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# The Reactivity and Structural Dynamics of Supported Metal Nanoclusters Using Electron Microscopy, *in situ* X-Ray Spectroscopy, Electronic Structure Theories, and Molecular Dynamics Simulations

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## Objectives

Heterogeneous catalysis is surface chemistry over a supported metallic nanoparticle, where the critical first step in understanding structure-reactivity relationships is the accurate 3-D atomic arrangement of metal atoms on the support. Despite the relatively large number of available techniques to characterize nanoparticles, most of them obtain the overall, volume-average properties of nanoparticles, and give little, if any, insight into sometimes very elaborate *actual* arrangement of atoms within the particle. Our focus is the synthesis of stable nanoparticles (Nuzzo) on a variety of supports, and determination of the structure of metal clusters by utilizing existing techniques and developing new methods of synchrotron X-ray absorption spectroscopy (Frenkel) and transmission electron microscopy (Yang) with the validation/prediction of these shapes by theoretical simulations (Johnson).

## Technical Barriers

Our coordinated experimental and theoretical program on nano-structural dynamics utilizing state-of-the-art synthesis, specialized nanoparticle characterization methods, and first-principles theory will provide a full 3-dimensional model of the structural habits at a *non-precedented accuracy*, both individually and as an ensemble, and the elucidation of the energy landscapes that lead to these structural habits. The development of *in situ* methods with these advanced

methodologies will provide critical insights into the fundamental catalytic mechanisms.

## Abstract

Our accomplishments to date are that ultra-small, monodisperse Au<sub>13</sub> clusters have been synthesized via a ligand-exchange and deposited on different supports, including C and TiO<sub>2</sub>, and the beneficial effect of ozone, and limited beneficial effects of atomic oxygen, post-treatments to reduce sintering has been determined. Both XAFS and TEM revealed the structures of these Au nanoclusters, e.g icosahedral Au<sub>13</sub> clusters for ligand-protected Au on C, and XAFS determined the charge transfer between the Au atom and ligand. The theoretical effort focused on Pt-Ru systems because of the large amount of previous experimental data on this system. Theoretical analysis demonstrated that the experimentally observed bond disorders are due to changes in bond-lengths within a particle because of the metal-substrate interactions. Initial efforts into *in situ* experiments are being carried out. Our results demonstrate the strengths and necessity of a multi-disciplinary approach for accurate determination of supported nanostructures utilized in heterogeneous catalysis.

## Progress Report

**Monodisperse sub-nanometer Au<sub>13</sub>** particles provided a model system suitable for demonstrating the wealth of structural information obtainable using X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM). Recent synthetic efforts have been focused on preparing supported Au nanoparticles using the ligand-protected Au<sub>13</sub> clusters as precursors. In order to remove the ligands from the deposited clusters, we compared annealing treatments versus reactive oxygen flow. The supports used in these studies included carbon black, g-alumina, titania (anatase form), and silica (mesoporous SBA-15). The structures of both mixed-ligand and fully-thiolated nanoparticles were investigated using X-ray absorption fine structure (XAFS), scanning TEM (STEM), and high resolution TEM (HREM).

Full multiple-scattering EXAFS study of mixed-ligand and fully-thiolated Au nanoclusters was performed. Visual observation of the EXAFS data reveals difference between the local order in the mixed-ligand clusters and the fully thiolated nanocluster.

The quantitative multiple-scattering analysis on bond lengths revealed that the mixed-ligand clusters,  $\text{Au}_{13}[\text{PPh}_3]_4[\text{SC12}]_2\text{Cl}_2$  and  $\text{Au}_{13}[\text{PPh}_3]_4[\text{SC12}]_4$  is icosahedral and the fully thiolated cluster are cuboctahedral.

Transmission electron microscopy of the mixed-ligand and fully-thiolated clusters confirmed XAFS data. Quantitative Z-contrast on a dedicated STEM identified the mixed-ligand clusters as sub-nanometer, highly monodisperse nanoparticles with an average core of 13 atoms. Determination of the icosahedral shape of the  $\text{Au}_{13}$  clusters was achieved by the trace analysis of the particle edges. Similarly, the cuboctahedral shape of gold particles with fully-thiolated shells can be determined from microdiffraction of single particles. The Au-Au bond length can be obtained as 2.82 Å, which is in excellent agreement with the Au-Au bond distance ( $2.81 \pm 0.01$  Å) obtained by our EXAFS analysis.

**Charge transfer** from gold to thiol and phosphine ligands was studied by S and P K-edge X-ray absorption near edge structure (XANES). Transition states “1” and “3” of P and “2” of S absorption edges regions in references triphenylphosphine ( $\text{PPh}_3$ ) and dodecanethiol, respectively, are modified in their complexes with Au nanoparticles.

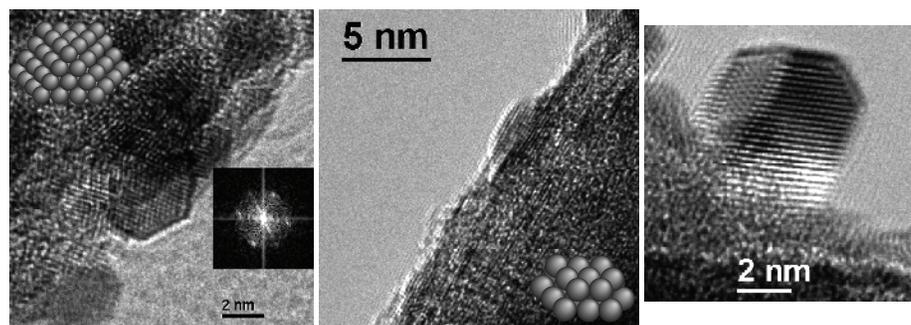
Analysis revealed no significant difference in P peak positions and intensities for the two different mixed ligand clusters:  $\text{Au}_{13}[\text{PPh}_3]_4[\text{SC12}]_2\text{Cl}_2$  and  $\text{Au}_{13}[\text{PPh}_3]_4[\text{SC12}]_4$ . However, the XANES in the two clusters differ from that of pure  $\text{PPh}_3$ . According to the literature, the oxidation state changes of P and S by 1 cause their XANES peaks shifts by ca. 2 eV and 1.7 eV, respectively. Therefore, our experimental results correspond to the Au-ligand charge transfer of an average of 0.5e per P and 0.7e per S atom, in agreement with the difference in their electronegativities (P: 2.1 and S: 2.5). Thus, the total charge transfer from the  $\text{Au}_{13}$  core to the  $\text{PPh}_3$ - $\text{SC}_{12}$  ligands in the  $\text{Au}_{13}[\text{PPh}_3]_4[\text{SC12}]_4$  cluster is 4.8e. Our results allow, for the first time, to measure the charge transfer from Au to phosphine and thiol ligands and compare with theoretical predictions.

**Gold nanoparticles supported on  $\text{TiO}_2$**  is of particular relevance to recent studies of catalysis. Inspection of the nanoparticles at the edges of the particle (i.e. those imaged in a profile view) suggests hemispherical geometry. Extensive quantitative-STEM analyses tallying the number of atoms in the supported particles and their projected

diameters to better qualify the particle morphology are in progress. HREM profiles for a number of particles were collected – all indicating a different truncation of particles on the  $\text{TiO}_2$  support (suggesting a (100) basal plane) compared to Au on carbon black.

**Post-treatments of the ligand-protected  $\text{Au}_{13}$  clusters** on anatase  $\text{TiO}_2$  by reactive oxygen exposure was compared to thermal annealing. The EXAFS spectra of the supported gold nanoparticles after ozone removal of the protecting ligands did show apparent nanoparticle growth as a result of the ozone treatment. This growth is least for Au on  $\text{TiO}_2$ , intermediate for Au on carbon black and on  $\text{Al}_2\text{O}_3$ , and greatest for Au on mesoporous silica (SBA-15). Scanning transmission electron microscopy was used to confirm that reactive oxygen treatment prevented sintering better than annealing alone. Both the ozone post-treatment and thermal annealing lead to sintering of the  $\text{Au}_{13}$  nanoparticles, but the ozone yielded less Au nanoparticles sintering than conventional thermal treatment. The truncated cuboctahedral structure of Au nanoparticles is observed in ozone treatment process while the thermal treatment results in mostly cuboctahedral structure. The average particle size for the UV-ozone treated sample is smaller on average and has a narrower range of sizes centered on an average particle dimension of  $3.7 \pm 1.5$  nm containing 40 atoms on average, while the average particle size for the calcined  $\text{Au}/\text{TiO}_2$  is  $6.2 \pm 3.6$  nm with 320 atoms on average. Atomic oxygen exposure also reduced sintering as compared to thermal annealing, but not as effective as ozone where the average particle diameter was 1.5 nm with more spread in sizes corresponding to different cluster shapes (Figure 1).

**PtRu<sub>5</sub> bimetallic clusters** were also investigated by combined HREM, STEM and XAFS along with modeling. Combined HREM, STEM and XAFS revealed that the PtRu<sub>5</sub> structure on C black was a truncated cuboctahedron, with 1.5 nm diameter, and Pt segregation to the surface. Modeling revealed that the Pt segregation is due to an electronic size effect, and the



**FIGURE 1.** HREM images of different 3-dimensional shapes of Au nanoparticles produced by the exposure of ligand-protected  $\text{Au}_{13}$  clusters to atomic oxygen.

bond disorder, noted by XAFS, is due to the support interaction with a nanoparticle.

**Future directions** include examining bimetallic catalysts such as Pt-Ir, and *in situ* reactions such as quick EXAFS, with time resolution of 1 sec.

### Publications acknowledging the grant

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