The Selective Oligomerization of Ethylene with Metal-Organic Frameworks

by

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B.A., St. Olaf College (2013)

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ABSTRACT

The benefits of heterogeneous catalysis for industry and the society at large cannot be overstated, with approximately 90% of all industrial catalysis being performed with heterogeneous catalysts. Despite the undeniable operational advantages of heterogeneous catalysts, several large volume industrial processes involved in the production of commodity chemicals remain impenetrable to solid catalysts. Among them are the selective dimerization of ethylene and the selective trimerization of ethylene, which require fine steric and electronic tuning to optimize the production of the desired olefin.

In this thesis, I describe the development of new heterogeneous catalysts to address the lack of activity and selectivity found among heterogeneous catalysts for selective ethylene oligomerizations, with an emphasis on developing new metal-organic framework (MOF) catalysts for the selective dimerization of ethylene to 1-butene. The ability to tune the catalytically active site of a solid at the molecular level places MOFs in prime position to answer challenges in heterogeneous catalysis that no other class of solids has been able to address. Chapter 2 of this thesis describes the development of Ni-MFU-4, a nickel-substituted MOF with excellent activity and selectivity for the dimerization of ethylene to 1-butene. Although the active sites in the MOF are designed to mimic homogeneous Ni-trispyrazolylborate dimerization catalysts, the selectivity observed for the solid catalyst is considerably higher than that of the homogeneous system, highlighting the importance of active site isolation in the porous solid. Chapter 3 details a combination of studies utilizing isotopic labeling and mechanistic probes to demonstrate that Ni-MFU-4 dimerizes ethylene via the Cossée-Arlman mechanism. Chapter 4 reports the preparation of Ni-CFA-1, a related heterogeneous ethylene dimerization catalyst that is far more synthetically accessible than Ni-MFU-4. Lastly, chapter 5 relays initial results towards the development of MOF-based ethylene trimerization catalysts.

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Selective Ethylene Oligomerizations
1.1 Introduction

Linear \( \alpha \)-olefins (LAOs) are among the most versatile building blocks in the chemical industry, used as precursors for detergents, synthetic lubricants, plasticizer alcohols, and as comonomers in the production of linear low-density polyethylene (LLDPE). Increasing demand for LLDPE has led to renewed interest in selective ethylene oligomerizations, as 1-butene, 1-hexene, and 1-octene impart superior mechanical properties to polymers when used as comonomers. In this introduction, I will provide a historical perspective on the development of ethylene oligomerization. Aiming to be descriptive rather than exhaustive, I will first discuss the nonselective oligomerization of ethylene, followed by developments in selective ethylene dimerization, trimerization, and tetramerization. A special emphasis will be given to heterogeneous systems, as my research aims to address key limitations with existing heterogeneous catalysts.

1.2 Ethylene Oligomerization Mechanisms

Two mechanisms are commonly invoked to explain ethylene oligomerization.\(^1\)-\(^3\) The Cossee-Arlman mechanism involves the successive insertion of ethylene monomers into a growing metal alkyl chain prior to chain termination, typically leading to an unselective distribution of oligomers determined by the relative rates of ethylene insertion and chain termination (Figure 1-1). In principle, however, catalysts operating via this mechanism can be selective for dimers if the rate of chain termination is much faster than the rate of ethylene insertion, resulting in catalysts that terminate the metal alkyl chain after a single insertion.\(^1\) Although both early and late transition metal catalysts are known to operate via this mechanism, many early transition metal catalysts have a slow rate of chain termination, often resulting in the formation of polyethylene. In contrast, late transition metal catalysts typically have much faster rates of \( \beta \)-hydride elimination, resulting in faster chain termination and the
release of ethylene dimers or oligomers. Nonetheless, steric and electronic factors can slow the rate of chain termination such that late transition metal catalysts also selectively produce polyethylene.

In contrast to Cossee-Arlman catalysts, which often produce nonselective distributions of oligomers, catalysts that operate via metallacyclic intermediates typically result in the selective oligomerization of ethylene. In addition to a handful of nonselective oligomerization catalysts, selective dimerization, trimerization, and tetramerization catalysts have all been proposed to operate via metallacyclic intermediates, although the exact mechanistic details differ between each system. Of the many oligomerization systems that operate via metallacycles, selective trimerization catalysts are the most extensively studied. For these trimerization catalysts, two ethylene molecules initially coordinate to the metal center (Figure 1-2). Following the formation of the bis(ethylene) intermediate, oxidative (with respect to the metal) coupling of the olefin monomers generates a metallacyclopentane. Sterically restricted metallacyclopentanes decompose slowly, enabling the insertion of another ethylene

Figure 1-1. The Cossee-Arlman mechanism. The product distribution is controlled by the rate of ethylene insertion relative to chain termination.
monomer into a metal-carbon bond to form a metallacycloheptane. The more flexible metallacycloheptane decomposes much more rapidly than the smaller metallacyclopentane, resulting in the selective trimerization of ethylene to 1-hexene. Metallacyclic mechanisms are most commonly proposed for early transition metals such as titanium, chromium, and tantalum, although some late transition metal oligomerization catalysts also operate via metallacyclic intermediates.

![Selective Ethylene Trimerization](image)

**Figure 1-2.** The mechanism of selective ethylene trimerization via metallacyclic intermediates.

Although it is broadly accepted that selective ethylene tetramerization relies upon metallacyclic intermediates, the exact nature of the mechanism is under debate. It has been proposed that a bimetallic mechanism may explain selective tetramerization, wherein two metallacyclopentanes couple to form a dimetallacyclodecane, which decomposes to release 1-octene. Although this proposal has been used as a guiding principle in the development of new ethylene tetramerization catalysts, experimental support for this mechanism is lacking. Theoretical work has implicated extended mononuclear metallacycles as the key intermediates.
for the most active ethylene tetramerization catalyst, although additional work is required to fully elucidate the mechanistic details for selective tetramerization.

1.3 Nonselective ethylene oligomerization

1.3.1 Shell Higher Olefin Process

First discovered in 1968, the Shell Higher Olefin Process (SHOP) remains one of the largest applications of homogeneous catalysis. Initially developed to prepare C_{12}-C_{18} olefins as precursors for detergents, the SHOP process utilizes homogeneous nickel complexes to carry out the nonselective oligomerization of ethylene via the Cossee-Arlman mechanism. The catalyst is readily prepared via the reaction of Ni(cod)₂ with Ph₂PCHOH, with the resulting complex oligomerizing ethylene in a two-phase system to enable catalyst recirculation. Given the nonselective olefin distribution, only 40-50% of the products were the desired C_{12}-C_{18} olefins. Numerous process improvements were made to address these limitations in selectivity, most notably the isomerization and metathesis of <C_{12} and >C_{18} olefins. SHOP's remarkable versatility has enabled its continued relevance, as the combination of ethylene oligomerization and olefin metathesis provides the backbone to a process that produces over 3 million tons of olefins per year.

1.3.2 Nickel α-diimine catalysts

In the 1990s, Brookhart and coworkers further demonstrated the versatility of late transition metal catalysts for olefin oligomerizations, establishing structure-function relationships with nickel complexes supported by α-diimine ligands. In early work, it was demonstrated that cationic nickel and palladium catalysts could polymerize ethylene and α-olefins via the Cossee-Arlman mechanism, a notable departure from the previously developed SHOP catalysts that merely produced ethylene oligomers. Supported by bulky diimine ligands,
these highly active nickel and palladium catalysts could be prepared by either the protonolysis of a dimethyl precursor or *in situ* by the treatment of the α-diimine nickel dibromide precatalyst with methylaluminoxane, affording catalysts with turnover frequencies as high as 390,000 moles of ethylene consumed per mole of nickel per hour (Figure 1-3A). Increasing the reaction temperature resulted in increased polymer branching, whereas increasing the ethylene pressure decreases the polymer branches. Importantly, the α-diimine ligands are easily synthesized via condensation reactions, enabling the preparation of a series of catalysts with varying steric and electronic properties. Reducing the steric bulk of the diimine ligand was shown to increase the rate of chain transfer relative to the rates of chain migration and chain propagation, producing less branched polymers with decreased molecular weight.

This structure-function relationship was further extended by the preparation of catalysts that removed much of the steric bulk found in the α-diimine polymerization catalysts (Figure 1-3B). These unhindered cationic nickel catalysts were highly active for the nonselective oligomerization of ethylene, with the resulting oligomers following the Schulz-Flory distribution. The selectivity for α-olefins is dependent on the ethylene pressure, with higher pressures leading to an increase in selectivity for α-olefins. This was proposed to be due to a competition between chain transfer and chain isomerization from an olefin hydride intermediate. Chain transfer was proposed to occur via the associative displacement of the...
olefin with an incoming ethylene monomer, a process first-order in ethylene, although calculations have suggested chain transfer may occur via a concerted β-hydride transfer to incoming ethylene. In contrast, chain isomerization is independent of ethylene pressure, relying only upon the olefin hydride intermediate. Thus, as ethylene pressure increases, the rate of chain transfer increases relative to the rate of chain isomerization, resulting in a higher abundance of α-olefins.

Figure 1-4. Simulated Schulz-Flory distribution for the catalyst depicted in figure 1-3B under the most active conditions reported (Schulz-Flory $\alpha = 0.61$). The mole fraction distribution was simulated according to reference 3.

Catalyst activity is dependent on the electronic properties of the α-diimine ligand, even among catalysts with similar steric bulk. In general, catalysts supported by electron-poor ligands are more active than more electron-rich systems, with turnover frequencies reaching 136,000 moles of ethylene consumed per mole of nickel per hour for a CF$_3$ substituted analog (Figure 1-3B). These electron-poor catalysts exhibit a first-order relationship between activity and ethylene pressure at pressures below 30 atmospheres, with the resulting Schulz-Flory distribution dependent on ethylene pressure. Longer oligomers are produced at higher pressures, as a result of an increased rate of ethylene insertion relative to the rate of chain insertions.
transfer. No substantial differences are observed in the resulting Schulz-Flory distribution for a series of catalysts as the electronic properties are varied, despite catalyst activity increasing as the metal center becomes more electrophilic. In contrast, reaction temperature has a substantial impact on the product distribution, as higher temperatures generate shorter oligomers with a decreased selectivity for \(\alpha\)-olefins. Brookhart \textit{et al.} rationalize these results with the decreased solubility of ethylene in toluene at higher temperatures, invoking similar selectivity arguments as those presented to explain the results obtained at different reaction pressures. Although these catalysts have high initial activities, these systems decay within two hours.

Detailed low temperature NMR studies have provided additional insight into the mechanism of ethylene oligomerization with this class of catalysts.\textsuperscript{19} More hindered catalysts have a somewhat lower barrier for ethylene insertion, presumably due to steric interactions destabilizing the alkyl olefin intermediate. For these sterically hindered catalysts, the resting state is an agostic nickel alkyl complex. Product isomerization occurs via metal migration along the alkyl chain, proceeding through a four-coordinate species that is inhibited by ethylene coordination. Thus, decreasing ethylene pressure increases the extent of product isomerization, whereas increasing the steric bulk of the \(\alpha\)-diimine ligand similarly leads to increased product isomerization. Increasing the steric profile of the catalyst inhibits the coordination of ethylene to the metal center, enabling prolonged metal migration along the alkyl chain. Although these \(\alpha\)-diimine nickel catalysts only produce a distribution of ethylene oligomers or polymers, the demonstration of structure-function relationships was crucial for the field of ethylene oligomerization.
1.3.3 Non-selective ethylene oligomerization with iron and cobalt

Although the majority of nonselective ethylene oligomerization catalysts utilize nickel as the metal of choice, a handful examples have been developed that use iron or cobalt. In concurrent contributions by Brookhart and Gibson, bulky pyridine(bis)imine iron and cobalt complexes were reported as ethylene polymerization catalysts, with the iron complexes showing remarkable activities. Analogous to the α-diimine nickel complexes, reducing the steric bulk of the pyridine(bis)imine iron complex results in nonselective ethylene oligomerization catalysts (Figure 1-5). Catalyst activity is dependent on ethylene pressure, although the distribution of oligomers is unaffected by ethylene pressure. This suggests that both chain propagation and chain transfer are first order in ethylene, consistent with chain transfer via an associative process. These catalysts are more than 99% selective for α-olefins at pressures above 200 psig, demonstrating that product isomerization can be minimized with some Cossee-Arlman catalysts.

1.3.4 Nonselective chromium catalysts

Although the majority of nonselective oligomerization catalysts function via the Cossee-Arlman mechanism, some nonselective chromium catalysts have been reported to function through metallacyclic intermediates. Although many catalysts that operate via metallacyclic intermediates selectively produce 1-
hexene due to the facile decomposition of the metallacycloheptane, nonselective oligomerization can occur with catalysts where ethylene insertion is more favorable than the ring decomposition of the metallacycle. Similar to nonselective Cossee-Arlman catalysts, when the rates of ethylene insertion and ring decomposition are comparable, a wide range of \( \alpha \)-olefins are produced. Bis(benzimidazole)pyridine chromium trichloride (Figure 1-6A) is one example of a chromium catalyst that catalyzes the nonselective oligomerization of ethylene with a turnover frequency reaching as high as 765,000 moles of ethylene consumed per mole of chromium per hour (85.7% selective for \( C_6 \) through \( C_{32} \) \( \alpha \)-olefins).\(^{24}\) Oligomerizing a mixture of ethylene and perdeuterioethylene shows that no \( \beta \)-hydride elimination occurs during the reaction, implicating metallacyclic intermediates. Reacting ethylene in the presence of 1-nonene does not produce olefins with an odd number of carbon atoms, indicating that oligomerization occurs via extended metallacycles rather than by secondary reactivity of higher olefins in solution. The exact features that govern this ring stability are not well understood, as some nonselective chromium catalysts are very closely related to selective trimerization catalysts.

Some of the most remarkable chromium catalysts are those that produce an alternating distribution of oligomers via metallacyclic intermediates. The earliest system reported to produce an alternating distribution of oligomers utilized a chromium cation supported by a bis(benzimidazole)amine ligand (Figure 1-6B).\(^{25}\) When treated with methylaluminoxane this catalyst is extremely active for ethylene oligomerization, with a maximum turnover frequency of 8,000,000 moles of ethylene consumed per mole of chromium per hour. Most remarkably, this systems produces an abundance of \( C_{(4n)} \) oligomers, while only producing a relatively diminished quantity of \( C_{(4n+2)} \) oligomers. The abundant \( C_{(4n)} \) olefins follow the Schulz-Flory distribution, whereas the \( C_{(4n+2)} \) olefins deviate substantially from the expected distribution.
This divergent behavior is unlikely to be due to two distinct catalysts, as these would require chain extension by four carbons at a time. Instead, it is believed that this alternating distribution is caused by the metallacycle occupying two distinct sites, which could be expected by the non-linearity of the ligand. These distributions have been modeled as second-order linear recursive relations, where each olefin fraction is related to the two previous fractions. An extensive series of related catalysts that produce an alternating distribution of oligomers have been prepared and theoretically modeled by Britovsek and coworkers. These studies suggest that both mono- and bis-ethylene adducts form after metallacyclic intermediate are generated, with the relative abundance of these intermediates dictating the composition of the olefinic products. Although many of these chromium catalysts are supported by tridentate chelating ligands, the proposed mechanism necessitates the hemilability of one of the donor ligands to generate a bis-ethylene adduct. Although not yet fully explored, ligand variation may provide a method towards the control of the resulting product distribution.

1.4 Selective ethylene dimerization

1.4.1 Homogeneous Catalysts for ethylene dimerization

1.4.1.1 Nickel-based catalysts for ethylene dimerization

Nickel catalysts are among the most extensively explored for ethylene dimerization. Catalysts following the Cossee-Arlman mechanism produce a Schulz-Flory distribution of olefin oligomers, which is statistically defined by the rates of chain growth and chain

![Figure 1-7. Example P,N- nickel catalysts for ethylene dimerization. While these catalysts are selective for ethylene dimers, they are only poorly selective for 1-butene, producing substantial amounts of isomerized products in addition to the desired alpha olefin.](image)
transfer. To develop a selective dimerization catalyst that functions via the Cossee-Arlman mechanism, the catalyst must have a faster rate of chain transfer than of chain propagation. This requirement makes nickel complexes ideally suited for ethylene dimerization, as β-hydride elimination is facile for many nickel complexes. Speiser et al. have generated a series of nickel catalysts supported by P,N- chelating ligands with different electronic and steric properties (Figure 1-7). These complexes are active for ethylene dimerization, with turnover frequencies typically ranging between 20,000 and 40,000 moles of ethylene consumed per mole of nickel per hour. The catalysts are also reasonably selective for dimers, with C₄ olefins accounting for roughly 80% of the products with most of the P,N- catalysts. Unfortunately, these P,N- catalysts are very poorly selective for α-olefins, with 1-butene typically accounting for only 10-30% of the dimeric products. This highlights a major challenge with many nickel catalysts for ethylene dimerization: although the facile β-hydride elimination of the nickel alkyl species enables selective dimer formation, the reinsertion of the olefin into the metal hydride bond with the opposite regiochemistry is a common side reaction, leading to substantial product isomerization.

Despite the challenges, some homogeneous nickel catalysts have been developed that are selective for dimers while producing primarily linear α-olefins. In 2003, nickel scorpionate complexes were reported to selectively dimerize ethylene to 1-butene with nickel (Figure 1-8). Both monomeric and dimeric complexes...
were prepared and tested for ethylene oligomerization, although the dimeric complex was inactive for ethylene dimerization. Upon treatment with methylaluminoxane the two monometallic complexes were active for ethylene dimerization, although decreasing the steric bulk around the metal center results in a more than tenfold reduction in catalyst activity. In tandem with the inactivity of the dimeric complexes, these results suggest that bimolecular pathways play a significant role in catalyst decomposition. In further support of this hypothesis, increasing the catalyst loading from 5 \( \mu \)mole to 25 \( \mu \)mole leads to a drop in catalyst activity of greater than 30 percent. Catalyst activity increases with increasing ethylene pressure in an apparent first-order relationship. Interestingly, the relative selectivity for dimers is independent of pressure, with dimers comprising approximately 86\% of the products. In contrast, increasing the ethylene pressure has a clear impact on the selectivity for \( \alpha \)-olefins. For example, increasing the pressure from 1.1 atm to 30 atm increases the selectivity for 1-butene among the dimers from 78\% up to 95\%. These results are similar to those found with the nonselective \( \alpha \)-diimine nickel oligomerization catalysts, where the Schulz-Flory distribution is independent of ethylene pressure and the selectivity for linear \( \alpha \)-olefins increases with increasing pressure. Temperature also plays an important role on the performance of the catalyst, with selectivity decreasing dramatically as the temperature is increased from 0 °C to 30 °C. Despite limitations related to catalyst decomposition, these scorpionate complexes demonstrate that nickel dimerization catalysts can be selective for \( \alpha \)-olefins.

Although the majority of nickel catalysts for ethylene dimerization function via the Cossee-Arlman mechanism, a few examples have been documented that dimerize ethylene through metallacyclic intermediates. In the late 1970s, Grubbs prepared nickelcyclopentanes supported by phosphine ligands via the addition of 1,4-dilithiobutane to a dichlorobisphosphinenickel(II) complex.\(^9\) In the presence of free phosphine in solution, the
coordination number of the nickel complex is dynamic, playing a critical role in determining the hydrocarbons produced by the thermal decomposition of the nickelcyclopentane. Complexes with high coordination numbers produce ethylene as the primary product, indicative of C-C bond cleavage via the isomerization of the nickelcyclopentane to a bis(ethylene)nickel complex. Four-coordinate nickelcyclopentanes decompose to release cyclobutane, whereas three-coordinate species decompose to produce 1-butene as the major product with 2-butene as a secondary product. Given the equilibrium between the nickelcyclopentane and the bis(ethylene)nickel complex, Grubbs and coworkers realized the potential for phosphine supported nickel complexes to serve as ethylene dimerization catalysts. Reacting tris(triphenylphosphene)tetramethylenenickel(II) with ethylene produced a mixture of cyclobutane and butenes. By varying the concentration of phosphine ligand in solution, cyclobutane formation was almost entirely suppressed, affording a mixture of butenes. The catalysts are not particularly active for ethylene dimerization, as optimal conditions affording 59.5 turnovers over the course of a 14 hour reaction. Nonetheless, these results demonstrated that metallacycles can play a significant role in the dimerization of olefins, even with nickel catalysts.

1.4.1.2 Vanadium based catalysts for ethylene dimerization

In recent years, (imido)vanadium(V) complexes have been reported as tremendously active and selective for ethylene dimerization. The most active of these complexes, V(NAd)Cl[8-(2,6-dimethylanilide)-5,6,7-trihydroquinoline] (Figure 1-9), has an optimized activity in excess of 10,000,000 moles of ethylene consumed per mole of vanadium per hour with
a selectivity for 1-butene exceeding 97.8%. Although the catalyst functions best at short reaction times with low catalyst loading – the optimized reactivity was observed with 100 nanomoles of catalyst in a 5 minute reaction – these results nonetheless demonstrate the incredible activity of some transition metal catalysts. The steric bulk of the imido ligand plays a critical role in the performance of the catalyst, as slight variations in ligand properties can dramatically decrease catalytic activity or instead produce a mixture of oligomers and polyethylene. These vanadium catalysts are proposed to function via a Cossee-Arlman mechanism.

1.4.1.3 Titanium Catalysts

Titanium catalysts are the basis for the AlphaButol commercial dimerization process, which is used to dimerize over 700,000 tons of ethylene per year. The active catalyst is formed \textit{in situ} via the treatment of a titanium(IV) alkoxide with minimal (~2 equivalents) triethylaluminum. The catalysts are very active, with turnover frequencies exceeding 100,000 moles of ethylene consumed per mole of titanium per hour. They also exhibit a selectivity of over 93% for 1-butene under optimized conditions, with only trace 2-butenes observed. Branched C6 olefins account for the bulk of the byproducts, although polyethylene formation leads to significant reactor fouling.

Although the structure of the active species is unknown, substantial work has been devoted to understanding the mechanism of these titanium catalysts. Given the exceedingly high selectivity for 1-butene among the C4 products, it has been assumed that these titanium systems dimerize ethylene via Ti(II) and Ti(IV) metallocyclic intermediates. Additionally, model complexes have been prepared that implicate the metallocyclic mechanism. However, recent work by Suttil \textit{et al.} have cast this assumption into doubt, demonstrating that
the titanium catalysts produce an isotopolog distribution more consistent with the Cossee-Arlman mechanism when a mixture of ethylene and perdeuteroethylene are dimerized. DFT studies have also suggested that the Cossee-Arlman mechanism is more energetically accessible than the metallacyclic mechanism. Further work is required to conclusively determine the mechanism of catalysis.

Catalyst stability and reactor fouling are the two main problems that plague these titanium catalysts for ethylene dimerization. Kinetic analysis demonstrates that these catalysts decompose in under thirty minutes, requiring a constant stream of catalyst. Even more problematic is that polyethylene accounts for 1-5% of the overall products. Although laboratory scale reactions are not adversely affected by this level of polymeric byproducts, this represents a major operational challenge for reactions performed on an industrial scale. Chronic reactor fouling necessitates frequent process shutdowns, as accumulated polymer may clog reactor valves and decrease the efficiency of cooling systems. Researchers at Saudi Aramco have recently reported that the inclusion of antifouling agents such as phosphonium salts can retard polymer formation during dimerization catalysis, typically leading to an 80% reduction of polyethylene formation without negatively impacting dimerization activity.

1.4.1.4 Tantalum catalysts

In the late 1970s, Schrock and coworkers reported tantalum catalysts that are extremely selective for the dimerization of ethylene to 1-butene. Model complexes have been prepared that implicate the metallacyclic mechanism for ethylene dimerization (Figure 1-10). Unlike many of the other developed catalysts, these tantalum systems do not require activation via the addition of an alkyl aluminum species. This unique

![Figure 1-10. An isolated tantalum compound, indicating a metallacyclic mechanism for ethylene dimerization.](image)
feature has enabled these catalysts to be used in tandem alkane upgrading systems, where alkyl aluminum species are incompatible with the other catalyst.48

1.4.2 Heterogeneous Catalysts for ethylene dimerization

1.4.2.1 Nickel-based heterogeneous catalysts

Although homogeneous catalysts continue to dominate selective ethylene dimerization, the existing technology poses significant challenges that could potentially be solved with heterogeneous catalysts. Some homogeneous catalysts are tremendously active for ethylene dimerization, but they often decompose rapidly via biomolecular decomposition pathways. Thus, in many publications the catalyst loading is minimized to achieve optimal performance, while reactions are commonly limited to 5 minutes, 10 minutes, 30 minutes, or one hour. Heterogeneous catalysts thus offer a promising path to extending catalyst lifetime, as biomolecular decomposition pathways are eliminated. Reactor fouling with polyethylene byproducts is another major challenge for existing homogeneous catalysts, as the resulting polymer will clog transfer lines and form strands around cooling systems, necessitating frequent reactor shutdown. Although it may be impossible to entirely suppress polyethylene formation with a heterogeneous catalyst, the morphology of the resulting polymer may be altered such that the reactor is not fouled as severely.

Much of the work on heterogeneous ethylene dimerization has been carried out with nickel supported on inorganic porous materials. Supported nickel oxides were the original nickel-based heterogeneous catalysts for ethylene dimerization.49–54 Although ethylene oligomerization was reported at temperatures ranging between 20 °C and 200 °C and selectivity for dimers was generally higher than 80%, activity never exceeded 200 moles of ethylene consumed per mole of nickel per hour, too low to be of any practical use. Ni-exchanged zeolites and nickel supported on mesoporous silica give much more promising
results.\textsuperscript{55} These catalysts are orders of magnitude more active than supported NiO, with turnover frequencies ranging between 10,000 and 48,000 moles of ethylene consumed per mole of nickel per hour.\textsuperscript{56-62} However, these catalysts are poorly selective for 1-butene, with selectivity inversely related with activity. Indeed, the most active of these systems, Ni-MCM-48, is only 42\% selective for dimers, with no data reported for the selectivity for 1-butene.\textsuperscript{55,63}

When supported on porous inorganic materials, catalyst activity is inversely related with the pore size of the material due to catalyst deactivation via pore filling with heavy reaction products.\textsuperscript{60,61} Larger pores allow longer oligomers to diffuse out of the material, resulting in a slower deactivation rate. Catalytic reactions were run at temperatures between 0 and 200 °C, with increasing temperatures increasing catalyst activity but decreasing selectivity for 1-butene. Although these materials demonstrate that high activities for ethylene oligomerization can be obtained with heterogeneous materials, the low selectivity renders these catalysts impractical for industrial applications.

A recent study by Agirrezabal-Telleria and Iglesia reports the optimization of Ni-MCM-41 to afford an extremely active, stable, and selective catalyst for ethylene dimerization.\textsuperscript{64} Differing from previous studies with Ni-MCM-41, ethylene dimerization was carried out at subambient temperatures (240-260 K), inducing the condensation of ethylene within the ordered mesopores of the material. At decreasing temperatures, this intrapore condensation of ethylene led to the abrupt suppression of catalyst deactivation. Furthermore, the high local concentration of ethylene facilitated the desorption of 1-butene prior to isomerization or additional insertion, affording a much higher selectivity at subambient temperatures than observed at 448 K. Activities as high as 77,800 moles of ethylene consumed per mole of nickel per hour were reported, with a selectivity for dimers of 98\% and 1-butene accounting for 92\% of the dimeric products.
1.4.2.2 Titanium-based heterogeneous catalysts

Titanium alkoxides supported on silica or alumina phosphate are some of the most successful heterogeneous catalysts for ethylene dimerization. High surface area supports are essential for catalysis, as solid titanium(IV) alkoxides have been reported to be inactive for the dimerization of ethylene. Optimal results were obtained when a reducing agent such as a dialkylmagnesium was supported on silica or alumina phosphate, which was subsequently treated with Ti(OEt)$_4$. Similar to homogenous catalysts, the supported materials were inactive unless also treated with a small amount of triethylaluminum, with the highest activity obtained at a ratio of triethylaluminum/titanium = 3. Trialkylaluminum species are uniquely capable of activating this system, as chloride containing cocatalyst such as diethylaluminum chloride completely suppressed ethylene dimerization in favor of polymerization. Despite the necessity of triethylaluminum, these supported catalysts are substantially more stable than the homogenous analogs. The activity of the heterogeneous catalyst decays by approximately 25% after a 30 minute reaction, whereas the activity of the homogeneous catalyst decreases by more than 75% under analogous conditions. Indeed, the peak activity for the supported catalyst exceeds that of the unsupported catalyst, a rare example of heterogenization improving catalyst activity. Unfortunately, selectivity data for the supported catalyst is not consistently reported, although it is mentioned that 1-butene is the primary oligomeric product, in one case accounting for up to 98.9% of the oligomers (trace 2-butenes are present, in addition to C$_6$ products). The major limitation for this catalyst is that polymeric products are formed in addition to oligomeric products, with polymers accounting for 1-5% of the total products. This is believed to be due to the leaching of titanium species into solution, which was demonstrated upon soaking the supported catalyst with a hot triethylaluminum solution. The possibility that the observed dimerization activity is due to leached homogeneous species has
not been excluded, which is particularly relevant given that the attachments to the support can be cleaved by triethylaluminum. Nonetheless, the stable reaction kinetics for the supported system suggest that catalyst leaching is slow and that the heterogenized catalyst is active in addition to any homogeneous species.

1.4.2.3 Metal-organic frameworks as heterogeneous catalysts for ethylene dimerization

Metal-organic frameworks (MOFs) are a class of materials that have found growing success as heterogeneous catalysts. The first example of ethylene oligomerization with MOFs used the framework Fe-MIL-101-NH$_2$ as a scaffold to immobilize a known homogeneous catalyst.\textsuperscript{67} The amine functionalized MOF was condensed with 2-pyridinecarboxaldehyde and metallated with NiCl$_2$ in a one-pot reaction, resulting in a supported organometallic nickel-based catalyst (Figure 1-11). The resulting material showed promise for ethylene oligomerization, with turnover frequencies between 3,215 hr$^{-1}$ and 20,000 hr$^{-1}$. Nickel loading greatly influences the activity of the MOF-supported catalyst, with the activity per nickel site increasing as the overall number of nickel sites decreases. This is likely due to mass transport limitations caused by the grafting of homogeneous catalysts onto the ligand of the MOF, as the surface area decreases from 1884 m$^2$/g to 155 m$^2$/g after the post-synthetic installation of the catalyst. Importantly, this catalyst affords a high selectivity for 1-butene, with dimers accounting for approximately 90\% of the products. It was reported that \(\alpha\)-olefins were the exclusive product formed by this catalyst,\textsuperscript{67} although in our hands 1-butene accounts for only 88\% of the dimeric products.\textsuperscript{68} Nonetheless, this is substantially more selective than other active nickel-based heterogeneous catalysts, demonstrating that the unique versatility of
MOFs can be exploited to produce excellent catalysts for ethylene dimerization. Similar MOF-based catalysts have been prepared by grafting the same catalytic unit onto other amine functionalized MOFs. Although these reports provide a proof of concept, further improvements are clearly necessary to make industrially competitive catalysts.

Another example of heterogeneous ethylene dimerization utilized the UiO-67 variant prepared from ZrCl$_4$ and 2,2'-bipyridine-5,5'-dicarboxylic acid, generating a MOF with 2,2'-bipyridine moieties lining the pores of the material. These ligands were subsequently post-metallated with NiBr$_2$, generating species similar to early ethylene oligomerization catalysts reported by Brookhart (Figure 1-12). Upon activation with diethylaluminum chloride, these MOF-based catalysts were proficient for ethylene oligomerization, with activities reaching 36,000 moles of ethylene consumed per mole of nickel per hour. As expected from the homogeneous analog, however, the MOF catalyst produced a wide range of olefins and were poorly selective for \( \alpha \)-olefins. Catalyst activity increased with decreased loading, an observation explained by mass transport limitations restricting access of both the alkyl aluminum activator and monomer to catalytic sites in the particle interior.

Surprisingly, the oligomeric products deviate from the Schulz-Flory distribution, with more short olefins observed than predicted. This could possibly be explained by the confinement of a catalyst in the interior of a porous material, effectively inhibiting chain growth past a certain length. Unfortunately, analysis of the product distribution is complicated by the formation of a second catalytically active nickel species. It has been repeatedly demonstrated that metals can be deposited on the secondary building units of zirconium MOFs such as UiO-67. As confirmed by experiments with unfunctionalized UiO-67, nickel species are deposited
upon the zirconium SBUs, generating catalytically active sites that exclusively produce C₄-C₁₀ olefins (albeit with poor selectivity for α-olefins). The presence of multiple nickel species makes it difficult to determine whether deviations from the Schulz-Flory distribution are due to catalyst confinement effects. Although alternative explanations cannot be ruled out, exploiting confinement effects in MOF catalysis deserves continued attention.

In addition to appending catalysts to MOF ligands, molecular catalysts have also been appended to the metal clusters of MOFs. Much of this work has been reported with zirconium MOFs, as the secondary building units have pendant hydroxyl groups that provide a handle for post-synthetic modification. Madrahimov et al. attached 5-methylphosphonate-2,2'-bypridine to the nodes of NU-1000, which was metallated with nickel chloride to afford a (bipyridyl)nickel dichloride species supported on the MOF (Figure 1-13). Upon treatment with diethylaluminum chloride this catalyst was active for ethylene dimerization, with turnover frequencies of 7,200 moles of ethylene per mole of nickel per hour. These catalysts could be recycled up to three times, and were used in a gas-solid phase reaction. As expected with a nonselective catalyst, substantial amounts of polyethylene was formed in addition to the desired oligomers. Interestingly, the selectivity for α-olefins was much higher than reported for the analogous homogeneous complex and with related heterogeneous catalysts, although the cause of this increased selectivity remains unclear.

In addition to the installation of molecular catalysts, isolated metal species have also been directly deposited upon the nodes of zirconium MOFs to produce ethylene dimerization catalysts. By reacting Ir(C₂H₄)₂ with pristine UiO-66 and pristine NU-1000, immobilized...
iridium sites were prepared that could be characterized by EXAFS and IR spectroscopy.\textsuperscript{72} Under a flow of ethylene and hydrogen, these iridium centers primarily hydrogenated ethylene to ethane, although trace ethylene dimerization products were formed (\textasciitilde7 ethylene molecules were converted into dimers per iridium center). Calculations suggest that ethylene is dimerized via a metallacyclic mechanism, although relatively high activation barriers cause the preference for ethylene hydrogenation relative to ethylene dimerization. Although these catalysts were relatively inactive, the uniformity of the supported catalytic species is a major advantage of MOFs, as the single-site nature of these catalysts will enable the formation of selective catalysts. Similar systems have been developed via the deposition of nickel upon the nodes of NU-1000, although these systems are also poorly active for ethylene dimerization.\textsuperscript{73,74}

In an alternative approach, Long \textit{et al.} reported using the metal sites intrinsic to Ni-MOF-74 as catalysts for olefin oligomerization.\textsuperscript{75} Although not a particularly active catalyst, this was the first report of using the secondary building units of MOFs to catalyze olefin oligomerizations. This report is primarily focused on the dimerization of propylene, although in the supporting information it is reported that Ni-MOF-74 is active for ethylene oligomerization as well, albeit only barely so, with just six moles of propylene oligomerized per mole of nickel per hour. This activity is almost certainly due entirely to defect sites, as the ideal secondary building unit of MOF-74 only has one open coordination site per metal, insufficient for olefin oligomerization. However, given that no additional units must be appended to the MOF, the porosity of the material is maintained, making this approach a promising avenue for future research.
1.5 Selective Ethylene Trimerization

1.5.1 Homogeneous Trimerization Catalysts

1.5.1.1 Chromium Catalysts

Chromium catalysts are the most extensively studied systems for ethylene trimerization. The earliest studies on ethylene trimerization were reported by Union Carbide Corporation researchers investigating related systems for ethylene polymerization. Treatment of chromium 2-ethylhexanoate with hydrolyzed triisobutyl aluminum under an ethylene atmosphere gave polyethylene with exclusively n-butyl branches, implicating a side reaction that selectively trimerized ethylene. These studies hinted at one of the challenges of developing selective trimerization catalysts, as both polyethylene and 1-hexene were formed in appreciable amounts. The rate of 1-hexene formation is second order in ethylene, leading to early proposals that selective ethylene trimerization involves a chromacyclopentane intermediate. This system was later optimized to limit polymer formation via the addition of 1,2-dimethoxyethane, with 1-hexene accounting for 74% of the products. Branched decenes were also observed, suggesting the cotrimerization of two ethylene molecules and a 1-hexene molecule.

The Phillips ethylene trimerization catalyst was the first selective trimerization technology to be commercialized, with a selectivity for 1-hexene above 90% while limiting polyethylene formation to just 2% of the products. The catalyst is prepared by combining chromium (III) 2-ethylhexanoate, 2,5-dimethylpyrrole, diethylaluminum chloride, and triethylaluminum in a ratio of 1:3.3:7.8:10.8. At 115 °C and 100 bar of ethylene catalyst activities exceeding 150,000 g/g Cr per hour are obtained with a 93% overall selectivity for 1-hexene. The catalyst can be further enhanced by the addition of a non-coordinating Lewis acid such as B(C₆F₅)₃. Despite the commercial success of the Phillips trimerization catalyst,
the fundamental aspects of this catalyst remain poorly understood. The pyrrole ligand is believed to flip between $\gamma^1$ and $\gamma^5$ throughout the catalytic cycle to compensate for changes in the coordination environment at chromium. The oxidation state of the active catalyst is still under debate, with evidence supporting both a Cr(II)/Cr(IV) mechanism and a Cr(I)/Cr(III) mechanism.

Modern chromium catalysts for ethylene trimerization have utilized multidentate ligands featuring P, N, O, and S donors. Bis(phosphino)amine chromium complexes - when activated with methylaluminoxane - were some of the first well-defined selective trimerization catalysts, which were quickly followed by bis(sulfanyl)amine chromium complexes with comparable activities and selectivities (Figure 1-14). The ease of preparation and the relative stability of the bis(sulfanyl)amine ligands make these systems generally preferred. Researchers at Sasol have optimized the bis(sulfanyl)amine chromium catalysts to demonstrate that with relatively few equivalents of MAO (30-100 equivalents) 1-hexene selectivities above 97% and turnover frequencies up to 300,000 hr$^{-1}$ can be obtained. However, these optimized catalyst conditions require very low catalyst loading levels. Recent studies have investigated whether the N-H functionality of the precatalyst is preserved upon treatment with methylaluminoxane. Deprotonation of bis(phosphino)amine chromium complexes generates dimeric species that are comparably active for trimerization as the protonated analog under analogous conditions.

![Figure 1-14. Bis(phosphino)amine and bis(sulfanyl)amine chromium complexes are active for ethylene trimerization. Both Cr(II) (B and D) and Cr(III) (A and C) precatalysts give similar performance, suggesting the same active species is prepared under reaction conditions.](image-url)
N-alkylated analogs were prepared and tested for ethylene trimerization, displaying low activity and between 30% and 70% of polyethylene, suggesting that the catalytically active species is deprotonated. However, when similar complexes were treated with 5 equivalents of either trimethylaluminum or isobutylalumoxane protonated chromium cationic dimer were isolated. The conditions of these model reactions are not directly comparable to the conditions of catalysis, making it unclear how relevant these conditions are for catalysis. To further probe the oxidation state of the metal, chromium(II) and chromium(III) analogs were prepared (Figure 1-14). Upon treatment with MAO both species behaved similarly catalytically, leading to the conclusion that the Cr(III) precursors are reduced to Cr(II) under reaction conditions.

Tris(pyrazolyl)methane chromium complexes and related heteroscorpionates have been developed by the Tosoh Corporation as ethylene trimerization catalysts. When treated with 360 equivalents of methylaluminoxane, tris(3,5-dimethyl-1-pyrazolyl)methane chromium trichloride (Figure 1-15) is extremely selective for the trimerization of ethylene, with 1-hexene accounting for more than 99% of the products. At 80 °C and 40 bar of ethylene the turnover frequency reaches 74,500 moles of ethylene consumed per mole of chromium per hour. The activity can be increased through subtle ligand variation, with the imidazolyl-based heteroscorpionate reaching a maximum activity of 98,000 hr⁻¹.

Diphosphinoamine ligands (P,N,P) support some of the most active and selective chromium catalysts for ethylene trimerization (Figure 1-16). Upon treatment of the free ligand with chromium and methylaluminoxane, the in situ generated catalysts have turnover frequencies in excess of 1,800,000 hr⁻¹ at 20 bar of ethylene. 1-hexene accounts for roughly
80-90% of the products, with C10 olefins being the major byproducts. The ortho-methoxy substituents on the aryl rings are necessary for this high selectivity, as catalysts without these methoxy groups produce 1-octene instead of 1-hexene.9 Asymmetric ligands with partial methoxy substitution shows decreased selectivity for 1-hexene, and the overall selectivity for 1-hexene versus 1-octene can be controlled by varying the total methoxy substitution.9 These effects are not strictly electronic, as ligands with para-methoxy groups also produce 1-octene instead of 1-hexene.9 Steric interactions play at least some role in the selectivity for 1-hexene relative to 1-octene, as ortho-ethyl substituents on the aryl ring shows an increased selectivity for 1-hexene relative to the unsubstituted analog.9 Nonetheless, of the P,N,P- catalysts the ortho-methoxy substituted variants are most selective for ethylene trimerization, likely due to the dative binding of the methoxy group to the metal center (Figure 1-16B).

Substantial mechanistic work has been devoted to understanding the nature of these P,N,P- chromium catalysts. In the mid-2000s, Bercaw and Agapie demonstrated that selective trimerization proceeds via a metallacyclic mechanism.92 A 1:1 mixture of ethylene and perdeuterioethylene was trimerized and the resulting isotopolog distribution was more consistent with the metallacyclic mechanism. Subsequent studies suggested that the proposed metallacycloheptane decomposes in a single intramolecular step, rather than a β-hydride elimination followed by reductive elimination.93 Although the catalyst is commonly formed in situ, well-defined precatalysts have also been prepared. Single crystal X-ray diffraction revealed
that the ortho-methoxy group is datively bound to the metal center, making these ligands ostensibly P,P,O-chelating ligands (Figure 1-15B). NMR studies have established that the methoxy binding to the metal center is dynamic, with exchange occurring between different methoxy substituents.

1.5.1.2 Titanium Catalysts

Although not as prevalent as chromium systems, titanium catalysts are well-developed for ethylene trimerization. One notable class of Ti catalysts are supported by cyclopentadiene-arene ligands (denoted Cp-arene Ti catalysts; Figure 1-17). Under optimal conditions, these catalysts are 90% selective for 1-hexene with activities in excess of 200,000 moles of ethylene consumed per mole of titanium per hour. The primary byproducts are C_{10} olefins resulting from the cotrimerization of 1-hexene with two molecules of ethylene, although polyethylene accounts for ~2% of the products as well. Polyethylene formation is believed to form via two different catalytic species. At the beginning of the reaction, a partially alkylated cationic titanium complex is responsible for the majority of the polymerization, while the slow decomposition of the trimerization catalyst leads to the formation of additional polyethylene throughout the course of the reaction. Pretreating the catalyst with trimethylaluminum to fully alkylate the precatalyst reduces initial polyethylene formation, although polyethylene still is formed as the reaction progresses.

Multiple studies have investigated the mechanism of trimerization with both experimental and computation methods. Although the catalyst is thought to proceed through a metallacyclic mechanism, catalyst activity is first order in ethylene, suggesting that ethylene insertion into the metallacyclopentane is the rate limiting step. Catalyst decomposition is
second order in titanium, indicating a bimolecular decomposition pathway. Treating the \((\text{Cp-arene})\text{TiCl}_3\) precatalyst with methylaluminoxane leads to a cationic Ti(II) species through alkylation, insertion, and reductive \(\beta\)-hydride transfer.\(^{98-100}\) Calculations suggest that trimerization occurs through Ti(II)/Ti(IV) intermediates, with the pendant arene group serving a crucial role in facilitating catalysis. Throughout the catalytic cycle ring-slipping takes place with the arene group, shuttling between \(\eta^1\)-, \(\eta^3\)-, and \(\eta^6\)- coordination. The bridge between the Cp ligand and the pendant arene is also crucial for catalysis. Single crystals of complexes with a CMe\(_2\) bridge display \(\eta^1\)- binding of the arene, whereas \(\eta^6\)- binding is observed in complexes with a CMe\(_2\)CH\(_2\) bridge.\(^{101}\) Variable temperature NMR studies demonstrate that the arene group in CMe\(_2\) bridged complexes display hemilabile coordination, whereas CMe\(_2\)CH\(_2\) bridged complexes show tight arene binding. Importantly, the CMe\(_2\) bridged complexes are active for ethylene trimerization whereas CMe\(_2\)CH\(_2\) bridged complexes are not.

Several variations of the Cp-arene Ti complexes have been prepared, although introduction of other functional groups typically decreases the catalytic performance of the catalyst. Indeed, one report even demonstrates some trimerization activity with just unsubstituted CpTiCl\(_3\), trimethylaluminum, and methylaluminoxane, although the activity is fiftyfold lower than that of the arene substituted analogs.\(^{102}\)

Perhaps the most notable development in ethylene trimerization of the past decade has been the introduction of phenoxyimine titanium catalysts (Figure 1-18) as extremely active and selective catalysts for ethylene trimerization.\(^8\) Developed by researchers at Mitsui chemicals as an extension of extremely active polymerization catalysts based upon phenoxyimine ligands, these complexes feature pendant methoxy donors that coordinate and

![Figure 1-18. Phenoxyimine catalysts are extremely active for ethylene trimerization.](image-url)
stabilize the metal center. The best of these catalysts features an activity in excess of 1,000,000 moles of ethylene consumed per mole of titanium per hour with a selectivity for 1-hexene in excess of 92%. Unlike the Cp-arene catalysts, phenoxyimine titanium catalysts display a second-order dependence on ethylene pressure, suggesting that the formation of the metallacyclopentane intermediate is the rate-determining step. Patents filed by Mitsui have shown that a wide range of related complexes are similarly active and selective. Replacing the methoxy group with other ethers has perhaps the most substantial influence on catalyst performance, decreasing both activity and selectivity for 1-hexene. However, decreasing the steric bulk around the metal center also leads to a decrease in both selectivity and activity. Presumably the decreased steric bulk enables secondary reactivity of 1-hexene in the reactor, while also increasing the rate of catalyst decomposition.

Bercaw and coworkers have made substantial contributions to our understanding of phenoxyimine based catalysts for ethylene trimerization. They have shown that in addition to treating the chlorinated precatalyst with methylaluminoxane, a methylated precatalyst can be treated with B(C₆F₅)₃ to generate the active species. Crystal structures show that the methoxy group is not coordinated to the (Fl)TiMe₃ precatalyst, although NMR studies suggest the coordination of the methoxy group upon methyl abstraction. Over the course of 120 minutes the catalyst decomposes, with EPR studies indicating the decomposition product is a Ti(III) complex, suggesting the comproportionation of Ti(II) and Ti(IV) intermediates. Other decomposition pathways are also active, including the gradual decomposition of the ligand.

1.5.1.3 Tantalum Catalysts

Tantalum catalysts have also been utilized for ethylene trimerization, although these are far less developed than chromium or titanium catalysts. TaCl₅ is capable of selectively trimerizing ethylene when treated with an alkylating agent such as AlR₃ or ZnR₂, although the
activity of this system is just 500 moles of ethylene consumed per mole of tantalum per hour.\textsuperscript{105} This diminished activity has enabled characterization of intermediates, with the TiCl\textsubscript{3}Me\textsubscript{2} intermediate being observed by \textsuperscript{1}H NMR after treatment of TaCl\textsubscript{5} with AlR\textsubscript{3}. This species subsequently undergoes insertion and \(\alpha\)-hydride abstraction to generate the catalytically active species. The metallacyclopentane is the catalyst resting state (identified by \textsuperscript{1}H NMR), as ethylene insertion into the metallacyclopentane is the rate limiting step.\textsuperscript{106} Alternative routes to the reduction of TaCl\textsubscript{5} have been explored, leading to somewhat more active systems (\(\sim 2500\) hr\textsuperscript{-1}) when reduced with bis(trimethylsilyl)cyclohexadiene.\textsuperscript{107}

1.5.2 Heterogeneous Trimerization Catalysts

As with ethylene dimerization, a number of attempts have been made to develop heterogeneous ethylene trimerization catalysts, although to date no options have proven superior to their homogeneous analogs or sufficiently attractive to afford commercialization. The earliest examples were based on variations of the Phillips trimerization catalyst supported on AlPO\textsubscript{4}, SiO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3}. Activities in excess of 10000 g/g Cr per hour were obtained with alumina supported Cr\textsubscript{5}(C\textsubscript{4}H\textsubscript{4}N)\textsubscript{10}(C\textsubscript{4}H\textsubscript{4}O)\textsubscript{4}, although liquid oligomers accounting for only 31% of the overall products, with undesirable polyethylene being the predominant product formed.\textsuperscript{102} Treating Cr(III) pyrrole polymers with triethylaluminum afford a catalyst that was 99% selective towards liquid oligomers, although it was unclear whether the catalyst was truly heterogeneous or if the activity was due to leached species.\textsuperscript{82,108} In either case, the activity of the Cr(III) polymer was drastically lower, with an activity of just 1030 g/g Cr per hour. Other variants on the Phillips catalyst have been immobilized on silica, although significant quantities of polyethylene are produced in these reactions and the activities reported are rather low, providing no clear benefit over the homogeneous systems.\textsuperscript{109}
Some efforts have demonstrated that the Phillips polymerization catalyst can be converted into a trimerization catalyst when treated with appropriate ligands. For instance, when the reduced Phillips polymerization catalyst was treated with triazacyclohexane and activated with [Me₂PhNH]-[B(C₆F₅)₄]/AlBu₃, a small amount of 1-hexene was formed in addition to polymeric products that account for 80% of the products. However, turnover frequencies for 1-hexene are below 10 moles of ethylene consumed per mole of chromium per hour, multiple orders of magnitude less active than other trimerization catalysts reported.

Perhaps the most successful approach towards heterogeneous ethylene trimerization has been the immobilization of homogeneous trimerization catalysts on silica/MAO composites. In these materials, the silica support is first treated with MAO, immobilizing the cocatalyst on the silica surface. The trimerization precatalyst is subsequently exposed to the silica/MAO support, which activates the precatalyst and effectively heterogenizes the catalyst via electrostatic interactions. Although some catalysts are incompatible with this method – instead switching to polymerization catalysts – phenoxylamine based trimerization catalysts have shown some aptitude for heterogenization. Bercaw et al. have demonstrated that heterogenization of (Fl)TiCl₃ on silica/MAO leads to a more than tenfold increase in productivity of the titanium species relative to its homogeneous analog under analogous conditions. This is attributed to a decreased rate of catalyst decomposition, as one major pathway of deactivation for the homogeneous catalyst is the comproportionation of Ti(II) and Ti(IV) intermediates to inactive Ti(III) species. Although some catalyst mobility remains with the silica/MAO immobilized species – in addition to the presence of other deactivation pathways – the lifetime of the catalyst is significantly increased, resulting in a higher turnover number. Heterogenizing catalysts in this manner is very versatile and has the potential alter the morphology of resulting polyethylene byproducts such that they do not foul the reactor.
One MOF-based catalyst for selective ethylene trimerization has been reported. This system exploits the chromium secondary building units available in Cr-MIL-100 to develop a catalyst with a maximum oligomerization activity of 33,100 moles of ethylene consumed per mole of chromium per hour, although 1-hexene only accounts for 40% of the oligomeric products. Remarkably, thermal activation of the MOF to remove bound solvent has a significant influence on the activity and selectivity of the catalyst, with lower activation temperatures affording catalysts that are more selective for 1-hexene. The authors propose this change in selectivity is due to variable amounts of Cr(II) and Cr(III) in materials activated at different temperatures, suggesting that Cr(II) centers are responsible for ethylene polymerization. The exact mechanism of ethylene oligomerization in this MOF remains unclear, as the idealized MOF structure only affords one open coordination site per chromium. Nonetheless, this report demonstrates that the metal nodes of MOFs can serve as catalysts for ethylene trimerization.

1.6 Ethylene Tetramerization

The best developed ethylene tetramerization catalysts are closely related to the diphosphinoamine chromium ethylene trimerization catalysts. Although the trimerization catalysts have ortho-methoxy substituents on the aryl rings of the ligand, the tetramerization catalyst lacks this functionality (Figure 1-19). These tetramerization catalysts are comparably active to the trimerization systems and display selectivities for 1-octene in excess of 80%. Mechanistically, these P,N,P-ethylene tetramerization catalysts are believed to operate through extended metallacyclic intermediates, although it has been proposed that 1-octene may be produced via the coupling of two metallacyclopentanes. Nonetheless, a monometallic mechanism best
explains the byproducts observed with 1-octene. Relative to the trimerization catalysts, these
tetramerization catalysts have an additional coordination site that can participate in ethylene
oligomerization. Calculations suggest the formation of a bis(ethylene)chromacyclopentane
adduct, which undergoes double ethylene insertion into a metallacyclopentane to form a
metallacyclonone. Lastly, this metallacyclonone decomposes to release 1-octene and
regenerate the catalyst. Cyclopentanes are produced as a minor byproduct with these
tetramerization catalysts via the insertion of a distal alkene into a chromium-carbon bond.
These side products are not produced with the analogous trimerization catalysts, as they lack
available coordination sites to enable the insertion.

Gambarotta et al. have reported two additional ethylene tetramerization catalysts
featuring chromium supported by amino substituted phosphine ligands (Figure 1-20). In
one case, the 1-octene selectivity exceeds 91%, although the turnover frequency is orders of
magnitude lower than those of the P,N,P- tetramerization catalysts. In both cases the authors propose that bimetallic intermediates may be responsible for selective ethylene
tetramerization, although direct evidence is lacking. Increasing the steric bulk of the ligand switches the catalyst from selective
tetramerization to selective trimerization, which the authors claim is due to disfavoring the
required bimetallic intermediates for ethylene tetramerization. Nonetheless, this increased
steric bulk may simply favor the formation of a mono-ethylene adduct relative to a
bis(ethylene) adduct, leading to the formation of 1-hexene instead of 1-octene. It should be
noted that these systems are very sensitive to the reaction conditions, only selectively
producing 1-octene in methylcyclohexane. The development of new selective tetramerization catalysts remains an area of great interest.
Selective Dimerization of Ethylene with a Porous Catalyst

2.1 INTRODUCTION

The process advantages afforded by continuous throughput and the ready separation of products have made heterogeneous catalysis an enabling technology for the large-scale manufacture of chemical commodities. However, conventional solid catalysts lack the capacity for precise structural design inherent in molecular catalysts that allows fine-tuning of reactivity and selectivity. The multiplicity and intractability of active sites often observed in heterogeneous catalysts complicates structure/activity-based control over reactivity. Consequently, many chemical processes requiring high selectivity rely on homogeneous molecular catalysis. The AlphaButol process, which produces 1-butene through the dimerization of ethylene on a 700,000 metric ton scale annually, remains one of the largest applications of homogenous catalysis, exceeded industrially by only a few others. Despite substantial academic and industrial efforts, new heterogeneous catalysts for ethylene dimerization have suffered from either a lack of activity or poor selectivity. Controlling the selectivity remains a paramount challenge because the product 1-butene is required in high purity for application as a comonomer in polyolefin synthesis and because the accumulation of higher molecular weight byproducts leads to reactor fouling. The product distribution is defined by the relative rates of ethylene insertion versus chain termination, which can be profoundly influenced by variations in the ligand sphere or electronic structure of the active metal. However, fine-tuning of ligand design to control this reactivity has not traditionally been available to heterogeneous systems.

Metal-organic frameworks (MOFs) are a class of materials that offer tunability in the solid state at the molecular level. These materials are built from metal clusters bridged by organic ligands, which define highly porous three-dimensional structures. Because both the metal clusters and the organic ligands can be modified, MOFs provide the level of control
necessary to develop effective heterogeneous catalysts.\textsuperscript{122-125} A growing number of examples utilize these materials for catalysis, with the majority of work installing well-known homogeneous catalysts into the organic ligand.\textsuperscript{67,69,71} In contrast, the metal clusters, also known as secondary building units (SBUs), provide unique platforms to establish chemical reactivity without decreasing the surface area of the material.\textsuperscript{75,126-128} The SBUs behave like site-isolated molecules suspended throughout a heterogeneous matrix, a structural configuration which may extend the lifetime of the catalyst by eliminating bimolecular decomposition pathways and which potentially provides additional selectivity by pore shape and size. Furthermore, reactive transition metals may be incorporated into these SBUs by mild cation exchange,\textsuperscript{128} offering a rational strategy for installing well-defined active sites based on a crystallographically characterized coordination environment. In this work, we demonstrate that the SBUs in nickel-substituted MFU-4/ (Ni-MFU-4) catalyze the selective dimerization of ethylene with a combination of activity and selectivity that is premier among all heterogeneous catalysts.

In developing new heterogeneous catalysts for ethylene dimerization, we sought to employ SBUs that are structurally homologous to promising homogeneous catalysts which could benefit from site isolation. Molecular \([\text{Tp}^{\text{Mes}}\text{Ni}]^+\) (\(\text{Tp}^{\text{Mes}} = \text{HB}(3\text{-mesitylpyrazolyl})\)) complexes are particularly attractive candidates in this sense: they display turnover frequencies of \(\sim 30,000\) moles of ethylene converted per mole of nickel per hour, with butenes accounting for up to 87\% of the products,\textsuperscript{32} but suffer from inactivation by catalyst aggregation. We thus surmised that isolating Tp-like moieties in a MOF would offer a more robust environment for catalytic ethylene dimerization. Four of the five \(\text{Zn}^{2+}\) ions in each SBU of MFU-4/ are coordinated in such a manner: the SBUs contain a central Zn atom that is octahedrally coordinated by six nitrogen atoms, and four tetrahedral \(\text{Zn}^{2+}\) ions coordinated by three nitrogen atoms and a chloride (Figure 2-1). These tetrahedral \(\text{Zn}^{2+}\) ions are exposed to the
MOF’s cubic pores (Figure 2-6), which have been found to have aperture diameters between 1.1-2.0 nm. Because the bond angles and lengths surrounding these Zn2+ ions are almost identical to those found in Tp complexes, we reasoned that Ni-MFU-4 could indeed serve as a very proficient heterogeneous catalyst for ethylene dimerization.

Figure 2-1. Structure of Ni-MFU-4 and TpMeNiCl. A. A representation of the three dimensional structure of Ni-MFU-4 highlighting the exposure of the SBUs to the pores. B. Ball-and-stick model of the inorganic secondary building unit in Ni-MFU-4. C. Ball-and-stick model of TpMeNiCl. D. A space-filling model of the inorganic cluster of Ni-MFU-4. E. A space-filling model of TpMeNiCl.
2.2 RESULTS AND DISCUSSION

Direct solvothermal synthesis of a nickel-doped MFU-4/ from mixtures of Ni$^{2+}$ and Zn$^{2+}$ starting materials was unsuccessful, producing only amorphous solids. However, simple exchange of the parent zinc framework by soaking in an N,N-dimethylformamide (DMF) solution of Ni(NO$_3$)$_2$$\cdot$6H$_2$O, under conditions mimicking those reported previously,$^{131,132}$ afforded nickel-substituted materials with a Ni content that could be tuned by varying the soaking time and temperature. Exchanging Zn$^{2+}$ ions for Ni$^{2+}$ does not affect the structural integrity or the porosity of the MOF, as verified by comparisons of the exchanged materials with the parent Zn materials using powder X-ray diffraction and N$_2$ gas sorption analysis (Figure 2-7, Figure 2-8).

To verify the Ni$^{2+}$ coordination environment, Ni(Cl)-MFU-4/ was examined by X-ray absorption spectroscopy (XAS). The XAS spectra of Tp$_2$Ni and anhydrous NiCl$_2$ were also collected for comparison. The edge energy obtained for Ni-MFU-4/ agrees well with both of these standards (Table 2-4), consistent with a Ni(II) oxidation state in Ni-MFU-4/. Furthermore, Ni-MFU-4/ displays a more intense pre-edge feature than either NiCl$_2$ or Tp$_2$Ni, consistent with a lower-symmetry, pseudo-tetrahedral coordination environment (Figure 2-4). Fitting the X-ray absorption fine structure (EXAFS) data resulted in three Ni-N bonds (1.99 Å, Table 2-3) and one Ni-Cl bond (2.14 Å), similar in length to those of DFT models of Ni-MFU-4/ (1.95 Å and 2.12 Å respectively). Fitting a different coordination number and a different combination of scattering atoms both gave significantly worse fits, allowing us to rule out other potential coordination modes for Ni$^{2+}$ in Ni-MFU-4/.

Ni-MFU-4/ displays excellent activity for ethylene dimerization, whereas the parent Zn analog remains inactive. A typical catalytic protocol consisted of the addition of methylaluminoxane (MAO) to a rapidly stirred suspension of Ni-MFU-4/ in toluene, with


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Table 2-1. Results of ethylene dimerization with Ni-MFU-4\(^{l}\), as determined by GC analysis. \(^{a}\)Catalyst is Ni(10\%)\(-\)MFU-4\(^{l}\); \(^{b}\)Catalyst is Ni(30\%)\(-\)MFU-4\(^{l}\); \(^{c}\)Catalyst is Ni(3\%)\(-\)MFU-4\(^{l}\); \(^{d}\)Catalyst is Ni(1\%)\(-\)MFU-4\(^{l}\). \(^{e}\)Moles of ethylene converted per mole of nickel per hour, determined by GC analysis. \(^{f}\)Percent oligomeric products that are C\(_4\) olefins. \(^{g}\)Percent oligomeric products that are C\(_6\) olefins. \(^{h}\)Percent 1-butene relative to all C\(_4\) products. The overall selectivity for 1-butene among all products.
subsequent pressurization with ethylene gas. Upon completion, the reactor was rapidly cooled with a dry ice/acetone bath to condense the oligomerized products and the reaction was quenched with ice-cold water. After a 60 minute reaction at 25 °C, 30 bar of ethylene, and in the presence of 100 equivalents of MAO, a Ni-MFU-4/ sample with a Ni:Zn ratio of ~ 1:9 (Ni(10%)-MFU-4/) shows a turnover frequency of 21,000 moles of ethylene consumed per mole of Ni per hour. The products contain 94.9% butenes, 4.8% hexenes, and no other detectable higher oligomers, with only trace polyethylene (0.3% by weight). Leaching experiments indicate that the observed activity is not attributable to homogeneous decomposition products (Figure 2-13). Further optimization of the reaction conditions showed that temperature has a dramatic effect on the catalytic performance of Ni-MFU-4/. For a given ethylene pressure, the dimerization activity is comparable at 0 °C and 25 °C, although no polymeric residues are isolable at 0 °C. There is, however, a marked drop-off in oligomerization activity when the reaction temperature is increased to 50 °C, with a concomitant decrease in the selectivity for 1-butene in favor of the isomerized, less desirable product 2-butene (Table 2-1, entries 5 – 13).

The reaction pressure also plays a key role in the catalytic performance of Ni-MFU-4/. Two distinct reactivity regimes are present for Ni(10%)-MFU-4/ when the ethylene pressure is varied between 5 and 50 bar at 25 °C in the presence of 100 equivalents of MAO (Figure 2-2B). The activity of Ni(10%)-MFU-4/ has a first order dependence on ethylene at pressures below 25 bar, which is consistent with the Cossee-Arlman mechanism that is commonly proposed for ethylene oligomerization with homogeneous nickel complexes (Figure 2-2A). The activity of Ni(10%)-MFU-4/ plateaus at pressures higher than 25 bar, although the selectivity for 1-butene continues to increase at higher pressures of ethylene (Figure 2-2C).
This trend suggests that higher ethylene pressure suppresses the competitive reinsertion of 1-butene, which would contribute to the 2-butene and hexene byproduct formation.\textsuperscript{133}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2-2.pdf}
\caption{Mechanism, activity, and product distribution of ethylene dimerization with Ni-MFU-4. A. Proposed catalytic cycle for ethylene dimerization in Ni-MFU-4. B. The pressure and Ni content dependence of ethylene dimerization in Ni-MFU-4. C. The product distribution at various ethylene pressures for Ni(10\%)-MFU-4 at 25 °C with 100 equivalents of MAO.}
\end{figure}

Activation of Ni-MFU-4 by an alkyl aluminum reagent is essential for catalysis, and reactivity is strongly influenced by the identity and relative loading of this activator. No catalytic activity is observed in the absence of an aluminum activator, and the replacement of MAO with diethylaluminum chloride (Et\textsubscript{2}AlCl) or triethylaluminum (Et\textsubscript{3}Al) leads to a greatly diminished activity. For instance, replacement of MAO with an equivalent amount of Et\textsubscript{2}AlCl retards the turnover frequency of Ni(10\%)-MFU-4 at 50 bar and 25 °C from 21,000 h\textsuperscript{-1} to
4,700 h\(^{-1}\). The amount of MAO also correlates positively with the observed catalytic activity. This is most obvious when the quantity of MAO is doubled from 50 to 100 equivalents (Table 2-1, entries 3 and 4). Increasing the amount of MAO beyond 100 equivalents nevertheless leads to incremental improvements in activity, which reaches 27,000 moles of ethylene consumed per mole of nickel per hour in the presence of 500 equivalents of MAO at 50 bar and 25 \(^{\circ}\)C (Table 2-1, Entry 1). Under these conditions, Ni(10\%)\'-MFU-4/ shows a selectivity of 96.5\% for butenes, with an overall selectivity of 89.1\% for 1-butene. The selectivity for 1-butene increases even further when catalysis is run with 100 equivalents of MAO at 50 bar and 0 \(^{\circ}\)C (Table 2-1, Entry 5). These conditions lead to a turnover frequency of 22,600 moles of ethylene consumed per mole of nickel per hour and an optimized selectivity of 98.4\% for butenes, a record among all active heterogeneous catalysts, with 1-butene making up 97.8\% of the C\(_4\) fraction. Indeed, the optimized overall selectivity for 1-butene is thus 96.2\%, a technologically significant improvement over the industrial process, whose selectivity for 1-butene under operating conditions is 93\%\(^2,37-39\) Importantly, under these optimized conditions, Ni(10\%)\'-MFU-4/ produces C\(_6\) olefins as the sole observable byproducts, with no higher oligomers observed by GC, and no isolable polymers. In an industrial setting these C\(_6\) byproducts do not foul the reactor, can readily be separated using technology currently employed in the AlphaButol process\(^9\), and are valuable themselves as copolymerization monomers.

Having identified optimal reaction conditions for catalysis, we sought to evaluate the role of mass transport on the activity of Ni-MFU-4/ by examining the impact of nickel loading on the turnover frequency. Subjecting Ni-MFU-4/ samples with molar Ni loadings of 1\%, 3\%, 10\%, and 30\% of the total metal content to the optimal catalytic conditions revealed clear differences in turnover frequency. Thus, the turnover frequency decreased from 27,000 moles
of ethylene consumed per mole of nickel per hour for Ni(10%)-MFU-4/ to 9,100 h⁻¹ for Ni(30%)-MFU-4/. Potential deactivation stemming from the agglomeration of Ni sites on the same or neighboring SBUs notwithstanding, the decreasing turnover frequency with increased nickel loading is consistent with mass transport limitations typical of porous catalysts. Accordingly, decreasing the nickel loading should improve the activity per nickel site. Indeed, under optimized catalytic conditions Ni(1%)-MFU-4/ exhibits a turnover frequency of 41,500 h⁻¹ (Table 2-1, entries 22-25). This value is commensurate with the activity of homogeneous [Tp₃MCSNi]+, which has a maximum reported activity of 34,600 h⁻¹ when treated with MAO. Assuming that the intrinsic activities of Ni-exchanged SBUs and [Tp₃MCSNi]+ are within the same range, these results suggest that the Ni-SBUs act as heterogenized molecular catalysts and are the active species in Ni-MFU-4/, with the majority of nickel sites contributing to catalysis, not just those on the surface.

Surprisingly, although the maximum observed turnover frequency of Ni-MFU-4/is similar to that of the [Tp₃MCSNi]+, its maximum selectivity for 1-butene, 96.2%, is notably superior to the latter, which only reaches 80.8%. This superior selectivity is not solely attributable to differences in reaction conditions, because Ni-MFU-4/ still has a selectivity of 93.0% for 1-butene when operated under the most selective conditions for the molecular [Tp₃MesNi]+ complexes. Although shape or size selectivity induced by the pores of Ni-MFU-4/ may explain the preference for butenes relative to hexenes, they do not account for the higher 1-butene selectivity observed with the heterogeneous catalyst. An alternative explanation is that the less sterically encumbered active site in Ni-MFU-4/ enhances the rate of chain transfer relative to chain propagation or chain isomerization. By analogy, cationic Ni²⁺ α-diimine complexes are well-known catalysts for ethylene oligomerization, but turn into ethylene polymerization catalysts when steric bulk is added in positions axial to the active site.¹⁷,¹⁸ It is
Table 2-2. Heterogeneous catalysts for ethylene dimerization.

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<th>T (°C)</th>
<th>TOF (h⁻¹)</th>
<th>Selectivity (wt %)</th>
<th>Reference</th>
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<td>50</td>
<td>10,482</td>
<td>67, 10, N.R.</td>
<td>55, 61</td>
</tr>
<tr>
<td>Ni-MCM-36</td>
<td>40</td>
<td>150</td>
<td>16,000</td>
<td>45, 25, 35</td>
<td>118</td>
</tr>
<tr>
<td>Ni-MCM-36</td>
<td>40</td>
<td>70</td>
<td>4,200</td>
<td>81, 8, 55</td>
<td>118</td>
</tr>
<tr>
<td>MixMOF-Ni-b</td>
<td>20</td>
<td>40</td>
<td>16,400</td>
<td>92.7, 6.1, N.R.</td>
<td>69</td>
</tr>
<tr>
<td>MixMOF-Ni-b</td>
<td>20</td>
<td>20</td>
<td>2,500</td>
<td>79.5, 6.9, N.R.</td>
<td>69</td>
</tr>
<tr>
<td>IRMOF-3-Ni-a</td>
<td>20</td>
<td>20</td>
<td>2,200</td>
<td>35.0, 9.3, N.R.</td>
<td>69</td>
</tr>
<tr>
<td>Ni@(Fe)MIL-101</td>
<td>15</td>
<td>20</td>
<td>9,400</td>
<td>89.3, 9.5, N.R.</td>
<td>67</td>
</tr>
<tr>
<td>Ni@(Fe)MIL-101</td>
<td>15</td>
<td>10</td>
<td>6,300</td>
<td>95, 4.5, N.R.</td>
<td>67</td>
</tr>
<tr>
<td>Ni@(Fe)MIL-101</td>
<td>15</td>
<td>0</td>
<td>10</td>
<td>N.R., N.R., N.R.</td>
<td>67</td>
</tr>
<tr>
<td>Ni@(Fe)MIL-101</td>
<td>15</td>
<td>30</td>
<td>3600</td>
<td>93, 6.5, N.R.</td>
<td>67</td>
</tr>
<tr>
<td>Ni@(Fe)MIL-101</td>
<td>15</td>
<td>30</td>
<td>3600</td>
<td>93, 6.5, N.R.</td>
<td>67</td>
</tr>
<tr>
<td>Ni@(Fe)MIL-101</td>
<td>30</td>
<td>25</td>
<td>17,700</td>
<td>89.6, 3.6, 94.5</td>
<td>This work</td>
</tr>
<tr>
<td>Ti(OEt)₄/AlPO₄</td>
<td>38</td>
<td>85</td>
<td>28,700</td>
<td>N.R., N.R., N.R.</td>
<td>66</td>
</tr>
<tr>
<td>Ti(OEt)₄/AlPO₄</td>
<td>38</td>
<td>85</td>
<td>22,500</td>
<td>N.R., N.R., N.R.</td>
<td>66</td>
</tr>
<tr>
<td>Ti(OEt)₄/Silica</td>
<td>38</td>
<td>85</td>
<td>25,400</td>
<td>N.R., N.R., N.R.</td>
<td>66</td>
</tr>
<tr>
<td>Ti(OEt)₄/Silica</td>
<td>38</td>
<td>85</td>
<td>18,400</td>
<td>N.R., N.R., N.R.</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 2-2. Selected heterogeneous catalysts for ethylene dimerization. aMoles of ethylene converted per mole of nickel per hour. N.R. = not reported. bThe percentage of oligomeric products that are C₄ olefins. cThe percentage of oligomeric products that are C₆ olefins. dThe percentage of 1-butene relative to all C₄ products.
thus apparent that the Ni environment within Ni-MFU-4 balances active site accessibility and pore-induced shape/size selectivity, thereby leading to the high selectivity for 1-butene.

One of the major attractions in heterogenizing homogeneous catalysts stems from the possibility of extending the catalyst lifetime by eliminating bimolecular decomposition pathways. To study the lifetime of Ni-MFU-4/ and the potential for catalyst recycling, we constructed a two-reactor system that allows us to distill the reaction products without exposing the Ni-MFU-4//MAO slurry to the atmosphere. This experimental setup allows the removal of products by distillation and repressurization of the reactor for evaluating reactivity in consecutive catalytic runs. A reactor charged with Ni(10%)-MFU-4/ was thus cycled continuously over 72 hours (8 cycles), with only a minor decrease in catalyst activity (Figure 2-15). In contrast, the activity of the industrially employed homogeneous catalysts for ethylene dimerization decreases by 50% over the course of one hour.7

Ni-MFU-4/ compares favorably to other heterogeneous catalysts for ethylene dimerization. A large amount of work has focused on using nickel-exchanged zeolites and mesoporous silica as catalysts for the oligomerization of ethylene, with some degree of success.5,6,11,17 However, these catalysts are poorly selective for dimerization, with butenes typically comprising only 40-45% of the resulting products. Furthermore, Ni-exchanged zeolites and mesoporous silica are also poorly selective for α-olefins, with overall selectivity for 1-butene of only ∼15%. Recent work optimizing Ni-MCM-41 has demonstrated it can function as an extremely active, selective, and long-lived catalyst, although the reaction must be maintained at sub-ambient temperatures.64 Previous efforts to develop MOF catalysts for ethylene dimerization have focused on installing well-known homogeneous catalysts into the organic linkers67,69 or onto the inorganic SBUs.71 Although these catalysts show activities ranging from 6,000 to 20,000 h⁻¹, reasonable selectivities for butenes of at least 90% were
associated only with the lower activities. Moreover, some of these catalysts form substantial polymeric deposits that lead to catalyst deactivation. To ensure that differences in reaction conditions were not the cause of the superior catalytic performance of Ni-MFU-4, we prepared Ni@(Fe)MIL-101 and tested it for ethylene dimerization under our optimized reaction parameters (Methods). These conditions do increase dimerization activity for Ni@(Fe)MIL-101, instead resulting in the formation of polyethylene (Figure 2-16). Supported titanium alkoxides come closest to Ni-MFU-4 in terms of activity. However, these supported titanium catalysts produce substantial polymeric deposits accounting for as much as 5% of the total products. Polymeric byproducts present a more substantial liability for large-scale production due to reactor fouling and are much less desirable as end products than the C_6 olefins observed under optimized conditions with Ni-MFU-4.

2.3 CONCLUSION AND OUTLOOK

The foregoing results demonstrate the considerable potential for using MOFs to catalyze industrially significant reactions that currently have no viable solutions in heterogeneous catalysis. Under optimized conditions, the selectivity of Ni-MFU-4 for 1-butene surpasses that of the industrial homogeneous catalyst, whereas its activity is on par with the analogous homogeneous [Tp^{Me}Ni]^+ complexes. The outstanding activity and selectivity of Ni-MFU-4 demonstrate the power in utilizing cation exchange in MOFs to develop well-defined heterogeneous catalysts. We anticipate that exploring further reactivity at the metal nodes of MOFs will lead to important new applications for these highly tunable materials in heterogeneous catalysis.
2.4 METHODS

General Remarks.
Nickel nitrate hydrate (99.9%, Strem), methylaluminoxane (10 wt. % in toluene, Sigma), modified methylaluminoxane (MMAO-12, 7 wt% Al in toluene, Sigma), diethylaluminum chloride (25 wt. % in toluene, Sigma), triethylaluminum (25 wt. % in toluene, Sigma), 1-pentene (analytical standard, 99.5%, Sigma), and ethylene (99.9%, Airgas) were used as received. Dry, deaerated toluene (HPLC Grade, 99.8%) was obtained by passing the solution through two silica columns in a Glass Contour Solvent System and degassing with a flow of argon gas for 30 min followed by three freeze-pump-thaw cycles.

Nickel and zinc analyses for Ni-MFU-4/ samples were performed by Robertson Microlit Laboratories, Ledgewood, New Jersey. Nickel and iron analyses were conducted at the MIT Center for Environmental Health Sciences (MIT CEHS) using an Agilent 7900 inductively coupled plasma mass spectrometer (ICP-MS). Standards were prepared from solutions purchased from VWR designated suitable for ICP analysis.

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker Advance II diffractometer equipped with 0/20 Bragg-Brentano geometry and Ni-filtered Cu-Kα radiation (Kα1 = 1.5406 Å). The tube voltage and current were 40 kV and 40 mA, respectively.

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure nitrogen adsorption isotherms. An oven-dried sample tube equipped with a S3 TranSeal™ (Micrometrics) was evacuated and tared. The sample was transferred to the sample tube, heated to 200 °C for 12 h, and held at that temperature until the outgas rate was less than 2
mTorr/minute. The evacuated sample tube was weighed again and the sample mass was determined by subtracting the mass of the previously tared tube. N\textsubscript{2} isotherms were measured using liquid nitrogen baths (77 K). UHP grade (99.999% purity) N\textsubscript{2} and He, oil-free valves and gas regulators were used for all free space corrections and measurements.

The ethylene dimerization reaction mixtures were analyzed with an Agilent 7890B gas chromatograph (30 meter PoraBOND Q PT capillary column) equipped with a 5977A mass spectrometer and a flame ionization detector.

MFU-4/ was prepared according to the literature.\textsuperscript{12,130,131}

**Synthesis of Ni(30\%)\textsuperscript{-}MFU-4.** Ni(NO\textsubscript{3})\textsubscript{2}\textperiodcentered 6H\textsubscript{2}O (1.8 g, 6.2 mmol) was dissolved in 15 mL of DMF. MFU-4/(100 mg; 7.93 \times 10\textsuperscript{-2} mmol) was suspended in an additional 5 mL of DMF and added to the Ni(NO\textsubscript{3})\textsubscript{2}\textperiodcentered 6H\textsubscript{2}O solution. The resulting suspension was left in an oven heated to 75 °C for 48 hours. The solution was decanted, and the remaining powder was soaked in 20 mL fresh DMF. This process was repeated once daily for three days. The powder was subsequently suspended in 20 mL of fresh methanol. The methanol was replaced once daily for three days. The resulting powder was transferred as a slurry into activation glassware. The material was activated at 150 °C under high vacuum. Number of Ni\textsuperscript{2+} ion in the molecular formula: 1.34, as determined by ICP-OES.

**Synthesis of Ni(10\%)\textsuperscript{-}MFU-4.** Ni(NO\textsubscript{3})\textsubscript{2}\textperiodcentered 6H\textsubscript{2}O (5.5 g, 19 mmol) was dissolved in 100 mL of DMF. An activated sample of MFU-4/ (600 mg, 0.475 mmol) was suspended in an additional 50 mL of DMF and added to the Ni(NO\textsubscript{3})\textsubscript{2}\textperiodcentered 6H\textsubscript{2}O solution. The resulting
suspension was allowed to sit at room temperature for one month. The solution was decanted,
and the remaining powder was soaked in 100 mL fresh DMF. This process was repeated once
daily for three days. The powder was subsequently suspended in 100 mL of fresh methanol.
The methanol was replaced once daily for three days. The resulting powder was collected via
gravity filtration and was transferred into activation glassware. The material was activated by
heating at 150 °C under high vacuum for 18 hours. Number of Ni$^{2+}$ ion in the molecular
formula: 0.46, as determined by ICP-OES.

**Synthesis of Ni(3%)-MFU-4.** Ni(NO$_3$)$_2$$\cdot$6H$_2$O (0.5 g, 1.7 mmol) was dissolved in
15 mL of DMF. MFU-4/(100 mg; $7.93 \times 10^{-2}$ mmol) was suspended in an additional
5 mL of DMF and added to the Ni(NO$_3$)$_2$$\cdot$6H$_2$O solution. The resulting suspension was left at room temperature
for 48 hours. The solution was decanted, and the remaining powder was soaked in 20 mL
fresh DMF. This process was repeated once daily for three days. The powder was subsequently
suspended in 20 mL of fresh methanol. The methanol was replaced once daily for three days.
The resulting powder was transferred as a slurry into activation glassware. The material was
activated at 150 °C under high vacuum. Number of Ni$^{2+}$ ion in the molecular formula: 0.17,
as determined by ICP-OES.

**Synthesis of Ni(1%)-MFU-4.** Ni(NO$_3$)$_2$$\cdot$6H$_2$O (0.2 g, 0.4 mmol) was dissolved in 15 mL of
DMF. MFU-4/(100 mg; $7.93 \times 10^{-2}$ mmol) was suspended in an additional 5 mL of DMF and
added to the Ni(NO$_3$)$_2$$\cdot$6H$_2$O solution. The resulting suspension was left at room temperature
for 24 hours. The solution was decanted, and the remaining powder was soaked in 20 mL
fresh DMF. This process was repeated once daily for three days. The powder was subsequently
suspended in 20 mL of fresh methanol. The methanol was replaced once daily for three days.
The resulting powder was transferred as a slurry into activation glassware. The material was
activated at 150 °C under high vacuum. Number of Ni$^{2+}$ ion in the molecular formula: 0.04, as determined by ICP-OES.

**Synthesis of Ni@(Fe)MIL-101.** The supported catalyst Ni@(Fe)MIL-101 was prepared according to a literature procedure.$^{67}$

**General procedure for ethylene oligomerization.** In a typical catalytic protocol, a magnetic stir bar and desolvated Ni-MFU-4/ (5.0 mg, 4.0 × 10$^{-3}$ mmol) were introduced into a 50-mL stainless steel Parr reactor in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of the specified number of equivalents of MAO. The reactor was sealed, transferred out of the glovebox, and brought to the reaction temperature specified with a temperature controller and internal temperature probe. Thirty minutes after the addition of MAO, the reactor was pressurized with ethylene through a dip tube and magnetic stirring was turned on. After one hour, the reactor was rapidly cooled in a dry ice/acetone bath. When the internal temperature reached -20 °C, the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was treated with ice-cold deionized water. Cooled 1-pentene (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2-μm syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography. The recovered solids were digested in a 10:1 mixture of methanol and concentrated aqueous HCl to isolate any polymeric products.

Control experiments with the parent all-Zn MFU-4/and with alternative aluminum activators were carried out in an analogous manner as described above.
**Lifetime experiment with Ni-MFU-4I.** We constructed a two-reactor system that allows us to distill the reaction product without exposing the Ni-MFU-4I/MAO slurry to air in order to study the lifetime of Ni-MFU-4I and the potential for catalyst recycling. As with typical oligomerization experiments, a magnetic stir bar and activated Ni-MFU-4I (5.0 mg, 4.0 \times 10^{-3} \text{ mmol}) were introduced into a 25 mL stainless steel Parr reactor, referred to as reactor 1, in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of 100 equivalents of MAO. The reactor was sealed, transferred out of the glovebox, and the temperature of the reactor was monitored with an internal temperature probe. A 50 mL stainless steel Parr reactor, referred to as reactor 2, was connected to reactor 1 with three feet of 1/8" copper tubing, with the valve connecting reactor 1 to reactor 2 remaining closed. Reactor 2 was evacuated to remove ambient water and oxygen inside the vessel. After evacuation, reactor 2 was cooled below -20 °C with a dry ice/acetone bath, and monitored with an internal temperature probe. Thirty minutes after the addition of MAO to Ni-MFU-4I, reactor 1 was pressurized to 50 bar with ethylene through a dip tube and magnetic stirring was turned on. After one hour, reactor 1 was placed in a water bath at room temperature and the connection between reactor 1 and reactor 2 was opened, allowing butenes to condense in the second reactor. After allowing the system to equilibrate for 30 minutes, the connection between reactor 1 and reactor 2 was closed. Reactor 2 was opened, and precooled toluene (10 mL) and 1-pentene (0.1 mL) were added to the vessel. This organic mixture was analyzed via gas chromatography. Reactor 1 was repressurized with ethylene and allowed to react for one hour, while reactor 2 was cleaned and evacuated. This process was repeated over 8 cycles.

**Leaching Experiment with Ni-MFU-4I.** To verify that leached nickel species were not responsible for the observed catalytic activity, a magnetic stir bar and activated Ni-MFU-4I (5.0 mg, 4.0 \times 10^{-3} \text{ mmol}) were introduced into a 50-mL stainless steel Parr reactor in a
nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of 100 equivalents of MAO. The reactor was sealed, transferred out of the glovebox, and brought to the reaction temperature specified with a temperature controller and internal temperature probe. Thirty minutes after the addition of methylaluminxoane, magnetic stirring was turned on and the reactor was pressurized with ethylene through a dip tube. After one hour, the reactor was transferred into a nitrogen glove bag and slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was sparged with dry nitrogen for 15 minutes to remove any residual butenes in solution. The solution was subsequently filtered through three 0.2-μm syringe filters and transferred into a second 50-mL stainless steel Parr reactor. This new reactor was sealed, transferred out of the glove bag, and pressurized with ethylene through a dip tube. Internal stirring was maintained throughout the reaction, and after one hour the reactor was rapidly cooled to -20 °C with a dry ice/acetone bath. Once the internal temperature reached -20 °C the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was treated with precooled deionized water. Precooled 1-pentene (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2-μm syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography.

**Ethylene dimerization comparison with Ni@*(Fe)MIL-101.** To ensure that the increased activity of Ni-MFU-4/ relative to other MOF catalysts is not due to reaction conditions, we prepared Ni@*(Fe)MIL-101 and treated it analogously to Ni-MFU-4/. During the preparation of Ni@*(Fe)MIL-101, the aluminoxane blend provided by our supplier changed slightly from MAO to MMAO-12, a modified methylaluminxoane activator in which 5% of the methyl groups have been replaced with octyl groups. To ensure that this MAO blend modification does not unfairly bias our comparison between the MOF catalysts, control experiments were
performed demonstrating the equivalent catalytic performance of Ni-MFU-4 when activated with either MAO or MMAO-12 (Table 2-6, entries 1-4). Following these controls, Ni@**(Fe)MIL-101** was tested under our optimized conditions (Table 2-6, entry 5), demonstrating the superior performance of Ni-MFU-4. Furthermore, the PXRD pattern of the recovered Ni@**(Fe)MIL-101** shows the formation of substantial polymeric deposits (Figure 2-16).

**Computational Modeling of Ni-MFU-4**

First-principles total energy and electronic structure calculations were performed within the Kohn-Sham DFT construct. A delocalised plane-wave basis set with PAW scalar-relativistic frozen-core potentials were employed as implemented in the Vienna ab initio simulation package (VASP). A 500 eV plane-wave kinetic energy cutoff and a $2 \times 2 \times 2$ k-grid were combined to provide total energy convergence to within 0.01 eV/atom. Beginning with the experimentally determined crystallographic primitive cell of MFU-4, all unit cell vectors and internal ionic positions were relaxed to their equilibrium values using the PBEsol functional. This functional provides a good description of the solid-state structures of MOFs, with all equilibrium lattice vectors being within 1% of experimental values. Nickel substitutions were then installed by manually modifying the structural file to 0.5 Ni$^{2+}$ per cluster with appropriate charge compensating metal-bound Cl$^{-}$ included. The structure was then further optimized using the same convergence criteria as the native framework. The resulting geometry-optimized structure is hereafter referred to as DFT-1.

**Table 2-3. Structural Comparison of Nickel Coordination in DFT-1 and Tp$^{Me}$NiCl (2).**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-1</td>
<td>1.945 Å</td>
<td>2.121 Å</td>
<td>97.06°</td>
<td>120.07°</td>
</tr>
<tr>
<td>Tp$^{Me}$NiCl (2)</td>
<td>2.004 Å</td>
<td>2.147 Å</td>
<td>92.88°</td>
<td>128.81°</td>
</tr>
</tbody>
</table>
X-Ray Absorption Spectroscopy Analysis of Ni-MFU-4/

X-ray absorption spectroscopy measurements at the Ni K edge (8.333 keV) were performed on the 10-BM bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source (APS), Argonne National Laboratory. Data was acquired in transmission and step-scan mode using ionization chambers optimized for the maximum current with linear response (~10¹⁰ photons detected/sec) with 10 % absorption in the incident ion chamber and 70 % absorption in the transmission X-ray detector. A Ni foil spectrum was acquired simultaneously with each sample measurement for energy calibration. Catalyst samples were pressed in a N₂ glovebox into a cylindrical sample holder consisting of six wells, forming a self-supporting wafer which was then placed in a quartz tube (2.5 cm. OD, 10.0 cm. length) sealed with Kapton windows by two Ultra-Torr fittings. Artemis software was used to fit the XAS data.

Below are the X-ray absorption near-edge spectroscopy (XANES) plots (Figure 2-3) and zoom in pre-edge feature (Figure 2-4) of Ni-MFU-4/ (1) and corresponding references. From the shape of the XANES curve, Ni-MFU-4/ clearly has a different coordination environment compared to NiCl₂ and Tp₂Ni (3). Although the edge position and shape corresponding to Ni-MFU-4/ more closely resembles that of Tp₂Ni (with a lower white line intensity), the shape of Ni-MFU-4/s XANES spectra after the white line more closely resembles that of NiCl₂.
Figure 2-3. XANES plot for Ni-MFU-4/ and corresponding references.
The values of the edge energy (inflection point of the leading edge) and pre-edge energy can be determined from the spectra and are summarized below (Table 2-4). Ni-MFU-4/ has an edge and pre-edge energy similar to that of NiCl₂ and Tp₂Ni, consistent with an oxidation state of Ni(II) in the former. The pre-edge energy of Tp₂Ni is slightly higher than that of Ni-MFU-4/, which can be explained by the difference in coordination geometry. In the octahedral structure of Tp₂Ni, the e₉ orbitals are higher in energy than t₂₉ orbitals. The pre-edge is due to the transition of 1s-e₉, since all the t₂₉ orbitals are filled. In a tetrahedral structure, the t₂₉ orbitals would be higher in energy than the e₉, so the pre-edge would due to the transition of 1s-t₂₉. Thus the higher XANES pre-edge energy in Tp₂Ni compared to Ni-MFU-4/ would be consistent with the larger crystal field splitting for Oh compared to Td symmetry. Although Ni(II) resides in an octahedral geometry for both Tp₂Ni and NiCl₂, Tp⁻ is a stronger field

Figure 2-4. XANES Pre-edge plot for Ni-MFU-4/ and corresponding references.
ligand than Cl⁻, consistent with the higher pre-edge energy observed for Tp₂Ni. Furthermore, the pre-edge features are higher in intensity for Ni-MFU-4/ than the two standards (Figure 2-4), indicating less symmetric coordination. Taken together, the pre-edge data are consistent with the proposed pseudo-tetrahedral environment modeled in DFT-1.

Table 2-4. XANES edge energy and pre-edge energy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Edge Energy (keV)</th>
<th>Pre-Edge Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni foil</td>
<td>8.3330</td>
<td>8.3332</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>8.3410</td>
<td></td>
</tr>
<tr>
<td>Tp₂Ni</td>
<td>8.3426</td>
<td>8.3336</td>
</tr>
<tr>
<td>Ni-MFU-4/</td>
<td>8.3416</td>
<td>8.3330</td>
</tr>
</tbody>
</table>
Figure 2-5. EXAFS plot for Ni-MFU-4/ and corresponding first shell fit.

**Quantitative Coordination Structure by EXAFS.** Figure 2-5 displays the EXAFS plot of Ni-MFU-4/ and the optimal first shell fits evaluated using Artemis software. The initial bond lengths and coordination number were derived from DFT-1, and the model was adjusted until reasonable amplitude reduction factor (S_r^2), energy shift (ΔE_o) and bond length difference (ΔR) values are obtained. When comparing multiple samples, the S_r^2 value is typically determined from fitting a reference compound (in this case Tp₂Ni). Guided by this value, the optimal bond lengths for the fit (3 Ni-N at 1.99 Å and 1 Ni-Cl at 2.14 Å) are slightly longer than those of DFT-1 (3 Ni-N at 1.95 Å and 1 Ni-Cl at 2.12 Å). Nevertheless, the first coordination sphere in the proposed model fits the EXAFS data well. Fitting Ni-MFU-4/ with other models have
been examined, including a total coordination number of 6 or a coordination number of 4 but with different numbers of neighbor (N versus Cl), which all lead to significantly poorer fits.

Table 2-5. Quantitative evaluation of the EXAFS fit (Artemis Software)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scattering Pair</th>
<th>$S_0^2$</th>
<th>CN</th>
<th>Bond Length ($\AA$)</th>
<th>$\Delta E_0$ (eV)</th>
<th>$\sigma^2$ ($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tp$_2$Ni</td>
<td>Ni-N</td>
<td>0.77</td>
<td>6</td>
<td>2.06</td>
<td>-5.9</td>
<td>0.006</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>Ni-Cl</td>
<td>0.77</td>
<td>6</td>
<td>2.40</td>
<td>0.0</td>
<td>0.009</td>
</tr>
<tr>
<td>Ni-MFU-4/</td>
<td>Ni-N</td>
<td>0.77</td>
<td>3</td>
<td>1.99</td>
<td>-5.6</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Ni-Cl</td>
<td></td>
<td>1</td>
<td>2.14</td>
<td></td>
<td>0.003</td>
</tr>
</tbody>
</table>

* The error of all the fitted parameters are very close. The average error in $S_0^2$ is 0.10, in bond length is 0.01 $\AA$, in $\Delta E_0$ is 1.5 eV and in $\sigma^2$ is 0.002 $\AA^2$.

The fitting ranges for Tp$_2$Ni and Ni-MFU-4/ are $\Delta k = 3.0-11.0$ $\AA^{-1}$ and $\Delta R = 1.0-2.0$ $\AA$. For NiCl$_2$, the ranges are $\Delta k = 3.0-10.0$ $\AA^{-1}$ and $\Delta R = 1.4-2.4$ $\AA$. 

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Table 2-6. Comparison between Ni-MFU-4/ and Ni@(Fe)MIL-101.

<table>
<thead>
<tr>
<th>Entry</th>
<th>MOF</th>
<th>Activator</th>
<th>TOF (h(^{-1}))(^{a})</th>
<th>Selectivity (wt %)</th>
<th>Overall 1-butene(^{e})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni(1%) - MFU-4/</td>
<td>MAO</td>
<td>41500</td>
<td>97.4</td>
<td>94.5</td>
</tr>
<tr>
<td>2</td>
<td>Ni(1%) - MFU-4/</td>
<td>MMAO-12</td>
<td>41100</td>
<td>97.0</td>
<td>95.9</td>
</tr>
<tr>
<td>3</td>
<td>Ni(10%) - MFU-4/</td>
<td>MAO</td>
<td>27000</td>
<td>96.5</td>
<td>92.3</td>
</tr>
<tr>
<td>4</td>
<td>Ni(10%) - MFU-4/</td>
<td>MMAO-12</td>
<td>26500</td>
<td>96.1</td>
<td>91.7</td>
</tr>
<tr>
<td>5</td>
<td>Ni@(Fe)MIL-101</td>
<td>MMAO-12</td>
<td>17700</td>
<td>89.6</td>
<td>94.0</td>
</tr>
</tbody>
</table>

Table 2-6. Comparison of Ni-MFU-4/ with Ni@(Fe)MIL-101. All reactions run at 25 °C with 500 equivalents of the alkyl aluminum activator. \(^{a}\)Moles of ethylene converted per mole of nickel per hour. \(^{b}\)The percentage of oligomeric products that are \(C_4\) olefins. \(^{c}\)The percentage of oligomeric products that are \(C_6\) olefins. \(^{d}\)The percentage of 1-butene relative to all \(C_4\) products. \(^{e}\)The overall selectivity for 1-butene among all oligomeric products.
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Chapter 3

Mechanism of Catalytic Ethylene Dimerization in Ni-MFU-41

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3.1 INTRODUCTION

Metal-organic frameworks (MOFs) have tremendous potential for heterogeneous catalysis due to their unparalleled tunability in the solid state. Indeed, numerous reports detail the development of catalytically active MOFs through the modification of either the organic ligands or inorganic clusters that define the materials, although detailed mechanistic studies on MOF catalysts remain conspicuously absent. To fully leverage the unique tunability that MOFs provide for the development of improved heterogeneous catalysts, rigorous mechanistic studies are necessary to enable rational catalyst design. In this work, we demonstrate that standard organometallic techniques can be translated to study the reaction mechanisms of catalytic MOFs by fully elucidating the mechanism of ethylene dimerization in Ni-MFU-4.

The catalytic oligomerization of ethylene to form linear alpha olefins (LAOs) is one of the most commercially successful applications of catalysis in the petrochemical industry, with more than 1.1 million tons of oligomers produced annually. Because the majority of oligomerization catalysts provide a wide distribution of products primarily consisting of C_{14}-C_{20} olefins, the advent of linear low-density polyethylene (LLDPE) has led to an increasing demand for just the short LAOs that are valuable as comonomers in LLDPE production. With the growing interest in 1-butene, 1-hexene, and 1-octene, both academia and industry have expended considerable efforts on the development and study of
catalysts for the *selective* dimerization, trimerization, and tetramerization of ethylene.\textsuperscript{3,37,38,47,79,82,91,93,105,139-150}

Figure 3-12. Structure of Ni-MFU-41. Teal – nickel; Green – chlorine; Black – zinc; Grey – carbon; Blue – nitrogen; Red – oxygen. Hydrogens omitted for clarity.

As reported in chapter 2 of this thesis, Ni-MFU-41 is a heterogeneous catalyst whose combined activity and selectivity for the production of 1-butene from ethylene surpasses analogous homogeneous catalysts and all other heterogeneous catalysts (Figure 3-1).\textsuperscript{68} This highlighted the utility of MOFs in solving long-standing industrial challenges in heterogeneous catalysis. Indeed, despite decades of research devoted to displacing homogenous catalysts for ethylene dimerization, solids tested for this process were either poorly active or unselective,\textsuperscript{55} their performance plagued by the intractability and multiplicity of their active sites, a common problem in conventional heterogeneous catalysts. In contrast, metal-organic frameworks (MOFs) provide well-defined platforms for reactivity, as inorganic clusters are held together by organic ligands to form periodic three-dimensional structures. MFU-41 is an ideal model system for investigating ethylene reactivity, because it is chemically robust and contains
scorpionate-like coordination motifs that are known to activate small molecules.\textsuperscript{129-131,151} Although we initially investigated Ni-MFU-4/ due to the structural homology between the inorganic clusters and molecular [Tp\textsuperscript{Mes}Ni]\textsuperscript{+} catalysts for ethylene dimerization (Tp\textsuperscript{Mes} = HB(3-mesitylpyrazoly)\textsubscript{3}), we found that the MOF's selectivity for 1-butene is considerably higher than that of the homogeneous system.\textsuperscript{32,68} With Ni-MFU-4/, selectivities of up to 96.2\% for 1-butene are obtained, although the molecular [Tp\textsuperscript{Mes}Ni]\textsuperscript{+} catalyst is only 82.8\% selective under identical conditions (Table 3-1). This was surprising because typical heterogenization techniques applied to homogeneous catalysts often lead to severe penalties in selectivity and/or activity.\textsuperscript{152-154} Given the immense importance of selective heterogeneous catalysis, developing a detailed mechanistic understanding of ethylene dimerization in Ni-MFU-4/ is of considerable fundamental interest and is crucial for ongoing efforts in catalyst development. Here, we elucidate this mechanism and demonstrate that methods common to molecular organometallic chemistry can similarly be applied to studying reaction mechanisms in well-defined heterogeneous materials such as MOFs. This study provides clear precedent and a blueprint for translating molecular design principles and applying the vast toolbox of mechanistic organometallic chemistry to this emerging class of heterogeneous catalysts.

Two mechanisms have commonly been invoked for ethylene dimerization. The Cossee-Arlman mechanism (Scheme 3-1A) involves the successive insertion of ethylene monomers into a growing metal alkyl chain prior to chain transfer, typically leading to an unselective distribution of higher oligomers determined by the relative rates of ethylene insertion and chain transfer.\textsuperscript{1,155} In principle, however, catalysts operating via this mechanism can be selective for dimers if the rate of chain transfer is much faster than the rate of chain propagation. In contrast, the metallacyclic mechanism (Scheme 3-1B) involves the initial coordination of two ethylene molecules to a metal center followed by the reductive coupling
of the olefin monomers to generate a metallacyclopentane. The metallacycle subsequently decomposes in either a stepwise fashion or a concerted process to selectively release the desired 1-butene. Although the metallacyclic mechanism is most often proposed for early transition metals such as titanium, chromium, and tantalum, nickel systems have also been shown to dimerize olefins through metallacyclic intermediates. Furthermore, nickel-catalyzed reductive couplings are well-established in organic synthesis. In this work, we report isotopic labeling experiments and reactions with mechanistic probes to conclusively determine the operative mechanistic pathway for ethylene dimerization in Ni-MFU-4/.

Scheme 3-1. The two commonly proposed mechanisms for ethylene dimerization.
Some of the most elegant studies on selective ethylene oligomerization have analyzed the isotopolog distribution resulting from the oligomerization of a 1:1 mixture of ethylene and perdeuteroethylene to determine the oligomerization mechanism.\textsuperscript{2,93,143,158} When coloading C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}D\textsubscript{4} over a catalyst that operates via the metallacyclic mechanism, only C\textsubscript{4}H\textsubscript{8}, C\textsubscript{4}H\textsubscript{4}D\textsubscript{4}, and C\textsubscript{4}D\textsubscript{8} should be present, in a 1:2:1 ratio (Figure 3-4). In contrast, \(\beta\)-hydride crossover that accompanies chain transfer causes H/D scrambling for catalysts operating via the Cossee-Arlman mechanism, yielding C\textsubscript{4}H\textsubscript{8}, C\textsubscript{4}H\textsubscript{7}D, C\textsubscript{4}H\textsubscript{5}D\textsubscript{3}, C\textsubscript{4}H\textsubscript{4}D\textsubscript{4}, C\textsubscript{4}H\textsubscript{3}D\textsubscript{5}, C\textsubscript{4}HD\textsubscript{7} and C\textsubscript{4}D\textsubscript{8} (Figure 3-5). However, the mass fragmentation pattern of 1-butene shows substantial C-H bond fragmentation, giving rise to ions over the range 49-57 m/z (Figure 3-6), substantially complicating the isotopolog analysis.\textsuperscript{2} Previous studies have modeled hydrocarbon fragmentation whereby the probability of H or D loss via EI ionization is proportional to the ratio of H and D in the isotopolog.\textsuperscript{2,158,159} Building upon this prior work, we added corrections to account for the natural abundance of \(^{13}\)C in ethylene and C\textsubscript{2}D\textsubscript{4}, as the fragmentation pattern shows a substantial spectral ion at m/z = 57 that is due to \(^{13}\)C incorporation in 1-butene (Figures 3-6 through 3-20). Once these corrections are applied, it is facile to analyze the product mixture by gas chromatography/mass spectrometry to distinguish between the two mechanisms.

3.2 RESULTS AND DISCUSSION

We initially sought to dimerize an equimolar mixture of C\textsubscript{2}D\textsubscript{4}/C\textsubscript{2}H\textsubscript{4} with Ni-MFU-4/ and modified methylaluminoxane (MMAO-12)\textsuperscript{161} for one hour, mimicking our previously reported conditions. Although the resulting mass fragmentation pattern fits the Cossee-Arlman mechanism better than the metallacyclic mechanism, the observed intensities at m/z = 58 and 62 are both higher than expected (Figure 3-22). This slight mismatch between the
experimental results and the theoretical distribution suggests that some secondary H/D scrambling occurs, generating additional isotopologs such as C₄H₆D₂ and C₄H₂D₆ and leading to an enrichment of observable species at these m/z values. Indeed, GC/MS analysis of the leftover ethylene/perdeuteroethylene mixture after one-hour dimerization experiments show substantial H/D scrambling between C₂H₄ and C₂D₄ (Figure 3-2). This H/D scrambling among ethylene monomers accounts for the perceived mismatch between experimental results and theoretical predictions; theoretical isotopolog distributions for both mechanisms assume all starting monomers to be either pure C₂H₄ or C₂D₄, with no contribution from C₂H₃D, C₂H₂D₂, or C₂HD₃. The scrambled ethylenes are nevertheless clearly present by the end of the reaction. Together, these results suggest that ethylene dimerization with Ni-MFU-4/ occurs via the Cossee-Arlman mechanism. Importantly, high selectivity is only possible with the Cossee-Arlman mechanism if the rate of ethylene insertion is slower than the rate of chain termination via β-hydride elimination. Because high selectivity is indeed observed with our catalyst, it implies that the rate of ethylene insertion is indeed slow relative to chain termination, which necessarily leads to H/D scrambling between C₂D₄ and C₂H₄.

![Figure 3-13. The mass fragmentation pattern of a mixture of ethylene/d₂-ethylene before and after a one-hour reaction with Ni-MFU-4//MMALLO-12. Note the increased relative abundance of spectral ions 29 and 31 after the reaction, indicative of H/D scrambling.](image-url)
Although the isotope labeling studies were strongly suggestive of a Cossee-Arlman mechanism, we nonetheless sought to make a more conclusive determination by shortening the reaction time to obtain the initial isotopolog distribution prior to extensive H/D scrambling. As expected, when dimerization experiments under a C₂H₄/C₂D₄ atmosphere were quenched after only 3 minutes (Figure 3-3A), much less H/D scrambling among the ethylene monomers was observed, making the assumption that all of the monomeric species participating in dimerization were unscrambled C₂H₄ or C₂D₄ much more accurate. Indeed, a

![Figure 3-3](image-url)

**Figure 3-3.** (A) The mass fragmentation pattern of a mixture of ethylene/d₄-ethylene before and after a three-minute reaction with Ni-MFU-4//MMAO-12. (B) The mass fragmentation pattern of the 1-butene resulting from a mixture of ethylene/d₄-ethylene after a three-minute reaction.
close match is observed between the experimental mass fragmentation pattern for dimerized products and the predicted mass fragmentation pattern for products resulting from the Cossee-Arlman mechanism (Figure 3-3B), providing additional evidence that Ni-MFU-4/ operates via this mechanism. At these short reaction times, we also observe increased abundance at m/z = 56 m/z. This is due to trace decomposition products from quenched MMAO-12 that co-elute with 1-butene (Figures 3-24, 3-25), and which naturally become more prominent components of the overall reaction mixture as the reaction time decreases. Further validation of the Cossee-Arlman mechanism comes from an analysis of the 2-butenes produced, which do not suffer from issues of co-elution with MMAO-12 decomposition products. Indeed, when H/D scrambling among olefins is limited by reducing the reaction time, the mass fragmentation pattern of the resulting 2-butenes is nearly identical to the theoretical distribution for the Cossee-Arlman mechanism (Figure 3-26).

Having established that ethylene dimerization with Ni-MFU-4/ proceeds by the Cossee-Arlman mechanism, we next focused upon the mechanism of initiation. When ethylene dimerization reactions are run under low conversion, substoichiometric amounts of propylene are detected (Figures 3-27 – 3-29, 3-24). This suggests the formation of an initial nickel methyl species, which subsequently undergoes ethylene insertion. Deuterium labeling studies confirm that the observed propylene is not attributable to quenched MMAO-12 products formed after the reaction, but indeed to reaction with ethylene substrate. Interestingly, the amount of propylene detected increases with increasing equivalents of MMAO-12, following a similar trend to that observed for turnover frequency versus equivalents of MMAO-12. This suggests that the large excess of MMAO-12 is in part necessary to activate all of the nickel sites dispersed throughout the MOF. Given that methylaluminoxane exists in toluene as a set of dynamic oligomers with sizes similar to the
MOF's pore window, we hypothesize that the large excess of MMAO-12 is necessary to support the formation of a sufficiently large concentration of small aluminoxane oligomers to allow these to diffuse into the MOF and activate internal nickel sites.\textsuperscript{161-163}

Our isotopic labeling experiments clearly demonstrate dynamic binding and release of olefins at the nickel sites in Ni-MFU-4. We sought to gain further insight into this process by utilizing substrates whose dynamic binding to the active site is trapped with a subsequent irreversible step that affords structurally distinct products. Nonconjugated dienes such as 1,6-heptadiene are ideal mechanistic probes for this purpose, as the irreversible insertion of the pendant alkene into either the primary or secondary alkyl species leads to different cyclic products (Scheme 3-2). Indeed, literature examples show that when zirconocene catalysts are treated with 1,6-heptadiene, the tethered alkene solely inserts into the primary Zr alkyl species, selectively producing methylenecyclohexane.\textsuperscript{164} In contrast, the cyclopolymerization of 1,6-heptadiene with cobalt and iron catalysts yields exclusively 1,2-cyclopentanediyl rings,\textsuperscript{165} demonstrating that late transition metal catalysts prone to chain walking can selectively insert alkenes into secondary alkyls. Given previous results with molecular catalysts demonstrating olefin insertion into primary and secondary nickel alkyls in roughly equivalent amounts,\textsuperscript{18} we anticipated observing a mixture of methylenecyclohexane and 1-methyl-2-methylenecyclopentane upon treatment of Ni-MFU-4 with 1,6-heptadiene. Surprisingly, we observed only the latter along with isomerized linear dienes (Scheme 3-2), indicating that the tethered alkene selectively inserts into the secondary nickel alkyl species.
DFT calculations provide further insight into the selective insertion of the pendant alkene into the secondary nickel alkyl species. Experimentally, the presence of isomerized dienes implies a highly dynamic nickel alkyl in Ni-MFU-4, as the formation of internal olefins requires the formation of a secondary nickel alkyl species prior to β-hydride elimination (Scheme 3-2). Calculations reveal that the primary nickel alkyl species is in fact 3.5 kcal more
stable than the secondary alkyl, and that the Ni–C bond is elongated by 2% in the latter (Figure 3-32). These results are consistent with literature examples of group 10 metal alkyl complexes, which show that secondary metal alkyl complexes are commonly less stable than primary metal alkyls, with a slight elongation of the M–C bond for the secondary alkyl species.\textsuperscript{166–168} This elongation suggests that the Ni–C bond is weaker in the secondary Ni-alkyl species, which therefore favors olefin insertion and the formation of 1-methyl-2-methylenecyclopentane. Furthermore, 5-exo ring closures are often kinetically favored,\textsuperscript{169} providing additional kinetic selectivity for 1-methyl-2-methylenecyclopentane. Thus, we propose that the selectivity for 1-methyl-2-methylenecyclopentane results from the kinetically favored alkene insertion into the less thermodynamically stable secondary nickel alkyl species. Indeed, when the molecular Cossee-Arlman catalyst (2,2'-bipyridine)nickel bromide/MMAO-12\textsuperscript{17} was treated with 1,6-heptadiene, the resulting product mixture was similar to that obtained with Ni-MFU-4: isomerized dienes and 1-methyl-2-methylenecyclopentane. This provides further confirmation that our MOF catalyst operates via the Cossee-Arlman mechanism and suggests that the selectivity for 1-methyl-2-methylenecyclopentane results from the kinetically favorable 5-exo ring closure relative to the 6-exo ring closure.\textsuperscript{170}

Control experiments further ruled out the formation of 1-methyl-2-methylenecyclopentane by a metallacyclic mechanism. When a prototypical system for reductive coupling via metallacyclic intermediates – Ni(cod)\textsubscript{2} with two equivalents of triphenylphosphine\textsuperscript{9,10,157} – was allowed to react with 1,6-heptadiene, the starting material was recovered quantitatively, despite noticeable color changes indicating the formation of a nickel alkene complex. This, in tandem with the results obtained with (2,2'-bipyridine)nickel bromide/MMAO-12 (see above), strongly suggests that Ni-MFU-4/ forms 1-methyl-2-methylenecyclopentane via the Cossee-Arlman mechanism.
3.3 CONCLUSION AND OUTLOOK

Due to the tremendous utility of short linear alpha olefins and the recent development of a heterogeneous catalyst that can selectively dimerize ethylene, determining the catalyst's mechanism of operation is a question of fundamental interest with substantial practical implications. In this study, we have conclusively shown that Ni-MFU-4/ selectively dimerizes ethylene via the Cossee-Arlman mechanism with a combination of isotopic labeling experiments, molecular probes, and DFT calculations. Importantly, we have shown that the toolbox of homogeneous organometallic chemistry can be applied to rigorously elucidate catalytic mechanisms in MOFs. Continued research in MOF catalysis should leverage the unique opportunities afforded by these materials to address unsolved challenges in heterogeneous catalysis and exploit the molecular nature of active sites in these systems to provide insight into the fundamental chemistry that enables the catalytic transformation.

3.4 METHODS

General Remarks.

Nickel nitrate hydrate (99.9%, Strem), MMAO-12 (7 wt. % Al in toluene, Sigma-Aldrich), 1-pentene (99.5%, Sigma-Aldrich), 1-hexene (99%, Sigma-Aldrich), ethylene (99.9%, Airgas), \( d_1 \)-ethylene (98%, Cambridge Isotope Laboratories), 1,6-heptadiene (99%, Sigma-Aldrich), bis(1,5-cyclooctadiene)nickel(0) (98%, Strem), and triphenylphosphine (99%, Alfa Aesar) were used as received. Dry, deaerated toluene (HPLC Grade, 99.8%) was obtained by passing the solution through two silica columns in a Glass Contour Solvent System and degassing with a flow of argon gas for 30 min followed by three freeze-pump-thaw cycles. Dry, deaerated \( d_6 \)-benzene (99.6%, Cambridge Isotope Laboratories) was obtained by distillation under nitrogen after drying over 4Å molecular sieves, followed by three freeze-pump-thaw cycles. CDCl₃ (99.8%, Cambridge Isotope Laboratories) was used as received.
Nickel and zinc analyses were performed by Robertson Microlit Laboratories, Ledgewood, New Jersey. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker Advance II diffractometer equipped with 0/20 Bragg-Brentano geometry and Ni-filtered Cu-Kα radiation (Kα1 = 1.5406 Å). The tube voltage and current were 40 kV and 40 mA, respectively. NMR spectra were obtained at the MIT DCIF on Bruker Avance 400 instruments equipped with Magnex Scientific superconducting magnets.

Ethylene dimerization reactions were analyzed with an Agilent 7890B gas chromatograph (30 meter PoraBOND Q PT capillary column) equipped with a 5977A mass spectrometer and a flame ionization detector using helium (99.9995%, Airgas) as the carrier gas. The experimental parameters for the mass spectrometer were optimized with Agilent’s built-in autotuning methods. This set of parameters was not changed throughout the course of the dimerization experiments.

**Experimental details.**

Ni-MFU-4/ was prepared according to the literature procedure. Per molecular formula, there are 0.46 nickel atoms. (2,2’-bipyridyl)nickel dibromide was prepared according to the literature procedure. HB(3-mesitylpyrazolyl)3 NiCl (TpMcNiCl) was prepared according to the literature procedure.

**General procedure for ethylene dimerization.** In a typical catalytic protocol, a magnetic stir bar and desolvated Ni-MFU-4/ (5.0 mg, 4.0 × 10⁻³ mmol) were introduced into a 25-mL Schlenk flask in a nitrogen filled glovebox. Toluene (5 mL) was added to the flask. The flask was capped with a septum, transferred out of the glovebox, and degassed with five freeze-pump-thaw cycles. Upon completion of the freeze-pump thaw cycles, ethylene (30 mL, 20 kPa) and d₄-ethylene (30 mL, 20 kPa) were delivered into the flask via a syringe. A 1 mL
sample of the headspace was analyzed via the gas chromatograph/mass spectrometer (GC/MS) to establish the initial ethylene:d<sub>4</sub>-ethylene ratio, and thus allow the calculation of the theoretical isotopolog distributions. MMAO-12 (Al/Ni = 500) was added to the flask to start the reaction. Long reactions were stirred at room temperature for 1 hour, while short reactions were only allowed to stir at room temperature for 3 minutes. After the specified time, the reaction was rapidly cooled in a liquid nitrogen bath. Ice-cold deionized water was added dropwise to quench the MMAO-12, and cooled 1-pentene (0.1 mL, cooled to 0 °C on an ice bath) was added to the solution to serve as an internal standard. The organic layer was filtered through a precooled 0.2-µm Supor® syringe filter and an aliquot of the organic layer was quickly analyzed via gas chromatography/mass spectrometry.

**General procedure for reactions with 1,6-heptadiene.** In the glovebox, Ni-MFU-4/ (5.0 mg, 4.0 × 10⁻³ mmol) was added to a 20-mL scintillation vial. Toluene (5 mL) was added to the vial, followed by 500 equivalents of MMAO-12 (Al/Ni = 500). 1,6-heptadiene (150 µL, 1.1 mmol) was added to the vial, which was subsequently sealed and stirred vigorously for two hours. After cooling on an ice bath, the reaction was quenched with a few drops of water and then treated with mesitylene to serve as a standard (50 µL, 0.359 mmol). An aliquot was diluted with CDCl₃ and analyzed by ¹H-NMR (vinyllic protons of 1-methyl-2-methyleneyclopentane at δ 4.69 (s, 1H) and δ 4.77 (s, 1H)). Analogous conditions were employed for the reaction between 1,6-heptadiene and (2,2'-bipyridyl)nicker dibromide/MMAO-12.

**Procedure for reactions with 1,6-heptadiene in C₆D₆.** In the glovebox, a toluene solution of MMAO-12 was transferred to a vial that was subsequently placed under vacuum for one hour, resulting in a glassy looking solid. The solid was dissolved in 2 mL C₆D₆ Ni-MFU-4/ (5.0 mg, 4.0 × 10⁻³ mmol) was added to the scintillation vial (Al/Ni = 500). 1,6-heptadiene (150
µL, 1.1 mmol) was added to the vial, which was subsequently sealed and stirred vigorously for two hours. After cooling on an ice bath, the reaction was quenched with a few drops of water and then treated with mesitylene to serve as a standard (50 µL, 0.359 mmol). An aliquot was diluted with CDCl₃ and analyzed by ¹H-NMR to ensure the reaction in C₆D₆ was representative of reactions run in toluene (vinyl protons of 1-methyl-2-methylenecyclopentane at δ 4.70 (s, 1H) and δ 4.78 (s, 1H)). The undiluted reaction mixture was analyzed by ¹H NMR, quantitative ¹³C NMR (δ 138.65, δ 104.31, δ 39.11, δ 35.74, δ 24.31, δ 19.23), and HSQC.

Procedure for reactions between 1,6-heptadiene and bis(cyclooctadiene)nickel(0)/PPh₃. In the glovebox, bis(cyclooctadiene)nickel(0) (15.3 mg, 0.0555 mmol) was combined with two equivalents of triphenylphosphine (29.1 mg, 0.111 mmol) in a scintillation vial. Toluene (2 mL) was added to afford a dark red solution. 1,6-heptadiene (150 µL, 1.11 mmol) was added to the vial to afford a pale yellow solution. The reaction was stirred for two hours, after which it was exposed to air and treated with mesitylene (50 µL, 0.359 mmol). An aliquot was diluted with CDCl₃ and analyzed by ¹H NMR.

Ethylene dimerization with TpMesNiCl. A magnetic stir bar and TpMesNiCl (1.5 mg, 2.3 × 10⁻³ mmol) were introduced into a 50-mL stainless steel Parr reactor in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of 500 equivalents of MMAO-12. The reactor was sealed, transferred out of the glovebox, and brought to 0 °C with an ice bath, as monitored by an internal temperature probe. Thirty minutes after the addition of MMAO-12, the reactor was pressurized with ethylene through a dip tube and magnetic stirring was turned on. After one hour, the reactor was rapidly cooled in a dry ice/acetone bath. When the internal temperature reached -20 °C, the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was
treated with ice-cold deionized water. Cooled 1-pentene (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2-μm syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography.

**Determination of the theoretical mass spectral ion (m/z) ratios for 1-butene isotopologs resulting from the Cossee-Arlman mechanism and the metallacyclic mechanism.** As can be seen in Figures 3-4 and 3-5, a 1:1 mixture of ethylene:perdeuteroethylene leads to different theoretical isotopolog distributions depending on if a catalyst operates by either the metallacyclic mechanism (Figure 3-4) or the Cossee-Arlman mechanism (Figure 3-5). A catalyst that operates via the metallacyclic mechanism should only give rise to $C_4H_8$, $C_4H_4D_4$, and $C_4D_8$ in a 1:2:1 ratio, while a catalyst that proceeds via the Cossee-Arlman mechanism leads to $C_4H_8$, $C_4H_2D$, $C_4H_3D$, $C_4H_4D_4$, $C_4H_3D_3$, $C_4HD_7$, and $C_4D_8$ in a 1:1:1:2:1:1:1 ratio. These calculated ratios neglect kinetic isotope effects, an assumption that has previously been made for ethylene dimerization catalysts, as any kinetic isotope only provides a minor perturbation relative to the presence of different isotopologs. However, translating these ratios to a predicted mass spectrum is substantially complicated by the fragmentation of 1-butene in the mass spectrometer (Figure 3-3). The molecular peak at m/z = 56 is the most prominent mass spectral ion, although non-negligible fragments between m/z = 48 and m/z = 55 represent the loss of between one and eight hydrogens in the mass spectrometer. In addition to these fragments, a peak at m/z = 57 is present due to the natural abundance of $^{13}C$. An authentic sample of 1-butene was injected onto the GC/MS to precisely determine the mass spectrum for 1-butene in our mass spectrometer. Using the natural abundance of $^{13}C$, we translated this observed mass spectrum to the percentage of fragments.
that lost one hydrogen ([M-1]+), two hydrogens ([M-2]+), etc. (Figure 3-7). To predict the mass spectra for isotopologs besides C\textsubscript{4}H\textsubscript{8}, we employed a model of where the loss of either H or D is proportional to the relative abundance of H and D in the parent ion, similar to other models reported in the literature.\textsuperscript{2,158,159} These fragmentation trees are depicted in figures 3-8 – 3-16. This model does not take into account any kinetic isotope effects for H or D loss due to fragmentation, although prior work has shown that these effects are negligible for isotopologs of 1-butene.\textsuperscript{2} The calculated percentages (depicted below the fragment in figures 3-8 through 3-16) represents the relative abundance of a fragment within the [M-x]+ family of fragments for a given isotopolog. Scaling the abundance of each fragment with the [M-x]+ percentages determined for C\textsubscript{4}H\textsubscript{8} provides the overall contribution of a fragment to the observed mass spectrum for the parent isotopolog (Figure 3-17). Summation of the intensity for each fragment by mass and correcting for the natural abundance of \textsuperscript{13}C gives the expected mass spectrum for a given isotopolog, an example of which is shown in Figures 3-18. Differentiating our model from others that investigate 1-butene fragmentation is the correction for \textsuperscript{13}C. This process was repeated for all of the possible isotopologs. The different isotopolog distributions predicted by the Cossee-Arlman mechanism (Figure 3-19) and the metallacyclic mechanism (Figure 3-20) allows for the differentiation of each mechanism by measuring the mass spectrum for the 1-butene products.

To compare the theoretical distributions with the experimental data, all of the graphs were normalized to the spectral ion \textit{m/z} = 60. This spectral ion is the base peak in all of our experimental runs, and is the predicted base peak for both mechanistic models.

To experimentally validate the model, we dimerized C\textsubscript{2}D\textsubscript{4} and compared the mass fragmentation pattern of the resulting 1-butene products with our calculated fragmentation
pattern for C_{4}D_{8}. As seen in Figure 3-31 there is an excellent agreement between the calculated and experimental fragmentation patterns.

**Computational Methods.** First-principles total energy and electronic structure calculations were performed within the Kohn-Sham DFT construct. A delocalized plane-wave basis set with PAW scalar-relativistic frozen-core potentials was employed as implemented in the Vienna *ab initio* simulation package (VASP).

A 500 eV plane-wave kinetic energy cutoff and 1x1x1 k-grid were combined to provide total energy convergence to within 0.001 eV/atom. Beginning with the experimentally determined 100% Zn-containing crystallographic cell, all unit cell vectors and internal ionic positions were relaxed to their equilibrium values using the PBEsol functional. This functional provides a good description of the solid-state structures of MOFs, with all equilibrium lattice vectors being within 1% of experimental values. Then a single Ni substitution was made at a Ni site, and the structure was further geometrically and electronically optimized with spin polarization enabled. Subsequent Ni-alkyl models were then constructed and optimized with freedom in the geometric positions of the Ni site, and the bound alkyl species. Energetics were computed using the PBEsol functional.
<table>
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<th>Catalyst</th>
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<th>C\textsubscript{4}</th>
<th>C\textsubscript{6}</th>
<th>(\alpha)-C\textsubscript{4}</th>
<th>1-butene</th>
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<td>9.4</td>
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Table 3-1. Comparison of Ni-MFU-4/ with the molecular scorpionate complex Tp\textsuperscript{Me3}NiCl. Both reactions were run under 50 bar of ethylene at 0 °C with 500 equivalents of MMAO-12 for 1 hour.
Figure 3-4. Theoretical 1-butene isotopolog distribution predicted by the metallacyclic mechanism.
Figure 3-5. Theoretical 1-butene isotopolog distribution predicted by the Cossee-Arlman mechanism.
Figure 3-6. Mass spectrum obtained for 1-butene (C₄H₈, as received).
### Observed Spectral Ions

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### Fragmentation Correction

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</tr>
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<td>[M-8]+</td>
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*Figure 3-7. Translating the observed mass spectrum to the percentage of fragments that lost one hydrogen ([M-1]+), two hydrogens ([M-2]+), ..., eight hydrogens ([M-8]+) to account for the natural abundance of $^{13}$C.*
Figure 3-8. Model of $C_4D_8$ fragmentation pattern. The $[M-X]^+$ percentages on the right indicate the overall abundance of that $[M-X]^+$ group relative to the molecular peak $[M]^+$, as determined from the fragmentation of $C_4H_8$ (Figure 3-6).
Figure 3-9. Model of C₄HDD₇ fragmentation pattern. The [M-X]⁺ percentages on the right indicate the overall abundance of that [M-X]⁺ group relative to the molecular peak [M]⁺, as determined from the fragmentation of C₄H₈ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]⁺ group.
Figure 3-10. Model of $C_4H_2D_6$ fragmentation pattern. The [M-X]$^+$ percentages on the right indicate the overall abundance of that [M-X]$^+$ group relative to the molecular peak [M]$^+$, as determined from the fragmentation of $C_4H_8$ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]$^+$ group.
Figure 3-11. Model of C₄H₅D₃ fragmentation pattern. The [M-X]+ percentages on the right indicate the overall abundance of that [M-X]+ group relative to the molecular peak [M]+, as determined from the fragmentation of C₄H₈ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]+ group.
Figure 3-12. Model of C₄H₄D₄ fragmentation pattern. The [M-X]+ percentages on the right indicate the overall abundance of that [M-X]+ group relative to the molecular peak [M]⁺, as determined from the fragmentation of C₄H₈ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]+ group.
**Figure 3-13.** Model of C$_4$H$_3$D$_3$ fragmentation pattern. The [M-X]$^+$ percentages on the right indicate the overall abundance of that [M-X]$^+$ group relative to the molecular peak [M]$^+$, as determined from the fragmentation of C$_4$H$_8$ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]$^+$ group.
Figure 3-14. Model of $\text{C}_4\text{H}_6\text{D}_2$ fragmentation pattern. The $[\text{M-X}]^+$ percentages on the right indicate the overall abundance of that $[\text{M-X}]^+$ group relative to the molecular peak $[\text{M}]^+$, as determined from the fragmentation of $\text{C}_4\text{H}_8$ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated $[\text{M-X}]^+$ group.
Figure 3-15. Model of C₄H₇D fragmentation pattern. The [M-X]⁺ percentages on the right indicate the overall abundance of that [M-X]⁺ group relative to the molecular peak [M]⁺, as determined from the fragmentation of C₄H₈ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]⁺ group.
Figure 3-16. C₄H₈ fragmentation pattern. The [M-X]+ percentages on the right indicate the overall abundance of that [M-X]+ group relative to the molecular peak [M]+, as determined from the fragmentation of C₄H₈ (Figure 3-6). Below each fragment is the mass and its relative abundance within the associated [M-X]+ group.
### C₄D₃H₃ Fragments

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<td>100.00</td>
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**Figure 3-17.** Theoretical contribution of each fragment relative to the mass spectrum of the C₄H₃D₃ 1-butene isotopolog.
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<th>(^{13}\text{C}_4) fragments (%)</th>
<th>(^{12}\text{C}_4) and (^{13}\text{C}_4) fragments (%)</th>
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Figure 3-18. The calculated mass spectrum for the 1-butene isotopolog \(\text{C}_4\text{H}_3\text{D}_5\). The second column in this table results from the summation of the intensity of each fragment listed in figure 3-17 by the mass of the fragment. After a correction is applied to account for the natural abundance of \(^{13}\text{C}\), the predicted mass spectrum for this isotopolog is depicted in the rightmost column.
Figure 3-19. The predicted mass spectrum for reactions proceeding via the Cossee-Ariman mechanism. The predicted intensities for each 1-butene isotopolog are depicted in the column block on the left. Scaling these predicted isotopolog fragmentation patterns by the predicted isotopolog distribution for the Cossee-Ariman mechanism (displayed in the grayed out row above the isotopolog fragmentation patterns) provides the anticipated mass spectrum for 1-butene products in the rightmost column.
**Figure 3-20.** The predicted mass spectrum for reactions proceeding via the metallacyclic mechanism. The predicted intensities for each 1-butene isotopolog are depicted in the column block on the left. Scaling these predicted isotopolog fragmentation patterns by the predicted isotopolog distribution for the metallacyclic mechanism (displayed in the grayed out row above the isotopolog fragmentation patterns) provides the anticipated mass spectrum the 1-butene products in the rightmost column.

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Figure 3-21. Gas chromatogram for a reaction run for 1 hour. The butene peaks appear wide due to the presence of numerous isotopologs with slightly different retention times. For comparison see figure 3-27.
Figure 3-22. Mass spectrum averaged over the entire 1-butene distribution resulting from a reaction run for 1 hour. The experimental data fits better with the Cossee-Arlman mechanism, with the most notable differences at m/z = 57, 59, 61, and 63. These are the molecular peaks for C₄H₇D, C₄H₅D₃, C₄H₃D₅, and C₄H₂D₇.
Figure 3-23. The gas chromatogram for a reaction run for 3 minutes. The butene peaks appear wide due to the presence of numerous isotopologs with slightly different retention times.
Figure 3-24. The gas chromatogram for the quenched MMAO-12 products. Note the presence of a C₄ species at 5.4 minutes, overlapping with the butene products.
Figure 3-25. The mass spectrum for the quenched MMAO-12 products present at 5.4 minutes.
Figure 3-26. The mass spectrum of the 2-butene from a reaction run for 3 minutes. The experimental data clearly fits better with the Cossee-Armann mechanism.
Figure 3-27. The equivalents of propylene with respect to nickel versus the equivalents of MMAO-12. This is plotted with the previously reported turnover frequency versus equivalents of MMAO-12.
Figure 3-28. Zoomed in region of Figure 3-23, highlighting the trace propylene products detected after a 3 minute reaction.
Figure 3-29. Gas chromatogram of ethylene, showing no quantifiable propylene impurities.
Figure 3-30. The gas chromatogram of a dimerization reaction of C$_2$D$_4$. 
Figure 3-31. The mass spectrum for the C$_4$D$_8$ obtained in Figure 3-30 and the predicted fragmentation of C$_4$D$_8$. 
Figure 3-32. The calculated structures for 1,6-heptadiene interacting with Ni-MFU-4/
Chapter 4

Heterogeneous Ethylene Dimerization with a Synthetically Accessible Catalyst
4.1 INTRODUCTION

The catalytic oligomerization of ethylene to produce linear alpha olefins is one of the hallmark reactions of the petrochemical industry, with more than 1.1 million tons of oligomers produced annually.\textsuperscript{15} Increasing demand for linear low-density polyethylene (LLDPE) has renewed interest in the selective dimerization of ethylene, as the resulting 1-butene imparts superior mechanical properties when used as a comonomer in the production of LLDPE.\textsuperscript{5} The existing technology for the dimerization of ethylene - the AlphaButol process - remains one of the largest applications of homogeneous catalysis, despite rapid catalyst deactivation and reactor fouling with polymeric byproducts.\textsuperscript{5,37,39} As such, substantial work has been dedicated to developing heterogeneous alternatives, with the goal of producing long-lived catalysts. Traditional heterogeneous materials like zeolites and mesoporous silica are robust catalysts for ethylene oligomerization, although an intractable tradeoff between activity and selectivity plagues these systems, with the most active mesoporous silica catalyst exhibiting selectivities for butenes below 40\%.\textsuperscript{5,63,118} It is particularly challenging to develop proficient heterogeneous catalysts for ethylene dimerization because the selectivity depends on the ability to fine tune both the electronic structure and the steric environment of the catalytic site. Such degree of control is not typically available in the solid state, necessitating the development of new catalytic platforms.

Metal-organic frameworks (MOFs) are a class of materials with tremendous potential for heterogeneous catalysis.\textsuperscript{76,171-177} Built from metal clusters and organic ligands, these three-dimensional materials offer molecular level control in the solid-state.\textsuperscript{122} Numerous examples have functionalized the organic ligands of MOFs to heterogenize homogeneous catalysts in a manner similar to that found in the field of surface organometallic chemistry.\textsuperscript{67,69,124} Indeed, the earliest examples of ethylene dimerization in MOFs utilized this approach, although the
resulting materials had a greatly reduced porosity, which raises concerns about mass transport through the particles. In contrast, the metal clusters of MOFs, also known as secondary building units (SBUs), provide unique platforms for establishing chemical reactivity without decreasing the porosity of the material. Recent years have seen an increasing number of transformations catalyzed by SBUs, and we have used the SBU of Ni-MFU-4/ to catalyze the dimerization of ethylene. Ni-MFU-4/ is an exceptional catalyst for ethylene dimerization, with a combination of activity and selectivity for 1-butene superior to all other heterogeneous dimerization catalysts. Unfortunately, Ni-MFU-4/ requires a relatively expensive multistep ligand synthesis, complicating scale-up and prompting us to develop alternative catalysts. In this work, we report Ni-CFA-1, a much more synthetically accessible dimerization catalyst that maintains the superior activity and selectivity of Ni-MFU-4/.

The ability to maintain the connectivity and chemical composition of an SBU while varying the length and topology of the organic ligand is one of the defining features of metal-organic frameworks. This unique tunability has been previously exploited to encapsulate large molecules and optimize ammonia sorption, and in this work we leverage this structural versatility to produce an easily prepared heterogeneous ethylene dimerization catalyst. Our lab and others have demonstrated that the metal clusters found within MFU-4/ behave analogously to molecular scorpionate complexes, enabling selective dimerization catalysts to be prepared by incorporating Ni\textsuperscript{2+} cations into pore exposed sites. With the goal of developing more synthetically accessible catalysts for ethylene dimerization, we targeted MOFs with similar SBUs prepared from more synthetically accessible ligands. CFA-1 is just such a MOF (Figure 4-1). Unlike MFU-4/, whose ligand requires a lengthy, expensive synthesis, the ligand for CFA-1 can be prepared in one straightforward step for less than one fortieth of the cost (see Methods section for additional details). Furthermore, CFA-1 consists
of two types of metal clusters, wherein the orientation of the phenyl ring provides different steric profiles (Figure 4-1B and C). Although the presence of multiple SBUs makes it challenging to isolate the steric effects of a given orientation, the cluster depicted in Figure 4-1C is far more accessible than that found in Ni-MFU-4. Nickel scorpionate complexes with similar steric profiles have been tested for ethylene dimerization, although these are far less active than more sterically hindered catalysts, presumably due to bimolecular decomposition pathways. We hypothesized that site-isolation of a similar Ni-substituted motif within a MOF would suppress these decomposition pathways, providing an excellent, easily accessible catalyst for ethylene dimerization.

Figure 4-14. Structure of Ni-CFA-1. (A) A representation of the three-dimensional structure of Ni-CFA-1. (B) and (C) Ball-and-stick models of the two inorganic secondary building units in Ni-CFA-1. Disordered anions are omitted for clarity.
4.2 RESULTS AND DISCUSSION

Ni-CFA-1 is easily prepared via cation exchange methods. Mimicking the conditions reported to generate Ni-MFU-4, Ni substituted variants of Ni-CFA-1 were prepared by soaking the all zinc CFA-1 in an N,N-dimethylformamide (DMF) solution of Ni(NO$_3$)$_2$•6H$_2$O. Altering the time and stoichiometry of the cation exchange reaction enables control over the level of nickel incorporation in the material. The cation exchange does not affect the structural integrity or the porosity of the MOF, as verified by comparisons of the exchanged materials with the parent Zn materials using X-ray diffraction (Figure 4-4) and N$_2$ gas sorption analysis (Figure 4-5).

Ni-CFA-1 is an extremely active and selective catalyst for ethylene dimerization. Initial catalytic runs were carried out in a 50 mL stainless steel Parr reactor with Ni(7.5%-CFA-1, a material where 7.5% of the Zn cations were replaced with Ni. In these small-scale batch reactions, modified methylaluminoxane (MMAO-12) was added to a vigorously stirred suspension of the MOF in toluene, with subsequent pressurization with ethylene. Upon completion of the reaction, the reaction was rapidly cooled in a dry ice/acetone bath, vented, and quenched with ice-cold water. After a 60 minute reaction at 25 °C with 1000 equivalents of MMAO-12 under 25 bar of ethylene, the Ni-substituted material shows a turnover frequency (TOF) of 16,600 moles of ethylene consumed per mole of nickel per hour (Table 4-1, entry 15, Figure 4-10 and 4-11). The products contain 95.1% oligomers dimers with an overall selectivity for 1-butene of 83.1%. Control experiments demonstrate that the nickel sites dispersed throughout the MOF are necessary for catalysis, as the parent Zn-CFA-1 is inactive for ethylene dimerization under identical conditions (Figure 4-10). Similarly, hot filtration experiments show that the filtrate is inactive for ethylene dimerization (Figure 4-11),
demonstrating that homogeneous decomposition products are not responsible for the observed reactivity.

Modified methylaluminoxane (MMAO-12) is critical for ethylene dimerization catalysis with Ni-CFA-1. A series of experiments varying the equivalents of modified methylaluminoxane (MMAO-12) added relative to nickel highlight the importance of using an excess of the alkyl aluminum reagent (Table 4-1, entries 1-7). Reactions run in the absence of MMAO-12 do not generate oligomeric products, as modified methylaluminoxane is necessary to convert the precatalyst to a catalytically active site. Increasing the equivalents of MMAO-12 added to Ni(7.5%)-CFA-1 monotonically increases the observed activity, although the benefit of additional MMAO-12 is much more pronounced at low Al/Ni ratios (Al/Ni < 250). For example, increasing the equivalents of MMAO-12 added to reactions run with Ni(7.5%)-CFA-1 at 25 °C under 50 bar of ethylene from Al/Ni = 50 to Al/Ni = 250 results in a substantial increase in the turnover frequency from 13,100hr⁻¹ to 30,600hr⁻¹, whereas further increasing the Al/Ni ratio to 2000 results in the more modest improvement of the TOF up to 37,100hr⁻¹. Catalyst selectivity is largely maintained at Al/Ni ratios between 100 and 2000, suggesting that at higher Al/Ni ratios a higher percentage of nickel sites throughout the material are activated, although the specific nature of each catalytic site is essentially unchanged. When testing the influence of MMAO-12 on Ni(1%)-CFA-1, a material where nickel makes up 1% of the overall metal content, the same monotonic increase in activity with higher equivalents of MMAO-12 is observed, although the absolute Al/Ni ratio must be much higher to obtain the same activity as observed with Ni(7.5%)-CFA-1 (Table 4-1, entries 19-23). Instead, we observe an excellent agreement between the activities with Ni(7.5%)-CFA-1 and Ni(1%)-CFA-1 when compared with the concentration of aluminum species introduced to the reaction via MMAO-12 (Figure 4-6), despite the differences in catalyst loading. This
observation suggests that the activator concentration may be a more meaningful metric when comparing porous heterogeneous catalysts, as diffusion may play a role in limiting access to internal precatalysts. We expect that these concentration effects are particularly significant for methylaluminoxanes, as these cocatalysts are known to be an ensemble of oligomeric species of varying size. This system is further complicated by the presence of pore exposed zinc species that may also react with alkylaluminum activators. As such, a high aluminum concentration is necessary to alkylate all of the nickel sites throughout the MOF. That Ni(1\%)\-CFA-1 and Ni-(7.5\%)\-CFA-1 both reach comparable maximum activities under individually optimized conditions makes this system notably different from many homogeneous catalysts, where catalyst activity is optimized by decreasing the catalyst loading while maintaining the same Al/Ni. Indeed, even the related nickel scorpionate complex shows decreased activity at higher catalyst loading,\textsuperscript{32} highlighting the unique behavior of the heterogeneous catalyst Ni-CFA-1.

Reaction pressure and reaction temperature also play key roles in the catalytic performance of Ni-CFA-1. When the ethylene pressure is varied between 5 bar and 50 bar at 25 °C in the presence of 1000 equivalents of MMAO-12 (Table 4-1, entries 11-18; Figure 4-2), the turnover frequency of Ni(7.5\%)\-CFA-1 increases with an apparent first-order dependence, consistent with the Cossee-Arlman mechanism (Figure 4-2C). Comparable activities are observed with Ni(1\%)\-CFA-1, indicating that mass transport limitations do not play a limiting role at these nickel loading levels (Table 4-1, entries 24-26). As observed with Ni-MFU-4/ and homogeneous nickel scorpionate complexes, the selectivity of Ni-CFA-1 for 1-butene increases with increasing pressure (Figure 4-2B). This increased selectivity is primarily driven by a higher selectivity for 1-butene relative to isomerized dimers, demonstrating that higher ethylene pressure suppresses the chain-walking and isomerization
characteristic of many nickel catalysts. Optimal activity is observed at 25 °C, with substantially lower activities observed at both 0 °C and 50 °C (Table 4-1, entries 8-10). However, selectivity dramatically increases with decreasing temperature. For example, the overall selectivity for 1-butene of Ni(7.5%) CFA-1 at 0 °C with 1000 equivalents of MMAO-12 under 50 bar of ethylene reaches an exceptional 96.1% (Figure 4-9), whereas the selectivity drops to 74.9% when the reaction is run at 50 °C. This highlights that the rate of isomerization increases at higher temperatures, a phenomenon observed with many homogeneous nickel catalysts.

Figure 4-15. Activity, product distribution, and mechanism of ethylene dimerization with Ni-CFA-1. (A) The pressure dependence of ethylene dimerization with Ni(7.5%) CFA-1 and Ni(1%) CFA-1. (B) The product distribution at various ethylene pressures for Ni(7.5%) CFA-1 with 1000 equivalents of MMAO-12, demonstrating the increased selectivity for 1-butene at higher pressures. (C) The proposed mechanism for ethylene dimerization with Ni-CFA-1.
Having identified optimal conditions for catalytic performance, we sought to evaluate Ni-CFA-1 for potential commercial application by scaling up the ethylene dimerization reaction and determining the turnover number and lifetime of Ni-CFA-1. Our initial experiments were performed with Ni(7.5%)-CFA-1, although immediate exotherms led to rapid catalyst decomposition. To maintain temperature control over the reaction, we carried out dimerization reactions with Ni(1%)-CFA-1 in a 1 L stainless steel reactor equipped with an internal cooling coil set to -15 °C. Maintaining the MMAO-12 concentration used in our 50 mL batch reactions, we carried out a semi-batch experiment with Ni(1%)-CFA-1 under a continuous atmosphere of 50 bar for 96 hours (Figure 4-3, Table 4-2). As seen in figure 4-3, the initial activity of the catalyst is maintained for the first 10 hours of the reaction, followed by a gradual decay in catalytic activity. Accompanying this loss of activity, the crystallinity of Ni(1%)-CFA-1 decreases as dimerization reactions exceed 8 hours (Figure 7-14), suggesting that the gradual structural decomposition of the MOF is one pathway responsible for catalyst decay. Nonetheless, over 400,000 moles of ethylene were consumed per mole of nickel over the course of the reaction (Table 4-2), demonstrating the exceptional stability and activity of the heterogenized catalyst. Both the selectivity for dimers and the selectivity for 1-butene decrease over time, likely due to secondary insertion and isomerization of 1-butene accumulating in the reactor. However, even after 96 hours the selectivity for dimers is 83.9% and the selectivity for 1-butene among the dimers remains at 87.9% (Table 4-2). We anticipate that the selectivity for 1-butene can be further optimized in reactors where the residence time
of the product is minimized, although this 96 hour reaction demonstrates the robustness of Ni(1%)-CFA-1.

Figure 4-16. Cumulative turnovers for Ni(1%)-CFA-1 throughout a 96 hour ethylene dimerization reaction.

Among heterogeneous systems, Ni-CFA-1 is a rare example of a catalyst that is both active and selective for ethylene dimerization. While our previously reported Ni-MFU-4/ is comparably active and selective, cost considerations and ease of preparation make Ni-CFA-1 a superior choice for implementation. Traditional solids like Ni-exchanged zeolites or nickel supported on mesoporous silica are active for ethylene oligomerization, but typically only 40-45% selective for dimers. A full discussion of relevant heterogeneous catalysts for ethylene dimerization can be found in chapter 1 of this thesis.55
Table 4-1. Ethylene dimerization with Ni-CFA-1.*

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<th>Pressure (bar)</th>
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<td>22</td>
<td>5000</td>
<td>0.24</td>
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*As determined by GC analysis. Initial reaction temperature as measured by an internal temperature probe. Moles of ethylene converted per mole of nickel per hour, determined by GC analysis. Percent of oligomeric products that are C₄ olefins. Percent 1-butene relative to all C₄ products. The overall selectivity for 1-butene among all oligomeric products.
4.3 CONCLUSION AND OUTLOOK

We have shown that Ni-CFA-1 is a robust catalyst for ethylene dimerization, whose activity and selectivity for 1-butene are matched only by our previously developed Ni-MFU-4 among heterogeneous catalysts. Ni-CFA-1 provides undeniable practical advantages over Ni-MFU-4, as the ligand can be prepared in one-step and affords a fortyfold cost in savings relative to Ni-MFU-4. Large scale reactions have demonstrated over 400,000 moles of ethylene are consumed per mole of nickel with Ni-CFA-1, while the selectivity for 1-butene remaining high throughout the course of the reaction. The outstanding results obtained with Ni-CFA-1 show that the unique tunability of MOFs can be leveraged to develop alternative catalysts that are far better candidates for implementation.

4.4 METHODS

General Remarks.

Nickel nitrate hydrate (99.9%, Strem), modified methylaluminoxane (MMAO-12, 7 wt.
% Al in toluene, MilliporeSigma), 3,3'-diaminobenzidine (99%, MilliporeSigma) n-pentane
(analytical standard, 99.9%, MilliporeSigma), 1-pentene (analytical standard, 99.5%,
MilliporeSigma), and ethylene (99.9%, Airgas) were used as received. Dry, deaerated toluene
(HPLC Grade, 99.8%) was obtained by passing the solution through two silica columns in a
Glass Contour Solvent System, degassed with a flow of argon gas for 30 min followed by three
freeze-pump-thaw cycles, and stored over 4Å molecular sieves.

Elemental analysis were performed by Robertson Microlit Laboratories, Ledgewood,
New Jersey. Nickel and zinc analyses were performed on an Agilent 7900 ICP-MS in the MIT
Center for Environmental Health Sciences. Powder X-ray diffraction (PXRD) patterns were
recorded on a Bruker Advance II diffractometer equipped with 0/20 Bragg-Brentano
geometry and Ni-filtered Cu-Kα radiation (Kα1 = 1.5406 Å). The tube voltage and current were 40 kV and 40 mA, respectively.

Surface area measurements were conducted on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. In an Argon glovebox, each activated sample was loaded in an oven-dried sample tube of known mass, which was weighed again to determine the sample mass. The tube was equipped with a S3 TranSeal™ (Micrometrics) and transferred out of the glovebox. The sample was placed on the analysis port of the instrument and evacuated at room temperature for 2 hours. N2 isotherms were measured using liquid nitrogen baths (77 K). UHP grade (99.999% purity) N2 and He, oil-free valves and gas regulators were used for all free space corrections and measurements. BET surface area was determined using Micromeritics fitting software and MOF specific criteria.

Ethylene dimerization reaction mixtures were analyzed with an Agilent 7890B gas chromatograph (30 meter PoraBOND Q PT capillary column) equipped with a 5977A mass spectrometer and a flame ionization detector.

Experimental details.

Synthesis of CFA-1. The synthesis of CFA-1 was adapted from literature procedures. In a 250 mL glass jar, zinc acetate dehydrate (1.5491 g, 7.06 mmol) and 5,5'-bibenzotriazole were dissolved (403.9 mg, 1.71 mmol) in 160 mL N-methylformamide. The precipitate was washed with N,N-dimethylformamide (3 x 50 mL) and MeOH (5 x 50 mL) and dried at 150 °C under high vacuum overnight.

Synthesis of Ni(7.5%)-CFA-1. Ni(NO₃)₂•6H₂O (8.0 g, 27.5 mmol) was dissolved in 150 mL of DMF in a 250 mL wide mouth glass jar. A sample of CFA-1 (1.0 g, 0.79 mmol) was suspended in an additional 50 mL of DMF and added to the Ni(NO₃)₂•6H₂O solution. The
resulting suspension was allowed to sit at room temperature for two weeks. The solution was
decanted, and the remaining powder was soaked in 200 mL fresh DMF. This process was
repeated twice daily for three days. The powder was subsequently suspended in 200 mL of
fresh methanol. The methanol was replaced once daily for three days. The resulting powder
was collected via gravity filtration and was transferred into activation glassware. The material
was activated by heating at 150 °C under high vacuum for 18 hours.

Number of Ni²⁺ ion in the molecular formula: 0.37, as determined by ICP-MS.

**Synthesis of Ni(1%)-CFA-1.** Ni(NO₃)₂·6H₂O (6.75 g, 23.2 mmol) was dissolved in 120 mL
of DMF in a 250 mL wide mouth glass jar. CFA-1 (500 mg ; 4.0 mmol) was suspended in an
additional 30 mL of DMF and added to the Ni(NO₃)₂·6H₂O solution. The resulting
suspension was left at room temperature for 24 hours. The solution was decanted, and the
remaining powder was soaked in 200 mL fresh DMF. This process was repeated twice daily
for three days. The powder was subsequently suspended in 200 mL of fresh methanol. The
methanol was replaced once daily for three days. The resulting powder was transferred as a
slurry into activation glassware. The material was activated at 150 °C under high vacuum.
Number of Ni²⁺ ion in the molecular formula: 0.04, as determined by ICP-OES.

**General procedure for ethylene oligomerization.** In a representative experiment,
desolvated Ni(1%)-CFA-1 (10.6 mg, 8.4 × 10⁻³ mmol) was directly loaded into a 50-mL
stainless steel Parr reactor in a nitrogen filled glovebox. Toluene (5 mL) was added to the
reactor, followed by the addition of 2000 equivalents of MMAO-12. A magnetic stir bar was
added and the reactor was sealed. The reactor was transferred out of the glovebox and brought
to the desired reaction temperature with a Parr temperature controller and internal
temperature probe. The ethylene line was purged for fifteen minutes and immediately
connected to the Parr reactor. Thirty minutes after the addition of MMAO-12 to the MOF, the reactor was pressurized with ethylene through a dip tube and magnetic stirring was turned on. The ethylene tank was left connected to the reactor for 5 minutes, after which the reactor was completely sealed. One hour after the initial reaction pressurization, the reactor was rapidly cooled in a dry ice/acetone bath. When the reactor temperature reached -20°C as measured by the internal temperature probe, the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was treated with 1 mL ice-cold deionized water. Cooled n-pentane (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2-μm syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography.

**Leaching Experiment with Ni-CFA-1.** To verify that leached nickel species were not responsible for the observed catalytic activity, a magnetic stir bar and desolvated Ni(1%)-CFA-1 (10.1 mg, $8.0 \times 10^{-3}$ mmol) were introduced into a 50-mL stainless steel Parr reactor in a nitrogen filled glovebox. Toluene (5 mL) was added to the reactor, followed by the addition of 2000 equivalents of MMAO-12. The reactor was sealed, transferred out of the glovebox, and brought to the reaction temperature specified with a temperature controller and internal temperature probe. Thirty minutes after the addition of modified methylaluminoxane, magnetic stirring was turned on and the reactor was pressurized with ethylene through a dip tube. After one hour, the reactor was transferred into a nitrogen glove bag and slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was sparged with dry nitrogen for 30 minutes to remove any dissolved butenes in solution. The solution was subsequently filtered through three 0.2-μm syringe filters and transferred into a second 50-mL stainless steel Parr reactor. Modified methylaluminoxane was added and the reactor was sealed, transferred out of the glove bag, and pressurized with ethylene through a dip tube. Internal
stirring was maintained throughout the reaction, and after one hour the reactor was rapidly cooled to -20 °C with a dry ice/acetone bath. Once the internal temperature reached -20 °C the reactor was slowly vented to atmospheric pressure. The reactor was opened and the reaction solution was treated with precooled deionized water. Precooled n-pentane (0.1 mL) was added to the solution to serve as an internal standard before the organic layer was filtered through a precooled 0.2-μm syringe filter. A small sample of the organic layer was quickly analyzed via gas chromatography.

**Reaction scale-up and lifetime studies with Ni(1%)-CFA-1.** A 1 L stainless steel reactor was sealed and heated to 120 °C. The reactor was purged with a slow stream of dry nitrogen overnight to fully dry the reactor. The next morning, the 1 L reactor was allowed to cool to room temperature, the internal cooling system was set to -15 °C, and the reactor was sparged with ethylene for 30 minutes. In a nitrogen glovebox, a 500 mL transfer vessel was loaded with Ni(1%)-CFA-1 (100 mg, 8.3 × 10⁻² mmol), 400 mL of a diluted MMAO-12 solution (1.17 wt. % Al in toluene), and 1 mL n-pentane (standard). The transfer vessel was sealed, removed from the nitrogen glovebox, and attached to the 1 L stainless steel reactor. The connection between the transfer vessel and the large reactor was sparged with ethylene for 30 minutes. The transfer vessel was opened and its contents were dispensed into the 1 L reactor. The contents of the reactor were stirred at 800 rpm. The reactor was slowly pressurized with ethylene via a headspace valve over the course of 10 minutes, taking care that the internal temperature of the reactor never exceeded 27 °C. Thirty minutes later, the headspace valve was sealed and the ethylene pressure was instead maintained with an internal dip. Due to the gradual increase in temperature - as measured by an internal temperature probe – an additional external cooling bath was added after 5 hours to prevent the reaction temperature from
exceeding 30 °C. Aliquots (~1 mL) of the reaction mixture were collected throughout the course of the reaction via an internal dip tube and analyzed quickly via GCMS. C₈ olefins were unable to be quantified due to quenched MMAO-12 products.

To investigate the structural stability of Ni-CFA-1 over extended ethylene dimerization, a series reactions in 50 mL Parr reactors were carried out for 2 hours, 4 hours, 8 hours, and 24 hours. These reactions were performed at room temperature under 50 bar of ethylene with Ni(1%)-CFA-1 (5 mg, 4.0 × 10⁻³ mmol), toluene (5 mL), and MMAO-12 (1 mL, 7 wt% Al in toluene). After the reaction the solids were collected and analyzed by PXRD.
Cost Analysis. A comparison of the price to produce one gram of ligand for MFU-4/ versus one gram of ligand for CFA-1 is included below. Prices for each material were calculated from the lowest vendor price per gram.

**MFU-4/ligand cost estimate**

<table>
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<th>Amount</th>
<th>Cost</th>
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<td>dibenzo[1:4]dioxin</td>
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<td>$256.76</td>
<td>TCI America*</td>
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<tr>
<td>fuming nitric acid (90%)</td>
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<td>tin powder (99%)</td>
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<td>hydrochloric acid (37%)</td>
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<td>acetic acid (99%)</td>
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<td>sodium nitrite (97%)</td>
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Total cost = $268.55/g

*dibenzo[1:4]dioxin available from Aldrich for $1,060/g as oxanthrene.

**CFA-1 ligand cost estimate**

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Total cost = $6.27/g

*3,3’-diaminobenzidine available for $1.21/g from Research Products International Corp.
Figure 4-4. PXRD patterns of CFA-1, Ni(1%)-CFA-1, and Ni(1%)-CFA-1 after exposure to MMAO-12, and Ni(1%)-CFA-1 after an ethylene dimerization reaction.
Figure 4-5. Isotherm for the adsorption of N\textsubscript{2} in CFA-1 (top), Ni(1\%)\textendash CFA-1 (middle) and Ni(7.5\%)\textendash CFA-1 (bottom) at 77 K. BET analysis of this isotherm gives an apparent surface area of 1,974 m\textsuperscript{2}/g for CFA-1, 1964 m\textsuperscript{2}/g for Ni(1\%)\textendash CFA-1, and 1894 m\textsuperscript{2}/g for Ni(7.5\%)\textendash CFA-1.
Figure 4-6. The activity dependence of ethylene dimerization on MMAO-12 with Ni(1%)-CFA-1 and Ni(7.5%)-CFA-1. (A) The activity dependence of Ni(1%)-CFA-1 and Ni(7.5%)-CFA-1 plotted as a function of the aluminum to nickel ratio. (B) The activity dependence of Ni(1%)-CFA-1 and Ni(7.5%)-CFA-1 plotted as a function of the concentration of aluminum species introduced by MMAO-12. When comparing these heterogeneous catalysts with different nickel loading levels, the catalyst activity is very similar when using the same cocatalyst concentration, while the activity differs substantially at the same Al/Ni ratio.
Figure 4-7. Example chromatogram after ethylene dimerization with Ni(7.5%)-CFA-1.
Figure 4-8. Expanded view of product region in the chromatogram in Figure 4-7.
Figure 4-9. Example chromatogram after the most selective conditions for ethylene dimerization with Ni(7.5%)-CFA-1.
Figure 4-10. Chromatogram after a control ethylene dimerization experiment with all-zinc CFA-1 and MMAO-12. No detectable product is observed. The control experiment was performed with 5 mg of desolvated CFA-1 under 50 bar of ethylene at 25 °C. An equivalent amount of MMAO-12 (as determined by the amount added relative to catalyst mass) was added as in standard ethylene dimerization experiments with Ni(7.5%)-CFA-1.
Figure 4-11. GC-FID chromatogram after a leaching experiment where the filtrate was sparged prior to repressurization with ethylene. No oligomerization products can be observed.
Figure 4-12. GC-FID chromatogram of the scaled-up ethylene dimerization reaction with Ni(1%)-CFA-1 after 30 minutes.
Figure 4-13. GC-FID chromatogram of the scaled-up ethylene dimerization reaction with Ni(1%)-CFA-1 after 96 hours.
Figure 4-14. PXRD patterns of Ni(1%)-CFA-1 after ethylene dimerization reactions of different lengths, demonstrating the slow loss of crystallinity throughout the course of dimerization reactions.
Table 4-2. Tabulated results of large-scale ethylene dimerization reaction with Ni(1%)-CFA-1.

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<th>Time (h)</th>
<th>T (°C)</th>
<th>TON (h⁻¹)</th>
<th>Selectivity (wt %)</th>
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<td>α-C₄</td>
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<td>404900</td>
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<td>87.9</td>
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As determined by GC analysis. Reaction temperature as measured by an internal temperature probe. moles of ethylene converted per mole of nickel, determined by GC analysis. Percent of oligomeric products that are C₄ olefins. Percent 1-butene relative to all C₄ products. The overall selectivity for 1-butene among all oligomeric products. An external cooling bath was placed around the reactor at 5 hours to prevent the internal temperature from exceeding 28 °C.
Chapter 5

Towards Selective Ethylene Trimerization in Metal-Organic Frameworks
5.1 INTRODUCTION

Linear α-olefins (LAOs) are among the most versatile building blocks in the chemical industry, with α-olefin length dictating suitable chemical applications. Since the development of the SHOP process, the nonselective oligomerization of ethylene has served as a major route for the production of LAOs, yielding a broad distribution of oligomers. Recently, however, demand for short linear α-olefins has risen relative to longer olefins, with nonselective technologies unable to meet market needs for 1-hexene. This has led to new on-purpose plants for the selective trimerization of ethylene to 1-hexene, relying upon homogeneous catalysts to facilitate this transformation. Although some of the homogeneous catalysts are remarkably active and selective for 1-hexene, these systems are nonetheless plagued by rapid catalyst deactivation and reactor fouling stemming from undesired polyethylene, prompting continued research into developing heterogeneous alternatives.

Heterogeneous catalysts are desirable for industrial processes due to the tremendous operational advantages they afford. Supported polyolefin catalysts have been extensively studied, demonstrating that reactor fouling can be prevented by utilizing heterogenized polymerization and oligomerization catalysts. The most commonly employed support for the immobilization of polyolefin precatalysts consists of silica and methylaluminoxane (MAO), wherein silica is treated with MAO to coat the particle surface with alkyl aluminum species. In a process analogous to the activation of homogeneous polyolefin catalysts, the MAO/silica support activates polyolefin catalysts via alkylation and abstraction to generate a cationic species. Crucially, electrostatic interactions immobilize this cationic species on the MAO/silica support, affording the heterogeneous catalyst. Although this method of catalyst heterogenization has been most commonly employed with polymerization catalysts, this approach has also enabled the heterogenization of a selection of ethylene trimerization
catalysts. Thus, Bercaw and coworkers have reported that immobilization of a phenoxyimine-based titanium catalyst ((FI)TiCl₃; Figure 5-1B) significantly retards catalyst decomposition, resulting in a substantially higher turnover number relative to the homogeneous catalyst. However, heterogenization is not always successful, with various reports demonstrating significantly diminished activity and/or selectivity upon heterogenization. Given the promising results obtained with MAO/silica immobilized species and the importance of the supporting material, we sought to expand the range of available platforms for catalyst heterogenization.

Metal-organic frameworks are a class of materials that have found growing success as heterogeneous catalysts or supports for homogeneous precatalysts. Consisting of metal clusters and organic ligands, these crystalline materials offer molecular level control in the solid-state. Although most MOF-based catalysis has been carried out with the metal clusters or with functionalized metalloligands, a growing number of examples have utilized metal species immobilized onto the metal cluster of the MOF. Zirconium MOFs are particularly amenable for this method of heterogenization, as their metal clusters contain hydroxy groups that provide a chemical handle for immobilization. Species supported on zirconium MOFs have been used as heterogeneous catalysts for numerous reactions, ranging from alkene epoxidation to the oxidative dehydrogenation of propane. In an alternative approach to MOF-based catalysis, enzymes, metal nanoparticles, and homogeneous catalysts have been trapped within the pores of metal-organic frameworks. This method can be particularly effective in developing heterogeneous catalysts when electrostatic interactions help immobilize the molecular species, as our lab has recently demonstrated with heterogeneous epoxide carbonylation by cooperative ion-pair catalysis. I hypothesized that treating zirconium MOFs with methylaluminoxane would coat the material with a layer of
alkyl aluminum species, which would subsequently platform to immobilize homogeneous ethylene trimerization catalysts via electrostatic interactions. In this chapter, I report my initial efforts to develop heterogeneous catalysts for ethylene trimerization with MAO/MOF materials. In particular, I immobilized two titanium trimerization catalysts – (η⁵-C₆H₄CMe₂Ph)TiCl₃ ((Cp-arene)TiCl₃; Figure 5-1A; catalyst 1)²⁸ⁱ and [N-(5-methyl-3-(1-adamantyl)salicylidene)-2’-(2”-methoxyphenyl)anilinato]titanium(IV) trichloride ([Fl]TiCl₃; Figure 5-1B; catalyst 2)⁸,₁⁰,₁¹,₁² – on four distinct MOF/MMAO-12 supports. Although neither catalyst is as selective or as active as its homogeneous counterpart, this chapter demonstrates that MOFs can be used to heterogenize ethylene trimerization catalysts.

![Catalysts](image)

**Figure 5-1.** The two catalysts immobilized on MOF/MMAO-12 supports. (A) (Cp-arene)TiCl₃; Catalyst 1 (B) [Fl]TiCl₃; Catalyst 2.

### 5.2 RESULTS AND DISCUSSION

The supported catalysts were prepared in a two-step process. First, a slurry of the zirconium MOF in toluene was treated with an excess of modified methylaluminoxane (MMAO-12) under a nitrogen atmosphere for 18 hours. After treatment with MMAO-12, the MOF was decanted and washed extensively with toluene before drying under reduced pressure to afford a free flowing solid. The MOF/MMAO-12 composite was treated with a dilute solution of the precatalyst of choice in toluene for one hour, after which the volatiles were
removed under reduced pressure to afford the immobilized catalyst. Powder X-ray diffraction confirmed that the MOFs were stable to this heterogenization protocol (Figures 5-6, 5-8, 5-10, and 5-11). The catalyst is presumably similar to species supported on MAO/silica, wherein the catalyst is immobilized via electrostatic interactions (Figure 5-2).^{112}

![Figure 5-2. Representation of electrostatic immobilization of a titanium catalyst on a zirconium MOF/MMAO-12 support.](image)

The titanium catalysts were first immobilized on NU-1000/MMAO-12. NU-1000 (Figure 5-3) provided an ideal support for catalyst heterogenization, as numerous metals have been grafted on its nodes and the MOF features large pores with widths of approximately 3 nm, which facilitate mass transport and catalyst incorporation.^{211} Heterogenization has a clear impact on the selectivity and activity of both catalysts. While homogeneous Cp-arene catalysts are over 90% selective for ethylene trimerization,^{97,211} the MOF-immobilized analog exclusively polymerizes ethylene (Table 5-1, entry 7). Similar attempts to heterogenize Cp-arene catalysts on MgCl₂ have also lead to ethylene polymerization rather than heterogenization.^{114} In contrast, the heterogenized phenoxyimine titanium catalyst retains some selectivity for ethylene trimerization (Table 5-1), although polymeric products account
for 18-35% of the products. The supported catalyst is substantially less active and selective than the homogeneous analog, and less active than when immobilized on MAO/silica.  

As the phenoxyimine titanium catalyst supported on NU-1000/MMAO-12 displayed some competency for ethylene trimerization, we sought to further explore catalyst reactivity. The catalyst is only active at elevated pressures, with no polyolefin products detected when the immobilized species was reacted with ethylene at atmospheric pressure. A maximum activity of 12,400 moles of ethylene consumed per mole of titanium per hour was observed when the reaction was pressured to 50 bar of ethylene (Table 5-1, entry 15; Figure 5-14). Although the homogeneous catalyst is far more active in methylcyclohexane than in toluene, the supported catalyst exclusively gives polyethylene when reacted with ethylene in methylcyclohexane. Likewise, supported catalysts open up the possibility of solventless catalysis, a result that has been reported with silica immobilized systems. However, the MOF supported phenoxyimine catalyst only affords polyethylene, clearly demonstrating the importance of solvent selection with these supported catalysts. Suspending the supported
catalyst in toluene, filtering the suspension, and testing the filtrate for ethylene reactivity confirm that homogeneous species are not responsible for the observed catalysis (Figure 5-13). Additional hot filtration experiments demonstrate that the recovered solid is active for ethylene trimerization, while the filtrate is inactive, establishing the heterogeneous nature of the reactivity (Figure 5-4).

![Figure 5-4. Hot filtration experiments demonstrate that the catalysis observed with (FT)TiCl₃@NU-1000/MMAO-12 is heterogeneous.](image)

Seeking to understand the impact of the MOF support on ethylene trimerization, we supported both titanium catalysts upon UiO-66 (Zr₆O₄(OH)₄(OOC-C₆H₄-COO))₆, Figure 5-5), UiO-67 (Zr₆O₄(OH)₄(OOC-C₁₂H₈-COO))₆, Figure 5-7), and MOF-808 (Zr₆O₄(OH)₄(HCOO)₆(C₆H₅(COO))₂, Figure 5-9) in an manner analogous to the prior
heterogenization with NU-1000. The SBUs of each of these Zr MOFs contain $\mu_3$-OH, enabling the formation of MOF/MMAO-12 composites. By preparing heterogenized catalysts supported on a series of MOF/MMAO-12 composites, we are able to compare the activity and selectivity of the supported catalysts based on the pore size of the MOF support. Although the exact nature of the interaction between the support and the catalyst is unclear, the choice of support clearly influences the activity and selectivity of both catalysts. ICP-MS results show that neither catalyst is efficiently supported with UiO-66/MMAO-12, as titanium is not detected in the digested samples. This can potentially be explained by the narrow pore apertures of UiO-66 (6 Å), which are too small to permit diffusion of either catalyst throughout the material. The absence of titanium also implies that the catalysts do not load efficiently onto the surface of UiO-66/MMAO-12 particles. The catalysts are more readily supported upon the isoreticular UiO-67/MMAO-12 composite, where the parent MOF has pore apertures between 8 Å and 11.5 Å. Nonetheless, upon exposure to ethylene the supported catalysts solely produce polyethylene. Increasing the pore aperture of the MOF to 14 Å by moving to MOF-808/MMAO-12 provides a more effective support for (Fl)TiCl$_3$. The supported phenoxyimine catalyst 2 selectively trimerizes ethylene, albeit with a lower activity than when immobilized upon NU-1000. Of the MOFs tested as a supporting material NU-1000 has the largest pore window, with one-dimensional hexagonal channels with a 31 Å diameter. The phenoxyimine catalyst 2 is most active when supported upon NU-1000/MMAO-12, consistent with the previous results that the catalytic performance of the supported (Fl)TiCl$_3$ generally improves with increasing pore size of the MOF. Interactions with the support and confinement seem to disrupt the activity and selectivity of the phenoxyimine catalyst, suggesting that future studies seeking to immobilize ethylene trimerization catalysts upon MOF/MMAO-12 composites should explore MOFs with large mesopores. Similarly,
heterogenization of (Cp-arene)TiCl₃ upon UiO-67/MMAO-12, MOF-808/MMAO-12, and NU-1000/MMAO-12 all lead to the exclusive polymerization of ethylene, consistent with results from the literature where (Cp-arene)TiCl₃ was heterogenized upon MgCl₂/MAO.¹¹⁴ In the homogeneous analog, the pendant arene group is believed to serve as a hemilabile ligand that stabilizes metallacyclic intermediates necessary for ethylene trimerization,²⁰⁴ and it is possible that heterogenization disrupts this essential interaction. Alternatively, studies with homogeneous Cp-arene titanium catalysts have demonstrated that at the beginning of ethylene trimerization reactions that polyethylene is formed due to partially alkylated cationic titanium complexes.⁵ It is possible that only these partially alkylated complexes form upon heterogenization, leading to the exclusive formation of polyethylene. More studies are necessary to determine the origin of polyethylene formation with the heterogenized Cp-arene titanium catalyst, although these preliminary results demonstrate that the impact of heterogenization varies from catalyst to catalyst.

5.3 CONCLUSION AND OUTLOOK

In conclusion, I have prepared supported titanium trimerization catalysts on MOF/MMAO-12. Although supported (Cp-arene)TiCl₃ catalysts exclusively polymerize ethylene, supported phenoxyimine catalysts are active for the trimerization of ethylene to 1-hexene. Surface immobilized catalysts contribute to the overall catalytic behavior of the supported materials, although the MOF supported systems are much less active than their homogeneous counterparts. Future MOF-based catalysts should focus on alternative approaches towards the development of heterogeneous trimerization catalysts.
Table 5-1. Ethylene reactivity with immobilized catalysts.

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<th>Catalyst</th>
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<th>TOF (hr(^-1))(^a)</th>
<th>C(_6) (%)(^b)</th>
<th>C(_{10}) (%)(^c)</th>
<th>Oligomer Fraction (%)(^d)</th>
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<td>9</td>
<td>NU-1000</td>
<td>(Ft)TiCl(_3)</td>
<td>25</td>
<td>7900±2100</td>
<td>83.8</td>
<td>16.2</td>
<td>65.4</td>
</tr>
<tr>
<td>10</td>
<td>NU-1000</td>
<td>(Ft)TiCl(_3)</td>
<td>32</td>
<td>5800±5100</td>
<td>94.4</td>
<td>5.6</td>
<td>68.2</td>
</tr>
<tr>
<td>11</td>
<td>NU-1000</td>
<td>(Ft)TiCl(_3)</td>
<td>50</td>
<td>12400±4400</td>
<td>92.5</td>
<td>7.5</td>
<td>81.7</td>
</tr>
</tbody>
</table>

All reactions carried out at room temperature. Control experiments were carried out with the MOF/MMAO-12 composite to determine background reactivity. No oligomers form, but some background polymerization activity is observed. \(^a\)Moles of ethylene consumed per mole of titanium per hour. \(^b\)C\(_6\) products as a weight percent of all oligomeric products, as determined by gas chromatography. \(^c\)C\(_{10}\) products as a weight percent of all oligomeric products, as determined by gas chromatography. \(^d\)The percentage of the overall products that are oligomeric. Results are corrected for background polymerization reactivity observed with the MOF/MMAO-12 composites.
5.4 METHODS

General Remarks.

\[(\text{Cp-arene})\text{TiCl}_3, (\text{FI})\text{TiCl}_3, \text{UIO-66}, \text{UIO-67}, \text{MOF-808}, \text{and NU-1000} \]

were prepared according to literature procedures. Modified methylaluminoxane (MMAO-12, 7 wt.
% A in toluene, MilliporeSigma), pentane (analytical standard, 99.9%, MilliporeSigma), 1-
pentene (analytical standard, 99.5%, MilliporeSigma), mesitylene (analytical standard, 99.8%,
MilliporeSigma), and ethylene (99.9%, Airgas) were used as received. Dry, deaerated toluene
(HPLC Grade, 99.8%) was obtained by passing the solution through two silica columns in a
Glass Contour Solvent System, degassed with a flow of argon gas for 30 min followed by three
freeze-pump-thaw cycles, and stored over 4Å molecular sieves.

Elemental analysis were performed by Robertson Microlit Laboratories, Ledgewood, New
Jersey. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker Advance II
diffractometer equipped with 0/2θ Bragg-Brentano geometry and Ni-filtered Cu-Kα radiation
\((\text{K}\alpha 1 = 1.5406 \text{ Å})\). The tube voltage and current were 40 kV and 40 mA, respectively.

Ethylene trimerization reactions were analyzed with an Agilent 7890B gas chromatograph (30
meter PoraBOND Q PT capillary column) equipped with a 5977A mass spectrometer and a
flame ionization detector.

Experimental details.

The supported catalysts were prepared in a manner analogous to that found in the
literature.\textsuperscript{104}
Preparation of (Fl)TiCl$_3$@NU-1000/MMAO-12. NU-1000 (100 mg, 4.8 x $10^{-2}$ mmol) was suspended in 10 mL MMAO-12 (2.32M in toluene) and gently stirred for 18 hours. After treatment with MMAO-12, the solution was decanted and washed with fresh toluene (5 x 10 mL). The MOF was dried under reduced pressure to afford a free flowing powder. The aluminum to zirconium ratio was measured by ICP-OES (Al:Zr = 7.7:1). A 50 mg sample of the NU-1000/MMAO-12 composite was suspended in 5 mL toluene and treated with 1 mL of a 1.6 mM solution of (Fl)TiCl$_3$ in toluene. The suspension was gently stirred for one hour, the solution was decanted, and the volatiles were removed under reduced pressure to afford a light yellow powder. Ti:Zr:Al = 1:31:238. (Cp-arene)TiCl$_3$@NU-1000/MMAO-12 was prepared in an analogous manner (Ti:Zr:Al = 1:40:290).

Preparation of (Fl)TiCl$_3$@MOF-808/MMAO-12. MOF-808 (110 mg, 8.3 x $10^{-2}$ mmol) was suspended in 10 mL MMAO-12 (2.32M in toluene) and gently stirred for 18 hours. The solution was decanted and washed with fresh toluene (5 x 10 mL). The MOF was dried under reduced pressure to afford a free flowing powder. The aluminum to zirconium ratio was measured by ICP-OES (Al:Zr = 14.0:1). The MOF-808/MMAO-12 composite was suspended in 15 mL toluene and treated with 2.1 mL of a 1.6 mM solution of (Fl)TiCl$_3$ in toluene. The suspension was gently vigorously for one hour, the solution was decanted, and the volatiles were removed under reduced pressure to afford a light yellow powder. Ti:Zr:Al = 1:58:812. (Cp-arene)TiCl$_3$@MOF-808/MMAO-12 was prepared in an analogous manner (Ti:Zr:Al = 1:33:220).

Preparation of (Fl)TiCl$_3$@UiO-67/MMAO-12. UiO-67 (250 mg, 1.2 x $10^{-1}$ mmol) was suspended in 10 mL MMAO-12 (2.32M in toluene) and gently stirred for 18 hours. The solution was decanted and washed with fresh toluene (5 x 10 mL). The MOF was dried under reduced pressure to afford a free flowing powder. The aluminum to zirconium ratio was
measured by ICP-OES (Al:Zr = 5.2:1). A 50 mg sample of the UiO-67/MMAO-12 composite was suspended in 5 mL toluene and treated with 1 mL of a 1.6 mM solution of (Ft)TiCl₃ in toluene. The suspension was gently stirred for one hour, the solution was decanted, and the volatiles were removed under reduced pressure to afford a light yellow powder. Ti:Zr:Al = 1:295:1525. (Cp-arene)TiCl₃@UiO-67/MMAO-12 was prepared in an analogous manner (Ti:Zr:Al = 1:90:570).

**Preparation of (Ft)TiCl₃@UiO-66/MMAO-12.** UiO-66 (300 mg, 1.8 x 10⁻¹ mmol) was suspended in 10 mL MMAO-12 (2.32M in toluene) and gently stirred for 18 hours. The solution was decanted and washed with fresh toluene (5 x 10 mL). The MOF was dried under reduced pressure to afford a free flowing powder. The aluminum to zirconium ratio was measured by ICP-MS (Al:Zr = 4.6:1). A 50 mg sample of the UiO-66/MMAO-12 composite was suspended in 5 mL toluene and treated with 1 mL of a 1.6 mM solution of (Ft)TiCl₃ in toluene. The suspension was gently stirred for one hour, the solution was decanted, and the volatiles were removed under reduced pressure to afford a light yellow powder. The error in the quantification of Ti by ICP-MS exceeds the level of titanium detected. (Cp-arene)TiCl₃@UiO-66/MMAO-12 was prepared in an analogous manner.

**Ethylene reactivity experiments.** In a typical experiment, a freshly prepared sample of the supported catalysts (50 mg, 1.6 x 10⁻³ mmol Ti) was suspended in toluene (10 mL) and loaded into a 50 mL Parr reactor under a nitrogen atmosphere. The reactor was sealed and removed from the glovebox. The ethylene line was purged for 5 minutes before the reactor was pressurized to 32 bar and allowed to react at room temperature for one hour. After one hour, the reactor was depressurized, mesitylene (100 uL) was added as standard, the mixture was filtered, and the organics were analyzed by GCMS. The solids were dried under vacuum for one hour and weighed.
**Hot Filtration experiments.** A freshly prepared sample of (FI)TiCl₃@NU-1000/MMAO-12 (50 mg, $1.6 \times 10^{-3}$ mmol Ti) was suspended in toluene (10 mL) and loaded into a 50 mL Parr reactor under a nitrogen atmosphere. Mesitylene (100 uL) was added as an internal standard and the reactor was sealed and removed from the glovebox. The ethylene line was purged for 5 minutes before the reactor was pressurized to 50 bar and allowed to react at room temperature for one hour. After the reaction was complete, the reactor was slowly depressurized through a stainless steel bubbler, resealed and pumped into the glovebox. The solution was filtered. An aliquot of the filtrate (0.1 mL) was collected and analyzed by GCMS. The rest of the filtrate was loaded into a 50 mL Parr reactor and 0.5 mL of 2.32 M MMAO-12 was added. The reactor was sealed and removed from the glovebox. The ethylene line was purged for 5 minutes before the reactor was pressurized to 50 bar and allowed to react at room temperature for one hour. The mixture was quenched with ice-cold water (1 mL), and the organics were analyzed by GCMS. In a separate reactor, the solids recovered from the initial ethylene trimerization reactor were suspended in toluene. The reactor was sealed and pressurized to 50 bar under an ethylene atmosphere. After one hour at room temperature, the reactor was depressurized, the solution was filtered, and the filtrate was analyzed by GCMS.
Figure 5-5. Three-dimensional representation of UiO-66.
Figure 5-6. PXRD patterns of UiO-66. From bottom to top, as synthesized UiO-66, the MOF/MMAO-12 composite, after treatment with (FTiCl₃, and after ethylene trimerization reactivity with (FTiCl₃. The crystallinity of the material is maintained throughout.
Figure 5-7. Three-dimensional representation of UiO-67.
Figure 5-8. PXRD patterns of UiO-67. From bottom to top, as synthesized UiO-67, the MOF/MMAO-12 composite, after treatment with (Fl)TiCl₃, and after ethylene trimerization reactivity with (Fl)TiCl₃. Substantial polyethylene formation occurs, although features at 5.5° and 6.5° are still present.
Figure 5-9. Three-dimensional representation of MOF-808.
Figure 5-10. PXRD patterns of MOF-808. From bottom to top, as synthesized MOF-808, the MOF/MMAO-12 composite, after treatment with (FL)TiCl₃, and after ethylene trimerization reactivity with (FL)TiCl₃. The crystallinity of the material is maintained throughout.
Figure 5-11. PXRD patterns of NU-1000. From bottom to top, as synthesized NU-1000, the MOF/MMAO-12 composite, after treatment with (FI)TiCl₃, and after ethylene trimerization reactivity with (FI)TiCl₃. The crystallinity of the material is maintained throughout, although amorphous features grow in with the formation of polyethylene after reaction of the supported catalyst with ethylene.
Figure 5-12. Gas chromatogram (flame ionization detector) of NU-1000/MMAO-12 without (FI)TiCl₃ loaded onto the support.
Figure 5-13. Gas chromatogram (flame ionization detector) analysis shows that no homogeneous species are responsible for the observed reactivity. Suspending NU-1000/MMAO-12 in toluene, filtering the suspension, and testing the filtrate for ethylene reactivity provides this chromatogram.
Figure 5-14. Gas chromatogram (flame ionization detector) of a 1 hour reaction with NU-1000/MMAO-12 in toluene pressurized with ethylene to 50 bar.
Bibliography


(2) Suttil, J. A.; McGuinness, D. S. Mechanism of Ethylene Dimerization Catalyzed by Ti(OR')₄/AlR₃. *Organometallics* 2012, 31 (19), 7004–7010.


2007.


(32) Kunrath, F. A.; de Souza, R. F.; Casagrande Jr., O. L.; Brooks, N. R.; Young Jr., V. G. Highly Selective Nickel Ethylene Oligomerization Catalysts Based on Sterically


Canivet, J.; Aguado, S.; Schuurman, Y.; Farrusseng, D. MOF-Supported Selective Ethylene Dimerization Single-Site Catalysts through One-Pot Postsynthetic


Tobisch, S.; Ziegler, T. Catalytic Linear Oligomerization of Ethylene to Higher α-


(145) Overett, M. J.; Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F.; Killian, E.; Maumela,


(168) Reger, D. L.; Garza, D. G.; Lebioda, L. Synthesis of Extremely Stable Alkylpalladium Complexes of the Type (Me₂NCS₂)Pd(PEt₃)(alkyl). Crystal and Molecular Structures of the Isomers [Cyclic] (CH₃CH₂CH₂CH₂NCS₂)Pd(PEt₃)(n-Propyl) and [Cyclic] (CH₃CH₂CH₂CH₂NCS₂)Pd(PEt₃)(isopropyl). *Organometallics* 1991, 10 (4), 902–906.


(170) An alternative hypothesis is the selective 2,1-insertion of 1,6-heptadiene into the Ni–H species followed by a 1,2-insertion of the tethered alkene. This is also consistent with the data and has some literature support (for example, see Widenhoefer, R. A. *Acc. Chem. Res.* 2002, 35, 905. and references therein).


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