

Supplementary materials

The effects of Ce and W promoters on the performance of alumina supported nickel catalysts in CO₂ methanation reaction

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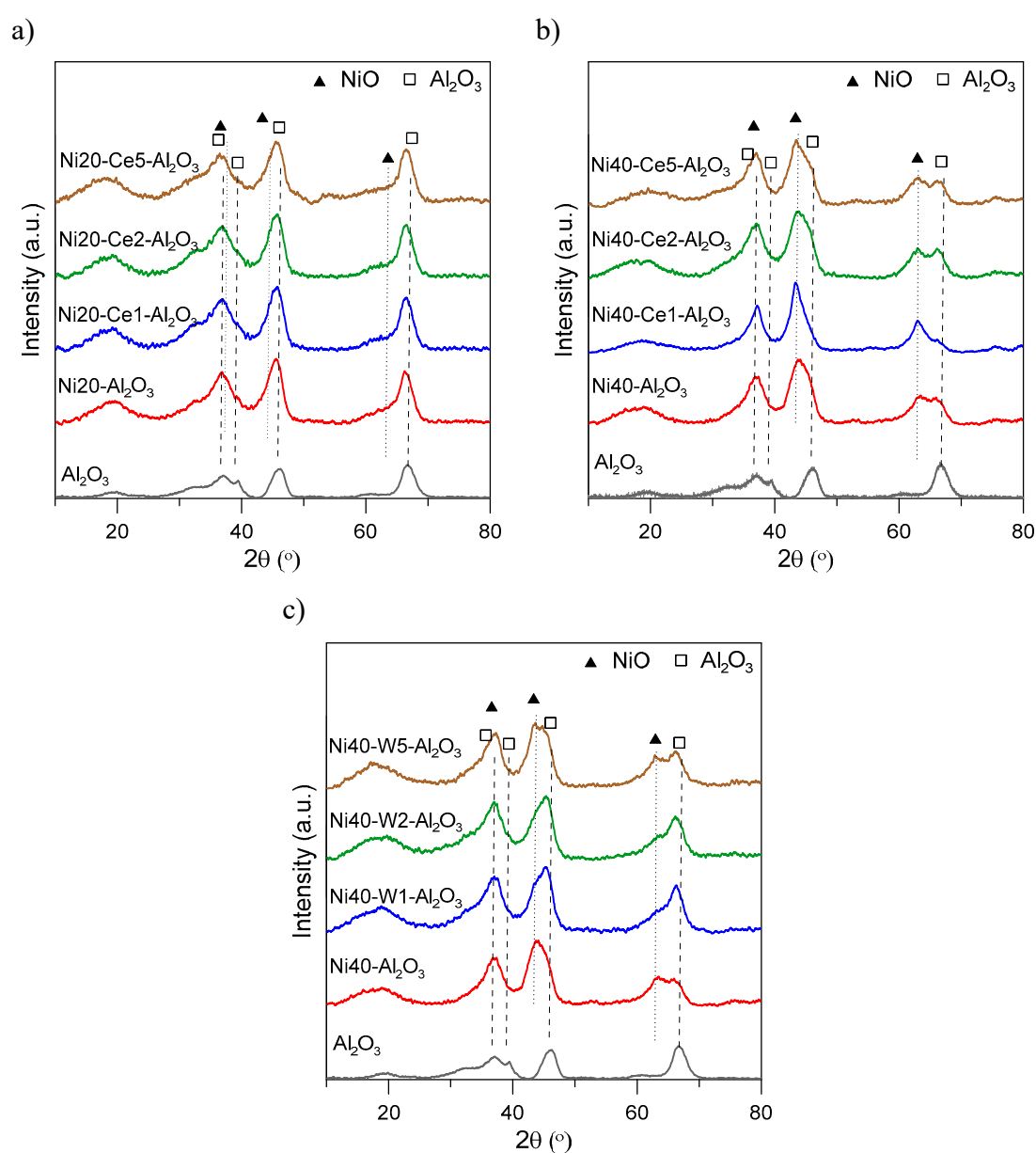


Figure S1. X-ray diffraction patterns of catalysts after calcination (a-c).

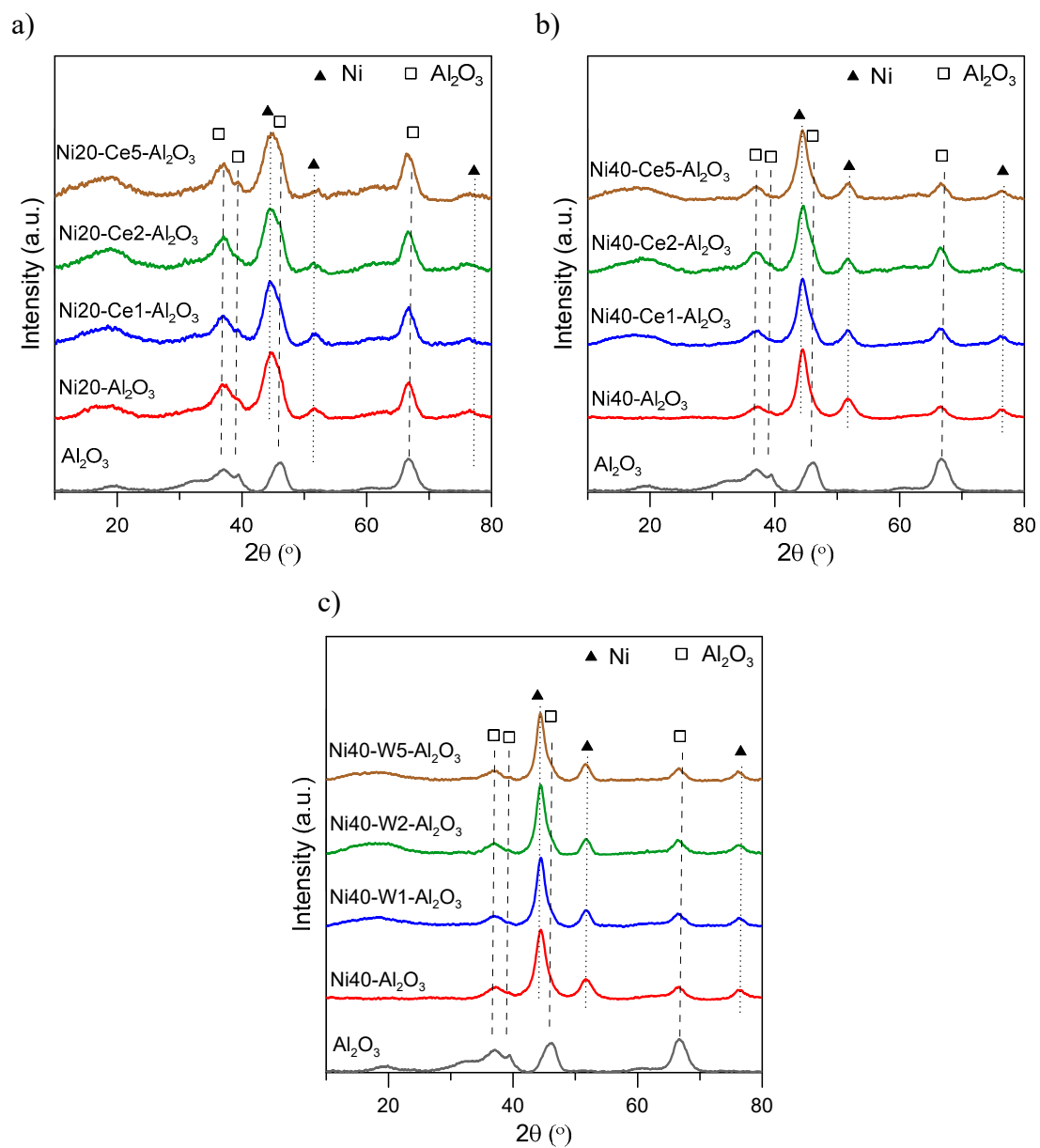


Figure S2. X-ray diffraction patterns of catalysts after reduction (a-c).

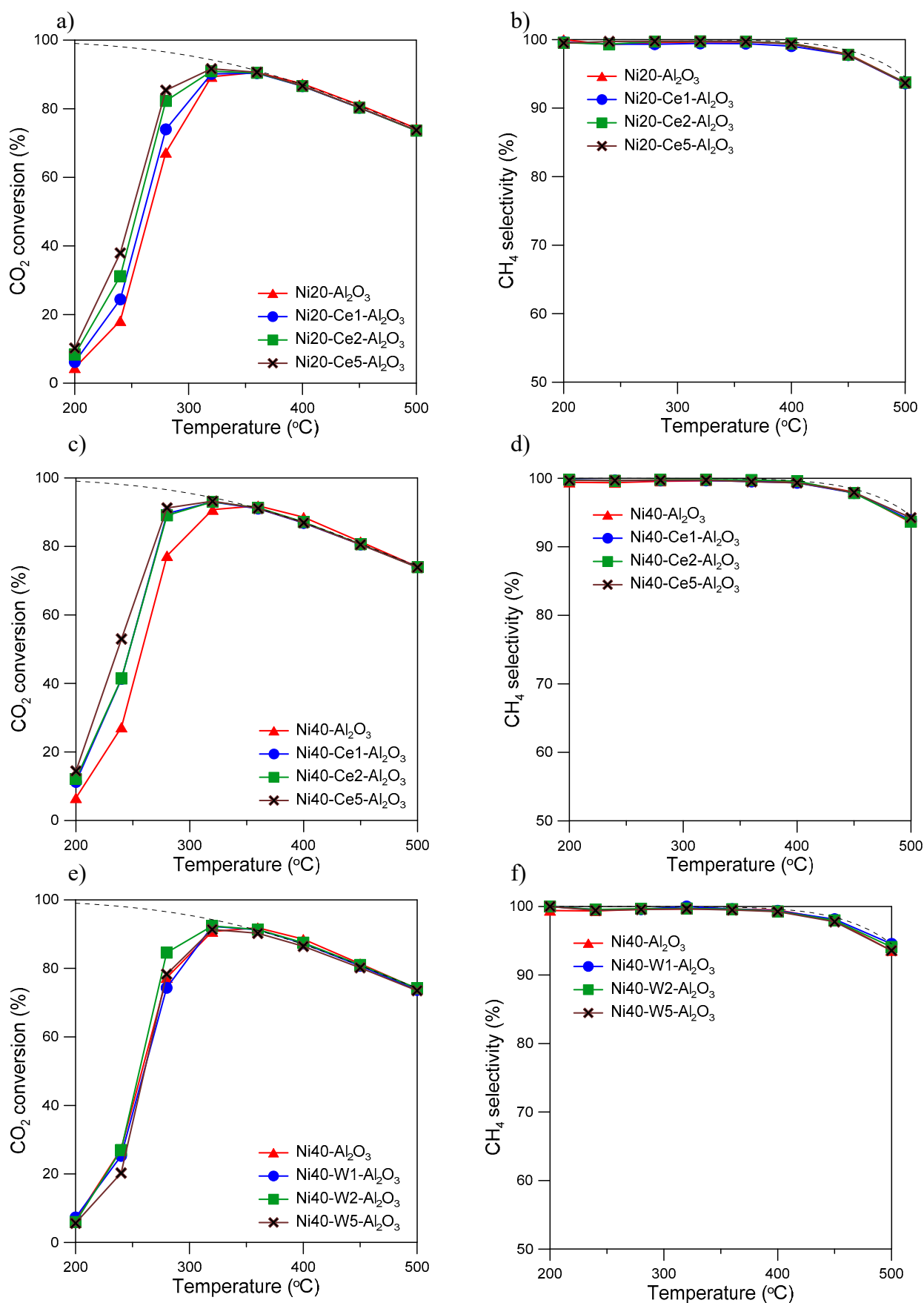


Figure S3. CO₂ conversion (a,c,e) and selectivity to CH₄ (b,d,f) of cerium and tungsten promoted alumina supported nickel catalysts in CO₂ methanation reaction.

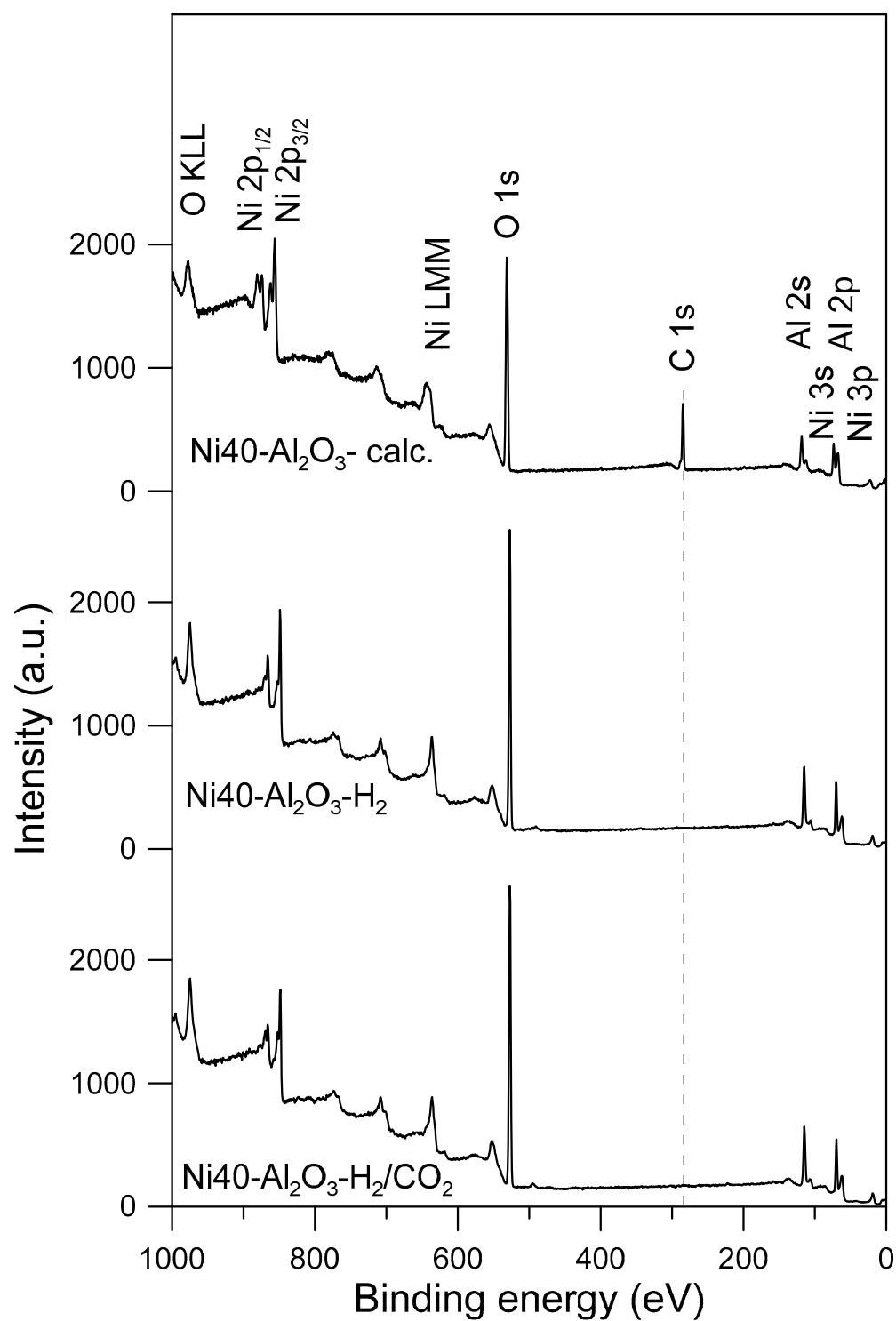


Figure S4.a. Survey XPS scans of Ni₄₀-Al₂O₃ catalyst after calcination (“-calc.”), activation in hydrogen (“-H₂”) and CO₂ methanation reaction (“-H₂/CO₂”).

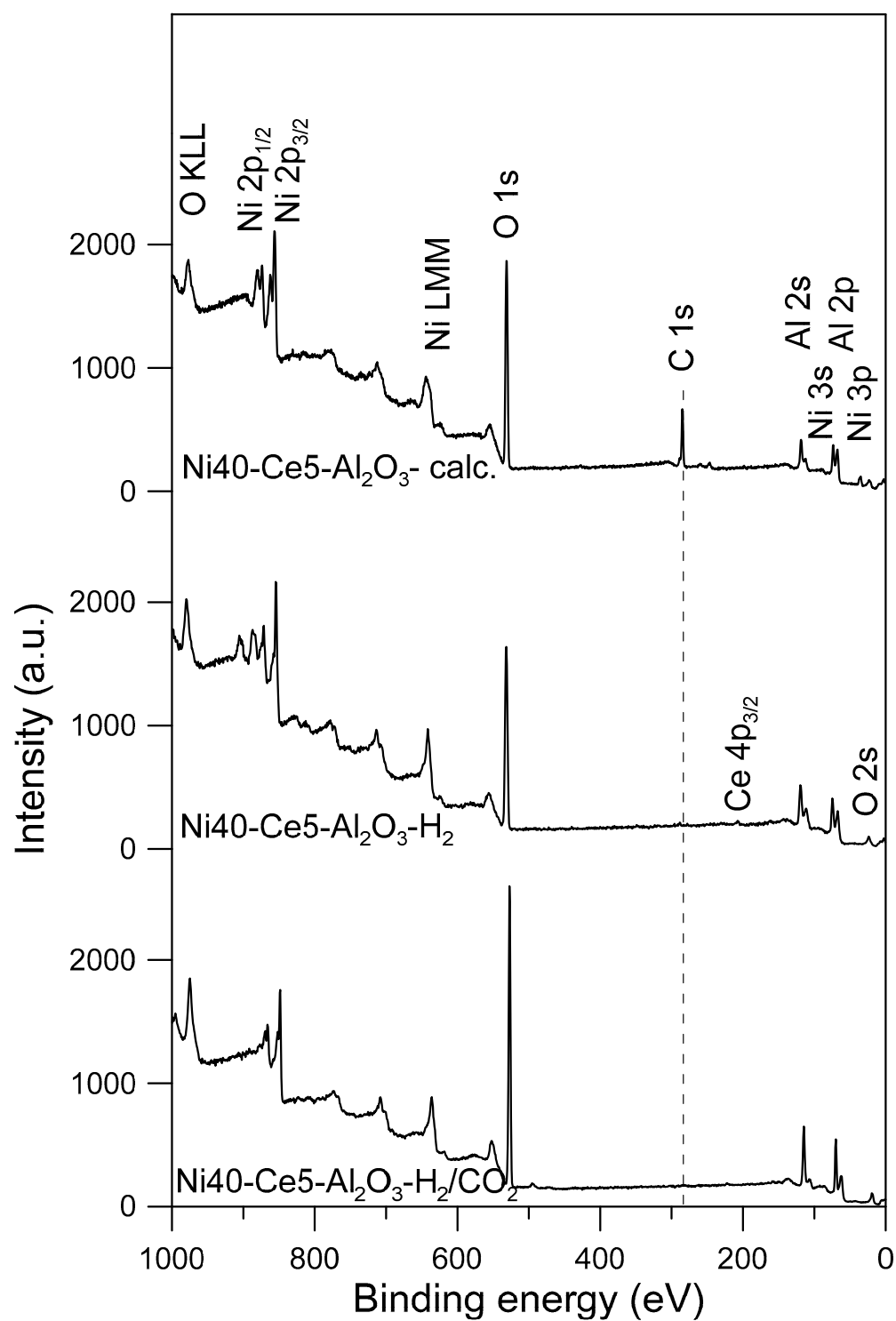


Figure S4.b. Survey XPS scans of Ni₄₀-Ce₅-Al₂O₃ catalyst after calcination (“-calc.”), activation in hydrogen (“-H₂”) and CO₂ methanation reaction (“-H₂/CO₂”).

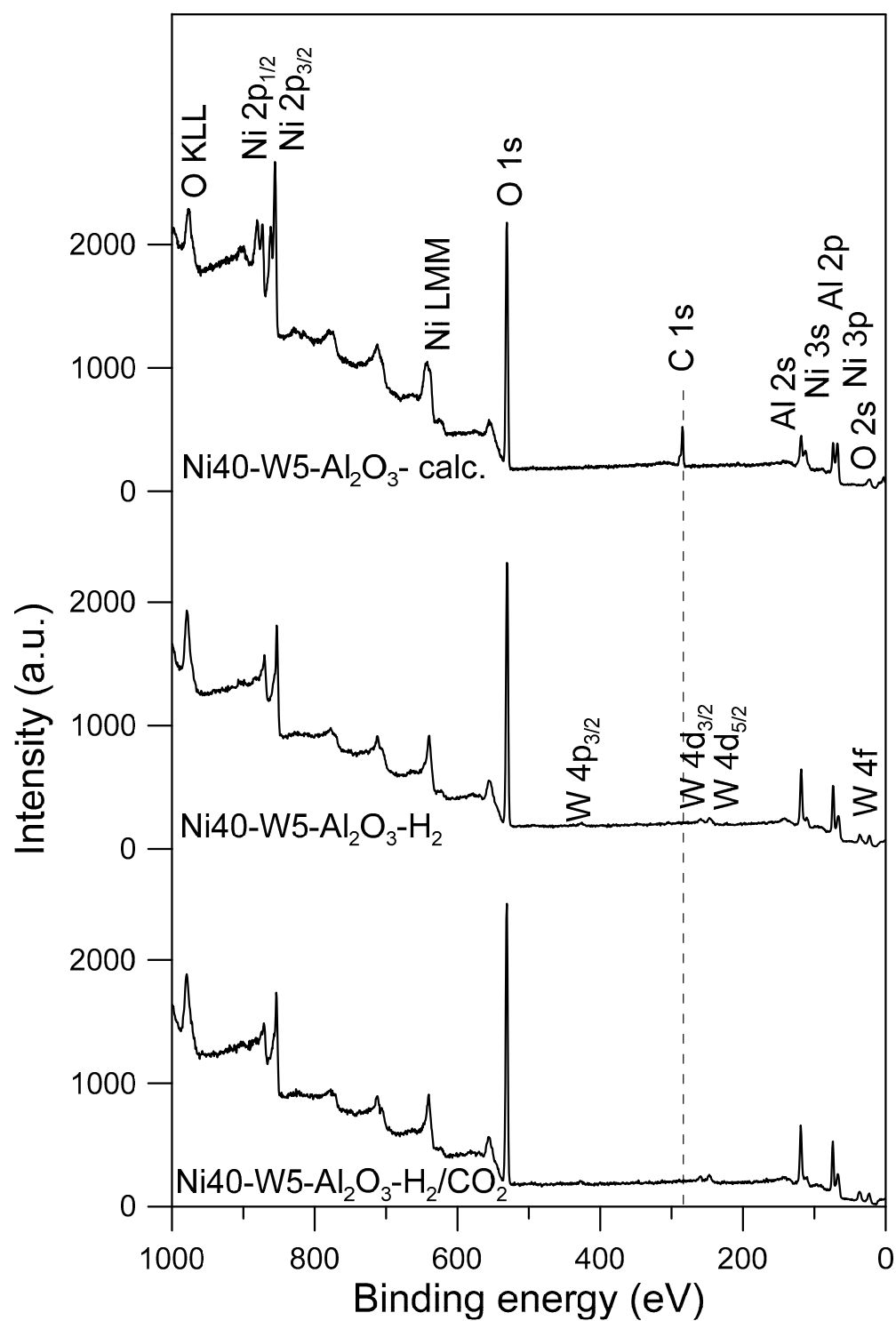


Figure S4.c. Survey XPS scans of Ni40-W5-Al₂O₃ catalyst after calcination (“-calc.”), activation in hydrogen (“-H₂”) and CO₂ methanation reaction (“-H₂/CO₂”).

Table S1. The analysis of XPS peaks from the XPS studies of catalysts after calcination (“-calc.”), activation in hydrogen (“-H₂”) and CO₂ methanation reaction (“-H₂/CO₂”).

Sample identifier	Name	Position	FWHM	Raw area
Ni 2p _{3/2}				
Ni40-Al ₂ O ₃ -calc.	NiAl ₂ O ₄	854.6	2.54	8.885
Ni40-Al ₂ O ₃ -calc.	NiAl ₂ O ₄	856.1	2.51	7.765
Ni40-Al ₂ O ₃ -calc.	NiAl ₂ O ₄	857.9	2.07	0.890
Ni40-Al ₂ O ₃ -calc.	NiAl ₂ O ₄	861.3	4.41	10.764
Ni40-Al ₂ O ₃ -calc.	NiAl ₂ O ₄	865.7	3.06	0.984
Ni40-Ce5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	854.62	2.54	8.885
Ni40-Ce5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	856.14	2.51	7.765
Ni40-Ce5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	857.86	2.07	0.890
Ni40-Ce5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	861.28	4.41	10.764
Ni40-Ce5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	865.74	3.06	0.984
Ni40-W5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	854.89	2.17	9.968
Ni40-W5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	856.56	2.40	12.861
Ni40-W5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	858.28	2.46	1.845
Ni40-W5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	861.91	4.27	15.077
Ni40-W5- Al ₂ O ₃ -calc.	NiAl ₂ O ₄	866.21	3.69	2.116
Ni40-Al ₂ O ₃ -H ₂	Ni ⁰	852.5	1.14	15.422
Ni40-Al ₂ O ₃ -H ₂	Ni ⁰	856.2	3.28	1.197
Ni40-Al ₂ O ₃ -H ₂	Ni ⁰	858.5	2.50	1.934
Ni40-Al ₂ O ₃ -H ₂	NiOOH	854.5	1.35	0.113
Ni40-Al ₂ O ₃ -H ₂	NiOOH	855.2	6.96	0.405
Ni40-Al ₂ O ₃ -H ₂	NiOOH	855.6	1.50	0.317
Ni40-Al ₂ O ₃ -H ₂	NiOOH	856.4	1.50	0.676
Ni40-Al ₂ O ₃ -H ₂	NiOOH	857.7	2.04	0.284
Ni40-Al ₂ O ₃ -H ₂	NiOOH	861.8	2.94	0.240
Ni40-Al ₂ O ₃ -H ₂	NiOOH	864.3	4.71	0.372
Ni40-Ce5-Al ₂ O ₃ -H ₂	Ni ⁰	852.54	1.14	15.426
Ni40-Ce5-Al ₂ O ₃ -H ₂	Ni ⁰	856.19	3.27	1.197
Ni40-Ce5-Al ₂ O ₃ -H ₂	Ni ⁰	858.49	2.49	2.127
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	854.90	2.70	0.716
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	856.57	2.99	1.315
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	858.29	3.06	0.189
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	861.82	5.30	1.890
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	866.22	4.59	0.216
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiOOH	854.19	1.41	0.071

Ni40-Ce5-Al ₂ O ₃ -H ₂	NiOOH	854.87	1.52	0.166
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiOOH	855.29	1.57	0.201
Ni40-Ce5-Al ₂ O ₃ -H ₂	NiOOH	856.09	1.57	0.429
Ni40-Ce5-Al ₂ O ₃ -H ₂	x	850.78	2.28	3.298
Ni40-W5-Al ₂ O ₃ -H ₂	Ni ⁰	852.63	1.71	7.697
Ni40-W5-Al ₂ O ₃ -H ₂	Ni ⁰	856.28	4.91	0.597
Ni40-W5-Al ₂ O ₃ -H ₂	Ni ⁰	858.66	3.74	0.965
Ni40-W5-Al ₂ O ₃ -H ₂	Ni ⁰ -W	854.13	1.41	4.432
Ni40-W5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	857.94	2.17	1.365
Ni40-W5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	859.61	2.40	1.560
Ni40-W5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	861.33	2.46	0.224
Ni40-W5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	864.95	4.27	0.537
Ni40-W5-Al ₂ O ₃ -H ₂	NiAl ₂ O ₄	869.26	3.69	0.257
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	854.58	1.34	0.147
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	855.26	1.44	0.340
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	855.68	1.49	0.412
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	856.48	1.49	0.879
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	857.78	2.02	0.370
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	861.88	2.92	0.400
Ni40-W5-Al ₂ O ₃ -H ₂	NiOOH	864.38	4.67	0.484
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	852.6	1.33	14.084
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	856.3	3.81	1.093
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	858.6	2.90	2.512
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	854.4	1.50	0.221
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	855.1	4.41	0.650
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	855.5	1.67	0.509
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	856.3	1.67	1.086
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	857.6	2.26	0.648
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	861.7	3.27	1.008
Ni40-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	864.2	5.24	0.598
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	852.60	1.21	15.773
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	856.25	3.47	1.224
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	858.63	2.64	2.248
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	854.89	1.80	0.748
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	856.56	1.99	0.965
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	858.28	2.04	0.138
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	861.90	3.53	1.131
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	866.21	3.06	0.159
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	854.93	1.41	0.105
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	855.60	1.52	0.244
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	856.03	1.57	0.296
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	856.83	1.57	0.632
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	858.13	2.13	0.266
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	862.23	3.07	0.224
Ni40-Ce5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	864.73	4.92	0.348

Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	852.29	1.68	6.342
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	855.94	4.81	0.492
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰	858.32	3.66	0.795
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	Ni ⁰ -W	853.77	1.45	4.215
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	857.94	2.17	1.365
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	859.61	2.40	1.560
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	861.33	2.46	0.224
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	864.95	4.27	0.537
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	869.26	3.69	0.257
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiAl ₂ O ₄	857.94	2.17	1.365
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	854.58	1.34	0.180
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	855.26	1.44	0.418
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	855.68	1.49	0.507
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	856.48	1.49	1.082
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	857.78	2.02	0.455
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	861.88	2.92	0.492
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	NiOOH	864.38	4.67	0.596
W 4f _{7/2}				
Ni40-W5-Al ₂ O ₃ -H ₂	W ⁰	30.93	0.93	0.127
Ni40-W5-Al ₂ O ₃ -H ₂	W-O	32.07	1.11	0.222
Ni40-W5-Al ₂ O ₃ -H ₂	WO ₂	33.15	1.01	0.121
Ni40-W5-Al ₂ O ₃ -H ₂	WO ₃	34.55	1.04	0.212
Ni40-W5-Al ₂ O ₃ -H ₂	WO ₃ /Al ₂ O ₃	35.66	1.04	0.392
W 5p _{3/2}				
Ni40-W5-Al ₂ O ₃ -H ₂	W ⁰	36.60	1.13	-
Ni40-W5-Al ₂ O ₃ -H ₂	W-O	37.70	1.13	-
W 4f _{7/2}				
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	W ⁰	30.85	0.87	0.051
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	W-O	32.08	0.83	0.064
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	WO ₂	33.07	1.05	0.069
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	WO ₃	34.60	1.14	0.422
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	WO ₃ /Al ₂ O ₃	35.44	1.04	0.356
W 5p _{3/2}				
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	W ⁰	36.38	1.48	-
Ni40-W5-Al ₂ O ₃ -H ₂ /CO ₂	W-O	37.62	1.48	-