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Plate Anodic Alumina-supported Nickel Catalysts in Steam Reforming of Methane: Effects of Hydrogen Addition, Electrical Heating, and Pt Doping

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A porous anodic alumina-supported 4.9 wt % nickel catalyst showed deactivation in steam reforming of methane at 700 °C, and this was mainly ascribed to Ni oxidation. The influence of hydrogen additive was examined by adding hydrogen into feed, and no deactivation was found during 20 h when hydrogen with $H_2/H_2O = 1/3$ was added. The influence of electrical heating over catalyst stability was also examined, and the results showed a stable 93% methane conversion for 30 h. 0.078 wt % Pt-doped 4.9 wt % nickel catalyst showed a stable SRM reactivity even without the prereduction with hydrogen.

In our previous research,[1] a plate-type porous anodic alumina-supported Ni catalyst, 4.9 wt % Ni/Al_2O_3/alloy, was synthesized for steam reforming of methane (SRM), which would be conducted in wall reformers, rather than out of style fixed-bed reformers.[2] Besides the high thermal stability and possibility of being prepared into varieties of shapes, such as mesh, honeycomb, serrated honeycomb, and spiral, this kind of plate-type catalysts can be heated from room temperature to 1000 °C over 23 s by applying current through the alloy interlayer of this catalyst.[3] However, this catalyst showed deactivation over 1 h in SRM at 700 °C, $F/W = 157000\,\mathrm{mL\,h^{-1}\,g_{cat}{}^{-1}}$, and the oxidation of reduced Ni was thought to be the main reason.[1]

In this study, the influence of hydrogen additive, electrical heating, and Pt doping on the 4.9 wt % Ni/Al_2O_3/alloy catalyst SRM reactivity was investigated. It was found that H_2 presented positive effect while no deactivation was found when hydrogen with $H_2/H_2O = 1/3$ was added. Under the electrically heating SRM, the catalyst showed a stable 93% methane conversion for as long as 20 h. The 0.079 wt % Pt-doped 4.9 wt % Ni/Al_2O_3/alloy catalyst showed no deactivation in 10 h, while the prereduction with hydrogen was not necessary.

A commercial plate Al/Cr–Ni–alloy/Al clad base material was used to prepare the support in Figure 1. The 4.9 wt % Ni/Al_2O_3/alloy was prepared by impregnation method with $Ni(CH_3COO)_2\cdot 4H_2O$ precursor.[1] Pt was doped by impregnation with H_2PtCl_6 solution. The impregnated samples were dried at 120 °C overnight and calcined at 500 °C for 3 h.

Metal loadings were analyzed with an inductively coupled plasma spectrometer (ICPS-7510, Shimadzu Corp.) and reported here based on alumina quantity. H_2-TPR with 65% H_2/Ar and O_2-TPO with 40% O_2/He analyses were performed on ChemBET 3000 (Quantachrome Instruments, Co.). Details are available in our previous research.[1]

Figure 1. The preparation of anodic alumina supported Ni SRM catalysts.

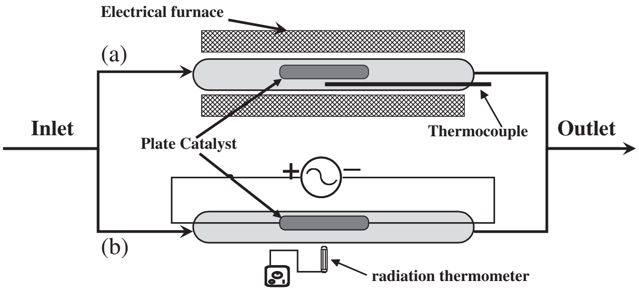

Figure 2. The SRM reaction system: (a) electrical furnace heating and (b) electrically heating.

SRM tests were carried out in a plug-flow integrated reactor (i.d. 10 mm). In Figure 2, a $0.5 \times 10\,\mathrm{cm^2}$ plate catalyst (the loaded quantity of alumina layers was about 76 mg) was packed into the reactor. The catalyst was heated by two methods as shown in Figure 2: (a) electrical furnace and (b) electrical heating. 100 mL min^{-1} N_2 was introduced as the inner inference gas for GC analyses. In all SRM tests, the total flow of feed was fixed at 200 mL min^{-1} (i.e., $F/W = 157000\,\mathrm{mL\,h^{-1}\,g^{-1}}$), while the ratio of $CH_4/H_2O/H_2$ in the feed was changed between 1:3:0 and 1:3:1. Before each test, the catalyst was purged with N_2 (100 mL min^{-1}) at 500 °C for 1 h and then reduced in H_2 (100 mL min^{-1}) at 800 °C for 0.5 h. The dry outlet gases were analyzed with an online gas chromatograph (GC-2014AT, Shimadzu Corp.). The results obtained were evaluated in terms of CH_4 conversion and H_2 concentration.

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

$$\mathrm{H_2\ concentration\ (\%)} = \frac{\mathrm{H_{2\,outlet}}}{\mathrm{CH_{4\,outlet}} + \mathrm{H_{2\,outlet}} + \mathrm{CO_{outlet}} + \mathrm{CO_{2\,outlet}}} \times 100\% \qquad (1)$$

CH_4, CO, H_2, and CO_2: molar flow rates

In Figure 3, in the SRM without H_2 additive (i.e., $H_2/H_2O = 0$), the catalyst provided a high initial methane conversion, but it deactivated significantly in 1 h. Figure 4 shows the TPR and TPO profiles over the fresh and spent catalysts. The anodic alumina support was also included for comparison, while no noticeable signal was detected. Over a fresh 4.7 wt % Ni/Al_2O_3/alloy catalyst, three reduction peaks were detected in TPR, reported as NiO at 470 °C, nonstoichiometric nickel aluminate ($x\mathrm{NiO}\cdot Al_2O_3$, $x < 1$) at 650 °C, and $NiAl_2O_4$ at

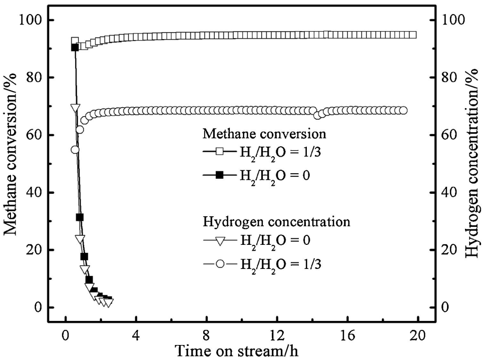

Figure 3. The influence of H_2 additive during SRM at 700 °C over 4.7 wt% Ni/Al_2O_3/alloy catalyst.

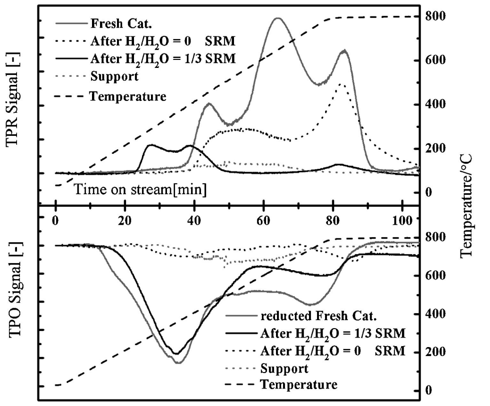

Figure 4. The TPR and TPO profiles over 4.7 wt% Ni/Al_2O_3/alloy catalyst.

800 °C in our previous work.[1] Although H_2 prereduction was conducted before SRM, the deactivated catalyst after $H_2/H_2O = 0$ SRM, exhibited a H_2-TPR profile with NiO and $NiAl_2O_4$ reduction peaks. On the other hand, although the H_2-reduced catalyst showed two oxidation peaks in TPO, the catalyst after $H_2/H_2O = 0$ SRM exhibited no TPO signal. These implied that the reduced Ni was turned into nickel oxides after SRM without H_2 additive. Our previous research[1] and other researchers[4–8] explained that the oxidation of metallic Ni particles with steam into inactive NiO and/or $NiAl_2O_4$ was the main reason for the catalyst deactivation. In the stage of H_2 reduction, microcrystalline nickel would be precipitated throughout the support from the highly dispersed nickel oxides, giving a high surface of nickel and hence a high catalytic activity. However, because of the effect of solid-state diffusion, the highly dispersed nickel then reacted with the steam and alumina support forming inactive nickel oxides.

Therefore, the key of acquiring excellent SRM stability over 4.7 wt% Ni/Al_2O_3/alloy catalyst is to maintain the metallic state of Ni during SRM reaction. As an approach, the hydrogen reductant additive was logically considered. Laosiripojana et al.[9] reported that during SRM reaction over 5 wt% $Ni/Ce–ZrO_2$, H_2 addition presented positive effect on the CH_4 conversion when a small amount of H_2 was introduced, due to the reduction of oxidation state on the surface-active site of Ni by hydrogen. This is the same case for our catalyst. In Figure 4 showing TPR and TPO profiles, by adding hydrogen with $H_2/H_2O = 1/3$ into the feed, sufficient H_2 will be provided to prevent the oxidation of active nickel to the inactive NiO and/or $NiAl_2O_4$. Thus, a stable methane conversion of 93% was maintain for as long as 20 h. In Figure 5, even for the entirely deactivated catalyst, by adding $H_2/H_2O = 1/3$ hydrogen into the feed, the methane conversion was regenerated from 0 to 83% in 5 h and no deactivation was found in the next 6 h. This was explained why part of the nickel oxide was reduced to metallic nickel particle, and due to the existence of sufficient H_2, the reduced could be kept active and thus performed a regeneration and stable SRM reactivity. However, according to Takemura et al.,[10] $NiAl_2O_4$ would be largely unreduced at 700 °C; therefore, the lower methane conversion of deactivated catalyst than that of initial catalyst could be explained by metallic Ni particle in catalyst at 14 h in Figure 5 less active than that of fresh catalyst at 0 h, as part of the nickel still remained as $NiAl_2O_4$. Meanwhile, the sintering of the Ni during the SRM in the initial 2 h could also be responsible for the lower conversion.

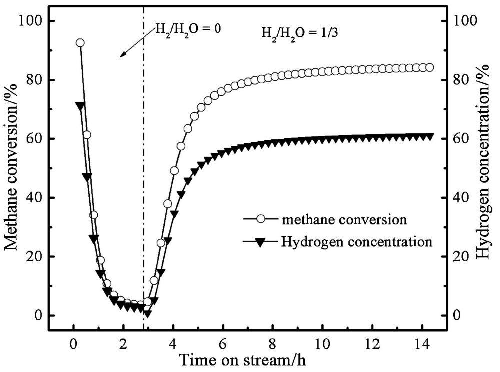

Figure 5. The influence of H_2 additive for the deactivated 4.7 wt% Ni/Al_2O_3/alloy catalyst during SRM at 700 °C.

Because of the alloy interlayer existence in the support (Figure 1), it allows for an electrical heating pattern for our catalysts. In Figure 6, a swift heating and cooling speed was found by the electrical heating, because the support was heated from room temperature to 1000 °C in just 23 s. This is a novel approach for the long start-up time issue of fuel cells.

Figure 7 shows the SRM reactions under electrical heating over 4.7 wt% Ni/Al_2O_3/alloy catalyst by using homemade electrical testing equipment (Figure 2). During the experiment, the temperature of catalyst surface was controlled at 700 °C by adjusting the electric current (16 A, 80 V and 14 A, 70 V are required for heating the catalyst to 800 and 700 °C, respectively). But, as shown in Figure 6, the color of catalyst surface is not uniform at 700 and 800 °C, respectively, which means that there are distribution of surface temperature profile. But, actually there is just 30–50 °C temperature difference during the test, and the highest temperature on the catalyst surface is taken as the reaction temperature. Different from the catalyst that deactivated over 2 h in SRM under furnace heating, the catalyst under electrical heating SRM performed excellent methane conversion as 93%, and no deactivation was evidenced over 30 h. It is well known that when an electrified metal or metal oxide is heated, electrons can boil off its surface, leading to thermal emission of electrons from the surface,[11] which would play an important role in reduction (e.g., $O_2 + 4e^- \rightarrow 2O_2^-$), occurring on the cathode of

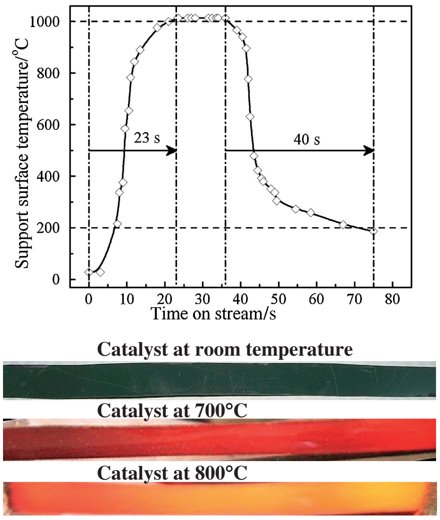

Figure 6. The surface temperature of 4.7 wt % Ni/Al_2O_3/alloy catalyst under electrically heating in 100 mL min^{-1} N_2.

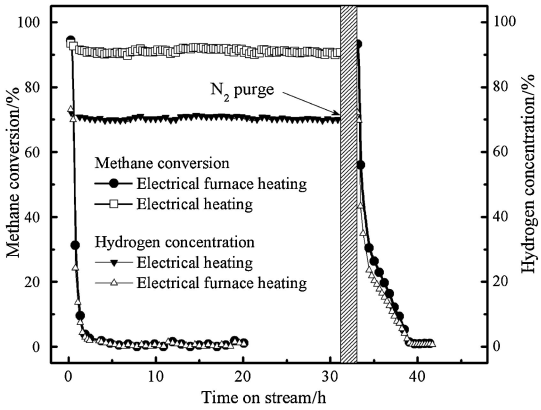

Figure 7. The SRM test over 4.7 wt % Ni/Al_2O_3/alloy catalyst under electrically heating mode at 700 °C.

a solid oxide fuel cell. From this point, it is assumed that when a current was applied on the 4.7 wt % Ni/Al_2O_3/alloy catalyst, the emitted thermal electrons would enter the Al_2O_3 body and thus could supply electrons onto the catalyst surface to reduce the ionic state Ni^{2+}. Therefore, by continually applying current through the catalyst, the Ni over the catalyst would be maintained as active metallic Ni to provide stable SRM reactivity. In order to check the effect of current, after 30 h SRM under electrical heating mode, the catalyst was purged in 100 mL min^{-1} N_2 and then subjected to SRM under electric furnace heating. This showed a quick and entirely catalyst deactivation.

This showed that besides the shortened start-up time and intense heat transmission, the electrical heating would surprisingly increase the SRM stability.

In order to suppress Ni oxidation in SRM, Ni catalysts are always modified with noble metal such Ru, Pt, and Rh in view of their hydrogen spillover function.[12–14] In this study, a 0.078 wt % Pt was doped over the 4.7 wt % Ni/Al_2O_3/alloy catalyst. Figure 8 shows the TPR over Pt-doped Ni catalyst. By the addition of Pt, the Ni reduction peak shifted toward lower temperature, which suggested that either a formation of alloy or a strong interaction between Pt and Ni, resulting in an easy reduction of Ni on the Pt–Ni bimetal catalyst. The SRM over Pt–Ni catalyst without prereduction with hydrogen in Figure 9 demonstrated a stable methane conversion for 10 h, which implied that the hydrogen spillover from doped Pt could reduce the nickel oxides to metallic Ni and keep the nickel in the form of metallic Ni.

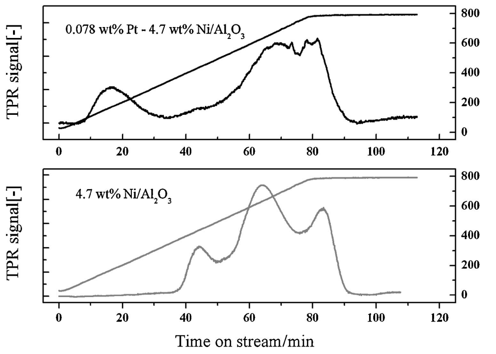

Figure 8. The TPR profiles over 0.078 wt % Pt doped 4.7 wt % Ni/Al_2O_3/alloy catalyst.

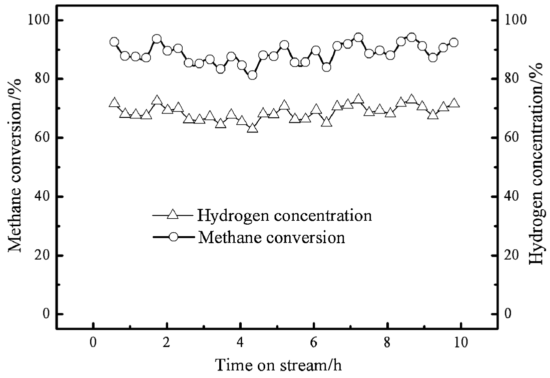

Figure 9. The SRM without hydrogen prereduction at 700 °C over 0.078 wt % Pt doped 4.7 wt % Ni/Al_2O_3/alloy catalyst.

References

1 Y. Guo, T. P. Tran, L. Zhou, Q. Zhang, H. Kameyama, *J. Chem. Eng. Jpn.* **2007**, *40*, 1221.
2 C. Fukuhara, A. Igarashi, *J. Chem. Eng. Jpn.* **2004**, *37*, 415.
3 L. Zhou, Y. Guo, M. Yagi, M. Sakurai, H. Kameyama, *Int. J. Hydrogen Energy* **2009**, *34*, 844.
4 N. Sahli, C. Petit, A. C. Roger, A. Kiennemann, S. Libs, M. M. Bettahar, *Catal. Today* **2006**, *113*, 187.
5 Y.-S. Oh, H.-S. Roh, K.-W. Jun, Y.-S. Baek, *Int. J. Hydrogen Energy* **2003**, *28*, 1387.
6 H.-S. Roh, K.-W. Jun, S.-E. Park, *Appl. Catal., A* **2003**, *251*, 275.
7 E. Ruckenstein, X. D. Hu, *J. Catal.* **1986**, *100*, 1.
8 S. Natesakhawat, R. B. Watson, X. Wang, U. S. Ozkan, *J. Catal.* **2005**, *234*, 496.
9 N. Laosiripojana, D. Chadwick, S. Assabumrungrat, *Chem. Eng. J.* **2008**, *138*, 264.
10 Y. Takemura, Y. Morita, K. Yamamoto, *Int. Chem. Eng.* **1996**, *6*, 725.
11 G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, New York, Wiley-Interscience, **1994**.
12 D. Li, T. Shishido, Y. Oumi, T. Sano, K. Takehira, *Appl. Catal., A* **2007**, *332*, 98.
13 J. H. Jeong, J. W. Lee, D. J. Seo, Y. Seo, W. L. Yoon, D. K. Lee, D. H. Kim, *Appl. Catal., A* **2006**, *302*, 151.
14 T. Suzuki, H. Iwanami, T. Yoshinari, *Int. J. Hydrogen Energy* **2000**, *25*, 119.