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Studies of Nanocatalysts with Single-Atom Sensitivity

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Studies of Nanocatalysts with Single-Atom Sensitivity

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Aberration-corrected Z-contrast (HAADF) STEM offers significant advantages for materials research due to its superior resolution and sensitivity, which allows observation of atomic-scale phenomena with unprecedented detail. ORNL's 300 kV VG Microscopes' HB603U STEM with Nion aberration corrector has a demonstrated resolution of 0.61 Å and routinely allows imaging of single atoms inside materials and on their surfaces. Such observations also provide a direct link to first-principles calculations thus facilitating the solution of complex materials problems.

In particular, aberration corrected STEM is a powerful tool for the studies of heterogeneous catalysts, where it becomes possible to connect the structure of metal clusters on the oxide support with the macroscopic properties of the system. In the studies of La-doped _-Al_2O_3 catalytic supports, the single-atom imaging and theoretical calculations allowed identification of isolated La atoms adsorbed on _-Al_2O_3 surface as the instruments of the dopant-induced thermal stabilization [1]. In a related system, accurate measurements of the interatomic distances of the Pt_3 clusters on the surface of _-Al_2O_3 and thorough theoretical analysis led us to discover that these units are capped with OH-groups, which affect electron density distribution within the clusters and, consequently, the catalytic activity of the system. Improved signal-to noise ratio of the aberration-corrected microscope allows visualization of the substrate and dopant structure simultaneously, providing more details on their interaction, as we were able to demonstrate for Cr_2O_3-_-Al_2O_3 and other cases. In the catalytic systems where several metals are involved, Z-contrast imaging can provide atom-by-atom identification and thus distinguish bimetallic and segregated particles.

Most importantly, the high convergence angle of the probe in aberration-corrected HAADF STEM results in depth sensitivity, enabling vertical resolution in the nanometer range in addition to sub- Ångstrom lateral resolution. Focal series of the STEM images can thus be used for determination of the three-dimensional structure of mesoporous or polycrystalline substrates and characterization of the vertical distribution of the catalytic particles. It was demonstrated effective for the systems such as (Pt, Ru)/_-Al_2O_3 and (Pt, Au)/anatase, where the vertical location of single atoms and nanometer-size particles with respect to the substrate was determined. Work is currently underway to establish the best conditions for a similar observation of a single atom within a crystal. Prospects for in-situ aberration-corrected HAADF STEM in ORNL will also be discussed.

[1] S. Wang, A. Y. Borisevich *et al*., *Nature Materials* **3**, 143 (2004).