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An Efficient Catalyst System at Mild Reaction Conditions Containing Rare Earth Metal Complexes

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An efficient rare earth metal complex-catalyzed cycloaddition reaction of CO_2 with propylene oxide using Hdpza (di(2-pyrazyl)amine) as a *N*-donor ligand has been accomplished in good to excellent yields with high selectivity. The effects of different rare earth metal salts, ligands and reaction conditions were examined. Catalytic reaction tests demonstrated that the incorporation of $ErCl_3$ and Hdpza can significantly enhance the catalytic reactivity of the TBAB ($^{n}Bu_4NBr$, tetra-*n*-butyl ammonium bromide) towards cycloaddition reaction of CO_2 and propylene oxide that produce cyclic carbonates under mild conditions without any co-solvent.

Keywords: Rare earth metal; Metal complexes catalyst; Carbon dioxide transformation; Propylene oxide.

INTRODUCTION

The development of environmentally friendly processes based on carbon dioxide, one of the key greenhouse-effect gases, has attracted considerable attention in recent years.[1] Carbon dioxide is recognized to be highly naturally abundant, inexpensive, recyclable, and nontoxic carbon source of various organic reactions.[2] The chemical fixation of carbon dioxide into valuable chemicals, such as cyclic carbonate,[3] dimethyl carbonate,[4] methanol, dimethyl ether, and formic acid,[5] is generally regarded as an excellent solution both from an environmental protection and resource utilization standpoint.[6] Propylene carbonate (PC) is not only a low toxicity and high boiling point solvent, but also an important organic product that has been used widely in the fields of organic synthesis, gas separation, electrochemistry.[7] Although the synthesis of PC from carbon dioxide and propylene oxide has been applied in industrial scales, the process requires high temperature and pressure (180-206 °C, 7-8 MPa). Therefore, great efforts are still being made to develop novel and efficient catalyst system to catalyze cycloaddition reaction of carbon dioxide under mild reaction conditions.[8]

The catalysts of this transformation include heterogeneous catalysts and homogeneous catalysts.[9] Most heterogeneous catalysts consist of metal oxides,[10] supported catalysts,[11] polymer catalysts and so on, which are easy to be separated from product.[12] The inherent problems, however, are their low activity, high pressure, high temperature conditions and they also need the use of co-solvents.[13] Homogeneous catalysts comprise quaternary ammonium salts,[14] alkali metal salts,[15] ionic liquids,[16] and metal complexes.[17] Prominent among these are transition metal complex catalysts.[18] In particular, metal complexes based on nickel, copper, zinc, cobalt and chromium are remarkable.[19] Various ligands have been developed, such as pyridine, quinoline, acridine, porphyrins, salen, phthalocyanines, *et al.*[20] In many cases, salen complexes are moisture sensitive, and low-valent metal complexes are oxygen sensitive.[21] Metal porphyrin and phthalocyanine complexes agglomerate with each other and need to be used in large quantities and require co-solvents to achieve excellent activity.[19]

Up to now, reports on rare earth complex catalysts on the cycloaddition of carbon dioxide to propylene oxide for the synthesis of PC remain extremely scarce, and the catalytic function of heterocyclic amine ligand complexes for this series has been rarely explored. Considering that rare earth metal ions have high charges, high coordination numbers and incompact room compared with common transition metal ions, it is our interest to investigate the novel and efficient rare earth metal catalyst system for synthesizing PC under relatively mild reaction conditions.[22]

In this study, we report our recent research results using various rare earth metal complexes catalyst systems to catalyze the reaction of carbon dioxide with propylene oxide to generate PC. The effects of various components in the rare earth metal complex catalytic system on the cata-

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lytic activity and different reaction condition were also investigated.

RESULTS AND DISCUSSION

IR spectra of the PC showed strong absorption bands at 1,793 and 1,053-1,184 cm^{-1}, characteristic of stretching vibration of C=O bond and C-O-C bond of the carbonate group, respectively. Fig. 1 shows the ^{1}H and ^{13}C-NMR spectra of the reaction product after purification, which is consistent with PC as a sole main product.

In a general process, the synthetic reaction of PC from carbon dioxide and propylene oxide were examined at 100 °C, 1.5 MPa with the catalyst containing different rare earth metal salts and *N*-heterocyclic ligands. Table 1 summarizes the performance of different types of catalysts in the PC synthesis from propylene oxide and CO_2. Although the yield is relatively low (Table 1, entry 1), TBAB (^{n}Bu$_4$NBr, tetra-*n*-butyl ammonium bromide) is shown essential and plays a pivotal role for their function as a catalyst (Table 1, entries 2 and 5). The catalyst systems without TBAB showed no catalytic activity (Table 1, entries 2 and 3). The use of rare earth complex increased the reaction yield significantly from 35% up to 56% (Table 1, entry 4), and the introduction of the reducing agent Zn powder enhanced the activity and improved the yield even more (80%, Table 1, entry 5). Therefore, the in-depth study was carried out based on this catalyst system. The effects of different rare earth chlorides on the catalytic activity were also investigated *via* three kinds of metals, Er^{3+}, Nd^{3+} and Gd^{3+}, and the sequence of the effect with the same ligand is: $Er^{3+} > Nd^{3+} > Gd^{3+}$ (Table 1, entries 5-7, 8-10 and 11-13). The catalytic activity is inversely proportional to their ionic radii: with the smallest radius and the highest charge density among the three metals, Er^{3+} showed the best yield. This is consistent with that the Er^{3+} is harder and stronger Lewis acid than Nd^{3+} and Gd^{3+}, which allows a stronger metal-ligand interactions.[23]

Table 1. Synthesis of propylene carbonate with metal catalyst/ ligand/ Zn/ TBAB[a]

Entry	Catalyst	Temperature	Yield[b]
1	TBAB	100	35
2	$ErCl_3$/Hdpza	100	0
3	$ErCl_3$/Hdpza/Zn	100	0
4	$ErCl_3$/Hdpza/TBAB	100	56
5	$ErCl_3$/bipy/TBAB/Zn	100	80
6	$NdCl_3$/bipy/TBAB/Zn	100	73
7	$GdCl_3$/bipy/TBAB/Zn	100	71
8	$ErCl_3$/Hdpa/TBAB/Zn	100	80
9	$NdCl_3$/Hdpa/TBAB/Zn	100	77
10	$GdCl_3$/Hdpa/TBAB/Zn	100	69
11	$ErCl_3$/Hdpza/TBAB/Zn	100	95
12	$NdCl_3$/Hdpza/TBAB/Zn	100	84
13	$GdCl_3$/Hdpza/TBAB/Zn	100	76
14	$ErCl_3$/Hdpza/TBAB/Zn	80	77
15	$Er(NO_3)_3$/Hdpza/TBAB/Zn	100	61

[a] Reaction condition: metal catalyst 0.05 mmol, ligand 0.15 mmol, Zn powder 1 mmol, TBAB 0.2 mmol (1.5 MPa) at 100 °C for 1 h. [b] Isolated yield.

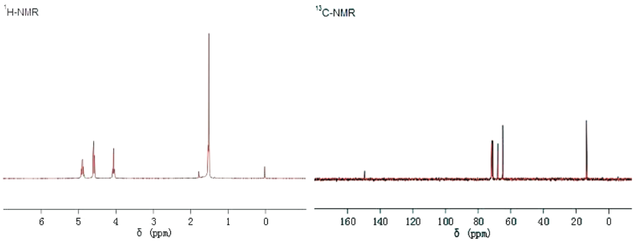
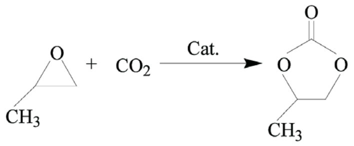


Fig. 1. ^{1}H and ^{13}C-NMR data of Propylene carbonate at 100 °C, 1.5 MPa, 1 h, with $ErCl_3$/Hdpza/ TBAB/Zn. Propylene carbonate: yellow liquid, ^{1}H-NMR (400 MHz, $CDCl_3$, TMS) δ: 1.497 (d, $J = 6.4$ Hz, 3H, CH_3), 4.046 (t, $J = 7.6$ Hz, 1H, CH), 4.576 (t, $J = 8.0$ Hz, 1H), 4.837-4.921 (m, 1H, CH); ^{13}C-NMR (400 MHz, $CDCl_3$, TMS) δ: 13.740, 64.997, 67.900, 149.392 (C=O); IR ν/cm^{-1} = 2988 m, 1793 s, 1389 m, 1354 m, 1184 s, 1120 s, 1053 s, 777 m, 712 m.

Three different ligands, Bipy, Hdpa and Hdpza (Bipy = 2,2'-bipyridine, Hdpa = di(2-pyridyl)amine and Hdpza = di(2-pyrazyl)amine)) were examined to understand the effects of ligands on the catalytic activity. The ligand sequence of the effect with the same metal chlorides is: Hdpza > Hdpa ≈ Bipy (Table 1, entries 5-7, 8-10 and 11-13). The results revealed the following important points: (1) The amine group of the ligands plays minor role and is unnecessary for the catalytic activity, which was indicated by the similar results of Hdpa and Bipy. Reactivity remains almost the same in two groups of parallel tests (Table 1, entries 5-7 and 8-10). (2) The heterocyclic rings in ligands are vital for their function as a catalyst. When ligand Hdpa was changed to Hdpza, the yields increased significantly (Table 1, entries 8-10 and 11-13). The introduction of pyrazine instead of pyridine to the ligands resulted in more electronegative nitrogen atoms in the ligand and stronger basicity than pyridine ligand, and therefore a stronger metal-ligand interaction from the viewpoint of HSAB theory.[24]

The catalytic efficiency is quite sensitive to the reaction temperature. When the reaction temperature was de-

Scheme I The reaction of PC from carbon dioxide with propylene oxide



creased from 100 °C to 80 °C, the yield decreased from 95% to 77% (Table 1, entries 11 and 14). When the rare earth nitrate was employed instead of chlorides, the catalytic activity reduced markedly (Table 1, entry 15). This indicates the importance of the cooperative effect related to anions, and the reaction favors chlorides other than nitrates.

Based on the above results, the mechanism of this reaction using the rare earth metal complex-based catalyst can be envisioned as being very similar to that previously proposed by Li and co-workers.[25] First, the RE(III) complex (RE = rare earth metal) was reduced to a RE(II) complex by the reducing agent Zn powder. Then the RE(II) complex could efficiently activate the inert carbon dioxide to afford a three-membered active intermediate.[26] In another catalytic cycle, the TBAB opens the ring of the PO by nucleophilic attack, which generates an oxyanion species and attacks the three-membered intermediate to afford another oxyanion species which eventually generate the PC product. The facts that there is almost no reaction in the absence of TBAB while the reaction is very excellent in the presence of TBAB (Table 1, entries 2, 3 and 11) insists on this mechanism. The role of RE(II) complexes is evidenced by the good performance of ligand Hdpza and metal Er^{3+}. Our previous research on the complexes of oligo-α-pyridylamino ligands and their pyrazine-modulated catalogues indicated that the introduction of more electronegative nitrogen atoms changes electrochemistry properties of the complexes, makes the complexes easier to be reduced and more resistant to oxidation.[27] The metal Er^{3+}, with the smallest radius, the highest charge density, and therefore the most trend to undergo reduction, exhibits the best catalytic efficiency.

EXPERIMENTAL

The catalytic reactions of CO_2 with PO were performed in a 100 mL titanium autoclave equipped with a magnetic stirrer. In a typical run, the catalyst was charged into the dry reactor, followed by adding a desired amount of purified PO. Then, the reactor was pressurized to 1.5 MPa with carbon dioxide and heated to the desired temperature (100 °C) with stirring. After 1 h of reaction, the autoclave was cooled to room temperature, the CO_2 pressure was released by opening the outlet valve. The solid residue was separated from the reaction mixture by filtration. The reaction mixture was transferred to a round bottom flask. The product PC was obtained through distillation under reduced pressure. Qualitative analysis of the liquid products was performed on IR spectrum. For quantitative determination, the products were analyzed on an Agilent 6890 Plus GC with flame ionization detection. The PC yield was obtained by internal standard method (Biphenyl as the internal standard substance). ^1H NMR and ^{13}C NMR spectra were obtained on a Varian INOVA 400 MHz spectrometer with TMS as an internal standard.

CONCLUSIONS

In summary, we have successfully developed an efficient catalyst system containing rare earth metal complex for the cycloaddition reaction of CO_2 with propylene oxide. Using RE(III) chlorides and Hdpza as a *N*-donor ligand, the reaction goes very quickly under mild conditions. The cooperative effect between the RE(III) complex, reduction agent and TBAB was attributed to the excellent activity and high selectivity.

Catalytic reaction tests demonstrated that the incorporation of $ErCl_3$ and Hdpza can significantly enhance the catalytic reactivity of the TBAB ($^nBu_4NBr$, tetra-*n*-butyl ammonium bromide) towards cycloaddition reaction of CO_2 and propylene oxide that produce cyclic carbonates under mild conditions without any co-solvent.

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