

**Catalysis Club of Philadelphia's
Graduate Student Poster Competition
March 18, 2010**

1. In Situ Time Resolved Spectroscopic Studies of Metal Oxide Photocatalysts for Water Splitting

Charles A. Roberts¹, Alexander A. Puretzky², Somphonh Peter Phivilay¹, and Israel E. Wachs¹
(1) Department of Chemical Engineering, Lehigh University and (2) Nanomaterials Synthesis and Properties Group Materials Science & Technology Division, Oak Ridge National Laboratory

2. Fundamental Surface Structure-Photoactivity Relationships of Advanced Photocatalysts

Somphonh Peter Phivilay and Israel E. Wachs, Department of Chemical Engineering, Lehigh University

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8. Scale-out of Microreactor Stacks for Syngas Production from Methane

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9. Molten-Metal Electrodes for Solid Oxide Fuel Cells

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

10. Characterization of the fractal geometry of SBA-15, and its use as a vanadia oxide support for the partial oxidation of methanol

Tom Baldassare and Michael Smith, Department of Chemical Engineering, Villanova University

11. Experimental and theoretical study of glycolaldehyde activity on Ni/Pt(111) bimetallic system

Weiting Yu, Mark A. Barteau, Jingguang G. Chen, Center for Catalytic Science and Technology (CCST), Department of Chemical Engineering, University of Delaware

12. Structure Property Relationships of Supported Pt/Ni Bimetallic Catalysts: Correlating the Extent of Pt-Ni Bimetallic Bond Formation with Low-Temperature Hydrogenation Activity

W. Lonergan, D. G. Vlachos, J. G. Chen, Department of Chemical Engineering, University of Delaware

13. Reverse micelle synthesis and characterization of supported bimetallic catalysts

Beth Cheney, Jingguang Chen, Jochen Lauterbach, Chemical Engineering Department, University of Delaware

14. Doped Ceria Films on YSZ Prepared by Infiltration as Reaction Barriers in SOFCs

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

15. Analysis of Ga Coordination Environment in Novel Spinel Zinc Gallium Oxy-Nitride Semiconductors

Bharat Boppana, Raul Lobo, University of Delaware

16. Stability and Performance of SOFC Cathodes Prepared by Infiltration

Fred Bidrawn, J. M. Vohs, R.J. Gorte, Department of Chemical and Biomolecular Engineering, University of Pennsylvania

17. Raman, UV-Vis and IR-ATR Study of Vanadium Haloperoxidase Functional Mimics

Julie E. Molinari and Israel E. Wachs, Lehigh University, Bethlehem, PA 18015 (USA)

18. A Study of the Water-Gas-Shift Reaction on Pd@CeO₂/Al₂O₃ Core-Shell Catalysts

Noah L. Wieder¹, Matteo Cargnello², Tiziano Montini², Kevin Bakhmutsky¹, Paolo Fornasiero², and Raymond J. Gorte¹, ¹ *Department of Chemical and Biomolecular Engineering, University of Pennsylvania,* ² *Chemistry Department, ICCOM-CNR, INSTM, Center of Excellence for Nanostructured Materials (CENMAT), University of Trieste*

19. Development of Structural Model of the Orthorhombic M1 Phase in the Mo-V-Te-Nb-O Catalyst by Rietveld Refinement

Xin Li, Douglas Buttrey and Mark Barteau, Catalytic Center for Science and Technology, Department of Chemical Engineering, University of Delaware

20. Studies of the active sites on supported cobalt catalysts for the steam reforming of ethanol

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

21. Microstructure-Based Design for Replacing Rh with Co in a Synergistic Catalyst for the Reduction of NO with H₂

Paul S. Dimick^a, Richard G. Herman^b, and Charles E. Lyman^c, Department of Chemical Engineering^a, Department of Chemistry^b, and Department of Materials Science and Engineering^c, Lehigh University

22. Model Based Prediction of Bimetallic Catalysts for Hydrogen Production from Ammonia Decomposition

Danielle A. Hansgen, Jinguang G. Chen, Dionisios G. Vlachos, Chemical Engineering, University of Delaware

23. Cell performance and chemical stability of La_{0.8}Sr_{0.2}Co_xFe_{1-x}O₃ (LSCF)

Lawrence Adjanto, Fred Bidrawn, J. M. Vohs, R. J. Gorte, Department of Chemical & Biomolecular Engineering, University of Pennsylvania

Post Doctoral Submissions:

PD1. Examining the Co/ZnO towards the steam reforming of ethanol using model surfaces

Matthew P. Hyman and John M. Vohs, University of Pennsylvania

PD2. A Study of Methane Tolerance in LSCM-YSZ Composite Anodes with Pt, Ni, Pd and Ceria Catalysts

Ju-Sik Kim, Vineet V. Nair, J. M. Vohs, and R. J. Gorte, Department of Chemical and Biomolecular Engineering, University of Pennsylvania

In Situ Time Resolved Spectroscopic Studies of Metal Oxide Photocatalysts for Water Splitting

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Photocatalysis involves phenomena occurring at high time resolutions under unique conditions. Studies probing these time scales under relevant *in situ* conditions will lead to improved photocatalysts. Thus, novel catalysts containing Ga₂O₃, ZnO, GaN, GaN:ZnO, GaN-RhCr, and GaN:ZnO-RhCr were dehydrated under flowing 10% O₂ at 400 °C, the last of which has been proven to be superior for the water splitting reaction under visible light irradiation.¹ Using a pulsed laser for excitation and a gated detector with picosecond time resolution, the lifetime of excited states of the samples was determined *in situ* at room temperature. The water splitting reaction's intermediate and product formation will also be monitored using ATR FT-IR during transient irradiation.

The ability to probe reactions under *in situ* conditions and with time resolutions relevant to the photo-excitation process will yield deeper insight into the reaction mechanism and ultimately allow for improved rational design of future photocatalysts for water splitting. Therefore, studies were conducted using *in-situ* photoluminescence (PL) spectroscopy to determine how the various structures present in the novel metal oxide samples affects the emission spectrum's decay characteristics. Samples were dehydrated under flowing 10% O₂ at 400 °C in order to avoid the quenching effect of water on PL emission. Spectra were *in situ* using a 76 MHz pulsed tunable laser, tuned to 400 nm excitation, and a gated Picostar detector with time resolution in picoseconds. The same dehydration procedure was used and the lifetime of excited states of the various nano-domain containing samples was determined by changing the delay time of the detector.

The results initially show several main trends. The PL spectra show that a complex interplay of the several components of the GaN:ZnO-RhCr catalyst (the most active) come together to create a catalyst with an apparent ideal decay of emission. It was found that the emission generally displays a second order decay containing a "fast" and "slow" component. The fast component is essential as it is believed to be responsible for a high turnover of available electrons, while the slow component serves as a deterrent to electron-hole pair recombination.

In situ attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectroscopy will be done using a Thermo Nicolet 8700 equipped with a Harrick Horizon ATR cell with a ZnSe crystal. Thin films of catalysts can be coated on the crystal to obtain spectra under aqueous, irradiated conditions.

(1) Kudo, A; Miseki, Y. *Chem. Soc. Rev.* **2009**, 38, 243-278.

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.

Alternative Anode Electrocatalysts for Direct Ethanol Fuel Cells

Thomas Kelly

University of Delaware, Chemical Engineering

Adviser: Jingguang Chen

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 predict the binding energies of ethanol and ethoxy on the Rh/Pt bimetallic system and on Rh/WC surfaces. By comparing the binding energy of ethanol on these surfaces, it is potentially possible to predict their activity towards ethanol decomposition. Within the Rh/Pt system, it was predicted that the surface activity would follow the trend RhPtPt(111) > Rh(111) > Pt(111) > PtRhPt(111). The overall goal of this research is an anode electrocatalyst composed of a WC bulk with a Rh monolayer deposited on the surface. As a proof of concept, the Rh/Pt bimetallic system has been studied experimentally before moving to the Rh/WC surface. Temperature-programmed desorption (TPD) was used with a Pt(111) single crystal to quantitatively determine the activity of the surfaces and their selectivity towards certain decomposition pathways. High resolution electron energy loss spectroscopy (HREELS) showed the reaction intermediates adsorbed on the crystal surface at different temperatures. TPD confirmed that the RhPtPt(111) and Rh(111) surfaces have a higher activity towards ethanol decomposition than the Pt(111) and PtRhPt(111) surfaces. HREELS showed that the reaction intermediates were the same on all four surfaces. Similar experimental and theoretical approaches are applied to investigate the Rh/WC system for ethanol electrooxidation.

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.

Controlling the Bond Scission Sequence of Methanol Decomposition as an Example of Rational Catalyst Design

Alan L. Stottlemeyer and Jinguang G. Chen

The so called "Holy Grail" of heterogeneous catalysis is a fundamental understanding of catalyzed chemical transformations which span multidimensional scales of both length and time, enabling rational catalyst design. Such an undertaking is realizable only with an atomic level understanding of bond formation and destruction with respect to intrinsic properties of the metal catalyst. In this study, we investigate the bond scission sequence of methanol on bimetallic transition metal catalysts and transition metal carbide catalysts, with the simplicity of methanol allowing us to follow the different reaction pathways both experimentally and with density functional theory (DFT) modeling. Additionally, methanol is of interest both as a hydro-gen carrier for reforming to H₂ and CO and as a fuel in direct methanol fuel cells (DMFC). In order to bridge the "materials gap" and "pressure gap" this work adopted three parallel research approaches: (1) ultra-high vacuum (UHV) studies including temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS); (2) electrochemical studies including cyclic voltammetry (CV) and chronoamperometry (CA); (3) DFT studies including thermodynamic and kinetic calculations.

The Ni/Pt bimetallic system was studied as an example for using methanol as a hydrogen source. There are two well characterized surface structures for the Ni/Pt system [1]: the surface configuration, in which the Ni atoms reside primarily on the surface of the Pt bulk, and the subsurface configuration, in which the second atomic layer is enriched in Ni atoms and the surface is enriched in Pt atoms. These configurations are denoted NiPtPt and PtNiPt, respectively. TPD studies revealed that the NiPtPt surface was more active to methanol reforming than the Pt or PtNiPt surfaces. HREELS confirmed the presence of strongly bound reaction intermediates [2], including aldehyde-like species [3], and suggested that the first decomposition step was likely O-H bond scission. Thus, the binding energies of the deprotonated reaction intermediates are likely important parameters in controlling the decomposition of methanol.

Recent studies have suggested that tungsten monocarbide (WC) may behave similarly to Pt for the electrooxidation of methanol [4, 5]. TPD was used to quantify the activity and selectivity of methanol decomposition for WC and Pt-modified WC (Pt/WC) as compared to Pt[5]. WC appeared to be more active than Pt, but C-O bond scission on WC resulted in gas phase CH₄, an undesired reaction for DMFC. When Pt was added to WC by physical vapor deposition, the CH₄ reaction pathway was eliminated, suggesting that Pt synergistically modifies WC to improve the selectivity toward C-H bond scission to produce hydrogen and CO. Additionally, TPD confirmed WC and Pt/WC to be more CO tolerant than Pt[6]. DFT calculations suggested that the bond scission sequence of CH₃OH could be controlled using monolayer coverage of Pt on WC and that the resulting mechanism was different for Pt/WC as compared to either parent surface. HREELS results verified that surface intermediates were different on Pt/WC as compared to Pt or WC.

Both studies demonstrated that the bond scission sequence of methanol can be controlled using either bimetallic or carbide catalysts. Such success was only possible using a methodology that combines both calculations to predict catalytic properties and experiments to fine-tune theoretical predictions.

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Atomic Layer Deposition of Pt on WC for Fuel Cell Applications

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The most commonly preferred method to produce heterogeneous catalysts is incipient wetness impregnation, which is favored because the procedure is straightforward and is successful in producing high surface area catalysts. However, this technique has limited control over catalyst particle size and distribution, and in order to make more effective and complex catalyst systems, such as bimetallic catalysts or core shell nanoparticles, a synthesis method that provides more control is desired. One proposed method is atomic layer deposition (ALD), a technique which 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 repeatedly until a specified film thickness is achieved; however, its use as a catalyst synthesis method has recently been explored to make uniform and well-distributed nanoparticles.

In this work, we explore the use of ALD to make Pt-WC catalysts. Pt-modified WC has previously been demonstrated to show increased activity for some electrocatalytic reactions, such as methanol oxidation. Planar WC thin films are first used as model surfaces for Pt ALD, with the intent of later making powder catalysts. Pt-WC film samples of increasing number of ALD cycles were characterized using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) for surface composition and scanning electron microscopy (SEM) to determine the surface morphology and Pt particle size. Cyclic voltammetry (CV) was also used to demonstrate that ALD Pt on WC shows improved oxygen reduction activity over Pt foil.

Copper Coordination in Cu-SSZ-13 and Cu-SSZ-16 Investigated by Variable-Temperature XRD

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Nitrogen oxides (NO_x) are a major atmospheric pollutant produced through the combustion of fossil fuels in internal combustion engines. Copper-exchanged zeolites are promising as selective catalytic reduction catalysts for the direct conversion of NO into N_2 and O_2 , and recent reports have shown the enhanced performance of Cu-CHA catalysts over other zeolite frameworks in the NO decomposition of exhaust gas streams. In the present study, Rietveld refinement of variable-temperature XRD synchrotron data obtained for Cu-SSZ-13 and Cu-SSZ-16 is used to investigate the location of copper cations in the zeolite pores and the effect of temperature on these sites and on framework stability. The XRD patterns show that the thermal stability of SSZ-13 is increased significantly when copper is exchanged into the framework compared with the acid form of the zeolite, H-SSZ-13. Cu-SSZ-13 is also more thermally stable than Cu-SSZ-16. From the refined diffraction patterns, the atomic positions of atoms, copper locations and occupancies, and thermal displacement parameters were determined as a function of temperature for both zeolites. Copper is found in the cages coordinated to three oxygen atoms of the six-membered rings. This study also shows the enhanced performance of copper exchanged small-pore zeolites towards the selective catalytic reduction of nitric oxide compared to Cu-ZSM-5 after hydrothermally treating the zeolites.

* **Fickel, D.W.**, Lobo, R.F., *Copper Location Study of Cu-SSZ-13 and Cu-SSZ-16 Variable Temperature XRD Rietveld Refinement*, J. Phys. Chem. C, DOI: 10.1021/jp9105025

The Effect of Support on Redox Properties and Methanol-Oxidation Activity of Vanadia

Catalysts

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Abstract

The effect of support composition on the catalytic properties of vanadia catalysts was studied using reaction rates of the methanol oxidation and oxygen binding energy from coulometric titration measurements on isolated monovanadates 2.5-wt% V_2O_5/ZrO_2 , 2.5-wt% V_2O_5/TiO_2 , 5-wt% V_2O_5/Al_2O_3 and bulk oxides V_2O_5 , ZrV_2O_7 , $AlVO_4$, $Mg_3(VO_4)_2$, and $CeVO_4$. Redox characterization showed that the environment surrounding the V cations can have a dramatic effect on the redox properties for bulk oxides, but the majority of sites on supported catalysts showed nearly identical properties, with ΔG of oxidation being -375 ± 25 kJ/mol at 748 K. The steady-state turnover frequencies for methanol oxidation were also similar (within a factor of 3) on all of the supports over the temperature range from 463 to 528 K.

Scale-out of Microreactor Stacks for Syngas Production from Methane

Matthew S. Mettler, George Stefanidis, and Dion G. Vlachos

Microreactor technology has become an attractive means to intensify methane-to-syngas production processes for portable power applications as well as off-shore methane steam reforming. Conventional methane steam reforming reactors are characterized by residence times on the order of seconds while syngas generation processes using microreactor technology have demonstrated reaction time scales on the order of milliseconds^[1]. This reduction in residence time is a product of shorter characteristic heat and mass transfer distances and it ultimately results in reduced equipment size. In this work, a scale-out strategy for microreactor stacks with alternating combustion and reforming channels with sub-millimeter gap size is proposed. The effect of scaling-out the stacks is then studied as a function of heat loss to the ambient.

Microreactor geometries were simulated using the computational fluid dynamics (CFD) software package Fluent®. Catalytic surface reaction rates were implemented using recently published reduced rate expressions derived from previous microkinetic models for methane combustion and steam reforming^{[2], [3]}. Using this model, microreactor stacks of several sizes with alternating combustion and reforming channels were studied under varying degrees of heat loss. The maximum heat loss coefficient of each stack size where combustion processes are sustained and the stack is autothermal was determined and used to compare the stability of the different stack sizes.

It was found that for a given set of flow rates and material properties, there is a minimum number of combustion and reforming channels below which heat losses to the ambient are too high relative to heat generation via methane combustion. Below this stack size, combustion processes are not sustained and syngas is not produced. Significant transverse thermal gradients develop as the external heat loss coefficient is increased from adiabatic to the critical value. This causes the outer and inner channels to exhibit dissimilar methane conversions in both combustion and steam reforming channels. Temperature as well as methane conversion profiles for the individual channels were studied in order to understand the mechanism of extinction. It was found that near the critical heat loss coefficient of the stack, methane conversion within the combustion channel closest to the stack edge decreases significantly while inner combustion channels remain relatively unaffected by the heat losses. It is clear that the outermost combustion channel fails first, causing the entire stack to extinguish. The final part of the work examines methods for stabilizing microstacks for various power generation applications.

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Molten-Metal Electrodes for Solid Oxide Fuel Cells

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Abstract

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 to 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 impedance increased dramatically at all temperatures after drawing current due to formation of an insulating, oxide barrier at the electrolyte interface. Similar results were observed for Pb at 973 and 1073 K, but the impedance remained low even after PbO at 1173 K because this is above the melting temperature. Similarly, the impedance of molten Sb electrodes at 973 K was 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.

Characterization of the fractal geometry of SBA-15, and its use as a vanadia oxide support for the partial oxidation of methanol

Tom Baldassare and Michael Smith, Villanova University

The reactivity and selectivity of a vanadia catalyst on a mesoporous silica support is studied using the partial oxidation of methanol to formaldehyde. SBA-15 was used as the support and synthesized using the procedure developed by Zhao et.al. [1] The calcinations of the support were also done at higher temperatures (500, 700, 850 °C) to vary the porosity of the support. Vanadia oxide catalysts were grafted on the support using a processes researched by the Gary Haller group at Yale [2] as well as a new grafting technique developed at Villanova. The fractal geometry and catalyst structure were thoroughly characterized using N₂-physisorption, X-ray diffraction, small angle X-ray scattering (SAXS), scanning electron microscopy (SEM), and X-ray fluorescence (XRF). The results of a decrease in surface area and a smoothing of the topographical surface of SBA-15 were confirmed using N₂-physisorption. The partial oxidation experiments performed have shown greater catalytic performance when compared to incipient wetness techniques, as well as conversion and selectivity differences due to the changes made to the support porosity.

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Experimental and theoretical study of glycolaldehyde activity on Ni/Pt(111) bimetallic system

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Biomass derived molecule is a promising class of alternative energy to fossil fuels because of its advantages of widely available, renewable, and potentially carbon-neutral, the wide use of which helps to solve the problems of global warming and global energy shortage. In this work, glycolaldehyde with both –OH and –CHO structure similar to glucose was for the first time studied on its activity to produce H₂ and CO(syngas). Glycolaldehyde was studied on Ni/Pt(111) bimetallic surfaces using both density functional theory (DFT) modeling and temperature programmed desorption (TPD) experiments. We found the binding energy of glycolaldehyde on the surface increases as the surface d-band center approaches the Fermi level with NiPtPt(111) surface having the highest binding energy. In all of the Pt(111), NiPtPt(111), PtNiPt(111) and thick Ni/Pt(111) surfaces, NiPtPt (111) surface showed the highest reforming activity and total activity, consistent with the DFT prediction. In addition, a comparison between the activity of glycolaldehyde and the reported ethylene glycol activity was made in this study.

Structure Property Relationships of Supported Pt/Ni Bimetallic Catalysts: Correlating the Extent of Pt-Ni Bimetallic Bond Formation with Low-Temperature Hydrogenation Activity

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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 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.

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.

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Reverse micelle synthesis and characterization of supported bimetallic catalysts

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Previous research has reported that the activity and selectivity of a metal catalyst can be altered by the incorporation of a second metallic element.[1] Explanations for these altered properties have been extensively studied using density functional theory calculations on unit cell models and verified by single crystal and polycrystalline foil experiments.[2],[3] However, there exists an increase in structure complexity when moving from experiments performed on single crystals and polycrystalline foils to oxide-supported catalysts, which makes it often difficult to correlate surface science experiments with catalysis.

Traditionally, supported bimetallic catalysts have been synthesized using incipient wetness impregnation wherein metal salt precursors are dissolved in water and impregnated on an oxide support.[4] While this technique produces active catalysts with small particles there is little control over final nanoparticle size and larger agglomerated particles often result after calcination and reaction pretreatments.[5] An alternative synthesis technique which has been shown to control nanoparticle size is reverse micelle synthesis. A reverse micelle is a nanometer-sized, surfactant-stabilized droplet of water suspended in an oil phase in which metal salt precursors can be dissolved and subsequently reduced chemically.[6] In order to validate the synthesis technique, transmission electron microscopy images of supported Pt and Pt/Co catalysts were taken to determine particle size distributions. Extended X-ray absorption fine structure measurements on the Pt L3 edge were used to verify bimetallic bond formation and determine interatomic distances. The results presented demonstrate that reverse micelle synthesis produces supported bimetallic nanoparticles with a narrower particle size distribution than nanoparticles synthesized using incipient wetness impregnation. While monometallic Pt catalysts were active for benzene hydrogenation and 1,3 cyclohexadiene hydrogenation, bimetallic Pt/Co catalysts were inactive. Due to the low hydrogenation activity observed for the present chemistry, optimization of synthesis materials and parameters is being pursued to take advantage of this technique to control nanoparticle size.

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Doped Ceria Films on YSZ Prepared by Infiltration as Reaction Barriers in SOFCs

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Strontium-doped lanthanum cobaltite (LSCo) can provide outstanding performance for solid oxide fuel cell cathodes. However, the tendency of LSCo to react with yttria-stabilized zirconia (YSZ), along with its poor coefficient of thermal expansion (CTE) match, makes the use of LSCo with YSZ electrolytes difficult. The CTE problem can be solved by using composites prepared by infiltration. However, solid-state reactions between LSCo and YSZ are found to occur at temperatures as low as 700°C. Even with low-temperature processing, deactivation is still a problem at operating temperatures.

To prevent solid-state reactions from taking place, the common approach is to incorporate a layer of doped ceria between the LSCo and YSZ. Unfortunately, traditional screen-printing and deposition methods that introduce a thick additional layer at the cathode-electrolyte interface still suffer from the high CTE mismatch between YSZ and LSCo. Therefore, in order to avoid reaction between LSCo and YSZ, while maintaining a CTE match, we investigated infiltrated LSCo electrodes in which a samaria-doped ceria (SDC) layer had been coated onto the YSZ pores.

Our studies show that doped ceria forms a uniform layer over the YSZ (Fig. 1) that successfully inhibits the solid state reaction between YSZ and LSCo.

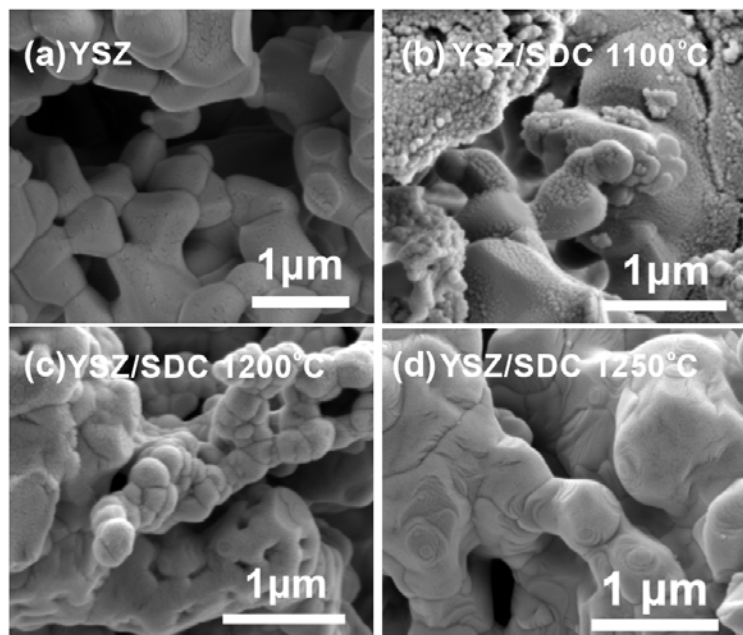


Figure 1. The microstructure of a) the YSZ matrix, b-d) YSZ-SDC composites with 20-wt% SDC fired to b) 1100°C, c) 1200°C, and d) 1250°C.

Analysis of Ga Coordination Environment in Novel Spinel Zinc Gallium Oxy-Nitride Semiconductors

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Abstract for the Catalysis Club of Philadelphia Annual Poster Contest

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 long considered a plausible technology to reduce the impact of these problems. The photocatalyst (semiconductor) utilized for the majority of applications is TiO_2 because it is stable, non-toxic and inexpensive. The major drawback of TiO_2 is that it has limited visible light absorption capability. We have developed Zinc Gallium Oxy-Nitrides (ZGONs) with the spinel crystal structure which show enhanced photocatalytic efficiencies to the degradation of methylene blue in visible light. These novel photocatalysts were synthesized from sol-gel derived zinc gallium oxide precursors upon nitridation in ammonia at 550°C . The reduction in the band gap for the spinel oxy-nitrides is associated with the incorporation of N2p orbitals in the valence band with corresponding changes in the anion position parameter. We established that the presence of a small fraction of gallium tetrahedral centers and anion vacancies that might affect its unique electronic properties. The changes associated with the gallium coordination environment as the spinel precursor becomes an oxynitride at 550°C and further transforms into a wurzite crystal structure at higher temperatures (850°C) are studied through x-ray diffraction, ultraviolet-visible diffuse reflectance spectroscopy, neutron powder diffraction, x-ray absorption spectroscopy and other techniques. The protocol developed opens a different avenue for the synthesis of semiconductors possessing the spinel crystal structure and with band gaps engineered to the visible region with potential applications for both opto-electronics and photocatalytic applications.

Stability and Performance of SOFC Cathodes Prepared by Infiltration

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The most commonly used cathodes for solid oxide fuel cells (SOFC) are composites of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) and yttria stabilized zirconia (YSZ). These LSM-YSZ composite electrodes are typically manufactured by sintering a physical mixture of the two materials and although they initially perform well at high temperatures ($>1073\text{K}$), this performance is seen to decline over extended operation times. In addition to improving upon the stability of these cathodes, it is also desirable to improve their performance at more intermediate temperatures.

Previously, our laboratory has developed a method of composite cathode fabrication by which aqueous solutions of La, Sr, and Mn nitrate salts are infiltrated into a preexisting porous YSZ scaffold and the calcined to form the desired perovskite phase. In this work, the performances of LSM - YSZ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (LSF) - YSZ composite electrodes are examined and possible explanations for degradation in cathode performance are discussed. It is also shown that the performance of degraded or deactivated electrodes can be improved through the infiltration of various “promoter” materials. Finally, a model for cathode degradation is proposed and solved numerically.

Raman, UV-Vis and IR-ATR Study of Vanadium Haloperoxidase Functional Mimics

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Introduction

Vanadium haloperoxidases (VHPOs) are a class of redox enzymes characterized by their vanadate-dependent active site and are named for their ability to catalyze the two-electron oxidation of halide ions (Cl^- , Br^- , or I^-) in the presence of hydrogen peroxide to produce hypohalous acids (HOCl , HOBr , or HOI) [1]. In pharmaceuticals and fine chemical applications, vanadium enzymes and vanadium-organic ligand enzyme mimic complexes can be employed as oxidation catalysts in aqueous media at mild temperatures and pressures.

To bridge the gap between inorganic and protein based vanadate oxidation catalysts, we have used *in-situ* and *operando* Raman, UV-Vis, and IR-ATR spectroscopy during methanol oxidation to examine two types of vanadium haloperoxidase functional mimics initially designed by Colpas *et al.*: vanadia complexed with N-(2-amidomethyl) iminodiacetic acid and vanadia complexed with N-(2-hydroxyethyl) iminodiacetic acid (VAda and VHeida respectively) [2]. The proposed structures of VAda and VHeida are given in figure 1. In addition, a novel form of immobilized VHeida was synthesized. These VHPO functional mimics are highly active methanol oxidation catalysts reactions in the presence of molecular oxygen or hydrogen peroxide at mild reaction temperatures required for condensed phases [2, 3].

Density Functional Theory (DFT) and isotope experiments were also used to compliment experiments.

Results and Discussion

UV-Vis spectroscopy confirms the presence of a Vanadium peroxo type structure due to the observation of a strong band centered at 450 nm. UV-Vis also confirms the +5 oxidation state of vanadium. In-situ during methanol oxidation with 10% oxygen shows no reduced vanadium.

VHeida and VAda in solid and aqueous forms show similar Raman and IR spectra. A doublet peak for both solid and aqueous VHeida between 900 and 970 cm^{-1} and strong bands between 460 and 640 cm^{-1} appear only after the vanadium chelate has been oxidized to the peroxo form in figure 1. DFT vibrational frequency analysis is in strong agreement with experimental Raman vibrations found for the $\text{V}=\text{O}$ stretching mode, the $\text{O}-\text{O}$ stretching mode, and the vanadium peroxo $\text{V}-\text{O}-\text{O}$ stretching modes. The differences between solid and aqueous spectra are attributed to hydrogen bonding and crystal lattice interactions. $\text{V}-\text{O}-\text{O}$ band assignments have also been confirmed by tracking VAda and VHeida Raman bands during different synthesis steps and by isotope exchange studies. Isotopic vanadium peroxo Raman experiments clearly distinguish the signature vanadium peroxo raman bands from other $\text{V}-\text{O}$ bands. *Operando* Raman spectra during methanol oxidation in the presence of 10% oxygen show a significant decrease in intensity for the vanadium peroxo signature bands indicating that the peroxo structure is involved in the methanol oxidation mechanism. Both VHeida and VAda were found to be highly active catalysts for the oxidation of methanol to formaldehyde.

This study elucidates the aqueous and solid VOx active phase, reaction intermediates, and the important role of the vanadium peroxo structure. These studies will be used as a benchmark for future studies of vanadium haloperoxidase (VHPO) enzymes.

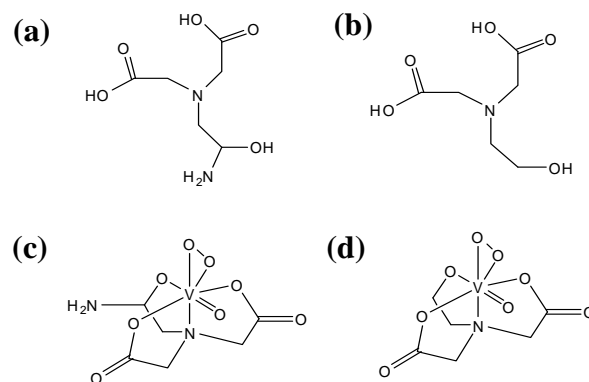


Figure 1. Structures of ligands (a) Ada and (b) Heida and corresponding vanadium peroxo chelate VHPO

A Study of the Water-Gas-Shift Reaction on Pd@CeO₂/Al₂O₃ Core-Shell Catalysts

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An alumina-supported, Pd@CeO₂, core-shell catalyst having 1-wt% Pd and 9-wt% ceria was prepared and characterized for the water-gas-shift (WGS) reaction. Although the catalyst initially exhibited similar WGS rates to that of a conventional Pd/ceria catalyst at 623 K in 25 torr each of CO and H₂O, the Pd@CeO₂ catalyst deactivated severely over a period of 1 h. The WGS activity of the Pd@CeO₂ could be completely restored by mild oxidation and oxygen-titration measurements showed that the ceria shell in the Pd@CeO₂ catalyst was significantly reduced after being used for the WGS reaction. These observations are in sharp contrast to that found with a conventional Pd/ceria catalyst, for which the ceria remains almost fully oxidized under WGS conditions. CO adsorption measurements, using FTIR at room temperature and CO uptakes at 195 K, indicated that Pd in the oxidized Pd@CeO₂ catalyst was accessible to CO but that adsorption was completely suppressed on the reduced catalyst. A model is presented to explain the results, which assumes that cracks and fissures in the oxidized ceria shell allow access to the Pd core but that reduction blocks access; either due to changes in the density of the ceria, which closes the fissures, or to coverage of the metal surface with ceria.

Development of Structural Model of the Orthorhombic M1 Phase in the Mo-V-Te-Nb-O Catalyst by Rietveld Refinement

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The biphasic M1/M2 Mo-V-Te-Nb-O mixed oxides are generally regarded as the most efficient catalytic system for selective ammoxidation of propane to acrylonitrile^[1]. The orthorhombic M1 phase is believed to be the key component for propane activation and the [001] face of the crystal is proposed to be catalytically active^[2]. Previous studies based on electron microscopy and powder diffraction have developed a structural model through simultaneous refinement of synchrotron and neutron diffraction data^[3]. Recent studies using HAADF aberration-corrected STEM imaging suggest new modifications to the model^[4, 5]. In the present work, we report an improved model accomplished by including new assumptions.

These modifications include: assigning new sites of mixed Mo and V; grouping oxygen sites based on their locations (linking site, pentagonal ring, and other); using a V-substituted Mo₅O₁₄ phase instead of Mo₅O₁₄; Including a (V, Mo)₂O₅ phase as a new impurity. The refinement progress showed all these assumptions contribute to the improvement of the model, while the major part results from the introduction of the (V, Mo)₂O₅ impurity.

The final results show that Site 4 is a Mo/V mixed site with similar V occupancy as site 7, in agreement with HAADF imaging results. Interestingly, V also occupies three of the five pentagonal ring sites in small quantity leaving the other two 100% Mo. Unlike the previous model, bond valence sum (BVS) results suggest that site 7 is likely to be a d¹ configuration which is also consistent with electroneutrality testing results. BVS results also suggest that Te site in the heptagonal channel might be of zero valence. Future work will employ atomic resolution EELS to investigate the specific coordination for each atomic column down the [001] projection trying to further understand the crystal chemistry as well as the catalytic mechanism.

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Studies of the active sites on supported cobalt catalysts for the steam reforming of ethanol

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Co/ZnO catalysts exhibit high selectivity for the steam reforming of ethanol (SRE) at low temperatures (<700 K) and are highly resistant towards coking. The ZnO support is thought to stabilize the active form of the cobalt and may also help to minimize carbon buildup. Previous studies of these catalysts have indicated that both Co^0 and Co^{2+} are present under reaction conditions, but the active form of the Co species has yet to be conclusively identified. In this research project we are studying model catalysts consisting of Co particles and thin films supported on a ZnO (0001) single crystal in order to determine how the support influences the reactivity of the Co. The growth mode and oxidation states of Co layers on the ZnO support at temperatures ranging from 600 to 900 K were investigated using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and Atomic force microscopy (AFM). Vapor deposited Co films were found to grow in a nearly layer-by-layer fashion at room temperature followed by agglomeration into particles upon heating to 700 K. Further heating to 800 K resulted in an oxidation of the Co and its re-dispersion over the support. These studies provide a new insight into how interactions at the metal–support interface influence both the structure and oxidation state of the Co, and we are currently studying how they affect the reactivity towards ethanol.

Microstructure-Based Design for Replacing Rh with Co in a Synergistic Catalyst for the Reduction of NO with H₂

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A novel microstructure-based design methodology was used to design and synthesize synergistic Pt(98wt%)-Co(2wt%)/□-Al₂O₃ catalysts for the reduction of NO with H₂. This method involves selecting metals with desirable catalytic properties, determining whether these metals will alloy, evaluating surface segregation phenomena, and selecting a preparation procedure and thermal treatment schedule that will result in forming nanoparticles with the desired microstructure[1]. The synergistic Pt-Co catalysts in this study were designed by mimicking the idealized nanoparticle surface microstructure of a synergistic Pt-Rh/□-Al₂O₃ catalyst and replacing Rh with Co [2]. The Pt-Co alloy nanoparticles were formed by reduction of metal salt precursors added to the support by co-impregnation, sequential impregnation, and sequential impregnation with an intermediate calcination step. Synergistic performance was not obtained until the surface of the bimetallic nanoparticles was tailored via conditioning, which involves exposing the catalyst to a selected atmosphere at temperature for a specified time. Three successful conditioning procedures have been identified and will be discussed. Although the design process resulted in the selection of a single catalyst composition to achieve synergy, the effect of varying the percentage of total metal loaded that is Co was explored according to the feasible range for synergy defined by the design procedure. The originally selected composition resulted in optimal performance for selectivity to N₂ by producing 2.8 times more N₂ compared to N₂O + NH₃ than Pt/□-Al₂O₃. The prepared catalysts were characterized by *in-situ* FTIR spectroscopy, UV/Vis diffuse reflectance spectroscopy, and aberration-corrected scanning transmission electron microscopy to support our hypothesis for the microstructure of the active Pt-Co nanoparticles.

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Model Based Prediction of Bimetallic 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 Pt, Pd, Ir, Ni, Rh, Co, Ru, Re, 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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Cell Performance and Chemical Stability of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_x\text{Fe}_{1-x}\text{O}_3$ (LSCF)

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Lanthanum Strontium Manganite (LSM) is currently the commercially preferred cathode material in Solid Oxide Fuel Cells due to its high chemical stability with Ytria-stabilized Zirconia (YSZ) electrolytes. Unfortunately, LSM-YSZ composite cathodes exhibit good performance only at operating temperatures above 973 K. Two materials that show promising results at lower temperatures are Lanthanum Strontium Ferrate (LSF) and Lanthanum Strontium Cobaltate (LSCo). Although LSCo provides superior initial performance relative to both LSM and LSF, it is susceptible to solid state reaction when in the presence of YSZ and forms a nonconductive $\text{La}_2\text{Zr}_2\text{O}_7$ phase, leading to a degradation in performance. LSF is chemically stable with YSZ up to 1473 K, but the performance of LSF cathodes provides only a modest improvement over LSM and has area specific resistances (ASR) over an order of magnitude greater than those of LSCo. In this work, the effects of varying the B site dopant in LSCF composite cathodes are examined, with the goal of obtaining the improved performance of LSCo matched with the improved chemical stability of LSF. XRD data is used to detect the formation of secondary phases, which is then correlated with decline in cell performance.

Post Doctoral Submission 1

Examining the Co/ZnO towards the steam reforming of ethanol using model surfaces

Matthew P. Hyman and John M. Vohs

The steam reforming of ethanol is a potential method for the production of hydrogen from a biorenewable feedstock. While Co/ZnO shows promise as an effective catalyst, more understanding is necessary to tailor the catalyst to enhance selectivity and stability.

In the Vohs laboratory, we are examining the Co/ZnO interface by vapor depositing Co films onto ZnO single crystals, as well as examining the reactivity of ethanol on Co foils. Experiments have been performed to understand the influence of this interface on the activity of Co.

A Study of Methane Tolerance in LSCM-YSZ Composite Anodes with Pt, Ni, Pd and Ceria Catalysts

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The carbon formation from methane was investigated in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ (LSCM)-yttria-stabilized zirconia YSZ composites with different metals (Pt, Ni, Pd) and ceria. For this purpose, the composite symmetric cells were prepared by aqueous impregnation of nitrate salts with LSCM, ceria and metal in a porous YSZ scaffold. SEM results show that composite anodes with Ni or Pd was found to form large amounts of carbon exposure to CH_4 at 1073 K for 24 h, while the electrode with Pt formed small amounts of carbon filaments for the same condition. This suggests that Pt does not promote the carbon deposition when operating on methane, while Ni and Pd significantly catalyze the formation of carbon. When CH_4 was switched back to pure H_2 , it was confirmed that the polarization resistance did not returned to its original value for the cell with Pd, indicating that the carbons formed from CH_4 degraded the catalytic ability of Pd for hydrogen oxidation. In addition, a comparison of the metal-containing electrodes with and without ceria showed that the addition of ceria effectively suppressed the carbon deposition reactions on metals under CH_4 .