Effect of NiAl$_2$O$_4$ formation on Ni/Al$_2$O$_3$ Stability during Dry Reforming of Methane

Lu Zhou, [a] Lidong Li,[a] Nini Wei, [b] Jun Li,[b] Kazuhiro Takanabe, [a] and Jean-Marie Basset*[a]

A series of alumina-supported Ni catalysts were prepared to examine their activity and carbon deposition during dry reforming of methane (DRM). By increasing the final calcination temperature to 900°C to form exclusively NiAl$_2$O$_4$, a catalyst with strong metal–support interactions was obtained. During a long-term DRM reaction (of about 100 h) at 700°C and with CH$_4$/CO$_2$ = 1:1, reduced Ni (from NiAl$_2$O$_4$) showed a high resistance to sintering and coking. The DRM kinetics behaviours of the catalysts calcined at different temperature were also investigated. Carbon growth models were proposed to rationalize the different carbon morphologies observed on the catalysts.

Introduction

Dry reforming of methane (DRM) (Eq. (1)) has become an important research topic over recent years.[1-2] This process uses both greenhouse gases CO$_2$ and CH$_4$ to produce syngas H$_2$/CO at a low ratio of ~1:1 that is a suitable feedstock in Fischer–Tropsch synthesis.

$$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2, \Delta H_{298} = +247 \text{ kJ/mol} \quad (1)$$

Numerous supported “monometallic” catalysts have been studied for DRM; more specifically, noble metals based catalysts such as Rh, Ru and Pt are known to exhibit promising performance.[3] However, considering the high cost and the limited availability of noble metals, Ni-based catalysts are more attractive for industrial applications. As for the support, Wang and Lu[4] reported that the use of Al$_2$O$_3$ as support for Ni catalysts resulted in a supported Ni catalyst with superior initial activities over Ni catalysts than that used SiO$_2$, TiO$_2$, MgO, ZrO$_2$, CeO$_2$, La$_2$O$_3$, clay, or zeolites as a support. Therefore, Ni/Al$_2$O$_3$ catalysts are the most commonly reported DRM catalysts in the literature.

Nevertheless, it must be pointed out that owing to carbon deposition accompanied with Ni oxidation and/or sintering, NiAl$_2$O$_4$ catalysts suffer from severe deactivation.

Regarding carbon deposition on NiAl$_2$O$_4$ catalysts during DRM, it is reported that the mechanism of coke formation is similar to that of steam reforming of methane (SRM).[5] However, the potential for coke formation on Ni catalysts during DRM is much higher. Methane cracking (Eq. (2)) and the Boudouard reaction (Eq. (3)) are believed to be the two main routes of carbon formation.

$$\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2, \Delta H_{298} = +74.9 \text{ kJ/mol} \quad (2)$$
$$2\text{CO} \rightarrow \text{CO}_2 + \text{C}, \Delta H_{298} = -172.5 \text{ kJ/mol} \quad (3)$$

Wang and Lu[4] reported a coke deposit of 62.76 wt.% on 12 wt.% Ni/Al$_2$O$_4$ after 2 h DRM at 700°C; the reaction conditions were CH$_4$/CO$_2$ = 1:1, pressure = 1 atm, F/W = 18000 mLh$^{-1}$g$_{\text{cat}}^{-1}$. De Miguel et al.[6] reported a coke deposit of 22 wt.% on 10 wt.% NiAl$_2$O$_4$ after 108 h DRM at 750°C; the reaction conditions were CH$_4$/CO$_2$ = 1:1, pressure = 1 atm, F/W = 7000 mLh$^{-1}$g$_{\text{cat}}^{-1}$. As demonstrated in the literature,[7] by adjusting the reaction conditions, thermal dynamical coking can be inhibited and Ni/Al$_2$O$_3$ catalysts can thus maintain their activity. Xu et al.[8] reported a 120-h stable DRM activity over a 9.17 wt.% NiAl$_2$O$_4$ catalyst at 700°C, with a CO$_2$/CH$_4$ ratio of 1:3.1. Gadalla et al.[9] and many other researchers also suggested that higher CO$_2$/CH$_4$ ratios could suppress coke deposition on NiAl$_2$O$_4$ catalysts. However, for industrial processes, a ~1:1 CO$_2$/CH$_4$ ratio is preferred. Higher CO$_2$/CH$_4$ ratios could improve the reverse water–gas shift (RWGS) reaction (Eq. (4)), thus resulting in lower H$_2$ selectivity. Furthermore, methane sources, such as biogas, usually comprise CO$_2$/CH$_4$ ratios of less than one.

$$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}, \Delta H_{298} = +46.1 \text{ kJ/mol} \quad (4)$$

Based on the above discussion, a catalyst that kinetically inhibits carbon formation under conditions that are thermodynamically favourable for carbon deposition is urgently required for the DRM process. Therefore, the investigation of coking-resistant Al$_2$O$_3$-supported Ni catalysts has become a very important subject and much effort has recently been devoted to the design of coking-resistant Ni/Al$_2$O$_3$-based catalysts by decorating the Ni particles with trace amounts of noble metals.[10] In our previous research,[11] we also reported a good DRM stability over Ni/Pt bimetallic catalysts. Nevertheless, it is obvious that these noble metal decorated catalysts are unsuitable on a commercial scale because of their high cost.

The formation of NiAl$_2$O$_4$ spinel has generally been considered to be another route leading to the deactivation of NiAl$_2$O$_4$ catalysts during methane reforming reactions.[3, 5] NiAl$_2$O$_4$ can easily form under reaction between Ni and Al$_2$O$_3$; however, it is believed that the NiAl$_2$O$_4$ spinel cannot be easily reduced to Ni(0) and thus its formation should lower the amount of active Ni. Only limited literature reports demonstrate the positive influence of NiAl$_2$O$_4$ on catalyst activity. Alternatively, Enger et al.[12] recently reported that reducing the NiAl$_2$O$_4$ at 800°C to nano-sized (15–25 nm) Ni particles afforded a catalyst with good SRM activity. Ribeiro et al.[13] prepared a NiAl$_2$O$_4$ catalyst with a high surface...
area that was activated with CH₄/O₂. The resulting catalyst displayed excellent DRM stability for more than 40 h. In our recent study,[14] we reported the excellent SRM activity of a plate-type anodic alumina-supported Ni catalyst featuring an interfacial NiAl₂O₄ layer; moreover, coke deposition was suppressed and the Ni particle sintering rate was reduced. The catalyst was examined in DRM, and showed good initial activity. Chen and Ren[15] studied the influence of calcination temperature on the activity of a 13 wt.% Ni/Al₂O₃ catalyst for DRM. They concluded that the formation of NiAl₂O₄ suppressed coke deposition. However, the DRM process was only conducted over a relatively short period of 3 h at 750°C, and the applied CH₄/CO₂ ratio of 1:2 was above the normal industrial requirement.

As a consequence of these preliminary published results, we investigated in detail, in the present work, the effect of NiAl₂O₄ formation on the Ni/Al₂O₃ catalyst performance during a long-term DRM process (of about 100 h) at 700°C and with a CH₄/CO₂ of 1:1. The aim was to develop a relatively cheap catalyst without any added promoters. The catalyst structure, catalyst reducibility, and Ni particle dispersion, size, morphology and amount of deposited carbon were characterized with X-ray diffraction (XRD), thermo gravimetric analysis (TGA), transmission electron microscopy (TEM), temperature-programmed reduction (TPR), and temperature-programmed desorption (TPD). The DRM and carbon formation kinetic behaviours of the catalysts are also reported.

Results and Discussion

Influence of NiAl₂O₄ formation on catalysts structure

The XRD patterns of the as-prepared catalysts, calcined at different temperatures, are shown in Figure 1 (patterns a–c). With increasing calcination temperatures, the Al₂O₃-supported Ni catalysts exhibited stronger NiAl₂O₄ but weaker NiO diffraction peaks. It is well known that under a high-temperature calcination condition, nickel ions have sufficient energy to overcome the surface barrier of alumina and integrate into the alumina lattice to form the spinel structure, i.e., NiO reacts with Al₂O₃ to form NiAl₂O₄. This is evident from the XRD results that show that high temperatures, such as 900°C, favour such reaction; the sample Ni/Al₂O₃(900) that was calcined at 900°C displayed only NiAl₂O₄ peaks as Ni-oxides.

Stating that in the DRM the metallic state of Ni is required, a pre-reduction of the catalyst is in principle needed. Figure 2 shows the reducibility performance of different catalysts by H₂-TPR analysis.

The TPR results confirmed the existence of different types of nickel oxides present in the as-prepared catalysts. According to our previous report,[14] the reduction peaks observed below 600°C can be ascribed to the reduction of NiO to Ni(0) nanoparticles, whereas the peaks observed between 600 and 800°C can be ascribed to the reduction of “NiO-Al₂O₃” (or better described as surface NiAl₂O₄). The peaks observed above 800°C were attributed to the reduction of crystalline spinel NiAl₂O₄ to Ni(0) nanoparticles. Consequently, it can be concluded that Ni/Al₂O₃(350) mainly consists of NiO, Ni/Al₂O₃(700) consists of NiO·Al₂O₃, and Ni/Al₂O₃(900) consists of NiAl₂O₄ only.

In this study, the catalysts pre-reduction was performed with pure H₂ at 800°C. The reduction degree was calculated by the TPR profiles done at 800°C, while assuming that the Ni exists as Ni²⁺. The calculated results showed that, following H₂ reduction at 800°C, Ni/Al₂O₃(350) primarily featured metallic Ni (also see Figure 1 pattern d), whereas 61% and 7% of the nickel oxide in Ni/Al₂O₃(700) and Ni/Al₂O₃(900), respectively, were reduced to metallic Ni. Because the nickel oxides in Ni/Al₂O₃(700) and Ni/Al₂O₃(900) could not be completely reduced at the selected
temperature (i.e., 800°C), the resulting two catalysts are best referred to as Ni-NiAl₂O₄-Al₂O₃. These were confirmed by the XRD patterns of the catalysts that underwent H₂ reduction at 800°C. As observed in Figure 1 (patterns e–f), the co-existence of Ni and NiAl₂O₄ were observed for Ni/Al₂O₃(700) and Ni/Al₂O₃(900).

The Ni metal morphology and size distribution of the reduced catalysts were investigated by TEM (Figure 3). The average particle size of metallic Ni measured by TEM on each sample is listed in Table 1. According to the TPR profiles in Figure 2, the reduction temperature of 800°C is too low to reduce the NiAl₂O₄. Perhaps this is the reason why, among these reduced catalysts (Figure 3a–c), little difference on the particle size can be seen. The NiAl₂O₄(350) shows the smallest mean Ni particle size of 9 nm. The NiAl₂O₄(900) shows the largest mean particle size of around 13 nm.

Therefore, the influence of different nickel oxides supported on alumina, especially NiAl₂O₄, on Ni sintering was investigated by assessing the change in Ni size would follow reduction of the catalysts under pure H₂ at a relatively high temperature of 1100°C for 1 h. As observed in Figure 3A–C, the presence of NiAl₂O₄ exerted a positive effect on Ni sintering. The particle size decreases from 32 nm for NiAl₂O₄(350) to 29 nm for NiAl₂O₄(700) and to only 21 nm for NiAl₂O₄(900). Considering the different Ni-oxides over these samples, it is reasonable to conclude that the NiAl₂O₄ existence helps to stabilize the Ni particles toward sintering under high reaction temperature. And this stabilizing effect of nickel aluminate was most likely because of a stronger nickel bonding to nickel aluminate relative to that with the alumina. The nickel aluminate, in turn, bonded well to alumina, and the nickel aluminate was effectively incorporated into the surface of the alumina support. [16] It is likely that

<table>
<thead>
<tr>
<th>Table 1. Change of catalysts structure properties with different pre-reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Samples</strong></td>
</tr>
<tr>
<td>NiAl₂O₄(350)</td>
</tr>
<tr>
<td>NiAl₂O₄(700)</td>
</tr>
<tr>
<td>NiAl₂O₄(900)</td>
</tr>
</tbody>
</table>

[a] Particle size detected by TEM
[b] Crystallite size calculated from Sherrer equation

<table>
<thead>
<tr>
<th>Table 2. Characterization of catalysts in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Samples</strong></td>
</tr>
<tr>
<td>NiAl₂O₄(350)</td>
</tr>
<tr>
<td>NiAl₂O₄(700)</td>
</tr>
<tr>
<td>NiAl₂O₄(900)</td>
</tr>
<tr>
<td>Al₂O₃</td>
</tr>
</tbody>
</table>

[a] Catalysts reduced by H₂ at 800°C for 1h

Figure 3. TEM images of H₂ reduced samples. After reduction at 800°C for 1h: (a) NiAl₂O₄(350), (b) NiAl₂O₄(700), (c) NiAl₂O₄(900); After reduction at 1100°C for 1h: (A) NiAl₂O₄(350), (B) NiAl₂O₄(700), (C) NiAl₂O₄(900).
incomplete reduction of NiAl₂O₄ produces Ni sites that can strongly interact with a NiₓAlᵧOₘ support. The NiₓAlᵧOₘ support can be considered as a deficient NiO–Al₂O₃ solid solution-like species featuring a number of Ni²⁺ defects. It is proposed that such defects play an important role in stabilizing the catalytic size of Ni.

The Ni loading in Table 2 was ~16 wt.%. Because of the alumina support sintering under increasing calcination temperatures, the BET areas decreased in the order of Ni/Al₂O₃(350) > Ni/Al₂O₃(700) > Ni/Al₂O₃(900). The dispersion was consistent with the Ni particle size in Table 1.

Kinetic investigation of the DRM catalytic activity

The effect of temperature (500–800°C) on the reaction rates of methane and CO₂ consumption and product formation (CO and H₂) over the three types of as-prepared alumina-supported Ni catalysts was investigated. For each temperature case studied, the reaction rates were calculated from the initial reaction stage (20 min) to ensure precise control of catalytic activity of the preformed catalyst. The TOF for the reactants CH₄ and CO₂ and the product H₂/CO ratio as a function of temperature are presented in Figure 4. It is obvious that both CH₄ and CO₂ conversions and H₂/CO ratio increased with increasing temperatures regardless of the catalyst studied. The H₂/CO ratio determined at 500°C was only 0.45 and increased to 0.7 at 800°C. These values were far away from the values predicted from the thermodynamic calculations. At low temperatures (500–600°C), all catalysts exhibited similar activity in terms of CH₄ and CO₂ conversion and H₂/CO ratio, whereas at high temperatures (650–800°C), the activity increased in the order of Ni/Al₂O₃(900) < Ni/Al₂O₃(700) < Ni/Al₂O₃(350). The difference in the initial TOF activities among these three samples may be related to the size of the Ni particles. Similar results were reported by Wang et al.[17] who prepared a series of NiO/MgO catalysts with different Ni particle sizes (3–20 nm) and observed that the activity, as measured by CH₄ TOF, increased with reducing Ni particle sizes. They suggested that the coordinatively unsaturated surface atoms prevail in small crystallites and are significantly more active than those in the low-index planes predominately exposed on large crystallites.

The apparent activation energies calculated from the Arrhenius plots are shown in Figure 5. Regardless of catalyst studied, the activation energy for CH₄ consumption was in agreement with that reported by Osaki et al.[18] (i.e., ~33 kJ/mol).

The activation energy of CO₂ consumption was higher than that of CH₄ consumption, indicating that the activation of CO₂ is more temperature sensitive than that of methane. Lower CO₂ activation energies (relative to those of CH₄) are usually reported for catalyst supports with a strong Lewis base character such as MgO, ZrO₂, and TiO₂. Guo et al.[19] reported CH₄ and CO₂ activation energies of 26.39 and 40.43 kJ/mol, respectively, over 5% Ni/MgAl₂O₄, consistent with the findings of the present study. Both CH₄ and CO₂ activation energies were lower than those for CO and H₂ production, suggesting that the rate-determining steps for CO and H₂ formation are different from those for CH₄ and CO₂ consumption. The activation energy for H₂ production is significantly higher than that for CO, thereby indicating that the RWGS reaction (which consumes H₂ and produces CO) strongly influences the formation of H₂, thus generating an H₂/CO ratio of less than 1 (Figure 4c). It has been reported that supports can significantly influence the activation energy by altering the rate-controlling step in the reaction sequence.[20] The difference in the activation energies of these three catalysts is thus most likely because of the different support composition. A higher amount of non-reduced NiAl₂O₄ will remain supported on the alumina support and act as the “real” support for catalysts...
prepared at higher calcination temperatures, thereby altering the surface mechanism.

Table 3 presents the catalytic DRM stability performance over the three types of catalysts prepared in this study. Catalysts prepared at higher calcination temperatures showed better stability. Both Ni/Al2O3(350) and Ni/Al2O3(700) suffered severe deactivation within the early stages of the process. Ni/Al2O3(350) catalyst showed a 50% loss of its initial activity within the first 15 h of reaction and only retained 30% of its initial activity after 100 h of reaction, whereas Ni/Al2O3(700) lost 40% of its initial activity within the first 15 h of reaction and retained almost 50% of its initial activity after 100 h of reaction. Ni/Al2O3(900) only lost 10% of its initial activity within the first 15 h of reaction, and negligible catalyst deactivation was evidenced within the remaining 85 h of reaction, which we consider as a remarkable result. The coking amount of the three catalysts after 100 h DRM, as shown in Table 3, clearly demonstrating that the NiAl2O4 reduced the extent of carbon deposition on the reduced catalyst. The “Ni” from the reduction of NiAl2O4 over Ni/Al2O3(900) resulted in only a 8-wt.% coking, whereas the “Ni” from the reduction of NiO over Ni/Al2O3(350) resulted in a 37-wt.% coking after 100 h DRM. The “Ni” from reduced Ni/Al2O3(700) comprising both NiO·Al2O3 and NiAl2O4 resulted in moderate 16-wt.% coking.

Small Ni particles are often reported to limit the level of coking during DRM. Hu and Ruckenstein [21] concluded that large Ni particles stimulate carbon deposition. However, according to the present data (Table 1) it could be seen that the Ni particle size

![Figure 5](image_url)

**Figure 5.** Arrhenius plots and apparent activation energies over different catalysts at N2:CH4:CO2 = 2:1:1, F/W = 480 L/gcat·h: (a) Ni/Al2O3(350); (b) Ni/Al2O3(700); (c) Ni/Al2O3(900); (d) Apparent activation energies.
was not the only factor influencing carbon deposition. Although
the Ni particles sizes of three reduced samples were similar, the
level of coke deposition was totally different. These results
indicate that in addition to the Ni particle size, the
physicochemical state of the nickel oxide species in the as-
prepared catalyst sample influenced carbon deposition. Juan-
Juan et al.\cite{22} indicated that besides the particle size, other
factors, such as particle morphology or structure, influence
carbon deposition. It is reasonable to conclude that the “Ni” from
the reduction of NiAl_{2}O_{4} would suppress coking to a higher
degree than that the “Ni” from NiO and/or NiO-Al_{2}O_{3} during DRM.
NiO species that are prone to reduction would produce Ni sites
with weak metal–support interactions, which could be
responsible for the severe sintering and coking observed for
Ni/Al_{2}O_{3}(350) and Ni/Al_{2}O_{3}(700). The Ni particles reduced in
Ni/Al_{2}O_{3}(900), i.e., partial reductive extraction of Ni^{2+} ions from
NiAl_{2}O_{4}, are expected to adequately strongly interact with the
support to inhibit carbon deposition. Enger et al.\cite{12} reported that
the reduction of NiAl_{2}O_{4} does not simply yield Ni/Al_{2}O_{3}, but
bimetallic species such as NiAl/Al_{2}O_{3}. Considering that in a
reducing atmosphere Ni from NiAl_{2}O_{4} forms such kind of a
defective NiAl_{2}O_{4} phase, which has probably a higher oxygen
surface mobility, the high stability of the samples containing
NiAl_{2}O_{4} can be also related to a higher rate of carbon
gasification over these samples.

**Carbon deposition on different catalysts**

Figure 6 shows the TGA–DTA data for the spent catalysts after
undergoing 100 h DRM. As noted, an increase in the sample
weight was observed at temperatures of 300–430°C that could
be due to the oxidation of Ni to nickel oxides. The amount of
deposited coke on the different catalysts was calculated based
on the TGA curves and the results are shown in Table 3. Oxidation of carbonaceous deposit with oxygen in air is an
exothermic process, and DTA was employed to investigate the
decoking of catalysts. All three spent samples displayed two
distinct exothermic peaks at 500–550°C and 680–700°C. This
indicates the deposit of more than one type of carbon species on
the catalyst surface. According to the literature,\cite{23} deposited
carbon on Ni-based catalyst surfaces can be classified into three
types: amorphous carbon C_{α}, filament carbon C_{β}, and graphite
carbon C_{γ}. Deposited C_{α} is often reported to be an active carbon
species during DRM and can easily be eliminated by oxidation
or H_{2}-reduction at temperatures as low as 250–350°C. Some
researchers\cite{24} explain that C_{α} originates from nickel carbide
that is produced during methane decomposition and does not affect
the catalyst DRM activity. C_{γ} is an inert carbon species and
requires temperatures higher than 600°C for removal. C_{β} is
known to possess a relatively high activity and can be eliminated
at a relatively low temperature. Therefore, the DTA peak
observed at 680–700°C could be ascribed to the oxidation of
graphite carbon C_{γ}, whereas the peak at 500–550°C can be
attributed to filament carbon C_{β}. XRD patterns of the spent
catalysts following 100 h DRM, shown in Figure 7, also
demonstrate the existence of graphitic carbon in all three
samples; the intensity of graphite carbon in spent Ni/Al_{2}O_{3}(900)
was the lowest. The DTA result also showed that the intensity of
the C_{γ} peak decreased in the order of Ni/Al_{2}O_{3}(350) > Ni/Al_{2}O_{3}(700)
> Ni/Al_{2}O_{3}(900). These findings support the different DRM stability
observed in Table 3. As reported,\cite{24} C_{α} and C_{β} can gradually

---

**Figure 6.** TGA-DTA behaviour of different catalysts after DRM in Table 3: (a)(A) Ni/Al_{2}O_{3}(350); (b)(B) Ni/Al_{2}O_{3}(700); (c)(C) Ni/Al_{2}O_{3}(900).
transform into C\(_\gamma\) with time. This may explain the absence of amorphous carbon C\(_\alpha\) in the DTA curves of all three samples that were subjected to 100 h DRM.

Figure 8 shows TEM images of the morphologies of deposited carbon on the spent catalysts. Filament carbon with a multi-wall carbon nanotube (MWCNT) morphology was present on all three samples. Only Ni/Al\(_2\)O\(_3\)(350) additionally featured carbon nano onions (CNO), whereby Ni particles were encapsulated within graphite carbon in Figure 8(a). The MWCNT morphology displayed different structural properties: chain-like (with or without embedded Ni particles) (Figure 8(B) or (c)), close end (Figure 8(C)), and open mouth (with or without Ni particles on the tip of the nanotube) (Figure 8(A) or (b)).

Figure 9 summarizes the different morphologies of carbon deposited on the three catalysts that originated from variations in the nature of the metal–support interaction. The coking process in DRM is believed to proceed in three steps: carbon deposition on Ni particles, carbon diffusion through the bulk Ni particles, and carbon precipitation. Besides the metal–support interaction, the coke morphology is very likely directly related to the balance between the carbon deposition and carbon diffusion–precipitation rates. Regarding Ni/Al\(_2\)O\(_3\)(350), Ni particles from the bulk NiO sinter into larger Ni particles (40 nm) onto which the carbon deposition rate is relatively higher than the diffusion–graphite formation rate, resulting in rapid encapsulation of Ni particles into graphite carbon to form CNO, consequently leading to complete catalyst deactivation. For the Ni reduced from highly dispersed NiO, with a relatively strong interaction with the alumina support, comparable carbon deposition and diffusion–precipitation rates are expected. In this case, the deposited carbon would follow the tip–growth model: the carbon initially deposits on the top surface of the Ni metal, carbon diffuses down through the metal, and MWCNTs precipitate at the bottom of the Ni metal, driving the entire metal particle off.
the support. The Ni on the tip of the MWCNTs is accessible and acts as an active site for carbon deposition. The presence of a concentration gradient in Ni promotes carbon diffusion and continual growth of the MWCNTs.

Regarding Ni/Al₂O₃, the Ni-support interaction is relatively high, with an obtuse contact angle between Ni and the support. Initial carbon deposition and carbon diffusion proceed similarly to that in the tip-growth mechanism; however, the MWCNT precipitation fails to drive the Ni metal particles upwards. Hence, precipitation is forced to occur at the Ni apex, thus resulting in carbon precipitation on the other side of the exposed surface of the Ni particles rather than at the interface between the lower portion of Ni and support. This would lead to the formation of carbon nanotubes on the surface of Ni particle at the gas-solid interface. As a result, the Ni particles would be fixed on the support, but with the carbon tube growing with a closed end with Ni at the bottom of the nanotube. This is referred to as the base-growth model. Furthermore, Lee and Park used this model to rationalize the formation of chain-like MWCNTs, whereby the compartment graphite sheets grew by forming joints with the wall. Because Ni from NiO·Al₂O₃ in Ni-b may not have adequately strong interaction with the support, during DRM at 700°C, the Ni particles behave as a quasi-liquid and can be easily split into smaller particles and absorbed into the interior of the chain-like MWCNTs. Similar results were also reported by Hua and Wang.

In all, the carbon deposition happened over all three catalysts and this explained the initial catalyst deactivation. However, the strong metal-support interaction would not only help to fix the Ni particles into the support to suppress them towards sintering, but also favour the carbon tube growing with an active Ni at the bottom of the nanotube.

Conclusions

In this study, three types of alumina-supported Ni catalysts were prepared by the incipient impregnation method. The influence of calcination temperature during the catalyst preparation process on the catalyst physical structure, Ni dispersion, DRM activity, and carbon deposition was fully investigated. The findings are summarized as follows:

1. Catalysts prepared at low calcination temperatures showed high initial DRM activities, but poor stability. Ni reduced from NiO·Al₂O₃ showed better resistance to sintering and coking during DRM. It is likely that incomplete reduction of NiO·Al₂O₃ produces Ni sites that interact strongly with the support. It is believed that this strong interaction plays an important role in stabilizing the catalytic activity of Ni during DRM.

2. Carbon growth models were proposed to rationalize the different carbon morphologies observed on the three catalysts. Ni from bulk NiO is believed to sinter into larger Ni particles during DRM that were encapsulated by graphite carbon to form carbon nano onions. Based on the tip-growth and base-growth models, strong interaction between Ni and the support favors the formation of filament carbon including chain-like structures and MWCNTs with Ni on the tip.

![Figure 9](image-url)  
Figure 9. Image of different carbon deposition over three catalysts during DRM.
Experimental Section

Catalyst preparation

The alumina-supported Ni catalysts were prepared by incipient impregnation using Ni(NO3)2·6H2O solution. Al2O3 (AEROSID® Alu 130; Brunauer–Emmett–Teller (BET) surface area of 130 m²/g) was used as a support. The Ni loading was controlled at 16 wt.%. After impregnation, the supported Ni samples were dried at 110°C overnight and then calcined in air at 350, 700, or 900°C for 5 h. The resulting Ni catalysts are respectively referred to as Ni/Al2O3(350), Ni/Al2O3(700), and Ni/Al2O3(900).

Catalyst characterization

The elemental composition of the samples dissolved in H2SO4/HNO3 was determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES) on a Thermo-Scientific 3580 instrument.

N2 adsorption–desorption isotherms were obtained on a Micromeritics ASAP2420. Prior to measurements, the samples were degassed for 2 h at 300°C. The surface areas of the samples were determined by a multi-point BET analysis method, and pore volumes were estimated at P/P0 = 0.99.

XRD patterns were recorded on a Bruker D8 Advanced A25 diffractometer using a Bragg–Brentano geometry with a copper tube operating at 40 kV and 40 mA. The catalyst powder was compacted into disks and mounted in the chamber. The mean crystallite size of nickel was calculated using the Scherrer equation.

H2-TPR was performed on an Altamira instrument. The catalyst powder (50 mg) was placed in a U-shaped quartz reactor and pre-treated in flowing Ar (50 mL/min) for 0.5 h at 300°C, followed by cooling to room temperature. The temperature was then raised from room temperature to 1000°C at a rate of 10°C/min under a 5% H2/Ar flow (50 mL/min). A thermal conductivity detector (TCD) was employed to monitor the H2 consumption.

Combined H2-TPR and TPD measurements were conducted to analyse the dispersion of the Ni particles. Following TPR measurements from room temperature to 800°C, followed by isothermal heating at 800°C for 1 h, the sample was cooled to room temperature in 5% H2/Ar mixture and allowed to stand for 1 h. The sample was then purged with pure Ar (50 mL/min) to remove the physically adsorbed H2. Upon stability of the TCD baseline, the sample was heated at a rate of 10°C/min to 800°C in pure Ar (50 mL/min) to perform H2-TPD measurements. The ratio of 2 × (TPD signal area)/(TPR signal area) enabled estimation of the dispersion of reduced nickel.

The catalyst reduction degree was evaluated using TGA–DTA (differential thermal analysis) (NETZSCH STA 449 F1 Jupiter). The catalyst powder (20 mg) was placed in an alumina crucible and pretreated in flowing Ar (50 mL/min) for 0.5 h at 300°C, followed by cooling to room temperature. The temperature was then raised from room temperature to 1000°C at a rate of 10°C/min under a 5% H2/Ar flow (50 mL/min). The sample remained heated at 1000°C for a time period until no weight change was detected. The catalyst reduction degree at different temperatures was calculated by the ratio of weight loss at that temperature to the total weight loss.

The amount of carbon deposited on the catalyst was also analyzed using TGA–DTA. The spent catalyst powder (20 mg) was placed in an alumina crucible and pretreated in flowing Ar (50 mL/min) for 0.5 h at 300°C, followed by cooling to room temperature. The temperature was then raised from room temperature to 1000°C at a rate of 10°C/min under air flow (50 mL/min). The sample remained heated at 1000°C for a time period until no weight change was detected. The deposited carbon amount was calculated based on the weight loss.

TEM images were taken on a Titan G2 transmission electron microscope (FEI, Hillsboro, OR, USA), operating at 80–300 kV and equipped with a 4 k × 4 k charge-coupled device (CCD) camera (US4000) and an energy filter (GIF Tridiem, Gatan Inc., Pleasanton, CA, USA). The specimens were prepared by ultrasonically suspending the sample in ethanol. A drop of the suspension was then applied onto clean, highly polished copper grids and dried in air.

Activity evaluation

Activity measurements of the DRM process were conducted in a PID micro-activity reactor equipped with a long quartz tube reactor (internal diameter: 4 mm; length: 305 mm), which was heated by an electrical furnace under atmospheric pressure. First, 20 mg of catalyst (size: 250–300 µm) was loaded into the reactor, and the reaction temperature was controlled by a thermocouple placed in the center of the catalyst layer. Conversions of CH4 and CO2 were typically adjusted to be 2:1:1 over a temperature range of 500–800°C. A pre-reduction treatment was performed by heating the catalyst at 800°C for 1 h in pure H2 atmosphere. The outlet gases were analysed by online gas chromatography (GC; Varian 450) and micro GC (Soprane MicroGC 3000). The DRM catalyst activity was determined by evaluating both the turnover frequency (TOF) of CH4 and CO2. The TOF was calculated by normalizing the reaction rates to the number of exposed surface Ni atoms. The apparent activation energy (Ea) was calculated from the Arrhenius plots of the TOF.

Carbon deposition study

Thermogravimetric analyses of carbon deposits were performed on a TGA-DTA analyser under a CO2/CH4 (1:1) atmosphere. A 10-mg catalyst with a particle size of 250–300 µm was loaded
into an alumina crucible. The catalyst was reduced in pure H2 for 1 h at 800°C until no further weight change was detected. The temperature was then decreased to the reaction temperature for isothermal reaction studies under a CO2+CH4 flow of 40 mL/min. The rate of carbon formation was obtained from the slope of the curve at the early reaction stage (<2 min). Therefore, rates of coking obtained can be regarded as the initial rates. These values were accordingly used to calculate the $E_a$ of coking on the different catalysts studied.

**Keywords:** methane • dry reforming • nickel • spinel • carbon deposition

The Ni reduced from NiAl$_2$O$_4$ showed an excellent performance against sintering and coking during a long-term methane dry reforming reaction.