
Beamtime report 01-01-921

" ON THE SYNERGY OF AU-CU CLUSTERS IN SILICA AEROGELS AND HIERARCHICAL SAPO-34 IN SELECTIVE PROPENE OXIDATION REACTIONS "

We collected transmission in situ XAS data and high resolution powder X-ray diffraction on single site copper-gold silica aerogels during separated reaction stages of selective oxidation of propene. The XAS data was collected in the quick-scan mode, and powder diffraction data was collected at the end point of individual treatments. The CuAu aerogel has previously been studied at SNBL for this reaction with promising results (CH-3593). The aerogels were compared to the hierarchical SAPO-34 (HSAPO-34) and the conventional microporous analogue, two carriers with different surface functionality and catalytic behavior. These three materials were found to be active and particularly selective for this reaction, however, they display entirely different catalytic behavior during H₂ co-feed and H₂ regeneration steps than the aerogel.

We conducted four studies with focus on formation of bimetallic Au-Cu clusters, possible sintering effects in C₃H₆ and O₂ feed and regeneration steps with H₂ or H₂ as co-feed. The samples were reduced in H₂ (5 %) to 350 °C using a ramp rate 5 °C/min, and was treated in C₃H₆ (1.1 %) and O₂ (1.1 %) feed for speciation of selective oxidation of propene. Due to time limitations, we chose to prioritize screening of several samples and study reversibility over several cycles for this beamtime. We planned to study particularly interesting samples in the upcoming beamtime in april (01-01-939) with longer scans to improve their data quality.

RESULTS

Figure 1 show XANES at the Au L3 edge and Cu k-edge of the AuCu aerogel during C₃H₆/O₂, H₂ regeneration cycles and in C₃H₆/O₂/H₂. The aerogel and HSAPO-34 both formed CuAu bimetallic particles during reduction in H₂, shown by the characteristic features in Au XANES upon reduction of Cu(II) to Cu(0). The feature remains in HSAPO-34 after switching to C₃H₆/O₂ feed, and disappears when H₂ was co-fed. EXAFS analysis confirms Cu...O + Cu/Au contribution in C₃H₆/O₂, whereas prolonged Cu...Au distances are found in H₂ co-feed. This structural change when adding H₂ to C₃H₆/O₂ is not visible in Cu XANES. Cycling between C₃H₆/O₂ and H₂-regeneration show reversibility in the aerogel, which is partly re-oxidised to Cu(I)/Cu(II) in C₃H₆/O₂ and was completely re-reduced to the initial AuCu bimetallic particles in the H₂-regeneration step. The AuCu synergy is not observed in Au XANES for the aerogel in neither C₃H₆/O₂ feed, nor in H₂ co-

feed, however, EXAFS analysis shows Cu...O+Cu/Au interaction in reoxidised state. The data quality at the Au L3 edge was insufficient and cannot confirm Au...Cu interaction for these samples.

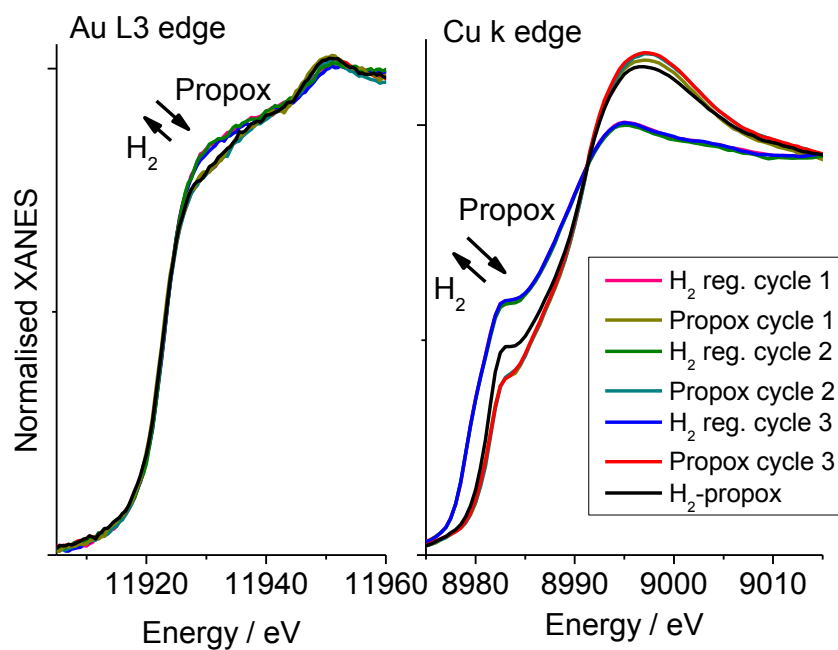


Figure 1: Au L3 edge and Cu k-edge of AuCu silica aerogel during C₃H₆/O₂ ("propox"), H₂ regeneration ("H₂ reg."), and in C₃H₆/O₂ while co-feeding H₂ ("H₂-propox").