

Direct synthesis of dimethyl carbonate from methanol and carbon dioxide over transition metal oxide/Ce_{0.6}Zr_{0.4}O₂ catalysts: Effect of acidity and basicity of the catalysts

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Abstract—Ce_xZr_{1-x}O₂ 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. Among these catalysts, Ce_{0.6}Zr_{0.4}O₂ showed the best catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. To see the effect of acidity and basicity of transition metal oxide/Ce_{0.6}Zr_{0.4}O₂ catalysts on the catalytic performance in the direct synthesis of dimethyl carbonate, MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) catalysts were prepared by an incipient wetness impregnation method. NH₃-TPD and CO₂-TPD experiments were carried out to measure acidity and basicity of the supported catalysts, respectively. 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. The amount of dimethyl carbonate produced over MO/Ce_{0.6}Zr_{0.4}O₂ catalysts increased with increasing both acidity and basicity of the catalysts. Among the catalysts tested, Ga₂O₃/Ce_{0.6}Zr_{0.4}O₂, which had the largest acidity and basicity, exhibited the best catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide.

Key words: Dimethyl Carbonate, Methanol, Carbon Dioxide, Acid-base Property, Ceria-zirconia, Supported Transition Metal Oxide

INTRODUCTION

Dimethyl carbonate (DMC) is an environmentally benign chemical product and important intermediate with versatile chemical reactivity. It can be used as a non-toxic substitute for dimethyl sulfate and phosgene, which are highly toxic and corrosive methylation and carbonylation agents [1,2]. DMC can also be used as a good solvent, a monomer for the synthesis of functional resins, and a fuel additive that can replace MTBE [1,2]. The traditional synthesis route of DMC requires highly toxic phosgene as a reagent [3]. Oxidative carbonylation of CH₃OH with CO and O₂ using a cuprous chloride catalyst [4] or a palladium catalyst with methyl nitrate promoter [5] has also been attempted. However, these conventional processes involve many drawbacks 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. Transesterification of ethylene carbonate or propylene carbonate with methanol [6,7] and urea methanolysis [8] have also been studied. However, direct synthesis of DMC from methanol and carbon dioxide has attracted much attention as an environmentally benign chemical process [9-13]. Although DMC yield in the direct synthesis reaction still remains low due to the thermodynamic equilibrium limitation, it has been reported that this problem can be solved by shifting the equilibrium through pressurizing carbon dioxide and adding effective dehydrating agents [1]. Thus, developing an appropriate catalyst for the direct synthesis of DMC from methanol and carbon dioxide would be worthwhile.

According to the mechanism for the direct synthesis of DMC from methanol and carbon dioxide [2,9], 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 [2,9]. These imply 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 used for the direct synthesis of DMC from methanol and carbon dioxide, including organometallic compounds [10,11], metal tetra-alkoxides [12], potassium carbonate [13], Ni(CH₃COO)₂ [14], zirconia [9], CeO₂-ZrO₂ [15,16], H₃PW₁₂O₄₀/ZrO₂ [17], H₃PW₁₂O₄₀/Ce_xTi_{1-x}O₂ [18], and H₃PW₁₂O₄₀/Ce_xZr_{1-x}O₂ [19].

It has been reported that transition metal oxides retain both acid and base properties, and these transition metal oxides supported on metal oxide can modify the acidity and basicity of the support [20-23]. Therefore, many supported transition metal oxide catalysts have been investigated for various acid-base catalytic reactions [22,23]. To the best of our knowledge, however, transition metal oxides supported on metal oxide have never been applied to the direct synthesis of DMC from methanol and carbon dioxide. Therefore, a systematic investigation on the supported transition metal oxide as a feasible catalyst for the direct synthesis of DMC would be meaningful.

In this work, Ce_xZr_{1-x}O₂ catalysts were prepared by a sol-gel method with a variation of cerium content (X) in order to find an appropriate support for transition metal oxides. Among the Ce_xZr_{1-x}O₂ cata-

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lysts, $Ce_{0.6}Zr_{0.4}O_2$ was found to show the best catalytic activity in the direct synthesis of DMC from methanol and carbon dioxide. Based on this result, transition metal oxides (Ga_2O_3 , La_2O_3 , Ni_2O_3 , Fe_2O_3 , Y_2O_3 , Co_3O_4 , and Al_2O_3) were supported on $Ce_{0.6}Zr_{0.4}O_2$ by an incipient wetness impregnation method to improve the acidity and basicity of $Ce_{0.6}Zr_{0.4}O_2$. The prepared $MO/Ce_{0.6}Zr_{0.4}O_2$ ($MO=Ga_2O_3$, La_2O_3 , Ni_2O_3 , Fe_2O_3 , Y_2O_3 , Co_3O_4 , and Al_2O_3) catalysts were applied to the direct synthesis of DMC from methanol and carbon dioxide. Acidity and basicity of $MO/Ce_{0.6}Zr_{0.4}O_2$ 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.

EXPERIMENTAL

1. Catalyst Preparation

$Ce_xZr_{1-x}O_2$ 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 a similar method in the literature [24]. A known amount of $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich) and $ZrO(NO_3)_2 \cdot xH_2O$ (Sigma-Aldrich) was dissolved in distilled water. A known amount of citric acid ($C_6H_8O_7$, 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 $80^\circ C$ for 3 h, it was evaporated to obtain a gel. The gel was then dried at $100^\circ C$ for 24 h. After the dried gel was ground, it was finally calcined at $500^\circ C$ for 3 h in an air stream to yield $Ce_xZr_{1-x}O_2$ catalysts.

$MO/Ce_{0.6}Zr_{0.4}O_2$ ($MO=Ga_2O_3$, La_2O_3 , Ni_2O_3 , Fe_2O_3 , Y_2O_3 , Co_3O_4 , and Al_2O_3) catalysts were prepared by an incipient wetness impregnation method using an aqueous solution of nitrate precursor. The loading of transition metal oxides on $Ce_{0.6}Zr_{0.4}O_2$ was fixed at 5 wt% in all cases. After transition metal oxides were impregnated onto $Ce_{0.6}Zr_{0.4}O_2$, the $MO/Ce_{0.6}Zr_{0.4}O_2$ catalysts were dried at $100^\circ C$ for 24 h and calcined at $500^\circ C$ for 3 h in an air stream.

2. Catalyst Characterization

Crystalline phases of $MO/Ce_{0.6}Zr_{0.4}O_2$ ($MO=Ga_2O_3$, La_2O_3 , Ni_2O_3 , Fe_2O_3 , Y_2O_3 , Co_3O_4 , and Al_2O_3) catalysts were investigated by XRD measurements (Rigaku, D-MAX2500-PC) using $Cu-K\alpha$ 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).

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 $200^\circ C$ 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 the flow of helium (5 ml/min), until the acid sites were saturated with NH_3 . Physisorbed NH_3 was removed by evacuating the catalyst sample at $50^\circ C$ for 1 h under the flow of helium (15 ml/min). Furnace temperature was increased from room temperature to $500^\circ C$ at a heating rate of $5^\circ C/min$ under the flow of helium (10 ml/min). Desorbed ammonia was detected by using a GC-MSD (Agilent, 5975MSD-6890N GC). Basicity of the catalysts was measured by CO_2 -TPD experiments. 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.

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 the reactor was heated to the reaction temperature with constant stirring, the autoclave was pressurized up to 60 bar by using carbon dioxide. Catalytic reaction was carried out at $170^\circ C$ for 3 h. After the reaction, the reactor was cooled to room temperature and depressurized. Reaction products were sampled and analyzed with a gas chromatograph (HP 5890 II, FID) on the basis of mole balance. In the catalytic reactions, DMC was selectively produced without any by-products. Formation of DME (dimethylether) was under detection limit. No products were also observed in the gas phase.

RESULTS AND DISCUSSION

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

To find an appropriate support for transition metal oxide catalysts 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) ($X=0, 0.2, 0.4, 0.5, 0.6, 0.8$, and 1.0). Fig. 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 $170^\circ C$ 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 important for the direct synthesis of DMC from methanol and carbon dioxide [9]. This indicates that acid-base properties of $Ce_xZr_{1-x}O_2$ catalysts were different depending on cerium content

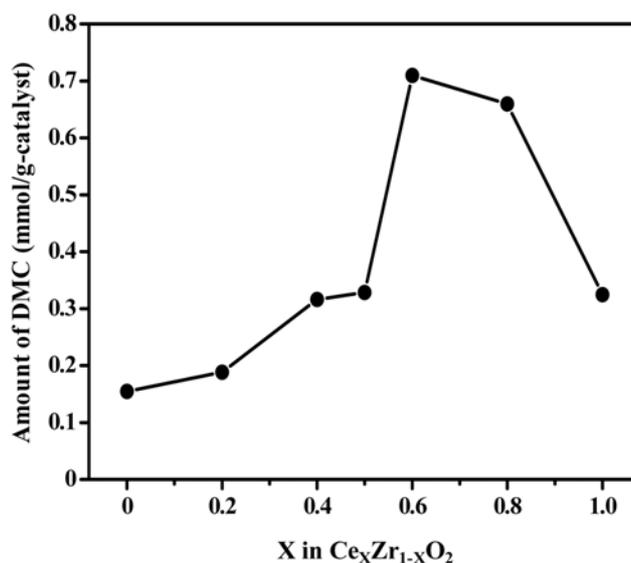


Fig. 1. Catalytic performance of $Ce_xZr_{1-x}O_2$ ($X=0, 0.2, 0.4, 0.5, 0.6, 0.8$, and 1.0) in the direct synthesis of DMC from methanol and carbon dioxide at $170^\circ C$ after a 3 h-catalytic reaction.

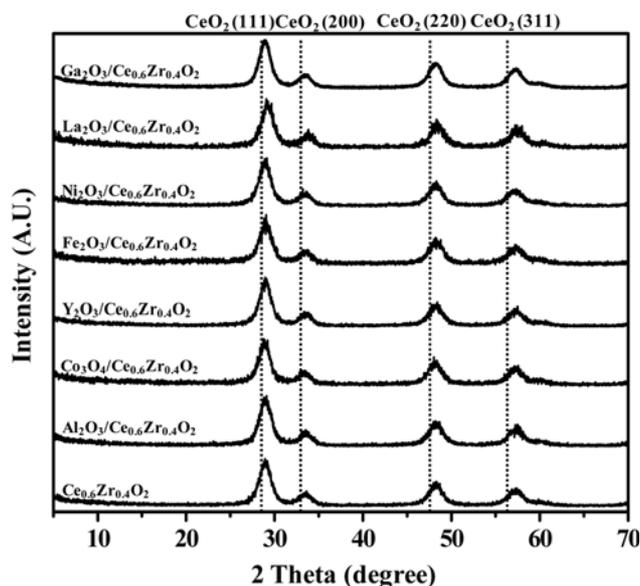


Fig. 2. XRD patterns of Ce_{0.6}Zr_{0.4}O₂ and MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) catalysts.

(X), leading to the different catalytic activity in the direct synthesis of DMC from methanol and carbon dioxide. Among the Ce_xZr_{1-x}O₂ catalysts, Ce_{0.6}Zr_{0.4}O₂ exhibited the best catalytic performance in this reaction. Therefore, Ce_{0.6}Zr_{0.4}O₂ was chosen as an efficient support for further investigation of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts in the direct synthesis of DMC from methanol and carbon dioxide.

2. Catalyst Characterization

Fig. 2 shows the XRD patterns of MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) catalysts. For comparison, the XRD pattern of Ce_{0.6}Zr_{0.4}O₂ is also presented in Fig. 2. In our previous work [19,25], we found that Ce_{0.6}Zr_{0.4}O₂ retained a single cubic fluorite phase (characteristic phase of CeO₂) without a detectable tetragonal phase (characteristic phase of ZrO₂), although the characteristic XRD peaks of Ce_{0.6}Zr_{0.4}O₂ slightly shifted to higher angles compared to the peaks for cubic fluorite phase of CeO₂. We also found that the shift of XRD peaks was due to the shrinkage of lattices originating from the replacement of Ce⁴⁺ (ionic radius=0.098 nm) with a smaller Zr⁴⁺ (ionic radius=0.084 nm) in the Ce_{0.6}Zr_{0.4}O₂ catalysts [26,27]. XRD peaks of Ce_{0.6}Zr_{0.4}O₂ were in good agreement with those of previous works [28,29], indicating successful formation of Ce_{0.6}Zr_{0.4}O₂.

On the other hand, no characteristic diffraction peaks for transition metal oxides (Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) were found in the MO/Ce_{0.6}Zr_{0.4}O₂ catalysts. This indicates that supported transition metal oxides were finely dispersed on the surface of Ce_{0.6}Zr_{0.4}O₂. This result was well consistent with the previous works reporting that no characteristic XRD peaks for transition metal oxides were detected for impregnated transition metal oxide samples such as Ga₂O₃/Al₂O₃ [30], Ga₂O₃/Nb₂O₅ [31], Al₂O₃/ZrO₂ [23], La₂O₃/ZrO₂ [24], La₂O₃/Al₂O₃ [32], Fe₂O₃/SiO₂ [33]. These results indicate that MO/Ce_{0.6}Zr_{0.4}O₂ catalysts were successfully prepared in this work. BET surface areas of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts are summarized in Table 1. For comparison, the BET surface area of Ce_{0.6}Zr_{0.4}O₂ is also listed in Table 1. It was found that BET sur-

Table 1. Surface area, acidity, and basicity of MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) catalysts

Catalyst	Surface area (m ² /g) ^a	Acidity (mol-NH ₃ /g-catalyst) ^b	Basicity (mol-CO ₂ /g-catalyst) ^c
Ce _{0.6} Zr _{0.4} O ₂	53.8	85.7	17.0
Ga ₂ O ₃ /Ce _{0.6} Zr _{0.4} O ₂	50.0	226.3	121.8
La ₂ O ₃ /Ce _{0.6} Zr _{0.4} O ₂	52.2	210.4	110.8
Ni ₂ O ₃ /Ce _{0.6} Zr _{0.4} O ₂	42.8	188.6	94.2
Fe ₂ O ₃ /Ce _{0.6} Zr _{0.4} O ₂	48.1	180.1	88.0
Y ₂ O ₃ /Ce _{0.6} Zr _{0.4} O ₂	45.8	164.5	84.6
Co ₃ O ₄ /Ce _{0.6} Zr _{0.4} O ₂	43.4	146.5	78.3
Al ₂ O ₃ /Ce _{0.6} Zr _{0.4} O ₂	41.9	132.6	68.2

^aCalculated by the BET (Brunauer-Emmett-Teller) equation

^bDetermined by NH₃-TPD measurement

^cDetermined by CO₂-TPD measurement

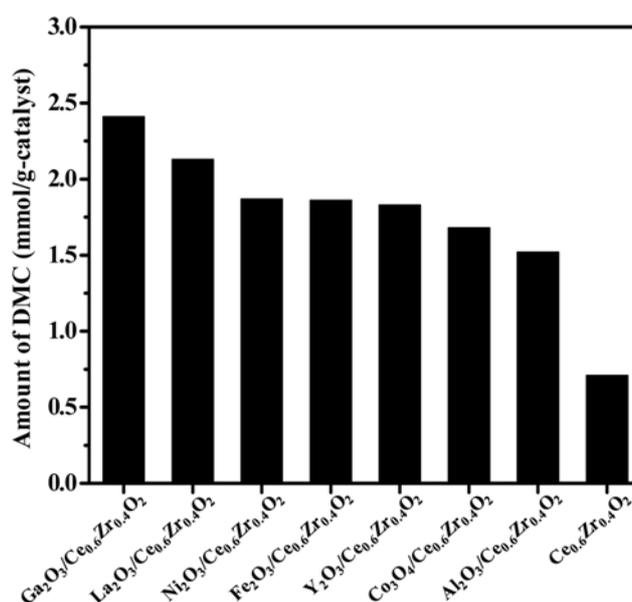


Fig. 3. Catalytic performance of Ce_{0.6}Zr_{0.4}O₂ and MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction.

face areas of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts showed no significant difference.

3. Catalytic Performance of MO/Ce_{0.6}Zr_{0.4}O₂ Catalysts

Fig. 3 shows the catalytic performance of MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction. For comparison, the catalytic performance of Ce_{0.6}Zr_{0.4}O₂ is also presented in Fig. 3. No by-products were observed in the reaction over Ce_{0.6}Zr_{0.4}O₂ and MO/Ce_{0.6}Zr_{0.4}O₂ catalysts, indicating that both Ce_{0.6}Zr_{0.4}O₂ and MO/Ce_{0.6}Zr_{0.4}O₂ were highly selective for the formation of DMC. All the MO/Ce_{0.6}Zr_{0.4}O₂ catalysts exhibited better catalytic performance than Ce_{0.6}Zr_{0.4}O₂ catalyst. We also found that catalytic performance of MO/Ce_{0.6}Zr_{0.4}O₂

catalysts was strongly affected by the identity of supported transition metal oxide. As shown in Fig. 3, $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

4. Effect of Acidity on the Catalytic Performance of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

According to the mechanism study [1], methanol is activated to methyl species on the acid sites, while methanol is converted into methoxy species on the base sites of the catalyst. Methoxy species then react with carbon dioxide on the base sites to form methoxy carbonate [2]. DMC is finally produced by the reaction of methoxy carbonate with methyl species on the acid sites of the catalyst [2,9]. Among these reaction steps, the activation of methanol to methyl species on the acid sites of the catalyst is known to be the rate-determining step [34,35]. Therefore, a large amount of acid sites would be favorable for the direct synthesis of DMC from methanol and carbon dioxide.

NH_3 -TPD experiments were conducted over the catalysts in order to see the effect of acid properties on the catalytic performance of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($\text{MO}=\text{Ga}_2\text{O}_3, \text{La}_2\text{O}_3, \text{Ni}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Y}_2\text{O}_3, \text{Co}_3\text{O}_4,$ and Al_2O_3) catalysts. Fig. 4 shows the NH_3 -TPD profiles of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts. All the catalysts exhibited a broad NH_3 -TPD peak. $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts exhibited a significant difference in acidity (peak area) depending on the kind of supported transition metal oxide. Acidity of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts calculated from NH_3 -TPD peak area is summarized in Table 1. Acidity of the catalysts decreased in the order of $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{La}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Ni}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Fe}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Y}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Co}_3\text{O}_4/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2 > \text{Al}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$.

Fig. 5 shows the correlation between acidity and catalytic performance of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$. Acidity (NH_3 -TPD peak area) was directly correlated with the catalytic performance. The amount of DMC produced over $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts increased with increasing acidity of the catalysts. Among the catalysts tested, $\text{Ga}_2\text{O}_3/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ with the largest acidity exhibited the best catalytic performance in the direct synthesis of DMC from methanol and car-

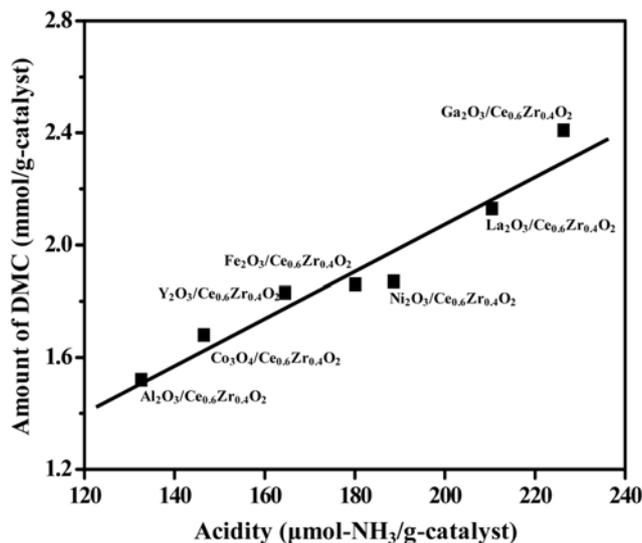


Fig. 5. A correlation between acidity and catalytic performance of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($\text{MO}=\text{Ga}_2\text{O}_3, \text{La}_2\text{O}_3, \text{Ni}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Y}_2\text{O}_3, \text{Co}_3\text{O}_4,$ and Al_2O_3).

bon dioxide. As mentioned earlier, methanol is activated to methyl species on the acid sites for the DMC formation [34,35]. This indicates that the acidity of the catalyst plays a crucial 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 [34,35].

5. Effect of Basicity on the Catalytic Performance of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$

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 [34, 35]. Base sites of the catalyst are responsible for the formation of

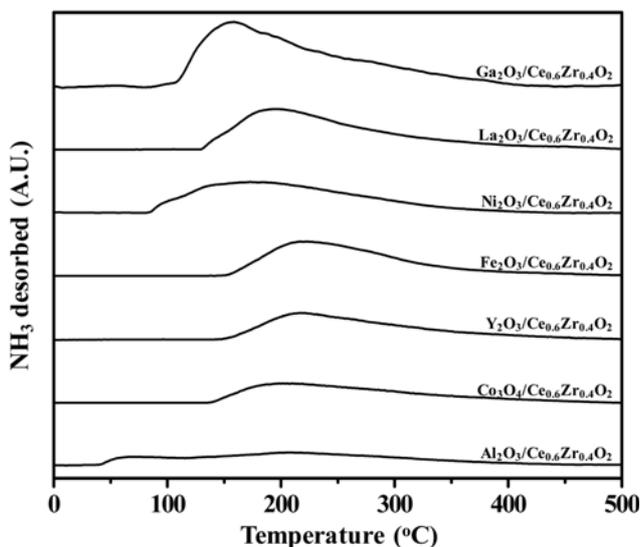


Fig. 4. NH_3 -TPD profiles of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($\text{MO}=\text{Ga}_2\text{O}_3, \text{La}_2\text{O}_3, \text{Ni}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Y}_2\text{O}_3, \text{Co}_3\text{O}_4,$ and Al_2O_3).

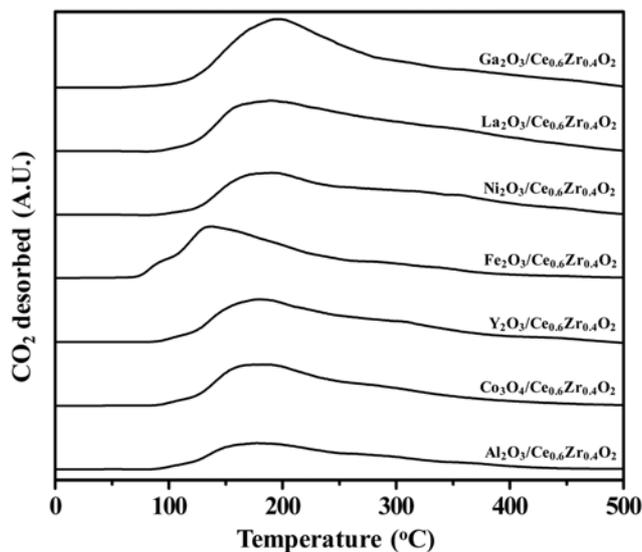


Fig. 6. CO_2 -TPD profiles of $\text{MO}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ ($\text{MO}=\text{Ga}_2\text{O}_3, \text{La}_2\text{O}_3, \text{Ni}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Y}_2\text{O}_3, \text{Co}_3\text{O}_4,$ and Al_2O_3).

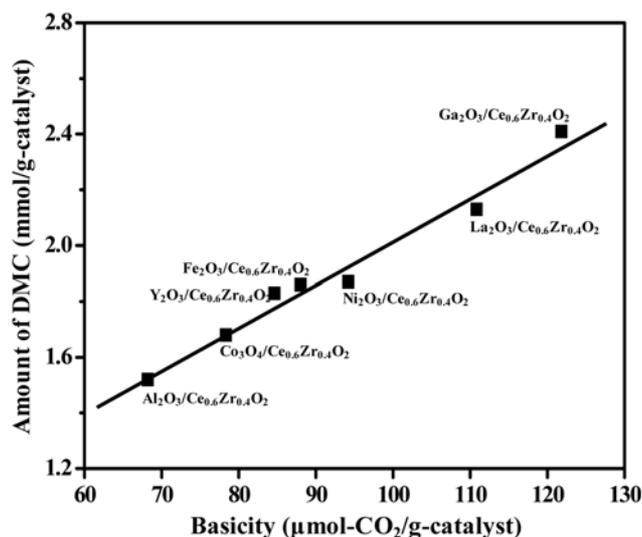


Fig. 7. A correlation between basicity and catalytic performance of MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃).

methoxy carbonate anion through the reaction of carbon dioxide with methoxy species [1,2]. CO₂-TPD experiments were conducted with an aim of investigating the effect of base properties on the catalytic performance of MO/Ce_{0.6}Zr_{0.4}O₂ (MO=Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃) catalysts. Fig. 6 shows the CO₂-TPD profiles of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts. The basicity of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts calculated from CO₂-TPD peak area is listed in Table 1. The basicity of the catalysts decreased in the order of Ga₂O₃/Ce_{0.6}Zr_{0.4}O₂>La₂O₃/Ce_{0.6}Zr_{0.4}O₂>Ni₂O₃/Ce_{0.6}Zr_{0.4}O₂>Fe₂O₃/Ce_{0.6}Zr_{0.4}O₂>Y₂O₃/Ce_{0.6}Zr_{0.4}O₂>Co₃O₄/Ce_{0.6}Zr_{0.4}O₂>Al₂O₃/Ce_{0.6}Zr_{0.4}O₂. Interestingly, the basicity of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts showed the same trend as acidity of the catalysts. This implies that both acidity and basicity of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts were simultaneously enhanced by impregnating transition metal oxide on Ce_{0.6}Zr_{0.4}O₂.

Fig. 7 shows the correlation between basicity and catalytic performance of MO/Ce_{0.6}Zr_{0.4}O₂. The correlation clearly shows that the catalytic performance was closely related to the basicity of MO/Ce_{0.6}Zr_{0.4}O₂ catalysts. The amount of DMC produced over MO/Ce_{0.6}Zr_{0.4}O₂ catalysts increased with increasing basicity of the catalysts. Among the catalysts tested, Ga₂O₃/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 [9]. Therefore, it is believed that large basicity of the catalyst can facilitate the formation of DMC from methanol and carbon dioxide [34,35].

As shown in Figs. 5 and 7, the catalytic performance of MO/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. The amount of DMC produced over MO/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 served as crucial factors in determining catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Among the catalysts tested, Ga₂O₃/Ce_{0.6}Zr_{0.4}O₂, which had the largest acidity and basicity, exhibited the best catalytic performance in this reaction.

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 efficient support for transition metal oxides (Ga₂O₃, La₂O₃, Ni₂O₃, Fe₂O₃, Y₂O₃, Co₃O₄, and Al₂O₃). On the basis of this result, transition metal oxides were supported on Ce_{0.6}Zr_{0.4}O₂ by an incipient wetness impregnation method for use in the direct synthesis of DMC from methanol and carbon dioxide. Experimental results revealed that the catalytic performance of MO/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, Ga₂O₃/Ce_{0.6}Zr_{0.4}O₂ with the largest acidity and basicity exhibited 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 play an important role in determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

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