

An Integrated Approach to the Rational Design of Chemical Catalysts

Participants

Institutions

Robert J. Harrison: PI

Oak Ridge National Laboratory,
University of Tennessee

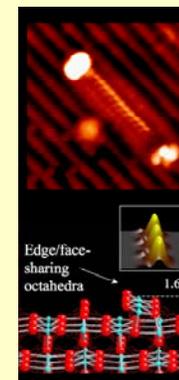
Jerzy Bernholc
A.C. Buchanan III
Marco Buongiorno Nardelli
James M. Caruthers
W. Nicholas Delgass
David A. Dixon
Sharon Hammes-Schiffer
Duane D. Johnson
Manos Mavrikakis
Djamaladin Musaev
Mathew Newrock
Steven H. Overbury
William F. Schneider
William A. Shelton
David Sherrill
Bobby G. Sumpter
Kendall T. Thomson

North Carolina State University
Oak Ridge National Laboratory
North Carolina State University
Purdue University
Purdue University
University of Alabama
Pennsylvania State University
University of Illinois at Urbana Champaign
University of Wisconsin at Madison
Emory University
University of Virginia
Oak Ridge National Laboratory
University of Notre Dame
Oak Ridge National Laboratory
Georgia Institute of Technology
Oak Ridge National Laboratory
Purdue University

Summary

- o The Chemical Endstation brings together researchers from 12 academic and government laboratories representing research projects funded by DOE, NSF and other agencies, with the common interest in the rational design of catalysts
- o The large collaboration has been very successful: several important publications including articles in Physical Review Letters and an article which made the cover of Physical Chemistry Chemical Physics.
- o 11 Journal Articles, 22 presentations, 8 post-doctoral students and 3 graduate students

Surface reconstructions of TiO₂ (110) driven by suboxides — Pan, Meunier



- Recent experiments of highly dispersed gold on titanium oxide show remarkable catalytic activity
- Defects are believed to play a crucial role in the formation of nano-clusters on surface
- A part of the challenge in understanding defects is that transition metal oxides range of stoichiometry and structure.
- From the comparison between experimental and theoretical studies
- the formation of face- sharing octahedra is a mechanism through which a "bulk-like" (1x1) surface can be restored in sub-stoichiometry: 2(TiO) instead of 2(TiO₂) per unit cell. When the row of 2(TiO) is reduced, the remaining structure relaxes into a Ti-rich double row of Ti₂O, which exhibits key characteristics consistent with previously reported double strands.

Surface Strain



Grabow, Xu, Mavrikakis

- o Surface strain plays a major role in determining the rate limiting step and catalytic activity of platinum for CO oxidation.
- o Density functional theory (DFT) calculations were used to investigate the change of thermodynamics and kinetics with variations in surface strain on the Pt(111) surface.
- o ORNL resources were used to perform part of the DFT calculations in this work.

Hybrid ab initio DFT/Thomas-Fermi method

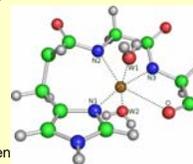
Hodak, Lu, Bernholc

- Hybrid model features:
 - Overlap of densities
 - Exchange of solvent molecules between *ab initio*/TF subsystems
 - No additional parameters are needed (unlike QM/MM) once TF density is specified
- Suitable for (bio)molecules in solution
 - *ab initio* DFT: biomolecule (chemically active part), nearby solvent molecules
 - TF: all other solvent molecules (>1000)
- Initial application: Prion protein PrP^C
 - Involved in neurodegenerative diseases: Creutzfeldt-Jacob disease, Bovine spongiform encephalopathy (BSE)
 - misfolding into scrapie form PrP^{Sc}
 - *ab initio*: PrP^C, 12 waters (109 atoms)
 - Thomas-Fermi: 1469 waters (4407 atoms)
 - *ab initio* part takes 97% of CPU time

Cu-PrP^C binding site geometry

- Copper-HGGGW bond distances (Å):

| | Dry protein | partial solvation | full solvation |
|-------|-------------|-------------------|----------------|
| Cu-N1 | 1.99 | 1.98 | 1.98 |
| Cu-N2 | 2.01 | 2.00 | 2.01 |
| Cu-N3 | 1.91 | 1.91 | 1.92 |
| Cu-O | 2.23 | 2.41 | 2.36 |
| Cu-W1 | - | 2.78 | 2.82 |
| Cu-W2 | - | 2.79 | 2.7 |



- Solvation is important for non-covalent bonds

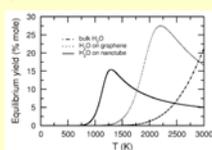
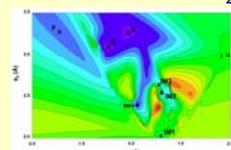
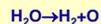
Gap between unoccupied and occupied states:
Dry PrP^C-Cu: 2.11 eV
Partial solvation: 2.25 eV
Full solvation: 2.38 eV

Solvation is important for electronic properties and cannot be neglected

Also important for reaction energetics

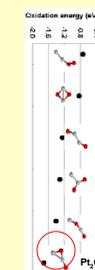
Catalytic role of defective carbon substrates in the dissociation of water

Kostov, Santiso, George, Gubbins and Buongiorno-Nardelli

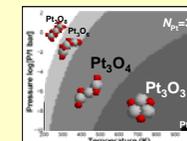


Potential energy surface for water dissociation on a vacancy in graphene - low energy barriers wrt the direct thermal splitting due to the ability of the carbon substrate to keep the reaction on the spin singlet surface

Defective carbon substrate can produce hydrogen from water at temperatures at least a factor of 2 lower for hydrogen yields comparable to the free space reaction



Supported metal nanoclusters have been gaining research interest in catalysis new materials distinct from bulk metals (e.g., Au) synthesis techniques becoming more sophisticated exciting possibility of potentially tunable catalytic properties Activity of metal catalysts depends on chemical environment fluid phase (*T, p, C*), support, surface species, ... e.g., the active phase of several transition-metal oxidation catalysts is not metallic but metal oxides Nanoclusters may be very sensitive to environment effects of particle size and environment on structure, composition, reactivity DFT calculations performed to better understand these effects focus is on Pt in oxidizing environment



O₂ atmosphere affects the composition and structure of Pt clusters Reactivity of Pt clusters very different from Pt bulk surface Strong size dependence observed in both the oxidation and reactivity of P clusters

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