Ni catalysts for dry methane reforming prepared by A-site exsolution on mesoporous defect spinel magnesium aluminate

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ABSTRACT

In dry methane reforming, the selection of a suitable support is critical due to coke formation and metal particle sintering. We prepared two types of mesoporous defect spinel magnesium aluminate support, namely DS09, with a Mg/Al molar ratio of 0.1, and DS19 with Mg/Al = 0.24. Each support has a high surface area, large mesopore volume, and a phase between its defect spinel (Mg0.388Al2.408O4) and spinel (MgAl2O4) structures. Magnesium aluminate with a Mg/Al of 0.5 (MG30), which has a low surface area and is devoid of mesopores, was used as the reference support. Ni was supported on DS09 (Ni-DS09) and DS19 (Ni-DS19) by A-site exsolution. These catalysts display significant advantages over Ni-supported MG30 (Ni-MG30); Ni-DS19 exhibited a higher coke resistance than Ni-DS09, due to its lower acidity, while DS19, which contains a defect spinel structure, optimized acidity, and well-developed mesopores, was the best support for the DMR.

1. Introduction

Dry methane reforming (DMR) uses two abundant greenhouse gases (i.e., CO2 and CH4) for the production of syngas, which is an industrially important, mixture of CO and H2 [1,2]. DMR was first reported by Fischer and Tropsch in 1928 and is currently attracting growing attention in an environmental context due to ongoing concerns related to global warming promoted by greenhouse gases [3]. High temperatures are required to produce syngas in high yields, which results in the rapid catalyst deactivation due to coke formation as well as sintering of the support and/or active metal particles [4,5]. Although noble metals such as Pt and Ru are the most highly active and robust catalysts for DMR [6], these metals are not suitable for practical applications due to their high costs.

Ni-based catalysts which are used in industrial steam methane reforming have been also considered as promising DMR catalysts because of their low costs and high activities [1,5,7]. Indeed, significant effort has been devoted to the development of thermally stable Ni-based catalysts that exhibit high resistance against both coke formation and Ni sintering [4,7,8]. The selection of a suitable support that can maintain a high Ni dispersion during the high temperature reaction is critical to obtaining highly active and coke-resistant catalysts [5,9]. In this context, two physical approaches that modulate the structural and morphological properties of the support material have generally been introduced.

More specifically, the first approach, which involves placing the Ni phase within well-defined crystalline structures, such as spinel or perovskite phases, has been applied to DMR catalysts [10–13]. Highly dispersed Ni active site on the support surface can be obtained by the exsolution-based in situ growth of Ni nanoparticles in a reducing atmosphere, especially for perovskite phases that contain Ni in B-site [10,13–17]. Ni nanoparticles with strong metal-support interactions and high thermal stabilities, which are highly promising catalyst characteristics for a wide variety of chemical and energy-conversion applications, can be prepared using this approach [15]. Zubenko et al. introduced the LaFeO3 perovskite phase, which was further doped with Ni and Re active phases and tested in DMR reactions. Although the catalysts showed strong resistance against coke formation and sintering, the exsolved active phase is a precious Re-based alloy [13]. Pure exsolution of the Ni phase has been reported for the development of solid oxide fuel-cell anodes, which are mostly based on perovskite phase [14,16]. Ni exsolution has been rarely reported in Ni-MgAl2O4 spinel...
catalysts or MgO-promoted Ni-Al\textsubscript{2}O\textsubscript{3} catalysts, which are conventionally known to be highly stable and active DRM catalysts with high coke and sintering resistance [18–20].

Secondly, Ni nanoparticles can be confined in the well-developed mesopores of support materials [9,21], where such nano-scale compartmentalization physically inhibits the Ni nanoparticles from sintering [4]. This approach is also advantageous for catalytic reaction as it results in a high specific surface area and an interconnected porosity. Although mesoporous materials, such as MCM-41 and SBA-15, have been reported as supports for Ni-based DMR catalyst, such acidic silica-based mesoporous materials are susceptible to coke deposition and often require the use of noble metals as promoters [22,23]. Indeed, from a chemical point of view, basic supports or catalysts with basic promoters are highly desirable for the DMR reaction, as proven with Ni-MgAl\textsubscript{2}O\textsubscript{4} spinel for MgO-promoted Ni-Al\textsubscript{2}O\textsubscript{3} catalysis [18–20].

With the above-discussion in mind, herein, we devised a Ni-based mesoporous magnesium aluminate catalyst that satisfies both the chemical requirement (i.e., basic in nature) and the two above-mentioned physical requirements of well-defined crystalline materials with well-developed mesopores. To achieve this goal, we first prepared a mesoporous A-site-deficient magnesium aluminate defect spinel. The A-site was then filled with Ni by impregnation and subsequent calcination, after which the Ni phase was exsolved by reduction. Consequently, we expect strong interaction between metal particle and support. Thermal stability and the provision of vacant A-sites for Ni are two advantages associated with the use of the defect spinel phase as the support materials. Mesoporous magnesium aluminate support materials were synthesized using the evaporation-induced self-assembly method, with the Mg/Al molar ratio (Mg/Al) maintained below 0.5 during the formation of the defect spinel phase. The effect of Mg/Al on the porosity of the mesoporous catalyst and catalyst acidity were examined, and the optimal Mg/Al was finally evaluated to give a species that satisfies both the physical and chemical requirements of a support for the Ni-based DMR catalyst.

2. Experimental

2.1. Support material synthesis

The solvent was prepared by dissolving the Pluronic P123 triblock copolymer (6.57 g, P123, Mn \approx 5800, EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}, Sigma-Aldrich) in mixture of absolute ethanol (135.6 mL, CH\textsubscript{3}CH\textsubscript{2}OH, ACS reagent, \geq 99.5 %, Sigma-Aldrich) and nitric acid (10.6 mL, HNO\textsubscript{3}, 60.0 %, OCI) with vigorous stirring. Subsequently, aluminum isopropoxide (12.42 or 11.03 g, Al(OCH(CH\textsubscript{3})\textsubscript{2})\textsubscript{3}, \geq 98 %, Sigma-Aldrich) and magnesium chloride (0.56 or 1.21 g, MgCl\textsubscript{2}, anhydrous, \geq 98 %, Sigma-Aldrich) were dissolved in the solvent over 5 h with vigorous stirring. The Al(OiPr)\textsubscript{3}+MgCl\textsubscript{2}: P123:EtOH:HNO\textsubscript{3} molar ratio was 1:0.017:34.1:2.09, with the MgCl\textsubscript{2}:Al(OiPr)\textsubscript{3} molar ratio fixed at 8.8:91.2 or 19:81 for DS09 or DS19, respectively. The obtained solution was then dried in an oven at 333 K for 48 h, and the resulting dried sample was calcined at 1073 K for 4 h in air with a ramp rate of 0.5 K/min. To prepare MG30, the hydrotalcite-like MgO–Al\textsubscript{2}O\textsubscript{3} mixed oxide (MgO = 30 wt%, SASOL) was calcined at 1073 K in air for 4 h.

2.2. Ni catalyst preparation

The Ni catalysts were prepared as follows: the three support materials (DS09, DS19, and MG30) were impregnated with 10 wt% Ni using the incipient wetness method. More specifically, nickel(II) nitrate hexahydrate (1.69 g, Ni(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O, \geq 98.5 %, Sigma-Aldrich) was dissolved in deionized water (2 mL) to give a Ni solution, which was subsequently added to the support material (3 g) in a drop-wise manner in an agate mortar with mixing. Each impregnated sample was then dried in an oven at 333 K for 48 h, and the resulting dried sample was calcined at 1073 K for 4 h under air with a ramp rate of 1 K/min. To prepare MG30, the hydrotalcite-like MgO–Al\textsubscript{2}O\textsubscript{3} mixed oxide (MgO = 30 wt%, SASOL) was calcined at 1073 K in air for 4 h, with a ramp rate of 1 K/min.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>MG30</th>
<th>DS19</th>
<th>DS09</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m\textsuperscript{2}/g)a</td>
<td>90</td>
<td>146</td>
<td>171</td>
</tr>
<tr>
<td>Pore volume (cm\textsuperscript{3}/g)b</td>
<td>0.24</td>
<td>0.58</td>
<td>0.62</td>
</tr>
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aSurface area was calculated from the N\textsubscript{2} adsorption isotherm using the BET method.
bTotal pore volume was calculated at partial pressure of P/P\textsubscript{0} = 0.99.

Ni-DS19-I, and Ni-MG30-I. Following subsequent reduction at 1073 K for 2 h in an atmosphere of 10 % H\textsubscript{2} and 90 % N\textsubscript{2}, samples Ni-DS09-R, Ni-DS19-R and Ni-MG30-R were obtained, respectively.
2.3 Catalyst reactivity testing

The three prepared samples (Ni-MG30, Ni-DS19 and Ni-DS09) were used as catalysts in DMR reactions. For this purpose, a fixed-bed type 1/4-inch quartz reactor was used, along with a sample mass of 0.15 g and a quartz wool mass of 0.012 g. The reaction was performed at 973 and 1073 K with a weight hourly space velocity (WHSV) of $24,200 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ and a CH$_4$:CO$_2$:N$_2$ gas feed ratio of 1.00:1.06:1.00. Reduction was performed (H$_2$:N$_2$ = 1:9, total 100 mL/ min) at 1073 K for 2 h prior to commencing the reaction. The effluent gas was analyzed by micro-gas chromatography (GC, Infiicon 3000) using two thermal conductivity detectors (TCDs).

2.4 Characterization

The crystal structures of the support materials and the catalysts were analyzed by powder X-ray diffractionometry (XRD, D/MAX-2500, RIGAKU, Japan) using a Cu Kα source. To confirm the oxidation state of Ni on the reduced sample surface, the X-ray photoelectron spectroscopy (XPS) analysis was performed using a K-Alpha+ (Thermo-Fisher Scientific™). Morphological information of supports was obtained using field emission transmission electron microscopy (FE-TEM, JEM-2100 F HR, JEOL, Japan) with an accelerator voltage of 200 kV at the National Nanofab Center, Daejeon, Republic of Korea. N$_2$ physisorption experiments were carried out using a BELSORP-mini II instrument (MicrotracBEL Corp., Japan) at 77 K after degassing at 573 K for 3 h. The surface area of each sample was calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distribution and pore volume were characterized using the Barrett–Joyner–Halenda (BJH) method. H$_2$-temperature-programmed reduction (H$_2$-TPR) and NH$_3$-temperature-programmed desorption (NH$_3$-TPD) were performed.

Fig. 2. N$_2$-physisorption results for the prepared samples: (a) N$_2$ isotherms and (b) Pore size distributions obtained by the BJH method (desorption branch): (■) MG30, (●) DS19, and (▲) DS09.

Fig. 3. XRD patterns of the supports (MG30, DS19 and DS09) after calcination at 1073 K for 4 h.

Fig. 4. XRD patterns of the prepared catalysts (Ni-MG30-I, Ni-DS19-I, and Ni-DS09-I) after calcination at 1073 K for 4 h.

Fig. 5. XRD patterns for Ni-MG30-R, Ni-DS19-R and Ni-DS-09-R after reduction at 1073 K for 2 h.
using a chemisorption analyzer (BEL-CAT, BEL Japan Inc.). Pre-treatment was performed at 473 K for 1 h under He. NH3-adsorption testing was then carried out by placing the sample in 5 vol% NH3 in He gas at 373 K, while NH3 desorption was measured between 323 and 1273 K at 10 K/min. H2 consumption and NH3-desorption were detected using TCDs. The carbon deposition rates of the spent catalysts were measured by thermogravimetric analysis (TGA2, METTLER) under air. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments at low temperature were performed on a Nicolet iS10 FTIR spectrometer equipped with a mercury-cadmium-telluride (MCT) detector. CO gas was used as a probe molecule to investigate the acid-base properties of the MgAl2O4 surface. All spectra were collected and are averages of 128 scans at a resolution of 4 cm⁻¹. Samples of magnesium aluminate or Ni impregnated magnesium aluminate (5 mg) samples were loaded into a high-temperature reaction chamber (Harrick Scientific) with ZnSe windows, installed in a Praying Mantis diffusion reflection accessory. All samples were pretreated under flowing He (flow rate = 1 mL/sec) at 423 K for 1 h and then cooled to room temperature. To provide hydroxyl-groups information, we collected the KBr background spectrum. After cooling to 273 K, CO-adsorption experiments were performed on magnesium aluminate and the Ni-impregnated magnesium aluminate under a flow 0.2 % CO/He with repeated pulses (1 mL) at 273 K. Negligible CO was adsorbed on bare magnesium aluminate at 273 K. After cooling to 123 K, background spectra were collected on the catalyst saturated with CO on the Ni surface. CO adsorption was carried out until no spectral change was observed under a flow of 0.2 % CO/He, after which the spectrum was collected following purging with a flow of He for 5 min to remove gas-phase CO.

3. Results and discussion

3.1. Characterizing the supports and prepared catalysts

Due to its basic nature, the MgAl2O4 spinel structure is known to have a higher coke resistance than the commonly employed alumina support [24]. In addition, MgAl2O4 has a number of advantageous properties, including a superior chemical resistance, mechanical strength, and thermal stability. As such, various strategies have been introduced for the preparation of magnesium aluminates that exhibit well-ordered mesopores, with examples including the use of structure directing agents, such as triblock copolymers and surfactants [25–28]. However, the well-developed mesopores of this spinel phase are easily deformed by sintering above 973 K [29]. Zhang et al. carefully analyzed the optimum temperature ranges for the DMR reaction [2] and found that the catalyst-deactivating carbon deposition was mainly caused by CO disproportionation that takes place at 830–973 K, while high reaction temperatures lead to the formation of carbon deposits through deep methane cracking. However, a reaction temperature greater than 1000 K is favorable for the reforming reaction, and therefore it is highly desirable to develop a mesoporous magnesium aluminate support that is thermally stable at such temperatures. TEM images of the prepared support materials are shown in Fig. 1, where it is apparent that the well-developed and ordered mesopores of DS19 (Mg/Al = 0.24) and DS09 (Mg/Al = 0.1) are clearly maintained after calcination at 1073 K. In contrast, such mesopores were not observed in the magnesium aluminate prepared by the same procedures but at a Mg/Al = 0.5 to give the MgAl2O4 spinel phase (Fig. S1). Considering that Mg/Al < 0.25 was employed for the synthesis of DS09 and DS19, it is apparent that lowering the Mg content is essential to increasing the sintering resistance of the mesoporous magnesium aluminates. Magnesium aluminate with Mg/Al = 0.5 (MG30) prepared by calcination of the hydrotalcite (MgO = 30 wt%, SASOL) at 1073 K for 4 h, showed no well-defined mesopores, as seen in Fig. 1(c).

Nitrogen physisorption analysis was then used to investigate the physical properties of the three support materials. As shown in Table 1,
the surface areas of the MG30, DS19, and DS09 supports are 90, 146, and 171 m²/g, respectively. In addition, Fig. 2(a) shows the nitrogen isotherms of MG30, DS19, and DS09, where it is apparent that the isotherms of DS19 and DS09 exhibit type IV hysteresis loops, which indicates that these materials have mesoporous structures with ink bottle-shaped pores. Fig. 2(b) shows the BJH pore-size distributions of the samples. Although MG30 did not exhibit any distinct mesopores, DS19 and DS09 were found to contain well-developed mesopores, which correlates with the TEM images shown in Fig. 1.

Fig. 3 shows the XRD patterns of the prepared MG30, DS19, and DS09. It should be noted that the JCPDS cards indicate that the peak positions of the MgAl₂O₄ (PDF #21-1152) and NiAl₂O₄ (PDF #10-0339) spinel structures are very similar, while those of NiAl₂O₄ are very slightly right-shifted from those of MgAl₂O₄ (e.g., by 0.294° for the (440) plane at ~65°, Table S1). In the case of the defect spinel structure of Mg₀.₃₈₈Al₂.₄₀₈O₄ (PDF #48-0528), the peak positions and intensities are also similar to those of the spinel structure, but the peaks are more right-shifted than those of NiAl₂O₄ (i.e., by 1.092° for the (440) plane of MgAl₂O₄) as shown in Fig. 3. To allow careful peak identification, the (440)-plane peak pattern was enlarged, as shown on the right-hand side of the XRD patterns. As indicated, the peaks corresponding to MG30 are similar to those of the MgAl₂O₄ or NiAl₂O₄ phase. As no nickel is present in MG30, which was obtained by the thermal treatment of hydrotalcite containing 30 wt% MgO and 70 wt% Al₂O₃ at 1073 K, this support was identified to the MgAl₂O₄ spinel phase. In addition, the XRD peaks of DS09 are identical to those of the JCPDS card for Mg₀.₃₈₈Al₂.₄₀₈O₄, while the XRD peak of the DS19 (440) plane was right-shifted from that of MgAl₂O₄ by 0.46° (Table S1), which indicates that DS19 has a partially Mg-deficient spinel phase between MgAl₂O₄ spinel and Mg₀.₃₈₈Al₂.₄₀₈O₄ defect spinel. Fig. 4 shows the XRD patterns of the various support following the impregnation of 10 wt% Ni and subsequent calcination at 1073 K for 4 h. Interestingly, the XRD pattern of Ni-MG30-I exhibits signals corresponding to NiO (PDF #71-1179) at 44 and 63°, while no such peaks are observed for Ni-DS19-I and Ni-DS09-I. Compared to the XRD patterns of DS19 and DS09 shown in Fig. 3, it is clear that these peaks have been left-shifted (Fig. 4, Table S1), with the XRD peaks of Ni-DSS-I now similar to those of the JCPDS card for NiAl₂O₄, which indicates that nickel ions (Ni²⁺) filled the Mg-deficient tetrahedral sites of DS19 through nickel
imregnation and subsequent calcination. In the case of Ni-DS09-I, the XRD peak of the (440) plane lies between that of the MgAl2O4 spinel and the Mg0.388Al2.408O4 defect spinel, which indicates that the tetrahedral sites remain Mg or Ni deficient. The defect spinel phase is formed when the stoichiometric ratio of A to B is \(\leq1:2\) in \(\text{AB}_2\text{X}_4\). As the stoichiometric ratios of A to B employed in the preparation of MG30, DS19, and DS09 were 1.09:2 (0.5), 0.47:2 (0.24) and 0.19:2 (0.1), respectively, it is apparent that the Ni\(^{2+}\) fills the Mg-deficient sites (A sites) of DS19 and DS09 without the formation of a NiO phases, which means that Ni\(^{2+}\) is incorporated into the lattice structure of the defect spinel at A-sites during calcination. In contrast, the Ni\(^{2+}\) was impregnated on the surface of MG30, a fully stoichiometric spinel phase, resulting in the formation of a NiO phase.

Following the reduction of Ni-DS19-I and Ni-DS09-I, a NiO phase was formed in both cases (i.e., Ni-DS19-R and Ni-DS09-R), as indicated by the red dashed lines in Fig. 5. In addition, a metallic Ni phase was formed in the case of Ni-DS19-R, as indicated by the yellow dashed lines. Taking only the support materials into consideration, the XRD peaks of MG30 (Fig. 3) were not significantly shifted following Ni impregnation (Fig. 4) and reduction (Fig. 5). However, in the cases of DS19 and DS09, the XRD peaks were left-shifted following Ni impregnation and subsequently right-shifted after reduction. In particular, the defect spinel phase (Mg0.388Al2.408O4) of DS09 was recovered following the Ni impregnation and reduction processes, likely due to the exsolution of Ni\(^{2+}\) from A-sites in the spinel or defect spinel structures. Exsolution is known to be a process by which, in a reducing atmosphere, highly dispersed metal nanoparticles are formed by the diffusion of easily reducible cations such as Mn, Co or Ni, that are incorporated into the A or B sites of the spinel (\(\text{AB}_2\text{O}_4\)) or perovskite (\(\text{ABO}_3\)) structure [31]. The formation of metallic nickel by A-site exsolution was confirmed using XPS analysis as shown in Fig. 6 and Table 2. XPS analysis was performed to confirm the oxidation state of nickel on the reduced catalysts surface. As expected from XRD results, not only metallic nickel but also nickel ion corresponding to nickel aluminate was found in XPS spectra.

Fig. 7 shows a schematic summary of our interpretation of the XRD patterns shown in Figs. 3–5. Ni\(^{2+}\) can reside in the A-site-deficient unit cells of DS19 following Ni impregnation and calcination, to form a MgAl2O4/NiAl2O4 spinel (Fig. 7b), while subjecting MG30 to the same treatment resulted in the formation of separate NiO and MgAl2O4 spinel phases (Fig. 7a), as confirmed by XRD studies (Fig. 4). In the case of DS09, which contains the Mg0.388Al2.408O4 defect spinel phase, the A sites of the unit cells remain deficient following Ni impregnation and calcination (Fig. 4 and 7c). After reduction, the metallic Ni present in Ni-DS19-I and Ni-DS09-I become exsolved from the A-sites to form Ni\(^+\) and/or NiO, with recovery of the crystal phases of the support materials (Fig. 5). This is meaningful in that Ni nanoparticles exsolved from the spinel or defect spinel phases can more strongly interact with the supports. Indeed, Neagu et al. reported that exsolved Ni particles are socketed in the parent perovskite; they also found that the resulting catalysts showed enhanced resistance to coking, in addition to strong metal-oxide interfaces compared to conventionally prepared Ni catalysts [32]. Indeed, H\(_2\)-TPR analyses of Ni-MG30-I, Ni-DS19-I, and Ni-DS09-I (see Fig. 8) confirmed that different interactions exist between the Ni species and the prepared supports.

As shown in Fig. 8, H\(_2\)-TPR was used to determine the reduction temperatures of the nickel species (i.e., NiO and NiAl2O4) present in the sample. The sharp peaks visible at high temperatures (> 1000 K) correspond to the reduction of NiAl2O4, while the broad peaks visible at low temperatures (< 600 K) are assigned to NiO [18,33–35]. It should be noted that the formation of NiAl2O4 could not be confirmed by XRD, as the corresponding signals appeared at similar positions to those of MgAl2O4. In addition, we found that the TPR peak temperatures of the NiAl2O4 present in Ni-DS19-I and Ni-DS09-I were higher than that in the Ni-MG30-I sample, likely due to strong interactions between the support and the nickel species, since DS09 and DS19 have larger numbers of Mg-deficient sites than MG30.

Following reduction of the prepared sample, TEM was performed to determine the sizes of the metallic nickel particles. As shown in Fig. 9(c), a Ni particle size of \(~19\) nm was obtained when MG30 was used as the support. In the cases of the DS19 and DS09 supports, the Ni particle sizes were \(~15\) and \(~4\) nm, respectively (Fig. 9(a) for Ni-DS19-R, Fig. 9(b) for Ni-DS09). DS09 which has larger number of defect sites than DS19 or MG30 generates the smaller Ni particles in Ni-DS09-R than those in Ni-DS19-R or Ni-MG30-R. Based on these results, we speculate that the exsolved Ni particle size is related to the number of Mg-deficient defect site.
3.2. Catalytic testing of the prepared Ni catalysts

To evaluate the catalytic activities of the prepared samples, the DMR reaction was carried out at 973 and 1073 K using a WHSV of 24,000 mLg_{cat}^{-1} h^{-1} over 2 h. We found that the methane conversions of Ni-MG30, Ni-DS19 and Ni-DS09 were comparable at both reaction temperatures (973 and 1073 K) despite their Ni particle sizes, surface areas, and mesopore volumes differing. In addition, each catalyst displayed a higher CO\textsubscript{2} conversion considering the corresponding CH\textsubscript{4} conversion. Hence, to suppress coke formation, excess quantities of CO\textsubscript{2} (CO\textsubscript{2}/CH\textsubscript{4} = 1.06) were supplied during the DMR reaction. As a result, the conversion of CO\textsubscript{2} should be reduced compared to that of CH\textsubscript{4} since the consumption of 1 mol of CH\textsubscript{4} corresponds to the consumption of 1 mol of CO\textsubscript{2}. For example, the CO\textsubscript{2} conversion of Ni-MG30 should be 75 % with a CH\textsubscript{4} conversion of 80 %. The white lines shown in Fig. 10(b) indicate the calculated CO\textsubscript{2} conversions that correspond to the CH\textsubscript{4} conversions; however, the various CO\textsubscript{2} conversions shown in Fig. 10(b) are higher than the calculated conversions, indicative of the occurrence of a reverse water gas shift (RWGS) reaction. We also note that the degree of RWGS decreased as the reaction temperature was increased from 973 to 1073 K. Thus, from the viewpoint of initial catalytic activity, our results indicate that all prepared catalysts exhibit similar catalytic activities.

To evaluate the catalyst stability during the DMR reaction, long-term reactions (≤30 h, Fig. 11) were performed for each catalyst. Although the three catalysts exhibited similar initial catalytic activities (Fig. 10), their activities differed in the long-term reactions. For example, in the case of Ni-MG30, it was only possible to carry out the reaction for 6 h due to reactor plugging. Where Ni-DS09 was employed, the DMR reaction was sustained for 20 h, but was again halted due to reactor plugging. However, the CH\textsubscript{4} and CO\textsubscript{2} conversions of Ni-DS19 were maintained beyond 30 h without plugging, which indicates that, in terms of long-term stability, Ni-DS19 appears to be the most suitable catalyst for the DMR reaction among three catalysts examined herein.

The reactor plugging observed for Ni-MG30 and Ni-DS09 is attributable to coke deposition; the longer reaction time possible for Ni-DS09 is due to its larger mesopore volume and higher surface area compared to Ni-MG30. To explain this phenomenon more precisely, the coke deposition of each catalyst should be investigated after long-term reactions.

3.3. Characterizing the spent catalysts

After the reaction, the characterization of the spent catalysts was performed by Raman and TEM. The Raman spectra of spent catalysts were displayed in Fig.S2. In Ni-MG30 and Ni-DS09, the peak intensity
of the D band corresponding to amorphous carbon was higher than that of the G band corresponding to graphitic carbon. It means that the major carbon species in Ni-MG30 and Ni-DS09 were amorphous carbon. On the other hand, the Raman peak intensity of the spent catalysts of Ni-DS19 was higher in the G band than in the D band, suggesting that the major carbon species deposited in Ni-DS19 was graphitic carbon. This trend was also confirmed by the TEM images (Fig.S3). Ni-MG30 (Fig.S3(a)) and Ni-DS09 (Fig.S3(c)) had small amount of filament and fiber carbons. However, Ni-DS19 (Fig.S3(b)) displayed a large amount of filament and fiber carbons. Summarizing Raman and TEM results, the major carbon species deposited on Ni-DS19 was graphitic carbon. It strongly suggests that metallic nickel was the major coke formation site. On the other hand, the major carbon species in Ni-MG30 and Ni-DS09 were amorphous carbon. It means that not only metallic nickel, but also acid sites contributed the carbon formation.

It is well known that the amount of coke deposited on a catalyst is closely related to the catalyst lifetime. Hence, we used TGA to determine the amount of coke present on each catalyst after the long-term reaction. For this purpose, the amount of coke determined by TGA was divided by the reaction time, and the quantity of catalyst employed in the reaction was used to calculate the coke deposition rate (see Fig. 12). Among the three catalysts, the coke deposition rate of Ni-DS19 was the lowest, while that of Ni-DS09 was the highest. In terms of the reaction duration (see Fig. 11), the reaction employing Ni-MG30 as the catalyst had the shortest duration (6 h) and the highest coke deposition rate. The higher coke deposition rate of Ni-MG30 compared to that of Ni-DS19 is easily explained by considering that Ni-MG30 contains larger Ni particles, a lower surface area, and almost no mesopore volume. However, the high deposition rate observed for Ni-DS09 was unexpected, since DS09 has the highest surface area, highest mesopore volume, and smallest Ni particle size. This result is therefore attributed to catalyst acidity, which is closely related to coke deposition. Summarizing these experimental results of spent catalysts, the catalytic lifetime, reaction duration time, was affected closely with the total amount of carbon deposited on the surface of catalysts.

The acid sites in the catalysts were then investigated to determine their effect on coke formation. Fig. 13 shows the NH$_3$-TPD curves for the three supports (MG30, DS09, and DS19) and the three catalysts (Ni-MG30, Ni-DS19, and Ni-DS09), where the peak area of each sample is proportional to the total number of acid sites for a given sample. More specifically, as shown in Fig. 13(a), DS09 bears the highest number of acid sites, while DS19 and MG30 contain similar numbers of acid sites. Since both DS19 and DS09 have defect spinel structures, and their Mg/Al ratios are related to their total acidities; DS09 has a higher number of acid sites than DS19 due to its lower Mg/Al ratio (i.e., 0.1, 0.24, respectively). After Ni loading, this trend was maintained, with Ni-DS09 containing a greater number of acid sites than Ni-DS19 and Ni-MG30. Therefore, the total number of acid sites can indeed be correlated with the coke deposition rate of a given catalyst, with Ni-DS09 containing the greatest number of acid sites and exhibiting the highest coke deposition rate.

3.4. Acidity analysis by CO adsorption and DRIFTS

The surface acid properties of magnesium aluminate with different Mg and Al content ratio were also investigated by DRIFTS after CO adsorption at low temperature (123 K). IR studies of CO adsorbed on alumina surfaces have demonstrated that CO interacts with both Lewis and Bronsted acid sites on the alumina surface [36,37]. On the basis of these studies, the high-frequency peak at 2194−2186 cm$^{-1}$ is assigned to CO at Lewis acid sites, while the low-frequency peak at 2158−2155 cm$^{-1}$ could be assigned to CO on Bronsted acid sites [36,37]. Two distinctive bands are observed at 2170 and 2152 cm$^{-1}$ in the DRIFT spectrum of Ni-MG30-R after CO adsorption (Fig. 14). Interestingly, compared with the spectrum of Ni-MG30-R, the Lewis acid site band is shifted by about 5 cm$^{-1}$ toward higher wavenumber in the spectra of Ni-DS09 and Ni-DS19 (2175 cm$^{-1}$), which suggests that the Lewis acid sites on Ni-DS09-R and Ni-DS19-R bind more strongly than the Lewis acid sites on Ni-MG30-R, despite Ni-MG30-R containing a considerable number of Lewis acid sites [38,39]. Furthermore, the 2175 cm$^{-1}$ band in the spectrum of Ni-DS09-R was notably less intense than that observed for Ni-DS19-R, indicating that Ni-DS09-R has more Lewis acid sites than Ni-DS19-R [40]. These results are in good agreement with the reaction data, which reveal that the strength of Lewis acid site binding significantly affects the coke-resistance of the catalyst. In addition, the number of acid sites also plays an important role in determining the coke-resistance of catalyst.

4. Conclusions

Herein, we employed Ni which is supported on mesoporous defect-
spinel structured magnesium aluminate (DS19 and DS09) as catalysts for dry methane reforming (DMR). A-site exsolution induced Ni nanoparticles on the surface of the defect-spinel structure of the magnesium aluminate (DS19 and DS09). Ni supported on the spinel-structured magnesium aluminate support (MG30) was also employed as a reference catalyst. The defect spinel magnesium aluminate support with a low Mg/Al molar ratio (DS09) contains a higher number of acid sites than that with a high Mg/Al molar ratio (DS19). Following long-term DMR stability testing for over 30 h, Ni-DS19 exhibited a significant advantage over Ni-DS09 and Ni-MG30 in terms of the degree of coke deposition. Indeed, the carbon deposition rate was notably different between Ni-DS19 and Ni-DS09, as the less acidic DS19 displayed a higher coke resistance than Ni-DS09. These results indicate that DS19 is the most suitable support for DMR, as it is based on the defect spinel structure, contains the optimal volume of mesopores, and exhibits an optimized acidity. The information obtained in this study is expected to be useful when designing DMR catalysts.

CRedit authorship contribution statement


Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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