One-pot synthesis of dimethyl carbonate catalyzed by \( n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N} \) from methanol, epoxides, and supercritical \( \text{CO}_2 \)

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Received 29 September 2005; received in revised form 27 November 2005; accepted 4 December 2005

Available online 18 January 2006

Abstract

A homogeneous binary catalyst system, \( n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N} \), was found to be active for the synthesis of dimethyl carbonate from styrene oxide (SO), methanol, and supercritical \( \text{CO}_2 \). Under the optimized conditions, the dimethyl carbonate yield could reach 84\% at SO conversion of 98\%. Several parameters were studied, i.e. catalyst precursors, reaction time and temperature, methanol/epoxide feed ratio in moles, and \( \text{CO}_2 \) pressure. The best compromise for the one-pot synthesis was achieved with an equimolar amount of \( n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N} \). A possible mechanism for the present \( n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N}\)-catalyzed one-pot synthesis of dimethyl carbonate was proposed.

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Keywords: Supercritical carbon dioxide; Epoxide; Dimethyl carbonate; Methanol; Binary catalyst system \( (n\text{-Bu}_4\text{NBr}/n\text{-Bu}_3\text{N}) \); Homogeneous catalysis

1. Introduction

In recent years, much attention has been paid to utilization of \( \text{CO}_2 \) because it is an abundant and cheap carbon resource, a greenhouse compound, and a non-toxic reaction medium \([1–4]\). Dimethyl carbonate synthesis starting from \( \text{CO}_2 \) is one of the promising projects in the development of environmentally benign processes based on the utilization of naturally abundant carbon resources. Dimethyl carbonate is an important raw material in organic synthesis due to its versatile chemical reactivity and unique physical properties \([5,6]\), which is widely used as an important intermediate for polycarbonate resins as well as a useful carbonylation and methylation agents \([7]\).

Recently, dimethyl carbonate application has attracted more and more attention. Because of its negligible toxicity, it is promising as a safe substitute for toxic and corrosive phosgene, dimethyl sulfate, or methyl iodide. Therefore, it can be regarded as a so-called environmentally benign building block \([8]\). In addition, dimethyl carbonate has also been mentioned as a potential gasoline octane enhancer due to its very high oxygen content and good octane, good gasoline/water distribution coefficient, low toxicity, and rapid biodegradability \([9]\).

Furthermore, it has also been widely used as an electrolyte in lithium batteries due to its high dielectric constant \([10]\).

Currently, there are three processes commercialized for the large-scale production of dimethyl carbonate \([11–14]\): the phosgene process, the oxidative carbonylation of methanol process, and the two-step transesterification process. A considerable effort has been devoted to the non-phosgene accesses to dimethyl carbonate \([6–8,15–17,27,29]\). In this context, the two-step transesterification process is very attractive in view of the so-called “Sustainable Society” and “Green Chemistry” \([1–4]\). The two-step process, one of industrial synthetic processes utilizing \( \text{CO}_2 \) as a raw material, consists of two steps: (1) the production and separation of cyclic carbonates and (Eq. (1)), Scheme 1 and (2) the transesterification (Eq. (2), Scheme 1). For step 1, quaternary ammonium salts or alkali halides are typically used as efficient catalysts \([18–20]\); on the other hand, various acid and base catalysts have been reported to be effective for transesterification \([21–28]\). However, major disadvantages of this process are high energy consumption and high investment and production.
costs, due to the requirement of separation of the intermediate, i.e. cyclic carbonate. In a word, this two-step manipulation is one of the main drawbacks of this process.

The other synthetic methods for dimethyl carbonate starting from CO$_2$ are represented by the following two procedures. The first method is the reaction of methanol with methyl iodide and CO$_2$. The consumption of an equimolar amount of methyl iodide for producing 1 mol of dimethyl carbonate is the disadvantage of this method. The second approach is the direct synthesis of dimethyl carbonate only from methanol and CO$_2$. The problem of this procedure is the low methanol conversion that is ascribed to the thermodynamic limitations and/or deactivation of the catalysts by H$_2$O, and high production cost [29].

To eliminate the separation process of cyclic carbonate in the two-step manufacture, it is very desirable to integrate the cycloaddition of CO$_2$ with epoxide and the transesterification of cyclic carbonate with methanol into one-pot reaction, which could be regarded as the third access to dimethyl carbonate from CO$_2$ (Eq. (3), Scheme 1). Recently, various heterogeneous basic metal oxides [24,27,28,30–38], such as alkaline metals and alkaline earth metal salts [32–35], solid base supported on molecular sieve [37,38], and homogeneous catalysts [39], have been used in this process. However, these catalysts were not highly effective from a practical point of view, and significant amount of the by-product via the methanolysis of epoxide was produced [30]. Accordingly, the keys to carry out the one-step reaction are the choice of active catalysts for both reactions (Scheme 1, Eqs. (1 and 2)), and tuning of reaction parameters to suppress the side reactions like methanolysis of epoxides.

In this article, in order to realize one-pot synthesis of dimethyl carbonate, i.e. the sequential reaction of epoxide, CO$_2$, and methanol in one reactor, we designed the binary catalysts (cat. I/cat. II), between which one would be active towards cycloaddition reaction (Scheme 1, Eq. (1)) and another could be effective for the transesterification process (Eq. (2)). Styrene oxide (SO) was selected as a model epoxide for this study (Scheme 2). Interestingly, it was found that a homogeneous binary catalyst system of $n$-Bu$_4$NBr/$n$-Bu$_3$N was the most effective one for one-pot synthesis of dimethyl carbonate. At 423 K, total pressure 15 MPa after 8 h, SO conversion was up to 98%, dimethyl carbonate yield reached 84%. The effects of reaction conditions, such as reaction time, methanol/epoxide feed ratio in moles, reaction temperature, and pressure, on the yields of dimethyl carbonate and styrene carbonate were also investigated in detail.

2. Experimental

2.1. Chemical reagents

Methanol (99.5%) was purified using magnesium [40] and stored under a dinitrogen atmosphere. Other reagents were of analytical grade and were used without further purification.
2.2. A representative procedure for one-pot synthesis of dimethyl carbonate in the presence of a catalytic amount of \(n\)-Bu\(_4\)NBr/n-Bu\(_3\)N

The experiment was carried out in a stainless-steel autoclave reactor with an inner volume of 25 ml. A typical procedure was as follows: styrene oxide (5 mmol), methanol (0.2 mol), \(n\)-Bu\(_4\)NBr (2.5 mol%), and \(n\)-Bu\(_3\)N (2.5 mol%) and dibutyltin oxide \([41]\), and titanium (80 mg, an internal standard for GC analysis) were charged in an autoclave under nitrogen at room temperature. The CO\(_2\) (liquid, ca. 5.0 MPa) was introduced to the above reactor. The initial pressure was adjusted to 15 MPa at 423 K and the autoclave was heated at that temperature for 8 h. After cooling, the products were analyzed by gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector, and further identified by GC–MS (HP G1800A) by comparing retention times and fragmentation patterns with authentic samples. The side-products were detected by GC and identified by GC–MS.

3. Results and discussion

3.1. Catalysts for the one-pot synthesis of dimethyl carbonate

The quaternary ammonium salts or alkali halides \([18–20]\) were reported to be active for the cycloaddition of epoxide and CO\(_2\). On the other hand, Lewis bases and acids \([21–27,30]\) were successfully used to promote the transesterification reaction. Accordingly, it could be possible to effectively integrate the cycloaddition reaction and the transesterification reaction in the presence of the binary catalyst, which could be effective for both reactions, to realize the one-pot reaction (Scheme 1).

Table 1 summarizes some typical experimental results on catalyst screening. The yields are defined in this paper as follows: yield of product (i) = moles of product (i)/moles of epoxide added. Neither \(2a\) nor \(3\) was obtained at all without any catalyst (entry 20, Table 1). Hexamethylenetetramine \([39]\), dibutyltin oxide \([41]\), and titanium \(n\)-butoxide \([42,43]\) were reported to be active for transesterification reactions, but they catalyzed hardly one-pot synthesis of dimethyl carbonate in this study (entries 1–3, Table 1).

Therefore, the binary catalyst system was designed for the one-pot reaction of CO\(_2\), SO, and methanol simultaneously in one reactor (Scheme 2). It was reported that \(n\)-Bu\(_4\)NBr \([44,45]\) and LiBr \([46]\) were typically used as homogeneous catalysts for the cycloaddition reaction. In order to find an effective binary catalyst for the one-pot reaction, LiBr and \(n\)-Bu\(_4\)NBr, respectively, in combination with some Lewis acids/bases, were examined. Using LiBr or \(n\)-Bu\(_4\)NBr alone (Table 1, entries 4 and 5), SO conversion was up to ca. 90%, but only a trace amount of 3 was detected. However, LiBr in conjunction with different bases, such as KOH, 4,4-methylenebis(N,N-dimethylaniline) (MBDA), \(N\,N\)-dimethylformamide (DMF), triethyamine (Et\(_3\)N), CH\(_3\)ONa, and BaCO\(_3\) was not highly effective for the one-pot synthesis of dimethyl carbonate (Table 1, entries 7–12). Then the combination of \(n\)-Bu\(_4\)NBr with some bases and Lewis acids were also evaluated (Table 1, entries 13–15). Apparently, the results show that the binary catalyst system of \(n\)-Bu\(_4\)NBr and \(n\)-Bu\(_3\)N is the most effective (Table 1, entry 15), which could presumably be attributed to the cooperative effect between the two catalyst precursors as shown in Scheme 4. When the reaction was carried out at 423 K, 15 MPa, 8 h, the yield of 3 was up to 84%. Consequently, this binary catalyst system of \(n\)-Bu\(_4\)NBr/n-Bu\(_3\)N displayed better catalytic activity than the typical catalysts like KI/K\(_2\)CO\(_3\) \([33]\) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene): 20 \([39]\).

\(^{a}\) Reaction conditions: styrene oxide, 5 mmol; methanol, 0.2 mol; catalyst I, 0.125 mmol (2.5 mol%); catalyst II, 0.125 mmol (2.5 mol%); total pressure, 15 MPa; reaction temperature, 423 K; reaction time, 8 h. 

\(^{b}\) Determined by GC using an internal standard technique. All of the yields in this paper are based on the starting epoxides. Each entry is the average of three tests.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst I/mol%</th>
<th>Catalyst II/mol%</th>
<th>Conversion (%)</th>
<th>Yield(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(CH(_3)_3N(_4))/10</td>
<td>/</td>
<td>24</td>
<td>22  0  2</td>
</tr>
<tr>
<td>2</td>
<td>Bu(_4)SnO/5</td>
<td></td>
<td>34</td>
<td>30  3  2</td>
</tr>
<tr>
<td>3</td>
<td>Tr(OCH(_3)H(_4))/5</td>
<td></td>
<td>20</td>
<td>18  0  0</td>
</tr>
<tr>
<td>4</td>
<td>LiBr/2.5</td>
<td></td>
<td>90</td>
<td>85  4  5</td>
</tr>
<tr>
<td>5</td>
<td>(n)-Bu(_4)NBr/2.5</td>
<td></td>
<td>/</td>
<td>82  2  4</td>
</tr>
<tr>
<td>6</td>
<td>/</td>
<td>(n)-Bu(_2)N/2.5</td>
<td>38</td>
<td>5   34 33</td>
</tr>
<tr>
<td>7</td>
<td>LiBr/2.5 KOH/2.5</td>
<td></td>
<td>97</td>
<td>92  4  5</td>
</tr>
<tr>
<td>8</td>
<td>LiBr/2.5 MBDA(_2)/2.5</td>
<td></td>
<td>88</td>
<td>79  10  5</td>
</tr>
<tr>
<td>9</td>
<td>LiBr/2.5 DMF/100</td>
<td></td>
<td>97</td>
<td>75  20  21</td>
</tr>
<tr>
<td>10</td>
<td>LiBr/2.5 BaCO(_2)/2.5</td>
<td></td>
<td>97</td>
<td>89  6  8</td>
</tr>
<tr>
<td>11</td>
<td>LiBr/2.5 Et(_3)N/2.5</td>
<td></td>
<td>96</td>
<td>72  23  22</td>
</tr>
<tr>
<td>12</td>
<td>LiBr/2.5 CH(_3)ONa/2.5</td>
<td></td>
<td>99</td>
<td>77  21  21</td>
</tr>
<tr>
<td>13</td>
<td>(n)-Bu(_4)NBr/2.5</td>
<td>ZnBr(_2)/2.5</td>
<td>92</td>
<td>85  5  3</td>
</tr>
<tr>
<td>14</td>
<td>(n)-Bu(_4)NBr/2.5</td>
<td>K(_2)CO(_3)/2.5</td>
<td>92</td>
<td>68  25  23</td>
</tr>
<tr>
<td>15</td>
<td>(n)-Bu(_4)NBr/2.5</td>
<td>(n)-Bu(_2)N/2.5</td>
<td>89</td>
<td>62  26  25</td>
</tr>
<tr>
<td>16</td>
<td>(n)-Bu(_4)NBr/2.5</td>
<td>(n)-Bu(_2)N/2.5</td>
<td>98</td>
<td>13  84  83</td>
</tr>
<tr>
<td>17</td>
<td>(n)-Bu(_4)NBr/2.5</td>
<td>Et(_2)N/2.5</td>
<td>96</td>
<td>75  22  20</td>
</tr>
<tr>
<td>18</td>
<td>(n)-Bu(_3)N/2.5</td>
<td></td>
<td>96</td>
<td>94  /  /</td>
</tr>
<tr>
<td>19</td>
<td>/</td>
<td>(n)-Bu(_2)N/2.5</td>
<td>75</td>
<td>/   73  72</td>
</tr>
<tr>
<td>20</td>
<td>None</td>
<td>None</td>
<td>/</td>
<td>0   0  0</td>
</tr>
</tbody>
</table>

The turnover number (TON: moles of 3 per mole of catalyst) = 34; for comparison, the TONs of the most active catalysts for one-pot synthesis of dimethyl carbonate under the optimal conditions in the literature are given herein: KI/K\(_2\)CO\(_3\): 28 \([33]\); and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene): 20 \([39]\). 

\(^{a}\) Hexamethylenetetramine.

\(^{d}\) 4,4-Methylenebis(N,N-dimethylaniline).

\(^{e}\) \(N\,N\)-Dimethylformamide.

\(^{f}\) Reaction temperature, 413 K.

\(^{g}\) The turnover number (TON: moles of 3 per mole of catalyst) = 34; for comparison, the TONs of the most active catalysts for one-pot synthesis of dimethyl carbonate under the optimal conditions in the literature are given herein: KI/K\(_2\)CO\(_3\): 28 [33]; and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene): 20 [39]. 

\(^{b}\) Styrene oxide, 5 mmol; in the absence of methanol, 0.2 mol. 

\(^{c}\) Styrene carbonate, 5 mmol; methanol, 0.2 mol. 

\(^{d}\) Triethylamine, 5 mmol; in the absence of methanol, 0.2 mol. 

\(^{e}\) N,N-Dimethylformamide.

The experiment was carried out in a stainless-steel autoclave reactor with an inner volume of 25 ml. A typical procedure was as follows: styrene oxide (5 mmol), methanol (0.2 mol), \(n\)-Bu\(_4\)NBr (2.5 mol%), and \(n\)-Bu\(_3\)N (2.5 mol%) and dibutyltin oxide \([41]\), and titanium (80 mg, an internal standard for GC analysis) were charged in an autoclave under nitrogen at room temperature. The CO\(_2\) (liquid, ca. 5.0 MPa) was introduced to the above reactor. The initial pressure was adjusted to 15 MPa at 423 K and the autoclave was heated at that temperature for 8 h. After cooling, the products were analyzed by gas chromatograph (Agilent 6890) equipped with a capillary column (HP-5, 30 m × 0.25 μm) using a flame ionization detector, and further identified by GC–MS (HP G1800A) by comparing retention times and fragmentation patterns with authentic samples. The side-products were detected by GC and identified by GC–MS.
3.2. Effect of reaction time

The dependence of yields of 2a and 3 on reaction time for n-Bu₄NBr/n-Bu₃N is illustrated in Fig. 1. Reactions were performed in the presence of n-Bu₄NBr (2.5 mol%) and n-Bu₃N (2.5 mol%) at 423 K under 15 MPa, and were monitored in the range of 0.5–14 h at regular intervals. Obviously, the transesterification of intermediate (2a) started before SO was quantitatively consumed, and the cycloaddition reaction proceeded faster than the transesterification at the initial stage. The yield of 2a reached a maximum with a 2-h reaction time, and then decreased with extended reaction time, kept a constant after ca. 8 h, whereas yield of 3 got the maximum value when the reaction time was about 8 h. This hints that the transesterification reaction reaches equilibrium after ca. 8 h, depending on the reversible nature of the transesterification. Conclusively, a reaction time of 8 h was appropriate for the one-pot synthesis of 3 from SO, methanol, and supercritical CO₂.

3.3. Effect of methanol/styrene oxide ratio

The influence of the feed molar ratio of methanol to SO is given in Table 2. The effect of methanol/styrene oxide ratio was investigated in the reaction with n-Bu₄NBr (2.5 mol%) and n-Bu₃N (2.5 mol%) at 423 K for 8 h at the pressure of 15 MPa (Fig. 1). Within the range of MER of 10–40, an increase in the methanol/styrene oxide ratio resulted in the decrease of 2a yield and the increase of 3 yield (Table 2, entries 1–3), which is consistent with the reversible nature of the transesterification of 2a with methanol. When the methanol/styrene oxide ratio was up to 60–80, the conversion of SO and the yields of both 2a and 3 decreased (Table 2, entries 4 and 5), whereas a side product 5 by the methanolysis of SO increased. The similar phenomenon was reported by Kishimoto and Ogawa [39]. Summarily, increasing the feed molar ratio of methanol to SO can improve 3 formation; however, much higher methanol/styrene ratio up to 60–80 presumably can accelerate the methanolysis of SO (entry 5, Table 2), and reduce the rate of 3 formation due to low concentration of SO and the catalyst caused by methanol dilution, and retard 3 formation by promoting the formation of methyl carbonate ammonium salts and the attack of methanol on SO [39]. Indeed, a prolonged reaction of 24 h resulted in an increase in the yield of product 3–45%.

3.4. Effect of reaction temperature

To investigate the catalytic activity at different temperatures, we carried out the experiments in the range of 363–463 K (Fig. 2). A relatively high temperature (363–423 K) was favorable to an efficient reaction. The reaction was almost complete within 8 h at 423 K and the yield of 3 was up to 84% (Table 1, entry 16). When the mixture was heated to 403 K, a considerable amount of 2a was produced, and almost all of 2a survived without undergoing the transesterification. However, further decrease in the reaction temperature to 363 K led to a much slower reaction, the yield of 2a was very low, and there was no transesterification of 2a with methanol. When the reaction temperature was higher than 443 K, 2a and 3 were detected only in trace amounts because the number of side reaction increased (Scheme 3). Therefore, the appropriate temperature is 423 K.

3.5. Effect of reaction pressure

The influence of pressure on the reaction is depicted in Fig. 3. The most selective production of 3 with high conversion of SO was accomplished at 15 MPa. A higher pressure (8–
15 MPa) was favorable to cycloaddition reaction, and lower pressure led to the lower yields of \( 3 \) and \( 2a \), probably due to increase of side reaction (Scheme 3). On the other hand, the yield of dimethyl carbonate decreased gradually over 15 MPa, which could be attributed to a suppression of the transesterification of \( 2a \). The visual inspection revealed that the presence of both supercritical CO\(_2\) phase and liquid phase in the reactor was detected, and the reaction mainly took place in the liquid phase because of the high solubility of the catalyst in the liquid phase. Accordingly, high pressure decreased the polarity of the liquid phase and was unfavorable to the transesterification of \( 2a \) with methanol [33]. So, the optimal pressure should be 15 MPa.

### 3.6. Effect of epoxides

To survey the applicability of other epoxides to this binary catalytic system for one-pot synthesis of dimethyl carbonate, reactions employing glycidyl methyl ether, phenyl oxide, propylene oxide, and chloromethyl oxide were investigated. The results are summarized in Table 3. At 423 K, 15 MPa, 8 h, the epoxides (1a–c) exhibited significant activity with negligible side reaction of the methanolysis except \( 1d \). Interestingly, dimethyl carbonate yields were also good when using glycidyl methyl ether (entry 1, Table 3) and propylene oxide (entry 3). However, intermediate (cyclic carbonate) was the main product (50%), and the yield of \( 3 \) was merely 12% with incomplete conversion (70%) when chloromethyl oxide (1d) was employed (entry 4). Hence, the order of activity for dimethyl carbonate formation under the same reaction conditions was found to be \( 1a \approx 1b > 1c > 1d \) as shown in Table 3, which is dependent on the electronic property of the substituent on the ring of the epoxide. Particularly, \( 1d \) with electron-withdrawing group shows the lowest activity towards the cycloaddition step and the transesterification step (Schemes 1 and 4), while the relatively high yield of by-product 5 (Scheme 3) was obtained (entry 4, Table 3).

### 3.7. A possible mechanism for the present n-Bu\(_4\)NBr/n-Bu\(_3\)N-catalyzed one-pot synthesis of dimethyl carbonate

From Table 1, it can be concluded that dimethyl carbonate was produced from the transesterification of methanol with \( 2a \) that was formed from SO and CO\(_2\). As easily seen from Fig. 1, the transesterification of \( 2a \) started before SO was consumed quantitatively, the cycloaddition reaction proceeded faster than the transesterification at the initial stage. The esterification reaction is the rate-controlling step in one-pot reaction [30,47]. Hence, a possible catalytic cycle for the present \( n \)-Bu\(_4\)NBr/\( n \)-Bu\(_3\)N-catalyzed one-pot synthesis of dimethyl carbonate has been proposed as illuminated in Scheme 4, which involves two cycles of the \( n \)-Bu\(_4\)NBr-prompted cycloaddition of CO\(_2\) to epoxide [18,45,48] and the \( n \)-Bu\(_3\)N-mediated transesterification step [49] of cyclic carbonate with methanol.

We separately examined the catalytic activities of \( n \)-Bu\(_4\)NBr, \( n \)-Bu\(_3\)N, and \( n \)-Bu\(_4\)NBr/\( n \)-Bu\(_3\)N towards cycloaddition reaction, and the transesterification of cyclic carbonate with methanol, one-pot reaction, respectively. As given in Table 1, \( n \)-Bu\(_4\)NBr (entries 18 and 5, Table 1) was highly active for cycloaddition and \( n \)-Bu\(_3\)N (entry 19) had excellent effect on
the transesterification reaction. But a considerable amount of SC remained intact in the case of \(n\)-Bu4NBr (entry 5), indicating its low transesterification activity. On the other hand, \(n\)-Bu3N displayed low activity for the cycloaddition of SO with CO2, while significantly effective for the transesterification reaction. Overall, catalyst alone either \(n\)-Bu4NBr (entry 5) or \(n\)-Bu3N (entry 6) has little effect on the one-pot synthesis of dimethyl carbonate. As expected, a combination of \(n\)-Bu4NBr and \(n\)-Bu3N showed much higher activity for one-pot synthesis of dimethyl carbonate, probably due to cooperative effects between \(n\)-Bu4NBr \([15,42]\) and \(n\)-Bu3N \([45]\) leading to the results, which can be explained by a possible mechanism as shown in Scheme 4.

The data in Tables 1 and 3 show that there are certain amounts of cyclic carbonates in the products, presumably due to the reversible property of the transesterification reaction.

The pressure effect on the reaction could be well explained by this possible mechanism. The high pressure of CO2 retarded the transesterification of cyclic carbonate with methanol partially by weakening the activation of methanol by \(n\)-Bu3N or interaction of methanol with catalyst II (Bu3N) due to the interaction of CO2 with the amine (catalyst) \([39]\). In addition, as deduced from the proposed mechanism (Scheme 4), high polarity could be favorable to the transesterification, whereas the polarity of the liquid phase can be decreased because of the swelling of liquid high pressure of CO2 \([33]\). Indeed, higher CO2 pressure than 15 MPa retarded the formation of dimethyl carbonate.

4. Conclusions

In conclusion, an effective homogeneous catalyst system comprising \(n\)-Bu4NBr and \(n\)-Bu3N was investigated for one-pot synthesis of dimethyl carbonate from epoxide, methanol, and supercritical CO2. The mixture of \(n\)-Bu4NBr and \(n\)-Bu3N exhibited good performance at 423 K and total pressure 15 MPa, with SO conversion of 98% and dimethyl carbonate yield up to 84%. The choice of efficient binary catalysts for two steps, i.e. cycloaddition and transesterification, and the optimization of reaction condition are keys to the highly efficient, one-pot synthesis of dimethyl carbonate. This process eliminates the requirement for toxic and wasteful feedstocks such as phosgene and carbon monoxide.

Acknowledgements

Gratitude is expressed to the National Natural Science Foundation of China (Grant Nos. 20472030, 20421202), the Tianjin Natural Science Foundation (Grant No. 03360931), Ministry of Education of China, and Nankai University for financial support.

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