CeO_2–ZrO_2 solid solution catalyst for selective synthesis of dimethyl carbonate from methanol and carbon dioxide

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CeO_2–ZrO_2 solid solution catalysts are very effective for the selective synthesis of dimethyl carbonate from methanol and CO_2. The activity was much dependent on the calcination temperature. The higher the calcination temperature, the higher the activity of the catalyst for DMC formation, though the BET surface area is lower on the catalyst calcined at higher temperature.

KEY WORDS: dimethyl carbonate; CeO_2–ZrO_2 solid solution; methanol; CO_2; acidity; basicity

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]. Three kinds of large-scale production methods of DMC have been known: (1) DMC produced by the stoichiometric reaction of methanol and phosgene, (2) a process based on the oxidative carbonylation of CH_3OH with carbon monoxide and oxygen catalyzed by cuprous chloride [3–5], and (3) an oxidative carbonylation process using a palladium catalyst and methyl nitrite promoter [6]. In the last two cases, raw materials of DMC production are CH_3OH, CO and O_2. In contrast, the utilization of carbon dioxide as the raw material of the DMC synthesis process has been attempted [7]. Some catalysts have been reported to be effective for the synthesis of DMC from CH_3OH and CO_2,

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

It has been reported that DMC was synthesized by equation (1) in the presence of organotin compounds [8,9], Sn(IV) and Ti(IV) alkoxides and metal acetates [10]. Recently we have reported that DMC was selectively synthesized from CH_3OH and CO_2 using zirconia as a solid catalyst [11]. From this study, it was suggested that both acid and base functions on the catalyst surface play a major role on DMC synthesis from CH_3OH and CO_2 (equation (1)). ZrO_2 has been known to exhibit both weak acidic and basic properties [12–16]. Furthermore, we investigated the addition effect of H_3PO_4 to ZrO_2 for the promotion of activity [17,18]. Weak Brønsted acid sites, which seem to be the active sites for DMC formation, were formed on the catalyst by the modification of zirconia. Weak acidity is very important in the selective DMC synthesis since the expectable by-product dimethyl ether (DME) is easily formed on the rather strong acid sites [18]. When DME is formed together with the same amount of H_2O, no DMC was observed due to the more favorable hydrolysis reaction of DMC.

It has been reported that ZrO_2, CeO_2 and CeO_2–ZrO_2 solid solution have both acid and base properties [19]. The strength of acidity on CeO_2 and CeO_2–ZrO_2 is lower than that on ZrO_2. In this letter, a new catalyst system effective to the synthesis of DMC from CH_3OH and CO_2 is reported.

2. Experimental

CeO_2–ZrO_2 catalysts were prepared by calcining the hydroxides (available from Daiichi Kigenso, Japan) for 3 h under air atmosphere at various temperatures. The preparation method of the hydroxides was on the basis of the patent [20]. The molar ratio Ce/(Ce + Zr) of the catalysts is 0, 0.2, 0.33 and 0.5.

The reaction was carried out in a stainless-steel autoclave reactor with an inner volume of 70 ml. The standard procedure is as follows: 6.1 g CH_3OH (192 mmol, Kanto Chemical, 99.8% min.) and 0.5 g catalyst were put into an autoclave, and then the reactor was purged with CO_2. After that, the autoclave was pressurized with CO_2 (200–1000 mmol, Takachiho Trading Co., Ltd., 99.99%). The reactor was heated and magnetically stirred constantly during the reaction. The total pressures at 383 K are about 6 MPa (200 mmol CO_2), 12 MPa (500 mmol) and 21 MPa (1000 mmol). Products in both gas phase and liquid phase were analyzed by a gas chromatograph (GC) equipped with FID and TCD. The separation column packing is PEG-6000 + Porapak N and Gaskuropak 54 for FID-GC, MS-13X and Porapak Q for TCD-GC. All the products were also identified by GC-MS. In the gas phase, almost no products

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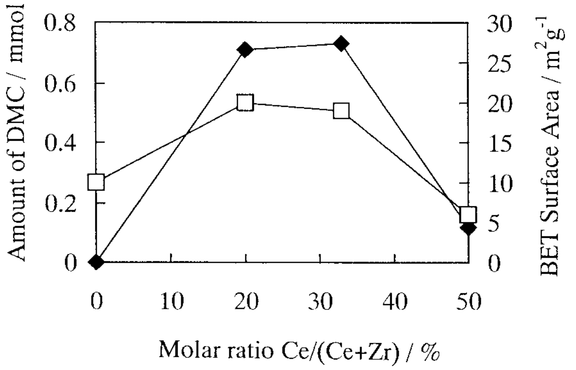

Figure 1. Dependence of the amount of DMC formation (◆) and BET surface area (□) on Ce content in CeO_2–ZrO_2. Reaction conditions: reaction temperature 383 K, $CH_3OH : CO_2 = 192$ mmol : 200 mmol, reaction time 2 h, catalyst weight 0.5 g. Calcination temperature of catalysts 1273 K.

were observed. CO was below the detection limit of FID-GC equipped with a methanator. Under the reaction conditions shown in this letter, DMC was the only product and DME, which is the expectable by-product, was below the detection limit of FID-GC.

XRD spectra and BET surface area of the catalyst samples were measured with RINT-2400 (Rigaku) and Gemini (Micromeritics, N_2), respectively.

3. Results and discussion

Figure 1 shows the dependence of DMC amount on the Ce content in CeO_2–ZrO_2 solid solution catalysts. In this experiment, the calcination temperature was 1273 K. The results of BET surface area are also shown in figure 1. ZrO_2 calcined at 1273 K exhibited almost no activity of DMC formation, whereas the ZrO_2 calcined at lower temperature exhibited the activity to some extent as is shown later. CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2 and 0.33) showed much higher activity than the ZrO_2 catalyst. Although the BET surface area of CeO_2–ZrO_2 is twice that of ZrO_2, it does not explain the high activity. On the catalyst with higher Ce content, DMC amount was not so high.

Table 1 shows the DMC amount on CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) and ZrO_2 under various reaction conditions. Even under higher CO_2 pressure, ZrO_2 had very low activity. On the other hand, CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) gave larger DMC amount under higher CO_2 pressure. After longer reaction time (16 h), the increase of DMC amount was small. This indicates that the conversion is near the equilibrium level. The effect of catalyst weight was also investigated here. After 16 h, the product amount was almost the same on 0.5 and 1.5 g CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2). This supports that the conversion is limited by the equilibrium. From the comparison, Zr-rich CeO_2–ZrO_2 has much higher performance in DMC formation from methanol and CO_2 than the ZrO_2 catalyst.

Table 1
DMC formation from methanol and CO_2 on CeO_2–ZrO_2 catalysts.[a]

Ce content Ce/(Ce + Zr) (%)	Reactant (mmol) CH_3OH	Reactant (mmol) CO_2	Reaction time (h)	DMC amount (mmol)
0	192	200	2	0.05
0	192	500	2	0.00
0	192	500	16	0.04
20	192	200	2	0.71
20	192	200	16	0.78
20	192	500	2	0.88
20	192	500	16	1.1
20	192	1000	2	0.97
20	192	1000	16	1.6
20[b]	192	1000	16	1.6

[a] Reaction conditions: temperature 383 K, calcination temperature 1273 K, catalyst weight 0.5 g.

[b] Catalyst weight 1.5 g.

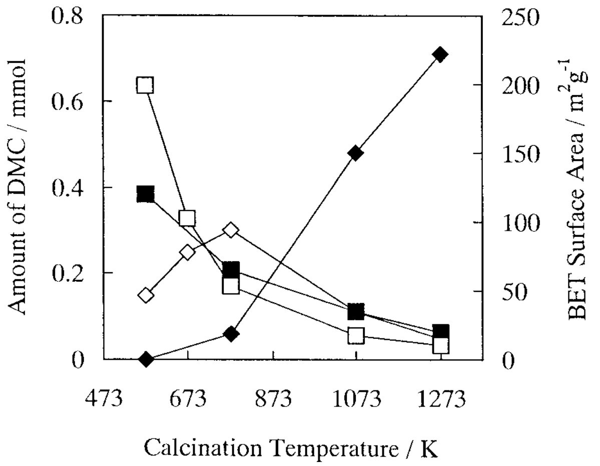

Figure 2. Dependence of the amount of DMC formation (◆, ◇) and BET surface area (■, □) on the calcination temperature over ZrO_2 (◇, □) and CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) (◆, ■). Reaction conditions: reaction temperature 383 K, $CH_3OH : CO_2 = 192$ mmol : 200 mmol, reaction time 2 h, catalyst weight 0.5 g.

Figure 2 shows the dependence of DMC amount over ZrO_2 and CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) on the calcination temperature. BET surface area of the samples is also shown in this figure. The BET surface area of the samples decreased with higher calcination temperature. The amount of DMC formation on ZrO_2 reached the maximum at the calcination temperature of 773 K. Similar behavior was often observed in the previous reports [11,16]. Above 773 K, the amount of DMC and the BET surface area decreased on ZrO_2 with increasing calcination temperature. On the other hand, the amount of DMC increased with increasing calcination temperature, though the BET surface area decreased. This tendency on CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) was completely inverse to that on ZrO_2. The tendency on CeO_2 catalyst prepared by calcining the hydroxide was similar to that on CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) although the details of the data are not shown in this letter. As a result, the catalyst with lower surface area exhibited the higher performance.

Figure 3 shows XRD patterns of CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) calcined at various temperatures. The peak position was not changed with the calcination temperature. The

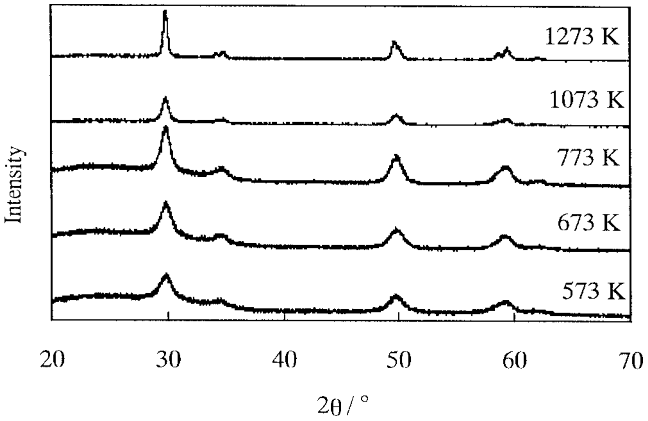

Figure 3. XRD patterns of CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) calcined at various temperatures. X-ray source Cu Kα.

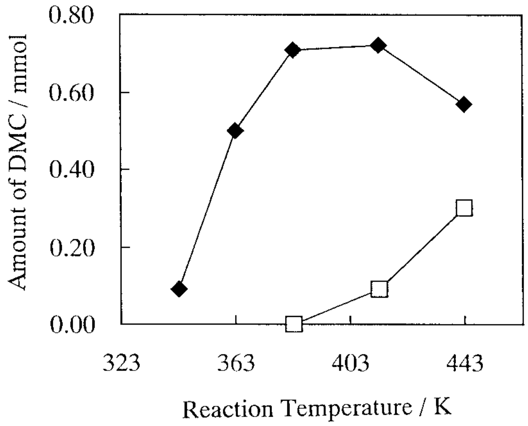

Figure 4. Dependence of the amount of DMC formation over CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) (◆) and ZrO_2 (☐) catalysts on reaction temperature. Reaction conditions: reaction temperature 383 K, $CH_3OH : CO_2$ = 192 mmol : 200 mmol, reaction time 2 h, catalyst weight 0.5 g. Calcination temperature: 1273 K (CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2)), 773 K (ZrO_2).

peak width became sharp on the samples at higher calcination temperature. These results indicate that the crystal size becomes larger with the calcination temperature, though the crystal structure remains the same. This is attributed to the lower surface area of the catalyst calcined at higher temperature. From the diffraction angle of the peaks, CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) has tetragonal structure. It is known that a shift of the CeO_2 peak toward higher values of 2θ was observed when Zr content increased with respect to that of cerium. This can be explained by the insertion of zirconium atoms in the CeO_2 cubic matrix with the contraction of its cell parameter and the deformation of the cubic phase to be transformed into the tetragonal phase for higher zirconium content [21].

Figure 4 shows the dependence of the amount of DMC formation over CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) and ZrO_2 catalysts on reaction temperature. The activity of ZrO_2 prepared in this study was almost the same level as that of zirconia catalysts developed in our previous study [11]. From the comparison, it is characteristic that CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) has much higher activity than ZrO_2 catalysts, especially at lower reaction temperature. In the case of ZrO_2 calcined at 773 K, the amount of DMC formation was zero below the reaction temperature of 373 K. On the other hand, CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) gave large amount of DMC even at this low temperature.

From the XRD results, the bulk structure of CeO_2–ZrO_2 (Ce/(Ce + Zr) = 0.2) is not changed with the calcination temperature. However, the performance becomes higher with the higher calcination temperature and lower BET surface area. In this case, it is estimated that the activity per surface area is enhanced drastically by the calcination. It is expected that the surface structure and properties, especially acidity and basicity which influence the activity and selectivity of DMC formation [16], can be modified with high temperature of calcination. In addition, it is possible that the surface composition approaches the bulk composition with the formation of crystal growth of solid solution. This is related to the results that the activity was much dependent on the composition of CeO_2–ZrO_2, as shown in figure 1. Further investigation about the surface structure and acid–base properties is necessary for the elucidation of the promoting effect of high-temperature calcination. In addition, if it is possible to prepare the catalyst with both high surface area and the active surface which is formed by calcining at high temperature, it is expected that the activity of DMC formation will be enhanced dramatically.

4. Conclusions

(1) Zirconium-rich CeO_2–ZrO_2 solid solution catalysts had higher activity in the selective dimethyl carbonate formation from methanol and CO_2 than ZrO_2.

(2) Especially, it is characteristic that CeO_2–ZrO_2 catalysts maintained high performance even at low reaction temperature.

(3) High calcination temperature is more favorable though BET surface area of the catalyst is considerably low.

(4) The bulk structure of CeO_2-ZrO_2 solid solution was tetragonal and the structure was not changed with the calcination temperature, though crystal size became larger on the catalyst calcined at higher temperature.

(5) The elucidation of the mechanism of the activity enhancement enables catalyst design for much higher performance.

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