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RESEARCH NOTE

Cyclic Carbonate Synthesis from Supercritical Carbon Dioxide and Epoxide over Lanthanide Oxychloride

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Lanthanide oxychloride, especially SmOCl, is an efficient solid catalyst for propylene carbonate synthesis from supercritical CO_2 and propylene oxide. The process requires no additional organic solvents and the product is automatically separated out from the CO_2 phase.

Key Words: **propylene carbonate; propylene oxide; supercritical carbon dioxide; lanthanide oxychloride.**

INTRODUCTION

Organic cyclic carbonates such as ethylene carbonate and propylene carbonate are widely used as electrolyte components for lithium batteries, polar solvents, and chemical intermediates (1) and are currently synthesized by cycloaddition of carbon dioxide to epoxides. The reaction is one of a few industrial synthetic processes utilizing CO_2 as a raw material, very attractive from the viewpoint of "green chemistry" and "atom economy" because CO_2 is a renewable resource and can be incorporated without producing any coproducts (2).

A large number of organic and inorganic compounds, including amines, phosphines, quaternary onium salts, alkali metal salts with or without crown ether, and main-group metal and transition metal complexes, homogeneously catalyze the cycloaddition of CO_2 to epoxides to form five-membered cyclic carbonates (3). However, the utilization of homogeneous catalysts is disadvantageous in terms of catalyst separation. On the other hand, a few solid catalysts, such as polymer-supported quaternary onium salts (4), magnesia (5), Mg–Al mixed oxide (6), and Cs-loaded zeolite and alumina (7), are reported to be active for the cycloaddition reactions. In most cases, however, a polar organic solvent like DMF (*N*,*N*-dimethylformamide) is added in order to achieve high yields.

Lanthanide oxides generally act as basic catalysts (8), while lanthanide chlorides show various Lewis acidic catalysis (9). Therefore, we expected that lanthanide oxychlorides would provide the synergistic combination of the activation of CO_2 by the Lewis basic O^{2-} sites and the activation of propylene oxide by the Lewis acidic Ln^{3+} sites. The importance of the cooperative actions of base and acid sites for the cyclic carbonate synthesis has also been proposed by others (6, 7b). Lanthanide oxychlorides (LnOCl) with the lanthanide elements from La to Ho are structurally well-defined crystalline compounds consisting of a combination of the chlorine layer and the metal oxygen layer and taking a tetragonal PbFCl-type structure (10). The materials have been known to catalyze the oxidative coupling of methane (11) and the oxidative cracking of *n*-butane (12). Here, we report that the lanthanide oxychlorides can efficiently catalyze the propylene carbonate synthesis from CO_2 and propylene oxide under supercritical CO_2 conditions, where propylene carbonate is obtained in high yields even in the absence of any additional organic solvents.

EXPERIMENTAL

Catalyst Preparation and Characterization

The LnOCl (Ln = La, Pr, Nd, Sm, Eu, Gd, Dy) were prepared by calcining the corresponding lanthanide chloride hydrate in air at 873 K for 6 h. Sm_2O_3 (Wako Pure Chemical Industries, 99.9%, 2.0 m^2/g) and $SmCl_3$ (Wako, 99.5%) were used as received. MgO (JRC-MGO-4, 99.98%, 17.2 m^2/g) and γ-Al_2O_3 (JRC-ALO-8, 99.99%, 148 m^2/g) were supplied by the Catalysis Society of Japan as reference catalysts. Mg–Al mixed oxide (the Mg/Al molar ratio of 5) was prepared by calcining Mg–Al hydrotalcite in air at 673 K for 3 h. The Mg–Al hydrotalcite was synthesized according to Ref. (13).

The crystal structure of the LnOCl was determined by powder X-ray diffraction (XRD) (Mac Science M18XHF22) using Cu$K\alpha$ radiation. The XRD patterns of the LnOCl showed only the PbFCl-type structure except that very small unidentified phases were observed for DyOCl. The specific surface area was measured by means

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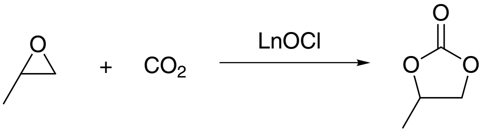
of the BET method using N_2 adsorption at 77 K after the evacuation of the sample at 573 K.

Reaction

The cycloaddition reaction of CO_2 to propylene oxide was carried out with a stainless steel autoclave (20 cm^3 inner volume). Prior to the reaction, the catalyst (250–425 μm) was evacuated at 573 K for 3 h. In an autoclave, CO_2 (liquid, 5.0 MPa) was added to a mixture of propylene oxide (57.2 mmol), a catalyst (1 g), and biphenyl (200 mg, internal standard for GC analysis) at room temperature. The initial pressure was generally adjusted to 14 MPa at 473 K and the autoclave was heated at that temperature for 8 h. After cooling, product yield was determined by GC (Shimadzu GC-17A) using capillary columns (J&W Scientific DB-1 (60 m) and DB-WAX (30 m)). The products were further identified using GC–MS (Shimadzu QP-5000) by comparing retention times and fragmentation patterns with authentic samples.

RESULTS AND DISCUSSION

The LnOCl (Ln = La, Pr, Nd, Sm, Eu, Gd, Dy) catalyzed the cycloaddition reaction of CO_2 to propylene oxide to afford propylene carbonate over 373 K (Scheme 1). The temperature dependence of the yield and selectivity of propylene carbonate is shown for SmOCl in Fig. 1. The yield increased with reaction temperature up to 473 K, whereas further increase in the temperature caused a decrease in the selectivity. Table 1 summarizes the surface area, the yield, and the selectivity of propylene carbonate for the LnOCl catalysts. The products other than propylene carbonate were isomers of propylene oxide, such as acetone and propionaldehyde, and oligomers of propylene oxide and their derivatives, such as 2-ethyl-4-methyl-1,3-dioxolane and 2-(1-methylethoxy)-1-propanol. Note that no chlorinated organic compounds were detected by GC–MS. It is interesting that there is an optimal lanthanide element for the catalysis. Among the LnOCl catalysts, SmOCl showed the highest activity and selectivity for the propylene carbonate synthesis from CO_2 and propylene oxide. The SmOCl catalyst was most active even when the differences in surface area were taken into account. No changes in the crystal structure of the SmOCl catalyst were observed by XRD after the reaction. Insolubility of the SmOCl catalyst into the product solution was confirmed by elemental analyses. The SmOCl catalyst was thoroughly filtered from the product solution, and the content of samarium and chloride ions in the resulting filtrate was measured by ICP and ion chromatography, respectively. The content of samarium ion was below the detectable limit (<0.2 ppm) whereas that of chloride ion was at the level of detectable limit (0.15 ppm). In addition, the SmOCl catalyst could be recovered and reused. Although the yield in the second run slightly decreased (58 to 49%) possibly due to the deposition of carbonaceous species on the catalyst surface, the yield in the second run was practically maintained in the third run.



SCHEME 1

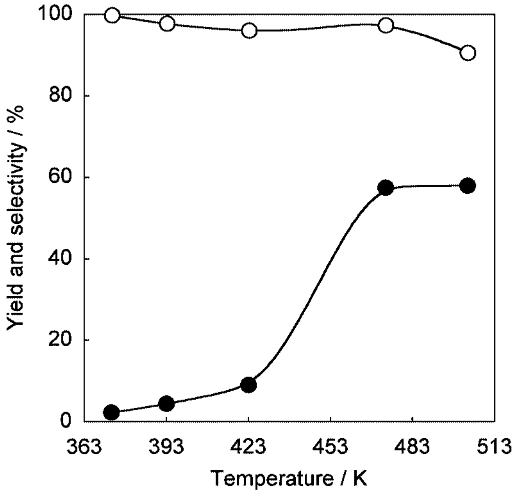


FIG. 1. Temperature dependence of the yield (●) and selectivity (○) of propylene carbonate for SmOCl. Propylene oxide, 57.2 mmol; SmOCl, 1 g; CO_2, 14 MPa; 8 h.

The SmOCl catalyst was much more effective than the Sm_2O_3 and $SmCl_3$ catalysts (Table 2, entries 1–3). The use of Sm_2O_3 resulted in a low conversion of propylene oxide while the reaction in the presence of $SmCl_3$ produced a large number of isomers and oligomers of propylene oxide as by-products. The simple physical mixture of Sm_2O_3 and $SmCl_3$ (the $SmCl_3/Sm_2O_3$ molar ratio of 2) was not

TABLE 1

Propylene Carbonate Synthesis from Carbon Dioxide and Propylene Oxide Catalyzed by Lanthanide Oxychlorides[a]

Entry	Catalyst	Surface area (m^2/g)	Yield (%)	Selectivity[b] (%)
1	LaOCl	3.9	10.9	89.3
2	PrOCl	6.1	16.6	93.3
3	NdOCl	6.4	20.2	76.2
4	SmOCl	8.5	57.5	97.4
5	EuOCl	8.3	18.9	82.5
6	GdOCl	10.2	20.4	81.6
7	DyOCl	9.0	18.8	83.2

[a] Propylene oxide, 57.2 mmol; catalyst, 1 g; CO_2, 14 MPa; 473 K; 8 h.

[b] Isomers of propylene oxide, such as acetone and propionaldehyde, and oligomers of propylene oxide and their derivatives were formed as by-products.

TABLE 2

Propylene Carbonate Synthesis from Carbon Dioxide and Propylene Oxide[a]

Entry	Catalyst	Additive	Yield (%)	Selectivity[b] (%)
1	SmOCl	None	57.5	97.4
2	Sm_2O_3	None	7.1	91.0
3	$SmCl_3$	None	3.3	4.0
4	$Sm_2O_3 + SmCl_3$[c]	None	11.8	12.5
5	MgO	None	22.6	78.2
6	Mg–Al oxide	None	23.7	31.4
7	γ-Al_2O_3	None	<0.1	<0.1
8	SmOCl	DMF[d]	99.0	99.0
9	MgO	DMF	52.2	83.4
10	Mg–Al oxide	DMF	74.2	75.3
11	γ-Al_2O_3	DMF	55.4	77.8
12	None	DMF	2.4	96.0
13	SmOCl	PC[e]	70.8	98.2

[a] Propylene oxide, 57.2 mmol; additive, 5 cm^3; catalyst, 1 g; CO_2, 14 MPa; 473 K; 8 h.

[b] Isomers of propylene oxide, such as acetone and propionaldehyde, and oligomers of propylene oxide and their derivatives were formed as by-products.

[c] Physical mixture of Sm_2O_3 (0.405 g) and $SmCl_3$ (0.595 g) (a $SmCl_3$/Sm_2O_3 molar ratio of 2).

[d] *N*,*N*-Dimethylformamide.

[e] Propylene carbonate.

effective for the reaction (entry 4). As we postulated, the coexistence of oxide ion and chloride ion in the same crystal structure seems important for promoting the reaction. For Mg–Al mixed oxide and Cs/Al_2O_3 catalysts, it has been suggested that acid–base bifunction is the key to catalyzing the cycloaddition reaction (6, 7b). For the SmOCl catalyst, therefore, we propose a postulated reaction mechanism, in which propylene oxide and CO_2 are activated by the Lewis acidic Sm^{3+} sites adjacent to Cl^- and the Lewis basic O^{2-} sites adjacent to Sm^{3+}, respectively (Scheme 2).

It is noteworthy that the yield and selectivity of the SmOCl catalyst was higher than those of the previously reported MgO (5), Mg–Al mixed oxide (6), and γ-Al_2O_3 (Table 2, entries 5–7). The yield of propylene carbonate for the SmOCl catalyst was improved by adding polar organic solvents such as DMF or propylene carbonate (entries 8 and 13). It is reported that DMF alone promotes the carbonate formation from styrene oxide under supercritical CO_2 conditions (14). In this study, however, DMF hardly catalyzed the reaction (entry 12). Note that the addition of DMF was necessary for MgO, Mg–Al oxide, and γ-Al_2O_3 to achieve high yields (entries 9–11). The reason the addition of DMF promotes the propylene carbonate formation is not clear, but DMF may increase the diffusion or the solubility of the propylene carbonate formed.

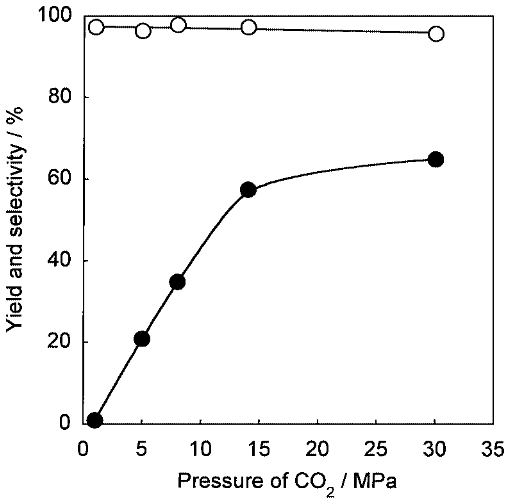
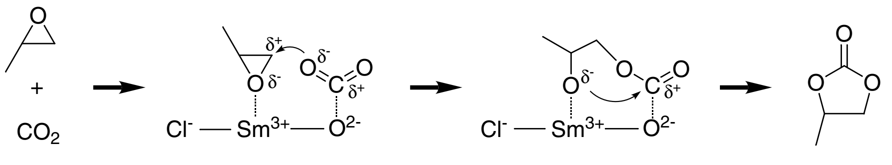


FIG. 2. Effect of CO_2 pressure on the yield (●) and selectivity (○) of propylene carbonate for SmOCl. Propylene oxide, 57.2 mmol; SmOCl, 1 g; 473 K; 8 h.

Figure 2 shows the effect of CO_2 pressure on the yield and selectivity of propylene carbonate for the SmOCl catalyst. The yield strongly depended on CO_2 pressure, and supercritical CO_2 was effective for the reaction. The reaction in supercritical CO_2 was also advantageous in terms of product separation from the reaction media. Thus, visual observation through a sapphire window revealed that propylene oxide and supercritical CO_2 initially formed a uniform phase while propylene carbonate was separated out from the supercritical CO_2 phase after the reaction. Therefore, supercritical CO_2 can be recycled, maintaining the high pressure.

In conclusion, the SmOCl catalyst showed excellent activity and selectivity for the propylene carbonate synthesis from supercritical CO_2 and propylene oxide even in the absence of additional organic solvents. The new procedure has the advantage of easy product separation from catalyst and reaction media. If one considers the small surface area of the SmOCl catalyst, the enlargement of the surface area, for example, by dispersing SmOCl on high-surface-area supports would further enhance productivity.



SCHEME 2. Postulated mechanism for the cycloaddition reaction of CO_2 to propylene oxide over SmOCl.

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