

**The Catalysis Club of Philadelphia**  
**2013 Student Poster Contest**

**Thursday, October 24, 2013**

**DoubleTree Hotel**

**4727 Concord Pike, Wilmington, DE 19803**

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## An *Operando* Molecular Spectroscopic and DFT Calculation Investigation of Methane Aromatization by Supported Mo/ZSM-5 Catalysts

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Supported Mo/ZSM-5 catalysts are able to convert methane to aromatics, but despite intensive studies many fundamental issues still remain unresolved: nature of supported Mo species on ZSM-5 (monomer, dimer or cluster), anchoring site(s) of Mo species (Al-Al, Al-Si or Si-Si), and active Mo phase during CH<sub>4</sub> activation (MoO<sub>x</sub>, MoO<sub>x</sub>C<sub>y</sub>, MoC<sub>y</sub> or Mo<sub>2</sub>C).

This study aims to resolve the fundamental issues for CH<sub>4</sub> dehydroaromatization (DHA) by supported Mo/ZSM-5 catalysts with the application of *in situ* and *operando* spectroscopy (Raman, IR, UV-vis, XANES/EXAFS) and DFT calculations for a systematic series of catalysts (Si/Al from 1/15-1/140 and 1-5% MoO<sub>3</sub>). *In situ* UV-vis DRS revealed that the initial supported MoO<sub>x</sub> are exclusively present as isolated surface sites on the ZSM-5 support. Combined *in situ* Raman spectroscopy and DFT calculations, however revealed the presence of four distinct surface MoO<sub>x</sub> structures on the Mo/ZSM-5 support: 1) isolated dioxo (O=)<sub>2</sub>MoO<sub>2</sub> surface site over two Brønsted acid sites at low Mo loading and high Al content; 2) isolated dioxo (O=)<sub>2</sub>MoO<sub>2</sub> surface site over one Brønsted acid site and an adjacent Si-OH group at increasing Mo loading; 3) isolated dioxo (O=)<sub>2</sub>MoO<sub>2</sub> surface site over two Si-OH groups at low Al content; 4) isolated mono-oxo O=MoO<sub>4</sub> surface site over extra framework Al-OH groups at high Al content. *In situ* FT-IR showed that MoO<sub>x</sub> prefers to anchor at Brønsted acid sites at low Mo loading, and at Si-OH and external Al-OH groups at higher Mo loading and low Al content. The addition of MoO<sub>x</sub> to ZSM-5 also induces dealumination and forms extra-framework Al<sub>2</sub>O<sub>3</sub> NPs. Kinetic studies and DFT calculations demonstrate that the surface MoO<sub>x</sub> sites anchored at Al sites are the catalytic active site because of their much lower activation energy for activating methane. During CH<sub>4</sub> DHA, *Operando* Raman and EXAFS/XANES spectroscopy indicate that the surface MoO<sub>x</sub> sites become reduced to MoO<sub>x</sub>C<sub>y</sub> when aromatics are formed during the CH<sub>4</sub> DHA reaction. The MoO<sub>x</sub>C<sub>y</sub> sites activate CH<sub>4</sub> to C<sub>2</sub> hydrocarbons and the ZSM-5 Brønsted acid sites oligomerize the C<sub>2</sub> fragments to aromatics. These new studies demonstrate how systematic studies with modern approaches to catalysis research are able to resolve the fundamental issues of complex catalytic systems.

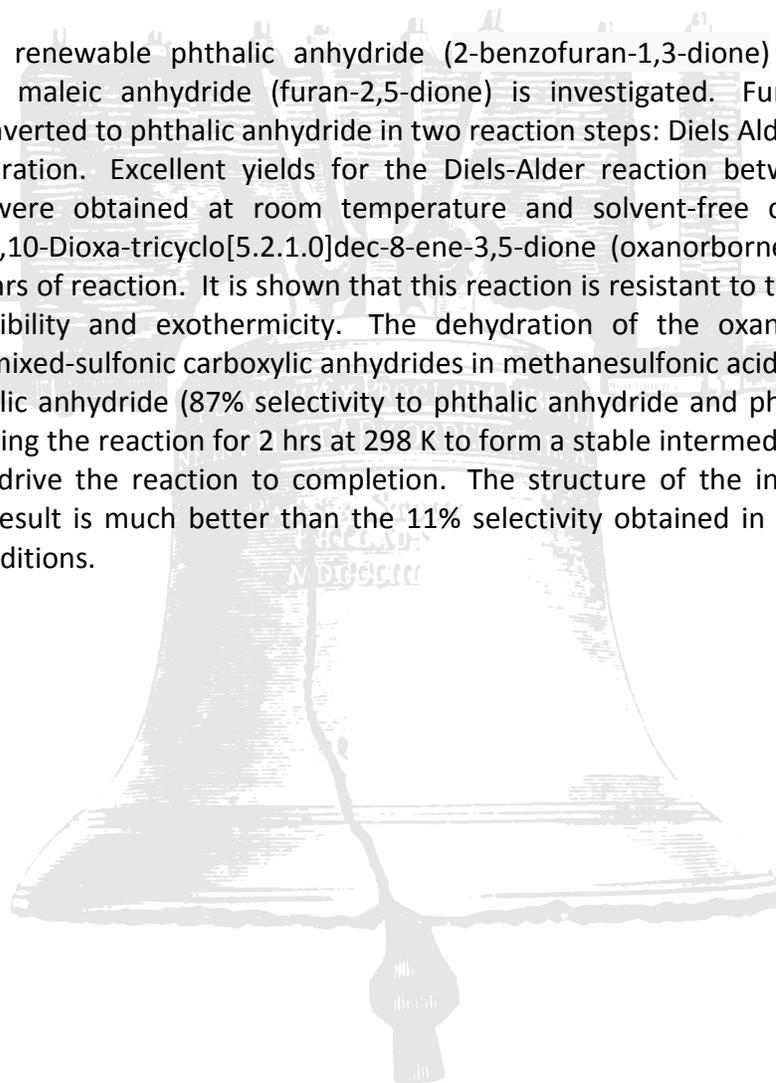
## Renewable Production of Phthalic Anhydride from Biomass-Derived Furan and Maleic Anhydride

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A route to renewable phthalic anhydride (2-benzofuran-1,3-dione) from biomass-derived furan and maleic anhydride (furan-2,5-dione) is investigated. Furan and maleic anhydride were converted to phthalic anhydride in two reaction steps: Diels Alder cycloaddition followed by dehydration. Excellent yields for the Diels-Alder reaction between furan and maleic-anhydride were obtained at room temperature and solvent-free conditions (SFC) yielding 96% *exo*-4,10-Dioxo-tricyclo[5.2.1.0]dec-8-ene-3,5-dione (oxanorbornene dicarboxylic anhydride) after 4 hrs of reaction. It is shown that this reaction is resistant to thermal runaway because its reversibility and exothermicity. The dehydration of the oxanorbornene was investigated using mixed-sulfonic carboxylic anhydrides in methanesulfonic acid (MSA). An 80% selectivity to phthalic anhydride (87% selectivity to phthalic anhydride and phthalic acid) was obtained after running the reaction for 2 hrs at 298 K to form a stable intermediate followed by 4 hrs at 353 K to drive the reaction to completion. The structure of the intermediate was determined. This result is much better than the 11% selectivity obtained in neat MSA using similar reaction conditions.

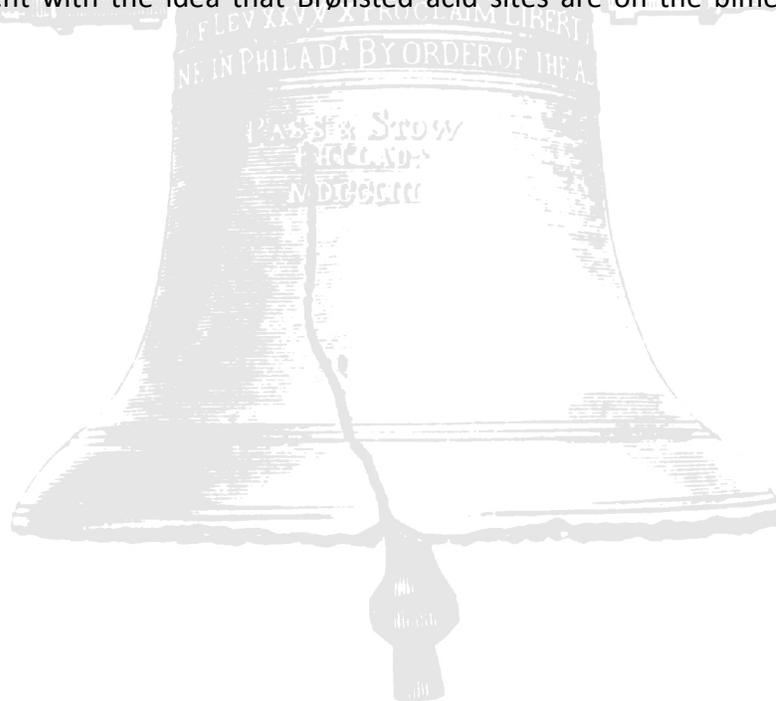


## A Mechanistic Investigation of Selective Glycerol Hydrogenolysis

*Derek D. Falcone and Robert J. Davis*

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Several chemical intermediates can be derived from renewable glycerol, a byproduct of the biodiesel transesterification process. In this work the selective hydrogenolysis of the secondary C-O bond in glycerol to produce 1,3-propanediol was studied over Pt-Re bimetallic catalysts. Prior work has suggested that a Brønsted acid site is associated with the Re component in liquid water, which catalyzes the dehydration reaction at the secondary carbon of glycerol. Rhenium also promoted the rate of glycerol hydrogenolysis by more than an order of magnitude compared to monometallic Pt. Nevertheless, the role of Re is still a matter of debate in the literature. In this work, ATR-FTIR spectroscopy was used to characterize the acidity of Pt-Re nanoparticles supported on silica using aqueous pyridine as an acid probe. In addition, batch reaction experiments showed that dilute NaOH substantially decreased the rate of glycerol hydrogenolysis, presumably by the neutralization of acid sites on the catalyst. These results are consistent with the idea that Brønsted acid sites are on the bimetallic catalyst in liquid water.



## ***In situ* Raman and UV-Vis Diffuse Reflectance Spectroscopy (DRS) of the Phillips catalyst for ethylene polymerization**

*Anisha Chakrabarti and Israel E. Wachs*

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In the early 1950s at Phillips Petroleum Company, J.P. Hogan and R.L. Banks discovered that ethylene could be converted to high-density polyethylene (HDPE) by supported Cr/SiO<sub>2</sub>, known as the Phillips catalyst. This catalyst is now responsible for over half of the production of HDPE sold globally. The reason for the widespread use of the Phillips catalyst lies in its ability to synthesize over 50 different types of HDPE and linear low-density polyethylene (LLDPE), without the use of additional activators, which simplifies the catalyst preparation and production process. The process is also important because HDPE is produced at lower temperatures (65-180°C) and atmospheric pressure. The supported Cr/SiO<sub>2</sub> polymerization catalyst has been one of the most studied catalysts, but the same fundamental structural and mechanistic questions are still being debated today with researchers being no closer to a common view. For example, the initial molecular structure of the surface chromia(+6) site has been proposed to be isolated dioxo CrO<sub>4</sub>, isolated mono-oxo CrO<sub>5</sub> and dimers of Cr<sub>2</sub>O<sub>7</sub> and its oxidation state to reduce to Cr(+2) or Cr(+3) during ethylene polymerization.

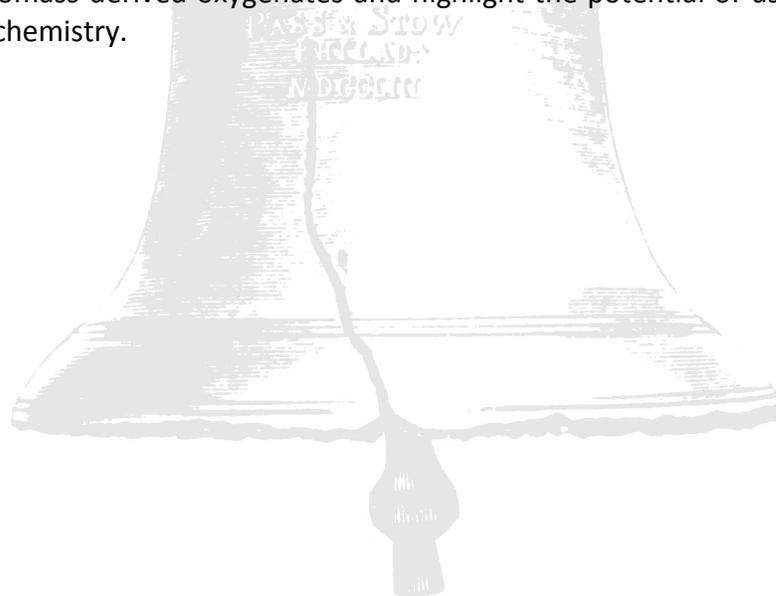
The initial supported Cr/SiO<sub>2</sub> catalyst was characterized with UV-vis and Raman spectroscopy to determine the molecular nature of the surface chromia(+6) site. UV-vis spectroscopy exhibited a high edge-energy consistent with only isolated surface chromia sites and Raman spectroscopy revealed the presence of two distinct surface chromia sites: dioxo CrO<sub>4</sub> and mono-oxo CrO<sub>5</sub>. Raman spectroscopy during the ethylene polymerization reaction demonstrated that the surface dioxo CrO<sub>4</sub> site is more reactive than the surface CrO<sub>5</sub> site for this reaction. The corresponding UV-vis analysis showed that the surface chromia sites become partially reduced during ethylene polymerization reaction conditions. This poster will address the structure-activity relationships of the catalytic active chromia sites present on SiO<sub>2</sub> for ethylene polymerization.

## Zn Modification of Pt(111) for the Hydrodeoxygenation of Aldoses

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The high oxygen content and multiple functional groups in biomass-derived platform molecules like glucose pose an interesting reaction engineering challenge for the conversion of biomass to value-added fuels and chemicals. The key to understanding the reaction pathways necessary for these conversions lies in elucidating reaction active sites on catalytically relevant surfaces and identifying the role of each functionality exhibited by the feed molecule in the reaction mechanism. In this study, temperature programmed desorption (TPD) and high resolution electron energy loss (HREEL) spectrometry are utilized to probe the reaction pathway of the biomass-relevant glucose molecule, as well as model aldoses glyceraldehyde and glycolaldehyde, and simple aldehyde acetaldehyde on a Pt catalyst surface. The effects of modification of the Pt(111) surface with oxyphilic Zn adatoms are explored with regard to hydrodeoxygenation chemistry, and reaction mechanisms are proposed. With all molecules studied, it was found that Zn addition to Pt(111) resulted in an increase in the barrier for C-H and C-C scission, as well as notable activity for deoxygenation at the aldehyde oxygen as a function of polyalcohol content. These results help elucidate the role of multiple alcohol functionalities in biomass-derived oxygenates and highlight the potential of using alloy effects to modify catalytic chemistry.



## The Coupling of Ethanol to Butanol over Calcium Hydroxyapatites

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The use of corn-based bioethanol as a domestic and renewable transportation fuel alternative has led to a recent surge of ethanol production in the United States. This increased availability combined with reduced market prices has made ethanol an economically viable platform feedstock for higher-value fuels and chemicals, such as butanol. Butanol is an important industrial chemical commodity and has recently generated interest as a potential gasoline fuel additive because of its high energy density and ability to improve fuel economy for biofuel blended gasoline.

The catalytic conversion of ethanol to butanol is thought to occur via the Guerbet reaction – a well-known industrial route for higher alcohol synthesis that ultimately couples two short-chain alcohol molecules to produce a longer chain saturated alcohol. The most commonly-accepted path for this reaction involves an initial dehydrogenation of ethanol to form acetaldehyde, which then undergoes an aldol condensation reaction followed by hydrogenation of the resulting unsaturated condensation products. Recent reports have demonstrated that the highest activity and butanol selectivity in ethanol coupling reactions can be obtained over hydroxyapatite (HAP) catalysts [1]; however the active site on these materials is unknown, which complicates catalyst design and optimization. This work explores the surface acid and base sites on calcium hydroxyapatite to determine their influence on catalytic performance during the Guerbet coupling of ethanol.

Ethanol conversion studies were performed at atmospheric pressure in a gas-phase, fixed-bed reactor system equipped with an on-line gas chromatograph. Acid and base sites of the catalytic materials were characterized using adsorption microcalorimetry of probe molecules such as NH<sub>3</sub> and CO<sub>2</sub>, as well as diffuse reflectance FT-IR spectroscopy (DRIFTS) during stepwise temperature programmed desorption (TPD) and during reaction at elevated temperatures. Results from TPD indicated that the ethanol is weakly held to the HAP surface compared to that on MgO, which is consistent with the affinity of the surface for other adsorbates as probed by adsorption microcalorimetry [2]. Results from characterization and reactivity testing will be used to determine important structure-function relationships for HAP materials.

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[1] Tsuchida, Takashi, Shuji Sakuma, Tatsuya Takeguchi, and Wataru Ueda. "Direct synthesis of n-butanol from ethanol over nonstoichiometric hydroxyapatite." *Industrial & engineering chemistry research* 45, no. 25 (2006): 8634-8642.

[2] Birky, Theodore W., Joseph T. Kozlowski, and Robert J. Davis. "Isotopic transient analysis of the ethanol coupling reaction over magnesia." *Journal of Catalysis* 298 (2013): 130-137.

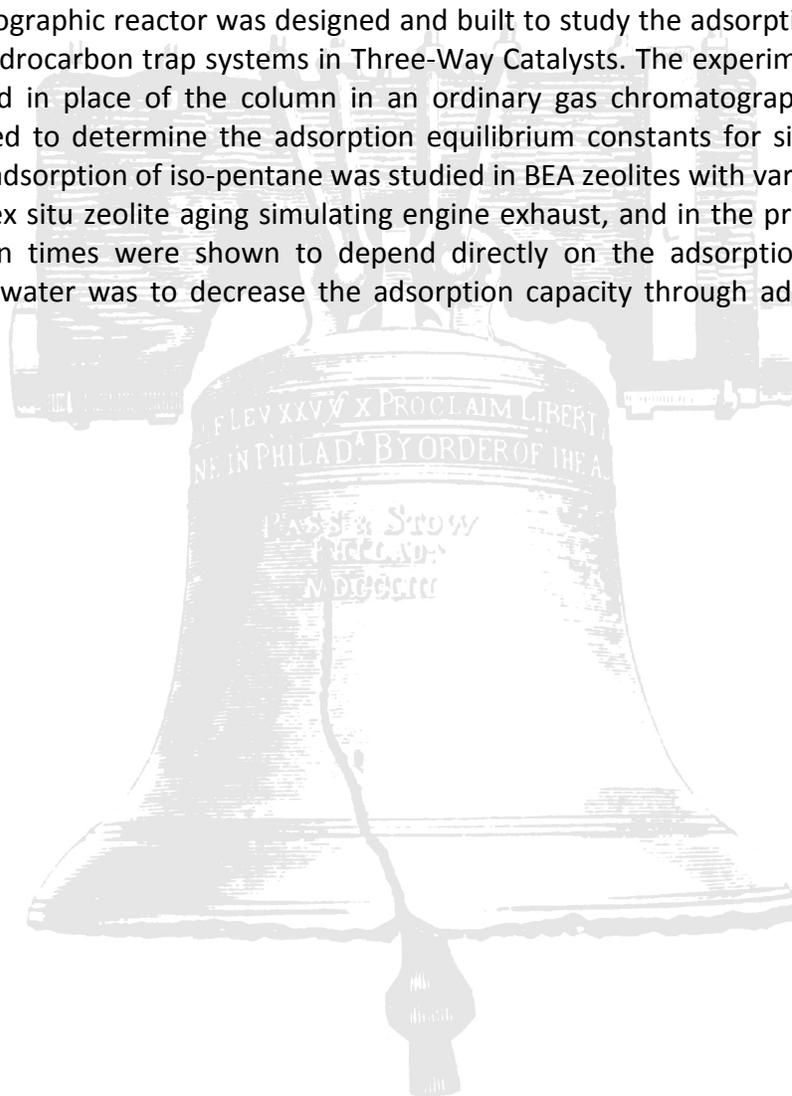
## A Study of Hydrocarbon Trapping for Automotive Three-Way Catalysts

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A chromatographic reactor was designed and built to study the adsorption of alkanes in zeolites for the hydrocarbon trap systems in Three-Way Catalysts. The experimental apparatus used a zeolite bed in place of the column in an ordinary gas chromatograph and could be accurately modeled to determine the adsorption equilibrium constants for simple alkanes in MFI zeolites. The adsorption of iso-pentane was studied in BEA zeolites with varying Si/Al ratios, before and after ex situ zeolite aging simulating engine exhaust, and in the presence of water vapor. The elution times were shown to depend directly on the adsorption capacity. The primary effect of water was to decrease the adsorption capacity through adsorption at acid sites.

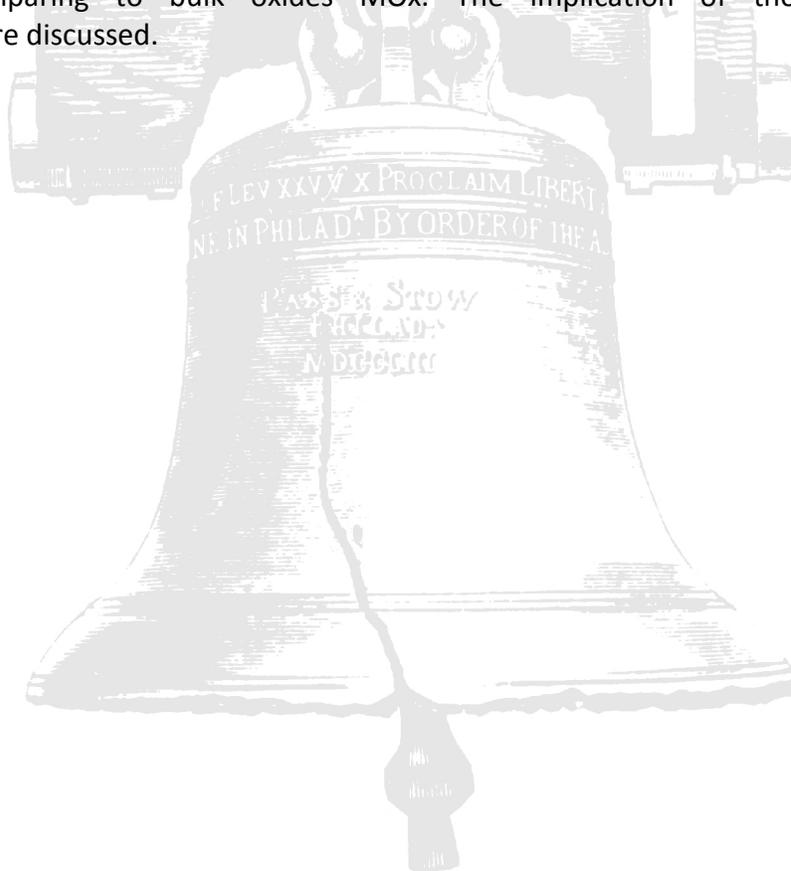


## Characterization of acidic properties of $ZrO_2$ , $TiO_2$ and $Al_2O_3$ , after deposition on SBA-15

*Jingye Yu and Raymond J. Gorte*

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$ZrO_2$ ,  $TiO_2$ , and  $Al_2O_3$  are common and widely used catalyst in industrial reactions. In this work, TPD (Temperature programming desorption) of different alcohols on these oxides are carefully studied. Peak temperature of alkene desorption are similar on  $TiO_2$  and  $ZrO_2$ , slightly higher than  $Al_2O_3$ , indicates a similar reaction mechanism. After deposition on SBA-15, acidic properties of these materials are significantly changed. TPD of isopropyl-amine on  $MO_x/SBA-15$  and IR studies indicate Bronsted acid sites formed on those materials. Alcohol TPD studies show that peak temperature of alkene desorption on  $MO_x/SBA-15$  (M= Zr, Ti, Al) shift to much lower temperature comparing to bulk oxides  $MO_x$ . The implication of those results for characterization are discussed.

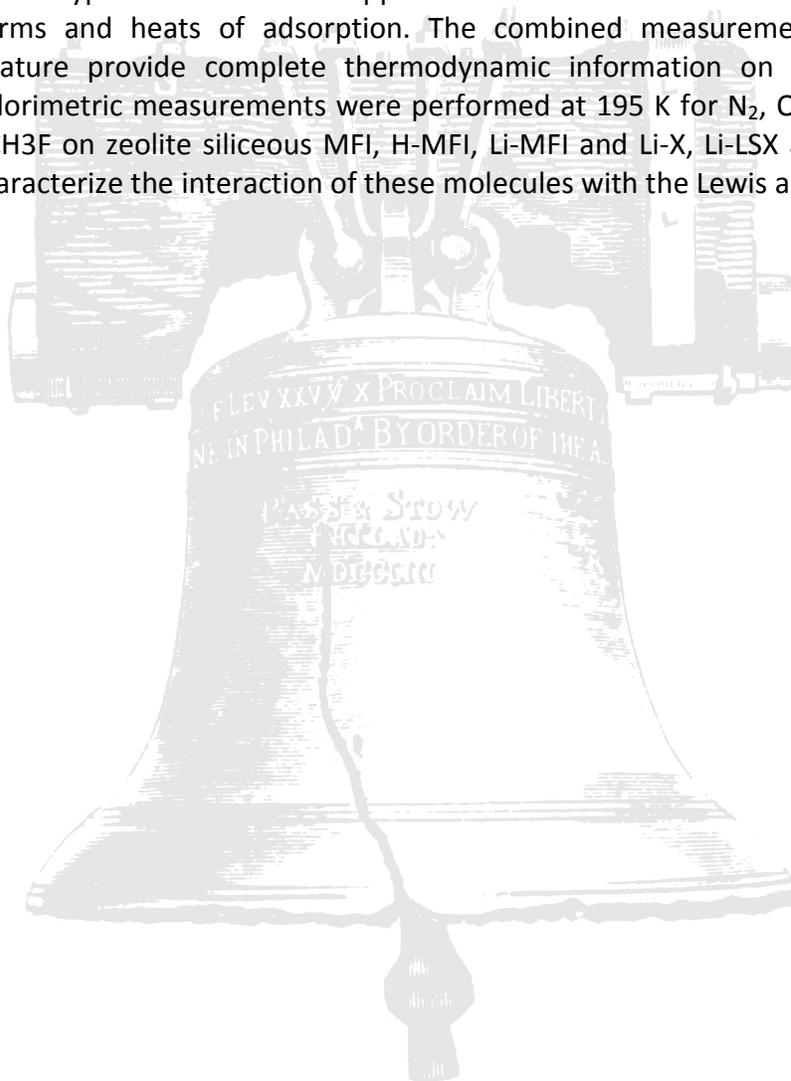


## Calorimetric Investigation of N<sub>2</sub>, O<sub>2</sub>, CO and CH<sub>3</sub>F in zeolites for Characterization of Lewis Acidity

Junjie Cao

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A Tian-Calvet type calorimeter is applied to the simultaneous determination of adsorption isotherms and heats of adsorption. The combined measurements at a single reference temperature provide complete thermodynamic information on the equilibrium behavior. Microcalorimetric measurements were performed at 195 K for N<sub>2</sub>, O<sub>2</sub>, CO and room temperature for CH<sub>3</sub>F on zeolite siliceous MFI, H-MFI, Li-MFI and Li-X, Li-LSX and other Lewis acid in order to characterize the interaction of these molecules with the Lewis acid sites.



## Phase Transfer-Catalyzed Fast CO<sub>2</sub> Absorption by MgO-Based Absorbents with High Cycling Capacity

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Purified syngas from coal or biomass gasifiers can be utilized through subsequent catalyzed processes for the production of fuels and chemicals, as well as for fuel cell-based power generation. Capture of CO<sub>2</sub> during syngas preparation provides benefits, both in reducing greenhouse gas emissions as well as through facilitating the generation of optimal syngas (H<sub>2</sub>/CO) compositions through driving the water gas shift reaction equilibrium. CO<sub>2</sub> capture must occur at the same (warm) temperature as water gas shift in order to preserve energy efficiency.

CO<sub>2</sub> capture with metal oxide absorbents, notably MgO and CaO, through a gas-solid reaction is an attractive approach based on thermodynamic considerations. However, this promise is thwarted by slow kinetics, arising from the high reaction barrier resulting from the strong lattice energy of the solid metal oxide and diffusion resistance from carbonate product layer. In this work, we report a novel phase transfer catalysis process that can provide an active absorbent by partially dissolving the solid absorbent materials in the supported molten salt liquids at moderate temperatures. Dynamic MgO dissolution/precipitation equilibrium in molten nitrate provides activated MgO species accessible to CO<sub>2</sub> at gas-solid-liquid triple phase boundaries. As a result, we develop a novel NaNO<sub>3</sub>-MgO “solid” absorbent that can efficiently capture CO<sub>2</sub> with very high sorption rate and cycling capacity in the range 300-400 °C, which falls into the normally inactive temperature range for metal oxide reaction with CO<sub>2</sub>. This methodology is also applicable to CaO and other basic metal oxides and molten salts, inspiring the design of absorbents that require activation of the bulk material. Furthermore, we provide comprehensive experimental and DFT calculation results to reveal the origin of the significant promotion effects of molten salts.

## Adsorption of Monosaccharide Dehydration Reagents in Zeolites

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Catalysis Center for Energy Innovation, Department of Chemical & Biomolecular Engineering,  
University of Delaware, Newark, DE*

Biomass carbohydrates are the most abundant renewable resources available and have the potential to replace petroleum as a source of both energy and chemicals, leading to more environmentally friendly processes and reducing the dependence on crude oil. A promising reaction in this field is the acid-catalyzed dehydration of monosaccharides, such as fructose and glucose, towards 5-hydroxymethylfurfural (HMF), an important intermediate for the production of valuable chemicals.<sup>1</sup> When zeolites are used as catalysts, the preferential adsorption of reactants, products or byproducts could markedly affect the yield to the desired product. In this regard, studying the adsorption of the compounds present in the reaction media in the zeolite catalyst becomes crucial to understand the reactivity of the system and it is necessary to calculate the intrinsic reaction rate constants from kinetic data. Zeolites can also be used as adsorbents for the selective removal of the HMF from the reaction media. In this respect understanding the effect of the framework type, composition, and presence of co-solvent (e.g. dimethylsulfoxide (DMSO)) on HMF adsorption are important for the design of an adsorptive separation process.

Adsorption loadings from solution are usually estimated from changes of the solute concentration assuming that the solution volume is not affected by adsorption. This quantity is called excess adsorption loading and sometimes it is quite different from the real loading. We formulated and used a method for the estimation of the real adsorption loading from the experimentally measured excess adsorption.

The adsorption isotherms of fructose, glucose, HMF, levulinic and formic acid from aqueous solutions in the protonated form of zeolite beta with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 18 (zeolite proposed as catalyst by Kruger et al.<sup>2</sup>) were measured experimentally and fitted to different adsorption models. The limiting heats of adsorption at zero coverage were calculated from isotherms measured at 0, 25 and 40 °C. Adsorption experiments from multi-solute solutions were also carried out and the data were found to be in good agreement with predictions made using Ideal Adsorbed Solution Theory (IAST) and the single solute isotherm experimental data.

Adsorption of HMF was studied in more detail in BEA and MFI zeolites with different Si/Al ratios. In addition, adsorption of HMF/DMSO/water ternary mixtures was approached both experimentally and computationally (using Grand Canonical Monte Carlo - Expanded Ensemble (GCMC-EE)) in silicalite-1 and dealuminated zeolite Y.

Overall, our findings could shed light on the acid catalyzed dehydration of monosaccharides and the HMF separation, and serve as a hint to the rational design of microporous adsorbents for liquid-phase separations in biomass processing.

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  2. Kruger, J. S.; Choudhary, V.; Nikolakis, V.; Vlachos, D. G. Elucidating the Roles of Zeolite H-Bea in Aqueous-Phase Fructose Dehydration and HMF Rehydration. *ACS Catal.* 2013.



## High Temperature Calcination Improves the Catalytic Properties of Alumina-Supported Pd@Ceria Prepared by Self Assembly

*Chen Chen, Junjie Cao, Matteo Cargnello, Paolo Fornasiero, and Raymond J. Gorte*  
*Department of Chemical & Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA*

The effect of varying the calcination temperature from 773 to 1073 K was examined on catalysts prepared from Pd@CeO<sub>2</sub>, core-shell nanoparticles adsorbed on silane-functionalized  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Pd@CeO<sub>2</sub>/Si-Al<sub>2</sub>O<sub>3</sub>). Calcining to higher temperatures increased rates per gram catalyst for the methane-oxidation reaction significantly. The Pd@CeO<sub>2</sub>/Si-Al<sub>2</sub>O<sub>3</sub> catalyst calcined to 773 K was unstable for methane-steam reforming (MSR) due to deep reduction of the catalyst while the catalyst calcined at 1073 K showed reasonable stable rates. CO adsorption, monitored using volumetric uptakes and FTIR, indicated adsorption on the Pd was suppressed following reduction at 673 K in H<sub>2</sub> when the catalyst had been calcined at only 773 K, but not after 1073 K. Pulse-reactor measurements demonstrated that catalysts calcined at either 773 K or 1073 K were heavily reduced under MSR reaction conditions at 673 K but that the catalyst heated to 1073 K could be reoxidized by H<sub>2</sub>O at this temperature, while the 773-K sample could not be. It is suggested that increasing calcination temperature modifies the structure of the ceria shell, which in turn changes the ceria redox properties.



## Liquid Phase Catalytic Transfer Hydrogenation of Furfural over Ru/C Catalyst

*Paraskevi Panagiotopoulou and Dionisios G. Vlachos*

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Diminishing fossil resources, in combination with environmental concerns related to reducing atmospheric pollution and global greenhouse gas emissions, dictate the development of alternative renewable sources and new technologies for the production of fuels and chemicals. In this regard, conversion of lignocellulosic biomass is of special interest, since it is widely available around the world at a relatively low cost. However, biomass is highly oxygenated and highly functionalized, and therefore, for fuels, the energy density should be increased and for high value chemicals, the reactive oxygenated organic compounds should be selectively deoxygenated at high yields. This can be achieved by catalytic hydrodeoxygenation of furanic components. Biomass derived furfural, produced by acidic degradation of hemicelluloses, is an important intermediate for a number of potential biofuels components and chemicals. Selective hydrogenolysis of furfural is a vital way to transform it into more valuable products such as furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), methyl furan (MF) or cyclopentanone. Among various products, MF is attractive due to its intrinsically good fuel properties and its potential use for chemicals, such as toluene. Moreover, one of its two reactive  $\alpha$ -positions is protected by an unreactive methyl group, which could reduce side reactions.

In the present work the production of MF through catalytic transfer hydrogenation of furfural has been investigated in the liquid phase over Ru/C catalyst. Experiments have been conducted in the temperature range of 120-200 °C in a Parr batch reactor, with the use of an alcohol solution of furfural. It has been found that the reaction of furfural hydrogenation in the liquid phase proceeds toward production of FA, which is further hydrogenated to MF. Small amounts of furan and traces of THFA are also produced via furfural decarbonylation and FA hydrogenation, respectively. Production of MF is enhanced with increasing reaction temperature and/or reaction time. Optimum results have been obtained after 10 h of reaction at 180 °C, where furfural conversion and MF yield reach 100% and 76%, respectively. Mechanistic aspects of the reaction have been investigated by analysing the evolution of reaction intermediates and final products. Production of intermediates, as well as MF, are taking place faster when FA is used as reactant, rather than furfural, via intermediate production of FA. Catalyst recycling experiments over spent Ru/C catalyst showed that although furfural conversion is not decreased significantly, FA yield increases at the expense of MF. However, the initial catalytic activity and selectivity is completely regained after regeneration.

## Role of Cu in Promoting the Bulk Cu/Cr/Fe Water-Gas Shift (WGS) Catalyst

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Industrial hydrogen production is achieved by the water-gas shift (WGS) reaction ( $\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2$ ). Traditionally, the  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$  catalyst was used to perform the high temperature WGS and  $\text{Cu-Fe}_2\text{O}_3$  catalyst to perform the low temperature WGS to enhance hydrogen production. Addition of Cu to  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$  was found to increase the performance of the HT WGS catalyst, but the promotion mechanism of Cu is still not well understood because of the lack of characterization studies under reaction conditions.

To advance our understanding of the promotion of Cu for this important industrial reaction, a series of  $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$  catalysts were synthesized and investigated with modern cutting edge *in situ* (TPR, TP-DRIFTS and Raman) and *operando* (Raman and ambient pressure XPS) spectroscopy during the WGS reaction. The unsupported  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$  and  $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$  catalysts were synthesized by the Co-precipitation method from the corresponding nitrates. The fresh calcined  $\text{CuO-Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$  catalyst consists of surface  $\text{Cr}^{6+}$  species, and bulk  $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$  and  $\text{CuO}$  phases. During the WGS reaction, surface  $\text{Cr}^{6+}$  is reduced to  $\text{Cr}^{3+}$ , bulk  $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$  transforms to bulk  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  and the smaller  $\text{CuO}$  particles become reduced to larger metallic Cu particles. Addition of Cu was found to promote both the initial transformation of  $\text{Fe}_{2-x}\text{Cr}_x\text{O}_3$  to  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  and, more importantly, the  $\text{H}_2$  reduction step during the WGS reaction. It appears that the supported metallic Cu particles promote the HT WGS reaction by facilitating  $\text{H}_2$  dissociation and supplying hydrogen to the  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  surface via hydrogen spillover.

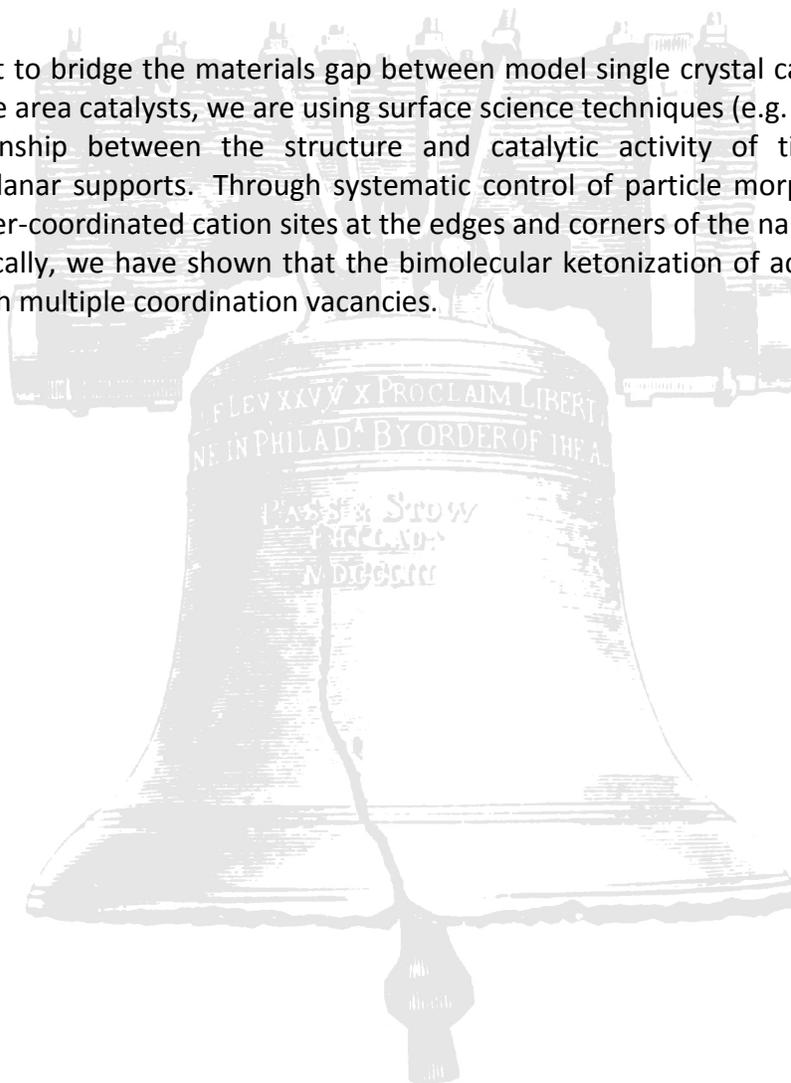
## Studies of Thin Film Metal Oxide Nanocrystal Model Catalysts

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In an effort to bridge the materials gap between model single crystal catalysts and real world, high surface area catalysts, we are using surface science techniques (e.g. XPS and TPD) to study the relationship between the structure and catalytic activity of titanium dioxide nanocrystals on planar supports. Through systematic control of particle morphology, we are studying how under-coordinated cation sites at the edges and corners of the nanocrystals affect reactivity. Specifically, we have shown that the bimolecular ketonization of acetic acid occurs on cation sites with multiple coordination vacancies.

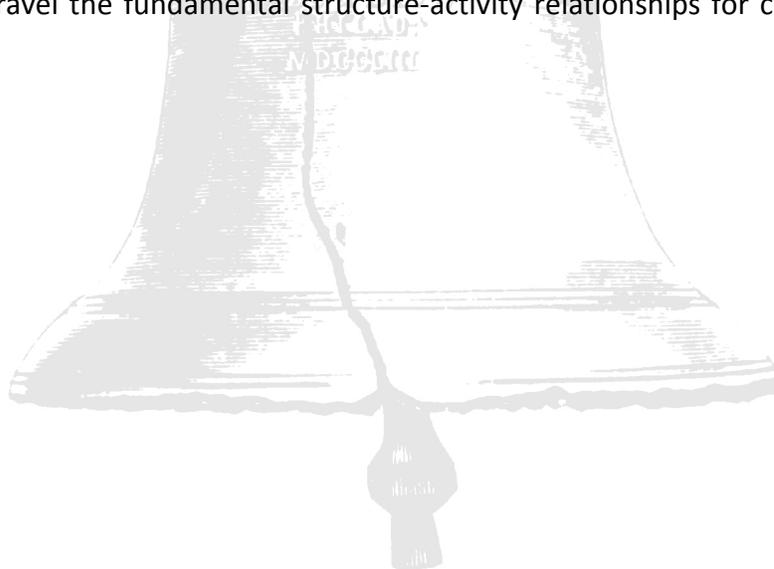


## ***Operando* Molecular Spectroscopy during Catalytic Biomass Pyrolysis**

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This work will focus on the molecular events taking place on the surface of solid acid catalysts (HZSM-5 and supported  $\text{Al}_2\text{O}_3/\text{SiO}_2$ ) during biomass pyrolysis since recent biomass pyrolysis studies have only investigated pyrolysis product yield and bio-oil composition under various reaction conditions. Little fundamental information has been reported about the molecular events taking place during the catalytic biomass pyrolysis reaction over solid acid mixed oxide catalysts: catalytic active sites, their activation and deactivation as well as promotion, surface reaction intermediates and surface reaction pathways. In order to elucidate the molecular events taking place on the catalyst surface, cutting edge *in situ* and *operando* spectroscopic characterization studies (Raman and IR) during the catalytic biomass pyrolysis reaction are undertaken with representative model biomass compounds such as D-glucose, cellulose, furan, furfural, and others. Time resolved spectroscopy and mass spectrometry *operando* style experiments during catalytic biomass pyrolysis provide a direct correlation between catalyst structure, surface reaction intermediates, and pyrolysis products. These fundamental studies during pyrolysis with well-defined solid acid catalysts and model biomass compounds will unravel the fundamental structure-activity relationships for catalytic biomass pyrolysis.

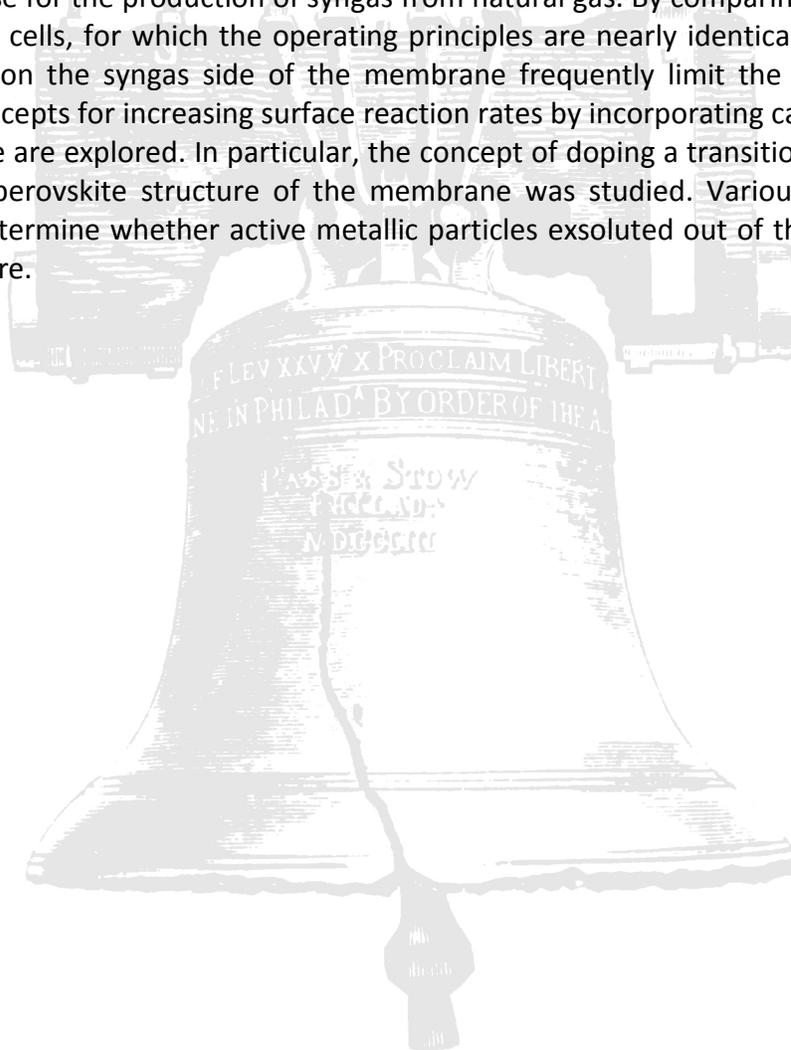


## Interfacial Reactions in Ceramic Membrane Reactors for Syngas Production

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Ceramic membranes reactors based on Mixed Ionic and Electronic Conductors (MIEC) show great promise for the production of syngas from natural gas. By comparing these reactors to solid oxide fuel cells, for which the operating principles are nearly identical, we argue that surface reactions on the syngas side of the membrane frequently limit the performance of these devices. Concepts for increasing surface reaction rates by incorporating catalysts onto the membrane surface are explored. In particular, the concept of doping a transition metal catalyst directly into the perovskite structure of the membrane was studied. Various dopants were investigated to determine whether active metallic particles exsolved out of the membrane in the fuel atmosphere.

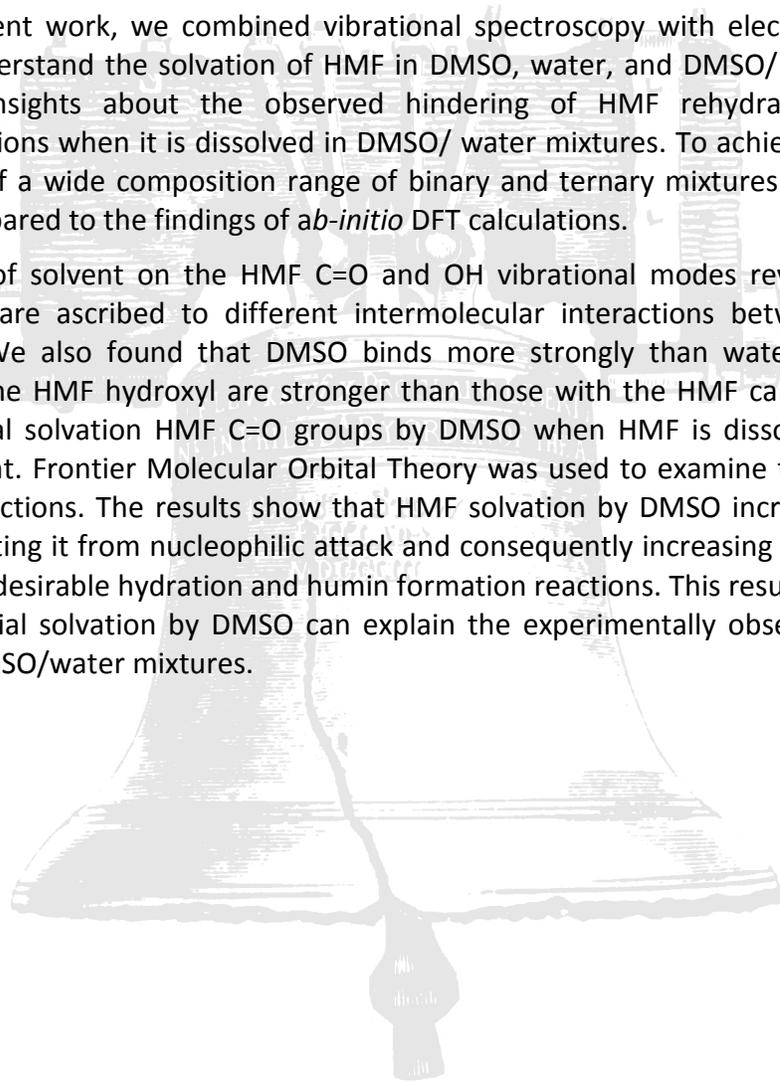


## Elucidating the solvation of 5-hydroxymethylfurfural (HMF) in DMSO/water mixed solvents and its effect in hydration and humin formation reactions

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In the present work, we combined vibrational spectroscopy with electronic structure calculations to understand the solvation of HMF in DMSO, water, and DMSO/ water mixtures and to provide insights about the observed hindering of HMF rehydration and aldol condensation reactions when it is dissolved in DMSO/ water mixtures. To achieve this goal the ATR/FTIR spectra of a wide composition range of binary and ternary mixtures was measured, analyzed, and compared to the findings of *ab-initio* DFT calculations.

The effect of solvent on the HMF C=O and OH vibrational modes reveals significant differences which are ascribed to different intermolecular interactions between HMF and DMSO or water. We also found that DMSO binds more strongly than water to HMF, and interactions with the HMF hydroxyl are stronger than those with the HMF carbonyl. We also showed preferential solvation HMF C=O groups by DMSO when HMF is dissolved in DMSO/ water mixed solvent. Frontier Molecular Orbital Theory was used to examine the influence of solvent on side reactions. The results show that HMF solvation by DMSO increases its LUMO energy thus protecting it from nucleophilic attack and consequently increasing significantly the HMF stability to undesirable hydration and humin formation reactions. This result together with the HMF preferential solvation by DMSO can explain the experimentally observed enhanced HMF stability in DMSO/water mixtures.



## Mechanisms of Ethanol Conversion to Ethylene and Diethyl Ether on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Using Density Functional Theory and Microkinetic Modeling

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There is substantial ongoing research into the production of fuels and chemicals from biomass-derived feedstocks. These feedstocks are often over-functionalized and must have some chemical functionality removed via catalytic upgrade (e.g., dehydration, hydrodeoxygenation, etc.). Identifying materials to execute such transformations and understanding the catalytic cycle will enable the rational development of superior catalysts.

Metal oxides are an important class of materials that catalyze dehydration reactions, but there is little mechanistic understanding of the role that they play in the catalytic conversion of oxygenated hydrocarbons and sugars, including how they affect selectivity. For the specific case of alcohol dehydration and etherification over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the reaction mechanisms are still under debate despite decades of study. Part of the complexity arises because bulk Al atoms occupy both tetrahedral and octahedral sites, and consequently exposed surface Al sites can display three-, four-, or five-fold coordination. In addition,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles expose various facets including (100), (110) and (111). In order to delve deeper into the fundamentals of reaction kinetics and selectivity for this system, we used periodic density functional theory (DFT) calculations and microkinetic modeling to explore the reactions of ethanol on a diversity of Al surface sites and on different  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> facets.

DFT calculations demonstrate that ethanol is most stable when bound to a surface Al site, pointing to the role of Lewis acidity in these reactions. Multiple pathways for dehydration were explored including sequential and concerted bond-breaking mechanisms. A concerted elimination (E2) pathway was the most energetically favorable pathway, consistent with earlier results using an Al<sub>8</sub>O<sub>12</sub> cluster<sup>1</sup> and with an observed C-H kinetic isotope effect.<sup>2</sup> We also identified new pathways for diethyl ether formation; a bimolecular nucleophilic substitution (S<sub>N</sub>2) mechanism was most favorable. The rate expression for ethylene formation requires both an adsorbed ethanol and a vacant surface O site, while ether formation requires an adsorbed ethanol and an adsorbed ethoxy. These two pathways form a mechanistic branching point originating from adsorbed ethanol. The lowest-energy barriers for the two pathways are similar on each of the (100), (110), and (111) facets; thus the relative coverages of ethoxy and vacant O sites critically affect selectivity. In order to explicitly account for the effect of coverage on the reaction rates and compare to experimental reaction orders,<sup>2</sup> a microkinetic model was developed using data from the (111) facet. The model successfully replicates key experimental trends with minimal parameter adjustment. Ethoxy, OH, and H are the most abundant intermediates on the catalyst surface. O-H bond dissociation/formation reactions are equilibrated, while the E2 and S<sub>N</sub>2 mechanisms are irreversible and rate-controlling. These results have answered key questions about (1) the mechanisms for alcohol conversion on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (2) the origin of observed selectivity trends. They are also leading to additional

insights about reactions on other metal oxides, suggesting that there may be a common alcohol dehydration mechanism on solid Lewis acid catalysts.

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1. S. Roy, et al. *ACS Catal.* **2012**, 2 (9), 1846–1853.
2. J.F. DeWilde, et al. *ACS Catal.* **2013**, 3 (4), 798–807.



## Synthesis of Pt@Oxide Core-Shell Nanoparticles onto Hydrophobic Alumina Support

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Pt@oxide (oxide = CeO<sub>2</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub> and ZnO) core-shell catalysts were synthesized and deposited onto hydrophobic alumina (H-Al<sub>2</sub>O<sub>3</sub>). The supported core-shell nanoparticles were synthesized in solution using a method based on self-assembly. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and CO chemisorption techniques were used for the characterization of the catalysts. The measurements of water gas-shift (WGS) rates for Pt@CeO<sub>2</sub>/H-Al<sub>2</sub>O<sub>3</sub> catalyst exhibit activity higher to the conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. The results showed that Pt@ZnO/H-Al<sub>2</sub>O<sub>3</sub> catalysts have activity towards methanol steam reforming with high selectivity to CO<sub>2</sub>. We successfully demonstrated the versatility of the method to prepared Pt@oxide core-shell nanostructures well dispersed onto hydrophobic support.

