

Catalysis Club of Philadelphia Annual Student Poster Contest

March 19, 2009

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Polarization dependence of adsorption on ferroelectric BaTiO₃ surfaces

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Ferroelectric material has a net dipole associated with the bulk structure. The ability to manipulate the orientation of the dipoles in ferroelectric ceramics holds promise as a method to tailor the surface reactivity of these materials for specific applications. While over the last 50 years multiple studies have suggested that the orientation of ferroelectric domains may affect the energetics of adsorption on ferroelectric oxides, definitive evidence is still lacking. In this talk I will present the first unambiguous observations of differences in the energetics of adsorption on ferroelectric domains for adsorption of methanol, ethanol and 2-fluore-ethanol on barium titanate thin film as a model system to study polarization impact on ferroelectric surface reactivity in gas phase. Domain-dependent sticking coefficients are observed using temperature-programmed desorption (TPD). Results indicate that the ferroelectric orientation alters the strength of the interaction of adsorbed species with the surface. Furthermore, in ethanol and 2-fluore-ethanol reaction on barium titanate, the desorption peak temperature and the relative product yields were found to be polarization dependent suggesting that ferroelectric polarization may also affect the intrinsic reactivity of the surface. The polarization effect on the energetics of adsorption was quantified in the surface reaction of 2-fluore-ethanol on barium titanate.

Structure-Photocatalytic Relationships of Well-Defined TiO₂ Nanodomains

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The goal of this study was to examine the photocatalysis of well-defined TiO₂ nanodomains supported on SiO₂ and to determine their structure-photocatalytic relationships. Understanding how catalytic structure relates to photocatalytic properties (photoluminescence, electron excitation, intermediate and product formation) in these catalysts of known structure will lead to more rapid development in the discovery of improved photocatalysts for specific reactions. Thus, 1-60% TiO₂/SiO₂ catalysts were synthesized by incipient wetness impregnation of Ti-isopropoxide into the SiO₂ support (Cab-O-Sil), with drying followed by calcination at 500 °C. The molecular and electronic structures of the TiO₂ nanodomains were determined with *in-situ* Raman and UV-vis spectroscopy. The nature of the TiO₂ nanodomain was found to change in the following manner as a function of the titania loading: isolated site (1% TiO₂/SiO₂) < polymeric chain (12% TiO₂/SiO₂) < 2D sheets (20-40% TiO₂/SiO₂) < 3D nanoclusters (60% TiO₂/SiO₂). Studies were conducted using *in-situ* photoluminescence (PL) spectroscopy to determine if the type of TiO₂ nanodomain present in the sample affects the emission spectrum. Samples were dehydrated under flowing 10% O₂ at 400 °C in order to avoid the quenching effect of water on PL emission. Spectra were collected on a Jobin-Yvon Fluorolog system which also allowed collection of PL maps. Studies were also conducted *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. Production of H₂ was monitored by gas chromatography for the water splitting reaction in a UV irradiated batch reactor at room temperature.

The results show several main trends. The PL spectra show that as the percent loading of titania increases, the peak emission occurs at higher wavelength excitation, meaning those samples are more easily excited with lower energy irradiation. However, the excitation lifetime measurements indicate that the lower percent loading samples (those containing isolated TiO₄ sites) have slower decay rates, meaning there is a greater opportunity for reactions to occur. This finding offers an explanation for the observed higher production of H₂ during water splitting by the lower titania loading catalysts when normalized by exposed Ti site.

Raman and UV-Vis Spectroscopy Study of Vanadium-Containing Heteropoly Acids in Aqueous Solutions

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Introduction

To advance liquid phase spectroscopic techniques, we have selected two types of heteropoly acids (HPAs) in aqueous solutions to serve as our experimental catalysts: $H_3PW_{12}O_{40}$, (TPA-tungstophosphoric acid) and $H_3PMo_{12}O_{40}$, (MPA-molybdophosphoric acid). The cage-like structure that these HPAs assume is called the Keggin structure [1,2]. Distorted forms of the Keggin structure are also known to exist. For example, the Dawson structure is composed of two Keggin anions which have each expelled three WO_3 or MoO_3 units and joined together as a dimeric unit [1,3].

The initial objectives of this investigation were (1) to compare the ambient and aqueous solution spectra of the HPAs and (2) to determine differences or similarities in their structures between their ambient and aqueous states. Varying levels of vanadium were introduced into the primary and secondary structure of each HPA in order to investigate the influence of vanadium when the HPAs are in solution. TPA and MPA samples containing vanadium in the primary structure are denoted as TPAV $_x$ and MPAV $_x$. The chemical formulas for solid TPAV $_x$ and MPAV $_x$ are $H_{3+x}PW_{12-x}V_xO_{40}$ and $H_{3+x}PMo_{12-x}V_xO_{40}$ (where $x=1, 2, \text{ and } 3$). TPA and MPA which contain vanadia on the secondary structure are denoted as VOTPA and VOMPA.

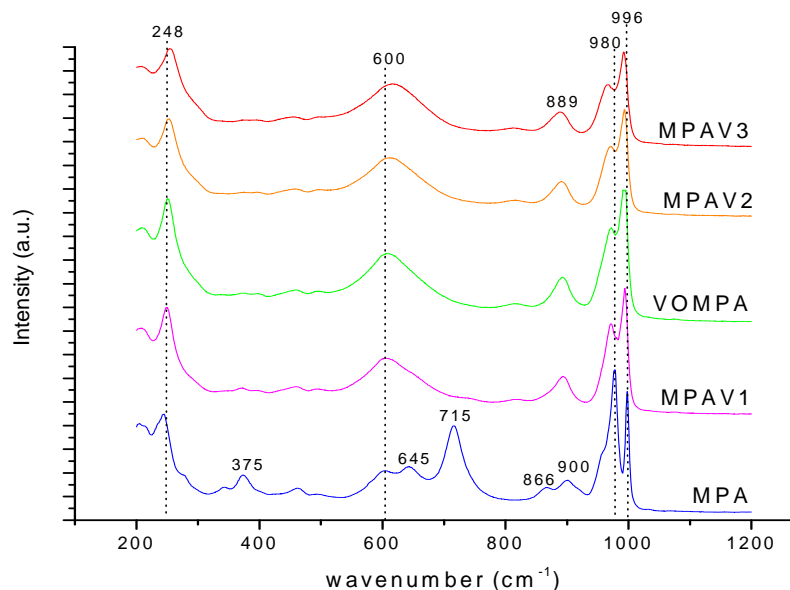


Figure 1: RT Raman spectra for 100 mM aqueous MPA, VOMPA, and MPAV $_x$ solutions.

Results and Discussion

The Raman spectra (shown in Figure 1 for the MPA series) exhibit the characteristic bands of the Keggin structure reported in the literature for both the aqueous and solid state hydrated samples [6], but the bands broaden as the vanadium content increases. This indicates that the Keggin structures remain intact in the aqueous solutions for TPA, TPAV $_x$, VOTPA, MPAV $_x$ and VOMPA, and that the addition of vanadium causes

the well-ordered Keggin structure to become somewhat disordered. The Raman spectrum for MPA in aqueous solution, however, displays an additional band at 715 cm^{-1} (see Figure 1). This

Raman band is characteristic of the Dawson structure [7] and indicates that the MPA Keggin structure in aqueous solution is unstable and breaks down to form a Dawson structure.

The E_g values for the HPAs were found to correlate with the total number of bridging bonds (V-O-Mo and V-O-W) indicating that the correlation published by Gao *et al.* is somewhat insensitive to type of neighboring metal atom in the second coordination sphere [8].

Significance

In this study we have demonstrated that the Raman and UV-vis spectra of aqueous mixed metal oxides can be readily obtained. Comparison of the ambient and aqueous solution spectra reveals that the HPAs remain intact in aqueous environments. However, MPA transforms from the Keggin to the Dawson structure in aqueous solutions. These findings set the stage for spectroscopic characterization of aqueous solutions found during biocatalysis and biomass reforming.

OPTIMIZATION OF SOLID OXIDE FUEL CELL MATERIALS BY EXPERIMENTAL DESIGN

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The electrochemical performance of intermediate temperature solid oxide fuel cell single-cells of general formula $\text{Ni/Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}|\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}|\text{Ln}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$, $\text{Ln} = \text{La, Pr, Gd}$, was optimized for the lanthanide cobaltite cathode material, the specific surface area of the anode starting powder, as well as for the amount of carbonaceous pore former in the anode in a single designed experiment (Fig. 1) combining the strengths of electrochemical impedance spectroscopy with these of mathematical statistics.

The optimal cell was found to have either an $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ or $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ cathode, an anode active layer prepared of a starting powder of SBET, powder = 135 m^2/g , and a pore former content of 2 wt%. The combination of electrochemical impedance spectroscopy (EIS), equivalent circuit fitting, and mathematical statistics methods proved to be a powerful tool for interpreting solid oxide fuel cell data.

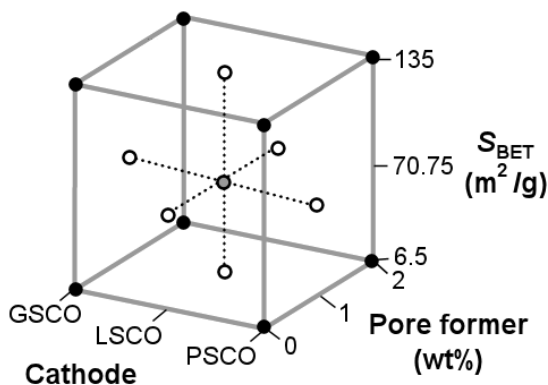


Figure 1. Schematic representation of the face-centered cubic response surface design used in this study.

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The Effect of Redox Thermodynamics on the Water-Gas-Shift Reaction over Pd/Ceria-Praseodymia

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Ceria and ceria-supported metals have been widely studied recently as catalysts for the water-gas-shift (WGS) reaction and steam reforming reactions. According to one of the leading proposed WGS reaction mechanisms, CO adsorbs on the precious-metal sites and reacts with ceria's oxygen to form CO₂, followed by desorption and ceria reoxidation by steam. Much research has also been done on modifying ceria's reducibility and while better performance has been achieved in some instances, further improvements are needed. Praseodymia (Pr₆O₁₁) and ceria-praseodymia solid solutions are known to release their loosely-bound oxygen at lower temperatures than ceria, which would appear especially favorable for a reaction such as the WGS which requires a low-temperature catalyst. This study demonstrates that although Pr doping of the support does enhance reducibility, the catalysts exhibit poor WGS performance because the associated oxygen is too reducible and cannot be easily replaced in the lattice by a reaction with steam.

Pd-promoted PrO_x and Ce_{0.5}Pr_{0.5}O_{2-x} both exhibited an order of magnitude decrease in WGS performance compared to ceria at differential reaction conditions. Despite this disparity in steady state activity, both praseodymium-based samples were observed to initially perform as well as Pd/ceria, but conversions decreased gradually over time until a lower steady state conversion was reached. Once the samples were "deactivated", higher catalytic activities could only be restored by oxidizing the Pr samples in air. Exposure to water-gas-shift conditions and the reduction of the oxides by H₂ with subsequent exposure to steam demonstrated that significantly more reoxidation occurred with ceria than either of the praseodymium-based catalysts. These results suggested that in the Pr samples, a significant amount of oxygen was consumed by CO in the WGS which cannot be replaced by steam, causing the gradual decrease in catalytic activity. Examination of the redox properties of the studied supports at significant WGS conversions determined by coulometric titration revealed that ceria is expected to be completely oxidized, PrO_x is expected to be completely reduced, and Ce_{0.5}Pr_{0.5}O_{2-x} is expected to be between the two, but deficient of the weakly-bound oxygen associated with Pr addition available for removal.

Water-gas-shift studies on Pd supported on ceria-praseodymia mixed oxides reveal the importance of selecting a support whose redox properties are suited for the reaction conditions. Although kinetics should still be foremost criteria, optimal support reducibility should lead to the most active catalysts for the WGS and other reactions.

Structure-Property Relationships of Supported Pt/Ni Bimetallic Catalysts

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Bimetallic catalysts are of great interest because they often display properties that differ from either of their parent metals. Previous studies on the Ni/Pt(111) bimetallic system have shown that the location of Ni atoms in the Pt(111) surface has a strong influence on the electronic and chemical properties of the surface. 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.

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 hydrogenation was used as a probe reaction and it was found that the bimetallic catalysts outperformed both monometallic catalysts. 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.

Controlling the Bond Scission Sequence of Methanol Decomposition on Platinum-Modified Tungsten Carbide

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Recent studies have suggested that tungsten monocarbide (WC) may behave similarly to Pt for the electrooxidation of methanol. Temperature programmed desorption (TPD) was used to quantify the activity and selectivity of methanol decomposition for WC and platinum-modified WC (Pt/WC) as compared to Pt. While WC appeared to be more active than Pt in ultra-high vacuum (UHV), C-O bond scission resulted in gas phase CH₄, an undesired reaction for DMFC. When Pt is added to WC by physical vapor deposition, the CH₄ reaction pathway is eliminated, suggesting that Pt synergistically modifies WC to improve the selectivity for reforming products. Additionally, TPD confirmed WC and Pt/WC to be more CO tolerant than Pt.

Density functional theory (DFT) was used to study the reaction network of methanol on Pt/WC(0001) as compared to Pt(100) and WC(0001). Results suggested that the bond scission sequence of CH₃OH could be controlled using submonolayer coverages of Pt on WC and that the resulting mechanism was different for Pt/WC as compared to either parent surface.

High-resolution electron energy loss spectroscopy (HREELS) verified that surface intermediates were different on Pt/WC as compared to Pt or WC and that methanol decomposition occurred at lower temperatures for the WC surfaces.

Ultimately, this study suggests that Pt-modified carbide surfaces can be used to control the bond scission sequence of small oxygenates and that WC is a more CO tolerant material than Pt; thus, WC and Pt/WC could be promising alternatives to Pt electrocatalysts for low temperature fuel cells.

Dehydrogenation of Hydroxyl Nest Groups in Silicalite-1

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A hydroxyl nest is a common defect in zeolite frameworks where a tetrahedral atom (T=Si, Al, etc.) is missing from the structure. In the absence of a T-atom a cluster of four silanol groups are left forming medium-strength hydrogen bonds with each other. Hydroxyl nests can be formed in aluminosilicate and other zeolite materials by leaching or steaming at high temperatures. Silicalite-1 synthesized in basic media is well known for containing large numbers of silanol nests. The source of silica (tetraethyl-orthosilicate or colloidal silica) has proven to be crucial in the number of missing T-atoms leading to varying sizes of these defect sites. The OH region of the IR spectra ($3760\text{-}3300\text{ cm}^{-1}$) shows two characteristic peaks that have been assigned to isolated silanol groups in the exterior and interior of the zeolite ($3760\text{-}3720\text{ cm}^{-1}$), and to hydrogen-bonded groups of silanol units that give a much broader signal centered at about 3400 cm^{-1} . Upon heating to temperatures exceeding 873K , these bands decrease in intensity, and a new triplet is formed in the $911\text{-}896\text{ cm}^{-1}$ region. Previously, the disappearance of these signals has been attributed to dehydration of the silanol groups. Using temperature-programmed-desorption (TPD), we show that the product of the dehydroxilation of hydroxyl nests in silicalite-1 (made with colloidal silica) is hydrogen and not water. We propose that the disappearance of hydrogen from the hydroxyl nests is accompanied by the formation of bisperoxysilyl groups (Si-O-O-Si). Ultraviolet-Visible Light Spectroscopy (UV-Vis) measurements support the claim of this bond formation due to an increase in an UV absorption band at $\sim 260\text{ nm}$ with increasing temperatures. Silicalite-1 samples made with tetraethyl-orthosilicate show distinctly different characteristics in their IR and UV-Vis spectra compared to samples made with colloidal silica. It appears that the source of silica plays an important role in the structure of the internal defects and thus hydrogen production capabilities.

Development of Visible Light Based Photocatalysts with Improved Band Gaps

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Introduction

Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids and include a variety of chemicals (i.e., benzene, trichloroethylene), some of which may have short- and long-term adverse health effects. Photocatalytic oxidation has the potential to decompose these VOCs but there is still considerable work to be done in the development of visible light based photocatalysts with activities comparable to standard materials such as TiO₂. Research has recently progressed in the development of various oxynitrides of Zn, Ga, Ti, Li, Ge and the combination of these metals, in the hope of preparing photocatalysts with band gaps less than 3 eV. The substitution for the orbitals of O by orbitals of N raises the energy of the highest occupied molecular orbital, and thereby lowers the band gap for catalysts with d-orbitals in the conduction band. Zinc gallium oxynitrides (ZGONs) are being investigated for the degradation of acetaldehyde. Earlier, ZGONs have been the focus of research by Domen's group who have split water under visible light upon co-loading these with RuO₂ to produce 1000 μmol/hr of H₂. The band gaps of these samples are also known to be related to the final zinc content in the sample.

Results and Discussion

The XRD patterns show that the samples prepared at higher temperatures are solid solutions of ZnO and GaN with surface areas less than 10 m²/g BET, whereas the samples prepared at lower temperatures are a combination of the two phases (confirmed also by SEM images). The bulk (ICP) and surface (XPS) zinc content are found to decrease with increasing nitridation temperatures. The surface is predominantly GaN with little ZnO. Figure 1 shows the UV – visible diffuse reflectance spectra of the samples prepared at various temperatures along with reference spectra for gallium nitride (3.4 eV) and zinc oxide (3.2 eV). The spectra for samples prepared at 650°C, 750°C & 850°C tend to red shift and the band gaps are consequently between 2.6 to 2.8 eV. The reduction in band gap is attributable to the presence of zinc acceptor levels in between the valence and the conduction bands confirmed by photoluminescence spectra. These samples are also photocatalytically active in visible light by their 60% degradation of rhodamine B dye compared to just 20% with no catalyst in 6 hours of irradiation.

Improvement of these ZGONs hinges on optimizing the zinc content, a sol-gel technique is then employed to crystallize zinc gallium oxide which is subsequently nitrided to produce a sample with a combination of the oxide and oxyniride phases having a much lower band gap (2.4 eV) attributed to lower volatilization of zinc.

Significance

ZGONs can be employed for a variety of catalytic applications, decomposition of VOCs being one; they can also be employed in air conditioning units and possibly production of H₂ from water. These photocatalysts being active in visible light also makes it unnecessary to use expensive UV light sources.

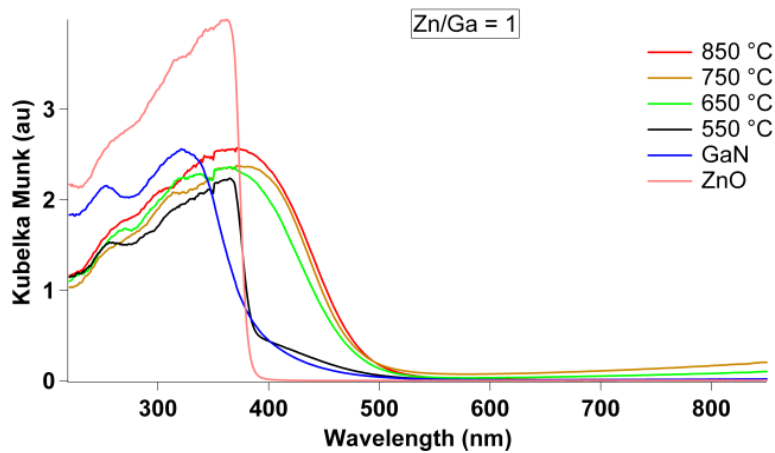


Figure 1. UV-Vis spectra of ZGONs with Zn/Ga =1

The Structure/Photocatalytic Activity Relationship of TiO₂/SiO₂ Nanocatalyst

Somphonh Peter Phivilay and Israel E. Wachs

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The relationship between TiO_x domain size and photocatalytic activity of supported TiO₂/SiO₂ catalysts was investigated in this study along with the effect of anchoring surface WO_x and VO_x species onto the TiO_x sites. The catalysts were synthesized by impregnating isopropanol solutions of titanium isopropoxide, (Ti(O-Pr)ⁱ)₄, onto the SiO₂ support. After impregnation, the catalyst samples were dried overnight and then calcined at 500 °C. The TiO₂ loading was varied between 1% and 60%. Surface WO_x and VO_x species were subsequently impregnated onto the TiO₂/SiO₂ in aqueous solutions of ammonium metatungstate, (NH₄)₁₀W₁₂O₄₁·5H₂O and isopropanol solutions of vanadium triisopropoxide VO[CHO(CH₃)₂]₃, respectively, to form WO₃/TiO₂/SiO₂ and V₂O₅/TiO₂/SiO₂ multicentered catalysts. *In situ* Raman and UV-vis spectroscopy and TEM characterization revealed that the supported TiO₂ phase varied its domain size from isolated surface species to polymeric surface species to NPs (3 - 9 nm). UV-vis spectroscopy also revealed that E_g values increased with decreasing titania domain size. The photocatalytic activity of the catalysts was determined for H₂O splitting under UV irradiation (λ > 290 nm). H₂ production was found to decrease by over an order of magnitude with increasing titania domain size. The anchoring of VO₄ species resulted in a ~9 fold increase in H₂ production and the anchoring of WO₅ species resulted in a ~14 fold increase in H₂ production. These results show that isolated TiO₄ sites are the most activity for photocatalytic H₂O splitting and the anchoring of surface VO₄ and WO₅ species leads to increased photocatalytic activity.

The Effect of Thermodynamic Properties of Zirconia-Supported Fe₃O₄ on Water-Gas Shift Activity

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Thermodynamics of oxidation and reduction were investigated in connection with reactivity studies for a series of zirconia- and alumina-supported iron-oxide catalysts, using coulometric titration to measure oxidation isotherms. For all supported samples, from weight loadings of 5-wt% (one monolayer) up to 30 wt%, the Gibbs free energy of transition between Fe₂O₃ and Fe₃O₄ has decreased by factor of 2 compared to bulk iron oxide to -109 kJ/mole at 973 K. Water-Gas Shift (WGS) reaction rates on supported iron oxide have decreased by factor of 10 or more compared to bulk iron oxide, suggesting that the changes in thermodynamic properties are related to changed in catalytic properties.

Anchoring Pt-3d Bimetallic Surfaces on Tungsten Carbide

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Bimetallic surfaces often exhibit catalytic properties that are not present on either of the parent metal surfaces. To gain insight into these novel properties, the electronic and chemical properties of Pt(111) modified by 3d transition metals were studied using a combination of experimental methods and theoretical modeling. Temperature programmed desorption (TPD) experiments were performed with various probe molecules, and density functional theory (DFT) was utilized as a tool to provide insight into the interaction between these molecules and the model surfaces. The overall objective was to correlate the electronic and chemical properties of bimetallic surfaces.

For the 3d transition metals studied (Fe, Co, Ni, Cu), deposition on Pt(111) at 300 K results in the formation of a surface configuration, 3d-Pt-Pt(111), where the first atomic layer is concentrated in the 3d metal. In contrast, when the Pt(111) substrate is held at 600 K during deposition, the 3d metal diffuses into the bulk resulting in a subsurface configuration, Pt-3d-Pt(111), where the second atomic layer is enriched in the 3d metal and the surface layer in Pt. The general results of the TPD experiments on these surfaces are that hydrogen binds weaker on Pt-3d-Pt(111) surfaces and stronger on 3d-Pt-Pt(111) in comparison to Pt(111). This is consistent with DFT calculations, which further show that several hydrocarbons, including ethylene and cyclohexene, also bind strongly to 3d-Pt-Pt(111) and weakly to Pt-3d-Pt(111). These results help to explain the unique hydrogenation activity and selectivity on the Pt-3d-Pt(111) surface as determined by TPD experiments with cyclohexene and acrolein, respectively.

From these results it was evident that Pt-3d-Pt(111) surfaces are active for hydrogenation reactions, with Pt-Ni-Pt(111) having the highest activity for cyclohexene and acrolein hydrogenation. With this insight, and the idea that WC has demonstrated similar electronic properties to Pt, it was desired to replace bulk platinum in the Pt-Ni-Pt(111) surface with WC. Using WC to replace Pt has two important benefits. The obvious one is cost. Perhaps more important, however, is the fact that WC is an effective diffusion barrier layer. This property prevents the diffusion of Pt and Ni into the bulk of a tungsten carbide substrate at elevated temperatures, which is crucial to applications in heterogeneous catalysis. TPD experiments have been performed on WC and Pt and/or Ni-modified WC substrates, and these results are compared to those on Pt(111) surfaces. In doing so, it was found that the Pt-Ni-WC and Pt-Ni-Pt(111) surfaces have qualitatively similar chemical properties.

Structure and colloidal stability of nanosized zeolite beta precursors

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The crystal growth of zeolite beta in solutions of molar composition $1 \text{ Si}(\text{OCH}_2\text{CH}_3)_4 / 80 \text{ H}_2\text{O} / 0.5 \text{ TEAOH} / 0.1 \text{ NaOH} / 0.02 \text{ NaAlO}_2$ proceeds by aggregation of nanosized zeolite precursor particles near zeolite nucleation (between 6 and 20 days heating at 120°C) and by solution mediated monomer dissolution an addition after 20 days of heating. Amorphous silica nanoparticles ($< 3 \text{ nm}$) form spontaneously in solution at room temperature. When these solutions are heated some of the primary particles transform into larger secondary particles (6 - 50 nm). After 4 days of heating some of the secondary particles are stable as spheroidal monomers and others are unstable and aggregate. In the absence of aluminum the monomers have a mean diameter of $16.2 \pm 0.3 \text{ nm}$ and less than 5 percent have aggregated. In the presence of aluminum the monomers have a mean diameter of $9.4 \pm 0.2 \text{ nm}$ and about half of the particles have aggregated. The long-range and short-range order of the silica tetrahedra comprising these secondary particles is similar to amorphous (Ludox HS) silica but their composition is similar to zeolite beta showing that organization of the silica tetrahedra occurs after structure directing agents are occluded into the precursor particles. It appears that the secondary particles evolve structurally over the induction time of the synthesis from amorphous silica to zeolite beta. Simultaneously, the surface charge of the particles is changing and those particles that are highly organized aggregate among themselves forming tertiary particles (zeolite beta crystals). Other more amorphous secondary particles are electrostatically stable and remain in solution. The secondary population of particles continues to aggregate into crystalline tertiary particles over a period of a few days until they are depleted. The coherence length of the zeolite beta crystal structure increases between 6 to 30 days of heating. After 20 days of heating aluminum is depleted from solution. Electrostatically stable precursor nanoparticles ($< 3 \text{ nm}$) remain in solution. Other less stable primary particles are consumed after 20 days of heating as the zeolite beta crystals ripen into well organized square bipyramidal zeolite beta. This mechanism for zeolite beta nucleation is different from classical nucleation theory where the crystalline order changes simultaneously with the density since we have observed that there is a step wise aggregation of zeolite beta precursor particles and continuous evolution of their structure to zeolite beta.

Gas-phase coupling of reactive surfaces by oscillating reactant clouds

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The collective, global behavior of a catalytic system depends on the effective communication of local reactivity variations to distant points in the system. One particularly efficient mode of communication occurs via partial pressure fluctuations in the gas-phase above the catalytically active surface. This gas-phase coupling mode is widely considered to be most effective under vacuum conditions, where the mean free path between molecular collisions is relatively large. However, this hypothesis has gone untested over the years due to a number of experimental challenges associated with systematically creating and characterizing spatially resolved catalytic activity. In this study, we take advantage of a spatially distributed system of spatially isolated chemical oscillators to investigate the details of gas-phase communication for heterogeneous systems in the 10^{-3} Torr range. Characterization of local gas-phase variations, in conjunction with local kinetic activity on the surface, provided a novel description of the surface/gas-phase interaction which differs from the conventional assumption of a gradient free, molecular flow environment near the surface. This analysis provides, for the first time, a quantitative estimate of the effective gas-phase coupling length in a heterogeneous system. This coupling length was found to be in agreement with surface imaging results which qualitatively showed coupling between oscillators.

Nanoporous Carbon Mediated Shape Selective Catalysts

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Synthesis of nanoporous carbon with controlled pore size distribution is paramount in the development of carbon based supports and adsorbents for catalysis and gas storage applications. Herein, we have synthesized nanoporous carbon derived from polyfurfuryl alcohol. The pore size distribution was optimized for specificity. The carbon is tuned to perform as a shape selective catalyst support for liquid phase hydrogenation. We have shown that the parameters influencing the synthesis of the polymer precursor such as polymerization temperature, types of solvent used, and curing have a profound effect on the yielding porosity of the nanoporous carbon after pyrolysis at high temperatures.

Specifically, 4nm Pt nanoparticles are formed by reducing platinum acetylacetonate in furfuryl alcohol, the monomer, under refluxing conditions. This solution is then polymerized and the yielding polymer is cured at 100°C. The cured, rigid polymer inhibits the sintering of the Pt nanoparticles during pyrolyzation at 800°C over inert gas for 6 hours. This resulted in sequestering the active sites within the pore structure of the carbon. The Pt nanoparticles are kinetically frozen in the carbon network thus resisting sintering even at forced conditions, 900°C. The pore network induces shape and size selectivity based on molecule configuration with respect to pore opening and pore wall constraints. The pore structure is easily manipulated by the solvent used in the synthesis. It was determined that Triton X-100, a non-ionic surfactant, resulted in the right combination of micropores and mesopores to perform liquid phase hydrogenation reactions of alkenes. We have explored the effect of Pt nanoparticles on the polymer during carbonization, particularly, its role in pore formation. The size and shape selectivity of these catalysts were thoroughly analyzed in terms of their reactivity with respect to alkene chain length, excluded volume, position of double bonds and stereoregularity. The synthesized catalysts were extensively characterized using XRD, TEM, H₂ Chemisorption, Gas adsorption tests (Nitrogen and Methyl Chloride) and TGA-MS.

A Computational Study of Oxygenate Thermal Decomposition and Reforming

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There has been recent interest in the utilization of biomass for renewable energy and chemical production. Development of distributed, catalytic reforming technology can lead to improved conversion, higher hydrogen product selectivity, and faster reaction rates over the current large-scale biomass reforming processes. Increased domestic distribution in biomass utilization can also decrease transportation inefficiencies and increase national energy security. Microkinetic modeling can provide insight into the surface reaction mechanisms of oxygenate thermal decomposition and reforming. Model results can be applied to reactor design and catalyst optimization for conversion of biomass to hydrogen.

A surface reaction mechanism consisting of 122 reversible elementary reactions has been developed to model thermal decomposition and reforming of ethylene glycol and methanol on a Pt(111) catalyst surface. Thermochemical properties of reaction intermediates were calculated using both quantum mechanical and statistical mechanical methods. Order of magnitude estimates of pre-exponential factors were tuned to published experimental data. Preliminary results and analysis will be presented.

Scale-out of Microreactor Stacks for Syngas Production from Methane

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Microreactor technology is an attractive means to intensify methane-to-syngas production processes as microreactors have shorter characteristic heat and mass transfer distances relative to conventional methane-to-syngas reactors. Current industrial syngas production processes are characterized by contact times on the order of seconds while syngas generation processes using microreactor technology have demonstrated reaction time scales on the order of milliseconds. In this work a scale-out strategy for microreactor stacks with alternating combustion and reforming channels with sub-millimeter gap size is proposed. Microreactor geometries were simulated using the computational fluid dynamics (CFD) software package Fluent® and catalytic surface reaction rates were implemented using recently published reduced rate expressions derived from microkinetic modeling for methane combustion over Pt and methane steam reforming and water-gas-shift reactions over Rh. Using this model, microreactor stacks of several sizes were studied under varying degrees of heat loss by changing the external heat loss coefficient. The maximum heat loss of a stack occurs at the critical heat loss coefficient and this quantity was used to compare the stability of the different stacks. It was found that for a given set of flow rates and material properties, there is a minimum stack size below which methane combustion cannot be sustained and thus the stack will not function. For a wall thermal conductivity of 100 W/m-K, the minimum size was seven channels while at 23 W/m-K the minimum size was eleven channels. The behavior of individual channels within one stack was investigated in order to understand the extinction mechanism as well as heat generation and consumption within the stacks. It was found that near the critical heat loss coefficient of the stack, methane conversion within the combustion channel closest to the stack edge drops significantly and upon further heat loss combustion in this channel dies and causes extinction of the entire stack.

Zn modification of the reactivity of Pd(111) towards alcohols, aldehydes and formates

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Methanol and ethanol have been proposed as 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. Pd/ZnO is one potential catalyst for this reaction since it exhibits an 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. Pd/ZnO also exhibits high selectivity to CO₂ for the steam reforming of ethanol. Recent results from our group have identified the alloying of Pd and Zn as a significant step in the activation of the Pd/ZnO catalyst. In this poster, we will present TPD and HREELS studies on the adsorption and reactivity of alcohols, aldehydes and formate on model catalysts consisting of sub-monolayer amounts of Zn on Pd(111). Overall, these studies provide new fundamental insight into how Zn alters the reactivity of Pd and provides evidence of the intriguing reactivity of small coverages of Zn in the Pd lattice, providing information which might be useful in elucidating the mechanism of the steam reforming of alcohols on Pd/ZnO.

Using Aberration-Corrected HAADF Imaging to Develop Structural Models for Multicomponent Mo-V-M-O (M=Nb or Ta, Te) Complex Oxide Catalysts

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In our work, we use high-angle annular dark-field (HAADF) STEM imaging to develop preliminary structural models for several Mo-V-M-O (M=Nb or Ta, Te) complex oxide catalysts used for the selective oxidation of light alkanes. Current processes used to produce high-demand C3 derivatives, namely acrylic acid and acrylonitrile, require the use of multicomponent bismuth molybdates with propene as the feed. Significant cost savings can be achieved by replacing propene with propane. Top candidates for this replacement are based on the multiphase Mo-V-O based materials and the best current formulation is the MoVTenbO complex oxide system. The optimal MoVTenbO catalysts with respect to selectivity and activity are two-phase mixtures comprised of an orthorhombic network bronze (M1) and a hexagonal tungsten bronze (HTB)-type phase (M2). By using HAADF imaging and applying the Z^2 contrast approximation, we are able to evaluate several catalyst formulations and estimate the chemical composition of individual atomic columns, the atomic coordinates of the metal framework, and the occupancy of the intercalation species enclosed within polyhedral rings. Using the structural models for several different Mo-V catalyst formulations, we can begin to develop structure-property relationships that connect catalytic performance to trends in crystal structure, active site composition, or the inclusion/exclusion of various substitutional elements. Furthermore, these HAADF-derived models can be developed in short periods of time (~1-2 weeks) and can serve as starting models for rigorous refinements that otherwise may require several months or even years to complete due to difficulties in estimating the large number of parameters necessary for full structure refinement. Rapid evaluation of complex catalyst formulations can assist with efficient assessment of relationships between crystal chemistry, structure, and catalyst performance.

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

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

The mechanism consists of 12 elementary reaction steps and 5 surface species, namely N, H, NH, NH₂, and NH₃. For many of the metals, a large portion of the surface is covered by adsorbates. For these metals, repulsive adsorbate-adsorbate interactions were expected to change the binding energies of the surface species, thereby changing the elementary reaction activation barriers and modifying the catalytic activity. 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. and activation barriers were calculated through the bond-order conservation (BOC) method.

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. The maximum activity was found at a nitrogen heat of chemisorption of approximately 136 kcal/mol.

A DFT study of nitrogen binding energies on Pt-3d bimetallic surfaces showed a binding energy of 138 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, currently the most active single metal catalyst.

Synthesis of Pt-modified Tungsten Monocarbide and Its Activity Towards the Hydrogen Evolution Reaction

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Hydrogen has been touted as the energy carrier of the future because it represents a means for carbon-free energy storage and can be produced from biomass or water using renewable energy. When produced from water in an electrolyzer or photoelectrochemical cell (PEC), $\text{H}_2(\text{g})$ is evolved at the cathode via the hydrogen evolution reaction (HER) while water is split at the anode to produce $\text{O}_2(\text{g})$. For electrolysis in acidic solutions, the best HER catalysts are precious metals such as Pt, Rh, and Pd, but their prohibitively high costs and limited supplies are major hurdles for the widespread production of H_2 by this means. One approach for overcoming this challenge is to disperse the active precious metal catalyst in sub-monolayer or monolayer coverages on a low-cost, stable, supporting catalyst.

In this work, we investigate the performance of tungsten monocarbide (WC), modified by sub-monolayer amounts of Pt, as a HER catalyst. WC is an attractive material for this purpose, as it has shown an appreciable activity for the HER, is known for its electrocatalytic stability in acidic solutions, and has demonstrated synergistic effects when combined with Pt as an electrocatalyst. In recent years, several research groups have reported high HER activity for Pt-modified tungsten carbides in acidic solutions, but these carbides are phase mixtures of WC, WC_{1-x} , and W_2C . One of the goals of our research is to distinguish between the effectiveness of these various carbide phases as HER catalysts. Initial studies have looked at the activity of phase-pure WC and Pt-WC thin film electrodes for the HER in 0.05 M H_2SO_4 . The composition and phase purity of these films has been verified using XPS and GIXRD, and their activity towards the HER investigated using a unique set-up which allows for XPS analysis of electrode surfaces before and after electrochemistry without being exposed to atmospheric conditions. This set-up consists of a UHV chamber where samples are synthesized and characterized, and a side chamber where electrochemistry is performed in an inert N_2 environment. Using this set-up, linear sweep voltammetry (LSV) measurements show a significant improvement in WC HER activity upon modification by sub-monolayer Pt. Current work is focused on investigating the effect of different coverages of Pt on the HER activity on WC and its comparison to polycrystalline Pt foils.

Catalysis Science of Bulk Mixed Metal Oxide Catalysts: An Operando IR-TPSR Spectroscopic Study

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The bulk iron-molybdate ($\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$) catalyst is widely used for commercial production of HCHO from CH_3OH . Recently, FeVO_4 has been studied for the same process and found to be a promising alternative to $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ because of its stability and selectivity at high reaction temperature. In the present investigation, the catalytic science of bulk mixed metal oxides have been studied (with FeVO_4 model) by employing *Operando* temperature programmed surface reaction-Infrared spectroscopy (TPSR-IR) with well defined V_2O_5 , Fe_2O_3 , FeVO_4 , and supported $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ catalysts. Raman spectroscopy confirmed the phase purity of bulk metal oxides and the exclusive presence of a surface V_2O_5 monolayer on the Fe_2O_3 support. The *Operando* IR-TPSR spectroscopes showed the presence of CH_3O^* and Lewis methanol intermediate species on bulk Fe_2O_3 surface and their subsequent conversion to dimethyl ether and methanol/HCHO products respectively. However, predominantly CH_3O^* intermediate species were observed for V_2O_5 , FeVO_4 and monolayer $\text{V}_2\text{O}_5/\text{Fe}_2\text{O}_3$ catalysts. They exclusively form HCHO product from exposed surface VO_x sites. The TEM images also confirmed the presence of an amorphous surface layer for FeVO_4 catalyst. The selectivity and activity of FeVO_4 are comparable with that of industrial $\text{Fe}_2(\text{MoO}_4)_3\text{-MoO}_3$ catalyst, which has a problem of MoO_3 volatilization at high reaction temperatures. Therefore, the surface of bulk mixed metal oxide catalyst FeVO_4 is enriched with active and stable VO_x species, responsible for methanol oxidation to formaldehyde.

Size Optimization of Ru Nanoparticles for the Generation of CO_x-free H₂ from Ammonia

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The on-board generation of hydrogen for mobile fuel cell applications by the decomposition of ammonia boasts high H₂ storage density and zero CO_x emissions, rendering this option superior to many other proposed H₂ storage alternatives. Since NH₃ can in principle be synthesized using completely green processes, the environmental benefits are clear. However, in order to realize ammonia decomposition as an economically viable possibility for mobile hydrogen delivery, discovery of an inexpensive catalyst that is active at low temperatures is paramount. Supported alkali-promoted ruthenium (Ru) is known to be the most active ammonia decomposition catalyst. In addition, it has been proposed through modeling efforts that the formation of highly active Ru reaction sites is highly dependent upon particle size. Toward this end, we have directed our efforts to optimizing a K-promoted Ru system that was found to form a single crystal morphology belonging to the Hollandite family of structures. Recently, we have sought to systematically control Ru particle size using microemulsion synthesis.

The catalyst containing Hollandite improved catalyst performance at 350°C from 10% NH₃ conversion in the case of the unpromoted catalyst to over 65% in the Hollandite-containing catalyst. Formation of Hollandite was found to depend on promoter weight loading and for a 4 wt% Ru catalyst, the optimum K loading was 12 wt%. The apparent promotional mechanism is primarily structural, as Hollandite breaks down in reducing preparation conditions and Ru dispersion changed with K loading. Through manipulation of the co-surfactant concentration in the microemulsion, we have achieved control of the size of the reverse micelles between approximately 25 and 2.5 nm to limit the particle size growth of Ru clusters. Our initial studies indicate that by using a Ru catalyst synthesized using microemulsions, a reduction in the T₅₀ from a Ru catalyst synthesized using wet impregnation of 100°C is achievable.

La-doped SrTiO₃-based Composite Anode of SOFC Prepared by Infiltration

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Composite anode formed by infiltrations of 45-wt% La_{0.3}Sr_{0.7}TiO₃ (LST), 5-wt% ceria, and 0.5-wt% Pd into 65% porous yttria-stabilized zirconia (YSZ) were examined for application as solid oxide fuel cell (SOFC). The structure of the LST deposits was strongly affected by the calcination temperature. For example, the LST formed loosely-packed, 0.1- μ m particles that filled the YSZ pores when it was calcined to 1373K. The conductivity of this composite was greater than 0.4 S/cm after heating to 1173 K in humidified (3% H₂O) H₂. Following calcination at 1573 K, the LST had sintered significantly, decreasing the conductivity of the composite by a factor of approximately 5. Microstructural changes of LST on YSZ with temperature will be discussed with the AFM observation of LST particles behavior on YSZ single crystal. The presence of a catalyst was critical for achieving reasonable electrochemical performance. With the addition of Pd and CeO₂, the powder density of the identical cells increased from 20 mW/cm² to 780 mW/cm² for operation in humidified (3% H₂O) H₂ at 1073 K.

Undergraduate

The High Temperature Water-Gas Shift Over Supported CrO₃/Fe₂O₃ Catalysts

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The high temperature water-gas shift reaction is commercially conducted over Cr₂O₃*Fe₂O₃ (~10% CrO₃) catalysts. A series of model supported CrO₃/Fe₂O₃ catalysts were prepared by aqueous impregnation of Cr-nitrate onto a Fe₂O₃ support and subsequent calcination at 350 °C. The molecular structures and surface chemistry of the supported CrO₃/Fe₂O₃ catalysts (1, 2, 3, 5, 7 and 9% CrO₃) were investigated by combined in situ Raman and IR spectroscopy under dehydrated conditions. The in situ Raman and IR studies revealed that surface CrO_x species are present as a two-dimensional monolayer on the Fe₂O₃ support. Crystalline Cr₂O₃ nanoparticles, however, are not formed above monolayer coverage (~3% CrO₃/Fe₂O₃) as is normally the case. It appears that the excess Cr₂O₃ formed a solid solution with the isostructural Fe₂O₃ support. Analysis of the OH region revealed the formation of acidic surface OH groups in the CrO_x monolayer. The surface chemistry of these catalysts were chemically probed with IR spectroscopy of adsorbed CO, CO₂, and HCOOH monolayers. The surface HCOO* is frequently invoked as a reaction intermediate for the WGS reaction. The supported CrO₃/Fe₂O₃ catalysts were found to weakly interact with CO, while surface bicarbonates were shown to decompose to surface HCOO* by room temperature on supported CrO₃/Fe₂O₃ catalysts, but not on the support itself. The IR analysis of HCOOH showed that surface HCOO* are present and their reactivity was a function of the catalyst composition. The steady-state WGS shift reaction was investigated at high temperatures with *operando* IR spectroscopy (simultaneous spectroscopic and reaction conversion analysis). These fundamental experiments provide new insights into the WGS reaction mechanism over supported CrO₃/Fe₂O₃ catalysts that will be elaborated upon.