Alumina coated nickel nanoparticles as a highly active catalyst for dry reforming of methane

Elham Baktash [a,d,*], Patrick Littlewood [b], Reinhard Schomäcker [b], Arne Thomas [a], Peter C. Stair [c,**]

[a] Functional Materials, Department of Chemistry, Technische Universität Berlin, Hardenbergstr. 40, 10623 Berlin, Germany
[b] Chemical Reaction Engineering, Department of Chemistry, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany
[c] Center for Catalysis and Surface Science, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA
[d] Chimie de la Matière Condensée de Paris, Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, 11 Place Marcelin Berthelot, 75005 Paris, France

ARTICLE INFO

ABSTRACT

Alumina coated nickel nanoparticles were prepared employing atomic layer deposition (ALD) on nickel oxide (NiO) nanoparticles and subsequent reduction of the NiO core. The materials showed impressive activity and stability for dry reforming of methane at elevated temperatures (700–800 °C), especially when compared to the uncoated and reduced NiO nanoparticles. The stabilization against sintering at high temperatures is the crucial factor explaining the high catalytic activity of alumina coated Ni nanoparticles.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Dry reforming is a process for syngas production from methane and carbon dioxide ($CH_4 + CO_2 \rightarrow 2H_2 + 2CO$). Syngas can be used for the production of numerous chemicals, including methanol, dimethyl ether, Fischer–Tropsch chemicals, ammonia, acetic acid, and formic acid [1–4]. Methane and carbon dioxide are two of the cheapest and most abundant carbon-containing materials. Furthermore, they are greenhouse gases; thus, their conversion into value added chemicals is of great interest. DRM is an endothermic reaction which even at higher temperatures needs suitable catalysts to observe sufficient conversions. Noble metals show high catalytic activity in dry reforming of methane (DRM) [5–9]; however, applying cheap and abundant metals such as Ni, which is also an active catalyst for this process, is certainly preferred [10]. However, Ni-based catalysts suffer from severe deactivation during the catalytic

process [11]. Generally, catalyst deactivation is one of the major problems in heterogeneous catalysis. The time scale for deactivation can vary considerably depending on the operation conditions (temperature, pressure, reactants, etc.) type of catalyst and the reactor. Especially, in the case of endothermic processes, such as the DRM reaction, which require elevated temperatures for reasonable conversions, deactivation of catalysts is a serious problem. For Ni based catalysts in DRM, two major sources of deactivation have been identified, namely carbon deposition at lower (500–700 °C) and sintering at higher temperatures (700–800 °C) [10,12].

In order to decrease the cost of catalyst replacement and process shut down, tremendous efforts have been undertaken to improve catalyst stability in harsh conditions. Formations of alloys [13–17], partial passivation of the active sites with sulfur, tin or bismuth [14,15,18–20] are some examples of strategies employed for achieving this goal. Moreover, in order to avoid sintering which changes the active sites and accelerates coke formation, shells out of silica, [21,22] tin oxide [23] and zirconia [24] have been formed around the active catalysts by employing techniques such as chemical vapor deposition, dendrimer encapsulation or grafting. However, the formed shells often decreased the catalyst activity probably due to mass transfer limitation or active site coverage. Therefore, shell formation around active catalysts (also called

"inverse catalysts") [25–27] in a more controlled manner is necessary, to inhibit catalyst sintering but also maintain catalytic activity. Moreover, the preparation of inverse catalysts can give the opportunity to enhance selectivity of catalysts by partial coverage of catalytic active but unselective sites.

We report here on the preparation of alumina coated nickel-based catalysts from commercially available nickel oxide nanopowders. For conventional supported catalysts used in DRM, Al_2O_3 was considered to be an excellent support material due to its basicity, promoting a high conversion of CO_2 [28]. For the here presented inverse catalyst, Al_2O_3 coatings were prepared in a highly controlled manner using atomic layer deposition (ALD), by sequential exposures of NiO nanopowders to trimethyl aluminum (TMA) and water vapors. Different numbers of Al_2O_3 ALD cycles (5–20) were performed to generate protective layers of progressively increasing thickness on the NiO nanopowder. A pre-reduction of the Al_2O_3 covered NiO nanoparticles with hydrogen at 500 °C is carried out before the catalytic tests, yielding alumina coated Ni(0)-nanoparticles.

2. Experimental

2.1. Catalyst preparation

Ni oxide nanopowder (∼50 nm particle size (TEM), 99.8% trace metals basis) was purchased from Sigma–Aldrich.

ALD was performed using a viscous flow reactor system similar to the one previously described [29] and a fixed-bed powder sample holder. Ultrahigh pure nitrogen (99.999%) was used as the carrier gas with a mass flow rate of 360 sccm. The system pressure was between 1 and 2 Torr. In traditional ALD, two precursors, A and B, are alternately dosed and purged through the reactor with the time sequence t_1–t_4. Here, A is trimethyl aluminum (TMA, Sigma–Aldrich, 97%); B is deionized water (H_2O); t_1 is the dose time for A; t_2 is the purge time for A; the t_3 is dose time for B; and t_4 is the purge time for B. The time sequence of 300–300–300–300 s was chosen for our system due to the porous nature of the NiO nanopowder which usually needs longer dosing and purging time than for flat substrates. [30] The over-coated samples were prepared using 5, 10, 15, and 20 cycles of Al_2O_3 ALD at 50 °C to generate the protective layers (NiO-X, X: number of alumina ALD).

2.2. Characterization

Nitrogen sorption isotherms were measured at liquid-nitrogen temperature (−196 °C) with an Autosorb-1. The samples were degassed at 120 °C overnight before the measurement. The Brunauer–Emmett–Teller (BET) surface area was calculated by multiple-point (five-point) measurement in the relative pressure range of 0.05–0.30.

The mass content of aluminium was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES), Optina 2100 DV (PerkinElmer, USA).

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 20 S-TWIN transmission electron microscope equipped with a LaB$_6$-source at 200 kV acceleration voltages, using amorphous carbon-coated copper grids. The specimens were dispersed in ethanol with ultrasonication and loaded onto a copper grid.

Temperature programmed oxidation (TPO) was carried out under 8 ml per min flow of 20% O_2 in He. The oxidation temperature was increased from room temperature to 800 °C with a heating ramp of 2 °C per minute. Outlet gas was analyzed using a quadrupole mass spectrometer (Inprocess Instruments GAM 200).

XRD was performed using a Bruker D8 Advance X-ray diffractometer with Cu Kα1 = 1.5418 Å radiation between 2° and 90° (2θ).

2.3. Catalytic testing

Catalyst testing was carried out in a fixed-bed quartz tube reactor (internal diameter 5 mm). The catalyst mass was diluted in quartz sand or glass balls with a total volume of 1.25 ml. The amount of catalyst used was typically 1 mg, although less was used for highly active catalysts in certain experiments to measure the catalytic activity away from thermodynamic equilibrium. The reactor was heated using an external furnace (HTM Reetz) controlled by a temperature probe within the catalyst bed. Each catalyst was reduced in-situ in pure H_2 for 1 h at 500 °C before testing; in-situ catalyst oxidation consisted of heating (20 K min^{-1}) and 1 h oxidation at 750 °C under 15 ml min^{-1} synthetic air flow. Typical reaction conditions were 30 or 60 ml min^{-1} reaction gas with composition CH_4:CO_2:He = 1:1:8 at atmospheric pressure. Outlet gases were analyzed (typically every 10 min) using an Agilent 7890A gas chromatograph equipped with thermal conductivity and flame ionization detectors.

3. Results and discussion

Al_2O_3 ALD performed using TMA and water is one of the most investigated and successful ALD procedures. [31–35] In this process:

1. TMA reacts with hydroxyl groups on the surface forming Al(CH$_3$)$_x$* (*surface species, x = 1–2) and CH_4.
2. Evacuation or purging with an inert gas like nitrogen removes the non-reacted reactants and the gaseous reaction by-products.
3. After the following H_2O exposure, the Al(CH$_3$)$_x$* transforms to Al(OH)$_x$* (x = 1–2) and releases CH_4.
4. After the formation of a monolayer on the substrate, excess precursors are purged by the inert gas.

The film growth occurs in a layer-by-layer fashion. These cycles are repeated until the target film thickness is achieved. Recently, ALD Al_2O_3 protective layers with precise thicknesses were utilized to inhibit the sintering of Pd NPs. The catalytic performance of the resulting material was tested in the methanol decomposition reaction [36]. The catalytic activity of the Al_2O_3 protected Pd NPs was maintained or even slightly enhanced up to a certain thickness. It has been shown that catalyst deactivation due to sintering or coke formation could be effectively prevented by alumina coating with a thickness of 8 nm [37]. The same process might be applicable for the protection of other supported/unsupported nanoparticles or porous materials with catalytic application in reactions perform at elevated temperatures.

5, 10, 15 and 20 cycles of alumina ALD were applied to NiO nanoparticles. XRD patterns of the nanoparticles before and after coating showed the typical pattern of the nickel oxide phase (Fig. S1). N_2 physisorption was performed on the uncoated and coated samples (Table 1). The BET measurements on the uncoated nanoparticles yield a surface area of 99.2 m^2 g^{-1}. After 5 cycles of alumina ALD, the surface area reduced to 51 m^2 g^{-1}. The decrease in surface area becomes more pronounced with increasing the number of alumina ALD cycles. This gradual decrease of surface area by increasing the ALD cycles could be a consequence of partial filling of the nanoparticle voids by alumina layers. The increasing aluminum content, measured by ICP elemental analysis (Table 1) furthermore proves the successful deposition of thicker alumina layers with increasing cycle number. The morphology of the Ni oxide nanoparticles before and after coating was studied by transmission electron