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Activation of Carbon Dioxide and Synthesis of Propylene Carbonate

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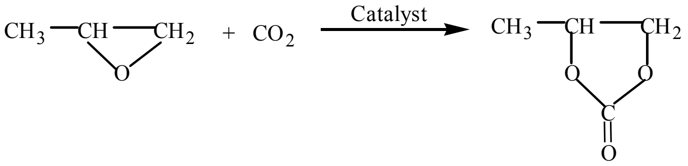
Abstract: Cycloaddition of carbon dioxide and propylene oxide to propylene carbonate catalyzed by tetra-*tert*-butyl metal phthalocyanine in the presence of tributylamine (TBA) shows higher yield than catalyzed by unsubstituted metal phthalocyanine. Comparing different catalysts of diverse metals, (t-Bu)$_4$PcMg is more active than (t-Bu)$_4$PcFe. But (t-Bu)$_4$PcCo and (t-Bu)$_4$PcNi only have low catalytic activities towards the reaction. Moreover, the yield will increase as the temperature increases.

Keywords: Cycloaddition reaction, carbon dioxide, propylene oxide, propylene carbonate, tetra-*tert*-butyl metal phthalocyanine.

Global warm, caused by increasing emissions of greenhouse gases such as carbon dioxide has been recognized as a serious environmental problem. Therefore, the reuse of existing CO_2 as a source of carbon for producing chemicals has received much attention recently[1]. So far CO_2 has been used in the synthesis of urea, cyclic carbonates, salicylic acid and methanol as a one-carbon precursor[2].

Cyclic carbonates are important intermediates and organic solvents for industrial purpose. It is well known that the photosynthetic process in nature can convert CO_2 and H_2O into carbohydrate, and the catalyst operating in this process is magnesium porphyrin. Therefore cycloaddition of CO_2 and cycloalkylene oxides to cyclic carbonates catalyzed by metal phthalocyanines were previously studied in our laboratory[3-4] (as shown in **Scheme 1**).

Scheme 1



In this paper we will discuss the cycloaddition of CO_2 and propylene oxide to propylene carbonate catalyzed by a series of *tert*-butyl substituted metal phthalocyanines,

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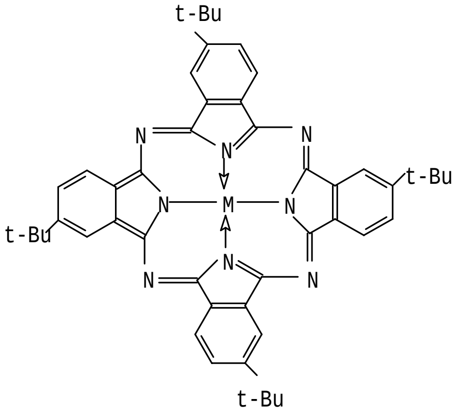
(t-Bu)$_4$PcMg **A**, (t-Bu)$_4$PcFe **B**, (t-Bu)$_4$PcCo **C** and (t-Bu)$_4$PcNi **D**, whose structures are shown in **Scheme 2**.

Scheme 2



A M=Mg; **B** M=Fe; **C** M=Co; **D** M=Ni

Experimental

Precatalysts (t-Bu)$_4$PcMg **A**, (t-Bu)$_4$PcFe **B**, (t-Bu)$_4$PcCo **C** and (t-Bu)$_4$PcNi **D** were prepared[5-7] while metal phthalocyanine were supplied by Shenyang Research Institute of Chemical Engineering, and carbon dioxide was purified by passing through a column packed with 4 A molecular sieves. The other chemicals with A. R. purity or C. P. grade level were purchased commercially and used without further purification. The cycloaddition reaction was carried out in a 75 mL stainless steel autoclave with magnetic stirring, as the autoclave charged by substituted or unsubstituted metal phthalocyanines, propylene oxide and tributylamine was maintained at constant temperature and under constant CO_2 pressure. After the reaction, the autoclave was cooled to room temperature and the excess gas was vented. The remnant mixture was distilled in vacuum (88-90°C/ 2 mmHg) in order to obtain pure propylene carbonate. The spectral data are listed as follows: IR: $\upsilon_{C=O}$ 1793 cm^{-1}, $\upsilon_{C\text{-}O}$ 1183, 1120, 1075, 1052 cm^{-1}. ^{1}H-NMR ($CDCl_3$/TMS): δ 1.4 (d, 3H), δ 3.9~4.1 (q, 1H), δ 4.4~4.6 (t, 1H), δ 4.7~4.9 (m, 1H).

Results and Discussion

In the previous papers[3-4], we reported that metal phthalocyanines could effectively catalyze the cycloaddition reaction to form cyclocarbonates at higher temperature. In this paper, the yields of cycloaddition reaction catalyzed by FePc, MgPc, PcAlCl, (t-Bu)$_4$PcFe and (t-Bu)$_4$PcMg under the same reaction condition were listed in **Table 1**, and the result indicated that tert-butyl substituted metal phthalocyanines showed higher catalytic activities than unsubstituted metal phthalocyanines.

Table 1 The yield of Propylene Oxide: Comparing (t-Bu)$_4$PcM/TBA with PcM/TBA

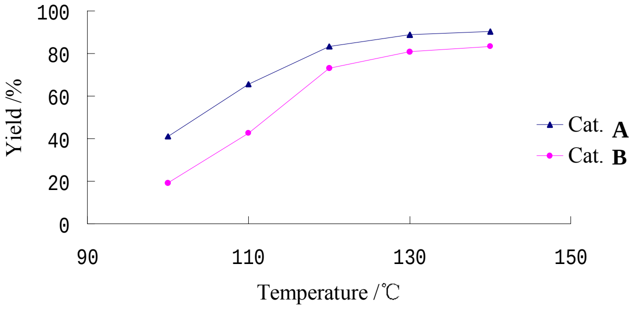
Cat/TBA	FePc	MgPc	PcAlCl	(t-Bu)$_4$PcFe	(t-Bu)$_4$PcMg
Yield(%)	5.6	28.3	53.9	42.5	65.5

Reaction condition: Propylene Oxide 0.15 mol; Cat 0.2 mmol; TBA 0.4 mmol; CO_2 4.0 MPa; reaction temperature 110°C; reaction time 3 h.

It is reasonable that homogeneous catalytic systems resulted from good solubility of (t-Bu)$_4$PcM favors the cycloaddition reaction, but the poor solubility of unsubstituted metal phthalocyanines in organic solvents results a heterogeneous catalytic system, so the yield of PC with unsubstituted metal phthalocyanines is lower than that with the tert-butyl metal phthalocyanines. Another possible reason is that the increased charge densities of (t-Bu)$_4$PcM caused by introducing *tert*-butyl, a donor group, could favor the insertion of CO_2 for the cycloaddition reaction, which possibly proceeds *via* insertion of propylene oxide and carbon dioxide between the metal ion and the axial ligand[8].

The catalytic properties of various tetra-*tert*-butyl metal phthalocyanines **A**, **B**, **C** and **D** in the presence of tributylamine in the cycloaddition reaction of CO_2 and propylene oxides to synthesize propylene carbonates are studied. We abandon **C** and **D** because they show low catalytic activities, and the yields of propylene carbonates catalyzed by **A** and **B** under different temperatures are listed in **Figure 1.**

Figure 1 The yields of propylene carbonates catalyzed by **A** and **B** under different temperature



Reaction condition: Propylene Oxide 0.15 mol; Cat 0.2 mmol; TBA 0.4 mmol; CO_2 4.0 MPa; reaction time 3 h.

The experimental results (**Figure 1**) indicated that catalytic properties of these catalytic systems were strongly affected by reaction temperature since the yield of PC increased with the increase of the reaction temperature from 100°C to 140°C. Moreover the yield of PC with **A**/TBA increased 50 percent from 100°C to 140°C and with **B**/TBA it increased 60 percent. The yield of PC with **A**/TBA increased almost linearly from 100°C to 120°C, while it increased very slowly beyond 120°C, inclined steadily. For **B**/TBA, it showed similar tendency. At 120°C, only little amount of PC with **C**/TBA or **D**/TBA was obtained. This probably resulted from the selfpolymerization of PO or the formation of polycarbonate.

The data listed in **Figure 1** also described that **A**/TBA showed higher catalytic activity than **B**/TBA under the same condition, which indicated that the main metal had higher catalytic activity than the transition metal. The catalytic activities of all tetra-*tert*-butyl metal phthalocyanines studied in this paper were in the following order: (t-Bu)$_4$PcMg> (t-Bu)$_4$PcFe> (t-Bu)$_4$PcCo, (t-Bu)$_4$PcNi, which was in good agreement with our previous work[4].

Conclusions

Tetra-*tert*-butyl metal phthalocyanines such as (t-Bu)$_4$PcMg , (t-Bu)$_4$PcFe, (t-Bu)$_4$PcCo, (t-Bu)$_4$PcNi are used as catalysts for the cycloaddition of carbon dioxide and propylene oxide to prepare propylene carbonate in the presence of tributylamine. Compared with unsubstituted metal phthalocyanines, the tetra-*tert*-butyl metal phthalocyanines show higher catalytic activities towards the cycloaddition reaction, such as (t-Bu)$_4$PcFe>FePc, (t-Bu)$_4$PcMg>MgPc. For the metal phthalocyanines with the same substituent, the catalytic activities of the cycloaddition reaction are in the following order: (t-Bu)$_4$PcMg > (t-Bu)$_4$PcFe> (t-Bu)$_4$PcCo, (t-Bu)$_4$PcNi.

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