Catalytic Activity of Porphyrin-Supported Iron Oxide Clusters for Methane Oxidation

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Current environmental concerns and the rising cost of fossil energy are driving the search for cleaner alternative feedstocks for chemical production with lower carbon dioxide emissions. The escalating production of natural gas is evidence that shale gas reserves surpass those of oil, and therefore, natural gas is likely to become one of the main sources of carbon-based chemicals in the next century. Methane monooxygenase (MMO), an enzyme found in biological systems, is capable of oxidizing methane to methanol using O_2 at mild conditions. MMO has two different forms: (1) particulate MMO (pMMO), which is postulated to have a dicopper-oxo active site, and (2) soluble MMO (sMMO), which contains a diiron site.[2] The identification of different iron and copper sites in these enzymes has inspired the synthesis of catalysts that mimic their activity towards the partial oxidation of methane.[3]

Using density functional theory, we have studied the catalytic activity of iron oxide nanoclusters that can be grown via atomic layer deposition (ALD) on a porphyrinic substrate and mimic the structure of the active site in the enzyme for the oxidation of methane to methanol. The porphyrin-supported iron oxide active site consists of an $Fe^{IV}_2(\mu\text{-}O)_2(OH)_2$ diamond core supported by a bridging $Al^{III}(\mu\text{-}O)_2(OH)$ moiety. After a series of ALD cycles to deposit the Al atom and the Fe^{II} sites on the porphyrin substrate, the bridging oxygen atoms that initiate the catalytic cycle can be incorporated via O_2 or N_2O activation. Two mechanisms for the oxidation of methane using the $Fe^{IV}_2(\mu\text{-}O)_2(OH)_2$ active site and N_2O as the oxidant are proposed: (1) a concerted mechanism in which the C-H bond is cleaved heterolytically and (2) a rebound mechanism in which a bridging oxygen or a terminal oxo group abstracts a hydrogen atom from methane. Our preliminary computational results show that the rebound mechanisms are more likely to occur due to lower activation barriers of about 70 kJ/mol. We also find activation barriers between 100-120 kJ/mol for N_2O activation and CH_3OH desorption. Population analysis reveals the addition of electrons from C-H activation and CH_3OH formation to the lowest unoccupied molecular orbitals (LUMOs). Furthermore, the highest occupied molecular orbital (HOMO) has a significant contribution from the p orbitals of the oxygen active site. Understanding the nature and electronic structure of the active site can help us identify possible reactivity descriptors for the most important steps of the catalytic cycle (C-H activation and N_2O activation) for a series of ALD-grown metal oxide clusters.

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A Computational Investigation of Ethylene Dimerization and Hydrogenation Mechanisms on Iridium Deposited NU-1000 and UiO-66

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Metal-organic frameworks (MOFs) are crystalline, nanoporous materials built by a combination of metal nodes and organic linkers. They may provide great opportunities for many areas such as catalysis, gas storage/separation, sensing etc. due to their highly versatile structures since there are almost infinitely many structures that can be formed from numerous inorganic and organic building block combinations.

Recently, it has been shown by experimentalists that metals can be precisely inserted on MOFs using a technique called atomic layer deposition (ALD). This technique, ALD in MOFs (AIM)[1], opens a way for the synthesis of catalytically active materials possessing uniform active sites and support which are relatively facile to characterize.

It is known that Zr based MOFs have high structural stability due to strong Zr-O bonds. This computational study focuses on two such MOFs, NU-1000 and UiO-66, to study the mechanisms of ethylene dimerization and hydrogenation on them using density functional theory (DFT) with M06-L functional[2]. The MOF clusters are carved from their DFT optimized periodic unit cells and truncated with acetate groups. Several reaction mechanisms have been characterized not only by comparing the activation energies but also contrasting them with experimental selectivities. To better comprehend the local structure, CO stretching frequencies are computed for $Ir(CO)_2$ deposited structures and compared with experimental IR frequencies. Lastly, thanks to EXAFS measurements, the interatomic distances in the DFT models and experimental samples have been contrasted to understand the level of agreement between the structures.

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Semi-hydrogenation of alkynes using a MOF based heterobimetallic catalyst

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A pervasive goal in chemistry is to discover new ways to utilize transition metals as catalysts for selective chemical transformations. In principle, catalysts featuring multiple metals in close proximity may exhibit selectivity profiles that are different from their monometallic counterparts. Our lab investigates bimetallic catalysts featuring two metals where an active metal centre is electronically tuned by a second metal via metal-metal interactions. The enforced proximity between the metal centres facilitates strong electronic coupling which has resulted in unprecedented modes of reactivity that are powerful and selective.[1] Furthermore, we are interested in building well-defined heterobimetallic clusters onto a heterogeneous metal organic framework (MOF) support. MOFs provide a highly tuneable platform for integrating catalytically desirable properties, including high surface area, porosity, recyclability, and crystallinity. Our approach to functionalize MOFs relies on using a preassembled bimetallic unit to deliver two metals of choice in a controlled fashion.[2]

By employing a simple solution-based technique we were able to graft a rhodium-gallium bimetallic complex onto the node of NU-1000, a MOF known for its high thermal stability and large pore size distribution.[3] XAS studies confirm that the bimetallated MOF features a Lewis acid (Ga)-transition metal (Rh) interaction and several characterization techniques independently demonstrate that the active sites in the bimetallated MOF are homogeneous in nature. Interestingly, this bimetallic system is an efficient catalyst for *(E) selective hydrogenation* of a wide variety of alkynes. However, in the absence of the Lewis acid, the surface immobilized rhodium-only species over-hydrogenates alkynes to alkanes. Overall, this talk showcases our efforts at exploiting transition metal-Lewis acid interactions in a heterogeneous MOF support to achieve selective hydrogenation of alkynes.

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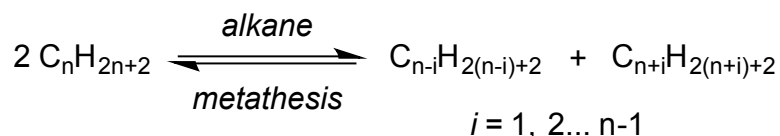
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Deposition of Organometallic Tungsten Precursors on NU-1000 for Alkane Metathesis

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Alkane metathesis is a reaction that directly transforms a given alkane into its higher and lower molecular weight homologues (Figure 1).[i] This is a critically important reaction when considering petrochemical feedstocks: a significant amount of the carbon feedstock is either too low or too high in carbon count for effective use as a chemical fuel or feedstock, and thus is wasted or used as a low-value stock. Alkane metathesis represents a potential route to homologation of these simple precursors to more useful feedstocks such as diesel fuel. The majority of alkane metathesis catalysis has been carried out by Bassett on single-site catalysts consisting of metal (typically Ta and W) hydrides that were developed out of surface organometallic chemistry (SOMC)-modified oxides such as SiO_2 and Al_2O_3.

$$2\ C_nH_{2n+2} \xrightleftharpoons[\text{metathesis}]{\text{alkane}} C_{n-i}H_{2(n-i)+2}\ +\ C_{n+i}H_{2(n+i)+2}$$

$$i = 1,\ 2...\ n-1$$

NU-1000 provides an ideal support for alkane metathesis chemistry as its well-defined node surfaces will allow for homogenous catalytic sites and protic residues will allow for facile deposition of metal alkyl species. Accordingly, we have prepared a variety of different organometallic tungsten precursors for their solution phase deposition on NU-1000. Tungsten alkyl species such as $W(=O)Cl(Np)_3$, $W(=O)Np_4$, $W(CC\text{-}tBu)(Np)_3$, and $W(Me)_6$ were prepared and depositions attempted. Surprisingly, all precursors showed minimal loading ($<1W/Zr_6$) by SEM-EDS. However, tungsten amide based precursors, $W(NMe_2)_2(NPh)_2$ and $W_2(NMe_2)_6$, can be easily depostited on NU-1000 via solution phase deposition giving loadings of $\sim 3W/Zr_6$. Both materials maintain the integrity of NU-1000 (pXRD) and show decreased pore volume (BET), consistent with metal deposition. We are currently investigating the hydrogenation of these materials to achieve tungsten hydrides, our desired precatalysts for alkane metathesis. Other precatalysts such as tungsten halides and carbonyls will be investigated as well, where reactions with silanes and hydrogen, respectively, could allow for hydride generation.

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

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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] Very 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. 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 so called multiconfigurational calculations.

In this contribution we focused on the use of multiconfigurational quantum methodologies for analyzing the electronic structure of the cluster model with two cobalt atoms and the models with same valent dopants (Ni, Fe, Cu, Zn), starting from DFT structures. Owing to the large active space required to accurately describe the electronic structure, we used the RAS (restricted active space) approach. For recovering the dynamic correlation, we employed RASPT2 (when affordable) and MCPDFT[3] in top of the RASSCF wavefunction. The activation barriers, spin states energetics as well as descriptors for this catalysis have been analyzed and directly compared with previous DFT studies.

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Development of Heterobimetallic Precursors toward Preparation of Lewis Acid-Modified Group 10 Single Sites on NU-1000

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Previous work in the Lu group has demonstrated the ligand N,N,N-tris[2-(2-pyridylamino)ethyl]amine (L) as a useful scaffold for the controlled solution-phase deposition of isolated bimetallic moieties onto the nodes of NU-1000.[1] The NU-1000 support was shown to impart good site isolation, improved recyclability and thermal stability while maintaining catalytic activity and accessibility to substrate molecules. Subsequent calcination of the metal-organic framework-supported precursors in air has allowed access to catalytically active mixed-metal oxide single sites.

Recent efforts have turned toward the preparation of a series of new bimetallic precursor complexes featuring a group 10 metal (Ni, Pd, Pt) coupled with a redox-inert secondary metal such as Zn or Sn. Supported group 10 metal sites are targeted as potential catalytic species for the partial hydrogenation of alkyne substrates. The presence and variation of a secondary metal in close proximity to the active metal is proposed as a handle for tuning the selectivity of these materials.

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Quantum Monte Carlo Calculations of Energy Barrier Heights

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An important aspect of rational and predictive design of catalytic systems is the ability to accurately calculate energy barriers of key reaction steps in the reaction chain. Such calculations can be done accurately, once the correct initial, transition, and product states and their geometries have been identified using quantum chemical methods. However, such methods rapidly become prohibitively expensive for reasonably large systems as the computational cost grows as N^6. Quantum chemical methods are certainly not possible for investigating the catalytic activity of Zr_6 nodes decorated with transition metals in the NU-1000 metallorganic framework (MOF). Instead, various flavors of density functional theory (DFT)-based methods are used, in which the exchange and correlation interactions are treated very approximately, and these approximations become especially questionable for transition metals. In contrast, Quantum Monte Carlo (QMC) methods treat the electron-electron interactions exactly using stochastic methods to minimize the energy by sampling the many-body wavefunction. Recent advances in algorithms and hardware have made QMC methods applicable to real chemical and solid state systems, and the results are typically accurate to beyond chemical accuracy.

We have used QMC to calculate energy barriers between reaction state (RS), transition state (TS), and product state (PS) for ethylene hydrogenation on single-Ni decorated Zr_6 nodes in the NU-1000 MOF. As input, we use geometries obtained and optimized using DFT with truncated benzoate linkers[1]. We compare the results obtained from QMC (in particular diffusion Monte Carlo) with different generalized gradient and range-separated hybrid functional approximations for the DFT exchange-correlation functional. The energy barriers in DFT range from about 0.19 eV to 0.29 eV for the RS➔TS reaction, and from 0.72 eV to 0.90 eV for the TS➔PS transition (with PS having lower energy). In contrast, the corresponding values obtained from diffusion Monte Carlo are 0.64 eV and 0.47 eV with error bars of 0.1 eV. This means that the DFT error is about 0.4 eV or about 9 kcal/mol – significantly larger than chemical accuracy. DFT significantly underestimates the RS➔TS energy barriers, which will lead to exponentially large errors in the reaction rate.

We are presently working on obtaining QMC RS➔TS energy barriers for a number of metal-decorated Zr_6 nodes[2], and we will present results in the near future.

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Theoretical Insights into Selective Oxidation of Methane to Methanol on Porphyrin-supported Copper Oxide Nanoclusters

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In nature, methane can be converted to methanol in a single step under mild conditions by methane monooxygenase (MMO), an enzyme found in some bacteria. In the industry, methane-to-methanol conversion is a multi-step, high temperature and pressure process that requires large-scale operations. Such sharp existing contrasts in the era of ubiquitous natural gas/methane production have inspired us to follow nature's footstep to achieve more efficient utilization of this resource. In this regard, it was discovered that Cu-exchanged zeolites composed of similar active sites to those of particulate MMO can selectively oxidize methane to methanol at low temperature.[1] More recently, copper oxide nanoclusters grown by atomic layer deposition (ALD) on metal nodes of NU-1000 metal-organic framework (MOF) have shown catalytic activity for the same reaction.[2] Although these findings are encouraging, low methane-to-methanol conversions are generally observed among the aforementioned systems and therefore necessitate further research and development in this area.

In the spirit of employing MOFs for catalysis, we want to explore the possibility of forming copper active sites on organic linkers for selective oxidation of methane to methanol. In comparison to a metal node as a substrate, an organic linker such as porphyrin can be metallated to provide a single nucleation site[3] and may allow for more control over the subsequent Cu-ALD steps. In this work, we examined the prospect of using ALD-grown copper oxide nanoclusters on porphyrins for selective methane-to-methanol oxidation by means of theoretical calculations. Ab initio thermodynamic analysis indicated that an active site in the form of Cu(μ-O)Cu can be stabilized under dry oxygen activation conditions at 437 K. Furthermore, a feasible methane activation energy barrier (E_a = 54 kJ/mol) was observed, and hydrogen abstraction activity could be attributed to the radical character of the bridging oxygen in the active complex. Methanol extraction in this system is limited by a thermodynamic barrier of ΔG^{473K} = 57 kJ/mol; however, it can be facilitated by the presence of water. Overall, our results indicate similar catalytic activity between porphyrin-supported copper oxide nanoclusters and existing Cu-exchanged zeolites and provide a computational proof-of-concept of using functionalized organic linkers for selective oxidation of methane to methanol.

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Towards Single-Site Catalysts: Achieving a Simpler Node Structure in NU-1000 via Active Site Blocking Approach

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Recently, functionalization of a high surface area support, Zr-based metal-organic frameworks (MOFs), has attracted much attention for applications in heterogeneous catalysis owing to their thermal/chemical stability, high surface area, as well as potential for sinter-resistance. Among various routes to functionalize MOFs, a vapor phase approach utilizing atomic layer deposition (ALD), a process we refer to as AIM (ALD in MOFs) herein, offers several distinct advantages over conventional approaches such as site-specificity and spatial uniformity.

While AIM presents a versatile approach to functionalizing MOFs, NU-1000 reacts in numerous and complex ways under a wide range of ALD conditions. For example, a high density of functional groups in NU-1000 generates a significant amount of heat which ultimately causes node distortion and/or metal migration. Furthermore, we cannot completely rule out the possibility of precursor insertion at the linkers. As such, we seek to achieve a rational synthesis of size-selected clusters by generating a simpler node via selective active site blocking approach. In an idealized scheme, the approach utilizes a blocking agent (e.g. alcohols, acetylacetone), which is introduced prior to the metal precursor to passivate certain functional groups. Once passivated, the metal precursor is only able to react with unpassivated functional groups. Finally, introduction of H_2O removes not only the ligands from the precursor, but also the blocking agent.

With the introduction of blocking agents, we not only see a decrease in the metalation, but we also see a wide range of –OH stretches associated with ZnO utilizing different blocking agents based on the in situ FTIR data. With the use of complimentary blocking agents (e.g. methanol and acetylacetone), we anticipate achieving a much simpler node for the AIM process paving the way for the synthesis of a truly single-site catalyst.

Fine-Tuning the Activity of Metal–Organic Framework-Supported Cobalt Catalysts for the Oxidative Dehydrogenation of Propane

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Few-atom cobalt-oxide clusters, when dispersed on a Zr-based metal–organic framework (MOF) NU-1000, have previously been shown to be active for the oxidative dehydrogenation (ODH) of propane at low temperatures (< 230 °C), affording a selective and stable propene production catalyst. In our current work, a series of promoter ions with varying Lewis acidity, including Ni(II), Zn(II), Al(III), Ti(IV) and Mo(VI), are anchored to NU-1000 via solvothermal deposition in a MOF (SIM) followed by incorporation of Co(II) ions in the support via vapor-phase atomic layer deposition (ALD) in a MOF (AIM). This process leads to the formation of a series of NU-1000-supported bimetallic materials. Using difference envelope density (DED) analyses, the location information for the promoter and Co ions in the materials are determined. The SIM-anchored promoter ions are in between the two Zr_6 nodes along the c axes for all samples whereas the location of the AIM-anchored Co ions vary. They grow (1). selectively on the promoter sites when Ni/Al/Ti ions are used; (2). exclusively on the Zr sites when Mo is used; (3). both the Zr and promoter sites in the Zn case. These NU-1000-supported bimetallic materials are active for the propane ODH process upon activation, where the Co component is demonstrated to be exclusively responsible for the observed catalysis. The catalytic activity decreases in order of Ni(II)>Zn(II)>Al(III)>Ti(IV)>Mo(VI), in accord with the decreasing Lewis acidity of the promoter ions. In-situ X-ray absorption spectroscopy at the Co K-edge indicates a slight reduction in the coordination number of the first coordination shell of the cobalt sites and the appearance of Co(III) during catalysis for all five samples. As evidenced by cyclic voltammetry, the onset potential for the appearance of Co(III) in these samples shifts anodically as the Lewis acidity of the promoter ion increases. The ease of accessibility of Co(III) is proposed to affect the formation of a Co(III)−O• species involved in the rate-determining step in the catalytic cycle, which accounts for the fine-tuning of the propane ODH catalytic activity.

Tuning Catalytic Reactivity and Selectivity of MOF-Supported Nickel through Electronic Effect of Modified Ligands

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Ni-oxo clusters, when supported on a Zr metal–organic framework (MOF), NU-1000, are active for gas-phase ethylene hydrogenation and oligomerization reactions upon activation. Mechanistic investigation via computational modeling implies the critical role of the electronic structures of Ni (II) sites in controlling catalytic activity and product selectivity (ethylene oligomerization).

In this work, we focus on tuning the electron environment around the Ni (II) center in the similar vein to the approach used in homogeneous catalysis, where a highly electron-withdrawing ligand, hexafluoroacetylacetone (Facac), was introduced to NU-1000 via atomic layer deposition (ALD) in a MOF (AIM) before Ni ions were deposited the same way to produce Ni-Facac-AIM-NU-1000. The binding mode of the Facac ligands in the MOF was determined via single crystal X-ray crystallographic studies whereas the Ni ions were located via differential electron density (DED) map study, from which both species were shown to be attached to the Zr_6 nodes. The resulting material was subsequently tested for gas-phase ethylene hydrogenation where a decreased catalytic activity was observed as compared to Ni-AIM-NU-1000 presumably due to the strong electron-withdrawing ability of the Facac ligands. This observation prompted us to use it for ethylene oligomerization in aim of higher selectivity towards the C4 products. With a lower activity, Ni-Facac-AIM-NU-1000 is shown to be more selective towards C4 products upon activation, which is well explained by computational modeling. The results presented herein reiterate the important roles of the electronic structure of the active sites play in controlling the catalytic activity/product selectivity of heterogenous catalysts and highlight the ease of modifying it in MOF-supported catalysts.

Hydrolysis of Chemical Warfare Agents on Metal Organic Frameworks

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Accurate quantum mechanical calculations are performed using both periodic and cluster models for computing reaction mechanism of hydrolysis of chemical warfare agents on a wide variety of water stable/soluble Zr metal organic frameworks (MOFs). The goal of this study is to establish possible trends which might be useful in designing new effective heterogeneous catalysts. We also aim to investigate accuracy of using cluster *vs.* periodic models for studying the hydrolysis reaction. Results of this study are central in appreciating the role of O-H groups in ever-expanding applications of these 3D crystalline materials.

Pushing the limits on NU-1000 as a catalyst support

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In the past year, two projects have advanced the use of NU-1000 towards more aggressive reaction conditions characteristic of current hydrocarbon processing. Under these conditions, the NU-1000 supported catalysts are well-defined models for ill-structured conventional catalysts and can present paths for new reactivity. In the first project, strongly acidic tungsten oxide polyoxometallates (POMs) were loaded into NU-1000 and used in the catalytic isomerization of o-xylene. Industrially, a number of strong solid acids are used for this reaction, but the reactivity of WOx/ZrO_2 has been shown to be strongly dependent on the surface density of the WOx. Thus, WOx/NU-1000 offers opportunities to understand these commercial catalysts through well-defined analogues. The MOF-supported catalysts are stable at temperatures exceeding 250°C, and are only active when synthesized with the POM precursor – AIM or SIM gives 'isolated' W sites by EXAFS and does not give an active catalyst – consistent with predictions from conventional catalysts. Finally, the MOF-supported catalysts are unusually active for transmethylation to toluene and trimethylbenzene, which may be a consequence of the NU-1000 pore structure.

In the second project, we are beginning to investigate the ability of metal sulfides, and specifically MoS_2, to catalyze alkane dehydrogenation. While a critical reaction for alkane dehydrogenation, it has not been studied to any significant extent over metal sulfides. The dehydrogenation of isobutane to isobutene has quantifiable rates at 360°C over various morphologies of MoS_2, including materials prepared by deposition within NU-1000. In spite of a reaction temperature at the upper limit of thermal stability of the MOF, reaction rates decrease minimally over several hours TOS and display rates per Mo atom comparable to MoS_2 dispersed on purely inorganic matrices. MoS_2 is a particularly complex structure under catalytic conditions, so again, the MOF support presents opportunities for increased understanding through the synthesis of well-defined materials.

Screening Supported Nanocatalysts for Ethene Conversions

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One of the major challenges in catalysis research is finding novel catalysts that are active and selective for the conversion of light hydrocarbons from shale gas into liquid products. Currently, the largest drawback for converting natural gas into liquid fuels is that it requires steam reforming, which is a high-temperature / high-pressure process. Thus, a primary goal of realizing the full utility of shale gas is developing technologies that convert natural gas into liquid fuels in energy-efficient ways. Our groups and others have demonstrated that catalysts comprised of a small number of transition metal cations are promising for natural gas upgrading. Particularly, our group has focused on single-site transition metal cation catalysts supported on the nodes of the meta–organic framework (MOF) NU-1000. To determine optimal or novel catalysts, density functional theory-based computational screening was applied to nanocatalysts comprising one or two transition metal cations for the upgrading of ethene. We identified descriptors of catalytic activity and use them in microkinetic modeling to identify the descriptor values that maximize the production rate of ethene conversion reactions. Formation energies of co-adsorbed hydrogen and ethene (i.e., $(H/C_2H_4)^*$) were identified as catalytic descriptors for dimerization and hydrogenation reactions. For ethene dimerization the formation energy of adsorbed ethyl (i.e., $C_2H_5^*$) was additionally used as a descriptor, while for ethene hydrogenation, co-adsorbed dihydrogen and ethyl (i.e. $(H_2/C_2H_5)^*$) was used.

Localizing catalyst-substrate interactions in NU-1000 catalysts

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The interaction of molecules at active sites is key to the catalytic activity and mechanism of heterogeneous catalysts, including metal-organic frameworks (MOFs). For a series of modified NU-1000 catalysts with different activity for the hydrogenation of ethylene, we compare the interactions of the molecular substrate and product within the lattice using structure envelope analyses of synchrotron powder X-ray diffraction (XRD) data. *In-situ* XRD data was collected under exposure to ethylene and ethane at different temperatures relevant for catalysis, for two different supports (i.e. bare and Facac-NU-1000, where Facac: fluoroacetylacetonate) and their Ni-analogues.

Through difference envelope density (DED) analysis of these data, we demonstrate that the catalytic activity of these Ni-MOFs is correlated to the proximity of the reactant to the framework surface; for the most active catalyst (Ni-NU-1000), the closest reagent-Ni interaction is observed (Figure 1). The molecular reagent/substrate interacts more strongly with the catalytic sites than the molecular product, based on the temperature series. Based on the closest/strongest adsorption site for the molecular reagent, the results suggest that the active site might be associated with the face of the nickel cluster. The presence of withdrawing electron ligands within the Zr_6-nodes hinders the interaction of ethylene with the Ni-oxo clusters. This observation helps explain the slower catalytic activity determined for this system, compared to Ni-NU-1000.
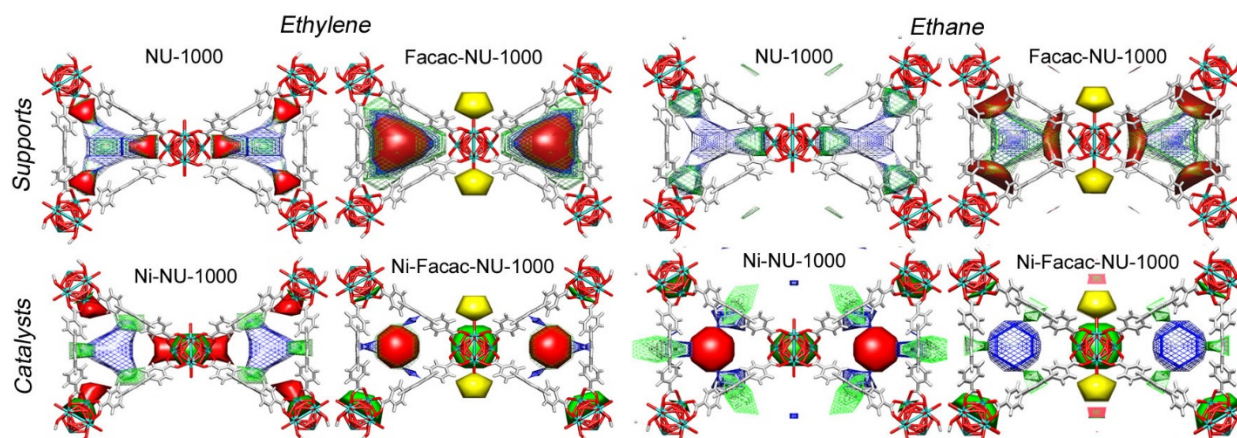
DEDs: location of the gases at 40 °C, 80 °C anc 100 °C. shown in blue, green, and red, respectively.

Figure 1. Representation of the triangular pores within NU-1000 viewed perpendicular to the c axis. The yellow and green surfaces represent the location of the Facac ligands and the Ni-oxo clusters within the NU-1000 framework, respectively.

Computational Screening and Predictive Catalyst Design of Metal- Organic Frameworks for the Oxidation of Methane and Ethane

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Metal-organic frameworks (MOFs) are a promising class of materials for catalytic reactions, as they can act as single-site heterogeneous catalysts with uniform, fine-tuned active sites that provide precise control over activity and selectivity. The modular nature of MOFs also makes them particularly appealing for computational screening studies with the goal of predictive catalyst design. In this work, we provide insight into MOF-based catalyst optimization for the direct oxidation of methane and ethane, the two most abundant components of natural gas, into methanol and ethanol.

Active sites composed of a single Fe atom with a range of ligands commonly used as MOF linkers were theoretically investigated to enable the design of MOFs for ethane oxidation.[1] We found linear scaling relations between the Fe-O binding enthalpy and common descriptors for catalytic reactions, such as the Fe 3d energy levels in different reaction intermediates. In addition, we found that the Fe 3d energy levels are positively correlated with the electron-donating strength of functional groups on the linkers. With these trends, volcano plots based on the Sabatier principle were constructed. This catalyst screening approach was further validated by comparing the energy barriers associated with MOF-74 Fe sites both with and without NH_2-functionalization of the linkers.

Inspired by recent work involving the synthesis of porphyrin-supported metal oxide clusters via site-selective atomic layer deposition (ALD),[2] we are also currently screening the catalytic properties of first-row transition elements on porphyrinic supports for the conversion of methane to methanol. We investigate both homobimetallic and heterobimetallic metal oxide nanoclusters that can be incorporated in the functionalized linkers of porphyrin-based MOFs. With regards to the methanol desorption step, we find that bimetallic M(I) clusters (M = Mn, Fe, Co, Ni, Cu, Zn) follow trends similar to the Irving-Williams series, with the energy of methanol desorption generally increasing across the period to a maximum at Cu. This trend is reversed, however, for bimetallic M(III) clusters. Combining these and related screening results, including relevant linear scaling relations, with those of the N_2O activation and C-H activation steps will help identify optimal candidates for experimental investigation.

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Correlated-Participating-Orbitals Pair-Density Functional Method for Calculating the Bond Dissociation energies of FeX and NiX (X= C, S, Se)

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Accurate prediction of the bond dissociation energies between transition metal atoms and the main group atoms is challenging and highly desired. In the present work, we investigate the performance of multi-configuration pair-density functional theory[1] (MC-PDFT) for computing the bond dissociation energies of diatomic FeC, NiC, FeS, NiS, FeSe, and NiSe for which accurate experimental data are recently available.[2] We define three correlated participating orbitals (CPO) schemes[3] (nominal, moderate, and extended, abbreviated nom, mod, and ext) to define the constitution of complete active spaces[4] (CAS) and separated-pair generalized active spaces[5] (SP-GAS), and we test them systematically. We found that the moderate SP-PDFT scheme with the "translated" tPBE on-top pair-density functional has the smallest mean unsigned error. This level of theory provides a balanced treatment of the static and dynamic correlation effects for the studied systems.

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C–H Bond activation on bimetallic two-cation Co-M oxide clusters deposited on Zr-based MOF nodes: Effects of doping at the molecular level

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Cluster-based density functional theory calculations show that energy barriers for dissociative adsorption of propane on two-atom heterobimetallic Co-M clusters supported on Zr-based nodes of NU-1000, a metal–organic framework material, decrease with decreasing valence of the dopant metal. Systematic changes in spin density and charge on the bridging oxygen atom (M-O-Co) are noted upon addition of a low-, same-, and high-valent dopant to cobalt. Observed correlations between the energy barrier and charge and spin on the bridging oxygen atom can be rationalized in terms of Lewis acid-base pair interactions on oxide surfaces.

Extending the Scope of Nanocasting in Metal–Organic Frameworks

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The process of nanocasting in metal-organic frameworks (MOFs) is a versatile strategy to modify these porous materials by introducing supporting scaffolds. The nanocast scaffolds can stabilize oxo-metal clusters in MOFs at high temperatures and modulate their chemical environments to extend the application of the highly tunable metal active sites in MOFs to high temperature catalysis. We previously demonstrated that a silica skeleton introduced into the mesopores of the MOF NU-1000 was able to keep the catalytically-active oxozirconium clusters and clusters modified with bimetallic groups isolated and accessible, even after high temperature treatment at 500 ˚C or higher.

We recently extended nanocasting to other skeletal compositions (titania, carbon) and other MOFs with oxometallate clusters of interest for catalytic applications (UiO-66, UiO-67, DUT-9 and post-metalated NU-1000 MOFs containing hexazirconium, hexacerium and pentanickel oxide-based clusters). In this presentation, we describe the necessary differences in nanocasting conditions to achieve these nanocomposite structures. The responses of NU-1000 towards different scaffold precursors are discussed, including the effects on morphology, precursor distribution, and porosity after nanocasting. Upon removal of organic linkers in the MOF by calcination/pyrolysis, or by a recently developed extraction process, the Zr_6 clusters remained accessible and maintained their Lewis acidity in SiO_2 and TiO_2 nanocast samples, whereas additional treatment was necessary for Zr_6 clusters to become accessible in carbon nanocast samples. Aggregation of Zr_6 clusters was prevented at temperatures exceeding 500 ˚C with all three of the nanocast scaffold compositions (SiO_2, TiO_2, C). The ability to maintain high densities of discrete Lewis acidic Zr_6 clusters on an oxide or carbon support at high temperatures provides a starting point for designing new thermally stable catalysts.

Immobilization of Earth Abundant Metals Coordinated in Heterobimetallic Ligand Scaffolds on Metal Organic Frameworks (MOFs)

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The synthesis of catalysts possessing enzyme-like active sites is a long standing dream because of the high performances reached also in reactions not favored thermodynamically. The goal of this project is to isolated well defined single-site, bimetallic oxide clusters of the mid-to-late first-row metals (Mn, Fe, and Co) on a metal organic framework (MOF) support and use it to catalyze oxidative reactions using O_2 with the high activity and specificity of enzymatic active sites.

Exploiting a synthetic procedure developed at the University of Minnesota for Co-Co[1,2] and Co-Al species,[3] single bimetallic units comprising earth abundant metals (Co-Mn and Fe-Mn) were installed on the Zr_6O_8 nodes of NU-1000 by grafting and calcination of $CoMnOPh(py_3tren)$ and $FeMnOPh(py_3tren)$ precursors (H_3py_3tren=N,N,N-Tris(2-(2-pyridylamino)ethyl)amine).

The structure of the $CoMn(OH)_2$ and $FeMn(OH)_2$ clusters on the NU-1000 nodes was investigated by DFT methods and by X-ray absorption spectroscopy. The position of the Mn-based species before and after calcination in the MOF pores was determined through indirect (N_2 volumetry) and direct techniques (difference envelope density analysis, DED), providing the same description of the complex position within the material. Electron dispersion spectroscopy associated with transmission electron microscopy (TEM) imaging allows to evidence a uniform distribution of the metallic species along the MOF crystals. The effective loading of one unite per MOF node was evaluated by means of ^{1}H NMR of digested MOF and inductively coupled plasma optical emission spectrometry (ICP-OES).

These materials were then tested for their ability to perform heterogenous catalysis such as olefin epoxidation[4] and oxidative dehydrogenation of N-heterocycles.[5] The larger activity of these species with respect to previously reported metal-organic catalysts is promising for their use in catalyzing more challenging reactions such as dehydrogenation of propane or the oxidation of methane in analogy with their Co-Co and Cu and analogues, respectively.[1, 6]

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Carbon Nanocasting in NU-1000

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Nanocasting is a useful synthetic technique to achieve specific nanostructures with predetermined geometries. In previous work, our group reported a method of nanocasting silica into NU-1000. The oxozirconium (Zr_6) clusters remained isolated after nanocasting and removal of the linkers. The product showed activity in the isomerization of glucose to fructose. Additionally, we found that this silica nanocasting method could be applied to metalated NU-1000, e.g. NU-1000 modified with Co_2 or CoAl complexes. The calcined products $Co_2Zr_6@SiO_2$ and $CoAlZr_6@SiO_2$ showed similar conversion values and turn-over numbers as the original metalated NU-1000 in the catalytic oxidation of benzyl alcohol to benzaldehyde.

Here we extend the concept of nanocasting to carbon skeletons that are introduced into NU-1000. Carbon was chosen as a possible scaffold, because a conductive scaffold may enable electrocatalytic processes, such as the conversion from methane to methanol under mild conditions. Furfuryl alcohol is used as the carbon precursor. The strategy of infiltrating furfuryl alcohol into the pores involves vapor treatment, followed by heating to induce further polymerization. The linkers are then removed at 600 °C under N_2 flow. N_2 sorption experiments showed that the surface area and porosity of the final product could be tuned by adjusting the time of furfuryl alcohol infiltration in the MOF and hence, the carbon loading. Difference-envelope-density maps of the infiltrated samples showed that the precursor occupied both the large and small mesopore channels and also the pockets between oxozirconium clusters during nanocasting. This distribution of precursor in the MOF host was also verified by the pore size distributions derived from N_2 and Ar sorption experiments. X-ray diffraction data showed no evidence for aggregation of ZrO_2 after pyrolysis, which suggests that the Zr_6 clusters remained isolated. Pyridine adsorption experiments indicated that in the pyrolyzed product, the Lewis-acidic sites in the oxozirconium clusters were not accessible to the pyridine probe but became accessible after a post-treatment involving partial oxidation of the carbon.

Role of Modulator in the Synthesis of Phase-Pure NU-1000

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NU-1000 is a robust, mesoporous metal organic framework with hexazirconium nodes ($[Zr_6O_{16}H_{16}]^{8+}$, referred to as oxo-Zr_6 nodes) that can be synthesized by combining a solution of $ZrOCl_2 \cdot 8H_2O$ and a benzoic acid modulator in N,N-dimethylformamide with a solution of linker (1,3,6,8-tetrakis(p-benzoic acid)pyrene, referred to as H_4TBAPy) and aging at elevated temperature. Typically, the resulting crystals are primarily composed of NU-1000 domains that crystallize with a more dense phase that shares structural similarity with NU-901, which is a MOF composed of the same linker molecules and nodes. Density differences between the two polymorphs arise from differences in the node orientation: in NU-1000 the oxo-Zr_6 nodes rotate 120° from node to node, whereas in NU-901 all nodes are aligned in parallel. Considering this structural difference lead to the hypothesis that changing the modulator from benzoic acid to the larger and more rigid biphenyl-4-carboxylic acid might lead to stronger steric interaction between the modulator coordinating on the oxo-Zr_6 node and misaligned nodes or linkers in the large pore and inhibit growth of the more dense NU-901-like material, resulting in phase-pure NU-1000. Side-by-side reactions comparing the products of synthesis using benzoic acid or biphenyl-4-carboxylic acid as modulator produce structurally heterogeneous crystals and phase-pure NU-1000 crystals, respectively. It can be concluded that the larger and more rigid biphenyl-4-carboxylate inhibits incorporation of nodes with alignment parallel to neighboring nodes already residing in the crystal.

Combined Quantum Mechanical and Molecular Mechanical Method for Catalyst Design on the NU-1000 Metal-Organic Framework

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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 time and computational resources; therefore we have developed a combined quantum mechanical and molecular mechanical (QM/MM) method to investigate these systems.

Our method is illustrated by calculations on MOF NU-1000 [$Zr_6(\mu_3$-$O)_8(O)_8(H)_{16}(TBAPy)_2$], which is a superb candidate for use as a catalytic support for various reactions (e.g., alkane metathesis and ethylene dimerization). We study the relative energetics for various proton topologies of the NU-1000 node. Because of the high partial charges on the atoms of the highly polar bonds in this structure, this provides a challenging test of the adequacy of the QM/MM boundary treatment. In our QM/MM calculations, we use a cluster model of the node [$Zr_6(\mu_3$-$O)_8(O)_8(H)_{16}(PhCOO)_8$] with eight phenyl rings (88 atoms) treated classically while the other atoms (62 atoms) are treated quantum mechanically. Two kinds of link atoms (in particular H atoms and tuned F atoms) are used to cap the dangling bonds in the QM subsystem, and six kinds of charge modification schemes are considered for the treatment of boundary charge. By comparing with full QM calculations, we found that the QM/MM method can give remarkably accurate results with a mean unsigned error of only 2 kJ mol^{-1} in the relative energies of seven proton topologies.

To facilitate the design of MOF-based catalysts, it can be desirable to further reduce the number of atoms in the QM subsystem. To do this for NU-1000 we have to cut through two types of polar bonds (Zr-O and O-Zr) in the same calculation. We are developing a new method based on a tuned F link atom to treat this situation.

Inorganometallic Catalyst Design: Alkane Metathesis Catalysis in NU-1000 MOFs Functionalized with Transition Metals

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Mid-weight (C_3-C_8) *n*-alkanes are petrochemical raw materials that are available in large quantities from oil and gas reserves. They are also produced in Fischer-Tropsch catalysis, which is the major route for the conversion of natural gas and coal to liquid fuels. It is desirable to convert mid-weight *n*-alkanes into higher-value molecules. Alkane metathesis, in which alkane molecules are transformed into higher and lower homologs, is a potential method for achieving such conversion.

The majority of single-site alkane metathesis catalysts are metal hydrides on amorphous SiO_2 and Al_2O_3. In each case, the metal plays dual roles: first, dehydrogenation of alkanes to alkenes, and second, perform alkene metathesis to form C–C bonds. The present work considers using a metal–organic framework (MOF), in particular NU-1000 (molecular formula $[Zr_6(\mu_3–O)_4(\mu_3–OH)_4(OH)_4(OH_2)_4](TBAPy)_2$, H_4TBAPy = 1,3,6,8-tetrakis(p-benzoic-acid)pyrene), as a support for new catalyst development. Because of their tunable surface structures, MOFs are ideal for rational heterogeneous catalyst design based on structure–reactivity relationships.

We used Kohn–Sham density functional calculations with the M06-L exchange-correlation functional for computational screening of NU-1000 functionalized with various transition metals, in particular screening for propane metathesis. We considered eight transition metals (V, Nb, Ta, Cr, Mo, W, Mn, Re) along with two variations of the NU-1000 framework: fully hydrated NU-1000 and NU-1000 decorated with yttrium oxide. The activation energies for C–H bond activation and [2+2] cycloaddition were identified as descriptors of catalytic activity of different catalysts. Using the Sabatier principle, we constructed volcano plots to evaluate the expected efficacy of the trial catalysts. This identified vanadium-functionalized, yttrium oxide-decorated NU-1000 ($VYO_x@NU-1000$) as the most suitable catalyst among the trial catalysts for the propane metathesis. The complete reaction cycle for $VYO_x@NU-1000$ catalyst was computed and the free energy of activation is predicted to be 37.8 kcal/mol. This relatively high activation energy obtained by using a dual-role single-site catalyst indicates that the overall performance of the catalyst is compromised in order to achieve a balance between different reactions. We conclude that future developments in alkane metathesis catalysis should focus on dual-site catalysts and/or tandem systems.

Ethanol Dehydration Catalyzed by Zr_6O_8 Nodes in Metal–Organic Frameworks: Probing the Structure and Dynamics of Node Surfaces in UiO-66, UiO-67, and NU-1000

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The Zr_6O_8 nodes in UiO-66 and NU-1000 have been characterized by IR spectroscopy and DFT calculations, leading to structural models including hydroxo and aqua ligands on the nodes. We have now combined IR spectra with ^{1}H nuclear magnetic resonance (NMR) spectra of unzipped MOFs to reexam the identities of ligands on the node vacancies. The results demonstrate that the majority of the node vacancies on the as-synthesized MOFs were covered by formate ligands and small number by DMF molecules. The NMR spectra provide quantitative data determining the numbers of the various ligands on the node vacancies. When the as-synthesized MOF samples are treated with methanol or ethanol, alkoxide ligands are formed, and these have been converted to hydroxo ligands upon exposure to water vapor.

We used ethanol dehydration as catalytic probe reaction to test the active sites on the nodes of the Zr-based MOFs UiO-66, UiO-67, and NU-1000. The activity is determined by the number of vacancies on the MOF nodes and by the MOF particle size. Ligands bonded to the MOF node vacancies, including hydroxo, alkoxy, and carboxylate, play various roles influencing the catalytic activity. UiO-66 has a higher catalytic activity than metal oxides for ethanol dehydration, and it is uniquely selective for ether formation, but it is less stable. The DFT calculations show that the key to the selectivity is the breaking of node-linker bonds to allow catalytically fruitful bonding of the reactant ethanol to the nodes to facilitate the bimolecular ether formation. Indeed, these calculations suggest that only *highly defective* nodes account for the selective formation of diethyl ether through S_N2-type transition state structures.

MOFs with metal oxide clusters as nodes offer new opportunities for catalysis and for anchoring essentially molecular catalysts, and, with guidance by theory, ultimately for design of catalysts.

Computational Study of MOF-Supported Transition Metal Catalysts for Ethylene Dimerization

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Metal-organic frameworks (MOFs) with ultrahigh porosity and large surface area have recently emerged as excellent heterogeneous supports for transition metal catalysts, either through functionalization of the linker or direct modification of the nodes. The mesoporous MOF, NU-1000, is of particular interest due to its chemical and thermal stability as well as its large pore size (~30 Å), which facilitates the diffusion of gaseous molecules. More importantly, the coordinatively unsaturated metal sites at the inorganic nodes provide specific sites for metal oxide species to anchor, enabling the synthesis of a highly dispersed and isolated single-site metal catalysts on the internal surface of NU-1000. Through atomic layer deposition, a highly dispersed Ni catalyst (Ni-NU-1000) was successfully synthesized; it shows good activity and stability for ethylene hydrogenation and was predicted to be a potential catalyst for ethylene oligomerization.[1,2]
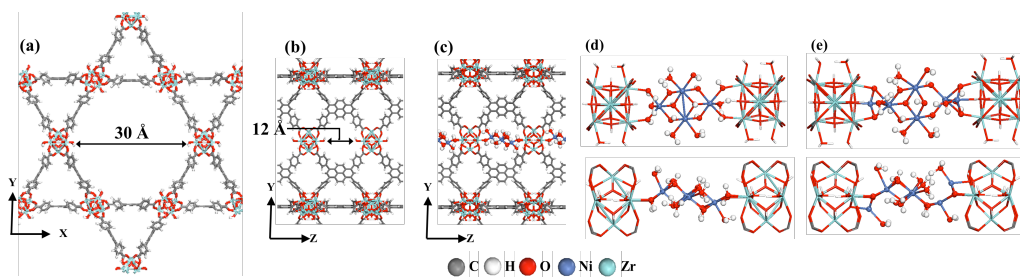
In this work, we aim to develop a Ni-NU-1000 catalyst model and from there to identify the catalytic active sites for ethylene dimerization. Furthermore, a variety of metals have been screened to search for potential catalyst candidate the ethylene dimerization with higher selectivity.

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Non-Innocent Catecholate Ligand on the Activity of Metal-Organic Frameworks-Supported Cu Catalysts

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Metal-organic frameworks (MOFs) have been widely studied over the past two decades due to their high surface area, porosity and versatile tunability. Both the inorganic nodes and organic linkers (e.g. 2,2'-bipyridine) can serve as metal anchoring sites for catalytically active metal species. Redox-active organic species such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), tetrathiafulvalene (TTF) naphthalenediimide (NDI), anthraquinone and pyridinium units, have been incorporated in MOFs for a variety of applications including magnetism, electrical conductivity, batteries and molecular switches. However, these redox-active linkers are under-explored for the purpose of catalysis, as they usually lack the versatility for further functionalization with catalytically active metal species.

In order to study the interactions between redox-active organic linkers and the anchored metal catalysts, and their effect on the catalytic activity, we have synthesized two new UiO-68-like MOFs with catechol-diphenylcarboxylates as the functional MOF scaffolds. The catechol sites also serve as bidentate chelating ligands for postsynthetic metalation to give the MOF-supported catalysts. When the MOFs were metalated with Cu(II) precursors, Cu(I) species were generated via the redox interactions between Cu(II) and the catechol moieties. In comparison, a similar catalyst with only Cu(II) species was produced in the absence of the redox interactions. It has been found that these catalysts are selective toward the allylic oxidation of cyclohexene to produce *tert*-butyl-2-cyclohexenyl-1-peroxide, 2-cyclohexe-1-ol and 2-cyclohexe-1-one. A higher catalytic activity has been observed for the Cu(I) containing catalyst than the Cu(II) catalyst. This work provides a new strategy for the design and synthesis of MOF-supported catalyst with enhanced catalytic activities that take advantage of the redox activity of MOF linkers.

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

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TiO$_2$ is a well-known redox and photocatalyst. As a catalyst support, it exhibits strong metal-support interactions that can be exploited to modify electronic and catalytic properties of metal or oxo-metal clusters.[1] In mixed TiO$_2$ and ZrO$_2$ oxides, the dispersion of Lewis acidic Zr atoms and surface structure of the material can be tuned through the synthetic conditions to optimize the material for different applications such as dehydrogenation, hydrogenation and hydroprocessing.[2] However, in most ZrO$_2$-doped TiO$_2$ materials, ZrO$_2$ is present in the form of a ceramic mixture with TiO$_2$, forming ZrTiO$_4$ with poorly-defined active sites, which leads to decreased surface area and compromises catalytic activity and selectivity.[2] A proposed approach to overcome these problems is to synthesize TiO$_2$ loaded with well-defined oxozirconium clusters by means of nanocasting metal-organic frameworks (MOFs). Through nanocasting the MOF NU-1000 with TiO$_2$, followed by removal of organic linkers from the MOF, we have prepared oxozirconium cluster-loaded TiO$_2$, which is thermally stable up to 600 °C.

Titanium ethoxide (TEOT) and tetrakis(dimethylamido)titanium (TDMAT) were suitable for the nanocasting process in NU-1000. X-ray diffraction (XRD) confirmed that the structure of NU-1000 was intact after infiltration. The surface area and pore volume of the infiltrated NU-1000 determined from N$_2$ sorption isotherms showed a moderate decrease, indicative of successful infiltration of the MOF with the TiO$_2$ precursor. The ability of the TiO$_2$ skeleton to prevent extended cluster aggregation during linker removal was confirmed by XRD. Pyridine sorption experiments showed that the Lewis acidic sites from oxozirconium clusters remained accessible. Our goal after synthesis optimization is to provide a single-site, multifunctional catalyst with tunable environment, and high catalytic efficiency and selectivity for high temperature hydrocarbon upgrading.

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Pt clusters and nanoparticles deposited on the nodes of NU-1000 for ethylene hydrogenation

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In this work, Pt is deposited on the nodes of NU-1000 metal-organic framework (MOF) via ion-exchange (IE) and strong electrostatic adsorption (SEA) routes. After exchange or adsorption, the samples are further reduced under H_2 at 200 °C overnight. XRD and BET results show that deposited Pt by IE has negligible influence on the crystallinity and the porosity of NU-1000. However, we see a 15% decrease in the surface area on the Pt-NU-1000-SEA sample. With scanning transmission electron microscopy (STEM) image, we do not see Pt particles (> 1 nm) for Pt-NU-1000-IE, but clear Pt particles with diameter of 2-3 nm for Pt-NU-1000-SEA. Extended X-ray absorption fine structure (EXAFS) analysis shows that the first shell Pt-Pt coordination number for the IE and SEA samples are 3 ± 1.2 and 7.5 ± 1.1, respectively. It further confirms the very small Pt clusters with several Pt atoms in Pt-NU-1000-IE and ~2 nm particles in Pt-NU-1000-SEA. Thus ion-exchange method is an efficiency route to deposit sub-nanometer Pt clusters on the nodes of NU-1000 MOF.

The obtained Pt-NU-1000 samples are used as catalysts in the ethylene hydrogenation. Both samples are highly active at room temperature. In particular, Pt-NU-1000-IE offers 3 time higher activity than Pt-NU-1000-SEA if it is normalized to the amount of Pt in the samples. Kinetic study shows that the two samples have similar energy barrier (Ea) in the reaction, which are 8.48 ± 1.0 kcal/mol and 9.32 ± 0.9 kcal/mol for Pt-NU-1000-IE and Pt-NU-1000-SEA, respectively. It indicates that ethylene hydrogenation on Pt-NU-1000 might be a structure-insensitive reaction. In addition, Density Functional Theory (DFT) calculations are being performed to elucidate the detailed energetics and structural properties for the formation of several platinum clusters interacting with the nodes of the NU-1000. Moreover, the DFT calculations, coupled with microkinetic modeling, are used to elucidate the dominant pathway from the many different elementary reactions considered.

Ion-exchanged Cu-NU-1000 for selective methane oxidation

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We have developed an ion-exchange (IE) method for depositing Cu on the nodes of NU-1000 metal–organic framework (MOF) using aqueous solutions. XRD and N_2-sorption demonstrate that the crystallinity and the porosity of NU1000 are largely preserved after Cu deposition. STEM images proves that Cu particles over 1nm are not formed. X-ray absorption spectroscopy (XANES, X-ray absorption near edge structure, and EXAFS, extended X-ray absorption fine structure) indicates that Cu is present as $Cu(OH)_2$-like structure and gave 100% Cu^{2+} in the as-synthesized material. FEFF fitting of the EXAFS spectra shows first the shell Cu-Cu coordination number of 0.6 ± 0.3. Combined with density functional theory (DFT), this suggests that monomer and dimer species are the predominant Cu species in the samples.

The sample prepared by IE (Cu-NU-1000-IE) is used as a catalyst on selective methane oxidation. Under mild reaction conditions (1 bar 150 °C), the material oxidizes methane to methanol with a yield of 128.7 $\mu mol/g_{Cu}$ and a methanol selectivity of about 70%. We see substantial decreases in the activity in the following cycles. However, the surface area and pore volume are retained after three catalytic cycles. In situ XAS are employed to track the local structure of Cu species along catalysis. Upon loading with CH_4, ~7% of Cu^{2+} is reduced to Cu^+. EXAFS spectra show no agglomeration of Cu species in the post-catalysis material. Overall, ion exchange is an efficient, low-cost, scalable, and controlled method to deposit Cu on MOF nodes.