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A Facile and Scalable Approach to Ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ Solid Solution Nanoplates and Their Performance for Carbon Dioxide Reforming of Methane

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Abstract: Carbon dioxide reforming of methane (CRM) represents a promising method that can effectively convert CH_4 and CO_2 into valuable energy resources. Herein, ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ nanoplate catalysts were synthesized using a scalable and facile process involving a one-pot, co-precipitation method in the absence of surfactants. This approach resulted in the synthesis of planar $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts that were much thinner (<8 nm) with larger specific surface area (>120 m^2/g) in comparison to $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts prepared by conventional methods. The ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ nanoplate catalysts exhibited high thermal stability, catalytic activity, and durability for CRM. Especially, these novel catalysts exhibited excellent anti-coking behavior with a low carbon deposition of 2.1 wt.% after 36 h of continuous reaction compared with the conventional catalysts, under the reaction conditions of the present study. The improved performance of the thin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ nanoplate catalysts was attributed to the high specific surface area and the interaction between metallic nickel nanocatalysts and the solid solution substrates to stabilize the Ni nanoparticles.

Keywords: $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution; carbon dioxide reforming of methane; high surface area; anti-coking

1. Introduction

The most abundant greenhouse gases of carbon dioxide (CO_2) and methane (CH_4) reputedly cause the climate change on a global scale. At present, controlled release and effective utilization of these reputed greenhouse gases have received considerable attention [1,2]. Carbon dioxide reforming of methane (CRM) is regarded as the most efficient processes, which can simultaneously convert CO_2 and CH_4 into hydrogen (H_2) and carbon monoxide (CO) (known as syngas). As we know, syngas can be widely used for chemical synthesis in many industrial applications as fuel or an intermediate. An optimal ratio of $\sim 1:1$ $\text{H}_2:\text{CO}$ in the CRM reaction is most optimal for downstream synthesis to convert syngas into useful chemicals by subsequent reactions, such as Fisher–Tropsch reactions and oxosynthesis [3–11]. Unfortunately, no mature industrial technology is established for CRM, despite the potentially attractive economic and environmental incentives. That can be attributed to the lack of sustainable catalysts for CRM, most of which are quickly deactivated by the high temperature stream of CO_2 and CH_4 [2,3,12].

Although noble metals (Pt, Rh, Ir, et al.) are highly active and remarkably stable for CRM, utilization of these is limited due to their high cost and rarity [13–17]. By contrast, the transition metal

Ni catalysts, which are less expensive and readily available with comparable activity, have recently attracted much attention [2,3,12]. However, serious carbon deposition and easy Ni agglomeration at the high temperatures induce rapid deactivation of the Ni catalysts, which significantly limits their catalytic lifetime at high temperatures [9,18–20]. To attain desirable catalytic performance, Ni-based catalysts for CRM have to satisfy a minimum of four factors. First is the rigid support, which is required to resist the structural collapse of the catalyst at high temperatures and maintain available surface area to host a large number of small Ni particles [16,21,22]. Moreover, a small size for the metallic nickel catalysts (<6.0 nm) is desired, which can deliver high catalytic activity and inhibit carbon deposition at high temperatures [3,23,24]. The high thermal stability of Ni nanocatalysts is required to produce extended life in a CRM reaction process. Finally, basic supports for the Ni are preferred, because acidic supports favor carbon deposition, which is suppressed by basic supports [3,25].

Among the various Ni-based catalysts, the catalysts of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution are widely investigated and used for converting CH_4 and CO_2 into syngas because their high activity and obvious high temperature anti-carbon deposition performance [3,7,25–29]. When the solid solution is treated with H_2 at high temperature only a part of surface NiO is reduced to small Ni^0 nanoparticles on the surface of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts. Notably, the migration of Ni nanocatalysts on the support at high temperatures can be effectively suppressed due to the strong metal-support interaction for the solid solution between Ni and MgO [3]. Moreover, as a strong basic support, MgO exhibits high thermal stability, which induces strong CO_2 adsorption and reduces or restrains carbon deposition under the catalytic conditions of CRM [30–32].

Various synthetic methods have been employed to prepare the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution catalysts including impregnation, co-precipitation, and sol-gel methods [25,33–38]. Generally, capping agents or surfactants are used to obtain a high surface area $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution [25]. However, the effect of the capping agents on the catalyst surface is still under debate [39]. The residues from surfactants removed by high temperature treatment may poison the active sites. By contrast, in the absence of the capping agents, the surface area of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution is small, in the range of 3–60 m^2/g [33,34,38]. Development of a facile method for synthesis of high surface area $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution catalysts in the absence of surfactants is still a challenge. Herein, in contrast to the conventional co-precipitation, ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution nanoplates with a large surface area (>120 m^2/g) were successfully synthesized on a large scale from a one-pot co-precipitation approach in the absence of surfactants. Then the catalytic performances and structural evolution of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts and deposited coke were also investigated. The ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ nanoplate catalysts exhibited high thermal stability, high catalytic activity, high durability, and good anti-carbon deposition for CRM.

2. Results and Discussion

2.1. Catalyst Characterization

For comparing with conventional catalysts, the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts were also prepared by Chen et al. [29] by co-precipitation method from an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using K_2CO_3 as the precipitant. In Figure 1, the XRD patterns of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts containing various Ni/Mg ratios are displayed. The XRD peaks located at $2\theta = 37.0^\circ$, 42.9° , 62.4° , 74.8° , and 78.6° for all $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts were consistent with previous reports [25,26]. It is clear from Figure 1 that the peaks indicated that the NiO-MgO solid solution was successfully prepared in the synthesis process [25,26]. Meanwhile, the XRD signal of the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts was stronger and narrower, and, comparing with the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ catalysts, indicated that the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts have bigger crystallite size [25]. The microstructures of three synthesized catalysts were further examined using transmission electron microscopy. As shown in Figure 2a, the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ catalysts displayed a thin plate-like morphology with an irregular shape and a broad particle size distribution ranging from tens to hundreds of nanometers. This feature of thin (~8 nm) could be seen in the vertically aligned nanoplates shown in Figure 2a. Increasing the concentration of Ni in the

synthesis process did not lead to significant changes in morphology of the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ (Figure 2b) and $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ (Figure 2c). Figure 2d showed that the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts were also comprised of nanoparticles and platelet shaped. The thickness of $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts, though, was ca. 50 nm, which was obviously thicker than our catalysts.

Figure 1. The XRD patterns of the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$, $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$, and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts.

Figure 2. TEM images of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts, (a) $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, (b) $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$, (c) $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$, and (d) $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$.

The values of surface area for $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ and $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ catalysts were 123.9, 124.5, and 133.9 m^2/g (Table 1), respectively, which was significantly greater than that of the samples synthesized using co-precipitation methods (3 ~ 60 m^2/g) [25,35,37]. For the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts, the values of surface area was only 12.5 m^2/g . Meanwhile, Figure 3a,b show the N_2 adsorption/desorption profiles and pore size distributions of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts, respectively. The N_2 adsorption/desorption isotherms were type III isotherm by the IUPAC (International Union of Pure and Applied Chemistry) classification, typical of mesoporous materials. In Figure 3b, the mesopores and macropores between 2 and 100 nm of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts can be observed from the pore size distributions of the catalysts.

Table 1. Structural properties of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts.

Catalyst	BET ¹ (m^2g^{-1})	V_{pore} (cm^3)	Pore Size (nm)	BET ¹ _{spend} (m^2g^{-1})	Carbon ² (wt.%)
$\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$	117.8	0.35	50.62	94.5	2.0
$\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$	140.3	1.20	121.8	89.5	2.1
$\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$	164.9	1.16	95.10	76.5	31.6
$\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$	12.5	0.11	33.45	10.5	8.1

¹ BET (Brunauer–Emmett–Teller) results were analyzed by the ASAP 2020, Micromeritics Inc. ² The thermogravimetry was used to quantify the coke deposition after 36 h on stream.

Figure 3. (a) N_2 adsorption/desorption isotherms of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts, (b) pore size distributions of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts.

It should be mentioned that the synthesis of the binary $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution catalysts was performed in the absence of surfactants. This can potentially avoid possible contamination induced by the surfactants or organic capping agents with subsequent high temperature annealing. To demonstrate that the synthetic method was scalable, the reaction was amplified 20 times in a 2-L Pyrex bottle. Figure 4 shows the optical graphs of a 2-L reaction and the fabricated $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ plates. As a result, the same properties of $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ plates were obtained and the yield of catalysts was about 99%. These results confirmed that the reported synthetic approach provided a facile and scalable method for the one-pot synthesis of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution catalysts with high surface area.

H_2 -TPR (H_2 temperature-programmed reduction) properties of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution catalysts (Figure 5) were used to evaluate the reducibility of the catalysts, which contained additional information of the interaction between metallic nickel nanocatalysts and the solid solution substrates. The strong metal-support interaction can prevent the sintering of small nickel species into big particles and the coke formation. The $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$, and $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ catalysts showed a broad reduction peak in the range of 625–1000 $^\circ\text{C}$, which was attributed to the reduction of Ni^{2+} species in the crystal lattice and the formation of the metallic Ni^0 nanoparticles [37]. No reduction peaks for the catalysts could be observed at low temperatures, which precludes the existence of a free NiO phase in the catalysts, consistent with the XRD results. The $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ had two reductions, at 520 $^\circ\text{C}$ and 1000 $^\circ\text{C}$. The first reduction peak was related to small Ni particles or to the reduction of Ni species in low interaction with MgO . The second peak was associated to strong interaction with MgO . Compared

to $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con and previous literature reports, the reduction peaks of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts in the range of 625–1000 °C significantly shifted toward high temperatures, demonstrating a very strong interaction between Ni and solid solution in the nanoplate catalysts [34,37]. This result indicated that Ni successfully incorporated into the structure of NiO-MgO solid solutions.

Figure 4. The optical graphs of a 2-L reaction and the as-obtained $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ nanoplates.

Figure 5. H_2 -TPR (H_2 temperature-programmed reduction) profiles of the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$, $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$, and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts.

2.2. Catalytic Performances of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$

The $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$, $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$, and $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ catalysts were employed for the CRM reaction. The methane conversion as a function of temperature on all catalysts is exhibited in Figure 6a. CH_4 conversion was mainly dependent on the temperature of reaction. Specifically, as the reaction temperature increased, the ratio of the conversion of CH_4 increased correspondingly. As shown in Figure 6a, the methane conversion for the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ catalysts was 16.4%, 33.8%, 52.6%, 68.3%, 80.3%, and 88.5%, when the reaction temperatures were 550 °C, 600 °C, 650 °C, 700 °C, 750 °C, and 800 °C, respectively, revealing the highly endothermic nature of the CRM reaction. As shown in Figure 6b, the conversion of carbon dioxide exhibited the similar tendency. The catalytic activity

of the nanoplate catalysts followed the trend of $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O} > \text{Ni}_{0.1}\text{Mg}_{0.9}\text{O} > \text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$. Among these catalysts, the $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ catalysts exhibited the best catalytic activity, which was attributed to the higher surface area, the pore volume, and the pore size of the catalysts. For the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$, the CH_4 and CO_2 conversions are shown in Figure 6a,b, exhibiting similar catalytic activity. Although the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ had a low surface area, the similar catalytic activity with the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ catalysts was shown. It was due to the additional content of Ni on the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts' surface in low temperature ($\leq 800^\circ\text{C}$), which was revealed from the H_2 -TPR properties of the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts.

Figure 6. Catalytic activity of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ solid solution nanoplate catalysts and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts for the CRM (Carbon dioxide reforming of methane). (a)–(c) CH_4 conversion, CO_2 conversion, and H_2/CO ratio as a function of the reaction temperatures. (d)–(f) CH_4 conversion, CO_2 conversion, and H_2/CO ratio for a 36 h continuous CRM reaction at 700°C .

Despite feeding equimolar amounts of CH_4 and CO_2 into the CRM, CO_2 conversion was slightly larger than CH_4 conversion at all temperatures for all catalysts. The reason for this phenomenon was the simultaneous reaction of the reverse water–gas shift reaction (RWGS) ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$, $\Delta H_{298} = +41 \text{ kJ/mol}$), which led to additional amounts of CO_2 and H_2 being consumed to yield CO and H_2O [7,16]. Figure 6c shows the plots of H_2/CO ratios as a function of reaction temperature. The H_2/CO ratios increased with the increase of the reaction temperature for the three catalysts. Theoretically, the ratios of H_2/CO should be around 1.0. However, these ratios were less than 1 when temperature was low, which was attributed to consumption of H_2 through some side reaction, such as methanation and RWGS reactions [16]. The rise of the reaction temperatures led to the increased ratio of H_2/CO by facilitating the carbon gasification, water–gas shift reaction (WGS), and methane decomposition to

produce more H_2 [16]. In the low temperature range ($<700^\circ C$), the H_2/CO ratios of $Ni_{0.03}Mg_{0.97}O$ were lower than those of $Ni_{0.1}Mg_{0.9}O$ and $Ni_{0.2}Mg_{0.8}O$ at each temperature point, indicating that small Ni nanoparticles may favor the RWGS and methanation reactions [16]. Elevating the reaction temperature resulted in a greatly increased H_2/CO ratio on the $Ni_{0.03}Mg_{0.97}O$, reaching 0.96 and 1.06 at $750^\circ C$ and $800^\circ C$, respectively.

2.3. Durability Tests of $Ni_xMg_{1-x}O$ Catalysts

Figure 6d–f shows the conversions of CH_4 and CO_2 and the molar ratios of H_2/CO for the $Ni_xMg_{1-x}O$ nanoplate catalysts and $Ni_{0.1}Mg_{0.9}O$ -con catalysts as a function of reaction time at $700^\circ C$. The three $Ni_xMg_{1-x}O$ solid solution catalysts displayed remarkable stability during the whole process of the continuous reaction for 36 h. As shown in Figure 6d, the CH_4 conversions were slightly decreased from 70.4% to 68.4%, from 72.0% to 71.6%, and from 81.5% to 80.4% for $Ni_{0.03}Mg_{0.97}O$, $Ni_{0.1}Mg_{0.9}O$, and $Ni_{0.2}Mg_{0.8}O$, respectively, indicating the high catalytic stability for the ultrathin nanoplate catalysts. The decrease of $Ni_{0.1}Mg_{0.9}O$ -con in methane conversion from 70.0% to 64.6% (namely, 5.6%) was more serious than that (0.4%) of $Ni_{0.1}Mg_{0.9}O$ nanoplates after 36 h reaction. Similarly, trends in CO_2 conversions for all the catalysts were observed, as given in Figure 6e. The H_2/CO ratios were also recorded during the continuous reactions. As shown in Figure 6f, the H_2/CO ratios of the $Ni_xMg_{1-x}O$ nanoplate catalysts fluctuated in the range of 0.83–0.94, further confirming the stability of their catalysis towards CRM reaction.

Characterization of the $Ni_xMg_{1-x}O$ nanoplate catalysts after the 36 h continuous reactions may explain their remarkable catalytic stability. The surface areas of the spent catalysts (in Table 1) were 94.5, 89.8, and $76.5\text{ m}^2/\text{g}$ for the $Ni_{0.03}Mg_{0.97}O$, $Ni_{0.1}Mg_{0.9}O$, and $Ni_{0.2}Mg_{0.8}O$ nanoplate catalysts after 36 h reactions, which preserved 76.5%, 72.1%, and 57.1% of those of the fresh $Ni_{0.03}Mg_{0.97}O$, $Ni_{0.1}Mg_{0.9}O$, and $Ni_{0.2}Mg_{0.8}O$, respectively. Although the structural collapse of the $Ni_xMg_{1-x}O$ catalysts was reflected in BET (Brunauer–Emmett–Teller) measurements, the values of the available surface areas of the $Ni_{0.03}Mg_{0.97}O$, $Ni_{0.1}Mg_{0.9}O$, and $Ni_{0.2}Mg_{0.8}O$ nanoplate catalysts were still much larger than those of the freshly prepared NiO - MgO catalysts by the co-precipitation method [33–35,38]. Therefore, they can provide enough surface areas and preserve enough active sites in the CRM reaction. The results also indicated the solid solution nanoplates with a low content of Ni and highly dispersed Ni nanocatalysts could deliver a better thermal stability in their microstructures at the high temperatures.

In the CRM reaction, the nickel catalysts deactivated quickly due to the thermal sintering of the metallic nickel catalysts at high temperature [16,18,24]. Herein, the unexpected catalytic stability of the $Ni_xMg_{1-x}O$ catalysts for the CRM reaction can be ascribed to their unique structural features and intrinsic physicochemical properties. First of all, both NiO and MgO have the face-centered cubic structure with the close lattice parameters and bond lengths [3]. Therefore, MgO and NiO can form a solid solution with a very strong interaction. This has been demonstrated by the XRD spectra (Figure 1) and H_2 -TPR profiles (Figure 5), which displayed a single phase of the solid solution. Due to the very strong interaction between active sites and supports, the small Ni nanocatalysts can be effectively immobilized on the surface of the solid solution and largely avoid the nickel sintering during the CRM reaction [3]. The highly stable catalytic activity of the $Ni_xMg_{1-x}O$ catalysts can be maintained even after 36 hours of continuous reactions at $700^\circ C$. To monitor the size change of the Ni^0 active component of the catalysts, the XRD patterns of the spent catalysts after 36 h continuous reactions were also recorded. In Figure 7b, the $Ni_{0.03}Mg_{0.97}O$ and $Ni_{0.1}Mg_{0.9}O$ catalysts revealed that the peaks of the metallic nickel phase were still weak and broad, indicating that a small amount of Ni^0 particles appeared after the continuous 36-hour reaction at the high temperature of $700^\circ C$ [40]. In contrast, the much stronger XRD peaks of the metallic Ni phase for the $Ni_{0.2}Mg_{0.8}O$ and $Ni_{0.1}Mg_{0.9}O$ -con catalysts were observed, indicating a serious aggregation of Ni^0 at the operational temperatures.

In order to quantify the aggregation of the Ni nanocatalysts, the integral area ratios of $Ni(200)$ and $NiMgO(220)$ ($S_{Ni-200}/S_{NiMgO-220}$) in XRD patterns were calculated for both the freshly reduced and the spent catalysts (Figure 7). The metallic nickel aggregation of the $Ni_{0.03}Mg_{0.97}O$ and $Ni_{0.1}Mg_{0.9}O$

catalysts was indeed observed, as evidenced by the apparent XRD peaks of metallic nickel. As shown in Figure 8, the values of $S_{Ni-200}/S_{NiMgO-220}$ for the spent $Ni_{0.03}Mg_{0.97}O$ (0.02) and $Ni_{0.1}Mg_{0.9}O$ (0.028) catalysts were still lower than the freshly reduced $Ni_{0.2}Mg_{0.8}O$ catalysts (0.18). The results indicated that the small size of the metallic nickel and good dispersion of nickel for the spent $Ni_{0.03}Mg_{0.97}O$ and $Ni_{0.1}Mg_{0.9}O$ catalysts was preserved, while the value (0.84) of $S_{Ni-200}/S_{NiMgO-220}$ for the spent $Ni_{0.2}Mg_{0.8}O$ catalysts and the value (0.084) of $S_{Ni-200}/S_{NiMgO-220}$ for the spent $Ni_{0.1}Mg_{0.9}O$ -con catalysts indicated a serious sintering of Ni^0 at the reaction temperature.

Figure 7. (a) The XRD patterns of the $Ni_xMg_{1-x}O$ catalysts reduced at 800 °C by H_2 . (b) XRD patterns of the $Ni_xMg_{1-x}O$ catalysts after the continuous CRM reaction at 700 °C for 36 h.

Figure 8. The calculated integral area ratios of $S_{Ni-200}/S_{NiMgO-220}$ for the freshly reduced and spent $Ni_xMg_{1-x}O$ catalysts.

Moreover, the catalytic stability of the $Ni_xMg_{1-x}O$ catalysts came from MgO, a strong basic support [3,41,42]. MgO as the substrate can avoid the strong acidity of the catalysts and subsequently suppress the carbon deposition (discussed below) and the aggregation of the metallic nickel nanocatalysts. In addition, MgO has a high thermal stability due to its very high melting point (2850 °C). As a result, MgO can keep a relatively large surface area at high temperatures compared to most oxides used as catalyst supports. Besides, the large surface areas of the catalysts provide a large amount of the reactive sites for the catalytic reaction. Although the surface areas of the three spent catalysts were reduced (Table 1), they were still larger than those of the $Ni_xMg_{1-x}O$ catalysts synthesized by the conventional method and $Ni_{0.1}Mg_{0.9}O$ -con. Hence, the thin nanoplate catalysts still preserved enough active sites for the efficient CRM reaction after a long, life-time testing for 36 hours at 700 °C.

2.4. Coking Characteristics of $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ Catalysts

Carbon accumulation is another critical factor corresponding to the degradation of the CRM catalysts, in which the carbon layer deposited on the surface Ni active particles blocks the approach of the reactants towards the catalytic sites [21]. Generally, CH_4 decomposition reaction ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$, $\Delta H_{298} = 75 \text{ kJ/mol}$) and CO disproportionation reaction ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$, $\Delta H_{298} = -172 \text{ kJ/mol}$) are two possible side reactions resulting in the coke formation [43,44]. The latter has been demonstrated to be the dominant mechanism of carbon deposition on Ni-based catalysts for the CRM reaction [21]. The carbon diffusion of carbon nanotubes, filamentous whisker carbon, and shell-like graphite are formed by a metal particle [33,45–47]. The SEM analyses on the spent catalysts after 36 hours of CRM reactions are presented in Figure 9. For the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ catalysts (Figure 9a,b), no obvious tubular and wire-like carbon nanostructures were observed, indicating a low carbon deposition. In contrast, the filamentous carbon was observed for the used $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$ catalysts.

Figure 9. SEM images of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts after the continuous CRM reactions at 700°C for 36 h. SEM images of the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts after the continuous CRM reactions at 700°C for 36 h, (a) $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$; (b) $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$; (c) $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$; (d) $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O-con}$.

After the 36 h of continuous reactions, the temperature-programmed oxidation of the spent $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts was also performed with the TG-DSC (Thermogravimetry-differential scanning calorimetry) techniques to estimate the coke deposition for each catalyst. The weight loss over the higher Ni content of catalysts (in Table 1) was obviously larger than that of catalysts with the lower Ni content in a sequence: $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ (2.0 wt.%) < $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ (2.1 wt.%) < $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ (31.6 wt.%). This suggested that the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ catalysts with a low nickel content could significantly inhibit carbon deposition and largely maintain the higher dispersion of Ni species. The heavy carbon

deposition is generally accompanied by the serious aggregation of catalysts and the decreased surface area, which are consistent with the BET measurements on the freshly reduced and the used catalysts. In Figure 9d, the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts also had the filamentous nature of the deposited coke and 8.1% carbon deposition. The $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts exhibited more carbon deposition than $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ nanoplates. From the H_2 -TPR results, the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con had Ni species in low interaction with MgO and same small Ni particles, which led to the easy sintering of Ni on $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts at high temperature. Moreover, compared with the reduced $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts, the spent $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts showed a shoulder at 44.4° and a broad peak at 51.7° for metallic nickel phase. These results indicated that the metallic Ni^0 particles of the $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts became bigger. Thus, it can be concluded that a strong metal-support interaction for thin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ nanoplates prevented the sintering of small nickel species into big particles and the coke-formation.

To further monitor the coke formation, the XRD spectra were recorded for all catalysts. In Figure 7b, strong diffraction peaks of the spent $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ catalysts at 26° was corresponding to the graphitic carbon, confirming the serious coke deposition of the $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ catalysts for the CRM reactions at 800°C [48]. In contrast, the scarce XRD peaks at 26° were not observed for the used $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ and $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ catalysts, illustrating the excellent resistance to the coke formation of ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ nanoplates with the low Ni content for the CRM reactions.

3. Materials and Methods

3.1. Catalysts' Synthesis

All reagents in this research were analytical grade and used without further purification.

Synthesis of Ultrathin $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ Solid Solution Nanoplates

The aqueous solutions of Ni (NO_3) $_2$ ·6 H_2O (Sigma-Aldrich, America), Mg (NO_3) $_2$ ·6 H_2O (Sigma-Aldrich, America), and NaOH (Sigma-Aldrich, America) were used for preparing the $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ ($x = 0.03, 0.1, 0.2$) catalysts by co-precipitation method. For the synthesis of the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ catalyst, Ni(NO_3) $_2$ ·6 H_2O (0.1163 g) and Mg(NO_3) $_2$ ·6 H_2O (0.9231 g) was dissolved in 10 mL Millipore water (Milli-Q water, 18.2 M Ω ·cm). Meanwhile, NaOH (12.8 g) was dissolved in 70 mL MQ water. These two solutions were thoroughly mixed and aged in the Pyrex bottle under the continuous stirring about 30 min. Then, the mixture was put into an electric oven for 24 h and the temperature was controlled at 100°C . After cooling down naturally, the products were obtained by centrifugation and washed with MQ water and ethanol three times alternatively. Then, the $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$ nanoplate precursors were dried at 60°C overnight. At last, the obtained powders were calcined at 800°C in air for 4 h. The synthesis of $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ and $\text{Ni}_{0.2}\text{Mg}_{0.8}\text{O}$ was similar to that of $\text{Ni}_{0.03}\text{Mg}_{0.97}\text{O}$. The conventional $\text{Ni}_{0.1}\text{Mg}_{0.9}\text{O}$ -con catalysts were also synthesized by co-precipitation using K_2CO_3 as the precipitant.

3.2. Characterization

X-ray diffraction (XRD) of the catalysts were performed on a PW 1710 Philips Powder X-ray diffractometer (Philips Co. Ltd., Japan). Transmission electron microscopy (TEM) of the catalysts was analyzed at an accelerating voltage of 120 kV on a Hitachi HT7700 microscopy (Hitachi, Japan). Scanning electron microscopy (SEM) (Hitachi, Japan) of the catalysts was taken by a Zeiss Merlin system operated at 5 kV. Nitrogen adsorption and desorption measurements of the catalysts were conducted on an ASAP 2020 (Micromeritics Co. Ltd., America) apparatus. In order to ensure a clean, dry surface, the catalysts were degassed at 200°C under vacuum. Using the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) method to calculate the specific surface area and the pore size distribution of the catalysts.

H_2 temperature-programmed reduction (H_2 -TPR) of catalysts was operated in a quartz fixed-bed micro-reactor. Generally, 90 mg of catalysts were pretreated for 30 min at 300°C with 30 mL/min

of high-purity argon. After cooling to 25 °C, a 30 mL/min of 10% H₂ in Ar was imported and the temperature was controlled by programming with a ramping rate of 10 °C/min from room temperature to 1000 °C. The consumption of H₂ during the reduction was measured by gas chromatography (GC) equipped with a thermal conductivity detector (TCD).

The amount of carbon deposition of the used catalysts was evaluated by TG-DSC (thermogravimetry-differential scanning calorimetry) with a Netzsch STA449C thermoanalyzer (NETZSCH Co. Ltd., Germany). The spent catalysts were held in an alumina crucible for which an empty alumina crucible was taken as a reference. The temperature was heated from room temperature to 800 °C in air with a rate of 5 °C/min.

3.3. Catalytic Reaction

The catalytic activity of the samples was measured at the atmospheric pressure in a fixed-bed quartz reactor. Calcined catalysts (90 mg) were reduced in a 100 mL/min of 5% H₂/Ar mixture at 800 °C and isothermally kept for 1 h at this temperature. The CRM was conducted with a gas composition of CH₄:CO₂:Ar with a 9:9:27 volume ratio and a total 45 mL·min^{−1} flow rate (GHSV, Gaseous Hourly Space Velocity, 30,000 mL·g^{−1}·h^{−1}). The catalytic activity was performed from 500 °C to 800 °C with a 5 °C/min ramping rate. For each temperature, the reaction efficiency of the catalysts was evaluated after 30 min steady state. Process gas analysis was performed by gas chromatography equipped with methanizer, TCD, FID (flame ionization detector) and the mole sieve 5A and TDX-01 columns (Stainless steel filled column). The stability of the catalysts was carried out for 36 h at 700 °C. The CH₄ and CO₂ conversions and H₂/CO ratio were used to evaluate the properties of catalysts. The equations were as follows [40]:

$$\text{CH}_4\text{conversion}(\%) = \frac{\text{moles of CH}_4 \text{ converted}}{\text{moles of CH}_4 \text{ in feed}} \times 100$$

$$\text{CO}_2\text{conversion}(\%) = \frac{\text{moles of CO}_2 \text{ converted}}{\text{moles of CO}_2 \text{ converted in feed}} \times 100$$

$$\frac{\text{H}_2}{\text{CO}}\text{ratio} = \frac{\text{moles of H}_2 \text{ produced}}{\text{moles of CO produced}}$$

4. Conclusions

In summary, the ultrathin Ni_xMg_{1−x}O solid solution nanoplates with high surface areas (>120 m²/g) were synthesized by a facile and scalable co-precipitation method. The ultrathin Ni_xMg_{1−x}O solid solution nanoplates displayed high catalytic activity and stability for the CRM reactions, which can be attributed to their unique physicochemical properties, providing high surface area and strong metal-support interaction to prevent coke formation and sintering of small nickel species into large particles. The characterization of the spent catalysts indicated that the Ni_xMg_{1−x}O solid solution nanoplate catalysts with a low nickel content can improve the thermal stability of the catalysts, preserve the small size of the metallic nickel, and resist carbon deposition. Therefore, the Ni_xMg_{1−x}O catalysts were prepared via a hydrothermal method exhibited good activity and stability for the CRM reaction for industrial applications.

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