

Catalysts via First Principles

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Physical Chemistry of Materials, Materials
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**DOE VEHICLE TECHNOLOGIES
PROGRAM ANNUAL MERIT
REVIEW, FY 2010**

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Project PM011

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start: Oct. 2004
- Finish: Sep. 2011

Budget

- Funding received in 2008
 - 225,000
- Funding received in 2009
 - 225,000
- Funding received in 2010
 - 166,137

Barriers

- Performance: Materials needed to achieve the performance objectives in specific engine and ancillary components may not exist today as
 - durable
 - reliable
 - well-characterized and understood materials.

Partners

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

Objectives

To assist DOE complete the development of materials solutions that will enable improvement of fuel economy of light-duty gasoline vehicles by 25%, light-duty diesel vehicles by 40% compared to 2009 gasoline vehicles while meeting EPA 2010 emissions standards.

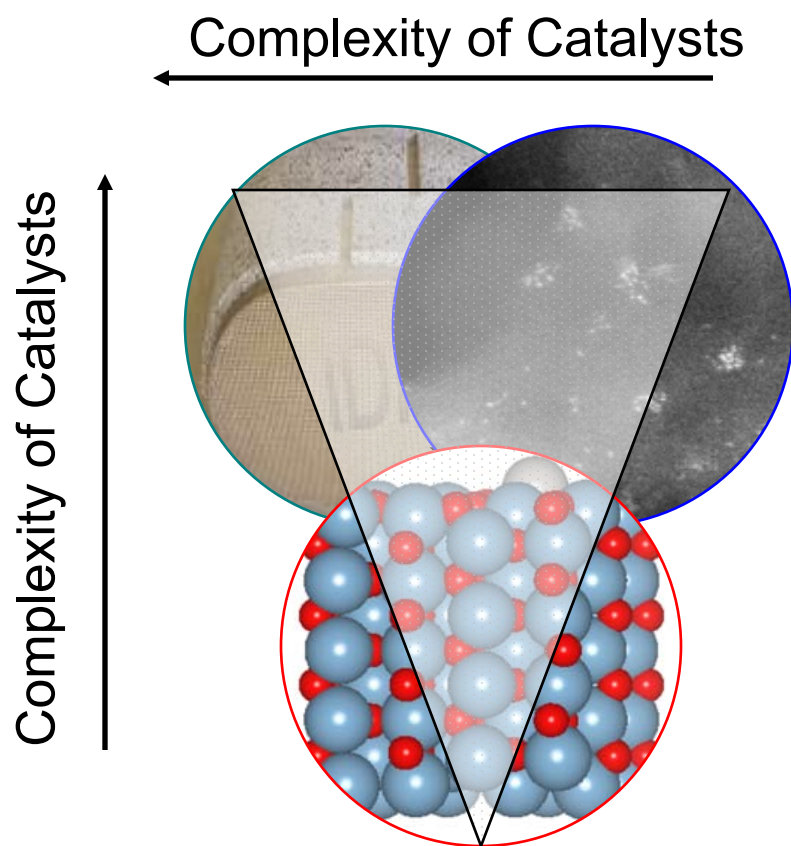
- The project is precursor to "Materials by Design" approach including "Catalyst by Design" and is focusing on designing catalyst systematically rather than by trial and error.
- To demonstrate that we can examine catalyst system by first principle theoretical models, experimental studies, and nanostructural 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

- Performance: Materials needed to achieve the performance objectives in specific engine and ancillary components may not exist today as durable, reliable, well-characterized and understood materials.
 - 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

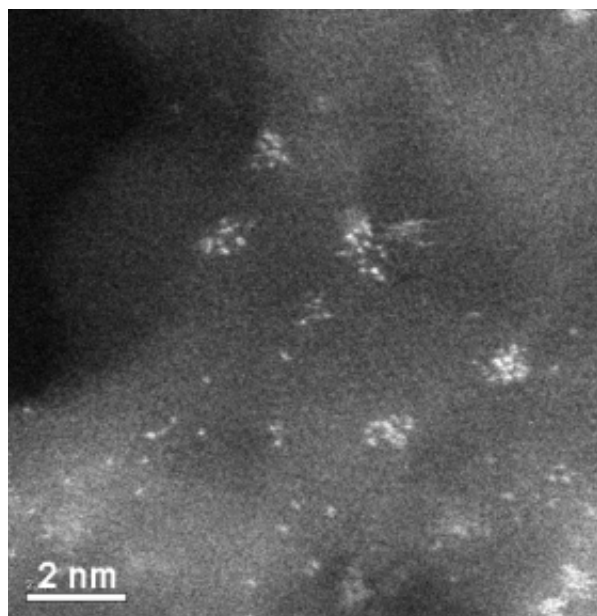
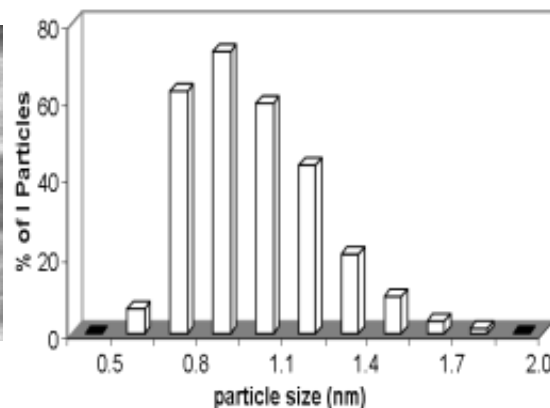
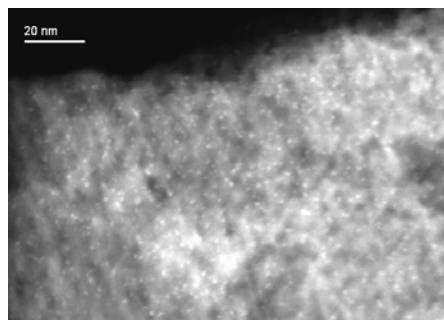
Supported clusters (Pt, Rh) are integral part of vehicle emission treatment catalysts such as oxidation catalyst, three-way catalyst, lean NO_x traps, diesel particulate filters. For lean burn NO_x treatment, urea-selective catalytic reduction (SCR) is currently leading technology and is based on zeolites.



- 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

C.K. Narula, "Catalyst by Design", Encyclopedia of Nanoscience and Nanotechnology, Taylor & Francis, New York, 2008, pp 771-782.

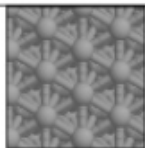
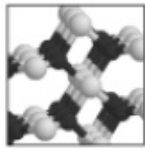
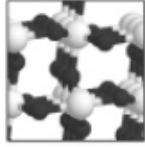
Pt/ γ -Al₂O₃



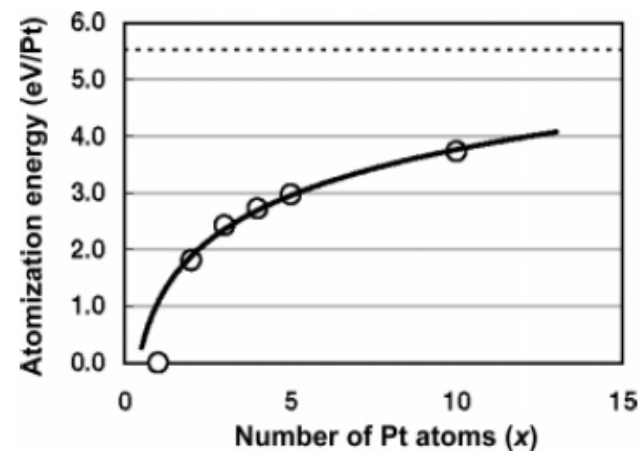
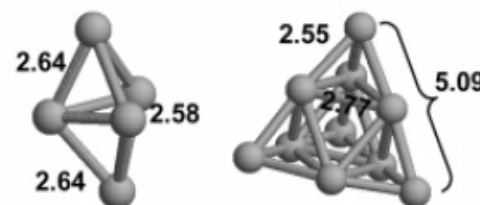
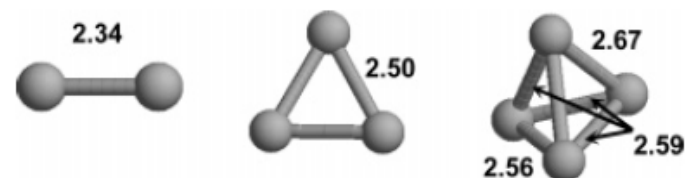
- STEM analysis shows that platinum particle size ranges from 0.6-1.9 nm and the distribution is centered at 1.0 nm
 - A common observation reported in literature
 - Recent EXFAS & XANES study suggest thermally mediated interaction between Pt and support resulting in Pt-Pt bond contraction (JACS, 128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

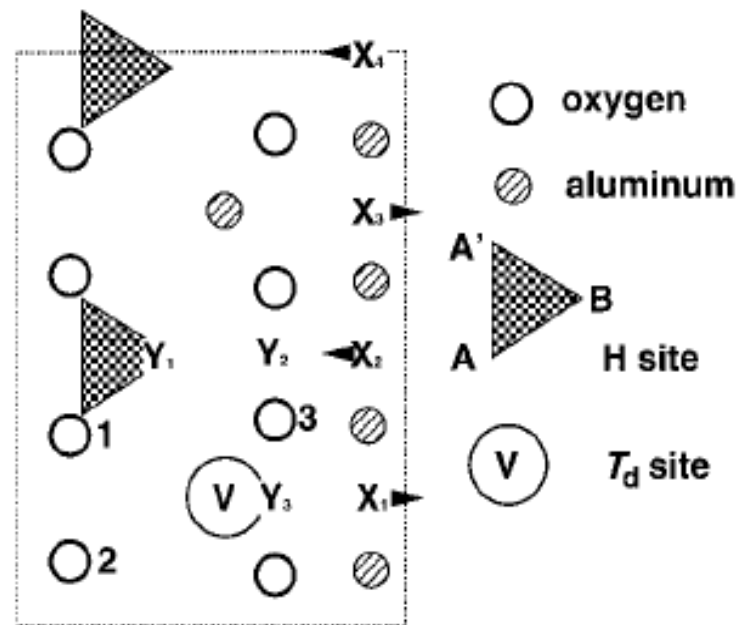
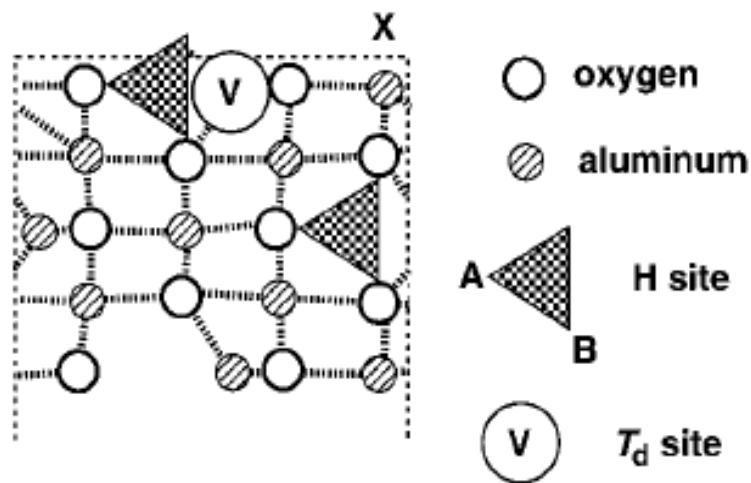


- **3-D structures generally preferred. Optimal structures are shown with some bond distances that match with experimentally observed ones for dimers.**
- **Atomization energy increases monotonically with cluster size i.e. atoms are held together more strongly as the cluster size increases**

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



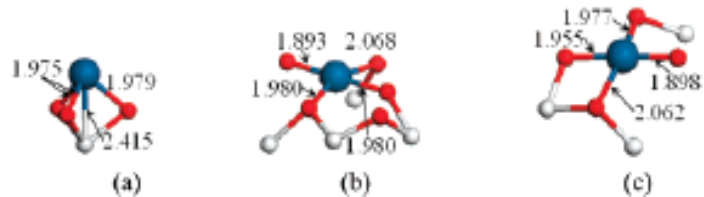
This structure has Pt-Pt bond distances of 2.6, 2.6, and 3.3 Å. If this structure is capped with –OH, the bond distances are 2.6, 3.1, 3.6 Å which are in good agreement with experimental values.

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.

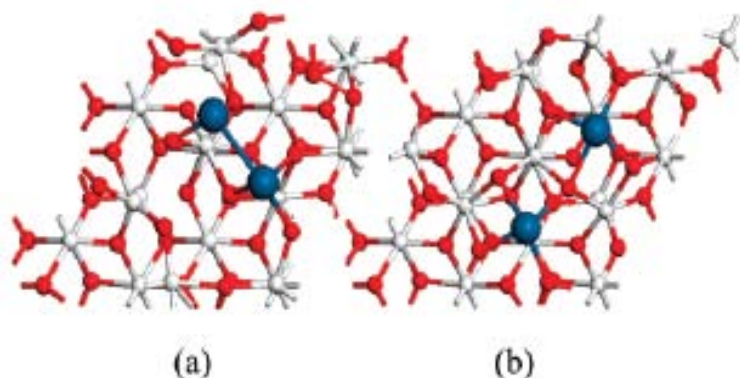
Oversimplified structure of $\gamma\text{-Al}_2\text{O}_3$ employed in these models

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

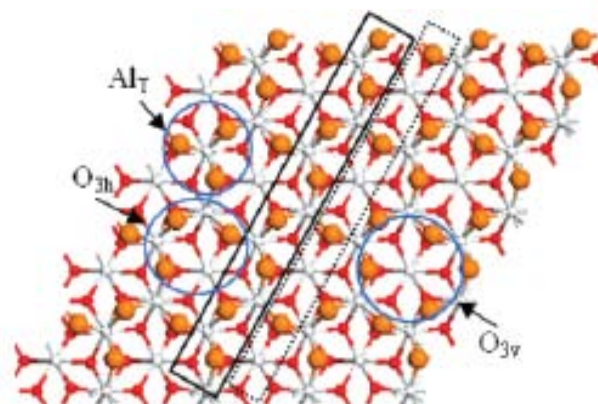
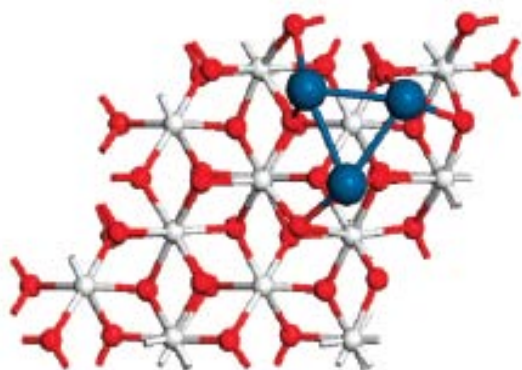
Pt/ α - Al_2O_3



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



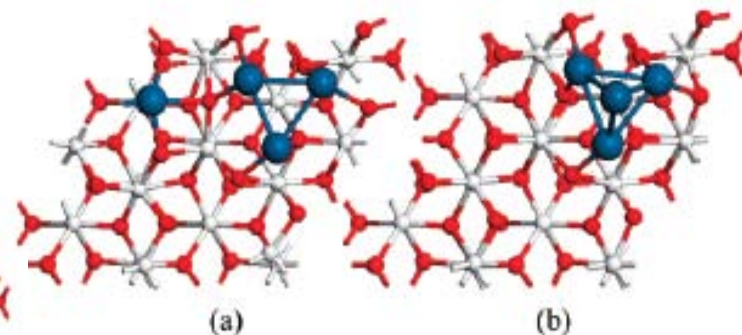
a. $\text{Al}_T\text{-Al}_T$ b. $\text{O}_3\text{-O}_3$



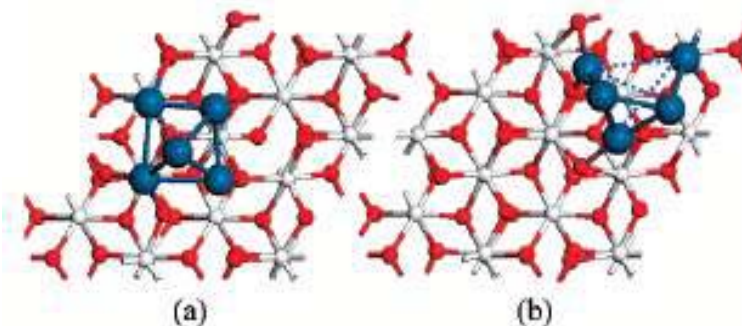
Al_T = 2 zigzag O and 1 linear O attached to single Al

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

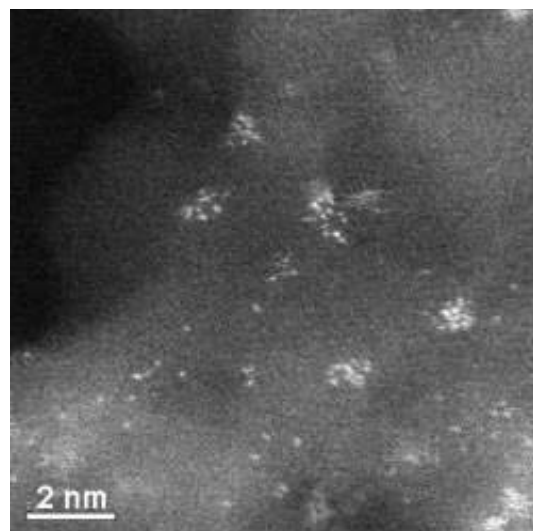


a. Square pyramid b. triangular bipyramid

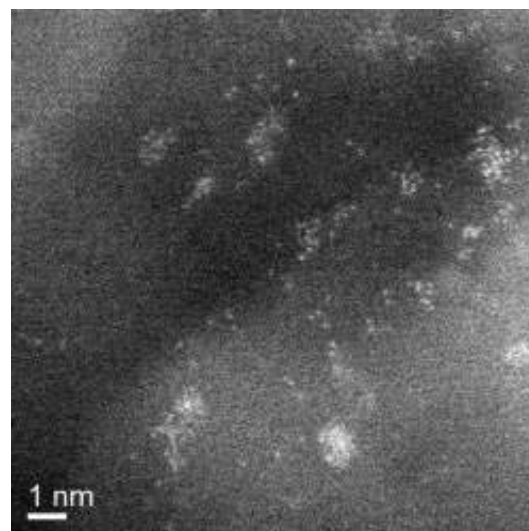
- O_3 site strongly preferred
- Clusters larger than 3 prefer to interact with substrate via its triangular face
- Adhesion declines with increase in size

Pt₃ equilateral triangle adsorption structure

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



Pt/ γ -alumina

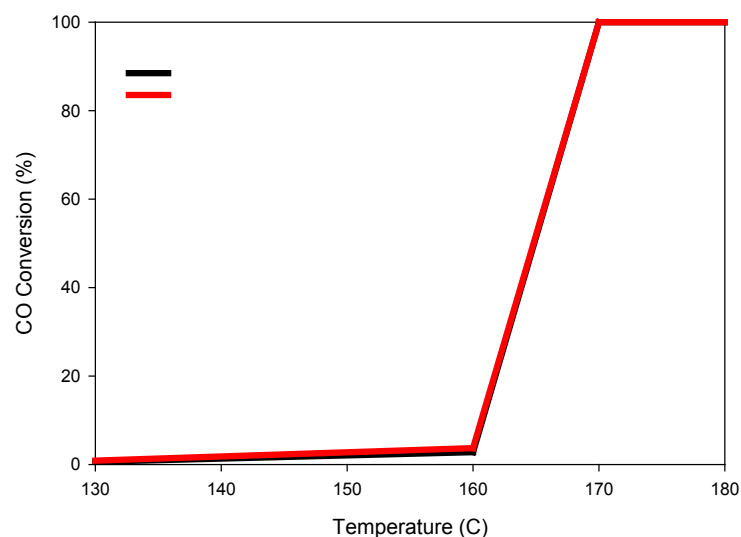


Pt/ θ -alumina

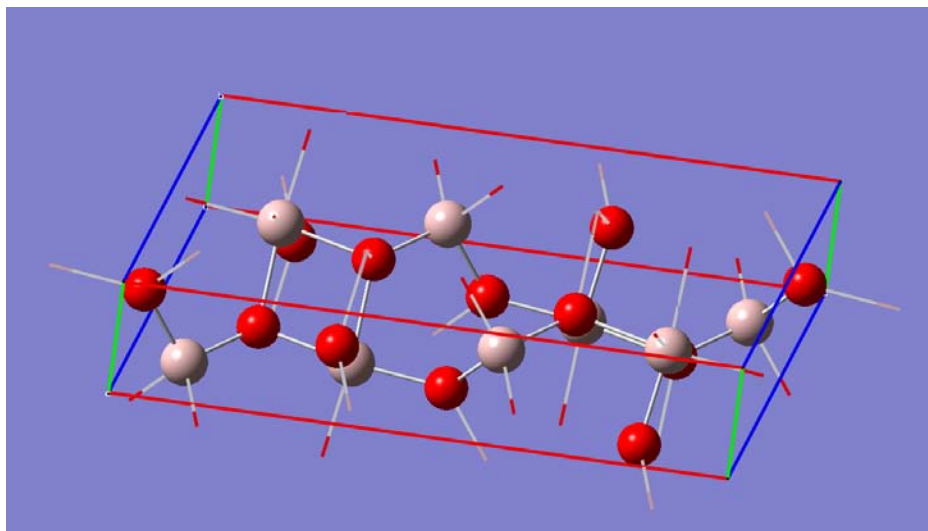
- ACEM ADF-STEM images of fresh Pt/ γ -alumina and Pt/ θ -alumina show a bimodal distribution – single atoms and 10-20 atom agglomerates.

- The BET surface areas of γ - and θ -alumina are 200 m²/g and 100 m²/g, respectively

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

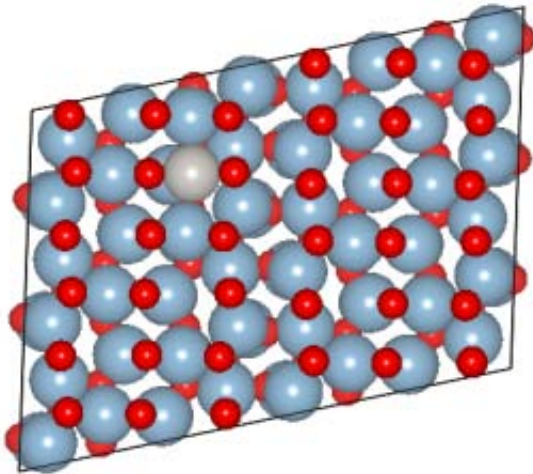
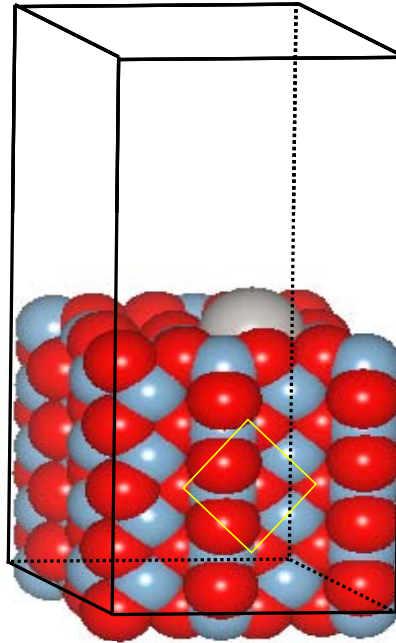
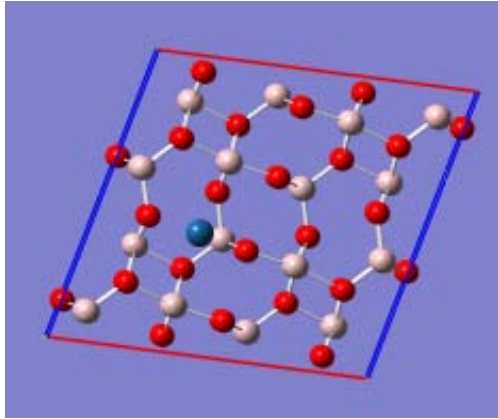


Modeling Pt/ θ -Al₂O₃

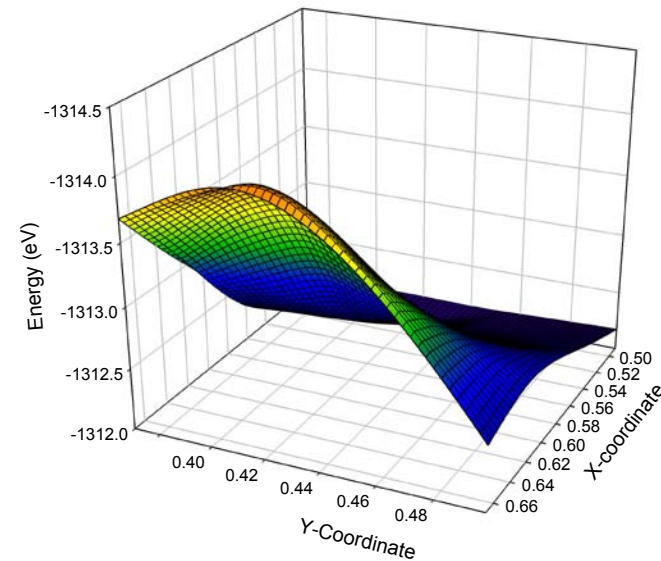
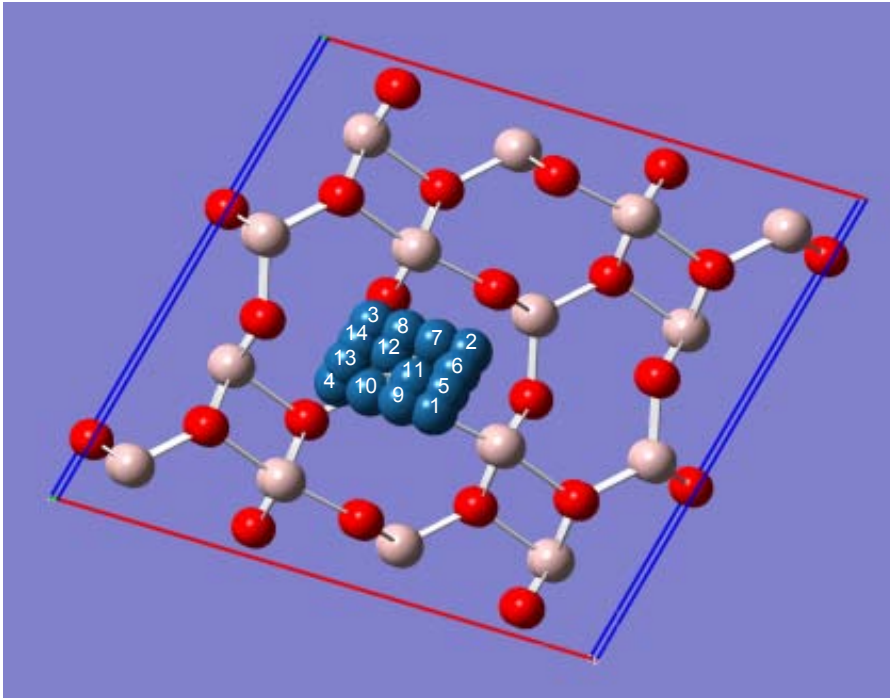


Density Functional Theoretical Calculations were performed for generalized gradient approximation (GGA) of Perdew and Wang. The structure was fully relaxed with respect to volume as well as cell-internal and –external coordinates. Extensive test indicated that 600 eV was a sufficient cut-off to achieve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

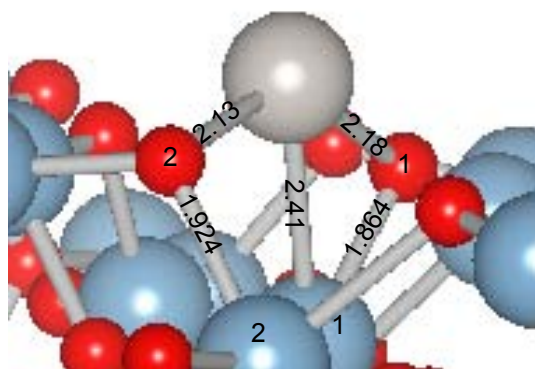


- The charge neutral surface was constructed from a 2x4x2 supercell and a vacuum of 15Å. This cell contains 180 atoms
 - Lodziana, Z.; Topsoe, N-Y. ; Norskov, J.K.; Nature Materials, 2004, 3, 289
- A larger charge neutral surface was constructed from 2x3x3 supercell and a vacuum of 15Å. This cell contains 420 atoms



- **Platinum surface mapping by fixing x- and y-coordinate and allowing z-coordinate to vary. Lowest energy deviation from optimized position is for position 13 which is just above the optimized position.**

Pt - Bonding



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

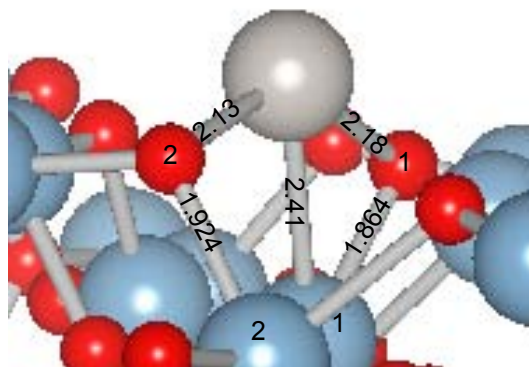
- Platinum occupies a position between two surface oxygen atoms

- 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)
- Noticeably, Pt-O1 and Pt-O2 distances bond distances are not identical because the Pt-O1 bond distance is influenced by the bonding of O1 to subsurface aluminum which is 2.41 Å apart from platinum atom
- The O1-Al1 bond is 1.864 Å which is shorter than O2-Al2 bond (1.9238 Å). Strengthening of O1-Al1 bond affects Pt-O1 interaction.

- This structure is different from Pt/ α -Alumina where Pt atom is atop surface oxygen and

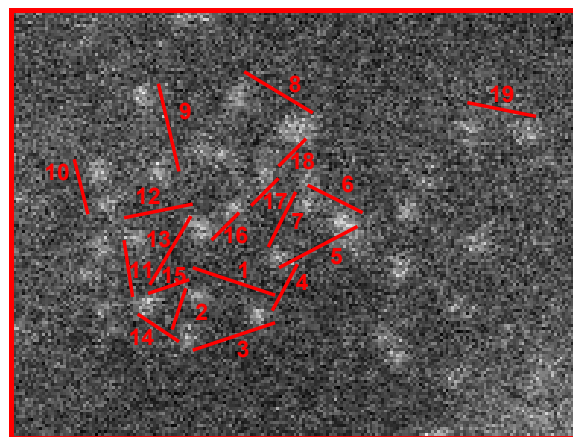
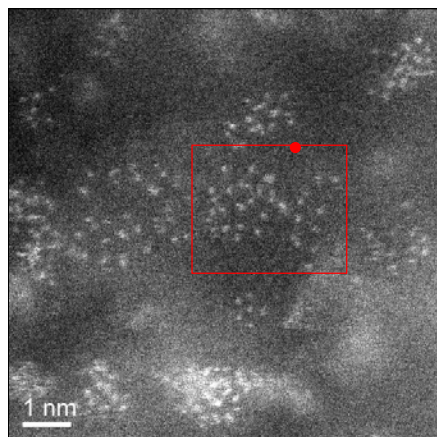
- Calculated Pt-O distance is 2.02Å. The adsorbed platinum atom is paramagnetic
- The interaction of Pt with surface is summarized as localized covalent bonding between Pt and O enabled by nearly Al-centered electron-accepting empty states available to accept excess electron density

Bonding of other noble metals



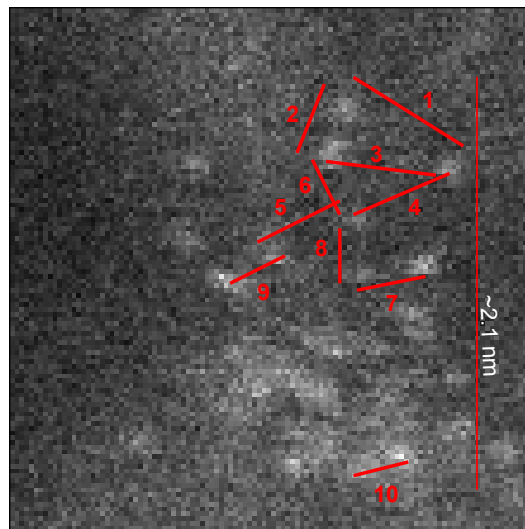
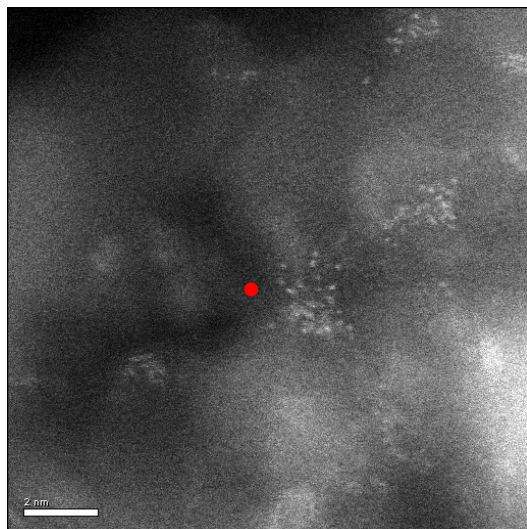
M	Adsorption Energy (Kcal/mole)	M-O1 (Å)	M-O2 (Å)	M-H1 (Å)
Pd	-44.84	2.227	2.201	2.49
Au	-20.21	2.45	2.69	2.706
Ag	-13.23	2.483	2.549	3.08

Larger Agglomerates



Pt/ θ -Al₂O₃

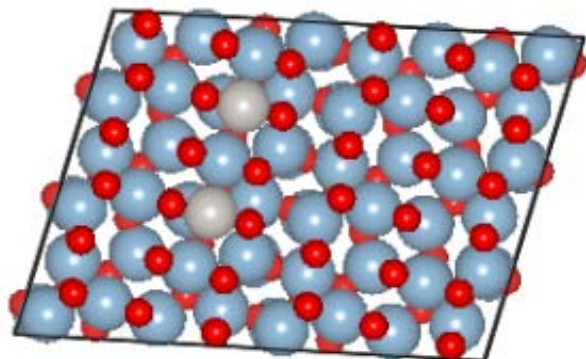
1	3.82	6	2.6	11	4.0	16	2.27
2	2.61	7	3.64	12	3.8	17	2.79
3	4.53	8	3.97	13	5.53	18	3.14
4	3.45	9	4.87	14	3.28	19	3.65
5	3.45	10	2.09	15	3.3		



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

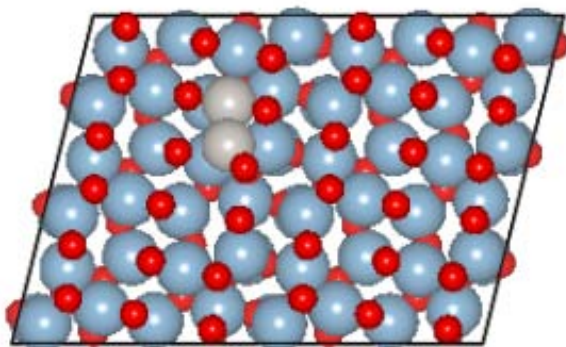


Pt1-O1	2.192Å
Pt1-O2	2.13Å
Pt1-Al	2.395Å
Pt2-O1	2.198Å
Pt2-O2	2.135Å
Pt2-Al	2.387Å

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

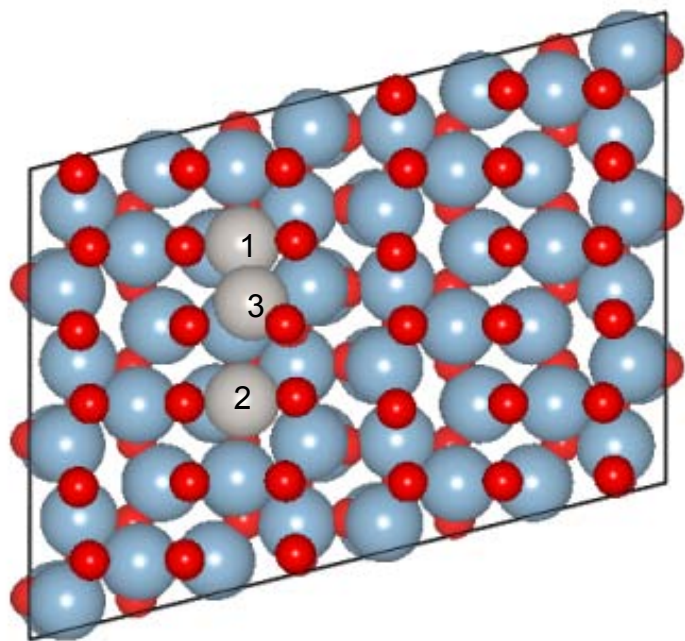
0.6 Kcal/mole



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

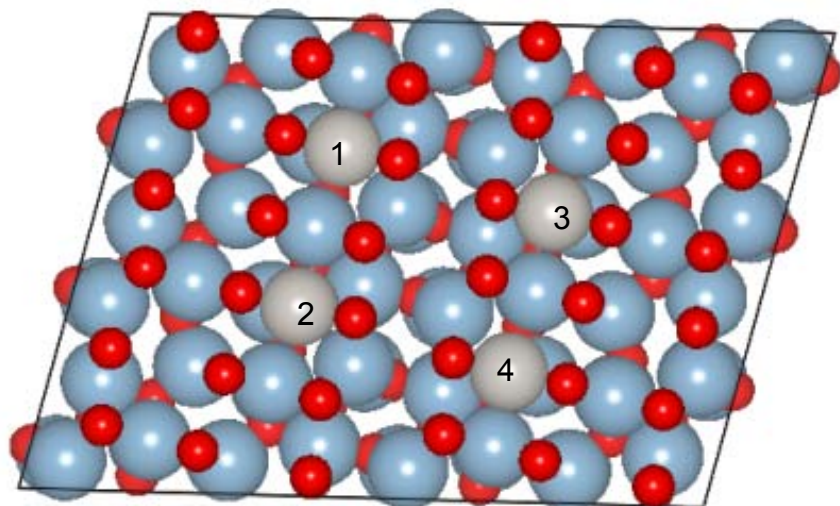
Pt-O1	2.176Å
Pt-O2	2.095Å
Pt-Al	2.428Å
Pd-Pt	2.57Å
Pd-Al	2.52Å

More than two 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	2.517Å
Pt3-Al	2.439Å

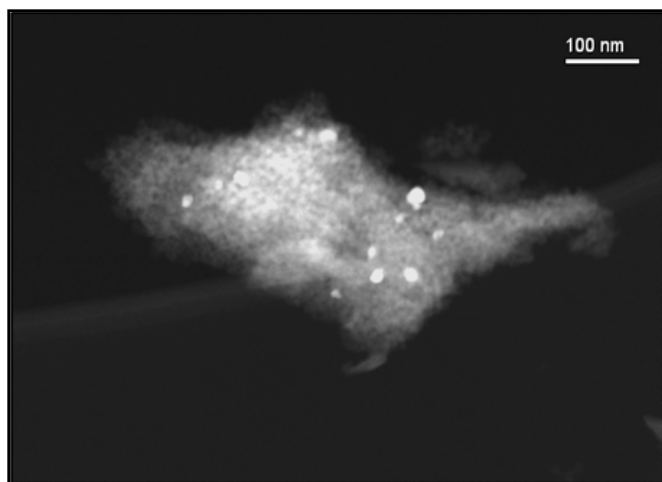
Pt1-O1	2.20Å
Pt1-O2	2.121Å
Pt1-Al	2.429Å
Pt2-O1	2.20Å
Pt2-O2	2.126Å
Pt2-Al	2.419Å
Pd-Pt1	2.763Å
Pt3-Al	2.38Å



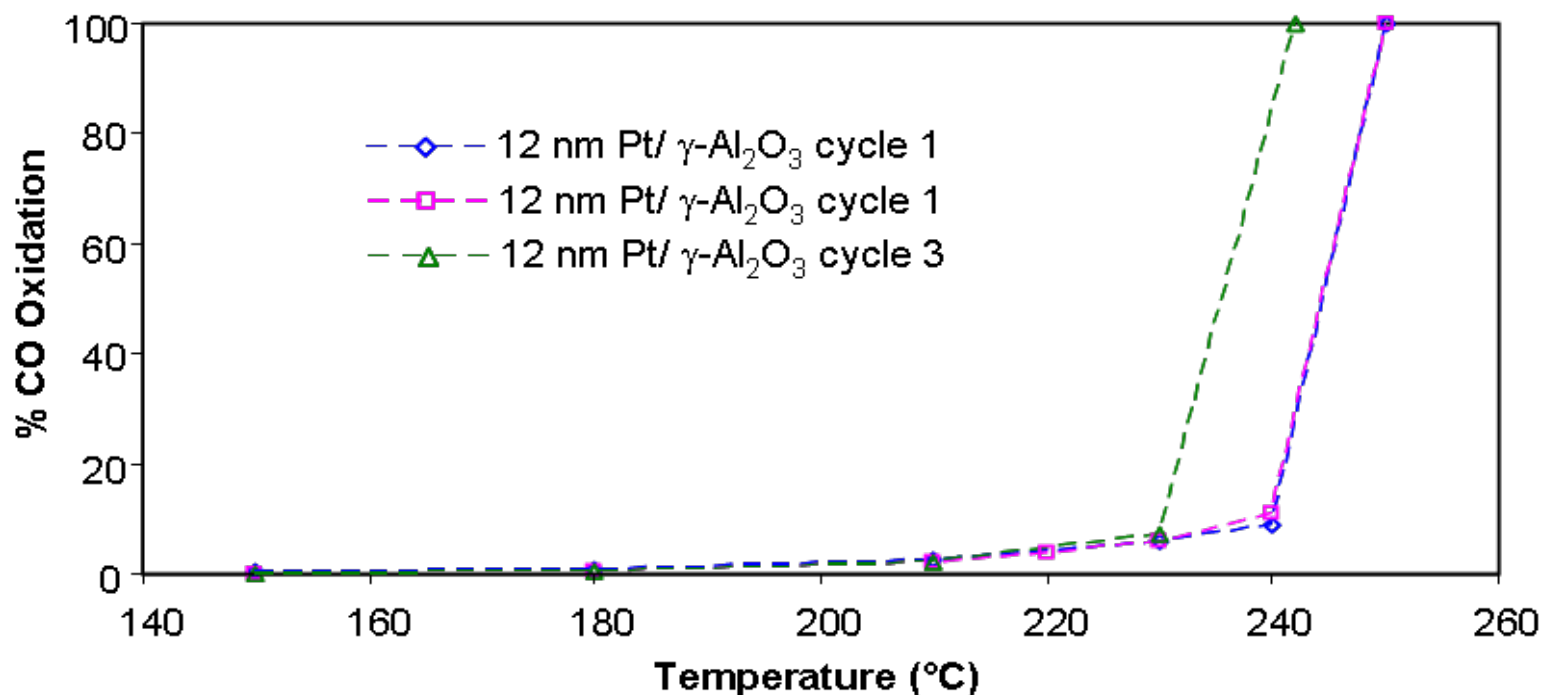
Pt1-O1	2.192Å	Pt1-O2	2.132Å
Pt2-O1	2.202Å	Pt2-O2	2.129Å
Pt3-O1	2.135Å	Pt3-O2	2.213Å
Pt4-O1	2.138Å	Pt4-O2	2.214Å
Pt1-Pt2	5.73Å	Pt1-Pt3	7.67Å

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

CO Oxidation – Structural Changes in Pt-Particles supported on γ -Al₂O₃: Particle Size Effect

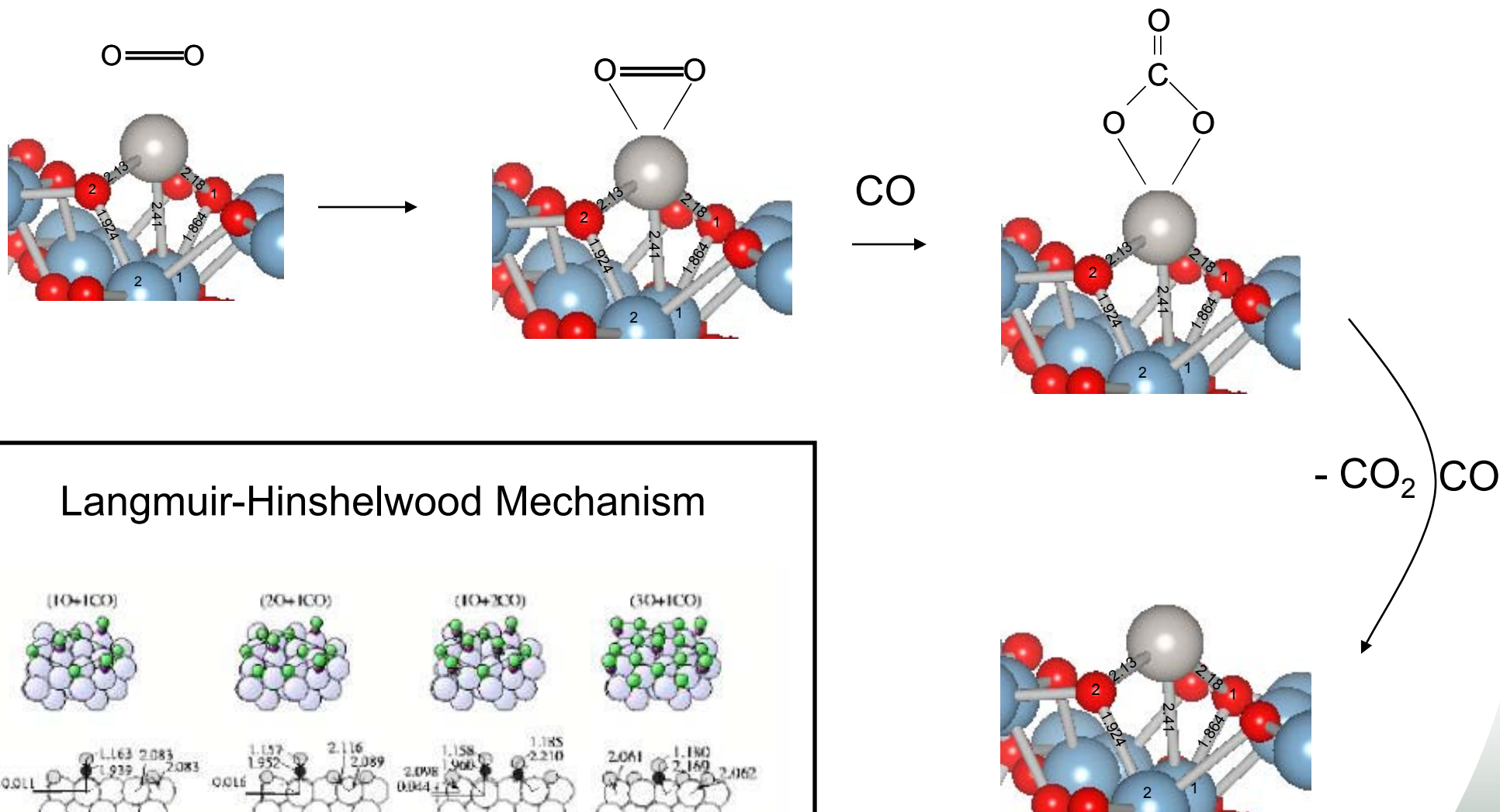


STEM analysis shows that platinum particle size distribution is centered at ~12 nm with some large particles in 20-40 nm range

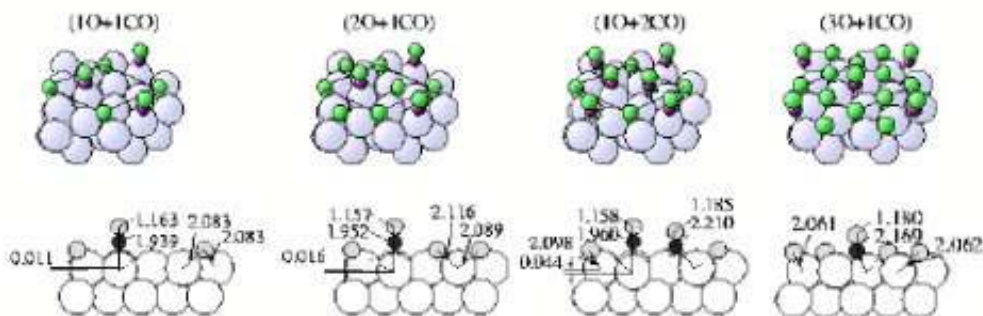


Metal – CO Oxidation

Eley-Rideal Mechanism

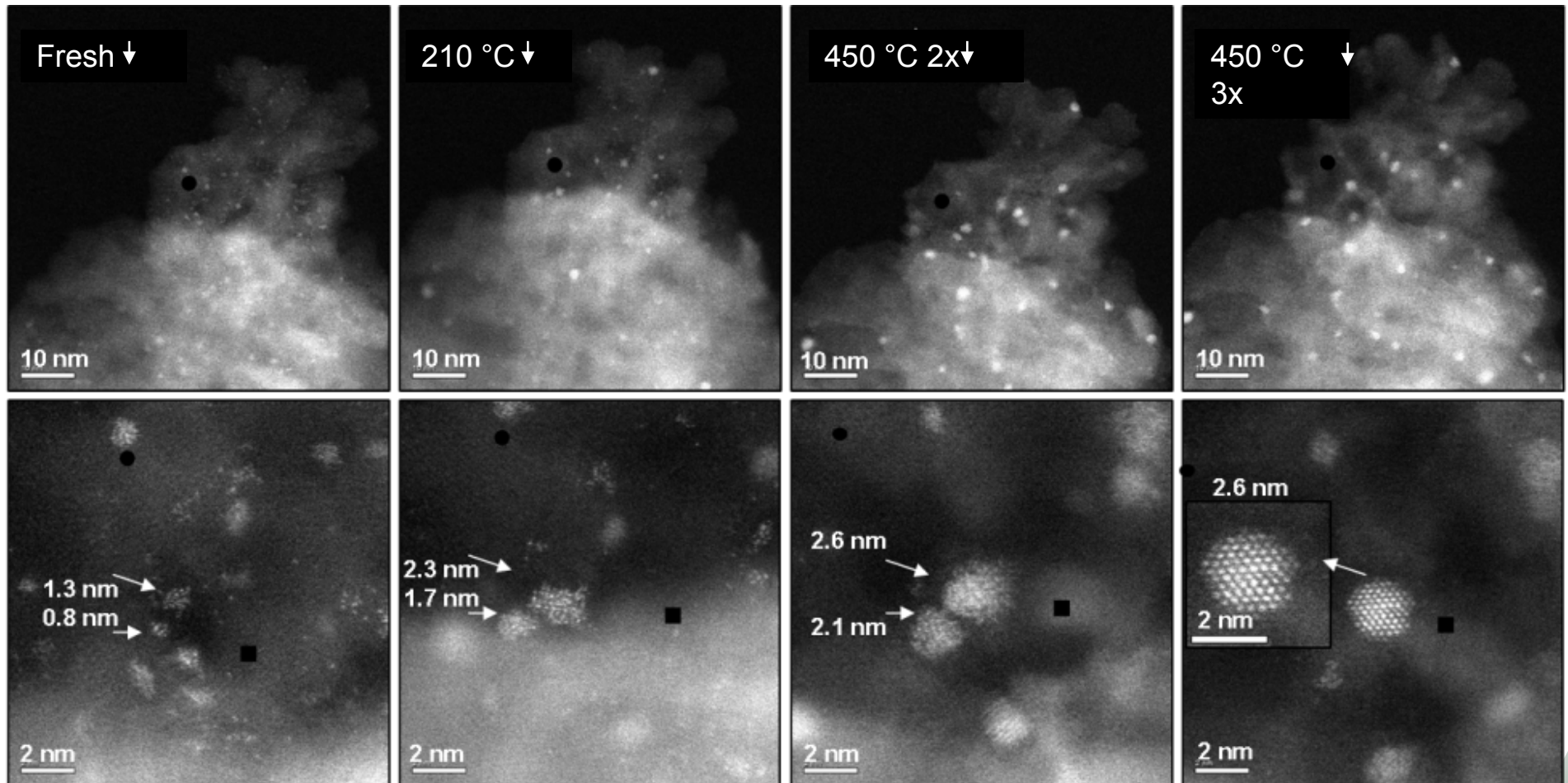


Langmuir-Hinshelwood Mechanism



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

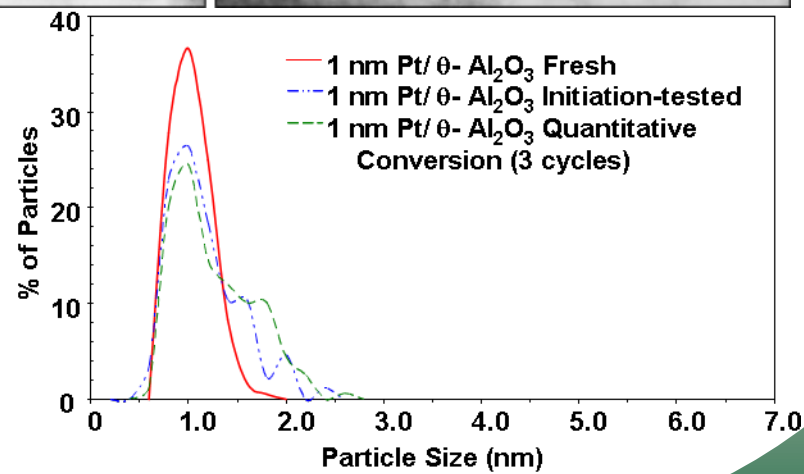
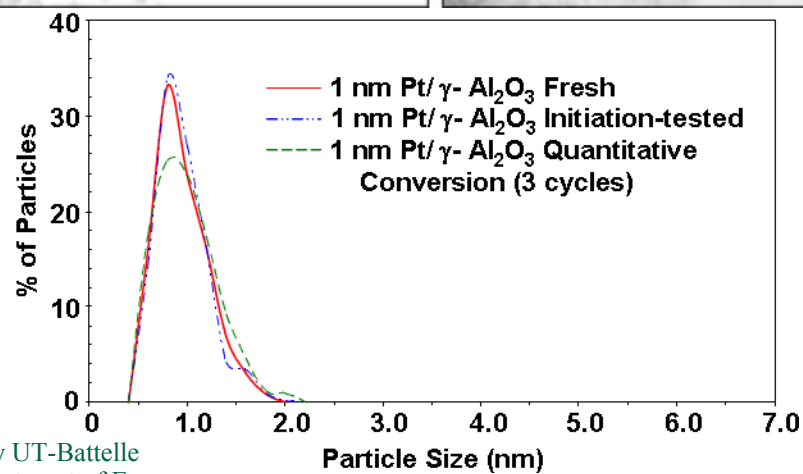
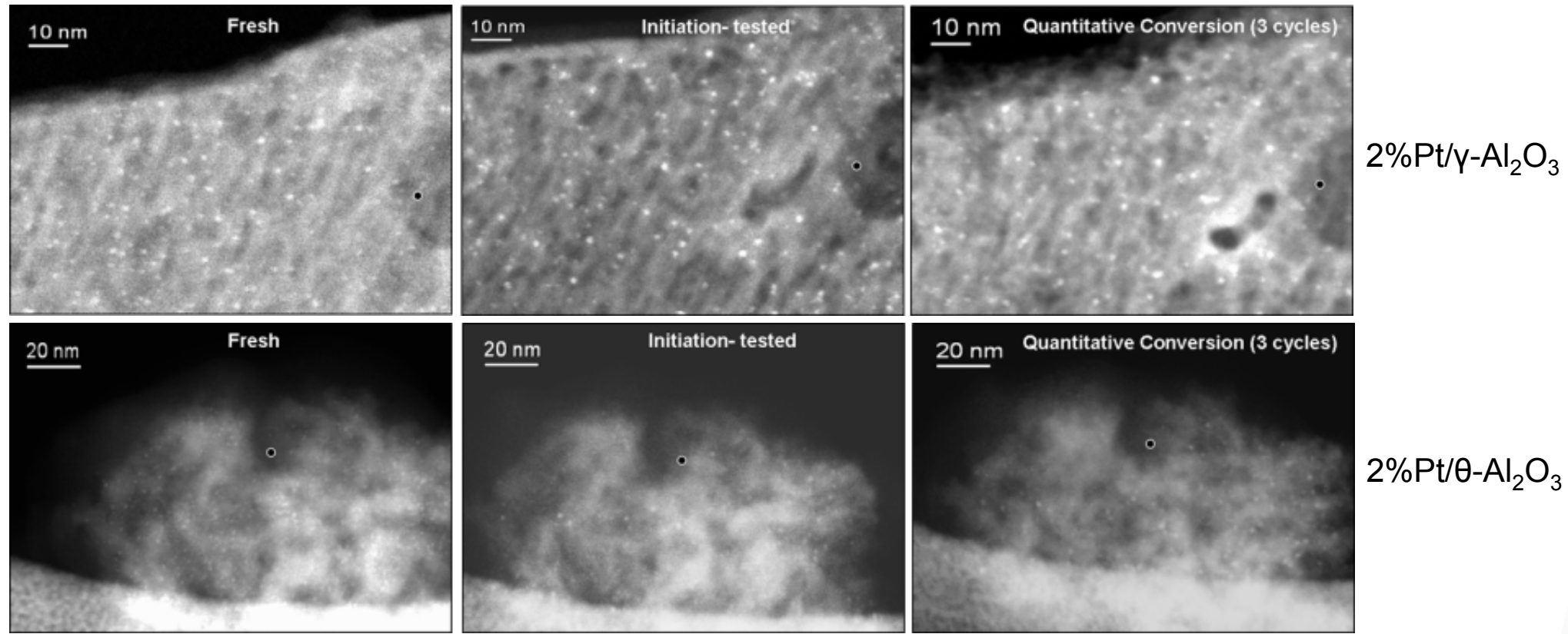
Ex-situ Reactor Studies



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

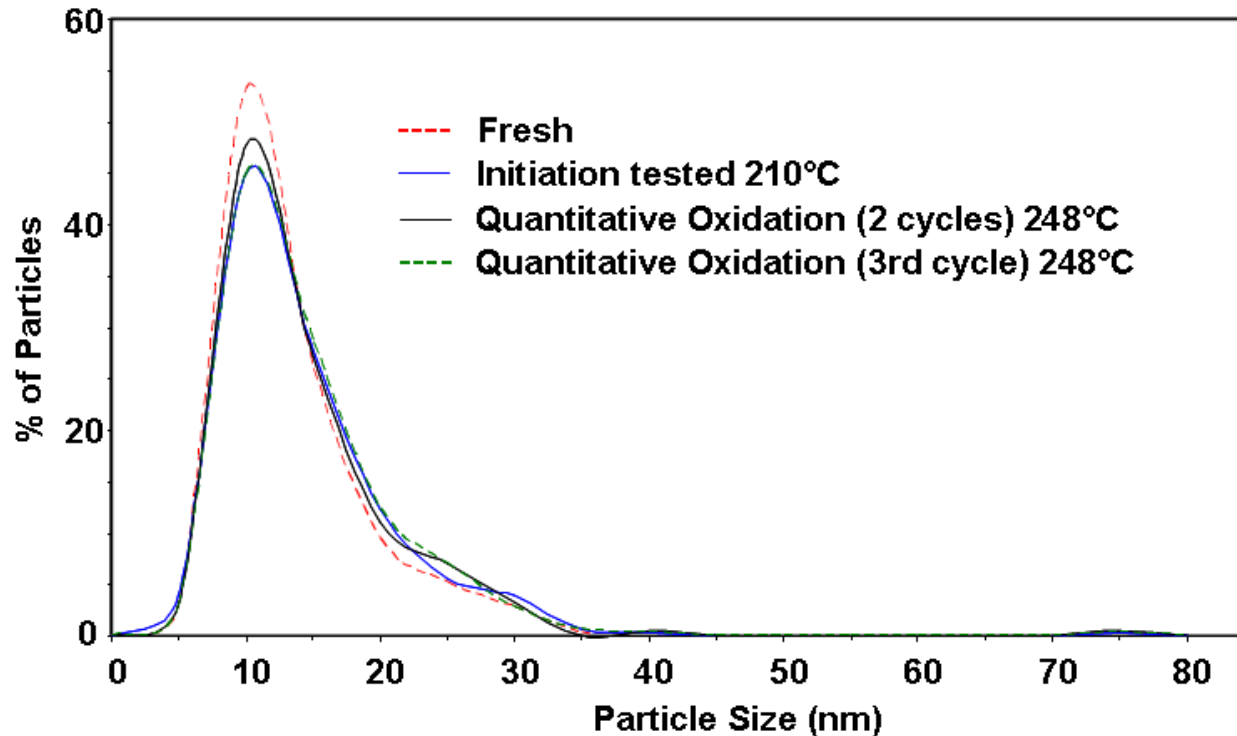
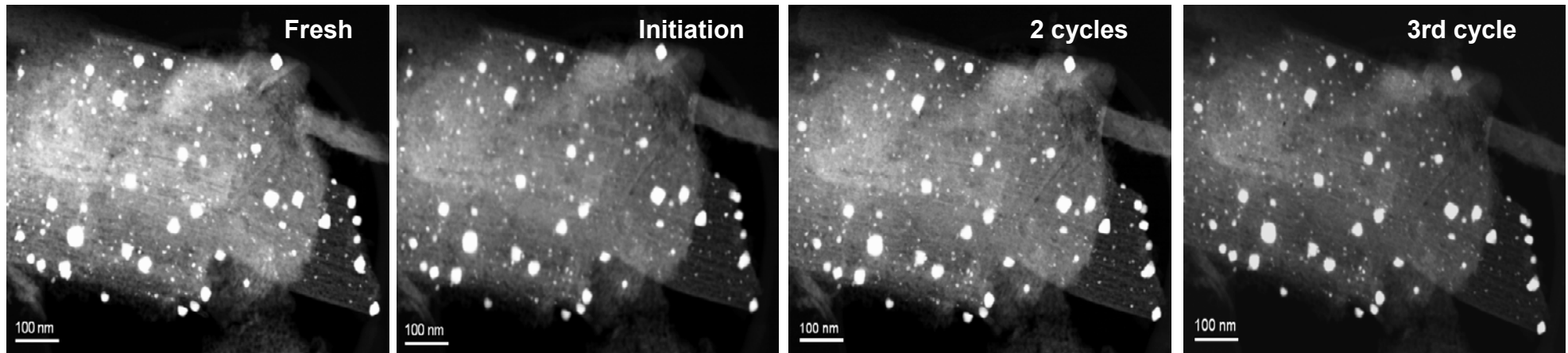
CO Oxidation – Structural Changes in Pt-Particles supported on θ - Al_2O_3 : Substrate Morphology Effect

CO oxidation *Ex-situ* Reactor Studies



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

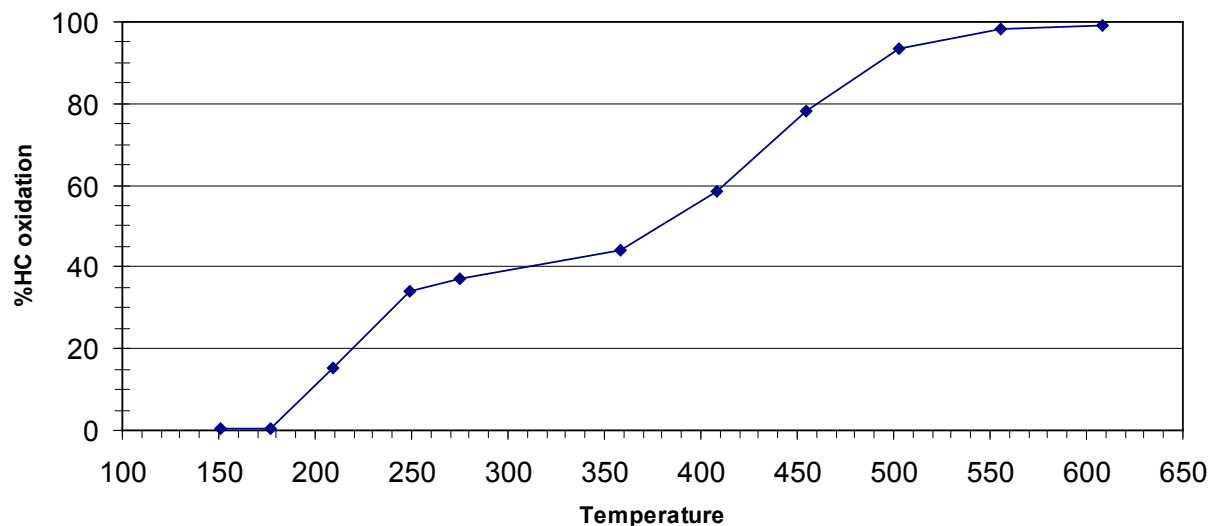
Ex-situ Reactor Studies



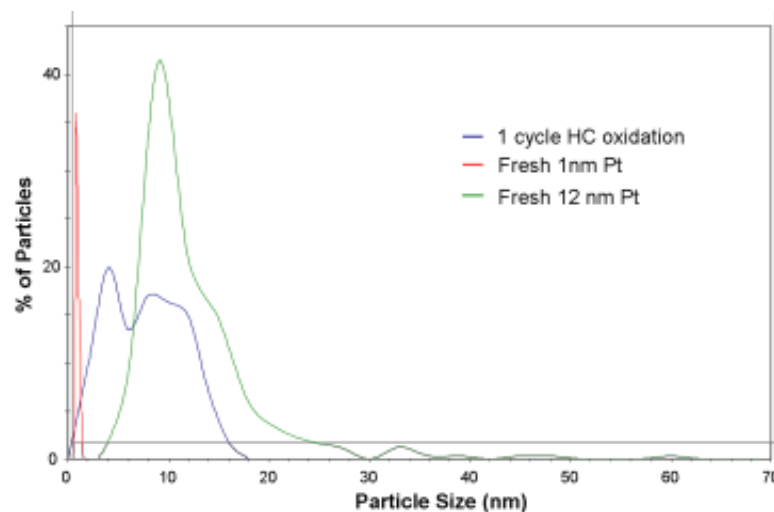
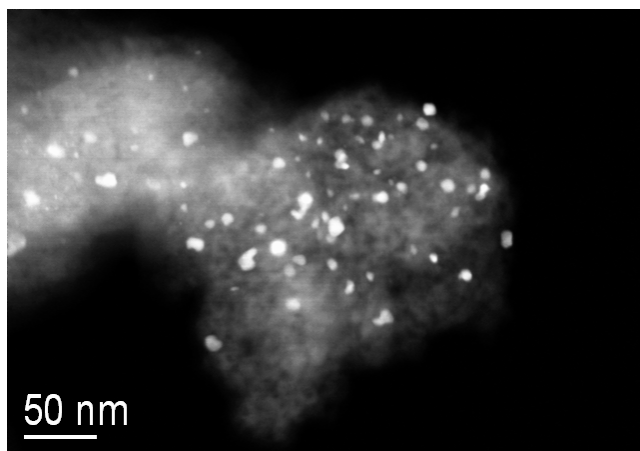
Ex-situ reactor study suggests essentially no change after three cycles of CO oxidation

Hydrocarbon Oxidation – Structural Changes in Pt-Particles supported on γ -Al₂O₃

1 nm 2% Pt/ γ -Al₂O₃

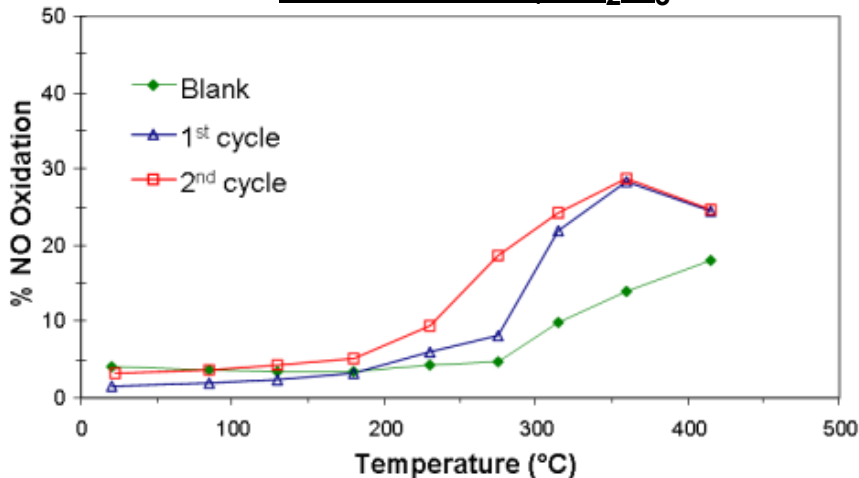


- A 500 ppm mixture of Propane and Propene in 1:2 ratio with 10% O₂ and balance N₂ at ~50k h⁻¹ space velocity
- The oxidation begins at 180°C and completes at 600°C
- Pt particles grow rapidly (range 1.3-15.2 nm). This is not surprising since thermal treatment at 650°C can also lead to ~12 nm particles.

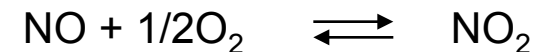


NO Oxidation – Structural Changes in Pt-Particles supported on γ -Al₂O₃

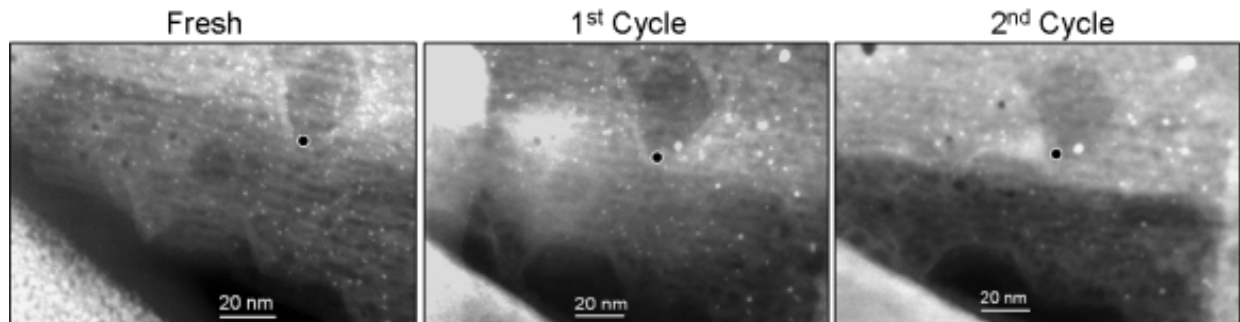
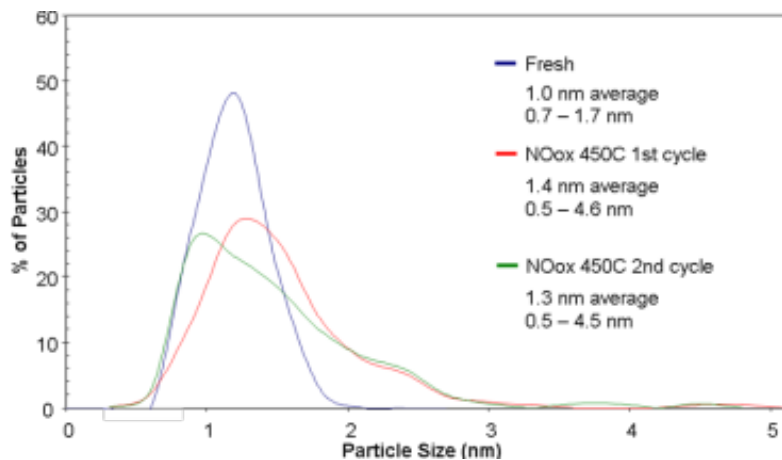
1 nm 2% Pt/ γ -Al₂O₃



- 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



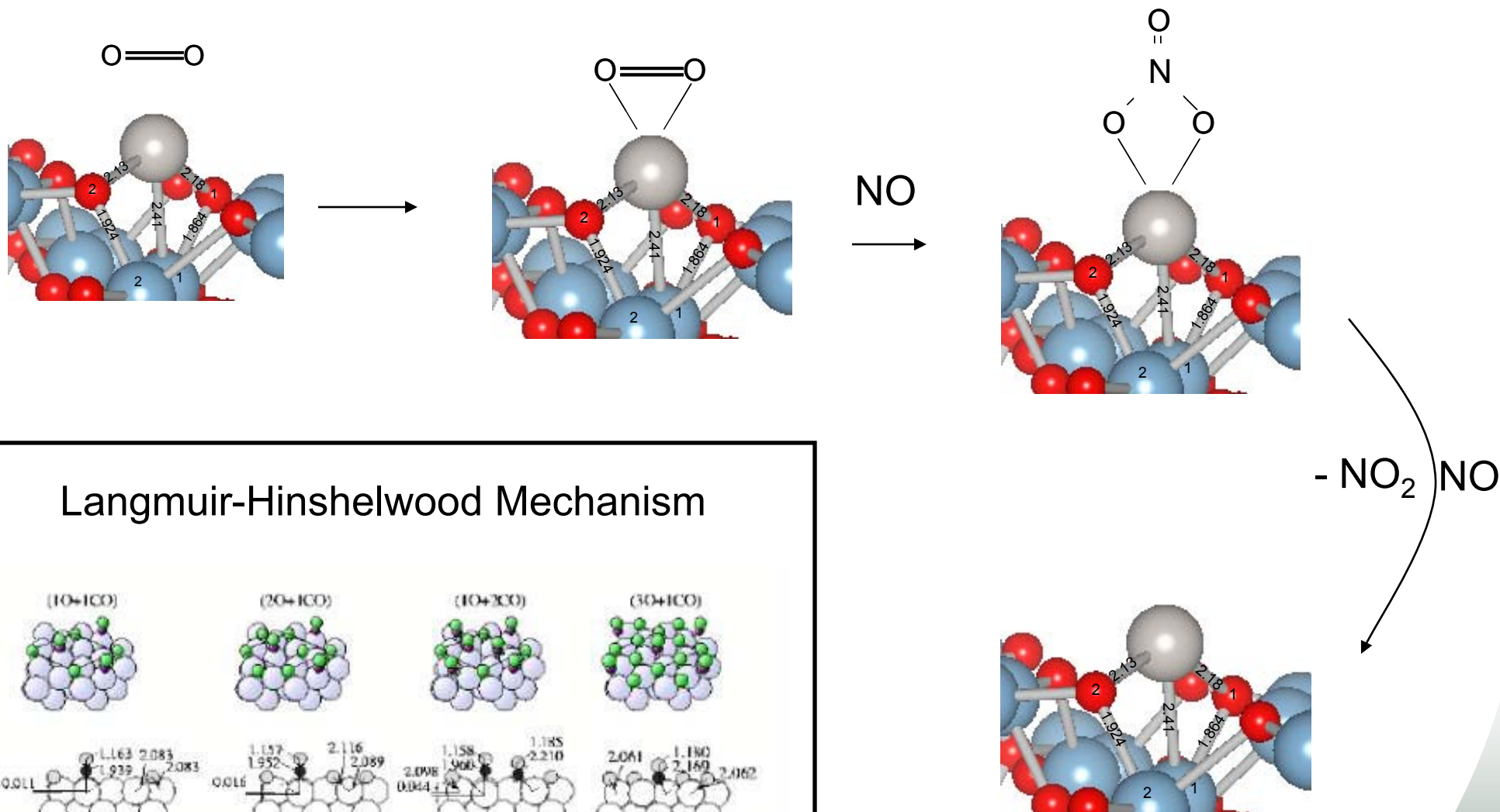
- Under NO oxidation conditions at this temperature, no significant Pt growth is observed.



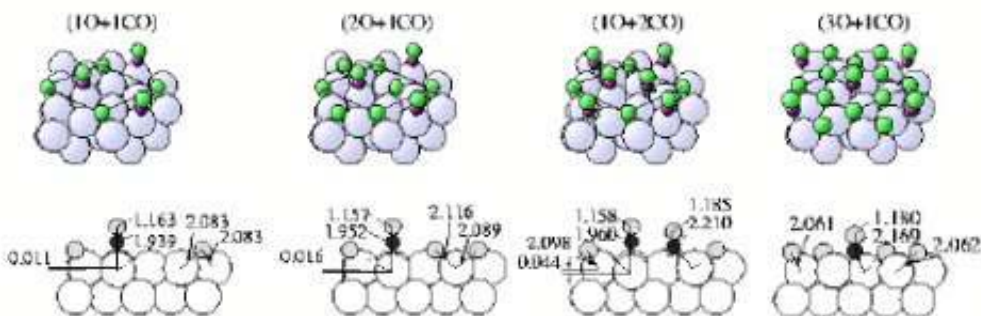
- Results of *ex-situ* studies suggest that the average particles size under these conditions is not effected by the density of Pt particles but the degree of particle growth possible is increased. Since the fresh sample has already been calcined at 450 C/5h prior to testing, the sintering observed in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

Metal – NO Oxidation

Eley-Rideal Mechanism



Langmuir-Hinshelwood Mechanism



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

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

- Our preliminary results demonstrate “catalyst by first principles” concept.
- First principle DFT studies show that supported Pt atoms are in zero oxidation state. Nanostructural studies by ACEM of Pt/alumina, synthesized by us, show that Pt is present as single atoms and 10-20 atom agglomerates with only a few Pt-Pt bonds (if any!).
- Since platinum atoms are in zero oxidation state, the CO or NO_x oxidation can occur by Eley-Rideal mechanism. We are working on energetics of intermediates in Eley-Rideal mechanism scenario.
- Experimental studies show that
 - CO oxidation occurs at lower temperature on subnanometer agglomerates than that on large particles supporting theoretical study that subnanometer agglomerates involve Pt(0) species (Eley-Rideal mechanism) while particles involve Pt surfaces (Langmuir Hinshewood pathway). Pt agglomerates grow under CO oxidation conditions to particles gradually resulting in high temperature requirement for CO oxidation.
 - Pt agglomerates rapidly grow into particles under hydrocarbon oxidation conditions.
 - Pt agglomerates growth under NO oxidation conditions is mild at 450°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 CO oxidation, theoretical studies suggest that subnanometer Pt (single atoms or 10-20 atom agglomerates) can catalyze CO and NO_x oxidation. Experimentally, we validated it by synthesizing supported subnanometer Pt, characterizing them, and determining their CO and NO_x reactivity.
- Well-characterized and understood materials

Collaboration

➤ Commercialization of technology

- Now that we are beginning to develop understanding of the catalyst sites in supported catalyst, we can develop pathways to improve the catalyst
 - Stabilize catalysts as sub-nanometer particles – more catalyst sites means less catalyst! (CO oxidation)
 - Durable, reliable, well-understood materials

➤ 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
 - Catalytic activity of fresh and hydrothermally aged samples

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