Catalyst Design for Decarbonization Center (CD4DC)
EFRC Director: Laura Gagliardi
Lead Institution: University of Chicago
Class: 2022 – 2026

Mission Statement*: To discover and develop reticular metal-organic framework materials as catalysts for the decarbonization energy transition and to optimize the key catalytic reactions involved.*

The call to decarbonize the chemical and energy industries requires the reduction and eventual elimination of fossil carbon resources and the adoption of radically new approaches for producing chemicals and storing electric power harvested from the wind and sun. To respond to this call, the *central research mission of CD4DC* is to discover and develop reticular metal-organic framework materials (MOFs) as catalysts for the decarbonization energy transition and to optimize the key catalytic reactions involved. This is being accomplished by a symbiotic combination of synthesis, catalysis and kinetics, computational modeling and active learning, and characterization.

Using widely abundant hydrogen as a primary energy vector would reduce the need for carbon rejection and replace it with hydrogen addition, which requires comparatively lower operating temperatures that will reduce the overall carbon footprint. Future approaches must include processes that convert electric power to chemical energy, and the initial transformation of electric energy to chemical energy will involve electrolysis and generation of H_2. A large percentage of hydrogen will be intermittently stored in liquid organic hydrogen carriers (LOHCs) that can release H_2 at the time and place of the target application. The extraction reaction is endothermic, and its utility will depend critically on a combination of the efficiency of dehydrogenation and separation of the dehydrogenated carrier and hydrogen. These processes require highly precise, robust, and stable catalysts for the key generic transformations, namely *the addition and release of hydrogen to and from organic molecules* and the *manipulation of C-C bonds*. Catalysts with these desired properties that operate with high efficiency and at low temperatures are not currently available.

CD4DC targets the development of three types of catalysts: (1) MOFs with components that provide a high degree of polarizability and softness for superior hydrogen transfer catalysis, (2) MOFs that enable the use of an external electric potential to facilitate catalytic transformations, and (3) MOFs that provide bio-inspired environments for highly selective chemical transformations. Project objectives are being achieved through interactive and iterative efforts of synergistic computational and experimental techniques that leverage our unique, multi-disciplinary team. These themes systematize the design of catalysts that drive the two proposed reaction classes: H_2 addition and release from LOHCs, and the efficient combination of C–C bond formation with H_2 management.

MOFs are the central component of the design strategy because of their unmatched diversity within the boundaries of a well-defined class of materials, the uniformity of their characterizable active centers, the tailorable sterically and chemically well-defined environments near the active site, and the ancillary components that modulate transport and selectivity. These properties facilitate explanatory and exploratory molecular-level computational modeling of catalyst properties for molecular-level control of catalytic transformations. The theoretical and computational component of our center, aided by active learning, is working to identify key structure–function relationships for catalytic activity and aid hypothesis-driven understanding and design of catalysts and catalytic pathways. Such design—particularly of the catalytic active center, environment, and reaction mechanism—creates a synergistic cycle between theory, experiment, and active learning that drives success.

Our choice of target reactions addresses the emerging challenges in catalysis science for decarbonization. As society seeks to transition from C-centered energy and industrial schemes, processes that enable efficient addition and removal of H_2 will become increasingly important. Therefore, we investigate the fundamental mechanisms of (bio)alcohol dehydrogenation to aldehydes and aldehyde oligomers and hydrogen addition and removal from aromatic LOHCs. The move away from a petroleum-based economy requires selective, low-energy processes for generating higher-order chemical feedstocks from biogenic sources or recycled waste. We also examine reaction mechanisms for C–C bond formation, such as the coupling of CO, carboxylates, or alcohols, which also require close management of H_2. A particular challenge is to realize C–C coupling reactions (i.e., ones involving H_2 addition) with high selectivity. Highly active and selective versions of these reactions could be truly transformative for decarbonization of the chemical industry.

At the end of the four-year program, we will have laid the foundation for the decarbonization transition by understanding and validating the requirements for targeted chemical transformations using MOFs and will have advanced the tools for *de novo* design of catalysts via modular synthesis. Moreover, the active learning-driven integration of high-throughput experimentation and computation will generate significant new knowledge on MOF-based catalysis that will be available to the broader energy research community.

Catalyst Design for Decarbonization Center (CD4DC)	
University of Chicago	Laura Gagliardi (Director); John Anderson; Chibueze Amanchukwu; Andrew Ferguson; Ian Foster; Juan de Pablo; Anna Wuttig
Argonne National Laboratory	Massimiliano Delferro
Northwestern University	Omar Farha; Joseph Hupp (Deputy Director); Justin Notestein
Ohio State University	Rachel Getman
Pacific Northwest National Laboratory	Johannes Lercher
Stony Brook University	Karena Chapman
University of Illinois at Chicago	Ksenija Glusac
University of Minnesota	Matthew Neurock; Donald Truhlar

Contact: Mónica Lugo, Managing Director, lugom@uchicago.edu
312-320-3751, cd4dc.center.uchicago.edu