Promoting effect of phosphoric acid on zirconia catalysts in selective synthesis of dimethyl carbonate from methanol and carbon dioxide

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The addition of phosphoric acid to zirconia catalysts promoted the activity for dimethyl carbonate synthesis from methanol and carbon dioxide with high selectivity, and the reactions proceeded at much lower temperature on H_3PO_4/ZrO_2 than on zirconia catalysts. This suggested that the surface acidity enhanced by phosphoric acid contributed to higher activity.

Keywords: dimethyl carbonate, phosphoric acid, zirconia, surface acidity

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 fuel [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 second and third production methods, raw materials 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 organo-tin 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, though dimethyl ether (DME) was formed on various other catalysts and DMC was not detected at all [11]. It was found that the DMC formation rate was much dependent on the structure of ZrO_2. On ZrO_2 prepared by the calcination of zirconium hydroxide at 673 K, the highest rate of DMC formation was observed [11].

From this study, it was suggested that both acid and base functions on the catalyst surface are necessary for DMC synthesis from CH_3OH and CO_2 (equation (1)) [11]. ZrO_2 has been known to exhibit both weakly acidic and weakly basic properties [12–15]. We performed the surface modification of ZrO_2 in order to enhance the surface acidity and to promote the reaction activity. Best known method for the enhancement of surface acidity is the modification of zirconia with sulfate ions, known as superacidic catalyst [16]. As a suitable acid-strength modification, we chose phosphoric acid. H_3PO_4 supported on silica is used in the vapor-phase industrial process for the synthesis of isopropylbenzene from benzene and propylene [17]. H_3PO_4/SiO_2 has medium strength acidity, which inhibits propylene polymerization. In this letter the promoting effect of H_3PO_4 on ZrO_2 in the synthesis of DMC from CH_3OH and CO_2 is reported.

2. Experimental

ZrO_2 catalyst was prepared by calcining a commercially available zirconium hydroxide ($ZrO_2 \cdot xH_2O$, Nakarai Tesque Inc.) at 673 K for 3 h under air atmosphere. The calcination temperature was optimized by our previous study [11]. H_3PO_4/ZrO_2 catalysts were prepared by impregnating $ZrO_2 \cdot xH_2O$ with aqueous H_3PO_4 solution (Aldrich, 85 wt%). Water was removed by heating and the sample was dried at 393 K for 10 h, followed by calcining at different temperatures (573–923 K) for 3 h under air atmosphere. This preparation method was referred to that of sulfated zirconia. Another preparation method was attempted. H_3PO_4 was loaded directly on ZrO_2 calcined at 673 K. After the impregnation, the catalyst was dried at 393 K and at 673 K for 3 h. This catalyst is represented by

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H_3PO_4/ZrO_2(D). The loading of P is denoted as the molar ratio P/Zr in parentheses. Fine-powder catalysts were used.

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, CO_2 (200 mmol, Takachiho Trading Co. Ltd., 99.99%) was introduced into the autoclave and 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 (383–443 K) for 2 h. Products in both gas phase and liquid phase were analyzed by a gas chromatograph (GC) equipped with FID and TCD. The separate 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, no products were observed. CO was below the detection limit of FID-GC equipped with methanator. Under all 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 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 reaction temperature over ZrO_2 and H_3PO_4/ZrO_2 (P/Zr = 0.025, 0.05, 0.1). DMC formation on ZrO_2 is controlled by the reaction rate. The dramatic additive effect of H_3PO_4 to ZrO_2 catalyst was easily observed at all reaction temperatures. It seems that the amount of DMC on H_3PO_4/ZrO_2 (P/Zr = 0.025) at 443 K reached the equilibrium level. The DMC amount on H_3PO_4/ZrO_2 at 423 K became about four times larger than that on ZrO_2. The amount of DMC on H_3PO_4/ZrO_2 at 403 K was comparable to that on ZrO_2 at 443 K. While DMC formation was not observed on ZrO_2 at 383 K, about 0.20 mmol g-cat^{-1} DMC was formed on H_3PO_4/ZrO_2. It should be noted that the surface modification of ZrO_2 with H_3PO_4 promoted this reaction remarkably. Besides, the amounts of DME and CO, which are expectable by-products, were also smaller than the detection limit on H_3PO_4/ZrO_2 under these reaction conditions. Therefore, we estimated the selectivity of DMC formation on H_3PO_4/ZrO_2 as 100%. By the addition of H_3PO_4, the reaction temperature could be lowered by 40 K.

Figure 2 shows the dependence of DMC amount and surface area of H_3PO_4/ZrO_2 on H_3PO_4 loading. The amount of DMC and the surface area increased with the loading of H_3PO_4 in the range of low P/Zr. The amount of DMC reached a maximum at P/Zr = 0.05, and then decreased at P/Zr > 0.05. DMC formation was not observed at P/Zr > 0.5. The surface area reached a maximum at P/Zr = 0.1, and then decreased at P/Zr > 0.1.

XRD patterns of H_3PO_4/ZrO_2 with various H_3PO_4 loadings are shown in figure 3. On ZrO_2, both metastable tetragonal phase and monoclinic phase were observed. The metastable tetragonal phase increased and the monoclinic phase decreased with the loading of H_3PO_4. Metastable tetragonal phase was predominantly formed on H_3PO_4/ZrO_2 (P/Zr = 0.05), which exhibited the highest activity, as shown in figure 2. On higher H_3PO_4 loading, a new peak appeared around $2\theta = 20°$. This peak has not been identified, but it may be due to the salt formed between Zr ions and H_3PO_4. These results in figures 2 and 3 sug-

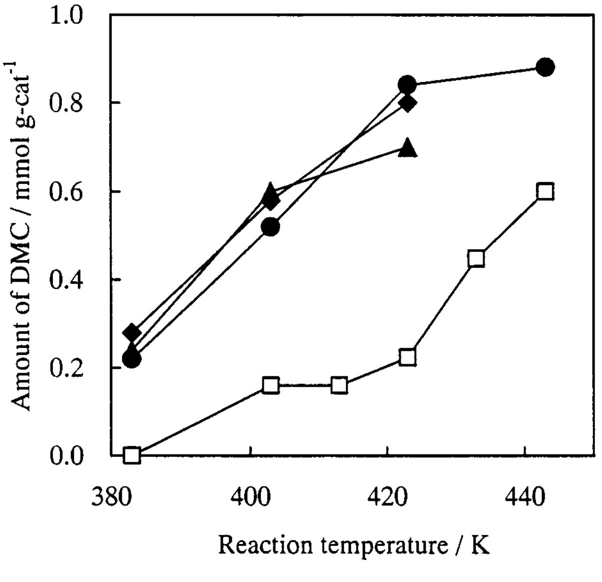

Figure 1. Dependence of DMC amount on reaction temperature over ZrO_2 (□) and H_3PO_4/ZrO_2 (P/Zr = 0.025 (●), 0.05 (▲) and 0.1 (◆)). Reaction conditions: $CH_3OH : CO_2$ = 192 mmol : 200 mmol, catalyst weight 0.5 g, reaction time 2 h.

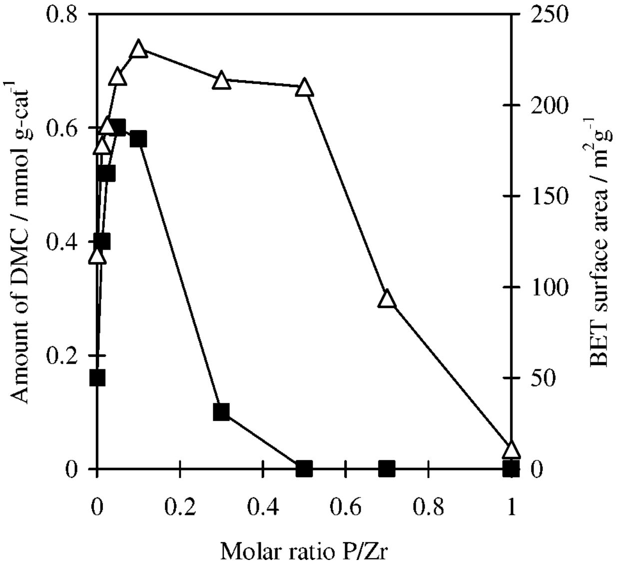

Figure 2. Dependence of DMC amount (■) and surface area (△) of H_3PO_4/ZrO_2 on H_3PO_4 loading. Reaction conditions: $CH_3OH : CO_2$ = 192 mmol : 200 mmol, catalyst weight 0.5 g, reaction temperature 403 K, reaction time 2 h.

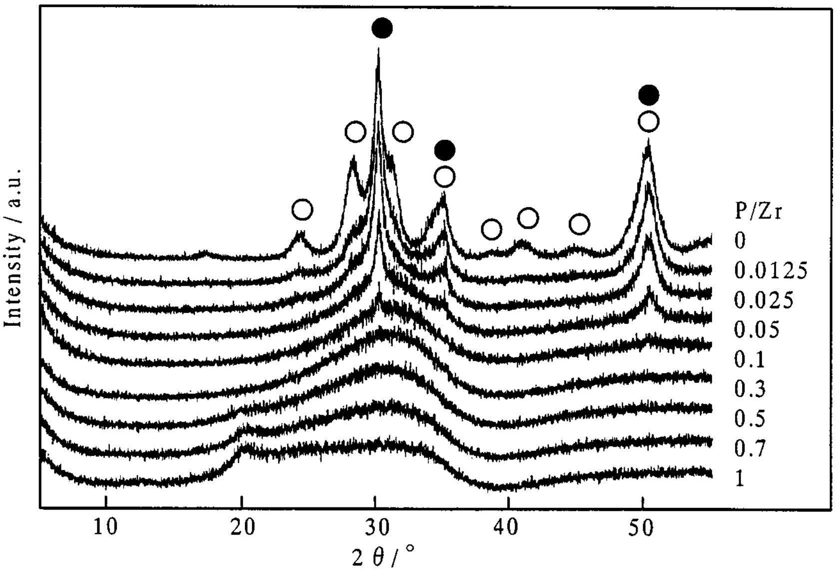

Figure 3. Cu K_α XRD patterns of H_3PO_4/ZrO_2 with various H_3PO_4 loadings. Crystal structure: metastable tetragonal (●), monoclinic (○).

Table 1
Dependence of DMC amount and surface area on calcination temperature of catalysts.[a]

Catalyst	Calcination temp. (K)	Amount of DMC (mmol g-cat^{-1})	BET surface area (m^2 g^{-1})
H_3PO_4/ZrO_2 (P/Zr = 0.05)	573	0.46	260
	673	0.60	216
	773	0.20	154
	923	not detected	106
H_3PO_4/ZrO_2(D) (P/Zr = 0.05)	673	not detected	106

[a] Reaction conditions: $CH_3OH : CO_2 = 192$ mmol : 200 mmol, catalyst weight 0.5 g, reaction temperature 403 K, reaction time 2 h.

gested that the most active phase for DMC formation is metastable tetragonal ZrO_2 modified with H_3PO_4. The formation amount is not directly related to the surface area of catalysts, as shown in figure 2.

Table 1 shows the dependence of DMC amount and surface area on calcination temperature of H_3PO_4/ZrO_2 (P/Zr = 0.05). The surface area decreased with calcination temperature. The amount of DMC increased to a maximum at 673 K and then decreased as the temperature was increased further. From the comparison between figure 2 and table 1, the catalyst can be optimized: the optimum calcination temperature is 673 K and the optimum composition of the catalyst is P/Zr = 0.05. In addition, we prepared H_3PO_4/ZrO_2 by another method. H_3PO_4 was loaded directly on ZrO_2 which was calcined at 673 K. This catalyst is represented by H_3PO_4/ZrO_2(D) in table 1. DMC formation on H_3PO_4/ZrO_2(D) was not observed. This result indicates that the effective active site is formed by the interaction between H_3PO_4 and zirconium hydroxide. Similar tendency has been observed in the case of sulfated zirconia catalysts [18]. It is suggested that the surface modification of ZrO_2 with phosphoric acid enhances the surface acidity and this causes higher activity. At the present stage, the structure of the catalytic active site is not clear. Further investigation and catalyst characterization are necessary for the catalyst development.

4. Conclusions

The modification of ZrO_2 catalysts with phosphoric acid was found to be very effective for the enhancement of the catalytic activity in DMC synthesis from methanol and CO_2. This modification can decrease the reaction temperature drastically compared to the unpromoted zirconia. From the results of catalyst characterization, it is suggested that the active phosphoric species on metastable tetragonal ZrO_2 is formed by the interaction between H_3PO_4 and zirconium hydroxide during catalyst preparation.

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