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Effect of Ru and Pt Addition over Plate-type Catalysts for Methane Steam Reforming during Daily Start-up and Shut-down

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A plate-type anodic-alumina-supported 17.9 wt % Ni catalyst quickly deactivated in daily start-up and shut-down (DSS) steam reforming of methane at 700 °C. When 0.05 wt % Ru or Pt was doped, the catalyst exhibited self-activation, self-regeneration, and self-redispersion. The Pt–Ni catalyst showed better stability than Ru–Ni. A wave-shape Pt–Ni catalyst was prepared, while 3000 h continual and 500-time DSS stability was achieved. Nevertheless, for industrial application, some effort should be made to suppress the catalyst sintering.

A plate-type anodic-alumina-supported alumite Ni catalyst, 17.9 wt % Ni/Al_2O_3/alloy, was prepared in our previous research[1] for steam reforming of methane (SRM) at 700 °C, $F/W = 157000\,mL\,h^{-1}\,g_{cat}{}^{-1}$. Although an excellent continual activity was shown while no deactivation was evidenced over 100 h, this catalyst deactivated entirely during the steam-purge DSS SRM.[2] Our previous research[2] showed that the steam purge at 700 °C resulted in Ni sintering and oxidation and that a re-reduction with H_2 was required to regenerate the catalyst. In order to suppress Ni oxidation and sintering in DSS SRM, Ni catalysts are always modified with noble metal such Ru and Pt in view of their hydrogen spillover function.[3–6]

In this study, the influence of Ru and Pt doping on the Ni catalyst during DSS SRM reactivity was investigated. It was found that the 0.079 wt % Ru or Pt doped 17.9 wt % Ni/Al_2O_3/alloy catalyst showed stable activity during 400–700 °C steam-purge DSS SRM, while prereduction with H_2 was not necessary. Further, it was found that the Pt-doped Ni catalyst showed better steam-purge resistance, because the Pt–Ni catalyst could even recover reactivity under 800 and 900 °C steam-purge DSS SRM. Furthermore, with the cooperation of TOKYO GAS Co., Ltd., a wave-shape Pt–Ni catalyst was fabricated to investigate its application possibility in fuel cells. The result demonstrated 3000 h continual and 500-time DSS SRM stability over this catalyst at 680 °C, $F/W = 34000\,mL\,h^{-1}\,g_{cat}{}^{-1}$ with the 13 A city gas in Japan.

A commercial plate Al/Cr–Ni–alloy/Al clad base material was used to prepare the alumite catalysts.[1] The 17.9 wt % Ni/Al_2O_3/alloy was prepared by impregnation with $Ni(NO_3)_2 \cdot 6H_2O$ precursor.[1] Ru was doped by impregnating Ni catalyst with $RuCl_3$ solution, while Pt was doped with H_2PtCl_6 solution. The impregnated samples were dried at 120 °C overnight and calcined at 500 °C for 3 h. As control, 0.079 wt % Ru and Pt catalysts were also prepared by impregnation. These catalysts were simply designated as Ni, Ru, Pt, Ru–Ni, and Pt–Ni catalysts.

Metal loadings were analyzed with an inductively coupled plasma spectrometer (ICPS-7510, Shimadzu Corp.) and reported here based on alumina quantity. The morphology of the catalysts was examined by field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Ltd.). H_2-TPR with 65% H_2/Ar analysis was performed on a ChemBET 3000 (Quantachrome Instruments, Co.). Thermogravimety (TG) (TGA-51, SHIMADZU Corporation) was used to investigate the mechanism of methane decomposition over the catalysts. After prereduction with hydrogen, the sample was heated from room temperature to 200 °C in $50\,mL\,min^{-1}$ CH_4 gas with a heating rate of $10\,°C\,min^{-1}$. The sample was kept at 200 °C for 1 h to remove adsorbed H_2O and other gases on the sample, and then the temperature was increased to 700 °C by $10\,°C\,min^{-1}$, while the sample weight changes was continuously recorded. Details are available in our previous research.[1,2]

SRM tests were carried out in a plug flow integrated reactor (i.d. 10 mm) under atmospheric pressure by cutting the plate catalyst into small pieces. N_2 was introduced as the inner inference gas for GC analyses. In all SRM tests, the ratio of $CH_4/H_2O/N_2$ in the feed gas was controlled at 1:3:2, while the CH_4 feed flow was changed between 50 and $150\,mL\,min^{-1}$ (i.e., $F/W = 157000$ and $471000\,mL\,h^{-1}\,g_{cat}{}^{-1}$). During the DSS SRM, the catalyst was purged with steam at 700 °C when the reactant gas was stopped. The prereduction was conducted with $100\,mL\,min^{-1}$ H_2 at 800 °C for 0.5 h. The dry outlet gases were analyzed by an online gas chromatograph (GC-2014AT, Shimadzu Corp.). The results obtained were evaluated in terms of CH_4 conversion and H_2 concentration. CH_4, CO, H_2, and CO_2: molar flow rates.

$$\mathrm{CH_4\ conversion\ (\%)} = \frac{\mathrm{CH_{4\,inlet}} - \mathrm{CH_{4\,outlet}}}{\mathrm{CH_{4\,inlet}}} \times 100 \tag{1}$$

$$\mathrm{H_2\ concentration\ (\%)} = \frac{\mathrm{H_{2\,outlet}}}{\mathrm{CH_{4\,outlet}} + \mathrm{H_{2\,outlet}} + \mathrm{CO_{outlet}} + \mathrm{CO_{2\,outlet}}} \times 100 \tag{2}$$

Figure 1 shows the DSS SRM reactivity over Ni, Ru, Pt, Ru–Ni, and Pt–Ni catalyst. The Ni catalyst deactivated quickly after 700 °C steam purge. Our previous study stated that during the steam purging, metallic Ni particles were sintered to form large-sized particles and that simultaneously the surface layer of Ni particles was oxidized to form a sintered structure with hard-to-reduce Ni^{2+} species while the core remained as metallic Ni particles. But for both Ru–Ni and Pt–Ni catalysts, no deactivation was shown during 700 °C steam purge DSS SRM (this was termed self-regeneration). Moreover, it was found that both the Ru–Ni and Pt–Ni catalysts could activate themselves (termed self-activation, i.e., reduce Ni^{2+} to Ni automatically), because stable SRM activity was achieved by applying the fresh Ru–Ni and Pt–Ni catalysts to the SRM at 700 °C without prereduction with H_2 in Figure 1. After 700 °C steam purge DSS SRM, a test was also conducted under 800 and 900 °C steam purge. For Pt–

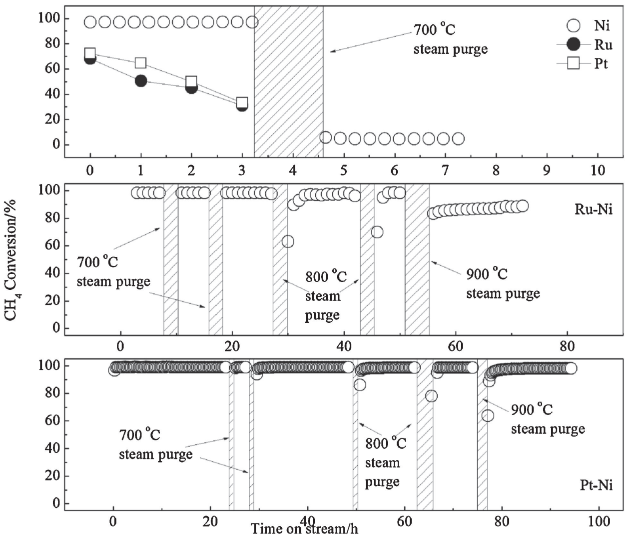


Figure 1. DSS SRM over Ni, Ru, Pt, Ru–Ni, and Pt–Ni catalysts at 700 °C, $S/C = 3$, $F/W = 157000\,\mathrm{mL\,h^{-1}\,g_{cat}^{-1}}$. Ni: 800 °C H_2 reduction for 0.5 h; Ru–Ni and Pt–Ni: without prereduction.

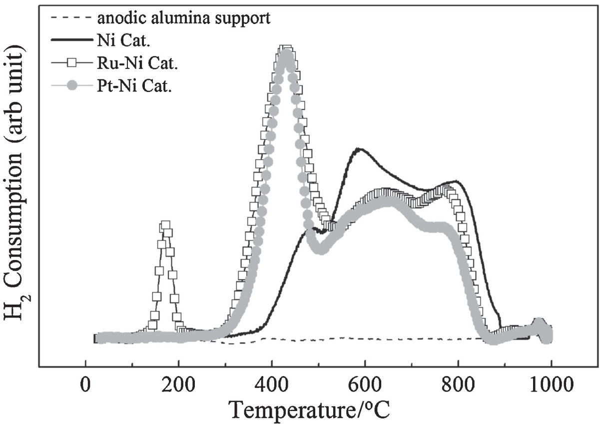


Figure 2. The TPR profiles of Ni, Ru–Ni, and Pt–Ni catalysts.

Ni catalyst, the catalyst showed self-regeneration during <1 h under both 800 and 900 °C steam-purged DSS SRM. However, it took more than 4 h for Ru–Ni catalyst to recover initial methane conversion under 800 °C steam-purged DSS SRM. As to the 900 °C steam-purged DSS SRM, the Ru–Ni catalyst showed a lower methane conversion near 88%. As we know, the higher temperature steam purge would result in more severe Ni sintering. The recovery time here was thought to be the time for catalyst to redisperse its Ni metallic particles (this was termed self-redispersion).

Figure 2 showed the TPR analyses over fresh Ni, Ru–Ni, and Pt–Ni catalysts. The anodic alumina support was also examined as a control. NiO, $x\mathrm{NiO{\cdot}Al_2O_3}$, $x < 1$ and $NiAl_2O_4$ peaks[1] were detected over all three catalysts. For the Ru–Ni catalyst, the peak at ca. 200 °C resulted from the reduction peak of RuOx species.[7] It was apparent that by adding Ru or Pt, the Ni reduction peak shifted toward lower temperature. The formation of Ru–Ni alloy and Pt–Ni alloy was believed to be the main reason for the low reduction of Ru–Ni and Pt–Ni catalysts. The XRD analysis over the Pt–Ni catalyst after DSS SRM in Figure 1 showed the existence of Pt–Ni alloy in Figure 3. A similar conclusion was also suggested by Miyata et al.,[6] who reported that the formation of Ru–Ni alloy or a strong interaction between Ru and Ni resulted in an easy reduction of Ni catalysts. Furthermore, as shown in Figure 1, the SRM test over 0.079 wt% Ru and 0.079 wt% Pt was conducted. This showed negligible reactivity over both Ru and Pt catalysts. Comparing this result and the high stability over Ru (Pt)–Ni catalyst, the synergy between Ni and Pt or Ru can be concluded.

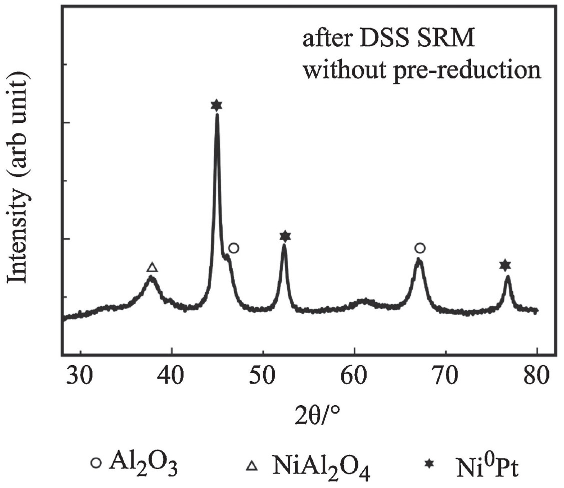


Figure 3. XRD analysis over Pt–Ni catalyst after DSS SRM.

When the fresh Ru (Pt)–Ni catalyst or steam-purged Ru (Pt)–Ni catalyst were subjected to the flow of CH_4 and H_2O, we considered that CH_4 decomposition and/or SRM reaction over some of the free Ru (Pt) species at 700 °C initiated the autoreduction of the catalyst. Further reduction of Ru (Pt)–Ni–oxide clusters would be facilitated by increased availability of hydrogen. According to this, the Ni^{2+} on this catalyst was self-activated by H_2 spillover from Ru (Pt), while Ru (Pt)–Ni alloy was formed on the surface of metallic Ni particles. The formation of Ru (Pt)–Ni alloy was vital for self-regeneration and self-redispersion of the catalyst. While the mechanism is still unknown, it is thought to be as follows: Ni^0 is oxidized and incorporated into the $NiAl_2O_4$ layer under steam purge, whereas the Ni^{2+} is released as small Ni^0 particles on the catalyst surface by the spilled hydrogen from methane.

However, it should be noted that the Ru–Ni catalyst showed weaker DSS SRM under 800 and 900 °C steam purge than Pt–Ni catalyst. This was associated with the hydrogen spillover ability of the noble metals. As shown in Figure 4, the comparison of hydrogen produced by methane dissociation on noble metal was tested with TG analyses. When the temperature of methane gas was increased from 200 °C at 3.5 h to 700 °C at 4.3 h, owing to coking resulting from methane decomposition, three samples showed a quick increment in weight: increases of 5.15 wt% for Ni catalyst, 19.6 wt% for Ru–Ni, and 80.3 wt% for Pt–Ni catalyst. After the temperature was stable at 700 °C, the weight of these samples continually increased with a seemingly gradual decline in rate and reached an increase of 6.5 wt% for Ni, 30.5 wt% for Ru–Ni, and 94 wt% for Pt–Ni. No increment was found for anodic alumina support. This shows that the ability

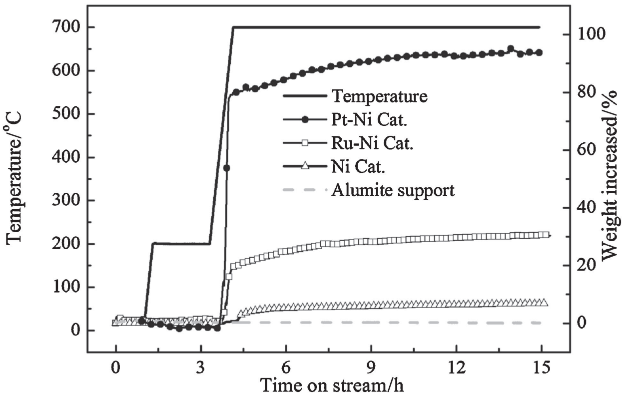


Figure 4. TG analyses over Ni, Ru–Ni, and Pt–Ni catalysts.

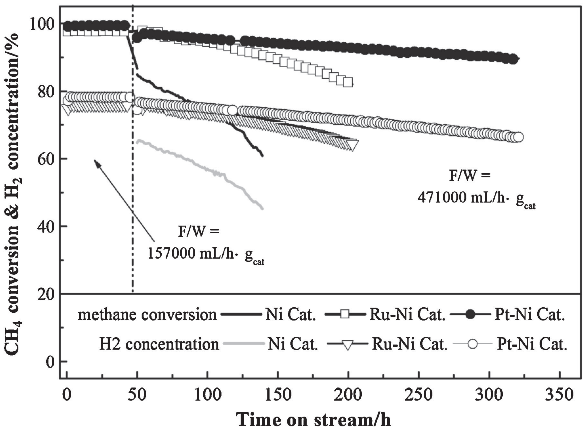
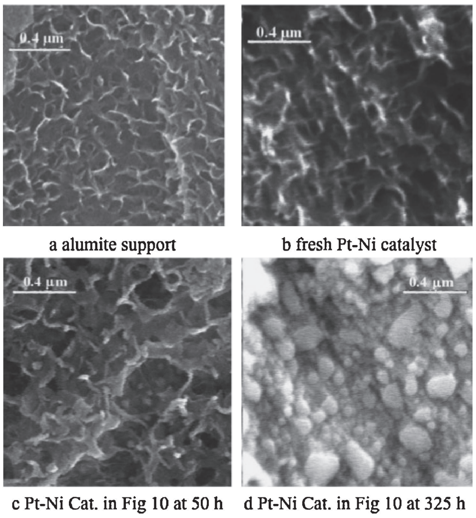


Figure 5. The accelerated SRM test over Ni, Ru–Ni, and Pt–Ni catalyst at 700 °C, S/C = 3. Ni: 800 °C H_2 reduction for 0.5 h; Ru–Ni, and Pt–Ni: without prereduction.

of hydrogen produced by methane dissociation following the sequence is Pt > Ru ≫ Ni. Thus, the Pt-doped Ni catalyst would show greater DSS SRM than Ru, while the Ni showed deactivation under DSS SRM.

It is known that a durability of over 90000 h is required for fuel cell systems, the minimum life of household appliances to be economical. Therefore, it is meaningful to establish the long-term durability of SRM catalysts. In this study, an accelerated life testing was conducted on the Pt–Ni, Ru–Ni, and Ni catalysts by increasing the F/W to investigate its potential deactivation in actual long-term testing. In Figure 5, under the $F/W = 157000$ mL h^{-1} $g_{cat}{}^{-1}$, all catalysts showed stable methane conversion near 97%. When the F/W was increased by three times to 471000 mL h^{-1} $g_{cat}{}^{-1}$, the methane conversion over Ni catalyst declined from 97% to 61% over 90 h, while only a 7% (from 97% to 90%) decline of methane conversion was shown over Ru–Ni catalyst over 150 h, and the Pt–Ni catalyst showed the best SRM stability while a 7% (from 97% to 90%) decline was shown over as long as 330 h. According to our previous research,[2] the deactivation under the higher F/W resulted from the higher Ni sintering speed. Although doping Ru or Pt suppressed the Ni sintering to some degree, which must be associated with the self-redispersion ability, the FE-SEM in Figure 6 showed the sintering of catalyst, where some large particles could be seen over the catalyst surface after 50 h SRM in $F/W = 157000$ mL h^{-1} $g_{cat}{}^{-1}$, while the particles became larger to ca. 150 µm after the catalyst was subjected to $F/W = 471000$ mL h^{-1} $g_{cat}{}^{-1}$ for 325 h. This shows that the sintering of the catalyst resulted in the deactivation. Therefore, some efforts should be made to suppress the sintering of Pt–Ni catalysts. These are now in progress by modifying supports with lanthanum species, and the results will be reported later elsewhere.



a alumite support b fresh Pt-Ni catalyst
c Pt-Ni Cat. in Fig 10 at 50 h d Pt-Ni Cat. in Fig 10 at 325 h

Figure 6. The FE-SEM of Pt–Ni catalyst in Figure 4.

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