Effects of Metal Oxide Support and Non-noble Metal Active Species on Catalytic Steam Reforming of Ethanol for Hydrogen Production

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Dependence of hydrogen production via the catalytic steam reforming of ethanol on the metal oxide support and first row transition metal catalyst was investigated. Ni supported on CeO₂ was more easily reduced and began to produce hydrogen at a lower temperature than Ni supported on ZrO₂, SiO₂, Al₂O₃, and MgO. Ni/CoO also maintained a high activity at a constant reaction temperature of 673 K and inhibited carbon deposition. Therefore, CeO₂ was adopted as the catalytic support. Compared with Ni/CoO, Fe/CoO and Mn/CoO were less active. Contrarily, Co/CoO was slightly less active at 673 K, but exhibited a comparable hydrogen yield at 873 K. The Cu/CoO system was reduced more readily and produced hydrogen at a lower temperature, but its activity gradually deteriorated by carbon deposition. Thus we concluded that Ni/CoO exhibited the best combination of properties with the highest hydrogen yield at 673 K and a long stability.

Keywords
Ethanol steam reforming, Metal oxide support, Transition metal catalyst, Carbon deposition

1. Introduction

Hydrogen demand is expected to increase precipitously for fuel cells in the near future. Currently, hydrogen is mainly produced by steam reforming of fossil fuels such as natural gas and petroleum. However, there are environmental concerns associated with this technology: emission of CO₂ as a greenhouse gas, resource depletion, destruction of nature due to drilling, etc. Recently, biomass ethanol has attracted significant attention as an alternative resource for hydrogen production. It is a renewable and environmentally-friendly fuel because it can be produced by fermenting sugars, starches, and cellulosics in plants and the CO₂ released during its combustion is reused for the growth of the plants.

Steam reforming of ethanol (SRE):

\[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 \]

is the most promising method for converting biomass ethanol to hydrogen. It differs principally from the steam reforming of methanol (SRM), which is used in methanol-converting fuel cells, because it involves the cleavage of a C-C bond. Cu is an excellent catalyst for SRM, but is relatively inactive for SRE because of its poor ability to mediate C-C bond breaking. In addition, the reaction pathway for SRE is more complicated, and many side reactions may occur. According to literature, Co, Ni, Pd, Rh, and Pt have catalytic activity for SRE. In particular, Co and Ni have been extensively investigated because of their high activities and low cost. It is well known that the catalytic activity and stability of Co and Ni are highly dependent on the support. Sun et al. reported that Ni/Al₂O₃ exhibited lower activity for SRE than Ni/Y₂O₃ and Ni/La₂O₃. Alberton et al. also found that a γ-Al₂O₃-supported Ni catalyst was more active for H₂ production than the catalyst supported on α-Al₂O₃. However, activation with a CH₄/O₂ mixture significantly increased the stability of Ni/α-Al₂O₃ compared with that observed during standard activation using hydrogen reduction. The increased stability was attributed to the migration of Ni particles on carbon filaments during CH₄/O₂ activation. The effect of modification of the metal in Ni/Al₂O₃ on the SRE was examined by Sanchez-Sanchez et al., who demonstrated that a Ni catalyst supported on Mg-modified Al₂O₃ exhibited higher reforming activity due to the lower acidity and enhanced Ni dispersion in the modified system. They also found that Ce and Zr promoted water adsorption/dissociation on Ni–Ce and Ni–Zr interfaces for improved catalytic activity, and La and Ce additives prevented the formation of fibrous carbon deposits on Ni surfaces.
The goal of the present study was to determine the best combination of catalytically-active component and support for low-temperature SRE. First, the crystalline structures, reduction properties, catalytic activities, and carbon deposits of Ni catalysts supported on CeO$_2$, SiO$_2$, ZrO$_2$, Al$_2$O$_3$, and MgO were investigated to elucidate the effects of the support on SRE. The results of this analysis indicated that CeO$_2$ as a support provided catalysts with high activity at lower temperatures and inhibited carbon deposition. The activities of different CeO$_2$-supported first row transition metals (Ni, Co, Cu, Fe, and Mn) as catalysts for SRE were evaluated.

2. Experimental

2.1. Catalyst Preparation

Nine supported catalysts (Ni/CeO$_2$, Ni/ZrO$_2$, Ni/SiO$_2$, Ni/Al$_2$O$_3$, Ni/MgO, Co/CeO$_2$, Cu/CeO$_2$, Fe/CeO$_2$, and Mn/CeO$_2$) were prepared in this study. The precursors of the transition metals were commercial Ni(NO$_3$)$_2$$·$6H$_2$O, Co(NO$_3$)$_2$$·$6H$_2$O, Cu(NO$_3$)$_2$$·$3H$_2$O, Fe(NO$_3$)$_3$$·$9H$_2$O, and Mn(NO$_3$)$_2$$·$6H$_2$O (Kishida Chemical). Commercial ZrO$_2$ (Wako Pure Chemical Industries), SiO$_2$ (Nippon Aerosil), γ-Al$_2$O$_3$ (Nippon Light Metal), and MgO (Kishida Chemical) were also used as catalytic supports. CeO$_2$ was prepared via a precipitation method with urea$^{22)}$, Ce(NO$_3$)$_3$$·$6H$_2$O (11.9 g) and urea (50 g) were dissolved in water (500 mL) and stirred at 363 K for 24 h. After filtration, washing with water, and drying at 383 K for 12 h, the obtained precipitate was calcined at 773 K for 5 h. The BET surface area of the supports is summarized in Table 1.

Each catalyst was prepared by impregnating the support powder with an aqueous solution of the metal nitrate, followed by evaporation to dryness. Each obtained powder was dried at 383 K for 12 h and then calcined at 773 K for 3 h, and the metal loading was adjusted to 10 wt%.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku Rint2000 diffractometer with Ni-filtered Cu K$_{α}$ radiation generated at an accelerating voltage of 30 kV and a tube current of 30 mA. Specific surface areas were estimated by applying the BET theory to the nitrogen adsorption isotherms determined at liquid nitrogen temperature. The temperature programmed reduction (TPR) was determined by heating the sample at a rate of 10 K min$^{-1}$ in a flow of 10 % H$_2$/Ar. The amount of H$_2$ consumed was detected by a thermal conductivity detector. The quantity and combustion properties of the carbon deposited on the catalyst during the reaction were evaluated via thermogravimetry (TG) using a Rigaku TG8120 Thermo Plus Evo. The catalyst was heated at a rate of 10 K min$^{-1}$ in air. The carbon amount was calculated by assuming that the weight loss in the TG profile was caused only by combustion of the carbon deposits. In addition, the weight increase due to reoxidation of the catalysts was ignored because it was not detected by TG. The carbon deposits were also observed via field emission scanning electron microscopy (FE-SEM, Hitachi High-Technologies S-4800).

2.3. Activity Test

Catalytic activity was evaluated in two types of reactions: temperature-programmed SRE (TP-SRE) with a stepwise temperature increase of 50 K per 30 min from 473 to 873 K and isothermal SRE at 673 K and 873 K. For each reaction, the unreduced catalyst (0.2 g) was loaded into a tubular quartz reactor (i.d. 8 mm). No reduction pretreatment was carried out because although it shortened the time needed for the catalyst activation, it had little influence on SRE in the steady state. A mixed solution of H$_2$O/C$_2$H$_5$OH with a molar ratio of 3 : 1 was fed at 30 µL min$^{-1}$, vaporized at the top of the reactor, and then sent to the catalyst bed with nitrogen flow of 30 mL min$^{-1}$. The gaseous products were passed through an ice-chilled trap in order to remove any liquids and then analyzed using two gas chromatographs with thermal conductivity detectors, one equipped with a column packed with 13X molecular sieve and nitrogen as the carrier gas for H$_2$ detection and the other with a column packed with active carbon and helium as the carrier gas for C1 gases (CO, CO$_2$, and CH$_4$). The product yields Y(H$_2$) and Y(C1) were calculated according to the ideal SRE equation (Eq. (1)) as follows:

$$Y(H_2)(\%) = \frac{F(H_2)}{6 \times F(C_2H_5OH)} \times 100$$  \hspace{1cm} (2)
where \( F(C_2H_5OH) \) represents the feed rate of \( C_2H_5OH \) in mol min\(^{-1}\) and \( F(H_2) \) and \( F(C_1) \) represent the quantities of \( H_2 \) and \( C_1 \) gases produced in mol min\(^{-1}\), respectively. The quantitative determination of ethanol and liquid products in the trap was difficult because of a poor sensitivity of the gas chromatogram, and therefore the catalytic performance was evaluated via \( Y(H_2) \) and \( Y(C_1) \) in the present investigation.

3. Results and Discussion

3.1. Effect of the Support on SRE over Ni Catalysts

3.1.1. Characterization of the Supported Ni Catalysts before SRE

XRD patterns of the as-prepared Ni catalysts are shown in Fig. 1. The unmarked peaks in the figure are due to the catalytic supports. No XRD peak due to the Ni species was observed for Ni/MgO (Fig. 1(e)). The other catalysts exhibited reflections for the (111), (200), and (220) lattice planes of NiO crystals at 37.3°, 43.3°, and 62.9°, respectively. The peaks observed for Ni/SiO\(_2\) (Fig. 1(c)) were relatively intense. In contrast, the XRD pattern for Ni/Al\(_2\)O\(_3\) (Fig. 1(d)) consisted of exceedingly weak peaks, indicating very high dispersion of NiO.

The surface areas of the catalysts are summarized in Table 1. The CeO\(_2\)-, SiO\(_2\)-, and Al\(_2\)O\(_3\)-supported catalysts had smaller surface areas than the unloaded supports, and those of ZrO\(_2\) and MgO increased after metal loading. In particular, Ni/MgO had 6 times the surface area of the raw MgO. This extraordinary increase suggests partial dissolution of the MgO surface during Ni loading.

Fig. 2 shows the TPR profiles of the Ni catalysts and NiO powder as a reference. The NiO crystallites supported on ZrO\(_2\) were reduced at approximately 673 K, which was nearly the same as that for the unsupported NiO. Ni/SiO\(_2\) also provided a peak maximum at the same temperature, but \( H_2 \) consumption continued beyond 900 K. The higher-temperature peak is likely due to the reduction of Ni\(^{2+} \) ions from surface nickel philosilicates\(^{23} \).

Ni/CeO\(_2\) was reduced at approximately 100 K lower than NiO, indicating that CeO\(_2\) promoted the reduction of NiO to the metal. In contrast, Ni/Al\(_2\)O\(_3\) and Ni/ MgO exhibited reduction peaks at higher temperatures. The broad peak with a maximum at 845 K and a shoulder peak at approximately 1030 K observed for Ni/ Al\(_2\)O\(_3\) is attributed to the reductions of NiO species weakly interacting with the Al\(_2\)O\(_3\) support and of a diluted NiAl\(_2\)O\(_4\)-like phase, respectively\(^{20} \). In the spectrum of Ni/MgO, the percentage of the higher-temperature peak was much larger than that for the other materials. Considering the absence of XRD peaks due
to Ni species and the marked increase in surface area following Ni loading, this behavior is attributed to the reduction of Ni$^{2+}$ ions located more deeply in the MgO bulk (NiO-MgO solid solution)$^{24,26}$.

3.1.2 SRE over the Supported Ni Catalysts

The yields of H$_2$, CO$_2$, CO, and CH$_4$ during TP-SRE over the Ni catalysts on various supports are shown in Fig. 3. Ni/CeO$_2$ began to produce H$_2$ and CO$_2$ at 623 K, and the other catalysts required higher temperatures for initiation of the reaction. In the temperature range below 750 K, the H$_2$ yield decreased in the order Ni/CeO$_2$ > Ni/ZrO$_2$ > Ni/Al$_2$O$_3$ > Ni/MgO, which was in agreement with the order of the reduction temperature (Fig. 2). These results indicated that the catalytically active phase consists of metallic Ni crystallites.

In the case of Ni/CeO$_2$, the H$_2$ yields initially increased with increasing temperature then decreased at 773 K, at which point the CH$_4$ yield reached a maximum, and then increased again with a decrease in the CH$_4$ yield. These results suggest that it is important to suppress CH$_4$ production to achieve higher H$_2$ yields. A relatively large quantity of CH$_4$ was also generated over the ZrO$_2$- and SiO$_2$-supported catalysts, which exhibited H$_2$ yields nearly equivalent to those for Ni/CeO$_2$ above 750 K. On the other hand, Ni/Al$_2$O$_3$ and Ni/MgO exhibited relatively low activities over the entire temperature range.

Figure 4 shows the product yields at 9 h after the initiation of SRE at 673 K and 873 K. Although the H$_2$ yields at 673 K in TP-SRE (Fig. 3(a)) over the ZrO$_2$- and SiO$_2$-supported catalysts were less than 10%, those for SRE at a constant temperature of 673 K were constant at approximately 40%, which was comparable to that for the CeO$_2$-supported catalyst. These three catalysts produced C1 gases with a total yield of more than 70%, approximately half of which was CH$_4$. Raising the reaction temperature to 873 K resulted in a decrease in CH$_4$ production and an increase in H$_2$ generation.

On the other hand, barely reducible Ni/Al$_2$O$_3$ and Ni/MgO exhibited much lower H$_2$ and C1-gas yields at 673 K. However, their activities significantly increased and the clear differences between the supports disappeared at 873 K, which was different from the results in Fig. 3. The fact that higher yields were obtained for the isothermal SRE reaction than TP-SRE indicates that the reduction of the Ni species during the latter was incomplete, and a larger amount of catalytically-active metal sites were generated in the former at the same temperature over a longer reaction time.

3.1.3 Characterization of the Supported Ni Catalysts after SRE

XRD patterns of the catalysts after SRE at 673 K and 873 K are also shown in Fig. 1 ((a) 2-(e) 2 and (a) 3-(e) 3, respectively). The peaks due to NiO crystallites on the CeO$_2$ and SiO$_2$ supports decreased in intensity, and very small peaks for Ni(111) reflections

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Fig. 5 TG Profiles of the Supported Ni Catalysts after SRE at (a) 673 K and (b) 873 K for 9 h

appeared at approximately 44.5° after SRE at 673 K (Figs. 1(a) 2 and (c) 2), respectively, indicating the partial reduction of NiO to metallic Ni. Despite the absence of XRD peaks due to Ni metal, the NiO peaks in the XRD patterns for Ni/ZrO$_2$ after reaction at 673 K (Fig. 1(b) 2) were also less intense than those in the pattern for the catalyst before reaction (Fig. 1(b) 1). Ni/ZrO$_2$ exhibited catalytic activity comparable with that of Ni/CeO$_2$ and Ni/SiO$_2$ (Fig. 4(a)), and it is therefore considered that the NiO on ZrO$_2$ was partially reduced to form small metal particles as catalytically active species at 673 K. At 873 K, the NiO crystallites on these three catalysts were completely reduced to Ni metal, as can be seen in Figs. 1(a) 3-(c) 3.

The XRD pattern of Ni/Al$_2$O$_3$ remained nearly unchanged after SRE at 673 K (Fig. 1(d) 2), but the reduction of NiO to Ni metal was observed at 873 K (Fig. 1(d) 3). In contrast, no indication of Ni reduction was detected for Ni/MgO, even at 873 K (Fig. 1(e) 3). Nevertheless, it is assumed that part of the Ni was reduced, because Ni/MgO exhibited high catalytic activity at 873 K (Fig. 4(b)) and H$_2$ consumption was observed below 873 K during TPR (Fig. 2).

In addition to the peaks due to Ni metal and the support, a new XRD peak appeared at 26.0° in the XRD patterns shown in Figs. 1(b) 3, (c) 3, and (d) 3. This peak indicates the formation of graphite-like carbon on the ZrO$_2$-, SiO$_2$-, and Al$_2$O$_3$-supported catalysts during SRE at 873 K. In particular, the XRD pattern for Ni/ SiO$_2$ contained an extremely intense peak (Fig. 1(c) 3), which was also detected at 673 K (Fig. 1(c) 2).

The quantity of carbon deposited after a reaction time of 9 h was determined via TG analysis in air. The profiles are shown in Fig. 5, and the quantities of carbon estimated from the weight losses during combustion are summarized in Table 1. It was found from Fig. 5 that the carbon deposited on the catalysts during SRE at 673 K began to burn in the temperature range 660-740 K, and the carbon formed at 873 K required higher ignition temperatures (750-810 K). Furthermore, the quantity of deposited carbon increased with increasing reaction temperature for all of the catalysts. These results suggest the formation of burn-resistant graphite at a higher temperature.

Notably, while Ni/CeO$_2$ had comparable catalytic activities at 673 K and 873 K to those of Ni/ZrO$_2$ and Ni/SiO$_2$, much less carbon was deposited on the Ni/CeO$_2$ catalyst, indicating an inhibiting effect of CeO$_2$ on carbon deposition. In contrast, Ni/SiO$_2$ produced the greatest amount of carbon at 673 K and 873 K; this result is consistent with the XRD analysis presented in Fig. 1. In addition, although Ni/Al$_2$O$_3$ and Ni/MgO were catalytically inactive at 673 K, only a relatively minor amount of carbon was deposited on these catalysts. After raising the reaction temperature to 873 K, a 3-fold increase in carbon deposits was observed for Ni/Al$_2$O$_3$, and Ni/MgO appeared to greatly inhibit carbon formation despite its high activity, which was, as mentioned above, comparable to that of the other catalysts.

As described in the 1. Introduction, the goal of the present study was to develop a catalyst with high activity for SRE at lower temperatures, and therefore CeO$_2$ was selected as the most effective catalytic support because of its stimulatory effect on Ni reduction, which resulted in a relatively high activity at a lower temperature, and its inhibitory effect on carbon deposition. In the next stage, the catalytic performance of CeO$_2$-supported Co, Cu, Fe, and Mn catalysts for SRE was compared to that of Ni/CeO$_2$.

3.2 Effect of the Transition Metal on SRE over CeO$_2$-supported Catalysts

3.2.1 Characterization of the CeO$_2$-supported Transition Metal Catalysts before SRE

Figures 6(b) 1-(e) 1 present the XRD patterns of the as-prepared Co, Cu, Fe, and Mn catalysts supported on CeO$_2$. For comparison, that of Ni/CeO$_2$ is also redisplayed in Fig. 6(a) 1. The unmarked peaks in the figure are assigned to CeO$_2$ crystallites. XRD peaks due to Co$_3$O$_4$ and CuO were observed in the XRD patterns in Figs. 6(b) 1 and (c) 1, respectively. In the spectrum of Fe/CeO$_2$ (Fig. 6(d) 1), the very small peak at approximately 35.7° was assigned to the reflection for the (110) lattice planes of α-Fe$_2$O$_3$ crystallites. No apparent XRD peak due to Mn species was observed in the XRD pattern for Mn/CeO$_2$ shown in Fig. 6(e) 1.

Figure 6(f) shows an enlarged view near the most intense XRD peak due to the (111) lattice planes in CeO$_2$. As evident from the figure, the peak for Fe/CeO$_2$ was shifted to a higher angle (~0.2°); the peaks in the XRD patterns of the other catalysts were completely in accord with the CeO$_2$(111) reflection. Notably, the other XRD peaks due to CeO$_2$ in the pat-
tern for Fe/CeO2 were also shifted to higher angles, suggesting penetration of Fe ions into the CeO2 crystallites.

The surface areas of the different transition metal catalysts are summarized in Table 2. Loading CeO2 with Ni, Cu, Fe, and Mn resulted in a decrease in the surface area, and no change was observed for Co/CeO2. Fe/CeO2 had the smallest surface area. The TPR curves can be seen in Fig. 7. For Co/CeO2, two peaks at 540 K and 594 K assigned to reduction of Co3+ to Co2+ and Co2+ to Co0, respectively, were observed in the TPR curve14). Similar peaks were also observed at 530 K and 608 K for Mn/CeO2. Cu/CeO2 was reduced at the lowest temperature (474 K). In addition to obvious peaks below 800 K, the Ni, Co, and Cu catalysts exhibited small and broad peaks at temperatures above 1000 K, which are likely due to partial reduction in the CeO2 support. A high-temperature peak above 1000 K was also observed for Mn/CeO2, but the hydrogen consumption of this catalyst was relatively large over a wide temperature range.

On the other hand, the TPR profile of Fe/CeO2 was significantly different from that of the other catalysts: four reduction peaks were observed at 654, 767, 972, and 1120 K. A similar TPR spectrum for an Fe–Ce mixed oxide with an Fe content of 30 mol% was reported by Li et al.27). According to these researchers, the lowest-temperature peak is due to the surface reduction of independent Fe2O3 dispersed on the CeO2 surface, and the second and third peaks result from the reduction of Ce4+ and Fe3+ in the surface layer of the solid solution, which is in close contact with surface iron species and to bulk reduction of Fe2O3 to FeO in the ceria lattice, respectively. The highest-temperature peak is related to the further reduction of bulk iron oxides and the consumption of isolated CeO2 particles without interaction with iron ions. The formation of an Fe–Ce–O solid solution in Fe/CeO2 is also supported by its smaller surface area and the shift of the XRD peaks due to CeO228),29).

3.2.2. SRE over the CeO2-supported Transition Metal Catalysts

Figure 8 shows the results of TP–SRE over the CeO2-supported transition metal catalysts. The most easily reduced Cu catalyst began to produce H2 at the lowest temperature (523 K), and the other catalysts required higher reaction temperatures for H2 generation. Although Ni/CeO2 and Co/CeO2 exhibited low activities below 650 K, the yields of H2 and CO2 increased rapidly and exceeded those of Cu/CeO2 at 673 K. Notably, the Ni catalyst led to the production of a larger quantity of CH4 than the other metals above 700 K. In addition, the catalytic activity of Fe/CeO2 and Mn/CeO2 increased above 650 K and was approximately the same as that of Cu/CeO2 at 873 K.
The yields of H2, CO2, CO, and CH4 during isothermal SRE at a reaction time of 9 h are shown in Fig. 9. The catalytic activity of the Fe and Mn catalysts was relatively low. At 673 K, Ni/CeO2 exhibited the highest H2 and C1-gas yields, followed by Co/CeO2 and Cu/CeO2. The Ni catalyst was also characterized by the production of a large amount of CH4, as expected from Fig. 8. By raising the reaction temperature to 873 K, the catalytic activity of Ni/CeO2 and Co/CeO2 was significantly enhanced, and the Cu/CeO2 catalyst became less active. In addition, the H2 and CO2 yields over Cu/CeO2 at 673 K were nearly the same as those during TP-SRE, but at 873 K were much smaller than those at the same temperature during TP-SRE (Fig. 8). This result is likely due to deactivation by carbon deposition during the long-term reaction at 873 K.

To verify this speculation, changes in the yields during SRE over Ni/CeO2 and Cu/CeO2 at 873 K as a function of reaction time and the effects of catalyst regeneration using air were investigated. The results are illustrated in Fig. 10. For the Ni/CeO2 catalyst, the H2 and C1-gas yields remained constant at approximately 70 % and 90 %, respectively, for 5 h, which were in approximate agreement with the values at 9 h in Fig. 9 with an uncertainty of 10 %. The catalytic performance also remained constant after the catalyst was exposed to an air flow at 873 K for 1 h. On the other hand, the H2 and C1-gas yields over the Cu/CeO2 catalyst were 52 % and 68 %, respectively, during the first 30 min, but decreased to 26 % and 20 %, respectively, after 5 h. While the catalytic activity was recovered following air
treatment at 873 K, the catalyst was deactivated during the second SRE run in the same manner as observed in the first run. Similar deactivation was also observed for Fe/CeO$_2$ and Mn/CeO$_2$. These results lead to the conclusion that the carbon deposited on Cu, Fe, and Mn greatly inhibited SRE, and carbon deposition on Ni/CeO$_2$ did not influence the reaction.

3.2.3. Characterization of the CeO$_2$-supported Transition Metal Catalysts after SRE

The XRD patterns of the CeO$_2$-supported catalysts after SRE at 673 K and 873 K are shown in Figs. 6(a-2)-(e-2) and (a-3)-(e-3), respectively. The unmarked peaks due to CeO$_2$ increased in intensity compared with those observed in the XRD patterns in Figs. 6(a-1)-(e-1), indicating the growth of CeO$_2$ crystallites during SRE. In Fig. 6(b), it can be seen that the CoO in the as-prepared Co catalyst was reduced to CoO and Co metal during SRE at 673 K and completely reduced to the metal at 873 K. It is also evident from Fig. 6(c) that the CuO on CeO$_2$ was fully reduced to metallic Cu, even at 673 K. Two small peaks due to MnO appeared at 34.9° and 40.6° in the XRD pattern of Mn/CeO$_2$ after SRE at 673 K (Fig. 6(e-2)) and increased in intensity after SRE at 873 K, but no XRD peak for metallic Mn was observed (Fig. 6(e-3)). It was therefore concluded that the two TPR peaks for Mn/CeO$_2$ at 530 K and 608 K in Fig. 7 were not due to the reduction of manganese ions to the metal, which likely requires higher temperatures than 1000 K, as suggested by the higher-temperature TPR peak in Fig. 7.

In the case of Fe/CeO$_2$, the small peak at 35.7° in the XRD pattern in Fig. 6(d-1) disappeared, and two peaks appeared at 35.5° and 43.1° after SRE at 673 K (Fig. 6(d-2)), whose intensities increased when the reaction temperature was raised to 873 K (Fig. 6(d-3)). These peaks were assigned to the diffractions of the (311) and (400) planes of Fe$_3$O$_4$ lattices. In addition, the shift of the XRD peaks due to CeO$_2$ (Fig. 6(d-1)) was no longer detected after the reaction. These results indicated that the Fe–Ce–O solid solution in the as-prepared Fe/CeO$_2$ catalyst was decomposed to Fe$_3$O$_4$ and CeO$_2$ in the reductive atmosphere.

TG profiles of the catalysts employed for SRE at 673 K and 873 K for 9 h are shown in Fig. 11, and the quantities of carbon deposits estimated from the weight losses are summarized in Table 2. Ni/CeO$_2$ and Co/CeO$_2$ after SRE at 673 K contained a relatively large amount of deposited carbon that required higher temperatures for burning than the other catalysts. In addition, after reaction at 873 K, the burning temperatures of the carbon deposited on the catalytically-active Ni and Co catalysts clearly increased, and those of the other catalysts remained nearly unchanged. Furthermore, the carbon content of Ni/CeO$_2$ increased by approximately 30 %, whereas Co/CeO$_2$ showed a decrease in the carbon content which may be attributable to the significant increases in C1 gases. Finally, the inactive Cu, Fe, and Mn catalysts maintained a low level of carbon deposition.

Table 2: BET Surface Areas of the CeO$_2$-supported Catalysts and the Amount of Deposited Carbon after SRE at 673 K and 873 K for 9 h

| Catalyst  | Surface area [m$^2$ g$^{-1}$] | Carbon deposit [g g$^{-1}$ cat$^{-1}$] |
|-----------|------------------------------|----------------------------------------|
|           | SRE at 673 K                 | SRE at 873 K                           |
| Ni/CeO$_2$| 100                          | 0.21                                   |
| Co/CeO$_2$| 110                          | 0.22                                   |
| Cu/CeO$_2$| 75                           | 0.03                                   |
| Fe/CeO$_2$| 70                           | 0.06                                   |
| Mn/CeO$_2$| 80                           | 0.03                                   |

Figure 12 shows the SEM images of the CeO$_2$-supported Ni, Co, and Cu catalysts after SRE at 873 K for 9 h. Ni/CeO$_2$ and Co/CeO$_2$ produced carbon fibers with a diameter of 20-70 nm and 10-30 nm, respectively. On the other hand, no obviously-carbonaceous matter was observed on the surface of Cu/CeO$_2$. Therefore, it can be concluded from Figs. 10, 11, and 12 that a minor amount of carbon deposits covered the metallic Cu sites, resulting in a remarkable decrease in the activity of Cu/CeO$_2$. In contrast, the long-term stability of Ni/CeO$_2$ suggests that the fibers of the deposited carbons had a porous structure through which the react...
SiO₂-supported Ni catalysts had a similar level of activity as the CeO₂-supported Ni catalyst at 673 K, but larger temperature. In contrast, Al₂O₃ and MgO partly sites³⁰).

Cu on CeO₂ was reduced at the lowest temperature and exhibited the highest activity below 650 K, but was remarkably deactivated by a minor amount of carbon deposition at a reaction temperature of 873 K. Although Co/CeO₂ exhibited activities as high as that of Ni/CeO₂ at 873 K, the latter afforded higher yields of H₂ and C₁ gases at 673 K. In conclusion, Ni/CeO₂ exhibited both high catalytic activity and low-temperature stability for low-temperature SRE, despite the deposition of a large quantity of fibrous carbon.

Fig. 12 SEM Images of the CeO₂-supported Ni, Co, and Cu Catalysts after SRE at 873 K for 9 h

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要  旨

エタノール水蒸気改質による水素製造における金属酸化物担体と非貴金属活性種の効果

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エタノール水蒸気改質による水素製造における金属酸化物担体と第一遷移金属触媒の影響を検討した。CeO_2担体上の Ni は ZrO_2，SiO_2，Al_2O_3，MgO 担体上の Ni よりも容易に還元され，より低温で水素を生成した。また，Ni/CoCeO_2触媒は反応温度 673 K において高い活性を維持するとともに炭素の析出を抑制した。以後，担体として CeO_2 を用いることとした。Ni/CoCeO_2 と比べると Fe/CoCeO_2 や Mn/CoCeO_2 是不活性であった。Ce/CeO_2 は 673 K ではわずかに活性が低かったが，873 K では同等の水素収率を示した。Cu/CoCeO_2 は還元されやすく，より低温で水素を生成し始めたが，炭素析出により活性は次第に低下した。したがって，Ni/CoCeO_2 は 673 K での最高水素収率と長時間安定性を有する最良の組み合わせであると結論した。