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## Highly efficient conversion of $\text{CO}_2$ to cyclic carbonates with a binary catalyst system in a microreactor: intensification of “electrophile–nucleophile” synergistic effect<sup>†</sup>

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An intensification of the “electrophile–nucleophile” synergistic effect was achieved in a microreactor for the coupling reaction of  $\text{CO}_2$  and epoxides mediated by the binary Al complex/ternary ammonium salt catalyst system. The microreactor technology is proven to be a powerful tool for the preparation of cyclic carbonates with an improved reaction rate and a wide substrate scope.

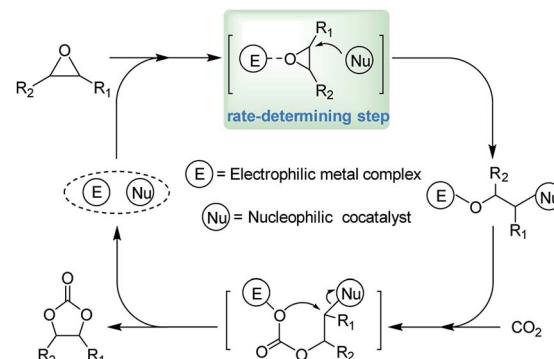
### Introduction

The chemical fixation of carbon dioxide ( $\text{CO}_2$ ) into economically competitive products has attracted much attention, as  $\text{CO}_2$  is one of the most important greenhouse gases, as well as being an abundant, inexpensive, nontoxic, and renewable C1 resource.<sup>1–6</sup> One of the most studied reactions for the use of  $\text{CO}_2$  is the coupling reaction of  $\text{CO}_2$  with epoxides to afford cyclic carbonates,<sup>7–10</sup> which are widely used as electrolytes in lithium-ion secondary batteries<sup>11,12</sup> and polar aprotic solvents,<sup>13,14</sup> as well as intermediates in organic synthesis.<sup>15–19</sup> Successful industrial processes for the preparation of cyclic carbonates from the  $\text{CO}_2$ /epoxides coupling reaction have been realized for more than 50 years, however, efficient transformations usually required high catalyst loadings, elevated  $\text{CO}_2$  pressures, and long reaction time.

In the past decades, various catalysts have been developed for the coupling reaction of  $\text{CO}_2$  with epoxides, such as metal oxides,<sup>20,21</sup> alkali metal salts,<sup>22,23</sup> organic bases,<sup>24,25</sup> ionic liquids,<sup>26–28</sup> metal complexes,<sup>29–31</sup> and so on. Prominent among these are the homogeneous catalyst systems based on well-defined metal complexes.<sup>32–37</sup> These catalyst systems provide a high activity and product selectivity for the coupling reaction of  $\text{CO}_2$  with various epoxides even under mild reaction conditions. For example, Ema *et al.* developed a bifunctional magnesium porphyrin catalyst showing a very high turnover number (TON up to 103 000) for this coupling reaction.<sup>38</sup> Kleij and coworkers also reported an aluminium complex exhibiting an unprecedented high activity (TOF up to 36 000  $\text{h}^{-1}$ ) in the formation of cyclic carbonates.<sup>39</sup> It is worth noting that the

presence of a nucleophilic co-catalyst, such as organic base or quaternary ammonium salt, is beneficial to obtain cyclic carbonates efficiently for most metal complexes.<sup>40</sup> A widely accepted mechanism concerning epoxide ring-opening and  $\text{CO}_2$  activation was shown in Scheme 1 when a binary metal complex/quaternary ammonium salt system was employed. According to this mechanism, the activation of epoxide coordinated to the electrophilic metal center and further ring-opened by the attack of nucleophilic agent is the rate-determining step during the coupling reaction. In this context, an intensification of the “electrophile–nucleophile” synergistic effect might help to further improve the catalytic activity of the binary systems.

Microreactor technology is regarded as a promising process intensification strategy for chemical synthesis due to its unique characteristics, such as high effective surface-to-volume ratio, enhanced heat- and/or mass-transfer rates, and excellent process safety.<sup>41–45</sup> In 2013, Chen and co-workers studied the coupling reaction of  $\text{CO}_2$  with propylene oxide (PO) in a microreactor using a hydroxyl-functionalized quaternary ammonium



Scheme 1 Catalytic cycle for  $\text{CO}_2$ /epoxide coupling reaction mediated by the binary “electrophile–nucleophile” system.

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salt as catalyst.<sup>46</sup> The reaction rate is significantly improved compared to the conventional stirred reactor with the use of the same reaction conditions. Herein, we wish to further explore the application of microreactor technology in the coupling reaction of  $\text{CO}_2$  with epoxides. The aluminium salen complex in conjunction with a quaternary ammonium salt was chosen as a binary catalyst system for this transformation since it is robust, easily prepared and recyclable. The main purpose of this study is to verify the intensification of the “electrophile–nucleophile” synergistic effect for epoxides ring-opening, decrease the reaction time from hours to seconds, and expand the substrate scope.

## Experimental

### Materials

PO and tetrabutylammonium bromide (TBAB) purchased from Sinopharm Chemical Reagent Co. Ltd. Carbon dioxide (99.99%) was used as received.

### Experimental procedure

The microreactor is consisted of two stainless-steel plates with microstructures that combine to form a complex sloped structure channel (Fig. 1). The geometric size of the mixing channel is  $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m} \times 1\text{ cm}$  (length). The fluid continuously rises and falls as it flows through the channel, achieving multiple separation and recombination to complete the ample mixing process.

The aluminium catalyst and TBAB were dissolved in epoxides and pumped by a flow pump into the reaction system. On the other hand, the  $\text{CO}_2$  high-pressure gas cylinder was connected to the pipeline *via* a gas flow meter and the flow rate was controlled by the gas quality controller. The two-phase materials were mixed in microreactor and fully reacted *via* a delay reactor (1/8 inch 316L stainless steel tube, wall thickness 0.5 mm, 22.83 mL). Both the microreactor and the delay reactor located in the oil bath were regarded as the residence time unit for regulating the reaction time. The temperature and pressure controlled by the back pressure valve of the reaction system were detected by sensors and transmitted to the data acquisition system, making the data fluctuation observation more intuitive. Then, the gas–liquid reaction mixture was separated

in the gas–liquid separator. The liquid product sample was collected and weighted for the calculation of the yield. Additionally, a small amount of the crude product was dissolved in methanol, and analyzed by Agilent 7890B gas chromatography (GC with flame ionization detector, HP-5 column,  $30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) for determining the cyclic product selectivity. Each set of experiments was repeated three times to ensure the accuracy of the data.

## Results and discussion

We initially chose PO as a model substrate to test the catalytic activity of the binary system in the microreactor. Neither the aluminium complex (0.5% mol) nor TBAB (1% mol) alone can mediate the PO/ $\text{CO}_2$  coupling reaction with satisfactory conversion (0 and 36%, respectively) at  $150\text{ }^\circ\text{C}$  and  $2.0\text{ MPa}$   $\text{CO}_2$  pressure (Table 1, entries 1 and 2). When the aluminium complex (0.5% mol) in combination with TBAB (1% mol) was employed as a binary catalyst system for the coupling reaction, the conversion of PO increased dramatically (entry 3). With a further increase in the loading of TBAB, quantitative conversion of PO was achieved with a residence time of 48.8 s (entry 5). In this case, the turnover frequency (TOF) value was up to  $14\ 700\text{ h}^{-1}$ , which is significantly higher than the value ( $5160\text{ h}^{-1}$ ) in a conventional stirred reactor (entry 6).<sup>47</sup> In contrast, a yield of 90% was observed under the same conditions when TBAB (5% mol) was used exclusively (entry 7). These results suggest that the “electrophile–nucleophile” synergistic effect of the binary catalyst system can be intensified in the microreactor.

In order to further verify the intensification, the effects of the residence time on the conversion of PO was studied. The residence time can be defined as the total volume of the reaction line divided by the gas–liquid mixing flow rate in the microreactor. In this text, changing the flow rate of  $\text{CO}_2$  and PO in the

Table 1 Coupling reaction of  $\text{CO}_2$  and PO<sup>a</sup>

Entry	[Al]/[PO]	[TBAB]/[PO]	Yield <sup>b</sup> (%)	TOF <sup>c</sup> ( $\text{h}^{-1}$ )
1	0.5%	0	<1	—
2	0	1%	36	—
3	0.5%	1%	62	9150
4	0.5%	3%	85	12 540
5	0.5%	5%	>99	14 700
6 <sup>d</sup>	0.5%	5%	35	5160
7	0	5%	90	—

<sup>a</sup> Typical reaction conditions:  $150\text{ }^\circ\text{C}$ ,  $2.0\text{ MPa}$ ,  $[\text{CO}_2]/[\text{PO}] = 2 : 1$ , ( $\text{CO}_2$  flow rate of  $385\text{ mL min}^{-1}$  under standard conditions and PO flow rate of  $0.6\text{ mL min}^{-1}$ ) residence time 48.8 s for entries 1–5. The propylene carbonate selectivity is >99% based on GC. <sup>b</sup> Yield of propylene carbonate. <sup>c</sup> Turnover frequency (TOF) = moles of cyclic carbonate per mole of Al-catalyst per hour. <sup>d</sup> The coupling reaction was performed in a conventional stirred reactor for 49 s.

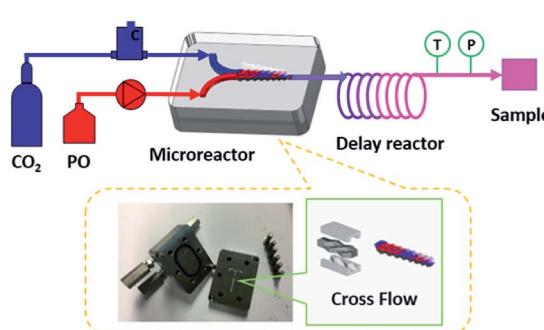


Fig. 1 The experimental setup and illustration of the microreactor inner structure.



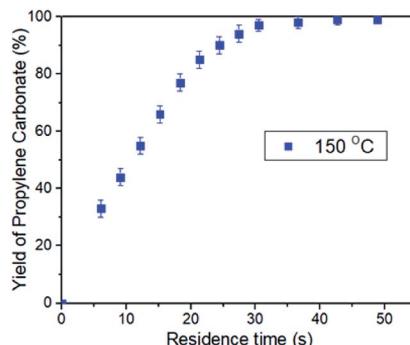


Fig. 2 Plots of PC conversion vs. time, with the use of the binary catalyst system at 150 °C and 2.0 MPa CO<sub>2</sub> pressure. [Al]/[TBAB]/[PO] = 0.5%/5%/1, [PO]/[CO<sub>2</sub>] = 1/2.

same proportion can adjust the residence time of the reaction while maintaining other conditions unchanged. For example, the residence time of 48.8 s corresponded to CO<sub>2</sub> flow rate of 385 mL min<sup>-1</sup> and PO flow rate of 0.6 mL min<sup>-1</sup>, while the residence time of 6.1 s can be got by increasing the CO<sub>2</sub> flow rate to 3080 mL min<sup>-1</sup> and PO flow rate to 4.8 mL min<sup>-1</sup>. Thus, a series of plots of conversion *versus* residence time was obtained with a reaction condition of 150 °C and 2.0 MPa CO<sub>2</sub> pressure (Fig. 2). The results show that the yield of propylene carbonate reaches >98% when the residence time is 30 s. More importantly, the reaction rate did not show an obvious decrease even the yield of propylene carbonate up to 95%. By contrast, the reaction rate was gradually decreased after the yield of cyclic carbonate reaches 60% in a conventional stirred reactor, and it may take about half of the total reaction time to convert the remaining ~20% PO.<sup>48</sup>

Another advantage of the microreactor, compared with the conventional stirred reactor, is that changing the ratio of CO<sub>2</sub> to PO does not affect the reaction pressure.<sup>49</sup> Therefore, we examined the effects of the molar ratio of CO<sub>2</sub> to PO on the reaction rate under the same CO<sub>2</sub> pressure. When the coupling reaction was performed at 140 °C and 2.0 MPa CO<sub>2</sub> pressure with the residence time of 48.8 s or 24.4 s, an increase in the molar ratio of CO<sub>2</sub> to PO from 2/1 to 4/1 does not lead to an observable change in the yield of propylene carbonate (Fig. 3). These results imply the variation of the CO<sub>2</sub>/PO molar ratio has little effect on the “electrophile-nucleophile” synergistic effect for epoxides ring-opening. The very slight fluctuation in the yield of propylene carbonate may be due to the small change of PO concentration in the liquid phase with the different CO<sub>2</sub>/PO molar ratios. Unfortunately, we did not obtain the data with a CO<sub>2</sub>/PO molar ratio of 1/1, because the consumption of CO<sub>2</sub> may lead to a loss of accuracy in the calculation of the residence time.

To explore the wider applicability of the microreactor, a series of monosubstituted terminal epoxides and ethylene oxide were tested. All the terminal cyclic carbonates were obtained with excellent yields (>90%) and high selectivity (99%) under 150 °C and 2.0 MPa CO<sub>2</sub> pressure within the residence time of less than 100 s (Table 2, entries 1–7). When ethylene oxide was employed as a substrate, the quantitative formation

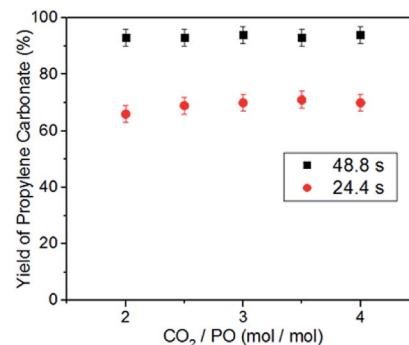
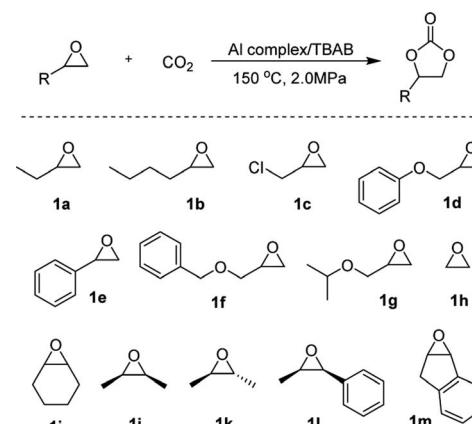


Fig. 3 Effect of the molar ratio of CO<sub>2</sub>/PO on the yield of propylene carbonate, with the use of the binary catalyst system at 140 °C and 2.0 MPa CO<sub>2</sub> pressure. [Al]/[TBAB]/[PO] = 0.5%/5%/1.

of ethylene carbonate with a high reaction rate of TOF up to 29 000 h<sup>-1</sup> was achieved under a residence time of 24.4 s (entry 8). For further expanding the substrate scope, some disubstituted or internal epoxides were chosen as reaction partners. All of the substrates studied were conveniently

Table 2 Coupling reaction of CO<sub>2</sub> and various epoxides<sup>a</sup>



Entry	Substrate	Residence time (s)	Yield <sup>b</sup> (%)	TOF <sup>c</sup> (h <sup>-1</sup> )
1	<b>1a</b>	48.8	>99	14 700
2	<b>1b</b>	97.6	>99	7300
3	<b>1c</b>	48.8	>99	14 700
4	<b>1d</b>	97.6	97	7100
5	<b>1e</b>	97.6	96	6860
6	<b>1f</b>	97.6	96	7000
7	<b>1g</b>	97.6	98	7200
8	<b>1h</b>	24.4	>99	29 000
9	<b>1i</b>	97.6	97	7100
10	<b>1j</b>	97.6	91 <sup>d</sup>	6700
11	<b>1k</b>	97.6	92 <sup>e</sup>	6800
12	<b>1l</b>	97.6	87 <sup>f</sup>	6400
13	<b>1m</b>	97.6	81	6000

<sup>a</sup> Typical reaction conditions: 150 °C, 2.0 MPa, [Al]/[TBAB]/[PO] = 0.5%/5%/1, [CO<sub>2</sub>]/[PO] = 2 : 1. The cyclic carbonate selectivity is >99% based on GC or NMR spectroscopy. <sup>b</sup> Yield of cyclic carbonate. <sup>c</sup> Turnover frequency (TOF) = moles of cyclic carbonate per mole of Al-catalyst per hour. <sup>d</sup> Cis/trans = 86 : 14. <sup>e</sup> Cis/trans = 12 : 88. <sup>f</sup> Cis/trans = 38 : 62. The cis/trans ratios were determined by <sup>1</sup>H NMR spectroscopy.

converted into the corresponding carbonates with high selectivity (>99%) and good to excellent yields, indicating the high versatility of the microreactor technology.

## Conclusions

In summary, the conversion of  $\text{CO}_2$  to various cyclic carbonates proceeds effectively in a microreactor using a binary Al complex/quaternary ammonium salt catalyst system. All the tested epoxides can be transformed to the corresponding cyclic carbonates with >95% yield under the residence time of less than 100 s due to the intensification of “electrophile-nucleophile” synergistic effect for epoxides ring-opening. It is clear that the microreactor technology presented here might be ideally suited for the industrial preparation of cyclic carbonates.

## Conflicts of interest

There are no conflicts to declare.

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47 The reaction was carried out in a 75 mL conventional stirred reactor, with the reaction conditions: 150 °C, 2.0 MPa CO<sub>2</sub> pressure, PO 15 mL, [Al]/[TBAB]/[PO] = 0.5%/5%/1 and performed for 49 s.

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49 Reaction pressure was regulated by a back pressure valve, and the flow rate of the mixture mainly depended on the CO<sub>2</sub>. Therefore, the same pressure, same residence time with different molar ratio of PO and CO<sub>2</sub> can be realized, which is more controllable than the conventional stirred reactor.

