Development of Ni- and Co-based Alloy Catalysts for Steam Reforming of Biomass Tar

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Improvement of catalysts for the steam reforming of tar derived from the pyrolysis of biomass is needed in terms of activity, stability, and resistance to coke deposition. Ni and Co are known to be active components for the steam reforming reaction, and one effective method to improve the catalytic performance is the alloying of the active metal with another suitable metal. The development of Ni-Fe, Ni-Co, and Co-Fe alloy catalysts is described. The relationship between the promoting effect of alloy formation and the characterization of alloy particles is introduced. The catalytic performance of alloy particles is greatly influenced by the properties such as components, compositions, crystal structures, uniformity, and so on. In particular, utilization of hydrotalcite-like compounds as the catalyst precursors can produce alloy particles with uniform composition as well as higher catalytic activity than those prepared by the conventional impregnation method, demonstrating an effective method for preparing excellent alloy catalysts.

Keywords
Biomass, Tar, Steam reforming, Alloy catalyst, Synthesis gas, Hydrogen production

1. Introduction

Utilization of biomass for power generation and production of liquid fuels and chemicals has attracted much attention because of the renewability and sustainability of biomass resources. One of the common technologies for power generation, the production of liquid fuels by Fischer-Tropsch synthesis and chemicals by methanol synthesis, is the conversion of biomass to synthesis gas and hydrogen1). A conventional method for biomass conversion to synthesis gas and hydrogen is non-catalytic gasification with air, which has usually been carried out at very high temperature (>1073 K). In particular, reduction of the tar content as a by-product requires operation at very high temperature3). In the non-catalytic gasification system, the product gas is diluted with nitrogen because air is usually used as the gasifying agent. The diluted product gas is not suitable for the catalytic conversion of synthesis gas to hydrocarbons and methanol because these reactions require high pressure. In order to avoid dilution of the product gas, steam is used as the gasifying agent. The reactivity of steam as a gasifying agent is not as high as that of air. Therefore, the gasification of biomass with steam needs higher reaction temperature, which can decrease the energy efficiency, whereas higher energy efficiency in the production of synthesis gas and hydrogen requires that the reaction temperature should be lowered.

To solve this problem, catalytic steam reforming of tar derived from the pyrolysis of biomass at lower temperature has been developed. Biomass pyrolysis at low temperature such as 773 K gives high yield of a mixture of volatile organic compounds called tar or biooil2). If the catalytic conversion of this tar can be achieved by steam reforming at lower temperature, gasification of biomass to synthesis gas and hydrogen at low temperature will be feasible. This process requires the development of catalysts for the steam reforming of biomass tar, in particular, improved activity and stability of the catalyst.

Noble metals such as Rh are effective components for the conversion of biomass to synthesis gas4). However, the high cost and limited availability of noble metals demands the further development of catalysts not based on noble metals. Ni and Co metals are known to catalyze the steam reforming reactions of hydrocarbons and oxygenates, and the modification of Ni and Co metals with suitable oxides or other metals can improve the catalytic performance5). Our group has reported that the addition of cerium oxide6) and
manganese oxide to Ni catalysts enhanced the catalytic performance in terms of activity and suppression of coke formation in the steam reforming of the biomass tar. The interface between the metal and the added oxides was shown to be important, and the synergy between the activation of tar components on the metal surface and the activation of steam based on the redox property of the added oxides were important in the high catalytic performance. However, the interface between the metal and the metal oxide is difficult to expand. On the other hand, the interface between the metal and other metals can be expanded, in particular, through alloy formation of two metals. The combination of the metal and other metals with different oxygen affinities and redox properties such as Rh-Sn, Pt-Ni, Pd-Ni, and Rh-Co can also improve the catalytic performance in various reactions. The oxygen affinity of various metals is listed in Table 1.

This review article describes the development of Ni- and Co-based catalysts alloyed with other metals (Ni-Fe, Ni-Co) for the steam reforming of tar derived from the pyrolysis of cedar wood.

2. Ni–Fe and Ni–Co Alloy Catalysts for Steam Reforming of Tar

Ni-Fe/Al2O3 and Ni-Co/Al2O3 alloy catalysts were prepared by the co-impregnation method using mixed aqueous solution of the corresponding metal nitrates (Ni(NO3)2·6H2O, Fe(NO3)3·9H2O, Co(NO3)2·6H2O). The support material of α-Al2O3 (BET surface area: 8 m² g⁻¹-cat) was prepared by the calcination of γ-Al2O3 (JRC-ALO-1, Catalysis Society of Japan, 143 m² g⁻¹-cat, grain size 2-3 mm) in air at 1423 K, followed by crushing and sieving to obtain particle sizes between 0.6-2.0 mm. After impregnation, the catalyst was dried at 383 K for 12 h, followed by calcination at 773 K for 3 h under air atmosphere. Cedar wood was used as the biomass feedstock. Steam reforming of tar was conducted in a laboratory-scale continuous feed dual-bed reactor. In this system, tar is formed by the pyrolysis of cedar wood in the presence of steam, and is then introduced to the secondary catalyst bed together with steam. Before catalytic reaction, the catalyst was pre-reduced in H2 at 773 K for 0.5 h.

**Table 1 Oxygen Affinity of Metals**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>pΟ⁰⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtO</td>
<td>-1.3</td>
</tr>
<tr>
<td>PdO</td>
<td>-1.1</td>
</tr>
<tr>
<td>RhO</td>
<td>4.2</td>
</tr>
<tr>
<td>CoO</td>
<td>16.2</td>
</tr>
<tr>
<td>NiO</td>
<td>16.2</td>
</tr>
<tr>
<td>SnO2</td>
<td>19.7</td>
</tr>
<tr>
<td>FeO</td>
<td>20.6</td>
</tr>
</tbody>
</table>

a) pΟ = -logPΟ₂ for oxygen in equilibrium at 1273 K.

Figure 1A shows the catalytic performance of Ni-Fe/Al2O3 for the steam reforming of tar at 823 K. In the case of Ni(12 wt%)/Al2O3, the amount of the residual tar was large and the H2/CO ratio was rather low, indicating Ni(12 wt%)/Al2O3 had low reforming activity. In addition, Fe(6 wt%)/Al2O3 showed much lower activity than Ni(12 wt%)/Al2O3. In contrast, the promoting effect of Fe addition to Ni(12 wt%)/Al2O3 was maximum at Fe/Ni = 0.5. The amount of H2 adsorption on Ni-Fe/Al2O3 (Fe/Ni = 0.5) (11 μmol g⁻¹-cat) was smaller than that of Ni(12 wt%)/Al2O3 (44 μmol g⁻¹-cat). Therefore, the high activity of Ni-Fe/Al2O3 is considered to result from the synergy between Ni and Fe. In particular at Fe/Ni ≤ 0.5, not only the activity increased but also the amount of coke deposited on the catalyst decreased with higher Fe addition, indicating that Fe addition improves the resistance to coke deposition.

Ni and Co tend to be effective catalyst components for the catalytic reforming of hydrocarbons and oxygenates, respectively. On the basis that the biomass tar contains various kinds of hydrocarbons and oxygenates, Ni-Co catalysts can be multifunctional. As shown in Fig. 1B, the additive effect of Co to

Reaction conditions: biomass; 60 mg min⁻¹ (H2O 7.22 %; C 2358 μmol min⁻¹, H 3351 μmol min⁻¹, O 1454 μmol min⁻¹), N2 flow rate 60 mL min⁻¹, (added H2O)/C = 0.47 (steam flow rate 1110 μmol min⁻¹), T = 823 K, Wcat = 0.75 g.

Fig. 1 Catalytic Performance in Steam Reforming of Tar over (A) Ni-Fe/Al2O3 and (B) Ni-Co/Al2O3 at 823 K.
Ni(12 wt%)/Al2O3 was most remarkable at Co/Ni = 0.25. The catalytic performance of Ni-Co/Al2O3 (Co/Ni=0.25) was also higher than those of Ni(15 wt%)/Al2O3 and Co(15 wt%)/Al2O3, where total metal loading was adjusted to Ni-Co/Al2O3 (Co/Ni=0.25, 12 wt% Ni). The amount of H2 adsorption on Ni-Co/Al2O3 (Co/Ni=0.25) (47 µmol g⁻¹-cat) was only a little higher than that on Ni(12 wt%)/Al2O3 (44 µmol g⁻¹-cat) and on Co(15 wt%)/Al2O3 (30 µmol g⁻¹-cat), and so this observation cannot explain the superiority of Ni-Co/Al2O3 (Co/Ni=0.25). Therefore, the high activity of Ni-Co/Al2O3 in the tar steam reforming is also interpreted as the synergy between Ni and Co. Another important point is that Co(12 wt%)/Al2O3 exhibited higher activity than Ni(12 wt%)/Al2O3 under the present reaction conditions, and this may be related to the previous observations that Co-based catalysts were effective for the tar removal.

Figure 2A shows the X-ray diffraction (XRD) patterns of Ni-Fe/Al2O3 after H2 reduction at 773 K. The peak due to Ni metal was observed at 2θ 44.4° on Ni/Al2O3. In contrast, the peak gradually shifted to smaller angle around 2θ 44-45° on Ni-Fe/Al2O3 (Fe/Ni=0.13-0.5) with increasing Fe amount, indicating the formation of Ni-rich Ni-Fe solid solution alloy with fcc structure. Based on Vegard’s rule, the composition of the Ni-Fe alloy was determined to be Fe/Ni = 0.05, 0.07, 0.12 on Ni-Fe/Al2O3 (Fe/Ni=0.13, 0.25, 0.5), respectively (Fig. 2B). The observed composition of the fcc Ni-Fe alloy phase was lower than the composition in Ni-Fe/Al2O3 catalysts, and this tendency suggests that the composition of the alloy phase is not uniform. The small peak assigned to tetragonal NiFe phase was detected at Fe/Ni = 0.5, and this phase increased at Fe/Ni > 0.5. Therefore, Fe-rich bcc Fe-Ni alloy was probably formed at Fe/Ni > 165. In addition, Ni-Fe fcc alloy phase was observed on Ni-Fe/Al2O3 (Fe/Ni=0.5) after tar steam reforming, and the composition was determined to be Fe/Ni = 0.29 (Fig. 2A(p)). The composition of the fcc Ni-Fe alloy phase increased after the reaction, which can be interpreted as the solid reaction of the fcc Ni-Fe alloy phase with the NiFe tetragonal phase.

Figure 3A shows the XRD patterns of Ni(12 wt%)/Al2O3, Co(12 wt%)/Al2O3, and Ni-Co/Al2O3 after the H2 reduction at 773 K. The peaks were located between the peaks of Co and Ni metal on Ni-Co/Al2O3 (Co/Ni=0.06-0.5), indicating the formation of Ni-Co solid solution alloy. In particular, the d spacing as a function of the molar ratio of Co/(Ni + Co) showed an almost linear relationship as suggested by Vegard’s rule (Fig. 3B).

Figure 4 shows the transmission electron microscope (TEM) images of the fresh Ni-Fe/Al2O3 (Fe/Ni=0.5) and Ni-Co/Al2O3 (Co/Ni=0.25) catalysts after H2 reduction at 773 K. In the case of Ni-Fe/Al2O3 (Fe/Ni =0.5), the average size of metallic particles was estimated to be 22 ± 2 nm. The size was almost the same as that of Ni metal particles on Ni/Al2O3 obtained from the XRD pattern. On the other hand, based on the average particle size (d) from the TEM result, the dispersion (D) was calculated as 4.4 % using the equation $D = 9.71/d$ nm, assuming the size of the Fe atom is the same as that of the Ni atom. The difference in the dispersion measured from H2 adsorption (Table 2) and from TEM can be explained by the suppression of H2 adsorption by the addition of Fe. In addition, the elemental composition of the various positions on the catalysts was measured by energy dispersive X-ray fluorescence spectrometer (EDX) analysis. Although the average molar ratio is Fe/Ni = 0.5, particles with com-
positions far from the average were also present, indicating that the composition of metallic particles was not homogeneous (Fig. 4C). In the case of Ni-Co/Al2O3 (Co/Ni = 0.25), the average size of the metallic particles was estimated to be 22 ± 2 nm, which was comparable to the estimate from XRD (26 nm). The composition was not homogeneous in a strict sense, but the local composition of the Ni-Co/Al2O3 (Co/Ni = 0.25) was much more homogeneous than that of Ni-Fe/Al2O3 (Fe/Ni = 0.5), as shown in Fig. 4C.

Metal particle sizes of Ni(12 wt%)/Al2O3 and Co(12 wt%)/Al2O3 estimated by XRD were 22 and 25 nm (Table 2), respectively. Assuming that the composition of the Ni-Co solid solution was homogeneous, the average particle size can also be estimated for Ni-Co/Al2O3 (Table 2). Moreover, the dispersion of Ni-Co alloy particles can be calculated using the relationship between the average metal particle size (d/nm) and the dispersion (D) \(D \% = A_{Ni,Co} d \times 100, A_{Ni} = A_{Ni} \times Ni/(Ni + Co) + A_{Co} \times Co/(Ni + Co), A_{Ni} = 0.971, A_{Co} = 0.963\), which are also listed in Table 2. The amount of H2 adsorption on the fresh catalysts after the reduction at 773 K and the dispersion are listed in Table 2. The agreement of dispersion estimated from H2 adsorption and from XRD also suggests rather homogeneous composition of the Ni-Co solid solution.

Figure 5A shows the TPR profiles of Ni-Fe/Al2O3 as well as Ni/Al2O3 and Fe/Al2O3. Considering the H2 reduction pretreatment temperature (773 K), the reduction degree of Fe (Fe0/(Fe total)) was calculated and is shown in Fig. 5A. Almost all Ni species on Ni/Al2O3 were reduced. However, the reduction degree of Fe was not as high as that of Ni. On Ni/Al2O3, H2 consumption was observed in the temperature range between 573 K and 800 K. In contrast, the temperature range of the reduction of Fe species on Fe/Al2O3 was very broad and higher. In the case of the Ni-Fe/Al2O3 catalysts, the reduction of Fe was strongly promoted by the presence of Ni. This tendency can be explained by the spillover of activated hydrogen species from Ni to Fe. Similar behavior has been observed on NiO-MgO solid solution catalysts modified with noble metals38),39),41),67) and physically-mixed noble metal catalysts with solid acid catalysts70) and 72.

Figure 5B shows the temperature-programmed reduction (TPR) profiles of Ni-Co/Al2O3, Ni/Al2O3 and Co/Al2O3, the findings of H2 consumption below 773 K (Table 2) show that almost all Ni and Co species were reduced to the metallic state. This behavior may be due to the higher reducibility of Co species on Co/Al2O3 than that of Ni species on Ni/Al2O3. As shown above, the composition of Ni-Co alloy particles was rather uniform, which was due to the simultaneous reduction of Co and Ni, because the reducibility of Ni and Co is similar. In contrast, in the case of Ni-Fe/Al2O3, the reducibility of Fe species on Al2O3 was not high even if reduction of Fe was promoted by the presence of Ni. The difference in the reducibility of Ni and Fe prevents simultaneous reduction, resulting in non-uniform composition. In addition, the surface segregation of Fe species on the Ni-Fe alloy particles was verified, and this observation can be supported by the reduction of Ni species followed by that of Fe species. Similarly, surface segregation of Ni and high probability of noble metals occur inside the Ni–noble metal alloy particles on Ni catalysts modified with noble metals prepared by the co-impregnation method(37),42)). Based on these results, to form alloy particles with uniform composition, the reducibility of two components should be adjusted.

3. Preparation of Uniform Ni–Fe Alloy Catalyst

The comparison between the Al2O3 supported Ni–Fe
Fig. 4 TEM-EDX Images of (A) Ni-Fe/Al₂O₃ (Fe/Ni = 0.5) and (B) Ni-Co/Al₂O₃ (Co/Ni = 0.25) after H₂ Pretreatment at 773 K and (C) Composition of Alloy Particles Determined by EDX Analysis²⁵,²⁶.

### Table 2 Properties of Ni-Co/Al₂O₃ Catalysts after H₂ Reduction at 773 K²⁶

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co/Ni Content</th>
<th>H₂ consumption⁹</th>
<th>H₂ consumption in TPR²⁶</th>
<th>Particle size³</th>
<th>H₂ adsorption⁶</th>
<th>Dispersion [%]</th>
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</thead>
<tbody>
<tr>
<td>Ni/Al₂O₃</td>
<td></td>
<td>2.0</td>
<td>2.0</td>
<td>22</td>
<td>44</td>
<td>4.4</td>
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<tr>
<td>Ni-Co/Al₂O₃</td>
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<td>38</td>
<td>4.9</td>
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<tr>
<td></td>
<td>0.13</td>
<td>2.0</td>
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<td>26</td>
<td>37</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.26</td>
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<td>26</td>
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<td>4.7</td>
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<tr>
<td></td>
<td>0.50</td>
<td>2.0</td>
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<td>26</td>
<td>37</td>
<td>4.8</td>
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<tr>
<td></td>
<td>0.50</td>
<td>1.0</td>
<td>3.5</td>
<td>26</td>
<td>37</td>
<td>4.8</td>
</tr>
<tr>
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<td>1</td>
<td>2.0</td>
<td>4.7</td>
<td>34</td>
<td>28</td>
<td>5.7</td>
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<tr>
<td>Co/Al₂O₃</td>
<td>-</td>
<td>2.0</td>
<td>4.9</td>
<td>25</td>
<td>39</td>
<td>3.0</td>
</tr>
</tbody>
</table>

a) The stoichiometry assumed is: NiO + H₂ → Ni + H₂O and Co₃O₄ → 3Co + 4H₂O.
b) H₂ consumption below 773 K in TPR profiles shown in Fig. 5B.
c) Calculated by the Scherrer equation using the full width at half height of the diffraction peak at 2θ = 44-45° in XRD (Fig. 3A).
d) H₂ adsorption is total adsorption at room temperature.
e) Calculated by \( \frac{A_{Ni} \times Ni(Ni + Co) + A_{Co} \times Co(Ni + Co)}{\text{particle size} \times 100} \), where \( A_{Ni} = 0.971 \) and \( A_{Co} = 0.963 \).
f) Calculated by \( 2 \times H₂ \text{ adsorption}(\text{Ni content} + \text{Co content}) \), assuming H/Ni = 1 and H/Co = 1.

and Ni-Co catalysts with optimized composition suggests that the Ni-Co catalyst is superior to the Ni-Fe catalyst. However, non-uniform composition of alloy particles on the Ni-Fe catalysts can be disadvantageous, and the potential of uniform Ni-Fe may be high. As mentioned above, it is important to adjust the reducibility of Ni and Fe, and the interaction between Ni and MgO is strong and decreases the reducibility of Ni, which is particularly remarkable for NiO-MgO solid solution69,73). Here, we attempted to prepare Ni-Fe catalysts containing MgO using a hydrotalcite-like precursor.

Hydrotalcite-like compounds, also known as layered double hydroxides (LDHs), are a class of anionic clays consisting of positively charged brucite-like layers, interlayer charge-balancing anions, and water molecules74). The chemical composition of the hydrotalcite-like compounds is expressed by the general formula [M²⁺ₓ₋ₓM³⁺ₓ(OH)$_{2x}$]^{x⁺}·mH$_2$O, where M²⁺ and M³⁺ represent divalent and trivalent metal ions within the brucite-like layers, and A⁺ represents an interlayer charge-balancing anion. Calcination converts the hydrotalcite-like compounds to mixed oxides that exhibit several good properties such as high dispersion, thermal stability, large surface area, and basic character. Moreover, the mixed oxides form well-dispersed and thermally stable metal particles by reduction treatment if reducible cations are incorporated into the hydrotalcite-like compounds75-83).

Ni/Mg/Al catalyst with optimized composition of Ni/Mg/Al = 9/66/25 prepared from Ni-Mg-Al hydrotalcite-like compound exhibits much higher activity, stability, and resistance to coke deposition than Al$_2$O$_3$- and MgO-supported Ni catalysts in the steam reforming of tar84). The high catalytic performance of Ni/Mg/Al is attributed to the formation of nanocomposite consisting of Ni metal particles (about 8.5 nm) and Mg(Ni, Al)O particles (about 11.5 nm).

Ni-Mg-Fe-Al hydrotalcite-like compounds were prepared by co-precipitation of the corresponding metal nitrates (Ni(NO$_3$)$_2$·6H$_2$O, Mg(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, Al(NO$_3$)$_3$·9H$_2$O). The precipitate was dried at 383 K and then calcined at 1073 K. The reduction of oxides with hydrogen at 1073 K can give Ni-Fe alloy nanoparticles. The reduced catalyst is denoted as Ni-Fe/Mg/Al. The structural changes of the samples during the preparation of Ni-Fe alloy nanoparticles were investigated by XRD and scanning transmission electron microscope (STEM) (Fig. 6). The hydrotalcite structure of as-synthesized precursor was verified from Figs. 6A(a) and 6B. After calcination at 1073 K (Fig. 6A(b)), the diffraction peaks of hydrotalcite phase completely disappeared and the diffraction pattern of Mg(Ni, Fe, Al)O phase appeared. Even after hydrogen reduction at 1073 K, the structure of the Mg(Ni, Fe, Al)O phase was maintained. Meanwhile, a diffraction peak at 2θ = 51.4° appeared after the reduction (Fig. 6A(c)), which shifted to lower angle compared to 51.8° for Ni metal on Ni/Mg/Al (Fig. 6A(d)), suggesting the formation of Ni-Fe alloy. According to the reduction degrees of Ni and Fe, about half of the Ni and Fe components were reduced to form Ni-Fe alloy51). The unreduced portions of Ni and Fe were probably incorporated in the MgO-like phase (Mg(Ni, Fe, Al)O). The composition of Ni-Fe alloy particles in Fig. 6A(c) was estimated to be Fe/Ni = 0.2 from the peak shift, using Vegard’s rule. Ni-Fe alloy formation was also confirmed by STEM-EDX analysis (Fig. 6C), and the Fe/Ni ratio in the alloy particles was determined to be in the range of 0.17-0.22. These compositions agreed well with that obtained from the XRD analysis, indicating the uniform composition of Ni-Fe alloy nanoparticles. The average diameter of the particles in

![TPR Profiles](image)
Figs. 6C and 6D \((\Sigma n_i d_i^3/\Sigma n_i d_i^2)\) was determined to be 9.5 nm, and the distribution of the particle size was rather narrow. On the other hand, from the Brunauer-Emmett-Teller (BET) surface area (127 m²/g-cat), the size of the Mg(Ni, Fe, Al)O particles was calculated to be ~13 nm, which is comparable to the size of alloy particles. Therefore, Ni_Fe/Mg/Al had a nanocomposite structure consisting of uniform Ni_Fe alloy particles and Mg(Ni, Fe, Al)O particles.

The catalytic performance of the Ni_Fe/Mg/Al catalysts was investigated in the steam reforming of toluene, which is one of the typical compounds used to model tar derived from the pyrolysis of wood biomass containing cellulose, hemicellulose, and lignin\(^{2,4}\). The steam reforming of toluene was carried out using a continuous flow reaction system with a fixed-bed reactor. Before the reaction, the Ni_Fe/Mg/Al catalyst was reduced at 1073 K with a H₂/N₂ (30/30 mL/min) gas flow.

**Fig. 6** (A) XRD Patterns and (B-D) STEM Images\(^{51}\)

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Next, the promoting effect of Fe on the suppression of coke formation, which can be connected to the catalyst stability\(^{41,68}\), was investigated. In order to evaluate the catalyst stability, Ni_Fe/Mg/Al (Fe/Ni = 0.25) and Ni/Mg/Al were tested in the steam reforming of toluene for longer reaction times. As shown in **Fig. 8A**, Ni_Fe/Mg/Al (Fe/Ni = 0.25) maintained toluene conversion of more than 99 % for 20 h, indicating high activity and stability for the steam reforming of toluene. On the other hand, the activity of Ni/Mg/Al was lower than that of Ni_Fe/Mg/Al (Fig. 8B). The pressure difference between catalyst bed inlet and outlet increased for Ni/Mg/Al after 17 h, but this behavior was not observed for Ni_Fe/Mg/Al. This pressure increase can be due to plugging by the deposited coke. The amounts of the deposited coke on Ni_Fe/Mg/Al and Ni/Mg/Al after 20 h reaction were determined to be 15 and 750 mg g⁻¹-cat, respectively, as measured by thermogravimetry. One explanation for this observation could be that the formation of uniform Ni_Fe alloy nanoparticles results
in Ni–Fe bimetallic sites with homogeneous and advantageous composition, in which Ni atoms can activate hydrocarbon molecules and neighboring Fe atoms can activate H₂O to H₂ and adsorbed oxygen atoms. This function is based on the higher oxygen affinity of Fe compared to that of Ni. The oxygen atoms supplied from Fe react with adsorbed hydrocarbon, leading to high activity and resistance to coke formation. The transfer of oxygen atoms from the metal with higher oxygen affinity to the metal with lower oxygen affinity on the alloy surface has been also suggested on Rh-M (M = Co, Ni, Fe) catalysts for the partial oxidation of methane⁴⁵,⁴⁸.

Figure 9 shows the XRD patterns recorded after the reduction and the catalytic use of both catalysts. In the case of Ni/Mg/Al, the size of Ni metal particles was almost constant and the coke peak was not observed at all. Regarding the suppression of aggregation of nanoparticles, two characteristics of Ni–Fe/Mg/Al can be considered: the high resistance to coke deposition and the nanocomposite structure. Coke deposition can weaken the interaction between metals and oxide supports, so the high resistance to coke deposition of Ni–Fe/Mg/Al may also contribute the inhibition of aggregation⁸⁵. Meanwhile, the Mg(Ni, Fe, Al)O particles are located between the Ni–Fe alloy nanoparticles, and may be important in inhibiting contact between the Ni–Fe alloy nanoparticles even at rather high reaction and reduction temperatures (1073 K).

The catalytic performance of Ni–Fe/Mg/Al in the steam reforming of tar derived from the biomass pyrolysis will be investigated in the near future.

4. Co–Fe Alloy Catalyst for Steam Reforming of Tar⁵³

The Ni catalysts were mainly investigated for the steam reforming of methane and biomass tar. As mentioned above (Fig. 1B), Co/Al₂O₃ catalyst showed higher performance than Ni/Al₂O₃. In addition, Co catalysts were effective in the steam reforming of tar⁶¹–⁶³,⁸⁶. Based on these reports and our findings, the catalyst development of Co-based alloy, in particular, Co–Fe alloy, has been carried out.

Figure 10 shows the catalytic performance of Co–Fe/Al₂O₃ as well as Co/Al₂O₃ and Fe/Al₂O₃ in the steam reforming of tar at 823 K. Similarly to the case of Ni–Fe/Al₂O₃, volcano-type dependence of the activity on the amount of added Fe was observed. Using 0.75 g
of catalyst, almost all tar was converted over the catalysts with Fe/Co = 0.25-0.5. Therefore, the difference in the activity was too small for the optimization of the added Fe amount. In order to verify the optimum Fe amount, the catalyst amount of Co$_2$Fe/Al$_2$O$_3$ (Fe/Co = 0.25-0.5) was decreased to 0.3 g, and the result showed that Co$_2$Fe/Al$_2$O$_3$ (Fe/Co = 0.25) exhibited the highest performance. Therefore, addition of the optimum amount of Fe to Co/Al$_2$O$_3$ catalyst improved the catalyst performance in terms of activity and suppression of coke deposition. As in the case of Ni$_2$Fe/Al$_2$O$_3$ and Ni$_2$Co/Al$_2$O$_3$, the performance is not determined by the number of surface metal atoms, but by the surface property of the alloy. From the comparison of the results of the activity tests (Figs. 1 and 10), Co$_2$Fe/Al$_2$O$_3$ (Fe/Co = 0.25) showed the highest activity in the steam reforming of tar.

Figure 11 shows the XRD patterns of Fe/Al$_2$O$_3$, Co/Al$_2$O$_3$ and Co$_2$Fe/Al$_2$O$_3$ after H$_2$ reduction at 773 K for 0.5 h. The peak due to Fe metal with the bcc structure was observed at 2θ 44.7° on Fe/Al$_2$O$_3$, whereas the peak due to Co metal with the fcc structure was observed at 2θ 44.28° on Co/Al$_2$O$_3$. In the case of Co$_2$Fe/Al$_2$O$_3$ (Fe/Co = 0.13-0.5), two peaks in the range of 2θ 44.0-45.3° were observed. The peak around 2θ 44.1° was gradually shifted to smaller angle with increasing Fe amount, and the intensity of the peak decreased. This peak disappeared on Co$_2$Fe/Al$_2$O$_3$ (Fe/Co = 0.75 and 1). According to previous reports, the peak at 44.1° is assigned to Co$_2$Fe solid solution alloy with the fcc structure. The other peak around 2θ 45.1° was shifted to smaller angle with increasing Fe content approaching that due to Fe metal with the bcc structure, and this peak is due to Co$_2$Fe solid solution alloy with the bcc structure on the basis of the previous reports. In the case of Ni$_2$Fe/Al$_2$O$_3$, the formation of the bcc alloy was not detected at Fe/Ni ≤ 1 (Fig. 2A), in contrast, the formation of the bcc alloy was recognized even at Fe/Co = 0.13 (Fig. 11A). This suggests that Co tends to form the bcc alloy with Fe.

Since two alloy phases were detected, we attempted to determine the composition and distribution of the alloy phases. Figure 11B shows the d-spacing of the fcc and bcc Co$_2$Fe alloy phases as a function of the composition (Fe/(Co + Fe)) on Co$_2$Al$_2$O$_3$, Fe/Al$_2$O$_3$ and Co$_2$Fe/Al$_2$O$_3$ catalysts. In order to apply the Vegard’s rule to the results, the d-spacings of bcc and fcc Co$_2$Fe alloy were calculated using the lattice constant of bcc Co metal 0.2827 nm and fcc Fe metal 0.3646 nm, as shown in Fig. 11B. From the line of Vegard’s rule and the d-spacings obtained from the experimental results in Fig. 11A, the actual compositions in the fcc and bcc Co$_2$Fe alloy phases were estimated assuming uniform composition of each phase. In addition, since all Co and Fe species are reduced to metallic species on Co$_2$Fe/Al$_2$O$_3$ catalysts after the reduction pretreatment, the distribution of Co and Fe in the fcc or bcc alloy phase could be calculated easily from the obtained composition of each phase. Figures 11C and 11D show the obtained composition (Fe/Co) of the fcc and bcc Co$_2$Fe alloy phases, and distribution of Co and Fe in each alloy phase, respectively. The Fe/Co ratio of fcc Co$_2$Fe alloy phase was lower than that on Co$_2$Fe/Al$_2$O$_3$ catalysts, whereas the Fe/Co ratio of bcc Co$_2$Fe alloy was higher than that on Co$_2$Fe/Al$_2$O$_3$. The distribution of Co and Fe in the bcc Co$_2$Fe alloy phase

\[ \text{Reaction conditions: biomass; 60 mg min}^{-1} (\text{H}_2\text{O} 7.22 \%, \text{C} 2358 \mu\text{mol min}^{-1}, \text{H} 3351 \mu\text{mol min}^{-1}, \text{O} 1454 \mu\text{mol min}^{-1}), \text{N}_2 \text{ flow rate; } 60 \text{ mL min}^{-1}, (\text{added } \text{H}_2\text{O})/\text{C} \leq 0.47 (\text{steam flow rate } 1110 \mu\text{mol min}^{-1}), T = 823 \text{ K}, W_{\text{cat}} = 0.75 \text{ g}. \]

*Fig. 10* Catalytic Performance in Steam Reforming of Tar over Co$_2$Fe/Al$_2$O$_3$ Catalysts at 823 K.
increased with increasing Fe/Co on Co–Fe/Al₂O₃ cata-
lysts. Overall, bcc Co–Fe alloy phase tended to be
formed preferentially at higher Fe/Co ratio. It should
be noted that Fe tends to give bcc alloy much preferen-
tially on Co–Fe/Al₂O₃ catalysts than on Ni–Fe/Al₂O₃
catalysts at the same molar ratio based on
Figs. 1A and 11A.

Figure 12 shows the formation rates of gaseous prod-
ucts in the steam reforming of biomass tar as a function
of time on stream over Co–Fe/Al₂O₃ (Fe/Co = 0.25) at
873 K. According to the previous report⁵², Co(12 wt%)/Al₂O₃
was deactivated after 40 min under the same reaction conditions. On the other hand, Co–Fe/Al₂O₃ (Fe/Co = 0.25) maintained the activity for
60 min. Co–Fe/Al₂O₃ (Co/Ni = 0.25) was clearly more stable than Co(12 wt%)/Al₂O₃. One possible explanation for the high stability of Co–Fe/Al₂O₃ (Fe/Co = 0.25) is the higher resistance to coke deposition.

Next, toluene steam reforming was investigated. Figure 13 shows the formation rate of the products and toluene conversion as a function of time on stream over Co–Fe/Al₂O₃ (Fe/Co = 0.25). In the absence of H₂ addi-
tion, the activity decreased significantly with increasing reaction time. Co/Al₂O₃ showed stable activity in the steam reforming of toluene without hydrogen addi-
tion (details are not shown). Under this condition, Co/Al₂O₃ gave 55.3 % toluene conversion. The steady state activity in the toluene steam reforming in the ab-

Crystalline phases: (▲) Al₂O₃, (●) Co, (□) Fe, (■) fcc Co–Fe solid solution alloy, (●) bcc Co–Fe solid solution alloy.

Fig. 11 (A) XRD Patterns of the Reduced Catalysts, (B) d-Spacing of the Peaks of Co, Fe, fcc Co–Fe and bcc Co–Fe as a Function of Fe/(Co + Fe), (C) Fe/Co in fcc and bcc Co–Fe Alloy, and (D) Amount of Co and Fe in fcc and bcc Alloy⁵³
Sence of hydrogen addition was Co Fe/Al2O3 (Fe/Co 0.25) Co/Al2O3, which was different from the order in the steam reforming of the biomass tar. The toluene conversion at the initial stage on Co Fe/Al2O3 (Fe/Co 0.25) was over 60 %, and the conversion was expected to be much higher than 60 % based on the conversion decrease during the initial 5 min. Judging from this reaction time dependence, Co Fe/Al2O3 (Fe/Co 0.25) apparently has high catalytic activity in the steam reforming of toluene. After the activity test in toluene steam reforming (Fig. 13A), the amount of the deposited coke on Co Fe/Al2O3 (Fe/Co 0.25) was determined to be 5 mg g⁻¹-cat. This coke amount is quite small, and cannot explain the deactivation of Co Fe/Al2O3 (Fe/Co 0.25). One possible reason for the deactivation is thought to be catalyst oxidation with steam. Therefore, addition of hydrogen to the reactant gas for toluene steam reforming was evaluated. The stability of Co Fe/Al2O3 (Fe/Co 0.25) was improved by hydrogen addition (Fig. 13B). After this activity test, the amount of the deposited coke on Co Fe/Al2O3 (Fe/Co 0.25) was also as small as 15 mg g⁻¹-cat, only a little higher than found in the steam reforming of toluene in the absence of hydrogen.

Figure 14 shows the XRD patterns of Co Fe/Al2O3 (Fe/Co 0.25) after reduction and steam reforming of biomass tar and toluene. After reduction, both fcc and bcc Co-Fe alloys were detected as explained above. After steam reforming of the biomass tar, the peak due to bcc Co-Fe alloy decreased and that due to fcc Co-Fe alloy slightly increased. Considering the constant activity in the steam reforming of tar (Fig. 12), oxidation of the bcc Co-Fe alloy proceeded to some extent at initial stage, and further oxidation was suppressed. The difference in the resistance to oxidation with steam between the alloy phases can be explained by the Fe/Co ratio: the content of Fe in bcc Co-Fe alloy was much higher than that in fcc Co-Fe alloy, as shown in Fig. 11C. In the case of the toluene steam reforming in the absence of H₂ addition, the peak due to bcc Co-Fe alloy disappeared (Fig. 14(c)), suggesting that fcc Co-Fe is not oxidized and bcc Co-Fe is oxidized almost completely during the reaction. Here, the obtained Fe/Co (0.18) in the fcc Co-Fe alloy was slightly higher than after the reduction (0.11). The increase of Fe/Co in the fcc Co-Fe alloy may be explained by the phase transition from the bcc Co-Fe alloy with higher Fe/Co to the fcc Co-Fe alloy with oxidation. This phenomenon indicates that preferential oxidation of Fe in the bcc Co-Fe alloy can decrease the Fe/Co in the reduced phase, and promote the phase transition to fcc Co-Fe alloy which is more stable at lower Fe/Co. The comparison between the reaction time dependence of the activity test and the XRD results after the reaction suggests that the activity of the fcc Co-Fe alloy is not high. On the other hand, after steam reforming of toluene with hydrogen addition, peaks due to both fcc and bcc Co-Fe alloy phases were maintained (Fig. 14(d)).
Here, the Fe/Co ratio was slightly increased by steam reforming of toluene in both fcc and bcc Co-Fe alloys. The oxidation of Co is preferable to that of Fe based on passivation of the surface of metal particles from extended X-ray absorption fine structure (EXAFS) analysis\(^{53}\). Therefore, the Fe/Co ratio in the alloys can be increased by preferential oxidation of Co.

Comparison of the reaction time dependence of the activity and the structure after the reaction showed that the addition of H\(_2\) to the reactant gas maintained the bcc Co-Fe alloy structure and high activity in the steam reforming of toluene. In the steam reforming of hydrocarbons, the ratio of the oxidation rate of active metal species to the reduction rate of oxidized species can determine the state of the metal species under steady-state reaction conditions. In the steam reforming of toluene without H\(_2\) addition, the reduction rate with toluene was higher than the oxidation rate with steam for the Co-rich fcc Co-Fe alloy phase, whereas the oxidation rate is higher for the Fe-rich bcc Co-Fe phase. If hydrogen was added to the reactant gas, the reduction rate was accelerated and the bcc Co-Fe alloy phase was maintained in the metallic state, and these phenomena may be related to the high reforming activity.

The reason why bcc Co-Fe alloy phase is maintained during the steam reforming of biomass tar without the addition of hydrogen may be because the tar contains more highly reactive components than toluene\(^6\), suggesting that the reduction rate with tar is much higher than that with toluene. This difference can be related to the presence of the bcc Co-Fe alloy phase after the steam reforming of tar, which can lead to higher activity of Co-Fe/Al\(_2\)O\(_3\) (Fe/Co = 0.25) than of Co/Al\(_2\)O\(_3\). Another important point is the composition of the bcc Co-Fe alloy. The bcc Co-Fe alloy phase was mainly formed on Co-Fe/Al\(_2\)O\(_3\) (Fe/Co = 0.75 and 1.0) in Fig. 11A. However, the activity of Co-Fe/Al\(_2\)O\(_3\) (Fe/Co = 0.75 and 1.0) was lower than that of Co-Fe/Al\(_2\)O\(_3\) (Fe/Co = 0.25). The composition of Fe/Co in the bcc Co-Fe alloy phase increased significantly with increasing Fe content on Co-Fe/Al\(_2\)O\(_3\). Excessively high Fe composition reduced the catalytic performance in steam reforming because Fe has very low reforming activity. However, the synergy between Co and Fe at the optimum composition can increase the reforming activity and suppress the coke deposition. This can be interpreted as the synergy between the activation of tar on the Co species and the supply of oxygen atoms to the carbonaceous intermediate from neighboring Fe atoms. Similar synergistic effects have been proposed for other systems using Ni-CeO\(_2\)\(^{26}\) and Ni-MnO\(_x\)\(^{31}\) in various reforming reactions as well as the Ni-Fe\(^{50}\) catalysts in the previous section.

At present, the composition of individual Co-Fe alloy particles cannot be uniform on Co-Fe/Al\(_2\)O\(_3\) as for Ni-Fe/Al\(_2\)O\(_3\), but bcc Co-Fe alloy with uniform composition is expected to exhibit higher performance. In particular, if uniform bcc Co-Fe becomes available, the optimum composition of the alloy can be evaluated and the reason why the surface of the bcc Co-Fe alloy has high steam reforming activity will be elucidated.

### Conclusions

In this review article, we introduce the development of Ni-Fe, Ni-Co, and Co-Fe bimetallic particles for the steam reforming of tar. The catalytic performance of the alloy particles is strongly dependent on their components, compositions, crystal structures, uniformity, and other characteristics. It is very important to optimize these parameters for the development of alloy catalysts with high catalytic performance.

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要 旨
バイオマスタールの水蒸気改質用ニッケルおよびコバルト合金触媒の開発

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バイオマス熱分解由来タールの水蒸気改質用触媒については、活性、安定性、炭素析出耐性といった観点において改良が必要とされている。ニッケルおよびコバルトは水蒸気改質反応における活性成分であることが知られている。そして、その触媒性能を向上させる有効な方法の一つが活性金属に対して、適切な異なる金属を合金化させることである。ここでは、Ni-Fe, Ni-Co, およびCo-Fe合金触媒の開発を行い、合金形成による促進効果と、合金粒子の構造との関係について紹介する。合金粒子の成分、組成、結晶構造および均一性などは合金粒子の触媒活性に大きな影響を与えることが明らかになった。特に、バイオマスタールタールの二段階反応を有する触媒を用い、二段階の反応をより効率的に進行させることが可能であることが示された。