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Polyvinyl alcohol-potassium iodide: An efficient binary catalyst for cycloaddition of epoxides with CO_2

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ABSTRACT

In this study, we have for the first time demonstrated that polyvinyl alcohol (PVA) and potassium iodide (KI) can form an efficient catalytic system for synthesis of cyclic carbonates from epoxide and CO_2. The catalytic reaction happens in solvent-free conditions. A synergetic effect occur between PVA and KI which considerably increases the reaction yield. This binary catalytic system is mainly suitable for mono-substituted terminal epoxides. In the optimized reaction condition, over 90% reaction yield can be achieved. The binary catalyst is reusable and can be recycled at least five times without significant loss of the catalytic activity. The PVA hydrolysis degree affect the catalytic activity as well. A possible mechanism of synergetic effect of the binary system was proposed. PVA and KI may form a non-toxic, low cost, recyclable, highly-efficiency catalyst for fixing CO_2 through cycloaddition with epoxides.

1. Introduction

In recent decades, conversion of carbon dioxide into usable materials has gained much attention [1–4]. A coupling reaction between epoxide and CO_2 has been considered as an efficient method for the chemical fixation of CO_2 [2–4], and the reaction products, cyclic carbonates, have show wide application potential in chemical synthesis, catalysis, and electrochemistry [5,6]. Since the epoxide-CO_2 reaction is required to proceed via catalysis, a considerable effort have been made to develop high efficiency catalysts for this reaction. Catalysts such as metal oxides [7], alkali metal halides [8], ionic liquids (ILs) [9–13], transition metal complexes [14–16], and metal-organic frameworks (MOFs) [17] have been reported, and potassium iodide (KI) is the most promising one because of the abundance and low price. However, KI alone typically has low catalytic activity, and a co-catalyst is commonly used to improve the catalytic efficiency [18–37]. It has been reported that hydrogen bond donors (HBDs), such as tetraethylene glycol [22], β-cyclodextrin [23], cellulose [24], lignin [25], C60 fullerenol [26], pentaerythritol [27], sugarcane bagasse [28], hydroxyl-functionalized imidazoles [29], triethanolamine [30], amino alcohols [31], polydopamine [32], formic acid [33], amino acids [34,35] and tannic acid [36] can be used as KI co-catalysts for epoxide-CO_2 coupling. HBDs can activate the ring-opening of epoxides by forming hydrogen bond with the oxygen atom of epoxide, through which to promote the coupling reaction. Despite of the studies, most of the HBDs are either toxic, expensive, unrecyclable or involving using organic solvents. Non-toxic, cheap, recyclable, readily available and environmentally benign co-catalysts are highly desirable, but much less reported in research literature.

Polyvinyl alcohol (PVA) is a linear polymer with enriched hydroxyl groups. PVA is prepared by hydrolysis of poly(vinyl acetate). It is a non-toxic, low price polymer with high excellent biocompatibility and biodegradability [37]. PVA has wide applications in the fields of textile, papermaking, adhesives, food, biomedical, pharmaceutical and biocatalysis [38–41]. The abundant hydroxyl groups, which can be served as HBDs, make PVA an ideal co-catalyst candidate with KI to accelerate epoxide-CO_2 coupling reaction. However, the co-catalysis ability to of PVA has not been reported to date.

In the study, we have for the first time demonstrated that PVA-KI is an excellent catalyst system for the epoxide-CO_2 coupling reaction in solvent-free condition. PVA-KI can promote the coupling reaction in relatively mild conditions. We further showed that the residual acetate groups in the PVA had a positive effect on the yield and PVA of 87–89 mol% hydrolysis degree combined with KI showed the best catalytic efficiency. A synergetic effect happened between PVA and potassium halides. Effects of various parameters on their catalytic activity were examined. A possible mechanism of synergetic effect of the binary system was proposed.

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2. Experimental section

2.1. Chemicals

CO_2 with a purity of 99.99% was obtained commercially. All the epoxides and potassium halides (all analytical grade) were purchased from the Aladdin Chemicals and were used as received. PVA1788 (polymerization degree: 1700; degree of hydrolysis: 87–89 mol%) and PVA1799 (polymerization degree: 1700; degree of hydrolysis: 98–99 mol%) were obtained from the Aladdin Chemicals. PVAs were ground into powder and the sizes of PVAs powder below 500 mesh was obtained through sieves. PVA1788 and PVA1799 have surface area of 0.995 m^2/g and 1.407 m^2/g (Fig. S1), respectively.

2.2. Characterizations

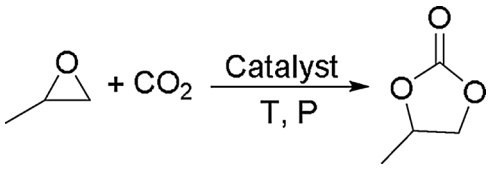
The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane as an internal standard. LC–MS spectra were recorded on an AmaZon SL spectrometer. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer equipped with nickel monochromatized Cu Kα radiation (λ = 1.5406 Å). The crystallinity degree of PVA was estimated by the ratio of the crystalline signal areas to the total area of the diffractogram. Scanning electron microscopy (SEM) was undertaken using a JSM-7610F scanning electromicroscope at 5 kV accelerating voltage. The specific surface area of PVA1788 and PVA1799 powder were measured by N_2 isothermal adsorption/desorption (77 K) using Autosorb-IQ-MP-C system (Quantachrome, USA).

2.3. Cycloaddition reactions of epoxides with CO_2

The cycloaddition reactions were carried out in a 100 mL stainless steel reactor equipped with a magnetic stirrer. In the typical procedure, the desired amounts of potassium halides and PVA1788 were placed into the reactor and purged with CO_2 three times. Then 143 mmol epoxide was added into the reactor and the reactor was sealed. CO_2 was introduced into the reactor until desired pressure reached. Subsequently, the reactor was heated to the reaction temperature. After a certain time, the autoclave was cooled to ambient temperature in a water bath, and the excess CO_2 was vented slowly. Dichloromethane (CH2Cl2) was added into the reaction mixture. The solid catalyst was separated from the reaction mixture by centrifugation. It was rinsed three times with CH2Cl2 and dried in vacuum. The recycled catalyst was used directly for the next round of experiment. Isolated yields were obtained by distillation or silica gel column chromatography using a mixture consisting of petroleum ether and ethyl acetate as an eluent. The products were confirmed by ^1H and ^{13}C NMR spectra.

3. Results and discussion

Three potassium halides (i.e. KCI, KBr and KI) and two PVA materials (i.e. PVA1788 and PVA1799) were used to examine the catalytic activity, and propylene oxide (PO) was used as epoxide model to react with CO_2. The main difference between the two PVA materials is in the hydrolysis degree. Both PVAs have a polymerization degree of 1700. PVA1788 has a slightly lower hydrolysis degree than PVA1799. Scheme 1 shows the



Scheme 1. Cycloaddition reaction between CO_2 and PO.

Table 1
Catalysis results for different substances.[a]

Entry	Cat.	Co-Cat.	PC yield (%)[b]	TOF[c]
1	KI	PVA1788	93	23.3
2	None	PVA1788	Trace	–
3	KI	None	8	2.0
4	KBr	PVA1788	19	4.8
5	KCl	PVA1788	10	2.5
6	KBr	None	4	1.0
7	KCl	None	Trace	–
8	KI	PVA1799	83	20.8
9	None	PVA1799	Trace	–

[a] Reaction conditions: PO (8.3 g, 143 mmol), potassium halide (1.0 mol% relative to PO),PVA(593 mg) g),CO_2 (initial pressure 1.5 MPa), 120 °C, and 4 h.
[b] Isolated PC Yield.
[c] TOF: mole of synthesized PC per mole of KI per hour.

coupling reaction and the product propylene carbonate (PC).

Table 1 summarizes the results. For KI-PVA1788, the reaction yield was 93%, whereas the reaction catalyzed by KI alone had a very low yield, only 8%. When PVA was used alone as catalyst, no matter which sample used, only trace amount of PC was obtained, indicating very low catalysis activity. These results suggest that PVA1788 and KI forms an efficient catalytic system for cycloaddition of PO with CO_2 and there exists a synergistic effect between the two catalyst components.

When KBr or KCl was combined with PVA1788 for the reaction, the yields were very low although the yields were slightly higher than that using KBr or KCl alone. This can be explained by the difference in nucleophilicity and leaving ability. I^- has stronger nucleophilicity and leaving ability when compared with Cl^- and Br^- [23,25,28,30,32,34,36].

When PVA1799 was used as a co-catalyst with KI, the reaction yield was 83%, 10% lower than that using PVA1788 in the same condition. This indicates that lower hydrolysis degree of PVA could lead to higher reaction yield. For PVA1788, which has a hydrolysis degree of 87–89 mol%, there still acetate groups in the polymer (around 11–13 mol%). However, the un-hydrolysis acetate remained in PVA1799 was only 1–2 mol%. The 10% more acetate group content for PVA1788 might increase the CO_2 content in PVA due to the CO_2-philicity of poly(vinyl acetate), hence contributing to the interaction with reagents and facilitating the cycloaddition.

It is known that PVA is a semi-crystalline polymer and its hydrolysis degree have a significant effect on the degree of crystalline [37]. The crystalline region of a semi crystalline polymer is hard to access during chemical reaction. To examine the effect of crystalline content on the coupling reaction, we measured the crystallinity of the two PVA materials using XRD. As expected, PVA1799 had higher degree of crystallinity (40.2%) than PVA1788 (31.7%) (Fig. S2). To verify the effect of crystallinity on the coupling reaction, we used an isothermally annealing method to treat PVA1788 at 120 °C for 10 h. After treatment, the degree of crystalline increased to 47.8%, which is higher than that of PVA1799. When the annealed PVA1788 and KI were used to co-catalyze the reaction, the PC yield was 84%, which is similar to that of KI-PVA1799 in the same condition. Therefore, the effect of PVA hydrolysis degree on the PO-CO_2 coupling reaction should be stemmed from the effect on PVA crystallinity.

The effect of PVA1788 and KI amount on the coupling reaction was examined. As shown in Fig. 1(a), when keeping KI/PO ratio unchanged, while changing the PVA1788/KI ratio, increasing the PVA1788 amount could initially increase the PC yield. 93% PC yield reached when KI/PO molar ratio was 1:100 and PVA1788/KI mass ratio was 2.5:1. The PC yield remained almost unchanged when further increasing the PVA1788 amount. When KI/PO molar ratio was changed to 1.5:100, while PVA1788/KI mass ratio was kept at 2.5:1, the PC yield was only slightly higher than that of the KI/PO molar ratio at 1:100. Thus, the optimum amount of catalyst was KI content at 1 mol% (based on the