Direct synthesis of dimethyl carbonate from methanol and carbon dioxide over Ga₂O₃-CeO₂-ZrO₂ catalysts prepared by a single-step sol-gel method: Effect of acidity and basicity of the catalysts

Hye Jin Lee*, Wangrae Joe*, Ji Chul Jung**, and In Kyu Song*,†

*School of Chemical and Biological Engineering, Institute of Chemical Processes,
Seoul National University, Shinlim-dong, Gwanak-gu, Seoul 151-744, Korea
**Department of Chemical Engineering, Myongji University, Yongin 449-728, Korea

Abstract−XGa₂O₃-CeO₂-ZrO₂ (X=0, 1, 3, 5, 7, and 9) catalysts were prepared by a single-step sol-gel method with a variation of Ga₂O₃ content (X, wt%) for use in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. The ratio of cerium oxide:zirconium oxide in the XGa₂O₃-CeO₂-ZrO₂ catalysts was fixed to be Ce₀.₆Zr₀.₄O₂. Effect of acidity and basicity of XGa₂O₃-CeO₂-ZrO₂ on the catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide was investigated using NH₃-TPD and CO₂-TPD experiments, respectively. Experimental results revealed that both acidity and basicity of the catalysts played important roles in determining the catalytic performance in the reaction. The amount of dimethyl carbonate increased with increasing both acidity and basicity of the catalyst. Among the catalysts tested, 3Ga₂O₃-CeO₂-ZrO₂, which retained 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, Ga₂O₃-CeO₂-ZrO₂, Acid-base Property

INTRODUCTION

Dimethyl carbonate (DMC) is a promising green chemical with a wide range of applications: as an environmentally benign substitute for methyl halides, 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 good solvent, a monomer for the synthesis of functional resins, an intermediate in the synthesis of isocyanates, and a fuel additive [1,2].

Conventional processes for the synthesis of DMC, including methanolysis of phosgene [3], oxidative carbonylation of methanol [4], oxidative carbon monoxide-methyl nitrite processes [5], and transesterification of ethylene carbonate or propylene carbonate with methanol [6,7], and urea methanolysis [8], have many drawbacks from an environmental point of view. Highly toxic phosgene has been employed as a reagent for the synthesis of DMC in the methanolysis of phosgene. In the oxidative carbonylation of methanol and the oxidative carbon monoxide-methyl nitrite processes, flammable, explosive, and corrosive gases such as nitric oxide and carbon monoxide are used. On the other hand, direct synthesis of DMC from methanol and carbon dioxide has attracted much attention as a green chemical process for the synthesis of DMC [9-13]. The major drawback of this process is low DMC yield due to the thermodynamic equilibrium limitation. However, this problem can be substantially 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 is one of the key technologies for the production of DMC.

It has been reported that acid-base bifunctional catalysts are efficient for the direct synthesis of DMC from methanol and carbon dioxide [1,2]. Fig. 1 shows the reaction pathway for the direct synthesis of DMC from methanol and carbon dioxide over acid-base bifunctional catalyst. Methanol is activated to methyl species and methoxy species on the acid and base sites of the catalyst, respectively [2,9]. Methoxy carbonate anion is then formed by the reaction of methoxy species with carbon dioxide adsorbed on the base sites of the catalyst [1,2]. Methoxy carbonate anion further reacts with methyl species to produce DMC [2]. From this reaction pathway, it can be inferred that both acid and base sites of the catalyst play important roles in the direct synthesis of DMC from methanol and carbon dioxide. So it is expected that acid-base bifunctional catalysts will show an excellent catalytic activity in this reaction. A number of catalysts have been investigated 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], ZrO₂ [9], CeO₂-ZrO₂ [15,16], H₃PW₁₂O₄₀/ZrO₂ [17], H₃PW₁₂O₄₀/CeₓTi₁₋ₓO₂ [18], and H₃PW₁₂O₄₀/CeₓZr₁₋ₓO₂ [19]. Among these catalysts, CeO₂-ZrO₂ showed an excellent catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide due to its superior acid-base bifunctional property.

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, we have attempted to enhance the acidity and basicity of CeO₂-ZrO₂ catalyst by impregnating various transition metal oxides onto CeO₂-ZrO₂ [24]. Among various transition metal oxides,

†To whom correspondence should be addressed.
E-mail: inksong@snu.ac.kr

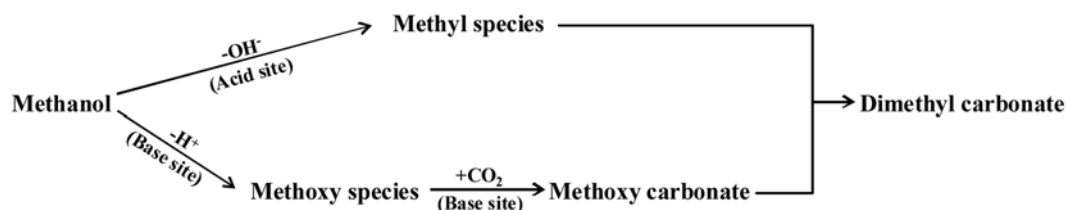**Fig. 1. Reaction pathway for the direct synthesis of DMC from methanol and carbon dioxide over acid-base bifunctional catalyst.**

Ga_2O_3/CeO_2-ZrO_2 with the largest acidity and basicity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide [24]. Also, $Ce_{0.6}Zr_{0.4}O_2$ was found to be the most efficient support for Ga_2O_3/CeO_2-ZrO_2 catalyst [24]. However, $Ga_2O_3/Ce_{0.6}Zr_{0.4}O_2$ catalyst prepared by an incipient wetness impregnation method required a number of calcination and drying steps.

It is known that a single-step sol-gel method for the preparation of mixed metal oxide catalysts provides a simple synthesis route and leads to the finely dispersed metal oxide species [25,26]. It has also been reported that a mixed metal oxide prepared by a single-step sol-gel method has an enhanced acid-base property compared to pure metal oxide [25,26]. Therefore, it is expected that Ga_2O_3-CeO_2-ZrO_2 catalyst prepared by a single-step sol-gel method will show an excellent catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

In this work, XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, and 9) catalysts were prepared by a single-step sol-gel method with a variation of Ga_2O_3 content (X, wt%). In our previous investigations [24, 27] on the $Ce_xZr_{1-x}O_2$ catalysts (X=0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0), $Ce_{0.6}Zr_{0.4}O_2$ catalyst was found to show the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Therefore, the ratio of cerium oxide:zirconium oxide in the XGa_2O_3-CeO_2-ZrO_2 catalyst was fixed to be $Ce_{0.6}Zr_{0.4}O_2$. For example, $0Ga_2O_3$-CeO_2-ZrO_2 (X=0) catalyst represents $Ce_{0.6}Zr_{0.4}O_2$ catalyst. The prepared XGa_2O_3-CeO_2-ZrO_2 catalysts were applied to the direct synthesis of DMC from methanol and carbon dioxide. Acidity and basicity of XGa_2O_3-CeO_2-ZrO_2 catalysts were determined by NH_3-TPD and CO_2-TPD experiments, respectively, with an aim of investigating the effect of acidity and basicity of the catalysts on the catalytic performance in the reaction.

EXPERIMENTAL

1. Catalyst Preparation

XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, and 9) catalysts were prepared by a single-step sol-gel method with a variation of Ga_2O_3 content (X, wt%), according to the similar method in literature [28]. Based on our previous works [24,27], the ratio of cerium oxide:zirconium oxide in the XGa_2O_3-CeO_2-ZrO_2 catalyst was fixed to be $Ce_{0.6}Zr_{0.4}O_2$. 6.513 g of $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich), 2.336 g of $ZrO(NO_3)_2 \cdot xH_2O$ (Sigma-Aldrich), and a known amount of $Ga(NO_3)_3 \cdot xH_2O$ (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, zirconium, and gallium precursors. After the mixed solution was stirred at 80 °C for 3 h, it was evapo-

rated to obtain a gel. The gel was then dried at 100 °C for 24 h. After grinding of the dried gel, it was finally calcined at 500 °C for 3 h in an air stream to yield XGa_2O_3-CeO_2-ZrO_2 catalysts. The prepared catalysts were denoted as XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9), where X represented wt% of Ga_2O_3 in the XGa_2O_3-CeO_2-ZrO_2. The ratio of CeO_2 : ZrO_2 was fixed to be $Ce_{0.6}Zr_{0.4}O_2$ in all the catalysts.

2. Catalyst Characterization

Crystalline phases of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts were investigated by XRD measurements (Rigaku, D-MAX2500-PC) using Cu-Kα radiation (λ=1.54056 Å) operated at 50 kV and 100 mA. Surface areas of the catalysts were measured using 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 °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. Physisorbed NH_3 was removed by evacuating the catalyst sample at 50 °C for 1 h under a flow of helium (15 ml/min). Furnace temperature was increased from room temperature to 500 °C at a heating rate of 5 °C/min under a 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 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 with a gas chromatograph (HP 5890 II, FID) on the basis of mole balance.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Fig. 2 shows the XRD patterns of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts. For comparison, XRD patterns of CeO_2, ZrO_2, and Ga_2O_3 are also presented in Fig. 2. $0Ga_2O_3$-CeO_2-ZrO_2
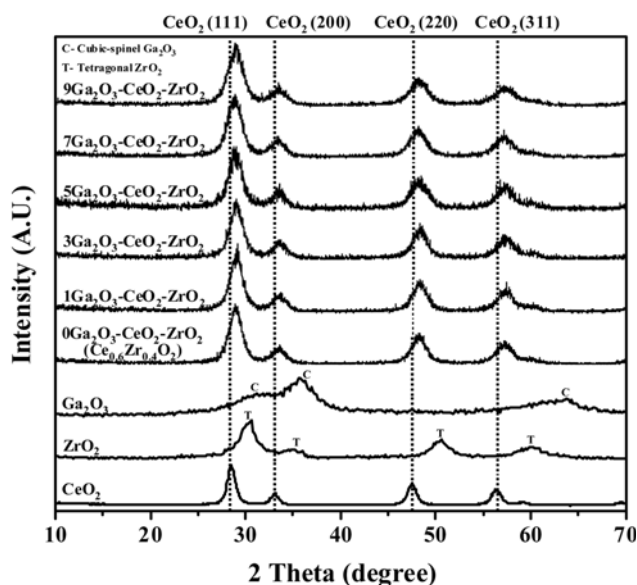
Fig. 2. XRD patterns of CeO_2, ZrO_2, Ga_2O_3, and XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts.

Fig. 3. Catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) 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). The catalytic performance data for $5Ga_2O_3$/$Ce_{0.6}Zr_{0.4}O_2$ was taken from a literature [27].

($Ce_{0.6}Zr_{0.4}O_2$) retained a single cubic fluorite phase (characteristic phase of CeO_2) without a detectable tetragonal phase (characteristic phase of ZrO_2), although the characteristic XRD peaks of $0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$) 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 originating from the replacement of Ce^{4+} (ionic radius=0.098 nm) with a smaller Zr^{4+} (ionic radius= 0.084 nm) in the $0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$) catalyst [29-32]. It is interesting that no characteristic diffraction peaks for Ga_2O_3 were found in the XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) catalysts. XGa_2O_3-CeO_2-ZrO_2 showed only characteristic XRD peaks corresponding to $Ce_{0.6}Zr_{0.4}O_2$ catalyst. This indicates that Ga_2O_3 was finely dispersed or incorporated into $Ce_{0.6}Zr_{0.4}O_2$ in the preparation of Ga_2O_3-CeO_2-ZrO_2 catalysts. This result was well consistent with the previous works reporting that no characteristic XRD peaks for Ga_2O_3 were detected in the mixed metal oxides prepared by a single-step sol-gel method such as Ga_2O_3-ZrO_2 [26] and Ga_2O_3-NiO [33]

Table 1. Surface area, acidity, and basicity of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts

Catalyst	Surface area $(m^2/g)^a$	Acidity (μmol-NH_3/ g-catalyst)^b	Basicity (μmol-CO_2/ g-catalyst)^c
$0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$)	53.8	85.7	17.0
$1Ga_2O_3$-CeO_2-ZrO_2	40.4	247.2	429.9
$3Ga_2O_3$-CeO_2-ZrO_2	47.5	323.7	528.0
$5Ga_2O_3$-CeO_2-ZrO_2	32.3	245.2	368.8
$7Ga_2O_3$-CeO_2-ZrO_2	30.3	190.2	280.1
$9Ga_2O_3$-CeO_2-ZrO_2	36.9	159.9	172.4

^{a}Calculated by the BET (Brunauer-Emmett-Teller) equation
^{b}Determined by NH_3-TPD measurement
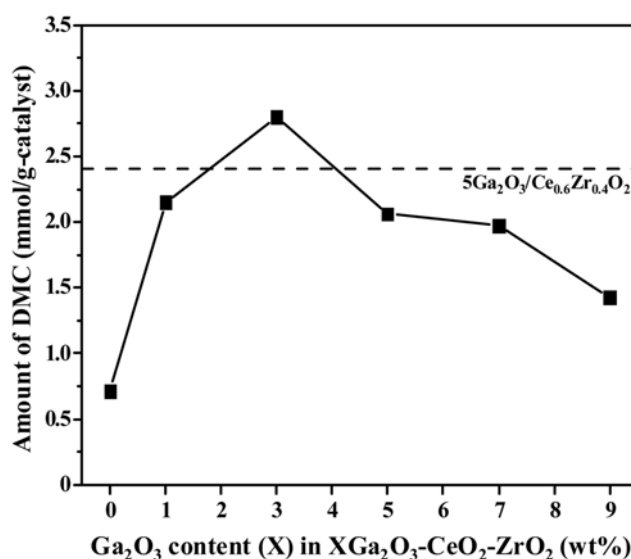^{c}Determined by CO_2-TPD measurement

with incorporated Ga_2O_3. The above results indicate that XGa_2O_3-CeO_2-ZrO_2 catalysts were successfully prepared in this work. BET surface areas of XGa_2O_3-CeO_2-ZrO_2 catalysts are summarized in Table 1. It was found that BET surface areas of XGa_2O_3-CeO_2-ZrO_2 catalysts showed no significant difference.

2. Catalytic Performance of XGa_2O_3-CeO_2-ZrO_2 Catalysts

Fig. 3 shows the catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) 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). For comparison, catalytic performance $5Ga_2O_3$/$Ce_{0.6}Zr_{0.4}O_2$ prepared by an impregnation method is also presented in Fig. 3. $5Ga_2O_3$/$Ce_{0.6}Zr_{0.4}O_2$ was the best catalyst in our previous work [27]. In the catalytic reactions, DMC was selectively produced without any by-products, indicating that the catalysts employed in this work were highly selective for the formation of DMC.

XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) catalysts exhibited a better catalytic performance than $0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$) catalyst. This indicates that XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) catalysts were more efficient than $0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$) catalyst in the direct synthesis of DMC from methanol and carbon dioxide. It is believed that Ga_2O_3 increased both acidity and basicity of $Ce_{0.6}Zr_{0.4}O_2$ catalyst, leading to the enhanced catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) in the reaction. As shown in Fig. 3, the amount of DMC produced over XGa_2O_3-CeO_2-ZrO_2 catalysts showed a volcano-shaped curve with respect to Ga_2O_3 content (X). Among the catalysts tested, $3Ga_2O_3$-CeO_2-ZrO_2 catalyst showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

The amount of DMC produced over $3Ga_2O_3$-CeO_2-ZrO_2 catalyst prepared by a single-step sol-gel method was larger than that over $5Ga_2O_3$/$Ce_{0.6}Zr_{0.4}O_2$ catalyst prepared by an incipient wetness

impregnation method. This indicates that a single-step sol-gel method was more efficient than an incipient wetness impregnation method in the preparation of Ga_2O_3-CeO_2-ZrO_2 mixed metal oxide catalyst for the direct synthesis of DMC from methanol and carbon dioxide.

3. Effect of Acidity on the Catalytic Performance of XGa_2O_3-CeO_2-ZrO_2

According to the reaction pathway shown in Fig. 1, direct synthesis of DMC from methanol and carbon dioxide involves several reaction steps [1,2]. 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 [34,35]. Therefore, a large number of acid sites would be favorable for the direct synthesis of DMC from methanol and carbon dioxide.

To see the effect of acid properties on the catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9), NH_3-TPD experi-

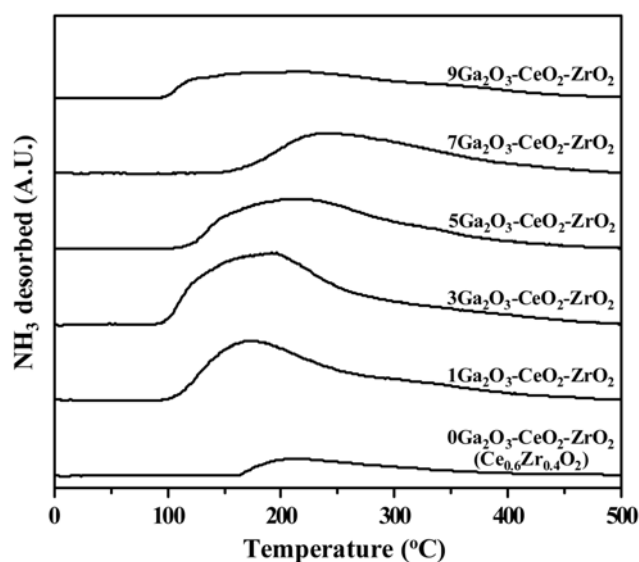ments were conducted over the catalysts. Fig. 4 shows the NH_3-TPD profiles of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts. All the catalysts exhibited a broad NH_3-TPD peak. XGa_2O_3-CeO_2-ZrO_2 catalysts exhibited a significant difference in acidity (peak area) with a variation of Ga_2O_3 content (X). Acidity of XGa_2O_3-CeO_2-ZrO_2 catalysts calculated from NH_3-TPD peak area is summarized in Table 1. Acidity of the catalysts decreased in the order of $3Ga_2O_3$-CeO_2-ZrO_2>$1Ga_2O_3$-CeO_2-ZrO_2>$5Ga_2O_3$-CeO_2-ZrO_2>$7Ga_2O_3$-CeO_2-ZrO_2>$9Ga_2O_3$-CeO_2-ZrO_2>$0Ga_2O_3$-CeO_2-ZrO_2.

Fig. 5 shows the correlation between acidity and catalytic performance of XGa_2O_3-CeO_2-ZrO_2. Acidity (NH_3-TPD peak area) was directly correlated with the catalytic performance. The amount of DMC produced over XGa_2O_3-CeO_2-ZrO_2 catalysts increased with increasing acidity of the catalysts. Among the catalysts tested, $3Ga_2O_3$-CeO_2-ZrO_2 with the largest acidity exhibited the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. When considering the fact that methanol is activated to methyl species on the acid sites for the DMC formation [2,9], it is believed that large acidity of the catalyst was favorable for the activation of methanol to methyl species, leading to a facile formation of DMC in the reaction.

4. Effect of Basicity on the Catalytic Performance of XGa_2O_3-CeO_2-ZrO_2

As presented in Fig. 1, base sites of the catalyst are responsible for the formation of methoxy carbonate anion through the reaction of carbon dioxide with methoxy species [2,9]. This indicates that large basicity of the catalyst would be favorable for the formation of methoxy carbonate anion, leading to a facile formation of DMC from methanol and carbon dioxide. Therefore, CO_2-TPD experiments were conducted with an aim of investigating the effect of base properties on the catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts. Fig. 6 shows the CO_2-TPD profiles of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts. Basicity of XGa_2O_3-CeO_2-ZrO_2 catalysts calculated from CO_2-TPD peak area is listed in Table 1. Basicity of the catalysts decreased in the

Fig. 4. NH_3-TPD profiles of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts.

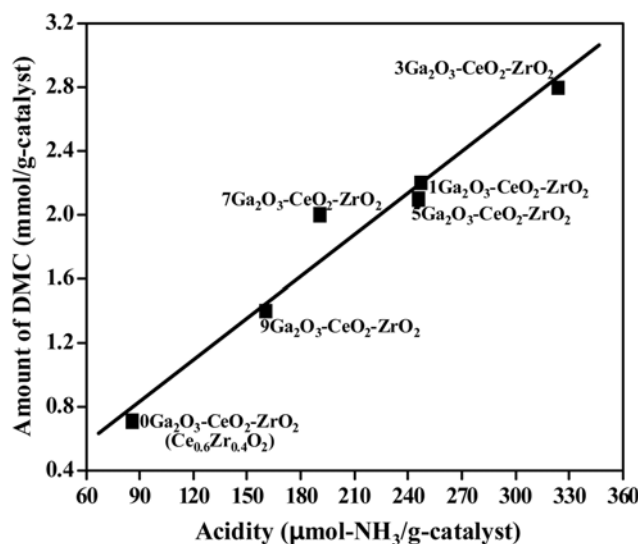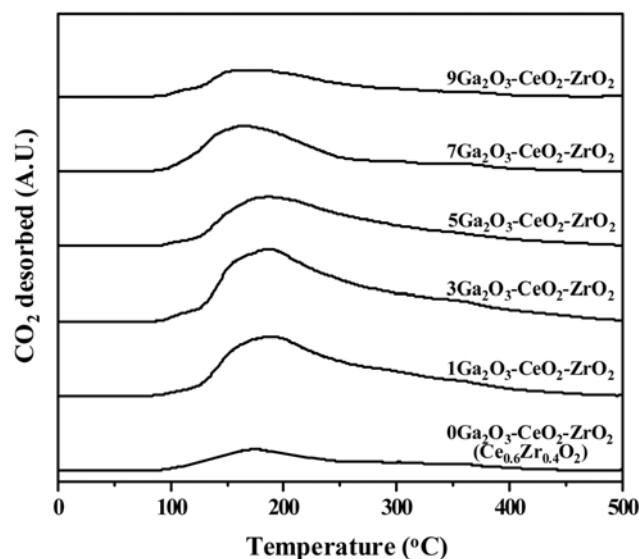**Fig. 5. A correlation between acidity and catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9).**

Fig. 6. CO_2-TPD profiles of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts.

Fig. 7. A correlation between basicity and catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9).

order of $3Ga_2O_3$-CeO_2-ZrO_2>$1Ga_2O_3$-CeO_2-ZrO_2>$5Ga_2O_3$-CeO_2-ZrO_2>$7Ga_2O_3$-CeO_2-ZrO_2>$9Ga_2O_3$-CeO_2-ZrO_2>$0Ga_2O_3$-CeO_2-ZrO_2. Note that the basicity of XGa_2O_3-CeO_2-ZrO_2 catalysts showed the same trend as acidity of the catalysts.

Fig. 7 shows the correlation between basicity and catalytic performance of XGa_2O_3-CeO_2-ZrO_2. The correlation clearly shows that the catalytic performance was closely related to the basicity of XGa_2O_3-CeO_2-ZrO_2 catalysts. The amount of DMC produced over XGa_2O_3-CeO_2-ZrO_2 catalysts increased with increasing basicity of the catalysts. This means that basicity of the catalyst played an important role in determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Among the catalysts tested, $3Ga_2O_3$-CeO_2-ZrO_2 with the largest basicity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. As mentioned earlier, base sites of the catalyst are required for the formation methoxy carbonate anion [2]. The methoxy carbonate anion formed on the base sites of the catalyst reacts with methyl species formed on the acid sites of the catalyst to produce dimethyl carbonate [34,35]. Therefore, it is believed that large basicity of the catalyst was favorable for the formation of DMC from methanol and carbon dioxide.

From two correlations (Fig. 5 and Fig. 7), we found that the catalytic performance of XGa_2O_3-CeO_2-ZrO_2 was closely related to both acidity and basicity of the catalyst in the direct synthesis of DMC from methanol and carbon dioxide. From the fact that XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) showed a better catalytic performance than $0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$) in the direct synthesis of DMC from methanol and carbon dioxide (Fig. 3), we also came to know that Ga_2O_3 increased both acidity and basicity of $Ce_{0.6}Zr_{0.4}O_2$, leading to the enhanced catalytic performance of XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) in this reaction. The amount of DMC produced over XGa_2O_3-CeO_2-ZrO_2 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 important factors determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Among the catalysts tested,

$3Ga_2O_3$-CeO_2-ZrO_2 with the largest acidity and basicity exhibited the best catalytic performance in this reaction.

CONCLUSIONS

XGa_2O_3-CeO_2-ZrO_2 (X=0, 1, 3, 5, 7, and 9) catalysts were prepared by a single-step sol-gel method with a variation of Ga_2O_3 content (X, wt%). Based on our previous work, the ratio of cerium oxide : zirconium oxide in the XGa_2O_3-CeO_2-ZrO_2 catalyst was fixed to be $Ce_{0.6}Zr_{0.4}O_2$. The prepared catalysts were applied to the direct synthesis of DMC from methanol and carbon dioxide. XGa_2O_3-CeO_2-ZrO_2 (X=1, 3, 5, 7, and 9) showed a better catalytic performance than $0Ga_2O_3$-CeO_2-ZrO_2 ($Ce_{0.6}Zr_{0.4}O_2$) in the reaction due to the enhanced acidity and basicity provided by Ga_2O_3. Among the catalysts tested, $3Ga_2O_3$-CeO_2-ZrO_2 catalyst showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Furthermore, the amount of DMC produced over $3Ga_2O_3$-CeO_2-ZrO_2 catalyst prepared by a single-step sol-gel method was larger than that over $5Ga_2O_3$/$Ce_{0.6}Zr_{0.4}O_2$ catalyst (the best catalyst in our previous work) prepared by an incipient wetness impregnation method. This indicates that a single-step sol-gel method was more efficient than an incipient wetness impregnation method in the preparation of Ga_2O_3-CeO_2-ZrO_2 mixed metal oxide catalyst for the reaction. NH_3-TPD and CO_2-TPD experiments were conducted to investigate the effect of acidity and basicity of the catalyst on the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Experimental results revealed that the catalytic performance of XGa_2O_3-CeO_2-ZrO_2 was closely related to both acidity and basicity of the catalyst in this reaction. The amount of DMC increased with increasing both acidity and basicity of the catalyst. It is concluded that both acidity and basicity of the catalyst played important roles in determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

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