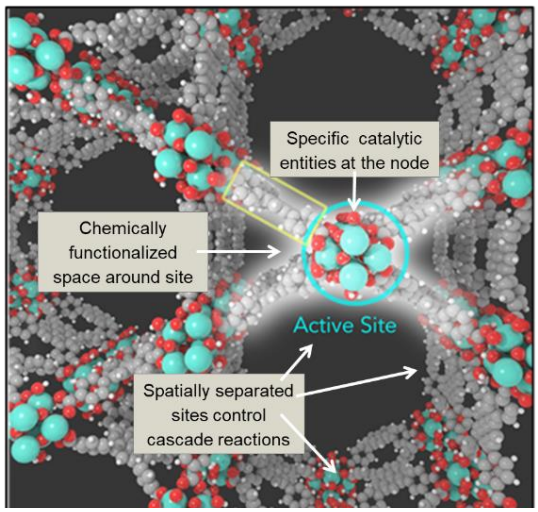
Inorganometallic Catalyst Design Center (ICDC)
EFRC Director: Laura Gagliardi
Lead Institution: University of Minnesota
Class: 2014 – 2022

Mission Statement*: To discover new classes of energy-science relevant catalytic materials, especially through the exploitation of computational modeling to identify underlying structure-function relationships that are critical to advancing further, predictive catalyst discovery.*

ICDC pursues hypothesis-driven experimental, computational, and theoretical research in heterogeneous catalysis. Our **experimental vision** is a) to devise and apply synthetic methods to yield stable, uniformly organized arrays of catalytic sites with single-atom or close-to-single-atom precision with respect to both composition and placement, and b) to use these catalysts to answer fundamental questions in catalysis science. Paramount to our approach is the synthetic accessibility of chemically and thermally stable metal-organic frameworks (MOFs), featuring controlled porosities, ultra-high surface areas, and well-defined catalytic sites, or anchoring sites for catalysts, along with tailored environments around such sites.

Our **vision for theory and computation** is to develop novel quantum chemical, molecular mechanical, and combined quantum mechanical and molecular mechanical approaches to explore the structures, stabilities, activities, and selectivities of realized and as-yet-unrealized catalytic materials, where the latter can be proposed as targets for synthesis by the experimental teams in the Center. Using transferrable advances in theory developed by ICDC, we augment detailed characterizations of elementary reaction steps with microkinetic modeling to identify key descriptors that can be used to rapidly screen potential catalysts and tune catalyst behavior.

Central to our efforts is the use of frameworks based on hexa-zirconium(IV) nodes and oxy-anion terminated linkers. $Zr^{4+}O^{2-}$ bonds are among the strongest known ionic bonds. Oxyanion-terminated linker-node bonds are not so strong but are among the strongest known for MOFs. Known members of this MOF family exhibit especially desirable properties for catalysis science and technology.



Schematic representation of a catalytically active site in hexa-zirconium(IV)-node based MOF and the elements critical to constituting this site.

To address the most challenging and compelling questions at the forefront of catalysis science, **the mission of ICDC** will be to develop and promulgate:

- Concerted experimental/computational approaches to (i) make and interpret structural and spectroscopic observations, (ii) measure, interpret, and predict catalytic properties, and (iii) guide new MOF syntheses.
- Experimental methods for rapid, robust synthesis of previously unexplored, well-defined, catalytic structures in MOFs—including those with compositions unattainable on the macroscopic scale.
- Theoretical models able to guide experiment for discovery and rationalization of structure–function relationships in catalysts incorporating inorganometallic structures ranging from single metal atoms to clusters smaller than bulk-like nanoparticles.

Having demonstrated the reproducible synthesis of many catalytically active sites embedded in the three-dimensional environments of MOFs, we are now positioned to design novel catalysts that master the

complexity of catalyzed transformations, guided by computational insights into elementary steps and enabled by advanced synthesis. To achieve this goal we will exploit: (i) confinement of the locations of active sites; (ii) nuclearity of active centers; (iii) tailored chemical environments surrounding centers; (iv) controlled under-coordination (defects) to create new access to key MOF elements; and (v) steric separation of sites with different functions to enable multiple reaction steps.

Focusing on the catalytic chemistry of shale-gas substrates, we will address the selective conversion of light alkanes, including methane, as well as the synthesis of fuel and chemical components from light alkane conversion. The target catalytic transformations will be those that can best answer important, fundamental questions in energy-relevant catalysis science and in energy-relevant materials synthesis. At the highest level, these catalytic transformations will address the fundamental challenges of controllably making and breaking C-H, C-C, C-O, C-N, and C-S bonds, as well as bonds between these various atoms and metal or metal-oxide catalysts.

We envision five groups of deliverables from our program:

- Advanced computational methods and strategies to aid interpretation of mechanistic information, as well as structural and spectroscopic observations to guide synthesis.
- Advanced methods to synthesize electronically and structurally defined catalytically active sites in heterogeneous catalysts with unprecedented precision.
- Methods for precisely siting active sites in mesoscale, uniform, and hierarchically structured environments that both isolate sites and provide ready access to them.
- Advanced characterization methods of (operando) catalyst function and structure.
- Stringent approaches for the discovery and theoretical rationalization of structure/function relationships in atomically precise catalysts in cluster size ranges of less than 100 atoms.

Research Approach. It has been a central tenet of ICDC that theory would not only help to post facto interpret spectroscopic and chemical observations, but that it would also guide experimental priorities, as the nearly infinite number of possibilities imposes need for a hypothesis-based, step-by-step approach to catalyst development. Our ongoing hypotheses are informed by observations from ICDC and current, preliminary experiments. Theory and physicochemical evaluations of catalysts and their reactions have synergistically provided the tools to understand their chemical and structural properties, and we see substantial promise for making rational future predictions.

Inorganometallic Catalyst Design Center (ICDC)	
University of Minnesota	Laura Gagliardi (Director), Aditya Bhan, Chris Cramer, Connie Lu, R. Lee Penn, Donald Truhlar
Northwestern University	Joseph Hupp (Deputy Director), Omar Farha, Justin Notestein
Clemson University	Rachel Getman
MIT	Heather Kulik
Stony Brook University	Karena Chapman
University of California, Davis	Bruce Gates
Argonne National Laboratory	Massimiliano Delferro, Alex Martinson
Pacific Northwest National Laboratory	Johannes Lercher, Oliver Gutierrez Tinoco
NuMat Technologies	William Morris

Contact: Melanie Burns, Managing Director, mburns@umn.edu
(612) 301-1491, http://www1.chem.umn.edu/icdc