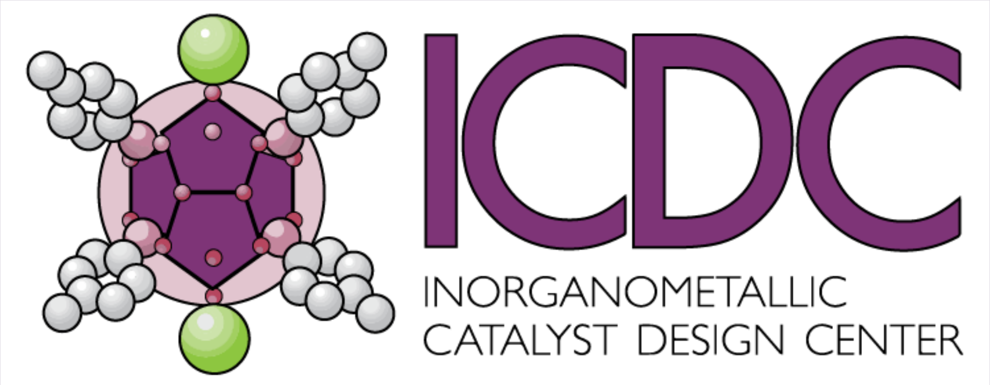

Inorganometallic Catalyst Design Center

2018 ALL-HANDS MEETING

October 8 – 9, 2018

University of Minnesota
Graduate Hotel
Minneapolis, Minnesota

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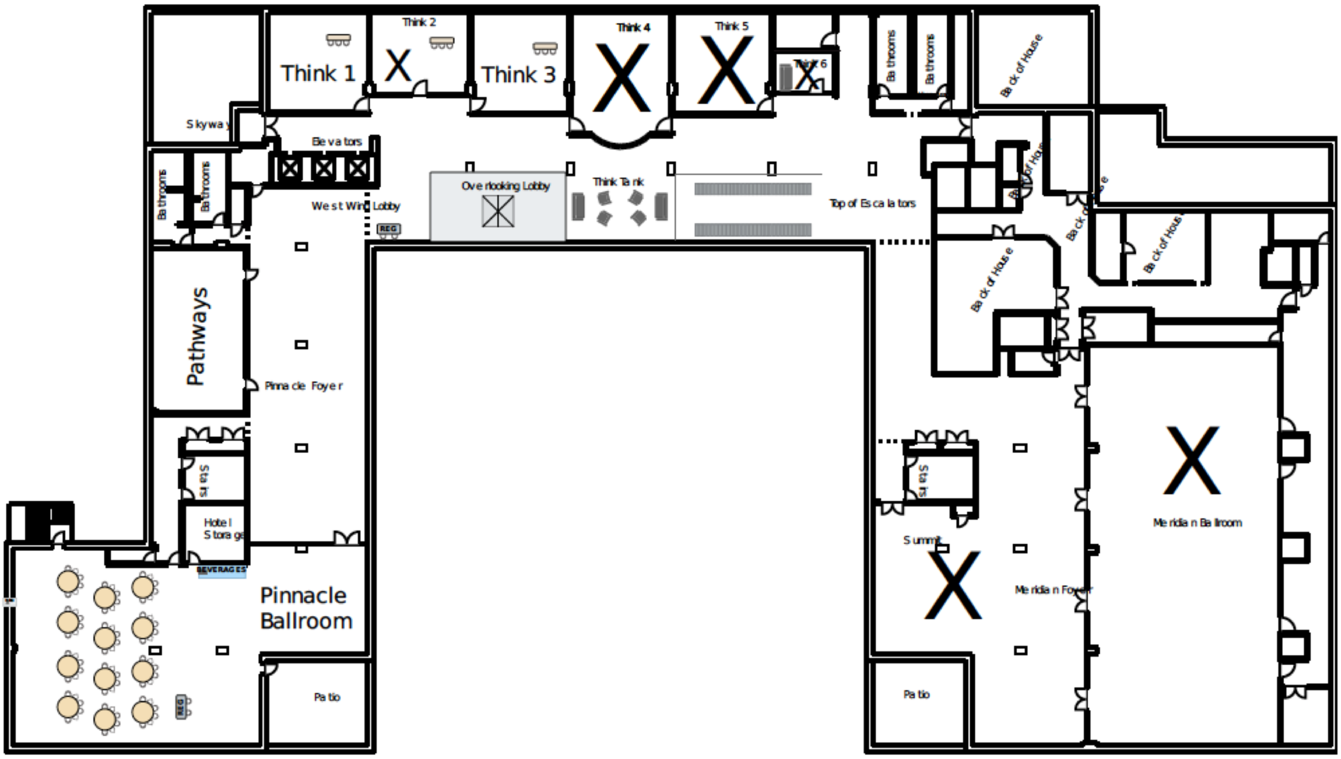

LOCATION
Graduate Hotel, University of Minnesota
615 Washington Ave SE, Minneapolis, MN 55414
www.graduatehotels.com/minneapolis

Monday, October 8, 2018

All events held in Pinnacle Ballroom, unless otherwise noted

7:15 am	**Registration opens, Continental Breakfast available**
8:00 am	**Advisory Board Members meet with Director and Deputy Director (Pathways Room)**
8:30 am	**Meeting Begins**
	Welcome by Mostafa Kaveh, Dean of the College of Science and Engineering
	Laura Gagliardi: "Grand Challenges and Mission of ICDC-2"
9:00 am	**Parallel Sessions 1, 2**
	Topic 1 Oxidative Dehydrogenation, Moderator: Cramer (Think 1)
	Topic 2 Metathesis/Oligomerization, Moderators: Gagliardi/Lercher (Think 3)
9:50 am	**Break**
10:10 am	**Parallel Sessions 3, 4**
	Topic 3 Reductive Catalysis with Metal-Chalcogen Clusters, Moderator: Hupp (Think 1)
	Topic 4 Borylation with Different Transition Metal Catalysts, Moderator: Farha (Think 3)
11:00 am	**Session 5**
	Topic 5 Selective Oxygenation, Moderators: Hupp/Lercher
11:50 am	**Group Picture**
12:00 pm	**Working lunch and preparation of reports**
2:00 pm	**Topic Session Reports: All PIs who want to work on a topic have to report**
	Topic 1 (2.00-2.30); Topic 2 (2.30-3.00); Topic 3 (3.00-3.30)
3:30 pm	**Break**
4:00 pm	**Topic Session Reports: All PIs who want to work on a topic have to report**
	Topic 4 (4.00-4.30); Topic 5 (4.30-5.00)
5:00 pm	**Collaboration time**
5:00 pm	**Advisory Board Members meet (Pathways Room)**
6:00 pm	**Dinner**
7:00 pm	**Public Lecture "Arranged Scientific Marriages"** **Marc A. Hillmyer, McKnight Presidential Endowed Chair** **Director of the Center for Sustainable Polymers**
7:30 pm	**Poster Session (Pinnacle Foyer)** Students and Postdocs present posters on their current and future ICDC research
9:30 pm	**End of Poster Session**

Tuesday, October 9, 2018

All events held in Pinnacle Ballroom, unless otherwise noted

7:30 am	**Continental Breakfast**
9:00 am	**Advisory Board Members meet with Director and Deputy Director (Pathways Room)**
9:30 am	**Joe Hupp: Future challenges for mid-term review in 18 months**
9:40 am	**Junior Investigator Awards for Best Posters**
10:00 am	**Closing Remarks and more time for collaborations**
12:00 pm	**Box lunches available (Pinnacle Foyer)**

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Presenters of odd-numbered posters are kindly requested to stay near their posters during the first hour and presenters of even-numbered abstracts are kindly requested to stay near their posters during the second hour of the poster session.

No.	Title	First / Joint Co-Author(s)
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12	Computational Study of the Stability and Reactivity of Copper-Exchanged NU-1000 Metal–Organic Framework for Methane Oxidation to Methanol	Jingyun Ye (UMN)
13	Organic Linker Effect on the Nucleation and Diffusion of Cu Clusters in a Metal-Organic Framework	Jingyun Ye (UMN)
14	Catalytic Chemo-Selective Functionalization of Methane in a Microporous Metal-Organic Framework	Xuan Zhang (Northwestern)
15	High pressure catalytic methane oxidation to methanol over copper exchanged stable Metal–Organic Frameworks	Jian Zheng (PNNL)
16	Expanding Methods from Computationally-Driven Design of Metal/Alloy Catalysts to Designing Single Atom Catalysts	Jiazhou Zhu (Clemson)

Multiconfigurational calculations on bimetallic decorated NU-1000 for C–H activation: comparison with DFT

<u>Carlo Alberto Gaggioli</u>[a] , Joachim Sauer[b], and Laura Gagliardi[a]

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In the last years, Zr-based Metal Organic Frameworks (MOFs) have revealed their potential for heterogeneous catalytic applications, due to their high stability.[1] Recently, the installation of Co(II) ions to the Zr_6 nodes of the MOF NU-1000 has been successfully achieved. This Cobalt decorated NU-1000, upon activation in a flow of O_2 at 230 °C, has been shown to catalyze the oxidative dehydrogenation (ODH) of propane to propene under mild conditions.[2] A DFT study for this Co-NU 1000 catalyzed propane ODH process using a cluster model containing one Co atom has been carried out, elucidating the reaction mechanism.[2] However, polynuclear sites may also be competent for this reaction; in this regard, the mechanism of the ODH with a two Co atoms model has been analyzed, demonstrating the C-H activation of propane to be the rate determining step.[3]

Knowing the mechanism, a further DFT study has been done in order to lower the barrier of the C-H activation step, improving therefore the catalysis.[3] This work has been focused on computing the activation energies by doping one of the two cobalt atoms with another transition metal (namely, Mo, Ti, Mn, Ag, Fe, Ni, Cu, Zn). Encouraging results for Cu and Zn have been found, which lower the activation barrier. After this work, the question of whether DFT could be accurate enough to describe the challenging electronic structure of these systems arose. For example, it has been recently shown that for some bimetallic systems, different functionals localize the unpaired electrons on different metals, and yield different reaction energies.[4] Furthemore, the quantum chemical study of metals that present electronic states close in energy (which very often happens when dealing with transition metals) requires a detailed analysis in terms of multiconfigurational calculations.

In this contribution we focused on the use of multiconfigurational quantum methodologies for first analyzing the electronic structure of the bimetallic cluster model, with one fixed cobalt and the second metal being Zn, Cu, Ni, Co, Fe, Mn and Ti. We noticed substantial differences with respect to DFT in the oxidation states for some metals and oxygen atoms spin densities. This can in turn switch the C-H abstraction mechanism from a Hydrogen Atom to a Proton Coupled Electron Transfer. We then analyzed the reaction energies of the C-H bond activation, and found sizable differences with respect to DFT, pointing out the challenge of accurately modeling these catalytic systems.

References

[1] S. Odoh et al., *Chem. Rev.*, **2015**, *115*, 6051- 6111; Y. Huang et al., *Chem. Soc. Rev.,* **2017**, *46*, 126-157; D. Yang et al., *J. Am. Chem. Soc.*, **2015**, *137*, 7391-7396; D. Yang et al., *ACS catalysis*, **2016**, *6*, 235-247
[2] Z. Li et al., *ACS Cent. Sci.*, **2017**, *3*, 31-38
[3] M. Simons et al., *ACS Catal.*, **2018**, *8*, 2864-2869
[4] G. Rugg et al., *J. Phys. Chem. A*, **2018**, *122*, 7042-7050

Ligand Modification to Tune the Activity of Metal−Organic Framework-Supported Ni Catalysts for Ethylene Hydrogenation

Jian Liu[a], Zhanyong Li[a], Xuan Zhang[a], Ken-ichi Otake[a], Lin Zhang[a], Aaron W. Peters[a], Matthias J. Young[b], Omar K. Farha*,[a,c,d], and Joseph T. Hupp*,[a]

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Our previous work has shown that modifying the ligand environment near the Ni(II) active centers supported on the Zr-based metal–organic framework (MOF), NU-1000, yields desirable catalytic performance for the gas-phase ethylene dimerization process. To systematically investigate the impact of the electronic environment surrounding the Ni(II) active centers on its catalytic properties, a series of benzoate ligands with varying para-substituents (R-BA, R = $-NH_2$, $-OCH_3$, $-CH_3$, –H, –F and $-NO_2$) but similar steric hindrance were introduced to NU-1000 *via* a solvent-assisted ligand incorporation (SALI) process before the Ni(II) ions were deposited *via* atomic layer deposition in a MOF (AIM). Ni binding energy shifts observed from X-ray photoelectron spectra indicate the ligands have an electronic influence on the metal center, which is similar to strategies used in homogeneous catalyst design to tune the electronic density of organometallic metal center by adjusting the surrounding ligands. The newly formed materials, Ni-AIM-R-BA-NU-1000, exhibited a linear correlation between the Hammett sigma constants (σ) of the corresponding para-substituents and their catalytic activities for the ethylene hydrogenation reaction. Benefiting from the structural well-defined nature of the MOF support, this approach provides a versatile way of predictably modifying the activity of supported catalysts, where fine-tuning of the electronic properties of the MOF supports can be readily achieved.

Microkinetic modeling of single-site catalysts for hydrogenation of ethene to ethane on NU-1000

Hafeera Shabbir[a], **Steven Pellizzeri**[b], **Magali Ferrandon**[c], **In Soo Kim**[d, e], **Massimiliano Delferro**[f], **Alex Martinson**[d *], **and Rachel Getman**[a]

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[b] Department of Chemistry, Clemson University
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[d] Materials Science Division, Argonne National Lab
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The recent shale oil and gas boom has given rise to a pressing need to develop new catalysts for converting small-chain hydrocarbons (C_1-C_4) to long-chain hydrocarbons (C_8-C_{12}) for their effective utilization in petrochemical and fuel applications. We are interested in single site catalysts supported on the metal-organic framework (MOF) NU-1000 for this purpose, since they have been shown to catalyze hydrogenation/dehydrogenation and oligomerization reactions of small hydrocarbons like ethene. Our research focuses on elucidating the reaction mechanism of ethene hydrogenation for three metals – Cu, Zn, and Ni – supported on the $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4(OH)_4(OH_2)_4$ nodes of NU-1000. Our experimental results show Ni to be the most active at all temperatures and Zn to be the least with intermediate reactivity for Cu. We propose a multistep reaction mechanism with multiple branch points leading toward both ethene hydrogenation and dimerization. We perform Density Functional Theory (DFT) calculations using the Gaussian-09 software to calculate the free energies of reaction intermediates and transition states along the reaction pathways. Then, we use a C++ program MKMCXX to calculate the rates and perform microkinetic modeling, which we compare with experimental observations. We make general conclusions about the catalytic mechanism, including that the pathway that is pursued depends on the metal cation that is deposited on NU-1000.

Light Alkane Hydroxylation over MIL-100(Fe)

Matthew Simons[a,b], Jenny Vitillo[b], Christopher Cramer[b], Connie Lu[b], Laura Gagliardi[b], and Aditya Bhan[a]

[a] Department of Chemical Engineering and Materials Science, University of Minnesota
[b] Department of Chemistry, University of Minnesota

Direct oxidative routes for the valorization of light alkanes, the primary components of natural gas, to olefin and alkanol platform chemicals involve the activation of the carbon-hydrogen bond as the rate limiting step. Enzymes oxidatively activate light alkanes and selectively upgrade them at room temperature utilizing iron(IV)-oxo active centers. Formulating active centers in zeolites and Metal Organic Frameworks (MOFs) that mimic the reactivity of biological systems is an active topic of research with the potential to open new catalytic pathways for the enhancement of underutilized chemical feedstocks.

MIL-100(Fe) is an iron based MOF that forms Fe(II) species upon thermal pretreatment. We show our progress thus far utilizing N_2O as an oxidant with these sites to form transient Fe(IV)=O species capable of converting light alkanes. We detail our synthesis methods, characterization (IR, and Raman Spectroscopy, N_2 Isotherms, XRD), results for the reactivity of the catalyst, and an enumeration of the active site using chemical titrants.

Single Fe(II) sites in MIL-type metal organic frameworks for the oxidation of light alkanes to alcohols

Jenny G. Vitillo[a], **Aditya Bhan**[b], **Christopher J. Cramer**[a],
Connie C. Lu[a], **and Laura Gagliardi**[a]

[a] Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota
[b] Department of Chemical Engineering and Materials Science, University of Minnesota

Site-isolated Fe(II) centers have been recently linked to the activity of synthetic catalysts for methane oxidation to alcohols.[1-2] Isolation of the iron species requires metal loading lower than few mass%, thus limiting the number of active sites in the materials studied so far. We report the results of a computational study assessing single non-heme Fe(II) ions present as structural metals in several metal organic frameworks (e.g. MIL-100) as promising catalysts for C-H bond activation. The barriers associated with the homolytic C-H bond scission are as low as 40 kJ mol^{-1} for ethane and 60 kJ mol^{-1} for methane that is lower than those reported previously for other iron-based MOFs.[3] Through consideration of the full reaction profile leading to the corresponding alcohols ethanol and methanol, we have identified key changes in the chemical composition of the node that would modulate catalytic activity. The thermal and chemical stability of these MOFs together with the scalability of their syntheses make them attractive catalysts for the selective low temperature conversion of light alkanes to higher-value oxygenates.

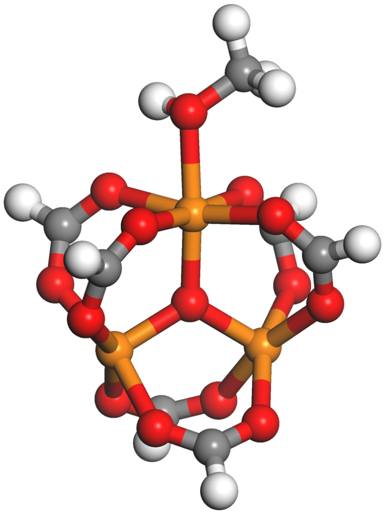

Figure: Single non-heme Fe(II) sites in MIL-100 coordinating a methanol molecule. Color code: orange (Fe), red (O), grey (C) and white (H).

References

[1] Bols, M. L., et al., *J. Am. Chem. Soc.* **2018**, 10.1021/jacs.8b05877.
[2] Snyder, B. E. R. et al., *Nature* **2016**, *536*, 317.
[3] Verma, P et al., *J. Am. Chem. Soc.* **2015**, *137*, 5770.

Synthesis of NU-1000:
Effect of Concentration of NaOH, Linker, Modulator, and Water

Thomas E. Webber, Rebecca L. Combs, Sophie Socha, Sai Puneet Desai,
Connie C. Lu, and R. Lee Penn*

Department of Chemistry, University of Minnesota

NU-1000 is a robust, mesoporous metal organic framework (MOF) with hexazirconium nodes ($[Zr_6O_{16}H_{16}]^{8+}$) that are responsible for relatively low toxicity and high chemical and thermal stability. The MOF can be synthesized by combining a solution of a Zr precursor and a biphenyl-4-carboxylic acid modulator with a solution of linker (1,3,6,8-tetrakis(p-benzoic acid)pyrene, referred to as H_4TBAPy) and aging at elevated temperature. Previously, we showed that replacing the traditional modulator (benzoic acid) with a longer modulator (like biphenyl-4-carboxylic acid) we can obtain phase-pure NU-1000 particles. Current efforts are being applied to understanding the effects of the solvent, the Zr precursor, and the concentrations of the linker, modulator, and any additives. The identity of the solvent can have a marked effect on the resulting aspect ratio of the NU-1000 particles in the microscale range. Work is underway to determine the size range at which this effect holds true in an effort to controllably synthesize NU-1000 particles with different sizes and aspect ratios. Modifying the concentrations of the linker, modulator, and any additives such as water or NaOH can alter the equilibrium between the modulator and linker molecules attached to the nodes. Data will be presented on how this equilibrium can be shifted resulting in either faster reactions and smaller particles or slower reactions and larger particles. Ongoing work includes catalytic testing on a variety of particle sizes to probe the effect of external surface area vs inner pore volume.

Combined Quantum Mechanical and Molecular Mechanical Method for Metal-Organic Frameworks

Xin-Ping Wu, Bo Yang, Indrani Choudhuri, Laura Gagliardi, and Donald G. Truhlar

Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota

Metal-organic frameworks (MOFs) have high internal surface area and tailorable nodes and organic ligands, and for these reasons they are very promising for heterogeneous catalysis, hydrogen storage, and gas separation. Fully quantum chemical investigations of these systems are usually quite demanding in terms of computer time and computational resources; therefore, combined quantum mechanical and molecular mechanical (QM/MM) methods are desirable to investigate these systems. This will be especially important as we move into the era of more demanding simulations enabled by exascale computing; therefore, it is important to develop improved methods and software for QM/MM calculations.

The treatment of the QM–MM boundary strongly affects the accuracy of QM/MM calculations and is especially challenging for the treatment of Zr-based MOFs because of the high due to the presence of high atomic charges on the inorganic nodes. The difficulty of treating high electrostatic fields is exacerbated when the boundary between the QM fragment and the MM fragment must pass through a covalent bond, which is unavoidable in treating MOFs. For QM/MM calculations having covalent bonds cut by the QM–MM boundary, it has been proposed previously to use a scheme with system-specific tuned fluorine link atoms. Here, we propose a broadly parametrized scheme where the parameters of the tuned F link atoms depend only on the type of bond being cut. In the proposed new scheme, the F link atom is tuned for systems with a certain type of cut bond at the QM–MM boundary instead of for a specific target system, and the resulting link atoms are call bond-tuned link atoms. In principle, the bond-tuned link atoms can be as convenient as the popular H link atoms, and they are especially well adapted for high-throughput and accurate QM/MM calculations. We confirm that the proposed bond-tuned link-atom scheme can be as accurate as the system-specific tuned-F link-atom scheme.

Current and proposed work includes the following:

- applying the bond-tuned link-atom scheme to NU-1000 and UiO-67
- developing new parameters for nodes and linkers to allow a more realistic treatment of a variety of MOFs, including accurate lattice constants and intracell structural parameters
- making the parameters in force fields more physical, for example by developing noncovalent parameters suitable for use with CM5 charges
- improving the self-consistent-field convergence of the *QMMM* computer program [Lin, H.; Zhang, Y.; Pezeshki S.; Wang, B.; Wu, X.-P.; Gagliardi, L.; Truhlar, D. G.; QMMM 2017; University of Minnesota, Minneapolis, 2017] to make it exascale ready
- adding periodic boundary conditions capability to the *QMMM* computer program to enable the treatment of crystalline systems without truncating to clusters
- improving the documentation of the *QMMM* computer program
- applications to catalysis

Computational Study of Electrocatalytic Hydrogen Evolution from Water by a Mononuclear Molybdenum Sulfide-Functionalized Metal-Organic Framework

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A molybdenum sulfide functionalized NU-1000, the latter a Zr_6-based metal-organic framework, was synthesized via SIM (solvothermal deposition in MOFs) of molybdenum(VI) and subsequent exposure to H_2S. The catalyst, named **MoS_x-SIM**, is established to be mononuclear via single crystal X-ray diffraction measurement and exhibits low electrocatalytic behavior for evolution of molecular hydrogen from aqueous acid. Meanwhile, introduction of a redox mediator (RM), methyl viologen (MV^{2+}), enhances the catalytic performance, presumably through facilitation of electron transfer from the reduced RM. Kinetic study reveals an unexpected square-root dependence of the overall reaction rate on the mediator concentration and a potential-dependent pH-effect and potential-dependent isotope effect.

To gain a microscopic understanding of the mechanism of hydrogen evolution from aqueous acid by this MOF-affixed mononuclear **MoS_x-SIM** catalyst, we performed density functional theory calculations on a cluster model (Figure 1). We substituted the linkers with formate or benzoate and used the M06-L/6-31G(d)&SDD method in the Gaussian 09 software package. An electrocatalytic cycle of hydrogen evolution requires the addition of two protons, two electrons, and the release of H_2, with the proton and electron transfer steps potentially proceeding in any order. A metal-hydride intermediate is formed, followed by reacting with a proton from the system to form H_2. Considering multiple possible protonation sites, -Mo, –O, –OH, and –HS, several mechanisms were explored. Preliminary results suggest the favored pathway is protonation → reduction → protonation → reduction → H_2 release, and that the formation of H_2 on the metal is the rate limiting step. Our current model suggests that using MV^{2+} as the redox mediator, proton transfers and electron transfers are highly feasible.

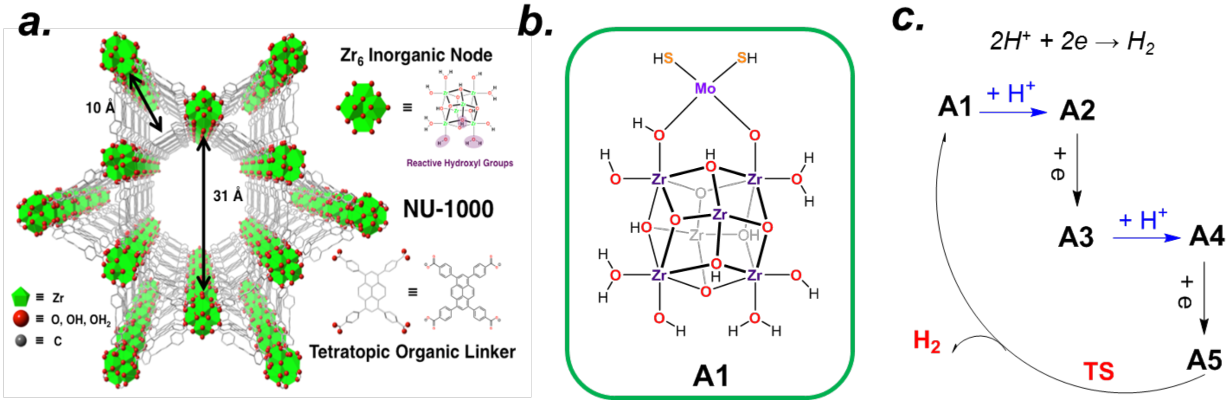

Figure 1. ***a***. Non-functionalized metal–organic framework, NU-1000. ***b***. Cluster model of MoS_x-SIM. ***c***. Catalytic hydrogen evolution reaction scheme.

Computation Study of Methane Borylation in Transition Metal Functionalized Metal-Organic Frameworks

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Unconventional natural gas production using hydraulic fracturing has unlocked a massive supply of lightweight alkanes (C1-C4). It is desirable to convert low-cost alkanes into higher-value chemicals. The conversion of methane (CH_4) is challenging due to its strong C−H bonds. The methane borylation reaction over organometallic catalysts that utilize bis(pinacolborane) is a promising method for activating the methane molecule under mild reaction conditions. Metal-organic frameworks (MOFs) are a class of porous materials that offer a high degree of structural and functional modifiability by the selection of inorganometallic nodes and organic linkers as building blocks and provide a promising way for heterogenization of organometallic catalysts with high activity, selectivity, and improved stability. A new MOF UiO-67-based catalyst was synthesized and experimentally examined for methane borylation. The catalyst involves an Ir(III) complex supported on MOF UiO-67 through modified linker groups. MOF UiO-67 is composed of inorganic nodes ($Zr_6(\mu^3\text{-}O)_4(\mu^3\text{-}OH)_4$) and 4,4′-biphenyl dicarboxylate linkers. The newly synthesized complex is found to have excellent chemoselectivity (>99%) for methane borylation to produce monoborylated methane. [Zhang, X.; Huang, Z.; Ferrandon, M.; Yang, D.; Robison, L.; Li, P.; Wang, T. C.; Delferro, M.; Farha, O. K.; *Nat. Catal.* 2018, **1**, 356−362]

Density functional theory (DFT) can yield valuable information on the structures and thermodynamics of the catalytic materials. In this project, we use DFT calculations to determine the atomic-scale reaction pathway and to verify the steric effect of the UiO-67 framework for methane borylation over the Ir-based complex. In addition to full DFT calculations, we use combined quantum mechanical and molecular mechanical (QM/MM) methods to facilitate the investigation of the large systems that are computationally less affordable in a full QM calculation. In this way, we can accurately simulate MOFs at a lower cost and thereby make progress toward the rational design of improved catalysts for methane borylation.

Current and proposed work includes the following:

- investigating methane borylation reaction mechanisms using homogeneous cluster models to determine the energetically most favorable reaction pathway
- applying the QM/MM method) to study the shape-selective effect of the metal−organic framework and pore structures
- computational screening of various transition metals, including – but not limited to – Fe, Co, Ni, and Cu, as catalytically active centers to identify more affordable, earth-abundant, and catalytically efficient heterogeneous borylation catalysts

Accelerating catalyst discovery with machine learning and automation

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Despite the rapid advances in high-throughput screening, we know very little about the vast number of feasible materials or catalysts. The highly tunable electronic structure properties of inorganic complexes make them attractive as functional materials targets but also make their rational design difficult. Transition metal chemical space is neither well-defined nor easily enumerable. Approximate DFT is both too computationally costly for full enumeration of vast numbers of compounds and also too inaccurate for robust property prediction. In this abstract, we present our work to overcome these challenges to enable predictive catalyst design.

Firstly, we present our efforts in the development of the open-source python software toolkit, molSimplify, for catalyst design and discovery. We introduced an automated method to generate transition metal complexes by combining the established methods for organic chemistry with pretrained metal-organic binding geometry. Structures of metal complexes can be generated from metal atoms and ligands or modifying upon templates. Transition state (TS) structures can also be generated by molSimplify by the specification of a substrate. Structural diversity is incorporated in molSimplify by direct mining of the multi-million molecule database ChEMBL.

Catalyst and materials discovery are realized through the use of virtual high-throughput (VHT) and diverse structures generation enabled by molSimplify and hardware-accelerated QM calculations. For example, we examined the reaction between 210 combinations of $In(O_2CR)_3$ and PH_3 for the synthesis of InP quantum dots using GPU-accelerated ab initio molecular dynamics (AIMD) and TS theory. We also examined the scaling relations between the N_2O activation and hydrogen atom transfer reactions catalyzed by various transition metal complexes. We also present our recent efforts in enabling VHT TS calculations for catalyst discovery.

ML is employed to accelerate materials discovery. QM data of bond length and spin splitting are used to train artificial neural network (ANN) models. First, we introduced two numerical representations for inorganic complexes, MCDL-25 and RAC-155. We then trained ANN models using these representations for property predictions. ANN predict the correct spin splitting in 97% of cases and excellent bond length, as compared to density functional theory (DFT) results. Chemical diversity is introduced to our ANN-accelerated materials discovery by genetic algorithm (GA). Random mutation of the ligands with the control by a fitness function that penalizes according to the property of interest (i.e. spin splitting) and Euclidean distance from training data. The combination of ANN and GA for the exploration of diverse metal complexes as potential spin crossover materials lead to over 50% success against DFT results.

Lastly, predictions from the trained ML models are validated against experimental data through data/text-mining. We have shown that catalyst and materials discovery can be accelerated by the combination of molSimplify, QM codes, and ML. To further substantiate our methods, we compared ML-predicted bond length and spin splitting to 175 crystal structures obtained from the Cambridge Structural Database and variable temperature magnetic susceptibility measurements for spin crossover complex. We found that our ML methods successfully predict the trend of bond length in 80% of cases and good agreement with experimental spin crossover is observed.

Nanoscale Confinement of Bimetallic Catalysts within Metal−Organic Frameworks for CO_2 Hydrogenation

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Zirconium-based metal−organic frameworks (MOFs) have been known to be excellent supports due to their exceptional thermal and chemical stability, advantageous in heterogeneous catalysis. Additionally, the spatially distributed hydroxyl/aqua groups on Zr_6 node can serve as grafting sites for metal ions, which upon reduction form nanoparticles with the particle size confined by the MOF pores. Here, we designed bimetallic catalysts for CO_2 hydrogenation, aiming to enhance the stability, activity and selectivity of copper-based catalysts. By solvothermal deposition in MOFs (SIM) and/or atomic layer deposition (ALD) in MOFs (AIM), we successfully installed bimetallic nanoparticles, Ga/Cu and In/Cu, into two Zr-based MOFs, NU-1000 and UiO-66, named Cu-SIM-Ga-SIM-MOF, Cu-SIM-In-SIM-MOF, and Cu-SIM-In-AIM-MOF, respectively. Catalysis under high pressure and temperature showed that Cu-SIM-Ga-SIM-UiO-66 exhibited the highest selectivity towards methanol over CO as compared to other bimetallic nanoparticles supported in the same framework or in NU-1000. Structure-activity relationship (*i.e.* nanoparticle size/composition vs. catalytic activity/selectivity) that can be interrogated in this work further implies the extension of this versatile approach beyond the current bimetallic systems with eventual target of optimum (hetero)metallic catalysts for renewable-energy related catalysis.

Computational Study of the Stability and Reactivity of Copper-Exchanged NU-1000 Metal–Organic Framework for Methane Oxidation to Methanol

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Methane (CH_4), the major component of natural gas, is a clean and important energy source. Direct conversion of methane to an easier-to-handle fuel, such as methanol, is both technically and economically viable. Very recently, researchers in ICDC have reported the synthesis and characterization of Cu-oxo clusters deposited on the nodes of the metal–organic framework NU-1000.[1] This new material was shown to catalyze the conversion of methane to methanol with a carbon selectivity of 45–60% at 150 °C.[1] The structures of the synthesized Cu-NU-1000 prior to activation have been identified by highly collaborative experimental and theoretical work. In the present work, we will apply density functional theory calculations to study the structures of the Cu-NU-1000 catalysts after activation by O_2 and using a thermodynamic analysis to study the stabilities of these structures as functions of temperature and pressure. We will investigate different reaction pathways on different catalyst structures to identify the most active sites for the selective oxidation of methane to methanol. The goal is to understand the observed catalytic properties and provide guidance on the synthesis of catalysts and the optimization of reaction conditions.

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Organic Linker Effect on the Nucleation and Diffusion of Cu Clusters in a Metal-Organic Framework

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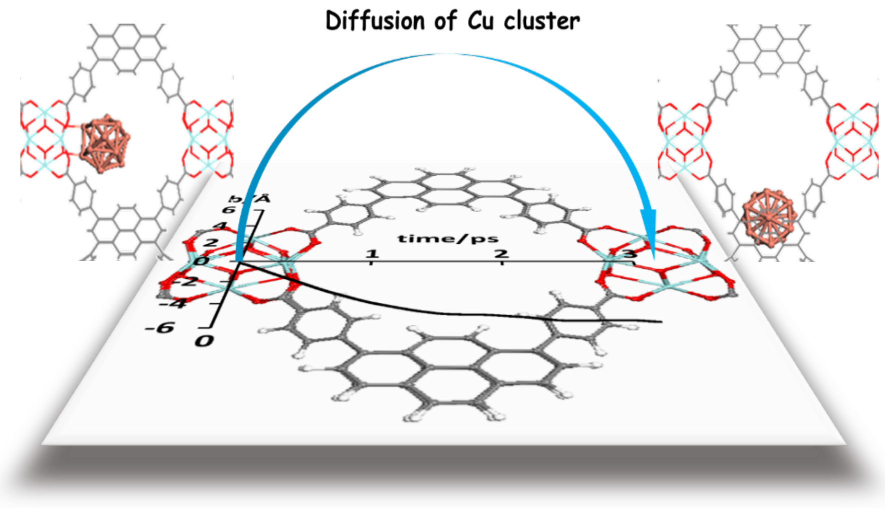
Metal nanoparticles encapsulated in metal organic frameworks are of interest because confinement effects on the particle size and shape may lead to superior catalytic activity. The interior of a metal–organic framework (MOF) has the potential to influence nucleation and aggregation of metal nanoparticles and to strongly to affect their *in situ* shape and electronic properties. We apply density functional theory and ab initio molecular dynamics (AIMD) to model the nucleation and diffusion of Cu_n (n = 1–19) clusters on the tetratopic 1,3,6,8-(p-benzoate)pyrene ($TBAPy^{4-}$) linkers of NU-1000 frameworks. We find that Cu atoms and Cu clusters are stabilized by the TBAPy linker, especially by the edge site of aromatic rings. The stabilization increases when the Cu cluster interacts with two linkers. We identified the most favorable site for Cu cluster adsorption as the window site that connects the c pore and the triangular pore. A Pt atom is found to bind much stronger than a Cu atom on the TBAPy linker, and AIMD simulations show that this promotes Pt atom diffusion from the center of a Cu_{15} cluster to the interface between the linker and the cluster. The strong interaction between a Pt atom and a linker is attributed to the greater metal-to-linker charge transfer.



Catalytic Chemo-Selective Functionalization of Methane in a Microporous Metal-Organic Framework

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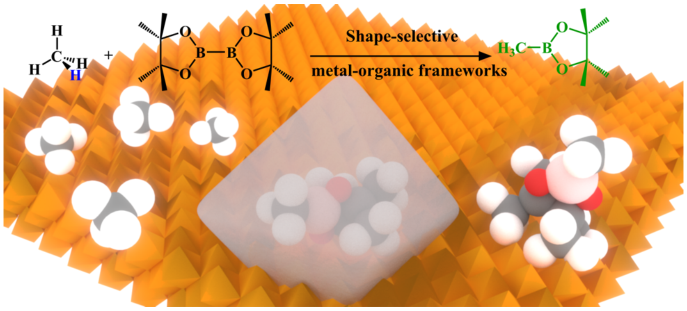

Methane, the largest fraction of natural gas, constitutes an abundant and low-cost starting material for the synthesis of value-added chemicals and fuel. However, catalytic selective functionalization of methane remains a "Holy Grail" in chemistry due to its low intrinsic reactivity. Borylation has recently emerged as a promising route for the catalytic functionalization of methane. A major challenge in this regard is the selective borylation toward of the monoborylated product that is more active than methane and can easily lead to over-functionalization. Herein a highly selective metal-organic frameworks (MOFs)-supported iridium(III) catalyst for methane borylation is reported, which exhibits an overall chemo-selectivity of >99% toward the monoborylated methane with bis(pinacolborane) as the borylation reagent in dodocane, at 150 °C and 34 atom of methaneThe shape-selective effect of MOF has been found to be crucial for the selective monoborylation of methane.

High pressure catalytic methane oxidation to methanol over copper exchanged stable Metal–Organic Frameworks

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Previous work showed that Cu-oxo clusters stabilized in the pores of NU-1000 MOF are active for selectively oxidizing methane into methanol at low temperature (150 - 200 °C). At 1 bar methane at 150 °C, the methanol productivity per copper atom is about 0.01, thus, there is a great opportunity for improvement. In current work we are investigating the effect of methane pressure on methanol productivity over Cu exchanged Zr-based MOFs, including NU-1000 and UIO-66. We hypothesized that increasing the chemical potential of methane would enable higher methanol productivity. As shown in the Figure, for Cu/NU-1000, we observed ~9 $\text{mmol}_{\text{MeOH}}/\text{mol}_{\text{Cu}}$ and ~70% methanol selectivity in the reaction performed at 150 °C and 1 bar methane. Upon heating the reactor to 200 °C, methanol yield increased to ~14 $\text{mmol}_{\text{MeOH}}/\text{mol}_{\text{Cu}}$ with similar selectivity. Methanol yield further increased to ~30 $\text{mmol}_{\text{MeOH}}/\text{mol}_{\text{Cu}}$ with ~90% selectivity (a small amount of dimethyl ether was observed) after the system was pressurized to 40 bar with methane. Similar results have been observed for the Cu/UIO-66. At 1 bar and 40 bar, we collected ~21 and ~44 $\text{mmol}_{\text{MeOH}}/\text{mol}_{\text{Cu}}$ of methanol, and the methanol selectivity of about 75% and 92%, respectively. These results demonstrate that increase methane pressure is an advantageous strategy to improve the methanol productivity for methane oxidation at low temperature. Efforts are under way to understand whether there are different kind of active sites enabled at high pressure or if the mechanism changes with pressure regime.

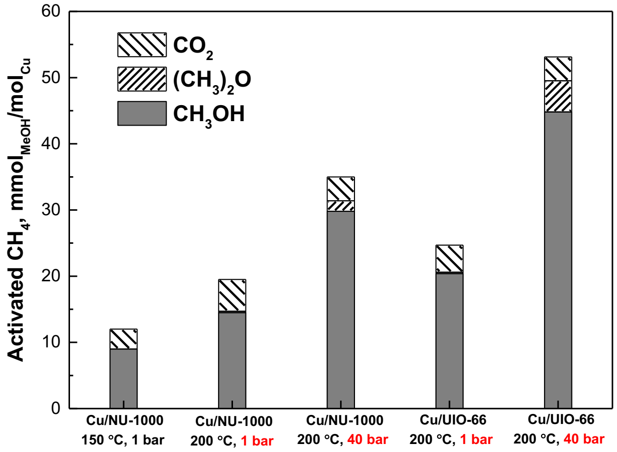

Figure. Tests of copper exchanged MOFs for methane oxidation. The materials were activated in oxygen at 200 °C for 2 h, then loaded with methane (150 or 200 °C, 1 bar or 40 bar). The products were extracted with a gas flow contained 10% water plus 90% helium and on-line analyzed with a mass spectrometer.

Expanding Methods from Computationally-Driven Design of Metal/Alloy Catalysts to Designing Single Atom Catalysts

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In this work, we expand methods from computationally-driven design of catalysts to designing single atom catalysts. Specifically, computational catalysis involves using density functional theory (DFT) to calculate thermodynamic and kinetic quantities of chemical reactions as they occur over a handful of catalysts. The thermodynamic and kinetic quantities are analyzed statistically in order to identify one or two "descriptors". These descriptor quantities are well-correlated to all of the other thermodynamic and kinetic quantities and are used to construct "scaling relationships," which are linear equations that take the descriptors as independent variables and produce as dependent variables estimates of the remaining thermodynamic and kinetic quantities. The scaling relationships are input to a microkinetic model, which combines the thermodynamic and kinetic quantities with models from statistical thermodynamics, in order to construct rate equations for the elementary steps. These are coupled with reactor design equations to produce a system of equations, which, when solved yields information about the catalytic rate. In computational catalyst design, the goal is to identify the optimal descriptor values, which maximize the rate and/or selectivity of the desired product. The material properties that control these optimal descriptor values can then be sought using a machine learning regression procedure. In this poster, we discuss how machine learning can be used to predict the descriptor value from the material, electronic properties (e.g., electronegativity, valence electron, ionization) and structure information. Those features we selected are information we can learn from the composition of catalysts, periodic table and books without performing any calculations beforehand. In that case, we can do rational catalyst design in the future without the DFT calculations.

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