Evolution of Au$_{25}$(SR)$_{18}$ Nanoclusters on Ceria Surfaces during in situ Electron Beam Irradiation

Wenpei Gao,$^{1,2}$ Zili Wu,$^2$ George Graham,$^3$ Xiaoping Pan,$^{1,4}$ Karren L. More,$^2$ and Miaofang Chi$^2$

$^1$ Dept. of Chemical Engineering and Materials Science, University of California - Irvine, CA 92697
$^2$ Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831
$^3$ Dept. of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109
$^4$ Department of Physics and Astronomy, University of California - Irvine, Irvine, CA 92697.

Gold nanoclusters (NCs) containing less than ~200 atoms with sizes smaller than 2nm have demonstrated significantly enhanced catalytic activities compared to their nanoparticle (NP) counterparts [1]. The improved activity is largely attributed to their well-controlled homogenous size and morphology, offering a high density of unsaturated atomic sites. Colloidal sols and surfactants are used during NC synthesis to stabilize the structure and select the preferable surfaces; however, such additives can complicate the catalyst-reactant interactions and often degrade the catalytic performance. The molecules adsorbed on the NC surfaces are typically removed via thermal annealing and oxidative etching and the NCs without surfactant assume a metastable state and become highly active. The nature of the NC atomic configurations upon the removal of ligands, and the NC structural and chemical evolution during specific post-synthesis treatments or reactions remain essentially unknown. Here, we directly observe the atomic structural evolution of Au$_{25}$(SR)$_{18}$ NCs supported on CeO$_2$ during the in situ removal of surface ligands in a scanning transmission electron microscope (STEM).

Au$_{25}$(SR)$_{18}$ NCs were synthesized and then loaded onto CeO$_2$ nanocubes in solution, which were then dispersed on lacey carbon coated Cu grids. In situ STEM imaging was performed using an aberration corrected FEI Titan S 80/300 microscope operated at 300kV. A sub-A electron probe (0.08nm) with controlled beam current (0.65 nA) and dose (220 e/nm$^2$s) was used as the heating source to remove surface ligands on individual NCs. Sequential high angle annular dark field (HAADF)- and bright field (BF)-STEM images were acquired simultaneously every 3s for each frame.

A HAADF-STEM image of a Au$_{25}$(SR)$_{18}$ NC supported on a CeO$_2$ NP is shown in Fig. 1a. The CeO$_2$ nanocube is orientated along the (100) zone axis. Ce atomic columns are resolved in the HAADF-STEM image while O atoms are not due to its weak scattering of electrons. The structure of the Au$_{25}$(SR)$_{18}$ NC shown in Fig. 1a has an icosahedron core of 13 Au atoms and the rest of the 12 Au atoms form a disordered exterior shell, with 18 thiolate ligands encapsulating the entire cluster [2], as the inset in Figure 1a. The atoms in Au$_{25}$ are not resolved since the atomic columns are not aligned with respect to the electron beam, and since the NC is surrounded by ligands. Under electron beam irradiation, the atomic structure of the Au$_{25}$ NC changes with time while the CeO$_2$ remains stable. The structure of the Au$_{25}$ NC evolved through four different stages during the course of ligand removal via electron beam irradiation: (1) increased anchoring of the NC onto the CeO$_2$ support during partial removal of the surface ligands; (2) the full removal of all surface polymer molecules, which results in an FCC-structured single-crystal Au NC; (3) the atoms on Au nanoparticle gradually, surface-layer by surface-layer, migrate and spread onto the surface of the CeO$_2$; and (4) finally, a single atomic layer forms on the CeO$_2$ surface, as shown in Fig. 1b. This in situ study revealed a complete reconstruction of a single Au$_{25}$ NC on a CeO$_2$ (100) surface upon the removal of surface molecular ligands during electron beam irradiation indicating that the NCs do not maintain the same atomic framework as in the as-
processed/untreated Au$_{25}$(SR)$_{18}$ due to a very strong interaction between the NC and the CeO$_2$ surface. The true active structural state of such NCs prior to catalytic reaction, after the complete removal of surface ligands, may not be as expected or predicted.

References:

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Figure 1. (a) A HAADF STEM image of Au$_{25}$(SR)$_{18}$ on the (100) surface of CeO$_2$ nanocube, the inset shows the atomic model of Au$_{25}$(SR)$_{18}$ cluster. (b) A STEM image of a single layer of Au on CeO$_2$ surface after electron beam irradiation, with an atomic model and simulated HAADF STEM image of CeO$_2$ overlay on the image. (c) The atomic model of a single layer of Au on CeO$_2$ surface.