

**Catalysis Club of Philadelphia's
Graduate Student Poster Competition
October 21, 2010**

1. Catalyst by Design: Tuning the Selective Oxidation of CH₃OH to Dimethoxymethane over Supported V₂O₅ – WO₃/TiO₂/SiO₂ with TiO₂ Nanoligands

Kevin F. Doura, Israel E. Wachs, *Operando* Molecular Spectroscopy and Catalysis Research Laboratory, Department of Chemical Engineering, Lehigh University

2. A Raman and IR Investigation of Supported Na₂O/Al₂O₃ and K₂CO₃-Promoted Hydrotalcite for Reversible CO₂ Capture

Christopher J. Keturakis^a, Michael G. Beaver^b, Hugo S. Caram^b, and Israel E. Wachs^a
^a*Operando* Molecular Spectroscopy and Catalysis Research Laboratory, Chemical Engineering Department, Lehigh University; ^bDepartment of Chemical Engineering, Lehigh University

3. Ammonia Decomposition Using Supported Bimetallic Catalysts

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7. The Influence of Cobalt Loading on Oxidation of Supported Catalysts for Fischer-Tropsch Synthesis

Kevin Bakhmutsky¹, Noah Wieder¹, Thomas Baldassare², Michael A. Smith² and Raymond J. Gorte¹; ¹Department of Chemical and Biomolecular Engineering, University of Pennsylvania, ²Department of Chemical Engineering, Villanova University

8. Ab initio Investigation of Stable Surface Phases and Active Sites for Hydrocarbon Combustion on Palladium-Ceria

Adam D. Mavernick, Michael J. Janik Department of Chemical Engineering, Pennsylvania State University, University Park

9. Design and analysis of novel d10 Photocatalysts

Bharat Boppana, Douglas J Doren, Raul F Lobo, Center for Catalytic Science and Technology University of Delaware

10. Tungsten Monocarbide (WC) and Surface-Modified WC Catalysts for Solar Fuel Applications

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11. Kinetics of oxygenate reforming on Pt based catalysts

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12. First Principles Design of Electrocatalysts for Direct Borohydride Oxidation

Gholamreza Rostamikia and Michael J. Janik, Dept. of Chemical Engineering, Pennsylvania State University, University Park

13. Photoreforming of Glycerol and Biomass Using Metal-Loaded Titanium Dioxide

Kevin Brodwater, D.W. Skaf, Department of Chemical Engineering, Villanova University

14. Presence of Surface Vanadium Peroxo-oxo Umbrella Structures in Supported Vanadium Oxide Catalysts: Fact or Fiction?

Julie E. Molinari and Isreal E. Wachs, *Operando* Molecular Spectroscopy and Catalysis Research Laboratory, Department of Chemical Engineering, Lehigh University

15. Synthesis and Characterization of Platinum-Modified Tungsten Carbide Using Atomic Layer Deposition

Irene Hsu, J. G. Chen and B. G. Willis, University of Delaware

16. Systematic Studies of the Cathode-Electrolyte Interface for More Active and Stable Solid Oxide Fuel Cell Electrodes

Rainer Küngas, J. M. Vohs, and R. J. Gorte, Department of Chemical and Biomolecular Engineering, University of Pennsylvania

17. Glucose Reformation on Pt (111) and Pt Bimetallic Catalysts for the Production of Hydrogen

Jesse R. McManus, R. J. Gorte, & J. M. Vohs, Department of Chemical and Biomolecular Engineering, University of Pennsylvania

18. Ethanol Reactivity Studies on Supported Cobalt Catalyst

Eddie Martono and John M. Vohs, Department of Chemical and Biomolecular Engineering, University of Pennsylvania

19. Oxidative dehydrogenation of ethanol to acetaldehyde and ethyl acetate by graphite nanofibers

Andrew Ferens, Randy Weinstein, Department of Chemical Engineering, Villanova University

20. Molten-Metal Anodes for Solid Oxide Fuel Cells

Abhimanyu Jayakumar, J. M. Vohs, and R. J. Gorte, Department of Chemical and Biomolecular Engineering, University of Pennsylvania

21. Fundamental Surface Structure-Photoactivity Relationships of Advanced Photocatalysts

Somphonh Peter Phivilay^a, Xiaofang Yang^b, Guangzhi Frank Liu^b, Bruce Koel^b, and Israel Wachs^a, ^a*Operando* Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, ^bDepartment of Chemistry, and Center for Advanced Materials and Nanotechnology, Lehigh University

22. Theoretical and Experimental Studies of Optimal Catalysts for Hydrogen Production from Ammonia Decomposition

Danielle A. Hansgen, Jingguang G. Chen, and Dionisios G. Vlachos, University of Delaware

23. Estimating number of surface active sites of redox catalysts using transient kinetic measurements

Ivan Baldychev, Raymond J. Gorte, John M. Vohs, University of Pennsylvania

24. Selective Oxidation of Propane to Acrylic Acid over Single Phase M1 MoVTenNbOx Catalysts

Xin Li, Mark A. Barteau and Douglas J. Buttrey, Department of Chemical Engineering, University of Delaware

25. Oxidation resistant boron substituted carbons for high surface area catalyst supports

Ali Qajar^a, Billy-Paul Matthew Holbrook^b, Ramakrishnan Rajagopalan^c, Henry C. Foley^a
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^bDepartment of Chemistry, Université Claude Bernard Lyon 1, Lyon, France, ^cThe Materials Research Institute, The Pennsylvania State University, University Park

26. Synthesis and characterization of shape selective platinum embedded microporous carbon sphere catalysts

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^aDepartment of Chemical Engineering, The Pennsylvania State University, University Park,
^bDepartment of Chemistry, Université Claude Bernard Lyon 1, Lyon, France, ^cThe Materials Research Institute, The Pennsylvania State University, University Park

27. High Temperature Decomposition and Reactivity of Bronsted Acid Sites in Zeolites

Khalid A. Al-majnouni, Dionisios G. Vlachos, Raul F. Lobo, Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware

28. Reaction Mechanisms of Glycerol Conversion to Value-Added Chemical Products

Tim Courtney, Jingguang Chen, Dionisios Vlachos, University of Delaware

Post Doctoral Submissions:

PD1. Structural Sensitivity of the Water Gas Shift Reaction in Platinum Surfaces

Michail Stamatakis, Ying Chen, and Dionisios G. Vlachos, Department of Chemical Engineering, University of Delaware

Catalyst by Design: Tuning the Selective Oxidation of CH₃OH to Dimethoxymethane over Supported V₂O₅–WO₃/TiO₂/SiO₂ with TiO₂ Nanoligands

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The selective oxidation of methanol over a catalyst with surface redox sites primarily produces formaldehyde (HCHO) as the reaction product, with low selectivity's to other redox products. The conversion of CH₃OH over acid sites, however, primarily yields CH₃OCH₃ as the reaction product. The selective oxidation of CH₃OH to (CH₃O)₂CH₂ (DMM: dimethoxy methane) requires redox sites to initially form HCHO and acid sites to combine HCHO with two methanol molecules to form DMM. Recently, DMM has been investigated for its potential benefit as an oxygenated additive in diesel fuel. The objective of this study was to molecularly design a supported V₂O₅-WO₃/TiO₂/SiO₂ catalyst whereby methanol could be selectively oxidized to give DMM as the main reaction product by changing the titania domain size.

The experimental results demonstrate that varying the local electron density of oxide nanoligand supports allows tuning of the specific activity characteristics of surface metal oxide catalytic active sites. In the low temperature regime (150°C - 190°C), the selectivity to DMM is highest due to a high concentration of methoxy species present on the surface. These methoxy species are able to react to form HCHO, and still in a high enough concentration on the surface to further react with HCHO to produce DMM. However, in the high temperature regime (200°C - 230°C), the concentration of methoxy species is significantly lower. As a result, it takes longer for two methoxy species to diffuse on the catalyst surface and react with HCHO to produce DMM. Therefore, we find the selectivity decrease as we approach our highest temperature. Ultimately, the ability to engineer the catalyst structure at the nanoscale and the fundamental understanding of the synthesis-structure-property relationships of supported metal oxides enabled the rational design of a supported metal oxide that could selectively oxidize methanol to DMM.

A Raman and IR Investigation of Supported Na₂O/Al₂O₃ and K₂CO₃-Promoted Hydrotalcite for Reversible CO₂ Capture

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Donated industrial CO₂ sorbents Na₂O/Al₂O₃ and K₂CO₃-promoted hydrotalcite were studied by means of diffuse reflectance infrared spectroscopy (DRIFTS) and Raman spectroscopy, along with X% Na₂O/Al₂O₃ sorbents synthesized by the incipient wetness impregnation method. As expected, the addition of promoters sequentially consumed basic surface hydroxyls from both supports (bare Al₂O₃ and hydrotalcite). It was found that the surface of the Na₂O/Al₂O₃ sorbents (both industrial and synthesized) is terminated by sodium carbonate groups in both the monodentate and polydentate coordinations, while the K₂CO₃-promoted hydrotalcite surface is terminated mainly by monodentate potassium carbonate groups. The presence of crystalline nanoparticles on the surface (Na₂CO₃ or K₂CO₃) was also detected for samples with high promoter loading. CO₂ adsorption studies revealed that samples with low promoter loading form surface bicarbonate species due to remaining surface hydroxyls, while samples with high promoter loading form mainly surface bidentate carbonate species, with a minor amount of surface monodentate coordinated carbonate also present.

Ammonia Decomposition Using Supported Bimetallic Catalysts

Jacob Weiner, Jingguang Chen and Dionisios Vlachos
University of Delaware

Ammonia decomposition is an important reaction due to the impact that it will have on the hydrogen economy. Hydrogen has been found to be a possible source of alternative energy with the application of hydrogen fuel cells. However, the major difficulty with hydrogen, as an alternative energy source, is its low energy density. Hydrogen is a low-density gas, and in order for its use in automobiles to be economically plausible, large bulky tanks or tanks under high pressure would have to be employed. The result would limit space available for other purposes and pose significant safety issues. Ammonia has been proposed as a means to store hydrogen chemically, due to its increased energy density.¹ At moderate pressures (~9 atm) ammonia is a liquid, and could be adapted into the current infrastructure.² In addition, the decomposition of ammonia would not produce carbon monoxide, which poisons fuel cell electrodes. Thus, the ammonia decomposition reaction is one piece of the mechanism that could make hydrogen a viable alternative energy source.

The work of Hansgen et al. examined ammonia decomposition through computational studies and surface science experiments on monolayer bimetallic surfaces. The Ni-Pt-Pt(111) configuration of NiPt was found to show favorable results for ammonia decomposition.³ In a reducing environment, the subsurface configuration of Pt-Ni-Pt(111) is thermodynamically preferred, and the surface configuration of Ni-Pt-Pt(111) is most stable in an oxidizing environment.⁴ The focus of this work is on reactor experiments under pressure with supported catalysts to validate predictions made by computations and surface science experiments. The importance of supported catalysts is that they bridge the pressure and materials gap from surface science experiments.

Various NiPt catalysts, of varying metal ratios and impregnation sequences, were synthesized and characterized. The co(1Pt10Ni)/ γ -Al₂O₃ catalyst shows very promising activity for ammonia decomposition, which also had the most bimetallic interactions with respect to the EXAFS data fittings. The observations of increased activity of the bimetallic catalyst provide early evidence of the necessary surface Ni being present to some extent in the ammonia decomposition environment. This finding would validate the DFT calculations and surface science experiments performed previously within the group. However, more work is still to be done to obtain proof of the surface Ni conformation on the support, and to model and quantify the extent to which this conformation exists on the support.

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- (2) Deshmukh, S. R.; Mhadeshwar, A. B.; Vlachos, D. G. *Industrial & Engineering Chemistry Research* **2004**, 43, 2986.
- (3) Hansgen, D. A.; Vlachos, D. G.; Chen, J. G. *Nat Chem* **2010**, 2, 484.
- (4) Menning, C. A.; Chen, J. G. *The Journal of Chemical Physics* **2009**, 130, 174709.

Alternative Anode Electrocatalysts for Direct Alcohol Fuel Cells

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Direct ethanol fuel cells (DEFCs) have been proposed as an alternative to hydrogen and methanol fuel cells. Ethanol is easier to transport, less toxic, and more readily obtained from biorenewable sources than other fuels. The anode material most widely studied for DEFCs is currently a PtRu alloy; however, Pt is scarce and expensive. Additionally, Pt is not active towards scission of the C-C bond in ethanol. Recently, researchers reported using a Pt/Rh/SnO₂ alloy that is more active towards ethanol electrooxidation than Pt, and Rh was determined to be crucial for effective C-C bond cleavage.¹ Tungsten monocarbide (WC) has been shown to have Pt-like properties and is active towards methanol electrooxidation.^{2,3} Density Functional Theory (DFT) was used to calculate the binding energies of ethanol and ethoxy on WC and Rh/WC; it may be possible to correlate reactivity with binding energy. Temperature-programmed desorption (TPD) was used with a WC polycrystalline foil modified with Rh to quantitatively determine the activity of the surfaces and their selectivity towards ethanol decomposition. High resolution electron energy loss spectroscopy (HREELS) showed the reaction intermediates adsorbed on the surface at different temperatures. The predominant reaction product on clean WC was ethylene; adding small amounts of Rh shifted the selectivity towards CO and H₂. HREELS showed that cleavage of the C-C bond occurred by 200 K on the Rh/WC surfaces. Extending the work to higher alcohols, propanol showed similar behavior on Rh/WC. Future work will focus on electrochemical experiments on Rh/WC in an acidic medium.

- [1] A. Kowal, *et al. Nat. Mater.* **8** (2009) 325-330.
- [2] R.B. Levy and M. Boudart, *Science* **181** (1973) 547-549.
- [3] E.C. Weigert, *et al. J. Phys. Chem. C.* **111** (2007) 14617-14620.

Sodium tungsten bronze (Na_xWO_3)-YSZ composite anode for SOFCs

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Sodium tungsten bronze (Na_xWO_3) is a promising composite anode material for solid oxide fuel cells (SOFCs) due to its extremely high electronic conductivity for an oxide based material under reducing conditions. The composites prepared by infiltration into porous yttria-stabilized zirconia (YSZ) were investigated. They exhibited very high electronic conductivities, greater than 100 S/cm at 973 K in humidified H_2 . X-ray diffraction (XRD) patterns of Na_xWO_3 composite electrodes calcined at temperatures ranging from 823K to 1073K for 2 hours demonstrated that the sodium tungsten bronze phase was formed. Electrochemical impedance measurements of the electrodes operated at 973K in humidified H_2 had a non-ohmic impedance of $1.1 \Omega\text{cm}^2$. Upon the addition of 1wt% Pd, the non-ohmic impedance improved to $0.5 \Omega\text{cm}^2$. The good electrochemical performance and the high electronic conductivity of Na_xWO_3 -YSZ show that it is a potential SOFC anode material that can be operated at intermediate SOFC operating temperatures.

Structure Property Relationships of Supported Pt/3d Bimetallic Catalysts

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Bimetallic catalysts are of great interest because they often display properties that differ from either of their parent metals. Previous studies on the Ni/Pt(111) bimetallic system have shown that the location of Ni atoms in the Pt(111) surface has a strong influence on the electronic and chemical properties of the surface [1]. The bimetallic surface consisting of a monolayer of Ni on top of bulk Pt(111), designated Ni–Pt–Pt(111), binds hydrogen and alkenes much more strongly than either parent metal, resulting in decreased hydrogenation activity. In contrast the surface consisting of a monolayer of Ni atoms in the subsurface region designated as Pt–Ni–Pt(111), has been shown to weaken metal-hydrogen bonds in comparison to Ni–Pt–Pt(111) or either parent metal surface. The resulting abundance of weakly bound hydrogen and alkenes on the Pt–Ni–Pt(111) surface increases its activity for novel low temperature hydrogenation pathways [2, 3].

The objective of current study is to extend previous investigations of Pt/Ni on single crystal surfaces to supported catalysts in an attempt to bridge the materials gap. Both monometallic and bimetallic catalysts were synthesized on γ -Al₂O₃ via incipient wetness. Two series of bimetallic catalysts were synthesized in order to study the effects of Pt:Ni metal atomic ratio and impregnation sequence. Benzene and 1,3-butadiene hydrogenations were used as probe reactions and it was found that for both hydrogenations the bimetallic catalysts were more active than either monometallic catalyst. Fourier transform infrared (FTIR) spectroscopy was used to characterize CO chemisorption, which showed that the bimetallic catalysts bound CO in a different manner than either monometallic catalyst. The results of both the hydrogenation and chemisorption experiments suggested that there was a bimetallic effect, which justified further physical characterization using extended X-ray absorption fine structure (EXAFS) and transmission electron microscopy (TEM). EXAFS of the Pt L_{III} edge confirmed the presence of bimetallic Pt-Ni interactions, and the magnitude of these interactions was found to correlate with the observed trends in hydrogenation activities for the two series of bimetallic catalysts. TEM imaging was performed in high angle annular dark field (HAADF) mode, and the resulting images showed a majority of particles with diameters on the order of 1 to 2 nm. In addition, several Pt/3d bimetallic catalysts (Pt/Co, Pt/Ni, and Pt/Cu) were synthesized, characterized, and tested for hydrogenation activity. The hydrogenation activity was observed to correlate well with hydrogen and 1,3-butadiene binding energies calculated from theory.

These catalysts are also expected to perform well for reforming chemistry based on previous surface science studies in which the Ni–Pt–Pt(111) showed increased reforming activity over either monometallic surface as well as the Pt–Ni–Pt(111) surface [4]. Experiments to test these catalysts are currently in progress.

- [1] Kitchin, J.R., Khan, N.A., Barteau, M.A., Chen, J.G., Yakshinskiy, B., and Madey, T.E., *Surf. Sci.* 544, 295 (2003).
- [2] Hwu, H.H., Eng, J., and Chen, J.G., *J. Am. Chem. Soc.* 124, 702 (2002).
- [3] Chen, J.G., Menning, C.A., and Zellner, M.B., *Surf. Sci. Rep.* (2008).
- [4] Skoplyak, O., Barteau, M. A., Chen, J.G., *J. Phys. Chem. B* 110, 1686 (2006)

The Influence of Cobalt Loading on Oxidation of Supported Catalysts for Fischer-Tropsch Synthesis

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High demand for petroleum and rising costs of the crude oil feedstock have spurred a great deal of interest in the conversion of natural gas into liquid fuels via the gas-to-liquids (GTL) process. As a key step in the process, the Fischer-Tropsch synthesis (FTS) converts syngas (CO and H₂) to produce hydrocarbons. Cobalt catalysts are preferentially used in the low temperature Fischer-Tropsch synthesis because of their high activity, paraffin selectivity and relative resistance to oxidation [1,2]. However, studies have shown that dispersed cobalt on catalyst supports tends to deactivate into stable cobalt (II) oxide or irreducible cobalt support mixed compounds [3-5]. This decrease of active cobalt metal sites has primarily been attributed to oxidation by water. Thermodynamic data for bulk cobalt suggests otherwise, as oxidation of cobalt at FTS operating conditions would not be expected. Coulometric titration was used to examine redox characteristics of cobalt supported on mesoporous silica and zirconia. Experimental data of cobalt constrained by pore size in a mesoporous silica support suggests that oxidation energetics of Co nanoparticles are nearly identical to those of bulk particles. However, thermodynamic measurements of cobalt supported on zirconia revealed that low cobalt loading samples do appear to undergo partial oxidation at FTS conditions, unlike bulk cobalt and higher cobalt loading samples. Further experiments have suggested that the apparent distinction in redox properties is likely due to support interactions of cobalt oxide with the zirconia rather than an inherent difference in thermodynamics of bulk and dispersed cobalt.

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4. Dalai, A. K. and Davis, B. H., *Appl. Catal., A*, 348, 1 (2008).
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Ab initio Investigation of Stable Surface Phases and Active Sites for Hydrocarbon Combustion on Palladium-Ceria

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Ceria (CeO_2) offers unique properties as a heterogeneous catalyst or catalyst support due to its ability to store and release oxygen, or more generally to readily transition between oxidation states. For Pd/ CeO_2 systems, strong interactions between Pd and ceria influence the stable surface structure and catalytic activity. This work utilizes ab initio thermodynamics evaluated with density functional theory (DFT+U) methods to evaluate the stability of Pd atoms and PdO_x species, in varying configurations on CeO_2 (111), (110), and (100) single crystal surfaces. The ceria support shifts the transition between formal Pd oxidation states (Pd⁰, Pd²⁺, Pd⁴⁺) relative to bulk palladium, and stabilizes certain oxidized palladium species on each surface. Over specific oxygen partial pressure and temperature ranges, palladium incorporation to form a mixed surface oxide is thermodynamically favorable versus other single Pd atom states. For example, Pd atoms may incorporate into Ce fluorite lattice positions in a Pd⁴⁺ oxidation state on the CeO_2 (111) surface.

We evaluate the thermodynamics and kinetics of methane combustion over pure CeO_2 (111), single supported Pd atoms on CeO_2 (111), single incorporated atoms in CeO_2 (111), the extended Pd(111) surface, and PdO(100) to identify rate limiting steps and stable intermediates on possible surface phases present in Pd-supported ceria. Methane activation is more exothermic over the mixed Pd-ceria surface than over pure ceria, Pd metal, PdO, or supported Pd atoms, and the apparent barrier for methane oxidation is also lowest over the mixed Pd-ceria surface. Our results show that the catalytic activity of ceria-based metal oxides for methane oxidation is a function of surface reducibility, and that the rate of combustion is limited by C-H activation. The combustion rate over the surface mixed oxide of Pd-ceria is four orders of magnitude larger than over Pd metal, evidencing the unique combustion activity of noble metal-ceria mixed oxides.

Design and analysis of novel d¹⁰ Photocatalysts

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There is currently a tremendous focus on the development of renewable energy sources and pollution abatement. Photocatalysis involving visible light i.e., the energy of the sun is considered a plausible technology to reduce the impact of these problems. The photocatalyst (semiconductor) utilized for the majority of applications is TiO₂ (d⁰) because it is stable, non-toxic and inexpensive. The major drawback of TiO₂ is that it has limited visible light absorption capability. To offset this, we have developed multiple photocatalysts which show activities in visible light by either anion (N) or cation doping (Sn²⁺) with d¹⁰ mixed metal oxides. One such photocatalyst is zinc gallium oxy-nitride (ZGON)^{1,2} with the spinel crystal structure which show enhanced photocatalytic efficiencies to the degradation of organics in visible light than the precursor zinc gallate or P25 TiO₂. These novel photocatalysts were synthesized from sol-gel derived zinc gallium oxide precursors upon nitridation in ammonia from 550°C to 650°C. Interestingly, the spinels synthesized at 650°C show the maximum activity for degradation of cresol, which we believe could be from lower oxygen vacancies. The reduction in the band gap for the spinel oxy-nitrides is associated with the mixing of N 2p orbitals with O 2p orbitals in the valence band. Our other approach involved the introduction of Sn 5s orbitals which also leads to mesoporous photocatalysts with high surface areas than the ZGONs (250 m²/g compared with < 40 m²/g). These novel materials also show activities in visible light and the electronic and material properties are investigated using multiple techniques. The protocols developed by us opens different avenues for the synthesis of d¹⁰ semiconductors possessing the spinel crystal structure and with band gaps engineered to the visible region with potential applications for both opto-electronics and photocatalytic fields.

Tungsten Monocarbide (WC) and Surface-Modified WC Catalysts for Solar Fuel Applications

Yannick Kimmel

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Photoelectrochemical cell (PEC) devices offer a unique solution to storing solar energy. A PEC device uses a semiconducting photo-anode to drive an electrochemical reaction to evolve oxygen at the anode and reduce a chemical species into fuel, such as hydrogen, at the cathode. Almost all hydrogen is produced from fossil fuels^[1]; the use of hydrogen producing PEC devices could lead to the development of a hydrogen based economy. The most active catalysts for evolving hydrogen are the platinum group metals, but Pt is too expensive and scarce for large scale use^[2]. Pt and tungsten monocarbide (WC) have been shown to have similar bulk electronic properties^[3], and tungsten is more than three orders of magnitude less expensive and more abundant than Pt. A shift in energy of the surface of WC compared to the Pt surface prevents WC from being as active as Pt for hydrogen evolution. The modification of the surface of WC greatly influences the catalytic properties of WC, while retaining the less costly bulk properties of WC. This work studies the effect of modification of WC with surface Pt and carbon on the electrocatalytic activity.

WC with various amounts of surface carbon was synthesized by carbonizing tungsten foil under an atmosphere of methane and hydrogen. Pt was deposited onto WC foils by thermal evaporation under high vacuum conditions. The hydrogen evolution activity was tested by performing a linear sweep voltammogram (LSV) of the foils in an acidic solution, and the stability of the hydrogen evolution activity was tested by performing chronopotentiometric (CP) measurements for two hours that mimicked a PEC device operation. X-ray photoelectron spectroscopy and X-ray diffraction were used to identify and quantify the foils before and after electrochemical testing. The results show that the hydrogen evolution activity of WC decreases with increasing amounts of surface carbon. The activity of WC modified with Pt was shown to have activity approaching that of bulk Pt; however, surface carbon on WC was found to have a detrimental effect on the long-term stability of the Pt modified WC catalysts. The strong stability of Pt on WC compared to Pt on carbon under hydrogen evolution conditions agree with previous work showing the similarities between WC and Pt.

^[1] US DOE Hydrogen Program fact sheet.

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Kinetics of oxygenate reforming on Pt based catalysts

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There has been increasing interest in the utilization of biomass for renewable energy and chemical production. Biomass, which is made up of oxygenated hydrocarbon building blocks, can be more efficiently utilized for chemical and energy production through the use of small-scale catalytic reforming technologies. Small-scale reactors can increase localization of synthesis gas production and increase reaction rates over current large-scale and enzymatic technologies. Distributed synthesis gas will allow for local production of methanol, ammonia, liquid fuels (Fischer-Tropsch process) and hydrogen for fuel cell applications. Recent technological successes in catalytic reforming of biomass derived oxygenates have shown high reaction rates and high product selectivity towards hydrogen for smaller oxygenates such as methanol, ethylene glycol and glycerol. Future improvements and extensions of this technology to larger oxygenates will require rational design for reactor and catalyst optimization.

Microkinetic models provide necessary insights into surface chemistry that are useful for reactor design and catalyst optimization. The focus of this study is the development of a thermodynamically consistent microkinetic model that describes the detailed mechanisms of thermal decomposition and reforming of ethylene glycol on a Pt(111) surface. A hierarchical methodology was implemented for refinement of sensitive kinetic parameters via DFT and allows for the inclusion of adsorbate-adsorbate interactions for abundant surface species. The surface mechanism describing oxygenate chemistry on Pt(111) includes over 100 reversible elementary reactions of the following classifications: adsorption/desorption, hydrogen extraction, carbon-carbon bond cleavage, hydrogen oxidation, carbon monoxide oxidation, hydrogen and carbon monoxide coupling reactions via the carboxyl intermediate, and oxidative dehydrogenation. Sensitivity analysis on rate constants shows that early dehydrogenation reactions are kinetically important.

Additionally, previous experimental research has shown that Ni/Pt bimetallic catalysts have increased activity toward oxygenate reforming compared to that of the parent metals. This work also explores fundamental descriptors for catalytic activity which explain the increased activity of the Ni/Pt bimetallic catalyst, and offers insight into future catalyst design for oxygenate reforming.

This poster will focus on key model results and interpretation to reactor design applications and extensions of the model to other chemistry sets. A key focus will be on the mechanistic differences of the reforming of ethylene glycol on platinum compared to the reforming of ethylene glycol on the Ni/Pt bimetallic catalyst.

First Principles Design of Electrocatalysts for Direct Borohydride Oxidation

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Direct Borohydride Fuel Cells (DBFCs) have the potential to generate high power densities for use in portable power applications. Current applications are limited, in part, by the lack of an effective anode electrocatalyst. Though a number of pure metals have been tested as anodes, no previously tested electrocatalyst demonstrates both the required activity and selectivity. Overpotentials on Au anodes limit the overall cell efficiency to low values and little is known of the elementary electrocatalytic mechanisms. Platinum demonstrates a sizable current at lower overpotentials, but non-selective hydrolysis reactions compete with direct oxidation. Difficulties associated with experimental characterization of elementary kinetics for the 8 electron reaction motivate our application of density functional theory (DFT) methods. DFT calculations examine the mechanism of borohydride electro-oxidation over Au(111) and Pt(111) surfaces. Stable surface intermediates and limiting steps are identified. Key energetic parameters are identified and evaluated for pure and bimetallic electrocatalysts. Au-Cu alloys are determined from DFT calculations to be encouraging for improved performance, and initial experimental testing will be discussed.

Photoreforming of Glycerol and Biomass Using Metal-Loaded Titanium Dioxide

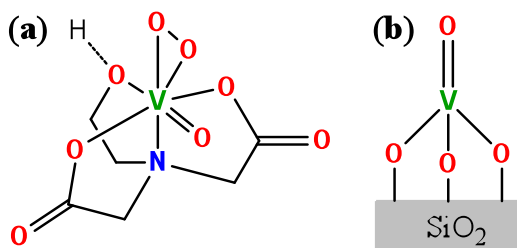
Kevin Brodwater
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Photocatalytic reaction of aqueous glycerol and crude glycerol solutions in the presence of a metal-loaded titanium dioxide catalyst under solar-simulating lights is being investigated. Previous researchers used noble metal catalysts, however, this work focuses on copper catalyst. Preliminary results confirm that hydrogen and carbon dioxide are produced in the gas phase. The reaction has a high initial selectivity for hydrogen, however the selectivity decreases as the reaction progresses. Catalyst metal loading, temperature, and pH effects are tested. Gas phase and liquid phase analysis are performed to determine the products. Among the liquid phase products, methanol and acetic acid have been successfully identified. Various biomass components will be screened to determine whether they are candidate substrates for hydrogen generation from this photoreaction.

Presence of Surface Vanadium Peroxo-oxo Umbrella Structures in Supported Vanadium Oxide Catalysts: Fact or Fiction?

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(a) $K[V(O)(O_2)(heida)]$ mimic of vanadium bromoperoxidase and (b) surface structure of vanadia supported on silica

Recent debates over the active site structure of supported vanadia/silica catalysts have suggested the existence of a surface vanadium peroxo-oxo “umbrella” structure. This study definitively demonstrates with Raman and UV-vis spectroscopy that the surface vanadia peroxo-oxo umbrella-like structure is not present for both hydrated and dehydrated supported vanadia catalysts such as supported vanadia on silica. The vanadia peroxo-oxo umbrella structure, however, is present in vanadium haloperoxidases (VHPOs) enzymes and metal-organic compounds designed to mimic VHPOs.

Synthesis and Characterization of Platinum-Modified Tungsten Carbide Using Atomic Layer Deposition

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Pt-modified tungsten carbide (WC) has been demonstrated to show increased methanol electro-oxidation activity for direct methanol fuel cells (DMFC).[1],[2] One proposed method of producing Pt nanoparticles is to use atomic layer deposition (ALD), a method that is normally used in the semiconductor industry to produce thin films with sub-monolayer control. ALD consists of a series of gas-solid interactions that are cycled over and over again until a specified film thickness is achieved. However, when few cycles are used nanoparticles can be produced rather than full films.[3]

Planar WC thin films are first used as model surfaces for Pt deposition using ALD to produce particles with the intention of later making powder catalysts using the same deposition method. The WC films were produced using physical vapor deposition (PVD), followed by a carburization step. X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) show that the films are phase pure WC, while scanning electron microscopy (SEM) shows that the WC films have large grains and a rough surface. Pt ALD was demonstrated on both clean WC, which was sputtered with Ar ions to remove W-oxides and carbonaceous carbon, and passivated WC, which contains the surface contaminants. These samples were then characterized using electrochemical methods (cyclic voltammetry and chronoamperometry) to determine the active surface area as well as methanol oxidation activity. XPS and SEM were also used to further characterize the composition and morphology of the film surfaces.

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Systematic Studies of the Cathode-Electrolyte Interface for More Active and Stable Solid Oxide Fuel Cell Electrodes

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Solid oxide fuel cells (SOFCs) are ceramic energy conversion systems that are attractive due to their high efficiency, fuel flexibility, and the possibility to operate with zero local emissions. However, the wider use of SOFCs is held back by high material costs and long-term durability issues. Lowering the operating temperature of SOFCs to 600 C-800 C may help to solve degradation problems, as electrochemical degradation rates decrease exponentially with temperature. Additionally, lower operating temperatures allows for a number of cheaper materials (e.g. stainless steel) to be used as cell construction and current collection materials.

SOFC performance at 600 C-800 C is generally governed by slow oxygen reduction reaction kinetics on the cathode (air electrode) side of the cell. Perovskite materials, such as strontium-doped lanthanum ferrite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$, LSF) and lanthanum cobaltite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, LSCo) can provide outstanding performance for fuel cell cathodes, especially if low-temperature processing methods, such as infiltration, are used. However, the performance degrades significantly over time. In this study, the two main causes of degradation are identified and addressed (Fig. 1).

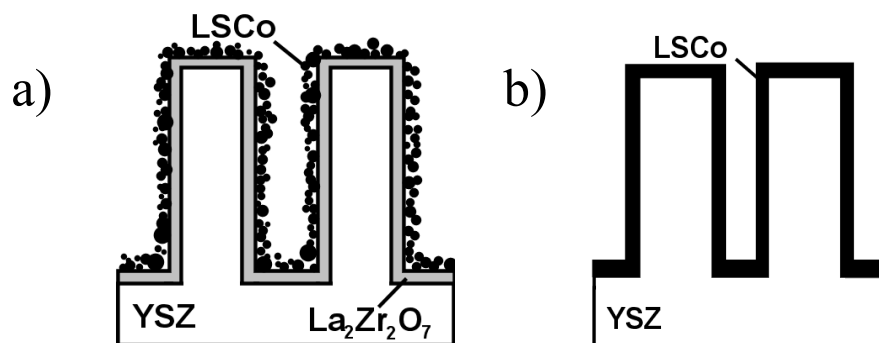


Figure 1. Main causes of degradation in SOFC cathodes: a) solid state reaction between the cathode and the electrolyte, b) coarsening of the cathode material.

In particular, the extent of degradation in LSCo-YSZ cathodes related to the solid-state reaction between LSCo and YSZ was significantly reduced by the introduction of a thin samaria-doped ceria interlayer prepared by infiltration.

Secondly, the degradation due to the coarsening in LSF-YSZ cathodes was addressed by increasing the surface area of the underlying YSZ porous matrix by HF treatment.

Finally, a systematic study investigating the effect of the ionic conductivity of the electrolyte on composite cathode performance was carried out. The results of the study agree well with a model developed in our laboratory.

Glucose Reformation on Pt (111) and Pt Bimetallic Catalysts for the Production of Hydrogen

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The environmentally motivated shift towards a carbon neutral, sustainable hydrogen economy has spotlighted the need for advances in biomass reforming science. Catalytic production of hydrogen from simple, model oxygenates has been demonstrated using platinum bimetallics; however, the catalytic conversion of complex biomass feed molecules is not well understood, therefore there is a distinct need to elucidate the fundamental science for oxygenate bond scission. An approach for bond scission characterization of the cellulosic monomer Glucose on Pt catalysts is presented.

Characterization difficulties arising from the cellulosic sugars' low vapor pressures are addressed and successful dosing of Glucose onto a Pt(111) crystal is demonstrated in ultra high vacuum. Also, temperature programmed desorption (TPD) results are presented for low and high Glucose coverages on clean Pt(111), with low coverages resulting in complete decomposition into H₂, CO, CO₂ and CH₃OH.

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Ethanol Reactivity Studies on Supported Cobalt Catalyst

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As traditional fossil fuels become more difficult and expensive to mine and as the public looks towards more environmentally friendly energy sources for the future, the need to explore alternative sources of power becomes critical. Ethanol is one fuel that can be produced from numerous biomass feedstocks via fermentation and it is not toxic. Co/ZnO catalysts exhibit high selectivity for the steam reforming of ethanol (SRE) at low temperatures (<700 K) and are highly resistant towards coking, although the lack of knowledge regarding the reaction mechanism and intermediate pathways has prevented further optimization. The ZnO support is thought to stabilize the active form of cobalt and help to minimize carbon buildup. Previous studies using model catalysts of vapor deposited Co on a ZnO (0001) single crystal have provided details on the structure and oxidation state of the Co as a function of operating temperature; hence, using this information and through the use of Temperature Programmed Desorption (TPD), we are trying to identify the reaction pathway of ethanol on different sites available on these catalysts, namely, ZnO, Co⁰, CoO_x, and interface of Co/ZnO.

Oxidative dehydrogenation of ethanol to acetaldehyde and ethyl acetate by graphite nanofibers

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Three types of graphite nanofibers (GNFs), with varying orientations of the graphene sheets (herringbone, platelet, and ribbon), were used as catalysts for the gas-phase oxidative dehydrogenation of ethanol to acetaldehyde and ethyl acetate in the presence of oxygen. The effects of fiber type, temperature, oxygen concentration, and ethanol concentration on conversion and product ratio were explored. When identical processing conditions were employed, herringbone fibers produced higher conversions of ethanol compared to platelet and ribbon fibers, which yielded similar results to one another. Altering equilibrium conditions by increasing oxygen concentration tended to increase conversion as well as increase the percentage of acetaldehyde produced. Adjusting oxygen concentration had a more significant affect on the platelet and ribbon fibers. Temperature also altered the conversion and product ratios as expected. It is believed that the oxygen groups terminating the prismatic edge sites of the graphene planes are responsible for the catalytic activity in oxidative dehydrogenation reactions such as the one explored here.

Molten-Metal Anodes for Solid Oxide Fuel Cells

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Molten In, Pb, and Sb were examined as anodes in solid oxide fuel cells (SOFC) that operate between 973 and 1173 K. The results for these metals were compared with those reported previously for molten Sn electrodes. Cells were operated under “battery” conditions, with dry He or N₂ flow in the anode compartment, to characterize the electrochemical oxidation of the metals at the yttria-stabilized zirconia (YSZ)-electrolyte interface. In most cases, the open-circuit voltages (OCVs) were close to that based on equilibrium between the metals and their oxides. With Sn and In, the cell impedances increased dramatically at all temperatures after drawing current due to formation of insulating, oxide barriers at the electrolyte interface. Similar results were observed for Pb at 973 and 1073 K, but the impedance remained low even after PbO formation at 1173 K because this is above the melting temperature of PbO. Similarly, the impedances of molten Sb electrodes at 973 K were low and unaffected by current flow because of the low melting temperature of Sb₂O₃. The potential of using molten-metal electrodes for direct-carbon fuel cells and for energy-storage systems is discussed.

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Fundamental Surface Structure-Photoactivity Relationships of Advanced Photocatalysts

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Numerous photocatalytic materials (i.e. TaON, GaN:ZnO, NaTaO₃:La) have been shown to catalyze the water splitting reaction. The activity of these bulk materials is greatly enhanced by loading precious metal cocatalysts (NiO, RuO₂) onto the surface. The molecular and electronic structures of these catalysts were characterized using optical spectroscopic characterization methods (Raman, IR, and UV-vis). LEIS spectroscopy will be used to determine the surface composition of the bulk photocatalytic material and the effect of loading a cocatalyst onto the material. Steady state attenuated total reflection (ATR) FT-IR will be used to determine the nature of surface species during UV irradiation to elucidate further insight into the fundamental structure-photoactivity of these catalytic materials.

Theoretical and Experimental Studies of Optimal Catalysts for Hydrogen Production from Ammonia Decomposition

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The ammonia decomposition reaction has recently received increased attention due to the possibility of ammonia being used as a hydrogen storage medium in a possible hydrogen economy. We have explored this decomposition reaction through multiscale microkinetic modeling for a number of transition metal catalysts, including Cu, Pt, Ir, Ru, Pd, Rh, Co, Ni, Re, W, and Mo, to better understand the reaction mechanism. An understanding of the reaction mechanism and electronic properties of these metals has given insight into how to tailor catalysts to improve catalytic activity for this reaction.

The mechanism consists of 12 elementary reaction steps and 5 surface species, namely N, H, NH, NH₂, and NH₃. For many of the metals, a large portion of the surface is covered by adsorbates. For these metals, repulsive adsorbate-adsorbate interactions were expected to change the binding energies of the surface species, thereby changing the elementary reaction activation barriers and modifying the catalytic activity [1]. Coverage dependant atomic heats of chemisorption were calculated through DFT using the Vienna Ab-initio Simulation Package (VASP) for the various transition metal catalysts. Coverage dependant molecular binding energies were calculated using a method based on scaling relationships published by Abild-Pederson et al. [2] and activation barriers were calculated through the bond-order conservation (BOC) method [3].

Inclusion of the interaction parameters to the models resulted in reduced nitrogen coverages and a peak shift in the volcano curve. The conversions were plotted against the characteristic nitrogen heat of chemisorption for each metal, which was found to be an adequate descriptor for this reaction. The volcano curve of the conversions calculated through the microkinetic models are in good agreement with experimental data of single metal catalysts by Ganley and coworkers [4]. The maximum activity was found at a nitrogen heat of chemisorption of approximately 130 kcal/mol.

A DFT study of nitrogen binding energies on Pt-3d bimetallic surfaces showed a binding energy of 131 kcal/mol on the Ni-Pt-Pt surface, indicating that it could be a potentially active catalyst; therefore surface science experiments were performed to assess the microkinetic model and DFT results. The Ni-Pt-Pt surface was found to be more active at decomposing ammonia at low temperatures and desorbed nitrogen at lower temperatures than a Ru(0001) surface [5], currently the most active single metal catalyst.

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Estimating number of surface active sites of redox catalysts using transient kinetic measurements

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Using quantitative monitoring of anaerobic reduction of a redox catalyst, number of active surface sites can be estimated. A catalyst was pre-oxidized in air, flushed with helium and then subjected to reduction by step increase in reducing agent's concentration. Reducing agents used were methanol and carbon monoxide. By integrating oxidation products, number of active surface sites was determined. In case of bulk compounds, surface and bulk reduction can be distinguished by performing the experiment at low temperatures where oxygen mobility in a lattice is essentially zero. Transient kinetic measurements were performed over series of bulk vanadates and sub-monolayer vanadia supported on silica, titania and alumina. Number of active surface sites of bulk vanadates was close to values from literature determined using other techniques. On supported vanadia, number of active sites corresponded to amount of vanadia loaded, except in silica case number of sites was significantly less. Reactivity of catalysts during aerobic steady state and anaerobic transient oxidation of methanol was found to be similar.

Selective Oxidation of Propane to Acrylic Acid over Single Phase M1 MoVTaNbO_x Catalysts

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Advisors: Prof. Mark A. Barteau and Prof. Douglas J. Buttrely

The MoVTaNbO_x mixed metal oxides developed by Mitsubishi Chemical Corporation are currently the most efficient catalytic system for selective ammoxidation and oxidation of propane to acrylonitrile and acrylic acid, respectively ^[1]. Up to 62% yields of acrylonitrile and 50% yields of acrylic acid have been reported ^[2]. Two phases have been identified as the effective components: the orthorhombic M1 and pseudo-hexagonal M2. A biphasic M1/M2 mixture has been reported to give better long-term catalytic performance than either pure phase, but M1 is generally believed to be the key factor for propane activation ^[3].

The slurry method can be used for catalyst synthesis, but simultaneous formation of M1 and M2 is often encountered. In this work, we focus on the investigation of single phase M1 catalyst in order to better understand the true crystal chemistry and intrinsic structure-property relationships. For the synthesis part, several parameters have been studied and it is found that besides M1 and M2, TeMo₅O₁₆, V-Mo₅O₁₄, and Mo-V₂O₅ are often formed as impurity phases. The formation of TeMo₅O₁₆ is favored at relatively high slurry pH, while the formation of V-Mo₅O₁₄ is significantly affected by the heating rate of calcination. The formation of this Te-free phase can be related to the Te loss during the heat treatment. The Mo-V₂O₅ phase is usually formed when V is in excess and can be removed by washing with 30% hydrogen peroxide solution. In general, highly pure M1 can be produced by gently heating the precursor during calcination and then washing the resulting product in concentrated hydrogen peroxide.

A fixed-bed reactor is used to evaluate the catalytic performance of single phase M1 catalyst. It is found that M1 phase alone is capable of converting propane to acrylic acid at fair yields. Introduction of steam is not necessary for better acrylic acid selectivity but higher conversion can be obtained with an excess of water. In addition to acrylic acid, CO_x, acetic acid, and acetone are major byproducts over the temperature range tested. Water-rich conditions also increased the selectivity to acetic acid significantly, which indicates that acetic acid might be primarily formed through acetone decomposition. The formation of acetone is highly favored at lower temperatures as compared to acids, even though the conversion is low. Product distribution analysis suggests that propylene is likely to be the first dominant intermediate although it is too reactive at high temperatures. In propane oxidation to acrylic acid, dehydrogenation occurs prior to terminal oxygen insertion. These results agree well with the reaction networks proposed earlier ^[4, 5].

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Oxidation resistant boron substituted carbons for high surface area catalyst supports

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In this work, the influence of substitutional boron on carbon oxidation behavior is studied. High concentration of boron in carbon lattice changes the carbon micro-structure, physical properties and oxidation behavior. Boron oxide blocks active carbon sites and inhibits oxidation of carbon. This leads to a new approach to develop novel high surface area, high porosity and reducible carbon catalyst supports. Boron substituted carbon was prepared by CVD reaction of benzene and BCl_3 to form BC_x . Then, anti-oxidative behavior of boron substituted carbon was investigated by coating carbon fibers and activated carbon spheres with BC_x .

Synthesis and characterization of shape selective platinum embedded microporous carbon sphere catalysts

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The goal in this study is to synthesize and use carbon microspheres within which are embedded even smaller platinum nanoparticles as more efficient shape selective catalyst for liquid phase hydrogenation reactions. Previously in our group, platinum particles embedded in a molecular sieving carbon support were prepared and shape selectivity was demonstrated using different alkenes hydrogenation rates. However, the activity of these catalysts was limited by their relatively low effectiveness arising from the poor accessibility of active sites embedded deeply within the carbon. Diffusion lengths and resistance were so high that much of the platinum was simply uninvolved in reaction. In this study, to increase the activity of the catalyst and to maintain the shape selectivity, platinum is embedded within carefully prepared carbon microspheres that were synthesized in a multistep process. Catalyst particles with the average size of 400 nm were synthesized by pyrolysis of preformed platinum/polyfurfuryl alcohol spheres. Platinum preformed particles were sequestered within the carbon support by adding them during the polymerization step. The activity of the synthesized particles was demonstrated using liquid phase hexene hydrogenation reaction.

High Temperature Decomposition and Reactivity of Bronsted Acid Sites in Zeolites

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The thermal decomposition of Bronsted acid sites (BAS) has been proposed to proceed through a dehydration process. The aluminum sites formed after dehydroxilation show distinct IR vibration due to CO adsorption in the range of 2230-2220 cm^{-1} compared with 2175-2168 cm^{-1} for BAS. However, the structure of these sites is not unambiguity known. The dehydroxilation of BAS is studied using XRD, MS-TPD, FTIR and XAFS using Ga-beta and Ga-ZSM5. The MS-TPD showed that hydrogen in addition to water is produced. The XANES and EXAFS reveal that Ga is present only in tetrahedral and octahedral coordination. The dehydrogenation pathway of BAS leaves unpaired electron on the oxygen surrounding the Ga atoms. To confirm the presence of such electrons, the dehydroxilated samples are dosed with hydrogen and monitored with FTIR. Partial recovery of BAS is observed. Two distinct sites with different reactivities are observed when propane is reacted over the dehydroxylated sites.

Reaction Mechanisms of Glycerol Conversion to Value-Added Chemical Products

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The threat of peak oil and climate change has contributed to rapidly increasing production of biodiesel both in the US and abroad. The glycerol produced as a byproduct requires extensive purification for use in glycerol-consuming industries such as foods, cosmetics, and pharmaceuticals. It is often more economical to simply burn it.¹ Process simulations have shown the profitability of biodiesel production is significantly impacted by the value of glycerol which has ironically declined in recent years as a result of the excess supply produced concomitantly with biodiesel.² Processes that convert glycerol to more valuable chemicals therefore have twofold benefit in providing commodity chemicals from renewable feedstock while encouraging production of biofuels.

One particular upgrade of interest is the conversion of glycerol to acrolein, used in production of acrylic acid, methionine, and various polymers and detergents. Acrolein is currently produced from propylene, so use of glycerol as a feedstock will further reduce dependence of fossil fuels. Glycerol forms acrolein and water via two acid-catalyzed dehydration reactions. Other byproducts include olefins, acetone, and acetaldehyde. Zeolites and other catalysts have been shown experimentally to have selectivity towards acrolein production in excess of 60%.³

In this study, the Gaussian quantum chemistry package was used to calculate energies of intermediates and transition states in the acrolein conversion reaction using Density Functional Theory (DFT). The reaction was studied both in the aqueous solution phase and within the cage of zeolite HZSM-5. Solution phase results predict an activation energy of 37 kcal/mol for the first dehydration and 35 kcal/mol for the second when catalyzed with HCl. Zeolite-catalyzed results predict an activation energy of 39 kcal/mol for the initial dehydration with substantially lower barriers in subsequent reaction steps. Further study will be in examining mechanisms for byproduct formation and in tuning zeolite structure and composition to obtain optimal catalytic properties.

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Structural Sensitivity of the Water Gas Shift Reaction in Platinum Surfaces

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In view of recent economical and environmental pressures, the necessity of a paradigm shift in the production and utilization of energy has emerged. In this shift, hydrogen is envisioned to play a central role, being regarded as a potential “fuel of the future”. Hydrogen can be produced via the water-gas shift (WGS) reaction taking place during the catalytic reforming of oxygenated hydrocarbons derived from biomass. Latest research focuses on the use of precious metals, such as platinum and gold, as catalysts for WGS, and several studies have elucidated the underlying reaction mechanism. However, the contribution of different site types, namely steps and terraces, on the overall reaction rate is an open question and it remains unclear how structure sensitive is the WGS reaction.

The present work addresses these questions using a multiscale modeling approach that integrates density functional theory (DFT) calculations and kinetic Monte Carlo (KMC) simulation. Using DFT we calculate the reaction barriers for the elementary steps of the WGS mechanism occurring at the two different site types, steps or terraces. These elementary steps include adsorption-desorption events, water and hydroxyl decomposition, and the formation of carboxyl and formate intermediates. We subsequently incorporate the calculated values into a KMC framework, and perform simulations for different step-site densities. For an extended temperature range we show that the reaction rates of stepped surfaces depend on step-site density. Our results indicate that the WGS reaction is structure sensitive and that the steps are the active sites for this chemistry.