

Catalysis Center for Energy Innovation Final Technical Report

Overview of CCEI Accomplishments and Impact

CCEI was founded in 2009 as a transformative catalysis center for energy innovation that combines fundamental science with technology transfer to address one of today's most challenging problems: **transforming lignocellulosic biomass into renewable transportation fuels and chemicals**. Center members made significant progress toward solving this grand challenge by creating new heterogeneous catalysts and developing processes involving their use.

In the first funding cycle, we primarily focused on the low-temperature sugar platform of biomass conversion. The scientific thrusts are shown in Figure 1. We invented numerous CCEI technologies, namely:

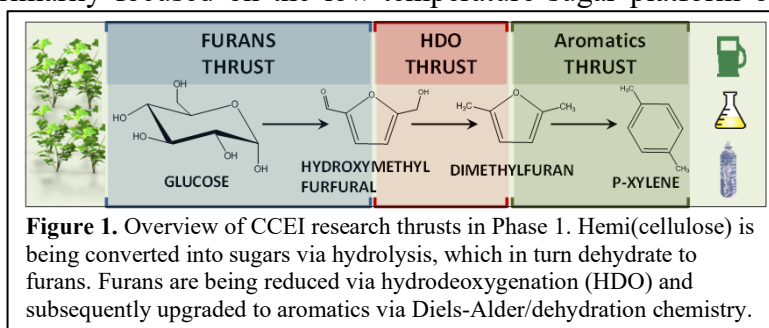


Figure 1. Overview of CCEI research thrusts in Phase I. Hemi(cellulose) is being converted into sugars via hydrolysis, which in turn dehydrate to furans. Furans are being reduced via hydrodeoxygenation (HDO) and subsequently upgraded to aromatics via Diels-Alder/dehydration chemistry.

- (1) The first-of-its-kind heterogeneous catalyst (Sn- or Ti-Beta zeolite, a Lewis acid) for the isomerization (epimerization) of glucose to fructose (mannose)—the *CCEI-ISO process*—to replace the existing, costly enzymatic process;¹⁻³ the first stereospecific isomerization of D-glucose to L-sorbose using Ti-Beta zeolite;⁴ and the extension of this chemistry to C5 sugars^{5,6} and di-saccharides.⁷
- (2) The production of renewable para-xylene (PX) from 2,5-dimethyl furan (DMF) (derived from glucose) and ethylene (can be derived from bioethanol at commercial scale) with an unprecedented yield of 90% for a heterogeneous catalyst, using a bifunctional Lewis/Brønsted acid zeolite (*the CCEI-PX process*);^{8,9} and from more complex feedstocks using fast pyrolysis.^{10,11}
- (3) The first synergistic Lewis/Brønsted acid catalytic conversion of glucose (and even starch) to 5-hydroxymethyl furfural (HMF) with high yield in a single-pot cascade of reactions;¹² and its extension to the xylose conversion to furfural (FUR).^{13,14}
- (4) High-yield catalytic transfer of hydrogen (CTH), followed by hydrodeoxygenation (HDO), to reduce furans into high research octane number (RON) additives and chemical precursors, on dual metal/Lewis acid site catalysts, without external H₂.¹⁵⁻¹⁷
- (5) High-yield diesel-grade fuels from HMF on a Lewis acid catalyst (Sn-Beta) via a cascade of Meerwein-Ponndorf-Verley (MPV) and etherification reactions, without external H₂.¹⁸
- (6) Inexpensive and selective carbide-based catalysts for propylene production from C3 bio-oil oxygenates, filling a market need arising from the recent abundance of shale gas.^{19,20}
- (7) Reactive adsorption, as process-intensification, in the production of furans to selectively remove HMF from the reacting phase and improve HMF yields;²¹⁻²⁴ and
- (8) Solid carbon-based fuel cells that can directly convert solid biomass into electricity.²⁵⁻²⁷

A key point is that Center members created new heterogeneous catalysts and fundamental science in all these technologies (e.g., reaction mechanisms, active site, etc.), seeded the foundations for **interpretive science** in an otherwise empirical field, and demonstrated **predictive science** in some cases. In parallel, we advanced many *enabling technologies*:

- (1) We synthesized new, hydrothermally stable materials with hierarchical (zeolites). We

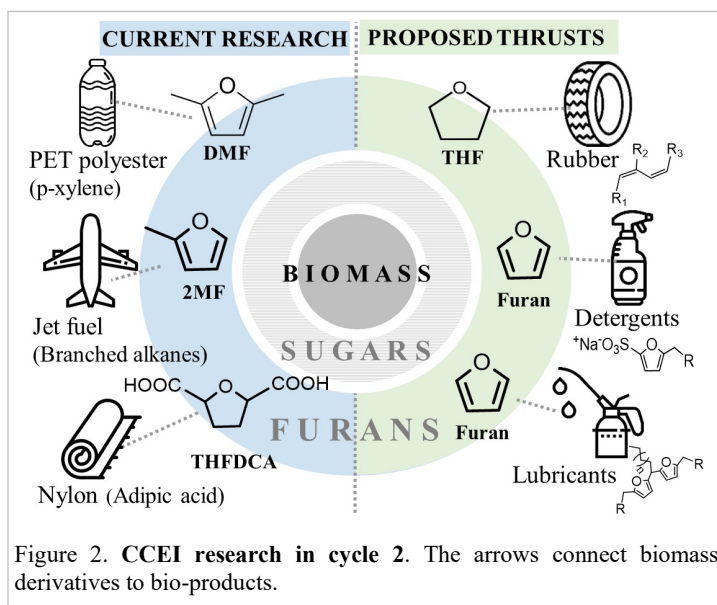
ordered porosity (carbons, ZrO₂, and TiO₂) by scalable nanofabrication techniques (e.g., multi-modal colloidal assembly, multi-step to ‘one-pot’ colloidal templating, crystal growth from intrinsic crystal defects)²⁸⁻³² for hosting catalytic reactions, overcoming diffusion limitations, and achieving selective adsorption. We also introduced new strategies for rapid synthesis of Sn-Beta zeolite (an alternative to the fluorite route).³³

- (2) We performed (i) the first multiscale simulations of sugar dehydration chemistry and exposed the importance of considering *explicit, dynamic solvent effects*;³⁴⁻³⁶ (ii) developed *first-principles semi-empirical methods (FPSEM) on metal catalysts*^{37,38} to predict selectivity and activity maps and thus *new materials*;^{39,40} (iii) developed the first descriptors for *predicting acid-catalyzed chemistry in renewable aromatics*;⁴¹ and (iv) introduced a methodology for *molecular simulation of adsorption from solution*.⁴²⁻⁴⁴
- (3) We introduced a powerful methodology to *characterize, with atomic resolution, the catalyst structure under in situ conditions* and exposed restructuring of bimetals.⁴⁵
- (4) We developed the thin-film pyrolysis method to obtain intrinsic kinetics of solid biomass.⁴⁶

In the second funding cycle, CCEI continued its impactful research on numerous fronts: heterogeneous Lewis acid catalysis in zeolitic and hierarchical materials with framework

metal atoms and metal-organic frameworks (MOFs); the discovery of a new class of catalysts, phosphorous-modified all-silica zeolites (P-zeosils), with dynamic active sites, for selective dehydrative Diels-Alder aromatization, dehydration, and dehydra-decyclization of oxacyclopentanes; elevated our comprehension of cooperativity among active sites; and synthesis of stable, ultra-selective nanocrystals (NCs) for HDO. Below we highlight some of the most important achievements.

- (1) A novel material, the zeolitic self-pillared pentasil (SPP), engaged multiple PIs in its synthesis and characterization,^{28,47,48} transport properties,⁴⁹ and catalytic testing.^{50,51} We demonstrated synthesis of Lewis acidic Sn-SPP with Sn atoms incorporated exclusively into the framework. Testing in the isomerization of glucose to fructose in alcoholic solvents showcased its superior selectivity and catalytic performance over Sn-BEA, establishing a new benchmark.^{50,51} Computational studies revealed **site cooperativity—a thread running through CCEI’s research—being responsible for the superior performance of Sn-SPP**; in this case the synergistic combination of readily accessible framework Sn sites and Sn-O-Si-OH groups in the mesopores.⁵² By Monte Carlo simulations,⁴⁹ we supplied a framework to understand and optimize hierarchical zeolites as efficient catalysts and separation media.
- (2) We discovered that P-zeosils with BEA, MFI and SPP architectures allow unprecedented control over selectivity in Brønsted-catalyzed reactions by curbing undesired alkylation and oligomerization reactions.⁵³ We demonstrated benchmark *p*-xylene yield (97%) in the Diels-



Alder aromatization of DMF,⁵³ and promising yields of dienes from dehydra-decyclization of oxacyclopentanes over P-SPP (e.g., 75% butadiene yield at 90% tetrahydrofuran (THF) conversion).⁵⁴ **P-zeosils have intrinsically new catalytic properties.** Preliminary spectroscopic and computational studies point to **active sites that are dynamic in nature, clearly falling outside the conventional boundaries of heterogeneous catalysis.**

- (3) Our quest for novel catalysts continued by leveraging site manipulation and the high surface-area, well-defined porosity and widely tunable composition of MOFs as heterogeneous catalysts. In collaboration with the ICDC EFRC, we initially explored MOF-derived oxide catalysts for glucose isomerization.⁵⁵ This experience led CCEI to explore MOFs as sugar isomerization catalysts. We synthesized the MOF MIL-101(Cr) in the presence of glycine and were able to create a novel chromium hydroxide/MIL-101(Cr) composite that surpasses all other MOF-derived materials in alcohol solvents⁵⁶ and matches the performance of optimized zeolite catalysts, e.g., Sn-SPP. Interestingly, isotopic labeling studies revealed a proton transfer isomerization mechanism. We also demonstrated that the MOF UiO-66, appropriately modulated, can achieve similar performance (by an intramolecular hydride transfer mechanism) and attain 72% fructose selectivity at 82% glucose conversion in propanol.⁵⁷
- (4) We undertook a rigorous study of acylation of furans in microporous and mesoporous catalysts. H-BEA proved superb in rate and selectivity (nearly 100%).⁵⁸ **This reaction opens up the door to using acid derivatives (e.g., fatty acids) from various feedstocks for synthesis of specialty bio-products, e.g., surfactants and lubricants.**
- (5) We have shown that sugar-derived furans can be linked with triglyceride-derived fatty acid anhydrides via Friedel–Crafts acylation within single-layer Al-SPP catalysts. The performance of the resulting alkyl-furan surfactants surpasses that of known products (a technology commercialized by SIRONIX Renewables). Their tunability (in size, structure and function)⁵⁹ forms the basis for further studies in funding cycle 3.
- (6) We discovered that improved graphene oxide (IGO) contains Brønsted acid sites and effectively couples MF and carbonyl-containing compounds via HAA; yields up to 95% (C₁₂-C₁₅ condensates) were achieved at low temperatures.⁶⁰ Subsequent DEHDO over Ir-ReO_x/SiO₂ yields 99% of branched alkanes for jet fuel.⁶¹ Combined with furan acylation (*cf.* (4) and (5) above), HAA allows unprecedented control over specificity, size and molecular structure, laying the foundations for building up lubricants.
- (7) We developed a disruptive pathway to sugars from lignocellulose that attains yields up to 95% of the theoretical values.⁶² With one-pot strategy that combines saccharification under mild conditions and subsequent biphasic dehydration to HMF and FUR, **we achieved process intensification by leveraging the cooperativity of Brønsted and Lewis acidity in inorganic salt solutions.**^{63,64} The drastic reduction in the cost of producing furans **enables profitable downstream processing**, which further motivates the focus of this proposal.
- (8) Computer simulations have been integral to our work and to elevate our understanding of mechanisms and site cooperativity—a theme that runs through our efforts to formulate guiding principles for advancing catalysis science. Three examples stand out: (a) Site cooperativity in Sn-SPP, presented in (1) above;⁵² (b) Acid-base pair synergy between metal Lewis centers and basic OH groups or framework O atoms in the partially hydrolyzed “open” site of homomorphously substituted zeolites, such as Sn-BEA;⁶⁵⁻⁶⁷ (c) The extraordinary synergy between metal atoms, surface oxygen atoms and oxygen vacancies in the hydrogenolysis of furfurals over metal/metal-oxide surfaces, exemplified by Ru/RuO₂.^{68,69} Mechanistic understanding⁶⁸⁻⁷¹ has culminated in the guiding principle **that stable thin**

surface-oxide layers with vacancies can be prototypical materials for hydrogenolysis. This has guided solvothermal synthesis to develop metal-core/metal oxide-shell NCs (e.g., Pt-CoO_x) that achieve 98% yield of DMF from HMF.⁷² This control of catalyst structure was extended by introducing a versatile, **two-step solvothermal/atomic layer deposition synthesis** and demonstrated in DEHDO chemistry.⁷³ Our understanding of multi-site control will be instrumental for hydrogenolysis of furfural derivatives to produce substrates for surfactants and lubricants and for tandem DEHDO to lubricants.

- (9) We performed multiscale kinetics simulations that account for selectivity change due to coverage and/or solvent effects.⁷⁴ We developed a fast-estimation, descriptor-based microkinetic-model for HDO⁷⁵ to provide insights into catalyst selection; and a multiscale methodology for accurate modeling in microporous materials.⁷⁶ We improved the COSMO-SAC model⁷⁷ to predict high-performance extractants in biphasic sugar conversion. We are developing a functional to correct the self-interaction error in the generalized gradient approximation of density functional theory (DFT) to accurately model metal-oxide surfaces.
- (10) We developed a universal carbon detector⁷⁸ that formed the basis of Polyarc™, a microreactor technology commercialized by the Activated Research Company. We developed a new microreactor for *in situ* temperature-programmed reaction (TPR) measurements *in solvent*⁷⁹ and advanced surface-enhanced infrared absorption spectroscopy (SEIRAS)^{80,81} to probe solid-liquid interfacial species. We invented an automated Reactive Gas Chromatography method to quantify the Brønsted acid site density using alkylamine Hofmann elimination.⁸² We also developed a method to identify the location of Brønsted acid sites by combining alkylamine Hofmann elimination with competitive adsorption of inert titrants of varying size.

A summary of the key accomplishments of CCEI in funding cycles 1 and 2 is shown in Figure 3.

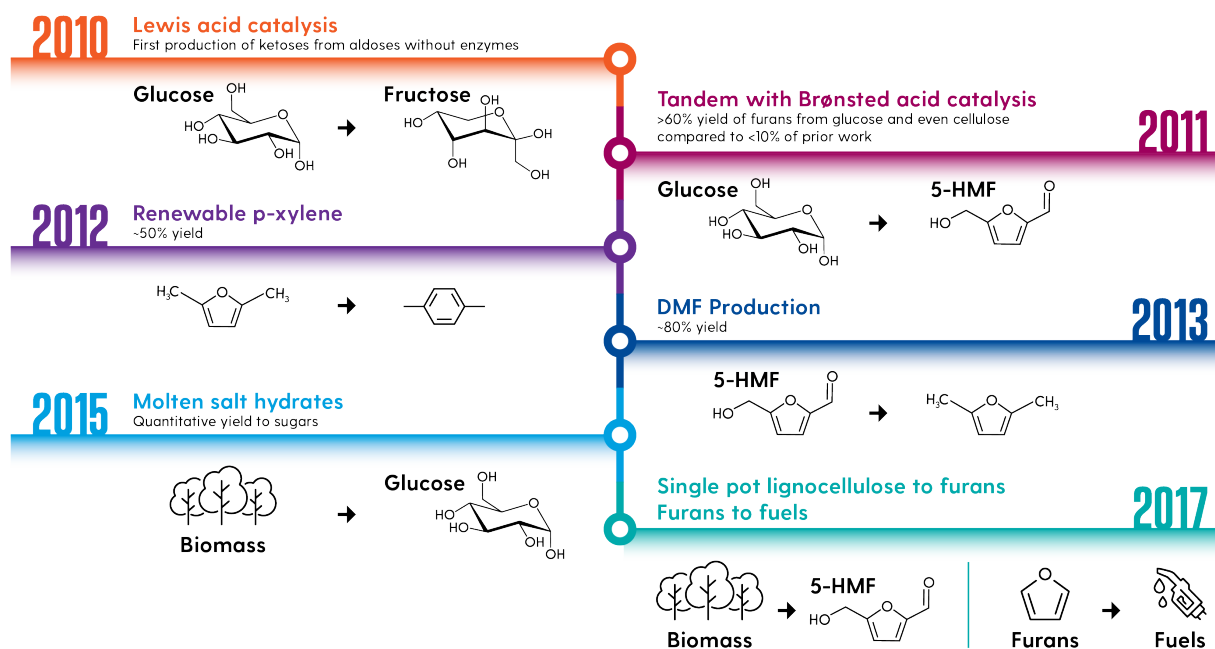


Figure 3. Overview of key developments of CCEI in funding cycles 1 and 2.

In funding cycle 3, we made significant progress in various new directions. These include:

- (1) Following up on our discovery (2nd funding cycle) that P-zeosils (phosphoric acid supported on inert, *all-silica zeolites*) are a new class of selective *Brønsted acidic* catalysts with catalytic properties *distinct from typical aluminosilicate zeolites*, our overarching goal is to characterize them and to develop new, dynamically confined acids in zeolite and metal-organic frameworks (MOFs). We characterized the state of phosphorus in P-zeosils using solid-state Nuclear Magnetic Resonance (SS-NMR) spectroscopy. We elucidated the effect of water on the distribution of possible P-sites and the effect of the framework (dealuminated BEA vs self-pillared pentasil SPP) on the hydrolytic stability of the P-sites. Achievements include:
 - a) Dry P-SPP and P-BEA have different distributions of P- sites. P-SPP shows almost only rigid, surface-bound Q³ sites, whereas P-BEA shows Q² and Q¹ sites that are framework-bound or oligomeric polyphosphoric acids.
 - b) Hydrolysis of P-O-X (X=P, Si) linkages proceeds rapidly upon exposure to humidity but is slower in P-BEA than in P-SPP due to the former's hydrophobic nature.
 - c) Hydrolysis of P-O-X (X=P, Si) linkages changes the acidity of the materials, as inferred from DFT calculations.
- (2) Following up on strong evidence that the activity of P-zeosils can be modulated by hydrolysis of inactive framework Q³ sites (by co-feeding precise amounts of water), we have made the remarkable discovery that pre-activation of the catalyst with *tert*-butylamine (TBA) greatly facilitates the effect of hydrolysis of P-sites, leading to a ~ 300-fold increase in catalytic activity compared to the parent, dry catalyst. Extensive characterization (XRD, XANES, and SS-³¹P-NMR) of samples pre-activated by water and TBA revealed that:
 - a) They undergo structural changes, manifested by the appearance of an amorphous phase.
 - b) They have far fewer rigid (i.e., inactive) Q³ structures as water alone is not enough to fully hydrolyze them into the less coordinated and more active Q¹ and Q⁰ sites.
- (3) We pursued the synthesis, post-synthetic modification (PSM), and characterization of inorganic-functionalized frameworks as a way of systematically tuning the Brønsted acidity of multiple families of porous materials. We successfully installed phosphonic acid functionalities into MIL-140C, a series of robust, large-pore MOFs, notoriously recalcitrant to modification. We demonstrated that the P-modified MIL-140C is catalytically active for the dehydration of *tert*-butanol.
- (4) We began to explore metal oxide catalysts for the conversion of furans to dienes. After testing various metal oxides, we discovered that ZrO₂ consistently exhibited the highest selectivity for 1,3-butadiene (~90%) when reacted with tetrahydrofuran (THF) without compromise in conversion. In addition, ZrO₂ is very selective for dienes (>80%) when reacted with other cyclic ethers as well, such as 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran and tetrahydropyran. Moreover, ZrO₂ is highly selective for a single diene isomer when multiple dienes can form (C5+).
- (5) We have extended CCEI's prior work on lubricant synthesis by introducing a new, two-step strategy to synthesize benzene and branched cyclic alkane lubricant base-oils from lignin-derived guaiacol and lauryl aldehyde (obtained from natural oils). The procedure involves Brønsted acid-catalyzed hydroxyalkylation/alkylation followed by hydrodeoxygenation (HDO). Measurements of viscosity properties indicate that the synthesized lubricant base-oil is comparable to commercial poly- α -olefin Group III, IV, and refrigerant base-oils. This is a unique pathway for replacing petroleum-derived base oils with lignin-derived ones.

- (6) We continued our studies to characterize the putative BASs on supported WO_x/Pt catalysts. Following up on our finding that BASs on WO_x form facily either by H_2 dissociative adsorption on Pt and spillover onto WO_x , or by direct H_2O dissociative adsorption on WO_x , we delved into the dynamical behavior of WO_x/Pt by considering the kinetics of BAS creation, WO_x reduction/oxidation, and WO_x hydration/dehydration. Among our findings:
- The kinetics of WO_x protonation and reduction depends on the oxidation state of tungsten.
 - The *ab initio* phase diagram of a model sub-monolayer $\text{WO}_x/\text{Pt}(111)$ predicts the facile reduction of WO_x even at low H_2 partial pressures. Progressive reduction of WO_x is self-inhibited and accompanied by a decrease in BAS density and an increase in redox center density.
 - In parallel, we have undertaken UHV mechanistic studies on well-characterized WO_x on Pt(111) surfaces. Using isopropanol (IPA) as a probe molecule, we found that Pt promotes dehydrogenation to acetone and H_2 whereas WO_x sites promote dehydration to propylene. DFT calculations revealed the adsorption and activation barriers of IPA on Pt(111) and $\text{WO}_x/\text{Pt}(111)$ surfaces, as well as the most active, *in-situ* formed BAS on the $\text{WO}_x/\text{Pt}(111)$ interface.
- (7) We exploit diverse feedstock portfolios for future biorefineries that utilize olefins and dienes from shale gas to produce functionalized substrates, such as aldehydes and acids, for hydroxy alkylation-alkylation and acylation chemistries. Focusing on hydroformylation as a strategy to synthesize aldehydes, we demonstrated that heteroatom single-site pairs consisting of an early transition metal (W) and a late transition metal (Rh) on Al_2O_3 exhibit bifunctional reaction pathways for CO insertion into alkenes. This work showcased how heteroatom pair sites could be designed and synthesized to enable bifunctional reaction pathways in CO insertion reactions. The tunable nature of such pair sites opened new avenues for selectively driving challenging heterogeneous catalytic processes.
- (8) We made great strides in developing oxide-supported ultra-low-loading metal catalysts, including stable, atomically dispersed metal sites. We have used two methods: a) Laser-induced Thermal Shock treatment followed by fast quenching to prevent further growth of small metal centers into larger particles; and b) redispersion of metal nanoparticles by iodomethane/ CO treatment. Both techniques successfully treated Pt/ TiO_2 ; extensive characterization was performed to confirm the presence of isolated Pt atoms, and the catalysts were evaluated for their performance.
- (9) We reported the synthesis of new amide-based insecticidal active ingredients from biomass-derived monomers, specifically furfural and vanillin. The process involves reductive amination followed by carbonylation. The synthesis of the furfural-based carbamate yield reaches a cumulative 88%, with catalysts Rh/ Al_2O_3 and La(OTf) $_3$ being recyclable at each stage. Insecticidal activity assessments reveal that the furfural carbamate exhibits competitive performance, achieving an LC_{50} of $6.35 \mu\text{g}/\text{cm}^2$, compared to $6.27 \mu\text{g}/\text{cm}^2$ for carbofuran. Ecotoxicity predictions indicate significantly lower toxicity levels toward non-target aquatic and terrestrial species. The importance of the low octanol-water partition coefficient of the biobased carbamate, attributed to the oxygen heteroatom and electron density of the furan ring, is discussed in detail. Building on these promising results, the synthesis strategy was extended to six other biobased aldehydes, resulting in a diverse portfolio of biomass-derived carbamates. A techno-economic analysis revealed a minimum selling price of 11.1\$/kg, only half that of comparable carbamates, demonstrating the economic viability of these new biobased insecticides.

- (10) We advanced the knowledge of metal-metal oxide (M-MO) inverse catalysts.⁸³⁻⁸⁶ For example, we investigated the role of the metal core (M = Pt, Ru, Rh, Pd, Ni) in the formation and dynamics of Brønsted acid sites on the WO_x overlayer. By in situ and ex situ characterizations (XPS, H₂-TPR, CO chemisorption), the kinetics of probe reactions (alcohol dehydration and H-D exchange), and DFT calculations, we demonstrated that metals promote the dispersion of WO_x domains which exhibit stronger Brønsted acidity than three-dimensional crystalline WO_x domains on the carbon support at submonolayer average coverages. Metals (with varying work functions) modulate the dispersion of WO_x on them and the Brønsted acid density and acidity of the dispersed WO_x domains by tuning the extent of reduction (i.e., the oxidation state) of W, which correlates with the dehydration reactivity of those domains. Hydrogen co-feeding strongly enhances the initial dehydration rate on Pt-WO_x, Pd-WO_x, and Ni-WO_x but not on Ru-WO_x and Rh-WO_x, likely due to a deeper reduction of WO_x. The hydroxylation of the WO_x species by H₂O is significantly influenced by metal. DFT calculations, air-free XPS, and H₂ periodic pulsing show that splitting water on Ru-WO_x is thermodynamically favorable compared to Ni-WO_x, resulting in order of magnitude increase in dehydration reactivity on the former and no enhancement on the latter. The catalyst activity was enhanced 10x by increasing the frequency of the H₂ pulse.
- (11) We advanced significantly nitrogen-doped, carbon-supported transition metal catalysts, which are excellent for several reactions, and showed that it is often Fe impurities that impart the catalytic activity.^{84,87-90} Structural engineering of metal-N_x sites to boost catalytic activity is rarely studied. In one of the most impact works,⁸⁷ we demonstrate that the structural flexibility of Fe-N₃ site is vital for tuning the electronic structure of Fe atoms and regulating the catalytic transfer hydrogenation (CTH) activity. By introducing carbon defects, we construct Fe-N₃ sites with varying Fe-N bond lengths distinguishable by X-ray absorption spectroscopy. We investigate the CTH activity by density functional theory and microkinetic calculations and reveal that the vertical displacement of the Fe atom out of the plane of the support, induced by the Fe-N₃ distortion, raises the Fe 3d_{z²} orbital and strengthens binding. We propose that the activity is controlled by the relaxation of the reconstructed site, which is further affected by Fe-N bond length, an excellent activity descriptor. We elucidate the origin of the CTH activity and principles for high-performing Fe-N-C catalysts by defect engineering.

The overall technological achievements of CCEI, mainly of cycles 2 and 3, are depicted in Figure 4.

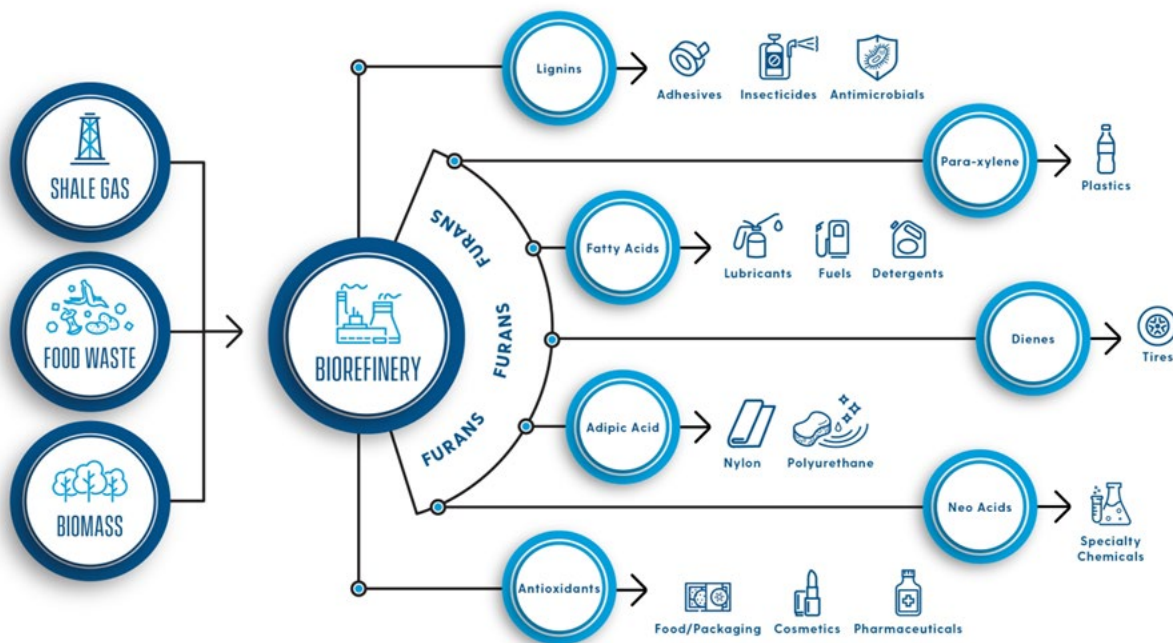


Figure 4. CCEI's major chemical innovation space.

Publications and Scientific Impact

CCEI formally published 550 papers and received 35,489 citations with an h factor of 98 (data from Web of Science, 10/15/2024). Annual statistics is shown in Figure 5.

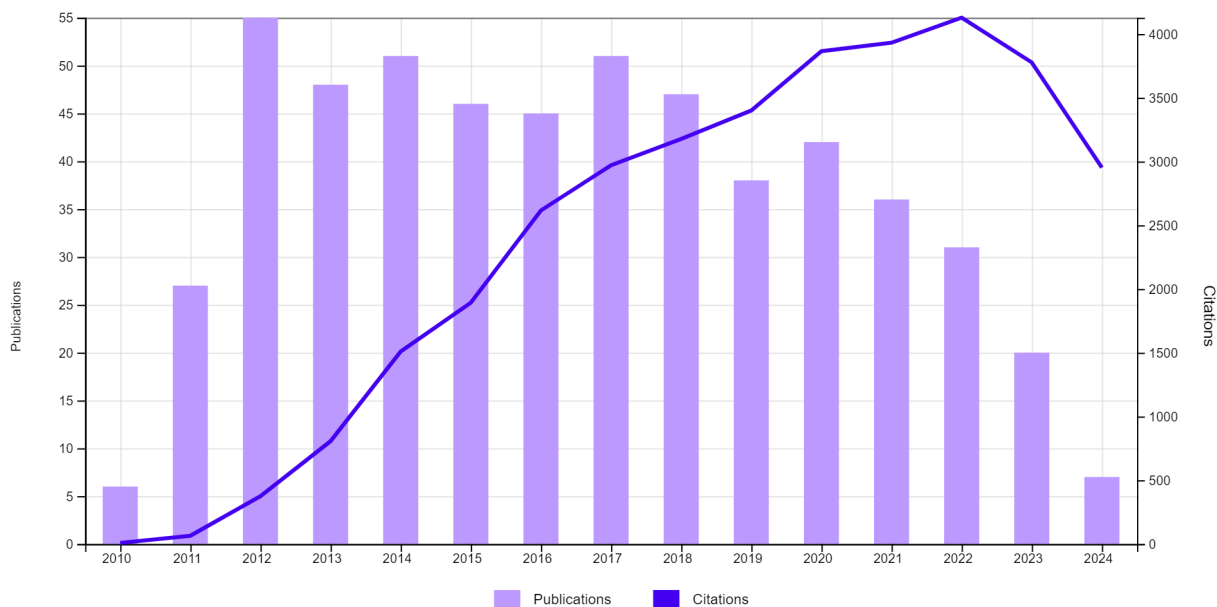


Figure 5. Web of Science CCEI's publications and citations as of 10/15/2024.

Intellectual Property and Technology Transfer

We produced >40 disclosure agreements, >10 patents, 6 start-up companies, and licensed several technologies.

Education and Workforce Development Accomplishments

In addition, we have also *educated* 153 Ph.D. students and 68 postdoctoral fellows and provided summer research opportunities to 103 undergraduate and high school students.

A summary of the statistics of the center is given in Figure 6.

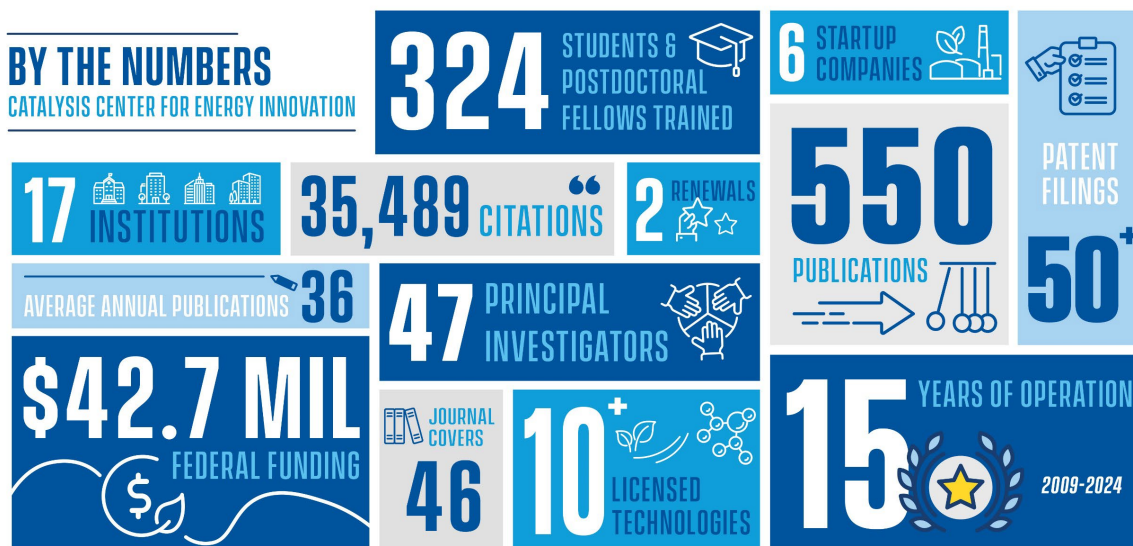


Figure 6. CCEI accomplishments by numbers.

Technical Report References

1. M. Moliner, Y. Roman-Leshkov, and M. E. Davis, Tin-containing zeolites are highly active catalysts for the isomerization of glucose in water. *Proc. Nat. Acad. Sci.* **107**(14), 6164-6168 (2010). DOI:10.1073/pnas.1002358107.
2. Y. Roman-Leshkov, M. Moliner, J. A. Labinger, and M. E. Davis, Mechanism of Glucose Isomerization Using a Solid Lewis Acid Catalyst in Water. *Angew. Chem. Int. Ed.* **49**(47), 8954-8957 (2010). DOI:10.1002/anie.201004689.
3. R. Bermejo-Deval, R. Gounder, and M. E. Davis, Framework and Extraframework Tin Sites in Zeolite Beta React Glucose Differently. *ACS Catal.* **2**(12), 2705-2713 (2012). DOI:10.1021/cs300474x.
4. R. Gounder, and M. E. Davis, Titanium-Beta Zeolites Catalyze the Stereospecific Isomerization of D-Glucose to L-Sorbose via Intramolecular C5–C1 Hydride Shift. *ACS Catal.* **3**, 1469-1476 (2013). DOI:10.1021/cs400273c.
5. V. Choudhary, A. B. Pinar, S. I. Sandler, D. G. Vlachos, and R. F. Lobo, Xylose Isomerization to Xylulose and its Dehydration to Furfural in Aqueous Media. *ACS Catal.* **1**, 1724-1728 (2011). DOI:10.1021/cs200461t.
6. C. M. Lew, N. Rajabbeigi, and M. Tsapatsis, Tin-containing zeolite for the isomerization of cellulosic sugars. *Micr. Meso. Mat.* **153**, 55-58 (2012). DOI:10.1016/j.micromeso.2011.12.020.
7. R. Gounder, and M. E. Davis, Monosaccharide and disaccharide isomerization over Lewis acid sites in hydrophobic and hydrophilic molecular sieves. *J. Catal.* **308**, 176-188 (2013). DOI:10.1016/j.jcat.2013.06.016.

8. C. L. Williams, C.-C. Chang, P. Do, N. Nikbin, S. Caratzoulas, D. G. Vlachos, R. F. Lobo, W. Fan, and P. J. Dauenhauer, Cycloaddition of Biomass-derived Furans for Catalytic Production of p-Xylene. *ACS Catal.* **2**, 935-939 (2012). DOI:10.1021/cs300011a.
9. C.-C. Chang, S. K. Green, C. L. Williams, P. J. Dauenhauer, and W. Fan, Ultra-Selective Cycloaddition of Dimethylfuran for Renewable p-Xylene with H-BEA. *Green Chem.*, In press DOI: 10.1039/C1033GC40740C (2014). DOI:10.1039/C3GC40740C.
10. Y.-T. Cheng, Z. Wang, C. J. Gilbert, W. Fan, and G. W. Huber, Production of p-Xylene from Biomass by Catalytic Fast Pyrolysis Using ZSM-5 Catalysts with Reduced Pore Openings. *Angew. Chem. Int. Ed.* **51**(44), 11097-11100 (2012). DOI:10.1002/anie.201205230.
11. T. R. Carlson, Y.-T. Cheng, J. Jae, and G. W. Huber, Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust. *Energy Environ. Sci.* **4**(1), 145-161 (2011). DOI:10.1039/c0ee00341g.
12. E. Nikolla, Y. Roman-Leshkov, M. Moliner, and M. E. Davis, 'One-Pot' Synthesis of 5-(Hydroxymethyl)furfural from Carbohydrates using Tin-Beta Zeolite. *ACS Catal.* **1**(4), 408-410 (2011). DOI:10.1021/cs2000544.
13. V. Choudhary, S. I. Sandler, and D. G. Vlachos, Conversion of Xylose to Furfural using Lewis and Brønsted Acid Catalysts in Aqueous Media. *ACS Catal.* **2**(9), 2022-2028 (2012). DOI:10.1021/cs300265d.
14. V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, and D. G. Vlachos, Insights into the Interplay of Lewis and Brønsted Acid Catalysts in Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media. *J. Am. Chem. Soc.* **135**(10), 3997-4006 (2013). DOI:10.1021/ja3122763.
15. J. Jae, W. Zheng, A. Karim, W. Guo, R. F. Lobo, and D. G. Vlachos, The role of Ru and RuO₂ in the Catalytic Transfer Hydrogenation of 5-Hydroxymethylfurfural for the Production of 2,5-Dimethylfuran. *ChemCatChem*, Accepted (2014).
16. J. Jae, W. Zheng, R. F. Lobo, and D. G. Vlachos, Production of Dimethylfuran from Hydroxymethylfurfural through Catalytic Transfer Hydrogenation with Ruthenium Supported on Carbon. *ChemSusChem* **6**(7), 1158-1162 (2013). DOI:10.1002/cssc.201300288.
17. P. Panagiotopoulou, and D. G. Vlachos, Liquid Phase Catalytic Transfer Hydrogenation of Furfural Over Ru/C Catalyst. *Appl. Catal. A-Gen.*, Submitted (2013).
18. J. Jae, E. Mahmoud, R. F. Lobo, and D. G. Vlachos, Cascade of Liquid- Phase Catalytic Transfer Hydrogenation and Etherification of Hydroxymethylfurfural to Potential Biodiesel Components over Lewis Acid Zeolites. *ChemCatChem*, Accepted (2014).
19. H. Ren, Y. Chen, Y. Huang, W. Deng, D. G. Vlachos, and J. G. Chen, Tungsten carbides as selective deoxygenation catalysts: experimental and computational studies of converting C3 oxygenates to propene. *Green Chem.*, In press (2014). DOI:10.1039/c3gc41256c.
20. H. Ren, W. Yu, M. Saliccioli, Y. Chen, Y. Huang, K. Xiong, D. G. Vlachos, and J. G. Chen, Selective Hydrodeoxygenation of Biomass-Derived Oxygenates to Unsaturated Hydrocarbons using Molybdenum Carbide Catalysts. *ChemSusChem* **6**(5), 798-801 (2013). DOI:10.1002/cssc.201200991.
21. T. D. Swift, C. Bagia, G. Peklaris, P. Dornath, V. Nikolakis, W. Fan, and D. G. Vlachos, Reactive Adsorption for the Selective Dehydration of Sugars to Furans: Modeling and Experiments. *AIChE J.* **59**(9), 3378-3390 (2013). DOI:10.1002/aic.14090.

22. N. Rajabbeigi, R. Ranjan, and M. Tsapatsis, Selective Adsorption of HMF on Porous Carbons from Fructose/DMSO Mixtures. *Micr. Meso. Mat.* **158**(1), 253-256 (2012). DOI:10.1016/j.micromeso.2012.03.047.
23. E. E. Mallon, I. J. Babineau, J. I. Kranz, Y. Guefrachi, J. I. Siepmann, A. Bhan, and M. Tsapatsis, Correlations for Adsorption of Oxygenates onto Zeolites from Aqueous Solutions. *J. Phys. Chem. B* **115**(39), 11431-11438 (2011). DOI:10.1021/jp208143t.
24. W. C. Yoo, N. Rajabbeigi, E. E. Mallon, M. Tsapatsis, and M. A. Snyder, Elucidating structure-properties relations for the design of highly selective carbon-based HMF sorbents. *Micr. Meso. Mat.* **184**(0), 72-82 (2014). DOI:<http://dx.doi.org/10.1016/j.micromeso.2013.10.001>.
25. A. Javadekar, A. Jayakumar, R. Pujara, J. M. Vohs, and R. J. Gorte, Molten silver as a direct carbon fuel cell anode. *J. Power Sources* **214**, 239-243 (2012). DOI:10.1016/j.jpowsour.2012.04.096.
26. A. Jayakumar, A. Javadekar, J. Gissing, J. M. Vohs, G. W. Huber, and R. J. Gorte, The stability of direct carbon fuel cells with molten Sb and Sb-Bi alloy anodes. *AIChE J.* **59**(9), 3342-3348 (2013). DOI:10.1002/aic.13965.
27. A. Jayakumar, R. Kungas, S. Roy, A. Javadekar, D. J. Buttrey, J. M. Vohs, and R. J. Gorte, A direct carbon fuel cell with a molten antimony anode. *Energy Environ. Sci.* **4**(10), 4133-4137 (2011). DOI:10.1039/c1ee01863a.
28. X. Y. Zhang, D. X. Liu, D. Xu, S. Asahina, K. A. Cychosz, K. Varoon, Y. Al Wahedi, A. Bhan, S. Al Hashimi, O. Terasaki, M. Thommes, and M. Tsapatsis, Synthesis of Self-Pillared Zeolite Nanosheets by Repetitive Branching. *Science* **336**(6089), 1684-1687 (2012). DOI:10.1126/science.1221111.
29. W.-G. Kim, X. Zhang, J. S. Lee, M. Tsapatsis, and S. Nair, Epitaxially Grown Layered MFI-Bulk MFI Hybrid Zeolitic Materials. *ACS Nano* **6**(11), 9978-9988 (2012). DOI:10.1021/nn3036254.
30. K. Varoon, X. Y. Zhang, B. Elyassi, D. D. Brewer, M. Gettel, S. Kumar, J. A. Lee, S. Maheshwari, A. Mittal, C.-Y. Sung, M. Cococcioni, L. F. Francis, A. V. McCormick, K. A. Mkhoyan, and M. Tsapatsis, Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane. *Science* **334**(6052), 72-75 (2011). DOI:10.1126/science.1208891.
31. H. Chen, J. Wydra, X. Y. Zhang, P.-S. Lee, Z. Wang, W. Fan, and M. Tsapatsis, Hydrothermal Synthesis of Zeolites with Three-Dimensionally Ordered Mesoporous-Imprinted Structure. *J. Am. Chem. Soc.* **133**(32), 12390-12393 (2011). DOI:10.1021/ja2046815.
32. D. Xu, G. R. Swindlehurst, H. Wu, D. H. Olson, X. Zhang, and M. Tsapatsis, On the Synthesis and Adsorption Properties of Single-Unit-Cell Hierarchical Zeolites Made by Rotational Intergrowths - Invited contribution for Special Issue on Porous Materials, **Featured as frontispiece of the issue**. *Adv. Func. Mat.*, In press (2014). DOI:10.1002/adfm.201301975.
33. C.-C. Chang, Z. Wang, P. Dornath, H. J. Cho, and W. Fan, Rapid Synthesis of Sn-Beta for the Isomerization of Cellulosic Sugars. *RSC Adv.* **2**, 10475-10477 (2012). DOI:10.1039/C2RA21381H.
34. S. Caratzoulas, and D. G. Vlachos, Converting Fructose to 5-Hydroxymethylfurfural: A Quantum Mechanics/Molecular Mechanics Study of the Mechanism and Energetics. *Carbohydr. Res.* **346**(5), 664-672 (2011). DOI:10.1016/j.carres.2011.01.029.

35. S. Caratzoulas, T. D. Courtney, and D. G. Vlachos, Hybrid Quantum Mechanics/Molecular Mechanics-Based Molecular Dynamics Simulation of Acid-Catalyzed Dehydration of Polyols in Liquid Water. *J. Phys. Chem. A* **115**(32), 8816-8821 (2011). DOI:10.1021/jp203436e.
36. N. Nikbin, S. Caratzoulas, and D. G. Vlachos, A First Principles-Based Microkinetic Model for the Conversion of Fructose to 5-Hydroxymethylfurfural. *ChemCatChem* **4**(4), 504-511 (2012). DOI:10.1002/cctc.201100444.
37. M. Saliccioli, S. M. Edie, and D. G. Vlachos, Adsorption of Acid, Aster, and Ether Functional Groups on Pt: Fast Prediction of Thermochemical Properties of Adsorbed Oxygenates via DFT-Based Group Additivity Methods. *J. Phys. Chem. C* **116**, 1873-1886 (2012). DOI:10.1021/jp2091413.
38. M. Saliccioli, Y. Chen, and D. G. Vlachos, Density Functional Theory-Derived Group Additivity and Linear Scaling Methods for Prediction of Oxygenate Stability on Metal Catalysts: Adsorption of Open-Ring Alcohol and Polyol Dehydrogenation Intermediates on Pt-Based Metals. *J. Phys. Chem. C* **114**(47), 20155-20166 (2010). DOI:10.1021/jp107836a.
39. M. Saliccioli, and D. G. Vlachos, Kinetic Modeling of Pt Catalyzed and Computation-Driven Catalyst Discovery for Ethylene Glycol Decomposition, **Cover Art.** *ACS Catal.* **1**(10), 1246-1256 (2011). DOI:10.1021/cs2003593.
40. M. Saliccioli, M. Stamatakis, S. Caratzoulas, and D. G. Vlachos, A review of multiscale modeling of metal-catalyzed reactions: Mechanism development for complexity and emergent behavior. *Chem. Eng. Sci.* **66**(19), 4319-4355 (2011). DOI:10.1016/j.ces.2011.05.050.
41. N. Nikbin, S. Caratzoulas, and D. G. Vlachos, On the Brønsted Acid-Catalyzed Homogeneous Hydrolysis of Furans. *ChemSusChem* **6**(11), 2066-2068 (2013). DOI:10.1002/cssc.201300432.
42. R. Xiong, S. I. Sandler, and D. G. Vlachos, Alcohol Adsorption onto Silicalite from Aqueous Solution. *J. Phys. Chem. C* **115**(38), 18659-18669 (2011). DOI:10.1021/jp205312k.
43. R. Xiong, M. León, V. Nikolakis, S. I. Sandler, and D. G. Vlachos, Adsorption of HMF from Water/DMSO Solutions onto Hydrophobic Zeolites: Experiment and Simulation. *ChemSusChem*, In press, DOI: 10.1002/cssc.201300408 (2014). DOI:10.1002/cssc.201300408.
44. J. E. Santander, M. Tsapatsis, and S. M. Auerbach, Simulating Adsorptive Expansion of Zeolites: Application to Biomass-Derived Solutions in Contact with Silicalite. *Langmuir* **29**(15), 4866-4876 (2013). DOI:10.1021/la300932a.
45. S. Tupy, A. Karim, C. Bagia, W. Deng, Y. Huang, D. G. Vlachos, and J. G. Chen, Correlating ethylene glycol reforming activity with in-situ EXAFS detection of Ni segregation in supported NiPt bimetallic catalysts. *ACS Catal.* **2**, 2290-2296 (2012). DOI:10.1021/cs3004227.
46. M. S. Mettler, S. H. Mushrif, A. D. Paulsen, A. D. Javadekar, D. G. Vlachos, and P. J. Dauenhauer, Revealing pyrolysis chemistry for biofuels production: Conversion of cellulose to furans and small oxygenates. *Energy Environ. Sci.* **5**(1), 5414-5424 (2012). DOI:10.1039/C1EE02743C.
47. D. Xu, G. R. Swindlehurst, H. Wu, D. H. Olson, X. Zhang, and M. Tsapatsis, On the Synthesis and Adsorption Properties of Single-Unit-Cell Hierarchical Zeolites Made by

- Rotational Intergrowths. *Adv. Funct. Mater.* **24**(2), 201-208 (2014). DOI:10.1002/adfm.201301975.
48. P. Kumar, K. V. Agrawal, M. Tsapatsis, and K. A. Mkhoyan, Quantification of Thickness and Wrinkling of Exfoliated 2-Dimensional Zeolite Nanosheets. *Nature Commun.* **6**, Article 7128 (2015). DOI:10.1038/ncomms8128.
 49. P. Bai, E. Haldoupis, P. J. Dauenhauer, M. Tsapatsis, and J. I. Siepmann, Understanding Diffusion in Hierarchical Zeolites with House-of-Cards Nanosheets. *ACS Nano* **10**(8), 7612-7618 (2016). DOI:10.1021/acsnano.6602856.
 50. L. M. Ren, Q. Guo, P. Kumar, M. Orazov, D. D. Xu, S. M. Alhassan, K. A. Mkhoyan, M. E. Davis, and M. Tsapatsis, Self-Pillared, Single-Unit-Cell Sn-MFI Zeolite Nanosheets and Their Use for Glucose and Lactose Isomerization. *Angew. Chem. Int. Ed.* **54**(37), 10848-10851 (2015). DOI:10.1002/anie.201505334.
 51. L. M. Ren, Q. Guo, M. Orazov, D. D. Xu, D. Politi, P. Kumar, S. M. Alhassan, K. A. Mkhoyan, D. Sidiras, M. E. Davis, and M. Tsapatsis, Pillared Sn-MWW Prepared by a Solid-State-Exchange Method and its Use as a Lewis Acid Catalyst. *ChemCatChem* **8**(7), 1274-1278 (2016). DOI:10.1002/cctc.201600120.
 52. T. R. Josephson, Swagata, J. I. Siepmann, D. Vlachos, and S. Caratzoulas, Selective Fructose Ketalization on Hierarchical Sn-SPP Zeolite. **In preparation**, (2018).
 53. H. J. Cho, L. M. Ren, V. Vattipalli, Y. H. Yeh, N. Gould, B. J. Xu, R. J. Gorte, R. Lobo, P. J. Dauenhauer, M. Tsapatsis, and W. Fan, Renewable p-Xylene from 2,5-Dimethylfuran and Ethylene Using Phosphorus-Containing Zeolite Catalysts. *ChemCatChem* **9**(3), 398-402 (2017). DOI:10.1002/cctc.201601294.
 54. O. A. Abdelrahman, D. S. Park, K. P. Vinter, C. S. Spanjers, L. Ren, H. J. Cho, D. G. Vlachos, W. Fan, M. Tsapatsis, and P. J. Dauenhauer, Biomass-Derived Butadiene by Dehydra-Decyclization of Tetrahydrofuran. *ACS Sustain. Chem. Eng.* **5**(5), 3732-3736 (2017). DOI:10.1021/acssuschemeng.7b00745.
 55. C. D. Malonzo, S. M. Shaker, L. M. Ren, S. D. Prinslow, A. E. Platero-Prats, L. C. Gallington, J. Borycz, A. B. Thompson, T. C. Wang, O. K. Farha, J. T. Hupp, C. C. Lu, K. W. Chapman, J. C. Myers, R. L. Penn, L. Gagliardi, M. Tsapatsis, and A. Stein, Thermal Stabilization of Metal-Organic Framework-Derived Single Site Catalytic Clusters through Nanocasting. *J. Am. Chem. Soc.* **138**(8), 2739-2748 (2016). DOI:10.1021/jacs.5b12688.
 56. Q. Guo, L. Ren, P. Kumar, V. J. Cybulskis, K. A. Mkhoyan, M. E. Davis, and M. Tsapatsis, A Chromium Hydroxide/MIL-101(Cr) Composite Catalyst and its Use for Selective Glucose Isomerization to Fructose. *Angew. Chem. Int. Ed.*, In press, DOI: 10.1002/anie.201712818 (2018). DOI:10.1002/anie.201712818.
 57. M. D. d. Mello, and M. Tsapatsis, Selective Glucose to Fructose Isomerization over Modified Zirconium UiO-66 in Alcohol Media. *ChemCatChem*, In press, DOI: 10.1002/cctc.201800371 (2018).
 58. M. Koehle, E. Saraci, P. Dauenhauer, and R. F. Lobo, Production of p-Methylstyrene and p-Divinylbenzene from Furanic Compounds. *ChemSusChem* **10**(1), 91-98 (2017). DOI:10.1002/cssc.201601554.
 59. D. S. Park, K. E. Joseph, M. Koehle, C. Krumm, L. M. Ren, J. N. Damen, M. H. Shete, H. S. Lee, X. B. Zuo, B. Lee, W. Fan, D. G. Vlachos, R. F. Lobo, M. Tsapatsis, and P. J. Dauenhauer, Tunable Oleo-Furan Surfactants by Acylation of Renewable Furans. *ACS Central Sci.* **2**(11), 820-824 (2016). DOI:10.1021/acscentsci.6b00208.
 60. S. Dutta, A. Bohre, G. R. Jenness, W. Zheng, M. Núñez, D. G. Vlachos, and B. Saha,

- Solventless C-C Coupling of Low Carbon Furanics to High Carbon Fuel Precursors Using an Improved Graphene Oxide Carbocatalyst. *ACS Catal.* **7**, 3905–3915 (2017).
61. S. B. Liu, S. Dutta, W. Q. Zheng, N. S. Gould, Z. W. Cheng, B. J. Xu, B. Saha, and D. G. Vlachos, Catalytic Hydrodeoxygenation of High Carbon Furylmethanes to Renewable Jet-fuel Ranged Alkanes over a Rhenium-Modified Iridium Catalyst. *ChemSusChem* **10**(16), 3225-3234 (2017). DOI:10.1002/cssc.201700863.
 62. W. Deng, J. R. Kennedy, G. Tsilomelekis, W. Zheng, and V. Nikolakis, Cellulose hydrolysis in acidified LiBr molten salt hydrate (MSH) media. *Ind. Eng. Chem. Res.* **54**(19), 5226–5236 (2015). DOI:10.1021/acs.iecr.5b00757.
 63. S. Sadula, O. Oesterling, A. Nardone, B. Dinkelacker, and B. Saha, One-pot integrated processing of biopolymers to furfurals in molten salt hydrate: understanding synergy in acidity. *Green Chem.* **19**(16), 3888-3898 (2017). DOI:10.1039/c7gc01709j.
 64. S. Sadula, A. Athaley, W. Q. Zheng, M. Ierapetritou, and B. Saha, Process Intensification for Cellulosic Biorefineries. *ChemSusChem* **10**(12), 2566-2572 (2017). DOI:10.1002/cssc.201700183.
 65. S. K. Brand, T. R. Josephson, J. A. Labinger, S. Caratzoulas, D. G. Vlachos, and M. E. Davis, Methyl-ligated tin silsesquioxane catalyzed reactions of glucose. *J. Catal.* **341**, 62-71 (2016). DOI:10.1016/j.jcat.2016.06.013.
 66. T. R. Josephson, S. K. Brand, S. Caratzoulas, and D. G. Vlachos, 1,2-H- versus 1,2-C-Shift on Sn-Silsesquioxanes. *ACS Catal.* **7**(1), 25-33 (2017). DOI:10.1021/acscatal.6b03128.
 67. S. Li, T. Josephson, D. G. Vlachos, and S. Caratzoulas, The origin of selectivity in the conversion of glucose to fructose and mannose in Sn-BEA and Na-exchanged Sn-BEA zeolites. *J. Catal.* **355**, 11-16 (2017). DOI:https://doi.org/10.1016/j.jcat.2017.09.001.
 68. A. V. Mironenko, M. J. Gilkey, P. Panagiotopoulou, G. Facas, D. G. Vlachos, and B. Xu, Ring Activation of Furanic Compounds on Ruthenium-Based Catalysts. *J. Phys. Chem. C* **119**(11), 6075-6085 (2015). DOI:10.1021/jp512649b.
 69. M. J. Gilkey, P. Panagiotopoulou, A. V. Mironenko, G. R. Jenness, D. G. Vlachos, and B. Xu, Mechanistic Insights into Metal Lewis Acid-Mediated Catalytic Transfer Hydrogenation of Furfural to 2-Methylfuran. *ACS Catal.* **5**(7), 3988–3994 (2015). DOI:10.1021/acscatal.5b00586.
 70. G. R. Jenness, and D. G. Vlachos, DFT Study of the Conversion of Furfuryl Alcohol to 2-Methylfuran on RuO₂ (110). *J. Phys. Chem. C* **119**(11), 5938-5945 (2015). DOI:10.1021/jp5109015.
 71. A. V. Mironenko, and D. G. Vlachos, Conjugation-Driven "Reverse Mars-van Krevelen"-Type Radical Mechanism for Low-Temperature C-O Bond Activation. *J. Am. Chem. Soc.* **138**(26), 8104-8113 (2016). DOI:10.1021/jacs.6b02871.
 72. J. Luo, H. Yun, A. V. Mironenko, K. Goulas, J. D. Lee, M. Monai, C. Wang, V. Vorotnikov, C. B. Murray, D. G. Vlachos, P. Fornasiero, and R. J. Gorte, Mechanisms for High Selectivity in the Hydrodeoxygenation of 5-Hydroxymethylfurfural over PtCo Nanocrystals. *ACS Catal.* **6**(7), 4095-4104 (2016). DOI:10.1021/acscatal.6b00750.
 73. C. Wang, J. D. Lee, Y. Ji, T. M. Onn, J. Luo, C. B. Murray, and R. J. Gorte, A Study of tetrahydrofurfuryl alcohol to 1,5-pentanediol over Pt-WOx/C. *Catal. Lett.* **148**, 1047–1054 (2018). DOI:https://doi.org/10.1007/s10562-018-2323-6.
 74. S. G. Wang, V. Vorotnikov, and D. G. Vlachos, Coverage-Induced Conformational Effects on Activity and Selectivity: Hydrogenation and Decarbonylation of Furfural on Pd(111). *ACS Catal.* **5**(1), 104-112 (2015). DOI:10.1021/cs5015145.

75. V. Vorotnikov, and D. G. Vlachos, Group Additivity and Modified Linear Scaling Relations for Estimating Surface Thermochemistry on Transition Metal Surfaces: Application to Furanics. *J. Phys. Chem. C* **119**(19), 10417-10426 (2015). DOI:10.1021/acs.jpcc.5b01696.
76. R. E. Patet, S. Caratzoulas, and D. G. Vlachos, Adsorption in zeolites using mechanically embedded ONIOM clusters. *Phys. Chem. Chem. Phys.* **18**(37), 26094-26106 (2016). DOI:10.1039/c6cp03266d.
77. R. C. Xiong, J. Miller, M. Leon, V. Nikolakis, and S. I. Sandler, Evaluation of COSMO-SAC method for the prediction of the alcohol-water partition coefficients of the compounds encountered in aqueous phase fructose dehydration. *Chem. Eng. Sci.* **126**, 169-176 (2015). DOI:10.1016/j.ces.2014.12.014.
78. S. Maduskar, A. R. Teixeira, A. D. Paulsen, C. Krumm, T. J. Mountziaris, W. Fan, and P. J. Dauenhauer, Quantitative carbon detector (QCD) for calibration-free, high-resolution characterization of complex mixtures. *Lab Chip* **15**(2), 440-447 (2015). DOI:10.1039/c4lc01180e.
79. M. J. Gilkey, C. Brady, D. G. Vlachos, and B. Xu, Characterization of Oxidation States in Metal/Metal Oxide Catalysts in Liquid-Phase Hydrodeoxygenation Reactions with a Trickle Bed Reactor. *Ind. Eng. Chem. Res.*, Accepted, DOI: 10.1021/acs.iecr.1028b00797 (2018).
80. M. Dunwell, Y. Yan, and B. Xu, In Situ Infrared Spectroscopic Investigations of Pyridine-Mediated CO₂ Reduction on Pt Electrocatalysts. *ACS Catal.* **7**(8), 5410-5419 (2017).
81. M. Dunwell, Q. Lu, J. M. Heyes, J. Rosen, J. G. Chen, Y. Yan, F. Jiao, and B. Xu, The Central Role of Bicarbonate in the Electrochemical Reduction of Carbon Dioxide on Gold. *J. Am. Chem. Soc.* **139**(10), 3774-3783 (2017).
82. O. A. Abdelrahman, K. P. Vinter, L. M. Ren, D. D. Xu, R. J. Gorte, M. Tsapatsis, and P. J. Dauenhauer, Simple quantification of zeolite acid site density by reactive gas chromatography. *Catal. Sci. Technol.* **7**(17), 3831-3841 (2017). DOI:10.1039/c7cy01068k.
83. J. Zhou, J. Fu, P. Yang, K. Yu, S. Caratzoulas, W. Zheng, and D. G. Vlachos, Controlling oxide promoter coverage and microstructure on metals of inverse catalysts: Application to liquid phase tetrahydrofurfuryl alcohol conversion to 1,5-pentanediol. *Appl. Catal. B-Environ.* **346**, 123724 (2024). DOI:<https://doi.org/10.1016/j.apcatb.2024.123724>.
84. J. Zhou, P. Yang, P. A. Kots, M. Cohen, Y. Chen, C. M. Quinn, M. D. de Mello, J. Anibal Boscoboinik, W. J. Shaw, S. Caratzoulas, W. Zheng, and D. G. Vlachos, Tuning the reactivity of carbon surfaces with oxygen-containing functional groups. *Nat. Commun.* **14**(1), 2293 (2023). DOI:10.1038/s41467-023-37962-3.
85. J. Zhou, A. Worrada, Y. Wang, K. Yu, S. Deshpande, J. A. Boscoboinik, S. Caratzoulas, W. Zheng, and D. G. Vlachos, The role of the metal core in the performance of WO_x inverse catalysts. *Chem Catalysis*, 100756 (2023). DOI:<https://doi.org/10.1016/j.checat.2023.100756>.
86. Y. R. Wu, S. Sourav, A. Worrada, J. H. Zhou, S. Caratzoulas, G. Tsilomelekis, W. Q. Zheng, and D. G. Vlachos, Dynamic Formation of Bronsted Acid Sites over Supported WO_x/Pt on SiO₂ Inverse Catalysts: Spectroscopy, Probe Chemistry, and Calculations. *ACS Catal.* **13**(11), 7371-7382 (2023). DOI:10.1021/acscatal.3c00279.
87. P. Yang, J. Li, D. G. Vlachos, and S. Caratzoulas, Tuning Active Site Flexibility by Defect Engineering of Graphene Ribbon Edge-hosted Fe-N₃ Sites. *Angewandte Chemie International Edition* **n/a**(n/a), e202311174 (2023).

- [DOI:https://doi.org/10.1002/anie.202311174](https://doi.org/10.1002/anie.202311174).
88. S. Shi, P. P. Yang, C. Dun, W. Q. Zheng, J. J. Urban, and D. G. Vlachos, Selective hydrogenation via precise hydrogen bond interactions on catalytic scaffolds. *Nat. Commun.* **14**(1), 429 (2023). [DOI:10.1038/s41467-023-36015-z](https://doi.org/10.1038/s41467-023-36015-z).
 89. J. Li, H. Liu, Z. An, Y. Kong, L. Huang, D. Duan, R. Long, P. Yang, Y.-Y. Jiang, J. Liu, J. Zhang, T. Wan, J. Fu, R. Pan, X. Wang, and D. G. Vlachos, Nitrogen-doped carbon for selective pseudo-metal-free hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran: Importance of trace iron impurity. *J. Catal.* **417**, 396-407 (2023). [DOI:https://doi.org/10.1016/j.jcat.2022.12.021](https://doi.org/10.1016/j.jcat.2022.12.021).
 90. Z. An, P. Yang, D. Duan, J. Li, T. Wan, Y. Kong, S. Caratzoulas, S. Xiang, J. Liu, L. Huang, A. I. Frenkel, Y.-Y. Jiang, R. Long, Z. Li, and D. G. Vlachos, Highly active, ultra-low loading single-atom iron catalysts for catalytic transfer hydrogenation. *Nat. Commun.* **14**(1), 6666 (2023). [DOI:10.1038/s41467-023-42337-9](https://doi.org/10.1038/s41467-023-42337-9).