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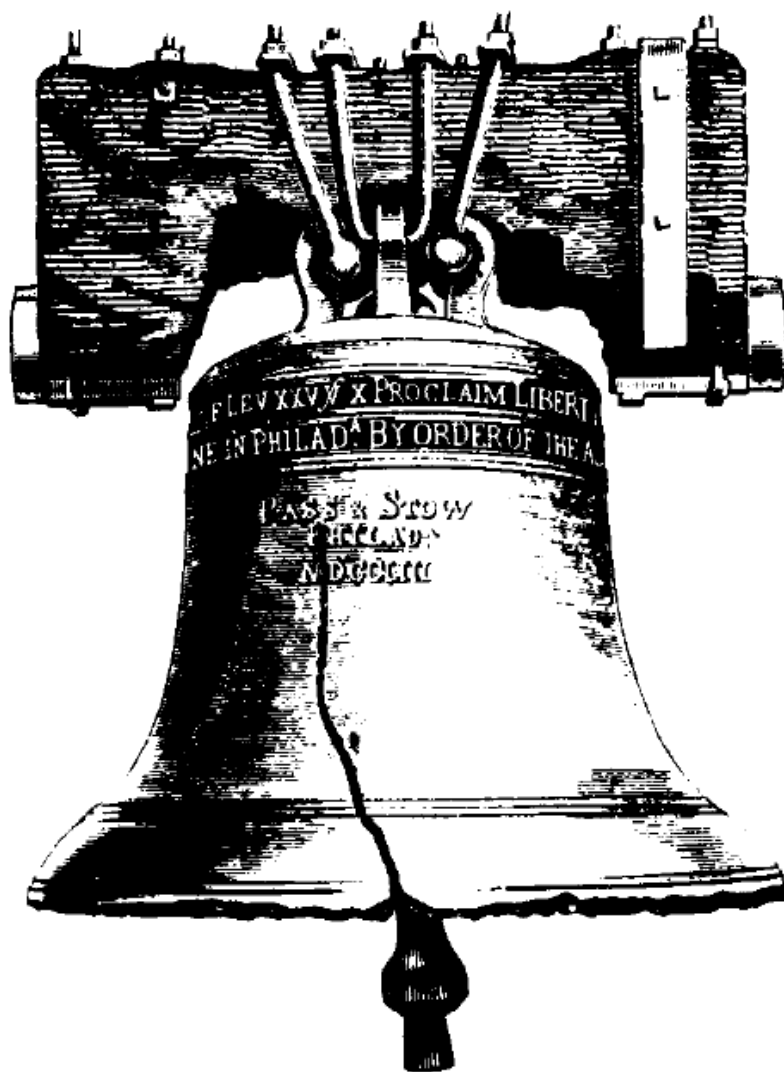
2020-2021 Virtual Poster Program

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Thursday, February 4, 2021.
6:00pm ~ 8:00pm

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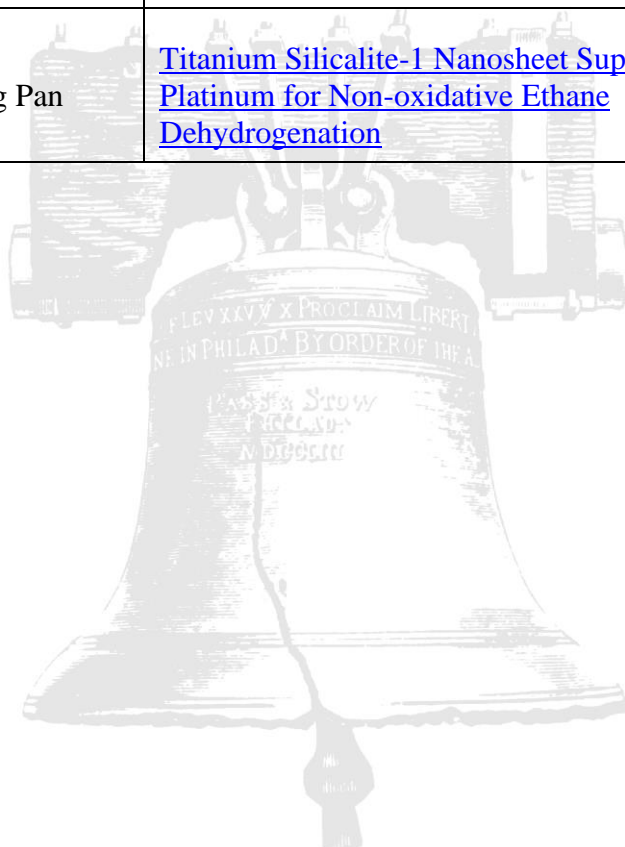| Affiliation	Presenter	Title & Zoom Link	Page #
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Nature and Role of Mn_aO_b Surface Sites in SiO_2-supported, Mn- & Na-Promoted Tungsten Oxide Catalysts (Mn-Na-WOx/SiO_2) for Oxidative Coupling of Methane (OCM)

Daniyal Kiani, Sagar Sourav, Jonas Baltrusaitis,* Israel E. Wachs*

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Due to a lack of evidence-based molecular level understanding of OCM surface reaction mechanism over the Mn_2O_3-Na_2WO_4/SiO_2 catalyst, most historically accepted OCM mechanisms like the Lunsford mechanism and the Li mechanism speculate Mn-O bonds to be critically involved in either CH_4 or O_2 activation during OCM reaction, respectively. The Lunsford mechanism postulates that WO_x serves only as the stabilizing agent while all catalytic steps occur over Mn-O-Na sites. On the other hand, the Li mechanism posits a two-site mechanism where $W^{6+}O_4$ and adjacent $Mn^{3+}_2O_3$ sites are involved in a redox cycle, switching between W^{5-6+} and Mn^{2-3+} states.

This presentation will focus on elucidating the nature and role of surface Mn_aO_b and Na-WO_x catalytic sites based on *in-situ* characterization (UV-vis DRS, Raman), temperature-programmed surface reaction (TPSR), steady-state catalytic tests, and DFT modelling. Specifically, the validity of both Lunsford mechanism (site: Mn-O-Na) and Li mechanism (site: adjacent WO_4, Mn_2O_3) will be tested based on advanced experimental characterization of a series of model catalysts and *ab initio* computational insights.
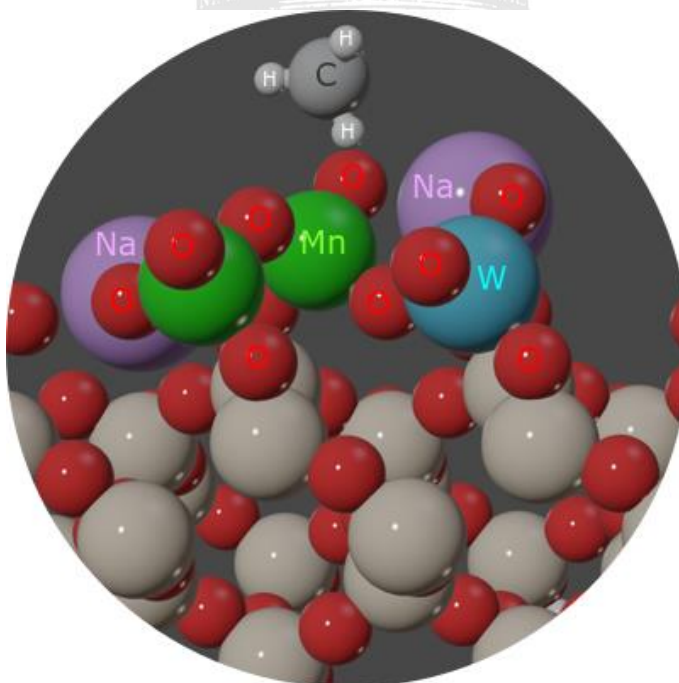
2020-2021 CCP Poster Abstract
Type: Graduate
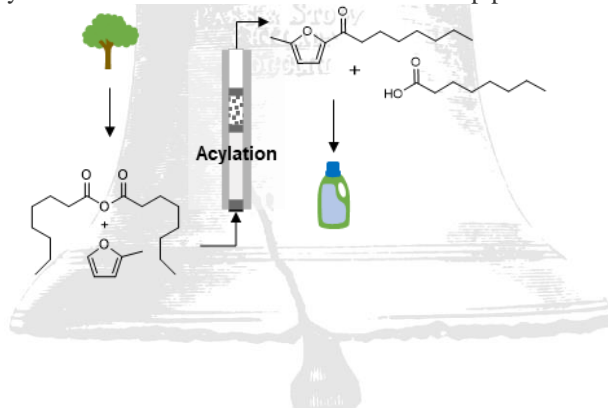Consideration in poster competition: Yes

Kinetics of acylation of 2-methylfuran with fatty acid anhydride and Al-MCM-41

Ankita Naik, Kristeen Joseph, Manish Shetty, M. Alexander Ardagh, and Paul Dauenhauer[1]

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The increasing consumer demand and the burden on fossil fuels has prompted the need for sustainable and bio-based alternatives in several consumer products. For example, oleo-furan sulphonate surfactants (OFS)[1] are a potential bio-based alternative to commercial petroleum derived surfactants in laundry detergents. These surfactants are synthesized from furans obtained from biomass and long-chain (C_{12}-C_{20}) fatty acid derivatives such as anhydrides obtained from plant-oils. The key step in their synthesis is the Friedel Crafts acylation reaction in the presence of solid Brønsted acid catalysts. There is limited understanding of the acylation kinetic of furanic substrates and fatty acid anhydrides. In this work, we study the acylation of 2-methylfuran and n-octanoic anhydride as a model system using Al-MCM-41 as a mesoporous catalyst. The apparent activation energy and rate orders are reported. An Eley-Rideal type of a mechanism is proposed to explain the apparent reaction rate orders. The study will benefit the design of catalysts to promote the acylation of furanic substrates and the scale-up process of OFS surfactants.

References:

[1] Park, D. S., Joseph, K. E., Koehle, M., Krumm, C., Ren, L., Damen, J. N., Shete, M. H., Lee, H. S., Zuo, X., Lee, B., Fan, W., Vlachos, D. G., Lobo, R. F., Tsapatsis, M. and Dauenhauer, P. J. ACS Cent. Sci. 2, 820–824 (2016).

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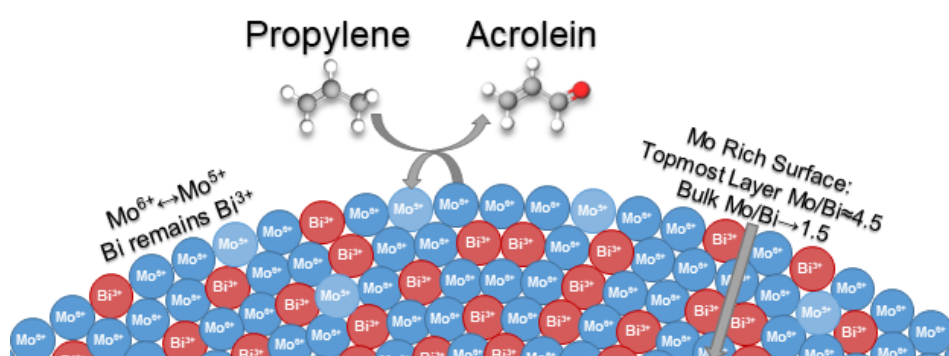Consideration in poster competition: No

A Paradigm Shift in the Nature of the Active Surface of the Bismuth Molybdate Catalyst during the Selective Oxidation of Propylene

<u>Bar Mosevitzky Lis</u>,[1] Michael E. Ford[1], Jih-Mirn Jehng[2], Israel E. Wachs[1,*]

[1] *Department of Chemical and Biomolecular Engineering, Lehigh University, 111 Research Drive, Bethlehem, 18015, USA*
[2] *Department of Chemical Engineering, National Chung Hsing University, 145 Xingda Road, Taichung, 40227, Taiwan*

Bulk bismuth molybdate mixed oxide catalysts have found application in the industrial production of acrolein and acrylonitrile from oxidation/ammoxidation of propylene since the early 1960s, thereby, revolutionizing the textile manufacturing industry in a short period of time[1]. Despite the impact of bismuth molybdate catalysts, *operando* spectroscopic surface information vital to decipher the fundamental surface structure-performance relations of these catalysts is still missing from the literature[2]. In the present work, *operando* near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) is used to monitor the elemental composition and oxidation states in the near-surface region (~1-3 nm) of the α-Bi$_2$(MoO$_4$)$_3$ catalyst under propylene oxidation reaction conditions. The *operando* NAP-XPS measurements are complemented with *in situ* high sensitivity low-energy ion scattering spectroscopy (HS-LEIS) to determine the elemental composition of the outermost surface layer (~0.3 nm) and depth profiling down to ~1.2 nm of the α-Bi$_2$(MoO$_4$)$_3$ catalyst. The corresponding bulk-phase of the α-Bi$_2$(MoO$_4$)$_3$ catalyst under reaction conditions is monitored with *in situ* Raman and XRD. The bulk phase of the α-Bi$_2$(MoO$_4$)$_3$ catalyst is stable during propylene oxidation and even after 60 minutes of propylene in the absence of molecular O$_2$. In contrast, the surface region is dynamic since Mo undergoes the Mo^{6+} $\leftrightarrow$ Mo^{5+} redox cycle while Bi^{3+} is always present and does not undergo redox during the selective oxidation of propylene. Furthermore, the topmost layer of α-Bi$_2$(MoO$_4$)$_3$ is significantly surface enriched in Mo. The pronounced surface enrichment of Mo and redox behavior of MoO$_x$ suggests that the surface Mo^{6+}O$_x$ sites are the catalytic active sites while the Bi^{3+} sites are not active sites and only t indirectly participate as ligands that moderate the MoO$_x$ redox cycle in the selective oxidation of propylene. These new molecular level insights about the surface characteristics of α-Bi$_2$(MoO$_4$)$_3$ catalysts during propylene oxidation reaction conditions are creating a paradigm shift of the previously proposed models for propylene oxidation by α-Bi$_2$(MoO$_4$)$_3$ catalysts that are based on the bulk phase of bismuth molybdate.

References
[1] J. L. Callahan, R. K. Grasselli, E. C. Milberger, H. A. Strecker, *Ind. Eng. Chem. Prod. Res. Dev.*, **9** (1970) *134*.
[2] P. Sprenger, W. Kleist, J. D. Grunwaldt, *ACS Catal.*, **7** (2017) *5628*.

OCM Reaction Pathways over Supported Na$_2$WO$_4$/SiO$_2$ Catalysts

Sagar Sourav,[1, 2] **Yixiao Wang,**[1] **Daniyal Kiani,**[2] **Jonas Baltrusaitis,**[2, *] **Rebecca R. Fushimi,**[1, *] **and Israel E. Wachs**[2, *]

[1] *Biological and Chemical Science and Engineering, EES&T, Idaho National Laboratory, 775 M K Simpson Blvd, Idaho Falls, 83415*

[2] *Department of Chemical and Biomolecular Engineering, Lehigh University, 111 Research Dr, Bethlehem, 18015*

Oxidative coupling of methane (OCM) over supported the Na$_2$WO$_4$/SiO$_2$ catalyst (prepared by incipient-wetness impregnation) was studied to identify the catalyst structure, roles of various oxide phases and catalytic active sites using multiple *in-situ* spectroscopic techniques (Raman, NAP-XPS and HS-LEIS) along with transient kinetic analysis and steady-state (SS) OCM reaction performance. The *in-situ* Raman spectra of this catalyst under dehydrated conditions (400 °C, 10% O$_2$/Ar) reveal the presence of surface Na-WO$_x$ species along with the crystalline Na$_2$WO$_4$ phase and the β-cristobalite phase of the SiO$_2$ support. Stability analysis of above metal oxide phases under OCM reaction conditions (900 °C, CH$_4$+O$_2$+N$_2$ 3.3:1:4), through *in-situ* Raman spectroscopy (see Figure 1 (left)), established that only surface Na-WO$_x$ sites, anchored to the SiO$_2$ support, are thermally stable under OCM environment; whereas the crystalline Na$_2$WO$_4$ phase is unstable and melts.

To further understand the nature and types of oxygen species associated with the two different types of metal oxide phases (surface Na-WO$_x$ and molten Na$_2$WO$_4$), ^{16}O$_2$-^{18}O$_2$ pump-probe experiments were conducted in a Temporal Analysis of Products (TAP) reactor (see Figure 1 (Right)). The evolution of molecular ^{16}O$_2$* species (after ^{18}O$_2$ introduction) from the lattice of the supported 5%Na$_2$WO$_4$/SiO$_2$ catalyst was observed at 800 °C. At lower temperature (650 °C) where the Na$_2$WO$_4$ phase crystallizes or when only dispersed Na-WO$_x$ sites are present (0.5%Na-5%WO$_x$/SiO$_2$ catalyst), the evolution of molecular ^{16}O$_2$* does not occur. This suggests that the evolved O$_2$* species are associated with the molten Na$_2$WO$_4$ phase. Additional CH$_4$ series pulsing experiment in the TAP reactor studies revealed the presence of an O* type species during anaerobic OCM.

To determine the roles of these two oxygen species towards the catalytic OCM reaction, experimental protocols were undertaken with transient O$_2$-CH$_4$, O$_2$-C$_2$H$_6$ and O$_2$-C$_2$H$_4$ pump-probe experiments in the TAP reactor and SS-OCM reaction in a flow reactor. These studies showed that (*i*) the O$_2$* species are mostly involved in the over-oxidation of CH$_4$ to CO$_2$ and in the catalytic dehydrogenation of C$_2$H$_6$ to C$_2$H$_4$ and (*ii*) the O* species selectively activate CH$_4$ to form C$_2$H$_6$ and oxidize CH$_x$ to form CO.
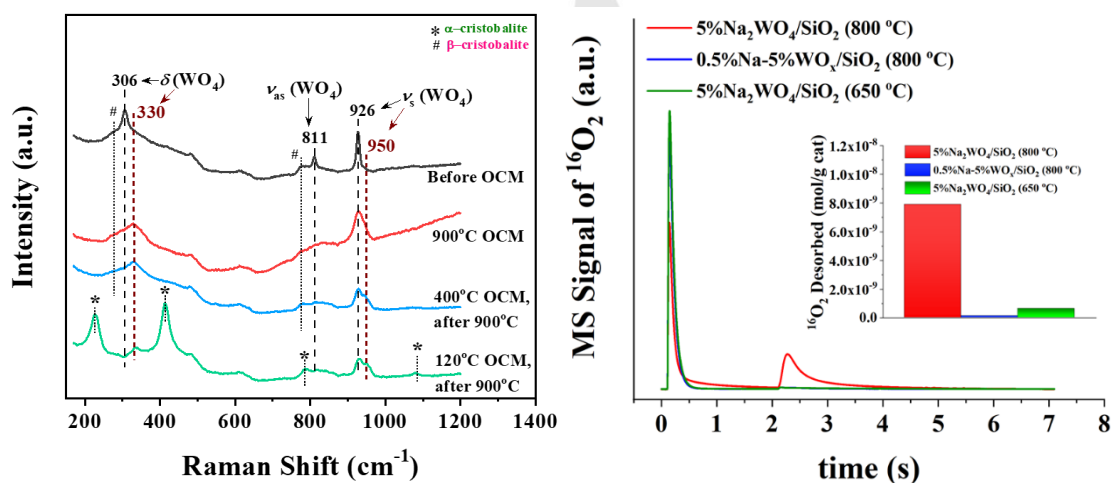
Figure 1. (Left) *In-situ* Raman spectra showing the dynamics of 5 wt% Na$_2$WO$_4$/SiO$_2$ catalyst structure as a function of different environmental conditions. (Right) Evolution of ^{16}O$_2$* from catalyst lattice from TAP ^{16}O$_2$-^{18}O$_2$ pump-probe experiment (pump-probe spacing, Δt = 2 s).

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Tuning the Surface Active Sites by Surface Modification of Supported ReO$_x$/(SiO$_2$-Al$_2$O$_3$) Catalysts for Olefin Metathesis

Bin Zhang[1], Soe Lwin[1], Shuting Xiang[2], Anatoly I. Frenkel[2,3], Israel E. Wachs[1]

[1] *Operando Molecular Spectroscopy and Catalysis Laboratory, Department of Chemical & Biomolecular Engineering, Lehigh University, Bethlehem, PA, 18015, United States*
[2] *Department of Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, NY, 11794, United States*
[3] *Division of Chemistry, Brookhaven National Laboratory, Upton, NY 11973, United States*

Due to the global shortage of propylene, the chemical industry is turning to metathesis of ethylene and 2-butene to produce on purpose propylene. Heterogeneous supported ReO$_x$/Al$_2$O$_3$, MoO$_x$/Al$_2$O$_3$ and WO$_x$/SiO$_2$ catalysts have been found to be most efficient for metathesis of olefins. Although the supported ReO$_x$/Al$_2$O$_3$ catalyst has received much attention for olefin metathesis, the effect of the oxide support on olefin metathesis by supported ReO$_x$ catalysts is still not well understood. For the most common Al$_2$O$_3$ support, not all rhenia anchoring sites lead to activation of rhenia for olefin metathesis. Modified Al$_2$O$_3$-SiO$_2$ mixed oxide supports are highly effective supports for promoting surface ReO$_x$ sites for olefin metathesis. The improved metathesis performance of the Al$_2$O$_3$-SiO$_2$ mixed oxide supports has been attributed to the modified surface Lewis and Brønsted acidity, but supporting data were not provided in these studies. The nature of the surface AlO$_x$, SiO$_x$ and ReO$_x$ sites present in these mixed oxide supports are still unknown. The objective of the present study is to determine the origin of enhanced performance of the surface ReO$_x$ sites on Al$_2$O$_3$-SiO$_2$ mixed oxide supports.

Modern *in situ* molecular spectroscopy (UV-Vis, Raman, IR and XAS) and chemical probe studies (ammonia chemisorption, C$_2^=$/C$_4^=$-titration, C$_3$H$_6$-TPSR and steady-state propylene self-metathesis) of the surface ReO$_x$ sites on Al$_2$O$_3$ and SiO$_2$, and surface modified mixed oxide supports (SiO$_2$/Al$_2$O$_3$, Al$_2$O$_3$/SiO$_2$, and ZSM-5 (Si/Al=15)) were applied to address the origin of the promotional effect. The characterization studies of the supported rhenia catalysts demonstrated that the enhanced activity on Al$_2$O$_3$-SiO$_2$ mixed oxide supports is due to anchoring rhenia at Brønsted acidic Al-(OH)$^+$-Si surface hydroxyls that results in a greater number of activated surface ReO$_x$ sites.

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2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Direct Conversion of Ethylene to Propylene Through Simultaneous Ethylene Dimerization and Olefin Metathesis with 8%NiSO$_4$/8%ReO$_4$/γ-Al$_2$O$_3$ Catalyst

E. Ream[1], E. Li[1], I.E. Wachs[1]

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Propylene is a major petrochemical building block used to generate a variety of important chemicals. Historically, propylene has been produced as a byproduct of steam cracking. With an increase in shale gas production, however, steam cracking processes are switching to lighter feedstocks that produce less propylene.[1] Thus, there is a need for the development of "on-purpose" methods for producing propylene. The direct conversion of ethylene to propylene (ETP) through simultaneous ethylene dimerization and olefin metathesis is a promising method for propylene production that is currently in development. In ethylene dimerization, two ethylene molecules dimerize to form butene molecules and through olefin metathesis, ethylene and 2-butene form two propylene molecules. Many catalysts have been proposed for this reaction. One method for designing a catalyst for ETP is to combine elements of catalysts for ethylene dimerization and catalysts for olefin metathesis. Ethylene dimerization catalysts are typically Ni-based and olefin metathesis catalysts are typically Mo-, W-, or Re-based.[2,3] In the present study, a supported NiSO$_4$/ReO$_4$/γ-Al$_2$O$_3$ catalyst was synthesized for the direct conversion of ethylene to propylene, in which NiSO$_4$ performs ethylene dimerization to butenes and ReO$_4$ performs olefin metathesis to propylene. The catalyst was extensively characterization at the molecular level with *in situ* IR spectroscopy, *in situ* UV-vis spectroscopy, C$_2^=$-TPSR spectroscopy, and ammonia adsorption to probe the nature of the surface acid sites. Preliminary findings at 60°C achieved an ethylene conversion of 63% and a selectivity towards propylene of 76%. The structure-activity relationships of this catalytic system will be discussed during the presentation.

References
[1] V. Blay; E. Epelde, R. Miravalles; L.A. Perea. *Catalysis Reviews*, **Vol. 60** (2018) *278-335*.
[2] A. Finiels; F. Fajula; V. Hulea. *Catal. Sci. Technol.*, **4** (2014) *2412-2426*
[3] S. Lwin; I.E. Wachs. *ACS Catal.* **4** (2014), *2505-2520*

2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Unraveling the Reactivity of Ethylene with Oxygen Species on/in Silver Catalysts

Tiancheng Pu,[1] Bar M. Lis,[1] Adhika Setiawan,[2] Srinivas Rangarajan,[2,*] Israel E. Wachs[1,*]

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[2] *Computational catalysis and materials design group, Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, 18015*

Silver catalysts find wide industrial application for ethylene oxidation because of its uniquely high selectivity towards ethylene oxide (EO). The nature of the selective oxygen species on/in silver responsible for EO formation have been extensively debated in the literature because of the scarcity of molecular level measurements and computational calculations. Integration of *in situ* Raman spectroscopy and Temperature Programmed Surface Reaction (TPSR) spectroscopy allowed for chemically probing the reactions of ethylene with the oxygen species on/in Ag powder and Ag/α-Al$_2$O$_3$ catalysts. Although multiple oxygen species are present on/in Ag (surface, subsurface and bulk), the oxygen species that give rise to a Raman band at ~ 820 cm^{-1} are associated with selective formation of ethylene oxide. The Raman band at ~820 cm^{-1} is found to selectively exchange under mild conditions (T < 100 ºC) with C^{18}O$_2$ indicating that this oxygen species is present on the surface of Ag. Near Atmospheric Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) studies indicate that the oxygen species with a binding energy of ~532 eV is consumed by reacting with ethylene. Density Functional Theory (DFT) calculations bring further insights into the detailed structures of the corresponding oxygen species. The methodologies and insights developed are widely applicable to the understanding of a wide range of catalytic oxidation reactions.

2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Ethylene Dimerization to n-Butene with Nickel Sulfate on Zirconia: Investigation of the Molecular Structure and Activity of Surface Nickel and Sulfate Species

Erin M. Sobchinsky, Shiao-Chien Tsai, Israel E. Wachs[1]

Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, United States

The shift to lighter hydrocarbon feedstocks due to the growing abundance of natural gas has led to a global shortage of *n*-butene, stimulating interest in ethylene dimerization as an effective means for producing butene from natural gas derived ethylene. Industrial ethylene dimerization processes, however, frequently rely on homogenous catalyst that present several environmental and operational challenges. Consequently, there has also been interest in developing heterogeneous catalyst that can achieve comparable activity and selectivity to their homogeneous counterparts. Numerous heterogenous catalysts for ethylene dimerization have been investigated, with Ni-based catalysts typically reported to have high activity and selectivity to *n*-butene. This work investigates sulfated nickel zirconia as a heterogeneous ethylene dimerization catalyst, owing to its strong surface acidity and well-dispersed nickel phase. The molecular structure of the surface NiO and sulfate species, the oxidation state of the Ni active site, and the importance of sulfate-Ni interactions in catalytic activity for ethylene dimerization on sulfated nickel zirconia catalysts remain controversial. Few studies on sulfated nickel zirconia have applied *in situ* characterization under reaction which is vital for understanding the nature of the catalyst during operating conditions. In this work, a series of nickel sulfated zirconia catalysts were synthesized by varying the loading of the active components, the zirconia support and the order of impregnation of Ni and sulfate species. Critical characterization techniques including *in-situ* UV-vis, *in-situ* IR, NH_3-IR and $C_2^=$-TPSR spectroscopy were utilized to investigate the nature of the active site, surface species and catalytic activity. The surface sulfate species were found to anchor at terminal hydroxyl groups while Ni_{2+} sites may be anchoring to adjacent surface hydroxyl sites or defect sites. The order of impregnation of nickel and sulfate affects the catalytic activity as well as the Bronsted to Lewis acid ratio. The molecular level structure-activity relationships will also be discussed during the presentation.

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Towards Data-Driven Structure-Property Relations for Predicting Adsorption Entropy in Siliceous Zeolites

<u>Christopher Rzepa</u>,[1] Daniel W. Siderius,[2*] Harold W. Hatch,[2] Vincent K. Shen,[2] Srinivas Rangarajan[1], Jeetain Mittal[1]

[1] Department of Chemical and BioMolecular Engineering, Lehigh University, Bethlehem, PA, USA
[2] Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, MD, USA

A thorough understanding behind shape selective zeolite catalysis and its relationship to entropy remains elusive[1]. Furthermore, the interaction of both the adsorbent pore structure and adsorbate molecular structure on entropic transfer quantities is largely unexplored and, consequently, significant opportunities exist for the development of systems or correlations for relating the adsorption-catalysis-thermodynamics to fundamental and more easily measured physical properties. Previous works using experimental data have demonstrated simple linear scaling relationships between the gas- and adsorbed-phase entropies[2,3], allowing for sensible predictions based on more-easily obtained physical parameters. However, the resultant conclusions were based on experimental data for a relatively small subset of industrially relevant alkanes and a few alcohols.

Motivated by these results in the literature, here we computationally explore the generality of such relationships across multiple classes of molecules and frameworks. We model our adsorption systems (i.e., the adsorbates and adsorbents) by implementing TraPPE forcefields[4] and quantify the adsorbate entropy by performing canonical Monte-Carlo integrations (cf. Widom test particle method)[5] using the FEASST[6] molecular simulation package. Our dataset was composed of thirty-seven adsorbates, across ten functional categories, adsorbed within five siliceous zeolite structures. Our results show that simple linear correlations between the gas- and adsorbed-phase entropies, to a good first approximation, continued to exist for our larger and more diverse set of molecules.[7] Moreover, we have found that each correlation was largely dependent on the zeolite's size, characterized by physical descriptors such as the largest cavity diameter and occupiable volume, indicating that the adsorbate entropy may be predicted using such metrics. To further elicit such "structure-topology-thermochemistry" relations, we have expanded our dataset to include over eight thousand combinations between molecules and zeolites, each consisting of twenty-four unique topological features for zeolites and eleven unique molecular descriptors. Ultimately, our effort is to develop an interpretable data-driven model, which, given framework and molecular descriptors of the system, may be used to predict the adsorbate entropies of novel systems.

References

[1] Smit, B., & Maesen, T. L. M. (2008). Towards a molecular understanding of shape selectivity. Nature, 451, 671.
[2] Campbell, C. T.; Sellers, J. R. V. The entropies of adsorbed molecules. J. Am. Chem. Soc. 2012, 134 (43), 18109−18115.
[3] P. J. Dauenhauer, O. A. Abdelrahman, ACS Central Science 2018 4 (9), 1235-1243
[4] M. G. Martin and; J. Ilja Siepmann, J. Physical Chemistry B 1998 102 (14), 2569-2577
[5] Widom, B. Some Topics in the Theory of Fluids.J. Chem. Phys.1963,39, 2808–2812.
[6] Hatch, H. W., Mahynski, N. A., and Shen, V. K. (2018) FEASST: Free Energy and Advanced Sampling Simulation Toolkit. J. Res. Natl Inst Stan, 123, 123004.
[7] Rzepa, C., Siderius, W. D., Hatch, H. W., Shen, V. K., Rangarajan, S., and Mittal, J., J. Physical Chemistry C 2020 124 (30), 16350-16361

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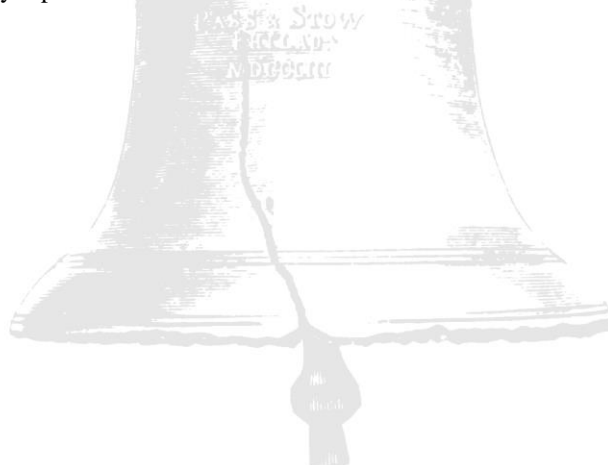2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Exploring chemically active sites on Ceria-supported Single-Atom Catalysts from Experiments and First principles

Shyam Deo,[1] **Linxi Wang**[1]**, Ahana Mukhopadhyay**[1]**, Rob Rioux**[1]**, Michael Janik**[1]

[1] *Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States*

The active sites for single-atom catalysts (SACs) remain highly debated, and fundamental insights are limited due to experimental challenges. We used CO oxidation over metals like Ni, Pd and Pt supported on ceria as a test case for understanding the role and effectiveness of different metal SACs. DFT calculations in conjugation with experiments examine the variation of catalytic performance across the metals and identify the synergy between individual metal atoms and the support towards CO oxidation. Also, since oxidation reactions consume oxygen, the oxidation state of the metal sites as well as specific metal-support interactions are crucial in understanding and predicting the catalytic performance. Therefore, more broadly than understanding CO oxidation, we evaluate the active site, catalyst oxidation state, and reaction mechanism under working conditions of SACs, by leveraging first-principles calculations and spectroscopic experimental techniques. Further on, we also introduce first principles microkinetic modeling of CO oxidation over the metal atoms to provide further insights into the dynamic states of single atoms under reaction conditions. This is especially important for single-atom catalysts whose reaction mechanism is less established and different from the one of extended surfaces. Together we gather evidence for correlation between active single atom states and the resulting variation in kinetics across Ni, Pd, Pt single atoms and those previously reported over extended surfaces/nanoclusters.

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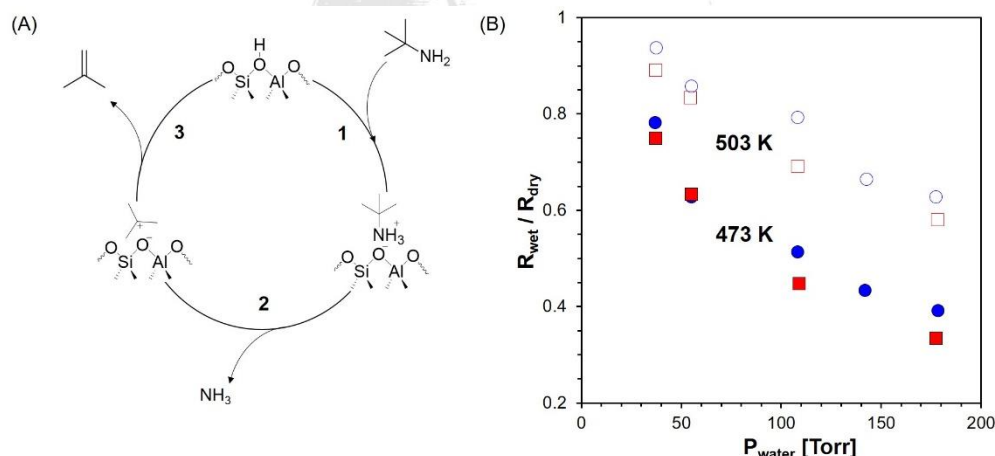2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Kinetic Investigation into the Effect of Water on Alkylamine Hofmann Elimination over H-ZSM-5

<u>Han Chen</u>,[1] Omar A. Abdelrahman[1]

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Catalytic transformations over solid acid catalysts frequently involve water as a solvent, particularly when considering sustainable chemical conversions related to biomass upgrading. While it is well recognized that water can significantly affect catalytic kinetics over solid acids, the means by which this occurs remains debated. The challenge usually arises from the highly non-ideal thermodynamics of the aqueous phase, further complicated by reactions that already involve water as a reactant or product. We present a kinetic investigation of the vapor phase Hofmann elimination of tert-butylamine (TBA) over H-ZSM-5 as a model reaction for deciphering the effect of water on solid acid catalysis. The Hofmann elimination offers a purely Brønsted acid catalyzed and water-free chemistry, allowing us to systematically study the effect of a solvent like water in the more thermodynamically ideal vapor phase. Kinetic measurements in the absence of water reveal a tert-butylammonium adsorbate as the most abundant reaction intermediate, with its E1-like unimolecular decomposition as the rate determining step (Figure 1A). This reduces the apparent kinetic measurements to those of the rate determining step, which we interrogate in the presence of controlled water partial pressures. Water reduces the rate of Hofmann elimination (Figure 1B) and increases the apparent activation energy. Linearization of rates based on Langmuir isotherm indicates that water cluster formation around the Brønsted acid site is unlikely. Rate measurements with increasing total pressure but at a fixed ratio of P_{water}/P_{TBA} reveal a mechanism by which water hinders the rate of reaction, without competing for adsorption on the catalytically active Brønsted acid sites. We propose two hypotheses based on the results: water preferentially de-stabilizes the kinetically relevant transition state; alternatively, water occupies a neighboring framework site crucial to the Brønsted acid catalytic cycle. Lastly, microkinetic modeling is carried out trying to capture the kinetic effect of water over various partial pressures and temperatures.

Figure 1. A. Proposed E1 mechanism of Hofmann elimination over a Brønsted acid site in an aluminosilicate zeolite; B. Rate ratios of wet and dry condition against varying P_{water}, over H-ZSM-5 with Si/Al = 11.5 (■/□) and Si/Al = 140 (●/○) at 473 K and 503 K, with P_{TBA} = 10 Torr.

2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Olefin methylation and chain initiators in the methanol to hydrocarbon reaction over iron zeolites

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The methanol to hydrocarbons (MTH) reaction is a pathway for taking methanol or dimethyl ether (DME) and converting it into fuels and chemicals. The reaction is catalyzed by various acid zeolites and using the large-pore zeolite H-[Al]Beta, the products contain predominantly triptane and isobutane. The alkanes are formed via hydrogen transfer reactions of the isostructural olefins formed through the successive methylation of small olefins in the olefin cycle of the MTH reaction. The hydride donors (other olefins) then undergo further reactions to give aromatic products such as n-methylbenzenes; these side products are not valuable as a fuel and lead to catalyst deactivation. Zeolite catalysts containing framework iron (instead of aluminum) reduce the rate of hydrogen transfer reactions due to their weaker Brønsted acid strength but also reduce methylation rates: on Fe-zeolites thus, reaction temperature must be relatively high also leading to rapid deactivation. To reduce reaction temperatures, a chain initiator can be added to the feed to jumpstart chain growth and the olefin cycle. We have found, for example, that pure DME is essentially unreactive at 240 °C over H-[Fe]Beta, but after the addition of isobutene, the consumption rate of DME increased significantly as shown in Figure 1. After stopping the isobutene flow, DME consumption rate decreased back to its initial low value. Co-feeding isobutene thus overcomes low catalytic rates by increasing the DME consumption rate at otherwise low reaction temperatures where the precursors to stimulate the formation of the carbon pool, do not form. These results suggest that, over Fe-zeolites, isobutene can initiate the methylation of olefins and the olefin cycle. This allows for the carbon from shale gas to be incorporated into larger molecules more suited for uses as fuels and chemicals then traditional MTH reaction products.
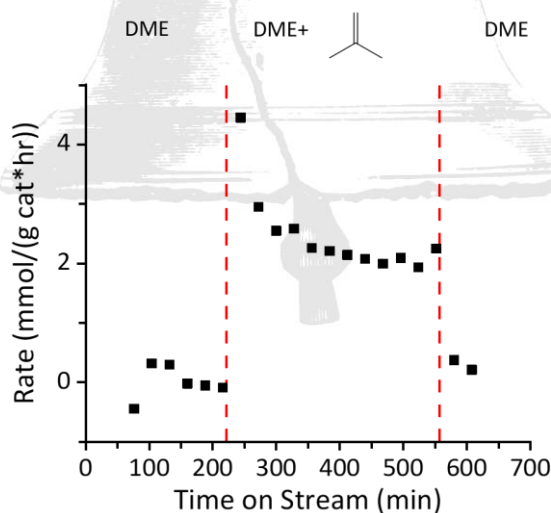

Figure 1: **240 °C**, 20 PSIG, and WHSV 6.12 $g_{DME}g_{Catalyst}^{-1}$ hour $^{-1}$ 15.2/1 DME/Isobutene Ratio, $\approx$**1.5-2% DME Conversion,** The red lines correspond to Isobutene being turned on and off.

2020-2021 CCP Poster Abstract
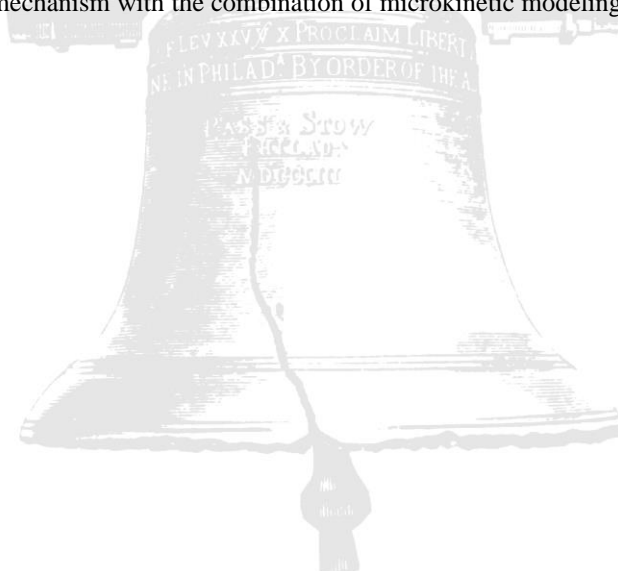Type: Graduate
Consideration in poster competition: Yes

Mechanism Inference from Information-Rich Time-Varying Spectrokinetic Data: A Conceptual Framework

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Combining the microkinetic modeling, reaction kinetics studies, and operando molecular spectroscopy experiments together has been applied to identify the reaction mechanism of heterogeneous catalytic reaction. Traditionally, kinetic experiments are performed at steady state reaction conditions. On the other hand, time varying kinetic experiments such as modulated excitation spectroscopy (MES) and temporal analysis of product (TAP) allows for capturing fast-time scale transients of the reaction system which are often missed in steady state kinetic study. Despite providing rich information about the reaction system, such time-varying data in combination with DFT is rarely used to develop mechanistic models of heterogeneously catalyzed reaction systems beyond simple demonstrations of few step first order reactions.

In this work, we develop a statistical and microkinetic modeling framework to extract the kinetic information from modulated kinetic experiments. We showcase MES signal (peak position, shape, number of peaks, phase lag, etc.) is recovered via regularized optimization. We further discuss the feasibility of identifying the reaction mechanism with the combination of microkinetic modeling and modulated kinetic experiments.

2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Understanding the Entropic Contributions of Irreversibly Bound Adsorbates on Zeolite Surfaces

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The design of solid acid catalysts has greatly benefitted from understanding the energetics of adsorbates (enthalpy and entropy), where the relative stability of surface species dictates the overall catalytic turnover frequency. While enthalpic contributions are relatively well understood, limited information exists for entropic contributions to adsorption,1 particularly for strongly bound species, representative of reaction intermediates and transition states. This is due to the fact that existing methods to measure an adsorbate's entropy, require the adsorption/desorption process to equilibrate 2. Strongly bound intermediates like alkylamines adsorbed on a Brønsted acid site, however, do not equilibrate on relevant timescales given their negligible rate of desorption, limiting the applicability of existing methods. To overcome this issue, we leverage the concept of adsorption assisted desorption through the co-adsorption of multiple strongly bound adsorbates. While one strongly bound adsorbate does not equilibrate due to limited desorption, two or more strongly bound adsorbates can continuously displace one another from an active site and attain adsorption-desorption equilibrium. Applying this concept to alkylamine adsorption on Brønsted acid sites in H-ZSM-5 (Si/Al = 140), we demonstrate for the first time the experimental ability to measure the overall adsorption thermodynamics of strongly bound species. Despite the relatively strong adsorption, we find that the Langmuir adsorption isotherm can capture the adsorption of multiple alkylamines varying in size and basicity over a wide range of conditions. Comparing a homologous family of sec-alkylamines, varying only in alkyl chain length (C3-C5), we find a fixed contribution to both the enthalpy and entropy of adsorption per methylene unit. Terminal adsorption of n-alkylamines is favored on H-ZSM-5 when compared with the central adsorption of sec-alkylamines; relative to isopropylamine, n-propylamine adsorbs with an enthalpy and entropy of 21 kJ mol-1 and 45 J mol-1 K-1, respectively. Similar to the adsorption energetic trend observed for sec-alkylamines, n-alkylamines exhibit a fixed contribution to the enthalpy and entropy of adsorption per methylene unit (C3-C5, **Figure 1**).
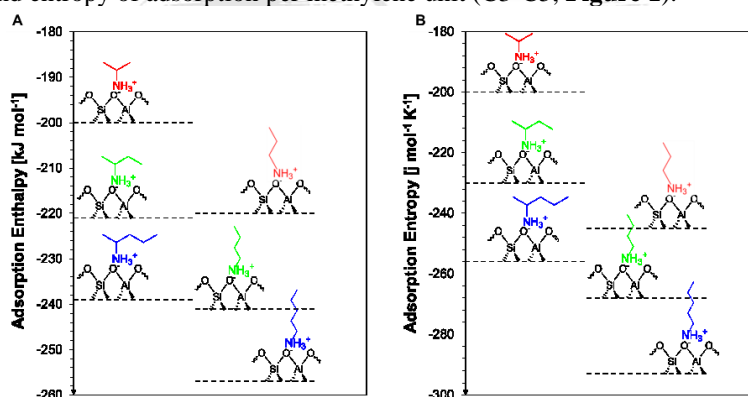
Figure 1: Adsorption Energetics of iso and n-propylamine (red), sec and n-butylamine (green), sec and n-pentylamine (blue), over H-ZSM-5 (Si/Al = 140) A. Adsorption Enthalpy difference for every methylene unit increase **B.** Adsorption entropy difference for every methylene unit increase.

References
1. C.T. Campbell, and J.R.V. Sellers, *The Entropies of Adsorbed Molecules.* Journal of the American Chemical Society, 2012. **134**(43): p. 18109-18115.
2. G. Sastre, and A. Corma, *The confinement effect in zeolites.* Journal of Molecular Catalysis A: Chemical, 2009. **305**(1): p. 3-7

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Structure-activity relationships in the conversion of ethanol to 1,3-butadiene over supported ZnO/ZrO2/SiO2 catalysts

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Abundant and low-cost shale gas has replaced naphtha as the feedstock of choice for C_2-C_4 olefin production. This change has led to a shortage of 1,3-butadiene (BD), a critical intermediate for the manufacture of synthetic rubber. The constrained BD supply has triggered price fluctuations and interest in on-purpose BD production. Cellulosic ethanol is a sustainable feedstock quickly becoming mainstream and its conversion into BD significantly reduces lifecycle greenhouse gas emissions when compared to petroleum-derived BD. Supported ZnO/ZrO2/SiO2 catalysts show particular promise for the one-pot conversion of ethanol to BD, yet little is known about the atomic structures giving rise to catalytic activity. We report how insights about catalytic activity and selectivity, as probed by temperature-programmed surface reaction spectroscopy, are made possible via *in situ* X-ray absorption, Raman, and UV-vis spectroscopies. These new fundamental insights point towards structure-activity/selectivity relationships to guide the rational design of improved catalyst performance.

2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

High selectivity of Sn-modified alumina for propane dehydrogenation under H₂S treatment and co-feed

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A large share of natural gas reserves is sour and can contain a significant amount of H_2S. These streams are typically treated using energy-intensive separation methods to remove sour gas molecules to preserve downstream catalysts and equipment. In contrast, we investigate sour gas tolerant catalysts to devise catalytic processes for sour natural gas monetization without prior CO_2 and H_2S removal.

The catalytic dehydrogenation of propane (PDH) is the most direct and selective way to produce propylene and valorize propane from abundant natural and shale gas resources. Recent experimental and computation work has demonstrated that earth-abundant and environmentally benign bulk metal oxide, such as Al_2O_3, TiO_2, and ZrO_2 can exhibit good activity and selectivity for PDH. Recently, we showed that bulk γ-Al_2O_3 catalyst shows high selectivity for propane dehydrogenation upon pretreatment and co-feeding with H_2S.[1] Subsequently, to improve catalyst selectivity, we have modified alumina by the introduction of Sn to reduce cracking reaction over alumina catalyst. The selectivity is further enhanced from ~94% over Al_2O_3-S to 98% on 1.5-10 Sn/Al_2O_3-S at identical operating conditions although a decrease in rate was observed with Sn loading during the first few dehydrogenation cycles. Interestingly, gradual loss of Sn with time on stream leads to regaining original rate comparable to Al_2O_3-S which was verified using atomic absorption spectroscopy (AAS). We postulate that the active sites are defect sites on the 110 facet comprised of a tri-coordinated Al atom and Sn-based species poison unselective sites on the catalyst. Further, complementary kinetic studies and DFT calculations show that the catalyst surface is under dynamic thermodynamic equilibrium which is dependent on H_2S and H_2 partial pressure. For deriving key insights into the structure, reactivity, selectivity, with time on-stream stability, the catalysts were characterized by XRD, AAS, NH_3-TPD, in situ IR, CO_2-DRIFTS, NH_3-DRIFTS, AC-STEM, and TPO. This study shows that Sn modified alumina as (i) highly selective, (ii) regenerable, (iii) environmentally benign, and (iv) low-cost sulfur tolerant catalysts for large-scale non-oxidative dehydrogenation of propane to propene (PDH) for sour gas up-gradation.

References:
[1] L. Sharma, X. Jiang, Z. Wu, J. Baltrus, S. Rangarajan, J. Baltrusaitis, Elucidating the origin of selective dehydrogenation of propane on γ-alumina under H2S treatment and co-feed, J. Catal. (2020). doi:https://doi.org/10.1016/j.jcat.2020.12.018.

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Enhancing the Activity of LST-YSZ Electrodes with Ultra-Low Catalyst Loadings via ALD

Julian M. Paige[1], Duytam Vu[1], Tianyu Cao[1], Steven McIntosh[2], Raymond J. Gorte[1], and John M. Vohs[1]

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The enhancement of the catalytic activity of $La_{0.3}Sr_{0.7}TiO_3$ (LST) – yttria-stabilized ZrO_2 (YSZ) Solid Oxide Electrochemical Cell (SOC) fuel electrodes by using Atomic Layer Deposition (ALD) to decorate their surfaces with very low weight loadings of catalytic materials (Ni, Pt, Pd, Fe, Co and CeO_2) was studied. The electrochemical performance of the ALD-modified cells was compared to those in which much higher weight loadings of Ni or Pt were added to the electrodes using wet infiltration. The results of the study show that for the highly-active metal catalysts, Ni, Pt, and Pd, weight loadings as small as 0.01 wt % were sufficient to achieve performance similar to that of the infiltrated cells that had catalyst weight loadings in excess of 0.5 wt%. Thermal stability of the ALD-deposited catalysts was an issue, however, indicating that methods to stabilize metal catalyst dispersion on the electrode surface is still needed.
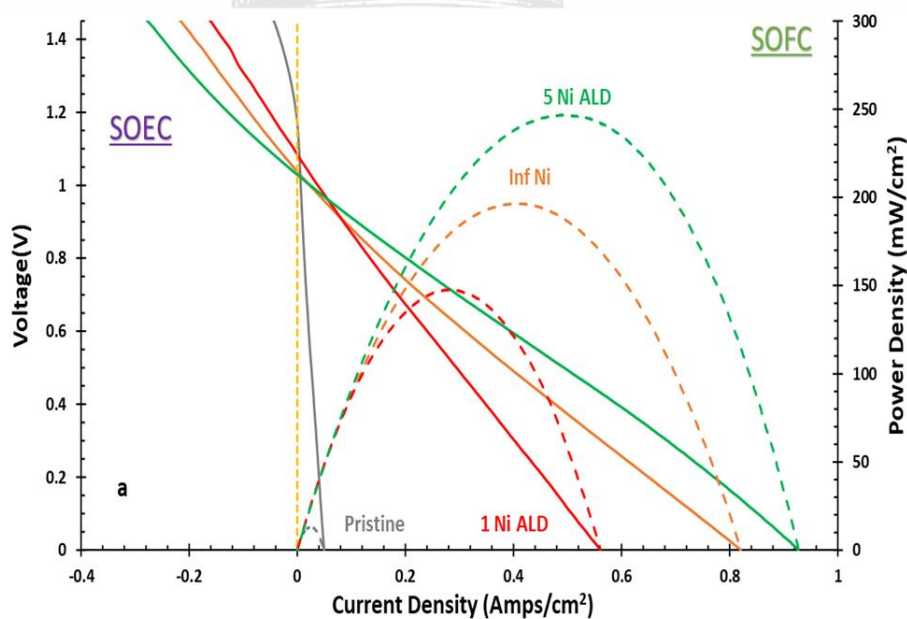
Performance of Pristine & Ni modified LST-YSZ/LSF-YSZ cells at 973 K: a. IV-curves (solid) & power density curves (dashed)

2020-2021 CCP Poster Abstract
Type: Postdoc
Consideration in poster competition: No

Catalytic Performance and Crystallinity of Perovskite Thin Films Supported on Different Oxides
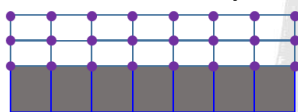
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Perovskite thin films decorated with catalytic metals supported on high-specific-area oxides have demonstrated fascinating catalytic performance and impressive stability in reforming reactions of hydrocarbons [1] and automotive emission control [2]. In present research, we investigated the interaction between the perovskite overlayer and its supporting oxide. $LaFeO_3$ and $CaTiO_3$ thin films with equivalent thickness of ~0.5 nm were deposited to different supporting materials such as $MgAl_2O_4$, γ-Al_2O_3 and amorphous SiO_2. X-ray diffraction results shown that films deposited to the crystalized supports tend to possess high degree of crystallinity after high temperature oxidation, while those deposited to the amorphous support (SiO_2) did not crystalize themselves during the same oxidation process. Catalytic performance of Pt-$LaFeO_3$ thin film supported on SiO_2 was tested and compared with Pt-$LaFeO_3$ supported on $MgAl_2O_4$. Both catalysts showed similar catalytic performances in CO oxidation reaction, however $LaFeO_3$ thin film deposited to SiO_2 was less stable than its analog supported on $MgAl_2O_4$. Metallic Fe and La_2O_3 were found in the XRD pattern of the SiO_2 supported sample after reduction at 1073 K, which has never been seen in the $MgAl_2O_4$ supported systems.

Perovskite film formed on crystalized support · Film formed on amorphous support
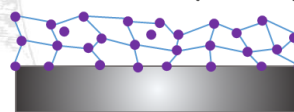
References
[1] Lin, C.; Jang, J.B.; Zhang, L.; Stach, E.A.; Gorte, R.J, *ACS Catal., 8* (2018) *7679*.
[2] Mao, X.; Foucher, A.C.; Montini, T.; Stach, E.A.; Fornasiero, P.; Gorte, R.J, *J. Am. Chem. Soc., 142* (2020), *10373*.

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The effects of SMSI on m-Cresol Hydrodeoxygenation over Pt/Nb$_2$O$_5$ and Pt/TiO$_2$

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The hydrodeoxygenation (HDO) of m-cresol was studied on Pt/Nb$_2$O$_5$ and Pt/TiO$_2$ catalysts to understand the effects of Strong Metal Support Interactions (SMSI). The Nb$_2$O$_5$ and TiO$_2$ supports were prepared as 0.7-nm films on MgAl$_2$O$_4$ by Atomic Layer Deposition (ALD) to ensure that the structures of the catalyst were the same. When reduced at 773 K to place it in the SMSI state, Pt/Nb$_2$O$_5$/MgAl$_2$O$_4$ was much less active than Pt/MgAl$_2$O$_4$ at 573 K but much more active at 623 K. While Pt/MgAl$_2$O$_4$ deactivated rapidly due to coking, Pt/Nb$_2$O$_5$/MgAl$_2$O$_4$ showed significantly better coke tolerance and was almost 100% selective towards toluene production. Pt/Nb$_2$O$_5$/MgAl$_2$O$_4$ reduced at lower temperatures exhibited intermediate catalytic properties. The effect of reduction temperature on Pt/TiO$_2$/MgAl$_2$O$_4$ was much less and this catalyst was more similar to Pt/MgAl$_2$O$_4$ than its Nb$_2$O$_5$ counterpart. The implications of these results for understanding the nature of oxide promoters on HDO of m-cresol are discussed.
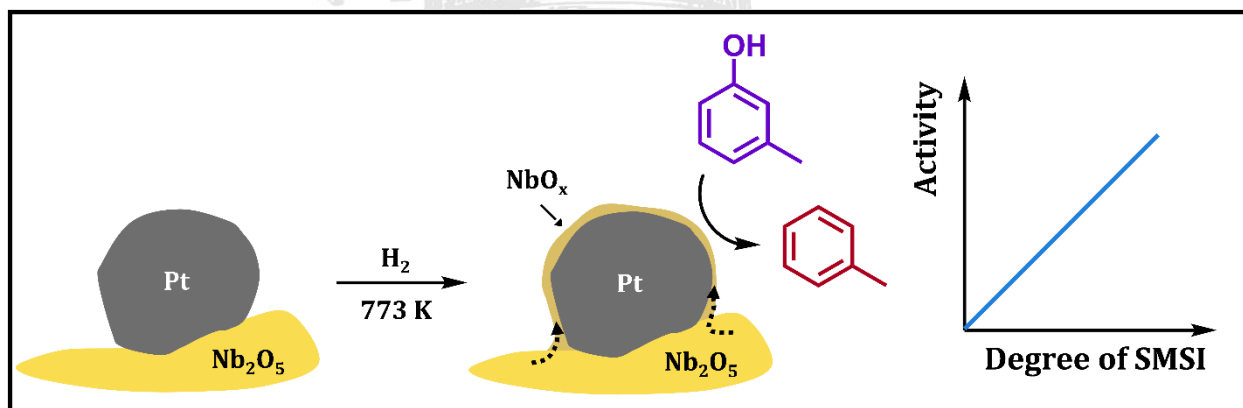
References
[1] C. Wang, A. V. Mironenko, A. Raizada, T. Chen, X. Mao, A. Padmanabhan, D.G. Vlachos, R.J. Gorte, J.M. Vohs, Mechanistic Study of the Direct Hydrodeoxygenation of m-Cresol over WOx - Decorated Pt/C Catalysts, ACS Catal. 8 (2018) 7749–7759.
[2] C. Wang, G.R. Wittreich, C. Lin, R. Huang, D.G. Vlachos, R.J. Gorte, Hydrodeoxygenation of m-Cresol Over Pt-WOx/C Using H2 Generated In Situ by n-Hexane Dehydrogenation, Catal. Letters. 150 (2020) 913–921.
[3] T. Chen, J.M. Vohs, Direct Hydrodeoxygenation of m-Cresol to Toluene over Bifunctional NbOx –Pt, J. Phys. Chem. C. 124 (2020) 14253–14261.

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2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

## Dehydra-decyclization of Tetrahydrofuran to 1,3-butadiene over ZrO$_2$

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Butadiene, one of the most important conjugated dienes, plays an important role in the rubber industry. Currently, butadiene is produced as a side product of naphtha cracking for production of ethylene in the United States. However, such production of butadiene is considered unsustainable because of the use of fossil sources and inefficient since it is not the main target reaction. Thus, a sustainable and more effective pathway is required. Recent studies have shown that conjugated dienes can be obtained from dehydro-decyclization of cyclic ethers, which can be derived from biomass sources, over Brønsted acidic catalysts through a carbocation pathway. However, most of these reactions are industrially undesirable because of their reaction activities.

In finding a proper catalyst to carry this reaction, zirconia appeared to be a promising catalyst and a series of metal oxides with Lewis acidity were tested to compare with it. While most of the Lewis catalysts showed activity to this reaction at similar temperature, zirconia has shown high selectivity to butadiene (~90%) and promising reaction rate. Near quantitative yields to butadiene could be achieved over tetragonal zirconia (t-ZrO2) at 673 K and a WHSV of 0.93 g THF gcat−1 h−1. Methyl-substituted THF gave only moderate increases in rates and the products showed minimal isomerization of the carbon backbone. The t-ZrO2 catalyst was found to be relatively stable with time on stream, experiencing alkene products polymerization as a likely source of deactivation. Complete regeneration of the catalyst was demonstrated through calcination alone, allowing for multiple regenerations with no irreversible loss in activity or selectivity. The catalytic activity of zirconia was found to be structure insensitive, with t-ZrO2 and monoclinic zirconia (m-ZrO2) exhibiting similar initial activities; however, m-ZrO2 was observed to deactivate much more rapidly.
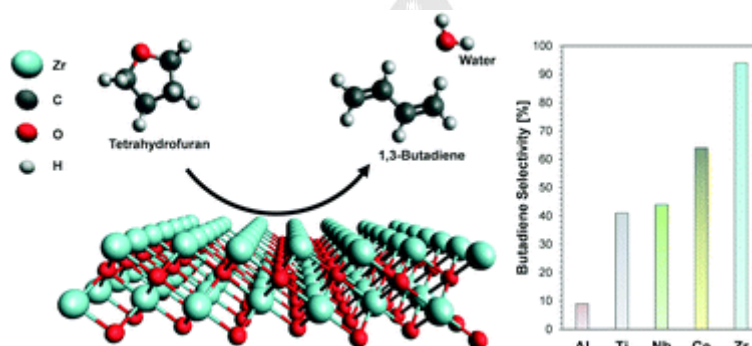
2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Diode behavior in $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3−δ}$ Proton-Conducting Ceramic Electrolyzers

Jian Chang, Colin Lehman, Aleksandra Vojvodic, John M. Vohs, Raymond J. Gorte*

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The proton-conducting ceramic, $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3−δ}$ (BZCYYb), was used as the electrolyte with a goal of electrochemically synthesizing NH_3. While a metal catalyst is necessary for dissociation of H_2, H_2 evolution was observed even in the absence of a catalyst on the BZCYYb surface. This leads to diode behavior for Pt-LST ($La_{0.7}Sr_{0.3}TiO_3$) ‖ LST cells, with current passing from the Pt-containing electrode but not in the opposite direction. Initial studies show with Ru, Fe, Re and W added to the cathode show that Ru easily dissociates H_2 and recombines protons. W was ineffective for hydrogen dissociation, while Fe, and Re showed intermediate behavior. Attempts are ongoing to suppress the hydrogen evolution reaction on the BZCYYb surface.
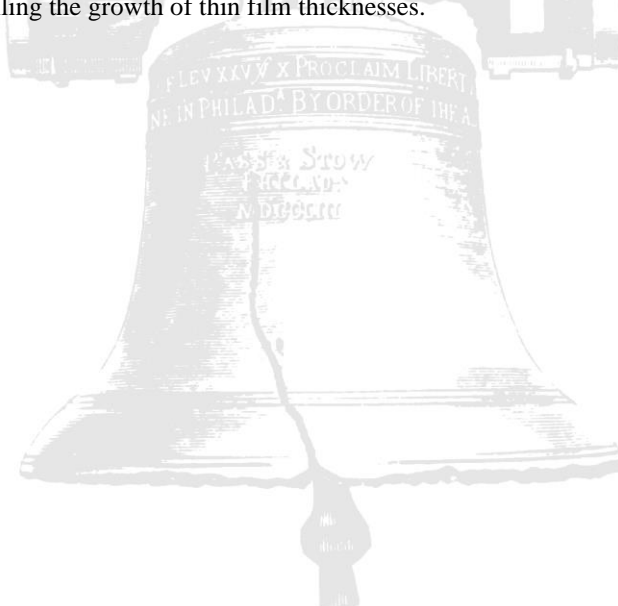
2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Thermodynamic tunability of FeO_x through thickness of ultra-thin film

Kai Shen,[1] Xinyu Mao[1], Chao Lin[1], Julian M. Paige[1], John M. Vohs[1,*], Raymond J. Gorte[1,*]

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In this study, thin film FeO_x of different thicknesses were uniformly deposited on high-surface-area γ-alumina support by Atomic Layer Deposition (ALD) method. Thermodynamic properties were then measured by flow titration and coulometric titration. From flow titration, oxygen capacity of ALD-prepared thin film samples was shown to be dependent on both iron oxide loadings and film thicknesses. Thin film samples also showed improved stability than bulk after redox cycles. Coulometric titration demonstrated thin film samples tended to be more easily reduced. As film gets thicker, the reducibility decreases. However, increased reducibility does not always mean increased reactivities. Thin film samples with higher reducibility showed lower Water Gas Shift Reaction (WGSR) rates. This may be explained by the fact that oxidation of Fe_3O_4 by H_2O, one of the rate limiting step of WGSR, is harder to occur on more reducible samples. This study suggests a promising thermodynamic and catalytic tunability of iron-based catalysts through precisely controlling the growth of thin film thicknesses.

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"Intelligent" Ni catalysts based on LaMnO$_3$ films prepared by atomic layer deposition

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Thin films of LaMnO$_3$ were deposited onto MgAl$_2$O$_4$ by atomic layer deposition (ALD) and studied as catalyst supports for Ni in the dry reforming of methane. X-ray diffraction (XRD) showed that the 0.5 nm films presented a simple perovskite structure after 5 redox cycles at 1073 K. And scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDS) demonstrated that MgAl$_2$O$_4$ powders were uniformly covered by the LaMnO$_3$ films. In addition, Ni was dispersed uniformly on the supports after oxidation at 1073 K. However, the Ni nanoparticles having roughly 5 nm diameter were exsolved after reduction at 1073 K and well aligned with LaMnO$_3$ films, which is confirmed by high-resolution TEM. The Ni-LaMnO$_3$/MgAl$_2$O$_4$ catalysts exhibited excellent redox stability and catalytic performances for dry reforming of methane. The strong metal-support interaction between Ni and LaMnO$_3$ are suggested to be the main characteristics for the improved carbon coking tolerance and catalytic activities.
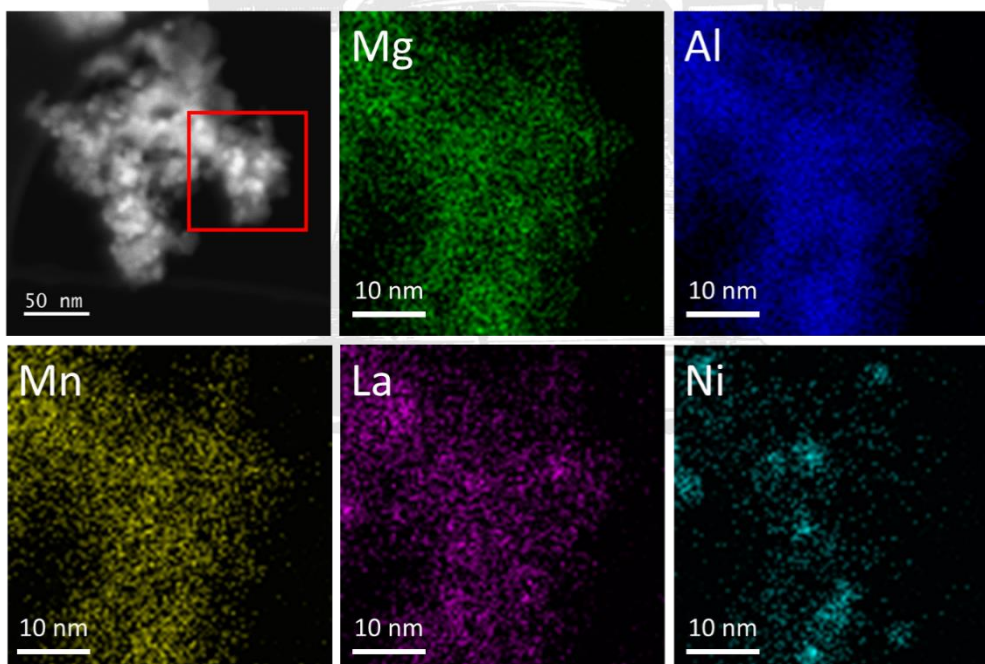
Figure. High angle annular dark-field (HAADF) STEM results for reduced Ni-LaMnO$_3$/MgAl$_2$O$_4$ with EDS elemental maps of Mg, Al, Mn, La, and Ni taken from the region indicated by the red box.

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2020-2021 CCP Poster Abstract
Type: Graduate
Consideration in poster competition: Yes

Thermochemical Data Fusion Using Graph Representation Learning

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Large databases are required for "Big Data" applications in catalysis and materials science. Thermochemical databases can be created by combining data from various sources and by correcting low-fidelity datasets to higher accuracy with minimal computation. To achieve this "data fusion", thermochemical quantities of interest, calculated at various levels of density functional theory (DFT), need to be mapped to the same, high levels of theory. We propose a graph theoretical, statistical framework for such tasks. We learn linear fusion maps with automated descriptor selection. The method is explainable, generalizable, and provides a diagnostic tool for outlier identification.

We model the difference between two thermochemical quantities A and B at different levels of theory: $\Delta A^{(1)} B^{(2)} = B^{(2)} - A^{(1)}$. A molecule is represented by a molecular graph whose nodes and edges represent the nuclei and bonds, respectively. A data matrix for the entire set is constructed where each molecule is featurized my its subgraph frequencies. These subgraph frequency descriptors are thus semantically meaningful, 2D, and trivially computed from the chemical representation of the molecule. Finally, we use an L1-regularized machine learning model on a dataset of 10, 000 molecules. We learn maps across the B3LYP -> CBS-QB3 functional and three different thermochemical quantities of interest (QoI): electronic energy (0K), enthalpy and free energy (298.15K). Due to the L1 regularization, the model learns important molecular subgraphs contributing to these mappings and helps us tie our work back to chemical concepts of group additivity and functional groups.

Our models approach chemical accuracy of 1 kcal/mol using only a few hundred points for all tasks. Important molecular subgraphs are identified that are important for the mapping tasks. These subgraphs resemble chemically sensible functional groups. We propose statistical tests to guarantee model predictions and use PCA to suggest a qualitative failure test of all the models.
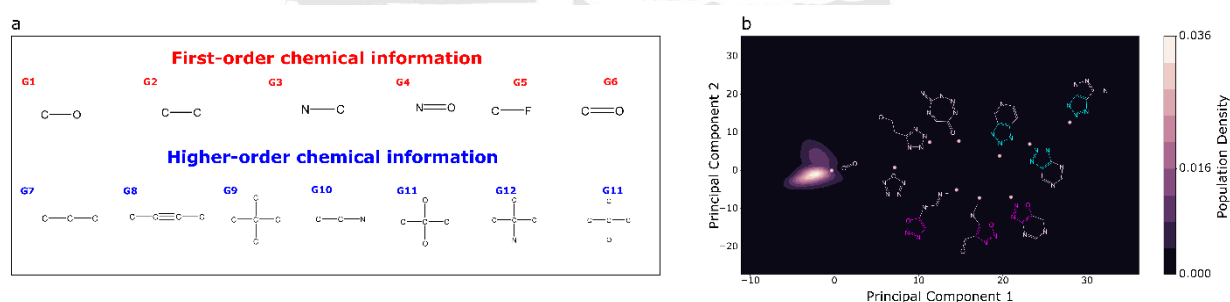

Figure 2. a) Important subgraphs identified by the model. The group G1-G6 are subgraphs which account for the kinds of bonds present in the data set and be considered as first order chemical information used by the model. G7 – 11 represents higher order chemical information involving multiple atoms and configurations. b) All the 133, 885 molecules of the QM9 database projected

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Titanium Silicalite-1 Nanosheet Supported Platinum for Non-oxidative Ethane Dehydrogenation

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Studies of stable catalysts for non-oxidative dehydrogenation of ethane (NDE) have been challenged by coke deposition from side reactions and thermal sintering of active species. Herein, we report a catalyst mechanism that overcome both challenges to enable highly stable, active and selective NDE. The catalyst is made of subnanometric platinum (Pt) species (i.e. single atoms and clusters) habituated on the two-dimensional (2D) multilamellar titanium silicalite-1 (M-TS-1) zeolite nanosheet support[1] (i.e. Pt/M-TS-1). The ultra-thin (~3 nm) M-TS-1[2] nanosheets provide high external surface area, high terminal silanol/titanol (-OH) groups and weak Lewis acid sites[3]. The first two characteristics enhance molecular transport and Pt dispersion in the catalyst support. The third characteristic prohibits side-reactions to avoid coking and create strong Pt-support interaction leading to well-dispersed Pt species against thermal sintering. The M-TS-1 nanosheet supported Pt catalyst exhibited durable catalytic activity and high ethylene selectivity in the NDE.
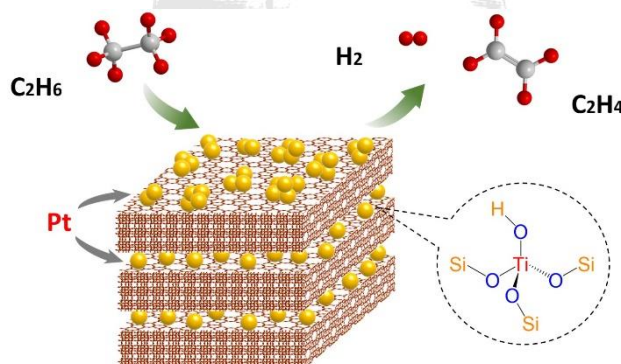
References

[1]   E. Schulman; W. Wu; D. Liu, *Materials*, **13** (2020).

[2]   W. Wu; D. T. Tran; X. Wu; S. C. Oh; M. Wang; H. Chen; L. Emdadi; J. Zhang; E. Schulman; D. Liu, *Micropor. Mesopor. Mater.*, **278** (2019)_414-422.

[3]   W. Wu; D. T. Tran; S. Cheng; Y. Zhang; N. Li; H. Chen; Y.-H. Chin; L. Yao; D. Liu; *Micropor. Mesopor. Mater.*, **311** (2021)_110710.