Structural insight into an atomic layer deposition (ALD) grown Al₂O₃ layer on Ni/SiO₂: impact on catalytic activity and stability in dry reforming of methane

Sung Min Kim a,§, Andac Armutlulu a, Wei-Chih Liao b,§, Davood Hosseini a, Dragos Stoian c, Zixuan Chen a, Paula M. Abdala a, Christophe Copéret b and Christoph Müller a,*

a Department of Mechanical and Process Engineering, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland
* e-mail: muelchri@ethz.ch
b Department of Chemistry and Applied Sciences, ETH Zurich, Vladimir Prelog Weg 1-5, 8093 Zurich, Switzerland
Swiss–Norwegian Beamlines, ESRF, BP 220, Grenoble, 38043, France

Abstract
The development of stable Ni-based dry reforming of methane (DRM) catalysts is a key challenge owing to the high operating temperatures of the process and the propensity of Ni for promoting carbon deposition. In this work, Al₂O₃-coated Ni/SiO₂ catalysts have been developed by employing atomic layer deposition (ALD). The structure of the catalyst at each individual preparation step was characterized in detail through a combination of in situ XAS-XRD, ex situ ²⁷Al NMR and Raman spectroscopy. Specifically, in the calcination step, the ALD-grown Al₂O₃ layer reacts with the SiO₂ support and Ni, forming aluminosilicate and NiAl₂O₄. The Al₂O₃-coated Ni/SiO₂ catalyst exhibits an improved stability for DRM when compared to the benchmark Ni/SiO₂ and Ni/Al₂O₃ catalysts. In situ XAS-XRD during DRM together with ex situ Raman spectroscopy and TEM of the spent catalysts confirm that the ALD-grown Al₂O₃ layer suppresses the sintering of Ni, in turn reducing also coke formation significantly. In addition, the formation of an amorphous aluminosilicate phase by the reaction of the ALD-grown Al₂O₃ layer with the SiO₂ support inhibited catalysts deactivation via NiAl₂O₄ formation, in contrast to the reference Ni/Al₂O₃ system. The in-depth structural characterization of the catalysts provided an insight into the structural dynamics of the ALD-grown Al₂O₃ layer, which reacts both with the support and the active metal, allowing to rationalize the high stability of the catalyst under the harsh DRM conditions.
1. Introduction

To mitigate anthropogenic climate change, carbon dioxide capture, storage and utilization (CCSU) is a promising technology.\textsuperscript{1-5} In this context the dry reforming of methane (DRM) has emerged as a process to convert two major greenhouse gases, CH\textsubscript{4} and CO\textsubscript{2}, into a synthesis gas (CH\textsubscript{4} + CO\textsubscript{2} → 2CO + 2H\textsubscript{2} \(\Delta H^0_{298K} = +247\ \text{kJ/mol}\)). Synthesis gas is a versatile chemical feedstock that can be converted further into synthetic liquid fuels and chemicals, e.g., via the Fischer-Tropsch process.\textsuperscript{6,7} In DRM the development of Ni-based catalyst has received considerable attention, owing to its high activity combined with its relatively low cost when compared to noble metals.\textsuperscript{8}

Ni\textsuperscript{0} is proposed to be the catalytically active state for DRM, and a linear relationship between the DRM activity and the quantity of surface Ni has been reported.\textsuperscript{5,9-12} However, under DRM conditions, Ni-based catalysts are prone to rapid deactivation due to a combination of various factors including coke formation,\textsuperscript{13} metal oxidation followed by the migration of Ni into the support\textsuperscript{11,15-17}, and sintering of the Ni particles.\textsuperscript{18}

The fact that the Tammann temperature of Ni (≈ 700 °C) is below the envisioned operating temperatures of the DRM process (≈ 900 °C) makes sintering a serious issue. Coke formation during DRM can proceed through methane decomposition (CH\textsubscript{4} → C + 2H\textsubscript{2}, \(\Delta H^0_{298K} = +75\ \text{kJ/mol}\)) and CO disproportionation, i.e., Boudouard reaction (2CO → C + CO\textsubscript{2}, \(\Delta H^0_{298K} = -171\ \text{kJ/mol}\)). Carbon species accumulate on the catalyst surface thereby blocking the active sites for DRM or leading to the detachment of Ni particles from the support. Coke formation is also linked to sintering since the nature and the rate of coke deposition is sensitive to the size of the Ni nanoparticles.\textsuperscript{20, 21} When Ni (111) facets and step edges are too small, nucleation of C\textsuperscript{*} does not proceed, restricting the formation of a graphene layer.\textsuperscript{20} Thus, the formation and the stabilization of small Ni particles (< 10 nm) is a key requirement towards the development of highly active and stable Ni-based DRM catalysts.\textsuperscript{21-24} A further challenge with regards to Ni-based DRM catalysts that has to be overcome is the inhibition of the reaction of Ni with the (metal oxide) support. Although Al\textsubscript{2}O\textsubscript{3} support is known to stabilize Ni particles more effectively against sintering compared to SiO\textsubscript{2}, the reaction of Ni with Al\textsubscript{2}O\textsubscript{3} can lead to its oxidation and formation of inactive NiAl\textsubscript{2}O\textsubscript{4}.\textsuperscript{11, 15, 16} Hence conceiving and generating highly active and stable Ni-based DRM catalysts, several strategies have been proposed, including (i) controlling the Ni particle size with the aim of minimizing the fraction of edge and step sites on the nickel surface;\textsuperscript{11,22,25} (ii) coating Ni-based DRM catalyst by metal oxide layers (e.g., Al\textsubscript{2}O\textsubscript{3}, MgO, ZrO\textsubscript{2} and SiO\textsubscript{2})\textsuperscript{13, 26-32} to alleviate sintering and coke formation; (iii) deposition of Ni particles on basic supports (e.g., MgO and La\textsubscript{2}O\textsubscript{3}) to reduce coke formation;\textsuperscript{11,16} (iv) promotion with alkaline (e.g., K and Na),\textsuperscript{33, 34} alkaline earth (e.g., Mg, Ca and Ba)\textsuperscript{33, 35} or lanthanide (e.g., La)\textsuperscript{16, 36} metals to facilitate CO\textsubscript{2} activation to gasify carbon; and (v) the alloying of Ni with a noble (e.g., Pt, Rh, Pd, and Ru)\textsuperscript{37-41} or non-noble (e.g., Fe, Cu, Mn, and Co)\textsuperscript{9, 10, 37, 42-44} transition metal to improve its activity and stability for DRM.
SiO₂-supported Ni DRM catalysts have been plagued by a lower metal dispersion and poor sintering resistance against sintering under DRM conditions owing to a weak metal-support interaction. To stabilize Ni nanoparticles on a SiO₂ support, several strategies have been employed. For example, nickel-silicide colloids have been deposited on SiO₂ and CeO₂ supports. Treatment in H₂ leads to the formation of small, supported Ni nanoparticles (1–2 nm). Further, the addition of metal oxide overcoats (SiO₂, Al₂O₃, MgO, ZrO₂ and TiO₂) on Ni/SiO₂ has shown to reduce sintering and coke formation.

In order to precisely control the thickness of the metal oxide overcoat with atomic scale precision, atomic layer deposition (ALD) has been employed. ALD-grown TiO₂, Al₂O₃, MgO, ZrO₂ and TiO₂ coatings demonstrated an enhanced catalytic activity and stability. Although the deposition of Al₂O₃ coating onto Ni/Al₂O₃ alleviated the sintering of Ni under DRM conditions, Ni was found to interact with the overcoat to form NiAl₂O₄. Currently, the structural and electronic interaction of Ni with an Al₂O₃ overcoat is only poorly understood, hindering the further development of this class of material systems.

This work aims at obtaining an atomic-level understanding of how an ALD-grown Al₂O₃ overcoat reacts with Ni and the SiO₂ support during pretreatment and DRM. To this end, Al₂O₃-coated Ni/SiO₂ DRM catalysts have been obtained by ALD. The structure of the catalysts were interrogated in detail by in situ X-ray absorption spectroscopy (XAS) and X-ray powder diffraction (XRD) to probe the local structure of Ni, the average crystalline structure and changes therein with time-on-stream (TOS) during catalyst pretreatment and DRM. Further spectroscopic (Raman, FTIR and ²⁷Al magic-angle spinning (MAS) solid-state NMR) and electron microscopy (TEM) characterizations were applied to scrutinize the structural dynamics of the Al₂O₃ coating during synthesis and pretreatment and to elucidate the driving forces behind sintering and coking under DRM conditions.

2. Experimental

2.1. Preparation of bare Ni/SiO₂ and Ni/Al₂O₃ catalysts

5 wt. % Ni/SiO₂ and Ni/Al₂O₃ catalysts were prepared by incipient wetness impregnation using Ni(NO₃)₂ as the Ni precursor and, respectively, Aerosil 300 SiO₂ (S_BET = 275 m²/g) and γ-Al₂O₃ (S_BET = 220 m²/g) supports. The catalysts were calcined at 300 °C under static air to yield NiO.

2.2. Atomic layer deposition of Al₂O₃

An Al₂O₃ overcoat was deposited onto calcined catalyst at 300 °C (NiO/SiO₂ and NiO/Al₂O₃) and onto the supports (SiO₂ and Al₂O₃) via ALD (Picosun R-200, equipped with a powder coating system). Electronic grade trimethylaluminum (TMA) and deionized (DI) water (or ozone) were used as the Al₂O₃ precursor and oxidants, respectively. High-purity N₂ served as both the carrier and purge gas. In a typical ALD deposition cycle the following pulse and purge (N₂) times were used: 0.1 s TMA - 15 s N₂ purge - 0.1
s oxidant (H₂O or O₃) - 15 s N₂ purge. The deposition was carried out at 300 °C. High-resolution TEM allowed us to determine the deposition rate, i.e. ≈ 1.0 Å/ALD cycle, which is in good agreement with the thickness of an Al₂O₃ layer, grown simultaneously on a Si wafer and measured by ellipsometry (SENTECH SE850). To prepare the Al₂O₃-coated catalysts, approximately 300 mg of the catalyst (pre-calcined at 300 °C) were loaded into the reactor via a powder cartridge and then heated to 300 °C under vacuum, followed by repeated ALD cycles. The as-synthesized catalyst was subsequently calcined at 800 °C in static air in a muffle furnace.

2.3. Characterization

Elemental analysis. The elemental composition of the calcined materials was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5100 VDV) and inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCap 6500, Dual View).

Nitrogen physisorption. Nitrogen physisorption was performed in a NOVA 4000e (Quantachrome) instrument at -196 °C. Prior to the experiment, the samples were degassed at 300 °C under vacuum (10⁻³ mbar) for 3 h. The specific surface area and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models, respectively.

Hydrogen temperature-programmed reduction (H₂-TPR). H₂-TPR was conducted in Autochem2920 equipped with a thermal conductivity detector (TCD). In a typical experiment, 50 mg of a calcined catalyst were loaded into a U-shaped quartz reactor and heated up to 1000 °C under a flow (50 ml/min) of 5 vol. % H₂ in Ar. The concentration of H₂ in the off-gas was measured using a TCD after having passed through a cold trap (-10 °C).

Ammonia temperature-programmed desorption (NH₃-TPD). NH₃-TPD was conducted in Autochem2920 equipped with a TCD detector. In a typical experiment, 50 mg of a calcined catalyst was loaded into a U-shape quartz reactor and subsequently heated to 500 °C in He (50 ml/min) for 1 h, followed by cooling down to 150 °C. The catalyst was then exposed to a flow (50 ml/min) of 5 vol. % NH₃ in He for 1 h followed by a He purge (50 ml/min) for 1 h. The TPD profile of NH₃ was continuously recorded using a TCD.

Pyridine infrared spectroscopy (Py-IR). The infrared (IR) spectra of the samples onto which pyridine was adsorbed were recorded with a Nicolette FTIR (Thermoscientific) at a resolution of 4 cm⁻¹. The catalyst samples were prepared as self-supporting wafers and exposed to vacuum (p = 10⁻⁶ mbar) at 450 °C for 1 h (heating rate of 10 °C/min). After cooling down to 150 °C, the sample was equilibrated with 0.1 mbar pyridine for 0.5 h followed by outgassing for 1 h and the acquisition of a spectrum. The concentrations of Brønsted (BAS) and Lewis acid sites (LAS) were quantified using the integrated areas under the peaks at
1540 cm$^{-1}$ and 1450 cm$^{-1}$, respectively. For quantification, molar extinction coefficients of 0.73 cm μmol$^{-1}$
and 0.96 cm μmol$^{-1}$ were used for Brønsted and Lewis acid sites, respectively.$^{47}$

**Hydrogen chemisorption.** H$_2$ chemisorption was conducted in Autochem2920 equipped with a TCD detector. 50 mg of the calcined catalyst were loaded into a quartz reactor and reduced in 5 vol. % H$_2$ in Ar at the temperature determined by H$_2$-TPR for 1 h. Subsequently, the sample was purged with Ar at 450 °C for 30 min in order to desorb H$_2$ on the surface followed by cooling down to 50 °C. The quantity of chemisorbed hydrogen was determined at 45 °C by periodically injecting pulses of 5 vol. % H$_2$ in Ar over the reduced catalyst. The stoichiometry factor between dissociated H$_2$ and the active metal was assumed to be 1.0 (H/Ni).$^{48-50}$

$^{27}$Al magic angle spinning solid-state nuclear magnetic resonance ($^{27}$Al MAS NMR). $^{27}$Al solid state NMR spectra were obtained at a static field of 9.4 T (104.26 MHz of $^{27}$Al operating frequency) with a Bruker 2.5 mm DR MAS probe. All $^{27}$Al NMR chemical shifts were referenced externally to (NH$_4$)$_2$Al(SO$_4$)$_2$·12H$_2$O at -0.6 ppm. The sample spinning frequency was set to 25 kHz. $^{27}$Al direct-excited spin-echo spectra were acquired with a recycle delay of 1 second. The excitation pulse was optimized to yield maximal signal intensity. One rotor period was used as the echo delay. The numbers of scans were adjusted to obtain good to moderate signal-to-noise ratios (ca. 8000 scans for 100 ALD cycles; ca. 40000, 20000, and 80000 scans for calcined Al$_2$O$_3$-coated SiO$_2$, Al$_2$O$_3$-coated NiO/SiO$_2$, and reduced Al$_2$O$_3$-coated Ni/SiO$_2$, respectively). The raw FID was shifted by 142 points towards the start of FID acquisition. All spectra were fitted with the CzSimple model using the DMFit software,$^{51}$ simulating the $^{27}$Al central transitions with a Gaussian distribution of sites (d = 5).

**X-ray absorption spectroscopy (XAS) and X-ray powder diffraction (XRD):** *In situ* combined XAS (Ni K-edge, 8.2 keV)-XRD experiments were performed at the Swiss-Norwegian Beamlines (SNBL, BM31) at the European Synchrotron Radiation Facility (ESRF). The catalyst (≈ 2 mg) was loaded into a capillary quartz reactor (1.0 mm of outer diameter).$^9$ The as-synthesized catalyst was calcined in synthetic air (20 vol. % O$_2$/N$_2$) at 800 °C. The calcined catalyst was then reduced at the temperature determined by H$_2$-TPR with a ramping rate of 10 °C/min under 10 vol. % H$_2$/He (10 ml/min). Subsequently, the DRM reaction was performed at 700 °C in a total flow rate of 10 ml/min of the feed gas (4.5 ml/min CH$_4$, 4.5 ml/min CO$_2$ and 1 ml/min He). During reduction and DRM tests, XAS-XRD data were collected alternatingly. XAS spectra were collected at the Ni K-edge using a Si (111) double crystal monochromator in transmission mode. XRD data were collected with a 2D DEXELA detector using a Si (111) channel-cut monochromator set at a wavelength of 0.5060 Å. Alternating XAS-XRD data were collected during temperature-programmed calcination, reduction and DRM. For *ex situ* XAS measurements, the as-synthesized materials and references were mixed with cellulose (the sample to cellulose ratio was chosen such that XAS
measurements in transmission mode were optimized) and ground to a fine powder. The pelletized samples were measured in transmission mode. The XAS data were analyzed using the Athena and Artemis software.

**Electron microscopy:** The morphology, particle size and particle composition of the reduced and reacted catalysts were analyzed by transmission electron microscopy (TEM, Philips CM 12, 100 kV), high-resolution transmission electron microscopy (HR-TEM, FEI F30 FEG, 300 kV) and scanning transmission electron microscopy (STEM, Hitachi HD-2700). TEM and STEM were operated at 200 kV, which were equipped with a SuperX EDX consisting of four SDD detectors.

**Temperature-programmed oxidation (TPO):** Temperature-programmed oxidation (TPO) and carbon deposition experiments were performed in a thermogravimetric analyzer (TGA, Mettler Toledo TGA/DSC). A small amount of the reacted catalyst (≈ 15 mg) was placed in an alumina crucible and heated to 1000 °C (10 °C/min ramp) under an air flow (50 ml/min). The weight loss of the reacted material during oxidation was recorded continuously.

**Raman spectroscopy:** Coke deposition was characterized by Raman spectroscopy (Thermo Scientific). The Raman spectra were acquired in the range 500–3500 cm$^{-1}$ using a laser with a wavelength of 514.5 nm. The spectral resolution employed was 4 cm$^{-1}$.

### 2.4. DRM catalytic test

The DRM reaction was carried out in a fixed-bed quartz reactor (400 mm length, 12.6 mm internal diameter). The calcined catalyst (≈ 20 mg) was loaded into the reactor and reduced at the temperature determined by H$_2$-TPR in 10 vol. % H$_2$/N$_2$ (100 ml/min) for 2 h. Subsequently, the bed was cooled down to 700 °C to perform the DRM activity test. The total flow rate of the feed gas was 100 ml/min (270 L·g$^{-1}$·h$^{-1}$; 45 ml/min CH$_4$, 45 ml/min CO$_2$ and 10 ml/min N$_2$). The composition of the off-gas was analyzed by an online micro-GC equipped (CV-200, Thermo Scientific). N$_2$ was used as internal standard.

### 3. Results and discussion

#### 3.1. Deposition of an Al$_2$O$_3$ overcoat onto Ni/SiO$_2$ by ALD

Figure 1a schematically describes the surface reactions occurring during a half and full ALD cycle. To follow the surface reactions occurring during ALD, FTIR spectra were collected after one half (i.e., after injection of a TMA pulse) and a full (i.e., TMA and subsequent injection of a steam pulse) ALD cycle on dehydroxylated SiO$_2$ (Figure 1b). Due to high reactivity of TMA with air and moisture, the FTIR measurements were carried out in an inert atmosphere (glovebox). SiO$_2$ dehydroxylated at 500 °C in high vacuum (10$^{-6}$ mbar) shows isolated silanols at 3746 cm$^{-1}$. After one half cycle, i.e., after pulsing TMA, the intensity of the peak from isolated silanols is significantly reduced owing to their reaction with TMA. In addition, peaks associated with C-H stretching vibrations (2916 and 2966 cm$^{-1}$) appear owing to methyl
groups of surface-adsorbed (or chemisorbed) TMA. After injection of a pulse of steam, i.e., after the completion of a full ALD cycle, the intensity of the peak due to isolated silanols restores, albeit with a reduced intensity. In addition, a new broad band between 3461–3498 cm\(^{-1}\) appears, which is ascribed to an O-H interacting with Al and Si on the surface (or vicinal silanols)\(^52\). The regeneration of surface O-H groups provides the reactive sites for subsequent ALD cycles.

The growth rate of the Al\(_2\)O\(_3\) layer was estimated by HR-TEM (Figure 1c). The thickness of the Al\(_2\)O\(_3\) layer on Ni nanoparticle (5.0 ± 0.3 nm) supported on SiO\(_2\) after 40 ALD cycles (TMA/steam) was determined as 4.0 ± 0.3 nm, denoted as Al (4.0 nm)-Ni/SiO\(_2\), corresponding to a deposition rate of ~0.1 nm/ALD cycle.

XRD characterization of Ni/SiO\(_2\) calcined at 300 °C and as-synthesized Al (4.0 nm)-Ni/SiO\(_2\) (ALD temperature 300 °C) revealed the presence of cubic NiO (\(Fm-3m\) space group) in Ni/SiO\(_2\) (Figure 1d). A broad halo at 4.5–9.5° is ascribed to the amorphous SiO\(_2\) support. Similarly, in the case of as-synthesized Al (4.0 nm)-Ni/SiO\(_2\), only Bragg peaks due to NiO are present, indicating an amorphous nature of the as-deposited Al\(_2\)O\(_3\) layer.

As-synthesized, Al\(_2\)O\(_3\)-coated Ni/SiO\(_2\) catalysts with different thicknesses of the Al\(_2\)O\(_3\) layer (0.4 nm and 4.0 nm), i.e., Al (0.4 nm)-Ni/SiO\(_2\) and Al (4.0 nm)-Ni/SiO\(_2\), were characterized further by \(^{27}\)Al MAS NMR (Figure 1e). The fitting of the \(^{27}\)Al MAS NMR spectra was performed using the Czjzek model\(^51\). The \(^{27}\)Al MAS spectra of as-synthesized Al (0.4 nm)-Ni/SiO\(_2\) and Al (4.0 nm)-Ni/SiO\(_2\) contains tetra- (Al\(^{IV}\), NMR shift \(\delta = 75.9, 35.2, 8.6\) ppm and quadrupolar coupling constant \(C_Q = 8.4\) MHz, penta- (Al\(^{V}\), \(\delta = 35.2\) ppm and \(C_Q = 6.3\) MHz) and hexa- (Al\(^{VI}\), \(\delta = 8.6\) ppm and \(C_Q = 5.7\) MHz) coordinated Al sites, and no significant differences are observed between the spectra of as-synthesized Al (0.4 nm)-Ni/SiO\(_2\) and Al (4.0 nm)-Ni/SiO\(_2\). The broad and featureless \(^{27}\)Al NMR line feature is characteristic of amorphous Al\(_2\)O\(_3\),\(^53,55\) in line with the absence of diffraction peaks due to Al\(_2\)O\(_3\) in as-synthesized Al (4.0 nm)-Ni/SiO\(_2\).
Figure 1. Characterization of as-synthesized Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂: (a) Schematic illustrating the surface reactions occurring over a half and a full ALD cycle. (b) FTIR spectra obtained after a half and a full ALD cycle. The arrows indicate the direction of change during a full ALD cycle. (c) TEM image of Al (4.0 nm)-Ni/SiO₂, showing an amorphous Al₂O₃ layer on top of a Ni nanoparticle dispersed on a SiO₂ support. (d) XRD diffractograms of as-synthesized Al (4.0 nm)-Ni/SiO₂ and calcined Ni/SiO₂: (■) NiO. (e) Solid-state ²⁷Al NMR spectra of as-synthesized Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂.

3.2. Structural characterization of the materials after calcination at 800 °C: Probing the interaction of the Al₂O₃ layer with Ni and SiO₂

3.2.1. Physical, chemical, and textural properties of the calcined materials

As-synthesized Ni/SiO₂, Al (0.4 nm)-Ni/SiO₂, and Al (4.0 nm)-Ni/SiO₂ were subsequently calcined at 800 °C in static air for 1 h. HAADF STEM with elemental mapping (Figure S2) confirms that in calcined Al (4.0 nm)-Ni/SiO₂ Al is distributed homogeneously on the surface of the silica, indicating that the ALD-grown Al₂O₃ layer maintains its highly dispersed character after calcination at 800 °C.
The elemental composition of the materials, as determined by ICP-OES, is summarized in Table 1. As expected, the deposition of an Al$_2$O$_3$ layer onto Ni/SiO$_2$ leads to a reduction of the weight fraction of Ni from 5 wt. % to 4.8 wt. % and 3.7 wt. % for Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$, respectively (accompanied by an increase in the Al content from 0 wt. %, to 1.1 wt. % and 10.2 wt. %).

The N$_2$ isotherms and BJH pore size distributions of Ni/SiO$_2$ calcined at 300 °C, as-synthesized Al (4.0 nm)-Ni/SiO$_2$, and Al (4.0 nm)-Ni/SiO$_2$ calcined at 800 °C are shown in Figure S3. The specific surface area and BJH pore volume of Ni/SiO$_2$ are 198 m$^2$/g and 1.33 cm$^3$/g, respectively. After the deposition of a 4-nm-thick layer of Al$_2$O$_3$ onto Ni/SiO$_2$, i.e., as-synthesized Al (4.0 nm)-Ni/SiO$_2$, the pore volume in pores with a diameter d$_{\text{pore}}$ = 10–100 nm is significantly reduced (Figure S3b), resulting in a BET surface area and BJH pore volume of, respectively, 91 m$^2$/g and 0.64 cm$^3$/g. This reduction in surface area is ascribed to the filling of voids by the ALD-grown Al$_2$O$_3$. On the other hand, Al (4.0 nm)-Ni/SiO$_2$ after calcination (800 °C), shows a significant increase of the volume in small pores (d$_{\text{pore}}$ = 1–10 nm) (Figure S3b). Such an increase in the specific surface area and BJH pore volume was also observed in calcined Al (0.4 nm)-Ni/SiO$_2$ (Table 1). We hypothesize that the local restructuring of the ALD-grown Al$_2$O$_3$ layer during calcination (including the reaction of the Al$_2$O$_3$ layer with NiO and SiO$_2$ as discussed in more detail in the following section) is responsible for the formation of additional small pores.

### Table 1. Physical and chemical properties of Ni/SiO$_2$ and the Al$_2$O$_3$-coated Ni/SiO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Elemental composition$^a$</th>
<th>N$_2$ physisorption$^b$</th>
<th>H$_2$ uptake$^c$</th>
<th>Ni particle size$^d$</th>
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<tbody>
<tr>
<td></td>
<td>Ni [wt. %]</td>
<td>Al [wt. %]</td>
<td>S$_{\text{BET}}$ [m$^2$/g]</td>
<td>V$_{\text{pore, BJH}}$ [cm$^3$/g]</td>
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<tr>
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<td>197</td>
<td>1.33</td>
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<td>Al (0.4 nm)-Ni/SiO$_2$</td>
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<td>1.40</td>
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<td>10.2</td>
<td>204</td>
<td>1.44</td>
</tr>
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</table>

$^a$The weight percentage of Ni and Al in the calcined materials was determined by ICP-OES. $^b$The specific surface area, pore volume, and pore radius were calculated using the BET and BJH models for the calcined materials. $^c$The quantity of surface Ni in the reduced materials was determined by H$_2$ chemisorption using a stoichiometry factor of 1.0 for H/ Ni. $^d$The average Ni particle size of the reduced materials was determined by HR-TEM.

### 3.2.2. In situ XRD-XAS of Al (4.0 nm)-Ni/SiO$_2$ during calcination: NiAl$_2$O$_4$ formation

To elucidate the chemical reaction between the ALD-grown Al$_2$O$_3$ layer and the Ni/SiO$_2$ catalyst, *in situ* synchrotron XRD-XAS measurements were performed during the calcination of as synthesized Al (4.0 nm)-Ni/SiO$_2$ (Figure 2). The *in situ* diffractogram of as synthesized Al (4.0 nm)-Ni/SiO$_2$ shows peaks due
to a crystalline NiO phase, while no Bragg peaks due to crystalline Al$_2$O$_3$ were observed between 50–400 °C owing to the amorphous nature of the ALD-grown Al$_2$O$_3$ layer and the amorphous SiO$_2$ support. Bragg peaks due to spinel NiAl$_2$O$_4$ (Fd-3m space group) started to appear at ca. 500 °C (Figure 2a), which grew in intensity as the temperature increased to 800 °C; this was accompanied by a simultaneous decrease of the intensity of the NiO peaks. The diffraction pattern of NiAl$_2$O$_4$ is similar to that of γ-Al$_2$O$_3$, yet we can clearly assign the observed peaks to NiAl$_2$O$_4$ when taking into account the results of the analysis of the XANES spectra. The in situ XANES spectra at the Ni K-edge collected during calcination, in an alternating fashion with XRD, are plotted in Figure 2b. During calcination, the white line decreased in intensity and shifted from 8352 eV to 8354 eV. In addition, changes in the features of the post-edge region were observed, in line with the formation of NiAl$_2$O$_4$. Applying linear combination fitting (LCF) analysis, using references for NiO and NiAl$_2$O$_4$ (Figure S5) revealed the onset of NiAl$_2$O$_4$ formation at ca. 500 °C. The fraction of NiAl$_2$O$_4$ reached 0.68 at 800 °C, whereas the fraction of NiO was reduced correspondingly. Hence in situ XRD-XAS experimentation confirms the reaction of NiO with the ALD-grown Al$_2$O$_3$ layer forming NiAl$_2$O$_4$ (NiO + Al$_2$O$_3$ → NiAl$_2$O$_4$)$_{56}$. However it is worth noting that in situ XRD and XANES only allows to elucidate the reaction between the ALD-grown Al$_2$O$_3$ and NiO and cannot probe the interaction between Al$_2$O$_3$ and the SiO$_2$ support.

**Figure 2.** Combined in situ XRD-XAS characterization: (a) in situ XRD (λ = 0.5060 Å), (b) in situ Ni K-edge XANES and (c) corresponding LCF analysis for Al (4.0 nm)-Ni/SiO$_2$ during calcination in air. The symbols in the diffractogram mark the peaks due to NiO (ICSD 9866, ■) and NiAl$_2$O$_4$ (ICSD 9554, ●). The arrows indicate the direction of change in the XANES spectra with calcination.
3.2.3. ssNMR of Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ after calcination: formation of aluminosilicates

To shed light onto the possible reaction between the ALD-grown Al₂O₃ layer and the SiO₂ support, the structure of calcined Al (4.0 nm)-Ni/SiO₂ was characterized by ²⁷Al MAS NMR and Raman spectroscopy (Figure 3). Figure 3a plots the ²⁷Al NMR spectra of the references α-Al₂O₃, γ-Al₂O₃, and a commercial amorphous aluminosilicate (Siral 70, 70 wt. % of SiO₂). The ²⁷Al MAS NMR of the α-Al₂O₃ reference displays the expected signal for Al in an octahedral environment (Al⁴⁺, δ = 9.0 ppm and CQ = 2.5 MHz). The reference for NiAl₂O₄, i.e. (structurally related) γ-Al₂O₃ is composed primarily of Al⁴⁺ (δ = 74 ppm and CQ = 3.2 MHz) and Al⁴⁺-coordinated Al sites (δ = 11 ppm and CQ = 2.1 MHz) with a negligible amount of Al⁵⁺ (δ = 40.3 ppm and CQ = 4.2 MHz). For Siral 70, three types of Al sites, i.e., Al⁴⁺ (δ = 57.8 ppm and CQ = 4.3 MHz), Al⁵⁺ (δ = 38.9 ppm and CQ = 8.2 MHz), and Al⁶⁺ (δ = 6.7 ppm and CQ = 1.9 MHz) are observed, which are in good agreement with previous NMR data of amorphous aluminosilicates (AAS)⁵⁷-⁵⁹. Turning now to our catalysts, Figure 3b plots the ²⁷Al NMR spectra of calcined (800 °C) Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂. For calcined Al (0.4 nm)-Ni/SiO₂, three different Al sites are identified, i.e. Al⁴⁺ (δ = 63.4 ppm and CQ = 8.5 MHz), Al⁵⁺ (δ = 35.1 ppm and CQ = 6.4 MHz) and Al⁶⁺ (δ = 9.1 ppm and CQ = 5.8 MHz). Increasing the thickness of the ALD grown Al₂O₃ layer to 4.0 nm, i.e. calcined (800 °C) Al (4.0 nm)-Ni/SiO₂ similar ²⁷Al NMR resonance features are observed: Al⁴⁺ (δ = 59.0 ppm and CQ = 4.6 MHz), Al⁵⁺ (δ = 34.9 ppm and CQ = 7.9 MHz) and Al⁶⁺ (δ = 5.7 ppm and CQ = 2.6 MHz). The NMR features of Al (4.0 nm)-Ni/SiO₂, i.e. NMR shift (δ) and quadrupolar coupling constant (CQ) of the different Al sites are similar to the values of Siral 70 and previously reported data on and Al₂O₃-rich AAS⁵⁸,⁵⁹ and calcined (500 °C) ALD Al₂O₃-deposited SiO₂.⁶⁰ These NMR results point to a rearrangement of Al sites during calcination at 800 °C leading to the formation of AAS-like structures due to the reaction of Al₂O₃ with the SiO₂ support, for both thicknesses of the ALD-grown Al₂O₃ layer studied here.

To probe more quantitatively the differences in the Al environment in calcined Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ the respective samples were exposed to an ammonia pretreatment. Previous reports have shown that ammonia treatment of AAS leads to the transformation of its Al⁶⁺ sites into Al⁴⁺ sites, whereas such a transformation (upon ammonia treatment) has not been observed for γ-Al₂O₃.⁵⁸,⁵⁹, ⁶¹, ⁶² In this context, we applied ammonia treatment to calcined Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂, in order to probe the AAS content, following the hypothesis that only Al⁶⁺ sites in AAS will selectively transform into Al⁴⁺ sites by NH₃ treatment. Indeed, a comparison of the ²⁷Al NMR spectra of γ-Al₂O₃ before and after ammonia treatment (5 vol. % NH₃/He at 120 °C for 5 h) features a negligible difference between the two spectra (Table S1 and Figure S6a), confirming previously reported observations.⁵⁸,⁵⁹, ⁶¹, ⁶² On the other hand, for calcined Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂, a transformation of Al⁴⁺ sites to Al⁴⁺ sites was observed after ammonia treatment (Figure S6b compared to Figure 3b). The evaluated ratios of
the Al$^{IV}$, Al$^{V}$, and Al$^{VI}$ sites in Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$ before and after ammonia treatment are summarized in Table S1. After ammonia treatment the relative abundance of Al$^{VI}$ sites in Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$ decreased, while the relative abundance of Al$^{IV}$ sites increased, providing further evidence of the presence of AAS in both materials.

To complement the $^{27}$Al NMR studies, Raman spectroscopy was performed on calcined Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$ (Figure 3c). For bare Ni/SiO$_2$, a dominant band at 395 cm$^{-1}$, which is ascribed to Si-O-Si linkages in the tetrahedral unit of SiO$_4$, is observed. In addition, the Si-O stretching band in the Si-O-Si plane is detected at 802 cm$^{-1}$. The bands at 483 cm$^{-1}$ and 603 cm$^{-1}$ are associate with the breathing modes of oxygen in, respectively, four (D1) and three (D2) membered rings of tetrahedral SiO$_4$. An increase in the thickness of the ALD-grown Al$_2$O$_3$ layer leads to a reduction of the intensity of the Si-O-Si and SiO$_4$ bands, whereas new characteristic features appeared at 707 cm$^{-1}$ and 1043 cm$^{-1}$. The band at 707 cm$^{-1}$ is related to AlO$_4$ units and the band at 1043 cm$^{-1}$ is attributed to Si-O-Al, indicative of the presence of AAS in calcined Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$. These findings are in good agreement with $^{27}$Al NMR results.

![Figure 3](image.png)

**Figure 3.** Characterization of the interaction between silica and alumina: solid-state $^{27}$Al-NMR of (a) $\alpha$-Al$_2$O$_3$, $\gamma$-Al$_2$O$_3$, and aluminosilicate Siral 70 references; and (b) calcined Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$. (c) Raman spectra of calcined Ni/SiO$_2$, Al (0.4 nm)-Ni/SiO$_2$, and Al (4.0 nm)-Ni/SiO$_2$. 

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3.2.4. Acidic properties of calcined Al₂O₃-coated Ni/SiO₂ catalysts

The formation of amorphous aluminosilicates is expected to yield surface acid sites. To probe the presence of both Lewis and Brønsted acid sites, qualitative FTIR spectroscopy using pyridine as a probe molecule was performed (Figure 4a). The FTIR transmittance spectra were collected after pyridine adsorption at 150 °C followed by outgassing at 150 °C under high vacuum conditions (≈ 10⁻⁶ mbar) in order to remove physically adsorbed pyridine (Figure 4a). The FTIR spectra of calcined Al (4.0 nm)-Ni/SiO₂ features both Brønsted and Lewis acid sites. The bands at 1450 cm⁻¹ and 1610 cm⁻¹ are ascribed to strong Lewis acid-bound pyridine, while the bands at 1550 cm⁻¹ and 1640 cm⁻¹ are attributed to pyridine protonated by Brønsted acid sites (pyridinium).⁶⁹,⁷⁰ The band at 1492 cm⁻¹ is assigned to physically adsorbed pyridine on both Brønsted and Lewis acid sites.⁶⁹,⁷⁰ The reference α-Al₂O₃ and γ-Al₂O₃ exhibit Lewis acid sites, whereas the commercial AAS catalyst Siral 70 showed both Lewis and Bronsted acid sites. Bare Ni/SiO₂ features only Lewis acid sites. The spectral features of calcined Al (0.4 nm)-Ni/SiO₂ are similar to Ni/SiO₂, showing predominantly Lewis acid sites whereas the presence of Brønsted acidity is observed in calcined Al (4.0 nm)-Ni/SiO₂.

To quantify the amount of acid sites, we performed NH₃-TPD (Figure S7). Bare Ni/SiO₂ and α-Al₂O₃ showed a negligible desorption of NH₃, i.e. 0.007 mmol NH₃/gcat and 0.027 mmol NH₃/gcat, respectively. On the other hand, 0.373 mmol NH₃/gcat was desorbed from γ-Al₂O₃, attributed largely to Lewis acid sites. For commercial AAS, the quantity of desorbed NH₃ increases from 0.26 mmol NH₃/gcat to 0.65 mmol NH₃/gcat with an increase in the quantity of Al₂O₃ from 30 wt. % (Siral 70) to 70 wt. % (Siral 30). For the catalysts Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂, the amount of NH₃ desorbed was 0.021 mmol NH₃/gcat and 0.065 mmol NH₃/gcat, respectively. Overall, the amount of NH₃ desorbed showed a linear correlation with the amount Al₂O₃ in the AAS materials (Figure 4b). Nevertheless, the amount of NH₃ desorbed from Al₂O₃-coated Ni/SiO₂ is small compared to γ-Al₂O₃ likely due to the amorphous nature of the Al₂O₃ layer.⁷¹
Figure 4. **Acidic properties:** (a) Difference FT-IR spectra of pyridine adsorbed on calcined Ni/SiO₂, Al (4.0 nm)-Ni/SiO₂ and the references α-Al₂O₃, γ-Al₂O₃, and Siral 70. The labels L and B mark Lewis and Brønsted acid sites, respectively. (b) The quantity of NH₃ desorbed during TPD as a function of the mass fraction of Al₂O₃.

3.3. **Catalyst activation: Reduction of calcined Al₂O₃-coated Ni/SiO₂ catalysts**

The reduction behavior of the calcined Al₂O₃-coated Ni/SiO₂ catalysts was assessed by H₂-TPR (Figure 5a). The reducible Ni²⁺ species can be classified as: (i) α-type (weak interaction with support, 290–475 °C), (ii) β-type (mid-interaction with support, 475–753 °C), and (iii) γ-type (strong interaction with support, 753–894 °C). As references we used commercial NiO, NiAl₂O₄, Ni impregnated on Siral 70 and Ni impregnated on Al₂O₃-coated SiO₂ (Ni/Al (4.0 nm)-SiO₂). The TPR profiles of the NiO and NiAl₂O₄ references showed a reduction peak at 415 °C and 803 °C, respectively, corresponding to α- and γ-type reduction behaviors. Ni/Siral 70 and Ni/Al (4.0 nm)-SiO₂ calcined at 800 °C revealed a reduction peak at 611 °C and 617 °C, respectively, indicative of a β-type reduction. The β-type reduction is ascribed to an interaction of NiO with alumina (NiO-Al₂O₃). This observation suggests that the formation of AAS mitigates the further reaction of NiO with Al₂O₃ (forming NiAl₂O₄); however, the interaction of NiO with Al₂O₃ leads to a higher reduction temperature compared to bulk NiO. H₂-TPR of Ni/SiO₂ revealed a low reduction temperature of 450 °C indicative of a weak Ni-silica interaction, in agreement with literature. On the other hand, two reduction peaks were observed in the H₂-TPR of Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂. In Al (0.4 nm)-Ni/SiO₂ the reduction peaks at 450 °C and 600 °C are attributed to the reduction of NiO interacting with SiO₂ and free Al₂O₃. Increasing the thickness of the ALD-grown Al₂O₃ layer, i.e., Al (4.0 nm)-Ni/SiO₂, leads to reduction temperatures of 600 °C and 800 °C owing to the interaction of NiO with free Al₂O₃ on Al (4.0 nm)-Ni/SiO₂, and the reaction of NiO with Al₂O₃ forming NiAl₂O₄, respectively.

In the following, we utilize *in situ* XANES at the Ni K-edge (Figure 5b) and *in situ* XRD (Figure S8b) during reduction to probe in more detail the reduction pathway of Ni²⁺ species in the calcined catalysts. Calcined Ni/SiO₂ (α-type Ni²⁺) and Al (4.0 nm)-Ni/SiO₂ (β- and γ-type Ni²⁺) were chosen for *in situ* XAS-XRD experiments as they show the largest difference in the H₂-TPR experiments (whereby Al (0.4 nm)-Ni/SiO₂ can be considered, from a reduction behavior perspective, as a mixture of Ni/SiO₂ (α-type Ni²⁺) and Al (4.0 nm)-Ni/SiO₂ (β- and γ-type Ni²⁺) features). For bare Ni/SiO₂, *in situ* XANES revealed that the reduction of NiO started at 250 °C; NiO was fully reduced to metallic Ni at 450 °C. The appearance of (111), (200) and (220) reflections due to Ni⁰ (fcc) in the *in situ* XRD data at temperatures exceeding 300 °C is indicative of the formation of metallic Ni through the direct reduction of bulk NiO. LCF analysis of the XANES data of calcined Al (4.0 nm)-Ni/SiO₂ yielded a composition of 32 mol % NiO and 68 mol%
NiAl₂O₄. LCF of the in situ XANES and XRD showed that in calcined Al (4.0 nm)-Ni/SiO₂, NiO was reduced in the temperature range 500 - 600 °C, whereas NiAl₂O₄ was reduced between 550 °C and 800 °C.

To summarize, combining our insight of the structure of calcined Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ with its reduction behavior, we can deduce that the reduction occurring at 400 °C is ascribed to the reduction of NiO weakly interacting with SiO₂, whereas NiO interacting with free Al₂O₃ in Al₂O₃-modified SiO₂, i.e., AAS, reduces only at 600 °C. In addition, the availability of excessive, free Al₂O₃ domains in Al (4.0 nm)-Ni/SiO₂ results in the formation of NiAl₂O₄ (NiO + Al₂O₃ → NiAl₂O₄) which reduces at 800 °C. ²⁷Al NMR measurements of the reduced materials revealed no significant differences to the calcined material (Figure S6c), indicating that AAS remains as such in the catalysts after reduction. Overall, our structural characterization using XRD, XAS, Raman and ²⁷Al NMR point to the formation of both AAS, and NiAl₂O₄ in Al₂O₃-coated Ni/SiO₂ catalysts.
Characterization of the reduced materials: (a) H$_2$-TPR of the references (NiO, Ni/Al$_2$O$_3$, Ni/Al$_2$O$_3$ and Ni/Siral 70) and calcined Ni/SiO$_2$, Al (0.4 nm)-Ni/SiO$_2$ and Al (4.0 nm)-Ni/SiO$_2$. Contour plots of the acquired in situ Ni K-edge XANES data and the corresponding LCF analysis of (b) Ni/SiO$_2$ and (c) Al (4.0 nm)-Ni/SiO$_2$ during reduction.

Electron microscopy of reduced Al (4.0 nm)-Ni/SiO$_2$ was performed to visualize the morphology of the Ni nanoparticles and the ALD-grown Al$_2$O$_3$ layer (Figure 6). HR-TEM of reduced Al (4.0 nm)-Ni/SiO$_2$ (Figure 6a) shows metallic Ni nanoparticles with a size of 8 ± 1 nm. The Ni nanoparticles were partly embedded in the support and partly covered by an amorphous (ALD-grown) layer. Hence, increasing the thickness of the ALD-grown Al$_2$O$_3$ layer from 0.4 nm to 4.0 nm, will reduce the number of active (and accessible) active Ni active sites at the surface, which is in line with a decrease in the quantity of chemisorbed H$_2$ with increasing thickness of the ALD-grown Al$_2$O$_3$ layer, as tabulated in Table 1. To probe
further the morphology and composition of the $\text{Al}_2\text{O}_3$ layer, STEM images combined with elemental EDX analysis (Figure 6b-e and Figure S9) of reduced Al (4.0 nm)-Ni/SiO$_2$ were acquired. At the top of the silica spheres, an Al-containing layer forms. The overlap of the signals from Si and Al are indicative of a reaction between SiO$_2$ and $\text{Al}_2\text{O}_3$. The particle size of Ni after reduction, as determined by TEM (Figure S4 and Table 1) was similar for all of the reduced catalysts: Ni/SiO$_2$ (7 ± 2 nm), Al (0.4 nm)-Ni/SiO$_2$ (7 ± 2 nm) and Al (4.0 nm)-Ni/SiO$_2$ (8 ± 1 nm). However, the amount of surface Ni of the reduced catalysts, quantified by H$_2$ chemisorption using a stoichiometry factor of H/Ni = 1$^{48,50}$ decreased with increasing thickness of the ALD-grown $\text{Al}_2\text{O}_3$ layer, i.e., 102 $\mu$mol$_{\text{Ni}}$/g$_{\text{cat}}$ (Ni/SiO$_2$) > 91 $\mu$mol$_{\text{Ni}}$/g$_{\text{cat}}$ (Al (0.4 nm)-Ni/SiO$_2$) > 70 $\mu$mol$_{\text{Ni}}$/g$_{\text{cat}}$ (Al (4.0 nm)-Ni/SiO$_2$). This observation can be explained by the partial coverage of surface Ni by the ALD-grown $\text{Al}_2\text{O}_3$ layer.

![Figure 6. Electron microscopy-based morphological characterization: (a) HR-TEM and (b) HAADF-STEM images with (c-e) EDX mapping for reduced Al (4.0 nm)-Ni/SiO$_2$. The arrows represent the ALD-grown layer.](image)

### 3.4. Dry reforming of methane activity and selectivity

The catalytic activity tests for DRM were performed in a fixed-bed quartz reactor. In a typical experiment, prior to the activity test, the respective calcined catalysts were first reduced (based on the TPR results) at 400 °C (Ni/SiO$_2$), 600 °C (Al (0.4 nm)-Ni/SiO$_2$), and 800 °C (Ni/$\text{Al}_2\text{O}_3$ and Al (4.0 nm)-Ni/SiO$_2$) in 10 vol. % H$_2$/N$_2$ (100 ml/min) for 2 h. The DRM performance was evaluated in the kinetic regime, i.e., far from the equilibrium conversion of methane, at 700 °C using a GHSV of 300 L$\cdot$g$_{\text{cat}}^{-1}$$\cdot$h$^{-1}$ (100 mL/min of 45 % CH$_4$, 45 % CO$_2$ and 10 % N$_2$). The DRM performances of the $\text{Al}_2\text{O}_3$-coated Ni/SiO$_2$ based catalysts
(Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂) were compared with the following benchmark catalysts: (i) Ni supported on SiO₂ or Al₂O₃ (Ni/SiO₂ and Ni/Al₂O₃), ii) Ni supported on Al₂O₃-coated SiO₂ (Ni/Al (4.0 nm)-SiO₂) and Ni supported on Al₂O₃-coated Al₂O₃ (Ni/Al (4.0 nm)-Al₂O₃) and (iii) Al₂O₃-coated Ni/Al₂O₃ (Al (0.4 nm)-Al₂O₃).

As expected, we observe severe deactivation for Ni/SiO₂, exhibiting a drastic reduction of the methane consumption rate with TOS, i.e. from 33 mmolCH₄⋅min⁻¹⋅gcat⁻¹ to 5 mmolCH₄⋅min⁻¹⋅gcat⁻¹ after 10 h TOS (Figure 7a). A gradual decrease of the methane consumption rate was also observed for Ni/Al₂O₃ (from 27 mmolCH₄⋅min⁻¹⋅gcat⁻¹ to 20 mmolCH₄⋅min⁻¹⋅gcat⁻¹), Ni/Al (4.0 nm)-SiO₂ (from 38 mmolCH₄⋅min⁻¹⋅gcat⁻¹ to 30 mmolCH₄⋅min⁻¹⋅gcat⁻¹) and Ni/Al (4.0 nm)-Al₂O₃ (from 30 mmolCH₄⋅min⁻¹⋅gcat⁻¹ to 26 mmolCH₄⋅min⁻¹⋅gcat⁻¹).

These results show that the deactivation tendency of Ni catalysts when impregnated onto Al₂O₃ (Ni/Al₂O₃) and Al₂O₃-coated supports (Ni/Al (4.0 nm)-SiO₂ and Ni/Al (4.0 nm)-Al₂O₃) improves only partially.

Turning now to the catalysts for which the Al₂O₃ overcoat was deposited after Ni impregnation onto the SiO₂ support, the methane consumption rate at 1 h of TOS of Al (0.4 nm)-Ni/SiO₂ (30 mmolCH₄⋅min⁻¹⋅gcat⁻¹) Al (4.0 nm)-Ni/SiO₂ (23 mmolCH₄⋅min⁻¹⋅gcat⁻¹) and Al (4.0 nm)-Ni/Al₂O₃ (18 mmolCH₄⋅min⁻¹⋅gcat⁻¹) are reduced compared to the corresponding benchmarks Ni/SiO₂ and Ni/Al₂O₃ (Figure 7a and b). After 10 h of TOS, the methane consumption rate of Al (0.4 nm)-Ni/SiO₂ has reduced to 20 mmolCH₄⋅min⁻¹⋅gcat⁻¹, while a very stable methane consumption rate was observed for Al (4.0 nm)-Ni/SiO₂ (23 mmolCH₄⋅min⁻¹⋅gcat⁻¹ over 10 h TOS). For Al (4.0 nm)-Ni/Al₂O₃ the initial methane consumption rate (1 h TOS) was reduced from 18 mmolCH₄⋅min⁻¹⋅gcat⁻¹ to 16 mmolCH₄⋅min⁻¹⋅gcat⁻¹ after 2 h of TOS, but remained stable at 16 mmolCH₄⋅min⁻¹⋅gcat⁻¹ at 10 h TOS. These findings show that an Al₂O₃ overcoat of a thickness of 4 nm deposited onto Ni/SiO₂ or Ni/Al₂O₃ is effective to stabilize the DRM performance of the impregnated Ni catalysts. The inverse preparation route, i.e., the impregnation of Ni onto Al₂O₃-coated SiO₂ and Al₂O₃ supports did not yield stable catalysts.

It is important to note that the initial methane consumption rate (normalized by weight catalyst) decreases with increasing thickness of the Al₂O₃ overcoats. This is ascribed to (i) the reduced Ni content per mass catalyst and (ii) the reducing number of accessible active surface Ni sites (H₂ chemisorption data, Table 1) with an increasing quantity of Al₂O₃ deposited. Figure 7c confirms that there is a linear correlation between the methane consumption rate (1 h of TOS) with surface Ni, as quantified by H₂ chemisorption (H/Ni = 1.0), providing further evidence that surface metallic Ni is the active site for DRM. The methane consumption rate (1 h of TOS) normalized by surface Ni features very similar values (5.4–5.7 mmolCH₄⋅mmol_{surface Ni}⁻¹⋅s⁻¹) for Ni/SiO₂, Ni/Al₂O₃, Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂.
Figure 7. DRM performance: Rate of methane consumption for (a) Ni supported on bare SiO$_2$ and Al$_2$O$_3$-coated SiO$_2$ and Al$_2$O$_3$, and (b) Al$_2$O$_3$-coated Ni/SiO$_2$ and Ni/Al$_2$O$_3$ as a function of TOS, (c) rate of methane consumption at 1 h of TOS as a function of surface Ni as quantified by H$_2$ chemisorption (H/Ni = 1.0), and (d) rate of methane consumption normalized by surface Ni, quantified by H$_2$ chemisorption (H/Ni = 1.0), as a function of TOS.

3.5. Structure-stability relationship: Al$_2$O$_3$ overcoat stabilizing the catalyst against coking and sintering

To obtain further insight into the enhanced stability of Al (4.0 nm)-Ni/SiO$_2$ when compared to the uncoated benchmark catalysts (i.e., Ni/SiO$_2$ and Ni/Al$_2$O$_3$), additional in situ and post-reaction analyses were performed.

In situ XRD data acquired during the DRM at 700 °C (Figure 8a) revealed a noticeable (002) reflection due to graphitic carbon (space group P6$_3$/mmc) for Ni/SiO$_2$ and Ni/Al$_2$O$_3$ after 5 h of TOS. On the other hand, no crystalline carbon was detected for Al (4.0 nm)-Ni/SiO$_2$, implying that graphite C formation was at least one of the reasons leading to the deactivation of uncoated Ni/SiO$_2$ and Ni/Al$_2$O$_3$. For Ni/Al$_2$O$_3$ in situ XRD also reveals a decrease in the intensity of the Ni$^0$ peaks (with respect to the intensity of the support), likely due to the formation of NiAl$_2$O$_4$. However, due to overlapping diffraction peaks the distinction between spinel γ-Al$_2$O$_3$ and NiAl$_2$O$_4$ is difficult. Thus, the in situ XRD study was complemented by XAS
characterization of the post-reaction catalysts to determine the oxidation state of Ni. To examine the oxidation state of Ni in the catalyst materials, *in situ* and *ex situ* XANES spectra at the Ni K-edge after 5 h and 10 h of DRM were collected (Figure 8b and Figure S10). It should be noted that all of the catalysts were completely reduced to metallic Ni⁰ prior to DRM, i.e., TOS = 0 h. The *in situ* Ni K-edge XANES data (Figure 8b) does not show significant changes in the oxidation state of Ni for Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ after 5 h of DRM. On the other hand, the XANES spectra of spent Ni/Al₂O₃ showed a partial oxidation of metallic Ni forming NiAl₂O₄. The oxidation of metallic Ni to NiAl₂O₄ was also observed for Ni/Al (4.0 nm)-Al₂O₃ and Al (4.0 nm)-Ni/Al₂O₃ (Figure S10). From a LCF analysis of the *ex situ* XANES data we quantified that 10, 10 and 9 mol % of Ni in Ni/Al₂O₃, Ni/Al (4.0 nm)-Al₂O₃ and Al (4.0 nm)-Ni/Al₂O₃ were converted into NiAl₂O₄ during 10 h of DRM (Table S2). The migration of Ni⁰ into the Al₂O₃ lattice forming NiAl₂O₄ can explain (with carbon deposition) the deactivation of these three catalysts. Importantly, we did not observe any Ni oxidation in spent Al (4.0 nm)-Ni/SiO₂ and Ni/Al (4.0 nm)-SiO₂, i.e., Ni was maintained in its metallic form over 10 h of TOS. These peculiar results of the Al₂O₃-ALD/SiO₂-based catalysts are possibly due to the presence of aluminosilicates in Al (4.0 nm)-Ni/SiO₂ and Ni/Al (4.0 nm)-SiO₂ that prevent the formation of NiAl₂O₄. Hence, the presence of aluminosilicates resulting from the interaction of the ALD-grown Al₂O₃ layer with SiO₂ upon calcination seems to mitigate the migration (and oxidation) of Ni into the Al₂O₃ matrix.

The quantity of the carbon deposited was determined by temperature programmed oxidation (TPO) on the spent catalysts that were collected after the *in situ* XAS-XRD measurements under DRM conditions for 5 h. (inset in Figure 8c). The weight increase in the temperature range of 300–450 °C is mostly due to the oxidation of Ni to NiO. The weight loss due to the oxidation of deposited carbon species occurs at 600 °C for Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂, and at 715 °C for Ni/Al₂O₃. The quantity of deposited carbon followed the order: Ni/SiO₂ (45 wt. %) > Ni/Al₂O₃ (23 wt. %) >> Al (4.0 nm)-Ni/SiO₂ (4 wt. %).

Raman spectra of all of the spent catalysts showed characteristic D and G bands of carbon at 1250–1350 cm⁻¹ and 1500–1700 cm⁻¹, respectively (Figure 8c). The D bands represent disordered carbon species, e.g., amorphous or defective filamentous carbon, whereas the G band represents the stretching mode of the sp² bonds in ordered graphite.⁸¹,⁸² The very low intensity of the peaks in the Raman spectra for Al (4.0 nm)-Ni/SiO₂ is in line with the quantitative carbon analysis using TPO, i.e., very little carbon deposition on spent Al (4.0 nm)-Ni/SiO₂ compared to spent Ni/SiO₂ and Ni/Al₂O₃. The ratio of the intensities of the G and D bands (I_D/I_D) provides an indication on the degree of crystallinity of the deposited carbon,⁸³ whereby a high ratio of I_D/I_D points to a high crystallinity. For spent Ni/Al₂O₃ I_D/I_D = 1.3, which is higher than the values for spent Ni/SiO₂ (I_D/I_D = 1.0) and Al (4.0 nm)-Ni/SiO₂ (I_D/I_D = 1.0). The crystallinity of the carbon deposited affects the oxidation temperature of carbon, i.e., an increasing oxidation temperature with an increasing degree of carbon crystallinity.⁹ Hence our findings concerning the I_D/I_D values for the different
catalysts are in line with the higher oxidation temperature of carbon deposited onto Ni/Al₂O₃ (715 °C) compared to Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ (600 °C). These results confirm that the significant deposition of coke is a key reason for the deactivation of the uncoated catalysts, i.e. Ni/SiO₂ and Ni/Al₂O₃, whereas Al (4.0 nm)-Ni/SiO₂ shows a very high resistance to coke formation. An increasing degree of coke formation during DRM can be explained by the following factors: (i) surface acidity of the catalyst support (basic sites can alleviate coke deposition by promoting the oxidation of surface carbon⁸⁴) and (ii) sintering of Ni particles. Considering the observed trends in coke formation, particle size and acidity, we ascribe the main driver to coke formation in our set of model catalysts to differences in the growth of the Ni particle size during DRM. Coke formation and particle growth were also visualized by TEM. The formation of filamentous carbon on spent Ni/SiO₂ and Ni/Al₂O₃ was observed, whereas no coke formation was revealed in the TEM images of spent Al (4.0 nm)-Ni/SiO₂ (Figure 8d). Measuring the particle growth during DRM through the analysis of TEM images, a 3.1-fold (from 7 nm to 22 nm) and 1.7-fold (from 11 nm to 19 nm) increase in the Ni particle size was observed for Ni/SiO₂ and Ni/Al₂O₃, respectively. On the other hand, a significantly reduced increase in the particle size of Ni (from 8 nm to 10 nm, i.e., 25 %) was observed for Al (4.0 nm)-Ni/SiO₂, demonstrating the stabilizing effect of an ALD-grown overcoat of Al₂O₃ on the Ni nanoparticles, preventing in turn their sintering during DRM.

To summarize our detailed characterization of the as-prepared and spent catalysts attribute the remarkable stability of Al (4.0 nm)-Ni/SiO₂ during DRM to (i) the confinement of Ni nanoparticles by the Al₂O₃ overcoat preventing coke deposition on edge and step sites in large Ni particles, and (ii) the formation of aluminosilicates that mitigate the migration and oxidation of Ni preventing NiAl₂O₄ formation.
Figure 8. **Morphological and structural characterization of the spent catalysts:** Selected *in situ* (a) diffractograms and (b) Ni K-edge XANES acquired under DRM conditions and (c) Raman spectra of spent Ni/SiO$_2$, Ni/Al$_2$O$_3$ and Al (4.0 nm)-Ni/SiO$_2$. The asterisk in (a) represents γ-Al$_2$O$_3$ (ICSD 66559) or NiAl$_2$O$_4$ (ICSD 9554). The inset in (b) plots the weight loss of the spent catalysts as a function of temperature during a TPO experiment. (d) TEM images and Ni particle size distribution of the spent catalyst.

4. **Conclusions**

We have developed stable Ni-based DRM catalysts by employing atomic layer deposition (ALD) to ensure the deposition of a conformal layer of Al$_2$O$_3$ onto Ni nanoparticles supported on SiO$_2$. Al$_2$O$_3$-coated Ni/SiO$_2$ that showed a remarkable DRM stability when compared to the benchmark references Ni/SiO$_2$ and Ni/Al$_2$O$_3$. An in-depth structural characterization of the Al$_2$O$_3$-coated catalysts and several benchmark systems via *in situ* Ni K-edge XAS-XRD complemented by H$_2$-TPR and solid-state $^{27}$Al NMR revealed the reaction of the ALD-grown Al$_2$O$_3$ layer with the SiO$_2$ support and Ni during calcination, i.e., forming an aluminosilicate and NiAl$_2$O$_4$, respectively. The deactivation of the uncoated benchmark catalysts, i.e. Ni/Al$_2$O$_3$ and Ni/SiO$_2$, is ascribed to Ni particle growth and coke formation during DRM. An additional deactivation route of the Ni/Al$_2$O$_3$ benchmark is the migration/oxidation of Ni into the Al$_2$O$_3$ matrix forming (inactive) NiAl$_2$O$_4$. The best catalyst prepared, i.e. Al (4.0 nm)-Ni/SiO$_2$, showed a remarkable stability (maintenance of 89% of the initial methane consumption rate after 10 h of TOS) under DRM conditions owing to the confinement of Ni nanoparticles by the Al$_2$O$_3$ overcoat and the inhibition of the oxidation of Ni and reaction with Al$_2$O$_3$ in the presence of aluminosilicates.
Present address

§Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington 99352, United States (S. M. K.)

∥DSM Applied Science Center, P.O. Box 1066, 6160 BB Geleen, The Netherlands. (W.-C. L)

Notes

The authors declare no competing financial interest.

Acknowledgements

The authors acknowledge ETH (ETH 57 12-2) and the Swiss National Science Foundation (200020_156015) for financial support. ESRF and the Swiss Norwegian Beamlines (SNBL at ESRF) are gratefully acknowledged for providing access to the synchrotron facility. We would like to thank the Scientific Center for Optical and Electron Microscopy (ScopeM) and the Center for Micro- and Nanoscience (FIRST) at ETH Zurich for providing training and access to electron microscopes. This publication was created as part of NCCR Catalysis, a National Centre of Competence in Research funded by the Swiss National Science Foundation and partially supported by the European Research Council under the European Union’s Horizon 2020 research and innovation program Grant Agreement 819573.

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Supporting information for

Structural insight into an atomic layer deposition (ALD) grown Al₂O₃ layer on Ni/SiO₂: impact on catalytic activity and stability in dry reforming of methane

Sung Min Kim¹, Andac Armutlulu¹, Wei-Chih Liao⁵,
Davood Hosseini⁴, Dragos Stoian⁴, Zixuan Chen,² Paula M. Abdala¹, Christophe Copéret⁵ and Christoph Müller¹,*

¹ Department of Mechanical and Process Engineering, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland
² Department of Chemistry and Applied Sciences, ETH Zurich, Vladimir Prelog Weg 1-5, 8093 Zurich, Switzerland
³ Swiss–Norwegian Beamlines, ESRF, BP 220, Grenoble, 38043, France

*Corresponding author. e-mail: muelchri@ethz.ch

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Table S1. The coordination of Al sites in Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ after calcination and NH₃-treatment, and the distribution of Al₂O₃ and amorphous aluminosilicate (AAS) phase.

Table S2. Ni K-edge XANES-based linear combination fitting (LCF) quantification of NiAl₂O₄ (mol%) for the benchmarks and Al₂O₃ coated Ni-based DRM catalysts after calcination and DRM (10 h of TOS).

Figure S1. Schematic of the experimental setup for combined in situ XAS-XRD measurements BM31 beamline, SNBL at ESRF.

Figure S2. HAADF STEM with EDX analysis of Al (4.0 nm)-Ni/SiO₂ calcined at 800 °C.

Figure S3. (a) N₂ isotherm and (b) BJH pore size of calcined Ni/SiO₂, as-deposited Al (4.0 nm)-Ni/SiO₂, and calcined Al (4.0 nm)-Ni/SiO₂.

Figure S4. TEM images and particle size distribution of reduced Ni/Al₂O₃, Ni/SiO₂, Al (0.4 nm)-Ni/SiO₂, and Al (4.0 nm)-Ni/SiO₂.

Figure S5. Ni K-edge XANES spectra for calcined Ni/SiO₂, Ni/Al₂O₃, Al (4.0 nm)-Ni/SiO₂, Ni/Al (4.0 nm)-SiO₂, Al (4.0 nm)-Ni/Al₂O₃, and Ni/Al (4.0 nm)-Al₂O₃. NiO and NiAl₂O₄ references plotted for comparison.

Figure S6. Solid-state ²⁷Al NMR spectra of (a) γ-Al₂O₃ after calcination and NH₃-treatment, and Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ after (b) NH₃ adsorption and (c) reduction.

Figure S7. NH₃-TPD profile of (a) reference and (b) calcined materials.
Figure S8. Combined (a) in situ Ni K-edge XANES and (b) in situ XRD of calcined Ni/SiO$_2$ and calcined Al (4.0 nm)-Ni/SiO$_2$ during reduction. The arrows in (a) indicate the change of XANES upon reduction. The dashed line in (b) represents (111), (200) and (222) Bragg reflections of Ni.

Figure S9. HAADF-STEM images with EDX mapping for reduced Al (4.0 nm)-Ni/SiO$_2$.

Figure S10. Ex situ Ni K-edge XANES for spent catalysts after 10 h of DRM and references.
Table S1. The coordination of Al sites in Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ after calcination and NH₃-treatment, and the distribution of Al₂O₃ and amorphous aluminosilicate (AAS) phase.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>Al coordination</th>
<th>Al₂O₃</th>
<th>AAS</th>
<th>Al content [mmol/g]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al IV</td>
<td>Al V</td>
<td>Al VI</td>
<td>Al IV</td>
</tr>
<tr>
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<td>3</td>
<td>28</td>
<td>69</td>
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<tr>
<td></td>
<td>NH₃-treated</td>
<td>69</td>
<td>3</td>
<td>28</td>
<td>69</td>
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<tr>
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<tr>
<td></td>
<td>NH₃-treated</td>
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<td>41</td>
<td>11</td>
<td>41</td>
</tr>
<tr>
<td>Al (4.0 nm)-Ni/SiO₂</td>
<td>Calcined</td>
<td>35</td>
<td>41</td>
<td>24</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>NH₃-treated</td>
<td>39</td>
<td>38</td>
<td>23</td>
<td>38</td>
</tr>
</tbody>
</table>

aThe coordination of Al sites was fitted with the CzSimple model using the DMFit software with the assumption of all Al sites detected by ²⁷Al MAS NMR. The Al IV and Al VI sites in Al₂O₃ was calculated using the coordination of Al VI sites after NH₃ treatment, whereby a constant 3:7 ratio is available in γ-Al₂O₃ regardless of calcination and NH₃ treatments. The Al IV, Al V, and Al VI sites in AAS were calculated by the subtraction of Al IV and Al VI in Al₂O₃. Al content in calcined Al (0.4 nm)-Ni/SiO₂ and Al (4.0 nm)-Ni/SiO₂ was quantified by combination of elemental analysis and ²⁷Al NMR with the assumption that all Al species can be detected by ²⁷Al NMR. The parenthesis represented the relative ratio between Al₂O₃ and AAS.

Table S2. Ni K-edge XANES-based linear combination fitting (LCF) quantification of NiAl₂O₄ (mol%) for the benchmarks and Al₂O₃ coated Ni-based DRM catalysts after calcination and DRM (10 h of TOS).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Calcination</th>
<th>After DRM</th>
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</thead>
<tbody>
<tr>
<td>Ni/SiO₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni/Al₂O₃</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>Al (0.4 nm)-Ni/SiO₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al (4.0 nm)-Ni/SiO₂</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Al (4.0 nm)-Ni/Al₂O₃</td>
<td>100</td>
<td>9</td>
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<tr>
<td>Ni/Al (4.0 nm)-SiO₂</td>
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<td>0</td>
</tr>
<tr>
<td>Ni/Al (4.0 nm)-Al₂O₃</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>

aThe benchmark catalysts Ni/SiO₂ and Ni/Al₂O₃ were calcined at 300 °C, while the ALD Al₂O₃-coated Ni catalysts were calcined at 800 °C. bThe catalysts were completely reduced to metallic Ni⁰ at 400–800 °C under 10 vol.% H₂/N₂ prior to DRM tests. The amount of NiAl₂O₄ was quantified after 10 h TOS under DRM conditions at 700 °C.
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