

## Direct synthesis of dimethyl carbonate from methanol and carbon dioxide over $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts: Effect of acidity of the catalysts

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**Abstract**— $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were prepared by a sol-gel method, and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were then prepared by an impregnation method. Both catalysts were applied to the direct synthesis of dimethyl carbonate from methanol and carbon dioxide in a batch reactor.  $\text{NH}_3$ -TPD experiments were carried out to investigate the effect of acidity on the catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . Catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was closely related to the acidity of the catalysts. The amount of dimethyl carbonate produced over both  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts increased with increasing acidity of the catalysts. This indicates that acidity of the catalyst played a key role in determining the catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. Catalytic activity of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was higher than that of the corresponding  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . The enhanced catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was attributed to the Brønsted acid sites provided by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

Key words: Dimethyl Carbonate, Methanol, Carbon Dioxide, Heteropolyacid, Ceria-zirconia

### INTRODUCTION

Dimethyl carbonate (DMC) has been considered as a clean chemical product with a wide range of applications. It can serve as a green and alternative chemical for dimethyl sulfate and phosgene, which are highly toxic and corrosive methylation and carbonylation agents [1,2]. In addition, DMC can also be used as a fuel additive, a good polar solvent, and a monomer for the synthesis of polycarbonate and polyurethane [1,2]. Several commercial processes have been developed for the synthesis of DMC, including methanolysis of phosgene [3], oxidative carbonylation of methanol [4], and carbon monoxide-methyl nitrite processes [5]. However, these conventional processes involve many problems from an environmental point of view, because toxic, flammable, explosive, and corrosive gases such as phosgene, hydrogen chloride, nitric oxide, and carbon monoxide are used in the processes. Therefore, direct synthesis of DMC from methanol and carbon dioxide has attracted much attention as an environmentally benign chemical process [6-16]. Although DMC yield in this reaction is low due to the thermodynamic equilibrium limitation, it has been reported that low yield can be enhanced by shifting the equilibrium through pressurizing carbon dioxide and adding effective dehydrating agents [1]. Thus, developing an efficient catalyst for the direct synthesis of DMC from methanol and carbon dioxide would be worthwhile.

It has been reported that both acid and base sites on the catalyst surface play an important role in the direct synthesis of DMC from methanol and carbon dioxide [6]. Various catalysts have been utilized for the direct synthesis of DMC from methanol and carbon

dioxide, including organometallic compounds [7,8], metal tetraalkoxides [9], potassium carbonate [10],  $\text{Ni}(\text{CH}_3\text{COO})_2$  [11], zirconia [6,12],  $\text{CeO}_2\text{-ZrO}_2$  [13,14],  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$  [15], and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$  [16]. Among these catalysts,  $\text{CeO}_2\text{-ZrO}_2$  showed a considerable catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide due to its acid-base bifunctional property.

In this work,  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were prepared by a sol-gel method. Heteropolyacid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) was then supported on  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts by an impregnation method in order to enhance the acidity of the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts [17,18]. The prepared catalysts were applied to the direct synthesis of DMC from methanol and carbon dioxide in a batch reactor.  $\text{NH}_3$ -TPD experiments were conducted to investigate the effect of acidity on the catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide. A correlation between catalytic performance and acidity of the catalysts was then established.

### EXPERIMENTAL

#### 1. Preparation of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ Catalysts

$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were prepared by a sol-gel method with a variation of cerium content (X) from 0 to 1.0 (X=0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0). A known amount of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich) and  $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (Sigma-Aldrich) was dissolved in distilled water. A known amount of citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , Sigma-Aldrich) was separately dissolved in distilled water. The citric acid solution was then added to the solution containing cerium and zirconium precursors. After the mixed solution was stirred at 80 °C for 3 h, it was evaporated to obtain a gel. The gel was then dried at 100 °C for 24 h. After

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grinding the dried gel, it was finally calcined at 500 °C for 3 h in an air stream to yield  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts.

$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (Sigma-Aldrich). The loading of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  on  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was fixed at 1 wt% in all cases. After impregnating  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  onto  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ,  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were dried at 100 °C for 24 h and calcined at 300 °C for 3 h in an air stream.

## 2. Catalyst Characterization

Crystalline phases of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were investigated by XRD measurements (Rigaku, D-MAX2500-PC) using  $\text{Cu-K}\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ) operated at 50 kV and 100 mA. Surface areas of the catalysts were measured with a BET apparatus (Micromeritics, ASAP 2010). Chemical compositions of the catalysts were determined by ICP-AES (Shimadzu, ICP-1000IV) analyses.

$\text{NH}_3$ -TPD experiments were conducted to determine the acidity of the catalysts (BEL Japan, BELCAT-B). Each catalyst (0.1 g) was pretreated at 200 °C for 2 h under a flow of helium (50 ml/min) to remove any physisorbed organic molecules. Ammonia (50 ml/min) was introduced into the reactor at 50 °C for 30 min to saturate acid sites of the catalyst. Physisorbed ammonia was removed at 150 °C for 1 h under a flow of helium (50 ml/min). After the sample was cooled, the furnace temperature was increased from 50 °C to 500 °C at a heating rate of 5 °C/min under a flow of helium (30 ml/min). The desorbed ammonia was detected by using a TCD (thermal conductivity detector).

## 3. Direct Synthesis of DMC from Methanol and Carbon Dioxide

DMC was directly synthesized from methanol and carbon dioxide in a stainless steel autoclave reactor with a volume of 75 ml. Methanol (30 ml) and catalyst (0.7 g) were charged into the autoclave, and the reactor was then purged with carbon dioxide. After the reactor was heated to the reaction temperature with constant stirring, the autoclave was pressurized up to 60 bar using carbon dioxide. A catalytic reaction was carried out at 170 °C for 3 h. Reaction products were analyzed by gas chromatograph (HP 5890 II).

## RESULTS AND DISCUSSION

### 1. Formation and Characterization of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ Catalysts

Successful formation of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts was well confirmed by XRD measurement. Fig. 1 shows the XRD patterns of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts. The peaks for (111), (200), (220), and (311) planes of cubic fluorite phase were observed in the XRD pattern of  $\text{CeO}_2$  ( $X=1.0$ ) catalyst, while the peaks for tetragonal phase were found in the XRD pattern of  $\text{ZrO}_2$  ( $X=0$ ) catalyst. The  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0.2-0.8$ ) catalysts retained a single cubic fluorite phase without a detectable tetragonal phase, although the characteristic XRD peaks of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0.2-0.8$ ) shifted to higher angles with decreasing cerium content ( $X$ ). The shift of XRD peaks was due to the shrinkage of lattices that originated from the replacement of  $\text{Ce}^{4+}$  (ionic radius=0.098 nm) with a smaller  $\text{Zr}^{4+}$  (ionic radius=0.084 nm) in the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts [19-21]. The above results are in good agreement with previous reports [22,23], indicating suc-

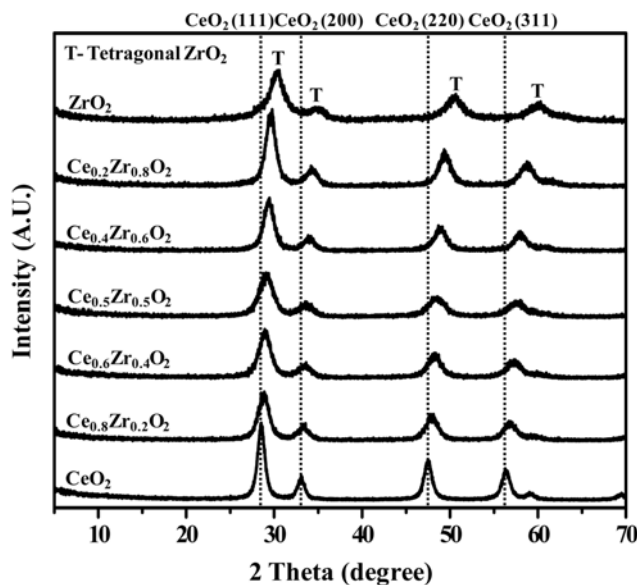


Fig. 1. XRD patterns of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts.

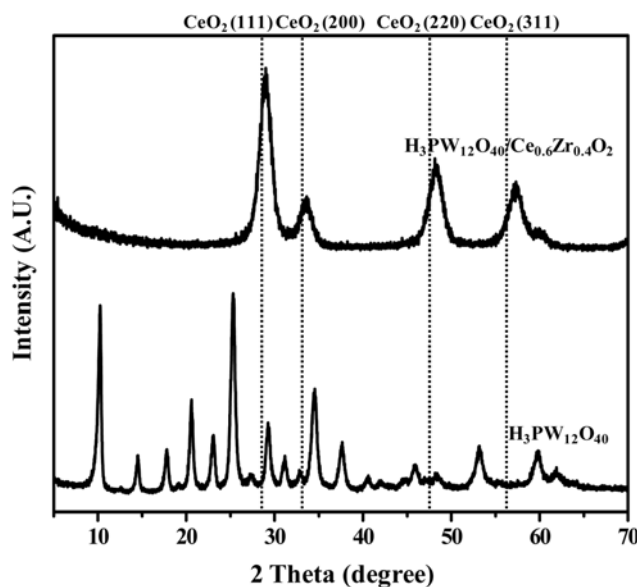


Fig. 2. XRD patterns of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  catalysts.

cessful formation of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts in this work.

Fig. 2 shows the XRD patterns of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  catalysts. No characteristic peaks for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  were found in the XRD pattern of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ . The XRD peaks for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  were not observed in all  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts, although these are not shown here. This indicates that  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was finely dispersed on the surface of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts. This result is consistent with earlier studies reporting that no characteristic XRD peaks for  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  were detected for impregnated samples with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  on zeolite NaY [24], SBA-15 [25],  $\text{SiO}_2$  [26], MCM-41 [27], and  $\text{ZrO}_2$  [28].

Atomic ratios of constituent metal components in the prepared  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts are listed in Table 1.

**Table 1. Chemical composition, surface area, and acidity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts**

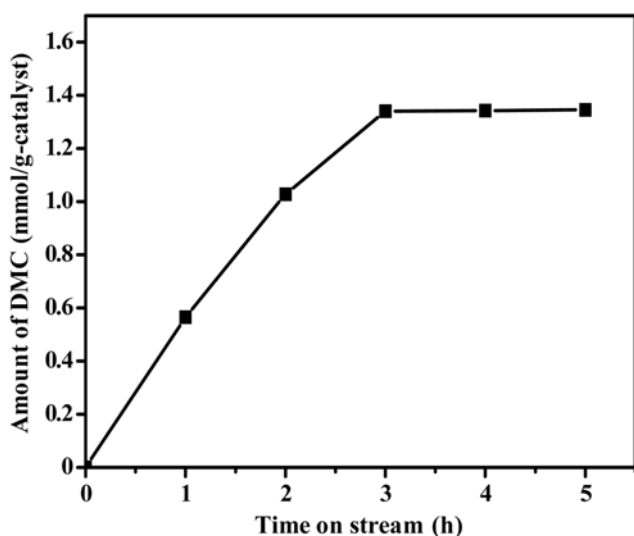
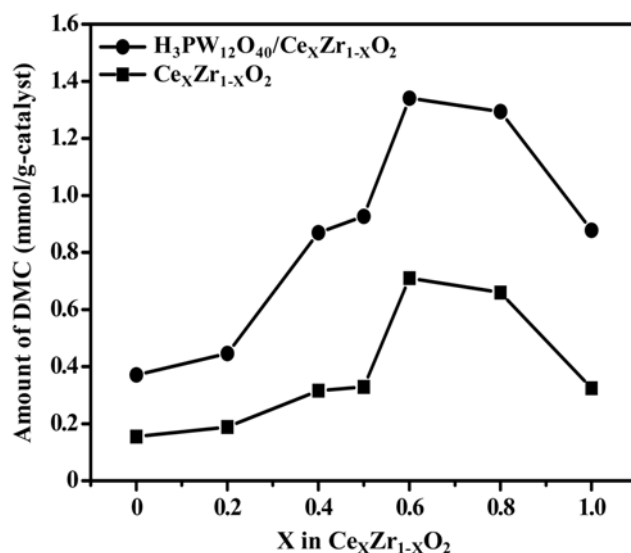
Catalyst	Atomic ratio <sup>a</sup>		Surface area (m <sup>2</sup> /g) <sup>b</sup>	Acidity (μmol-NH <sub>3</sub> /g-catalyst) <sup>c</sup>
	Ce	Zr		
$\text{CeO}_2$	1	0	53.8	35.7
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	0.81	0.19	64.8	48.2
$\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	0.64	0.36	54.4	51.3
$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.52	0.48	41.1	36.7
$\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$	0.37	0.63	34.0	33.5
$\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$	0.22	0.78	32.1	24.5
$\text{ZrO}_2$	0	1	38.4	20.4
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{CeO}_2$	1	0	51.2	50.1
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	0.81	0.19	62.3	59.3
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	0.64	0.36	51.4	63.4
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	0.52	0.48	37.6	52.4
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.4}\text{Zr}_{0.6}\text{O}_2$	0.37	0.63	32.1	47.2
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$	0.22	0.78	30.3	37.1
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$	0	1	36.3	34.6

<sup>a</sup>Determined by ICP-AES analysis<sup>b</sup>Calculated by the BET (Brunauer-Emmett-Teller) equation<sup>c</sup>Determined by NH<sub>3</sub>-TPD measurement

The atomic ratios determined by ICP-AES analyses are in good agreement with the designed values. Once again, this indicates that  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were successfully prepared in this work. BET surface areas of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts are also summarized in Table 1. BET surface areas of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts slightly decreased after the impregnation of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

## 2. Catalytic Performance in the Direct Synthesis of DMC from Methanol and Carbon Dioxide

Fig. 3 shows the typical catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

**Fig. 3. Typical catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide with time on stream at 170 °C.****Fig. 4. Catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction.**

$\text{Zr}_{0.4}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide with time on stream at 170 °C.  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  catalyst showed a stable catalytic performance after a 3 h-reaction. Therefore, steady-state catalytic performance data obtained after a 3 h-reaction were reported and used for further correlations in this work.

Fig. 4 shows the catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction. No by-products were observed in the reaction over  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts, indicating that the catalysts were highly selective for the formation of DMC. The catalytic performance of all catalysts with respect to reaction time was similar to that of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  catalyst (Fig. 3). The amount of DMC increased with increasing reaction time but no significant increase was observed after 3 h. As shown in Fig. 4, the amount of DMC produced over both  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $X=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts showed volcano-shaped curves with respect to cerium content ( $X$ ). Among the catalysts tested,  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  catalyst showed the best catalytic performance. What is noticeable is that  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  showed a better catalytic performance than the corresponding  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . It is known that  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  catalyst only retains Brønsted acid sites [18]. Compared to the acid sites of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ , therefore, it is believed that the acid sites of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts increased due to the Brønsted acid sites of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , leading to the enhanced catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide.

The leaching of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  during the reaction was confirmed by ICP-AES analysis. No detectable amount of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was found in the solution obtained after the catalytic reaction over  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ , indicating that there was no dissolution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  during the direct synthesis of DMC over  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts.

## 3. Acidity of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ Catalysts

NH<sub>3</sub>-TPD measurements were conducted to verify the effect of

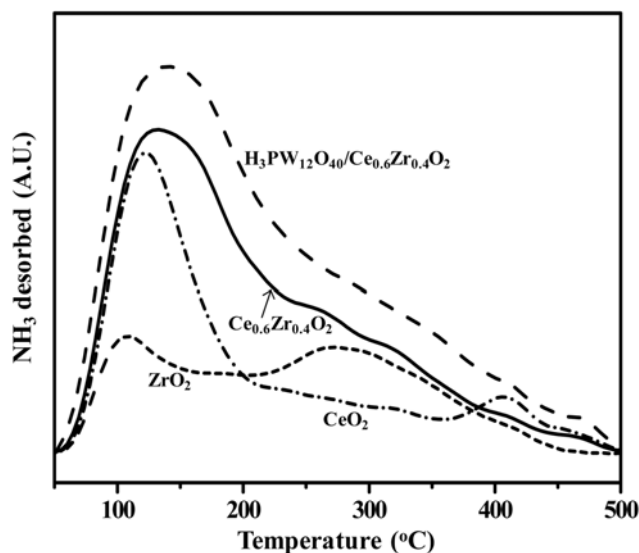


Fig. 5.  $\text{NH}_3$ -TPD profiles of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x=0, 0.6$ , and  $1.0$ ) and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ .

acidity on the catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide. Fig. 5 shows the  $\text{NH}_3$ -TPD profiles of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x=0, 0.6$ , and  $1.0$ ) and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ . Interestingly,  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts exhibited a significant difference in acidity (peak area) with a variation of cerium content ( $x$ ). This implies that acidity of the catalyst can serve as a crucial factor determining catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  in the direct synthesis of DMC from methanol and carbon dioxide. Acidity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts is summarized in Table 1. Acidity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts exhibited a volcano-shaped trend with respect to cerium content ( $x$ ). Among the  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts tested,  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  catalyst retained the largest acidity.

It is noteworthy that  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  retained a larger acidity than  $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ , as shown in Fig. 5. It is believed that the enhanced acidity of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  was attributed to the Brønsted acid sites provided by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . As listed in Table 1, acidity of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was larger than that of the corresponding  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . When considering the fact that  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  exhibited a better catalytic performance than the corresponding  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  (Fig. 4), it is believed that Brønsted acid sites of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  played an important role in enhancing the catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ .

#### 4. Correlation between Catalytic Performance and Acidity of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$

According to the reported mechanism for the reaction, methanol is activated to methyl species and methoxy species on the acid and base sites of the catalyst, respectively [1,2]. Methoxy carbonate anion is then formed by the reaction of methoxy species with carbon dioxide adsorbed on the base sites of the catalyst [2]. Methoxy carbonate anion further reacts with methyl species on the acid sites of the catalyst to produce DMC [2,29]. Among these reaction steps, activation of methanol to methyl species on the acid sites of the catalyst is known to be the rate-determining step [30,31]. Therefore, large amount of acid sites can facilitate the direct synthesis of DMC from methanol and carbon dioxide. Fig. 6 shows the correlation be-

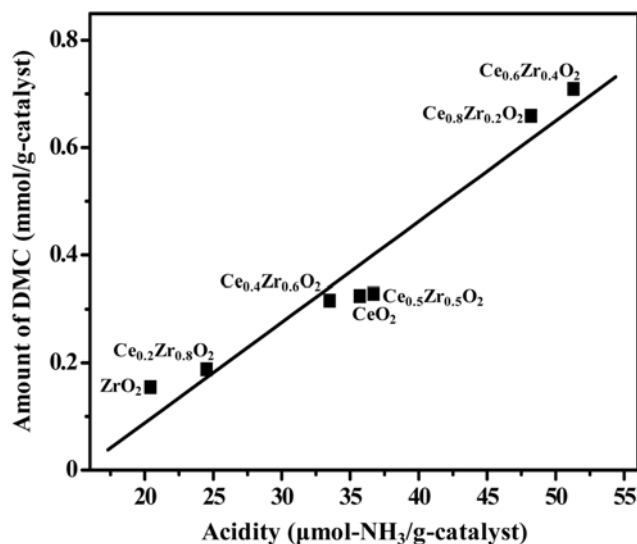


Fig. 6. A correlation between catalytic performance and acidity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ .

tween catalytic performance and acidity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . The correlation clearly shows that the catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was closely related to the acidity of the catalysts. The amount of DMC produced over  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  increased with increasing the acidity of the catalysts. This indicates that acidity of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts played a key role in determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

In the course of investigating the effect of acidity on the catalytic performance of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ , a similar correlation could be established. Fig. 7 shows the correlation between catalytic performance and acidity of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ . Once again, this correlation shows that acidity of the catalyst serves as a crucial factor determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Among the catalysts tested,  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  with the largest acidity showed the best cata-

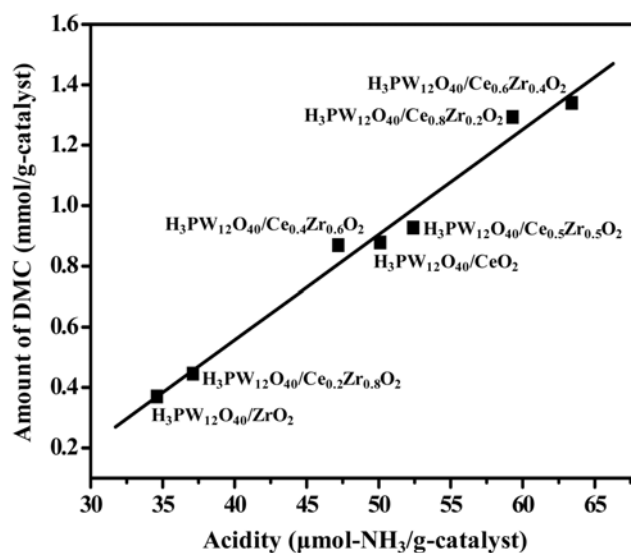


Fig. 7. A correlation between catalytic performance and acidity of  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ .

lytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

## CONCLUSIONS

$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts were prepared by a sol-gel method, and  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was then supported onto  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts by an impregnation method. The prepared  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  ( $x=0, 0.2, 0.4, 0.5, 0.6, 0.8$ , and  $1.0$ ) catalysts were applied to the direct synthesis of DMC from methanol and carbon dioxide. Successful formation of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts was well confirmed by XRD and ICP-AES analyses. The amounts of DMC produced over both  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  catalysts showed volcano-shaped curves with respect to cerium content ( $x$ ). Experimental results revealed that catalytic performance of  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  and  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  was closely related to the acidity of the catalysts. The amount of DMC increased with increasing acidity of the catalyst.  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  showed a better catalytic performance than the corresponding  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  due to the Brønsted acid sites provided by  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . Among the catalysts tested,  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$  with the largest acidity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

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