

# Supplementary Information: CO<sub>2</sub> Methanation over Ni/Al@MAl<sub>2</sub>O<sub>4</sub> (M = Zn, Mg, or Mn) Catalysts

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

## 1. Characterization of Catalysts

N<sub>2</sub> physisorption was analyzed using a Micromeritics ASAP 2020 instrument. The specific surface area ( $S_{\text{BET}}$ ) of the sample was determined according to the BET method. The pore size distribution for each catalyst was obtained using the Barrett–Joyner–Halenda desorption method.

ICP-OES was carried out on a Thermo Scientific iCAP 6500 instrument to determine the metal content for each catalyst.

XRD patterns were detected by a Rigaku D/Max instrument with a Cu K $\alpha$  source to assess the bulk crystalline structure of the samples.

H<sub>2</sub>-TPR was performed with a Micromeritics 2910 Autochem instrument to check the reducibility of the nickel oxide species in the sample. 0.20 g of the sample was contacted with 10 mol% H<sub>2</sub>/Ar at a flow rate of 30 mL/min in the temperature range of 40–900 °C.

Pulsed CO<sub>2</sub> chemisorption and CO<sub>2</sub>-TPD were carried out on a Micromeritics Autochem 2910 instrument to analyze the basicity of the catalyst surface. Pulsed CO<sub>2</sub> chemisorption was conducted at room temperature by injection of 0.50 mL of 15 mol% CO<sub>2</sub> balanced with He in a He stream at a flow rate of 30 mL/min. CO<sub>2</sub>-TPD was conducted in the He stream at a flow rate of 30 mL/min for the temperature range of 40–900 °C at a heating rate of 10 °C/min.

In-situ DRIFTS experiments were carried out on a NICOLET 6700 (Thermo Scientific) spectrometer equipped with a ZnSe window with a resolution of 3.857 cm<sup>-1</sup>. Before CO<sub>2</sub> adsorption, the sample was reduced in-situ in the DRIFTS cell at 500 °C for 1 h using H<sub>2</sub> at a flow rate of 30 mL/min, and cooled under He flow to 40 °C. The cell was purged with He before the introduction of CO<sub>2</sub> at a flow rate of 50 mL/min. A background spectrum was recorded under He flow. CO<sub>2</sub> adsorption was performed for 20 min at 40 °C, and the spectra were recorded while purging with He at a flow rate of 50 mL/min at different temperatures. The spectra were also recorded during CO<sub>2</sub> methanation under the same reaction conditions as described for the catalytic activity test. At each reaction temperature, the signal was recorded after 20 min of reaction time.

HRTEM image was obtained using Tecnai G2 TEM (FEI) operating at 200 kV with energy dispersed spectroscopy (EDS) to observe the catalyst morphology, Ni particle size, and the elemental distribution.

## 2. Catalytic Evaluation

CO and CO<sub>2</sub> methanation were carried out in a fixed-bed quartz reactor. 0.10 g of the catalyst with particulate sizes of 45–80 mesh was reduced at 500 °C for 1 h in a 30 mL/min H<sub>2</sub> stream and then contacted with the feed gas composed of 1 mol% CO (or CO<sub>2</sub>), 50 mol% H<sub>2</sub>, and 49 mol% He at a flow rate of 100 mL/min. The reaction was conducted at atmospheric pressure in the reaction temperature range of 140–450 °C.

The exit gas composition was analyzed using a gas chromatograph (YL Instrument 6100GC), equipped with a packed column filled with Carbosphere® for TCD and a capillary Porolot Q column for the flame ionization detector (FID). CO conversion ( $X_{\text{CO}}$ ), CO<sub>2</sub> conversion ( $X_{\text{CO}_2}$ ), CO yield ( $Y_{\text{CO}}$ ), and C<sub>1</sub>-C<sub>3</sub> hydrocarbon yield ( $Y_{\text{C}_x\text{H}_y}$ ) were calculated using the following equations.

$$X_{\text{CO}} (\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100 \quad (1)$$

$$X_{CO_2} (\%) = \frac{[CO_2]_{in} - [CO_2]_{out}}{[CO_2]_{in}} \times 100 \quad (2)$$

$$Y_{C_xH_y} (\%) = \frac{x[C_xH_y]_{out}}{[CO]_{in} + [CO_2]_{in}} \times 100 \quad (3)$$

where  $[CO]_{in}$ ,  $[CO_2]_{in}$ ,  $[CO]_{out}$ ,  $[CO_2]_{out}$ , and  $[C_xH_y]_{out}$  are the CO concentration in the feed stream, CO<sub>2</sub> concentration in the feed stream, CO concentration in the exit stream, CO<sub>2</sub> concentration in the exit stream, and C<sub>x</sub>H<sub>y</sub> concentration in the exit stream, respectively.

**Table S1.** Physical properties of the support.

Support	Specific surface area <sup>a</sup> (m <sup>2</sup> /g)	Pore volume <sup>a</sup> (cm <sup>3</sup> /g)	Average pore diameter <sup>a</sup> (nm)	Al core (wt%) <sup>b</sup>
ZnAl <sub>2</sub> O <sub>4</sub>	111	0.27	9.9	-
MgAl <sub>2</sub> O <sub>4</sub>	210	0.36	6.8	-
Al@ZnAl <sub>2</sub> O <sub>4</sub>	41	0.11	12.1	58
Al@MgAl <sub>2</sub> O <sub>4</sub>	136	0.27	7.9	10
Al@MnAl <sub>2</sub> O <sub>4</sub>	104	0.15	5.7	32

<sup>a</sup>The specific surface area, pore volume, and average pore diameter were determined by N<sub>2</sub> physisorption.

<sup>b</sup>The weight percentage of Al core was calculated by according to the previous work [1].

**Table S2.** Basic sites distribution of Ni/Al@MAl<sub>2</sub>O<sub>4</sub> (M = Zn, Mg, or Mn) (WI) and (DP) samples determined by deconvolution of DRIFT spectra after CO<sub>2</sub> adsorption at 40 °C.

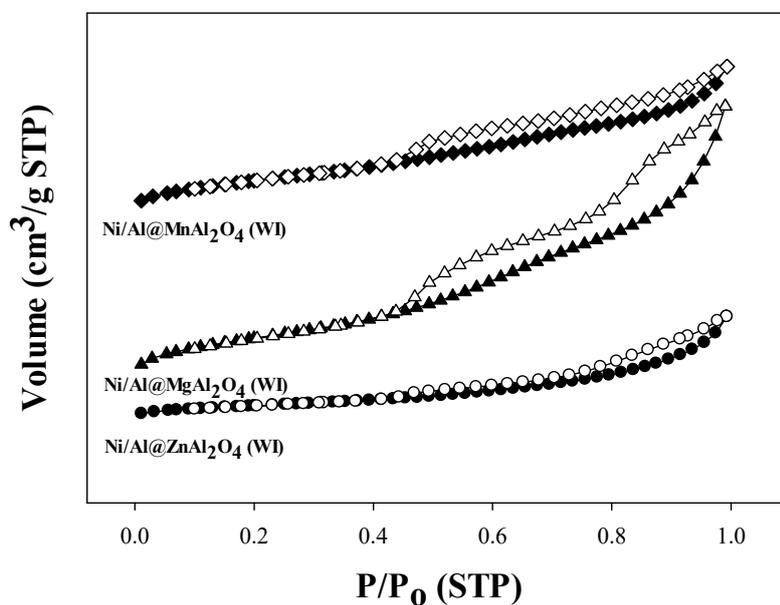
Catalyst	Percent of each basic site in wavenumber range 1130-1910 cm <sup>-1</sup> (%)	
	Weak basic sites	Strong basic sites
Ni/Al@ZnAl <sub>2</sub> O <sub>4</sub> (WI)	39.6	60.4
Ni/Al@MgAl <sub>2</sub> O <sub>4</sub> (WI)	41.6	58.4
Ni/Al@MnAl <sub>2</sub> O <sub>4</sub> (WI)	44.9	55.1
Ni/Al@ZnAl <sub>2</sub> O <sub>4</sub> (DP)	41.5	58.5
Ni/Al@MgAl <sub>2</sub> O <sub>4</sub> (DP)	43.4	56.6
Ni/Al@MnAl <sub>2</sub> O <sub>4</sub> (DP)	46.3	53.7

**Table S3.** Comparison of catalytic activity for CO and CO<sub>2</sub> methanation over supported Ni catalysts.<sup>a</sup>

Catalyst	CO methanation <sup>b</sup>		CO <sub>2</sub> methanation <sup>b</sup>	
	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)
Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> (WI)	274	299	338	388
Ni/Al@ZnAl <sub>2</sub> O <sub>4</sub> (WI)	336	348	310	337
Ni/Al@MgAl <sub>2</sub> O <sub>4</sub> (WI)	246	260	282	314
Ni/Al@MnAl <sub>2</sub> O <sub>4</sub> (WI)	226	238	246	272
Ni/ZnAl <sub>2</sub> O <sub>4</sub> (DP)	313	328	302	329
Ni/MgAl <sub>2</sub> O <sub>4</sub> (DP)	223	239	250	281
Ni/Al@ZnAl <sub>2</sub> O <sub>4</sub> (DP)	275	290	272	302
Ni/Al@MgAl <sub>2</sub> O <sub>4</sub> (DP)	211	223	243	272
Ni/Al@MnAl <sub>2</sub> O <sub>4</sub> (DP)	209	221	236	266

<sup>a</sup>The reaction conditions are same with those in Figures 5 and 6.

<sup>b</sup>T<sub>50</sub> and T<sub>90</sub> mean the temperature achieving 50 and 90% conversions of CO or CO<sub>2</sub>, respectively.



**Figure S1.** N<sub>2</sub> adsorption and desorption isotherms of supported Ni catalysts prepared by WI method.

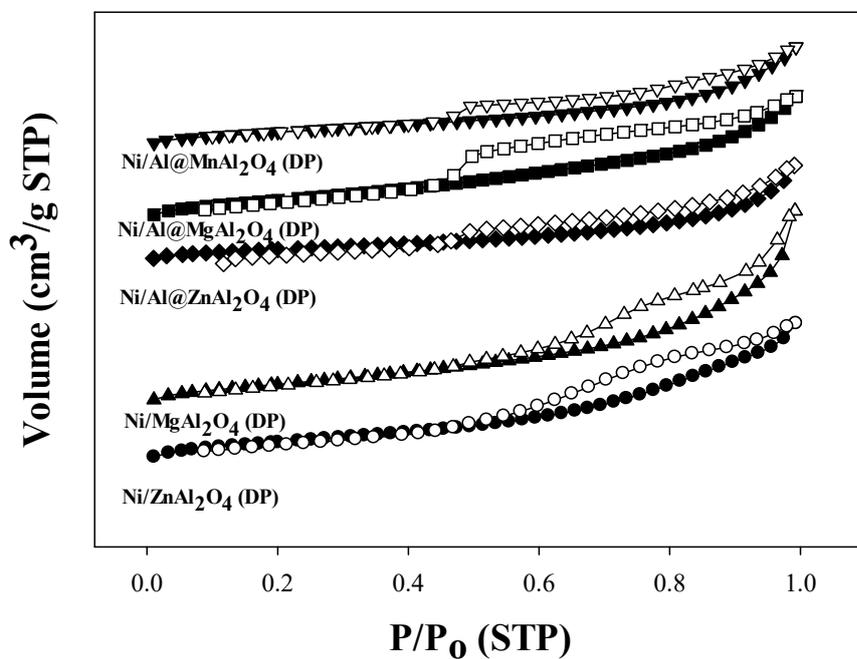


Figure S2. N<sub>2</sub> adsorption and desorption isotherms of supported Ni catalysts prepared by DP method.

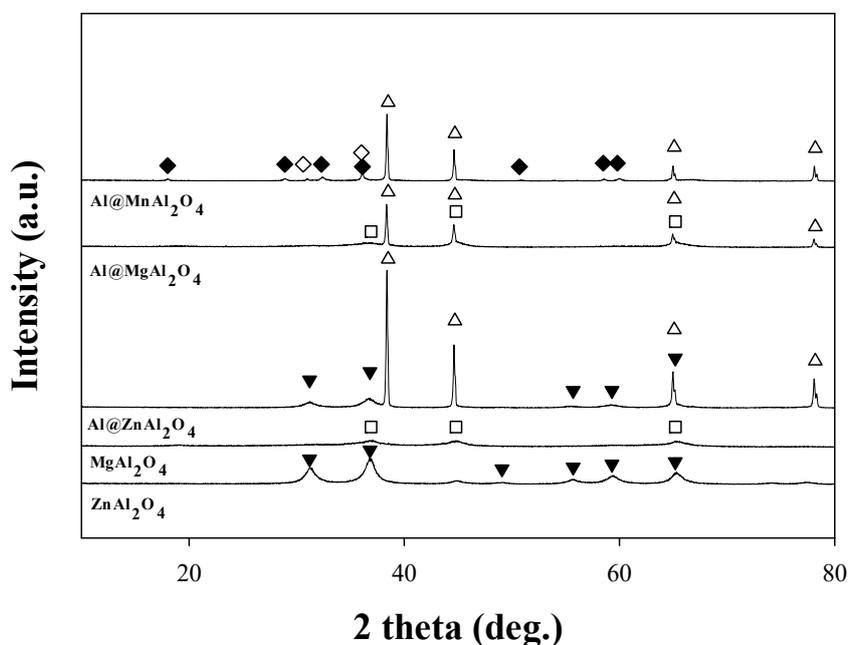
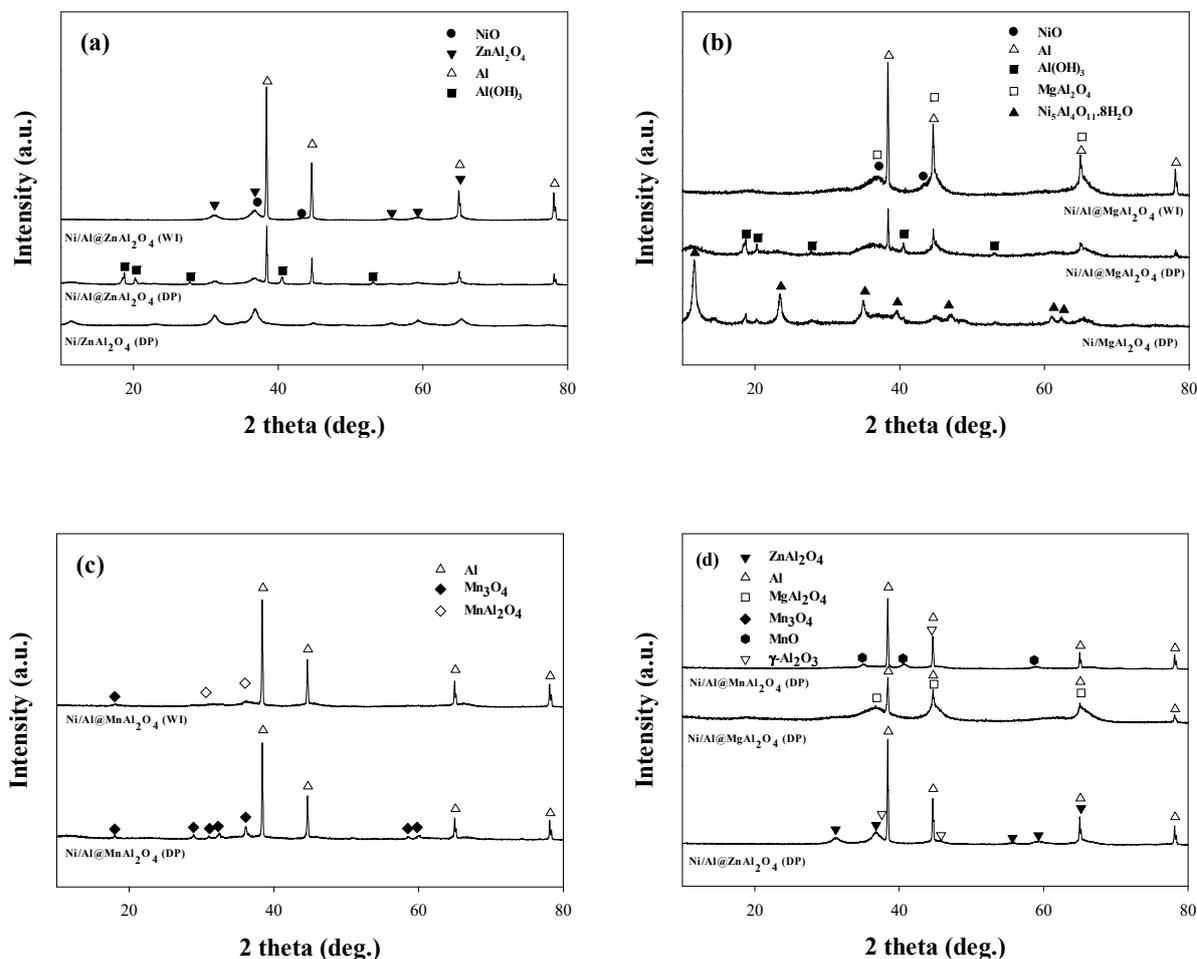
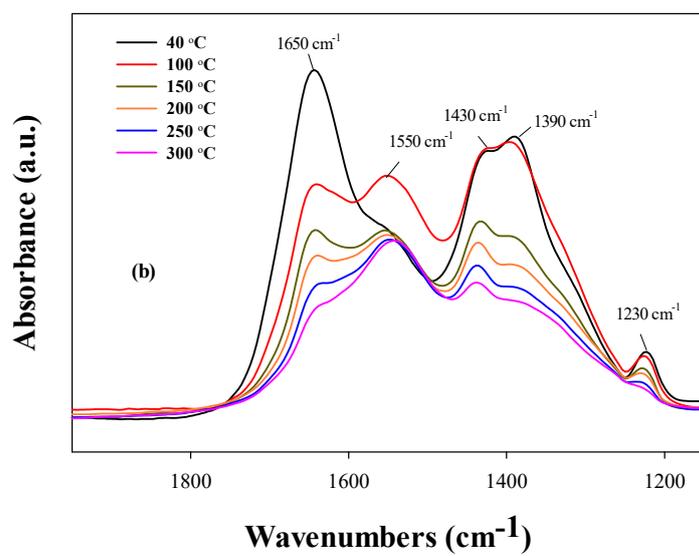
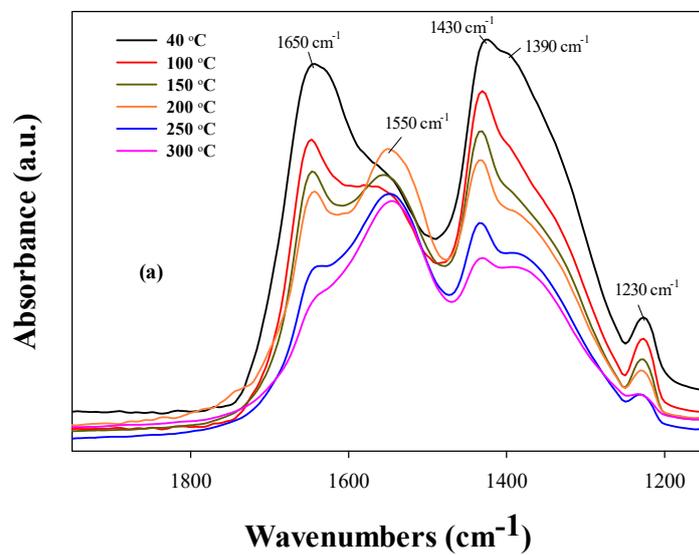


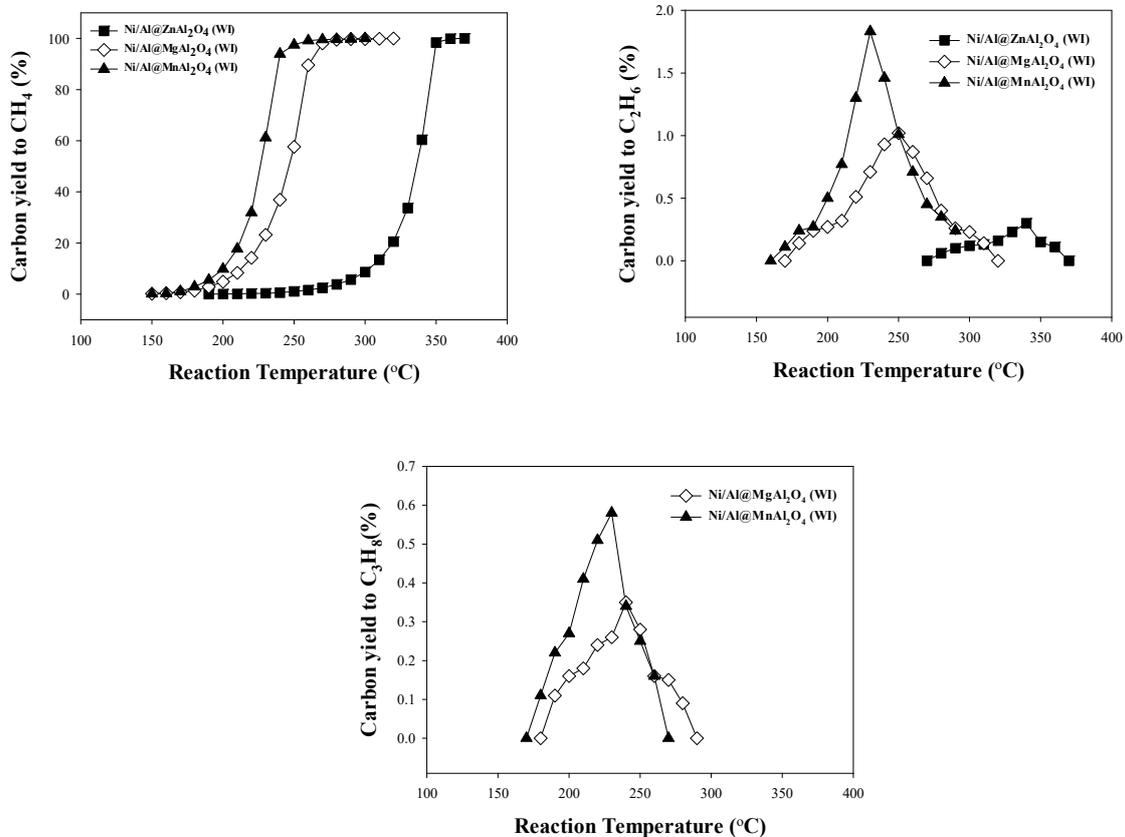
Figure S3. X-ray diffraction patterns of the prepared supports. ( $\Delta$ ) Al (JCPDS 04-0787), ( $\blacktriangledown$ ) ZnAl<sub>2</sub>O<sub>4</sub> (JCPDS 05-0669), ( $\square$ ) MgAl<sub>2</sub>O<sub>4</sub> (JCPDS 21-1152), ( $\diamond$ ) MnAl<sub>2</sub>O<sub>4</sub> (JCPDS 10-0310), and ( $\blacklozenge$ ) Mn<sub>3</sub>O<sub>4</sub> (JCPDS 24-0734).



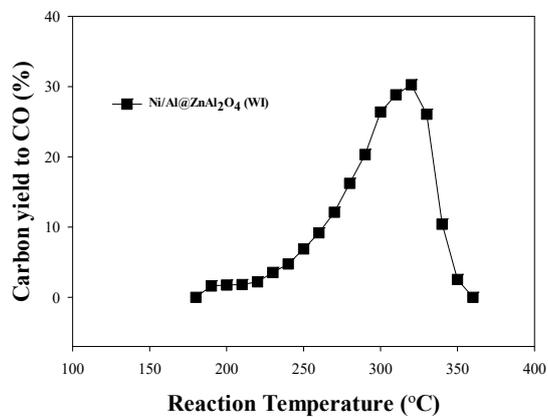
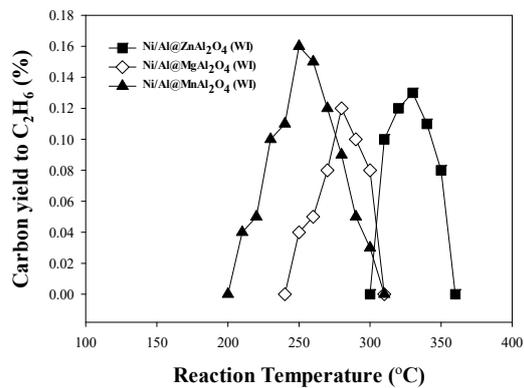
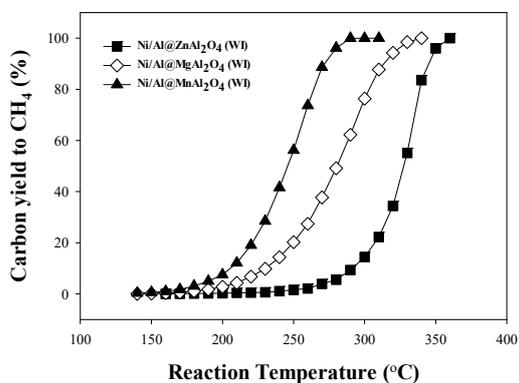
**Figure S4.** X-ray diffraction patterns of supported Ni catalysts calcined in air at 500 °C for WI samples (a, b, c), dried at 110 °C for DP samples (a, b, c), and core-shell supported Ni (DP) samples reduced in  $\text{H}_2$  at 500 °C (d). (●) NiO (JCPDS 47-1049), (▼)  $\gamma\text{-Al}_2\text{O}_3$  (JCPDS 29-0063), (△) Al (JCPDS 04-0787), (■)  $\text{Al(OH)}_3$  (JCPDS 20-0011), (▼)  $\text{ZnAl}_2\text{O}_4$  (JCPDS 05-0669), (□)  $\text{MgAl}_2\text{O}_4$  (JCPDS 21-1152), (◇)  $\text{MnAl}_2\text{O}_4$  (JCPDS 10-0310), (◆)  $\text{Mn}_3\text{O}_4$  (JCPDS 24-0734), (●) MnO (JCPDS 07-0230), and (▲)  $\text{Ni}_5\text{Al}_4\text{O}_{11}\cdot 8\text{H}_2\text{O}$  (JCPDS 22-0452).



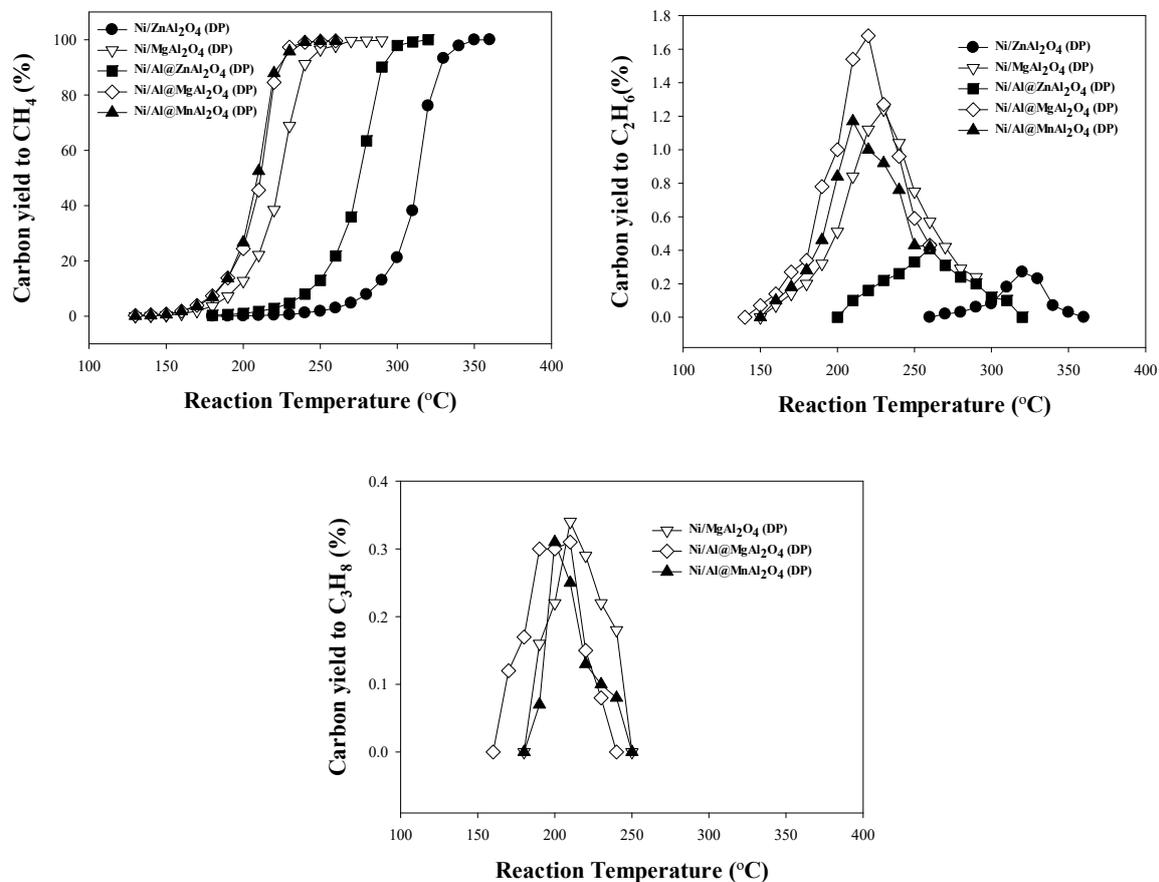
**Figure S5.** In-situ DRIFT spectra of CO<sub>2</sub> adsorption from 40 to 300 °C on (a) Ni/Al@MnAl<sub>2</sub>O<sub>4</sub> (WI) and (b) Ni/Al@MnAl<sub>2</sub>O<sub>4</sub> (DP).



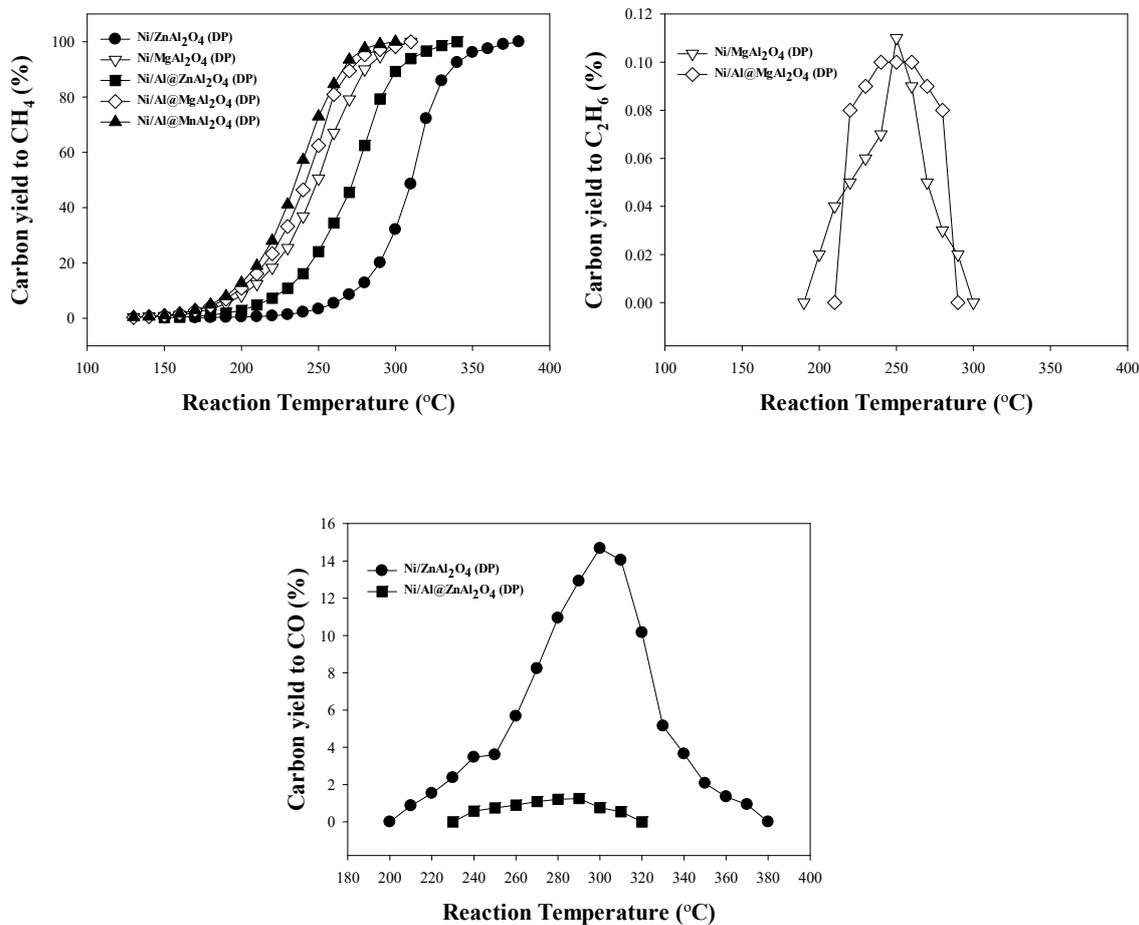
**Figure S6.** Product yield for CO methanation over Ni/Al@MAl<sub>2</sub>O<sub>4</sub> (M = Zn, Mg, or Mn) (WI). All the catalysts were reduced in H<sub>2</sub> at 500 °C. Reaction conditions: 1 mol% CO, 50 mol% H<sub>2</sub>, 49 mol% He, F/W = 1000 mL/min/g<sub>cat</sub>.



**Figure S7.** Product yield for CO<sub>2</sub> methanation over Ni/Al@MAl<sub>2</sub>O<sub>4</sub> (M = Zn, Mg, or Mn) (WI). All the catalysts were reduced in H<sub>2</sub> at 500 °C. Reaction conditions: 1 mol% CO<sub>2</sub>, 50 mol% H<sub>2</sub>, 49 mol% He, F/W = 1000 mL/min/g<sub>cat</sub>.



**Figure S8.** Product yield for CO methanation over Ni/MAl<sub>2</sub>O<sub>4</sub> (M = Zn or Mg) (DP) and Ni/Al@MAl<sub>2</sub>O<sub>4</sub> (M = Zn, Mg, or Mn) (DP). All the catalysts were reduced in H<sub>2</sub> at 500 °C. Reaction conditions: 1 mol% CO, 50 mol% H<sub>2</sub>, 49 mol% He, F/W = 1000 mL/min/g<sub>cat</sub>.



**Figure S9.** Product yield for CO<sub>2</sub> methanation over Ni/MAl<sub>2</sub>O<sub>4</sub> (M = Zn or Mg) (DP) and Ni/Al@MAI<sub>2</sub>O<sub>4</sub> (M = Zn, Mg, or Mn) (DP). All the catalysts were reduced in H<sub>2</sub> at 500 °C. Reaction conditions: 1 mol% CO<sub>2</sub>, 50 mol% H<sub>2</sub>, 49 mol% He, F/W = 1000 mL/min/g<sub>cat</sub>.

#### Reference

[1] J. Kim, J. Kim, D. Lee, Appl. Catal. A-Gen., 499 (2015) 197-204.