

Effect of CeO₂ on CO removal over CeO₂-modified Ni catalyst in CO-rich syngas

Sung Ho Kim, Weon-Doo Lee, and Ho-In Lee[†]

School of Chemical and Biological Engineering & Research Center for Energy Conversion and Storage,
Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea
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Abstract—A CeO₂-modified Ni catalyst has been studied as a substitute for Ni bulk catalyst in a CO removal reaction using various characterization methods. CO removal was enhanced slightly and presented at lower reaction temperatures following promotion of CeO₂ on Ni. The enhanced ability to reduce CO was mainly a result of methanation rather than WGS during a CO removal reaction. Based on X-ray diffraction and temperature-programmed reduction, CeO₂ appeared to change the Ni surface properties. Because the bond strength between C and O atoms in CO was weakened by the surface oxygen of CeO₂ on Ni, the CeO₂-promoted Ni catalyst showed higher CO conversion and lower selectivity to WGS than Ni bulk catalyst.

Key words: Fuel Processor, Water Gas Shift, CO Methanation, Cerium Oxide, Mobile Surface Oxygen

INTRODUCTION

Fuel cells promise highly efficient conversion of chemical energy into electrical energy with low emission of environmental pollutants. They require high purity hydrogen as their major fuel. To date, hydrocarbon (CH₄, C₃H₈, and CH₃OH) fuel processors have produced hydrogen gas containing CO, CO₂, and H₂O [1-3]. However, the CO level in the produced gas stream has to remain below 10 ppm to prevent deactivation of the fuel cell anode through CO poisoning. Typically, water gas shift (WGS) [4,5] and preferential oxidation (PROX) [6] reactions have been employed to remove CO in fuel processing systems.

WGS is composed of high temperature WGS (HTS) [7,8] and low temperature WGS (LTS) [9,10], and plays the role of conversion of CO producing H₂. A double-stage WGS process is disadvantageous in fuel processing systems due to its large volume [11, 12]. In previous research [11], we developed an Ni bulk catalyst as an alternative to using a single-stage WGS reaction. The Ni bulk catalyst was suggested as a substitute for the conventional WGS catalyst in order to overcome the size-related weakness of the WGS process, which can occupy *ca.* 70% of system volume in a fuel processor. That Ni bulk catalyst reduced high concentrations (15%) of CO to below 1% at 380-440 °C by a single-stage CO removal reaction. However, methanation could not be avoided during the CO removal reaction, resulting in the consumption of H₂, and thereby reducing fuel production efficiency. In fact, the Ni catalyst is active, but not selective for the WGS reaction, because methane/steam reforming [13] and methanation [14] are usually observed concurrently. Even though the Ni bulk catalyst resulted in methanation, the single-stage CO removal reaction was still advantageous to the fuel processing system.

CeO₂ is a well-known material for catalyst support and promoter [15-18]. The typical property of CeO₂ is the existence of mobile and active oxygen on the surface [19-21]. We studied the effects of CeO₂ on the Ni bulk catalyst and assessed catalyst status using various characterization methods. We also investigated and discussed how the catalytic properties of Ni were changed by CeO₂ promotion in a CO removal reaction by WGS and methanation.

EXPERIMENTAL

The Ni bulk catalyst was prepared by a tape-casting method and was cut to a doughnut-type disk shape for catalytic activity tests, details of which are described elsewhere [11,22]. CeO₂ was added to the Ni bulk catalyst rings by dip-coating. The Ni rings were dipped into a commercial CeO₂ sol (20% CeO₂ in H₂O, Alfa Aesar) for 30 sec and then dried at 100 °C in an oven. Catalyst rings coated with 3 wt% CeO₂/Ni, 6 wt% CeO₂/Ni, and 12 wt% CeO₂/Ni were obtained by varying the number of dips. Therefore, all the catalysts employed in this study were bulk catalysts regardless of promotion.

The reactor for the structural catalyst was made of stainless steel in order to withstand high reaction temperatures. The standard reactant gas, which simulated the gas reformed from an autothermal methane reforming process, was 15% CO, 40% H₂, 10% CO₂, with the balance being N₂. The reactant gas (400 cm³/min) was passed through an evaporator and introduced vertically into the reactor with a steam to CO ratio of 5 : 1, and flowed in parallel over the catalyst ring. An Inconel sheet layer was used to define the flow path.

The flow rate of the standard reactant gas was controlled by a mass flow controller (UFC-1100A, Unit Instruments, Inc.), and the amount of steam was controlled by adjusting the evaporator temperature. A line heater set at 250 °C maintained steam flow, without condensation, from the evaporator to the reactor inlet.

The product mixture of CO, CH₄, CO₂, and O₂ gases was analyzed by using a CO analyzer (Ultramat 23, Siemens) and a micro gas chromatograph (Agilent 3000A, Agilent Technologies) with two thermal conductivity detectors (TCDs) composed of a ϕ 0.32 mm ×

[†]To whom correspondence should be addressed.

E-mail: hilee@snu.ac.kr

This article is dedicated to Prof. Gon Seo on the occasion of his retirement from Chonnam National University.

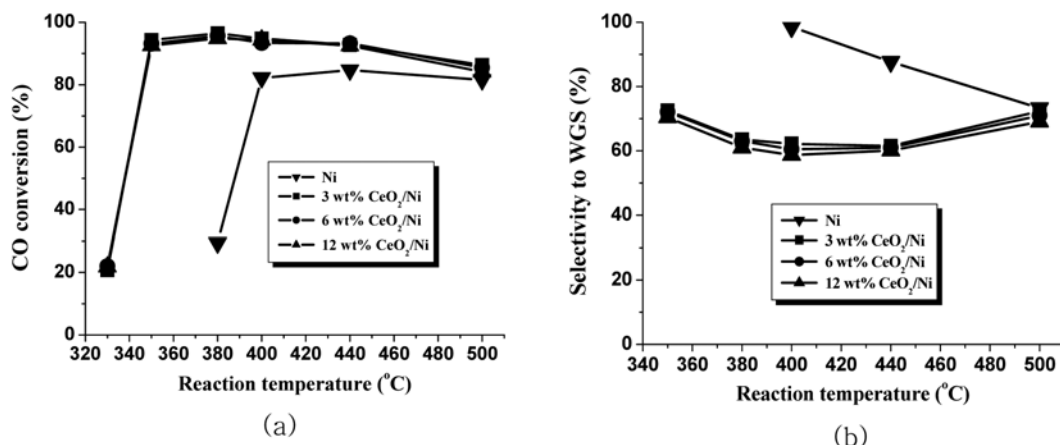


Fig. 1. (a) CO conversion and (b) selectivity to WGS of Ni bulk and CeO₂-promoted Ni catalysts.

10 m column of MolSieve 5A (Agilent Technologies) to separate H₂, CO, N₂, and CH₄, and a ϕ 0.32 mm \times 3 m pre-column of PLOT U (Agilent Technologies) to separate CO₂ using a 1.0 μ L backflush injector. The carrier gases for MolSieve 5A and PLOT U were Ar and He, respectively. For all conditions, N₂ was used as the balance gas to calculate CO conversion and product amount. CO conversion (X_{CO}) and the selectivity to WGS (S_{WGS}) during the CO removal reaction by WGS and methanation were calculated from the following formulae:

$$X_{CO} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100(\%)$$

$$S_{WGS} = \frac{[CO_2]_{out} - [CO_2]_{in}}{[CO_2]_{out} - [CO_2]_{in} + [CH_4]_{out}} \times 100(\%)$$

The temperature-programmed reduction (TPR) with hydrogen was performed by an automated catalyst characterization system (BEL CAT, BEL Japan, Inc.). The experiments were performed at a heating rate of 10 °C/min. The reactive gas was H₂ (10 vol%) in Ar and the flow rate was fixed at 30 cm³/min. The total reactive gas consumption during TPR analysis was measured by TCD. The surface morphology of the catalyst was observed by scanning electron microscopy (SEM; FEI XL-30 FEG, Philips FEI Company) and its crystal structure was measured by X-ray diffraction (XRD; D/MAX-III A, Rigaku) with CuK α radiation.

RESULTS AND DISCUSSION

Pretreatment to activate the catalysts, by oxidation process with air (400 cm³/min) at 600 °C and subsequent reduction process with a stream of steam (at 77.5 °C) and reformat gas (400 cm³/min) for 0.5 h at 600 °C as conducted in a previous study [11], was carried out before the catalytic activity tests.

The influence of reaction temperature on the CO removal reaction is shown in Fig. 1 and the activity tests for the Ni and CeO₂-promoted Ni catalysts were conducted between 330 and 500 °C. Fig. 1(a) shows that the X_{CO} (dry %) of the CeO₂-promoted Ni catalysts reached ca. 94% at 350 °C and decreased slightly with increasing reaction temperature, while the X_{CO} of the Ni bulk catalyst was ca. 84% at 400 °C with a similar trend to lower X_{CO} at increased reaction temperatures. Overall, CO removal was enhanced slightly,

and CO removal presented at a lower reaction temperature, 350 °C, by promotion of CeO₂ onto the Ni bulk catalyst.

Fig. 1(b) shows that the amount of methanation as a side reaction to WGS was considerable. S_{WGS} indicates which reaction is dominant: *i.e.*, WGS producing H₂ or methanation consuming H₂ during the removal of high concentrations of CO. As presented in Fig. 1(b), the Ni bulk catalyst showed different S_{WGS} values from 400 to 500 °C, while the CeO₂-promoted Ni catalysts showed lower S_{WGS} than the Ni bulk catalyst at all the reaction temperatures. S_{WGS} for the Ni bulk catalyst increased with decreasing reaction temperature from 500 to 400 °C because WGS is a slightly exothermic and thermodynamically preferential reaction at lower temperatures [23]. However, in the CeO₂-promoted Ni catalysts, S_{WGS} did not change markedly at all reaction temperatures. The results suggest that the lower values are due to improved methanation resulting from CeO₂ promotion. The results of Fig. 1 indicate that catalytic CO removal can be intensified by promoting CeO₂ to Ni, and that CeO₂ promotion affects methanation, rather than WGS. It suggests that H₂ was consumed when hydrogenating CO to CH₄ during the CO removal reaction,

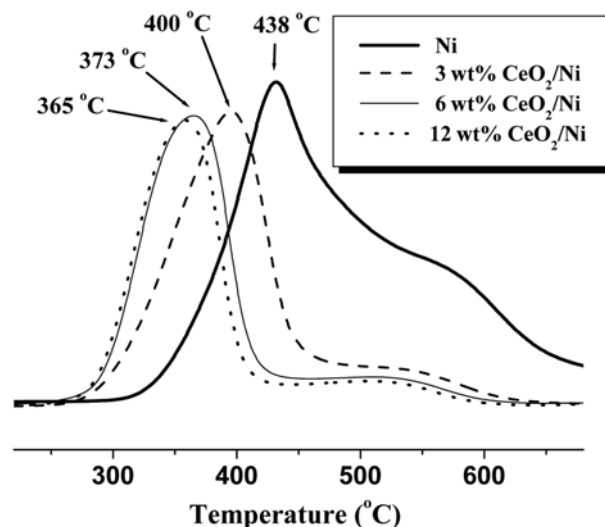


Fig. 2. H₂-TPR profiles of Ni bulk and CeO₂-promoted Ni catalysts after exposing to 400 cm³/min air for 2 h at 600 °C: sample weight, 0.03 g.

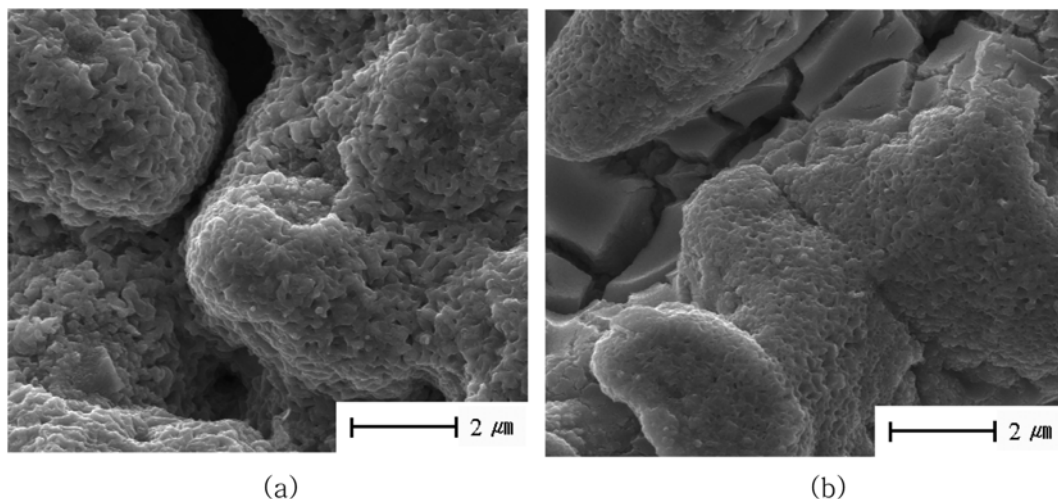


Fig. 3. SEM images of (a) Ni bulk and (b) 3 wt% CeO₂-promoted Ni catalysts after exposing to 400 cm³/min air for 2 h at 600 °C.

resulting in a decrease in overall efficiency of the fuel processor.

The reduction behavior of the CeO₂-promoted Ni catalyst was investigated by H₂-TPR, and the resultant profiles are shown in Fig. 2. The reduction of NiO to Ni was reported to follow Ni²⁺ → Ni^{δ+} → Ni⁰ [24,25]. Fig. 2 shows two peaks for NiO reduction by H₂ suggesting a stepwise reduction at *ca.* 438 and 550 °C. CeO₂ is reported to be reduced with two steps and partially changes the reducibility of the Ni bulk catalyst [26,27]. In Fig. 2, when 3 wt% CeO₂ was promoted to the Ni bulk catalyst, the NiO reduction temperature shifted, presumably due to the presence of CeO₂. The NiO reduction peak shift from *ca.* 438 to *ca.* 400 °C is assumed by a result of mobile CeO₂ surface oxygen affecting the surface oxygen of NiO [28]. The second NiO reduction peak in the CeO₂-promoted Ni catalyst was the result of the strong interaction between CeO₂ and NiO.

The H₂-TPR experiment was performed to investigate why methanation rather than WGS was enhanced by promotion of CeO₂ onto Ni, and to evaluate the interaction between Ni and CeO₂. Based on the mechanism of methanation [29,30], methanation could be improved by weakening the bond strength between C and O of the CO over the catalyst because the C atom in the weakened C-O bond reacts more easily with H₂ than with H₂O. It has also been reported that mobile oxygen on the catalyst surface might attenuate the bond strength of C-O adsorbed on the surface [31].

As reported previously [11], if NiO is completely reduced to Ni and CeO₂ has no effect on the catalytic activity of Ni, the reaction window over CeO₂-promoted Ni catalyst should decrease giving a lower activity at 380 °C like the Ni bulk catalyst. However, the CeO₂-promoted Ni catalyst sustained that activity level, and expanded the reaction window while maintaining the catalytic activity (Fig. 1). Therefore, we conclude that CeO₂ changed the Ni catalyst's surface characteristics, and thus, the catalytic activity of Ni. In addition, the CeO₂-promoted Ni affected methanation much more than WGS (Fig. 1(b)), resulting in a decrease of WGS selectivity.

To help explain the differences in TPR results, the surface morphologies of the two catalyst types were characterized. The SEM images in Fig. 3 show the surfaces of (a) Ni and (b) 3 wt% CeO₂-promoted Ni catalysts after oxidation with air for 2 h at 600 °C. While the Ni bulk catalyst had large intermolecular pores, the CeO₂-pro-

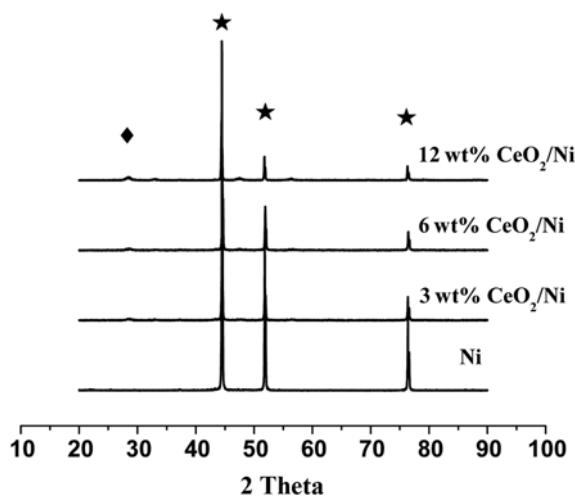


Fig. 4. XRD patterns of Ni bulk and CeO₂-promoted Ni catalysts after an activity test (★: Ni, ◆: CeO₂).

moted Ni catalyst exhibited smaller ones, apparently resulting from blockage by CeO₂ particles. The images suggest that CeO₂ did not affect the structure of the Ni bulk catalyst, but that it did interact with the Ni metal.

XRD was carried out to ascertain the properties of the CeO₂-promoted Ni catalysts that may be related to the enhancement of methanation. The XRD patterns of the catalysts are presented in Fig. 4, but even the 12 wt% CeO₂-promoted Ni catalyst showed no shift in the characteristic Ni peaks suggesting no influence of CeO₂ on the lattice of Ni.

The weak CeO₂ peaks shown in the CeO₂-promoted Ni catalysts are due to the lower instrument sensitivity toward CeO₂ than Ni. The CeO₂ particle in the CeO₂-promoted Ni catalyst was supposed to cover only the Ni surface as shown in the SEM image of Fig. 3(b), but, some property of CeO₂ affected the catalytic activity of Ni in the CO removal reaction, thus suggesting that CeO₂ played a chemical, not structural, role. Based on the TPR and XRD results, we conclude that the promotion of CeO₂ enhances the methanation reaction. In addition, we suggest that the mobile surface oxygen of

CeO₂ affects the bond strength between C and O in CO on the catalyst surface according to the methanation mechanism.

CONCLUSIONS

The CeO₂-promoted Ni catalyst reduced high concentrations of CO (15% in dry condition) contained in a standard reformat gas to less than 1% in a single-stage process, and might be a practical substitute to a double-stage WGS process (HTS and LTS). However, selectivity to WGS over the CeO₂-promoted Ni catalyst decreased while methanation increased. CeO₂ changed the properties of the Ni bulk catalyst and advanced its catalytic activity for CO removal. However, even though CeO₂ promotion positively affected CO conversion, the WGS reaction was inhibited and the methanation reaction was enhanced. This is seen as the result of surface oxygen formed by CeO₂ promotion weakening the C-O bond on the catalyst.

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REFERENCES

1. K.-Y. Kim, J. Han, S. W. Nam, T.-H. Lim and H.-I. Lee, *Catal. Today*, **131**, 431 (2008).
2. J. M. Sohn, Y. C. Byun, J. Y. Cho, J. Choe and K. H. Song, *Int. J. Hydrog. Energy*, **32**, 5103 (2007).
3. H. J. Seo and E. Y. Yu, *J. Ind. Eng. Chem.*, **3**, 85 (1997).
4. C. Rhodes, G. J. Hutchings and A. M. Ward, *Catal. Today*, **23**, 43 (1995).
5. G. Jacobs and B. H. Davis, *Appl. Catal. A*, **333**, 192 (2007).
6. C. R. Jung, A. Kundu, S. W. Nam and H.-I. Lee, *Appl. Catal. A*, **331**, 112 (2007).
7. C. Rhodes, B. P. Williams, F. King and G. J. Hutchings, *Catal. Commun.*, **3**, 381 (2002).
8. C. Kokkofitis, G. Karagiannakis and M. Stoukides, *Catal. Today*, **127**, 330 (2007).
9. V. Idakiev, T. Tabakova, K. Tenchev, Z.-Y. Yuan, T.-Z. Ren and B.-L. Su, *Catal. Today*, **128**, 223 (2007).
10. K. S. R. Rao, K.-W. Jun, W.-J. Shen and K.-W. Lee, *J. Ind. Eng. Chem.*, **6**, 287 (2000).
11. S. H. Kim, S. W. Nam, T.-H. Lim and H.-I. Lee, *Appl. Catal. B*, **81**, 97 (2008).
12. T. A. Semelsberger and R. L. Borup, *Int. J. Hydrog. Energy*, **30**, 425 (2005).
13. J.-S. Choi, J.-S. Yun, H.-H. Kwon, T.-H. Lim, S.-A. Hong and H.-I. Lee, *J. Power Sources*, **145**, 652 (2005).
14. H. Habazaki, M. Yamasaki, B.-P. Zhang, A. Kawashima, S. Kohno, T. Takai and K. Hashimoto, *Appl. Catal. A*, **172**, 131 (1998).
15. H. Kušar, S. Hoëvar and J. Levec, *Appl. Catal. B*, **63**, 194 (2006).
16. K. G. Azzam, I. V. Babich, K. Seshan and L. Lefferts, *J. Catal.*, **251**, 153 (2007).
17. Y. Denkwitz, A. Karpenko, V. Plzak, R. Leppelt, B. Schumacher and R. J. Behm, *J. Catal.*, **246**, 74 (2007).
18. L. Mendelovici and M. Steinberg, *J. Catal.*, **96**, 285 (1985).
19. D. Widmann, R. Leppelt and R. J. Behm, *J. Catal.*, **251**, 437 (2007).
20. N. Laosiripojana and S. Assabumrungrat, *Appl. Catal. B*, **60**, 107 (2005).
21. N. C. Park, Y.-C. Kim and D.-J. Kim, *Korean Chem. Eng. Res.*, **36**(2), 139 (1998).
22. S. H. Kim, J. H. Chung, Y. T. Kim, J. Han, S. P. Yoon, S.-W. Nam, T.-H. Lim and H.-I. Lee, *Catal. Today*, **146**, 96 (2009).
23. Y. Choi and H. G. Stenger, *J. Power Sources*, **124**, 432 (2003).
24. W. Shan, M. Luo, P. Ying, W. Shen and C. Li, *Appl. Catal. A*, **246**, 1 (2003).
25. S. Xu, X. Yan and X. Wang, *Fuel*, **85**, 2243 (2006).
26. G. Jacobs, P. M. Patterson, L. Williams, E. Chenu, D. Sparks, G. Thomas and B. H. Davis, *Appl. Catal. A*, **262**, 177 (2004).
27. W. Zheng, J. Zhang, Q. Ge, H. Xu and W. Li, *Appl. Catal. B*, **80**, 98 (2008).
28. K. O. Xavier, R. Sreekala, K. K. A. Rashid, K. K. M. Yusuff and B. Sen, *Catal. Today*, **49**, 17 (1999).
29. I.-G. Bajusz and J. G. Goodwin Jr., *J. Catal.*, **169**, 157 (1997).
30. J. Sehested, S. Dahl, J. Jacobsen and J. R. Rostrup-Nielsen, *J. Phys. Chem. B*, **109**, 2432 (2005).
31. M. A. Henderson, C. L. Perkins, M. H. Engelhard, S. Thevuthasan and C. H. F. Peden, *Surf. Sci.*, **526**, 1 (2003).