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# Silica grafted ammonium salts based on DABCO as heterogeneous catalysts for cyclic carbonate synthesis from carbon dioxide and epoxides

Abdol R. Hajipour [a,b*], Yasaman Heidari [a] and Gholamreza Kozehgary [c]

1, 4-diazabicyclo [2.2.2] octane (DABCO) based ammonium salts immobilized on functionalized silica ascertained to be an effective heterogeneous catalyst for the cycloaddition reaction of carbon dioxide with epoxide under green reaction conditions without utilization of metals and any organic solvents. N-Benzyl DABCO bromide as a homogeneous analog of catalyst exhibited a lower catalytic activity than the supported catalyst. This is probably due to Si-OH groups on the silica surface which exhibited a synergistic effect with the halide anions. The effects of the grafted ammonium salts' structures and various reaction parameters on the catalytic activity were also investigated. The catalyst could be recovered in a facile way from the reaction mixture and also exhibited good reusability.

## Introduction

Nowadays, the development of catalytic processes for the efficient utilization of naturally abundant carbon dioxide, one of the greenhouse gases, has drawn much attention.[1,2] Since $CO_2$ is an abundant, nontoxic, inexpensive, and highly functional carbon resource, it became a very attractive environmentally benign feedstock for manufacturing useful chemical compounds,[3,4] as nature uses the fixation of carbon dioxide by green plants to make glucose by photosynthesis and regulate the atmospheric $CO_2$.

One of the few commercial synthetic processes utilizing $CO_2$ as a raw material is the insertion of $CO_2$ into epoxides to produce five-membered cyclic carbonates.[5-7] This is an attractive process in terms of green chemistry and atom efficiency, since $CO_2$ reacts with epoxides without formation of any by-product.[8] Cyclic carbonate products are widely used not only as polar aprotic solvents in organic and polymeric synthesis but also as intermediates in the syntheses of pharmaceuticals.[9-11]

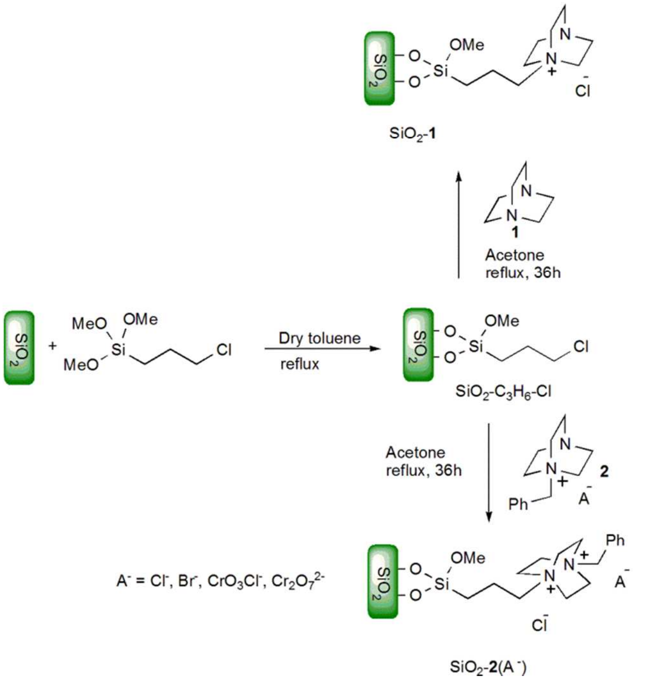
In the past decades, various homogeneous and heterogeneous catalytic systems such as quaternary ammonium and phosphonium salts,[12-17] various ionic liquids (ILs),[18-20] metal oxides,[21,22] alkali metal salts,[23-25] and other transition-metal complexes[26-28] have been developed for the cycloaddition reaction of carbon dioxide and epoxides. However, using solvents or homogeneous additives, metal based catalyst and harsh reaction conditions (high pressures and/or high temperatures) are needed in most of these catalyst systems. Hence, the development of new and environmentally friendly catalyst systems for efficient production of cyclic carbonates under mild conditions still remains a challenge.

It has been reported that the use of silica-supported catalysts, which have both acidic and basic characteristics, are effective for the reaction of epoxides with $CO_2$.[10,29,30] In these systems, the cooperative action of the silanol groups and the nucleophile promotes oxygen atom coordination and the nucleophilic ring-opening of the epoxide. This fact encouraged us to support ammonium salts based on DABCO as a basic molecular part on an acidic solid support to result in an effective acid-base catalyst for the transformations of epoxides to cyclic carbonates. Compared with other ammonium salts, the use of DABCO based ammonium salts has advantages such as the facile preparation of various structures from DABCO and benzyl halides or alkyl halides, facility of handling and stability under air.

In this work, silica-supported ammonium salts based on DABCO were examined as acid-base bifunctional catalysts for cycloaddition reactions of carbon dioxide and epoxide.

## Results and discussion

At first, a variety of $SiO_2$-supported ammonium salts based on DABCO were prepared from the reaction of 3-chloropropyl silica and DABCO or [BnDABCO] (A)[31] as shown in Scheme 1. The immobilization of catalysts was confirmed with FT-IR spectroscopy, elemental analysis, titrimetric analysis, inductively coupled plasma analysis (ICP), TGA-DTA techniques, and Brunauer–Emmett–Teller (BET).



Scheme 1. The preparation of $SiO_2$-supported ammonium salts based on DABCO

In the FT-IR spectrum depicted in Fig. 1, the characteristic peaks of C–N stretching (1390 $cm^{-1}$), C–H stretching (3014, 2958, 2900 $cm^{-1}$), $CH_2$ bending (1460 $cm^{-1}$), Si–C stretching (1212 $cm^{-1}$), and Si–O stretching (1050-1110 $cm^{-1}$) vibrations are assignable to the supported catalysts (curves b–g).

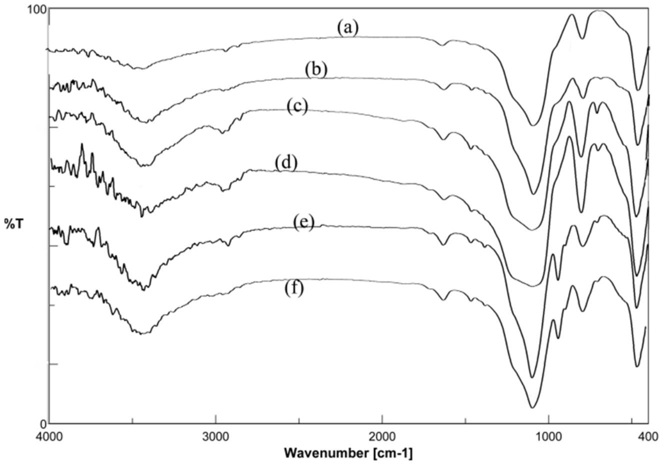


Fig. 1. FT-IR spectra of (a) $SiO_2$-$C_3H_6$-Cl, (b) $SiO_2$-**1**, (c) $SiO_2$-**2** (Cl), (d) $SiO_2$-**2** (Br), (e) $SiO_2$-**2** ($Cr_2O_7$), (f) $SiO_2$-**2** ($CrO_3Cl$)

The presence of the organic phase in the silica-supported ammonium salts was also confirmed by elemental and titrimetric analysis. The amount of grafted ammonium salts was determined by titrimetric analysis (TA) based on the chlorine content, with using a recent procedure[32] and by means of elemental analysis (EA) based on the nitrogen content. As shown in Table 1, the results obtained from titrimetric analysis are in good agreement with those of EA.

In the case of [BnDABCO]($CrO_3Cl$) and [BnDABCO]($Cr_2O_7$), the content of chromium was measured by ICP, which were 3.7% and 3.5%, respectively.

The supported catalyst N-Benzyl DABCO Bromide was investigated by thermogravimetric analysis in order to survey its thermal behaviour. The measurement was carried out in the temperature range of 30–800 °C at 20 °C/ min ramp in nitrogen atmosphere. As shown in Fig. 2, the TGA pattern showed three steps of weight reduction: The first mass loss, starting from 29 to 139 °C, was due to the elimination of water molecules adsorbed onto the surface of silica material[33,34], the second mass loss occurred between 194 and 289 °C and the third continuous weight loss occurred between 289–400 °C. Both of these mass losses were attributed to the decomposition of the organic groups on the silica surface. According to these mass losses, 0.61 mmol/g of N-Benzyl DABCO bromide was loaded on the silica support which is consistent with the elemental analysis and titrimetric analysis. Hence, it is indirect evidence for the successful grafting of N-Benzyl DABCO Bromide on the silica support.

Table 1. Elemental analysis (EA) and titrimetric analysis (TA) results

| Catalyst | N(Wt%) | H(Wt%) | C(Wt%) | Mmol/g$^{a}$ | Mmol/ g$^{b}$ |
|---|---|---|---|---|---|
| $SiO_2$-**1** | 1.74 | 2.27 | 9.08 | 0.62 | 0.61 |
| $SiO_2$-**2**(Cl) | 1.65 | 2.2 | 12.02 | 0.58 | 0.59 |
| $SiO_2$-**2**(Br) | 1.6 | 2.03 | 12.5 | 0.57 | 0.57 |
| $SiO_2$-**2**($Cr_2O_7$) | 1.6 | 2.12 | 9.71 | 0.57 | 0.56 |
| $SiO_2$-**2** ($CrO_3Cl$) | 1.9 | 2.33 | 9.7 | 0.68 | 0.66 |

$^{a}$Amount of catalyst based on EA
$^{b}$Amount of catalyst based on TA

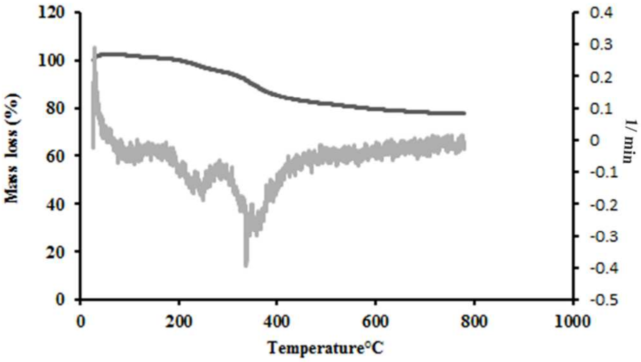


Fig. 2. The TGA/DTA analysis of $SiO_2$-**2** (Br) catalyst

Brunauer–Emmett–Teller (BET) gas-sorption was performed to determine the specific surface area and porous nature of the $SiO_2$-**2** (Br). Nitrogen adsorption–desorption isotherm curve of the catalyst is shown in Fig. 3 According to the IUPAC classification of physisorption isotherms, the catalyst exhibits the typical type IV with H1-shaped hysteresis loops which is associated with capillary condensation.[35] The BET analysis displayed the specific surface area of $SiO_2$-$C_3H_6$-Cl was 382 $m^2 g^{-1}$, while the specific surface areas of $SiO_2$-**2** (Br) was 296 $m^2g^{-1}$. The reduction in the surface area of $SiO_2$-**2** (Br) could result from the decrease of the surface sites due to the immobilization of N-benzyl DABCO bromide. In addition, the BET surface area, pore size and pore volume of the catalyst is listed in Table 2.

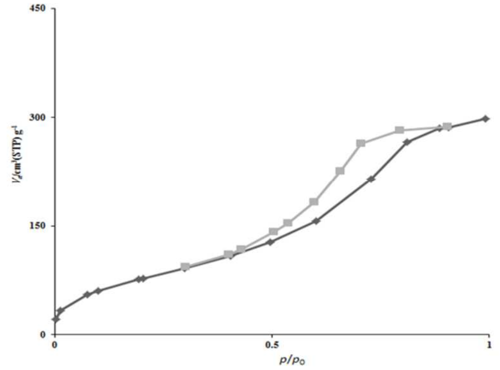


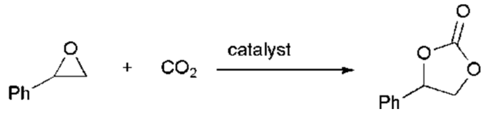
Fig. 3. $N_2$ adsorption–desorption isotherm of $SiO_2$-**2** (Br)

Table 2. The result of BET analysis for $SiO_2$-$C_3H_6$-Cl, $SiO_2$-**2** (Br).

| Sample | Specific surface area ($m^2 g^{-1}$) | Average pore volume($cm^3 g^{-1}$) | Average pore diameter (nm) |
|---|---|---|---|
| $SiO_2$-$C_3H_6$-Cl | 382 | 0.40 | 5.2 |
| $SiO_2$-**2** (Br) | 296 | 0.56 | 6.2 |

The catalytic performance of $SiO_2$-supported ammonium salts based on DABCO in the cycloaddition reaction of $CO_2$ to epoxides was initially probed using styrene oxide (SO) as a model substrate. The results are depicted in Table 3. The control reaction employing N-Benzyl DABCO bromide as a homogeneous catalyst was also conducted, which gave 1.7% yield (Table 3, entry 1). However, with the silica-immobilized catalyst, the materials dramatically became active, increasing the yield up to 91% (Table 3, entry 3). This is probably due to the activation of epoxide assisted by silanol groups on the silica surface which acts as an acid site (see scheme 2). It can be seen from Table 3, $SiO_2$-**1** which contains basic active site afforded styrene carbonate (SC) in 74% yield (Table 3, entry 2). While after the quaternisation, catalytic activity increased when $SiO_2$-supported N-Benzyl DABCO chloride (Table 3, entry 3) or bromide (Table 3, entry 4) was used, with yields of 80% and 91.4% respectively. since the bulkiness of $SiO_2$-supported N-Benzyl DABCO ion makes the electrostatic interaction between the anion and the cation weaker and consequently increases the availability of the anion. The cyclic carbonate product did not obtain when $SiO_2$-$C_3H_6$-Cl was used as catalyst (Table 3, entry 9).

Table 3. Reaction of styrene oxide with $CO_2$ utilizing various catalysts[a]



| Entry | Catalyst system | T/°C | Yield (%)[c] | Selectivity(%)[c] |
|---|---|---|---|---|
| 1[b] | [BnDABCO]Br | 100 | 1.7 | 38 |
| 2 | $SiO_2$-**1** | 100 | 74 | 88 |
| 3 | $SiO_2$-**2**(Cl) | 100 | 80 | 94 |
| 4 | $SiO_2$-**2**(Br) | 100 | 91.4 | 99 |
| 5 | $SiO_2$-**2**($Cr_2O_7$) | 100 | 15 | 25 |
| 6 | $SiO_2$-**2** ($CrO_3Cl$) | 100 | 19 | 30 |
| 7 | $SiO_2$-**2**(Br) | 120 | 92 | 99 |
| 8 | $SiO_2$-**2**(Br) | 80 | 76 | 78 |
| 9 | $SiO_2$-$C_3H_6$-Cl | 100 | Trace | 31 |

[a] Reaction conditions: SO (10 mmol), catalyst (0.5 g), $CO_2$ (4 atm), 24 h.
[b] [BnDABCO]Br (0.05mmol)
[c] Determined by GC using an internal standard technique.

It is generally known that the kinds of anions have a significant influence on catalytic activity during the cycloaddition of epoxides with $CO_2$.[36,37] Therefore, $SiO_2$-**2** (A) with different anions including $Br^-$, $Cl^-$, $Cr_2O_7^{2-}$and $CrO_3Cl^-$ were used to catalyzed this reaction. As shown in Table 3, the conversion decreased in the order of $Br^-$> $Cl^-$> $CrO_3Cl^-$>$Cr_2O_7^{2-}$ (Table 3, entries 3-6). Essentially, as easily seen, catalysts containing halide anions exhibited a considerable activity for cycloaddition reactions (Table 3, entries 2-4), probably because of the moderate nucleophilicity and leaving ability of these anions.[38] $SiO_2$-**2** (Br) showed higher catalytic activity than $SiO_2$-**2** (Cl) (entry 4 vs 3), since $Br^-$ have higher nucleophilicity and better leaving ability. Hence, the silica-supported N-Benzyl DABCO bromide was selected as benchmark structure for further studies on the reaction parameters.

The influence of some reaction parameters on the catalytic activity of $SiO_2$-**2** (Br) was then investigated. As illustrated in Table 3, the temperature had a noticeable positive influence on the coupling reaction. At lower temperatures (80 °C), the yield of SC was obtained 76% (Table 3, entry 8) due to the low activity of the catalyst, whereas both yield and selectivity of SC were increased at 100°C (Table 3, entry 4). Further increase in the temperature has a negligible effect on the yield and selectivity (Table 3, entry 7). As a consequence, 100 °C was optimal.

Table 4 depicted the relationship between amount of the catalyst and SC yield. The amount of $SiO_2$-**2** (Br) catalyst was calculated using the EA data. The catalytic activity was found to increase when the amount of $SiO_2$-**2** (Br) catalyst increased from 0.46 mmol% to 1.24 mmol% due to the increase in the number of active sites available. However, the further increasing in amount of catalyst did not yield any significant increase in the conversion. Thus, 0.93 mmol% was found to be the optimum amount of catalyst for the reaction.

The influence of $CO_2$ pressure on the reactivity of the $SiO_2$-**2** (Br) catalyst is also shown in Fig. 4. The concentration of styren carbonate increased from 69 % to 94 %, when the $CO_2$ pressure was increased progressively from 1 to 4 atm. A further increase in pressure reduced the activity of the catalyst. Such an impact of pressure on the reaction has also been found on other catalytic systems.[39-41] Based on these report, it could be explained that higher $CO_2$ pressure could cause low SO concentration in the vicinity of the catalyst, which may result in low SC yield. A $CO_2$ pressure of 4 atm was the optimum pressure for the reaction utilizing $SiO_2$-**2** (Br) as the catalyst.

Table 4. Effect of different ammount of $SiO_2$-**2** (Br)

| Catalyst amount (g) | Amount of $SiO_2$-**2** (Br) (mmol%) | SC yield (%) |
|---|---|---|
| 0.3 | 0.46 | 80 |
| 0.4 | 0.62 | 89.4 |
| 0.5 | 0.77 | 92.5 |
| 0.6 | 0.93 | 94 |
| 0.7 | 1.24 | 94.1 |

Reaction conditions: SO (10 mmol), T (100 °C), initial $CO_2$ pressure (4 atm), reaction time (24 h), selectivity of SC >99%.

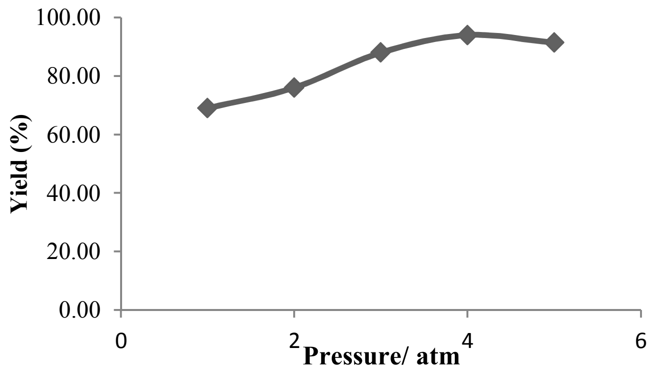


Fig. 4. Influence of the $CO_2$ pressure on the yield of SC. SO (10 mmol), cat. amount (0.6 g), 100 °C, 24 h.

The influence of reaction time on SC yield was investigated and the results are shown in Fig. 5. It can be seen that the yield of styrene carbonate at 4 h was 32 %, and this increased to a maximum of 94 % in 24 h. As expected, longer reaction times result in higher conversions because of the prolonged contact between the catalyst and the reactants. However, further increased in reaction time did not yield more reaction product. Therefore, a reaction time of 24 h was appropriate for the cycloaddition reaction in this study.

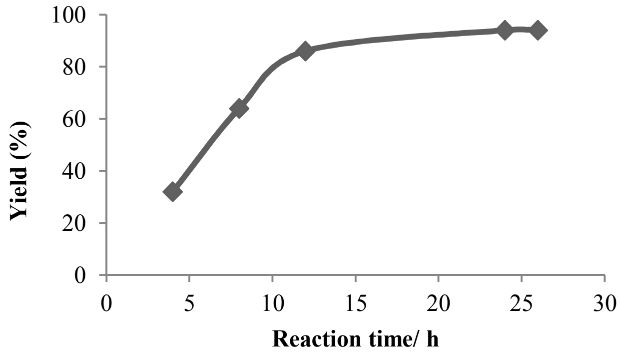


Fig. 5. Influence of the reaction time on the yield of SC for $SiO_2$-**2** (Br) (0.6 g) at 100°C and $CO_2$ pressure of 4 atm.

The reusability of $SiO_2$-**2** (Br) was carried out to probe the stability of the immobilized catalyst. In each case, the catalyst was separated by simple filtration from the reaction mixture and then rinsed with acetone and EtOAc, dried at 80 °C for 1 h and reused for next cycle. As shown in Fig. 6, the efficiency of the $SiO_2$-**2** (Br) decreased from 94% SC yield to closely 72% upon the fourth use, demonstrating some deactivation. Therefore, elemental analysis and titrimetric analysis carried out on four times used catalyst which exhibits that some of the active sites were lost, probably due to leaching (Table 5). The tendency of the catalyst to get leached being inevitable while recycling, this might come from the continuous heating. Poor reusability over catalysts of similar type has been reported in earlier studies.[40,42]

The FT-IR spectra of the fresh and four times used catalyst showed in Fig. 7. As can be seen, the recycled catalyst exhibited characteristic peaks of the $SiO_2$-**2** (Br) similar to those of the fresh one.

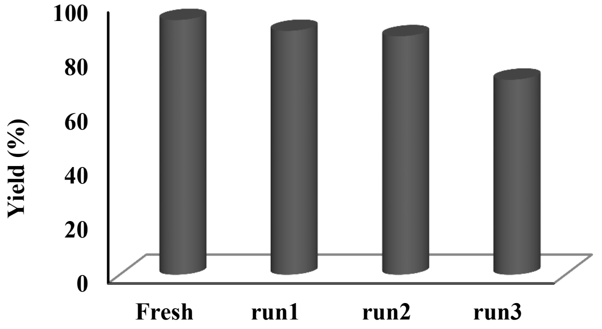


Fig. 6. The reusability results of the $SiO_2$-**2** (Br) catalyst Reaction condition: SO (10 mmol), catalyst (0.6 g), 100 °C, 24 h, $CO_2$ (4 atm),

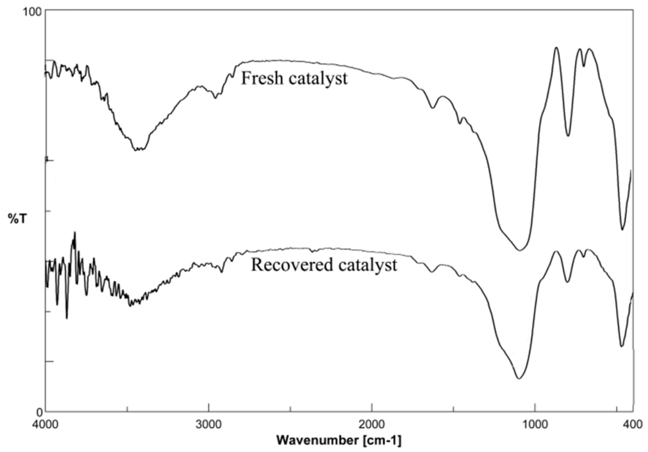


Fig. 7. The FT-IR spectrum of the fresh and recovered catalyst.

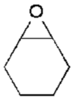
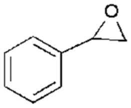
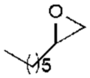
Table 5. EA results of the fresh and recovered catalyst.

| Catalyst | C (Wt%) | H (Wt%) | N (Wt%) | Mmol/g[a] | Mmol/g[b] |
|---|---|---|---|---|---|
| Fresh | 12.5 | 2.03 | 1.6 | 0.57 | 0.57 |
| Recovered | 12.1 | 1.01 | 1.12 | 0.36 | 0.37 |

[a]Amount of catalyst based on EA
[b]Amount of catalyst based on TA

in order to make it clear that the catalyst is thermally stable under the reaction conditions, the thermogravimetric analysis of the fresh catalyst and the four times used catalyst were made (Fig. S1, see ESI) This clearly indicates that the fresh and four times used catalyst showed two similar decomposition curves and could tolerate about 200 °C which is much higher than the reaction temperature (100 °C) in our catalytic experiments.
The performance of $SiO_2$-**2** (Br) in the cycloaddition reactions of other epoxides was investigated under the optimized reaction conditions and the results are shown in Table 6. The catalyst was found to be applicable to various terminal epoxides to afford the corresponding cyclic carbonates in high yields with excellent selectivity (up to 95%), whereas internal cyclohexene oxide exhibits the lowest activity even at prolonged reaction time ( Table 6, entry 3) probably due to steric hindrance which was also illustrated by other authors.[43-45]

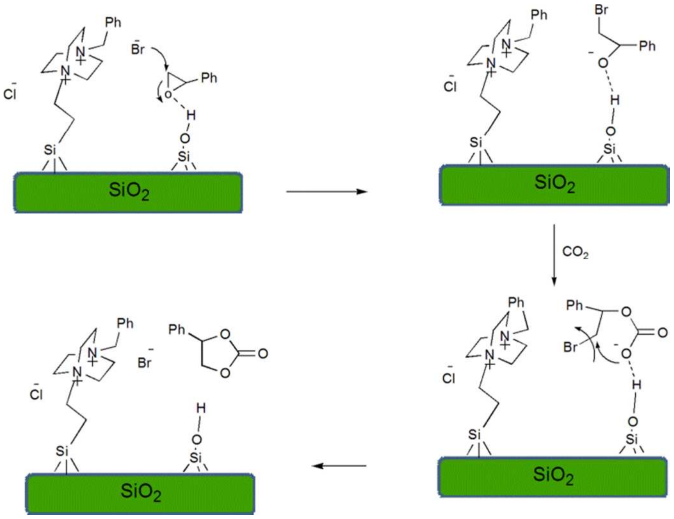
Table 6. Coupling of $CO_2$ with various epoxides catalyzed by $SiO_2$-**2** (Br)[a]

| Entry | Epoxide | Yield (%)[c] | Selectivity(%)[d] |
|---|---|---|---|
| 1 |  | 95 | 99 |
| 2 |  | 20 | 70 |
| 3[b] | | 21 | 81 |
| 4 |  | 94 | 99 |
| 5 |  | 90 | 98 |

[a]Reaction conditions: SO (10 mmol), catalyst (0.6 g), 100 °C, $CO_2$ (4 atm) 24 h, solventless.
[b] Reaction time:30 h
[c] Isolated yield.
[d] based on GC.

Since neither the reaction progress in the presence of homogeneous analog of $SiO_2$-**2** (Br) (Table 3, entry 1) nor silica itself exhibit catalytic activity for the coupling reaction (Table 3, entry 9), then the promotion effect of silica was significantly synergistic. Hence, not only N-Benzyl DABCO bromide moiety but also Si-OH groups on the silica surface are probably to contribute to catalyst, being compatible with those previously reported.[30,46]

A plausible acceleration mechanism is shown in scheme 2, in which the Si–OH groups on the silica surface act as acid sites to activate the styrene oxide, which subsequently undergoes nucleophile attack on the less sterically hindered carbon atom by the bromide anion to open the epoxy ring. Finally, the ring-opened epoxide reacts with $CO_2$ to form the styrene carbonate and regenerates the catalyst. This mechanism is a similar acid–base reaction mechanism to the Sakakura's silica-supported phosphonium[30] and Motokura 's silica-supported aminopyridinium[47] catalyst systems.



Scheme 2 The proposed mechanism for $SiO_2$-**2** (Br) catalyzed reaction.

## Conclusions

Silica-supported DABCO based ammonium salts was proved to be an excellent catalysts for the synthesis of cyclic carbonates from epoxides and $CO_2$ with no requirement for any organic solvent and metal co-catalyst. It was found that immobilized N-Benzyl DABCO bromide with a bulkier group and more nucleophilic halide anion showed much better catalytic performance. The catalyst can be easily recovered and reused at least three times without any significant loss of its initial activity.

## Exprimental

### General

Commercial reagents were purchased from Merck Company and were used without further purification. $CO_2$ of a purity of 99.99% was commercially available. Elemental analyses were performed by using a Leco, CHNS-932 elemental analyzer. Thermo gravimetric analysis (TGA) was carried out on TGA/DTA STA503 analyzer at a heating rate of 20 °C min−1. $^1H$ NMR spectra were recorded on a Bruker 250 spectrometer using TMS as an internal standard in $CDCl_3$. Mass spectra were recorded on a Shimadzu QP 1100 BX Mass Spectrometer and FT-IR spectra were obtained as KBr pellets on a JASCO 680-Plus spectrophotometer. Melting points were measured with a Gallenkamp melting apparatus. Gas chromatography (GC) (BEIFIN 3420 gas chromatograph equipped with a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm) were used for consideration of reactions conversions and yields.

### Synthesis of $SiO_2$-1 and $SiO_2$-2-(A)

Before immobilization, Silica-gel (60-120 mesh) (25 g) was dried at 300°C for 5 h and suspended in dry toluene (300 mL), and then an excess amount of 3-chloropropyltrimethoxysilane (25.0 mL) was added. The solution was refluxed for 48 h. Afterward, the reaction mixture was cooled to room temperature, the solvent was decanted and the silica was washed thoroughly with toluene, then extracted with dichloromethane for 5 h. The silica was then dried under vacuum drying for 8 h. 3-Chloropropyl functionalized silica (1 g) and DABCO (0.56 g, 5 mmol) were added in the flask containing 30 mL dry acetone and the reaction mixture was refluxed for 36 h. Afterward, the solid phase was filtered and extensively washed with acetone, ethanol, and methanol in turn at room temperature. The resulting solid was dried under vacuum at 50 °C for 4 h to obtain $SiO_2$-**1**. Following the similar procedure, a series of $SiO_2$-**2** (A) were also synthesized. A summary of this procedure is shown in Scheme 1.

### General procedure for the cycloaddition reaction

All the cycloadditions were conducted in a 100 mL stainless-steel reactor equipped with a magnetic stirrer under a $CO_2$ atmosphere and the reactor was put into a bath of 100°C and then pressurized to the appropriate pressure with $CO_2$. In the typical procedure, $SiO_2$-**2** (Br) (0.6 g), 1,2-dichlorobenzene (internal standard of GC) and 10 mmol of styrene oxide (SO) were placed into the reactor. The atmosphere inside the reactor was replaced with 4 atm of carbon dioxide and the mixture was vigorously stirred at 100 °C. After 24 h, the catalyst was separated by filtration, and GC analysis of the filtrate showed 94% yield of styrene carbonate. The recovered $SiO_2$-**2** (Br) was washed with EtOAc and acetone, and dried. Then the catalyst was reused under the same conditions. organic cyclic carbonate products were identified by IR, ESI-mass, $^1$H and $^{13}$C NMR spectra.[44,48-50]

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## Notes and references

[a] Pharmaceutical Research Laboratory, Department of Chemistry, Isfahan University of Technology, Isfahan 84156, IR Iran. Corresponding Author Tel.: +98 313 391 3262; fax: +98 313 391 2350.E-mail address: haji@cc.iut.ac.ir

[b] Department of Neuroscience, University of Wisconsin, Medical School, 1300 University Avenue, Madison, 53706-1532, WI, USA

[c] Department of Chemistry, Faculty of Science, Shahid Beheshti University, G. C., Evin, Tehran 1983963113, Iran

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## Graphical abstract

DABCO based ammonium salts immobilized on functionalized silica proved to be an effective heterogeneous catalyst for the synthesis of cyclic carbonate from epoxide and $CO_2$ without the utilization of any organic solvent and any additives.