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Chemical fixation of carbon dioxide to propylene carbonate using smectite catalysts with high activity and selectivity

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The reaction of propylene oxide and carbon dioxide to propylene carbonate was carried out using Mg-, Ni- and Mg-Ni-containing smectite catalysts which contain different amounts of alkali atoms such as sodium, potassium and lithium. These catalysts are highly active and selective for this reaction. The catalytic activity strongly depends on the elemental composition of the catalyst used. Particularly the amount of alkali atoms incorporated in the catalyst is the most important factor governing the catalytic performance. The most active catalyst among those prepared in the present study shows a turnover number of 105 mmol/g for the propylene carbonate formation, which is the highest turnover number compared with those reported so far (10 mmol/g) for the title reaction.

KEY WORDS: smectite; reaction of propylene carbonate; fixation of carbon dioxide; heterogeneous catalyst.

1. Introduction

The development of environmentally benign processes based on carbon dioxide, which is one of the greenhouse-effect gases, has gained considerable attention in recent years [1–3]. Chemical fixation of carbon dioxide to valuable chemicals is one of the important approaches in this direction. The addition of carbon dioxide to epoxides is a powerful candidate for CO_2 fixation to produce five-member cyclic carbonates [4]. The five-member cyclic carbonates have several applications; for example, ethylene carbonate is an excellent solvent for many polymers and resins [5]. Other important applications include their use as an intermediate for the manufacture of several important chemicals such as dialkyl carbonates, glycols, carbamates, pyrimidines, purines and so on [5]. The five-member cyclic carbonates are conventionally produced via corrosive, poisonous and hazardous routes using phosgene and glycols. Currently manufacturers have shifted to production based on carbon dioxide and epoxides as starting materials in the presence of base catalysts. Various catalysts such as alkali metal halides, onium halides, DMF, MgO, and Mg-Al mixed oxides have been explored earlier [4,6–8]. Commercial use of homogeneous catalysts including alkali metal halides and onium salts is restricted due to problems associated with the catalyst-product separation and side reactions such as decomposition and polymerization, which could also take place during the distillation after the reaction. Inorganic heterogeneous catalysts generally possess high thermal stability and their recycling is easy. There are only three reports on the use of heterogeneous catalysts, which use Mg-Al mixed oxides [6], alkali modified zeolite [7], and basic metal oxides [8]. However, the activity and/or the selectivity reported for these catalysts was not so high.

Smectite is one of the layered clay minerals, in which one layer consists of one octahedral sheet sandwiched by two tetrahedral sheets. The octahedral sheet contains divalent or trivalent cations such as Mg^{2+} and Al^{3+} surrounded by six oxygen atoms and the tetrahedral sheet contains Si^{4+} cations surrounded by four oxygen atoms. The trilayers are negatively charged and are held together by electrostatic interaction with exchangeable cations in the interlayer region. It is possible to introduce various transition metal cations in the octahedral sheet and alkali metal cations in the interlayer. We have earlier reported the synthesis of various smectites containing nickel [9] and magnesium [9,10] that have both acidic and basic sites. The acidic and basic properties of the smectites are tunable [9,10], being a great advantage for them to be used as catalysts. In this paper we report on application of these smectite materials as catalysts for the reaction of carbon dioxide and propylene oxide (PO) to propylene carbonate (PC). It is shown that the catalytic performance of the smectite catalysts strongly depends on the amount of alkali incorporated in them and specific activity observed is very high, as compared with those reported so far in the literature.

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Table 1
Composition of smectite catalysts prepared

Catalyst	Number of atoms in a unit cell							BET area (m^2/g)
	Si	Mg	Ni	Na	K	Li	F	
(a) S-Mg-Na	8	6.62	–	1.10	–	–	–	333
(b) S-Mg-Na-K-1	8	6.17	–	0.63	0.02	–	–	339
(c) S-Mg-Na-K-2	8	6.43	–	1.5	0.06	–	–	273
(d) S-Mg-Na-K-3	8	6.44	–	2.28	0.12	–	–	186
(e) S-Mg-Na-K-4	8	6.44	–	2.81	0.13	–	–	110
(f) S-Mg-Na-Li	8	5.58	–	0.66	–	0.61	–	293
(g) S-Ni-Na-1	8	–	5.75	0.14	–	–	–	413
(h) S-Ni-Na-2	8	–	5.97	0.56	–	–	–	394
(i) S-Ni-Na-3	8	–	5.9	1.4	–	–	–	333
(j) S-Ni-Na-Li-1	8	–	5.69	0.4	–	0.31	–	387
(k) S-Ni-Na-Li-2	8	–	5.61	0.97	–	0.39	–	302
(l) S-Ni-Na-Li-3	8	–	7.04	1.54	–	0.79	–	159
(m) S-Ni-Na-F	8	–	6.17	0.75	–	–	3	293
(n) S-Ni-Na-Li-F	8	–	6.84	1.22	–	0.6	3	256
(o) S-Mg-Ni-Na	8	3.08	3.08	1.21	–	–	–	370
(p) S-Mg-Ni-Na-K	8	2.87	3.45	1.5	0.74	–	–	154

2. Experimental

Magnesium and/or nickel containing smectite catalysts were synthesized according to the methods developed by Torri and Iwasaki [11,12]. In brief, an alkali solution was added to an acidic aqueous solution of sodium silicate and magnesium or nickel chloride. The precipitated hydrous oxide, after being filtered, was autoclaved at temperatures between 110 and 300 °C. The catalysts obtained were dried in an oven at 110 °C for 15 h. The composition of the smectite catalysts prepared was determined by an X-ray fluorescence method and the results obtained are listed in table 1. These catalysts were coded by the name of the atom incorporated in the catalyst except silicon and oxygen, as S-Mg-Na, S-Mg-Na-K, etc. For the catalysts of S-Mg-Na-K, S-Ni-Na, S-Ni-Na-Li, numbers are added such as S-Mg-Na-K-1, S-Mg-Na-K-2, etc. In these samples, the amount of the incorporated alkali atoms increases in numerical order.

All reaction experiments were carried out in a 50 ml stainless steel autoclave. Typical conditions and procedures are as follows. Propylene oxide (57 mol) and the catalyst (0.9 g) were charged into the reactor. Then CO_2 was injected up to 1 MPa. The reactor was heated up to 150 °C and then liquid CO_2 was further injected up to 8 MPa under stirring. The mixture was stirred for 15 h. After the reaction, the reactor was cooled to 0 °C by ice-water and depressurized by a back pressure regulator. The liquid reaction mixture was analyzed by a gas chromatograph with a flame ionization detector and a mass spectrometer.

Basic properties of the catalysts were measured by temperature programmed desorption (TPD) of adsorbed CO_2. After a stream of 20 vol% CO_2-He mixture was passed over 0.25 g of the catalyst at room temperature for 20 min, gases in the reactor were flushed with a helium stream at a flow rate of 100 cm^3/min. Then, the temperature was ramped at a heating rate of 10 °C/min while passing the helium carrier. The effluent from the reactor was analyzed by gas chromatography.

3. Results and discussion

The reaction results obtained are presented in table 2. S-Mg-Na catalyst gives 47.7% conversion of propylene oxide with a selectivity of 53.7% for propylene carbonate.

Table 2.
Results on the reaction of PO and CO_2 in the presence of smectite catalysts [a]

Catalyst	Conversion of PO (%)	Selectivity for PC (%) [b]	Yield of PC (%)
(a) S-Mg-Na	47.7	53.7	25.6
(b) S-Mg-Na-K-1	64.2	55.7	35.8
(c) S-Mg-Na-K-2	55.1	65.9	36.3
(d) S-Mg-Na-K-3	60.9	85.3	51.9
(e) S-Mg-Na-K-4	85.6	94.3	80.7
(f) S-Mg-Na-Li	24.2	82.6	20.0
(g) S-Ni-Na-1	31.6	43.9	13.9
(h) S-Ni-Na-2	21.0	99.2	20.9
(i) S-Ni-Na-3	44.2	84.5	37.4
(j) S-Ni-Na-Li-1	26.8	81.0	21.8
(k) S-Ni-Na-Li-2	39.3	96.9	38.1
(l) S-Ni-Na-Li-3	39.1	82.1	32.3
(m) S-Ni-Na-F	54.6	90.0	49.1
(n) S-Ni-Na-Li-F	21.8	70.2	15.3
(o) S-Mg-Ni-Na	77.7	14.7	11.4
(p) S-Mg-Ni-Na-K	32.6	89.2	29.1

[a] PO, 57 mmol; $CO_2 = 8$ MPa; catalyst, 0.9 g; temperature, 150 °C; time, 15 h.
[b] Selectivity = (the amount of PC formed/the amount of PO consumed) × 100.

Most byproducts other than PC consisted of compounds produced *via* the condensation of PO and/or PG, which could be catalyzed by acidic sites. When potassium is additionally introduced in the sample, the conversion of PO and the selectivity for PC increase (S-Mg-Na-K series). The yield of PC tends to increase with the total amount of sodium and potassium incorporated. The catalyst of S-Mg-Na-K-4, which contains the largest amounts of sodium and potassium, gives a high PO conversion of 85% with a high PC selectivity of 94.3%. A partial replacement of sodium with lithium also improves the selectivity for PC (S-Mg-Na-Li). Improvement of the PC selectivity is also observed when nickel replaces magnesium (S-Mg-Na and S-Ni-Na-3). The nickel-containing smectites, except for S-Ni-Na-1, show high selectivity values for PC. However, the smectites containing both magnesium and nickel (S-Mg-Ni-Na and S-Mg-Ni-Na-K) are found to be not effective.

The effect of fluorine atoms is complicated. When fluorine atoms are introduced into the sample of S-Ni-Na, there is an increase in the conversion of PO and selectivity for PC (S-Ni-Na-3, S-Ni-Na-F). In contrast with this, introduction of fluorine atoms into S-Ni-Na-Li causes a decrease in the conversion and the selectivity (S-Ni-Na-Li-3, S-Ni-Na-Li-F). Probably, the presence of lithium should cause such a difference.

Comparison between tables 1 and 2 clearly shows that there is no relationship between the BET area and the activity and/or selectivity. It is also suggested that the yield of PC tends to increase with the amount of alkali atoms in the catalyst. In figure 1 the yield of PC is plotted against the amount of alkali atoms in a unit cell. Although there is some deviation, the yield of PC increases with the amount of alkali atoms in a unit cell. Thus, it can be concluded that it is an important factor governing the catalytic performance of the smectites.

It has recently been suggested that both moderately and strongly basic sites are active for the title reaction [8]. To measure the basic properties of the smectite catalysts, TPDs of adsorbed CO_2 were carried out. Figure 2 illustrates the TPD spectra obtained for the catalysts of the series of S-Mg-Na-K, S-Ni-Na and S-Ni-K-Li. For all of the catalysts, a sharp peak is seen around 100 °C. This peak is assigned to the desorption of CO_2 physisorbed or adsorbed on weakly basic sites. In a temperature region above 200 °C, several peaks appear. The intensity and the temperature of these peaks are different between the catalysts. This means that the strength and the number of basic sites vary with the composition of the catalyst. Although a conclusive definition was difficult, the peaks seen between 200 and 600 °C were assigned to the desorption of CO_2 adsorbed on moderately basic sites, while the peaks above 600 °C were assigned to the desorption of CO_2 adsorbed on strongly basic sites. As figure 2 shows, larger CO_2 desorption peaks appear above 200 °C for the smectites having larger amounts of alkali atoms. Thus, it is highly probable that alkali atoms are involved in the basic sites which are active for the title reaction.

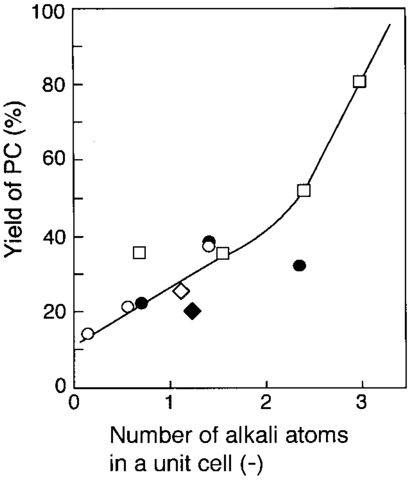

Figure 1. Effect of alkali content on the yield. ◇, S-Mg-Na; □, S-Mg-Na-K; ◆, S-Mg-Na-Li; ○, S-Ni-Na; ●, S-Ni-Na-Li.

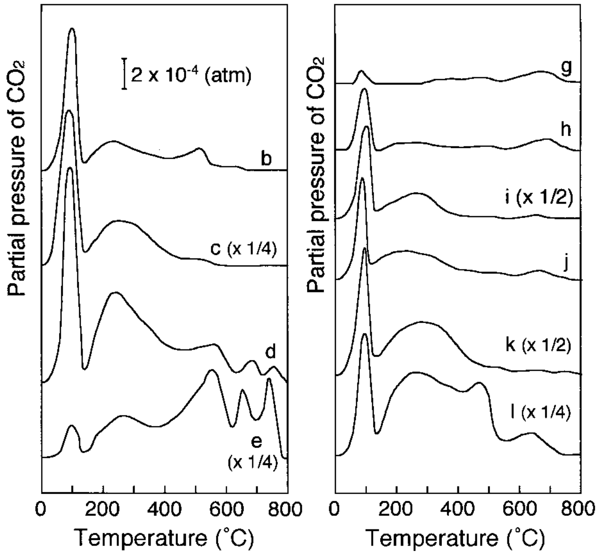

Figure 2. TPD spectra of CO_2 adsorbed on the smectite catalysts. Letters for the spectra correspond to those for the catalysts listed in table 1.

The catalyst performance has also been tested with various amounts of S-Mg-Na-K-2 catalyst. Figure 3 shows changes of the PC yield and of the turnover number (TON) for PC formation with the catalyst loading. Although the yield increases with increasing amount of catalyst, TON decreases. The selectivity (94.3%) for PC was not affected by the amount of the catalyst used. Among the TONs shown in the figure, the lowest one is 51 mmol/g but it is the highest value compared with those reported so far for this reaction using inorganic heterogeneous catalysts. Previously, Yamaguchi *et al.* [6] and Yano *et al.* [7] reported such TONs of 8 mmol/g and 10 mmol/g for the formation of PC, respectively, under reaction conditions similar to those employed in the present study. It is to be noted that

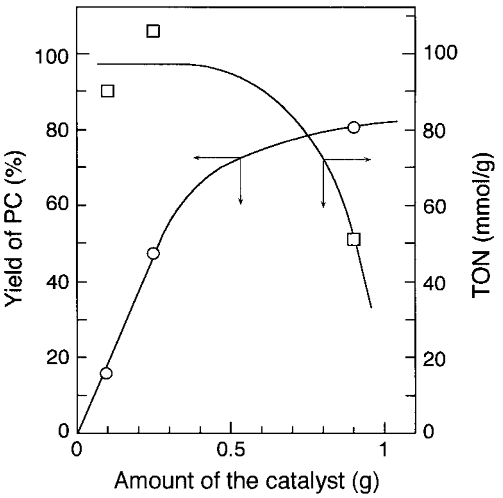

Figure 3. Effect of catalyst loading on the yield of PC and the turnover number.

they used DMF as an additional solvent, which itself is a catalyst for the reaction and has potential problems associated with the separation. The present reaction does not use any solvent, contributing to the development of more eco-friendly reaction and separation processes.

4. Conclusions

The reaction of propylene oxide and carbon dioxide to propylene carbonate was carried out by using magnesium, nickel and magnesium–nickel containing smectite catalysts which contain various amounts of alkali metals such as sodium, potassium and lithium. The catalysts give very high activity and selectivity. The yield of PC strongly depends on the amount of alkali atoms in a unit cell. TONs in a range of 46–118 mmol/g have been obtained using the catalyst of S-Mg-Na-K (Si 8, Mg 6.44, Na 2.81, K 0.13). This TON is the highest reported so far for this reaction.

References

[1] P.G. Jessop, T. Ikariya and R. Noyori, Science 269 (1995) 1065.
[2] M. Aresta and E. Quaranta, CHEMTECH (1997) 32.
[3] A.A. Shaikh and S. Sivaram, Chem. Rev. 96 (1996) 951.
[4] N. Kihara, N. Hara and T. Endo, J. Org. Chem. 58 (1993) 6198 and references cited therein.
[5] K. Weissermel and H. Arpe, *Industrial Organic Chemistry* (VCH, New York, 1997), third edition.
[6] K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, J. Am. Chem. Soc. 121 (1999) 4526.
[7] T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara and T. Maeshima, Chem. Commun. (1997) 1129.
[8] B.M. Bhanage, S. Fujita, Y. Ikushima and M. Arai, Appl. Catal. A 219 (2001) 259.
[9] Y. Nishiyama, M. Arai, S.L. Guo, N. Sonehara, T. Naito and K. Torri, Appl. Catal. A 95 (1993) 171.
[10] M. Shirai, K. Aoki, T. Miura, K. Torri and M. Arai, Chem. Lett. (2000) 36.
[11] K. Torri and T. Iwasaki, Chem. Lett. (1986) 2021.
[12] K. Torri and T. Iwasaki, Clay Sci. 7 (1987) 1.