CO and CO_2 methanation over promoted Ni/Al@Al_2O_3 catalysts

Thien An Le, Tae Wook Kim, Jieun Kim, Jong Kyu Kang, Eun Duck Park[*]
Department of Chemical Engineering and Department of Energy Systems Research, Ajou University, Suwon, 16499, Korea
**Corresponding author: 82-31-219-1612, edpark@ajou.ac.kr*

Abstract: The core-shell metal-ceramic microstructures (Al@γ-Al_2O_3 and Al@spinel-MAl_2O_4, M=Mn, Mg, Zn) were applied as supports for Ni-based catalysts to CO and CO_2 methanation reaction. The outstanding catalytic performance of the Ni catalysts supported on core-shell metal-ceramic microstructures on CO methanation and CO_2 methanation offers a new catalyst design strategy to improve the dispersion and reducibility of NiO nanoparticles. Besides, the addition of some metals (Mn, Ce, Zr, K, Mg, Zn, and V) to the Ni catalysts supported on Al@γ-Al_2O_3 was also investigated to enhance the catalytic activity. Mn-, Ce-, and Zr-doping to the supported Ni catalysts are beneficial to both CO and CO_2 methanation. The promotional effect of Mn is remarkable. On the other hand, the negative effect of K, Mg, Zn, and V on CO methanation was also observed.

Keywords: CO methanation, CO_2 methanation, Ni catalyst, core-shell metal-ceramic microstructures.

1. Introduction

The CO and CO_2 methanation reactions known as the Sabatier reaction have been studied to develop the better catalysts and related processes [1-4]. Ni-based catalysts have been widely used in the commercial process because of their relative fair activity, low cost, and high availability compared with noble metal catalysts [2-4]. Until now, the catalytic activity for these reactions over supported Ni catalysts has been reported to be strongly dependent on the nature of the support. Alumina occupies one of the most-employed industrial supports due to its high thermal stability and strong resistance to attrition [1]. However, the surface defect sites can strengthen the interaction between metal precursors and support resulting in low reducibility of metal oxides. Therefore, the modification Al_2O_3 by changing the alumina structures [3] or adding other metals as promoters [4] was investigated to develop the better alumina-supported metal catalysts. Nevertheless, the low thermal conductivity of the ceramic support might cause the sintering of the metal especially for the highly exothermic reactions including CO and CO_2 methanation reactions. Therefore, the support with a high thermal conductivity has its merit as long as the high dispersion of metal is guaranteed. The metal-ceramic core-shell microarchitectures [5] can be a solution to enhance the thermal conduction of a support and dispersion of metal particles. In this contribution, the Ni catalysts supported on Al@Al_2O_3 or Al@MAl_2O_4 were prepared and applied to CO and CO_2 methanation. For comparison, Ni/γ-Al_2O_3 catalyst was also prepared and tested.

2. Experimental

Metal-ceramic composites with core-shell microarchitecture (Al@γ-Al_2O_3 and Al@MAl_2O_4, M=Mn, Mg, and Zn) were obtained by a simple hydrothermal surface oxidation of Al metal particles in an aqueous solution of heterometal ions at elevated temperature (120-200 °C) and were used as the supports for Ni catalysts through the impregnation method. Some kinds of metals (Ce, K, Mn, Zr, Mg, Zn, and V) were also co-impregnated to modify supported Ni catalysts. For comparison, Ni/γ-Al_2O_3 catalyst was also prepared with an impregnation method.

The catalytic activity was measured at atmospheric pressure in the reaction temperature range 140 - 450 °C. The feed gas composed of 1 mol% CO (or CO_2), 50 mol% H_2, and 49 mol% He was contacted with 0.10 g of the catalyst at a flow rate of 100 mL/min. Various techniques including N_2 physisorption, CO_2, H_2 chemisorption, H_2-TPR, chemisorption, CO_2-TPD, XRD, ICP-OES, STEM-EDX, and TEM were employed to characterize the catalysts.

3. Results and discussion

The catalytic activity for CO and CO_2 methanation over supported Ni catalysts is shown in **Figure 1.** Among them, the Ni/Al@$MnAl_2O_4$ catalyst showed the highest activity. It achieved 100% CO and CO_2 conversion at 260 and 290 °C, respectively. The negative effect on CO and CO_2 methanation was observed over Ni/Al@$ZnAl_2O_4$. Note that Ni/Al@γ-Al_2O_3 is much superior to Ni/γ-Al_2O_3 for both CO and CO_2 methanation.

As shown in **Figure 2**, the promotional effect of the second metal in M-Ni/Al@γ-Al_2O_3 was examined for CO and CO_2 methanation. Compared with Ni/Al@γ-Al_2O_3, a remarkable enhancement in the catalytic activity was found over Mn-Ni/Al@γ-Al_2O_3 catalyst. On the other hand, V was confirmed as the second metal to selectively suppress the CO_2 methanation.

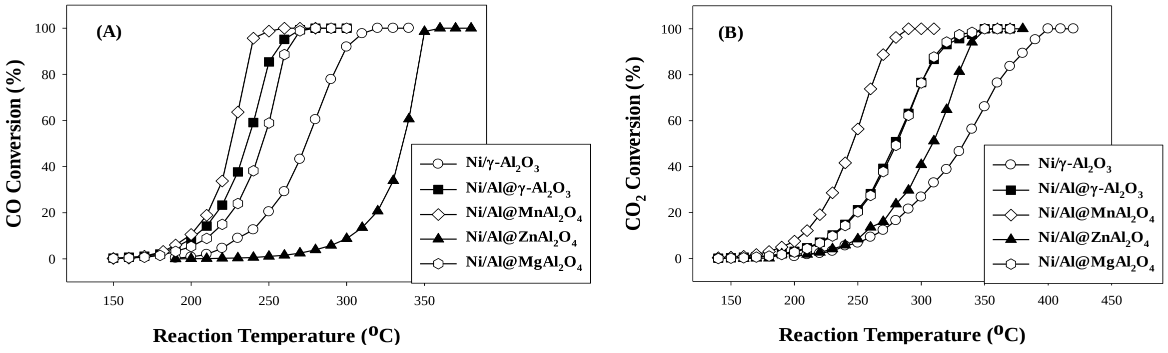

Figure 1. Catalytic performance of Ni supported catalysts via different kinds of supports on CO methanation (A) and CO_2 methanation (B). Reaction conditions: 1 mol% CO_x, 50 mol% H_2, 49 mol% He, F/W = 1,000 mL/min/g_{cat}.

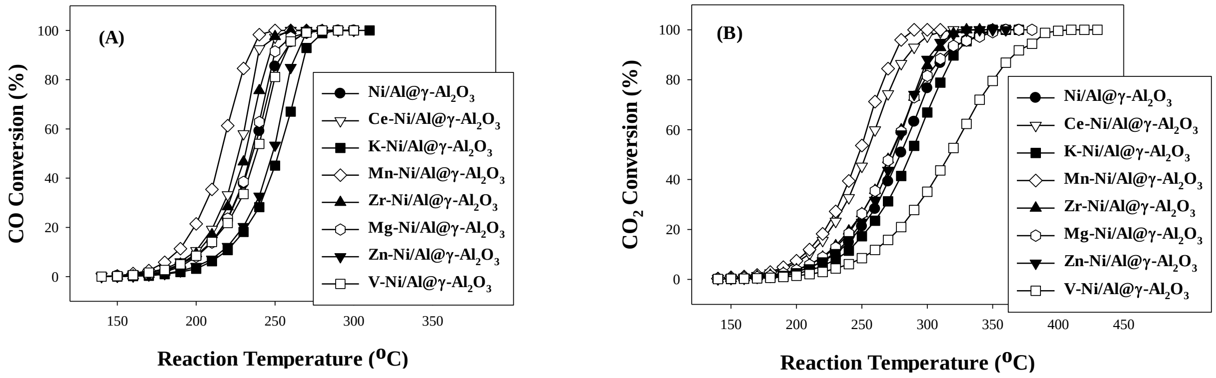

Figure 2. Catalytic performance of Ni/Al@ γ-Al_2O_3 modified by adding some kinds of metals on CO methanation (A) and CO_2 methanation (B). Reaction conditions: 1 mol% CO_x, 50 mol% H_2, 49 mol% He, F/W = 1,000 mL/min/g_{cat}.

4. Conclusions

The outstanding catalytic performance of the Ni supported on core-shell metal-ceramic microstructures for CO and CO_2 methanation was confirmed. Mn can be selected as the effective promoter to enhance the catalytic activity for both CO and CO_2 methanation. This is closely related to the Ni dispersion determined by H_2-chemisorption. On the other hand, the negative effect on CO methanation was observed over K-, Mg-, Zn-, and V-Ni/Al@γ-Al_2O_3. The negative effect on CO_2 methanation was also found over V-Ni/Al@γ-Al_2O_3.

References

1. J. Gao, Q. Liu, F. Gu, B. Liu, Z. Zhong, F. Su, RSC Adv. 5 (2015) 22759.
2. T.A. Le, M.S. Kim, S.H. Lee, T.W. Kim, E.D. Park, Cat. Today 293-294 (2017) 89.
3. T.A. Le, T.W. Kim, S.H. Lee, E.D. Park, Korean J. Chem. Eng. (2017) https://doi.org/10.1007/s11814-017-0257-0.
4. H. Lu, X. Yang, G. Gao, J. Wang, C. Han, X. Liang, C. Li, Y. Li, W. Zhang, X. Chen, Fuel 183 (2016) 335.
5. J. Kim, D. Lee, Chem. Mater. 28 (2016) 2786.