# Highly active and stable alumina supported nickel nanoparticle catalysts for dry reforming of methane

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## ARTICLE INFO

## ABSTRACT

A highly stable and extremely active nickel (Ni) nanoparticle catalyst, supported on porous γ-Al$_2$O$_3$ particles, was prepared by atomic layer deposition (ALD). The catalyst was employed to catalyze the reaction of dry reforming of methane (DRM). The catalyst initially gave a low conversion at 850 °C, but the conversion increased with an increase in reaction time, and stabilized at 93% (1730 L h$^{-1}$ g$_{Ni}^{-1}$ at 850 °C). After regeneration, the catalyst showed a very high methane reforming rate (1840 L h$^{-1}$ g$_{Ni}^{-1}$ at 850 °C). The activated catalyst showed exceptionally high catalytic activity and excellent stability of DRM reaction in over 300 h at temperatures that ranged from 700 °C to 850 °C. The excellent stability of the catalyst resulted from the formation of NiAl$_2$O$_4$ spinel. The high catalytic activity was due to the high dispersion of Ni nanoparticles deposited by ALD and the reduction of NiAl$_2$O$_4$ spinel to Ni during the DRM reaction at 850 °C. It was verified that NiAl$_2$O$_4$ can be reduced to Ni in a reductive gas mixture (i.e., carbon monoxide and hydrogen) during the reaction at 850 °C, but not by H$_2$ alone.

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## 1. Introduction

Methane reforming with carbon dioxide ($CH_4 + CO_2 \rightarrow 2H_2 + 2CO$), also called dry reforming of methane (DRM), obtained considerable attention due to the advances in shale gas recovery [1,2]. DRM is important because the two main greenhouse gases (carbon dioxide and methane) could be converted to syngas (carbon monoxide and hydrogen) in this reaction process. The H$_2$/CO ratio is always lower than 1 due to a reverse water-gas shift reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$). This gas mixture could be used to blend streams from methane steam reformation to produce syngas with the desired H$_2$/CO ratio, which could be applied in the Fischer–Tropsch (FT) synthesis [3,4]. Different metal catalysts (e.g., Rh [5,6], Pt [7,8], Ir [9], Pd [10], Ru [11,12], and Ni [13,14]) were employed to catalyze the DRM reaction. Among them, noble metal catalysts showed better resistance to coking, as compared to Ni catalysts [15,16]. However, due to the limited availability and high cost of noble metals, it was considered desirable to develop a Ni-based catalyst.

The main disadvantage of the Ni catalyst for DRM reaction is deactivation, due to coking and sintering of Ni metal nanoparticles to form larger particles with lower catalytic activity [17]. Coking could be decreased by running the reaction at high temperatures and using small Ni particles, because their step edges are small enough to limit carbon nucleation and growth [4,18]. However, the aggregation of small Ni nanoparticles will be more extreme at higher reaction temperatures. Therefore, there is a trade-off when Ni nanoparticles are used at higher temperatures. The supported Ni catalysts are normally synthesized by an impregnation method using an aqueous solution of nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) [13,14,19–21]. The Ni nanoparticles that are synthesized by the impregnation method are relatively large, typically tens of nanometers [22–24]. They have lower Ni surface areas, compared to smaller Ni nanoparticles, and are easier to get coked.

Atomic layer deposition (ALD) is a self-limiting and self-terminating gas phase deposition technique that has been successfully demonstrated for the synthesis of metal nanoparticles (e.g., Pd and Pt) on different substrates [25,26]. Small Ni nanoparticles ($\sim$3 nm) could be synthesized by ALD and have been demonstrated to be an excellent catalyst with high catalytic activity for catalyzing hydrogenation of propylene [27]. In addition, the ALD Ni nanoparticles strongly interacted with the substrate, which was more stable, when compared to the Ni nanoparticles prepared

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by conventional methods. Alumina was demonstrated to be a better catalyst support for the Ni catalyst, as compared to some other catalyst supports (e.g., $SiO_2$ and $MgO-SiO_2$). This could be due to the fact that the alumina support increased the overall basicity of the supported Ni catalyst and there was a stronger metal-support interaction between the Ni and alumina support [28,29].

Gould et al. [30] deposited Ni nanoparticles (~3 nm) on dense alumina nanoparticles by ALD to catalyze the DRM reaction and applied porous alumina film obtained from aluminum alkoxide (alucone) molecular layer deposition (MLD) films to stabilize the Ni nanoparticles. The idea was to use ALD to prepare highly dispersed Ni nanoparticles with high catalytic activity and to use porous alumina films to encapsulate the Ni nanoparticles for greater thermal stability. Their results showed that five cycles of alucone MLD could increase the thermal stability and steady-state activity of the catalyst. However, previous studies by Liang et al. indicated that the porous alumina film formed from ten cycles of alucone MLD by calcination could not completely encapsulate 1.8 nm average size Pt particles [31]. Similarly, it would be difficult to use porous alumina films obtained from 5 cycles of alucone MLD coating to encapsulate 3 nm Ni nanoparticles. Therefore, the increase in catalyst stability, with five cycles of MLD coating, should not result from stabilization of Ni particles by alumina film encapsulation. The interaction between the Ni nanoparticles and the deposited alumina film could be the key. In the study by Gould et al., dense alumina nanoparticles were used as catalyst support [30]. We hypothesize that the catalytic performance could be very different if we used porous alumina particles as the catalyst support. There will be more interaction between the Ni nanoparticles and the porous alumina support (as schematically shown in Fig. S1), since there is more interfacial contact between nanoparticles and the concave surface (porous support), compared to the case of a convex surface (dense particle support). Thus, the thermal stability of the highly dispersed ALD Ni nanoparticles would be improved. In this study, we synthesized a porous $\gamma-Al_2O_3$ supported Ni nanoparticles catalyst using the ALD technique. The DRM reaction was initially carried out at 850 °C, to activate the catalyst, and then run at different temperatures. The reduction mechanism of $NiAl_2O_4$ spinel was studied.

## 2. Experimental

### 2.1. Materials

Dense alumina nanoparticles (50–100 nm, gamma phase) and porous $\gamma-Al_2O_3$ particles were purchased from Sigma-Aldrich and Alfa Aesar, respectively. The porous alumina particles were 40 μm in diameter, with a Brunauer–Emmett–Teller (BET) surface area of 95.5 $m^2$/g. The dense alumina nanoparticles had a BET surface area of 137 $m^2$/g. Bis(cyclopentadienyl)nickel ($NiCp_2$) and $Ni(NO_3)_2\cdot6H_2O$ were purchased from Alfa Aesar and Fisher Scientific, respectively.

### 2.2. Catalyst preparation and characterization

Ni nanoparticle ALD was carried out using $NiCp_2$ and hydrogen as precursors at 300 °C in a fluidized bed reactor. The ALD reactor system has been previously described in detail [32]. Both porous $\gamma-Al_2O_3$ particles and dense alumina nanoparticles were used as the substrates and one cycle of Ni ALD was applied. These two catalysts were labeled as ALD Ni/$\gamma-Al_2O_3$, and ALD Ni/NP-$Al_2O_3$, respectively. To obtain a better characterization result, a porous $\gamma-Al_2O_3$ supported Ni catalyst with four cycles of Ni ALD (a Ni loading of 4 wt.%) was synthesized and labeled as ALD 4-Ni/$\gamma-Al_2O_3$. For comparison, Ni nanoparticles supported on porous $\gamma-Al_2O_3$ par-

ticles were also prepared by the incipient wetness (IW) method. An aqueous solution of $Ni(NO_3)_2$ $6H_2O$ was added to the porous $\gamma-Al_2O_3$ particles and dried at 110 °C, while stirring continuously. The sample was then calcined in air at 550 °C for 6 h. The catalyst prepared by the IW method was labeled as IW Ni/$\gamma-Al_2O_3$.

The Ni loadings of different catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP–AES, Model ARL 34101, Thermo Electron, Waltham, MA).

The average size and dispersion of the Ni nanoparticles supported on alumina nanoparticles were observed by transmission electron microscopy (TEM) with a FEI Tecnai F20 TEM.

In order to measure the coke content of the used catalyst, derivative thermogravimetric (DTG) analyses of the samples were made using a TA Instruments Q50 thermogravimetric analyzer. The DTG analyses were carried out with an air (40 mL/min) and $N_2$ (40 mL/min) stream. The temperature was increased from room temperature to 200 °C, at a heating rate of 10 °C/min, and kept at 200 °C for 60 min, and then increased to 1000 °C at the same rate.

X-Ray diffraction (XRD) spectra were recorded on a Philips X-Pert Multi-purpose Diffractometer, using Cu Kα 1 radiation (λ=0.15416 nm).

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis 165 X-ray photoelectron spectrometer with a monochromatic Al Kα radiation (h = 1486.6 eV). All binding energy values were corrected based on a C (1s) peak at 284.5 eV.

$H_2$-temperature programmed reduction (TPR) tests were performed using an AMI-300. Typically, 100 mg of the sample were charged in a quartz tube and reduced up to 900 °C at a heating rate of 10 °C/min in a stream of 10% $H_2$ in Ar. The ALD Ni/$\gamma-Al_2O_3$ and ALD Ni/NP-$Al_2O_3$ samples were oxidized at 550 °C for 1 h before the TPR test.

### 2.3. General procedure for dry reforming of methane

Different amounts of various catalysts were loaded into a quartz tube reactor (10 mm diameter) to keep the Ni content consistent (~0.64 mg). Quartz wool was employed to support the catalysts. The catalysts, using porous $\gamma-Al_2O_3$ as supports, were diluted with 0.5 g of quartz sands (60–120 mesh) and were well distributed in the quartz sands. A thermal couple was applied to measure the temperature. The ALD synthesized catalysts were oxidized at 550 °C to remove any residual organic components from the Ni ALD precursor. All of the catalysts were reduced with 20% $H_2$ and 80% Ar (with a total flow rate of 100 sccm) at 700 °C for 1 h before the DRM reaction. $CH_4$ and $CO_2$ that were balanced with Ar (20% $CH_4$, 20% $CO_2$, and 60% Ar, with a total flow rate of 100 sccm), were introduced into the reactor at different temperatures for a DRM reaction. The catalysts were regenerated after the reaction and applied to catalyze the DRM reaction again. In a typical regeneration process, the catalyst was first oxidized in 20% $O_2$ and 80% Ar at 700 °C for 1 h and then reduced in 20% $H_2$ and 80% Ar at the same temperature for 1 h. The gas flow rates were controlled by MKS® mass flow controllers. The reaction products were analyzed by an online gas chromatograph (SRI 8610C) equipped with a 6-foot HAYESEP D column, a 6-foot MOLECULAR SIEVE 13X column, and a thermal conductivity detector (TCD).

## 3. Results and discussion

### 3.1. Catalytic performance

The ALD Ni/$\gamma-Al_2O_3$ catalyst was first employed to catalyze the DRM. Fig. 1 shows the DRM reaction results at different temperatures as catalyzed by ALD Ni/$\gamma-Al_2O_3$. In the first cycle (here, one