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Superbase/cellulose: an environmentally benign catalyst for chemical fixation of carbon dioxide into cyclic carbonates†

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An environmentally benign catalytic system consisting of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) and cellulose was developed for CO_2 chemical fixation with epoxides under metal-free and halide-free conditions. Due to the dual roles played by DBU and cellulose on the activations of CO_2 and epoxide, the reaction could be performed with high activity and selectivity. A possible catalytic cycle for the hydrogen bond assisted ring-opening of epoxide and the activation of CO_2 induced by DBU was proposed. The process herein represents a simple, ecologically safe and efficient route for CO_2 chemical fixation into high value chemicals.

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Introduction

Recently, a great deal of effort has focused on the synthesis of cyclic carbonates from CO2 and epoxides. The synthesized cyclic carbonates have various purposes in synthesis, catalysis, electrochemistry and so on.^{1,2} A wide range of catalysts have been developed including alkali metal or transition metal based binary systems,3-5 ionic liquids (ILs),6 and supported catalysts.^{7,8} It is generally accepted that an efficient catalyst prefers to employ Lewis acid sites (Zn²⁺, Al³⁺, Co²⁺, etc.) along with highly nucleophilic and good leaving ability groups (e.g. Cl⁻, Br⁻ and I⁻). This has some advantages including high activity, good selectivity, and low energy demand. However, the inherent corrosion, toxicity and environmental problems associated with metallic cations and halide anions are concerns from the viewpoint of green chemistry. Therefore, although this area of research has been well explored, there is still a place for developing catalysts that are both halide-free and metal-free for an effective cycloaddition under mild conditions while respecting environmental considerations.

It is well known that the inherent thermodynamic stability and the kinetic inertness of CO_2 hinder the development of efficient catalysts that realize CO_2 activation and subsequently its functionalization.^{2c} To resolve this problem, the applications of organic bases have been considered, and among these bases, superbases have attracted much attention in green chemistry.9,10 They provide new opportunities not only for the development of reversible CO2 capture systems with a high capacity but a low desorption energy,9 but also for CO₂ chemical activation. As reported, previously developed superbase based CO2 capture systems generally include non-volatile weak proton donors like alcohols,^{9a,b} ILs or hydroxyl-functionalized ILs,^{9c,d} and phenol.9e An organic base has been found its activity in the presence of metallic compounds for the conversion of CO₂ into cyclic carbonates.^{10d} However, a metallic ion is still needed. On the other hand, it has been found that hydrogen bond donor (HBD) can accelerate the cycloaddition of epoxides with CO₂ through the hydrogen bond on the oxygen atom of the epoxide.^{6a-e} Thus, many kinds of HBDs have been reported for this transformation, such as lecithin, ${}^{3a}\beta$ -CD, 3b cellulose,^{3c} formic acid,^{3d} H₂O,^{6a} amino acids,^{11a} and lignin.^{11b} As a natural HBD, cellulose is a well known fascinating biopolymer with abundant hydroxyl groups and is readily available, inexpensive, biocompatible and stable.¹² Moreover, it has been considered as an almost inexhaustible source of raw material to supply the increasing demand for environmentally friendly and biocompatible products.¹² Thus, the utilization of cellulose is still a hot topic.

In our previous work, we have reported some strategies to avoid the use of metal based catalyst, such as through the combination of HBDs and halide based ILs, 6a,7a and through the covalent attachment of hydroxyl groups or carboxyl groups to the structure of the ILs. $^{6b-c,7b}$ However, one key drawback associated with these methods for the conversion of CO₂ is the still employment of halide anions from the viewpoint of activity. It has also been reported that N-heterocyclic carbene

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provides a possibility for the development of environmentally friendly catalysts for this kind of reaction, however, the activities need to be further improved.¹³ Could the combination of bases and HBDs be used as efficient catalysts for the chemical fixation of CO2 into cyclic carbonates, eliminating both the use of metallic and halide ions? As a continuing work, herein, we present a study on the combination of organic bases and HBDs as catalytic systems for the synthesis of cyclic carbonates from CO₂ and epoxides. The effects of reaction parameters like the choice of HBDs and organic bases, reaction temperature, CO₂ pressure, and reaction time have been investigated. Moreover, in situ FT-IR was used for the detection of the reaction process. It was found that these novel integrated systems effectively convert CO2 into cyclic carbonates under halide-free and metal-free conditions. The established process represents a protocol for an ecologically safe and cost-effective route to the synthesis of cyclic carbonates from CO_2 .

Results and discussion

To investigate the effects of bases and HBDs on the CO₂ chemical fixation into cyclic carbonates, several typical organic bases (Scheme 1) and HBDs were selected and explored. The were 1,8-diazabicyclo[5.4.0]-undec-7-ene bases (DBU), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), N-methylimidazole (MIm), imidazole (Im), N,Ndimethylaminopyridine (DMAP), pyridine (Py), monoethanolamine (MEOA), diethanolamine (DEOA), triethanolamine (TEOA), triethylamine (TEA), and diethylamine (DEA). The HBDs were cellulose, chitosan, PEG600, PEG400, glycerine, β -CD, deionized H₂O and 1,2-propylene glycol (PG).

The DBU superbase was first examined combining with the HBDs to study the effects of the different HBD on a probe reaction of propylene oxide (PO) and CO₂ to produce propylene car-



ÓН

TEA

DEA

TEOA

Scheme 1 Chemical structures of organic bases used in this work and

bonate (PC), and the corresponding results were summarized in Table 1. It was found that the influence of the HBDs on the reaction was moderate (Table 1). As can be seen, single DBU exhibits an 80% PO conversion (entry 1). The high activity obtained might be due to the nucleophilic capability of DBU and its CO₂ activation effect.^{9b,c} The yield of PC was negligible in the case of only using cellulose as the catalyst, although it is an excellent HBD for ring-opening of epoxides (entry 2).^{3c} However, the combination of DBU with cellulose realized a further enhancement in catalytic activity compared to that achieved by each one, indicating the necessary synergistic effect of DBU and cellulose for accelerating the reaction by which the PO conversion approaches 93% with a 99% PC selectivity (entry 3). The promoting effect of cellulose on the activity of DBU is more obvious at a lower reaction temperature (entry 4 vs. 5). Interestingly, when chitosan was substituted for cellulose, the activity decreased (entry 6) although chitosan can also be used for CO₂ capture and conversion.^{7a,14} In the other catalyst screening experiments, the effects of HBDs such as poly(ethylene glycol) (PEG), glycerine, β -cyclodextrin (β -CD) and H_2O on the reaction were investigated (entries 7–11). The corresponding activity order for the above HBDs is cellulose > chitosan, glycerine, PEG400 > PEG600, β -CD > H₂O (entries 3, 6-11). Compared to other HBDs, H₂O played an inhibiting role for the reaction, only a 50% PO conversion and a 45% PC yield were obtained, which is caused by the hydrolysis of PC to produce 1,2-propylene glycol in the presence of DBU. It is noted that in the 4th reuse, the DBU-cellulose catalyst still

Table 2 shows the effects of the employed different organic bases on the conversion of PO with the presence of cellulose, which was found to be quite strong. Among the organic bases, DBU was the most excellent (entry 3). When a bicyclic amidine

Table 1	Catalyst	screening	for the	cycloaddition	reaction	of PO	Ĵ
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F)> >o	+	CO ₂	 -	PC	

Entry	Base	HBD	Conversion ^{b} (%)	Selectivity ^{b} (%)
1	DBU	/	80	99
2	/	Cellulose	_	_
3	DBU	Cellulose	93	99
1^c	DBU	/	60	95
5 ^c	DBU	Cellulose	85	99
5	DBU	Chitosan	88	99
7	DBU	PEG600	83	99
3	DBU	PEG400	86	99
9	DBU	Glycerine	87	98
10	DBU	β-ČD	83	99
11	DBU	H_2O	51	89
12^d	DBU	Cellulose	92	99
13 ^e	DBU	Cellulose	89	99
14^f	DBU	Cellulose	85	99

^a Reaction conditions: PO (1 mL), base (225 mg), HBD (15 mg), 120 °C, 2.0 MPa, 2 h. ^{*b*} Determined by GC/GC-MS, main by-product is 1,2-propylene glycol. ^{*c*} 110 °C. ^{*d*} 2nd-reuse. ^{*e*} 3rd-reuse. ^{*f*} 4th-reuse.

DEOA

DBU

MIm

MEOA

their designations.

Table 2 The effect of organic bases on the conversion of PO^a

Entry	Base	pK _a ^b	Conversion ^c (%)	Selectivity ^c (%)
1	TBD	26.0	8	96
2	MTBD	25.5	15	99
3	DBU	24.3	93	99
4	TEA	18.8	41	95
5	DMAP	18.0	87	99
6	Py	12.5	30	92
7	DEA	(11.0)	34	92
8	MEOA	(9.5)	64	88
9	DEOA	(8.9)	74	94
10	DABCO	(8.7)	80	98
11	TEOA	(7.8)	81	93
12	MIm	(7.1)	74	99
13	Im	(7.0)	10	93

^{*a*} Reaction conditions: PO (1 mL), base (225 mg), cellulose (15 mg), 120 °C, 2.0 MPa, 2 h. ^{*b*} pK_a value of the conjugated acid in acetonitrile or water (brackets).^{9*a*,15 *c*} Determined by GC/GC-MS, main by-product is 1,2-propylene glycol.

(DBU) was replaced by a guanidine superbase (TBD or MTBD), an unsatisfactory result was obtained (entries 1, 2 vs. 3). This distinctly diminished performance might be related in part to a high steric hindrance of TBD or MTBD. As reported by Heldebrant et al., an organic base with a lower pK_a value had a less negative Gibbs free energy of reaction with CO₂.^{9b} Therefore, the ability of the organic bases to form ammonium salts with CO₂ might decrease in the order of TBD > MTBD > DBU > TEA > DMAP > Py > DEA > MEOA > DEOA, DABCO > TEOA > MIm, Im. However, Table 2 shows that the activity order of the above bases is not in strict accordance with the established pK_a , that is DBU > DMAP > DABCO, TEOA > DEOA, MIm > MEOA > TEA > DEA, Py > MTBD > Im, TBD (entries 1-13), which indicates that the basicity of the base is one important factor for a high activity to be obtained. Besides that, its steric hindrance as well as the synergistic effect of the hydroxyl group in its structure were also promotion factors in the reaction as reported in previous work.⁶

Since DMAP also showed an interesting activity in the presence of cellulose (entry 5, Table 2), and is a well known nucleophilic catalyst to promote the coupling and copolymerisation of CO₂ and epoxides,¹⁶ its activities were further evaluated in the presence of 1,2-propylene glycol (PG), chitosan, β -CD, and in the absence of any HBD, in order to demonstrate that the combination of DBU and cellulose was the best one under the employed conditions. The results compared to those of DBU were also summarized in Table 3. The results proved that DBU based catalytic systems could exhibit higher activities than the DMAP based systems employed (entries 1–4 *vs.* 5–8), which might be presumably due to the higher nucleophilicity and basicity of DBU compared to those of DMAP.¹⁷ Based on the above discussions from Tables 1–3, DBU–cellulose was selected as the catalyst for further investigations.

The effect of the mass ratio of DBU to cellulose on the cycloaddition of PO and CO_2 to produce PC was studied by a regular step change of the DBU amount at a fixed weight of cellulose. Table 4 depicts that every change had an obvious effect

Table 3 Screening for the cycloaddition reaction of PO^a

Entry	Base	HBD	Conversion ^{b} (%)	Selectivity ^b (%)
1	DBU	/	80	99
2	DBU	PG	89	98
3	DBU	Chitosan	88	99
4	DBU	β-CD	83	99
5	DMAP	,	76	96
6	DMAP	PG	86	97
7	DMAP	Chitosan	83	98
8	DMAP	β-CD	80	98

^{*a*} Reaction conditions: PO (1 mL), base (225 mg), HBD (15 mg), 120 °C, 2.0 MPa, 2 h. ^{*b*} Determined by GC/GC-MS, main by-product is 1,2-propylene glycol.

Table 4 Effect of DBU amount on cycloaddition reaction of PO and CO_2^a

Entry	DBU-cellulose	Conversion ^{b} (%)	Selectivity ^b (%)
1	1.1	16	00
1	1:1	10	99
2	3:1	25	99
3	5:1	50	99
4	7:1	69	99
5	10:1	85	99
6	15:1	93	99
7	20:1	95	99
8	25:1	96	99
9	30:1	99	98

 a Reaction conditions: PO (1 mL), cellulose (15 mg), 120 °C, 2.0 MPa, 2 h. b Determined by GC/GC-MS.

on the reaction. DBU–cellulose could exhibit a high activity at a mass ratio of 15:1. Thereafter, a continuous increase of DBU amount improved but little the PC yield, indicating an optimal mass ratio of 15:1 in DBU-cellulose system.

Subsequently, we investigated the effects of other parameters on the catalytic activity of DBU-cellulose. Fig. 1 shows the effect of catalyst mass concentration on the reaction. With the increase in catalyst amount, PO conversion increased quickly from 55% to around 96% in the range of catalyst



Fig. 1 Dependence of the PC yield on catalyst concentration. *Reaction conditions*: PO (1 mL), DBU-cellulose = 15 : 1 (wt/wt), 120 °C, 2.0 MPa, 2 h.

concentration increasing from 9 to 38 wt%, while PC selectivity increased first and then slightly decreased after the catalyst concentration increased beyond about 23 wt%. The increase in PO conversion is understandable, while the decrease in PC selectivity might be caused by a side-reaction of PO and water in the production of PG.

As illustrated in Fig. 2, the temperature had a pronounced positive effect on the coupling reaction when it varied from 80 to 120 °C. The PO conversion was enhanced from about 25% to above 90% correspondingly. 120 °C could be the optimal temperature. The lower selectivity may be due to possible side reactions such as the isomerization and hydrolysis of PO at lower temperatures.^{6/} When the reaction temperature was higher than 120 °C, the conversion of PO increased but a little. Whereas a further increase in the temperature caused a slight decrease in the selectivity, possibly due to more PG formed at the higher temperature.

Subsequently, we investigated the effect of reaction pressure on the cycloaddition reaction. Fig. 3 shows that the CO₂ pressure has also a great effect on the PC yield at 120 °C in the range of 1–4 MPa. A maximum PC yield could be obtained when the pressure varies from 1 to 4 MPa. Within a certain



Fig. 2 Dependence of the PC yield on reaction temperature. *Reaction conditions*: PO (1 mL), DBU (225 mg), cellulose (15 mg), 2.0 MPa, 2 h.



Fig. 3 Effect of the reaction pressure on the cycloaddition reaction of PO. Reaction conditions: PO (1 mL), DBU-cellulose = 15:1 (wt/wt), DBU (225 mg), 120 °C, 2 h.



Fig. 4 Dependence of the PC yield and selectivity on reaction time. *Reaction conditions*: PO (1 mL), DBU (225 mg), cellulose (15 mg), 120 °C, 2.0 MPa.

reaction time, the decrease in the product yield might be caused by the lowered PO concentration in the vicinity of the catalyst with the increasing concentration of CO₂,^{8e} which has also been observed in other catalytic systems.^{3b}

The dependence of the PC yield and selectivity on the reaction time were also evaluated. It was found that the reaction time had a remarkable influence on the reaction. As shown in Fig. 4, the reaction rate was fast in the initial stage and remained almost invariant after 4 h. The PC selectivity fluctuation is relatively small after a reaction time of 2 h. Since the further increase of reaction time from 2 to 4 h only resulted in a small increase in the PC yield, a reaction time of 2 h was used for the investigations.

Next, the characterization of DBU and cellulose before and after recycling was carried out by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), liquid chromatography (LC) and nuclear magnetic resonance (NMR) (Fig. S2-S7, ESI[†]). The FT-IR results shown in Fig. 5(top) reveal that the structure of the cellulose after the 2nd-reuse and 4th-reuse did not obviously change compared to the fresh cellulose. The XRD result showed that the recycled cellulose typically exhibited lower degrees of crystallinity than the native cellulose (Fig. S2[†]), which is also found in the case of cellulose after being dissolved in ILs.¹² No glucose was detected even when prolonging the reaction time from 2 to 12 h (Fig. S5[†]). The above results indicate the stability of cellulose in the reaction system. Fig. 5(bottom) shows a comparison of the FT-IR spectra of fresh and 4th-reuse DBU. The DBU was heated at 120 °C for one hour to remove CO2 before detection. The result also proved the stability of DBU in the recycling experiments.

To obtain more information on the cycloaddition process, the reaction between PO and CO_2 catalyzed by DBU–cellulose was investigated in a 100 mL stainless steel reactor using *in situ* FT-IR monitoring under identical conditions (PO 30 mL, DBU 6.75 g, cellulose 0.45 g, 120 °C and 2.0 MPa). During the reaction process, the CO_2 is in excess. Two selected



Fig. 5 FT-IR spectra: (top) the fresh, 2nd-reuse and 4th-reuse cellulose; (bottom) the fresh and 4th-reuse DBU.

results are shown in Fig. 6. The FT-IR spectra obtained synchronously in Fig. 6(top) indicated that a new species was formed as indicated by the peak at around 1788 cm^{-1} , which is a peak of PC. The three-dimensional spectra in Fig. 6(bottom) described a consistent reaction profile of the PC yield with the reaction time (Fig. 4).

Under the optimized reaction conditions, a range of terminal epoxides were explored in the presence of DBU and cellulose. The results were shown in Table 5. The catalyst was found to be applicable to the mono-substituted and disubstituted epoxides studied, providing the corresponding cyclic carbonates in high yields and selectivities. It is worth mentioning that ethylene oxide **1a** was the most active among the epoxides surveyed, and a 92% yield of ethylene carbonate with a 99% selectivity was obtained after a reaction time of 1 h (entry 1). Due to the higher steric hindrance of the disubstituted epoxides **1g** and **1h** compared to the epoxides **1a**–**1f**, longer reaction times were needed to obtain higher product yields (entries 7–8).

As is well known, cellulose is a carbohydrate polymer containing abundant hydroxyl groups in its structure. The existence of H-bond interactions between PO and the numerous hydroxyl groups in cellulose has been deduced as a main



Fig. 6 In situ IR spectra of the reaction system. Reaction conditions: PO (30 mL), DBU (6.75 g), cellulose (0.45 g), 120 °C, 2.0 MPa.

reason why cellulose could accelerate the synthesis of cyclic carbonates.^{3c,14c} Based on the previous reports^{3,6a-f,7a-c,10d,14c} and the results obtained, we propose a possible mechanism for this chemical fixation reaction of CO₂ (Scheme 2).

As shown in Scheme 2, the hydroxyl groups in cellulose coordinate with the oxygen of the epoxide ring through hydrogen bonds, resulting in activation of an epoxide molecule, and simultaneously, the nucleophilic attack of DBU on the less sterically hindered β-carbon atom of the epoxide ring, furnishes a possible ring-opened intermediate 1, by which the ring of the epoxide was opened easily. In parallel, another DBU might coordinate reversibly with CO₂,^{6f} to afford a carbonate salt 2, which might be an activated species of CO₂. Thereafter, the intermediate 1 made a nucleophilic attack on the carbonate salt 2 to produce a new alkyl carbonate compound 3. By the subsequent intramolecular ring-closure, a cyclic carbonate could be formed and the catalyst was regenerated. Cellulose is known as a promoting chemical for the ringopening of epoxides due to its hydrogen bonding and DBU is also known to activate CO2 by involving a zwitterionic adduct

Table 5 Cycloaddition of CO_2 to terminal epoxides catalyzed by DBU– cellulose^a

			Results ^b	
Entry	Epoxide	Product	Yield (%)	Selectivity (%)
1 ^{<i>c</i>}	°⊳ 1a	0 0 2a	92	99
2	°≻ 1b	2b	90	99
3 ^c	O └───CH ₂ CI 1c	CH ₂ CI 2c	80	93
4	^O ⊱− ^{Bu} 1d	O O Bu 2d	87	97
5	O ⊢Ph 1e	e^{O}	85	99
6	O └──OPh1f	O OPh 2f	88	99
7 ^{<i>d</i>}	→ 1g	°, 2g	75	99
8 ^e	° lh	of o 2h	80	96

 a Reaction conditions: epoxide (1 mL), DBU (225 mg), cellulose (15 mg), 120 °C, 2.0 MPa, 2 h. b Isolated yield. c 1 h. d 12 h. e 22 h.



Scheme 2 The proposed mechanism for the DBU-cellulose catalyzed reaction.

between the base and CO₂. This synergetic catalysis role played by cellulose and DBU made the reaction proceed smoothly.

Conclusions

We developed a simple and efficient binary system consisting of DBU and cellulose for the synthesis of cyclic carbonates from epoxides and CO_2 under metal-free and halide-free conditions. Under the optimal reaction conditions, the binary catalyst was found to be applicable to the mono-substituted and disubstituted epoxides. In addition, the catalyst could be reused with high activity and selectivity. A possible catalytic cycle for the hydrogen bond-assisted ring-opening of epoxide and the DBU-induced activation of CO_2 was proposed. The results of this work provided an example of the application of superbases combined with biomaterials as potentially environmentally benign alternatives in organic synthesis and catalysis.

Experimental

1. Chemicals

Chemicals including microcrystalline cellulose (with an average molecular weight of 5×10^4), chitosan (with a degree of deacetylation of 90% and an average molecular weight of 5×10^4), β -CD, PEG600, PEG400, glycerine, PG, DBU, MTBD, TBD, DMAP, DABCO, TEOA, DEOA, MEOA, Py, TEA, DEA, MIm, Im, epoxides (propylene oxide, ethylene oxide and epichlorohydrin), and solvents needed were all purchased from Beijing Chemical Reagent Company, and used directly without further purification. CO₂ was supplied by Beijing Analytical Instrument Factory with a purity of 99.95%. Other epoxides were purchased from Alfa Aesar China Co., Ltd.

2. Typical procedures for PC synthesis from PO and CO₂

In a typical procedure, DBU (225 mg), cellulose (15 mg), PO (1 mL, ~14 mmol) were added into a pressure reactor (25 mL inner volume) equipped with a magnetic stirrer and automatic temperature control system. Then, CO_2 was charged in the reactor and the pressure was adjusted to 2.0 MPa at 120 °C. The reactor was maintained at 120 °C for 2 h, and the pressure was kept constant during the reaction. After the reaction was completed, the autoclave was cooled to ambient temperature, and the excess CO₂ was vented. The conversion and selectivity were determined by 6820 GC and 6890-5973B GC-MS. Isolated yields were obtained via column chromatography using a mix of petroleum ether and ethyl acetate (e.g. 10:1, v/v) as an eluent. Catalyst recycling tests were performed with a large scale of 30X in a 100 mL stainless steel reactor. Due to the formation of the DBU-CO₂ carbonate salt with excess amounts of CO₂, DBU could be separated by distillation under vacuum together with the cellulose, and reused for the next run.

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