

Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide over $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ Catalysts: Effect of Acidity and Basicity of the Catalysts

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Abstract $\text{Ce}_X\text{Zr}_{1-X}\text{O}_2$ catalysts with different cerium content (X) ($X = 0, 0.2, 0.4, 0.5, 0.6, 0.8,$ and 1.0) were prepared by a sol–gel method for use in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. Among these catalysts, $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ was found to show the best catalytic performance. In order to enhance the acidity and basicity of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst, Ga_2O_3 was supported on $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15)) by an incipient wetness impregnation method with a variation of Ga_2O_3 content (X , wt%). Effect of acidity and basicity of $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ on the catalytic performance in the direct synthesis of dimethyl carbonate was investigated using NH_3 -TPD and CO_2 -TPD experiments. Experimental results revealed that both acidity and basicity of the catalysts played a key role in determining the catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. Large acidity and basicity of the catalyst facilitated the formation of dimethyl carbonate. The amount of dimethyl carbonate produced over $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts increased with increasing both acidity and basicity of the catalysts. Among the catalysts tested, $5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$, which retained the largest acidity and basicity, showed the best catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide.

Keywords Dimethyl carbonate · Methanol · Carbon dioxide · Gallium oxide · Ceria-zirconia

1 Introduction

Dimethyl carbonate (DMC) has attracted much attention as a green chemical that can replace dimethyl sulfate and phosgene, which are highly toxic and corrosive methylation and carbonylation agents [1, 2]. In addition, DMC has been widely employed as a good polar solvent and a chemical intermediate in the synthesis of various organic compounds and functional resins [3, 4]. Due to its high oxygen content and good blending nature with octane, DMC can also be used as a fuel additive [4, 5].

Several commercialized processes for the synthesis of DMC have been reported, including methanolysis of phosgene [3], oxidative carbonylation of methanol [4], oxidative carbon monoxide-methyl nitrite processes [5], and transesterification of alkene carbonate with methanol [6, 7]. However, these conventional processes involve many drawbacks in an environmental point of view, because toxic, flammable, explosive, and corrosive gases such as phosgene, hydrogen chloride, nitric oxide, and carbon monoxide are employed in the processes. Therefore, direct synthesis of DMC from methanol and carbon dioxide has been recognized as a green chemical process for the synthesis of DMC [8–12].

According to the mechanism for the direct synthesis of DMC from methanol and carbon dioxide [2, 8], 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 base sites of the catalyst [2]. Methoxy carbonate anion further

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reacts with methyl species on the acid sites of the catalyst to produce DMC [2, 8]. This implies that both acid and base sites of the catalyst play an important role in the direct synthesis of DMC from methanol and carbon dioxide. Therefore, it is expected that acid–base bifunctional catalysts will show an excellent catalytic activity in this reaction. Various catalysts have been utilized for the direct synthesis of DMC from methanol and carbon dioxide, including organometallic compounds [9, 10], metal tetraalkoxides [11], potassium carbonate [12], $\text{Ni}(\text{CH}_3\text{COO})_2$ [13], zirconia [8], $\text{CeO}_2\text{-ZrO}_2$ [14, 15], $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{ZrO}_2$ [16], and $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ce}_x\text{Ti}_{1-x}\text{O}_2$ [17]. 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 [14, 15].

It is known that gallium oxide (Ga_2O_3) retains both acid and base properties [18, 19]. It has also been reported that gallium oxide supported on metal oxide can modify the acidity and basicity of the support [20]. Therefore, many supported gallium oxide catalysts have been investigated for various acid–base catalytic reactions [19–22]. To our best knowledge, however, gallium oxide supported on metal oxide has never been applied to the direct synthesis of DMC from methanol and carbon dioxide. Therefore, a systematic investigation on the supported gallium oxide as a feasible catalyst for the direct synthesis of DMC would be worthwhile.

In this work, $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts were prepared by a sol–gel method with a variation of cerium content in order to find an appropriate support for Ga_2O_3 . Among the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts, $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ was found to show the best catalytic activity in the direct synthesis of DMC from methanol and carbon dioxide. Based on this result, Ga_2O_3 was supported on $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ by an incipient wetness impregnation method with a variation of Ga_2O_3 content to enhance the acidity and basicity of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$. The prepared $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts were applied to the direct synthesis of DMC from methanol and carbon dioxide. Acidity and basicity of $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts were measured by NH_3 -TPD and CO_2 -TPD experiments, respectively, with an aim of elucidating the effect of acidity and basicity of the catalysts on the catalytic performance in this reaction.

2 Experimental

2.1 Catalyst Preparation

$\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts were prepared by a sol–gel method with a variation of cerium content (X) ($X = 0, 0.2, 0.4, 0.5,$

$0.6, 0.8,$ and 1.0), according to the similar method in literature [23]. A known amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich) and $\text{ZrO}(\text{NO}_3) \cdot x\text{H}_2\text{O}$ (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 stirring the mixed solution at $80\text{ }^\circ\text{C}$ for 3 h, it was evaporated to obtain a gel. The gel was then dried at $100\text{ }^\circ\text{C}$ for 24 h. After grinding the dried gel, it was finally calcined at $500\text{ }^\circ\text{C}$ for 3 h in an air stream to yield $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ catalysts.

$\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich) with a variation of Ga_2O_3 content. Ga_2O_3 content in the $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts was adjusted to 1, 5, 10, and 15 wt%. After drying the impregnated catalysts overnight at $80\text{ }^\circ\text{C}$, they were calcined at $500\text{ }^\circ\text{C}$ for 3 h in an air stream. The prepared catalysts were denoted as $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15), where X represented wt% of Ga_2O_3 in $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$.

2.2 Catalyst Characterization

Crystalline phases of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15) 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 using a BET apparatus (Micromeritics, ASAP 2010). Chemical compositions of the catalysts were determined by ICP-AES (Shimadzu, ICP-1000IV) analyses.

Acidity of the catalysts was measured by NH_3 -TPD experiments. Each catalyst (0.2 g) was charged into the quartz reactor of the conventional TPD apparatus. It was pretreated at $200\text{ }^\circ\text{C}$ for 1 h under a flow of helium (20 mL/min) to remove any physisorbed organic molecules. 20 mL of ammonia was then pulsed into the reactor every minute at room temperature under a flow of helium (5 mL/min), until the acid sites were saturated with NH_3 . The physisorbed NH_3 was removed by evacuating the catalyst sample at $50\text{ }^\circ\text{C}$ for 1 h under a flow of helium (15 mL/min). Furnace temperature was increased from room temperature to $500\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under a flow of helium (10 mL/min). The desorbed ammonia was detected using a GC-MSD (Agilent, 5975MSD-6890N GC). Basicity of the catalysts was measured by CO_2 -TPD experiments. The experimental procedures for CO_2 -TPD were identical to those for NH_3 -TPD, except that CO_2 instead of NH_3 was employed as a probe molecule.

2.3 Direct Synthesis of DMC from Methanol and Carbon Dioxide

Direct synthesis of DMC from methanol and carbon dioxide was carried out 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 heating the reactor to the reaction temperature with constant stirring, the autoclave was pressurized up to 60 bar using carbon dioxide. Catalytic reaction was carried out at 170 °C for 3 h. After the reaction, the reactor was cooled to room temperature and depressurized. Reaction products were sampled and analyzed using a gas chromatograph (HP 5890 II).

3 Results and Discussion

3.1 Catalytic Performance of $Ce_xZr_{1-x}O_2$ Catalysts

In order to find an appropriate support for Ga_2O_3 catalyst in the direct synthesis of DMC from methanol and carbon dioxide, $Ce_xZr_{1-x}O_2$ samples were prepared by a sol-gel method with a variation of cerium content (X) ($X = 0, 0.2, 0.4, 0.5, 0.6, 0.8, \text{ and } 1.0$). Figure 1 shows the catalytic performance of $Ce_xZr_{1-x}O_2$ catalysts in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction. In the catalytic reaction, $Ce_xZr_{1-x}O_2$ catalysts were highly selective for the formation of DMC without any by-products. The amount of DMC increased with increasing reaction time, but no significant increase was observed after 3 h. What is interesting is that the amount of DMC produced over $Ce_xZr_{1-x}O_2$ catalysts showed a volcano-shaped curve with respect to cerium content (X). As mentioned earlier, both acid and base sites of the catalyst are required for the direct synthesis of DMC from methanol and carbon dioxide [8]. This implies that acid-base properties of $Ce_xZr_{1-x}O_2$ catalysts were different depending on cerium content (X), leading to the different catalytic activity in the direct synthesis of DMC from methanol and carbon dioxide. Among the $Ce_xZr_{1-x}O_2$ catalysts, $Ce_{0.6}Zr_{0.4}O_2$ showed the best catalytic performance in the reaction. Therefore, $Ce_{0.6}Zr_{0.4}O_2$ was chosen as an efficient support for further investigation of $Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$ catalysts in the direct synthesis of DMC from methanol and carbon dioxide.

3.2 Catalyst Characterization

Figure 2 shows the XRD patterns of $Ce_{0.6}Zr_{0.4}O_2$ and $XGa_2O_3/Ce_{0.6}Zr_{0.4}O_2$ ($X = 1, 5, 10, \text{ and } 15$) catalysts. For comparison, XRD patterns of CeO_2 and ZrO_2 are also

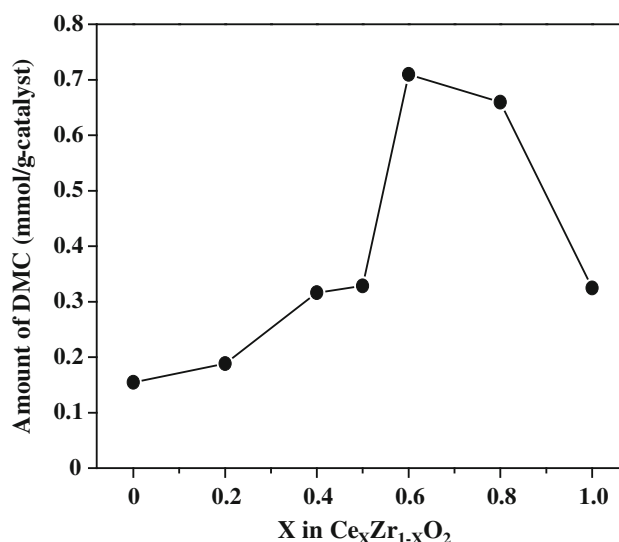


Fig. 1 Catalytic performance of $Ce_xZr_{1-x}O_2$ ($X = 0, 0.2, 0.4, 0.5, 0.6, 0.8, \text{ and } 1.0$) in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction

presented in Fig. 2. CeO_2 showed the peaks corresponding to (111), (200), (220), and (311) planes of cubic fluorite phase, while ZrO_2 exhibited the peaks for tetragonal phase. $Ce_{0.6}Zr_{0.4}O_2$ catalyst retained a single cubic fluorite phase without a detectable tetragonal phase, although the characteristic XRD peaks of $Ce_{0.6}Zr_{0.4}O_2$ slightly shifted to higher angles compared to the peaks for cubic fluorite phase of CeO_2 . The shift of XRD peaks was due to the shrinkage of lattices originated from the replacement of Ce^{4+} (ionic radius = 0.098 nm) with a smaller Zr^{4+} (ionic radius = 0.084 nm) in the $Ce_{0.6}Zr_{0.4}O_2$ catalysts [24, 25]. The above results are in good agreement with the previous reports [26, 27], indicating successful formation of $Ce_{0.6}Zr_{0.4}O_2$ in this work.

The formation of $XGa_2O_3/Ce_{0.6}Zr_{0.4}O_2$ ($X = 1, 5, 10, \text{ and } 15$) catalysts was confirmed by XRD and ICP-AES analyses. For XRD measurement of Ga_2O_3 , Ga_2O_3 was prepared by the thermal treatment of $Ga(NO_3)_3 \cdot xH_2O$ (Sigma-Aldrich) at 500 °C for 3 h in an air stream. The XRD pattern of Ga_2O_3 was presented in Fig. 2. It is noteworthy that no characteristic peaks for Ga_2O_3 were found in the $XGa_2O_3/Ce_{0.6}Zr_{0.4}O_2$ ($X = 1, 5, 10, \text{ and } 15$) catalysts. This indicates that Ga_2O_3 was finely dispersed on the surface of $Ce_{0.6}Zr_{0.4}O_2$ catalyst. This result is well consistent with the previous works [28, 29] reporting that no characteristic XRD peaks for Ga_2O_3 were detected for impregnated Ga_2O_3 samples such as Ga_2O_3/Al_2O_3 and Ga_2O_3/Nb_2O_5 . Ga_2O_3 contents (X) in the $XGa_2O_3/Ce_{0.6}Zr_{0.4}O_2$ catalysts determined by ICP-AES analyses were in good agreement with the designed values, although these are not shown here. This result indicates that $XGa_2O_3/Ce_{0.6}Zr_{0.4}O_2$ catalysts were successfully prepared

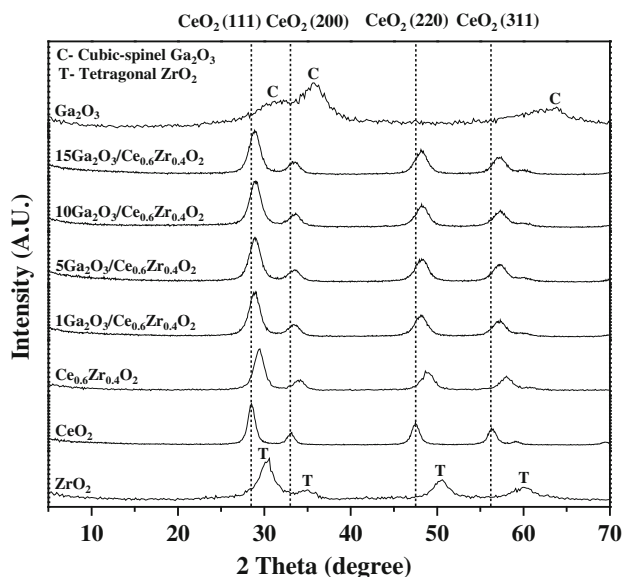


Fig. 2 XRD patterns of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10, \text{ and } 15$) catalysts

in this work. BET surface areas of $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts are summarized in Table 1. BET surface areas of $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts slightly decreased with increasing Ga_2O_3 content (X).

3.3 Catalytic Performance of $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ Catalysts

Figure 3 shows the catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10, \text{ and } 15$) in the direct synthesis of DMC from methanol and carbon dioxide at 170°C after a 3 h-catalytic reaction, plotted as a function of Ga_2O_3 content (X). No by-products were observed in the reaction over $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts, indicating that both $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ were highly selective for the formation of DMC. It is noticeable that all $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

catalysts showed a better catalytic performance than $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst. This indicates that $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts are more efficient than $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst in the direct synthesis of DMC from methanol and carbon dioxide. As shown in Fig. 3, the amount of DMC produced over $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts showed a volcano-shaped curve with respect to Ga_2O_3 content (X). Among the catalysts tested, $5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalyst showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

3.4 Effect of Acidity on the Catalytic Performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

In order to investigate the effect of acid properties on the catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10, \text{ and } 15$) catalysts, NH_3 -TPD experiments were conducted over the catalysts. Figure 4 shows the NH_3 -TPD profiles of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts. All the catalysts showed a broad NH_3 -TPD peak. $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts exhibited a significant difference in acidity (peak area) with a variation of Ga_2O_3 content (X). $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts also showed a slight difference in acid strength (peak temperature) with a variation of Ga_2O_3 content (X). We attempted to correlate the catalytic performance with the acid properties (acidity and acid strength) of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts. Unfortunately, acid strength was not directly correlated with the catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$. However, a reliable correlation between acidity and catalytic activity of the catalysts was observed. Acidity of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts calculated from NH_3 -TPD peak area is summarized in Table 1. Acidity of the catalysts decreased in the order of $5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > 1\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > 10\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > 15\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$.

Table 1 Surface area, acidity, and basicity of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10, \text{ and } 15$) catalysts

Catalyst	Surface area (m^2/g) ^a	Acidity ($\mu\text{mol-NH}_3/\text{g-catalyst}$) ^b	Basicity ($\mu\text{mol-CO}_2/\text{g-catalyst}$) ^c
$\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	53.8	85.7	17.0
$1\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	51.6	170.5	50.9
$5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	50.0	226.3	121.8
$10\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	43.5	143.7	45.4
$15\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$	34.9	110.7	36.7

^a Calculated by the BET (Brunauer–Emmett–Teller) equation

^b Determined by NH_3 -TPD measurement

^c Determined by CO_2 -TPD measurement

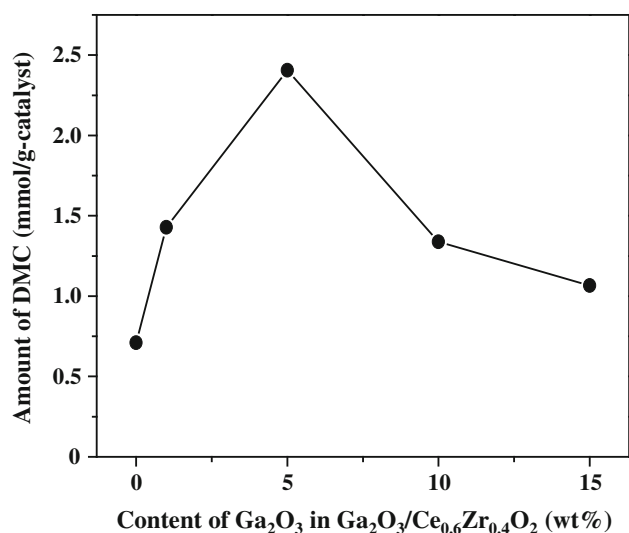


Fig. 3 Catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15) in the direct synthesis of DMC from methanol and carbon dioxide at 170°C after a 3 h-catalytic reaction

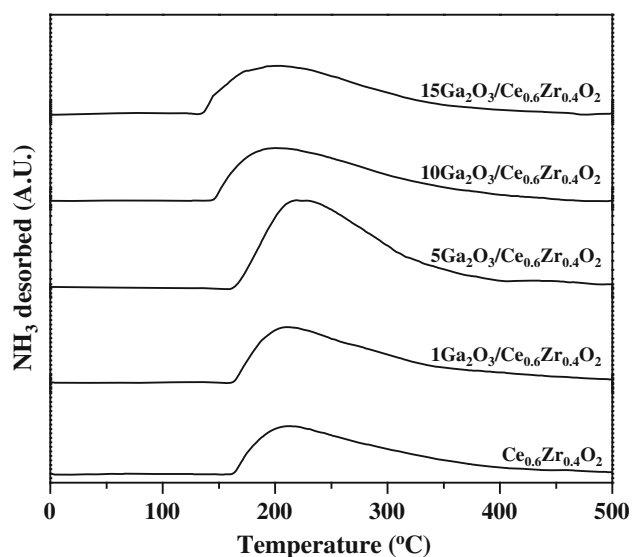


Fig. 4 NH_3 -TPD profiles of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15) catalysts

Figure 5 shows the correlation between acidity and catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15). Acidity (NH_3 -TPD peak area) was directly correlated with the catalytic performance. The amount of DMC produced over $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts increased with increasing acidity of the catalysts. Among the catalysts tested, $5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ with the largest acidity exhibited the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. As mentioned earlier, methanol is activated to methyl species on the acid sites for the DMC formation [30, 31]. This

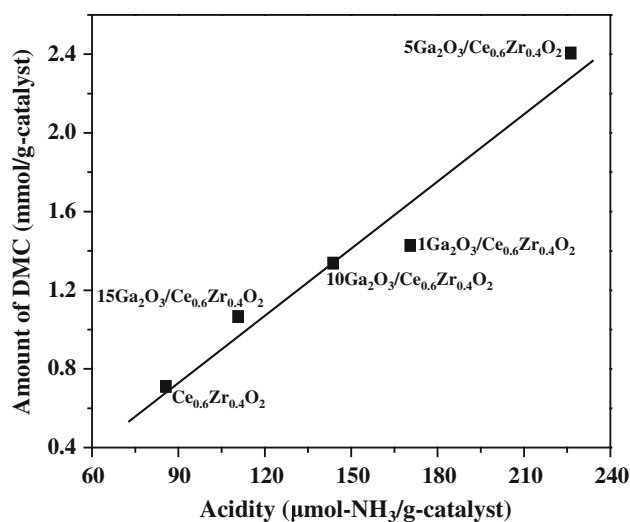


Fig. 5 Correlation between acidity and catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15)

indicates that acidity of the catalyst plays an important role in determining the catalytic performance in this reaction. Therefore, it is believed that large acidity of the catalyst was favorable for the activation of methanol to methyl species, leading to the facile formation of DMC in the direct synthesis of DMC from methanol and carbon dioxide [30, 31].

3.5 Effect of Basicity on the Catalytic Performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

According to the mechanism of DMC formation, not only acid sites but also base sites of the catalyst play an important role in the direct synthesis of DMC from methanol and carbon dioxide [30, 31]. Therefore, CO_2 -TPD experiments were conducted with an aim of investigating the effect of base properties on the catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($X = 1, 5, 10,$ and 15) catalysts. Figure 6 shows the CO_2 -TPD profiles of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts. As similarly observed in the effect of acid properties, no reliable correlation between base strength (peak temperature) and catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ was found, while a good correlation between basicity (peak area) and catalytic performance of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ could be established. Basicity of $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ and $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts calculated from CO_2 -TPD peak area is listed in Table 1. Basicity of the catalysts decreased in the order of $5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > 1\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > 10\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > 15\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$. Interestingly, basicity of $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts showed the same trend as acidity of the catalysts. This implies that both acidity and basicity of $X\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts

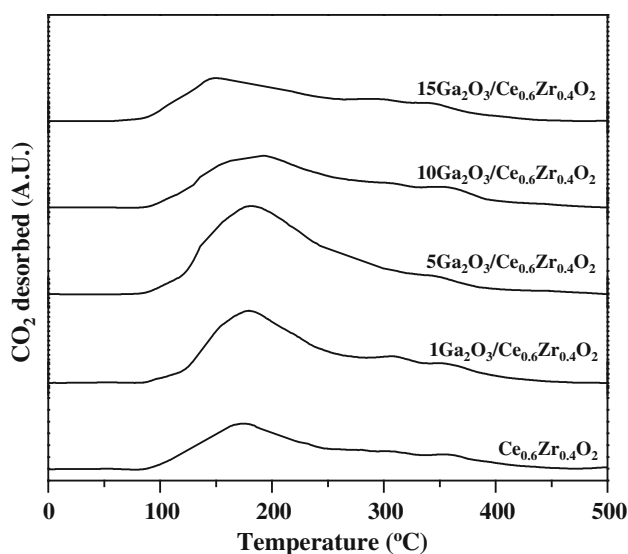


Fig. 6 CO₂-TPD profiles of Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ (X = 1, 5, 10, and 15) catalysts

were simultaneously enhanced by impregnating Ga₂O₃ on Ce_{0.6}Zr_{0.4}O₂.

Figure 7 shows the correlation between basicity and catalytic performance of Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ (X = 1, 5, 10, and 15). The correlation clearly shows that the catalytic performance was closely related to the basicity of Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ catalysts. The amount of DMC produced over Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ catalysts increased with increasing basicity of the catalysts. Among the catalysts tested, 5Ga₂O₃/Ce_{0.6}Zr_{0.4}O₂ with the largest basicity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. It has been reported that base sites of the catalyst are required for the formation methoxy carbonate anion through the reaction of carbon dioxide with methoxy species in the direct synthesis of DMC from methanol and carbon dioxide [1, 2]. The methoxy carbonate anion formed on the base sites of the catalyst reacts with methyl species on the acid sites of the catalyst to produce dimethyl carbonate [16]. Therefore, it is believed that large basicity of the catalyst can facilitate the formation of DMC from methanol and carbon dioxide [30, 31].

As shown in Figs. 5 and 7, the catalytic performance of XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ was closely related to both acidity and basicity of the catalyst in the direct synthesis of DMC from methanol and carbon dioxide. When considering the fact that all XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ (X = 1, 5, 10, and 15) exhibited a better catalytic performance than Ce_{0.6}Zr_{0.4}O₂ (Fig. 3) in the direct synthesis of DMC from methanol and carbon dioxide, it is thought that acid and base sites provided by Ga₂O₃ played an important role in enhancing the catalytic performance of XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ in this

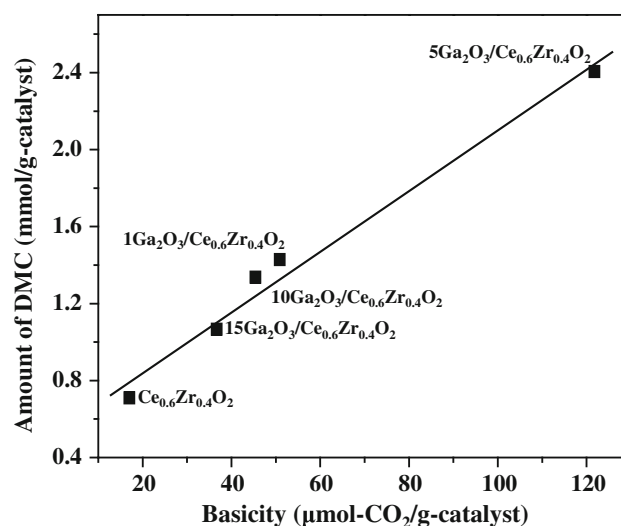


Fig. 7 Correlation between basicity and catalytic performance of Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ (X = 1, 5, 10, and 15)

reaction. In addition, the amount of DMC produced over Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ catalysts increased with increasing both acidity and basicity of the catalysts. Therefore, it is concluded that both acidity and basicity of the catalyst can serve as crucial factors determining catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Among the catalysts tested, 5Ga₂O₃/Ce_{0.6}Zr_{0.4}O₂, which retained the largest acidity and basicity, exhibited the best catalytic performance in this reaction.

4 Conclusions

Among various Ce_xZr_{1-x}O₂ samples prepared by a sol-gel method, Ce_{0.6}Zr_{0.4}O₂ was found to be the most favorable support for Ga₂O₃. On the basis of this result, Ga₂O₃ was supported on Ce_{0.6}Zr_{0.4}O₂ by an incipient wetness impregnation method with a variation of Ga₂O₃ content (X, wt%) for use in the direct synthesis of DMC from methanol and carbon dioxide. XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ showed a better catalytic performance than Ce_{0.6}Zr_{0.4}O₂ due to the enhanced acid and base sites provided by Ga₂O₃. Acid and base sites of the catalyst were responsible for activation of methanol to methyl species and methoxy species, respectively. Base sites of the catalyst were also required for the formation of methoxy carbonate anion through the reaction of carbon dioxide with methoxy species. Experimental results revealed that the catalytic performance of Ce_{0.6}Zr_{0.4}O₂ and XGa₂O₃/Ce_{0.6}Zr_{0.4}O₂ catalysts was closely related to the acidity and basicity of the catalysts. The amount of DMC increased with increasing both acidity and basicity of the catalyst. Among the catalysts tested,

$5\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ with the largest acidity and basicity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. It is concluded that both acidity and basicity of the catalyst played an important role in determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

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References

1. Keller N, Rebmann G, Keller V (2010) *J Mol Catal A Chem* 317:1–18
2. Delledonne D, Rivetti F, Romano U (2001) *Appl Catal A Gen* 221:241–251
3. Babad H, Zeiler AG (1973) *Chem Rev* 73:75–91
4. King ST (1997) *Catal Today* 33:173–182
5. Matsuzaki T, Nakamura A (1997) *Catal Surv Jpn* 1:77–88
6. Ju H-Y, Mampambath DM, Kim K-H, Park S-W, Park D-W (2007) *Korean J Chem Eng* 24:917–919
7. Kim K-H, Kim D-W, Kim C-W, Koh J-C, Park D-W (2010) *Korean J Chem Eng* 27:1441–1445
8. Tomishige K, Ikeda Y, Sakaiori T, Fujimoto K (2000) *J Catal* 192:355–362
9. Kizlink J (1993) *Collect Czech Chem Commun* 58:1399–1402
10. Sakakura T, Choi J-C, Saito Y, Sako T (2000) *Polyhedron* 19:573–576
11. Kizlink J, Pastucha I (1995) *Collect Czech Chem Commun* 60:687–692
12. Fang S, Fujimoto K (1996) *Appl Catal A Gen* 142:L1–L3
13. Zhao T, Han Y, Sum Y (2000) *Fuel Process Technol* 62:187–194
14. Tomishige K, Furusawa Y, Ikeda Y, Asadullah M, Fujimoto K (2001) *Catal Lett* 76:71–74
15. Tomishige K, Kunimori K (2002) *Appl Catal A Gen* 237:103–109
16. Jiang C, Guo Y, Wang C, Hu C, Wu Y, Wang E (2003) *Appl Catal A Gen* 256:203–212
17. La KW, Youn MH, Chung JS, Baeck S-H, Song IK (2007) *Solid State Phenom* 119:287–290
18. Petre AL, Auroux A, Gelin P, Caldararu M, Ionescu NI (2001) *Thermochim Acta* 79:117–185
19. Halasz J, Konya Z, Fudala A, Beres A, Kiricsi I (1996) *Catal Today* 31:293–304
20. Xu B, Zheng B, Hua W, Yue Y, Gao Z (2006) *J Catal* 239:470–477
21. Nakagawa K, Kajita C, Ide Y, Okamura M, Kato S, Kasuya H, Ikenaga N-O, Kobayashi T, Suzuki T (2000) *Catal Lett* 64:215–221
22. Yuliati L, Hattori T, Itoh H, Yoshida H (2008) *J Catal* 257:396–402
23. Seo JG, Youn MH, Cho KM, Park S, Lee SH, Lee J, Song IK (2008) *Korean J Chem Eng* 25:41–45
24. Rao GR, Rajkumar T (2008) *J Colloid Interface Sci* 324:134–141
25. Pantu P, Kim K, Gavalas GR (2000) *Appl Catal A Gen* 193:203–214
26. Dhage SR, Gaikwad SP, Muthukumar P (2004) *Mater Lett* 58:2704–2706
27. Postole G, Chowdhury B, Karmakar B, Pinki K, Banerji J, Auroux A (2010) *J Catal* 269:110–121
28. Shimizu K-I, Satsuma A, Hattori T (1998) *Appl Catal B Environ* 16:319–326
29. Petre AL, Perdigon-Melon JA, Gervasini A, Auroux A (2003) *Catal Today* 78:377–386
30. La KW, Jung JC, Kim H, Baeck S-H, Song IK (2007) *J Mol Catal A Chem* 269:41–45
31. Jung KT, Bell AT (2001) *J Catal* 204:339–347