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Los Angeles

Reaction Engineering with
Metal-Organic Framework Catalysts

A thesis submitted in partial satisfaction
of the requirements for the degree Master in Science
in Materials Science and Engineering

by

Arek Viken Melkonian

2013

ABSTRACT OF THE THESIS

Reaction Engineering with Metal-Organic Framework Catalysts

by

Arek Viken Melkonian

Master of Science in Materials Science and Engineering

University of California, Los Angeles, 2013

Professor Richard B. Kaner, Chair

To date, there has been no comprehensive attempt to perform and/or describe catalytic reactions in the gas phase that utilize metal-organic frameworks (MOFs) as catalysts. In addition, there has been no attempt to reaction engineer these MOF catalysts in order to determine their regimes of optimal catalytic activity and possible limitations to their use. A zinc-based MOF that has been post-synthetically modified with a homogeneous palladium catalyst, $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$, is used to catalyze the hydrogenation of propylene. The catalyst is assembled in a packed-bed reactor under a continuous flow of reactants. The reaction is optimized with respect to isorecticular metalation, reactant flow rate, and reactor temperature. Maximum catalytic conversion is found at intermediate metalations of 40% and 60%, high hydrogen flow of 50 ccm, and intermediate reactor temperatures of 100 °C and 150 °C.

The MOF-60 catalyst is exposed to a traditional catalyst poison, carbon monoxide (CO). It is found that the MOF is reversibly poisoned upon introduction of CO. Upon poisoning, catalytic conversions rates of 90%-100% are dramatically reduced to less than 10%-30%, depending on the CO flow rate and the reactor temperature. The CO poisoning is shown to be reversible, a similar effect as found with palladium on carbon (Pd/C). The time scale of poisoning and recovery is very fast for both the MOF catalyst and Pd/C (approximately 10-30 seconds).

Other effects of temperature on the MOF-40 are also investigated. At fixed reactant flow, the temperature grid is partitioned into finer steps of 10 °C to determine the temperature that yields the highest catalytic conversion. It is found that conversion is nearly uniform in the range between the highest conversions, i.e., conversion plateaus between the optimum temperatures. The catalyst also exhibits a weak thermal hysteresis. There is no significant improvement in conversion with thermal cycling after alternating the reactor temperature between 100 °C and 200 °C for 8 hours.

The thesis of Arek Viken Melkonian is approved.

Louis-Serge Bouchard

Christian Fischer

Richard Kaner, Committee Chair

University of California, Los Angeles

2013

DEDICATION

My time at UCLA has been eye-opening; I have learned many things in many fields, ranging from physical chemistry to musicology. More importantly, the more knowledge I have amassed, the more I have realized that I know close to nothing. The research I have conducted is an attempt to gain new insights directly—and such insight is the most valuable.

I am deeply grateful to my PIs, Professor Louis Bouchard and Professor Omar Yaghi, for rigorously introducing me to the world of research. I would like to thank Professor Richard Kaner, for being my graduate advisor in the MSE Department, and Professor Christian Fischer, who has taught me much about materials science and spectroscopy. Dr. Jane Strouse and Dr. Greg Khitrov at the Molecular Instrumentation Center have been a great help to me as well. The entire Bouchard lab, especially our “Catalysis Crew,” has been instrumental in these projects.

Nanette Jarenwattananon and Dr. Stefan Glöggler have helped me acquire much of my data thanks to their expertise in NMR, Jonathan Brown has helped me by synthesizing many a MOF, and Trenton Otto has been my Saturday-late-at-night-experiment date countless times. I couldn't have done any of this without you guys.

I would like to dedicate this work to my family: my mom, Arpi, my dad, Viken, and my sister, Arin, for always having my back. Whenever I need a break from the City of Angels, they welcome me back home to Laguna Niguel with open arms, comforting words, and the best Armenian food on this side of the world.

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Acknowledgements

Figure 1.1:

Reprinted (adapted) with permission from (Eddaoudi, M., Kim, J., O'Keeffe, M., Yaghi, O.M. Cu₂[o-Br C₆H₃(CO₂)₂]₂(H₂O)₂·(DMF)₈(H₂O)₂: A Framework Deliberately Designed To Have the NbO Structure Type. *J. Am. Chem. Soc.* **2002**, *124*, 376-377.) Copyright (2002) American Chemical Society.

Figure 1.2:

Left image is reprinted (adapted) with permission from (Kaye, S.S., Dailly, A., Yaghi, O.M., Long, J.R. Impact of Preparation and Handling on the Hydrogen Storage Properties of Zn₄O(1,4-benzenedicarboxylate)₃ (MOF-5). *J. Am. Chem. Soc.* **2007**, *129*, 14176-14177.) Copyright (2007) American Chemical Society.

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CHAPTER 1

Background and Introduction

Catalytic reactions are omnipresent in our world: the chemical reactions in our body are catalyzed by enzymes [1], the toxic exhausts of our automobiles are converted to CO_2 , H_2O , and N_2 [2], and the many polymeric materials we use on a daily basis are polymerized by a variety of homogeneous and heterogeneous catalysts [3]. Indeed, it is estimated that almost 85% of chemical industrial processes utilize catalysts of some sort [4]. This need for catalysts gives rise to a search for new classes of compounds that can either 1) catalyze new reactions, or 2) catalyze old reactions with some sort of advantage. The utility of the former is obvious; the utility of the latter can be in the form of higher conversion, higher selectivity, lower material cost, or lower energy cost.

One class of compounds that has recently seen use in catalysis is metal-organic frameworks (MOFs). MOFs are hybrid organic-inorganic crystalline compounds that are composed of metal clusters connected by organic linker molecules [5] (Figure 1.1).

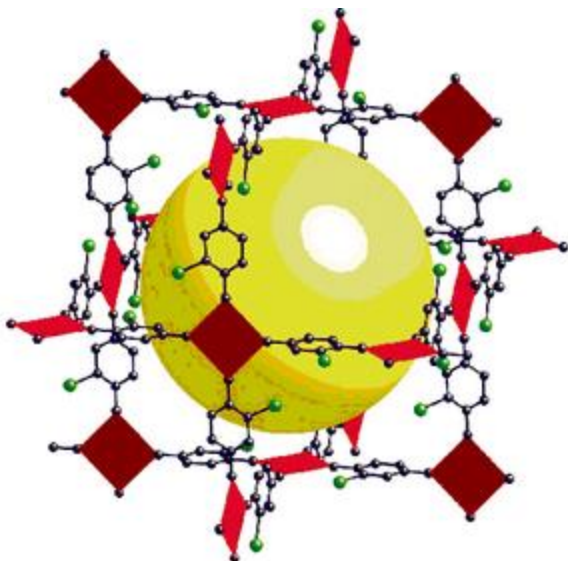


Figure 1.1: An example of a MOF (MOF-101); metal clusters (red squares) are connected to each other by organic linkers (black balls and lines).

The connected metal clusters form an array of cages, and these cages possess considerable void space. Because of this porosity, MOFs have been traditionally used to store gases such as H₂, CO₂, and CH₄ at atmospheric pressures [6]. This porosity is one reason why MOFs see use in catalysis, but there are other reasons that will be discussed later. MOFs have also been used for drug delivery [7,8] and gas separation [9].

MOFs have catalyzed numerous reactions in recent years: oxidations [10], photochemical oxidations [11], esterifications [12], carboxylations [13], and liquid-state hydrogenations [14]. Though there are many different reaction types that have been catalyzed with MOFs, these catalytic reactions fall into two general classes:

1. Use of the frameworks as hosts for other species that perform the catalysis
2. Use of the metal centers within the framework itself as catalytic centers

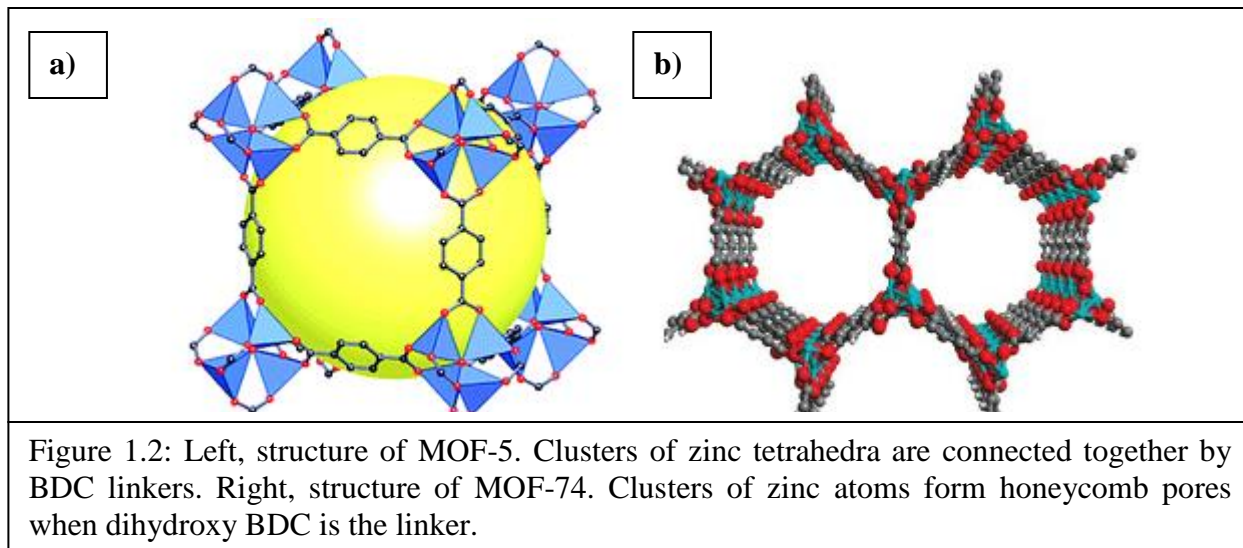
For example, the reaction that uses the impregnated Zr-MOF in ref. [11] falls into class 1. The authors doped the framework with iridium, ruthenium, and rhenium complexes. The main framework used in ref. [11] was found to be inactive, with the “dopants” being the catalytically active species. After the reactions, power x-ray diffraction patterns (PXRDs) were taken and the MOFs were found to be crystalline, i.e., they were still structurally intact. Other reactions utilize frameworks that do not have catalytically-active species trapped inside the pores. Rather, the framework’s metal centers catalyze the reaction. For example, the authors in [15] incorporate Mn-Salen bridging ligands with [Zn₄(μ₄-O)(O₂CR)₆] clusters into the frameworks to catalyze enantioselective epoxidation reactions. All reactions are reported to have relatively high conversions (60%-99%), while a smaller number of reactions have an enantiomeric excess (ee) of at least 60%.

There are a number of properties that make MOFs attractive for catalysis. They have some of the highest specific surface areas among all crystalline compounds [15] and possess highly tunable properties. The former is desirable, for higher surface areas result in higher catalytic activities. This is due to the availability of more catalytically-active sites to the reactants. In addition, the property of crystallinity allows one to determine the exact location of each moiety in the unit cell. The latter is useful in producing different MOFs with relatively small changes in the synthesis—one can synthesize new MOFs with the desired chemical and physical properties by altering the metal and/or the organic linkers. These altered properties can include:

- i. Pore size
- ii. Crystal structure, geometry, and topology
- iii. Coordination number of the metal center

For example, combining $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with benzene dicarboxylic acid (BDC) in N,N-dimethylformamide (DMF) produces MOF-5, which consists of corner-sharing zinc tetrahedra connected by the benzene dicarboxylate linker (Figure 1.2a). Alternatively, combining $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with dihydroxybenzene dicarboxylic acid (dihydroxy BDC) in DMF produces MOF-74. MOF-74 consists of zinc hexagons that form “honey comb” pores. The framework’s unit cell changes because of the inclusion of two hydroxyl groups on the linker, for the deprotonated hydroxyl groups interact with the metal centers in addition to the deprotonated carboxyl groups. The different structure is shown in Figure 1.2b. There are, however, instances in which a change in the linker produces a relatively small change in the framework, as in the case of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ combined with amino-BDC in DMF. In this case, the base structure of MOF-5 is retained, and the resultant MOF is called IRMOF-3. (IRMOF stands for “isoreticular MOF”; the term

isorecticular denotes that IRMOF-3 has an identical base structure to a parent MOF, in this case to MOF-5, except IRMOF-3 has amino groups off the edges of the framework.)



This thesis will cover the reaction engineering of MOF catalysts that are used in a relatively simple reaction, the hydrogenation of propylene to propane. There is a spectrum of MOFs used, and the base structure is that of MOF-5. Instead of using only BDC as the linker, these MOFs contain a mix of BDC and amino-BDC linkers. This is an instantiation of the so-called “MTV principle” (multivariate principle) [17] which states that MOFs can be made with multiple links, allowing the frameworks to contain multiple functional groups. In some cases, it is necessary to mix the links in a MOF, e.g., there has been no report of a MOF-5 analogue successfully synthesized with 100% nitro-BDC linker, but a mix of nitro-BDC and BDC produces a MOF-5 analogue. In other cases, the MTV principle is beneficial, as we will see with the MOFs that catalyze the hydrogenation of propylene. The amino groups of the amino-BDC are post-synthetically modified to form imines, and attached to these imines is the $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$ catalyst. Thus, higher ratios of amino-BDC result in higher amounts of catalyst attached to the framework, and this is termed isorecticular metalation or MOF metalation [18]. In

the rest of this thesis we will use the following abbreviation: the MOF with 20% amino-BDC and 80% regular BDC will be referred to as “MOF-20” and the MOF with 60% amino-BDC and 40% regular BDC will be referred to as “MOF-60.” This nomenclature helps to reduce the tedium of constantly referring to these MOFs by their official names: “MTV-Pd-MOF-AB.”

Most MOF catalysis studies describe the synthesis of the MOF used to catalyze a reaction (or class of reactions), run the reaction(s), and present porosity data. In contrast to this trend, this thesis will investigate the effects of isorecticular metalation (by varying the amount of amino-BDC incorporated into each framework), external reactor temperature, and reactant flow rate on catalytic activity. The effects of a carbon monoxide (CO) stream will also be studied, for CO is a poison/inhibitor to traditional palladium catalysts such as palladium on carbon (Pd/C). In addition, the effects of temperature will be studied in greater detail.

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CHAPTER 2

Reaction Engineering and Optimization of MOF Catalysts

Introduction

The overarching goal of reaction engineering is to optimize a chemical reaction by manipulating the relevant reaction conditions and parameters such as reactor design, catalyst used, the temperature of the reaction, and the pressure of the reaction. According to classical transition state theory, catalysts stabilize the transition state of a reaction, and this reduces E_a [1]. Different catalysts bind to the substrates in different manners to reduce E_a . The temperature of the reaction affects the kinetic energy of the reactants, and this determines whether or not the reactants can cross the activation energy barrier and initiate a reaction event. Thus, catalyst choice and temperature are two obvious ways of hastening a chemical reaction. Another method of improving the yield of a chemical reaction is reactor design [2-4]. Various reactor types can be used depending on a number of factors such as the delivery of the reactants to the reactor, e.g., stationary reactants versus pumped or flowed reactants. For this thesis, we will use a tubular packed bed reactor, for our reactants are gases that are being flowed through a reaction vessel packed with MOF catalyst. The flow rate through a packed bed affects the pressure drop that is observed across the reactor vessel. This pressure drop affects how the reactants interact with the catalyst bed that they are being flowed through [5]. Thus, reactant flow rate is also an important variable to consider. Since we are fixing the reactor variable to the packed bed reactor, we will examine three parameter spaces that affect our chemical reaction:

1. Catalyst choice (via isorecticular metalation)

2. Temperature
3. Reactant flow rate

Note that the emphasis will not be on the catalysts' ability to catalyze the hydrogenation of propylene—the optimization of this reaction has been studied in the past [6]. The relative optimization with respect to our MOF catalysts is the object of interest. Hence, we are performing reaction engineering with the MOF catalysts by altering the MOFs and the reaction conditions in the hydrogenation of propylene.

Experimental Details

General Setup and Data Analysis. A modular, copper packed-bed reactor is prepared with three parts: a coiled preheating element, the reactor vessel itself, and an outlet. The coiled preheating element provides a longer residence time for the gases in order to heat them to the external temperature. (Specifications of the heating element: 23 turns, 26.50 mm diameter for each turn, 88.85 mm long.) The external temperature is controlled using a Thermal Electric Corporation Lindberg/Blue M tube oven with a UT-150 temperature controller. The reactor vessel is stoppered on one end with a 1/8th inch diameter 316L stainless steel frit (McMaster-Carr Item 9446T38 machined to 1/8th inch by the Engineering Machine Shop) to allow gases to pass through but not catalyst particles. (Specifications of the reactor vessel: 57.04 mm long, inner diameter of 3.03 mm and outer diameter of 6.72 mm.) 30 mg of each catalyst is packed into the vessel, and a second 1/8th inch diameter stainless steel frit is put on top of the catalyst bed. The top frit is then stoppered with 25 mg of glass wool to prevent the frit from shifting its position while the reaction is run. The preheating element and outlet are attached to the reactor vessel by Swagelok connectors and the connectors are tightened to prevent leaks. The tube oven is

preheated to a temperature of interest, and after it reaches that temperature, the reactor is laid along the tube oven. The gas inlet and outlet are then connected to the reactor by Swagelok connectors. The two reactants, hydrogen and propylene, were bought from AirGas. Their regulators are set at 40 pounds per square inch (psi) and are controlled using Model 32907-59 Cole Parmer mass flow controllers. The control mode is volumetric flow.

The reactants are flowed from their sources to mix at a Swagelok T-joint, and this gas mixture is sent through the packed-bed reactor. After the reactants pass through the reactor vessel, they move through the outlet of the reactor into a 5 mm NMR tube that has been placed inside a vertical-bore Bruker 600 MHz Ultrashield NMR magnet. Before the reaction is run, a stream of pure propylene is flowed through the reactor to test for a suitable signal-to-noise ratio (SNR). Once this is done, the reaction is run at a flow rate of interest. ^1H -NMR spectra of the outlet gases are taken after each reaction reaches steady state. After each set of flow rates is run at a temperature of interest, the reactor is flushed with a stream of N_2 gas for 15 minutes. At that time, the tube oven temperature is changed to the next temperature of interest, and the process is repeated. The general schematic of the setup can be seen in Figure 2.1.

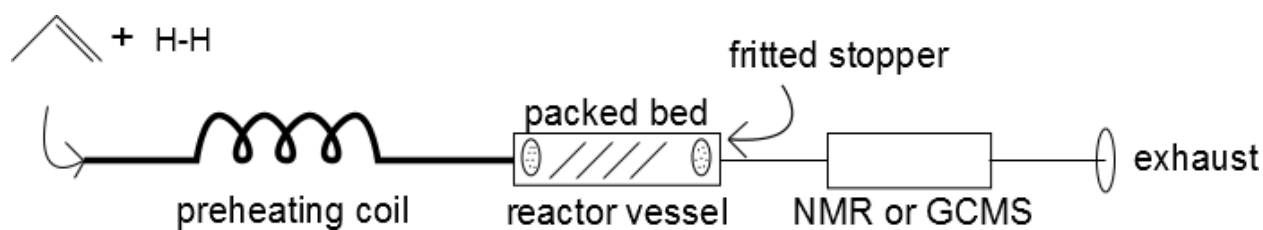


Figure 2.1: General setup of the reaction. The reactants are flowed through the coiled preheating element, pass through the packed bed in the reactor vessel, move through the outlet into the NMR or the GCMS, and are opened to an appropriate exhaust vent.

The catalytic conversions are calculated by integrating the peaks of the ^1H -NMR spectra. The area under the propane methyl resonance is compared to the area under the propylene methyl resonance. Since propane has two methyl groups, its peak area must be divided by two. The conversion is calculated using Equation 2.2:

$$\text{conversion} = \frac{(\text{area of propane resonance}/2)}{(\text{area of propane resonance}/2 + \text{area of propylene resonance})}$$

Equation 2.2

The areas are determined using the built-in integration feature of the NMR operating software, Topspin. The catalytic conversions determined through the NMR spectra are confirmed using gas chromatography/mass spectrometry (GCMS). The GCMS measurements are taken using an Agilent 6890N GC attached to a 5975 MSD in positive electron ionization mode. The column used is a GS-CarbonPlot column. The conversion is calculated in a similar manner to the NMR spectra-based conversion; the area under the peak for each chemical species is calculated using the built-in integration feature of the Agilent GCMS software. The conversion is given by Equation 2.3:

$$\text{conversion} = \frac{(\text{area of propane peak})}{(\text{area of propane peak} + \text{area of propylene peak})}$$

Equation 2.3

Examples of a gas chromatogram and an NMR spectrum containing both propylene and propane peaks can be found in Figures 2.2 and 2.3, respectively.

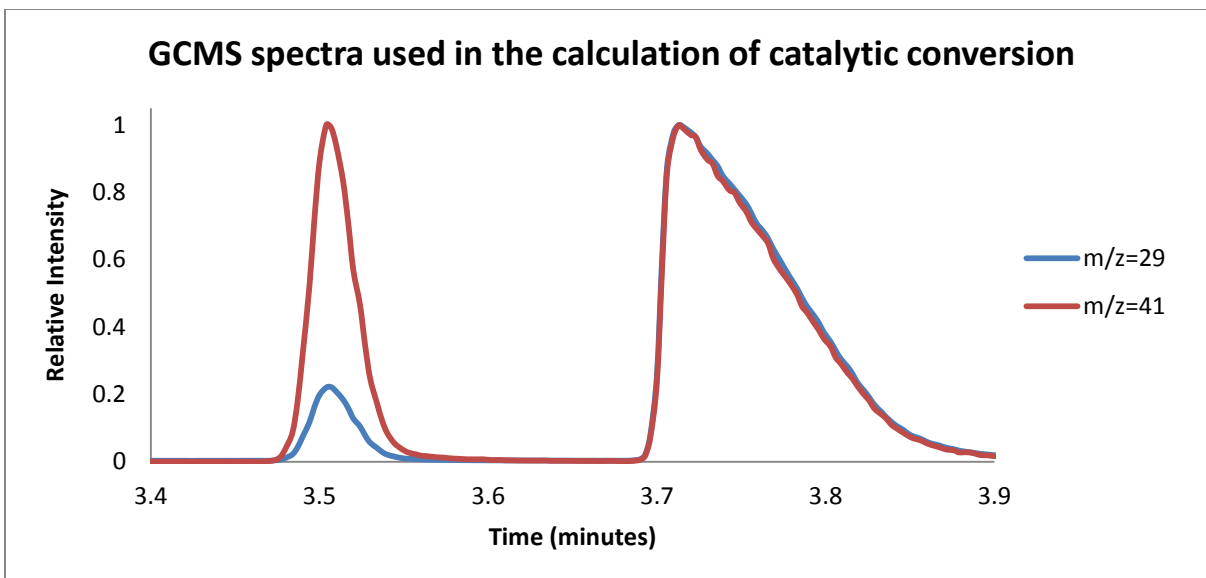


Figure 2.2: An example of the GCMS spectra used to calculate catalytic conversion. Since propylene and propane both share an m/z peak of 41, the molecular ion mode of the GCMS analysis is used to separate a unique m/z value for propane, $m/z=29$, from $m/z=41$. The propane peak from $m/z=29$ is compared to the propylene peak from $m/z=41$ for the conversions.

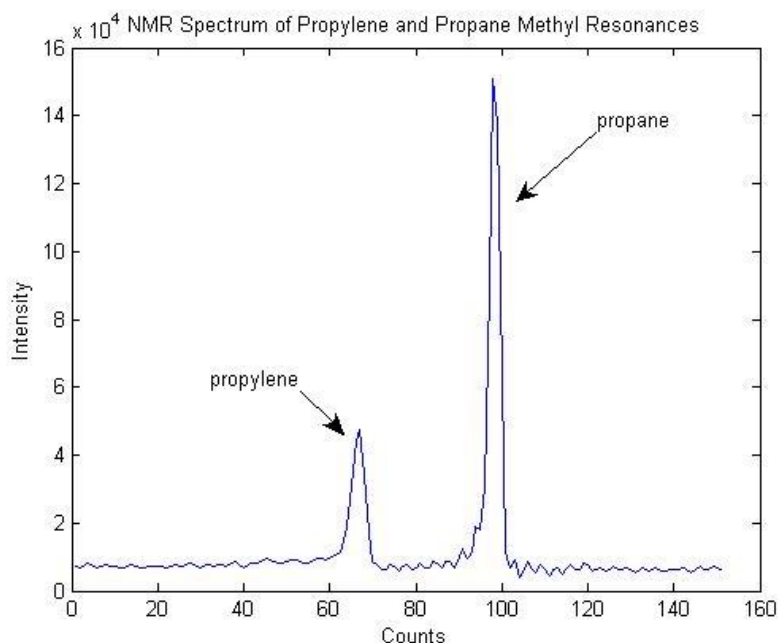


Figure 2.3: An example of the NMR spectra used to calculate catalytic conversion. The propylene methyl resonance is centered at around 70 counts and the propane methyl resonance is centered at around 100 counts. The area of the propane methyl resonance must be divided by two when comparing the areas since there are two chemically identical methyl groups in propane.

Propylene Flow Rate Testing. Before beginning the optimization of the MOF catalysts, the effect of propylene flow is investigated on the catalyst to determine whether or not both

reactant flow rates affect the outcome of the reaction. Uncertainty in flow rate is $\pm 0.8\%$. For these experiments, the tube oven is set to 100 °C and the MOF-40 is used. The reaction parameters are listed in Table 2.1.

Propylene Flow (ccm)	Hydrogen Flow (ccm)
2.5	10.0
5.0	20.0
7.5	30.0
	40.0
	50.0
	60.0
	70.0
	80.0
	90.0
	100.0

Table 2.1: Propylene flows paired with different hydrogen flows. This is a combinatorial table; each propylene flow rate on the left is paired with a hydrogen flow rate on the right. Thus, there is a total of 30 reactions.

Optimization of MOF Catalysts. For each isorecticular metalation (refer to Chapter 1 for the explanation of isorecticular metalation), an “optimization experiment” is performed to determine which temperatures and reactant flow rates deliver high catalytic conversions. Identical conditions are set up for each catalyst to also determine which isorecticular metalations deliver the highest catalytic conversion. The reaction parameters are listed in Table 2.2.

Metal Loading (%)	Temperature (°C)	Hydrogen Flow Rate (ccm)
20	30	10
40	50	20
60	100	30
80	150	40
100	200	50

Table 2.2: Different parameters used in the reaction engineering of propylene hydrogenation utilizing MOF Catalysts. Propylene flow is fixed at 5.0 ccm. Each MOF metalation on the left is combined with a temperature in the middle, which is then combined with a flow rate on the right. Each metal loading is considered to be one optimization experiment. Thus, there is a total of 125 reactions.

Results and Discussion

Propylene Flow Rate Testing. With each propylene flow rate, it is observed that increased hydrogen flow results in higher catalytic conversion. With a low propylene flow rate (5 ccm), the conversion reaches ~100% starting at 50 ccm hydrogen, whereas for higher propylene flow rates, it reaches ~100% at higher hydrogen flow rates. At low flow rates, catalytic conversion scales directly with the propylene:hydrogen ratio, e.g., 5 ccm propylene:20 ccm hydrogen yields the same almost the conversion as 10 ccm propylene:40 ccm hydrogen. Thus, though the total flow rate changes, the relative flow rate remains the same and results in close to the same conversion. This justifies the use of a single propylene flow rate for the optimization experiments performed on each MOF catalyst if the hydrogen flows are kept low. This scaling breaks down when increasing propylene flow. There are slight differences between the same ratios for 7.5 ccm propylene and 10 ccm propylene. This could be due to the saturation of the active sites on the catalyst, or to the shorter residence time of the reactants on the catalyst bed.

(Higher reactant flow rates result in the reactants passing through the catalyst more quickly, lowering the chances of forming the transition state, and in turn, the product.) The data for the propylene flow testing can be found in Figure 2.4, and one can see the differences in conversion for higher propylene flow rates in Figure 2.5. Horizontal error bars were obtained from the uncertainty in flow rate (reported by Cole Parmer) and vertical error bars were obtained from uncertainty in flow rate, standard error of three readings of conversion ($n=3$), and standard error in differences in peak integration ($n=3$).

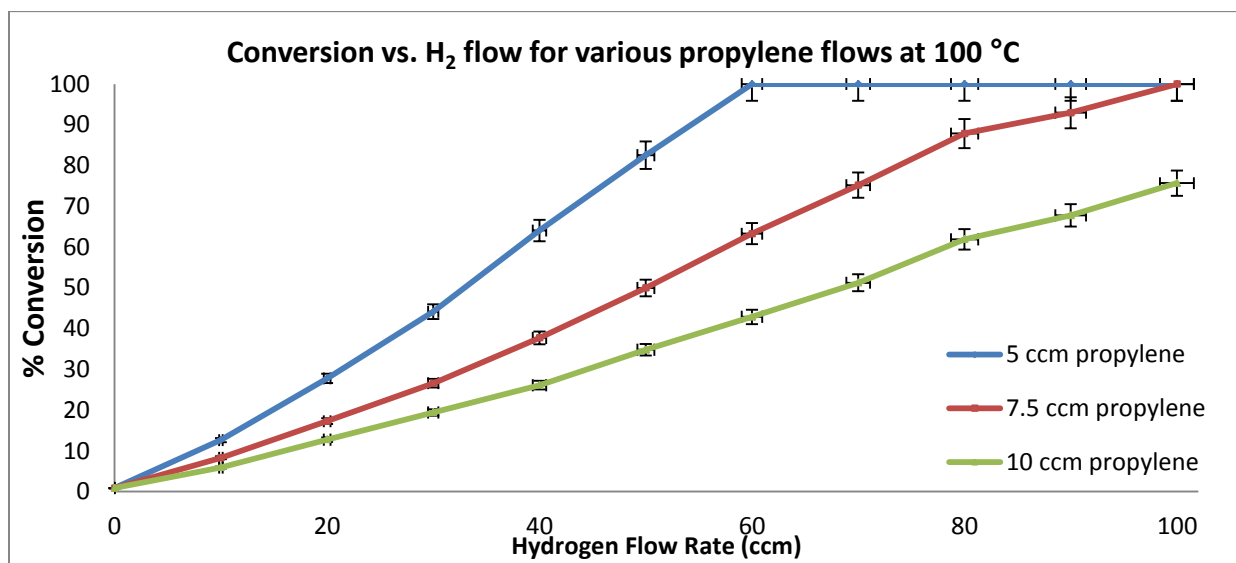


Figure 2.4: Propylene flow rate data for MOF-40. The 5 ccm propylene flow reaches 100% conversion at 50 ccm H₂, while the higher propylene flows do not reach 100% at 50 ccm H₂.

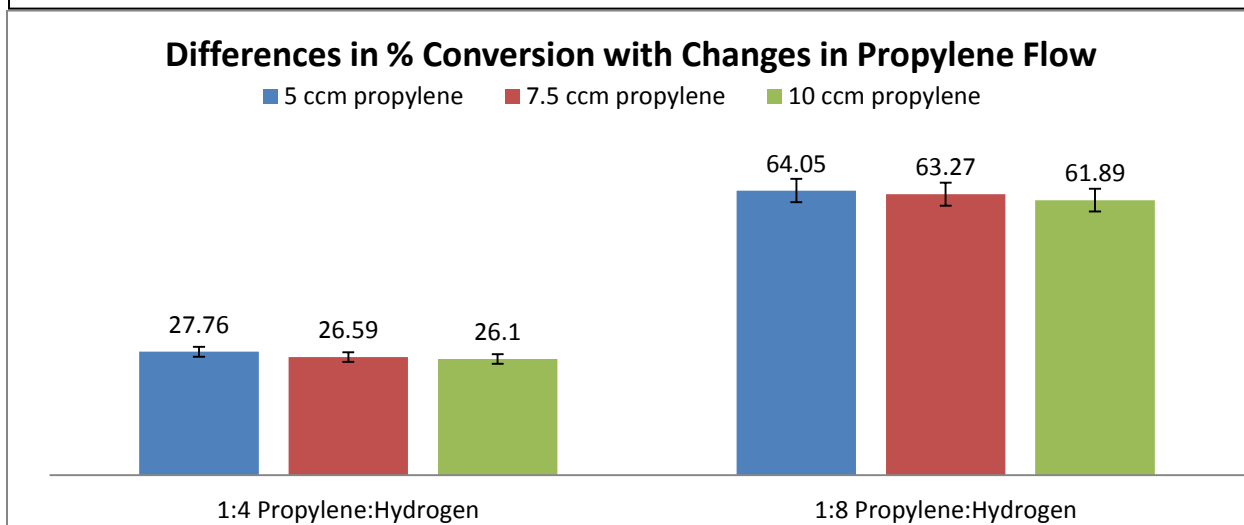


Figure 2.5: Differences in conversion at propylene:hydrogen ratios of 1:8 and 1:4. At higher propylene flows, the difference in conversion increases. At higher propylene flows (and thus total flows), conversion doesn't scale perfectly with flow ratio and decreases slightly.

Optimization of MOF Catalysts. At all temperatures and MOF metalations, higher hydrogen flow rates result in higher catalytic conversions. This trend can be seen in Figure 2.6. Error bars were obtained from the uncertainty in flow rate, standard error of three readings of conversion ($n=3$), and standard error in differences in peak integration ($n=3$).

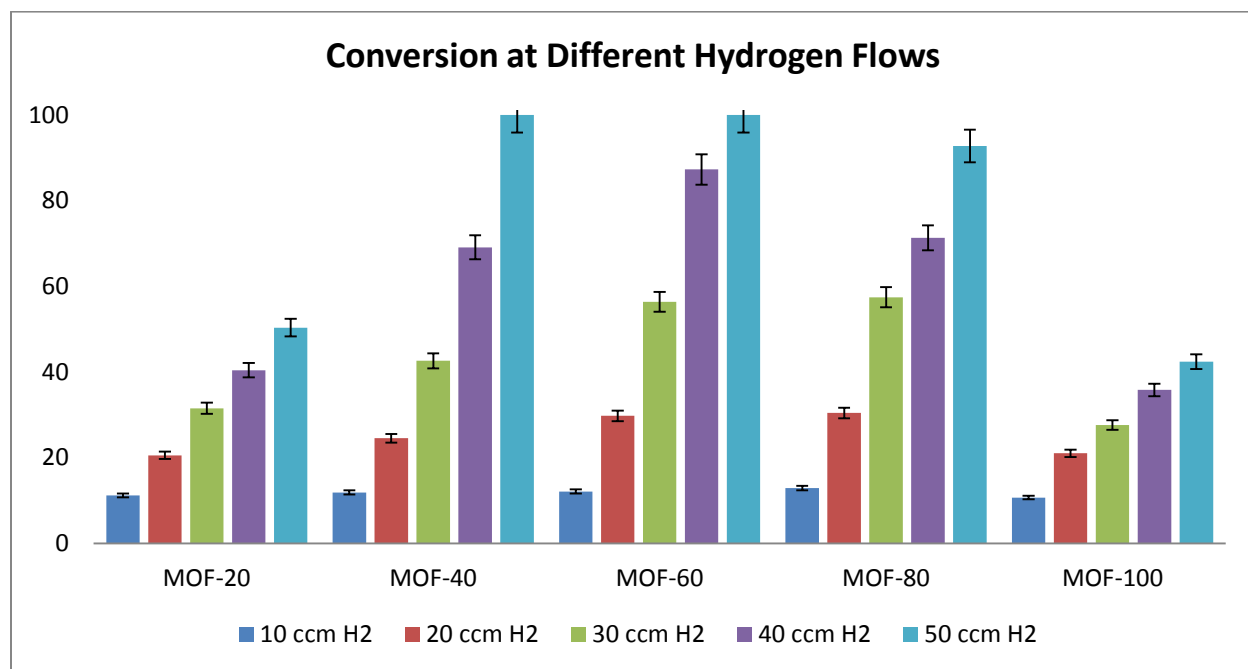


Figure 2.6: For all MOF metalations, higher hydrogen flow yields higher conversion when propylene flow is fixed at 5 ccm. This is expected, since an excess of the non-transformed reagent increases the chance of the transforming reagent to react, increasing % conversion.

This is an intuitive result: an excess of the non-transformed reagent increases the likelihood of the reaction taking place. When recasting the figure in the form of a scatter plot in Figure 2.7, the hydrogen flow dependence takes on certain forms. The dependence on hydrogen flow appears to be linear for some of the MOFs (MOF-20), but it appears to be curved or exponential for other MOFs (MOF-60). The MOFs that show lower catalytic conversions could have linear forms because of their poor abilities to scale with hydrogen flow, having either not enough palladium

catalyst or too little surface area. The MOFs that show higher catalytic conversions presumably have the right balance between palladium catalysts present and surface area in order to scale exponentially well with hydrogen flow. The MOF-80 appears to be different, but the middle point at 30 ccm hydrogen is likely an outlier. If the conversion at that point were slightly lower, the trend would appear linear as well.

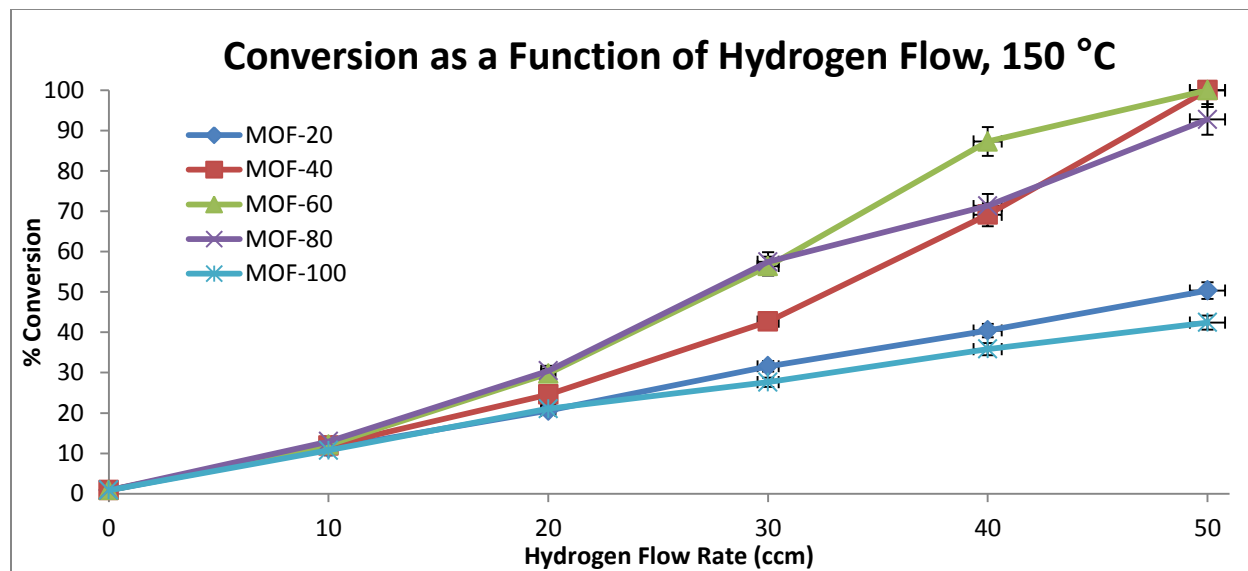


Figure 2.7: The same data portrayed in Figure 2.6 is recast into a scatter plot. The MOF profiles that appear linear scale poorly with hydrogen flow, while the MOF profiles that appear exponential scale well with hydrogen flow.

Regarding the effect of temperature, higher temperatures result in higher catalytic conversions in all MOFs, but there is a limit to this improvement. From 30 °C to 150 °C, a higher temperature improves the conversion of the reaction. An increase in temperature should result in a faster rate of reaction because the higher temperature should impart enough kinetic energy to the reactants to allow them to collide and react. Increasing the temperature to 200 °C, however, results in lower conversion. There are two possible reasons for this:

1. Higher temperatures result in the breakdown of the catalyst, rendering it inactive
2. Higher temperatures decrease the residence time of the reactants inside the framework

The former case is unlikely, since powder x-ray diffraction patterns (PXRDs) taken after the reaction show that the MOFs retain their crystallinity; Figure 2.7 shows the MOF-40 retaining its diffraction pattern after running the reaction at 200 °C.

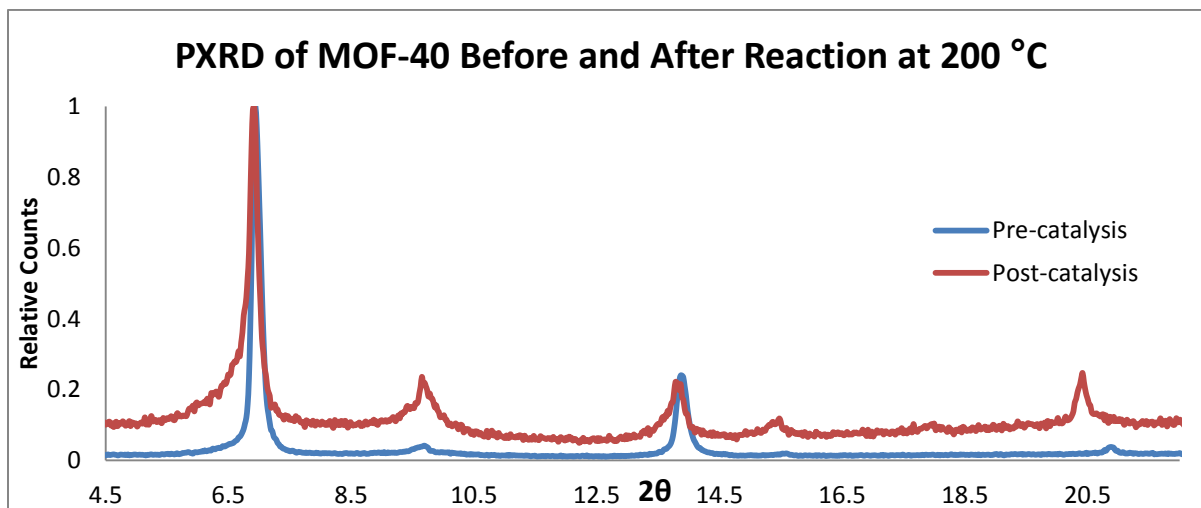


Figure 2.7: PXRDs before and after running the reaction at 200 °C show that the MOF retains its crystallinity and structural integrity. Though the positions of the peaks are shifted slightly, there is no loss or gain of peaks.

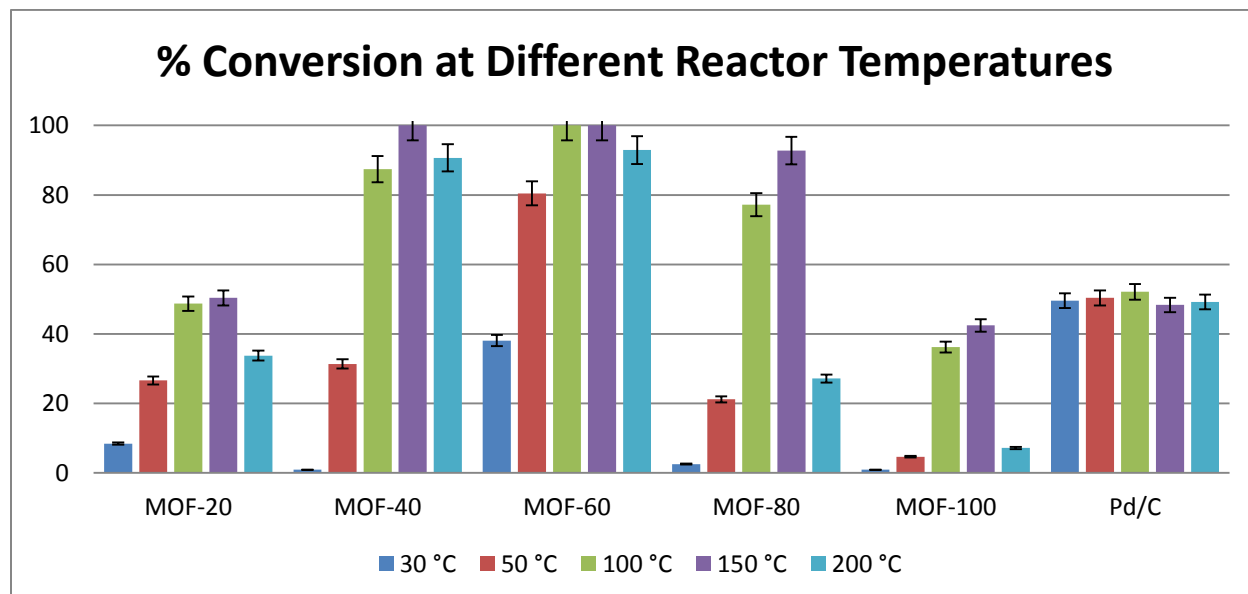


Figure 2.8: For all MOFs, increased temperatures up to 150 °C yield higher conversions. Past 150 °C, however, conversion is decreased. This is probably due to the decreased residence time of the gases inside the pores of the framework. Pd/C, on the other hand, shows temperature independence. Propylene:hydrogen is 5 ccm:50 ccm.

The second case is more likely, for lower residence times of the reactants inside the framework should result in lower conversions. Even though the residence time is long in at a temperature of 30 °C, there is not enough kinetic energy imparted to the reactants for a reaction event to take place. When performing the same test on palladium on carbon (Pd/C), this effect is not observed—catalytic activity is independent of temperature, as shown in Figure 2.8. This could be ascribed to the fact that Pd/C is not an ordered material with regards to its pore geometry/arrangement or its smaller pores; the mean free path of the gases could be the same at all temperatures. Figure 2.8 also shows the effect of temperature on catalytic conversion for each MOF. All MOFs show an increase in catalytic activity up to 150 °C and a drop in activity at 200 °C. Error bars were obtained by uncertainty in the tube oven reading (measured by comparing it at various temperatures to a thermocouple), standard error of three readings of conversion (n=3), and standard error in differences in peak integration (n=3).

The variation in metal loading is the most interesting, for it shows that the MTV principle can enhance catalytic activity. By controlling the metalation of these MOFs, one simultaneously controls two important properties:

1. Amount of palladium catalyst present on the framework
2. Porosity/surface area of the framework

At first thought, a larger amount of palladium catalyst on the framework should result in higher catalytic activity, suggesting that the MOF-100 is the best catalyst. This is, however, not the case. N₂ isotherms from Morris, et. al. [7] show that the presence of palladium catalyst on the framework crowds the framework pores, and this results in a lower surface area. Since good catalytic performance depends on a high surface area, this effect predictably results in a lower catalytic activity. Thus, the isorecticular metalations that yield the highest conversions strike a

balance between catalyst number and porosity. This is why the MOF-60 has the highest catalytic activity (~100%) at the optimal hydrogen flow rate (50 ccm) and optimal temperatures (100 °C and 150 °C). The MTV principle is validated for enhancement of catalysis, since the use of mixed links yields the highest catalytic activity. Figure 2.10 shows the effect of isorecticular metalation on catalytic conversion; it is apparent that the MOF-60 is the best catalyst across all temperatures. Error bars were obtained by uncertainty in flow rate, standard error of three readings of conversion (n=3), and standard error in differences in peak integration (n=3).

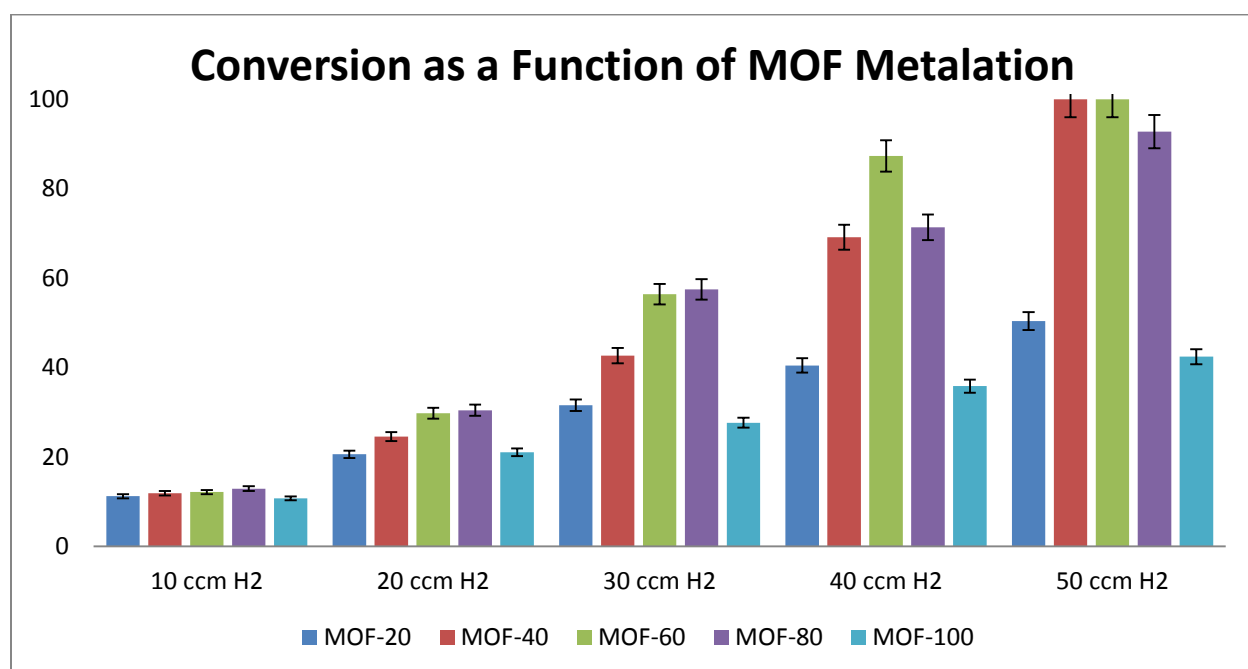


Figure 2.10: At all temperatures, the MOF-60 has the highest catalytic activity compared to the other MOFs because it balances isorecticular metalation with framework porosity. The MOF-40 and MOF-80 are the next best catalysts for the same reason. The propylene:hydrogen ratio is 5 ccm:50.

Conclusions

Determining that a fixed propylene flow rate is plausible given the results of the propylene flow testing, optimization of each MOF catalyst is done by cycling through various reaction parameters. The conditions specific to each MOF metalation are temperature and

hydrogen flow rate. The optimum temperature across all MOF metalations is found to be 150 °C, and the optimum hydrogen flow rate is found to be 50 ccm (the highest flow rate tested). The best MOF catalyst for the hydrogenation of propylene is the MOF-60 catalyst, for it balances the number of palladium catalysts on the framework and framework porosity. These results confirm that the MTV principle can be used to enhance catalytic activity with MOFs that incorporate catalytically-active species into the framework [7].

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CHAPTER 3

Poisoning/Inhibition of MOF Catalysts with Carbon Monoxide

Introduction

Reaction engineering seeks to improve the yield of a catalytic reaction. There are, however, reasons to limit the activity or investigate the inhibition of a catalyst. These reasons can include:

1. Altering the reaction products
2. Turning the catalyst's activity off
3. Knowing the limits of a catalyst when affected by external agents

The utility of the first point has been seen in the past. For example, when hydrogenating alkynes (e.g., 2-butyne), a conventional palladium catalyst such as Pd/C reduces the alkyne to the alkane. If instead one wishes to reduce the alkyne to a *cis* alkene, the palladium must be treated with lead compounds such as plumbous oxide (PbO). The catalysis community terms this "poisoning" because the active sites of the palladium catalyst are deactivated by the lead compounds. A quick note on definitions: poisoning refers to the permanent deactivation of a catalyst, while inhibition refers to the temporary deactivation of a catalyst. The literature often uses the former term for all cases of decreased catalytic activity, and as a result, I will use the term "poisoning" from now on to refer to a decrease in catalytic activity. These catalysts are called Lindlar catalysts, which were developed by Herbert Lindlar to partially reduce acetylenes [1]. The utility of the second point includes reversibly switching a catalyst on and off in a multistep reaction or achieving spatial/temporal control of reaction products.

With regards to the third point, the literature discusses the use of carbon monoxide as a poison for conventional palladium catalysts. Burrows and Stockmeyer discuss CO's effects on such a conventional catalyst in the reaction of molecular hydrogen and oxygen [2]. Some points of interest include:

- i. Minimal amounts of CO result in a great loss of catalytic activity.
- ii. The effects of CO poisoning decrease with temperature.
- iii. When passing H₂ gas through the CO + catalyst system, catalytic activity is not regained. However, when passing O₂ gas through the system, the CO is “unseated” from the surface of the catalyst, and activity is regained.

Instead of CO flow rates, they report CO concentrations and pressures that correspond to how many layers of CO are used to cover the surface of the catalyst. Their reaction vessel was made of quartz, and they introduced CO to the system for a period of 3 hours. The reaction was carried out at room temperature.

It would be useful to determine the effects of CO poisoning on our MOF catalysts, for the presence of CO in reactor vessels and reactant lines lowers the catalytic conversion of a number of reactions, e.g., the reactions of a catalytic converter in an automobile. Though the reactions involved in the operation of a catalytic converter are not the same as our reaction, various Pd-based catalysts suffer from CO poisoning, and this prevents the relevant reactions from achieving a high yield. There have been attempts to develop poison-resistant catalysts for catalytic converters to control hydrocarbon, nitrogen oxide, and CO exhausts [3].

Somorjai and coworkers have suggested that CO not only blocks catalytically active sites on Pd catalysts, but forms “perfect structures” that restrict the mobility of reactant atoms [4]. Somorjai also confirms that increased temperatures ameliorate the extent of poisoning in

conventional Pt-based catalysts (which are similar to conventional Pd-based catalysts). Hence, it would be not only practical, but interesting, to determine if MOF catalysts also exhibit the same behavior when poisoned with CO.

In this section, the MOF-60 catalyst will be poisoned with various CO flow rates and external temperatures. In addition to poisoning, the response to the removal of CO will be investigated to determine the time scale of recovery and whether or not external agents are needed to remove CO from the active sites. The same experiments will be performed on Pd/C for comparison.

Experimental Details

General Setup and Data Analysis. The general setup for the poisoning and recovery experiments is virtually identical to the catalyst optimization setup in Chapter 2, but there are key differences:

- i. CO flow is controlled by a Cole Parmer mass flow controller, and the hydrogen flow is controlled by a Key Instrumentals analogue rotameter.
- ii. NMR spectra are taken continuously, with one spectrum corresponding to one second in real time.

CO and propylene are premixed in one Swagelok T-joint, and this mixture is combined with hydrogen at a second T-joint. The first change is done to allow all three gases to premix at the second Swagelok T-joint before being flowed to the reactor. The second change is done to monitor the progress of the poisoning and recovery in real time. (The time scales of poisoning and recovery, as we will see, are quite fast and must be temporally resolved.)

Catalytic conversions are analyzed in a similar manner to the catalyst optimizations, but continuous monitoring of the reaction produces hundreds of NMR spectra that cannot be manually integrated through Topspin, the NMR operation and analysis software developed by Bruker Inc. Instead, the free induction decays (FIDs) are Fourier transformed and the resulting spectra are fit to Lorentzians. These Lorentzians are integrated numerically using the trapezoidal method. The final result is an array of conversions versus time. All of this is done through a MATLAB script.

Poisoning Experiments. MOF-60 and Pd/C are packed into the reactor vessel in an identical manner to the optimization experiments. The propylene and hydrogen flows are fixed at 2 ccm and 50 ccm, respectively. The carbon monoxide flows and temperatures are listed in Table 3.1:

Temperature (°C)	CO Flow Rate (ccm)
100	0.5
150	1.0
	2.0

Table 3.1: Experimental conditions for the poisoning and recovery experiments. This is a combinatorial table. Each temperature on the left is paired with a flow rate on the right, totaling in 6 poisoning experiments and 6 recovery experiments for each catalyst.

The NMR spectra are collected once the set point of the CO flow is input into the mass flow controller. The acquisition of spectra is halted once a large drop in catalytic activity is observed.

Recovery Experiments. At the end of each poisoning experiment, the set point of the CO flow is set to 0 ccm. NMR spectra are continuously collected to observe the recovery of catalytic activity. Spectra acquisition is halted once a large gain in catalytic activity is observed.

Results and Discussion

It is important to note that there is a slight delay between turning on the CO flow and observing its effects through the NMR. This delay depends on the CO flow rate, the temperature of the reactor, and the catalyst inside the reactor. The effect of CO poisoning (and recovery) doesn't begin until this delay time passes. Since CO adsorbs to the framework readily, it can be assumed that the delay is on the order of the onset of poisoning and recovery for each experiment.

In both the MOF-60 and Pd/C, the time scale of poisoning and recovery is very fast, and the extent of poisoning appears to depend on CO flow rate. For example, in the MOF-60, 0.5 ccm CO drops activity to around 20% conversion, whereas 2.0 ccm CO drops activity to around 8% conversion (Figure 3.1). The flat regime at the beginning of each curve corresponds to the “normal” reaction without the presence of CO. The delay in the drop in activity is due to the delay between turning on the CO flow and the travel time of the reaction output to the NMR.

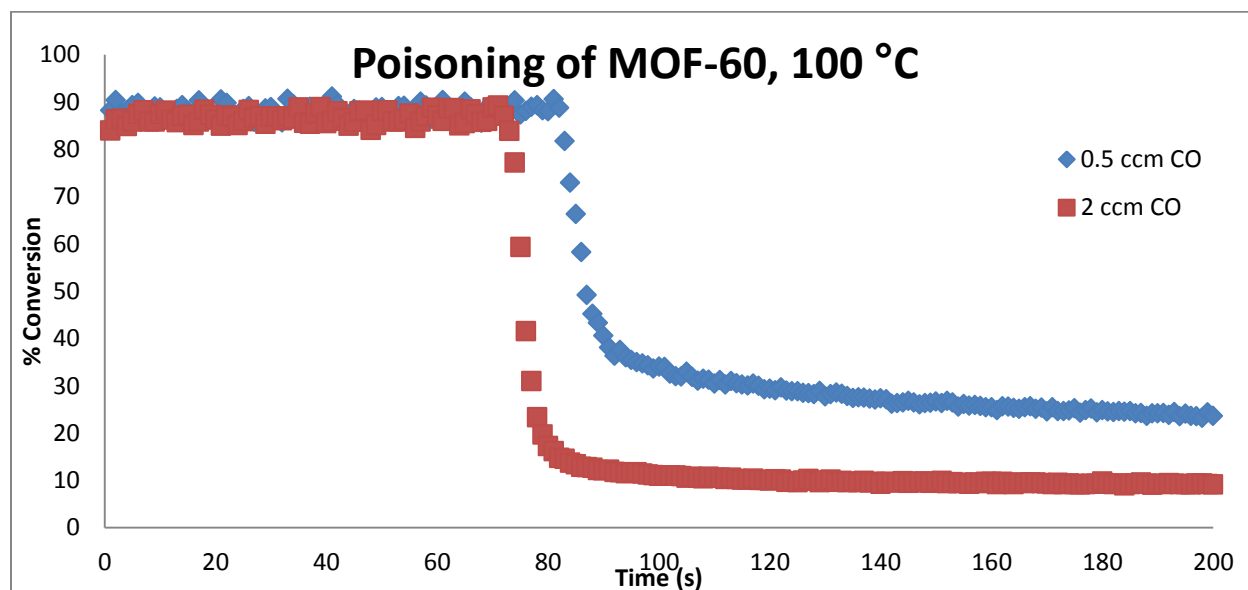


Figure 3.1: Poisoning of the MOF-60 at 1 ccm CO/100 °C with 2 ccm propylene:50 ccm hydrogen. After about 135 seconds of high conversion near 85%, the effects of CO are observed when the conversion plummets to around 12%.

As for the dependence on temperature, it is clear that higher temperatures mitigate the effects of the poisoning in all experiments. This trend is seen across all experiments. For example, with the MOF-60, poisoning at 100 °C under 1 ccm CO drops the conversion to around 11%, whereas the same experiment at 150 °C drops the conversion to around 30% (Figure 3.2). From these results, it seems that the results of Burrows and Stockmeyer hold for our MOF catalysts. More specifically, we now know that:

1. Small amounts of CO greatly decrease catalytic activity
2. Higher temperatures result in a smaller drop in catalytic activity

One interesting point is that some MOFs appear to slightly recover after the initial poisoning while still under CO flow. This can be seen in the MOF-60 at 150 °C and 1 ccm CO (Figure 3.3). After an initial drop to 29% conversion, the catalyst recovers to around 32% conversion. The exact reason for this is unclear, but almost all cases of this slight recovery occur at 150 °C.

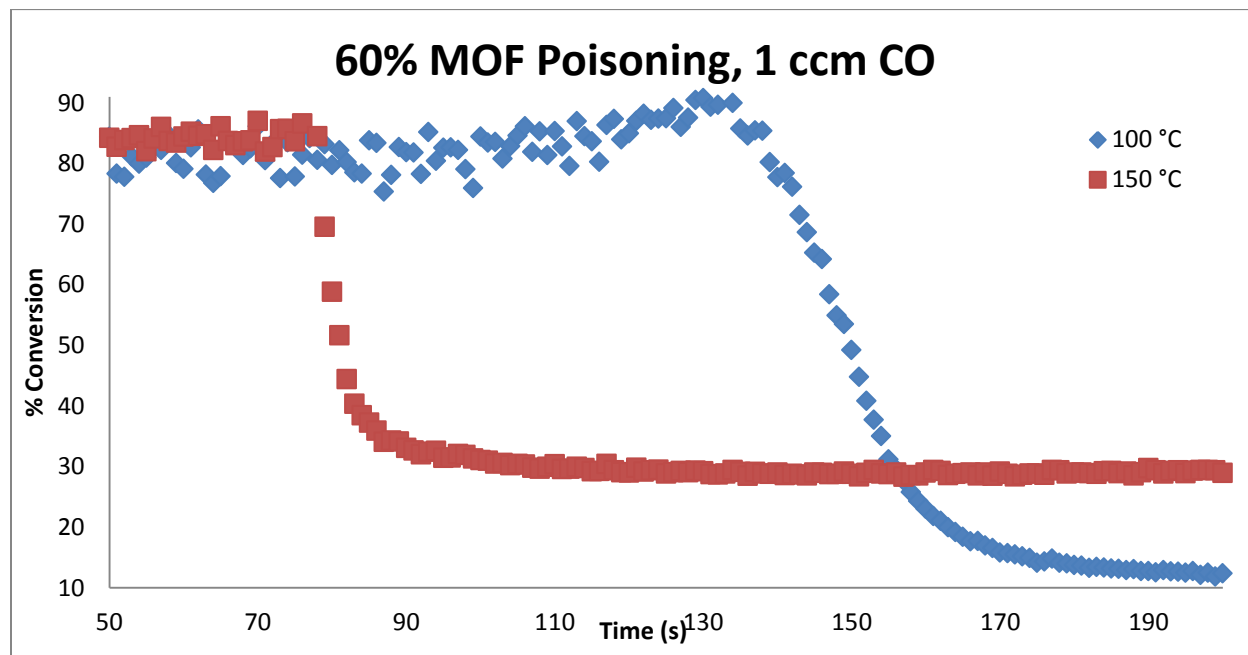


Figure 3.2: Poisoning of the MOF-60 at 100 °C (blue) and 150 °C (red). It can be seen that the MOF retains higher activity when poisoned at a higher temperature. In addition, the higher temperature produces a faster onset of poisoning.

Perhaps the higher temperature imparts enough energy to the adsorbed CO to break away from the surface of the MOF, allowing the reactants to occupy the active sites. Perhaps waiting longer would result in more significant gains in catalytic activity. This suggests that our MOF catalysts may be viable in catalytic converters as poison-resistant catalysts.

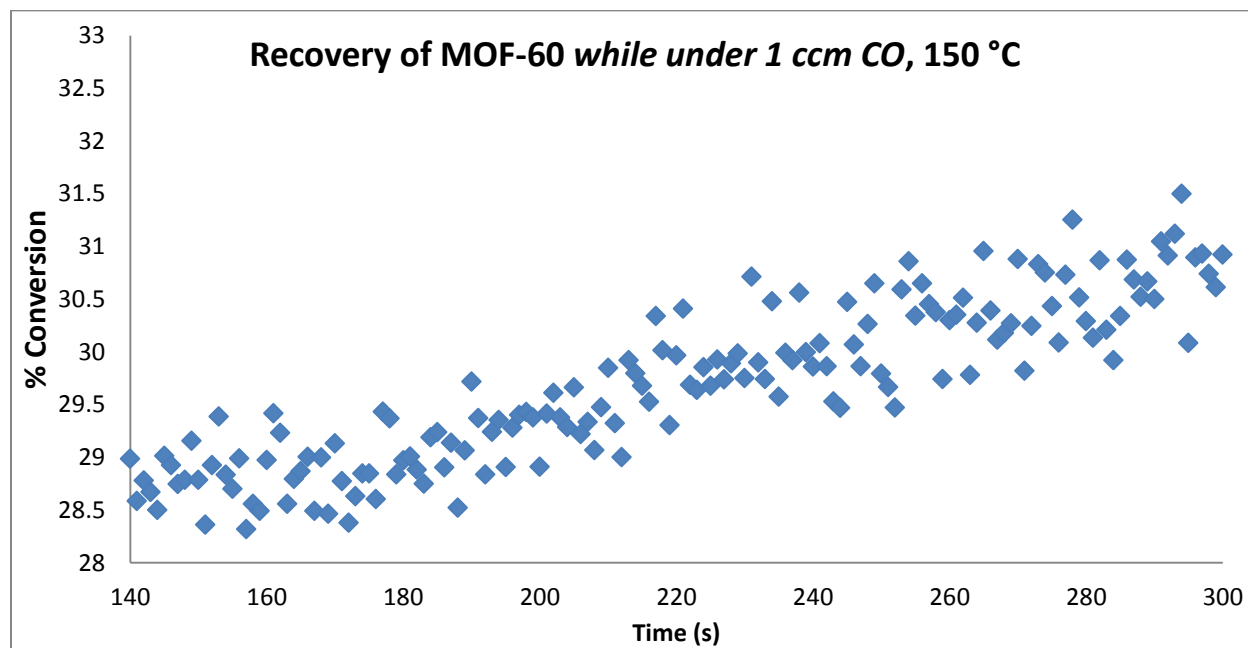


Figure 3.3: There is a slight recovery observed in the MOF-60 after it is initially exposed to CO and *while it is still under CO flow*. Over the course of 160 seconds, the MOF recovers around 3% of its catalytic activity. This effect is mostly seen at 150 °C.

Regarding the recoveries upon removal of CO, both catalysts quickly recover to (approximately) their original conversions on roughly the same time scale. (Recovery appears to be slightly slower than poisoning, taking around 8-10 seconds longer.) This is the case at all CO flow rates and both temperatures. For example, in Figure 3.4, one can see that at 1 ccm CO flow and 150 °C, the poisoning and recovery curves for the MOF-60 look almost identical, except they are reversed.

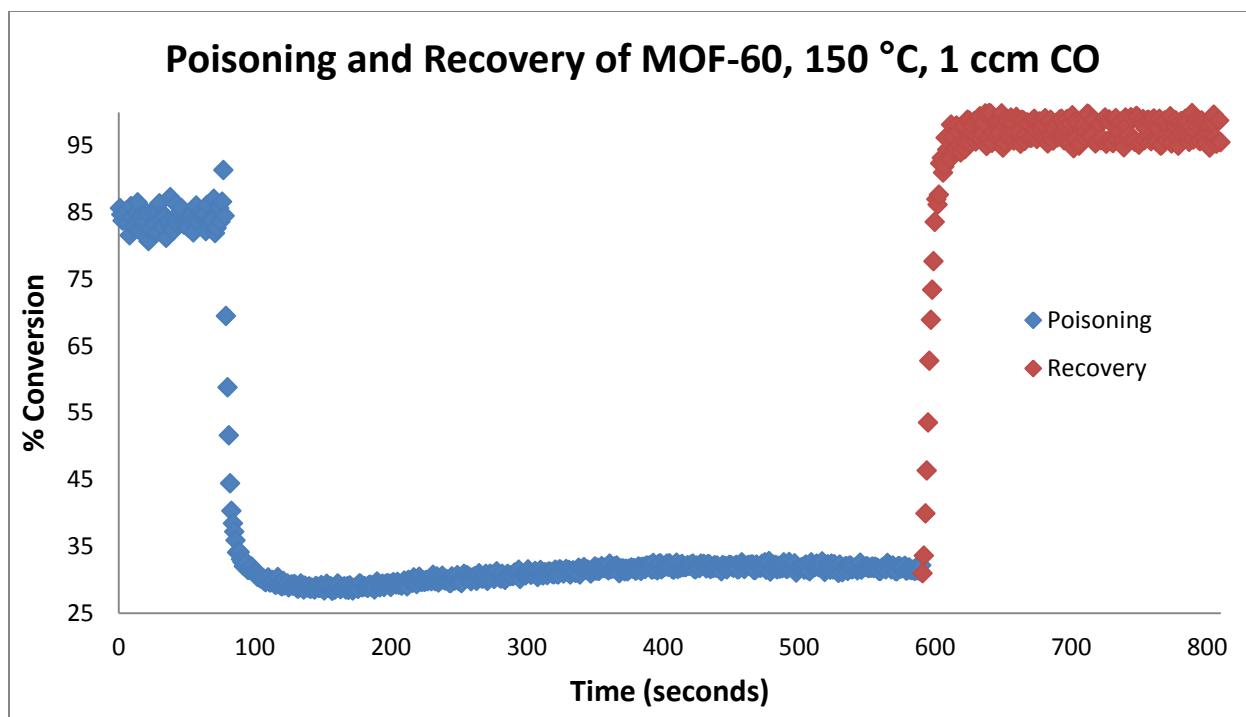


Figure 3.4: Poisoning (blue) and recovery (red) of MOF-60. The two processes are almost identical, except they are reverses of each other. The higher conversion at the end of the recovery curve can be ascribed to the integration of noise in the spectra at the site of the propylene resonance.

One difference observed between the MOF-60 and Pd/C is that Pd/C recovers significantly more quickly when the CO flow is turned off. This does not necessarily refer to the time scale of recovery when it begins; rather, it refers to the time when the recovery begins. For example, in Figure 3.5, one can see that at 2 ccm CO and 150 °C, the MOF-60 begins recovery around 72 seconds, whereas Pd/C begins recovery around 25 seconds. This delay for the onset of recovery could be due to the MOF's affinity for gases: MOFs adsorb gases very well, and compared to Pd/C, they bind CO more tightly. This results in the generally slower onsets of recovery.

Regarding the effect of temperature, higher temperatures hasten the time scale of recovery. This can also be seen in Figure 3.5, in which the MOF-60 recovers more quickly at 1 ccm CO/150 °C compared to 1 ccm CO/100 °C. Another key difference is that while Pd/C recovers more quickly

under the same conditions as the MOF-60, the MOF-60 retains more catalytic activity than Pd/C at 100 °C.

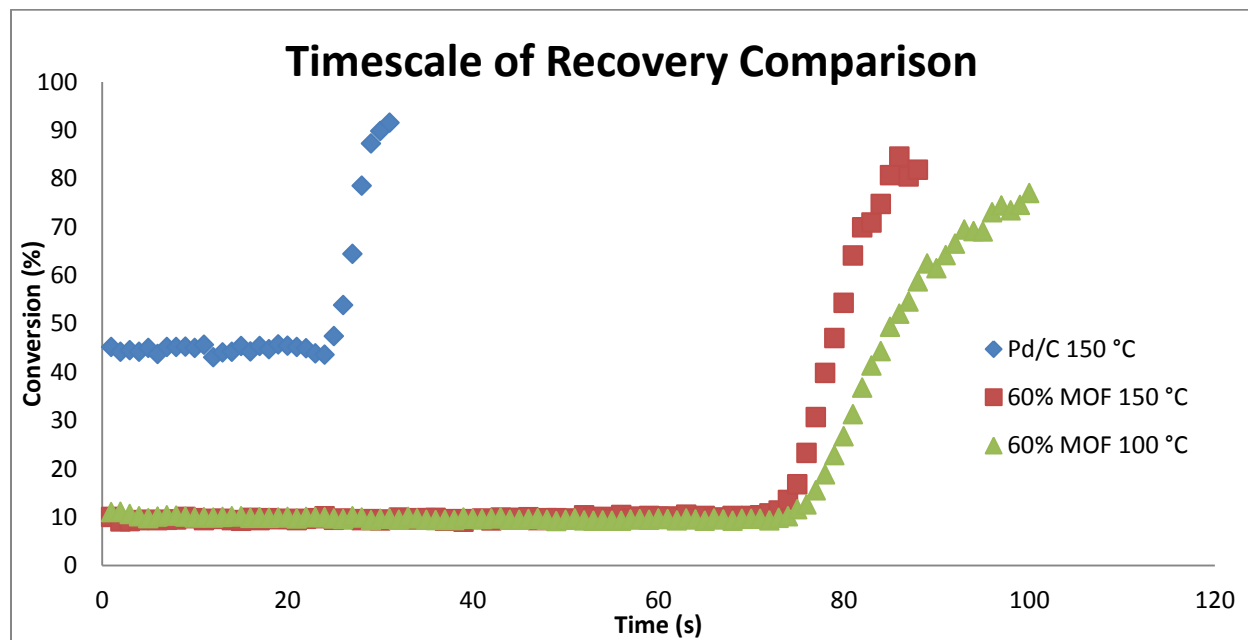


Figure 3.5: Comparison of recovery timescale between Pd/C and MOF-60. One can see that the Pd/C's onset of recovery is much earlier than that of the MOF. This is probably due to the framework's affinity for gases inside its pores—it takes more time for CO to leave the pores of the MOF. One can also see that higher temperatures hasten the recovery process. This is due to the higher kinetic energy of the CO inside the framework. Note that the onset of recovery doesn't change; rather, it is the timescale of recovery that changes.

This could be due to the fact that a MOF is crystalline: CO could adsorb to specific sites on the framework where the palladium has been attached, whereas CO could be adsorbed to random sites on Pd/C. If these random sites happened to be clustered together on the Pd/C, then a large number of reactants would remain unreacted. This trend does not hold at 150 °C, however; at all CO flow rates, Pd/C retains higher catalytic activity after poisoning. The higher temperature may mitigate the aforementioned effect.

There is one discrepancy between our results and the results of Burrows and Stockmeyer. Whereas Burrows and Stockmeyer observed that passing a stream of H₂ did not result in recovery of catalytic activity, we observe that both our MOF catalysts and Pd/C recover after a delay

when CO is removed (Figure 3.5); there is no extra treatment needed. Since there is no need to pass oxygen through the reactor (as Burrows and Stockmeyer did) with our MOF catalysts, poisoning on a large/industrial scale would not be a serious problem, especially if CO eventually dissipates or can somehow be eliminated through an auxiliary reaction.

If one attempts to fit the poisoning event to exponentials, another difference can be found between the MOF-60 catalyst and Pd/C. Using MATLAB, the MOF-60 is fit to a double exponential, while Pd/C is fit to a single exponential. Regarding the physical nature of the CO poisoning of MOF catalysts, a biphasic adsorption model is the most appropriate description; Fletcher and coworkers develop these model, as applied to MOFs, in [5]. The biphasic model states that the adsorbed species first forms a “surface transient state” with the adsorbant, and then forms a “stable chemisorbed” species with the adsorbant. These two processes occur on different timescales. In the MOF-60, the two timescales could correspond to the entry of the CO through the pore apertures of the framework and the diffusion of the CO once inside the pore. This model applies to crystalline materials in general, for similar work was done with Zn(0001) surface [6]. A fit of the Pd/C poisoning profile yields a single exponential, indicating that there is only one process occurring. The single process is most likely the random diffusion of CO. Recall that Somorjai and coworkers have suggested that the presence of carbon monoxide not only covers up catalytically active sites on catalysts, but that the formation of “perfect structures” with adsorbed CO restricts the mobility of reactant atoms to actually react [7]; this would likely correspond to the “stable chemisorbed” state of the framework some time after the exposure to CO. More experimental work would need to be done in order to ascertain the factors responsible for the two processes (MOF) versus the single process (Pd/C). These fits can be found in Figure 3.7.

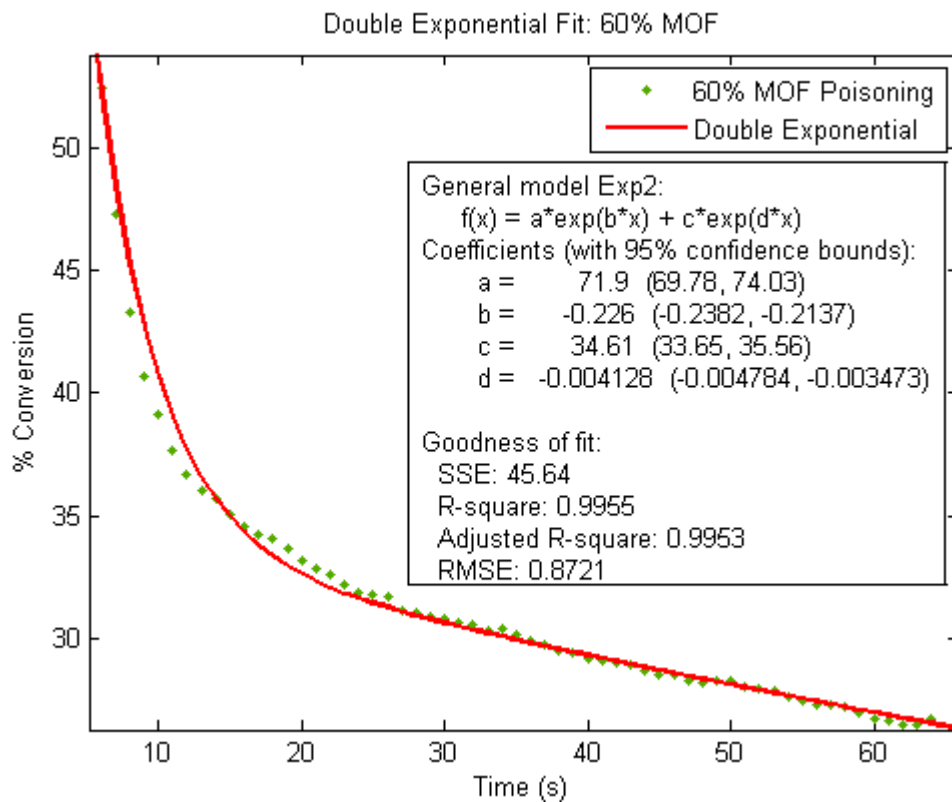
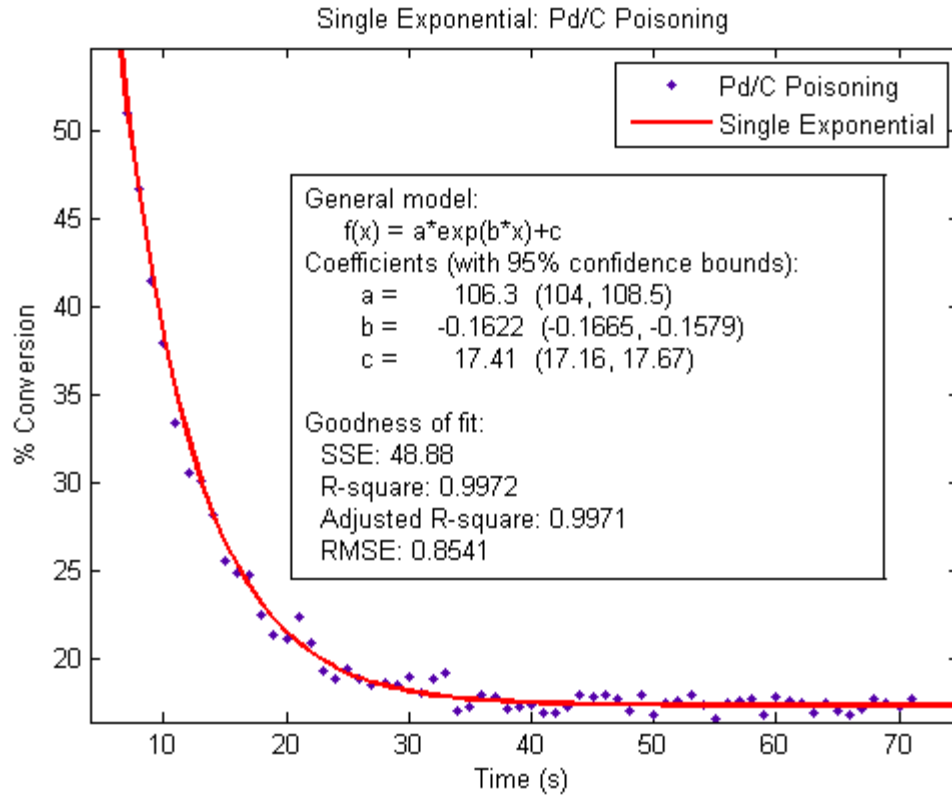


Figure 3.7: Exponential fits for Pd/C poisoning (above) and MOF-60 poisoning (below) at 0.5 ccm CO and 100 °C. The Pd/C poisoning profile can be fit to a single exponential, indicating that a single process is occurring when the Pd/C is being poisoned. The MOF-60 poisoning profile can be fit to a double exponential, indicating that two processes are occurring (e.g., entry of CO through the framework pore aperture followed by diffusion inside the pore).

Regarding the units of the fitting parameters, we must note that the end result must be a unitless number, for the y-axis is simply a number (percentage). To achieve this, the additive constant of the Pd/C fit and the multiplicative constants in both Pd/C and MOF-60 are unitless since each exponential term is of course unitless. This leaves the fitting parameters in the exponentials. The independent variable is time, which means that the exponential constants are in units of inverse time, or sec^{-1} . Thus, those values can be interpreted to be decay constants, for the negative signs on those constants correspond to exponential decay. The two decay constants of the MOF poisoning are likely the two different timescales of MOF poisoning mentioned previously: entry of CO through the pore apertures and diffusion of CO within the pores.

Conclusions

In this chapter, we observed that the MOF-60 is poisoned by CO just as conventional Pd catalysts are. The extent of poisoning increases with higher CO flow and decreases with higher temperature. The time scales of poisoning and recovery for the MOF-60 and Pd/C are very fast, on the order of 10-30 seconds depending on the conditions. Higher temperatures hasten both the recovery and poisoning time scales. The MOF-60 poisoning curve can be fit to a double exponential, while the Pd/C poisoning curve can be fit to a single exponential. This indicates that there are two processes occurring in the poisoning of the MOF while there is only process occurring in the poisoning of Pd/C. The MOF-60 retains more catalytic activity under identical poisoning conditions compared to the Pd/C, but the time scale of recovery is generally faster for

Pd/C. Thus, superiority cannot be established without the context of an application. A chemical process that requires quick “on and off” switching would likely benefit from Pd/C, whereas a chemical process that requires high conversions when faced with the possibility of poisoning would benefit from the MOF. Overall, these results indicate that our MOF catalysts perform well under poisoning conditions, and do not need external agents to recover from their poisoning as long as the source of poison is removed. Hence, our MOFs can be used in an industrial setting for their ability to be “turned off” and “turned on” with the introduction and removal of a relatively inexpensive gas (CO) and without the need of external agents.

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CHAPTER 4

Thermal Effects on MOF Catalysts

Introduction

In Chapter 2, our MOF catalysts were optimized in order to determine which conditions yielded the highest catalytic conversions in the hydrogenation of propylene. The effect of metalation is relatively straight forward: balancing catalyst number and porosity yields the best activity. The effect of reactant flow rate was straight forward as well: an excess of hydrogen results in more propylene hydrogenation. The effect of temperature, however, was not fully investigated. Temperatures were taken at intervals of 50 °C. For all catalysts, 150 °C was found to be the optimal temperature, and 100 °C was a close second. This suggests the question: what happens in between 100 °C and 150 °C? Conversion could reach 100% at a temperature between 100 °C and 150 °C, or it could reach 100% starting at 150 °C, stay at 100% past 150 °C, and decrease at 200 °C. One could partition the temperature range into finer grid points, of say, 10 °C instead of 50 °C in order to ascertain these regimes of high conversion. Apart from a finer control of temperature, the effects of thermal hysteresis and temperature cycling would be interesting to investigate since many catalysts exhibit hysteretic effects. The utility of hysteresis could include more convenient catalysts, e.g., having two forms of a catalyst that switch when the temperature is changed, or higher conversions, e.g., having different conversions in a certain reaction with different temperature profiles.

Indeed, the thermal hysteresis of a number of catalysts is reported in the literature. One example is the work by Farrauto and colleagues [1] involving the reversible oxidation of a Pd-

based catalyst to PdO when the catalyst is subjected to high temperatures. In their experiments, the Pd catalyst was prepared and taken to temperatures to 800-1100 °C after it was supported on a variety of ceramics (ZrO₂, Al₂O₃, CeO₂). When the catalyst was oxidized to PdO, it was cooled in air (~20 °C/min) and the original Pd form of the catalyst was recovered along with a residual layer of PdO. The temperature at which the original catalyst was recovered is different than the temperature at which it began to oxidize, indicating thermal hysteresis. PdO formation was inhibited when hydrogen was used to reduce the catalyst, and if it was used to reduce PdO to Pd, the catalyst did not reoxidize at high temperatures in air. A study by Sidwell and colleagues [2] investigated the thermal hysteresis of different Pd-based catalysts. They used saw-tooth temperature profiles between 600 °C to 900 °C with a 10 °C/min ramping rate and found that the alumina-supported Pd catalyst exhibited very weak hysteresis below a certain critical temperature. Catalyst activity began to drop at this point, and past this point, hysteresis was very strong. They also observed that the highest activity was achieved on the downward ramp (toward lower temperatures). They make two key observations:

- i. The Pd-based catalysts have strong hysteretic effects above 800 °C.
- ii. Above 900 °C, there is a permanent loss of activity.

Given that our reaction involves two highly flammable gases, the temperature range for our investigation will not exceed 200 °C.

Regarding temperature cycling, Abdul-Kareem and colleagues [3] undertook a study of temperature cycling in the oxidation of CO gas. They used 50/60 mesh particles in order to reduce the temperature gradients in the system. High flow rates reduced the effects of radial gradients. The shortest temperature cycle period used was 60 minutes, with 10 minutes to ramp to each temperature extremum. They conclude two important points:

- i. Shorter cycle periods result in reduced reaction rates.
- ii. Temperature cycling does not result in significant gains in activity. If a higher temperature can be used without destroying the catalyst, it is preferable to cycling the reactor temperature.

The utility of temperature cycling has been brought into question in recent years. Silveston and Hudgins [4] used simulation, theory, and previous experimental work to investigate the matter, and drew no decisive conclusion regarding whether or not temperature cycling of chemical reactions improved conversions. They did, however, postulate that microreactors may be able to sidestep the problem of the thermal capacity of conventional reactors. In their own words at the conclusion of their work: “The conflicting simulation, theoretical work and experiments, make it impossible to state confidently that temperature modulation is a useful tool for reaction engineering.” Presumably, if the temperature of the reactor could be changed quickly enough, investigators thought that the exponential dependence of the rate constant on temperature coupled with high activation energies could increase the yields of catalytic reactions by orders of magnitude.

Combining the idea of thermal hysteresis with temperature cycling, it would be useful to determine whether or not our MOF catalysts achieve enhanced catalytic activity through the cycling of the external temperature. (Enhancement of activity through thermal cycling is thus a special case of thermal hysteresis.)

Experimental Details

General Setup and Analysis. The setup for these reactions is almost identical to the setup of the optimization experiments described in Chapter 2, but the output of the reaction is

opened to a vent. Samples are collected for GCMS analysis through a syringe attached to a tube that has been connected to the outlet of the reactor via a Swagelok connector. The settings on the GCMS are unchanged. The catalytic conversions are calculated using Agilent's built-in integration tools through its Data Analysis program, as in the case of the optimization experiments.

Temperature Gradation Experiments. The reactor is assembled as it is in the optimization experiments. The catalyst used for these experiments is the MOF-40. The tube oven is first set to 50 °C, and the flows through the reactor are set at 2 ccm propylene and 50 ccm hydrogen for the first experiment. The flows are set to 5 ccm propylene and 50 ccm hydrogen for the second experiment. The reactor is kept at 50 °C for 30 minutes, and the output of the reaction is collected at the end of the 30 minute period. After the output is collected, the temperature on the tube oven is increased by 10 °C. This process of waiting 30 minutes and collecting the output is repeated until the tube oven reaches 200 °C.

Thermal Cycling Experiments. The setup is the same as in the temperature gradation experiments, but instead of 30 minute periods at incremental temperatures, the MOF-40 catalyst is subjected to 100 °C and 200 °C with a soak time of 60 minutes at each temperature. The catalyst is first heated to 100 °C for 60 minutes, at which point the output of the reaction is collected and the temperature of the tube oven set to 200 °C. The reaction is then run at 200 °C for 60 minutes, at which point the temperature is set to 100 °C again. This pattern is repeated 16 times.

Results and Discussion

Temperature Gradation Experiments. The previous result of increased conversion with increased temperature is observed at the first few temperatures tested with the MOF-40. Conversion starts near 77% at 50 °C (2 ccm propylene) and near 47% (5 ccm propylene). It increases until 80 °C (2 ccm propylene) and until 70 °C (5 ccm propylene). At this point, for both propylene flow rates, the conversion plateaus and stays nearly constant. There is some fluctuation for 5 ccm propylene, but the average value is above the conversion at lower temperatures. At 180 °C, the conversions begin to decrease. It appears that the conversion profiles for the catalyst resemble a trapezoid when plotted against temperature (Figure 4.1). The two different propylene flow rates were tested to confirm that the changes in conversion are not due to a flow effect such as catalyst saturation.

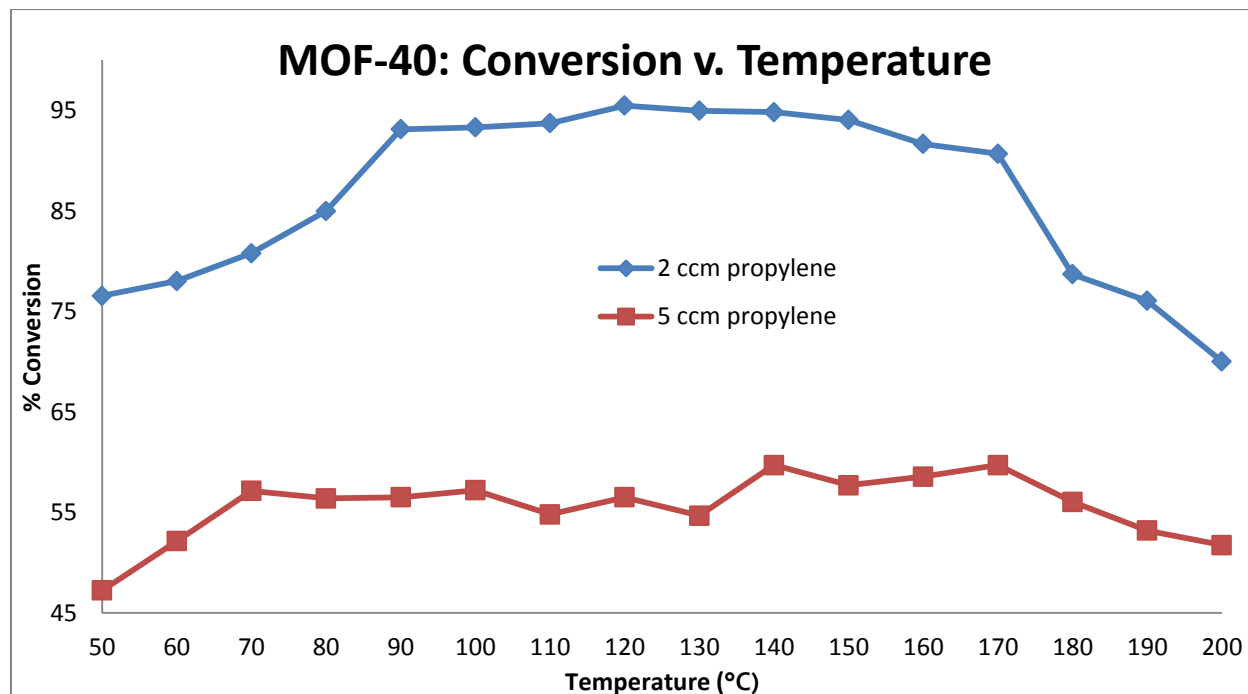
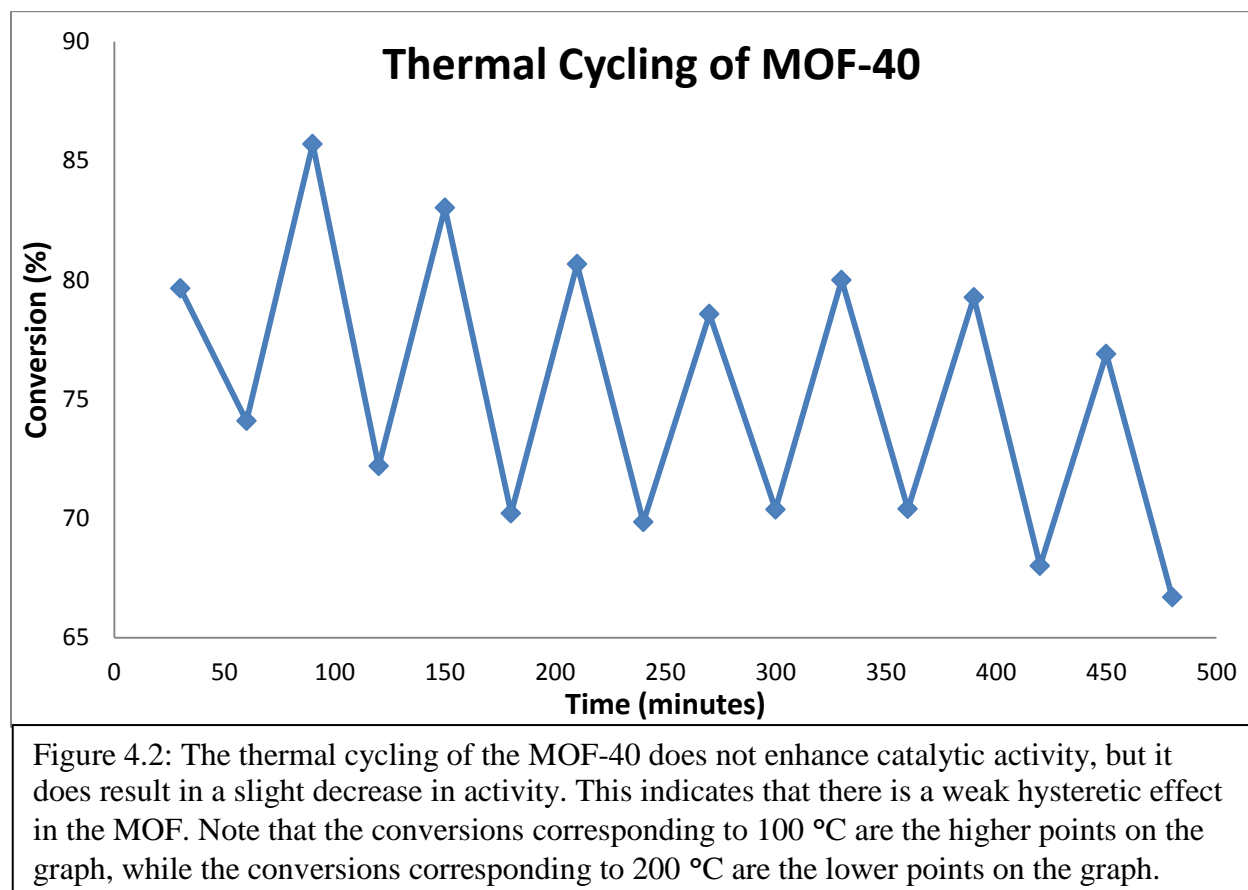


Figure 4.1: Effect of temperature on conversion at 2 different propylene flow rates. One can see that conversion increases with increasing temperature at the beginning, plateaus in the middle, and then decreases. This forms what appears to be a trapezoidal profile.

From the results of Chapter 2, one would not be faulted for thinking that the reactions should be run at 150 °C to achieve the highest conversion. These results, however, show that the reaction can be run at a lower temperature while still achieving a virtually identical conversion, e.g., running the reaction at 120 °C instead of 150 °C. On an industrial scale, this could translate to savings in energy costs. From Chapter 2, it was seen that Pd/C was temperature-independent in its conversion profiles, i.e., conversion at 30 °C is the same as conversion at 150 °C. If lower conversions are preferred in a certain application, using Pd/C could be more cost efficient. Otherwise, running the MOF-60 at the lower end of the trapezoidal profile could be more cost efficient. This is dependent on the assumption that the reactions are run at low propylene flows. More work would have to be done to elucidate the effects of higher propylene flows with finely divided temperature meshes to see if the trend holds if high throughput reactions are desired.

Thermal Cycling Experiments. Though this reaction utilized a microreactor (a reactor with a lateral dimension on the order of one millimeter), higher conversion was not observed by cycling the external temperature. There is a slight decrease in activity as the temperature is cycled between 100 °C and 200 °C, indicating weak thermal hysteresis. These results were produced from 8 hours of reaction with 9 temperature setpoints. Only one soak time was tested (30 minutes), so Abdul-Kareem's first point in ref. [3]—that shorter soak times decrease conversion—cannot be validated in these experiments. It must be noted that there is systematic error in the results due to the stability of the tube oven. The soak time includes the time to ramp/deramp to each temperature, which is about 2 minutes. His second point, that thermal cycling does not result in a significant increase in catalytic activity, applies to our MOF catalysts. It may be that our setup and reactor type are responsible for this observation, i.e., a different

reactor such as a plugged-flow reactor could produce different results. One can see the results in Figure 4.2.



Conclusions

In this chapter, the finer effects of temperature on the MOF-40 catalyst were investigated by dividing the temperature grid into finer mesh points and measuring the conversion at each mesh point. In addition, the effects of thermal cycling were investigated by alternating between 100 °C and 200 °C for 8 hours. There is a plateau in activity between the two best temperatures (taken from the optimization experiments) and the catalyst exhibits a weak thermal hysteresis, for activity slightly decreases after 8 hours of cycling. The physics behind temperature cycling and thermal hysteresis relate to the chemical identity of the catalyst. As mentioned previously,

temperature cycling sought to exploit the exponential dependence of the rate constant on temperature. Thermal hysteresis can change the identity of the catalyst depending on the temperature regime. As in the case of Farrauto in ref. [1], different chemical species of a single catalyst at different temperatures will alter the adsorption properties and the surface properties of the catalyst. This in turn affects the catalytic performance of the chemical species. To observe more drastic thermal hysteretic effects with our MOF catalysts, it is likely necessary to elevate them to higher temperatures.

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CHAPTER 5

Future Work

In these experiments, a number of points have been elucidated. These points include the optimization of our MOF catalysts in the hydrogenation of propylene, the effects of CO poisoning, the recovery from poisoning, and the finer effects of temperature. These points could be further investigated through more experiments that are similar in nature to the ones already conducted. For example, a finer mesh of hydrogen flows could be tested in order to obtain smoother hydrogen flow rate v. conversion curves. Or, one could test more temperatures when poisoning the MOFs with CO. These types of experiments would do little to innovate. Though further reaction engineering is useful from an engineering standpoint, it is less than interesting from a scientific standpoint. The investigation of the poisoning process in MOF catalysts and Pd/C would be interesting, however. The exact reasons for two processes occurring in MOF poisoning and one process occurring in Pd/C poisoning could lead to the design of MOF catalysts that are completely poison resistant. For example, if the metal centers of the MOF are affected by CO by a certain mechanism, new MOF catalysts could be synthesized to have metal centers that are unaffected by CO through that mechanism.

A different set of reactions that are catalyzed by palladium catalysts would be a worthwhile project to undertake. In much of the cited literature, the model reaction is the oxidation of CO to CO₂. (This is the reason why the effects of CO poisoning are eliminated in other catalysts when one passes a stream of O₂ through the reactor.) Apart from the oxidation of

carbon monoxide, other reactions such as Suzuki coupling would be useful to investigate since reactions that form carbon-carbon bonds are incredibly useful in organic synthesis.

As described in Chapter 1, there are two overarching motifs in the field of MOF catalysis:

- i. Trapping or immobilization of homogeneous catalysts in the framework
- ii. Use of the metal centers within the framework itself as catalytic centers

To date, there has been no study that compares these two cases with the same catalyst. For example, Eddaoudi and coworkers trapped a metalloporphyrin inside a *rho* ZMOF (zeolitic MOF) by utilizing an anionic indium-based framework [1]. The trapped porphyrin was cationic, allowing it to stay inside the pores instead of leaching out. This is a case of immobilizing a homogeneous catalyst inside the framework, and the reaction carried out was the epoxidation of alkenes in the liquid state. A case of using the framework itself would be that of Morris and coworkers [2]. Their MOF utilized a metalloporphyrin as a linker for the MOF. Though no catalysis experiments were carried out with these MOFs, the idea of incorporating a catalyst as a part of the framework stands. Apart from determining differences in catalytic activity, NMR imaging of the diffusion of reactants could ascertain the differences in reaction mechanism. A gas phase epoxidation, such as the epoxidation of propylene to form propylene oxide, would be industrially useful to catalyze. There is no method of epoxidating propylene using oxygen—though ethylene can be epoxidated with oxygen using silver catalysts [3]. (One can oxidize propylene with hydrogen peroxide [4], but it is not as cost efficient as using atmospheric oxygen.)

In a similar spirit, NMR imaging experiments could be performed to determine the velocity maps and thermodynamics of MOF-mediated gas separation. Olefins and paraffins are well separated by certain MOFs, such as Fe-MOF-74 [5]. Other experiments include the use of

complexes such as Crabtree's catalyst to observe parahydrogen-induced polarization (PHIP). Duckett and colleagues demonstrated that Crabtree's catalyst can hyperpolarize pyridine in the presence of pH_2 [6]. With Crabtree's catalyst, the polarization occurs homogeneously. This reaction could be heterogenized: an analogue of Crabtree's catalyst could be synthesized and attached to an amino group on a MOF linker through click chemistry. Multistep reactions involving parahydrogen-induced polarization could also be investigated, e.g., determining whether or not polarization is conserved in a series of reactions. For example, an alkyne could be reduced to an alkene using Lindlar's catalyst + pH_2 , and catalysis by a conventional hydrogenation catalyst would either conserve or destroy the polarization.

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CHAPTER 6

Conclusion

This thesis has discussed the reaction engineering of MTV-MOF catalysts that have attached palladium complexes to the amino groups on the linker. Three general areas were investigated in the reaction of propylene and hydrogen:

1. The optimization of these MOF catalysts when catalyzing this reaction with respect to:
 - a. Reactor temperature
 - b. Reactant flow rate
 - c. Isoreticular metalation
2. The poisoning and recovery of the MOF-60 catalyst when subjected to and relieved from the presence of CO in the reactor
3. Other effects of temperature on these catalysts:
 - a. Smaller temperature gradations and the effect on conversion
 - b. Thermal hysteresis

These ideas and methods could develop into more comprehensive studies in the reaction engineering of MOF catalysts in general. As mentioned before, most catalysis studies that use MOFs are limited to synthesis, a reaction to test for activity, and porosity data. If MOF catalysts are properly tailored and reaction engineered, they could be viably used in both the laboratory and the industry. Their unique physical and chemical properties allow for precise design and other utilities such as gas separation and storage. This being said, the field of MOF catalysis has many obstacles to overcome, such as the degradation of many MOFs when subject to moisture

and lower surface areas when compared to other, non-crystalline, compounds. Given enough time, MOF catalysis will flourish, especially with the recent attention that MOFs have received in the catalysis community.