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Short Communication

Biocompatible and recyclable amino acid binary catalyst for efficient chemical fixation of CO_2

Zifeng Yang [a], Jian Sun [b], Weiguo Cheng [b], Jinquan Wang [b], Qian Li [a,*], Suojiang Zhang [b,**]

[a] School of Chemistry and Chemical Engineering Henan University, Kaifeng 475001, PR China
[b] Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

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ABSTRACT

In this work, the cycloaddition reactions of CO_2 with various epoxides to form five-membered cyclic carbonates catalyzed by an efficient amino acid based biocompatible catalyst were investigated. It was found that the activity of amino acid could be obviously enhanced in the presence of alkali metal salts, and the L-tryptophan catalytic system was the most efficient among the catalysts employed. Based on the result, a possible mechanism for the synergetic effect of catalyst was proposed. The process reported here represents a simple, ecologically safer, cost-effective route to cyclic carbonates with high product quality, as well as easy catalyst recycling.

1. Introduction

Chemical conversion of carbon dioxide (CO_2) into useful organic compounds has attracted much attention in recent years [1], because CO_2 is not only a renewable, abundant and nontoxic resource, but also a primary greenhouse gas responsible for climate change [2]. It has been well known that the CO_2 fixation with epoxide to produce five-membered cyclic carbonates is an important contribution from the viewpoint of resource utilization [3].

In past decades, various homogeneous and heterogeneous catalysts have been developed to catalyze the reaction, such as metal oxides [4], alkali metal salts [5,6], transition metal salen complexes [7], functionalized ionic liquids [8,9], functionalized polymers [10,11], silica-supported ionic liquids [12,13], ion-exchange resin-supported gold nanoparticle [14], magnetic nanoparticle-supported porphyrin [15], choline chloride and urea supported on molecular sieves [16], biopolymer-supported catalyst [17], and so on. Among the above catalysts, alkali metal salts are one of the most important type of catalysts for the reaction due to they are cheap, stable and environmentally friendly [5,6]. Han et al. reported that alkali metal salts could be used as catalyst for the synthesis of cyclic carbonates together with natural products, such as β-cyclodextrin, cellulose, and lecithin [18–20]. Although the reaction process is ecologically safe, high pressure and long time are unsatisfied for this kind of catalyst, which still needs to be improved. The development of efficient, cheap, ecologically safe, and recyclable catalysts for a reaction under green reaction conditions is still a very attractive topic.

In recent years, using amino acids as catalysts have gained much interest [21,22]. Amino acids are natural, green, non-toxic chemicals which contain active N (e.g. $-NH_2$, $-NH$) and strong hydrogen bonding (e.g. $-COOH$ or $-OH$) in the molecule. He et al. [8] reported that amino acid and epoxide could form an amino acid-epoxide complex through hydrogen bonding, which could activate the epoxide. Several groups including us reported that the synergistic effect between halide anion and hydrogen bond could promote the cycloaddition reaction [19,23,24]. Owing to amino acids containing strong hydrogen bonding, the additional $-NH_2$ group in amino acid was proposed to activate CO_2 [25–30]. Therefore, we envisioned that alkali metal halide and amino acids could be utilized as efficient complex catalysts under solvent-free conditions for the cycloaddition reaction. Herein, a novel catalytic system prepared by combining one of five typical structure amino acids, glycine, L-aspartic acid, L-threonine, L-histidine, and L-tryptophan (Scheme 1) with potassium halide was examined for the CO_2 chemical fixation. The effects of various parameters, such as catalyst, catalyst amount, reaction time, temperature and CO_2 pressure on the reaction were investigated.

* Corresponding author. Tel./fax: +86 10 82627080.
** Corresponding author. Tel.: +86 378 3881589.
E-mail addresses: liq@henu.edu.cn (Q. Li), sjzhang@home.ipe.ac.cn (S. Zhang).

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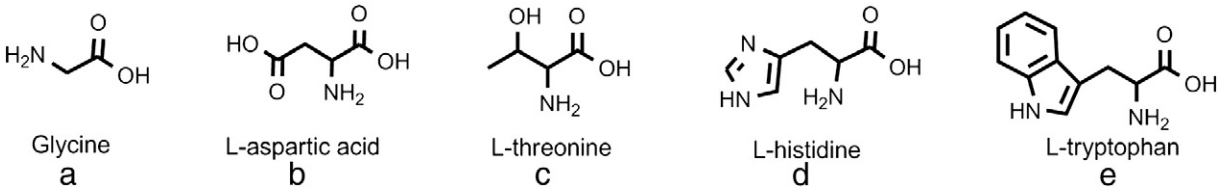


Scheme 1. Amino acids used in the study.

2. Experimental

2.1. Cycloaddition of propylene oxide with CO_2

All the cycloaddition reactions were conducted in a 25 mL stainless-steel reactor equipped with a magnetic stirrer and self-acting temperature control system. In the typical procedure, desired amounts of catalyst (KI/L-tryptophan) and propylene oxide (PO) were added into the reactor. Then, CO_2 was charged in the reactor and the pressure was adjusted to 2 MPa at 120 °C, and the stirrer was started. The reactor was maintained at 120 °C for 1 h, and the pressure was kept constant by means of a CO_2 cylinder connected to the reactor during the reaction. After the reaction was completed, the autoclave was cooled to ambient temperature, and the excess CO_2 was vented. The catalyst was separated from the reaction mixture by vacuum distillation, and the product yields were determined by GC and GC–MS.

3. Results and discussion

3.1. Screening of catalysts

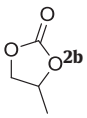
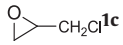
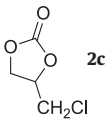
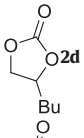
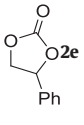
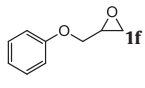
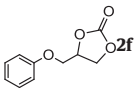
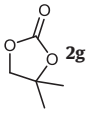
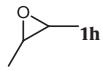
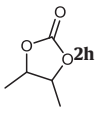
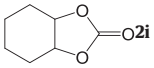
The activity of various catalysts was tested using the reaction of propylene oxide (PO) and CO_2 to produce propylene carbonate (PC), and the results are summarized in Table 1. Almost no product was detected when L-aspartic acid, L-threonine and L-tryptophan were used alone (entries 2, 3 and 5), except Glycine and L-histidine (entries 1, 4). Potassium halide alone could catalyze the cycloaddition, but the yield of PC was very low. The order of the activity of potassium halide was found to be KI > KBr > KCl (entries 6–8), which is consistent with the order of the nucleophilicity of these anions. Furthermore, we tested the halide anion in the presence of amino acids (entries 13–15), it was found that the catalytic activity improved with the increase of halide anion leaving ability, the leaving ability of the halide anions is $I^- > Br^- > Cl^-$. Thereafter, KI was selected combining with amino acids for further investigation under solvent-free conditions (entries 9–13). The conversion rate of PO was varied in an order of KI/glycine < KI/L-threonine < KI/L-aspartic acid < KI/L-histidine < KI/L-tryptophan (entries 9–13, Table 1), which indicated that halide anion in KI and hydrogen bonding in amino acids have a positive effect on promoting the synthesis of cyclic carbonate, as in our system, hydrogen bonding exists between amino acid and epoxides. In addition, the presence of other functional groups of amino-group, and imino group might also be the reason that the yield of PC increased dramatically when amino acid was added. KI/L-tryptophan catalytic system was the most efficient among the catalysts employed, and 99% PO conversion as well as more than 99% PC selectivity could be obtained under the reaction conditions of 120 °C, 2 MPa, and 1 h. The activity of KI/L-histidine catalytic system was little lower than that of KI/L-tryptophan catalytic system, the reason may be the

Table 1
Coupling of CO_2 and PO catalyzed by different catalysts.[a]

Entry	Catalyst	PO conversion (%)[b]	PC yield (%)[b]
1	a	4	4
2	b	Tr.	Tr.
3	c	Tr.	Tr.
4	d	1	1
5	e	Tr.	Tr.
6	KCl	Tr.	Tr.
7	KBr	1	1
8	KI	7	7
9	KI + a	18	18
10	KI + b	27	27
11	KI + c	22	22
12	KI + d	91	91
13	KI + e	99	99
14	KBr + e	31	30
15	KCl + e	6	5
16[c]	KI + e	96	96

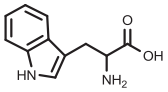
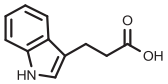
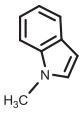
[a] Reaction conditions: PO (20 mmol), amino acid (0.2 mmol), metal halide (0.2 mmol), 120 °C, 2 MPa, 1 h.
[b] Determined by GC.
[c] Recycled five times.

Table 2
Synthesis of other cyclic carbonates catalyzed by KI/L-tryptophan.[a]

Entry	Epoxide	Product	Time (h)	Conversion (%)[b]	Yield (%)[b]
1	 1a	 2a	0.8	99	99
2	 1b	 2b	1	99	99
3	 CH_2Cl 1c	 2c CH_2Cl	2	50	48
4	 Bu 1d	 2d Bu	2	41	40
5	 Ph 1e	 2e Ph	2	22	22
6	 1f	 2f	2	85	84
7	 1g	 2g	2/15	15/96	14/93
8	 1h	 2h	2/24	9/98	9/95
9	 1i	 2i	2/9	5/21	5/20

[a] Reaction conditions: epoxide (20 mmol), catalyst (KI = L-tryptophan = 0.2 mmol), 120 °C, 2 MPa.
[b] Determined by GC.

Table 3
Effect of function group on the activity of catalyst in the reaction.[a]

Entry	Co-catalyst	PO conversion (%)[b]	PC yield (%)[b]
1		85	85
2		74	74
3		58	58
4		24	23

[a] Reaction conditions: PO (20 mmol), KI (0.2 mmol), co-catalyst (0.2 mmol), 110 °C, 2 MPa, 1 h.
[b] Determined by GC.

electronegativity of KI/L-tryptophan catalytic system more than KI/L-histidine catalytic system. In addition, after separated by distillation under vacuum, the catalyst could be used at least for five times without loss of its activity and selectivity (entries 16) indicating that the catalyst was stable.

3.2. Effect of reaction conditions on the synthesis of propylene carbonate

A study of the effect of reaction parameters on the activity of KI/L-tryptophan catalytic system in the cycloaddition of PO with CO_2 has been carried out. The molar ratio 1:1 of KI to L-tryptophan (Fig. S1), catalyst amount of 1 mol% (relative to PO) (Fig. S2), and under 2 MPa CO_2 pressure (Fig. S3), at 120 °C (Fig. S4) and reaction for 1 h (Fig. S5) were found to be ideal for the reaction (see supplementary data).

3.3. Applicability of substrates

The experiments of other epoxides with CO_2 to synthesize the corresponding cyclic carbonates were also investigated, and the results are summarized in Table 2. Among the mono-substituted terminal epoxides (**1a–1f**), it was found that with the growth of the substituent chain, the activity order of epoxides is ethylene oxide (**1a**) > propylene oxide (**1b**) > epichlorohydrin (**1c**) > butyloxirane (**1d**). On the other hand, glycidyl phenyl ether (**1f**) was good substrates to give cyclic carbonates in good yield and with excellent selectivity. However, in the case of styrene oxide (**1e**), the reaction was carried out with a relative low yield.

To further exemplify the catalytic potential of KI/L-tryptophan, disubstituted epoxides were also tested (Table 2, entries 7–9). Disubstituted epoxides such as 1,2-epoxy-2-methylpropane (**1g**) showed lower activity than mono-substituted terminal epoxides **1a–1f** (entries 7 *vs.* 1–6), and required a long time to give **2g** (entry 7). Compared to **1g**, a much longer reaction time (24 h) was needed to get a high yield (94%) when *cis*-2, 3-epoxybutane (**1h**) was used as substrate, In particular for **1i**, only 19% cyclic carbonate yield was achieved after 9 h, which is probably due to its higher steric hindrance [31].

3.4. Possible mechanism

As proposed by previous reports, carboxyl-groups in the catalyst might accelerate the ring-opening of epoxide by hydrogen bonding [13,23]. Moreover, $-NH_2$ is well known as efficient absorbents to form carbonate salts with CO_2 [25–30], thus, the additional $-NH_2$ group in amino acid was proposed to activate CO_2 by affording the carbonate salts in the similar way. In parallel, the –NH group in the amino acid may also activate the epoxy ring through a hydrogen bond [8,32,33], also resulting in enhanced reaction. In order to confirm the effect of functional group of –COOH, $-NH_2$, and –NH in amino acid studied, experiments in the cases of L-tryptophan, 3-indolepropionic acid, iodole, and 1-methylindole with or without function groups (–COOH, $-NH_2$, and –NH) were carried out in the presence of a given concentration of KI. The results summarized in Table 3 proved the necessary roles played by the above functional groups in promoting the reaction. The activity decreased in the order: L-tryptophan > 3-indolepropionic acid > iodole > 1-methylindole (entries 1–4). In the absence of $-NH_2$ group, the activity of KI/3-indolepropionic acid was obviously decreased compared to that of KI/L-tryptophan (entry 1 *vs.* 2). Further experiment showed that the activity of KI/iodole catalyst was much lower than that of KI/3-indolepropionic acid without –COOH group in the structure (entry 2 *vs.* 3). The above results confirmed the

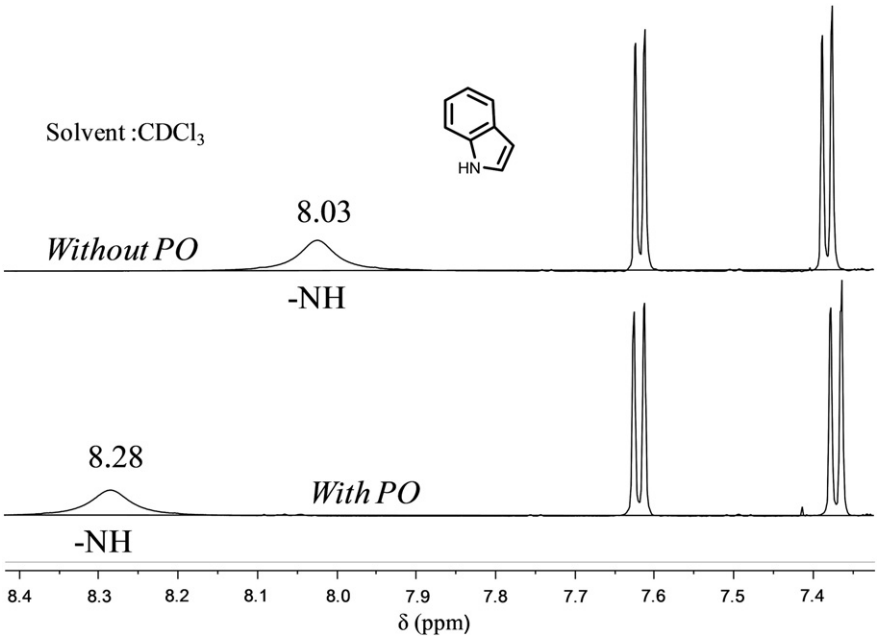


Fig. 1. The ^1H NMR spectrums of iodole with and without PO.

important roles of $-NH_2$, and −COOH. In addition, it was also found that the yield of PC reduced dramatically when the −NH function group was removed from the structure of catalyst (Table 3, enter 3, 4), which might be caused by the hydrogen bonding interaction between the −NH function group and epoxide ring (Fig. 1). This result of the shift of H signal in −NH after forming hydrogen bonding could also be found in previous report [24,34]. Based on the discussions above, a possible mechanism for the formation of cyclic carbonates was proposed. Firstly, the −COOH and −NH groups of amino acid possibly activate the epoxide via hydrogen bonding interaction. Secondly, the I^- anion of KI attacks the less hindered carbon atom of the activated epoxide, followed by ring-opening of epoxide. Then the CO_2 inserts and forms an alkyl carbonate anion. Finally, the cyclic carbonate is formed by subsequent intermolecular ring-closure and the catalyst is regenerated.

4. Conclusions

The effect of amino acids and KI system on the cycloaddition of CO_2 with epoxides to produce five-membered cyclic carbonates has been studied for the first time. It was found that the catalytic system of KI/L-tryptophan was an efficient, simple, green and stable for the coupling reaction. Under the optimized reaction conditions, 99% PO conversion and more than 99% selectivity could be achieved at 120 °C, 2 MPa and 1 h. The synergistic catalysis of KI and various parts of amino acid is necessary for the high efficient results to berealized. The process represents a simple, ecologically safer and cost-effective route to synthesize cyclic carbonate with high product quality, as well as easy catalyst recycling.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.07.025.

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