Oxidative Steam Reforming of Methane over Ni Catalysts Modified with Noble Metals

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The effects of addition of small amounts of noble metals such as Pt, Pd, and Rh to Ni/γ-Al₂O₃ and NiO-MgO solid solutions were investigated on the catalyst activation, catalyst bed temperature profile, and carbon formation behavior in oxidative steam reforming of methane. Addition of Pt and Pd by a sequential impregnation method to Ni/γ-Al₂O₃ had a much more remarkable effect than by a co-impregnation method on the resistance to deactivation by oxidation of Ni and suppression of hot-spot formation. Temperature-programmed reduction, extended X-ray absorption fine structure, and Fourier transform infrared spectroscopy suggested that the noble metal atoms introduced by the sequential impregnation method were preferentially located on the surface to form an alloy. Addition of noble metals (Pt, Pd, and Rh) to Niₓ₋ₓMgₓO solid solution catalysts inhibited carbon formation in the oxidative steam reforming of methane under pressurized conditions.

Keywords
Oxidative steam reforming, Nickel catalyst, Noble metal, Self activation, Hot spot, Carbon deposition

1. Introduction

Sulfur-free transportation fuels produced by gas-to-liquid (GTL) processes have become very important for reasons related to the soaring petroleum price, depletion of oil reserves, and environmental problems with exhaust gases. The GTL process combines synthesis gas production from natural gas and Fischer-Tropsch synthesis from the synthesis gas. Steam reforming is the conventional method for the production of synthesis gas from natural gas, and is utilized on the industrial scale. However, conventional steam reforming is an energy-consuming process, so oxidative steam reforming of natural gas is expected to provide a more energy-efficient syngas production method.

Steam and dry reforming of methane, which is the main component of natural gas, are highly endothermic reactions, as indicated below (Eqs. (1) and (2)). Therefore, the catalyst bed has to be heated from the outside of the reactor by the combustion of hydrocarbons, for instance, methane (Eq. (3)).

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \Delta \text{H}^{\circ}_{298 \text{K}} = +206 \text{kJ} \cdot \text{mol}^{-1} \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \Delta \text{H}^{\circ}_{298 \text{K}} = +286 \text{kJ} \cdot \text{mol}^{-1} \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \Delta \text{H}^{\circ}_{298 \text{K}} = -806 \text{kJ} \cdot \text{mol}^{-1}
\end{align*}
\]

Oxidative steam reforming of methane, in which O₂ is introduced to the catalyst bed together with methane and steam, is a promising method for synthesis gas production because the reaction conditions can be adjusted by balancing exothermic combustion and endothermic reforming to an autothermal system \(^{13−18}\). Therefore, oxidative steam reforming of methane can be more energy-efficient than conventional methane steam reforming.

Oxidative steam reforming of methane over Ni catalysts suffers from the inherent problems of deactivation by oxidation of active metal species, hot-spot formation and carbon deposition. Ni metal particles are the active species for reforming reactions, Ni ions and oxidized Ni species are not active. Therefore, the presence of oxygen will eliminate the reforming activity of Ni catalysts \(^{2,4,9,10}\).

Hot-spot formation is a common problem in the reforming of hydrocarbons to synthesis gas using oxygen \(^{13−15}\), and is attributable to the combustion reaction occurring at the inlet of the catalyst bed. Noble metal catalysts such as Pt and Rh are more effective for suppression of hot-spot formation than Ni catalysts \(^{8,14,15}\). However, high loading is required for suppression of hot-spot formation \(^{16−18}\).

Carbon deposition is another problem associated with oxidative steam reforming of methane, and is common to synthesis gas production by the reforming of hydrocarbons \(^{19−24}\). The carbon is formed by decomposition of the hydrocarbons and CO disproportionation. In particular, carbon deposition becomes more serious
with higher reaction pressure$^{25)−30)}$. The deposited carbon can deactivate the catalyst, so resistance to carbon formation will enhance the catalyst stability.

One strategy for the development of catalysts for oxidative reforming of methane with high resistance to hot-spot formation and carbon deposition is the use of Ni catalysts modified with a small amount of noble metals. The high reducibility of noble metals is considered to be effective for the suppression of hot-spot formation. Furthermore, noble metal catalysts have high resistance to carbon formation in the reforming reactions, so modification with a small amount of noble metals is expected to suppress carbon deposition in the oxidative steam reforming of methane, even under high pressure conditions.

The present study investigated the effect of modification of Ni catalysts such as NiAl2O3 and NiO-MgO solid solution with noble metals on the catalyst bed temperature profile and the resistance to coke deposition in the oxidative steam reforming of methane, as well as the relationship between the catalytic performance and the structure of bimetallic particles.

2. Experimental

Oxidative steam reforming of methane was conducted under atmospheric and high pressure conditions in a fixed-bed quartz reactor$^{31)−33)}$. The reaction temperature was monitored with a chromel-alumel thermocouple located at the outlet of the catalyst bed, and was used for temperature control. The temperature profile was measured using infrared thermograph equipment through a window installed in the electric furnace. Details of the thermographical observation were reported previously$^{36)}$. Catalyst weight and pretreatment conditions are described for each of the activity tests. Flow rates are also shown as $W/F$ (W (g) = catalyst weight, $F$ (mol·h$^{-1}$) = total flow rate of gases). The partial pressure ratios of the feed gases are also shown for each test. Details of gas analyses in the activity tests were reported previously$^{31)−33)}$. The methane conversion was calculated using the equations below.

Methane conversion (%) = \( \frac{C_{\text{CO}} + C_{\text{CO}_2}}{C_{\text{CH}_4} + C_{\text{CO}} + C_{\text{CO}_2}} \times 100 \)

CO selectivity (%) = \( \frac{C_{\text{CO}}}{C_{\text{CO}} + C_{\text{CO}_2}} \times 100 \)

$C$, concentration of each gas in the effluent gas.

Catalysts and their notations are listed in Table 1. Monometallic Ni catalysts were used in the sequential impregnation method. Before the second impregnation, the monometallic Ni catalysts were reduced using H2 at 1123 K for 0.5 h. The Pt was then loaded by impregnating the Ni catalysts with acetone solution of PtC2H5OH$_2$·H2O in air. After removal of the acetone solvent, the catalyst was dried at 383 K for 12 h and calcined in air at 573 K for 3 h. Details of the catalyst preparation were reported previously, and are listed in Table 1.

Catalysts were characterized by temperature-programmed reduction (TPR), extended X-ray absorption fine structure (EXAFS), and Fourier transform infrared (FTIR) spectra of CO adsorption. The EXAFS spectra were measured at the Photon Factory of the High Energy Accelerator Research Organization in Tsukuba (Proposal No. 2006G095) and at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2006A1058, 2007A1156). The procedures for catalyst characterization were described previously$^{32)−33)}$.

3. Resistance to Oxidation of Ni Enhanced by Modification with Noble Metals$^{9)−10)34)−36}$

Figure 1 shows the effect of partial pressure of the feed gases on methane conversion over Ni(2.6), Pt(0.1), and Pt(0.1)/Ni(2.6). The gases for the combustion reaction (CH$_4$/H$_2$O = x/2x; x = 2−10), called the combustion gas, were added to the methane steam reforming feedstock (CH$_4$/H$_2$O = 30/30). Condition A corresponds to the steam reforming of methane without the addition of oxygen. Conditions B to F include increasing partial pressure of oxygen. The order of methane conversion under condition A was as follows: Ni(2.6) > Pt(0.1)/Ni(2.6) > Pt(0.1). Under this reaction condition, the equilibrium methane conversion was 92%. Methane conversion decreased drastically over Ni(2.6), and was comparable to the conversion when the combustion gas was introduced. This behavior resulted from the deactivation of Ni metal species. Methane conversion over Pt(0.1) was low in the steam reforming of methane. However, the addition of combustion gas enhanced methane conversion. Methane conversion under condition F (oxidative steam reforming) over Pt(0.1) was much higher than that over Ni(2.6). The high activity of Pt(0.1) in the oxidative steam reforming may be related to the high reducibility of Pt compared to Ni. Although methane conversion over Pt(0.1)/Ni(2.6) under condition A was between Ni(2.6) and Pt(0.1), the highest methane conversion was given by Pt(0.1)/Ni(2.6) under condition F, where the equilibrium methane conversion was 99.6%. Modification of Ni/γ-Al$_2$O$_3$ with Pt by the sequential impregnation method enhanced the oxidative steam reforming of methane through inhibition of Ni oxidation.

Figure 2 shows the contact-time ($W/F$) dependence for methane conversion in the oxidative steam reforming of methane over Ni$_{0.2}$Mg$_{0.8}$O, 0.035%Rh/Ni$_{0.2}$Mg$_{0.8}$O and 0.035%Rh/MgO catalysts. In these experiments, $W/F$ first decreased stepwise from 1.2 to 0.1 g·h·mol$^{-1}$, and increased. Hysteresis of catalytic performance was observed over Ni$_{0.2}$Mg$_{0.8}$O in the oxidative steam.
Table 1 Catalysts and Catalyst Properties

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support material [BET surface area/m² g⁻¹]</th>
<th>Preparation methoda</th>
<th>Precursor</th>
<th>Composition</th>
<th>Noble metal</th>
<th>Reduction of N₂b [%]</th>
<th>Molar ratio of noble metals to Nib</th>
<th>Mean metal particle size [nm]c</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(0.1)/Ni(2.6)</td>
<td>Si</td>
<td>Ni(NO₃)₂, Pt(acac)₂</td>
<td>2.6</td>
<td>0.45</td>
<td>0.1</td>
<td>0.45</td>
<td>100</td>
<td>0.01</td>
<td>5.0 ± 0.4</td>
</tr>
<tr>
<td>Pt(0.1) + Ni(2.6)</td>
<td>Cl</td>
<td>Ni(NO₃)₂, H₂PtCl₆</td>
<td>2.6</td>
<td>0.45</td>
<td>0.1</td>
<td>0.45</td>
<td>100</td>
<td>0.01</td>
<td>4.5 ± 0.4</td>
</tr>
<tr>
<td>Pt(0.1)</td>
<td>I</td>
<td>H₂PtCl₆</td>
<td>—</td>
<td>—</td>
<td>0.1</td>
<td>0.45</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni(2.6)</td>
<td>I</td>
<td>Ni(NO₃)₂</td>
<td>2.6</td>
<td>0.45</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>100</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt(0.2)/Ni(0.9)</td>
<td>Si</td>
<td>Ni(NO₃)₂, Pt(acac)₂</td>
<td>0.9</td>
<td>0.15</td>
<td>0.2</td>
<td>0.9</td>
<td>100</td>
<td>0.06</td>
<td>—</td>
</tr>
<tr>
<td>Pt(0.2) + Ni(0.9)</td>
<td>γ-Al₂O₃ (110)</td>
<td>Ni(NO₃)₂, H₂PtCl₆</td>
<td>0.9</td>
<td>0.15</td>
<td>0.2</td>
<td>0.9</td>
<td>100</td>
<td>0.06</td>
<td>—</td>
</tr>
<tr>
<td>Pt(0.05)/Ni(2.6)</td>
<td>Si</td>
<td>Ni(NO₃)₂, Pd(acac)₂</td>
<td>2.6</td>
<td>0.45</td>
<td>0.05</td>
<td>0.45</td>
<td>100</td>
<td>0.01</td>
<td>8.1 ± 0.4</td>
</tr>
<tr>
<td>Pt(0.05) + Ni(2.6)</td>
<td>Cl</td>
<td>Ni(NO₃)₂, PdCl₆</td>
<td>2.6</td>
<td>0.45</td>
<td>0.05</td>
<td>0.45</td>
<td>100</td>
<td>0.01</td>
<td>4.8 ± 0.4</td>
</tr>
<tr>
<td>Pt(0.1)/Ni(0.9)</td>
<td>Si</td>
<td>Ni(NO₃)₂, Pd(acac)₂</td>
<td>0.9</td>
<td>0.45</td>
<td>0.1</td>
<td>0.9</td>
<td>100</td>
<td>0.06</td>
<td>—</td>
</tr>
<tr>
<td>Pt(0.1) + Ni(0.9)</td>
<td>Cl</td>
<td>Ni(NO₃)₂, PdCl₆</td>
<td>0.9</td>
<td>0.45</td>
<td>0.1</td>
<td>0.9</td>
<td>100</td>
<td>0.06</td>
<td>—</td>
</tr>
<tr>
<td>Pt(0.05)</td>
<td>I</td>
<td>PdCl₆</td>
<td>—</td>
<td>—</td>
<td>0.05</td>
<td>0.45</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni₉₂Mg₂₀O</td>
<td>I</td>
<td>—</td>
<td>—</td>
<td>4.2</td>
<td>—</td>
<td>—</td>
<td>3.4</td>
<td>0.0</td>
<td>6.2 ± 0.5</td>
</tr>
<tr>
<td>RhNi₉₂Mg₂₀O</td>
<td>I</td>
<td>Rh(NO₃)₃</td>
<td>—</td>
<td>—</td>
<td>4.2</td>
<td>0.035</td>
<td>0.34</td>
<td>6.4</td>
<td>0.001</td>
</tr>
<tr>
<td>PrNi₉₂Mg₂₀O</td>
<td>I</td>
<td>Pr(NO₃)₂(NH₄)₂</td>
<td>—</td>
<td>—</td>
<td>4.2</td>
<td>0.1</td>
<td>0.51</td>
<td>3.4</td>
<td>0.004</td>
</tr>
<tr>
<td>PdNi₉₂Mg₂₀O</td>
<td>I</td>
<td>Pd(NO₃)₂</td>
<td>—</td>
<td>—</td>
<td>4.2</td>
<td>0.1</td>
<td>0.94</td>
<td>4.8</td>
<td>0.005</td>
</tr>
<tr>
<td>PdNi₉₂Mg₂₀O</td>
<td>I</td>
<td>Pd(NO₃)₂</td>
<td>—</td>
<td>—</td>
<td>4.2</td>
<td>0.5</td>
<td>4.7</td>
<td>5.6</td>
<td>0.02</td>
</tr>
<tr>
<td>RhMgO</td>
<td>I</td>
<td>Rh(NO₃)₃</td>
<td>—</td>
<td>—</td>
<td>0.035</td>
<td>0.34</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PrMgO</td>
<td>I</td>
<td>Pr(NO₃)₂(NH₄)₂</td>
<td>—</td>
<td>—</td>
<td>0.1</td>
<td>0.51</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>PdMgO</td>
<td>I</td>
<td>Pd(NO₃)₂</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
<td>4.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a) Si: Sequential impregnation, Cl: Co-impregnation, I: Impregnation
b) Based on temperature-programmed reduction with hydrogen. c) TEM observation
reforming of methane, probably reflecting deactivation caused by the oxidation of Ni metal species under low W/F conditions. On the other hand, no hysteresis was observed over Rh/NiO-MgO and Rh/MgO. Another important point is that Rh/NiO-MgO provided much higher conversion than NiO-MgO and Rh/MgO, particularly under low W/F conditions. One of the additive effects of Rh is enhancement of the reduction of Ni species in NiO-MgO, as listed in Table 2. This promoting effect is also observed in methane reforming over the NiO-MgO solid solution catalysts. However, the observed difference in the activity at low W/F is too large to be explained by only enhancement of the reduction of Ni species. Similar behaviors were also observed in the cases of Pt and Pd additions. These results indicate that the synergy between Rh and NiO-MgO can contribute to the inhibition of oxidation deactivation.

Figure 3 shows oxidative reforming at increasing reaction temperature over 0.1% Pt/NiO-MgO, 0.1% Pt/MgO, and NiO-MgO without H2 pretreatment. In this experiment, the catalyst was first heated at 773 K under Ar flow; then the reactant gas (CH4/H2/O2 = 40/30/20) was introduced at 773 K. The catalyst was then heated stepwise to 1073 K at 50 K intervals. The reaction was observed for 30 min at each temperature. In the case of 0.1% Pt/NiO-MgO, the methane conversion was 25% at 773 K and the main carbon-containing product was CO2, indicating that only the methane combustion reaction proceeded. The methane conversion increased with reaction temperatures higher than 773 K, at which the reforming reaction yielded CO and H2. In contrast, in the case of 0.1% Pt/MgO, the methane conversion was much lower than 25% at 773-973 K. This behavior indicates that 0.1% Pt/MgO has much lower activity for the combustion and reforming of methane, although the methane conversion reached about 50% at 1023 K. In addition, NiO-MgO without H2 reduction showed much lower activity than 0.1% Pt/NiO-MgO and 0.1% Pt/MgO. The interesting point here is that addition of Pt to NiO-MgO enhanced the activity for oxidative reforming of methane without activation by the H2 reduction pretreatment. This finding can be explained by the self-activation mechanism, in which the active metal species are formed by reduction with the oxidative steam reforming feed gases at low temperatures such as 823 K. This function can be related to the high combustion activity and the high reducibility of the catalyst. This self-activation effect is promoted by the addition of noble metals.

We found that Ni catalysts were deactivated by the oxidation, but Ni catalysts modified with noble metals showed high resistance to such deactivation. In addition, modification with noble metals enabled the activation of Ni by the reactants and products such as CH4, CO, and H2 formed in the oxidative steam reforming of methane.
4. Suppression of Carbon Formation through Modification with Noble Metals\(^{40,53,41,42}\)

Synthesis gas production by natural gas reforming in the gas-to-liquid process is normally operated on the industrial scale under pressurized conditions. Therefore, catalytic performance must be evaluated under pressurized conditions, under which catalyst deactivation caused by carbon deposition proceeds more easily. The carbon formation rate increased drastically with increased reaction pressure\(^{29-30}\). In fact, carbon deposition was not detected over the catalysts by activity tests at atmospheric pressure. Recently, we found that no carbon was deposited and no deactivation was observed on 0.035% Rh and 0.1% Pt modified Ni\(_{0.2}\)Mg\(_{0.8}\)O catalysts even after reaction for 8 h under pressurized conditions (1.0 MPa) at 973 K. Moreover, 0.035% Rh/MgO and 0.1% Pt/MgO showed no carbon deposition or deactivation\(^{40}\). These findings indicate that modification of Ni catalysts with Rh and Pt is very effective for the inhibition of the carbon deposition. The behaviors of Pt-modified catalysts are different to those of catalysts modified with Rh or Pt because the resistance to carbon deposition of Pt/MgO was very low. However, Pd/Ni\(_{0.2}\)Mg\(_{0.8}\)O with suitable Pd loading exhibited much higher resistance compared with Ni\(_{0.2}\)Mg\(_{0.8}\)O and Pd/MgO.

Figure 4 shows the relationship between carbon deposition and deactivation in the oxidative steam reforming of methane over Pd/Ni\(_{0.2}\)Mg\(_{0.8}\)O and reference catalysts with various amounts of Pd loading. The amount of deposited carbon was determined from the weight decrease in air flow by thermogravimetric analysis of the used catalysts for 8 h\(^{13}\). The deactivation rate is defined as follows: \(\frac{([\text{CH}_4 \text{ conv. at 0.5 h}) - ([\text{CH}_4 \text{ conv. at 8 h}])/[\text{CH}_4 \text{ conv. at 0.5 h}] \times 100 \%}{\text{Pd loading amount}}\). The results showed that catalysts with larger amounts of the carbon deposition tended to have higher deactivation rates. Here, the important point is that 0.1% Pd/Ni\(_{0.2}\)Mg\(_{0.8}\)O shows almost no carbon formation and deactivation, which indicates that the catalyst has high resistance to carbon formation. This result is contrary to the findings for 0.1% Pd/MgO and Ni\(_{0.2}\)Mg\(_{0.8}\)O. The mean particle size of Ni was estimated to be 7.6 ± 0.6, 6.2 ± 0.5 and 4.7 ± 0.5 nm in 0.5% Pd/Ni\(_{0.2}\)Mg\(_{0.8}\)O, Ni\(_{0.2}\)Mg\(_{0.8}\)O and 0.1% Pd/Ni\(_{0.2}\)Mg\(_{0.8}\)O, respectively (Table 1). The differences in metal particle size are quite small, so cannot explain the resistance to carbon deposition. The interaction between the Pd and Ni species is thought to contribute to the suppression of carbon formation. Formation of the Pd–Ni alloy may occur in the Pd-modified catalysts, and the difference in the surface composition of the alloy consequently affects the performance \((\text{vide infra})\).

Figure 5 shows the relationship between carbon deposition and deactivation rate in the steam reforming, dry reforming, and oxidative steam reforming of methane. The amount of carbon deposition was in the order of dry reforming > steam reforming > oxidative

\[\begin{align*}
\text{CH}_4 + H_2O &\rightarrow \text{CO} + 3 \text{H}_2 \\
\text{Pt} &\rightarrow \text{Pt} + e^- \\
\end{align*}\]
reforming of methane. Although 0.1% Pd/NiO2MgO containing about 10 wt% of carbon deposits after the dry and steam reforming, this value was much smaller than that of NiO2MgO and 0.1% Pd/MgO. 0.1% Pd/NiO2MgO is characterized by complete suppression of carbon deposition in the oxidative reforming of methane even under pressurized conditions. Modification of NiO2MgO with Pd is also effective for the suppression of carbon deposition in the oxidative steam reforming of methane under pressurized conditions.

5. Suppression of Hot-spot Formation through Modification with Noble Metals

The formation of synthesis gas in conventional steam reforming of methane is limited by the rate of external heat supply. In contrast, oxidative steam reforming of methane can be operated at higher feed rates because the oxidative steam reforming of methane provides an internal heat supply. On the other hand, hot-spot formation becomes more serious at higher feed rates. Therefore, suppression of hot-spot formation will help to increase productivity.

Table 2 compares steam reforming of methane and oxidative steam reforming of methane over Pt(0.1)/Ni(2.6), Pt(0.1) + Ni(2.6) and reference catalysts. The order of catalytic activity in the steam reforming of methane was: Ni(2.6) > Pt(0.1) + Ni(2.6) > Pt(0.1)/Ni(2.6) > Pt(0.1); which is greatly different to the order for oxidative steam reforming of methane: Pt(0.1)/Ni(2.6) > Pt(0.1) + Ni(2.6) > Ni(2.6) > Pt(0.1). Pt(0.1)/Ni(2.6) showed the highest activity in oxidative steam reforming reaction, despite lower activity in conventional steam reforming without oxygen. This finding probably reflects the decrease in reforming activity resulting from the presence of oxygen over Ni(2.6) and Pt(0.1) + Ni(2.6), mainly because of the oxidation of Ni. In contrast, the activity was maintained even under the presence of oxygen over Pt(0.1)/Ni(2.6), with high resistance to oxidation as described above (Fig. 1).

Figure 6 shows the temperature profile of the catalyst bed in the oxidative steam reforming of methane. A very high temperature region at the inlet of the catalyst bed and a much lower temperature region in the downstream were observed over Ni(2.6). This large temperature gradient is due to the separation of the

Table 2 Catalytic Performance of Ni(2.6), Pt(0.1) and Corresponding Bimetallic Catalysts in Steam Reforming of Methane and Oxidative Steam Reforming of Methane

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>CH₄ conversion [%]</th>
<th>CO selectivity [%]</th>
<th>H₂/CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming</td>
<td>Pt(0.1)/Ni(2.6)</td>
<td>41</td>
<td>68</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>Pt(0.1) + Ni(2.6)</td>
<td>55</td>
<td>80</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>Ni(2.6)</td>
<td>58</td>
<td>82</td>
<td>3.9</td>
</tr>
<tr>
<td></td>
<td>Pt(0.1)</td>
<td>32</td>
<td>60</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>Equilibrium</td>
<td>87</td>
<td>96</td>
<td>3.2</td>
</tr>
<tr>
<td>Oxidative steam</td>
<td>Pt(0.1)/Ni(2.6)</td>
<td>&gt;99</td>
<td>82</td>
<td>2.7</td>
</tr>
<tr>
<td>reforming</td>
<td>Pt(0.1) + Ni(2.6)</td>
<td>&gt;99</td>
<td>81</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Ni(2.6)</td>
<td>&gt;99</td>
<td>81</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Pt(0.1)</td>
<td>87</td>
<td>79</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Equilibrium</td>
<td>&gt;99</td>
<td>81</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Reaction conditions: CH₄/H₂O/O₂/Ar = 30/30/0/40, temperature 1023 K for steam reforming; CH₄/H₂O/O₂/Ar = 40/30/20/10, temperature 1123 K for oxidative steam reforming; total pressure 0.1 MPa; catalyst weight 0.08 g; H₂ pretreatment 1123 K, w/F = 0.16 g·h·mol⁻¹.

Fig. 5 Relationship between Carbon Deposition and Deactivation Rate in Steam Reforming (CH₄/H₂O = 1/1), Dry Reforming (CH₄/CO₂ = 1/1) and Oxidative Steam Reforming (CH₄/H₂O/O₂ = 40/30/20) of Methane under High Pressure Conditions

![Graph showing relationship between carbon deposition and deactivation rate](image-url)
combustion and reforming reaction zones, which will be explained below. Pt(0.1) exhibited a flatter temperature profile than Ni(2.6). However, the temperature at the inlet was rather high. The temperature profile over Pt(0.1) + Ni(2.6) catalyst was similar to that over Ni(2.6), which indicates that the additive effect of Pt introduced by the co-impregnation method is small. In contrast, the temperature gradient over the Pt(0.1)/Ni(2.6) was much smaller than for the other three catalysts, which indicates that the additive effect of Pt introduced by the sequential impregnation method is remarkable. The additive effect of Pt can also be strongly dependent on the preparation method. 

**Figure 7** shows the highest temperature of the catalyst bed and the methane conversion in the oxidative steam reforming of methane over Pt-Ni, Pd-Ni, and corresponding monometallic catalysts. Pd(0.05) showed low methane conversion and high catalyst bed temperature; indicating that Pd(0.05) had high combustion activity and low reforming activity. The highest temperature over Pd(0.05) + Ni(2.6) was almost identical to that over Ni(2.6). In contrast, the highest temperature over Pd(0.05)/Ni(2.6) was much lower than those over Ni(2.6), Pd(0.05) and Pd(0.05) + Ni(2.6). The similarity between Pt and Pd suggests that hot-spot formation is suppressed mainly by the common properties of Pt and Pd such as high reducibility. This is supported by the different catalytic activities of Pt and Pd in the combustion and reforming reactions.

The TPR profiles of the catalyst near the inlet and outlet were obtained to elucidate the dependence of the catalyst oxidation state on the position in the catalyst bed. In this experiment, the catalyst was purged with Ar after the reaction treatment (CH\textsubscript{4}/H\textsubscript{2}O/O\textsubscript{2}/Ar = 40/30/20/10; reaction temperature 1123 K; total pressure 0.1 MPa; catalyst weight 0.08 g; H\textsubscript{2} pretreatment 1123 K). 

**Figure 7** Highest Temperatures of the Catalyst Beds and Methane Conversions in the Oxidative Steam Reforming of Methane over Various Catalysts at W/F = 0.07 g·h·mol\textsuperscript{-1}
Fig. 8 Temperature-programmed Reduction (TPR) Profiles for the Catalysts Located at the Inlet and Outlet of the Catalyst Bed after Oxidative Steam Reforming of Methane over Ni(2.6), Pt(0.1) + Ni(2.6) and Pt(0.1)/Ni(2.6)

Fig. 9 Hot-spot Formation Mechanism on Ni Catalysts (a) and Suppression Mechanism of Hot-spot Formation on Ni Catalysts Modified with Pt and Pd by the Sequential Impregnation Method (b)

The introduction of Pt by sequential impregnation method greatly increased the amount of reduced Ni at the catalyst bed inlet, even in the presence of gas-phase O₂ during the oxidative steam reforming of methane. The TPR profiles demonstrate that the reducibility of Pt-Ni bimetallic catalysts and the resistance to Ni oxidation are strongly influenced by the preparation method.

Figure 9 depicts the hot-spot formation and suppression mechanisms on Ni catalysts modified with Pt and Pd. A large temperature gradient was observed over Ni catalysts in the oxidative steam reforming of methane. Figure 8 shows that most Ni species were oxidized in the presence of oxygen at the catalyst bed inlet, because the rate of Ni oxidation by O₂ was much higher than the rate of reduction of the oxidized Ni species with reducing agents such as CH₄, CO, and H₂. Consequently, the oxidized Ni species lost reforming activity and only had combustion activity. Therefore, at the inlet of the catalyst bed, only the exothermic reaction proceeded, which increased the catalyst bed temperature. On the other hand, at the outlet of the catalyst bed where no oxygen was present, the Ni species remained in the metallic state; so the Ni species still had reforming activity. In this reaction zone, only the endothermic reaction proceeded and the catalyst bed temperature decreased, resulting in a large temperature gradient. In contrast, over the Pt/Ni and Pd/Ni catalysts, the ratios of the reduced to the oxidized species were much higher because of the modification effect in the presence of oxygen. In particular, the reduced species also acted as active sites for methane reforming as well as combustion even in the presence of oxygen. Therefore, the reforming reaction helps to reduce the temperature decrease at the inlet of the catalyst bed.
### Table 3 Curve-fitting Results of Pt L$_2$-edge and Pd K-edge EXAFS of Various Catalysts after Reduction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shell</th>
<th>C.N. $^a$</th>
<th>R (10$^{-1}$ nm)$^b$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(0.2) + Ni(0.9)</td>
<td>Pt-Pt</td>
<td>3.7</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-Ni</td>
<td>4.5</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Pt(0.2)/Ni(0.9)</td>
<td>Pt Pt</td>
<td>2.8</td>
<td>2.65</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>Pt Ni</td>
<td>4.3</td>
<td>2.52</td>
<td></td>
</tr>
<tr>
<td>Pt(0.2)</td>
<td>Pt Pt</td>
<td>10.5</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>Pd(0.1) + Ni(0.9)</td>
<td>Pd-Ni</td>
<td>7.1</td>
<td>2.54</td>
<td>31</td>
</tr>
<tr>
<td>Pd(0.1)/Ni(0.9)</td>
<td>Pd-Pd</td>
<td>2.5</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd Ni</td>
<td>5.4</td>
<td>2.53</td>
<td></td>
</tr>
<tr>
<td>0.5% Pd/MgO</td>
<td>Pd Pd</td>
<td>8.0</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>0.5% Pd/Ni$<em>{0.2}$Mg$</em>{0.8}$O</td>
<td>Pd Pd</td>
<td>8.6</td>
<td>2.71</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Pd-Ni</td>
<td>2.7</td>
<td>2.55</td>
<td></td>
</tr>
</tbody>
</table>

$a$ Coordination number. $b$ Bond distance.

### Table 4 Curve-fitting Results of Ni K-edge EXAFS of Various Catalysts after Reduction and Passivation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pretreatment</th>
<th>Shell</th>
<th>C.N. $^a$</th>
<th>R (10$^{-1}$ nm)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(0.9)</td>
<td>reduction</td>
<td>Ni-Ni</td>
<td>11.1</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>passivation</td>
<td>Ni-Ni</td>
<td>10.5</td>
<td>2.49</td>
</tr>
<tr>
<td>Pt(0.2) + Ni(0.9)</td>
<td>reduction</td>
<td>Ni Ni</td>
<td>10.2</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>passivation</td>
<td>Ni Ni</td>
<td>8.5</td>
<td>2.49</td>
</tr>
<tr>
<td>Pt(0.2)/Ni(0.9)</td>
<td>reduction</td>
<td>Ni Ni</td>
<td>10.3</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>passivation</td>
<td>Ni-Ni</td>
<td>10.3</td>
<td>2.50</td>
</tr>
<tr>
<td>Ni foil</td>
<td></td>
<td>Ni-Ni</td>
<td>12</td>
<td>2.49</td>
</tr>
</tbody>
</table>

Sample pretreatment: reduction (H$_2$, 1127 K, 0.5 h), passivation (0.5% O$_2$, 298 K, 1 h) after reduction. $a$ Coordination number. $b$ Bond distance.

### 6. Characterization of Ni Metal Particles Modified with Noble Metals$^{(1),(3),(33),(42)}$

The local structure was investigated by EXAFS analysis to evaluate the interaction of the noble metals with Ni. Table 3 lists the curve-fitting results of Pt L$_2$-edge and Pd K-edge EXAFS for various catalysts. Catalysts with different composition from the catalysts described above were used for EXAFS measurement to obtain spectra with high S/N ratios. We confirmed that these catalysts exhibited similar catalytic performances to the corresponding ones used in the experiments. The spectra of Pt(0.2) + Ni(0.9) and Pt(0.2)/Ni(0.9) could be fitted to the Pt-Pt and Pt-Ni bonds. The bond lengths of Pt-Pt and Pt-Ni were much shorter than those of the Pt and Ni intermetallic compounds (NiPt and Ni$_2$Pt$^6$). This disagreement indicates that the intermetallic compounds (NiPt and Ni$_2$Pt) were not formed on the catalysts. The bond length of Pt-Ni was nearly equal to that of Ni-Ni obtained from the Ni K-edge EXAFS results (0.249 nm). In addition, the bond lengths of Pt-Pt in Pt(0.2) + Ni(0.9) and Pt(0.2)/Ni(0.9) were shorter than those in Pt(0.2) and Pt foil (0.277 nm). These results suggest the formation of a Pt-Ni alloy phase. The Pt atoms partly substitute for Ni atoms in the Ni metal phase.

Curve-fitting results of Pd K-edge EXAFS for Pd(0.1) + Ni(0.9) and Pd(0.1)/Ni(0.9) are also listed in Table 3. The spectrum of Pd(0.1) + Ni(0.9) after reduction could be fitted only to the Pd-Ni bond. The bond length of Pd-Ni was nearly equal to that of the Ni-Ni bond (0.249 nm). On the other hand, the spectrum of Pd(0.1)/Ni(0.9) could be fitted to the Pd-Pd and Pd-Ni bonds. In contrast to the Pt-Ni catalysts, the bond length of the Pd-Pd bond on Pd(0.1)/Ni(0.9) was close to that of Pd foil (0.272 nm), which suggests that part of the Pd was present as Pd metal particles, although most of the Pd species were present as Pd-Ni alloy, judging from the coordination number of the Pd-Pd and Pd-Ni bonds. Formation of the Pd-Ni alloy was also suggested by a previous study$^{(3)}$. Similar tendency of the bond length of the Pd-Pd and Pd-Ni bonds was observed for 0.5% Pd/Ni$_{0.2}$Mg$_{0.8}$O. However, the contribution of the Pd-Pd bond for Pd/Ni$_{0.2}$Mg$_{0.8}$O was much larger than that of the Pd-Ni bond, which may explain the large amount of carbon deposition on 0.5% Pd/Ni$_{0.2}$Mg$_{0.8}$O in the oxidative steam reforming of methane under high pressure conditions.

The structure of the bimetallic particles was also investigated with Ni K-edge EXAFS analysis. Table 4 lists the curve-fitting results of Ni K-edge EXAFS for...
Ni(0.9), Pt(0.2) + Ni(0.9) and Pt(0.2)/Ni(0.9). The EXAFS spectra were measured after passivation and reduction pretreatments. The passivation was carried out using 0.5% O₂ in He, which corresponds to the superficial oxidation of metal particles. No contribution of Ni-Pt was not detected in the curve fitting analysis in Pt(0.2) + Ni(0.9) and Pt(0.2)/Ni(0.9), which was attributed to the low molar ratio of Pt to Ni (Pt/Ni = 0.06). The coordination number of the Ni-Ni bond over Ni(0.9) and Pt(0.2) + Ni(0.9) decreased after the passivation pretreatment, because of the oxidation of Ni metal and the breakage of the Ni-Ni bond. In these cases, no contribution of Ni-O was detected, even after the passivation, possibly due to the superficial oxidation, not to the deep oxidation of the Ni metal particles. In contrast, the coordination number over Pt(0.2)/Ni(0.9) after the passivation was almost equal to that after the reduction, indicating that oxygen was not accessible to the Ni species over Pt(0.2)/Ni(0.9). This phenomenon is interpreted as surface segregation of Pt atoms prepared by the sequential impregnation method. A similar tendency was also observed for Pd(0.1)/Ni(0.9)\(^{[51]}\). The FTIR spectra of CO adsorption also supported this characteristic property, which is caused by the sequential impregnation method.

The FTIR spectra of CO adsorption were measured to characterize the surface properties of Pt-Ni bimetallic particles, as shown in Fig. 10. The bands at 2070 cm\(^{-1}\) and 2050 cm\(^{-1}\) on Ni(2.6) were attributed to linear CO on Ni metal, the band at about 1930 cm\(^{-1}\) to bridge CO. Only one band at 2070 cm\(^{-1}\) was observed on Pt(0.1), which was assigned to linear CO. Two broad bands at 2070 and 2048 cm\(^{-1}\) with similar intensity were observed for Pt(0.1) + Ni(2.6). The bands resembled those of Ni(2.6) catalyst. In contrast, the intensity of the 2070 cm\(^{-1}\) band was much stronger than that of the 2048 cm\(^{-1}\) band for Pt(0.1)/Ni(2.6). The differences in spectra between Pt(0.1)/Ni(2.6) and Ni(2.6) were attributed to the peak intensity at 2070 cm\(^{-1}\), which can be caused by linear CO on Pt. Judging from the FTIR of CO adsorption, the Pt atoms were preferentially located on the surface of metal particles of the catalyst prepared by the sequential impregnation method. This tendency is also reflected in the Ni K-edge EXAFS results. The main implication is that the sequential impregnation method is more effective than the co-impregnation method in terms of surface modification, particularly with a small amount of Pt. The combination of EXAFS and FTIR results suggests that the Pt atoms were segregated on the surface of the Pt-Ni alloy particles, as illustrated in Fig. 10.

The results of catalyst characterization suggested that noble metal-Ni bimetallic particles with higher surface compositions of the noble metal provide higher performance in the oxidative steam reforming of methane. The effects of surface modification with noble metals on the resistance to the oxidation of Ni and the suppression of hot-spot formation are thought to be kinetic, because the products of oxidative steam reforming of methane can reduce the oxidized Ni species on the bimetallic catalysts. In fact, the ratio of the reduced to the oxidized Ni species strongly depended on the reduction rate of the oxidized species and the oxidation rate of the reduced species. The shift of the H₂ consumption peak to lower temperatures in TPR profiles (Fig. 8) indicated that Pt modification enhanced the reduction rate of the Ni species, which was interpreted as the hydrogen spillover effect\(^{[50,53]}\), of noble metals. Moreover, the much smaller sticking probability of O₂ on the Pt surface\(^{[52,53]}\) than on the Ni surface\(^{[54,55]}\) suggested that the oxidation rate of Ni\(^{\text{III}}\) was decreased on the noble-metal modified Ni surface. Therefore, the reduction rate of the oxidized Ni species was increased, whereas the oxidation rate of Ni\(^{\text{III}}\) species was decreased by the modification of the Ni surface with noble metals. In particular, the reduced species acted as the active site for methane reforming as well as combustion, even in the presence of oxygen, and the reforming reaction helped to decrease the temperature at the inlet of catalyst bed and suppress hot-spot formation. Furthermore, the modification of Ni catalysts with noble metals is effective for suppression of carbon formation in the oxidative steam reforming of methane under high pressure conditions. Noble metals such as Pt and Rh have higher resistance to carbon formation than Ni. The additive effect of Pt and Rh could be explained by the properties of the modifiers, but not for Pd. Ni\(_{0.2}\)Mg\(_{0.8}\)O catalyst modified with a suitable amount of Pd exhibited much higher resistance to carbon formation than Ni\(_{0.2}\)Mg\(_{0.8}\)O and Pd/MgO with the same amount of Pd. In this case, the high resistance could not be explained by the properties of Pd. At present, the mechanism of Pd-Ni synergy to the suppression of the carbon formation remains unclear.
Conclusions

The present study found that Ni catalysts modified with small amounts of noble metals such as Pt, Pd and Rh show reduced deactivation by oxidation of the Ni species, suppress hot-spot formation, and have higher resistance to carbon formation in the oxidative steam reforming of methane. The performance of the catalysts modified with noble metals strongly depends on the preparation method, which strongly influences the structure of the bimetallic particles. Addition of a small amount of noble metals by the sequential impregnation method resulted in the formation of segregated noble metal atoms on the surface of the bimetallic particles, indicating the sequential impregnation method is more suitable than the co-impregnation method. The results demonstrated structural control of the Ni and noble metal bimetallic particles and design of high performance catalysts with excellent deactivation, carbon deposition, and hot-spot formation characteristics.

Acknowledgments

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References

要  旨

貴金属修飾ニッケル触媒によるメタンの酸化的水蒸気改質反応

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アルミナ担持ニッケル触媒およびニッケル マグネシア固溶体触媒によるメタンの酸化的水蒸気改質反応において、微量貴金属（Pt, Pd, Rh）の添加が触媒の活性化、触媒層温度分布、炭素析出挙動に与える効果を検討した。逐次含浸法で調製したPtおよびPd修飾NiAl2O3触媒は、共含浸法で調製した触媒と比較して、触媒の酸化による劣化の抑制やホットスポット生成の抑制に対して顕著な効果を示した。昇温水分還元、広域X線吸収法および原子間相互作用、フェライト構造、蒸発光度分析法などの結果、逐次含浸法で導入された貴金属は金属微粒子の表面に偏析した表面合金を形成していることが分かった。貴金属で表面修飾したニッケルマグネシア固溶体は、加圧条件下における酸化的水蒸気改質反応においても高い炭素析出耐性を示すことを示した。