed with homogeneous ILs resulting in high activity and selectivity. However, the system suffers from a major separation and recovery problem. Heterogeneous IL catalysts prepared by grafting ILs onto a solid support such as silica (Han et al., 2011), polymer (Xie et al., 2007, Siewniak et al., 2014), graphite oxide (Luo et al., 2015) or carbon nanotubes (CNT) (Han et al., 2012b) via anchoring agent tends to be recoverable, regenerable and reusable. More recently, multiwall carbon nanotubes (MWCNT) supported imidazolium-based IL was successfully prepared and utilized for the synthesis of various cyclic carbonates (Han et al., 2012b).

It has also been reported that ILs containing zinc tetrahalide anion, exhibits higher performance towards the cycloaddition reaction (Lee et al., 2012). Zhu et al. (2007) reported that choline chloride/urea provide excellent results in the cycloaddition reaction because of the presence of a hydroxyl group in choline chloride. They have proposed that most of the ILs considered as promising heterogeneous catalysts are those containing a quaternary ammonium ion together with a halide anion, -OH or a -COOH group.

The silanol (Si-OH) group in silica supports aminopyridinium halide catalyst which acts as weak Brønsted acid to activate the epoxide. The silanol synergistically enhances the reaction between carbon dioxide with epoxide to form cyclic carbonates under atmospheric pressure (Motokura et al., 2009).

1.4 Factors influencing the production of cyclic carbonates

The production of cyclic carbonates not only dependents on the usage of catalyst, but on other reaction parameters such as temperature, pressure and solvent as well. These parameters should be studied to attain high yield of product. Basically, the condition varies depending on the type of epoxide and the catalyst. Table 1.1 summarizes most of the studies carried out for cycloaddition of CO_2 to styrene oxide (SO) on various types of catalysts.

Based on the Table 1.1, it can be concluded that, the performance of the metal oxide catalysts is not satisfactory. Much higher catalytic activities were observed over mixed metal oxides or mixed metal-nonmetal oxides. In some instances, the presence of co-catalyst and solvent are the main disadvantage with respect to "green chemistry" requirements. Compared to the homogeneous catalysts, heterogeneous catalysts such as supported ionic liquid showed better activity and selectivity in cycloaddition reactions. In most studies, the yield of respective product was higher since the active sites of the catalyst contain both acid and base bifunctional groups which could help synergistically activate the epoxide and CO_2 respectively. However, many parameters determine the activity of the catalyst. Therefore, it becomes important that rational design of novel catalytic systems should be supported by a rich experimental activity.

Table 1.1: Catalytic activity studies of cycloaddition of CO_2 to styrene oxide using various homogeneous and heterogeneous catalysts.

Catalyst[a]	Reaction conditions				Reaction results			References
	Solvent or co-catalyst	P_{CO2} (bar)	Temp (°C)	Time (h)	Yield (%)	Selectivity (%)	Conversion (%)	
MgO	DMF	80	150	15	15.8	17.2	92.3	(Bhanage et al., 2001)
MgO	DMF	20	135	12	60.0	-	-	(Yano et al., 1997)
Nb_2O_5	DMF	50	135	12	80.0	-	-	(Aresta et al., 2003)
Mg-Al-Oxide	DMF	5	100	15	90.0	97.8	-	(Yamaguchi et al., 1999)
DMF	-	79	150	15	85.0	-	-	(Kawanami and Ikushima, 2000)
Guanidine-MCM-41	CH_3CN	50	140	70	90.0	92.0	-	(Barbarini et al., 2003)
Al-SBA-15-*pr*-Ade	-	6.9	120	4	88.9	94.6	94.0	(Srivastava et al., 2006a)
Cr-salen-SiO_2	CH_2Cl_2	100	80	6	74.0	100	-	(Alvaro et al., 2004)
Mn-salen-SiO_2	-	35[b]	140	3	95.0	-	-	(Jutz et al., 2008)
ClAlPc-MCM-41	n-Bu_4NBr	40	110	2	384[c]	-	-	(Lu et al., 2002)
Al-salen-PEA	n-Methyl imidazole	100	80	15	78.0	87.6	89.0	(Alvaro et al., 2005)
Betaine based salt[d]	-	80	140	8	96.0	-	-	(Zhou et al., 2008)
Au/R201	-	40	150	4	92.5	97.0	95.4	(Xiang et al., 2009)
MCM-41[e]	CH_3CN	6.9	120	8	-	98.2	88.4	(Srivastava et al., 2006b)
	-	6.9	120	8	-	95.2	93.7	(Srivastava et al., 2006b)
Zn/Ps-IL[Br]	-	30	120	8	97.5	-	-	(Qiao et al., 2009)
SalenRu(II)$(PPh_3)_2$/PTAT	EtOH[f]	8.3	70	2	92.0	-	-	(Jing et al., 2007)
$CoCl_2$/onium salt	CH_2Cl_2	15	120	1	1238[c]	-	-	(Sibaouih et al., 2009)

Ti-SBA-15-*pr*-Ade	CH_3CN	6.9	120	8	-	87.0	79.8	(Srivastava et al., 2005a)
	-	6.9	120	8	-	94.6	94.0	(Srivastava et al., 2005a)
Diimine Ru(II) compex	-	16	100	2	73.1	-	-	(Ulusoy et al., 2009)
IL-polymer	-	60	110	7	79.1	-	-	(Wang et al., 2009)
Cellulose/KI	-	20	110	9	98.0	-	-	(Liang et al., 2011)
HEPIMBr	-	20	120	2	99.6	-	99.8	(Dai et al., 2010)
IL tetrabutylammonium chloride	-	9.7	100[g]	0.5	97.9	-	-	(Dharman et al., 2010)
$Au/Fe(OH)_3$-$ZnBr_2/Bu_4NBr$	-	40	80	10	53.0	-	-	(Wang et al., 2009)
Co(III) complex	DMAP	20	120	3	85.8	-	-	(Ghosh et al., 2010)
SLPC	Toluene	45	150	6	84.8	-	-	(Jagtap et al., 2006)
Co(III) Porphyrin/DMAP	CH_2Cl_2	20.7	120	4	97.0	-	-	(Paddock et al., 2004)
MNP-Co-Porphrin	CH_2Cl_2	10	25	36	48.7	-	-	(Bai et al., 2011)
$M(TTMAPP)I_4(X)$ M=Co;X= OAc	-	6.7	80	36	62.5	-	-	(Bai et al., 2010)
Bis-(phenoxyiminato) cobalt(III)/lewis base	CH_2Cl_2	10	145	1	600/640[c]	-	-	(Sibaouih et al., 2009)
Metal porphyrin/phenyltrimethyl -ammonium tribromide	-	6.9	20	10	20.0	-	-	(Jin et al., 2007)
$SnCl_4$-organic base	-	3.5	75	1.5	96.0	-	-	(Jing and Nguyen 2007)
DMF	-	50	110	15	8.0	-	-	(Jiang and Hua, 2006)
Zeolite-based- organic-inorganic	-	6.9	120	8	-	92.8	98.0	(Srivastava et al., 2005b)
CS-$[BuPh_3P]Br$	-	25	120	6	96.9	97.4	99.5	(Jing-Xian et al., 2014)

$[Ph_3PC_2H_4COOH]Br$		25	130	3	99.5	99.8	99.7	(Wei-Li et al., 2014a)
ChI	EtOH	10	85	6	99.0	94.0	-	(Amaral et al., 2013)
KI/PDA		20	120	5	34.7	99.0	35.0	(Yang et al., 2014)
$[P\text{-}Im\text{-}C_4H_8Ph_3P]Br_2$		25	130	4	99.3	99.8	99.5	(Wei-Li et al., 2014b)
SBA-15-IL1Br		20	110	3	80.0	99.0	80.8	(Cheng et al., 2013)
Si-Imi		6	130	10	76.6	97.0	79.0	(Sankar et al., 2015)
Cr-CMP		30	100	2	96.3	-	-	(Xie et al., 2014)
PDDA-Br		25	100	12	92.9	97.8	95.0	(Song et al., 2014)
PPN(I)	ZnI_2	1	100	7	89.0	94.7	94.0	(Motokura et al., 2014)
$OXCNT\text{-}(CH_2)(Me)_3N^+Cl^-$		20	110	6	22.0	96.0	23.0	(Baj et al., 2014)
P-DVB-HEImBr		20	140	5	98.9	100	98.9	(Dai et al., 2013)
PS-hexyl-MeI		12	120	12	96.7	-	-	(Lee et al., 2014)
PS-TBMAC	ZnI_2	9	110	2	71.0	99.0	70.3	(Siewniak et al., 2014)

[a] *Abbreviations*. *pr*: 3-chloro or 3-aminopropyltriethoxysilane; Ade: adenine; ClAlPc: aluminium phthalocyanine; PEA: poly(ethylene glycol bismethacrylate); PTAT: phenyltrimethylammonium tribromide; HEPIMBr: 3-(2-Hydroxyl-Ethyl)-Propylimidazolium Bromide; SLPC: supported liquid phase catalyst; MNP: magnetic nanoparticle; $M(TTMAPP)I_4(X)$: Bifunctional metalloporphyrins; CS: chitosan; ChI: choline iodide; PDA: polydopamine; CMP: conjugated Microporous polymer; Imi: imidazole; PDDA-Br: polydiallyldimethylammonium bromide; PPN(I): 4-Pyrrolidino-(3- (trimethoxysilyl)propyl)pyridinium Iodide; CNT: carbon nanotubes; PS: Polystyrene-supported quaternized ammonium salt; PS-TBMAC: polymer-supported tributylmethylammonium chloride.
[b] molar ratio of CO_2 to styrene oxide.
[c] Turnover frequency (h^{-1}) value.
[d] containing quaternary ammonium ion and carboxyclic acid group.
[e] as-synthesized MCM-41 (without calcination).
[f] recrystal with ethanol.
[g] Microwave assisted.

1.4.1 Influence of temperature

Temperature is one of the important parameters in a catalytic reaction. An effective collision happens during the reaction with sufficient speed, energy and force to break bonds in the colliding molecules. Therefore, the yield of the product is strongly dependent on the reaction temperature. Aresta et al. (2003) studied the influence of temperature on the formation of styrene carbonate (SC) from styrene oxide and CO_2 with Nb_2O_5 as a catalyst. The reaction did not yield any product below 100 °C. However, the product yield increased to 80 % as the temperature rose to 135 °C. This indicates that a slight change in the temperature can influence the product formation in a reaction.

Jutz et al. (2008) studied the influence of the reaction temperature on the performance of Mn(salen)Br catalyst by utilizing a broader range of temperature. Maximum yield was obtained at 160 °C, but reduced dramatically at a higher temperature. This behavior was accounted to phase distribution changes of the reactants which normally occur at higher temperatures. Zhou et al. (2008) reported that at 140 °C, the yield of propylene carbonate (PC) was 98 % and reduced to 78 % at 150 °C. The decrease in the yield was possibly due to the occurrence of side reactions, which happens after the entire propylene oxide (PO) was converted at the higher temperature. Bai et al. (2010) reported that the increase in the temperature caused a decrease in PC yield, due to the decomposition of the catalyst at the higher temperature. Qiao et al. (2009) explained that, SO is difficult to convert to SC compared to other epoxides due to its less reactive β-carbon atom. Thus, it requires a longer reaction time and higher temperature.

He found that the temperature of 120 ℃ (98 %) was the optimum condition compared to 130 ℃ (~80 %) and 140 ℃ (~95 %). However, the reaction temperature for optimal performance is dependent on the nature of the catalyst employed and it is widely known that cycloaddition reaction is an exothermic process (Dai et al., 2010).

Recently, Lee et al. (2014) studied the effect of reaction temperature on the cycloaddition reaction between ally glycidyl ether (AGE) and CO_2 using PS-*hexyl*-MeI at 12 bar of total pressure. They found that the yield of allyl glycidyl carbonate (AGC) increased from 80 to 140 ℃; however, it decreased at 160 ℃. The decreased was due to the formation of oligomers and some by-products such as 3-allyloxy-1,2-propanediol. Zhong et al. (2014) investigated the effect of temperature in the range of 120 ℃ to 160 ℃ on the propylene carbonate yield in the presence of little (0.78 mmol) and large amount (13.7 mmol) of DMF. They concluded that, the large amount of DMF used was favorable to decrease the reaction temperature.

1.4.2 Influence of pressure

The pressure of the carbon dioxide has been established as one of the most crucial factor affecting the cycloaddition reaction with epoxide (Qiao et al., 2009), since CO_2 acts as a reactant and as a reaction medium simultaneously (Jutz et al., 2008). There are two phases in the reaction system, where the top phase is rich with CO_2 and the bottom phase is rich with epoxide. According to Xie et al. (2007), the CO_2 acts as a reactant and favors the reaction when the bottom phase is under high pressure.

However, this condition is not favorable to the reaction at the high pressure (120 bar), because the concentration of epoxide (PO) which acts as a reactant, at the bottom phase decreases. Therefore, at high pressure, more epoxide can be extracted into CO_2 rich phases; hence greatly reduces the reaction rate.

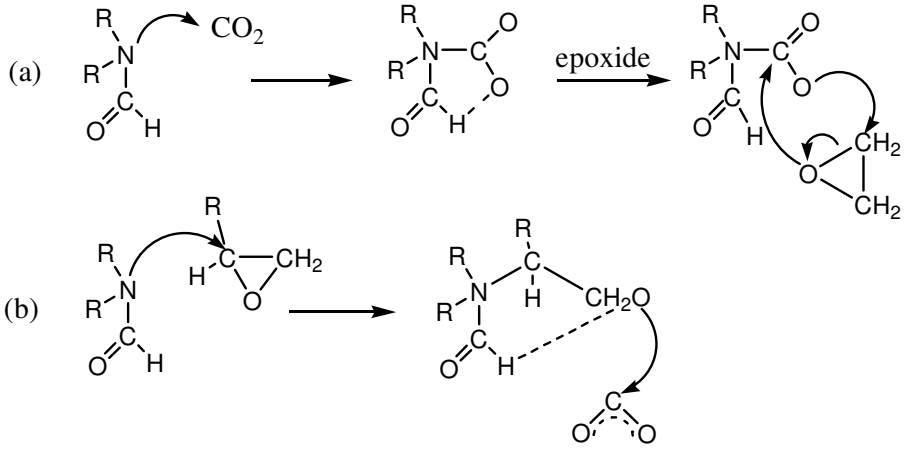
Ghosh et al. (2010) reported that at lower pressure (7 bar) the catalyst retains sizable activity (TOF: 312 h^{-1}) and with increasing pressure up to 20 bar higher TOF value of 351 h^{-1} was observed. However, the pressure higher than 20 bar diminishes the overall activity of the catalyst. This is due to the decrease in polarity of the reaction mixture and solubility of the catalyst in the reaction mixtures is lowered. Qiao et al. (2009) studied the influence of CO_2 at different pressure ranges, e.g., mild pressure (15 bar), medium pressure (80 bar) and supercritical pressure (140 bar) for the CO_2 cycloaddition with SO. By increasing the pressure to more than 60 bar, they observed a negative effect on the reaction, where, both yield and conversion reduced tremendously. This was due to changes in phase from gas to supercritical fluid, where a part of SO dissolves in the supercritical CO_2 and decrease the amount of reaction substrate in liquid phase where the reaction occurs.

Wang et al. (2009) observed, that the introduction of too much CO_2 dissolves in SO or "liquefies" the formation of CO_2-SO complex, and retards the interaction resulting in a lower conversion. Lately, similar results were also reported where the introduction of higher pressure of CO_2 dissolved in the PO and becomes an unfavorable factor due to the difficulty of separating CO_2 and PO, and inhibit the reaction between PO and catalyst, thus resulting in lower yield (Xiao et al., 2014, Wei-Li et al., 2014b).

Xiang et al. (2009) reports that many oligomers were produced as side products at high pressure. In a solvent-less reaction with (PO and SO) and CO_2, Jutz et al. (2008) reported that a ratio of 1:4 (epoxide: CO_2) was found to be optimum compared to a ratio of 1:16 for both epoxides. They also studied the phase behavior to investigate the influence of the fluid phases present in the catalytic reaction.

1.4.3 Influence of solvent

The synthesis of cyclic carbonate is carried out in the presence of solvents too. The solvent plays a vital role in removing the carbonaceous deposits from the catalyst surface and keeps the reaction system clean. Thus, the catalysts life is prolonged significantly (Bhanage et al., 2001). Aresta et al. (2003) demonstrated that, *N,N*-dimethylformamide (DMF) alone yields 34.7 % of SC at 50 bar. They also found that, the amide group acts as good promoter. Dimethylacetamide (DMA) produced 28 % of SC yield at 50 bar, 135 °C and for 12 h without the usage of any catalyst. The role of DMF in the cycloaddition of epoxides is shown in the Scheme 1.3.



Scheme 1.3: Role of DMF in the cycloaddition of epoxides (Aresta et al., 2003).

According to the mechanism, the role of amide is to increase the nucleophilicity of the relevant oxygen atoms in either epoxide or CO_2. To enhance the activity of the reaction, methylene chloride or 1,2-dichloroethane was added as an additive to DMF along with Nb_2O_5 catalyst. It was suggested that, methylene chloride could contribute to stabilize polar or ionic intermediates through the $C^{\delta-}$ -$H^{\delta+}$, $C^{\delta+}$ -$Cl^{\delta-}$ dipoles. Additives such as tetrachloromethane and ethanol when used together with DMF, shows a co-operative solvation effect.

In the case of dimethylsulfoxide (DMSO), several side products were observed in the presence of a catalyst. In the investigation, xylenes and toluene did not yield any product without catalyst. However, for xylenes, a very poor yield was observed in the presence of a catalyst. Kawanami and Ikushima (2000) used DMF as a catalyst and solvent under supercritical conditions, where CO_2 with epoxide were dissolved in DMF-scCO_2. Under this condition, the viscosity of the solution was reduced and the diffusion rate was increased when compared with the DMF of the liquid phase. Recently, Zhong et al. (2014) utilized DMF as co-catalyst together with $ZnBr_2$ as a catalyst for cycloaddition reaction of CO_2 to PO. They have described, DMF acted as solvent as well as CO_2 activator. A 100 % selectivity to PC were registered at 150 °C, 30 bar within very short reaction time of 10 min. Alvaro et al. (2004) used about 0.4 mL dichloromethane or dimethyl carbonate as a co-solvent to increase the solubility in the medium of SO and used the base as a co-catalyst. They have observed 70 % conversion with 100 % selectivity under supercritical condition (100 bar, 80 °C) in a 50 mL reactor for 6 h in the presence of a Cr-salen base catalyst.

A new approach was taken by Jiang and Hua (2006) in order to study the effect of various solvents during the synthesis of chloropropene carbonate from epichlorohydrin. They found that, protic alcohols such as methanol and ethanol were good solvents for the formation of chloropropene carbonate, which were 90 % and 82 % in methanol and ethanol respectively. However, high molecular weight of benzyl alcohol resulted in a decreased productivity (12 %). Nevertheless, they observed a maximum yield of > 99 % at 110 °C for 20 h with DMF as the solvent.

1.5 The mechanism of cycloaddition of CO_2 to epoxides

1.5.1 Ring opening of epoxide

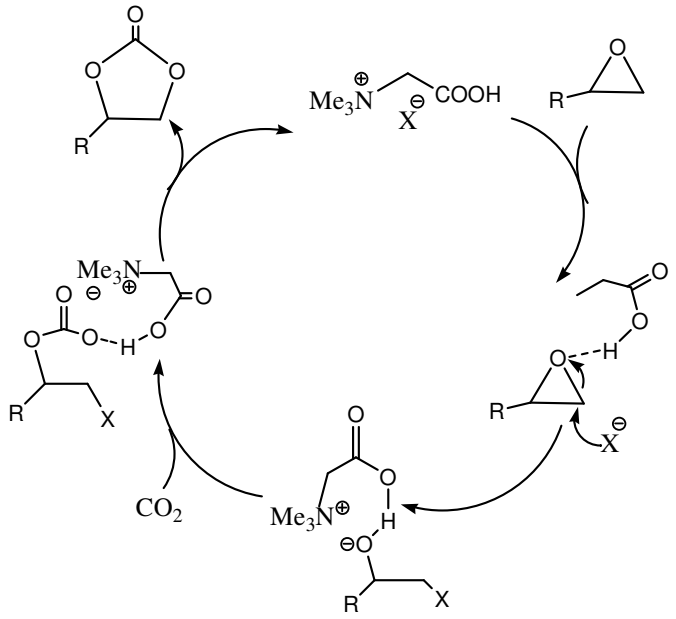
Basically, the ring opening of the epoxide is described in terms of two pathways; (i) Lewis-acid catalyzed cleavage and (ii) Lewis-base catalyzed cleavage. Bu et al. (2007) found that the ruthenium complex ((2,2'-bipy)$RuCl_3(CH_3OH)$) together with cetyltrimethylammonium chloride (CTAC) catalyzes the reaction of CO_2 with propylene oxide (PO) which forms a 100 % yield of propylene carbonate.

In this complex, Ru acted as a Lewis-acid to activate the PO to form adduct of Ru-PO. However, in this case they found that the adduct itself was not able to open the PO ring. The addition of CTAC is vital, in which it performs a crucial role in enhancing the ring opening intermediate. The chloride anion (Lewis-base) in CTAC attacks the less sterically hindered carbon atom to open the epoxide ring while forming the oxy anion species.

Bai et al. (2010) found that the bifunctional metalloporphyrins M(TTMAPP)I_4(X) (M = Co, Fe, Mn and Cr; X = OAc, CF_3COO, CCl_3COO, OTs, Cl, Br and I) were highly efficient catalysts for the cycloaddition reaction of PO and CO_2. They observed that, metal acts as a Lewis acid center to catalyze the reaction. The activity order of the metal was Co > Mn > Fe > Cr. The catalytic activity order in the presence of cobalt porphyrin and other different conterions was $OAC^- > I^- > Cl^- > Br^- > OTs^- > CF_3COO^- > CCl_3COO^-$.

Barbarini et al. (2003) reported that, MCM-41-supported guanidine catalysts which contains hydroxyl groups on the arm and silanols on the support surface. Both hydroxyl and silanol groups could activate the epoxide by H-bond formation but there were no evidence to prove this hypothesis. Zhou et al. (2008) investigated the synthesis of cyclic carbonate over betaine (HBetX) and choline cation (ChoX) catalysts. They found that either the hydroxyl group or the carboxyclic acid group affects the activity of the catalysts. Besides that, they reported the comparison among the anion such as Cl^-, Br^-, I^-, BF_4^- and PF_6^-. The yield for PC synthesis decreased in the order of $Cl^- > BF_4^- > PF_6^-$. Moreover, the leaving ability of the anions plays an important factor and their activity increases in the order of $I^- > Br^- > Cl^-$. The use of better nucleophilic anions will attack the epoxide ring effectively to form a reactive intermediate.

The carboxylic acid group was found to be more useful, where it shows a cooperative effect with halide anions to activate the ring opening of epoxides than hydroxyl group due to the stronger Brønsted acid and hydrogen bonding donor. The reaction mechanism for the cycloaddition reaction is shown in Scheme 1.4.



Scheme 1.4: The assumed reaction mechanism for the cycloaddition of epoxide with CO_2 catalyzed by HBetX (Zhou et al., 2008).

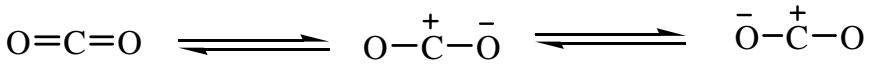
Qiao et al. (2009) described that ZnX, X= Br^-, Cl^-, BF_4^-, PF_6^- immobilized on soluble imidazolium-styrene copolymers was a suitable catalyst for the CO_2 cycloaddition to SO. Among the catalyst investigated, Zn/PS-IL[Br] was the most efficient, which gave 97.5 % yield with a TOF of 3800 h^{-1}. Although, this catalyst was considered as homogeneous, but it could be reused three times due to its immiscibility with ethanol without significant loss in activity. The Zn/PS-IL[Cl] showed a product yield of only 35 %, with TOF of 1300 h^{-1}. The authors suggested that, this could be due to the stronger nucleophilicity of Br^- than that of Cl^- under the reaction conditions. Jing et al. (2007) suggested that the high activity of the catalyst could be attributed to the good leaving group of Br^-.

Dai et al. (2010) reported that 3-(2-hydroxyl-ethyl)-1-propyl imidazolium bromide-SBA-15 (HEPIMBr) as an efficient catalyst for the synthesis of cyclic carbonates under mild conditions in a solvent-free environment and in the absence of a co-catalyst. They proposed that, the intermediate formation occurred when the H atom of the hydroxyl group coordinated with the O atom of epoxide through hydrogen bonding. Then, the halide anion makes a nucleophilic attack on the sterically less hindered β-carbon atom of the epoxide, due to the polarization of the C-O bonds and the ring opening of epoxide occurs concurrently.

Recently, Jing-Xian et al. (2014) reported biopolymer chitosan-grafted quarternary phosphonium ionic liquid (CS-[$BuPh_3P$]Br) as an excellent catalyst for the cycloaddition of epoxide with CO_2. They have proposed that the facilitation of ring opening of epoxides is due to a combined result of polarization. The bromide anion of the catalyst opens the epoxy ring, which was activated by the hydroxyl groups and phosphonium cation through hydrogen bonding as well as electronic interaction. A similar catalysts were developed by Wei-Li et al. (2014a) using phosphonium-based ionic liquid functionalized with carboxyl, hydroxyl and amino as a functional groups. Similarly, the epoxide ring is opened via the hydrogen bonding between the H atom of functional group and the O atom of epoxide, resulting in polarization of epoxide C-O bond and formation of intermediate. Then, there is nucleophilic attack of Br^- on the less sterically hindered β-carbon atom of epoxide, facilitating opening of epoxy ring and formation of another intermediate.

1.5.2 Activation of CO_2

Carbon dioxide chemical fixation is both important and possible due to two potential activation sites as shown in Scheme 1.5.

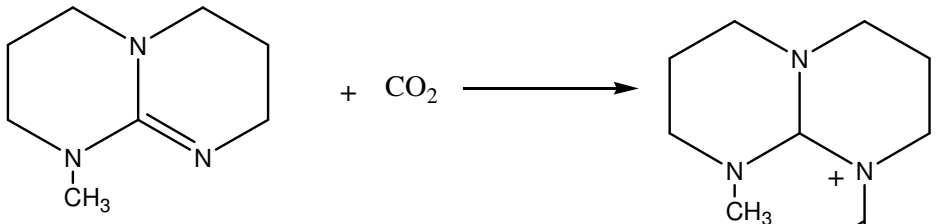


Scheme 1.5: The carbon and oxygen atoms act as Lewis acid and Lewis base respectively. Both are potential activation sites.

Carbon dioxide could be catalytically activated into valuable chemical when it reacted with the molecules containing an electron donor or an active hydrogen group. A catalyst plays an important role to activate the CO_2 for its participation in the chemical reaction to produce the respective cyclic carbonates.

Lu et al. (2002) prepared MCM-41 supported aluminium phthalocyanine complex for the reactions of CO_2 and epoxides and found that the co-catalyst, *n*-Bu_4NBr enhanced the reaction as well as giving high catalytic activity. In their studies, they found that the activation of CO_2 was initiated by the nucleophilic attack of the alcoholate (-OCH_2CH_2Br) at the carbon atom of CO_2, weak interaction between the central metal ion of ClAlPc and the lone pairs of one of the oxygen of CO_2. The catalyst showed a synergistic effect in promoting these reactions via the insertion of CO_2 to the Al-O bond of Pc(Cl)Al-OCH_2CH_2Br to form linear carbonates and it converts into cyclic carbonates by intramolecular substitution of halides.

On the other hand, Barbarini et al. (2003) observed that CO_2 was activated through the formation of the zwitterionic compound (Scheme 1.6), where it later adds to the epoxide via nucleophilic attack.



guanidine MTBD

Activated CO_2 carbamate anion

Scheme 1.6: Hypothesized MTBD-promoted CO_2 activation (Barbarini et al., 2003).

Srivastava et al. (2005a) critically investigated the properties of the catalyst in the activation of CO_2. FTIR spectroscopy was used to identify the structural features of CO_2 in the adsorbed state of the catalyst. The CO_2 reacted with the amine functional group in SBA-15-*pr*-Ade and Ti-SBA-15-*pr*-Ade which was confirmed with the presence of the carbamate bands at 1609 and 1446 cm^{-1}.

Conversion (62.3 %) of epichlorohydrin was obtained after the functionalization of adenine group compared to the bare SBA-15 (1.5 %). This increase in conversion was correlated with the intensity of the band at 1609 cm^{-1}, due to the CO_2 activation at the amine sites, highlighting the importance of such sites for CO_2 activation. In another report, Srivastava et al. (2006a) compared and investigated the importance of the basic sites of the catalysts such as alkyl amines ($-NH_2$), adenine (Ade), imidazole (Im) and guanine (Gua) in the activation of CO_2.