Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Boosting the performance of Ni/Al_2O_3 for the Reverse Water Gas Shift reaction through formation of copper-nickel nanoalloys

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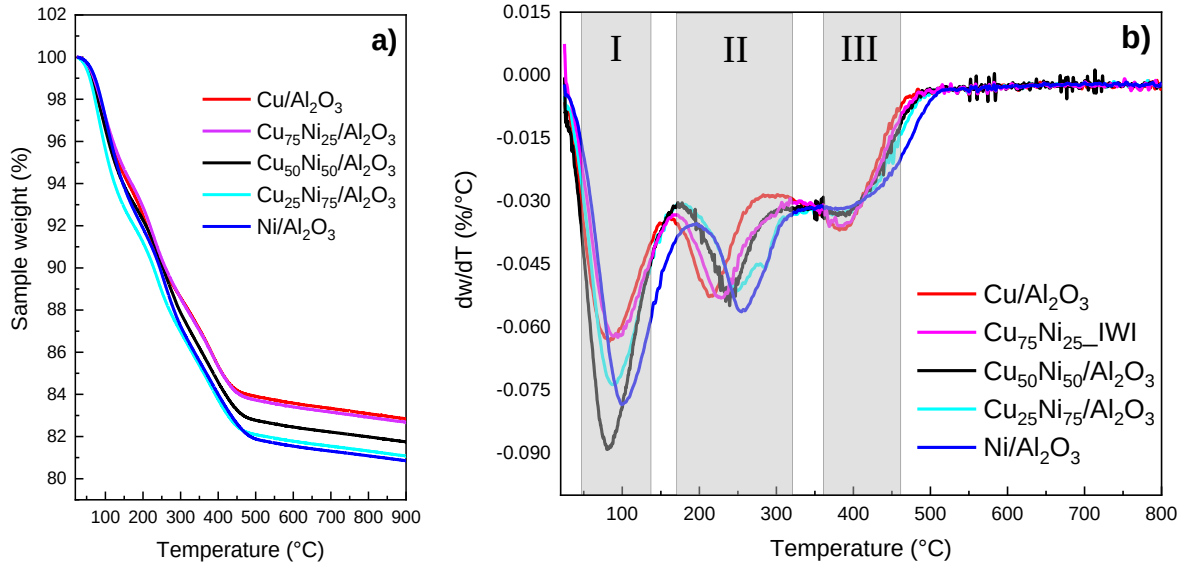


Figure S1. Thermogravimetric analysis of uncalcined samples.

a) TGA; b) DTGA analysis. Conditions: From 20°C up to 900°C, 10K min-1, 21% O_2 in Ar, 20 ml min^{-1}.

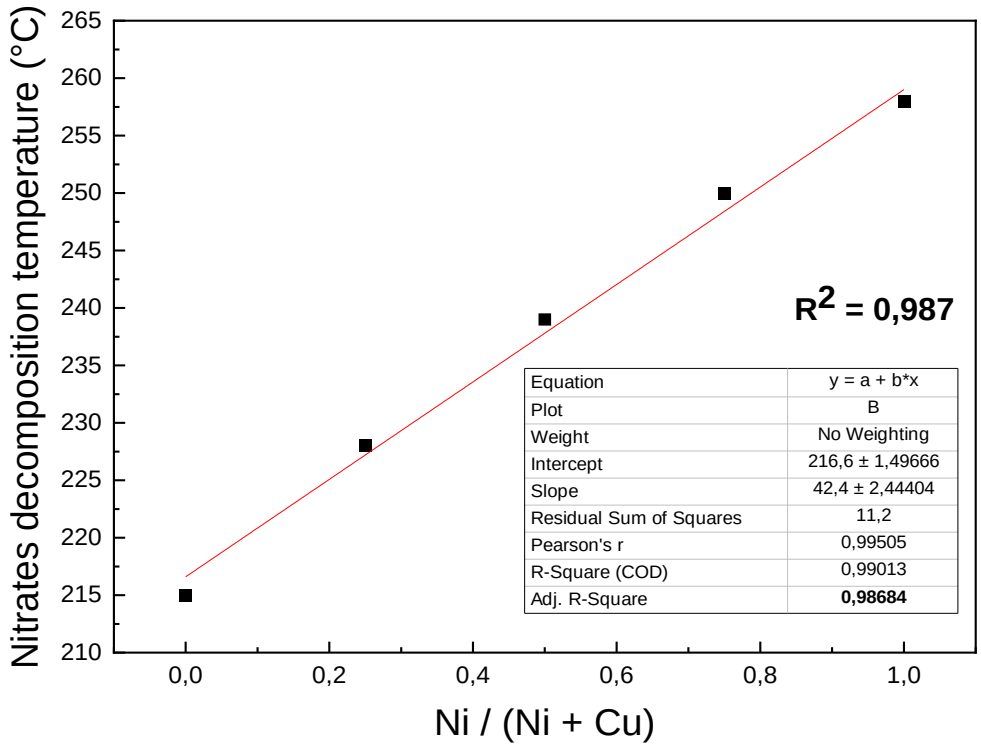


Figure S2. Nitrates decomposition temperature of copper, nickel, and copper-nickel catalyst. Prepared via impregnation of nitrates on γ-alumina. Conditions: 25mg of sample, 10K min^{-1}, 21% O_2 in N_2, 20 ml min^{-1}.

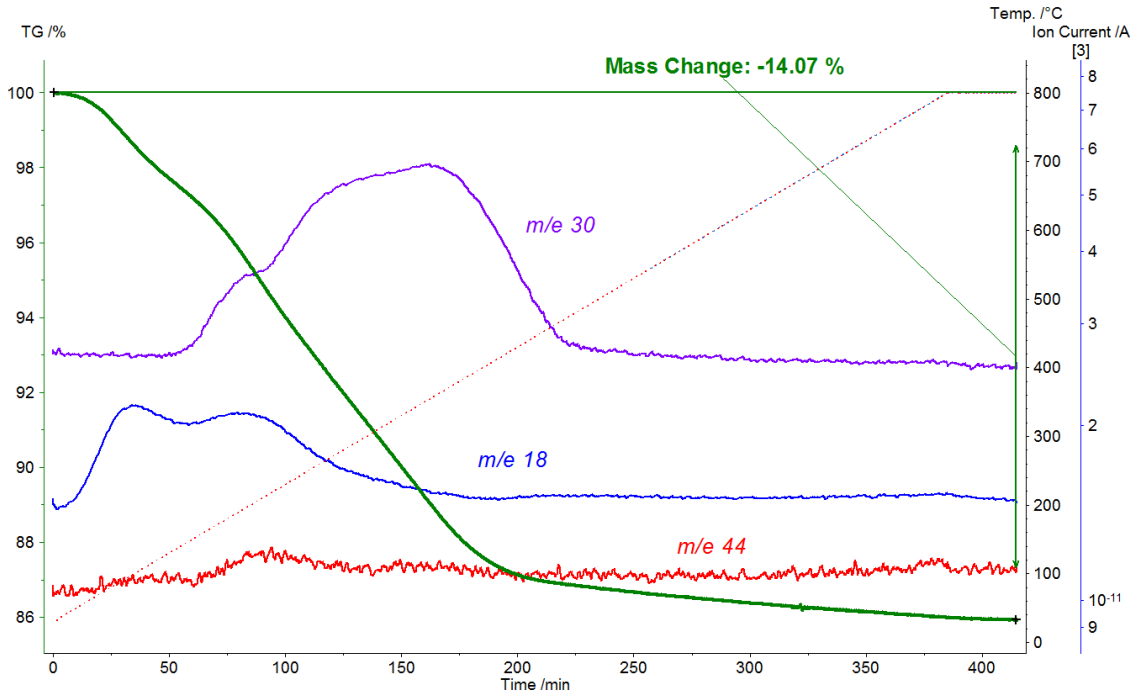


Figure S3. TGA – MS Study of $Cu_{50}Ni_{50}/Al_2O_3$ prepared via impregnation of nitrates.

Conditions: From 20°C to 800°C, 2Kpm, 30min hold, 21% O_2 in Ar, 100 ml min^{-1}. m/e = 18 (H_2O), 30 (NO) and 44 (NO_2).

CNHS Analysis (%)					
Sample	**Treatment**	**C**	**N**	**H**	**S**
Al_2O_3	Not Calcined	0,06	n/d	0,64	0
Cu/Al_2O_3	Impregnated	0,03	1,53	0,96	0
	Calcined	0,12	n/d	0,42	0
$Cu_{75}Ni_{25}/Al_2O_3$	Impregnated	0.01	1.55	1.05	0
	Calcined	0.23	n/d	0.69	0
$Cu_{50}Ni_{50}/Al_2O_3$	Impregnated	0,03	1,54	0,99	0
	Calcined	0,08	n/d	0,41	0
$Cu_{25}Ni_{75}/Al_2O_3$	Impregnated	0.01	1.61	0.96	0
	Calcined	0.20	n/d	0.71	0
Ni/Al_2O_3	Impregnated	0,02	1,51	1,03	0
	Calcined	0,07	n/d	0,42	0

Table S1. Elemental composition of the impregnated and calcined $CuNi/Al_2O_3$ catalysts. n/d: below detection limit.

Sample	m(cat) / mg	Theoretical H_2 consumption /mmol	Experimental H_2 consumption (Tmax=500°C) /mmol (Relative)	Experimental H_2 consumption (Tmax=900°C) /mmol (Relative)
Cu/Al_2O_3	256	0.20	0.19 (95)	0.20 (100%)
$Cu_{75}Ni_{25}/Al_2O_3$	255.7	0.19	0.14 (74%)	0.19 (100%)
$Cu_{50}Ni_{50}/Al_2O_3$	268.9	0.20	0.12 (60%)	0.20 (100%)
$Cu_{25}Ni_{75}/Al_2O_3$	249.5	0.18	0.06 (34%)	0.18 (100%)
Ni/Al_2O_3	262.9	0.22	0.03 (13%)	0.20 (91%)
Al_2O_3	203.8	0	0	0

Table S2. Hydrogen consumption of the different catalysts after reduction pretreatment at 900°C and 500°C.

The hydrogen consumption was calculated at 500°C (corresponding to the reduction pretreatment prior to catalysis) and 900°C 8corresponding to the highest temperature analyzed in the Belcat-II H_2-TPR setup).

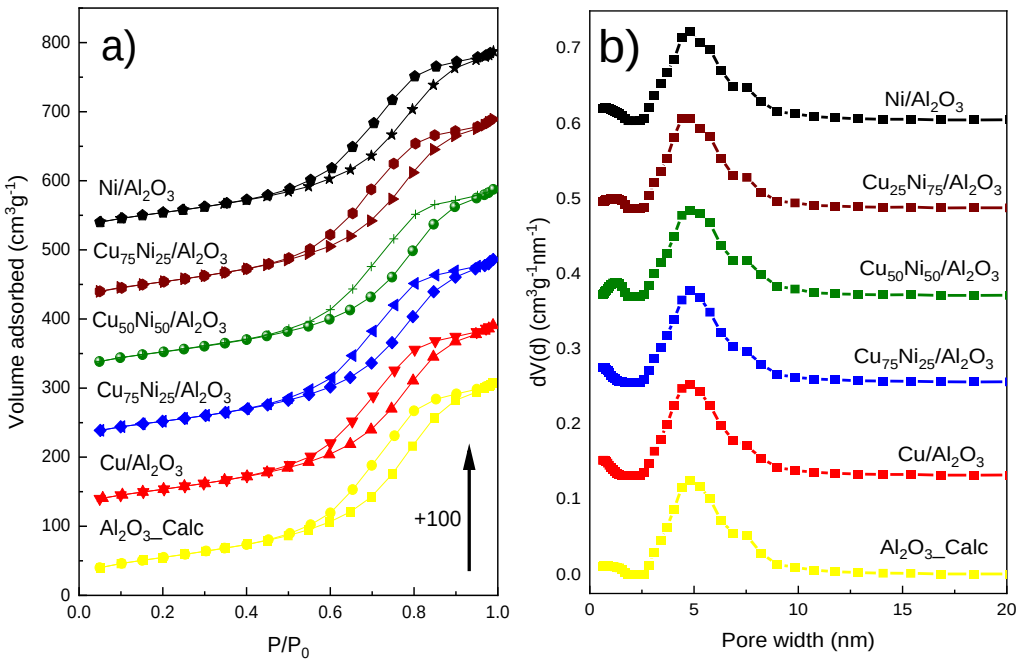


Figure S4. a) Nitrogen sorption isotherms and b) pore size distribution of $CuNi/Al_2O_3$ catalyst.

Sample	Name	Position (eV)	% at. XPS	Cu/Ni ratio	% at. ICP	Cu/Ni ratio
$Cu_{25}Ni_{75}/Al_2O_3$	Cu 2p	932.67	21	0.27	26	0.35
	Ni 2p	856.48	79		74	
$Cu_{50}Ni_{50}/Al_2O_3$	Cu 2p	932.49	53	1.12	49	0.96
	Ni 2p	856.59	47		51	
$Cu_{75}Ni_{25}/Al_2O_3$	Cu 2p	932,65	77	3.35	75	3
	Ni 2p	856,63	23		25	

Table S3. Comparison of the Cu/Ni atomic ratio determined by XPS and ICP analysis.

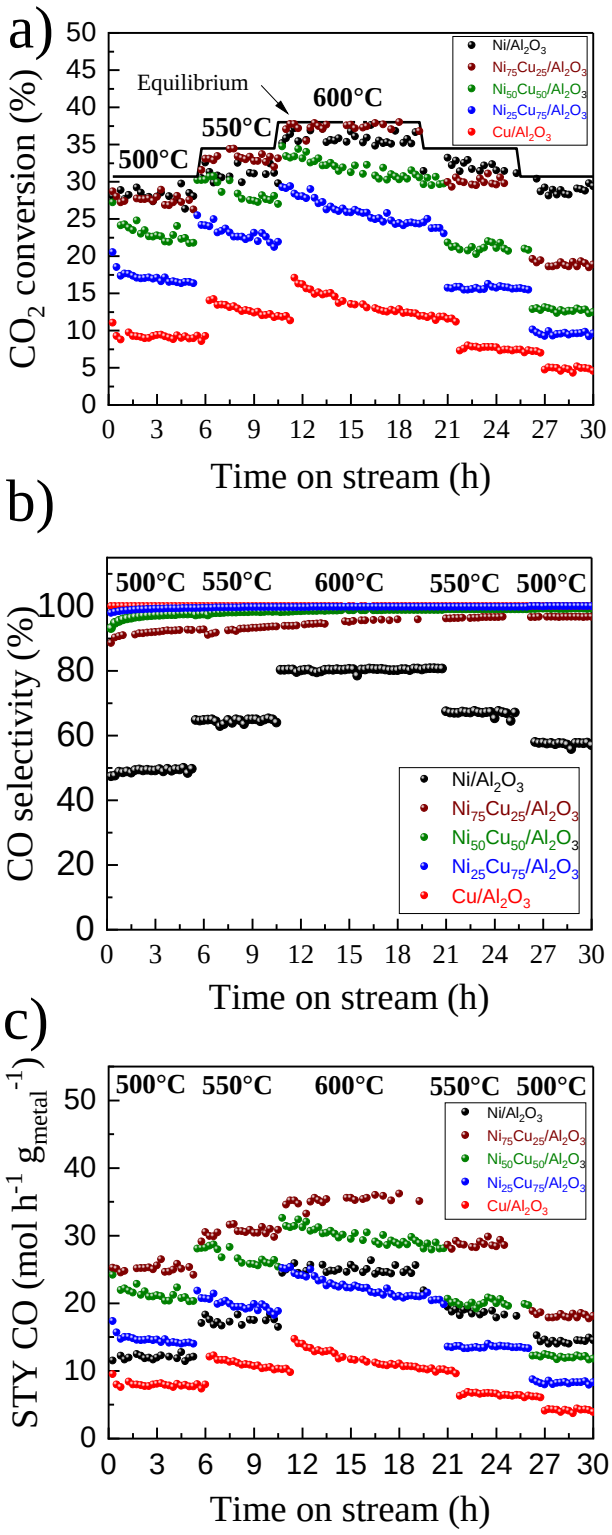


Figure S5. Catalytic performance of the CuNi/Al_2O_3 catalysts during the 30h of time on stream: a) CO_2 conversion; b) CO selectivity; c) space-time yield of carbon monoxide.

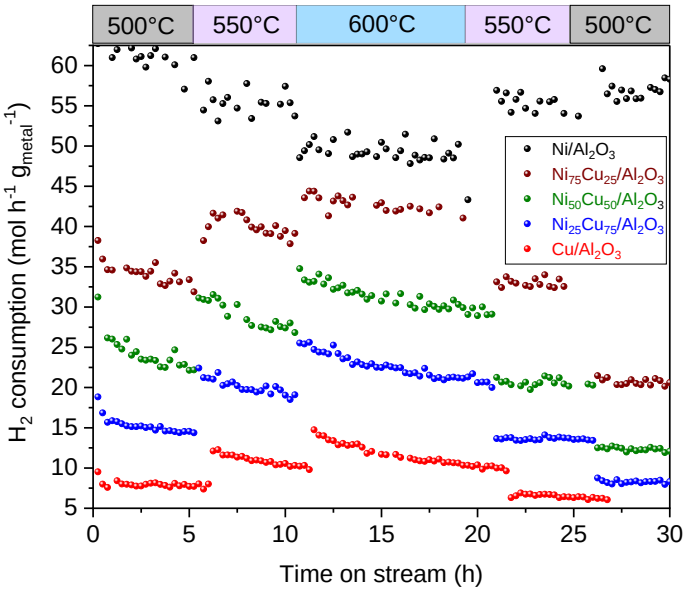


Figure S6. Hydrogen consumption of the different catalysts during time on stream.

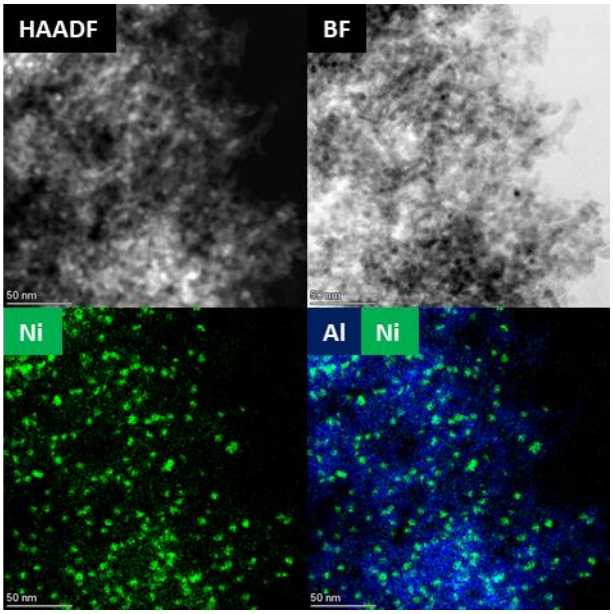
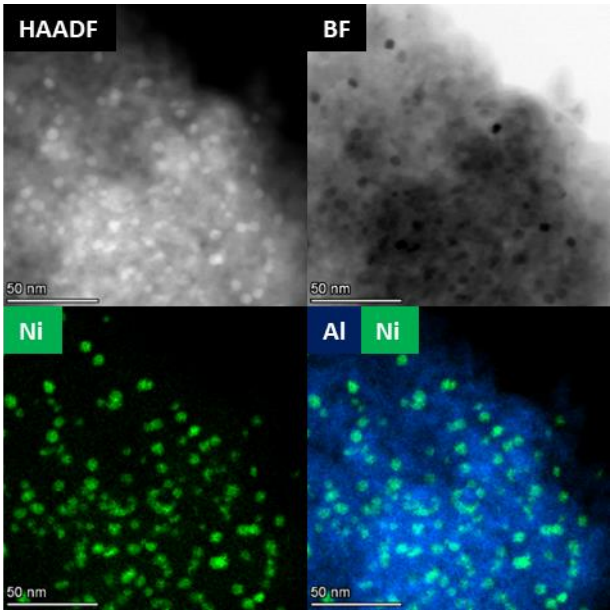


Figure S7. STEM-EDS study of fresh Ni/Al_2O_3 catalyst.



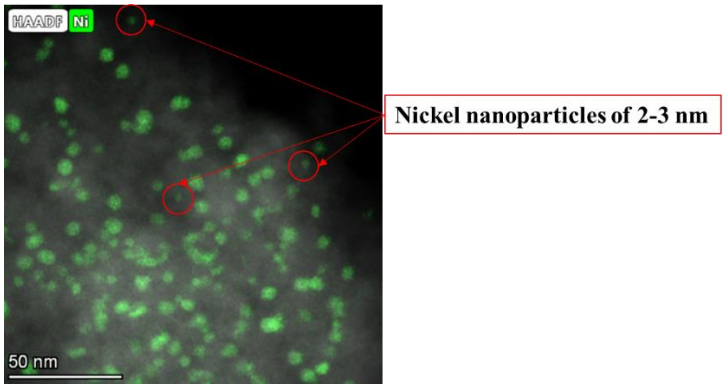


Figure S8. STEM-EDS study of spent Ni/Al_2O_3 catalyst (after reaction).

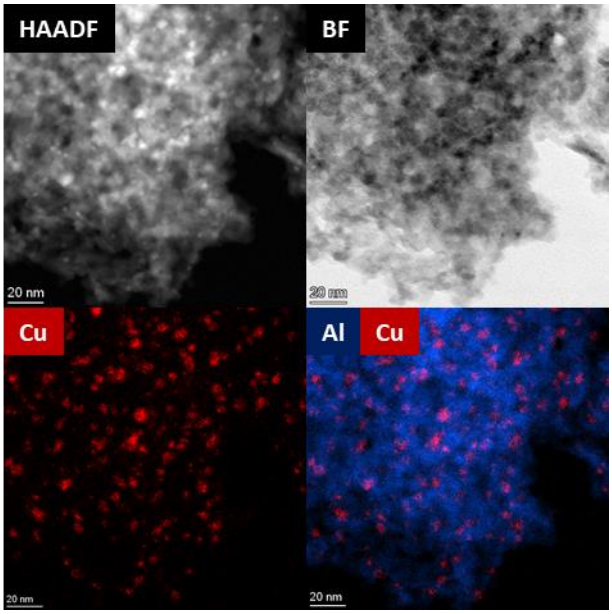


Figure S9. STEM-EDS study of fresh Cu/Al_2O_3 catalyst.

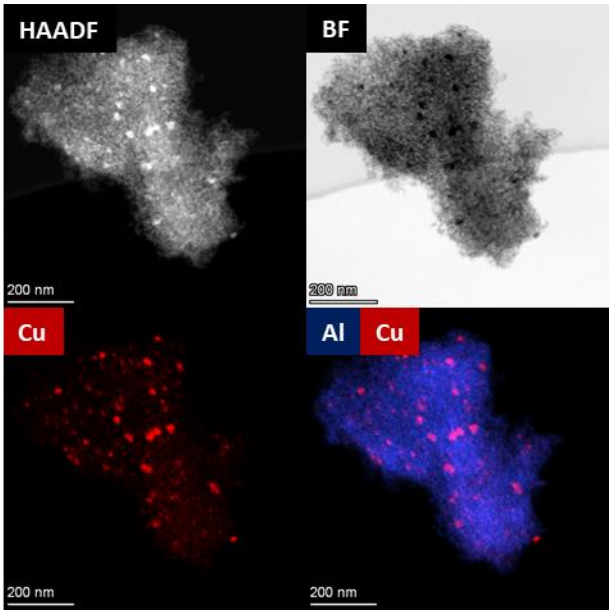


Figure S10.a. STEM-EDS study of spent Cu/Al_2O_3 catalyst.

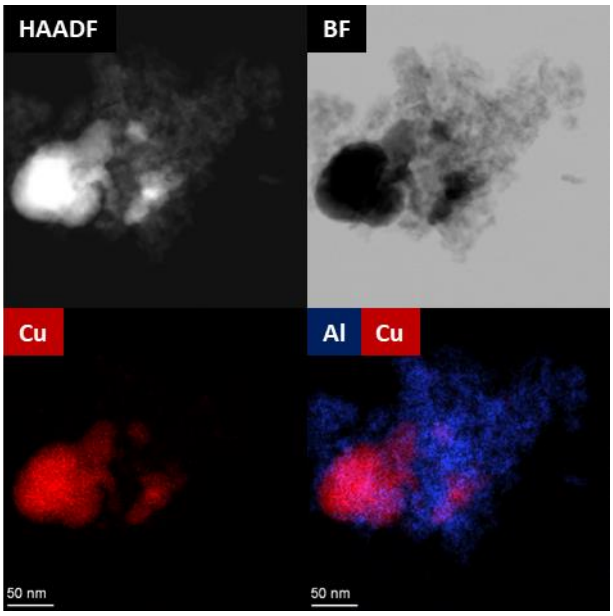


Figure S10.b. STEM-EDS study of spent Cu/Al_2O_3 catalyst.

Agglomerates up to 100 nm of copper could be observed in the spent Cu/Al_2O_3 catalyst.

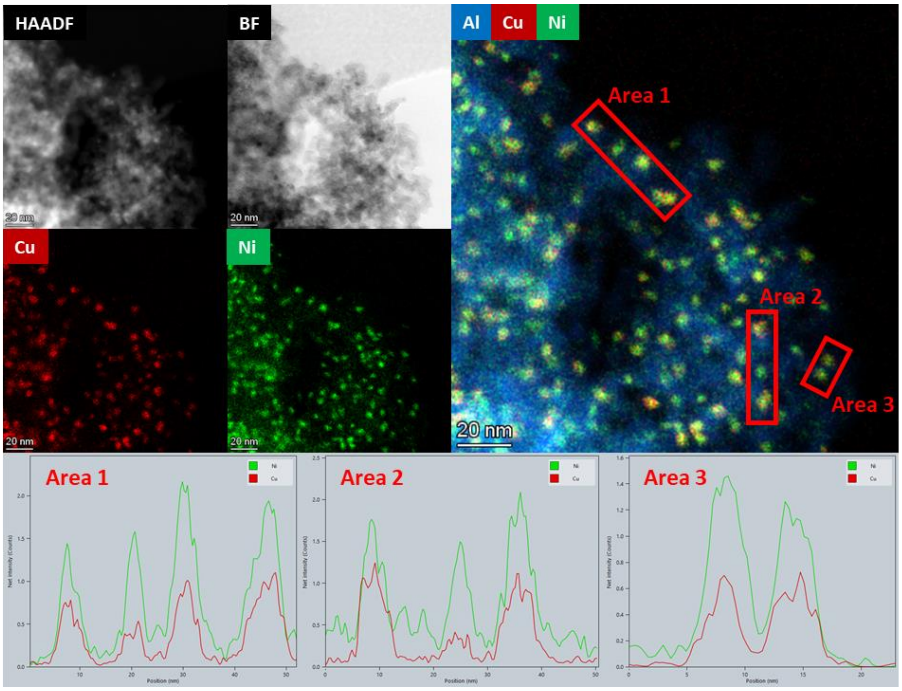


Figure S11. STEM-EDS study of fresh $Cu_{25}Ni_{75}/Al_2O_3$ catalyst.

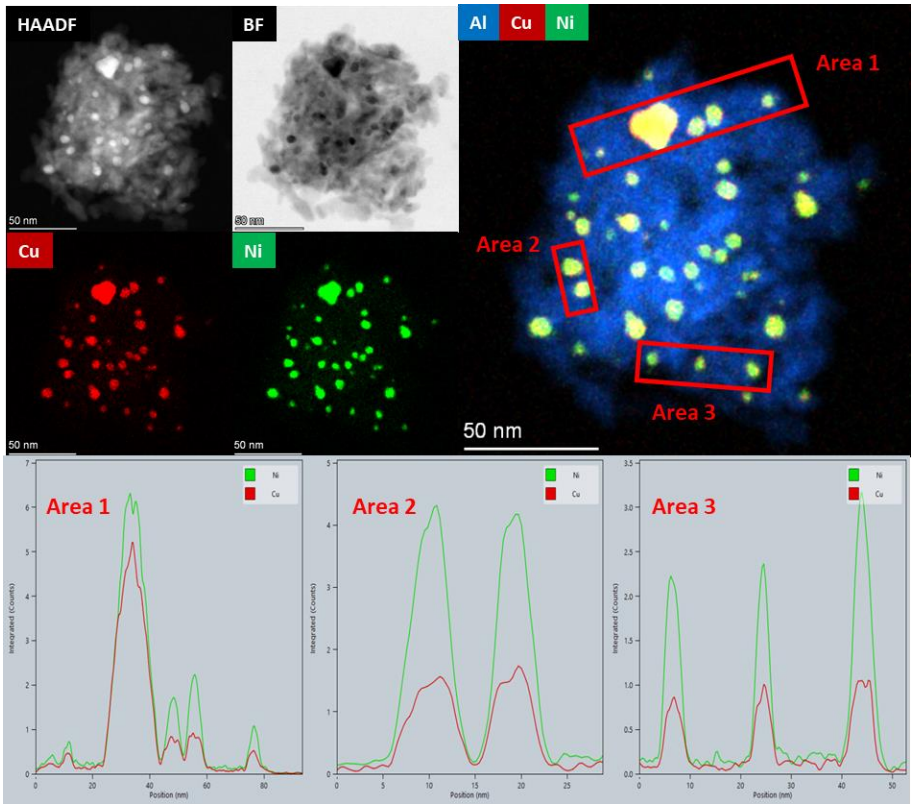


Figure S12. STEM-EDS study of $Cu_{25}Ni_{75}/Al_2O_3$ after reaction.

Some isolated agglomerates up to 20 nm could be observed in the spent $Cu_{25}Ni_{75}/Al_2O_3$ catalyst.

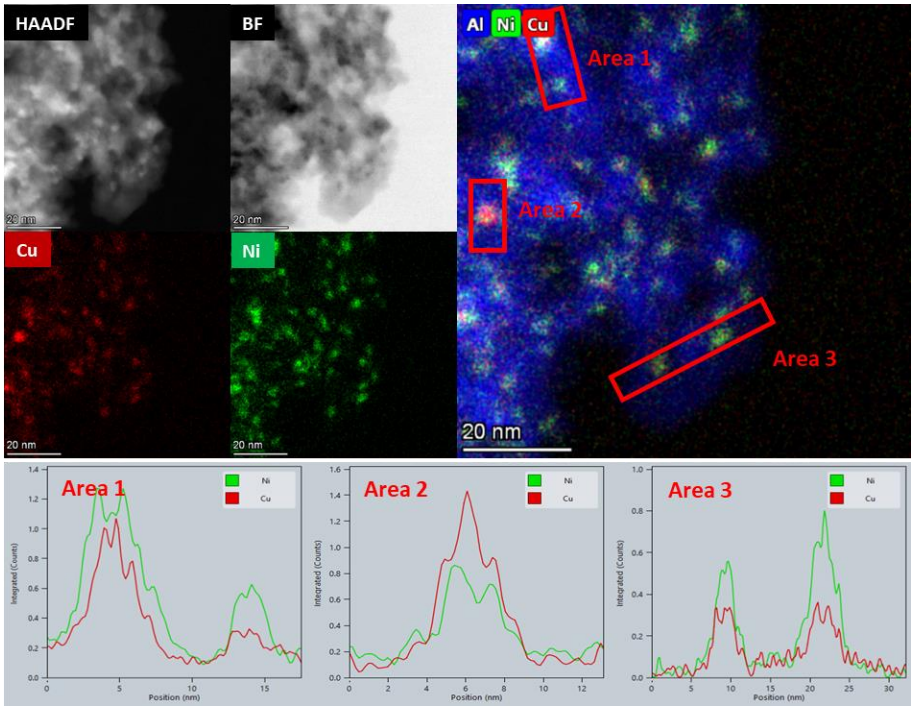


Figure S13. STEM-EDS study of fresh $Cu_{50}Ni_{50}/Al_2O_3$ catalyst.

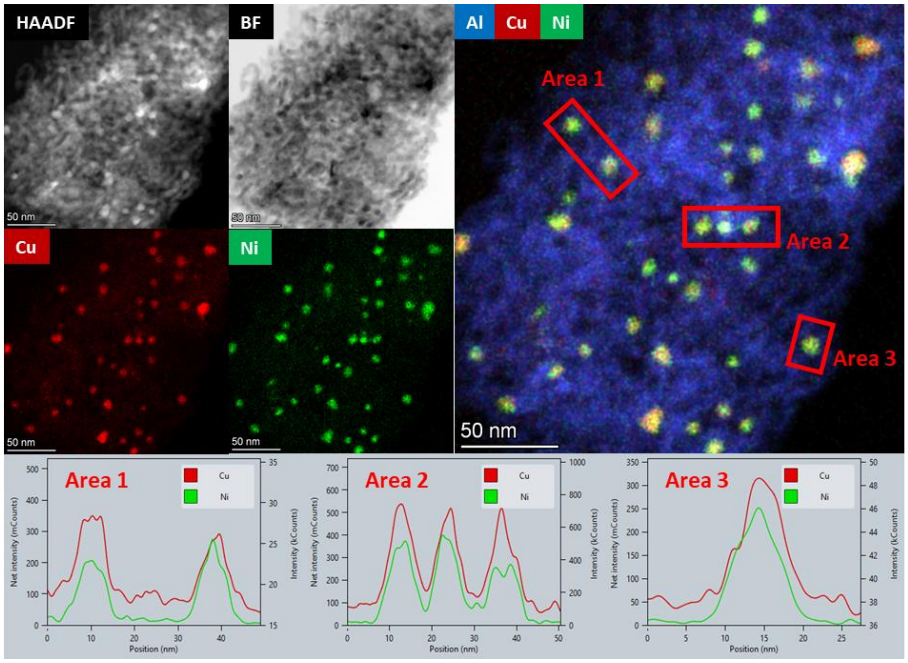


Figure S14.a. STEM-EDS study of spent $Cu_{50}Ni_{50}/Al_2O_3$ catalyst.

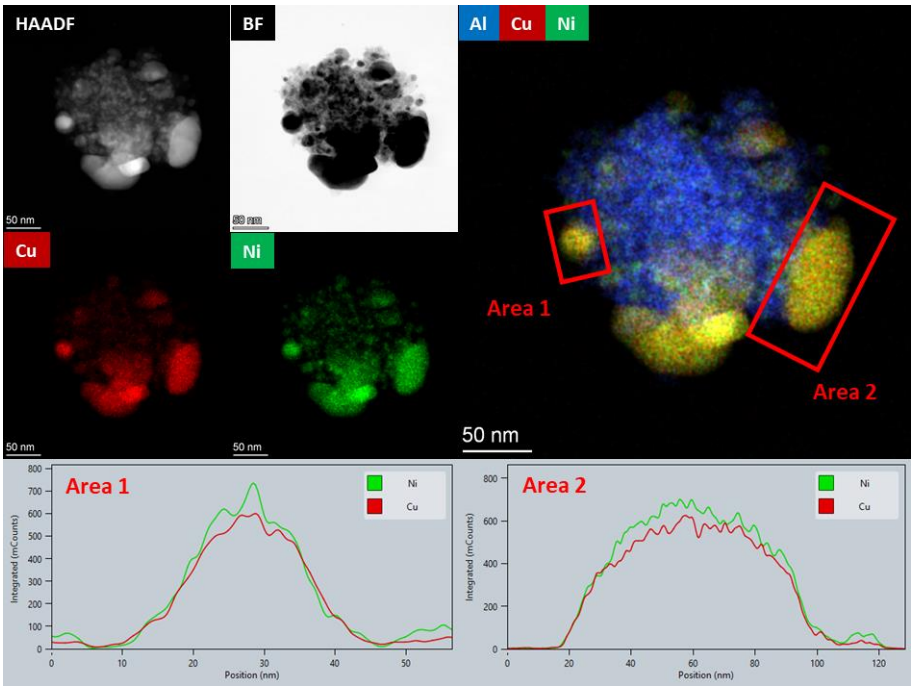


Figure S14.b. STEM-EDS study of spent $Cu_{50}Ni_{50}/Al_2O_3$ catalyst.

Agglomerates up to 80 nm of bimetallic $Cu_{50}Ni_{50}$ nanoparticles could be observed in the spent $Ni_{50}Cu_{50}/Al_2O_3$ catalyst.

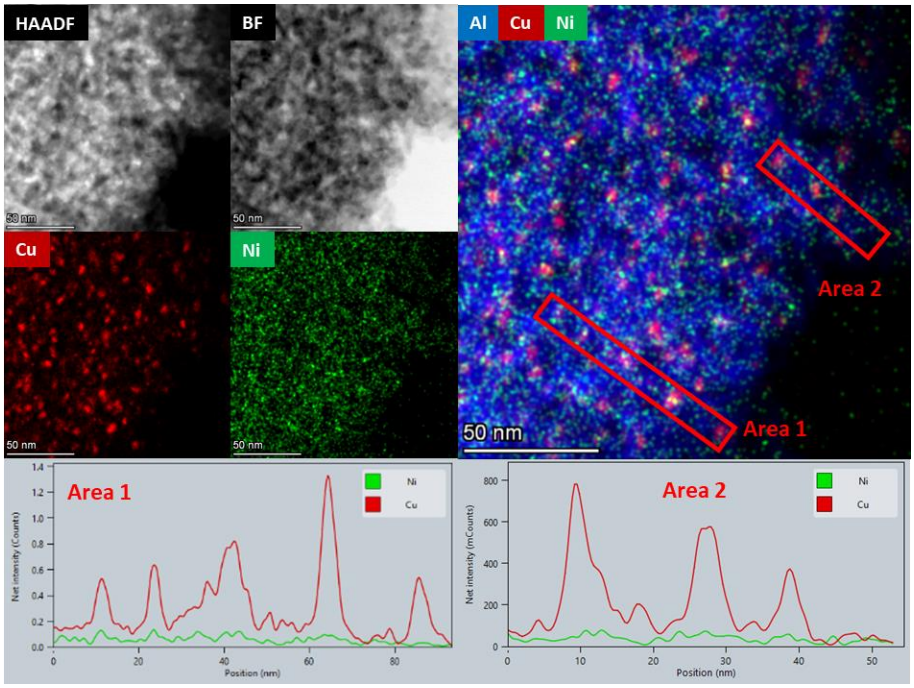


Figure S15. STEM-EDS study of fresh $Cu_{75}Ni_{25}/Al_2O_3$ catalyst.

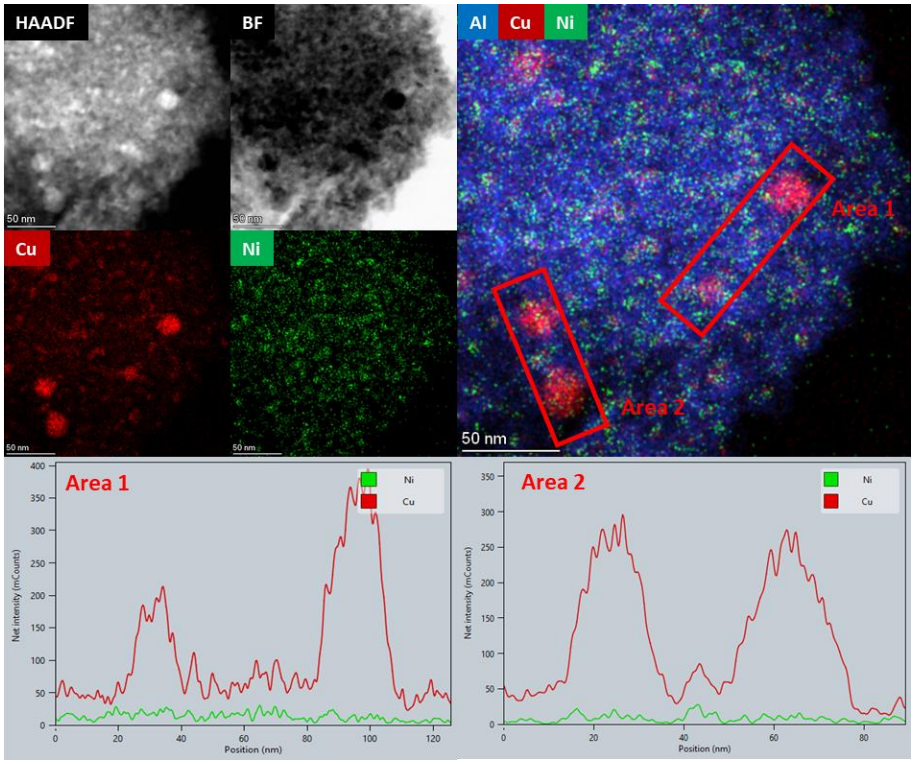


Figure S16.a. STEM-EDS study of spent $Cu_{75}Ni_{25}Al_2O_3$ catalyst.

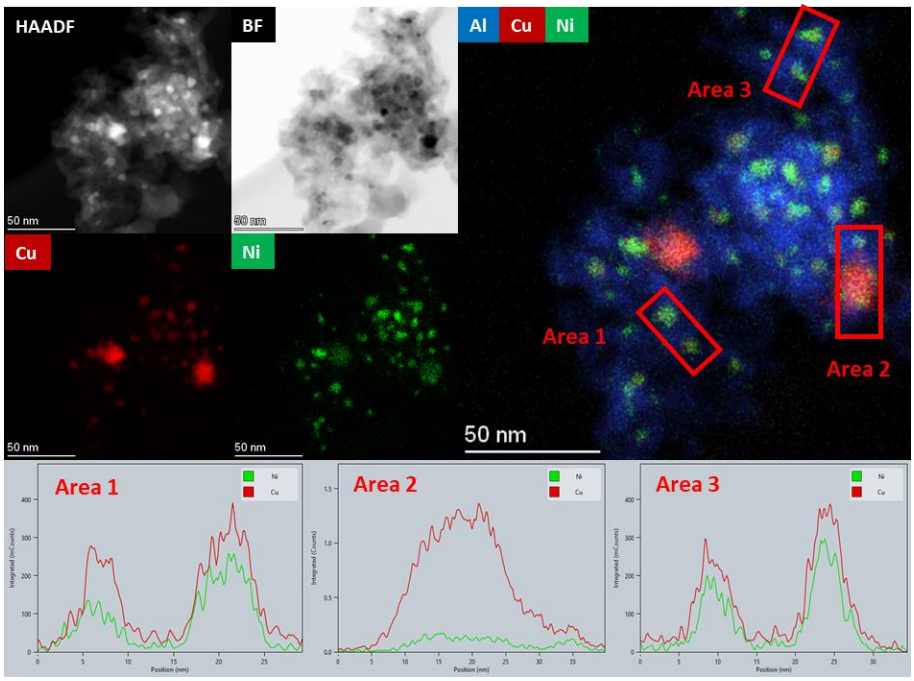


Figure S16.b. STEM-EDS study of spent $Cu_{75}Ni_{25}Al_2O_3$ catalyst.

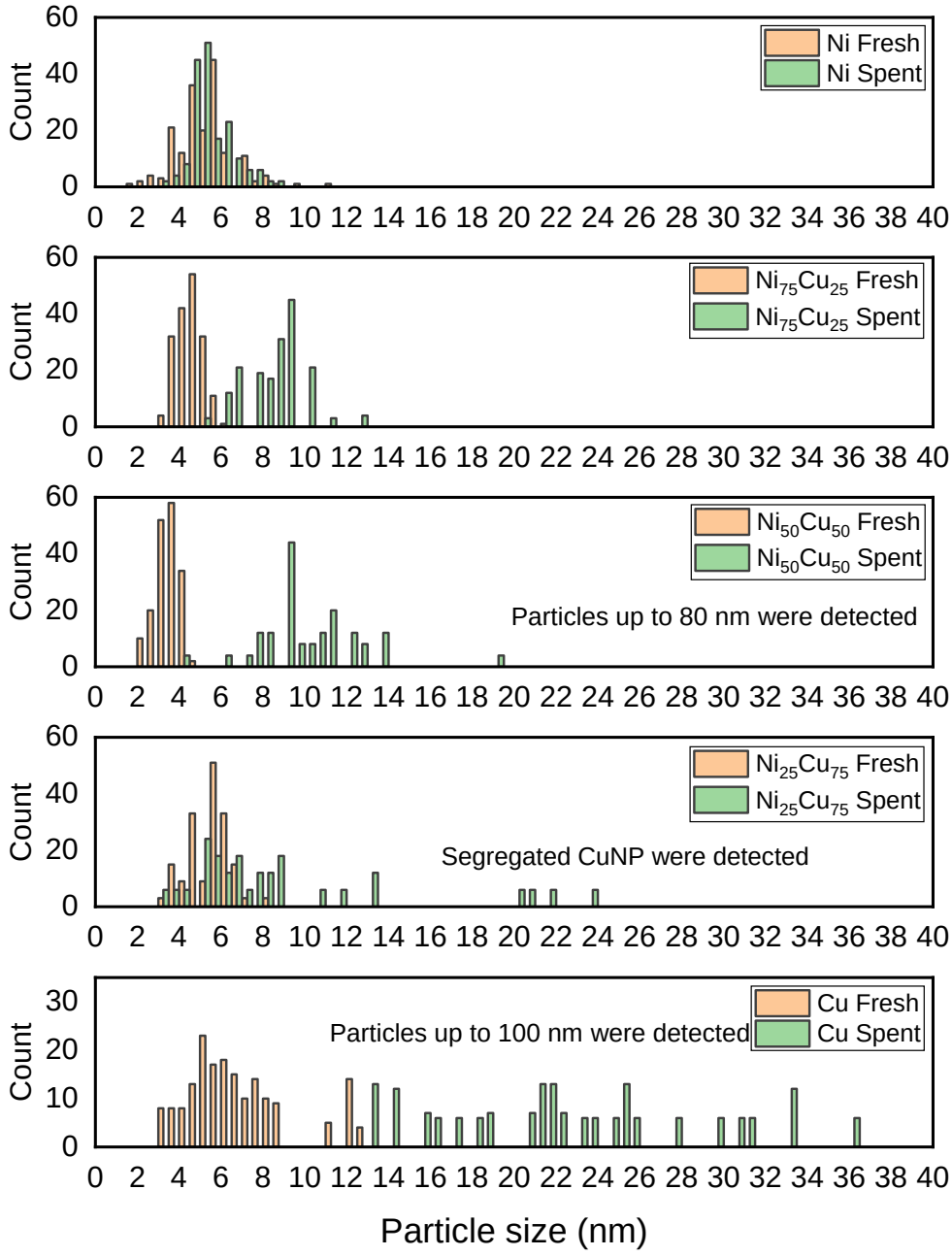


Figure S17. Particle size distribution of both fresh and spent $CuNi/Al_2O_3$ catalyst.

CNHS Analysis (%)					
Sample	**Condition**	**C**	**N**	**H**	**S**
Cu/Al_2O_3	Fresh	**0.297**	0.024	0.854	-
	Spent	**0.378**	0.029	0.829	-
$Cu_{75}Ni_{25}/Al_2O_3$	Fresh	**0.276**	0.032	0.795	-
	Spent	**3.711**	0.117	0.965	-
$Cu_{50}Ni_{50}/Al_2O_3$	Fresh	**0.997**	0.034	0.900	-
	Spent	**0.165**	0.138	0.938	-
$Cu_{25}Ni_{75}/Al_2O_3$	Fresh	**0.272**	0.037	0.843	-
	Spent	**0.160**	0.036	0.974	-
Ni/Al_2O_3	Fresh	**0.427**	0.017	0.917	-
	Spent	**0.201**	0.120	0.771	

Table S4. Elemental composition of both fresh and spent $CuNi/Al_2O_3$ catalysts.