Catalyst Characterization via Aberration-Corrected STEM Imaging

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Introduction

Modern electron microscopes equipped with aberration correctors are capable of providing image resolution in the deep sub-Ångström range [1]. When aberrations in the probe are minimized via a corrector on the incident illumination side, high-angle annular dark-field images can be obtained that are ideal for imaging the distribution of heavy metal species on low atomic number substrates, such as commonly encountered in the field of catalytic science. At ORNL, several such instruments are housed in a new, specially designed Advanced Microscopy Laboratory (AML) building that provides an environment in which the instruments can achieve their specification resolutions. The JEOL 2200FS-AC STEM/TEM aberration-corrected instrument (ACEM) equipped with a probe corrector by CEOS GmbH, and available through the High Temperature Materials Laboratory national user program [2], has been used in studies of a number of catalyst systems. Examples of the utility of ultra-high-resolution imaging for characterizing catalytic materials are given in this talk.

The Instrument

Figure 1 shows a view of the JEOL ACEM, which is housed in a sound-insulated room separate from a control room from which the instrument is operated. This allows precise control of the temperature (±0.1°C/hr), to minimize specimen drift effects. Many other environmental conditions are also optimized in the AML [3]. In STEM mode, with aberrations corrected to 3rd order [4], an illuminating aperture of 26.5mrad yields a computed probe diameter of ~0.07nm, at FWHM. Given a minimum of environmental disturbances, this offers the potential for recording images in high-angle annular dark-field mode well into the sub-Ångström range.

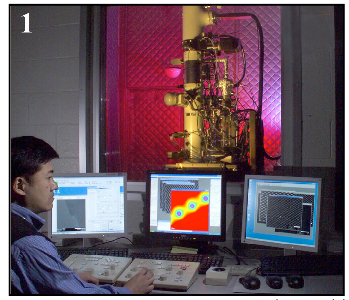
Results and Discussion

Figure 2 shows a HA-ADF image of Pt clusters on TiO_2 (rutile). Single atoms as well as "rafts" comprising a single layer of atoms are predominantly seen. The rutile support crystal is oriented near a zone axis in this image, showing the underlying lattice structure. The box inset shows an apparent "trimer" of Pt atoms, but an intensity profile suggests that the bright atoms compose a second layer, essentially perfectly aligned with the Pt layer below. The atoms in the first layer are represented by the peak at about half the intensity of the bright atom peaks, illustrating the direct correlation between number of atoms and intensity provided by the dark-field imaging process. We also note that this raft tends to align along the corresponding planes of the TiO_2 structure.

Figure 3 shows an aggregate of Au1Pd5 nanoparticles which show significant variations in intensity in atomic columns, e.g. as indicated in the inset. The particle is near a <100> projection. Intensity profiles over several single atoms on the adjacent thin carbon film indicated intensity levels of ~22 and ~40 units, suggesting that these represented Pd and Au atoms, respectively. The profile over the row in the inset suggests that the column with the highest intensity must contain one or more Au atoms. The observed intensity, if considering only Pd atoms in the column, would indicate a column thickness at least 3 atoms greater than surrounding columns, an energetically unfavorable situation.

Significance

Imaging catalytic materials with single-atom resolution provides an unequalled ability to understand the fundamental principles controlling behavior and performance.



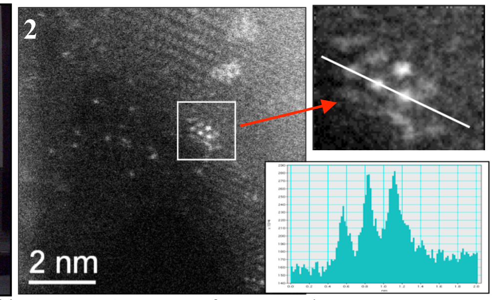


Figure 1. JEOL 2200FS-AC, housed in ORNL's AML, seen from control room.
Figure 2. Pt on TiO_2 (rutile). Single atoms and rafts are seen, overlying the rutile crystal. An intensity profile over a row of atoms in the inset raft suggests the "trimer" in bright contrast is the second layer on the raft, perfectly aligned with Pt atoms on the first layer.

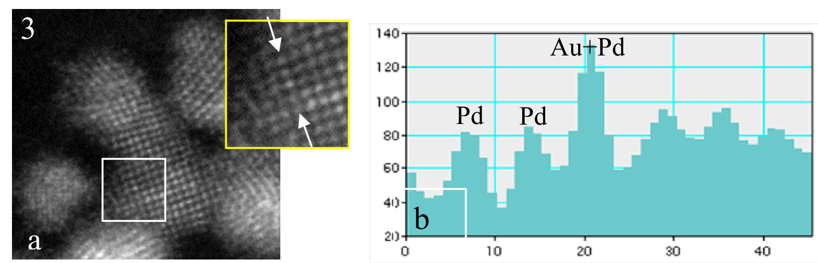


Figure 3. a) Nanoparticles of nominal composition Au1Pd5. Many atomic columns show anomalously high intensity, suggesting the presence of Au atoms, as indicated by the intensity profile (b). See text for details.

References

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