Selective Ethylene Dimerization by a Nickel-Exchanged Metal-Organic Framework Catalyst

by

Kathleen E. Martin

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Signature redacted

Signature redacted

Certified by: __________

Mircea Dincă
Associate Professor of Chemistry
Thesis Advisor

Accepted by: __________

Robert T. Haslam and Bradley Dewey Professor of Chemistry
Chairman, Departmental Committee on Graduate Students
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Submitted to the Department of Chemistry on August 5th, 2016 In Partial Fulfillment of the Requirements for the Degree of Masters of Science in Chemistry

Abstract

Short linear α-olefins such as 1-butene are valuable commodity chemicals due to their use as co-monomers in linear low-density polyethylene. Presently only homogeneous systems are used to catalyze ethylene dimerization in industry, causing many to suffer from quick deactivation and poor selectivity. The metal-organic framework (MOF) CPF-5 Mn₃(TBA)₃(HCOO)₃(OH)(H₂O)₂]₄•6DMF where TBA = 4-(1H-tetrazol-5-yl)benzoic acid provides an ideal structural template for the development of a heterogeneous catalyst for ethylene dimerization. Ni exchanged CPF-5 (Ni-CPF-5) treated with diethylaluminum chloride had a maximum turnover frequency of 23,000 mole ethylene per mole Ni per hour, and a maximum selectivity for 1-butene of 80% under optimized conditions. Ethylene pressure strongly influenced the activity and selectivity of Ni-CPF-5. Though the observed activity behavior is similar, the selectivity trends diverged significantly from previously reported MOF dimerization catalysts.

Thesis supervisor: Mircea Dincă
Title: Associate Professor of Chemistry
Dedicated to My Parents and My Significant Other

Kathleen E. Martin obtained her B.Sc. degree in Chemistry from the University of New Mexico (UNM) in 2014 and graduated with magna cum laude honors. During her time at UNM and Sandia National Laboratories (SNL), she developed an interest in chemical research and development. While working with Dr. John Shelnutt at SNL on photoconductive porphyrin microstructures, she authored and co-authored eight publications and obtained one patent. After graduating from UNM, Kathleen went on to pursue a graduate degree in chemistry at the Massachusetts Institute of Technology (MIT) with Dr. Mircea Dincă. While at MIT, she worked on developing catalytically active metal-organic frameworks for heterogeneous ethylene dimerization applications. Kathleen completed her M.Sc. degree in Inorganic Chemistry after two years of study at MIT.
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Reaction was run at room temperature for one hour at 50 bar and with 1900 equivalents of diethylaluminum chloride.

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GC trace of Ni-CPF-5 leach solution. Reaction was run at room temperature for one hour at 50 bar and with 1900 equivalents of diethylaluminum chloride.
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Figure 2.14  Catalytic behavior comparisons between Ni-MFU-4/ and Ni-CPF-5

A) A comparison of pressure dependent oligomer selectivities. The purple bars correspond to Ni-MFU-4/ selectivities and the blue bars to Ni-CPF-5 selectivities. B) A comparison of pressure dependent oligomer activities. The purple triangles correspond to Ni-MFU-4/ activity and the blue circles to NP-Ni-CPF-5 activity. All one-hour NP-NiCPF-5 reactions completed at room temperature and with 1900 equivalents of Et₂AlCl. All one-hour NiMFU-4/ reactions completed at room temperature and with 100 equivalents of MAO.

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Chapter 1- Background and Motivation

1.1 ETHYLENE DIMERIZATION

Linear α-olefins are straight chain hydrocarbons that contain a terminal double bond and are more desirable than their internal alkene isomers because they are more reactive to oxidants. By 2018, the global demand for α-olefins is expected to reach 4.6 million metric tons with a projected increase of 4.2% per year\(^1\). Much of this demand comes from the fact that α-olefins can be exploited for the synthesis of many industrial products including plasticizers, surfactants, and polyethylene\(^2\). Short chain linear α-olefins like 1-butene are of particular interest because they are co-monomers in the manufacture of linear, low-density polyethylene (LLDPE), a plastic that is favored for its resistance to puncture and tensile deformation while maintaining a relatively low melting point. The co-monomers need to be very pure or a significant amount of branching will occur and result in formation of weaker low-density polyethylene\(^3\). 1-butene is produced in large amounts by the thermal and acid-catalyzed cracking of paraffins\(^4\), but it is very energy intensive to distill from other short chain olefins. One way around this is to synthesize 1-butene directly from the dimerization of ethylene, a cheap and abundant reactant.

Most catalysts used in the oligomerization of ethylene follow the Cossee-Arlman mechanism (Figure 1.1) and produce a Shultz-Flory distribution of products\(^8,9\). To maximize the yield and purity of butenes, the rate of insertion of ethylene must be much lower than the rate of chain transfer\(^11\). Tuning the olefin product selectivity of a catalyst is largely dependent on the transition metal being used (often either titanium, nickel or zirconium\(^5\)), its coordination environment, and steric factors. There are many industrial catalysts that are active for ethylene oligomerization, including the nickel Shell Higher Olefin Process (SHOP) catalyst, the aluminum/zirconium Idemitsu Process catalyst, and the aluminum Albermarle and Chevron Processes catalysts, but all are homogeneous and relatively non-selective for 1-butene\(^6\).
Homogeneous ethylene oligomerization catalysts benefit from strong interactions with substrates, but often deactivate quickly and are difficult to separate from oligomer products. Therefore, many studies have been carried out to develop heterogeneous catalysts that are more robust than their homogeneous alternatives and are easier to recover without compromising selectivity.

1.2 METAL-ORGANIC FRAMEWORKS
Metal-organic frameworks (MOFs) are ordered, high surface area networks that comprise of organic linker molecules and metal clusters called secondary building units (SBUs). They are used in a large range of applications including gas storage/separation\textsuperscript{13}, ion conduction\textsuperscript{14}, and catalysis\textsuperscript{15}. Those that are well suited for heterogeneous catalysis have isolated and densely packed metal sites that are coordinatively unsaturated and contain large pores\textsuperscript{7,16-18}. These criteria among other more specific characteristics are vital when designing a MOF catalyst, though it often takes several attempts to design a working system. However, screening the Cambridge Crystallographic Data Centre (CCSD) for potential catalytically active MOFs instead of trying to design one from first principles allows for systematic and quick testing and does not rely on serendipity. Moreover, of the 54,000\textsuperscript{+} MOF crystal structures that can be found in the CCSD, very few of them have been fully characterized and their inherent properties exploited. Using the criteria stated above, an all-manganese MOF named CPF-5 was chosen from the CCSD to use as template for developing a heterogeneous ethylene dimerization catalyst.

\textbf{Figure 1.1.} The Cossee-Arlman mechanism for ethylene dimerization. This is an unofficial adaptation of an article that appeared in an ACS publication (reference 12). ACS has not endorsed the content of this adaptation or the context of its use.
1.3 THE CPF-5 MOF

CPF-5 ([Mn$_5$(TBA)$_3$(HCOO)$_3$(OH)(H$_2$O)$_2$]$_4$·6DMF) where CPF = Crystalline Porous Framework is a super-super-tetrahedral MOF in space group F-43c$^{19}$. The super-tetrahedral SBUs each contain octahedral Mn$^{2+}$ centers and 4-tetrazole-benzoic acid (TBA) ligands that are further bridged together by formate and N,N-dimethylformamide (DMF) molecules and are arranged to form larger tetrahedrons to make an octahedral pore (Figure 1.2). Each SBU vertex contains a solvated Mn$^{2+}$ site that points into the pore of the MOF for a total of four sites per pore. In order to make these solvated sites catalytically active for ethylene dimerization, they were cation exchanged for Ni$^{2+}$ to make the Ni-CPF-5 MOF. Ni-CPF-5’s catalytic success is described in the following chapter.

![Figure 1.2](image.png)
Chapter 2- Ethylene Dimerization of Ni-CPF-5

2.1 INTRODUCTION

1-butene is a desirable chemical commodity due to its use in industrial processes such as the production of linear low-density polyethylene and alkylate gasoline. In fact, the dimerization of ethylene alone accounts for around 700,000 metric tons of the \( \alpha \)-olefins produced per year\(^1\). Today, the most selective ethylene dimerization catalysts used in industry are homogeneous and prone to rapid deactivation and are difficult to separate from reaction mixtures. Other industrial homogeneous catalysts like those used in the Shell Higher Olefin Process contain immiscible liquid phases to aid in separation, but suffer poor short chain linear \( \alpha \)-olefin selectivity\(^10\). Therefore, much work has gone into the development of heterogeneous ethylene dimerization and oligomerization catalysts as they are often more selective and have longer lifetimes than their homogeneous counterparts, though their success has been limited\(^20\)-\(^24\). Metal-organic frameworks (MOFs) are particularly attractive materials for further optimizing heterogeneous catalysis since their metal sites are densely packed, evenly dispersed, and isolated within the framework lattice\(^25\).

Generally speaking, MOFs are highly porous, crystalline networks that contain metal clusters called secondary building units (SBUs) that are connected together by organic linker molecules. Due to their large surface areas and crystalline structure, they have a wide range of applications including gas storage/separation, ion conduction, and catalysis. In addition to isolated metal sites, MOFs suitable for catalysis also need to contain large pores to allow the adsorption and desorption of the desired substrate, have reaction condition stability, and contain metal centers that are coordinatively unsaturated or are bound to labile ligands\(^7\)-\(^16\)-\(^18\). Additionally, MOFs that contain open nickel centers in a nitrogen-rich coordination environment have been shown to be particularly active for ethylene dimerization. Such active sites are often found in homogeneous systems like the metal scorpionate complex nickel tris-pyrazolylborate (Tp\(^{Me}\)NiCl)\(^26\), and have recently been shown to produce selective and active 1-butene MOF heterogeneous catalysts using MFU-4\(^12\).
Using these design principles, we were able to investigate MOFs that may serve as effective heterogeneous catalysts instead of trying to design one from first principles. Using the criteria stated above, an all-Mn MOF named CPF-5 was chosen to use as template for developing a heterogeneous ethylene dimerization catalyst, as the solvated Mn sites could be cation exchanged for Ni (Ni-CPF-5) to form active sites similar to Ni-MFU-4/ and Tp\textsuperscript{Mes}NiCl (Figure 2.1). Herein, the effective ethylene dimerization of Ni-CPF-5 under mild reaction temperatures with an alkyl aluminum initiator is elucidated.

![Figure 2.1](image)

Figure 2.1. Cartoon structures of Tp\textsuperscript{Mes}NiCl, Ni-MFU-4/, and Ni-CPF-5. A) Three dimensional orientation of the active site within the CPF-5 MOF. B) Ball-and-stick model of CPF-5 and Ni-CPF-5 active sites. C) Space-filling model of Tp\textsuperscript{Mes}NiCl. D) Space-filling model of the Ni-MFU-4/ active site. E) Space-filling model of the Ni-CPF-5 active site. Pink balls correspond to boron, orange to zinc, purple to manganese, dark green to nickel, light green to chloride, blue to nitrogen, gray to carbon, red to oxygen, and white to hydrogen.
2.2 RESULTS AND DISCUSSION

The Ni-CPF-5 pre-catalyst could not be directly synthesized using conventional solvothermal techniques, but cation exchange techniques similar to those previously reported enabled the exchange of solvated Mn sites with nickel. In a typical cation exchange, a methanol solution containing 55 equivalents of nickel salt per solvated MOF site was allowed to sit at room temperature for one week, and was then washed with fresh methanol. Inductively coupled plasma mass spectrometry and elemental analyses found an average Mn to Ni ratio of 3.3 to 1. The crystallinity of the material was maintained upon nickel cation exchange, as confirmed by PXRD (Figure 2.2).

![Figure 2.2. Powder x-ray diffraction patterns of CPF-5 before and after Ni²⁺ exchange.](image)

If Ni-CPF-5 was suspended in methanol and allowed to dry, a different phase of the MOF was made. Interestingly, the new MOF phase (NP-Ni-CPF-5) maintained the same unit cell parameters, with only the two most intense PXRD pattern peaks being significantly reduced in intensity.
intensity (Figure 2.3). These two peaks corresponded to the (200) and (222) lattice planes and affected only the TBA ligands (Figures 2.4 and 2.6). These peak losses were likely due to significant ligand disordering as the original and new Ni-CPF-5 phases were chemically indistinguishable by CHN elemental analysis (Table 2.1). The (220) plane was not seen in the calculated structure for CPF-5, and could have corresponded to either the bridging DMF molecules that were partially omitted from the original CIF file (CCSD reference file FEBQIO), or from solvent ordering within the SBU void (Figure 2.5).

![Powder x-ray diffraction patterns of Ni-CPF-5 before and after rigorous drying. The PXRD peaks most strongly influenced have been labeled with their corresponding lattice planes.](image)

**Figure 2.3.** Powder x-ray diffraction patterns of Ni-CPF-5 before and after rigorous drying. The PXRD peaks most strongly influenced have been labeled with their corresponding lattice planes.
Figure 2.4. The (200) lattice plane of Ni-CPF-5. Only the TBA ligands intersect this plane.

Figure 2.5. The (220) lattice plane of Ni-CPF-5. This plane's peak is only observed in synthesized samples.
Figure 2.6. The (222) lattice plane of Ni-CPF-5. Only the TBA ligands intersect this plane.

Table 2.1 Elemental analyses for Ni-CPF-5 samples.

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<th>Exp. % New phase Ni-CPF-5</th>
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Under ethylene dimerization reaction conditions, Ni-CPF-5 samples with 1900 equivalents of diethyl aluminum chloride maintained their crystallinity and formed 1-butene, 2-butene, hexene products and 20 mg of polyethylene (Figure 2.7). Parent CPF-5 and Ni-CPF-5 without diethylaluminum chloride were both catalytically inactive. Homogenous leach solutions of Ni-CPF-5 and Ni-CPF-5 that had been heated to 40 °C showed significantly reduced activity for ethylene dimerization (Figures 2.8-2.12) by gas chromatography analysis.
Figure 2.7. Powder x-ray diffraction patterns of Ni-CPF-5 before and after ethylene. The peak at 22° in the gray curve corresponds to the formation of polyethylene. All one hour reactions completed at room temperature and with 1900 equivalents of diethylaluminum chloride.
Figure 2.8. Gas chromatography trace of Ni-CPF-5 with diethylaluminium chloride initiator. Reaction was run at room temperature for one hour at 50 bar and with 1900 equivalents of diethylaluminium chloride.
Figure 2.9. GC trace of CPF-5 with diethylaluminum chloride initiator. Reaction was run at room temperature for one hour at 50 bar and with 1900 equivalents of diethylaluminum chloride.
Figure 2.10. GC trace of diethylaluminum chloride without MOF. Reaction was run at room temperature for one hour at 50 bar and with 1900 equivalents of diethylaluminum chloride.
Figure 2.11. GC trace of Ni-CPF-5 without diethylaluminum chloride. Reaction was run at room temperature for one hour at 50 bar.
NP-Ni-CPF-5 had both higher activity and lower selectivity for ethylene dimerization than the native Ni-CPF-5 crystalline form, though its PXRD pattern peaks were overwhelmed by the amorphous formation of aluminum oxide by diethylaluminum chloride quenching (Figure 2.13). These experiments indicated that the new phase nickel-exchanged CPF-5 was a heterogeneous ethylene dimerization pre-catalyst and best operated at room temperature.
Figure 2.13. Powder x-ray diffraction patterns of NP-Ni-CPF-5 before and after ethylene. The broad peak below 15° corresponds to the formation of aluminum oxide upon initiator quenching, and the peak at 22° in the gray curve corresponds to the formation of polyethylene. Reaction was completed after one hour at room temperature and with 1900 equivalents of diethylaluminum chloride.

NP-Ni-CPF-5’s catalytic activity increased with respect to ethylene pressure upon initiation with diethyl aluminum chloride, and reached a maximum value of 23,000 hr⁻¹. This behavior agreed well with what has been previously reported for the Ni-MFU-4/ MOF system, though without the significant activity plateauing at higher pressures. The plateauing in Ni-MFU-4/ may be due in part to substrate mass transport limitations of the MOF. In the NP-Ni-CPF-5 system, this lack of observable plateauing could be due to a less sterically hindered active site, allowing for the quicker release of products and independence from ethylene pressure. Isomerization ratios did not appreciably change with pressure, but the selectivity for C₄ over C₆ products dropped. This diverged significantly from the behavior seen in the Ni-MFU-4/ system, which showed a marked decrease in C₆ products with increasing pressure (Figure 2.14).
Figure 2.14. Catalytic behavior comparisons between Ni-MFU-4/ and NP-Ni-CPF-5. A) A comparison of pressure dependent oligomer selectivities. The purple bars correspond to Ni-MFU-4/ selectivities and the blue bars to Ni-CPF-5 selectivities. B) A comparison of pressure dependent oligomer activities. The purple triangles correspond to Ni-MFU-4/ activity and the blue circles to NP-Ni-CPF-5 activity. All one-hour NP-NiCPF-5 reactions completed at room temperature and with 1900 equivalents of Et₂AlCl. All one-hour NiMFU-4/ reactions completed at room temperature and with 100 equivalents of MAO.
Again, nickel oligomerization catalysts are commonly proposed to operate via the Cossee-Arlman mechanism, resulting in a Shulz-Flory distribution of oligomeric products\(^9\). In the case of selective dimerization catalysts, the rate of insertion (\(k_i\)) is necessarily much lower than the rate of chain transfer (\(k_{tr}\))\(^11\). The first-order dependence on catalytic activity with respect to pressure for Ni-CPF-5 suggests \(k_{ii}\) is only influenced by the concentration of the ethylene when the temperature is held constant. The drop in selectivity for \(C_4\) over \(C_6\) products with pressure also indicates that \(k_i\) has a higher order dependence on ethylene pressure than \(k_{tr}\). The unchanging isomerization ratio points to the release of the butene product and the re-insertion of ethylene to regenerate the catalyst as two discrete \(k_i\) steps instead of being one concerted step because there is no apparent dependence on ethylene pressure (Figure 2.15).

**Figure 2.15.** Proposed Cossee-Arlman mechanisms for Ni-MFU-4l and Ni-CPF-5. The purple path corresponds to a concerted Ni-MFU-4l release of product and the blue path to a step-wise Ni-CPF-5 release of product.
One way this might be occurring is by the formation of a nickel hydride intermediate by β-hydride elimination of the olefin after release of the butene product and before the re-insertion of ethylene. In the concerted mechanism, the release of the product would be first-order dependent on ethylene and would disfavor the formation of higher chain olefins and isomers at higher pressures like what is observed in the Ni-MFU-4/ system. In contrast, the two-step mechanism would allow the release of the product to be independent of ethylene pressure. This would promote the formation of longer chain olefins at higher pressures since only the rate of ethylene re-insertion would be increasing. This also means the rate of isomerization to 2-butenes should not increase, both of which have been observed for the Ni-CPF-5 system.

Upon cation exchange with nickel and diethyl aluminum chloride initiation, CPF-5 has been shown to be a highly active and selective heterogeneous ethylene dimerization catalyst, with turnover frequencies exceeding 20,000 hr\(^{-1}\) and selectivity for 1-butene of around 80%. The steady increase in Ni-CPF-5 activity with ethylene pressure suggests that minimizing steric crowding at active sites help prevent mass transport limitations in heterogeneous catalytic systems. Additionally, the difference between Ni-MFU-4/ and Ni-CPF-5 in oligomer distribution with pressure points to the possible formation of a nickel hydride species in the Ni-CPF-5 system, and may help explain the marked differences in the final 1-butene selectivity.

2.3 EXPERIMENTAL DETAILS
A. General Remarks
Sodium azide, Na\(\text{N}_3\) (99%, Alfa Aesar), ammonium chloride, NH\(_4\text{Cl}\) (99.5%, Alfa Aesar), cyanobenzoic acid (98%, Alfa Aesar), anhydrous manganese chloride, MnCl\(_2\) (97%, Strem Chemicals), ammonium formate, NH\(_4\text{HCO}_3\) (97%, Alfa Aesar), nickel chloride hexahydrate, NiCl\(_2\)•6H\(_2\text{O}\) (99.9%, Strem Chemicals), diethylaluminum chloride, Et\(_2\text{AlCl}\) (25 wt. % in toluene, Sigma), 1-pentene (analytical standard, 99.5%, Sigma), ethylene (99.9%, Airgas), hydrochloric acid, HCl (1 M, Macron Fine Chemicals), N,N-dimethylformamide, DMF (99.8%, Macron Fine Chemicals), methanol (MeOH) (99.8%, Sigma-Aldrich) were used and received without further purification. Dry, deaerated toluene (HPLC Grade, 99.8%) was obtained by passing the solution through two silica columns in a Glass Contour Solvent System and degassed for 30 minutes.
followed by three freeze-pump-thaw cycles.

Nuclear magnetic resonance measurements of the organic linker was taken using a Bruker AVANCE-400 NMR spectrophotometer with a Magnex Scientific® superconducting magnet. Fourier-transform infrared spectroscopic measurements of the linkers were performed using a Bruker Alfa spectrometer. The data was averaged over 16 scans at 4 cm⁻¹ resolution between 4000-500 cm⁻¹. Nickel, and manganese analyses of Ni-CPF-5 MOF samples 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. CPF-5 and Ni-CPF-5 molecular formulas were conducted at Robertson Microlit Laboratories®, Ledgewood, New Jersey determined using carbon, hydrogen, nitrogen elemental analysis (CHN-EA). Samples were handled under inert atmosphere and were dried to constant weight. Optimal combustion conditions were used. 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 was 40 kV and the current was 40 mA. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 0.5 °C/min under a nitrogen gas flow of 90 mL/min. 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.

B. Synthesis of Ligand and MOFs

Synthesis of 4-tetrazole benzoic acid (TBA) TBA was synthesized according to a previous published preparation²⁸.

\[
\begin{align*}
\begin{array}{c}
\text{N} & \equiv & \text{N} \\
\text{O} & \equiv & \text{O} \\
\text{OH} & \equiv & \text{OH}
\end{array}
\end{align*}
\]

\[
\text{NaN}_3, \text{NH}_4\text{Cl} \quad \text{DMF, reflux, 20 hrs}
\]

\[
\begin{align*}
\begin{array}{c}
\text{N} & \equiv & \text{N} \\
\text{N} & \equiv & \text{N} \\
\text{OH} & \equiv & \text{OH}
\end{array}
\end{align*}
\]

Scheme 2.1. The synthetic route for 4-tetrazole benzoic acid.
Synthesis of CPF-5  
CPF-5 was synthesized according to a modified version of the provided literature preparation\(^\text{19}\). MnCl\(_2\) (100 mg, 0.79 mmol), TBA (80 mg, 0.42 mmol) and NH\(_4\)HCO\(_2\) (15 mg, 0.28 mmol) were dissolved in a solution of DMF (1.8 g) and deionized H\(_2\)O (0.200 g). The solution was then transferred to a pressure tube (Ace Glass Incorporated, 27 mL 30.5 cm long, 19 mmol, #7 front-seal plug) with a Teflon\(^\circ\) cap and was heated to 120 °C for 16 hours. The pressure tube was then allowed to cool to room temperature for 1.5 hours, and then reheated to 120 °C for two days. The supernatant was decanted, and the white precipitate was briefly washed in fresh DMF.

Synthesis of Ni(5\%)-CPF-5  
NiCl\(_2\)•6H\(_2\)O (0.250 g, 1.1 mmol) was dissolved in 20 mL of MeOH. Unactivated CPF-5 (100 mg; 2.2×10\(^{-2}\) mmol) was suspended in the NiCl\(_2\)•6H\(_2\)O solution. The resulting suspension was left at room temperature for one week. The solution was decanted, and the remaining powder was soaked in 20 mL fresh MeOH. This process was repeated once daily for two days. The solution was then again decanted and the MOF dried under vacuum (10\(^{-2}\) torr) for eight hours at room temperature.

Synthesis of New Phase Ni(5\%)-CPF-5  
Another 20 mL of fresh MeOH was then added and the MOF was agitated and centrifuged at 1000 rpm for five minutes to re-precipitate the MOF. The MeOH was then decanted and the MOF was allowed to dry for at least eight hours uncapped in a fume hood at room temperature to produce a different crystalline form of Ni-CPF-5.

C. Ethylene Dimerization Protocols

Pressure Dependence Experiment. Ethylene dimerization protocols were carried out according to a modified version of the provided literature preparation\(^\text{12}\). De-solvated Ni-CPF-5 (5.0 mg, 1.1 × 10\(^{-3}\) mmol) was placed into a 50 mL stainless steel Parr\(^\circ\) reactor under N\(_2\) atmosphere. Toluene (5 mL) and then Et\(_2\)AlCl (varied volumes) were then added to the reactor. The reactor was then sealed and brought to out to ambient conditions. Ten minutes after the Et\(_2\)AlCl was added, the reaction mixture was stirred vigorously on a stir plate, and the ethylene tank line to the reactor purged of O\(_2\) for at least five minutes. The reactor was then pressurized to a certain pressure under a constant feed of ethylene at room temperature. After one hour, the reactor was again sealed and was cooled in a dry ice/acetone bath. The reactor was vented to atmospheric
pressure after the temperature of the reaction mixture reached -20 °C to insure the condensation of oligomerization products. The reactor was then fully opened and 0.1 mL of cold 1-pentene internal standard was added to the mixture. The excess Et₂AlCl was then quenched with cold MeOH. To remove the residual Ni-CPF-5 and other solids, the cold reaction was then filtered through a precooled 0.2-µm Supor® syringe filter into a precooled GC vial. The filtrate was then analyzed via gas chromatography and mass spectroscopy. The recovered solids were analyzed using PXRD. Control experiments with the parent with no MOF present and all-Mn CPF-5 were carried out using the same protocol.

**Leaching Experiment.** De-solvated Ni-CPF-5 (8 mg, 1.8 x 10⁻³ mmol), toluene (8 mL) and Et₂AlCl (1.55 mL) were placed into a 20 mL glass scintillation vial under N₂ atmosphere. The reaction mixture was stirred briefly to and then allowed to sit for one hour at room temperature. The mixture was then filtered through a 0.2-µm Supor® syringe filter into a 50 mL stainless steel Parr® reactor. The reactor was then sealed and brought to out to ambient conditions. The pressurization of the reactor to 50 bar and resulting workup were carried out using the same protocol as above.

**Thermal Stability Experiment.** De-solvated Ni-CPF-5 (3.9 mg, 0.9 x 10⁻³ mmol), toluene (4 mL) and Et₂AlCl (0.77 mL) were placed into a 50 mL stainless steel Parr® reactor under N₂ atmosphere. The reactor was then sealed and brought to out to ambient conditions. Ten minutes after the Et₂AlCl was added, the reaction mixture was stirred vigorously on a stir plate. The reactor was then heated to 40 °C using a Parr® 4838 Reactor Controller for 30 minutes. The reactor was then cooled to 14 °C in an ice bath. The ethylene line purge, the pressurization of the reactor to 50 bar, and resulting workup were carried out using the same protocol as above.
References


KATHLEEN MARTIN

Business Address: Massachusetts Institute of Technology
Bldg. 2-316a
Cambridge, MA 02139
(617)-253-6192

Home Address: 95 Gordon St #15
Brighton, MA 02135
(505)-399-1063
martinke@alum.mit.edu

Education

Massachusetts Institute of Technology
MS, Department of Chemistry, September 2016
Thesis: Selective Ethylene Dimerization by a Nickel-Exchanged Metal-Organic Framework Catalyst

University of New Mexico
B.Sc, Department of Chemistry, May 2014
Magna Cum Laude

Awards

Department of Chemistry Award for Outstanding Teaching 2015
Massachusetts Institute of Technology

Dean’s List 2009-2014
University of New Mexico

Outstanding Science and Engineering Graduate 2014
University of New Mexico

Scholar’s Scholarship 2009-2013
University of New Mexico

Joan Willard Hemsing Tinoco Scholarship 2012-2013
University of New Mexico

International-Domestic Student Summit Travel Award 2012
American Chemical Society

First Place Undergraduate Poster 2012
Rio Grande Symposium of Advanced Materials

Dr. Thomas Whaley Endowed Memorial Scholarship 2012
University of New Mexico

J.L. Riebsomer Memorial Endowment 2011
University of New Mexico
<table>
<thead>
<tr>
<th>Research &amp; Teaching</th>
<th>MIT, Department of Chemistry</th>
<th>Cambridge, MA 2014-2016</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Advisor: Mircea Dinca</td>
<td></td>
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<tr>
<td></td>
<td>• Synthesized and refined metal-organic frameworks for heterogeneous ethylene oligomerization catalysis.</td>
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<tr>
<td></td>
<td>• Taught 5-310, an introductory laboratory chemistry course to undergraduate students for two semesters.</td>
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</table>

|                     | Center for Integrated Nanotechnology, Albuquerque, NM 2013-2014 |
|                     | Advisor: the late John Shelnutt | |
|                     | • Researched the deposition mechanisms and characterization of CBI porphyrin films onto surfaces for solar energy applications. | |
|                     | • Fabricated solar cell devices using CBI structures and chalcogenide nanowires. | |

|                     | UNM, Department of Chemistry and Biochemistry, Albuquerque, NM 2012-2013 |
|                     | Advisor: John Grey | |
|                     | • Studied charge transfer phenomena at the molecular donor-acceptor interface of hybrid nanostructures and spin-cast films as well as in non-fluorescent conjugated polymers. | |
|                     | • Taught CHEM-121L, an introductory laboratory chemistry course to undergraduate students for two semesters. | |
|                     | • Was a teaching assistant for CHEM 312, a thermodynamics physical chemistry course for undergraduate students for one semester. | |

|                     | Sandia National Laboratories, Albuquerque, NM 2008-2013 |
|                     | Advisors: John Shelnutt & Bernadette Hernandez-Sanchez | |
|                     | • Researched novel cooperative artificial photosynthetic solids formed from photosensitive organic dyes. | |
|                     | • Fabricated metallic nanostructures for nano-ampoules and oceanic anti-biofouling applications. | |

| Posters & Presentations | “Interfacial Charge Transfer Interactions in Donor/Acceptor Conjugated Polymers”, Martin, K. E.; Gao, J.; Grey, J. K.; Hernandez-Sanchez, B. A. Southeastern Regional Meeting of the American Chemical Society in Raleigh, NC. November 2012. | |


Patents