Parallel CASSCF Calculations Beyond the Limits of the Conventional CASSCF Implementations

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Strong correlation is central in modern electronic structure theory. Multiconfigurational wave functions can capture this type of correlation, but they are hindered from the size of active space. Currently, the size limit of a CASSCF calculation is about 18 electrons in 18 orbitals. The Generalized Active Space (GAS) method offers an efficient reduction of the ineffective configurations allowing the exploration of larger active spaces. [1,2] In the SplitGAS method, the GAS CI expansion is partitioned in two parts, the principal, which includes the most important configuration state functions (CSFs), and an extended part, containing less relevant but not negligible CSFs. [2,3] An effective Hamiltonian is then generated by means of Löwdin's partitioning technique, with the extended part acting as perturbation to the principal space.

We have developed a parallelization algorithm that allows the exploration of larger active spaces, beyond the limits of the conventional CASSCF. Our approach is based on the GAS concept, as it is implemented in the LUCIA code, which is now connected to the massively parallelized quantum chemistry package NWChem. The new algorithm is able to handle large active spaces, and a record CI calculation that includes 24 electrons in 24 orbitals (singlet state) was achieved.

Based on similar considerations, the parallel SplitGAS implementation will be presented and the scaling performance will be discussed.

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Synthesis of TiO$_2$-stabilized Single-site Oxozirconium Clusters through Nanocasting in NU-1000

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We recently demonstrated thermal stabilization of oxozirconium clusters derived from the metal-organic framework NU-1000 by nanocasting with silica.[1] Silica acted as a relatively inert skeleton that mitigated aggregation of the single-site oxozirconium clusters even in high temperature catalytic reactions. Here, we are investigating nanocasting processes of NU-1000 with titania as an active skeleton and support matrix for oxozirconium clusters. TiO$_2$ is a well-known redox and photocatalyst. As a catalyst support, it is known to exhibit strong metal-support interactions, which provides an approach for modifying electronic and catalytic properties of oxozirconium-based single-site catalytic clusters. In mixed TiO$_2$ and ZrO$_2$ oxides, the number of acidic surface sites can be dramatically increased and relative Lewis/Brønsted acidity tuned.[2] However, in most of the ZrO$_2$-doped TiO$_2$ materials, ZrO$_2$ appears to be in the form of a ceramic mixture with TiO$_2$, which leads to decreased surface area and compromises catalytic activity. In order to increase the accessibility of catalytic active sites, NU-1000 is used here as the matrix and source of oxozirconium clusters. Through nanocasting with TiO$_2$ followed by linker removal, usually calcination, we aim to prepare oxozirconium cluster-doped TiO$_2$ with enhanced catalytic properties relevant to hydrocarbon upgrading.

In order to nanocast NU-1000 with TiO$_2$, we used various titanium alkoxides as the precursor. NU-1000 was first immersed in titanium isopropoxide (TTIP) or titanium butoxide (TNBT) solution for infiltration. Further transformations, such as aging or steam treatment, were applied during the sol-gel synthesis of the titania skeleton. X-ray diffraction (XRD) confirmed that the structure of NU-1000 was intact after infiltration and the surface area and pore volume determined from N$_2$ absorption/desorption isotherms showed a moderate decrease as a result of the successful infiltration. Energy-dispersive X-ray spectroscopy (STEM-EDS) revealed that TiO$_2$ was distributed evenly throughout the whole particle. The ability of the TiO$_2$ skeleton to prevent cluster aggregation during linker removal by calcination depends on the heating program and highest applied temperature. Our goal after synthesis optimization is to provide a single-site, multifunctional catalyst with tunable environment, good accessibility and high catalytic efficiency, suitable for high temperature operation.

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Nanocasting NU-1000 with Carbon

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Nanocasting is a useful synthetic technique to achieve specific nanostructures with predetermined geometries. The template used for nanocasting here is the metal–organic framework (MOF) NU-1000, which consists of oxozirconium clusters and TBAPy linkers (1,3,6,8-tetrakis (p-benzoic acid) pyrene). Because NU-1000 possesses relatively large, 3.0 nm and 1.2 nm diameter, pores, a suitable precursor can penetrate these pores and form a scaffold inside them via suitable treatment. Ideally, functional single-site clusters are maintained after linker removal.

Our group has reported a method to nanocast silica into NU-1000, which shows strong Lewis acidity. Inspired by this work, we are investigating carbon precursors as the next step because a carbon backbone can separate the oxozirconium clusters after linker removal and be active for electrocatalytic processes, such as partial oxidation and functionalization of alkanes. Moreover, it may provide a method to control the electronic environment around the clusters through an applied potential, adding tunability to catalytic processes.

Furfuryl alcohol (molecular dimensions $0.84 \times 0.64 \times 0.43$ nm^3) is used as the precursor. The strategy of infiltrating furfuryl alcohol into the pores involves vapor treatment, followed by heating to induce further polymerization. A decrease in the average size of the 3.0 nm pores as determined by N_2 physisorption is attributed to infiltration of these pores by poly(furfuryl alcohol). After pyrolysis of the composite at 600 °C under N_2 flow to carbonize this polymer and remove the TBAPy linkers, X-ray diffraction data indicate that no extended zirconia aggregates are formed, which implies that the oxozirconium cluster sites remain separated, as desired for single-site catalysis.

Thermal Stabilization of Metal-Organic Framework-Derived Catalytic Single Sites Through Nanocasting

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We have developed a reproducible method of stabilizing MOF-based single catalytic sites by nanocasting the MOF with silica to provide a thermally stable secondary scaffold for the single sites, preventing them from aggregating even after heating to 600 °C in air.[1] We demonstrated the effectiveness of this nanocasting technique in the MOF NU-1000. By condensing tetramethylorthosilicate in the pores of NU-1000 via vapor phase HCl treatment, a silica layer is formed lining the pore walls of the MOF. This silica layer provided anchoring sites for the catalytic oxozirconium clusters in NU-1000, thereby maintaining their site isolation and keeping them catalytically active even after the organic linkers in the MOF were lost at high temperatures. The high temperature catalytic activity of the nanocast material has been demonstrated in the dehydrogenation reaction of cyclohexane, wherein the catalyst show activity up to 650 °C.

The silica nanocasting approach was extended to metal-exchanged NU-1000 materials with the aim to exploit the catalytic tunability of the MOF clusters for high temperature reactions. We have successfully made nanocasts of Co- and Fe-loaded NU-1000, in which aggregation of zirconia or metal oxide clusters was prevented at temperatures as high as 500 °C. We are also currently working on nanocasting In- and Sn-loaded NU-1000 samples. We are collaborating with the groups of Chapman and Gagliardi to determine the structures of the metal-modified clusters in the nanocasts, as well as with the groups of Bhan, Farha and Hupp for testing high-temperature catalytic activity of the nanocast materials. We have also studied sulfation of nanocast NU-1000 and achieved high sulfate loadings (Zr:SO_4^{2-} ~ 1:1), producing a sub-nanometer analogue of superacidic sulfated zirconia that is of interest for a variety of organic transformations, including olefin oligomerization and methanol-to-olefin conversion. Additionally, we will discuss doping the oxozirconium clusters with +3 metal ions (Y, Sc, and La), to achieve nanoscale analogues of industrial doped ZrO_2 catalysts.

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Multiconfigration Pair-Denity Dunctional Theory: Recent Developments for Ground and Excited-State Chemistry

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We will present on Multiconfiguration Pair-Density Functional Theory (MC-PDFT) and the latest developments for ground-state and excited-state chemistry. The electronic structure and spectroscopic properties of multiconfigurational systems can be a challenge for modern electronic structure theories. We benchmarked MC-PDFT on diverse data sets and find that MC-PDFT can describe bond energies and excitation energies accurately. We also discuss the latest work in on-top density functional development and configuration interaction coefficient optimizations.

Probing the Catalytic Activity of Bimetallic-Functionalized Metal Organic Frameworks

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Metal organic frameworks (MOFs) possess many desirable properties that make them advantageous for use in catalysis. The inherent crystallinity of MOFs allows for the installation of identical single-site catalysts that are uniformly dispersed, which offers the prospect of increased selectivity over traditional catalyst supports.[1-4]

Recent efforts in the Lu group have shifted towards the use of heterobimetallic complexes that function as precursors for solution state deposition onto MOF supports, such as NU-1000. The use of these heterobimetallic complexes allows for the installation of both metals in close proximity to one another in a controlled fashion. In particular, the use of two metals allows us to emulate biological systems by tuning the redox potentials of the catalytic metal sites, allowing for the optimization of the electronic environment required to achieve a given chemical transformation.

Heterobimetallic Al-M complexes (where M = Co, Rh) have been deposited onto NU-1000 with a loading of 1 complex per Zr_6-node and an Al:M ratio of 1:1. Catalytic screening studies have elucidated that the bimetallic functionalized NU-1000 is a competent catalyst for various chemical transformations. In particular, (Al-Co) NU-1000 is able to mediate the oxidation of benzyl alcohol, while (Al-Rh) NU-1000 mediates the hydrogenation of olefins under mild temperatures and pressures.

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Catechol-Ligated Transition Metals: A Quantum Chemical Study on a Promising System for Gas Separation

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Metal-organic frameworks (MOFs) have received a great deal of attention as having potential for atmospheric filtering, and recent work has shown that catecholate linkers can bind metals, creating monocatecholate metal centers with abundant open coordination sites. In this study, the binding energies of several small molecules to M-catecholate systems (with M = first-row transition metals) are calculated using density functional theory (DFT) and, in select cases, complete active space self-consistent field (CASSCF) with second order perturbation (CASPT2). The binding energies of different guests are compared for each metal and recommendations for further work based on the most promising selectivities are provided.

Oxidative Dehydrogenation of Propane
Catalyzed by Co-decorated NU-1000

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Zr-based metal–organic frameworks (MOFs) have been shown to be excellent catalyst supports in heterogeneous catalysis due to their high stability. More importantly, their crystalline nature affords the opportunity for molecular level characterization of both the support and the catalytic active site, expediting mechanistic investigations of the catalytic process.

Herein we describe the installation of Co(II) ions to the nodes of the mesoporous MOF, NU-1000, via two different preparative routes, namely solvothermal deposition in MOFs (SIM) and atomic layer deposition in MOFs (AIM), denoted as Co-SIM+NU-1000 and Co-AIM+NU-1000, respectively. Upon activation in a flow of O_2 at 230 °C, both materials can catalyze the oxidative dehydrogenation (ODH) of propane to produce propene under mild conditions (see Figure). Catalytic activity as well as propene selectivity of these two catalysts, however, is different under the same experimental conditions, corroborated by in-situ X-ray absorption spectroscopic studies where different Co species are generated in these two materials upon activation. A potential reaction mechanism for the propane ODH process catalyzed by Co-SIM+NU-1000 is proposed, yielding a low activation energy barrier in agreement with the observed low temperature catalytic activity.
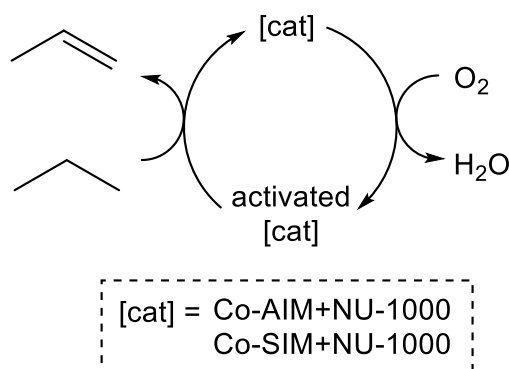
Figure. Propane oxidative dehydrogenation.

Cu-NU-1000: Structural Characterization and Catalytic Activity for Methane Oxidation

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In this work we have deposited Cu on the nodes of the metal–organic framework NU-1000 via atomic layer deposition (AIM). The new material, Cu-NU-1000, has been characterized using X-ray absorption spectroscopy (XANES, X-ray absorption near edge structure, and EXAFS, extended X-ray absorption fine structure) and density functional theory (DFT). The combined study indicates that the predominant cluster is likely to be a trimeric Cu-hydroxide-like structure that bridges two nodes across the small pore of NU-1000 (see Figure).

Cu-NU-1000 is then tested as catalyst for methane oxidation. The material oxidizes methane under mild reaction conditions (1 bar 150 °C) with up to 30% selectivity toward methanol, although substantial decreases in activity and surface area and pore volume are observed after the first cycle. Overall, Cu-NU-1000 appears as a promising first-generation MOF-based catalyst for selective methane oxidation.
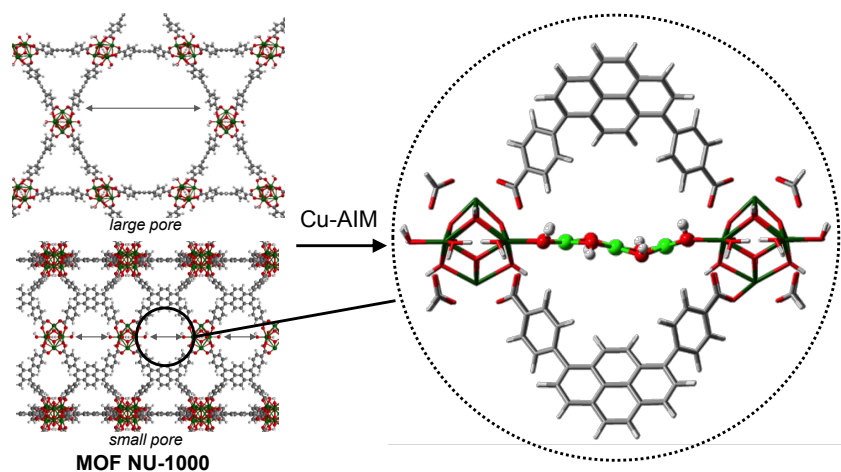

Figure. Cu clusters in Cu-NU-1000 after AIM.

Tuning the Sites on Metal Oxide-Like MOF Clusters as Supports for Well-Defined Metal Complex Catalysts

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The nodes of some MOFs closely resemble small pieces of metal oxides, exemplified by the Zr_6 nodes of UiO-66, UiO-67, and NU-1000. Understanding the precise structures of the node, including their vacancies and surface sites, is a central challenge of ICDC. Structural defect sites of UiO-66/67 and NU-1000 have been inferred on the basis of IR spectra and density functional theory (DFT) to consist of pairs of terminal OH and OH_2 groups (called site 1). An open challenge is to tune these sites as a basis for tuning the catalytic properties of metal complexes bonded to them. We developed a treatment process to convert site 1 into a new proton topology incorporating methoxy groups. IR and DFT results led to the identification of an intermediate methoxy-Zr structure incorporating structural vacancies on the node surface which facilitated the conversion of site 1 to a new dehydro-monohydroxo site, which provides new opportunities for anchoring of metal-containing catalytic groups to the MOFs and is the subject of ongoing experiments. The results show how the combination of DFT calculations and IR spectra can be used to determine the identity and chemistry of the functional groups on the defect sites on MOF nodes.

We have studied species formed by chemisorption of $Rh(C_2H_4)_2(acac)$, **I**, (acac is acetylacetonate) on the MOF nodes as catalysts. Bonding of the rhodium to site 1 of UiO-67 gave species identified by IR, EXAFS, and DFT results as mononuclear $Rh(C_2H_4)_2$ complexes. Conversion of these to rhodium *gem*-dicarbonyls resulted from reaction with CO; the ν_{CO} values provide distinguish electron-donor properties of the support sites and thereby provide a basis for comparison of various MOFs as catalyst supports. The catalytic activity and selectivity of the species initially present as $Rh(C_2H_4)_2$ for ethylene hydrogenation and dimerization were investigated experimentally and computationally, and the results show that the catalyst performance is strongly influenced by the node sites. We also formed $Pt(acac)_2$ and $Cu(acac)_2$ on the nodes of UiO-67 and NU-1000, but these are barely active as catalysts for ethylene conversion.

In summary, we are on track to tailoring the MOFs and their node surface sites as supports for metal complex catalysts quite generally.

NU-1000 Supported Niobium Catalysts:
In-situ Active Sites Titration & Cyclohexene Epoxidation

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Developing structurally well-defined supported catalysts has always been a challenge in the field of heterogeneous catalysis. In this study, we synthesized highly active and isolated metal oxide catalysts consisting of Nb(V) oxide on the metal node of NU-1000. Nb(V) oxide was deposited with high Nb(V) loading (up to 1.6 mmol/g) via two post-synthetic methods that are atomic layer deposition (ALD) in a MOF (AIM), solution-phase grafting in a MOF (SIM). One obvious advantage is that Nb(V) loadings (per g) can be much higher than for conventional oxide-supported catalysts, such as Nb-ZrO$_2$ or Nb-SiO$_2$.

Crystallinity and high porosity of NU-1000 were preserved after Nb(V) deposition, as confirmed by PXRD and nitrogen isotherms, respectively. The result from difference envelope density (DED) measurement indicates that two different synthetic methods result in difference in distribution of Nb(V) ions within NU-1000. Titration with phenylphosphonic acid (PPA) during cyclooctene epoxidation was used to quantify the number of active sites. Despite their high Nb(V) loading, nearly all Nb(V) sites of MOF-supported catalysts are kinetically active. MOF-supported catalysts were examined for the cyclohexene epoxidation with aqueous H$_2$O$_2$ at 65 °C. Both Nb-AIM and Nb-SIM are more selective and active than the control catalyst, Nb(V) on ZrO$_2$, on a gravimetric basis. Finally, we examined diffusion effects of both catalysts by reducing the size of the catalytic support, implying Nb-AIM can potentially be synthesized with high TOF approaching those of the oxide-supported catalysts.
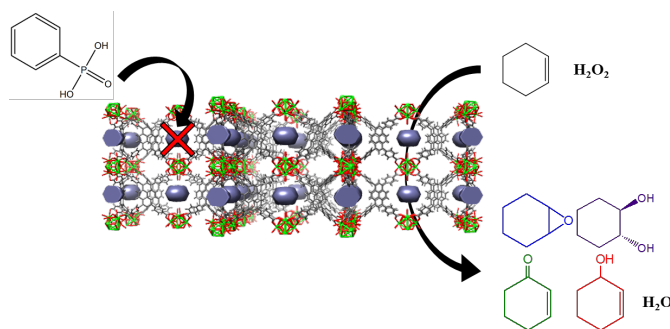
Figure. Phenylphosphonic acid titration and cyclohexene epoxidation with Nb-AIM

Extending scaling relationships from unsupported to supported metal cluster catalysts

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Traditional methods for screening catalysts have relied on brute-force high-throughput experiments that may test hundreds of thousands of different possibilities, while only producing a few promising variations. Computational catalysis has provided a more guided search methodology, by using scaling relationships to simplify the computational demands and expand the possible screening space beyond experimental limitations.

Computational catalyst screening methods have not been widely applied to atomic-scale catalysts and, in particular, single site catalysts. Single site catalysts are desirable since the active sites should be identical and spatially isolated. Most efforts in computationally studying these systems involves modeling the atomic catalyst on the support needed to stabilize the catalyst cluster in the experimental system. This support tends to be much larger than the actual active site therefore; most of the computational effort is associated with simulating this support. This limits the rate of catalyst screening since only the transition-metal catalyst directly influences the catalytic pathway. Therefore, to drive catalyst screening, the model needs to be simplified. We propose the use of small, unsupported atomic-scale clusters as models to study catalytic behavior.

In this work, we use small metal-based, gas phase clusters derived from a catalyst that could be grafted onto a porphyrin or NU-1000 support using atomic layer deposition (ALD). We show that scaling relationships derived from the unsupported gas phase catalytic clusters can predict catalytic behavior for their supported analogs along the same reaction pathway. Utilizing +2 oxidation state transition-metal catalysts, we analyze the direct catalytic oxidative upgrading of ethane to ethanol supported on the porphyrin support TCPP and the dimerization reaction of ethylene to 1-butene supported on the Zr6 node of NU-1000.

Exploring Catalysis Opportunities of Iridium Deposited NU-1000 and UiO-66

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Metal-organic frameworks (MOFs) are crystalline, porous materials which are built by connecting metal nodes with organic linkers. They possess great potential for many applications including catalysis, gas storage/separation, sensing etc. due to their chemically versatile structures, high porosity, high surface areas.

Recently, an experimental technique, atomic layer deposition (ALD), has been used to incorporate metals precisely in MOFs. This method, ALD in MOFs (AIM), provides synthesis of catalytically active materials that have uniform active sites and support which are easier to characterize.

It is known that Zr based MOFs have high structural stability due to strong Zr-O bonds. Two such Zr_6 based MOFs (NU-1000 and UiO-66) are modeled using clusters extracted from their density functional theory (DFT) optimized periodic structures. The clusters are loaded with $Ir(CO)_2$ and CO vibrational frequencies are characterized at site 1 to compare with experimental IR frequencies. Using $Ir(C_2H_4)_2$ deposited NU-1000 and UiO-66 structures, ethylene hydrogenation and dimerization reaction mechanisms are computationally studied which are used to explain experimental selectivity through calculated activation barrier values of both reactions. All cluster calculations employ M06-L functional.

Catalytic Activity of Porphyrin-Supported Mixed Metal Oxide Nanoclusters

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During the last decade, natural gas production in the United States has significantly increased every year, and it is predicted to increase even more rapidly during the coming years. This has opened new opportunities for selectively transforming natural gas components and their derivatives into more valuable chemicals through energy efficient and environmentally friendly processes. With this incentive in mind, we have performed two separate density functional theory studies of the activity of supported metal oxide nanoparticles that can be grown via atomic layer deposition on a porphyrinic substrate. We evaluated the catalytic performance of copper-oxide nanoparticles for the oxidative dehydrogenation of alkanes, while exploring different oxidants and reaction pathways. In addition, we studied the catalytic activity of vanadium-oxide nanoclusters for the oxidation of methane to methanol and the effect of the supporting metal on the C-H activation barrier. Efforts are currently underway to synthesize these systems and test their catalytic performance, and further studies will extend upon this work and explore other nanoclusters.

Hydrogenation and Oligomerization of Ethylene Catalyzed by Transition Metal Oxide Nanoclusters

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The hydrogenation and oligomerization of ethylene and other alkenes on transition metals are important reactions that could play roles in the conversion of ethane and other natural gas components into fuels or chemicals. To obtain high selectivity, the active sites of a catalyst should all be identical and should be isolated from each other. PCN-222 (a porphyrinic MOF) is an appealing, thermally-stable support for creating well-defined active sites that can catalyze the conversion of light hydrocarbons found in natural gas. We envision that atomic layer deposition (ALD) can be used to form isolated oxide nanoclusters on the metal centers of the porphyrin linkers, as has been shown by Avila et al[1] on a metallated meso-tetra(carboxyphenyl)porphyrin (TCPP) monolayer adsorbed parallel to a silica surface. Furthermore, the high porosity and surface area of PCN-222 are ideal for facilitating the catalytic reaction between active sites and reactants.

With these incentives in mind, we present well-defined transition-metal-oxide nanoclusters that could be formed via two ALD cycles on porphyrinic substrates. We employ a computational screening method to evaluate their catalytic activity and selectivity for the hydrogenation and oligomerization of ethylene. In addition to calculating the thermodynamics and kinetics of these catalyzed reactions using first principle calculations, we have also assembled them into three different microkinetic models: ethylene hydrogenation to ethane, ethylene oligomerization to butene, and a "competitive" reaction, in which both hydrogenation and oligomerization are allowed to occur simultaneously. Utilizing a descriptor-based approach, a set of scaling relationships is determined from the first principle energies to predict the theoretical production rates. With these scaling relationships, the catalytic performance of other potential nanoclusters can be quickly evaluated. The results and continuation of this study will lead to a better understanding of the catalytic process and provide guidance for experimental efforts to find improved catalysts for natural gas conversion.

[1] Avila, J. R.; Emery, J. D.; Pellin, M. J.; Martinson, A. B. F.; Farha, O. K.; Hupp, J. T. *"Porphyrins as Templates for Site-Selective Atomic Layer Deposition: Vapor Metalation and in situ Monitoring of Island Growth,"* submitted.

Testing a Simple Gaussian Model for Vibronic Band Shapes in Electronic Spectroscopy

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The interpretation of the electronic spectra of transition-metal complexes as aided by theory and computation can give useful information about their electronic structure, which is important for understanding their catalytic properties. It would be highly desirable if time-dependent density functional theory (TDDFT), which is affordable for large and complex molecules, can be used for this purpose. To understand the accuracy of TDDFT we need benchmark values against which to test it. This, however, poses a great challenge since it is difficult to compare to experiment because the experimental spectra of large molecules are not completely resolved and difficult to compare to more accurate electronic structure method because affordable calculations on large and complex molecules are not necessarily reliable. The vertical excitation energies predicted by TDDFT are not directly comparable to experiment, and electronic structure methods of benchmark quality are too costly for transition-metal complexes. Therefore we attempt to use a different strategy, namely to simulate full electronic spectra by TDDFT and compare to experimental ones. For this purpose we tested a simple Gaussian model for the vibronic band shape of electronic absorption spectra. We showed that, combined with accurate electronic structure calculations, the model can give an overall vibronic band shape comparable to more sophisticated vibronic methods and to experiment, and it is simple enough to be applied to complex systems. Therefore, the error in the spectra simulated by this model combined with TDDFT will be dominated by the TDDFT calculations, and we can evaluate the accuracy of TDDFT by comparing the simulated spectra to experiment.

Alkane Metathesis Catalysis in Ta/W-Functionalized NU-1000 MOFs

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Mid-weight acyclic alkanes, usually containing three to eight carbon atoms per molecule, are undesirable petrochemical feedstocks that are available in large quantities. It is desirable to convert mid-weight alkanes into higher-value alkane homologs. As a potential method for achieving such conversion, alkane metathesis is a class of reaction in which alkane molecules (C_nH_{2n+2}) are transformed into higher and lower homologs ($C_{n+i}H_{2(n+i)+2}$ and $C_{n-i}H_{2(n-i)+2}$).

The majority of single-site alkane metathesis catalysts are metal-hydride-modified oxides such as W-H and Ta-H functional groups on amorphous SiO_2 and Al_2O_3. In the present work, metal organic frameworks (MOFs), such as NU-1000, are utilized as supports for new catalyst development. Because of their tunable uniform surface structures, MOFs are ideal for rational heterogeneous catalyst design based on structure–reactivity relationships.

As an initial step, we performed computational screening using density functional calculations to identify suitable catalysts for propane metathesis. The reaction cycle for W-functionalized NU-1000 catalyst was computed, including energies for possible intermediates and transition states. This catalytic cycle involves: (a) C–H bond activation of the propane molecule, (b) propene metathesis through [2+2] cycloaddition and cycloreversion, and (c) hydrogenation and hydrogenolysis steps to generate alkane homologues. Tungsten hydride was examined as the catalyst precursor. A two-site mechanism involving metal hydride alkene and metal hydride alkylidene surface species has been verified. Activation barriers have been computed, and key reaction steps have been identified.

Evolution of metal distribution in metal-organic frameworks during atomic layer deposition: Single-site catalyst deposition in NU-1000 is directed to small pores by dispersion interactions

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The Zr-based NU-1000 MOF is an attractive platform for developing designer catalysts, including through atomically-precise atomic layer deposition (ALD). Specifically, -OH$_x$ groups around the equator of the Zr_6O_8 nodes in NU-1000 provide reactive surface sites at which a wide variety of ALD precursors can be deposited. While chemically equivalent -OH$_x$ groups are distributed around the equator of each node, directed into both large hexagonal channel and smaller perpendicular apertures, new electron density following ALD treatment has only been observed in the small apertures for the wide range of different ALD chemistries studied to date. This selective deposition of the ALD material on only half the node faces raises important questions on the mechanism and energetics of the ALD processes: Does the organometallic precursor selectively react at only half the sites? Or does the heat released during the B/H$_2$O cycle provide sufficient energy for evenly distributed metal species to be reorganized into the small apertures?

We applied *in situ* powder diffraction experiments and density functional computations to explore the structure mechanism and energetics of ALD with $Zn(Et)_2$ on NU-1000. These measurements show that $Zn(Et)_2$ reacts exclusively on faces within the smaller aperture, confirming that the selective deposition is associated with preferential reactivity and is not a consequence of rearrangement during the B cycle. Instead, the electron density changes to bridge adjacent nodes during the B cycle, resulting in a substantial contraction of the lattice along this axis.

We used periodic Kohn-Sham density functional theory with the M06-L and PBE-D2 exchange-correlation functionals to calculate the potential energy surface governing Zn-ALD. We examined both the transition state and the final product, the post-reaction complex that includes the produced ethane in the pore. For each of these two cases, both functionals give a lower energy in the small aperture. The PBE-D2 functional allows partitioning of the energy into a damped dispersion interaction and the rest, and this partitioning shows that the energy lowering in the apertures is mainly due to a larger dispersion interaction between $Zn(Et)_2$ and the MOF linkers.
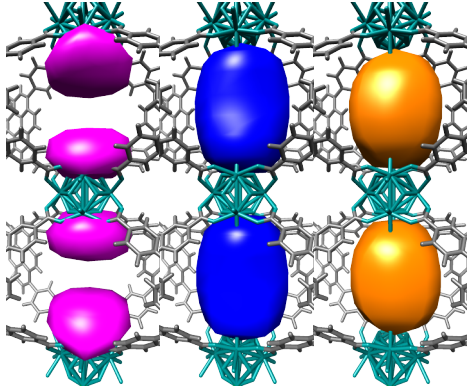
Difference envelope density maps of NU-1000 during atomic layer deposition of zinc viewed along c axis: (a) first A cycle (b) first B cycle and (c) Zn-AIM examined ex situ after a full ALD cycle.

Platinum Atomic Layer Deposition (ALD) in Metal-Organic Framework (MOF) for Ethylene Hydrogenation

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Metal-organic frameworks (MOFs) exhibit well-defined periodic structures with high thermal stability, and thus provide a unique platform to perform theoretical and experimental analyses on catalytic reactions. Recently, atomic layer deposition (ALD) in metal-organic framework (AIM) was demonstrated as a viable route to functionalize MOFs with reasonable scalability for a wide range of catalytically relevant materials. Here, we investigate structural integrity, reaction mechanism, and catalytic performance of Pt-NU-1000 before and after ethylene hydrogenation.

Structural analyses using XRD and BET measurements revealed structural integrity was retained upon Pt-AIM process with a uniform distribution of Pt. Pt was mainly in the form of Pt(IV), which formed clusters upon reduction in H_2 based on in-situ XAFS measurements. Density functional theory (DFT) calculations are conducted to elucidate the energetics and structural properties for the formation of several platinum clusters interacting with the nodes of the NU-1000. Additionally, we computationally investigate the ethylene hydrogenation catalyzed by small platinum clusters deposited on the nodes of NU-1000. A tetra-platinum cluster is used as a model for the deposited metal and DFT calculations are performed to investigate the reaction pathway for the ethylene hydrogenation. The DFT calculations, coupled with microkinetic modeling, are used to elucidate the dominant pathway from the many different elementary reactions considered and to identify the most important factors/descriptors for the hydrogenation reaction. By varying the residence time of ethylene, the turn over frequency (TOF) for the hydrogenation reaction catalyzed by Pt-NU-1000 is determined to be ~ 10 s^{-1} on a per-Pt-atom basis (Figure 1a). The apparent activation barrier of the reaction was ~ 7.9 kcal/mol, similar to other reported hydrogenation catalysts (Figure 1b).
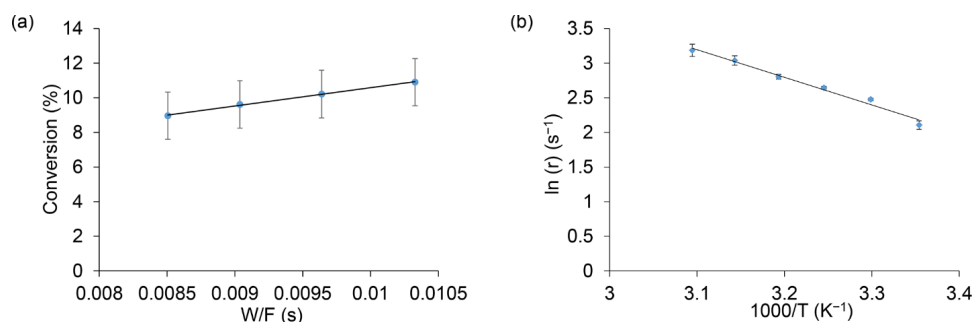
Diversifying and Understanding Atomic Layer Deposition (ALD) in Metal-Organic Frameworks (MOF) for High-Throughput Catalysis Testing

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Zr-based metal-organic frameworks (MOFs) have gained much attention for applications in catalysis and gas storage owing to their high surface area (porosity) and stability (thermal/chemical). Moreover, MOFs exhibit atomically well-defined structures, providing an ideal platform for computational modeling. Among various routes to functionalize MOFs, atomic layer deposition (ALD) in MOFs (AIM) utilizes self-limiting vapor phase reactions, which offers several distinct advantages such as site-specificity and spatial uniformity.

With a short-term goal of diversifying and scaling catalytically relevant AIM approach for high-throughput catalysis testing, we attempt to understand: 1) possible reaction pathways through DFT calculations and experimental verification via in-situ FTIR and QMS experiments, 2) precise location of metals and the evolution of local structure utilizing both in-situ and ex-situ PXRD/PDF, 3) distribution of metals within individual NU-1000 microcrystals investigated by S/TEM, and 4) the heat of reaction involved in AIM as well as its effect on structural integrity based on IR imaging and in-situ FTIR experiments.
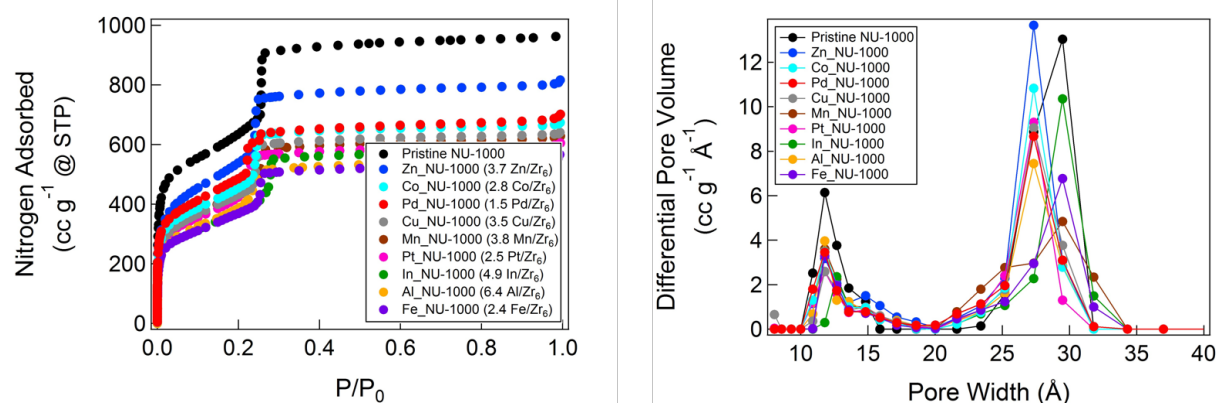
Computational investigation of ethylene hydrogenation with small metal clusters deposited on NU-1000

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Recent experiments have shown the successful deposition of small Pt clusters on the Zr_6O_8 nodes of the metal-organic framework NU-1000. The obtained platinum functionalized NU-1000 (Pt/NU-1000) has high reactivity for ethylene hydrogenation. In this work, we computationally investigate the ethylene hydrogenation catalyzed by small platinum clusters deposited on the nodes of NU-1000. A tetra-platinum cluster is used as a model for the deposited metal and Density Functional Theory (DFT) calculations are conducted to investigate the reaction pathway for the ethylene hydrogenation. Due to the pathway being relatively unknown several possible intermediate and transition state structures are calculated along the pathway. The mechanism is compared to the free, unsupported Pt_4 clusters and the effects of using the NU-1000 as support materials are presented.

The DFT calculations,coupled with microkinetic modeling, are used to elucidate the dominant pathway from the many different elementary reactions considered. With this knowledge, the study could be extended by including other metals (Pd, Rh, Ir). Additionally, we attempt to identify the most important factors/descriptors for the hydrogenation reaction.

Adsorption of ethylene by the mesoporous catalyst Ni-NU-1000

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The zirconium-MOF NU-1000 has successfully been utilized as a support for a high surface area nickel catalyst (Ni-NU-1000). The functionalization of NU-1000 with nickel via atomic layer deposition and the subsequent reductive activation required for catalysis induce significant local and long range structural changes in this material, which we have previ`ously examined via *in situ* total scattering and powder diffraction measurements. To better locate the active sites within this material, we have employed additional *in situ* powder diffraction measurements to study the localization of ethylene in the activated catalyst. Difference envelope density analysis revealed that ethylene not only interacts with both the deposited nickel oxide clusters and the zirconia nodes, but also adsorbs on the pyrene linkers of the MOF. This interaction is believed to be due to pi-pi interactions.
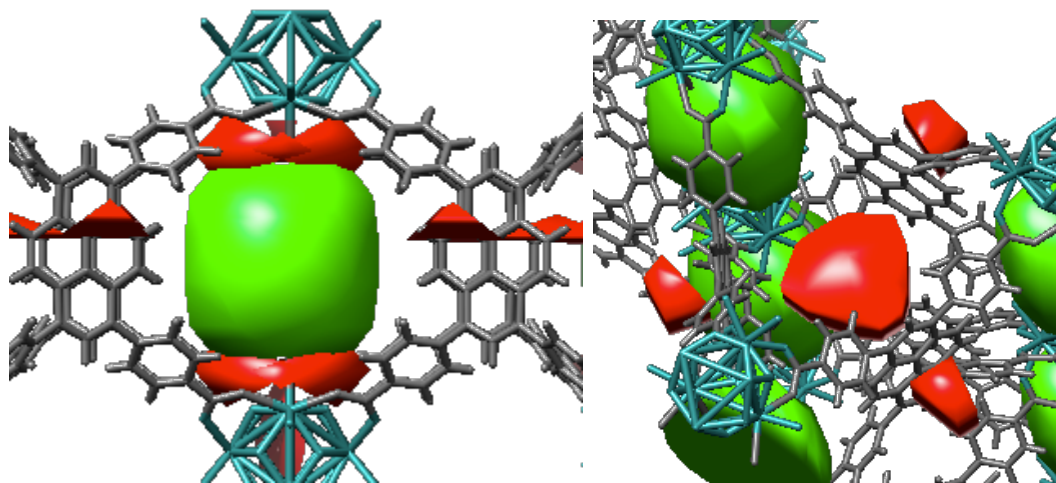
Difference envelope density maps of ethylene on NI-NU-1000: (a) ethylene-nickel and ethylene-zirconium interactions and (b) ethylene-pyrene interaction.

The nature and structure of Pt–NU-1000 for ethylene hydrogenation: an in situ XAFS and DFT study

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Atomic layer deposition (ALD) has been proposed as a superb technique for the deposition of metal on the node of metal-organic frameworks (MOFs). Pt has been loaded on NU-1000 via ALD. The obtained Pt-NU-1000 showed high activity for ethylene hydrogenation. In this work, we have performed the *in situ* XAFS analysis and DFT calculation on the deposited Pt species, particular attention was paid to the structure of the Pt species during the reduction and hydrogenation. The results indicate that the freshly prepared Pt-NU-1000 is in the form of Pt(IV) and is bonded to either C or O atoms. Reduction of the sample at room temperature under 100% H_2 (1 bar) leads to the formation of Pt clusters. Each Pt atom is coordinated by an average 6-7 Pt atoms in the first shell, which implies that the average diameter of the clusters is approximately 1 nm. During ethylene hydrogenation catalysis, the temperature of the sample pellet rose to an estimated 150℃ due the exothermicity of the reaction and high activity of the catalyst. No obvious change in the first shell Pt-Pt coordination number was observed (see Figure). It suggests that the Pt clusters have excellent resistance to sintering. In addition, Density Functional Theory calculations are being performed to elucidate the energetics and structural properties for the formation of several platinum clusters interacting with the nodes of the NU-1000. Based on this study, Pt-NU-1000 is demonstrated as a promising catalyst for ethylene hydrogenation at room temperature.
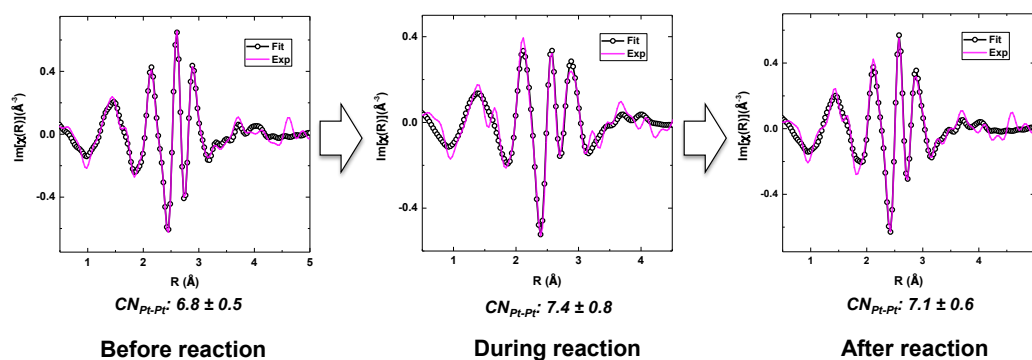

CN_{Pt-Pt}: 6.8 ± 0.5 **Before reaction**

CN_{Pt-Pt}: 7.4 ± 0.8 **During reaction**

CN_{Pt-Pt}: 7.1 ± 0.6 **After reaction**

Figure. The k^2-weighted Img[χ(R)] Pt-EXAFS spectra of Pt–NU-1000 and a comparison of the Pt-Pt first shell coordination number before, during, and after ethylene hydrogenation.

Deposition and Activity of Heterobimetallic Complexes onto NU-1000

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NU-1000 is a metal organic framework (MOF) that is an ideal support due to the stability of the framework and availability of reactive sites to bind metal precursors. Both atomic layer deposition in MOFs (AIM) and solvothermal deposition in MOFs (SIM) have been used to deposit metal catalysts resulting in either homometallic species, or layered bimetallic species. A complementary strategy is to use preassembled bimetallic precursors to ensure controlled deposition of both the metals. A potential benefit of this approach is the ability to systematically probe the effect of the supporting metal on the active metal with regards to activity and selectivity.

By using a simple solution phase technique wherein an organobimetallic complex of the general formula, $(py_3tren)M'MR$ (py_3tren = triply deprotonated N,N,N-Tris(2- (2-pyridylamino)ethyl)amine and R = alkyl, aryl or aryloxide), reacts with the – OH groups on the MOF, deposition of two systems(M' = Al, M = Co, Rh) has been achieved. Heating the anchored Co-Al or Rh-Al complex on NU-1000 in air completely removes the organic ligand of the complex while preserving the structural integrity of the MOF support. Both, AlCo and AlRh functionalized NU1000 are potent catalysts for the oxidation of benzyl alcohol and hydrogenation of olefins respectively. Preliminary investigations have indicated that $(py_3tren)AlRh$@NU-1000 can selectively (>95%) hydrogenate phenylacetylene to styrene, a much sought after reaction in the polymer industry.

It is of particular interest that the anchored material is active as previous calculations on the related AlCo system would suggest that the rhodium metal should be fully saturated with ligands and not have the open sites necessary to perform catalysis. To understand the active sites of these anchored materials DFT calculations were performed to determine how to liberate an active site and what is the identity of these potential active sites.

Size and Phase Control of a Metal-Organic Framework

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Metal-organic frameworks (MOFs) are promising catalysts due to their well-defined structures and high surface areas. NU-1000 is especially attractive for its 3.1 nm hexagonal channels, into which catalytically active species, such as bimetallic complexes, can be installed. The typical NU-1000 synthesis yields large hexagonal rods that are 4-10 µm in length and contain substantial amounts of an impurity phase, NU-901. The large particle size is detrimental for high-resolution imaging via electron microscopy and possibly the diffusion of catalytic species into the particles. NU-901 lacks the large 3.1 nm channels, which could inhibit diffusion and limit installation of catalytic sites. A focus of this work is to develop an effective and reproducible method for producing smaller, phase-pure NU-1000 particles. Small, uniform particles would also facilitate high-resolution imaging via electron microscopy. Data will be presented showing that the particle size varies with a number of factors including water concentration, NaOH concentration, and reaction time and temperature. Unfortunately, a reduction in particle size is generally accompanied by reduction of NU-1000 content and increase in NU-901 content. The relationship between particle size and phase will be discussed within the context of particle nucleation and growth.

High-angle annular dark field images of the typical NU-1000 particles exhibit enhanced brightness at the center of the particles, which means they are structurally heterogeneous. Images obtained using higher collection angles do not exhibit the same brightness at the center of the particles, which means that this contrast is most likely due to diffraction contrast. Such contrast is consistent with strain. One possibility is that the particle centers contain NU901, which would result in strain at the NU-901 / NU-1000 interface. Ongoing work is focused on detailed characterization of the structural difference between the centers and the rest of the particle as well as synthesizing phase-pure NU-1000 for direct comparison.

The third focus of this research is the characterization of NU-1000 before and after chemical modification. Using scanning transmission electron microscopy with energy dispersive X-ray spectroscopy, we characterize the distribution of elements throughout the particles after modification. In the case of nanocasting with silica, the silica seems uniformly
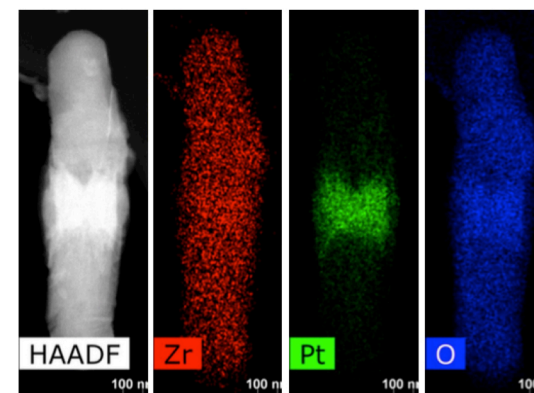
distributed throughout the NU-1000 particles. Interestingly, the installation by atomic layer deposition of catalytically active species (e.g., Pt, Pd, Co, Zn…) occurs preferentially at the particle centers, with sometimes more than an order of magnitude higher loading in the particle center as compared to the rest of the particle. Future experiments and advanced characterization will further probe the differences between the center and the rest of the particle.

Metal exchange in the zirconia node of NU-1000 for catalysis

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Metal exchange can be employed to modify the chemical properties of metal-organic frameworks (MOFs) without altering their topology. By retaining the initial framework, the resulting material can show different properties compared with its parent structure. This is especially useful to design novel catalysts by chemically changing selected active sites of the materials. Herein we report the results of a combined computational study, based on density functional theory calculations, and experimental study on the mixed Sn/Zr structure of NU-1000 obtained by partially substituting Zr^{4+} in the oxozirconium clusters with Sn^{4+}. Our results show that either one or two zirconium atoms in the metal node can be replaced as confirmed by SEM-EDX and FT-IR measurements.

Correlation and Holes: Visualizing Electron Correlation as a Function of Active Space

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Electron correlation arises from the constraint that electronic wave functions be antisymmetric with respect to the interchange of electrons and from the tendency of electrons to avoid one another due to Coulomb repulsion. The former effect is called Fermi correlation, and it affects electron pairs with the same spin; and the latter effect is called Coulomb correlation, and it affects both same-spin pairs and opposite-spin pairs. Coulomb correlation gives rise to the Coulomb hole, which is a region around a given electron where the probability of finding another electron is less than in the independent-particle model. Similarly, Fermi correlation can be visualized in terms of a region, called the Fermi hole, of significant depletion of same-spin electrons around a given electron. In Hartree–Fock theory, it is assumed that each electron interacts with an average charge distribution due to the other $N-1$ electrons, and therefore Hartree–Fock theory lacks Coulomb correlation. However, this kind of correlation is included in multiconfigurational calculations, such as complete-active-space self-consistent-field theory.

In this study, we analyze the effects of electron correlation on the pair density in molecules in terms of Fermi holes and Coulomb holes. The long-term goal of this study is to understand the dependence of the pair density on molecular geometry and on the choice of active space in order to design on-top density functionals to use with systematic active space choices in multi-configuration pair-density functional theory.

Catalytic Behavior of Few-atom Metal Sulfide Clusters Deposited Within the Metal–Organic Framework NU-1000

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The reactivity of transition-metal sulfides is often governed by the density of their coordinatively unsaturated metal sites. Given the exceptional chemical and thermal stability of Zr-based metal–organic frameworks (MOFs), paired with their well-isolated and well-defined grafting sites in the form of –OH and $-OH_2$ ligands on the zirconium oxide nodes, these high surface area materials afford a perfect scaffold for the deposition of structurally well-defined few-atom metal sulfide clusters.

Herein, complimentary deposition methods (solvothermal deposition in MOFs = SIM, and atomic layer deposition in MOFs = AIM) are used to synthesize Co, Cu, and Ni sulfide clusters in the MOF NU-1000 *via* a two-step process: anchoring metal ions and subsequent exposure to H_2S. These MOF-supported metal sulfides are explored for their propensity to photocatalyze hydrogen evolution in a pH 7 buffered aqueous solution, indicating both metal identity and deposition method affect the reactivity. Under UV light irradiation, hydrogen evolution activity follows the trend Ni>Cu>Co for both AIM and SIM materials.

A single-metal MS_x-AIM-NU1000 ((M = Co, Ni, and Cu) cluster model was developed computationally in order to study the catalytic hydrogen evolution reaction described above. The catalytic formation of hydrogen requires the addition of two protons and two electrons in some order, resulting in seven potential intermediates (labeled **A** – **I** in Figure 1c). Current calculations on structures of **A** to **I** and the TS for H_2 formation predict a trend of Co<Cu<Ni in catalytic efficacy. This result only partially agrees with the experimental trend, potentially indicating the necessity for a more complex model.
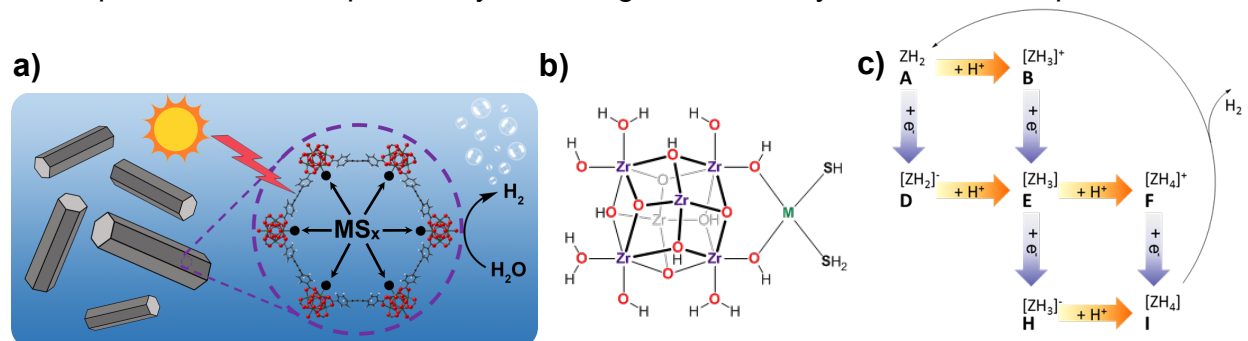

Figure1. a) Photocatallytic hydrogen evolution from water using MOF-supported metal sulfides, b) Single-metal cluster mode, c) Pourbaix diagram for catalytic hydrogen evolution.

DFT Study of MOF-Node as Support for Tungsten Metathesis Catalyst

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Typical heterogeneous catalysts for olefin metathesis are Mo, Re, and W species supported on oxides such as silica, alumina, and silica−alumina surface. Metal oxide or silica supports are terminated by surface hydroxyl and oxo groups. It is significant to understand the reactivity of a support surface toward reactive inorganic species, in order to synthesize heterogeneous catalysts using a molecular strategy.

Similar the surfaces of silica or metal oxide, the hydroxyl and oxo groups on Metal−organic frameworks (MOF) nodes can also provide sites for binding of organometallic catalyst precursors. Previously, such nodes (for instance, NU-1000 or UiO-66) have been used as catalyst supports that are comparable to metal oxides and zeolites. In this work, we focus on investigating the possibility that whether the MOF with Zr-node (NU-1000) can be act as a good support for tungsten species, aiming at synthesizing single-site catalyst for olefin metathesis reactions.

Using a previously reported molecular tungsten precursor, we first evaluated the NU-1000 node as a support for tungsten species. However, we found that the μ^3-OH group on NU-1000 node is poison to the metathesis active site due to facile hydrogen transfer from μ^3-OH to the carbene carbon. Considering that pre-decoration of NU-1000 with tri-valent metals (such as Al, In) could remove the H atom of the μ^3-OH group, we then investigated deposition of tungsten precursor on NU-1000 node pre-decorated with Al, In, Sc and Y, respectively, and found that NU-1000 modified by yttrium could be a good candidate for deposition of tungsten species.

Towards an Understanding of Supported Metal Oxides and Sulfides for Chemicals Synthesis

Justin Notestein, Northwestern University

Oxide catalysts are critical materials for a number of transformations that synthesize important commodity chemicals, and metal sulfides are beginning to attract attention as catalysts for reactions beyond their traditional domain of fuels hydrotreating. Research in the Notestein group seeks to better control and understand the catalytic surfaces of these materials through novel syntheses, probe molecules, and reaction modes. Two short vignettes on current developments will be described.

In the first area, we describe continuing efforts at creating and characterizing extremely highly dispersed metal oxide sites from groups IV-VI on silica and other conventional oxides,[1] and the nodes of MOFs,[2] principally for epoxidation, hydrolysis, and oxidative dehydrogenation. Additional insight is gained by employing novel site titration techniques[3] and by comparing materials with the same active site but different support environments, such as Nb-SiO$_2$ vs. Nb-MOF or an activated MOF vs. a supported Zr-SiO$_2$. Similar strategies are utilized for understanding and controlling the reactivity of clusters of redox-active oxides, which is known to be strongly dependent on structure. For example, we demonstrated that the precursor effects are significant in the first-ever report of Cu-catalyzed oxidative dehydrogenation of alkanes.[4]

In the second area, progress is reported on utilizing metal sulfides for reactions of interest to large-scale commodity chemicals. Others have reported that unsupported metal sulfides are active for methane oxidation with sulfur and for the direct dehydrogenation of alkanes.[5] As part of a larger project investigating sulfide catalysts for carbonylation,[6] we have demonstrated good activity for alcohol dehydrogenation over metal sulfides,[7] and are applying site-specific CO chemisorption to better understand the catalytic relevance of different surfaces in highly defected metal sulfides.

Overall, it will be shown how advances in materials synthesis can lead to improved understanding and breakout reactivity even in this very mature field of research.

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Mechanistic studies of heterogeneous catalytic systems: A case study on partial oxidation of light olefins

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Our research is focused on developing mechanistic and kinetic descriptions of catalytic chemistries involved in the conversion of natural gas, petroleum, and biomass-derived feedstock to energy carriers and polymer precursors. Specifically, we inquire the identity and reactivity of surface intermediates, the accessibility and reactivity of active sites, and the kinetic-relevance of elementary steps. On-going research in our program is focused on examining reaction pathways for (i) conversion of methanol to chemicals and transportation fuels, (ii) dehydrogenation and reforming of alkanes, (iii) partial oxidation of olefins to oxygen-containing molecules, and (iv) hydrodeoxygenation of biomass-derived monomers.

Case study on topic (iii)

We will describe the mechanistic origins of over-oxidation and C-C bond scission products in the partial oxidation of propylene to acrolein on mixed metal oxide catalysts. The complexity of multi-component oxidic formulations and the trace quantities (<10% total on a carbon basis) of acetaldehyde, acetic acid, acetone, acrylic acid, ethylene, butadiene, benzene, CO, and CO_2 that are formed as by-products have precluded so far a firm mechanistic understanding of structure-function correlations for this chemistry. We illustrate the detailed reaction network for this chemistry and develop a kinetic model that quantitatively describes the formation and consumption of all observed products.

New applications of early transition metals in catalysis

Ian Tonks

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The Tonks lab is designing early transition metal redox catalytic reactions for the synthesis of complex molecular architectures from simple precursors. The challenge of utilizing early transition metals for redox processes is that they typically do not undergo facile oxidation state changes because of the thermodynamic stability of their high oxidation states. As a result, we are exploring outside-the-box strategies for facilitating redox reactions at early transition metal centers. This talk will center on our recent results that capitalize on a unique oxidant, azobenzene, to access Ti(II)/Ti(IV) redox cycles that catalyze diverse oxidative coupling reactions to yield synthetically useful heterocycles and other products. Additionally, future plans involving alkane metathesis on MOF-supported early transition metal catalysts will be discussed.

Multiconfiguration Pair-Density Functional Theory: Affordability and Accuracy in Multireference Calculations

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For many cases an accurate description of chemical process from quantum chemical computation requires the application of multireference methodologies. Many current multireference methods, however, have unfavorable scaling or limited scope which can often restrict their use. Mulitconfiguration pair-density functional theory (MC-PDFT) is a new approach which combines a multireference wave function calculation with a special density functional, an on-top pair-density functional, generating a method that is both accurate and affordable. The improved scaling of MC-PDFT allows for calculations to be performed on much larger systems, including arbitrary spin and excited states. We perform a series of calculations to illustrate the time and memory cost as a function of active space size. We show that the MC-PDFT method is able to obtain results which are as accurate as those obtained from multireference perturbation theory at a significantly lower cost. We apply the MC-PDFT method to the calculation of the heterolytic dissociation enthalpy of ferrocene, and we find that MC-PDFT can obtain results that are within experimental accuracy and stable with respect to basis set selection.

Ir Complexes Deposited on Al(III) Decorated Nu-1000: A Highly Selective Catalyst for Ethylene Hydrogenation and Dimerization

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Metal organic frameworks (MOFs) are porous coordination materials formed by connection of inorganic metal oxide nodes with using organic linkers in a regular fashion. The structure and hence properties of MOFs can be readily tuned through the choice of different metal atoms and also organic linkers. This diversity in structure has led to very promising applications in MOFs for example in gas adsorption/separation, catalysis and so on.

Nu-1000 with $[Zr_6 (\mu_3\text{-O})_4 (\mu_3\text{-OH})_4 (OH)_4 (OH_2)_4]^{8+}$ metal oxide nodes and eight tetra-topic organic linkers of 1,3,6,8-tetrakis (p-benzoic acid) pyrene (H4TBPy) forms triangular and hexagonal pores. Eliminating one of the NU-1000 organic linkers opens up a site with dangling hydroxo and aqua groups ready to be coordinated to another metal complex for catalytic purposes.

In this computational study using DFT M06-L functional, complexes of Ir deposited on hydroxylated Al(III) modified NU-1000 MOF will be studied for catalytic hydrogenation and dimerization of ethylene. Comparisons with previous results with no Al(III) will shed light on the role of Al(III) ions in enhancing selectivity and reactivity in the abovementioned transformations.

Reaching consensus on the structural nature of the nickel sites within NU-1000

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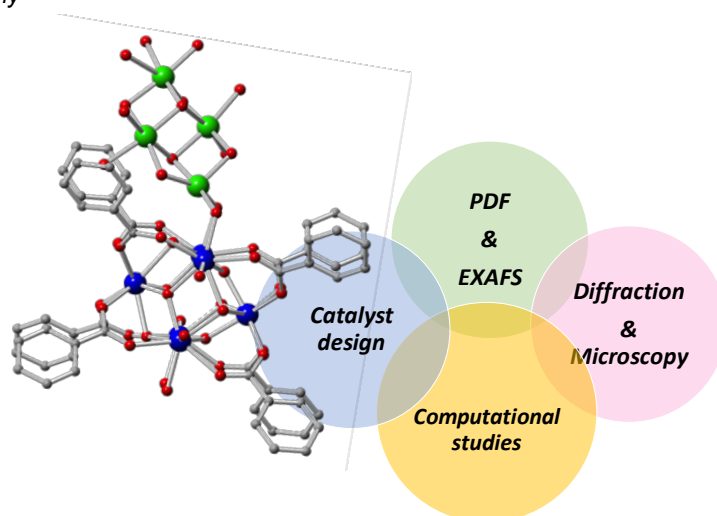
Multidisciplinary approach used within ICDC to study the Ni-NU-1000 system.

Ni-NU-1000 was the first catalytic system developed within ICDC through atomically-precise AIM (namely, atomic layer deposition in metal-organic frameworks) methods. This material is a very efficient and sintering-resistant gas-phase hydrogenation and dimerization catalyst.[1] The structural nature of the nickel sites on the active catalyst has been studied by using a wide variety of characterization techniques (including electron microscopy, X-ray diffraction, scattering (PDF) and absorption (EXAFS)) as well as computational methods available within the EFRC. These tools revealed a slightly different picture than original envisaged, evidencing a much richer structural variety of the metal-oxide clusters deposited *via* AIM on NU-1000 than expected. In light of all the knowledge gained on the Ni-NU-1000, are we reaching consensus about the *real* structure of these nickel clusters? Our findings provide a better understanding of the structure of the AIM-deposited clusters within NU-1000 and may be critical to deposit other transition-metal sites, such as copper or cobalt.

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