Catalysis Center for Energy Innovation

KEY ACCOMPLISHMENTS
AND CORE CAPABILITIES
# TABLE OF CONTENTS

Introduction and Overview of Discoveries and Breakthroughs .......................................................... 2

Core Capabilities: Multiscale Modeling .................................................................................................. 4
  Solution-phase Chemistry with Accelerated Molecular Dynamics Methods ........................................ 5
  High-throughput Computing: Predicting Thermochemistry and Kinetics of Biomass Derivatives on Transition Metals ......................................................... 6
  Computational Engine Drives Catalyst Discovery .................................................................................. 7

Core Capabilities: Hierarchical Multiscale Materials ........................................................................... 8
  House-of-Cards Structures Improve Catalyst Performance ................................................................. 8
  New Approach to Designing Zeolites ..................................................................................................... 9

Core Capabilities: Characterization Techniques and Evaluation ............................................................ 10

Furans Research:
  Sn-beta Catalyst Converts Selectively Biomass-derived Sugars to Chemicals ........................................ 12
  Functionality of a Novel Biomass Conversion Catalyst Explained at the Atomistic Level .................. 13
  The Magic of Sn: Converting Hemicellulose Building Blocks to Furfural in Aqueous Media ............... 14
  Solution-phase Mechanism of D-fructose Dehydration to 5-hydroxymethylfurfural (HMF) ............... 15
  Single-pot Technology by Coupling Lewis and Brønsted Acidity in Different Solvents ................... 16
  Quantum Mechanical Tunnelling in Aldose-Ketose Isomerization by Lewis Acids ............................ 17

Aromatics Research:
  CCEI-PX Process: Making Aromatic Chemicals from Biomass .......................................................... 18
  Elucidating the Chemical Network in the Making of Renewable P-xylene ....................................... 19
  Techno-economic Optimization of Renewable P-xylene Production ............................................... 20
  First-Principles Calculations Provide Insights into Pathways and Catalyst Discovery ...................... 21

Pyrolysis Research:
  Revealing Pyrolysis Chemistry for Biofuels Production ..................................................................... 22
  Production of Renewable P-xylene via Catalytic Fast Pyrolysis ......................................................... 23

Reforming and Hydrodeoxygenation Research:
  Identification of Glycolaldehyde as Probe Molecule for Biomass-derived Oxygenates .................... 24
  Catalysts with Lower Cost and Higher Stability: Replacing Ni/Pt With Ni/WC ................................. 25
  Theory and Surface Science Experiments Reveal the Mechanisms of Biomass Reforming on Noble Metal Catalysts ................................................................. 26

Fuel Cells Research:
  A Direct Carbon Fuel Cell with a Molten Antimony Anode ............................................................... 28
  Molten Antimony Fuel Cell Offers Potential for Low-footprint Management of Excess Electrical Power ................................................................................................. 29

Industrial Membership and Sponsorship Programs .......................................................................... 30

Partner Institutions of CCEI .................................................................................................................. 32
INTRODUCTION

The Catalysis Center for Energy Innovation (CCEI) was established in 2009 by a grant from the U.S. Department of Energy, Office of Science. Since inception, the center has been expanding its scope through industrial sponsorships on focused projects of interest to individual companies. The center's mission is to develop innovative heterogeneous catalytic technologies to transform lignocellulosic (non-food-based) biomass materials into fuels and chemicals. We have assembled an interdisciplinary team of faculty and scientific staff that brings together the expertise and synergism necessary to tackle the challenges and complexities in heterogeneous catalysis. Currently CCEI is a collaboration of over 25 faculty members and approximately 40 graduate students and postdoctoral researchers from 10 institutions nationwide. It offers an engaging environment that nurtures and educates the next generation of professionals needed to further develop and implement new catalytic technologies. The center provides an integrated approach to solving scientific and engineering problems that spans across scales and disciplines, including (1) synthesis and characterization of novel catalysts, (2) development and application of multiscale modeling, (3) reaction and reactor evaluation, and (4) technology transfer.

Biomass has been used as an energy source for thousands of years, since the first time wood was burned to cook food or to keep warm. With the evolution in technology, biomass can be used in producing other forms of energy while reducing the footprint of carbon dioxide. Plants and agricultural residue can be converted to fuels for transportation and to chemicals for making products that are typically made from petroleum. The U.S. Department of Energy (DOE) and the U.S. Department of Agriculture support expanding the role of biomass as a renewable energy source to reduce our country's dependency on foreign oil. According to the U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry\(^1\), it is estimated that the U.S. could produce over 1 billion dry tons of biomass per year without major changes in agricultural practices while meeting food demands—enough to displace at least 30% of the country's petroleum consumption. Biomass offers a unique opportunity for a sustainable society with unprecedented impact on the U.S. economy, energy security and independence. For this vision to be realized, we must overcome major scientific hurdles that are present due to the inherent complexity of biomass materials and associated processes.

FOCUS AND OBJECTIVES

Our overarching goal is to develop methods and concepts that form the foundations of modern biorefineries. The cornerstone of CCEI research lies in advancing catalysis and its integration into processes that deliver innovative technologies for the conversion of feedstocks of cellulose and hemicellulose, sugars (produced from the hydrolysis of biomass), and smaller oxygenated molecules. Since biomass feedstocks vary considerably by source and the number of candidate reactions is huge, CCEI mainly focuses on developing a fundamental science base for controlling the scission and formation of C-H, O-H, C-C and C-O bonds by choosing a select number of reactions from representative processes. CCEI researchers develop methods to cope with the complex, multiscale environment of biomass processing that renders the rational design of these processes and catalysts challenging.

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OVERVIEW OF DISCOVERIES AND BREAKTHROUGHS

In three years since its foundation, CCEI has established a diverse and innovative research portfolio in transforming lignocellulosic biomass, such as switchgrass and trees, into intermediate platforms that can be deployed for fuels and chemicals. Our faculty, staff, postdoctoral fellows and students have developed a number of signature research concepts and technologies, including the iconic technology for the isomerization of aldoses to ketoses production via Sn-beta zeolite. Sn-beta has been the first heterogeneous Lewis acid catalyst carrying this very hard reaction in water. Its high selectivity, activity, and stability set the foundations for replacing the current, costly enzymatic process converting glucose to fructose for syrup. Building on this success, we have integrated the Lewis acid catalyst (Sn-beta) and various Brønsted acid catalysts to produce furans and ethers in a single pot. Such process intensification has brought the production of intermediate biomass platforms one step closer to raw materials with a concomitant reduction in production cost.

By introducing bifunctional catalysts, we were able to successfully develop the CCEI-PX technology that demonstrates the highest ever yield in converting furans to p-xylene, a key precursor for the manufacturing of a number of polymers. This groundbreaking technology extends to complex catalytic pyrolysis, which enhances the yield to aromatics and thereby increases the suitability of the fuel as an add-on to gasoline. Starting with a high-risk idea, researchers ended up with an amazingly advanced—yet simple and scalable—technology for the direct conversion of solid biomass to electricity using molten metal electrolyte fuel cells.

Our thin-film pyrolysis technique is the first-of-its-kind method to overcome transport limitations and provide information for intrinsic kinetics. Combined with cutting-edge simulation, this elegantly simple method maps for the first time the molecular pathways via which cellulose breaks down to bio-oil. Major developments have also taken place in first-principles-based prediction of reforming and hydrodeoxygenation catalysts for key biomass derivatives. These developments can eventually assist in catalyst and process design for bio-oil upgrade.

Our diverse and innovative research portfolio would not have been feasible without a solid foundation of major breakthroughs in materials synthesis, in situ characterization, and multiscale computations. This brochure outlines the aforementioned major research accomplishments and the key capabilities that enable us to realize such significant scientific advances. We hope you find it valuable, and we welcome your feedback.

Dion Vlachos, Director
Elizabeth Inez Kelley Professor of Chemical & Biomolecular Engineering

MULTISCALE INTEGRATED APPROACH

We exploit various complementary catalytic technological platforms that are anticipated to play key roles in future biorefineries for energy, fuels, and chemical production: (1) novel pyrolysis methods to produce bio-oil, (2) bio-oil upgrade via hydrodeoxygenation, and (3) liquid-phase processing to selectively produce chemicals, such as aromatics and fuels.
Core Capabilities

The core capabilities of CCEI can be described as three crosscutting enablers that serve as the foundation of the center’s research: (1) multiscale modeling, (2) hierarchical multiscale materials, and (3) characterization. These enablers are integrated within all of the center’s research areas to more quickly address the inherent complexities of the environment in which reactions take place.

MULTISCALE MODELING

In CCEI, we have a world class program on multiscale modeling that uses tools at all scales, links models across scales, quantifies errors, and evaluates uncertainty in multiscale modeling. In addition to utilizing existing tools (ab initio, density functional theory, molecular dynamics, computational fluid dynamics, etc.), we developed and implemented new methodologies and approaches, including the following:

- A hybrid Grand Canonical Monte Carlo/Molecular Dynamics (GCMC/MD) simulation ensemble to allow seamless accounting for lattice flexibility in adsorption of biomass in microporous materials.
- A self-consistent Grand Canonical Monte Carlo/Expanded Ensemble methodology for adsorption of solutes into microporous materials directly from the liquid phase by relating the loadings to solution concentrations, thus obviating the need for an equation of state and very expensive simulations like two-phase Gibbs ensemble Monte Carlo.
- The first application of the hybrid quantum mechanics/statistical mechanics method (COSMO-SAC) to compute reaction-free energies in solvents with unprecedented accuracy, often within 1 kcal/mol.
- A framework and accompanying software for computing thermochemistry and kinetics of biomass derivatives (alcohols, polyols, esters, ethers, acids, etc.) on metal and metal-like surfaces with high accuracy and minimal computational cost.
- A high-throughput methodology for predicting activity and selectivity across the periodic table and new materials for reforming, (de)hydrogenation, and hydrodeoxygenation chemistries.
- A program for the study of reactions of biomass derivatives in solution that takes into account explicit solvent dynamics effects. The paradigms considered constitute first-of-their-kind simulations in catalysis. The program comprises development of aqueous-phase microkinetic models for testing and validation of deduced mechanisms.
- A graph-theoretical kinetic Monte Carlo (KMC) algorithm that takes quantum mechanical input and is applicable to both single crystals and nanoparticles, thus bridging the materials gap.
- The first-of-its-kind automatic mechanism generation code for metals, acids and pyrolysis of biomass.
Solution-phase Chemistry with Accelerated Molecular Dynamics Methods

At CCEI we have developed a strong, computational program for the comprehensive study of the solution chemistry of biomass derivatives.

Reaction mechanism studies that are carried out in the gas phase or even in implicit solvent by electronic structure calculations (ab initio or density functional theory) neglect a number of factors that are of great importance for the study of chemical reactions in solution. Under the umbrella term “solvent dynamics effects,” one has to account for (a) explicit solvation effects, which often give rise to free-energy barriers due to solvent reorganization or electronic polarization, especially in reactions that involve proton or hydride transfer, (b) friction, namely, energy dissipation from reactive modes to non-reactive ones directly affecting both the reaction energetics and rate, and (c) the possibility of active participation of the solvent molecules in the chemical reaction, implying that gas-phase mechanisms may not necessarily be transferable over to the solution phase.

To address these critically important issues, computational chemists at CCEI perform solution chemistry studies by employing state-of-the-art molecular dynamics acceleration techniques (umbrella sampling and its adaptive variants, such as metadynamics) within the frameworks of hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) and ab initio (Car-Parrinello) Molecular Dynamics. Hybrid QM/MM and Car-Parrinello Molecular Dynamics simulations are routinely performed to study solvation phenomena, to interpret spectroscopic data (IR, Raman), and to compute free energies of reaction and activation of elementary chemical reactions in solution.


Dimethylsulfoxide (DMSO) Water

Solvation of 5-hydroxymethylfurfural by water and DMSO determined via molecular dynamics simulations.
High-throughput Computing: Predicting Thermochemistry and Kinetics of Biomass Derivatives on Transition Metals

First-principle simulation of biomass processing is hindered by the sheer size of biomass derivatives and the associated computational cost of quantum codes. CCEI researchers developed a new framework for estimating thermochemistry of oxygenated species and rate constants on transition metals that drastically reduces the expense involved in kinetic modeling of biomass catalytic processing. This methodology allows for an inexpensive screening of a reaction mechanism that can be followed by refinement of sensitive mechanistic parameters via a limited number of (expensive) quantum calculations. The framework has been applied to ethylene glycol and glycerol decomposition chemistry on platinum to reveal interesting reactivity trends. It has been found that initial C-H bond scission reactions in the mechanism are rate controlling, whereas C-C bond cleavage is expected to be fast under typical thermal decomposition conditions. The oxygenate surface intermediate heat of formations calculated via group additivity are compared to those via density functional theory for ethylene glycol and glycerol decomposition intermediates in the figure.


Parity graph comparing first-principles density functional (DFT) theory calculations to semi-empirical, excel-based group additivity values along with snapshots of structures of oxygenated species on Pt manifesting the multi-dentate nature of binding of these adsorbates.
Computational Engine Drives Catalyst Discovery

Predicting catalysts from fundamental guiding principles has been the dream of the catalysis community for decades. With the advent in density functional theory (DFT), major inroads have been made in this direction using principally interpolation in the periodic table. The activity of mixed alloys is predicted from the properties of the parent metals drawing upon and reinforcing Sabatier’s principle. A tacit assumption in this modeling approach is that the ‘key’ surface intermediate and rate determining step are known and remain constant as operating conditions vary. Even more severe is the assumption of interpolation that breaks down for core-shell structures due to strain and ligand effects. Unlike activity, no underlying principle, similar to Sabatier’s, exists for predicting selective catalysts. Selectivity is truly determined from the complex interplay of pathways that eventually dictate the dominant intermediates and products. The lack of a computational framework that overcomes these hurdles has undermined until recently the realization of computer-driven catalyst design.

CCEI researchers have recently leveraged their development of semi-empirical thermochemistry techniques (group additivity and linear scaling relations) and combined it with linear free-energy (Børøssted-Evans-Polanyi) relations to develop a computational microkinetic modeling engine for approximate but rapid screening of the periodic table. Within hours to days of computation, maps of activity and selectivity can be constructed to identify properties of potential catalysts that maximize selectivity and yield of a given process without the underlying assumptions of prior work. This approach is capable of predicting the best performing catalysts subject to kinetic and thermodynamic constraints. More impactfully, when combined with DFT-based informatics tools, this approach can predict novel materials. It can zoom in efforts on identification and subsequently synthesis of potentially unknown materials, such as mixed alloys as well as core-shell structures (whose properties are not linear interpolations of those of the constituents) that hold best performance. The framework has been validated with small polyols (e.g., ethylene glycol and glycerol) and multifunctional compounds (e.g., glycol aldehyde) and can be applied to a large fraction of bio-oil compounds.


HIERARCHICAL MULTISCALE MATERIALS

CCEI has a growing portfolio of novel classes of materials with tunable micro-, meso-, and/or hierarchical pores and functional groups, including: (1) three-dimensionally ordered mesoporous (3DOM) carbons, titanias, and zirconias, (2) 3DOM-imprinted zeolites, (3) hollow mesoporous carbons, and (4) hierarchically porous MFI and MEL zeolites. These materials hold exciting implications for realizing both adsorption and reaction selectivity, enhancing hydrothermal stability, and reducing transport limitations specific to complex biorefinery streams. As such, the materials themselves and the strategies for their facile synthesis represent a unique and versatile capability of the center that cuts across various research areas and holds broader implications for impacting general chemicals processing.

House-of-Cards Structures Improve Catalyst Performance

CCEI researchers and their colleagues developed a novel and simple synthesis technique called repetitive branching that stacks thin zeolite sheets at right angles generating a house-of-cards shaped crystal. The large-pore channels act like highways that allow chemicals and molecules to travel more rapidly throughout the crystal to reach the smaller, reactive pores. Not only does this technique result in faster, more selective and stable catalysts, it costs the same as producing zeolites using traditional methods. A faster, improved catalyst at no extra cost could lower operating costs and reduce waste streams, having far-reaching impact worldwide.

This synthesis method significantly improves the effectiveness of traditional zeolites with no unwanted change in functionality and is the first cost-efficient route that can enable large-scale commercialization. Since both the pore size and the size of channels created between the zeolite thin sheets can be controlled, this technique can be applied to a variety of industries that use catalysts—including gasoline, plastics, biofuels, pharmaceuticals and other chemicals—and has the potential to lower consumer costs.

This technology has been licensed by Argilex Technologies, a Minnesota start-up company, and is a key component to the company’s materials-based platform.

Varoon, K; Zhang, X; Elyassi, B; Brewer, D; Gettel, M; Kumar, S; Lee, J; Maheshwari, S; Mittal, A; Sung, C-Y; Cococcioni, M; Francis, L; McCormick, A; Mkhoyan, K A; Tsapatsis, M, “Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane,” Science, 334, 72-75 (2011). [10.1126/science.1208891]
New Approach to Designing Zeolites

The race to produce new biofuels and sustainable biomass-derived chemicals has brought considerable research focus to zeolites, which are tiny crystals about the size of the tip of a pencil that are made out of inorganic materials similar to sand. Unlike sand, however, zeolites have sets of tiny identical pores that are just a little larger than many common chemicals. These pores can be engineered to separate chemicals, promote desirable chemical reactions, or serve as absorbant materials.

Researchers at CCEI have developed a new approach to designing zeolites allowing them to work faster and more efficiently than ever before. These novel materials have the conventional pores of zeolites, but are also comprised of a set of larger channels that allow molecules to get within the zeolite particle rapidly. The unique synthesis method allows researchers to control the zeolite pore structure by first producing a carbon template that is three-dimensionally ordered mesoporous (3DOm). The zeolite crystals are then grown within the 3DOm template by hydrothermal synthesis to produce the microchannels. Finally, the 3DOm template is removed, and the spaces remaining are the large channels. The combination of small pores (microchannels) and large channels (for fast chemical transfer) creates an engineered hierarchical system that can be optimized by varying the quantity and size of each particle structure.

The challenge of synthesizing zeolites inside 3DOm carbon is preventing crystal formation on the outside of the template while allowing zeolite growth on the inside. CCEI researchers overcame this obstacle by first growing zeolite seeds inside the 3DOm carbon and then adding the seeded carbon to a freshly prepared synthesis solution where the subsequent crystal growth was carried out.

This new route to hierarchical zeolite synthesis holds exciting opportunities for controlling mesopore (large channel) sizes with precision that was previously unattainable by other methods, and the mesoporosity can easily be tuned by varying the size of 3DOm carbon templates. In fact, a wide range of zeolite crystals can be achieved during synthesis by varying nucleation and crystal growth rates. These hierarchical zeolite materials have the potential to provide building blocks for new energy materials and a basis for quantitatively studying the mass-transfer limitation on the catalytic performance of zeolite catalysts. The outcome of this work will ultimately mean faster chemical reactions with better chemical control, and this will lead to less expensive, higher quality biofuels and renewable chemicals.

CHARACTERIZATION

CCEI researchers join efforts with collaborators in the Synchrotron Catalysis Consortium (SCC) at the Brookhaven National Laboratories (BNL) to develop state-of-the-art synchrotron techniques for in situ studies of chemical transformations, including biomass conversion. The primary goal is to investigate catalysts in action by (1) developing reactors for in situ operando research and (2) combining complementary techniques in a single experiment. Below are two techniques developed by the combined efforts of the SCC and CCEI team members.

Characterization Techniques

Combined EXAFS/XRD Instrument

The Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Diffraction (XRD) techniques give complementary information about the structure of catalytic materials: XRD is effective for crystalline materials (long-range), whereas XAFS provides short-range order structural features in disordered, amorphous and/or low-dimensional materials.

To analyze catalysts under their operating conditions, it is highly desirable to achieve the simultaneous collection of the XRD and EXAFS data under in situ conditions together with online product analysis.

The SCC and CCEI teams have finished building the first instrument in the U.S. for combined, time resolved XRD/XAFS experiments at Beamline X18A at the National Synchrotron Light Source at BNL. Such a combination allows the simultaneous measurement of changes in the actual structure (in the short-, medium- and long-range order), electronic properties, and chemical activity of heterogeneous catalysts.

Combined DRIFTS/XAFS/MS Measurements

The SCC and CCEI team members have designed and built a Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) cell for transmission EXAFS. The cell can be used for in situ measurement at temperatures up to 800 °C in a gaseous environment and allows identification of surface intermediates using DRIFTS, detection of reaction products using online mass spectrometry, and catalyst characterization using EXAFS. This is the first-of-its-kind instrument in the U.S.

Analysis of EXAFS Data

CCEI researchers are developing tools for atomistic reconstruction of particle size, shape and compositional order from the synchrotron data. Analysis can be expanded to account for additional characterization tools.

Catalyst Evaluation

Batch and flow reactors are available for evaluating the performance of different catalysts and for collecting data needed for understanding the reaction mechanisms. Of these, two high-throughput batch systems and a gas-phase flow high-throughput reaction system were designed and constructed by CCEI for efficient catalyst screening. The existing configurations of all reactors enable studies over a broad range of conditions ranging from vacuum (batch-IR reactor) to gas-phase fixed bed flow reactors and high-pressure systems for studying reactions in the condensed phase. Reactors are connected to the necessary analytical instruments (gas chromatograph, micro-gas chromatograph, GC/MS, HPLC, and MS).

UHV Spectroscopy

The ultra-high vacuum (UHV) characterization techniques available (XPS, TPD, HREELS, Auger, etc.) comprise a facility within the center that is used for studying the interaction of the reactants, products and intermediates on well-defined catalysts.

Vibrational Spectroscopy

CCEI has a state-of-the-art FTIR spectrometer that is equipped with a heated diamond Attenuated Total Reflection (ATR) plate (up to 300 °C) and a heated DRIFT reactor/cell (up to 910 °C under the flow of gases or in vacuum). The ATR plate is especially suitable for studies in the liquid phase, thus making it an extremely important tool for characterization of liquid-phase biomass conversion. It can be used for the investigation of interactions between solvents and biomass feedstocks or derived chemicals, as an analytical tool for determining the concentration of products in hexose dehydration reactions, to monitor in situ reactions, to study adsorption on the catalyst surface from the liquid phase, etc. The DRIFT cell can be used to study the structural changes of the catalyst as well as the species adsorbed from the gas phase on the catalyst surface. Complementary information about the vibrational properties of our samples is also obtained by measuring and analyzing their Raman spectra. These three techniques together with the UHV spectroscopy enable CCEI to have a holistic approach in the characterization of catalysts and biomass reaction systems.


Sn-beta Catalyst Converts Selectively Biomass-derived Sugars to Chemicals

CCEI researchers developed a novel catalyst that can have unprecedented impact on the production of renewable chemicals and fuels by efficiently converting biomass-derived sugars. Interest in carbohydrate chemistry has been revitalized by the push to produce chemicals from biomass. A reaction of particular importance and difficulty is the isomerization of glucose to fructose, an intermediate step in the production of biofuels. It has been shown that the use of Sn-beta zeolites as catalysts for this reaction offers significant advantages over the traditional enzyme catalyst. This catalyst has been shown to be more stable than the enzyme catalysts, is unaffected by impurities that harm enzyme activity and is compatible with harsh environments, such as acidic solutions. By coupling a dehydration reaction to the isomerization in hydrochloric acid solution, for instance, glucose was converted directly to 5-hydroxymethylfurfural (HMF) in high yields, proving Sn-beta as an attractive catalyst for a one-pot process.


Schematic of isomerization reaction of glucose to fructose using the Sn-beta zeolite.
Functionality of a Novel Biomass Conversion Catalyst Explained at the Atomistic Level

The core of catalytic chemistry research lies in understanding the role of a catalyst in a reaction. This understanding is crucial to the discovery of new materials leading to more energy efficient and benign chemical transformations. A critical reaction in utilization of the most abundant biomass ingredient, cellulose, is the conversion of glucose to fructose. Experiments have been designed to delineate the mechanism in this key chemical transformation catalyzed by a novel Sn-beta zeolite catalyst. The research team replaced the hydrogen atom attached to the C-2 carbon of the glucose molecule by a deuterium atom and performed the experiments with and without the Sn-beta catalyst in pure water. Nuclear magnetic resonance (NMR) experiments demonstrate the ability of the catalyst to facilitate the intramolecular hydrogen transfer from C-2 to C-1 carbon. This proves the first-of-its-kind Lewis acid catalysis in converting biomass in water, which is in stark contrast that Lewis acidity is generally suppressed by the presence of water. Given the fact that the Sn-beta catalyst is much more stable than the commercial enzymatic catalyst and active over a wide range of operating conditions, the findings of this work serve as a major milestone in developing catalysts for industrial scale biomass conversion process.


Isotopic labeling experiments reveal that an intra-hydride transfer rather than water mediated proton transfer convert abundant and inexpensive glucose to added-value fructose. In the transformation, the deuterium atom (D) shifts from the C-2 carbon in glucose to the C-1 carbon atom in fructose.
The Magic of Sn: Converting Hemicellulose Building Blocks to Furfural in Aqueous Media

Hemicellulose makes up a large fraction of lignocellulosic biomass. The majority of hemicellulose consists of C5 sugars (pentoses), such as xylose. Biological routes for xylose isomerization to xylulose have not been met with much success. As a result, the key C5 furan, furfural, is currently made from xylose by sulfuric acid heat treatment at high temperatures and is stripped away by steam. This is an energy intensive process, similar to the first industrial furfural production process established by Quaker Oats in 1921. The introduction of selective and active heterogeneous bifunctional catalysts for the transformation of xylose to furfural would be a transformative technology in efficiently utilizing hemicellulose.

CCEI researchers recently introduced the Sn-beta zeolite as a Lewis acid to selectively isomerize xylose to xylulose in water at low temperatures. Xylulose is then dehydrated using a Brønsted catalyst to furfural. Researchers demonstrated that it is possible to combine two heterogeneous catalysts to achieve furfural yields approaching 80% under certain conditions using a reactive separation scheme, and that the Sn-beta catalyst does its magic for additional aldo to keto sugar isomerization. This further enriched the portfolio of heterogeneous Lewis catalyzed chemistry in water, which was introduced by CCEI in 2010.


Solution-phase Mechanism of D-fructose Dehydration to 5-hydroxymethylfurfural (HMF)

Using hybrid Quantum Mechanics/Molecular Mechanics molecular dynamics (QM/MM MD) simulations, a computational technique that allows the study of chemical reactions in solution, CCEI computational chemists have recently mapped out the mechanism and energetics of the Brønsted acid-catalyzed dehydration of D-fructose to HMF and demonstrated the importance of the solvent in accounting for the free energy of activation of the reaction. This effort also marked the first time that the QM/MM MD method was used to fully study a solution chemistry consisting of ten elementary steps. Furfural and derivatives of it, such as HMF, show great promise as platform chemicals for the production of fine chemicals, plastics and fuels. The aqueous-phase synthesis of HMF from fructose exemplifies the difficulties in the conversion of highly functionalized biomass derivatives (carbohydrates) and the need for tight process optimization, as the reaction conditions (e.g., the pH) as well as the solvent in which the reaction is carried out can affect both the yield and the selectivity to HMF. Through modeling and molecular simulation, CCEI researchers elucidate these effects to ultimately control the numerous, undesired side reactions. One important milestone in this respect is that they have been able to predict that solvents with low static dielectric constant should accelerate the dehydration of fructose to HMF.


Furans Research

**Single-pot Technology by Coupling Lewis and Brønsted Acidity in Different Solvents**

Converting biomass to specific chemicals involves a series of several reactions that traditionally occur in separate steps. CCEI researchers developed a single-pot technology that allows two or more of these sequential reactions to be carried out in a single reactor vessel and demonstrated that it is possible to couple Lewis and Brønsted acidity to produce furans from aldoses in several cases. This technology is expected to have significant impact on the process economics because it eliminates the separation and purification needs, thereby reducing capital and operating costs while increasing product yield.

**Production of Furans from Aldoses and More Complex Biomass**

Even though glucose is the building block of cellulose or starch, it is difficult to directly convert it to intermediate platform chemicals like 5-hydroxymethylfurfural (HMF). On the other hand, HMF can be synthesized relatively easily by dehydration of fructose typically via homogeneous Brønsted acid catalysis. Thus the one-pot conversion of glucose to fructose followed by dehydration to HMF might have a profound impact on future biorefineries. Isomerization of glucose to fructose using immobilized enzymes is one of the largest biocatalytic processes worldwide. However, conversion to fructose is limited by thermodynamic equilibrium, and it cannot easily be coupled with fructose dehydration reactions due to limitations in temperature and pH of the bioreactor. Other studies coupled these two reactions using environmentally unfriendly catalysts and solvents.

CCEI researchers showed that it is possible to combine Sn-beta with HCl to carry out the one-pot synthesis of HMF starting from glucose. Using a biphasic system, it was possible to obtain more than 70% selectivity at 95% conversion. They also showed that it is possible to obtain high HMF yields starting from more complicated feedstocks like starch. In that case the reaction series includes the Bronsted catalyzed starch depolymerization to glucose, Lewis acid catalyzed isomerization of glucose to fructose using Sn-beta, and Bronsted catalyzed dehydration of fructose to HMF. It was also demonstrated that Sn-beta is active and stable over at least 4 cycles at reaction conditions (pH=1, water saturated with NaCl, and reaction temperatures up to 180 °C). This approach was subsequently extended to the conversion of xylose to furfural by combining Sn-beta with HCl or Amberlyst catalyst. This constitutes the first single-pot technology for C5 sugars derived from hemicellulose.

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Flow sheet of 5-hydroxymethylfurfural (HMF) production.
Quantum Mechanical Tunnelling in Aldose-Ketose Isomerization by Lewis Acids

CCEI researchers recently discovered that the zeolite beta with framework Sn or Ti Lewis acid centers can catalyze the aldose-ketose isomerization with remarkable efficiency and selectivity, even in acidic aqueous environments. This discovery sent CCEI theorists computing in an effort to understand this catalyst’s remarkable catalytic abilities. They performed gas-phase electronic structure calculations and solution-phase ab initio Molecular Dynamics simulations (Car-Parrinello Molecular Dynamics). The calculations verified $^1$H and $^{13}$C NMR spectroscopic studies and showed that the isomerization reaction follows a hydride transfer mechanism that resembles metalloenzymes, such as xylose isomerase—but with a quantum mechanical twist. Analysis and visualization of the molecular orbitals computed on the CCEI supercomputers has revealed that the hydride transfer is actually a coupled neutral hydrogen atom-electron transfer involving four different atoms, and that in the transition state the electron is shared by two oxygen atoms, indicating quantum mechanical tunneling (see image). Using this information, the CCEI theorists are currently using quantum mechanics to model the rate of the reaction from first principles.

Production of 5-Ethoxymethylfurfural (EMF) from Glucose

EMF can be used as a potential biofuel additive either directly or after hydrogenation to form EMF alcohol. It can be produced from HMF via etherification with alcohol. CCEI researchers demonstrated the single-pot synthesis of EMF from glucose in ethanol by combining a Lewis (Sn-beta) and a Brønsted (Amberlyst 131) acid catalysts. Sn-beta catalyzed isomerization of glucose to fructose in non-aqueous solvents (ethanol), while the Amberlyst 131 catalyzed the dehydration of fructose to HMF and the etherification between HMF and the ethanol solvent.

The CCEI-PX Process: Making Aromatic Chemicals from Biomass

CCEI researchers discovered a new process called CCEI-PX to produce renewable p-xylene, which is an isomer of the chemical xylene used to make a common plastic called polyethylene terephthalate (PET). The renewable p-xylene can be used in the existing chemical infrastructure to produce many everyday products, including food and beverage packaging, synthetic fibers and plastics.

Using conventional methods, sugars naturally found in biomass (such as glucose and xylose) are converted into five-atom ring structures called furans consisting of four carbons and one oxygen. However, most polymers and plastics need furans to be converted into six-carbon ring structures via a process that requires a series of chemical reactions. In combination with first-principles computation, the CCEI team reveals a two-step process that is ideally catalyzed by bifunctional zeolites that promote both reactions. Glucose derived from biomass is initially reacted to produce dimethylfuran (DMF), which is then reduced and reacted to make p-xylene with a 75% yield. Using zeolite catalysts, furans (C4 ring) react with ethylene (C2) to make six-carbon intermediates. Subsequent dehydration produces the ubiquitous benzene (C6) ring.

This two-step technique shows remarkable potential for renewable products, particularly bottles used to package soda and water. The same technology can be applied to replace other aromatic chemicals currently produced from non-renewable resources.

Elucidating the Chemical Network in the Making of Renewable P-xylene

Production of renewable p-xylene from biomass sugars relies upon catalytic control of the chemistry to minimize byproducts. In the final reaction to convert dimethylfuran (DMF) to six-carbon aromatic p-xylene, the main pathway consists of one major chemical intermediate (a cycloadduct). This major pathway is part of a larger reaction network that produces a few side products, which require more detailed understanding to maximize the main p-xylene pathway.

Through separation of reaction mixtures and identification of side products and intermediates via NMR and chromatography, CCEI researchers have identified three competing pathways for p-xylene production. The most important side reaction pathway (#1 in figure below) produces water by dehydration, which can further react with DMF to produce ring-opened products. A second pathway (#2 in figure below) involves the addition of ethylene to p-xylene or other compounds, which ultimately produces larger alkylated aromatics. The third pathway (#3 in figure below) involves the addition of DMF to the intermediate, which produces larger dimer species.

The reaction of water, ethylene, or DMF with starting materials or intermediates can lead to undesirable side products and loss of economic value. Elucidation of the complete chemical reaction network has led to fundamental understanding of reaction engineering challenges for optimizing p-xylene production. These initial findings in the reaction network will lead to an improved reactor design capable of separating product water and maximizing p-xylene production.

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**Reaction network for the conversion of 2,5-dimethylfuran and ethylene to p-xylene using zeolite HY at $P_{ethylen}=680$ psig and $T=220-250 \degree C$.**
Techno-economic Optimization of Renewable P-xylene Production

The recent discovery in the synthesis of renewable p-xylene with high yield, as well as the identification of the reaction network and byproducts, made it possible to estimate p-xylene production cost to that derived from oil. As a result, a team of CCEI researchers developed a realizable process design capable of accounting for all unit operations including separation, reaction and purification of p-xylene to very high purity levels.

Integration of the research team’s expertise in reaction engineering, thermodynamics, separation and process design has provided the necessary data to develop a process flow sheet that allows for optimization. The required unit operations were determined by considering the experimentally measured conversion and yields and by taking into account the physical properties of the product, reactants, intermediates and byproducts (e.g. boiling points, miscibility, etc.). Currently, simulations carried out using the ASPEN Plus and ASPEN Economic Analyzer have revealed the economic potential of the renewable p-xylene process. Furthermore, sensitivity analysis has been used to identify the key economic parameters and technological developments that will have the greatest impact on process efficiency and economics.

First-Principles Calculations Provide Insights into Pathways and Catalyst Discovery

The production of renewable chemicals relies upon the catalytic conversion of sugars to desirable products including monomers of plastics. This entire process occurs through several intermediate chemicals including furans, which exist as low-energy chemicals on the path to making the final products, such as p-xylene. CCEI’s computational techniques have led the way to developing new catalytic technologies in order to selectively make renewable chemicals and plastics.

The key challenge for producing renewable chemicals continues to be the development of catalytic systems that reduce the energy barriers between starting materials (such as sugars) and final products and direct the reaction in the most selective direction. CCEI researchers recently predicted two key barriers in the production of p-xylene from dimethylfuran, a chemical produced from glucose. These two barriers are separated by a chemical intermediate consisting of two oxygenated rings. A major breakthrough was the insight that each step is catalyzed effectively by a different type of site. Specifically, Brønsted acid catalysts can dramatically reduce the second barrier (dehydration of cycloadduct), which produces p-xylene.

A series of screening calculations has examined a set of Lewis acid catalysts for the first step (cycloaddition or Diels Alders reaction) and led to the invention of a bifunctional zeolite catalyst that has two catalytic sites, one for each step. Integration of both sites and tuning of the material to achieve comparable rates for both steps will lead to optimal catalytic materials for renewable chemical production from biomass.


Electron density in the interaction of reactants with the Lewis active site.

Energy diagram of the catalytic cycle.
Revealing Pyrolysis Chemistry for Biofuels Production

The next generation of biofuels will be produced by high-temperature (>1000 °F) pyrolysis or gasification of lignocellulosic biomass. At these temperatures, large biopolymers (such as cellulose) thermally fracture to smaller fragments, which can evaporate and be collected as bio-oil. Subsequent upgrading of bio-oil then produces gasoline, diesel and jet fuel. Thus, the future of biofuels depends on the production of high-quality, low-cost bio-oil.

CCEI researchers have developed a new technique called thin-film pyrolysis (TFP), which reveals for the first time the pathways of cellulose pyrolysis to bio-oil. This technique rapidly heats micro-scale (3-5 µm) films of cellulose to a high temperature, thereby allowing direct measurement of the intrinsic chemistry of pyrolysis. This approach has led to the discovery of a strong chain-length effect in cellulose, whereby the length of the cellulose chain dramatically alters the pyrolysis chemistry and product bio-oil composition.

Examination of pyrolysis chemistry for multiple carbohydrates has led to the first insight into the mechanisms of cellulose pyrolysis. Using the TFP technique, a small molecule surrogate that yields identical chemistry to the much larger cellulose polymer has been identified: α-cyclodextrin. This discovery opens the door for the use of first-principles molecular dynamics simulation, which in the past year has revealed mechanisms to major products (such as furans) that form directly from cellulose via a ring-contraction mechanism.

These insights have led to the first reaction map of the major pathways of cellulose pyrolysis all the way to the key products that comprise bio-oil. In addition to the formation of the primary products, the TFP technique has also led to an understanding of secondary reactions of major products (such as levoglucosan) that occur before evaporation. These pathways are the first step in moving toward detailed kinetic models of biomass pyrolysis that will lead to targeted production of higher quality bio-oils and biofuels.


In the Pyrolysis thrust, we develop novel methods to obtain intrinsic kinetics of the breakdown of biomass upon fast heating.

Production of Renewable P-xylene via Catalytic Fast Pyrolysis

A team of CCEI researchers developed a catalytic process that produces p-xylene from biomass via catalytic fast pyrolysis with >90% selectivity along all xylenes. P-xylene, one of the most valuable C8 chemicals, is primarily used as a starting material for the production of polyethylene terephthalate (PET) plastic bottles and polyester clothing and is currently being produced from petroleum. Using lignocellulosic biomass as the starting material to produce p-xylene with a high selectivity provides an alternative way to renewable chemicals and polymers while reducing our dependence on fossil fuels.

High selectivity to p-xylene was achieved by designing new catalysts in the catalytic fast pyrolysis process. During this process, particles of biomass thermally decompose to form pyrolysis vapors that enter zeolite catalysts, which are also inside the reactor. The pyrolysis vapors are converted into benzene, toluene, and xylenes. To maximize the production of p-xylene, the team used a surface-modified ZSM-5 catalyst that has a smaller pore opening compared to conventional ZSM-5. The narrowed pore opening allows only the smaller p-xylene to diffuse out of the catalyst and prohibits diffusion of the slightly larger isomers, m- and o-xylene. Using this advanced catalyst, the p-xylene selectivity was dramatically improved among xylenes from 32% to 96%. This study opens the door to producing renewable p-xylene from lignocellulosic biomass via pyrolysis.

Identification of Glycolaldehyde as Probe Molecule for Biomass-derived Oxygenates

Controlling the activity and selectivity during biomass conversion of derivatives to syngas (H₂ and CO) is critical for the utilization of biomass feedstocks as renewable sources for chemicals and fuels. One key chemistry in the conversion is the selective bond scission of the C-OH and C=O functionalities, which are present in many biomass derivatives. Due to the high molecular weight and low vapor pressure, it is relatively difficult to perform fundamental surface science studies of C₆ sugars, such as glucose and fructose, using UHV techniques. Glycolaldehyde (HOCH₂CH=O) is the smallest molecule that contains both the C-OH and C=O functional groups, as well as the same C/O ratio as C₆ sugars, and thus is selected as a probe molecule in the current study to determine how the presence of the C=O bond affects the reaction mechanism.

Using a combination of density functional theory calculations and experimental measurements, CCEI researchers found that the reaction pathway of glycolaldehyde to produce syngas can be enhanced by supporting monolayer Ni on a Pt substrate, which shows higher activity than either of the parent metals. Based on the comparison of the activity and reaction intermediates of ethylene glycol and glycolaldehyde, the presence of the C=O functionality enhances the activity on the Pt(111) surface. On the other hand, for surfaces with high activity toward the O-H bond scission, such as NiPtPt(111), the presence of the C=O bond does not significantly affect the activity or reaction pathway of C₂ oxygenates. These results demonstrate the feasibility in using glycolaldehyde as a useful model compound for mechanistic studies of larger sugar molecules.


Comparison of the activity from temperature programmed desorption (TPD) measurements of ethylene glycol and glycolaldehyde on Pt(111) and NiPtPt(111) surfaces.
Catalysts with Lower Cost and Higher Stability: Replacing Ni/Pt With Ni/WC

The reaction pathway of small oxygenates to produce syngas can be enhanced by supporting monolayer Ni on a Pt substrate; however, the favorable NiPtPt(111) bimetallic structure for reforming is not stable at high temperatures due to the diffusion of surface Ni atoms into the Pt bulk. In addition, Pt is expensive and scarce. CCEI researchers have explored the possibility of using Ni-modified tungsten monocarbide (WC) as a less expensive and more thermally stable reforming catalyst than Ni/Pt.

Experimental and theoretical results suggest that on a monolayer NiWC surface, glycolaldehyde undergoes C-C bond cleavage to produce syngas with similar reforming activity as NiPtPt(111) surface. This indicates monolayer NiWC may be preferable to NiPtPt(111) surface as active and selective catalyst for biomass reforming with higher stability and lower cost. In addition, on the clean WC surface, glycolaldehyde reacts via the deoxygenation pathway to produce ethylene, resulting from the selective C-O bond scission with the C-C bond remaining intact. The results found on WC and monolayer NiWC surfaces are also extended to other C2 oxygenates with different functional groups, including ethanol, ethylene glycol, acetaldehyde and acetic acid.


Theory and Surface Science Experiments Reveal the Mechanisms of Biomass Reforming on Noble Metal Catalysts

Understanding the catalytic decomposition reaction pathways of biomass-derived molecules can enable the design of more active and selective catalysts that facilitate the transformation of lignocellulosic biomass to fuels and chemicals. Toward this goal, CCEI researchers used a combination of quantum calculations and surface science experiments of isotopically labeled ethylene glycols to determine the decomposition pathways on Pt(111). Decomposition proceeds through initial O-H cleavage, followed by C-H cleavage to form adsorbed glycolaldehyde. Additionally, several low activation barriers to C-C bond-breaking exist in highly dehydrogenated surface intermediates. This implies that unlike hydrocarbons, the kinetically relevant steps in the decomposition of overfunctionalized oxygenates may not be C-C cleavage. Finally, surface modification of Pt with Ni increases the rate of decomposition and alters the reaction pathway. This indicates that catalysts for biomass transformation to fuels and chemicals can be selectively tuned for desired bond-breaking sequences.

In the hydrodeoxygenation thrust we selectively remove oxygen and add hydrogen to increase energy content and reduce over-functionality.


A Direct Carbon Fuel Cell with a Molten Antimony Anode

There is a great need for better technologies to efficiently produce useful forms of energy from cheap and abundant solid carbonaceous fuel resources, like coal and renewable biomass. To achieve this goal, CCEI researchers developed a concept for direct carbon fuels cells (DCFCs) that electrochemically converts solid carbonaceous fuels to electricity. Their technology is based on electrolytes that are ceramic oxygen-ion conductors, such as cubic zirconia. It uses molten antimony (Sb) as the fuel electrode. Inside the fuel cell, Sb is oxidized at the electrolyte interface to Sb$_2$O$_3$, producing electrical power. The Sb$_2$O$_3$, which is also molten at the fuel cell operating temperatures, is in turn reduced by carbon-based fuels to recover the Sb, allowing the cycle to start again. Figure 1a shows a schematic of the experimental configuration used in these studies. Figure 1b shows a diagram of the scientific principles.

Although initial studies were limited by the formation of an “ash” layer between the fuel and the Sb$_2$O$_3$, intermittent stirring of the molten Sb-Sb$_2$O$_3$ mixture has allowed stable performance for more than 200 hours on fuels ranging from pyrolysis oil to rice starch to charcoal. Power densities greater than 200 mW/cm$^2$ at 0.5 V and 700° C have been achieved on every fuel that has been tested. Figure 2 shows some elements of a preliminary stack design, which has been formulated in order to scale up this technology.

Based on this technology, DCFCs will be highly fuel flexible and tolerant to typical fuel impurities from both coal and biomass. They also offer the opportunity for considerable improvements in the efficiency of electricity generation while simultaneously allowing for easy CO$_2$ capture.


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![Fig. 1a](image1a.png) Longitudinal section of the fuel cell system.

![Fig. 1b](image1b.png) Solid oxide fuel cells with molten Sb anode and solid carbonaceous fuel.

![Fig. 2](image2.png) Schematic for a large-scale DCFC system based on molten Sb anodes.
Molten Antimony Fuel Cell Offers Potential for Low-footprint Management of Excess Electrical Power

One problem afflicting alternative electricity sources, particularly wind and solar power, is the inability to control output to match fluctuations in demand over the course of a day. CCEI researchers have proposed a solid oxide fuel cell (SOFC) with a molten Sb anode as a next-generation electrical storage device. Excess current reduces Sb$_2$O$_3$ to Sb, which can be physically stored for later use with a smaller footprint than similar technologies, such as hydrogen. Oxidation of Sb to Sb$_2$O$_3$ releases the stored energy back to the grid. Unlike most metal oxides, Sb$_2$O$_3$ is a liquid at an operating temperature of 973 K, allowing comparatively low-temperature fuel cell operation without deposition of a solid insulating layer on the electrolyte, which would decrease the performance of the cell. The anode consists of a molten mixture of Sb and Sb$_2$O$_3$, which was stirred to represent the flow conditions of a real installation. The electrolyte consists of a 100 μm thick scandia-stabilized zirconia (ScSZ) plate, and the cathode is a 50 μm thick composite of porous ScSZ filled with La$_{0.8}$Sr$_{0.2}$FeO$_3$. Low impedances for Sb/Sb$_2$O$_3$ compositions were demonstrated on at least 20-30% Sb.

INDUSTRIAL MEMBERSHIP PROGRAM

Our faculty are committed to collaborations with industry that align with the center’s mission of developing viable catalytic technologies for applications in renewable energy.

Membership Program Goals

- Develop innovative technologies for biomass conversion
- Promote technology transfer and deliverables
- Produce excellent engineers and scientists working on catalytic technology
- Provide a globally unmatched competitive advantage in catalytic renewable energy engineering

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