

## Catalysis Club of Philadelphia 2012 Graduate Student Poster Contest

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2	<b>Christopher J. Keturakis</b>	Israel E. Wachs	Lehigh University	<b>New Insights into the Water-Gas Shift Reaction over Bulk Cr<sub>2</sub>O<sub>3</sub>*Fe<sub>2</sub>O<sub>3</sub> Mixed Oxide Catalysts: A Combined Operando Raman-IR-XAS-XPS Investigation</b>
3	<b>Lawrence Adijanto</b>	John M. Vohs, and Raymond J. Gorte	University of Pennsylvania	<b>Approaches to mitigate catalyst deactivation in SOFC fuel electrodes</b>
4	<b>Vinit Choudhary</b>	Stanley I. Sandler, and Dionisios G. Vlachos	University of Delaware	<b>Furfural Production from Xylose in Aqueous Media in a Cascade of Reactions using Heterogeneous and Homogeneous Catalysis</b>
5	<b>Eyas Mahmoud</b>	Raul Lobo	University of Delaware	<b>Lewis Acid-Catalyzed Conversion of Biomass-Derived Dimethylfuran to p-Xylene</b>
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10	<b>Minghui Zhu</b>	Israel E. Wachs	Lehigh University	<b>Studies of Cu Promotion Effect in Cu/Cr/Fe Water-Gas Shift Catalyst</b>

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19	<b>Jing Luo</b>	Raymond J. Gorte	University of Pennsylvania	<b>High pressure cracking of n-hexane over H-ZSM-5</b>

20	<b>Timothy D Courtney</b>	Dionisios G. Vlachos	University of Delaware	<b>Liquid-Phase Dehydration of Propylene Glycol Using Solid-Acid Catalysts</b>
21	<b>Vassili Vorotnikov</b>	Dionisios G. Vlachos	University of Delaware	<b>Theoretical Insights into Reactions of Furans on Metal Surfaces</b>
22	<b>Ke Xiong</b>	Jingguang G. Chen	University of Delaware	<b>Converting Furfural Using Bimetallic Catalysts</b>
23	<b>Dr Jacob Kruger</b>	Dionisios G. Vlachos	University of Delaware	<b>Aqueous-Phase Fructose Dehydration and 5-Hydroxymethyl Furfural Rehydration Using H-BEA-18 Zeolite</b>
24	<b>Dr Paraskevi Panagiotopoulou</b>	Xenophon Verykios	University of Patras, Greece	<b>Low temperature steam reforming of ethanol over supported noble metal catalysts</b>
25	<b>Dr Marta Leon</b>	Dionisios G. Vlachos	University of Delaware	<b>Adsorption in zeolites of components encountered in hexose dehydration</b>

## Correlating Surface Chemistry of Glycolaldehyde and Glyceraldehyde with Glucose, a Mechanistic Study on Pd(111)

Jesse R. McManus<sup>†</sup>, Michael Saliccioli<sup>‡</sup>, Dion Vlachos<sup>‡</sup>, Jinguang G. Chen<sup>‡</sup>, John M. Vohs<sup>†</sup>

<sup>†</sup>*University of Pennsylvania*, <sup>‡</sup>*University of Delaware*

The catalytic conversion of biomass into fuels and chemicals requires an understanding of the adsorption and reaction of C<sub>5</sub> and C<sub>6</sub> sugars on catalytically active metals. In this investigation glycolaldehyde and glyceraldehyde were used as model compounds in a density functional theory (DFT) and experimental surface science study of the reaction of sugars on Pd(111). For the first time the stable intermediates formed by glucose on a single crystal metal surface were identified allowing for comparisons with the surrogate molecules. Adsorption was governed by aldehyde group-surface interactions forming  $\eta_1(\text{C}=\text{O})$  intermediates, which, upon heating, transformed into more stable di- $\sigma$   $\eta_2(\text{C}-\text{O})$  species followed by  $\alpha$ -O-H bond scission to produce an  $\alpha$ -oxo- $\eta_2$  intermediate. A consequence of the surface-carbonyl group interaction is that it precludes using simple alcohols or polyols as model compounds for biomass-derived sugars in mechanistic studies of heterogeneously catalyzed biomass reforming on metal surfaces and suggests that simple aldoses are more appropriate surrogates.

## New Insights into the Water-Gas Shift Reaction over Bulk Cr<sub>2</sub>O<sub>3</sub>\*Fe<sub>2</sub>O<sub>3</sub> Mixed Oxide Catalysts: A Combined *Operando* Raman-IR-XAS-XPS Investigation

Christopher J. Keturakis<sup>1</sup>, Emma Gibson<sup>2</sup>, Relja Vasic<sup>3,4</sup>, Franklin Tao<sup>5</sup>, Anatoly Frenkel<sup>3,4</sup>,

Marco Daturi<sup>2</sup> and Israel E. Wachs<sup>1\*</sup>

<sup>1</sup>*Operando Molecular Spectroscopy and Catalysis Laboratory, Chemical Engineering Department, Lehigh University, Bethlehem, PA 18015 USA*

<sup>2</sup>*Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen Cedex, France*

<sup>3</sup>*Department of Physics, Yeshiva University, New York, NY 10016 USA*

<sup>4</sup>*National Synchrotron Light Source, Brookhaven National Lab, Upton, NY 11973 USA*

<sup>5</sup>*Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA*

\*iew0@lehigh.edu

The bulk chromia-iron mixed oxide catalyst is the primary catalyst for the high temperature (310-450°C) water-gas shift (WGS) reaction for the production of hydrogen and carbon dioxide from steam and carbon monoxide. The commercial lifetime of pure magnetite catalysts is limited because of thermal sintering and chromium oxide addition, 8-12% Cr<sub>2</sub>O<sub>3</sub>, has been found to stabilize the surface area and extend the catalyst life to 2-5 years. Despite numerous characterization studies, the role of the chromia promoter is still not completely understood. The absence of fundamental *in situ* and *operando* spectroscopic studies of the bulk Cr<sub>2</sub>O<sub>3</sub>\*Fe<sub>2</sub>O<sub>3</sub> WGS shift catalyst during the WGS reaction in the catalysis literature has hindered the development of molecular level insights about the catalytic active sites, surface reaction intermediates and the reaction mechanism. In order to address the state of the iron oxide catalyst under reaction conditions, the role of the chromia promoter, and the nature of the catalytic active site, *in situ* and *operando* Raman spectroscopy, IR spectroscopy, X-ray Absorption Spectroscopy (XAS), and Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) studies under reaction conditions were undertaken in the present investigation.

The *operando* Raman spectroscopy studies during the high temperature WGS confirm that crystalline Fe<sub>3</sub>O<sub>4</sub> is the active bulk phase in Cr-doped samples and surface dioxo (O=)<sub>2</sub>CrO<sub>2</sub> species are reduced. The corresponding *operando* IR spectroscopy measurements revealed that no surface reaction intermediates are present, even when the reaction is performed at the temperature limit of ~225°C. *Operando* XANES measurements (Cr K-edge) confirm the reduction of Cr<sup>+6</sup> (dioxo species) to Cr<sup>+3</sup> during WGS reaction conditions. The EXAFS Fe K-edge data confirm that the Cr-doped samples stabilize as Fe<sub>3</sub>O<sub>4</sub> under steady-state WGS reaction conditions, while unpromoted Fe<sub>2</sub>O<sub>3</sub> is active as an amorphous phase consisting mostly of a core of metallic Fe with an Fe<sub>3</sub>O<sub>4</sub> shell. Recent *in situ* AP-XPS data has revealed, *for the first time*, that some Cr<sup>+6</sup> species remain on the catalyst surface under reaction conditions. The new fundamental insights are allowing for establishment of the WGS reaction mechanism and the nature of the catalytic active site during relevant WGS reaction conditions.

## **Approaches to mitigate catalyst deactivation in SOFC fuel electrodes**

Lawrence Adijanto, John M. Vohs, and Raymond J. Gorte

*Chemical and Biomolecular Engineering, University of Pennsylvania*

In the development of ceramic fuel electrodes for SOFC, high performance can only be achieved when a group VIII metal catalyst is added. Because of the high operating temperatures, deactivation of the metal catalyst sintering and coking is a severe problem. We present a study to mitigate the catalyst deactivation by: 1) designing a catalyst that is resistant to coking and sintering and 2) developing a new method for catalyst deposition.

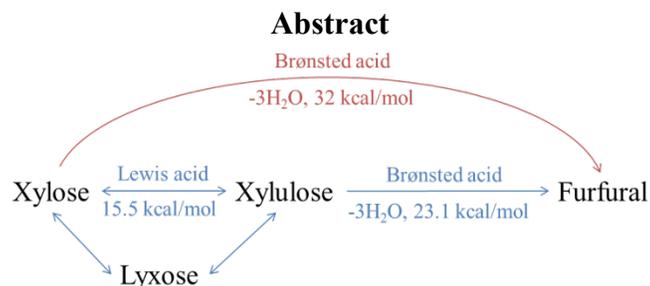
The first approach involved synthesizing the self-regenerating, “intelligent” catalyst, in which Co, Cu, or Ni can be inserted into the B-site of a perovskite oxide under oxidizing conditions and then brought back to the surface under reducing conditions. This restores lost surface area of sintered metal particles through an oxidation/reduction cycle. Results will be shown for each of the metals, as well as for Cu-Co mixed metal systems, which are found to exhibit good tolerance to carbon deposition and interesting catalytic properties.

The second strategy involves depositing Pd@ceria core-shell catalysts onto a substrate surface which was initially chemically modified to anchor the modular particles. The catalyst deposited onto the chemically modified, hydrophobic surface is shown to be uniform and well dispersed, with good thermal stability.

# Furfural Production from Xylose in Aqueous Media in a Cascade of Reactions using Heterogeneous and Homogeneous Catalysis

Vinit Choudhary, Ana B. Pinar, Stavros Caratzoulas, Vladimiro Nikolakis, Stanley I. Sandler, Dionisios G. Vlachos, and Raul F. Lobo

*Center for Catalytic Science and Technology and Catalysis Center for Energy Innovation, Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA*



Biomass conversion to biofuels and biochemicals has recently gained considerable attention as a result of the declining availability of petroleum reserves and growing environmental concerns over greenhouse gas emissions.<sup>1</sup> A challenge lies in developing economically efficient and environmentally benign technologies to transform lignocellulosic biomass into fuels and chemicals. Xylose is the most prevalent pentose in hemicellulose. An approach to utilize xylose entails its thermochemical conversion into furfural.<sup>2</sup> The cyclodehydration of xylose to furfural is typically catalyzed by Brønsted acids and requires high operating temperatures (>160 °C) in aqueous media, owing to the high activation energy of ~32 kcal/mol. This limits the development of an economically efficient process for this reaction.

In this work, we will present an experimental study that demonstrates the effect of molecular structure on the dehydration chemistry and the importance of aldose-to-ketose isomerization in preparing furfural and its derivatives from simple sugars. It was found that xylulose conversion to furfural is faster and results to much higher furfural yield compared to xylose conversion using a Brønsted acid catalyst. We recently achieved high yield (~75%) of furfural from xylose at moderate reaction temperatures (<140 °C) in aqueous media in a cascade of reactions: the isomerization of xylose (an aldose) to xylulose (a ketose), followed by xylulose dehydration to furfural.<sup>3-4</sup> This was achieved in a one-pot reactor using a Lewis acid (CrCl<sub>3</sub> or the zeolite Sn-beta) as an isomerization catalyst and Brønsted acid (HCl or Amberlyst-15) as a dehydration catalyst.

CrCl<sub>3</sub> speciation in aqueous media was investigated to study the distribution of various Cr(III) species under reaction conditions and their correlations with the isomerization reaction rate. Further, spectroscopic experiments were conducted to understand the interaction of the metal, a Lewis acid center, with the sugar molecule and to gain insight into the isomerization mechanism. These studies show remarkable similarities between homogeneous and heterogeneous catalysis of aldose-to-ketose isomerization. We shall also present *ab initio* mechanistic studies of the Lewis acid catalyzed xylose isomerization.

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## **Lewis Acid-Catalyzed Conversion of Biomass-Derived Dimethylfuran to p-Xylene**

Eyas Mahmoud, Phuong Do, and Raul Lobo

*Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy St., Newark, Delaware*

A renewable route to p-Xylene from biomass-derived dimethylfuran and ethylene is investigated with zeolite catalysts. This conversion consists of two steps: a Diels Alder cycloaddition of ethylene to dimethylfuran followed by dehydration of the oxabicyclic intermediate to p-Xylene. The capability of extra-framework cations in the zeolite framework—such as Na, Li, K, Ag, and Cu—in faujasites Y (Si/Al=40), Y (Si/Al=2.55) and X (Si/Al=1.25) to catalyze this reaction was investigated at low conversion ( $X_{\text{DMF}} \sim 10\%$ ). AgX zeolite was the most active catalyst for the formation of p-Xylene at 220 °C (1.80 moles of p-Xylene formed/ (mole cation\*hr)). NaX (Si/Al=1.25) was the most selective catalyst for the formation of p-Xylene at these conditions (75.5%). Competitive side reactions include hydrolysis of DMF to 2,5-hexanedione, alkylation of p-Xylene, and polymerization of 2,5-hexanedione. The observed trends may be explained by three main effects: the inherent Lewis acid strength of the cation, the site-distribution of cations in the zeolite framework, and the shielding effects associated with interaction between the cations and the zeolite framework

## Semi-Empirical Parameter Estimation Methods for Microkinetic Modeling

Jonathan E. Sutton and Dionisios G. Vlachos

*Center for Catalytic Science and Technology and Catalysis Center for Energy Innovation  
Department of Chemical and Biomolecular Engineering  
University of Delaware, Newark, DE 19711*

Bio-based materials have the potential to replace petroleum based feedstocks for fuels and chemicals, but new catalysts for the conversion processes need to be identified if this is to be successful. Traditionally, new catalysts have been identified primarily via trial and error. In an effort to more efficiently identify potential catalysts, there has been an increasing focus placed on detailed microkinetic modeling of reaction networks. For small networks, it is possible to calculate the needed kinetic parameters via, e.g., density functional theory. However, as the size of the reaction network increases, this approach quickly becomes computationally prohibitive. Because model results are usually insensitive to the vast majority of the parameters in a model, one way to deal with this challenge is to employ semi-empirical methods for the rapid estimation of the parameters and improve only the sensitive ones using more accurate methods.

A number of semi-empirical methods have been developed for this purpose. These include group additivity for surface heats of formation and Brønsted-Evans-Polanyi (BEP) correlations for the estimation of activation energies.[1, 2] Despite the work which has been done in this field in developing new techniques, little attention has been paid to characterizing the accuracy of the estimates afforded by these methods. We use theoretical and computational methods to explicitly characterize the distributions of errors inherent to these models when used both separately and in concert with each other. As a first step towards providing a practical benchmark for these methods, we have developed a DFT-based microkinetic model of ethanol steam reforming on Pt and compare our model results to experimental data.

In general, we find that errors resulting from regression (e.g., as in group additivity) are normally distributed. Interestingly, we find that the errors for the BEP estimated activation energies using group additivity heats of reaction are very similar to the errors when DFT heats of reaction are used, implying that the majority of the error stems from the use of the BEP correlation rather than group additivity. We also find that our DFT-based model is in qualitative agreement with experimental results, suggesting that this will be a useful benchmark for future investigations of the impact of errors in group additivity and the BEP correlations on microkinetic model results.

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## Catalytic role of the metal-support interface in d8-ceria systems prepared using artificial atoms

Matteo Cargnello,<sup>1,2</sup> Vicky Doan-Nguyen,<sup>2</sup> Thomas R. Gordon,<sup>3</sup> Kevin Bakhmutsky,<sup>4</sup> Rosa E Diaz,<sup>5</sup> Eric A. Stach,<sup>5</sup> Raymond J. Gorte,<sup>4</sup> Paolo Fornasiero,<sup>1</sup> and Christopher B. Murray<sup>2,3</sup>

<sup>1</sup>*Department of Chemical and Pharmaceutical Sciences, ICCOM-CNR, Consortium INSTM, University of Trieste, 34127 Trieste, Italy*

<sup>2</sup>*Department of Materials Science and Engineering, University of Pennsylvania, 19104 Philadelphia, Pennsylvania, United States*

<sup>3</sup>*Department of Chemistry, University of Pennsylvania, 19104 Philadelphia, Pennsylvania, United States*

<sup>4</sup>*Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 19104 Philadelphia, Pennsylvania, United States*

<sup>5</sup>*Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, United States*

Understanding size-activity relationships and the role of metal-support synergy in heterogeneous catalysts is fundamental for the preparation of materials with improved and tailored performance. In most cases, sample heterogeneity makes direct relationships difficult to extract. In this contribution, monodisperse Ni, Pd and Pt nanocrystals with tunable dimensions are prepared using high-temperature colloidal methods, with the aim of overcoming this problem. We prepare model catalysts with tailored metal-support interfaces by depositing preformed, monodisperse nanocrystals on ceria (CeO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) supports, creating catalytic systems that may be tested under realistic reaction conditions. We show that while carbon monoxide (CO) oxidation is size-independent for alumina-supported samples, as expected, there is size-dependency for metal-supported ceria-based catalysts. We demonstrate a direct relationship between the structure of the metal-support interface in ceria-based catalysts and their CO oxidation activity. Supported, highly monodisperse nanocrystals are introduced as model systems to demonstrate size-activity relationships under realistic reaction conditions.

***Nonaqueous Synthesis of TiO<sub>2</sub> Nanocrystals Using TiF<sub>4</sub> to Engineer Morphology, Oxygen Vacancy Concentration, and Photocatalytic Activity***

Thomas R. Gordon,<sup>†</sup> Matteo Cargnello,<sup>||</sup> Taejong Paik,<sup>†</sup> Filippo Mangolini,<sup>§</sup> Ralph T. Weber,<sup>⊥</sup>  
Paolo Fornasiero,<sup>||</sup> and Christopher B. Murray<sup>†,‡</sup>

<sup>†</sup>*Department of Chemistry*, <sup>‡</sup>*Department of Materials Science and Engineering*, <sup>§</sup>*Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, PA*

<sup>||</sup>*Department of Chemical and Pharmaceutical Sciences, ICCOM-CNR, INSTM, Center of Excellence for Nanostructured Materials (CENMAT), University of Trieste, Italy*

<sup>⊥</sup>*Bruker BioSpin Corporation, Billerica, Massachusetts*

We report the nonaqueous surfactant-assisted synthesis of highly uniform anatase TiO<sub>2</sub> nanocrystals (NCs) with tailorable morphology in the 10-100 nm size regime. Introduction of TiF<sub>4</sub> preferentially exposes the {001} facet of anatase through *in situ* release of HF, allowing for the formation of uniform anatase NCs based on the truncated tetragonal bipyramidal geometry. A method is described to engineer the percentage of {001} and {101} facets through the choice of co-surfactant and titanium precursor. The use of TiF<sub>4</sub> also results in TiO<sub>2</sub> NCs that are blue in color, resulting from the formation of oxygen vacancies. Preliminary experiments on the photoreforming of methanol from platinized TiO<sub>2</sub> NCs resulted in high volumes of evolved hydrogen under simulated solar illumination. Remarkably, the data suggest that the {101} facets of anatase are more active than the {001}.

## **Reactivity Studies of Pd@CeO<sub>2</sub> Nanoparticles Dispersed on ZrO<sub>2</sub>**

David Bennett, Lawrence Adijanto, John M. Vohs

*Chemical and Biomolecular Engineering, University of Pennsylvania*

Ultra-high vacuum systems are well established tools for characterizing the structure and reactivity of single crystal and polycrystalline model catalysts. We have utilized a technique to immobilize a uniform layer of Pd@CeO<sub>2</sub> core-shell particles on a flat ZrO<sub>2</sub> substrate by functionalizing the zirconia with triethoxy(octyl)silane in UHV. The particles remained dispersed after calcination at 770K. This was confirmed by atomic force microscopy measurements. We then used both X-ray photoelectron spectroscopy and temperature programmed desorption to investigate the reactive properties of Pd@CeO<sub>2</sub> core-shell particles. The ceria shell was found to reduce to Ce<sup>3+</sup> upon heating in vacuum to 700K. CO was found to adsorb to the Pd cores with an oxidized ceria shell, but not with a reduced shell. This gives insight into possible deactivation pathways for Pd@CeO<sub>2</sub> particles.

## **Studies of Cu Promotion Effect in Cu/Cr/Fe Water-Gas Shift Catalyst**

Minghui Zhu, Christopher J. Keturakis, Israel E. Wachs

*Operando Molecular Spectroscopy and Catalysis Research Laboratory, Chemical Engineering Department, Lehigh University, Bethlehem, PA 18015 USA.*

Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> and CuO/Cr<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> were analyzed by *in situ* and *operando* Raman spectroscopy, Temperature Programmed Surface Reaction (TPSR) spectroscopy and Temperature Programmed-Diffuse Reflectance Infrared Spectroscopy (TP-DRIFTS) with the expectation to understand structure - function relationship of Cu in Cu/Cr/Fe catalyst during high temperature WGS reaction. The Cr<sup>6+</sup> species are found exist on surface of Cr/Fe and Cu/Cr/Fe catalysts and Fe<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub> phase are also observed upon addition of Cr. H<sub>2</sub>/H<sub>2</sub>O-TPSR experiment reveals that addition of Cu makes both H<sub>2</sub> reduction peak and H<sub>2</sub>O reoxidation peak shift to lower temperature. Thus, it is proposed that Cu promotes high temperature WGS reaction by facilitating both H<sub>2</sub> reduction cycle and H<sub>2</sub>O reoxidation cycle during WGS reaction. This implies that the WGS mechanism occurs via a redox cycle over the Cu/Cr/Fe catalysts.

## Development of Manganese Oxide Water Oxidation Catalysts

Seif Yusuf, Feng Jiao

*Department of Chemical and Biomolecular Engineering, University of Delaware*

Oxygen evolution from water is one of the key reactions for solar fuel production. Here, we synthesized two nanostructured K-containing  $\delta$ -MnO<sub>2</sub>, K- $\delta$ -MnO<sub>2</sub> nanosheets and K- $\delta$ -MnO<sub>2</sub> nanoparticles, both of which exhibit high catalytic activities in visible light driven water oxidation reaction. The role of alkaline cations in oxygen evolution was first explored by replacing the K<sup>+</sup> ions in the  $\delta$ -MnO<sub>2</sub> structure with H<sup>+</sup> ions through proton ion exchange. The H- $\delta$ -MnO<sub>2</sub> catalysts with a similar morphology and crystal structure exhibited approximately one order magnitude lower activities per surface site compared with K- $\delta$ -MnO<sub>2</sub>, although both nanostructured H- $\delta$ -MnO<sub>2</sub> catalysts have much larger BET surface areas. Such a low TOF per surface Mn might be due to the fact that Ru<sup>2+</sup>(bpy)<sub>3</sub> sensitizer is too large to access the additional surface area created during proton exchange. Also, a Na-containing  $\delta$ -MnO<sub>2</sub> material with identical crystal structure was prepared and exhibited a similar TOF as the K-containing  $\delta$ -MnO<sub>2</sub>, suggesting that the alkaline cations are not directly involved into the catalytic water oxidation, but they stabilize the layered structure of  $\delta$ -MnO<sub>2</sub>.

## **Effect of CeO<sub>2</sub> addition by Atomic Layer Deposition on Surface Reactions in SOFC Cathodes**

Anthony Yu, Rainer Kungas, John M. Vohs, Raymond J. Gorte

*University of Pennsylvania, Department of Chemical and Biomolecular Engineering  
Philadelphia, PA 19104*

The influence of CeO<sub>2</sub> addition through atomic layer deposition (ALD) on solid oxide fuel cell (SOFC) cathodes was examined. Composite cathodes were prepared by infiltrating La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3-δ</sub> (LSF) into porous yttria-stabilized zirconia (YSZ) electrode scaffolds. The cathode performance was analyzed as a function of the thickness of the deposited ceria film, and compared to the performance of cathodes with infiltrated ceria. Impedance spectra measured on symmetric cells with no ceria deposited showed an initial polarization resistance of 1.1 Ω cm<sup>2</sup> at 873 K in air. While infiltration of ceria nano-particles decreased the polarization resistance to 0.6 Ω cm<sup>2</sup>, the addition of ceria ALD coatings of less than 1 nm in thickness increased the polarization resistance by an order of magnitude. The cause for the cathode deactivation by ceria ALD was examined by operating the symmetric cells at different current loadings, and by NO<sub>2</sub> flow titration measurements of the cathode surface oxygen vacancies. It is hypothesized that the ceria deposited by ALD is primarily depositing into the oxygen vacancies on the cathode surface therefore deactivating the active sites for oxygen reduction.

**Structure – Activity relationships of supported Molybdenum(VI) Oxide on TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> by means of In Situ/Operando Raman and FTIR spectroscopies combined with 18O/16O exchange**

George Tsilomelekis<sup>1,2,3</sup> and Soghomon Boghosian<sup>1,2</sup>

<sup>1</sup>*Department of Chemical Engineering, University of Patras, GR-26504, Greece*

<sup>2</sup>*Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation of Research and Technology—Hellas (FORTH/ICH-HT), GR-26504, Patras, Greece.*

<sup>3</sup>*Department of Chemical and Biomolecular Engineering, Catalysis Center for Energy Innovation, University of Delaware, 150 Academy Street, Newark, DE, 19716, USA*

Supported MoO<sub>3</sub> catalysts on TiO<sub>2</sub> (anatase), Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> with surface densities in the range of 0.5–18.5 Mo/nm<sup>2</sup> were extensively studied at temperatures of 400–540 °C for understanding the configuration and molecular structure of the deposited (MoO<sub>x</sub>)<sub>n</sub> species and examining their behavior for the ethane oxidative dehydrogenation (ODH). In situ Raman and in situ FTIR spectra under oxidizing conditions coupled with 18O/16O isotope exchange studies provide the mono-oxo configuration for the deposited (MoO<sub>x</sub>)<sub>n</sub> species on the different supports. A next-nearest-neighbor vibrational isotope effect perturbs the Mo=16O band as a result of 18O/16O substitution of O atoms that are next nearest neighbors to the terminal 16O atom and as a result the Mo=16O Raman band position is red shifted by 2–7 cm<sup>-1</sup> depending strongly on the nature of support. A consistent mechanism accounting for this effect is proposed at the molecular level for each support. Catalytic measurements for ethane ODH with simultaneous monitoring of operando Raman spectra were performed. The surface composition and the structural/vibrational properties of the deposited (MoO<sub>x</sub>)<sub>n</sub> species respond to changes in the catalyst gas environment, as evidenced by operando Raman spectra obtained under steady-state reaction conditions for the ODH of ethane. The operando Raman spectra and a quantitative exploitation of the relative normalized Mo O band intensities for various residence times show that the terminal Mo O sites are involved in non-selective reaction turnovers. Reaction routes follow primarily non-selective pathways at low coverage and selective pathways at high coverage. The apparent turnover frequencies of ethylene production as a function of Mo surface density and the nature of support are discussed extensively proposing that the oxygen site involved in the anchoring Mo–O–support is of relevance for the catalytic activity.

## **Catalytic Characterization of Hierarchical Meso-/microporous MFI and MWW Zeolites**

Yiqing Wu, Dongxia Liu

Chemical Engineering Department. University of Maryland

Three hierarchical meso-/microporous zeolites (pillared MWW, pillared MFI, and Self-pillared MFI) were synthesized and their Brønsted acid site location was quantified using dimethyl ether (DME) and 2,6-di-terbutyl pyridine (DTBP) titration reactions. Acid sites only accessible to DME molecules are designated as internal acid sites, while acid sites accessible to both DME and DTBP molecules are named as external acid sites. The catalytic behavior of the external and internal acid sites was studied using ethanol dehydration and alkylation of benzyl alcohol with aromatic solvents as probe reactions. The rate and apparent activation energy of the catalytic ethanol reaction in zeolites possessing dual micro- and mesoporosity was comparable to conventional microporous analogues, implying that the catalytic behavior of Brønsted acid sites in meso-/microporous zeolites is preferentially dominated by the microporous environment. The apparent rate of the catalytic conversion of benzyl alcohol in meso/micro-porous zeolites was higher than that of the microporous zeolite materials, revealing the important role of the mesoporosity of hierarchical zeolites in space-demanding catalytic reactions.

## **The Effect of High-Temperature Calcination on Pd@CeO<sub>2</sub>/Si-Al<sub>2</sub>O<sub>3</sub> Catalysts**

Chen Chen, R.J. Gorte

*Department of Chemical and Biomolecular Engineering, University of Pennsylvania*

A Pd@Ceria core-shell catalyst was synthesized and homogeneously deposited onto a modified hydrophobic alumina. The calcinations were conducted at 773K and 1073K. The redox properties of the catalysts were characterized by pulse-reactor studies. The results showed that further calcination lead to a less reducible ceria shell. Measurements of methane steam reforming rates showed that catalysts calcined at lower temperature exhibit transient deactivation, which is probably caused by a decrease in the exposed metal surface area due to the ease of reduction of the shells. Calcination at higher temperature enhanced the stability significantly.

# **A DFT study of the acid-catalyzed conversion of 2,5-dimethylfuran and ethylene to p-xylene**

Nima Nikbin, Stavros Caratzoulas, Dionisios G. Vlachos

*Department of Chemical and Biomolecular Engineering, Catalysis Center for Energy Innovation, University of Delaware, 150 Academy Street, Newark, DE, 19716, USA*

In this paper we present the detailed mechanism for the conversion of DMF and ethylene to p-xylene. The mechanism was calculated by gas-phase DFT (Density-Functional Theory) for the uncatalyzed, the Brønsted acid-catalyzed and the Lewis acid-catalyzed reaction. The conversion consists of Diels-Alder cycloaddition and subsequent dehydration of the cycloadduct, an oxanorbornene derivative. Even though the DMF-ethylene cycloaddition is thermally feasible, we find that Lewis acids can further lower the activation barriers by decreasing the HOMO-LUMO gap of the addends. The catalytic effect may be significant or negligible depending on whether the Diels-Alder reaction proceeds in the normal or the inverse electron-demand direction. We find that Brønsted acids are extremely effective at catalyzing the dehydration of the oxanorbornene derivative, which, according to our calculations, cannot proceed uncatalyzed. On the other hand, we find that Brønsted acids do not catalyze the cycloaddition. Although strong Lewis acids like  $\text{Li}^+$  can catalyze the dehydration, our calculations indicate that relatively elevated temperatures would be required as they are not as effective as Brønsted acids. We argue that the specific synthetic route to p-xylene is kinetically limited by the Diels-Alder reaction when Brønsted acids are used and by the dehydration when a Lewis acid is used, with the latter being slower than the former. Finally, we adduce experimental data that corroborate the theoretical predictions: we observe no activity in the absence of a catalyst and a higher turnover frequency to p-xylene in the Brønsted acidic zeolite HY than in the Lewis acidic zeolite NaY.

## **Design and Characterization of Photocatalysts for Solar Powered Hydrogen Generation**

Somphonh Peter Phivilay<sup>1</sup>, Anke Xiong<sup>2</sup>, Jun Kubota<sup>2</sup>, Kazunari Domen<sup>2</sup>, and Israel E. Wachs<sup>1</sup>

<sup>1</sup> *Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA*

<sup>2</sup> *Department of Chemical System Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

One of society's great challenges for the 21st century is the development of new energy sources. Hydrogen is considered to be one of the potential candidates especially if it can be generated from the photocatalytic conversion of cheap abundant H<sub>2</sub>O into clean non-carbon H<sub>2</sub> from solar energy resources. Development of this clean, renewable form of energy will help to address our reliance on depleted fossil fuel supplies and the environmental problems accompanying its use.

Numerous materials have been discovered which can photocatalytically convert H<sub>2</sub>O into H<sub>2</sub>/O<sub>2</sub>, with Rh-Cr/GaN:ZnO being the most active utilizing visible light irradiation. This study focuses on the use of in situ/operando optical spectroscopic characterization methods (Raman, UV-vis, photoluminescence (PL) and time-resolved picosecond PL-Raman) to give further insight into the bulk molecular and electronic structure of these photocatalysts. Surface science characterization techniques (high-resolution x-ray photoelectron spectroscopy (HR-XPS) and high-sensitivity low energy ion scattering (HS-LEIS)) were also utilized to determine the nature of the catalytic active sites for the photocatalysts which have not been done previously.

# Effect of High Temperature Hydrocarbon Reactions over Acid Zeolites

Jang Ho Yun, and Raul F. Lobo

*Center for Catalytic Science and Technology, Chemical and Biomolecular Engineering,  
University of Delaware, 150 Academy St., Newark, DE, 19716, USA*

Zeolites are crystalline materials that are widely used as solid acid catalysts in industry [1]. Bronsted acid sites (BAS), which are hydroxyl groups bridged between Al and Si (Al-OH-Si) tetrahedra, are responsible for many of the industrial catalytic application of zeolites. The OH-groups of BAS are detected in the range of 3600 – 3660  $\text{cm}^{-1}$  of IR spectroscopy. The intensity of IR spectrum decreases at high temperature (usually above 873K [2]) and these temperatures are found in the regenerator of a fluidized catalytic cracking (FCC) unit. Decomposition of BAS in zeolites, also called dehydroxylation, can proceed as a part of the normal FCC operation.

Dehydration of BAS has been believed to be the main mechanism of dehydroxylation [3], however, Nash et al. reported that hydrogen is also formed during dehydroxylation process [4]. The production of hydrogen indicates that electron deficient redox sites can be formed by decomposition of BAS. In a recent report, we investigated the reactivity of the active sites of H-ZSM-5 (MFI) after dehydroxylation using monomolecular propane reaction [5]. The selectivity is significantly different between the samples before and after dehydroxylation. However, the structure-activity relationship is still remaining unclear in part because of the complex structure of the H-ZSM-5 zeolite. Here we investigate the structure-activity relationships of H-SSZ-13 (CHA), a zeolite with a much simpler structure than H-ZSM-5.

SSZ-13 samples with Si/Al ratios of 14 and 6 are treated in an inert atmosphere at two temperatures; mild activation at temperature below 873K to prepare the “pristine” zeolite and activation at 1098K to generate dehydroxylated catalytic sites. The propane reaction is limited to the monomolecular reaction, in which  $\text{H}_2$ , propene, methane and ethene are produced.

High temperature activation shows dramatic effects on reaction rates and selectivity. The reaction rates are greatly increased after dehydroxylation with respect to the sample before dehydroxylation. For the sample before dehydroxylation, cracking-to-dehydrogenation ratios are  $\sim 2$  indicating that the cracking pathway is preferred. Cracking-to-dehydrogenation ratios for the sample after dehydroxylation are  $\sim 1.2$ . The dehydrogenation pathway is enhanced by dehydroxylation process. The measured activation energies for the dehydroxylated samples are also different from the ones calculated for the sample before dehydroxylation. The dehydrogenation pathway has higher activation energy than the cracking pathway for the sample before dehydroxylation. In contrast, the activation energy of cracking is higher than dehydrogenation for the sample after dehydroxylation. We further investigate if the presence of redox sites results in radical cation chemistry instead of protolytic chemistry in the sample after dehydroxylation.

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## **High pressure cracking of n-hexane over H-ZSM-5**

Jing Luo, Raymond J. Gorte

*Department of Chemical and Biomolecular Engineering, University of Pennsylvania*

Endothermic hydrocarbon cracking under supercritical conditions can be used for cooling of high-performance jet engines. In this study, we have examined n-hexane cracking over H-ZSM-5 at pressures from 0.03 to 137 bar, between 250 and 400 °C. The pressure dependences of the reaction rates exhibit the presence of 'sorption' effects in the high pressure region, following a Langmuir isotherm shape. This effect correlates well with the tabulated heat of adsorption for hexane.

## **Liquid-Phase Dehydration of Propylene Glycol Using Solid-Acid Catalysts**

Timothy D. Courtney, Vladimiro Nikolakis, Giannis Mpourmpakis, Jinguang G. Chen,  
Dionisios G. Vlachos

*Catalysis Center for Energy Innovation & Department of Chemical and Biomolecular  
Engineering, University of Delaware, Newark, DE 19716*

In this work we combine experiments with Density Functional Theory (DFT) calculations to investigate the heterogeneous dehydration of propylene glycol. Previous work in this area hasThe reactions are carried out with pure, liquid propylene glycol over MFI-framework zeolite catalysts or the mesoporous sulfonic-acid resin Amberlyst 36Dry. When Amberlyst 36Dry was used, propylene glycol dehydrated to form propionaldehyde with 77% selectivity. Most of the propionaldehyde further reacted with propylene glycol to form a cyclic acetal. This acetal made up 77% of the final products, dipropylene glycol made up an additional 13%, and the remaining 10% was composed of acetone and a different cyclic acetal formed from acetone. The zeolite catalysts demonstrated significantly higher selectivity towards dipropylene glycol compared to Amberlyst 36Dry. Furthermore, the zeolite had a lower conversion to cyclic acetals, improving the selectivity towards C3 products, acetone and propionaldehyde. DFT calculations confirmed that propionaldehyde is the favorable product in both catalysts, since it can be formed either through dehydration of the secondary hydroxyl group or via dehydration of the primary hydroxyl group with a concerted pinacol rearrangement. However, in the case of zeolites, the cyclic acetals experience steric hindrance since their size is comparable to that of the zeolite pores. Thus we argue that the cyclic acetals produced over the zeolite catalyst are formed homogeneously from the C3 products which have diffused out of the zeolite pores.

# Theoretical Insights into Reactions of Furans on Metal Surfaces

Vassili Vorotnikov and Dionisios Vlachos

*Department of Chemical and Biomolecular Engineering, University of Delaware,  
Newark, DE 19716*

With increasing interest in renewable fuels, fuel additives, and chemicals, a considerable attention has recently shifted towards biomass-derived building block molecules, such as 2,5-furandicarboxylic acid and furfural<sup>1</sup>. Furfural can be selectively hydrogenated to furfuryl alcohol or methylfuran, both of which potential fuel additives<sup>2</sup>. It has been found that the catalytic upgrade of furfural highly depends on the reactants' affinity to the metal. In addition, furfural is a multifunctional molecule and can potentially bind to a catalytic surface through its aromatic furan ring or through the carbonyl functional group. The type of binding as well as its strength may explain why furfural tends to decarbonylate easier on Pd catalyst while selectively hydrogenating to furfuryl alcohol and 2-methylfuran on Cu-based catalyst<sup>3-5</sup>.

In this study, we performed dispersion-corrected density functional theory calculations to investigate the adsorption and interconversion of furan, furfural, furfuryl alcohol, and 2-methylfuran on Pd(111) surface. The most stable configuration for furan, furfural, furfuryl alcohol, and 2-methylfuran entails the furan ring lying flat on the surface, centered over a hollow site. We performed an elementary step analysis for the reaction of furfural to furan, furfuryl alcohol, and 2-methylfuran. Thermodynamics favors the production of furan and CO. The activation energy for furfural reduction to furfuryl alcohol is lower than that for its decarbonylation to furan. The formation of 2-methylfuran occurs via dehydration of furfuryl alcohol or a dehydrogenation pathway through a methoxy intermediate. Our findings are in agreement with recently reported experimental results<sup>4</sup>.

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## Converting Furfural Using Bimetallic Catalysts

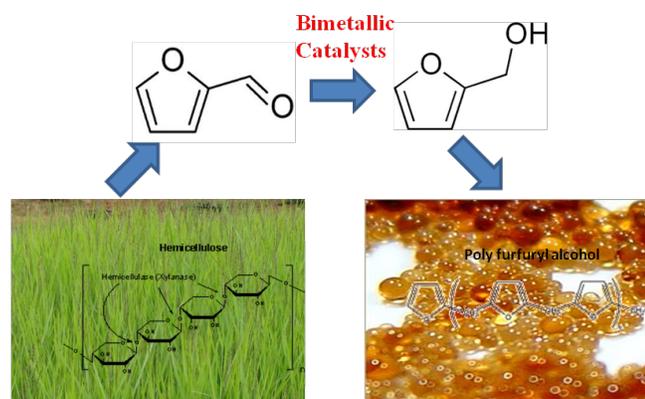
Ke Xiong, Jingguang G. Chen

*Chemical and Biomolecular Engineering, University of Delaware*

Furfural is considered as one of the platform chemicals in biomass conversion. Selectively activating the C=O bond of furfural is crucial to convert this important biomass-derived molecule to value-added chemicals like furfuryl alcohol. Copper chromite is the industrial catalyst of converting furfural to furfuryl alcohol but suffers from its high toxicity. Recently research efforts are devoted into exploiting more viable heterogeneous catalysts for hydrogenating furfural. Cu, Ni and Pt based catalysts are shown to be active for converting furfural. However, problems such as low selectivity and easy deactivation etc. limit the further application of these catalysts.

Previously Chen group has demonstrated the enhanced C=C and C=O bond hydrogenation activity of 3d/Pt(111) bimetallic catalysts using both surface science approach and reactor study[1, 2]. Particularly, Murillo et al. revealed the novel selectivity of hydrogenating the C=O bond of acrolein using PtNiPt(111) subsurface bimetallic surface[2]. These concepts are applied to biomass-derived molecules like furfural in this work. Using surface science techniques, it is found that furfural adopted desired adsorption configuration, adsorbing through the C=O bond, on Ni/Pt(111) bimetallic surfaces. The binding energy of furfural through this configuration seems a key to ensure the desired reaction pathway. However, Ni/Pt(111) was considered to have larger binding energy for furfural which subsequently remove the whole carbonyl group of furfural to make undesired products.

As one of the very few examples revealing the fundamental mechanisms of biomass-derived furans on bimetallic surfaces, this work lays the foundation for the future utilization of biomass-derived furans using bimetallic catalysts.



**Scheme** Converting biomass-derived furfural to furfuryl alcohol using bimetallic catalysts

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## **Aqueous-Phase Fructose Dehydration and 5-Hydroxymethyl Furfural Rehydration Using H-BEA-18 Zeolite**

Jacob S. Kruger, Vladimiro Nikolakis, Dionisios G. Vlachos

*Catalysis Center for Energy Innovation & Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716*

We investigate novel routes by which zeolites contribute to aqueous-phase dehydration of fructose and glucose to 5-hydroxymethyl furfural (HMF) and rehydration of HMF to levulinic acid using an acidic BEA zeolite as a model catalyst. We show by elemental analysis and comparative studies that dissolution of the zeolite occurs, producing homogeneous Al and Si species. The dissolved species homogeneously catalyze side reactions of fructose and sequential reactions of HMF. Both homogeneous and heterogeneous reactions can contribute to dehydration and the relative contribution can be controlled by varying the catalyst loading. Additionally, the zeolite preferentially adsorbs HMF and levulinic acid over sugars and formic acid. This competitive adsorption plays an important role in lower yields of HMF, but also facilitates rehydration of HMF to levulinic acid. Compared to homogeneous chemistry, zeolites can lead to a many-fold increase in conversion of HMF and selectivity to levulinic acid. We show that homogeneous Brønsted acid catalysis induced by the zeolite and reactions at the zeolite external surface play a minor role in the chemistry under the explored conditions. Finally, calcination can be used to introduce octahedrally-coordinated Al atoms in the zeolite, which act as Lewis acid sites and enable glucose isomerization to fructose. To our knowledge, this is the first mechanistic study unraveling the complexity of sugar dehydration and HMF rehydration using solid acid catalysts that can help us design better materials.

## Low temperature steam reforming of ethanol over supported noble metal catalysts

Paraskevi Panagiotopoulou\* and Xenophon E. Verykios

*University of Patras, Department of Chemical Engineering, GR-26504 Patras, Greece*

\* e-mail: ppanagiotopoulou@chemeng.upatras.gr

The use of hydrogen, in combination with fuel cells, is one of the most environmentally sound methods for the production of electrical energy, for both mobile and stationary applications. Among the various technologies which have been proposed for production of hydrogen, steam reforming of ethanol seems to be environmentally attractive, since ethanol can be produced from renewable biomass. Since ethanol can be decomposed at low temperatures, it is of interest to develop **alternative** processes and catalytic materials for hydrogen and/or power production. For example, ethanol could be reformed at low temperatures (300-400°C) toward a gaseous mixture containing H<sub>2</sub>, CH<sub>4</sub> and carbon oxides. The CO content can be significantly reduced if a WGS activity function is included on the catalyst formulation. The resulting gas mixture can then be used, without further treatment, to feed fuel cells for the production of electricity and heat. In the present study a detailed investigation has been carried out in an attempt to identify the key parameters which determine the performance of supported noble metal catalysts for the steam reforming of ethanol at low temperatures and to explore the reaction mechanism.

It has been found that, the reaction occurs in a bifunctional manner, with the participation of both the dispersed metallic phase and the support. Catalytic performance depends strongly on the nature of the dispersed metallic phase employed, with Pt and Pd exhibiting good activity and selectivity toward hydrogen. Catalytic activity and selectivity toward hydrogen is higher when Pt is supported on ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> rather than on CeO<sub>2</sub> carrier. Specific activity is defined primarily by metal crystallites and secondarily by metal/support interface. The reaction network of ethanol steam reforming over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst involves dehydration reactions on the Al<sub>2</sub>O<sub>3</sub> carrier, dehydrogenation reactions on Pt and decomposition/reformation and WGS reactions at the metal-support interface. Results of TPSR and DRIFT experiments provide evidence that the key step for ethanol reforming at low temperatures is ethanol dehydrogenation reaction, producing surface ethoxy species and subsequently acetaldehyde, which is further decomposed toward methane, hydrogen and carbon oxides. The ability of the catalyst to enhance the WGS reaction results in significant variations in the population of adsorbed surface species and in gas phase product distribution.

## **Adsorption in zeolites of components encountered in hexose dehydration**

Marta Leon Garcia, Dallas Swift, Vladimiro Nikolakis, Dionisios G. Vlachos

*Catalysis Center for Energy Innovation, Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, DE 19716*

The synthesis of chemical feedstocks from renewable sources, like biomass, has gained a lot of interest during the recent years. A promising reaction in this field is the acid catalyzed dehydration of carbohydrates, such as fructose and glucose, towards 5-hydroxymethylfurfural (HMF). HMF may serve as starting compound for several useful chemicals. Despite the fact that the dehydration of hexoses to HMF has been studied for many years, researchers are still searching for both the most suitable catalytic system and the best reaction medium. Zeolites have been proposed as advantageous heterogeneous catalysts compared to other materials, due to certain characteristics such as the possibility of tuning acidic and basic properties, hydrophilic and hydrophobic character, and adsorption and shape-selectivity. In fact, several interesting results on the dehydration of fructose and glucose using zeolites have been reported [1, 2]. However, HMF can undergo further rehydration to form levulinic acid and formic acid. Other side reactions are the oligomerizations of fructose and/or HMF leading to the so-called humins. In this regard, the study of the adsorption on the catalyst of the reactants, products and byproducts involved in the dehydration of sugars becomes crucial to understand the reactivity of such systems. Furthermore, zeolites without Bronsted acidity can also be considered as adsorbents that can selectively remove HMF from reaction medium before further degradation. Such a reactive adsorption process can be envisioned as an alternative to the bi-phasic reactive extraction configuration suggested in the literature [3]. In the present work, we studied the adsorption of fructose, glucose, mannose, 5-hydroxymethylfurfural, levulinic acid and formic acid in different zeolites as a function of temperature and zeolite  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . All zeolites tested adsorbed higher amounts of HMF than any other component and for each zeolite type HMF adsorption increased with the hydrophobicity of the zeolites (higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios). Different models of two parameters (Freundlich, Langmuir and Dubinin-Radushkevich) and three parameters (Sips, Redlich-Peterson and Toth) were evaluated to fit the experimental isotherms. The enthalpies of adsorption were also estimated from the adsorption isotherms measured at different temperatures. Finally, the competition between HMF and other components (fructose, formic acid and levulinic acid) for the active sites on H-BEA-18 was studied by performing the adsorption experiments with binary mixtures. Using the Ideal Adsorbed Solution Theory (IAST) the aqueous multicomponent adsorption equilibrium was predicted from single-solute adsorption data and compared with the experimental results.