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Functionalized dicyandiamide-formaldehyde polymers as efficient heterogeneous catalysts for conversion of CO\textsubscript{2} into organic carbonates

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Ammonium bromide modified dicyandiamide-formaldehyde polymer (ABMDFP) was the optimal catalyst among the four polymers and observed to be suitable for various substrates. A possible mechanism of ring-opening of epoxide assisted by the hydroxyl and activation of CO\textsubscript{2} induced by amines was proposed. Furthermore, the catalyst exhibited good activity in the synthesis of dimethyl carbonate (DMC) through transesterification reaction.
Functionalized dicyandiamide-formaldehyde polymers as efficient heterogeneous catalysts for conversion of CO$_2$ into organic carbonates

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The application of dicyandiamide-formaldehyde polymer (DFP), which is a kind of organic polymer flocculant, as a supporter for conversion of CO$_2$ into organic carbonates was studied in this work, and four kinds of dicyandiamide-formaldehyde polymers were synthesized and employed as efficient single component, metal-free, multifunctional, polyquaternium catalysts for cycloaddition of CO$_2$ with epoxides. The results indicated that the ammonium bromide modified dicyandiamide-formaldehyde polymer (ABMDFP) was the optimal catalyst among the four polymers and observed to be suitable for various substrates. A possible mechanism of ring-opening of epoxide assisted by the hydroxyl and activation of CO$_2$ induced by amines was proposed. In addition, the catalyst could be easily recovered and reused six times with only a slight loss of catalytic activity. Furthermore, the catalyst exhibited good activity in the synthesis of dimethyl carbonate (DMC) through transesterification reaction. The functional organic polymers in this study were proved to be efficient heterogeneous catalysts for the cycloaddition reaction of CO$_2$, which was applicable to the development of fix-bed continuous flow reactors.

1. Introduction

Carbon dioxide (CO$_2$) is considered to be the main component of the greenhouse gases, which is also a nontoxic, abundant, natural, inexpensive and renewable C1 building block. Therefore, the efficient transformation of CO$_2$ into useful organic compounds is of growing interest for resource utilization and sustainable development.$^1$ One of the typical routes for efficiently utilizing CO$_2$ is the synthesis of five-membered cyclic carbonates via the cycloaddition of CO$_2$ with epoxides (Scheme 1, step 1),$^{2-4}$ because cyclic carbonates can be extensively used as an intermediate in the production of pharmaceuticals and fine chemicals.$^5-7$

In the past decades, numerous of catalysts have been developed for the production of cyclic carbonates, including metal oxides,$^8$ alkali metal salts,$^9$ quaternary onium salts,$^{10}$ ionic liquids,$^{11}$ transition metal complexes$^{12}$ and functional organic compounds and polymers.$^{13}$ Although fixation of CO$_2$ with epoxides into cyclic carbonates has been researched extensively, the design of efficient, inexpensive, highly selective, stable, metal-free and reusable catalysts for this reaction is still a challenge.$^{14}$

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promoting the reaction. Furthermore, the catalysts can be easily polymers (AIMDFP) (Fig 1, slight loss of catalytic activity. Due to the structure of many hydroxyl functional polymers as active and insoluble catalysts for fixation of CO$_2$. Nevertheless, in most of these functional organic polymers, the synthetic method was complex as well as time-consuming. In addition, unsatisfactory activities, and harsh reaction conditions were still disadvantages that need to be improved. Therefore the design of inexpensive, simply synthesis, efficient, highly selective and reusable catalysts still remains to be studied toward effective CO$_2$ conversion.

The dicyandiamide-formaldehyde polymer (DFP) (Fig 1, a), which is well-known as a kind of organic polymer flocculant is a potential catalyst for the fixation of CO$_2$ not only because it has abundant amino and hydroxyl groups that can activate the CO$_2$ and epoxides but also the possibility of creating new functions via the addition of modifier, such as ammonium chloride, aluminum chloride, acrylamide, etc., especially ammonium chloride modified dicyandiamide-formaldehyde polymer (ACMDFP) (Fig 1, 1b). ACMDFP has functional groups of HBD and amino groups, as well as several halogen anions within the molecule, which have been proved much helpful for promoting the catalytic activity. Moreover, the relative simplicity of their synthesis method and the inexpensive raw materials make this class of catalysts very interesting particularly for the fixation of CO$_2$. Herein we synthesized ammonium bromide modified dicyandiamide-formaldehyde polymers (ABMDFP) (Fig 1, 2b) and ammonium iodide modified dicyandiamide-formaldehyde polymers (AIMDFP) (Fig 1, 3b), and investigated the activity of this class of catalysts for the cycloaddition of CO$_2$ with epoxides. All of these kinds of catalysts have shown an excellent impact on the addition of modifier, such as ammonium chloride, aluminum chloride, acrylamide, etc., especially ammonium chloride modified dicyandiamide-formaldehyde polymer (ACMDFP) (Fig 1, 1b). ACMDFP has functional groups of HBD and amino groups, as well as several halogen anions within the molecule, which have been proved much helpful for promoting the catalytic activity. Moreover, the relative simplicity of their synthesis method and the inexpensive raw materials make this class of catalysts very interesting particularly for the fixation of CO$_2$. Herein we synthesized ammonium bromide modified dicyandiamide-formaldehyde polymers (ABMDFP) (Fig 1, 2b) and ammonium iodide modified dicyandiamide-formaldehyde polymers (AIMDFP) (Fig 1, 3b), and investigated the activity of this class of catalysts for the cycloaddition of CO$_2$ with epoxides. All of these kinds of catalysts have shown an excellent impact on the reaction. Furthermore, the catalysts can be easily recovered by filtration and reused at least six times with only a slight loss of catalytic activity. Due to the structure of many amines within the molecule, the catalytic activity for DMC synthesis through transesterification reaction was also studied (Scheme 1, step 2), and the catalyst of 2b exhibited high activity, 90% yield of DMC together with 99% selectivity was obtained.

As shown in Table 1, all of the catalysts exhibited high selectivity (entries 1-4), which demonstrated negligible creation of by-products in the cycloaddition reactions. It was found that 2b showed much higher activity than 1b (entry 3 vs 2). However, 2b exhibited a lower PC yield than 3b. For comparison, we investigate the catalytic activity of dicyandiamide (DCD), NH$_4$X and hydroxyl-functionalized poly(ionic liquids) (PILs). The results revealed that activity of DCD was very low (entry 5), and the activity of NH$_4$X was in the order of NH$_4$I > NH$_4$Br > NH$_4$Cl (entries 6, 7, 8), which was in accordance with the reports that the activities of anions increased in the order of I$^-$ > Br$^-$ > Cl$^-$ with the same cation. Catalyst 2b could show a 96% PC yield, which was much higher than that of the NH$_4$Br (entry 3 vs 7). The better catalytic activity of 2b was most likely related to the synergistic catalysis effected by amino and hydroxyl groups in 2b. We studied the performances of the catalysts with and without halide anion (entries 2, 3, 4 vs 1), the results showed the activity of catalyst with halide anion (entries 2, 3, 4) was much higher than that without halide anion (entry 1). The heterogeneous catalyst of 2b, which could be easily prepared by ammonium bromide, dicyandiamide and methanol, was observed higher activity. Besides, the yield was better than the PILs (entries 9, 10) we prepared in our previous work. Compared with 3b, the starting materials to prepare 2b were relatively inexpensive and more stable. Therefore, 2b was chosen as the optimal catalyst for further investigation.

2.2 Effect of reaction conditions

The reaction conditions such as influence of temperature, CO$_2$ pressure, reaction time and dosage of catalysts on the cycloaddition reactions of CO$_2$ with PO were investigated to find...
the most appropriate and efficient reaction conditions. The effect of the temperature on the PC yield was showed in Fig 2. It could be observed that the yield of PC increased sharply from 20% to 98%, with temperature from 100°C up to 130°C. Then PC yield stayed almost constant when temperature increased further.

![Fig. 2 Effect of temperature. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), CO$_2$ pressure (2.0 MPa), reaction time (4 h).](image)

However, too high temperature would lead to reduction of PC yield, probably due to the result of side reactions such as the isomerization to acetone. To be delighted, the temperature did not appear to reduce the selectivity of PC, since no significant change in the selectivity with increasing temperature. Therefore, the optimal temperature for this reaction was chosen as 130°C.

![Fig. 3 Effect of pressure. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), reaction time (4 h), temperature (130°C).](image)

The influence of CO$_2$ pressure on the yield of PC was investigated at 130°C for 4 h with 2b as the catalyst (Fig. 3). It could be obviously seen that the reaction pressure showed great effect on PC yield. With the raise of CO$_2$ pressure in the low-pressure region (0.5-1.5 MPa), the PC yield increased rapidly, but CO$_2$ pressure was revealed little effect on the PC yield in the range of 1.5-2.5 MPa, and the PC yield decreased obviously when CO$_2$ pressure was above 2.5 MPa. Similar influence of CO$_2$ pressure on catalytic activity had been observed in other catalytic systems in the literature. According to these reports, it could be explained that PC was in its liquid form under the adopted reaction conditions. The concentration of CO$_2$ in the liquid phase raised with increasing pressure when the reaction was carried out in the low-pressure region, which promoted the reaction. But too high CO$_2$ pressure would decrease PC yield because of lower concentration of PO in the liquid phase since PO was also a reactant. So 2.0 MPa was chosen as the most suitable pressure.

![Fig. 4 Effect of reaction time. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), CO$_2$ pressure (2.0 MPa), temperature (130°C).](image)

The dependence of PC yield and selectivity on reaction time was also investigated under identical reaction conditions. As shown in Fig 4, the yield of PC increased rapidly in the initial stage and stayed almost steady after 4 h. Meanwhile, nearly all the PO could be converted within 4 h. Conclusively, a reaction time of 4 h was the optimal choice for the synthesis of PC.

![Fig. 5 Effect of catalyst amount. Reaction conditions: PO (14.3 mmol), CO$_2$ pressure (2.0 MPa), reaction time (4 h), temperature (130°C).](image)

Additionally, the effect of catalyst amount on the reaction was investigated under the same reaction conditions (Fig. 5). The results indicated that the catalyst amount had significant impact on the reactions. It could be found that the increase of catalyst amount resulted in a moderate increase in PC yield under a low catalyst amount level (0-1.5 mol%). Thereafter, the further increasing amount of catalyst exhibited little influence on PC yield, which indicated an optimal catalyst amount of 1.5 mol%.

2.3 Recycling of the catalyst

Recycle experiments were also conducted to examine the stability of the 2b catalyst for the reaction at 130°C, 2.0 MPa for 4 h.
During the cycle experiments, the catalysts were easily recovered by simple filtration, and then used for the next cycle. The results displayed in Fig 6 showed that the 2b catalyst could be reused for six runs with only a slight depression in its catalytic activity, while the selectivity of the product remained at 99%.

![Yield and selectivity (%)](Fig. 6)

**Fig. 6** Reuse of catalyst ABMDFP. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), CO$_2$ pressure (2.0 MPa), temperature (130°C), reaction time (4 h).

The FT-IR spectra of 2b which had been used six times was listed in Fig 7. And there was no obvious change of the two FT-IR curves which initially proved that the structure of the catalyst was stable after six times reuse. SEM images of the catalyst reused six times were also shown in Fig 8, and the morphology of

![FT-IR spectra](Fig. 7)

**Fig. 7** FT-IR spectra of the fresh and the six times reused ABMDFP.

The thermogram of the catalysts (fresh and reused six times) is shown in Fig 9. It was found that the 2b was still thermally stable up to 270°C after it had been used in the reaction, which was much higher than the temperature used for the cycloaddition of CO$_2$. Both the SEM and the thermogravimetric curve further proved the high stability of the catalyst structure, while the stability of the catalyst structure also provided evidence for the stability of the catalyst activity.

![Thermogram](Fig. 9)

**Fig. 9** The thermogram of the catalysts (fresh and reused six times).

2b hardly changed after being used six times. In addition, the thermogravimetric curve of 2b was exhibited in Fig 9. It was found that the 2b was still thermally stable up to 270°C after it had been used in the reaction, which was much higher than the temperature used for the cycloaddition of CO$_2$. Both the SEM and the thermogravimetric curve further proved the high stability of the catalyst structure, while the stability of the catalyst structure also provided evidence for the stability of the catalyst activity.

### 2.4 Catalytic activity of various epoxides with CO$_2$

In order to test the adaptability to different epoxides, a battery of epoxide substrates were examined under the optimized reaction conditions for the synthesis of corresponding cyclic carbonates in the presence of 2b, and the results are summarized in Table 2. The results indicated that the 2b was suitable for a variety of terminal epoxides with high yield and selectivity of the corresponding cyclic carbonates. The catalyst activity declined with the increase of carbon chain length (entries 1-4). Of all the epoxides surveyed, the activity of ethylene oxide (entry 1) was the highest, and 99% yield of ethylene carbonate (EC) was achieved in 4 h.

### 2.5 A possible mechanism for fixation of CO$_2$ into cyclic carbonates

![Mechanism](Scheme 3)

**Scheme 3** The interaction of ABMDFP, epoxide and CO$_2$ calculated by DFT study.
Based on the reports and the results above, we proposed a possible mechanism for chemical fixation reaction of CO$_2$ into cyclic carbonate catalyzed by ABMDFP (Scheme 2). Firstly, the hydrogen atom of hydroxyl group led to the C-O bond polarized by hydrogen bond interaction, which made the ring opening of epoxide easier. In the meantime, the nucleophilic attack of halide anion on the less sterically hindered carbon atom of the epoxide resulted in the ring opened easily and the epoxide transformed into ring-opened intermediate (step 1). Subsequently, the amines of the catalyst coordinated with CO$_2$ to form the carbamate salt (step 2). Then, nucleophilic attack of the intermediate on the carbamate salt produced the alkyl carbonate (step 3). Finally, the cyclic carbonate was obtained by intramolecular ring-closure and the catalyst was regenerated (step 4). Additionally, the interactions of 2b, epoxide and CO$_2$ were simulated by density functional theory (DFT) study. As shown in Scheme 3, the hydrogen atom of 2b was coordinated with the oxygen of epoxide through a hydrogen bond leading to the length of C-O bond increased from 1.434 Å to 1.459 Å, which made the ring-opening much easier. The DFT study also indicated that the bond angle of CO$_2$ was changed to 179° C from linear molecule after interaction with amines, which could activate the CO$_2$ in some degree.

2.6 Catalytic activity towards transesterification process for DMC production

The synthesis of DMC through transesterification reaction catalysed by ABMDFP with EC and PC as substrates was also studied due to the special structure of many amines within the molecule. As shown in Table 3, the 2b catalyst exhibited high activity and selectivity towards transesterification of EC or PC with methanol to the DMC. Furthermore, the results also demonstrated the activity of PC was much lower than EC under the same condition, presumably owning to its steric hindrance (entry 1 vs 2). By comparison, several conventional catalysts were also investigated under the same reaction conditions. It was found that the catalytic activity of ABMDFP was similiar with the conventional catalysts (entry 1 vs 4, 5, 6) or even better (entry 1 vs 3). According to the published reports and the results in this study, the catalytic activity of the catalysts for the transesterification process could be attributed to the activation of alcohol by amines.

**Table 2** Catalytic activity of the reaction of various epoxides with CO$_2$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxides</th>
<th>Carbonates</th>
<th>Time (h)</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
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<td>2</td>
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<td>6</td>
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<tr>
<td>7</td>
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</tr>
</tbody>
</table>

$^a$ Reaction conditions: epoxides (14.3 mmol), catalyst (1.5 mol%), CO$_2$ pressure (2.0 MPa), temperature (130°C). $^b$ Determined by GC.

**Table 3** Catalysts screening for the synthesis of DMC.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)$^b$</th>
<th>DMC Select. (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ABMDFP</td>
<td>90</td>
<td>99</td>
</tr>
<tr>
<td>2$^a$</td>
<td>ABMDFP</td>
<td>78</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>KOH</td>
<td>80</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>K$_2$CO$_3$</td>
<td>88</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>NaOH</td>
<td>87</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>MeONa</td>
<td>90</td>
<td>99</td>
</tr>
</tbody>
</table>

$^a$ Reaction condition: EC (12.5 mmol), CH$_3$OH (4.0 g, 125 mmol), Catalyst (2.5 mol%), ABMDFP was calculated by monomers, temperature (150°C), reaction time (6.0 h). $^b$ Determined by GC. $^c$ PC (12.5 mmol).
3. Experimental

3.1 Chemical reagents

Carbon dioxide was supplied by Beijing Analytical Instrument Factory with a purity of 99.95%. Ammonium iodide, 1,2-epoxyoctane and cyclohexene oxide were purchased from Alfa Aesar-A Johnson Matthey Company. Other reagents and chemicals (analytic grade) were bought from Sinopharm Chemical Reagent Co., Ltd, and were used without further purification.

3.2 Synthesis of dicyandiamide-formaldehyde polymers

We synthesized four kinds of dicyandiamide-formaldehyde polymers. In a typical reaction, NH₄Br (1.00 g) and dicyandiamide (1.12 g) were poured in sequence into a 25 mL three-necked flask with 4 mL of methanol, and the mixture was heated at reflux for 20 min in an oil bath at 60°C, then 0.60 g NH₄Br were added to the flask and heated for 3 h at 85°C. After the reaction, the mixture was cooled down to room temperature. The top phase was poured out and the residue was washed three times with ethyl acetate and then dried at 60°C for 12 h under vacuum. Subsequently, the solid polymer was obtained. Following a similar procedure, the catalysts of 1b and 3b were synthesized by using ammonium chloride and ammonium iodide instead of ammonium bromide respectively. The DFP was synthesized without any modifier.

3.3 Characterization of the catalysts

The catalysts were characterized by thermogravimetric analysis (TGA, PERKIN-ELMER7 Series Thermal Analysis System) at a heating rate of 10°C min⁻¹. The morphology of the polymer was observed using a scanning electron microscope (JEOL JSJ 6700F). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 380 spectrophotometer with anhydrous KBr as standard (Thermo Electron Co.). ¹³C NMR spectra were recorded on a Bruker Avance-III 400M Solid-State NMR Spectrometer.

FT-IR spectroscopic studies were carried out on DFP, 1b, 2b and 3b (Fig. 10). All of the samples were dried under vacuum at 60°C for 24 h before detected. The catalyst of DFP, 1b, 2b and 3b showed a typical strong peak related to -OH stretching at about 3500-3000 cm⁻¹. DFP displayed a characteristic bands of C≡N centered at 2172 cm⁻¹ peaks, while the other catalysts not, which demonstrated a completely reaction with NH₄I.

As shown in Fig. 11, the NMR signal at 165 ppm in DFP was attributed to the C≡N, and the signal apparently disappeared in 1b, 2b and 3b, which proved the success of their synthesis.

3.4 Procedure of the cycloaddition reaction of CO₂ with propylene oxide

The coupling reaction of carbon dioxide and epoxide was carried out in a 25 mL stainless-steel reactor equipped with a magnetic stirrer and an automatic temperature control system. In a typical reaction, appropriate amounts of PO and catalyst were charged into the reactor at room temperature, then CO₂ was added to a suitable pressure from a reservoir tank to maintain a constant pressure. Control the temperature within the desired range afterwards. After the reaction, the reactor was cooled to room temperature in a water bath and remaining CO₂ was vented out slowly. The organic products were separated from the catalyst by filtration and analysed by GC-MS and GC. Agilent 6890/5973 GC-MS was equipped with a FID detector and a DB-wax column. The catalyst was washed with ethyl acetate three times and dried under vacuum for the recycling experiment.

3.5 Procedure of transesterification of cyclic carbonate with methanol

A mixture of cyclic carbonate (12.5 mmol), CH₃OH (4.0 g, 125 mmol) and catalyst (0.1 g) was added to a 25 mL stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. The reaction was carried out for 150°C and 6 h. After the reaction, the reactor was then cooled to room temperature. The products were analyzed by GC using biphenyl as the internal standard and identified by GC-MS by comparing retention times and fragmentation patterns with authentic samples.

4. Conclusions

A series of dicyandiamide-formaldehyde polymers were synthesized and used as catalysts for conversion of CO₂ into...
organic carbonates. The ABMDFP was the best catalyst of all the polymers, which was applicable to various epoxides. Furthermore, the catalyst could be easily recovered by filtration and reused at least six times with high activity and selectivity. We proposed a possible mechanism of ring-opening of epoxide assisted by hydrogen bond and activation of CO$_2$ induced by amines. The catalytic activity for DMC synthesis through transesterification reaction was also studied, and the catalyst exhibited high activity, 90% yield of DMC together with 99% selectivity was obtained.

In conclusion, this class of functional organic polymers was inexpensive, easy to synthesize and recycle, and proved to be environmentally efficient catalysts for the cycloadition reaction of CO$_2$.

Acknowledgements

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Notes and references

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