Supporting Information

Unravelling the deactivation of CuZnO-based catalysts at industrial scale: a micro to macro scale perspective

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KEYWORDS: ZnO, crystal growth, sublimation, CuZnO based catalysts, industrial catalyst deactivation, pressure drop

Contents

1. X-ray diffraction after accelerating aging in the presence of H_2 or H_2/C_2H_5Cl

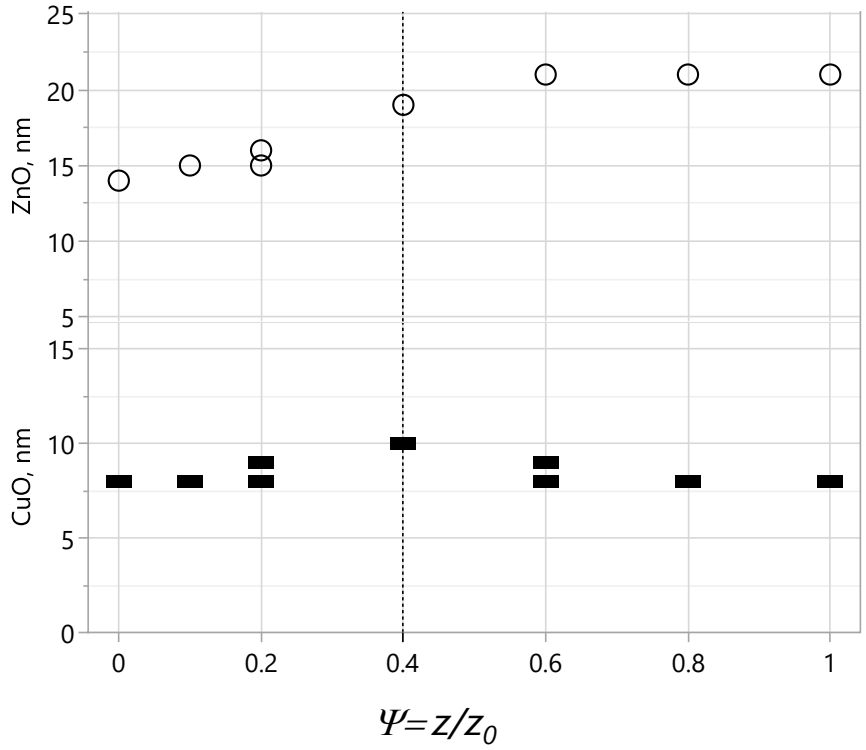

Figure S1 Crystal domain size determined by XRD on spent catalysts as a function of catalyst bed position ($\Psi=z/z_0$), where the inlet and outlet are $\Psi=1$ and $\Psi=0$, respectively. Fresh catalyst showed a crystal domain size ~11 nm for ZnO.

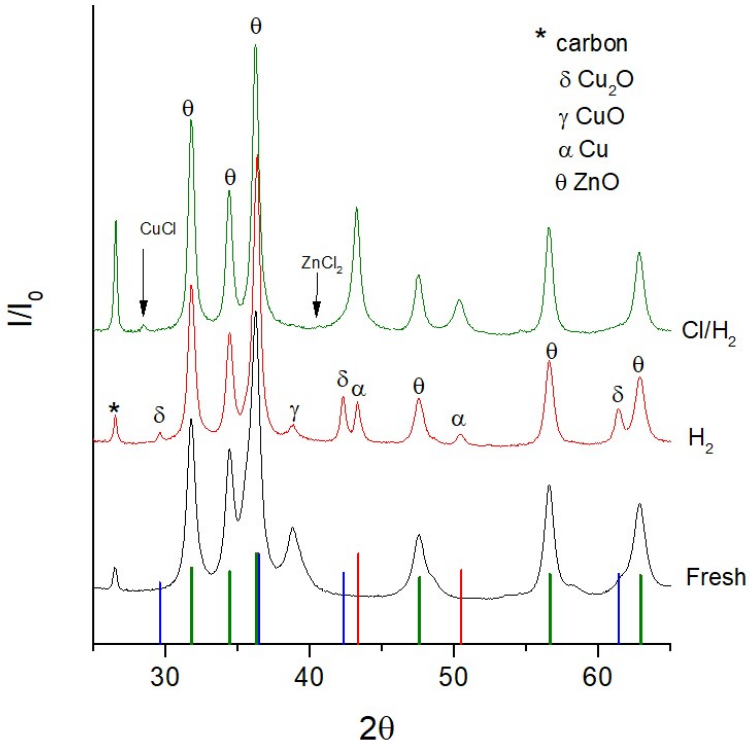

Figure S2 X-ray diffraction lines for fresh, H_2 treatment (7 days, 270 °C, 10% H_2/inert) and after chloride treatment (7 days, 270 °C, 10% H_2/10 ppm C_2H_5Cl/ inert).

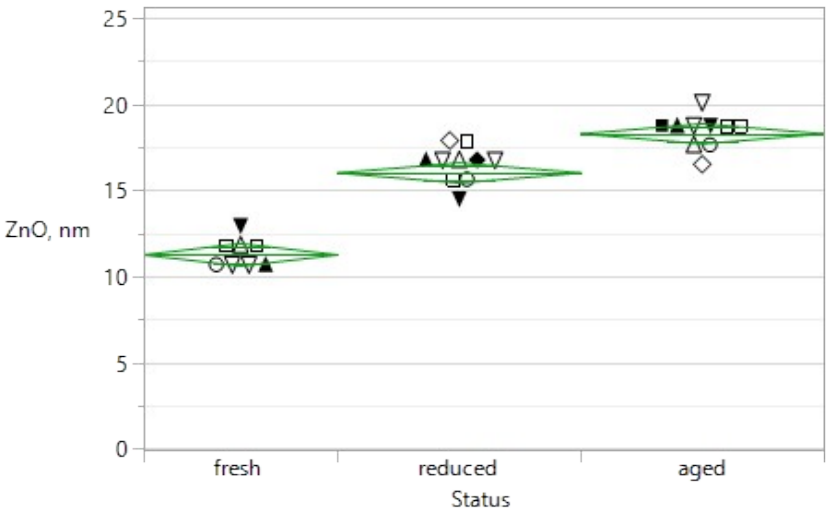

Figure S3 Crystal domain size determined by Scherrer equation for ZnO on as received, reduced and chloride treated samples (aged samples with chloride in the feed).

2. Evaluation of surface composition by XPS

Surface elemental compositions were determined by X-ray photoelectron spectroscopy (XPS) for the catalyst pellets aged with ethyl chloride (7 days, 270 °C, 10% H_2, 20 ppmv C_2H_5Cl, nitrogen (balance). The results are shown in Table S1.

Table S1 Surface elemental composition of catalyst pellets (surface side of the pellet) exposed to chlorine (relative atomic percentages **±** standard deviation).

CuZnO batch	Zn	Cu	Cl	Zn/Cu	Cl/ (Zn+Cu)
1	6.4 ± 2.7	9.3 ± 1.2	1.7 ± 0.3	0.69 ± 0.38	0.108
2	8.3 ± 1.6	5.5 ± 1.7	1.4 ± 0.1	1.51 ± 0.89	0.101
3	4.0 ± 1.4	5.7 ± 1.2	1.0 ± 0.1	0.70 ± 0.40	0.103
relative std dev (3 batches)	35%	31%	26%	49%	3%

3. Thermochemical analyses

Chloride is a known catalyst poison for these copper zinc oxide catalysts. Reactions of ethyl chloride are outlined below, where the values of ΔHrx and ΔSrx are determined from tabulated standard state enthalpies and entropies of formation, respectively (at 298 K or 25 °C). The ΔH/ΔS ratios are a reliable estimate of the temperatures at which the reactions are at thermodynamic equilibrium. The three reactions are all favorable thermodynamically under commercial operations (160-240 °C).

Table S2 Thermodynamic analysis

reaction	ΔH/ΔS (°C)	ΔHrx (kJ/mol)	ΔSrx (J/mol·K)
2 Cu + 2 C2H5Cl(g) → 2 CuCl + 2 C2H4(g) + H2(g)	150	53.5	126
Cu2O + 2 C2H5Cl(g) → 2 CuCl + 2 C2H4(g) + H2O(g)		-17.6	159
ZnO + 2 C2H5Cl(g) → ZnCl2 + 2 C2H4(g) + H2O(g)	-112	23.2	144

Figure 4 a) Pressure drop readings at the end of life for inlet, middle and outlet sections of

4. Stereomicroscopy

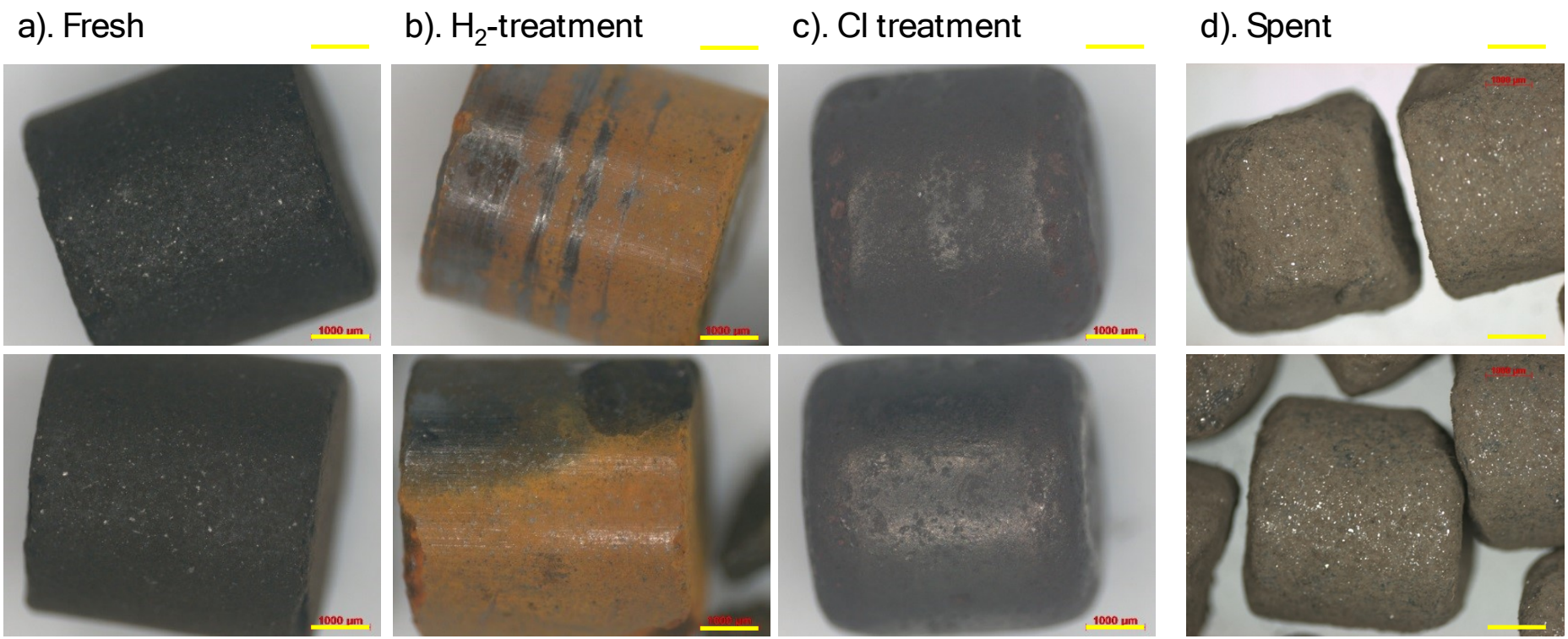

Figure S4 Stereomicroscopy of selected pellets correspondent to batch 1 (first row) and batch 2 (second row) on a) fresh, b) after H_2 treatment, c) Cl treatment and d) spent catalyst.

5. Scanning electron microscopy (SEM)

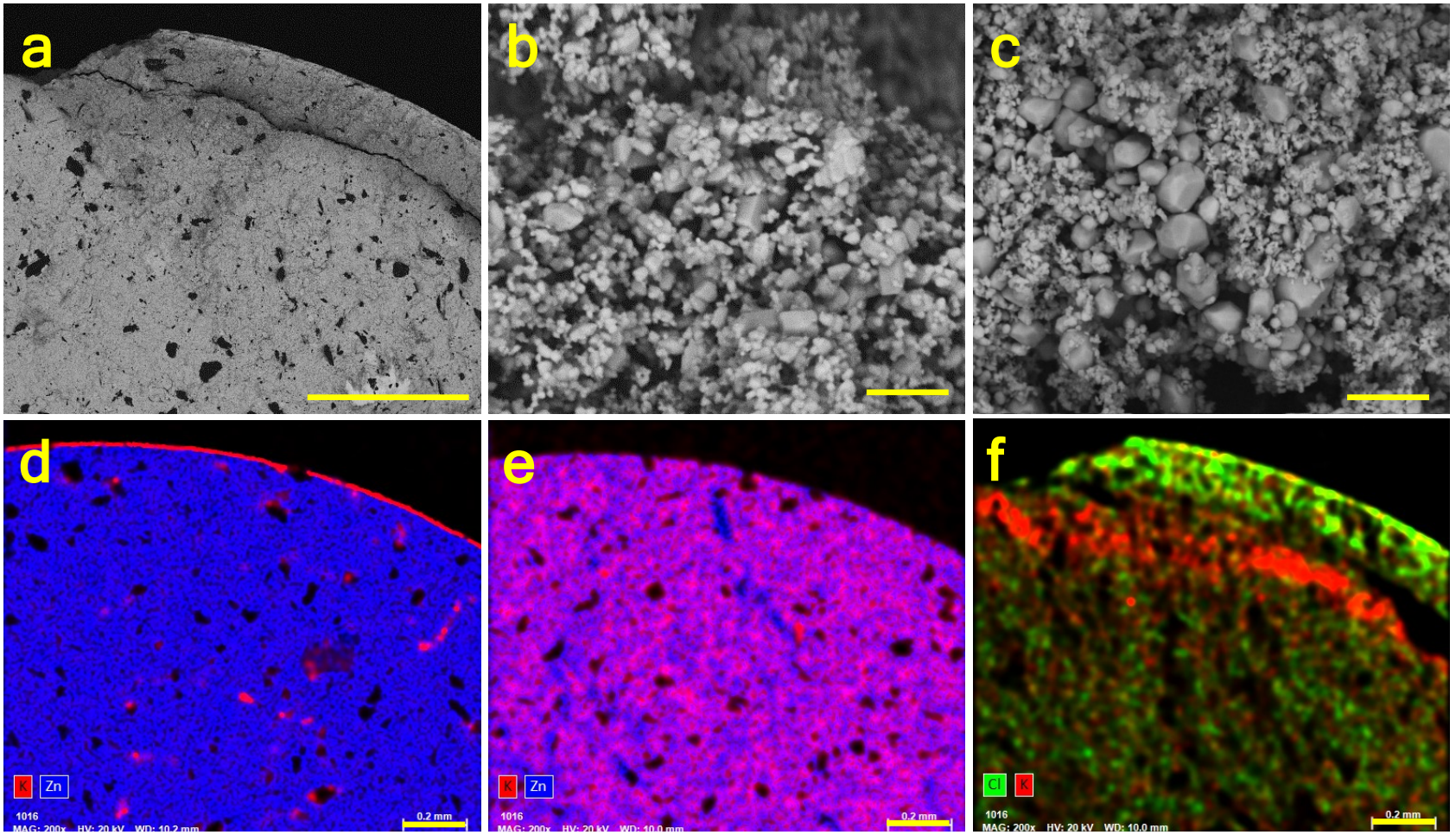

Figure S5. Morphology (a) and (b) after Cl_2 treatment, (c) spent. Scale bar represents (a) 500 µm, (b) and (c) 1 µm. Elemental maps of K (red) and Zn (blue) for (d) fresh and (e) H_2 treatment, (f) K (red) and Cl (green) distribution after aging with Cl. The scale bar represents 200 µm.

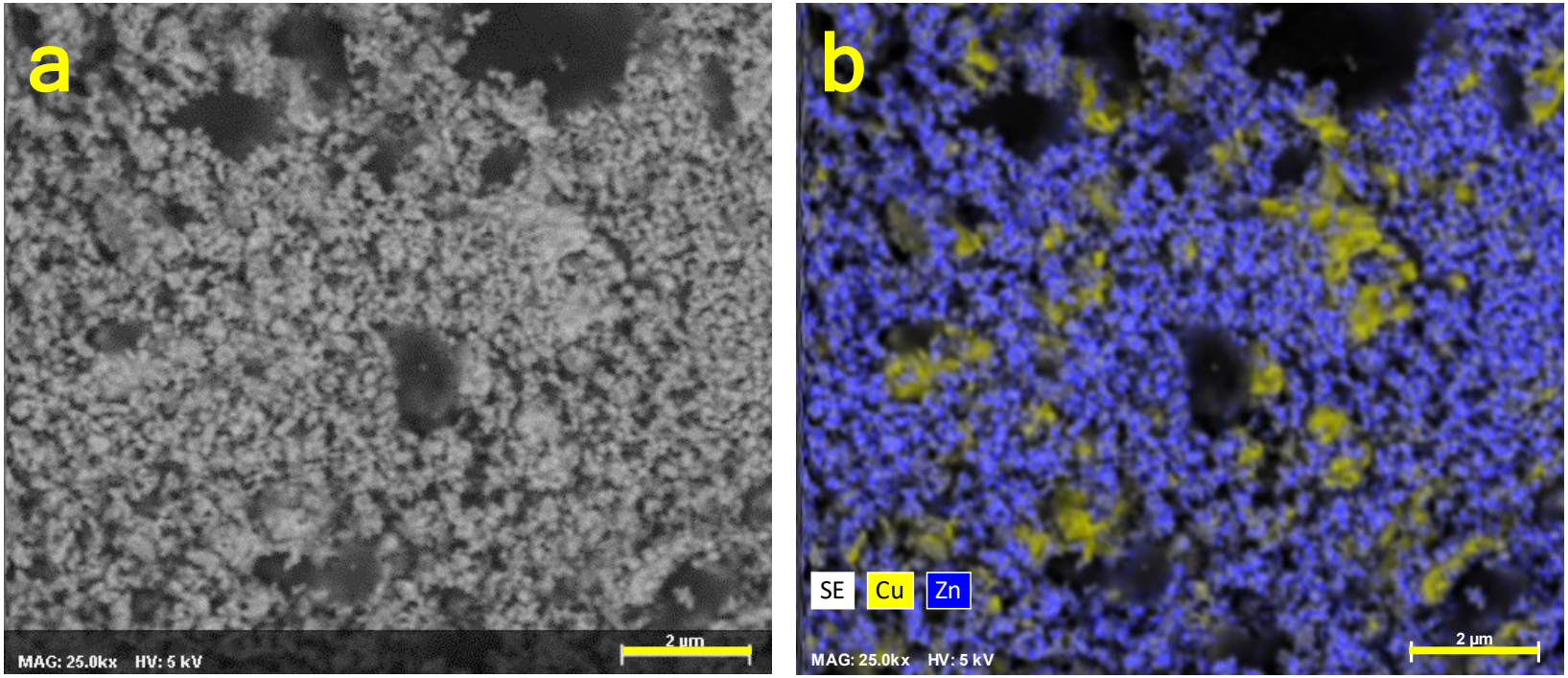

Figure S6 (a) SEM micrograph and (b) EDS map showing Cu and Zn element distribution after Cl-treatment experiment. The scale bar represents 2 µm.

6. Temperatures of melting and mobility

The temperatures of melting, bulk mobility (Tammann) and surface mobility (Hüttig) are given in the figure below. The temperatures for bulk and surface mobility are taken as $T_{melt}/2$ and $T_{melt}/3$, respectively. This analysis points to high mobility for the metal chlorides. As a result, chloride impurities can accelerate the sintering that leads to the weakening of the catalyst pellets, and subsequent early termination of the useful life of the catalyst.

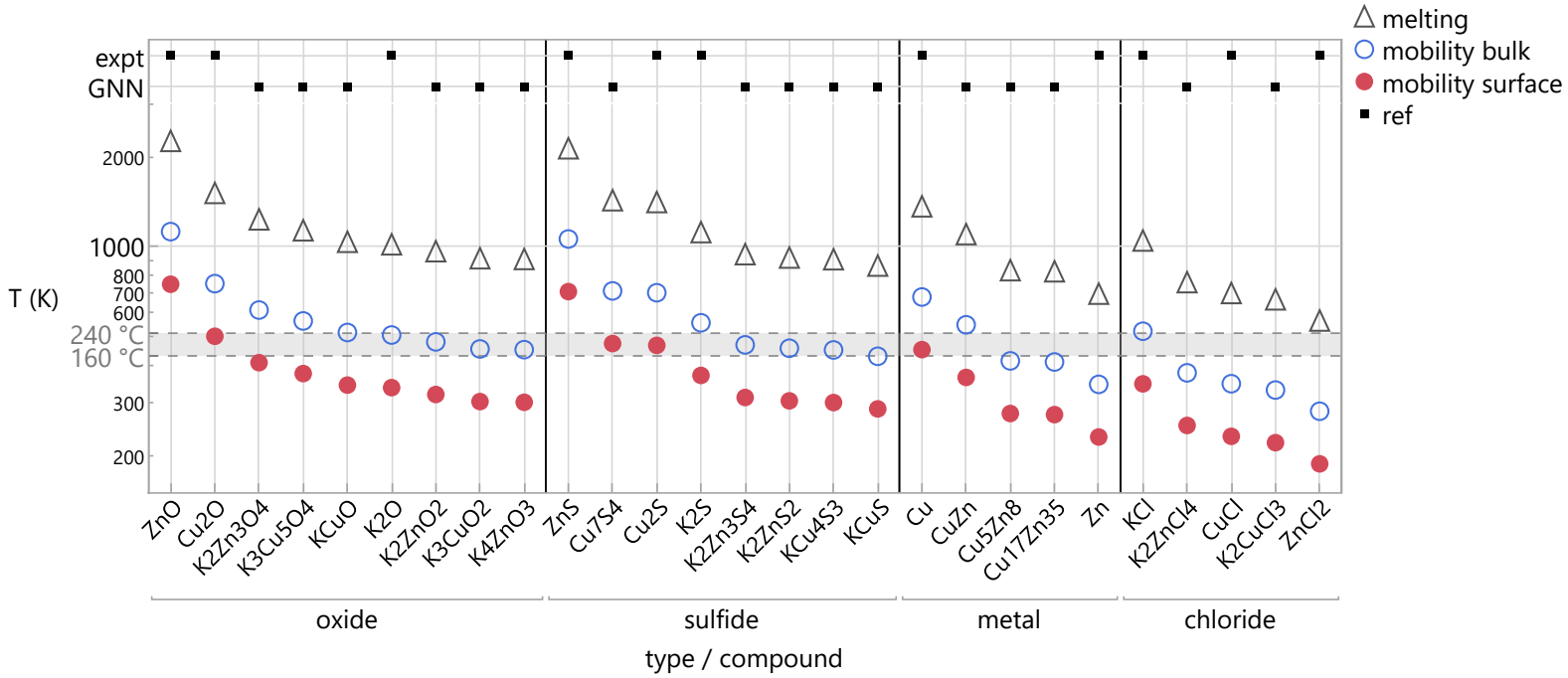

Figure S7. Temperatures of melting, bulk mobility, and surface mobility. Of the 27 compounds, data is from experiment for 11 and a GNN model for the other 16. The GNN model is implemented at https://next-gen.materialsproject.org/contribs/projects/melting_points, as described by Alexandra Navrotsky et al., Melting temperature prediction using a graph neural network model: From ancient minerals to new materials | PNAS.

7. X-ray Fluorescence (XRF)

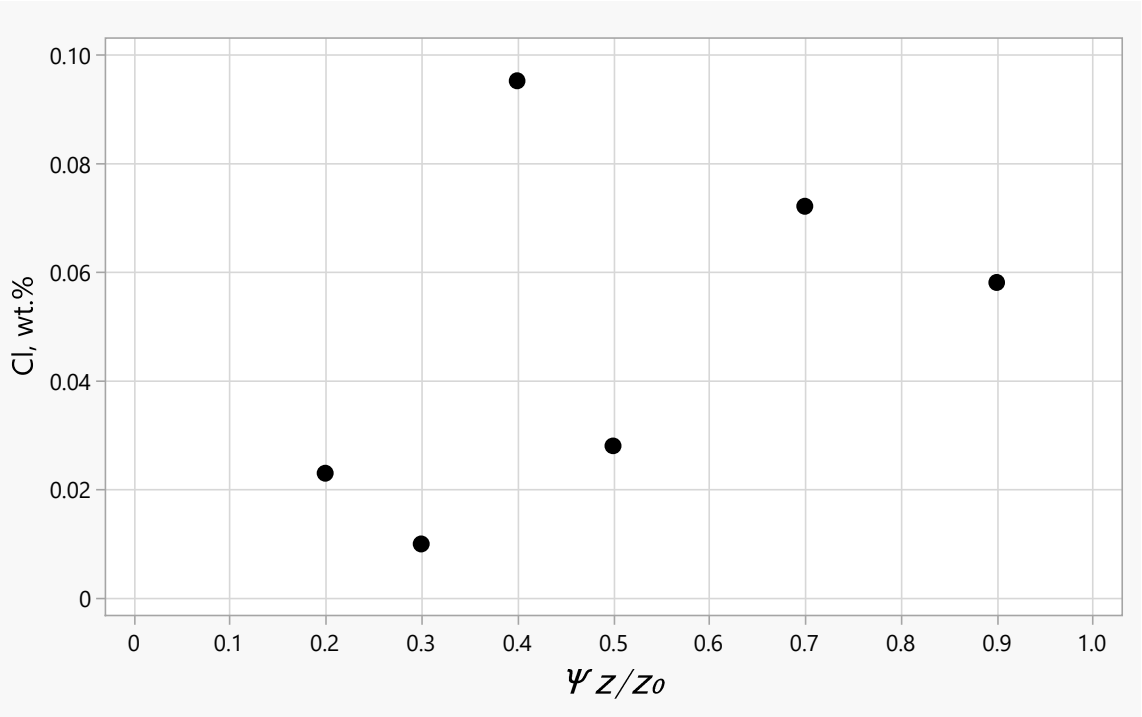

Figure S8 Chlorine impurity level determined by XRF on spent catalyst fines as a function of catalyst bed position (Ψ=z/z0), where the inlet and outlet are Ψ=1 and Ψ=0, respectively.