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Cyclic carbonate synthesis from epoxides and CO_2 over cyanocobalamin/*n*-Bu_4NI

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The synthesis of cyclic carbonates from epoxides and carbon dioxide catalyzed by cyanocobalamin and *n*-Bu_4NI system was achieved under 0.8 MPa CO_2 pressure at 140°C without organic solvents. Propylene carbonate was obtained in >99% yield within 6 h under the optimized reaction conditions. The cyanocobalamin catalyst could be recycled with water and retained moderate catalytic activity. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: epoxides; carbon dioxide; coupling reaction; cyclic carbonates; cyanocobalamin

Introduction

The chemical fixation of carbon dioxide (CO_2) has received much attention in the last two decades in view of abundant, inexpensive, non-toxic carbon sources and increasing concern regarding the environment.[1–3] One of the methodologies for CO_2 fixation is the cycloaddition of CO_2 to epoxides (Scheme 1) to form five numbered cyclic carbonates (CC). Cyclic carbonates are excellent organic synthetic intermediates, monomers, aprotic polar solvents and pharmaceutical/fine chemical intermediates.[4–6] Various catalyst systems have been successfully developed for the synthesis of cyclic carbonates from epoxides and CO_2 with varying yields and times of flight (TOFs), such as metal salts,[7–16] metal complexes,[17–20] organometallic compounds,[21–28] ionic liquids[29–34] and organic bases.[35] However, many of these catalytic systems suffer from high toxicity, low catalyst stability and selectivity, or addition of organic solvent. Hence, from an environmentally benign point of view, the quest for catalytic systems that combine toxicity or even zero toxicity, higher catalyst stability and selectivity without adding of any organic solvent remains a huge challenge.

In this paper, a natural edible product (cyanocobalamin) was explored as a greener biomimic catalyst for the synthesis of cyclic carbonates from epoxides and CO_2 under 0.8 MPa CO_2 pressure at 140°C without use of organic solvents. This is a new, simple, greener and safer route for the synthesis of cyclic carbonates.

Experimental

Materials

Propylene oxide (PO) was distilled from CaH_2. Other epoxides, *N*,*N*-dimethylaminopyridine (DMAP) and cyanocobalamin (VB_{12}) were purchased from Aldrich and used without further purification. Tetrabutylammonium fluoride (TBAF), tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB) and tetrabutylammonium iodide (TBAI) were obtained from Sinopharm Chemical Reagent Co. Ltd. Phenyltrimethylammonium tribromide (PTAT) was purchased from Aladdin.

General Procedure for Coupling Reaction of Epoxides and CO_2

All coupling reactions were performed in a 100 ml stainless steel autoclave equipped with a magnetic stir bar. The autoclave reactor was successively charged with cyanocobalamin (0.025 mmol), Lewis base (0.05 mmol) and epoxide (50 mmol). The reactor was pressurized with CO_2 to 0.8 MPa and then heated and stirred at 140°C. When the CO_2 pressure fell to 0.1–0.15 MPa, the reactor was cooled quickly to 0°C in ice-water and then vented. The remained mixture was distilled under reduced pressure or recrystallized with ethanol to obtain the pure cyclic carbonate.

Results and Discussion

Effect of Temperature on Cycloaddition of PO and CO_2 Catalyzed by VB_{12}-TBAI

Temperature is one of the most important factors for cycloaddition of CO_2 to epoxides. The influence of reaction temperature on propylene carbonate (PC) yield is shown in Fig. 1. There was no product generated when the coupling reaction was carried out at room temperature, so a higher temperature was desired. It can be seen from Fig. 1 that the PC yield increased up to >99% at 140°C under 0.8 MPa CO_2 pressure within 6 h, after which the PC yield remained almost constant with further increase of temperature, hinting that 140°C is the optimal temperature for the coupling reaction of propylene oxide and carbon dioxide.

Reaction Time Effect on PC Yield

The effect of reaction time on PC yield is presented in Fig. 2. The results indicate that the reaction proceeded slowly within the

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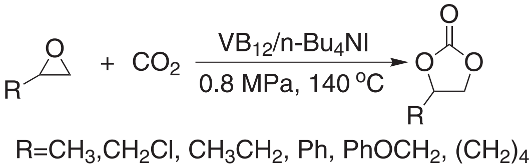


Scheme 1. Cycloaddition of epoxides and CO_2.

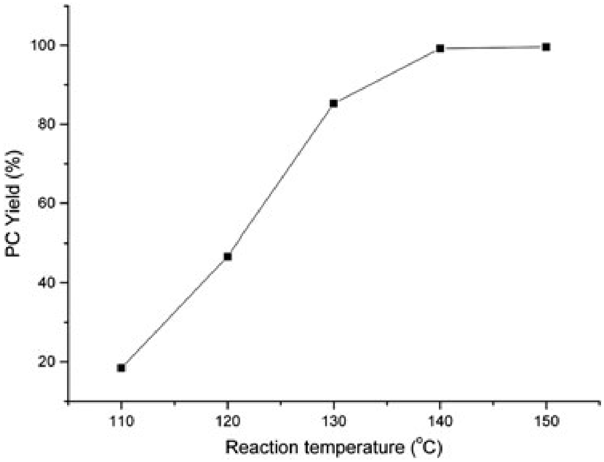


Figure 1. Influence of reaction temperature on PC yield.

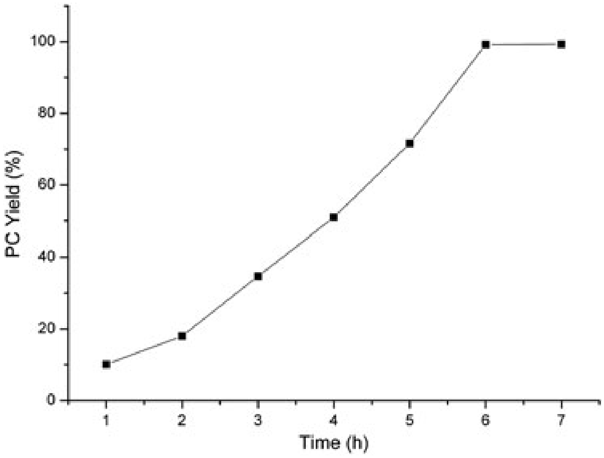


Figure 2. Reaction time effect on PC yield.

first 2 h, but the yield of PC was lower than 20%. In a relatively longer reaction time of 6 h, the reaction proceeded rapidly and the PC yield exceeded 99%. The reaction rate slowed down after 6 h, indicating that the reaction was completed. It can be seen that the CO_2 fixation onto PO was completed within 6 h.

Co-catalyst Effect on the Synthesis of PC

The catalytic activity of various catalytic systems was tested using the model coupling reaction of PO and CO_2. The results are summarized in Table 1. The activities of co-catalyst on this coupling reaction were found to be quite important, as seen from Table 1. Among different co-catalysts, TBAI showed superior activity: >99% PC yield was obtained within 6 h (Table 1, entry 4). Although TBAI could catalyze the cycloaddition of CO_2 to PO separately, PC yield was lower than any two-component catalytic system (Table 1, entry 8 vs. entries 1–6). The obtained PC yield catalyzed by VB_{12}/PTAT was higher than with VB_{12}/TBAB, because the large Br^{3-} anion in PTAT was a better leaving group than Br^- in TBAB, which corresponded to our previous research results.[17] DMAP as an organic base first activated CO_2 to form an organic

Table 1. Co-catalyst effect on the synthesis of propylene carbonate[a]

Entry	Co-catalyst	Time (h)	Yield (%)	TOF (h^{-1})[b]
1	TBAF	12	73	122
2	TBAC	6.5	60	185
3	TBAB	10	98	196
4	TBAI	6	>99	330
5	PTAT	7.5	>99	264
6	DMAP	10	99	198
7	—	12	—	—
8[c]	TBAI	12	6	10
9[d]	TBAI	12	<1.0	—

[a] Reaction conditions: VB_{12}, 0.025 mmol; co-catalyst, 0.05 mmol; PO, 50 mmol; $P(CO_2)$ 0.8 MPa, T 140°C.

[b] Moles of propylene carbonate produced per mole of catalyst per hour.

[c] Without VB_{12}.

[d] Room temperature.

Table 2. Recycling of cyanocobalamin catalyst[a]

Entry	Cycle	Yield (%)	TOF (h^{-1})[b]
1	Fresh	>99	330
2[c]	1	84	280
3[d]	2	76	253
4[e]	3	67	223

[a] Reaction conditions: VB_{12}, 0.025 mmol (34 mg); TBAI, 0.05 mmol; PO, 50 mmol; $P(CO_2)$ 0.8 MPa; T 140°C; reaction time, 6 h.

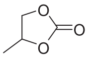
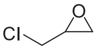
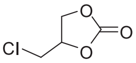
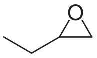
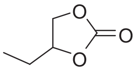
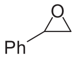
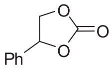
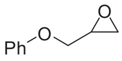
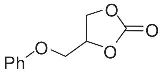
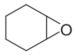
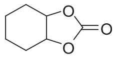
[b] Moles of propylene carbonate produced per mole of catalyst per hour.

[c] Amount of recycled cyanocobalamin = 31 mg.

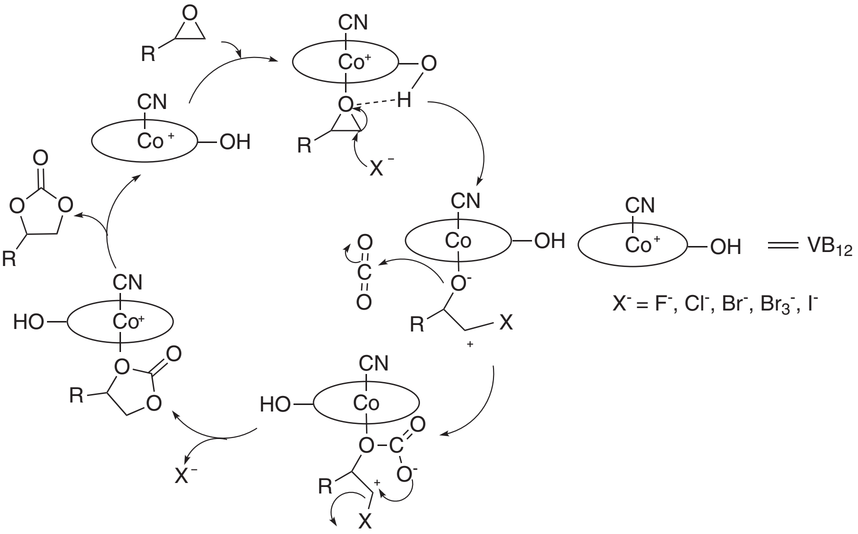
[d] Amount of recycled cyanocobalamin = 28 mg.

[e] Amount of recycled cyanocobalamin = 25 mg.

Table 3. The coupling results of various epoxides and CO_2 catalyzed by VB_{12}/TBAI[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1			6	>99
2			1.5	93
3			8	73
4			12.5	91
5			6.25	>99
6			9	9

[a] Reaction conditions: VB_{12}, 0.025 mmol; TBAI, 0.05 mmol; epoxide, 50 mmol; $P(CO_2)$ 0.8 MPa, T 140°C.



Scheme 2. Proposed mechanism of the cycloaddition of CO_2 to epoxides.

base–CO_2 intermediate, which was different from quaternary ammonium salt. It can be seen from Table 1 that DMAP showed almost the same catalytic activity as TBAB. The activity order of co-catalysts was TBAI > PTAT > DMAP > TBAB > TBAC > TBAF.

Recycling of Cyanocobalamin Catalyst

To examine the reusability of cyanocobalamin, we performed the recycling experiments under optimized reaction conditions using PO as substrate. The recycling results are summarized in Table 2. After a reaction recycle, cyanocobalamin was extracted with distilled water three times. The collected water layer was washed with CH_2Cl_2 three times, and then concentrated under vacuum. After drying in a vacuum oven, cyanocobalamin was reused for the next cycle directly, but TBAI was added for each run. The recycling results in Table 2 show that cyanocobalamin retained moderate activity in the coupling reaction of PO and CO_2, although the catalytic activity slightly decreased along with increased recycling.

Cycloaddition Reaction of Various Epoxides and CO_2 Catalyzed by VB_{12}/TBAI

To extend the scope of the coupling reaction, various epoxides were used as substrates and reacted with CO_2 under optimized and solventless reaction conditions. The cycloaddition results are shown in Table 3. Propylene oxide (Table 3, entry 1) and glycidyl phenyl ether (Table 3, entry 5) gave the relevant cyclic carbonate with >99% yield. 4-(Chloromethyl)-1,3-dioxolan-2-one was obtained with 93% yield from 2-(chloromethyl)oxirane and CO_2 (Table 3, entry 2). When butene oxide (Table 3, entry 3) and styrene oxide (Table 3, entry 4) were used as substrate, a longer reaction time was needed in order to obtain higher butene carbonate yield (73%) and styrene carbonate yield (91%). This may be due to the low reactivity of electron-rich substrates. The VB_{12}/TBAI system could also be realized the coupling reaction of cyclohexene oxide (CHO) and CO_2 to obtain the cyclohexene carbonate (9%; Table 3, entry 6), which is difficult to obtain in many catalytic systems.

Proposed Mechanism for Coupling Reaction of PO and CO_2

Considering the mechanism of the coupling reaction of epoxides and CO_2 described by Lu,[19] a proposed general mechanism is illustrated in Scheme 2, in which the epoxide was activated by cobalt center, and then attacked by nucleophilic reagent (co-catalyst) to produce the requisite metal/heteroatom alkoxide intermediates that was suffered insertion of CO_2 to lead corresponding cyclic carbonates. This mechanism insists that Lewis acidic center and Lewis base center have the importance for this coupling reaction. The higher activity of VB_{12}/*n*-Bu_4NI catalyst systems is attributed to both good nucleophilicity and leaving group.

Conclusions

In summary, we have developed a new, simple, greener and safer catalytic system of VB_{12}/*n*-Bu_4NI for the synthesis of cyclic carbonates from epoxides and CO_2 without organic solvents under 0.8 MPa CO_2 pressure at 140°C. Cyanocobalamin could be recycled three times and retained moderate activity.

Acknowledgments

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