

In-situ EXAFS/XANES Studies of Reactive Sorption of Hydrogen Sulfide by Copper Oxide Sorbents.

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Natural gas and oil-based streams contain a range of sulfur contaminants that require removal to meet environmental regulations and product specifications. One attractive yet not fully studied technique involves the reaction of copper oxide (CuO) with hydrogen sulfide (H₂S) to form copper sulfide. This reaction is thermodynamically favorable and results in environmentally benign products. However, the performance of CuO sorbents can be extremely sensitive to changes in the structure of CuO and process conditions. In this study, we implemented synchrotron-based in-situ X-ray absorption spectroscopy (XAS) along with fixed bed sorption experiments to investigate the effects of temperature and crystallite size on the kinetics of the sulfidation process and the removal capacity of CuO sorbents.

In-situ XAS experiments at both the Cu K-edge and S K-edge were performed at beam line 4-3 at SSRL using a custom designed reactor in which samples of CuO reacted in a gas flow of 1000 ppm-vol H₂S in helium under controlled conditions from which quantitative uptake kinetics were extracted. The fixed bed experiments were carried out in fixed-bed reactor under a flow of 1000 ppm-vol H₂S in nitrogen. The materials tested comprise of CuO nanoparticles synthesized via a hydrothermal method followed by calcination at different temperatures yielding a set of materials with crystallites ranging in size from 7 to 47 nm. Moreover, a commercial CuO-based sorbent containing CuO (63.5 wt%), ZnO (25 wt%), and Al₂O₃ (10 wt%) was tested.

The observations obtained from fixed bed and XAS experiments were consistent for both crystallite size and temperature change effects. Temperature proved to have greater influence on the absorbent capacity, kinetics and mechanism of the process. The bulk removal capacity doubled as temperature increased from 323 K to 353 K (9.5 wt% to 21 wt% and 12 wt% to 22 wt% based on XAS and fixed bed results, respectively). Sulfur uptake was also observed to be inversely proportional to crystallite size. Removal capacity of 12 wt% was achieved with 7 nm CuO nanoparticles compared to 5 wt% for 47 nm crystallite sizes. Moreover, the analysis of XAFS data showed that as temperature increases, the product copper sulfide phase resembled copper (II) sulfide rather than copper (I) sulfide. This phase change with temperature can be used to elucidate mechanistic aspects of the reaction that cannot be accomplished via conventional techniques.

In summary, this XAS based study served towards unraveling mechanistic and kinetic knowledge of CuO sulfidation reaction at various temperatures. It served also in studying the effects of structural differences between CuO sorbents on the sulfur removal performance which can be used to build a rational framework for the design of efficient CuO-based sorbents.

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