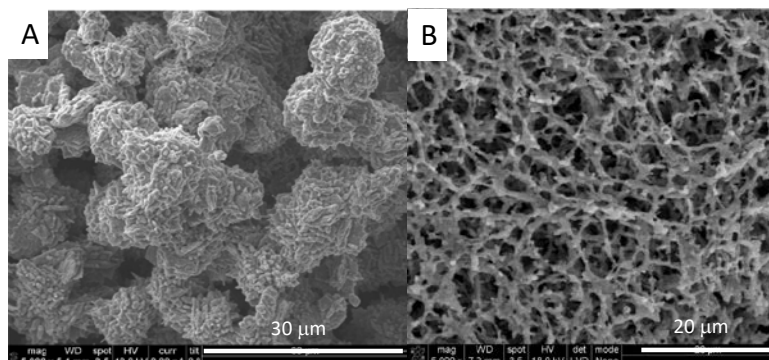


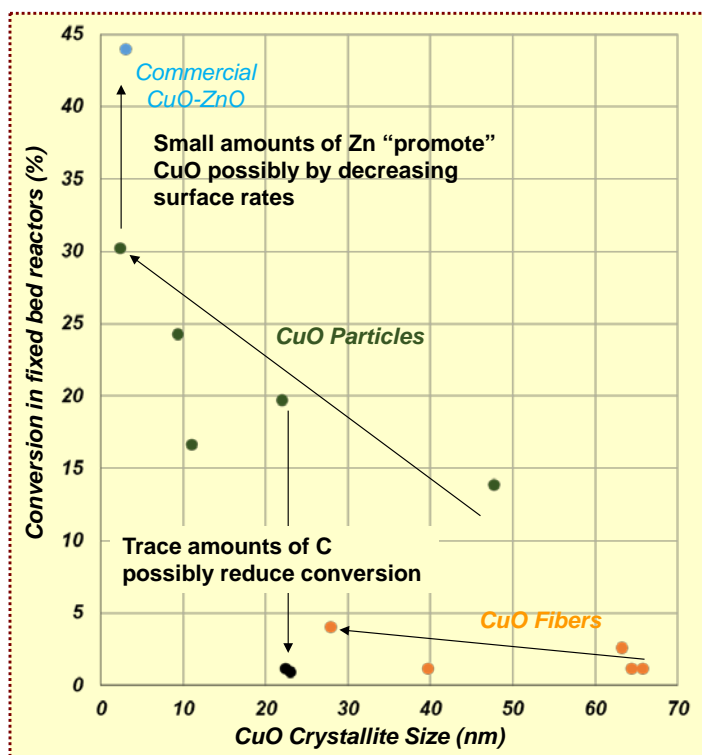
**Mechanistic studies of the reactive sorption of sulfur compounds using metal oxides**

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The objective of this project is to combine synthesis, characterization, and reaction kinetic experiments to create a microkinetic description that relates reaction mechanisms of sulfur-containing molecules to chemical and structural changes of copper oxide based materials. This objective was advanced by studying the reaction of CuO with H<sub>2</sub>S using fixed bed experiments and using X-ray Absorption Spectroscopy (XAS). The major findings during the second year of research were (i) further study of the effects of crystallite size, Zn content, and surface C-content on reactivity of CuO and (ii) identification of different Cu<sub>x</sub>S<sub>y</sub> phases during reaction of H<sub>2</sub>S with CuO. This knowledge is important because it elucidates the critical molecular features of CuO required to achieve high H<sub>2</sub>S capacity while also revealing that the reaction stoichiometry is more complex than the simple formation of CuS.



**Figure 1:** SEM images of A.) copper (II) oxide particles prepared by precipitation from copper (II) nitrate trihydrate, and B.) CuO fibers synthesized via electrospinning.



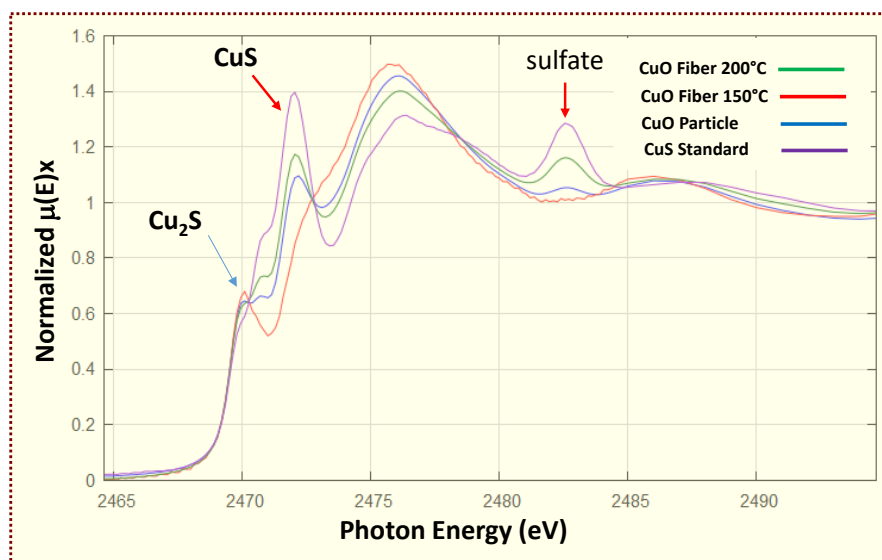
**Figure 2:** Effect of CuO crystallite size, Zn doping, and residual carbon on conversion of CuO sorbents in fixed bed reactors. Green circles are particles synthesized via precipitation, orange circles are fibers from electrospinning, black circles are particles synthesized via precipitation in the presence of PVP, and the blue circle is a commercial CuO-ZnO sample. Experiments were carried out at 294 K and 1.0 atm with 1000 ppm-vol H<sub>2</sub>S.

To probe the effect of micrometer scale morphology and microscale crystallite size of CuO materials, several CuO-based materials were synthesized via electrospinning to produce fibers, via precipitation to produce particles, and via hydrothermal and sol-gel techniques to produce CuO with different micrometer scale shapes (e.g., belts and flowers). Fibrous copper-PVP materials were synthesized via electrospinning and subsequently thermally treated to produce CuO materials with fiber-like reactive domains that are smaller and contain larger interstices compared to precipitated CuO (Figure 1). CuO fibers with different properties were synthesized by changing the ratio of the copper salt to the polymer in the precursor solution.

No apparent effect of surface area or pore size distribution on CuO conversion was observed. However, CuO conversions were higher for the particle materials (20%) compared to the fiber material (4%) for materials with small and similar crystallite sizes (28 and 22 nm). Crystallite size was observed to be linearly related to CuO conversion (Figure 2) for materials with the same microscopic shape (either fibers or particles). This data suggests that decreasing CuO crystallite size leads to higher conversions, possibly because of an increase in O-vacancies, with a critical CuO

crystallite size of ~40 nm (above which conversion appears to be constant at ~3%). A possible molecular reason for this is that decreasing crystallite size exposes more reactive surface facets in CuO that can facilitate H-S bond cleavage that is required to produce S atoms that can react with CuO moieties. Open facets can also lead to deep sulfuration by facilitating the migration of S from surface to subsurface layers. In addition to having different microscopic shape compared to precipitated CuO, the fibrous CuO (synthesized via electrospinning) may also contain residual carbon that is not decomposed upon thermal treatment. To probe the effect of this carbon on H<sub>2</sub>S uptake, PVP was added to the precipitate recipe to produce CuO particle samples with residual carbon (black circles in Figure 2). The conversions of the samples with PVP (1%) were lower than the non-PVP sample (20%), despite the similar crystallite sizes (~22 nm). This observation suggests that C species residing on the surface and possibly within CuO frameworks deleteriously impact conversion. Finally, Figure 2 shows that a small amount of Zn doping can lead to an increase in CuO conversion. These data will serve as a basis for future proposals that aim to conclusively identify the molecular explanations for the crystallite size, C content, and dopant effects.

Since the reactions between CuO and H<sub>2</sub>S involve complex chemical and structural changes that occur simultaneously, characterization techniques that can also simultaneously characterize these changes quantitatively are required to enhance the interpretation of reaction kinetics data. Toward this goal, S k-edge XAS measurements of sulfided samples of CuO particles and fibers were collected at SSRL (Figure 3). The spectral features of these three samples are quite different from each other and do not reflect all of the features of a CuS standard



**Figure 3:** XANES data at the S-k edge of sulfide species formed via reaction of CuO samples consisting of particles (blue line) and fibers (green and red lines) at 294, 423, and 473 K and 1 atm with 1000 ppm-vol H<sub>2</sub>S.

(purple line in Figure 3). Specifically, these samples contain features of Cu<sub>2</sub>S, CuS, and CuSO<sub>4</sub> as well as unidentified features that may indicate the presence of Cu<sub>x</sub>S<sub>y</sub> species with 1 < x/y < 2. This S-XAS data suggests that various Cu<sub>x</sub>S<sub>y</sub> species form during reaction of sulfur compounds with CuO and supports further S-XAS experiments to identify all possible reaction products for inclusion into fundamental microkinetic models that describe these reaction systems.

The results from this work have led to the publication of a full paper in the journal *Reaction Chemistry & Engineering* and to the completion of two additional papers to be submitted by the end of September 2018. Significant data was also collected at the Stanford Synchrotron Research Laboratory which is expected to contribute toward 2 additional publications and to support a renewal of a user proposal for 2018-2020. The continued collaboration with SSRL signifies the broader value of this research and has helped the PI expand XAS analysis to other projects in his lab. One master's student completed his thesis and one PhD student successfully advanced to candidacy during the second year of this project. One undergraduate student also participated in research related to this project to achieve 7.0 hours of course credit toward her BS degree. This student also presented her work as a poster at the 2017 AIChE student conference and as an oral presentation at the 2018 UCLA Engineering Undergraduate research symposium where she received the Best Presentation Award.

The results from this project also served as the basis for an NSF CAREER award submission by the PI. Through this project, the PI was able to leverage the research skills that he developed while working in catalysis to attack an adjacent research problem that is different and distinct from his PhD and postdoctoral work: understanding the complexity of the fundamentals of dynamic gas-solid reactions. Furthermore, the work in this project was able to introduce rarely used concepts (i.e., in-situ XAS analysis) into the gas-solid reaction chemistry and engineering research field. The advancement of in-situ techniques to analyze gas-solid reactions may create new directions of study, at the forefront of which, the PI will be considered a leader.