

**Catalysis Center for Energy Innovation (CCEI)**  
**EFRC Director: Dionisios G. Vlachos**  
**Lead Institution: University of Delaware**  
**Class: 2009 – 2022**

***Mission Statement:*** *To advance the catalysis science of complex systems with a focus on thermocatalytic transformation of lignocellulosic (non-food-based) biomass into chemicals and transportation fuels.*

CCEI has established itself as a transformative catalysis center with a mission to advance fundamental catalysis science in complex systems. We envision innovations toward feedstock diversification for co-processing of biomass with shale gas derivatives. To that end, we have established three new downstream research thrusts for the synthesis of: (1) *dienes* via dehydra-decyclization of oxacyclopentanes (saturated furans); (2) *surfactants* via acylation and aldol condensation of furan with fatty or shorter acids; and (3) *lubricants* via hydroxyalkylation/alkylation chemistry of furans with aldehydes and subsequent decyclization-hydrodeoxygenation of the intermediates. Major chemistry threads that emerge are: (1) C-C coupling chemistry to enable coupling of lignocellulose building blocks—among themselves or with shale gas derivatives; and (2) tandem furan ring opening and oxygen removal—as well as possible hydrogenation—to enable the design and synthesis of targeted functional molecules.

For the synthesis of dienes (e.g., butadiene)—important high-volume feedstock for polymers—we envision dehydra-decyclization of sugar-derived, oxacyclopentanes. To that end, we shall extend the use of *P-zeosils*, a new class of catalysts discovered by CCEI which consist of phosphoric acid supported on inert, all-silica zeolites. P-zeosils are Brønsted acids distinct from typical aluminosilicate zeolites, with P-speciation dynamically evolving on time scales comparable to those of the reactions they catalyze. Our goal is to improve catalytic activity and selectivity for dienes through fundamental understanding of the structure, dynamics, and catalytic properties of P-zeosils and through development of new, dynamically confined acids in zeosils and other microporous materials. Fundamentally, the description of weak acid catalysts requires new theoretical developments.

The synthesis of bio-renewable oleo-furan-sulfonate surfactants with unique properties will require development of a selective route for *direct*  $\alpha$ -site acylation of a sugar-derived furan with carboxylic acids (derived from shale gas, sugars, fatty acids or triglycerides) to produce a 2-furyl alkyl-ketone. Fundamental understanding of catalyst design to promote *direct* acylation by fatty acids or triglycerides can provide significant molecular efficiency over the *indirect* route that uses fatty acid anhydrides, the production of which is a multi-step, waste-generating process. Use of bulky acylating agents in porous solid acids introduces new challenges and scientific questions regarding their distribution in porous materials and interaction with the active site(s), reaction mechanisms, and active site catalyst design. Pore design for the control of the distribution, orientation and diffusion of bulky amphiphiles within porous materials adds one more layer of complexity to be addressed. In turn, understanding these phenomena requires the development of computational, spectroscopic, and scattering methods.

Our endeavors into the design and synthesis of bio-lubricants with tunable molecular architecture and properties from versatile carbon feedstocks (biomass, natural oils and shale gas) will require precise control over branching with precursors of suitable size as well as control over oxygen content and ring saturation. To that end, we shall synthesize atomically-controlled catalysts that perform C-C coupling, hydrogenolysis of targeted furfural derivatives to produce alkylfuran substrates, and decyclization-hydrodeoxygenation for producing poly- $\alpha$ -olefin lubricants. Our goal is to develop new hydrogenolysis catalysts that exhibit simultaneously high activity and stability and to understand weak acidity in liquid phase chemistry. The multifunctional nature of these catalysts will require new advances in spectroscopic methods and use of cutting-edge imaging techniques combined with multiscale computational methods.

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