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

In situ & Operando spectroscopy

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

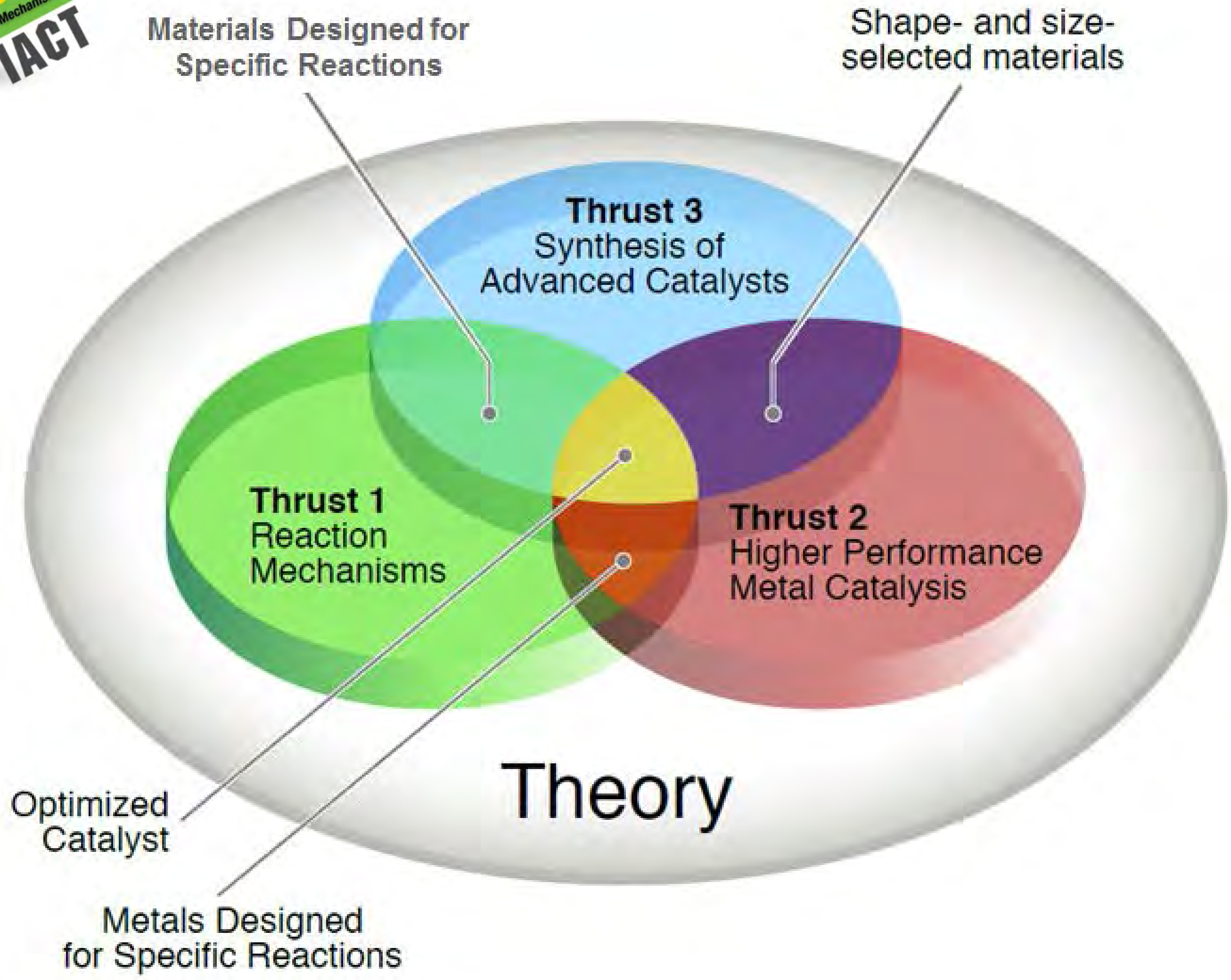
Computational studies tied to experimental work

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

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

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

- Relationships Between Thrusts



Materials Designed for
Specific Reactions

Shape- and size-
selected materials

Thrust 3
Synthesis of
Advanced Catalysts

Thrust 1
Reaction
Mechanisms

Thrust 2
Higher Performance
Metal Catalysis

Theory

Optimized
Catalyst

Metals Designed
for Specific Reactions

Hydrothermal synthesis of $SrTiO_3$ nanocubes

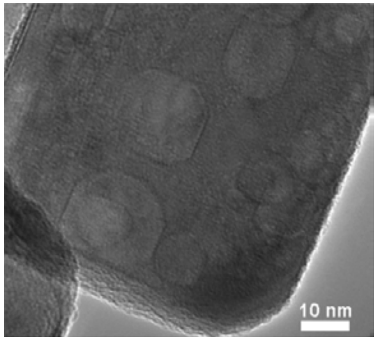
Sol-gel step:

Mix solutions of $Sr^{2+}_{(aq)}$ in 1M acetic acid and Ti^{4+} in EtOH, add NaOH until pH 13 – when gel forms

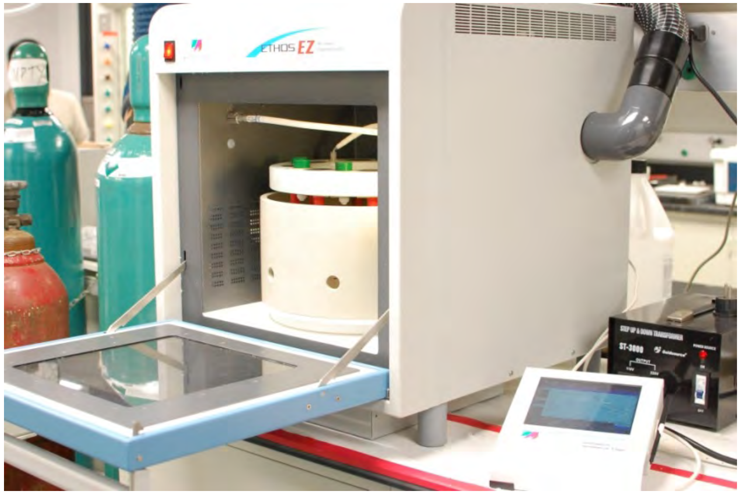
Hydrothermal synthesis step:

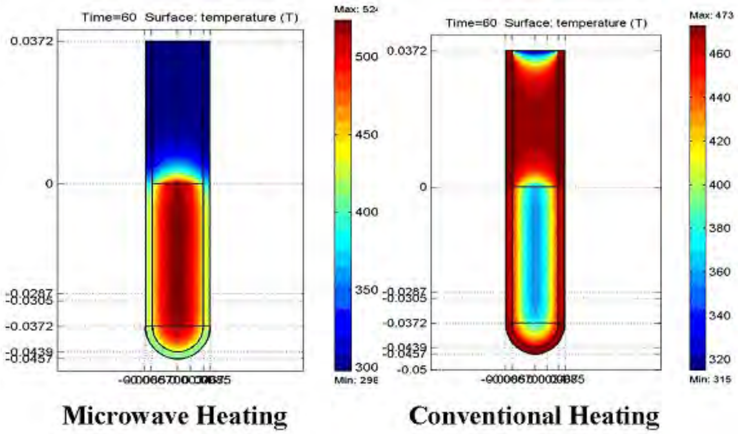
Parr autoclave
- Heat to 240°C, hold 36 hours

Microwave heating
- Heat to 240°C, hold 30 minutes



Chemistry of Materials **20** 5628-5635 (2008)





Promotional Material, Biotage, 2011

SAXS and PDF Analysis of Particles

SAXS and PDF capabilities

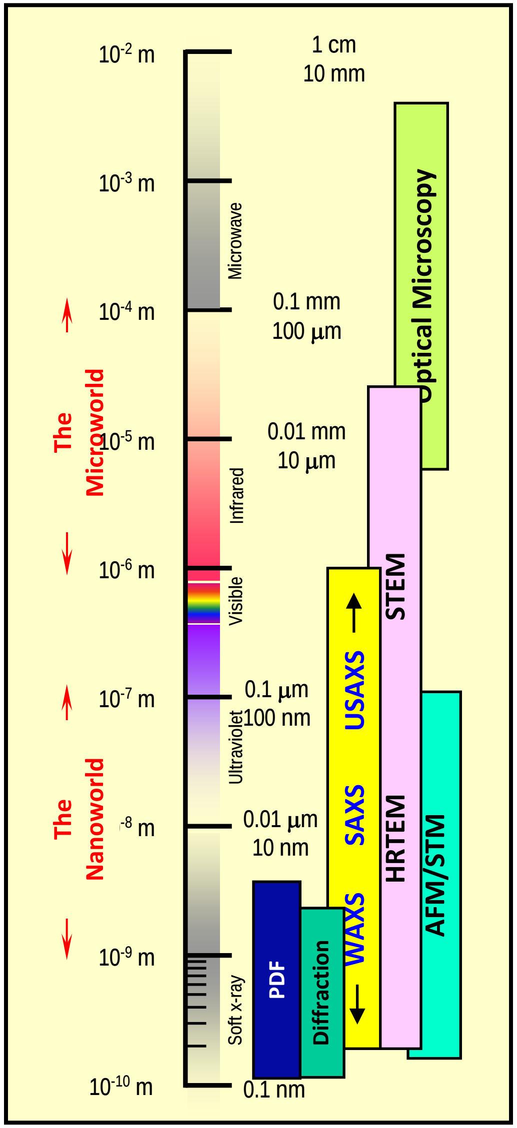
- Access length scales (nm)

  SAXS/WAXS: 0.5 – 500
  USAXS: 50 – 1000
  PDF: 0.1 – 4

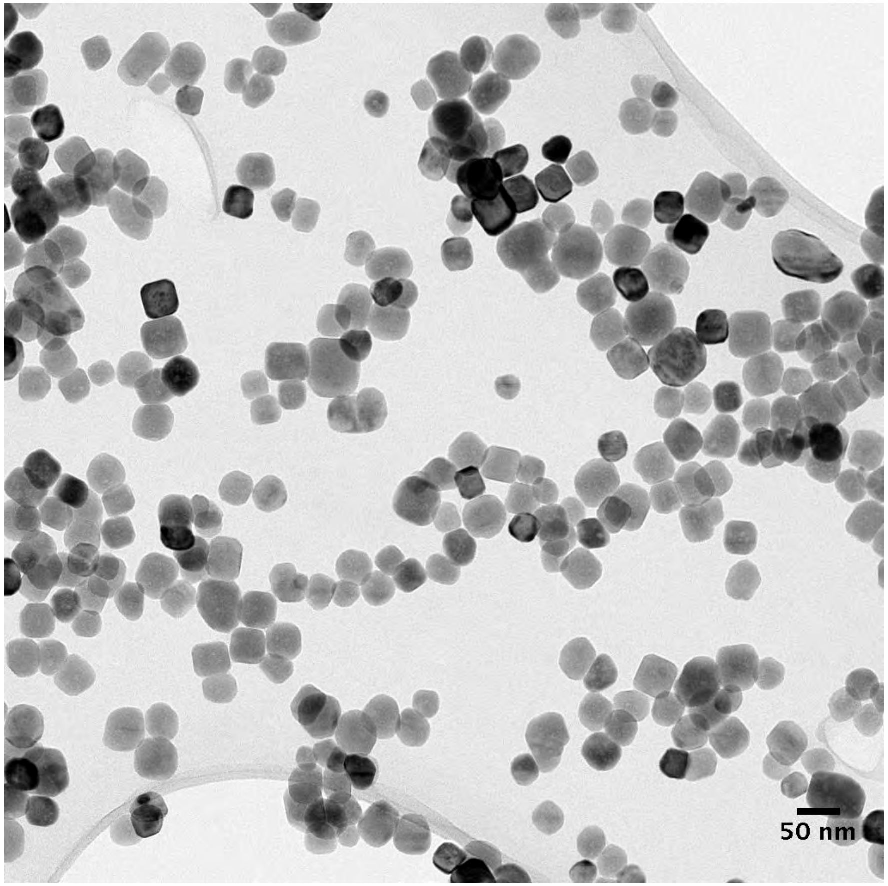
- SAXS provides particle size, size distribution, shape and surface morphology

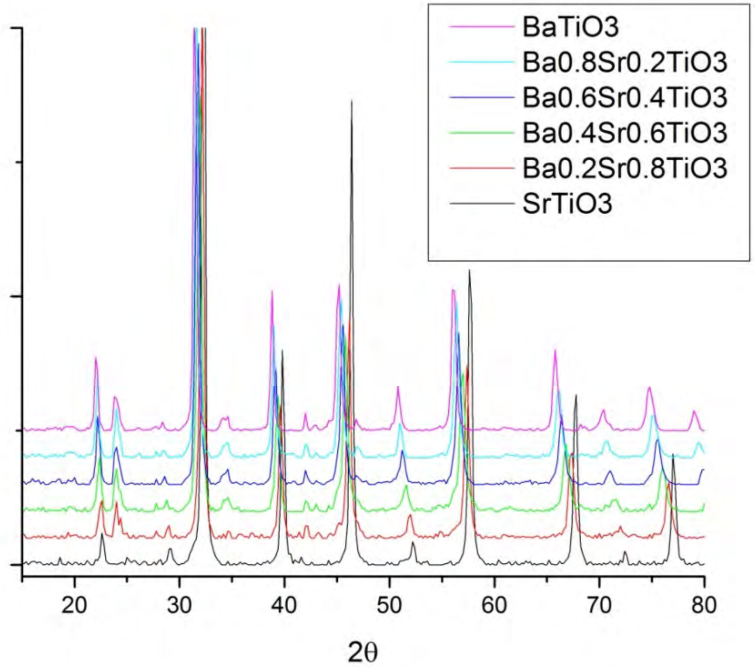
- PDF analysis provides the average separation of the pair of atoms (bond lengths), the coordination number of the pair of atoms and the underlying atomic probability distribution

- Both are in situ techniques and can work with high temperature conditions and a variety of high pressure cells.



Nanocube synthesis



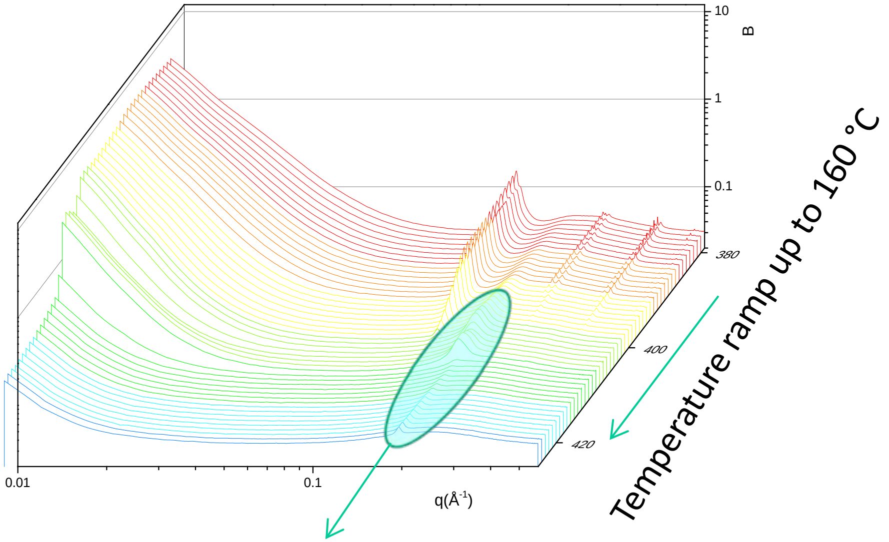


- Above: Powder X-ray diffraction of $Sr_{(1-x)}Ba_xTiO_3$ nanocubes
- Left: $Sr_{0.5}Ba_{0.5}TiO_3$ (SBTO) nanocubes synthesized by microwave hydrothermal synthesis

F. Rabuffetti, P. Stair, and K. R. Poeppelmeier, **2010** *J. Phys. Chem. C*, 114, 11056-11067

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

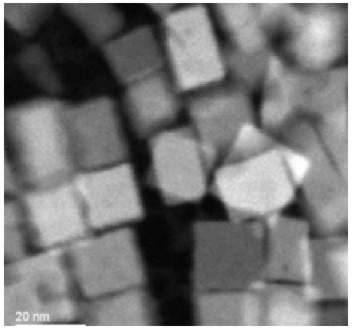
5 % : oleic acid

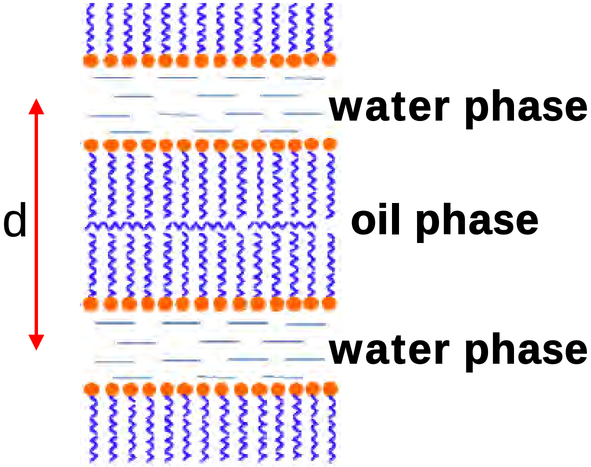


Temperature ramp up to 160 °C

well-defined structure even at high temperature

regular nanocuboid

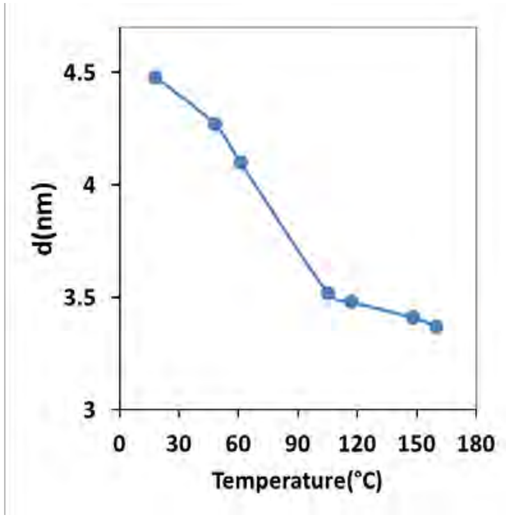




water phase

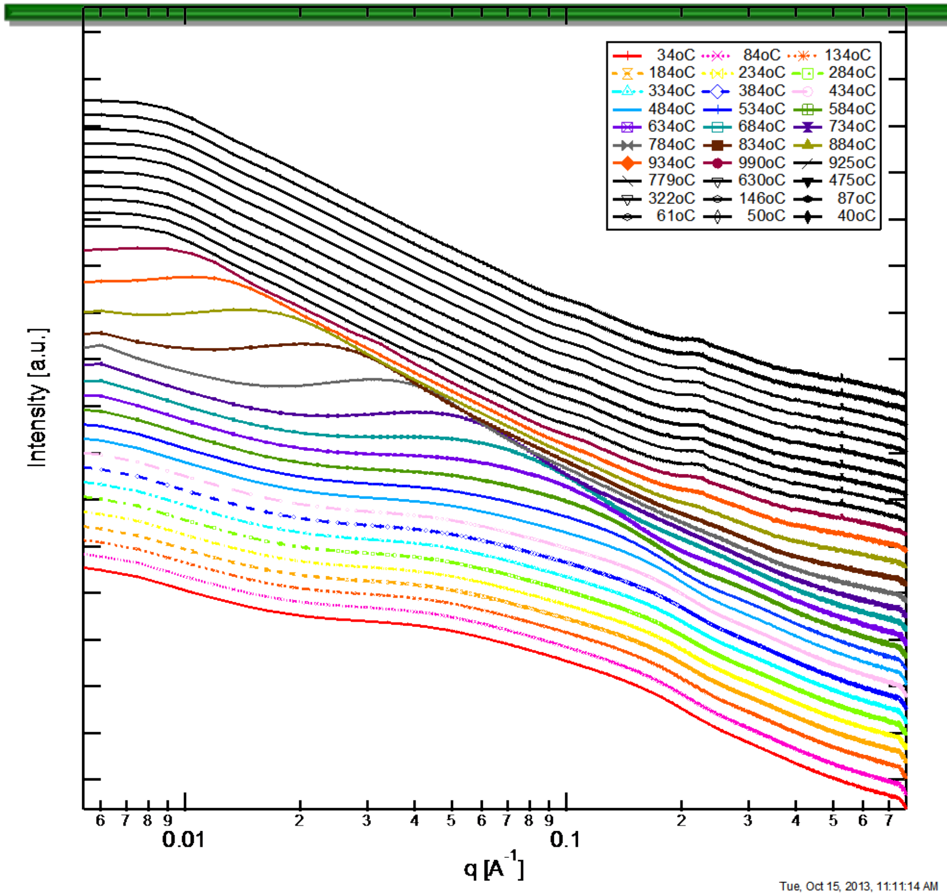
oil phase

water phase



Hu, Linhua; Wang, Chuandao; Lee, Sungsik; Winans, Randall E.; Marks, Laurence D.; Poeppelmeier, Kenneth R. Chemistry of Materials (2013), 25(3), 378-384.

In Situ SAXS Study of Modified ZrO_2 Support



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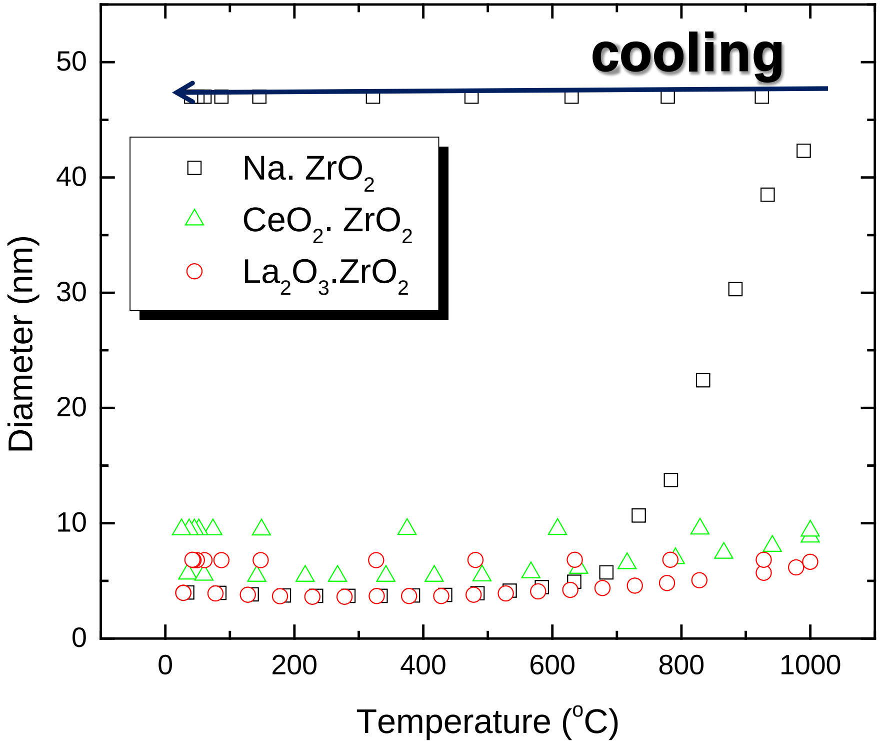
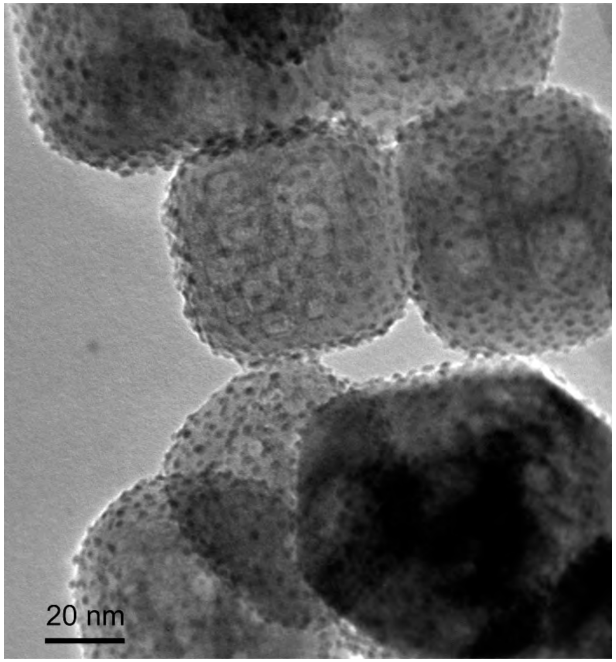
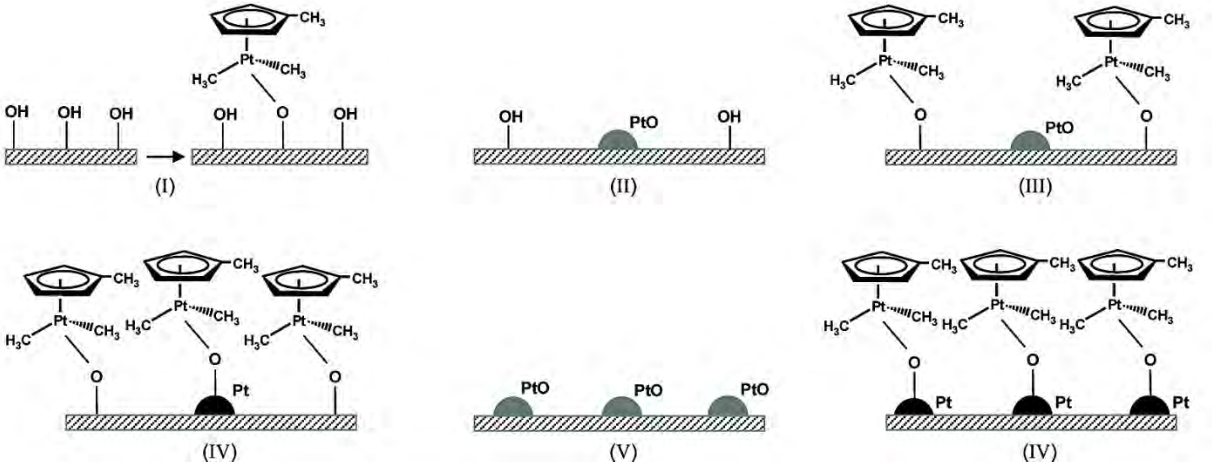


- In situ SAXS confirms that the particle size increases with the temperature increases. After calcination, the particle size remains the same upon cooling.
- Non-Na containing La_2O_3 / CeO_2-ZrO_2 supports show good thermal stability.

T. Li, R. E. Winans, K. R. Poeppelmeier, …..

Platinum by atomic layer deposition





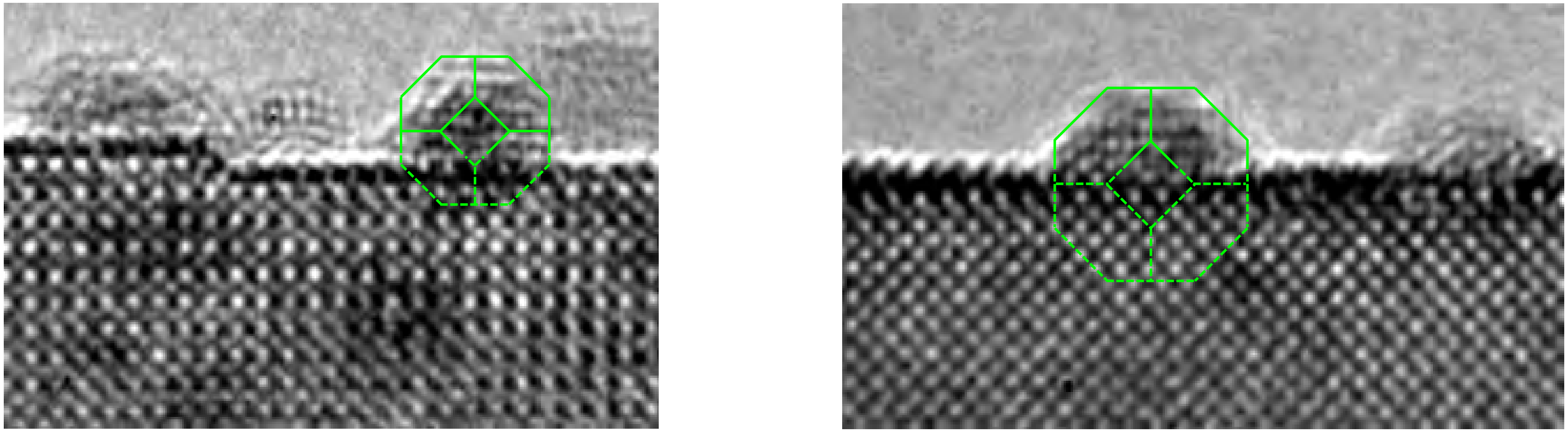
Above: Three cycles of Pt atomic layer deposition (ALD)

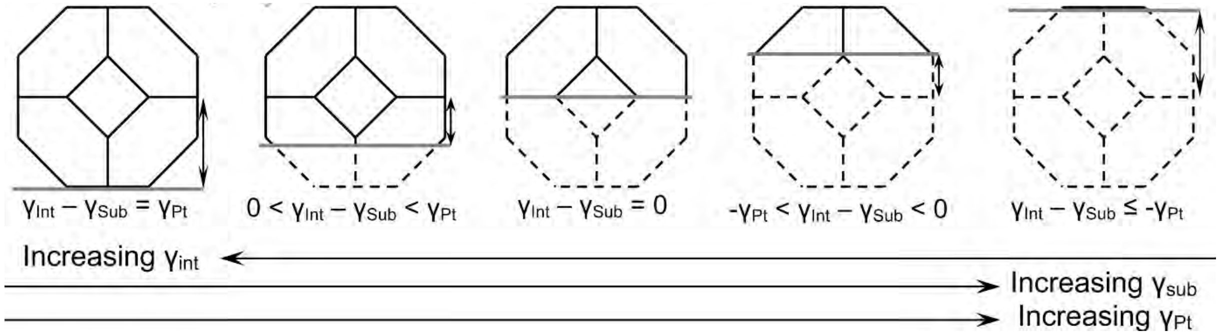
Left: Pt nanoparticles on $SrTiO_3$ nanocubes

- $MeCpPt(Me)_3$ 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 $Sr_{0.5}Ba_{0.5}TiO_3$ (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 $Ba_{0.5}Sr_{0.5}TiO_3$ is less than 50%.

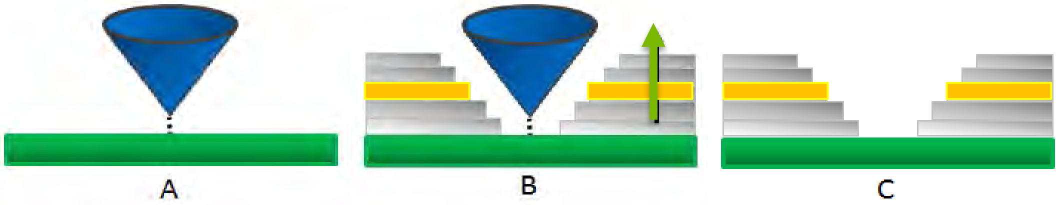
Below: Predicted Pt/substrate wetting as lattice mismatch increases

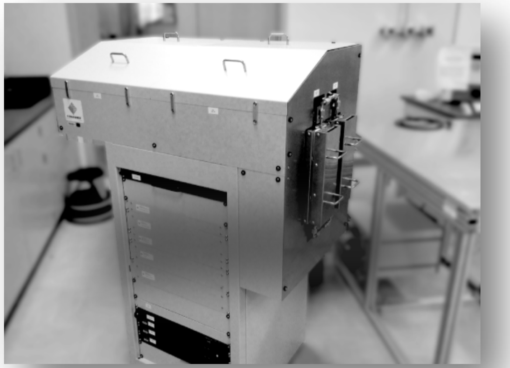
J. A. Enterkin, K. R. Poeppelmeier, and L. D. Marks, **2011**, *Nano Lett.*, 11, 993-997.

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.





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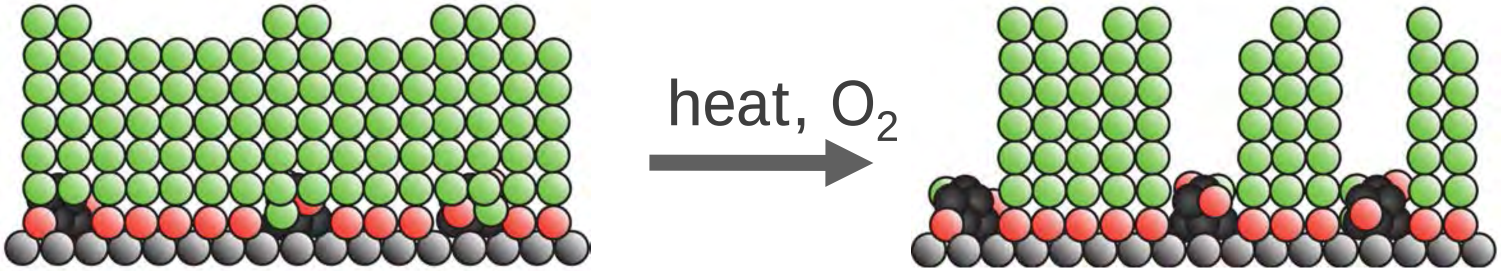
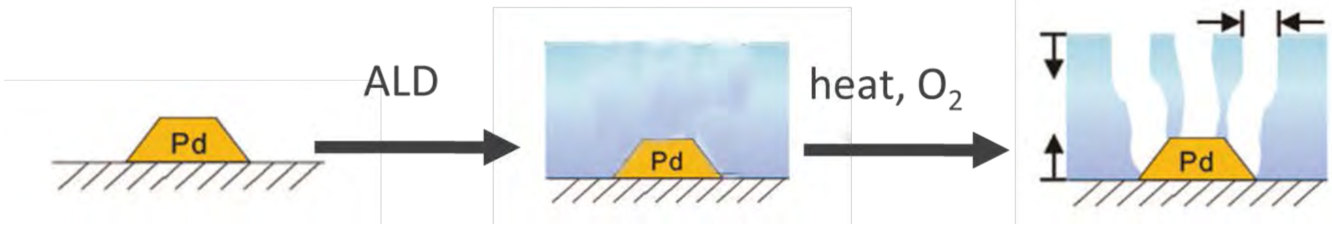
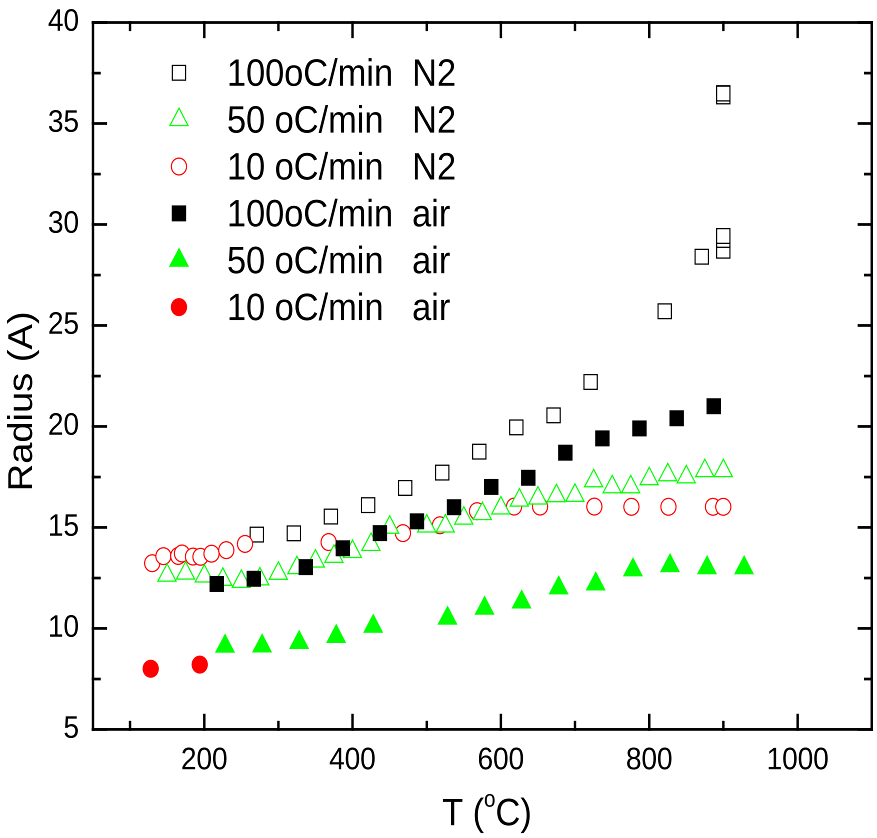
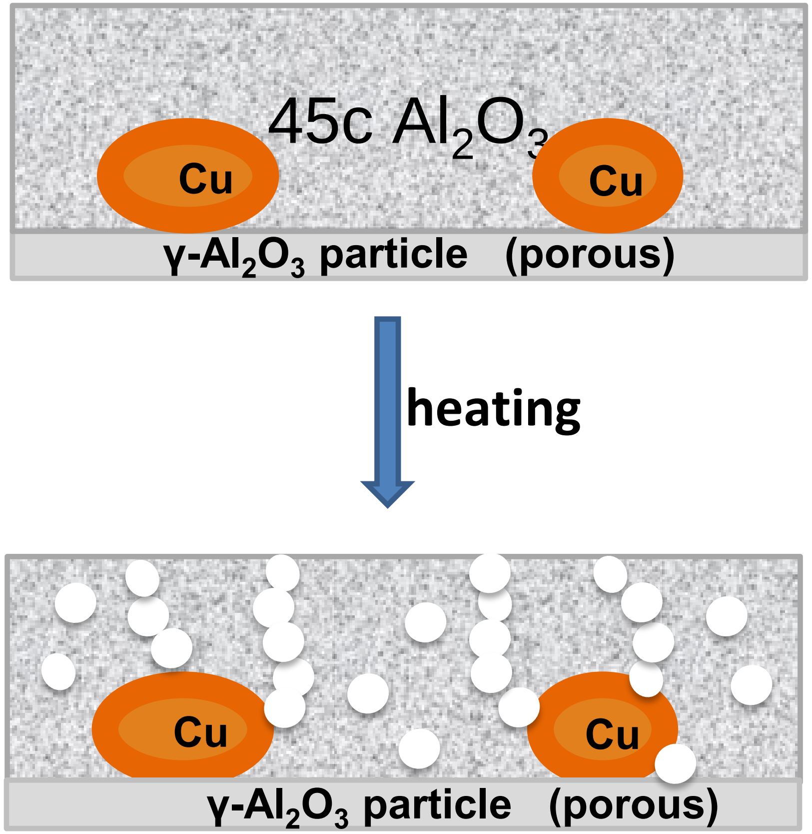




In situ SAXS of Calcination of ALD OverCoating

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.

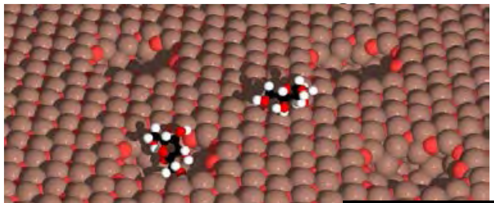
4GSR Strength:

- Small beams can be used to map out nano particles on the surface and how they change with temperature and pressure.

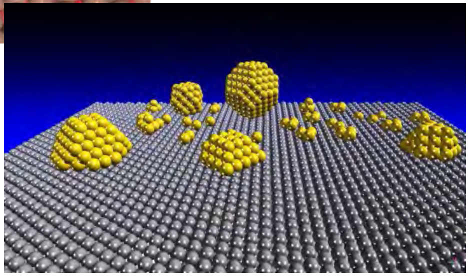
- GISAXS/WAXS can be combined with X-ray, Raman and FTIR spectroscopies.

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

Catalytic surfaces

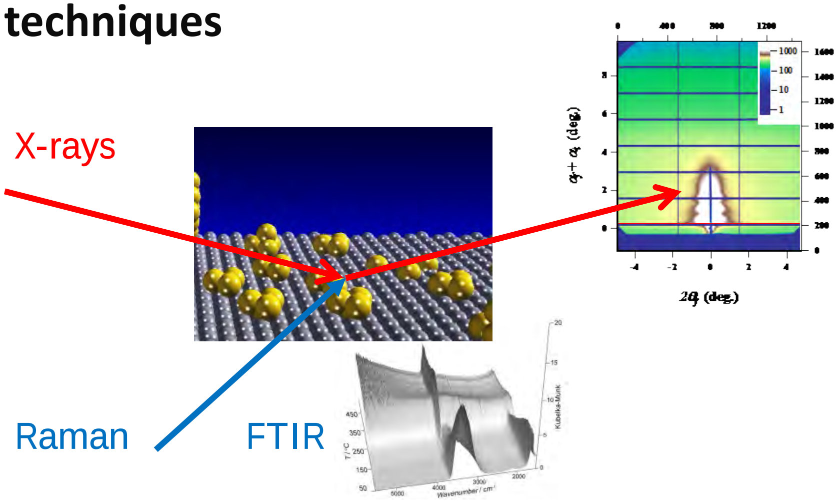


Bowls containing catalysts – size selective



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