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In situ Study of Dynamics of CuAu Alloy Nanoparticles on Oxide Supports

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The use of closed, electron transparent gas cells to perform *in situ* scanning/ transmission electron microscopy (S/TEM) now enables visualization of the atomic structure of catalysts at variable temperature in a gas environment, which may be close to real operational conditions [1]. When coupled with energy dispersive spectroscopy (EDS) detector, *in situ* composition analysis can be achieved at nm scale. Using this capability, here we demonstrate preliminary results from such an *in situ* study of the dynamics of CuAu alloy nanoparticles (NPs) supported on alumina and silica.

Cu-Au alloy catalysts have been shown to exhibit higher activity for CO oxidation and improved stability against sintering, compared with monometallic Au catalysts. This enhanced catalytic performance presumably arises from the synergetic effects provided by the bimetallic structure. A recent study has shown that colloidal CuAu NPs on alumina are more active after reducing pretreatment than after oxidizing treatment [2]. Experimental evidence suggested that Cu tends to segregate from the NP and is dispersed on the support outside the alloy NP when exposed to oxygen at elevated temperatures, while heating in hydrogen tends to restore the original alloy NP structure. We have thus begun to carry out an *in situ* study using an Atmosphere Protochips gas cell system on aberration corrected STEM for imaging and EDS mapping, to address the question of the atomic structure and composition of CuAu alloy NPs in different environments, and to study the structural dynamics that occur during various treatments.

CuAu alloy NPs supported on alumina or silica particles were dispersed on the heating chip in gas cell, for *in situ* study. *In situ* STEM was carried out on the aberration corrected FEI Titan operated at 300 kV at ORNL. During the *in situ* experiment, the sample was at 350 ℃ in gases at 710 torr. EDS mapping was done on the aberration corrected Jeol 2200FS at ORNL, operated at 200 kV.

Fig. 1 shows a series of STEM images of a CuAu NP on alumina upon heating in oxygen (100%) at 350 ℃. A small cluster forms at 44 s, as indicated by the red arrow. The cluster grows into a large particle at 108 s, after which the large newly grown particle splits into two smaller ones. Similar processes of small cluster formation around a large NP were observed at multiple places within the sample. Sequential STEM imaging revealed that a new particle could also form by consuming an entire existing particle via atomic diffusion, instead of particle migration. EDS mapping of the NPs after annealing in oxygen, as shown in Fig. 2, provides evidence of larger Cu concentration on the exterior edges, indicating that the formation of clusters could be attributed to the outward diffusion of Cu atoms. Upon heating in reducing gas, consisting of 5% hydrogen and 95% argon, small clusters near large particles were seen to disappear, and larger particles formed by consuming smaller ones. Compared to CuAu NPs supported by alumina, the NPs on silica were only seen to migrate slowly during annealing in oxygen, while no small clusters were seen to form.

References:
[1] S. Zhang, et al., ***Nature Communications***, 6 (2015), 7778
[2] S. Najafishirtari, et al., ***ACS Catalysis***, 5 (2015), 2154-2163.
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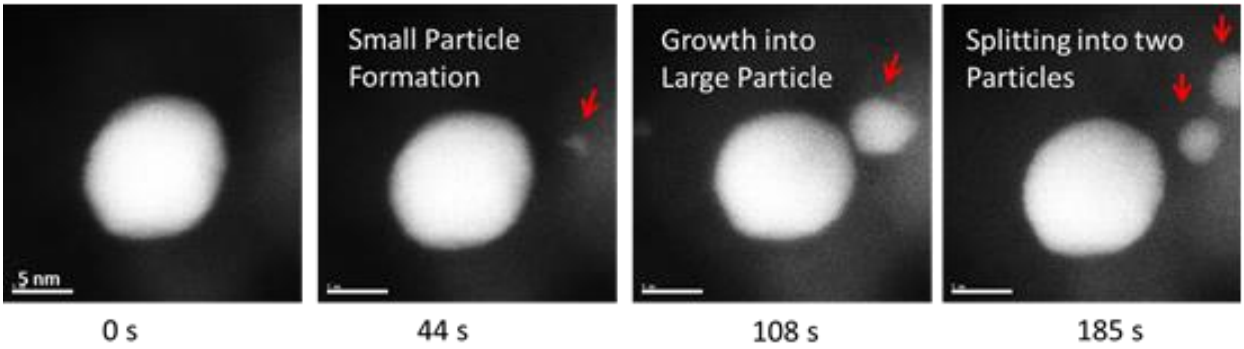

Figure 1. HAADF STEM images of a CuAu NP on alumina during annealing in O_2 at 350 ℃.

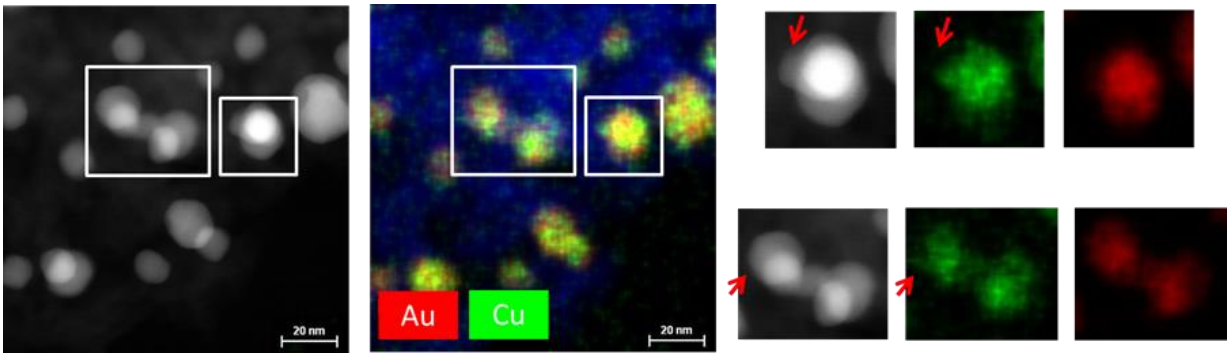

Figure 2. STEM image and EDS maps of CuAu NPs on alumina after annealing in oxygen.

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