

NiO/CeO₂–ZnO Nano-Catalysts for Direct Synthesis of Dimethyl Carbonate from Methanol and Carbon Dioxide

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XNiO/CeO₂(0.7)–ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts were prepared by a wet impregnation method with a variation of NiO content (X , wt%). The prepared catalysts were then applied to the direct synthesis of dimethyl carbonate from methanol and carbon dioxide. Successful formation of XNiO/CeO₂(0.7)–ZnO(0.3) nano-catalysts was confirmed by XRD and ICP-AES analyses. Acidity and basicity of XNiO/CeO₂–ZnO were measured by NH₃-TPD (temperature-programmed desorption) and CO₂-TPD experiments, respectively, with an aim of elucidating the effect of acidity and basicity of the catalysts on the catalytic performance in the reaction. It was revealed that the catalytic activity of XNiO/CeO₂(0.7)–ZnO(0.3) was closely related to both acidity and basicity of the catalysts. The amount of dimethyl carbonate produced over XNiO/CeO₂(0.7)–ZnO(0.3) increased with increasing acidity and basicity of the catalysts. Thus, both acidity and basicity of the catalysts played important roles in determining the catalytic performance in the direct synthesis of dimethyl carbonate from methanol and carbon dioxide.

Keywords: Dimethyl Carbonate, Methanol, Carbon Dioxide, NiO/CeO₂–ZnO Nano-Catalyst, Acid-Base Property.

1. INTRODUCTION

Dimethyl carbonate (DMC) has attracted extensive attention as a promising chemical for various industrial applications. The increasing interest of DMC is mainly due to its environmentally benign properties such as low toxicity and rapid biodegradability. DMC has been used as an eco-friendly substitute for dimethyl sulfate and methyl halides which are toxic and corrosive methylation agents.^{1–4} DMC has also been used as a fuel additive because of its high oxygen content.¹ In addition, DMC is reported to act as an organic solvent and electrolyte for a lithium ion battery due to its great solvation power and low viscosity.^{1,4}

Traditionally, DMC has been produced by the reaction of phosgene with methanol.^{5,6} Because of high toxicity of phosgene, however, several non-phosgene processes have been developed, including oxidative carbonylation of methanol (Enichem process) and oxidative carbon monoxide-methyl nitrite (UBE process).^{7,8} Nevertheless, these processes also suffer from many drawbacks in an environmental point of view. In the Enichem process,

formation of hydrochloric acid in the presence of CuCl₂ causes the plant corrosion. On the other hand, the UBE process involves safety problems because of the use of highly explosive Pd/NO/O₂ mixture and toxic methyl nitrite reactant. For this reason, direct synthesis of DMC from methanol and carbon dioxide has received much attention as an environmentally benign process.^{9–13}

Figure 1 shows mechanism for the direct synthesis of DMC from methanol and carbon dioxide over acid-base bifunctional catalyst.^{14–17} According to the mechanism, activation of methanol to methoxy species occurs on the base site of the catalyst.^{16,17} Methoxy carbonate anion is then formed via the insertion of carbon dioxide adsorbed on the base site into methoxy species.¹⁵ Methanol is also activated to methyl species on the acid site of the catalyst.¹⁵ DMC is finally formed by the reaction of methoxy carbonate anion with methyl species.^{15–17} From the reaction mechanism, it can be inferred that acid and base sites of the catalyst may serve as crucial factors in the reaction.

Various catalysts have been investigated for the direct synthesis of DMC from methanol and carbon dioxide,

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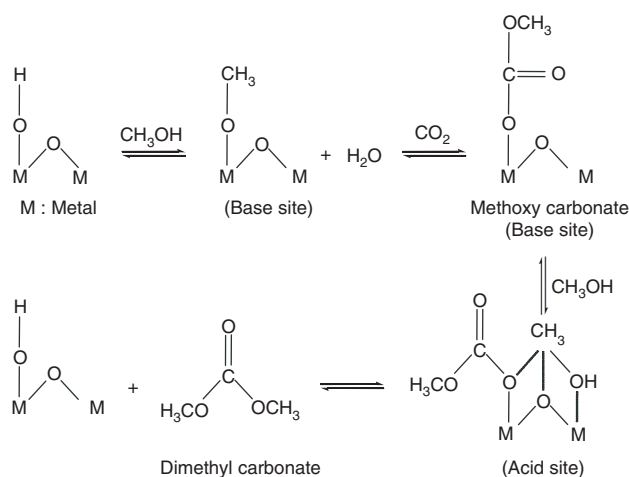


Figure 1. Mechanism for the direct synthesis of DMC from methanol and carbon dioxide over acid-base bifunctional catalyst.

including organometallic compounds,¹⁸ metal oxides,^{19–21} and bimetallic catalysts.²² Among these catalysts, mixed metal oxides are known to be the most efficient catalysts.^{19–21} In particular, it is reported that CeO₂-based metal oxide showed a superior catalytic activity due to its excellent acid-base property.²¹ Furthermore, it is also reported that the addition of NiO into metal oxide can modify the acid-base properties of metal oxide.^{23,24} In our previous work, we have developed a CeO₂(0.7)–ZnO(0.3) mixed metal oxide catalyst for direct synthesis of DMC from methanol and carbon dioxide, which showed a considerable catalytic performance in the reaction. In this work, CeO₂(0.7)–ZnO(0.3) was chosen as a support for NiO in order to increase the acid-base properties of the catalyst. To our best knowledge, NiO catalyst supported on CeO₂-based metal oxide has never been applied to the direct synthesis of DMC. Therefore, developing a NiO catalyst supported on CeO₂(0.7)–ZnO(0.3) with enhanced acid-base properties would be worthwhile.

In this work, XNiO/CeO₂(0.7)–ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts were prepared by a wet impregnation method with a variation of NiO content (X , wt%), and they were applied to the direct synthesis of DMC from methanol and carbon dioxide. Successful formation of XNiO/CeO₂(0.7)–ZnO(0.3) nano-catalysts was confirmed by XRD and ICP-AES analyses. NH₃-TPD (temperature-programmed desorption) and CO₂-TPD experiments were conducted to investigate the effect of acidity and basicity of XNiO/CeO₂(0.7)–ZnO(0.3) on the catalytic performance in the reaction.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

CeO₂(0.7)–ZnO(0.3) mixed metal oxide with a fixed molar composition (value in parenthesis) was prepared by a co-precipitation method according to the procedures

reported in the literature.²³ Known amounts of cerium precursor (Ce(NO₃)₃·6H₂O, Sigma-Aldrich) and zinc precursor (Zn(NO₃)₂·6H₂O, Sigma-Aldrich) were dissolved in ethanol under vigorous stirring. Ammonia solution was then slowly added into the solution containing cerium and zinc precursors to increase pH value to 10. The precipitate was aged for 3 h at 50 °C, and it was then filtered and washed with deionized water and ethanol. After drying the resulting product at 100 °C for 24 h, it was finally calcined at 500 °C for 3 h in an air stream to yield CeO₂(0.7)–ZnO(0.3) mixed metal oxide. A series of XNiO/CeO₂(0.7)–ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts with different NiO content (X , wt%) were prepared by a wet impregnation method using an aqueous solution of nickel precursor (Ni(NO₃)₂·6H₂O, Sigma-Aldrich). The impregnated catalysts were dried at 100 °C for 24 h, and they were calcined at 500 °C for 3 h in the presence of air to yield XNiO/CeO₂(0.7)–ZnO(0.3) nano-catalysts.

2.2. Characterization

Crystalline phases of XNiO/CeO₂(0.7)–ZnO(0.3) nano-catalysts were confirmed by XRD measurements (Rigaku, D-MAX2500-PC) using Cu-K α radiation ($\lambda = 1.54056$ Å) operated at 50 kV and 100 mA. Chemical compositions of the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis (Shimadzu, ICP-1000IV). Surface areas of the catalysts were determined using an ASAP-2010 (Micromeritics) instrument.

NH₃-TPD experiment was performed in order to investigate acidity of the catalysts. 0.2 g of each catalyst 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 NH₃. Physisorbed NH₃ 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 900 °C at a heating rate of 5 °C/min under a flow of helium (10 ml/min). Desorbed ammonia was detected using a GC-MSD (Agilent, 5975MSD-6890N GC). Basicity of the catalysts was measured by CO₂-TPD experiment. Experimental procedures for CO₂-TPD were identical to those for NH₃-TPD, except that CO₂ instead of NH₃ 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 conducted in a stainless steel autoclave reactor with a volume of 75 ml. 30 ml of methanol and 0.7 g of

each catalyst were charged into the reactor, and the reactor was then purged with carbon dioxide. After heating the reactor to the reaction temperature (170 °C) 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) equipped with a HP-5 column and a flame ionization detector (FID).

3. RESULTS AND DISCUSSION

3.1. Formation of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ Nano-Catalysts

Successful formation of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts was confirmed by XRD measurements as shown in Figure 2. It was revealed that all the $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts showed the mixed characteristic XRD peaks for CeO_2 and ZnO phases without a shift of diffraction angle, indicating that no solid solution between CeO_2 and ZnO was formed. This result was in good agreement with the previous work.²⁵ It is interesting to note that no characteristic XRD peaks for NiO were detected in the $1\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$, indicating that NiO was finely dispersed on the surface of $\text{CeO}_2(0.7)\text{-ZnO}(0.3)$. On the other hand, the intensity of characteristic XRD peaks for NiO in the $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 5, 10,$ and 15) catalysts increased with increasing NiO content.

Chemical compositions in the $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts are summarized in Table I. NiO contents measured by ICP-AES analyses were in good agreement with the designed

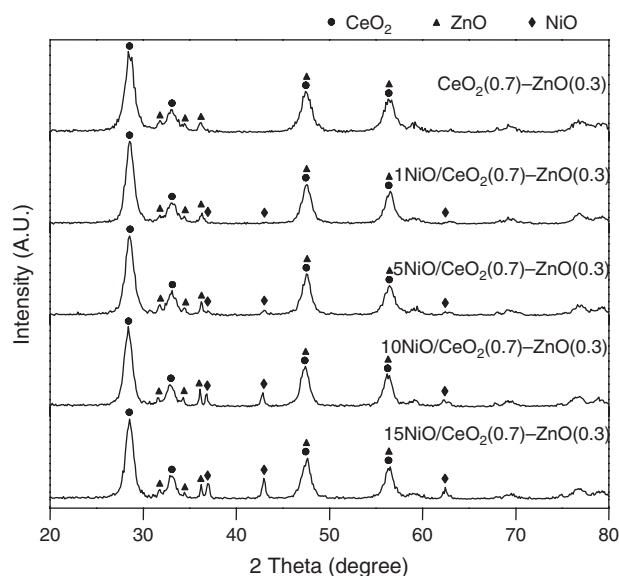


Figure 2. XRD patterns of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts.

Table I. NiO content, surface area, acidity, and basicity of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts.

Catalyst	NiO content (wt%)	Surface area (m^2/g) ^b	Acidity ($\text{mmol-NH}_3/\text{g-catalyst}$) ^c	Basicity ($\text{mmol-CO}_2/\text{g-catalyst}$) ^d
$\text{CeO}_2(0.7)\text{-ZnO}(0.3)$	0 (0) ^a	56.8	2.69	4.74
$1\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$	0.9 (1) ^a	28.1	3.36	6.58
$5\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$	5.1 (5) ^a	43.4	5.95	8.43
$10\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$	10.4 (10) ^a	36.2	4.94	6.79
$15\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$	14.7 (15) ^a	39.1	3.25	4.77

Notes: ^aDesigned value of NiO content in the $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ nano-catalysts; ^bCalculated by the BET (Brunauer-Emmett-Teller) equation; ^cDetermined by NH_3 -TPD measurement; ^dDetermined by CO_2 -TPD measurement.

values. Together with XRD result (Fig. 2), this result indicates that all the $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts were successfully prepared in this work. BET surface areas of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts are also summarized in Table I. It was observed that BET surface areas of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) showed no significant difference.

3.2. Catalytic Performance of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ Nano-Catalysts

Figure 3 shows the catalytic performance of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) in the direct synthesis of DMC from methanol and carbon dioxide performed at 170 °C and 60 bar for 3 h, plotted as a function of NiO content. It is noteworthy that no by-products were detected over the catalysts during the catalytic reaction. This implies that $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts were highly selective for the direct synthesis of DMC from methanol and carbon dioxide. $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$

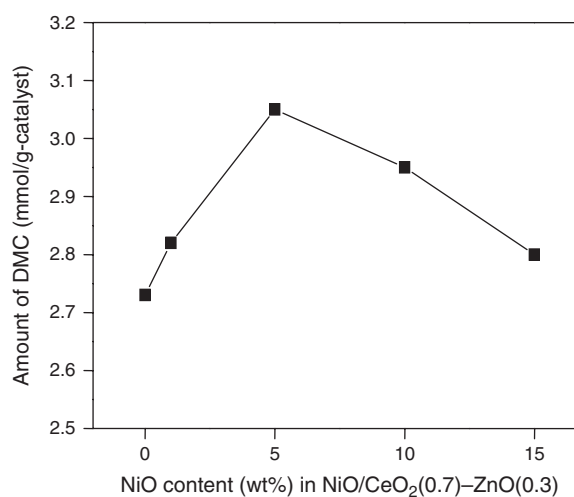


Figure 3. Catalytic performance of $X\text{NiO}/\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) in the direct synthesis of DMC from methanol and carbon dioxide at 170 °C after a 3 h-catalytic reaction.

($X = 1, 5, 10,$ and 15) showed a better catalytic activity than $\text{CeO}_2(0.7)\text{-ZnO}(0.3)$. This result implies that the addition of NiO increased the catalytic performance of $\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ in the reaction. It should be noted that the amount of DMC produced over $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts showed a volcano-shaped curve with respect to NiO content. Among the catalysts tested, $5\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. Thus, an optimal NiO content was required for maximum catalytic performance of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ in the direct synthesis of DMC.

3.3. Effect of Acidity on the Catalytic Performance of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ Nano-Catalysts

According to the reaction mechanism shown in Figure 1, activation of methanol to methyl species occurs on the acid site of the catalyst, which is known to be the rate-determining step.¹⁵ Thus, it is expected that the catalyst with large acidity is favorable for the direct synthesis of DMC from methanol and carbon dioxide. $\text{NH}_3\text{-TPD}$ experiment was conducted to investigate the effect of acidity on the catalytic performance of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15). Figure 4 shows the $\text{NH}_3\text{-TPD}$ profiles of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts. Although no great difference in acid strength (peak temperature) was observed with respect to NiO content, $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts showed a significant difference in acidity (peak area) with a variation of NiO content, as listed in Table I. $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 1, 5, 10,$ and 15) catalysts exhibited

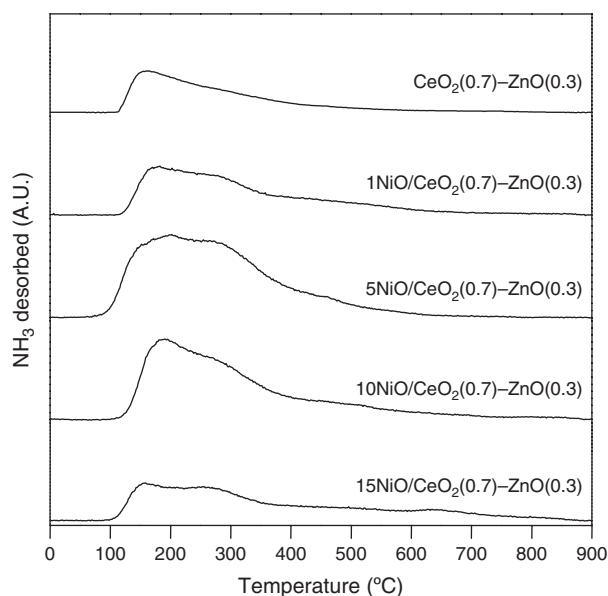


Figure 4. $\text{NH}_3\text{-TPD}$ profiles of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts.

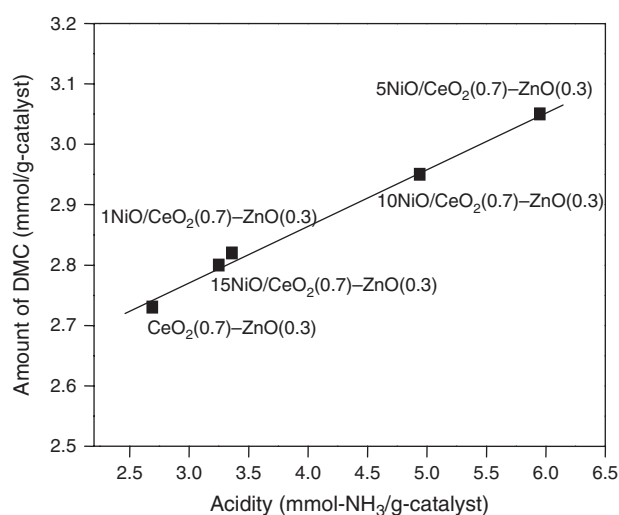


Figure 5. A correlation between catalytic performance and acidity of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) nano-catalysts.

larger acidity than $\text{CeO}_2(0.7)\text{-ZnO}(0.3)$, indicating that the addition of NiO to $\text{CeO}_2(0.7)\text{-ZnO}(0.3)$ increased the acidity of the catalysts. Acidity of the catalysts decreased in the order of $5\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3) > 10\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3) > 1\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3) > 15\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3) > \text{CeO}_2(0.7)\text{-ZnO}(0.3)$.

We attempted to correlate the catalytic performance with the acidity of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15), as presented in Figure 5. It is noteworthy that the catalytic performance was closely related to the acidity of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$. The amount of DMC produced over $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ increased with increasing acidity of the catalysts. Among the catalysts tested, $5\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ with the largest acidity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. When considering the fact that large acidity is favorable for the formation of DMC due to the facile formation of methyl species on the acid site, it can be concluded that acidity of the catalyst played an important role in determining the catalytic performance in the reaction.

3.4. Effect of Basicity on the Catalytic Performance of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ Nano-Catalysts

As presented in Figure 1, not only acid site but also base site of the catalyst are responsible for the formation of DMC, because methoxy carbonate is produced by the reaction of methoxy species with carbon dioxide on the base site of the catalyst.¹⁵⁻¹⁷ To elucidate the effect of basicity on the catalytic performance of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15), $\text{CO}_2\text{-TPD}$ experiment was performed. Figure 6 shows the $\text{CO}_2\text{-TPD}$ profiles of $X\text{NiO/CeO}_2(0.7)\text{-ZnO}(0.3)$ ($X = 0, 1, 5, 10,$ and 15) catalysts.

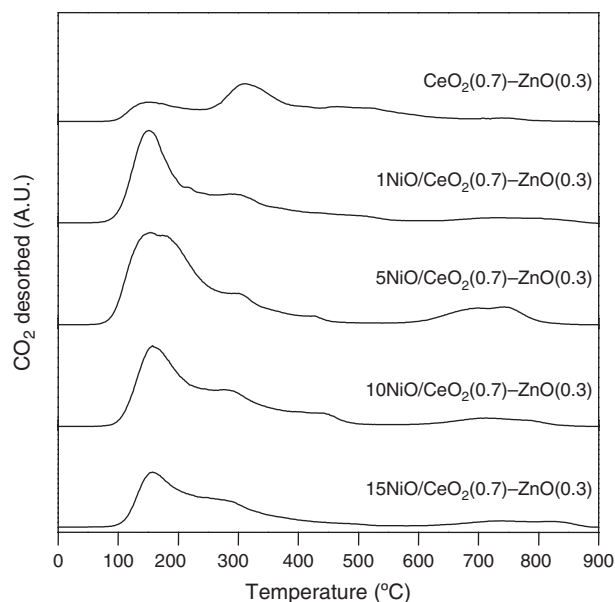


Figure 6. CO₂-TPD profiles of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts.

Interestingly, XNiO/CeO₂(0.7)-ZnO(0.3) nano-catalysts exhibited a significant difference in basicity (peak area) with a variation of NiO content. Basicity of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) catalysts calculated from CO₂-TPD peak area is listed in Table I. Basicity of the catalysts decreased in the order of 5NiO/CeO₂(0.7)-ZnO(0.3) > 10NiO/CeO₂(0.7)-ZnO(0.3) > 1NiO/CeO₂(0.7)-ZnO(0.3) > 15NiO/CeO₂(0.7)-ZnO(0.3) > CeO₂(0.7)-ZnO(0.3). It is noticeable that basicity of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) showed the same trend as acidity of the catalysts.

Figure 7 shows the correlation between basicity and catalytic performance of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15). The amount of DMC produced over XNiO/CeO₂(0.7)-ZnO(0.3) increased with increasing basicity of the catalysts. Among the catalysts tested, 5NiO/CeO₂(0.7)-ZnO(0.3) with the largest basicity showed the best catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide. As mentioned earlier, large basicity of the catalyst is favorable for the formation of methoxy carbonate anion. Thus, this result also demonstrates that basicity of the catalyst played a crucial role in determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

From Figures 5 and 7, it is inferred that the catalytic performance of XNiO/CeO₂(0.7)-ZnO(0.3) was closely related to both acidity and basicity of the catalysts in the direct synthesis of DMC from methanol and carbon dioxide. It was observed that XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 1, 5, 10,$ and 15) showed a better catalytic activity than CeO₂(0.7)-ZnO(0.3). This result implies that the addition

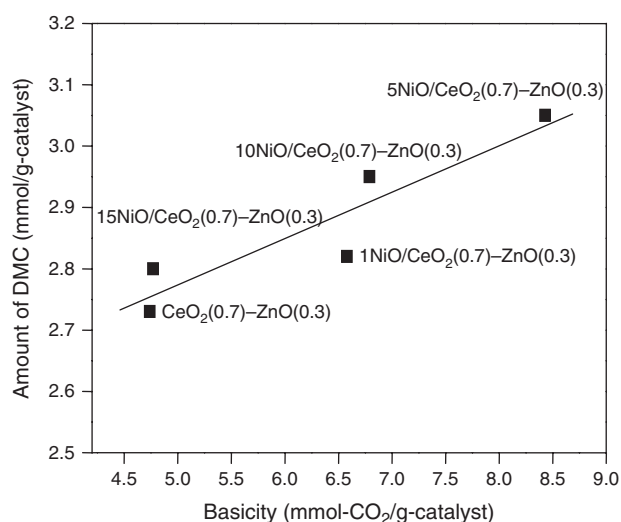


Figure 7. A correlation between catalytic performance and basicity of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts.

of NiO into CeO₂(0.7)-ZnO(0.3) enhanced the catalytic performance of XNiO/CeO₂(0.7)-ZnO(0.3) by increasing acidity and basicity of the catalysts. The amount of DMC produced over XNiO/CeO₂(0.7)-ZnO(0.3) increased with increasing both acidity and basicity of the catalysts. Among the catalysts tested, 5NiO/CeO₂(0.7)-ZnO(0.3) with the largest acidity and basicity showed the best catalytic performance in the reaction. Therefore, it is concluded that both acidity and basicity of the catalysts served as crucial factors determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

4. CONCLUSIONS

XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts were prepared by a wet impregnation method with a variation of NiO content (X , wt%). The prepared catalysts were then applied to the direct synthesis of DMC from methanol and carbon dioxide. Successful formation of XNiO/CeO₂(0.7)-ZnO(0.3) nano-catalysts was confirmed by XRD and ICP-AES analyses. XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 1, 5, 10,$ and 15) showed a better catalytic performance than CeO₂(0.7)-ZnO(0.3) in the reaction due to the enhanced acidity and basicity. The amount of DMC produced over XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) nano-catalysts exhibited a volcano-shaped curve with respect to NiO content. Acidity and basicity of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) were measured by NH₃-TPD and CO₂-TPD experiments, respectively, with an aim of elucidating the effect of acidity and basicity of the catalysts on the catalytic performance in the reaction. It was revealed that the catalytic performance of XNiO/CeO₂(0.7)-ZnO(0.3) ($X = 0, 1, 5, 10,$ and 15) was closely related to both acidity and basicity of the catalysts. The amount of DMC

increased with increasing acidity and basicity of the catalysts. Among the catalysts tested, 5NiO/CeO₂(0.7)–ZnO(0.3) with the largest acidity and basicity showed the best catalytic performance. It is concluded that both acidity and basicity of the catalysts served as key factors determining the catalytic performance in the direct synthesis of DMC from methanol and carbon dioxide.

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