Electronic supplementary information

Selective hydrogenation of CO_2 to CH_4 over two-dimensional nickel silicate molecular sieves†

Hyung-Ki Min,[a,‡] Haehyun Min,[b,‡] Sungjoon Kweon,[c] Young Woo Kim,[d] Siyeon Lee,[c] Chae-Ho Shin,*[d] Min Bum Park*[c] and Sung Bong Kang*[b]

[a]*LOTTE Chemical Research Institute, Daejeon 34110, Korea*

[b]*School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology, Gwangju 61005, Korea*

[c]*Department of Energy and Chemical Engineering, Incheon National University, Incheon 22012, Korea*

[d]*Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 28644, Korea*

†Electronic supplementary information (ESI) available. See DOI: xxx

‡These authors contributed equally to this work.

*Corresponding authors: chshin@chungbuk.ac.kr (C.-H.S.); mbpark@inu.ac.kr (M.B.P.); sbkang@gist.ac.kr (S.B.K.)

Table S1 Binding energies of XPS spectra for the catalysts employed in this study

Catalyst	Binding energy (eV)			
	Ni $2p_{1/2}$[a]	Ni $2p_{3/2}$[a]	Si 2p	ΔE_{Ni-Si}[b]
Ni-DML-100	873.8	856.2	103.2	753.0
Ni-DML-120	874.1	856.2	103.1	753.1
Ni-DML-140	874.1	856.6	103.6	753.0
Ni-DML-160	874.3	856.6	102.6	754.0
Ni-DML-180	873.9	856.4	102.9	753.5
Ni/B-MWW	876.0 (32) 872.9 (68)	856.5 (36) 854.5 (64)	103.5	753.0 751.0

[a] The values in parentheses indicate the relative area ratios. [b] Difference in Ni $2p_{3/2}$ and Si 2p binding energies.

Table S2 Comparison of TOF for catalysts prepared in this and previous studies

	CO_2 hydrogenation conditions			
Catalyst	Temp. (°C)	GHSV ($cm^3\ g_{-cat.}^{-1}\ h^{-1}$)	TOF (CO_2) (s^{-1})	Ref.
Ni-DML-100	330	84,000	0.008	This study
Ni-DML-120	330	84,000	0.010	This study
Ni-DML-140	330	84,000	0.079	This study
Ni-DML-160	330	84,000	0.025	This study
Ni-DML-180	330	84,000	0.012	This study
5 wt.% Ni/B-MWW	330	84,000	0.051	This study
5 wt.% Ni/Al_2O_3	330	84,000	0.046	This study
12 wt.% Ni/Al_2O_3	275	10,000	0.060	40
5 wt.% Ni/SiO_2	300	6,000	0.103	41
5 wt.% $NiRu/SiO_2$	300	6,000	0.087	41
10 wt.% $NiRu/SiO_2$	300	6,000	0.044	41
5 wt.% Ni/SiO_2	350	22,000	0.076	42
5 wt.% Ni/Al_2O_3	300	6,000	0.063	43
5 wt.% Ni_3Fe/Al_2O_3	300	6,000	0.083	43
3.4 wt.% $NiRh_{0.1}/Al_2O_3$	300	6,000	0.037	43
NiMgAl	350	2,400	0.034	44
Ru/NiMgAl	350	2,400	0.034	44

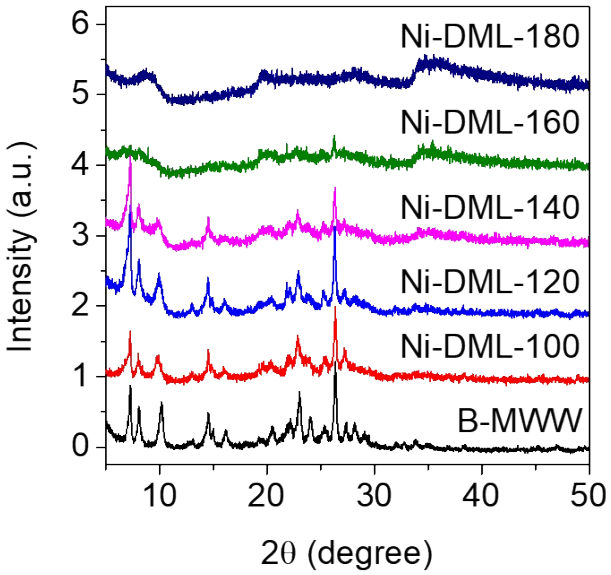

Fig. S1 Powder XRD patterns of calcined B-MWW and Ni-DML-*x* (*x* = 100−180 °C) catalysts.

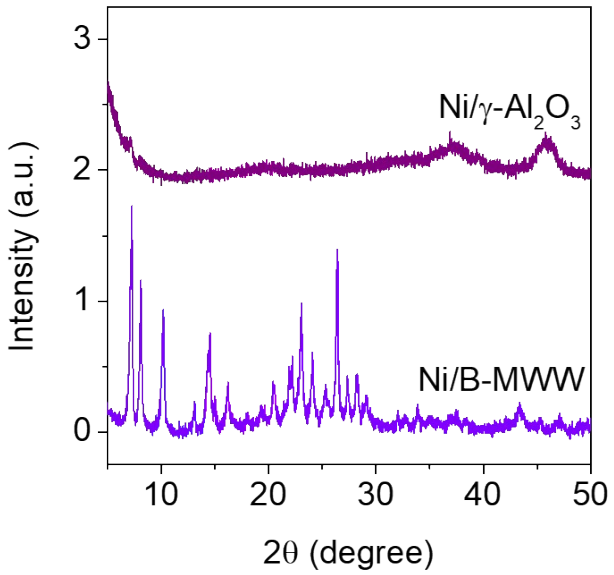

Fig. S2 Powder XRD patterns of calcined Ni/B-MWW and Ni/γ-Al_2O_3 catalysts.

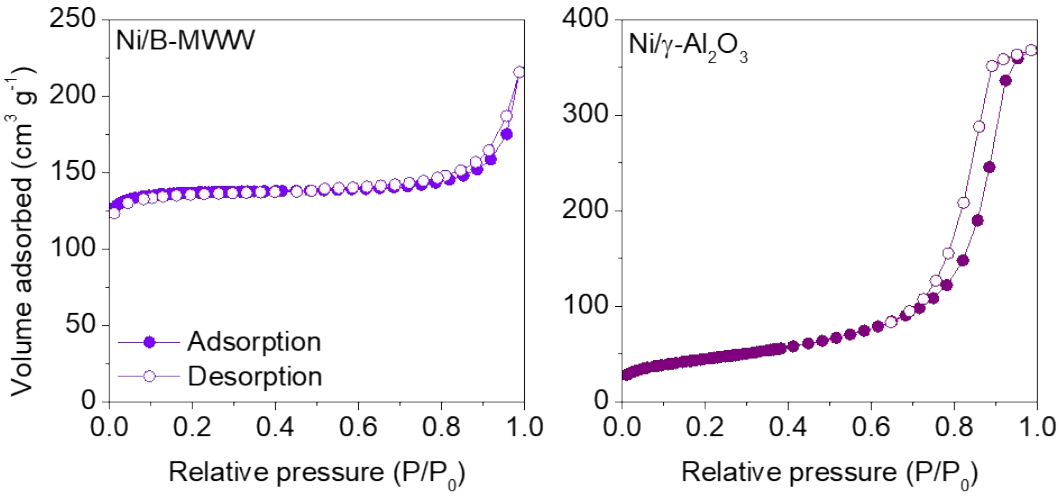

Fig. S3 N_2 sorption isotherms of Ni/B-MWW and Ni/γ-Al_2O_3 catalysts.

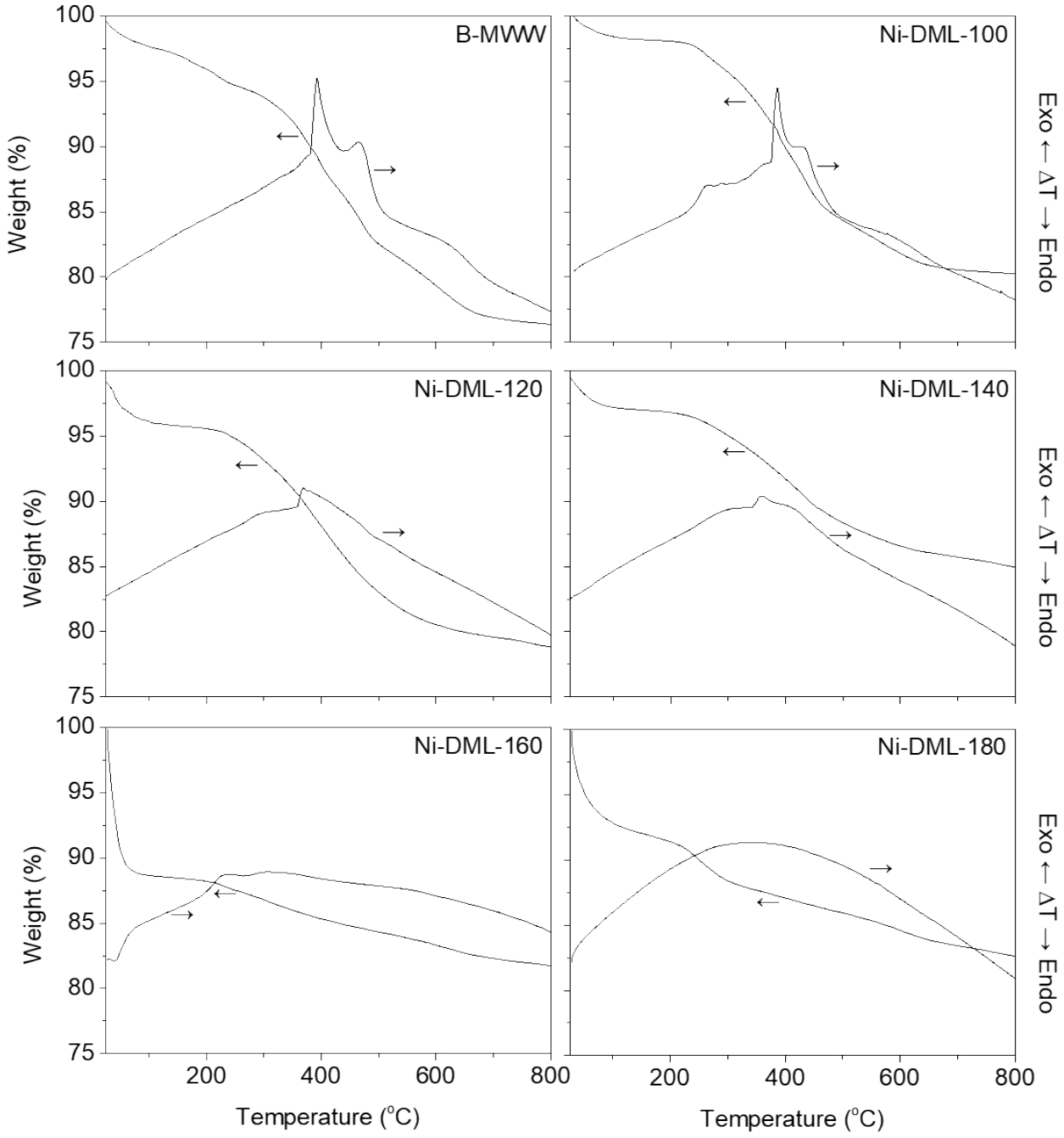

Fig. S4 TGA/DTA curves of as-synthesized B-MWW and Ni-DML-*x* (*x* = 100−180 °C) samples.

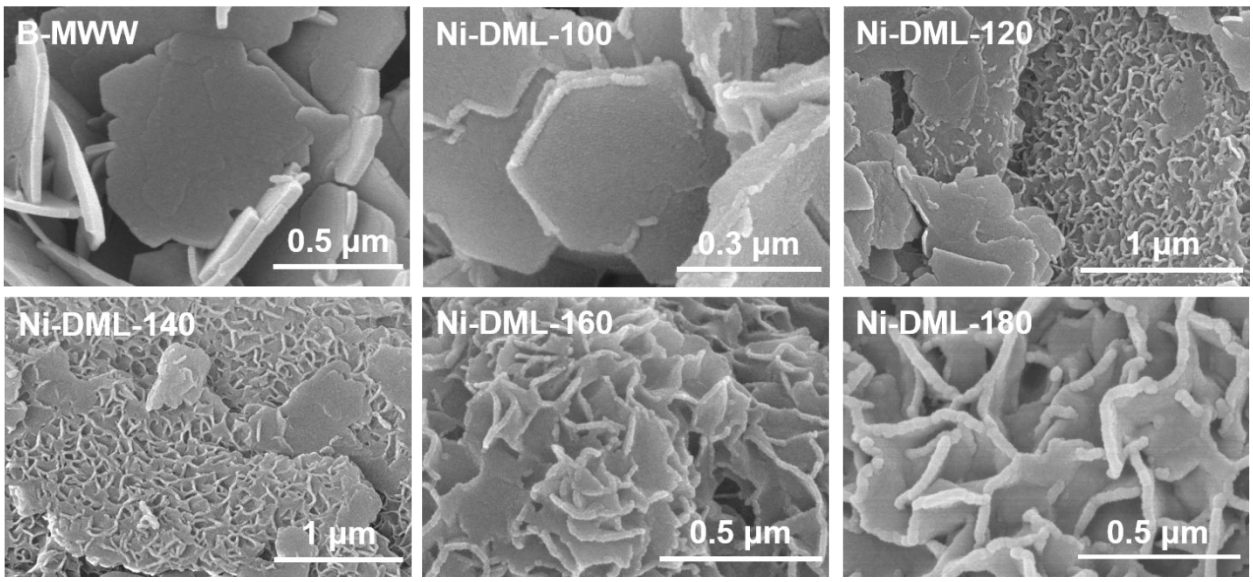

Fig. S5 SEM images of B-MWW and Ni-DML-*x* (*x* = 100−180 °C) catalysts.

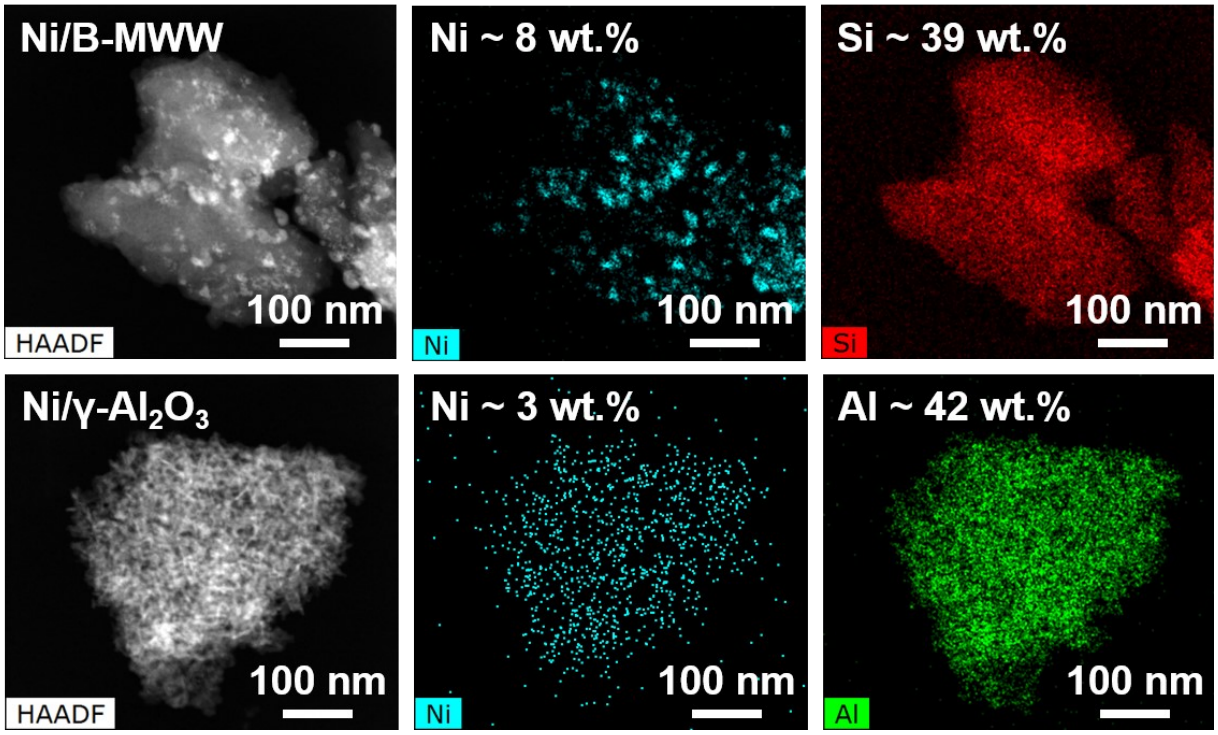

Fig. S6 STEM-EDS images of Ni/B-MWW and Ni/γ-Al_2O_3 catalysts.

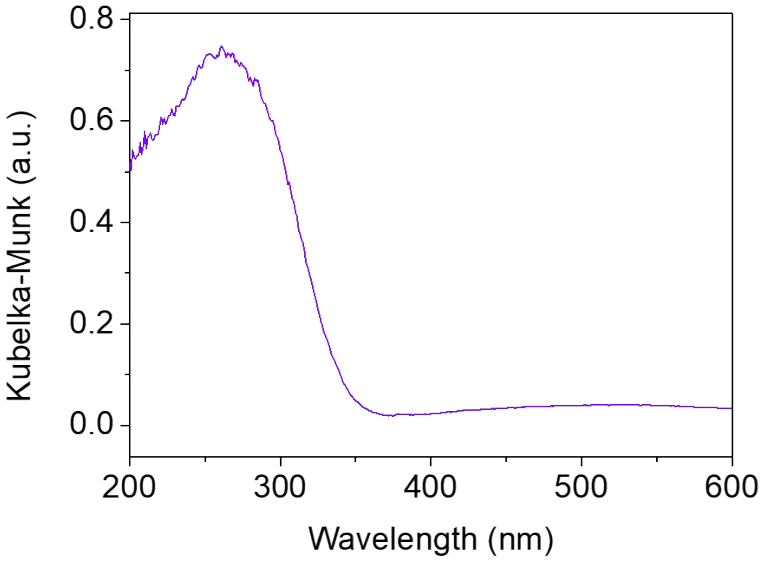

Fig. S7 UV-DRS spectrum of Ni/B-MWW catalyst.

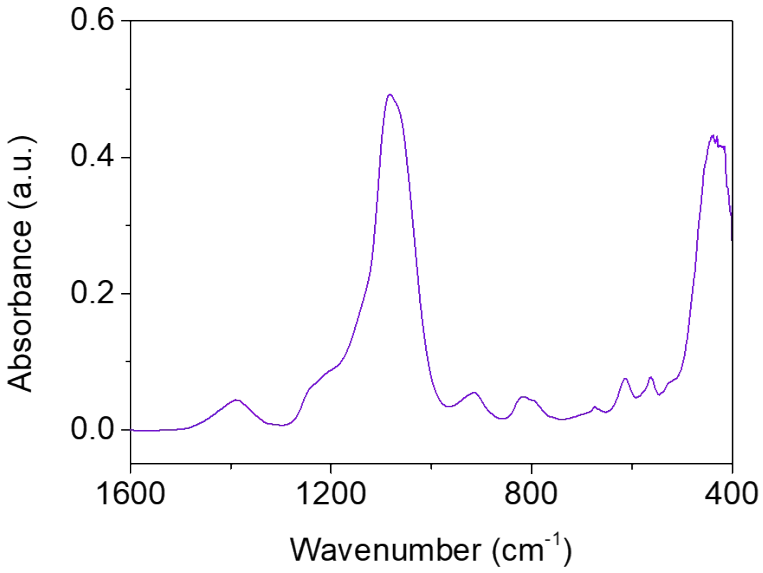

Fig. S8 IR spectrum in the structural region of the Ni/B-MWW catalyst.

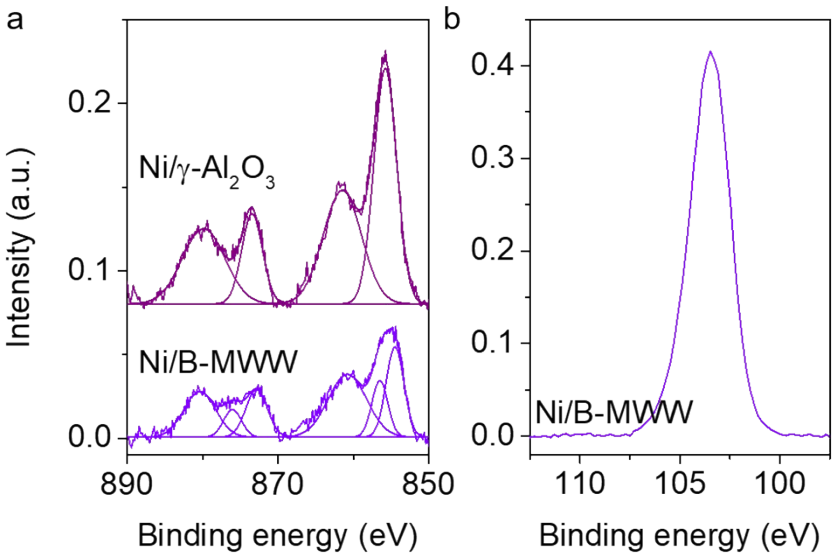

Fig. S9 (a) Ni 2p XPS and (b) Si 2p XPS spectra for Ni/B-MWW and/or Ni/γ-Al_2O_3 catalysts.

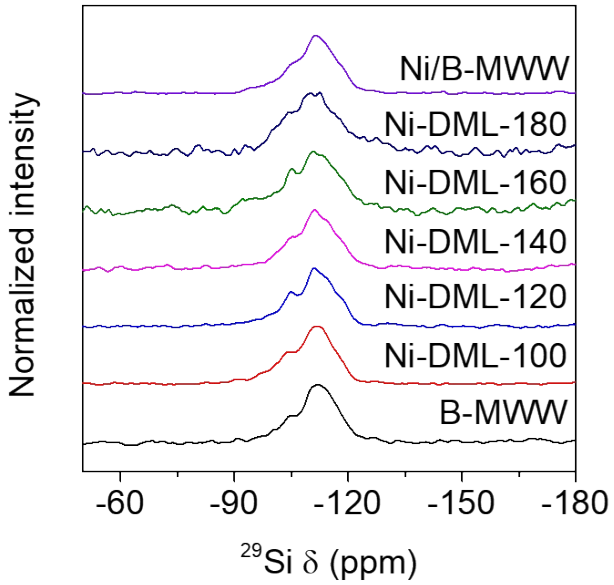

Fig. S10 ^{29}Si MAS NMR spectra of B-MWW, Ni-DML-*x* (*x* = 100−180 °C), and Ni/B-MWW catalysts.

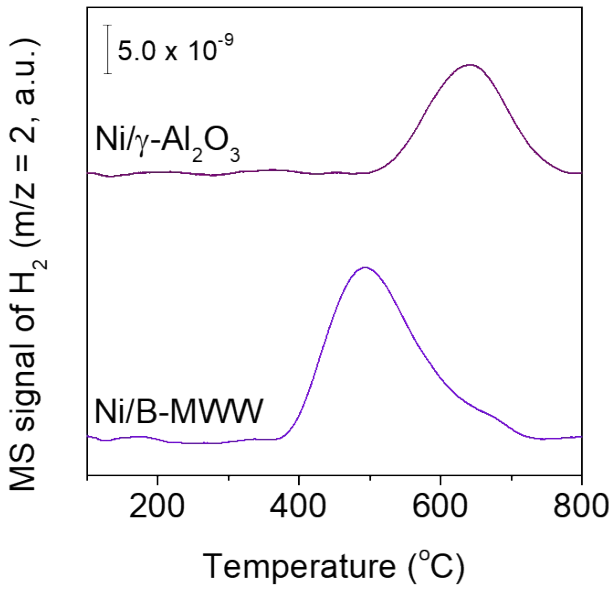

Fig. S11 H_2 TPR profiles of Ni/B-MWW and Ni/γ-Al_2O_3 catalysts.

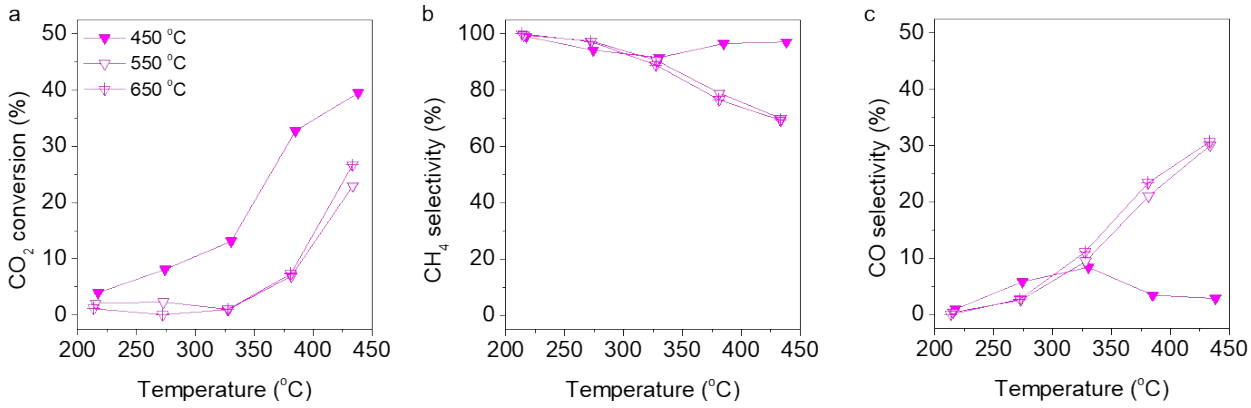

Fig. S12 (a) CO_2 conversion, (b) CH_4 selectivity, and (c) CO selectivity of Ni-DML-160 catalyst pre-reduced with 80 vol.% H_2 (Ar balance) at different temperatures (450−650 °C) as a function of reaction temperature at a GHSV of 30,000 h^{-1} for 1.5 h at each temperature.

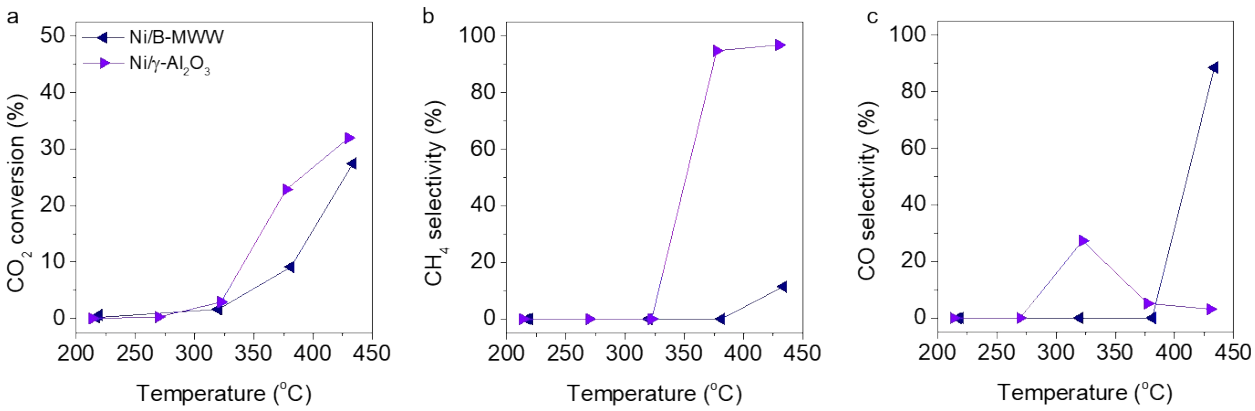

Fig. S13 (a) CO_2 conversion, (b) CH_4 selectivity, and (c) CO selectivity of Ni/B-MWW and Ni/γ-Al_2O_3 catalysts as a function of reaction temperature at a GHSV of 30,000 h^{-1} for 1.5 h at each temperature. The catalysts were routinely pre-reduced with 20 vol.% H_2 (Ar balance) at 450 °C for 1 h.

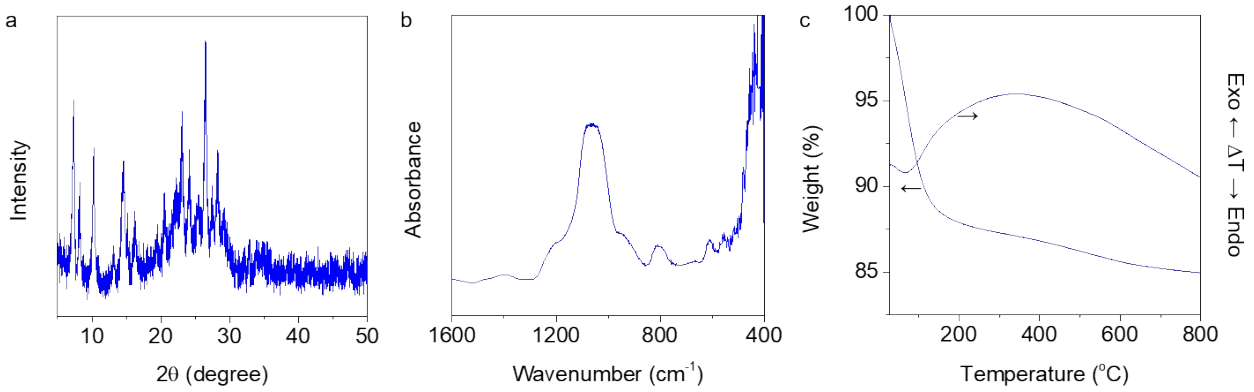

Fig. S14 (a) Powder XRD pattern, (b) IR spectrum in the structural region, and (c) TGA/DTA curves of the Ni-DML-140 catalyst after reaction.