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 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 (Heidelburg, Ger) 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.

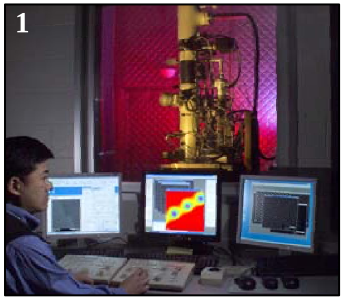
Results and Discussion

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 seen predominantly. 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 are comprise 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 is an example of the ability to image the behavior of single atoms and clusters, in this case Pt on γ-Al_2O_3. Sequential scans show rearrangement of atoms in a raft of about 20 atoms. But individual Pt atoms can be pinned to support sites, and are resistant to the effects of the electron beam, as indicated by the circled atoms in the two images.

Significance

The ability to routinely image catalytic materials at the level of single-atom resolution allows an unequalled potential for understanding of the most fundamental behavior of these materials, and the mechanisms by which they function and deteriorate.



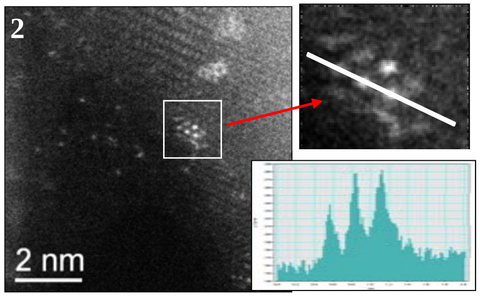


Figure 1. JEOL 2200FS-AC, housed in ORNL's AML, seen from control room.
Figure 2. Pt on TiO_2 (rutile). Single atoms and rafts are seen, overlying the rutile crystal. An intensity profile over a row of atoms in the inset raft suggests the trimer in bright contrast is the second layer on the raft, perfectly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

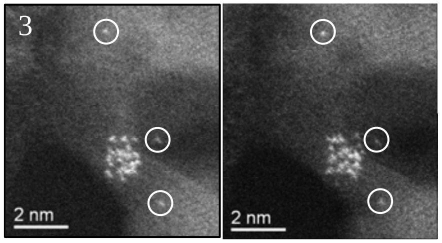


Figure 3. Two images of Pt on γ-Al_2O_3, taken from a series of sequential scans. Note 3 single atoms which remain pinned, while the cluster of ~20 atoms shows some rearrangement due to the influence of the electron beam.

References

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