

Post-doc

In Situ Raman and UV-Vis Spectroscopy Studies of Supported MoO₃/ZSM5 and MoO₃/Al₂O₃ Catalysts under Reactive Conditions

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The activation of methane into aromatic products over supported Mo/ZSM-5 catalysts has been intensively investigated over the last decade by many catalysis laboratories. The reactivity of this system and reaction pathways are still under discussion. The role of each element present in the zeolite-based catalyst (Mo, Al and Si), however, is not completely understood. Comparative studies of supported Mo/ZSM-5 and MoO₃/Al₂O₃ systems can provide insights about the interaction between the supported molybdenum oxide and alumina in these catalytic materials. The reducibility of the surface MoO_x species supported on alumina was investigated with *in situ* Raman and UV-Vis spectroscopy under H₂ and CH₄ conditions. The reducibility of supported MoO₃/Al₂O₃ increases with increasing surface MoO_x coverage or extent of MoO_x polymerization. Initially, the surface MoO_x species reduces in H₂ and the reduced Mo species subsequently interacts with alumina to form the aluminum molybdate (Al₂(MoO₄)₃), nanoparticles. The structural behavior of these catalytic systems in a CH₄ environment will also be discussed.

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New Fabrication Methods for Solid Oxide Fuel Cell Electrodes

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The electrochemical deposition of Cu into thick, highly porous Ni/YSZ (yttria-stabilized zirconia) and Co/YSZ cermets was investigated. An electrochemical cell in which the electrolyte solution was allowed to flow through the porous Ni and Co/YSZ substrate was used to allow for uniform Cu deposition throughout the porous substrates. The use of electrodeposition to make a Cu-coated Ni-YSZ cermet anode for a solid oxide fuel cell (SOFC) was also demonstrated.

New fabrication methods for Ni and Co/ceria/YSZ cermet anodes by use of electrochemical deposition were also examined. Uniform Ni and Co were successfully introduced electrochemically onto porous ceria-YSZ substrates which were made conductive enough for electroplating to take place by introducing conductive carbon layer in flowing of hydrocarbon at high temperature. Ni and Co/ceria/YSZ anodes thus prepared exhibited reasonable performance.

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The Stability of LSF-YSZ Electrodes Prepared by Impregnation

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Sr-doped LaFeO₃ (LSF) exhibits superior electrocatalytic activity for oxygen and outstanding oxygen permeability. It is one of the most promising materials as applied to solid oxide fuel cells (SOFCs), electrolyzer for hydrogen production, and oxygen separation membrane. However, YSZ-LSF composite electrode was reported to deactivate when operated at elevated temperatures. The deactivation might be due to interfacial chemical reaction and/or morphology change.

In this presentation, we report a study of the stability of LSF-YSZ electrodes prepared by impregnation. The performance of these cathodes was measured as a function of time and annealing temperature. We show that the performance at 973 K of LSF-YSZ electrodes is unstable if they were initially calcined to only 1123 K. The characteristics of an LSF-YSZ composite electrode calcined to 1373 K were similar to those of the 1123 K composite after long-time operation at 973 K. While there was no evidence for solid-state reaction between LSF and YSZ at either 1373 K or at SOFC operating temperatures, the LSF phase was found to sinter significantly following high-temperature treatment or after long times operating at 973 K. Based on the data, we conclude that the LSF forms a dense coating on the YSZ pores and that transport of oxygen through the dense film limits the performance. Possible methods for stabilizing the impregnated composites are discussed.

Key Words: Solid oxide fuel cells; cathode deactivation; yttria-stabilized zirconia; lanthanum ferrite;

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Combined IR/Raman Spectroscopy of Supported Pt/CeO₂ Catalysts: Probing the Metal-Support Interaction under Different Environmental Conditions

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The supported Pt/ceria catalyst represents an interesting class of catalysts that are attracting a lot of current attentions due to their unique properties and abilities of catalyzing the most demanding reactions related to environmental purifications and clean fuels emissions. In this investigation a combined *in situ* Raman and IR spectroscopic approach was set up to study the metal-support interactions of supported Pt/CeO₂ catalysts under oxidizing and reducing conditions that respectively mimic Lean and Rich conditions of the automotive exhaust environment. The supported Pt/CeO₂ catalyst was prepared by the incipient wetness impregnation method using a chlorine-free platinum precursor (Pt(NH₃)₄(NO₃)₂). The corresponding supported Pt/SiO₂ and Pt/Al₂O₃ catalysts were also synthesized as reference materials.

The calcined supported Pt/SiO₂ catalyst gives rise to the crystalline PtO₂ Raman band (~550 cm⁻¹) reflecting the weak interaction of Pt with the SiO₂ support. The calcined supported Pt/Al₂O₃ catalyst, however, exhibits a broad Raman band at ~610 cm⁻¹ reflecting the presence of distorted PtOx nanoparticles (NPs). For the calcined supported Pt/CeO₂ catalyst, Raman gives rise to a well-defined band at ~675 cm⁻¹ characteristic of two-dimensional surface PtOx species. Under reducing H₂ environment at elevated temperatures, the supported PtOx phases on SiO₂ and Al₂O₃ are easily reduced to metallic Pt at 50 °C (loss of PtOx Raman bands). Reduction of the supported PtOx/CeO₂ catalyst under reducing H₂ conditions, however, is retarded and only initiates at ~200 °C, reflecting the stronger interaction with the CeO₂ support.

Additional structural insights were provided by parallel DRIFT measurements. It was observed that CeO₂ reduction occurs at 200 °C as a consequence of H₂ spillover over the Pt sites. Reduction of the PtOx phase was also accompanied by chemisorption of CO on the reduced metallic Pt sites. Reduction of the CeO₂ support also changes the dispersion behavior of the supported PtOx component, which is also indicated by *in situ* Raman study of the re-oxidation of the reduced catalyst. Furthermore, re-oxidation of Pt/CeO₂ with ¹⁸O₂ resulted in the appearance of Pt¹⁶O, reflecting the supply of oxygen from the CeO₂ support rather than the gas phase molecular ¹⁸O₂.

In summary, the combination of Raman/IR spectroscopy is a very powerful characterization approach to study the metal-support interactions of the supported Pt/CeO₂ catalytic system. The Pt-support interactions determine the (i) dispersion of the supported PtOx phase, (ii) molecular structure of the supported PtOx phase under oxidizing conditions, (iii) ease of reduction of the supported PtOx phase and (iv) re-oxidation mechanism for supported Pt.

Is There A Relationship between the M=O Bond Length in Bulk Mixed Metal Oxides and Catalytic Activity?

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It's widely believed in the catalysis literature that the bulk M=O bond of bulk mixed metal oxides controls catalytic activity. In the present study, for the first time, the bulk Mo=O bond lengths and catalytic activity of bulk metal vanadates and molybdates are compared to allow examination of this long standing hypothesis. The bulk M=O bond lengths were measured with Raman spectroscopy and the corresponding catalytic activity was determined with CH₃OH-temperature programmed surface reaction (TPSR) spectroscopy. The CH₃OH-TPSR experiments provide the first-order rate constants for breaking of the C-H bond of the decomposition of the surface CH₃O* intermediate to H₂CO. The findings clearly show that there is no correlation between the rate constant, k_{rds} , and the bulk M=O bond length. This finding is not so surprising when one considers that the rate determining step involves C-H bond breaking, surface MO_x sites and doesn't involve bulk M=O bond breaking.

Fundamental Studies of CH₃OH Oxidation over Well-Defined Supported V₂O₅ Catalysts

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Methanol oxidation over supported V₂O₅ catalysts has received much interest in recent years because this catalytic reaction system represents a nice model for selective oxidation catalysis. In order to establish the molecular/electronic structure-activity/selectivity relationships, both CH₃OH-TPSR and steady-state studies with well-defined supported V₂O₅ catalysts were undertaken. The methanol oxidation TOF was found to be identical for isolated and polymerized surface VO₄ units on the same support in the sub-monolayer region. Relatively inactive crystalline V₂O₅ nanoparticles are also present above monolayer coverage and primarily decrease the number of exposed surface VO₄ catalytic active sites. The most dramatic effect on activity was observed when the specific oxide support was varied ($\sim 10^3$). The significant effect of the specific oxide support ligand and the absence of any effect of surface vanadia coverage (surface VO₄ polymer/monomer ratio), implicates the bridging V-O-Support bond as the catalytic active site for this and other redox reactions.

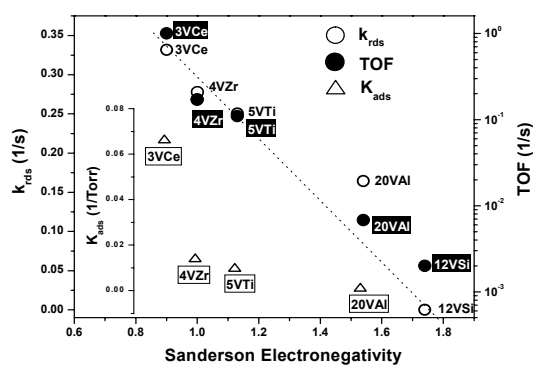


Fig. 1. The catalytic redox activity, TOF, K_{ads} , and k_{rds} , relationship with the support cation Sanderson electronegativity.

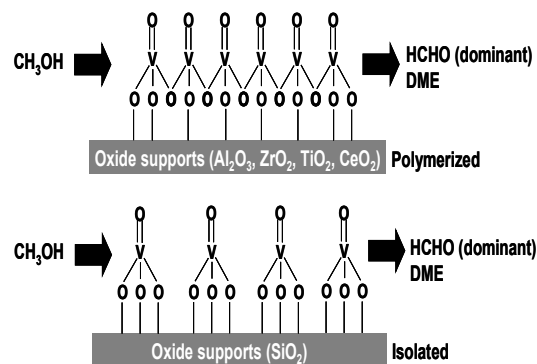


Fig. 2. Model of the supported vanadium oxide catalysts.

Conversion of Methanol over Solid Acidic WO₃/ZrO₂ Catalysts: Molecular/Electronic Structure-Activity Relationships

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Several different models have been proposed in the recent catalysis literature to explain the nature of the acidic catalytic active sites in supported tungsten oxide catalysts. The molecular level relationships between the different tungsten oxide structures present in these catalytic materials and their surface acidic characteristics, however, are not fully understood at present because of conflicting tungsten oxide structural assignments in the literature. In order to address these unresolved issues and determine the nature of the surface acidic sites present in both model supported WO₃ catalysts as well as the super-active WO₃/ZrO₂ catalysts, the relationships between the tungsten oxide molecular and electronic structures and the corresponding acidic catalytic activity for methanol dehydration to dimethyl ether were investigated.

Both “model” well-defined supported WO₃/ZrO₂ and calcined supported WO₃/ZrO(OH)₂ catalysts were synthesized by incipient wetness impregnation of preformed ZrO₂ and ZrO(OH)₂, respectively, and calcined in the 450-900 °C range. The molecular nature of the different supported tungsten oxide phases, two-dimensional surface and bulk crystalline phases was determined with *in situ* Raman spectroscopy because of the ability of Raman to readily discriminate among the different tungsten oxide structures. The corresponding electronic structures of the different tungsten oxide species were determined with *in situ* UV-vis DRS spectroscopy where the UV-vis DRS spectra were converted to edge energy, E_g, values. The catalytic surface chemistry of the supported tungsten oxide phases was chemically probed both by CH₃OH-Temperature Programmed Surface Reaction (TPSR) spectroscopy and steady-state CH₃OH dehydration studies. Fundamental information about the catalytic dehydration of CH₃OH to DME (k_{RDS}, K_{ADS}, TOF, reaction order and product selectivity) was obtained for the different catalysts from both the CH₃OH-TPSR and steady-state CH₃OH dehydration studies.

Monolayer surface WO_x coverage was determined to occur at 4.5-5 W/nm² for both sets of supported WO₃/ZrO₂ catalysts from Raman and XPS surface analysis. Although the UV-vis DRS E_g values are essentially the same below monolayer surface coverage, the corresponding Raman signals are not identical. The “model” WO₃/ZrO₂ catalysts exhibit the conventional dehydrated surface WO_x band at 1000-1020 cm⁻¹, but the WO₃/ZrO(OH)₂ catalysts possess this band as well as several others in the ~820-920 cm⁻¹ range. The additional Raman bands

present in the $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalysts arise from highly distorted WO_3 nanoparticles (NPs), which suggests that the $\text{ZrO}(\text{OH})_2$ precursor interacts with the WO_3 component during the synthesis and retards its crystallization. Above monolayer coverage, WO_3 NPs are present for both catalytic systems, but the WO_3 NPs present are not the same. For the “model” supported WO_3/ZrO_2 catalysts, the WO_3 NPs exhibit a Raman band at $\sim 805 \text{ cm}^{-1}$ characteristic of bulk-like WO_3 . For the supported $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalysts, the Raman bands of the WO_3 NPs are very broad and shifted to higher wavenumber values, $820\text{-}850 \text{ cm}^{-1}$, reflecting the distortion of these WO_3 NPs. Further, the corresponding UV-vis DRS E_g values are higher for the $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalysts than the WO_3/ZrO_2 catalysts above monolayer coverage, which reflects the smaller WO_3 NP domain size of the $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalysts at the same surface W/nm^2 density. Thus, the nature of the tungsten oxide species present in the supported $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalysts are very different than found in conventional “model” supported WO_3 catalysts because of the interaction of the $\text{ZrO}(\text{OH})_2$ precursor with the tungsten oxide component during calcination.

The surface chemistry of the zirconia supported tungsten oxide catalysts was chemically probed with both CH_3OH -TPSR and steady-state CH_3OH dehydration to DME. The catalytic TOF values for dehydration of CH_3OH to DME are significantly larger for the supported $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalysts, sometimes $> 10^2$, compared to the corresponding supported WO_3/ZrO_2 catalysts at the same surface W/nm^2 density. This catalytic enhancement is observed at all surface W/nm^2 density values and exhibits a maximum in TOF at $\sim 6 \text{ W}/\text{nm}^2$. This enhancement is related to the stabilization of the poorly ordered and distorted WO_3 NPs caused by their interaction with ZrO_x “impurities” that retard the crystallization of WO_3 . Above $6 \text{ W}/\text{nm}^2$ ordered WO_3 NPs are also present and the corresponding TOF values decrease. Thus, the dramatic enhancement in surface acidity and CH_3OH dehydration to DME specific reaction rate is related to poorly ordered and distorted WO_3 NPs caused by ZrO_x impurities that are only present in the supported $\text{WO}_3/\text{ZrO}(\text{OH})_2$ catalytic system. In the model supported WO_3/ZrO_2 catalyst system, the ZrO_2 support is encapsulated by the surface WO_x monolayer and can't interact with the WO_3 NPs during synthesis.

The current electronic and molecular structural information generated in this investigation are providing new insights into the nature of solid acidity for the supported WO_3/ZrO_2 catalysts that have lead to the development of a new solid acidity model.

Structural characterizations and surface reactivity of ferroelectric BaTiO₃ thin films on a conductive TiO₂(110) substrate

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The aim of this work is to understand how ferroelectric dipoles influence surface properties of BaTiO₃ and related materials. Barium titanate thin films supported on a TiO₂(110) single crystal have been prepared using a sol-gel process with a barium acetate and titanate butoxide precursor solutions. X-ray diffraction (XRD) was used to study the structure of the thin films and their morphology and their thickness were characterized using atomic force microscopy (AFM) and scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) Auger electron spectroscopy (AES) were also used to study the surface composition of the thin films. The grain size in the BaTiO₃ thin film was found to increase with the annealing temperature. After annealing to 800K in ultra high vacuum the TiO₂(110) substrate was found to undergo partial reduction and became electronically conductive, while the BaTiO₃ film remained fully oxidized. The BaTiO₃ film was also found to be ferroelectric and could be poled using an electric field applied by an AFM tip. The effect of polarization on the adsorption and reaction of methanol was also investigated using temperature programmed desorption (TPD). Preliminary results indicate that methanol adsorbs more strongly on the un-poled BaTiO₃ surface compared to a positively poled surface. Higher activity for the oxidation of adsorbed methoxide intermediates to formaldehyde was also observed for the positively-poled surface relative to the un-poled surface.

Structural characterizations and surface reactivity of ferroelectric BaTiO₃ thin films on a conductive TiO₂(110) substrate

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The interaction of organosulfur compounds, such as thiols and disulfides, with metal oxide surfaces is an increasingly important area of heterogeneous catalysis. While the reactions of sulfur containing compounds on oxide surfaces are important the mechanisms of these reactions are generally not well understood. In an effort to develop structure-activity relationships for the reaction of organosulfur compounds on catalytic oxides we have investigated the interaction of thiols and disulfides with several different single crystal surfaces of ZnO and compared them to higher surface area ZnO powder catalyst reactivity. TPD studies of the reaction of thiols and disulfides on the polar surfaces of ZnO showed that these molecules adsorb dissociatively on the (0001) surface to form thiolates and only molecularly on the (000-1) surface. The primary reaction pathways for adsorbed thiolates on ZnO(0001) are methyl transfer to produce dimethylsulfide and in the case of ethylthiolates dehydrogenation to produce ethylene. Oxydesulfurization to produce alkoxide intermediates was also observed to be a minor reaction pathway. Alkoxides produced in this manner either react further to produce gaseous aldehyde or are oxidized to CO and CO₂. All these pathways deposit sulfur atoms on the surface which are oxidized to SO₂ at temperatures above 800 K.

These TPD results in conjunction with the previously reported STM studies of the local atomic structure of the (0001) and (000-1) surfaces of Thornton et al [3] and Diebold et al.[4] have allowed the site requirements for the dissociative adsorption of thiols and disulfides and their subsequent reaction on these surfaces to be determined. For example we have proposed that thiols adsorb dissociatively on exposed, under-coordinated zinc-oxygen site pairs at step edges on the (0001) surface. These step edge sites are also active for the oxidation and oxydesulfurization of adsorbed thiolates. We recently expanded these studies to include the reactions of thiols and disulfides on the (10-10) surface which is also prevalent in high surface area ZnO powders. The reaction pathways for methylthiolates on this surface are similar to those on ZnO(0001) with the primary reaction being methyl transfer to produce dimethylsulfide. Also observed are oxydesulfurization to aldehydes, complete oxidation to CO₂ and SO₂ and coupling to produce ethylene. Studies of the reaction of ethylthiolates on this surface will also be presented. Ethylthiolates do not undergo coupling and instead undergo hydride abstraction, decomposition to methoxide and various levels of oxidation of the resultant alkoxide and surface sulfur. Combining the observed reactivity of the ZnO(0001), (000-1), and (10-10) surface compares favorably with TPD studies of thiols and disulfides on high surface area ZnO powders.

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Keywords: Barium titanate, surface reaction, ferroelectrics, methanol, TPD

Investigating the Volcano Curve Correlation for Formic Acid Decomposition on Bulk Metal Catalysts

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Formic acid (HCOOH) decomposition has been used as a common test of catalytic activity due to the presence of the same surface HCOO* intermediate (chemisorbed formate) on the majority of metal and metal oxide surfaces [1, 2]. The Sachtler-Fahrenfort volcano curve is a famous result of such a study on bulk metal catalysts [3]. The fundamental correlation that results in the volcano plot between bulk heat of formation of formate and catalytic activity has raised some questions in the literature [1, 2]. Primarily, work on bulk metal oxide catalysts analogous to that of Sachtler and Fahrenfort done by Fein and Wachs [2] showed weak or no correlations between formic acid decomposition activity and bulk heat of oxide formation. Thus the question is raised: Should one attempt to correlate bulk thermodynamic properties with a surface property such as specific catalytic activity? In an attempt to definitively answer this question, catalytic activity data for formic acid decomposition over bulk metal catalysts was gathered using a modern approach: temperature programmed surface reaction (TPSR) spectroscopy and *surface* heats of adsorption by calorimetry. The surface heats of adsorption of formic acid on bulk metals will be correlated with the formate TPSR decomposition temperatures, T_p . If the same volcano plot results when catalytic activity (surface property) is correlated with surface heat of adsorption (surface property), then one can conclude that the bulk thermodynamic property in question is related to the surface property. Thus, the volcano plot will hold or be shown to be a coincidence of linear free energy relationships [1].

The HCOOH-TPSR spectroscopy experiments were performed on an Altamira temperature programmed system (AMI-200) equipped with an online quadrupole mass spectrometer (Dycor Dymaxion DME200MS). Gas phase formic acid (2000 ppm in He) was allowed to adsorb over the various metal catalyst: Cu, Co, Fe, W, Ag, Ni, Au, Pt, Pd, and Ru in the temperature range of 35 -100 °C. In some cases the bulk metal oxide was used as a precursor to the bulk metal and was first reduced in 10% H₂ in Ar at appropriately elevated temperatures that were previously determined by temperature programmed reduction experiments. The HCOOH decomposition temperatures, T_p , for each metal were measured during temperature ramping after adsorption.

The newly generated T_p data were plotted versus the bulk heats of formation of the formate reported by Sachtler and Fahrenfort. Rather than a volcano trend, the results show a striking similarity to Mark Barteau's work on linear free energy relationships (LFERs) [1]. Barteau concluded that LFERs should be examined within groups on the Periodic Table, but should not be expected to carry over when one makes jumps across groups. This conclusion is significant because it is the Brønsted-Evans-Polanyi (BEP) relation, which is a LFER, which results in the linearity of the left- and right-hand sides of the volcano plot. Surface heats of adsorption data will definitively show if any correlation exists between the bulk heat of formation and activity.

The volcano curve has been widely accepted for many decades as a truth in catalyst design and this acceptance has led many researchers to search for similar volcano correlations in other catalyst systems. This work hopes to shed light on when it is and when it is not appropriate to look for such correlations or to attempt to correlate certain properties. Only if a relationship exist between the bulk and surface property should a strong correlation exist, but initially it would seem best to attempt to correlate surface/surface properties.

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Role of Excess MoO₃ in Iron-Molybdate Methanol Oxidation Catalysts

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The most widely used catalyst for commercial production of HCHO from CH₃OH oxidation is an iron-molybdate catalyst, which contains both crystalline MoO₃ and Fe₂(MoO₄)₃ phases. In the past, attempts have been made to unravel the role of the excess MoO₃ in the iron-molybdate catalyst and many different hypotheses have been put forth. In the present investigation, CH₃OH-temperature programmed surface reaction (TPSR) spectroscopy and steady-state methanol oxidation experiments were undertaken to address this interesting issue. CH₃OH-TPSR experiments reveal that when excess MoO₃ is introduced, the number of catalytic active redox sites (N_s) of the catalyst increases and the rate constant (k_{RDS}) for the surface CH₃OH intermediate decomposition to HCHO remains the same. Thus, the enhanced steady-state activity of iron-molybdate catalysts activity arises from an increase in the N_s and not in k_{RDS}. In addition, the steady-state HCHO selectivity also increases with excess MoO₃.

Mechanistic Studies of the Steam Reforming of Methanol on Pd/ZnO Catalysts

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Methanol and other alcohols are potential bio-renewable sources of hydrogen. The use of alcohols, however, as a source of H₂ or for H₂ storage requires stable reforming catalysts that have high activity at low temperatures. One such catalyst that has received much attention for steam reforming of CH₃OH (SRM) [CH₃OH + H₂O → CO₂ + 3H₂] is Pd supported on ZnO. Pd/ZnO catalysts have unusually high selectivity (>95%) for the production of CO₂ and H₂ from methanol, in spite of the fact that bulk Pd exhibits nearly 100 % selectivity for the dehydrogenation of CH₃OH to CO and H₂ under typical SRM conditions [1,2]. Iwasa and others have demonstrated that partial alloying of the Pd with Zn is required to obtain a highly selective Pd/ZnO SRM catalyst [3]. While the importance of alloy formation has been established, the mechanism by which Zn alters the selectivity to produce CO₂ rather than CO is not understood. Iwasa *et al.* have proposed, however, that the dramatic change in selectivity may result from the destabilization of η²-CH₂O intermediates in which the carbonyl group is parallel to the surface and bonding is by both the C and O atoms in favor of η¹-CH₂O in which the carbonyl is perpendicular to the surface and only the oxygen interacts with the metal [**]. Presumably this later species is more resistant to dehydrogenation and reacts with hydroxyl groups to produce CO₂ and H₂.

In order to elucidate how alloying with Zn affects the CH₃OH dehydrogenation activity of Pd, the structure and reactivity of model catalysts consisting of submonolayer amounts of Zn supported on a Pd(111) single crystal have been investigated. I will present temperature programmed desorption (TPD) data for the reaction of methanol and formaldehyde on Pd(111) as a function of Zn coverage as well as results of a high resolution electron energy loss spectroscopy (HREELS) study of the bonding configurations of CO, CH₂O, and CH₃OH on Zn/Pd(111) surfaces. TPD data for the reaction of methanol on Pd supported on ZnO(0001) single crystal surfaces will also be presented

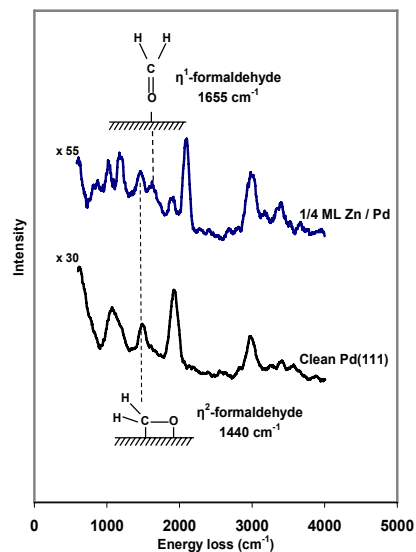


Fig. 1. HREEL spectrum of CH₃OH adsorbed on Pd(111) and 0.25 ML

Experiments were carried out in an ultra high vacuum (UHV) chamber equipped with a quadrupole mass spectrometer for TPD studies and a Kesmodel LK-2000 HREEL spectrometer. Zn and Pd were deposited on the single crystal substrates using an evaporative metal sources and a quartz crystal film thickness monitor was used to determine absolute coverages.

Methanol TPD data as a function of Zn coverage demonstrated that Zn is very effective in poisoning the activity of the Pd(111) surface for both the dissociative adsorption of CH₃OH and the subsequent dehydrogenation of adsorbed methoxide intermediates. For Zn coverages as low as 0.1 ML the amount of CO produced during a CH₃OH TPD experiment was less than 40 % of that produced on clean Pd(111).

Submonolayer amounts of Zn were also found to alter the bonding configuration of aldehydes on the Zn/Pd(111) surface. This is demonstrated by the HREELS data in Figure 1 which displays the vibrational spectrum of CH₃OH adsorbed on both clean Pd(111) and 0.25 ML Zn/Pd(111). The η^2 -CH₂O and η^1 -CH₂O species can be distinguished by their distinctive vibrational bands at 1450 cm⁻¹ and 1655 cm⁻¹, respectively

Note that on clean Pd(111) only the peak at 1450 cm⁻¹ is observed indicating an η^2 bonding configuration. In contrast for the 0.25 ML Zn/Pd(111) surface both the 1450 and 1655 cm⁻¹ peaks are observed demonstrating the presence of both η^2 -CH₂O and η^1 -CH₂O species on this surface.

Figure 1 also provides information about the bonding sites of the CO on the surface. The peak at 1860 cm⁻¹ corresponds to CO in threefold sites while that at 2070cm⁻¹ is CO in on top sites. Note the preferred CO bonding configuration changes from threefold to on top upon the introduction of Zn.

The results obtained in this study provides fundamental insight into how Zn alters the reactivity of Pd for the dehydrogenation of CH₃OH and this insight is useful in elucidating the mechanism of the steam reforming of methanol on Pd/ZnO catalysts.

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***Operando* Spectroscopy of Propylene Oxidation to Acrolein over Well-Defined Supported Vanadia Catalysts**

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The oxidation of propylene to acrolein was investigated over well-defined two-dimensional surface vanadia monolayer catalysts with Raman, IR, and *simultaneous* online product analysis (*operando* spectroscopy), temperature programmed surface reaction (TPSR) spectroscopy and isotopic labeling ($^{18}\text{O}_2$ and C_3D_6). The oxidation of propylene to acrolein proceeds via a combined Langmuir-Hinshelwood and Mars-van Krevelen surface reaction mechanism. The dissociative chemisorption of propylene forms surface $\text{CH}_2\text{CHCH}_2^*$ and H^* , and the presence of surface O^* , supplied by gas phase molecular O_2 , is required to remove the surface H^* as H_2O to prevent hydrogenation of the surface allyl intermediate to propylene (L-H step). The insertion of the second O^* , however, is only supplied by the surface vanadia monolayer (M-VK step). The rate-determining-step involves breaking of the surface allyl C-H bond. The elementary reaction steps and surface reaction kinetics for the selective oxidation of propylene over the model supported vanadia catalysts will also be discussed.

Propane ODH to Propylene over Supported Molybdena Catalysts: The Relation of Catalyst Structure to Catalytic Activity

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Much research in recent years has been devoted to understanding the molecular structure of supported molybdena catalysts. The objective of this presentation is to relate the molecular structure of supported molybdena catalysts (molybdena dispersed on zirconia, alumina, and silica supports) to catalytic activity. The molecular structures of the dispersed surface molybdena species were determined with *in situ* Raman, *in situ* IR and *in situ* UV-Vis spectroscopy. The corresponding catalytic activity was chemically probed by the propane oxidative dehydrogenation (ODH) reaction. Both low and high molybdena loaded catalysts were investigated in the sub-monolayer region ($< 5 \text{ Mo/nm}^2$). At low surface MoOx coverage, the surface MoOx species are isolated and possess isolated dioxo $(\text{S-O})_2\text{Mo(-O)}_2$ structures, where S represents a support site. At monolayer surface MoOx coverage ($\sim 4.6 \text{ Mo/nm}^2$), polymeric surface monoxo $\text{O=Mo(-O-Mo)}_2(\text{-O-S})_2$ structures are also present. The catalytic turnover frequency (TOF=propylene molecules/site-sec) for propane ODH was found to be identical for both surface molybdena structures. The catalyst support (S), however, was found to have a significant effect on the TOF values ($\text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{SiO}_2$). Thus, the most important parameter affecting the propane ODH catalytic activity is the nature of the bridging Mo-O-S bond, which controls the TOF.

Thermodynamic investigation of the redox properties of Ceria-based catalysts

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The thermodynamic redox properties for a series of ceria-zirconia solid solutions have been measured by determining their oxidation isotherms between 873 and 1073 K. Isotherms were obtained using Coulometric titration and using O₂ titration of samples equilibrated in flowing mixtures of H₂ and H₂O. While the oxidation enthalpy for CeO₂ was between -750 and -800 kJ/mol O₂, the oxidation enthalpies for each of the solid solutions were between -500 and -550 kJ/mol O₂ and essentially independent of the extent of reduction. The shapes of the isotherms for the solid solutions were affected by the oxidation entropies, which depended strongly on the sample composition and the extent of reduction. With CeO₂, Ce_{0.92}Zr_{0.08}O₂, and Ce_{0.14}Zr_{0.86}O₂, the samples remained single-phase after calcination at 1323 K and the thermodynamic redox properties were unaffected. By contrast, Ce_{0.59}Zr_{0.41}O₂ formed two phases following calcination at 1323-K, Ce_{0.78}Zr_{0.22}O₂ (71 wt%) and Ce_{0.13}Zr_{0.87}O₂ (29 wt%); and the isotherm changed to that which would be expected for a physical mixture of the two phases. A model is presented which views reduction of the solid solutions in terms of the local atomic structure, with the formation of "pyrochlore-like" clusters causing the increased reducibility of the solid solutions. Some of the changes in reducibility are associated with the number of sites from which oxygen can be removed in order to form pyrochlore-like clusters. Oxidation enthalpies for reduction of ceria surfaces were also investigated on high-surface-area ceria and ceria supported on La-modified alumina (LA). The surface area of pure ceria was found to be unstable under redox conditions, the extent of reduction at 873 K and a P(O₂) of 1.6x10⁻²⁶ atm increased with surface area. Because ceria/LA samples were stable, equilibrium isotherms were determined between 873 and 973 K on a 30-wt% ceria sample. Oxidation enthalpies on ceria/LA were found to vary with the extent of reduction, ranging from -500 kJ/mol O₂ at low extents of reduction to near the bulk value of -760 kJ/mol O₂ at higher extents. To determine whether +3 dopants could affect the oxidation enthalpies for ceria, isotherms were also measured for Sm⁺³-doped ceria (SDC) and Y⁺³-doped ceria. These dopants were found to remove the phase transition observed in pure ceria below 973 K but appeared to have minimal effect on the oxidation enthalpies. Implications of these results for catalytic applications of ceria are discussed.

Controlling the Molecular Structure and Reactivity of Supported Metal Oxide Catalytic Active Sites

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The surface molecular structures of dehydrated model supported catalysts have been determined, *for the first time*, by employing *in-situ* Raman, UV-Vis and O-18 isotopic labeling. Raman spectroscopy confirmed that the supported metal oxide phases were 100% dispersed on the SiO₂ support at low surface coverage. More importantly, the Group V, VI, and VII, represented by model systems, specifically V₂O₅/SiO₂, WO₃/SiO₂, and Re₂O₇/SiO₂ catalysts were revealed to consist of predominantly monoxo (O=M(-O)₄), dioxo ((O=)₂M(-O)₂), and trioxo ((O=)₃M(-O)) surface molecular structures, respectively. The monoxo and dioxo symmetric M=O vibrations were observed in the 1000-1020 cm⁻¹ and 970-985 cm⁻¹ regions, respectively, whereas the trioxo symmetric and antisymmetric M=O vibrations appeared at ~1010 ~cm⁻¹ and 970 cm⁻¹, respectively. The surface MO_x species were also confirmed by complementary UV-Vis diffuse reflectance spectroscopy (DRS) because of their different electronic features. The isotopic O-18 labeling and reduction studies identified the vibrations of the terminal M=O and bridging M-O-Si bonds.

The distribution of monoxo, dioxo, and trioxo surface MO_x molecular structures could be controlled by the addition of surface AlO_x, TiO_x, and ZrO_x species. The surface AlO_x and TiO_x additives were found to possess AlO₄/AlO₅ and TiO₄/TiO₅ coordination by solid-state NMR and XANES, respectively. According to literature reports, the Zr cations on SiO₂ should possess 5-fold or higher coordination. The surface MO_x species were found to preferentially self-assemble on the more reactive surface AlO_x, TiO_x, and ZrO_x sites over the relatively inert SiO₂ surface. For the supported VO_x species, the addition of these surface metal oxide additives was found to maintain monoxo surface structure. However, the WO_x species with the promoters were able to transform from predominantly dioxo to monoxo surface structure. Therefore, the ratio of monoxo/dioxo surface WO_x species can be tuned with the addition of AlO_x, TiO_x, and ZrO_x ligands. The ReO_x species were maintained as trioxo species even with the addition of the promoters, and were not able to transform to dioxo or monoxo species. The corresponding UV-Vis DRS electronic spectra revealed that a single LMCT (ligand to metal charge transfer) transition was identified, suggesting isolated surface species.

The structural modifications with AlO_x, TiO_x, and ZrO_x metal oxide additives lead to significant reactivity enhancements. The redox activity of the supported VO_x/SiO₂ was determined via methanol oxidation, where the TOF of the promoted systems increased by an order of magnitude over the model system. The acidity of the supported WO_x/SiO₂ was

chemically probed with CH₃OH-TPSR, where the formation of dimethyl ether (DME-CH₃OCH₃) from CH₃OH dehydration occurs on acidic catalytic surface sites. For exclusively monoxo WO_x species, the rate constant for DME, k_{rds} , were enhanced by greater than two orders of magnitude over dioxo species. The rate constant for surface redox products, primarily yielding HCHO, was found to be independent of the surface structure. These fundamental studies have shown *for the first time* that there are multiple surface species, monoxo, dioxo, and trioxo, were present on the SiO₂ support and that their relative surface concentrations can be *tuned* with the addition of secondary metal oxide additives (the promoted catalysts). The structural studies coupled with catalytic reactivity of these novel model catalysts allows for the establishment of molecular/electronic structure–activity/selectivity relationships.

High-Performance Ceramic Anodes For SOFC

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Ceramic anodes for solid-oxide fuel cells (SOFC) could speed the development of this technology because they can provide sulfur tolerance and redox stability, as well as allow direct utilization of hydrocarbon fuels. Performance has been investigated as a function of anode thickness, active component loadings, and catalytic metal dopants. We will describe cells with novel anode structures based on mixtures of Pd-doped CeO₂, YSZ, and La_{0.3} Sr_{0.7} TiO₃ (LST) that achieved power densities greater than 650 mW/cm² in humidified H₂ and 500 mW/cm² in humidified CH₄ at 1073 K, with 75- μ m YSZ electrolytes. Preliminary data shows that the anodes are stable in methane, have good thermal stability, and are reasonably tolerant towards oxidation.

Characterization of K-Promoted Ru Catalysts for Ammonia Decomposition Discovered Using High-Throughput Experimentation

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The necessity for alternative energy solutions is motivated from increasing fuel prices, stringent emission regulations, and depleting fuel resources. The most attractive option is H₂, as it has high-energy efficiency and H₂O is the only byproduct of its combustion [1]. Ammonia has emerged as an attractive source for H₂ because of its high hydrogen storage capacity (17.7 %), energy density (3000 Wh/kg), and the catalytic decomposition of NH₃ is free of CO_x emissions [1]. Ru catalysts have been successful for this reaction and we have examined this system in detail [2]. Using incipient wetness impregnation, we have investigated the effect of several promoters (K, Cs, Ba, Na, Rb, Li, Sr) and solvents (H₂O, DMSO, ACN, THF, MEK, 2-propanol) on the low-temperature ammonia decomposition over Ru catalysts supported on Al₂O₃. Using the high-throughput screening, we have determined that K promotion provides dramatic enhancement (up to 30%) in the conversion of NH₃ at a reduced temperature of 350°C. Using TEM and SEM, it was discovered that the addition of K to Ru induces the formation of potassium ruthenium oxide “nanowhiskers” as opposed to Ru agglomerates that appear to be responsible for the enhanced performance. Furthermore, it was discovered that changing the preparation solvent from H₂O to an alcohol for an identical Ru/K ratio provides an additional boost in the NH₃ conversion (up to 30%) at even lower temperatures (T=300°C).

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Reactions of Complex Epoxides on Silver Surfaces

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Direct oxidation processes, such as ethylene epoxidation to ethylene oxide, have been researched extensively due to their commercial significance. Despite the importance of epoxide production, the mechanistic details of olefin epoxidation remained obscure until recently and the majority of significant advances in Ag-catalyst development occurred primarily through empirical methods. Recent surface science studies of ethylene oxide and 1-epoxy-3-butene have identified an oxametallacycle species as the active intermediate in Ag-catalyzed epoxidation of both ethylene and 1,3-butadiene; expansion of the epoxide ring to incorporate surface silver atoms forms the oxametallacycle species. Oxametallacycles have been isolated by ring-opening ethylene oxide, 1-epoxy-3-butene, and styrene oxide on Ag(111) and 1-epoxy-3-butene on Ag(110).

Surface science techniques and density functional theory were used in this study to investigate the interactions of styrene oxide and isoprene oxide with Ag-surfaces. In agreement with previous studies of olefins on Ag(110) and Ag(111), these complex epoxides undergo activated ring-opening to form stable surface species on silver; these intermediates reform their parent epoxides during subsequent temperature-programmed desorption. Because the molecular forms of both styrene oxide and isoprene oxide desorb molecularly from silver below 250 K, the intermediate species derived from these epoxides are most likely surface oxametallacycles. Preliminary density functional theory calculations predict that cleavage of the epoxide ring occurs at the carbon bearing the substituent group to form surface oxametallacycle intermediates.

Comparison of Redox Thermodynamic Properties of V_2O_5 and $Mg_3(VO_4)_2$

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Coulometric titration, an electrochemical method for measuring oxidation isotherms, has been used to characterize the redox properties of V_2O_5 and $Mg_3(VO_4)_2$ between 823 and 973 K. V_2O_5 shows distinct regions in the isotherms corresponding to equilibrium with mixtures of V_2O_3 and V_2O_4 and of V_2O_4 and V_2O_5 . From this data, the enthalpies for oxidation of V_2O_3 to V_2O_4 and for V_2O_4 to V_2O_5 are shown to be -380 ± 10 kJ/mol O_2 and -285 ± 20 kJ/mol O_2 , respectively. Oxidation isotherms for $Mg_3(VO_4)_2$ exhibit a single step for between the oxidized sample (all V^{+5}) and a completely reduced sample (all V^{+3}). The enthalpy of oxidation is found to increase with the oxidation state of the sample, from -370 ± 30 kJ/mol O_2 at an O:V ratio of 1.5 to -460 ± 10 kJ/mol O_2 at an O:V ratio of 2.5.

General trends in hydrogen binding energy and hydrogenation activity on Pt-3d bimetallic surfaces

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This study utilizes a combination of density functional theory (DFT) and temperature-programmed desorption (TPD) to study the hydrogenation of cyclohexene on Fe, Co, Ni, and Cu-modified Pt(111) surfaces. It was found that the hydrogen binding energy (HBE) on the Pt-3d surface alloys is significantly lower than that on any of the parent metals. In addition, these Pt-3d bimetallic surfaces have been shown to display an increased activity for the hydrogenation of cyclohexene. Thus, it is concluded that accessibility of hydrogen by the reactant is a major factor in the reactivity of these surfaces. Ultimately, Pt-Ni-Pt(111) and Pt-Co-Pt(111) are found to have the highest hydrogenation activities with 0.030 and 0.006 molecules of cyclohexene converted to cyclohexane per metal atom on these two surfaces, respectively.

Controlling Hydrogenation Selectivity on Zeolite-Supported Bimetallic Catalysts

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Novel catalysts have been synthesized and evaluated by supporting Pd-based bimetallic nanocatalysts on zeolites to achieve higher selectivity for the selective hydrogenation of acetylene in a stream containing excess ethylene at relatively low temperatures (300-339K). Low-temperature hydrogenation offers the opportunity of using competitive adsorption on zeolite to achieve preferential hydrogenation of acetylene. Previous work from our group has found that bimetallic catalysts favor low-temperature hydrogenation.^[1-3] Results from many other groups have also shown that Pd is a good catalyst for the selective hydrogenation of alkynes in excess ethylene. Therefore the strategy of the present work was to modify Pd catalysts and to embed bimetallic nanoparticles in an environment that is highly selective for acetylene hydrogenation^[4].

Cation- π interaction offers the potential for selective adsorption of acetylene on the zeolite supports. In the current work we used the ion-exchanged zeolite^[4-6] as the support of the bimetallic catalysts. The zeolite structure should have multiple dimensions and contain large pores, in order to house the bimetallic nanoparticles inside the pores. Flow reactor studies using GC, batch reactor studies using FTIR, EXAFS, TEM and CO-Chemisorption evaluation have been performed. Our results indicate that the Pd-Ag bimetallic catalyst has a much higher selectivity for acetylene hydrogenation in ethylene than either Pd or Ag. Kinetic modeling of reactions in FTIR shows significant differences in the hydrogenation rate constant, adsorption equilibrium constant, as well as the selectivity of the γ -Al₂O₃ supported catalysts and cation exchanged β -zeolites supported catalysts, with the cation exchanged β -zeolite supported catalysts showing much higher selectivity than the γ -Al₂O₃ supported catalysts.

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Reforming of Oxygenates for H₂ Production on Bimetallic Surfaces

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Production of hydrogen for use in fuel cells can be achieved by selective reforming of oxygenates. The oxygenates may be derived from renewable biomass and offer advantages such as low toxicity, low reactivity and compatibility with the current infrastructure for transportation and storage. Platinum has been identified as one of the most promising catalysts for the reforming of oxygenates. Nickel catalysts have shown high activity, but also displayed decreased hydrogen selectivity. In this study, the reactions of oxygenates, such as methanol, ethanol and ethylene glycol, were investigated on 3d-Pt(111) bimetallic surfaces using temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), and Density Functional Theory calculations (DFT). The formation of bimetallic surfaces alters the physical and chemical properties of the parent metals, which can lead to novel catalytic activity in certain reactions. The bimetallic surfaces were prepared by physical vapor deposition (PVD) of the desired second metal onto Pt(111), using Auger electron spectroscopy (AES) to monitor surface compositions. Oxygenates reacted on 3d-Pt(111) to primarily form H₂ and CO. Surfaces prepared by deposition of a monolayer of Ni on Pt(111) at 300 K, designated as Ni-Pt-Pt(111), displayed increased reforming activity compared to Pt(111), subsurface monolayer Pt-Ni-Pt(111), and thick Ni/Pt(111). The experimentally measured reforming yield displayed a linear trend with the surface *d*-band center for both ethylene glycol and ethanol. The reforming activity increased as the surface *d*-band center moved closer to the Fermi level, opposite to the trend previously observed for hydrogenation reactions. DFT results indicated that the binding energy of methanol and ethanol increased as the *d*-band center of the bimetallic surface shifted closer to the Fermi level, which could be achieved by choosing 3d metals from the left side of the periodic table as the surface monolayer. Further studies are underway to investigate oxygenate reforming on other 3d-Pt-Pt(111) bimetallic surfaces.

Comparison among structured and packed-bed reactors for the catalytic partial oxidation of CH₄ at short contact times

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Three types of catalyst support (foams, honeycomb monoliths with square channels and spheres with approximately equal values of specific geometric surface) were examined and compared by simulation with a 1D, dynamic heterogeneous mathematical model for application to the autothermal partial oxidation of methane. The intrinsic reaction kinetics were accounted for after the results of an independent kinetic study of the process [1] and specific heat and mass transfer correlations were included for the different catalyst configurations [2-4]. Aim of the work was the analysis of the combined effect of chemical reaction and heat and mass transfer properties on the dynamic and steady-state performances of an adiabatic reactor at high flow rates; the reactor response during start up and the effect of increasing the space velocity on reactants conversion and syngas selectivity were investigated for each configuration up to the limit of reactor blow-out [5]. It was found that mass and, particularly, heat transfer properties markedly affect the reactor behaviour, both at start up and at steady state.

Thus, the choice of the catalyst support can lead to greatly different reactor performances. Concerning the reactor start-up, simulations revealed that better interphase heat transport properties and lower bed heat capacity are useful to minimize the total start-up time; on the other hand, more favorable transport properties reduce the maximum flow rate which allows to achieve and maintain an ignited steady state. At steady state, oxygen conversion is strictly governed by interphase mass transfer, while methane conversion depends on a more complex, mixed chemical-diffusional regime.

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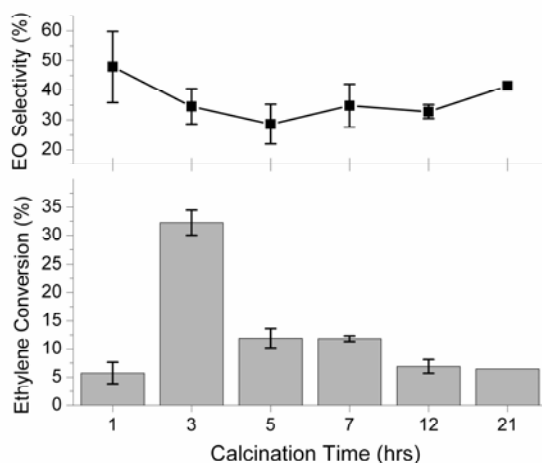
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Traditional and high-throughput reactor studies of Ag and Re-promoted Ag catalysts for ethylene epoxidation

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Current global production of ethylene oxide (EO) exceeds 14 million tons per year. The current industrial process, direct gas phase production of EO, is expensive with 20-25% of the main reactant, ethylene, being combusted due to an unselective reaction on the base catalyst, Ag. Several patents claim that promoters on Ag catalysts, such as rhenium, cesium, and co-fed organic chlorides, yield EO selectivities over 80%. However, only the effects of cesium and organic chlorides have been studied in detail. In order to establish a more fundamental understanding of the Ag and Re-Ag catalysts, single reactor and high-throughput reactor studies were executed. As Fig. 1 shows, the Ag catalyst activity was dramatically affected by the calcination conditions, without change to the selectivity. Based on this result, it is thought that catalyst sintering decreases the activity with longer calcination times. Results from studies with Re-Ag indicate that Re increases the EO selectivity at the expense of catalyst



activity. The optimum performance of 45% EO selectivity for the Re-Ag, compared to 30% for Ag, was found for catalysts with 25 ppm Re. Characterization, using SEM, shows that the addition of Re also causes an increase in the Ag particle size from 15-35 μm . An analysis of the oxygen reaction orders showed that the Re-Ag catalyst presents a more uniform distribution of sites for oxygen adsorption than do unpromoted catalysts. Thus, it is hypothesized that Re is blocking/destroying Ag step sites, increasing the EO selectivity.

Fig. 1. Ethylene conversion and EO selectivity for Ag catalysts calcined at 400°C for 1-21 hours

Effects of Transition Metal Substitution in a Microporous Titanosilicate PhotocatalystAnne Marie Shough¹, Raul F. Lobo², and Douglas J. Doren¹¹*Department of Chemistry and Biochemistry and* ²*Department of Chemical Engineering, University of Delaware, Newark, DE 19716*

ETS-10¹ is a microporous titanosilicate material with promise as a photocatalyst. It is composed of chains of TiO₆ octahedra, which act as 1-D semi-conducting wires, insulated by a SiO₂ shell. Titanium can be replaced in this structure by other transition metals, in some cases reducing the band gap and allowing excitation with visible light. We have developed computational models with varying concentrations of V, Nb and Fe dopants using a hybrid quantum mechanics/molecular mechanics (QM/MM) method. These models allow for the investigation of both bulk and end MO₆ groups within ETS-10. The first theoretical studies on metal-substituted ETS-10 materials are presented here, describing the geometric and electronic changes that occur upon transition metal substitution and their impact on the photocatalytic properties of this material.^{2,3} This work shows that increasing vanadium concentration decreases the band gap energy by lowering the conduction band, resulting in visible light photocatalytic materials at high [V]. This is consistent with experimental data. The calculations also allow assignment of features in the experimental UV-vis optical spectra to specific electronic transitions. Both V^{IV} and V^V states have been experimentally identified in V-substituted samples of ETS-10. Using the computational models, we have identified site and oxidation state preferences of substitutional V, predicted interactions between sites that may lead to clustering or structural instabilities, and discovered charge trapping sites localized on the V centers. This data suggests that substitution of V into ETS-10 will increase the photocatalytic activity at low to moderate [V] substitution and decrease it at high [V]. Additionally we find that the band gap energy and presence of electron traps can be controlled by the relative amount of V^{IV} and V^V within V-substituted samples of ETS-10, making this material a promising visible light photocatalyst. Comparable studies on Fe and Nb substituted models of ETS-10 are also presented. Finally, a statistical model has been developed, which can be used to predict the band gap lowering effect of transition metals substituted into the O-M-O chain of ETS-10. This model is a useful first step in directing more intensive computational and experimental studies to optimize the composition of ETS-10 for photocatalysis.

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Spatio-temporal Forcing of a non-linear Surface Reaction - Oxidation of CO on Pt(100)

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The oxidation of CO on Pt(100) exhibits complex, non-linear behavior, such as reaction rate oscillations and spatiotemporal adsorbate patterning¹. The current focus of our work is to investigate the dynamics of this system when it is subjected to external forcing. Using a novel gas microdosing technique to locally introduce reactants onto the catalytic surface and EMSI (Ellipsomicroscopy for Surface Imaging) to image changes in adsorbate activity, unique behavior has been observed for systems at pressures of 1×10^{-4} Torr. We are able to create metastable CO islands² under conditions where CO islands are not spontaneously formed, as well as trigger and annihilate reaction diffusion waves propagating across the surface. External forcing was also used to initiate unordinary patterning on the surface and to selectively transition a region of the surface from a monostable state into an oscillatory state.

The local dosing of several gasses (e.g. CO, O₂, NH₃, etc.) onto the catalytic surface modifies the surface in such a way as to lead to the formation of a ring shaped pattern generated by preferential adsorption of CO. Microdosing at temperatures below 125 °C resulted in a uniform CO spot on the dosed region, while dosing at temperatures above 150 °C led to initial CO adsorption on the fringe of the dosed area. Also, as the time between microdosing and the admission of CO into the reactor increases, the time required for the ring to form becomes longer.

External forcing was used to drive small areas of the surface from a monostable CO covered state into an oscillatory state. Initial reaction conditions were adjusted to produce a CO covered surface, lying close to the point at which the surface would become O saturated. Oxygen was then microdosed onto the surface creating an adsorbed O island that was eventually reacted away to leave the surface covered again with only CO. Decrease of the global CO pressure lead to the onset of oscillations, which were spatially restricted to the previously dosed regions. The oscillations persisted for several minutes until the global CO pressure was decreased to a point where the entire surface shifted to a monostable O covered state.

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Catalytic Oxidation of Methanol in Microreactors: Portable Power Generation or Syngas Generation

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Future portable and distributed energy production will happen at much smaller scales than the traditional economy of scales dominated by oil and petrochemical industry. Microchemical devices are an ideal platform to assist future energy generation due to compact size and process intensification. In this work, we present novel catalytic microreactor designs with variable gap size and thermal conductivity to overcome typical challenges at microscales. The fuel employed here is methanol, one of the simplest derivatives of bio-renewables. Methanol is heterogeneously oxidized over noble metal/anodic alumina catalysts. Depending on composition, one can use the fuel to produce either heat (fuel-lean conditions) or chemicals (fuel-rich conditions). In our system, methanol is found to be self-igniting and complete methanol combustion was achieved under fuel-lean conditions. High thermal conductivity inserts promote thermal uniformity across the reactor, allowing for optimal conditions for integrating a thermoelectric module and nearly isothermal conditions for extracting catalytic kinetics. Starting at room temperature, the combustor/thermoelectric system is shown to have a short startup time. Under fuel-rich conditions, partial oxidation at millisecond residence times is observed.

Stability of Pt-3d Bimetallic Cathode Electrocatalysts Under Oxidizing Environment

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The proton exchange membrane fuel cell (PEMFC) is one of the leading technologies for the next generation of power sources to be utilized in a wide range of applications. This technology offers high theoretical power density, high efficiency, low operating temperatures, and low vibration. One main hurdle preventing this technology from being commercially viable is the exceptionally high cost for the electrocatalysts for both the anode and the cathode. This study focuses on the cathode where the current leading electrocatalyst for the PEMFC cathode is pure Platinum for the oxygen reduction reaction (ORR)¹. The ORR reduces a stream of gaseous oxygen over an electrocatalyst to form water and complete the electrical circuit. The extraordinarily high cost of material for the cathode stems from two intertwined issues. First, due to the rarity of Platinum, its bulk cost is remarkably high in comparison to other transition metals². Second, even though Platinum has been found to have the highest activity for the oxygen reduction reaction (ORR) for pure catalysts, this activity is orders of magnitude lower than that found for other general electrode reactions such as the hydrogen oxidation reaction (HOR)³. This lower activity in turn requires the use of more expensive Platinum. One method of reducing the cost for this component of the fuel cell is to decrease the amount of Platinum loading necessary for the cathode while keeping the benefits of Platinum. This reduction of Platinum can be accomplished by replacing some of the Platinum with a cheaper transition metal such as the 3d group transition metals from Ti to Ni. In comparison to Pt, these 3d group transition metals are roughly 1000 times less expensive². Furthermore, these Pt-3d bimetallic catalysts have been shown to have superior chemical properties with higher activity for the ORR than either that of the pure parent metals. However, this increased activity has been attributed to the formation of a unique subsurface configuration where a layer of 3d group transition metal is sandwiched between the Pt bulk crystal layers and an outer “Pt-skin” layer⁴. While the increased activity for these bimetallic systems hold very promising avenues for the fuel cell industry, an issue yet to be quantified is the stability of these unique subsurface configurations in the presence of oxygen and water.

In the current study, we attempt to quantify the stability of the Pt-3d-Pt(111) subsurface electrocatalysts under an oxygen environment⁵. Experiments were performed for the Pt-Ni and Pt-Co bimetallic systems using ultra-high vacuum (UHV) techniques. The segregation of

Ni and Co was identified using high-resolution electron energy loss (HREELS). The activation barrier for the segregation of the 3d transition metal to the surface was determined using Auger electron spectroscopy (AES). The remaining Pt-3d bimetallic systems were compared using predicted thermodynamic stability calculated using density functional theory (DFT). Experimentally, the Pt-Ni subsurface configuration was determined to be more stable than the Pt-Co subsurface configuration when exposed to oxygen. Also, the Pt-Ni subsurface configuration has been predicted to be the most stable of the Pt-3d subsurface configurations when exposed to oxygen.

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Acid Site effects on the photocatalytic properties of ETS-10 & ETVS-10s toward the reduction of VOCs

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We have investigated ETS-10 and vanadium-incorporated ETS-10 as photocatalysts for the reduction of volatile organic components (VOCs) since their unique structure may help elucidate the material and surface properties needed to overcome some of the disadvantages of traditional semiconductors like anatase. ETS-10 is a microporous titanosilicate¹ composed of octahedral chains of TiO₆ embedded in a tetrahedral SiO₄ framework. These chains stack perpendicular to each other to form a 7.5 Å, three-dimensional channel structure with an ideal stoichiometry of (Na, K)₂TiSi₅O₁₃. Vanadium has been shown to substitute for the titanium along the chain forming (V/(V+Ti))ETVS-10s and can completely replace titanium forming an analogous structure to ETS-10, called AM-6.^{2,3} This incorporation of vanadium has also shown visible photocatalytic activity that has been explained experimentally and theoretically.^{4,5}

These chains of TiO₂ behave as 1D semi-conducting wires which are insulated by the SiO₂ framework. Therefore chain termination sites on the surface of the crystal or at defects along the chain play a crucial role in the electron-hole transfer from the chain to adsorbed organic molecules. Previous work has shown that ion exchange leads to an increase in chain termination for ETS-10 samples along with different photocatalytic properties.^{6,7} In this research we will determine the effects of acid site formation through NH₄ ion exchange in an attempt to maximize the photocatalytic reactivity of the ETVS-10 samples for VOCs decomposition.

Materials were characterized using X-ray diffraction (XRD), N₂ adsorption, scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), UV/vis spectroscopy, and Raman spectroscopy. A Diffuse Reflectance Infrared Fourier Transform Spectrometer (DRIFTS) coupled with a UV-lamp has been implemented to investigate the formation of electron-hole pairs upon excitation of ETS-10 and ETVS-10s.

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Thermodynamic Formation of ZSM-5

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Understanding zeolite growth mechanisms is important for further advancement in zeolite science. This work focuses on the formation of ZSM-5 through non-organic synthesis. To understand the formation of this zeolite, thermodynamics is used to quantify the relationship between the resulting zeolite and the supernatant remaining after synthesis. A complete range of Si/Al ratios for ZSM-5 formation, between approximately 10 and 50, is studied so that a complete phase equilibrium diagram can be formulated. In accomplishing this thermodynamic equilibrium equations along with regular solution theory are used. The techniques of x-ray diffraction, NMR, ICP, and small angle x-ray scattering are used in this research. Our research has shown a direct correlation between the amount of aluminum in the synthesis gel and that in the resulting ZSM-5. We have also shown that the supernatant contains exceedingly small amounts of aluminum, which implies that it is expended rapidly during the synthesis. Overall the results of this research will help in the understanding of ZSM-5 formation.