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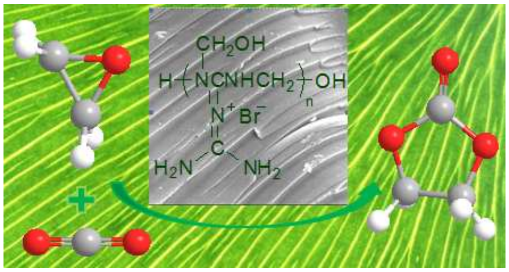

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

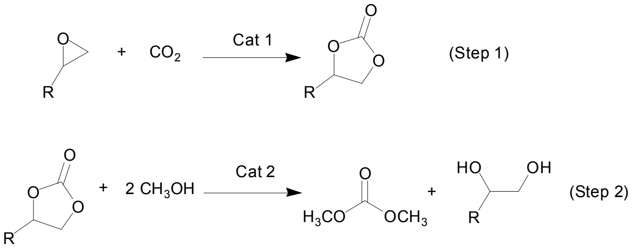
DOI: 10.1039/b000000x

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.



Scheme 1 Synthesis of cyclic carbonates (step 1) and transesterification process for DMC production (step 2).

Recently, functional organic polymers have received increasing interests in the fields of catalysis due to the macromolecular architecture and possibility of creating new properties and functions.[14] In this respect, He and co-workers reported that a quaternary ammonium salt-functionalized chitosan was an efficient and recyclable catalyst for the synthesis of cyclic carbonates from CO_2 and epoxides.[15] They also prepared polyethylene glycol (PEG)-supported quaternary ammonium salt as a recyclable catalyst for the reaction.[16] The PEG6000-supported catalyst was dissolved during the reaction and solidified by cooling after the reaction, which attained a homogeneous reaction and heterogeneous separation. Park and co-workers immobilized imidazolium ionic liquids on cellulose and proposed that the -COOH groups on the support material could stabilize the cyclic carbonate formed and promote the reaction.[17] North and co-workers reported polystyrene-supported one-component, bimetallic aluminium (salen) complexes, which using the ammonium group as a convenient linker, for the

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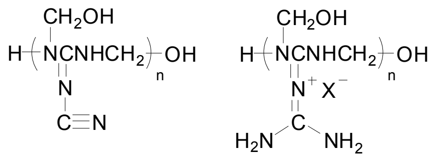
synthesis of cyclic carbonates at room temperature and atmospheric.[18] Han and co-workers prepared a highly cross-linked polymer-supported ionic liquid as a heterogeneous catalyst for the cycloaddition reaction,[13a] in which 3-butyl-1-vinylimidazolium chloride was covalently anchored on divinylbenzene-cross-linked polymer matrix. Current studies showed that hydrogen bond donors (HBD) could activate the ring-opening of epoxides and enhance the reaction for fixation of CO_2 with epoxides.[19-22] In this respect, we also synthesized hydroxyl functional polymers as active and insoluble catalysts for fixation of CO_2.[13e, f, 21d, f] 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,[23] 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 simpleness 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 promoting 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.



a

1b: X = Cl
2b: X = Br
3b: X = I

Fig. 1 Structures of the DFP (**a**), ACMDFP (**1b**), ABMDFP (**2b**) and AIMDFP (**3b**).

2. Results and discussion

2.1 Activities of various catalysts

After the four kinds of catalysts were achieved, their activities were investigated *via* the cycloaddition reaction of propylene oxide (PO) with CO_2 to synthesize propylene carbonate (PC), and the corresponding results were displayed in Table 1.

Table 1 Catalysts screening for the synthesis of propylene carbonate[a]

Entry	Catalyst	PO Conv. (%)[b]	PC Select. (%)[b]
1[c]	DFP	58	99
2[c]	ACMDFP	67	99
3[c]	ABMDFP	96	99
4[c]	AIMDFP	99	99
5	DCD	25	99
6	NH_4Cl	48	99
7	NH_4Br	85	99
8	NH_4I	92	99
9[d]	PILs[e]	90	99
10[d]	PILs[f]	94	99

[a] Reaction conditions: PO (14.3 mmol), catalyst (2.0 mol%), CO_2 pressure (2.0 MPa), reaction time (3.5 h) and temperature (130ºC). [b] Conversion and selectivity were determined by GC using biphenyl as the internal standard. [c] Catalyst (1.5 mol% calculated by monomers). [d] Catalyst (1.5 mol% calculated by ILs). Every experimnt was repeated 3 times. DCD = dicyandiamide. [e] PILs was synthesized by co-polymerization of 1-vinyl-3-carboxyethylimidazolium bromide with the cross-linker divinylbenzene.[13f] [f] PILs was synthesized by co-polymerization of 1-vinyl-3-hydroxyethyl-imidazolium bromide with the vinylpyridine.[13e]

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_4X and hydroxyl-functionalized poly(ionic liquids) (PILs). The results revealed that activity of DCD was very low (entry 5), and the activity of NH_4X was in the order of $NH_4I > NH_4Br > NH_4Cl$ (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.[24] Catalyst **2b** could show a 96% PC yield, which was much higher than that of the NH_4Br (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.[13e, f] 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.

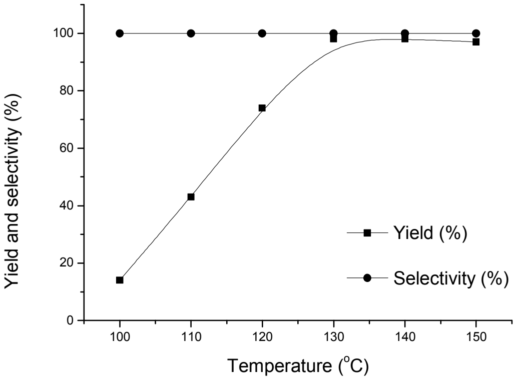


Fig. 2 Effect of temperature. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), CO_2 pressure (2.0 MPa), reaction time (4 h).

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.[25] 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.

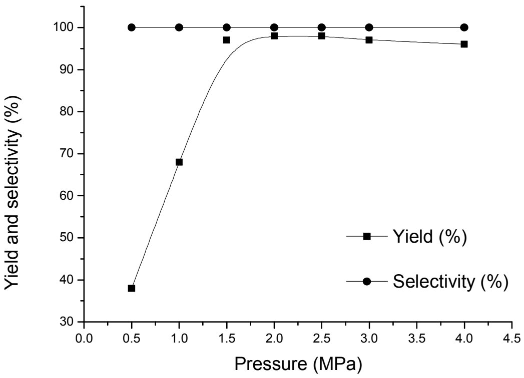


Fig. 3 Effect of pressure. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), reaction time (4 h), temperature (130°C).

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.[26-28] 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.[29] So 2.0 MPa was chosen as the most suitable pressure.

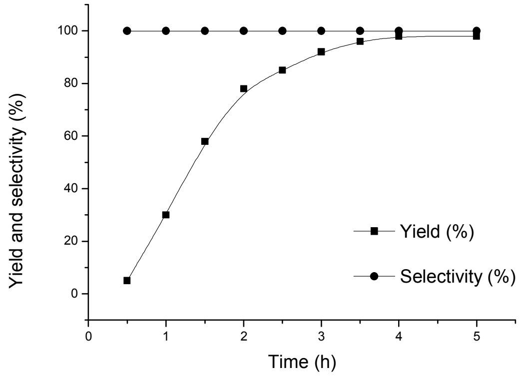


Fig. 4 Effect of reaction time. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), CO_2 pressure (2.0 MPa), temperature (130°C).

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.

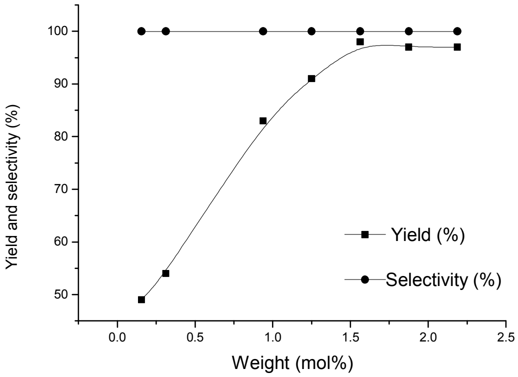


Fig. 5 Effect of catalyst amount. Reaction conditions: PO (14.3 mmol), CO_2 pressure (2.0 MPa), reaction time (4 h), temperature (130°C).

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%.

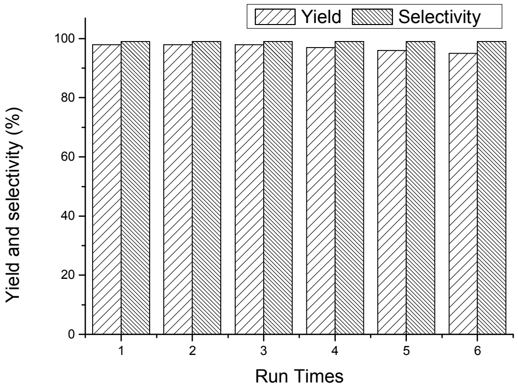


Fig. 6 Reuse of catalyst ABMDFP. Reaction conditions: PO (14.3 mmol), catalyst (1.5 mol%), CO_2 pressure (2.0 MPa), temperature (130°C), reaction time (4 h).

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 **2b** hardly changed after being used six times. In addition, the thermogravimatric 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 thermogravimatric 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.

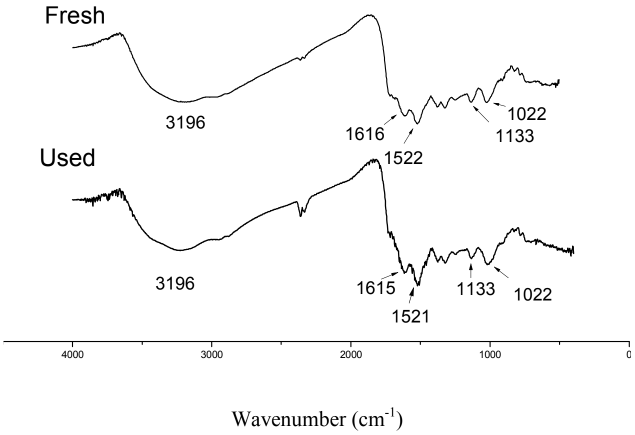


Fig. 7 FT-IR spectra of the fresh and the six times reused ABMDFP.

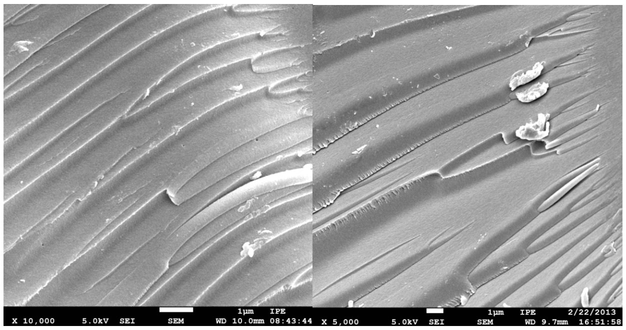


Fig. 8 SEM images of the fresh (left) and the six times reused (right) ABMDFP.

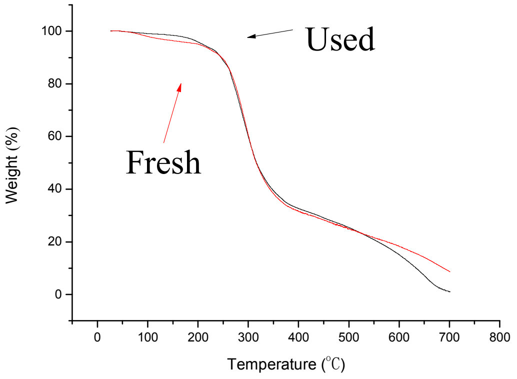
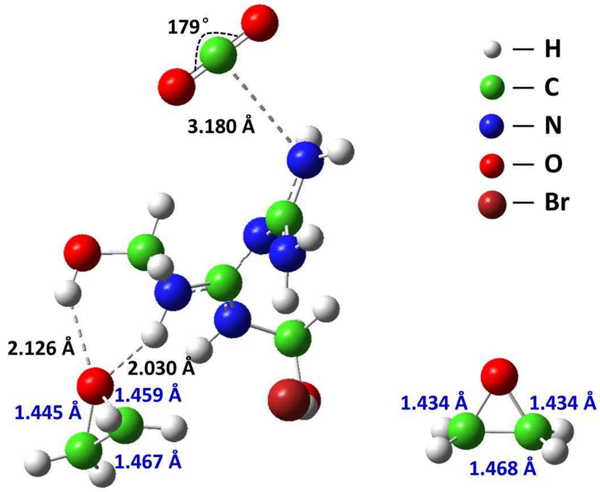


Fig. 9 The thermogram of the catalysts (fresh and reused six times).

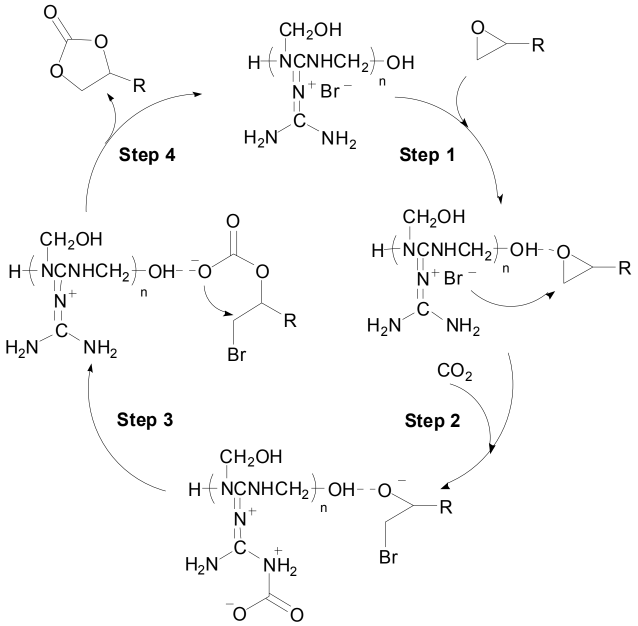
2.4 Catalytic activity of various epoxides with CO_2

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



Scheme 3 The interaction of ABMDFP, epoxide and CO_2 calculated by DFT study



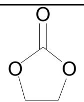
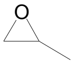
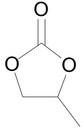
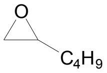
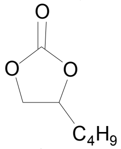
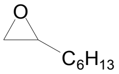
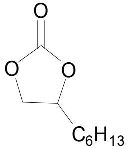
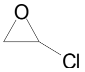
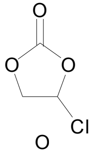
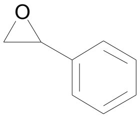
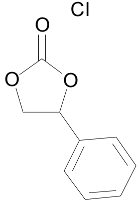
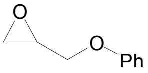
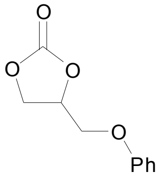
Scheme 2 The proposed mechanism for the cycloaddition reaction.

Based on the reports[21d, f, 30, 31] 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 ^{o}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 simalir with the conventional catalysts (entry 1 *vs* 4, 5, 6) or even better (entry 1 *vs* 3). According to the published reports,[32] 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[a]

Entry	Epoxides	Carbonates	Time (h)	Yield (%)[b]
1			4	99
2			4	98
3			4	98
4			4	91
5			4	97
6			5	99
7			5	99

[a] Reaction conditions: epoxides (14.3 mmol), catalyst (1.5 mol%), CO_2 pressure (2.0 MPa), temperature (130^{o}C). [b] Determined by GC.

Table 3 Catalysts screening for the synthesis of DMC[a]

Entry	Catalyst	Conv. (%)[b]	DMC Select. (%)[b]
1	ABMDFP	90	99
2[c]	ABMDFP	78	99
3	KOH	80	99
4	K_2CO_3	88	99
5	NaOH	87	99
6	MeONa	90	99

[a] Reaction condition: EC (12.5 mmol), CH_3OH (4.0 g, 125 mmol), Catalyst (2.5 mol%, ABMDFP was calculated by monomers), temperature (150^{o}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, NH_4Br (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 NH_4Br 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 JSM 6700F). Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet 380 spectrophotometer with anhydrous KBr as standard (Thermo Electron Co.). ^{13}C 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 3500-3000cm^{-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 NH_4X.

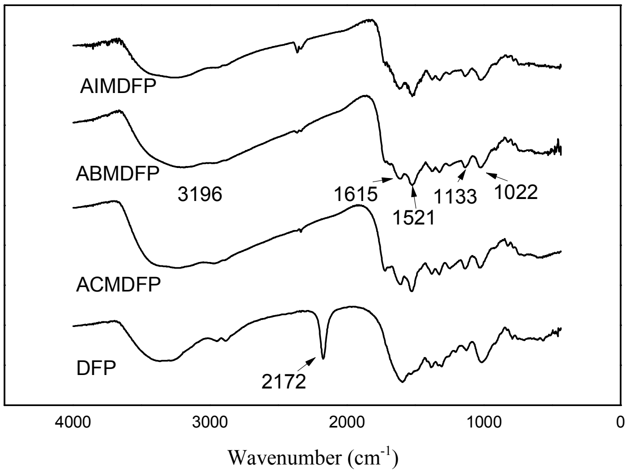


Fig. 10 The FT-IR spectra of DFP, ACMDFP, ABMDFP and AIMDFP.

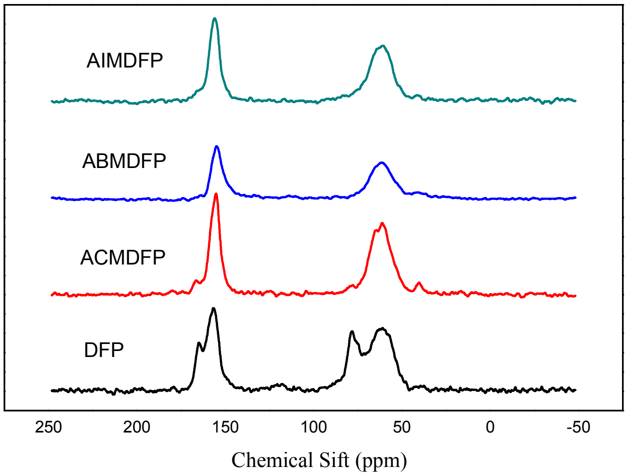


Fig. 11 The ^{13}C NMR spectra of DFP, ACMDFP, ABMDFP and AIMDFP.

The ^{13}C NMR spectra of the four catalysts were also studied. 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 CO_2 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, CO_2 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 CO_2 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), CH_3OH (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 CO_2 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 cycloaddition reaction of CO_2.

Acknowledgements

This work was supported by the Natural Science Foundation of China (21076113, 21003129 and 21006112).

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