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Synthesis of Cyclohexene Carbonate Catalyzed by Polymer-Supported Catalysts

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Abstract

A series of polystyrene-divinylbenzene cross-linked resin (PS) supported zinc chloride catalysts were prepared in this paper. They can efficiently catalyze the solventless cycloaddition of cyclohexene oxide with carbon dioxide in the presence of tetrabutylammonium bromide (TBAB) as co-catalyst under relatively mild reaction conditions. The catalyst is composed of carrier, connecting arm, ligand and active ingredient. The connecting arms of different lengths can significantly affect the catalytic activity. Among these catalysts, the one using diethylene glycol as connecting arm and 2-aminopyridine as ligand, which named PS-DEG-2ap-ZnCl₂, showed the optimal catalytic performance. The yield of cyclohexene carbonate was 95.18% calculated by GC analysis under the optimal conditions (393K, 5 MPa , 6 h). Moreover, the catalyst showed good stability and reusability. From the viewpoint of industrial application, the catalyst is attractive because of its excellent catalytic efficiency on the synthesis of cyclohexene carbonate.



Cyclohexene oxide

Cyclohexene carbonate



 $M=Fe \square Co \square Ni \square Zn \square X=Cl^{-} \square Br^{-} \square CH_{3}COO^{-};$ $n=0\sim15 \square a=1, 2, 3 \square b=1, 2, 3 \square$

KEYWORDS: Carbon dioxide; Cyclohexene carbonate; Chemical fixation;

Polymer-supported catalysts

INTRODUCTION

Recent researches show that carbon dioxide (CO_2), a major greenhouse gas, is a cheap, abundant, and environmentally benign C1 resource.^[1–10] In this context, the effective processes of CO₂ utilization have drawn much attention since they could heavily reduce the damage to environment and bring considerable economic benefits. One of the advantageous ways in this area is the cycloaddition of CO₂ with epoxide to afford cyclic carbonate, which can be widely used for various purposes, such as polar solvents, electrolytic materials and organic synthetic intermediates.^[11–18] However, it still remains a difficult target to incorporate CO₂ into other organic substances because of its inert nature. Therefore, it is urgent to find a cheap, effective, and environmentally benign catalyst system, which can activate CO₂ and make the cycloaddition reaction proceed smoothly. In the past years, a large number of catalysts have been developed for the cycloaddition of CO₂ with epoxide. These catalysts include alkali metal salts, ^[19–22] metal complexes, ^[23–31] ionic liquids, ^[32–45] metal oxides, ^[46] zeolites, ^[47] and so on. However, most cases suffer from low catalyst activity, ^[46,48] high costs, the need for co-solvents^[49,50] as well as the requirement for high pressure and high temperature. So, designing of highly efficient, easily separated catalysts still remains a challenge, especially a certain catalyst system for the cycloaddition reaction of CO₂ with cyclohexene oxide, because of the lower activity of cyclohexene oxide than that of other epoxides.

In our continuous study, we found that the polystyrene-divinylbenzene cross-linked resin (PS) supported catalysts exhibited excellent catalytic performance for some chemical reactions.^[51–59] In this article, we developed a series of PS supported metal salt catalysts and used them to catalyze the cycloaddition reaction of CO_2 with cyclohexene oxide (Scheme 1) to afford cyclohexene carbonate. And desirable results were achieved.

RESULTS AND DISCUSSION

Transition-metal ions are considered to be classical Lewis acids and they are often used to catalyze some organic reactions. In this work, several transition metal salts were selected to catalyze the cycloaddition of CO_2 with cyclohexene oxide. And the results were shown in Table 1. As shown in Table 1, $Zn(CH_3COO)_2$ (entry 2, Table 1), $Co(CH_3COO)_2$ (entry 3, Table 1), $NiCl_2$ (entry 5, Table 1), $FeCl_3$ (entry 6, Table 1) and $CoCl_2$ (entry 7, Table 1) could well catalyze the reaction, however, the yields of cyclohexene carbonate were not high, which were 76.47%, 70.19%, 34.35%, 58.24% and 70.35%, respectively. In contrast, $ZnCl_2$ (entry 1, Table 1) and $ZnBr_2$ (entry 4, Table 1) showed highly activity among the tested catalysts. The yields reached 88.24% and 88.07%, respectively.

In order to take advantage of relatively easy phase separation and catalyst recovery, a serial of PS supported metal salt catalysts were prepared, and their catalysis activities were investigated. The results were shown in Table 2.

As shown in Table 2, all the PS supported catalysts could well catalyze the reaction. Moreover, there was no significant decrease in the catalytic activity compared with that of the bare catalyst. That might be due to the finely dispersiveness of the metal salts on PS ruslting in the adequate contacts of the active ingredients with substrates. Another notable result was that the conversion and yield decreased significantly in absence of TBAB (entry 8, Table 2). This suggested that TBAB play an important role in the cycloaddition reaction. In a comprehensive consideration, ZnCl₂ was selected as the optimal metal salt for the following investigation.

The structure of catalytic materials has great influence on the activities of them. In order to find the optimized catalyst, the catalysts with different connecting arms were examined in the cycloaddition of CO_2 with cyclohexene oxide. The results were listed in Table 3.

As shown in Table 3, it was worth noting that all these catalysts were active for the cycloaddition reaction. The TOF was the highest when the reaction was catalyzed by PS-DEG-2ap-ZnCl₂. It was possibly due to the connecting arm with suitable length which could provide desirable degree of freedom to improve the collision probability of active ingredients and substrates. Another notable result was that the conversion of cyclohexene oxide was the highest when PS-PEG600-2ap-ZnCl₂ was used. It may suggest that the hydroxyl groups on PEG600 could also catalyze the reaction.^[60] The effects of the pore structure on the conversion and yield were studied. Some small but noticeable changes appeared in the pore volumes and pore diameters with the change of connecting arms. And the effects had not shown regularly changes. It suggested that the connecting arms are mainly grafted on the surface of PS. Overall, PS-DEG-2ap-ZnCl₂ was selected as the catalyst for the following investigation.

The dependence of cyclohexene carbonate yield on temperature was plotted in Figure 1. It was evident from the graph that the yield of cyclohexene carbonate reached 90.08% when the temperature was increased to 393 K, but a further increase in the temperature caused a decrease in the yield. This was possibly due to the damage of surface structure of the catalysts and the cycloaddition reaction being a exothermic reaction.^[61] Accordingly, 393K was chosen as the optimal temperature for the cycloaddition reaction of cyclohexene oxide with CO₂. Figure 2 revealed the effect of reaction time on the yield of cyclohexene carbonate. It can be noted that the yield reached maximum value (92.60%) after reacting for 6 h. Longer reaction time may result in side reactions and decreased the yield. It suggested that the optimum reaction time for this reaction was 6 h.

The effect of initial pressure was investigated at 393K over 6 h and the results were shown in Figure 3. The yield of cyclohexene carbonate increased with the pressure increasing from 2 MPa to 7 MPa. But the yield increased slightly (only from 95.18% to 96.47%) as the pressure was increased from 5MPa to 7 MPa. The reason may be that higher pressure, which could improve the concentration of CO_2 in the liquid phase, enhanced mass transfer between the two gas-liquid phases. Therefore, the optimum initial pressure was 5 MPa.

Experiments were carried out to examine the reusable performance of the catalyst. After each cycle, the catalyst was recovered by filtration, washed, dried in vacuum and then reused in the next batch. The results were shown in Figure 4. There is only a slight loss of its original catalytic activity.

Based on the above experimental results and analysis, the optimum conditions of the cycloaddition of cyclohexene oxide with CO₂ were obtained as follows: PS-DEG-2ap-ZnCl₂ 0.07mmol, cyclohexene oxide 200 mmol, TBAB 0.9mmol, 393K, 5 MPa and 6 h. Under these conditions, the yield of cyclohexene carbonate was 95.18% calculated by GC analysis. In order to demonstrate the general applicability of PS-DEG-2ap-ZnCl₂, we next investigated the cycloaddition of other epoxides with CO₂. The results were summarized in Table 4. As shown in Table 4, the catalyst was active for all the substrates used. The conversion and selectivity of the reactions were all above 90%. Among them, propylene oxide were the most active substrates, and the conversion and selectivity were 99.66% and 99.37% respectively (entry 4, Table 4). All in all, the PS-DEG-2ap-ZnCl₂ catalyst is very active and selective for the coupling of CO₂ onto a wide range of epoxides.

CONCLUSION

The PS supported zinc chloride catalysts were highly efficient for the solventless cycloaddition of cyclohexene oxide with carbon dioxide in the presence of tetrabutylammonium bromide (TBAB) as co-catalyst under relatively mild reaction conditions. Moreover, the synthetic process of cyclohexene carbonate was optimized and the yield reached 95.18% catalyzed by PS-DEG-2ap-ZnCl₂. And the catalyst is stable, environmentally benign, and reusable. Therefore, it is attractive for the synthesis of cyclohexene carbonate from an industrial viewpoint. The present work also provides new ideas for designing catalysts. The connecting arms with suitable length can provide desirable degree of freedom for the active ingredients to improve the collision probability with substrates, resulting in higher reaction yield. Furthermore, different active ingredients can be coordinated by changing ligands in order to use the catalysts for various reactions.

EXPERIMENTAL

All chemicals used in this study were commercially available. They were used without further purification unless otherwise mentioned. CO₂ (99.9%) was obtained from Zhengzhou Keyi Gas Co., Ltd.,China. Chloromethylated polystyrene-divinylbenzene crosslinked resin (PS) was supplied by Hebi Jiaxin Technology Co., Ltd.,China. Cyclohexene oxide was purchased from Yueyang Changde Chemical Industrial Co., Ltd.,China. Tetrabutylammonium bromide (TBAB) was obtained from Aladdin Industritrial Corporation.

¹H and ¹³C NMR spectra were obtained using a Bruker AVII-400 instrument. FT-IR spectra were recorded with a Nicolet Fourier transform infrared spectrometer (IR-200). Gas chromatography mass spectra (GC/MS) were obtained using a gas chromatograph Shimadzu GC-2010 detector linked to a Shimadzu GCMS-QP 2010 mass. BET surface areas and pore structure were measured by N_2 adsorption at the temperature of liquid nitrogen using a NOVA 4200e analyzer after the evacuation of the sample at 70°C for 6

h. The morphology of the samples was observed by scanning electron microscopy (SEM) (JEOL JSM-7500F). Contents of metal elements were determined by icp-aes (TJA IRIS Advantage). Thermogravimetric-differential scanning calorimetry (TG-DSC) analysis (from 20 to 650 °C) of samples was performed in N_2 flow on a NETZSCH-STA-409 PC equipment.

Catalysts Preparation And Structure Determination

The details of catalyst synthesis and characterization are presented in the **Supplemental** materials. The preparation procedure is illustrated in Scheme S1 (Supplemental **materials**). A series of modified PS were obtained after PS reacting with ethylene glycol, diethylene glycol, triethylene glycol and polyethylene glycol (PEG200, PEG300, PEG400, PEG600) in Step 1 (see Supplemental materials), named PS-EG, PS-DEG, PS-TEG, PS-PEG200, PS-PEG300, PS-PEG400 and PS-PEG600, respectively. Then the above modified PS further reacted with 2-aminopyridine to afford intermediates (Step 2, Supplemental materials), named PS-EG-2ap, PS-DEG-2ap, PS-TEG-2ap, PS-PEG200-2ap, PS-PEG300-2ap, PS-PEG400-2ap and PS-PEG600-2ap, respectively. And the catalysts were prepared after metal salts being coordinated (Step 3, **Supplemental materials**). FT-IR and surface properties studies were performed to characterize PS and the above modified PS. The FT-IR spectra were shown in Figure S1, Figure S2 (Supplemental materials). The BET surface areas and pore structure results were given in Table S1 (Supplemental materials). The contents of metal elements were determined by icp-aes and the results were given in Table S2 (Supplemental materials). The morphology of the samples, observed by scanning electron microscopy (SEM), was shown in Figure S3 (Supplemental materials). Figure S4 (Supplemental materials) showed the thermogravimetric-differential scanning calorimetry (TG-DSC) analysis.

General Procedure Of Cycloaddition Reaction Of Epoxides With CO₂

All the cycloaddition reactions were carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer. In a typical run, the reactor was charged with

cyclohexene oxide (200 mmol), catalyst (0.07 mmol, calculated by metal elements) and the desired amount of TBAB. The reactor was pressurized with CO₂ to 5 MPa and then was heated to 120 °C and stirred for a designated period of time. Then the reactor was cooled quickly to a low temperature by placing in an ice/water bath and pressure was released slowly. The reaction mixture was filtered and the catalysts was washed by dichloroethane for reusing. The remained liquid mixture was distilled under reduced pressure to obtain purified cyclohexene carbonate. The product was characterized by IR, ¹H NMR, ¹³C NMR and GC/MS (see **Supplemental materials, Figure S5, Figure S6, Figure S7**). The yield was calculated by the GC peak area with dimethyl succinate as an internal standard.

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SUPPORTING INFORMATION

Supplemental data for this article can be accessed on the publisher's website.

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Table 1 Coupling of carbon dioxide and cyclohexene oxide catalyzed by different catalysts^{*a*}

Entry	Catalysts	Conversion (%)	Yield $(\%)^b$	TOF $(h^{-1})^c$	
1	ZnCl ₂	95.85	88.24	504.2	
2	Zn(CH ₃ COO) ₂	80.26	76.47	436.8	
3	Co(CH ₃ COO) ₂	78.31	70.19	401.1	
4	ZnBr ₂	95.13	88.07	503.3	\mathbf{C}
5	NiCl ₂	43.67	34.35	196.3	
6	FeCl ₃	68.54	58.24	332.8	
7	CoCl ₂	87.91	70.35	402.0	

^{*a*}Reaction conditions: cyclohexene oxide 200 mmol, catalyst 0.07 mmol (calculated by metal elements), TBAB 0.9mmol, initial pressure 4MPa, 393K, 5h.

^{*b*}GC yield.

^cTOF: moles of cyclohexene carbonate produced per mole of a catalyst per hour.

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Entry	Catalysts	Conversion (%)	Yield $(\%)^b$	TOF $(h^{-1})^c$	
5	5				
1	PS-2ap-ZnCl ₂	95.69	87.93	502.5	
2	$PS-2ap-Zn(CH_3COO)_2$	77.45	74.50	425.7	
3	$PS-2ap-Co(CH_3COO)_2$	76.31	69.30	396.0	
4	PS-2ap-ZnBr ₂	94.03	88.16	503.8	
5	PS-2ap-NiCl ₂	41.98	36.10	206.3	
6	PS-2ap-FeCl ₃	67.52	58.90	336.6	
7	PS-2ap-CoCl ₂	87.77	65.68	375.3	
8^d	PS-2ap-ZnCl ₂	78.26	69.15	395.1	

Table 2 Coupling of carbon dioxide and cyclohexene oxide catalyzed by different PS supported catalysts^{*a*}

^aReaction conditions: cyclohexene oxide 200 mmol, catalyst 0.07 mmol (calculated by

metal elements), TBAB 0.9mmol, initial pressure 4MPa, 393K, 5h.

^{*b*}GC yield.

^{*c*}TOF: moles of cyclohexene carbonate produced per mole of a catalyst per hour.

^dWith catalyst in absence of TBAB.

Entry	Catalysts	Pore volume	Pore diameter	Conversion	Selectivity	TOF
		$(cm^{3}.g^{-1})$	(nm)	(%)	(%)	$(h^{-1})^{b}$
1	PS-2ap-ZnCl ₂	0.2019	10.65	95.69	91.89	502.5
2	PS-EG-2ap-ZnCl ₂	0.1564	13.82	96.41	87.35	481.2
3	PS-DEG-2ap-ZnCl ₂	0.1701	14.35	97.71	91.88	513.0
4	PS-TEG-2ap-ZnCl ₂	0.1726	13.91	95.62	83.65	457.1
5	PS-PEG200-2ap-ZnCl ₂	0.1788	12.69	96.92	84.69	469.0
6	PS-PEG300-2ap-ZnCl ₂	0.1769	12.21	98.38	87.09	489.6
7	PS-PEG400-2ap-ZnCl ₂	0.1961	12.17	98.07	90.13	505.1
8	PS-PEG600-2ap-ZnCl ₂	0.2014	11.68	98.43	90.51	509.1

Table 3 Effect of catalysts with different connecting arms^{a}

^aReaction conditions: cyclohexene oxide 200 mmol, catalyst 0.07 mmol (calculated by

zinc), TBAB 0.9mmol, initial pressure 4MPa, 393K, 5h.

^bTOF: moles of cyclohexene carbonate produced per mole of a catalyst per hour.

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Entry	Epoxide	Product	$X^{b}(\%)$	$S^{c}(\%)$
1			99.25	97.17
2			93.74	95.27
3			96.36	95.71
4			99.66	99.37

Table 4 Catalytic activities of the reactions of various epoxides with CO_2^a

^a Reaction conditions: epoxides 200 mmol, PS-DEG-2ap-ZnCl2 0.07 mmol (calculated

by zinc), TBAB 0.9mmol, initial pressure 5MPa, 393K, 6h.

^b X: epoxides conversion.

^c S: carbonates selectivity.

Scheme 1. Synthesis of Cyclohexene Carbonate Using CO_2 and Cyclohexene Oxide and the Structure of Catalysts



Figure 1. Effect of reaction temperature on cyclohexene carbonate yield. Reaction conditions: PS-DEG-2ap-ZnCl₂ 0.07mmol (calculated by zinc), cyclohexene oxide 200 mmol, TBAB 0.9mmol, initial pressure 4MPa, 5h.



Figure 2. Effect of reaction time on cyclohexene carbonate yield. Reaction conditions: PS-DEG-2ap-ZnCl₂ 0.07mmol (calculated by zinc), cyclohexene oxide 200 mmol, TBAB 0.9mmol, initial pressure 4MPa, 393K.



Figure 3. Effect of initial pressure on cyclohexene carbonate yield. Reaction conditions: PS-DEG-2ap-ZnCl₂ 0.07mmol (calculated by zinc), cyclohexene oxide 200 mmol, TBAB 0.9mmol, 393K, 6h.



Figure 4. Recycling of PS-DEG-2ap-ZnCl₂ in the cycloaddition of CO₂. Reaction conditions: PS-DEG-2ap-ZnCl₂ 0.07mmol (calculated by zinc), cyclohexene oxide 200 mmol, TBAB 0.9mmol, initial pressure 5MPa, 393K, 6h.

