

Catalysts via First Principles

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**DOE VEHICLE TECHNOLOGIES
PROGRAM ANNUAL MERIT
REVIEW, FY 2011**

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Project PM011

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Overview

Timeline

- Start: Oct. 2004
- Finish: Sep. 2012

Budget

- Funding received in 2010
 - \$300K
- Funding authorized in 2011
 - \$300K

Barriers

- Changing internal combustion engine combustion regimes
- Cost and durability of emission control systems
- Long lead times for materials commercialization
- Many advanced vehicle technologies rely on materials with limited domestic supplies

Partners

- Ongoing work with John Deere
 - Work-for-others arrangement on NO_x treatment

Objectives

Materials R&D expertise and enabling advanced materials that support the goals of the following VT subprograms discussed in the previous sections: Advanced Combustion Engine R&D; Batteries and Electric Drive Technology; and Fuels Technologies.

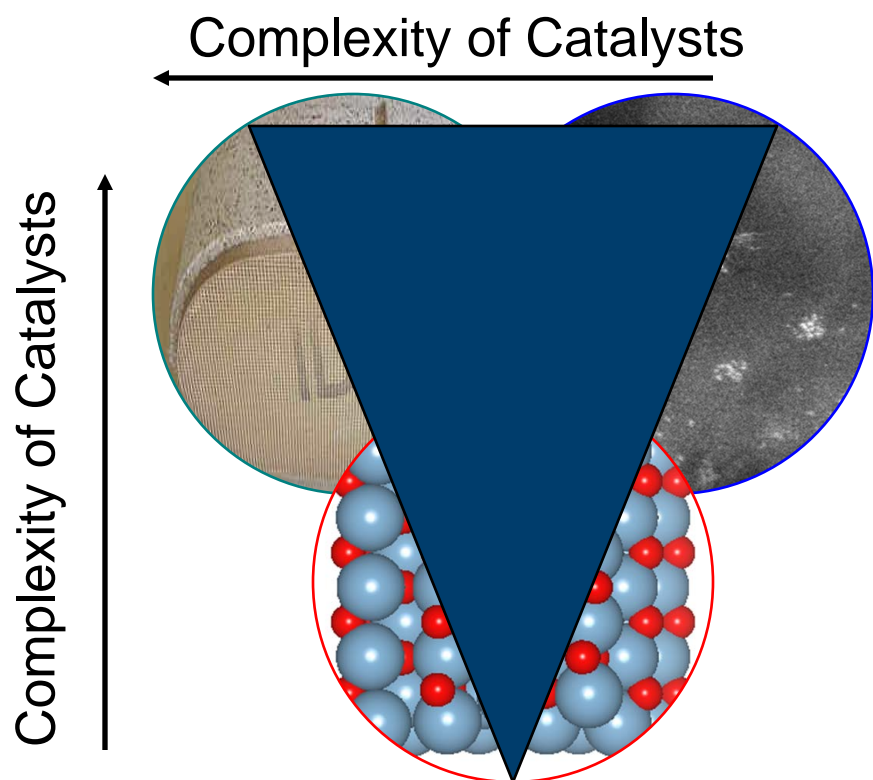
- To demonstrate that we can examine catalyst system by first principle theoretical models, experimental studies, and nanostructural characterization iteratively to forecast improvements to obtain optimum catalyst systems
- Identify optimum catalyst sites and develop durable, reliable, well-characterized catalyst materials with such sites

Barriers

- **Changing internal combustion engine combustion regimes. Many advanced vehicle technologies rely on materials with limited domestic supplies.**
 - Advances in emission catalysts from trial and error method
 - Although successful, very time consuming, resource intensive
 - 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?

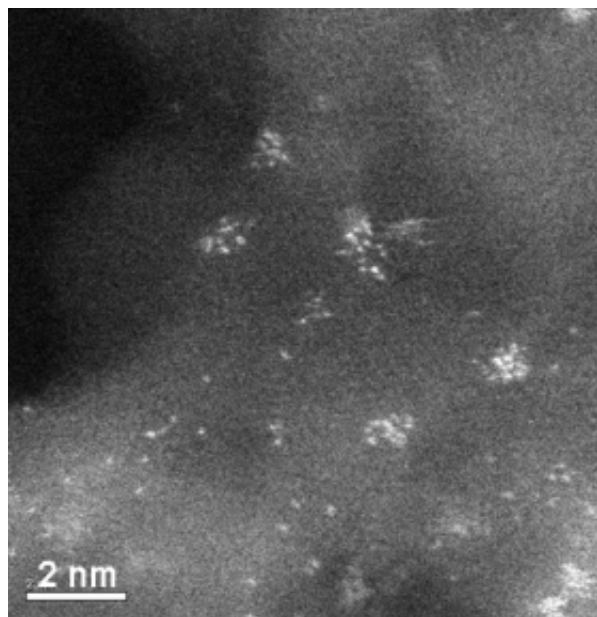
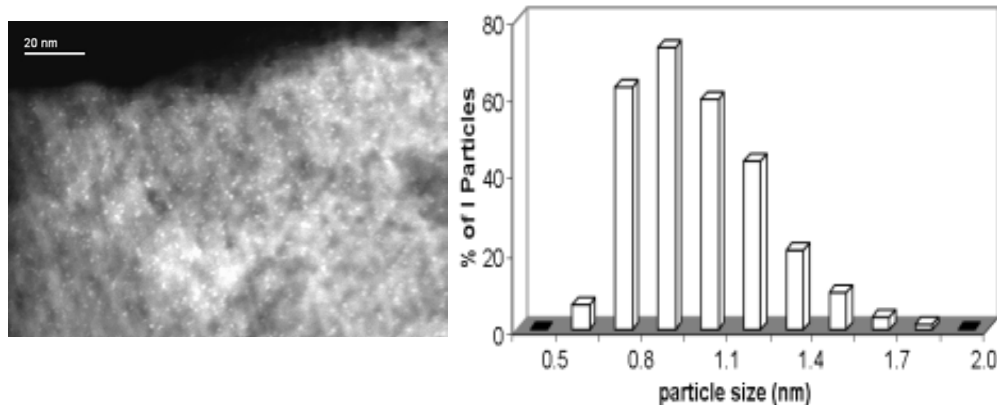
Approach

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. For lean burn NO_x treatment, urea-selective catalytic reduction (SCR) is currently leading technology and is based on zeolites.



- Theoretical Modeling
 - First Principles modeling of Pt clusters on oxide supports
 - Zeolite catalysts
 - 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
 - Zeolite catalysts for SCR (DOE-ITP project)
- Structure
 - Nano-structural characterization

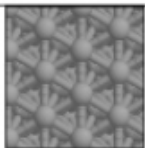
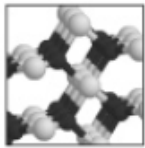
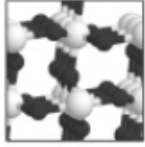
Supported Catalyst - Pt/ γ -Al₂O₃



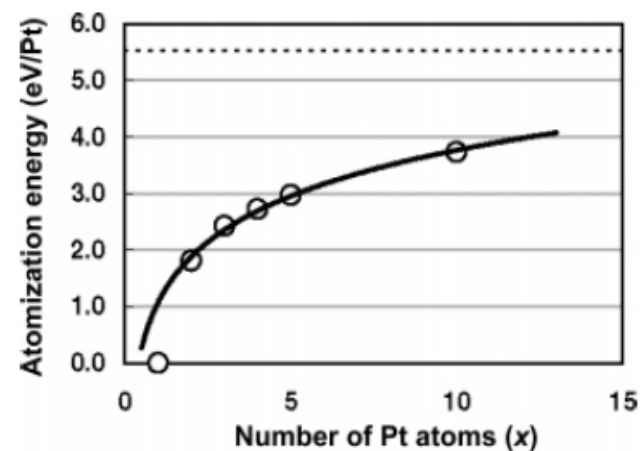
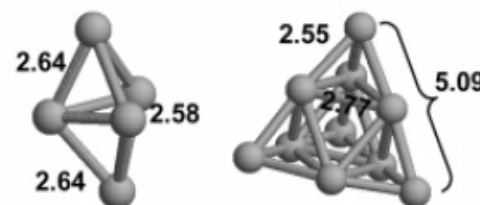
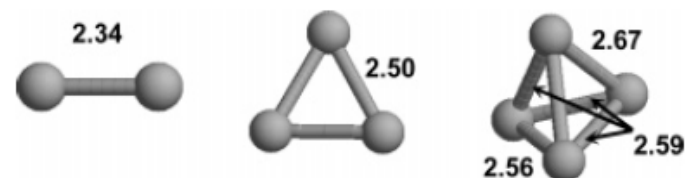
- STEM analysis shows that platinum particle size ranges from 0.6-1.9 nm and the distribution is centered at 1.0 nm
 - A common observation reported in literature
 - Recent EXFAS & XANES study suggest thermally mediated interaction between Pt and support resulting in Pt-Pt bond contraction (JACS, 128 (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 are also observed.
 - Only a 3-atom cluster has been observed previously

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

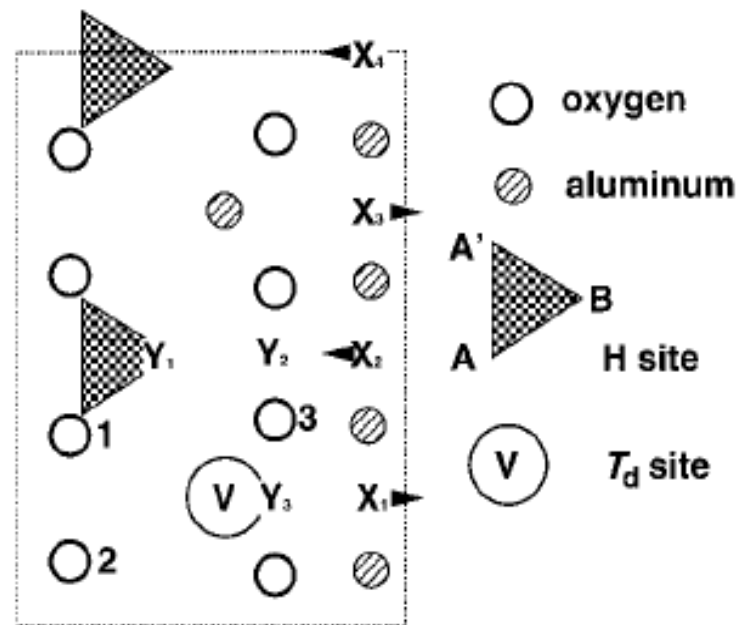
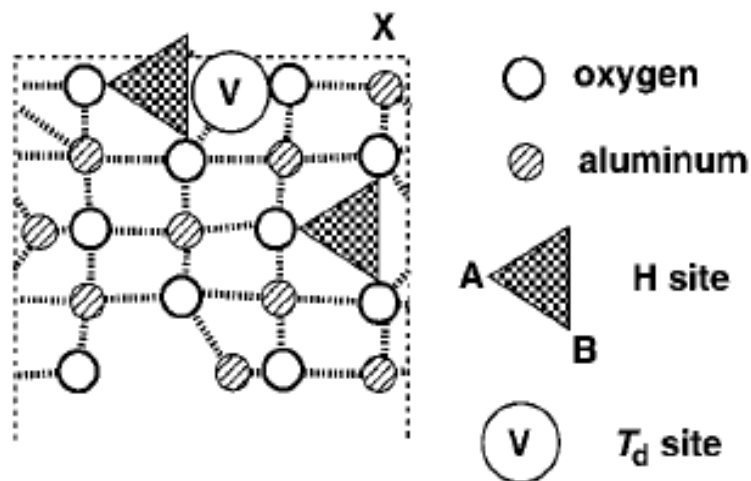


- **3-D structures generally preferred. Optimal structures are shown with some bond distances that match with experimentally observed ones for dimers.**
- **Atomization energy increases monotonically with cluster size i.e. atoms are held together more strongly as the cluster size increases**

Modeling Pt/ γ -Al₂O₃?

- Still disagreement on the bulk structure of γ -Al₂O₃. Poor crystallinity prevents structure optimization.
 - Defect-spinel lattice structure with one cation defect per Al₈O₁₂ 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 I4₁/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 -Al₂O₃ 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 -Al₂O₃ has been carried out but the results remain suspect till there is agreement on the structure of γ -Al₂O₃

Pt-Clusters on alumina



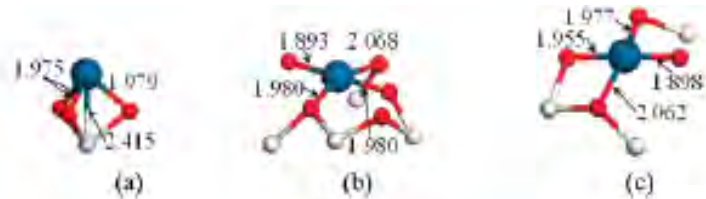
This structure has Pt-Pt bond distances of 2.6, 2.6, and 3.3 Å. If this structure is capped with -OH, the bond distances are 2.6, 3.1, 3.6 Å which are in good agreement with experimental values.

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 2.7, 3.2, 3.4 Å.

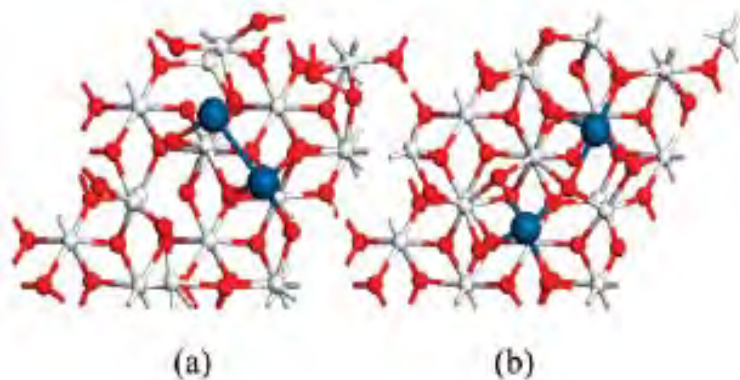
Oversimplified structure of $\gamma\text{-Al}_2\text{O}_3$ employed in these models

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

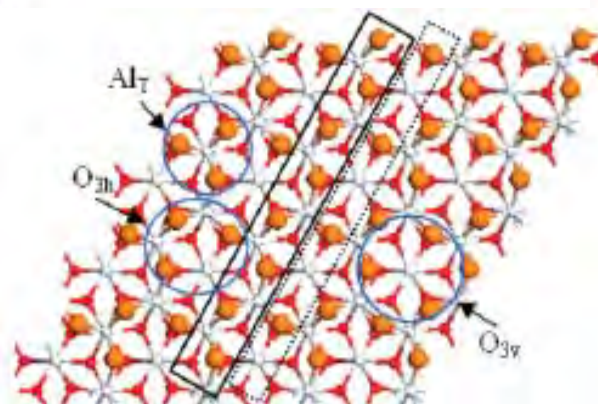
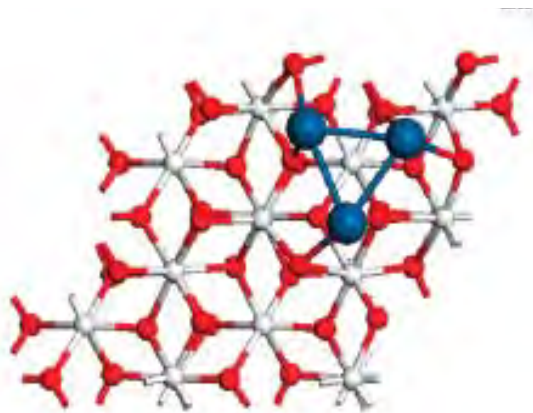
Pt/ α -Al₂O₃



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



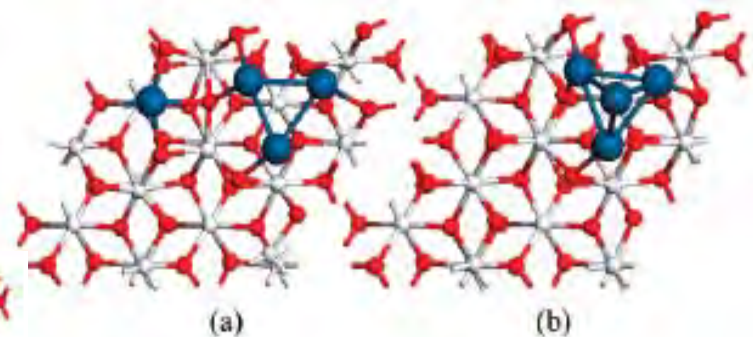
a. Al_T-Al_T b. O₃-O₃



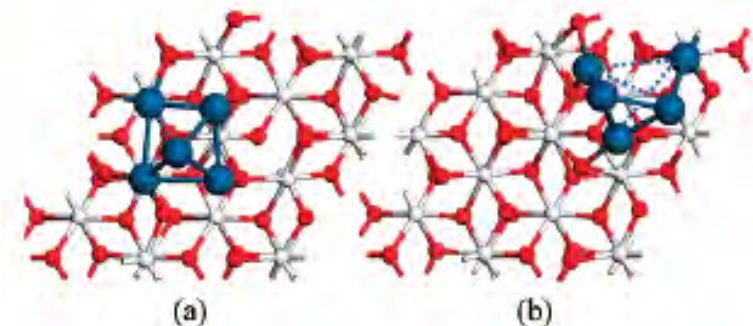
Al_T = 2 zigzag O and 1 linear O attached to single Al

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

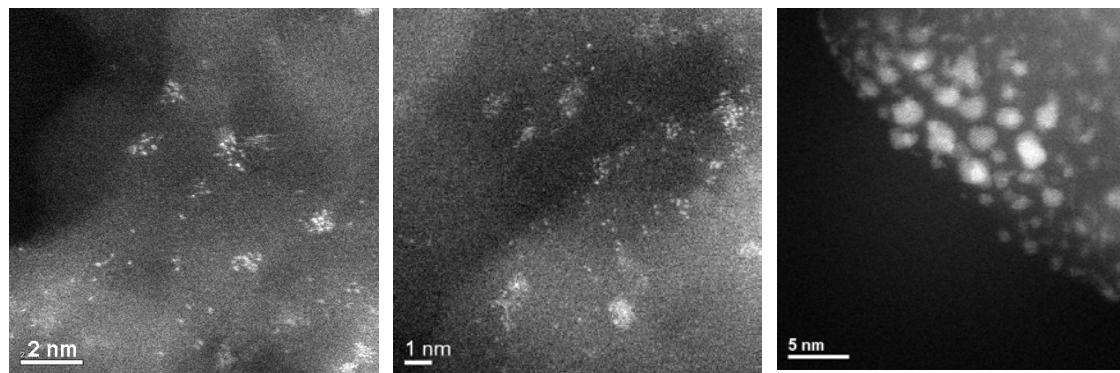


a. Square pyramid b. triangular bipyramid

- O₃ site strongly preferred
- Clusters larger than 3 prefer to interact with substrate via its triangular face
- Adhesion declines with increase in size

Pt₃ equilateral triangle adsorption structure

Is Pt/ θ -Al₂O₃ a good model for Pt/ γ -Al₂O₃?

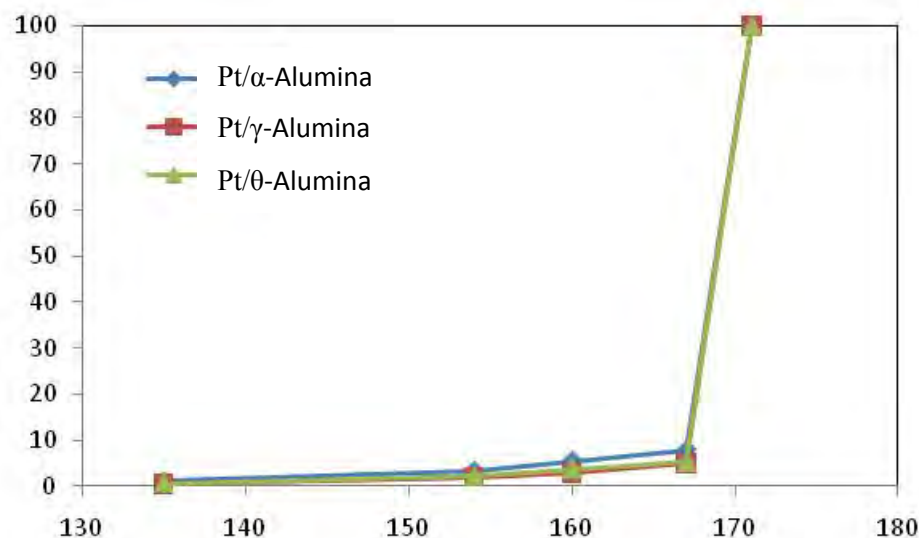


Pt/ γ -alumina Pt/ θ -alumina Pt/ α -alumina

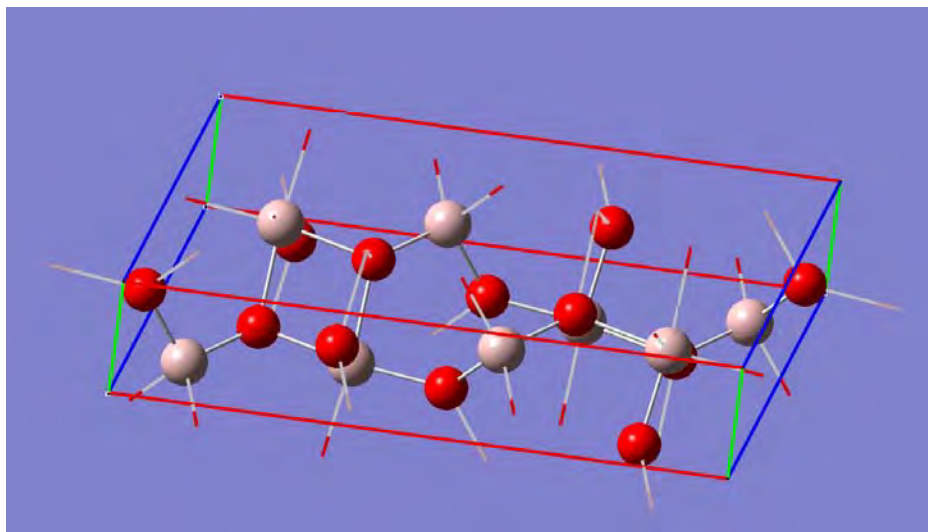
- ACEM ADF-STEM images of fresh Pt/ γ -alumina and Pt/ θ -alumina show a bimodal distribution – single atoms and 10-20 atom agglomerates. Pt/ α -alumina, on the other hand, several large particles.

- The BET surface areas of α -, γ - and θ - alumina are 8, 200, and 189 m²/g, respectively

- CO oxidation as a function of temperature with sampling after 15 minutes at the given temperature is identical for all catalysts

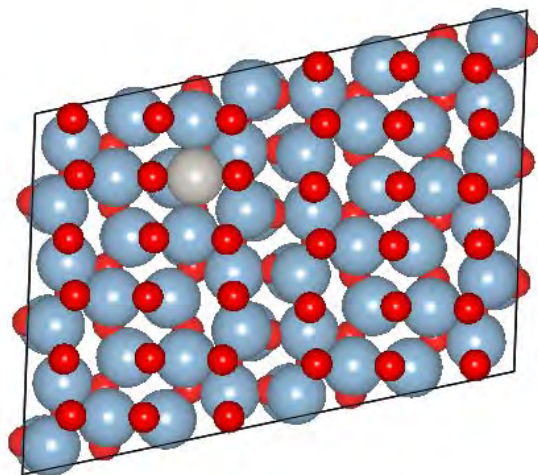
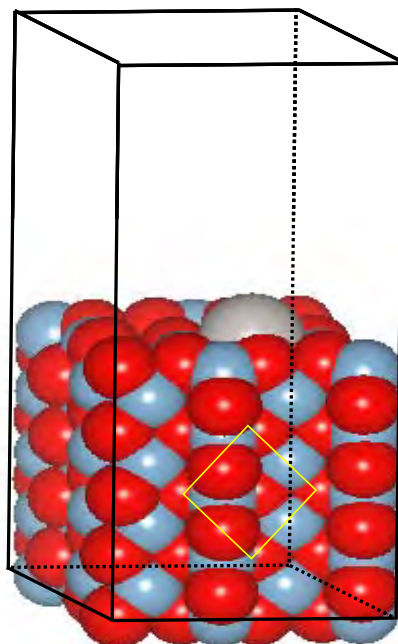
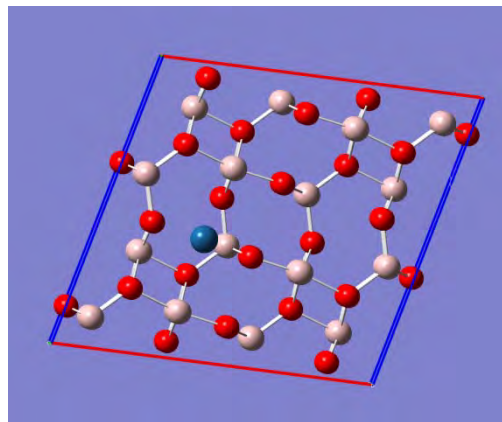


Modeling Pt/ θ -Al₂O₃



Density Functional Theoretical Calculations were performed for generalized gradient approximation (GGA) of Perdew and Wang. The structure was fully relaxed with respect to volume as well as cell-internal and -external coordinates. Extensive test indicated that 600 eV was a sufficient cut-off to achieve highly accurate energy differences.

Property	VASP (GGA) This Work	VASP (GGA) Lit	Experimental Lit
a	11.93	11.87	11.85
b	2.94	2.929	2.904
c	5.71	5.657	5.622
β	103.88	104	103.8
V	96.5	95.4	93.9
(x,z) Al ₁	(0.909, 0.204)	(0.910, 0.204)	(0.917, 0.207)
(x,z) Al ₂	(0.658, 0.317)	(0.658, 0.317)	(0.660, 0.316)
(x,z) O ₁	(0.160, 0.109)	(0.159, 0.109)	(0.161, 0.098)
(x,z) O ₂	(0.495, 0.257)	(0.495, 0.257)	(0.495, 0.253)
(x,z) O ₃	(0.826, 0.434)	(0.826, 0.432)	(0.827, 0.427)

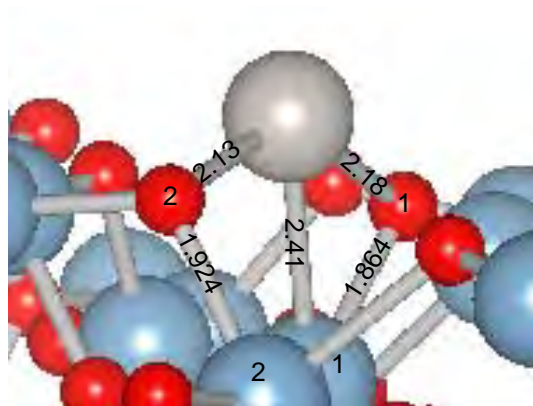


- The charge neutral surface was constructed from a 2x4x2 supercell and a vacuum of 15Å. This cell contains 180 atoms

— Lodziana, Z.; Topsoe, N-Y. ; Norskov, J.K.; Nature Materials, 2004, 3, 289

- A larger charge neutral surface was constructed from 2x3x3 supercell and a vacuum of 15Å. This cell contains 420 atoms

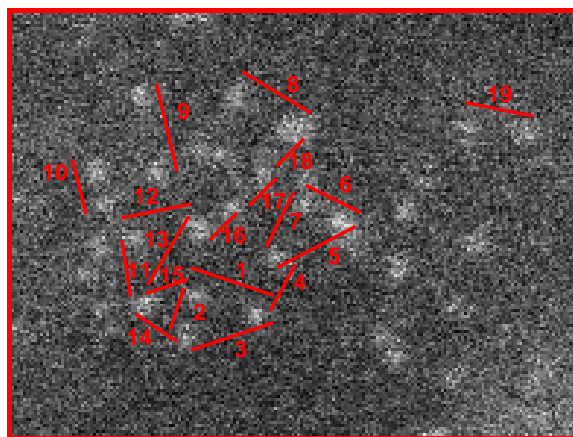
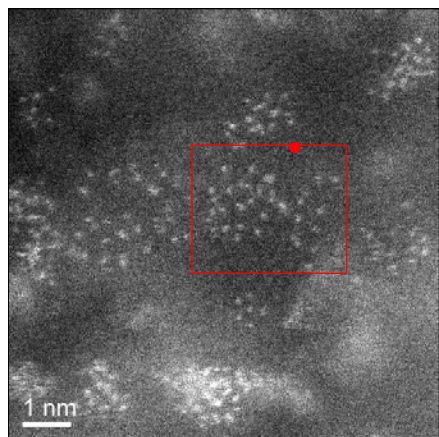
Pt - Bonding



Pt-O1	2.18Å
Pt-O2	2.13Å
Pt-Al	2.41Å
Absorption Energy	-62.29 kcal/mole

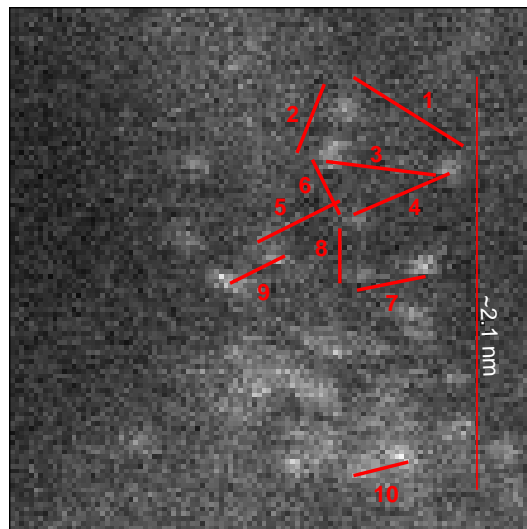
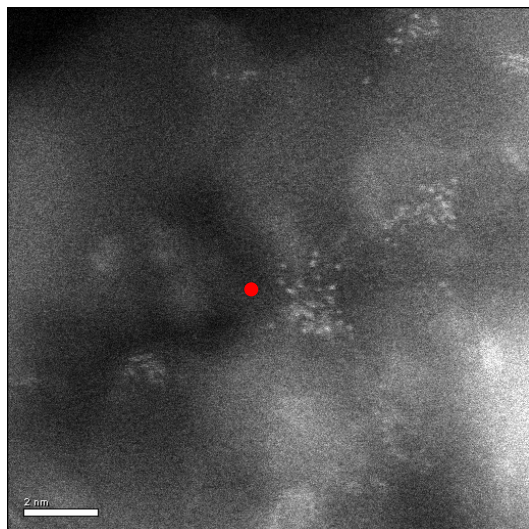
- Platinum occupies a position between two surface oxygen atoms
 - The adsorbed Pt is in zero oxidation state
 - Pt-O distances are larger than Pt-O bond distances calculated for Pt-O cluster in gas-phase (1.76 Å) or Pt/ α -alumina (2.0 Å) but are closer to bulk Pt-O (2.08 Å)
- This structure is different from Pt/ α -Alumina where Pt atom is atop surface oxygen and
 - Calculated Pt-O distance is 2.02Å. The adsorbed platinum atom is paramagnetic
 - The interaction of Pt with surface is summarized as localized covalent bonding between Pt and O enabled by nearly Al-centered electron-accepting empty states available to accept excess electron density

Larger Agglomerates



Pt/ θ -Al₂O₃

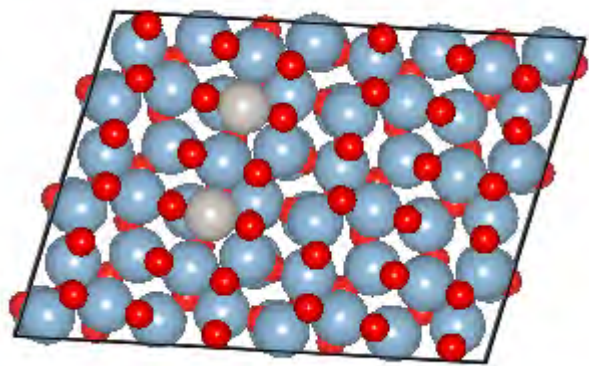
1	3.82	6	2.6	11	4.0	16	2.27
2	2.61	7	3.64	12	3.8	17	2.79
3	4.53	8	3.97	13	5.53	18	3.14
4	3.45	9	4.87	14	3.28	19	3.65
5	3.45	10	2.09	15	3.3		



Pt/ γ -Al₂O₃

1	6.94	6	3.97
2	2.53	7	3.36
3	6.75	8	3.33
4	6.19	9	3.07
5	5.35	10	2.24

Pt-Pt or Pt-Pd atoms on θ -Al₂O₃ surface

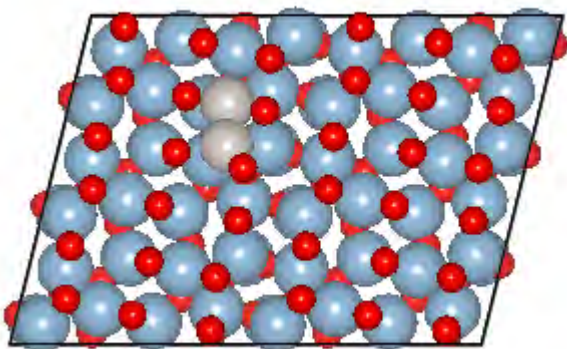


Pt1-O1	2.192Å
Pt1-O2	2.13Å
Pt1-Al	2.395Å
Pt2-O1	2.198Å
Pt2-O2	2.135Å
Pt2-Al	2.387Å

Favored by 1.27 Kcal/mole

Pt-O1	2.192Å
Pt-O2	2.13Å
Pt-Al	2.395Å
Pd-O1	2.24Å
Pd-O2	2.20Å
Pd-Al	2.45Å

0.6 Kcal/mole

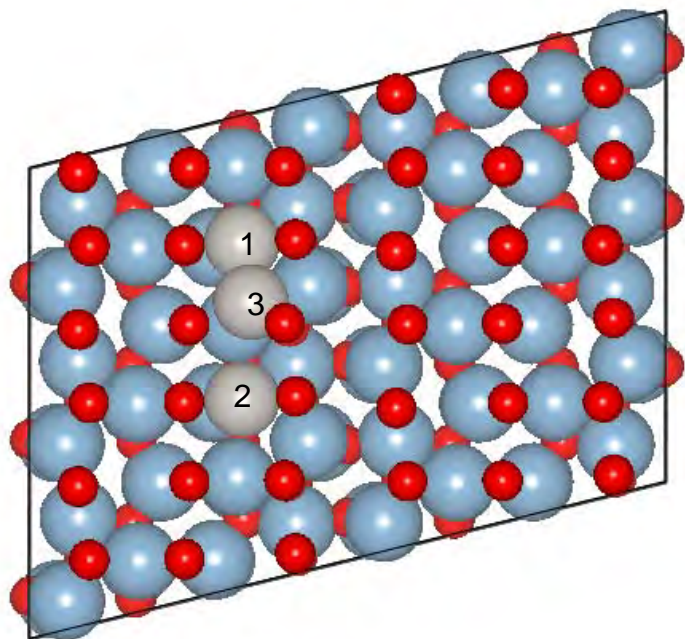


Pt1-O1	2.176Å
Pt1-O2	2.079Å
Pt1-Al	2.428Å
Pt2-Pt1	2.489Å
Pt2-Al	2.491Å

Pt-O1	2.176Å
Pt-O2	2.095Å
Pt-Al	2.428Å
Pd-Pt	2.57Å
Pd-Al	2.52Å

The barrier to sintering is very low in sub-nanometer Pt particles

2+ Pt atoms



Pt1-O1 2.183Å Pt1-O2 2.096Å

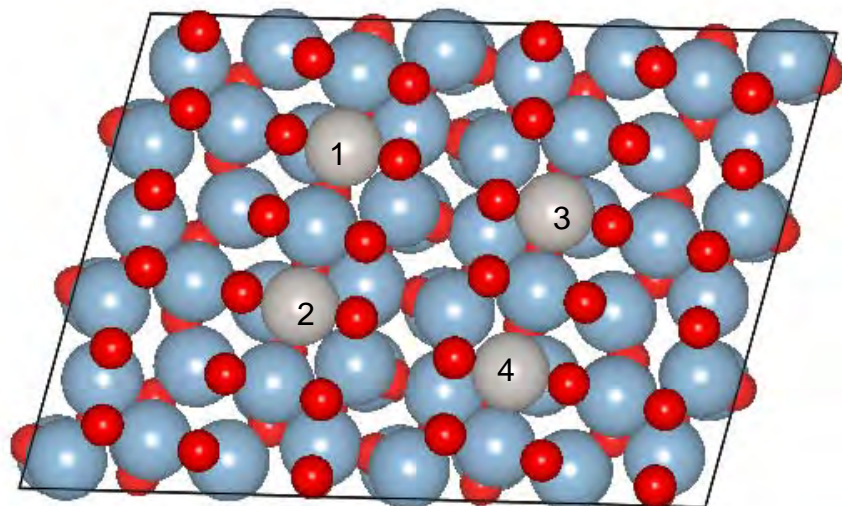
Pt1-Al 2.435Å

Pt2-O1 2.203Å Pt2-O2 2.119Å

Pt2-Al 2.417Å

Pt3-Pt1 2.517

Pt3-Al 2.439



Pt1-O1 2.192Å Pt1-O2 2.132Å

Pt2-O1 2.202Å Pt2-O2 2.129Å

Pt3-O1 2.135Å Pt3-O2 2.213Å

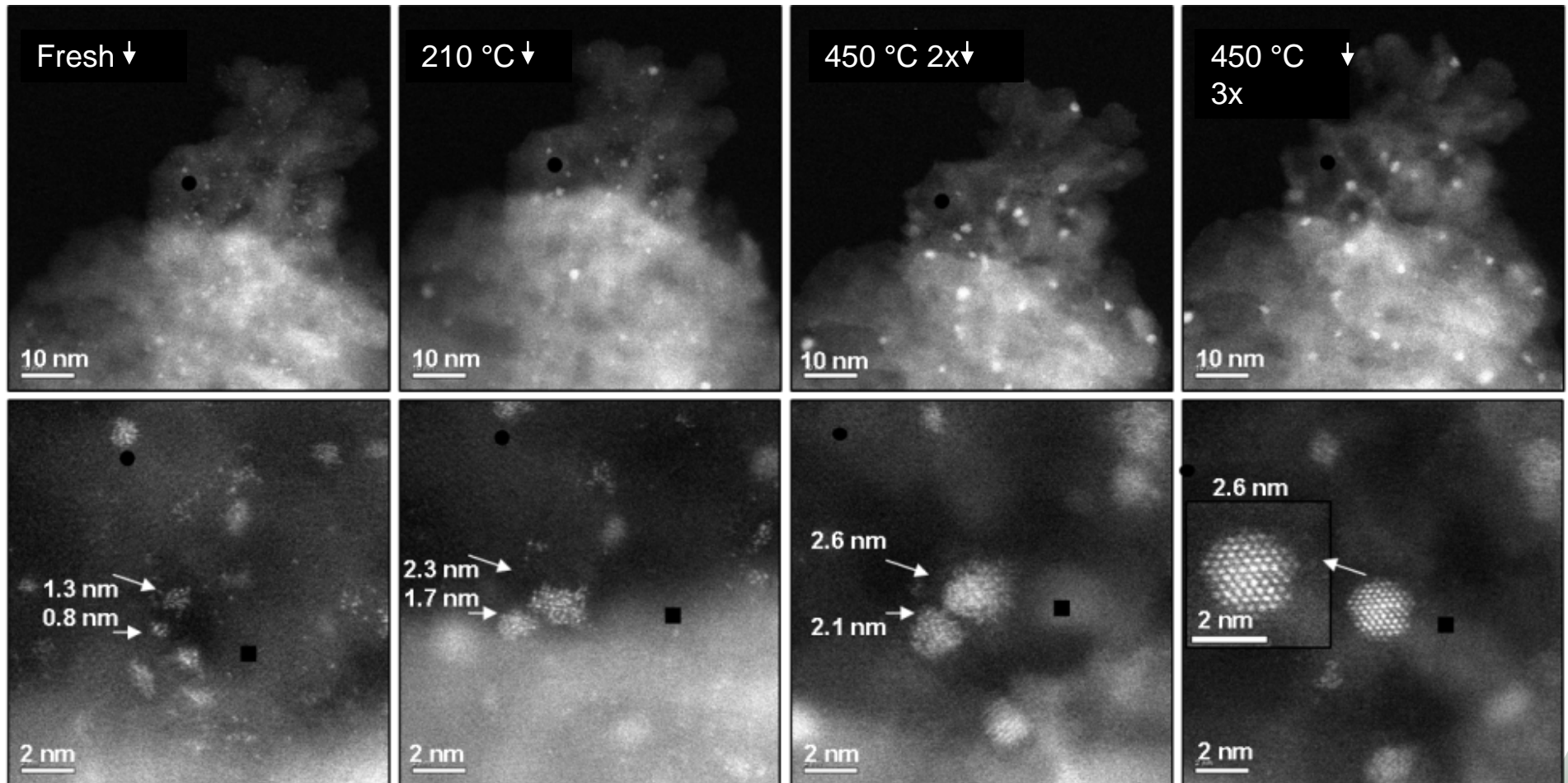
Pt4-O1 2.138Å Pt4-O2 2.214Å

Pt1-Pt2 5.73Å Pt1-Pt3 7.67Å

Do other surface oxygen sites become favorable after these 4-sites are occupied?

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

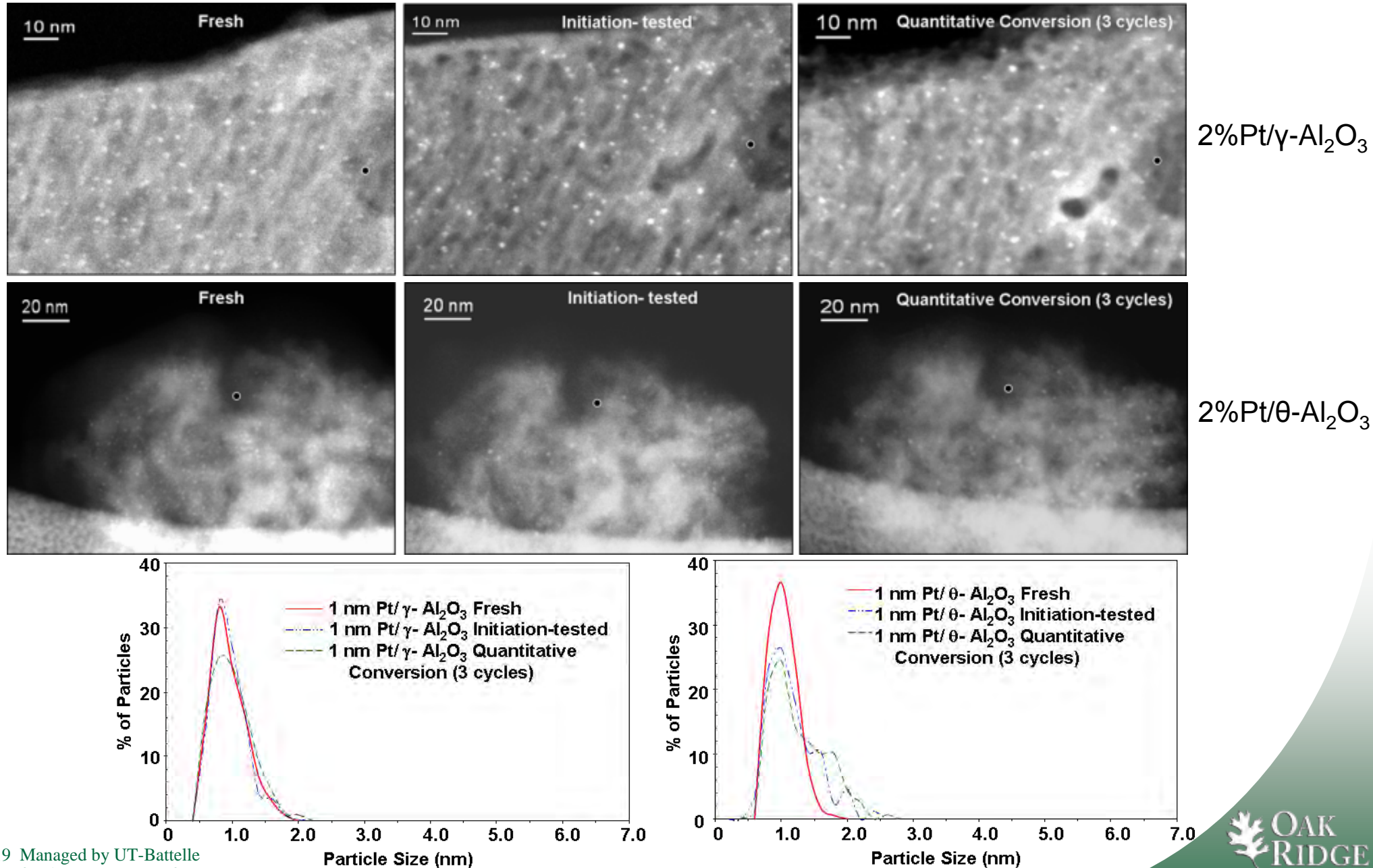
Ex-situ Reactor Studies



Rapid growth in Pt particles can be followed as a function of CO-oxidation conditions

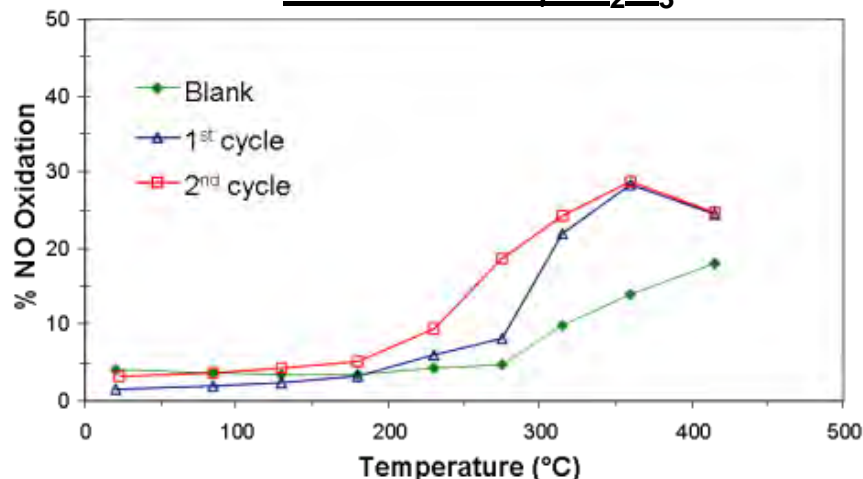
CO Oxidation – Structural Changes in Pt-Particles supported on θ - Al_2O_3 : Substrate Morphology Effect

CO oxidation *Ex-situ* Reactor Studies

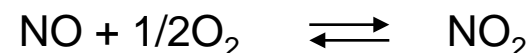


NO Oxidation – Structural Changes in Pt-Particles supported on γ -Al₂O₃

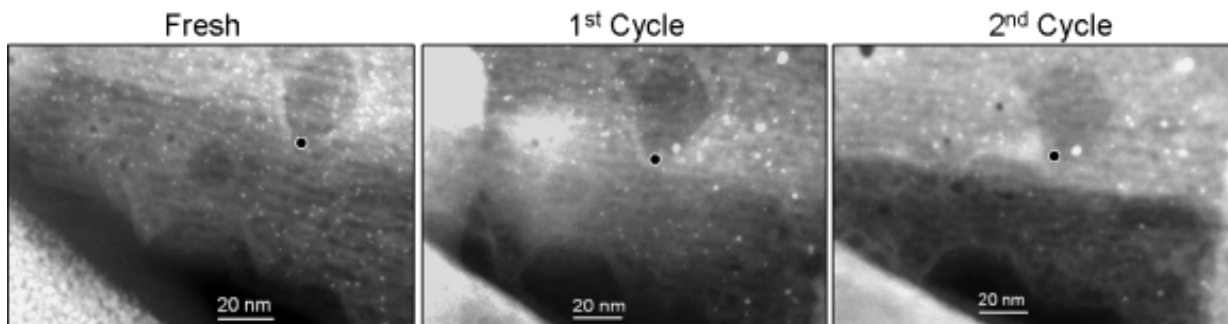
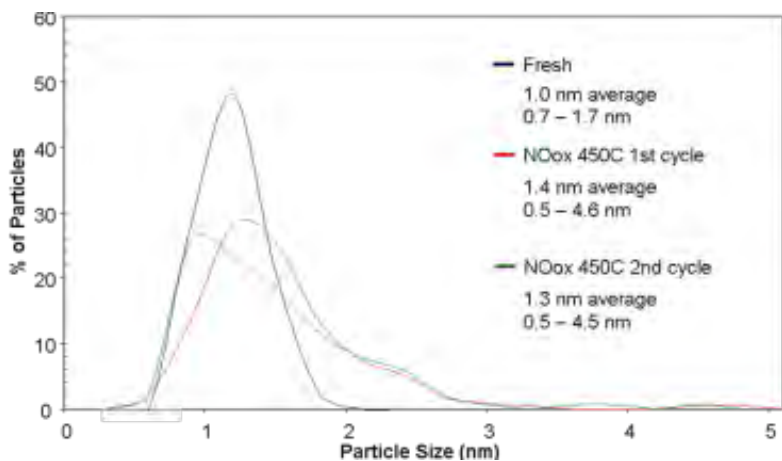
1 nm 2% Pt/ γ -Al₂O₃



- A 500 ppm mixture of NO with 10% O₂ and balance N₂ at ~50k h⁻¹ space velocity
- The 2nd cycle initiates at a lower temperature than the 1st cycle
- Reverse NO₂ reduction becomes favored at 400°C in both cycles



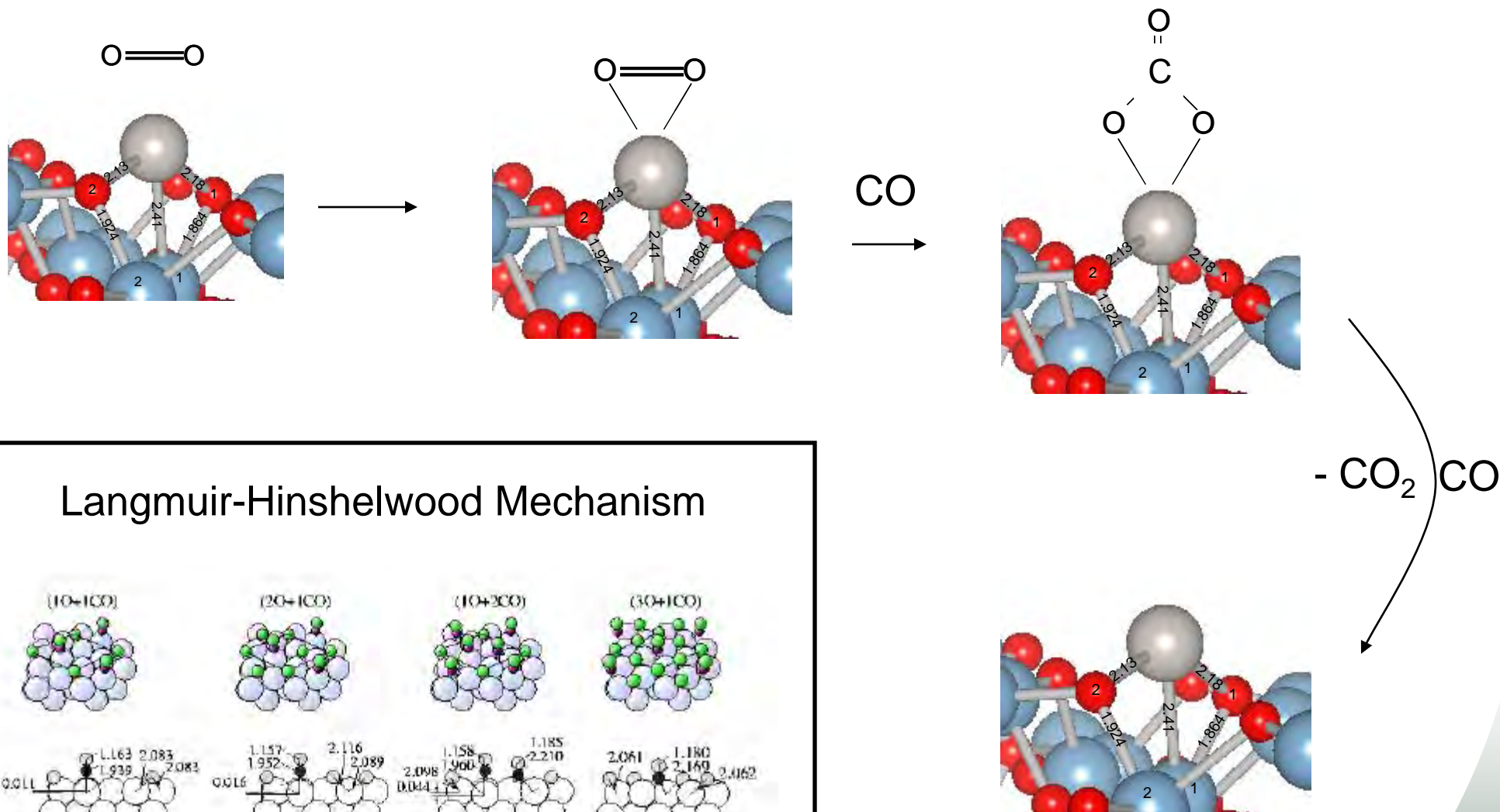
- Under NO oxidation conditions at this temperature, no significant Pt growth is observed.



- Results of *ex-situ* studies suggest that the average particles size under these conditions is not effected by the density of Pt particles but the degree of particle growth possible is increased. Since the fresh sample has already been calcined at 450 C/5h prior to testing, the sintering observed in the *ex-situ* studies can be primarily contributed to the NO oxidation environment.

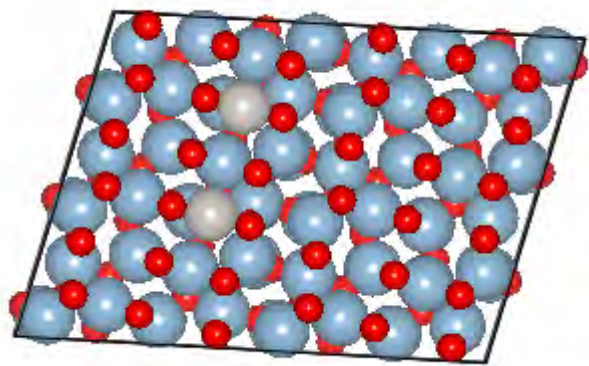
CO and NO Oxidation

Pt Oxidation



Strong NO₃ bond (as compared with CO₃ bond) to Pt atoms could explain low NO conversion on subnanometer Pt particles

Pt-Pt or Pt-Pd atoms on θ -Al₂O₃ surface

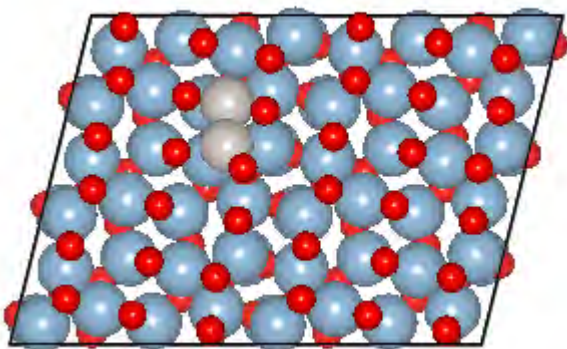


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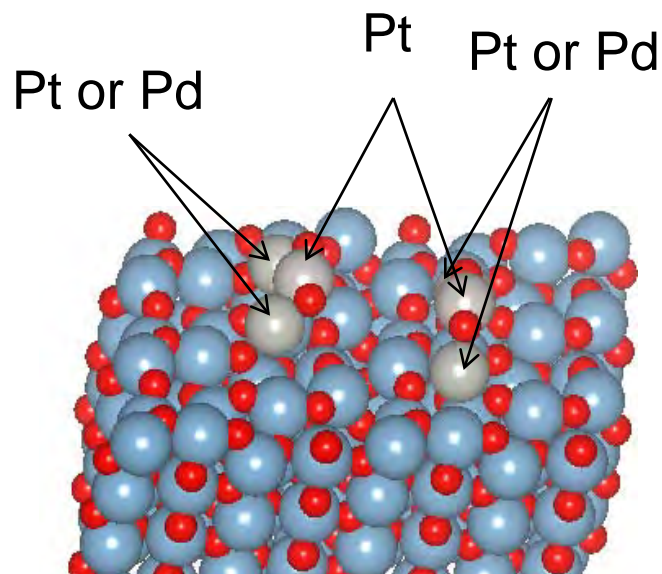
0.6 Kcal/mole



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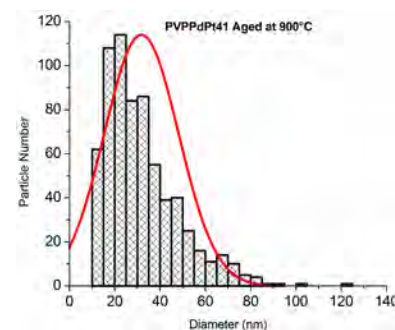
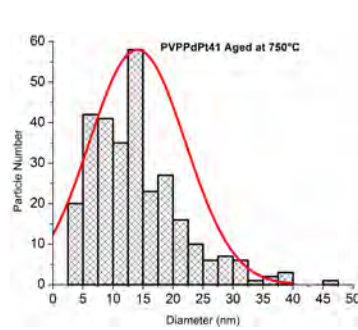
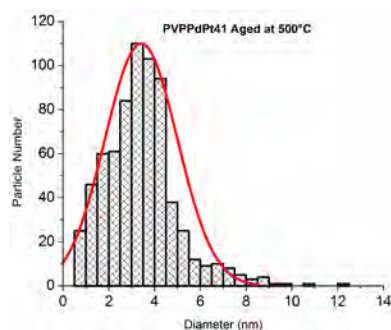
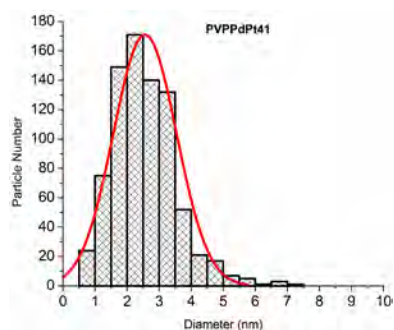
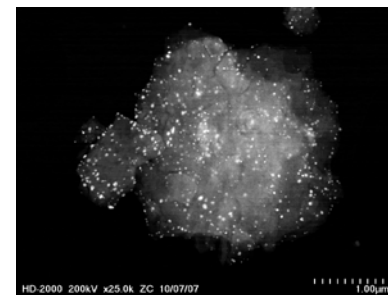
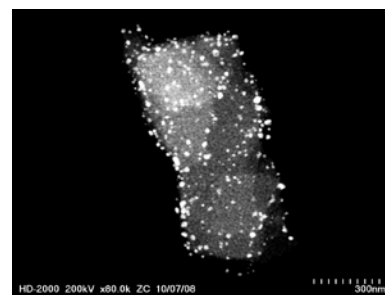
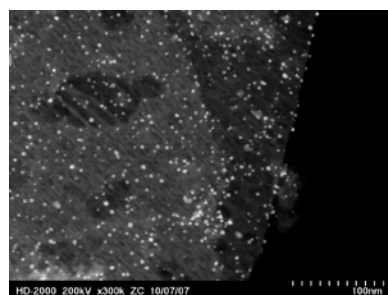
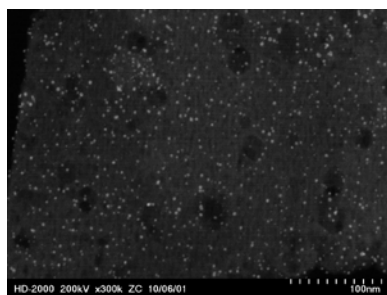
Pt-Pd Nanoparticles



- **Platinum atom bonded to oxygen atoms which are bonded to surface platinum or palladium atoms**
- **No difference in energy**

Pt-Pd alloying does not stabilize sub-nanometer Pt particles!

Pt-Pd Nanoparticles

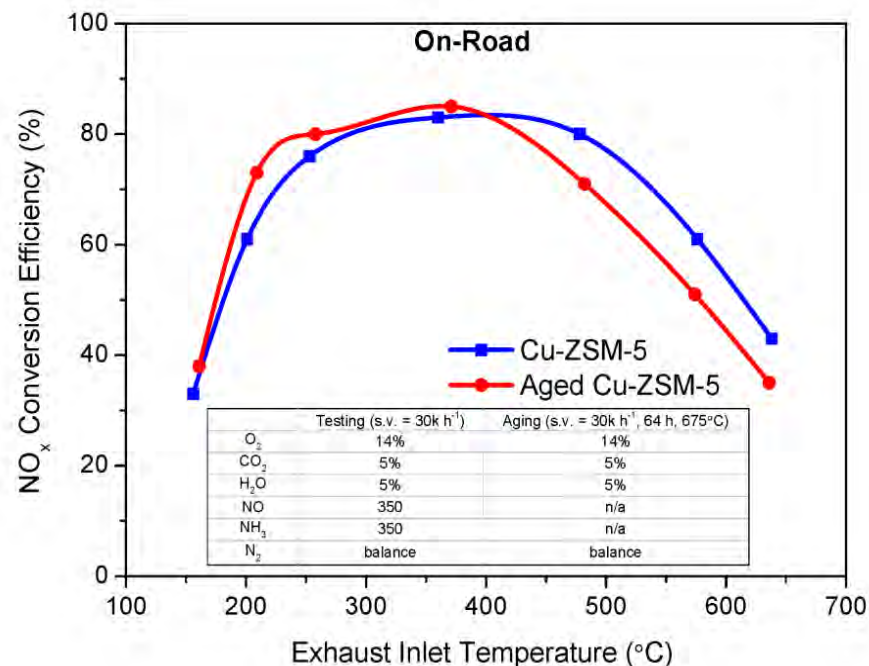
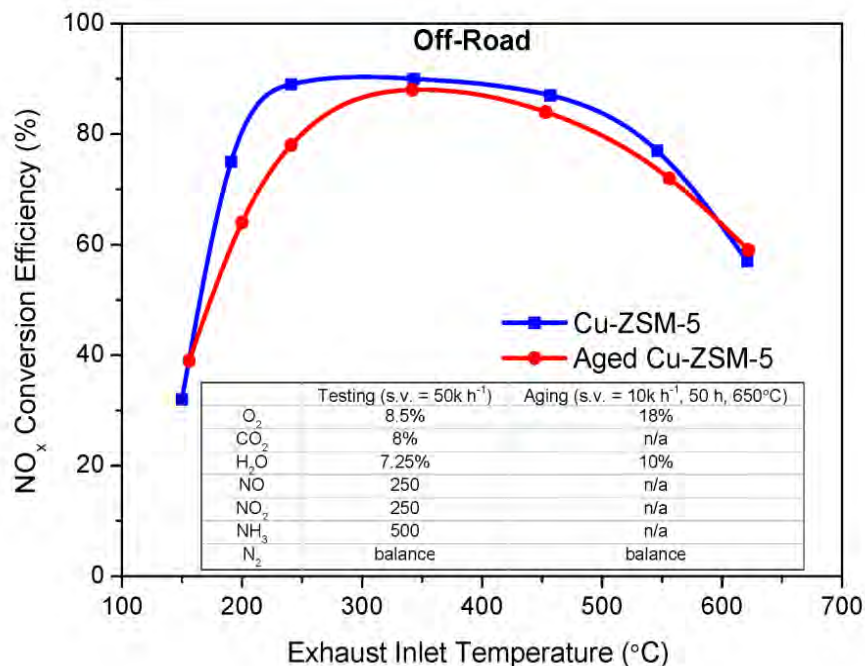


- A 0.7 g of PdPt/alumina sample was treated under a flow (5L/min) of N_2 , O_2 (5%) and H_2O (10%) for 3 hours at a series of temperatures (500°C, 600°C, 750°C and 900°C), held for 2.5 hours, and cooled under pure N_2
- Abnormally large particles, which are common in high temperature sintered samples of Pt/alumina were not observed.
- The results are comparable to the ones reported for Pt-Pd/alumina prepared by co-impregnation [Graham, G.W.; et al.; Catalysis Letters, 116 (2007) 1.

Pd reduced coarsening of Pt particles to abnormally large size.

Catalyst for Treatment of Emission from Off-Road Diesel Engines

- We initiated our research by employing Cu-ZSM-5 which has been shown to be highly effective NH_3 -SCR catalysts for passenger vehicles.
- Cu-ZSM-5 displayed a operating temperature window of 200-550°C for NO_x conversion.
- Hypothesis – Incorporation of heteroatoms in metal exchanged zeolite can impact NO_x conversion temperature

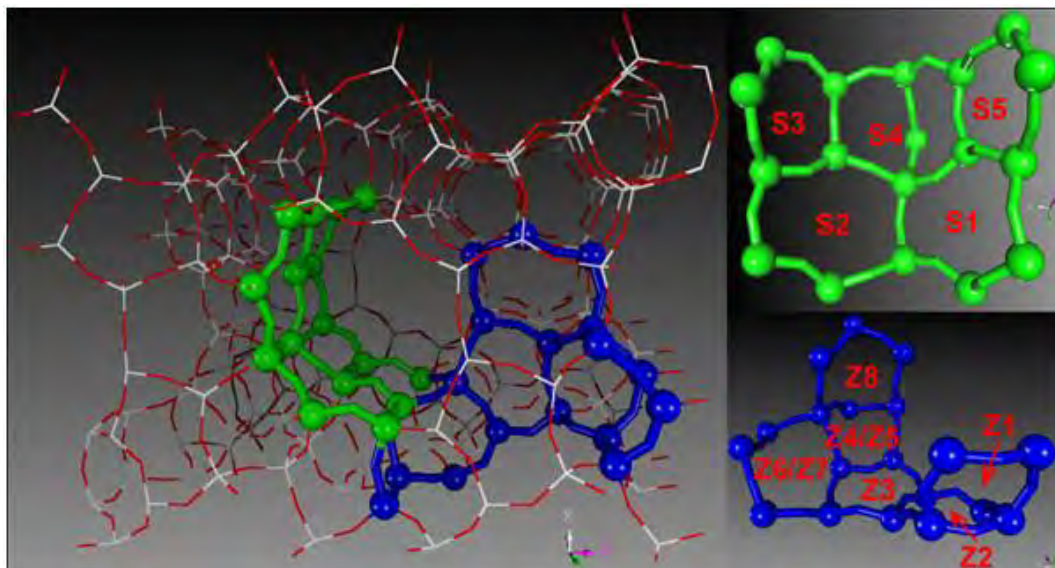


Heterobimetallic M-ZSM-5 zeolites

- **Location**

- **As oxide on surface**
 - No NO_x activity
- **As oxide in channels**
 - No NO_x activity
- **Partial replacement of aluminum**
 - Stores NH_3 and/or participate in NO_x reduction – Other cations should be able to store NH_3
- **Partial replacement of cation at M^+ sites**
 - Will act like a mixture of Cu-ZSM-5 and Fe-ZSM-5
- **Partial replacement of cation at $[\text{M-O-M}]^+$ sites**
 - Store NH_3 and/or participates in NO_x reduction

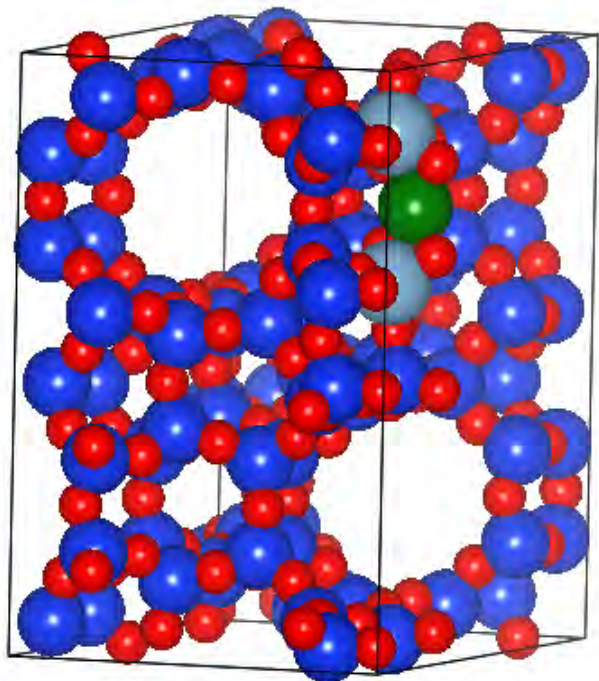
M-ZSM-5 catalysts



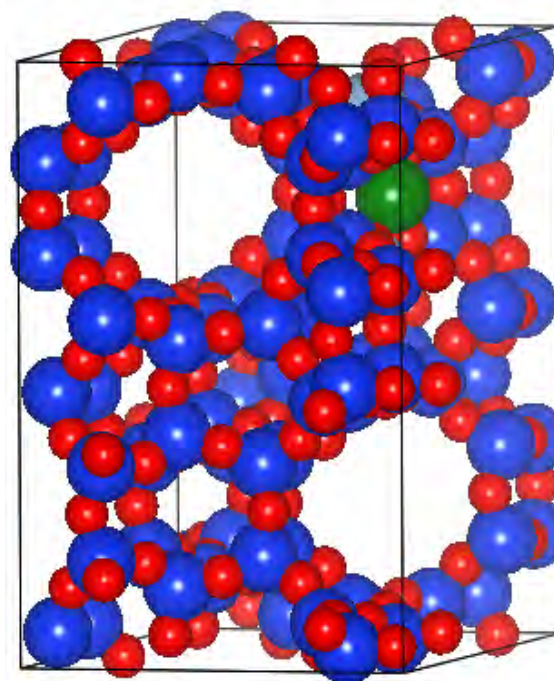
We carried our Density functional theory studies of Cu-ZSM-5 employing Vienna Ab Initio Software Package (VASP). We employed generalized gradient approximation (GGA) of Perdew and Wang. All Si ZSM5 structure was fully relaxed with respect to volume as well as cell-internal and –external coordinates.

- Possible locations of metal ions
- Mechanism
 - NO oxidation to NO_2
 - Reaction with NH_3

Lowest Energy Structures

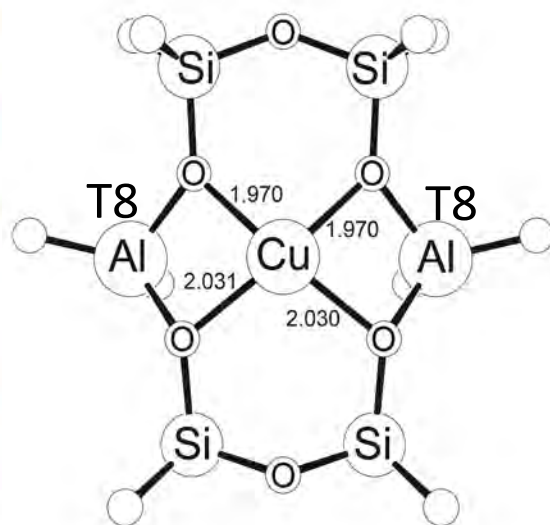
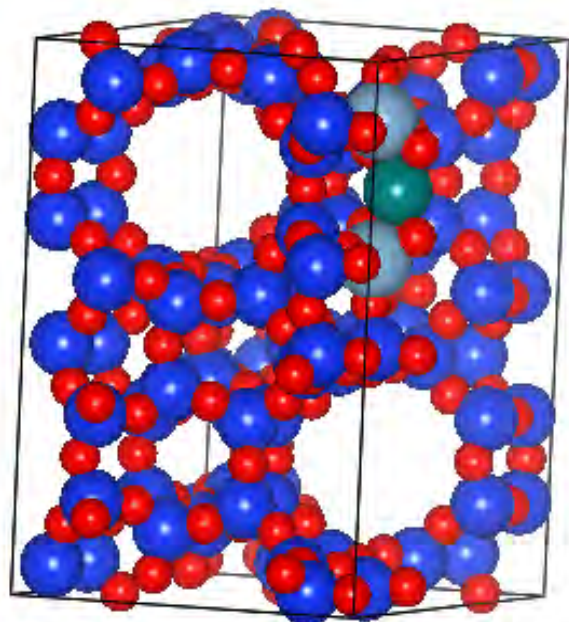


-2326.0142 eV
Cu-ZSM5 L1

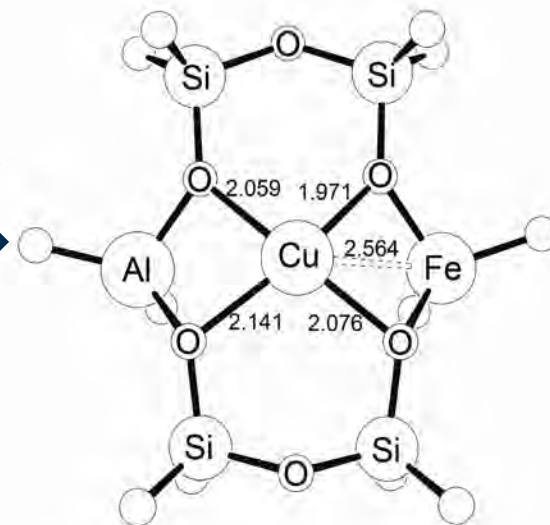


-2326.2133 eV
Cu-ZSM5 L2

Proposed Location of Fe in CuFe-ZSM5

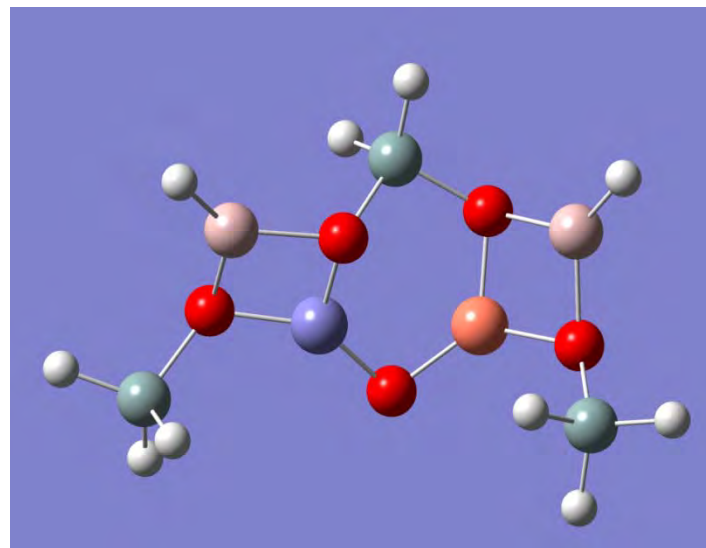
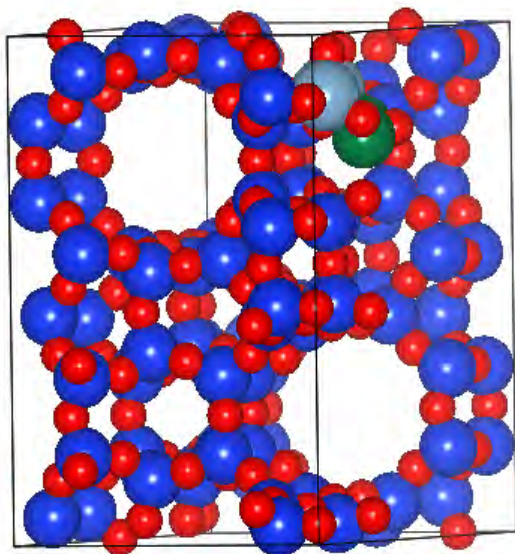
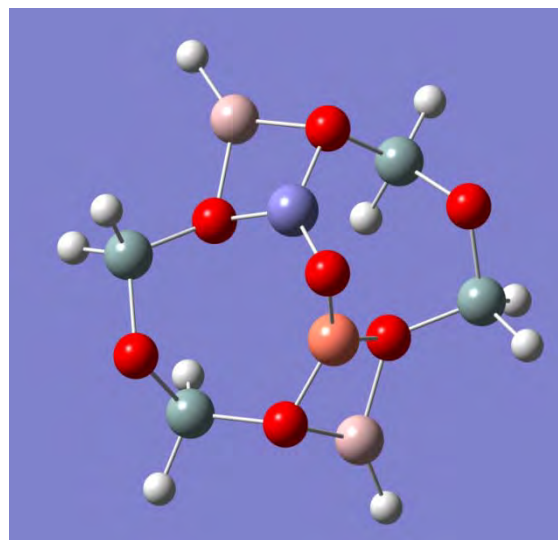
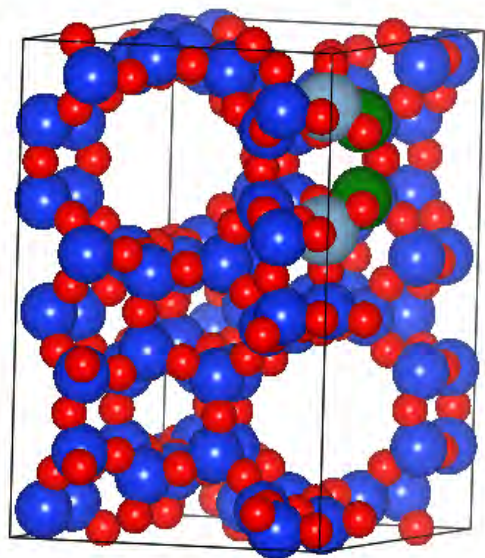


solution Fe^{3+}
exchange



- Single Cu^{2+} in Cu-ZSM-5 is generally believed to be in a square planar geometry, and coordinated by two anionic Al sites at T8 position.*
- We analyzed the electronic structure of the core using Gaussian 09', BP86/6-31G**(H, O, Si, Al) + LANL2DZ(Cu, Fe)
- One possible location analyzed i.e. replacement of Al with Fe
- No direct Cu-Fe interaction
- Possible NH_3 bonding site (i.e. iron) adjacent to NO oxidation site (i.e. Cu) can impact NO_x reduction
- If true, other elements which can bond NH_3 should also be effective e.g. In, Sc, La etc.

Partial Replacement of cations at [M-O-M]⁺ sites: Proposed Location of Fe in CuFe-ZSM5

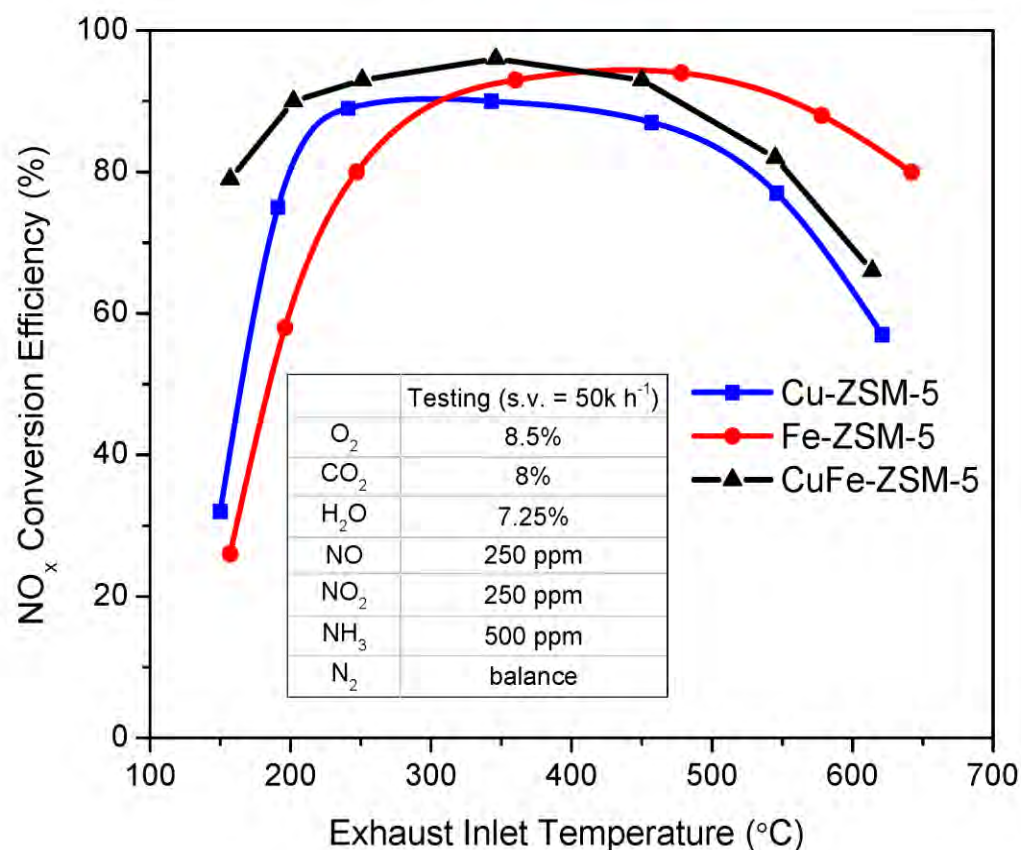


Heterobimetallic MFI Zeolite – A New Low Temperature NH₃ SCR Catalyst

a). Standard SCR reaction



b). Fast SCR reaction



➤ Cu-ZSM-5 and Fe-ZSM-5 are synthesized using literature procedures.

➤ Off-road degreening and testing protocols are provided by John-Deer Power System.

➤ CuFe-ZSM-5 shows **remarkable low temperature reactivity**, outperforming the mechanic mixture of Cu-ZSM-5 and Fe-ZSM-5. CuIn-ZSM-5 and Cu-Sc-ZSM-5 equally good.

➤ This research is sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC

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

- Catalyst by design approach can be effective in speeding up the discovery process
- The nanostructural studies of Pt nanoclusters on γ -alumina or θ -alumina show the presence of single atom and 10-20 atom Pt agglomerates. CO oxidation initiates at 160°C and completes at 170°C for both catalysts. Thus, the experimental evidence suggests that θ -alumina is a more appropriate model for γ -alumina than α -alumina.
- Single atoms of Pt are in zero oxidation state which is different from DFT structures of Pt on α -alumina.
 - Pt occupied a position between two surface oxygen atoms above aluminum
 - The adsorption energy is -62.9 kcal/mole .
 - The zero oxidation state suggests that CO oxidation can occur by O₂ addition and CO insertion intermediates..
- We describe new heterobimetallic MFI zeolites that exhibit high NO_x conversion efficiencies at 150°C.

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

➤ Overcoming Barriers

- We demonstrate that iterative application of theory, experimental studies, and nanostructural characterization can advance catalyst discovery process
- For supported catalyst, we are developing theoretical basis to new thermally stable catalyst discovery which can reduce the use of precious metals
- For NH_3 -SCR activity, the theoretical models facilitate discovery of new low temperature zeolites.

➤ Barriers addressed

- Changing internal combustion engine combustion regimes
- Long lead times for materials commercialization
- Many advanced vehicle technologies rely on materials with limited domestic supplies

Collaboration

➤ Technology Transfer

- Ongoing work with Dr. Danan Dou and Dr. Alex Kozlov of John Deere
 - Work-for-others arrangement on NO_x treatment for off-road vehicles
 - Jointly funded project on NO_x treatment from DOE-ITP office
- Technology is applicable to passenger vehicles also and will be implemented simultaneously in both off-road and on-highway sectors

Activities for Next Year

- Study of CO, NO_x and HC oxidation on Pt/ θ -Al₂O₃ system
 - Theoretical models
- Bimetallic systems to alleviate Pt sintering
 - Theoretical studies
 - Synthesis of sub nanometer particles
- SCR catalyst
 - Understanding the role of heteroatom

Acknowledgements

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- J. Gibbs, Technology Development Manager
- J. Eberhardt, Technology Area Development Specialist