

Prediction and accelerated laboratory discovery of heterogeneous catalysts



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Capabilities in Heterogeneous Catalysis

Synthesis for both classical and highly specific catalytic applications

- Wet Chemistry
- Atomic Layer Deposition (ALD)
 - Support Effects
 - Protecting groups
- Additives and poisons

Computational studies tied to experimental work

- Metals, Alloys, and Oxides
- Density Functional Theory
- Accelerated Scaling Methods from DFT
 - Cluster calculations
- Microkinetic modeling and mechanism search



In situ & Operando spectroscopy

- XAFS
- IR
- Raman
- SAXS/WAXS/PDF
 - NMR
- TEM/SEM/STEM
- Environmental

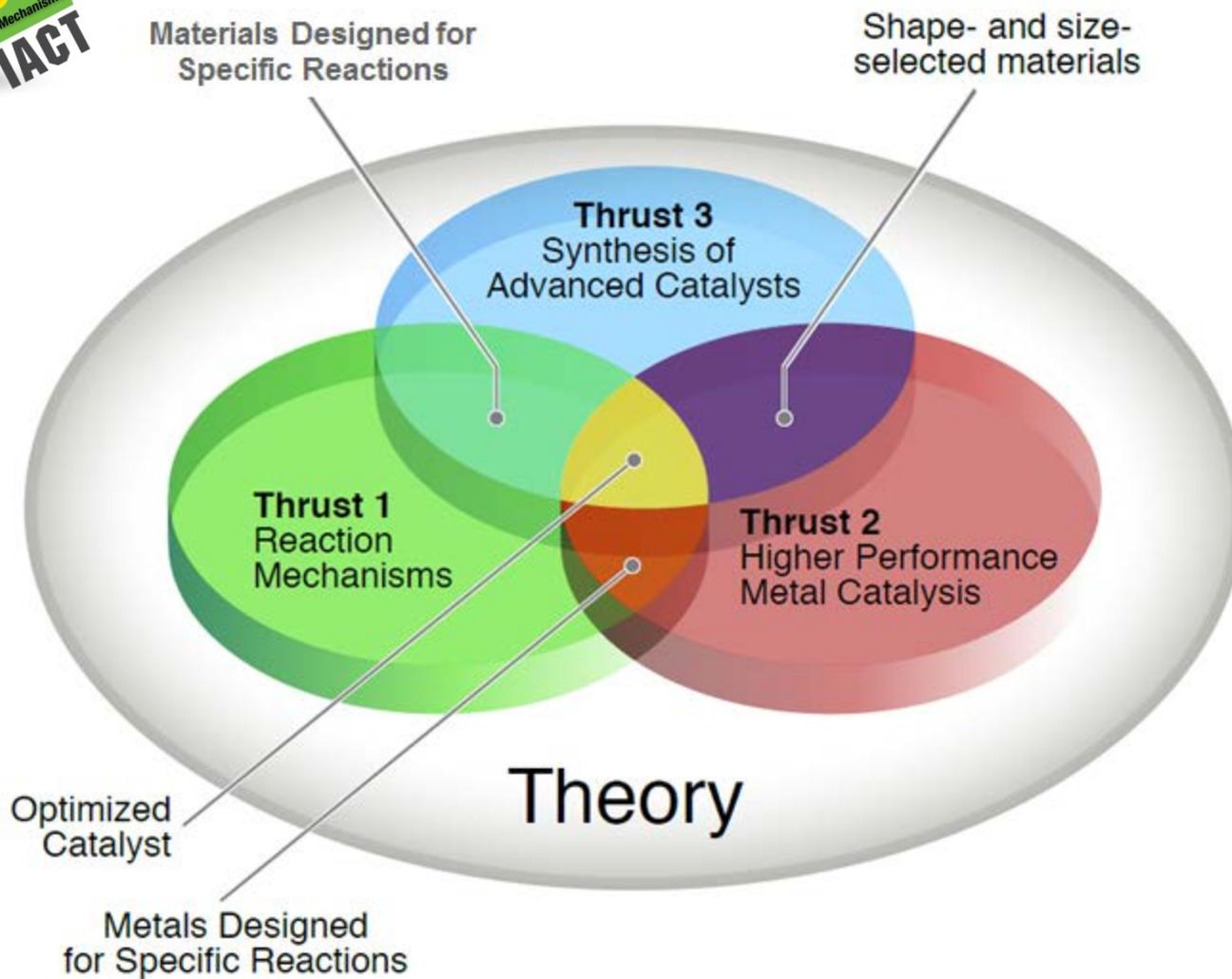
Reactors and reactor test cells for testing under a wide variety of conditions

- Batch
- Plug flow
- Trickle bed
- Combinatorial and fast screening units
 - T, P, solvents
- Kinetics and mechanisms





- Relationships Between Thrusts



Institute for Atom-efficient Chemical Transformations (IACT)

Supported by US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center



Hydrothermal synthesis of SrTiO₃ nanocubes

Sol-gel step:

Mix solutions of Sr²⁺_(aq) in 1M acetic acid and Ti⁴⁺ in EtOH, add NaOH until pH 13 – when gel forms

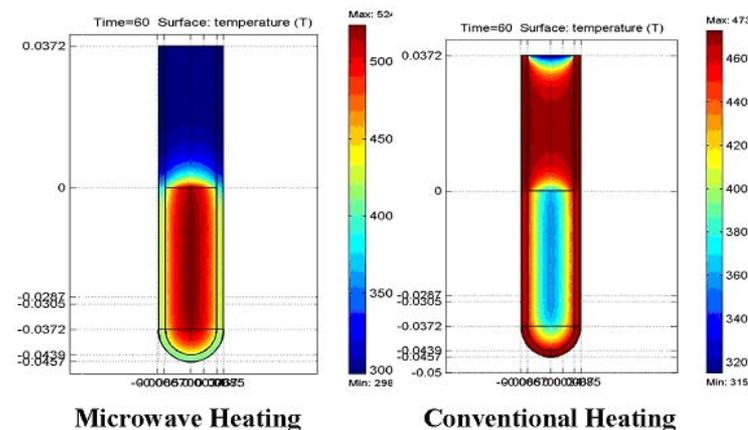
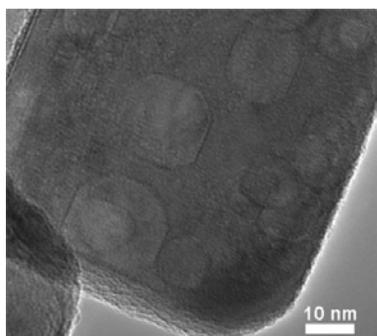
Hydrothermal synthesis step:

Parr autoclave

- Heat to 240°C, hold 36 hours

Microwave heating

- Heat to 240°C, hold 30 minutes

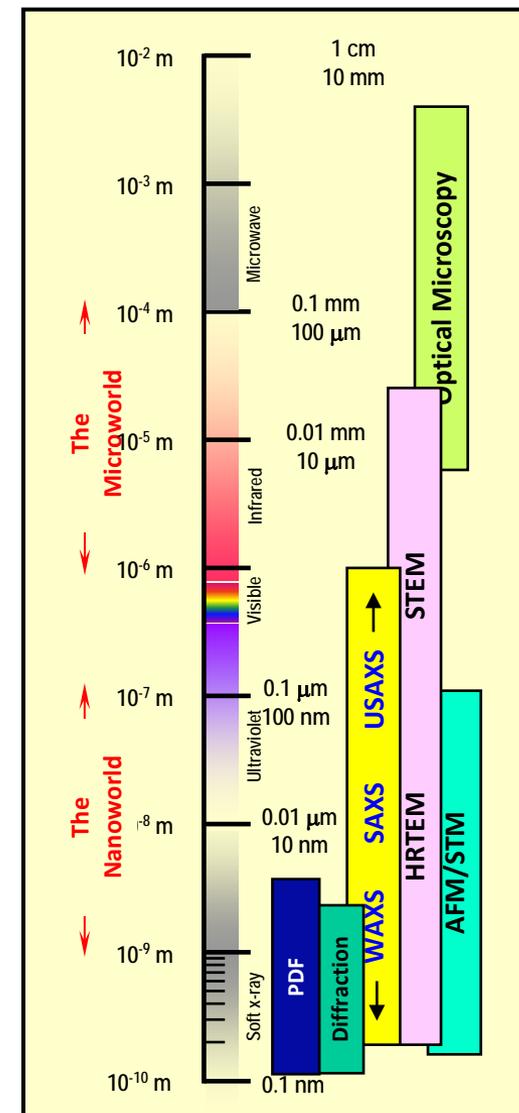


Promotional Material, Biotage, 2011

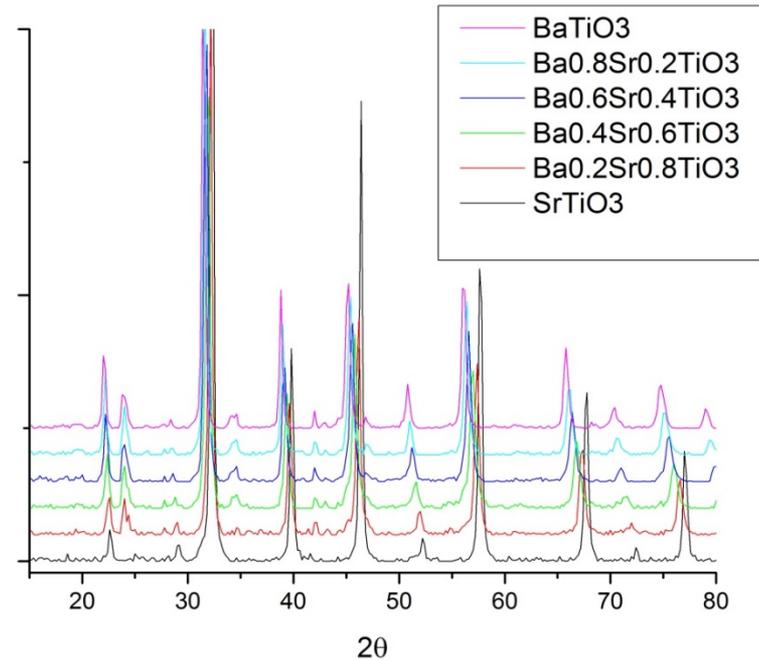
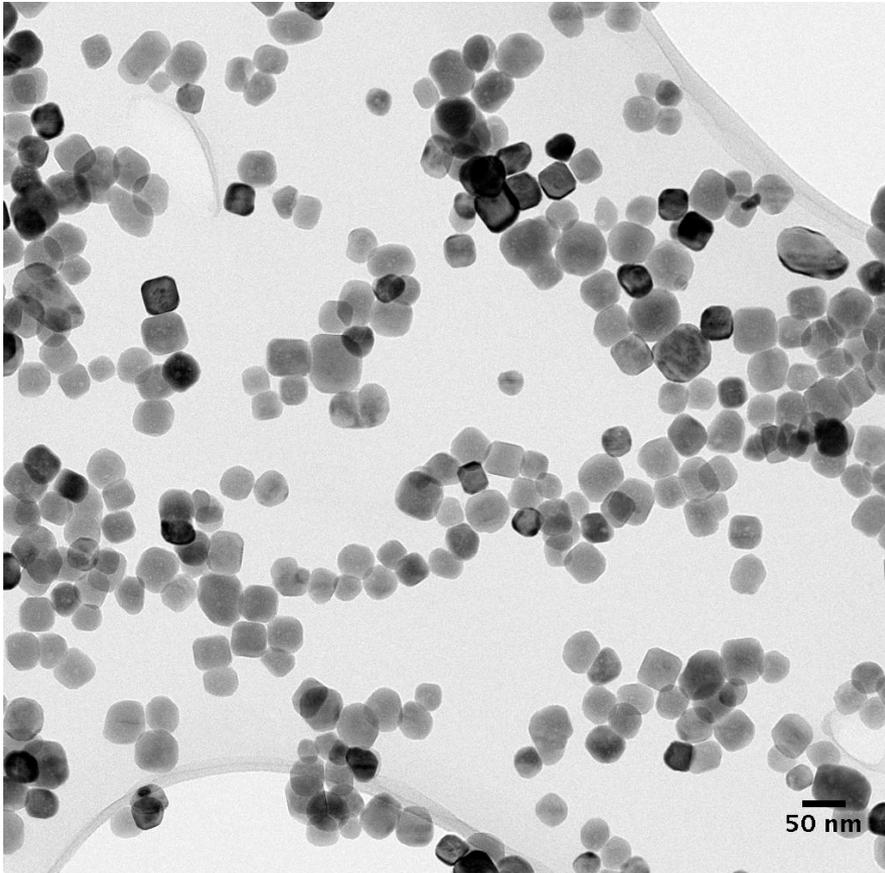
SAXS and PDF Analysis of Particles

SAXS and PDF capabilities

- Access length scales (nm)
 SAXS/WAXS: 0.5 – 500
 USAXS: 50 – 1000
 PDF: 0.1 – 4
- SAXS provides particle size, size distribution, shape and surface morphology
- PDF analysis provides the average separation of the pair of atoms (bond lengths), the coordination number of the pair of atoms and the underlying atomic probability distribution
- Both are in situ techniques and can work with high temperature conditions and a variety of high pressure cells.



Nanocube synthesis

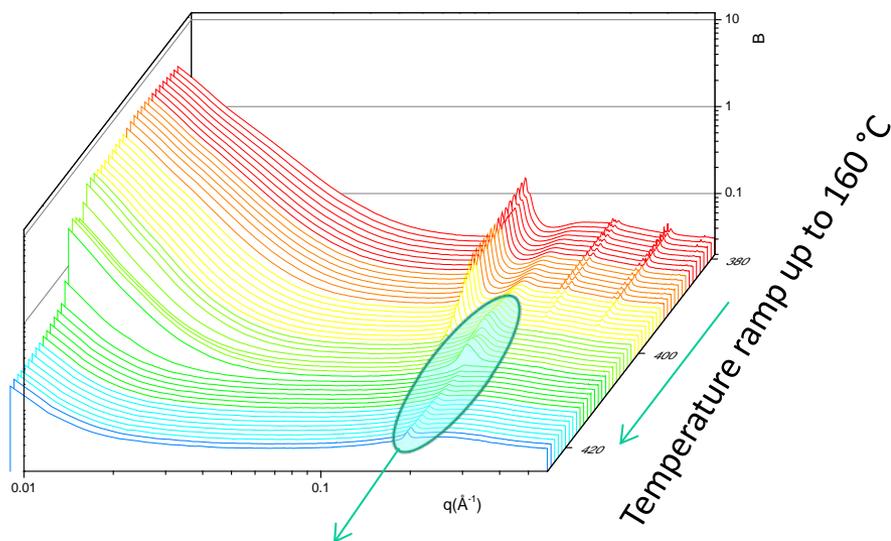


- Above: Powder X-ray diffraction of $\text{Sr}_{(1-x)}\text{Ba}_x\text{TiO}_3$ nanocubes
- Left: $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ (SBTO) nanocubes synthesized by microwave hydrothermal synthesis

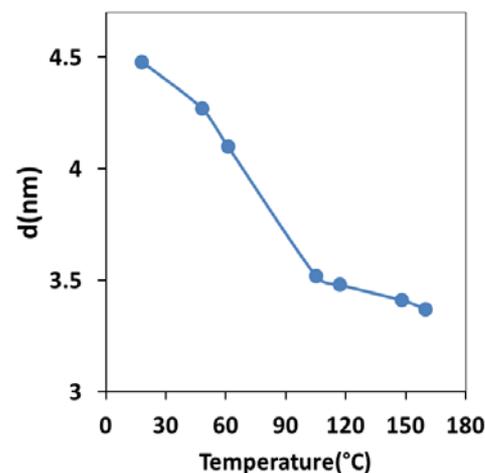
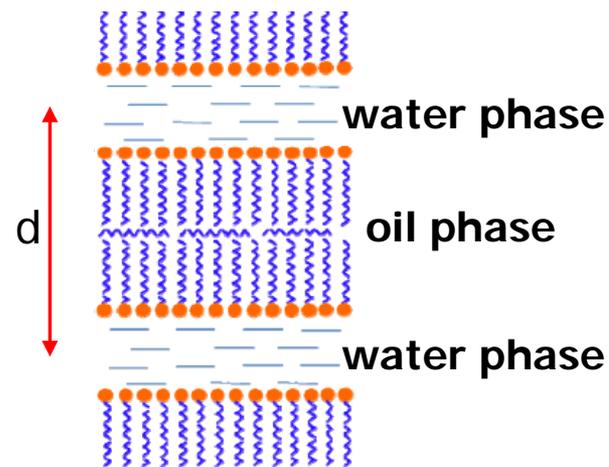
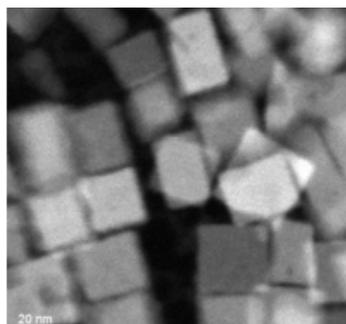
Ordered liquid crystalline phase to nanocrystalline nanocube(SrTiO_3 nanocubes) formation - SAXS results



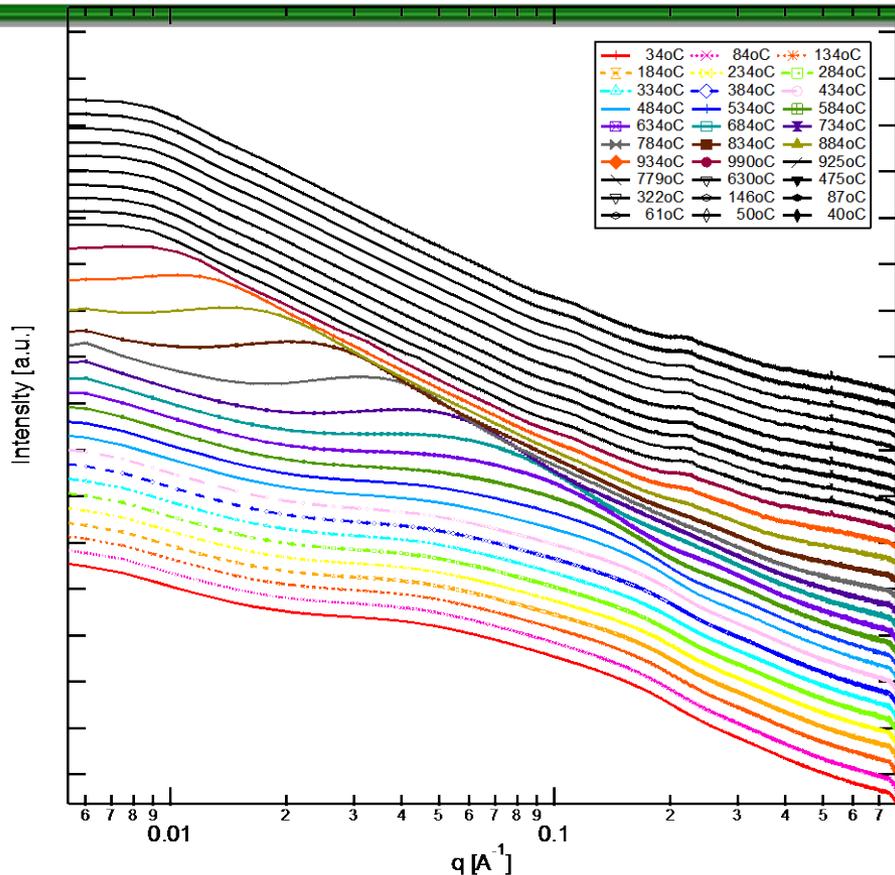
5 % : oleic acid



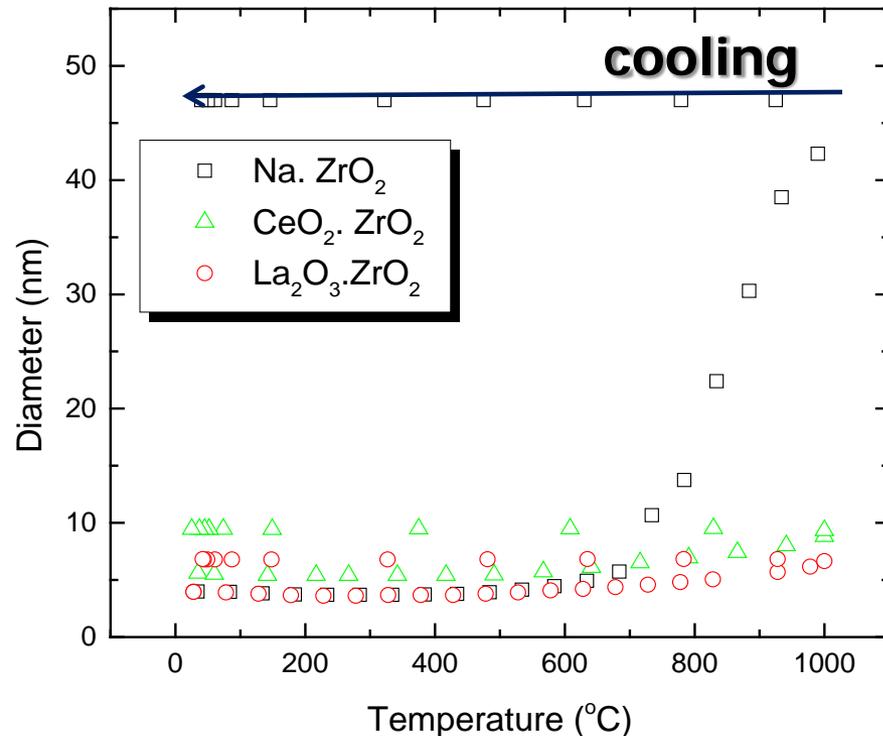
**well-defined structure
even at high temperature
regular nanocuboid**



In Situ SAXS Study of Modified ZrO₂ Support

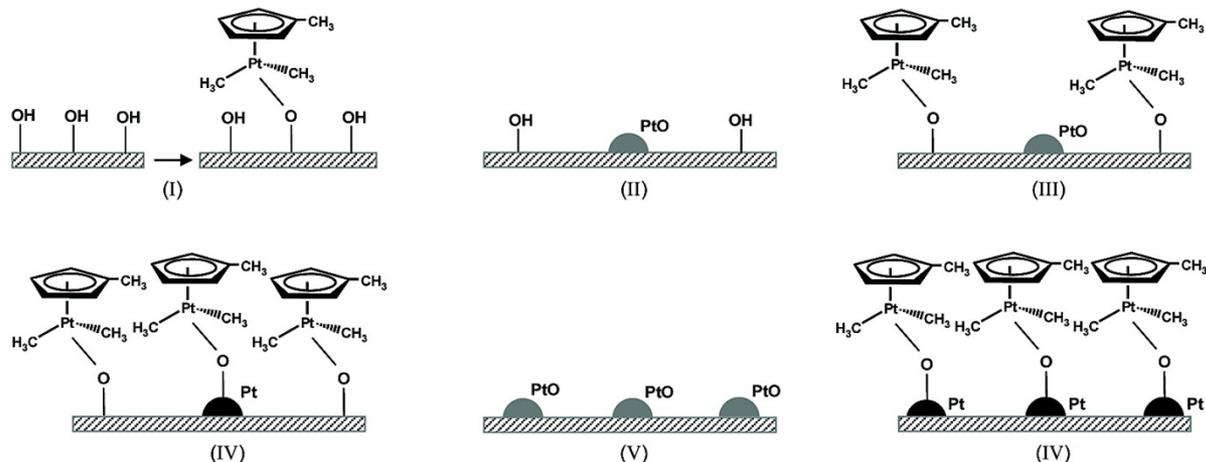
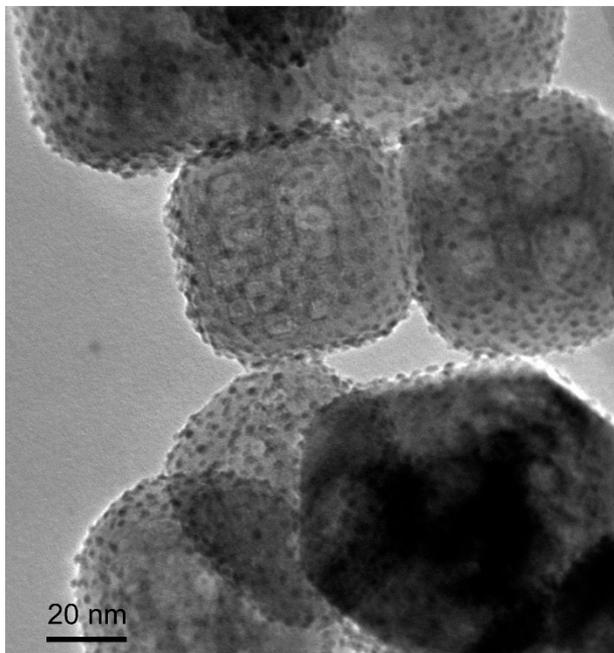


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- In situ SAXS confirms that the particle size increases with the temperature increases. After calcination, the particle size remains the same upon cooling.
- Non-Na containing La₂O₃ / CeO₂-ZrO₂ supports show good thermal stability.

Platinum by atomic layer deposition



Above: Three cycles of Pt atomic layer deposition (ALD)

Left: Pt nanoparticles on SrTiO₃ nanocubes

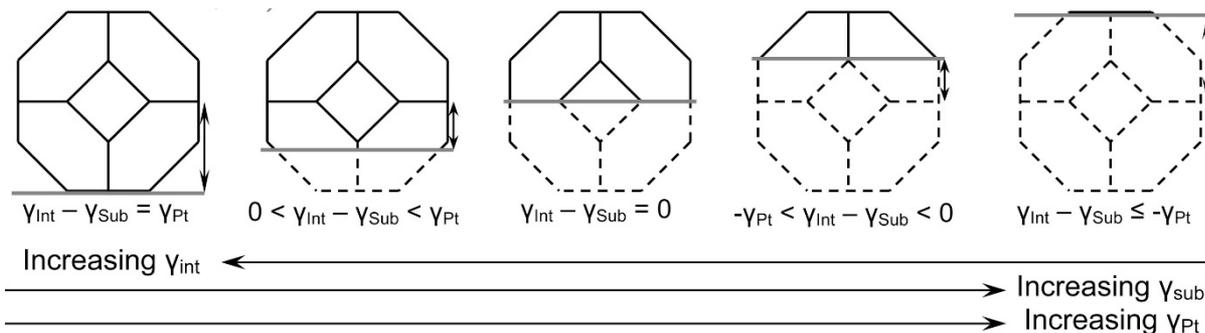
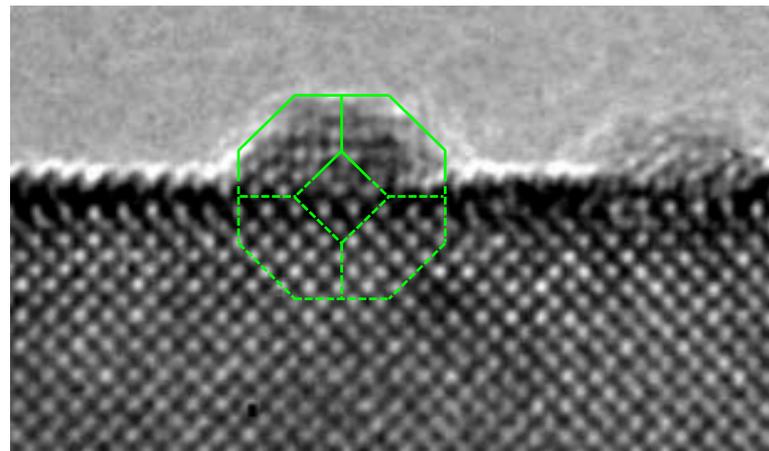
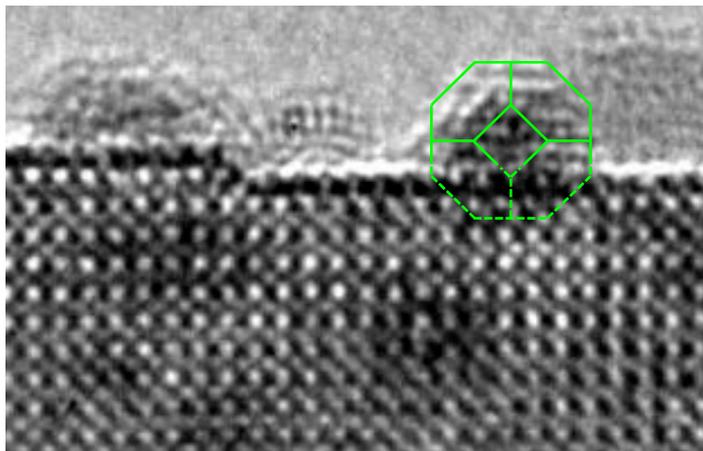
- MeCpPt(Me)₃ precursor forms monolayer on surface
- Oxygen flow removes ligands, nanoparticles form
- Size controlled by number of cycles

Worajit Setthapun, et. al. *J Phys Chem C* **2010** 114 (21), 9758-9771

S. T. Christensen, et. al., **2009**, *Small*, 5, 750-757

J.A. Enterkin, et. al. *Nano Letters* **2011** 11 (3), 993-997

Strain, surface wetting, and exposed facets



Above: HRTEM images of Pt on (100) facets of $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{TiO}_3$ (left) and SrTiO_3 (right) nanocubes. Winterbottom construction for Pt overlaid in green (color online), revealing that wetting on SrTiO_3 is greater than 50%, and wetting on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ is less than 50%.

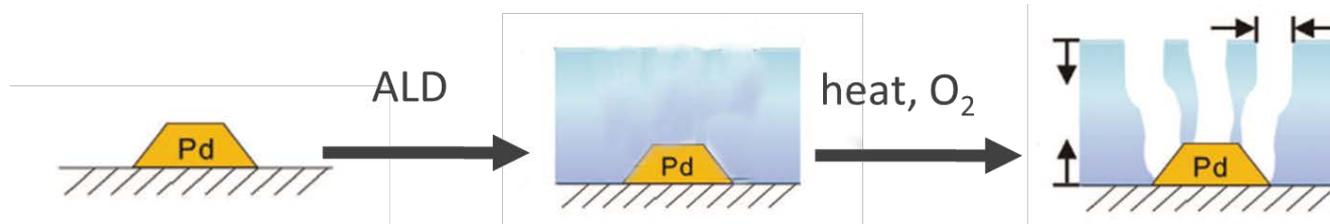
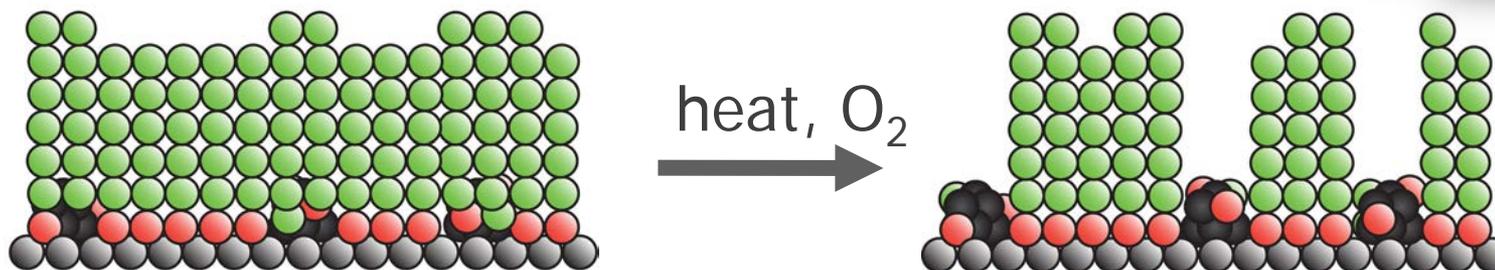
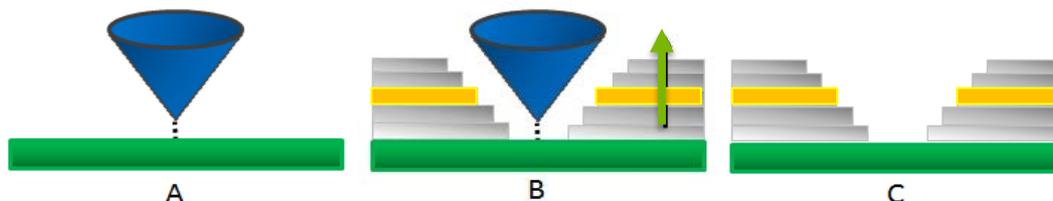
Below: Predicted Pt/substrate wetting as lattice mismatch increases

IACT Renewal - New Catalytic Materials



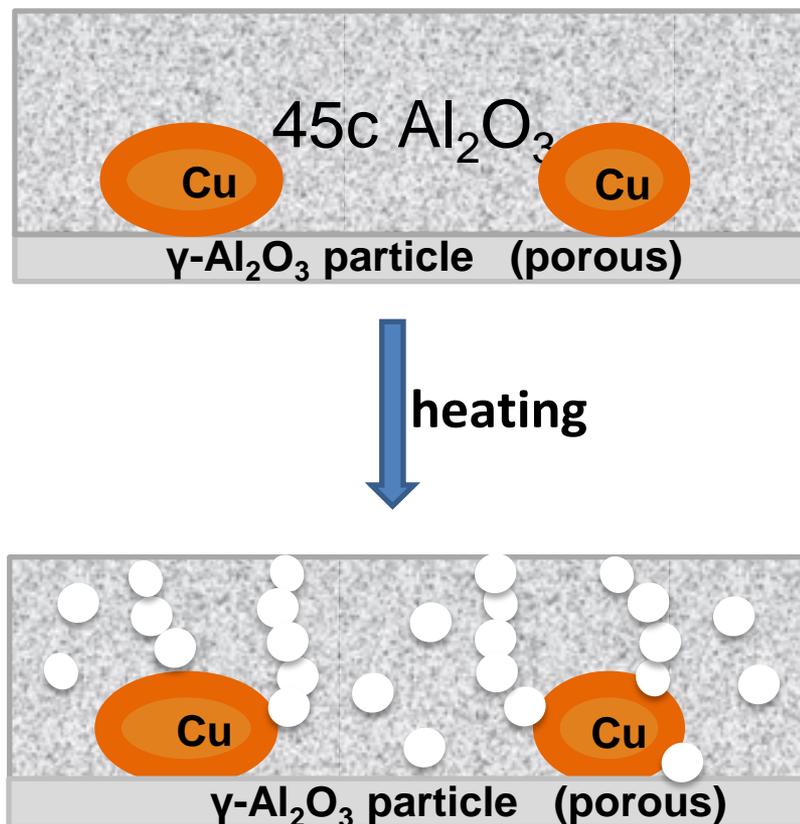
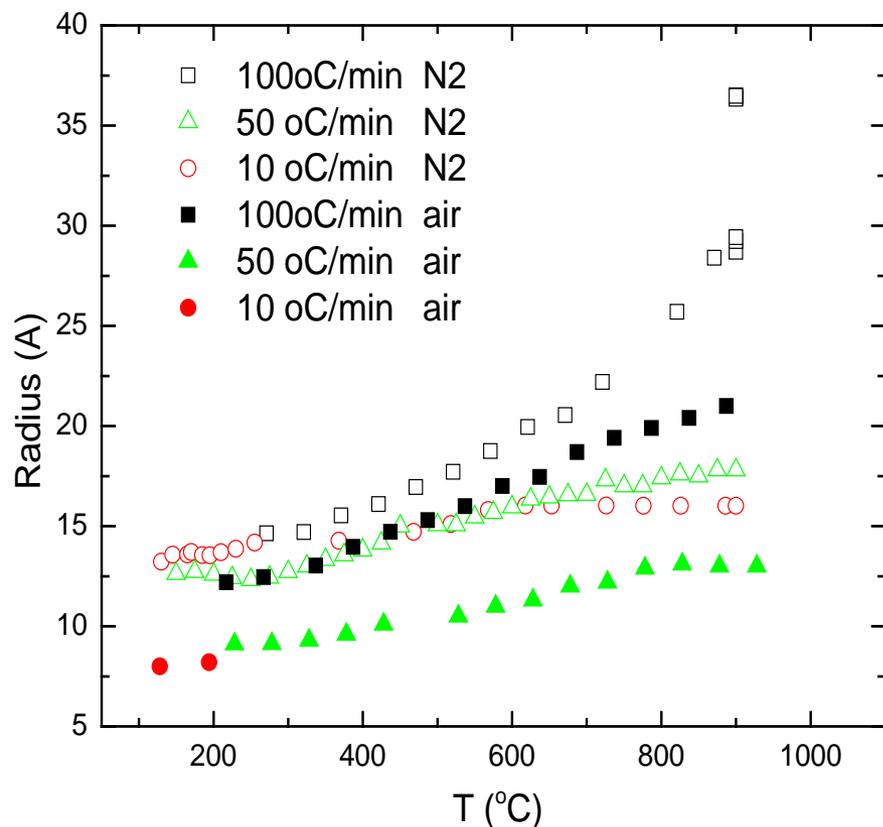
Goal: Expand overcoat and templating method

- Building nanobowls on catalytically active substrates.
- Adding active sites in the walls of pores and nanobowls.
- Control access to “single” metal atom of a nanoparticle.



In situ SAXS of Calcination of ALD OverCoating

Cu particles over coated with Al_2O_3 ALD



- The pore size increases as the temperature increases.
- With greater ramping rates, the larger pores form.
- The pore is larger heated in the N_2 than in the air.

T. Li, B. O'Neill, J. Dumesic, R. E. Winans

J. Elam and Saurabh Karwal (ANL) are doing a simulation of this pore forming process

In Situ X-ray Studies of Catalysis



Opportunity

- Surfaces designed for selectivity and nanometal particles are the trend in designer catalysts.
- The catalysts and reactants need to be studied under real reaction conditions.

Challenge

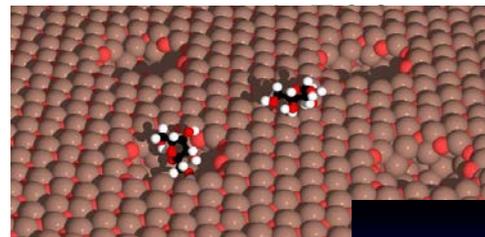
- Need a small beam with enough X-rays to see very dilute, very small nano catalysts.
- Currently it is very difficult to see nanobowls in surfaces and the very reactive nano particles.

4GSR Strength:

- Small beams can be used to map out nano particles on the surface and how they change with temperature and pressure.
- GISAXS/WAXS can be combined with X-ray, Raman and FTIR spectroscopies.

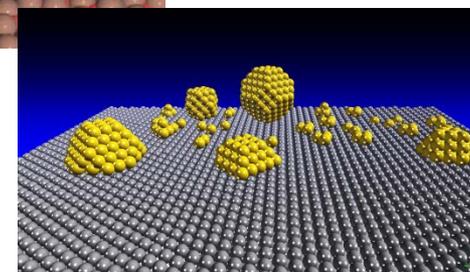
Credentials (Winans, Marshall, Elam, Miller/ANL, Poepelmeier, Stair, Notestein, NU)

Catalytic surfaces

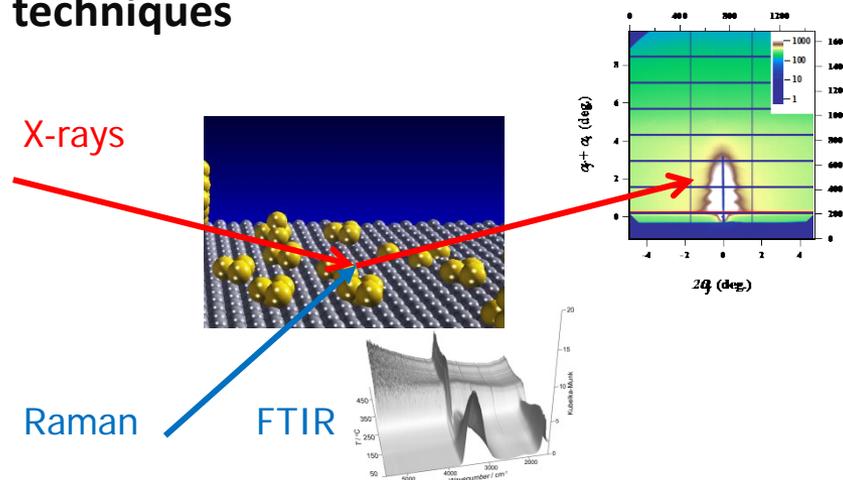


Bowls containing catalysts – size selective

Nano catalysts on surfaces



GISAXS combined with other techniques



IACT Renewal - Design of Catalysts for HDO of Biomass

Metal Functionality

Monometallic vs. Bimetallic

Hydrogenation
(aldehyde, ketones, ethers,
acids, carbohydrates)

C-C bond cleavage
(decarbonylation, retro-aldol
condensation)

C-O-C bond hydrogenolysis

Bifunctional Metal-Acid catalysts

Dehydration
(C-O bond cleavage)

Location of acid sites

Brønsted vs. Lewis

Isomerization

Support

High surface area
Hydrothermally stable

Regenerable

Acidity



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