Catalysts via First Principles

C.K. Narula, M. Moses-DeBusk, L.F. Allard

Physical Chemistry of Materials, Materials Science and Technology Division

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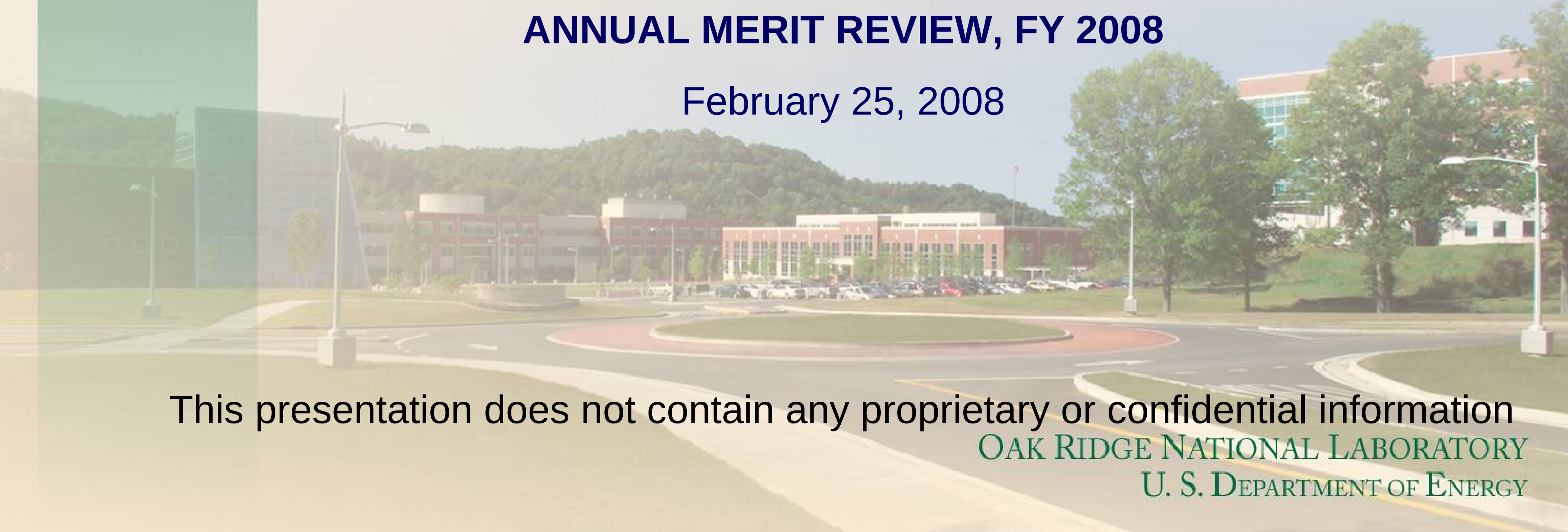

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OBJECTIVES

To assist DOE complete the development of materials solutions that will enable heavy-duty diesel engines to achieve efficiencies of 50% while meeting EPA 2010 emissions standards.

- The project is precursor to "Materials by Design" approach including "Catalyst by Design" and is focusing on designing catalyst systematically rather than by trial and error.
- To demonstrate that we can examine “computationally complex but experimentally simple” catalyst system by first principle theoretical models, experimental studies, and nanostructural characterization iteratively to forecast improvements to obtain optimum catalyst systems
- Identify optimum catalyst sites and develop durable catalyst materials with such sites

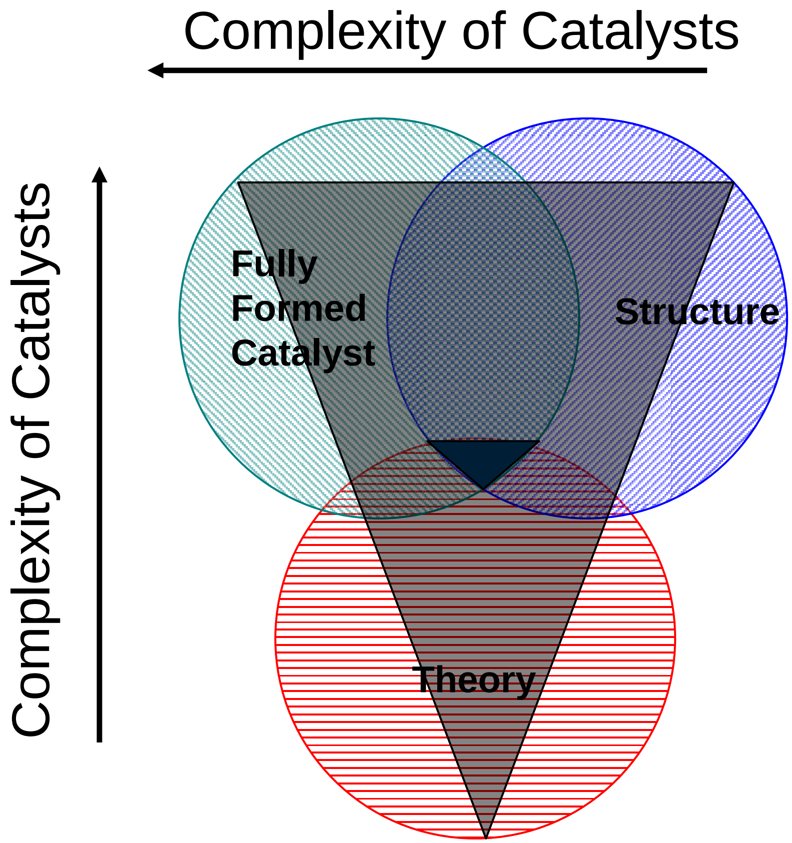
Barriers

- Advances in emission catalysts from trial and error method
  - Although successful, very time consuming
- In recent years, nanostructural characterization of catalysts has been helpful in advancing the state-of-the-research in emission catalysts
  - Provides information on gradual but persistent decrease in catalyst performance (e.g. catalyst coarsening, noble metal migration, changes in support etc.)
  - But, does not offer approaches to alleviate the problem
- Theoretical studies were limited to gas-phase very simple systems
  - Not adequate towards design of complex catalyst system

Can we benefit from the advances in catalyst synthesis, theory, and nanostructural characterization to better understand catalyst sites and reduce the iterations in emission catalyst design?

APPROACH

Supported clusters (Pt, Rh) are integral part of vehicle emission treatment catalysts such as oxidation catalyst, three-way catalyst, lean NO$_x$ traps, diesel particulate filters. We have carried out an extensive study of supported Pt clusters, their oxidation behavior, and their activity as CO, HC, and NO$_x$ oxidation catalyst.

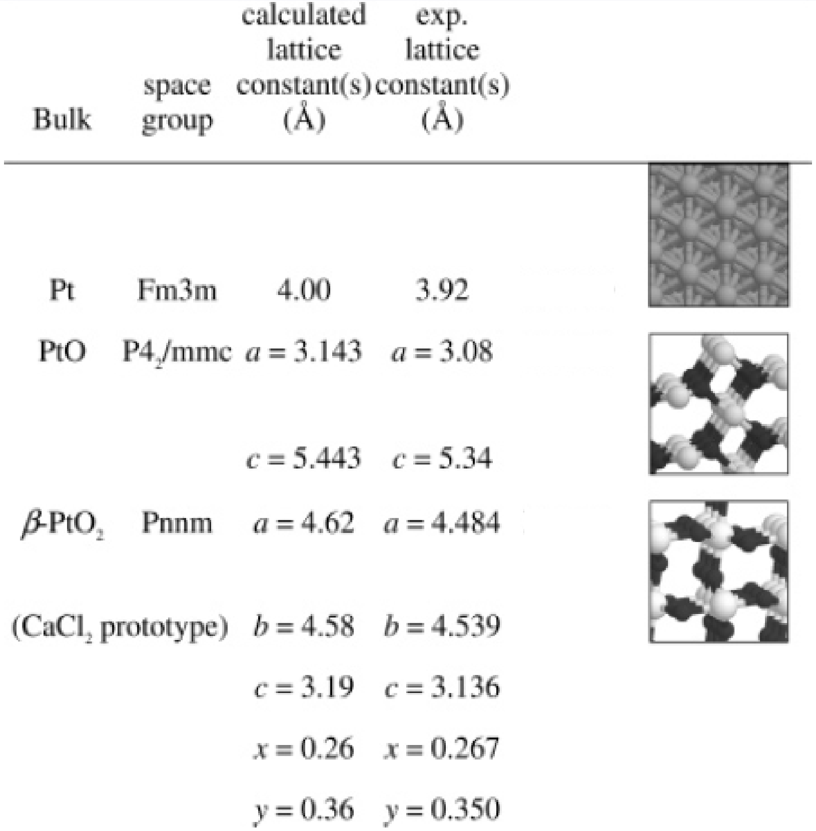


- Theoretical Modeling
  - Density functional theory calculations. Generalized gradient approximation (PW91 functional).
  - Optimization of Pt clusters on oxide supports
  - Interaction of CO, NO$_x$, and HC with catalysts
- Experimental System
  - Synthesis of Pt Nanoclusters on morphologically diverse oxide supports
  - Interaction of CO, NO$_x$, and HC with catalysts
- Structure
  - Nano-structural characterization

This approach can also be extended to zeolite based catalysts

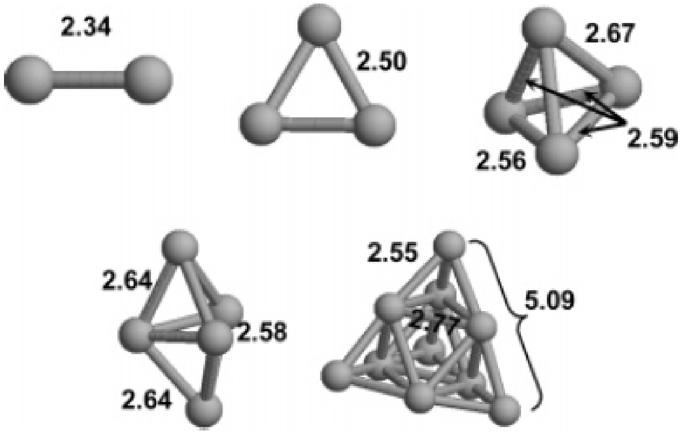
C.K. Narula, “Catalyst by Design”, Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis, New York, 2008 (invited).

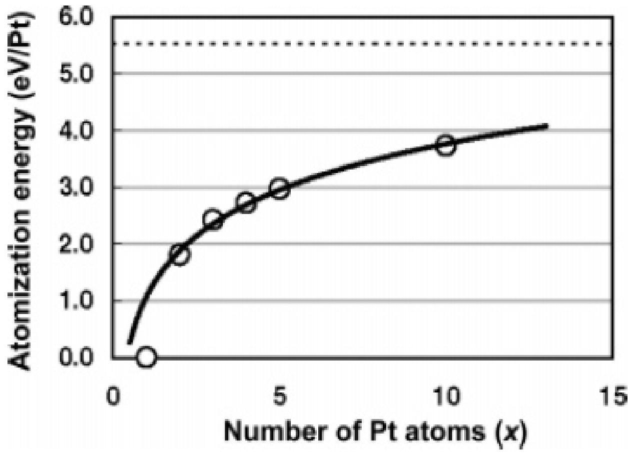
Gas-Phase Studies - Pt$_x$ clusters



Bulk	space group	calculated lattice constant(s) (Å)	exp. lattice constant(s) (Å)
Pt	Fm3m	4.00	3.92
PtO	P4$_2$/mmc	$a = 3.143$	$a = 3.08$
		$c = 5.443$	$c = 5.34$
β-PtO$_2$	Pnnm	$a = 4.62$	$a = 4.484$
(CaCl$_2$ prototype)		$b = 4.58$	$b = 4.539$
		$c = 3.19$	$c = 3.136$
		$x = 0.26$	$x = 0.267$
		$y = 0.36$	$y = 0.350$

[a] Experimental values are included for comparison; x and y refer to the fractional positions of the O atom.

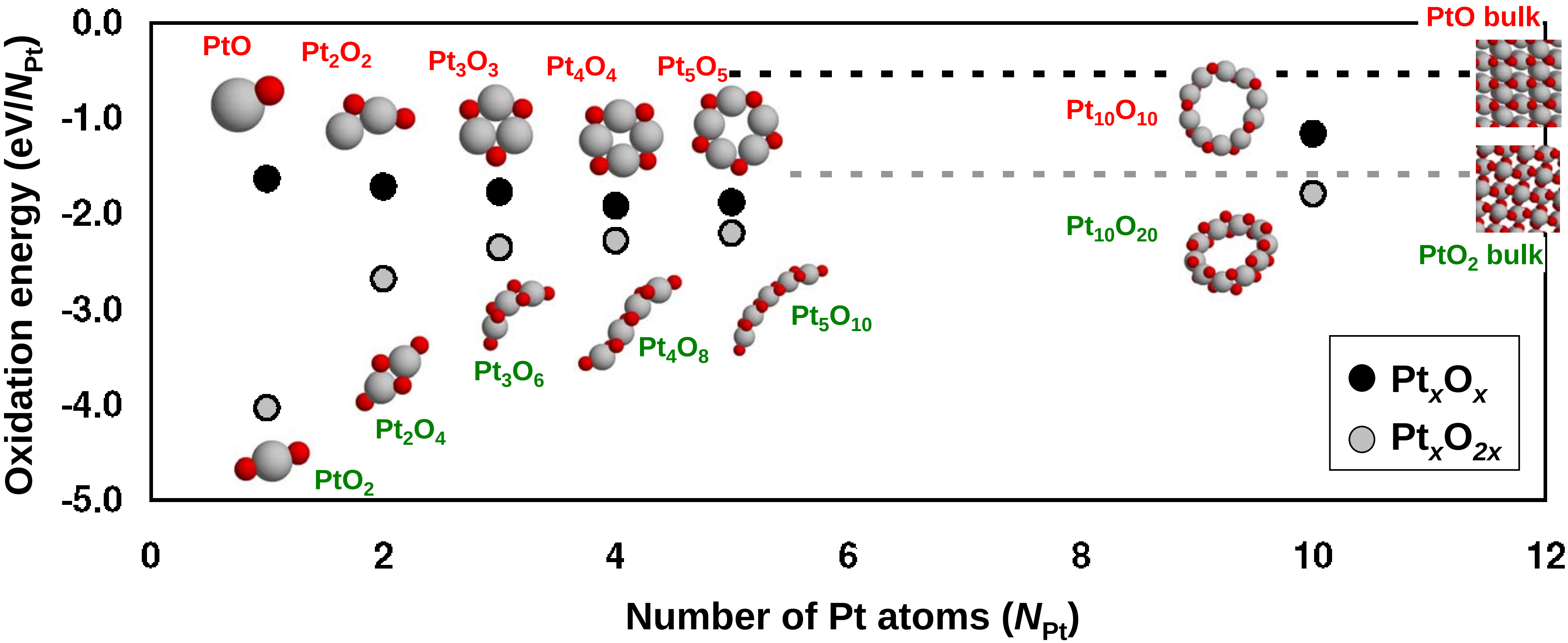




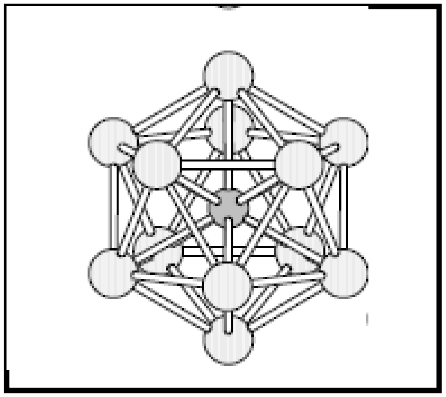
- **3-D structures generally preferred. Optimal structures are shown with some bond distances that match with experimentally observed ones for dimers.**
- **Atomization energy increases monotonically with cluster size i.e. atoms are held together more strongly as the cluster size increases**

Y. Xu, W. A. Shelton, and W. F. Schneider, *Journal of Physical Chemistry A*, 110 (2006) 5839.

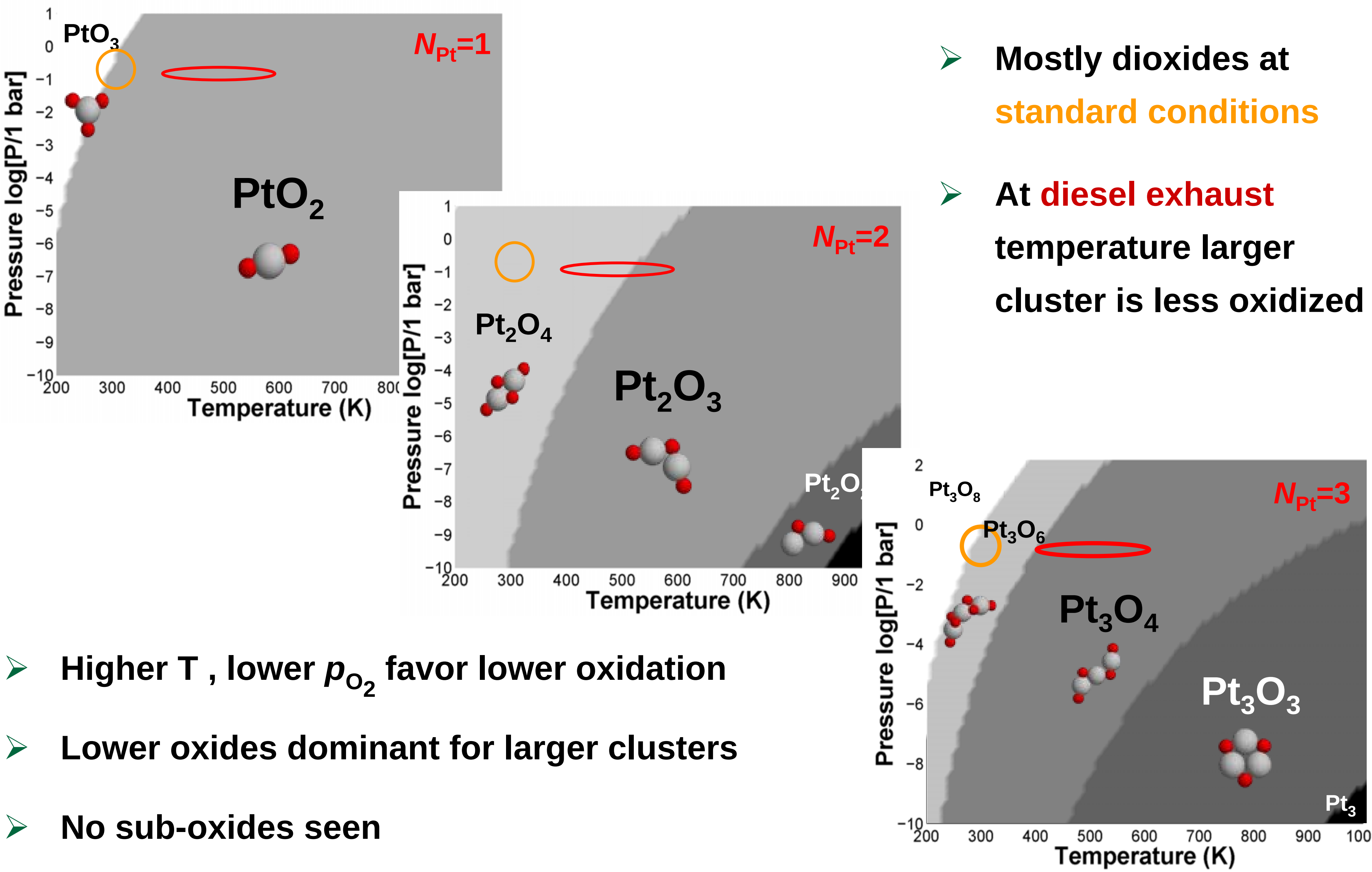
Oxidation of Pt_x clusters



- Oxidation energetically favorable; dioxides preferred to monoxides
- OE varies non-linearly with cluster size; small Pt clusters more prone to oxidation than bulk Pt



(T, p_{O_2}) phase diagrams for Pt_{1-3} clusters



- **Mostly dioxides at standard conditions**
- **At diesel exhaust temperature larger cluster is less oxidized**

- **Higher T , lower p_{O_2} favor lower oxidation**
- **Lower oxides dominant for larger clusters**
- **No sub-oxides seen**

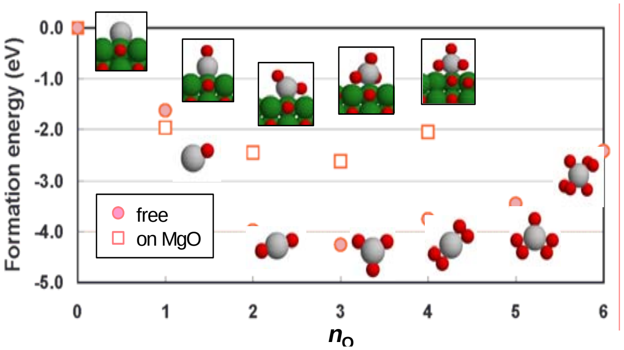
Y. Xu, W.A. Shelton, and W.F. Schneider, *Journal of Physical Chemistry B,* 110 (2006) 16591.

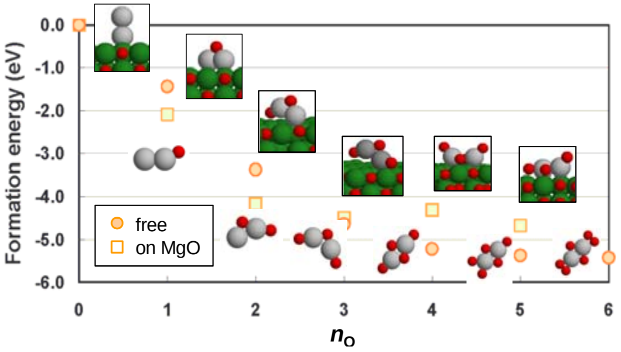
Modeling Pt/γ-Al_2O_3?

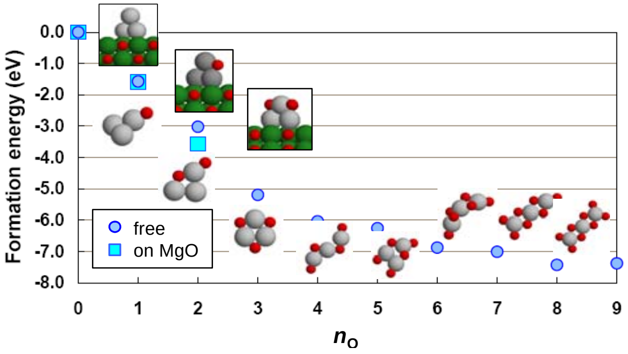
- Still disagreement on the bulk structure of γ–Al_2O_3. Poor crystallinity prevents structure optimization.
  - Defect-spinel lattice structure with one cation defect per Al_8O_{12} units to maintain charge balance
  - Debate on ratio of T_d and O_h sites which cation defects occupy
  - Not resolved by TEM, XRD, NMR
- Cubic $Fd\bar{3}m$ and tetragonal $I4_1/amd$ cells, restricting Al to spinel positions, results in about 1.47 billion configurations.
  - Paglia, G.; et al., Physical Review B 71 (2005) 224115
- Spinel-based structural models represent γ–Al_2O_3 structure better than non-spinel based models and can reproduce lattice parameters and other structural features
  - Nelson, A.E.; J. Phys. Chem. B, 110 (2006) 2310
- Theoretical modeling of supported catalysts on γ–Al_2O_3 has been carried out but the results remain suspect till there is agreement on the structure of γ–Al_2O_3

What happens on supported clusters?

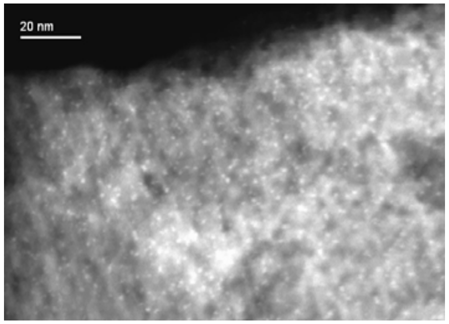
- Magnesia (MgO) is a model basic oxide surface that is relatively inert toward many adsorbates and its (100) facet is thermodynamically the most stable.
- The oxides of the Pt dimer and trimer exhibit very similar formation energies on MgO(100) compared to those of the free Pt2 and Pt3 clusters, while Pt1Oy clusters have markedly lower formation energies.
- The morphologies of the various Pt oxide clusters on MgO(100) closely resemble their gas-phase counterparts.
- These results show that the oxidation energetics and morphologies of the free Pt nanoclusters by and large are preserved on a relatively inert surface

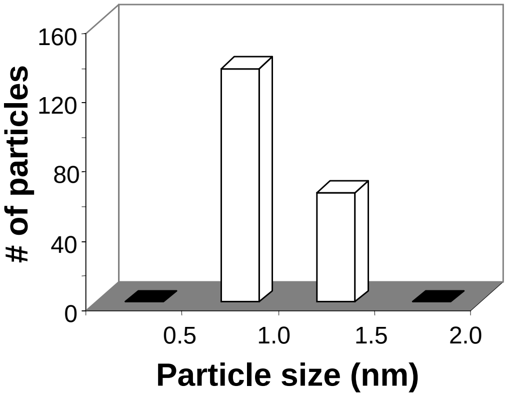


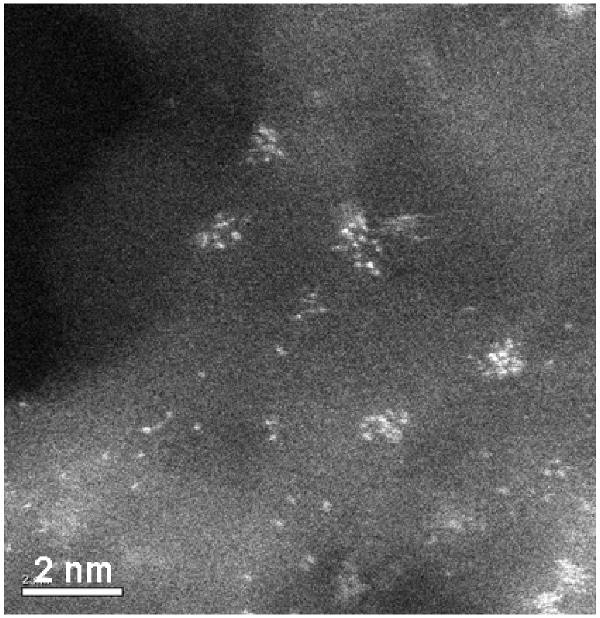




Oxidation Catalyst – Pt/**γ**-Al_2O_3



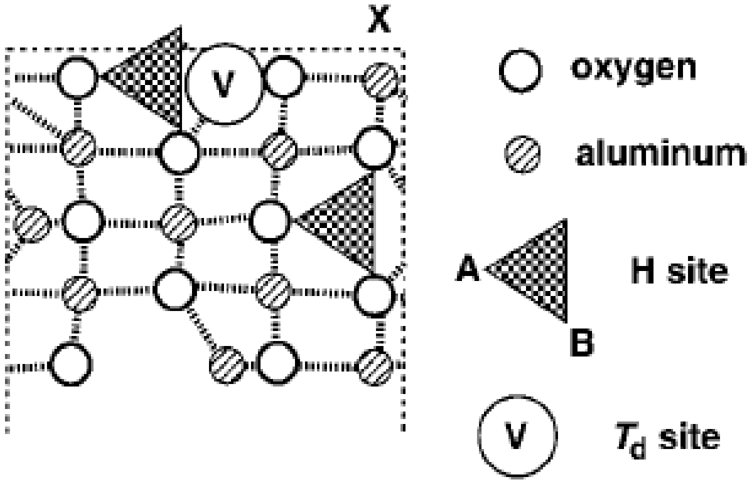


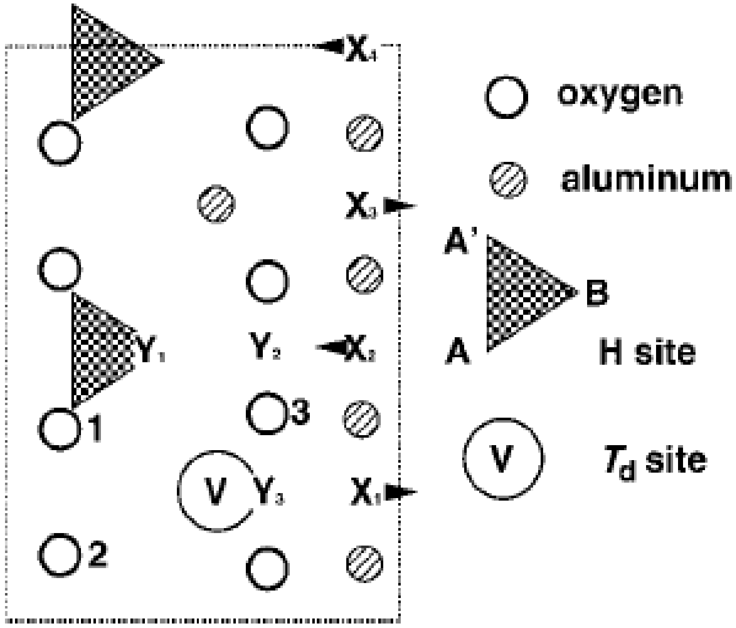


- STEM analysis shows that platinum particle size ranges from 0.6-1.4 nm and the distribution is centered at 0.9 nm
  - A common observation reported in literature
  - Recent EXFAS & XANES study suggest thermally mediated interaction between Pt and support resulting in Pt-Pt bond contraction (JACS, 128 (2006) 12068)
- HAADF-STEM mode clearly shows that the atomic make-up of these platinum nano-clusters involves on average between 10-20 atoms
- Single atoms and 2-3 atom clusters can also be observed
  - Only a 3-atom cluster has been observed previously
- The directly measured Pt-Pt bond distances are 2.35, 2.54, 2.7, and 3.2Å for 2-atom clusters, and 2.3, 2.8 Å for 3-atom clusters.

C.K. Narula, L.F. Allard, D.A. Blom, M.J. Moses, W. Shelton, W. Schneider, Y. Xu, SAE-2007-01-1018 (invited).

Pt-Clusters on alumina





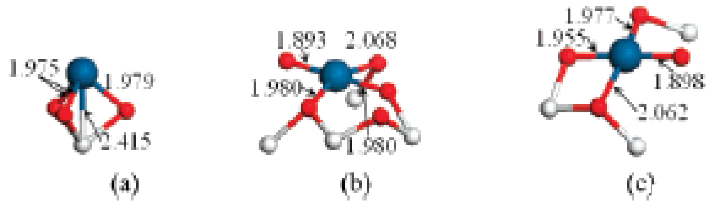
This structure has Pt-Pt bond distances of 2.6, 2.6, and 3.3 Å. If this structure is capped with –OH, the bond distances are 2.6, 3.1, 3.6 Å which are in good agreement with experimental values.

This structure has Pt-Pt bond distances of 2.59, 2.65, and 2.73 Å which do not agree with experimental values of are <u>2.7, 3.2, 3.4 Å.</u>

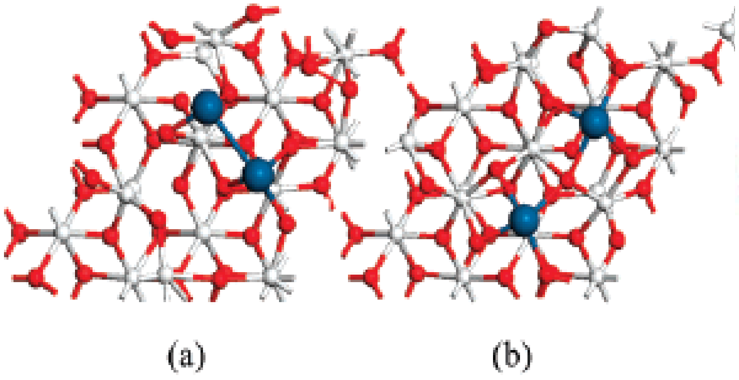
Oversimplified structure of γ-Al_2O_3 employed in these models

Sohlberg, K. et al., ChemPhysChem, 2004, 5, 1893

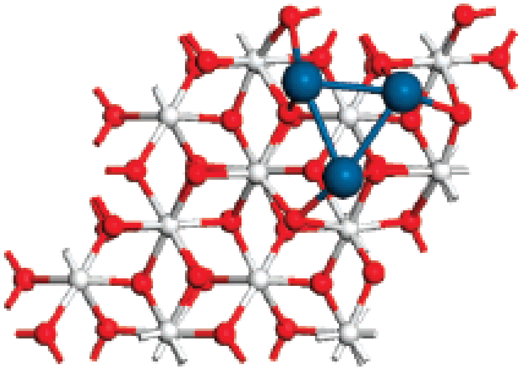
Pt/α-Al_2O_3



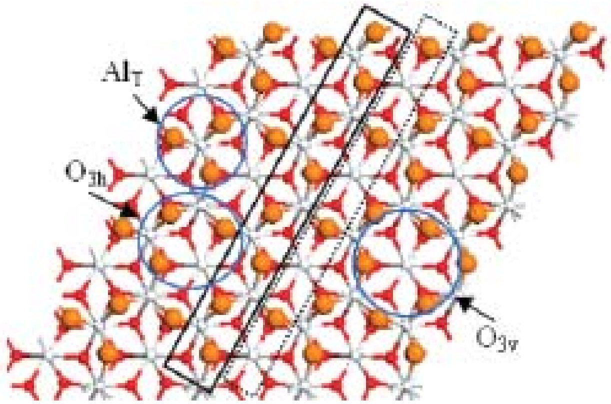
a. Al_T site b. O_{3h} c. O_{3v}



a. Al_T-Al_T b. O_3-O_3



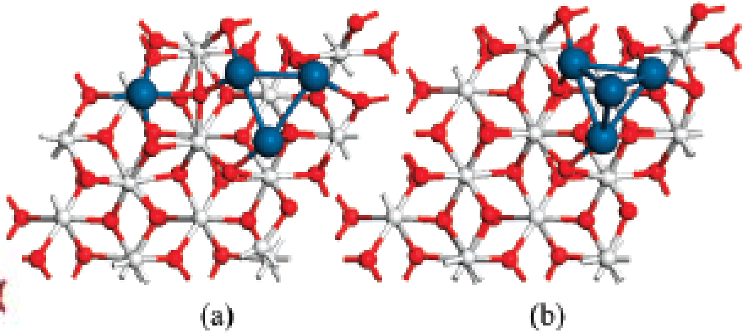
Pt_3 equilateral triangle adsorption structure



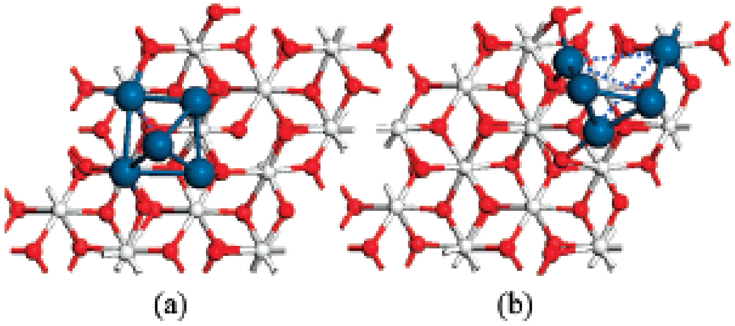
Al_T = 2 zigzag O and 1 linear O attached to single Al

O_{3h} = 2 zigzag O and 1 linear O attached to 2 Al

O_{3V} = 1 linear and 2 zigzag O from adjacent row



a. Planar b. tetrahedron



a. Square pyramid b. triangular bipyramid

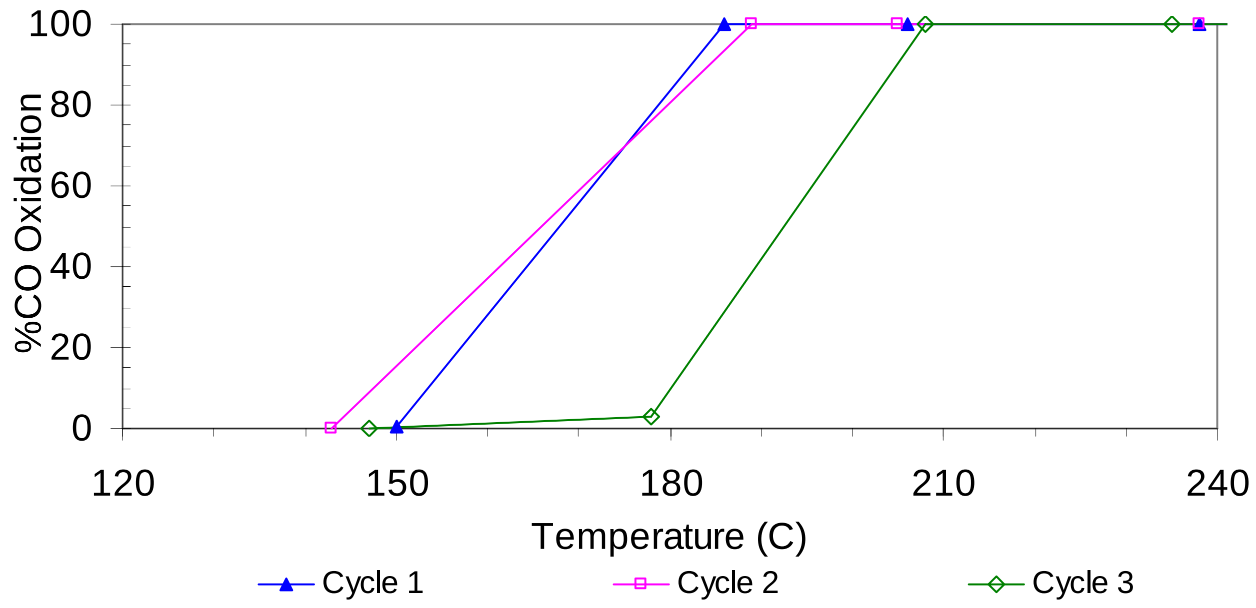
- **O_3 site strongly preferred**
- **Clusters larger than 3 prefer to interact with substrate via its triangular face**
- **Adhesion declines with increase in size**

Balakrishnan et al, J. Phys. Chem. C, 111(2007)13786

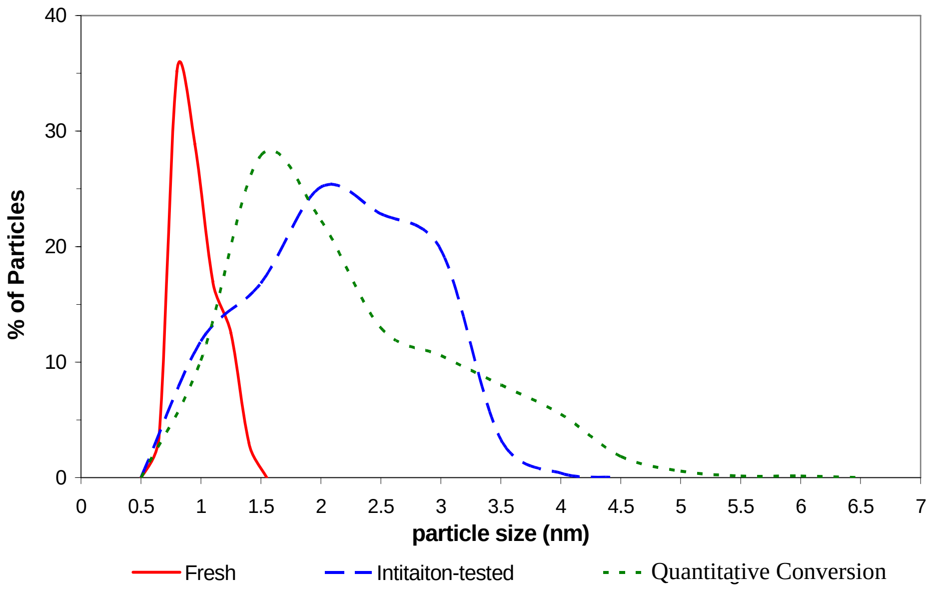
Pt-Pt bond distances

- Since our measured Pt-Pt bond distances are not from 3-dimensional images, we need to be very careful in assigning structures
- The directly measured Pt-Pt bond distances are 2.35, 2.54, 2.7, and 3.2Å for 2-atom clusters.
  - Gas phase Pt-Pt dimer 2.34 Å
  - Gas phase Pt_2O_4 cluster 2.77 Å
  - Pt dimer/α-Al_2O_3 2.723 Å
- The directly measured Pt-Pt bond distances for 3-atom clusters are 2.3, 2.8 Å. These are different from previously reported values of 2.7, 3.2, 3.4 Å
  - Gas phase Pt-Pt trimer 2.5 Å
  - Gas phase Pt_3O_6 cluster 2.75 Å
  - Pt trimer/α-Al_2O_3 2.696 Å

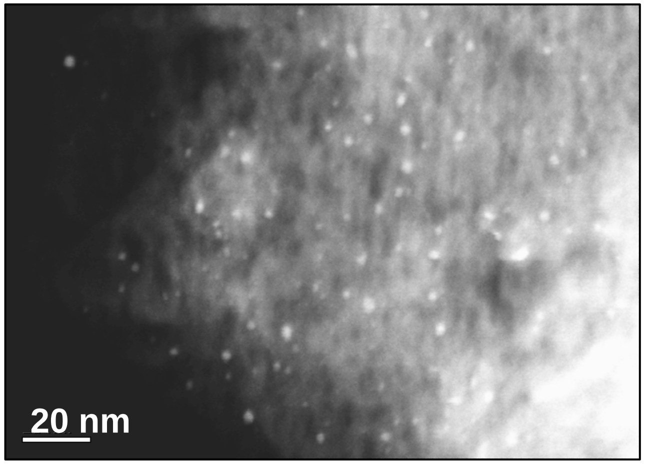
CO-Oxidation

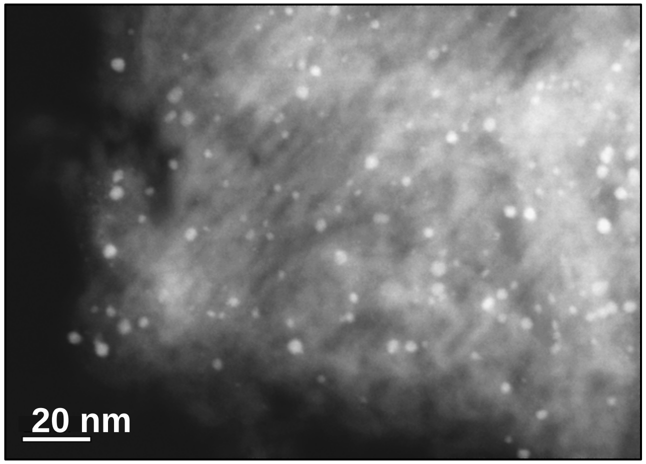


Pt-Particles post CO-Oxidation



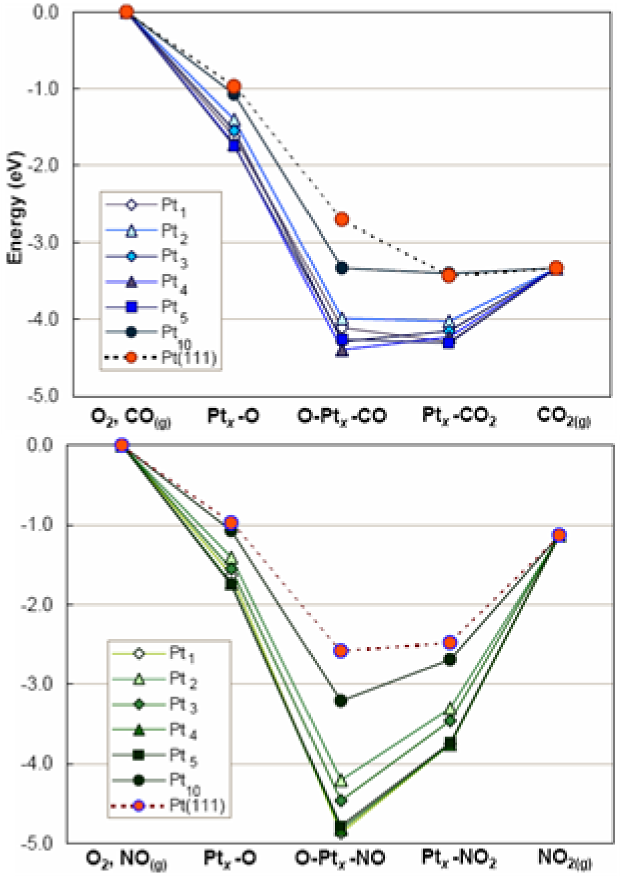
- ➢Pt particles start to grow even after exposure to CO-oxidation initiation conditions only
- ➢Is Pt-sintering effect real?

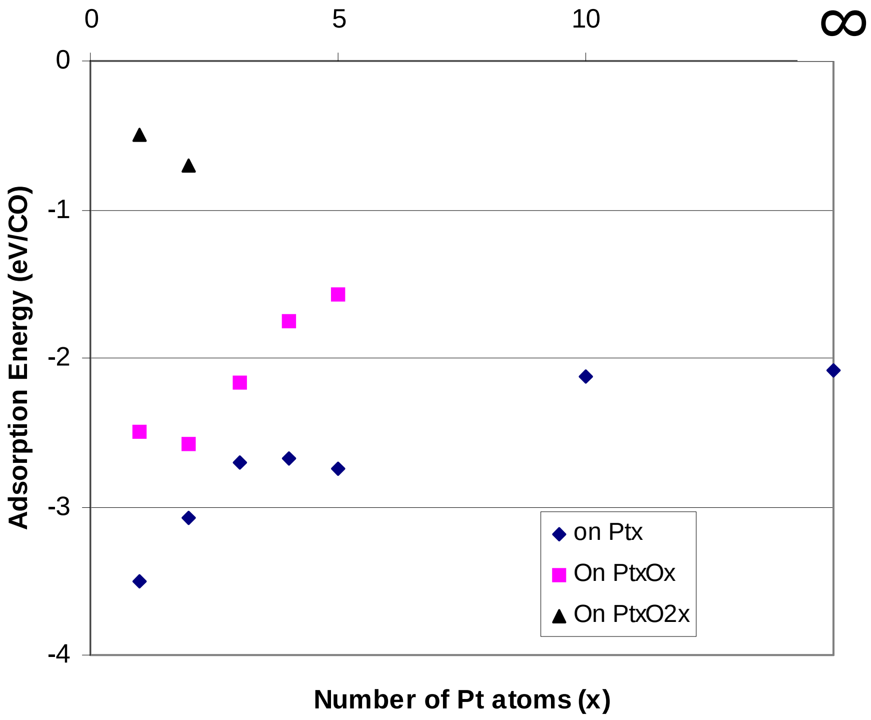




STEM images after CO oxidation were stopped at initiation (Top) and after 3 cycles of quantitative conversion (bottom)

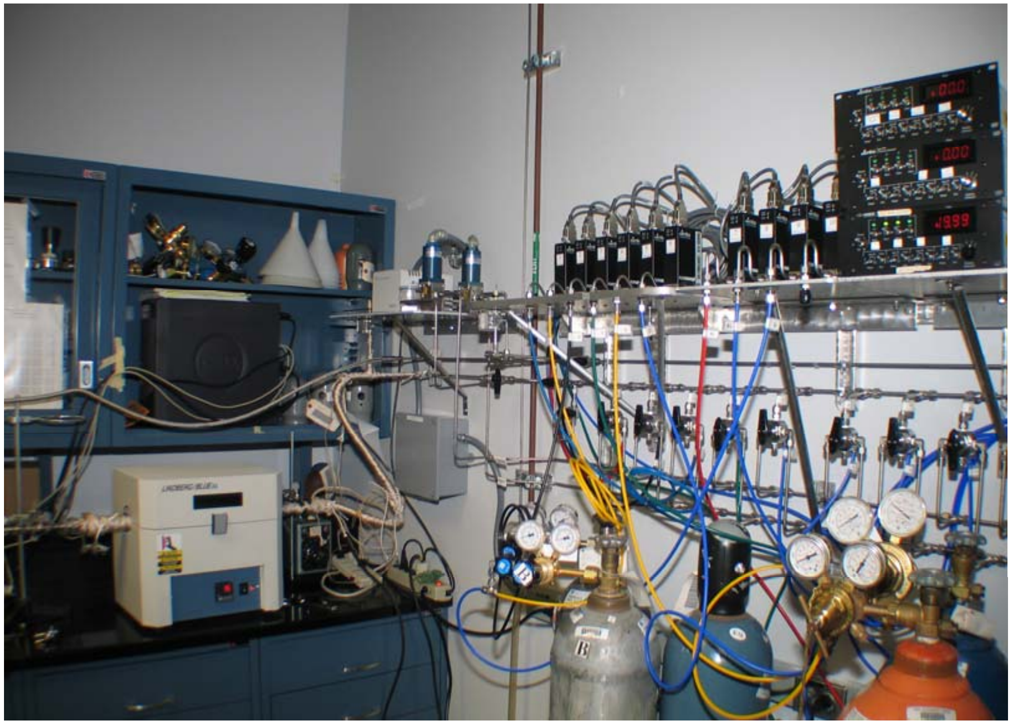
Reaction Energy Profiles





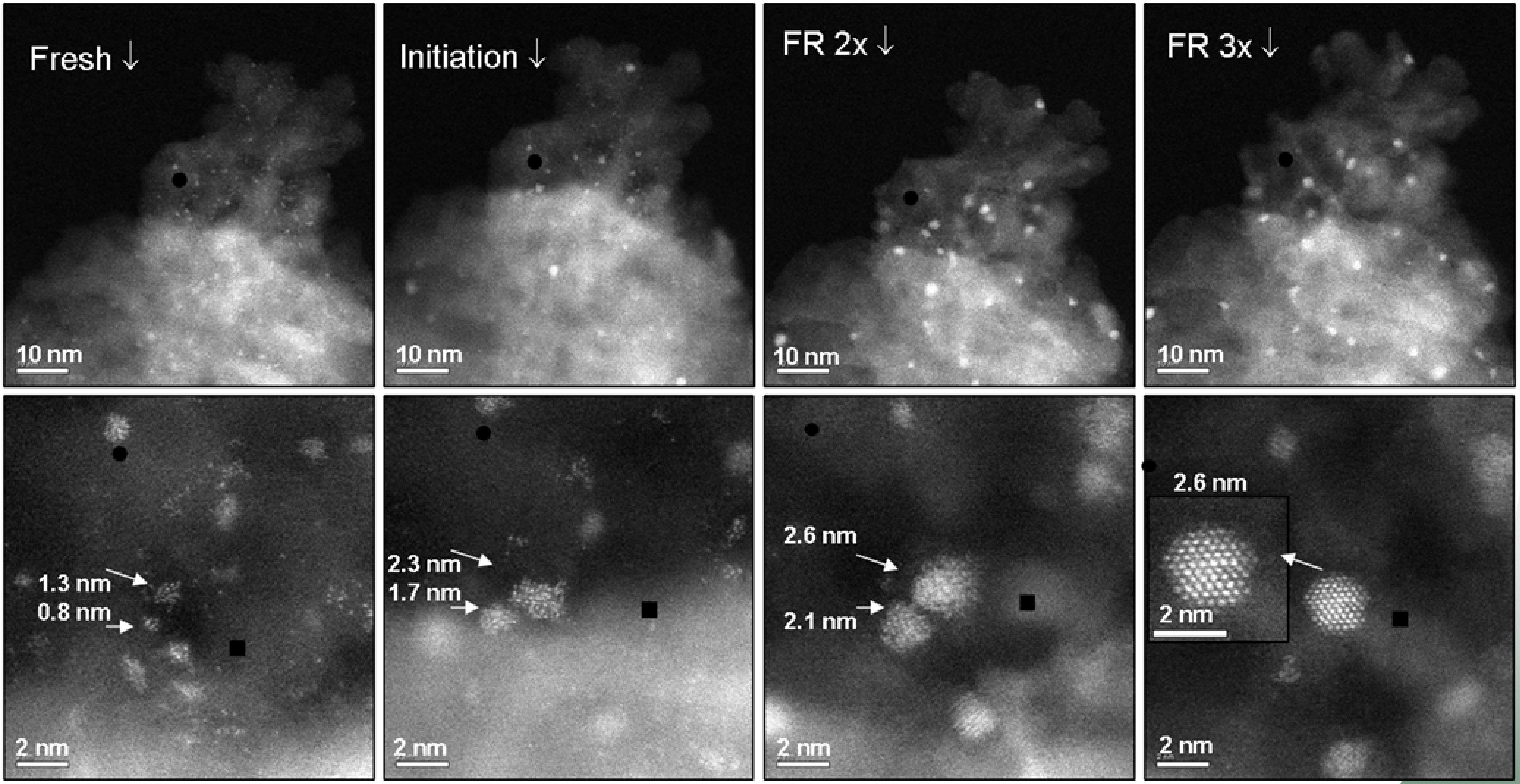
The reaction energy profiles for CO + ½O_2 → CO_2 and NO + ½O_2 → NO_2 on Ptx (x = 1-5 and 10). The profiles on the bulk Pt surface (represented by the Pt(111) surface) are included. As particle size increases, the adsorption energies trend toward the Pt(111) level That the adsorption of these species is enhanced compared to Pt(111) means that the energy profiles of CO and NO oxidation on Ptx also differ from their bulk-surface counterparts. CO oxidation on the bulk Pt surface is exothermic every step along the reaction path, but because of the enhanced adsorption of CO, there is a minimum in energy when CO adsorbs on the clusters. The same phenomenon can be seen in NO oxidation. This indicates that the ability of the Pt clusters to catalyze CO and NO oxidation may be inhibited by the strong adsorption of CO and NO.

Ex-Situ Reactor



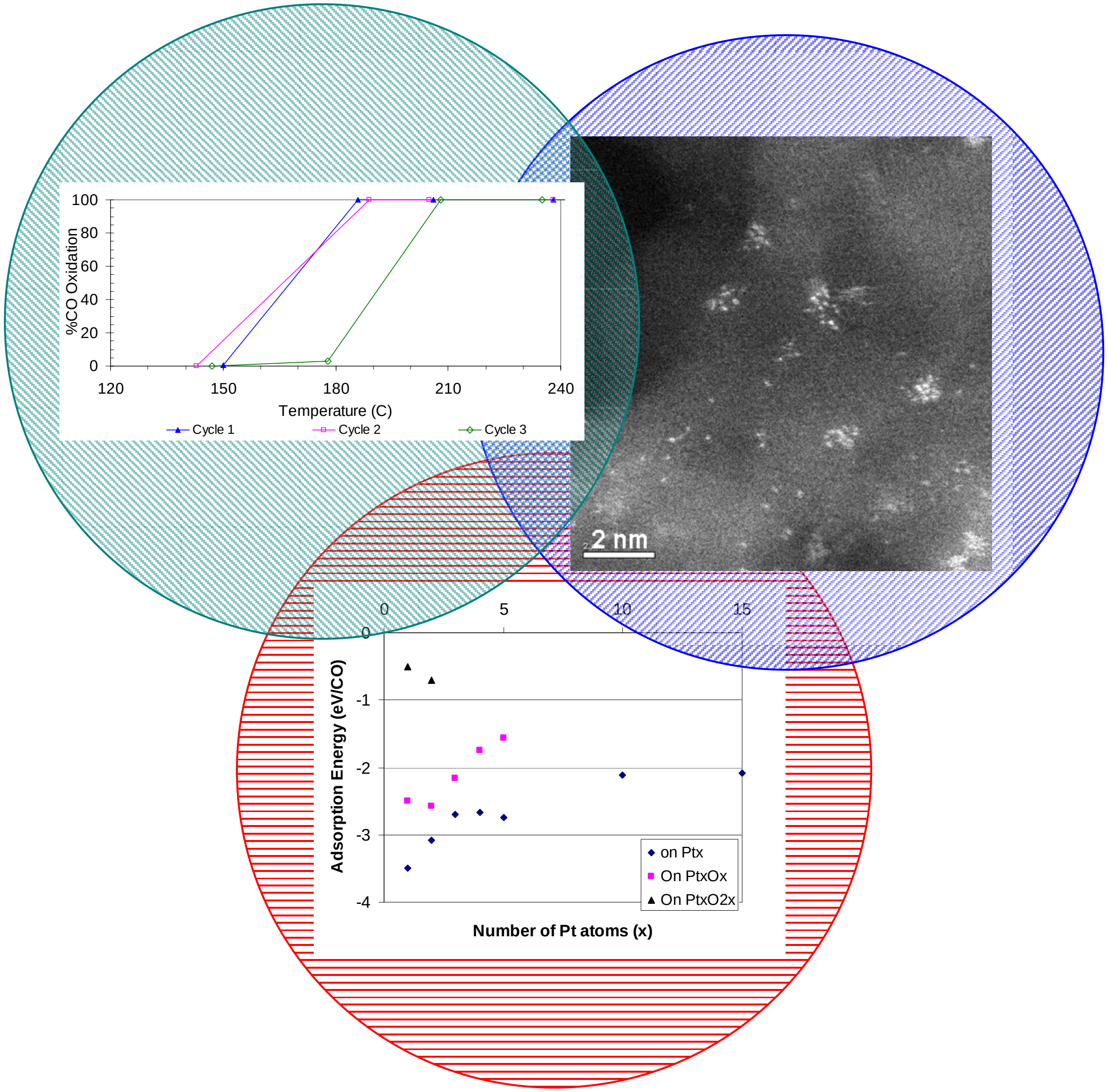
- ➢**Rapid Screening Method for Monitoring Nano-structural Changes**
- ➢**The catalyst was deposited on a TEM grid and placed in our *ex-situ* reactor where it was exposed to three different conditions 1) CO oxidation initiation, 2) quantitative CO conversion (2 cycles) , and 3) quantitative CO conversion (3rd cycle).**

ACEM HAADF-STEM images of the exact same sample area after exposure to CO-Oxidation conditions

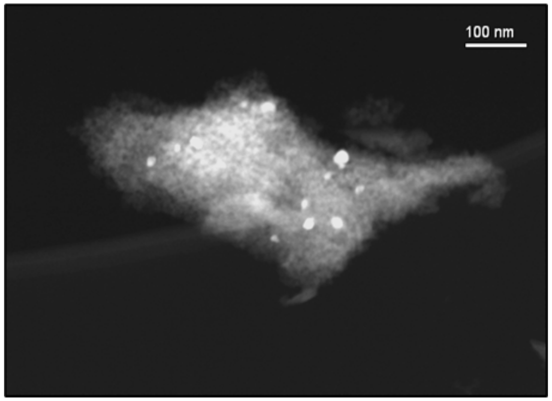


C.K. Narula, L.F. Allard, D.A. Blom, M. Moses-DeBusk, SAE-2008-01-0416.

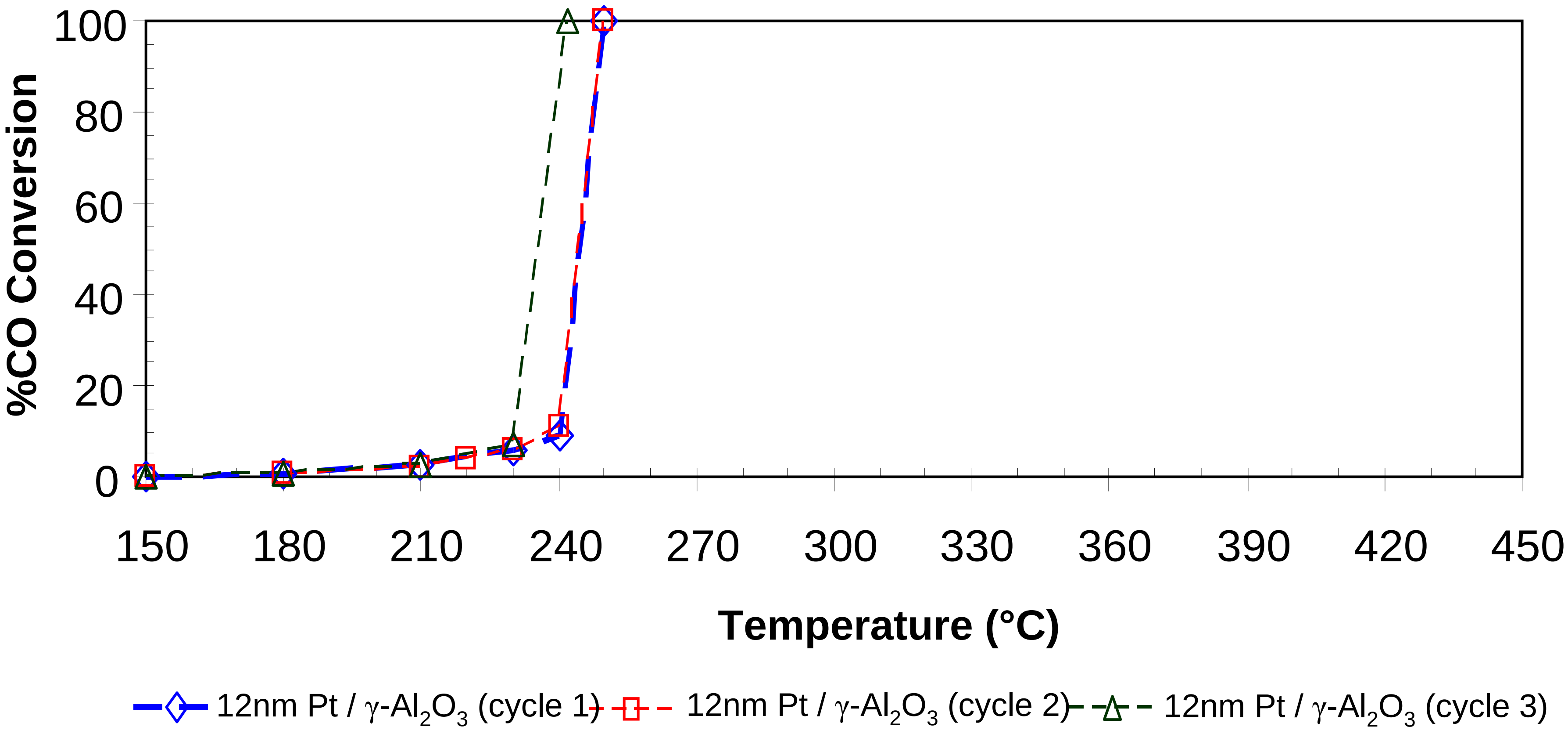
Catalyst by Design…



What happens when fresh catalyst contains larger particles?

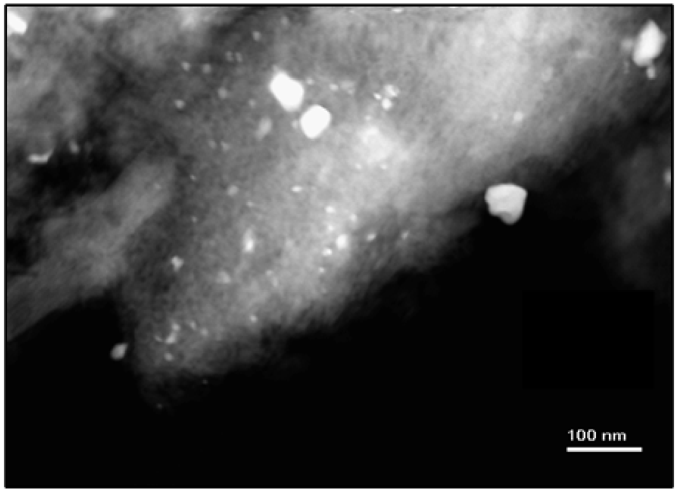


STEM analysis shows that platinum particle size distribution is centered at ~12 nm with some large particles in 20-40 nm range

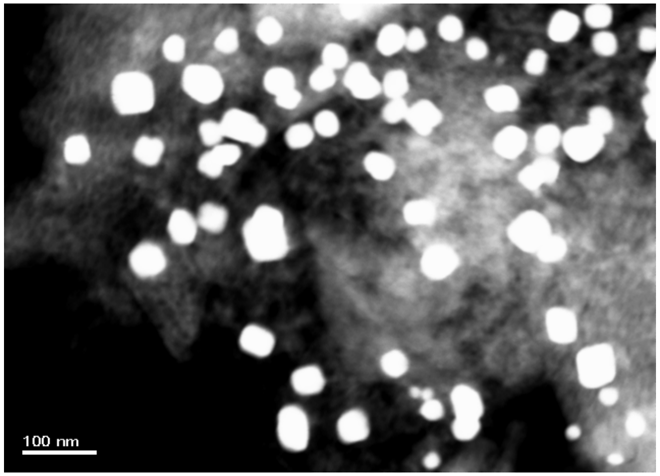


What happens when fresh catalyst contains larger particles?

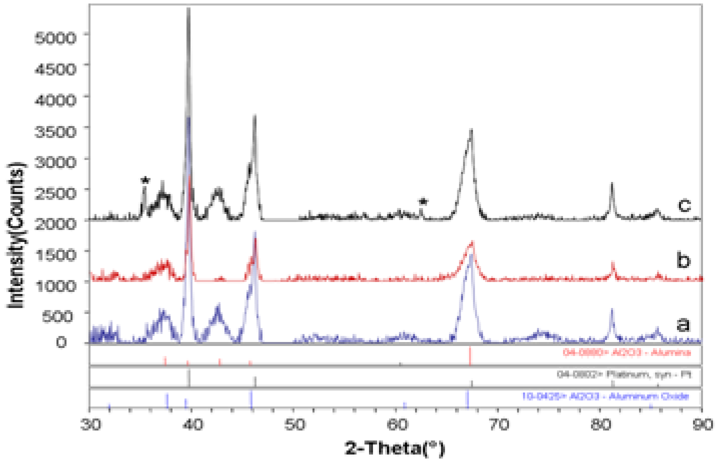
$Pt/\gamma\text{-}Al_2O_3$



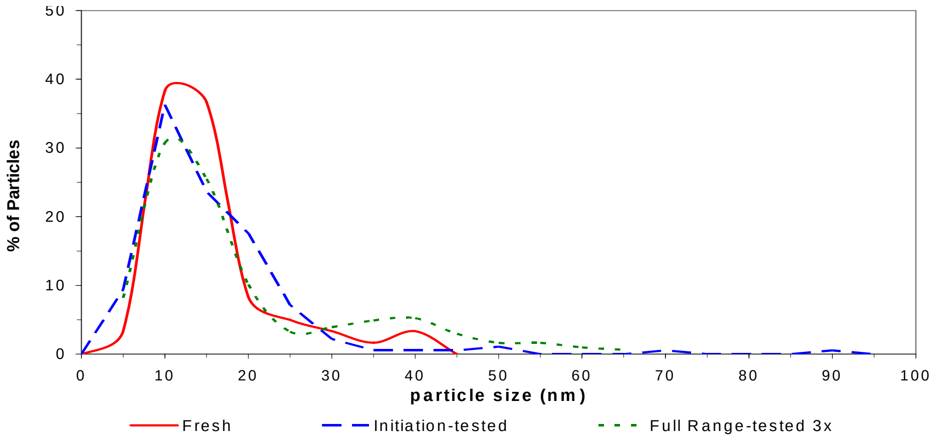
Fresh



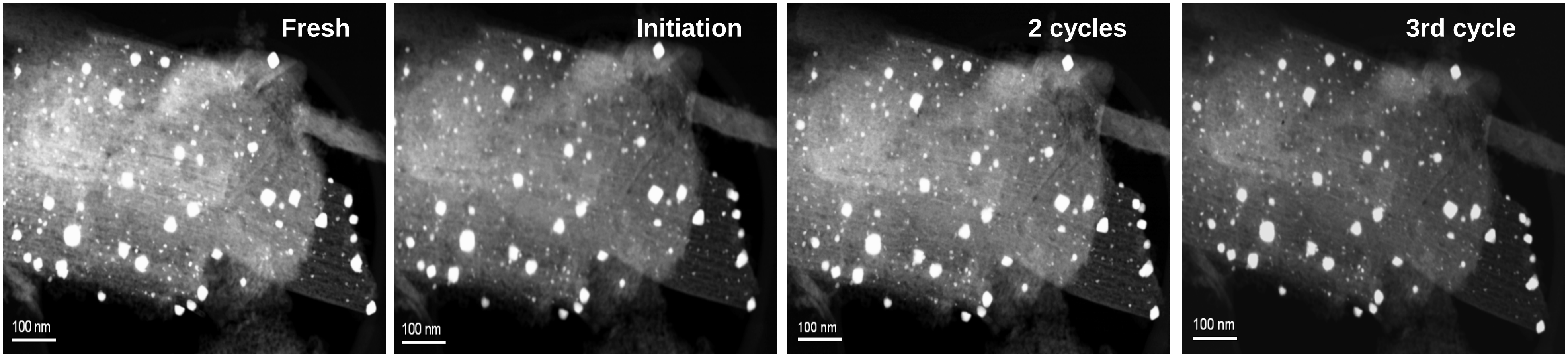
After 3 cycles of CO oxidation

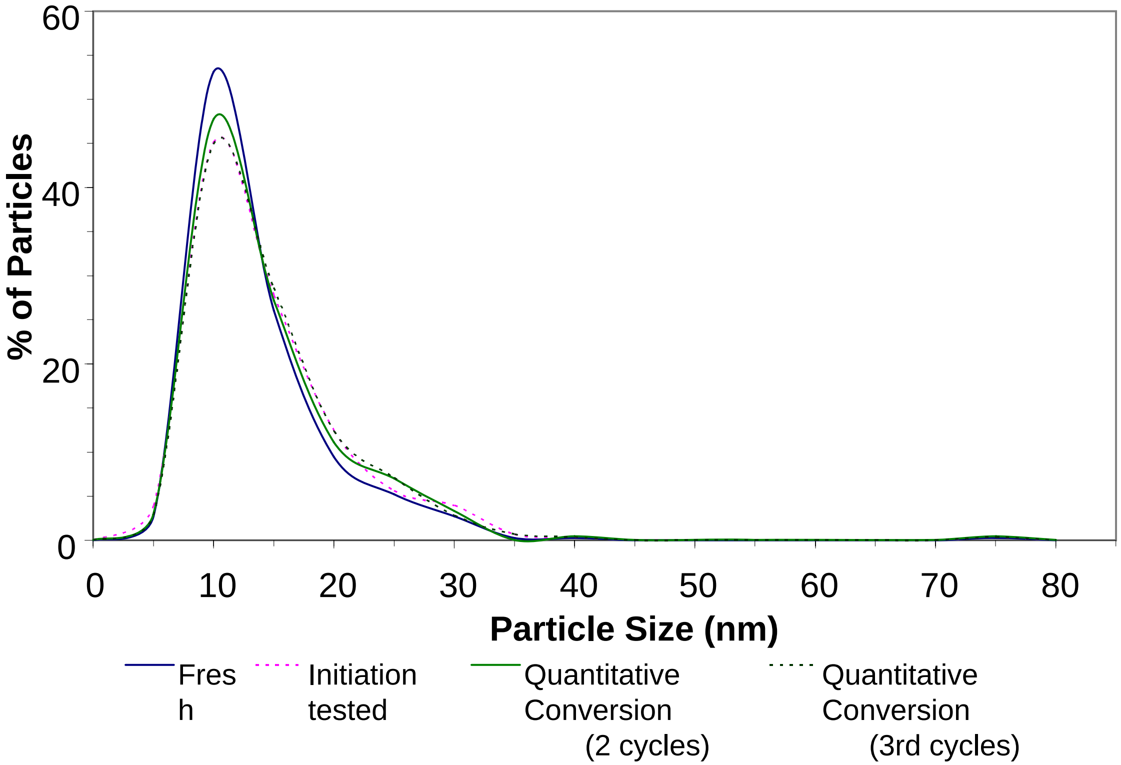


X-ray diffraction pattern of fresh 2% $Pt/\gamma\text{-}A_2O_3$ annealed at 650 °C (a) fresh and after CO oxidation tests: CO conversion (b) initiation (8.1%) (c) full range (3 cycles at 100%).* denotes a sample holder impurity.

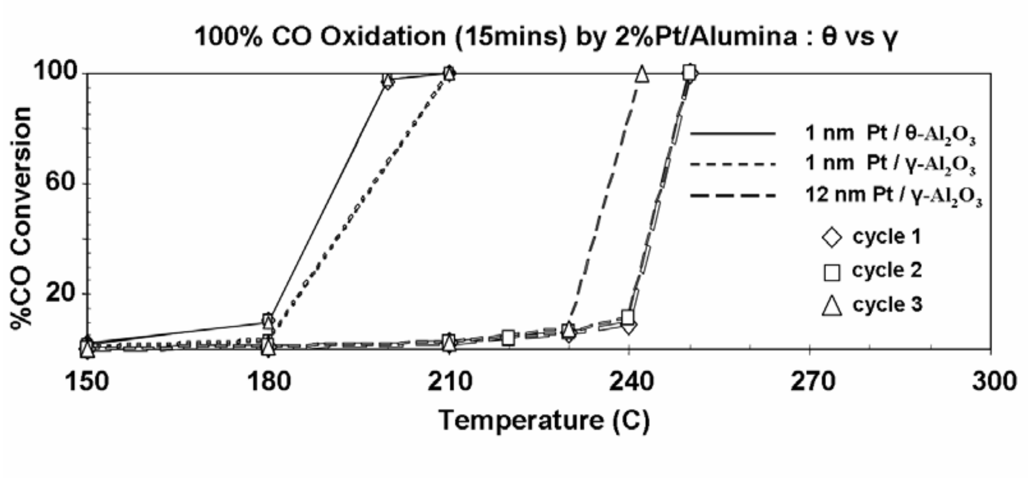


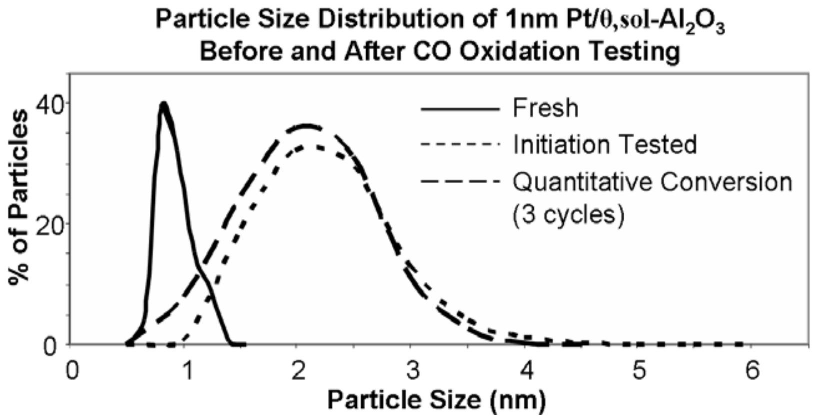
ACEM HAADF-STEM images of the exact same sample area after exposure to CO-Oxidation conditions

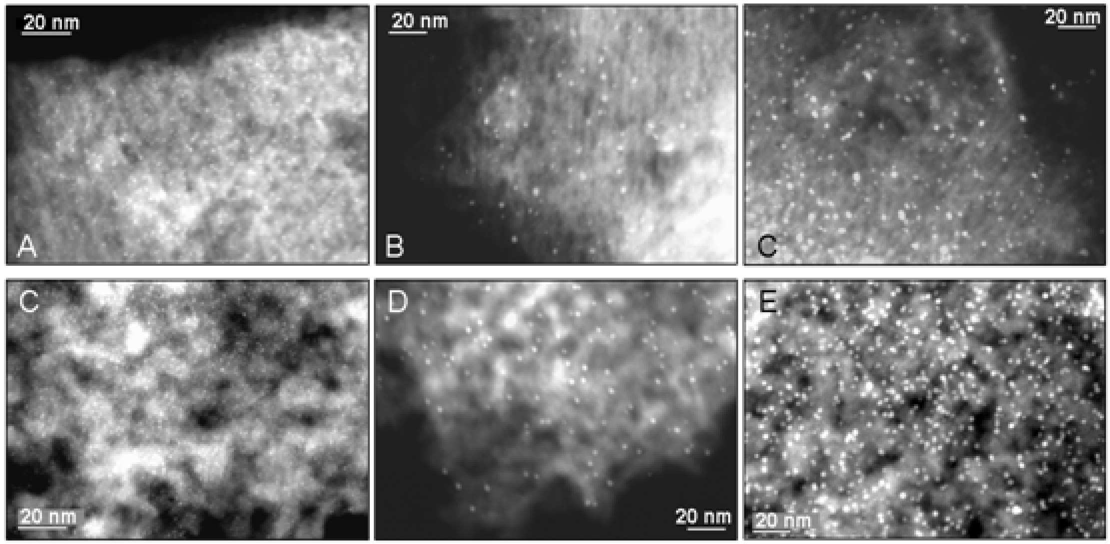




What happens if substrate morphology is different?

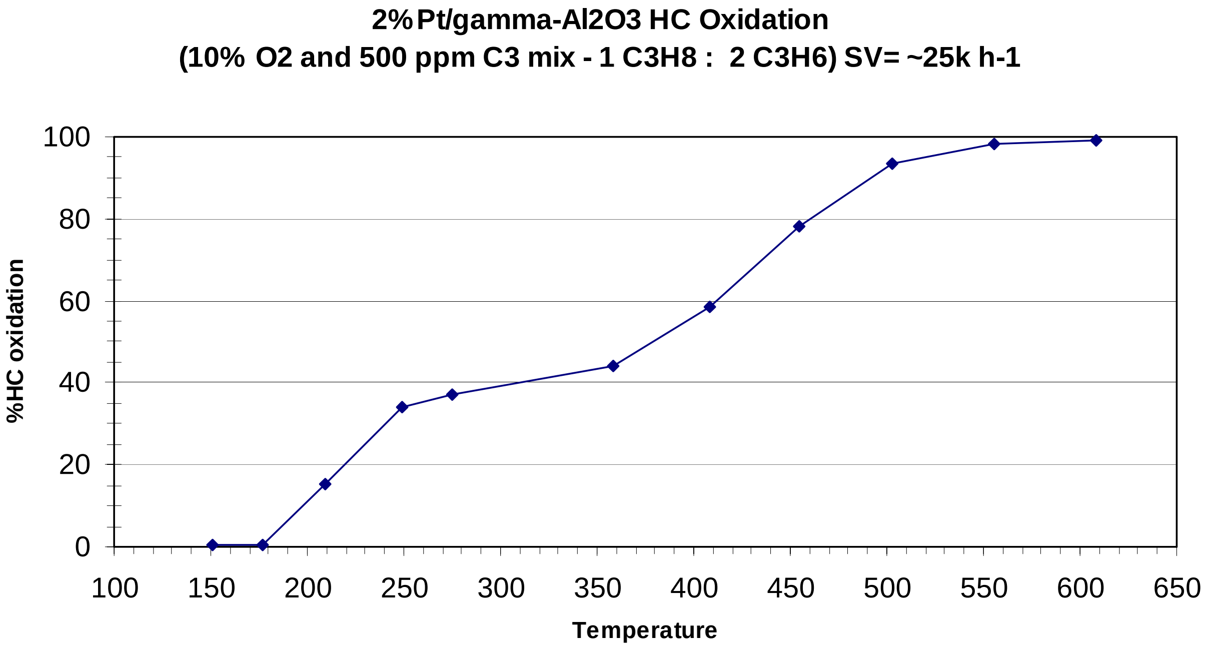


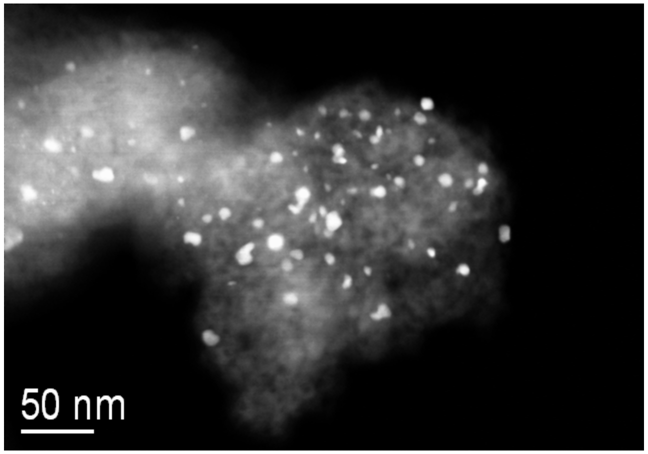


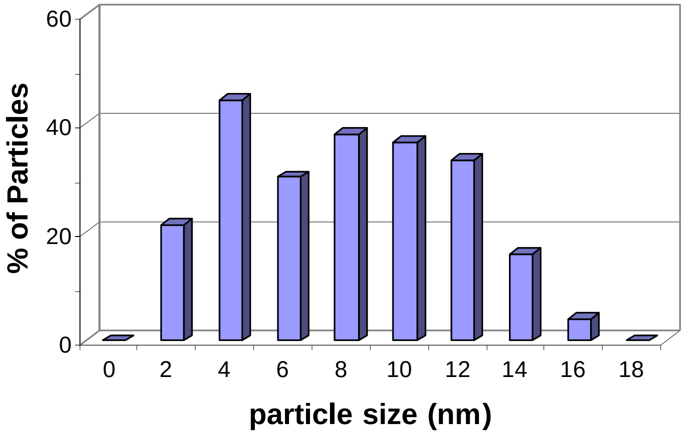


STEM images of 2%Pt/γ-Al_2O_3 (top row) and 2%Pt/θ-Al_2O_3 (bottom row) as fresh catalyst (A, C), after CO oxidation initiation (B, D) and after 3 cycles of quantitative CO oxidation (C, E)

Hydrocarbon Oxidation





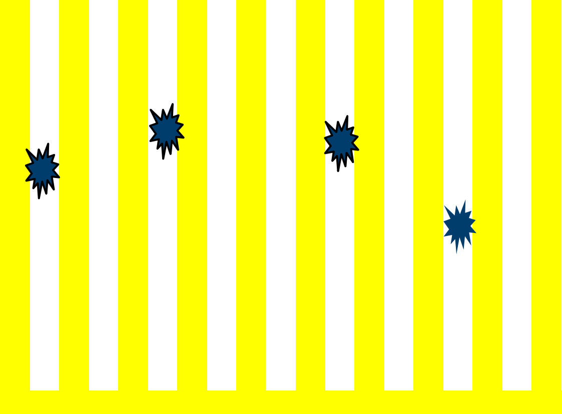


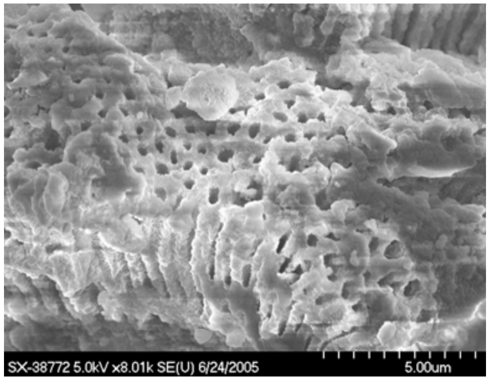
- A 500 ppm mixture of Propane and Propene in 1:2 ratio with 10% O2 and balance N2 at ~25k h-1 space velocity
- The oxidation begins at 180ºC and completes at 600ºC
- Pt particles grow rapidly (range 1.3-15.2 nm). This is not surprising since thermal treatment at 650ºC can also lead to ~12 nm particles

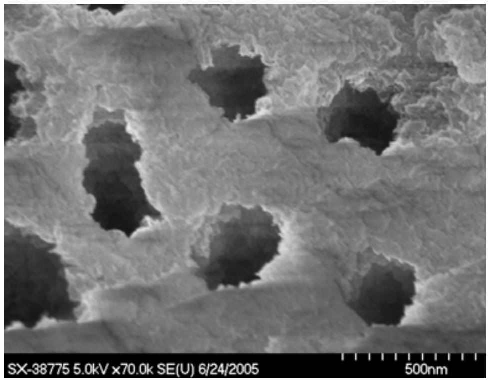
Conclusions -Theory, Experiments, and Structural Studies tell us…

- Nanostructural studies show that Pt nanoclustes on γ-alumina single atoms, 2-, 3-, and 10-20 atom clusters. Theoretical models suggest that metal clusters have extensive interaction with substrate oxygen. In gas phase, the oxidized nanoparticles are more stable.
- CO oxidation on Pt nanoclusters initiates and completes at lower temperature than that on Pt particles. Theoretical studies suggest that the adsorption of O, CO, and NO are weakened on Pt_xO_x and Pt_xO_{2x} clusters resulting into favorable CO and NO oxidation energetics on small oxidized clusters than on small metallic clusters or large particles.
- Experimental studies show that
  - Pt nanoclusters undergo rapid agglomeration even after exposure to CO oxidation initiation conditions.
  - When fresh catalysts comprises large Pt particles (~10nm), CO oxidation reaction does not induces rapid agglomeration.
  - Substrate has a major impact on the agglomeration rate.
  - Pt nanoclusters rapidly grow under hydrocarbon oxidation conditions.
- Overcoming Barriers
  - We demonstrate that iterative application of theory, experimental studies, and nanostructural characterization can advance catalyst discovery process
  - For CO oxidation, theory predicts that oxidized Pt nanoclusters are better catalysts than Pt-particles. Experimentally, we validate it by synthesizing supported Pt-nanoclusters, characterizing them, and determining their reactivity.
    - We also monitor nanostructural changes and show the impact on reactivtiy.

Can we do anything about agglomeration?

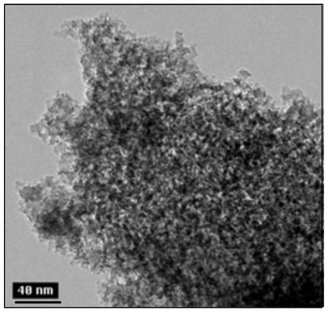






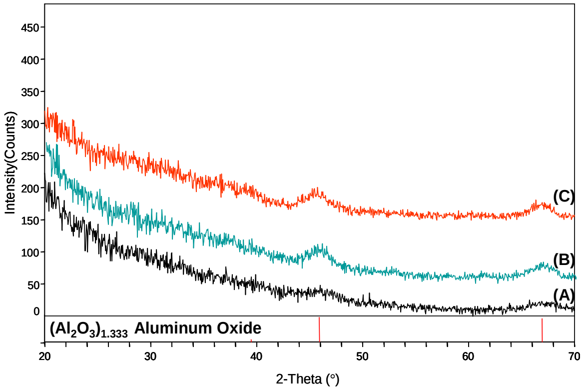
Stabilization

Ba or La Incorporation



Narula, C.K.; et al.,

AIChE Journal, **2001**, *47*, 744.



X-ray diffraction patterns of Al_2O_3 molecular sieves synthesized at 64 rpm, doped with 2 wt% La and calcined under flowing air at (A) 500 °C/ 5.5 h, followed by annealing under flowing air at (B) 700 °C/ 5.5 h, and finished with a final annealing under flowing air at (C) 900 °C/ 5.5 h.

$C_2H_5CH(CH_3)O]_3Al$

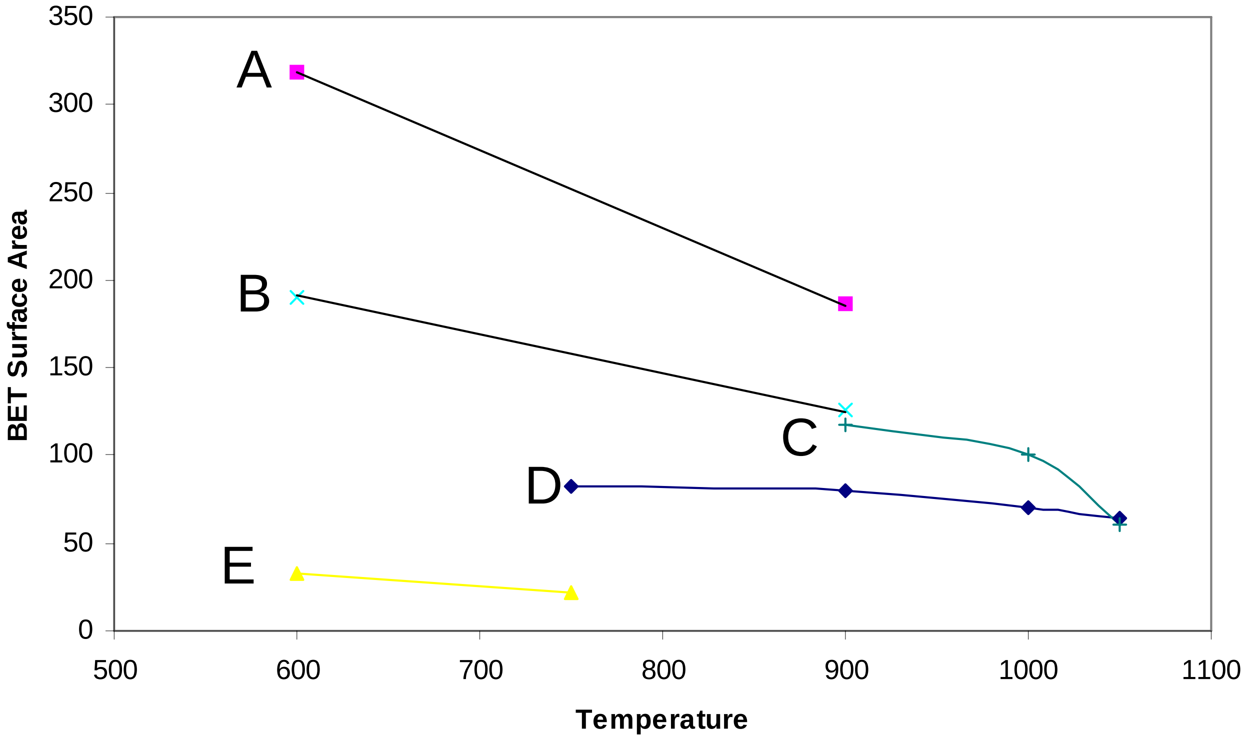
Or Tergitol + water ↓ Cetyltrimethylammonium bromide in water-ethanol + ammonium hydroxide

500ºC ↓ Calcination

Alumina
Molecular sieves

Shanks et al., Adv. Funct. Mater., **2003**,*13*, 61
Wenzhong, Z., T. J. Pinnavaia, *Chem. Comm.*, 1185 1998

Thermal Stability



A. Molecular Sieves [From Barium & Aluminum Alkoxides using Tergitol 15-S-12 as template]

B. BaO.6Al_2O_3 from Alkoxide hydrolysis

C. BaO.6Al2O3 [Lit., J. Mater. Sci, 29 (1994) 3441, carbonate method].

D. BaO.6Al_2O_3 [BaO impregnated Alumina]

E. BaO.6Al_2O_3 [From decomposition of a mixture of nitrates].

Technology Transfer

- **Ongoing work with Dr. Danan Dou and Dr. Gongshin Qi of John Deere under a work-for-others arrangement on NO_x treatment for off-road vehicles**
- **Collaboration with Dr. Yisun Cheng of Ford Motor Company**

PRESENTATIONS

- Narula, C.K.; Allard, L.F.; Blom, D.A.; Moses-DeBusk, M.; “Bridging the Gab between Theory and Experiments – Nanostructural Changes in Supported Catalysts under Operating Conditions”, Society of Automotive Engineers – international Congress, April 2008.
- Narula, C.K.; Moses, M.J.; Xu, Y.; Blom, D,A,; Allard, L.F.; Shelton, W.A.; Schneider, W.F.; ‘Catalysis by Design – Theoretical and Experimental Studies of Model Catalysts’, Nanomaterials for Automotive Applications, Society of Automotive Engineers – international Congress, March 2007 (invited)
- Blom, D.; Allard, L.; Narula, C.; Moses, M.; “Aberration-Corrected STEM ex-situ Studies of Catalysts” 8/8/07 Wednesday, Microscopy and Microanalysis Meeting, 2007, August 5-9, Ft. Lauderdale, Florida. *(Invited)*.
- Narula, C.K.; Moses, M.J.; Blom, D,A,; Allard, L.F.; ‘Catalysis by Design – Bridging the Gap Between Theory and Experiments– DEER 2007, Detroit, MI
- Allard, L.F.; Blom. D.A.; Narula, C.K.; Bradley, S.; Catalyst Characterization via Aberration-Corrected STEM Imaging, 20th North American Catalysis Society Meeting, Houston, Tx, June 17-22, 2007
- Blom, D.A.; Moses, M.; Narula, C.K.; Allard, L.F.; Aberration-Corrected STEM Imaging of Ag/Al2O3 Lean NOx Catalyst, 20th North American Catalysis Society Meeting, Houston, Tx, June 17-22, 2007
- Narula, C.K.; Moses, M.; Blom, D.A.; Allard, L.F.; Nano-structural Changes in Supported Pt Catalysts during CO oxidation, 20th North American Catalysis Society Meeting, Houston, Tx, June 17-22, 2007
- Moses, M.; Narula, C.K., Blom, D.A.; Allard, L.F.; Ex-situ Reactor Enabled Microstructural Monitoring: Elucidating Lean NOx Trap Deterioration Parameters, 20th North American Catalysis Society Meeting, Houston, Tx, June 17-22, 2007

PUBLICATIONS

- C.K. Narula, “Catalyst by Design – Bridging the Gap between Theory and Experiments at Nanoscale Level” Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis, New York, 2008 (invited).
- C.K. Narula, L.F. Allard, D.A. Blom, M. Moses-DeBusk, “Bridging the Gap between Theory and Experiments – Nano-structural Changes in Supported Catalysts under Operating Conditions” SAE-2008-01-0416.
- C.K. Narula, L.F. Allard, D.A. Blom, M.J. Moses, W. Shelton, W. Schneider, Y. Xu, "Catalysis by Design - Theoretical and Experimental Studies of Model Catalysts", SAE-2007-01-1018 (invited).
- C.K. Narula, M.J. Moses, L.F. Allard, “Analysis of Microstructural Changes in Lean NOx Trap Material Isolates Parameters Responsible for Activity Deterioration” SAE 2006-01-3420.
- Y. Xu, W.A. Shelton, and W.F. Schneider, “The thermodynamic equilibrium compositions, structures, and reaction energies of Pt_xO_y (x = 1-3) clusters predicted from first principles,” *Journal of Physical Chemistry B,* 110 (2006) 16591.
- Y. Xu, W. A. Shelton, and W. F. Schneider, “Effect of particle size on the oxidizability of platinum clusters,” *Journal of Physical Chemistry A*, 110 (2006) 5839.
- C.K. Narula, S. Daw, J. Hoard, T. Hammer, “Materials Issues Related to Catalysts for Treatment of Diesel Exhaust,” *Int. J. Amer. Ceram. Tech*., 2 (2005) 452 (invited).

Activities for Next Year

- Study of NO_x and HC oxidation on Pt/Al_2O_3 system
  - Theoretical models
  - Nanostructural Changes
  - Experimental studies
- Complex System “Oxidation Catalyst” for SCR
  - Nanostructural changes
  - Catalytic Activity
  - Comparison with individual gas interactions

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- J. Eberhardt, Technology Area Development Specialist