

Research Article

Cycloaddition Reaction of Carbon Dioxide to Epoxides Catalyzed by Polymer-Supported Quaternary Phosphonium Salts

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Polymer-supported quaternary phosphonium salt (PS-QPS) was explored as effective catalyst for the coupling reaction of carbon dioxide with epoxides. The results indicated that cyclic carbonates with high yields (98.6%) and excellent selectivity (100%) could be prepared at the conditions of 5 MPa CO₂, 150°C, and 6 h without the addition of organic solvents or cocatalysts. The effects of various reaction conditions on the catalytic performance were investigated in detail. The catalyst is applicable to a variety of epoxides, producing the corresponding cyclic carbonates in good yields. Furthermore, the catalyst could be recovered easily and reused for five times without loss of catalytic activity obviously. A proposed mechanism for synthesis of cyclic carbonate in the presence of PS-QPS was discussed. The catalyst was characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectrum. It is believed that PS-QPS is of great potential for CO₂ fixation applications due to its unusual advantages, such as easy preparation, high activity and selectivity, stability, low cost, and reusability.

1. Introduction

Due to the economic and environmental benefits, developing chemical synthesis processes using renewable resource becomes increasingly important [1]. From the green chemistry point of view, the use of CO₂ as feedstock in synthesis and industrial applications plays an important role in the protection of environment because it is a primary greenhouse gas which contributes to global warming, and the emission of CO₂ from combustion into the atmosphere continues to rise [2, 3]. Without action toward stemming CO₂ emissions, global warming could pose a massive threat to our modern life; crop failure due to changing climates, increasingly common freak weather conditions, and loss of habitat are all potential consequences of humans carbon-rich lifestyle which are already becoming apparent [4, 5].

Carbon dioxide is an attractive C1 building block, safe raw material, and environmentally friendly chemical reagent in organic synthesis since it is highly abundant, inexpensive, nontoxic, and nonflammable [6, 7]. Therefore, chemical fixation of CO₂ becomes more important from both an ecological and an economic points of view. Approximately

110 MT (megatons) of CO₂ are currently used for chemical synthesis annually. The chemicals synthesized include urea, salicylic acid, cyclic carbonates, and polycarbonates [8]. The cycloaddition reaction of CO₂ with epoxides to afford the five-membered cyclic carbonates represents a promising methodology in CO₂ chemical fixation [9, 10], these cyclic carbonates can be widely used for various purposes, such as electrolytic elements of lithium secondary batteries, polar aprotic solvents, monomers for synthesizing polycarbonates, chemical ingredients for preparing medicines or agricultural chemicals, alkylating agents, engineering plastics, and biomedical fields [11, 12]. In the last decades, many catalytic systems have been developed for coupling CO₂ and epoxides, such as metal salts [13], metal oxides [14], quaternary ammonium salts [15, 16], quaternary phosphonium salts [17, 18], transition metal complex, salen complex [19–25], ion-exchange resins [26], and ionic liquids (ILs) [27–31]. However, in some of the cases, organic solvents and expensive metal catalysts are used in the reactions or work-up procedures, and the products are commonly isolated from the reaction systems by distillation; the yield of the desired products still remained low. Therefore, development

TABLE 1: Cycloaddition reactions of CO₂ to ECH catalyzed by different catalysts.

Catalyst	P content (%)	Yield (%)	Selectivity (%)
PS-QPS-1	5.0	98.6	99.4
PS-QPS-2	2.1	78.9	97.9
PIL-1	8.7	93.3	100
PIL-2	9.4	92.4	97.4
PBu ₃	15.3	5.3	89.6
CMPS	0	—	—

Reaction conditions: ECH 3 mL, catalyst 0.08 g, 5 MPa CO₂, 150 °C, and 6 h.

of efficient catalysts for this transformation using cheap and nontoxic reagents and conducting the reactions under solvent-free conditions are still desirable [32].

In the previous works [33–35], we found that quaternary phosphonium salts demonstrated very high activity and excellent selectivity in the cycloaddition of CO₂ to epoxides. Herein, we highlight the use of high cross-linked polymeric material as support and develop the polymer-supported quaternary phosphonium salts (PS-QPS) for the synthesis of cyclic carbonate (as shown in Scheme 1). The catalytic performance of PS-QPS catalyst for cycloaddition of CO₂ to epoxides was investigated in detail.

2. Experimental

2.1. Materials. Highly cross-linked chloromethylated polystyrene (CMPS) (substitution: 4.7 mmol/g and 2% cross-linked with divinylbenzene, particle size: 100–200 mesh) was purchased from Tianjin Nankai Hecheng Sci. & Tech. Co. Ltd. Epichlorohydrin (ECH, AR) and propylene oxide (PO, CP) were commercially available and distilled before use. Tributylphosphine (PBu₃), cyclohexene oxide (Aladdin), styrene oxide (Aladdin 98%), allyl glycidyl ether (AGE, Aladdin > 99.0%) and carbon dioxide (99.99%), were used without further purification. Other chemicals were commercially available and used as received.

2.2. Synthesis of 4-Vinylbenzyl-Tributylphosphorous Chloride (PIL-1). 4-Vinylbenzyl-tributylphosphorous chloride was synthesized according to the reported method [33–35]. 4-Vinylbenzyl chloride (4.03 g, 26.4 mmol), PBu₃ (5.36 g, 26.5 mmol), and acetone (50 mL) were introduced into a dried flask with a magnetic stirrer. The mixture was stirred at 60 °C under nitrogen for 48 h. Then, 4-vinylbenzyl-tributylphosphorous chloride (PIL-1) was obtained by filtration after pouring the mixture into diethyl ether and washed with diethyl ether. The solid was dried overnight under vacuum at room temperature to give a white powder (yield: 78.6%). 4-Vinylbenzyl-tributylphosphorous chloride was characterized by proton nuclear magnetic resonance (¹H NMR, D₂O, 400 MHz, δ ppm): 0.68 (*t*, 9H), 1.12–1.36 (*m*, 6H), 1.88 (*s*, 6H), 3.39 (*t*, 6H), 5.11 (*d*, 2H), 5.65 (*d*, 1H), 6.45–6.63 (*m*, 2H), and 7.0–7.4 (*m*, 4H). Benzyl-tributylphosphorous chloride (PIL-2) was synthesized according to the same procedure (yield: 80.0%)—¹H NMR

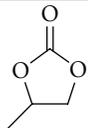
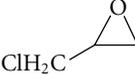
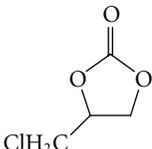
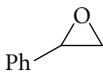
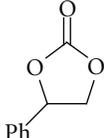
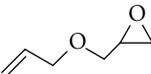
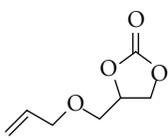
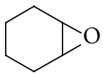
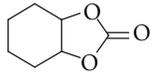
(D₂O, 400 MHz, δ ppm): 0.94 (*t*, 9H), 1.38–1.52 (*m*, 6H), 1.52–1.67 (*m*, 6H), 2.05–2.08 (*m*, 6H), 3.65–3.79 (*d*, 2H), and 7.31–7.58 (*m*, 5).

2.3. Preparation of Polymer-Supported Quaternary Phosphonium Salts. Preparation of immobilized quaternary phosphonium salts on chloromethylated polystyrene (CMPS) was conducted according to the procedure in the literature with a little modification [36]. A mixture of CMPS (0.38 g, 1.8 mmol), tributylphosphine (2.1 mmol), and acetonitrile (60 mL) was refluxed for 48 h under a nitrogen atmosphere in a 100 mL flask. After cooled down to room temperature, the solid residue was collected by filtration and washed three times with dehydrated ethanol. Then, the solid was dried under vacuum at 60 °C for 12 h to give polymer-supported quaternary phosphonium salt (PS-QPS).

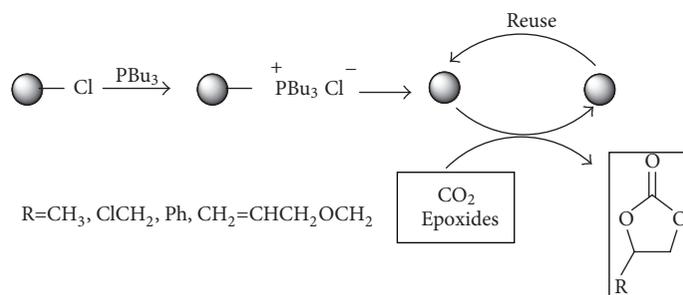
2.4. Characterization of Polymer-Supported Quaternary Phosphonium Salts. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AM 400 MHz spectrometer at 25 °C. Thermogravimetric analysis (TGA) was performed using a TG-DTA 2000S (Mac Sciences Co. Ltd., Yokohama, Japan) in a nitrogen atmosphere between 25 and 800 °C at a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were recorded on a DigiLab FTS-3000 IR-spectrometer with anhydrous potassium bromide (KBr) as standard. The morphology of PS-QPS was observed by scanning electron microscope (JSM 6701F, Japan). The content of P element was determined by atom absorbance spectrograph using a PerkinElmer optima 4300 DV as emission spectrometer (USA).

2.5. Typical Procedure for the Synthesis of Cyclic Carbonate from ECH and CO₂. The cycloaddition reactions were performed in a 100 mL stainless steel autoclave equipped with a magnetic stirrer. For each typical batch operation, epoxides and PS-QPS were charged into the reactor and then purged with CO₂. The reactor was then pressurized with CO₂ to a preset pressure at room temperature. The reactor was heated to a specified temperature with an addition of CO₂ from a high-pressure reservoir tank to maintain a specified constant pressure for a desired time, and then the reaction was started by stirring the reactant mixture at 300 rpm. The reactor pressure increased about 0.03–0.10 MPa depending on the reaction temperature due to vapor pressure of the reactants. After the proper reaction time, the reactor was cooled to 0–5 °C in an ice-water bath, and then the CO₂ was released through a cold trap with *N,N*-dimethylformamide to capture the reactants and products entrained by CO₂. The organic products were filtrated from the reaction mixture and the resulting filtrate, together with the absorbent, was analyzed by gas chromatography (GC, GC-16 A, 3 m · 3 mm OV-17 column, Shimadzu). The retention time of the products was compared with available authentic standards. The synthesized catalysts were pretreated by grinding before use.

TABLE 2: Cycloaddition reactions of CO₂ to different epoxides.

Entry	Epoxides	Products	Time (h)	Selectivity (%)	Yield (%)
1			6	99.9	93.0
2			6	99.4	98.6
3			10	98.6	95.8
4			9	79.2	73.7
5			48	88.2	72.3

Reaction conditions: epoxide 3 mL, PS-QPS-1 0.08 g, 5 MPa CO₂, 150 °C.

SCHEME 1: Preparation of PS-QPS and cycloaddition reaction of CO₂ to epoxides.

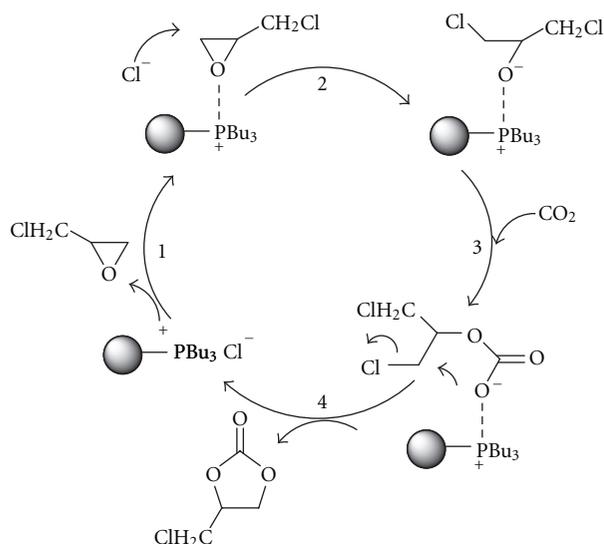
3. Results and Discussion

3.1. Characterization of Catalyst. Figure 1 shows the FT-IR spectra of CMPS, as well as fresh and used PS-QPS. The peaks at 1459 and 703 cm⁻¹, ascribing to the stretching vibration of P-C(Ar) and P-C, respectively, emerged in PS-QPS curve. In addition, there is a wide and strong peak at 3430 cm⁻¹, which is ascribed to absorption of H-O in water molecular. It is because PS-QPS becomes hydrophilic due to the introduction of quaternary phosphonium salts on the surface. However, the surface of CMPS is hydrophobic. The previous results indicate that tributylphosphine has been anchored onto CMPS successfully.

Figure 2 gives the TGA curves of PS-QPS and CMPS. It is observed that the weight loss of CMPS is less than 1% up to 260 °C. And then, polymer matrix decomposition goes

through two stages, at 270 °C and 430 °C, respectively. However, there is about 8% weight loss in PS-QPS below 110 °C. This may be attributed to the desorption of trapped water on the surface of PS-QPS. Polymer matrix decomposition of PS-QPS begins at 290 °C and higher than CMPS (270 °C). It can be drawn that the thermal stability of CMPS was enhanced a little due to the graft of tributylphosphine. Moreover, there is only 20% weight loss at 380 °C in CMPS, whereas the weight loss of PS-QPS is as high as 50% at the same temperature. It can be inferred that more weight loss is ascribed to the decomposition of tributylphosphine on the surface of PS-QPS.

As discussed earlier, the surface of PS-QPS became hydrophilic due to the anchoring of tributylphosphine. It can also be proved by SEM images. As shown in Figure 3, the surface of CMPS with the size about 100 μm is quite plain



SCHEME 2: Proposed mechanism for PS-QPS catalyzed cycloaddition of CO_2 with epoxides.

(Figures 3(a) and 3(d)). When CMPS was modified with quaternary phosphonium salts and recycled in the cycloaddition reaction, the size of CMPS particles did not change. However, it can be seen clearly that many spheric particles in the size of about 200 nm can be observed (Figure 3(e)). It is because quaternary phosphonium salt is hydrophilic, whereas CMPS is hydrophobic. As a result, phase separation occurs, and quaternary phosphonium salts tend to aggregate together to form spheric particles.

3.2. Coupling Carbon Dioxide and Epichlorohydrin. The catalytic performances of PS-QPS catalysts with different phosphorus content for the cycloaddition reaction of CO_2 to epichlorohydrin (ECH) were investigated. The phosphorus contents of different PS-QPS were determined by atom absorbance spectrograph. The results are summarized in Table 1. It can be seen that CMPS does not exhibit any activity for the cycloaddition reaction. However, PS-QPS presents high activity and selectivity at the same conditions, and the yield of cyclic carbonate increases with *P* content of PS-QPS microparticles. The catalytic activity of PS-QPS-1 is even higher than the unsupported quaternary phosphorous salts (PIL-1 and PIL-2). The main reason for this was that ionic liquids catalysts were immiscible with the substrate, and there were two phases in the reaction system at the beginning [36]. As a result, the interphase mass transfer reduced the reaction rate, while PS-QPS microparticles synthesized in this work could be well dispersed in the reaction mixture under stirring.

3.3. Influences of Pressure and Temperature on the Synthesis of Cyclic Carbonate. A disadvantage associated with using CO_2 as a reagent in organic synthesis is the potential dangers resulted from operating at high temperatures and pressures, especially in the presence of heterogeneous catalytic system. Therefore, the independences of the yields of cyclic carbonate on the reaction conditions were investigated. Figure 4 depicts

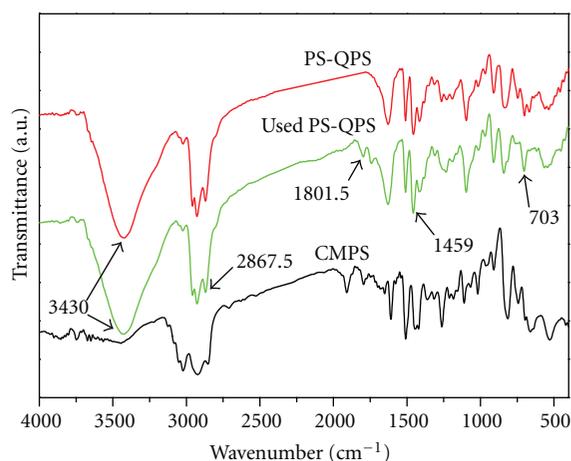


FIGURE 1: FT-IR spectra of chloromethylated bead and PS-QPS.

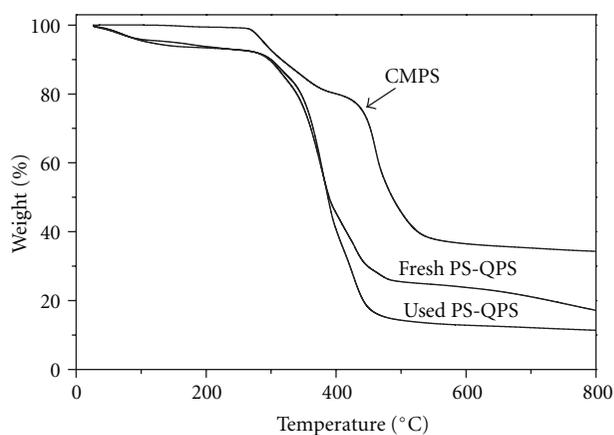


FIGURE 2: TGA curves of PS-QPS and chloromethylated bead.

the effect of CO_2 pressure on the yield of cyclic carbonate in the presence of PS-QPS. It can be seen that pressure plays great influence on the yield of cyclic carbonate. A yield of 77.5% can be obtained at lower pressure (2 MPa), and it increases with the CO_2 pressure from 2 to 5 MPa. The cyclic carbonate yield achieves as high as 98% when the reaction is conducted at 5.0 MPa CO_2 . However, the yield decreases to 91.6% when further increasing the pressure up to 5.5 MPa. This can be explained by the pressure effect on the concentrations of CO_2 and epoxide in the two phases [37]. The upper phase is the CO_2 -rich phase, and the bottom phase is the epoxide-rich phase. The reactions take place mainly in the liquid phase because the catalyst is dispersed in this phase. The change in reaction rate is related to the partition behavior of the substrate, and the increase in CO_2 pressure has two opposite effects on the reactions. First, the solubility of CO_2 in the epoxides increases with increasing pressure, which favors the reaction considering that CO_2 is a reactant. At higher pressures, however, more epoxides are in the CO_2 -rich phase and the concentration of epoxides in the liquid phase is too low, which reduces the reaction rate. At lower CO_2 pressure, the first factor is dominant because

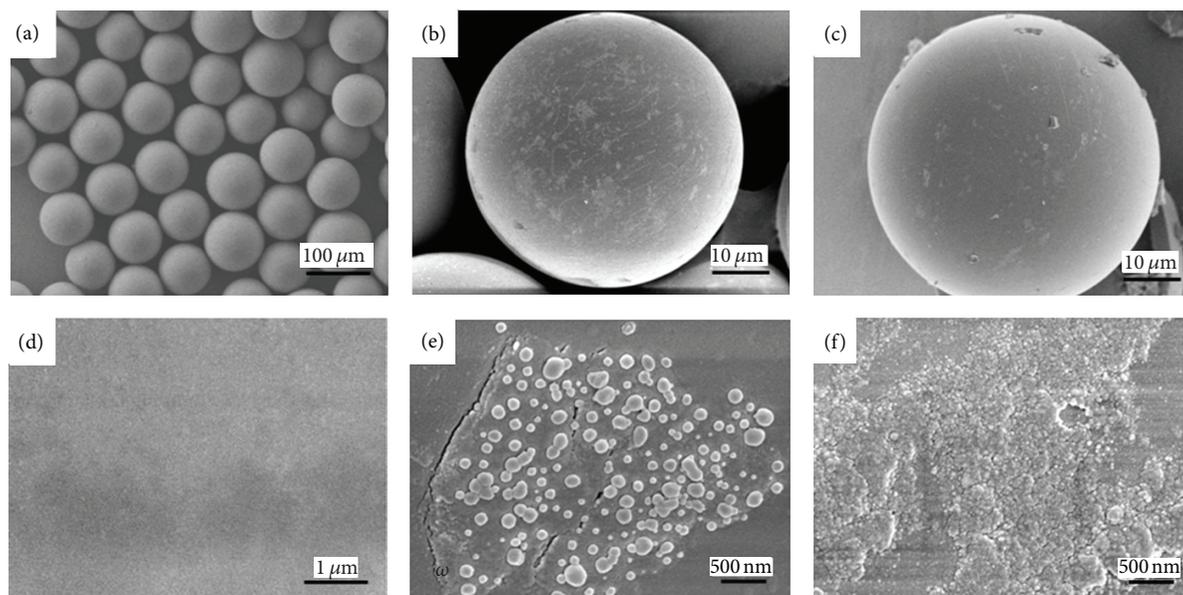


FIGURE 3: SEM images of chloromethylated bead (a and d), fresh PS-QPS (b and e), and used PS-QPS (c and f).

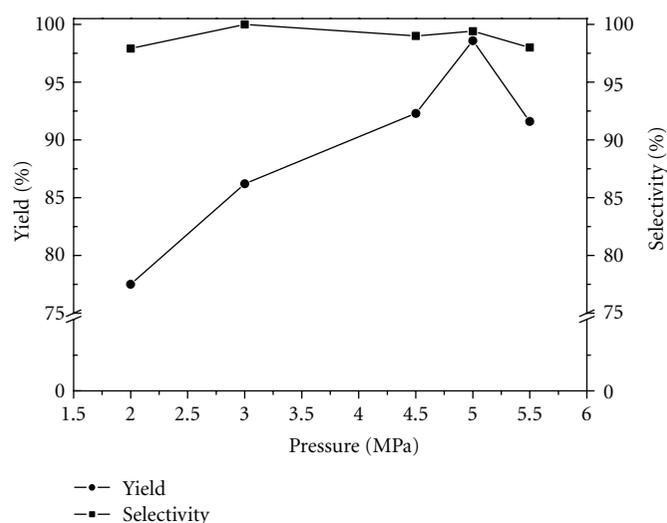


FIGURE 4: Dependence of the cyclic carbonate yield and selectivity on CO₂ pressure. Reaction conditions: ECH 3 mL, PS-QPS-1 0.08 g, 150°C, and 6 h.

the concentration of CO₂ in the liquid phase is lower. The second factor becomes dominant when the pressure of CO₂ is high enough. Therefore, a maximum appears in pressure versus yield curve [38]. The maximum occurs in yield versus pressure curves at about 5 MPa for ECH in the present system.

Figure 5 shows the influence of temperature on the yield and selectivity of cyclic carbonate. It can be seen clearly that the catalytic activity is sensitive to reaction temperature. The yield of cyclic carbonate increases dramatically with the temperature increasing from 130°C to 150°C. However, the yield decreases when further increasing the temperature. It has been reported that there were some side reactions, such as ECH polymerization, the isomerization to acetone

and the ring opening by water to propylene glycol [29, 39]. The GC study showed that the by-product in the present cycloaddition reaction of ECH was 3-chloro-1,2-propylene glycol. Therefore, the main side reaction was the ring opening of cyclic carbonate caused by the residual water on the surface of PS-QPS microparticles at higher temperature.

3.4. Influences of Reaction Time and Catalyst Amount on the Synthesis of Cyclic Carbonate. Dependence of the product yield on reaction time at 150°C and CO₂ pressure of 5 MPa is shown in Figure 6. It indicates that the yield increased with reaction time, and 98.6% ECH can be converted within 6 h. In other words, PS-QPS is an effective heterogeneous catalyst

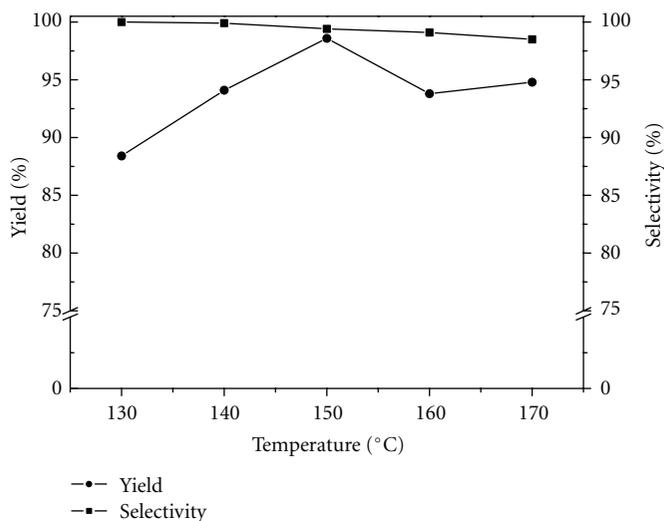


FIGURE 5: Temperature dependence of the cyclic carbonate yield and selectivity. Reaction conditions: ECH 3 mL, PS-QPS-1 0.08 g, 5 MPa CO₂, 6 h.

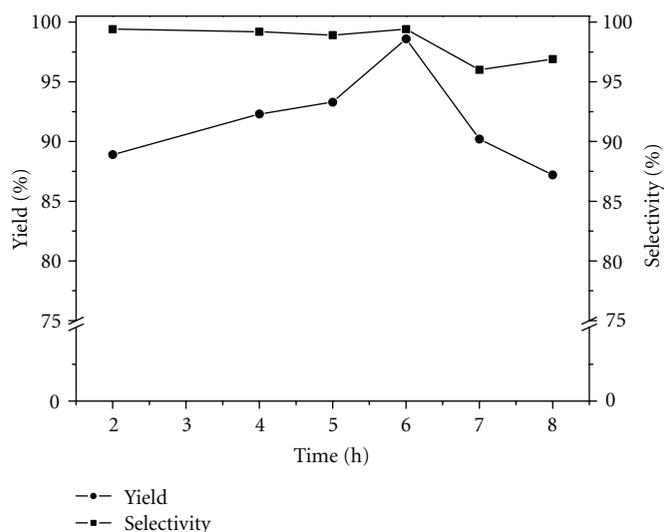


FIGURE 6: Influence of reaction time on the cyclic carbonate yield and selectivity. Reaction conditions: ECH 3 mL, PS-QPS-1 0.08 g, 5 MPa CO₂, and 150°C.

for the synthesis of cyclic carbonate from ECH and CO₂. However, both the yield and selectivity undergo decreases with the reaction time increasing, especially the yield. It has been reported that supported ionic liquid was also active catalyst for the hydrolysis reaction of cyclic carbonate to produce 1,2-propylene glycol [40]. As shown in Figures 2 and 3, the microparticles surface became highly hydrophilic, and some water was absorbed after quaternary phosphorous salts were anchored onto. Therefore, the reason for the decrease of cyclic carbonate yield with the reaction time over 6 hours is presumably due to the hydrolysis of cyclic carbonate to 3-chloro-1,2-propylene glycol. Similarly, GC results testified

the previous conclusion. Thus, all the following reactions are performed in 6 h.

The influence of catalyst amount on the reaction was also evaluated under otherwise identical reaction conditions. As summarized in Figure 7, the yield of cyclic carbonate remarkably increases to 87.9% with 0.07 g catalyst presented. Notably, cyclic carbonate could be obtained in almost quantitative yield (98.6%) with 99.4% selectivity within 6 h when the catalyst amount increased to 0.08 g. A lower cyclic carbonate yield was observed when the catalyst amount increased further. Because the catalyst microparticles are highly charged, there is electrostatic interaction between

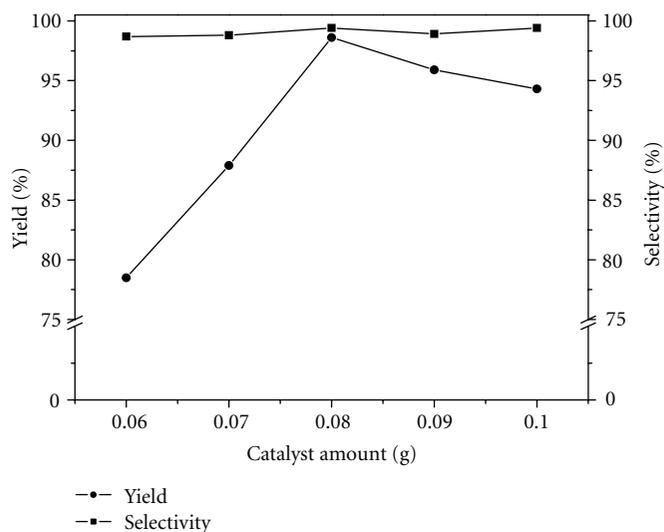


FIGURE 7: Effect of the amount of catalyst on the cyclic carbonate synthesis. Reaction conditions: ECH 3 mL, PS-QPS-1, 5 MPa CO₂, 150°C, and 6 h.

these catalyst microparticles. Therefore, the excess catalysts cannot be well dispersed in the reaction mixture and limit the mass transfer between the active sites and reactants [30]. As a result, there is an optimal catalyst amount in the present cycloaddition reaction process.

3.5. Coupling Carbon Dioxide and Other Epoxides. The results previous indicated that PS-QPS is an effective catalyst for the cycloaddition of ECH with CO₂ at solvent-free and cocatalyst-free conditions. In order to survey the scope of substrates, we examined the cycloaddition reactions of CO₂ with other epoxides by performing the reaction under the same conditions as elaborated in Table 2. PS-QPS is found to be applicable to a variety of terminal epoxides (entries 1–5, Table 2) to provide the corresponding cyclic carbonates with high yields and selectivity. Entries 1 and 2 demonstrate that ECH is more reactive than propylene epoxide when PS-QPS was used as catalyst. The possible reason is the presence of the electron-withdrawing chloromethyl group in ECH, which results in easy ring opening of ECH by nucleophilic attack. Due to the higher hindrance originated from the two rings, cyclohexene oxide (entry 5) presents relatively lower activity [11].

A possible mechanism for the PS-QPS-catalyzed cycloaddition of CO₂ with epoxide is proposed as shown in Scheme 2. As mentioned earlier, the quaternary phosphonium salt part is suggested to be the active species for the reaction. This proposal is analogous to that of the quaternary phosphonium salt-catalyzed version of the same reaction [5]. The proposed mechanism involves the activation of epoxide by the quaternary phosphonium cation (step 1), the ring opening of the epoxides via nucleophilic attack of chlorine at the less-hindered carbon, producing an oxy anion species (step 2), and the insertion of CO₂ into the P–O bond (step 3). Subsequent cyclization via an intermolecular nucleophilic attack (step 4) leads to the cyclic carbonate and

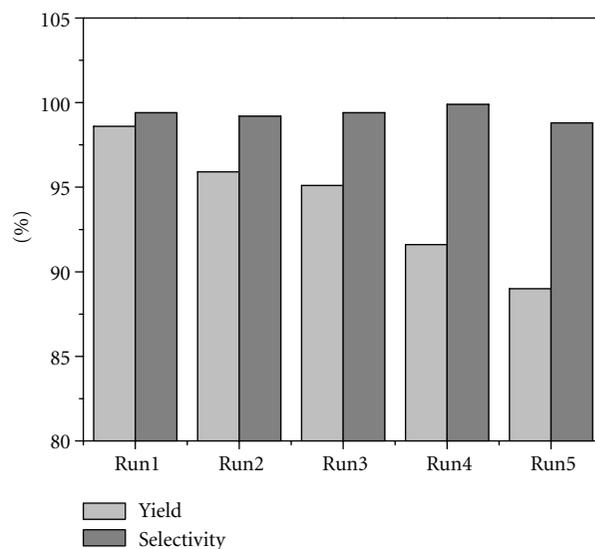


FIGURE 8: Recycling experiments for polymer-supported quaternary phosphonium salts. Reaction conditions: ECH 3 mL, PS-QPS-1 0.08 g, 5 MPa CO₂, 150°C, and 6 h.

the regeneration of the catalyst. It can be seen that the role of resin in this system was as a reusable supporter which can be easily separated.

It is well known that the constancy of the catalyst activity and reusability of catalyst are two important factors that determine whether it finds practical application in industry. In order to test this characteristic of PS-QPS catalyst, a series of catalytic cycles for the coupling reaction of CO₂ with ECH are investigated under the optimized reaction conditions [21, 29]. In each cycle, the catalyst was separated by filtration, washed with acetone, and then dried under vacuum before use in the succeeding run. The yields of cyclic carbonates after five repeated runs are shown in Figure 8. There is only about

10% activity loss after five recycles, indicating that the catalyst is not only insoluble in the reaction mixture but also very stable. The loss of catalytic activity may be due to the residual cyclic carbonate in PS-QPS. It is very difficult to remove cyclic carbonate from the catalyst completely due to its high boiling point (above 200 °C). The residual cyclic carbonate in the catalyst can be testified by FT-IR. As shown in Figure 1, the peak at 1801.5 cm^{-1} in the curve of used PS-QPS is ascribed to the stretch vibration of C=O in cyclic carbonate. Moreover, SEM image (Figure 3(f)) indicates that spheric particles on the surface of PS-QPS disappear, and the surface of used PS-QPS becomes rougher. It may be due to the solubilization of cyclic carbonate. TGA curve (Figure 2) illustrates that used PS-QPS is thermally stable.

4. Conclusions

Tributylphosphine was anchored on highly cross-linked chloromethylated polystyrene as effective catalyst for cyclic carbonates synthesis via the cycloaddition of epoxides with CO_2 . The results testified that high yields and excellent selectivity can be achieved using PS-QPS on the condition of 5 MPa CO_2 and 150 °C in 6 h. In addition, the catalyst can be easily separated from the products and reused for up to five times without considerable decrease in the yield of cyclic carbonate. The organic solvent-free green process presented here is of great potential application in industry due to its easy product separation, low cost, and high efficiency. In the future work, we will explore the application of PS-QPS catalyst in the transesterification reaction of cyclic carbonate and methanol for dimethyl carbonate synthesis. And our aim is the industry application of these quaternary phosphonium salt-based heterogeneous catalysts.

Acknowledgments

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