

Understanding Cu-Alumina Interactions in Redox Conditions for Chemical Looping Combustion (CLC) Application – A Multi-scale Correlative Electron and X-Ray Microscopy Study

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Chemical Looping Combustion (CLC) is a midterm solution for fossil fuel utilization with inherent carbon dioxide capture, based on the use of an oxygen carrier material. The oxygen carriers (OC) replace air to provide oxygen to a wide range of fuels for combustion, *via* reduction/oxidation cycles in a circulating fluidized bed reactor at high temperature [1]. Copper oxide supported on alumina grain (CuO/Al₂O₃) has been widely considered as a promising oxygen carrier (OC) for industrial use in CLC, due to its benign nature and flexible redox behaviour that ensures high reactivity and oxygen transfer capacity. However, the OC sustains successive high temperature (800-900°C) reduction (combustion) and oxidation (regeneration of oxide phase) reaction cycles which lead to chemical and morphological changes in the material causing the degradation in the oxygen-carrying properties. The evolution in the cycled material is attributed to the diffusion of the Cu-phases at the grain scale [2]. Herein, we are bridging the gap in understanding between the observed μm-scale migration of Cu-based phases and nanoscale transformations of the Cu nanoparticles (NPs) by employing a multi-scale characterization approach using Scanning Transmission X-ray (STXM) and Scanning Transmission Electron (STEM) Microscopies, respectively.

We have studied 13wt%CuO supported on 50-100 μm sized γ-Al₂O₃ grain produced *via* incipient wetness impregnation, calcined at 800 and 900 °C. To mimic the CLC cycling, the fresh samples were subjected to oxidation and reduction under air and H₂ at 900 °C, in a thermogravimetric analyser (TGA). Ultramicrotomy sections of 100 nm thickness were prepared for SEM, STXM and TEM characterizations. Energy stacks and mappings were performed at the Cu L-edge and Al K-edge to identify the specific spectral features of each compound. *In situ* TEM was performed using a probe Cs-corrected microscope equipped with Protochips' "Atmosphere" *in situ* gas setup with sealed environmental cell (e-Cell), operating at atmospheric pressure.

The fresh grains are composed of γ-Al₂O₃ with homogeneously dispersed CuO nanoparticles (10-20 nm). With progressive cycling (after 50 redox cycles), at the grain scale (μm), we observe the propagation of gamma to alpha reaction front in the solids (Figure 1). At a smaller scale (10×10 μm²), this front displays a well-defined structural-chemical gradient characterized by (Figure 1): zone 1, non-stoichiometric Cu (II) aluminate; zone 2, an intermediate thin layer (< 200 nm) of Cu (II) aluminate, enriched in Cu compared to zone 1; zone 3, α-Al₂O₃ phase containing large CuO particles. The proportion of copper shows a strong variation from 10 wt% Cu in zone 1, to ~25wt% at the edge of the reaction front in zone 2. In addition, *in-situ* STEM observation at 900 °C under H₂-reduction have shown the migration of copper to form copper nanoparticles from a starting oxidized sample mainly composed of homogeneous Cu (II) aluminate (Figure 2). It is suspected that the expelling of Cu from the spinel structure of Cu (II) aluminate favours

the formation of the α -Al₂O₃. This suggests that the mobility of copper during redox cycling is linked to the phase transition of γ to α -Al₂O₃. However, the γ to α -Al₂O₃ transition is not favoured in the pure Al-O system below 1000 - 1100 °C [3]. Reversely, the oxidative formation of spinel is only possible in the CuO+ γ -Al₂O₃ system and thermodynamically limited in the case of CuO+ α -Al₂O₃, at 900 °C [4]. To minimize the energy of the system, the mobility of copper on alumina during oxidation is sufficient to either form (1) CuAl₂O₄ at the expense of γ -Al₂O₃, and (2) larger CuO particles on α -Al₂O₃, by sintering. This study demonstrates the utilization of correlative multi-scale imaging techniques to reveal the dynamic interactions of metal/metal oxides and ceramic supports in complex reactive systems.

References:

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 [5] The authors acknowledge IFP Energies Nouvelles for the funding of this study.

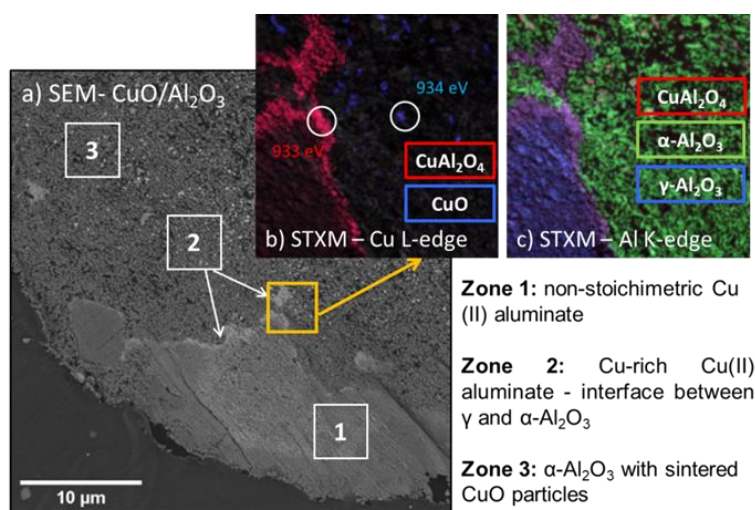


Figure 1. a) SEM image of ultramicrotomy cut of CuO/Al₂O₃ after 50 cycles, 10 x 10 μ m STXM map of the area represented by the yellow square at b) Cu L-edge and c) Al K-edge.

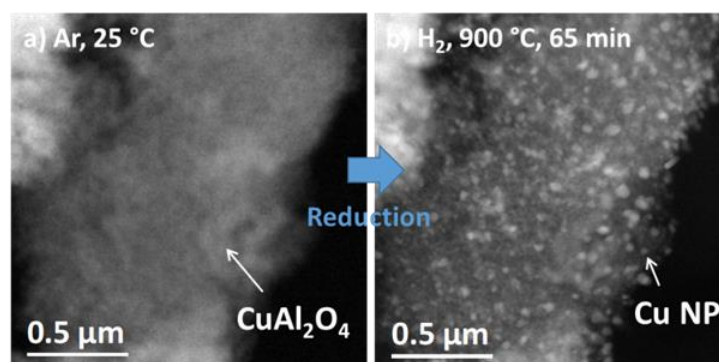


Figure 2. *In-situ* STEM characterisation of CuO/Al₂O₃ OC with starting phase containing CuAl₂O₄ under Ar atmosphere at 25 °C and b) after reduction by H₂.