Probing Atomic and Electronic Structure of Catalysts by Combination of In Situ and Ex Situ Chemical Imaging

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Pacific Northwest NATIONAL LABORATORY
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Purpose

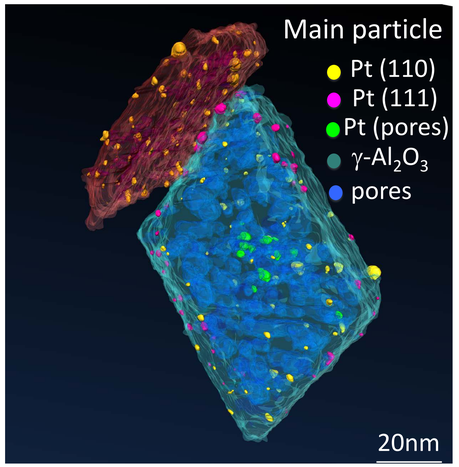
- Understand the structural and morphological evolution of catalytic materials under in situ/operando conditions
- Develop chemical imaging capabilities that enable this understanding
- Directly relate structural information with the catalytic performance, and establish guiding principles for accelerated discovery of next-generation catalytic materials

Key Successes

- Built gas control unit for environmental transmission electron microscope and established procedures for imaging of nanoparticles under reactive environment
- Identified complex reconstruction of transition Al_2O_3 surfaces
- Discovered crystal structure of δ-Al_2O_3 and derived the energy driving force for its formation
- Identified new mechanism of Pd oxidation and nature of surface oxide

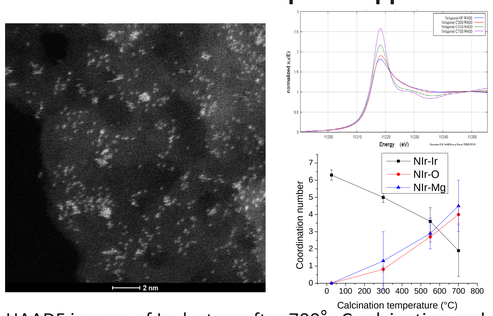
Research Accomplishments

1. Quantitative 3D analysis of particle attachment and surfaces of γ-Al_2O_3



Tomographically reconstructed volume of γ-Al_2O_3 decorated with Pt catalytic nanoparticles. (Kovarik L et al. 2013. *J. Phys. Chem. C* 117:179-186).

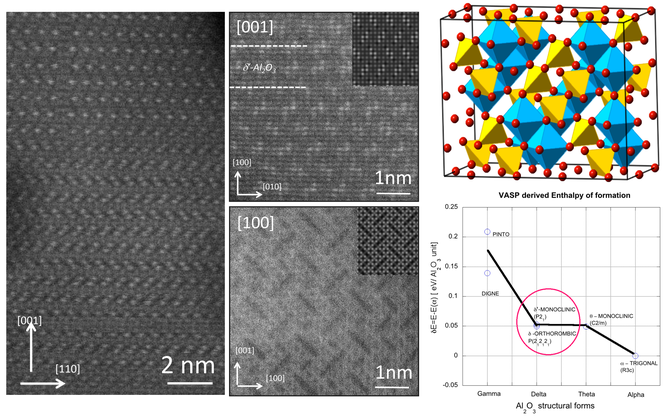
2. Combined high-angle annular dark-field imaging (HAADF) and extended X-ray absorption fine structure (EXAFS) analysis of bonding between Ir clusters and spinel support



HAADF images of Ir clusters after 700° C calcination and corresponding EXAFS nearest neighbor bonding analysis

3. In situ scanning TEM heating capabilities (Micro-electromechanical systems (MEMS) -based heating holder)

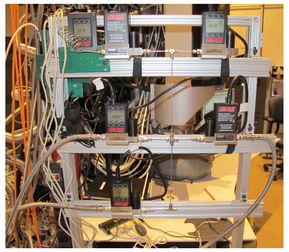
- Mechanism of phase transformations in γ-Al_2O_3 (γ->δ->θ transformation) (Determination of the structure of δ-Al_2O_3 since this phase has been identified for 50 years)
- Surface reconstruction in transition Al_2O_3
- Coarsening mechanism of precious metal catalytic clusters on the Al_2O_3 substrate)

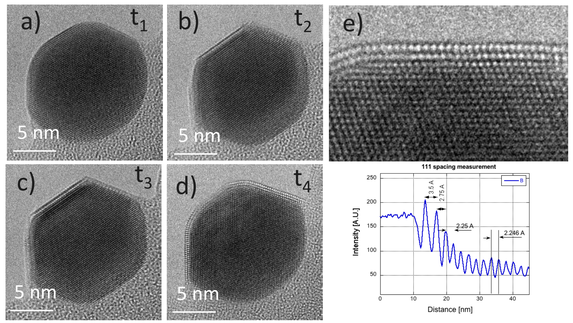


HAADF STEM atomic level of δ–Al_2O_3 from several low index zone axis. Derived crystal structure and enthalpy of formation of δ–Al_2O_3. analysis of structural intergrowth of δ– and θ–Al_2O_3

4. In situ imaging under reactive gas environment

- Developed gas control unit that allows customizable mixing of gases, and seamless switching between reactive gases to study transition phenomena
- Mechanism of Pd nanoparticle oxidation and the nature of Pd surfaces under reactive environment





HRTEM imaging of Pd nanoparticle during oxidation at 500° C. (a) initial state (b-c) strong faceting during the early stages of oxidation (d) further growth of PdO_x. (e) Detail view of the surface oxide formed on the (111) and corresponding bonding analysis.

Next Steps

- DOE Early Career proposal: "**Atomic level investigation of the phase stability of transition metal surfaces under reactive environment**"
- Partial funding from an existing BES project to study phase stability of transition Al_2O_3 and the interaction of transition Al_2O_3 with noble metal clusters and nanoparticles

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