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Jimmy Nelson Appaturi
University Sains Malaysia, Malaysia

Rajabathar. Jothi Ramalingam
King Saud University, Saudi Arabia

Muthu Kumaran Gnanamani
University of Kentucky, muthu.gnanamani@uky.edu

Govindasami Periyasami
King Saud University, Saudi Arabia

Prabhakarn Arunachalam
King Saud University, Saudi Arabia

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Authors

Jimmy Nelson Appaturi, Rajabathar. Jothi Ramalingam, Muthu Kumaran Gnanamani, Govindasami Periyasami, Prabhakarn Arunachalam, Rohana Adnan, Farook Adam, Mohammed D. Wasmiah, and Hamad A. Al-Lohedan

Review

Review on Carbon Dioxide Utilization for Cycloaddition of Epoxides by Ionic Liquid-Modified Hybrid Catalysts: Effect of Influential Parameters and Mechanisms Insight

Jimmy Nelson Appaturi ^{1,*}, Rajabathar. Jothi Ramalingam ^{2,*}, Muthu Kumaran Gnanamani ³, Govindasami Periyasami ^{2,*}, Prabhakarn Arunachalam ², Rohana Adnan ¹, Farook Adam ¹, Mohammed D. Wasmiah ², Hamad A. Al-Lohedan ^{2,4}

¹ School of Chemical Sciences, University Sains Malaysia(USM), Penang 11800, Malaysia; r_adnan@usm.mu (R.A.); farook@usm.my (F.A.)

² Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; parunachalam@ksu.edu.sa (P.A.); jot99ram@rediffmail.com (M.D.W); hlohedan@ksu.edu.sa (H.A.A.)

³ Center for Applied Energy Research, University of Kentucky, 2540 Research Park Drive, Lexington, KY 40511, USA; muthu.gnanamani@uky.edu (MKG)

⁴ Surfactant Research Chair, Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

* Correspondence: jimmynelson@usm.my (J.N.A.); rjabathar@ksu.edu.sa (R.J.R.); pkandhan@ksu.edu.sa (G.P.)

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Abstract: The storage, utilization, and control of the greenhouse (CO₂) gas is a topic of interest for researchers in academia and society. The present review article is dedicating to cover the overall role of ionic liquid-modified hybrid materials in cycloaddition reactions. Special emphasis is on the synthesis of various cyclic carbonate using ionic liquid-based modified catalysts. Catalytic activity studies have discussed with respect to process conditions and their effects on conversion and product selectivity for the reaction of cycloaddition of CO₂ with styrene oxide. The reaction temperature and the partial pressure of CO₂ have found to play a key role in cyclic carbonate formation. The role of other influential parameter (solvent effect) is also discussed for the conversion of cyclic/aromatic oxides to polycarbonate production. Our own research work that deals with ionic liquid-based halide-modified mesoporous catalyst (MCM-41 type) derived from rice husk waste has also been discussed. Finally, the role of carbon dioxide activation and ring-opening mechanisms involved in the cyclic carbonate product formation from CO₂ have been discussed.

Keywords: greenhouse gas; ionic liquid; mesoporous silica; cycloaddition; poly-carbonate

1. Introduction

Greenhouse gas (carbon dioxide—CO₂) in the atmosphere helps living things naturally by involving in photosynthesis [1]. About 32% of CO₂ is being produced by hydrocarbon combustion and gasification process that raises concern over environmental pollution [2,3]. The transportation sector contributes nearly 30% to total carbon dioxide emissions [4]. Figure 1 shows the carbon cycle, CO₂ storage, recycle and purification, and utilization mainly of fine chemicals formation by catalysis route. Figure 1 shows the global atmospheric CO₂ concentration for about half a decade from 1958 with respect to continuous research reports carried by the Mauna Loa Observatory in Hawaii [3]. The concentration of atmospheric CO₂ was 399.89 ppm till May 2013, and in 2020, it reached up to 412.78 ppm [5]. The continuous rise in greenhouse gas (CO₂) concentration creates global warming issues and continues damage to the green environment. In recent years, smart technologies are developed to store and utilize CO₂ reduction and which makes the pollution free atmosphere [6–8].

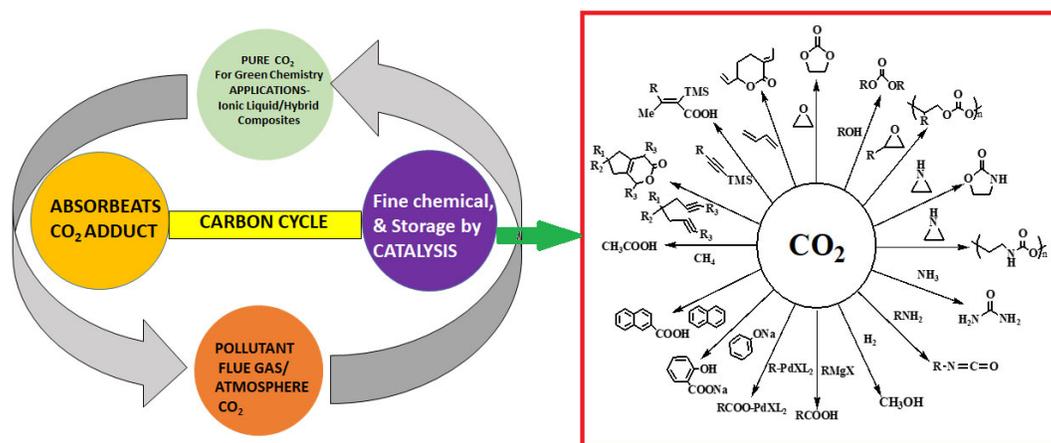
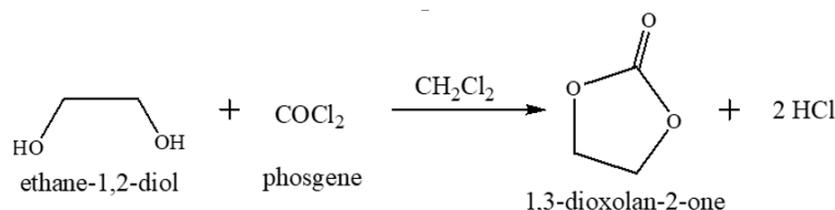


Figure 1. Schematic of carbon cycle for CO₂, recycle Storage and greenhouse gas utilization for possible fine chemicals production.

Carbon dioxide is recognized as a nonflammable [9], nontoxic [10], and inexpensive gas [11]. It is a renewable carbon source [12] and thermodynamically stable compound [13,14]. Interestingly, carbon oxide can replace the following toxic chemical compounds such as carbonyl dichloride known as phosgene (COCl₂), carbon monoxide (CO), and isocyanides (R-NCO) for fine chemical applications. Carbon dioxide can be utilized as a mild oxygen source [15]. It can be used as an alternate medium or solvent [16], also work as a supercritical fluid (sc) [17], and act 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 [16]. Hutchings [15,17] used supercritical CO₂ as an antisolvent for the preparation of Au/scCO₂ and sc-VPO (vanadium phosphate) catalysts. Currently, CO₂ has been used in various industrial applications such as chemical, pharmaceutical, foodstuff, laboratories and analysis, beverage, and pulp and paper industries [16]. The application of CO₂ as C1 raw material in the chemical industry was started in past few decades. It has been reported that approximately 110 million metric tons of CO₂ are currently used every year in the chemical industry. In the present decade, carbon dioxide utilization has reached around 110 million MT (metric tons) [18]. Carbon dioxide is also playing major role in the production of urea, [17] methanol [18], salicylic-acid [19], formic-acid [20], cyclic carbonates [21–23], copolymers, polymer building blocks, and fine chemicals [24–27]. Urea is one of the major fertilizers, and CO₂ is the source for it [26]. The urea is prepared from ammonia and CO₂ in fertilizer [28] and also in fabrication process of various types of polymers, such as melamine and urea-formaldehyde resin [29–32]. Salicylic acid is produced from phenol and CO₂ via the Kolbe-Schmitt reaction [33]. The product is used to produce acetyl salicylic acid which is also known as aspirin, used mostly in healthcare applications [34–36]. Everyday monitoring of Carbon dioxide emission in atmosphere have shown in online website (www.co2.earth) to monitor the Keeling Curve of Atmospheric CO₂ concentration emission between 1958 to 16 August 2020 [5,35].

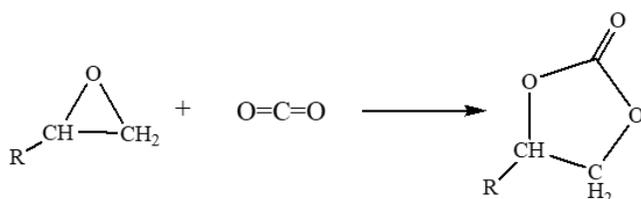
The cyclic carbonates are odorless, colorless, and biodegradable [37,38]. The cyclic carbonates are used in industries as aprotic polar solvents [39], as a monomer for polymer synthesis, and as additives [40]. Besides, it is also been used in electrolytic materials such as secondary batteries (lithium batteries) [41], cosmetics, resins, and cleaning utensils [42]. Cyclic carbonates are utilized as an intermediate compound in the biomedical and pharma industries [12]. Cyclic carbonates also play a key role in herbicides and disinfectants synthesis [43] as well as are fuel additives [44].

Traditionally, phosgene with ethane-1,2-diol in dichloromethane solvent was utilized to produce cyclic carbonates, and one of the products is hydrochloric acid obtained as a by-product, which is harmful to human beings [43]. Scheme 1 shows the conventional synthesis of organic cyclic carbonates.



Scheme 1. Synthesis of organic carbonate by the conventional route.

By considering the economic point of view and avoid toxicity generation, the CO₂ is a natural choice to phosgene as an alternate and the other advantage is that CO₂ can be incorporated into epoxides without side products [45]. However, due to the inert nature of CO₂, various catalysts were adopted to activate the epoxide [11]. The cycloaddition of CO₂ to epoxide is shown below (Scheme 2).



Scheme 2. Cycloaddition of CO₂ to epoxide forming cyclic carbonate.

To increase cyclic carbonates yield from cycloaddition of CO₂ and epoxides, a different kind of catalyst has been adopted. In the past decades, the wide range of homogeneous and heterogeneous catalysts have been developed to catalyze the so-called CO₂ fixation process. Homogeneous catalysts, such as CoCl₂/onium salt [44], diimine Ru (II) complex [46], Al-salen-PEA [4], betaine-based quaternary ammonium ion and carboxylic acid [12], *N,N*-dimethyl formamide (DMF) [47,48], SnCl₄-organic base [49], Au/Fe(OH)₃-ZnBr₂/Bu₄NBr [50], ionic liquid-highly cross linked polymer [51], BrBu₃PPEG₆₀₀PBU₃Br [52], cellulose/KI [53], and Au/R201 [54] have also been studied.

Several heterogeneous catalysts, such as metal oxides; MgO [55,56], Nb₂O₅ [43], Mg-Al oxide, guanidine-MCM-41 [57], Adecine-Pr-Al-SBA-15 [58], Cr-salen-SiO₂ [13], Mn-salen-SiO₂ [42], CIAIPC-MCM-41 [59], 3-(2-hydroxyl-ethyl)-1-propyl imidazolium bromide-SBA-15, and zeolite-based organic-inorganic hybrid catalysts have also been investigated [55–66].

Ionic liquid (IL) is recently explored as efficient catalysts with growing importance over the past decades [64]. Since 2003, ILs have widely been adopted in the chemical industry as a solvent as well as catalysts for many fine chemical productions [60–65]. Hence, a quaternary ammonium ion together with a halide anion, -OH, or a -COOH group with ionic liquid was considered as potential materials for heterogeneous catalysis.

2. Summary

The present review article described the effect of influential parameters such as temperature, pressure, and solvent on the conversion of cyclic epoxide into cyclic carbonate formation in presence of various ionic liquid modified hybrid catalysts. Another section describes the mechanisms insight into the activation of carbon dioxide and the ring-opening process in the process of substrate conversion and acidic/basic characteristics of the catalyst.

3. Results of Reaction Parameters and Influencing Factors for the Production of Cyclic Carbonates

The production of cyclic carbonates depends on various parameters including catalyst and reaction parameters such as solvents, temperature, and pressure condition. The optimization of all the above parameters could produce maximum product yield. Table 1 summarizes studies that were carried out for cycloaddition of greenhouse gas conversion to styrene oxide (SO) on different types of catalysts [66–99]. The produce yield was higher due to the presence of both acid and base bifunctional groups present on the catalyst and it synergistically activates the cycloaddition reactions.

Table 1. Catalytic activity studies of cycloaddition of CO₂ to styrene oxide using various homogeneous and heterogeneous catalysts.

Catalytic Materials ^a	Reaction Conditions				Reaction Results			References
	Solvent or Co-catalyst	P _{CO2} (bar)	Temp. (°C)	Time (h)	Yield (%)	Selectivity (%)	Conversion (%)	
Guanidine-MCM-41	CH ₃ CN	50	140	70	90	92	-	[11]
Al-SBA-15- <i>pr</i> -Ade	-	6.9	120	4	88.9	94.6	94	[58]
Cr-salen-SiO ₂	CH ₂ Cl ₂	100	80	6	74	100	-	[13]
Mn-salen-SiO ₂	-	35 ^b	140	3	95	-	-	[42]
ClAlPc-MCM-41	<i>n</i> -Bu ₄ NBr	40	110	2	384 ^c	-	-	[59]
Al-salen-PEA	<i>n</i> -Methyl imidazole	100	80	15	78	87.6	89	[4]
Betaine-based salt ^d	-	80	140	8	96	-	-	[12]
MCM-41 ^e	CH ₃ CN	6.9	120	8	-	98.2	88.4	[60]
	-	6.9	120	8	-	95.2	93.7	[60]
Zn/Ps-IL(Br)	-	30	120	8	97.5	-	-	[91]
SalenRu(II)(PPh ₃) ₂ /PTAT ^f	Ethanol	8.3	70	2	92	-	-	[92]
CoCl ₂ /onium salt	CH ₂ Cl ₂	15	120	1	1238 ^c	-	-	[44]
Ti-SBA-15- <i>pr</i> -Ade	CH ₃ CN	6.9	120	8	-	87	79.8	[1]
	-	6.9	120	8	-	94.6	94	[1]
Diimine Ru(II) complex	-	16	100	2	73.1	-	-	[46]
Ionic liquid-polymer	-	60	110	7	79.1	-	-	[50]
Cellulose/KI	-	20	110	9	98	-	-	[53]
HEPIMBr	-	20	120	2	99.6	-	99.8	[14]
Ionic liquid tetrabutylammonium chloride	-	9.7	100 ^g	0.5	97.9	-	-	[40]
Au/Fe(OH) ₃ -ZnBr ₂ /Bu ₄ NBr	-	40	80	10	53	-	-	[50]
Co(III) complex	DMAP	20	120	3	85.8	-	-	[38]
SLPC	Toluene	45	150	6	84.8	-	-	[81]
Co(III) Porphyrin/DMAP	CH ₂ Cl ₂	20.7	120	4	97	-	-	[82]
MNP-Co-Porphyrin	CH ₂ Cl ₂	10	25	36	48.7	-	-	[83]
M(TTMAPP)I ₄ (X) M = Co; X = OAc	-	6.7	80	36	62.5	-	-	[84]
Bis-(phenoxyiminato) cobalt(III)/Lewis base Metal	CH ₂ Cl ₂	10	145	1	600/640 ^c	-	-	[44]
porphyrin/phenyltrimethyl -ammonium tribromide	-	6.9	20	10	20	-	-	[85]
SnCl ₄ -organic base	-	3.5	75	1.5	96	-	-	[49]
P-DVB-HEImBr	Zn I ₂	20	140	5	98.9	96	23	[68]
SBA-15-IL1Br		20	110	3	80	99	80.8	[91]
Silica-immobilized		6	130	10	76.6	97	79	[92]
PDDA-Br		25	100	12	92.9	-	-	[93]
KI/PDA	OH	20	120	5	34.7	99	35	[94]
(P-Im-C ₄ H ₈ Ph ₃ P)Br ₂		25	130	4	99.3	99.8	99.5	[95]

PPN(I)	1	100	7	89	97.8	95	[95]
PS-hexyl-MeI	12	120	12	96.7	100	98.9	[98]
PS-TBMAC	9	110	2	71	-	-	[99]

^a SLPC: supported liquid phase catalyst; *pr*: 3-chloro or 3-aminopropyltriethoxysilane; PEA: poly(ethylene glycol bismethacrylate); PTAT: phenyltrimethylammonium tribromide; M(TTMAPP)₄(X): bifunctional metalloporphyrins; Ade: adenine; ClAlPc: aluminum phthalocyanine; HEPIMBr: 3-(2-Hydroxyl-Ethyl)-Propylimidazolium bromide; MNP: magnetic nanoparticle; CS: chitosan; ChI: choline iodide; PDA: 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 CO₂ to styrene oxide. ^c turn over frequency (h⁻¹). ^d quaternary ammonium ion and carboxylic acid group. ^e bulk MCM-41 catalyst. ^f recrystallization in ethanol. ^g microwave-irradiation method.

3.1. Effect of Influence of Reaction Temperature for Cycloaddition of Epoxides with CO₂

The reaction temperature is an important parameter in a catalytic reaction for an effective collision between molecules to enhance the bond-breaking step. Hence, the more molecular collision is the reason for the more yield of final products. Aresta et al. [26,41] reported the temperature effect on the production of styrene carbonate (SC) using Nb₂O₅ as a catalyst from styrene oxide by CO₂ addition. Below 100 °C, the reaction did not yield any product. However, it provides 80% yield at temperature of 135 °C. Jutz et al. [40] studied the effect of reaction temperature on the performance of Mn (salen) Br. The highest yield was obtained at 160 °C, and with a further increase in temperature, the yield was dramatically reduced. This was attributed to changes in the phase distribution observed at higher reaction temperatures. Zhou et al. [11] reported that the reaction carried out at 140 °C results in the formation of propylene carbonate (PC) with the highest yield of 98%. Increase in the temperature from 140 to 150 °C dropped the yield up to 78% due to problems of side product generation at high-temperature conditions. Bai et al. [83,84] reported that in some instances, high-temperature conditions are causing the catalyst to decompose resulting in a decrease in propylene carbonate (PC) yield [84]. Qiao et al. [91] explained that styrene oxide (SO) is difficult to convert to styrene carbonate (SC) compared to all other epoxides due to the lower reactivity of β-carbon atom. They found that the temperature of 120 °C (98%) with suitable catalyst was the best-optimized condition than the high-temperature condition (130 °C (~80%) and 140 °C (~95%)).

Recently, Lee et al. [98] studied the cycloaddition reaction between ally glycidyl ether (AGE) and carbon dioxide using PS-hexyl-Methyl iodide at 12 bar of total pressure and different temperature conditions. They reported that the yield of ally glycidyl carbonate (AGC) increases from 80 to 140 °C, and it decreased with a further increase in the temperature to 160 °C. The yield decreased was due to the generation of oligomers and other side products like 3-allyl oxy-1,2-propanediol. Zhong (2014) et al. [100] studied and reported the effect of temperature in the range between 120 and 160 °C for propylene carbonate formation. The yield of PC in the presence of 0.78 and 13.7 m/mol of DMF solvents for comparative purpose was studied. They found that the usage of a large amount of DMF was favorable to provide a higher yield at the lower reaction temperature.

3.2. Effect of Influence of Reaction Pressure Condition for Cycloaddition of Epoxides with CO₂

The reaction pressure of the carbon dioxide insertion has been established as one of the most crucial and critical conditions for affecting the epoxide cycloaddition reaction [91–98]. The inserted CO₂ acts as an important reactant for all catalytic transformations [42]. Two phases are established in the reaction system; the bottom phase is rich with epoxide and the top phase is enriched with CO₂. According to Xie et al. (2007), the reactant CO₂ favors the reaction when the bottom phase is under high pressure. However, the

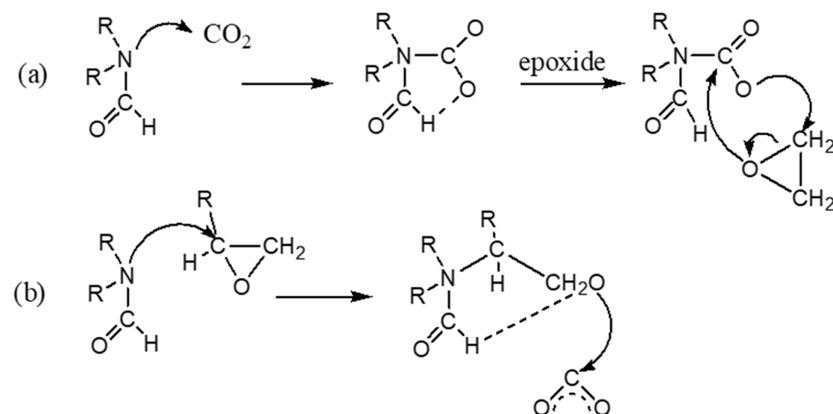
above condition is not favorable for the high-pressure reactions (120 bar) as concentration of epoxide for example propylene oxide [49].

Ghosh et al. [36] reported that at lower pressure (7 bar), the catalyst retains moderate reaction activity turn over frequency (TOF) of 312 h^{-1} and with increasing pressure up to 20 bar, increased TOF value of 351 h^{-1} was observed. However, the pressure more than 20 bar results in diminishes overall reactivity due to polarity and solubility problem of the catalysts. Qiao et al. [91] reported different pressure conditions, such as mild pressure (15 bar), medium pressure (80 bar), and supercritical pressure (140 bar), for the styrene oxide with CO_2 cycloaddition reactions. This was due to changes in the phase from gas to supercritical fluid, where a part of styrene oxide (SO) dissolves in the supercritical condition. On the other hand, Wang, et. al (2017) [65] approach was for the same reaction but different perspective, i.e., introduction of high concentration of CO_2 dissolves within a substrate or “liquefies” the formation of intermediate complex.

Xiang et al. (2009) [52] reported that the many oligomers were produced as the side products such as propylene oxide and styrene oxide due to insertion of CO_2 at high pressure in a solvent-less condition. Jutz et al. [40,53] reported that a ratio of 1:4 (epoxide: CO_2) was the best reactant ratio condition instead of 1:16 for conversion of both epoxides.

3.3. Effect of Influence of Solvent for Cycloaddition of Epoxides with CO_2

A variety of solvents are adopted to synthesis cyclic carbonate from cycloaddition reaction. A solvent plays a key role in minimizing carbonaceous deposits on the catalyst surface. [55]. Aresta et al. [26,41] exploited that the *N,N*-dimethyl formamide (DMF) alone yields 34.7% of styrene carbonate at 50 bar pressure of CO_2 and predict that amide group was a good promoter. Di-methyl acetamide (DMA) produced SC about 28% yield without the catalyst at 50 bar pressure and at temperature of $135 \text{ }^\circ\text{C}$ for 12 h. The role of DMF in the cycloaddition of epoxides mechanism and transformation is as follows (Scheme 3).



Scheme 3. (a) Role of *N,N*-dimethyl formamide (DMF) (a) initial CO_2 activation; (b) initial epoxide activation, in the cycloaddition of epoxides [43] (modified images and cited the related reference).

According to the mechanism, role of amide is to facilitate the nucleophilicity of the respective oxygen atoms in CO_2 or epoxides. From the results, it is evident that the methylene chloride could contribute to stabilize the polar or ionic intermediates through the dipole effect, i.e., $\text{C}^\delta- \text{H}^\delta+$ and $\text{C}^\delta+ - \text{Cl}^\delta-$. The cooperative solvation effect occurred in the presence of tetrachloro methane and ethanol-like additive used along with DMF for cycloaddition reactions. Kawanami et al. (2000)[45] used supercritical condition (sc) to study the effect of DMF as a catalyst and solvent on epoxide formation, which is dissolved in DMF- scCO_2 . Recently, Zhong (2000) et al. [100] utilized DMF as cocatalyst with ZnBr_2 as a catalyst for cycloaddition reaction of propylene oxide with carbon dioxide. In their study, they have observed that DMF acted as a solvent as well as carbon dioxide activator.

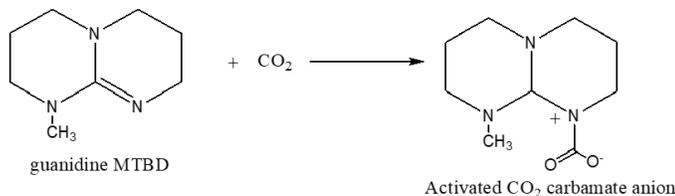
Both high conversion and 100% selectivity was obtained at 150 °C and pressure condition of 30 bar with very quick reaction time of 10 min [100]. Alvaro (2004) et al [12] used 0.4 mL dichloromethane (DMC) or dimethyl carbonate as a cosolvent to enhance product solubility in the supercritical medium and it serves as a cocatalyst as well. The results showed 70% conversion and 100% selectivity in presence of Cr-salen base catalyst under supercritical condition (100 bar, 80 °C, reactor volume = 50 m, 6 h reaction time).

A new approach was taken by Jiang et al. [46] in order to study the solvent effect for the synthesis of chloropropene carbonate from epichlorohydrin. Protic alcohols (methanol and ethanol) acted as good solvent for the formation of chloropropene carbonate with 90% and 82% yield. However, higher molecular weight alcohol such as benzyl alcohol was found to give less productivity yield (12%), whereas the same reaction carried out at 110 °C for 20 h with DMF as the solvent resulted in achieving for highest yield ($f > 99\%$).

4. Discussion of the Mechanism Insight of Cycloaddition of Epoxides with CO₂

4.1. Activation of CO₂ for Cycloaddition of Epoxides

Lu et al. [59] reported that aluminum phthalocyanine complex formation on MCM-41 support for the cycloaddition reaction of epoxides. They observed that CO₂ activated through nucleophilic attack at the carbon atom of CO₂ by the alcoholate group (-OCH₂CH₂Br). The weak interaction between the central metal ion of phthalocyanine complex and the lone pairs oxygen in CO₂ makes synergistic mechanism. The halide intramolecular substitution facilitate the epoxide into cyclic carbonates. In another related study, Barbarini et al. [10] argued that the mechanism of CO₂ activation through the formation of the zwitterion compound. Scheme 4 shows that the CO₂ adds to the epoxide via nucleophilic attack.



Scheme 4. Hypothesized 7-Methyl-1,5,7-triazabicyclo [4.4.0]dec-5-ene (MTBD)-promoted CO₂ activation [11].

[Srivastava et al,2005 \[1\]](#) exploited at first regarding the physico-chemical properties of the model catalyst in the activation of CO₂ molecules. Surface absorbing nature of CO₂ on catalyst was studied by Ft-IR spectroscopy. The CO₂ interacted with the amine functional groups in functionalized [SBA-15-*pr*-Ade(adenine) and Ti-SBA-15-*pr*-Ade(adenine)] was identified and confirmed by presence of the carbamate bands at 1609 and 1446 cm⁻¹.

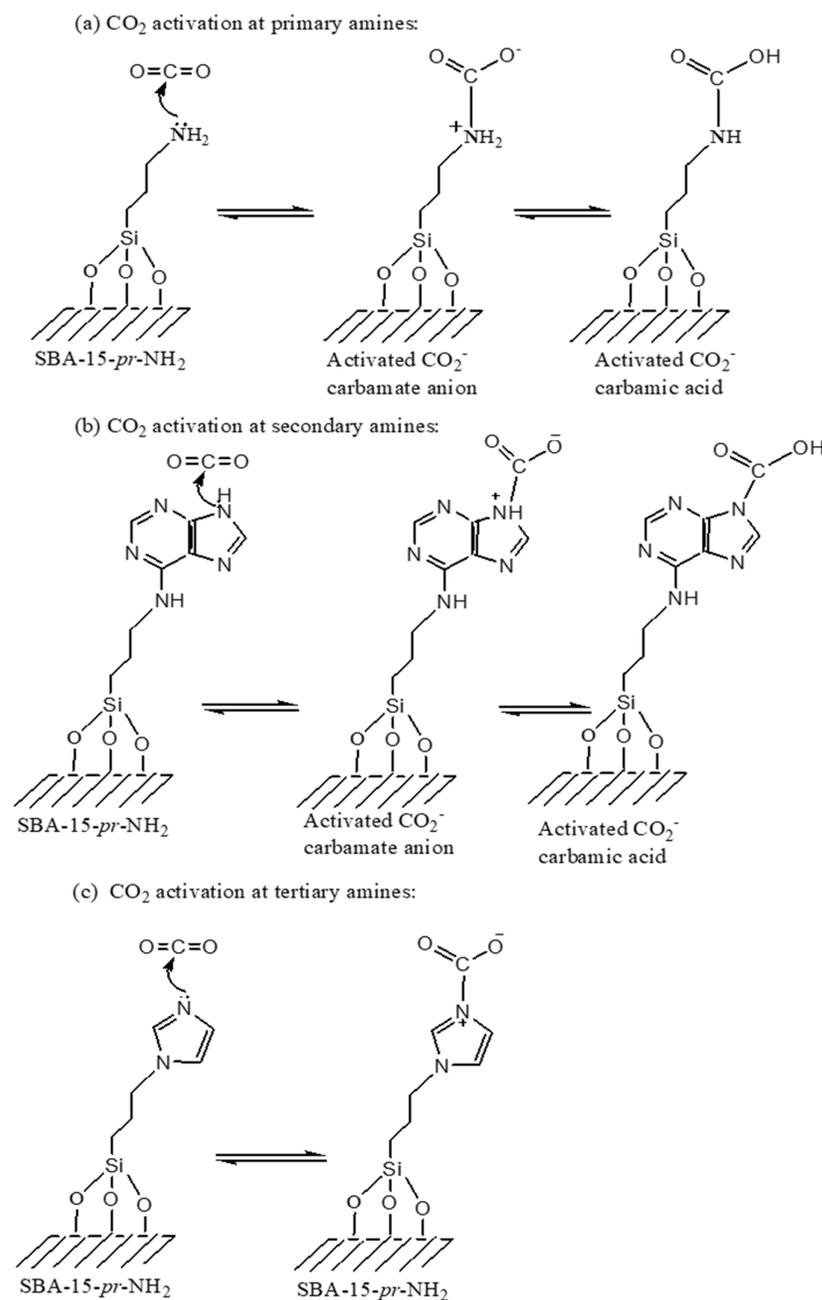
The efficient Epichlorohydrin conversion was obtained (62.3%) after functionalization of SBA-15 with adenine group compared to bulk SBA-15 (1.5%). This increased in conversion was related to the intensity of the band at 1609 cm⁻¹ ascribed due to CO₂ bonded with amine sites, which recognize the importance of such sites for CO₂ activation. In a related study, [Srivastava, et al, \[77,86\]](#) exploited and compared the importance of the basic sites present in the catalysts such as alkyl amines (-NH₂), adenine (Ade), imidazole (Im) and guanine (Gua) to activation process of carbon dioxide. Different types of coordination modes of CO₂ was discussed in detail in the past and its well known in the field of carbon dioxide chemistry [75].

Scheme 6 shows the stability of the activated CO₂ complex formation occurs *on the* basic amine sites at the catalyst surface decreased as follows: primary > secondary > tertiary amines [75,77 and 86]. The formation of carbamate anions from different type of

amine groups are demonstrated. The metal- electron deficient part of the catalyst facilitates the reaction rate for the formation of cyclic carbamate ions.

In Scheme 5 it is more clearly explained the role activation of CO₂ for their efficient conversion towards carbon dioxide activation process

From their point of view, Scheme 5 shows the stability of the activated CO₂ complex formation that occurring on the basic amine sites at the surfaces of catalyst decreased as follow: primary > secondary > tertiary amines [75,77,86]. The formation of carbamate anions from different types of amine groups are demonstrated. The metal-electron deficient part of the catalyst facilitates the reaction rate for the formation of cyclic carbamate ions.



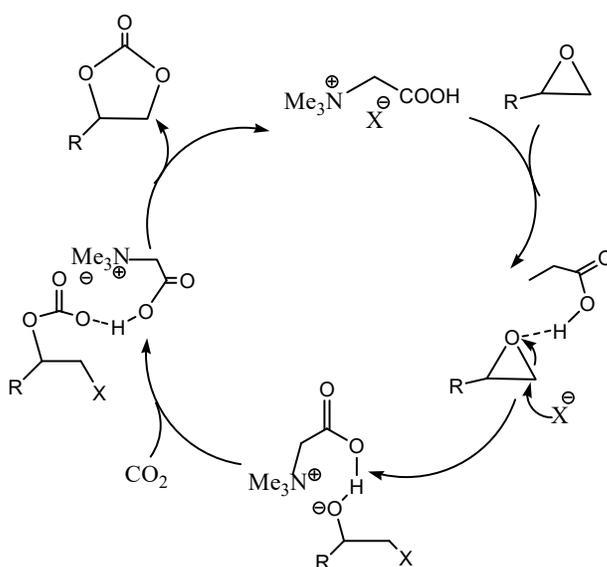
Scheme 5. CO₂ activation through primary, secondary, and tertiary amines [77,86].

4.2. Ring Opening of Epoxide

The ring-opening mechanism of the epoxide is described in two ways such as (i) Lewis-acid catalyzed cleavage and (ii) Lewis-base catalyzed cleavage. Bu et al (2007) [101] found that the ruthenium complex ((2,2'-bipy)RuCl₃(CH₃OH)) supported by cetyltrimethyl ammonium chloride (CTAC) catalyzes propylene oxide (PO) in the presence of CO₂ and achieved 100% yield for propylene carbonate (PC). In the above catalyst system, Ru acts as a Lewis-acid to activate the PO to form adduct of Ru-PO. CTAC addition enhances reaction rate and strikes the less sterically hindered carbon to break the epoxide ring while forming the oxy-anion species.

Bai et al. [83,96] reported that the bi-functional metal porphyrins M(TTMAPP)I₄(X) (M = Co, Mn, Fe, and Cr; X = OAc, CCl₃COO, CF₃COO, OTs, I, Cl, and Br) were highly efficient catalysts for the respective cycloaddition (formation of propylene carbonate). In the above catalyst system, metal ion incorporation acts as a Lewis acid center to facilitate the catalytic reaction rate. The order of activity of the catalysts was Co > Mn > Fe > Cr. The catalytic activity of cobalt porphyrin decreased with different counter ions as follows: CH₃COO⁻ > I⁻ > Cl⁻ > Br⁻ > OTs⁻ > CF₃COO⁻ > CCl₃COO⁻. Barbarini et al. [10] reported mesoporous silica (MCM-41) with hexagonal morphology in which Si-OH (hydroxyl and silanol functionalized)-supported guanidine catalysts are studied for cycloaddition reactions. The enhanced reactivity was obtained due to mechanisms involved in hydrogen bonding. Zhou et al. [11] studied the mechanism of cyclic carbonate formation in the presence of betaine (HBetX) and choline cation (ChoX) catalyst. They compared the anion effect and hydroxyl and carboxylic acid group activation towards catalyst function. The order of reactivity for PC conversion and yield decreased as follows: Cl⁻ > BF₄⁻ > PF₆⁻. The role of leaving group ability has also been studied, and the activity follows in this order: I⁻ > Br⁻ > Cl⁻. Adopting better nucleophilic anions could improve the epoxide ring opening/breaking efficiency of the catalyst.

The carboxylic acid group is found to be best for ring-opening mechanism with respect to suitable halide anions. The reason behind the halide anions to activate the ring opening is due to presence of stronger Brønsted acid and thereby involved in hydrogen bonding. Scheme 6 shows the reaction mechanism for the cycloaddition reaction and its halide anion interaction.



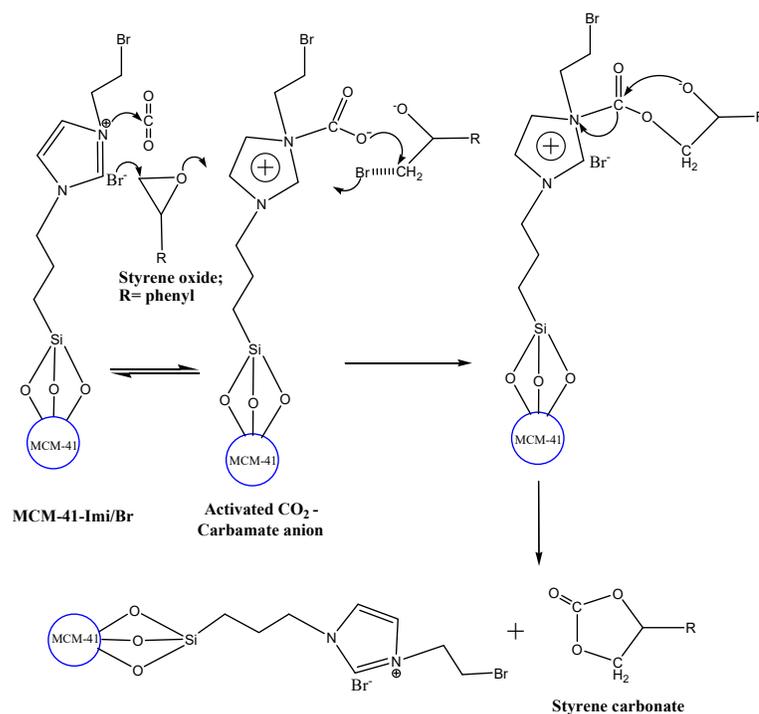
Scheme 6. The plausible cycloaddition reaction mechanism for epoxide ring opening with CO₂ by betaine (HBetX) catalysts [11].

Dai et al. [80,97] reported 3-(2-hydroxyl-ethyl)-1-propyl imidazolium bromide-SBA-15 (HEPIMBr), which is another type of mesoporous silica. The efficient synthesis of cyclic carbonates was achieved under mild conditions without solvent and in the absence of a co-catalyst.

Biopolymer chitosan-grafted quaternary phosphonium ionic liquid (CS-(BuPh₃P)Br) was reported as an excellent catalyst [98]. The authors proposed that the bromide anion of the catalyst played a major role in epoxy ring opening activated by the hydroxyl groups and phosphonium cation interaction. The same type of catalysts was developed by reported hydroxyl, carboxyl, and amino-functionalized phosphonium-based ionic liquid catalyst. They observed that a similar mechanism as mentioned above for the opening of the epoxide ring *via* polarization of epoxide C-O bond [90–98]. Excellent selectivity and good yield were obtained for cyclic carbonates under suitable or optimizable reaction conditions [90–101]. The following yields were obtained for the each cyclic carbonates such as epichlorohydrin (97.0%), glycidol (98.3%), styrene oxide (98.8%), phenyl glycidyl ether (96.7%) for allyl glycidyl ether (97.5%), and 1,2-epoxyhexane (100% for) at the reaction time of three hours (3h) [101,102].

Ramalingam et al. [102] and our group recently reported halide ion-modified mesoporous silica catalysts for solvent-free cycloaddition of styrene oxide with CO₂. For above reaction, imidazole was first immobilized on MCM-41 (derived from biomass materials) using 3-chloropropyltriethoxysilane (CPTES) as the anchoring agent followed by alkylation with 1,2-dibromoethane at 110 °C. The prepared catalyst was mentioned as MCM-41-Imi/Br. The catalyst was used in the cycloaddition of styrene oxide, glycidol, epichlorohydrin and phenyl glycidyl ether, and allyl glycidyl ether.

The halide ion (Br) and the tertiary amine from imidazole anchored over mesoporous support (MCM-41-Imi/Br) involved in the ring opening and activation of CO₂. In Scheme 7, the mechanism of ring opening of the epoxide carried out by a nucleophilic attack by the bromide ion at the less sterically hindered β-carbon resulted to the formation of haloalkoxy species.



Scheme 7. Mechanism of the halide ion (Br) and the tertiary amine from imidazole anchored over mesoporous support (MCM-41-Imi/Br) catalysts on cycloaddition of epoxide with CO₂.

5. Conclusions

The present review explained the different types of porous and mesoporous solid acid-base and ionic liquid-modified mesoporous catalysts for the effective conversion for cycloaddition reaction of various epoxide with CO₂. In addition, the influence of various parameters, such as reaction temperature, pressure, and usage of solvents or solvent-free conditions, is discussed.

Both excellent selectivity and good yield were obtained for cyclic carbonates under tuned reaction conditions by ionic liquid immobilized MCM-41 catalyst. The higher yields were obtained for the conversion of cyclic epoxides. The above higher conversion proves that the value of the development of ionic liquid-based mesoporous catalytic materials and their future applications. The mechanism insight of ring opening of epoxide at various catalyst systems has also been discussed. The Ft-IR spectroscopy is very useful to exploit the activation mechanism of CO₂ for cycloaddition reaction using the various amine-functionalized solid catalyst. Hence, the development of a hybrid composite catalyst based on ionic liquid could be the potential material for direct usage of emerging greenhouse gas for various chemical processes.

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