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Halide aided synergistic ring opening mechanism of epoxides and their cycloaddition to CO_2 using MCM-41-imidazolium bromide catalyst

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ABSTRACT

Imidazole was immobilized on MCM-41 using 3-chloropropyltriethoxysilane (CPTES) as the anchoring agent followed by alkylation with 1,2-dibromoethane at 110 °C. The resulting catalyst was designated as MCM-41-Imi/Br. The catalyst was used for the synthesis of cyclic carbonates via cycloaddition of CO_2 with several epoxides under solvent free condition. The use of MCM-41-Imi (without bromide ion) to catalyze the reaction led to the elucidation of the reaction mechanism involved in the synergistic catalysis. The catalyst was used in the cycloaddition of styrene oxide, epichlorohydrine, glycidol, allyl glycidyl ether and phenyl glycidyl ether. A high yield and excellent selectivity of cyclic carbonates were obtained under optimized conditions. The yields of the respective cyclic carbonates 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.

1. Introduction

Cyclic carbonates have been produced conventionally by reacting phosgene ($COCl_2$) with ethane-1,2-diol in the presence of an excess amount of dichloromethane as solvent. Hydrochloric acid and chlorinated solvents are produced as byproducts that are harmful to human and the environment [1]. Due to the extreme toxicity attributed to phosgene, CO_2 seems to be the most appropriate substitute. Carbon dioxide is a greenhouse gas found to be present in the atmosphere at a concentration of 398.58 ppm [2]. The rising demand of cyclic carbonates has also resulted in the need to look for safer and greener techniques for its synthesis. Scheme 1 shows the reactions used to synthesize cyclic carbonates using the traditional route and the new green route. The use of carbon dioxide will also help to reduce the amount of carbon dioxide in the atmosphere. Although this will not be enough to reduce global warming, it will at least help to reduce the amount of carbon dioxide in the environment. It has been known that CO_2 can be incorporated into epoxides without the formation of byproducts [3]. However, due to the inert nature of CO_2, its activation and incorporation into epoxides remains inadequately explained and are actively being investigated.

One of the main factors that can accelerate the reaction between CO_2 and epoxide are the catalysts that are used in the reaction. A wide range of homogeneous and heterogeneous catalysts has been developed to catalyze the reaction between CO_2 and epoxides to form cyclic carbonates. Homogeneous catalysts, such as $CoCl_2$/onium salt [4], diimine Ru(II) complex [5], Al-salen-PEA [6], betaine-based quaternary ammonium ion and carboxylic acid [7], DMF [8,9], $Au/Fe(OH)_3–ZnBr_2/Bu_4NBr$ [10], ionic liquid with highly cross linked polymer [11], $BrBu_3PPEG_{600}PBU_3Br$ [12], cellulose/KI [13], and Au/R201 [14] have been studied. Several heterogeneous catalysts, such as metal oxides; MgO [15,16], Nb_2O_5 [1], Mg–Al oxide [17], guanidine-MCM-41 [18], Adeine-Pr-Al-SBA-15 [19], Cr-salen-SiO_2 [20], Mn-salen-SiO_2 [21], ClAlPC-MCM-41 [22], as-synthesized MCM-41 [23], Ti-SBA-15-Pre-Ade [24], 3-(2-hydroxyl-ethyl)-1-propyl imidazolium bromide-SBA-15 [25] and zeolite based organic-inorganic hybrid catalyst [26] have also been investigated. Both homogeneous and heterogeneous catalysts have their own advantages and disadvantages. The major problem associated with most homogeneous catalyst is the difficulty in the separation of the catalyst from the reaction mixture and recycling of the catalyst. These drawbacks has been overcome in heterogeneous catalyst system.

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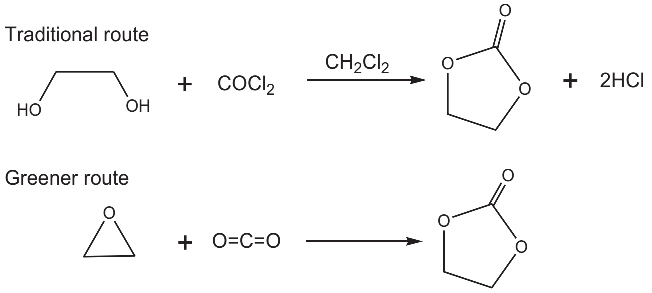


Scheme 1. The synthesis of cyclic carbonates via traditional route and greener route.

The catalyst is crucial to activate the CO_2 in the chemical reaction. Lu et al. [22] had used MCM-41 supported aluminium phthalocyanine (AlPc) complex for the reaction of CO_2 and epoxides. It required a co-catalyst, n-Bu_4NBr which enhanced the reaction as well as gave high catalytic activity. The activation of CO_2 was initiated by nucleophilic attack of the alcoholate ($-OCH_2CH_2Br$) on the carbon atom of CO_2 which was aided by the weak interaction between the central metal ion of (ClAlPc) and the lone pair electron of one of the oxygen of CO_2. The catalyst showed a synergistic effect during the reaction that resulted in the insertion of CO_2 to the Al—O bond of Pc(Cl)Al—OCH_2CH_2Br. This formed a linear carbonate, which converted into cyclic carbonates by the intramolecular substitution of the halides. Nevertheless, the mechanism for the formation of cyclic carbonates by this binary catalyst has not been reported. Qiao et al. [27] had reported that imidazolium-styrene copolymer supported zinc catalyst which was denoted as Zn/PS-IL[X] ($X = Br^-$, Cl^-, BF_4^-, PF_6^-) was a suitable catalyst for the cycloaddition of CO_2 to styrene oxide (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}.

In 1992, researchers at the Mobil Oil Cooperation successfully synthesized MCM-41 (hexagonal) [28] and MCM-48 (cubic) materials from silica [29]. These materials had amorphous silica wall with long range ordered framework with uniform mesopores. These materials have been used in catalysis, as adsorbents and recently in drug delivery systems. Due to the tremendous interest in the area of catalysis, MCM-41 has been utilized for various chemical reactions and has shown remarkable catalytic activity. These materials are of particular interest due to the well-ordered mesopores with high accessibility for reactants as well as products. Moreover, this materials can be used to synthesize hybrid organic-inorganic materials with an ionic liquid functionality unit as part of the solid network. The ionic liquid being connected to the surface of MCM-41 through an appropriate linker.

In this study, the silica from RHA [30–34] was converted to MCM-41 and used as support for heterogeneous catalyst to synthesize cyclic carbonates. The production of cyclic carbonates in high yield not only depends on the catalyst, but also on other reaction parameters such as temperature, pressure, catalyst amount and reaction time. The optimized conditions vary depending on the type of epoxide and the active site of the catalyst. In the past 10 years, there has been much research using a wide range of homogeneous and heterogeneous catalysts with different epoxides. However, none of them studied the detailed reaction parameters for various epoxides with the same catalyst.

Recently, the synthesis and catalytic activity of MCM-41-Imi/Br [35] was reported. It was found that MCM-41-Imi/Br catalyzed the cycloaddition reaction between CO_2 and styrene oxide effectively under solvent free condition. As an extension to this work, herein we describe the systematic investigation leading to the mechanism of the cycloaddition reaction. This paper describes the role of the quaternary imidazolium center and bromide ion which is shown to play a synergistic role in the activation of the CO_2 and the subsequent ring opening of the epoxide. To the best of our knowledge, this is the first report that also show the important role of water molecules in the formation of intermediates and byproducts under CO_2 free condition. Based on the data obtained, a most likely reaction mechanism has been proposed.

2. Experimental

2.1. Material

The rice husk (RH), for the preparation of MCM-41 was obtained from a rice mill in Penang. Other materials used were nitric acid (Qrec, 65.0%), sodium hydroxide pellets (R&M Chemicals, 99.0%), acetone (Qrec, 99.5%), cetyltrimethylammonium bromide (CTAB) (Riedel-de Haen, 98.0%), 3-chloropropyltriethoxysilane (CPTES) (Sigma-Aldrich, 95.0%), toluene (Qrec, 99.5%), acetonitrile (Qrec, 99.5%), 1,2-dibromoethane (Merck, >99.0%), imidazole (Scharlau, 99.0%), styrene oxide (SAFC, >97.0%), epichlorohydrin (FlukaChemika,99%), glycidol (Aldrich, 96%), allylglycidyl ether (Aldrich, >99%), phenyl glycidyl ether (Aldrich, 99%) and 1,2-epoxyhexane (Aldrich, 97%). The carbon dioxide was purchased from CAMBREX-HENKEL, Penang and used as received. All other reagents used were of analytical grade and used without further purification.

2.2. Synthesis of MCM-41-Imi/Br

The preparation of MCM-41-Imi/Br was carried out according to published method [35]. 2.0 g of MCM-41-Imi and 1.4 mL of 1,2-dibromoethane was refluxed at 110 °C for 24 h. The excess alkyl halide was filtered off, followed by repeated washing with dichloromethane. The resulting solid was dried in an oven at 100 °C. The yield of MCM-41-Imi/Br was 2.1 g with a BET surface area of 130 $m^2 g^{-1}$ [35].

2.3. Cycloaddition reaction and the analysis

In a typical catalytic reaction, epoxide (30 mmol) and 300 mg of the catalyst (MCM-41-Imi or MCM-41-Imi/Br) were charged into a high pressure laboratory autoclave, equipped with a magnetic stirrer and a heating mantle system. The reactor was carefully flushed once with CO_2. About 30 bar of CO_2 was dosed into the reactor, and heating and stirring started. Once the temperature reached 100 °C, the reaction was allowed to proceed for 4 h.

After the reaction was complete, the autoclave was allowed to cool down to room temperature, and the excess CO_2 was released by opening the outlet valve. After depressurization, the autoclave was opened slowly, and the reaction mixture was separated by filtration. To a 0.5 mL of the reaction product, 20 μL of cyclohexanol or acetophenone as internal standard was added. The resulting mixture was analyzed with gas chromatography (Clarus 500 Perkin Elmer) equipped with Elite Wax or Elite 1 capillary column (Perkin Elmer) and flame ionization detector. The reaction mixture was also analyzed by GC–MS (Clarus 600 Perkin Elmer) with a mass selective detector and helium as the carrier gas to identify the formation of products.

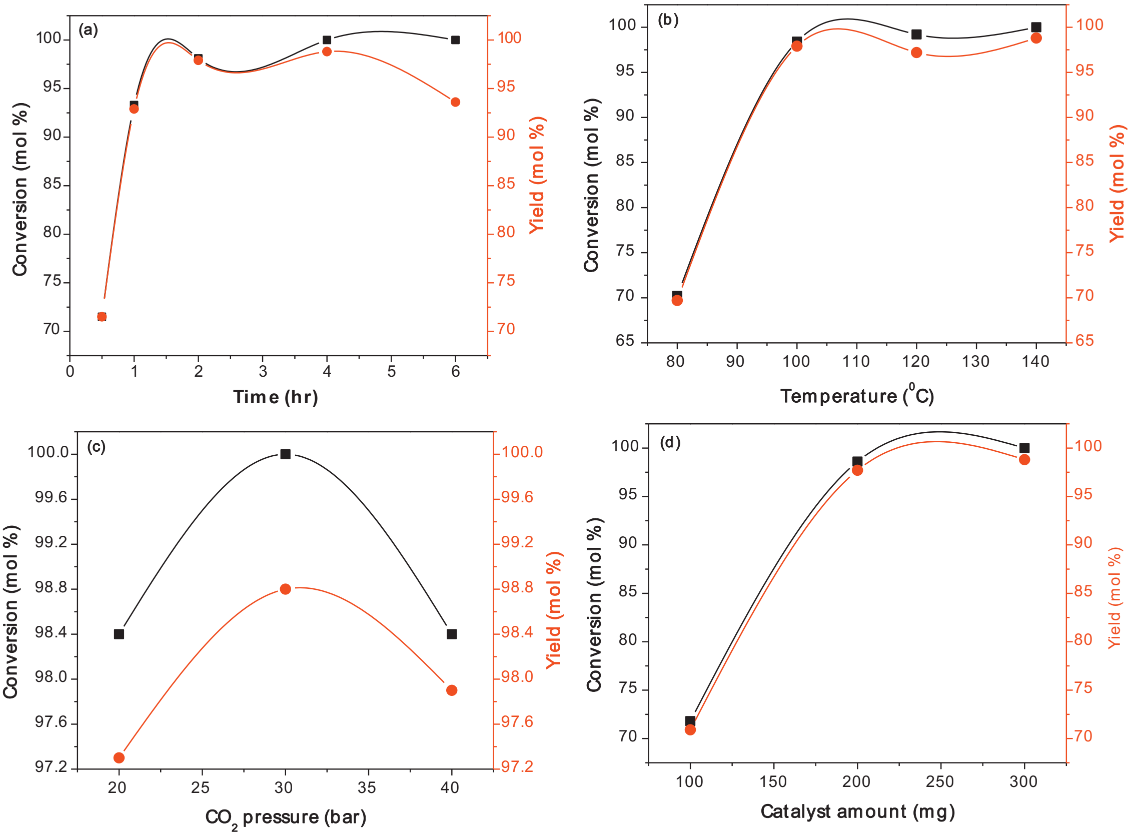


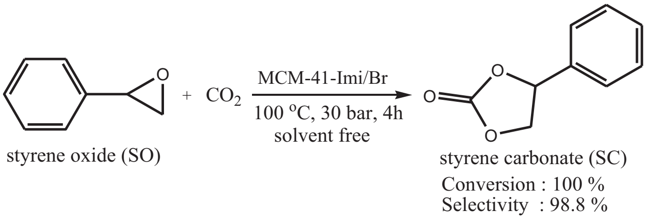
Fig. 1. The effect of different parameters on the synthesis of styrene carbonate (SC) from CO_2 under solvent free conditions. (a) The effect of reaction time (reaction conditions: temperature = 140 °C, pressure = 40 bar, catalyst amount = 300 mg), (b) The effect of temperature, (reaction conditions: time = 4 h, pressure = 40 bar, catalyst amount = 300 mg), (c) The effect of CO_2 pressure, (reaction condition: time = 4 h, temperature = 100 °C, catalyst amount = 300 mg), (d) The effect of catalyst amount, (reaction conditions: time = 4 h, temperature = 100 °C, pressure = 30 bar). In all the cases, the amount of styrene oxide = 3.5 mL (30 mmol).

3. Results and discussion

3.1. Catalytic performance of MCM-41-Imi/Br

3.1.1. Catalytic synthesis of styrene carbonate

The catalytic performance of MCM-41-Imi/Br was evaluated in the cycloaddition of CO_2 (40 bar) with styrene oxide (SO) (30 mmol) for 0.5–6 h to produce styrene carbonate (SC) as shown in Eq. (1).



(1)

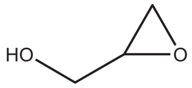
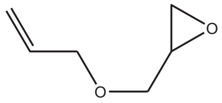
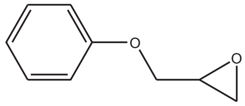
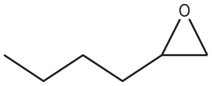
The effect of time, temperature, CO_2 pressure and catalyst amount on the cycloaddition of carbon dioxide with styrene oxide was investigated. No solvent was used in these reactions. The results are summarized in Fig. 1. As shown in Fig. 1(a), the SC yield increased with the reaction time up to a period of 4 h, after which no increase in SC yield was achieved. The results suggested that the CO_2 fixation of SO was completed within 4 h. On this basis, the experiment to assess other reaction parameters were performed for 4 h. Note that, a further increase in the reaction time led to a slight decrease in SC yield. This may be due to the formation of styrene glycol as byproduct. The yield of SC increased from 69.7 to 97.9% when the reaction temperature was raised from 80 to 100 °C, and remained unchanged at 120 °C (Fig. 1(b). It is known that, the activation energy for the synthesis of polycarbonates is usually lower than that for the thermodynamically favored cyclic carbonates.

Thus, at lower temperature (80 °C), the reaction rate was low but enhanced the selectivity toward the polycarbonates. The yield increased with the reaction temperature up to 140 °C. However, a slight reduction in the selectivity was observed at 140 °C as compared to 100 °C. The main reason may be that the high temperature might be favorable for the increase in the byproducts.

The influence of CO_2 pressure on the styrene oxide conversion and product yield are shown in Fig. 1(c). At 20 bar, the conversion of styrene oxide was 98.4% and achieved 100% at 30 bar. However, further increase in the pressure to 40 bar caused a decrease in the conversion. Thus, 30 bar was the optimum CO_2 pressure resulting in high yield. In addition, the CO_2 pressure and reaction temperature for optimum performance was dependent on the catalyst amount used. The use of 100 mg of the catalyst yielded lower conversion and SC yield compared with 200 and 300 mg (Fig. 1(d)). The higher catalyst mass (300 mg) led to maximum conversion of 100%. The complete conversion is not only due to the higher number of imidazolium units (1.03 mmol g^{-1}) but also to the influence of the electron density, the high surface area of the host material (1115 $m^2 g^{-1}$), and the ease of formation of ionic interactions with the styrene oxide, leading to favorable adsorption onto the active sites [35,36]. Therefore, the optimized conditions of the reaction was determined to be 100 °C, 30 bar CO_2 pressure, 300 mg catalyst and 4 h reaction time.

As comparison, a similar experiment was carried out with MCM-41-Imi (without bromide ion). MCM-41-Imi performed poorly

Table 1
Cycloaddition of CO_2 with epoxides catalyzed by MCM-41-Imi/Br under different optimized conditions.[a]

Entry	Substrate	Temperature (°C)	Pressure (bar)	Time (h)	Conversion (mol %)[b]	Selectivity (mol %)[b]	Yield (mol %)[b]	TOF[c]
1	 (EPCH)	90	25	4	100	97.0	97.0	23.5
2	 (GOH)	90	20	4	100	98.3	98.3	23.9
3	 (AGE)	120	60	6	99.0	98.5	97.5	15.8
4	 (PGE)	100	20	3	96.7	100	96.7	31.3
5	 (EH)	100	20	3	100	100	100	32.4

[a] Reaction conditions: 30 mmol substrate, 300 mg MCM-41-Imi/Br.
[b] Determined by GC.
[c] Turnover frequency: moles of cyclic carbonate produced per mole of quaternary imidazolium ion per hour.

(yield: 16.0%). The MCM-41-Imi/Br gave higher yield due to the synergistic effect of the quaternary imidazolium ion with the active (free) bromide ion. Such a free bromide ion is not present in MCM-41-Imi. Thus, we can conclude that the presence of the quaternary imidazolium ion and the Br^- ion helped to promote a synergistic effect to enhance the reaction. Note that a previously reported heterogeneous catalyst, MCM-41-TBD (a guanidine catalyst) required higher temperature (140 °C), 50 bar CO_2 pressure, with acetonitrile as solvent and took about 70 h to give 90.0% yield of styrene carbonate [18].

Lately, Zalomaeva et al. [37] had developed metal–organic-framework (MOF), i.e. Cr-MIL-101 as a heterogeneous catalyst for the production of styrene carbonate. The catalytic activity required a low temperature of 25 °C and low pressure of CO_2 (8 bar). However, a longer reaction time of 48 h was needed to obtain a yield of 95% with tetrabutylammonium bromide as the co-catalyst. This makes the MOF catalyst unfavorable from the points of view of reaction time.

3.1.2. *Parametric studies for other epoxides*

The effect of temperature, CO_2 pressure, catalyst amount and reaction time on the cycloaddition of CO_2 with epichlorohydrin (EPCH), glycidol (GOH), allyl glycidyl ether (AGE), phenyl glycidyl ether (PGE) and 1,2-epoxyhexane (EH) were investigated using MCM-41-Imi/Br as the catalyst. The number of moles of reactant was set at 30 mmol for all the respective epoxides. The result of the study is shown in Table 1.

The rate at which the cyclic carbonates are synthesized is given as turnover frequencies (TOF), calculated on the assumption that the imidazolium ion were the active site. The results shown in Table 1 clearly show that epichlorohydrin (entry 1) and glycidol (entry 2) converted to chloropropene carbonate (CC) and glycerol carbonate (Gc) with the yield of 97.0 and 98.3% respectively with the TOF values of ~24 h^{-1}. Both epoxides needed a lower reaction temperature of 90 °C and a reaction time of 4 h to attain the respective yields. However, the CO_2 pressure for optimal performance for both reactions were significantly lower than for SO. Epichlorohydrin required slightly higher CO_2 pressure as compared with glycidol. The selectivity of both cyclic carbonates was lower due to CO_2 pressure or temperature employed for the reaction. At low temperature, the CO_2 dissolves in the epoxides and liquefies, leading to the formation of a CO_2-epoxide complex. This will indirectly reduce the interaction between epoxide-catalyst or CO_2-catalyst and lead to low catalytic activity. Such observation of CO_2 pressure and temperature in catalysis has been observed by others [7,25].

In order to verify the advantage of this study, MCM-41-Imi/Br was compared with ZIF-8 functionalized ethylenediamine which was developed recently by Miralda et al. [38]. The ZIF-8 system consists of organic–inorganic active sites with a surface area of 1096 $m^2\ g^{-1}$. However, it has a major drawback due to the large number of byproducts at the optimum condition and thus the system still remains unfavorable.

In contrast, a relatively longer reaction time (6 h) and a much higher pressure (60 bar) was needed to convert AGE into allyl glycidyl carbonate (AGC) (Table 1, entry 3). When the reaction was carried out at low temperature (80 °C), about 67.1% yield was achieved. However, when the reation temperature was increased to 120 °C, AGC selectivity dramatically increased from 67.1% to 98.5%. The results indicated that a reaction temperature of 120 °C was necessary for the complete conversion (~99.0%) of AGE using

Table 2
Influence of the catalyst amount on the yield of the cycloaddition of CO_2 with epoxides.

Catalyst amount (mg)	Yield (mol %)				
	EPCH[a]	GOH[a]	AGE[b]	PGE[c]	EH[d]
100	91.2	83.6	72.0	88.1	98.3
200	92.4	92.6	100	97.9	99.1
300	97.0	98.3	97.5	99.2	100

Reaction condition: Substrate: 30 mmol, solvent less.

[a] Temperature: 90 °C, pressure: 25 bar, time: 4 h.

[b] Temperature: 120 °C, pressure: 60 bar, time: 6 h.

[c] Temperature: 100 °C, pressure: 20 bar, time: 6 h.

[d] Temperature: 100 °C, pressure: 20 bar, time: 4 h.

MCM-41-Imi/Br as the catalyst. The TOF value (15.8 h^{-1}) for this reaction is the lowest compared with other epoxides. As can be seen from (Table 1, entry 4 and 5) 100% selectivity of phenyl glycidyl carbonate (PGC) and 4-butyl-1-3-dioxolan-2-one could be obtained from PGE and EH respectively under the same reaction conditions, i.e. 100 °C, 20 bar and 3 h reaction time. These results are unexpected because both epoxides contain different substituents and different chemical and physical properties. However, a small decline in the conversion of PGE was observed possibly due to the side reaction of the cyclic carbonate. Similar work was carried out by Xiao et al. [39] and Zhou et al. [7] using immobilized ionic liquid–$ZnCl_2$ and betaine based catalyst respectively under harsher reaction conditions as compared with the present work.

Apart from the influence of temperature and pressure, the cycloaddition reaction was also affected by the amount of catalyst. Table 2 shows the influence of the catalyst amount on the yield for each epoxide. Increasing the amount of MCM-41-Imi/Br from 100 mg to 300 mg enhanced the catalytic activity. This is certainly due to the amount of quaternary imidazolium ion per unit surface area (7.92×10^{-3} mmol m^{-2}) and bromide ion (0.44 mmol g^{-1}) would increase, resulting in higher yield of the desired products, as shown in Table 2.

The influence of reaction time on the yield was also investigated as MCM-41-Imi/Br could offer a higher yield of product for the CO_2 cycloaddition with different epoxides. The results (Table 1) indicated that the reaction time of 4 h was necessary for the complete conversion of EPCH and GOH under the selected reaction conditions.

A relatively long reaction time (6 h) was needed to complete the reaction for AGE, resulting in a product yield of 97.5% (AGC). Interestingly, with PGE and EH, 96.7 and 100% conversion was achieved in 3 h. However, no plausible explanation can be put forward for this fast reaction time with respect to their chemical structure.

3.2. *The systematic steps leading to the mechanism of the cycloaddition*

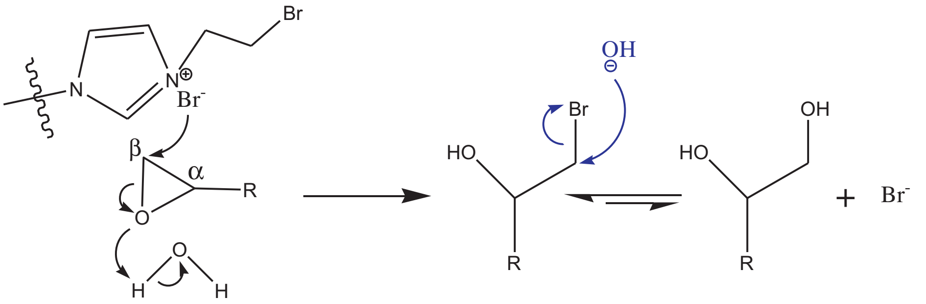
3.2.1. *Ring opening of epoxides using MCM-41-Imi/Br*

It is well known that the ring opening of the epoxide involves two pathways: (i) cleavage by Lewis acids and (ii) cleavage by Lewis base. Pescarmona et al. [40] in their recent review described the ring opening of SO via the α-carbon due to the electron-withdrawing inductive effect of the phenyl group. Thus, the electron-withdrawing nature of the aromatic ring favors the back-biting reaction after the insertion of CO_2 to an intermediate to form the SC [41]. However, in this work the ring opening of SO occurred at the less sterically hindered carbon atom of SO ring (β-carbon) (Schemes 2 and 3).

In order to demonstrate the opening of the epoxide ring by a nucleophilic reagent (Br^- ion) at the β-carbon, the MCM-41-Imi/Br was heated at 100 °C together with SO in the absence of CO_2 for 4 h. The resulting products were analyzed by GC–MS. The reaction between MCM-41-Imi/Br with styrene oxide showed two peaks in the GC–MS which correspond to 2-bromo-1-phenylethanol (as the major product) and a minor byproduct, styrene glycol (Fig. 1 of the Supplementry Information).

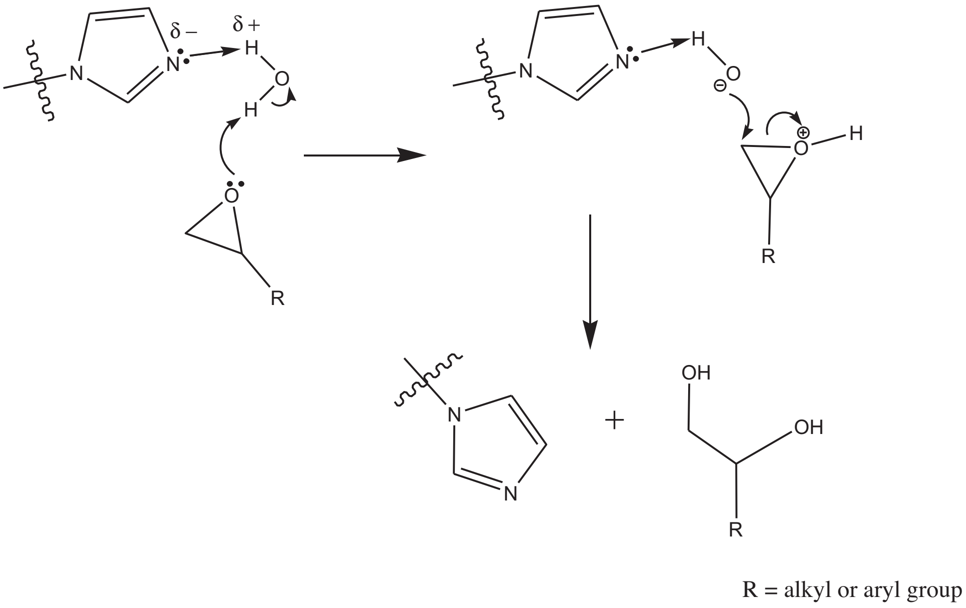
A possible reason for the presence of the hydroxyl group in the reaction intermediate and byproduct may be due to the interaction of H—OH molecules present in the catalyst. Recently, Dai et al. [25] reported the use of 3-(2-hydroxyethyl)-1-propyl imidazolium bromide-SBA-15 (HEPIMBr) catalyst for the synthesis of cyclic carbonates. They proposed that, the intermediate formation occurred when the H atom of the silyl-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. Nevertheless, no evidence was given for the ring opening process.

In the case of aliphatic terminal epoxide (EH), the nucleophilic attack also happens at the less sterically hindered carbon atom of the epoxide ring (β-carbon). This is due to higher accessibility and the electron-donating effect of the alkyl group. Thus, EH is more easily converted to 4-butyl-1,3-dioxolan-2-one without any byproducts in a shorter reaction time. On the other hand, for epoxide such as AGE, the ether group influenced the course of the reaction leading toward cyclic carbonate formation. However, harsher reaction condition was needed for the conversion of AGE to attain maximum yield. Surprisingly, milder reaction condition was observed for PGE in comparison with AGE. One plausible reason for this is the electronic π-system of the benzene ring in PGE is able to form a stable interaction with the quaternary imidazolium ion on the catalyst. This leads to a stable intermediate, thereby reducing the temperature and a shorter reaction time. Since the role of



R = alkyl or aryl group

Scheme 2. Reaction of MCM-41-Imi/Br with epoxide in the absence of CO_2: Most likely position for a nucleophilic attack of the ring and possible role of water molecule in the formation of intermediate and/or byproduct.



Scheme 3. Reaction of MCM-41-Imi with epoxide in the absence of CO_2: The role of water molecule in the formation of byproduct.

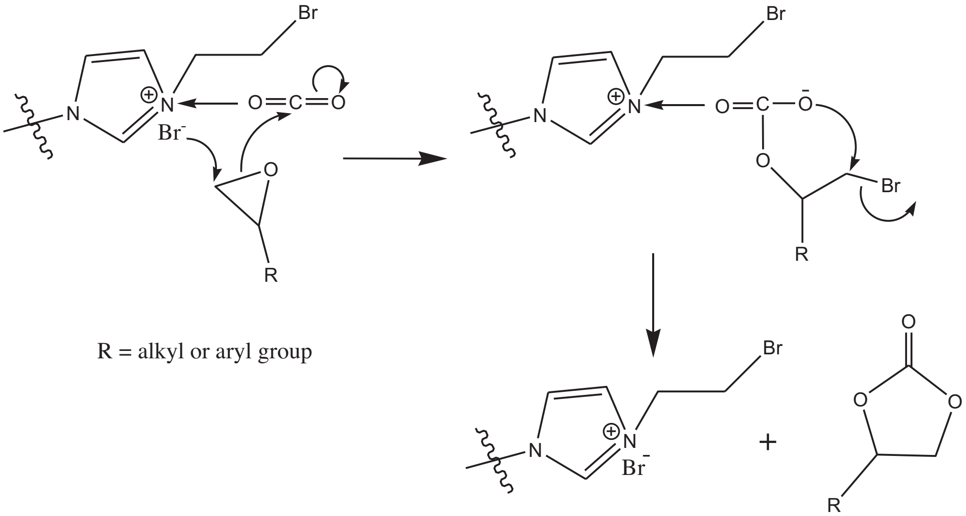
the quaternary imidazolium ion is also to fix the carbon dioxide on the catalyst, the proximity thus generated between the CO_2 and the epoxide would have reduced the activation energy much more significantly to afford much milder condition for the reaction of PGE with the CO_2. However, this needs to be investigated in more detail.

3.2.2. *Ring opening of epoxides using MCM-41-Imi*

The MCM-41-Imi (without Br^- ion) was employed as a control catalyst in the same manner to study the process of the ring opening of styrene oxide. The reaction between MCM-41-Imi and styrene oxide shows the formation of styrene glycol as a major product. However, a mixture of minor products, 2-phenylethoxy-1-phenylethanol and its isomer, 2-phenylethoxy-2-phenylethanol were also identified which could be formed due to the reaction between styrene oxide and styrene glycol (Fig. 6 of the supplementary Information). However, the GC–MS was not able to separate these isomers under the analytical condition used.

3.2.3. *Effect of water*

The effect of water in the cycloaddition reaction (CO_2 with SO) over MCM-41-Imi/Br was investigated to further proof the reaction mechanism. In the absence of water in the reaction, the SC yield was maximum at 98.8%. Further addition of water results in decline in SC yield; when the ratio of H_2O/SO was 0.3, the SC yield was found to be 86.3%. It can be concluded that, the addition of water has a negative effect on the selectivity to SC. The byproduct of styrene glycol was found to be higher in the presence of water in this reaction. A systematic investigation was conducted by Dai et al. [25] on the effect of water on the cycloaddition reaction over SBA-15-HEPIMBr. They found that when the ratio of H_2O/PO was 0.01, the PC yield was higher, and when it was 0.2, the PC yield decreased. A trace amount of water had



Scheme 4. The proposed reaction mechanism for cycloaddition of epoxide and CO_2 catalyzed by MCM-41-Imi/Br: The simultaneous activation of epoxide and CO_2 on the catalyst.

positive effect on PO conversion. It is proposed that the OH groups of water play a similar role to that of hydroxyl-functionalized ionic liquid (HIL) in the cycloaddition reaction.

3.3. Reaction mechanism

Based on the results and discussion above, a mechanism for the formation of cyclic carbonates is proposed, which is shown in Scheme 4. This mechanism is different from that proposed by Udayakumar et al. [42] in which there are two steps: (i) a reversible reaction between the oxirane and catalyst to form an intermediate complex and (ii) an irreversible reaction between the intermediate and CO_2 to form the cyclic carbonate. However, they did not furnish evidence for this mechanism.

In this study, however, it was demonstrated that the ring opening of the epoxide takes place by means of a nucleophilic attack by the bromide ion at the less hindered β-carbon, forming the haloalkoxy species. Simultaneously, the CO_2 is attached to the quaternary imidazolium ion by way of a coordinate bond. The proximity of these two species on the catalyst leads to an efficient interaction between the haloalkoxy anion species with the adsorbed CO_2, leading to the formation of a halocarbonate anion. Finally, the corresponding cyclic carbonate is formed through the intramolecular attack by the carboxyl anion on the halogen bearing carbon, releasing the catalyst and making it available to continue the reaction. Therefore, in this catalytic system the quaternary imidazolium ion and the bromide anion exhibit a synergistic effect to promote the reaction, which is responsible for the high catalytic activity and selectivity. It has been shown that, for the same catalyst, the reaction rate was different for different epoxides. Both stearic and electronic effects of the epoxides play a pivotal role in determining the efficacy of the synergistic active sites.

4. Conclusion

In conclusion, the quaternary imidazolium center and the bromide ion functionalized on MCM-41 promoted the cycloaddition of CO_2 with a wide range of epoxides to produce the corresponding cyclic carbonates in excellent yield under mild conditions. The catalyst showed a synergistic effect with the bromide anion. It was shown that the bromide ion attacks the epoxide on the less hindered carbon. This novel hybrid inorganic-organic catalyst system of MCM-41-Imi/Br enables a co-catalyst-free, phosgene-free, solvent-free reaction to be possible. Compared with the heterogeneous catalysts reported in the literature, MCM-41-Imi/Br catalyst is much more active and selective for the cycloaddition of CO_2 onto a wide range of epoxides. The use of this catalyst does not produce adverse byproducts and thus, is a zero-waste and 100% atom efficient system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.02.008.

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