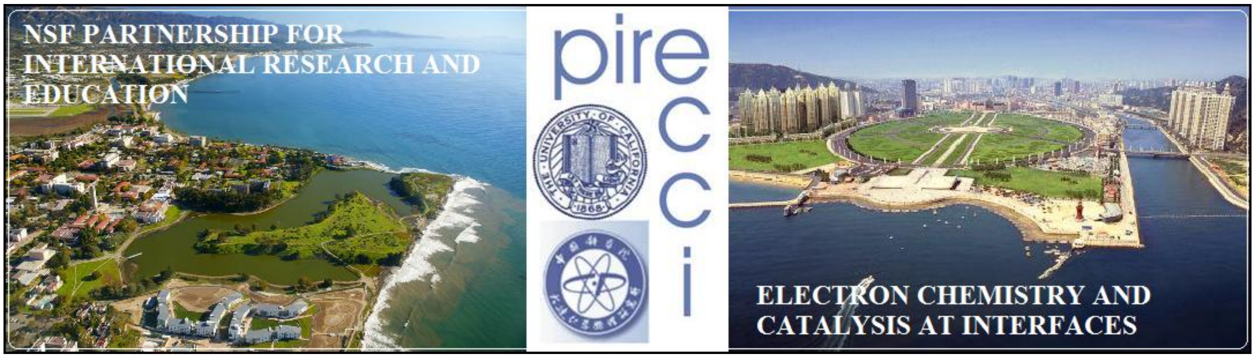

2010 PIRE-ECCI P.I. Planning Meeting

Dalian, China

Sept 8-10, 2010

Contents

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Schedule

Wednesday afternoon, September 8: Xueming Yang, chair		
2:00-2:10	Susannah Scott and Xueming Yang	Introduction: workshop goals
2:10-2:50	Susannah Scott	Using XAFS to elucidate catalyst structures
2:50-3:30	Brad Chmelka	Local order and disorder in zeolites and layered silicates
3:30-3:45	**Break**	
3:45-4:25	Baron Peters	Computational study of reactions between hydrogen peroxide and methyltrioxorhenium
4:25-5:05	An-Hui Lu	Designed synthesis of porous carbons and solid catalysts
5:05-5:45	Peter Ford	Adventures in biomass conversion
5:45	**Discussion**	
Thursday morning, September 9: Peter Ford, chair		
8:00-8:40	Alec Wodtke	H-atom Rydberg tagging: A new approach to studying energy transfer at surfaces
8:40-9:20	Qi-Kun Xue	Novel properties of topological insulator thin films of Bi_2Te_3 and Bi_2Se_3 prepared by molecular beam epitaxy
9:20-10:00	Xueming Yang	Photocatalytic chemistry of methanol on TiO_2(110) surface
10:00-10:15	**Break**	
10:15 -10:55	Jingping Zhang	Surface studies with sub-nano-scaled electron beam in transmission electron microscopes
10:55-11:35	Steve Buratto	Supported mass selected clusters: STM and thermal desorption
11:35	**Discussion**	
Thursday afternoon, September 9: Susannah Scott, chair		
2:00-2:40	Qihua Yang for Can Li	Synthesis and application of organic-inorganic hybrid materials
2:40-3:20	Qiang Fu for Xinhe Bao	
3:20-4:00	Mike Gordon	Synthesis, characterization, and catalytic evaluation of metal (oxide) nanoparticles
4:00-4:15	**Break**	
4:15-4:55	Horia Metiu	Local activation of oxide catalysts
4:55-5:35	Wei-Xue Li	Catalytic reactions on metal and oxide interface
5:35	discussion	
Friday morning, September 10: Alec Wodtke, chair		
8:00-8:40	Jie Fan	Nanoparticle/nanoporous catalysts for alcohol selective oxidation
8:40-9:20	Nanfeng Zheng	Catalysis-driven structural control of metal nanomaterials
9:20-10:00	Galen Stucky	Nanoparticle heterostructure design for energy transfer and catalysis
10:00-10:15	**Break**	
10:15 -10:55	Ram Seshadri	Understanding noble metal ions in oxide hosts
10:55-11:35	Liming Zhang	Gold(I)/gold(III) catalysis in synthetic method development, homogeneous systems vs supported gold nanoparticles
11:35	**Discussion**	
Friday afternoon, September 10: Horia Metiu, chair		
2:00-2:40	Zhenyu Li for Jinlong Yang	Towards atomic details of graphene growth on metal surfaces:Theoretical studies
2:40-3:00	**Break**	
3:00-6:00	**Discuss collaborations**	

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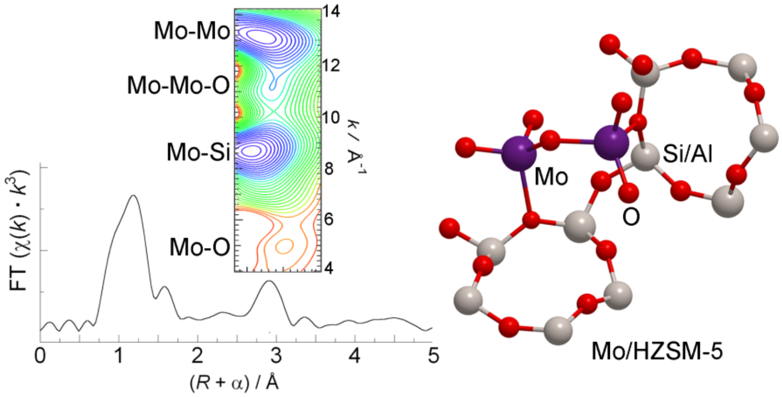
Using XAFS to elucidate catalyst structures

Evidence-based information about the structure of the active site enables us to generate testable hypotheses about reaction mechanisms, and to win insight into how to improve catalyst activity/selectivity. Non-crystalline systems, which are of high technological importance but are poorly amenable to diffraction-based techniques, are often easy to probe using X-ray absorption spectroscopy, and it is straightforward to obtain such spectra under operating conditions. Analysis of the XAFS is usually performed by curvefitting a model structure to the FT-EXAFS, and it may be difficult to choose between models that generate statistically similar fits. Recently, we showed that the use of a wavelet transform approach (WT-EXAFS) to complement FT-EXAFS analysis leads to additional model discrimination. For example, dimolybdate sites that are indistinguishable from monomolybdate sites in the FT-EXAFS were identified with confidence in the WT-EXAFS of Mo/ZSM-5.



Representative recent publications:

Robert O. Savinelli and Susannah L. Scott "Wavelet Transform EXAFS Analysis of Mono- and Dimolybdate Model Compounds and a Mo/HZSM-5 Dehydroaromatization Catalyst ," Phys. Chem. Chem. Phys. 2010, 12, 5660-5667.

X. Ouyang and S. L. Scott, "Mechanism for CO oxidation catalyzed by Pd-substituted $BaCeO_3$, and the local structure of the active sites", J. Catal., 2010, 273, 83-89.

Jagdeep Singh, Ryan C. Nelson, Brian C. Vicente, Susannah L. Scott and Jeroen A. van Bokhoven, "Electronic structure of alumina-supported monometallic Pt and bimetallic PtSn catalysts under hydrogen and carbon monoxide environment", Phys. Chem. Chem. Phys., 2010, 12, 5668-5677.

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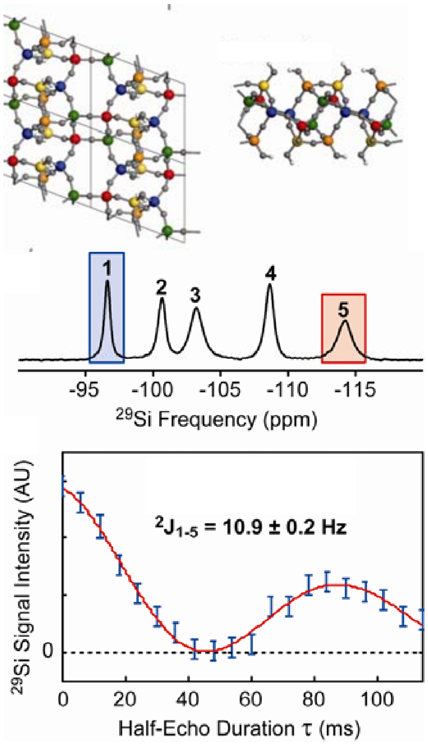
Local Order and Disorder in Zeolites and Layered Silicates

Zeolites and layered silicates often exhibit subtle combinations of short- and long-range structural order and disorder that reflect how their crystalline structures develop during synthesis and which can have important influences on their adsorption and reaction properties. Such heterogeneous features generally arise in the presence of organic structure-directing species that strongly interact with and direct the formation of crystallizing silicate or heteroatom-substituted networks. The structures of the resulting materials are often challenging to establish, particularly if single-crystals are not available. Solid-state NMR spectroscopy methods are sensitive to the local environments of atoms and can be used to provide complementary short-range compositional and structural information. For example, heteronuclear dipole-dipole couplings, such as between ^{29}Si-^{1}H or ^{29}Si-^{19}F nuclear spin pairs, allow interactions between the organic structure-directing species, fluoride ions, and silicate framework moieties to be measured. Furthermore, ^{29}Si-^{29}Si and heteroatom scalar interactions can be used to establish the interconnectivities and local bonding environments among different sites in ordered frameworks. In combination with X-ray scattering and molecular modeling analyses, such measurements yield new insights on the local compositions and structures of complicated zeolite and layered silicate frameworks and on the processes by which they become ordered.



S. Cadars, D.H. Brouwer, B.F. Chmelka, "Probing the Local Structures of Siliceous Zeolite Frameworks Using Solid-State NMR and DFT Calculations of ^{29}Si-O-^{29}Si Scalar Couplings," *Phys. Chem. Chem. Phys.*, *11*, 1825-1837 (**2009**).

S. Cadars, N. Mifsud, A. Lesage, J.D. Epping, N. Hedin, B.F. Chmelka, L. Emsley, "Dynamics and Disorder in Surfactant-Templated Silicate Layers Studied by Solid-State NMR Dephasing Times and Correlated Lineshapes," *J. Phys. Chem. C*, *112*, 9145-9154 (**2008**).

N. Hedin, R. Graf, S. C. Christiansen, C. Gervais, J. Eckert, R. Hayward, B.F. Chmelka, "The Structure of a Surfactant-Templated Silicate Framework in the Absence of 3D Crystallinity," *J. Am. Chem. Soc.*, *126*, 9425-9432 (**2004**).

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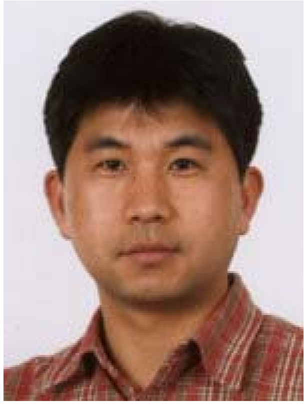
Computational study of reactions between hydrogen peroxide and methyltrioxorhenium

Methyltrioxorhenium (MTO) has interesting catalytic properties including activity for C-H bond activation and olefin metathesis. Computational studies using various model chemistries have been performed to understand reactions involving MTO. Earlier studies reveal that some commonly used functionals, basis sets, and effective core potentials do not accurately describe simple reaction thermodynamics and kinetics. The PW1PW91 functional with an extra *f*-function augmented def2-TZVP basis set and continuum solvent corrections bring computed results into better agreement with observed thermodynamic properties. However, calculations based on the mechanism in the literature still predict erroneously slow kinetics for reactions between MTO and H_2O_2. A water assisted mechanism brings theory and experiment into much closer agreement. Time permitting we will also discuss a framework that we are developing to model amorphous catalyst supports.



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Designed synthesis of porous carbons and solid catalysts

The synthesis of novel catalysts with well-designed composition and structure is an active research field. Porous materials have properties, such as high surface area, controllable pore structure and pore size distribution, associated with tailored composition and morphology, which are highly desired for catalysis applications. In the first part of this presentation, the recent achievement of controlled synthesis of pore carbons with tunable pore structures including hierarchical pores and ordered mesostructures, and with diverse morphologies covering monolith, sphere, fiber and core-shell, will be discussed. In the second part, selective deposition of catalytic particles/clusters in pre-defined regions of a support material on the nanometer scale will be discussed. The content covers, for example, design of magnetic solid acid catalyst, preparation of mushroom nanostructures, selective deposition of magnetic particles exclusively on the external surface or within the channel of ordered mesoporous materials by a reversible pore-blocking strategy. The prepared catalysts can be used for hydrogenation reaction, selective oxidation of alcohol to aldehyde, condensation reaction and ammonia decomposition.

Representative recent publications:

A.-H. Lu*, W.-C. Li, G.-P. Hao, B. Spliethoff, H.-J. Bongard, B. B. Schaack, F. Schüth, Easy Synthesis of Hollow Polymer, Carbon and Graphitized Microspheres, Angew. Chem. Int. Ed. 2010, 49,1615–1618.

G.-P. Hao, W.-C. Li, D. Qian, A.-H. Lu*, “Rapid Synthesis of Nitrogen-doped Porous Carbon Monolith for CO2 Capture”, Adv. Mater., 2010, 22, 853-857.

M. Feyen, C. Weidenthaler, F. Schüth and A.-H. Lu*, “Regioselectively Controlled Synthesis of Colloidal Mushroom Nanostructures and Their Hollow Derivatives” J. Am. Chem. Soc., 2010, 132, 6791–6799.

A.-H. Lu,* J.-J. Nitz, M. Comotti, C. Weidenthaler, K. Schlichte, C. W. Lehmann, O. Terasaki, F. Schüth, “Spatially and Size Selective Synthesis of Fe-based Nanoparticles on Ordered Mesoporous Supports as Highly Active and Stable Catalysts for Ammonia Decomposition”, J. Am. Chem. Soc., 2010, accepted.

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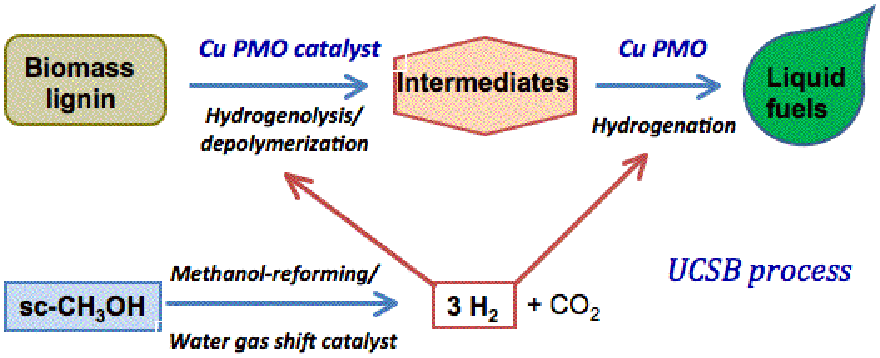
Adventures in Biomass Conversion

In this presentation I will outline recent studies into developing catalytic procedures for the conversion of various biomass components into chemicals and fuels with an emphasis on lignocellulose components. Our approach to the latter involves a one-pot transformation, which is achieved in supercritical methanol using a Cu-doped porous metal oxide derived from hydrotalcites as the catalyst, at a relatively mild temperature (300 ^{o}C). Results using the lignin model compounds dihydrobenzofuan and organosolv lignin will be described. This novel approach disassembles biomass-derived polymeric lignin into processible units via hydrogen transfer from methanol leading to complete hydrogenolysis of phenyl ether bonds, coupled with the hydrogenation of aromatic rings. The product is complex mixture composed principally of monomeric substituted cyclohexyl derivatives with greatly reduced oxygen content and negligible aromatics. Notably, no char formation was observed. The current status in similar treatments of the lignocellulose composite sawdust will be also be described.



1) Hydrogen Transfer from Super-critical Methanol over a Solid Base Catalyst. A Model for Lignin Depolymerization. Macala,_G. S.; Matson, T. D.; Johnson, C. L.; Lewis, R. S.; Iretskii, A. V.; Ford, P. C. *ChemSusChem* **2009**, *2*, 215-217.
2) Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol, Barta, K.; Matson, T. D.; Fettig, M. L.; Scott, S. L.; Iretskii, A. V.; Ford, P. C., *Green Chem.*, **2010**, Advance Article.

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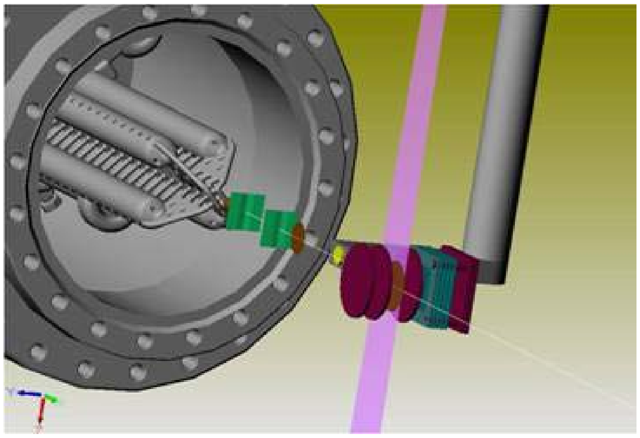
H-atom Rydberg tagging: A new approach to studying energy transfer at surfaces

We are interested in advancing understanding in problems related to electronically nonadiabatic energy transfer at surfaces. Electronically non-adiabatic effects refer to Born-Oppenheimer approximation (BOA) breakdown where energy can be converted back and forth between nuclear and electronic motion. While electronically nonadiabatic interactions have been observed in other physical contexts – for example gas-phase and liquid-phase energy transfer – for molecular interactions at surfaces; they appear to be of central importance. For example, observations of electron emission from low work function surfaces resulting from collisions of highly vibrationally excited molecules give direct evidence of the conversion of internal (vibrational) energy of a molecule to electronic excitation of a solid.

Such behavior is of significant interest as it represents an entirely new field of inquiry into how elementary atomic scale energy conversion processes take place, where chemical and electrical energy are intrinsically interrelated. The theoretical basis for the first-principles understanding of this class of phenomenology is still in its infancy. Thus, new experiments motivate new theoretical developments and vice versa. Furthermore, as our understanding of such elementary energy conversion processes improves, we may predict behavior and attempt to exploit our new knowledge to create conditions for unexpected new kinds of energy conversion.



Representative recent publications:

1. *Vibrational overtone excitation in electron mediated energy transfer at metal surfaces,* Russell Cooper, Igor Rahinov, Daniel Matsiev, Daniel J. Auerbach, Alec M. Wodtke, **1** 55-61 (2010)
2. *Efficient vibrational and translational excitation of a solid metal surface: State-to-state time-of-flight measurements of HCl (v=2,J=1) scattering from Au (111)*, Igor Rahinov, Russell Cooper, Cheng Yuan, Xueming Yang, Daniel J. Auerbach, Alec M. Wodtke, J. Chem. Phys. **129** 214708 (2008)

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Novel properties of topological insulator thin films of Bi_2Te_3 and Bi_2Se_3 prepared by molecular beam epitaxy

We have grown topological insulator thin films of Bi_2Te_3 and Bi_2Se_3 on Si(111) and 6H-SiC(0001) substrates by using state-of-art molecular beam epitaxy (MBE). We studied nontrivial surface states and their thickness-dependence of the films by *in situ* angle resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy/spectroscopy (STM/STS). By direct imaging standing waves associated with magnetic and nonmagnetic impurities and steps on Bi_2Te_3 and Bi_2Se_3 (111) surfaces, we show that the topological states have a surface nature and are protected by the time reversal symmetry. We demonstrated the high mobility of the Bi_2Se_3 films by direct observation of Landau quantization. We also discuss about the possibility for studying surface catalysis with chiral molecules on topological insulators in terms of their novel helical spin structure.

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Photocatalytic Chemistry of Methanol on TiO_2(110) Surface

Clean hydrogen production is highly desired for future energy needs, making the understanding of molecular-level phenomena underlying photocatalytic hydrogen production both fundamentally and practically important. It is known that water splitting on pure TiO_2 is inefficient, however, adding sacrificial methanol could significantly enhance the photocatalyzed H_2 production. Therefore, understanding the photochemistry of methanol on TiO_2 at the molecular level could provide important insights to its photocatalytic activity. Here, we report the clear evidence of photocatalyzed splitting of methanol on TiO_2 derived from time-dependent two-photon photoemission (TD-2PPE) results in combination with scanning tunneling microscopy (STM). STM tip induced molecular manipulation before and after UV light irradiation clearly reveals photocatalytic bond cleavage, which occurs only at Ti^{4+} surface sites. TD-2PPE reveals that the kinetics of methanol photodissociation appears to be fractal, an important characteristic of this intrinsically heterogeneous surface photoreaction.

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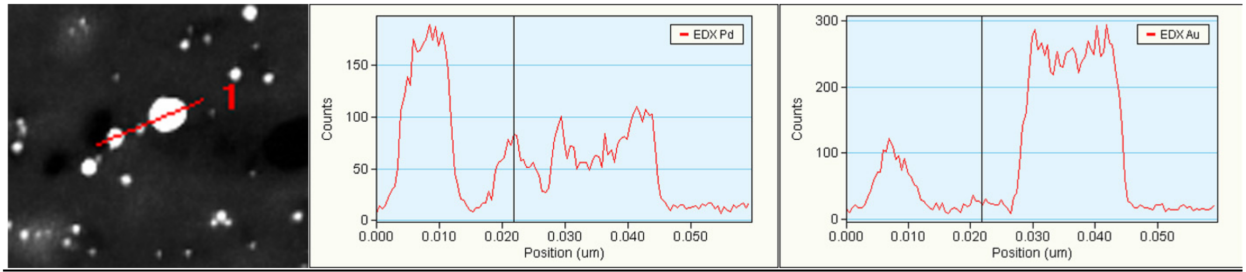
Surface Studies with Sub-nano-scaled Electron Beam in Transmission Electron Microscopes

One of the latest developments in transmission electron microscopy (TEM) is the Z-contrast imaging performed with a sub-nanometer probe in scanning TEM mode that the image intensity (I) presented is proportional to the atomic number (Z) of the specimen column illuminated, nearly $I \propto Z^2$. Moreover, the electron beam in that scale can also be used for chemical analysis with the attaché systems of electron dispersive X-ray spectrometer (EDS) and electron energy loss spectrometer (EELS). Here we present some applications of those techniques to the identifications of (1) Au-Pd core-shell catalytic particles; (2) unexpected P as a trace element appeared on the surface of Ni-particles, which played important role in TiO_2-nanowire formation; (3) Ti-O amorphous. In combine with conventional atomic imaging in TEM, the in-situ phase transformation from Ti-O amorphous to cubic TiO, induced by electron beam, will also be discussed.



Identification of Au-Pd core-shell nano-structure by Scanning TEM and EDS spectroscopy.

Representative recent publications:

Myung Hwa Kim, Jeong Min Baik, Jinping Zhang, Christopher Larson, Youli Li, Galen D. Stucky, Martin Moskovits, and Alec M. Wodtke, J. Phys. Chem. C 2010, 114, 10697–10702 “TiO2 Nanowire Growth Driven by Phosphorus-Doped Nanocatalysis”

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Supported mass selected clusters: STM and thermal desorption

Vanadium oxides supported on TiO_2 are known to catalyze a number of reactions. Despite being widely studied several questions regarding the catalytic activity remain including the exact compositions and structures of the active species. In an effort to gain a fundamental understanding of these catalysts, we utilize an apparatus that allows us to deposit mass-selected V_x and V_xO_y clusters on rutile TiO_2(110)-(1×1) in UHV. These model catalysts are characterized using STM to determine how the clusters bind to the support. We show that V_1 and V_2 clusters remain size-selected upon deposition, that there are clear differences in the morphologies of these clusters, and that the sizes and shapes observed for the clusters are consistent with density functional theory (DFT) calculations. We also show that that VO and VO_2 clusters remain size-selected upon deposition. These oxide clusters adsorb in sites that are predicted by lowest-energy structures calculated in DFT.

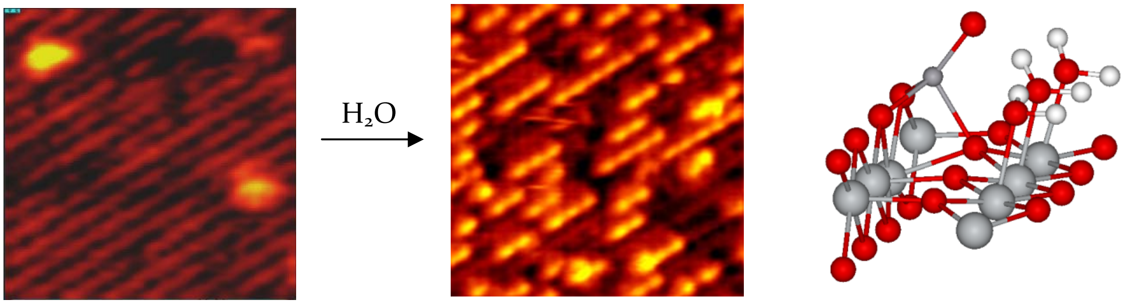

Figure 1: STM image of VO deposited on TiO_2(110) and 300K (left image), STM of water adsorbed to the VO/TiO_2 surface at 300K (middle image), and lowest energy structure for 3 water molecules bound to the VO/TiO_2 surface. The first water molecule has a desorption energy of 1.01 eV and the 2nd and 3rd water molecules have a desorption enrgy of 0.812 eV.

We have observed unusual reactivity of the VO-modified TiO_2(110)-(1×1) surface towards water and methanol adsorption. Room-temperature STM images (Figure 1) show adsorbed water molecules form chains along the five-fold coordinated Ti (5c-Ti) rows when a VO/TiO_2 surface is exposed to water. These chains of water molecules have been observed on bare TiO_2(110) at low temperature (~120K), but not at room temperature. Thermal desorption of water from a VO/TiO_2(110) surface shows a desorption state at 395K which is not present for bare TiO_2. These observations are supported by DFT calculations which predict room temperature adsorption of water along the 5c-Ti rows of a VO/TiO_2 surface, with adsorption energies of ~ 1 eV. Finally, we will present our most recent experiments describing the catalytic activity of VO and VO_2 clusters in the oxidation of methanol to produce formaldehyde.

Representative Publications

Kemper, P.; Kolmakov, A.; Tong, X.; Lilach, Y.; Benz, L.; Manard, M.; Metiu, H.; Buratto, S. K.; Bowers, M. T., Formation, deposition and examination of size selected metal clusters on semiconductor surfaces: An experimental setup. *Int. J. of Mass Spec.* **2006**, 254, (3), 202-209.

Tong, X.; Benz, L.; Kemper, P.; Metiu, H.; Bowers, M. T.; Buratto, S. K., Intact size-selected Au-n clusters on a TiO2(110)-(1 x 1) surface at room temperature. *Journal of the American Chemical Society* **2005**, 127, (39), 13516-13518.

Tong, X.; Benz, L.; Chretien, S.; Metiu, H.; Bowers, M.T.; Buratto, S. K., Direct Visualization of Water-Induced Relocation of Au Atoms from Oxygen Vacancies on a TiO2 (110) Surface. *Journal of Physical Chemistry C* **2010**, 114, (9), 3987-3990.

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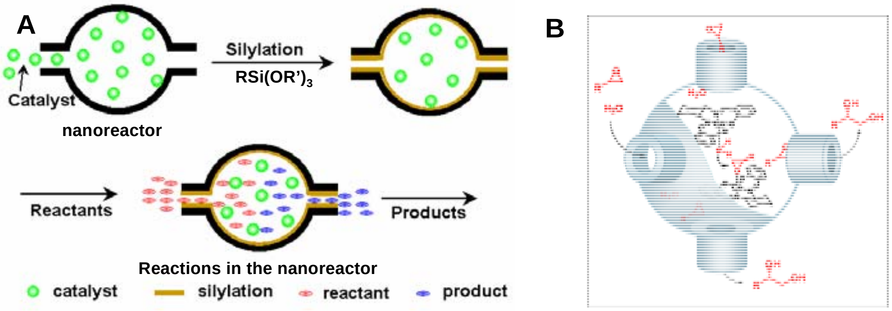
Synthesis and application of organic-inorganic hybrid materials

The synthesis of organo-modified mesoporous materials (OMM) with well-defined structure and morphology has attracted much research attention because of their wide applications in the fields of separation, chromatography, catalysis, large molecule sequestration and controlled release systems. The applications of OMM will be considerably broadened if OMM with various types of functional groups, structure, and morphology can be synthesized. Recently, we developed a method for the structure and morphology control of OMM in mild buffer solution. Also, the mesoporous silicas functionalized with chiral ligands were successfully synthesized and they show moderate to high enantioselectivity in asymmetric catalysis. Moreover, we developed an efficient method to encapsulate the metal complexes in the nanocage of the mesoporous materials, like SBA-16, through reducing the pore entrance size by silylation method (Scheme 1). It is noteworthy to mention that [Co(Salen)] encapsulated in the nanocage of SBA-16 exhibits even higher catalytic activity than the homogeneous counterpart in HKR of propylene oxide through cooperative activation(Scheme 1). This result indicates that the confined space of the nanopore can enhance the cooperative activation for the asymmetric catalysis. This provides a new opportunity for the preparation of efficient solid catalysts for the asymmetric reactions.



Scheme. A: General process for encapsulation of chiral catalyst within the nanocage of mesoporous silicas followed by tailoring the pore entrance size through silylation; B: Illustration of the cooperative activation in the nanocage.

Representative recent publications:
Shiyang Bai, Hengquan Yang, Peng Wang, Jinsuo Gao, Bo Li, Qihua Yang and Can Li “Enhancement of catalytic performance in asymmetric transfer hydrogenation by microenvironment engineering of the nanocage,” Chem. Commun. DOI: 10.1039/c0cc01401.
Jian Liu, Shiyang Bai, Hua Zhong, Can Li, Qihua Yang “Tunable Assembly of Organosilica Hollow Nanospheres,” J. Phys. Chem. C. 2010, 114, 953-961.
Qihua Yang,Jian Liu, Lei Zhang, and Can Li “Functionalized periodic mesoporous organosilicas for catalysis,” J. Mater. Chem. 2009, 19, 1945-1955.

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Architectural configurations of Pt-based bimetallic catalysts for CO oxidation

Bimetallic catalysts are widely used in many heterogeneous catalytic processes. With rational design of the surface structure of the bimetallic catalysts, improved catalytic performance can be achieved in comparison to their parent metals. In the bimetallic catalytic systems, three typical surface architectures can be constructed, including alloy, core-shell, and mixture of monometallic particles.[1] Furthermore, the chemical state of one of the two metals could be in either metallic or oxidized, which depends on the reaction atmosphere.[2-3] It has been demonstrated that the architectural configuration of the bimetallic catalysts is critical to their catalytic performance. Here, Pt-based bimetallic catalysts were applied for CO oxidation. In Pt-Fe systems, we demonstrate that the nanostructured ferrous oxides (FeO) grown on Pt present the best reactivity to the CO oxidation among various Fe-Pt(111) surface structures. Using surface science measurements and density functional calculations, we show that the interface confinement effect can be attributed to the stabilization of the monolayer-dispersed ferrous oxide nanoislands and coordinatively unsaturated ferrous (CUF) sites at the edges of the FeO nanoislands by taking advantage of strong adhesion between the nanostructured oxides and the metal substrates. The CUF sites together with the metal supports are active for O_2 activation, and the structural ensemble was highly efficient for CO oxidation using both model systems and practical supported catalysts.[4] The interface confinement effect could be extended to other oxide-metal systems as well. In Pt-Ni systems, we observe the formation of monolayer-dispersed NiO nanoislands on Pt(111) and the interface-confined coordinatively unsaturated Ni atoms. The NiO/Pt(111) is highly active for CO oxidation.[5]

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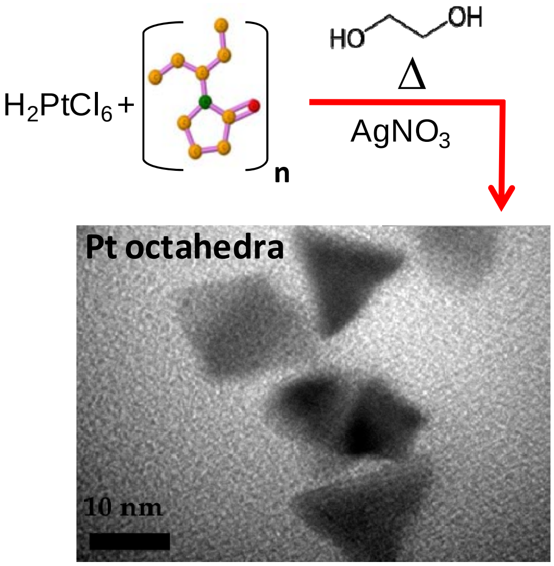
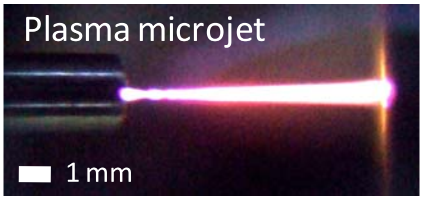
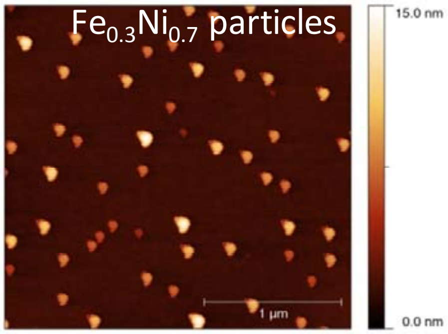
Synthesis, characterization, and catalytic evaluation of metal (oxide) nanoparticles

The exquisite structural and compositional control afforded by bottom-up synthesis of nanoparticles and nanostructure offers many opportunities to engineer novel catalytic materials with improved activity, selectivity, and functionality. In addition, fundamental studies aimed at correlating the catalytic behavior of such materials with nanoscale morphology and chemistry can potentially bridge the materials gap between single crystal studies in UHV and practical catalysts (e.g. metal(oxide) clusters or nanoparticles on oxide supports). In this talk, we will highlight our recent efforts using solution-phase synthesis and plasma-based deposition techniques to realize size, shape, and compositionally-controlled nanoparticles for catalytic applications. Shaped Pt nanoparticles (e.g. cubes, octahedra, etc.) <15 nm were created using wet chemical methods with polymer surfactants and Ag as a growth promoter; surfactant-free Fe_xNi_{1-x}, Pd, and Pd-decorated SiO_2 nanoparticles <10 nm were realized using a novel atmospheric-pressure microplasma jet approach which allowed direct growth of (bi)metallic and metal/oxide particles in a single step. The talk will focus on nanoparticle synthesis and characterization, scanning probe analysis and optical spectroscopy of catalysts and surface adsorbates via DRIFTS and Raman, and catalytic testing results.







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Local activation of oxide catalysts

H. Metiu and E. McFarland

Abstract: We are interested in catalysts consisting either of substitutionally doped oxides (e.g. $Ru_xCe_{1-x}O_2$) or of submonolayers of an oxide supported on another oxide (e.g. VO_x supported on ceria). Calculations and experiments show that in most cases these systems are more active catalysts than the original oxide (i.e. ceria). We use theory to try to find general patterns governing the activation by doping and to screen various oxide-dopant pairs. We perform experiments to find how the catalytic activity of a doped oxide depends on the method of preparation and the nature of the oxide and dopant. We are interested in alkane activation with a particular emphasis on methane and we study combustion, partial oxidation, steam reforming, dry reforming and the water-gas shift. We also use these catalysts to study CO_2 activation and the possibility of using CO_2 as a mild oxidant. More recently we started investigating the possibility of using anion dopants (e.g. replacing some oxygen atoms in the surface of the oxide with halogen atoms) to promote the activity of oxide catalysts. Finally, we are also planning to work on a two-step process in which an oxide is reduced with methane, to make syngas, and then is reoxidized with water to make hydrogen or is reoxidized with CO_2 to make CO.

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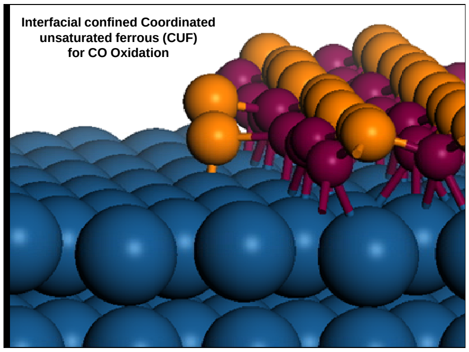
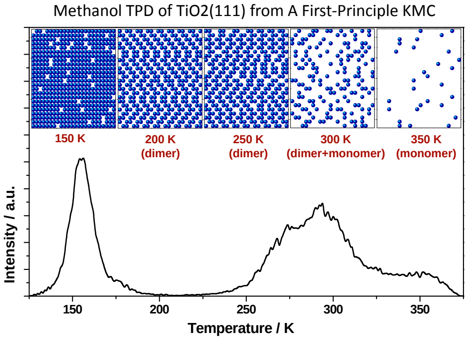
Catalytic reactions on metal and oxide interface

To rationalize the design of nano-catalysts supported on oxides and catalytic reactions under realistic conditions and bridge the so-called materials and pressure gaps, fundamental understanding of catalytic materials and corresponding activity taking into account of temperature and pressure at the microscopic level as well as the collaboration between experiments and theory are essential. In this talk, I will present our recent efforts along these directions. First, I will introduce a strategy of constructing a highly efficient and stable active site, namely coordinately unsaturated ferrous (CUF) site by taking advantage of interfacial confinement between FeO bilayer islands and Pt substrate, for CO oxidation in the presence of hydrogen with great implication for PEMFC. Secondly, I will talk about a first-principles kinetic Monte-Carlo study of methanol adsorption and desorption on TiO2(110) surfaces at wide range of T and P, which would provide valuable insights for relevant photocatalysis process under operational conditions.





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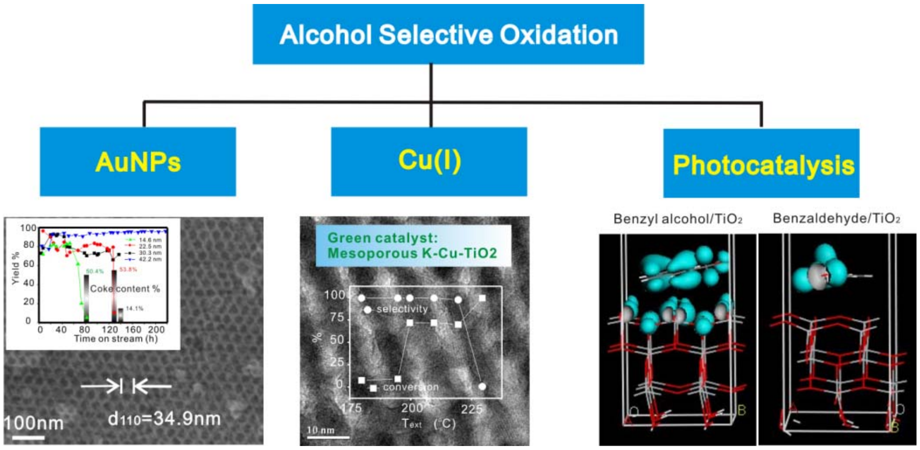
Nanoparticle/Nanoporous Catalysts for Alcohol Selective Oxidation

Selective oxidation of alcohols to aldehydes (SOAA) is one of the most common organic transformations and is of fundamental importance for laboratory and commercial processes. Currently, aldehydes are produced through stoichiometric oxidation by manganese and chromium salts in the laboratory or by liquid phase chlorohydrin processes.[1,2] In the wake of increasing concern about the environment, the alcohol-to-aldehyde transformation should preferably be accomplished by using a highly selective and recyclable “green” catalyst that is able to use molecular oxygen as the oxidant. In this report, three nanoparticle/nanoporous catalysts were developed to address this issue.

Many industry catalysts used today are metal nanoparticles that are spread over the internal surface of porous materials acting as carriers or supports. SOAA processes could benefit from the three-dimensional nanoporous networks that provide optimal mass diffusion. We demonstrated that supermolecular templating allows the tuning pore size of ordered mesoporous materials in the once elusive range spanning 30 nm to more than 60 nm through simple control of synthetic variables (salt/template concentration and hydrothermal temperature).[3] The pore size variation is important for the design of better porous catalysts. Gold nanoparticles (AuNPs) within the extra-large-pores exhibit dramatically increased lifetime in SOAA reaction than those located within relatively small mesopores due to the enhanced mass diffusion that suppresses the coke deposition on AuNPs.

In practice, the oxidation of alcohols with molecular oxygen can be performed in the liquid or gas phase, depending mainly on the thermal stability and volatility of the reagents and products. The convenience of catalyst separation and solvent-free condition make a gas-phase process more attractive for industrial applications. The biggest disadvantage of gas-phase oxidation is the high reaction temperature, which tends to favor energy consumption, low selectivity and deactivation of active sites. The reaction temperatures currently reported for gas-phase benzyl alcohol oxidation are generally above 300 ^{o}C, 100 ^{o}C higher than the boiling point (b.p.) of benzyl alcohol (203 ^{o}C), over various catalysts (e.g. Au/SiO2, K/Ag/SiO2, Cu/Na/ZSM-5, and Au-Cu/SiO2), and no appreciable benzyl alcohol-to-benzaldehyde oxidation below 250 ^{o}C has been reported. We reported a newly developed mesoporous ternary metal oxide (K-Cu-TiO2) that is capable of activating the selective gas-phase oxidation of benzyl alcohol at surprisingly low temperature —the b.p. of benzyl alcohol (203 ^{o}C).[4] The low-temperature reaction conditions and the homogeneous integration of K and Cu(I) components into the TiO2 matrix enable the stabilization of the active Cu(I) oxidation state and the resulting stable, excellent catalytic performance.

Finally, we show that the SOAA transformation can be achieved at exceptionally high yield (~ 99%) upon visible-light irradiation over mesoporous TiO2.[5] The origin of the high yields is further clarified based on DFT calculations and experimental observations. Briefly speaking, the antibonding π molecular orbitals (MOs) of benzyl alcohol (BA) can hybridize with the O2p atomic orbitals (AOs) of TiO2; such hybridization not only results in the band gap narrowing, making TiO2 responsive to visible light, but also enables the oxidation of BA to benzaldehyde (BAD) by photogenerated holes in the delocalized valence band. The DFT calculations also indicate that the local band gap of TiO2 is difficult to be modified by BAD molecules. Moreover, the calculation shows that BAD has a negative adsorption energy (-0.1 eV) on TiO2 surface, which is quite different from that for BA (5.45 eV). This result suggests that the BAD molecules are likely to bounce off the TiO2 surface once BA-to-BAD transformation is completed. It not only prevents the BAD from the over-oxidation, but also stop the hole-generation process. As a result, hole generation becomes controllable in this type of visible light photocatalytic system, and a so-labeled “self-adjustable photocatalytic system” can be established based on the interaction between BA/BAD and TiO2.



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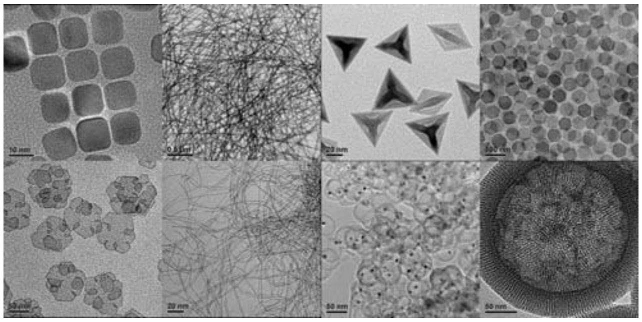
Catalysis Driven Structural Control of Metal Nanomaterials

To optimize the catalytic performance of a metal nanocatalyst, it is important to simultaneously design and precisely control the various parameters inside the catalyst. To achieve such a goal, our research efforts in catalysis are concentrated in the following two areas: 1) the morphology control of metal nanocrystals and the morphological effect on catalysis; 2) the hierarchical structures to stabilize metal nanocatalysts. Recently, we have demonstrated that the use of various small molecules (e.g., I^-, formaldehyde, CO) allows us to achieve the synthesis of several unique Pd/Pt nanostructures, such as nanocubes, ultralong nanowires/nanohairs, concave polyhedra, and ultrathin nanosheets. The as-prepared metal nanocrystals displayed a significant morphological effect on their catalysis / electrocatalysis properties. Together with the surface structure controlling, we are also developing strategies to convert pre-made well-defined metal nanoparticles into stable and efficient nanocatalysts(e.g., encapsulated, dual-supported catalysts).



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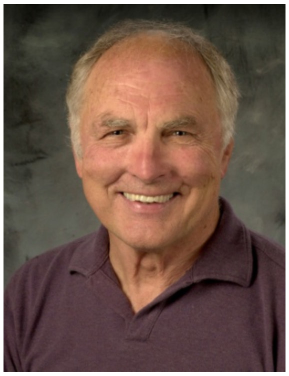

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Nanoparticle heterostructure design for energy transfer and catalysis

A successful catalytic system combines components that are defined by their function on atomic to macro length scales. The nanoscale integration of active heterostructures is of particular interest to our group in the context of interface control of energy transfer and catalytic processes. Two approaches that we have explored in this regard are single nanoparticle core/shell packaged catalysts and the the efficiency of electron/energy transfer between semiconductor and nanoparticle metallic components, which frequently limits system performance for selective catalytic oxidation and photovoltaic applications.

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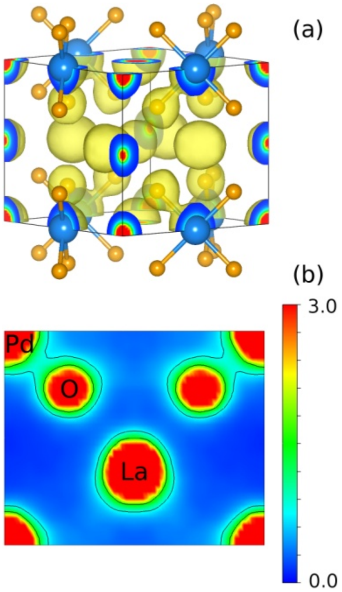
Understanding noble metals in oxide hosts

We have for some years, explored the role that ions such as Pd^{2+}, Rh^{3+}, and Au^{3+} play in catalytic processes, and in particular, in reactions where traditionally noble meal nanoparticles are implicated. To this end, we have devised systems of oxide hosts where the noble metal is either dilute, as in $BaCe_{1-x}Pd_xO_{3-x}$, or concentrated as in La_2BaPdO_5, and in collaboration with the group of Professor Susannah Scott, have examined the effectiveness of these compounds in CO oxidation reactions. In some cases, there is strong evidence that oxide systems with substituted Pd^{2+} ions are actually more effective catalysts that the equivalent oxides with supported Pd nanoparticles on the surface. The use of synchrotron x-ray and neutron scattering, including applications of the pair distribution function technique, as employed to better understand the substituted oxides, will be emphasized in this presentation.



The accompanying figure displays maximum entropy image restoration of the electron density from synchrotron x-ray scattering, in the unit cell of the catalyst La_2BaPdO_5. The highly electropositive La^{3+} and Ba^{2+} ions ensure that valence electron density is concentrated in the Pd-O bond.

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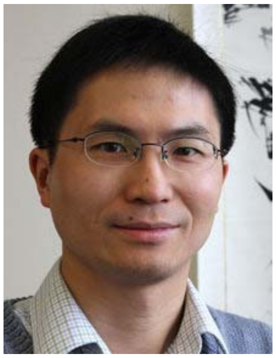

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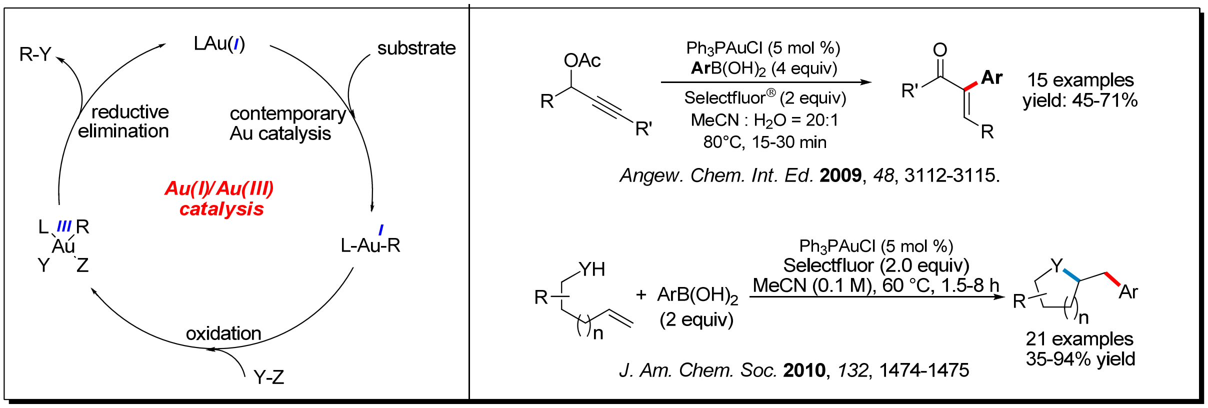
Au(I)/Au(III) Catalysis in Organic Synthesis: Homogeneous *vs* Heterogeneous Catalysis

Comparing to well studied isoelectronic Pd(0)/Pd(II) catalysis, organic reactions involving Au(I) and Au(III) catalytic cycles have little precedence. We have recently published first examples of homogeneous gold catalyzed oxidative cross-coupling reactions and carboheterofunctionalization of alkenes, demonstrating the feasibility of this novel catalytic manifold (see the Scheme below). Selectfluor, an electrophilic fluorine reagent, works instead as a uniquely effective oxidant to convert Au(I) into Au(III). While we are further exploring the synthetic potentials of this homogeneous reactivity, the much studied reactivities of supported gold NPs in oxidation reactions have prompted us to examine the Au(I)/Au(III) catalysis in heterogeneous systems. This approach would enable catalyst recycle, simplify separation and, perhaps most importantly, rendering new reactivities. Our preliminary data showed that indeed gold NP supported on TiO_2 could catalyze similar transformations as soluble gold complexes; moreover, in some cases, different reaction outcomes were observed. Our goal is to understand the difference between these two systems and use gold NPs of various sizes and support as platform to develop efficient synthetic methods for the construction of versatile and relatively complex structures.



Angew. Chem. Int. Ed. **2009**, *48*, 3112-3115.

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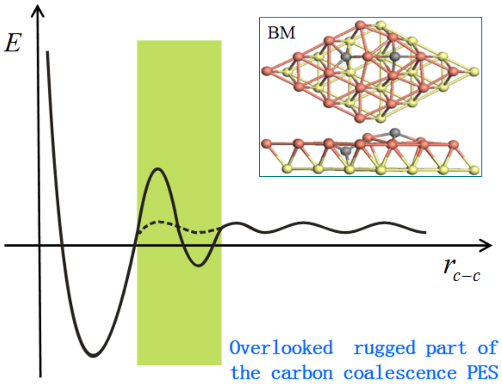
Towards Atomic Details of Graphene Growth on Metal Surfaces: Theoretical Studies

Graphene is an important material with many unique properties and a great application potential. A promising way to massively produce graphene is chemical vapor deposition (CVD) on metal surfaces. To improve sample quality, it is important to understand the atomic details during graphene CVD growth. First principles calculation is a powerful tool for this purpose. Recently, we have studied some relevant elementary processes on Cu and Ir surfaces. Although diffusion of atomic carbon on Cu (111) surface is almost barrierless, coalescence of carbon atoms on the surface is found to be hampered by an intermediate bridging-metal structure. The fact which makes things more complicated is that thermodynamic analysis indicates that the main species on the Cu surface during graphene growth is not the simplest atomic carbon. On Ir (111) surface, the experimentally observed cluster-attachment growth mode is confirmed. However, our calculations suggest that it is thermodynamically driven instead of kinetically driven as previously proposed.



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Ning Lu, Ying Huang, Hai-Bei Li, Zhenyu Li, and Jinlong Yang, " First principles nuclear magnetic resonance signatures of graphene oxide", *J. Chem. Phys.* 2010, 133, 034502-7.

Zhenyu Li, Wenhua Zhang, Yi Luo, Jinlong Yang, and Jian Guo Hou " How Graphene Is Cut upon Oxidation?" *J. Am. Chem. Soc.* 2009, 131, 6320-6321.

Upcoming Events

1. **Summer, 2011:** Advisory Board and All-PI Collaboration and Planning Meeting in Santa Barbara:

   Chinese PIs are invited to UCSB for a 3-day planning meeting, to tour campus and laboratories, and meet with additional UC faculty and students. The advisory board will also meet for the first time in Phase-II and help lay a course for the following year.
2. **Summer, 2012**: Summer Program in Santa Barbara & PI Collaboration Meeting in Dalian
3. **Summer 2013:** US-China Partnership in Dalian, Chinese Technology Transfer Study Tour, & PI Collaboration Meeting
4. **Summer 2014**: Summer Program in Santa Barbara & PI Collaboration Meeting in Dalian
5. **Summer 2015:** US-China Partnership in Dalian, Chinese Technology Transfer Study Tour, & PI Collaboration Meeting