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High CO Methanation Performance of Two-Dimensional Ni/MgAl Layered Double Oxide with Enhanced Oxygen Vacancies via Flash Nanoprecipitation

Mengjuan Zhang¹, Feng Yu^{1,*}, Jiangbing Li¹, Kai Chen^{1,3}, Yongbin Yao¹, Panpan Li¹, Mingyuan Zhu¹, Yulin Shi¹, Qiang Wang^{1,2,*} and Xuhong Guo^{1,3,*}

- Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, China; mengjuanzhang2017@126.com (M.Z.); ljbin@shzu.edu.cn (J.L.); chenkai@shzu.edu.cn (K.C.); yongbinyao0321@sina.com (Y.Y.); ppl_19910109@163.com (P.L.); zhuminyuan@shzu.edu.cn (M.Z.); shiyulin521@126.com (Y.S.)
- ² Environmental Functional Nanomaterials (EFN) Laboratory, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China
- ³ State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China
- * Correspondence: yufeng05@mail.ipc.ac.cn (F.Y.); qiang.wang.ox@gmail.com (Q.W.); guoxuhong@ecust.edu.cn (X.G.); Tel.: +86-993-205-7272 (F.Y. & Q.W. & X.G.); Fax: +86-993-205-7270 (F.Y. & Q.W. & X.G.)

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Abstract: As a methanation tool, two-dimensional (2D) carrier-loaded Ni has attracted the attention of many researchers. We successfully prepared 2D MgAl layered double oxides (LDO) carriers via flash nanoprecipitation (FNP). Compared to the LDO samples prepared by conventional co-precipitation (CP), the 2D MgAl-LDO (FNP) has more oxygen vacancies and more exposed active sites. The Ni/MgAl-LDO (FNP) catalyst demonstrates a CO conversion of 97%, a CH₄ selectivity of 79.8%, a turnover frequency of 0.141 s⁻¹, and a CH₄ yield of 77.4% at 350 °C. The weight hourly space velocity was 20,000 mL·g⁻¹·h⁻¹ with a synthesis gas flow rate of 65 mL·min⁻¹, and a pressure of 1 atm. A control experiment used the CP method to prepare Ni/MgAl-LDO. This material exhibits a CO conversion of 81.1%, a CH₄ selectively of 75.1%, a TOF of 0.118 s⁻¹, and a CH₄ yield of 61% at 450 °C. We think that this FNP method can be used for the preparation of more 2D LDO catalysts.

Keywords: CO methanation; oxygen vacancy; layered double oxide; synthesis gas; synthetic natural gas; flash nanoprecipitation

1. Introduction

Natural gas (i.e., methane) is a popular clean energy source that provides an important process to remedy air pollution. Coal currently accounts for 66% of the total energy consumption in China [1–3], which is produced by synthetic natural gas (SNG) by C1 chemical processes [4,5]. Another approach converts CO waste gas to methane [6–8]. Supported Ni-based catalysts are widely used for CO methanation due to their high catalytic activities and low cost [9]. In recent years, two-dimensional materials have been used to prepare catalyst carriers due to their larger surface area and more active sites. From previous reports, two-dimensional (2D) SiO₂ nanomesh was successfully prepared and supported Ni nanoparticles for CO methanation [10,11]. Versus three-dimensional (3D) MCM-41



molecular sieve catalysts (Ni/3D-MCM-41), the Ni/2D-SiO₂ catalyst showed remarkable catalytic activity with high CO conversion and CH₄ selectivity at 450 $^{\circ}$ C.

Natural mineral vermiculite (VMT) with a 2D structure as a catalyst support was reported [12]. Li et al. [13] attempted to expand multilayered vermiculite as a catalyst support and successfully synthesized NiO/VMT composite by microwave irradiation-assisted synthesis (MIAS). The Ni/VMT (MIAS) resulted in highly dispersed active sites and exhibited excellent catalysis performance, including a 99.6% CO conversion and 93.8% CH₄ selectivity at 400 °C. Zhang et al. [14] synthesized a 2D plasma-treated vermiculite (PVMT) with low Ni loading (0.5 wt %) via a plasma irradiation method (PIM). The PIM-Ni/PVMT exhibited superior catalytic performance, and the plasma-treated catalyst PIM-Ni/PVMT achieved a CO conversion of 93.5% and a turnover frequency (TOF) of 0.8537 s⁻¹ at a temperature of 450 °C and a pressure of 1.5 MPa.

Other 2D catalysts for CO methanation include 2D Ni-based layered double oxides (LDO) from layered double hydroxides (LDH). These systems are popular because of their high Ni dispersibility [15,16]. NiAl-LDO offers excellent activity for methanation under 2.0 MPa and 527 °C. NiAl-LDO catalysts with 56.5 wt % Ni achieved 97% CO conversion in a pilot methanation unit. Bian et al. [17] synthesized a NiAl-LDO catalyst that displayed high catalytic stability due to high Ni dispersion and strong resistance to coke deposition versus the impregnated catalyst. Nearly 100% CO conversion was achieved with reaction temperatures between 400 and 500 °C with a weight hourly space velocity (WHSV) of 300,000 mL·g⁻¹·h⁻¹.

Mg adulteration can also improve the anti-coke ability of Ni-based catalysts. Li et al. [18] synthesized Ni-Mg-Al LDO (i.e., NiMg8, Ni/Mg = 1/8) via a co-precipitation method. The as-obtained catalyst with 11 wt % Ni had the best CO methanation performance due to the small size of Ni particles and high Ni dispersion. The NiMg8 had excellent performance: 99.8% CO conversion and 73.6% CH₄ selectivity at 550 °C. Li et al. [19] synthesized Ni/VMT-LDO via an impregnation method. The results showed that Fe and Ca modification improved the dispersion of nickel. Additionally, the small Ni nanoparticles led to great performance. Furthermore, the Ni/VMT-LDO catalyst offered good low temperature activity with 87.9% CO conversion and 90% CH₄ selectivity at 400 °C.

From our previous work [20], the facile flash nanoprecipitation (FNP) method was used to synthesize Mn-Ce-Al mixed metal oxide as SCR catalysts for de-NO_x. Herein, we successfully synthesized 2D MgAl-LDO support with a high concentration of oxygen vacancies via the facile FNP method. The results showed that 2D MgAl-LDO (FNP) supports exhibited more oxygen vacancies than 2D MgAl-LDO (CP). The 2D MgAl-LDO (FNP)-supported Ni nanoparticles presented abundant active sites for CO methanation reactions and exhibited excellent catalytic performance. FNP is a simple, novel, and scalable method that can produce nanoparticles with a multi-inlet vortex mixer [21,22]. We think that FNP provides a powerful method to prepare 2D LDOs, which shows considerable potential as a catalyst.

2. Results and Discussion

Figure 1a,b show the catalytic performance of the obtained catalysts with a weight hourly space velocity (WHSV) of 20,000 mLg⁻¹ h⁻¹. Notably, the CO conversion of Ni/MgAl-LDO (CP) catalyst neared zero, whereas that of Ni/MgAl-LDO (FNP) achieved about 18% at 250 °C. With increasing temperature, for the Ni/MgAl-LDO (FNP) catalyst, CO conversion sharply rose and achieved a maximum CO conversion of 97% and a CH₄ selectivity of 79.8% at 350 °C. However, the Ni/MgAl-LDO (FNP) catalyst reached a maximum CO conversion of 81.1% and CH₄ selectivity of 75.1% at 450 °C. Compared with the Ni/MgAl-LDO (CP) catalyst, the Ni/MgAl-LDO (FNP) demonstrated remarkable catalytic activity at low temperature and a broader temperature range for target production.

The turnover frequency (TOF) value of the samples was a key dependent variable for the catalytic performance, as shown in Figure 1c. From the results, the TOF of Ni/MgAl-LDO (FNP) was considerably greater than Ni/MgAl-LDO (CP) [23,24], and the highest TOF value was obtained at

350 °C of about 0.14 s⁻¹. From Figure 1d, the CH₄ yield of Ni/MgAl-LDO (FNP) reached a maximum value at 350 °C of about 79.6%. However, that of Ni/MgAl-LDO (CP) reached a maximum at 450 °C of about 59.8%. Overall, in terms of CO conversion, CH₄ selectivity, and TOF, the catalytic performance of the Ni/MgAl-LDO (FNP) catalyst was clearly superior to that of the Ni/MgAl-LDO (CP) catalyst. Table 1 summarizes CO methanation from the literature using Ni/MgAl-LDO catalyst systems. The metrics for Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP) catalysts are also shown, which are comparable to those reported in the literature.

X-Ray Diffraction (XRD) was used to characterize the physical structure of the obtained materials and the results are shown in Figure 2. For the precursor supports, there were several diffraction peaks at 11.7°, 23.6°, 35.2°, 39.7°, 46.3°, 61.3°, 62.7°, 66.7°, and 75.7°, which were ascribed to the MgAl hydrotalcite phase (JCPDS NO. 22-0452). This indicated that both synthetic methods were effective methods of obtaining hydrotalcite. After being calcined, the characteristic diffraction peaks were observed at 36.9°, 42.9°, 62.3°, 74.7°, and 78.6°, which belong to MgO (PDF # 45-0946) [25]. There were no obvious peaks for aluminum, probably due to the Al amorphous lattice of hydrotalcite materials [19,26].



Figure 1. (a) Carbon monoxide (CO) conversion; (b) methane (CH₄) selectivity values; (c) turnover frequency (TOF) values; (d) CH₄ yield of the as-obtained Ni/MgAl-LDO co-precipitation (CP) and Ni/MgAl-LDO flash nano-precipitation (FNP).

Table 1.	Com	parison	of two-	dimens	sional	(2D)) cataly	vsts	prei	pared	via	different	method	ds.
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2D Catalysts	Ni Content	Preparation Method	Optimum Temperature (°C)	Pressure (Mpa)	Gas Hourly Space Velocity mL∙g ^{−1} ∙h ^{−1}	CO Conversion (%)	CH ₄ Selectivity (%)	Reference
Ni/VMT (MIAS)	10 wt.%	MIAS	400	1.5	12,000	99.6	93.8	[13]
PIM-Ni/PVMT	0.5 wt.%	PIM	450	1.5	6000	93.5	64	[14]
NiAl-LDO	56.5 wt.%	Urea hydrolysis	400	0.1	15,000	98	92	[17]
NiMg8	22 wt.%	CP method	400	0.1	30,000	98	90	[18]
Ni/VMT-LDO	10 wt.%	CP method	400	1.5	20,000	87.9	90	[19]
Ni/MgAl-LDO (CP)	10 wt.%	CP method	450	0.1	20,000	81.12	75.14	This work
Ni/MgAl-LDO (FNP)	10 wt.%	FNP method	350	0.1	20,000	97	79.76	This work

Note: Vermiculite and plasma-treated vermiculite are abbreviated as VMT and PVMT, respectively; LDO stands for layered double oxide. MIAS, PIM, CP, and FNP are microwave irradiation assisted synthesis, plasma irradiation method, co-precipitation, and flash nanoprecipitation, respectively.



Figure 2. X-ray diffraction (XRD) patterns of MgAl-LDH (CP), MgAl-LDH (FNP), MgAl-LDO (CP), and MgAl-LDO (FNP).

In order to confirm the layered structures of the MgAl-LDO (FNP) and MgAl-LDO (CP), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were used to obtain the images, as shown in Figure 3a–d. From the images, both samples exhibited lamination structures, and that of MgAl-LDO (CP) was thicker than the MgAl-LDO (FNP) catalyst. This indicated that the fast mixing speed and violent collision of the FNP method prevented the normal growth cycle of oxide crystals [27].

Figure 3e shows N₂ absorption and desorption isotherms of MgAl-LDO (CP) and MgAl-LDO (FNP) catalysts. These were type IV isotherms according to the IUPAC classification, which suggests that the materials were mesoporous [28]. From the pore size distribution curve of the MgAl-LDO (CP), a small peak at 10–70 nm was observed, and the average pore size was about 21.4 nm. However, the pore size distribution peak was centered at 10–90 nm, and the average pore size was about 19.3 nm. The BET surface areas of MgAl-LDO (FNP) of about 162 m²/g was higher than MgAl-LDO (CP) at about 119 m²/g. Additionally, the pore volume of the MgAl-LDO (FNP) also increased more than that of the sample using the CP method, as shown in Figure 3f. The enhanced pore structure was conducive to gas adsorption as well as heat and mass transfer in the CO methanation reaction, which was helpful to improve the catalyst efficient [29].



Figure 3. Cont.



Figure 3. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of (**a**,**c**) MgAl-LDO (CP); (**b**,**d**) MgAl-LDO (FNP); atomic force microscopy (AFM) images of (**c**) MgAl-LDO; (CP) and (**d**) MgAl-LDO (FNP). (**e**) N₂ adsorption-desorption isotherm. (**f**) Pore size distribution of Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP).

Atomic force microscopy (AFM) was used to study the thickness of the MgAl-LDO nanosheets, as shown in Figure 4. From previous reports, the AFM images demonstrated obvious bright specks, which represent the nanosheets of the samples [27]. From the results of the corresponding height curves, there was an obvious platform, which is a key characteristic of nanosheets. The thickness of the MgAl-LDO (CP) nanosheets was about 9.0 nm, and that of the MgAl-LDO (FNP) nanosheets was about 4.5 nm. This indicated that the hydrotalcate materials obtained using the FNP method prevented the accumulation of nanosheets, and resulted in thinner nanosheets, thereby improving the dispersion of Ni and offering many more active sites [30,31].



Figure 4. AFM images of (**a**) MgAl-LDO (CP), (**b**) MgAl-LDO (FNP) nanosheets, and the corresponding height curves of (**c**) MgAl-LDO (CP) and (**d**) MgAl-LDO (FNP).

X-ray photoelectron spectroscopy (XPS) was used to study the surface chemical composition and valence states of elements in the supports, as shown in Figure 5. From Figure 5a, there were obvious characteristic peaks of Al, O, and Mg elements in both samples. The peaks at 1303.3 eV and 1302.9 eV were attributed to the Mg1s spectrum of MgAl-LDO (CP) and MgAl-LDO (FNP) samples, respectively, as shown in Figure 5b. For the Al 2p orbitals, the spectra peaks of MgAl-LDO (CP) and MgAl-LDO (FNP) samples appeared at 73.6 eV and 73.9 eV, respectively, as shown in Figure 5c. Compared with MgAl-LDO (CP), the small peak shift toward higher binding energies for both Mg (0.4 eV) and Al (0.3 eV) suggested a decrease in the oxidation state of the transition metals [32]. From the findings, the XPS peak migration of metal oxides caused the lattice distortion of metal, which resulted in more defective sites and active sites [33,34]. Additionally, the introduction of oxygen vacancies was balanced by the lowered valence state of Mg and Al sites.



Figure 5. X-ray photoelectron spectroscopy (XPS) spectra of the as-obtained MgAl-LDO (CP) and MgAl-LDO (FNP). (**a**) Survey spectra, (**b**) Mg, (**c**) Al, and (**d**) O.

The O 1s peaks of the samples were divided into three peaks at about 530 eV, 531 eV, and 532 eV, as shown in Figure 5d. The peak at 530 eV was attributed to lattice oxygen from metallic oxide; the peak at 531 eV was attributed to the adsorbed oxygen from adsorbed H₂O, CO₂, and O₂; and the peak at 532 eV was attributed to surface oxygen from the -OH species [35,36]. From the diffraction pattern, the lattice oxygen peak area of MgAl-LDO (FNP) was bigger than that of MgAl-LDO (CP). This indicated that more oxygen vacancies existed on the surface of the MgAl-LDO (FNP) [37]. The abundant lattice oxygen provided external assistance to complete the oxygen cycle during the catalytic reaction [33].

After loading the active component Ni, XRD of the as-obtained materials was further characterized and the results are shown in Figure 6. The diffraction pattern of the Ni/MgAl-LDH (CP) and Ni/MgAl-LDH (FNP) materials highlights a hydrotalcite structure at $2\theta = 11.7^{\circ}$, 23.6° , 35.2° , 39.7° , 46.3° , 61.3° , 62.7° , 66.7° , and 75.7° , which were ascribed to the MgAl hydrotalcite phase (JCPDS NO. 22-0452) [38]. This confirmed that MgAl-LDO transformed into MgAl-LDH via the nickel solution treatment. The diffraction pattern of the Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP) materials

showed clear diffraction peaks corresponding to the MgO phase, including peaks at 36.9°, 42.9°, 62.3°, 74.7°, and 78.6° corresponding to MgO (PDF # 45-0946) [39]. There were no obvious peaks for nickel and aluminum, which was probably because nickel and aluminum were not detected in the hydrotalcite lattice or NiO was well-dispersed on the catalyst surface [18].



Figure 6. XRD patterns of Ni/MgAl-LDH (CP), Ni/MgAl-LDH (FNP), Ni/MgAl-LDO (CP), and Ni/MgAl-LDO (FNP).

Figure 7a–d show the TEM and HRTEM images of the Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP) catalysts. The layered structure of the supports was damaged after high temperature treatment. From Figure 7e, Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP) catalysts presented two type IV isotherms, which were is the key feature of mesoporous materials. The BET surface areas of Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP) were 218 m²/g and 214 m²/g, respectively. The slight increasing BET surface area of Ni/MgAl-LDO (CP) might be due to the tiny pores produced via Ni/MgAl-LDO transferred from Ni/MgAl-LDH (i.e., Ni-MgAl-LDH). The Ni/MgAl-LDH was easily formed from MnAl-LDO when added to Ni(NO₃)₂·6H₂O solution in the impregnation progress. Figure 7f shows that the pore volume and pore size of Ni/MgAl-LDO (CP) were 0.5 cm³/g and 10.2 nm, respectively. The corresponding MgAl-LDO (FNP) values were 0.4 cm³/g and 7.4 nm, which agreed with the HRTEM images results [18].

The XPS diffraction curves of the obtained materials are shown in Figure 8. For both samples, the peaks with a binding energy of 853 eV were attributed to Ni⁰. The peaks at 856.2 eV and 862.7 eV were assigned to Ni 2p3/2 and satellite peak, respectively. Similarly, the two peaks with binding energies of 873.7 eV and 879.6 eV were assigned to Ni2p1/2 and its satellite peak for Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP), respectively [40]. From Table 2, the proportion of Ni content was about 1.85% for the amount of elements on the Ni/MgAl-LDO (FNP) surface, and that of Ni/MgAl-LDO (CP) was 1.16%. This suggested that Ni was easily exposed to the catalyst surface via the FNP method, which was conducive to surface catalytic reaction. Furthermore, the radio of Ni⁰/Ni and Ni²⁺/Ni were about 4.7% and 48.6% for Ni/MgAl-LDO (FNP), respectively, which were higher than for Ni/MgAl-LDO (CP) at 4.0% and 42.6%. The abundant Ni⁰ and Ni²⁺ played a key role in the CO methanation reaction.

Notably, after loading the Ni, the peak shift to higher binding energies of Ni/MgAl-LDO (FNP) was still evident. In other words, more violent lattice distortion of metal existed on the surface of the Ni/MgAl-LDO (FNP) than the Ni/MgAl-LDO (CP) catalysts, which suggested that there were abundant oxygen vacancies for Ni/MgAl-LDO (FNP) [41].



Figure 7. TEM and HRTEM images of (**a**,**c**) Ni/MgAl-LDO (CP), (**b**,**d**) Ni/MgAl-LDO (FNP). (**e**) N₂ adsorption-desorption isotherm for Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP). (**f**) Pore size distribution of Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP).

Table 2. Elemental analysis of Ni, Mg, Al, and O elements content by X-ray photoelectron spectroscopy (XPS).

Sample	Ni (%)	Ni ⁰ /Ni (%)	Ni ²⁺ /Ni (%)	Mg (%)	Al (%)	O (%)
MgAl-LDO (CP)	-	-		17.86	13.06	53.90
Ni/MgAl-LDO (CP)	1.16	4.0	42.6	19.08	16.66	51.80
MgAl-LDO (FNP)	-	-		15.68	14.45	53.72
Ni/MgAl-LDO (FNP)	1.85	4.7	48.6	14.77	18.60	51.44



Figure 8. XPS spectra of the as-obtained Ni/MgAl-LDO (CP) and Ni/MgAl-LDO (FNP): (**a**) Ni, (**b**) Mg, (**c**) Al, and (**d**) O.

3. Materials and Methods

3.1. Coprecipitation Method

The requisite quantities of Al(NO₃)₃·9H₂O as the Al source, Mg(NO₃)₂·4H₂O as the Mg source, were dissolved in distilled water separately to obtain metal precursor solution, where the Mg:Al molar ratio was 2:1. The 1.0 mol/L mixed solution with a 1.5:1 molar ratio of NaOH:NaHCO₃ as the precipitant was added into the precursor solution, where the index of the salt-alkali ratio was 1:4, and was stirred for 1 h. The precipitate was aged for 24 h at 65 °C, and then washed several times with deionized water to keep the mixed solution pH at 7, and then dried in an oven to obtain MgAl-LDH (CP) at 80 °C for 12 h. The obtained materials were calcined in a muffle furnace at 550 °C for 4 h to obtain MgAl-LDO (CP).

For the Ni/MgAl-LDO (CP) catalyst, requisite quantities of Ni(NO₃)₂·6H₂O were dissolved in distilled water, and the MgAl-LDO (CP), as the support, was added into the obtained solution, where the Ni loading was 10%. After stirring for 12 h, the obtained material was placed in an 80 °C water bath for 2 h to evaporate water. Then, the sample was dried in an oven at 80 °C for 12 h, and the as-prepared precursor calcined at 550 °C for 4 h to obtain NiO/MgAl-LDO (CP). The as-obtained NiO/MgAl-LDO (CP) was reduced by in situ reduction to produce Ni/MgAl-LDO (CP) catalyst.

3.2. Flashnano-Precipitation (FNP) Method

The metal precursor solution and precipitant, as shown in Section 3.1., were injected into separate syringes. The liquid flow rate was controlled by the FNP equipment, and the as-raw materials crashed heavily in the FNP platform to produce the precipitate. Before the experiment, liquid flow rate was adjusted over several iterations to control the 1:4 salt-alkali ratio. The resulting precipitate was aged for 24 h at 65 °C and then filtered and washed several times with distilled water until there was no pH

change (pH = 7). Finally, the precipitate was dried in an oven to obtain MgAl-LDH (FNP) at 80 °C for 12 h. The obtained materials were calcined in a muffle furnace at 550 °C for 4 h to obtain MgAl-LDO (FNP). The NiO/MgAl-LDH (FNP), and Ni/MgAl-LDO (FNP), as described in Section 3.1.

3.3. Catalyst Characterization

The crystallographic properties of the supports and catalysts were determined through XRD analysis. The X-ray diffraction (XRD) patterns were obtained with a BrukerD8 Advance X-ray diffractometer (Bruker Biosciences Corporation, Billerica, MA, USA) with Cu K α radiation in the 2 θ range of 0 to 90°. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) investigations used a Tecnai F30 field-emission TEM (TecnaiG2 F20, FEI Instrument Ltd., Hillsboro, OR, USA). The support and catalysts were analysed by nitrogen physisorption at 77 K using Brunauer-Emmett-Teller (BET) (Micromeritics Instrument Ltd., Norcross, GA, USA) to calculate the surface area, pore volume, and pore size. The structures of the as-synthesized samples were elucidated via atomic force microscopy (AFM) with a Bruker Multimode 8 (Multimode 8, Bruker, Billerica, MA, USA). X-ray photoelectron spectroscopy (XPS) experiments used a Thermo ESCALAB 250XIelectron spectrometer from Kratos Analytical with Mg K α (20 mA, 12 kV) radiation (Escalab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA).

3.4. Activity Measurement

Experiments to determine the catalytic performance of the catalysts were evaluated by a fixed bed microreactor. In the test, a sample catalyst (about 0.2 g) was placed in a stainless steel tubular microreactor with a weight hourly space velocity (WHSV) of 20,000 mL·g⁻¹·h⁻¹. First, the sample was purged with N₂ at 60 mL·min⁻¹, and then the sample was heated to 500 °C. Next, the sample was reduced with 60 mL·min⁻¹ H₂ for 2 h to produce the as-needed catalyst. Then, the temperature was cooled down to 250 °C, and syngas (H₂:CO ratio of 3:1) was introduced into the microreactor at atmospheric pressure. The outlet gases were analyzed online every 50 °C between 250 and 550 °C by gas chromatography (GC-2014C, SHIMADZU, Kyoto, Japan).

4. Conclusions

Oxygen vacancies were introduced to the Ni/MgAl-LDO (FNP) via the FNP method to produce a highly-efficient catalyst for CO methanation. XPS analysis suggested that the FNP method produced more active sites, which was demonstrated by the remarkable CO conversion and CH₄ selectivity. The Ni/MgAl-LDO (FNP) exhibited a high CO conversion of 97%, CH₄ selectivity of 79.8%, a turnover frequency (TOF) of 0.141 s⁻¹, and a CH₄ yield of 77.4% at 350°C. The weight hourly space velocity was 20,000 mL·g⁻¹·h⁻¹, with a synthesis gas flow rate of 65 mL·min⁻¹, and a pressure of 1 atm. For the Ni/MgAl-LDO (CP) catalyst, this material exhibited a CO conversion of 81.1%, a CH₄ selectively of 75.1%, a TOF of 0.118 s⁻¹, and a CH₄ yield of 61% at 450 °C. This study demonstrates that MgAl-LDO could become an important catalyst. The FNP method offers a new strategy to easily and rapidly obtain catalysts with many oxygen vacancies.

Author Contributions: F.Y., Q.W. and X.G. designed and administered the experiments. M.Z. (Mengjuan Zhang) performed experiments. M.Z. (Mengjuan Zhang), J.L., K.C., Y.Y., P.L., M.Z. (Mingyuan Zhu) and Y.S. collected and analyzed data. All authors discussed the data and wrote the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interests.

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