

Rare Earth Complex Catalysts Transforming CO₂ into Cyclic Carbonate under Mild Conditions

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A highly efficient catalyst system was designed and fabricated based on the synthesis of cyclic carbonates from CO₂ and propylene oxide. The reaction of carbon dioxide with propylene oxide that generates propylene carbonate (PC) when catalyzed by N-heterocyclic ligands (Bipy, Hdpa, Hdpza and Napy) and rare earth metal salts system was investigated. Also, the influence of the ligand structure for catalytic performance was analyzed. Different reaction conditions including temperature, pressure and reducing metal were studied to optimize reaction conditions.

Introduction

As one of the key greenhouse effect gases, carbon dioxide has attracted considerable attention in recent years (Fujita et al., 2002). The chemical fixation of carbon dioxide into valuable chemicals is generally regarded as an excellent solution both from environmental protection and resource utilization standpoints. Carbon dioxide is recognized to be naturally abundant, cheap, recyclable, and a nontoxic carbon source for various organic reactions (Sakakura et al., 2007). PC is not only a low toxicity and high boiling point solvent, but also an important organic product that has been widely used in the fields of organic synthesis, gas separation, electrochemistry etc (Yu et al., 2009). Although the synthesis of PC from carbon dioxide and propylene oxide has been applied in industrial scales, the process demands considerably high temperature and pressure (180-206°C, 7-8 MPa). Therefore, great efforts are still being made to develop the novel and efficient catalyst system to catalyze cycloaddition reaction of carbon dioxide under mild reaction conditions (Han et al., 2012). The inherent problems, including heterogeneous catalysts and homogeneous catalysts, however, however, are their low activity, high

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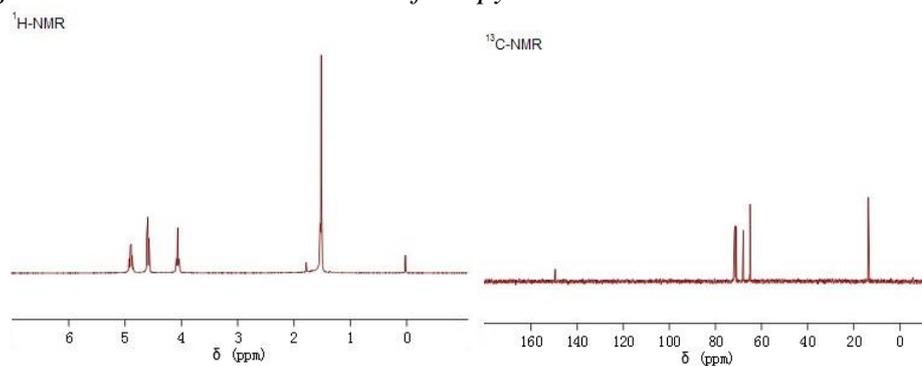
pressure, high temperature conditions and co-solvents as well (Dai et al., 2010). Generally, salen complexes are moisture sensitive, while low-valent metal complexes, oxygen sensitive (Baleiza & Garcia, 2006). Metal porphyrin and phthalocyanine complexes agglomerate with each other and need to be used in large quantities. They also require co-solvents to achieve excellent activity (Ghosh et al., 2010). 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 (Wang et al., 2013). Considering that rare earth metal ions have high charges, high coordination numbers and incompact room compared to 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 (Lin & Luo, 2006).

In this study a highly efficient catalyst system based on the synthesis of cyclic carbonates from CO₂ and propylene oxide was designed and fabricated, and the reaction catalyzed by ligands (Bipy, Hdpa, Hdpza and Napy) and rare earth metal salts was investigated. Meanwhile, the influence of the ligand structure on catalytic performance was also analyzed.

Results and Discussion

IR spectra of the PC showed strong absorption bands at 1,793 and 1,052-1,183 cm⁻¹, as well as characteristics of stretching vibration of C=O bond and C-O-C bond of the carbonate group, respectively. Fig. 1 demonstrated the ¹H and ¹³C-NMR spectra of the reaction product after purification, which is consistent with PC as a sole main product.

Figure. 1. ¹H and ¹³C-NMR Data of Propylene Carbonate



Propylene carbonate: yellow liquid, ¹H-NMR (400 MHz, CDCl₃, TMS) δ : 1.497 (d, J = 6.4 Hz, 3H, CH₃), 4.046 (t, J = 7.6 Hz, 1H, CH), 4.576 (t, J = 8.0 Hz, 1H), 4.837-4.921 (m, 1H, CH); ¹³C-NMR (400 MHz, CDCl₃, TMS) δ : 13.740, 64.997, 67.900, 149.392 (C=O)

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 summarized the performance of different types of catalysts in the PC synthesis from propylene oxide and CO₂.

The effects of different rare earth chlorides on the catalytic activity were also investigated *via* three kinds of metals, namely Er³⁺, Nd³⁺ and Gd³⁺. The sequence of the effect with the same ligand is: Er³⁺ > Nd³⁺ > Gd³⁺ (Table 1, entries 1-3, 4-6 and 7-9). The catalytic activity is inversely proportional to their ionic radii: with the smallest radius and the highest charge density among the three metals, Er³⁺ showed the best yield. This is consistent with the idea that the Er³⁺ is a harder and stronger Lewis acid than Nd³⁺ and Gd³⁺ are, which allows a stronger metal-ligand interaction.

Table 1. Synthesis of Propylene Carbonate Catalyzed by Metal/ Ligand/ Zn/ TBAB^a

Entry	Catalyst	Yield ^b / %	TOF ^c / h ⁻¹
1	NdCl ₃ / Napy/TBAB/Zn	86	375
2	GdCl ₃ / Napy/TBAB/Zn	85	370
3	ErCl ₃ / Napy/TBAB/Zn	90	392
4	NdCl ₃ / Hdpza /TBAB/Zn	84	366
5	GdCl ₃ / Hdpza /TBAB/Zn	76	331
6	ErCl ₃ / Hdpza /TBAB/Zn	95	414
7	NdCl ₃ / Bipy /TBAB/Zn	73	318
8	GdCl ₃ / Bipy /TBAB/Zn	71	309
9	ErCl ₃ / Bipy /TBAB/Zn	80	349
10	Nd(NO ₃) ₃ / Bipy /TBAB/Zn	75	327
11	Nd(acac) ₃ / Bipy /TBAB/Zn	80	349
12	Nd(NO ₃) ₃ / Hdpza /TBAB/Zn	76	331
13	Nd(acac) ₃ / Hdpza /TBAB/Zn	76	331
14	NdCl ₃ / Hdpa /TBAB/Zn	77	336
15	Nd(NO ₃) ₃ / Hdpa /TBAB/Zn	83	362
16	Nd(acac) ₃ / Hdpa /TBAB/Zn	84	366
17	ErCl ₃ / Hdpa /TBAB/Zn	80	349

[a] Reaction condition: metal catalyst 0.5 mmol, ligand 1.5 mmol, TBAB 2 mmol, Zn powder 10 mmol, 1.5 MPa at 100°C for 1 h. [b] Isolated yield. [c] Moles of propylene carbonate produced per mole of catalyst per hour.

Three different ligands, Napy, Hdpza and Bipy (Napy = 1, 8-naphthyridine, Hdpza = di(2-pyrazyl)amine, Bipy = 2,2'-bipyridine) were examined to reveal the effects of ligands on the catalytic activity. First of all, the amine group of the ligands plays a minor role and was unnecessary for the catalytic activity, as indicated by the similar results of Hdpa and Bipy (Table 1, entries 7 and 14). Second, the heterocyclic rings in ligands were vital for their function as a catalyst. When ligand Hdpa was changed to Hdpza, the yields increased significantly rising from 80% to 95%, and TOF also increased from 349 h⁻¹ to 414 h⁻¹ (Table 1, entries 6 and 17). With regard to different N-donor heterocyclic ligands, the anions of the rare earth metal salts affected the catalytic reaction differently. For Bipy ligand, the catalytic activity of acetate

salt was the best choice (Table 7, entries 1, 10 and 11); For Hdpa ligands, the nitrate catalyst worked best (Table 1, entries 14-16); For Hdpza ligand, the catalytic activity of chlorides was the best (Table 1, entries 4, 12 and 13). This indicated the importance of the cooperative effect related to anions, and that halide ion is more conducive to catalyze the process of nucleophilic attack, which also improved its catalytic efficiency.

The catalytic reaction tests demonstrated that the incorporation of ErCl₃ and Hdpza could significantly enhance the catalytic reactivity of the TBAB (tBu₄NBr, tetra-*n*-butyl ammonium bromide) towards cycloaddition reaction of CO₂ and propylene oxide that produced cyclic carbonates under mild conditions without any co-solvent. After that, the study mainly focused on the investigation of different reaction conditions, which included temperature (Table 2), pressure (Table 3), and reducing metals (Table 4).

Table 2. Synthesis of Propylene Carbonate Catalyzed by ErCl₃/ Hdpza /TBAB/Zn in Different Temperatures^a

Temperature / °C	60	80	100	120
Yield / %	84	83	95	83

[a] Reaction condition: metal catalyst 0.5 mmol, ligand 1.5 mmol, Zn powder 10 mmol, TBAB 2 mmol at 1.5 MPa for 1 h.

The test results showed that the catalytic efficiency was not sensitive to temperature. When the reaction temperature increased from 60 °C to 80 °C, the yield almost remained unchanged. However, when the temperature rose to 100 °C, the highest product yield was obtained with its yielding rate being 95%. When the temperature was further increased, the yield decreased to 83% (Table 2). Thus, it could be concluded that the optimum reaction temperature of the reaction was 100 °C.

Table 3. Synthesis of Propylene Carbonate Catalyzed by ErCl₃/ Hdpza /TBAB/Zn in Different Pressure^a

Pressure / Mpa	0.9	1.2	1.5
Yield / %	73	83	95

[a] Reaction condition: metal catalyst 0.5 mmol, ligand 1.5 mmol, Zn powder 10 mmol, TBAB 2 mmol at 100 °C for 1 h.

Pressure exerts have a significant influence on the catalytic activity. Judged from the above catalytic performance, it is seen that higher pressure was advantageous to the reaction. When the reaction pressure was 0.9 Mpa, the product yield was 73%; with the increase of the reaction pressure, the yield improved, and the highest value of 95% emerged at 1.5 Mpa.

Table 4. *Synthesis of Propylene Carbonate Catalyzed by ErCl₃/ Hdpza /TBAB/M in Different Reducing Metals^a*

Reducing metals (M)	Zn	Al	Fe
Yield / %	95	79	78

[a] Reaction condition: metal catalyst 0.5 mmol, ligand 1.5 mmol, Metal 10 mmol, TBAB 2 mmol (1.5MPa) at 100°C for 1 h.

Great influence by the reducing metal in the catalyst system was observed, and certain sorts of reducing metal can effectively improve the catalytic activity of the catalyst. When zinc powder was employed as the metal co-catalyst, the product yield reached 95%, while choosing iron or aluminum to be the metal co-catalyst, the yield decreased to 78% and 79%, respectively. This order differs from the standard electrode potential values of the three metal ions in aqueous solution: Al > Zn > Fe. Since our experiments were carried out in non-aqueous system, it was quite understandable that it led to different sequences.

Experimental

The catalytic reactions of CO₂ with propylene oxide (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 by stirring. After the reaction, the autoclave was cooled down to room temperature, and the CO₂ pressure was released by opening the outlet valve. The solid residue was separated from the reaction mixture by filtration. The product PC was obtained through distillation of the filtrate under reduced pressure. A qualitative analysis of the liquid products was performed on IR spectrum. ¹H NMR and ¹³C NMR spectra were obtained on a Varian INOVA400 MHz spectrometer with TMS as an internal standard. For quantitative determination, the products were analyzed on an Agilent 6890 Plus GC with flame ionization detection. The PC yield was obtained by an internal standard method (biphenyl as the internal standard substance).

Conclusions

In summary, an efficient catalyst system containing rare earth metal complex for the cycloaddition reaction of CO₂ with propylene oxide was successfully developed in the study. Using RE (III) chlorides as a metal source and Hdpza as a N-donor ligand, the reaction went fairly quickly with good yield and high selectivity. The synergy effect among the RE (III) complex, reduction agent and TBAB was attributed to the excellent activity and high selectivity. The catalytic reaction tests demonstrated that the incorporation of ErCl₃ and Hdpza could significantly enhance the catalytic reactivity of the

TBAB (ⁿBu₄NBr, tetra-*n*-butyl ammonium bromide) towards cycloaddition reaction of CO₂ and propylene oxide that produce cyclic carbonate under mild conditions without any co-solvent.

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