Computationally Assisted STEM and EXAFS Characterization of Tunable Rh/Au and Rh/Ag Bimetallic Nanoparticle Catalysts

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The acceleration of rational catalyst design by computational simulations is only practical if the theoretical structures identified can be synthesized and experimentally verified. Of particular interest are bi-functional/bimetallic catalysts, which can have the potential to exceed the selectivity and efficiency of a single-component system [1]. However, adding a second metal greatly increases the complexity of the system; variation in the elements' mixing patterns and reconfiguration can affect the reaction mechanisms and thus catalytic performance [2].

Most experimental tools for the characterization of nanoparticles (NPs) provide structural data at the relevant length scales, but not enough to unambiguously determine the structure. Extended X-ray absorption fine structure (EXAFS) spectroscopy samples particle ensembles to determine the average coordination number, interatomic distance, and disorder through fitting to a reference structure [3]. Scanning transmission electron microscopy (S/TEM) locally characterizes materials down to the atomic scale and can measure the particle size, morphology, and elemental distributions necessary to inform accurate input models for interpreting the EXAFS data [4]. Correlating the local characterization of TEM with the many-particle information from EXAFS, grants a multiscale understanding not achievable with either approach alone. Here we present our application of this correlative theory-experiment design approach to characterize Rh/Au and Rh/Ag bimetallic hydrogenation catalysts, which our calculations predict to have superior allyl alcohol hydrogenation performance compared to single-element catalysts due to the ability to tune the hydrogen binding on the surface. [5].

The NPs were synthesized via microwave heating (MARS 5, CEM Corp.) using previously reported methods [5]; however, metal precursors were added only once. EXAFS characterization was carried out at the Stanford synchrotron radiation lightsource (SSRL). Small metal NP structures were calculated by density functional theory (DFT) and interatomic potentials under the frame work the modified embedded-atom method (MEAM) were employed to simulate EXAFS spectra. STEM imaging, energy-dispersive X-ray spectroscopy (EDS), and *in situ* heating were performed using an FEI TitanX ChemiSTEM, an FEI Talos F200X with Super-X EDS, and an FEI Themis 300 with Super-X EDS.

Rh/Au and Rh/Ag bimetallic NPs of different metal mixing ratios (and their monometallic constituents) were studied under a range of experimental conditions (air and H_2-rich atmospheres; room, LN_2, and 400 °C temperatures) using synchrotron EXAFS. MEAM potentials for Au-Rh and Ag-Rh were developed – and validated by reproducing Au/Rh and Ag/Rh foil spectra – for simulating the EXAFS spectra of the Rh/Au and Rh/Aa bimetallic NPs. No single simple model – random alloy, partially segregated, or phase segregated – fully reproduced the experimental data (e.g., Figure 1). STEM

imaging and EDS mapping observations of the synthesized Rh/Au samples revealed heterogeneous, multimodal morphologies: larger (~3-10 nm), core-shell-like Rh/Au NPs (Au@Rh); smaller (1-3 nm) unalloyed Rh-only NPs; and a Rh-rich background of sub-nm clusters and non-associated individual atoms (See Figure 2a-b). Both the nanoparticle size and relative abundance of particle type depended on the stoichiometry. The morphology of the core-shell particles also varied with stoichiometry, with Rh in the 50:50 mixture showing a greater tendency for preferential attachment to certain facets of the Au cores than in the 90:10 mixture (e.g., Figure 2b-c). The Rh/Ag samples were found to possess a similar structural heterogeneity as the Rh/Au, though the "background" was Ag-rich. These TEM results provided the necessary information to develop the more accurate heterogeneous model needed to interpret the EXAFS data. Preliminary testing of this new model shows better agreement with the experimental spectra and DFT. [6]

References:
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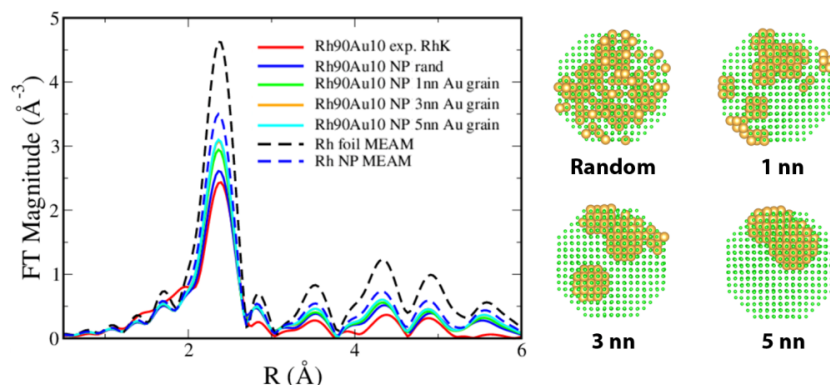

Figure 1. Experimental and simulated Rh K-edge EXAFS at 298 K for Rh90Au10 for different Au grain sizes; the K-edge height discrepancies arise from the use of an oversimplified input model.
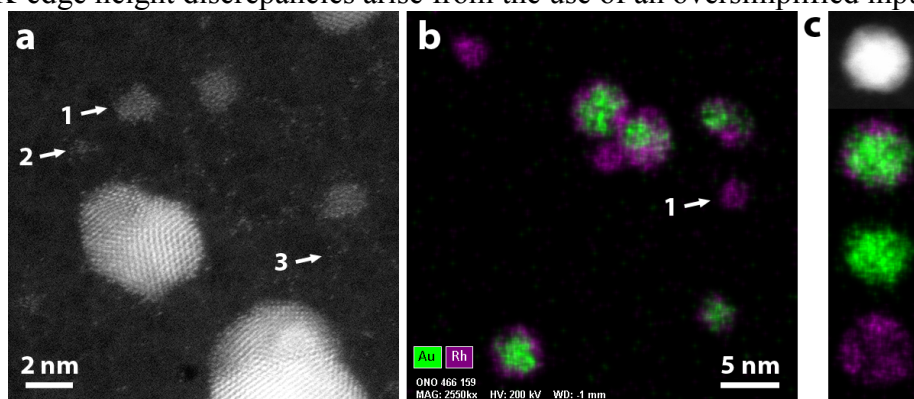

Figure 2. (a) HAADF-STEM image from the Rh90Au10 sample, showing larger, mixed Rh-Au NPs, (1) smaller Rh-only NPs, and Rh-rich (2) ultrasmall clusters and (3) non-associated atoms. (b) EDS map from the Rh50Au50 specimen showing the core-shell structure of the mixed particles; Au is green, Rh is purple. (c) A clear example of preferential Rh-attachment to certain facets of the Au core.