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Effect of CeO_2 on CO removal over CeO_2-modified Ni catalyst in CO-rich syngas

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Abstract−A CeO_2-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 CeO_2 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, CeO_2 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 CeO_2 on Ni, the CeO_2-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 (CH_4, C_3H_8, and CH_3OH) fuel processors have produced hydrogen gas containing CO, CO_2, and H_2O [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 H_2. 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 H_2, 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.

CeO_2 is a well-known material for catalyst support and promoter [15-18]. The typical property of CeO_2 is the existence of mobile and active oxygen on the surface [19-21]. We studied the effects of CeO_2 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 CeO_2 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]. CeO_2 was added to the Ni bulk catalyst rings by dip-coating. The Ni rings were dipped into a commercial CeO_2 sol (20% CeO_2 in H_2O, Alfa Aesar) for 30 sec and then dried at 100 °C in an oven. Catalyst rings coated with 3 wt% CeO_2/Ni, 6 wt% CeO_2/Ni, and 12 wt% CeO_2/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% H_2, 10% CO_2, with the balance being N_2. The reactant gas (400 cm^3/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, CH_4, CO_2, and O_2 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×

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

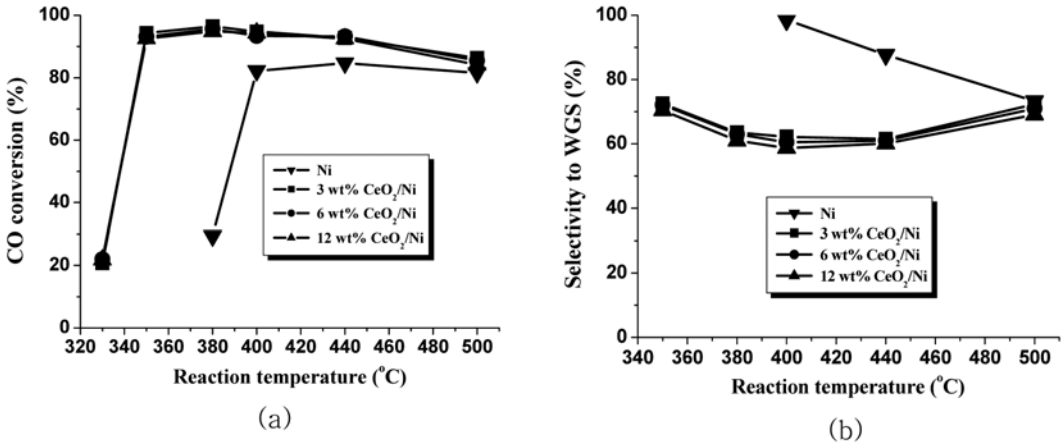

Fig. 1. (a) CO conversion and (b) selectivity to WGS of Ni bulk and CeO_2-promoted Ni catalysts.

10 m column of MolSieve 5A (Agilent Technologies) to separate H_2, CO, N_2, and CH_4, and a ϕ 0.32 mm×3 m pre-column of PLOT U (Agilent Technologies) to separate CO_2 using a 1.0 μL backflush injector. The carrier gases for MolSieve 5A and PLOT U were Ar and He, respectively. For all conditions, N_2 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 H_2 (10 vol%) in Ar and the flow rate was fixed at 30 cm^3/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-IIIA, Rigaku) with CuKα radiation.

RESULTS AND DISCUSSION

Pretreatment to activate the catalysts, by oxidation process with air (400 cm^3/min) at 600 °C and subsequent reduction process with a stream of steam (at 77.5 °C) and reformate gas (400 cm^3/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 CeO_2-promoted Ni catalysts were conducted between 330 and 500 °C. Fig. 1(a) shows that the X_{CO} (dry %) of the CeO_2-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 CeO_2 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 H_2 or methanation consuming H_2 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 CeO_2-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 CeO_2-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 CeO_2 promotion. The results of Fig. 1 indicate that catalytic CO removal can be intensified by promoting CeO_2 to Ni, and that CeO_2 promotion affects methanation, rather than WGS. It suggests that H_2 was consumed when hydrogenating CO to CH_4 during the CO removal reaction,

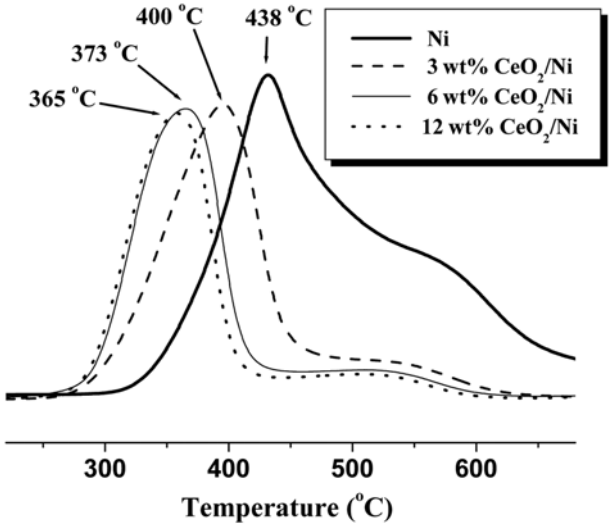

Fig. 2. H_2-TPR profiles of Ni bulk and CeO_2-promoted Ni catalysts after exposing to 400 cm^3/min air for 2 h at 600 °C: sample weight, 0.03 g.

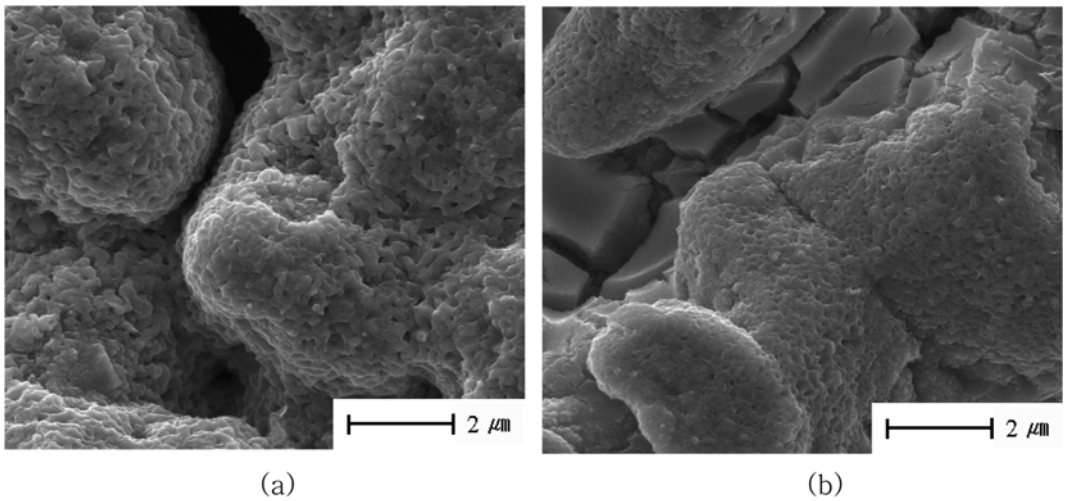

Fig. 3. SEM images of (a) Ni bulk and (b) 3 wt% CeO_2-promoted Ni catalysts after exposing to 400 cm^3/min air for 2 h at 600 °C.

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

The reduction behavior of the CeO_2-promoted Ni catalyst was investigated by H_2-TPR, and the resultant profiles are shown in Fig. 2. The reduction of NiO to Ni was reported to follow $Ni^{2+} \rightarrow Ni^{\delta+} \rightarrow Ni^0$ [24,25]. Fig. 2 shows two peaks for NiO reduction by H_2 suggesting a stepwise reduction at *ca.* 438 and 550 °C. CeO_2 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% CeO_2 was promoted to the Ni bulk catalyst, the NiO reduction temperature shifted, presumably due to the presence of CeO_2. The NiO reduction peak shift from *ca.* 438 to *ca.* 400 °C is assumed by a result of mobile CeO_2 surface oxygen affecting the surface oxygen of NiO [28]. The second NiO reduction peak in the CeO_2-promoted Ni catalyst was the result of the strong interaction between CeO_2 and NiO.

The H_2-TPR experiment was performed to investigate why methanation rather than WGS was enhanced by promotion of CeO_2 onto Ni, and to evaluate the interaction between Ni and CeO_2. 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 H_2 than with H_2O. 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 CeO_2 has no effect on the catalytic activity of Ni, the reaction window over CeO_2-promoted Ni catalyst should decrease giving a lower activity at 380 °C like the Ni bulk catalyst. However, the CeO_2-promoted Ni catalyst sustained that activity level, and expanded the reaction window while maintaining the catalytic activity (Fig. 1). Therefore, we conclude that CeO_2 changed the Ni catalyst's surface characteristics, and thus, the catalytic activity of Ni. In addition, the CeO_2-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% CeO_2-promoted Ni catalysts after oxidation with air for 2 h at 600 °C. While the Ni bulk catalyst had large intermolecular pores, the CeO_2-promoted Ni catalyst exhibited smaller ones, apparently resulting from blockage by CeO_2 particles. The images suggest that CeO_2 did not affect the structure of the Ni bulk catalyst, but that it did interact with the Ni metal.

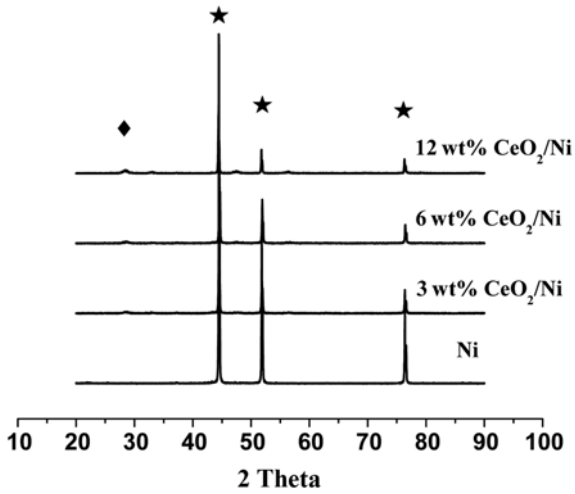

Fig. 4. XRD patterns of Ni bulk and CeO_2-promoted Ni catalysts after an activity test (★: Ni, ◆: CeO_2).

XRD was carried out to ascertain the properties of the CeO_2-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% CeO_2-promoted Ni catalyst showed no shift in the characteristic Ni peaks suggesting no influence of CeO_2 on the lattice of Ni.

The weak CeO_2 peaks shown in the CeO_2-promoted Ni catalysts are due to the lower instrument sensitivity toward CeO_2 than Ni. The CeO_2 particle in the CeO_2-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 CeO_2 affected the catalytic activity of Ni in the CO removal reaction, thus suggesting that CeO_2 played a chemical, not structural, role. Based on the TPR and XRD results, we conclude that the promotion of CeO_2 enhances the methanation reaction. In addition, we suggest that the mobile surface oxygen of

CeO_2 affects the bond strength between C and O in CO on the catalyst surface according to the methanation mechanism.

CONCLUSIONS

The CeO_2-promoted Ni catalyst reduced high concentrations of CO (15% in dry condition) contained in a standard reformate 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 CeO_2-promoted Ni catalyst decreased while methanation increased. CeO_2 changed the properties of the Ni bulk catalyst and advanced its catalytic activity for CO removal. However, even though CeO_2 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 CeO_2 promotion weakening the C-O bond on the catalyst.

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