Catal Lett (2012) 142:1376–1381
DOI 10.1007/s10562-012-0909-y

Low-Cost Polymer-Supported Quaternary Ammonium Salts as High-Efficiency Catalysts for Cycloaddition of CO_2 to Epoxides

**Yuan-Yuan Zhang · Lang Chen · Shuang-Feng Yin ·
Sheng-Lian Luo · Chak-Tong Au**

Received: 7 August 2012 / Accepted: 15 September 2012 / Published online: 26 September 2012

Abstract Polystyrene grafted with quaternary ammonium salts were obtained by direct quaternarization of chloromethylated polystyrene with *N*,*N*-dimethylethylamine, *N*,*N*-dimethylglycine (denoted as PS-QNS and PS-CQNS, respectively). These two polymer-supported ionic liquids were found to show high catalytic efficiency towards the cycloaddition of CO_2 to epoxides. The effects of catalyst amount, reaction temperature, initial CO_2 pressure, and reaction time on the yield of cyclic carbonates were investigated systematically. Under the optimal reaction conditions (150 °C, initial CO_2 pressure 2.0 MPa and 5 h), propylene carbonate yield and selectivity in the cycloaddition of CO_2 to propylene oxide over PS-CQNS were 96.2 and 99.3 % whereas those over PS-QNS were 97.9 and 99.5 %, respectively. It was observed that the reusability of PS-QNS was excellent. From the viewpoint of industrial application, PS-QNS is attractive in terms of catalytic efficiency, cost and simplicity in preparation.

Keywords Polymer-supported quaternary ammonium salts · Carbon dioxide · Epoxide · Cyclic carbonate

1 Introduction

Carbon dioxide is a major green-house gas. Motivated by the idea of environmental protection, scientists are paying much attention to the fixation of CO_2. An important reaction is the synthesis of five-membered cyclic carbonates via the cycloaddition of CO_2 to epoxides. The reaction is desirable because of three main reasons: (i) reactants are cheap (ii) atom utilization is high, and (ii) generation of by-product is low [1, 2]. Besides, five-membered cyclic carbonates are important chemicals and intermediates that are extensively applied in organic syntheses for the production of pharmaceuticals and fine chemicals [1, 3, 4]. They can also be used as aprotic polar solvents, electrolytic components of lithium secondary batteries, and cosmetics additive [5–7].

Up to now, many materials having been explored to catalyze the cycloaddition of CO_2 to epoxides, such as alkali metal salts [8, 9], organic bases [10, 11], metal oxides [12, 13], ion exchange resins [2], and modified molecular sieves [14]. So far, ionic liquids (ILs) containing imidazolium salts [15, 16], quaternary ammonium salts [17, 18], and quaternary phosphonium salts [19–21] have been used as catalysts for the synthesis of cyclic carbonates. In terms of separation, reusability, and cost effectiveness, the application of homogeneous catalysts has its limitation. Compared with homogeneous catalysts, heterogeneous catalysts could be easily separated and reused. In order to fabricate stable and reusable heterogeneous catalysts, ionic liquids were immobilized on solid materials such as magnetic nanoparticles [22] and inorganic materials [5, 23, 24], as well as on mesoporous materials such as SBA-15 and MCM-41 [25, 26]. However, as pointed out by Xiao et al. [23] and Dai et al. [26], due to leaching of ILs, there was decrease of catalytic activity, thus leading to poor reusability of catalysts. Another problem one should

---

Y.-Y. Zhang · L. Chen · S.-F. Yin (✉) · S.-L. Luo · C.-T. Au
State Key Laboratory of Chemo/Biosensing and Chemometrics,
College of Chemistry and Chemical Engineering,
Hunan University, Changsha 410082, Hunan, China
e-mail: sfyin73@yahoo.com.cn; sf_yin@hnu.edu.cn

C.-T. Au
Department of Chemistry, Hong Kong Baptist University,
Kowloon Tong, Hong Kong, China

not overlook is that the immobilization of ILs on inorganic materials is complex and costly.

In our previous research, we grafted ILs onto cross-linked divinylbenzene polymer and observed excellent catalytic efficiency in the synthesis of cyclic carbonates from CO_2 and epoxides [27, 28]. Although the catalysts could be obtained easily by a one-step chemical reaction, the high cost of synthesis limited their application on a large scale. Therefore, the development of low-cost solid catalysts that are highly efficient for the cycloaddition of CO_2 to epoxides under mild conditions is a challenge. Herein, we selected chloromethylated polystyrene (a relatively cheap material) as support, and reacted it with *N*,*N*-dimethylethylamine and *N*,*N*-dimethylglycine to prepare low-cost polystyrene that bears a quaternary ammonium salt. We systematically investigated the effects of catalyst amount, reaction temperature, initial CO_2 pressure, and reaction time on the yield of cyclic carbonate.

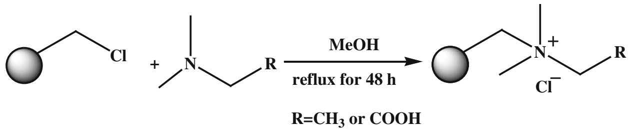
2 Experimental

2.1 Chemicals

The chloromethylated polystyrene (denoted hereinafter as PS; 100–200 mesh; Cl loading: 4.69 mmol g^{-1}, 2 % cross-linked with divinylbenzene) was supplied by Tianjin NanKai Hecheng S&T Co., Ltd. *N*,*N*-dimethylethylamine and 1,2-butylene oxide were provided by TCI Company. *N*,*N*-dimethylglycine was bought from Alfa Aesar China (Tianjin) Co., Ltd. Analytical grade absolute methanol, THF and propylene oxide (PO) were purchased from Sinopharm Chemical Reagent Co., Ltd. Other epoxides were bought from Acros Organics. All the chemicals were used as received except for PS and the epoxides. The PS was washed with a mixture of THF and H_2O ($V_{THF}/V_{H_2O} = 4/1$) repeatedly, then by THF twice, and dried in vacuum (60 °C for 6 h). The epoxides were dried by distillation over CaH_2 before use. CO_2 (purity: 99.9 %) was from Changsha Gas Co., and was dehydrated before use over 4A molecular sieve installed in a stainless-steel tube that could stand high pressure.

2.2 Preparation of Polymer-Supported Quaternary Ammonium Salts

The procedure for the preparation of polymer-supported quaternary ammonium salts is shown in Scheme 1. Hereinafter, when R is CH_3, the catalyst is denoted as PS-QNS; whereas when R is COOH, it is denoted as PS-CQNS. The typical preparation procedure of PS-CQNS is as follows: 2 ml of absolute methanol was added to a mixture of *N*,*N*-dimethylglycine (2.0 mmol) and PS (0.2 g) under the protection of N_2, followed by reflux for 48 h at 80 °C. After cooling to room temperature, the as-obtained solid was filtered out, washed with absolute methanol (three times to remove excess *N*,*N*-dimethylglycine), and dried in vacuum at 60 °C for 4 h to afford the generation of PS-CQNS. In a similar manner, PS-QNS was prepared following the above procedure with *N*,*N*-dimethylglycine being replaced by *N*,*N*-dimethylethylamine.



Scheme 1 Synthesis of polymer-supported quaternary ammonium salts catalysts

2.3 Catalyst Characterization

The FT-IR spectra were determined using a Bruker vector 22 FT-IR spectrophotometer (KBr tablets). Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis of samples from 25 to 700 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere was performed on a NETZSCH-STA-449C equipment. Elemental analysis was performed by using a Vario EL III analyzer.

2.4 Coupling Reactions

The coupling of CO_2 and epoxides to cyclic carbonates were carried out in a 30 ml stainless steel autoclave equipped with a magnetic bar. In a typical run, a desired amount of catalyst, an appropriate amount of biphenyl (as internal standard for gas chromatography analysis), and epoxide (28.6 mmol) were successively introduced into the reactor. Then, the reactor was pressurized with an appropriate amount of CO_2 and heated to a desired temperature in an oil bath. After a designated reaction time, the reactor was quickly cooled to 0 °C (in an ice-water bath), followed by slow venting of the remaining CO_2. The catalyst was separated from the reaction mixture by centrifugation. Qualitative analysis of the liquid products was performed on a GC/MS instrument (6890 N/5973 N) using an Agilent HP-5MS capillary column (30 m × 0.45 mm × 0.8 μm). For quantitative determination, the products were analyzed on an Agilent 7820A GC with flame ionization detection and Agilent AB-FFAP capillary column (30 m × 0.25 mm × 0.25 μm). The GC yield was obtained with reference to biphenyl (the internal standard substance).

3 Results and Discussion

3.1 Characterization

Figure 1 shows the FT-IR spectra of PS and PS-CQNS. The weak peak of OH appeared in the spectra of PS

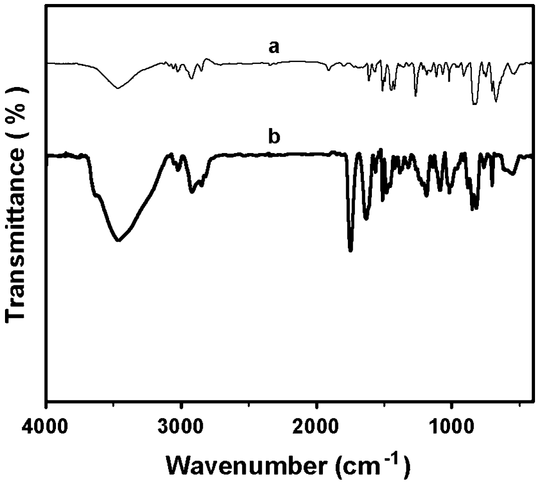


Fig. 1 FT-IR spectra of *a* PS and *b* PS-CQNS

(Fig. 1a) is due to adsorbed H_2O. The sharp peak at 1,750 cm^{-1} of C=O and the broad peak at 3,470 cm^{-1} of OH in Fig. 1b are indicative of the successful grafting of the quaternary ammonium salt onto the support.

The TG and DSC curves of PS, PS-CQNS and PS-QNS are showed in Fig. 2. One can see that PS is stable up to 300 °C, and decomposition of PS occurs above 300 °C (Fig. 2a). The slight weight loss observed over PS-CQNS below 100 °C is due to the removal of physisorbed water. One can see that PS-CQNS is stable up to 200 °C. There are two endothermic peaks above 200 °C, one at 206 °C and the other at 432 °C which are ascribable to the decomposition of IL and polymer, respectively (Fig. 2b). On the other hand, PS-QNS is thermally stable up to 220 °C and the decomposition of IL and support occurs at 249.3 and 417.3 °C, respectively (Fig. 2c). It is apparent that both PS-CQNS and PS-QNS are suitable catalysts for cycloaddition reaction of CO_2 and epoxides that occurs under 200 °C. Moreover, elemental analysis results showed the contents of N in the fresh PS-QNS and PS-CQNS were 5.56 and 4.95 %, respectively, which were very close to the theoretical values of 5.58 and 4.99 %. Therefore, the active components of the catalysts have been successfully grafted onto the support.

3.2 Catalytic Performance

In the present study, PO was chosen as model substrate to fix CO_2. We investigated the effect of PS-CQNS amount, reaction temperature, initial CO_2 pressure, and reaction time on the cycloaddition reaction. Furthermore, PS-CQNS

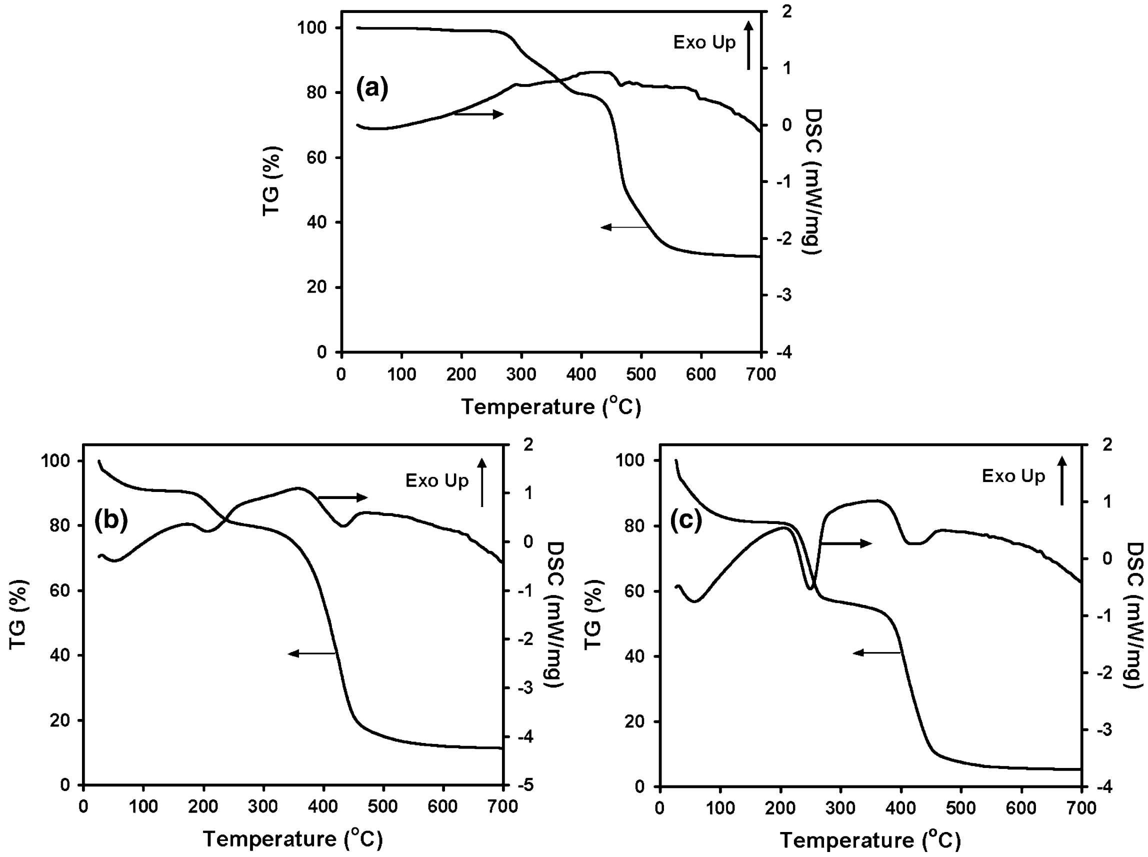


Fig. 2 TG and DSC curves of **a** PS, **b** PS-CQNS and **c** PS-QNS

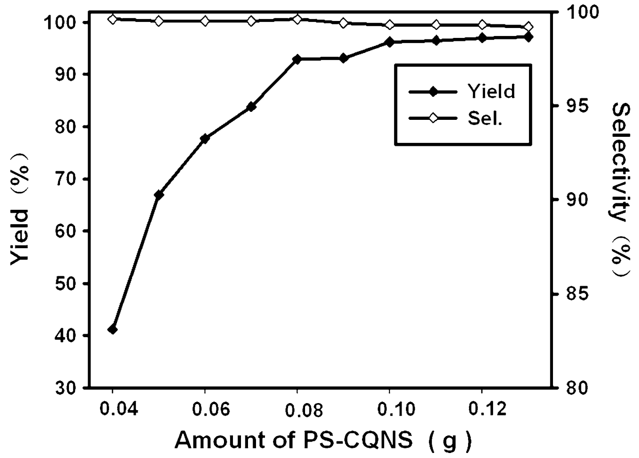


Fig. 3 Effect of the amount of PS-CQNS on catalytic performance (reaction conditions: PO 28.6 mmol, temperature 150 °C, initial CO_2 pressure 2.0 MPa, time 5 h)

was also used to catalyze the cycloaddition of CO_2 to selected epoxides.

3.3 Effect of the Amount of PS-CQNS

The effect of the amount of catalyst on the yield of propylene carbonate (PC) is illustrated in Fig. 3. With the amount of catalyst being raised to 0.10 g, there is rise of PC yield; but further rise of catalyst amount shows little effect on the yield. It is because an increase of catalyst amount would improve the substrate contact with the active constituent of catalyst, thus accelerating the coupling reaction. Once the active constituent of catalyst becomes plentiful at catalyst amount higher than 0.01 g, further rise in the amount of catalyst would have little effect on product yield. In the subsequent studies, we adopted 0.01 g as the most suitable amount of PS-CQNS for the coupling reaction.

3.3.1 Effect of Reaction Conditions

Figure 4 shows the influence of reaction temperature on PC yield and selectivity. With temperature rise from 130 to 150 °C, PC yield reaches 96.2 % rapidly under the condition of 5 h and 2.0 MPa of initial CO_2 pressure. The PC yield can reach 98.6 % at 170 °C. It appears that a rise in temperature is beneficial for the reaction. However, Xie et al. [29] reported that high temperature could have a negative effect on PC yield. It is plausible that at high temperature, there is the promotion of side reaction(s). With the formation of by-product(s), there is decline in the yield of cyclic carbonates [29]. It is noted that in the present investigation, a rise in temperature has no effect on PC selectivity (always >98.0 %).

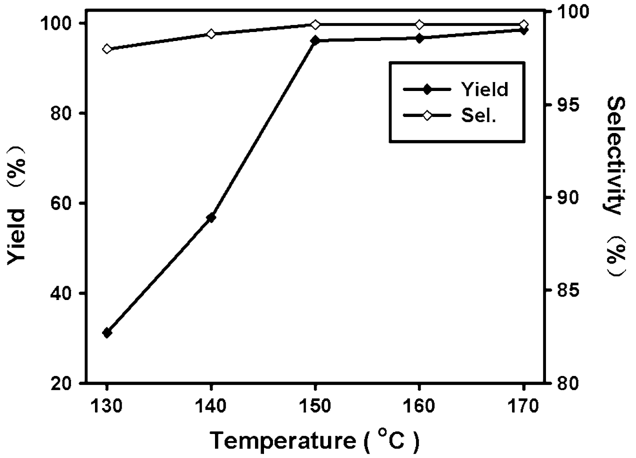


Fig. 4 Effect of reaction temperature on catalytic performance of PS-CQNS (reaction conditions: PO 28.6 mmol, initial CO_2 pressure 2.0 MPa, time 5 h)

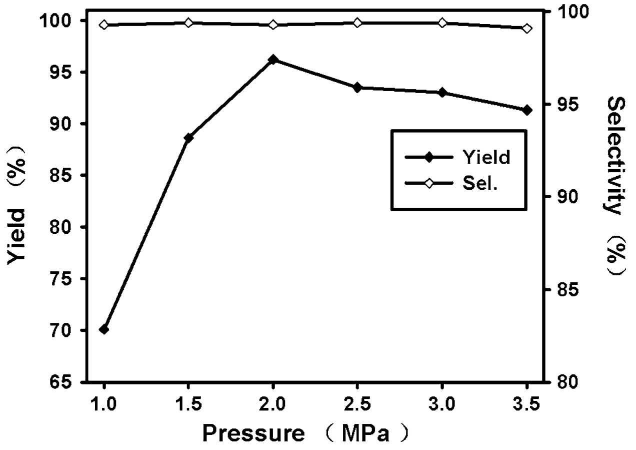


Fig. 5 Effect of initial CO_2 pressure on catalytic performance of PS-CQNS (reaction conditions: PO 28.6 mmol, temperature 150 °C, time 5 h)

As shown in Fig. 5, the PC yield is greatly affected by initial CO_2 pressure. An initial CO_2 pressure of 2.0 MPa affords the maximum yield of PC (96.2 %) under the condition of 150 °C and 5 h. A pressure higher or lower than 2.0 MPa would result in decline of PC yield. Similar phenomena were observed in other investigations [16, 20, 27]. Han et al. [16] explained that a high CO_2 pressure means a high concentration of CO_2 in the reaction mixture. Due to the strong presence of CO_2 in the vicinity of the catalyst, there is decline in interaction between epoxide and catalyst, and consequently decrease in PC yield.

Besides temperature and initial CO_2 pressure, reaction time could also have an effect on PC yield. As shown in Fig. 6, PC yield increases with reaction time. At a reaction time of 1 h, PC yield is still extremely low (15.0 %), but it reaches 90.2 % at the 4th hour. There is slight rise of PC yield afterwards and at 6 h, PC yield is 97.1 %. We also

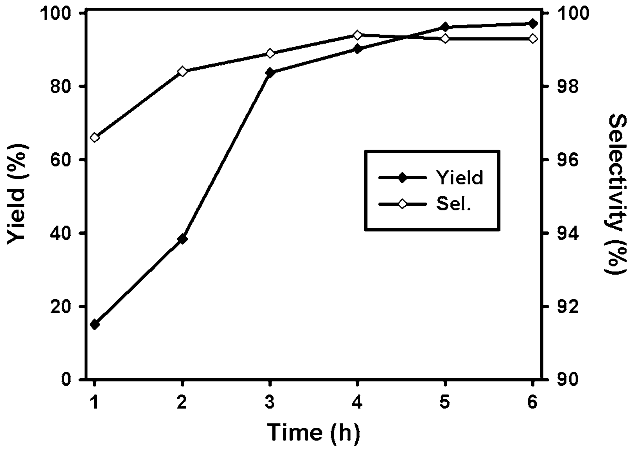


Fig. 6 Effect of reaction time on catalytic performance of PS-CQNS (reaction conditions: PO 28.6 mmol, temperature 150 °C, initial CO_2 pressure 2.0 MPa)

Table 1 Cycloaddition of CO_2 to epoxides catalyzed by PS-CQNS

Entry	Epoxides	Catalytic results	
		Yield (%)	Sel. (%)
1	Propylene oxide	96.2	99.3
2	Epichlorohydrin	96.3	98.3
3	Styrene oxide	93.1	98.2
4	1,2-Butylene oxide	94.1	99.6

Reaction conditions: PO 28.6 mmol, catalyst 0.1 g, temperature 150 °C, initial CO_2 pressure 2.0 MPa, time 5 h

found the PC selectivity slightly increased within the first 4-h period and then kept almost constant. Similar phenomenon was observed for other catalysts in the cycloaddition reaction [27, 28]. Therefore, proper reaction time is indispensable for this catalytic system.

3.3.2 *Cycloaddition of CO_2 to Selected Epoxides*

Under the optimized conditions (150 °C, initial CO_2 pressure 2.0 MPa, 5 h), PS-CQNS was tested for the cycloaddition of CO_2 to selected epoxides. As shown in Table 1, PS-CQNS is active for all the substrates. The activity (yield) order of the epoxides is: epichlorohydrin (96.3 %) $\approx$ PO (96.2 %) $>$ 1,2-butylene oxide (94.1 %) $>$ styrene oxide (93.1 %). It is noted the selectivity to the corresponding cyclic carbonates is high as well.

3.4 Comparison of Catalysts

Some researchers pointed out that imidazole-based ionic liquids containing COOH group show high catalytic activity, and the probable reason is the synergistic effect between COOH and halogen anions [16, 24, 28, 30]. In the present study, we compared the catalytic performance of PS-QNS and PS-CQNS under equal conditions with the latter containing the COOH group (Table 2).

Table 2 Comparison of cycloaddition of CO_2 to PO over various catalysts

Entry	Catalysts	Catalytic results	
		Yield (%)	Sel. (%)
1	PS	0	0
2[a]	*N*,*N*-Dimethylglycine	50.7	95.9
3[a]	PS + *N*,*N*-dimethylglycine	94.9	99.5
4[b]	*N*,*N*-Dimethylethylamine	47.3	99.5
5	PS-CQNS	96.2	99.3
6	PS-QNS	97.9	99.5
7[c]	HBetCl	94	–
8[c]	ChoCl	83	–

Reaction conditions: PO 28.6 mmol, catalyst 1.1 mol%, temperature 150 °C, initial CO_2 pressure 2.0 MPa, time 5 h

[a] *N*,*N*-Dimethylglycine: 1.1 mol%

[b] *N*,*N*-Dimethylethylamine: 1.1 mol%

[c] Reaction conditions: catalyst 2.5 mol%, temperature 140 °C, CO_2 pressure 8 MPa, time 8 h [18, 31]

As shown in Table 2, the support PS has no catalytic activity for the cycloaddition of CO_2 to PO (Entry 1). When *N*,*N*-dimethylglycine is selected as catalyst, the PC yield is extremely low (Entry 2). However, with the copresence of PS and *N*,*N*-dimethylglycine (Entry 3), there is big rise of PC yield, reaching an amount that is only slightly lower than that detected over PS-CQNS (Entry 5). The results indicate that there is synergistic effect between PS and *N*,*N*-dimethylglycine.

In order to investigate the role of COOH in the cycloaddition reaction, we compared the activity of *N*,*N*-dimethylethylamine and *N*,*N*-dimethylglycine under the conditions of: 150 °C, initial CO_2 pressure 2.0 MPa, and reaction time 5 h. As shown in Table 2 (Entries 2 and 4), despite *N*,*N*-dimethylethylamine and *N*,*N*-dimethylglycine both are low in catalytic activity, the latter shows slightly higher activity than the former, indicating that to some extent COOH could promote the reaction in the homogeneous system. Nonetheless, it is observed that PS-QNS shows higher catalytic activity than PS-CQNS (Table 2, Entries 5 and 6). Therefore, in the heterogeneous system, COOH does not promote the reaction; on the contrary, as a larger substituent group compared to CH_3, COOH hinders the reaction.

Compared to the works of Han et al. [18, 31], the catalytic activity of PS-QNS and PS-CQNS are higher than that of betaine hydrochloride (HBetCl) and choline chloride (ChoCl) under the conditions of CO_2 pressure 8 MPa and reaction time 8 h (Table 2, Entries 7 and 8).

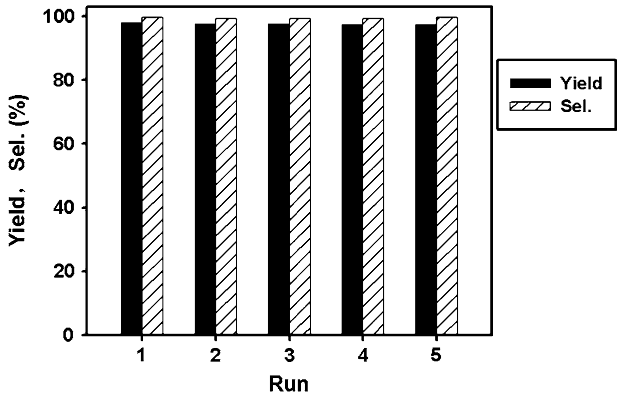


Fig. 7 Recycling of PS-QNS in the cycloaddition of CO_2 (reaction conditions: PO 28.6 mmol, temperature 150 °C, initial CO_2 pressure 2.0 MPa, time 5 h)

3.5 Catalyst Recycling

Using PO as substrate, we examined the reusability of PS-QNS under the conditions of 150 °C, initial CO_2 pressure 2.0 MPa and reaction time 5 h. After each cycle, the catalyst was recovered by simple filtration, washed with PO and dried in vacuum. Then the catalyst was reused for the next run. From Fig. 7, one can see that there is no significant decrease of PC yield across the five repeated runs, indicating that the PS-QNS catalyst is stable and reusable. What is more, the selectivity to PC is always above 99.2 %. We also employed elemental analysis technique to investigate the used catalyst after five recycles. It was found that its N content was 5.61 %, further confirming that PS-QNS has good stability. With such high catalytic activity and reusability, the PS-QNS catalyst is currently being tested in a fix-bed continuous flow reactor for the coupling reaction in our laboratory.

4 Conclusions

In summary, polystyrene bearing quaternary ammonium salts were obtained by direct quaternarization. The catalysts are relatively cheap and simple to prepare. They show high catalytic efficiency towards the cycloaddition of CO_2 to epoxides. Under relatively mild reaction conditions (150 °C, initial CO_2 pressure 2.0 MPa and 5 h), the PC yield and selectivity in the cycloaddition of CO_2 to PO over PS-QNS were 97.9 and 99.5 %, respectively. Besides, PS-QNS shows excellent reusability and stability. As a low-cost and high-efficient catalyst for the synthesis of five-membered cyclic carbonates, PS-QNS has potential in industrial application.

Acknowledgments This study was financially supported by the program for New Century Excellent Talents in Universities (NCET-10-0371), NSF of Hunan Province (10JJ1003), and the Fundamental Research Funds for the Central Universities. C. T. Au thanks the Hunan University for an adjunct professorship.

References

1. Xiong YB, Wang YJ, Wang H, Wang RM, Cui ZP (2012) J Appl Polym Sci 123:1486
2. Du Y, Cai F, Kong DL, He LN (2005) Green Chem 7:518
3. Zhang SJ, Chen YH, Li FW, Lu XM, Dai WB, Mori R (2006) Catal Today 115:61
4. Chen X, Sun J, Wang JQ, Cheng WG (2012) Tetrahedron Lett 53:2684
5. North M, Villuendas P (2012) ChemCatChem 4:789
6. Gao J, Song QW, He LN, Liu CL, Yang ZZ, Han X, Li XD, Song QC (2012) Tetrahedron 68:3835
7. Sakakura T, Choi JC, Yasuda H (2007) Chem Rev 107:2365
8. Sako T, Fukai T, Sahashi R (2002) Ind Eng Chem Res 41:5353
9. Huang JW, Shi M (2003) J Org Chem 68:6705
10. Jing HW, Nguyen ST (2007) J Mol Catal A 261:12
11. Kawanami H, Ikushima Y (2000) Catal Commun 36:2089
12. Yamaguchi K, Ebitani K, Yoshida T, Yoshida H, Kaneda K (1999) J Am Chem Soc 121:4526
13. Dai WL, Yin SF, Guo R, Luo SL, Du X, Au CT (2010) Catal Lett 136:35
14. Fujita SI, Bhanage BM, Ikushima Y, Shirai M, Torii K, Arai M (2002) Catal Lett 79:95
15. Kawanami H, Sasaki A, Matsui K, Ikushima Y (2003) Catal Commun 7:896
16. Han LN, Choi SJ, Park MS, Lee SM, Kim YJ, Kim MI, Liu YB, Park DW (2012) React Kinet Mech Catal 106:25
17. Du Y, Wang JQ, Chen JY, Cai F, Tian JS, Kong DL, He LN (2006) Tetrahedron Lett 47:1271
18. Zhou YX, Hu SQ, Ma XM, Liang SG, Jiang T, Han BX (2008) J Mol Catal A 284:52
19. He LN, Yasuda H, Sakakura T (2003) Green Chem 5:92
20. Wu SS, Zhang XW, Dai WL, Yin SF, Li WS, Ren YQ, Au CT (2008) Appl Catal A 341:106
21. Tian JS, Miao CX, Wang JQ, Cai F, Du Y, Zhao Y, He LN (2007) Green Chem 9:566
22. Zheng XX, Luo SZ, Zhang L, Cheng JP (2009) Green Chem 11:455
23. Xiao LF, Li FW, Peng JJ, Xia CG (2006) J Mol Catal A 253:265
24. Han LN, Choi HJ, Choi SJ, Liu BY, Park DW (2011) Green Chem 13:1023
25. Udayakumar S, Lee MK, Shim HL, Park SW, Park DW (2009) Catal Commun 10:659
26. Dai WL, Chen L, Yin SF, Luo SL, Au CT (2010) Catal Lett 135:295
27. Dai WL, Chen L, Yin SF, Li WH, Zhang YY, Luo SL, Au CT (2010) Catal Lett 137:74
28. Zhang YY, Yin SF, Luo SL, Au CT (2012) Ind Eng Chem Res 51:3951
29. Xie Y, Zhang ZF, Jiang T, He JL, Han BX, Wu TB, Ding KL (2007) Angew Chem Int Ed 119:7393
30. Sun J, Han LJ, Cheng WG, Wang JQ, Zhang XP, Zhang SJ (2011) ChemSusChem 4:502
31. Zhu AL, Jiang T, Han BX, Zhang JC, Xie Y, Ma XM (2007) Green Chem 9:169