

# Gas-Solid and Gas-Liquid Interfaces

Moderators: Daniel E. Resasco, Miquel Salmeron

The aim of this break-out session was the discussion of ideas about research opportunities and challenges in the area of “Gas-Solid” and “Gas-Liquid” interfaces. The main theme of the discussion was the development of fundamental knowledge of the interfaces at the atomic level.

From a list of rather specific topics presented at the beginning of the session, four major areas that incorporate all the specific topics were selected for discussion:

1. Experimental model systems
2. Particle size effects
3. Building nanostructured surfaces
4. Elementary steps of reactions

## 1. Experimental model systems

- Model systems are expected to faithfully represent a real catalyst. Therefore, not only the well-known “pressure gap” between studies on model and real systems needs to be addressed, but also the “materials gap” is a problem. That is, in addition to studies on well-defined single-crystals, more complex (more realistic) models need to be studied.
- The study of model system is important as they provide a well-defined, simplified reaction system that can be used in cooperation with theory and molecular simulations to understand the catalytic phenomenon at the atomic level. Models also provide catalytic activity benchmarks (turnover frequencies) that can be used for comparison with real systems without the limitation of mass/heat transfer limitations that may affect real systems.
- Model systems can provide a direct measurement of the identity and the density of active sites on a surface.
- The role of promoters and poisons can be readily studied and quantified on model systems.
- In-situ characterization of the liquid-solid interface. Use of polarization allows for discrimination between adsorbed and dissolved species as well as adsorption geometries
- Research opportunities:
  - Solid integration of the experimental studies on model systems with powerful theoretical simulations
  - Use of model systems in predicting reactivity of real catalysts to guide discovery, in addition to the more conventional role of explaining reactivity of known catalysts.
  - Well-structured model systems (beyond single-crystals)
    - Clusters, multimetallic and oxide nanoparticles
    - Carbide, sulfide nanoparticles
    - 3D nano/meso-structured porous systems
  - Multi-functional model systems incorporating different functionalities – adsorption, diffusion, reaction - in the same system with controlled spacing and defined paths.
  - Increasing the structural and compositional complexity of models by novel techniques such as (MBE, CVD, magnetron sputtering, and PLD)

- **What can we learn from other fields?**
  - Microelectronics (patterning, e-beam lithography, nano-imprints, etc.)
  - Sensors (multifunctionality, “smart” materials that respond to stimuli)
  - Solution and surfactant chemistry (templating, self-assembly)
  - Link to homogeneous catalysis (single-site chemistry)

## 2. Particle size effects

- The effect of particle size in Catalysis has been a subject of detailed investigations for years. However, the relationship between particle size and reactivity may have not been fully explained.
- Example: dramatic reactivity changes with particle size in supported Au particles
- Studies of particle size effects on systems with well-characterized particle size distributions are needed. “Next generation” models for metals and oxides need well-defined and uniform particle sizes.
- Stability of small clusters under reaction. As in most cases, the structure of the synthesized clusters is not retained under reaction conditions, there is a need for in-situ characterization.
- Combination of techniques for determining shape and texture of particles (Electron microscopy, X-Ray absorption spectroscopy, Molecular modeling)

## 3. Building nanostructured surfaces

Development of more complex, more realistic systems, that still retain the well-defined structure of models can be accomplished by a variety of novel techniques such as:

- Self assembly (e.g nano-templating, non-covalent templating)
- Wet-chemistry (e.g. colloidal and nano particles)
- Nanoparticles in uniform-pore supports (e.g. SB15, MCM-41, carbon nanotube)
- Organometallic precursors
- Anchoring homogeneous catalysts to inorganic or organic supports
- Micro and Nano-patterning (e-beam lithography, nanoimprint, stencil masking, soft lithography, etc)

## 4. Elementary steps of reactions

The study of elementary steps and the intermediates that are kinetically relevant (as opposed to mere spectators) is an important aspect to gain fundamental knowledge of the gas-solid or liquid-solid phenomena. Important aspects of this type of studies are:

- Time-resolved measurements in the time-scale of the TOF
- Relationships between reactivity and electron structure
- Detailed mechanisms of the energy transfer phenomena
- Need to conduct kinetic measurements at steady state to be able to focus on the kinetically relevant rates. Use of isotopically labeled compounds

# Break-out Session on Gas-Solid Interfaces

Moderators: Daniel E. Resasco – Miquel Salmeron

## Themes for this session:

- What do we know at the atomic level about catalysts under operating conditions?–Building, characterizing, and preserving structure and kinetic functionality in solids.
- From uniform “single sites” to multifunctional interfaces and bulks.
- Dynamics of electrons, atoms, defects, molecules, and solids

## Outcome:

- Brief picture of what is the program **today**
- What are the **hot** issues ?
- What have we **missed** ?
- What are the **challenges** ?
- Recommendations for **future** research

**Product:** *(It will be incorporated in the proceedings)*

–**Document** (2 pages) with opportunities for fundamental discovery - list of topics with some specific examples

## Format of session:

1)	Brief description of 15 topics selected by coordinator from contributions	10 min
2)	Vote (show of hands) to choose 6 most appealing topics (of potentially greatest impact) to discuss first	5 min
3)	Discussion and examples to illustrate the 6 selected topics	30 min
4)	Brainstorming. ( think <i>outside the box</i> ) Propose and discuss new topics	30 min
5)	CONVERGENCE	5 min

## Some topics suggested by participants

- 1. How can we choose model systems that faithfully represent real systems ?
- 2. Have we overlooked interesting particle size effects in catalysis, and if so, should we explore this avenue more thoroughly ?
- 3. Can patterning methods from the semiconductors industry be used to design heterogeneous catalysts at the nano- scale?
- 4. How to make surface nano-structures from nano-templated substrates ? Can we control particle size and shape ?
- 5. Can we control size and structure of nano-particle catalysts by controlling rates of nucleation, growth, and diffusion during deposition of organometallics?
- 6. How to make surface nano-structures by varying angle and deposition temperature with molecular beams?
- 7. Oxygen vacancies are important in all oxide-catalyzed oxidation reactions. What is the role of adsorbed molecular oxygen on the diffusion of these vacancy sites?
- 8. Crystal defects induce local strain. How does strain affect chemical reactivity and/or diffusivity inside the crystal? What is its effect on catalysis?
- 9. Can we obtain TOF bench-marks from single-crystal systems to help evaluate support effects and/or mass/heat transport limitations in real catalysts?
- 10. Metal carbide clusters of varying sizes have different activities. Can they be prepared and used on oxide supports?
- 11. How chemical substituents affect reactivity on surfaces ? How can they be used to prepare nano-structures on surfaces?
- 12. Instrumentation. What new techniques are available, particularly for “in-situ” studies?
- 13. Identification of elementary steps of solid-catalyzed reactions by characterization of short-lived radicals
- 14. Can we obtain stereo-selective control at surfaces? Enantioselective production of isomers from chirally modified surfaces.

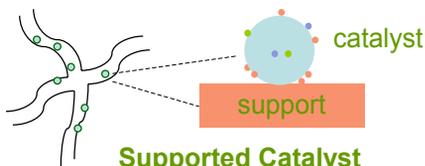
### **Other Potential Topics**

- Bridging the materials and pressure gap
- Anchoring homogeneous catalysts to inorganic or organic supports
- Novel, nano-structured supports with improved molecular transport properties, functionalities, etc.
- Single sites at interfaces
- Solid and surface dynamics of catalyst activation.
- Modeling solid-liquid reactions
- Sensors, molecular motors, pattern recognition

## Single Crystal Catalyst



Single Crystal Catalyst



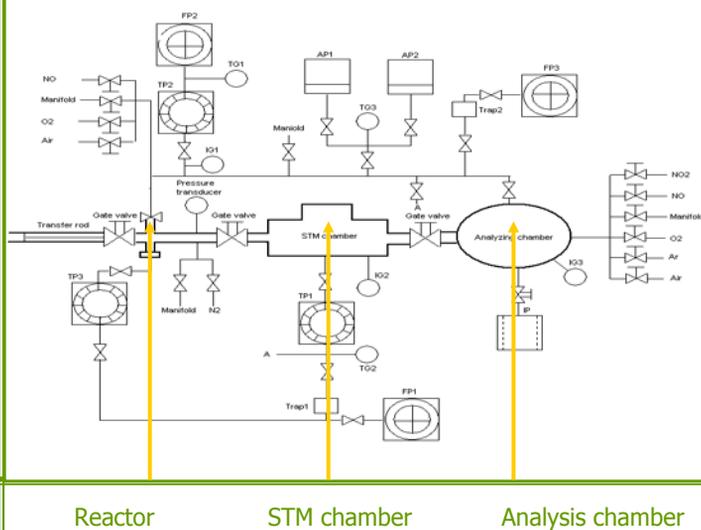
Supported Catalyst

### Advantages of using single crystal catalyst

- No support & impurity effect
- No internal mass and heat transfer limitations for reactions carried out at high temperature
- Control of chemical and morphological surface properties

Catalytic  $\text{CH}_4$  combustion was carried out on Pd(111), Pd(100) and Pd(110)

## Experimental Setup



## Methane Combustion -- Turnover Rate

Benchmark turnover rate on the crystals is determined to be 0.7-0.9 s<sup>-1</sup>

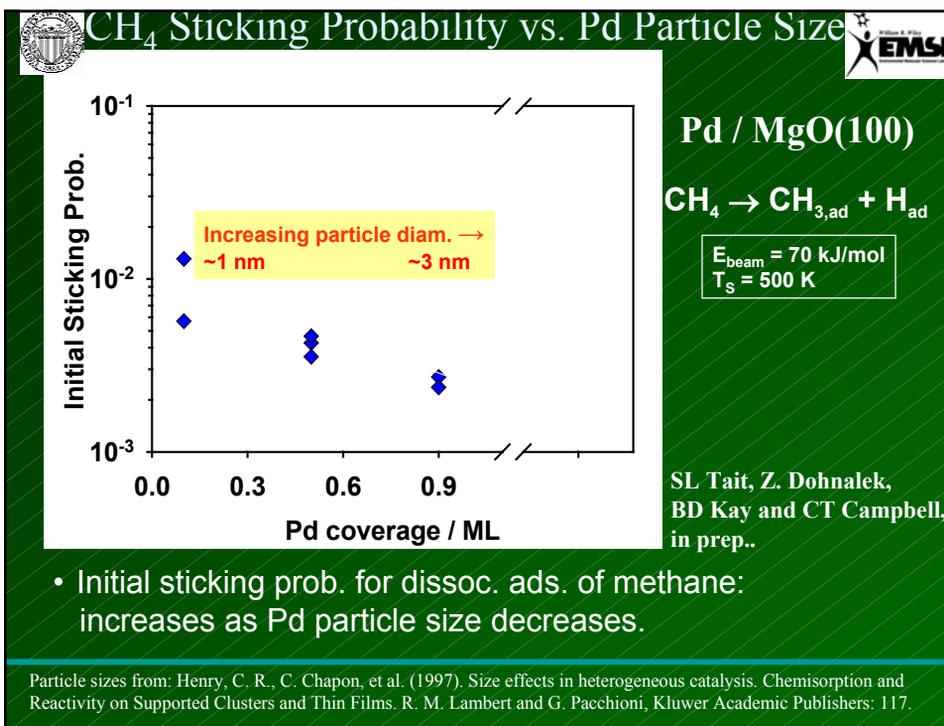
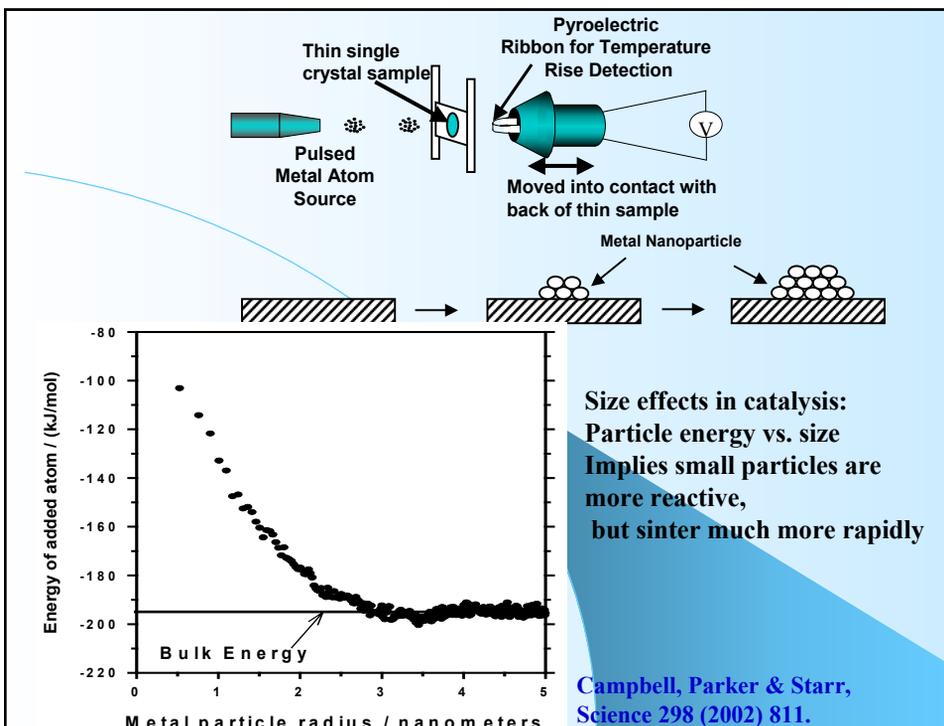
Catalyst	Particle Size (nm)	Turnover rate <sup>a</sup> (s <sup>-1</sup> )	Reference
Pd black	10	0.5 <sup>b</sup>	[1]
Pd/Si-Al <sub>2</sub> O <sub>3</sub>	2.6-6.2	0.1 <sup>c</sup>	[2]
Pd/Al <sub>2</sub> O <sub>3</sub>	49-134	0.07-0.16 <sup>c</sup>	[2]
Pd/ZrO <sub>2</sub>	4.3-81	0.1-0.7 <sup>c</sup>	[2]
Pd/ZrO <sub>2</sub>	3-9	0.5-3.0 <sup>c</sup>	[3]
Pd/ZrO <sub>2</sub>	5.5-12.5	0.3 <sup>c</sup>	[4]

<sup>a</sup> TOR calculated at 600 K, 16 Torr CH<sub>4</sub>, 1 Torr H<sub>2</sub>O. Reaction orders were assumed to be 1 for CH<sub>4</sub>, 0 for O<sub>2</sub> and -1 for H<sub>2</sub>O

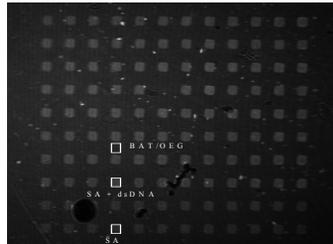
<sup>b</sup> Number of sites measured from BET surface area (47 m<sup>2</sup>g<sup>-1</sup>)

<sup>c</sup> For plug flow reactor, partial pressures for reactants and products are the average of values of inlet and exit concentration

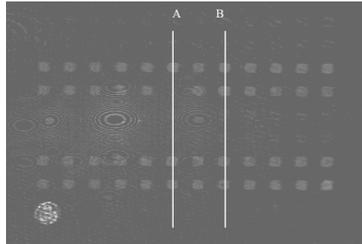
- [1] Monteiro, R.S., Zemlyanov, D., Storey, J.M., Ribeiro, F.H., *J. Catal.* **199**, 291 (2001).  
[2] Ribeiro, F.H., Chow, M., Betta, R.A.D., *J. Catal.* **146**, 537 (1994).  
[3] Fujimoto, K.-i., Ribeiro, F.H., Avalos-Borja, M., Iglesia, E., *J. Catal.* **179**, 431 (1998).  
[4] Mueller, C.A., Maciejewski, M., Koepfel, R.A., Baiker, A., *J. Catal.* **166**, 36 (1997).



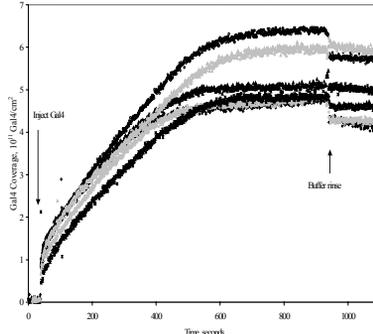
**High-throughput studies of protein-DNA interactions using surface plasmon resonance microscopy**  
 Jennifer Shumaker-Parry, Ruedi Aebersold and Charles Campbell, *Anal. Chem.* 76 (2004) 2071



- Control →
- Control →
- Operator →
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- S A only →
- S A only →



SPR microscope images of dsDNA arrays on gold. "Operator" refers to rows of spots which have a dsDNA sequence containing the binding site for the Gal4 protein. "Control" refers to spots with other DNA sequences but no binding site. "SA only" refers to spots with only the streptavidin (SA) linker layer, but not functionalized with any biotinylated dsDNA. Left: initial array. Right: intensity difference image, after Gal4 binding from



**Protein chip specific for DNA-binding proteins like transcription factors: label-free analysis with 1 s time resolution, absolute quantitation, and sensitivity to <0.5 pg protein.**

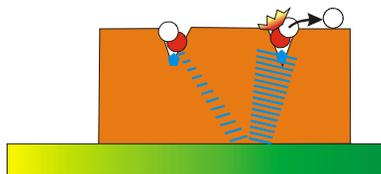
Simultaneous, real-time, quantitative measurement of Gal4 binding and unbinding kinetics to 6 different spots on the above array surface, all functionalized with its dsDNA operator sequence, to show reproducibility. This demonstrates sensitivity to  $<5 \times 10^6$  proteins molecules per spot, with time resolution of 1 s.

## Conscious Design of Heterogeneous Metal Catalysts

Conscious design may be required to exceed properties of combinations of materials in a random arrangement. Nanoscience and the Semiconductor Industry provide us with methods of patterning on the nanometer scale, which render the realization of conscious design of heterogeneous nanoparticles feasible. Our paradigm is to regard a catalyst as a nano-machine that has parts tailored to specific tasks and arranged in a predetermined, optimized fashion.

### Designs may exploit:

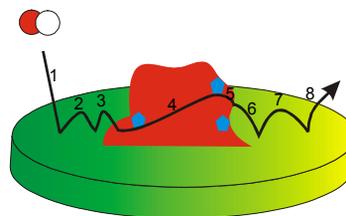
A) Prevention of **thermalization** of reaction energy by bandgap engineering and cluster design so as to provide highly energetic quanta for the activation of successive reactions.



### Entropy control

Two reactants are attached to active sites (blue) of a supported catalyst. We envision fabrication of catalysts, in which energy released by one reaction, is directly transferred to a neighboring active site where it will support the next reaction.

B) Steering of **molecular diffusion** to reactive sites and to/from sites specifically designed to facilitate adsorption and desorption of reactants



### Requires knowledge about:

- (a) interaction between reactants and substrate
- (b) chemical properties and reactivity of adsorbed reactant
- (c) adsorbate-adsorbate interaction and adsorbate diffusivity

### Knowledge provided by:

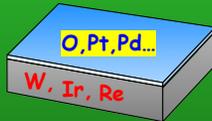
- (a,c) TPD and STM studies of adsorbate layers
- (b) local excitation of molecules and high temperature transient experiments (under development)

### Spatial Separation of the Reaction Steps and Controlled Reactant Transfer

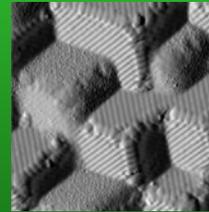
Reactant interaction with a compound nanocatalyst particle: 1) adsorption, 2) diffusion on one phase, 3) crossing of phase boundary, 4) diffusion on second phase to active site, 5) diffusion on second phase away from active site, 6) crossing of phase boundary, 7) diffusion on third(first) phase, 8) desorption.

# Control of catalysts at the nano scale

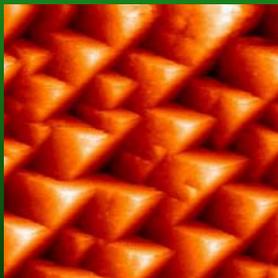
Motivation: Well controlled particle sizes, shapes important for reaction selectivity  
Nanometer-scale faceting of metals - a form of nanoreplication



anneal

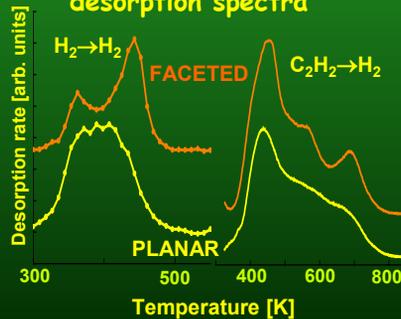


Faceted Pd/W(111)  
15 nm x 15 nm



Faceted Ir(210)  
100 nm x 100 nm

## Structure sensitivity: desorption spectra



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THE STATE UNIVERSITY OF NEW JERSEY  
**RUTGERS**

## Future directions - nanotemplated substrates: Can we control particle sizes, shapes in supported catalysts?

- Metals on planar oxide substrates - difficult to control growth and sizes
- Lithography has limitations
- Possible approaches: Nanotemplating by self assembly - strain effects, surface texture

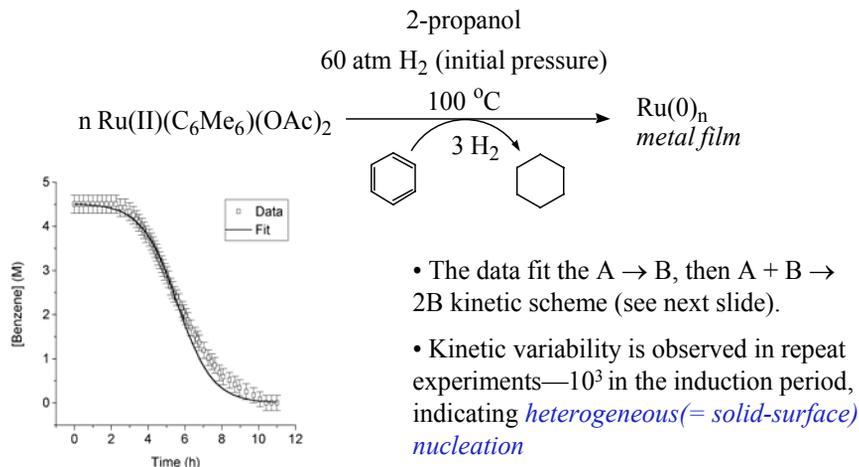
Proposed approach: Use oxidized, faceted surfaces as nanotemplates for catalyst particles; characterize nucleation and growth at specific sites



Challenge: generate 3D nanotemplated oxide substrates for controlling particle size and morphology in supported catalysts

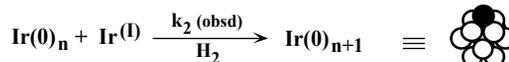
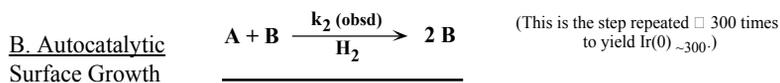
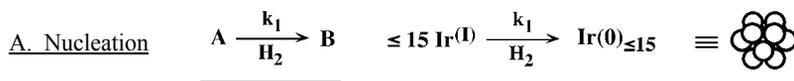
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## Re: Use of Organometallics to Deposit Catalytic, Solid Phases: The Surface Autocatalytic Growth Mechanism Extends to Heterogeneous Nucleation and Metal-Film Formation [1]

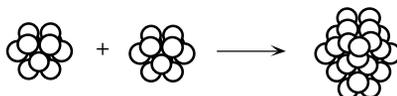
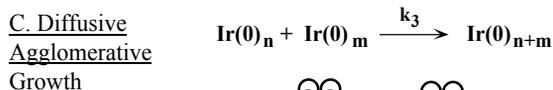


[1] Widegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **2003**, 125, 10301.

## The One Kinetically Supported Mechanism of Transition-Metal Nanocluster Formation



Where  $k_2 \text{ (obsd)} = k_2 \left[ \frac{1 + x_{\text{growth}}}{2} \right]$



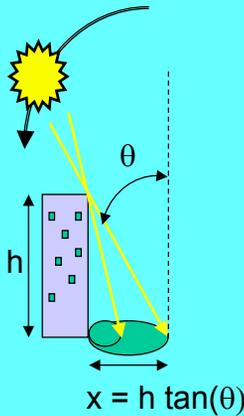
[1] Watzky, Finke *JACS* **1997**, 119, 10382 (plus 4 subsequent papers).

## **Important, But Untested, Predictions of the Deposition Mechanism Include:**

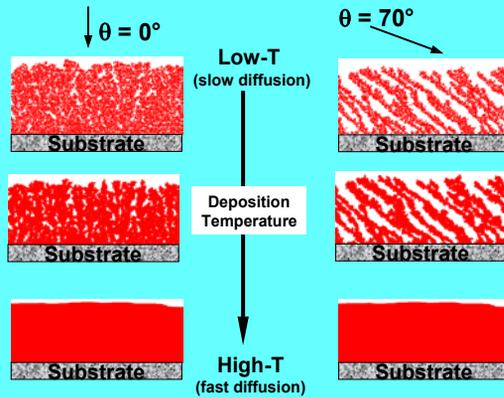
- (1) That the  $k_2/k_1$  ratio will correlate with, and can be used to control, “size” (the layer thickness in this case);
- (2) That seeded (controlled nucleation site, or other deliberately pre-nucleated) growth is a route to controlling deposition location;
- (3) That an initially deposited layer can be expanded simply by adding more organometallic precursor (living-metal-layer / polymer concept);
- (4) That novel bi-, tri- and higher- multimetallic layer formation is possible—including all possible geometric isomers thereof, as well as true alloys from the kinetics of single-layer deposition;
- (5) That lattice mismatch—and hence island, mound or other irregular growth—is a potential complication to the above predictions of the mechanism.

**Exploiting the Directionality of Molecular Beams to Synthesize Novel Nano-Materials - Zdenek Dohnalek, Bruce D. Kay, PNNL**

**Shadowing effect**



“Hit and Stick” model with limited surface mobility.

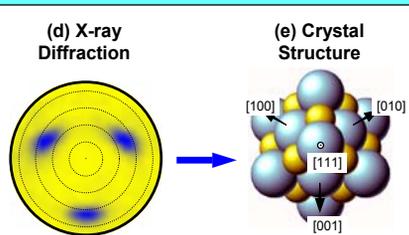
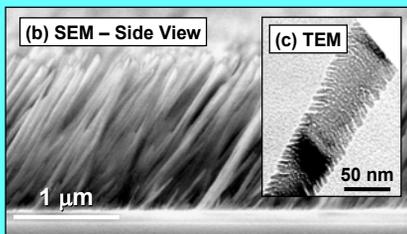
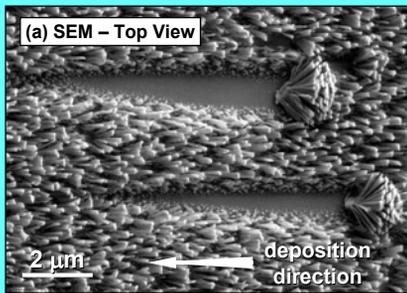


KP Stevenson, GA Kimmel, Z Dohnálek, RS Smith, and BD Kay, *Science* **283** (1999) 1505.  
 GA Kimmel, KP Stevenson, Z Dohnálek, RS Smith, and BD Kay, *J. Chem. Phys.* **114** (2001) 5284.  
 GA Kimmel, Z Dohnálek, KP Stevenson, RS Smith, and BD Kay, *J. Chem. Phys.* **114** (2001) 5295.

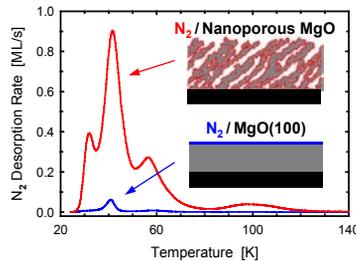
Pacific Northwest National Laboratory



**Molecular Beam Synthesis and Characterization of Nanoporous MgO Films**



**(f) Temperature Programmed Desorption**



Z. Dohnálek, G. A. Kimmel, D. E. McCreedy, J. S. Young, A. Dohnálková, R. S. Smith, and B. D. Kay  
*Journal of Physical Chemistry B* **106** (2002) 3526.

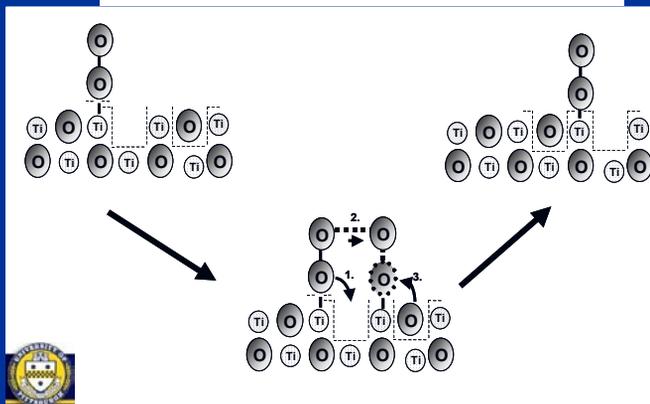
Pacific Northwest National Laboratory



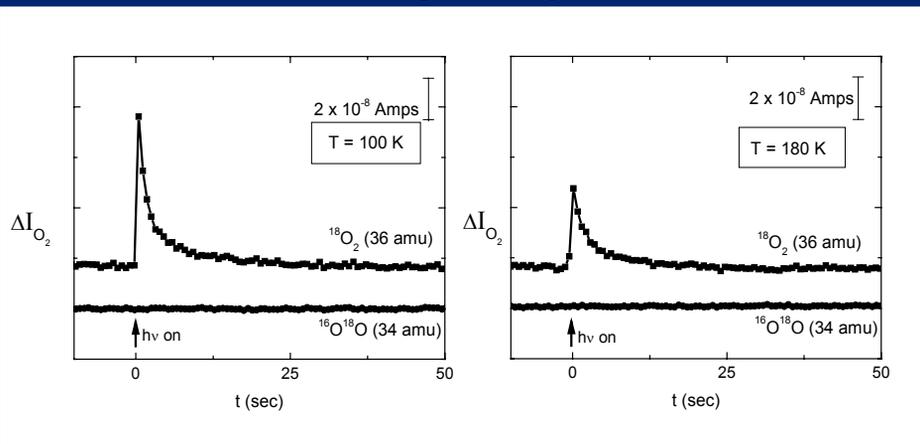
## Oxygen-Mediated Diffusion of Oxygen Vacancies on the $\text{TiO}_2(110)$ Surface

Renald Schaub, Erik Wahlström, Anders Rønnow, Erik Lægsgaard, Ivan Stensgaard, Flemming Besenbacher\*

Defects such as oxygen vacancies play a crucial role in the surface properties of transition metal oxides. By means of time-resolved, high-resolution scanning tunneling microscopy, we unraveled an adsorbate-mediated diffusion mechanism of oxygen vacancies on rutile  $\text{TiO}_2(110)$ . Adsorbed oxygen molecules mediate vacancy diffusion through the loss of an oxygen atom to a vacancy and the sequential capture of an oxygen atom from a neighboring bridging oxygen row, leading to an anisotropic oxygen vacancy diffusion pathway perpendicular to the bridging oxygen rows.

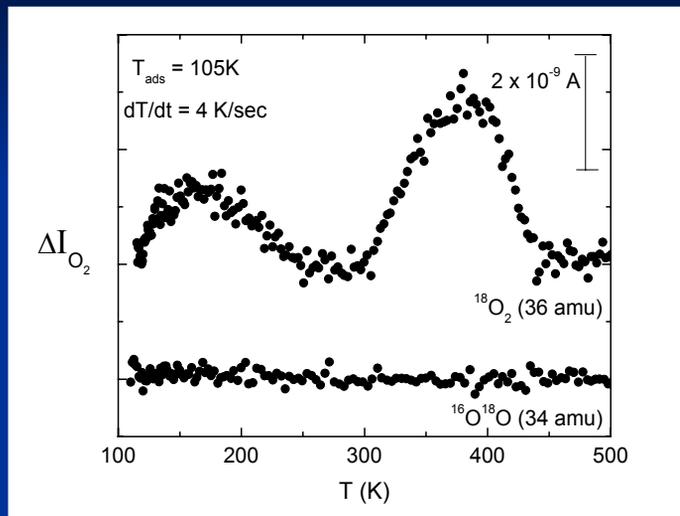


## Isotopomer $\text{O}_2$ Photodesorption from $\text{TiO}_2(110)$ Containing Vacancy Sites



T. Thompson, O. Diwald, J. T. Yates, Jr. Chem. Phys. Lett. Accepted for Publication, 2004.

## Isotopomer O<sub>2</sub> Thermal Desorption from TiO<sub>2</sub>(110) Containing Vacancy Sites



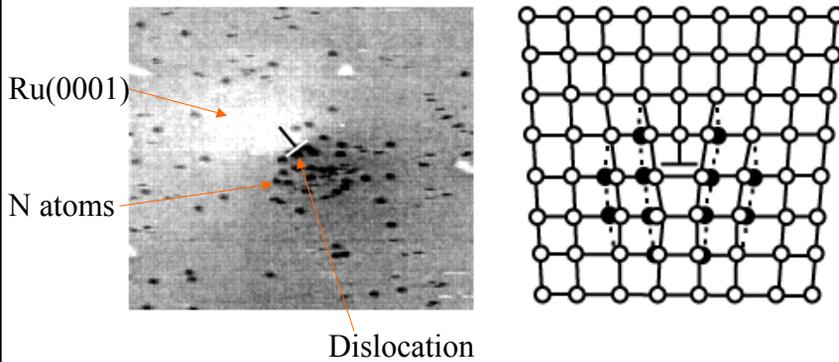
T. Thompson, O. Diwald, J. T. Yates, Jr. Chem. Phys. Lett. Accepted for Publication, 2004.

## Summary

1. O<sub>2</sub>-Mediated vacancy diffusion on TiO<sub>2</sub>(110) is observed by STM.
2. The mechanism proposed is incorrect since isotopic exchange does not occur from lattice oxygen to molecular oxygen.
3. Single Question: What other O<sub>2</sub>-mediated models can be imagined?

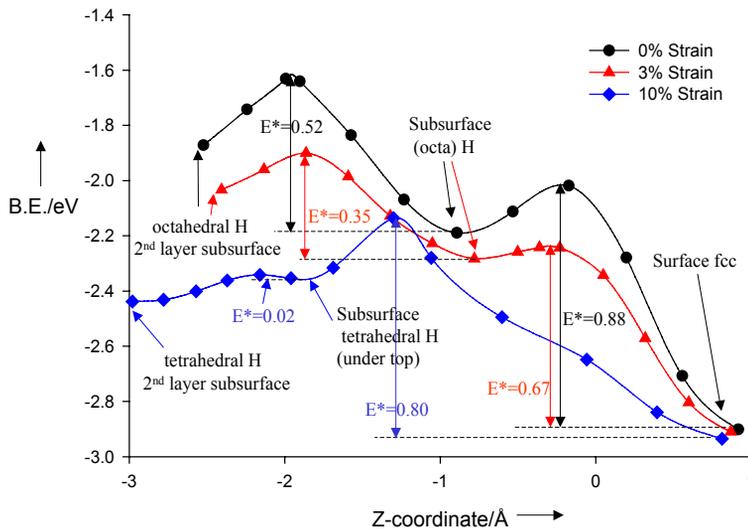


## Defects induce local *strain*

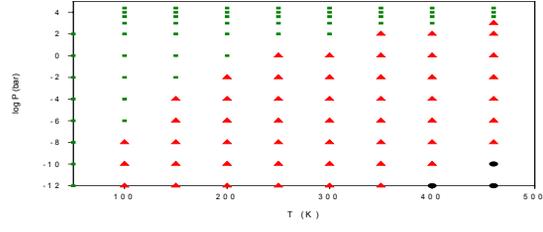
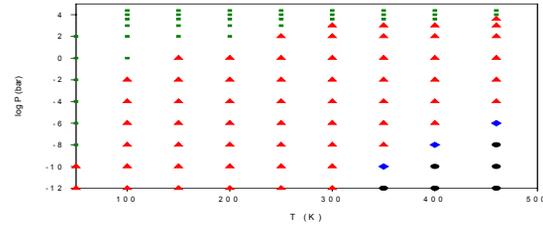
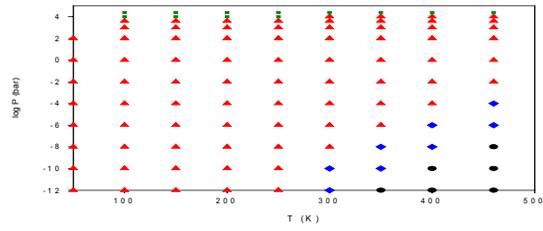


T. Zambelli, J. Winterlin, J. Trost, J. Greeley, M. Mavrikakis, *Angewandte Chemie International Edition*, **42**, 2849 (2003).

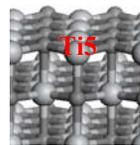
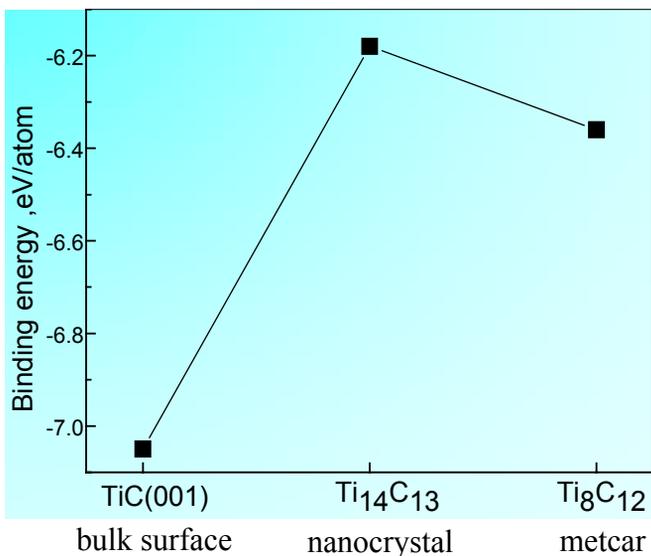
## Effect of *strain* on H diffusion into Ni(111)



J. Greeley and M. Mavrikakis, *Angew. Chem. Int. Ed.* (in press)



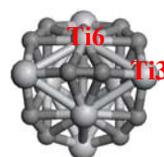
## RPBE DFT Calculations of the Stability of Ti carbides



TiC(001)

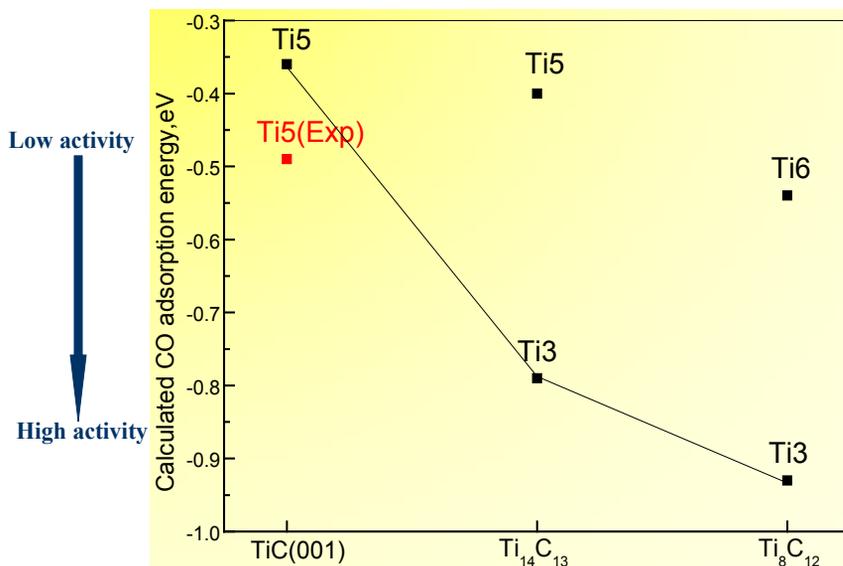


Ti<sub>14</sub>C<sub>13</sub>



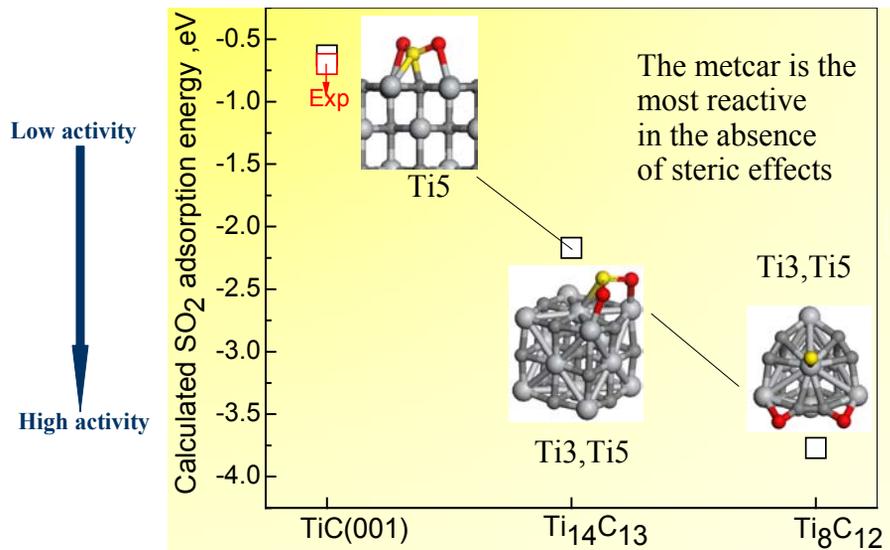
Ti<sub>8</sub>C<sub>12</sub>

## ... of CO adsorption on Ti carbides



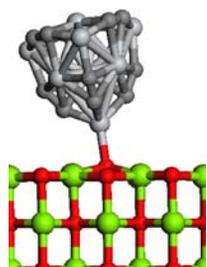
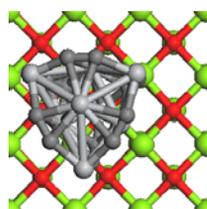
Exp: S.V. Didziulis, et al., J. Phys. Chem. B 105, 5196 (2001).

### ... of SO<sub>2</sub> adsorption on Ti carbides

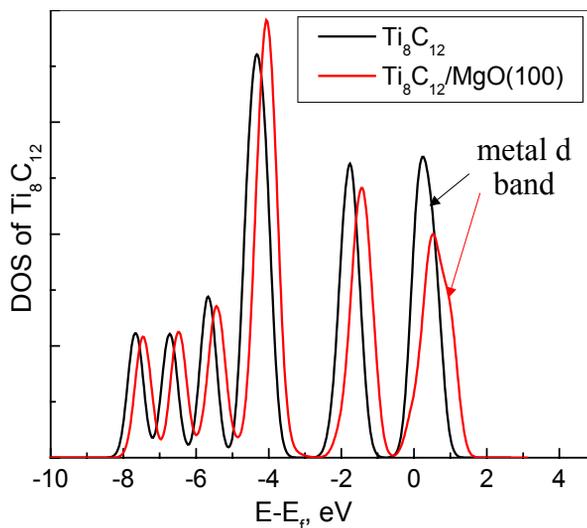


Exp: J. A. Rodriguez, et al., Surf. Sci. (2003), in press.

### ...of supported metcar: Ti<sub>8</sub>C<sub>12</sub>/MgO(100)



$\Delta E = -2.13 \text{ eV}$



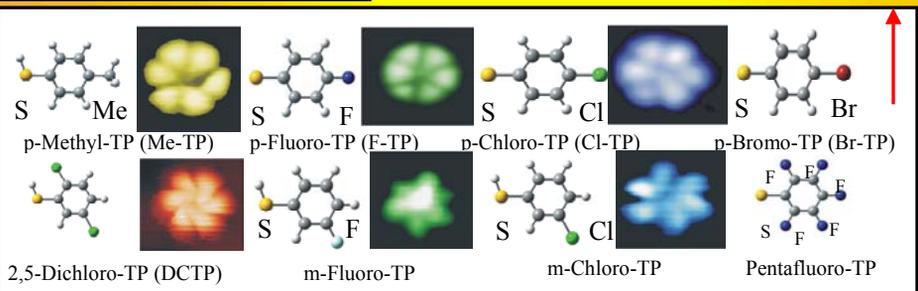
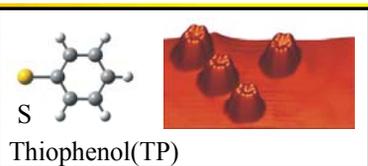
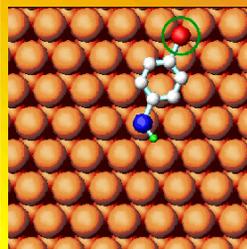
The supported metcar should be more active than in the gas phase.

## Substituent Effects in Adsorbate Dynamics



The impact of substitution on the physical and chemical properties of reactants is well studied in the solution phase. We investigate the surface reactivity and pattern formation depending on the substitution of thiophenols.

Following adsorption on Cu(111) at 15K, substituted thiophenols rotate around the sulfur anchor while maintaining the S-H bond. This lets them appear as flower-shapes in STM (below).

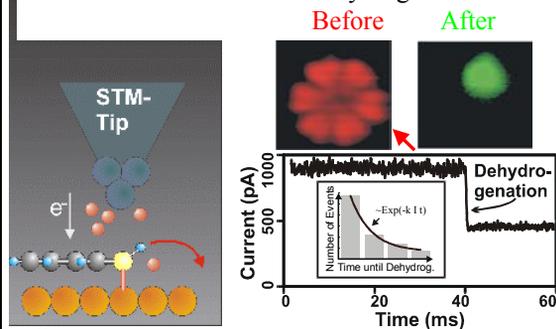


Adzic, Bartels, Feibelman, Heinz, Murray, O'Brien, Rahman

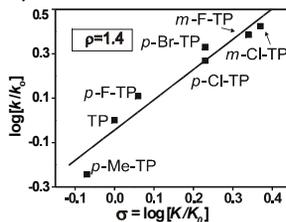
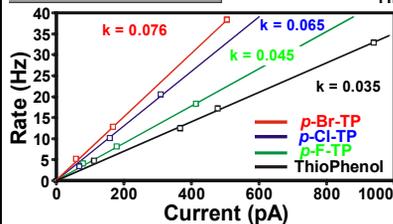
## Substituent-Dependent Surface Reactivity



### STM-Based Excitation of Dehydrogenation



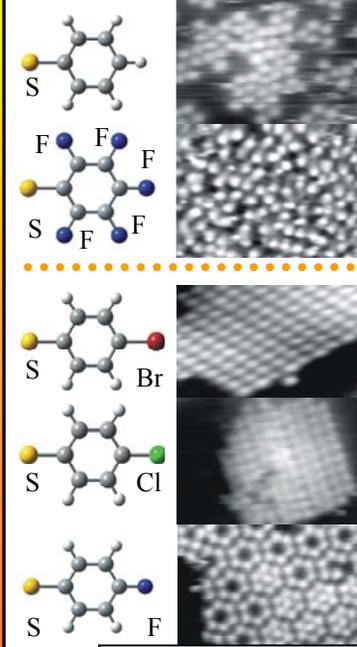
Excitation from the tunneling current can cause the dehydrogenation of substituted thiophenols, which stops their rotation by locking them into the substrate (left). Statistical evaluation of the time until dehydrogenation, establishes a dehydrogenation time constant  $k$ , which turns out to be independent of current (ie. first order process).



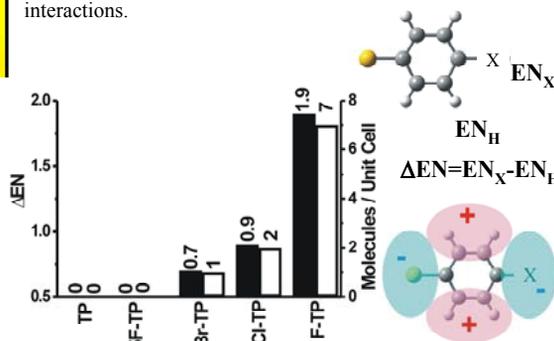
The STM-based dehydrogenation rates obtained for differently substituted thiophenols follow closely the sequence of  $\sigma$  values established by Hammett 70 years ago.

Adzic, Bartels, Feibelman, Heinz, Murray, O'Brien, Rahman

### Substituent Electronegativity vs. Film Patterns



Substitution of thiophenols has a pronounced impact on molecule-molecule interactions, diffusivity and film formation. Thiophenols, that have isotropic substituents, are mobile at LN<sub>2</sub> temperatures and form no ordered structures. With increasing difference in electronegativity between the para and the meta substituent, the complexity of the film increases, which we attribute to quadrupolar intermolecular interactions.



Adzic, Bartels, Feibelman, Heinz, Murray, O'Brien, Rahman

**Synchrotron Small Angle X-ray Scattering Methods for In Situ Studies**

Randall E Winans, Chemistry Division, Argonne National Laboratory  
 Collaborators: Soenke Seifert, Byeongdu Lee, Jan Hessler and Nancy Tomczyk

**SAXS capabilities**

- Access length scales 1 – 6000 Å
- Determine particle and molecular Size, shape, surface properties, porosity
- Time resolution with new detector(5/04) and pink beam  
 Ring timing 3.7 microsec  
 Pump – probe 100 ps
- High temperature, high pressure reactors

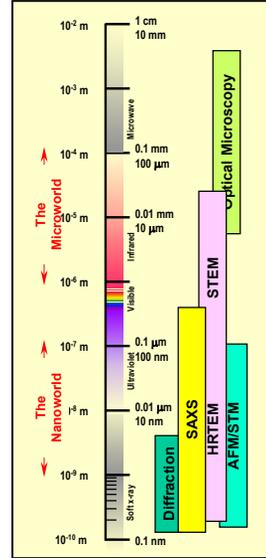
**Grazing Incidence SAXS (GISAXS)**

- Study particles and clusters on surfaces
- All information from regular SAXS plus Depth information  
 Particle distribution  
 Orientation relative to the surface
- *In Situ* heat, pressure



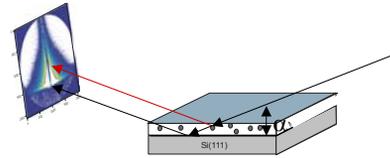
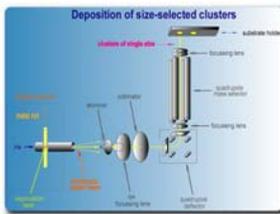
**Anomalous SAXS (ASAXS)**

- Study scattering at the edge of an element
- Determine local environment
- Reduce background scattering effects

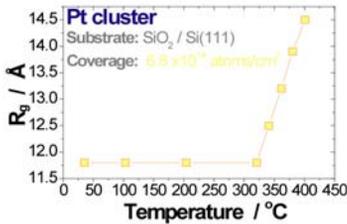


**Thermal stability of metal particles on surfaces – GISAXS results**

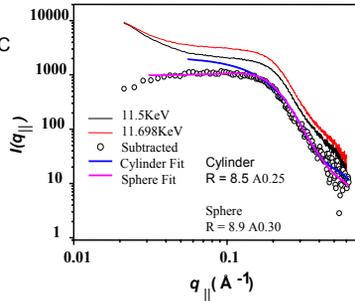
Randall E Winans, Chemistry Division, Argonne National Laboratory  
 Collaborators: Stefan Vajda, Soenke Seifert, Byeongdu Lee, Jan Hessler and Nancy Tomczyk



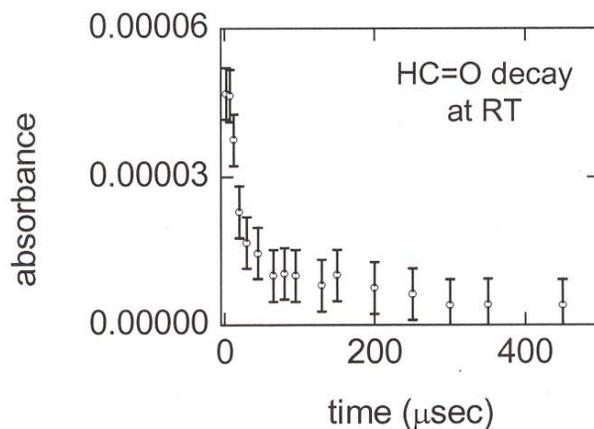
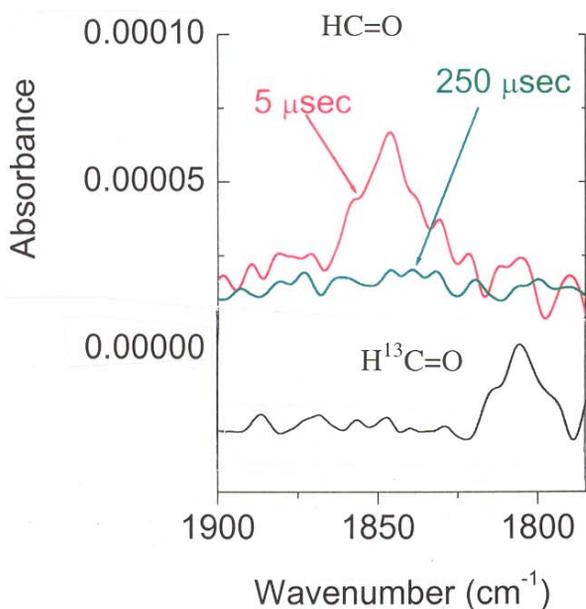
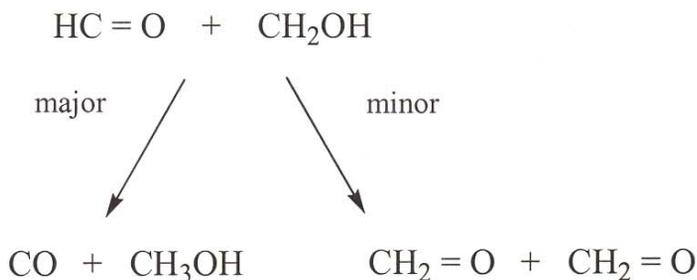
GISAXS results – size increased in horizontal but not vertical direction, Pt clusters stable to 320 C



**Anomalous GISAXS  
 Pt on Si (111)**



# Mechanistic Studies By Step-Scan FT-IR Spectroscopy of Small Radicals in Zeolites



Radicals in zeolites live for tens to hundreds of microseconds at room temperature

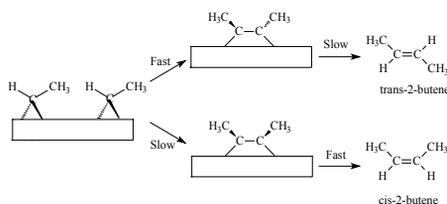
Geminate and non-geminate radical reactions observed

# Selectivity Control with Model Catalysts

Wilfred T. Tysoe, University of Wisconsin-Milwaukee

We have primarily focused on steric control of surface chemical reactions using single crystals:

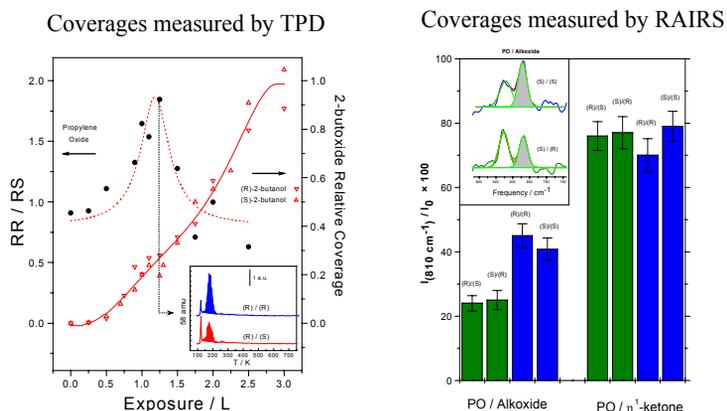
1. Stereoselective dimerization of ethylidene to 2-butene.



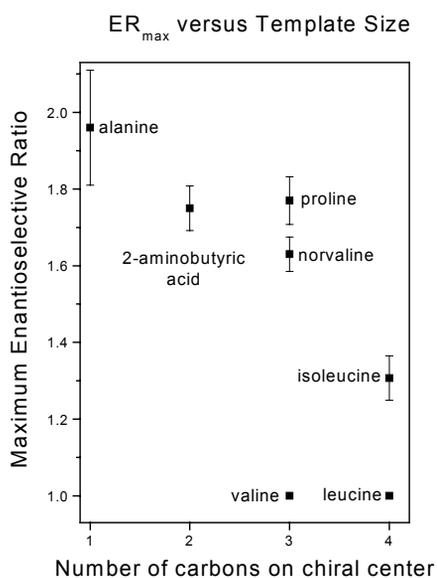
Ethylidene species that are formed from 1,1-diiodoethane on silver preferentially dimerize to form adsorbed trans-2-butene due to steric control of the approaching carbenes.

Wu *et al.*, *J. Am. Chem. Soc.*, **122**, 8232 (2000)

2. Enantioselective chemisorption on chirally modified surfaces.



R- or S-2-butanol-modified Pd(111) surfaces preferentially absorb propylene oxide with the same chirality (where propylene oxide coverages are measured using TPD or RAIRS). It is found that enantioselective chemisorption is expressed over a narrow modifier coverage range. This is ascribed to the formation of chiral “pockets”



When 2-methyl butanoic acid used as a template, there is no enantioselectivity to propylene oxide adsorption – this is proposed to be due to the rotation of the butyl group averaging out any asymmetry.

Anchoring the butyl group by functionalizing it with an amine restores the enantioselectivity.

As shown in the figure, the size of the group attached to the amino acid also changes the enantioselectivity.

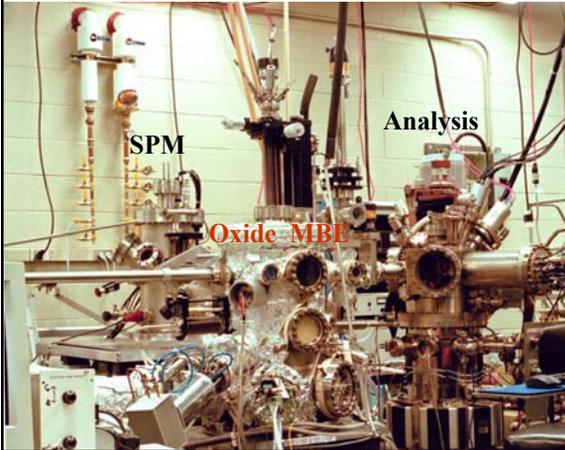
This effect is being explored further but may be due to changes in the size of the chiral “pocket”.

Stacchiola *et al*, *J. Am. Chem. Soc.*, **124**, 8984 (2002)

## Increasing the structural and compositional complexity of model catalysts

- A number of techniques have been developed to grow complex materials in a single phase and orientation with atomic level control over thickness and interface abruptness.
- Includes: MBE, CVD, magnetron sputtering, and PLD.
- Can be exploited to create model systems that better reflect actual catalysts, and to create well controlled systems to test fundamental hypotheses and for screening studies.

### Yale Multi-Chamber Growth and Characterization System (Eric Altman)



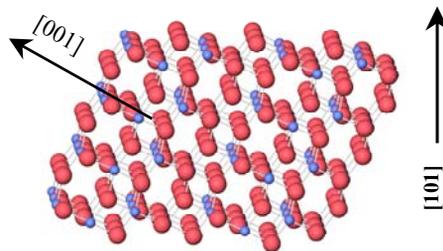
#### Techniques:

STM  
RHEED, LEED  
XPS, UPS, AES  
TPD

#### Films Grown:

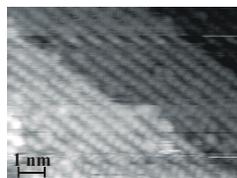
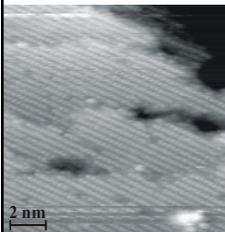
Anatase (001)  
Anatase (101)  
V-doped Anatase (101)  
 $\text{WO}_3$  (100)  
 $\text{NiO}$  (001)/ $\text{Fe}_3\text{O}_4$  (001)  
Ni-doped MgO (001)  
PdO (001)

### Example – Anatase $\text{TiO}_2$

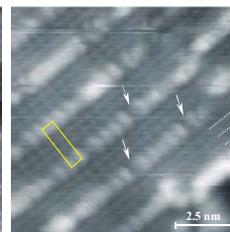
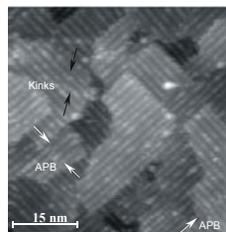


Although the anatase phase is most often used in real catalysts, model studies have focused on rutile because of the widespread availability of rutile single crystals.

STM of Epitaxial Anatase (101)

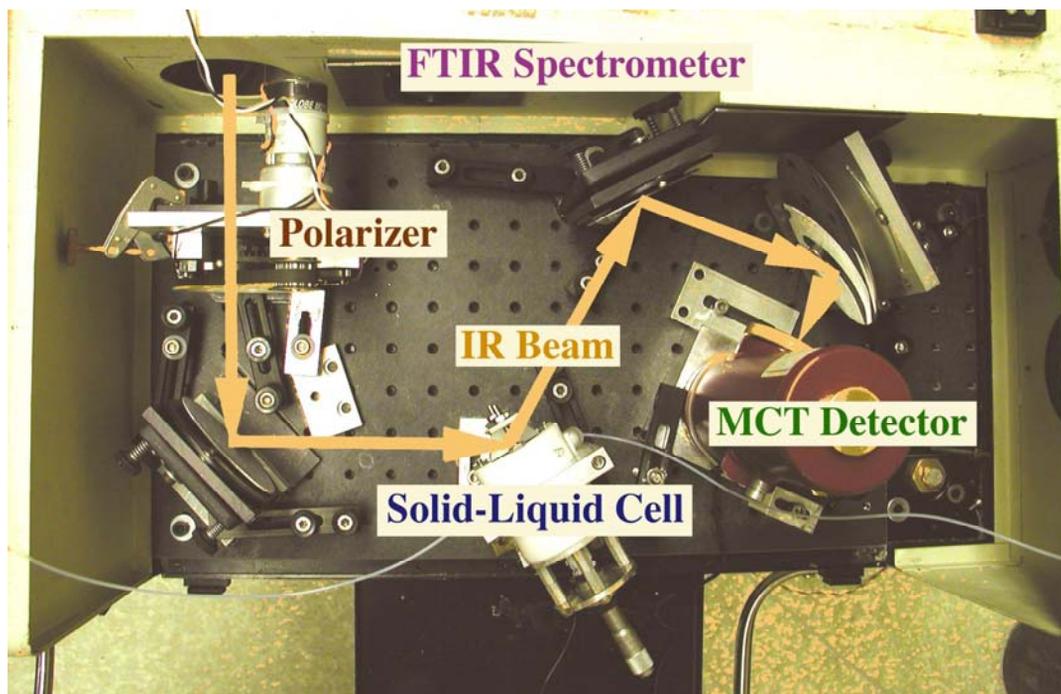


STM of Epitaxial Anatase (001)-(4x1)



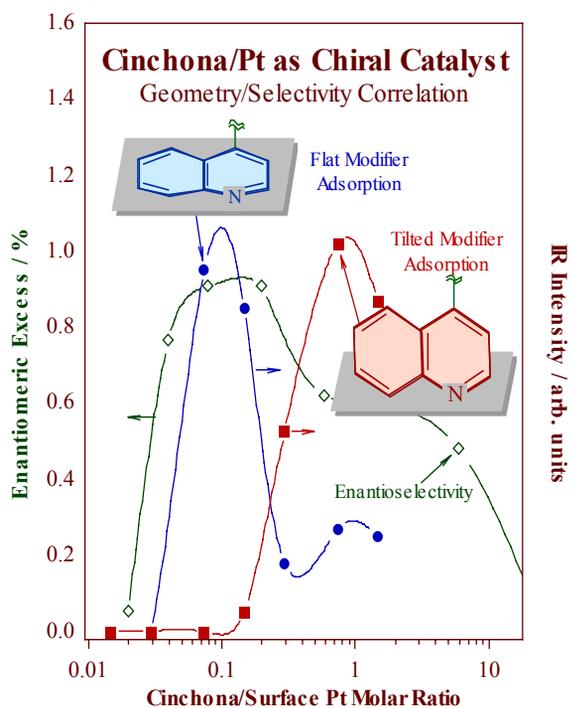
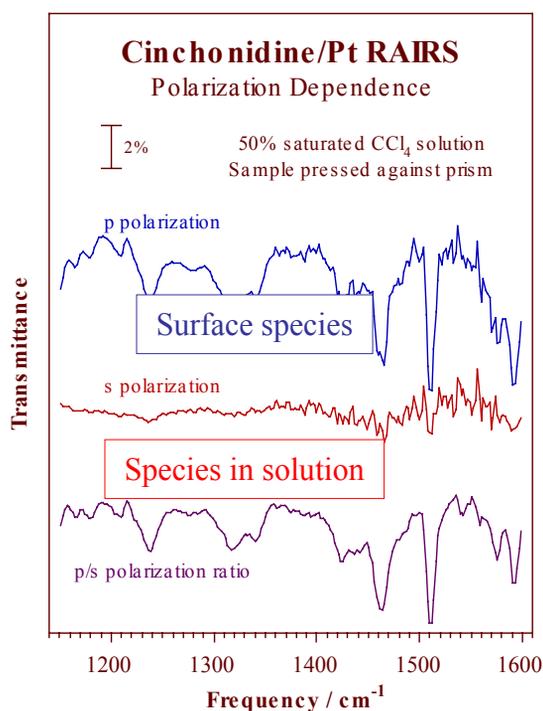
We have doped it with V to study matrix effects, and grown vanadium oxides on top to study support effects.

# Reflection-absorption infrared spectroscopy to probe the liquid-solid interface in situ

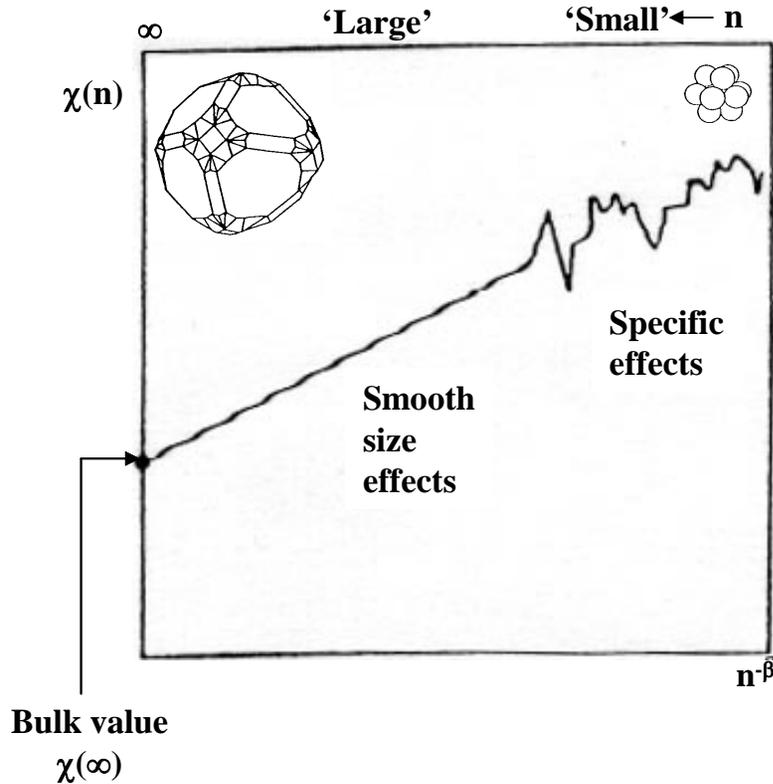


Use of polarization allows for:

- Discrimination between adsorbed and dissolved species
- Determination of adsorption geometries

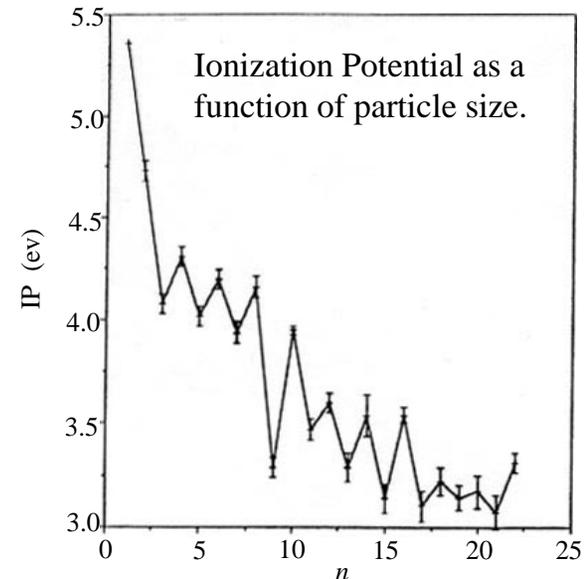
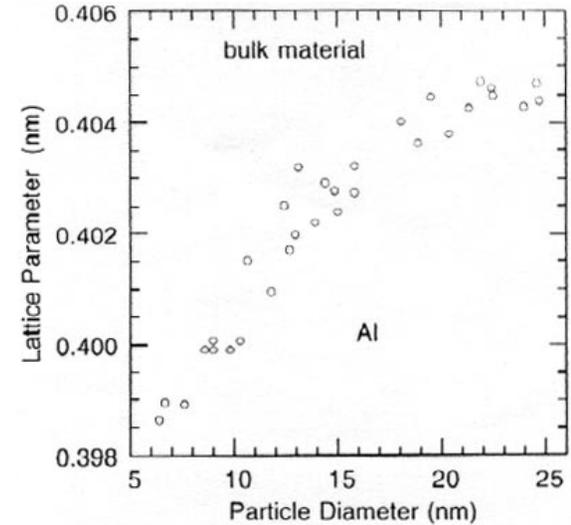


# Size Effects in Nanoscale Materials



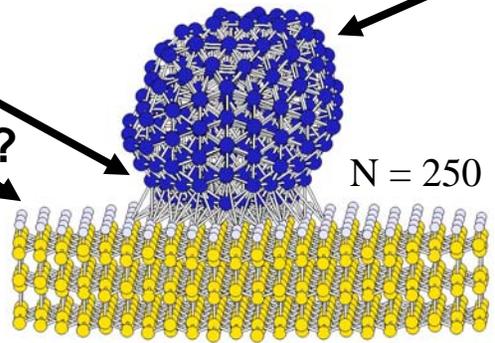
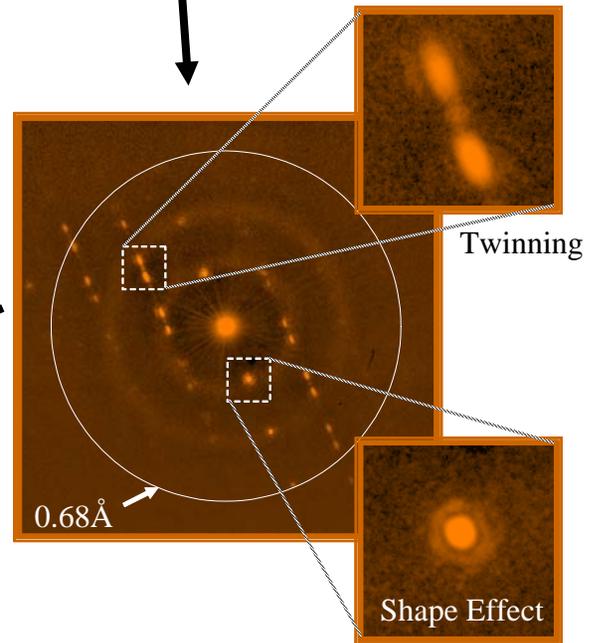
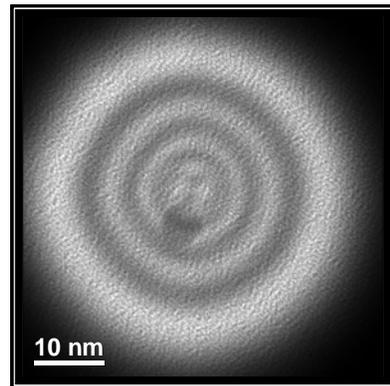
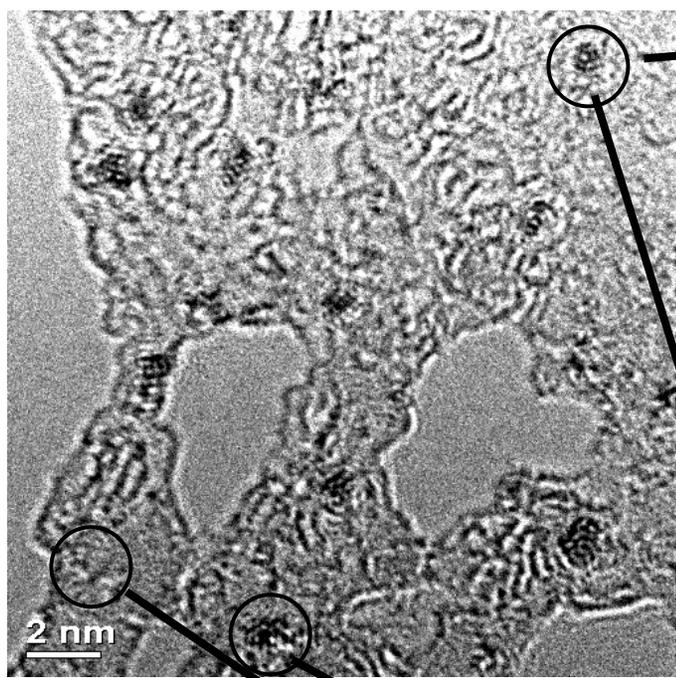
Adapted from: Jena, P; Khanna, S.N.; Rao, B.K. *Physics and Chemistry of Finite Systems: From Clusters to Crystals (NATO-ASI Series)*. 1992 (Deventer: Kluwer).

Woltersdorf, J.; Nepijko, A.S.; Pippel, E. *Surf. Sci.* 1968, 12, 134.



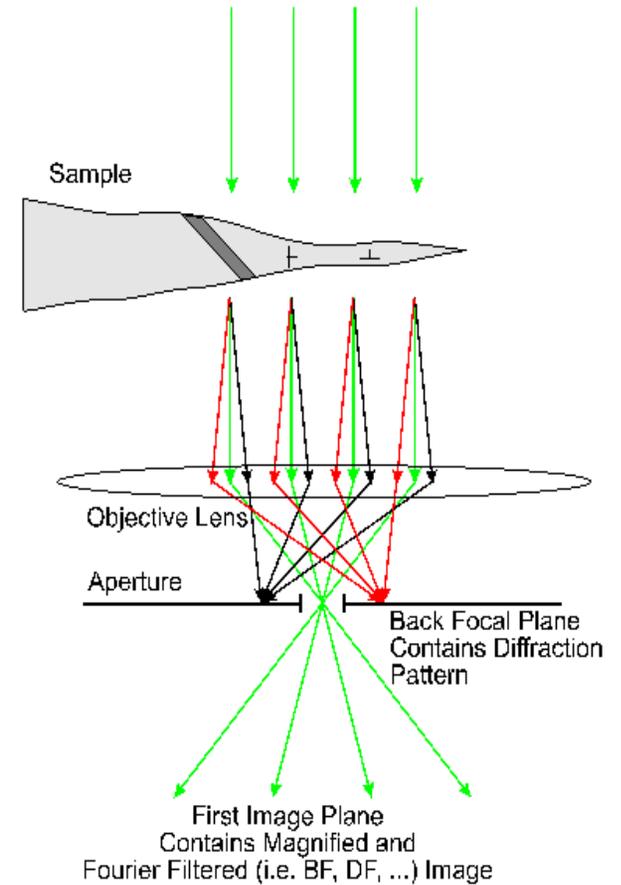
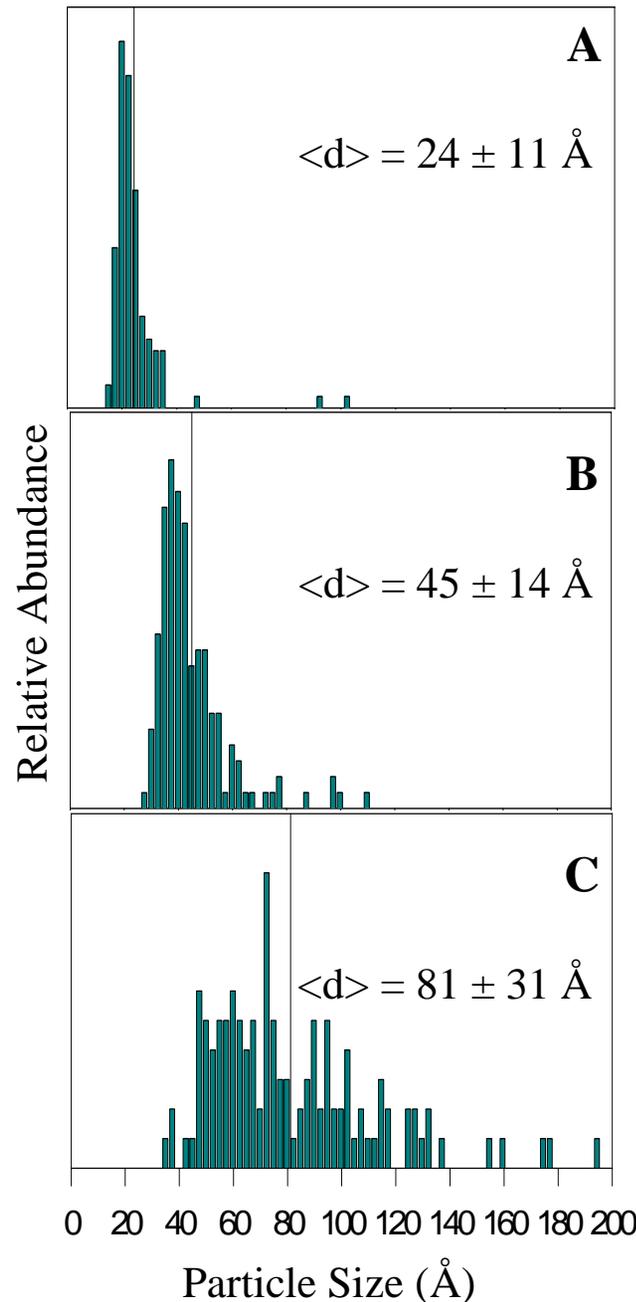
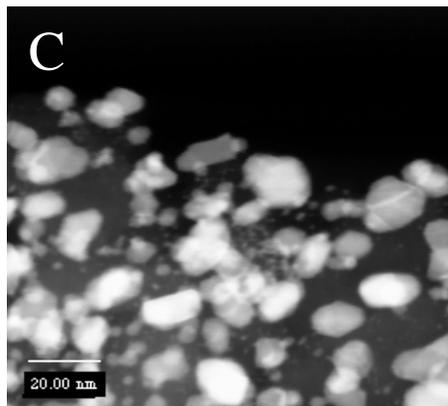
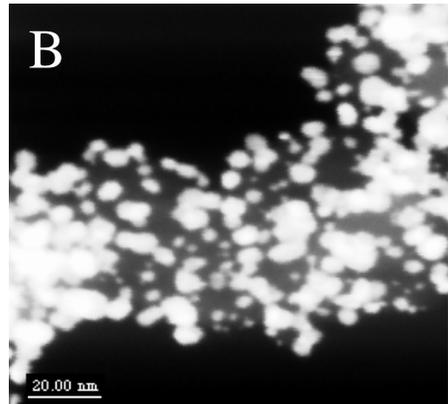
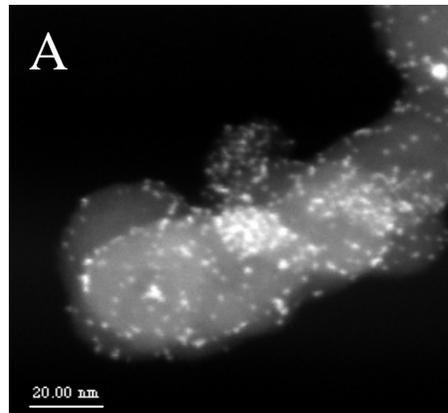
**The Need: Full Characterization/Understanding of Structure and Properties at all Length Scales**

**A Nanoscience for Catalysis Focused on Synthesis and (*and frequently limited by capacities for nanoscale*) Characterization**



**Structure, Function, Dynamics**  
• Accessible to Theory?  
• Accessible to Experiment?

# Particle Size Distributions



**Pt supported on Vulcan XC-72 carbon black.**

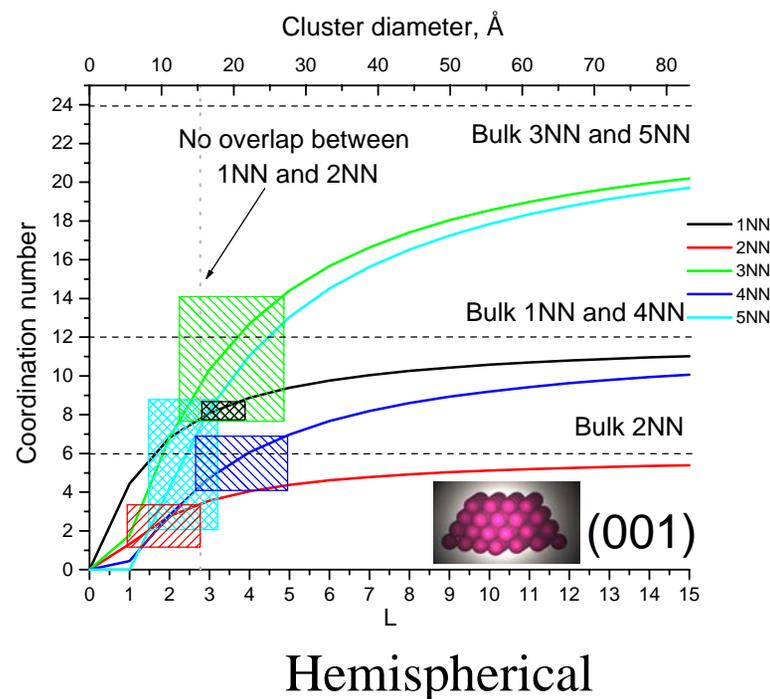
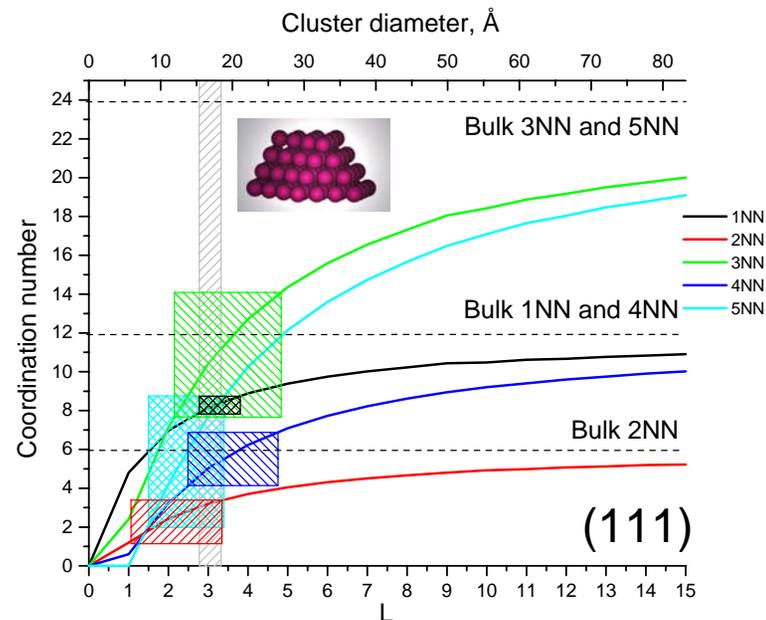
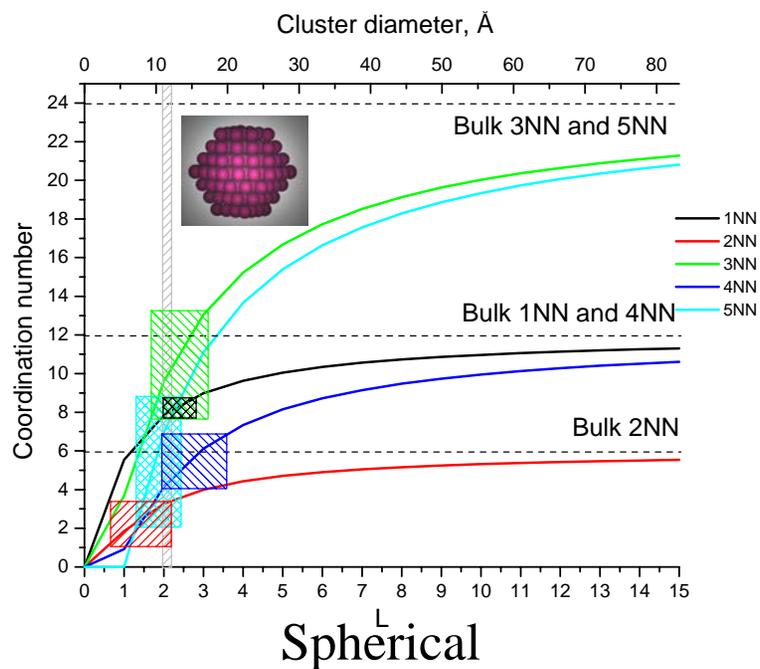
**A)10%**

**B)40%**

**C)60%**

# Model vs. Experiment

- Texture
- Size
- Support Interactions?
- Other Information?



# Support Interactions

## (The Dark Matter of Catalysis?)

***Use Accurate First-Principles Methods***

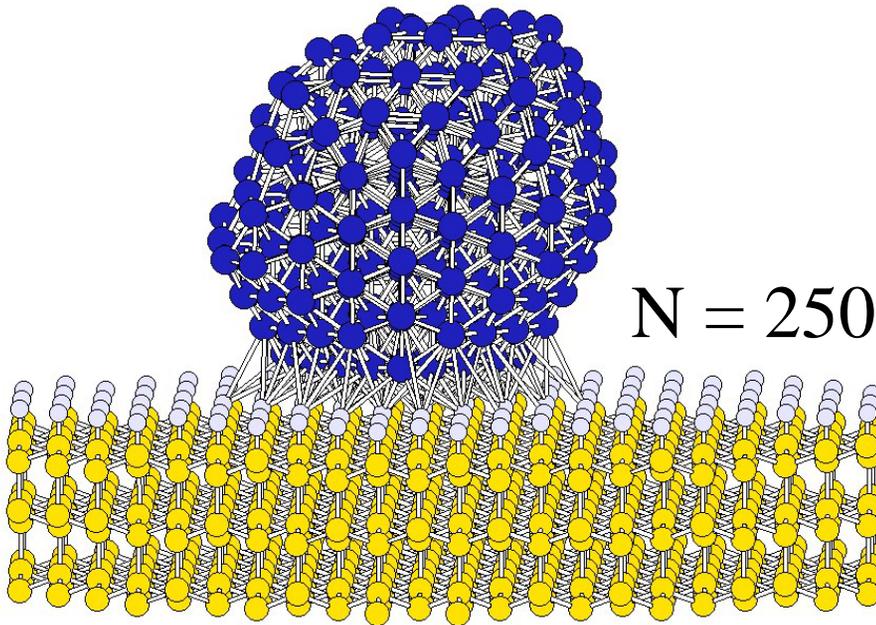
**VASP (Vienna Atomic Simulation Package)**

**G. Kresse and J.**

**Hafner, PRB 47, R558 (1993); J. Phys:  
CM 6, 8245 (1994);**

**PRB 54, 11169 (1996); Comp. Mat. Sci.  
6, 15 (1996).**

- Full-potential method with force evaluations.
- Ultrasoft Vanderbilt pseudo-potentials.
- Energy cut-off of 18 Ry for PW basis.
- Supercells from 1.4-2 nm on a side for free clusters.
- 4x4 hexagonal 2D supercell with 2-atom basis to mimic graphite sheet.
- Employed Special k-point mesh and checked convergence.
- For fixed k-mesh, accuracy  $\pm 1$  meV in energies and  $\pm 30$  meV/Å in forces.
  - *Bond distances will be small by 0.5-2.0% from well-known LDA errors.*



***(Examine Structural Dynamics and Support Interactions via Theory)***

# Applications of Heterogeneous Catalysis for the Production of controlled Nano-structures

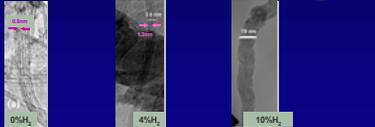
The diameter of carbon nanotubes can be controlled by modifying the rate of carbon nucleation and metal-cluster growth.

Adding hydrogen to the feed delays the nucleation process and increases the diameter of the SWNT.

In the competition between :

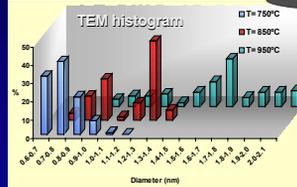
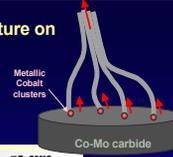
- Nucleation (C incorporation into Co)
- Particle growth (sintering)

Particle growth is favored



## Effect of Reaction Temperature on SWNT Diameter

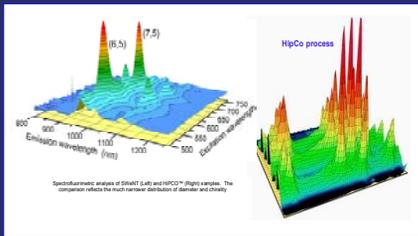
The nanotube diameter increases as the reaction temperature increases



Careful design of solid catalysts may have an impact on the synthesis of nanostructured materials:  
e.g. nanotubes and nanowires

Daniel E. Resasco, University of Oklahoma

## Comparison of Diameter Distribution SWeNT Vs. HiPCO 3D-Fluorescence

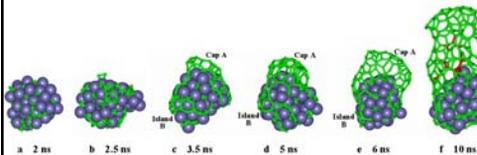
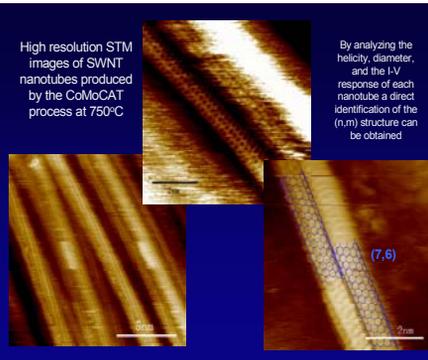


Spectrofluorimetric analysis of SWeNT (Left) and HiPCO<sup>®</sup> (Right) SWNT samples. Courtesy of Prof. R. Bruce Weisman (Rice University)<sup>9</sup>

Uniquely narrow distributions of nanotube diameters and chiralities are ONLY obtained over solid catalysts. All other synthesis methods (arc discharge, laser, vapor phase HiPCO) result in broad distributions

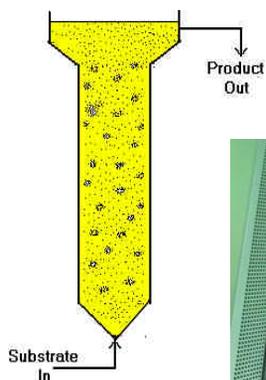
High resolution STM images of SWNT nanotubes produced by the CoMoCAT process at 750°C

By analyzing the helicity, diameter, and the I-V response of each nanotube a direct identification of the (n,m) structure can be obtained



Daniel E. Resasco, University of Oklahoma

Another advantage of synthesis on solid catalysts is that it can be operated in a continuous mode and scaled-up while keeping high quality product. These are significant elements for a cost-effective production of nanotubes. Use of fluidized beds is particularly advantageous and cost-effective



Daniel E. Resasco, University of Oklahoma