
Beamtime report 01-01-939

"AUCU NANOALLOYS IN POROUS CARRIERS: TUNING CATALYTIC PERFORMANCE IN SELECTIVE OXIDATION REACTIONS"

We collected transmission in situ XAS data and high resolution powder X-ray diffraction on single site copper-gold silica aerogels, hierarchical SAPO-34 and the conventional SAPO-34 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. This beamtime is a follow-up from our SNBL beamtime in February (01-01-921) with focus on reproduction of the most interesting results and improvement of data quality.

We conducted three extensive studies. The samples were reduced in H₂ (5 %) to 350 °C using a ramp rate 5 °C/min to study the formation of AuCu bimetallic particles, possible sintering effects in C₃H₆ (1.1 %) and O₂ (1.1 %) feed for selective oxidation of propene. Subsequently, H₂ (0.33 %) was co-fed to study possible bimetallic regeneration.

RESULTS

Both samples (Cu-Au aerogel and H-SAPO-34) show the formation of bimetallic clusters at 350°C in H₂. Figure 1 shows average coordination numbers obtained by EXAFS analysis of the CuAu aerogel in H₂, C₃H₆/O₂ (propox) and during H₂ co-feed (H₂-propox). Least-squares refinement at the Cu k-edge show small Cu(0) clusters with N_{Cu-Cu} ~ 4, while Cu...Au interaction was not confirmed. However, the Au L3-edge reveal predominant Au...Cu interaction with N_{Au...Cu} ~3, and the XANES-features at the Au L3-edge show characteristic AuCu bimetallic features rather than the bulk-like features. These results indicate a mixture of well-dispersed Cu(0) clusters and CuAu clusters. The switch C₃H₆/O₂ feed led to partial reoxidation to Cu(I)/Cu(II) causing the characteristic AuCu bimetallic features in Au XANES to disappear. However, a composite O + Cu/Au contribution is confirmed at both Cu and Au edges. Co-feeding with H₂ causes a significant increase in the Cu...Au contribution (Figure 1). The cluster sizes are rather small in both systems, indicating that they are within the confines of the micropores present in the aerogel and H-SAPO-34 structure.

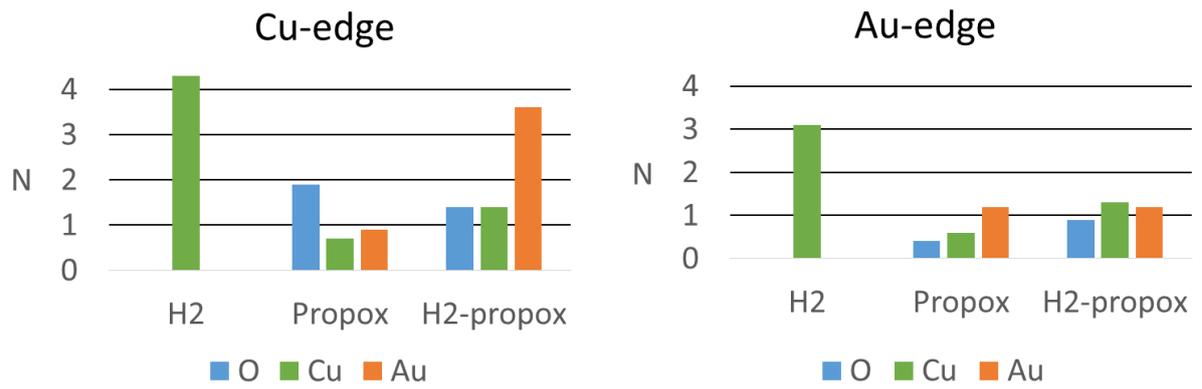


Figure 1: The average coordination number N at the Cu k -edge and Au $L3$ -edge for the AuCu aerogel in H_2 , C_3H_6/O_2 ("propox") and $C_3H_6/O_2/H_2$ ("H₂-propox").