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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/CeO₂ 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/CeO₂, Fe/CeO₂ and Mn/CeO₂ were less active. Contrarily, Co/CeO₂ was slightly less active at 673 K, but exhibited a comparable hydrogen yield at 873 K. The Cu/CeO₂ 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/CeO₂ 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^{1)~3)}. It is a renewable and environmentally-friendly fuel because it can be produced by fermenting sugars, starches, and celluloses in plants and the CO₂ released during its combustion is reused for the growth of the plants.

Steam reforming of ethanol (SRE):

is the most promising method for converting biomass ethanol to hydrogen^{2)~7)}. 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^{8)~10)}, 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 occur²⁾.

According to literature^{2),3),5),11)~18)}, 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^{3),13),15),19)~21)}. Sun *et al.*¹³⁾ reported that Ni/Al₂O₃ exhibited lower activity for SRE than Ni/Y₂O₃ and Ni/La₂O₃. Alberton *et al.*¹⁹⁾ 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.*²⁰⁾, 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.

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Table 1 BET Surface Areas of the Supports and Supported Ni Catalysts and the Amount of Deposited Carbon after SRE at 673 K and 873 K for 9 h

Support	Surface area [m ² g ⁻¹]		Carbon deposit [g g-cat ⁻¹]	
	Unloaded	Ni-loaded	SRE at 673 K	SRE at 873 K
CeO ₂	110	100	0.21	0.28
ZrO ₂	30	40	0.65	1.21
SiO ₂	300	200	0.93	2.37
Al ₂ O ₃	240	150	0.07	0.24
MgO	10	60	0.07	0.10

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 CeO₂, SiO₂, ZrO₂, Al₂O₃, and MgO were investigated to elucidate the effects of the support on SRE. The results of this analysis indicated that CeO₂ as a support provided catalysts with high activity at lower temperatures and inhibited carbon deposition. The activities of different CeO₂-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/CeO₂, Ni/ZrO₂, Ni/SiO₂, Ni/Al₂O₃, Ni/MgO, Co/CeO₂, Cu/CeO₂, Fe/CeO₂, and Mn/CeO₂) were prepared in this study. The precursors of the transition metals were commercial Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, Fe(NO₃)₃·9H₂O, and Mn(NO₃)₂·6H₂O (Kishida Chemical). Commercial ZrO₂ (Wako Pure Chemical Industries), SiO₂ (Nippon Aerosil), γ -Al₂O₃ (Nippon Light Metal), and MgO (Kishida Chemical) were also used as catalytic supports. CeO₂ was prepared *via* a precipitation method with urea²². Ce(NO₃)₃·6H₂O (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 areas of the supports are 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 % H₂/Ar. The amount of H₂ 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 H₂O/C₂H₅OH with a molar ratio of 3 : 1 was fed at 30 μ L 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 chromatograms with thermal conductivity detectors, one equipped with a column packed with 13X molecular sieve and nitrogen as the carrier gas for H₂ detection and the other with a column packed with active carbon and helium as the carrier gas for C1 gases (CO, CO₂, and CH₄). The product yields $Y(\text{H}_2)$ and $Y(\text{C1})$ were calculated according to the ideal SRE equation (Eq. (1)) as follows:

$$Y(\text{H}_2)(\%) = \frac{F(\text{H}_2)}{6 \times F(\text{C}_2\text{H}_5\text{OH})} \times 100 \quad (2)$$

(a) CeO₂-, (b) ZrO₂-, (c) SiO₂-, (d) Al₂O₃-, and (e) MgO-supported Ni catalysts (1) before and (2) after SRE at 673 K and (3) 873 K for 9 h. The marks in the parentheses represent overlaps with XRD peaks due to the supports.

Fig. 1 XRD Patterns of the Supported Ni Catalysts before and after SRE

$$Y(\text{Cl})(\%) = \frac{F(\text{Cl})}{2 \times F(\text{C}_2\text{H}_5\text{OH})} \times 100 \quad (3)$$

where $F(\text{C}_2\text{H}_5\text{OH})$ represents the feed rate of $\text{C}_2\text{H}_5\text{OH}$ in mol min^{-1} and $F(\text{H}_2)$ and $F(\text{Cl})$ represent the quantities of H_2 and Cl 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* $Y(\text{H}_2)$ and $Y(\text{Cl})$ 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)** 1). 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/SiO₂ (**Fig. 1(c)** 1) were relatively intense. In con-

Fig. 2 TPR Profiles of the Supported Ni Catalysts and NiO Powder

trast, the XRD pattern for Ni/Al₂O₃ (**Fig. 1(d)** 1) consisted of exceedingly weak peaks, indicating very high dispersion of NiO.

The surface areas of the catalysts are summarized in **Table 1**. The CeO₂-, SiO₂-, and Al₂O₃-supported catalysts had smaller surface areas than the unloaded supports, and those of ZrO₂ 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.

Figure 2 shows the TPR profiles of the Ni catalysts and NiO powder as a reference. The NiO crystallites supported on ZrO₂ were reduced at approximately 673 K, which was nearly the same as that for the unsupported NiO. Ni/SiO₂ also provided a peak maximum at the same temperature, but H₂ consumption continued beyond 900 K. The higher-temperature peak is likely due to the reduction of Ni²⁺ ions from surface nickel phyllosilicates²³⁾.

Ni/CeO₂ was reduced at approximately 100 K lower than NiO, indicating that CeO₂ promoted the reduction of NiO to the metal. In contrast, Ni/Al₂O₃ 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/Al₂O₃ is attributed to the reductions of NiO species weakly interacting with the Al₂O₃ support and of a diluted NiAl₂O₄-like phase, respectively²⁰⁾. 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

Fig. 3 Product Yields for Temperature-programmed SRE over the Supported Ni Catalysts

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/CeO₂ 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 $\text{Ni/CeO}_2 > \text{Ni/SiO}_2 \approx \text{Ni/ZrO}_2 > \text{Ni/Al}_2\text{O}_3 > \text{Ni/MgO}$, 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/CeO₂, 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 ZrO₂- and SiO₂-supported catalysts, which exhibited H_2 yields nearly equivalent to those for Ni/CeO₂ above 750 K. On the other hand, Ni/Al₂O₃ and Ni/MgO exhibited relatively low activities over the entire temperature range.

Figure 4 shows the product yields at 9 h after the

Fig. 4 Product Yields at 9 h after the Initiation of SRE at (a) 673 K and (b) 873 K over the Supported Ni Catalysts

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 ZrO₂- and SiO₂-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 CeO₂-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/Al₂O₃ 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 CeO₂ and SiO₂ supports decreased in intensity, and very small peaks for Ni(111) reflections

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/ZrO₂ 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/ZrO₂ exhibited catalytic activity comparable with that of Ni/CeO₂ and Ni/SiO₂ (Fig. 4(a)), and it is therefore considered that the NiO on ZrO₂ was also 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/Al₂O₃ 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 H₂ 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 ZrO₂-, SiO₂-, and Al₂O₃-supported catalysts during SRE at 873 K. In particular, the XRD pattern for Ni/SiO₂ 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/CeO₂ had comparable catalytic activities at 673 K and 873 K to those of Ni/ZrO₂ and Ni/SiO₂, much less carbon was deposited on the Ni/CeO₂ catalyst, indicating an inhibiting effect of CeO₂ on carbon deposition. In contrast, Ni/SiO₂ 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/Al₂O₃ 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/Al₂O₃, 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 CeO₂ 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 CeO₂-supported Co, Cu, Fe, and Mn catalysts for SRE was compared to that of Ni/CeO₂.

3. 2. Effect of the Transition Metal on SRE over CeO₂-supported Catalysts

3. 2. 1. Characterization of the CeO₂-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 CeO₂. For comparison, that of Ni/CeO₂ is also redisplayed in Fig. 6(a) 1. The unmarked peaks in the figure are assigned to CeO₂ crystallites. XRD peaks due to Co₃O₄ and CuO were observed in the XRD patterns in Figs. 6(b) 1 and (c) 1, respectively. In the spectrum of Fe/CeO₂ (Fig. 6(d) 1), the very small peak at approximately 35.7° was assigned to the reflection for the (110) lattice planes of α -Fe₂O₃ crystallites. No apparent XRD peak due to Mn species was observed in the XRD pattern for Mn/CeO₂ 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 CeO₂. As evident from the figure, only the peak for Fe/CeO₂ was shifted to a higher angle ($\sim 0.2^\circ$); the peaks in the XRD patterns of the other catalysts were completely in accord with the CeO₂(111) reflection. Notably, the other XRD peaks due to CeO₂ in the pat-

(a) Ni/CeO₂, (b) Co/CeO₂, (c) Cu/CeO₂, (d) Fe/CeO₂, and (e) Mn/CeO₂ (1) before and (2) after SRE at 673 K and (3) 873 K for 9 h, (f) an enlarged view of the XRD patterns of the catalysts before SRE.

Fig. 6 XRD Patterns of the CeO₂-supported Transition Metal Catalysts before and after SRE

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

Fig. 7 TPR Profiles of the CeO₂-supported Transition Metal Catalysts

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 CeO₂^{28),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.

Fig. 8 Product Yields for Temperature-programmed SRE over the CeO₂-supported Transition Metal Catalysts

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

Fig. 9 Product Yields at 9 h after the Initiation of SRE at (a) 673 K and (b) 873 K over the CeO₂-supported Transition Metal Catalysts

Fig. 10 Change in the SRE Yield over Ni/CeO₂ and Cu/CeO₂ at 873 K and the Effects of Catalyst Regeneration Using Air

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/CeO₂ and Mn/CeO₂. These results lead to the conclusion that the carbon deposited on Cu, Fe, and Mn greatly inhibited SRE, and carbon deposition on Ni/CeO₂ did not influence the reaction.

3. 2. 3. Characterization of the CeO₂-supported Transition Metal Catalysts after SRE

The XRD patterns of the CeO₂-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 CeO₂ increased in intensity compared with those observed in the XRD patterns in **Figs. 6(a) 1-(e) 1**, indicating the growth of CeO₂ crystallites during SRE. In **Fig. 6(b)**, it can be seen that the Co₂O₃ 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 CeO₂ 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/CeO₂ 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/CeO₂ 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/CeO₂, 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 Fe₃O₄ lattices. In addition, the shift of the XRD peaks due to CeO₂ (**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/CeO₂ catalyst was decomposed to Fe₃O₄ and CeO₂ 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/CeO₂ and Co/CeO₂ 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/CeO₂ increased by approximately 30 %, whereas Co/CeO₂ 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.

Figure 12 shows the SEM images of the CeO₂-supported Ni, Co, and Cu catalysts after SRE at 873 K for 9 h. Ni/CeO₂ and Co/CeO₂ 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/CeO₂. 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/CeO₂^{30)~32)}. In contrast, the long-term stability of Ni/CeO₂ suggests that the fibers of the deposited carbons had a porous structure through which the reac-

Fig. 11 TG Profiles of the CeO₂-supported Transition Metal Catalysts after SRE at 673 K and 873 K for 9 h

Table 2 BET Surface Areas of the CeO₂-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-cat ⁻¹]	
		SRE at 673 K	SRE at 873 K
Ni/CeO ₂	100	0.21	0.28
Co/CeO ₂	110	0.22	0.14
Cu/CeO ₂	75	0.03	0.03
Fe/CeO ₂	70	0.06	0.02
Mn/CeO ₂	80	0.03	0.02

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

tants could pass, enabling contact with metallic Ni sites³⁰.

4. Conclusion

The effects of the metal oxide support and first row transition metal catalyst on SRE were investigated. Because the catalytic sites for SRE are reduced metallic crystallites, the reducibility of the transition metals strongly affected their low-temperature activity. The CeO₂ support promoted the reduction of NiO crystallites to the metal, resulting in a higher activity at a low temperature. In contrast, Al₂O₃ and MgO partly formed solid solutions with Ni and consequently hindered its reduction and catalytic activity. ZrO₂- and SiO₂-supported Ni catalysts had a similar level of activity as the CeO₂-supported Ni catalyst at 673 K, but larger amounts of carbon deposits were formed with these systems, and therefore CeO₂ was adopted as the support.

Fe/CeO₂ and Mn/CeO₂ required relatively high temperatures for reduction of the metal and were less

active. 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 long-term stability for low-temperature SRE, despite the deposition of a large quantity of fibrous carbon.

References

- 1) Dunn, S., *Int. J. Hydrogen Energ.*, **27**, (3), 235(2002).
- 2) Ni, M., Leung, D. Y. C., Leung, M. K. H., *Int. J. Hydrogen Energ.*, **32**, (15), 3238 (2007).
- 3) Fatsikostas, A. N., Kondarides, D. I., Verykios, X. E., *Catal. Today*, **75**, (1-4), 145 (2002).
- 4) Haryanto, A., Fernando, S., Murali, N., Adhikari, S., *Energy & Fuels*, **19**, (5), 2098 (2005).
- 5) Vaidya, P. D., Rodrigues, A. E., *Chem. Eng. J.*, **117**, (1), 39 (2006).
- 6) Ye, J. L., Wang, Y. Q., Liu, Y., Wang, H., *Int. J. Hydrogen Energ.*, **33**, (22), 6602 (2008).
- 7) Zhang, B., Tang, X., Li, Y., Xu, Y., Shen, W., *Int. J. Hydrogen Energ.*, **32**, (13), 2367 (2007).
- 8) Huang, Y. H., Wang, S. F., Tsai, A. P., Kameoka, S., *Ceram. Int.*, **40**, (3), 4541 (2014).
- 9) Jones, S. D., Hagelin-Weaver, H. E., *Appl. Catal. B: Environmental*, **90**, (1-2), 195 (2009).
- 10) Pérez-Hernández, R., Gutiérrez-Martínez, A., Gutiérrez-Wing, C. E., *Int. J. Hydrogen Energ.*, **32**, (14), 2888 (2007).
- 11) Urasaki, K., Fukuda, Y., Sekine, Y., Matsukata, M., Kikuchi, E., *J. Jpn. Petrol. Inst.*, **51**, (2), 83 (2008).
- 12) Nagai, M., Akiyama, M., Oki, Y., *J. Jpn. Petrol. Inst.*, **55**, (1), 67 (2012).
- 13) Sun, J., Qiu, X. P., Wu, F., Zhu, W. T., *Int. J. Hydrogen Energ.*, **30**, (4), 437 (2005).
- 14) Pang, X., Chen, Y., Dai, R., Cui, P., *Chin. J. Catal.*, **33**, (2), 281 (2012).
- 15) Haga, F., Nakajima, T., Miya, H., Mishima, S., *Catal. Lett.*, **48**, (3-4), 223 (1997).
- 16) Casanovas, A., Llorca, J., Homs, N., Fierro, J. L. G., Piscina, P. R., *J. Mol. Catal. A: Chem.*, **250**, (1-2), 44 (2006).
- 17) Erdöhelyi, A., Raskó, J., Kecskés, T., Tóth, M., Dömök, M., Baán, K., *Catal. Today*, **116**, (3), 367 (2006).
- 18) Ciambelli, P., Palma, V., *Appl. Catal. B: Environmental*, **96**, (1-2), 190 (2010).
- 19) Alberton, A. L., Souza, M. M. V. M., Schmal, M., *Catal. Today*, **123**, (1-4), 257 (2007).
- 20) Sanchez-Sanchez, M. C., Navarro, R. M., Fierro, J. L. G., *Int. J. Hydrogen Energ.*, **32**, (10-11), 1462 (2007).
- 21) Trane-Restrup, R., Dahl, S., Jensen, A. D., *Int. J. Hydrogen Energ.*, **38**, (35), 15105 (2013).
- 22) Cai, W., Wang, F., Zhan, E., Van Veen, A. C., Mirodatos, C., Shen, W., *J. Catal.*, **257**, (1), 96 (2008).
- 23) Hadjiivanov, K., Mihaylov, M., Klissurski, D., Stefanov, P., Abadjieva, N., Vassileva, E., Mintchev, L., *J. Catal.*, **185**, (2), 314 (1999).
- 24) Frusteri, F., Freni, S., Chiodo, V., Spadaro, L., Blasi, O. D., Bonura, G., Cavallaro, S., *Appl. Catal. A: General*, **270**, (1-2), 1 (2004).
- 25) Zanganeh, R., Rezaei, M., Zamaniyan, A., *Int. J. Hydrogen Energ.*, **38**, (7), 3012 (2013).

- 26) Yamazaki, O., Tomishige, K., Fujimoto, K., *Appl. Catal. A: General*, **136**, (1), 49 (1996).
- 27) Li, K., Haneda, M., Ning, P., Wang, H., Ozawa, M., *Appl. Surf. Sci.*, **289**, 378 (2014).
- 28) Li, G., Smith, R. L., Inomata, H., *J. Am. Chem. Soc.*, **123**, (44), 11091 (2001).
- 29) Pérez-Alonso, F. J., Granados, M. L., Ojeda, M., Terreros, P., Rojas, S., Herranz, T., Fierro, J. L. G., Gracia, M., Gancedo, J. R., *Chem. Mater.*, **17**, (9), 2329 (2005).
- 30) Vicente, J., Montero, C., Ereña, J., Azkoiti, M. J., Bilbao, J., Gayubo, A. G., *Int. J. Hydrogen Energ.*, **39**, (24), 12586 (2014).
- 31) Djinić, P., Črnivec, I. G. O., Erjavec, B., Pintar, A., *Appl. Catal. B: Environmental*, **125**, 259 (2012).
- 32) Wang, F., Li, Y., Cai, W., Zhan, E., Mu, X., Shen, W., *Catal. Today*, **146**, (1-2), 31 (2009).

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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。CeO₂担体上のNiはZrO₂, SiO₂, Al₂O₃, 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/CeO₂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CeO₂を用いることとした。Ni/CeO₂

と比べるとFe/CeO₂やMn/CeO₂は不活性であった。Co/CeO₂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/CeO₂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/CeO₂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。

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