Heavy-Vehicle Propulsion Materials

Catalyst via First Principles

C.K. Narula
Oak Ridge National Laboratory
September 14, 2005

Project ID # 10455

This presentation does not contain any proprietary or confidential information

Catalyst via First Principles

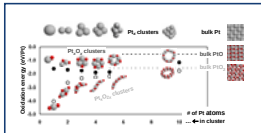
21CTP Technical Goal: Develop and demonstrate an emissions compliant engine system for Class 7-8 highway trucks that improves the engine system efficiency from ~42% today to 50% by 2010.

Project Objectives
Our goal is to demonstrate that we can examine "computationally complex but experimentally simple" system by both first principle theoretical models and experimental work to forecast improvements to obtain optimum catalyst systems

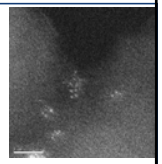
FY 2005 Focus
Our focus has been on the computational and experimental study of supported Pt and Re clusters. The theoretical efforts, which are based on the Density Functional Theory (DFT), have so far been focused on the oxidation behavior of Pt nanoclusters. The experimental studies have been focused on synthesis and characterization of Pt and Re nano catalyst systems.

Planned Duration
October 2004 to September 2007

DOE Funding/Industry Cost Share
FY04: $x00K; FY05: $x00K



Oxidation energies of the Pt_nO_x (filled circles) and Pt_nO_{2x} (open circles) clusters. In stick-and-ball representations red spheres represent O atoms, and grey spheres represent Pt atoms.



ACEM HAADF-STEM image of 2% Pt/γ-Al_2O_3. Pt atoms in Pt-nanoclusters can be seen.

Principal Investigators
Chaitanya Narula Oak Ridge National Laboratory/,UT-Battelle
(865) 574-8445; narulack@ornl.gov

Technology Development Manager
Sid Diamond, DOE/OFCVT
(202) 586-8032; sid.diamond@ee.doe.gov

Collaborators
W. Shelton, ORNL
B.C. Gates, UC Davis
W. Schneider, Univ. Notre Dame (formerly Ford)
Cummins has expressed interest

Accomplishments
- We have synthesized computationally complex but experimentally simple Pt and Re nanoclusters, carbonylated Re clusters, and decarbonylated Re clusters on commercial alumina.
- We have also synthesized sol-gel and mesoporous molecular sieve alumina. We are using these supports to synthesize carbonylated, decarbonylated, and nanoclusters of Pt and Re to understand the impact of substrate morphology by computational and experimental methods.
- We have completed theoretical studies of oxidation behavior of Pt nano-clusters.

Significant Future Milestones
- Complete the synthesis of carbonylated, decarbonylated, and nanoclusters of Pt and Re using sol-gel and mesoporous molecular sieve as support materials. Evaluate these catalysts for their CO, NO_x, and hydrocarbon oxidation efficiency (9-06). Synthesized catalysts based on insights from theoretical models (9/07) .
- Use experimentally observed structures as input for theoretical models of Pt or Re clusters on alumina (9-06). Investigate the adsorption of several atomic and molecular species relevant to CO oxidation, including O, O_2, CO, and CO_2, on the Pt and Pt oxide nanoclusters (9-07).

Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
PM_10455	Materials Technology	HV Propulsion Materials	Applied Research	8-15-05

OBJECTIVES

Project Objectives

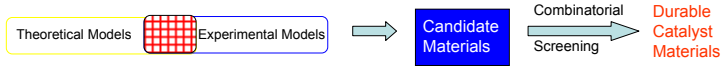
Our goal is to demonstrate that we can examine "computationally complex but experimentally simple" systems by both first principle theoretical models and experimental work to forecast improvements to obtain optimum catalyst systems.

- Deterioration of emission treatment catalyst materials – what can we do about it?
- Identify optimum catalyst sites
  - Examine "computationally complex but experimentally simple" systems by first principle theoretical models. Based on experimental results, iteratively optimize models to forecast improvements leading to optimum catalyst systems
  - Synthesize and evaluate model catalyst systems for CO, HC, and NO_x oxidation. Validate theoretical models from experimental results. Based on theoretical models synthesize and evaluate optimum catalysts systems.
- Identify optimum catalyst sites for emission catalysts and develop candidate durable catalyst materials containing such sites
- Employ combinatorial approach to screen candidates

Approach

Project Objectives

Our focus has been on the computational and experimental study of supported Pt and Re clusters. The theoretical efforts, which are based on the Density Functional Theory (DFT), have so far been focused on the oxidation behavior of Pt nanoclusters. The experimental studies have led to synthesis and characterization of Pt and Re nanocatalyst systems.



- Theoretical Modeling
  - Density functional theory calculations. Generalized gradient approximation (PW91 functional).
  - Optimization of Pt clusters supported on alumina
  - Interaction of CO, NO_x, and HC with supported Pt clusters
- **Experimental System**
  - Synthesize Pt and Re Nanoclusters on morphologically diverse alumina supports
  - Evaluate systems for CO, NO_x, HC oxidation

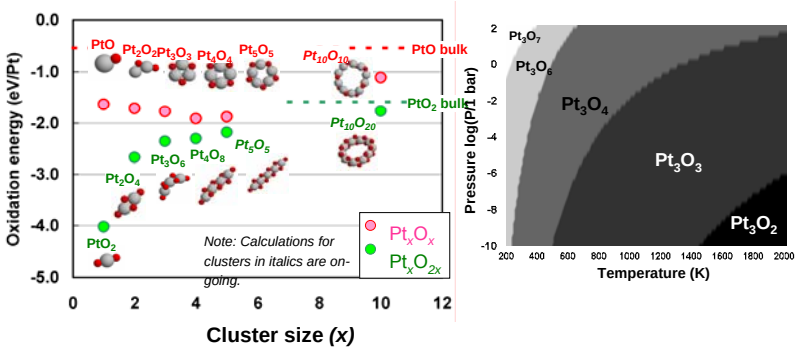
Relevance to 21 CT Goals

- Develop and demonstrate an emissions compliant engine system for class 7-8 highway trucks that improve the engine system efficiency from ~42% today to 50% by 2010
- The emission treatment systems are essential to achieve 21 CT goals. At present, Lean NO_x traps and Urea SCR are leading technologies to meet emission standards. While urea-SCR has been ready for implementation for several years, the EPA reluctance to approve it due to infrastructure issues has led to exploration of LNT. The success of LNT depends on catalyst materials development to improve durability. The success of the project will establish a new protocol for catalyst discovery by making it possible to forecast improvements. The implementation of the results is not limited to LNT's but to all systems containing supported catalysts e.g. three-way catalysts, oxidation catalysts for diesel etc.
- The partners on this project at initiation included: Dr. W. Schneider (Ford), Prof. B. Gates (UC, Davis) and Dr. W. Shelton (ORNL). Dr. Schneider left Ford to join University of Notre Dame. Dr. George Graham of Ford has expressed interest in this project. We are also discussing this project with Cummins.
- The demonstration of science based protocol in combination with combinatorial approaches will establish a new catalyst discovery protocol beneficial to other DOE programs as well as industries that employ catalyst based production. (e.g. our DOE-OIT program on ethylene production from ethane).

Technical Accomplishments/ Progress/Results

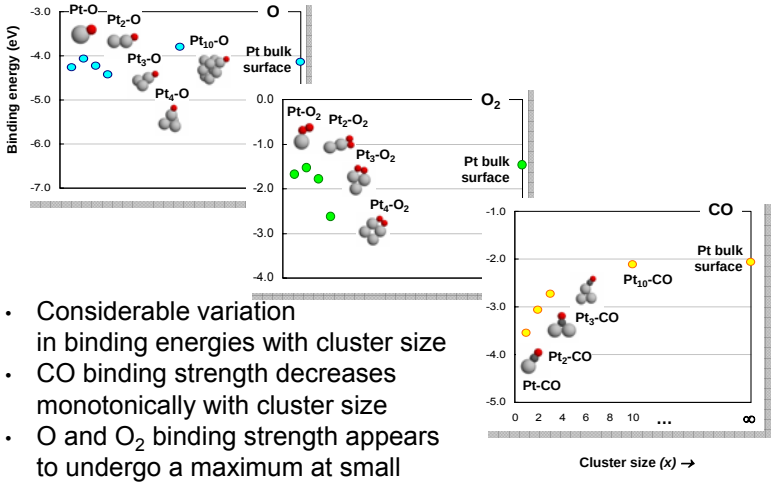
- We have demonstrated that the nano-clusters of platinum and rhenium supported on alumina do not have bulk metal structure. Theoretical models on gas-phase studies suggest that such small cluster of Pt are oxides rather than metal. The theoretical model of Pt nano-clusters supported on alumina will be identical to experimentally synthesized structure.
- These studies demonstrate that it is possible to examine "theoretically complex by experimentally simple systems" iteratively by first principle theoretical modeling and experimental work. Our next set of studies on CO, NO_x, and HC oxidation by both theoretical and experimental work will define the catalyst sites necessary for such reactions.
- Our target is "durable emission treatment catalysts".

Theoretical Models - 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)

Theoretical Models - 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

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

Experimental Results - Noble Metal-Al_2O_3 System

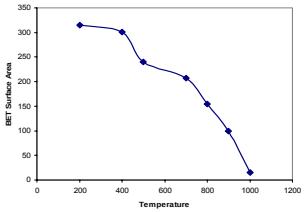
- γ- Alumina
  - Commercial
  - Sol-Gel
  - Molecular Sieves
- Precious Metals
  - Carbonyl clusters
  - Decarbonylated clusters
  - Metal Nanoparticle (M_n) >1nm
  - Metal Particle Pt_x (M_x) 1-5nm

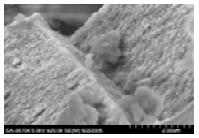
	Commercial γ-Al_2O_3	Sol-Gel γ-Al_2O_3	Mol. Sieve γ-Al_2O_3
La_2O_3	√√	√√	√√
$[Pt_6(CO)_{12}]^{2-}$	√		
Decarbonylated $[Pt_6(CO)_{12}]^{2-}$	√		
Pt_n	√√		
Pt_x	√√		
$H_3Re_3(CO)_{12}$	√√		
Decarbonylated $H_3Re_3(CO)_{12}$	√√		
Re_n	√√		
Re_x	√√		

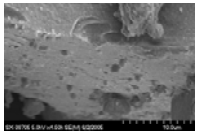
Support: Sol-Gel Alumina

$C_2H_5CH(CH_3)O]_3Al$ —(>80ºC, Water)→ γ-AlOOH —(>90ºC, Acid)→ Stable γ-AlOOH —(Gelling, Drying)→ γ-AlOOH gel

γ-AlOOH gel —(Calcination)→ Stable γ-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**

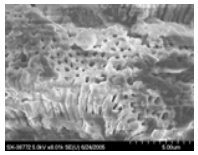
Support: Alumina Molecular Sieves

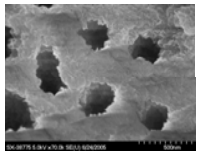
$C_2H_5CH(CH_3)O]_3Al$ —(Cetyltrimethylammonium bromide in water-ethanol + ammonium hydroxide; Or Tergitol + water)→ —(Calcination, 500ºC)→ Alumina Molecular sieves

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

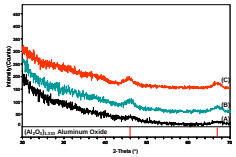
Stabilization

Alumina Molecular Sieves



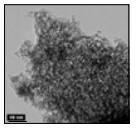


La Incorporation



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.

Ba or La Incorporation



Easy synthesis from a mixture of $Al(O^iPr)_3$ and $Ba[Al(O^iPr)_4]_2$. Thermally stable up to 900ºC.

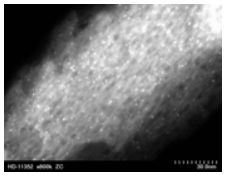
Narula, C.K.; et al., AIChE Journal, **2001**, *47*, 744.

Noble Metals on Supports

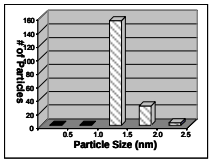
- Pt/γ–Al_2O_3 system
  - Pt_n/γ–Al_2O_3
    - Impregnation of Pt salts on commercial γ–Al_2O_3 and subsequent thermal treatment
  - Pt_x/γ–Al_2O_3
    - Thermal treatment of Pt_n/γ–Al_2O_3
- Re/γ–Al_2O_3 system
  - $H_3Re_3(CO)_{12}$/γ-Al_2O_3
    - $H_3Re_3(CO)_{12}$ was synthesized by literature methods and adsorbed on commercial γ–Al_2O_3 powder
  - Decarbonylated $H_3Re_3(CO)_{12}$/γ-Al_2O_3
    - The sample after treatment in H_2 at 673K was completely decarbonylated
  - Re_n/γ–Al_2O_3
    - Impregnation of Re salts on commercial γ–Al_2O_3 and subsequent thermal treatment
  - Re_x/γ–Al_2O_3
    - Thermal treatment of Re_n/γ–Al_2O_3

The smallest experimentally synthesized Pt/alumina clusters is $[Pt_6(CO)_{12}]^{2-}$.
A decarbonylated cluster will not be significantly different from alumina supported Pt nanoclusters that we synthesized by impregnation method. Instead of designing synthesis of smaller clusters, we are working with Re systems that allows us to synthesize alumina supported 3-atom clusters.

Pt_n/γ-Al_2O_3 Materials

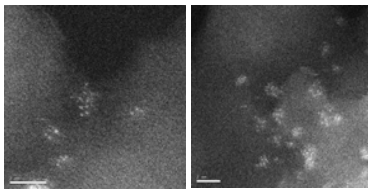


STEM images of the 2% Pt/ γ-Al_2O_3 sample

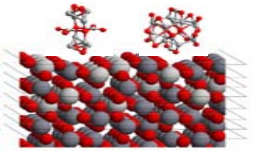


particles size distribution

- 80% particles in 1-1.5 nm range
- Structures assumed to be crystallites with symmetry of bulk metals
  - Pt_6: Octahedron with edge 0.55 nm
  - Pt_{20}: Edge 1.0 nm

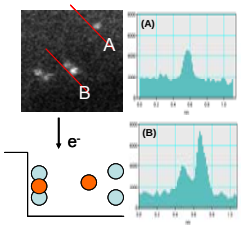


ACEM HAADF-STEM images of 2% Pt/ γ-Al_2O_3



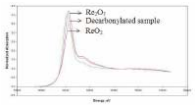
- ACEM images show the particles to be clusters of 10-20 atoms
- Theoretical models suggest that such clusters could be in oxidized state

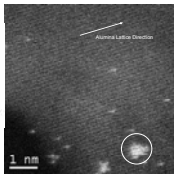
$H_3Re_3(CO)_{12}/\gamma\text{-}Al_2O_3$ Materials



- $H_3Re_3(CO)_{12}/\gamma\text{-}Al_2O_3$
  - –The IR data indicate the initial formation of rhenium tricarbonyl species as intermediates on the support surface, consistent with the EXAFS data characterizing the sample.
  - –3 x 3 smoothed image (top left) shows an isolated atom and two apparent dimers. Intensity profiles taken along lines A and B shown at right.
  - – Cartoon (bottom left) depicts cluster B orientation with front and side views. The cluster may be tethered to a ledge parallel to beam direction
  - –Intensity profile (B) shows double height of one "atom", as would be expected with the geometry suggested by the cartoon.

- Decarbonylated $H_3Re_3(CO)_{12}/\gamma\text{-}Al_2O_3$
  - The EXAFS parameters (coordination number $N_{Re\text{-}Re}$ = 2.3, distance $R_{Re\text{-}Re}$ = 2.69Å) indicate tri-rhenium raft-like structure on the support.
  - Re-support interaction via short Re-O bonds ($N_{Re\text{-}O}$ = 1.0, $R_{Re\text{-}O}$ = 2.04Å) and a long Re-O contribution ($N_{Re\text{-}O}$ = 0.7, $R_{Re\text{-}O}$ = 2.56Å) is evident.
  - XANES studies indicate that rhenium rafts are highly electron deficient and cationic in nature and Re is in +4 to +6 oxidation state
  - ACEM - Rhenium atoms and clusters form "rafts" that orient along the alumina lattice as time under the beam increases.





Comparison of Re L_{III} absorption edges of supported trirhenium rafts and reference materials

Experimental Results

- Pt and Re nano-clusters supported on alumina clearly are different from meso-particles/alumina and bulk metals. Theoretical models (in gas phase) suggest that experimentally observed Pt nano-clusters might be oxidized. Theoretical models of supported clusters will propose most stable structure for such clusters.
- Experimental and theoretical studies of nano-clusters supported on morphologically diverse alumina (sol-gel, molecular sieve) will enable us to determine the influence of support structure on catalyst sites.
- The experimental synthesis of carbonylated, decarbonylated, and small clusters of noble metals supported on alumina allows us to study the effect of nano-cluster size and oxidation state on catalytic oxidation of CO, NO_x, and HC.

Technology Transfer

- Tech transfer activities
  - Presentation at CLEERS, DEER2005, National Catalysis Society, and AIChE Meetings
  - Publications in refereed Journals
  - Establishing collaboration with OEMs – Ford, Cummins
- Collaborators
  - W. Shelton (ORNL), W. Schneider (University of Notre Dame), Y.Xu (Post-doctoral fellow, ORNL) – Theoretical Modeling
  - B. Gates (UC, Davis), V. Bhirud (Post-doctoral fellow, UC Davis), M. Moses (Post-doctoral fellow, ORNL) – Experimental Results
- Consideration of manufacturing, materials, design, supply chain
  - Does not require changes in manufacturing, design, or supply chains
- Timeframe for potential tech transfer
  - Ongoing

Future Work

- Understanding of the structures of nano-clusters on support. Our results show that nano-clusters are 10-15 atoms
  - Theoretical models to understand cluster size and their oxidation state (oxidized, reduced, in equilibrium)
    - Dependence on cluster size
    - Rapid or gradual equilibrium
  - Experimental studies on the structures of these systems using EXAFS, XANES
- Support interaction with clusters and its impact on the structure and reactivity
  - Cationic or zero-valent metals or both
- Reactivity of the clusters
  - Theoretical and experimental studies on structure-reactivity correlation
    - CO, NO_x, and HC oxidation studies
- The impact of cluster size on reactivity
- Project End-Point
  - Establish a new protocol for catalyst discovery with ability to forecast improvement

Publications, Presentations, Patents

- Publications
  - Y. Xu, W. A. Shelton, W. F. Schneider, Effect of particle size on the oxidizability of platinum clusters, J. Phys. Chem., B (submitted)
  - 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
- Presentations
  - 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)
  - 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)
  - 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). The poster received first place award.
  - Narula, C.K.; Shelton, W.A.; Allard, L.F.; Xu, Y.; M. Moses, M.; Schneider, W.; Gates, B.; Combining Theory and Experiments in Studies of Structural Changes in LNT Materials, Eighth DOE Crosscut Workshop on Lean Emissions Reduction Simulation, University of Michigan - Dearborn, Dearborn, Michigan 48128, May 17-19, (2005).
  - Narula C.K.; Allard, L.F.; Moses, M.J.; Xu, Y.; Shelton, W.; Schneider, W.F.; Graham, G.; Hoard, J.; Lean NOx Traps - Microstructural Studies of Real World and Model Catalysts, DEER 2005, Palmer Hilton, Chicago, Aug. 21-25, (2005).