

Article

CO₂ Methanation over Ni/Al@MAl₂O₄ (M = Zn, Mg, or Mn) Catalysts

Thien An Le, Jieun Kim, Yu Ri Jeong and Eun Duck Park * 

Department of Chemical Engineering and Department of Energy Systems Research, Ajou University, Suwon 16499, Korea

* Correspondence: edpark@ajou.ac.kr

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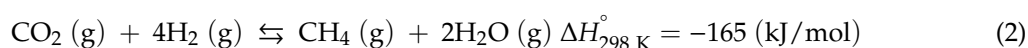
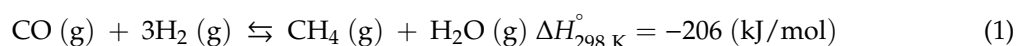


Abstract: In this study, unique core-shell aluminate spinel supports, Al@MAl₂O₄ (M = Zn, Mg, or Mn), were obtained by simple hydrothermal surface oxidation and were applied to the preparation of supported Ni catalysts for CO₂ methanation. For comparison, CO methanation was also evaluated using the same catalysts. The prepared catalysts were characterized with a variety of techniques, including N₂ physisorption, CO₂ chemisorption, H₂ chemisorption, temperature-programmed reduction with H₂, temperature-programmed desorption of CO₂, X-ray diffraction, high-resolution transmission electron microscopy, and in-situ diffuse reflectance infrared Fourier transform spectroscopy. The combination of supports with core-shell spinel structures and Ni doping with a deposition–precipitation method created outstanding catalytic performance of the Ni catalysts supported on Al@MgAl₂O₄ and Al@MnAl₂O₄ due to improved dispersion of Ni nanoparticles and creation of moderate basic sites with suitable strength. Good stability of Ni/Al@MnAl₂O₄ catalyst was also confirmed in the study.

Keywords: CO methanation; CO₂ methanation; Ni catalyst; deposition–precipitation; core-shell; Al@MAl₂O₄; Ni/Al@MAl₂O₄

1. Introduction

CO₂ conversion technologies have been identified as being crucial for mankind in order to mitigate global warming [1]. Since CO₂ is the most stable and fully oxidized state of carbon, its chemical transformation requires either highly reactive chemicals or additional energy. Recently, much attention has been paid to the power-to-gas (P2G) concept, in which surplus electricity from a renewable energy source can be used to produce hydrogen from water, which can then be reacted with carbon oxides (CO and CO₂) to form synthetic natural gas. The syngas can then be either stored as it is or distributed to users through a gas grid [2]. This concept revives CO and CO₂ methanation reaction research—applying a process known as the Sabatier reactions—that was initiated in the early 1900s [3]:



Since these reactions are thermodynamically limited and highly exothermic, low-temperature operation is preferred in order to achieve a high single-pass conversion. Therefore, development of a catalyst that is very active at low temperatures, as well as application of a highly thermal conduction material, is desirable to guarantee low-temperature operation without hotspots in the catalyst bed. Ni-based catalysts have been widely used in commercial methanation processes, based on their reasonable activity level, low cost, and high availability, compared with noble metal catalysts [4–16]. It has been reported that the low thermal conductivity of the ceramic support might cause metal

sintering, especially for highly exothermic reactions [17,18]. Therefore, supports with high thermal conductivity would have merit, if the high dispersion of metal was guaranteed, to support Ni-based catalysts. Among various supports documented in the literature [5,9,10,14,19–21], spinel MAl_2O_4 (M represents a divalent metal cation that usually occupies a tetrahedral site) materials are of great interest, as they embody a combination of desirable properties including high thermal stability, high mechanical resistance, high cation diffusion ability, and low surface acidity [22–24]. MgAl_2O_4 has been nominated as a good catalyst carrier, in Ni/ MgAl_2O_4 , for high CO selective methanation [25], for CO_2 methanation [15], and for its high level of coking resistance in CO_2 reforming of CH_4 [26]. Until now, only a few studies have been conducted on the application of the spinel structure to methanation processes.

Spinel samples have reportedly been synthesized using different methods, including a polymeric precursor method [23], by surfactant-assisted precipitation method [24], using a sol–gel method [27], by impregnation and coprecipitation methods [28,29], and combustion method [30]. Recently, unique core-shell $\text{Al@MAl}_2\text{O}_4$ (M = Mg, Ni, Co, Zn, or Mn) materials, prepared using a simple hydrothermal surface oxidation (HTSO) method, have been reported as providing superior heat conductivity and surface properties and having potential as a heterogeneous catalyst substrate for highly exothermic and endothermic reactions [31]. In addition, a deposition–precipitation (DP) approach has been proposed as an effective catalyst preparation method in which a catalytically active precursor can be deposited onto the support by precipitation [12,21,32]. Using this technique, by controlling pretreatment conditions, smaller metal particles can be formed on the support, compared with the conventional wet impregnation (WI) method.

In this study, the combination of different core-shell spinel $\text{Al@MAl}_2\text{O}_4$ (M = Zn, Mg, or Mn) and the DP method for the fabrication of supported Ni catalysts have been shown to be able to provide outstanding catalytic performance in CO and CO_2 methanation at low reaction temperatures. Various characterization techniques have been employed to investigate key factors affecting methanation activity, and a possible CO_2 methanation mechanism has been identified based on an in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study.

2. Results and Discussion

2.1. Characterization of Catalysts

Textural properties of Ni/ $\text{Al@MAl}_2\text{O}_4$ (M = Zn, Mg, or Mn) catalysts prepared by WI and DP method and Ni/ MAl_2O_4 (M = Zn or Mg) catalysts prepared by DP method were revealed when probed with N_2 physisorption (Figures S1 and S2), showing that they all had the type IIb isotherms [33]. Specific surface areas calculated from the Brunauer–Emmett–Teller (BET) method (S_{BET}), the corresponding specific pore volumes (V_{Pore}), and average pore diameters (D_{Pore}) have been listed in Table 1. The S_{BET} of supported Ni catalyst prepared using the WI method was slightly smaller than that of the support itself (Table S1), which was a result considered to be reasonable since the Ni precursor was able to block pores during the impregnation step. On the other hand, it was remarked that the S_{BET} of core-shell-supported Ni catalyst prepared using the DP method was noticeably larger than that of the core-shell support itself (Table S1), Ni/ MgAl_2O_4 (DP) excepted. This implied that the core Al metal may have been partly transformed into $\text{Al}(\text{OH})_3$ during the DP process.

Table 1. Textural properties of Ni-supported catalysts.

Catalyst	Ni Content ^a (wt.%)	S _{BET} ^b (m ² /g)	V _{Pore} ^b (cm ³ /g)	D _{Pore} ^b (nm)	Ni Dispersion ^c (%)	CASA ^c (m ² /g _{cat.})	CO ₂ Uptake ^d (μmol/g _{cat.})
Ni/γ-Al ₂ O ₃ (WI) [12]	10	94	0.22	9.2	1.7	1.2	28
Ni/Al@ZnAl ₂ O ₄ (WI)	8	36	0.10	9.5	1.3	0.9	23
Ni/Al@MgAl ₂ O ₄ (WI)	10	124	0.24	7.8	3.0	2.0	47
Ni/Al@MnAl ₂ O ₄ (WI)	10	97	0.13	5.3	3.4	2.3	41
Ni/ZnAl ₂ O ₄ (DP)	9	163	0.31	7.6	3.6	2.3	29
Ni/MgAl ₂ O ₄ (DP)	8	179	0.42	9.5	7.4	4.9	46
Ni/Al@ZnAl ₂ O ₄ (DP)	8	119	0.22	7.4	6.1	4.1	29
Ni/Al@MgAl ₂ O ₄ (DP)	9	171	0.28	6.6	9.2	6.1	57
Ni/Al@MnAl ₂ O ₄ (DP)	9	129	0.22	7.0	9.7	6.4	48

^a The metal content in each catalyst after calcination (for WI samples) or drying (for DP samples) was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-OES). ^b The specific surface area, pore volume, and average pore diameter for each catalyst after calcination (for WI samples) or drying (for DP samples) were determined using N₂ physisorption. ^c The Ni dispersion and catalytic active surface area (CASA) for each catalyst after reduction with H₂ at 500 °C were determined based on the H₂ chemisorption. ^d The amount of chemisorbed CO₂ for each catalyst after reduction with H₂ at 500 °C was measured at room temperature.

X-ray diffraction (XRD) patterns were obtained to identify the bulk structures of the prepared supports and catalysts, and the spinel structure of the supports was confirmed to be as illustrated in Figure S3. For calcined Ni catalysts, the NiO crystalline phase (Joint Committee on Powder Diffraction Standards (JCPDS) number 47-1049) could not be identified due to the overlapping XRD peaks of the NiO and the MAI₂O₄ spinel phase (Figure S4). In the case of Ni/Al@MnAl₂O₄ (DP), the Mn₃O₄ phase (JCPDS 24-0734) was seen as well as the MnAl₂O₄ structure (JCPDS 10-0310). XRD peaks corresponding to the Al phase (JCPDS 04-0787) were confirmed for all core-shell supports-supported Ni catalysts, and it was noted that the Al metal peak intensity for supported Ni catalysts (DP) was weaker than that of Al metal for supported Ni catalysts (WI). This implied that using NH₄OH solution in the DP process caused partial transformation of the Al core into Al(OH)₃, which decreased the intensity of the XRD peak caused by Al metal. At that time, the Al(OH)₃ phase (JCPDS 20-0011) was developed, and nickel-aluminum oxide hydrate (JCPDS 22-0452) was observed for Ni/Al@MgAl₂O₄ (DP).

H₂ chemisorption was performed to determine the Ni dispersion, and the catalytically active surface areas (CASA) of all catalysts have been listed in Table 1. It is worth mentioning that the supported Ni catalyst prepared by the DP method showed much higher Ni dispersion and CASA than the Ni catalyst prepared using the WI method. This clearly supported the hypothesis that the DP method was better than the WI method for preparing highly dispersed Ni metal on the support. Moreover, the core-shell Al@MAI₂O₄ (M = Zn or Mg) support appeared to be more beneficial in providing for higher Ni dispersion than the MAI₂O₄ (M = Zn or Mg) spinel version. Among the prepared Ni catalysts, Ni/Al@MnAl₂O₃ (DP) showed the highest Ni dispersion and largest CASA.

CO₂ uptake was measured to determine the amounts of basic sites on the supports and catalysts. Table 1 shows that Mg was the most effective in increasing CO₂ uptake, with Zn the least effective. Mn was also seen as an effective component for CO₂ accommodation. Note that the supported Ni catalyst prepared using the DP method had higher CO₂ uptake than the Ni catalyst (WI) supported on the same support.

To further investigate the surface basicity of the prepared catalysts, temperature-programmed desorption of CO₂ (CO₂-TPD) was carried out to determine the basic strength of surface basic sites. Figure 1 shows that similar CO₂-TPD patterns were obtained for all Ni catalysts supported by spinel supports. A TPD peak for each catalyst appeared at ~100 °C, which can be assigned to the desorption of CO₂ from weak basic sites. The broad CO₂ desorption peak in the temperature range of 150–400 °C was reported to be attributed to the presence of medium basic sites, while CO₂ desorption peaks observed at temperatures > 500 °C, which only appeared for DP samples, were reported to be due to the strong basic sites [9].

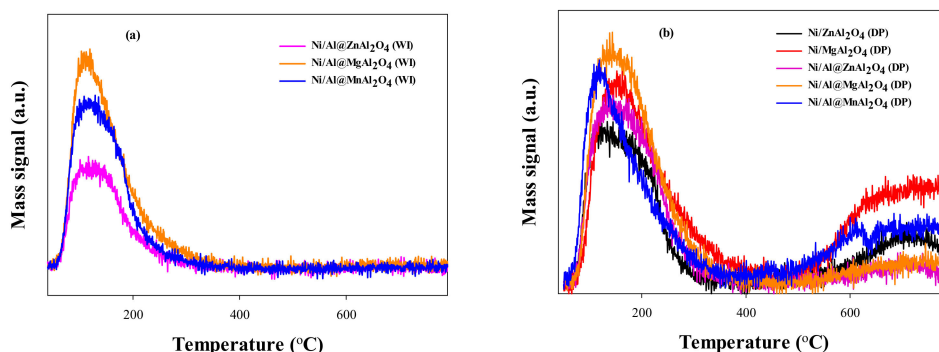


Figure 1. Temperature-programmed desorption of CO₂ (CO₂-TPD) profiles of supported Ni catalysts prepared using: (a) the wet impregnation (WI) method and (b) the deposition–precipitation (DP) method.

Note that CO₂ adsorption on weak and medium basic sites was a favorable outcome for the methanation process, whereas the strong basic sites could not participate in CO₂ activation [9,34]. It is still controversial to nominate which out of the weak or medium basic sites would be more favorable for CO₂ activation [7,9,35].

Figure 2 shows the infrared spectra recorded after the adsorption of CO₂, for 20 min at 40 °C, to consider distinct surface basicity. Two different basic sites on the Ni/Al@MAI₂O₄ (M = Zn, Mg, or Mn) can be distinguished: the weak basic site binding bicarbonate (at $\nu = 1650\text{ cm}^{-1}$, $\nu = 1430\text{ cm}^{-1}$ and $\nu = 1230\text{ cm}^{-1}$) and the strong basic site binding monodentate carbonate ($\nu = 1390\text{ cm}^{-1}$ and $\nu = 1550\text{ cm}^{-1}$) [7,36,37]. The density ratio of weak basic sites to strong basic sites, measured on Ni/Al@MAI₂O₄ (M = Zn or Mg) (DP), was higher than those measured for Ni/Al@MAI₂O₄ (M = Zn or Mg) (WI); Ni/Al@MnAl₂O₄ (DP) showed the highest figure comparing to Ni/Al@MgAl₂O₄ (DP) and Ni/Al@ZnAl₂O₄ (DP) (Table S2). Thus, Ni/Al@MnAl₂O₄ (DP) could support the achievement of high catalytic activity in CO₂ methanation, although Ni/Al@MgAl₂O₄ (DP) was also considered to be a potential candidate as it adsorbed the largest amount of CO₂. The similar trend was also observed for Ni/Al@MAI₂O₄ (M = Zn, Mg, or Mn) (WI) (Figure 2a, Table S2).

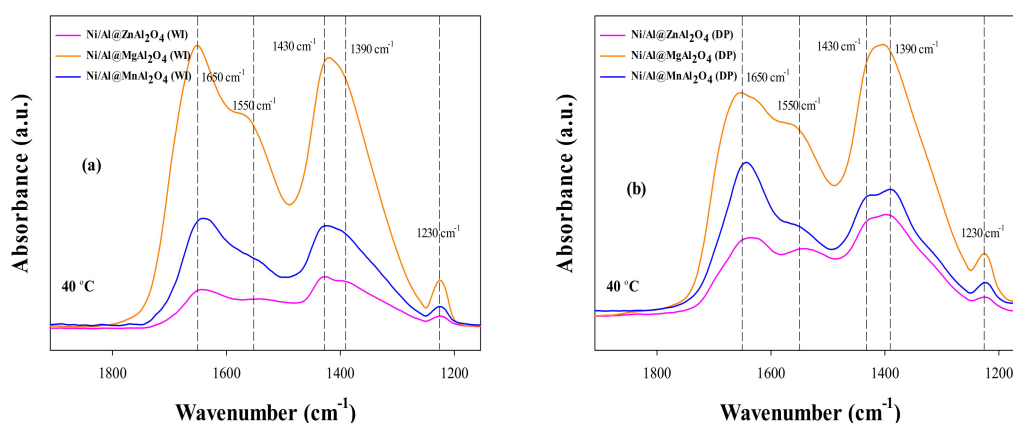


Figure 2. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) spectra for CO₂ adsorption at 40 °C on (a) Ni/Al@ZnAl₂O₄ (WI), Ni/Al@MgAl₂O₄ (WI), and Ni/Al@MnAl₂O₄ (WI) samples, and (b) Ni/Al@ZnAl₂O₄ (DP), Ni/Al@MgAl₂O₄ (DP), and Ni/Al@MnAl₂O₄ (DP) samples.

In order to investigate the effect of the catalyst preparation method on the interaction between CO₂ and surface basic sites on the catalyst surface, the in-situ CO₂ adsorption DRIFT spectra from 40 to 300 °C, on Ni/Al@MnAl₂O₄ (WI) and Ni/Al@MnAl₂O₄ (DP), were determined and have been collected in Figure S5. Based on the DRIFT spectra at 40 °C, it could be obtained that Ni/Al@MnAl₂O₄ (WI) had a lower fraction of weak basic sites than Ni/Al@MnAl₂O₄ (DP). As expected, this fraction of weak basic sites decreased with increasing reaction temperature due to the quick desorption of weakly

adsorbed CO₂. This in-situ DRIFTS study supported the concept that the DP method was better for providing weak basic sites than the WI method (Table S2).

Figure 3 shows the temperature-programmed reduction with H₂ (H₂-TPR) profiles of the supported Ni catalysts (WI) calcined at 500 °C (Figure 3a), and supported Ni catalysts (DP) dried at 110 °C (Figure 3b). In general, the TPR peak in the low-temperature range (210–250 °C) was due to the presence of NiO interacting weakly with the support. The high-temperature TPR peak in the temperature range (400–500 °C) indicated reduction of NiO species interacting strongly with the support [6,9,12]. A small negative TPR peak could be seen around 600 °C for the catalysts supported by Al@MnAl₂O₄ (M = Zn, Mg, or Mn), which could be attributed to the melting of Al core material. The comparison of H₂-TPR profiles implied that the DP method was more favorable for providing the NiO weakly interacting with the support, which resulted in a higher fraction of reduced Ni metal at the same reduction temperature.

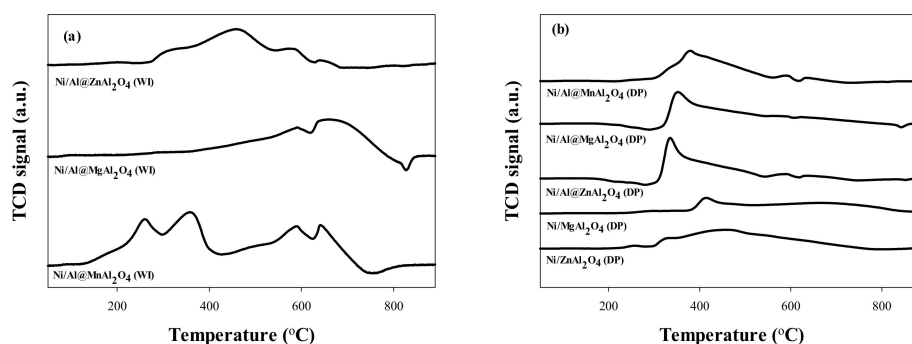


Figure 3. Temperature-programmed reduction with H₂ (H₂-TPR) profiles for supported Ni catalysts, prepared by (a) the WI method and (b) the DP method.

High-resolution transmission electron microscopy (HRTEM) images of Ni/Al@MnAl₂O₄ (WI) and Ni/Al@MnAl₂O₄ (DP) are presented in Figure 4. A rather uniform Ni metal particle size distribution with the average Ni particle size of ~10 nm and ~4 nm was obtained for Ni/Al@MnAl₂O₄ (WI) and Ni/Al@MnAl₂O₄ (DP), respectively. The typical scanning transmission electron microscope (STEM) dark field image and corresponding elemental maps confirmed that Mn, Ni, Al, and O elements were well distributed in both Ni/Al@MnAl₂O₄ (WI) and Ni/Al@MnAl₂O₄ (DP).

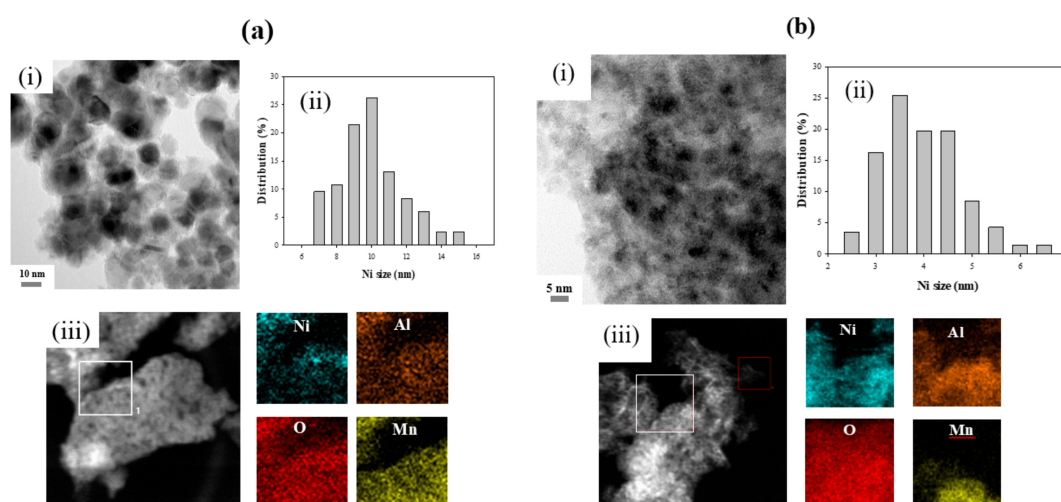


Figure 4. (i) High-resolution transmission electron microscopy (HRTEM) image, (ii) Ni particle size distribution, and (iii) elemental mapping for (a) reduced Ni/Al@MnAl₂O₄ (WI) and (b) reduced Ni/Al@MnAl₂O₄ (DP).

2.2. Catalytic Performance

CO and CO₂ methanation were carried out to examine the influences of the supports and the preparation method. Figure 5 shows that Al@MgAl₂O₄ and Al@MnAl₂O₄ were better supports than γ -Al₂O₃ in the provision of active Ni catalysts for CO and CO₂ methanation. On the other hand, Ni/Al@ZnAl₂O₄ (WI) was significantly inferior to Ni/ γ -Al₂O₃ (WI) for CO methanation. In CO methanation, the dispersed metallic Ni plays a key role because both H₂ and CO are adsorbed and activated on metallic Ni species [6]. Enhanced CO methanation activity was consistently related to improvement in the active Ni sites, when the catalytic activity for CO methanation decreased by the decrease of CASA in the following order: Ni/Al@MnAl₂O₄ (WI) > Ni/Al@MgAl₂O₄ (WI) > Ni/ γ -Al₂O₃ (WI) > Ni/Al@ZnAl₂O₄ (WI). The same trend can also be seen in Figure 6a for the catalysts prepared by the DP method. The DP method was confirmed as being better than the WI method to fabricate Ni-based catalysts with high metallic dispersion [12], so as a result, the significant improvement of Ni dispersion with the higher CASA of Ni/Al@MAl₂O₄ (DP), compared with Ni/Al@MAl₂O₄ (WI), contributed to the improved CO methanation. Figure 6 shows that Al@MAl₂O₄ was a better support than MAl₂O₄ for CO and CO₂ methanation over supported Ni catalysts.

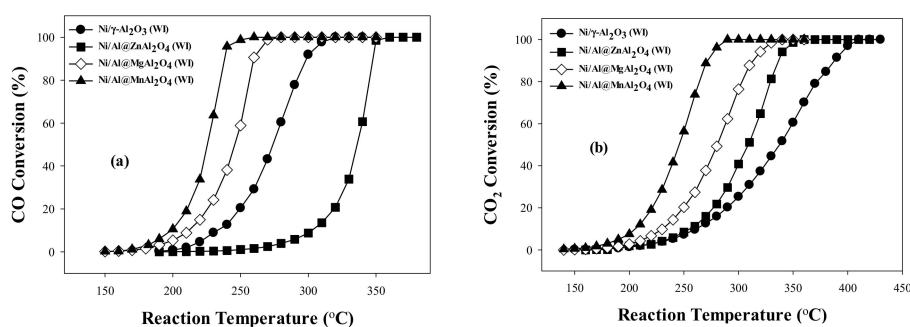


Figure 5. Catalytic performance of supported Ni catalysts prepared using the WI method for (a) CO methanation and (b) CO₂ methanation. All catalysts were reduced in H₂ at 500 °C. Reaction conditions: 1 mol.% CO (or CO₂), 50 mol.% H₂, 49 mol.% He, F/W = 1000 mL/min/g_{cat}. The catalytic activity of Ni/γ-Al₂O₃ [12] has been reproduced for comparison.

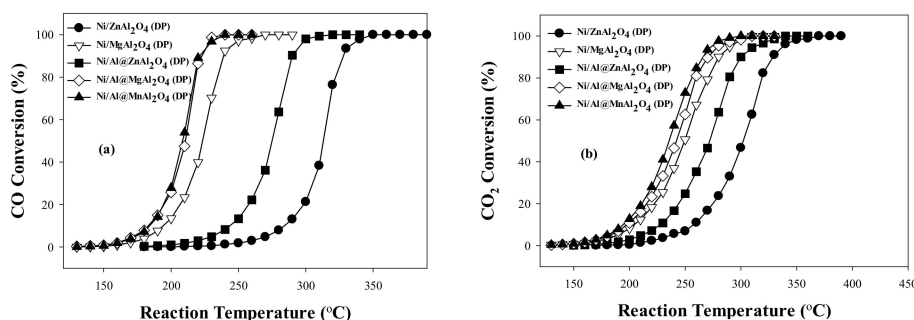


Figure 6. Catalytic performance of supported Ni catalysts prepared using the DP method for (a) CO methanation and (b) CO₂ methanation. All catalysts were reduced in H₂ at 500 °C. Reaction conditions: 1 mol.% CO (or CO₂), 50 mol.% H₂, 49 mol.% He, F/W = 1000 mL/min/g_{cat}.

In terms of product yield, methane was the predominant product at all reaction temperatures, while ethane and propane were also detected as CO methanation process byproducts (Figures S6 and S8). It was notable though that although Al@ZnAl₂O₄ and ZnAl₂O₄ did not help to improve Ni dispersion, they did show potential for providing high selectivity for methane by inhibiting long-chain hydrocarbon formation. On the other hand, the adsorption and activation of CO₂ mainly occurred on the support through the intermediate formation of either CO or carbonate and hydrogenate species [38]. High CASA supplied high surface H concentration for the hydrogenation of intermediates species, and the high CO₂ uptake capacity, coupled with strong interactions with catalyst surfaces,

promoted high catalytic activity for CO₂ methanation. The DP method was also better here in enhancing the amounts of basic sites, as well as strengthening CO₂ adsorption, than the WI method. Typically, the desorbed CO₂ peaks over Ni/Al@MnAl₂O₄ (DP) in Figure 1 were observed at higher temperatures and showed increased peak intensity when compared to Ni/Al@MnAl₂O₄ (WI).

These results, combined with the high CASA, showed that Ni/Al@MnAl₂O₄ (DP) (Figure 6b) outperformed Ni/Al@MnAl₂O₄ (WI) (Figure 5b) in CO₂ methanation. Ni/Al@MgAl₂O₄ (DP) exhibited slightly lower CO₂ methanation activity than Ni/Al@MnAl₂O₄ (DP), although both catalysts had similar Ni dispersion. Note that the former catalyst had the higher fraction of weak basic sites than the latter; and also note that Ni/Al@MnAl₂O₄ (WI), with lower fraction of basic sites, still showed greater catalytic activity than Ni/Al@MgAl₂O₄ (WI), which illustrated the synergistic effect in CO₂ methanation between Ni dispersion and CO₂ uptake.

In terms of product selectivity, methane was the predominant product for all Ni-based catalysts during CO₂ methanation (Figures S7 and S9). C₂H₆ was also obtained, though as a byproduct with a very small yield (up to 0.2%). The formation of CO as an intermediate was observed over supported Ni catalysts containing the ZnAl₂O₄ phase, with in-situ DRIFTS analysis (not shown here). The core-shell Al@ZnAl₂O₄ was better than ZnAl₂O₄ as a support for supported Ni catalysts in obtaining much less byproduct CO. The activity comparison between Ni/MAl₂O₄ (DP) and Ni/Al@MAl₂O₄ (DP) showed that the latter was superior, irrespective of the model reactions. In order to easily compare the catalytic performance among catalysts in this study, the reaction temperatures achieving 50% and 90% conversions of CO or CO₂ were determined for each catalyst and summarized in Table S3. Ni/Al@MnAl₂O₄ (DP) catalyst exhibited the best catalytic activity both for CO and CO₂ methanation (Table S3), which could be explained by the fact that it had the largest CASA among the tested catalysts and comparable CO₂ uptake with the Ni/Al@MgAl₂O₄ (DP)—which had the largest CO₂ uptake. Apart from their high catalytic activity, Ni/Al@MAl₂O₄ (DP) catalysts had an additional advantage for heat transfer across the catalyst particulates, as the Al metal core had high heat conductivity.

The stability of Ni/Al@MnAl₂O₄ (DP) during CO and CO₂ methanation was also examined. Figure 7a shows that the stable catalytic performance was maintained, for both CO and CO₂ methanation, for 50 h. XRD data (Figure 7b) and HRTEM images (Figure 7c) for the spent catalysts showed neither coke deposition nor Ni particle agglomeration.

The best Ni/Al@MnAl₂O₄ (DP) was chosen for further study in order to investigate the different surface intermediate evolution routes during CO₂ methanation at different temperatures. As shown in Figure 8, the immediate appearance of new bands at 3016, 2840, 1595, 1376, and 1304 cm^{−1}, accompanied by apparent attenuation of the carbonates bands at 1650, 1550, 1430, and 1230 cm^{−1}, could be seen at low reaction temperatures, with the new bands at 3016 and 1304 cm^{−1} evidently methane. The other new peaks were divided into two groups: (i) 2840, 1595, and 1376 cm^{−1} and (ii) 1340 cm^{−1}, and these were assigned to bidentate and monodentate formate species, respectively [7,9,21,39–42].

With increased reaction temperature, the bands corresponding to formate species became larger, reaching a maximum at 250 °C with the continuous consumption of carbonates, suggesting that the steady supply of H₂ facilitated transformation of carbonates into formate species. The peaks of the formate species decreased along with the continuous formation of surface methane species. Consequently, the possible mechanism for the CO₂ methanation over Ni/Al@MnAl₂O₄ (DP) catalyst was deduced to be that the CO₂ was first adsorbed onto the support as carbonates species, which was hydrogenated into formate species and subsequently further hydrogenated to produce methane as the final product—which is consistent with some previous reports on CO₂ methanation over supported Ni catalysts [4,8,21,34,40]. In this study, CO was also observed under our reaction conditions over Ni/ZnAl₂O₄ (DP), and Ni/Al@ZnAl₂O₄ (DP), which implied that the catalytic reaction mechanism involving CO as an intermediate [39,43], was also working over these catalysts.

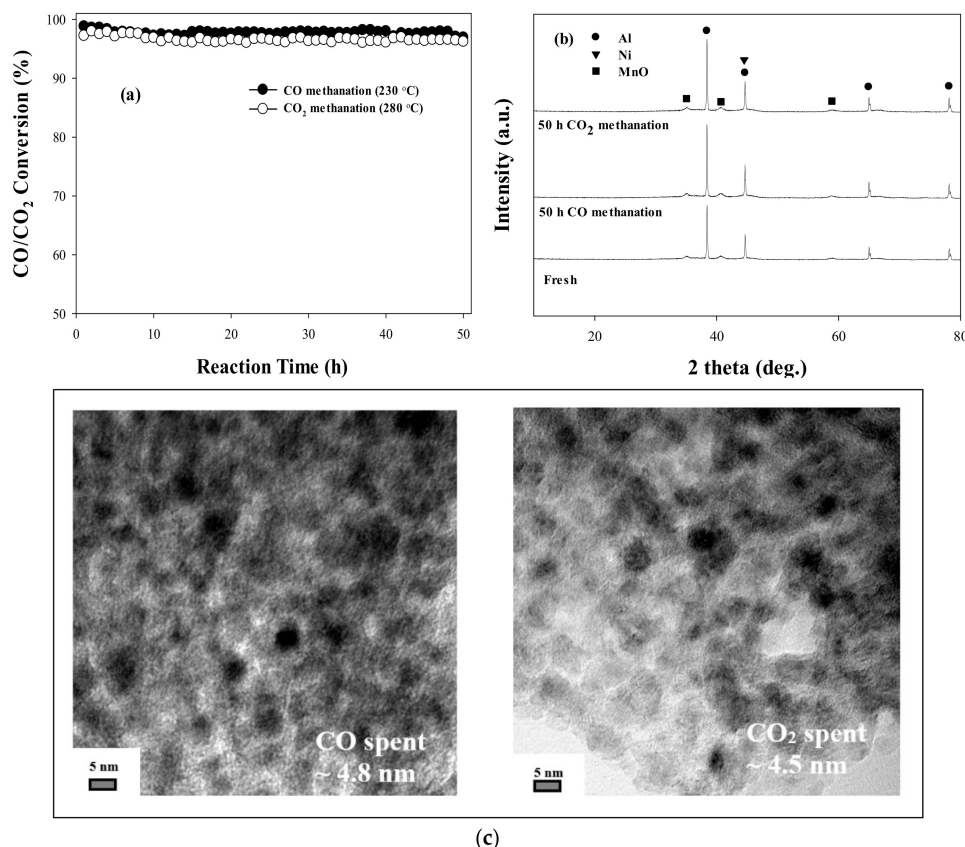


Figure 7. (a) Stability test for Ni/Al@MnAl₂O₄ (DP) for CO and CO₂ methanation during 50 h, (b) XRD patterns of fresh and spent catalysts, (c) HRTEM images of spent catalysts. Reaction conditions: 1 mol.% CO (or CO₂), 50 mol.% H₂, 49 mol.% He, F/W = 1000 mL/min/g_{cat}.

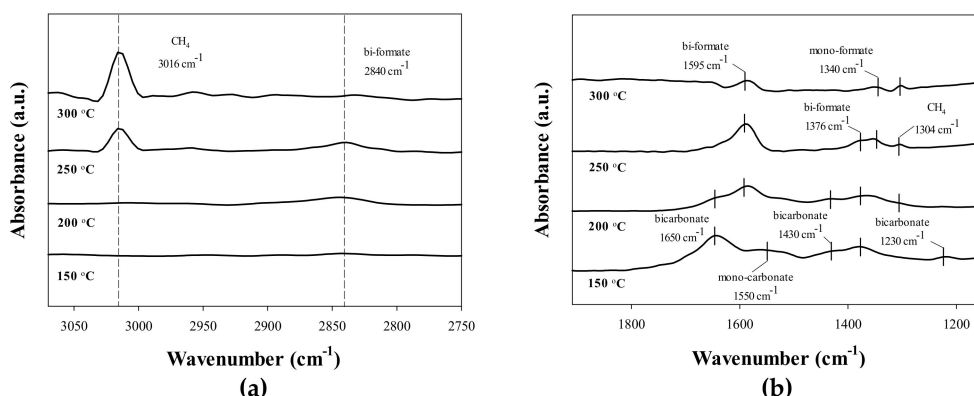


Figure 8. In-situ DRIFT spectra of CO₂ methanation on Ni/Al@MnAl₂O₄ (DP) from 150 to 300 °C in wavenumber range 2750–3070 cm⁻¹ (a) and in wavenumber range 1150–1910 cm⁻¹ (b). Total flow of 50 mL/min: 1 mol.% CO₂, 50 mol.% H₂, 49 mol.% He.

3. Experimental

3.1. Support Synthesis

Core-shell Al@MAl₂O₄ (M = Zn, Mg, or Mn) supports were prepared using the HTSO method, as previously described [31].

Spinel MgAl₂O₄ and ZnAl₂O₄ were synthesized using the coprecipitation method. 0.1 mol of either Mg(NO₃)₂·6H₂O (Kanto Chemical Co. Ltd., Tokyo, Japan) or Zn(NO₃)₂·6H₂O (Daejung

Chemicals & Metals Co. Ltd., Siheung, Korea) and 0.2 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Junsei Chemical Co. Ltd., Tokyo, Japan) were dissolved in deionized (DI) water, to which 1 M NH_4OH (Samchun Pure Chemical Co. Ltd., Pyeongtaek, Korea) was added dropwise with constant stirring to reach the pH 9.5. The precipitate mixture was aged for 4 h under stirring and was then filtered, washed thoroughly with DI water, and then dried in a vacuum oven at 110 °C for 12 h. The dried precipitate was then calcined in air at 600 °C for 4 h to obtain the spinels ZnAl_2O_4 and MgAl_2O_4 .

3.2. Catalyst Preparation

The supported Ni catalyst, prepared from an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Junsei Chemical Co. Ltd., Tokyo, Japan) and core-shell spinel support using the conventional WI method, has been denoted as $\text{Ni}/\text{Al}@\text{MAl}_2\text{O}_4$ (WI). For comparison, the $\gamma\text{-Al}_2\text{O}_3$ -supported Ni catalyst was also prepared with $\gamma\text{-Al}_2\text{O}_3$ (neutral, Alfa Aesar) using the WI method, and has been designated as $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ (WI) in the previous study [12]. Both $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ (WI) and $\text{Ni}/\text{Al}@\text{MAl}_2\text{O}_4$ ($\text{M} = \text{Zn}, \text{Mg}, \text{or Mn}$) (WI) were obtained after calcination in air at 500 °C and subsequent reduction in an H_2 stream at 500 °C.

The DP method was applied to prepare the spinel-supported Ni catalysts [12]. Typically, 2.91 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Junsei Chemical Co. Ltd., Tokyo, Japan) was dissolved in 50 mL DI water. This solution was contacted with 5.3 g of spinel support, and 1.0 M aqueous NH_4OH solution was added to this slurry drop by drop until reaching pH 9 and was then left being stirred for 12 h at room temperature. The slurry was filtered and washed several times with DI water until there was no further pH change (pH = 7). The recovered powder was dried in an oven at 110 °C for 12 h. This dried sample was further reduced in the H_2 stream at 500 °C for 1 h before catalytic checking. The resulting catalysts have been denoted as $\text{Ni}/\text{MAl}_2\text{O}_4$ ($\text{M} = \text{Zn}$ or Mg) (DP) and $\text{Ni}/\text{Al}@\text{MAl}_2\text{O}_4$ ($\text{M} = \text{Zn}, \text{Mg}, \text{or Mn}$) (DP). The Ni content for all supported Ni catalysts was intended to be 10 wt.%, which was confirmed using inductively coupled plasma-atomic emission spectroscopy (ICP-OES).

3.3. Catalyst Characterization

N_2 physisorption, ICP-OES, XRD, H_2 -TPR, pulsed CO_2 chemisorption and CO_2 -TPD, in-situ DRIFTS, and HRTEM analyses were carried out as described in the Supporting Information. CASA and Ni dispersion were determined for each catalyst by H_2 chemisorption using a Micromeritics ASAP 2020 instrument, as described previously [6].

3.4. Catalytic Evaluation

CO and CO_2 methanation were carried out as done previously [5] with the methodology reproduced in the Supplementary Information.

4. Conclusions

Application of core-shell $\text{Al}@\text{MAl}_2\text{O}_4$ ($\text{M} = \text{Zn}, \text{Mg}, \text{or Mn}$) spinel materials to supported Ni catalysts improved the Ni dispersion in comparison to $\gamma\text{-Al}_2\text{O}_3$. This high Ni dispersion appeared to be responsible for high catalytic activity in CO methanation. Furthermore, the improved number of basic sites with proper basic strength observed on $\text{Ni}/\text{Al}@\text{MAl}_2\text{O}_4$ benefitted CO_2 methanation. A CO_2 methanation mechanism via the formate route was proposed over $\text{Ni}/\text{Al}@\text{MnAl}_2\text{O}_4$, based on the in-situ DRIFTS study. Core-shell $\text{Al}@\text{MnAl}_2\text{O}_4$ spinel was determined to be the most active and stable support—in terms of high catalytic activity and excellent stability in CO and CO_2 methanation—for supported Ni catalyst prepared using the DP method.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/7/599/s1>. The detailed procedure for the catalyst characterization and catalytic evaluation. Figure S1: N_2 adsorption and desorption isotherms of supported Ni catalysts prepared by WI method. Figure S2: N_2 adsorption and desorption isotherms of supported Ni catalysts prepared by DP method. Figure S3: X-ray diffraction patterns of the prepared supports. Figure S4: X-ray diffraction patterns of supported Ni catalysts calcined in air at 500 °C for WI samples (a, b, c), dried at 110 °C for DP samples (a, b, c), and core-shell supported Ni (DP) samples reduced in H_2 at 500

°C (d). Figure S5: In-situ DRIFT spectra of CO₂ adsorption from 40 to 300 °C on (a) Ni/Al@MnAl₂O₄ (WI) and (b) Ni/Al@MnAl₂O₄ (DP). Figure S6: Product yield for CO methanation over Ni/Al@MnAl₂O₄ (M = Zn, Mg, or Mn) (WI). Figure S7: Product yield for CO₂ methanation over Ni/Al@MnAl₂O₄ (M = Zn, Mg, or Mn) (WI). Figure S8: Product yield for CO methanation over Ni/MAl₂O₄ (M = Zn or Mg) (DP) and Ni/Al@MnAl₂O₄ (M = Zn, Mg, or Mn) (DP). Figure S9: Product yield for CO₂ methanation over Ni/MAl₂O₄ (M = Zn or Mg) (DP) and Ni/Al@MnAl₂O₄ (M = Zn, Mg, or Mn) (DP). Table S1: Physical properties of the support. Table S2: Basic sites distribution of Ni/Al@MnAl₂O₄ (M = Zn, Mg, or Mn) (WI) and (DP) samples determined by deconvolution of DRIFT spectra after CO₂ adsorption at 40 °C. Table S3: Comparison of catalytic activity for CO and CO₂ methanation over supported Ni catalysts. Table S1. Physical properties of the support. Table S2. Basic sites distribution of Ni/Al@MnAl₂O₄ (M = Zn, Mg, or Mn) (WI) and (DP) samples determined by deconvolution of DRIFT spectra after CO₂ adsorption at 40 °C. Table S3. Comparison of catalytic activity for CO and CO₂ methanation over supported Ni catalysts.

Author Contributions: T.A.L. and E.D.P. designed and administered the experiments; T.A.L. performed and collected data; J.K. synthesized core-shell supports; Y.R.J. conducted temperature-programmed analysis; and T.A.L. and E.D.P. analyzed and wrote the paper.

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