

# Synthesis of cyclic carbonates from epoxides and carbon dioxide over silica-supported quaternary ammonium salts under supercritical conditions

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## Abstract

A silica-supported quaternary ammonium salt is reported for the first time as a recyclable and efficient catalyst for the synthesis of propylene carbonate from propylene oxide and carbon dioxide under supercritical conditions, which requires no additional organic solvents either for the reaction or for the separation of product. Moreover, the catalyst can be easily recovered by a simple filtration and reused over four times without obvious loss of its catalytic activity. The effects of the types of cation and anion of quaternary ammonium salts, and other reaction parameters on the reaction are investigated. This organic solvent-free process presented here could show much potential application in industry due to its simplicity, easy product separation from reaction medium and catalyst recycling. It could be profitably applied to the development of fix-bed continuous flow reactors, avoiding the use of solvent to isolate the products.

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**Keywords:** Supercritical carbon dioxide; Propylene carbonate; Propylene oxide; Cycloaddition; Silica-supported quaternary ammonium salts

## 1. Introduction

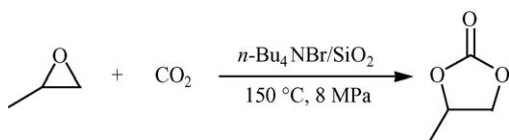
Chemical fixation of CO<sub>2</sub> is a very attractive subject from the viewpoints of better utilization of carbon resource and increased concern on our environment [1–3]. One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates via the coupling of CO<sub>2</sub> and epoxides (Schemes 1 and 2) [4]. These organic cyclic carbonates such as ethylene carbonate and propylene carbonate (PC) are widely used for various purposes, for instance, electrolytic elements of lithium secondary batteries, polar aprotic solvents, monomers for synthesizing polycarbonates, chemical ingredients for preparing medicines or agricultural chemicals, and alkylating agents [5–9].

In current processes for cyclic carbonate production employed by industry, various homogeneous catalysts are used [4–6]. However, homogeneous catalysts are undesirably dissolved in a phase containing cyclic carbonates, thus it is necessary to separate the catalysts from the products through a

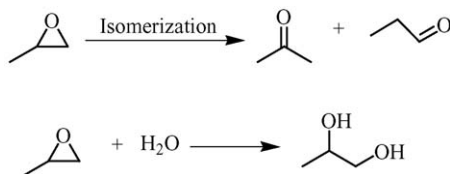
purification process. In order to facilitate the separation of catalyst, a large number of solid catalysts have been developed, for example, polymer-supported quaternary onium salts [10,11], magnesia [12,13], Mg–Al mixed oxide [14], Cs-load zeolite and alumina [15], lanthanide oxychloride [16,17]. More recently, niobium (V) oxide and other heterogeneous catalysts have been found to be efficient catalysts for the carboxylation of epoxides with CO<sub>2</sub> [18–25]. Unfortunately, these solid catalysts have insufficient activity and most of them are essentially required to contain a polar solvent as an additive for realizing activity and selectivity, which may have caused catalyst leaching and required additional processes for product separation. Solid supported catalysts have received much more attention [26,27], because they may offer several advantages in preparative procedures [28,29] e.g. simplifying work-up and separation and recycling of the catalyst. In heterogeneous catalysis, supercritical CO<sub>2</sub> properties can help reduce mass and heat transfer limitations and avoid coke formation or catalyst poisoning [29]. Development of a more efficient and environmentally benign catalyst for cyclic carbonate synthesis under mild conditions still remains a challenging issue.

Quaternary ammonium salts (e.g., Et<sub>4</sub>NBr) or alkali iodides (e.g., KI) are typically used as homogeneous catalysts for cyclic

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Scheme 1. Propylene carbonate synthesis.



Scheme 2. Possible side reactions.

carbonate synthesis [30–32]. Our strategy is that quaternary ammonium salts can be heterogenized by dispersing it on high-surface-area inorganic supports in order to get a better catalyst separation and make the catalyst recovery more facile [33]. Herein, we would like to describe a simple, efficient and recyclable catalyst of silica-supported quaternary ammonium salt for the cycloaddition reaction of CO<sub>2</sub> and propylene oxide to produce PC, as shown in Scheme 1. In the present work, high PC yield and selectivity were obtained at 140 °C under 8 MPa in a short reaction time of 5 h, even in the absence of any additional organic solvents.

## 2. Experimental section

### 2.1. Reagents

Silica gel (HG/T2534-92 chromatography grade, specific surface area: 550 m<sup>2</sup>/g; pore volume: 0.70–0.90 ml/g; particle size: 400 mesh) in this study was commercially supplied by Qingdao Haiyang Chemical Reagents Co. Ltd. Epoxides were supplied from Aldrich Company and carbon dioxide with a purity of 99.99% was commercially available. Tetra-*n*-propylammonium bromide (*n*-Pr<sub>4</sub>NBr) was purified by recrystallization from methanol prior to use. Other reagents were analytical grade and were used as received.

### 2.2. Catalysts preparation and characterization

Silica gel-supported catalysts were prepared according to the recently reported procedure [33] In a typical preparation, *n*-Bu<sub>4</sub>NBr was added in desired amounts 15% (w/w) to silica gel, dissolved in methanol. The solvent was removed by evaporation and the support was heated in an oven at 100 °C for 15 h. The specific surface area was determined by means of the BET method using N<sub>2</sub> adsorption at 77 K with a Quantachrome NOVA 2000e instrument. Prior to measurement, the sample was heated in vacuum at 100 °C for 3 h. The BET surface area of the typical supported catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>) was 217.8 m<sup>2</sup>/g. The FT-IR spectra were recorded on a Bruker vector 22 FT-IR spectrophotometer using KBr tablets. The FT-IR spectra comparison of the typical supported catalyst Bu<sub>4</sub>NBr/SiO<sub>2</sub> with the

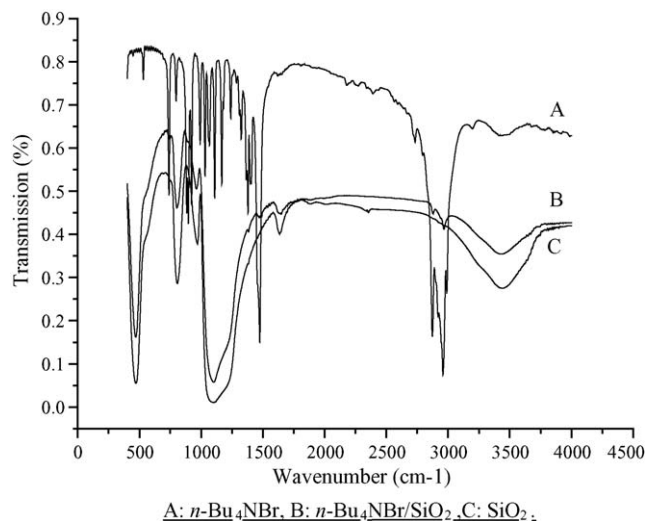


Fig. 1. The FT-IR spectra comparison of the typical supported catalyst Bu<sub>4</sub>NBr/SiO<sub>2</sub> with the support SiO<sub>2</sub> and the active species Bu<sub>4</sub>NBr. (A) *n*-Bu<sub>4</sub>NBr; (B) *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>; (C) SiO<sub>2</sub>.

support SiO<sub>2</sub> and the active species Bu<sub>4</sub>NBr was illustrated in Fig. 1, undoubtedly indicating the active catalyst was successfully immobilized in the support of silica.

### 2.3. Procedure for the cycloaddition reaction<sup>1</sup>

In a typical reaction, the cycloaddition reaction of CO<sub>2</sub> to propylene oxide was carried out in a stainless steel autoclave (25 cm<sup>3</sup> inner volume). Prior to the reaction, the catalyst was evacuated at 150 °C for 3 h. CO<sub>2</sub> (liquid, 4.0 MPa) was introduced to a mixture of propylene oxide (57.2 mmol), catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>) 1.41 g (1 mmol%), and biphenyl (80 mg, an internal standard for GC analysis) at room temperature. The initial pressure was adjusted to 8 MPa at 150 °C and the autoclave was heated at that temperature for 10 h. After cooling, the products were analyzed on a gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector. The structure and the purity of the products were further identified using GC-MS (HP G1800A) by comparing retention times and fragmentation patterns with those of authentic samples. The products were also characterized by NMR. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury-plus 400 spectrometer. Chemical shifts were given as δ values referenced in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard.

Spectral characteristics of the products (cyclic carbonates **2a–e**) in Table 3 were provided as follows: 4-methyl-1, 3-dioxolan-2-one (**2a**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.43 [d, <sup>3</sup>J (H, H)=6.0 Hz, 1H, CH<sub>3</sub>], 3.98 [t, <sup>3</sup>J (H, H)=8.4 Hz, 1H, OCH<sub>2</sub>], 4.51 [t, <sup>3</sup>J (H, H)=8.4 Hz, 1H, OCH<sub>2</sub>], 4.82 [m, 1H, CHO]. <sup>13</sup>C {<sup>1</sup>H} NMR (100.4 MHz in CDCl<sub>3</sub>): δ 19.14, 70.52, 73.47, 154.95; 4-chloromethyl-1, 3-dioxolan-2-one (**2b**): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.71 [dd, <sup>3</sup>J (H,

<sup>1</sup> Caution: Operations of high-pressure equipment should take proper precautions to minimize the risk of personal injury.

H) = 3.2 Hz,  $^2J$  (H,H) = 12.0 Hz, 1H, ClCH<sub>2</sub>], 3.80 [dd,  $^3J$  (H,H) = 5.2 Hz,  $^2J$  (H,H) = 12.0 Hz, 1H, ClCH<sub>2</sub>], 4.39 [dd,  $^3J$  (H,H) = 6.0 Hz,  $^2J$  (H,H) = 8.4 Hz, 1H, OCH<sub>2</sub>], 4.58 [t,  $^3J$  (H,H) = 8.4 Hz, 1H, OCH<sub>2</sub>], 4.98 [m, 1H, CHO].  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100.4 MHz in CDCl<sub>3</sub>):  $\delta$  43.83, 66.84, 74.29, 154.28; 4-phenyl-1, 3-dioxolan-2-one (2c):  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  4.35 [t,  $^3J$  (H,H) = 8.4 Hz, 1H, OCH<sub>2</sub>], 4.80 [t,  $^3J$  (H,H) = 8.4 Hz, 1H, OCH<sub>2</sub>], 5.70 [t,  $^3J$  (H,H) = 8.0 Hz, 1H, OCH], 7.36 [d,  $^3J$  (H,H) = 7.6 Hz, 2H, C<sub>6</sub>H<sub>5</sub>], 7.44 [d,  $^3J$  (H,H) = 6.4 Hz, 3H, C<sub>6</sub>H<sub>5</sub>].  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100.4 MHz in CDCl<sub>3</sub>):  $\delta$  66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65, 157.71; 4-phenoxyethyl-1, 3-dioxolan-2-one (2d):  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  4.15 [dd,  $^3J$  (H,H) = 4.4 Hz,  $^2J$  (H,H) = 10.8 Hz, 1H, OCH<sub>2</sub>], 4.24 [dd,  $^3J$  (H,H) = 3.6 Hz,  $^2J$  (H,H) = 10.8 Hz, 1H, OCH<sub>2</sub>], 4.55 [dd,  $^3J$  (H,H) = 8.4 Hz,  $^2J$  (H,H) = 6 Hz, 1H, PhOCH<sub>2</sub>], 4.62 [t,  $^3J$  (H,H) = 8.4 Hz, 1H, PhOCH<sub>2</sub>], 5.03 [m, 1H, OCH], 6.91 [d,  $^3J$  (H,H) = 8.0 Hz, 2H, C<sub>6</sub>H<sub>5</sub>], 7.02 [t,  $^3J$  (H,H) = 7.4 Hz, 2H, C<sub>6</sub>H<sub>5</sub>], 7.31 [t,  $^3J$  (H,H) = 8.0 Hz, 2H, C<sub>6</sub>H<sub>5</sub>].  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100.4 MHz in CDCl<sub>3</sub>):  $\delta$  66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65, 157.71; 4-isopropoxy-1, 3-dioxolan-2-one (2e):  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.08 [t,  $^3J$  (H,H) = 6.4 Hz, 6H, 2 × CH<sub>3</sub>], 3.62–3.51 [m, 3H, (CH<sub>3</sub>)<sub>2</sub>CHO, (CH<sub>3</sub>)<sub>2</sub>CHOCH<sub>2</sub>], 4.30 [dd,  $^3J$  (H,H) = 8.0 Hz,  $^2J$  (H,H) = 15.6 Hz, 1H, OCH<sub>2</sub>], 4.42 [dd,  $^3J$  (H,H) = 8.0 Hz,  $^2J$  (H,H) = 15.6 Hz, 1H, OCH<sub>2</sub>], 4.74 [m, 1H, CHO].  $^{13}\text{C}$  { $^1\text{H}$ } NMR (100.4 MHz in CDCl<sub>3</sub>):  $\delta$  21.52, 21.64, 66.15, 66.88, 72.58, 75.18, 155.02.

### 3. Results and discussion

#### 3.1. The counter anion effect of the silica-supported tetra-*n*-butyl ammonium halides on PC synthesis

Listed in Table 1 are the results for the propylene carbonate synthesis catalyzed by quaternary ammonium halides. Various silica-supported quaternary ammonium halides were screened for the cycloaddition of CO<sub>2</sub> to propylene oxide. For comparison with the silica-supported catalysts, the catalytic activities of the corresponding lower molecular weight catalysts such as *n*-Bu<sub>4</sub>NF, *n*-Bu<sub>4</sub>NCl, *n*-Bu<sub>4</sub>NBr, *n*-Bu<sub>4</sub>NI (Table 1, entries 9–12) were also examined for the reaction of propylene oxide and supercritical CO<sub>2</sub>. It was worth mentioning that silica gel alone was found to be inactive for PC synthesis under reaction conditions (entry 13). In general, the silica supported ammonium salts had higher catalytic activities than such low molecular weight catalysts under the same reaction conditions, probably due to the synergistic effect between silica gel and quaternary ammonium salts for the activation of CO<sub>2</sub> and propylene oxide. The products besides propylene carbonate were isomers of propylene oxide, such as acetone, propionaldehyde and 1,2-propanediol as shown in Scheme 2. It is noteworthy that no halogenated organic compounds were detected by GC-MS.

Notably, the catalytic activity among quaternary ammonium salts strongly depended on the anion. The order of activity was found to be *n*-Bu<sub>4</sub>NBr > *n*-Bu<sub>4</sub>NI ≈ *n*-Bu<sub>4</sub>NCl > *n*-Bu<sub>4</sub>NF (entries 9–12, Table 1), which was in accord with the order of nucleophilicity of the anion except *n*-Bu<sub>4</sub>NI [34–36], which could likely be unstable under reaction conditions. Interestingly,

Table 1

Propylene carbonate synthesis catalyzed by tetra-*n*-butyl ammonium halides: the counter anion effect on PC yield<sup>a</sup>

| Entry           | Catalyst                                       | Yield <sup>b</sup> (%) | Selectivity <sup>c</sup> (%) |
|-----------------|--|------------------------|------------------------------|
| 1               | <i>n</i> -Bu <sub>4</sub> NF/SiO <sub>2</sub>  | 84                     | 86                           |
| 2               | <i>n</i> -Bu <sub>4</sub> NCl/SiO <sub>2</sub> | 90                     | 90                           |
| 3               | <i>n</i> -Bu <sub>4</sub> NBr/SiO <sub>2</sub> | 97                     | 98                           |
| 4               | <i>n</i> -Bu <sub>4</sub> NI/SiO <sub>2</sub>  | 96                     | 98                           |
| 5 <sup>d</sup>  | <i>n</i> -Bu <sub>4</sub> NF/SiO <sub>2</sub>  | 50                     | 70                           |
| 6 <sup>d</sup>  | <i>n</i> -Bu <sub>4</sub> NCl/SiO <sub>2</sub> | 81                     | 85                           |
| 7 <sup>d</sup>  | <i>n</i> -Bu <sub>4</sub> NBr/SiO <sub>2</sub> | 87                     | 93                           |
| 8 <sup>d</sup>  | <i>n</i> -Bu <sub>4</sub> NI/SiO <sub>2</sub>  | 86                     | 92                           |
| 9               | <i>n</i> -Bu <sub>4</sub> NF                   | 66                     | 83                           |
| 10              | <i>n</i> -Bu <sub>4</sub> NCl                  | 84                     | 87                           |
| 11              | <i>n</i> -Bu <sub>4</sub> NBr                  | 95                     | 96                           |
| 12              | <i>n</i> -Bu <sub>4</sub> NI                   | 85                     | 88                           |
| 13 <sup>e</sup> | Silica gel                                     | Trace                  | –                            |
| 14 <sup>f</sup> | <i>n</i> -Bu <sub>4</sub> NBr/SiO <sub>2</sub> | 95                     | 98                           |

<sup>a</sup> Reaction conditions: propylene oxide (PO, 57.2 mmol), catalyst (1 mmol%), CO<sub>2</sub> (8 MPa), 150 °C, 10 h.

<sup>b</sup> Determined by GC using an internal standard technique. The yield in this work is defined as follows: yield of product (%) = (moles of product/moles of PO added) × 100.

<sup>c</sup> The selectivity in this work is defined as follows: selectivity (%) = [moles of product/(moles of PO added – moles of PO remained)] × 100.

<sup>d</sup> Reaction conditions: 2-chloromethyl-oxirane (**1b**, 57.2 mmol), catalyst (1 mmol%), CO<sub>2</sub> (8 MPa), 150 °C, 5 h.

<sup>e</sup> Propylene oxide (57.2 mmol), silica gel (1.0 g), CO<sub>2</sub> (8 MPa), 150 °C, 10 h.

<sup>f</sup> Reaction conditions: propylene oxide (PO, 57.2 mmol), catalyst (0.5 mmol%), CO<sub>2</sub> (8 MPa), 150 °C, 10 h.

the silica-supported catalysts containing different anions e.g. F<sup>–</sup>, Cl<sup>–</sup>, Br<sup>–</sup>, I<sup>–</sup> (entries 1–4 in Table 1) possessed similar reactivity except *n*-Bu<sub>4</sub>NF/SiO<sub>2</sub>. The low activity of fluoride can be explained by its poor leaving ability [34,35]. However, the difference of the catalytic activities among Cl<sup>–</sup>, Br<sup>–</sup> and I<sup>–</sup> became narrow, which is different from the corresponding unsupported catalysts (entries 1–4 and 9–12, Table 1). The same trend of activity was also found using 2-chloromethyl-oxirane (**1b**), relatively lower active substrate (entries 5–8 in Table 1). Accordingly, the anions of silica-supported ammonium salts except F<sup>–</sup> have little influence on the performance of the catalysts. Conclusively, bromide anion was chosen as the counter ion in the case of silica supported tetra-*n*-butyl ammonium salts, from a practical and economical point of view.

#### 3.2. The cation effect of the quaternary ammonium bromides on PC synthesis

Table 2 summarizes PC synthesis promoted by the quaternary ammonium bromides containing alkyl group with different alkyl chain lengths. The results showed that the silica-supported catalysts possessed slightly higher catalytic activity for PC synthesis than the unsupported counterparts (Table 2, entries 1–4 versus entries 9–12). Obviously, in the cases of both the quaternary ammonium bromides and their silica-supported ones, the cation had little influence on the cycloaddition of CO<sub>2</sub> to propylene oxide for PC synthesis, except that Me<sub>4</sub>NBr alone was found to be inactive for PC synthesis under the same reaction conditions (entry 9, Table 2), possibly owing to its causing

Table 2  
Propylene carbonate synthesis catalyzed by quaternary ammonium halides: the cation effect on PC yield<sup>a</sup>

| Entry | Quaternary salt                                | Yield (%) | Selectivity (%) |
|-------|--|-----------|-----------------|
| 1     | Me <sub>4</sub> NBr/SiO <sub>2</sub>           | 96        | 98              |
| 2     | Et <sub>4</sub> NBr/SiO <sub>2</sub>           | 96        | 98              |
| 3     | <i>n</i> -Pr <sub>4</sub> NBr/SiO <sub>2</sub> | 97        | 97              |
| 4     | <i>n</i> -Bu <sub>4</sub> NBr/SiO <sub>2</sub> | 97        | 98              |
| 9     | Me <sub>4</sub> NBr                            | 0.7       | 2               |
| 10    | Et <sub>4</sub> NBr                            | 94        | 98              |
| 11    | <i>n</i> -Pr <sub>4</sub> NBr                  | 95        | 97              |
| 12    | <i>n</i> -Bu <sub>4</sub> NBr                  | 95        | 98              |

<sup>a</sup> Reaction conditions: propylene oxide (57.2 mmol), catalyst (1 mmol%), CO<sub>2</sub> (8 MPa), 150 °C, 10 h.

isomerization of propylene oxide to acetone and propionaldehyde. It is interesting to note that the support, namely, silica gel would play a dramatic role in promoting cyclic carbonate synthesis and restraining side reactions using Me<sub>4</sub>NBr/SiO<sub>2</sub> as a catalyst. *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> exhibited high catalytic activity and excellent selectivity for PC synthesis at 150 °C, 8 MPa, and 10 h. Hence, *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> was selected as our benchmark catalyst for further investigation. On the basis of the above results, the silica-supported ammonium bromides all displayed the similar activity (almost quantitative yields were obtained), implying the cation of the ammonium bromides, namely the carbon chains of C1–C4 has no effect on PC synthesis under the reaction conditions.

### 3.3. Effect of reaction time on the PC synthesis

As shown in Fig. 2, the yield of PC increased with reaction time within 10 h. The results indicated that the reaction proceeded rapidly within first 5 h. It was important to note that almost quantitative yield (95%) could be achieved with 98% selectivity within 8 h. In other words, a reaction time of 8 h was required for complete propylene oxide conversion. Notably, selectivity remained ca. 98% for the entire course of the reaction.

### 3.4. Pressure effect on PC synthesis

Showed in Fig. 3 is the effect of CO<sub>2</sub> pressure on the yield of PC for the catalyst *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>. The selectivity was independent of CO<sub>2</sub> pressure in the range of 3–18 MPa, whereas, PC

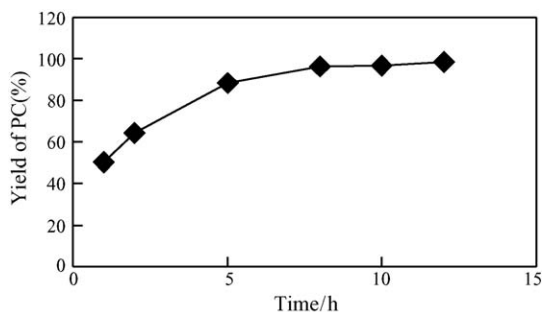


Fig. 2. Dependence of PC yield on reaction time. Reaction conditions: propylene oxide (57.2 mmol); catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>, 1 mmol%); CO<sub>2</sub> (8 MPa), 150 °C.

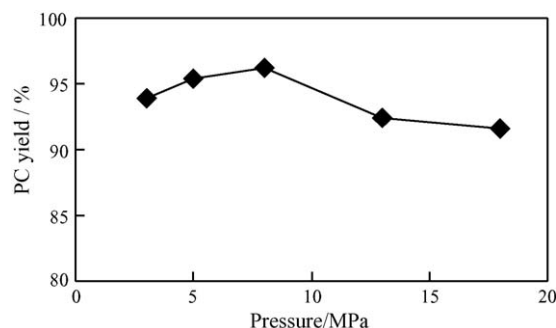


Fig. 3. Dependence of PC yield on CO<sub>2</sub> pressure. Reaction conditions: propylene oxide (57.2 mmol); catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>, 1 mmol%), 150 °C, 8 h.

yield slightly changed with variation of CO<sub>2</sub> pressure, demonstrating the preferential effect of the supercritical conditions for promoting the reactivity of CO<sub>2</sub>. The isomerization to acetone increased at low CO<sub>2</sub> pressure, while too high CO<sub>2</sub> pressure might retard the interaction between epoxide and the catalyst [37–39], and might cause a low concentration of epoxide in the vicinity of the catalyst, thus resulting in a low yield.

The reaction in supercritical CO<sub>2</sub> is also advantageous in terms of product separation from the reaction media. Thus, the phase behavior of the reaction visually inspected through a sapphire window attached to the autoclave revealed that propylene oxide and supercritical CO<sub>2</sub> initially formed a uniform phase while propylene carbonate was separated out and formed a new phase after the reaction. In addition, the catalyst *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> existed as solid during the reaction. Therefore, CO<sub>2</sub> could be recycled, maintaining the high pressure. Accordingly, this procedure could be applied to development of fixed-bed continuous flow reactors, avoiding the use of organic solvent to isolate the products.

### 3.5. Effect of reaction temperature on PC synthesis

It was found that the yield of cyclic carbonate was strongly affected by the reaction temperature. As shown in Fig. 4, the yield and selectivity of PC increased with the reaction temperature up to 150 °C, whereas, further increase in the temperature caused a decrease in the selectivity and catalytic activity, possibly due to more side-products formed at the higher temperature, such as, the isomerization to acetone and the ring opening by water to propylene glycol. The relatively low selectivity for the

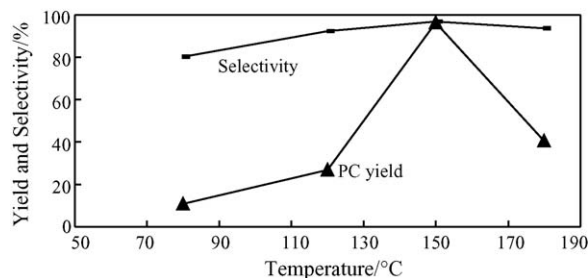


Fig. 4. Temperature dependence of the yield and selectivity. Reaction conditions: propylene oxide (57.2 mmol); catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>, 1 mmol%); CO<sub>2</sub> (8 MPa), 8 h.



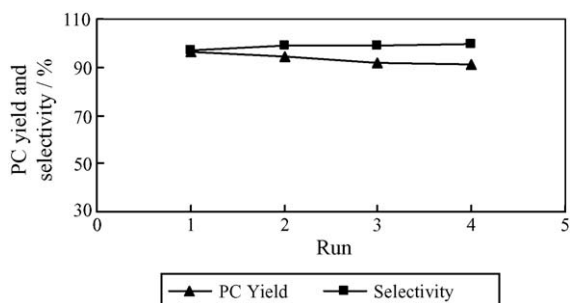


Fig. 5. Recycle of catalyst. Reaction conditions: propylene oxide (57.2 mmol); catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>, 1 mmol%); CO<sub>2</sub> (8 MPa), 150 °C, 8 h.

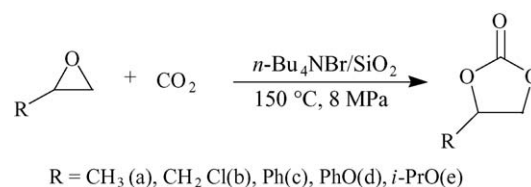
product was possibly due to the lower catalytic activity at lower temperature (below 120 °C). Conclusively, 150 °C could be the optimal temperature for the reaction.

### 3.6. Catalyst recycling

A series of catalytic cycles were run to investigate the constancy of the catalyst activity and recycle. In each cycle, *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> as solid catalyst could be easily recovered via a simple filtration, followed by rinsing with ether and drying, and reused as a catalyst for subsequent reactions. The work-up procedure is reasonably simple due to heterogeneous catalysis under organic solvent-free condition. The high purity (over 99%) of product is automatically separated by filtration of *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>. Catalyst reusability was checked by performing reactions using the optimized reaction conditions, namely, 150 °C, 8 MPa, 8 h. The results were summarized in Fig. 5. It is interesting to note that PC yields and selectivities in subsequent runs (runs 2–4) are similar to that of the fresh catalyst (in the first run), suggesting that silica-supported quaternary ammonium salt could be reused for at least up to four times with slightly loss of its catalytic activity, while the selectivity of catalyst could be kept constant. The characteristic FT-IR peaks of active species Bu<sub>4</sub>NBr did insignificantly change after four runs. We also tested the leaching of the active ingredient of the catalyst. The supported catalyst was thoroughly filtered from the product solution, and the content of bromide ion in the resulting filtrate was measured by ion chromatography with a DIONEX DX-120 Ion Chromatographic instrument. The content of bromide ion was at the level of 8 ppm. The experimental results also confirmed that *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> in the fourth run was still maintained high activity. Indeed, *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> still exhibited high activity even at low catalyst loading (0.5 mol%, entry 14, Table 1). Consequently, the recyclability of the catalyst makes the process economically and potentially viable for commercial applications.

### 3.7. Effect of various epoxides using silica-supported tetra-*n*-butyl ammonium bromine (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>)

Under the optimized reaction conditions, we examined the reactions of other terminal epoxides with CO<sub>2</sub>, in order to survey the applicability of various epoxides to this process (Scheme 3). The results are summarized in Table 3, the silica-supported tetra-



Scheme 3. Coupling of epoxides and CO<sub>2</sub> by *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>.

Table 3

Various carbonates synthesis using *n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub> as a heterogeneous catalyst<sup>a</sup>

| Substrate | Product | Yield (%) | Selectivity (%) |
|-----------|---------|-----------|-----------------|
|           |         | 96        | 97              |
|           |         | 89        | 95              |
|           |         | 97        | >99             |
|           |         | 98        | >99             |
|           |         | 91        | 95              |

<sup>a</sup> Reaction conditions: epoxide (57.2 mmol), catalyst (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>, 1 mmol%), CO<sub>2</sub> (8 MPa), 150 °C, 8 h.

*n*-butyl ammonium bromine (*n*-Bu<sub>4</sub>NBr/SiO<sub>2</sub>) was found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in high yields and selectivities. Glycidyl phenyl ether (**1d**) was found to be the most active epoxide, while epichlorohydrin (**1b**) exhibited relatively low activity among the epoxides surveyed.

## 4. Conclusion

In conclusion, the silica-supported quaternary ammonium salt is very effective for cyclic carbonate synthesis under supercritical carbon dioxide conditions, where CO<sub>2</sub> could act both as a reagent and a solvent. High cyclic carbonate yield together with excellent selectivity was achieved even in a short reaction time of 5 h. The silica-supported quaternary ammonium salts as heterogeneous catalysts were easily recovered by a simple filtration and reused over four times with slightly loss of its catalytic activity. Moreover, this organic solvent-free process presented here could show much potential application in industry due to its simplicity, easy product separation from reaction medium and

catalyst recycling. It could be profitably applied to the development of fix-bed continuous flow reactors, avoiding the use of solvent to isolate the products.

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