Concurrent synthesis of dimethyl carbonate and ethylene glycol via transesterification of ethylene carbonate and methanol using smectite catalysts containing Mg and/or Ni

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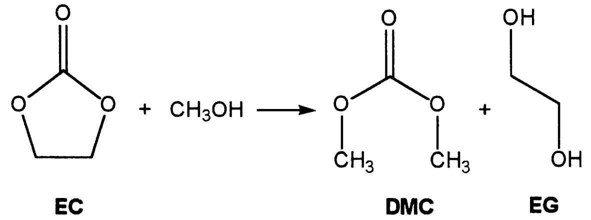
Smectites containing magnesium and/or nickel in the lattice were found to be excellent heterogeneous catalysts for the concurrent synthesis of dimethyl carbonate and ethylene glycol by transesterification of ethylene carbonate with methanol. The catalytic activity strongly depends on the elemental composition of the catalysts and is correlated with the number of moderately basic sites present on the catalyst.

KEY WORDS: smectite; ethylene carbonate; methanol; transesterification; dimethyl carbonate; ethylene glycol.

1. Introduction

Dimethyl carbonate (DMC) is a non-toxic carbonylation and methylation reagent and a precursor for polycarbonate resins, replacing poisonous phosgene and dimethyl sulfate [1–5]. Currently, DMC is manufactured by oxidative carbonylation of methanol (non-phosgene route) or by phosgenation of methanol. Both routes involve the use of poisonous and/or corrosive gases such as chlorine, phosgene and carbon monoxide and also have potential explosion hazards in the case of methanol carbonylation [2,3]. Many research works have been pursuing the direct synthesis of DMC using methanol and carbon dioxide [5]; however, most of the works are at a preliminary stage for practical application.

DMC can be synthesized concurrently with ethylene glycol (EG) by the transesterification reaction between methanol and ethylene carbonate (EC).



EC can be synthesized via the reaction of carbon dioxide and ethylene oxide [6,7]. There are some reports on the synthesis of DMC from EC and methanol [8–13]. Use of alkali metals or alkali metal compounds in homogeneous solution has been reported [8]. Commercial use of these homogeneous catalysts is restricted due to problems associated with the catalyst-product separation and side reactions such as decomposition or polymerization, which would also take place during distillation after the reaction. Various heterogeneous catalysts have also been proposed. Knifton and Duranleau [9] used free organic phosphines supported on partially cross-linked polystyrene for the reaction. Heterogeneous catalysts such as alkali-treated zeolite [10,11], basic metal oxides [12–14], and hydrotalcite [15] were also reported. However, with some of these catalysts, activity or selectivity was not so high. Most of the earlier investigators had not paid much attention to another commercially important product of EG. EG selectivity remains a key issue in this reaction.

Smectite is one of the layered clay minerals. 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. This allows the acidic and basic properties of the smectites to be tunable [16,17], being a great advantage for smectite as a catalyst. Previously, it was pointed out that controlling the

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strength of basic sites is important for the transesterification reaction between methanol and EC [13,14]. Hence, smectite could be a good catalyst for this reaction.

In the present study, various smectite catalysts have been prepared and applied for the transesterification reaction between methanol and EC. It is shown that the catalytic activity strongly depends on the number of alkali atoms incorporated in the smectite catalyst.

2. Experimental

Magnesium- and/or nickel-containing smectite catalysts were synthesized according to the methods developed by Torri and Iwasaki [18,19]. In brief, an alkali solution was added to an acidic aqueous solution of sodium silicate and magnesium and/or nickel chloride. The hydrous oxide precipitated was separated by filtration and washed with distilled water. The precipitates were mixed with an alkali hydroxide solution and then autoclaved at 200 °C for 2 h. 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, along with BET surface areas and average pore diameters, which were measured with nitrogen adsorption. 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 as S–Mg–Na–K-l, S–Mg–Na–K-2, etc., where the amount of the alkali atoms increases in numerical order. XRD spectra of the samples were measured on an XRD diffractometer (JEOL, JDX-8020) by using Ni-filtered Cu K_α radiation.

All activity measurements were carried out with a 50 ml stainless steel autoclave. Typical conditions and procedures are as follows. Ethylene carbonate (EC) (25 mmol), methanol (200 mmol), and the catalyst (0.45 g) were charged into the reactor. Then CO_2 was injected up to around 1 MPa and the reactor was heated up to 150 °C. Although CO_2 is not required for the transesterification, the presence of CO_2 prevents the decomposition of EC, as reported in our previous work [14]. The mixture was stirred for 4 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

Table 2 summarizes the results of the reaction. Most of the catalysts are highly active, as well as highly selective for DMC and EG. The high selectivity towards both products is a key issue in the title reaction, since EG has a tendency to form dimer, trimer or oligomers in the presence of base catalysts. Another issue is that EC can decompose to epoxide under such conditions [14,20]. In the presence of the smectite catalyst, these reactions are minimized.

Table 1
Composition of smectite catalysts prepared.

Catalyst	Number of atoms in a unit cell						S_{BET} [a] (m^2/g)	d_{av} [b] (nm)
	Si	Mg	Ni	Na	K	Li		
(a) S–Mg–Na	8	6.62	–	1.10	–	–	333	2.38
(b) S–Mg–Na–K-1	8	6.17	–	0.63	0.02	–	339	2.47
(c) S–Mg–Na–K-2	8	6.43	–	1.5	0.06	–	273	2.27
(d) S–Mg–Na–K-3	8	6.44	–	2.28	0.12	–	186	2.38
(e) S–Mg–Na–K-4	8	6.44	–	2.81	0.13	–	110	2.58
(f) S–Mg–Na–Li	8	5.58	–	0.66	–	0.61	293	2.41
(g) S–Ni–Na-1	8	–	5.75	0.14	–	–	413	3.32
(h) S–Ni–Na-2	8	–	5.97	0.56	–	–	394	2.68
(i) S–Ni–Na-3	8	–	5.9	1.4	–	–	333	2.40
(j) S–Ni–Na–Li-1	8	–	5.69	0.4	–	0.31	387	2.43
(k) S–Ni–Na–Li-2	8	–	5.61	0.97	–	0.39	302	2.27
(1) S–Ni–Na–Li-3	8	–	7.04	1.54	–	0.79	159	2.40
(m) S–Mg–Ni–Na	8	3.08	3.08	1.21	–	–	370	2.26
(n) S–Mg–Ni–Na–K	8	2.87	3.45	1.5	0.74	–	154	2.71

[a] BET surface area.

[b] Average pore diameter measured from nitrogen desorption isotherms.

Table 2
Results on DMC and EG synthesis via transesterification of EC and methanol. [a]

Catalyst	EC conversion (%)	Selectivity (%) [b]	
		DMC	EG
(a) S–Mg–Na	70.4	77.8	89.8
(b) S–Mg–Na–K-1	57.6	72.9	85.4
(c) S–Mg–Na–K-2	73.2	86.9	94.0
(d) S–Mg–Na–K-3	74.4	83.9	91.9
(e) S–Mg–Na–K-4	74.0	86.5	91.4
(f) S–Mg–Na–Li	61.6	89.0	96.1
(g) S–Ni–Na-1	20.8	76.9	67.3
(h) S–Ni–Na-2	32.4	80.2	74.0
(i) S–Ni–Na-3	56.4	85.1	87.2
(j) S–Ni–Na–Li-1	52.0	91.5	82.3
(k) S–Ni–Na–Li-2	70.0	85.1	89.1
(1) S–Ni–Na–Li-3	71.2	92.7	97.8
(m) S–Mg–Ni–Na	65.2	83.4	91.4
(n) S–Mg–Ni–Na–K	75.2	87.8	89.9

[a] EC, 25 mmol; methanol, 200 mmol; catalyst, 0.45 g; temperature, 150 °C; time, 4 h.

[b] Selectivity = (amount of DMC or EG formed/amount of EC consumed) × 100.

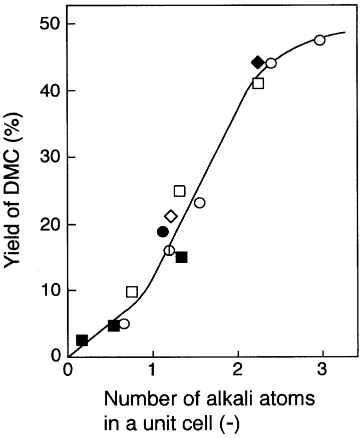

Figure 1. The relationship between the yield of DMC and the number of alkali atoms incorporated in magnesium-containing smectites. (●), (a) S–Mg–Na; (○), (b–e) S–Mg–Na–K; (⦶), (f) S–Mg–Na–Li; (■), (g–i) S–Ni–Na; (□), (j–k) S–Ni–Na–Li; (◇), (l) S–Mg–Ni–Na; (◆), (m) S–Mg–Ni–Na–K. For the reaction, the amount of catalyst was 0.25 g and the time was 1 h.

The activity and the selectivity of smectite are high as compared with earlier reports on the title reaction. For example, Tatsumi *et al.* reports 68% EC conversion with a 57% yield of DMC for the titanium silicate molecular sieve catalyst containing potassium [11]. Watanabe and Tatsumi reported that Mg–Al hydrotalcite materials are active catalysts for this reaction, and EC conversion of 70% with 58% DMC yield was reported [15]. In both of these reports they did not report EG yield and reported the formation of 2-hydroxyethyl methyl carbonate, which is thought to be an intermediate product of the DMC formation. This byproduct formation was not observed in the present study. Urano *et al.* [12] report 59% EC conversion with 30% EG and 32% DMC yield, using rare earth oxides such as yttrium oxide, cerium oxide, etc. The present authors also carried out this reaction with various basic metal oxides [14]. Although some of them were selective, the activity was lower than that of the present smectite catalysts.

Comparison of tables 1 and 2 shows that the conversion of EC depends on the catalyst composition rather than the BET surface area. The conversion tends to increase with an alkali amount up to 1.5. Above this level, the EC conversion is practically constant. This should result from the reaction being limited by the thermodynamic equilibrium, since the yield did not increase even if the reaction was carried out with a doubled amount of S–Mg–Na–K-3 or S–Mg–Na–K-4. Hence, the reaction was carried out with reduction of the catalyst amount and reaction time. In figure 1, the yields of DMC formed are plotted against the number of alkali atoms in the unit cell. It is seen that all of the data are plotted in one line, suggesting that the natures of the alkali atom and the transition metal cation present in the smectite lattice do not affect the activity of the catalyst.

It was previously suggested that moderately basic sites are active for the title reaction [13,14]. To measure the basic properties of the smectite catalysts, TPD of adsorbed CO_2 was carried out. Figure 2 illustrates the TPD spectra obtained. 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

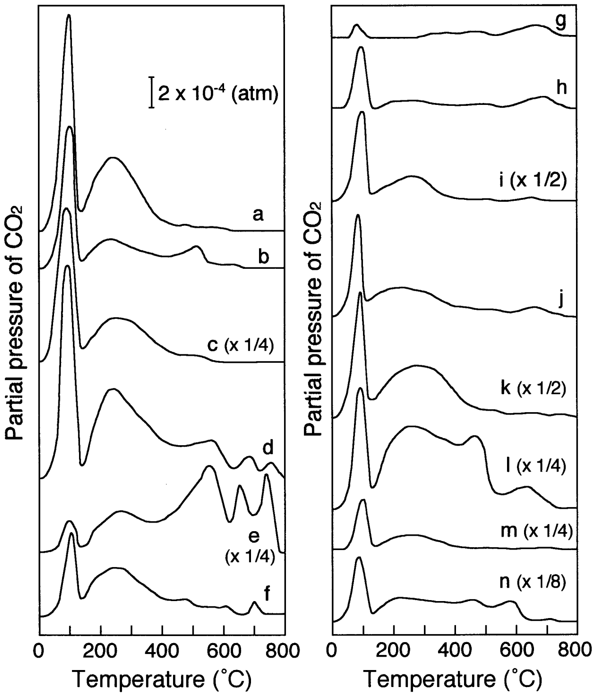

Figure 2. TPD spectra of CO_2 adsorbed on the smectite catalysts. The letters for the spectra correspond to those for the catalysts listed in table 1.

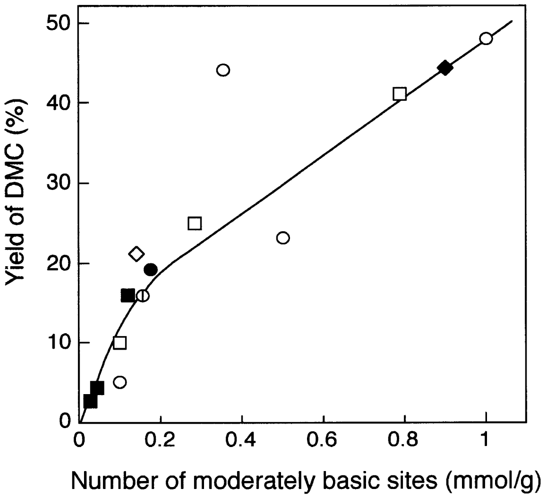

Figure 3. The relationship between the yield of DMC and the number of moderately basic sites, which was determined from the peak area between 200 and 600 °C in the TPD run. The symbols represent the same catalysts as those in figure 1. The amount of catalyst was 0.25 g and the reaction time was 1 h.

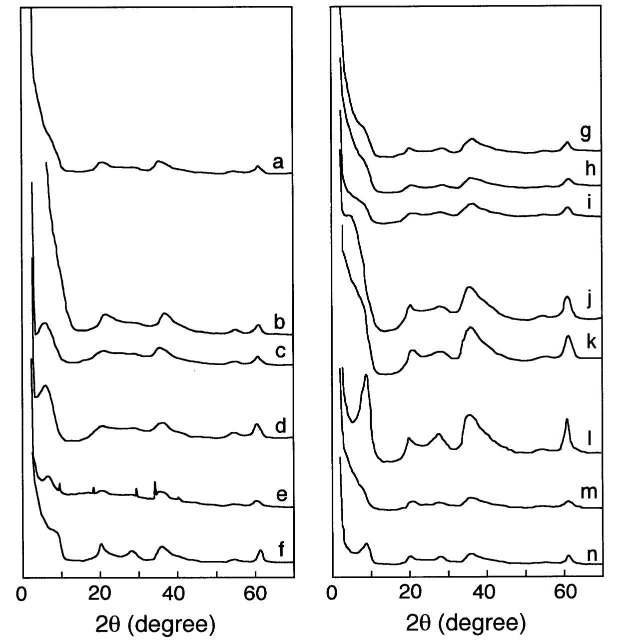

Figure 4. XRD patterns of smectite catalysts. The letters for the spectra correspond to those for the catalysts listed in table 1.

weakly basic sites. In the 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 now difficult, the peaks seen between 200 and 600 °C were assigned to the desorptions 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. The number of basic sites was estimated from the peak area in the TPD run. No good correlation of the activity with the total number of weakly and strongly basic sites or the total number of basic sites was obtained, but it was correlated with the number of moderately basic sites, as shown in figure 3. An exception is the catalyst of S–Mg–Na–K-3. Hence, moderately basic sites present on the smectite catalyst may be responsible for the title reaction. As shown above, the activity for the title reaction of the smectite catalyst mostly depends on the number of alkali atoms incorporated. The exact structure of moderately basic sites, which is responsible for the reaction, has not been given at the present stage. However, it is highly probable that alkali atoms are involved in such sites.

Figure 4 illustrates the XRD patterns of the samples of the S–Mg–Na–K series. All of the samples show the XRD pattern of smectite. Only in the pattern of S–Mg–Na–K-4 (e in figure 4) are small spikes seen together with the peaks of smectite, suggesting a small amount of another compound such as sodium magnesium silicate hydroxide is formed in this sample. The samples of c, d, e, l and n, which contain large amounts of alkali metals, exhibit the (001) peak of smectite between 5 and 9°. The distance between the (001) faces was determined from the (001) peak position, and the values of the distance were 1.67, 1.64, 1.47, 1.02, and 1.03 nm for the catalysts of c, d, e, l, and n, respectively. If the thickness of the trilayer of smectite is taken into account, the space between the interlayers is not enough for the substrates to diffuse into, particularly for the Ni-containing samples of l and m. However, as shown previously [21,22], small fragments of smectite existing as pillars between silicate layers would result in the formation of mesopores between the layers. Actually, the average pore diameters of these catalysts are above 2 nm (table 1). Hence, the reaction can proceed in the mesopores produced by the pillars. On the other hand, the other samples containing smaller amounts of alkali atoms show the (001) peak as a shoulder of the intense reflection signal starting around 2.5°, suggesting that the distance between the (001) faces of these catalysts should be larger than 3 nm. The reaction could proceed inside the interlayers. Naturally, it cannot be completely excluded that the mesopores produced by the pillars of the fragments exist in these catalysts and the reaction can proceed in the mesopores.

4. Conclusions

In conclusion, smectites containing Mg and/or Ni in the lattice were found to be excellent heterogeneous catalysts for the concurrent synthesis of dimethyl carbonate and ethylene glycol by transesterification of ethylene carbonate with methanol. The catalytic performance is dependent upon the amount of alkali metals introduced in the lattice. It was found that the activity depends on the number of moderately basic sites present on the catalyst.

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