Steam Methane Reforming Using an Anodic Alumina Supported Nickel Catalyst (Ni/Al₂O₃/Alloy): Analysis of Catalyst Deactivation

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A plate-type metal-monolithic anodic alumina supported nickel catalyst (Ni/Al₂O₃/Alloy) was employed to investigate the reactivity and the catalyst deactivation in the SMR reaction, and several methods of activation treatments were proposed. After H₂ reduction, a fresh Ni/Al₂O₃/Alloy catalyst only provided a short-term SMR activity, and then quickly deactivated. The oxidation of metallic nickel with steam into oxidation state was believed to be the most serious reason for the catalyst deactivation. After the second H₂ reduction, a deactivated catalyst (or a catalyst with the treatments of H₂ reduction and subsequent air oxidation) was observed to provide a more favorable SMR stability, compared a reduced fresh catalyst.

Introduction

Ni supported catalyst (10–25 wt%) has been preferred as a catalyst for the steam methane reforming reaction (SMR) due to its cheap price and high reactivity, although it requires a high molar ratio of steam/methane (3.0–3.5). Likewise, γ-Al₂O₃ and α-Al₂O₃ have been employed as supports owing to their cheap price and stabilities at high temperature. However, Ni/α-Al₂O₃ was reported to be unstable in oxy-reforming of methane (ORM) and SMR due to the carbon formation (Roh et al., 2001, 2002). Some researches showed that Ni/γ-Al₂O₃ was also unstable at high temperature (>973 K), due to the carbon deposit and the formation of inactive nickel aluminate at high temperature (700–1000 K). Consequently, last 10 years, tremendous exploratory researches focus on the modification of the alumina support to obtain a thermally stable support for the SMR reaction. A main approach is to add second metals such as K, Mg, Ce, and Mo, or to impregnate nickel catalyst on various supports such as ZrO₂, SiO₂, MgAl₂O₄ and mixed oxides. Especially, Ce–ZrO₂ support was found to be highly effective to suppress coke formation and provide a favorable reactivity and stability (Roh et al., 2002). However, it must be pointed out that Ce–ZrO₂ system is difficult to commercialize due to the high price. On the other hand, Lif et al. (2004) implied another modification approach that the formation of an interfacial nickel aluminate layer between metallic nickel particles and alumina support would effectively suppress nickel sintering. A similar result was also reported by Bolt et al. (1995). However, the effect of the interfacial nickel aluminate layer on the real SMR reaction was seldom reported up to now.

Many reviews on the SMR reaction discuss the conventional process, which is carried on bead Ni catalysts in multi-tubular reactors operated at the temperature and pressure respectively ranging from 773 K (inlet) to 1073 K (outlet) and 20 to 40 bar and steam/methane in the feed 2–4 (Zanfir and Gavrilidis, 2003). However, this process suffers from several drawbacks, such as a poor heat transfer coefficient, diffusion limitations, great pressure drop and large volume size. Consequently, the constructed wall type reactors have become the focus of recent research on the steam reformer, due to their excellent performances in gas diffusion, heat transmission and compact size. For the preparation of a plate catalyst, though various methods have been reported, such as sol–gel coating and nano-particle-based coating, thermal endurance of the catalysts was seldom mentioned. At high temperatures, it is difficult to prevent the coating layers peeling off from the base materials due to the difference of their thermal expansion. To avoid such a problem, a novel metal-monolithic plate-type anodic alumina catalyst with high thermal endurance and conductivity was developed by Kameyama (1995). Porous alumina film can be formed on the surface of Al plate by anodization. Hot water treatment and subsequent calcination greatly
increase its surface area (Guo et al., 2003). Since the alumina layer is derived from the base material, a close uniformity between the alumina layer and its inside can effectively prevent the mismatch in thermal expansion.

However, this catalyst is limited to be used in low temperature (<823 K), due to the low melting point of Al (ca. 915 K). To solve this problem, a commercial Al/Cr-Alloy/Al clad plate was used in this study. By the same anodization technology, γ-Al2O3/Alloy/γ-Al2O3 could be obtained. The thermal endurance test at 1073 K showed a high heat resistance, and the alumina layer peeling off from the catalyst was not observed during repeating the same test up to 40000 times. In particular, the existence of alloy interlayer allows an electrically heating pattern, which makes it possible to heat up the reformer inside the reactor promptly (Zhang et al., 2005). Therefore, the application of this catalyst in the SMR reformer is a promising area, especially in shortening start-up time and intensifying heat transmission.

In this paper, we prepared an anodic alumina supported nickel clad catalyst to investigate its SMR reactivity, with an aim to gain new insights into the practicality of this catalyst in SMR reaction. Here, we focused on the investigation of the SMR reactivity under no-electricity conditions; the electrically heated performance will be discussed elsewhere later.

1. Experimental

1.1 Catalyst preparation

Details regarding the preparation of an anodic γ-alumina support have been given elsewhere (Guo et al., 2003). An anodic alumina supported nickel catalyst with Ni loading of 4.9 wt%, designated Ni/Al2O3/Alloy, was prepared with the solution impregnation method. The support was impregnated by using an aqueous solution containing required amount of Ni(CH3COO)2·4H2O for 2 h under ambient conditions. The plate was then dried naturally, and calcined in air at 773 K for 3 h. The calcination and calcination were repeated twice.

1.2 Catalyst characterization

Nickel loading was analyzed by atomic absorption spectrometry (AA-680, Shimadzu Corp.), and is reported here based on the quantity of the surface alumina layer. Powder X-ray diffraction (XRD) analyses were performed on a XRD-6000 (Shimadzu Corp.), using Cu Kα radiation.

H2-TPR (temperature programmed reduction with H2) was performed in a U-type quartz fixed bed reactor (i.d., 6 mm) coupled to a TCD detector (CHEMBET-3000, Quantachrome Instruments Corp.). Generally, plate-type samples (5 cm2) were cleaned at 773 K for 1 h in flowing Ar of 70 mL·min−1 to remove adsorbed H2O and other gases. H2-TPR run was started from ambient temperature at a ramping rate of 10 K·min−1 in 65% H2/Ar of 70 mL·min−1, and the outlet dry gas was continuously monitored by the TCD detector. O2-TPO (temperature programmed oxidation with O2) was performed by using the same apparatus. Similarly, 5 cm2 of plate-type samples were cleaned at 773 K for 1 h in flowing He of 70 mL·min−1. O2-TPO run was started from ambient temperature at a ramping rate of 10 K·min−1 in 40% O2/He 70 mL·min−1.

1.3 Reactivity tests

A fixed bed quartz reactor (i.d., 10 mm) was used to test the SMR activity of the Ni/Al2O3/Alloy catalyst. The plate-type catalyst was cut into small pieces (ca. 5 mm3) and packed in the reactor, using quartz sand for dilution with a loading density of 1.0 cm-cat2(g-quartz)−1. The bed temperature was monitored by a K-type thermocouple placed in the center of the catalyst bed. The overall gas stream consisted of CH4, H2O and N2 with a molar ratio of 1:3:2. The SMR reaction was conducted at 1073 K and F/W = 157000 mL·(g−h)−1 (excluded nitrogen stream and the quantity of interlayer alloy) under atmospheric pressure. A cold trap was set at the outlet of the reactor to condense steam. N2 was simultaneously introduced into the system, used as an inner inference gas for GC analysis. Outlet dry gas was analyzed by a gas chromatograph with a TCD detector (GC-2014AT, Shimadzu Corp.). The results obtained were evaluated in terms of CH4 conversion and H2 production.

In this paper, three pre-treatment processes were discussed. (1) Direct H2 reduction: the catalyst was reduced in 50% H2/N2 mixture (200 mL·min−1) for 4 h at 1073 K, and then was applied to the SMR reaction. (2) H2 reduction → random deactivation → H2 re-reduction (RDR): The catalyst was spent in the SMR reaction after the direct H2 reduction. Then, the same reduction was repeated when CH4 conversion < 10%. (3) H2 reduction → air oxidation → H2 re-reduction (ROR): After the direct H2 reduction, air of 100 mL·min−1 was used to oxidize the catalyst at 1073 K for 2 h. Then, the same H2 reduction was repeated after N2 purge. After different pre-treatments, the SMR activity was measured at the same F/W, molar ratio of reactants, temperature, and pressure.

2. Results and Discussion

2.1 Catalyst deactivation and possibilities

After the direct H2 reduction, the SMR activity of the Ni/Al2O3/Alloy catalyst was tested at 1073 K, and the result was showed in Figure 1. The reduced fresh catalyst provided a short-term reactivity only in the initial 0.5 h, and then quickly deactivated in a short time. With regard to the catalyst deactivation, the following potential possibilities were discussed: a) Exposure of minim Fe impurity in the alloy interlayer to SMR reactants, which maybe accelerates carbon cok-
ing; b) Residual Al (2–3 µm) between the alumina layer and the alloy interlayer, which probably diffuses into the surface alumina layer at a high temperature to decrease the surface area of the catalyst; c) Start-up sequence of methane and steam; d) Deactivation of active compound, i.e., Ni.

To investigate the influences of minim Fe (a) and Al (b), a comparative experiment was carried out under the same H₂ reduction and SMR conditions by using a powder-type catalyst, which was prepared by scraping off the surface alumina layer from the plate-type catalyst. The powder experiment did not show any remarkable improvement on the SMR stability (not shown here). In the meantime, an approximate 100% of C atom mass balance also excluded the possibility of carbon coking. The SMR start-up sequence (c) was also studied by introducing steam ahead of CH₄ for 10 min, or introducing CH₄ ahead of steam for 10 min. Similar to (a) and (b), no remarkable improvement was found (not shown here). Therefore, the influence of (a), (b) or (c) could not be considered as the main reason for the catalyst deactivation, though they probably have some influence on the SMR stability to some extent.

In view of the deactivation of active compound nickel (d), a XRD analysis was conducted to obtain the information about nickel supported. However, there were no obvious diffraction lines attributable to nickel supported, and the XRD result exhibited a similar pattern of diffraction peaks to the parent associated with alumina. A relatively low Ni loading of 4.9 wt% was a possible interpretation.

2.2 H₂-TPR analyses

As an alternative method, H₂-TPR test was carried out to analyze the oxide form of nickel supported. It should be pointed out that a strong peak of H₂ consumption was found at 1206 K over a plate-type A₇O₃/Alloy support. The reaction of residual Al with H₂ into AlH₃ might be a plausible interpretation. For this reason, powder-type samples are recommended for H₂-TPR analyses. However, it is difficult to obtain sufficient sample amount, especially for a deactivated catalyst because it has been cut into small pieces in the SMR test. Therefore, hereinafter, most of H₂-TPR analyses were conducted by using the plate-type catalyst and maximum reduction temperature was set at 1073 K.

The H₂-TPR profile of a fresh plate-type Ni/A₇O₃/Alloy catalyst (Sample 1) was presented in Figure 2. Sample 1 exhibited three significant reduction peaks in low, moderate and high temperature regions, respectively. At first, the H₂ consumption signal climbed up with increasing temperature from 659 K and gave the maximum at 742 K, and then dropped gradually. After that, a very strong reduction peak was displayed from 789 to 1043 K, and peaked at 923 K. At last, a relatively weak peak appeared in the constant temperature stage of 1073 K. It should be noted that when using a powder-type sample the third peak peaked at 1116 K and disappeared in background at 1203 K. Considering the interpretation of H₂-TPR and XRD data reported by several groups (Bolt et al., 1995; Teixeira and Giudici, 1999; Roh et al., 2003), the peak located in 742 K was assigned to the reduction of more reducible NiO. The third reduction peak of 1073 K or (or 1116 K) was attributed to the nickel aluminate spinel (Ni₃AlO₅), because a temperature of 1073 K or greater is necessary for the reduction of nickel spinel (Takemura et al., 1966). Generally, the second reduction peak could be ascribed as a transitional product between NiO and Ni₃AlO₅, i.e., non-stoichiometric nickel aluminate (₃NiO·Al₂O₃, x < 1) (Teixeira and Giudici, 1999). In some relevant literature, it was also described as NiO strongly interacting with alumina support compared with NiO (Roh et al., 2003).

O₂-TPO analyses (not shown here) showed that the deactivated catalyst (spent in Figure 1) did not give any noticeable oxidation peak at lease until 1073 K, whereas a fresh catalyst spent in H₂-TPR test (Sample 1 spent in Figure 2) depicted two strong oxidation peaks.
located at 627 and 884 K. On the other hand, the deac-
tivated catalyst (Sample 5 in Figure 2) and the fresh
catalyst exhibited a striking similarity of \( \text{H}_2 \)-TPR pro-
file in reduction temperature and peak shape, regard-
less of the disappearance of the \( x \text{NiO} \cdot \text{Al}_2\text{O}_3 \) peak in
the deactivated catalyst. These results revealed that a
reduced fresh catalyst could be oxidized in the SMR
test, and steam was considered as the oxidant because
it was the only O-containing reactant. Tremendous re-
searches reported that nickel in alumina supported sys-
tems showing high SMR activity occurred mainly in
metallic form, and oxidation form (e.g., \( \text{NiO} \), \( x \text{NiO} \cdot \text{Al}_2\text{O}_3 \), \( \text{NiAl}_2\text{O}_4 \)) was almost inactive (Takemura
et al., 1966). Accordingly, the change of the redox form
of Ni was suggested to be the main reason for the de-
activation of our catalyst. In addition, the absence of
\( \text{O}_2 \) consumption signal in the deactivated catalyst (in
\( \text{O}_2 \)-TPO) indicated that there was no serious carbon
coking occurred during the SMR test.

In Figure 2, Sample 1 gave three kinds of oxida-
tion form of Ni (\( \text{NiO} \), \( x \text{NiO} \cdot \text{Al}_2\text{O}_3 \), \( \text{NiAl}_2\text{O}_4 \)). To in-
vestigate the influence of the different oxidation form
of Ni on the SMR reactivity, several samples were pre-
pared with different pre-treatments. A reduced fresh
catalyst (direct \( \text{H}_2 \) reduction) was oxidized with air of
100 mL·min\(^{-1}\) at 623 K for 2 h, and the resulting cata-
lyst was used as Sample 2. The difference between
Sample 2 and Sample 3 lay in the last oxidation stage
that the latter was oxidized with air at 1073 K for 2 h.
A fresh catalyst was directly calcined in an electric
furnace at 973 K for 2 h under air atmosphere, and
was named Sample 4. \( \text{H}_2 \)-TPR analyses of Samples
2–4 were shown in Figure 2. Due to the low oxidation
temperature of Sample 2, only one low-temperature
peak at 675 K was detected and assigned to \( \text{NiO} \). In
Sample 3, similar to a deactivated catalyst (Sample 5),
two reduction peak was observed, i.e., \( \text{NiO} \) and
\( \text{NiAl}_2\text{O}_4 \). When a fresh catalyst was directly calcined
in air at 973 K, however, only the high-temperature
peak of \( \text{NiAl}_2\text{O}_4 \) was found. In comparison of Sample
3 with Sample 4, the appearance of the reduction peak
at 739 K in Sample 3 indicated that the reducibility
into Ni(0) was considerably improved by the previous
\( \text{H}_2 \) reduction and the subsequent air oxidation, though
it seems contradictory that the previous oxidation tem-
perature of Sample 3 (1073 K) was higher than the
calcination temperature of Sample 4 (973 K), which
maybe requires some new explanation. The detailed
discuss will be carried out later (Figure 4).

After the \( \text{H}_2 \) reduction, Samples 2–4 were tested
in the SMR reaction at 1073 K (Figure 3). Samples 2
and 4 were observed to give short-term initial SMR
activity, and then quickly deactivated. Surprisingly,
when using Sample 3, the initial high activity was sta-
ably maintained at least for one day. These results indi-
cated that the catalyst pre-treatment had great influ-
ence on its SMR reactivity. Regarding to the initial high

SMR activity, El-Bousiffi and Gunn (2007) proposed
that the initial high activity was due to the formation
of micro-crystallites of nickel throughout the catalyst
structure arising from the micro-distribution of nickel.
The fall of the SMR reactivity was associated with the
solid-state diffusion allowing the nickel to react with
alumina to form nickel aluminate. Similar results and
interpretations were also reported by Takemura et al. (1966). These results and interpretations were coincident with our experimental phenomena that the formation of the oxidation form of Ni was definitely observed in the deactivated catalyst (Sample 5).

As mentioned above, the redox form of Ni played an extremely important role in the SMR reactivity. In order to gather further information about the complete redox cycle of Ni, a multiple loop of reduction-oxidation test was carried out on a fresh catalyst by using the TPR apparatus, and the result was shown in Figure 4. First, a fresh Ni/Al2O3/Alloy catalyst was reduced in 65% H2/Ar of 70 mL·min⁻¹ from ambient temperature to 1073 K at a ramping rate of 10 K·min⁻¹ and maintained at 1073 K for 1 h. After that, it was cooled to ambient temperature. Then, 40% O₂/He of 70 mL·min⁻¹ was introduced into the sample cell to oxidize the reduced catalyst at a ramping rate of 10 K·min⁻¹ up to different maximum temperatures, and was maintained for different periods. Subsequently, a same H2 reduction was repeated on this catalyst after it was cooled. All H2 reduction tests were monitored by a TCD detector. The number of sample tested in Figure 4 and the test sequence were summarized in Table 1.

In comparison of Sample b with Sample a (a fresh catalyst), the most obvious difference was the disappearance of the xNiO-Al2O3 peak after the oxidation operation (1073 K, 2 h). Similar results were observed when comparing Samples 3 and 5 with Sample 1 (a fresh catalyst) in Figure 2. Thus, xNiO-Al2O3 was considered very unstable at high temperature and in the presence of oxygen or steam. In addition, shortening the oxidation time to 0.5 h (Sample c), or decreasing the oxidation temperature to 873 K (Sample e), produced a small and ambiguous peak around 907 K which was near to the reduction temperature of xNiO-Al2O3 in a fresh catalyst. However, a complete recovery of xNiO-Al2O3 did not be achieved compared with a fresh catalyst. These results indicated that the phase composition and structure of Ni in a fresh catalyst were unstable and unrecoverable, due to the existence of the non-stoichiometric nickel aluminate. On the other hand, similar H2-TPR profiles between Sample b and Sample d showed catalyst recoverability, though the previous treatments before the oxidation operation (1073 K, 2 h) were different between Sample b and Sample d. That is, the pre-reduction and pre-oxidation could produce a more stable catalyst than a fresh catalyst. Moreover, in Figure 2, a directly calcined catalyst (Sample 4) provided only a reduction peak associated with NiAl2O4. However, when a pre-reduction was conducted before oxidation (Sample 3), the reducibility into Ni(0) was considerably improved. Consequently, the appropriate pretreatment conditions of pre-reduction and subsequent pre-oxidation brought not only more stable, but also more reducible phase composition and structure of Ni than a fresh catalyst. Takemura et al. (1966) reported a similar effect of the previous reduction and subsequent oxidation on the catalyst reducibility of a 10 wt% Ni/α-Al2O3. They attributed the increased catalyst reducibility to crystal fragmentation of the catalyst occasioned by the previous reduction and subsequent oxidation. Bolt et al. (1995) stated that due to the high onset temperature for the reduction of NiAl2O4, nickel sintering was inevitable during the reduction of deactivated Ni/Al2O3 catalysts by NiAl2O4 formation, and as a result, such a reduction treatment would not lead to a fully regenerated catalyst. This is true even for catalysts still containing some Ni which has not reacted to spinel: the presence of such nickel species may lead to a lowering reduction onset temperature of the NiAl2O4 due to hydrogen spillover.

2.3 Activation treatments

In our experiment, an interesting result was observed that a stable activity could be achieved when a deactivated catalyst was re-reduced (i.e., RDR treatment). A reduced fresh catalyst quickly lost its reactivity, and the deactivated catalyst was re-reduced with H2 when CH4 conversion became less than 10%. In the second SMR test, an approximate 100% of CH4
conversion was maintained at least for 55 h at 1073 K, as shown in Figure 5.

As mentioned above, steam was considered as the catalyst poison due to the oxidation of Ni(0) with steam. In Figure 6, the negative influence of steam on the SMR reactivity was verified again by measuring the dynamic responses of CH₄ conversion upon step feed and shut-off steam at 1073 K. Using a RDR treated catalyst, first, the SMR test was maintained for 3 h in the presence of CH₄/H₂O/N₂, and then CH₄ was switched off and only H₂O/N₂ was introduced into the reactor for 30 min. Subsequently, methane was re-added into the H₂O/N₂ stream. The catalyst almost completely lost its reactivity, due to steam poisoning. Furthermore, this poisoning was found that it could not be recovered by the CH₄/H₂O/N₂ stream, and a re-reduction with H₂ was required to regenerate the deactivated catalyst.

Generally, it is accepted that the particle size of nickel will considerably increase in H₂ reduction and subsequent SMR test, i.e., sintering of nickel via particle migration and coalescence. Teixeira and Giudici (1999) stated that reaction between the nickel particles and the feed, for instance steam and carbon monoxide, also accelerated the sintering of nickel. They verified that the rate of sintering was strongly affected by steam, with more than a two-fold increase with respect to the rate in H₂. On the other hand, Lif et al. (2004) reported that a double impregnation method with high temperature calcination in between could give a more stable Ni/γ-Al₂O₃ catalyst to suppress sintering due to the existence of a NiAl₂O₄ layer between the Ni particles and the γ-Al₂O₃ support. And, they pointed out that the stabilizing effect of NiAl₂O₄ was most likely due to a stronger Ni bonding to NiAl₂O₄ than to the Al₂O₃. The NiAl₂O₄ layer, in turn, bound well to Al₂O₃, and the NiAl₂O₄ was actually incorporated in the surface of the Al₂O₃ support.

In our case, the relatively low nickel loading (4.9 wt%) suggested that the impregnation of the low concentration Ni²⁺ produced a high dispersion of nickel, i.e., small particle size of nickel. In the SMR test, on the influences of high-temperature and steam, the particle size was remarkably increased. Accompanying with this increase, the effect of solid-state diffusion allowed more nickel to react with steam and alumina support into oxidation form of Ni, as observed in Figure 2. After the second H₂ reduction, as stated in Figures 2 and 4, the catalyst with the pre-reduction and subsequent pre-oxidation (with oxygen or steam) treatments provided a more stable and more reducible phase composition and structure of Ni, and resulted in a stable SMR activity in the second SMR test. With regard to the formation of the stable and more reducible phase structure, the appearance of an interfacial NiAl₂O₄ layer might be a plausible interpretation. After the second H₂ reduction, the oxidation form of Ni in the deactivated catalyst was mostly reduced into Ni(0). However, once the SMR reactants (especially steam) were introduced into the reactor again, the formation of NiAl₂O₄ was still inevitable, in particular at the bottom of nickel particles, where the contact of nickel and alumina support was the closest. In the light of the conclusions reported by Lif et al. (2004) and Bolt et al. (1995), this interfacial NiAl₂O₄ formed in the second SMR test was believed that: 1) it suppressed the further sintering of nickel; 2) as a result of 1), it cut off the contact between the top metallic nickel and alumina support, due to the anchorage of NiAl₂O₄. That is, it halted the further reaction of the top nickel particles with alumina, and maintained sufficient active Ni(0). The change of H₂-TPR profile of the catalyst in the process of the RDR treatment was shown in Figure 7. The result of the catalyst spent in the second SMR test for 40 h (in Figure 5) unambiguously showed that the oxidation of nickel with steam was substantially suppressed compared with the catalyst spent in the first SMR test, maybe due to the existence of the
weak high-temperature peak of NiAl$_2$O$_4$. However, the small particle size of Ni in a reduced fresh catalyst was believed that it could not support this complicated steric-structure. That is, the increased Ni particle size to some extent was favorable to the formation of the steric-structure. Upon these results, our recent research showed that a new Ni/Al$_2$O$_3$/Alloy catalyst with a high Ni loading of 17.9 wt%, which was prepared by a double impregnation method and was calcined at a high temperature after the first impregnation with an aim to produce a effective interfacial NiAl$_2$O$_4$ layer, gave a high and stable SMR activity for 1000 h at 973 K after the first H$_2$ reduction (Zhou et al., 2007).

In Figure 3(b), a ROR treated catalyst (H$_2$ Reduction $\rightarrow$ air Oxidation $\rightarrow$ H$_2$ re-Reduction) also gave a high and stable SMR reactivity after the second H$_2$ reduction. Comparison of the H$_2$-TPR result of a deactivated catalyst with that of the catalyst with the ROR treatment (before the second H$_2$ reduction, in Figure 2) showed an evident similarity in the peak number, peak shape and reduction temperature, suggesting that the reason for the positive effect of the ROR treatment was probably similar to that of the RDR treatment. That is, with the particle size of nickel increasing in the twice reduction stages and the air oxidation stage, the appearance of the effective interfacial NiAl$_2$O$_4$ layer in the subsequent SMR test was responsible for the high and stable SMR reactivity in the second SMR test. However, it should be noted that the effect of the ROR treatment closely depend on the ROR conditions, for instance the temperature and time of air oxidation. A catalyst with a similar ROR treatment, in which the temperature of air oxidation was set at 623 K (Sample 2 in Figure 2), did not showed notable improvement on the SMR stability, as shown in Figure 3(a), maybe due to the relatively low oxidation temperature which could not produce sufficiently big particle size to support the complicated steric-structure of the interfacial NiAl$_2$O$_4$ layer.

However, we do not yet have more direct evidence to support these hypotheses, especially to verify the existence of the interfacial nickel aluminate layer. Further research into chemical phase transition, the change of the particle size and the effect of the interfacial nickel aluminate by using FESEM-EDX, TEM and XPS, becomes an urgent need and is in progress. It is also necessary to investigate further the similarity and difference between the RDR treatment and the ROR treatment. In addition, the disappearance of $\text{NiO} \cdot \text{Al}_2\text{O}_3$ (in Figure 2) should be further studied.

Conclusions

A plate-type metal-monolithic anodic alumina supported nickel catalyst (Ni/Al$_2$O$_3$/Alloy) was employed to investigate the reactivity and the catalyst deactivation in the SMR reaction, and several methods of activation treatments were proposed. After H$_2$ reduction, a fresh Ni/Al$_2$O$_3$/Alloy catalyst only provided a short-term SMR activity, and then quickly deactivated. The oxidation of metallic nickel with steam into oxidation state was believed to be the most serious reason for the catalyst deactivation. After the second H$_2$ reduction, a deactivated catalyst (or a catalyst with the treatments of H$_2$ reduction and subsequent air oxidation) was observed to provide a more favorable SMR stability, compared a reduced fresh catalyst.

Literature Cited


