First principles studies of nanoscale effects on catalytic activity and selectivity

Larry A. Curtiss
Materials Science Division
Center for Nanoscale Materials

Outline

- Introduction to complexity involved in catalysis by small cluster
- Examples of complexity in catalytic reaction mechanisms and the need for experiment
- Design of new catalysts.

Introduction

- Understanding the effect of size, composition, and support on the catalytic properties of nanoscale clusters is very important.
  - Insight into the special reactivity properties exhibited by supported metal and metal oxide clusters not observed in their bulk analogs
  - Attractive as new materials for catalysis.
  - May lead to the development of new classes of catalytic materials with control of their bond breaking and making capabilities.
- ANL has an integrated synthesis, characterization, catalytic testing, and computational study is of supported nanoscale metal clusters.
  - resulting in the discovery of structure-property relationships
  - Special catalytic properties

Introduction – computational studies

- Computational studies (DFT) can provide information on the structural and electronic properties of the intermediates involved in the reaction mechanisms
  - it is difficult to experimentally obtain information on these intermediates and, thus confirm the computational modeling.
- Several examples will be given of catalytic reaction mechanisms and the complexities of intermediate states involved
  - Small silver clusters for environmentally friendly catalysis
  - Learning how to increase the reactivity of VOx clusters

Propylene oxide (PO)

- An important chemical and intermediate for many other industrial chemicals
- Current methods of production involve large amount of chlorinated waste
- Direct partial oxidation of propylene by molecular oxygen can overcome the waste problem

$$2CH_3\text{-}CH{=}CH_2 + O_2 \rightarrow 2PO$$

catalyst

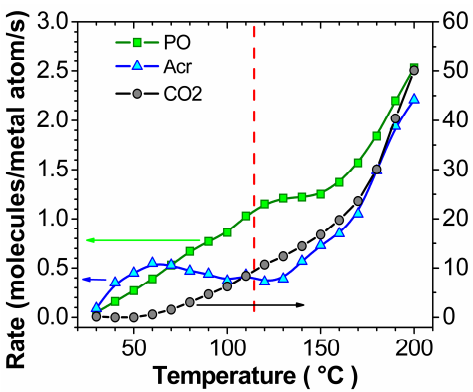
- Problems:
  - no industrial scale catalyst has been identified
  - Ag shows high selectivity for <u>ethylene</u> epoxidation in both lab and at industrial scale
  - Ag shows poor selectivity for propylene epoxidation

- Hayashi, Tanaka, Haruta, J. Catal. 178, 566 (1998)
- Lambert, Williams, Cropley, A. Palermo, J. Mol. Catal. A: Chem. 228, 27 (2005)
- Serafin, Liu, Seyedmonir, J. Mol. Catal. A: Chem. 131, 157 (1998)
- Barteau and Madix, JACS 105, 344 (1983)

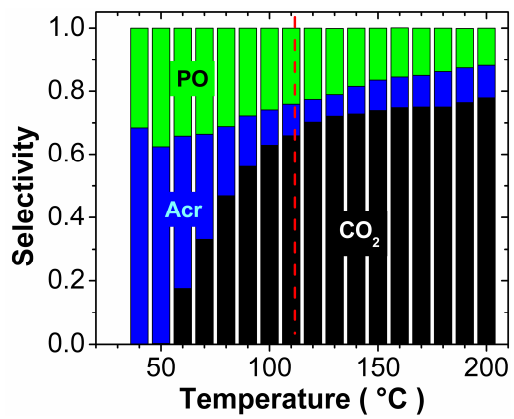
Size-selected Ag trimers on alumina: propylene epoxidation

(Vajda, Greeley, Pellin, Winans, Curtiss et al, Science, 2010)

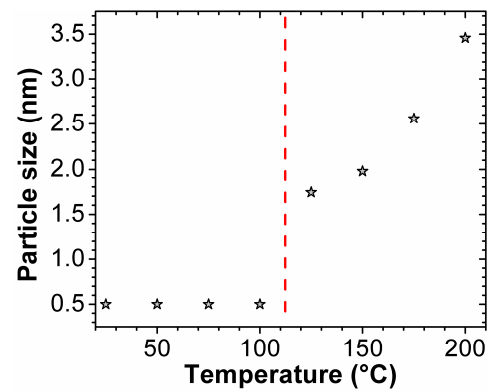
- **At 110 C abrupt sintering to 2x4nm Ag aggregates**
- **Very high activity and selectivity for propylene oxide (PO) formation**
- **CO_2 increase coupled to acrolein (AC) decrease**
- **Expt. activation barriers: PO: 0.25 eV; AC: 0; CO_2: 0.7 eV**



Activity



Selectivity



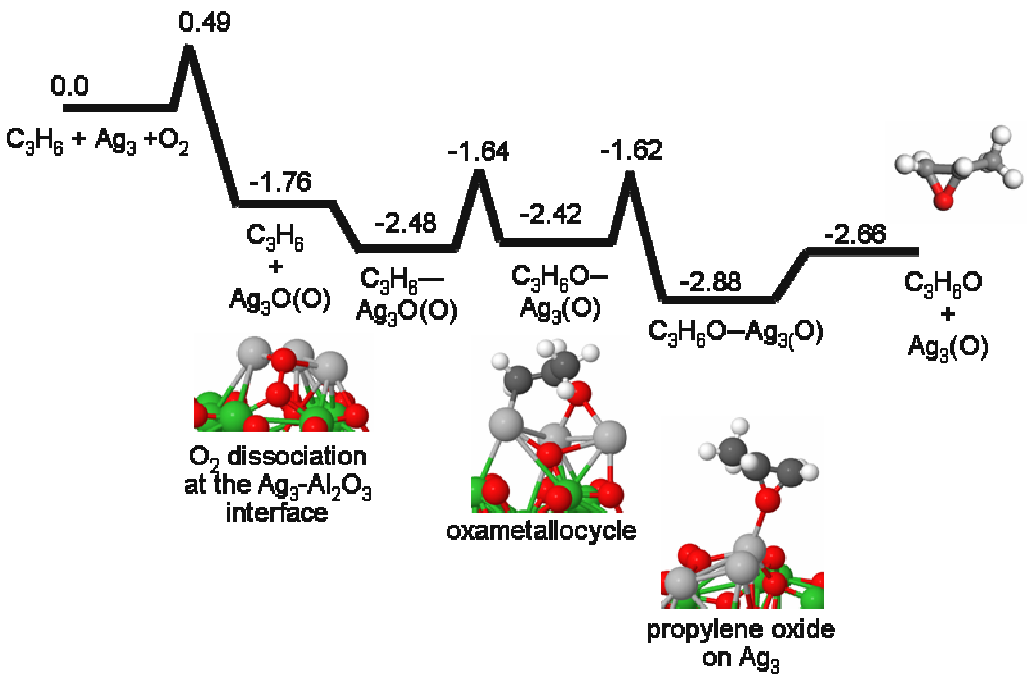
GISAXS cluster size study

- **Questions?**
  - **What is the mechanism for O_2 dissociation (O_2 dissociation on a Ag_3 gas phase cluster has a very large barrier (2.5 eV))**
  - **Why is Ag_3 cluster is more active and selective than silver surface as a propylene epoxidation catalyst?**
  - **What is the mechanism for acrolein formation**

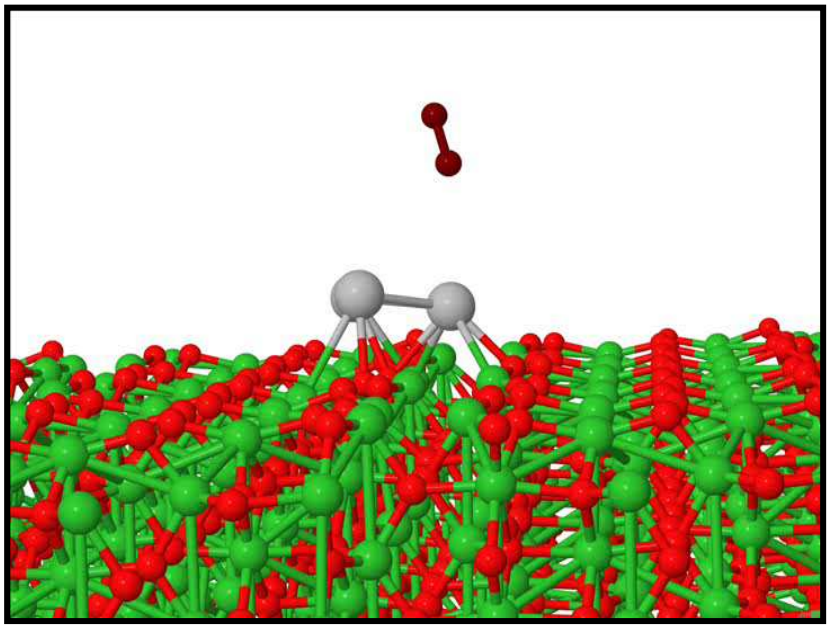
- **Theoretical methods**
  - **B3LYP density functional theory for clusters**
  - **Periodic calculations with cluster supported on θ-Al_2O_3(010); PW91 functional**
  - **Model system for experiment**

Extensive potential energy surface investigation of reactions of O_2, propylene oxide with supported Ag_3 cluster

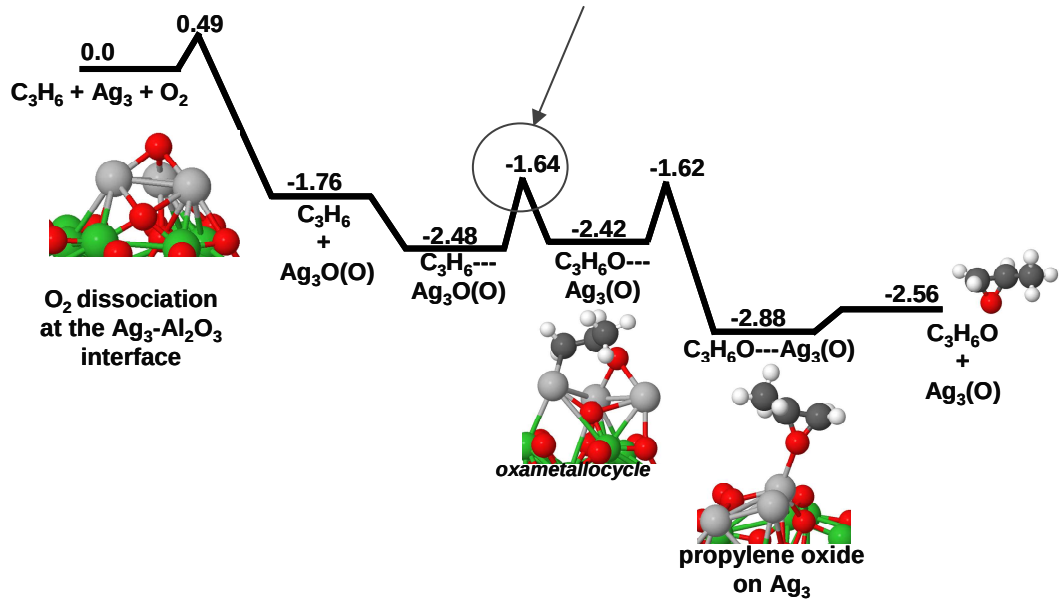
- Fully investigated about 20 pathways for formation of acrolein, propylene oxide, acetone, propanal

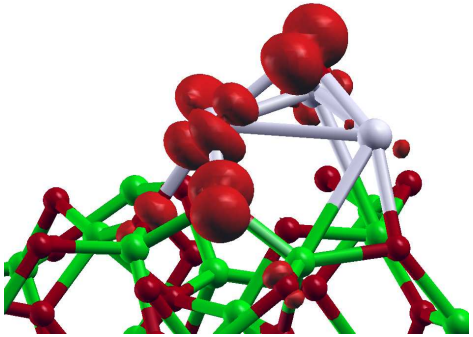


Ag trimer Al_2O_3: propylene epoxidation pathway



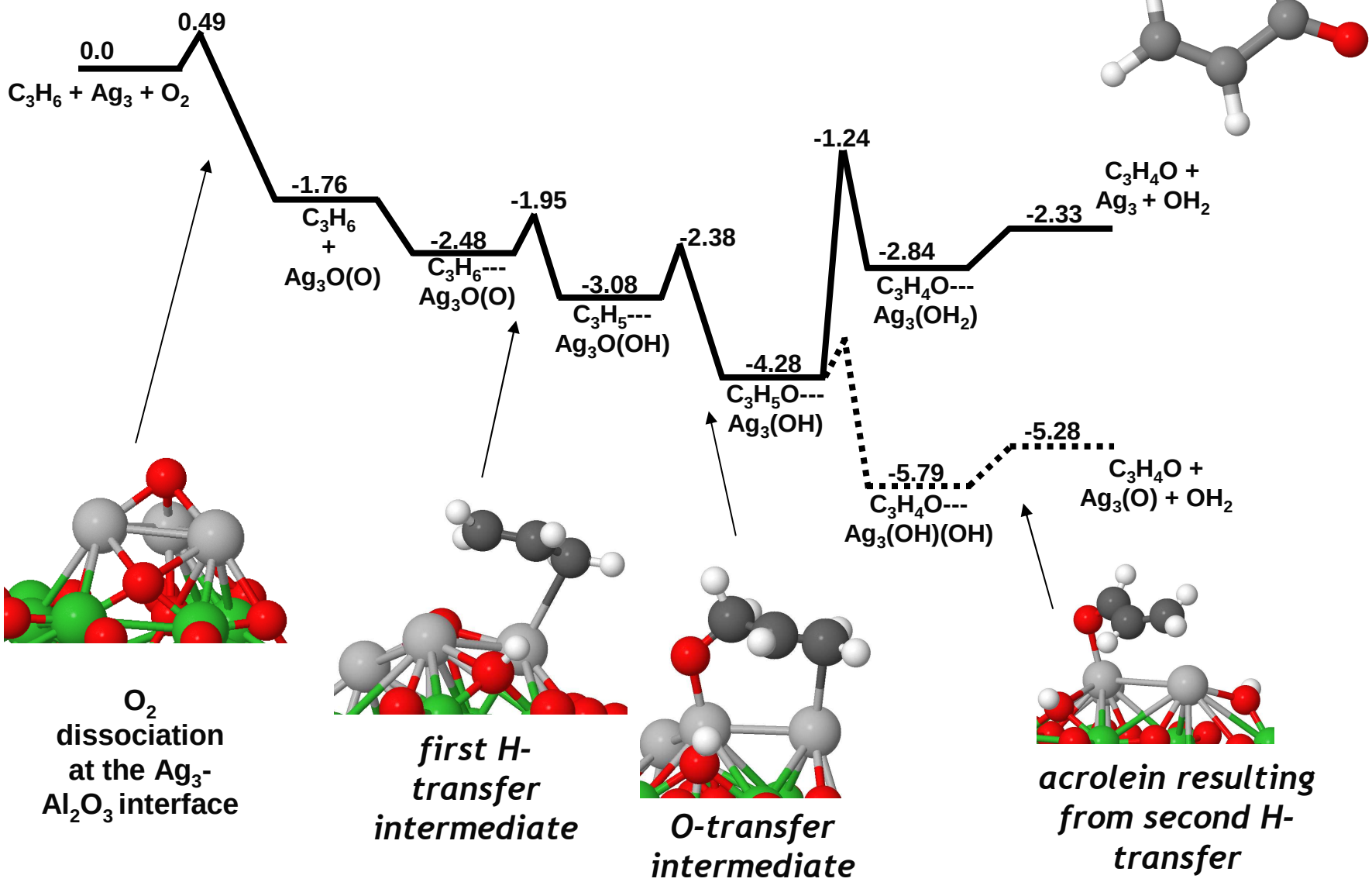
Apparent barrier of 0.12 eV for oxametallacyle formation compared to 0.7 eV on Ag surface → reason for higher propylene oxide activity on the trimer





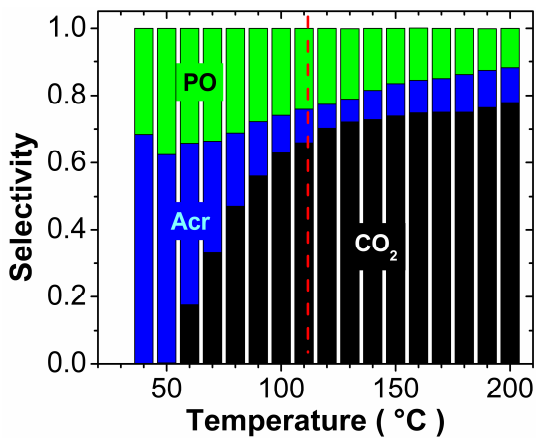
Electron spin density (in red) on the silver trimers is responsible for their high activity

Ag trimer: Al_2O_3 acrolein pathway

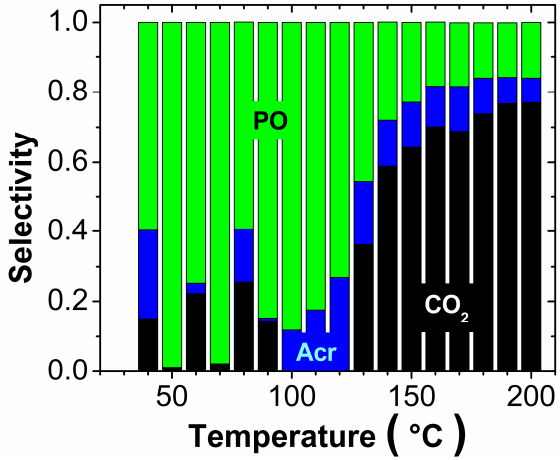


Ag aggregates on alumina: propylene epoxidation

- **Agregates**
  - **Same activity per surface site as trimers - same mechanism?**
  - **More selective towards PO at low temperatures - why?**



Ag_3



Ag 2x4nm aggregates

Ag aggregates - preliminary calculations

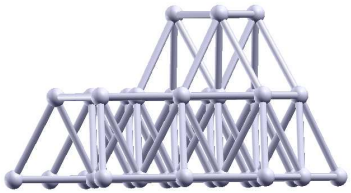
Starting geometry

Optimized geometries

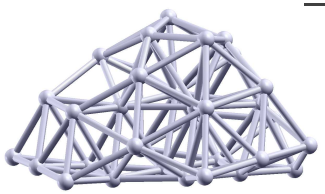
Rel. energies, eV

Spin densities

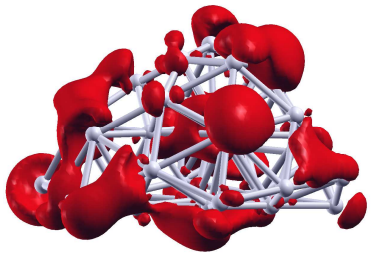
Ag_{33}



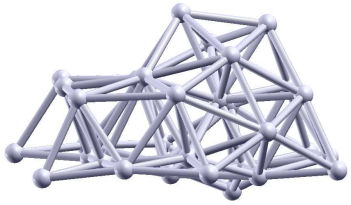
μB = 3



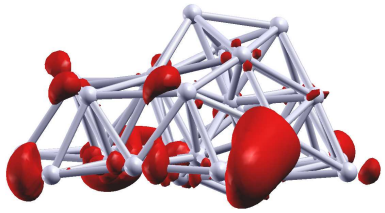
0.07



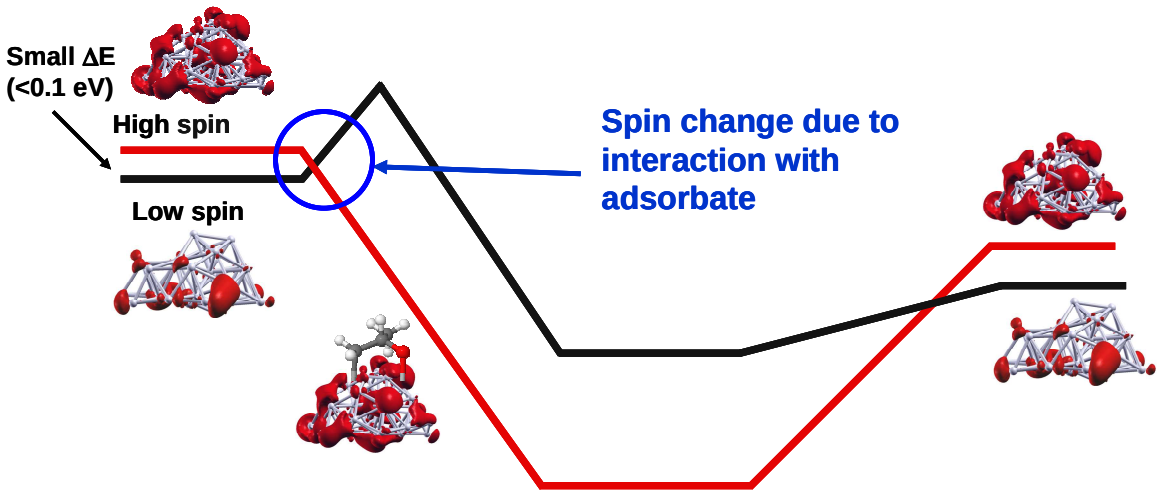
μB = 1



0.0



Many structures are possible; more complete studies needed!



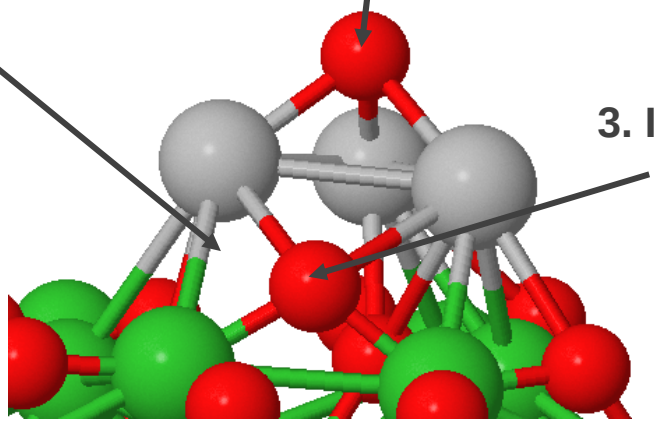
Strong adsorbate interaction with higher spin states may result in spin curve crossing

– may be the the reason for the high activity for Ag aggregates compared to Ag bulk.

Summary

2. O in 3-fold site is very active for oxygen addition to C=C double bond (PO formation)

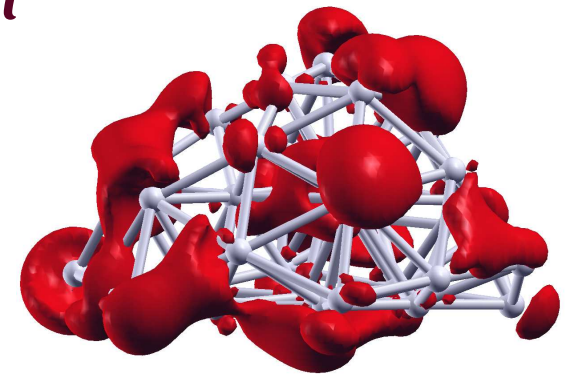
1. O_2 dissociation most favorable at interface



3. Interface O is very active for hydrogen abstraction (acrolein/CO_2 formation coupled)

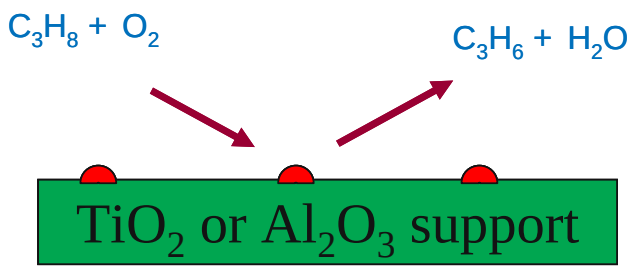
Preliminary results

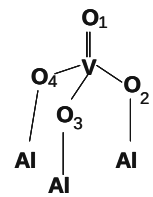
4. Spin density on surface sites results in similar surface site reactivity due to low energy high spin states



5. Less interface O results in higher selectivity towards PO vs acrolein/CO2

Vanadium oxide catalysts for propane oxidative dehydrogenation



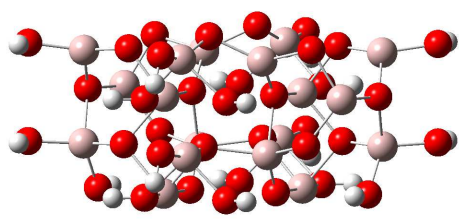


First step: Insertion of O from catalyst into a C-H bond (Mars and van Krevelen mechanism)

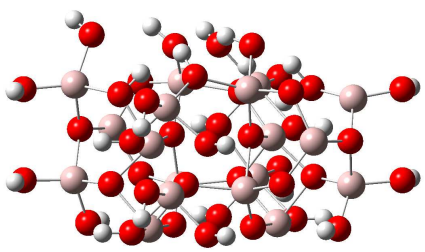
Current work

- New insight into the structure and reactivity of vanadium oxide monomer catalysts from theory and experiment (with P. Stair)

- Density functional theory (B3LYP)
- Models for supports
  - Hydrogen terminated clusters

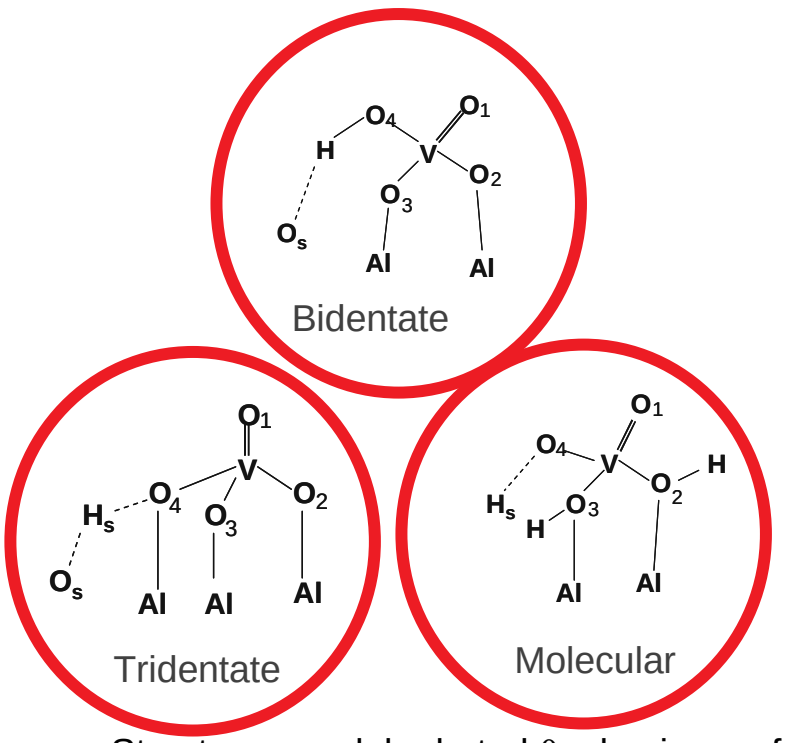


Dehydrated θ–alumina surface

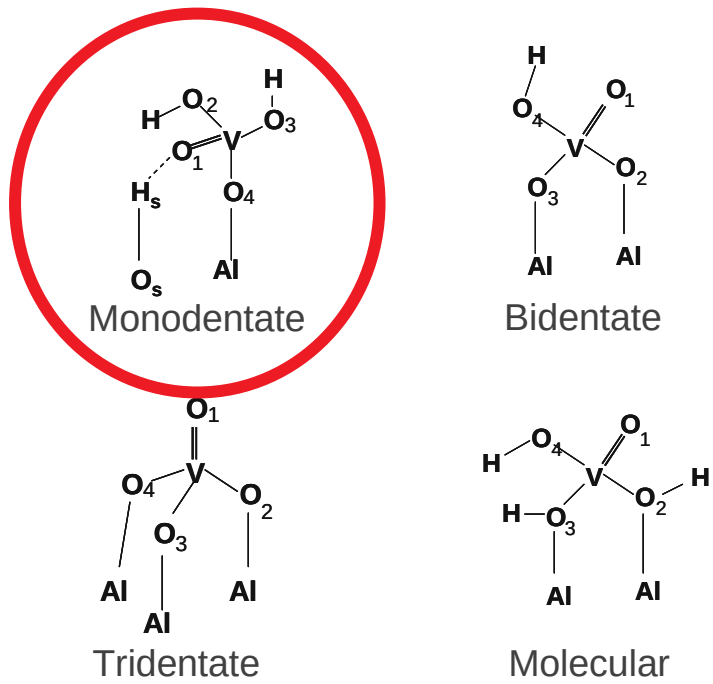


Hydrated θ–alumina surface

Optimized VO_x monomeric structures on cluster models of dehydrated and hydrated θ–alumina surfaces.



Structures on dehydrated θ–alumina surface

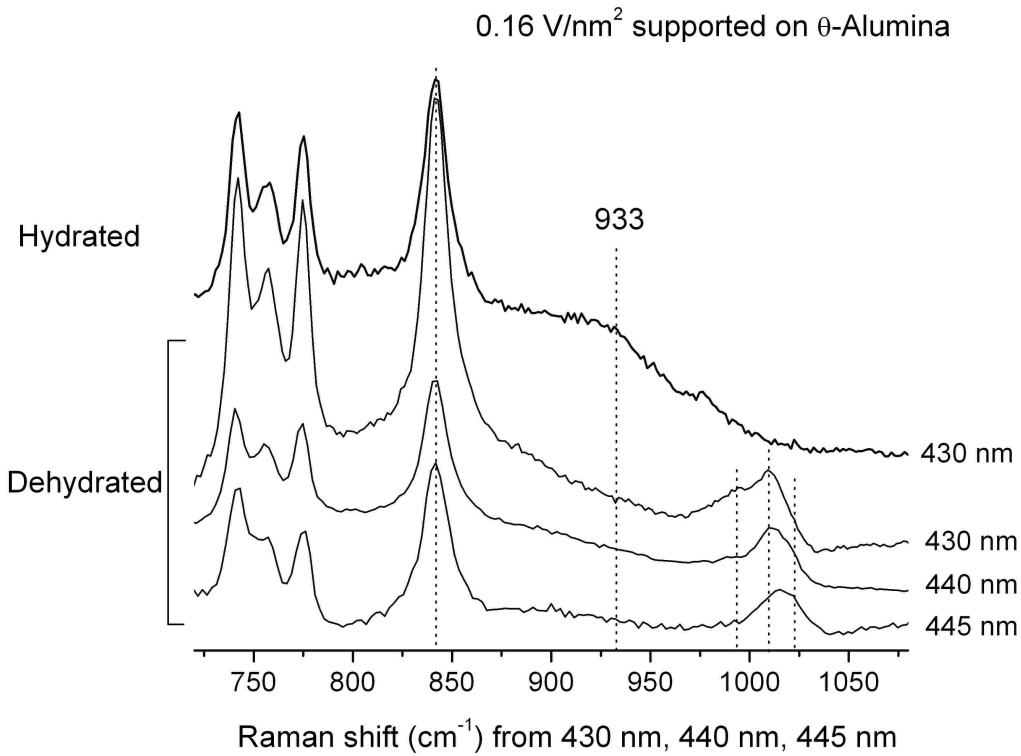


Structures on hydrated θ–alumina surface

- UV-Raman combined with theory provide evidence that **three** of the structures exist under dehydrated conditions and **one** under hydrated conditions!

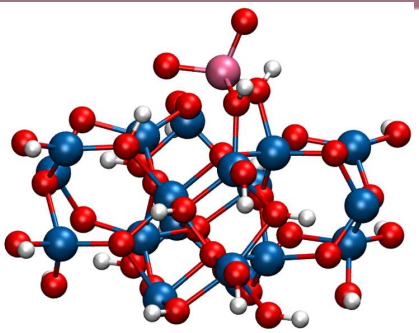
(Kim, Zygmunt, Stair, Zapol, Curtiss, JPC, 2009)

UV-Raman spectra of VOx monomers

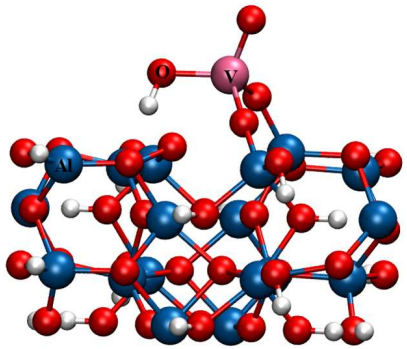


Raman spectra excited at three different excitation wavelengths of 430 nm, 440 nm, and 445 nm for 0.16VO_x obtained at dehydrated and hydrated conditions.

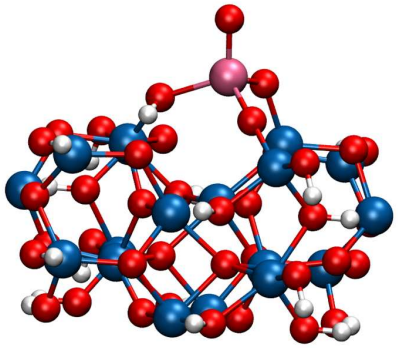
(Kim, Zygmunt, Stair, Zapol, Curtiss, JPC, 2009)



Molecular



Bidentate



Tridentate

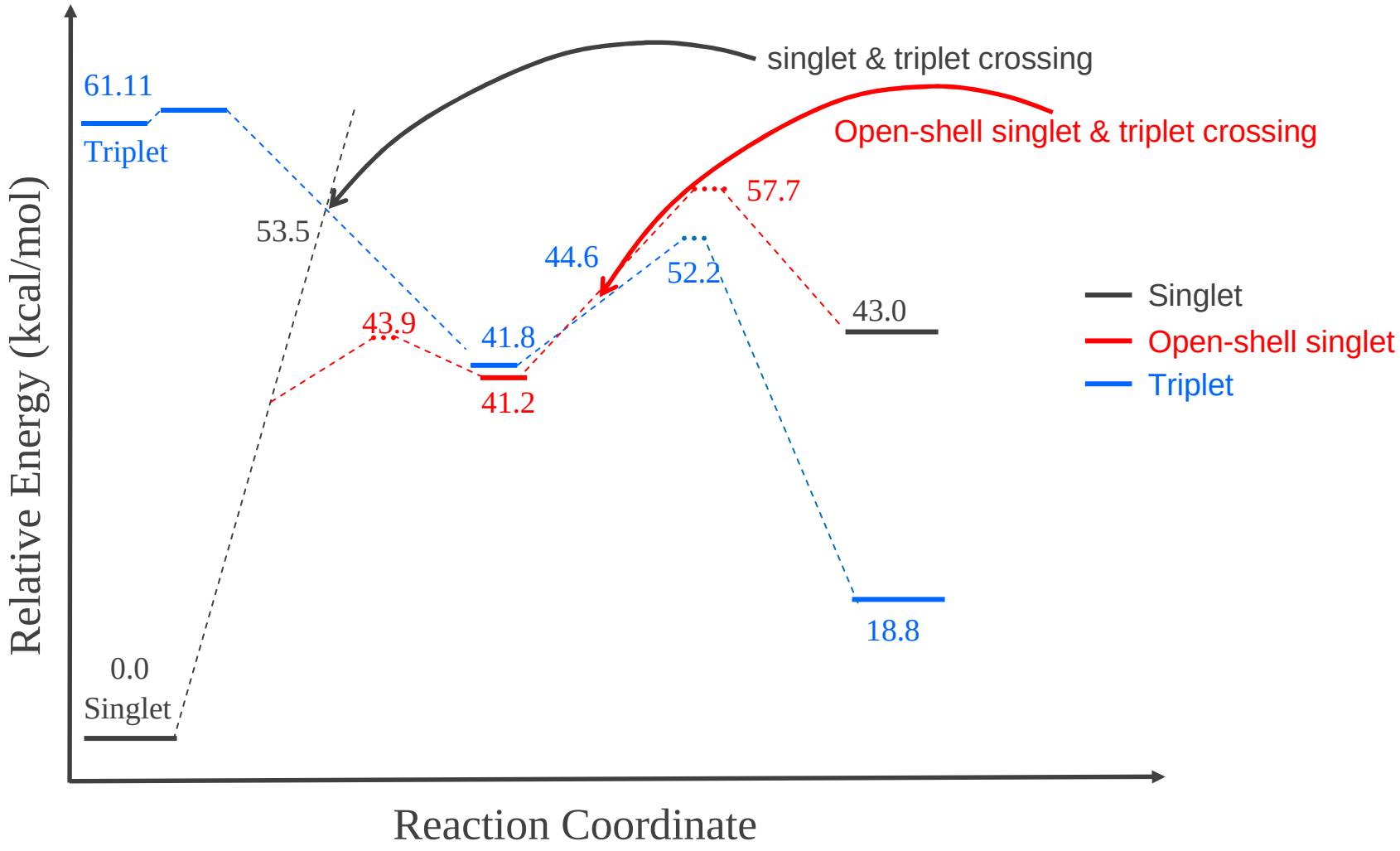
<u>Question:</u> how does the reactivity of the metal oxide clusters depend on structure?

Comparison of theoretical predictions and experiment (Stair and Kim) for reducibility by H_2 on VOx monomers on Al_2O_3

- *Rozanska, Fortrie, Sauer, J. Phys. Chem C 111 6041 (2007) Oxidative Dehydrogenation of Propane by Monomeric Vanadium Oxide Sites on Silica Support*
  - A key transition state is an open-shell singlet (broken symmetry solution)
  - Rate determining step involves H transfer from propane to V=O.

- Potential energy surface issues
  - Do curve crossings such as between electronic states play a role? Importance of open-shell singlet
  - How accurate are simple approximations to the curve crossings to a full search of the surface
  - Is the spin-orbit coupling large enough

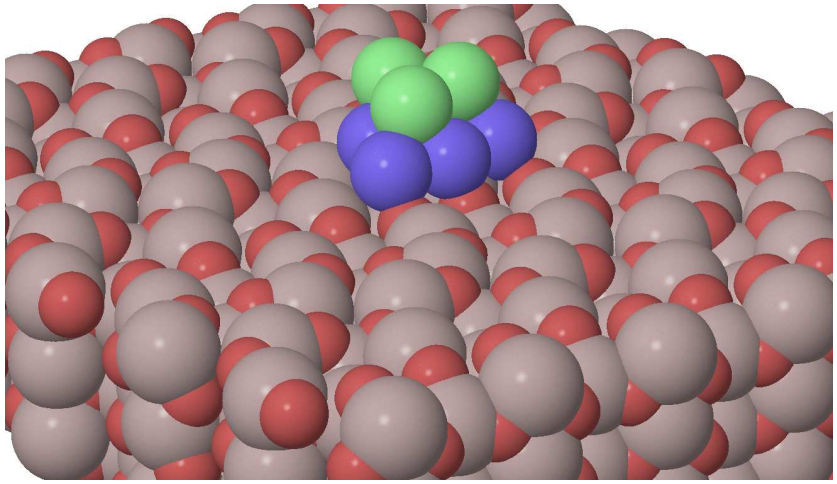
Complexity of potential energy surfaces for catalysis reaction mechanism: spin state changes



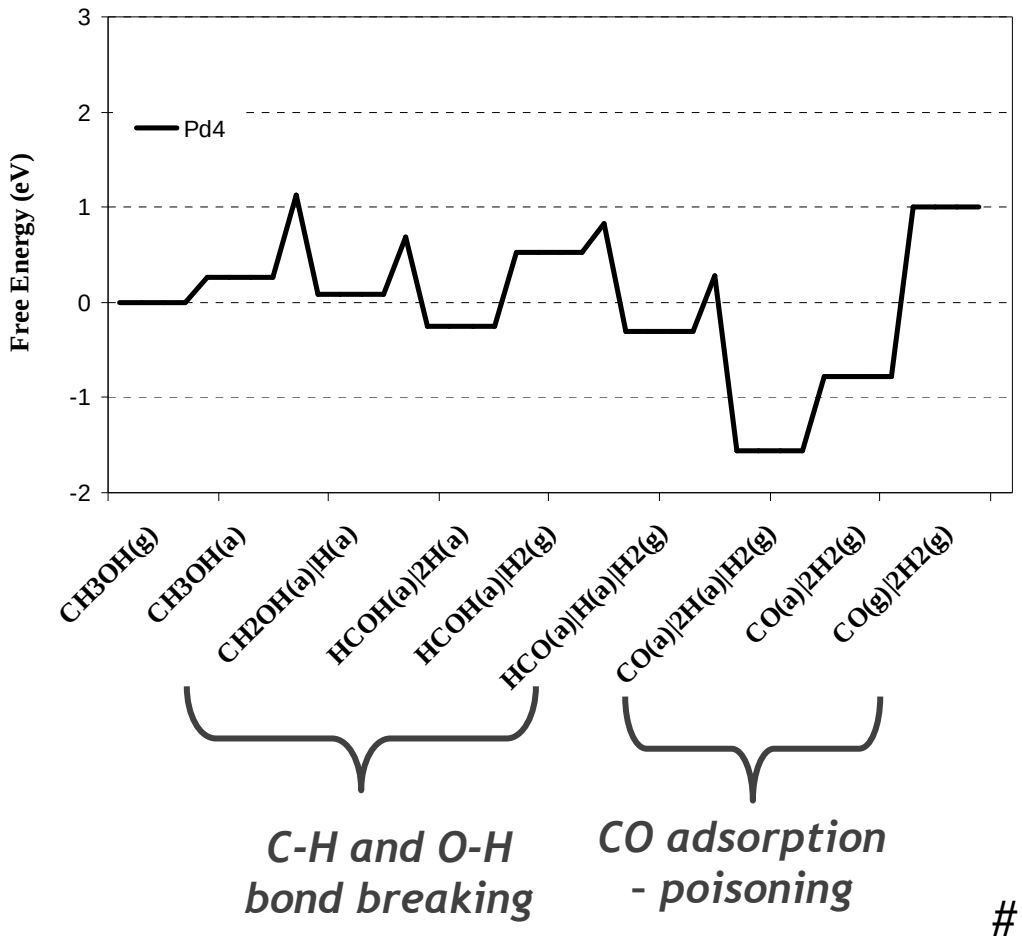
Outline

- **Understanding of catalytic reaction mechanisms on subnanometer and nanoscale clusters**
  - **Ag_n clusters**
  - **VO_x clusters**
- **Catalytic materials design**

Tailor metal alloy clusters for specific bond breaking and making reactions; bifunctional catalytic capabilities.



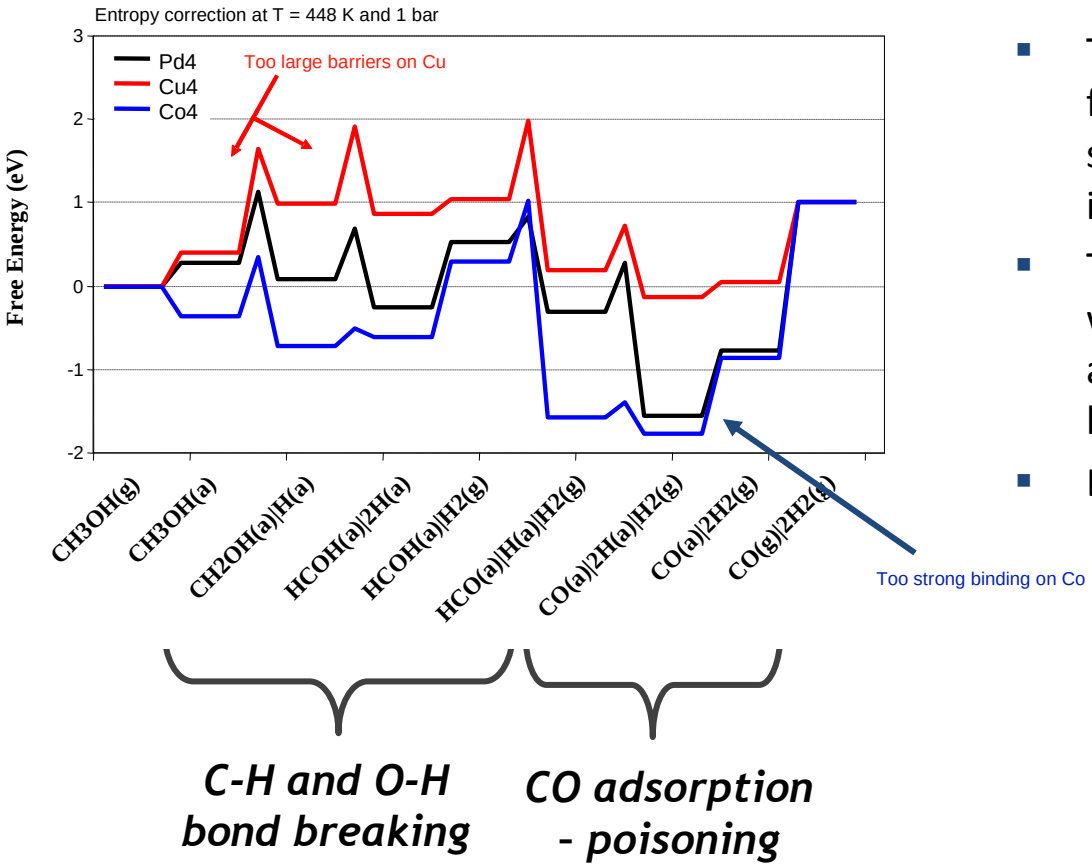
Methanol decomposition to H_2 and CO on Pd clusters



- Expt:# small Pd clusters on alumina were found to promote decomposition of methanol to CO and hydrogen, however with mediocre activity
- DFT studies* (PW91 functional) : CO adsorption likely poisons the catalyst and is the likely reason for the mediocre activity
- Can cluster size and composition be optimized for low temperature methanol decomposition to H_2?

Vajda et al, JPC 2010
* Mehmood, Greeley, Curtiss, JPC 2009

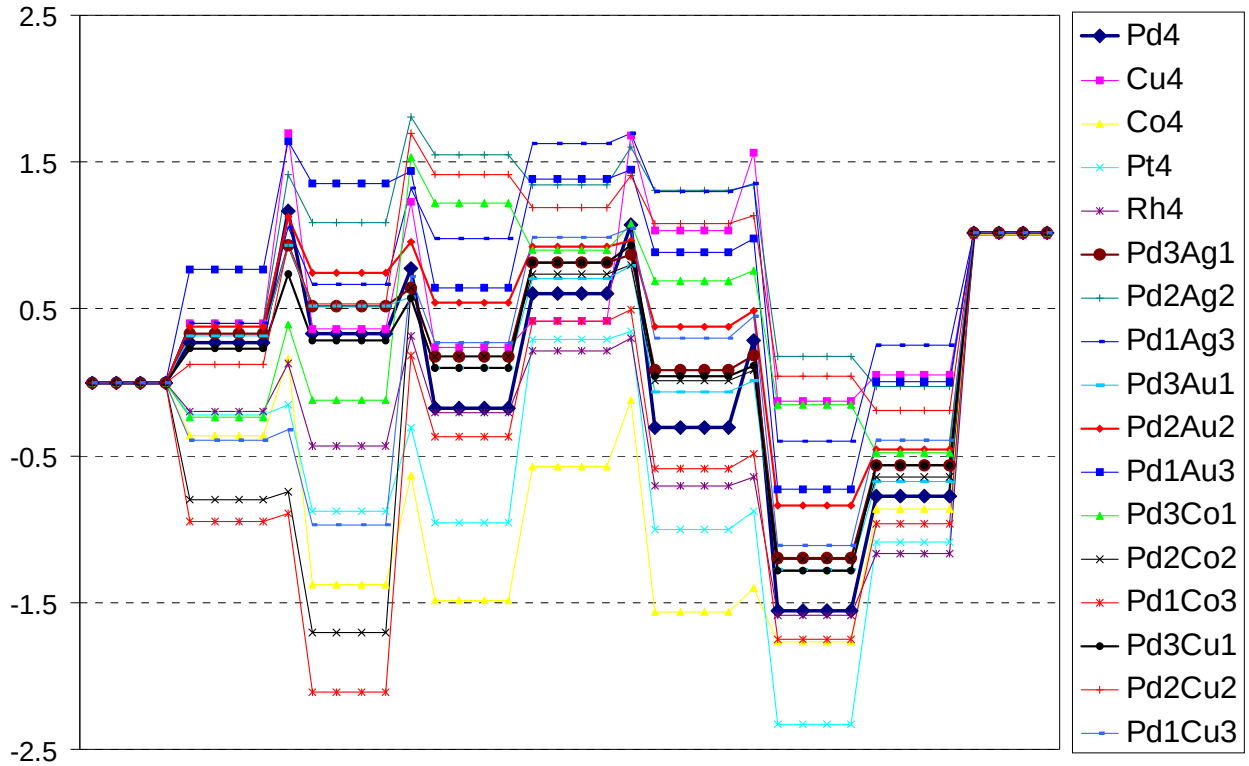
Methanol decomposition to H_2 and CO on Co_4 and Cu_4 clusters: comparison to Pd_4 cluster



- The Co_4 cluster was found to active for C-H and O-H bond breaking; but strong binding CO would likely result in poisoning
- The Cu_4 cluster was found to have weak binding for CO; but was not very active for active for C-H and O-H bond breaking
- Explore metal alloy clusters

Mehmood, Greeley, Zapol, Curtiss, JPC 2010

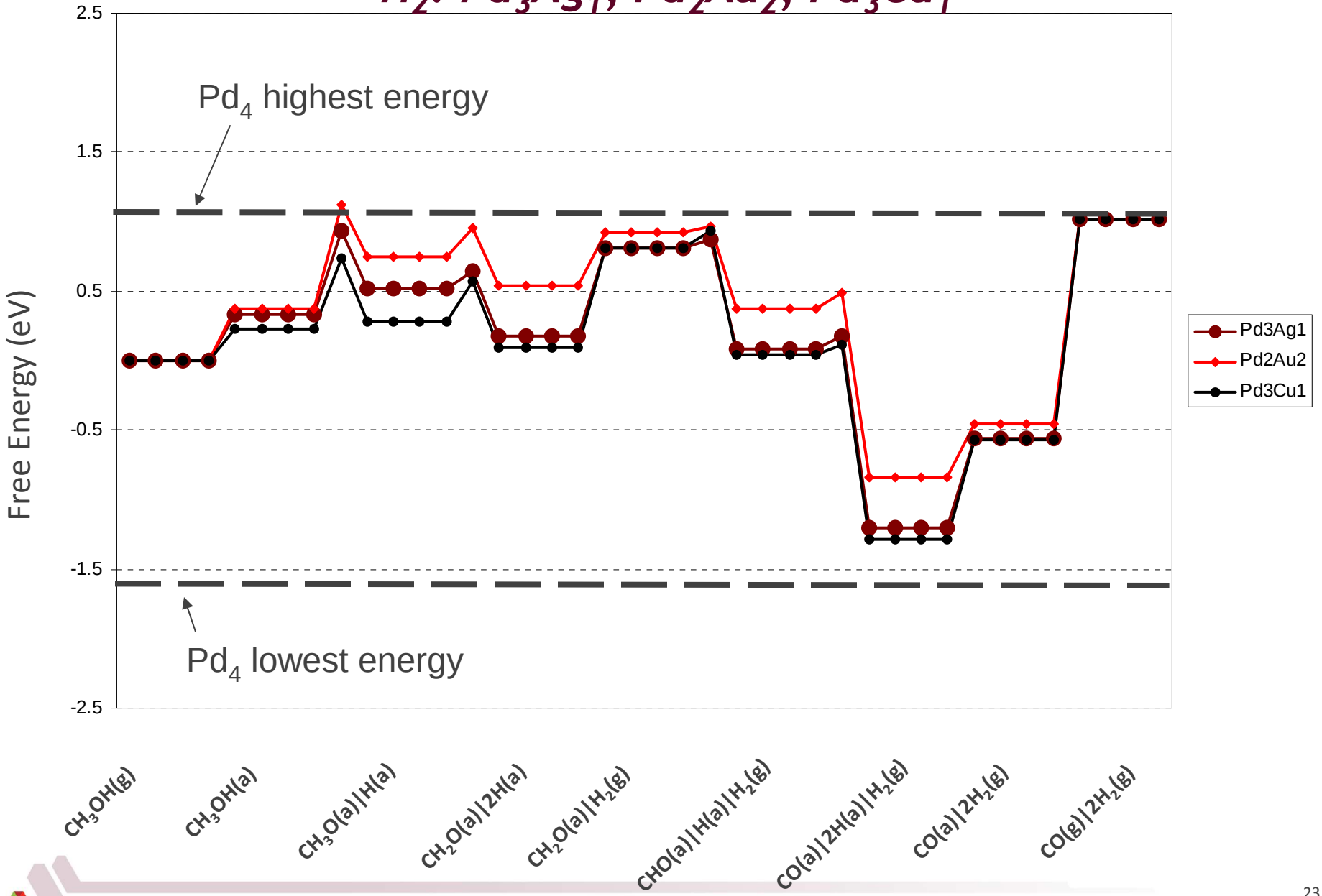
Screening of metal alloy clusters



Based on the estimated reaction energies from the scaling relationship and reaction energies from BEP relationships between E(TS) and E(FS), free energy diagrams are obtained

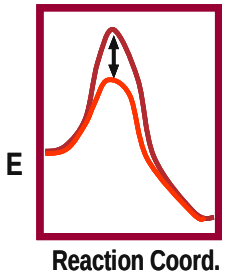
This enables identification of bimetallic alloys with weaker CO binding energies and smaller methanol activation energy barriers

Candidates for improved methanol decomposition to H_2: Pd_3Ag_1, Pd_2Au_2, Pd_3Cu_1



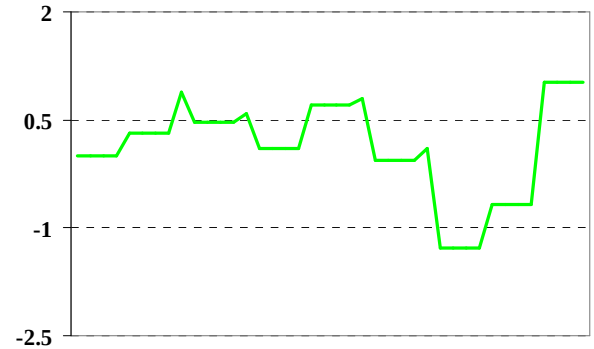
Materials Design Workbench

Data from computations

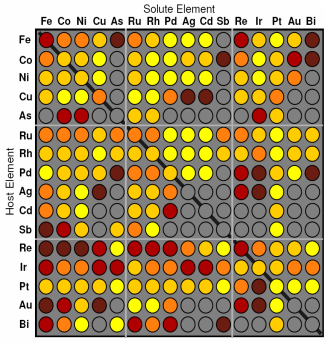


Scaling relationships to speed up reaction pathway calculation

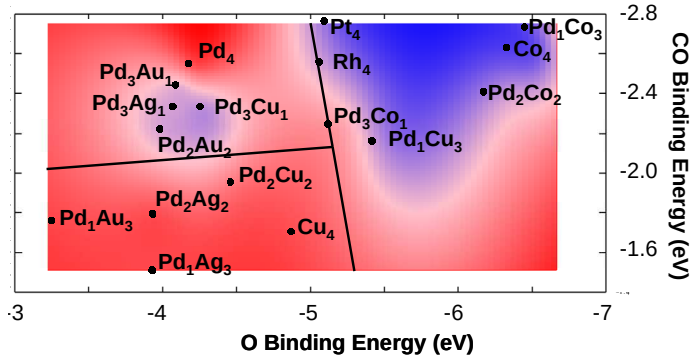
Reaction pathways



Find descriptors to optimize activity

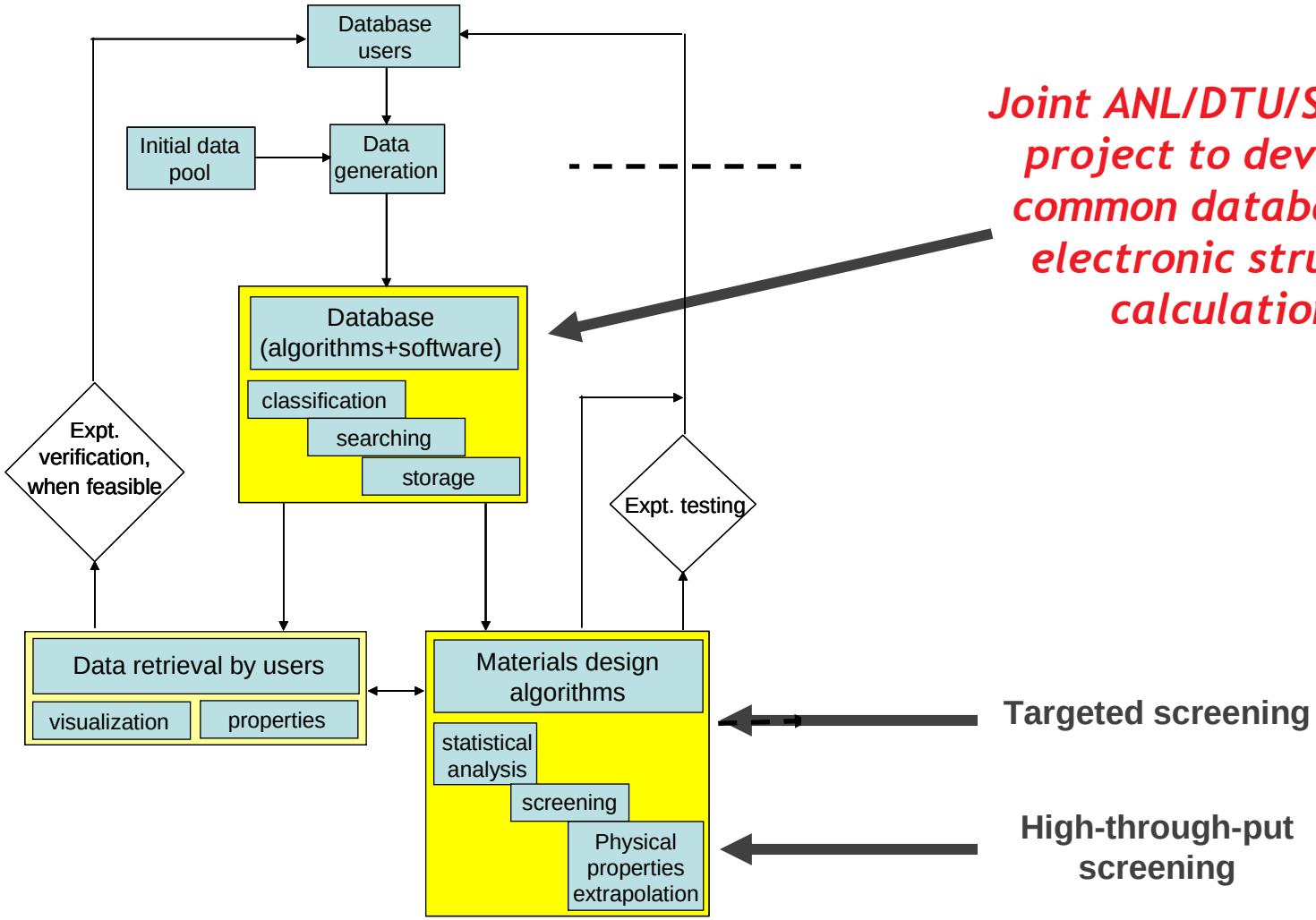


Screening many candidates based on descriptors



Materials Design Workbench for Catalysis

Ian Foster (CI), Svetlozar Nestorov (CI)



Joint ANL/DTU/Stanford project to develop a common database for electronic structure calculations

Summary

- Computational studies (DFT) can provide information on the structural and electronic properties of the intermediates involved in catalytic reaction mechanism
- However, it is difficult to experimentally obtain information on these intermediates and, thus confirm the computational modeling.
- Any information on reaction intermediates and catalytic sites that can be very helpful to validate the modeling work and to develop model, e.g electronic states, structures
- Several examples given of catalytic reaction mechanisms and the complexities involved.
  - Small silver clusters for environmentally friendly catalysis
  - Learning how to increase the reactivity of VOx clusters
- Can lead to the development of new classes of catalytic materials with control of their bond breaking and making capabilities for more environmentally friendly catalysis