

The effective synthesis of propylene carbonate catalyzed by silica-supported hexaalkylguanidinium chloride

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We have described that both homogeneous and a silica-supported hexaalkylguanidinium chloride were effective catalysts for CO₂ fixation to carbonate without any solvent under mild reaction conditions (4.5 MPa, 120 °C, 4 h), the silica-supported hexaalkylguanidinium chloride showing the great advantage that it could be recycled easily at least 5 further times without any obvious decrease in its catalytic activity, after simple filtration.

1. Introduction

The chemical fixation of carbon dioxide into industrially useful compounds has been given much attention in recent years due to the following two reasons. Firstly, carbon dioxide is regarded as the primary greenhouse effect gas, therefore, developing an efficient way to reduce carbon dioxide in our environment is intriguing work. Secondly, as an inexpensive, non-toxic and non-flammable gas, carbon dioxide has been considered an attractive C₁ building block for producing useful organic compounds.¹

The formation of cyclic carbonate *via* the cycloaddition of epoxides and carbon dioxide, which is one of the routes for the chemical fixation of CO₂, has been investigated widely, since the cyclic carbonates show interesting applications as polar aprotic solvents, as precursors for polycarbonate materials, and in general, as intermediates in organic synthesis.² Numerous catalyst systems, including alkali metal salts,³ metal complexes,⁴ MgO,⁵ Mg–Al mixed oxides,⁶ ionic liquids,⁷ biopolymer-supported zinc chloride,⁸ NaI/PPh₃/PhOH,⁹ DMAP/PhOH¹⁰ and homogeneous/heterogeneous guanidine catalyst systems,¹¹ have been developed for this transformation. While the advances have been significant, all suffer from low catalyst stability and activity, air sensitivity, the need for co-solvents or co-catalysts, or the requirement for high pressures and/or high temperatures. Hence the exploration of highly efficient, easily separated and recycled catalyst systems for this transformation, under mild conditions, still remains a challenge.

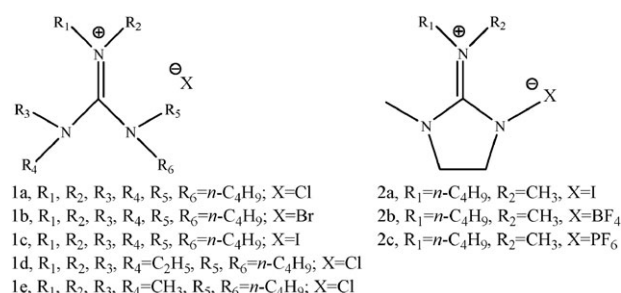
Recently, we demonstrated that hexabutylguanidinium chloride (HBGCl) is an effective catalyst for the reaction of styrene oxide with CO₂ to afford cyclic carbonate at 60 °C and atmospheric pressure.¹² The high catalytic efficiency may be due to the Lewis acidic guanidinium cation activating the ring opening of epoxides with electrophiles. Due to the great interest in this topic, the efforts made to obtain a better catalyst separation, and to make the catalyst recovery simpler, here we present a study of an effective coupling of CO₂ and propylene oxide to give cyclic carbonate, in the presence of a silica-supported pentabutylpropylguanidinium chloride (PBGSiCl) catalyst.

2. Experimental

GC was carried out on a Hewlett-Packard III 5720 instrument. ¹H and ¹³C NMR spectra were determined on a Bruker spectrometer (300 MHz) with TMS as the internal standard. Mass spectra were measured on a Hewlett-Packard HP-5989A apparatus. Elemental analyses were obtained on a VarioEL analyzer. FTIR spectra were obtained with a Bio-Rad Digilab Division FTS-80 spectrometer. Melting points were determined on a RY-1 melting point apparatus. All the epoxides were used after distillation over CaH₂.

2.1 The synthesis of ionic liquids¹³

The ionic liquids **1a**, **1d**, **1e**, **2a**, **2b** and **2c** were synthesized according to the literature. The ionic liquids **1b** and **1c** were synthesized by anion exchange between ionic liquid **1a** and the corresponding inorganic salt (Scheme 1).



Scheme 1

Synthesis of 1c. A mixture of HBGCl (4.32 g, 10 mmol) and KI (3.32 g, 20 mmol) in acetone (10 mL) was stirred at room temperature for 24 h and a white salt (KCl) precipitated out. After the filtration of the solid, further KI (3.22 g, 20 mmol) was added to the solution and it was stirred at room temperature for 24 h in order for the exchange to complete. Finally after the filtration of the solid, the solution was concentrated in a rotary evaporator and then diluted with dichloromethane.

The solution was again filtered and concentrated in a rotary evaporator. The concentrated solution was evaporated to dryness in a vacuum drying oven (0.1 mmHg and 80 °C), yielding 5.18 g (99%) of a white solid of **1c**. The ionic liquid **1b** was prepared by the same procedure.

Ionic liquid 1a. mp: 142–144 °C. δ_{H} (300 MHz, CDCl_3) 0.96 (18 H, t, $J = 6.8$ Hz), 1.30–1.45 (18 H, m), 1.74–1.78 (6 H, m), 3.06–3.12 (6 H, m) and 3.13–3.38 (6 H, m). δ_{C} (100 MHz, CDCl_3) 12.98, 19.35, 28.88, 48.82 and 163.34. Calc. C, 69.52; H, 12.51; N, 9.73; Cl, 8.24%; Found C, 69.23; H, 12.85; N, 9.70; Cl, 8.22%. IR (KBr, ν) 1540 cm^{-1} (C=N).

Ionic liquid 1b. mp: 132 °C. δ_{H} (300 MHz, CDCl_3) 0.96 (18 H, t), 1.30–1.44 (18 H, m), 1.73–1.78 (6 H, m), 3.06–3.12 (6 H, m) and 3.13–3.38 (6 H, m). Calc. C, 63.04; H, 11.35; N, 8.83; Br, 16.78%; Found C, 62.95; H, 11.40; N, 8.95; Br, 16.70%. IR (KBr, ν) 1540 cm^{-1} (C=N).

Ionic liquid 1c. mp: 138 °C. δ_{H} (300 MHz, CDCl_3) 0.96 (18 H, t), 1.30–1.45 (18 H, m), 1.74–1.78 (6 H, m), 3.06–3.12 (6 H, m) and 3.13–3.38 (6 H, m). Calc. C, 57.37; H, 10.33; N, 8.03; I, 24.27%; Found C, 57.26; H, 10.22; N, 8.15; I, 24.37%. IR (KBr, ν) 1540 cm^{-1} (C=N).

Ionic liquid 1d. δ_{H} (300 MHz, CDCl_3) 0.89 (6 H, t), 1.17–1.66 (20 H, m) and 3.20–3.42 (12 H, m). IR (KBr, ν) 1540 cm^{-1} (C=N). MS m/z 284 (A^+ , 100%). Calc. C, 63.85; H, 11.89; N, 13.15; Cl, 11.11%; Found C, 63.55; H, 11.95; N, 13.04; Cl, 11.46%.

Ionic liquid 1e. δ_{H} (300 MHz, CDCl_3) 0.96 (6 H, t), 1.37 (4 H, m), 1.54 (4 H, m) and 3.09–3.23 (16 H). IR (KBr, ν) 1540 cm^{-1} (C=N). MS m/z 228 (A^+ , 100%). Calc. C, 59.20; H, 11.39; N, 15.94; Cl, 13.47%; Found C, 59.05; H, 11.43; N, 15.82; Cl, 13.70%.

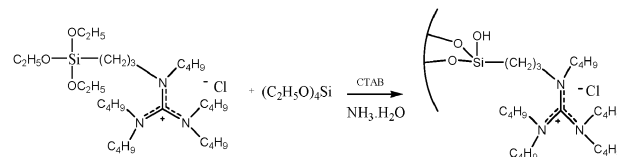
Ionic liquid 2a. δ_{H} (300.1 MHz, CDCl_3) 3.87 (4 H, s, N-CH₂-CH₂-N), 3.28 (2 H, t, $J = 7.4$ Hz, -CH₂-N=), 3.03 (9 H, s, CH₃-N=C(NCH₃)₂), 1.55–1.65 (2 H, m, -CH₂-), 1.25–1.35 (2 H, m, -CH₂-) and 0.90 (3 H, t, $J = 7.3$ Hz, CH₃-C). δ_{C} (75.4 MHz, CDCl_3) 164.5, 53.2, 50.4, 38.9, 37.7, 30.1, 20.0 and 14.1. MS m/z 184.2 (A^+ , 100%) ($\text{A}^+ = [\text{BuMeN}^+=\text{C}(\text{CH}_3\text{NCH}_2)_2]$).

Ionic liquid 2b. δ_{H} (300.1 MHz, CDCl_3) 3.79 (4 H, s, N-CH₂-CH₂-N), 3.29 (2 H, t, $J = 7.5$ Hz, -CH₂-N=), 3.04 (9 H, s, CH₃-N=C(NCH₃)₂), 1.62–1.66 (2 H, m, -CH₂-), 1.31–1.36 (2 H, m, -CH₂-) and 0.95 (3 H, t, $J = 7.3$ Hz, CH₃-C). MS m/z 184.2 (A^+ , 100%) ($\text{A}^+ = [\text{BuMeN}^+=\text{C}(\text{CH}_3\text{NCH}_2)_2]$). IR (KBr, ν) 1619 (N=C) and 2961 (CH₃-N).

Ionic liquid 2c. δ_{H} (300.1 MHz, CDCl_3) 3.77 (4 H, s, N-CH₂-CH₂-N), 3.28 (2 H, t, $J = 7.5$ Hz, -CH₂-N=), 3.03 (9 H, s, CH₃-N=C(NCH₃)₂), 1.59–1.69 (2 H, m, -CH₂-), 1.28–1.38 (2 H, m, -CH₂-) and 0.96 (3 H, t, $J = 7.3$ Hz, CH₃-C). MS m/z 184.2 (A^+ , 100%) ($\text{A}^+ = [\text{BuMeN}^+=\text{C}(\text{CH}_3\text{NCH}_2)_2]$). IR (KBr, ν) 1619 (N=C) and 2961 (CH₃-N).

2.2 The synthesis of PBGSiCl

The triethoxysilylated pentabutylpropylguanidinium chloride was prepared according to the literature.¹⁴ The silica material containing covalently-linked pentabutylpropylguanidinium halides were prepared from alkaline mixtures containing tetraethoxysilane (TEOS), triethoxysilylated pentabutylpropylguanidinium chloride, water, ammonia and the surfactant



Scheme 2

cetyltrimethylammonium bromide (CTAB) in the respective molar composition 0.9 : 0.1 : 114 : 8 : 0.12 (Scheme 2). The resulting mixture was heated to 80 °C for 48 h and a white precipitate obtained after filtration. The material was washed with acidic ethanol repeatedly and then extracted in a Soxhlet's extractor by ethanol for 48 h to remove the surfactant. The material was finally dried at 110 °C for 24 h. The incorporation of the organic entities within the silica network was monitored by FT-IR and ¹³C CP-MAS spectroscopy and quantified by elemental analysis. The obtained mesoporous silicas, containing covalently-linked guanidinium ionic liquid, had an average pore diameter of 3.6 nm, and whose surface area and porous volume (determined by nitrogen adsorption) were 627.5 m² g⁻¹ and 0.57 mL g⁻¹ respectively. FTIR (diffuse reflectance) ν Si-O-Si 1088.7, ν C=N 1546.0 (guanidinium) and ν C-H 2938.4. Found C, 18.81; H, 5.67; N, 2.57; Cl, 3.93%. Active site concentration = 1.12 mmol guanidinium g⁻¹ of support.

2.3 General procedure for the homogeneous process

A mixture of propylene oxide (5.8 g, 100 mmol) and hexabutylguanidinium halide (0.5–1.5 mmol) was charged in a 100 mL high pressure stainless steel reactor, an excess of CO₂ with respect to the epoxide was introduced (2.5–4.5 MPa), and the mixture heated at 90–120 °C for 2–6 h. The reaction mixture was then cooled to room temperature and the product purified by distillation.

2.4 General procedure for the PBGSiCl catalytic process

A mixture of epoxide (100 mmol) and PBGSiCl (1.34 g, 1.5 mmol catalyst) was charged in a 100 mL high pressure stainless steel reactor, an excess of CO₂ with respect to the epoxide introduced (0.1 or 4.5 MPa), and the mixture heated to 120 °C for 2–20 h. The reaction mixture was then cooled to room temperature and ethyl acetate added. The catalyst was removed by filtration and the products purified by a silica gel column using hexane/ethyl acetate (v/v, 1 : 5). All products were characterized by ¹H NMR, IR and elemental analysis.

2.5 General procedure for the blank experiment

A mixture of propylene oxide (100 mmol) and silica gel (purchased from Aldrich, surface area 500 m² g⁻¹, average pore diameter 6 nm, containing many silanol groups on the walls of the pores) (1.34 g) was charged in a 100 mL high pressure stainless steel reactor, an excess of CO₂ with respect to the epoxide introduced (4.5 MPa), and the mixture heated at 120 °C for 4 h. The reaction mixture was then cooled to room temperature and ethyl acetate added. The silica gel was removed by filtration and the product obtained after distilling the solvent.

3. Results and discussion

3.1 The effect of reaction parameters on the cycloaddition of CO₂ to propylene oxide with homogeneous guanidinium salts

At first, a variety of homogeneous catalysts of guanidinium salts (Scheme 1) were prepared. Their catalytic activities for the cycloaddition of CO₂ to propylene oxide were investigated to

Table 1 The effect of the structure of guanidinium salts on the cycloaddition of CO₂ to propylene oxide with homogeneous HBGCl^a

Entry	Ionic liquid	Anion	Time/h	Yield (%) ^b
1	1a	Cl	3	100
2	1b	Br	3	92
3	1c	I	3	90
4	1d	Cl	3	85
5	1e	Cl	3	80
6	2a	I	6	95
7	2b	BF ₄	6	99
8	2c	PF ₆	6	55

^a Reaction conditions: Propylene oxide 100 mmol, ionic liquid 1.5% mmol to the substrate, temperature 110 °C, CO₂ pressure 4.5 MPa.

^b Isolated yield; the selectivity is >99% based on GC.

obtain structural information on the grafting of the guanidinium units. As shown in Table 1, the cations and anions of the guanidinium units have a strong effect on catalytic activities. Essentially, the halide anions show a considerable activity among the anions, probably because halide anions exhibit a moderate nucleophilicity and high leaving ability. The order of the activity of hexabutylguanidinium halide salts was found to be Cl[−] > Br[−] > I[−] (Table 1, entries 1–3). It is known that the nucleophilicity of an anion depends on the solvent used, the order of the nucleophilicity of halides in S_N2-type reactions in aprotic solvent being Cl[−] > Br[−] > I[−].¹⁵ Thus, the order of activity of halide anions is consistent with the order of nucleophilicity. In this case, the propylene oxide and carbonate act as an aprotic solvent. Among the various guanidinium salts, hexabutylguanidinium chloride, **1a**, shows the highest activity. This could be ascribed to its structural features. Two references^{14,16} have reported the structural features of **1a** based on ¹H, ¹³C and ¹⁵N NMR spectroscopic studies, suggesting the existence of an electron-deficient state at the central carbon atom surrounded by the three nitrogen atoms. It is postulated that the epoxide is activated along the electron-deficient guanidinium central carbon axis, not unlike Lewis acid activation. On the other hand, the bulkiness of hexabutylguanidinium ion makes the electrostatic interaction between the cation and the anion weaker, which renders the counter anion more nucleophilic.

Besides the effect of the guanidinium's structure, the influence of several parameters have been studied with catalyst **1a**, so as to optimize the performance of the guanidinium salt's catalytic system. As shown in Table 2, the catalytic system is quite sensitive to reaction temperature and pressure; when the temperature was decreased from 120 °C to 90 °C and the CO₂ initial pressure was decreased from 4.5 MPa to 2.5 MPa, the yields were decreased (entries 3, 5–8). Hence, 120 °C and 4.5 MPa were the optimum reaction temperature and pressure respectively.

Table 2 The effect of reaction parameters on the cycloaddition of CO₂ to propylene oxide with homogeneous HBGCl^a

Entry	Catalyst amount/mmol	Pressure/MPa	Temperature/°C	Time/h	Yield (%) ^b
1	1.5	4.5	110	3	100
2	1.5	4.5	110	2	94.5
3	1.0	4.5	110	3	95.3
4	0.5	4.5	110	3	80.5
5	1.0	4.5	120	3	100
6	1.0	4.5	90	6	85.5
7	1.0	4.5	100	3	91.5
8	1.0	2.5	110	3	90.0

^a Reaction conditions: Propylene oxide 100 mmol. ^b Isolated yield; the selectivity is >99% based on GC.











The effect of the amount of **1a** on the reaction was also investigated. The results (Table 2, entries 1–4) indicate that the yield was improved by the increase in the amount of catalyst. The yield is only 80.5% when the catalyst amount is 0.5 mmol (0.5% mol to substrate), and it can be up to 100% using 1.5 mmol catalyst under otherwise the same conditions. To our knowledge, this is the best result obtained when using non-metal Lewis acid species to catalyze this reaction. Kawanami *et al.* reported that 1-octyl-3-methylimidazolium tetrafluoroborate can catalyze quantitatively the coupling of CO₂ to propylene carbonate in 5 min at 100 °C by applying supercritical CO₂ (14 MPa); however, only 71% yield and 78% selectivity were attained under 6 MPa at 100 °C after 2 h.^{7c}

3.2 The cycloaddition of CO₂ with epoxides to give cyclic carbonates catalyzed by PBGSiCl catalyst

The PBGSiCl catalyst was prepared by the direct hydrolysis–polycondensation of TEOS with triethoxysilylated pentabutylpropylguanidinium chloride under alkaline conditions. The optimum homogeneous reaction conditions were used for the cycloaddition of CO₂ with propylene oxide using PBGSiCl as catalyst. As shown in Table 3, after being supported, the catalytic activity of hexaalkylguanidinium halide made almost no obvious change (Table 2, entry 1; Table 3, entry 2). However in 2003, Barbarini *et al.*¹¹ reported that the reactivity of guanidine catalyst supported on MCM-41 was very much lower than that of homogeneous guanidine catalyst. This may be attributed to the high activity of hexaalkylguanidinium halide and a different catalytic mechanism.

A series of epoxide substrates were examined for the synthesis of the corresponding carbonates in the presence of PBGSiCl catalyst at 120 °C, 4.5 MPa and without any solvent (Table 3, entries 2–5, 8–10). All the corresponding carbonates were successfully synthesized from each epoxide in good yield and with excellent selectivity, except for the cyclohexene oxide. In order to investigate the effect of the silanol groups on the silica gel, a blank experiment was carried out under the same conditions. The result (entry 1) shows that no cyclocarbonate was obtained when using the unfunctionalised silica molecular sieve as the catalyst, demonstrating that the observed catalysis is due to the hexaalkylguanidinium chloride linked onto the

Table 3 The cycloaddition of CO₂ with epoxides to give cyclic carbonates, catalyzed by silica-supported hexaalkylguanidinium chloride^a

Entry	Substrate	Time/h	Yield (%) ^b	Selectivity (%) ^c
1 ^d		4	—	—
2		4	100	> 99
3		2	92	> 99
4		4	94	> 99
5		4	95	> 99
6 ^e		4	65	> 99
7 ^e		20	85	> 99
8		4	95	> 99
9		4	95	> 99
10		4	57	> 99

^a Unless otherwise indicated, the reaction conditions are as follows: Oxides 100 mmol, PBGSiCl 1.34 g (1.5 mmol catalyst), 1.5% mmol to the substrate, temperature 120 °C, CO₂ pressure 4.5 MPa. ^b Isolated yield. ^c The selectivity is >99% based on GC. ^d Using the unfunctionalised silica as catalyst. ^e The pressure of carbon dioxide is 0.1 MPa.

Table 4 Catalyst recycling studies in the coupling of carbon dioxide with propylene oxide^a

Entry	Recycle no.	Yield (%) ^b	Selectivity (%) ^c
1	Fresh	100	> 99
2	1	100	> 99
3	2	98	> 99
4	3	99	> 99
5	4	98	> 99
6	5	97	> 99

^a Reaction conditions: Propylene oxide 0.1 mol, PBGSiCl 1.34 g, temperature 120 °C, time 4 h, pressure 4.5 MPa. ^b Isolated yield.

^c Based on GC.

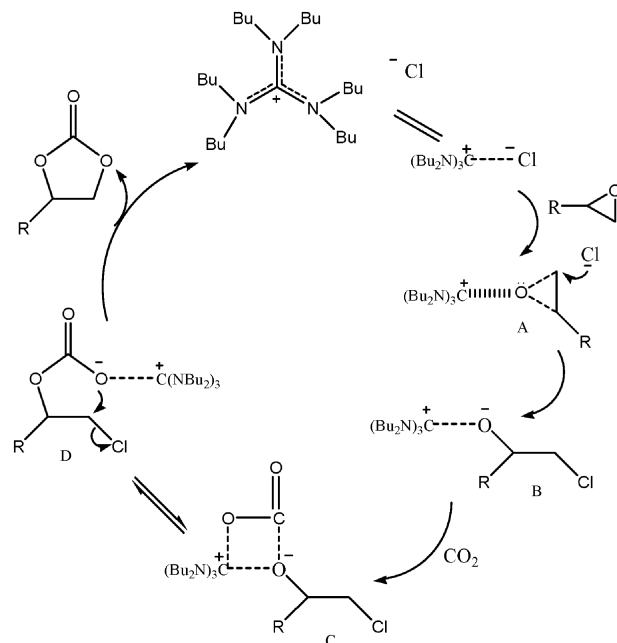
silica and not to the silanol group. It is quite noteworthy that the PBGSiCl catalyst is also very efficient for the cycloaddition of styrene oxide and carbon dioxide under these mild conditions without any solvent, and that the yield is up to 95% (entry 5). It is well known that styrene oxide, due to the low reactivity of its β -carbon, has a lower activity compared to propylene oxide. Furthermore, decreasing the CO₂ pressure down to 0.1 MPa at a constant temperature of 120 °C and time of 4 h leads to a remarkable decrease in yield, down to 65% (entry 6). If we prolong the reaction time to 20 h, we can also obtain satisfactory yields up to 85% (entry 7).

3.3 The possibility of recycling PBGSiCl catalyst

One of our greatest motivations is to get a better catalyst separation and make the catalyst recovery simpler. The efficiency of PBGSiCl catalyst in the cycloaddition of CO₂ to propylene oxide is shown in Table 4 by the possibility of recycling the catalyst for a further 5 cycles, without there being any obvious decrease in catalytic activity after simple filtration, washing with ethyl acetate and immediate reuse. In 1998, Sheldon *et al.* described that the catalysis observed during some heterogeneous liquid oxidation processes was due to homogeneous catalysis by small amounts of leached catalyst.¹⁷ In order to verify whether there is a similar phenomena occurring during our process, we undertook the same test by filtering the catalyst at reaction temperature, washing it with hot ethyl acetate and then immediately reusing it. The results were consistent with our initial results, which further proved that heterogeneous hexaalkylguanidinium chloride was responsible for the observed catalysis in the present study.

3.4 Mechanism consideration

Taking account of the reaction mechanism for the cycloaddition of CO₂ with epoxides to give cyclic carbonates catalyzed by an onium salt catalyst, *i.e.* tetrabutylammonium bromide salt, it has been proposed that this reaction involves the ring opening of the epoxide by means of a nucleophilic attack by the anion, yielding an oxy-anion species. This then reacts with CO₂ and the resulting cyclic carbonate subsequently cyclizes so that the catalytic activity is mostly based on the nucleophilicity and leaving ability of the anion.^{7f} Considering the high catalytic activity of HBGCl during this transformation and the special structure of it, we can speculate that its better performance could be ascribed to the cooperation of the nucleophilic attack of the anion (Lewis base), and the Lewis acid activation of the hexabutylguanidinium cation to the epoxide. This is a similar catalytic mechanism to that of metal complex catalysts,^{3a,5,6,7e,18} and it has been proposed that this reaction promotes both Lewis base activation of CO₂ for the nucleophilic attack at epoxide or the Lewis base nucleophilic attack at epoxide directly and the Lewis acid activation of epoxide. It is also called a “bi-functional catalyst system”. Based on the experimental results obtained and the above mentioned dis-



Scheme 3 A proposed mechanism for the addition of CO₂ to epoxide, catalyzed by HBGCl.

cussion, the mechanism for the cycloaddition of epoxides to CO₂, catalyzed by HBGCl, has been postulated in Scheme 3. The following steps are involved: Firstly, the epoxide is coordinated to the Lewis acid site (the central carbon) of hexabutylguanidinium chloride to form complex **A**, the Cl[−] anion then preferentially makes a nucleophilic attack on the lesser substituted site of the coordinated epoxide; this is followed by ring opening, producing an oxy-anion species **B**; next, a CO₂ molecule is coordinated to the complex through interaction of the O[−] and C⁺, resulting in the formation of **C** and **D** in equilibrium; finally, the cyclocarbonate is produced by intramolecular cyclic elimination, releasing the catalyst for recycling.

4. Conclusion

We have demonstrated that under mild reaction conditions (4.5 MPa, 120 °C, 4 h) both homogeneous and a silica-supported hexaalkylguanidinium chloride were effective catalysts for fixation of CO₂ to carbonate without solvent, and that the silica-supported catalyst had the great advantage of being easily recycled at least 5 times without any obvious decrease in its catalytic activity, after simple filtration. The possible mechanism was also discussed. We realized that the hexaalkylguanidinium chloride acted as a bi-functional catalyst during this transformation due to its strong steric and electrophilic effects.

References

- For recent reviews see: (a) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259; (b) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475; (c) X. D. Xiao and J. A. Moulijn, *Energy Fuels*, 1996, **10**, 305; (d) D. J. Darensbourg and M. W. Holtcamp, *Coord. Chem. Rev.*, 1996, **153**, 155; (e) M. Yoshida and M. Ihara, *Chem.-Eur. J.*, 2004, **10**, 2886.
- For a recent review about applications of cyclic carbonates see: J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663.
- (a) R. L. Addock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498; (b) R. L. Paddock and S. T. Nguyen, *Chem. Commun.*, 2004, 1622; (c) N. Kihara, N. Hara and T. Endo, *J. Org. Chem.*, 1993, **58**, 6198.
- (a) H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang and S. O. Kang, *Angew. Chem.*, 2000, **112**, 4262; (b) H. S. Kim, J. J. Kim, B. G. Lee, O. S. Jung, H. G. Jang and S. O. Kang, *Angew. Chem.*,

- Int. Ed.*, 2000, **39**, 4096; (c) H. S. Kim, J. J. Kim, S. D. Lee, M. S. Lah, D. Moon and H. G. Jang, *Chem.–Eur. J.*, 2003, **9**, 678; (d) Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 1559.
- 5 T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Rujihara, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 1997, 1129.
 - 6 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526.
 - 7 (a) J. J. Peng and Y. Q. Deng, *New J. Chem.*, 2001, **25**, 639; (b) H. Yang, Y. Deng and F. Shi, *Chem. Commun.*, 2002, **274**; (c) H. Kawanami, A. Sakaki, K. Matsui and Y. Ikushima, *Chem. Commun.*, 2003, 896; (d) H. S. Kim, J. J. Kim, H. Kim and H. G. Jang, *J. Catal.*, 2003, **220**, 44; (e) J. Sun, S. Fujita, F. Y. Zhao and M. Arai, *Green Chem.*, 2004, **6**, 613; (f) V. A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561.
 - 8 L. F. Xiao, F. W. Li and C. G. Xia, *Appl. Catal., A*, 2005, **279**, 125.
 - 9 Y. M. Shen, W. L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 6705.
 - 10 Y. M. Shen, W. L. Duan and M. Shi, *Adv. Synth. Catal.*, 2003, **345**, 337.
 - 11 A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartorio, *Tetrahedron Lett.*, 2003, **44**, 2931.
 - 12 H. F. Duan, S. H. Li, Y. J. Li, H. B. Xie, S. B. Zhang and Z. M. Wang, *Chem. Res. Chin. Univ.*, 2004, **20**(5), 568.
 - 13 (a) D. J. Brunelle, D. A. Haitko and J. P. Barren, *US Patent* 5,132,423, 1992; (b) H. B. Xie, S. B. Zhang and H. F. Duan, *Tetrahedron Lett.*, 2004, **45**, 2013; (c) H. F. Duan, Y. J. Lin, S. B. Zhang, Z. M. Qiu and Z. M. Wang, *Chem. Res. Chin. Univ.*, 2003, **24**, 2024; (d) D. J. Brunelle and N. Y. Scotia, *US Patent* 5,082,968, 1990.
 - 14 P. Gros, P. L. Percec and J. P. Senet, *J. Org. Chem.*, 1994, **59**, 4925.
 - 15 K. Nobuhiro, H. Nobutaka and E. Takeshi, *J. Org. Chem.*, 1993, **58**, 6198.
 - 16 A. V. Santoro, *J. Org. Chem.*, 1979, **44**, 117.
 - 17 H. E. B. Lempers and R. A. Sheldon, *J. Catal.*, 1998, **175**, 62.
 - 18 (a) D. Ji, X. Lu and R. He, *Appl. Catal., A*, 2000, **203**, 329; (b) X. B. Lu, R. He and C. X. Bai, *J. Mol. Catal. A: Chem.*, 2002, **186**, 1; (c) F. W. Li, C. G. Xia, L. W. Xu, W. Sun and G. X. Chen, *Chem. Commun.*, 2003, 2042; (d) R. L. Paddock, Y. Hiyama, J. M. McKay and S. T. Nguyen, *Tetrahedron Lett.*, 2004, **45**, 2023.