Copper Stabilization via Spinel Formation during the Sintering of Simulated Copper-Laden Sludge with Aluminum-Rich Ceramic Precursors

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Supporting Information

Including 1 tables and 9 figures in 11 pages

Table S1. Results of quantitative phase analysis and the calculated transformation ratio (TR, %) of the authentic **CuO/CuAl₂O₄/amorphous** phase mixtures determined by using Rietveld refinement analysis on the XRD data.

Known ^(c)		Refinement Results					
Composition (wt %)	TR (%)	Crystalline Composition (wt %)	TR (%)	R _F ² ^(a) (%)	Chi ² ^(b)	R _p (%)	R _{wp} (%)
20.00:80.00:0.00	63.68	18.87:81.13: --	65.33	2.80	1.35	2.95	3.79
40.00:60.00:0.00	39.66	38.47:61.53: --	41.21	2.71	1.42	2.98	3.85
60.00:40.00:0.00	22.61	59.13:40.87: --	23.25	2.64	1.56	3.16	4.13
80.00:20.00:0.00	9.87	80.49:19.51: --	9.60	2.57	1.63	3.13	4.17
32.00:48.00:20.00	39.66	36.51:63.49: --	43.25	2.90	1.26	2.86	3.66
24.00:36.00:40.00	39.66	38.19:61.81: --	41.50	3.16	1.22	3.06	3.85
48.00:32.00:20.00	22.61	58.98:41.02: --	23.36	2.81	1.34	2.93	3.76
36.00:24.00:40.00	22.61	57.67:42.33: --	24.34	3.04	1.22	2.96	3.73

Note:

$$(a) R_F^2 = \frac{\sum |F_{k,o}^2 - F_{k,c}^2|}{\sum F_{k,o}^2}, R_P = \frac{\sum |y_{i,o} - y_{i,c}|}{\sum |y_{i,o}|}, R_{wp} = \left[\frac{\sum w_i (y_{i,o} - y_{i,c})^2}{\sum w_i y_{i,o}^2} \right]^{1/2},$$

where y_i and F_k^2 are the (observed or calculated) profile intensity and squared structure factor, respectively; w_i is a statistical weighting factor; i is the corresponding data point; k is the space group permitted reflection; and χ^2 (goodness of fit) = $[\sum w_i (y_{i,o} - y_{i,c})^2 / (N - P)]$, where P = number of refined variables and N = number of extracted and integrated reflections.

(b) The goodness of fit (χ^2) equals one in an ideal refinement, although, practically, the background and the peak profile mismatch lead to a goodness of fit greater than one. It is generally considered that the χ^2 value between 1.0 and 2.9 is satisfactory¹. The random errors calculated using this refinement method are generally below 2%, with an observed goodness of fit of around 1.2 to 1.7.

(c) The compositions were expressed as the relative quantities of CuO: CuAl₂O₄: amorphous phase. The CuAl₂O₄ used in this test was synthesized by combining CuO and γ -Al₂O₃ with a Cu/Al molar ratio of 1:2 sintered at 990 °C for 20 d, and was confirmed by XRD with CuAl₂O₄ as the only phase in the sample. The amorphous phase used in the test was the finely-ground silica glass powder.

¹ Fansuri, H.; Zhang, D. K.; French, D.; Elcombe, M.; Studer, A. An X-ray and neutron diffraction study of the structure of α -Bi₂Mo₃O₁₂ as a catalyst for partial oxidation of propylene to acrolein. *In Proceedings of the CHEMECA symposium*. **2004**, 234.

Figure S1. Phase changes of HiQ-7223 alumina powder after thermal treatment. XRD patterns of HiQ-7223 alumina powder (AlOOH, boehmite; PDF#74-1895); HiQ-7223 alumina powder heated at 650 °C for 3 h (γ -Al₂O₃, Reference #17), and HiQ-7223 alumina powder further heated at 1500 °C for 6 h (α -Al₂O₃, corundum; PDF#10-0173). The weight loss in the process of transferring boehmite to γ -Al₂O₃ was measured to be $15.10 \pm 0.51\%$, which is consistent with the complete dehydration of boehmite (15%) calculated from its chemical formula.

Figure S2. XRD patterns of USP-grade acid-washed kaolin powder (kaolinite, PDF#78-1996) and after calcining at 1350 °C for 24 h. “M” represents mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; PDF#79-1455), and “C” represents cristobalite (SiO_2 ; PDF#76-0938).

Figure S3. Particle size distributions of the four CuO-containing raw materials after 18 h ball milling: (a) $\text{CuO}+\gamma\text{-Al}_2\text{O}_3$, (b) $\text{CuO}+\text{corundum}$, (c) $\text{CuO}+\text{kaolinite}$, and (d) $\text{CuO}+\text{mullite}+\text{cristobalite}$.

Figure S4. XRD pattern of the product obtained from the reaction of CuO with γ -alumina sintered at 990 °C for 20 d. “S” represents CuAl_2O_4 spinel (PDF#78-1605).

Figure S5. XRD patterns of the reaction products obtained from the reactions of CuO with Al-rich precursors sintered at (a) 1000 °C and (b) 1150 °C for 3 h. “S” represents CuAl₂O₄ (PDF#78-1605); “C” represents CuO (PDF#89-2529); “A” represents corundum (α -Al₂O₃, PDF#10-0173); “Si” represents cristobalite (PDF#76-0938); “Q” represents cuprous aluminate (CuAlO₂, PDF#75-2356); “P” represents Cu₂O (PDF#77-0199); and “M” represents mullite (PDF#79-1455).

Figure S6. Graphical plot of Rietveld refinement of the product sintered at 1050 °C for 3 h from γ -Al₂O₃ precursor and CuO (red line = experimental XRD pattern, green line = calculated XRD pattern and magenta line = difference curve between the experimental and calculated patterns). The observed goodness of fit (χ^2) (noted in Table S1) is 1.59.

Figure S7. Graphical plot of the final cycle of Rietveld refinement of the product sintered at 1050 °C for 3 h from corundum precursor and CuO. The observed goodness of fit (χ^2) is 1.86.

Figure S8. Graphical plot of the final cycle of Rietveld refinement of the product sintered at 1050 °C for 3 h from kaolinite precursor and CuO. The observed goodness of fit (χ^2) is 1.75.

Figure S9. Graphical plot of the final cycle of Rietveld refinement of the product sintered at 1050 °C for 3 h from mullite precursor and CuO. The observed goodness of fit (χ^2) is 1.63.