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Direct synthesis of organic carbonates from the reaction of CO_2 with methanol and ethanol over CeO_2 catalysts

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Abstract

The catalytic properties of CeO_2 catalysts in direct synthesis of dimethyl carbonate (DMC) from CH_3OH and CO_2 were investigated. The formation rate of DMC over the catalysts calcined at 873 K and above was almost proportional to the surface area of catalysts. However, CeO_2 calcined at 673 K showed lower activity than expected from the surface area. From the results of catalyst characterization, CeO_2 calcined at 673 K contained considerable amount of amorphous phase. In contrast, the ratio of amorphous phase decreased on the catalysts calcined at 873 K and above. This suggests that stable crystallite surface is active for the reaction.

In the $CH_3OH + C_2H_5OH + CO_2$ reaction at low temperature, ethyl methyl carbonate (EMC) was formed, and selectivity of EMC formation was comparable to that of DMC. The formation route is discussed by the comparison with transesterification reaction.

Keywords: CO_2; CeO_2; Organic carbonate; Methanol; Ethanol; Transesterification

1. Introduction

Development of CO_2-based methods for the synthesis of carbonic acid diesters is very attractive in terms of CO_2 chemical fixation and green chemistry, and this can also contribute to the substitute for phosgene with CO_2 [1]. Dimethyl carbonate (DMC), the lowest homologue of this family, is drawing attention as a safe, noncorrosive, and environmentally acceptable alternative to methylating and carbonylating agents [2]. In addition, it has been proposed that DMC can be used as an octane booster in gasoline and as an additive to diesel fuel to decrease the emission of particulate matter [3].

It has been known that synthesis of the organic carbonate by the reaction of alcohols with CO_2 is one of potential routes. It has been reported that DMC can be synthesized directly from CH_3OH and CO_2 (Eq. (1)) in the presence of dialkoxydibutyltin as a homogeneous catalyst [4].

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (1)$$

It has been also reported that DMC was synthesized from CH_3OH and CO_2 in the presence of Sn(IV) and Ti(IV) alkoxides and the metal acetates [5]. These alkoxide catalysts can be decomposed with H_2O and this can cause catalyst deactivation.

In contrast, it has been also reported that DMC was selectively synthesized from CH_3OH and CO_2 using ZrO_2 and H_3PO_4/ZrO_2 as heterogeneous catalysts [6]. From the result of catalyst characterization, it is suggested that the acid–base bifunction is an important factor for the selective DMC synthesis from CH_3OH and CO_2 [7,8]. Furthermore, CeO_2–ZrO_2 solid solution is more effective catalyst for DMC synthesis from CH_3OH and CO_2 than ZrO_2 and H_3PO_4/ZrO_2 [9]. Recently, it has been also reported that these catalysts are effective to the direct synthesis of cyclic carbonate from CO_2 and diols such as ethylene glycol and propylene glycol [10,11].

In this article, we prepared CeO_2 using various kinds of precursors under various calcination temperatures, and catalytic performance in the synthesis of DMC from CH_3OH and CO_2 was investigated. Combined with the characterization results by means of BET, X-ray diffraction (XRD), and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), we discuss the relation between activities and catalyst properties. Furthermore, one of CeO_2 catalysts was applied to the synthesis of ethyl methyl carbonate in $CH_3OH + C_2H_5OH + CO_2$ reaction.

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2. Experimental

CeO_2 catalysts were prepared by calcining cerium hydroxides (commercially available from Wako Pure Chemical Industries and Soekawa Chemicals) or cerium oxides (commercially available from Daiichi Kigenso, Japan) for 3 h under air atmosphere at various temperatures (673–1273 K). The details are listed in Table 1.

The reaction was carried out in a stainless-steel autoclave reactor with an inner volume of 70 mL. The standard procedure was as follows: 6.1 g CH_3OH (192 mmol, Wako Pure Chemical Industries, 99.8% min.) and the catalyst were put into the autoclave, and then the reactor was purged with CO_2. After that, the autoclave was pressurized with CO_2 (200 mmol; Takachiho Trading Co. Ltd., 99.99%). The reactor was then heated and magnetically stirred constantly during the reaction. After the reaction, 2-propanol was added to the liquid phase as a standard substance for quantitative analysis. Products in liquid and gas phases were analyzed by a gas chromatograph (GC, GL-science, GC353) equipped with FID. The capillary column TC-WAX was used for separation. In all the experiments, the formation of ethers, which are expected byproducts during the carbonate synthesis, were under the detection limits of FID-GC.

The surface area of catalysts was measured with BET method (N_2 adsorption) using Gemini (Micromeritics). DRIFT spectra were obtained using a Magna 550 (Nicolet) with an MCT detector. An in situ cell (Spectra-Tech) was used for high-temperature and high-pressure observations. Catalyst powder was placed in a sample cup in the cell. This cell was connected to the high-pressure gas flow system. Pretreatment was carried out in N_2 flow at 673 K for 0.5 h. CH_3OH (Wako Pure Chemical Industries, 99.8% min.) was introduced by pulsed gas under atmospheric pressure at 403 K with N_2 as a carrier gas until the coverage reached the saturation level. Then, CO_2 (Takachiho Trading Co. Ltd., 99.99%) was introduced onto the CH_3OH-preadsorbed sample under atmospheric pressure, and CO_2 was pressurized stepwise up to 5 MPa while the sample temperature was kept at 403 K. Each spectrum was obtained 3 min after the introduction of CO_2 at each pressure.

XRD was measured by an X-ray diffractometer (PHILIPS, Philips X'Pert MRD) with Cu Kα (40 kV, 20 mA) radiation.

Table 1
List of prepared CeO_2 catalysts

Precursor	Company	Calcination temperature (K)	BET surface area (m^2/g)
CeO_2-HS	Daiichi Kigenso	1273	13
		1073	41
		873	80
		673	131
CeO_2-FN	Daiichi Kigenso	1273	4
		1073	6
		873	45
		673	91
CeO_2-FP	Daiichi Kigenso	1273	4
		1073	12
		873	20
		673	23
$Ce(OH)_4$	Wako Pure Chemical	1273	2
		1073	14
		873	42
		673	66
$Ce(OH)_4$	Soekawa Chemicals	1273	2
		1073	12
		873	34
		673	68

3. Results and discussion

3.1. Performance and characterization of CeO_2 in DMC formation in $CH_3OH + CO_2$ reaction

Fig. 1 shows the relation between surface area and the amount of DMC formation in $CH_3OH + CO_2$ reaction over CeO_2 catalysts prepared from different precursors calcined at various temperatures. As listed in Table 1, the BET surface area of every sample decreased with increasing calcination temperature. Under these reaction conditions, the equilibrium level of DMC formation is 0.71 mmol, and the DMC amount in Fig. 1 did not reach the equilibrium level. This indicates that catalytic activities of CeO_2 catalysts can be reflected in Fig. 1. Except for the catalysts calcined at 673 K plotted in the circle in the figure, DMC amount was closely correlated with BET surface area as shown in Fig. 1 by dotted line. In the case of catalysts calcined at 873 K and above, it is found that the activity of DMC formation was almost proportional to BET surface area of catalysts. Low activity per surface area over the catalysts calcined at lower temperature can be due to the catalyst structure as shown and discussed later. The CeO_2-HS calcined at 873 K (BET: 80 m^2/g, Table 1), which was used in the following experiments, exhibited the highest activity in all the CeO_2 catalysts as shown in Fig. 1.

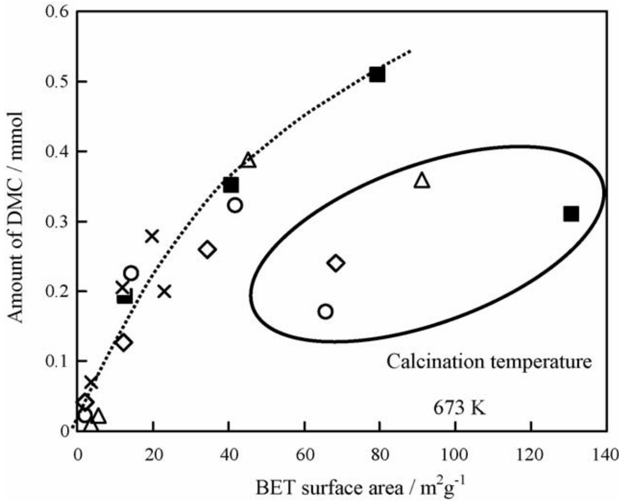

Fig. 1. Surface area dependence of DMC formation from CH_3OH and CO_2 on CeO_2. *Reaction conditions*: $CH_3OH:CO_2 = 192$ mmol:200 mmol, catalyst weight: 50 mg, reaction temperature: 403 K, reaction time: 2 h, precursor: CeO_2-HS (■), CeO_2-FN (△), CeO_2-FP (×), $Ce(OH)_4$ from Wako Pure Chemical (○), and $Ce(OH)_4$ from Soekawa Chemicals (◇).

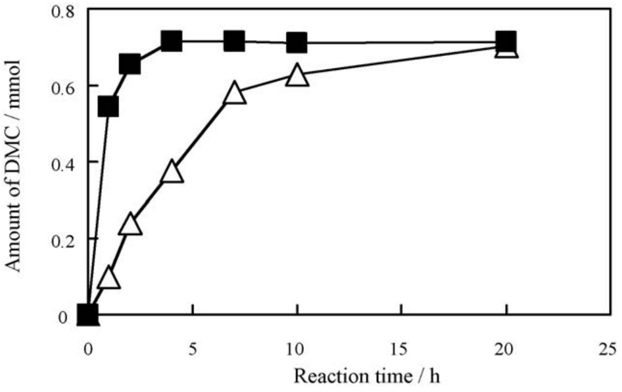

Fig. 2. Reaction time dependence of DMC formation from CH_3OH and CO_2 on CeO_2-HS calcined at 873 K. Catalyst weight: 10 mg (△) and 100 mg (■). *Reaction conditions*: $CH_3OH:CO_2$ = 192 mmol:200 mmol, and reaction temperature: 403 K.

Fig. 2 shows the reaction time dependence of DMC formation in $CH_3OH + CO_2$ reaction on CeO_2-HS calcined at 873 K. When 10 mg catalyst was used, the DMC amount increased with the reaction time and it reached about 0.71 mmol after 20 h reaction. In contrast, when 100 mg catalyst was used, the formation rate became much higher and the DMC amount reached about 0.71 mmol even after 4 h reaction. Although catalyst weight was changed, the saturation level of DMC amount was almost the same in both cases. This indicates that the plateau in Fig. 2 is not due to catalyst deactivation, but due to the reaction equilibrium of DMC formation from CH_3OH and CO_2. In addition, 10 mg CeO_2 catalyst contains 0.058 mmol of Ce ions, which is lower than 0.71 mmol. Considering that only a part of Ce ions is located at the surface, it is found that the reaction of DMC formation proceeded catalytically.

Fig. 3 shows the CO_2 amount dependence of DMC formation in $CH_3OH + CO_2$ reaction on CeO_2-HS calcined at 873 K. At 0.5 or 2 h reaction condition, the DMC amount did not reach the equilibrium level. For example, when the CO_2 amount is 200 mmol, the equilibrium level of DMC formation is about 0.71 mmol as demonstrated in Fig. 2. The formation rate of DMC increased with increasing CO_2 amount below 50 mmol of CO_2. However, above 50 mmol of CO_2, the DMC amount was almost constant in both reaction times. From these results, DMC can be synthesized from CH_3OH and CO_2 even at low CO_2 pressure although the formation rate of DMC was low at low CO_2 pressure.

Fig. 4 shows XRD patterns of CeO_2-HS calcined at various temperatures. The bulk structure of CeO_2-HS was the fluorite structure [12] and it was not affected by calcination temperature. The XRD peaks became sharper for the samples calcined at higher temperature. This indicates that the crystal growth of CeO_2 proceeded more significantly at higher calcination temperature, and this behavior is also supported by the decrease in BET surface area with increasing calcination temperature as listed in Table 1.

Fig. 5A shows the DRIFT spectra of CH_3OH adsorption and successive CO_2 introductions at 403 K on CeO_2-HS calcined at 873 K. Before the CH_3OH adsorption, the bands at 3724, 3631, and 3499 cm^{-1} were observed. These bands can be assigned to the O–H stretching modes of terminal OH (t-OH), bridged OH (b-OH), and OH on the amorphous CeO_2, respectively [13]. After CH_3OH adsorption, the bands due to t-OH and b-OH on CeO_2 disappeared, and new bands at 2913 and 2806 cm^{-1} appeared. These bands can be assigned to C–H stretching vibrations of methoxy species [14,15]. These results suggest that CH_3OH reacts with surface terminal and bridged OH groups to form methoxy species and H_2O. On the other hand, the OH group on the amorphous CeO_2 remained even after CH_3OH adsorption and successive CO_2 introductions. This indicates that CH_3OH is not adsorbed on the surface of amorphous CeO_2, and this suggests that amorphous CeO_2 cannot contribute to DMC synthesis. In addition, the bands in OH region in Fig. 5A(c) are due to the CO_2 in the gas phase.

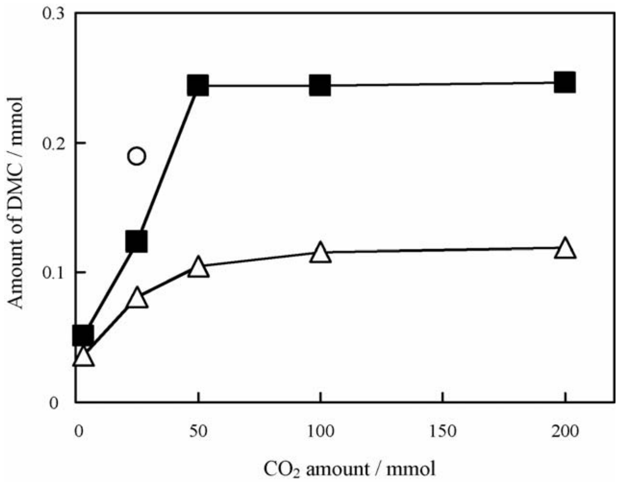

Fig. 3. CO_2 amount dependence of DMC formation from CH_3OH and CO_2 on CeO_2-HS calcined at 873 K. Reaction time: 0.5 h (△), 2 h (■), and 20 h (○). *Reaction conditions*: CH_3OH: 200 mmol, catalyst weight: 10 mg, and reaction temperature: 403 K.

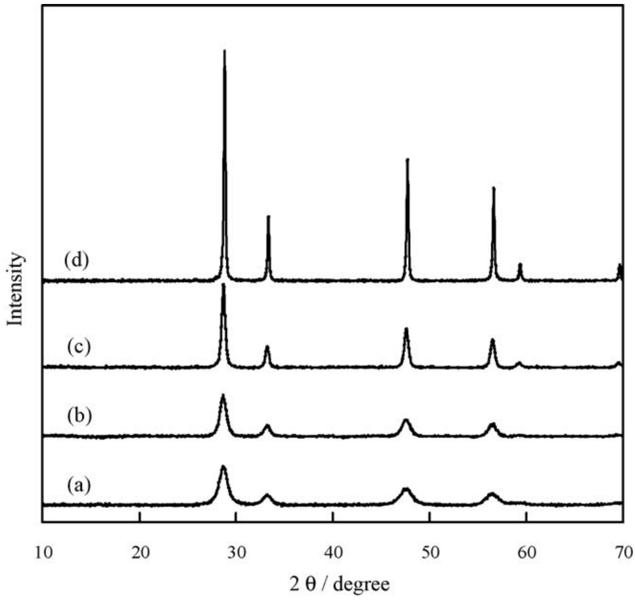

Fig. 4. XRD patterns of CeO_2-HS calcined at (a) 673 K, (b) 873 K, (c) 1073 K, and (d) 1273 K. X-ray source: Cu Kα.

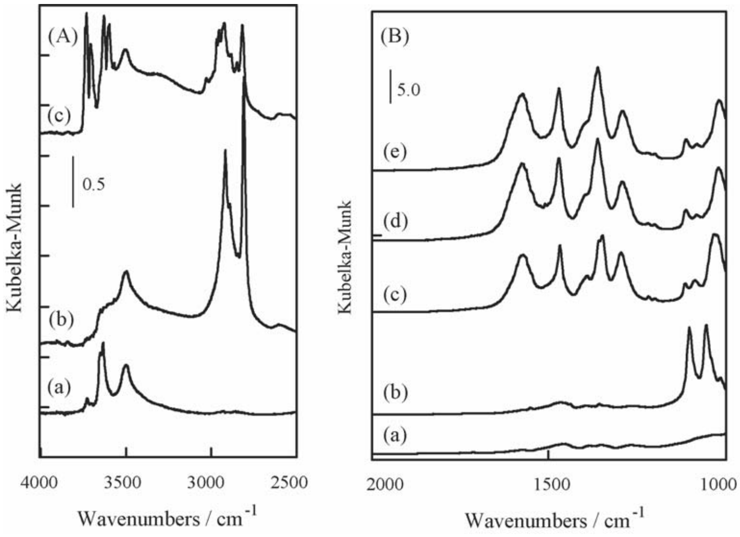

Fig. 5. DRIFT spectra of CH_3OH adsorption and successive CO_2 introductions at 403 K on CeO_2-HS calcined at 873 K: (a) in N_2 flow, (b) after CH_3OH adsorption, (c) after CO_2 introduction at 0.1 MPa, (d) at 0.5 MPa, and (e) at 5.0 MPa. Pretreatment: 773 K for 0.5 h in N_2 flow.

Fig. 5B shows the DRIFT spectra of CH_3OH adsorption and successive CO_2 introductions on the sample in the range of lower wavenumbers. CH_3OH adsorption led to the appearance of bands at 1101 and 1052 cm^{-1}. These can be assigned to the C–O stretching modes of terminal (t-OCH_3) and bridged (b-OCH_3) methoxy species, respectively [14,15]. When 0.1 MPa of CO_2 was introduced to the CH_3OH-preadsorbed catalysts, the band intensity at 1101 cm^{-1} decreased drastically, and at the same time, the bands at 1572, 1469, 1360, 1292, and 1109 cm^{-1} appeared. The bands of 1572, 1469, 1360, and 1109 cm^{-1} can be assigned to the monodentate methyl carbonate species [16,17]. At present, the band at 1292 cm^{-1} cannot be assigned. Although the intensity of these bands increased slightly with the increase in CO_2 pressure, the formation of adsorbed methyl carbonate species can be observed clearly even at 0.1 MPa of CO_2. CO_2 introduction did not affect the band at 1052 cm^{-1} assigned to b-OCH_3. These results indicate that the methyl carbonate species easily formed by the interaction between CO_2 and t-OCH_3. The similar behavior has been observed on ZrO_2 catalysts [7]. In addition, the OH group on amorphous CeO_2 remained even after the introduction of $CH_3OH + CO_2$.

Fig. 6 shows the DRIFT spectra of CO_2 adsorption at 403 K on CeO_2-HS calcined at 873 K. After CO_2 adsorption, bands at 1600, 1460, 1417, 1398, 1278, and 1217 cm^{-1} appeared. Bands at 1600, 1417, 1398, and 1217 cm^{-1} can be assigned to bicarbonate species [15,18]. Bands at 1460 and 1278 cm^{-1} are assigned to internal polydentate carbonate and bidentate carbonate, respectively [15,18]. Judging from these results, unidentified band at 1292 cm^{-1} in Fig. 5 is not originated from adsorbed CO_2 species on CeO_2 observed in Fig. 6. It is found that the band intensity was dependent on the pressure of CO_2, but the effect was very small. This indicates that CO_2 is strongly adsorbed on CeO_2 surface, which is also supported by the temperature programmed desorption of CO_2 adsorption [11].

Fig. 7 shows the DRIFT spectra of surface hydroxyl groups of CeO_2-HS calcined at various temperatures before and after CH_3OH adsorption. Before CH_3OH adsorption, the bands at 3724, 3631, and 3499 cm^{-1} assigned to the surface OH groups were observed at all samples, however, the intensity ratio of the bands was strongly dependent on the calcination temperature. On the CeO_2-HS calcined at 673 K, the intensity of the bands was stronger than those of other catalysts. This can be related to high surface area of CeO_2-HS calcined at 673 K. The relative band intensity at 3724 cm^{-1} increased with increasing calcination temperature. On the other hand, the intensity of OH on the amorphous CeO_2 decreased with increasing calcination temperature. In addition, after CH_3OH adsorption, both of bands assigned to t-OH and b-OH disappeared on all the samples, and the band assigned to OH on amorphous CeO_2 was unchanged. This result indicates that the ratio of amorphous

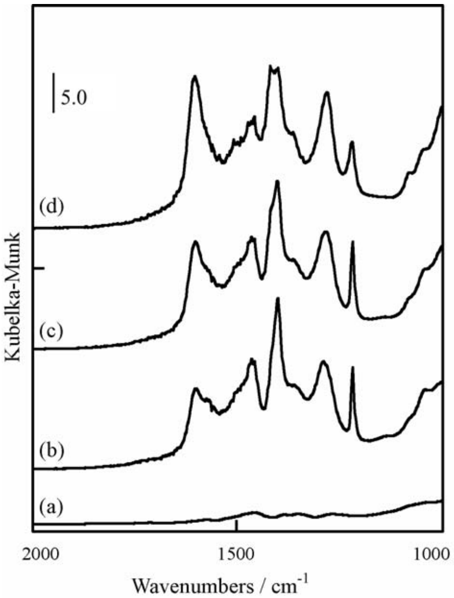

Fig. 6. DRIFT spectra of CO_2 adsorption at 403 K on CeO_2-HS calcined at 873 K: (a) in N_2 flow, (b) after CO_2 introduction at 0.1 MPa, (c) at 0.5 MPa, and (d) at 5.0 MPa. Pretreatment: 773 K for 0.5 h in N_2 flow.

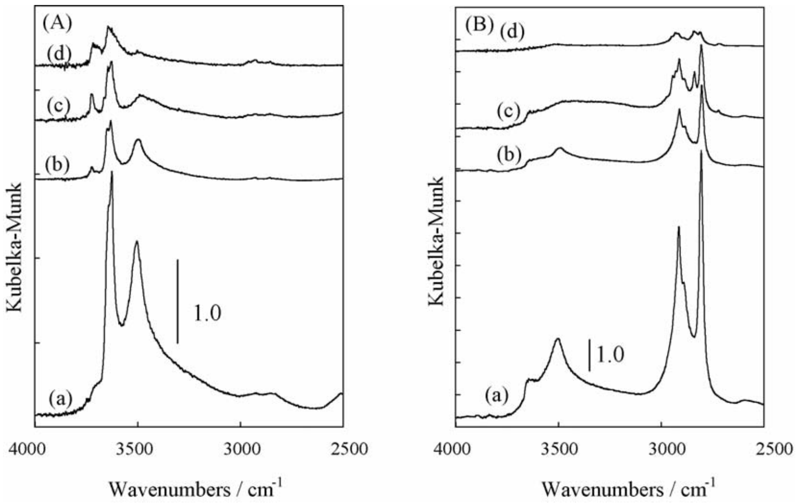

Fig. 7. DRIFT spectra of surface hydroxyl groups of CeO_2-HS calcined at (a) 673 K, (b) 873 K, (c) 1073 K, and (d) 1273 K. (A) Before CH_3OH adsorption and (B) after CH_3OH adsorption. Pretreatment: (a) 673 K and (b–d) 773 K, 0.5 h in N_2 flow.

phase to crystal phase decreases with increasing calcination temperature. This can be interpreted by the crystallization of CeO_2, which is promoted by calcination at higher temperature as shown in Fig. 4. Furthermore, this result can explain the tendency of catalyst activity shown in Fig. 1. On the CeO_2 catalysts calcined at 673 K, the activity of DMC formation per BET surface area was lower than that on the catalysts calcined at higher temperature. It is suggested that not the amorphous but the crystallite CeO_2 can be active for this reaction. Although CeO_2 calcined at 673 K has high surface area, the crystallite phase is not major and this can decrease the activity per surface area. In contrast, the crystallite phase becomes major on CeO_2 catalysts calcined at temperatures higher than 673 K. Considering that the activity of DMC formation is almost proportional to the surface area, it is suggested that the surface structure is also the same on these CeO_2 catalysts. It has been reported that the most stable surface among the low index planes is a (1 1 1) surface [19–21]. Therefore, in the case of DMC formation from $CH_3OH + CO_2$, the active surface is thought to be a stable surface like CeO_2(1 1 1). In the case of dehydration of 1,3-butanediol to unsaturated alcohols, it has been reported that the active site can be defected CeO_2(1 1 1) surface [22]. Since the number of the defect sites can decrease with the growth of CeO_2 crystallites and higher calcination temperature, if the defect site is an active site, the activity cannot be proportional to the surface area.

3.2. Synthesis of ethyl methyl carbonate in $CH_3OH + C_2H_5OH + CO_2$ reaction

Fig. 8 shows the reaction temperature dependence of $CH_3OH + C_2H_5OH + CO_2$ reaction on CeO_2-HS calcined at 873 K, which exhibited highest activity of DMC formation in $CH_3OH + CO_2$ reaction. In $CH_3OH + C_2H_5OH + CO_2$ reaction, DMC, ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) were produced, and the amount of ethers was also lower than the detection limits of GC. When the catalyst of 10 mg weight was used at low reaction temperature like 383 and 403 K, the selectivities of EMC and DMC formation were almost the same level, while in contrast, that of DEC was much lower than EMC and DMC. From the comparison of the results using 10 and 100 mg catalysts, it is found that the reaction using 10 mg at 383–423 K did not reach the equilibrium level. This means that the formation rate of DMC is almost the same as that of EMC. DEC amount

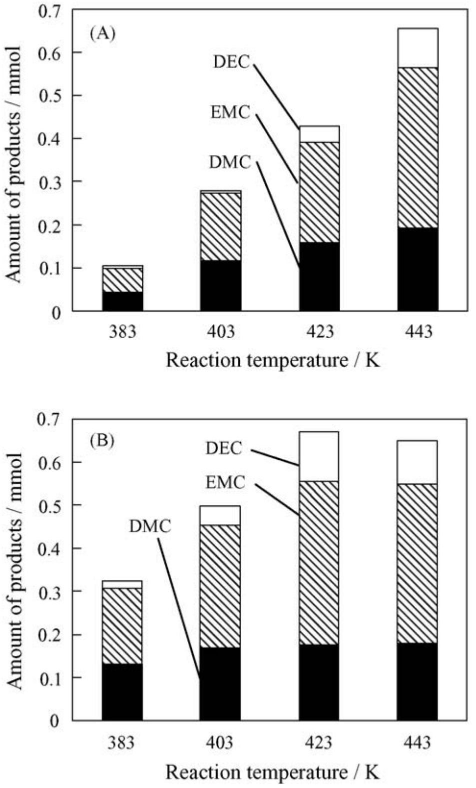

Fig. 8. Reaction temperature dependence of $CH_3OH + C_2H_5OH + CO_2$ on CeO_2-HS calcined at 873 K. Catalyst weight: (A) 10 mg and (B) 100 mg. Reaction time: 2 h, CH_3OH:C_2H_5OH:CO_2 = 100 mmol:100 mmol:200 mmol. DMC: dimethyl carbonate, EMC: ethyl methyl carbonate, and DEC: diethyl carbonate.

increased with increasing reaction temperature. In addition, the sum of these three carbonates over 100 mg catalyst increased in the range of 383–423 K, however, the sum at 443 K became smaller than that at 423 K. This kind of temperature dependence of carbonate formation has been also reported [7]. This tendency indicates that the reaction at 423 and 443 K using 100 mg catalyst reached the equilibrium level. When the reaction approaches the equilibrium level, the selectivity of DEC increased to some extent. For reference, we show the results of DMC synthesis in $CH_3OH + CO_2$ reaction and DEC synthesis in $C_2H_5OH + CO_2$ reaction in Table 2. From the comparison between DMC and DEC formation at low reaction temperature, the amounts of carbonates were dominated by the reaction rate, and the results indicate that the formation rate of DMC is much higher than that of DEC. Furthermore, from the comparison at high reaction temperature, the amount of equilibrium level of DMC was larger than that of DEC. Next, we compare the amount of DEC formation in $C_2H_5OH + CO_2$ reaction (Table 2) and $CH_3OH + C_2H_5OH + CO_2$ reaction (Fig. 8A) at 403 K using 10 mg catalyst. The DEC amount in $CH_3OH + C_2H_5OH + CO_2$ reaction was 0.006 mmol, while that in $C_2H_5OH + CO_2$ reaction was 0.09 mmol. This suggests that DEC formation is inhibited in $CH_3OH + C_2H_5OH + CO_2$ reaction. However, an important point is that the selectivity of EMC formation is as high as that of DMC formation, and it is suggested that EMC formation can be promoted from this viewpoint. In addition, the EMC selectivity was higher than that of DMC at the equilibrium level as shown in Fig. 8B at high temperature.

Here, it is necessary to discuss the formation mechanism of EMC. When EMC is directly formed from alcohols and CO_2, there are two possible formation routes. One is the reaction between adsorbed methylcarbonate species and C_2H_5OH, and the other is the reaction between adsorbed ethylcarbonate species and CH_3OH judging from the reports [7,16,23]. Although the details are not shown here, it is found that adsorbed ethylcarbonate species was formed from the reaction of preadsorbed ethoxy species with CO_2 by means of FTIR studies and similar behavior to that shown in Fig. 5 was observed. In both cases, all the terminal OH species were converted to alkylcarbonate species easily and the formation rate of these species was much higher than that of dialkylcarbonates. This indicates that both methylcarbonate and ethlycarbonate species are formed on the catalyst surface in $CH_3OH + C_2H_5OH + CO_2$ reaction and it is thought that the coverage ratio of methylcarbonate to ethylcarbonate can be dependent on the molar ratio of methanol to ethanol. In this case, the coverage ratio can be 1:1. In contrast, since the formation rate of DMC in $CH_3OH + CO_2$ is higher than that of DEC in $C_2H_5OH + CO_2$ as listed in Table 2, it is suggested that the reaction rate of adsorbed alkylcarbonate species with CH_3OH can be higher than that with C_2H_5OH, whose elementary step corresponds to the rate-determining step of dialkylcarbonate from alcohol and CO_2 [7,23]. This can explain that EMC is formed by the reaction of ethylcarbonate species with CH_3OH.

On the other hand, it is possible to form EMC via transesterification of DMC with C_2H_5OH. In order to evaluate the reaction rate of transesterification over the CeO_2 catalyst, the tests of $CH_3OH + C_2H_5OH + CO_2 + DMC$ reaction using 10 mg CeO_2 catalyst were carried out, and the results are shown in Fig. 9. Under the reaction conditions of the $CH_3OH + C_2H_5OH + CO_2 + DMC$ reaction (Fig. 9), EMC also can be formed via transesterification. At low reaction temperatures such as 383 and 403 K, the reaction rate of DMC with C_2H_5OH was much lower than the formation rate of EMC in $CH_3OH + C_2H_5OH + CO_2$ (Fig. 8A). This indicates that the transesterification route is not the main route in the formation of EMC at low reaction temperatures such as 383 and 403 K. In contrast, at higher reaction temperature, the distribution of

Table 2
Dialkyl carbonate formation in alcohol + CO_2 reaction on the CeO_2-HS catalyst

Alcohol	Reaction temperature (K)	Catalyst weight (mg)	Amount of DMC or DEC (mmol)
CH_3OH	383	10	0.05
		100	0.38
	403	10	0.24
		100	0.66
	423	10	0.47
		100	0.65
	443	10	0.62
		100	0.62
C_2H_5OH	383	10	0.02
		100	0.13
	403	10	0.09
		100	0.41
	423	10	0.22
		100	0.42
	443	10	0.37
		100	0.37

CeO_2 catalyst prepared by the calcination of CeO_2-HS at 873 K.
Reaction conditions: CH_3OH or $C_2H_5OH:CO_2$ = 200 mmol:200 mmol, and reaction time: 2 h.

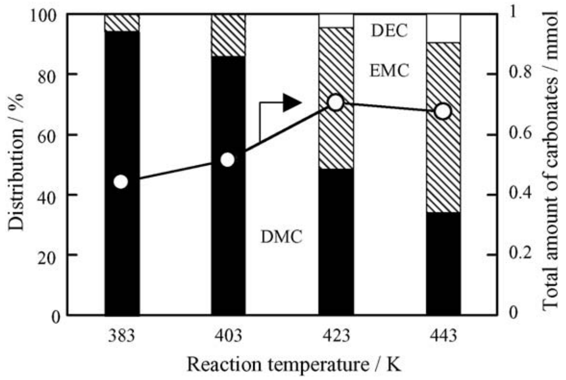

Fig. 9. Reaction temperature dependence of distribution and amount of carbonates in the $CH_3OH + C_2H_5OH + CO_2 + DMC$ reaction over CeO_2-HS calcined at 873 K. Catalyst weight: 10 mg, reaction time: 2 h, $CH_3OH:C_2H_5OH:CO_2:DMC$ = 100 mmol:100 mmol:200 mmol:0.5 mmol. DMC: dimethyl carbonate, EMC: ethyl methyl carbonate, and DEC: diethyl carbonate.

products in $CH_3OH + C_2H_5OH + CO_2 + DMC$ reaction was similar to that in $CH_3OH + C_2H_5OH + CO_2$ reaction. This indicates that the reaction rate of transesterification cannot be neglected compared to the reaction rate of carbonate formation from alcohol and CO_2, and the distribution is also influenced by the transesterification reaction. From these results, it is concluded that EMC can be formed by the reaction of adsorbed ethylcarbonate species with CH_3OH as the first step. At higher temperature, the transesterification can parallel with the reaction of alcohols with CO_2.

4. Conclusions

(1) The formation rate of DMC in $CH_3OH + CO_2$ reaction over various CeO_2 catalysts calcined at 873 K and above was almost proportional to the BET surface area of catalysts. This suggests that the active site of this reaction is on a stable crystal surface such as (1 1 1) of CeO_2.

(2) The activity of DMC formation per surface area over CeO_2 calcined at 673 K was not so high as that expected from the results on the CeO_2 calcined at 873 K and above. This can be because the amorphous phase of CeO_2, which was significantly observed by means of FTIR on the CeO_2 calcined at 673 K, does not have the activity of DMC formation.

(3) In the $CH_3OH + C_2H_5OH + CO_2$ reaction at low temperatures such as 383 and 403 K, EMC was formed and the selectivity of EMC was comparable to that of DMC. It is found that the reaction rate of the transesterification was much lower than that of the carbonate formation from alcohols and CO_2. This means that EMC is formed from the reaction adsorbed ethylcarbonate species and CH_3OH.

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