EMSL Research and Capability Development Proposals

Combining *In Situ* Buffer-Layer-Assisted-Growth with Scanning Probe Microscopy for Formation and Study of Supported Model Catalysts

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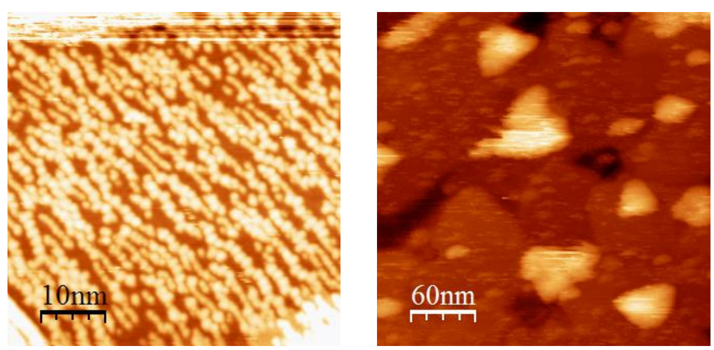
EMSL Lead Investigator:
Igor Lyubinetsky
Microscopy Group, EMSL, PNNL

Co-investigators:
Yingge Du
Spectroscopy and Diffraction Group, EMSL, PNNL
Wayne Goodman
Department of Chemistry, Texas A&M University, College Station, Texas

The objective of the project is to implement *in situ* advanced buffer-layer-assisted growth (BLAG) technique by combining EMSL's ultra-high vacuum scanning probe microscopy (UHV SPM) and applying the resulting novel tool for formation and structural study of BaO nanoclusters on Al_2O_3 ultra-thin crystalline film. The BaO/Al_2O_3 model is an important catalyst system, which virtually cannot be produced by conventional growth techniques. This work should enhance the instrumental capability on the base of the UHV SPM system.

The concept of this work involves examining—*in a model system approach—the synthesis, structure, and potentially active sites* of BaO nanoclusters supported on Al_2O_3 *on a particle-by-particle basis* using *in situ* SPM to provide the *critical structural information* necessary for a better molecular-level understanding of the relationships between catalysis and nanocluster properties.



STM images showing the morphology of BaO film (7 ML–left and 80 ML–right) formed by the direct evaporation of the BaO.

Among materials fundamentally important in heterogeneous catalysis, metal oxides are widely used as both a support and an active catalyst. For example, the BaO/Al_2O_3-based NO_x storage reduction (NSR) catalysts are used to remove harmful NO_x emissions originating from the lean-burn engine operation. Ever since the BaO was used as an active NO_x storage component in the NSR catalysts, there has been considerable interest in controlled synthesis and studies of the corresponding model system of BaO clusters on planar alumina substrate. Since bulk Al_2O_3 is an insulator, model systems of well-ordered, ultra-thin alumina films on crystalline metal substrates have to be synthesized to allow measurements by modern surface science techniques. However, during preparation of the BaO/Al_2O_3 model system by evaporation of Ba metal on ultra-thin θ-Al_2O_3 film (formed on NiAl(100)), the highly reactive Ba strongly interacts with and causes damage to the ultra-thin Al_2O_3. To overcome this problem, a model system can be fabricated by employing the BLAG method, which would separate barium from alumina film with a buffer layer, and/or the BaO clusters can be formed via direct sublimation of metal oxide material.

It is essential to evaluate the fundamental structural issues of the growth mode of the model catalyst systems employing the scanning tunneling microscopy (STM) and/or non-contact atomic force microscopy (NC AFM) *in situ* with other analytical methods of X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED).

Products and Output

New Capability for EMSL Users

In situ oxide nanocluster formation capabilities, developed as part of this EMSL Research and Capability Development project, are now available for EMSL users.

Publications

Lyubinetsky I., N.A. Deskins, Y. Du, E.K. Vestergaard, D.J. Kim, and M. Dupuis. 2010. "Adsorption states and mobility of trimethylacetic acid molecules on reduced TiO_2(110) surface." *Physical Chemistry Chemical Physics* 12(23):5986-5992. DOI: 10.1039/b921921h.

Presentations

Du Y., J. Szanyi, D.J. Kim, and I. Lyubinetsky. 2009. "*Growth of Single-Phase Barium Oxide Film from BaO Effusion Cell*." *Pacific Northwest Chapter-AVS Symposium 2009,* September 9-10, 2009, Edgefield, Oregon.