

Effect of support on hydrogen production by auto-thermal reforming of ethanol over supported nickel catalysts

Min Hye Youn, Jeong Gil Seo, Kyung Min Cho, Ji Chul Jung, Heesoo Kim, Kyung Won La,
Dong Ryul Park, Sunyoung Park, Sang Hee Lee and In Kyu Song[†]

School of Chemical and Biological Engineering, Research Center for Energy Conversion and Storage,
Seoul National University, Shinlim-dong, Gwanak-gu, Seoul 151-744, Korea
(Received 24 April 2007 • accepted 13 June 2007)

Abstract—Nickel catalysts supported on various supports such as ZnO, MgO, ZrO₂, TiO₂, and Al₂O₃ were prepared by an impregnation method to investigate the effect of support on catalytic performance in hydrogen production by auto-thermal reforming of ethanol. Among the supported catalysts, the Ni/ZrO₂ and Ni/TiO₂ catalysts showed better catalytic performance than the other catalysts. The electronic structure of nickel species supported on ZrO₂ and TiO₂ was favorably modified for the reaction, and thus, the reducibility of nickel species supported on ZrO₂ and TiO₂ was increased due to the weak interaction between nickel and support. On the other hand, the Ni/MgO and Ni/ZnO catalysts exhibited poor catalytic performance in the auto-thermal reforming of ethanol due to the formation of a solid solution phase.

Key words: Auto-thermal Reforming of Ethanol, Hydrogen Production, Effect of Support, Supported Nickel Catalyst

INTRODUCTION

Hydrogen has attracted much attention as a promising and clean energy source because of its potential applicability in fuel cell systems for stationary power plants and moving vehicles [1-7]. Among the various fuel sources for the production of hydrogen, light alcohols such as methanol and ethanol have been considered because they can be easily handled and are widely distributed over the world [8-10]. In particular, ethanol has been utilized as a promising source for the production of hydrogen because of its low toxicity, high volumetric energy density, and availability [11,12].

Ethanol has been converted into hydrogen via several catalytic reforming reactions. Among the catalytic reforming technologies, auto-thermal reforming, which consists of a combination of steam reforming and partial oxidation, has been recognized as a feasible method to produce hydrogen from ethanol in terms of both heat management and oxygen utilization [13]. In hydrogen production by auto-thermal reforming of ethanol, nickel-based catalysts have been widely investigated due to their excellent C-C bond cleavage activity and low cost [14,15]. The identity of support generally affects the catalytic performance of supported nickel catalysts in the auto-thermal reforming of ethanol, because the dispersion and stability of the nickel catalyst strongly depends on the nature of supporting material.

In this work, a series of nickel catalysts supported on various supports were prepared by an impregnation method, and were applied to hydrogen production by auto-thermal reforming of ethanol. The effect of support on the catalytic performance of supported nickel catalysts was investigated.

EXPERIMENTAL

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

A series of supported nickel catalysts were prepared by impregnating appropriate amounts of nickel precursor (Ni(NO₃)₂·6H₂O) onto ZnO, MgO, ZrO₂, TiO₂, and Al₂O₃ (γ -Al₂O₃). In all cases, the Ni loadings were fixed at 20 wt%. The impregnated catalyst samples were dried at 120 °C, and then they were calcined at 600 °C for 5 h. The reducibility and the acidity of supported nickel catalysts were measured by TPR (temperature-programmed reduction) [14,15] and NH₃-TPD (temperature-programmed desorption) [16] experiments, respectively, according to the methods in the literature [14-16]. The supported nickel catalysts were further characterized by XRD (MAC Science, M18XHF-SRA) using Cu-K α radiation (λ =1.54056 Å) operated at 50 kV and 100 mA.

Auto-thermal reforming of ethanol was carried out in a continuous flow fixed-bed reactor at atmospheric pressure. Each calcined catalyst (50 mg) was charged into a tubular quartz reactor, and then it was reduced with a mixed stream of H₂ (10 ml/min) and N₂ (30 ml/min) at 600 °C for 3 h. Ethanol and water were sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor together with N₂ carrier (30 ml/min). The molar feed ratios of H₂O/C₂H₅OH and O₂/C₂H₅OH were fixed at 3.0 and 0.5, respectively. The contact time was maintained at 175 g-catalyst·min/C₂H₅OH-mole. The catalytic reaction was carried out at 500 °C. Reaction products were periodically sampled and analyzed using an on-line gas chromatograph (Younglin, ACME 6000) equipped with a thermal conductivity detector.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of supported nickel catalysts calcined at 600 °C. Except for Ni/MgO catalyst, the calcined catalysts showed intrinsic XRD patterns of individual support and relatively narrow XRD peaks corresponding to NiO. In the case of Ni/MgO catalyst, however, XRD peaks representing a solid solution of NiO-MgO were observed. It was reported that the formation of a NiO-

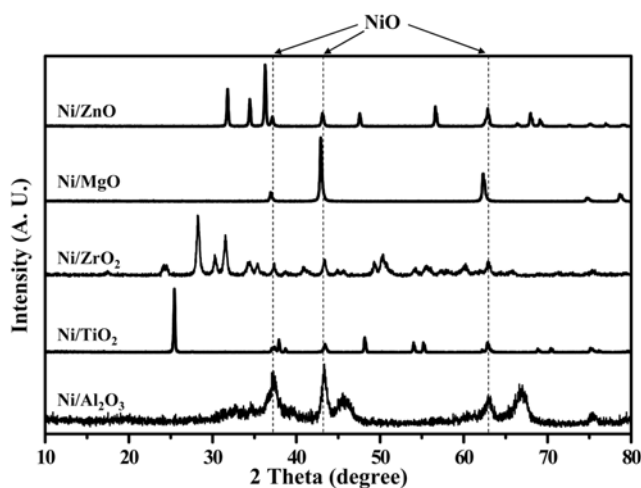


Fig. 1. XRD patterns of supported nickel catalysts calcined at 600 °C.

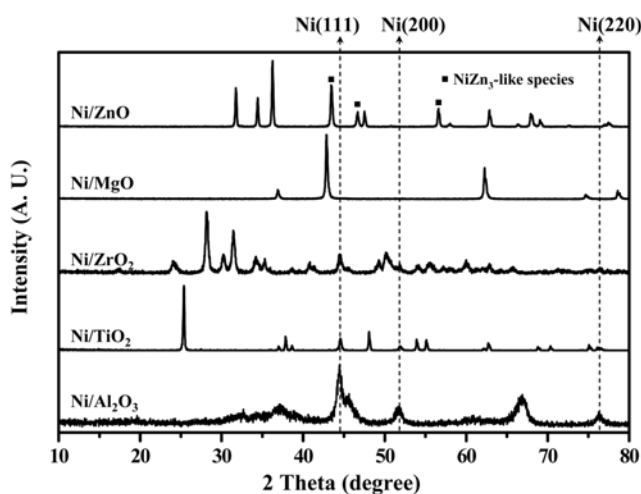


Fig. 2. XRD patterns of supported nickel catalysts reduced at 600 °C.

MgO solid solution was attributed to the incorporation of Ni^{2+} ion into the lattice of MgO occurred during the calcination step [17].

Fig. 2 shows the XRD patterns of supported nickel catalysts reduced at 600 °C for 3 h. The reduced $\text{Ni}/\text{Al}_2\text{O}_3$, Ni/TiO_2 , and Ni/ZrO_2 catalysts showed XRD peaks for metallic nickel. However, the Ni/ZnO and Ni/MgO catalysts exhibited somewhat different XRD patterns from the other three catalysts. In other words, the XRD peaks for metallic nickel disappeared in the Ni/ZnO and Ni/MgO catalysts after the reduction. In particular, the XRD peaks corresponding to NiZn_3 -like species (JCPDS 47-1019) were observed in the Ni/ZnO catalyst. These results indicate that no metallic nickel particles were formed in the Ni/ZnO and Ni/MgO catalysts, and that metallic phases were transformed into different forms during the reduction step.

Fig. 3 shows the TPR profiles of supported nickel catalysts. The TPR patterns of supported nickel catalysts were different depending on the identity of support. It is known that unsupported nickel oxide is reduced at around 400 °C [18]. Therefore, it can be inferred

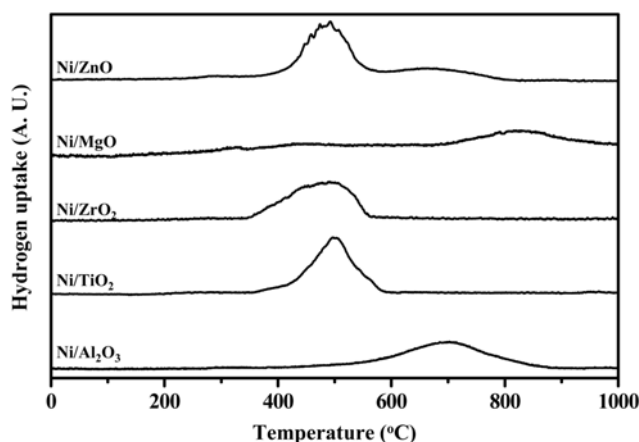


Fig. 3. TPR profiles of supported nickel catalysts.

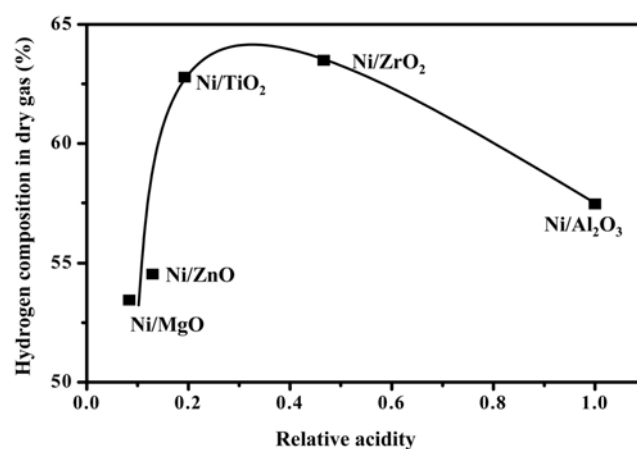


Fig. 4. Hydrogen compositions in dry gas in the auto-thermal reforming of ethanol over supported nickel catalysts at 500 °C. The catalytic performance data were obtained after a 3 h-reaction.

that the reduction peak of Ni/ZrO_2 and Ni/TiO_2 catalysts appearing at around 500 °C was attributed to the reduction of NiO species weakly interacted with the support. Although the Ni/ZnO catalyst also showed a reduction peak at around 500 °C, the reduction peak might be due to the reduction of NiO-ZnO, which was eventually transformed into the Ni-Zn solid solution after the reduction [19,20]. The weak reduction peak of Ni/MgO catalyst appearing at around 800 °C was due to the reduction of NiO-MgO solid solution. On the other hand, the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst exhibited a reduction peak at around 700 °C, which was attributed to the reduction of nickel aluminate species [18,21].

Fig. 4 shows the hydrogen compositions in dry gas in the auto-thermal reforming of ethanol over supported nickel catalysts at 500 °C, plotted as a function of relative acidity of the supported nickel catalyst. The relative acidity was defined as the ratio of acidity of a supported nickel catalyst with respect to that of $\text{Ni}/\text{Al}_2\text{O}_3$. All the supported nickel catalysts examined in this work exhibited 100% ethanol conversion. The hydrogen composition showed a volcano-shaped curve with respect to relative acidity of the supported nickel catalyst. It was observed that the Ni/ZrO_2 and Ni/TiO_2 catalysts with an

intermediate relative acidity exhibited high catalytic performance. It was reported that metal sites became more electron deficient due to the interaction between metal species and acid sites of the support with increasing acidity [22]. However, it was found that a strong acidic support such as Al_2O_3 led to side reactions and caused rapid deactivation of nickel catalyst. It is believed that the electronic structure of nickel species was favorably modified for the auto-thermal reforming of ethanol when a supported catalyst retained an optimum level of acidity. It can be inferred that the electronic structure of nickel species supported on ZrO_2 and TiO_2 was favorably modified to increase the reducibility of nickel species by forming a weak interaction between nickel and support.

CONCLUSIONS

Nickel catalysts supported on various supports such as ZnO , MgO , ZrO_2 , TiO_2 , and Al_2O_3 were prepared by an impregnation method, and were applied to hydrogen production by auto-thermal reforming of ethanol. Among the supported catalysts, the Ni/ZrO_2 and Ni/TiO_2 catalysts showed better catalytic performance than the other catalysts. It was found that the electronic structure of nickel species supported on ZrO_2 and TiO_2 was favorably modified for the reaction, and consequently, the reducibility of nickel species supported on ZrO_2 and TiO_2 was increased due to the weak interaction between nickel and support. However, the Ni/MgO and Ni/ZnO catalysts exhibited poor catalytic performance in the auto-thermal reforming of ethanol, because the solid solution phase prevented the formation of an active metallic nickel. The acidity of supported nickel catalysts also played an important role in determining the catalytic performance. It was revealed that the Ni/ZrO_2 and Ni/TiO_2 catalysts with moderate acidity exhibited high catalytic performance in the auto-thermal reforming of ethanol.

ACKNOWLEDGMENTS

The authors wish to acknowledge support from the RCECS (Research Center for Energy Conversion and Storage: R11-2002-102-00000-0) and Seoul Renewable Energy Research Consortium (Seoul R & BD Program).

REFERENCES

1. C. Diagne, H. Idriss and A. Kiennemann, *Catal. Comm.*, **3**, 565 (2002).
2. M. H. Kim, E. K. Lee, J. H. Jun, C. Y. Han, S. J. Kong, B. K. Lee, T. J. Lee and K. J. Yoon, *Korean J. Chem. Eng.*, **20**, 835 (2003).
3. D. J. Moon, J. W. Ryu, S. D. Lee and B. S. Ahn, *Korean J. Chem. Eng.*, **19**, 921 (2002).
4. A. N. Fatsikostas and X. E. Verykios, *J. Catal.*, **225**, 439 (2004).
5. J. K. Lee and D. Park, *Korean J. Chem. Eng.*, **15**, 658 (1998).
6. S. W. Nam, S. P. Yoon, H. Y. Ha, S.-A. Hong and A. P. Maganyuk, *Korean J. Chem. Eng.*, **17**, 288 (2000).
7. J. Zhang, Y. Wang, R. Ma and D. Wu, *Korean J. Chem. Eng.*, **20**, 288 (2003).
8. Y. Liu, T. Hayakawa, T. Tsunoda, K. Suzuki, S. Hamakawa, K. Murata, R. Shiozaki, T. Ishii and M. Kumagai, *Topics Catal.*, **22**, 205 (2003).
9. S. Velu, N. Satoh, C. S. Gopinath and K. Suzuki, *Catal. Lett.*, **82**, 145 (2002).
10. P. D. Vaidya and A. E. Rodrigues, *Chem. Eng. J.*, **117**, 39 (2006).
11. M. H. Youn, J. G. Seo, P. Kim and I. K. Song, *J. Mol. Catal. A*, **261**, 276 (2007).
12. S. J. Kong, J. H. Jun and K. J. Yoon, *Korean J. Chem. Eng.*, **21**, 793 (2004).
13. S. Cavallaro, V. Chiodo, A. Vita and S. Freni, *J. Power Sources*, **123**, 10 (2003).
14. M. H. Youn, J. G. Seo, P. Kim, J. J. Kim, H.-I. Lee and I. K. Song, *J. Power Sources*, **162**, 1270 (2006).
15. J. G. Seo, M. H. Youn and I. K. Song, *J. Mol. Catal. A*, **268**, 9 (2007).
16. K. W. La, J. C. Jung, H. Kim, S.-H. Baek and I. K. Song, *J. Mol. Catal. A*, **269**, 41 (2007).
17. A. Djaidja, S. Libs, A. Kiennemann and A. Barama, *Catal. Today*, **113**, 194 (2006).
18. P. Kim, Y. Kim, C. Kim, H. Kim, Y. Park, J. H. Lee, I. K. Song and J. Yi, *Catal. Lett.*, **89**, 185 (2003).
19. G. Drazic and D. Lisjak, *Mikrochim. Acta*, **132**, 289 (2000).
20. A. M. Rubinshtein, A. V. Sagalovich, A. L. Klyachko-Gurvich, A. A. Slinkin, G. A. Ashavskaya and N. V. Melnikova, *Russian Chem. Bull.*, **16**, 1639 (1967).
21. P. Kim, Y. Kim, H. Kim, I. K. Song and J. Yi, *Appl. Catal. A*, **272**, 157 (2004).
22. X. Qin, S. Xianxiang, Y. Pinliang and G. Xiexian, *React. Kinet. Catal. Lett.*, **31**, 279 (1986).