Synergistic effects of CeO₂-supported bimetallic Ni–Cu, Co–Cu, and Ni–Fe catalysts on steam reforming of ethanol

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The synergistic effects of CeO₂-supported bimetallic Ni–Cu, Co–Cu, and Ni–Fe catalysts on the reduction properties, crystal structure, and catalytic performance during steam reforming of ethanol were investigated. Both metals in the bimetallic catalysts were reduced at lower temperatures than were the metals in the associated monometallic catalysts, and they formed alloy crystallites. It was confirmed from activity tests of the monometallic catalysts that Ni and Co were relatively active components and that Cu and Fe were less active. The combination of Ni and Co with Cu (Ni–Cu/CeO₂ and Co–Cu/CeO₂) resulted in increases in H₂ and CO₂ yields and inhibition of carbon deposition during reactions at 673 K. On the other hand, the incorporation of Ni with Fe (Ni–Fe/CeO₂) showed a lower activity than did Ni/CeO₂ at 673 K but exhibited a higher H₂ yield and higher resistance to carbon deposition at 873 K, in which case NiFe alloys were formed. These results indicate the advantages of alloying a catalytically active metal with a less active metal during steam reforming of ethanol.

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Key-words : Ethanol steam reforming, CeO₂-supported catalyst, Bimetallic alloy, Synergistic effect, Carbon deposition

[Received March 23, 2015; Accepted July 23, 2015]

1. Introduction

Hydrogen fuel has attracted attention as a clean energy source because it generates only water upon burning. However, its major drawback is that enormous quantities of carbon dioxide (a greenhouse gas) are emitted during its industrial production from petroleum and natural gas; therefore, other manufacturing approaches are desired. Steam reforming of ethanol (SRE), which is characterized by the reaction

is a promising method of producing hydrogen from biomass ethanol.^{1)–3)} Carbon dioxide is also generated in this process, but its net quantity in the atmosphere can be assumed constant because it is absorbed during the growth of the plants that are raw materials for biomass ethanol. Hence, biomass ethanol is widely accepted as an environmentally friendly energy source.

It is well known that noble metals such as Ru, Rh, Pd, and Pt exhibit catalytically high activities.^{4)–7)} Apart from the noble metals, Ni and Co have also been used for SRE because of their high activities and low costs.^{8)–15)} We previously investigated the effects of metal oxide support in SRE over supported Ni catalysts¹⁶⁾ and found that Al₂O₃ and MgO supports partially formed solid solutions with Ni and consequently hindered its reduction and catalytic activity. ZrO₂- and SiO₂-supported Ni catalysts had relatively high activities at 673 K but large amounts of carbon were deposited during the reaction. As a result, CeO₂ was adopted as the support in this study because it promotes the reduction of the Ni ions to metallic crystallites that act as the catalytically active sites and, consequently, leads to high activ-

ities at low temperatures. In addition, the CeO₂ support inhibits carbon deposition during the reaction.

The bimetallic effects of SRE have been investigated for Ni–Cu,^{17)–21)} Ni–Co,^{22),23)} Ni–Fe,^{24),25)} and Ni–Pt.^{26)–28)} Wang et al.¹⁹⁾ found that the unsupported Ni–Cu catalyst exhibited stable performance, while the Ni catalyst showed severe deactivation due to heavy coke deposition. A decrease in carbon deposition was also reported for Co–Ni supported on perovskite-type LaFeO₃.²³⁾ Chen et al.²⁰⁾ investigated the effect of the Cu/Ni ratio on SRE over Cu–Ni/SiO₂ catalysts and concluded that adding Ni to Cu catalysts improves C–C bond rupture in ethanol, inducing synergistic enhancement in ethanol conversion at temperatures below 673 K. Shi et al.²⁴⁾ reported that bimetallic Ni–Fe catalysts supported on La₂O₂CO₃ exhibited higher activities than did monometallic catalysts, which was attributed to the coexistence of well-dispersed Ni, Fe, and LaFe₃Ni_{1–3}O₃. Moraes et al.²⁸⁾ found that the Ni/CeO₂ catalyst for low temperature SRE significantly deactivated during the reaction due to the formation of a nickel carbide phase. Pt addition minimized the formation of a nickel carbide phase and consequently enhanced catalyst activity and decreased catalyst deactivation. As mentioned above, the combination of metallic components is expected to improve catalytic performance in SRE.

In the present study, we investigated the bimetallic effects of CeO₂-supported Ni–Cu, Co–Cu, and Ni–Fe catalysts on the reduction properties, crystal structure, and catalytic performance during SRE. As mentioned in our previous report,¹⁶⁾ Ni and Co catalysts supported on CeO₂ maintained high activities for long reaction times, in spite of relatively large amounts of carbon deposition, whereas Cu and Fe catalysts were significantly deactivated by very small amounts of carbon. The objective of this investigation was to elucidate the effects of combining the catalytically active Ni and Co with the less active Cu and Fe supported on pure CeO₂.

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2. Experimental

2.1 Catalyst preparation

Three types of CeO₂-supported bimetallic catalysts, denoted by Ni5Cu5 (5 wt % Ni–5 wt % Cu), Co5Cu5 (5 wt % Co–5 wt % Cu), and Ni5Fe5 (5 wt % Ni–5 wt % Fe), were prepared. The CeO₂ support was synthesized via a precipitation method.²⁹ Precursory precipitation was obtained by stirring a mixed solution (500 mL) of Ce(NO₃)₃·6H₂O (11.9 g) and urea (50 g) at 363 K, followed by filtration, washing with water, drying at 383 K for 12 h, and then calcination at 773 K for 5 h. The BET surface area of the resultant CeO₂ powder was 110 m²·g^{−1}. Each catalyst was prepared by an impregnation method using commercial Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, and Fe(NO₃)₃·9H₂O (Kishida Chemical). The CeO₂ support was immersed in a mixed solution of the metal nitrates and evaporated to dryness in a boiling water bath. After drying at 383 K for 12 h, the obtained powder was calcined at 773 K for 3 h. For comparison, CeO₂-supported monometallic Ni, Co, Cu, and Fe catalysts with metal loadings of 10 wt % (Ni10, Co10, Cu10, and Fe10, respectively) were also prepared in the same manner.

2.2 Characterization

The crystal structure of the catalysts was analyzed by X-ray diffraction (XRD) 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. For the reduced catalysts, a liquid paraffin coating was employed to prevent sample reoxidation. The temperature-programmed reduction (TPR) was recorded with an apparatus consisting of a flow controller, a reaction tube, an electric furnace, and a thermal conductivity detector (Shimadzu GC-8A). The sample was heated at a temperature-increase rate of 10 K·min^{−1} in a flow of 10% H₂/Ar. Carbon deposited on the catalyst during the reaction was examined via thermogravimetry (TG) (Rigaku TG8120 Thermo Plus Evo) in air, at a temperature-increase rate of 10 K·min^{−1}.

2.3 Activity test

The catalytic activity was evaluated in two types of reaction: temperature-programmed SRE (TP-SRE) at 473–873 K, with a stepwise temperature increase of 50 K per 30 min, and isothermal SRE at 673 and 873 K. For each reaction, the unreduced catalyst (0.2 g) was loaded into a tubular quartz reactor (ID 8 mm). A mixed solution of H₂O/C₂H₅OH with a molar ratio of 3:1 was fed into the reactor at 30 μ L·min^{−1}, vaporized at the top of the reactor, and then sent to the catalyst bed using a 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 (Shimadzu GC-8A): one, for H₂ detection, was equipped with a column packed with a 13X molecular sieve and used nitrogen as the carrier gas; the other, for detection of C1 gases (CO, CO₂, and CH₄), was equipped with a column packed with active carbon and used helium as the carrier gas. The product yields, $Y(\text{H}_2)$ and $Y(\text{C1})$, were calculated according to the ideal SRE equation, Eq. (1), with

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

and

$$Y(\text{C1})(\%) = \frac{F(\text{C1})}{2 \times F(\text{C}_2\text{H}_5\text{OH})} \times 100, \quad (3)$$

where $F(\text{C}_2\text{H}_5\text{OH})$ represents the feed rate of C₂H₅OH in mol·min^{−1}, and $F(\text{H}_2)$ and $F(\text{C1})$ respectively represent the quantities of H₂ and C1 gases produced in mol·min^{−1}. The quantitative determination of ethanol and liquid products in the trap was difficult because of their tiny amounts and the poor sensitivity of the gas chromatogram, and therefore the catalytic performance was evaluated via $Y(\text{H}_2)$ and $Y(\text{C1})$ in the present investigation.

3. Results and discussion

3.1 Reduction property and crystalline structure

Figure 1 shows the TPR profiles of the CeO₂-supported monometallic and bimetallic catalysts. The XRD patterns of the catalysts before and after reduction at 473–873 K for 1 h with hydrogen are also given in Fig. 2. The TPR profile of Cu10 is characterized by two partially overlapping peaks with small widths and high intensities, and demonstrates that Cu10 is reduced at the lowest temperatures among the monometallic catalysts. Ni10 and Co10 required higher reduction temperatures of 510–575 and 540–590 K, respectively. These are consistent with the XRD results that the CuO crystallites in Cu10 were reduced to the metal at 473 K, whereas the oxide phases in Ni10 and Co10 remained at 473 K but were reduced to the metal phases at 573 K. On the other hand, the TPR and XRD profiles of Fe10 indicate that the oxidized Fe species in the as-prepared catalyst are reduced at high temperatures above 650 K. The less reducibility of Fe10 is attributable to a strong interaction with the CeO₂ support and a partial formation of Fe–Ce–O solid solution.³⁰⁾

The bimetallic Ni5Cu5 and Co5Cu5 catalysts yielded the sharp and intense TPR peaks due to the reduction of the Cu oxide phases, which were obviously shifted to the lower temperatures compared to Cu10, indicating a bimetallic effect on the Cu reducibility. In addition, small TPR peaks are also observed promptly after the completion of the Cu reduction in Figs. 1(e) and 1(f). Although the reduction temperatures are much lower than those for Ni10 and Co10, these peaks can be assigned to the reductions of the Ni and Co species.

Fig. 1. TPR profiles of the CeO₂-supported monometallic and bimetallic catalysts.

Fig. 2. XRD patterns of (a) Ni10, (b) Co10, (c) Cu10, (d) Fe10, (e) Ni5Cu5, (f) Co5Cu5, and (g) Ni5Fe5 (A) before and (B) after reduction at 473 K, (C) 573 K, (D) 673 K, (E) 773 K, and (F) 873 K with hydrogen for 1 h.

A decrease in the reduction temperature of the Ni phase in Ni5Cu5 was also confirmed by XRD. A comparison between Figs. 2A(e) and 2B(e) clearly demonstrates that not only CuO but also NiO crystallites are reduced to the metals even at 473 K in contrast to the non-reduced behavior of Ni10. The diffraction angles of 43.42 and 44.36° for the two peaks in Fig. 2B(e) fall between those for the 111 reflections from pure Cu (43.33°) and Ni (44.55°) crystals. This feature clearly indicates the formation of Cu- and Ni-rich alloy particles with face-centered cubic (fcc) structures.³¹⁾ Raising the reduction temperature to 573 K resulted in a marked decrease in the intensity of the XRD peak due to the Ni-rich alloys, but, at 873 K, a very broad peak re-emerged at 43.8–44.9°, indicating the formation of very fine NiCu alloy particles having a wide variety of Ni/Cu ratios.

The as-prepared Co5Cu5 catalyst exhibited a broad XRD peak due to small Co₃O₄ crystallites, but no peak due to Cu was observed. After the hydrogen reduction at 473 K, the peak due to the oxide disappeared and an extremely weak peak appeared at around 44.3°, which was identical to the diffraction angle of the 111 reflection from a cubic β-Co crystal. Finally, the peak slightly increased in intensity at a reduction temperature of 873 K and was accompanied by a tail toward the low-angle side, which suggests the formation of a CoCu alloy.³²⁾

Ni5Fe5 yielded two major TPR peaks. The lower-temperature peak has a maximum at 543 K after a gradual increase in the H₂ consumption. Although the peak temperature is about 30 K lower, this feature corresponds approximately to that of the oxidized Ni phase in Ni10. The broad TPR peak at 600–700 K is probably due

to the reduction of the Fe species. A lack of the higher-temperature peaks above 750 K observed for Fe10 may suggest that the broad peak consists of overlapped peaks due to the hardly reducible Fe species which are shifted to the lower temperatures by the presence of the reduced Ni. The XRD results of Ni5Fe5 indicate that, at a reduction temperature of 573 K, highly-dispersed α-Fe₂O₃ and NiO particles were reduced to the crystallites which provided a weak peak at 43.9°. This peak increased in intensity with increasing temperature. The final diffraction angle of 43.7° at 873 K indicates the formation of fcc NiFe alloy crystallites with a Ni/Fe atomic ratio of about 1.³³⁾

In conclusion, the combinations of Ni–Cu, Co–Cu, and Ni–Fe resulted in the decreases in the reduction temperatures of both metals and the formations of the alloy crystallites. The improvements in the metal reducibilities are possibly caused by a synergistic interaction between the metal oxide phases and by a decrease in their crystallite size.³⁴⁾ In addition, the significant decrease in the reduction temperatures of the less reducible metals is probably attributable to the catalytic effects of the more reducible metals.

3.2 Catalytic performance and structure in SRE

In addition to H₂ and CO₂, CO and CH₄ were produced from ethanol mainly via the following reactions:^{1),3),35)}

The following are also accepted as the significant side reactions for the byproducts.^{1),3),35)}

It is well known that ethylene is also generated via dehydration of ethanol on acid catalysts such as Al₂O₃.^{1),3)} Indeed, using the gas chromatogram, it was detected during SRE over Al₂O₃-supported catalysts, but it was not observed for the CeO₂-supported catalysts employed in this study.

The yields of H₂, CO₂, CO, and CH₄ for TP-SRE over the CeO₂-supported monometallic and bimetallic catalysts are shown in Fig. 3. The Cu-containing catalysts (Cu10, Ni5Cu5, and Co5Cu5) began to produce H₂ even at 523 K. In contrast, the other catalysts (Ni10, Co10, Fe10, and Ni5Fe5) generated H₂ at reaction temperatures of ≥623 K. As mentioned above, the metal oxides in the Cu-containing catalysts were reduced to the metal and alloy crystallites at temperatures below 523 K, whereas the remaining catalysts required higher reduction temperatures. These results suggest that the metallic phases are the catalytically active sites for SRE.

The H₂ yield for Cu10 was relatively high at ≤573 K, but its increase with increasing temperature was attenuated above 600 K. This behavior was probably caused by carbon deposition on the Cu surfaces.¹⁶⁾ Ni10 was characterized by the generation of a large amount of CH₄ and a related decrease in H₂ yield at 723–823 K. In contrast, Ni5Cu5 strongly suppressed them and consequently maintained relatively high H₂ yields across the whole temperature range. Co5Cu5 also exhibited higher H₂ yields than both Co10 and Cu10 at 623–723 K, and its activity was maintained as high as that of Co10 at higher temperatures. Although Fe10 was comparatively less active, the addition of Fe to Ni/CeO₂ (Ni5Fe5) inhibited CH₄ formation over the Ni atoms and improved the yields of H₂ and CO₂ at 773–823 K.

Figure 4 shows the product yields 9 h after the initiation of SRE at 673 and 873 K over the monometallic and bimetallic

Fig. 3. Product yields for temperature-programmed SRE over the CeO₂-supported monometallic and bimetallic catalysts.

Fig. 4. Product yields at 9 h after the initiation of SRE at (a) 673 K and (b) 873 K over the CeO₂-supported monometallic and bimetallic catalysts.

catalysts. Ni10, Co10, and Cu10 exhibit relatively high H₂ yields, but Fe10 was less active at 673 K. In addition, Ni10 produced much larger amounts of CO and CH₄, but these were not detected for Cu10. By raising the reaction temperature to 873 K, Ni10 and Co10 increased in the activities but Cu10 and Fe10 were inactivated by carbon deposition.¹⁶⁾

At 673 K, the addition of Cu to Ni/CeO₂ (Ni5Cu5) resulted in a significant decrease in CH₄ and a significant increase in H₂ and

Fig. 5. XRD patterns of (a) Ni10, (b) Co10, (c) Cu10, (d) Fe10, (e) Ni5Cu5, (f) Co5Cu5, and (g) Ni5Fe5 after SRE at (A) 673 K and (B) 873 K for 9 h.

CO₂. Co5Cu5 also exhibits a higher H₂ yield than both Co10 and Cu10. These results clearly indicate the synergistic effects of a combination of the two metals. However, these effects were not observed at 873 K. In contrast, although Ni5Fe5 yielded no bimetallic effect at 673 K, it exhibited the highest yields of H₂ and C1-gases, and the inhibitory effect of the CH₄ formation at 873 K. As a result, the advantages of Ni5Cu5 and Co5Cu5 at 673 K and of Ni5Fe5 at 873 K over the monometallic catalysts demonstrate the effectiveness of the combination of a catalytically active metal with a less active metal.

The XRD patterns of the catalysts after SRE at 673 and 873 K for 9 h are shown in Fig. 5. At a reaction temperature of 673 K, Cu10 was completely reduced to the metal, but the unreduced oxides were detected for the other monometallic catalysts, indicating a less reducibility during SRE than during hydrogen reduction at the same temperature. On the other hand, the bimetallic Ni5Cu5 and Co5Cu5 catalysts exhibited no XRD peak due to the oxides phase. The XRD peak observed for Ni5Cu5 is located at a slightly larger diffraction angle than is the 111 reflection from the Cu crystallites in Cu10. In addition, it is asymmetric and slightly broadened to the high-angle side, and therefore assigned to Cu-rich NiCu alloy particles. Co5Cu5 also yielded an asymmetric peak broadened to the low-angle side, which is due to CoCu alloy crystallites. These results demonstrate an improvement effect of the Cu doping on the reducibility of Ni and Co which may contribute to enhance the catalytic activities at 673 K. In the case of the less active Ni5Fe5 catalyst, the peak due to Fe oxides was observed but the peak due to NiFe alloys was not. The alloy phases were formed by raising the reaction temperature to 873 K, at which Ni5Fe5 exhibited the excellent catalytic properties. These results clearly indicate that the bimetallic effects on SRE are strongly associated with the alloy formations.

Figure 6 shows the TG profiles of the catalysts employed for SRE at 673 and 873 K for 9 h. The total quantities of the carbon deposits, estimated from the weight losses, are also summarized in Table 1. The weight losses due to the combustion of deposited carbon are classified into two groups: small weight loss at 490–570 K and relatively large weight loss at ≥600 K. As mentioned in our previous report,¹⁶⁾ the latter is attributed to the combustion of fibrous carbon deposited on the highly active Ni10 and Co10. On the other hand, the carbon related to the former weight loss

Fig. 6. TG profiles of the CeO_2 -supported monometallic and bimetallic catalysts after SRE at (A) 673 K and (B) 873 K for 9 h.

Table 1. The amount of deposited carbon after SRE at 673 K and 873 K for 9 h

Reaction temp. [K]	Carbon deposit [g g-cat ⁻¹]						
	Ni10	Co10	Cu10	Fe10	Ni5Cu5	Co5Cu5	Ni5Fe5
673 K	0.21	0.22	0.03	0.04	0.04	0.06	0.04
873 K	0.28	0.14	0.03	0.02	1.58	0.65	0.09

significantly deactivated Cu10 and Fe10 in spite of the very small amount that was undetectable by SEM. Although at 673 K, Ni5Cu5 and Co5Cu5 exhibited higher activities than did Ni10 and Co10, respectively, carbon deposition was strongly inhibited. However, raising the reaction temperature to 873 K resulted in approximately 40- and 10-fold increases in carbons deposited on Ni5Cu5 and Co5Cu5, respectively, most of which were the higher-temperature-combustible carbon generated on Ni and Co. On the other hand, Ni5Fe5, which presented the best catalytic performance at 873 K, showed excellent resistance to carbon deposition when compared with Ni10.

In conclusion, the combination of Ni and Co with Cu promoted their reductions to form the alloys during SRE at 673 K, leading to the high catalytic activities and the inhibition of carbon deposition. Similar advantages of Ni5Fe5 arose at 873 K, in which case NiFe alloy crystallites were formed. These results demonstrate that the alloy formations are closely related to the improvement in the catalytic performances. Miranda et al.³⁶⁾ reported that deep hydrogenolysis of glycerol to CH_4 was inhibited by the addition of Cu to the Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. They also found, by IR spectroscopy, that the bridge-bonded CO adsorbed on metallic Ni progressively decreased due to the incorporation of Cu, and they therefore concluded that CH_4 formation requires an ensemble of adjacent active Ni atoms. Since CH_4 generated in SRE not only reduces H_2 production but also promotes carbon deposition via its decomposition,^{2,3)} a decrease in the adjacent array of active metal atoms by alloying with the less active metal is presumed to be useful in the inhibition of CH_4 formation and the subsequent carbon deposition and thereby in the enhancement of H_2 production.

4. Conclusion

In this study, we investigated the bimetallic effects of CeO_2 -supported Ni-Cu, Co-Cu, and Ni-Fe catalysts on SRE. A combination of the two metals on CeO_2 decreased the reduction

temperatures of both components and formed NiCu, CoCu, and NiFe alloys with fcc structures. Ni/ CeO_2 had the highest ability among the monometallic catalysts to form H_2 but produced a large amount of CH_4 and deposited carbon. Co/ CeO_2 also exhibited a relatively high activity, but the Cu and Fe catalysts were less active. Incorporation of Ni with Cu inhibited CH_4 formation and heavy carbon deposition (which arose predominantly on Ni) and thereby enhanced the H_2 yield. Similar synergistic effects were observed for the Co-Cu catalyst. It was confirmed that alloy crystallites were formed in these catalysts during the reactions, leading to the adequate synergistic effects. However, these advantages were lost by raising the temperature to 873 K. In the case of the Ni-Fe catalyst, the NiFe alloys were generated at a reaction temperature of 873 K and exhibited excellent catalytic performances. These improvements were probably generated by an ensemble effect of the alloy catalysts through which CH_4 formation on an adjacent array of the active metal atoms was inhibited and H_2 production was enhanced.

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