1648
doi:10.1017/S1431927616009089
Microsc. Microanal. 22 (Suppl 3), 2016

Ex-situ TEM: Gaining Fundamental Insights into the Reduction-Oxidation-Reduction (ROR) Process in Small, Bimetallic Particles

C.E. Kliewer[1], S.L. Soled[1] and S. Miseo[1]

[1.] ExxonMobil Corporate Strategic Research, 1545 Route 22 East, Annandale, NJ

Air regeneration of bimetallic catalysts remains an important but poorly understood area of science. The effects of the reduction-oxidation-reduction (ROR) steps on a multi-component material's nanostructure are often unknown. However, with ex-situ electron microscopy-based techniques,[1,2] new insights into these structure/process variable relationships are possible. Earlier TEM studies conducted using ExxonMobil's ex-situ treatment facility revealed that the air oxidation of solid Cu particles resulted in the development of Cu oxide hollow domes (torus structures).[3,4,5] However, the effect of alloying the Cu was not examined.

In this study, the reduction, air oxidation, and re-reduction of small, 50/50 atomic percent CuAu alloy particles was studied. The particles were first formed by high vacuum vapor deposition onto an amorphous, Al oxide-coated carbon support film. The alloy was given a series of ex-situ thermal treatments beginning with an initial 500 °C, 1 hour, H_2 anneal. The material was inertly transferred from the treatment facility into the TEM.[2] The resulting structures consisted of discrete CuAu alloy particles (Figure 1a). The material was then given a 200 °C, 6 hour, air oxidation treatment. Re-examination of the same particles in the TEM indicated that those particles had developed a core-shell morphology (Figure 1b). Energy dispersive spectrometry (EDS) data indicated that the shells were enriched in Cu while the particle cores remained enriched in Au. These data suggest that Cu ions had diffused through the CuAu alloy matrix to the particles' surfaces and had begun to oxidize, while Au remained within the particles' cores. A subsequent 300 °C, 1 hour, H_2 treatment revealed a mix of particles similar to the parent structures and a new population of small Cu-rich particles. Thus, the ROR treatments had significantly changed the original material by creating: (1) bimetallic structures that were slightly depleted in Cu relative to their parent particles and (2) a new population of small Cu-rich metal particles. Thus, the ROR treatments changed both the metal particle chemistry and the metal particle size distribution. The insights gained via these types of ex-situ studies lend unique understanding to the effects of the air regeneration process on small, bimetallic metal catalyst systems.

References:

[1] L.F. Allard *et. al*. *Proceedings Microscopy & Microanalysis* **3** (1997) 595
[2] C.E. Kliewer *et. al*. *Proceedings Microscopy & Microanalysis* **1** (1999) 926
[3] C.E. Kliewer *et. al*. *Proceedings Microscopy & Microanalysis* **6** (2000) 378
[4] C.E. Kliewer *et. al*. *Proceedings Microscopy & Microanalysis* **7** (2001) 1214
[5] C.E. Kliewer *et. al*. *Microscopy & Microanalysis* **12** (2006) 135-144

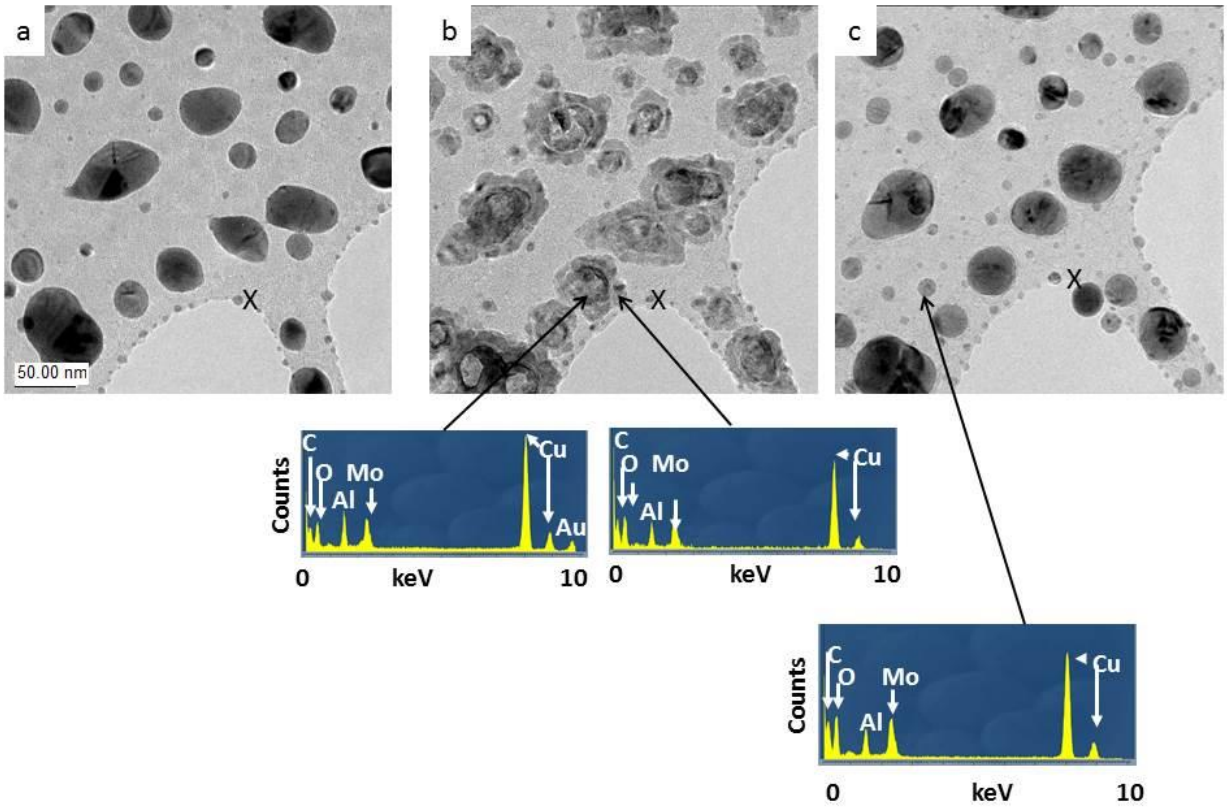

Figure 1. Bright field TEM images reveal CuAu metal particles supported on an amorphous, aluminum oxide-coated holey carbon film after various ex-situ treatments: (a) 500 °C for 1 h under H_2, (b) 200 °C for 6 h under air, and (c) 300 °C for 1 h under H_2. The initial reduction treatment (a) presents uniform metal particles across the support film. The oxidation treatment (b) results in the formation of distinct core-shell structures in which the shell is enriched in Cu and the core is enriched in Au. The final reduction treatment (c) results in uniform Cu_{1-x} Au metal particles and a new population of small, Cu-rich metal particles.

https://doi.org/10.1017/S1431927616009089 Published online by Cambridge University Press