Understanding CuO/Al2O3 Interactions during Thermochemical Redox Reactions: TEM, X-ray Microscopy, and XAS Study

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Background
Chemical Looping Combustion (CLC) presents a midterm solution for fossil fuel utilization with inherent carbon dioxide capture, utilizing oxygen carrier materials. These carriers replace air to provide oxygen for combustion across a wide range of fuels, operating through reduction/oxidation cycles in a circulating fluidized bed reactor at high temperatures [1]. Copper oxide supported on alumina grain (CuO/Al2O3) is widely considered a promising oxygen carrier (OC) for industrial CLC use due to its benign nature and flexible redox behavior, ensuring high reactivity and oxygen transfer capacity. However, successive high-temperature (800-900°C) reduction (combustion) and oxidation (regeneration of oxide phase) cycles induce chemical and morphological changes in the material, leading to degradation in its oxygen-carrying properties. The evolution in the cycled material is attributed to the diffusion of Cu-phases at the grain scale [2]. Herein, we bridge the gap in understanding between the observed µm-scale migration of Cu-based phases and nanoscale transformations of Cu nanoparticles (NPs) by employing a multi-scale characterization approach, both temporally and spatially, using Scanning Transmission X-ray (STXM) and Scanning Transmission Electron (STEM) Microscopies, and operando Quick X-ray Absorption Spectroscopy.

Methods
We conducted a study on CuO supported on 50-100 µm sized γ-Al2O3 grains, synthesized via incipient wetness impregnation and calcined at 900°C. To replicate the cyclic nature of (CLC), we subjected the fresh samples to oxidation and reduction under air and H2 at 900°C using a thermogravimetric analyzer (TGA). Ultramicrotomy sections with a thickness of 100 nm were prepared for SEM, STXM, and TEM characterizations. Energy stacks and mappings were generated at the Cu L-edge and Al K-edge to identify specific spectral features of each compound. In situ TEM analysis was conducted using a probe Cs-corrected microscope equipped with closed-cell in situ gas setup featuring a sealed environmental cell (e-Cell), operating at atmospheric pressure. Finally, operando XAS measurements were performed in a capillary tube under identical reaction conditions as in the TGA. By acquiring relevant reference material spectra and utilizing chemometric data processing, we extracted chemical-structural phase distribution over the course of 50 redox cycles at 900°C.

Results
The microscopic study reveals significant transformations in the CuO/γ-Al2O3 system during redox cycling (Figure 1 a and b) [3]. Initially, fresh grains consist of γ-Al2O3 with uniformly dispersed CuO nanoparticles (10-20 nm). After 50 redox cycles, observation at the grain scale (µm) demonstrates the progression of the gamma to alpha reaction front within the solids. This front exhibits a distinct structural-chemical gradient, characterized by three zones: zone 1 displaying non-stoichiometric Cu (II) aluminate, zone 2 with an intermediate thin layer (< 200 nm) of Cu (II) aluminate enriched in Cu, and zone 3 composed of α-Al2O3 phase containing large CuO particles. The proportion of copper varies significantly across these zones, ranging from 10 wt% Cu in zone 1 to ~25 wt% at the edge of the reaction front in zone 2. In situ STEM observation at 900°C under H2-reduction reveals the migration of copper,

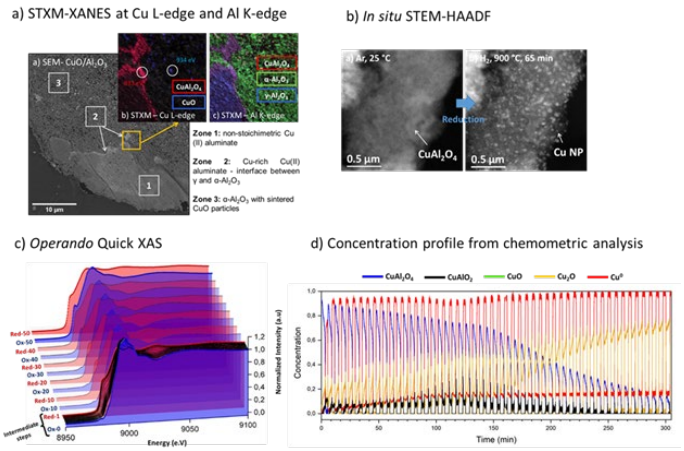
forming copper nanoparticles from a starting oxidized sample predominantly composed of homogeneous Cu (II) aluminate. This suggests that copper mobility during redox cycling is associated with the phase transition of γ to α-Al2O3.

Furthermore, the spectral evolution during oxidation and reduction reactions, depicted in Figure 1c, highlights changes in the concentration of different Cu-Al species [4]. The oxidized state initially consists of CuxAlyO4, gradually transforming into the metallic copper phase with increasing redox cycles. Notably, a threshold circa 25 cycles indicate a drastic conversion from the aluminate phase to copper oxide. At the end of the redox cycles, the oxygen carrier predominantly comprises α- Al2O3 and CuO. The transition point is linked to the growth and propagation of α- Al2O3, suggesting a mechanism involving particle size influencing the alpha alumina phase transition, proceeding through an initial slow seeding phase followed by rapid propagation.

Conclusion

The integration of spectroscopic and microscopic techniques, both in situ and post-mortem modes, provided a comprehensive understanding of the material evolution in terms of morphology and the diverse phase interactions across spatial dimensions and over extended reaction durations.

Graphic:



Keywords:

STEM, STXM, Quick XAS, Copper

Reference:

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