Platinum on High-Entropy Aluminate Spinels as Thermally Stable CO Oxidation Catalysts

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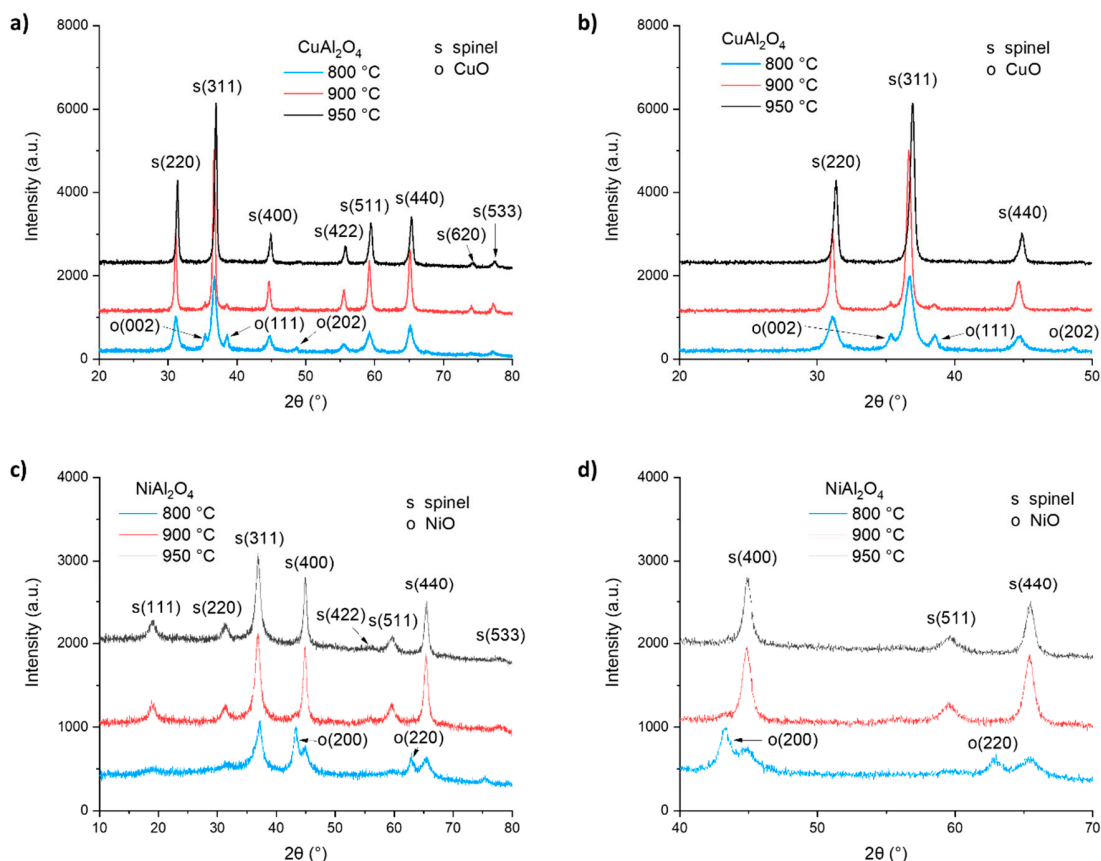[*] Correspondence: crriley@sandia.gov

Supporting Information

Figure S1. PXRD patterns of (a,b) $CuAl_2O_4$ and (c,d) $NiAl_2O_4$ spinel samples calcined at 800 °C and aged at 900 and 950 °C. Aged samples were quenched in ambient air.
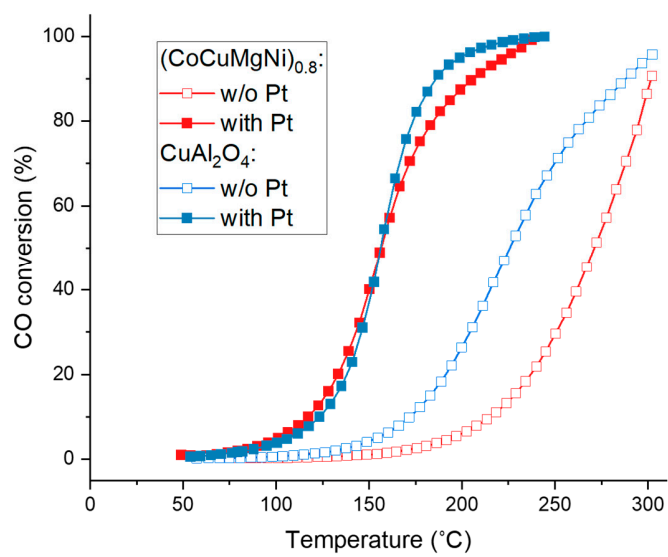
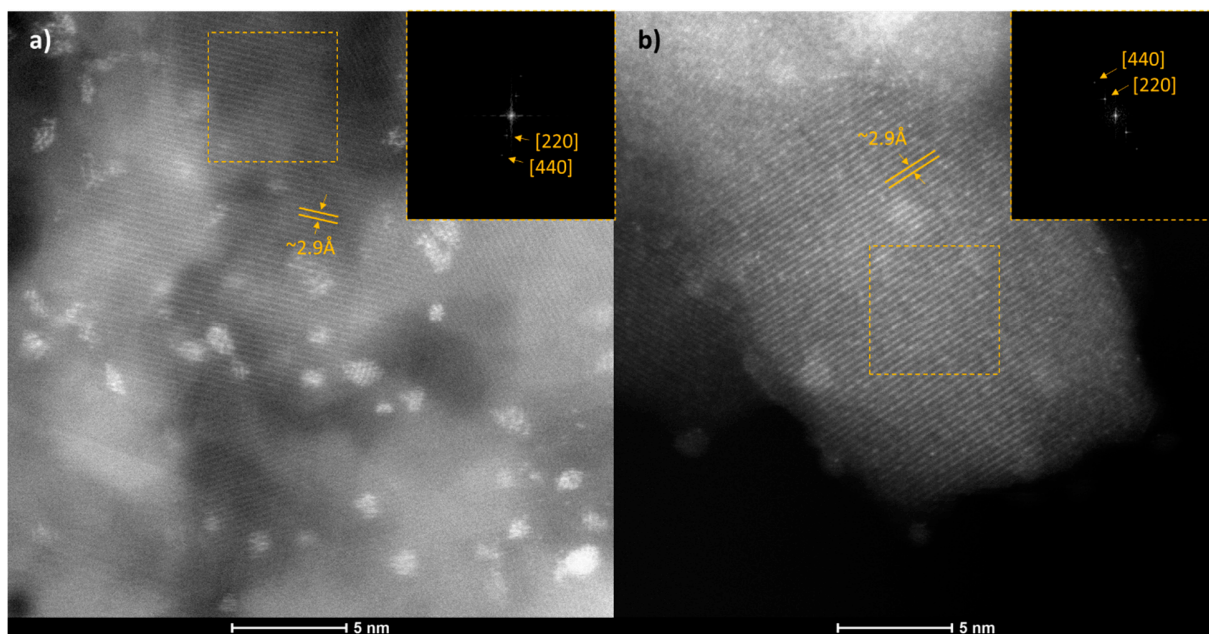**Figure S2.** CO conversion over $CuAl_2O_4$ and $(CoCuMgNi)_{0.8}$ with and without loaded platinum.

Figure S3. STEM images of (a) Pt – Mg after calcination and (b) Pt – $(CoCuMgNi)_1$ after aging.

Table S1. XRD and BET characterization of aged Pt-loaded samples

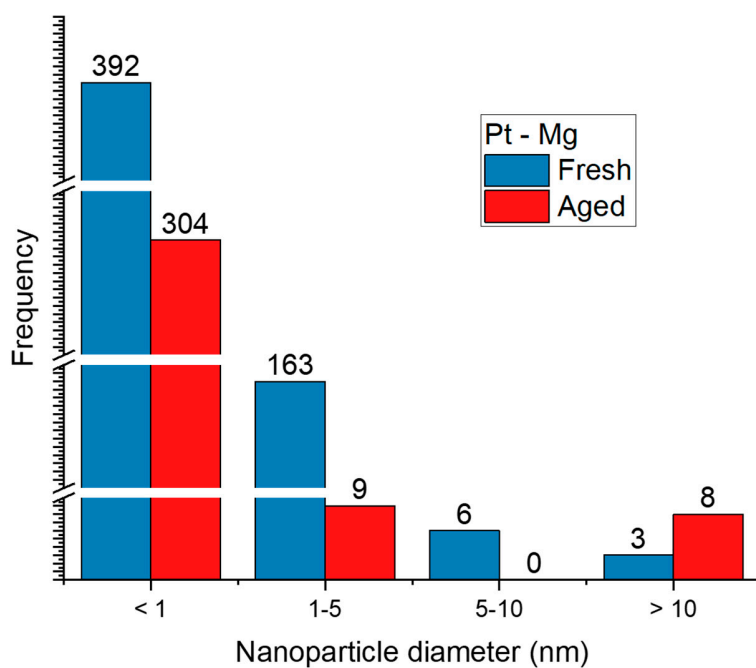| Sample	Spinel lattice parameter (Å)	Spinel crystallite size (nm)	Spinel lattice strain (%)	Specific surface area (m^2/g)
Pt – Co	8.090	18.3	0.06	75
Pt – Cu	8.083	47.3	0.035	4
Pt – Mg	8.035	19.5	0.21	107
Pt – Ni	8.044	8.6	-0.31	55
Pt – $(CoCuMgNi)_1$	8.071	15.6	0.06	24
Pt – $(CoCuMgNi)_{0.8}$	8.071	13.8	0.106	35

Figure S4. Estimated platinum particle size distribution measured from STEM imaging of Pt – Mg before and after aging.

Table S2. Compilation of previous PGM on HEO catalysts and performance in CO oxidation.

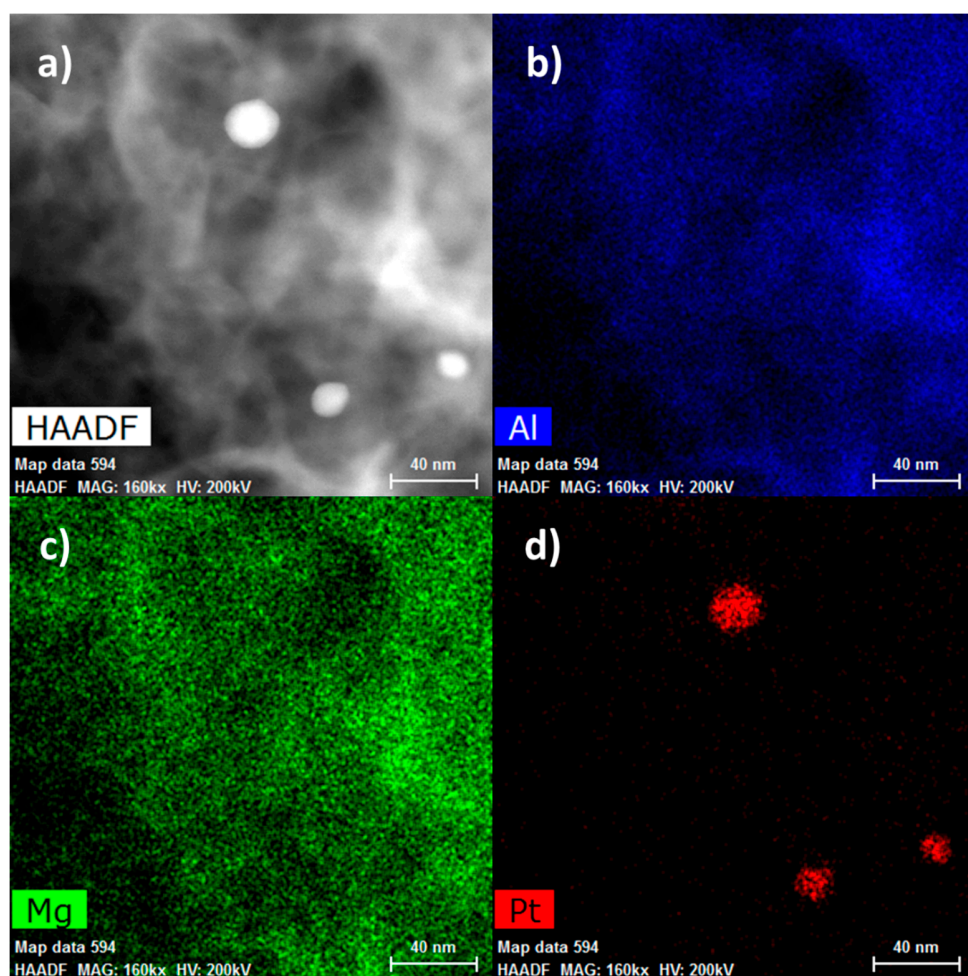| HEO composition	HEO synthesis method	Feed gas composition	Gas hourly space velocity (ml/g_{cat}/h)	Approximate T_{100} (°C)	Reference
Pt- (CoFeNiCuZn)-Al_2O_3	Sol-gel synthesis with calcination at 900°C	1% CO, 16% O_2, 83% N_2	30,000	180	[1]
Au- (MgNiZnCuCo)O	Solid state mixing of binary metal oxides	1% CO, 99% dry air	30,000	230	[2]
Ru- (BaSrBi)(ZrHfTiFe)O_3	Ultrasonication of metal precursor and precipitation agent solution	1% CO, 99% dry air	30,000	120	[3]
Pd- (CeZrHfTiLaO$_x$)-SiO_2	Ball milling of metal salt precursors, followed by 900 °C calcination	-	200,000	165	[4]
Pt- (CoCuMgNi)$_1$Al$_2$O$_4$	Sol-gel synthesis with calcination at 800°C	1.9% CO, 1.3% O_2, 96.8% He	232,500	222	This work

Figure S5. STEM imaging of 1wt% Pt-MgAl$_2$O$_4$-standard after aging at 800 °C for 8hrs via (a) HAADF mode and EDS imaging showing (b) aluminum, (c) magnesium, and (d) platinum within the sample.
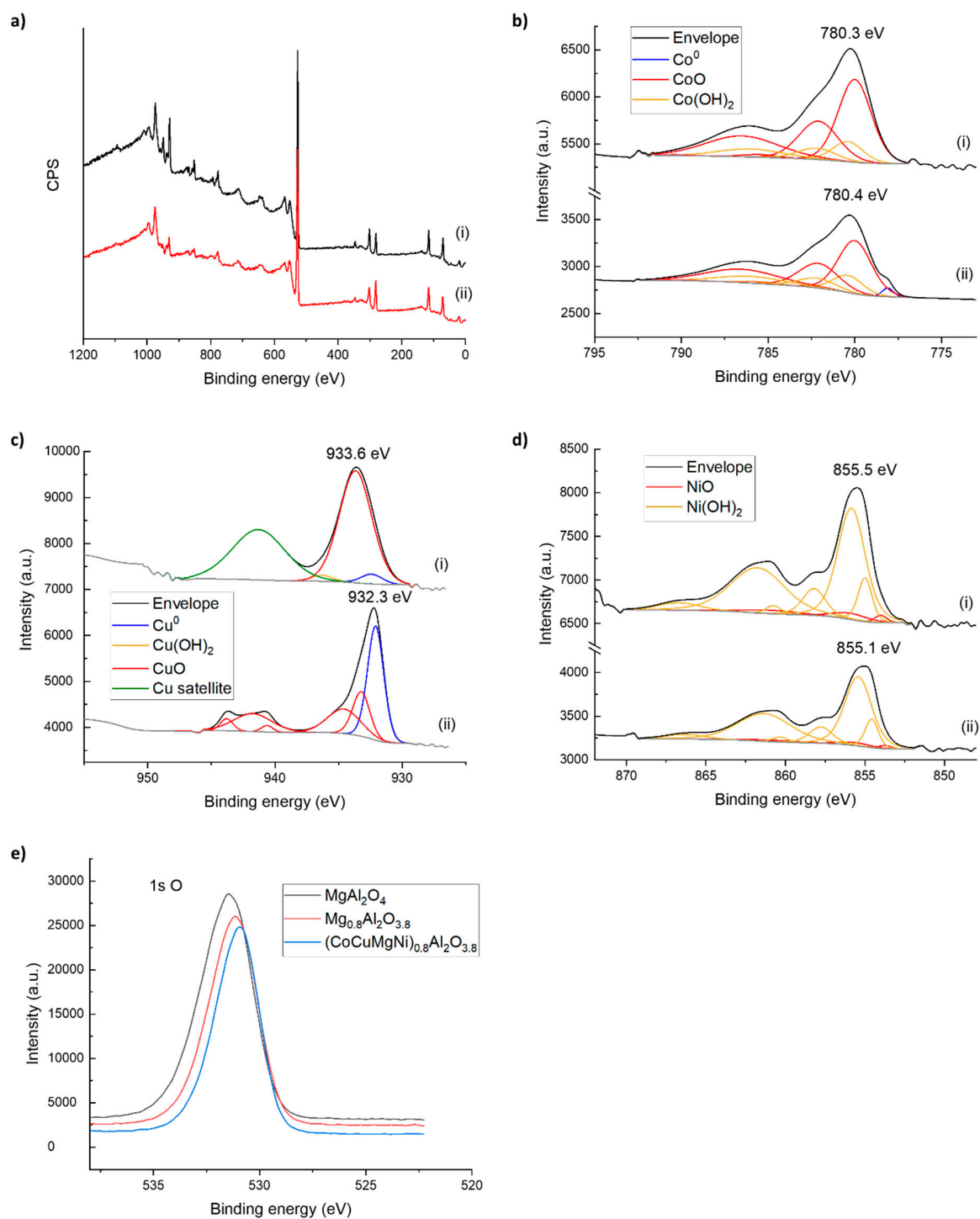
Figure S6. XPS (a) survey, (b) 2p Co, (c) 2p Cu, and (d) 2p Ni spectra of (i) the (CoCuMgNi)$_{0.8}$Al$_2$O$_{3.8}$ support as prepared and (ii) Pt – (CoCuMgNi) after aging, and (e) 1s O spectra of select spinel supports.[5, 6]

Table S3. Oxidation state of cobalt, copper, and nickel calculated from XPS spectra

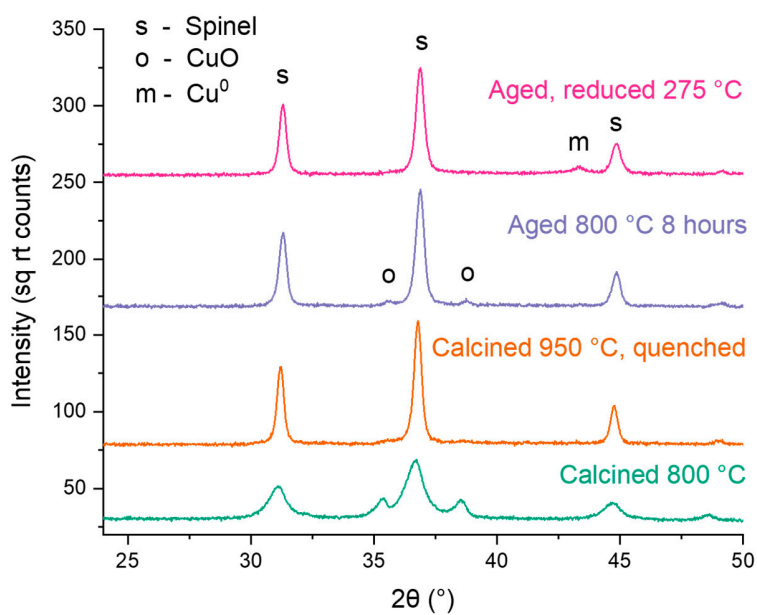| Sample	Relative oxidation state (%)								
	$Co(OH)_2$	CoO	Co^0	$Cu(OH)_2$	CuO	Cu^0	$Ni(OH)_2$	NiO	Ni^0
Aged Pt – $(CoCuMgNi)_1$	25.9	71.8	2.3	0	57.2	42.8	94.9	5.1	0

Figure S7. PXRD patterns of $CuAl_2O_4$ after varying calcination, aging, and reduction heat treatments.

References

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