A novel method of direct synthesis of dimethyl carbonate from methanol and carbon dioxide catalyzed by zirconia

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Dimethyl carbonate was synthesized from methanol and CO_2 with high selectivity using ZrO_2 catalysts. In this reaction, the amount of dimethyl ether and CO was below the detection limit. The catalytic activity seems to be related to acid–base pair sites of the ZrO_2 surface from the results of temperature-programmed desorption of NH_3 and CO_2.

Keywords: dimethyl carbonate, DMC synthesis from CO_2, zirconia

1. Introduction

Dimethyl carbonate (DMC) has attracted much attention in terms of a non-toxic substitute for dimethyl sulfate and phosgene, which are toxic and corrosive methylating or carbonylating agents [1]. In addition, DMC is considered to be an option for meeting the oxygenate specifications for transportation fuels [2]. There have been three commercial production schemes: (i) DMC produced by the reaction of methanol and phosgene, (ii) a process based on the oxidative carbonylation of methanol by CO and O_2 with copper catalysts [3–5], and (iii) an oxidative carbonylation process using a palladium catalyst and methyl nitrite promoter [6]. In the oxidative carbonylation, the raw materials are methanol, CO and oxygen, therefore CO_2 is formed as a by-product. Recently, we found that DMC can be synthesized from CH_3OH and CO_2 using CH_3I and K_2CO_3 as the promoters [7]. Whereas this reaction was very fast, the deactivation was very rapid. From this study, we found that two functions are necessary for DMC formation: one is to supply methyl species from CH_3I and the other is the basic function for the activation of methanol and CO_2. In the direct DMC synthesis from only methanol and CO_2, it seems to be important to supply methyl species from methanol, which can be proceeded by the acidic function. From this point of view, both acid and base functions are necessary for DMC synthesis (equation (1)) from only methanol and CO_2:

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

ZrO_2 has been reported to have both acidic and basic properties [8–11]. In this letter we report the reaction properties of DMC synthesis from methanol and CO_2; in addition we investigated the relation between the activity and surface properties of the catalysts, which were characterized by temperature-programmed desorption of CO_2 and NH_3 and the measurement of their adsorption amount.

2. Experimental

ZrO_2 catalysts were prepared by calcining a commercially available $ZrO_2 \cdot xH_2O$ (Nakarai Tesque Inc.) at different temperatures (388–1073 K) for 3 h.

The reaction was carried out in a stainless steel autoclave reactor with an inner volume of 70 or 30 ml. The standard procedure is as follows: 6.1 g methanol (192 mmol) and 0.5 g ZrO_2 (4.1 mmol) were put into an autoclave, and then the reactor was purged with CO_2. After that, CO_2 (200 mmol) was introduced into the autoclave and the initial pressure is about 5 MPa at room temperature. The reactor was heated and magnetically stirred constantly during the reaction. The reaction was carried out at different temperatures (413–463 K) for different reaction times (1–40 h). The products in both gas phase and liquid phase were analyzed by a gas chromatograph equipped with FID and TCD detector. Products were also identified by GC-MS. In the gas phase, almost no products were observed. CO was below the detection limit of GC with FID detector equipped with a methanator.

The XRD spectra and the BET surface area were measured by RINT-2400 (Rigaku) and Gemini (Micromeritics, N_2), respectively. The amount of CO_2 adsorption was measured by a volumetric method using a vacuum line, which has 30 cm^3 dead volume. Temperature-programmed desorption (TPD) profiles of CO_2 and NH_3 were obtained by a mass spectrometer (Balzers, Prisma QMS 200). Mass signals of $m/e = 44$ and 16 were monitored in CO_2 and NH_3 TPD, respectively. Sample pretreatment and gas adsorption were performed in a closed circulating vacuum system. Before exposing it to gas, the sample was evacuated for 0.5 h at the same temperature as the calcination temperature. The pressure of gas adsorption was 6.6 kPa. In the CO_2 and

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NH_3 coadsorption experiment, at first CO_2 was introduced to the sample and evacuated, and then NH_3 was introduced. Before the measurement of TPD profiles, the sample was evacuated for 1 h. Sample weight was 0.05 g. Heating rate is about 7 K/min.

3. Results and discussion

Figure 1 shows the amount of DMC formation over ZrO_2 at 433 K at various reaction times. The product was only DMC. It is clear that the formation rate of DMC was high at the initial stage, and its amount reached a constant level at about 5 h. The plateau in figure 1 may indicate that the zirconia catalyst deactivated. But it was also found that almost the same amount of DMC was formed even over this used ZrO_2 repeatedly several times. This indicates that ZrO_2 did not lose its activity. Therefore, the plateau in figure 1 seems to be due to reaching equilibrium of the reaction (equation (1)). When 0.25 g catalyst was used, the saturation level of DMC amount was almost the same as that shown in figure 1. In addition, we made sure that the reverse reaction of equation (1) proceeded rapidly. These results supported that DMC formation from methanol and CO_2 is a reversible reaction and DMC amount is possibly limited by reaction equilibrium. The amounts of dimethyl ether and CO as expectable by-products were lower than the detection limitation. Therefore, we estimated the selectivity of DMC formation on zirconia catalysts as 100% under all the reaction conditions in this study. The equilibrium level of DMC formation from methanol and CO_2 was estimated using the recent report [12]. This has reported the thermodynamic calculation data of DMC on the basis of the method described in [13]. We calculated the equilibrium level of methanol conversion under our reaction conditions in figure 1 to be about 1% (DMC $=$ 0.96 mmol). This value is higher than the experimental result, but this seems to be because the calculation did not consider H_2O as an impurity. The reactor, reactants, and catalyst surface should contain water as an impurity, the amount of which is difficult to estimate. H_2O may decrease the equilibrium level of DMC formation.

Figure 2 shows the dependence of reaction temperature on the amount of DMC formation over ZrO_2 calcined at 673 K. From the comparison of the results of 2 h reaction, the DMC amount was increased with the reaction temperature, reached maximum at 443 K, and decreased above 443 K. At 453 K, the DMC amount was constant at the reaction time longer than 2 h. On the other hand, the equilibrium level of DMC formation at 443 K is 0.36 mmol and higher than that at 453 K, as shown in figure 1. This indicated that DMC formation is more favorable at lower reaction temperature, and this is because this reaction is endothermic as expected from the thermodynamic calculation data [12,13]. In figure 2, the DMC amount of 2 h reaction is controlled by the formation rate at lower reaction temperature than 453 K, and it is controlled by the reaction equilibrium at higher than 453 K.

The effect of the amount of CO_2 on DMC formation rate is listed in table 1. At this reaction condition, the DMC amount has not reached the equilibrium level. The amount of DMC formation increased with CO_2 amount, and the formation rate of DMC was almost proportional to the amount of CO_2.

Figure 3 shows the dependence of the DMC amount, the BET surface area and amount of CO_2 adsorption on the calcination temperature of $ZrO_2{\cdot}xH_2O$. Since the equilibrium level of DMC amount is 0.36 mmol at reaction temperature 443 K, as shown in figure 1, the DMC amount did not reach the equilibrium level under the reaction conditions in figure 3. The activity showed a maximum at the calcination temperature around 573–773 K and then it decreased with calcination temperature higher than 773 K. The BET

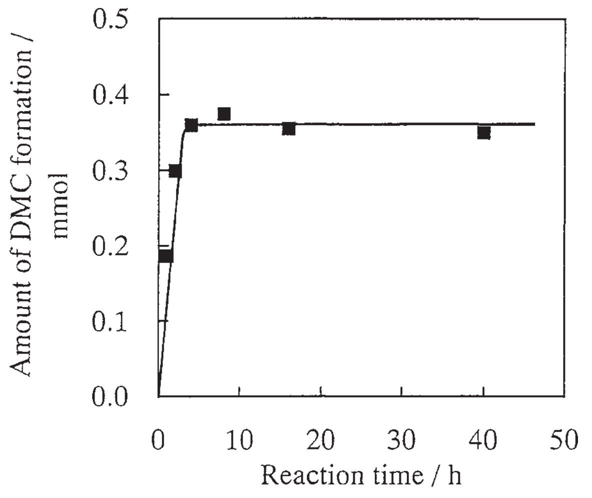

Figure 1. Reaction time dependence of dimethyl carbonate formation from methanol and CO_2 on ZrO_2 calcined at 673 K. Reaction temperature 433 K, $CH_3OH : CO_2 = 192$ mmol : 200 mmol, ZrO_2 weight 0.5 g.

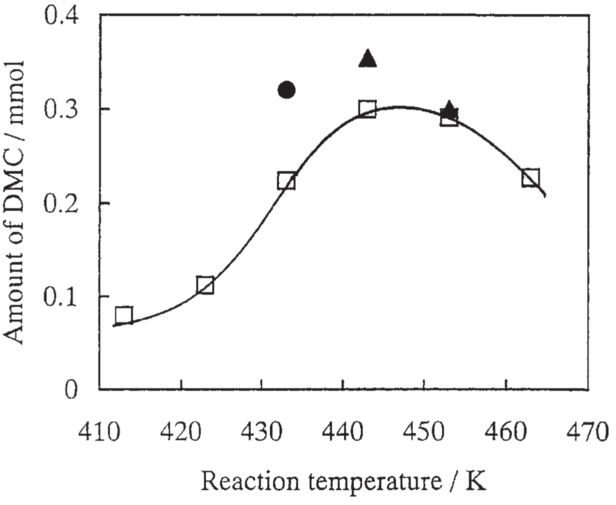

Figure 2. Reaction temperature dependence on the amount of DMC formation over ZrO_2 calcined at 673 K. Reaction time: 2 h (□), 4 h (▲), and 16 h (●). Reaction conditions: $CH_3OH : CO_2 = 192$ mmol : 200 mmol, ZrO_2 weight 0.5 g.

Table 1
Effect of DMC formation on the amount of CO_2 reactant over ZrO_2 catalyst.[a]

Catalyst weight (g)	Reaction time (h)	Reactant (mmol)		Product (mmol)
		CO_2	CH_3OH	DMC
0.5	2	150	192	0.24
0.5	2	200	192	0.30
0.5	2	250	192	0.33
0.04[b]	16	250[b]	82	0.42

[a] ZrO_2 catalyst prepared by the calcination of zirconium hydroxide at 673 K, reaction temperature: 433 K.

[b] The reaction was carried out in a stainless steel autoclave reactor with inner volume of 30 ml.

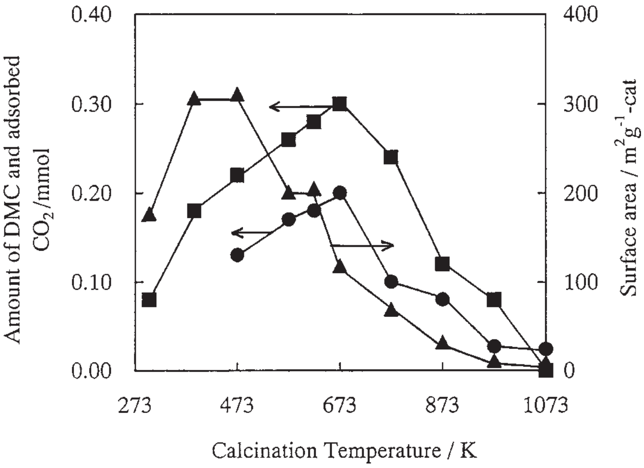

Figure 3. The dependence of dimethyl carbonate formation (■), surface area (▲), and amount of CO_2 adsorption (●) on calcination temperature of zirconium hydroxide. Reaction conditions: 433 K, 2 h, $CH_3OH:CO_2 = 192$ mmol : 200 mmol, sample weight 0.5 g. Surface area: BET method; the amount of CO_2 adsorption: volumetric method, 293 K, $P_{CO_2} = 6.6$ kPa.

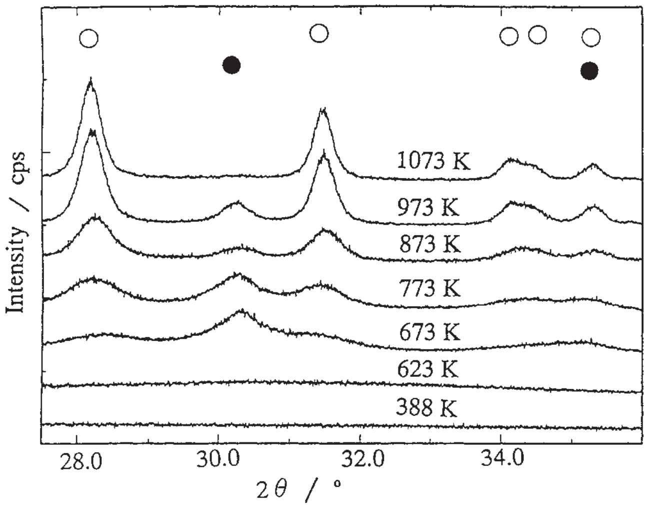

Figure 4. XRD spectra of zirconim oxides prepared by calcination at various calcination temperatures. Crystal structure: monoclinic (○), metastable tetragonal (●). X-ray source: Cu Kα.

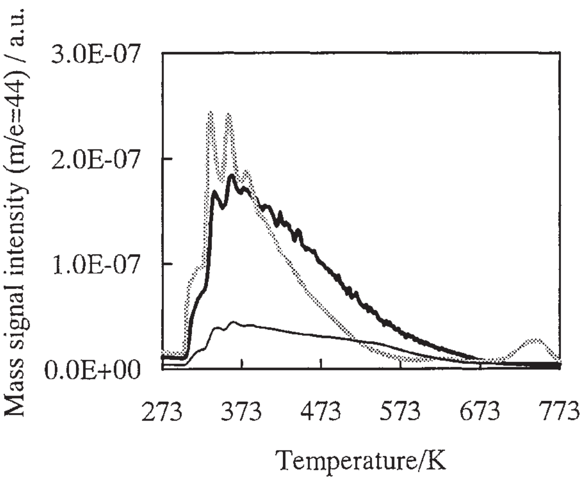

Figure 5. Profile of temperature-programmed desorption of CO_2 adsorbed on zirconium oxides prepared by the calcination of zirconium hydroxide at 573, 673 and 873 K. Calcination temperature: 573 K (bold gray line), 673 K (bold black line) and 873 K (thin black line). CO_2 adsorption: $P_{CO_2} = 6.6$ kPa, 293 K; TPD conditions: heating rate 7 K/min, sample weight 0.05 g.

surface area of the sample decreased with higher calcination temperature. A relation between DMC formation and BET was not observed. The amount of CO_2 adsorption is also shown in figure 3. DMC formation seems to be related to the amount of CO_2 adsorption. This correspondence suggests that the DMC formation is closely related to the acid–base surface properties of ZrO_2.

The crystal structure of ZrO_2 was determined by XRD and the spectra are shown in figure 4. ZrO_2, which was prepared by the calcination of zirconium hydroxide below 623 K, had amorphous structure. Metastable tetragonal structure was mainly formed by the calcination at 673–773 K. Monoclinic phase was predominant at higher calcination temperature above 773 K. The most active phase for DMC formation is metastable tetragonal ZrO_2 from the comparison between figures 3 and 4.

Figure 5 shows TPD profiles of CO_2 adsorption on ZrO_2 calcined at 573, 673, and 873 K. CO_2 was desorbed in a wide temperature range (300–700 K). In this experiment, both weakly and strongly adsorbed CO_2 were observed. Experimental conditions of TPD are almost the same as those of the measurement of adsorption amount. The ripples on the TPD profiles in the lower temperature range are caused by the gap of the electrical furnace from proportionally programmed heating. The amount of CO_2 desorption from ZrO_2 calcined at 573 K was considerably large, but in the higher temperature range, its amount was considerably small. This indicated that ZrO_2 calcined at 573 K had few strong basic sites. On the other hand, calcination at 673 K formed a considerably large amount of strong base sites on the surface. On the sample calcined at 873 K, little CO_2 desorption occurred.

Figure 6 shows TPD profiles of NH_3 (figure 6(a)) and CO_2 (figure 6(b)) from ZrO_2 on which CO_2 and NH_3 were coadsorbed. At the temperature of 450–600 K in TPD profiles of CO_2, another peak was observed. This peak was observed on all these samples, but most obvi-

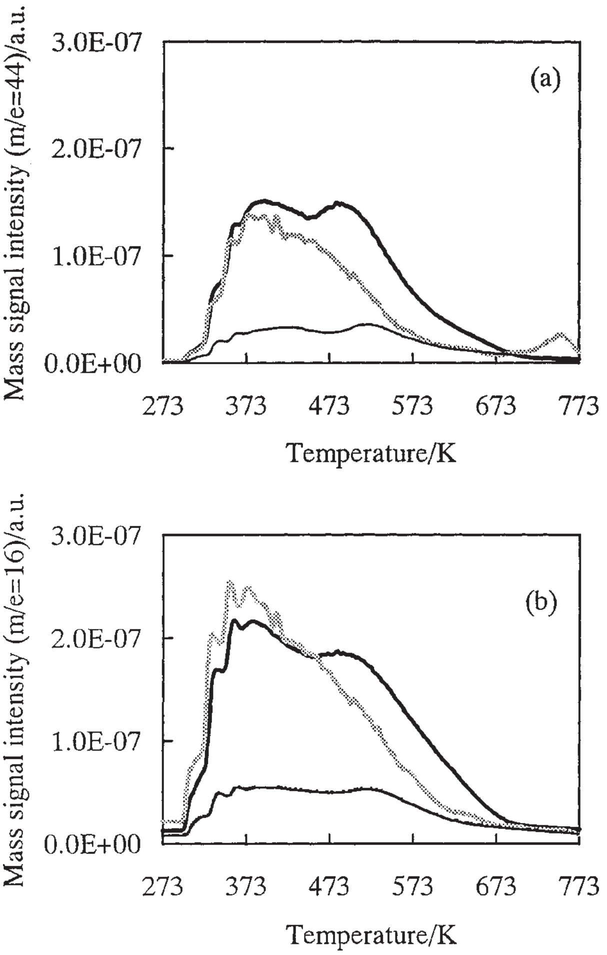

Figure 6. Profiles of temperature-programmed desorption of CO_2 (a) and NH_3 (b) from CO_2 and NH_3 coadsorbed on zirconium oxides prepared by the calcination of zirconium hydroxide at 573, 673 and 873 K. Calcination temperature: 573 K (bold gray line), 673 K (bold black line) and 873 K (thin black line). CO_2 and NH_3 adsorption: $P_{CO_2} = P_{NH_3} = 6.6$ kPa, 293 K, NH_3 adsorption after CO_2 adsorption; TPD conditions: heating rate 7 K/min, sample weight 0.05 g.

ously on ZrO_2 calcined at 673 K. At the same temperature range, NH_3 desorption was also observed. As previously reported, this peak indicated acid–base bifunctional behavior of the ZrO_2 catalysts [8]. Especially this phenomenon was observed significantly on ZrO_2 calcined at 673 K in our study. The amount of CO_2 at this peak on ZrO_2 calcined at 673 K can be estimated to be 0.02 mmol/0.5 g-ZrO_2. On the basis of this CO_2 amount, the saturated level in DMC formation corresponds to the turnover number TON = 18. In addition, we carried out the reaction under other reaction conditions, as listed in table 1. Under $CH_3OH : CO_2 = 82$ mmol : 250 mmol at 443 K, 0.42 mmol DMC was formed using 0.04 g ZrO_2 catalyst (0.30 mmol-Zr) after 16 h. The DMC amount went beyond the total Zr amount in the ZrO_2 catalyst. This result is evidence that this reaction proceeded catalytically. Furthermore, if the active sites correspond to the peak at high temperature in figure 6 and the number is 1.6×10^{-3} mmol/0.04 g-ZrO_2, TON can be estimated to be about 260. And if the active sites have all the CO_2 adsorption and the number is 0.016 mmol/0.04 g-ZrO_2, TON can be estimated to be 26.

Table 2
Results of $CH_3OH + CO_2$ reaction over various catalysts.[a]

Catalyst	Amount of formation (mmol)	
	DMC	DME
ZrO_2 (calcined at 673 K)	0.30	n.d.
ZrO_2 (commercial)	0.22	n.d.
SiO_2	n.d.	n.d.
Al_2O_3	n.d.	0.11
TiO_2	n.d.	0.16
H-ZSM5	n.d.	72.1
H-USY	n.d.	11.3
H-mordenite	n.d.	11.6
ZnO	n.d.	n.d.
MoO_3	n.d.	n.d.
Bi_2O_3	n.d.	n.d.

[a] Reaction conditions: reaction temperature 433 K, $CH_3OH : CO_2 =$ 192 mmol : 200 mmol, catalyst weight: 0.5 g, reaction time 2 h; n.d.: not detected. Catalysts except ZrO_2 (calcined at 673 K) were purchased from the manufacturers.

Table 2 shows the results of CH_3OH+CO_2 reaction over various catalysts. DMC was formed on zirconia catalysts, but on some catalysts DME was formed and DMC was not at all. It is found that ZrO_2 catalysts are effective for the DMC synthesis from methanol and CO_2.

The weak point of this DMC formation from methanol and CO_2 is that the conversion is limited by the reaction equilibrium at low level. But this limitation is avoidable by the removal of water from the reaction system, for example, by introducing trimethyl orthoformate, as described below:

$$HC(OCH_3)_3 + H_2O \rightarrow 2CH_3OH + HCOOCH_3 \quad (2)$$

This reaction has been utilized in oxalate synthesis by the direct oxidative coupling of CO as dehydrant to keep water-free conditions in the reaction system [4]. In fact, the DMC amount was increased by the addition of trimethyl orthoformate [14]. But in economical terms, the utilization of trimethyl orthoformate is not advantageous since this chemical is not so cheap. In our study, we tried Molecular Sieve 3A and $CaCl_2$, but DMC amount was almost the same as the amount observed in the experiment without them. This is because the reaction temperature is too high for Molecular Sieve 3A and $CaCl_2$to remove water from the reaction system. If it is possible to get a suitable method for the removal of water, DMC yield will be improved drastically. On the other hand, if we modify ZrO_2 catalyst and then DMC formation at lower reaction temperature comes true, inorganic dehydrating agents can be utilized. Further development of catalyst and process is very necessary.

4. Conclusions

(1) Dimethyl carbonate was directly and selectively synthesized from methanol and CO_2 using ZrO_2.

(2) The DMC formation rate was much dependent on the structure of the zirconia. On zirconia prepared by the

calcination of zirconium hydroxide at 673 K, the highest rate of DMC formation was observed.

(3) DMC amount was limited by the equilibrium of this reaction at the long reaction time. Since the maximum amount of DMC was beyond the amount of total Zr ions in ZrO_2, it is demonstrated that this reaction proceeded catalytically.

(4) From the results of catalyst characterization, it is suggested that the acid–base bifunction on the zirconia surface is related to the DMC formation from methanol and CO_2.

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