Atomic-level Investigation of the Phase Stability of Transition Metals under Reactive Environment

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Purpose

- Investigate stability of platinum (Pt) group catalytic nanoparticles during exposure to elevated temperature and reactive environment
- Develop capabilities for atomic-level imaging of transition phenomena with environmental TEM (ETEM)
- Establish guiding principles for accelerated discovery of next-generation catalytic materials

Expected Outcomes

- Establish mechanisms that govern stability of supported noble nanoparticles under environmental conditions

Key Successes

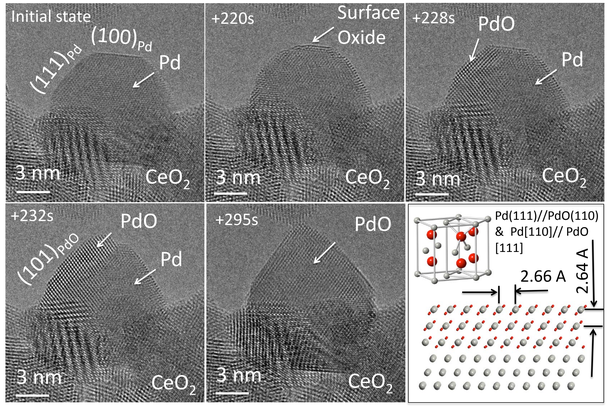
- Identified distinct atomic processes controlling oxidation of palladium (Pd) nanoparticles on CeO_2, SiN substrates.

Research Accomplishments

Atomic-level investigation of phase stability of Pd nanoparticles

A) Transformation pathways of nanoparticles oxidation

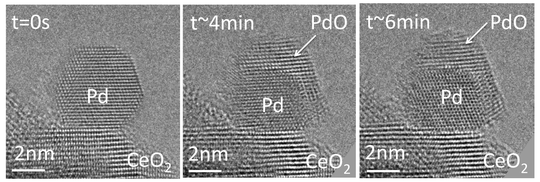
- Kinetics of nucleation and growth determined to not follow classical theory of oxidation
- Mechanisms and crystallographic features of phase transformation identified.



Atomic-resolution ETEM observation of Pd to PdO transformation at oxygen partial pressure of ~1 mbar, temperature of 400°C. Last frame depicts crystallographic relationship/mechanism of transformation.

B) Role of crystallographic interaction with the support

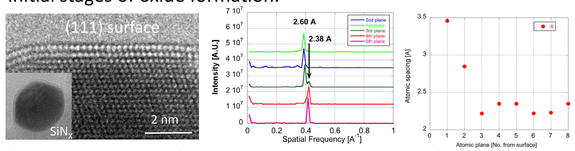
Coherency strains from the substrate identified as strong inhibition of phase transformation.



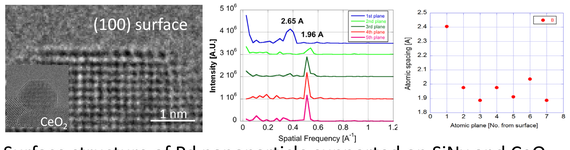
Atomic-resolution ETEM observation of Pd nanoparticles during exposure to oxidizing environment ~0.3 mbar O_2 and temperature of 400°C.

C) Chemical interaction with the support

Distinct chemical interaction with the substrate significantly changes initial stages of oxide formation.

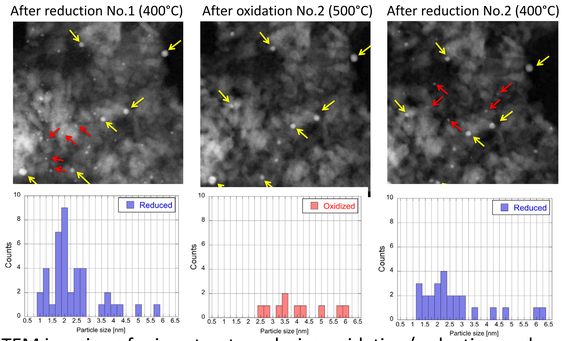


Surface structure of Pd nanoparticle supported on SiN_x during initial stages of oxidation at 500°C. Formation of $PdSiO_x$ surface layer was identified.



Surface structure of Pd nanoparticle supported on SiNx and CeO_2 during initial stages of oxidation at 300°C.

D) Stability of Pd clusters on γ-Al_2O_3 during oxidation/reduction cycling

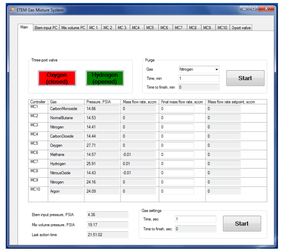


STEM imaging of microstructure during oxidation/reduction cycles demonstrating size stability Pd clusters supported on γ-Al_2O_3.

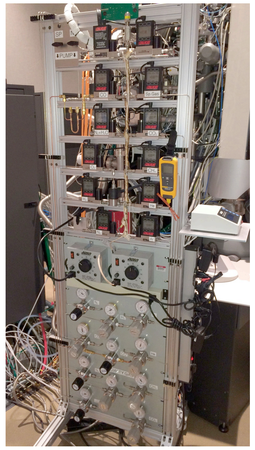
Methodology

Development of gas control unit

- Developed gas-handling system for precise mixing of gases (N_2, He, Ar, N_2+H_2O, O_2, H_2, CO2, CO, CH_4, SG)
- Designed and developed computer controls for seamless switching between reactive gases (A capability that enables high-resolution studies of transition phenomena).



Computer interface of the gas control unit



Gas control unit

Publications

- Kovarik L et al. 2014. *Journal of Physical Chemistry C*, Accepted
- Xin HL et al. 2014. *Nano Letters* 14(6):3203-3207
- Ewbank JL et al. 2014. *Green Chemistry* 16(2):885.

Next Steps

- DOE Early Career proposal "Development and Application of Compressive Sensing to Study Phase Stability of Transition Metal Nanoparticles under Reactive Gas Environment"