

Supplementary Information

Influence of 0.25% indium addition to Ni/CeO₂ catalysts for dry reforming of methane

Anita Horváth^a, Andrea Beck^a, Miklós Németh^a, György Sáfrán^b, Matevž Roškarič^c,

Gregor Žerjav^c, Albin Pintar^{c,*}

^aCentre for Energy Research, Institute for Energy Security and Environmental Safety,
Department of Surface Chemistry and Catalysis, Konkoly-Thege M. street 29-33, H-1121
Budapest, Hungary

^bCentre for Energy Research, Institute of Technical Physics and Materials Science, Thin Film
Physics Department, Konkoly-Thege M. street 29-33, H-1121 Budapest, Hungary

^cDepartment of Inorganic Chemistry and Technology, National Institute of Chemistry,
Hajdrihova 19, SI-1001 Ljubljana, Slovenia

*Corresponding author. Tel.: +386 1 47 60 237. *E-mail address:* albin.pintar@ki.si (A. Pintar).

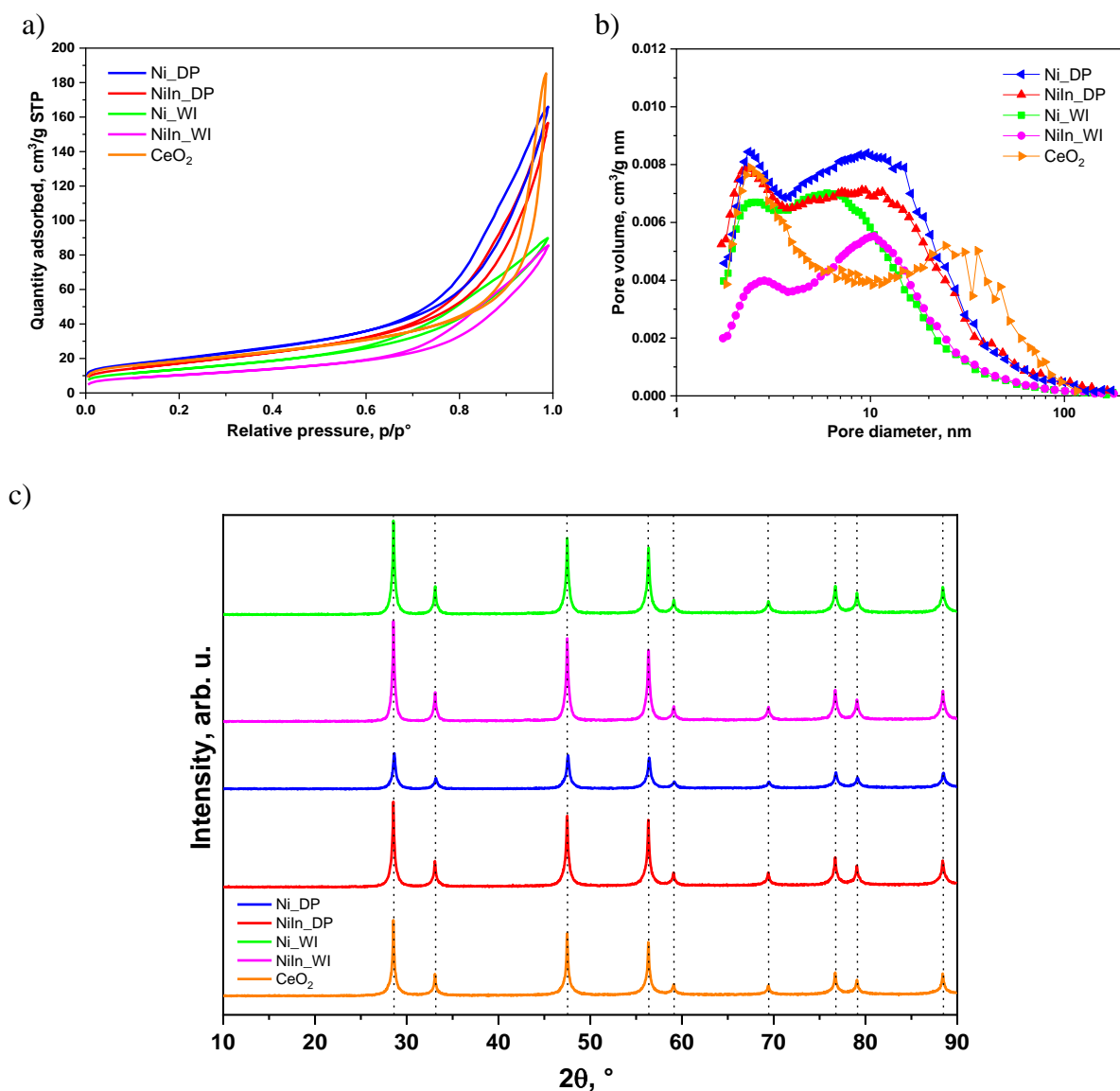


Figure S1. (a) Nitrogen adsorption-desorption isotherms, (b) pore size distribution and (c) XRD diffractograms of the studied catalysts in the calcined state. The dotted lines in the diffractograms represent the standard diffractions for PDF ICDD 04-015-0377, 01-080-6915 and 04-0102-0220 of cubic CeO₂.

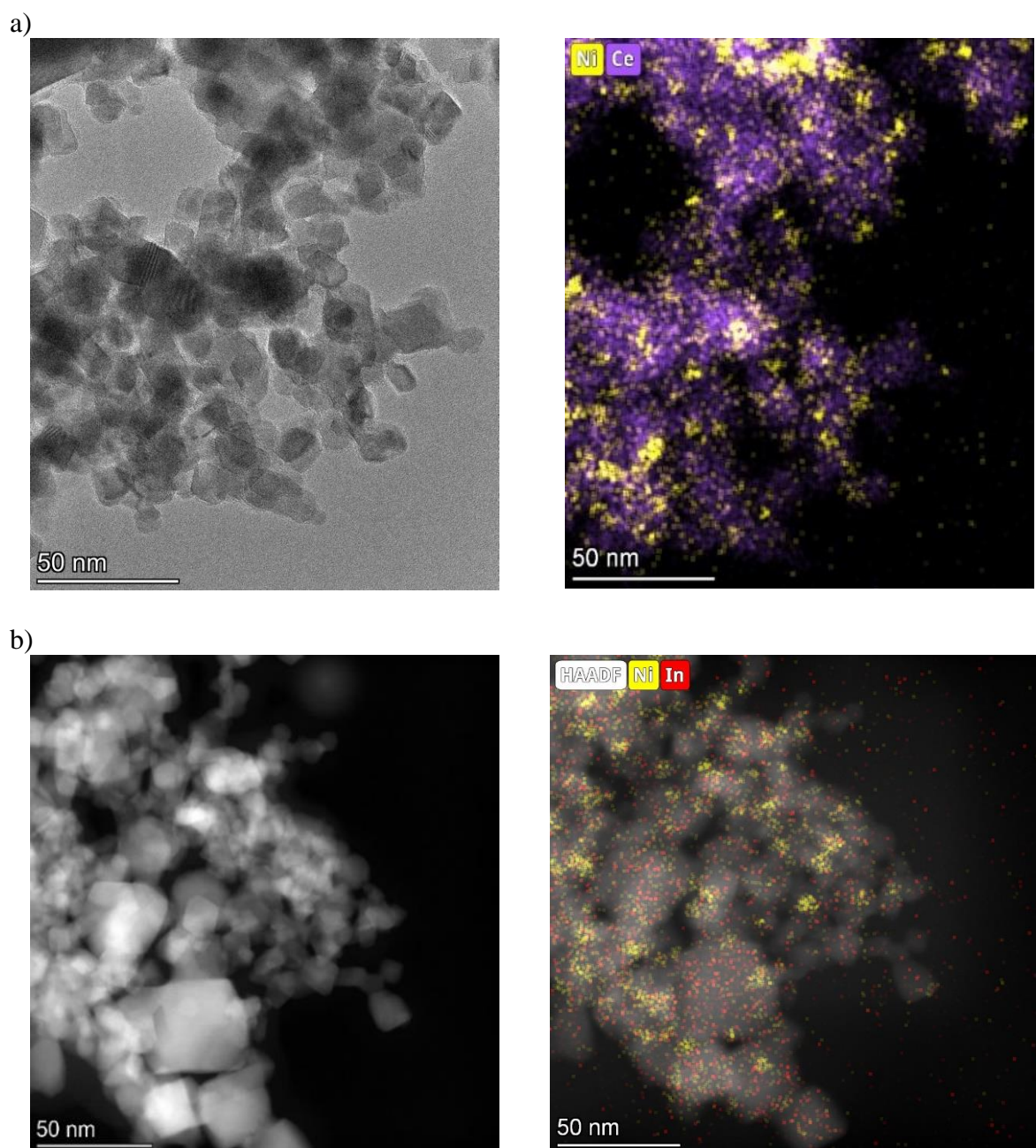


Figure S2. Comparison of TEM images and elemental maps of Ni and In for fresh (a) Ni_DP and (b) NiIn_DP catalyst samples.

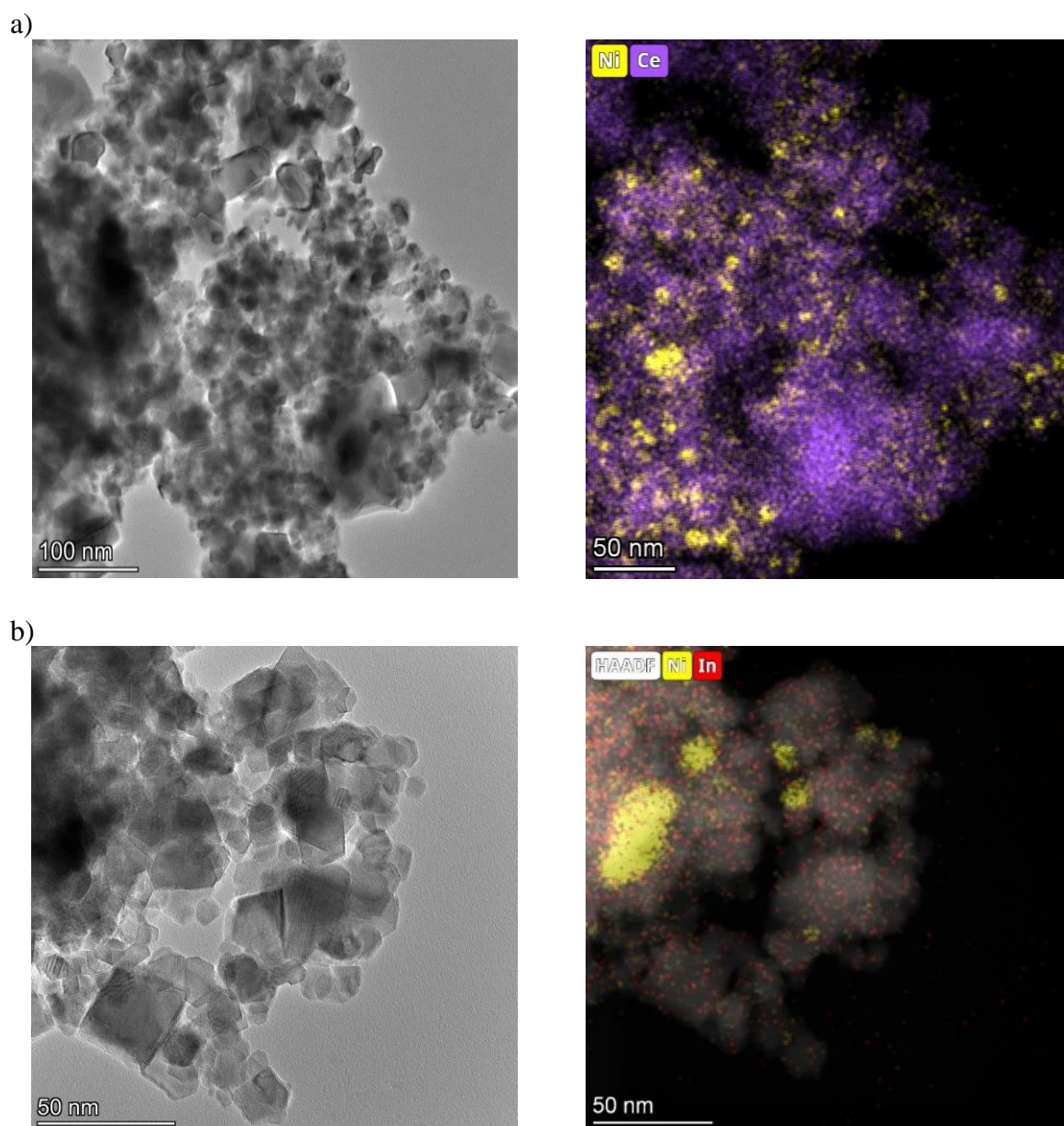


Figure S3. Comparison of TEM images and elemental maps of Ni and In for fresh (a) Ni_WI and (b) NiIn_WI catalyst samples.

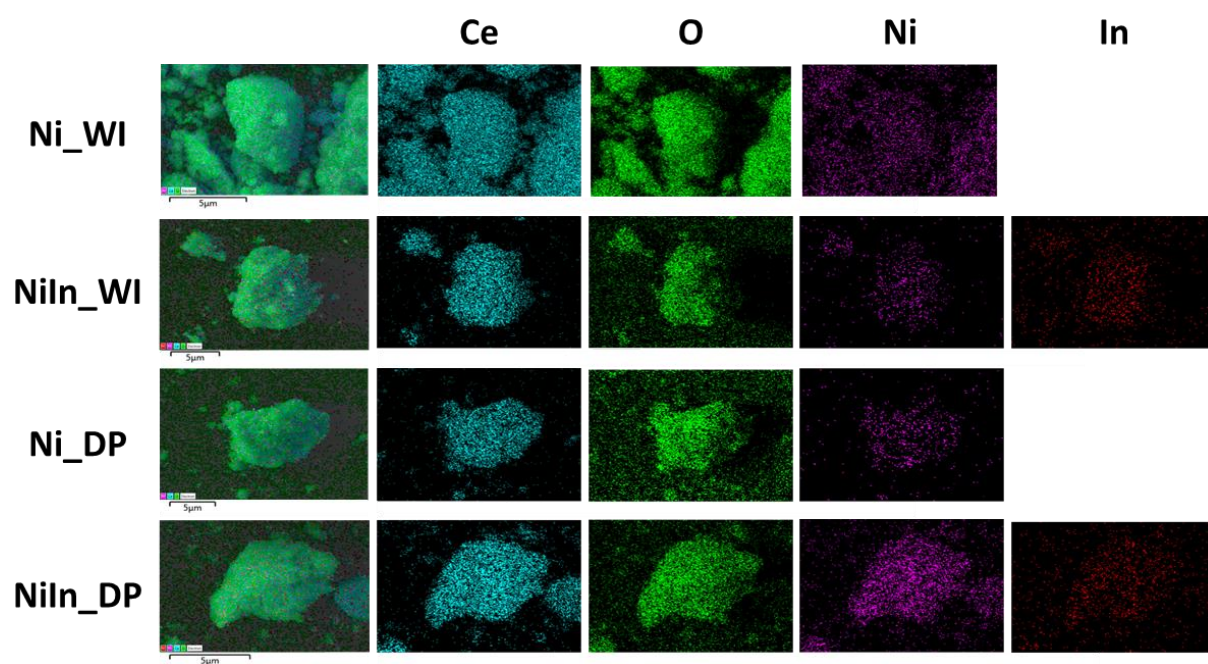


Figure S4. SEM-EDS mapping images of Ni_WI, NiIn_WI, Ni_DP and NiIn_DP samples.

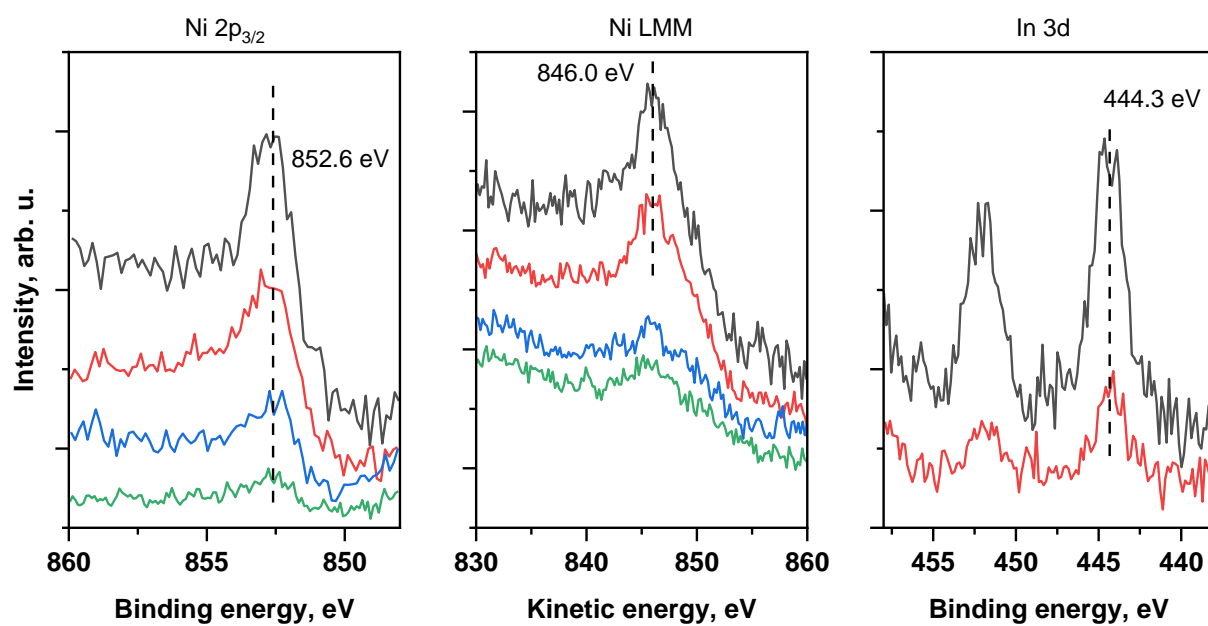


Figure S5. XPS spectra of the *in situ* reduced Ni_DP (red), NiIn_DP (black), Ni_WI (blue) and NiIn_WI (green) catalysts in the Ni 2p_{3/2} and Ni LMM region and the In 3d region for the bimetallic catalysts.

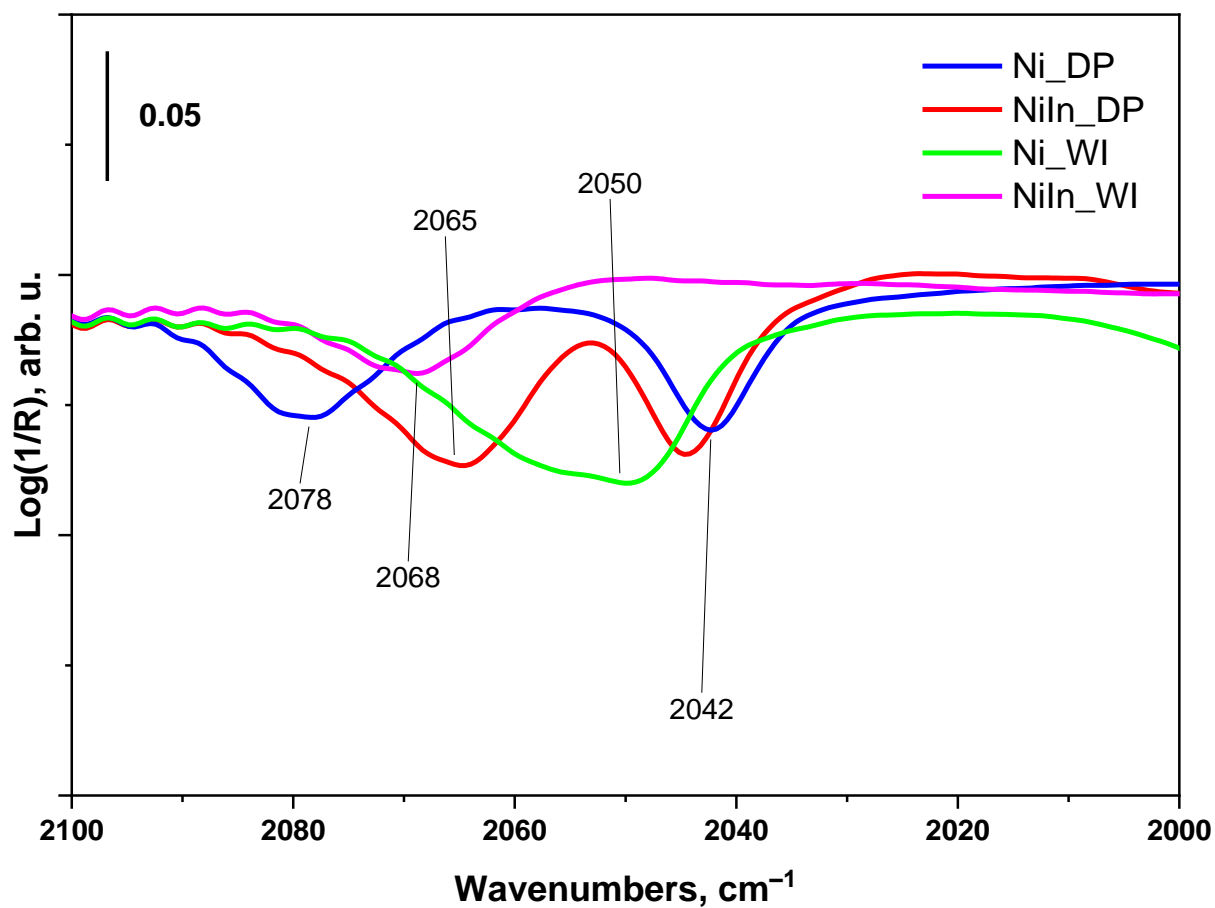
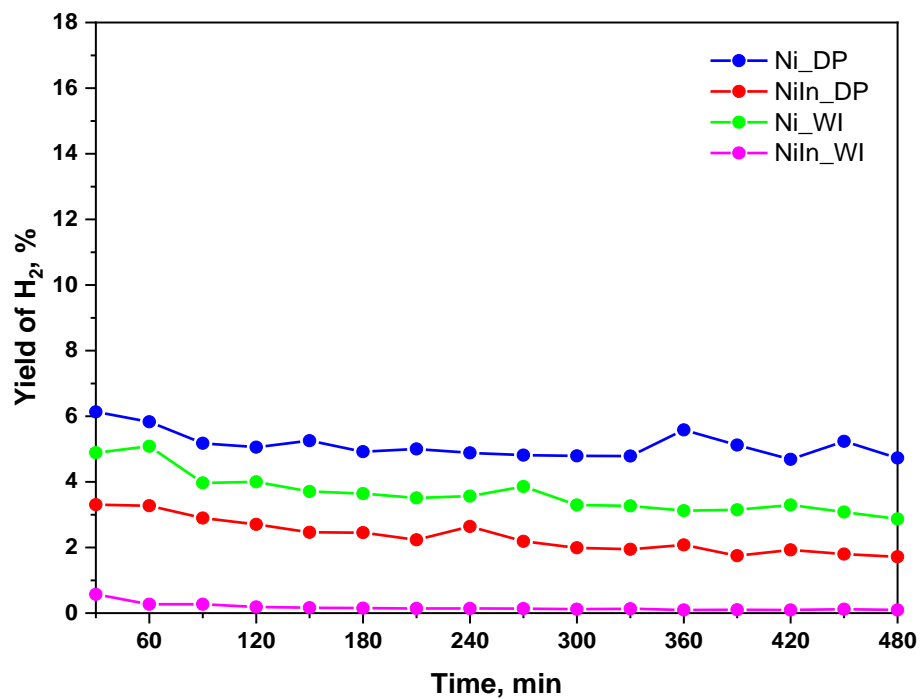


Figure S6. Difference spectra of DRIFT spectra recorded at room temperature after after CO adsorption followed by 5 minutes of purging with 5% H₂/Ar (red curves in Fig. 4) minus those previously recorded in 1% CO/Ar after 5 minutes of exposure (dashed curves in Fig. 4) on the catalyst samples.

a)



b)

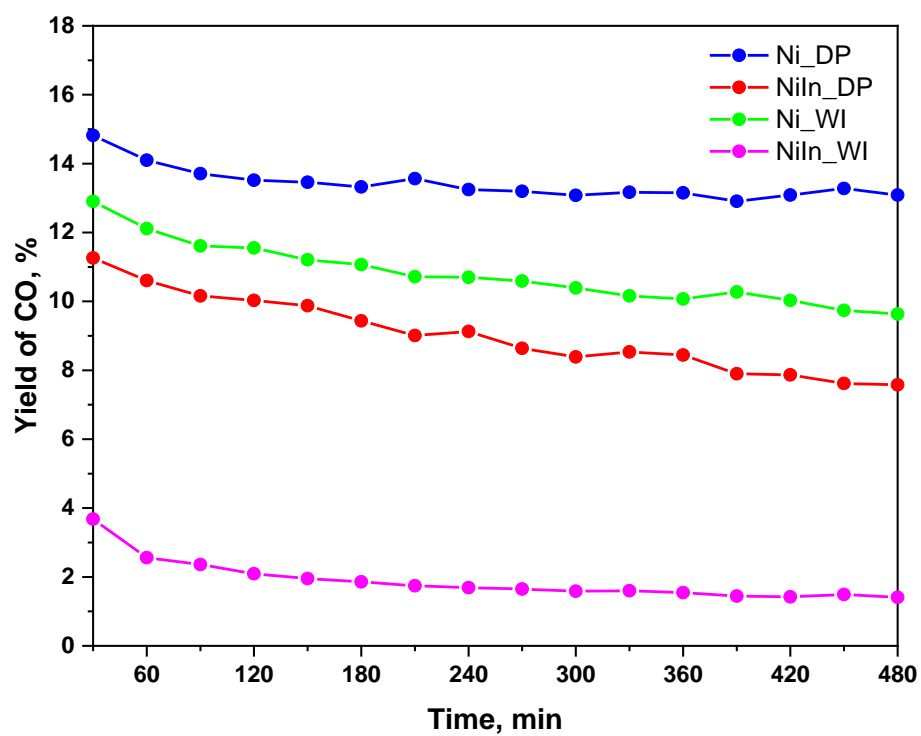
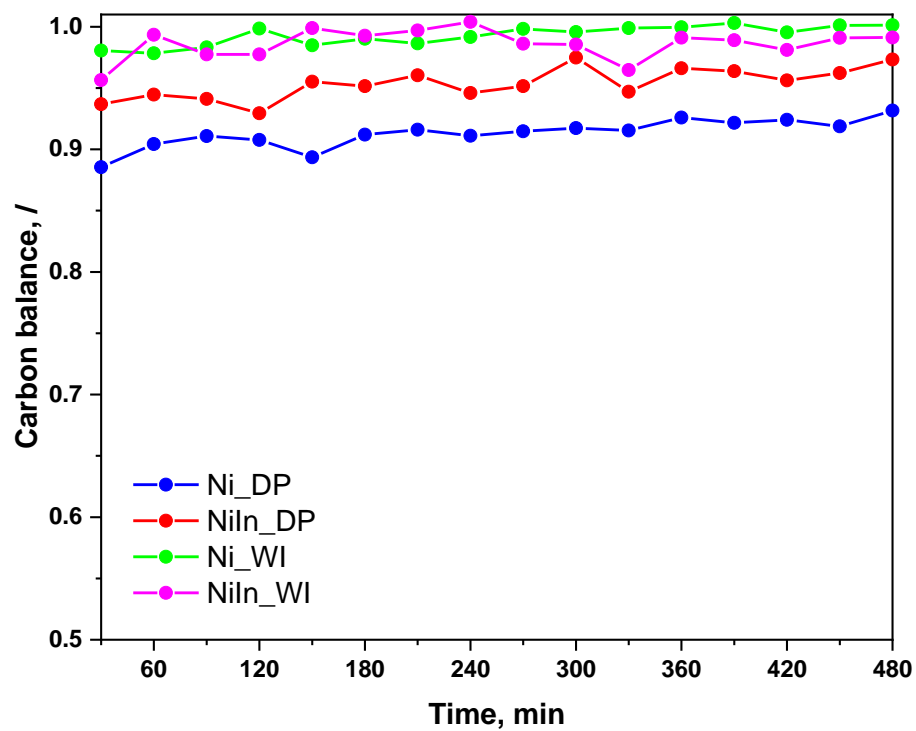


Figure S7. Yields of (a) H₂ and (b) CO obtained by DRM of the catalysts under study, reduced at 650 °C.

a)



b)

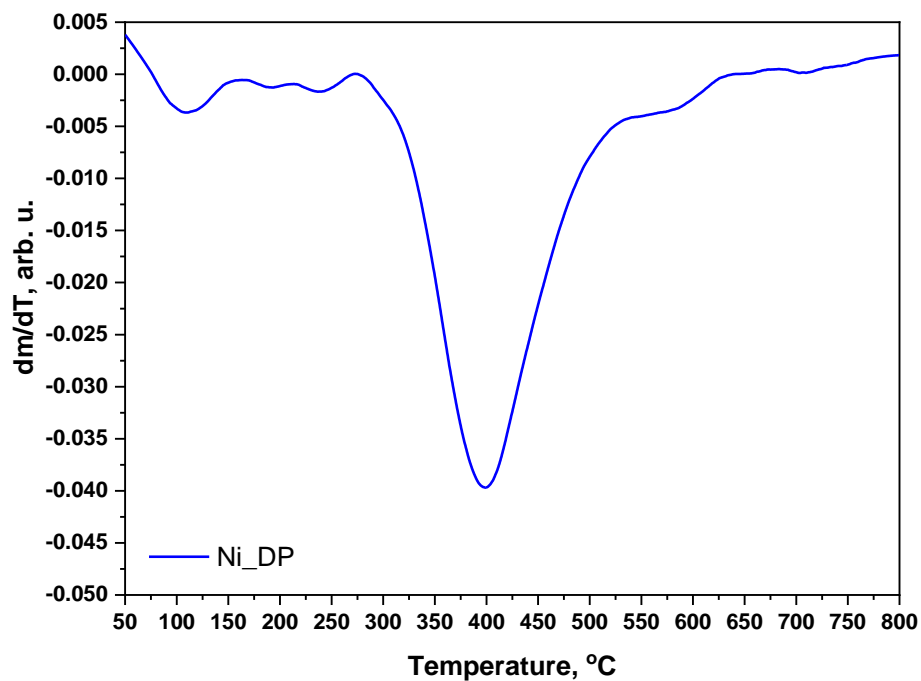


Figure S8. Graphical representation of the (a) carbon balance of the catalysts studied and (b) TGA of the spent Ni_DP catalyst conducted in air.

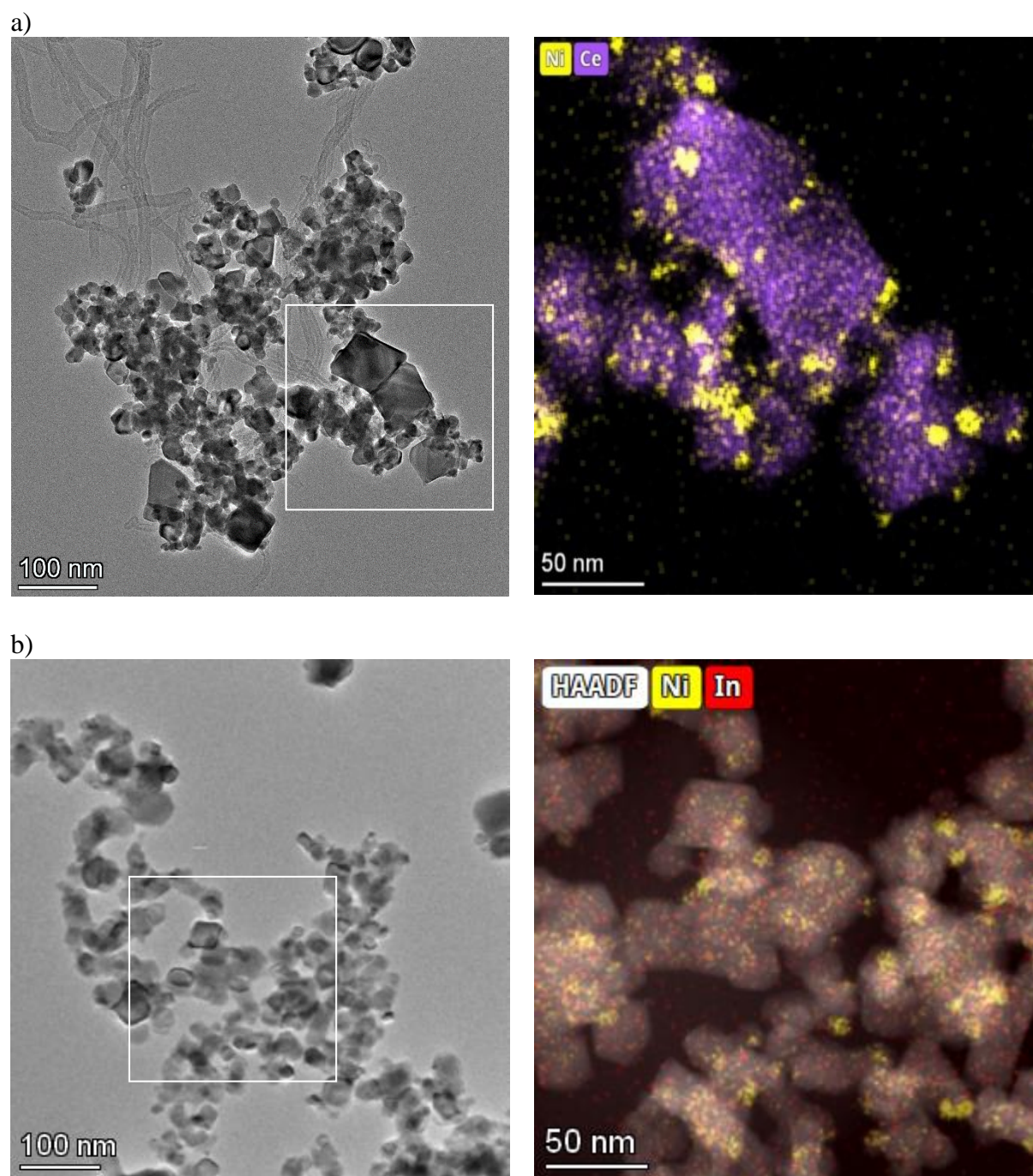


Figure S9. TEM images (left) and elemental maps (right) of spent (a) Ni_DP and (b) NiIn_DP catalysts. The Ni/In atomic ratio on the measured area of NiIn_DP sample is 31.

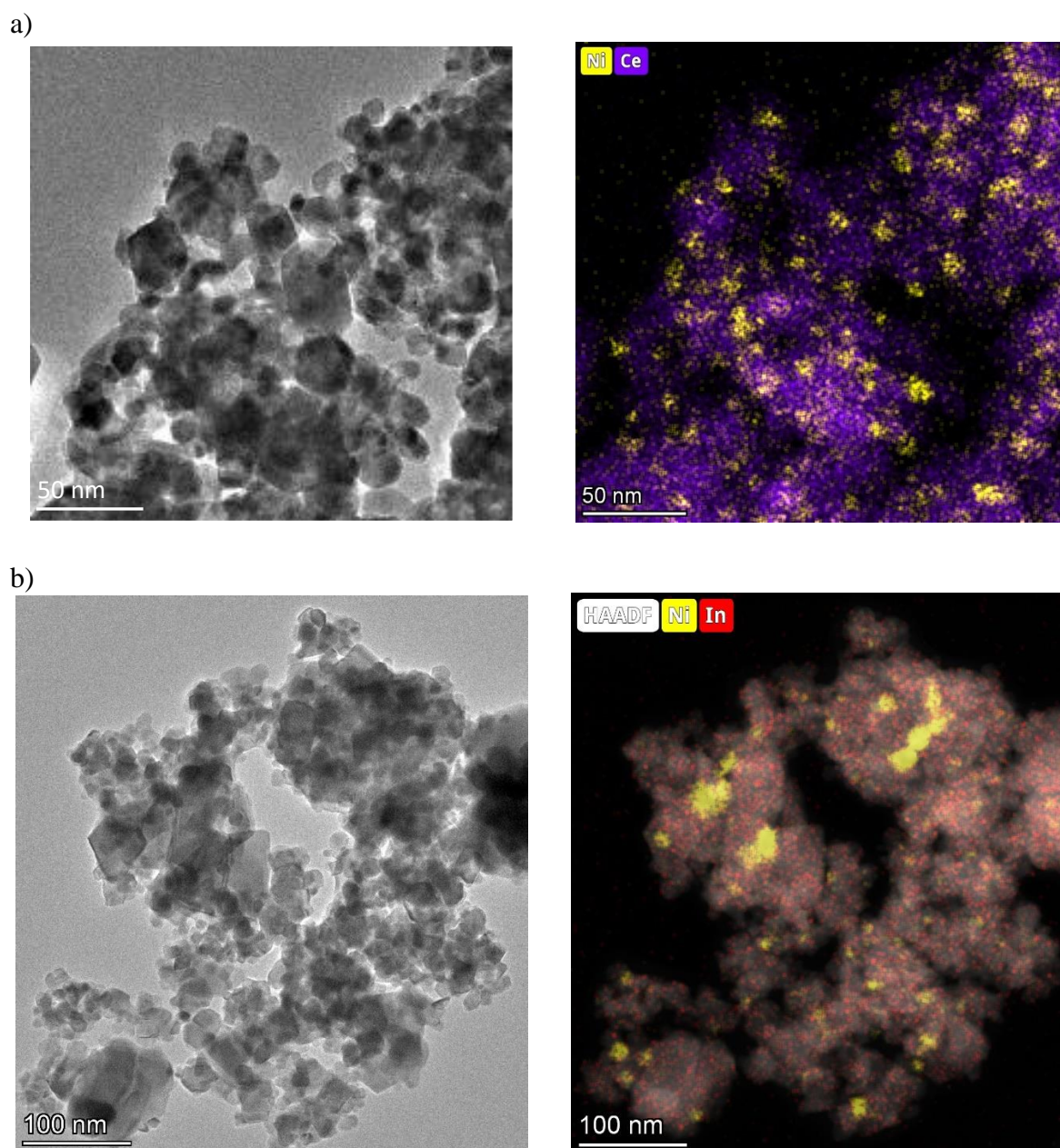


Figure S10. TEM images (left) and elemental maps (right) of spent (a) Ni_WI and (b) NiIn_WI catalysts. The Ni/In atomic ratio on the measured area of NiIn_WI sample is 28.

Table S1

Experimental values of cell unit obtained by XRD measurements (Figure. S1c) and corresponding cell volume.

Sample	a	b	c	Volume of cell
	nm			10^6 pm^3
CeO ₂	0.541	0.541	0.541	158.5
Ni_WI	0.541	0.541	0.541	158.4
NiIn_WI	0.541	0.541	0.541	158.4
Ni_DP	0.382	0.382	0.540	79.0
NiIn_DP	0.541	0.541	0.541	158.5

Table S2

Results of SEM-EDS elemental analysis of the studied materials.

Sample	Ce	O	Ni	In
	wt.%			
Ni_WI	80.8±2.8	16.5±3.1	2.7±0.8	/
NiIn_WI	81.6±1.6	15.8±1.9	2.3±0.3	0.2±0.1
Ni_DP	79.9±2.3	17.0±2.4	3.2±0.2	/
NiIn_DP	77.3±3.0	19.2±3.0	3.2±0.2	0.3±0.1

Note: The sodium content in the samples tested was below the LOD.