UT-BATTELLE

Combining Theory and Experiments in Studies of Structural Changes in LNT Materials

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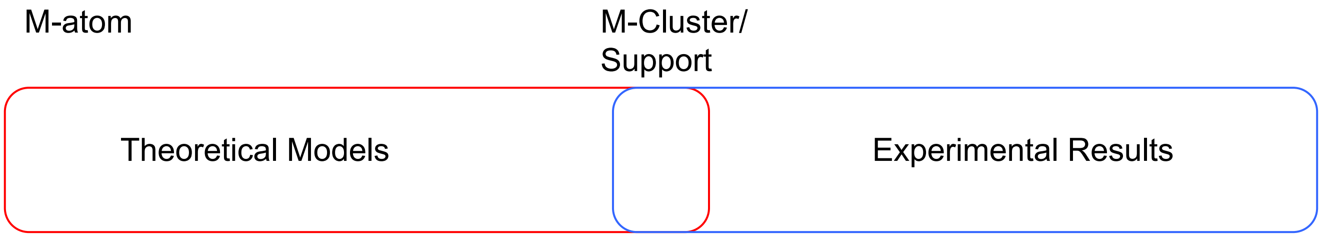
OAK RIDGE NATIONAL LABORATORY
U. S. DEPARTMENT OF ENERGY

Combining Theory and Experiments

- ➢ **Is it possible to examine computationally complex but experimentally simple systems by both theoretical and experimental methods?**
  - **Forecast improvements**
  - **Optimize Performance**



M-atom

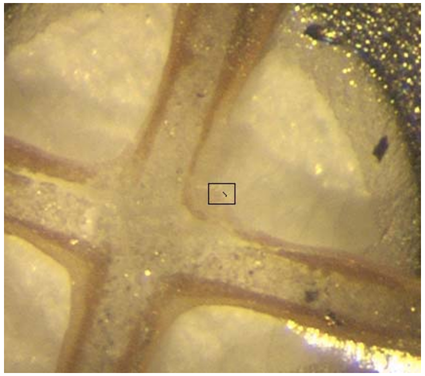
M-Cluster/
Support

Theoretical Models

Experimental Results

What happens in the Real World?

- **Supplier NO_x Traps [Collaboration with Ford]**
  - **Flow-Reactor Aging**
  - **Dyno Aging**
  - **Passenger Vehicle (DISI Fleet) Aging**
    - **30K km**
    - **53K km**
    - **82K km**



Microstructural Studies of Supplier NO_x Traps - Pulsator Aging

- **Lean and rich aged samples showed that the**
  - **Sintering of platinum particles occurs during aging**
  - **Barium migrates into ceria-zirconia layer.**
  - **Both of these factors reduce platinum-barium oxide surface area where NO_x adsorption and reduction takes place during lean and rich cycles respectively.**
- **The stoichiometric aging also leads to the migration of barium into ceria-zirocnia layer but the sintering of platinum is less severe.**

Microstructural Studies of Supplier NO$_x$ Traps – Dyno Aging

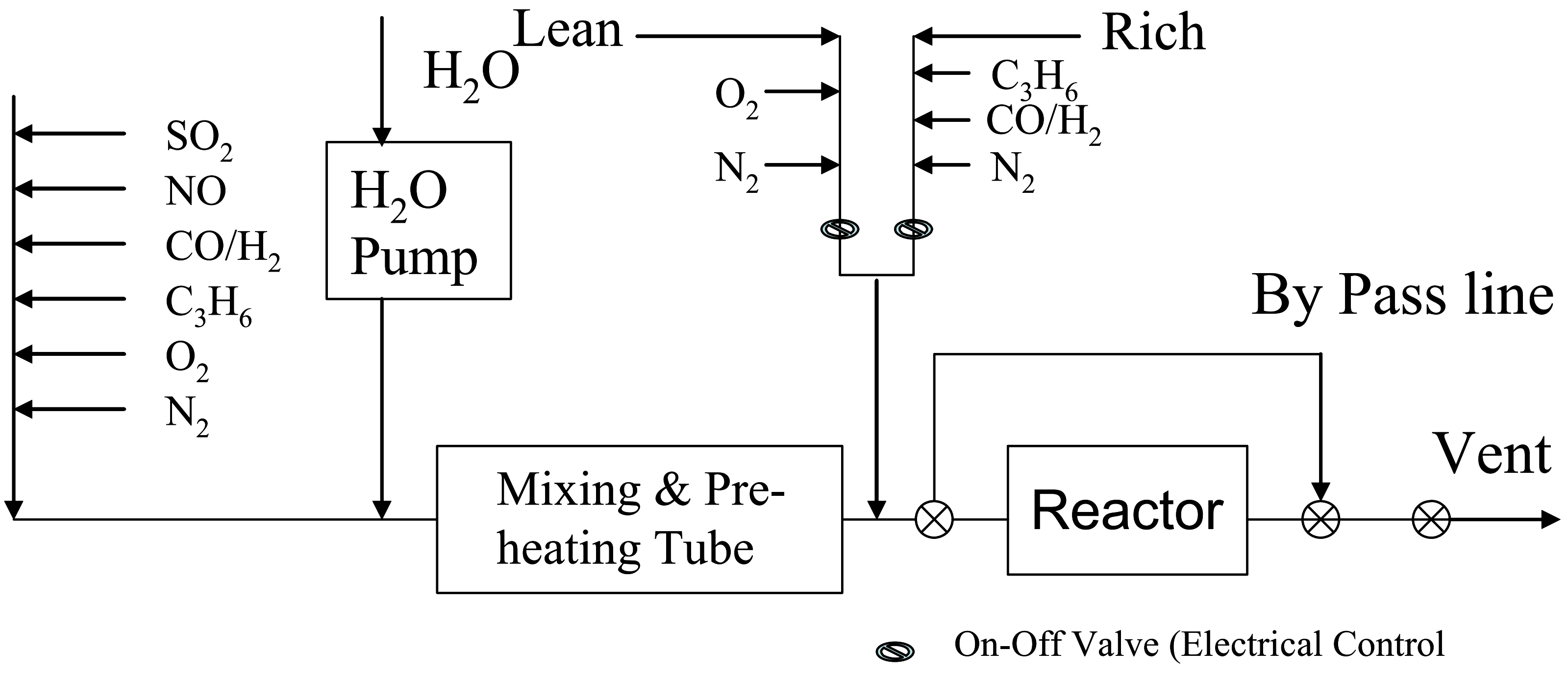
- The dyano aged samples showed extensive sintering of platinum and its migration in ceria-zirconia layer.
- The sintering of rhodium as well as the migration of barium into ceria-zirconia was also observed
- These observation explain the deterioration in LNT performance over time

Microstructural Studies of Supplier NO_x Traps - Passenger Vehicle (DISI Fleet) Aging

- **The analysis of on vehicle evaluated samples after 32K km and 80km showed that the bulk of precious metal sintering occurred in the early stages of on vehicle aging**

Ex-Situ Reactor

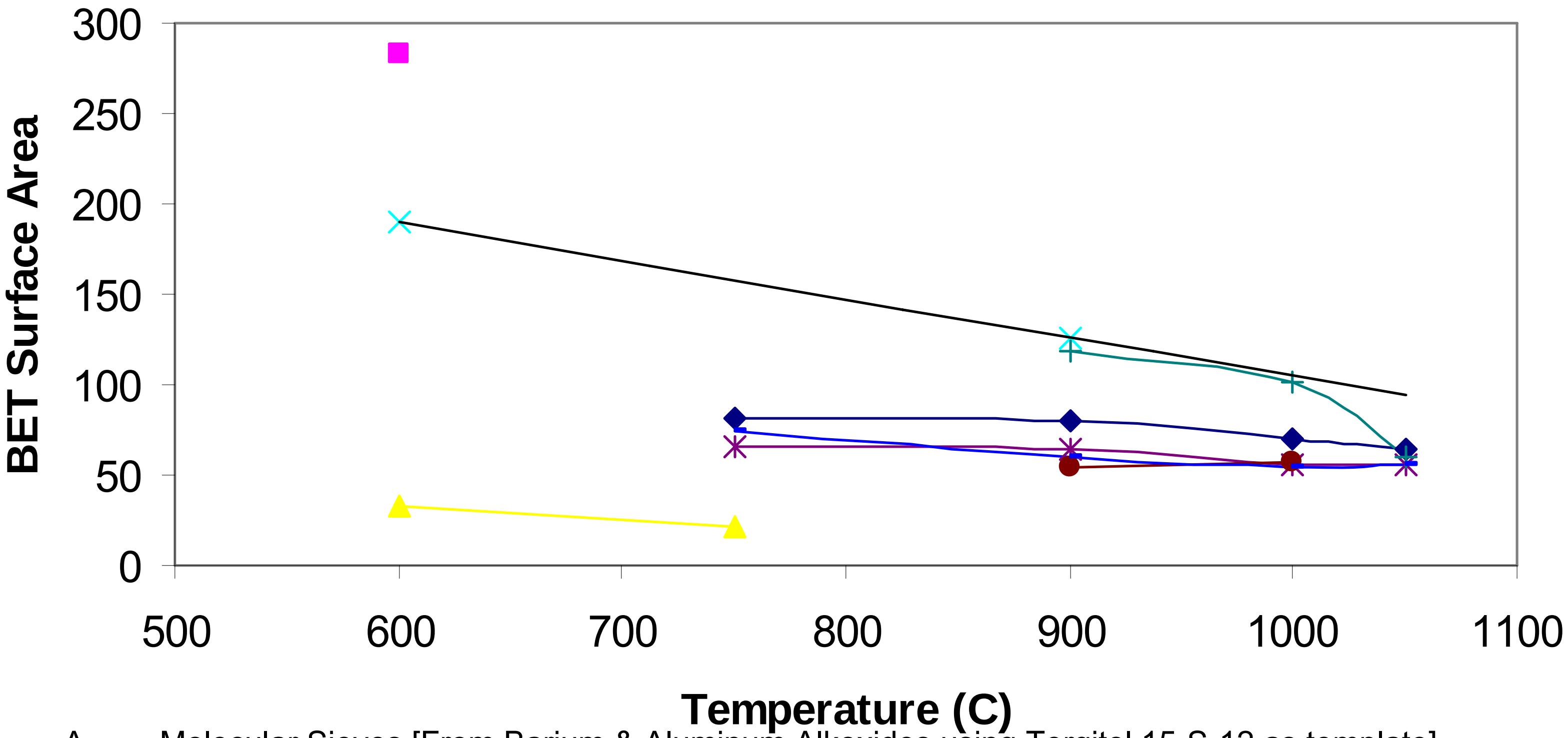
- Rapid Screening Method for Monitoring Microstructural Changes



Model Catalysts

- Model Catalysts were prepared by step-wise impregnation of commercial alumina
- 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%$BaO.6Al_2O_3$)]
  - Impregnate alumina with barium salts and thermally treat in air to obtain $BaO.6Al_2O_3$
  - Impregnate $BaO.6Al_2O_3$ with Lanthanum salt and thermally treat in air to obtain 2%La_2O_3-98%$BaO.6Al_2O_3$
  - Ball mill 2%La_2O_3-98%$BaO.6Al_2O_3$ with commercial CeO_2-ZrO_2
  - Impregnate 10%CeO_2-ZrO_2-90%(2%La_2O_3-98%$BaO.6Al_2O_3$ with Pt salts and thermally treat to obtain model NO_x trap
- Pt/Al_2O_3
  - Impregnate alumina with Pt salts and thermally treat to obtain model NO_x trap
- 2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% $BaO.6Al_2O_3$)]
  - Impregnate 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98%$BaO.6Al_2O_3$)] with manganese salts and thermally treat to obtain model NO_x trap

Thermal Stabiltiy of Impregnation $BaO.6Al_2O_3$



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

B. $BaO.6Al_2O_3$ from Alkoxide hydrolysis

C. $BaO.6Al_2O_3$ [BaO impregnated Alumina]

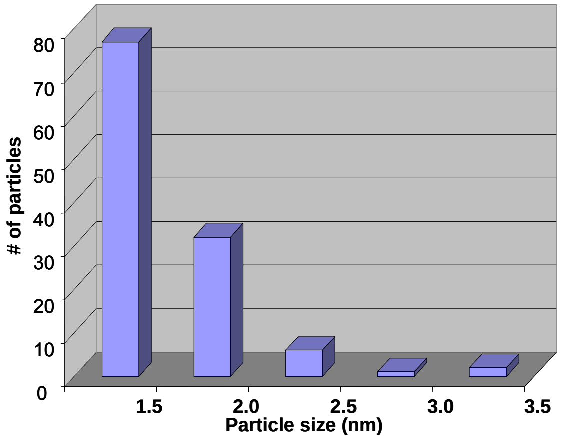
D. 2% La_2O_3 impregnated on $BaO.6Al_2O_3$; D’. 90% D + 10% CeO_2-ZrO_2

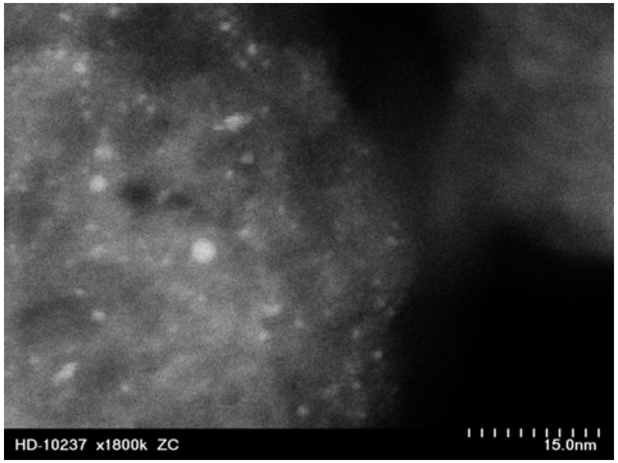
E. 10% ZrO_2 impregnated on $BaO.6Al_2O_3$.

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

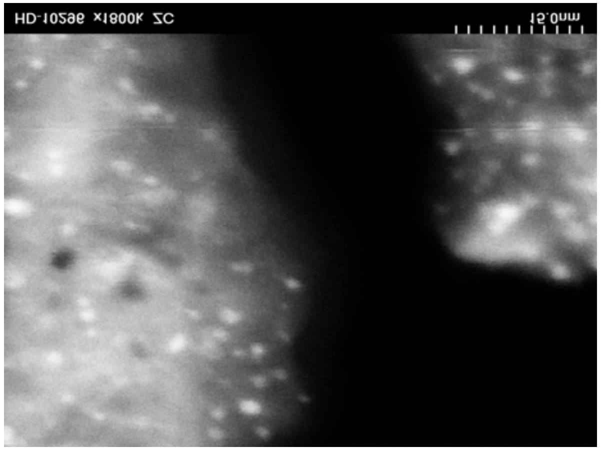
G. $BaO.6Al_2O_3$ [Lit., J. Mater. Sci, 29 (1994) 3441, carbonate method].

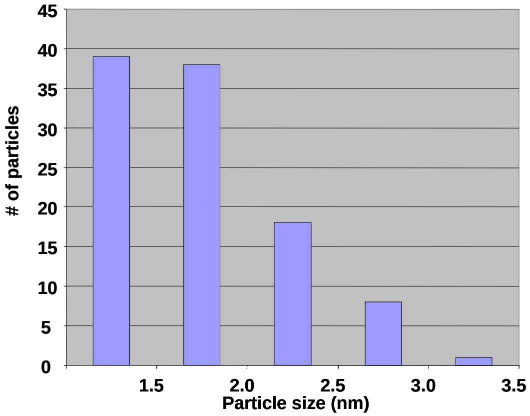
Lean-Rich Cycle Aging of (500°C, 4hrs) 2%Pt, 98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)] [60s-5s cycle]





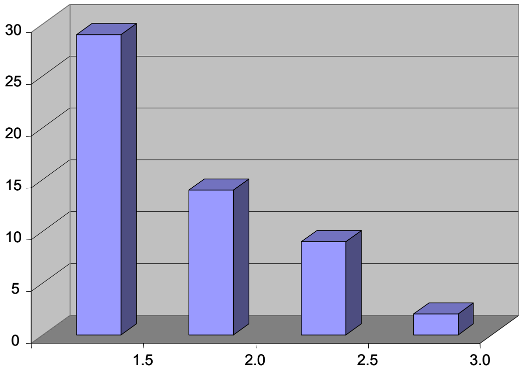
Fresh

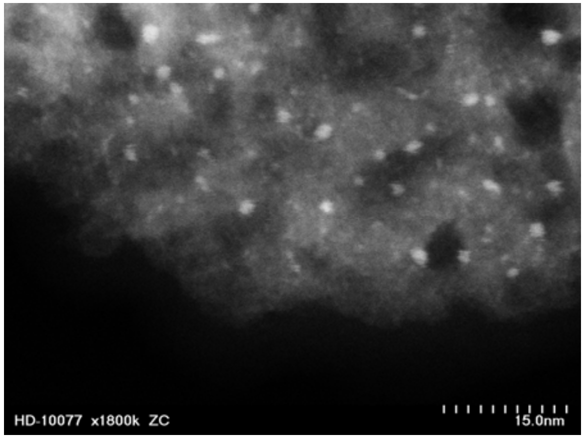




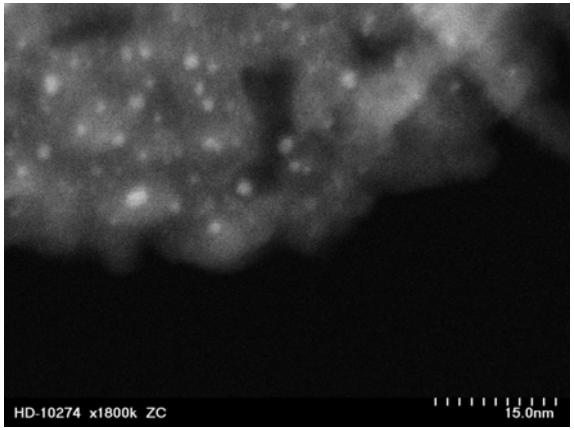
1.23nm → 1.49nm

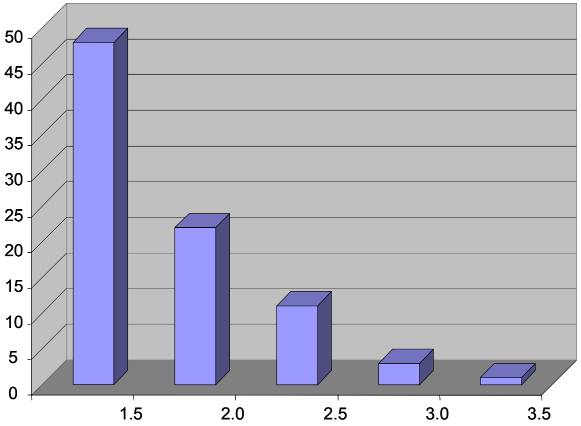
Fresh and Lean/Rich Aged (500°C, 4hrs) 2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90% (2%La_2O_3-98% $BaO\bullet 6Al_2O_3$)] [60s-5s cycle]





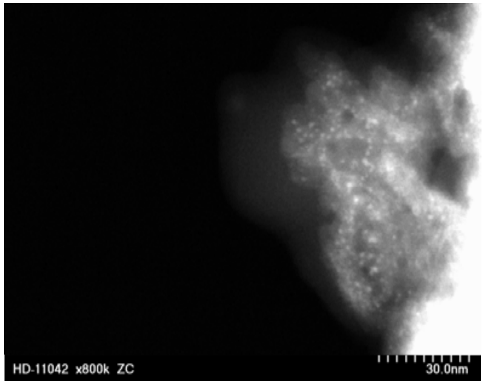
Fresh



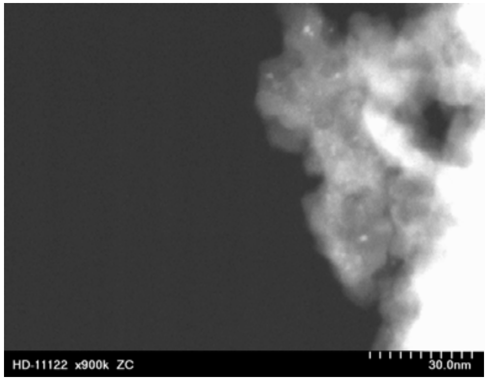


1.4nm → 1.3nm

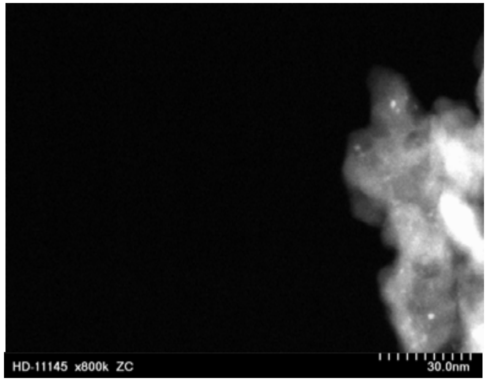
DF-STEM of fresh and lean-rich diesel Cycle (60s, 5s) aged 2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% $BaO \bullet 6Al_2O_3$)] at 700 ^oC



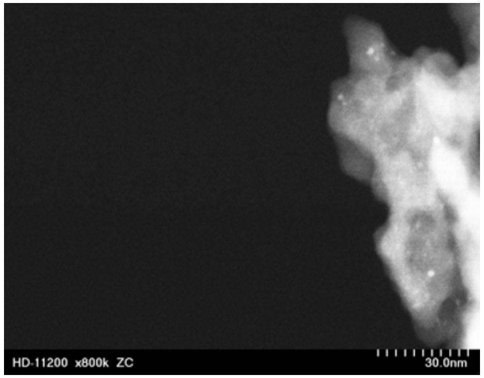
Fresh



1st 4h period



2nd 4h period



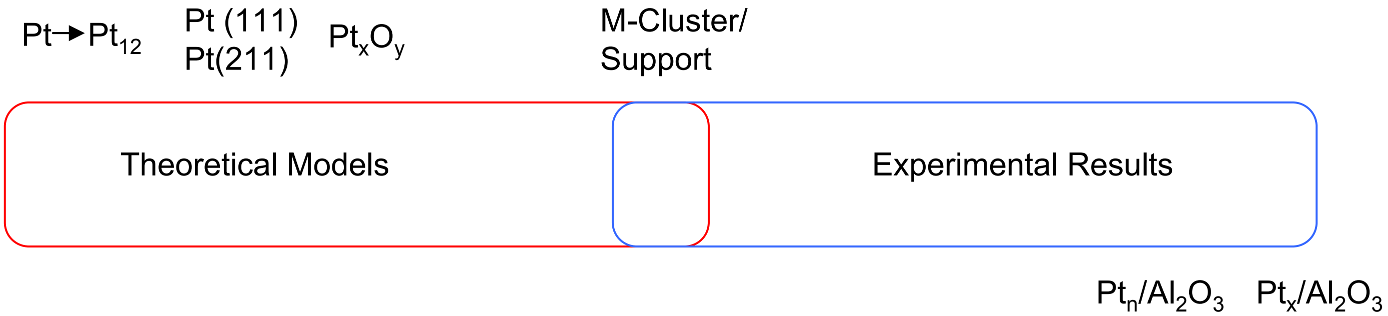
3rd 4h period

Summary of Pt particle size change under various treatments of the model catalysts

	Fresh Sample[1]	Thermal Aging In Air (XRD of powder)	Lean Diesel Aging 500 °C/ 4h	Rich Diesel Aging 500 °C/ 4h	Lean/ Rich Cycle (60s/5s) Diesel Aging 500 °C/ 4h[1]	Lean/Rich Thermal Diesel Aging 700 °C[1]
2% Pt / γ-Al_2O_3	0.5 - 1.0 nm (0.9 nm)	600ºC, 3.4 nm 700ºC, 17.1nm 800ºC, 26.1nm 900ºC, 39.5nm	1.0 - 1.5 nm[1] (1.3 nm)	2.0 - 4.0 nm		
2%Pt-98%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	1.0 – 1.5 nm (1.45 nm)	600ºC, 2.6 nm 700ºC, 21.3nm 800ºC, 37.2nm 900ºC, 48.4nm	1.0 -2.0 nm	1.5 - 3.5 nm	1.0 - 1.5 nm (1.7 nm)	1.0 nm F (1.4 nm) 1.5 – 2.0 nm 4h (2.1 nm) 1.5 - 2.0 nm 8h (2.1 nm) 1.5 nm 12h (2.0 nm) _______nm 16h
2%Pt, 5%MnO_2-93%[10%CeO_2-ZrO_2-90%(2%La_2O_3-98% BaO•6Al_2O_3)]	1.0 - 1.5 nm (1.6 nm)	700ºC, 20.7nm 800ºC, 27.0nm 900ºC, 34.0nm	2 - 3 nm	1 - 2 nm	1.0 – 1.5 nm (1.7 nm)	

1. The distribution is centered on these values. Averages are reported in brackets.

Combining Theory and Experiments



$Pt \rightarrow Pt_{12}$

Pt (111)
Pt(211)

Pt_xO_y

M-Cluster/
Support

Theoretical Models

Experimental Results

Pt_n/Al_2O_3 Pt_x/Al_2O_3

- **Noble Metal**
  - **Pt, Rh, Ru, Re**
- **Substrate**
  - **Commercial, sol-gel, molecular sieve**
  - **Al_2O_3, SiO_2, MgO**

Theoretical Modeling - Method

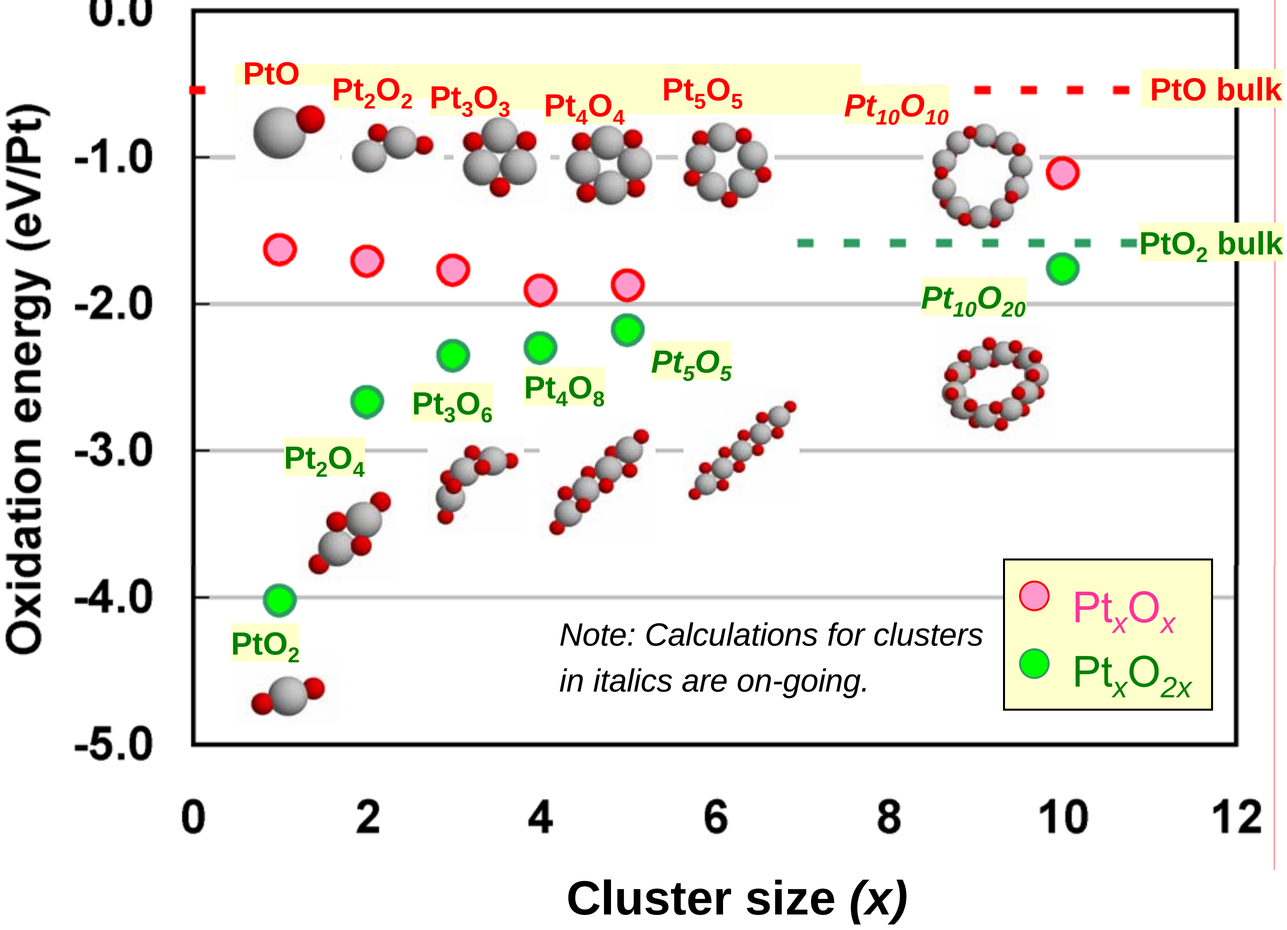
- **Density functional theory calculations**
- **Generalized gradient approximation (PW91 functional)**
- **Spin polarization to capture correct ground state**
- **Oxidation energy of Pt_xO_y clusters calculated as:**

$$OE = (E_{\text{cluster}} - E_{Pt_x} - ½\, y \cdot E_{O_2}) \,/\, x$$

(1 eV ≈ 100 kJ/mol ≈ 23 kcal/mol)

- **Convergence of results verified**

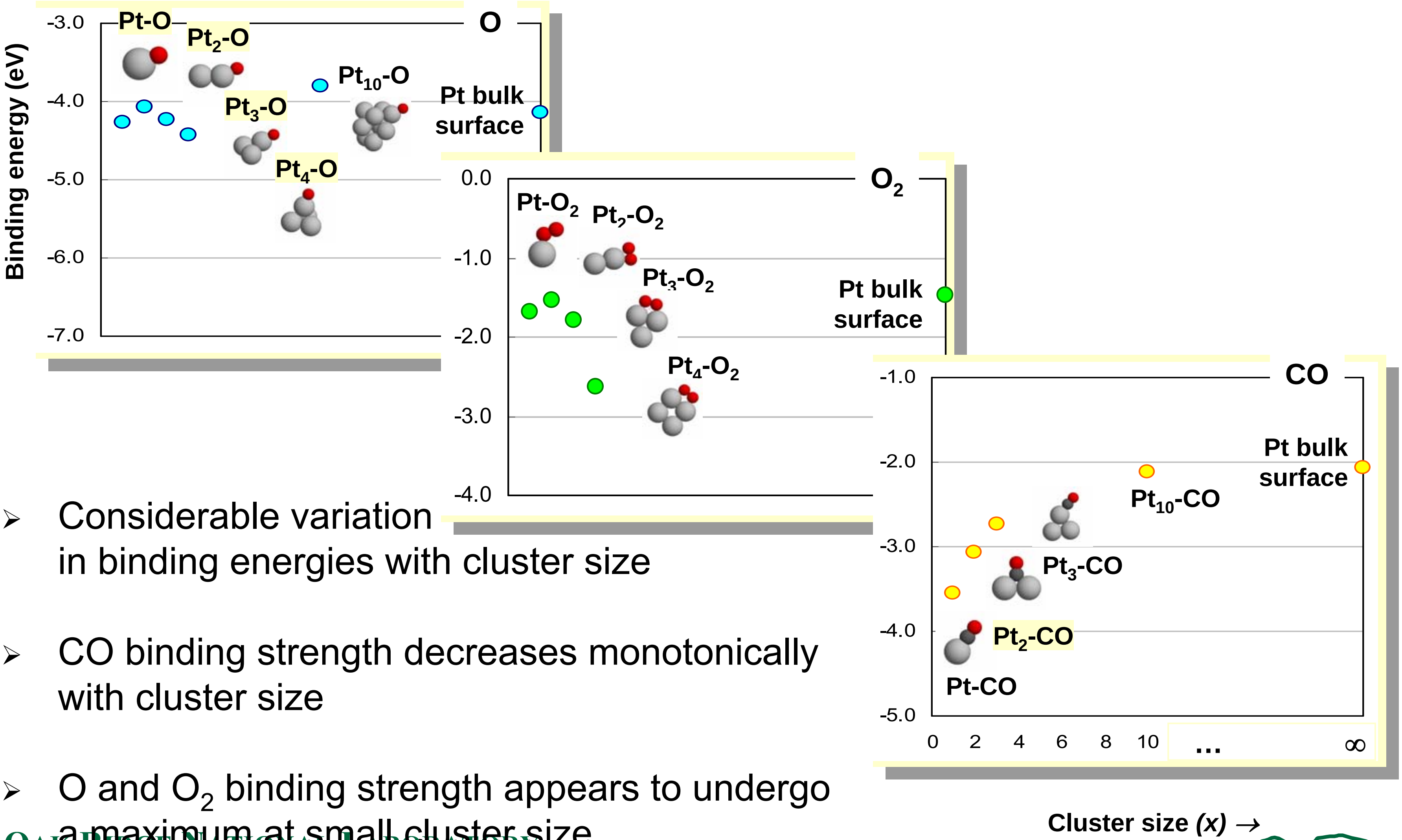
Oxidation thermodynamics of Pt oxide clusters



- Size matters… smaller Pt clusters oxidized much more readily than Pt bulk
- For a given number of Pt atoms (x), the Pt_xO_{2x} stoichiometry is most favorable
- Pt clusters can absorb more than $2x$ O atoms but won't be "over-oxidized" (except for PtO_3)

Y. Xu, W. A. Shelton, W. F. Schneider, J. Phys. Chem. B, to be submitted

Binding energies of single O, O_2, and CO on Pt clusters



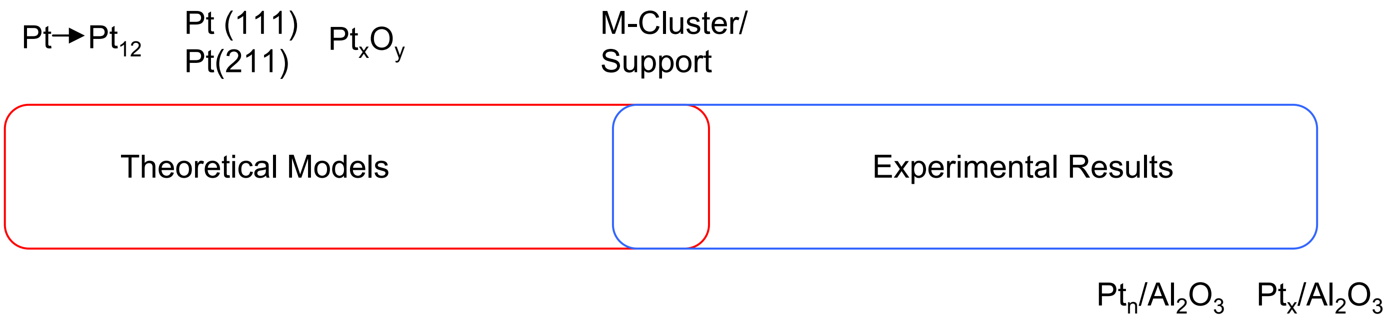
- Considerable variation in binding energies with cluster size
- CO binding strength decreases monotonically with cluster size
- O and O_2 binding strength appears to undergo a maximum at small cluster size

Y. Xu, W. A. Shelton, W. F. Schneider, J. Phys. Chem. B, to be submitted

Theoretical Model tells us that…

- Pure Pt clusters are easily oxidized; supported Pt nanoparticles should primarily be in oxidized forms in oxidizing environment
- +4 oxidation state (i.e., Pt:O=1:2) is favored thermodynamically for Pt atoms
- Pt clusters have very different oxidation energetics and oxidized structures compared to the bulk phase
- Adsorption properties of O, O_2, and CO on Pt clusters very different compared to extended Pt surface
- Even small Pt oxide clusters are structurally complex, although patterns can be detected and aid in future analysis

Combining Theory and Experiments



Pt→Pt$_{12}$

Pt (111)
Pt(211)

Pt$_x$O$_y$

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Theoretical Models

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Pt$_n$/Al$_2$O$_3$

Pt$_x$/Al$_2$O$_3$

- **Noble Metal**
  - **Pt, Rh, Ru, Re**
- **Substrate**
  - **Commercial, sol-gel, molecular sieve**
  - **Al_2O_3, SiO_2, MgO**

Pt-Al_2O_3 System

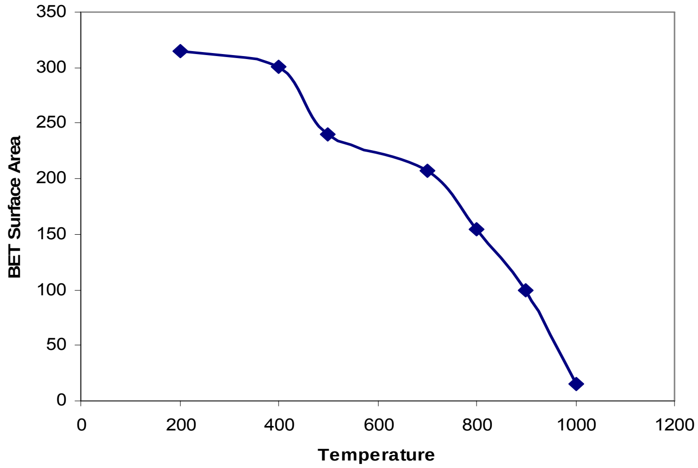
- γ- **Alumina**
  - **Commercial**
  - **Sol-Gel**
  - **Molecular Sieves**
- **Pt**
  - **Carbonyl clusters**
  - **Decarbonylated clusters**
  - **Pt_n**
  - **Pt_x**

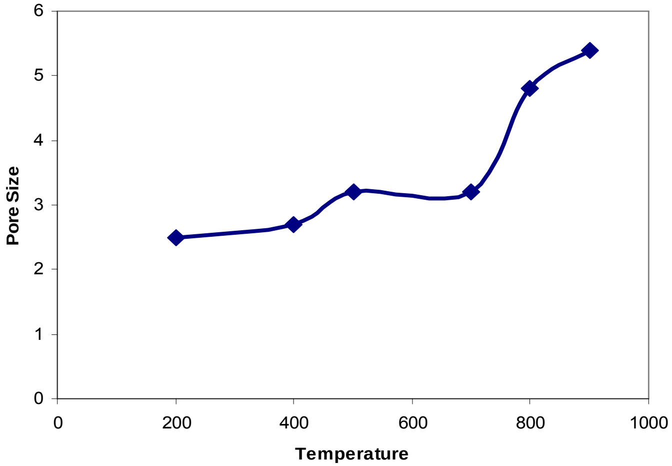
	Comm. **γ-Al_2O_3**	**Sol-gel** **γ-Al_2O_3**	Mol. Sieve γ-Al_2O_3
Pt carbonyl	√	√	√
Decarbonylated	√	√	√
Pt_n	√√	√	√
Pt_x	√√	√	√

Support: Sol-Gel Alumina

$$C_2H_5CH(CH_3)O]_3Al \xrightarrow[\text{Water}]{>80^{o}C} \gamma\text{-AlOOH} \xrightarrow[\text{Acid}]{>90^{o}C} \text{Stable } \gamma\text{-AlOOH} \xrightarrow[\text{Drying}]{\text{Gelling}} \gamma\text{-AlOOH gel}$$

$$\xrightarrow[\text{Calcination}]{} \text{Stable } \gamma\text{-}Al_2O_3$$





Burggraaf, A.J.; et al.; J. Materials Sc., **1984**, *19*, 1077

Narula, C.K.; et al.; US Patent 5,210,062, May 11, **1993**

Support – Alumina Molecular Sieve

$C_2H_5CH(CH_3)O]_3Al$

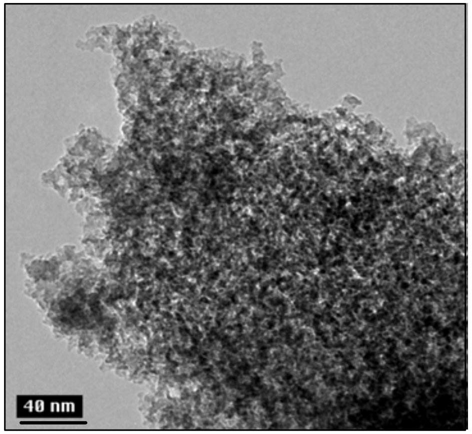
\+

$[(C_2H_5CH(CH_3)O)_4Al]_2Ba$

$\longrightarrow$ Tergitol + 2-Propanol + Water $\longrightarrow$ Alumina-20%BaO Molecular sieves

$\xrightarrow[500^\circ C]{\text{Calcination}}$ Stable Alumina Molecular sieves

Narula, C.K.; et al., AIChE Journal, **2001**, *47*, 744.



Support: Alumina Molecular Sieves

$C_2H_5CH(CH_3)O]_3Al \longrightarrow$ Cetyltrimethylammonium bromide in water-ethanol + ammonium hydroxide $\longrightarrow$ Alumina Molecular sieves

$\xrightarrow[500^{\circ}C]{\text{Calcination}}$ Stable Alumina Molecular sieves

Shanks et al., Adv. Funct. Mater., **2003**,*13*, 61

Support: Alumina Molecular Sieves

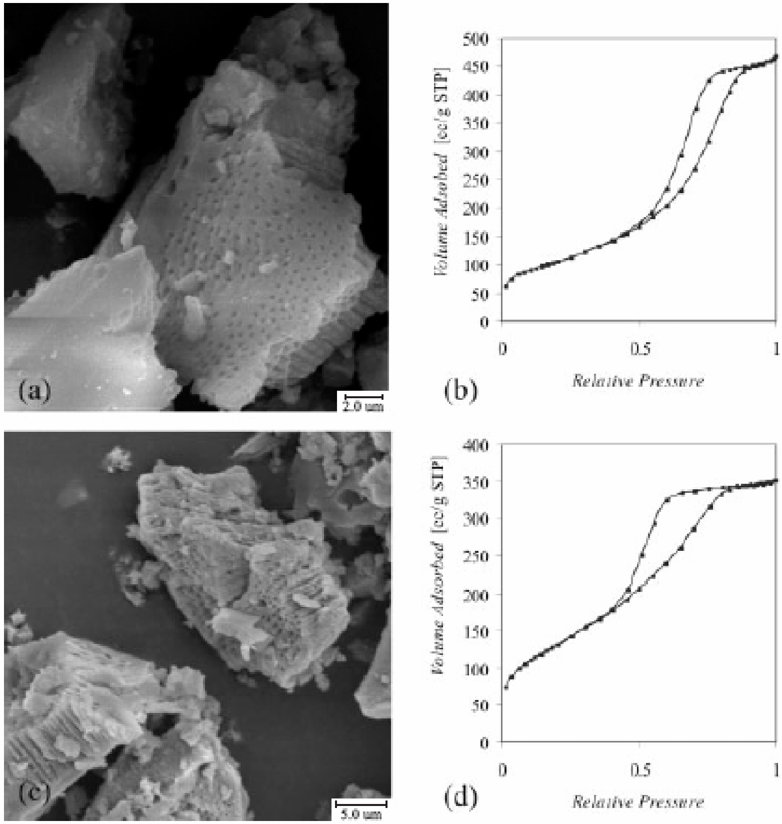


Fig. 1. SEM images and adsorption/desorption isotherm plots for Sample 1 (a,b), with 2 μm scale bar on SEM image, and for short synthesis time alumina (c,d), with 5 μm scale bar on SEM image.

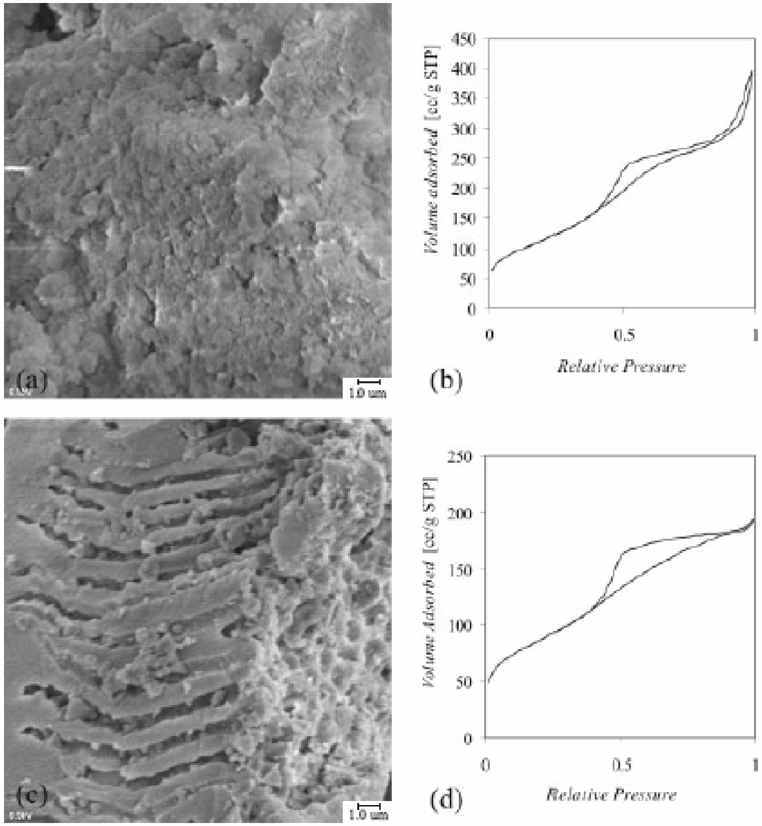
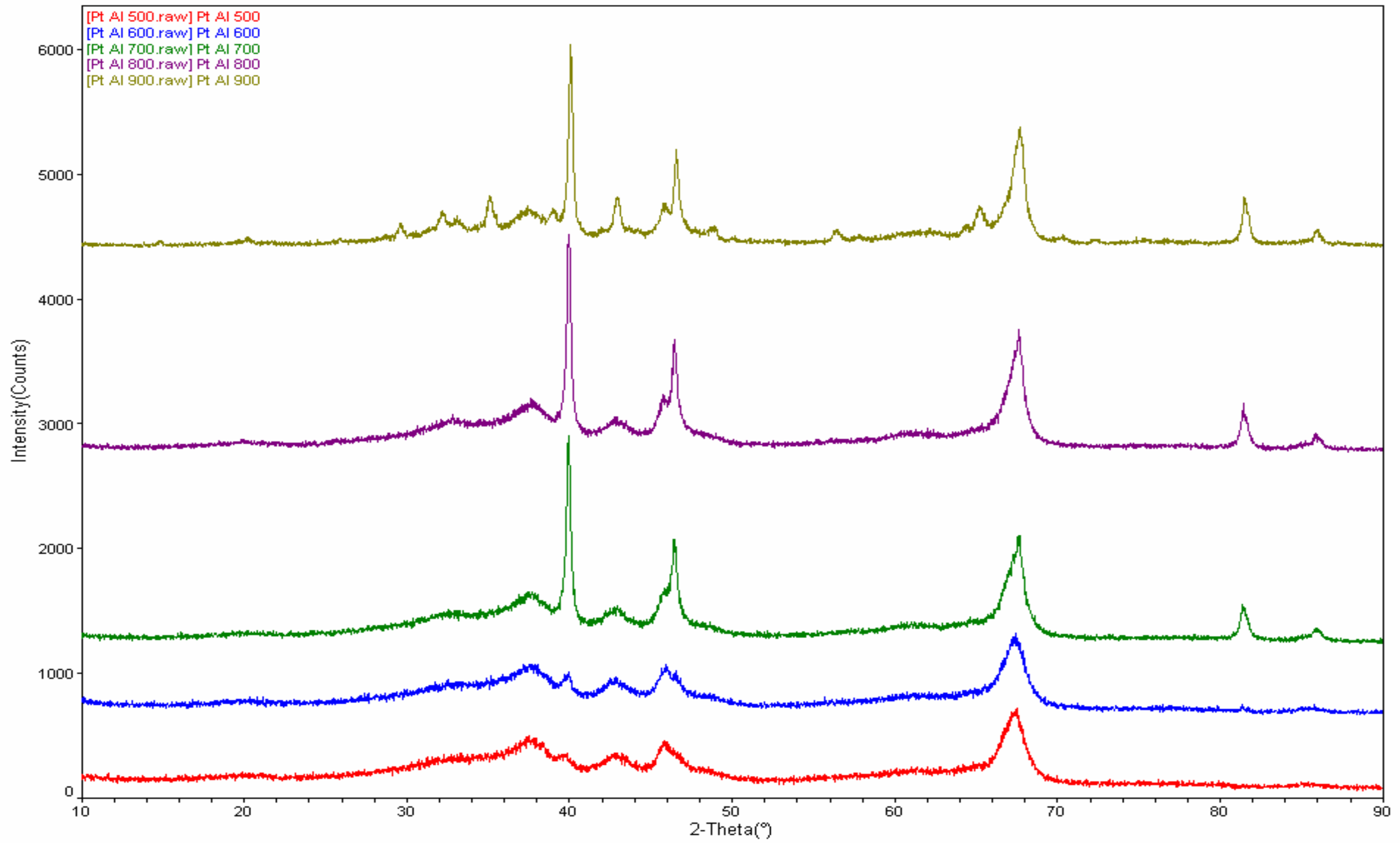


Fig. 2. SEM images and adsorption/desorption isotherm plots for Sample 3 (a,b), with 1 μm scale bar on SEM image, and Sample 2 (c,d), with 1 μm scale bar on SEM image.

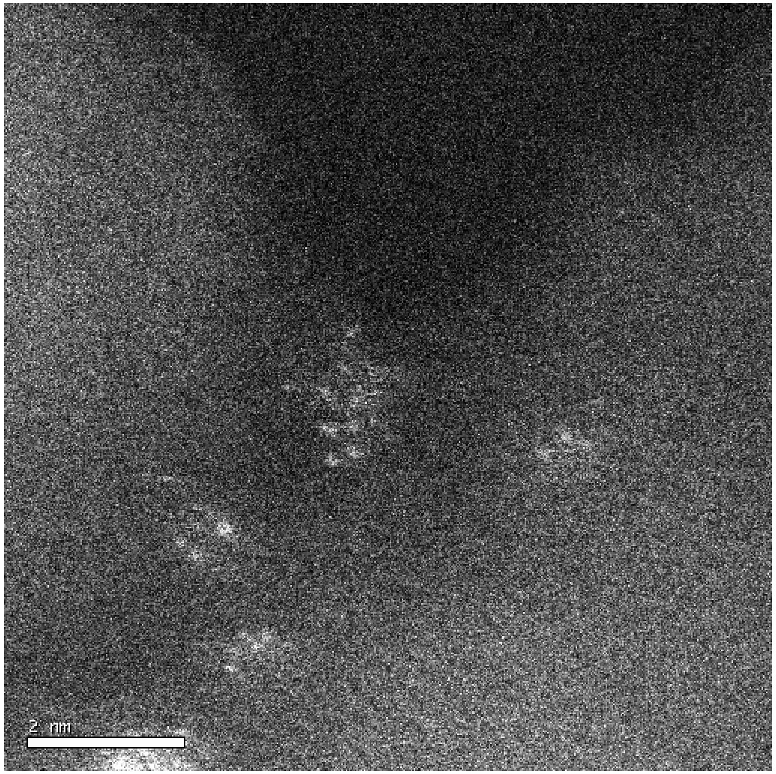
Noble Metal On Support: Pt_n and Pt_x supported on Commercial γ-Al_2O_3

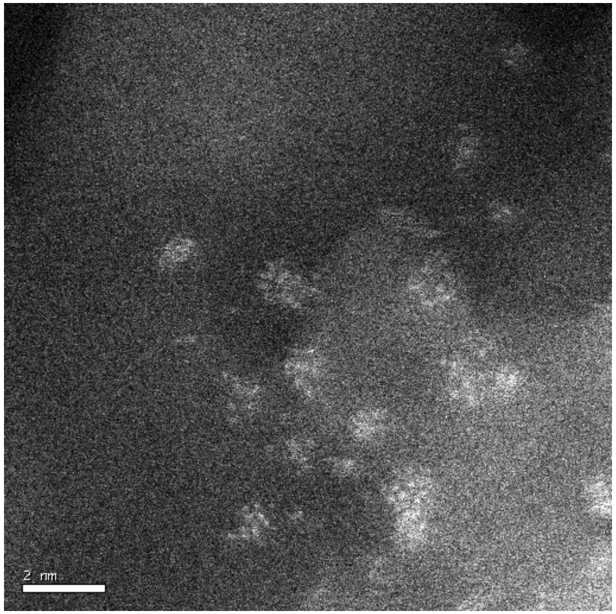


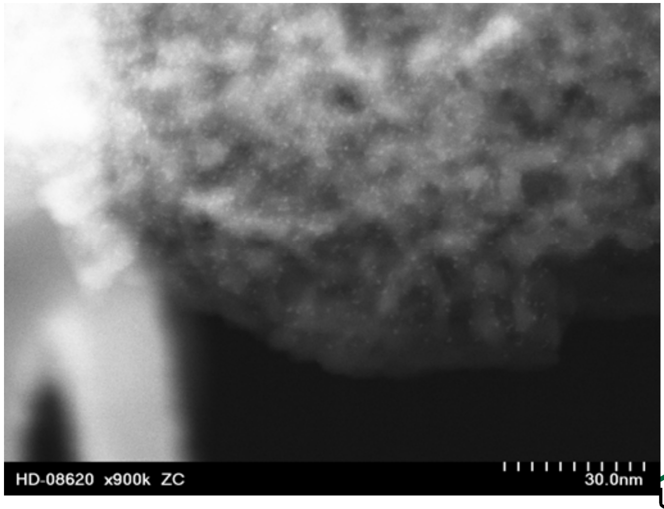
Oak Ridge National Lab

500ºC, 1.2 nm
600ºC, 3.4 nm
700ºC, 17.1nm
800ºC, 26.1nm
900ºC, 39.5nm

Noble Metal on Support: Pt_n supported on Commercial γ-Al_2O_3







Re-Al_2O_3 System

- γ- Alumina
  - Commercial
  - Sol-Gel
  - Molecular Sieves
- Re
  - Carbonyl clusters
  - Decarbonylated clusters
  - Pt_n
  - Pt_x

	Comm. γ-Al_2O_3	Sol-gel γ-Al_2O_3	Mol. Sieve γ-Al_2O_3
Re carbonyl	√ √	√	√
Decarbonylated	√ √	√	√
Re_n	√	√	√
Re_x	√	√	√

Noble Metal on Support: $H_3Re_3(CO)_{12}$/commercial γ-Al_2O_3 System

- **$H_3Re_3(CO)_{12}$ was synthesized by literature methods and adsorbed on commercial γ–Al_2O_3 powder**
- **IR and EXAFS indicate that rhenium tricarbonyl clusters are present on the sample**

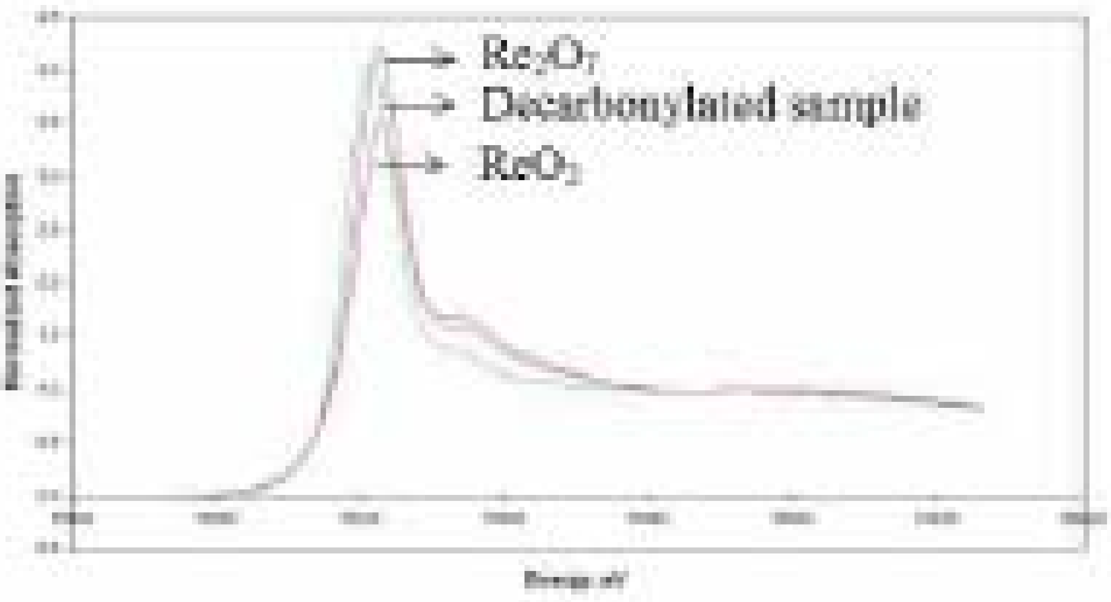
Noble Metal on Support: Decarbonylated Re Clusters on Commercial γ-Al_2O_3

- **The $H_3Re_3(CO)_{12}$/commercial γ–Al_2O_3 powder was decarbonylated in flowing He and in flowing H_2.**
  - **The sample after treatment in H_2 at 673K was completely decrbonylated.**
- **The EXAFS parameters (coordination number N_{Re-Re} = 2.3, distance R_{Re-Re} = 2.69Å) indicate tri-rhenium raft-like structure on the support.**
- **Re-support interaction via short Re-O bonds (N_{Re-O} = 1.0, R_{Re-O} = 2.04Å) and a long Re-O contribution (N_{Re-O} = 0.7, R_{Re-O} = 2.56Å) is evident.**

Bhirud, V.A., Narula, C., Gates, B.C., "γ-Al_2O_3 Supported Trirhenium Rafts: Spectroscopic and Microscopic Characterization", 19th North American Catalysis Society Meeting, Philadelphia, USA, May 22-27, **2005**

Noble Metal on Support: Decarbonylated Re Clusters on Commercial γ-Al_2O_3

- **XANES studies indicate that rhenium rafts are highly electron deficient and cationic in nature and Re is in +4 to +6 oxidation state.**



Experimental Results

- Alumina Substrate materials with controlled surface properties are available.

- Carbonylated, decarbonylated, and small clusters of noble metals can be deposited on the substrates.

- While bulk analysis techniques such as IR, XRD, EXAFS and XANES provide substantial information on these materials, the availability of ACEM makes it possible to carry out microtructural characterization of catalyst sites.

Publications

- Bhirud, V.A., Narula, C., Gates, B.C., γ-Al_2O_3 Supported Trirhenium Rafts: Spectroscopic and Microscopic Characterization, 19th North American Catalysis Society Meeting, Philadelphia, USA, May 22-27, (2005)
- Xu, Y.; Shelton, W.A.; Schneider, W.F.; Nanoscale Effects in the Reactivity of Pt Clusters towards CO oxidation, 19th North American Catalysis Society Meeting, Philadelphia, USA, May 22-27, (2005)
- Xu, Y.; Shelton, W.A.; Schneider, W.F.; Theoretical studies based on post-Hartree-Fock and DFT methods, *Synthesis and applications of oxide nanoparticles and nanostructures*, Ed. Rodriguez, J.A.; John Wiley & Sons
- Bhirud, V.A.; Moses, M.J.; Blom, D.A.; Allard, Jr. L. F.; Aoki, T.; Mishina, S.; Narula, C.K.; Gates, B.C.; Alumina-supported Tri-rhenium Clusters Visible by Aberration-Corrected Dark-field STEM, Microscopy and Microanalysis 2005, Honolulu, USA July 31-August 4, (2005).
- Y. Xu, W. A. Shelton, W. F. Schneider, J. Phys. Chem. B, to be submitted
- C.K. Narula, S. Daw, J. Hoard, T. Hammer, Materials Issues Related to Catalysts for Treatment of Diesel Exhaust, I.J. Amer. Ceram. Tech., (invited)

Next Steps

- Effect of T and *p* on stability and distribution of gas-phase PtO_y, Pt_2O_y, and Pt_3O_y clusters – current results valid for 0 K
- Reactivity of Pt and Pt oxide nanoclusters
  - the adsorption of O, O_2, and CO (already under way for pure Pt clusters)
  - the oxidation of CO
- Effect of support on the reactivity of Pt oxide nanoclusters
- Synthesis and microstructural characterization of Pt/Al_2O_3 and Re/Al_2O_3 systems
- Initiate CO-oxidation studies on these systems
- Microstructural changes in model NO_x trap materials after aging cycle on ex-situ reactor in presence of SO_2
- NO_x-trap efficiency studies on bench-top flow reactor

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- K. Lester (ORNL)
- G. Graham, J. Theis, J. Hoard, (Ford Motor Co.)
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  - Sid Diamond
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