

Review

Atomic Layer Deposition for Preparation of Highly Efficient Catalysts for Dry Reforming of Methane

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Abstract: In this article, the structural and chemical properties of heterogeneous catalysts prepared by atomic layer deposition (ALD) are discussed. Oxide shells can be deposited on metal particles, forming shell/core type catalysts, while metal nanoparticles are incorporated into the deep inner parts of mesoporous supporting materials using ALD. Both structures were used as catalysts for the dry reforming of methane (DRM) reaction, which converts CO_2 and CH_4 into CO and H_2 . These ALD-prepared catalysts are not only highly initially active for the DRM reaction but are also stable for long-term operation. The origins of the high catalytic activity and stability of the ALD-prepared catalysts are thoroughly discussed.

Keywords: atomic layer deposition; dry reforming of methane; nickel; shell-core type nanoparticle; mesoporous media; surface basicity

1. Introduction

Carbon dioxide is the most important greenhouse gas responsible for climate change; therefore, suppression of its concentration in the atmosphere has been of particular importance over the last several decades [1–4]. Thus, how to efficiently capture and store CO_2 from the emissions of vehicles and power plants has been extensively studied. A variety of storage media such as porous materials including a metal-organic framework (MOF) or compounds with high CO_2 affinity such as CaO or MgO have been studied [4–12]. More recently, chemical conversion of CO_2 has been drawing more attention, since this process is not only able to contribute to the reduction of CO_2 levels in the atmosphere but also produces value-added products from CO_2 [2,13–31].

There are diverse ways of converting CO_2 into more valuable chemical compounds. CO_2 can be electrochemically or photo-chemically reduced to many valuable chemicals such as CO, CH₃OH, and HCOOH [14–17]. In these processes, it is often important to use a proper heterogeneous catalyst to increase the selectivity of a specific reaction product as well as the total reaction yield. Using chemical reactions between CO_2 and other compounds, valuable materials such as polycarbonate plastics can be produced [18–20]. There are also thermal catalytic reactions such as hydrogenation of CO_2 , in which CO_2 reacts with H₂ to form CO and H₂O [21–23]. The abovementioned reactions using CO_2 as a reactant are generally endothermic due to the high thermodynamic stability of CO_2 . Therefore, energy needs to be provided in various forms (electric, thermal, or photon energy) to carry out these reactions even in the presence of highly active catalysts. Therefore, these reactions should be coupled with



alternative energy sources such as solar or wind energy [2,24-26]. The CO₂ chemical conversion can be considered as a possibility to store sustainable energy.

Dry reforming of methane (DRM) uses CO_2 and CH_4 as reactants to produce CO and H_2 . This reaction is highly endothermic, typically operating at 800 °C or higher [27–29]. Once this reaction can operate with long-term stability, the efficient production of syngas (CO and H_2) from two major greenhouse gases (CO₂ and CH₄) can be realized. However, even if alternative energy sources are available to maintain the reactor temperature sufficiently high enough for the catalytic DRM reaction, the catalysts used for this reaction generally do not endure such high temperatures for a long time as they rapidly undergo catalytic deactivation with time, which is the major hurdle of the DRM reaction [13,28,30].

Ni has been considered as a DRM catalyst in the past, yet bare Ni catalyst was shown to be inappropriate for this reaction since its catalytic activity drastically decreases with time due to the formation of a graphitic carbon layer on the Ni surface, which blocks catalytically active Ni sites [13,30,32]. Either disproportionation of CH₄ into $C_{(s)}$ and H₂ or CO into C and O₂ (or H₂O by reaction with H₂) can result in deposition of a graphitic carbon layer (coke) on the surface of Ni [30,33–36].

There are several different strategies for preparing coke-resistant DRM catalysts. For example, diverse composite materials consisting of catalytically active Ni and other metal oxides can be used, resulting in reduced coke formation due to, for example, the high adsorption energy of CO_2 on metal oxide surfaces [13,31,37–40]. Please note that CO_2 can react with coke to form CO, releasing the deposited coke from the catalyst surface. Nanoparticles of Ni were deposited on supporting materials, and the supported catalyst was used for the DRM reaction. Here, nanoparticles were shown to be more resistant toward coke formation than larger Ni terraces, since small Ni nanoparticles with a high curvature can suppress the formation of two-dimensional graphite domains [41–43]. Nevertheless, the low thermal stability of nanoparticles against agglomeration is a problem that needs to be solved [44–46].

Atomic layer deposition (ALD) has been widely used in the thin film deposition process of electronic and optical device fabrication [47–53]. Over the past few decades, application of ALD in the synthesis of heterogeneous catalysts has been vigorously considered [13,30,54–59]. In this article, the operation principles and advantages of ALD are briefly summarized. In addition, the structure, chemical uniqueness, and catalytic behavior toward the DRM reaction of ALD-prepared heterogeneous catalysts are reviewed together with potential applications. Two different types of structures prepared by employing ALD as heterogeneous catalysts for the DRM reaction are discussed: (1) shell/core-type, metal-oxide/metal catalyst prepared by depositing additional metal-oxide thin films (MgO, TiO₂, ZnO) onto Ni particles using ALD and (2) Ni nanoparticles confined in the mesoporous supporting templates prepared via ALD deposition of NiO on mesoporous materials (silica, alumina) followed by thermal annealing in a reducing atmosphere.

2. Shell-Core-Type DRM Catalysts Prepared by ALD

Figure 1a shows a schematic of the ALD process [47,60–63]. In principle, one can use more than two precursors to deposit thin films of diverse chemical compositions. In Figure 1a, a simple situation for depositing metal oxide thin films using an inorganic metal precursor and an oxidizing agent such as H_2O is described. In the first step, a sufficiently large amount of the metal precursor vapor consisting of metal atoms and organic ligands (e.g., Ti[OCH(CH₃)₂]₄, Mg(Cp)₂, or Ni(Cp)₂) is supplied into the vacuum chamber where substrates are located. Then, only precursors chemisorbed on the substrate surface remain, whereas physiosorbed species and precursor vapors in the gas phase are removed by purging with inert gases and pumping. Subsequently, oxidizing agent vapor such as $H_2O(g)$ or $O_2(g)$ is introduced into the chamber and reacts with chemisorbed metal precursors to form the metal oxide and $CO_2(g)$ and $H_2O(g)$ upon oxidation of the organic ligands. The aforementioned steps constitute one cycle of ALD, and 2–6 cycles of ALD generally form a metal-oxide monolayer, depending on the molecular structures of the inorganic precursors [63–68].



Figure 1. (a) The operating principle of atomic layer deposition is schematically described. (b) Scanning Electron Microscopy (SEM) images of TiO_2 thin films on anodic aluminum oxide substrates deposited using atomic layer deposition (ALD). Edited from Reference [69].

A clear advantage of ALD with respect to chemical vapor deposition (CVD), in which two different precursors are provided at the same time onto the substrate surface, is that the thickness of thin films can be controlled on the atomic scale. ALD has been widely employed for fabrication of diverse functional thin films of electronic and optical devices owing to its ability to finely control film thickness [70–82]. Another advantage of ALD is the formation of conformal thin films on complex structured surfaces. As an example, TiO₂ thin films with thicknesses less than 10 nm were deposited on an anodic aluminum oxide (AAO) membrane consisting of regularly ordered 200-nm-sized pores using ALD and the resulting structure consisted of a homogeneous coating of TiO₂ without deteriorating the original porous substrate structure of AAO (Figure 1b,c) [69]. The ALD-prepared nanostructure TiO₂ with a regularly ordered pore structure demonstrated a superior toluene adsorption efficiency of 3.8 toluene molecules/nm² by applying 300 ALD cycles [69].

Conventionally, catalytic active metals supported by metal oxides are considered heterogeneous catalysts. Both the geometrical structure (size, shape, morphology) and electronic nature (oxidation states) of the supported metal are related to its catalytic activity. The catalytic activity of conventional metal/metal oxide catalysts can also be influenced by underlying metal oxide supports. The geometrical and electronic structures of the supported metals can be influenced by underlying metal oxides. In addition, the catalytic behaviors of metal/metal oxide catalysts can be varied

depending on the choice of metal oxide materials as supports by providing dissimilar metal/metal oxide interface sites as well as the participation of metal oxides in the catalytic reaction. Alternatively, the metal oxide can be deposited on metal particles (metal oxide/metal) which is often referred to as an inverse catalyst [83–86]. These metal oxide/metal systems have been studied to elucidate the contribution of the metal oxide interface on catalytic activity since the 1940s [83–86]. A large number of research groups have investigated inverse catalysts, and it has been reported that some inverse catalysts exhibit even higher activities than regularly structured catalysts (metal/metal oxides) consisting of the same compounds [84,87].

Owing to the excellent trench filling capability and controllability of the metal oxide film thickness of ALD, as mentioned above, the ALD technique can be very useful in studies of inverse catalysts by fabricating various thin metal oxide films with different thicknesses on metal particles. The experimental results showing the utilization of ALD in the fabrication of various metal oxide thin films (MgO, TiO₂, ZnO) on Ni particles are summarized below including their catalytic behaviors towards the DRM reaction.

Ni particles (Sigma Aldrich) with diameters of $0.5-1 \ \mu m$ were loaded into a home-made sample container, in which particles are maintained and where precursor vapors can penetrate into the container and be purged during the ALD process. ALD was used to deposit metal oxide thin films on Ni particles and, as shown in Figure 2, either TiO₂ or MgO thin layers homogeneously wrapping the Ni particles could be prepared [13,30]. Ti[OCH(CH₃)₂]₄ bought from Sigma Aldrich (St. Louis, MO, USA) was used as the Ti precursor for deposition of TiO₂ films, while Mg(Cp)₂ purchased from EG Chem Co. Ltd (Daegu, Korea) was used as the Mg precursor for deposition of MgO films. For both cases (TiO₂ and MgO deposition), H₂O vapor was used as the oxidizing agent. By altering the number of ALD cycles, the thickness of the metal oxide thin layers could be finely altered [88].



Figure 2. Transmission electron microscopy (TEM) images of (**a**) TiO₂/Ni particles and (**b**) MgO/Ni particles prepared by applying 500 and 200 cycles of ALD, respectively. Edited from Reference [13,30].

The ALD process generally operates below 300 °C, where metal oxide layers tend to show amorphous structures with rather ill-defined oxidation numbers of metal atoms as opposed to highly crystalline structures [69]. During ALD under relatively low-temperature conditions, organic ligands and metal atoms are not completely oxidized, resulting in the formation of thin films with ill-defined structural properties. Only upon a proper post-annealing process of the ALD-prepared structure can stoichiometric metal oxide layers be formed, for example, annealing for 5 h at 800 °C under an N₂ atmosphere led to the formation of stoichiometric TiO₂ layers [13,30]. The specific areas and pore volumes of the samples (bare Ni, MgO/Ni, TiO₂/Ni) were determined by Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, respectively, and they are summarized in Table 1. An interesting aspect of the post-annealed metal-oxide/Ni structure compared to a bare Ni substrate is that the specific surface area or pore volume can increase with increasing thickness of metal oxide films prepared by ALD. For example, the surface area of TiO_2/Ni prepared by 500 ALD cycles was 25 m²/g and this value is much larger than that of bare Ni ($3.5 \text{ m}^2/\text{g}$) [30]. On the other hand, MgO/Ni prepared by 200 ALD cycles had a specific surface area of $1.9 \text{ m}^2/\text{g}$ which is lower than the respective value of bare Ni. It is likely that a MgO thin film with a smooth surface structure deposited on a rough Ni surface decreases the specific surface area. However, the pore volume increases from 0.005 to 0.008 cm³/g by depositing MgO on Ni particles [13]. These results can only be understood in terms of crack formation in the oxide layers prepared by ALD and post-annealing. The formation of cracks during fabrication of TiO₂ or MgO crystalline layers on Ni can result from the non-flat substrate surface structure of Ni particles since the curvature of the crystalline layer can induce strain on the thin film layer and result in crack formation.

Table 1. Brunauer-Emmett-Teller (BET) surface area and Barret-Joyner-Halenda (BJH) pore volume of bare Ni, MgO/Ni (50 and 200 ALD cycles), and TiO_2/Ni (100 and 500 ALD cycles). The ALD-deposited metal oxide thicknesses of MgO/Ni (200 cycles) and TiO_2/Ni (500 cycles) determined by TEM analysis are also summarized.

Catalyst	Number of Cycles	BET Surface Area (m²/g)	BJH Pore Volume (cm ³ /g)	Mean Thickness of Metal Oxide	Reference
Bare Ni	-	3.5	$5.5 imes 10^{-3}$	-	[13,30]
MgO/Ni	50	3.5	$4.3 imes 10^{-3}$	-	_ [13]
	200	1.9	$7.5 imes 10^{-3}$	~20	
TiO ₂ /Ni	100	4.9	$5 imes 10^{-3}$	-	_ [30]
	500	25	$1.3 imes 10^{-3}$	~40	

The metal-oxide-wrapped Ni particles were used as catalysts for the DRM reaction at 800 °C and the catalytic activity patterns of bare and oxide-wrapped Ni particles are presented in Figure 3 [13,30]. The DRM reaction was carried out using a vertical fixed-bed quartz reactor under atmospheric pressure. Quart wool loaded with 0.1 g of catalysts was placed in the center of the quartz reactor. The gas mixture of CH₄ and CO₂ at a ratio of 1:1 was continuously fed into the reactor at a constant total flow rate (20 mL/min) [13,30]. Generally, bare Ni as a catalyst shows high initial activity for conversion of CO₂ and CH₄ and high initial yields of H₂ and CO, which are syngas products. The production of CO is generally slightly higher than that of H₂ since H₂ produced in the DRM can further react with CO₂ to form CO and H₂O which is the reverse process of the water-gas shift reaction [89]. This process also contributes to the phenomenon in which CO₂ conversion is generally higher than that of CH₄ during the DRM reaction. As a function of reaction time, however, the conversion rates of the reactants and the formation rates of the products, as well as the H₂/CO ratio, drastically decrease. Such a deactivation process of the DRM reaction using Ni as a catalyst is a well-known phenomenon and is attributed to coke formation on the Ni surfaces, poisoning catalytically active bare Ni sites [30,90–92].

For Ni particles wrapped by MgO using ALD, improvement in both initial catalytic activity and sustainability of the catalytic activity with respect to bare Ni are observed. On the other hand, the initial catalytic activities of TiO_2/Ni catalysts were slightly higher or lower than those of bare Ni depending on the number of ALD cycles applied for TiO_2 deposition (100 cycles or 500 cycles). However, ALD deposition of TiO_2 thin layers (either 100 or 500 cycles) always resulted in improved catalytic sustainability of Ni particles. These results indicate that TiO_2 or MgO deposited on Ni does not completely block the active Ni sites, which can be attributed to the aforementioned crack formation within TiO_2 or MgO layers wrapping Ni particles. CH₄ and CO₂ molecules can diffuse via the cracks of TiO_2 and MgO and react to form CO and H₂ on catalytically active Ni sites. In addition, with increasing thickness of TiO₂ or MgO layers within 20 nm of the film thickness, the initial reactivity and stability of catalyst are enhanced [13,30]. Even though the TiO₂ shell shows higher surface areas corresponding to the higher crack density than MgO, MgO produces much higher enhancement effects of the catalytic activity and stability of Ni for DRM than TiO₂ shells. The origin of this result will be discussed in detail later. Ultimately, MgO/Ni with an MgO shell thickness of ~20 nm did not show any deactivation for DRM under ambient pressure conditions for longer than 3 days (Figure 3a–c).



Figure 3. (a) CO₂ conversion, (b) CH₄ conversion, and (c) H₂/CO ratio, which are products of the DRM reaction, are compared for bare Ni and MgO-wrapped Ni with two different MgO thicknesses. (d–f) show the respective data for bare and TiO₂-wrapped Ni. The dry reforming of methane (DRM) reactions were carried out at 800 °C under atmospheric conditions with a constant flow of the gas mixture (CH₄:CO₂ = 1:1, total flow rate of 20 mL/min). The number of ALD cycles used for preparing each metal oxide-wrapped Ni is denoted in the respective figure legend. Edited from Reference [13,30].

To shed light on the origin of the enhanced catalytic activity upon TiO₂ or MgO deposition on Ni particles, detailed characterization of the catalysts using X-ray diffraction (XRD) and scanning electron microscopy (SEM) was carried out (Figure 4a–d) after the catalysts were used for DRM reactions [13,30]. A generally observed phenomenon from TiO₂- or MgO-wrapped Ni particles is the formation of carbon filaments on the surface of catalysts after the DRM reaction. In contrast, on bare Ni particle surfaces, two-dimensional graphitic carbon layers are formed. These results are schematically summarized in Figure 4e. There is another effect of the MgO film, which is Lewis-basic and therefore shows high affinity to CO₂, which was verified by CO₂ temperature programmed desorption [13,93–95]. With increasing MgO thickness, the number of moderate MgO adsorption sites decreased, whereas that of stronger adsorption sites of CO₂, which can be attributed to under-coordinated surface O species of MgO, increased. When the CO₂ affinity of the catalyst surface increases, the reverse Boudouard reaction (C + CO₂ \rightarrow 2CO) can become faster, which can contribute to the removal of coke from the catalyst surface.



Figure 4. (**a**) X-ray diffraction (XRD) and (**b**–**d**) SEM results of bare and MgO-wrapped Ni particles after 72 h of the DRM reaction. (**e**) Schematic of the various deactivation behaviors. Edited from Reference [13].

Shells of thin layers of TiO₂ (100 ALD cycles) and MgO (50 and 200 ALD cycles) on Ni showed improved DRM catalytic activity and stability. In terms of catalytic activity for the DRM reaction, MgO/Ni is superior to TiO₂/Ni both in terms of initial activity and long-term stability. The primary roles of MgO and TiO₂ layers for enhancing DRM catalytic stability seem to be analogous to a geometric perturbation of coke formation by inducing carbon filament growth. MgO is a Lewis base, whereas TiO₂ is not; therefore, MgO shows a higher affinity towards CO₂, resulting in higher catalytic activity and stability for DRM [13,31,37]. This suggests that the chemical composition of the metal oxide shell is crucial to obtain a high catalytic activity for DRM. In order to further shed light on this issue,

we recently performed the DRM reaction with ZnO-wrapped Ni catalysts and showed (Figure 5) that the ZnO layer increases the deactivation of Ni catalyst during the DRM reaction. It is likely that ZnO layers induce a more facile formation of the coke layer on Ni, which clearly demonstrates that to obtain a high-performing shell-core-type catalyst for DRM, not only the geometric structure of the metal oxide shell/Ni core is beneficial, but the chemical composition and thickness of the oxide shell are crucial. The influence of the chemical nature of metal oxide supports, such as acidity/basicity and reducibility, on the catalytic behaviors of metal particles towards the DRM reaction has been highlighted by many researchers. For instance, basic sites existing on metal oxides such as La₂O₃ and MgO can enhance the activation of CO₂, which can reduce carbon formation and catalyst deactivation [96]. On the other hand, some research groups demonstrated that CO₂ activation can also take place on acidic metal oxides via reaction with hydroxyls on the surface of acidic supports, but CO_2 activation on acidic supports is weaker than that on basic supports [28,97,98]. The catalytic DRM reaction of Rh catalysts supported on various reducible and irreducible metal oxides was examined and the irreducible metal oxide supports generally led to higher catalytic activity of the supported metal catalyst than in the case of irreducible metal oxide supports [96]. However, it has also been reported that reducible CeO₂ can promote the catalytic activity of the Ni catalysts for DRM reaction by acting as an oxygen accumulator [99].



Figure 5. (a) CO₂ conversion and (b) ratio of H₂ to CO, which are products of the DRM reaction, for bare Ni and ZnO-wrapped Ni. The DRM reactions were carried out at 800 °C under atmospheric conditions with a constant flow of the gas mixture (CH₄:CO₂ = 1:1, total flow rate of 20 mL/min).

Considering that ALD is able to finely tune the oxide film thickness and can be applied for a wide range of oxide materials, ALD can be regarded as a proper technique for obtaining highly efficient DRM catalysts. It should be emphasized that when the oxide shell becomes much thicker than the oxide shells presented here, collision of CO_2 and CH_4 with the Ni surface could be hindered and the catalysts will become less active. It is promising that the catalytic activity of metal particles for reactions other than DRM can be also finely controlled by adopting diverse structures of metal oxide shells on catalytically active metal particles, which can be realized by employing ALD.

3. DRM Catalysts Consisting of Nanoparticles Implemented in a Mesoporous Template Prepared by ALD

When ALD is used for depositing materials into a pre-formed mesoporous template, one can often observe the formation of nanoparticles confined in the mesopores instead of formation of homogeneous layers on the internal walls of mesoporous substrates. Nanoparticles are formed not only at the outermost surfaces of mesoporous particles with a diameter around several micrometers, but also in the deeper areas of mesoporous particles far from the particle surface. This can be achieved due to the high trench-fill capability of ALD. As shown in Figure 6, Pt was deposited on carbon aerogel substrate-formed nanoparticles with a mean diameter of 1–2 nm and these structures were shown to be extremely active for CO oxidation [100].



Figure 6. TEM image of Pt nanoparticles deposited in carbon aerogel by employing ALD. Reprinted with permission from Reference [100]. Copyright (2008) ACS Publications.

In the case of a metal-organic-framework (MOF), a NiO layer deposited into MIL-101(Cr) by employing ALD resulted in an almost unchanged pattern of pore size distribution compared to that before NiO deposition, where only the total pore volume decreased upon ALD of NiO (Figure 7) [101]. This result implies that some pores of MOF were clogged by NiO nanoparticles, whereas other pores were barely decorated by NiO. The result in Figure 7 also confirms NiO decoration of not only the outermost surface of the MOF particles with a mean size of several hundred nanometers but also a substantially large portion of their internal pores.



Figure 7. Pore-size distribution of MIL-101 with an increasing number of ALD cycles of NiO deposition. Reprinted with permission from Reference [101]. Copyright (2016) Elsevier.

For layer-by-layer deposition of thin films on the internal wall of mesoporous substrates, smaller micropores with a dimension of less than 1 nm can be easily clogged in the early stages of ALD with only several deposition cycles, which would further inhibit incorporation of materials into the deeper parts of mesoporous particles by additional ALD. It is possible to load a substantially large amount of additional materials into a mesoporous substrate since some pores are occupied by additional ALD.

materials, whereas others remain vacant. These vacant pores serve as diffusion channels of precursor vapor into the deeper parts of mesoporous particles. It seems that, at the very initial stage of ALD, some deposited materials form small seeds and a subsequent increase in the number of ALD cycles results in nucleation at the seeds, whereas other vacant places remain unoccupied. In an ideal situation with a relatively strong chemical interaction between the substrate and thin films, a layer-by-layer growth mode should be valid and one can observe atomically homogeneous and conformal thin film formation on the substrate surface [55,60,62,102]. In this case, one cannot easily understand the formation of nanoparticles inside mesoporous materials. However, it is well-known that the growth of thin films can change depending on the substrate-film interaction. With a moderate interaction between the film layer and substrate, the Stranski-Krastanov mode with monolayer formation followed by three-dimensional island formation can be found. With an even weaker film-substrate interaction, three-dimensional growth of a film from the earliest stage of deposition is found and is referred to as the Volmer-Weber growth mode (Figure 8b) [103]. It is often assumed that the ALD process results in layer-by-layer growth of thin films. However, detailed studies of thin film growth on the nanometer scale show diverse growth modes of thin films by employing ALD [88,104].



Figure 8. Schematic illustration of thin film growth based on (**a**) Frank-van der Merwe and (**b**) Volmer-weber modes.

NiO nanoparticles were prepared inside commercially available mesoporous silica using 50 ALD cycles and the resulting structure was used as a catalyst for DRM [57,58]. Mesoporous silica with a mean pore size of ~12 nm and a pore size distribution from 2–20 nm was purchased from Sigma Aldrich and used as the mesoporous supporting materials. NiO nanoparticles were randomly distributed in a ~10 μ m slab from the outermost surface part of the silica beads, demonstrating that ALD shows

excellent trench fill capability. The amount of Ni loading was 2.9 wt.%, which was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) [105].

The DRM reaction was conducted with NiO nanoparticles embedded into mesoporous silica at 800 °C using a horizontal fixed-bed quartz reactor [57]. For this, 0.1 g of Ni/SiO₂ catalyst was loaded on a ceramic holder and the holder was placed in the center of the quartz reactor. The gas mixture of CH₄ and CO₂ with a 1:1 mixing ratio was continuously fed into the reactor and the total flow rate was 20 mL/min [57]. For comparison, the DRM reaction was also carried out with non-supported Ni particles (<1 μ m) under the same experimental conditions.

As shown in Figure 9a,b, the ALD-prepared Ni/silica exhibited higher catalytic activity and stability in terms of reactant (CH₄ and CO₂) conversion and CO evolution ratio compared to non-supported catalysts (Ni particles). These results were attributed to the confined Ni particle size to less than 10 nm in the mesoporous substrate during the DRM reaction at 800 °C (Figure 9c). Even when the reaction time was extended to 168 h (7 days) at 800 °C, the catalytic activity of the ALD-prepared Ni/silica catalysts remained at almost the same level, showing excellent catalytic stability (Figure 9d).



Figure 9. (a) CH₄ and CO₂ conversions of Ni/Silica catalyst at 800 °C for 72 h. (b) CH₄ and CO₂ conversions of Ni catalyst at 800 °C for 72 h. (c) TEM image of Ni/silica obtained after 72 h of the DRM reaction. (d) CH₄ and CO₂ conversions of the Ni/silica catalyst at 800 °C for 168 h (7 days). Edited from Reference [57].

It is interesting to note that coke formation was suppressed in the Ni nanoparticles confined in the mesopores, most likely due to the small nanoparticles with high curvature not showing high efficiency for two-dimensional graphitic carbon formation on Ni nanoparticles. This size-confinement effect on the catalytic activity and stability of Ni nanoparticles has been also reported elsewhere [27]. Recently, many scientific investigations were carried out to realize the effective incorporation of Ni nanoparticles inside porous substrates.

Ni nanoparticles can also be embedded into the pores of porous substrates utilizing conventional wet methods such as impregnation or co-precipitation. Recently, some research groups managed to improve the efficiency of selective dispersion of Ni nanoparticles at the interior of the mesoporous structure by modifying classical impregnation methods [106,107]. However, it has been shown that the formation of Ni particles outside of pores is not avoidable during the wet chemical process [106,107]. It is important to mention that the catalytic activity and stability can be influenced by experimental conditions (amount of catalyst used, reactor design, temperature, gas mixing ratio, and total gas flow). Therefore, direct comparison of the catalytic performances of catalysts (e.g., Ni nanoparticles prepared by ALD vs. Ni nanoparticles prepared via a wet chemical method) reported in various literature is only meaningful if the experimental conditions are comparable. Recently, Gould et al. prepared dispersed Ni nanoparticles on porous alumina supports using either ALD or an incipient wetness (IW) process and their catalytic performances towards the DRM reaction at 600 °C were compared [32]. The ALD-prepared catalyst showed a higher rate of CH₄ reforming and stability over IW-prepared catalysts under the same experimental conditions, which was attributed to better dispersion and the smaller size of ALD-prepared Ni nanoparticles than those prepared by the IW process [32]. Shang et al. also reported similar results showing higher catalytic activity and stability of ALD-prepared Ni nanoparticles on porous alumina than IW-prepared Ni nanoparticles on porous alumina in the temperature range of 700 to 850 $^{\circ}$ C [108]. It was also suggested that the interaction between ALD-prepared Ni nanoparticles and supports was stronger than in IW-prepared Ni nanoparticles cases considering that smaller Ni nanoparticles were formed by ALD compared to the IW method.

Figure 10 shows the CH₄ and CO₂ conversion of Ni nanoparticles supported by mesoporous TiO₂ and alumina (Sasol, mean pore size of 11.6 nm) during the DRM reaction at 800 °C. Ni/TiO₂ and Ni/alumina catalysts were prepared by applying 50 ALD cycles for NiO deposition on mesoporous TiO₂ and alumina, respectively. The mesoporous TiO₂ substrate was prepared by depositing TiO₂ thin films on mesoporous silica (Sigma Aldrich, mean pore diameter of ~12 nm) using the ALD technique, whereas mesoporous alumina with a mean pore diameter of ~11.6 nm was used as purchased (Sasol). The DRM reactions were conducted at 800 °C in a fixed-bed quartz reactor with 0.1 g of Ni/TiO₂ and Ni/alumina catalysts. The CH₄ and CO₂ gas mixture at a 1:1 ratio was fed into the reactor and the total flow rate was 20 mL/min. Ni particles supported by mesoporous silica, TiO₂, and alumina showed very similar activities and stabilities for the DRM catalytic reaction. This indicates that for Ni nanoparticle catalysts (~10 nm) supported by a stable mesoporous substrate, the chemical composition of the substrate is less important for the catalytic behavior of Ni nanoparticles than the size of Ni nanoparticles confined by a porous structure of supporting materials [58].



Figure 10. (a) CH₄ and CO₂ conversion of Ni/TiO₂ catalysts at 800 °C for 72 h. (b) CH₄ and CO₂ conversion of Ni/alumina at 800 °C for 550 h. The DRM reactions were carried out at 800 °C under atmospheric conditions with a constant flow of the gas mixture (CH₄:CO₂ = 1:1, total flow rate of 20 mL/min). Edited from Reference [57].

4. Summary and Outlook

ALD can be utilized to deposit thin films with diverse chemical compositions. The important specifications of ALD, which are not available in other thin film deposition methods such as physical vapor deposition, CVD, and wet-chemical coating methods, include its highly efficient trench-fill capability and fine control of film thickness on the atomic scale. These characteristics are beneficial for preparing various heterogeneous catalyst structures, particularly those active for the DRM reaction at 800 °C. As an example, MgO- or TiO₂-wrapped Ni sub-micrometer-sized particles with an oxide shell thickness of ~20 nm were shown to be catalytically more active and stable for the DRM reaction compared to bare Ni particles or those wrapped with thinner oxide films. It was shown that these oxide shells suppressed coke formation on Ni surfaces, whereas cracks existing within these oxide shells are important for facile diffusion of reactant molecules (CH₄ and CO₂) onto the Ni surfaces. Also, ALD was used to deposit Ni nanoparticles into the deep parts of mesoporous particles and the Ni nanoparticles incorporated into a mesoporous substrate were highly resistant towards sintering and coke formation. As a result, they are more catalytically active and stable for the DRM reaction. These unique catalyst structures, either oxide shell-wrapped metal particles or metal nanoparticles incorporated into mesoporous oxide substrates, prepared by ALD can help explain catalytic behaviors of variously structured heterogeneous catalysts.

In terms of practical application of heterogeneous catalysts, ALD is regarded to be less effective for mass-scale production of catalysts, even if its use can produce various interesting catalyst structures which are otherwise difficult to achieve. In order to overcome the disadvantages of ALD for mass production, methods such as temperature-regulated chemical vapor deposition have been developed and considered for preparing heterogeneous catalysts, whose structures are comparable to those prepared by ALD [109–113]. ALD is probably not a method which can be ultimately used in the mass production of heterogeneous catalysts, yet studies of ALD-prepared catalysts can shed light on the structure-function relationship in heterogeneous catalysts owing to the ability of ALD to finely tune the structure of catalysts.

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