catalysts

MDPI

Review

Recent Scientific Progress on Developing Supported Ni Catalysts for Dry (CO_2) Reforming of Methane

Hyun Ook Seo

Department of Chemistry and Energy Engineering, Sangmyung University, Seoul 03016, Korea; hyun.ook.seo@smu.ac.kr; Tel.: +82-2-2287-6105; Fax: +82-2-2287-0070

Received: 20 February 2018; Accepted: 9 March 2018; Published: 11 March 2018

Abstract: Two major green house gases (CO_2 and CH_4) can be converted into useful synthetic gas (H_2 and CO) during dry reforming of methane (DRM) reaction, and a lot of scientific efforts has been made to develop efficient catalysts for dry reforming of methane (DRM). Noble metal-based catalysts can effectively assist DRM reaction, however they are not economically viable. Alternatively, non-noble based catalysts have been studied so far, and supported Ni catalysts have been considered as a promising candidate for DRM catalyst. Main drawback of Ni catalysts is its catalytic instability under operating conditions of DRM (>700 °C). Recently, it has been demonstrated that the appropriate choice of metal-oxide supports can address this issue since the chemical and physical of metal-oxide supports can prevent coke formation and stabilize the small Ni nanoparticles under harsh conditions of DRM operation. This mini-review covers the recent scientific findings on the development of supported Ni catalysts for DRM reaction, including the synthetic methods of supported Ni nanoparticles with high sintering resistance.

Keywords: dry reforming of methane; Ni; metal-oxide supports; surface basicity; confinement effect

1. Introduction

Human have largely relied on fossil fuels as an energy source for the last centuries and a large amount of CO_2 gas has been emitted into atmosphere by burning fossil fuels. This extensive amount CO_2 accumulated for centuries is considered to be the main reason for the global climate change, such as artic-sea ice melting and increase of sea-level [1,2]. Therefore, for last decades, a lot of attention has been paid for measures to reduce the amount of CO_2 gas from the atmosphere and extensive scientific researches have been done on CO_2 capturing, sequestration, and conversion of CO_2 into other valuable chemical resources [3–7].

CO_2 can be considered as a possible carbon source in chemical industry and CO_2 reforming of methane (CH_4), which is often referred as dry reforming of methane (DRM), has been attracted much attention [8–13]. In the DRM reaction, two major greenhouse gases (CH_4 and CO_2) are converted into H_2 and CO. The generated H_2 and CO are important syngas that can be used as reagents of other synthetic chemical reaction. In addition, DRM reaction can provide the syngas (H_2 + CO) with a desirable ratio (H_2/CO ratio < ~1) for the subsequent Fischer-Tropsh (FT) synthesis of liquid hydrocarbons and the synthesis of oxygenated chemical compounds [14,15].

DRM reaction can be assisted by heterogeneous metal catalysts and a variety of metal-based catalysts have been studied so far. The noble metals, such as Rh, Pt, Ir, Pd, and Ru, exhibit higher catalytic activity and stability for DRM reactions when compared to other transition metal-based catalysts (Co and Ni) [15,16]. It has been also proved that an addition of small amount of noble metals into transition metal-based catalysts resulted in enhanced catalytic performances [9,16–22]. However, to realize the industrial implementation of CRM reaction, the utilization of noble metals should be avoided due to their high cost and limited availability.

Among the non-noble metal-based catalysts, Ni-based catalysts are most practical choice in favor of their high catalytic activity, low cost and large abundance [10,23–25]. However, Ni-based catalysts have a critical drawback as DRM catalysts. Although initial catalytic activity of Ni-based catalyst is comparable to noble-based catalysts, its initial activity is easily deactivated during CRM reaction due to coke formation on active Ni surface and aggregation of catalytic Ni particles [23,24].

DRM is a highly endothermic reaction, and thus, it requires a lot of energy input as heat to move the reaction in forward direction. That is to say, inevitably DRM reaction should be performed at very high temperature (<700 °C), and at this high temperature catalytic Ni nanoparticles are easily aggregated together losing their initial activity and high resistance to coke formation.

There have been a lot of efforts devoted to improving the catalytic activity and stability of Ni-based DRM catalyst in the last decades. The formation of bimetallic states with noble-metals and other transition metal has been extensively studied [18–20,25], and it has also been demonstrated that catalytic performances of Ni catalysts are strongly related to the basicity of metal-oxide supports [26–34]. In addition, many scientific results indicate that coke formation on Ni catalysts is less favored when their size are in a nano meter scale [35–38]. Very recently, many efforts have been made towards the fabrication of small Ni nano particles with high thermal stability, which can retain their initial high reactivity and coke-resistance during long-term operation of DRM reaction.

The main scope of this mini-review is to discuss recent progress in developing supported Ni catalysts for DRM. The overview of DRM reaction is provided in the first part of this review (Section 2), which includes the thermodynamics nature of DRM, possible side reactions, and impacts of operating conditions on the performance DRM reactions. Then, recent scientific findings on supported Ni catalyst for DRM are covered in the second part (Section 3). A variety factors including parameters of DRM operation have been proved to have influence on catalytic performance of Ni-based catalysts. Catalytic activity and stability of Ni catalyst can be altered by chemical nature of supports, e.g., acidity, basicity, oxygen storing ability, and reducibility [23]. Recently, small Ni nanoparticles (<~10 nm) have been extensively studied as DRM catalyst and it has been suggested that chemical and geometrical structures of underlying supports play an important role in dispersion and thermal stability of Ni nanoparticles. In this mini-review, the influence of chemical and physical nature of metal-oxide supports on the catalytic performance of supported Ni catalysts will be mainly discussed. In addition, recent scientific findings showing the merit of utilization of Ni nanoparticles will be summarized together with the recently proposed synthetic methods of stable Ni nanoparticles.

2. Overview of DRM

DRM can be expressed as follow,

$$CH_4 + CO_2 \leftrightarrow 2\,CO + 2\,H_2 \left(\Delta H^{O}_{298K} = +247\ \text{kJ mol}^{-1}\right) \quad (1)$$

Since DRM is a highly endothermic reversible reaction, it requires a large amount of heat energy to drive the reaction in the forward direction to achieve high conversion ratio of two green house gases (CH_4 and CO_2) into syngas (CO and H_2). Figure 1 shows the influence of operating temperature on equilibrium conversion of DRM reaction [39].

Besides the main reaction (Equation (1)), there are a number of other reactions that can occur during the DRM process. Those possible reactions were well documented previously by Wang et al. [40] and Nikoo et al. [39] and recently revisited in the review paper by Aramouni et al. [41]. Among the possible side reactions, following 4 reactions (Equations (2)–(6) have been noticed as important ones by most of researchers, which are responsible for the carbon formation on catalysts surface during DRM reaction [39].

$$CH_4 \leftrightarrow C + 2\,H_2 \left(\Delta H^{O}_{298K} = +74.9\ \text{kJ mol}^{-1}\right), \text{ methane decomposition} \quad (2)$$

$$2CO \leftrightarrow C + CO_2 \left(\Delta H^{O}_{298K} = -172.4 \text{ kJ mol}^{-1}\right), \text{ Boudouard reaction} \quad (3)$$

$$CO_2 + 2H_2 \leftrightarrow C + 2\,H_2O \left(\Delta H^{O}_{298K} = -90 \text{ kJ mol}^{-1}\right) \quad (4)$$

$$H_2 + CO \leftrightarrow C + H_2O \left(\Delta H^{O}_{298K} = -131.3 \text{ kJ mol}^{-1}\right) \quad (5)$$

Among above four reactions, only the methane decomposition (Equation (2)) is an endothermic reaction that favored at high temperatures, whereas other reactions are exothermic disfavored at high temperature. Carbon formation is an undesired process during DRM process, which may lead to catalytic deactivation either by deactivating catalytic active sites or blocking the reactor [42]. The rapid carbon formation is a major cause of easy deactivation of Ni catalysts during DRM reaction. Thus, considering the thermodynamic natures of main and aforementioned side reactions of DRM, it is intuitive that operating DRM over Ni-based catalysts at high temperature is not only beneficial for obtaining higher syngas yield, but also minimizing carbon formation during DRM reaction. The temperature range of 870 to 1040 °C was suggested as an optimal temperature range where the deactivation of catalyst by carbon (coke) formation can be minimized [40]. The thermodynamic equilibrium analysis conducted by Nikoo et.al also showed that the carbon formation on catalyst surface can be suppressed at high temperature (>700 °C) (Figure 2) [39].

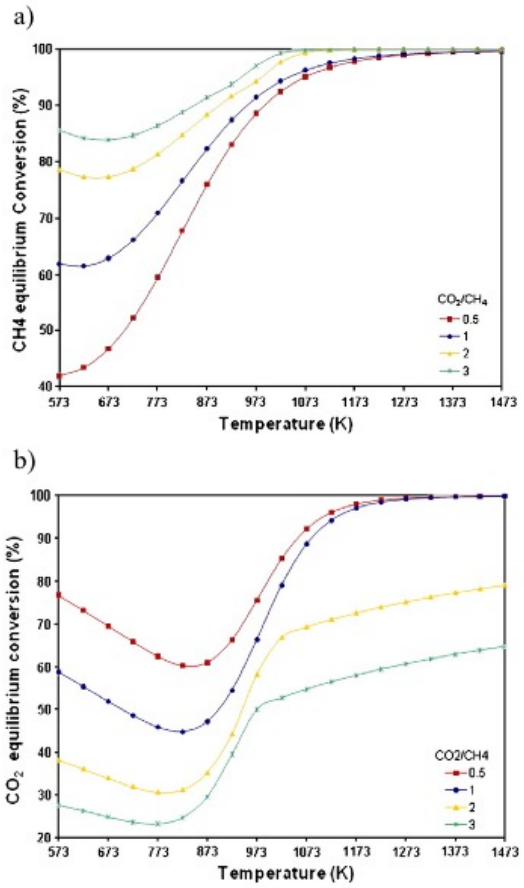

Figure 1. Equilibrium conversion of (**a**) CH_4 and (**b**) CO_2 as a function of temperature and CO_2/CH_4 ratio at atmospheric pressure for n(CH_4 + CO_2) = 2 mol. Reprinted with permission from Ref. [39]. Copyright (2011) Elsevier.

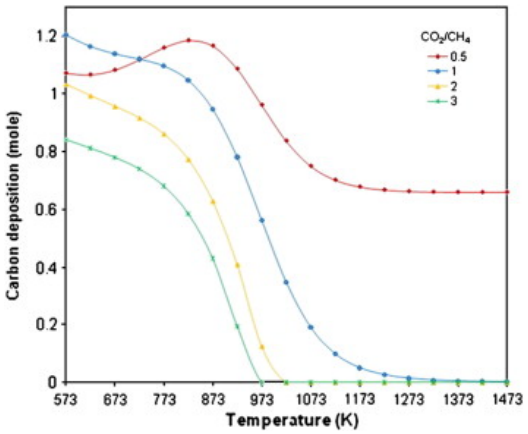

Figure 2. The amount of produced carbon species (mol) during dry reforming of methane (DRM) reaction as a function of temperature and CO_2/CH_4 ratio at atmospheric pressure for $n(CH_4 + CO_2) = 2$ mol. Reprinted with permission from Ref. [39]. Copyright (2011) Elsevier.

Many of recent studies on the catalytic DRM reaction have been performed at high temperature (>700 °C) and methane decomposition (Equation (2)) is a main pathway of carbon formation at such a high temperature whereas other reactions (Equations (3)–(5)) are less likely to proceed at the high temperature [24].

The dissociation of methane (Equation (2)) over Ni surface is sensitive to structure of Ni surface [43], and it leaves carbon atoms (Cα and Cβ) on Ni surface. Cα species are reactive that can be easily gasified by interacting with H_2O, CO_2, O, or H_2, whereas Cβ atoms are not reactive [44]. The less reactive Cβ atoms can dissolve in Ni surface generating Ni_3C species which may resulted in the growth of whisker carbon or nucleate forming coke layers on Ni surface. For the formation of coke layers, a large ensemble of Ni surface covered with carbon atoms is needed since carbon layers over more than ~80 atoms are thermodynamically stable [45–48].

The small Ni nanoparticles do not offer these large ensembles, therefore the deactivation of catalytic active Ni surface due to the coke formation can be suppressed by using small Ni nanoparticles as DRM catalysts. However, these small Ni nanoparticles are easily aggregated to each other forming larger particles at harsh operating conditions of DRM (>700 °C), which results in an increased carbon formation and catalyst deactivation [49].

There is another important side reaction which can be expressed as follows,

$$CO_2 + H_2 \leftrightarrow CO + H_2O \left(\Delta H^{O}_{298K} = +41 \text{ kJ mol}^{-1}\right), \text{ reverse water gas shift} \quad (6)$$

This process is often referred as reverse water gas shift (RWGS) and it lowers the syngas ratio of H_2/CO produced by the main reaction of DRM less than 1. Generally, the main reaction of DRM takes place with RWGS. However, RWGS is less endothermic than the main reaction of DRM, therefore its influence on syngas ratio is less significant with an increasing operating temperature of DRM. It has been reported that the produced syngas ratio (H_2/CO) gets higher as temperature of DRM operation increased and approaches to 1 above 800 °C [39,40,50].

In addition to the temperature, operating pressure also has influence on the equilibrium conversion of reagents and products, the produced syngas ratio (H_2/CO), and on the carbon formation. Nikoo and Amin performed thermodynamic analysis on DRM process based on direct minimization of Gibbs free energy method [39]. They reported that the equilibrium conversion of main reagents (CH_4 and CO_2) and products (H_2 and CO) were reduced as the operating pressure increased from the atmospheric pressure in the temperature range of 700~1000 °C [39]. This can be explained by Le Chatelier's principle; please note that the main reaction of DRM (Equation (1)) convert two equivalent

reagents ($CH_4 + CO_2$) into four equivalent products ($2CO + 2H_2$). In addition, the amount of carbon deposition on catalysts surface during DRM became larger at higher pressure.

The CO_2/CH_4 feed ratio also affect to equilibrium conversion of reagents and the syngas yields [50,51]. It has been reported that higher CO_2/CH_4 ratio resulted in higher CH_4 conversion and H_2 production, but lower CO_2 conversion and CO generation at high temperature above 700 °C. Furthermore, the feed ratio influenced not only on the amount of deposited carbon, but also on the production of other side products, including water. 800 °C and ambient pressure with reagent mixture of CH_4, CO_2, O_2 (feed ratio of 1:1:0.1) was suggested as an optimal operating conditions of DRM [39]. There are also other operating parameters that can influence on the performance of catalytic DRM reaction, including a reactor design and gas hourly space velocity (GHSV), thus one should be careful when comparing activity of catalysts reported in various literatures.

3. Ni Catalysts for DRM

A lot of scientific studies have been done on transition metal-based catalysts for DRM reaction and Ni catalysts supported on metal-oxides are most frequently investigated among them. Highly dispersed Ni nanoparticles supported on metal-oxide supports has been considered as a promising candidate as DRM catalyst since it can exhibit high catalytic activity and good long-term stability under the harsh operating conditions of DRM (>700 °C). Utilization of appropriate metal-oxide supports for Ni nanoparticles can not only increase thermal stability and coke-resistance of Ni nanoparticles at high temperature, but it can also promote the catalytic DRM reaction.

3.1. Reaction Mechanism of DRM over Supported Ni Catalysts; Influences of Metal-Oxide Supports

The DRM reaction over supported Ni catalyst mainly proceed via two steps: (1) decomposition of methane; and, (2) CO_2 dissociation. It is generally agreed that dissociation of methane on Ni surface is the rate determining step of DRM reaction. Dissociated CH_3 species are adsorbed on a top of Ni atom, whereas CH_2 species prefer to be adsorbed between two adjacent Ni atoms. The dissociative adsorption of CH_4 on Ni atoms is favored at step sites than that on terrace Ni atoms and this can explain higher catalytic activity of small Ni nanoparticles compared to bigger counterparts, which possess less amount of step Ni atoms per unit mass of Ni. Decomposition of a methane molecule leaves carbon atoms (atomic carbon, or CH_x species) on Ni surface and these carbon atoms need to be oxidized into carbon monooxide that will be desorbed from Ni surface regenerating active Ni surface. The oxidation of the carbon atom on Ni surface is mainly proceeded by interaction with an atomic oxygen either on the surface of Ni or supports. Dissociate adsorption of CO_2 is a major route for the generation of atomic oxygen on Ni surface during DRM and is generally considered as a fast process. When Ni particles are supported on inert metal-oxides, such as SiO_2, the CO_2 dissociation takes place on the surface of Ni particles. On the other hands, on the other active metal-oxide supports (e.g., MgO, La_2O_3, Ga_2O_3), chemisorption, and dissociation of CO_2 can take place on the surface of supports or Ni-supports interfaces [29,52,53]. It has been suggested that higher basicity of metal-oxides supports can facilitate CO_2 dissociation on the supports surface [26,54]. Some metal-oxides, such as CeO_2 and ZrO_2, can provide their lattice oxygen to oxidize carbon atoms on Ni surface into carbon monooxide [55–57]. The oxidation of carbon species from the Ni surface can also proceed via an interaction with hydroxyl groups on the surface, but this process has been suggested only significant at low temperature (<800 °C) [41,44].

3.2. Adjustment of Acidity and Basicity of Catalyst Surface

It has been generally believed that acidic supports (e.g., SiO_2, Al_2O_3) facilitate the dissociation of methane leading to predominant methane cracking reaction over CO_2 dissociation, which produce atomic oxygen and this, in turn, resulted in carbon formation on catalyst surface. In contrast, metal-oxide supports, such as MgO, La_2O_3 with high basicity promote dissociative adsorption of CO_2, which can result in the suppression of carbon formation by producing higher number of oxygen

atoms near the catalytic active metal surface [26–28,30,50]. The DRM reaction proceeds via three major step reactions (CH_4 cracking, CO_2 dissociation, and oxidation of carbon species on Ni surface) over Ni particles supported either by acidic metal-oxide (e.g., SiO_2) or basic metal-oxides (e.g., MgO) are schematically described in Figure 3.

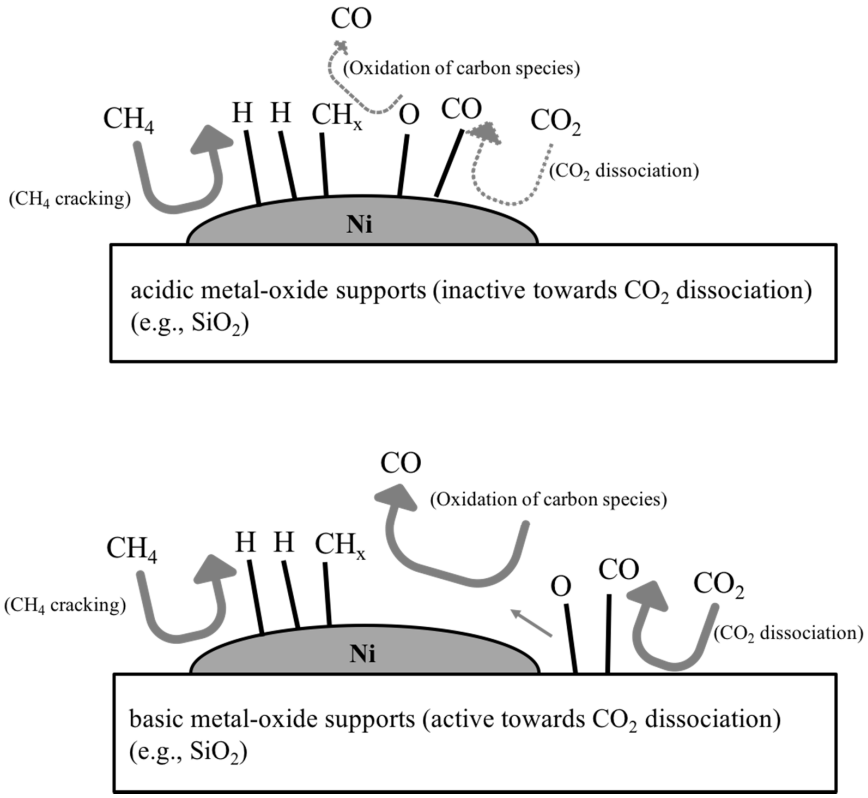

Figure 3. Schematic description of DRM reaction proceeds via three major steps (CH_4 cracking, CO_2 dissociation, and oxidation of carbon species) over Ni particles supported by either acidic (e.g., SiO_2) or basic metal-oxide supports (e.g., MgO).

Influence of basicity of supports on catalytic performances have been studied either by comparing Ni catalyst supported by various metal-oxides or by comparing supported Ni catalysts with different promoters. Zhang et al. prepared a variety of Ni catalysts that are supported by SiO_2, TiO_2, ZrO_2, Al_2O_3, MgO-modified Al_2O_3 (MA) [52]. In the presence of each catalyst inside a tubular fixed-bed continuous quartz reactor, DRM reaction was performed at 750 °C at ambient pressure with a reagent feed ratio of 1:1 (CH_4:CO_2). Ni catalyst supported by MA exhibited the best catalytic performances in terms of catalytic activity, stability, and anti-coking capability among them. They attributed the enhanced catalytic performances of MA-supported Ni catalysts to the promotion of dissociative CO_2 adsorption on basic MgO sites, which led to the suppression of carbon formation. However, one should note that those supports studied by Zhang et al. also exhibited various degree of metal-support interaction which can affect size, dispersion, and reducibility of Ni particles, as authors also discussed in detail [52].

It has been demonstrated that utilization of alkali or alkaline metal oxides, such as Na, K, Mg, and Ca, onto the supported Ni catalyst, as promoters can suppressed the carbon formation by promoting dissociative CO_2 adsorption on the basics sites of catalyst surface [58]. Recently, Pan et al. investigated promotion effects of Ga_2O_3 onto SiO_2 supports on CO_2 adsorption and catalytic DRM performance of supported Ni catalysts [53]. DRM was performed at 700 °C under ambient pressure with a feed ratio of 1:1:2 (CH_4:CO_2:Ar) over Ni/SiO_2 and Ni/SiO_2-Ga_2O_3, and they analyzed the states of adsorbed CO_2 by means of Fourier transformation infrared spectroscopy (FT-IR) [53]. The results showed that

Ga_2O_3 activated adsorbed CO_2 on its surface, whereas CO_2 only physically adsorbed on SiO_2 surface, which resulted in the enhanced resistance of Ni/SiO_2-Ga_2O_3 catalyst towards carbon formation during DRM reaction [53].

However, the promotion of CO_2 dissociation on catalysts surfaces by increasing basicity can also cause the deactivation of catalysts. The Boudouard reaction (Equation (3)) can be facilitated even at high temperature due to increased amount of reagents (CO), generating larger numbers of carbon atoms on catalysts surface. In addition, an excess amount of atomic oxygen can oxidize neighboring Ni atoms into NiO, which are not catalytically active towards DRM reaction. Very recently it has been demonstrated that excessive surface basicity led to catalyst deactivation by carbon formation and formation of metal-oxides [59]. The excessive surface acidity also caused the catalytic deactivation by carbon deposition through the promoted decomposition of methane. Das et al. suggested that the moderate acidity and basicity on catalyst surface is important factor, together with their homogeneous distribution that determines catalytic conversion ratio of DRM reaction and long-term stability of supported metal catalysts (Figure 4) [59].

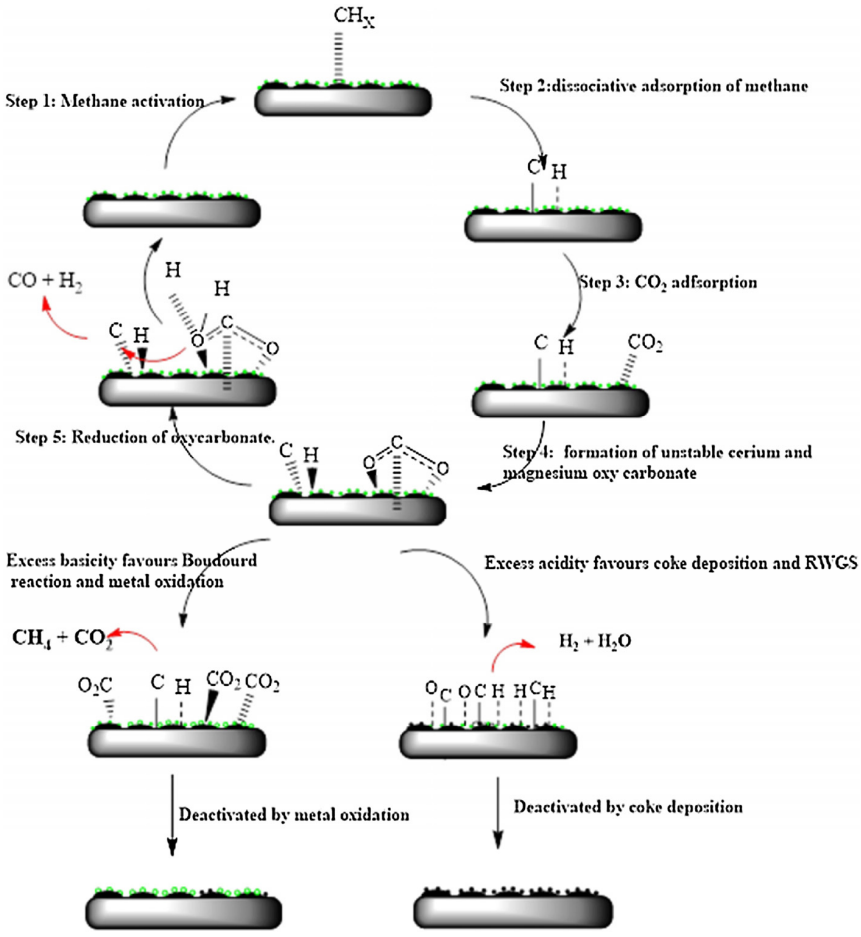

Figure 4. Suggested mechanism of deactivation of Ni catalysts supported by metal-oxides with excessive acidity or basicity. Reprinted with permission from Ref. [59]. Copyright (2017) Elsevier.

La_2O_3 has been also used either as a basic support or a basic promoter for supported Ni catalysts [60]. On the surface of Ni/La_2O_3 catalyst, methane dissociation takes place on Ni nanoparticles, whereas CO_2 dissociation occurs on the surface of La_2O_3 supports. Interaction of La_2O_3 supports with CO_2 can result in the formation of $La_2O_2CO_3$ species that can oxidize carbon deposits on adjacent Ni atoms producing CO and regenerating active species (Ni and La_2O_3), as follows,

$$La_2O_2CO_3 + C - Ni \rightarrow La_2O_3 + 2CO + Ni \quad (7)$$

This positive effects of the formation of $La_2O_2CO_3$ on the removal of carbon deposits has been confirmed by previous transient studies performed using isotopic molecules ($^{13}CH_4$, $^{13}CO_2$, ^{13}CO, and $C^{18}O$) [28]. Recently, it has been demonstrated that addition of Co on Ni/La_2O_3 catalyst facilitated the $La_2O_2CO_3$ formation during DRM reaction, which resulted in enhanced catalytic activity and stability [61].

3.3. Enhancement of Dispersion and Thermal Stability of Ni Nanoparticles

It has been demonstrated that the size of Ni particle plays an important role in its resistance towards carbon formation as well as catalytic activity. Very recently, Aramouni et al. studied the size effect of catalytic metal particles on carbon formation during DRM by performing thermodynamic analysis [62]. They used Gibbs energy minimization method taking into account the Gibbs energy deviation of carbon formation during DRM on metal surface with different particle sizes from the thermodynamics of graphite formation [62]. It was found that the formation of carbon depends on the particle sizes; larger metal particles are more prone to yield higher amount of carbon at moderate operating conditions. High conversion of CH_4 and CO_2 with an optimal ratio of H_2/CO (close to unity) can be achieved at higher temperature of 827–927 °C, however at this condition carbon formation can limit the efficiency of DRM process [62]. This highlighted the importance of developing highly dispersed small Ni nanoparticles (<5 nm) which possessing high resistance of carbon formation. This is in line with numerous experimental results previously performed by many researchers, indicating that the carbon formation on Ni surface during DRM reaction can be minimized by reducing the size of Ni particles [37,38,63,64].

Kim et al. reported the relationship between the carbon formation and size of Ni particles by performing DRM reaction over alumina supported Ni particles that were prepared via a sol-gel method and a subsequent supercritical drying process [63]. The average diameter of Ni particles drastically increased with increasing metal loading over 0.2 in Ni/Al mole ratio, while only the marginal change was found in the surface composition (Figure 5). This large increase of particle size with increasing metal loading attributed to the re-dispersion or aggregation of metal Ni particles during the thermal treatment. It was strongly correlated to the higher amount of filamentous carbon that formed on the surface Ni particles during DRM, as confirmed by TEM analysis performed after the DRM reaction at 773 °C for 30 h [63].

The thermal sintering of small Ni nanoparticles under harsh conditions of DRM operation (>700 °C) is a major problem that prevents the realization of their application as DRM catalysts. Many scientific results pointed that the size of Ni nanoparticles need to be below at least 8 nm to exhibit high resistance towards carbon formation [37,38,63,64]. However, those small Ni nanoparticles are prone to forming larger particles by the aggregation at high temperature (>700 °C).

The choice of metal oxides supports not only alters the catalytic activity of supported Ni particles towards DRM, but also influence on thermal stability of Ni nanoparticles. Strong metal-support interaction can stabilize the small Ni nanoparticles preventing them from thermal sintering, as well as enhance the catalytic activity by altering the electronic structure of Ni. The geometrical structure of metal-oxide supports is another parameter that can affect the catalytic performance of Ni nanoparticles; dispersion of Ni nanoparticles inside porous structure of metal-oxides supports has been demonstrated as a promising way to retain the size of small Ni nanoparticles.

The interaction between Ni and Al_2O_3 supports can lead to the formation of $NiAl_2O_4$ spinel structure, which can provide stable and highly dispersed metallic Ni particles via reduction [65]. The microstructural evolution of Ni-alumina catalyst at elevated temperature under reducing atmosphere has been investigated by in-situ XRD and TEM analysis [65]. Braidy et al. proposed the 3-step process of Ni particles formation from γ-$Ni_xAl_yO_4$; (1) the formation of $NiAl_2O_4$ spinel structure from the Ni-rich zone generated by the diffusion of Ni atoms from γ-$Ni_xAl_yO_4$, (2) the

precipitation of Ni by the further Ni diffusion into those Ni-rich zones, (3) the formation of Ni nanoparticles and γ-$Al_{2.67}O_4$ [65]. Guo et al. reported the higher activity and better stability of Ni particles on MgO-γ-Al_2O_3 when compared to those on γ-Al_2O_3 supports and it was attributed to the enhanced stability of the small Ni crystallites on $MgAl_2O_4$ spinel structure [66]. Very recently, Chamoumi et al. demonstrated a highly active and stable Ni catalysts supported by an upgraded slag oxide (UGSO), which were prepared by an improved solid-state reaction [67]. The mining residue consisting of various metal (Fe, Mg, Al, Ca, Mn, and etc.) oxides was used as a support material. The high catalytic activity and stability of the Ni/UGSO catalyst was attributed to the high dispersion of Ni particles resulted from the formation of the $NiAl_2O_4$ and $NiFe_2O_4$ spinel structure, and the presence of various elements, including basic promoters, such as (MgO, CaO, and MnO) [67].

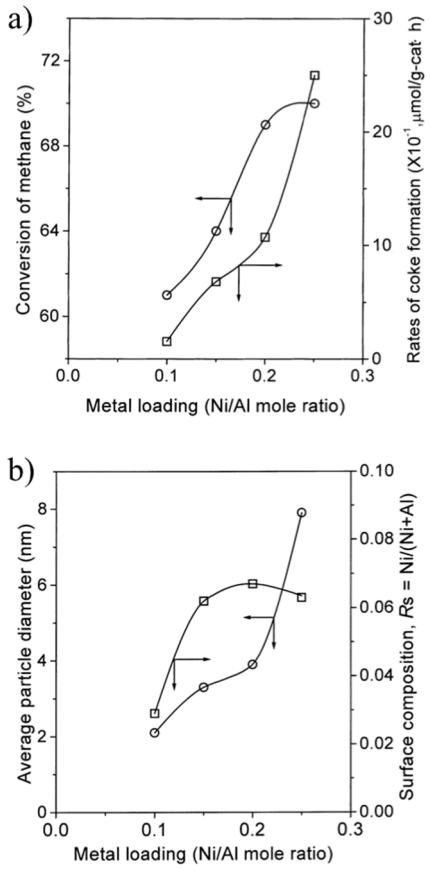

Figure 5. (**a**) Catalytic activity and the rate of coke formation, and (**b**) the particle size and the surface composition of Ni-alumina aerogel catalysts as a function of metal loading. The average particle size and surface composition were determined by TEM and XPS, respectively. The rate of coke formation was estimated from the total carbon contents in the spent catalysts. Reprinted with permission from Ref. [63]. Copyright (2000) Elsevier.

It was also found that poor dispersion of metal particles on La_2O_3 supports due to weak metal-support interaction can be improved by partial substitution of La with other metals such as Ca, Ce, Sr, etc. [60]. Chen et al. suggested that presence of small amount of Cu can also prevent deactivation of Ni particles due to aggregation or loss of Ni crystallites [67]. On the other hands, Dias et al. showed that addition of CaO could reduce the thermal stability of Ni particles that are supported by γ-Al_2O_3. Cu atoms competed with Ni atoms in interaction with Al_2O_3 supports, which reduced the metal-support interaction between Ni and Al_2O_3 supports. It, in turn, decreased the sintering resistance of the Ni particles although it improved the reducibility of Ni particles [68]. The degree of metal-support interactions was often measured by conducting temperature-programmed

reduction (TPR) analysis with a constant flow of reduction gas (e.g., H_2, CO_2). The shift of TPR peak position to higher temperature is an indication of stronger interaction between metal and support, i.e., higher temperature or longer time is needed to activate the Ni particles prior to DRM reaction with increasing metal-supports interactions. It is also worth to mention that metal-oxides exhibiting a strong interaction with metals can cover the surface of metal particles either by the diffusion of oxides over the metal particles or diffusion of metal particles into the supports, resulting in a decrease of the number of active Ni atoms exposed to the reagent gas. These results pointed that there is an appropriate level of metal-support interaction for optimum catalytic performance of supported Ni nanoparticles. It was reported that the strong capability of CeO_2 supports for metal-support interaction can lead to the reduced catalytic activity of metal particles [69,70].

Geometrical structure of metal-oxide supports also have a significant impact on the dispersion and sintering resistance of Ni nanoparticles. La_2O_3 supports derived from peroskite $LaNiO_3$ precursors have been extensively studied recently and it has been proved that Ni dispersion on those supports can be significantly improved. X. Li et al. also reported that La_2O_3 nanorod can not only improve dispersion of Ni nanoparticles but also stabilize Ni nanoparticles (Figure 6) [60]. Recently, it has been demonstrated that Ni particles fabricated by exsolution from parent perovskite structures exhibited better dispersion and thermal stability when compared to the respective ones prepared by a conventional deposition method [71]. It is attributed to the stronger interaction between exsoluted Ni particles and supports to their nano-socket structure [71]. Singh et al. reported that the shape of parent perovskites affected the degree of exsoluted Ni/supports interactions and the defective anisotropic perovskites were suggested as ideal parent perovskite presursors [72]. The Ni particles that were exsoluted from $LaNiO_3$ spheres and rods were highly dispersed on the supports and exhibited high catalytic activity and stability towards DRM reaction [72]. Recently, the fabrication Ni particles alloyed with Re and Fe by exsolution method has been also demonstrated [73]. The exsoluted Ni-alloy particles were firmly 'socketed' into a La_2O_3/LF supports and they exhibited high catalytic activity towards DRM reaction without showing carbon accumulation and particles sintering over 70 h of operation [73].

Recently, mesoporous silica and alumina has been received much attention as supports of Ni nanoparticles since Ni nanoparticles that are embedded in pores of those supports can exhibit good sintering resistance at high temperature [74–79]. Zhang et al. demonstrated that mesoporous structure of SBA-15 can prevent sintering of monometallic Ni particles by confining their size inside the pores [74].

Xu et al. prepared the ordered mesoporous alumina via improved evaporation-induced self-assembly (EISA) strategy and the synthesized mesoporous alumina exhibit large specific surface area, big pore volume, uniform pore size, and excellent thermal stability [80]. Ni particles were embedded inside the pores of the alumina via an incipient wetness impregnation method and their catalytic performances towards DRM reaction was investigated. The catalytic conversion of CH_4 and CO_2 at 700 °C reached the thermodynamic equilibrium conversion values and its high initial activity was retained for 100 h without a notable deactivation [80]. These results highlighted that the merit of utilization of mesoporous framework that can stabilize active Ni nanoparticles by the "confinement effect" and provide more accessible Ni active centers during DRM reaction [80].

Effective incorporation of Ni nanoparticles inside pores of mesoporous silica and alumina supports is a major key for the utilization of the confinement effect to retain the size of Ni nanoparticles. Xie et al. proposed a modified incipient wet process using polyols as new conveyors and removable carbon templates [77]. Polyol (ethylene glycol, EG) coordinated Ni^{2+} species can be effectively delivered into small channels of SBA-15 and polyol acted as carbon template during a subsequent pyrolysis process. As a result, highly dispersed Ni nanoparticles with an average diameter of 3.6 nm was synthesized inside the microchannel of silica SBA-15. The Ni/SBA-15-EG showed superior catalytic activity than Ni/SBA-15-H_2O towards DRM reaction and its activity did not change significantly during long-term operation of DRM at 750 °C. This attributed to high dispersion and thermal stability of Ni nanoparticles of Ni/SBA-15-EG samples, which was confirmed by TEM images of spent Ni/SBA-15-EG [77].

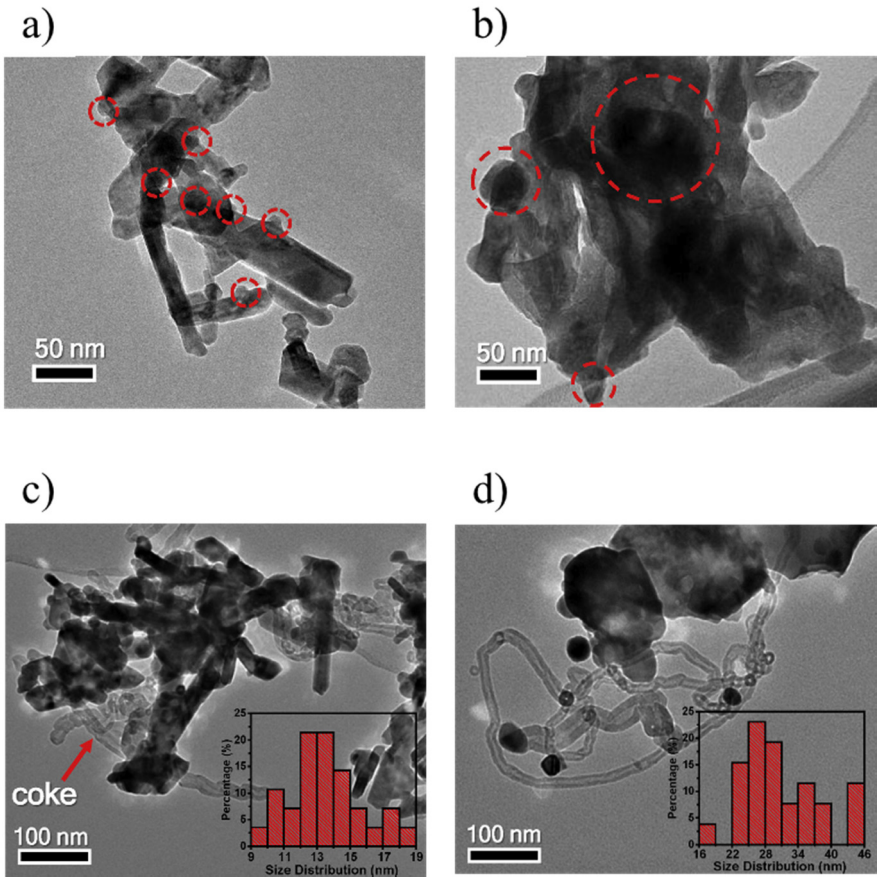

Figure 6. TEM image of (**a**) Ni nanoparticles synthesized on La_2O_3 nanorod (denoted as 5Ni/La_2O_3-LOC in Ref. [60]) and (**b**) on La_2O_3 supports via a wet impregnation method (denoted as 5Ni/La_2O_3-C in Ref. [60]) before DRM reaction. TEM image of (**c**) Ni nanoparticles on La_2O_3 nanorod (denoted as 5Ni/La_2O_3-LOC in Ref. (denoted as 5Ni/La_2O_3-C in Ref. [60]) Insets of (**c**,**d**) present the size distribution of Ni particles on each support. Reprinted with permission from Ref. [60]. Copyright (2017) Elsevier.

Kaydouh et al. demonstrated that the "two solvent" method resulted in much selective dispersion of Ni nanoparticles at interior of the mesoporous structure of SBA-15 silica [81]. Ni/SBA-15 catalysts were prepared via a "two solvent" method where aqueous Ni precursor solution is mixed into silica suspended hydrophobic solvents and they exhibited superior catalytic performances when compared to Ni/SBA-15 prepared by a classical impregnation method [81]. It was explained by better dispersion of Ni nanoparticles of "two solvent"-prepared Ni/SBA-15 than the classically-prepared one, as evidenced by TEM and XRD analysis [81].

Recently, some research groups presented the modified impregnation method using various chelating ligands to immobilize Ni nanoparticles in mesoporous silica. Kang et al. used a polyethyleneimine (PEI) as a chelating ligand of Ni precursors during impregnation processes [82]. Ni-PET complexes were well distributed inside the pores and strongly bound the SBA-15 silica surface through the strong interaction between NH_2 terminal groups of PEI and surface silanol groups of silica. Moreover, steric hindrance of PEI ligands prevented the aggregation of Ni-PEI complexes during the impregnation processes. It resulted in better dispersion of small Ni nanoparticles with narrower size distributions compared to the respective one prepared by classical impregnation method without using chelating ligands (Figure 7) [82]. The prepared catalysts showed stable catalytic activity towards DRM at 750 °C for 40 h and the size of Ni particles inside pores of SBA-15 silica was confined by pore structures of parent supports [82].

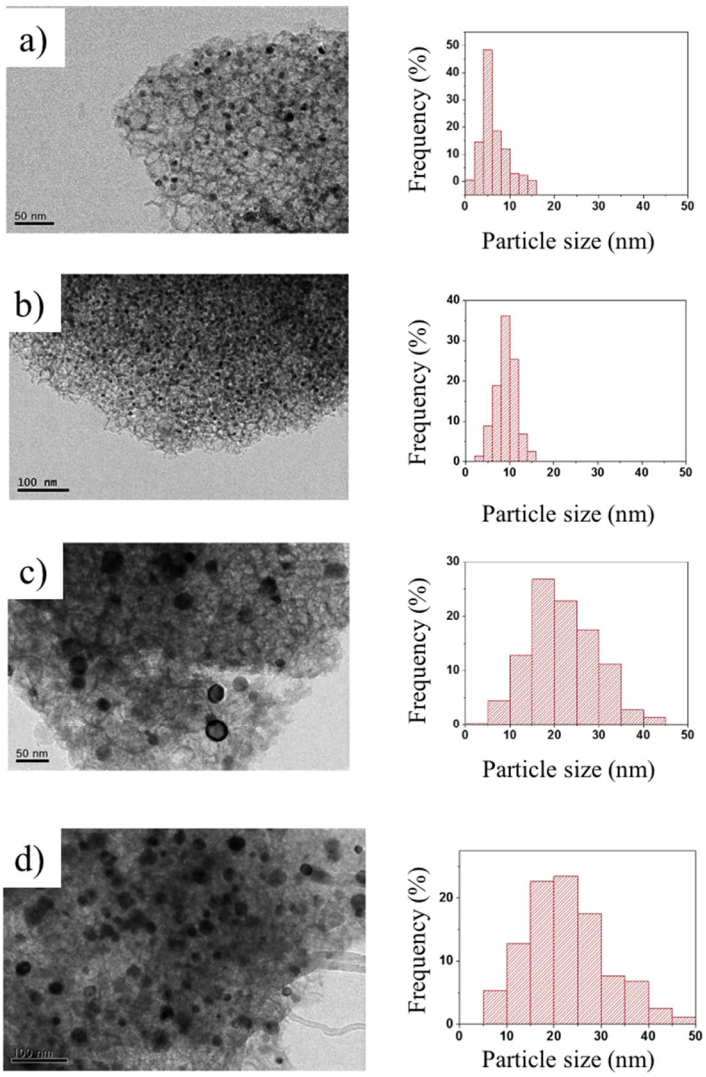

Figure 7. TEM image and size distribution of Ni nanoparticles synthesized on mesoporous silica via PET assisted impregnation method (**a**) before and after (**b**) DRM reaction (denoted as Ni/PST in Ref. [82]). TEM image and size distribution of Ni nanoparticles synthesized on mesoporous silica via classical impregnation method (**c**) before and (**d**) after DRM reaction (denoted as Ni/ST in Ref. [82]). Reprinted with permission from Ref. [82]. Copyright (2017) Elsevier.

Zhang et al. studied the promoting impacts of various chelating ligands during modified impregnation methods on the dispersion of Ni nanoparticles [83]. Three ligands (ethylenediamine, citric acid, and acetic acid) were tested as chelating agents of Ni precursors during impregnation methods. Utilization of each ligand resulted in the formation of smaller Ni nanoparticles with better dispersion compared to non-ligand assisted impregnation methods. The catalysts prepared via ligands assisted method exhibit higher catalytic activity and stability than the respective one that was prepared via a classical impregnation method, which was attributed to better dispersion of Ni nanoparticles inside the pores of SBA-15 silica [83].

Although utilization of ligand during the impregnation method can improve dispersion of Ni nanoparticles inside the pore structure of supports, it has been reported that the formation of some Ni particles outside of pores during wet-chemical processes is still not avoidable, which are subject to aggregation during the DRM reaction [82,83]. Alternatively, small Ni nanoparticles can be embedded inside pores of porous supports using dry-methods. It can be more advantageous for preparation of small metal nanoparticles on porous supports since incorporation of gas phase precursor into the

pore structure is much easier than aqueous precursors. Especially, atomic layer deposition (ALD) has been considered as a suitable technique for the preparation of small metal nanoparticles inside the pore structures of various supports. ALD is a self-limiting and self-terminating deposition technique where two gas phase precursors (metal precursor and oxidizing/reducing precursor) are injected onto the surface of substrates separately in a sequential manner. Gould et al. synthesized highly dispersed small Ni nanoparticles (particle size of ~4 nm) on alumina supports by ALD processes. The ALD-prepared Ni catalysts exhibited higher catalytic activity and carbon-formation resistance when compared to one prepared via incipient wetness (IW) process, which is attributed to smaller size of Ni particles with better dispersion of ALD-prepared sample than IW-prepared one [84]. Shang et al. prepared small Ni nanoparticles (mean diameter: ~3.6 nm) supported either by a porous γ-Al_2O_3 support using ALD process. The prepared catalysts showed high catalytic reactivity and exceptionally high stability towards DRM reaction performed in the range of 700 and 850 °C for 300 h (Figure 8) [85]. They also suggested that stronger bonding force between Ni nanoparticles and alumina supports was established for ALD-prepared sample than IW-prepared based on the larger size and lower catalytic performance of Ni nanoparticles that were prepared by IW method [86].

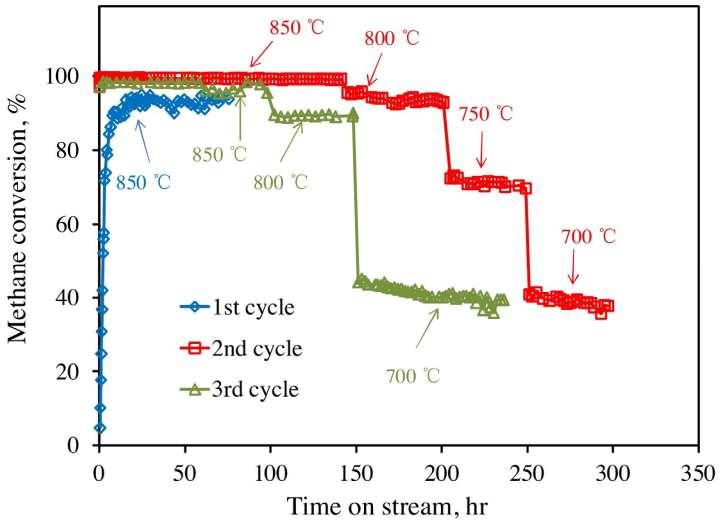

Figure 8. CH_4 conversion of DRM catalyzed by atomic layer deposition (ALD)-prepared Ni nanoparticles on mesoporous alumina at different temperatures (700~850 °C) (denoted as ALD Ni/γ-Al_2O_3 in Ref. [85]). Reprinted with permission from Ref. [85]. Copyright (2017) Elsevier.

4. Conclusions

Catalytic DRM reaction has been attracted much attention since its main reaction converts two major green house gases (CO_2 and CH_4) into useful synthetic gas (H_2 and CO). Due to high endothermic nature of the main reaction, it needs be operated at high temperature (>700 °C) to achieve high equilibrium conversion. The high temperature conditions are also beneficial to reduce the formation of carbon on the surface of active metal catalyst during DRM, which possibly deactivates the catalytic DRM reaction, since most of side reactions relating to carbon formation are exothermic.

Among many non-noble metal catalysts, supported Ni catalysts have been extensively studied due to high initial catalytic activity, which is comparable to other noble-based catalysts, and economic viability. However, easy deactivation of supported Ni catalysts due to coke-formation during the DRM operation remains as a main obstacle of its real application. Coke formation on active Ni surface at high temperature (>700 °C) mainly proceeds via methane cracking on Ni atoms and it has been suggested that this issue can be addressed either by adjusting the acidity-basicity of catalyst surface or reducing the size of Ni particles below ~8 nm.

Metal-oxide supports with higher basicity can alleviate the deactivation of Ni surface due to coke formation by promoting the CO_2 dissociation at basic sites. It can provide oxygen atoms to neighboring Ni sites covered with carbon species, which can facilitate gasification of the carbon species from Ni surface regenerating catalytic active sites. Recent studies on the influence of chemical nature of supports on the catalytic performances of Ni catalyst pointed the importance of even dispersion of moderate acidic and basic sites near the Ni atoms.

It has been generally acknowledged that coke formation on Ni surface can be inhibited when the size of Ni catalyst is below ~8 nm since carbon atoms on more than ~80 atoms are not thermodynamically stable. Many experimental results indicated that small Ni nanoparticles are less prone to deactivated due to coke formation, and recent results of theoretical simulation also pointed the importance of small size of Ni nanoparticles. However, small Ni nanoparticles are prone to easy aggregation at such a high temperature (>700 °C) due to its thermodynamic instability. This low stability issue of small Ni nanoparticles can be addressed by increasing metal-support interaction or by immobilizing Ni nanoparticles inside porous metal-oxide supports, as pointed by recent studies. It has been demonstrated that small Ni nanoparticles can be highly dispersed on porous silica and alumina supports via modified wetness impregnation methods or atomic layer deposition and they exhibited high stability as well as high catalytic conversion of DRM.

Utilization of porous substrates is a promising strategy to develop highly active and stable Ni catalysts for DRM reaction with good economically viability. It is further desirable to investigate the synergic effect of "confinement effects" of porous supports and the optimized chemical nature of supports, e.g., even distribution of moderate acidic and basic sites. ALD process possesses high potential for this purpose since the various metals can be loaded into the nanopores and the amount of metal loading can be finely controlled by ALD. For instance, one may prepare Ni nanoparticles with basic MgO promoter, of which sizes are confined by porous structures via a subsequent ALD deposition of Ni and Mg elements inside the porous substrates. Besides, in order to fully exploit the advantages of Ni nanoparticles that are supported by porous substrates, it is also the desire to find the optimum pore structures (pore size, distribution, pore network) of support to maximize the accessibility of reagents to confined Ni nanoparticles inside the pores.

Acknowledgments: This research was supported by a 2018 Research Grant from Sangmyung University.

Author Contributions: H.O. Seo searched the scientific papers and prepared the manuscript.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Knutson, T.R.; Tuleya, R.E. Impact of CO_2-Induced Warming on Simulated Hurricane Intensity and Precipitation: Sensitivity to the Choice of Climate Model and Convective Parameterization. *J. Clim.* **2004**, *17*, 3477–3495. [CrossRef]
2. Notz, D.; Stroeve, J. Observed Arctic sea-ice loss directly follows anthropogenic CO_2 emission. *Science* **2016**, *354*, 747–750. [CrossRef] [PubMed]
3. Sood, A.; Vyas, S. Carbon Capture and Sequestration—A Review. *IOP Conf. Ser. Earth Environ. Sci.* **2017**, *83*, 012024. [CrossRef]
4. Leung, D.Y.C.; Caramanna, G.; Maroto-Valer, M.M. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sustain. Energy Rev.* **2014**, *39*, 426–443. [CrossRef]
5. Arakawa, H.; Aresta, M.; Armor, J.N.; Barteau, M.A.; Beckman, E.J.; Bell, A.T.; Bercaw, J.E.; Creutz, C.; Dinjus, E.; Dixon, D.A.; et al. Catalysis Research of Relevance to Carbon Management: Progress, Challenges, and Opportunities. *Chem. Rev.* **2001**, *101*, 953–996. [CrossRef] [PubMed]
6. Kondratenko, E.V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G.O.; Perez-Ramirez, J. Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy Environ. Sci.* **2013**, *6*, 3112–3135. [CrossRef]
7. Aresta, M.; Dibenedetto, A. Utilisation of CO_2 as a chemical feedstock: Opportunities and challenges. *Dalton Trans.* **2007**, *28*, 2975–2992. [CrossRef] [PubMed]

8. Bradford, M.C.J.; Vannice, M.A. CO_2 Reforming of CH_4. *Catal. Rev.* **1999**, *41*, 1–42. [CrossRef]
9. Özkara-Aydınoğlu, Ş.; Aksoylu, A.E. CO_2 reforming of methane over Pt–Ni/Al_2O_3 catalysts: Effects of catalyst composition, and water and oxygen addition to the feed. *Int. J. Hydrogen Energy* **2011**, *36*, 2950–2959. [CrossRef]
10. Rostrupnielsen, J.R.; Hansen, J.H.B. CO_2-Reforming of Methane over Transition Metals. *J. Catal.* **1993**, *144*, 38–49. [CrossRef]
11. Kathiraser, Y.; Thitsartarn, W.; Sutthiumporn, K.; Kawi, S. Inverse $NiAl_2O_4$ on $LaAlO_3$–Al_2O_3: Unique Catalytic Structure for Stable CO_2 Reforming of Methane. *J. Phys. Chem. C* **2013**, *117*, 8120–8130. [CrossRef]
12. Ni, J.; Chen, L.; Lin, J.; Schreyer, M.K.; Wang, Z.; Kawi, S. High performance of Mg–La mixed oxides supported Ni catalysts for dry reforming of methane: The effect of crystal structure. *Int. J. Hydrogen Energy* **2013**, *38*, 13631–13642. [CrossRef]
13. Sutthiumporn, K.; Maneerung, T.; Kathiraser, Y.; Kawi, S. CO_2 dry-reforming of methane over $La_{0.8}Sr_{0.2}Ni_{0.8}M_{0.2}O_3$ perovskite (M = Bi, Co, Cr, Cu, Fe): Roles of lattice oxygen on C–H activation and carbon suppression. *Int. J. Hydrogen Energy* **2012**, *37*, 11195–11207. [CrossRef]
14. Centi, G.; Quadrelli, E.A.; Perathoner, S. Catalysis for CO_2 conversion: A key technology for rapid introduction of renewable energy in the value chain of chemical industries. *Energy Environ. Sci.* **2013**, *6*, 1711–1731. [CrossRef]
15. Kim, H.Y.; Park, J.-N.; Henkelman, G.; Kim, J.M. Design of a Highly Nanodispersed Pd–MgO/SiO_2 Composite Catalyst with Multifunctional Activity for CH_4 Reforming. *ChemSusChem* **2012**, *5*, 1474–1481. [CrossRef] [PubMed]
16. Pakhare, D.; Spivey, J. A review of dry (CO_2) reforming of methane over noble metal catalysts. *Chem. Soc. Rev.* **2014**, *43*, 7813–7837. [CrossRef] [PubMed]
17. Li, L.; Zhou, L.; Ould-Chikh, S.; Anjum, D.H.; Kanoun, M.B.; Scaranto, J.; Hedhili, M.N.; Khalid, S.; Laveille, P.V.; D'Souza, L.; et al. Controlled Surface Segregation Leads to Efficient Coke-Resistant Nickel/Platinum Bimetallic Catalysts for the Dry Reforming of Methane. *ChemCatChem* **2015**, *7*, 819–829. [CrossRef]
18. Wu, H.; Pantaleo, G.; La Parola, V.; Venezia, A.M.; Collard, X.; Aprile, C.; Liotta, L.F. Bi- and trimetallic Ni catalysts over Al_2O_3 and Al_2O_3-MO_x (M=Ce or Mg) oxides for methane dry reforming: Au and Pt additive effects. *Appl. Catal. B Environ.* **2014**, *156–157*, 350–361. [CrossRef]
19. Silverwood, I.P.; Hamilton, N.G.; McFarlane, A.R.; Kapitan, J.; Hecht, L.; Norris, E.L.; Mark Ormerod, R.; Frost, C.D.; Parker, S.F.; Lennon, D. Application of inelastic neutron scattering to studies of CO_2 reforming of methane over alumina-supported nickel and gold-doped nickel catalysts. *Phys. Chem. Chem. Phys.* **2012**, *14*, 15214–15225. [CrossRef] [PubMed]
20. Pawelec, B.; Damyanova, S.; Arishtirova, K.; Fierro, J.L.G.; Petrov, L. Structural and surface features of PtNi catalysts for reforming of methane with CO_2. *Appl. Catal. A Gen.* **2007**, *323*, 188–201. [CrossRef]
21. García-Diéguez, M.; Pieta, I.S.; Herrera, M.C.; Larrubia, M.A.; Alemany, L.J. Nanostructured Pt- and Ni-based catalysts for CO_2-reforming of methane. *J. Catal.* **2010**, *270*, 136–145. [CrossRef]
22. Jabbour, K.; El Hassan, N.; Casale, S.; Estephane, J.; El Zakhem, H. Promotional effect of Ru on the activity and stability of Co/SBA-15 catalysts in dry reforming of methane. *Int. J. Hydrogen Energy* **2014**, *39*, 7780–7787. [CrossRef]
23. Kawi, S.; Kathiraser, Y.; Ni, J.; Oemar, U.; Li, Z.; Saw, E.T. Progress in Synthesis of Highly Active and Stable Nickel-Based Catalysts for Carbon Dioxide Reforming of Methane. *ChemSusChem* **2015**, *8*, 3556–3575. [CrossRef] [PubMed]
24. Liu, C.; Ye, J.; Jiang, J.; Pan, Y. Progresses in the Preparation of Coke Resistant Ni-based Catalyst for Steam and CO_2 Reforming of Methane. *ChemCatChem* **2011**, *3*, 529–541. [CrossRef]
25. Bian, Z.; Das, S.; Wai, M.H.; Hongmanorom, P.; Kawi, S. A Review on Bimetallic Nickel-Based Catalysts for CO_2 Reforming of Methane. *ChemPhysChem* **2017**, *18*, 3117–3134. [CrossRef] [PubMed]
26. Alipour, Z.; Rezaei, M.; Meshkani, F. Effect of alkaline earth promoters (MgO, CaO, and BaO) on the activity and coke formation of Ni catalysts supported on nanocrystalline Al_2O_3 in dry reforming of methane. *J. Ind. Eng. Chem.* **2014**, *20*, 2858–2863. [CrossRef]
27. Tsipouriari, V.A.; Verykios, X.E. Kinetic study of the catalytic reforming of methane with carbon dioxide to synthesis gas over Ni/La_2O_3 catalyst. *Catal. Today* **2001**, *64*, 83–90. [CrossRef]

28. Tsipouriari, V.A.; Verykios, X.E. Carbon and Oxygen Reaction Pathways of CO_2 Reforming of Methane over Ni/La_2O_3 and Ni/Al_2O_3 Catalysts Studied by Isotopic Tracing Techniques. *J. Catal.* **1999**, *187*, 85–94. [CrossRef]
29. Verykios, X.E. Catalytic dry reforming of natural gas for the production of chemicals and hydrogen. *Int. J. Hydrogen Energy* **2003**, *28*, 1045–1063. [CrossRef]
30. García, V.; Fernández, J.J.; Ruíz, W.; Mondragón, F.; Moreno, A. Effect of MgO addition on the basicity of Ni/ZrO_2 and on its catalytic activity in carbon dioxide reforming of methane. *Catal. Commun.* **2009**, *11*, 240–246. [CrossRef]
31. Osaki, T.; Mori, T. Role of Potassium in Carbon-Free CO_2 Reforming of Methane on K-Promoted Ni/Al_2O_3 Catalysts. *J. Catal.* **2001**, *204*, 89–97. [CrossRef]
32. Lemonidou, A.A.; Vasalos, I.A. Carbon dioxide reforming of methane over 5 wt % $Ni/CaO\text{-}Al_2O_3$ catalyst. *Appl. Catal. A Gen.* **2002**, *228*, 227–235. [CrossRef]
33. Xu, L.; Song, H.; Chou, L. Carbon dioxide reforming of methane over ordered mesoporous $NiO–MgO–Al_2O_3$ composite oxides. *Appl. Catal. B Environ.* **2011**, *108–109*, 177–190. [CrossRef]
34. Liu, S.; Guan, L.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. CO_2 reforming of CH_4 over stabilized mesoporous $Ni–CaO–ZrO_2$ composites. *Fuel* **2008**, *87*, 2477–2481. [CrossRef]
35. Huo, M.; Li, L.; Zhao, X.; Zhang, Y.; Li, J. Synthesis of Ni-based catalysts supported on nitrogen-incorporated SBA-16 and their catalytic performance in the reforming of methane with carbon dioxide. *J. Fuel Chem. Technol.* **2017**, *45*, 172–181. [CrossRef]
36. Zhang, J.; Li, F. Coke-resistant $Ni@SiO_2$ catalyst for dry reforming of methane. *Appl. Catal. B Environ.* **2015**, *176–177*, 513–521. [CrossRef]
37. Han, J.W.; Park, J.S.; Choi, M.S.; Lee, H. Uncoupling the size and support effects of Ni catalysts for dry reforming of methane. *Appl. Catal. B Environ.* **2017**, *203*, 625–632. [CrossRef]
38. Han, J.W.; Kim, C.; Park, J.S.; Lee, H. Highly Coke-Resistant Ni Nanoparticle Catalysts with Minimal Sintering in Dry Reforming of Methane. *ChemSusChem* **2014**, *7*, 451–456. [CrossRef] [PubMed]
39. Nikoo, M.K.; Amin, N.A.S. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. *Fuel Process. Technol.* **2011**, *92*, 678–691. [CrossRef]
40. Wang, S.; Lu, G.Q.; Millar, G.J. Carbon Dioxide Reforming of Methane To Produce Synthesis Gas over Metal-Supported Catalysts: State of the Art. *Energy Fuels* **1996**, *10*, 896–904. [CrossRef]
41. Aramouni, N.A.K.; Touma, J.G.; Tarboush, B.A.; Zeaiter, J.; Ahmad, M.N. Catalyst design for dry reforming of methane: Analysis review. *Renew. Sustain. Energy Rev.* **2018**, *82*, 2570–2585. [CrossRef]
42. Zhu, X.; Huo, P.; Zhang, Y.; Cheng, D.; Liu, C. Structure and reactivity of plasma treated Ni/Al_2O_3 catalyst for CO_2 reforming of methane. *Appl. Catal. B Environ.* **2008**, *81*, 132–140. [CrossRef]
43. Hu, Y.H.; Ruckenstein, E. Catalytic Conversion of Methane to Synthesis Gas by Partial Oxidation and CO_2 Reforming. *Adv. Catal.* **2004**, *48*, 297–345.
44. Papadopoulou, C.; Matralis, H.; Verykios, X. *Utilization of Biogas as a Renewable Carbon Source: Dry Reforming of Methane BT—Catalysis for Alternative Energy Generation*; Guczi, L., Erdôhelyi, A., Eds.; Springer: New York, NY, USA, 2012; pp. 57–127.
45. Rostrup-Nielsen, J.R.; Sehested, J.; Nørskov, J.K. Hydrogen and synthesis gas by steam- and CO_2 reforming. *Adv. Catal.* **2002**, *47*, 65–139. [CrossRef]
46. Mortensen, P.M.; Dybkjær, I. Industrial scale experience on steam reforming of CO_2-rich gas. *Appl. Catal. A Gen.* **2015**, *495*, 141–151. [CrossRef]
47. Borowiecki, T. Nickel catalysts for steam reforming of hydrocarbons; size of crystallites and resistance to coking. *Appl. Catal.* **1982**, *4*, 223–231. [CrossRef]
48. Seo, H.O.; Sim, J.K.; Kim, K.-D.; Kim, Y.D.; Lim, D.C.; Kim, S.H. Carbon dioxide reforming of methane to synthesis gas over a TiO_2–Ni inverse catalyst. *Appl. Catal. A Gen.* **2013**, *451*, 43–49. [CrossRef]
49. Bengaard, H.S.; Nørskov, J.K.; Sehested, J.; Clausen, B.S.; Nielsen, L.P.; Molenbroek, A.M.; Rostrup-Nielsen, J.R. Steam Reforming and Graphite Formation on Ni Catalysts. *J. Catal.* **2002**, *209*, 365–384. [CrossRef]
50. Hassani Rad, S.J.; Haghighi, M.; Alizadeh Eslami, A.; Rahmani, F.; Rahemi, N. Sol–gel vs. impregnation preparation of MgO and CeO_2 doped Ni/Al_2O_3 nanocatalysts used in dry reforming of methane: Effect of process conditions, synthesis method and support composition. *Int. J. Hydrogen Energy* **2016**, *41*, 5335–5350. [CrossRef]

51. Abdullah, B.; Abd Ghani, N.A.; Vo, D.-V.N. Recent advances in dry reforming of methane over Ni-based catalysts. *J. Clean. Prod.* **2017**, *162*, 170–185. [CrossRef]
52. Zhang, R.; Xia, G.; Li, M.; Wu, Y.; Nie, H.; Li, D. Effect of support on the performance of Ni-based catalyst in methane dry reforming. *J. Fuel Chem. Technol.* **2015**, *43*, 1359–1365. [CrossRef]
53. Pan, Y.; Kuai, P.; Liu, Y.; Ge, Q.; Liu, C. Promotion effects of Ga_2O_3 on CO_2 adsorption and conversion over a SiO_2-supported Ni catalyst. *Energy Environ. Sci.* **2010**, *3*, 1322–1325. [CrossRef]
54. Alipour, Z.; Rezaei, M.; Meshkani, F. Effects of support modifiers on the catalytic performance of Ni/Al_2O_3 catalyst in CO_2 reforming of methane. *Fuel* **2014**, *129*, 197–203. [CrossRef]
55. Su, Y.-J.; Pan, K.-L.; Chang, M.-B. Modifying perovskite-type oxide catalyst $LaNiO_3$ with Ce for carbon dioxide reforming of methane. *Int. J. Hydrogen Energy* **2014**, *39*, 4917–4925. [CrossRef]
56. Huang, T.-J.; Wang, C.-H. Roles of Surface and Bulk Lattice Oxygen in Forming CO_2 and CO During Methane Reaction over Gadolinia-Doped Ceria. *Catal. Lett.* **2007**, *118*, 103–108. [CrossRef]
57. Sun, N.; Wen, X.; Wang, F.; Peng, W.; Zhao, N.; Xiao, F.; Wei, W.; Sun, Y.; Kang, J. Catalytic performance and characterization of Ni–CaO–ZrO_2 catalysts for dry reforming of methane. *Appl. Surf. Sci.* **2011**, *257*, 9169–9176. [CrossRef]
58. Horiuchi, T.; Sakuma, K.; Fukui, T.; Kubo, Y.; Osaki, T.; Mori, T. Suppression of carbon deposition in the CO_2-reforming of CH_4 by adding basic metal oxides to a Ni/Al_2O_3 catalyst. *Appl. Catal. A Gen.* **1996**, *144*, 111–120. [CrossRef]
59. Das, S.; Sengupta, M.; Patel, J.; Bordoloi, A. A study of the synergy between support surface properties and catalyst deactivation for CO_2 reforming over supported Ni nanoparticles. *Appl. Catal. A Gen.* **2017**, *545*, 113–126. [CrossRef]
60. Li, X.; Li, D.; Tian, H.; Zeng, L.; Zhao, Z.-J.; Gong, J. Dry reforming of methane over Ni/La_2O_3 nanorod catalysts with stabilized Ni nanoparticles. *Appl. Catal. B Environ.* **2017**, *202*, 683–694. [CrossRef]
61. Tsoukalou, A.; Imtiaz, Q.; Kim, S.M.; Abdala, P.M.; Yoon, S.; Müller, C.R. Dry-reforming of methane over bimetallic Ni–M/La_2O_3 (M=Co, Fe): The effect of the rate of $La_2O_2CO_3$ formation and phase stability on the catalytic activity and stability. *J. Catal.* **2016**, *343*, 208–214. [CrossRef]
62. Aramouni, N.A.K.; Zeaiter, J.; Kwapinski, W.; Ahmad, M.N. Thermodynamic analysis of methane dry reforming: Effect of the catalyst particle size on carbon formation. *Energy Convers. Manag.* **2017**, *150*, 614–622. [CrossRef]
63. Kim, J.-H.; Suh, D.J.; Park, T.-J.; Kim, K.-L. Effect of metal particle size on coking during CO_2 reforming of CH_4 over Ni–alumina aerogel catalysts. *Appl. Catal. A Gen.* **2000**, *197*, 191–200. [CrossRef]
64. Zhang, Q.; Zhang, T.; Shi, Y.; Zhao, B.; Wang, M.; Liu, Q.; Wang, J.; Long, K.; Duan, Y.; Ning, P. A sintering and carbon-resistant Ni-SBA-15 catalyst prepared by solid-state grinding method for dry reforming of methane. *J. CO2 Util.* **2017**, *17*, 10–19. [CrossRef]
65. Braidy, N.; Bastien, S.; Blanchard, J.; Fauteux-Lefebvre, C.; Achouri, I.E.; Abatzoglou, N. Activation mechanism and microstructural evolution of a YSZ/Ni-alumina catalyst for dry reforming of methane. *Catal. Today* **2017**, *291*, 99–105. [CrossRef]
66. Guo, J.; Lou, H.; Zhao, H.; Chai, D.; Zheng, X. Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels. *Appl. Catal. A Gen.* **2004**, *273*, 75–82. [CrossRef]
67. Chamoumi, M.; Abatzoglou, N.; Blanchard, J.; Iliuta, M.-C.; Larachi, F. Dry reforming of methane with a new catalyst derived from a negative value mining residue spinellized with nickel. *Catal. Today* **2017**, *291*, 86–98. [CrossRef]
68. Chen, H.-W.; Wang, C.-Y.; Yu, C.-H.; Tseng, L.-T.; Liao, P.-H. Carbon dioxide reforming of methane reaction catalyzed by stable nickel copper catalysts. *Catal. Today* **2004**, *97*, 173–180. [CrossRef]
69. Dias, J.A.C.; Assaf, J.M. Influence of calcium content in $Ni/CaO/\gamma$-Al_2O_3 catalysts for CO_2-reforming of methane. *Catal. Today* **2003**, *85*, 59–68. [CrossRef]
70. Wang, S.; Lu, G.Q. Role of CeO_2 in Ni/CeO_2–Al_2O_3 catalysts for carbon dioxide reforming of methane. *Appl. Catal. B Environ.* **1998**, *19*, 267–277. [CrossRef]
71. Ay, H.; Üner, D. Dry reforming of methane over CeO_2 supported Ni, Co and Ni–Co catalysts. *Appl. Catal. B Environ.* **2015**, *179*, 128–138. [CrossRef]
72. Neagu, D.; Oh, T.-S.; Miller, D.N.; Ménard, H.; Bukhari, S.M.; Gamble, S.R.; Gorte, R.J.; Vohs, J.M.; Irvine, T.S. Nano-socketed nickel particles with enhanced coking resistance grown in situ by redox exsolution. *Nat. Commun.* **2015**, *6*, 8120. [CrossRef] [PubMed]

73. Singh, S.; Zubenko, D.; Rosen, B.A. Influence of $LaNiO_3$ shape on its solid-phase crystallization into coke-free reforming catalysts. *ACS Catal.* **2016**, *6*, 4199–4205. [CrossRef]
74. Zubenko, D.; Singh, S.; Rosen, B.A. Exsolution of Re-alloy catalysts with enhanced stability for methane dry reforming. *Appl. Catal. B Environ.* **2017**, *209*, 711–719. [CrossRef]
75. Zhang, M.; Ji, S.; Hu, L.; Yin, F.; Li, C.; Liu, H. Structural Characterization of Highly Stable Ni/SBA-15 Catalyst and Its Catalytic Performance for Methane Reforming with CO_2. *Chin. J. Catal.* **2006**, *27*, 777–781. [CrossRef]
76. Sarkar, B.; Tiwari, R.; Singha, R.K.; Suman, S.; Ghosh, S.; Acharyya, S.S.; Mantri, K.; Konathala, L.N.S.; Pendem, C.; Bal, R. Reforming of methane with CO_2 over Ni nanoparticle supported on mesoporous ZSM-5. *Catal. Today* **2012**, *198*, 209–214. [CrossRef]
77. Moradi, G.; Khezeli, F.; Hemmati, H. Syngas production with dry reforming of methane over Ni/ZSM-5 catalysts. *J. Nat. Gas Sci. Eng.* **2016**, *33*, 657–665. [CrossRef]
78. Xie, T.; Shi, L.; Zhang, J.; Zhang, D. Immobilizing Ni nanoparticles to mesoporous silica with size and location control via a polyol-assisted route for coking- and sintering-resistant dry reforming of methane. *Chem. Commun.* **2014**, *50*, 7250–7253. [CrossRef] [PubMed]
79. Gálvez, M.E.; Albarazi, A.; Da Costa, P. Enhanced catalytic stability through non-conventional synthesis of Ni/SBA-15 for methane dry reforming at low temperatures. *Appl. Catal. A Gen.* **2015**, *504*, 143–150. [CrossRef]
80. Li, S.; Gong, J. Strategies for improving the performance and stability of Ni-based catalysts for reforming reactions. *Chem. Soc. Rev.* **2014**, *43*, 7245–7256. [CrossRef] [PubMed]
81. Xu, L.; Zhao, H.; Song, H.; Chou, L. Ordered mesoporous alumina supported nickel based catalysts for carbon dioxide reforming of methane. *Int. J. Hydrogen Energy* **2012**, *37*, 7497–7511. [CrossRef]
82. Kaydouh, M.N.; El Hassan, N.; Davidson, A.; Casale, S.; El Zakhem, H.; Massiani, P. Highly active and stable Ni/SBA-15 catalysts prepared by a "two solvents" method for dry reforming of methane. *Microporous Mesoporous Mater.* **2016**, *220*, 99–109. [CrossRef]
83. Kang, D.; Lim, H.S.; Lee, J.W. Enhanced catalytic activity of methane dry reforming by the confinement of Ni nanoparticles into mesoporous silica. *Int. J. Hydrogen Energy* **2017**, *42*, 11270–11282. [CrossRef]
84. Zhang, Q.; Long, K.; Wang, J.; Zhang, T.; Song, Z.; Lin, Q. A novel promoting effect of chelating ligand on the dispersion of Ni species over Ni/SBA-15 catalyst for dry reforming of methane. *Int. J. Hydrogen Energy* **2017**, *42*, 14103–14114. [CrossRef]
85. Gould, T.D.; Montemore, M.M.; Lubers, A.M.; Ellis, L.D.; Weimer, A.W.; Falconer, J.L.; Medlin, J.W. Enhanced dry reforming of methane on Ni and Ni-Pt catalysts synthesized by atomic layer deposition. *Appl. Catal. A Gen.* **2015**, *492*, 107–116. [CrossRef]
86. Shang, Z.; Li, S.; Li, L.; Liu, G.; Liang, X. Highly active and stable alumina supported nickel nanoparticle catalysts for dry reforming of methane. *Appl. Catal. B Environ.* **2017**, *201*, 302–309. [CrossRef]



© 2018 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).