

Tunable CuO Nanostructured Thin Films from Metal-Organic Frameworks for Dehydrogenation of Alcohols

Hans C. Anderson, Maren Rawlins, Allison A. Prue, Lindsey M. Alder, Felipe Rivera Kara J. Stowers *

Department of Chemistry and Biochemistry, Brigham Young University, C100 Benson Building, Provo, Utah, USA 84602

*kstowers@chem.byu.edu

Figure S1. XPS survey spectra of Si-CuBTC, 20 cycle spin coat.

Figure S2. SEM images of Si-20 H₂ decomposed samples at different ramp rates.

Figure S3. EDX analysis of various Cu particles found on Si-20 N₂ decomposed sample.

Figure S4. SEM image of Si-20 N₂ decomposed sample.

Figure S5. SEM image of Si-20 H₂ decomposed sample.

Figure S6. TEM HR-TEM SAED of the CuO/Cu nanoparticles

Figure S7. XPS profile spectrum of hydrogen treated Si-Cu₃(BTC)₂.

Figure S8. Temperature programmed desorption spectra of methanol off of hydrogen treated Si-Cu₃(BTC)₂.

Figure S9. Temperature programmed desorption spectra of methanol on Si-Cu₃(BTC)₂.

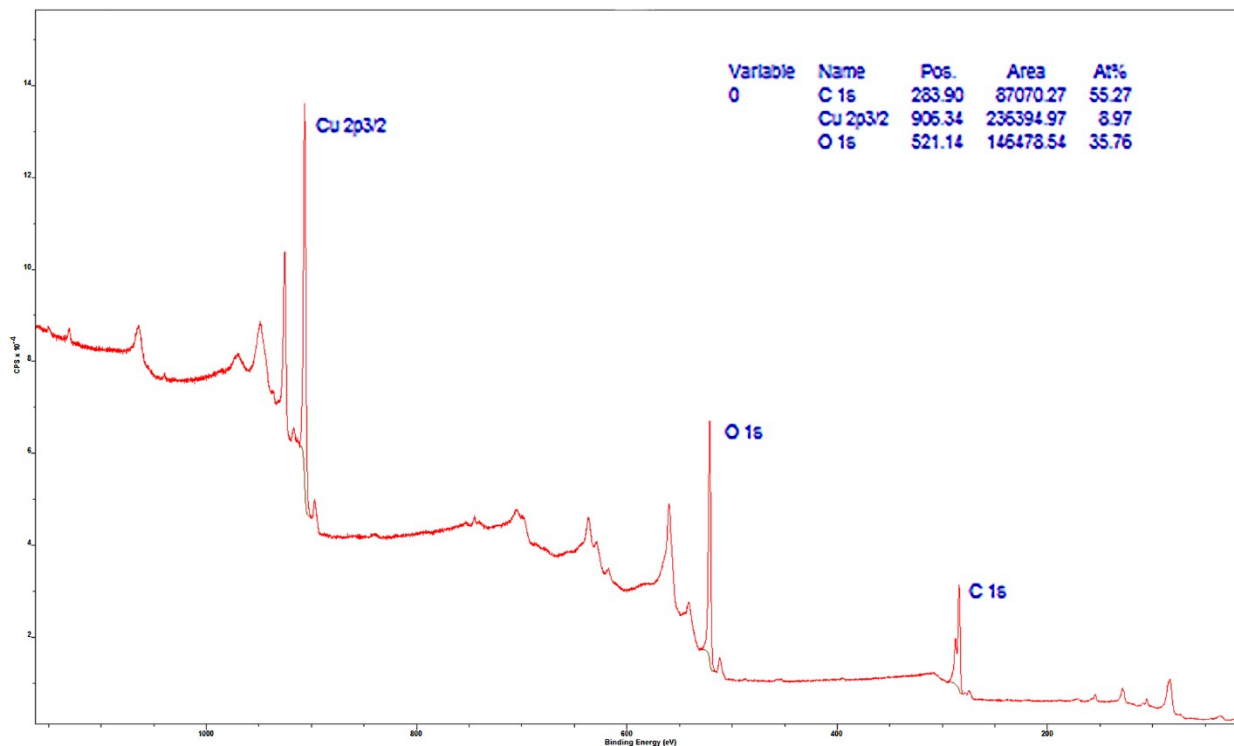


Figure S1. XPS survey spectra of Si-CuBTC, 20 cycle spin coat.

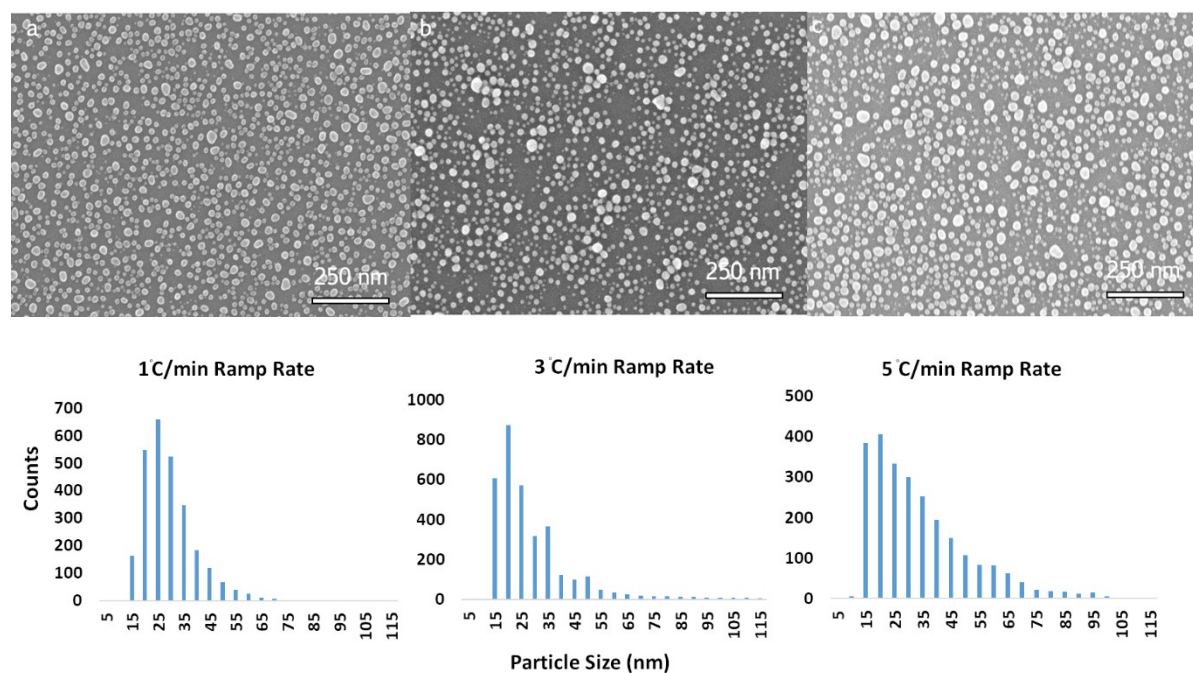


Figure S2. SEM and particle size histograms under varied ramp rates, with temperature ramps from ambient to 400 °C, and a hold at 400 °C for two hours. It is observed that under 5 °C/min ramp rate, the distribution of particles increases but holds within error for rates at 3 °C/min or lower. a) 1 °C/min, b) 3 °C/min, c) 5 °C/min.

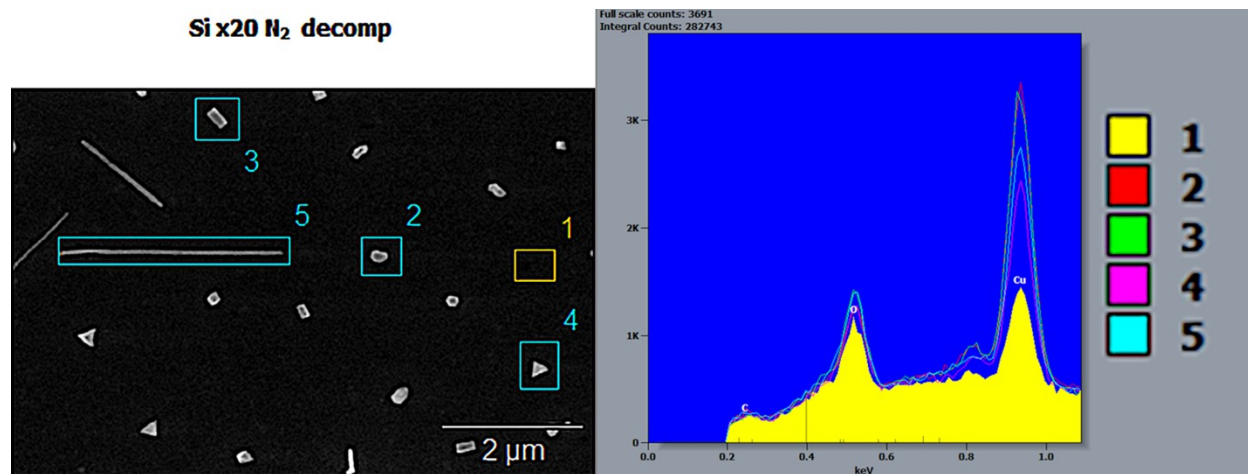


Figure S3. EDX analysis of various Cu particles found on Si-20 N₂ decomposed sample. The squares represent areas of interest probed, and corresponding binding energies are noted, with each square being represented by a unique colored trace. Of note, the CuO particles take on a number of morphologies, however, no significant difference in atomic concentration was observed. It is also noted that not all Cu is removed from the carbon phase, as a notable carbon peak is observed in area 1.

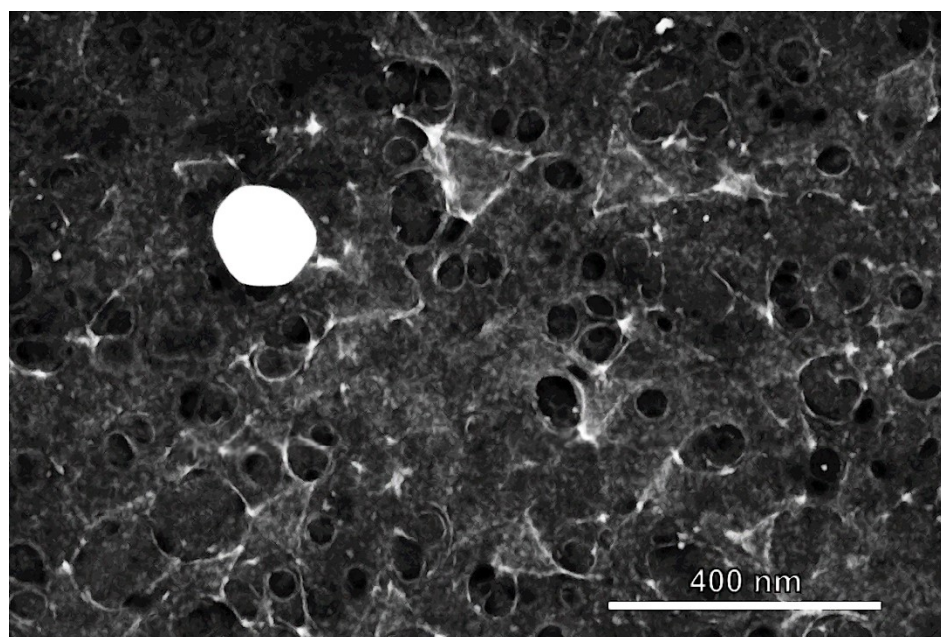


Figure S4. SEM image of Si-20 N₂ decomposed sample. The white particle is a CuO particle. Contrast between the carbon phase and the CuO results in either the carbon being crushed out, or the CuO being blown out. Contrast in the carbon phase is likely due to Cu remnants, not fully leached from the MOF. It appears this Cu aggregates on the edges of the crystal planes.

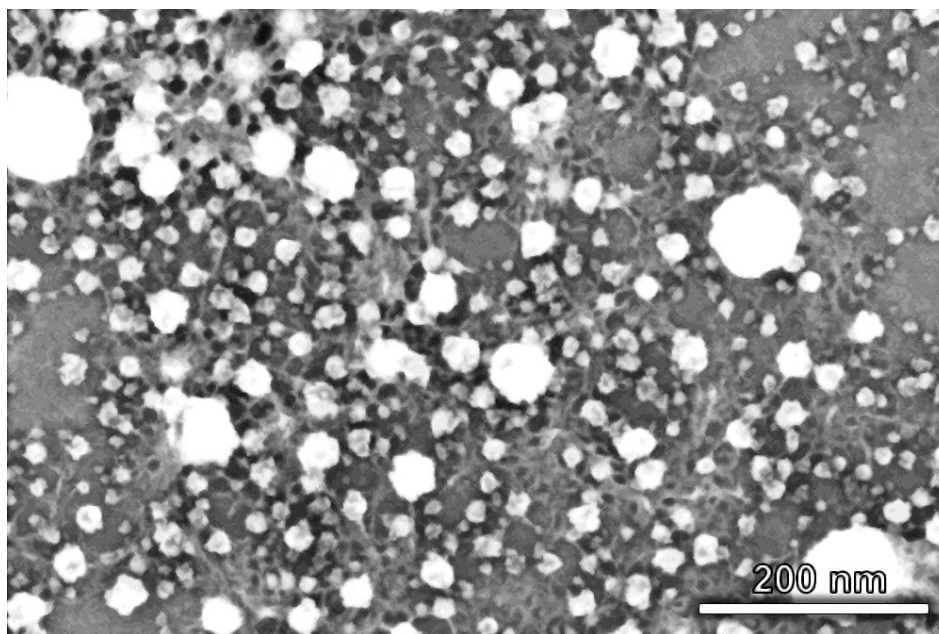


Figure S5. SEM image of Si-20 H₂ decomposed sample. When observing the carbon phase on these samples, again contrast in the carbon phase is only visible if the Cu particles are blown out.

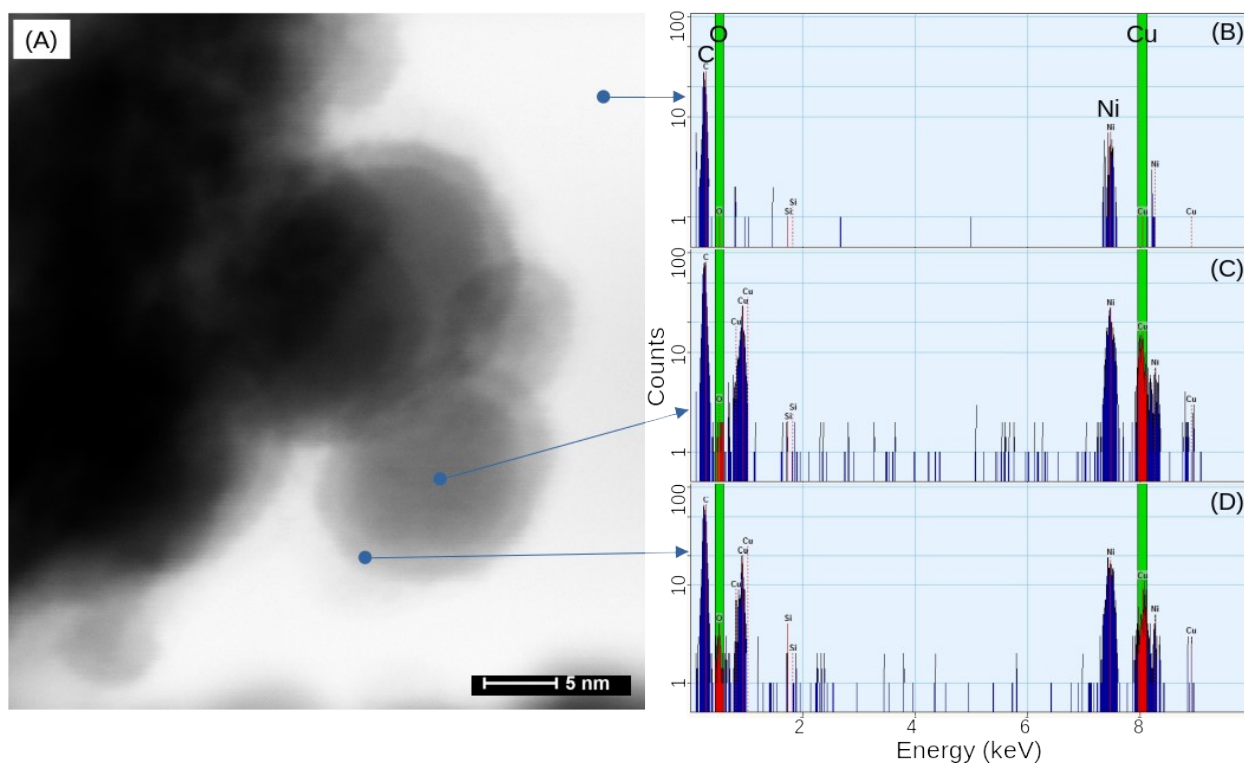


Figure S6. (A) STEM image of the Cu/CuO nanoparticles scraped from the Si-based substrate showing a coating layer. (B) Background of the C-support film on a Ni TEM grid. EDX of the Cu core of the nanoparticle (C) and the coating layer (D) show an increased relative concentration of O on the surface of the nanoparticle, supporting the presence of a CuO layer approximately 2-3 nm in thickness surrounding a Cu core.

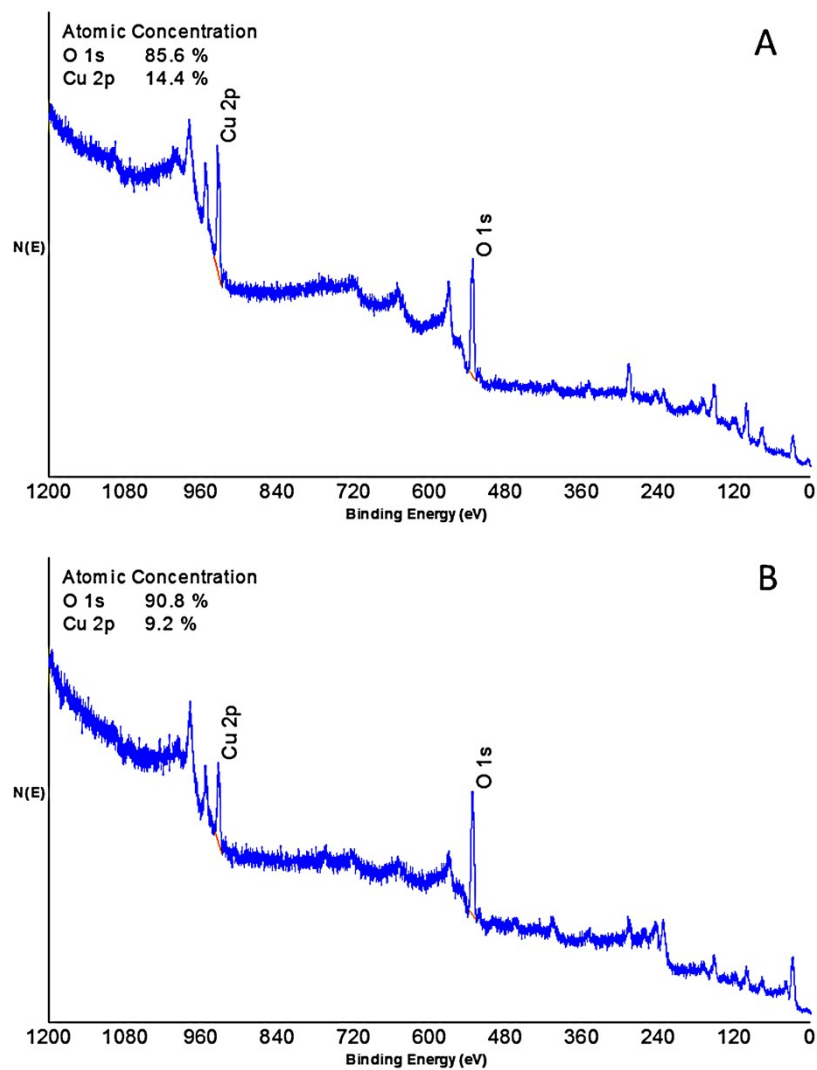


Figure S7. XPS profile spectrum of hydrogen treated $\text{Si-Cu}_3(\text{BTC})_2$ A) after a series of ethanol desorption runs B) after exposure to 50L of O_2

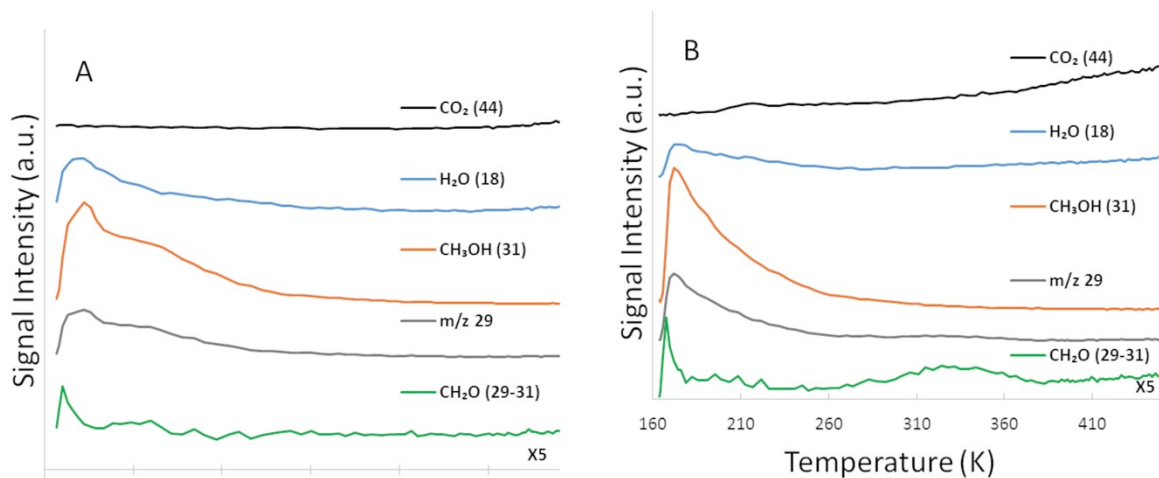


Figure S8. Temperature programmed desorption spectra of methanol off of H_2 treated $\text{Si-Cu}_3(\text{BTC})_2$ with significant mass fragments: A) 0.5 L methanol exposure at 200 K B) 50 L O_2 exposure at 300 K and 0.5 L methanol exposure at 200 K

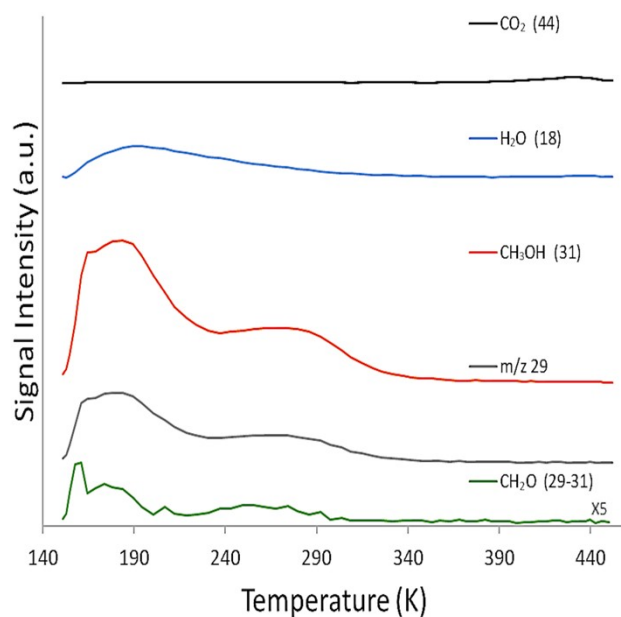


Figure S9. Temperature programmed desorption spectra of methanol off of $\text{Si-Cu}_3(\text{BTC})_2$ with significant mass fragments. 1L methanol exposure at 151K. Of interest, some formaldehyde formation does seem to occur on the bare MOF sample at lower temperatures.