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Tracking Cation Migration in Catalysts by Modulated Enhanced Powder Diffraction

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Mixtures of Cu-Fe oxides are used for numerous industrial catalytic processes including the Water-gas shift reaction (WGS: CO + H2O -> CO2 + H2). In this work we measure the structural changes of CuFe2O4 under redox (oxidizing and reducing) and WGS reaction conditions. A key component associated with the catalytic properties of this material is the reversible transfer of Cu in and out of the spinel structure during the reaction. The WGS reaction is the most active when Cu is metallic and on the surface of the spinel which has become Fe3O4. The reversible nature of the Cu migration preserves the activity of the catalyst and protects the Cu species from deactivation. We investigate the cation migration process from the octahedral site inside the spinel to the surface as Cu metal, using modulation measurements that perturb the dynamic structural properties of the spinel structure in a time resolved manner. The experiments termed MED [1] involve the switching of co-reactants (i.e. CO -> O2 -> CO -> O2) so that the residence time of specific adsorbates can be controlled, thus we can probe directly the role of the reactant and the redox sensitivity in the migration of the Cu cation. We demonstrate how distinguishable this technique is from previous steady-state measurements. The powder patterns are averaged over several cycles of gas (CO/H2/O2) variations. Phase-sensitive detection is applied to demodulate the data, picking up structural changes which occur in phase with reactant in-flow variations. Oscillations of the diffracted signal can be observed at the stimulation frequency ω, but also at the harmonic 2ω. Therefore the Fourier analysis of the components provides selective access to partial diffraction contributions otherwise merged into one average diffraction signal. This work is supported by the BNL LDRD program and experiments were performed at the APS and at the NSLS.

[1] *Chernyshov, D. et al. Acta Cryst. 2011, A67, 327*

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