Separation of Industrially-Relevant Gas Mixtures With Metal-Organic Frameworks

By

Zoey Rose Herm

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Professor Jeffrey R. Long, Chair
Professor T. Don Tilley
Professor Alexis T. Bell

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Abstract

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The work herein describes the investigation of metal-organic frameworks for industrial applications, specifically gas phase separations of mixtures. Metal-organic frameworks are crystalline molecular scaffolds built from cationic metal vertices and organic bridging ligands. They are porous on a molecular scale and can separate gas mixtures when one component interacts more strongly with the pore walls than others. The near-infinite combination of metals and ligands allows for optimization of metal-organic framework structures for specific separations.

Chapter 1 begins with an explanation of why gas separations are relevant to protecting the environment and preventing atmospheric CO$_2$ emissions, followed by an overview of the basic chemistry of metal-organic frameworks. The chapter then presents an extensive survey of previously reported literature on CO$_2$/H$_2$ separations and hydrocarbon separations using metal-organic frameworks, which are the two specific separations reported in this work.

Chapters 2, 3, and 4 focus on CO$_2$/H$_2$ mixtures. The first chapter describes the first experimental survey of metal-organic frameworks for this separation. Five materials were chosen as representative of different types of metal-organic frameworks: two with high internal surface areas, one with structural flexibility, and two with highly polarizing cationic metal sites lining the pores. The materials with these coordinatively-unsaturated metal centers demonstrated vastly improved behavior over the materials that are currently used industrially for this separation. Of these two, the framework with exposed Mg$^{2+}$ sites, Mg$_2$(dobdc), was deemed to be superior due to its high selectivity for CO$_2$ over H$_2$. The framework with exposed Cu$^{2+}$ sites, Cu-BTTri, had a lower selectivity but higher capacity for CO$_2$. Both selectivity and CO$_2$ capacity are important metrics in evaluating adsorbents, and in this case selectivity has been reported to be paramount.

Chapter 3 examines Mg$_2$(dobdc) in further detail due to its promising behavior in Chapter 2. Industrially, CO$_2$/H$_2$ mixtures are contaminated with a variety of impurities, primarily methane and carbon monoxide. Carbon monoxide is very reactive and therefore more manageable to remove. Methane, however, behaves very similarly to H$_2$ and therefore materials that isolate H$_2$ from both CO$_2$ and methane are highly desirable. Chapter 3 evaluates the performance of Mg$_2$(dobdc) when separating CO$_2$/H$_2$/CH$_4$ mixtures and describes its excellent performance.
Chapter 4 describes an attempt to improve upon the CO$_2$/H$_2$ selectivity of Cu-BTTri. Mg$_2$(dobdc) performs better than Cu-BTTri in part because Mg$^{2+}$ cations are more polarizing than Cu$^{2+}$ cations. By generating a material isostructural to Cu-BTTri but featuring Mn$^{2+}$ cations which are also more polarizing than Cu$^{2+}$, greater CO$_2$/H$_2$ selectivities can be achieved.

Chapter 5 is a departure from the previous chapters and investigates the separation of alkane isomers. Isomers are a particularly challenging mixture to separate because their reactivity and physical characteristics are very similar. This chapter presents the synthesis of a metal-organic framework with triangular channels that can separate hexane isomers based on their shape. The acute angles of the channels allow for isomers with a higher aspect ratio to wedge themselves into the channel corners, while the bulkier isomers have a weaker interaction.
This dissertation is dedicated to Prof. Paul J. Fischer, Bonnie P. Rose, and Joel E. Herm, all of whom share a wide-eyed belief in, love for, and devotion to the people around them.
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0.1 Introduction

There are four people without whom I would not be a chemist and would not have completed this dissertation: my parents, my college advisor Prof. Paul J. Fischer, and of course my devoted graduate supervisor Prof. Jeffrey R. Long. Many others have supported me and believed in me during graduate school, leading up to graduate school, and throughout my life from childhood.

0.2 Parents

Someone once told me that for things to work out, you have to get really lucky and you have to not mess it up when you do. I am so lucky to have been given the countless opportunities that have come my way, and I credit my Ph.D. to the people who and circumstances that have created that luck for me. My life is good. Really, really good. That’s the reason I have the strong foundation to pursue chemistry. I have an amazing family, great relationships, a stellar education, a passport full of stamps from across the world, good health, and a nice apartment. More than any other parents I know, mine came together as two people and each devoted their entire lives to only me. No other kids, no bigger priorities, just me. My life is beautiful and any contribution I have ever made or will ever get to make is a result of every resource they poured into me. And on top of all of that they’re simply really cool people and great role models. My mom has unbelievably big heart and personality, and my dad has his quiet thoughtfulness and excitement for all things technology. They both live intentionally, with purpose, and with a sense of humor. Because of their inherent beauty as people and their dedication to me, I get to do chemistry that is challenging and rewarding and that I believe in, all while being surrounded by brilliant scientists who support me and have fun with me.

0.3 Research Advisors and Chemistry Teachers

0.3.1 Professor Jeffrey R. Long, Graduate Advisor

0.3.1.1 One-on-One Mentorship

Over the past five years, Jeff has consistently offered me two of the greatest gifts that can be given to a graduate student: opportunities and patience. He has given me some of his best ideas and then let me struggle realizing them for what must have been an incredibly frustrating amount of time for him. When I felt like I was floundering, he made me feel like I had a safety net but the expectations of me were high. As a result, I feel ownership over every experiment I’ve done at Berkeley and I’ve developed the million skills it takes to be a scientist that I didn’t even know existed. I feel like a scientist, I am a scientist, and that is because of the vast time and effort Jeff put into me as an individual. He keeps it up with such thoughtful diligence, constantly nominating me for awards and suggesting new experiments. If I were his only graduate student, I would be impressed with his dedication. Considering that he has nearly twenty others, I am
blown away. I am also profoundly grateful for the personal relationship I have with Jeff. I have had so many very memorable, very fun times with him, devising fun activities together like putting temporary tattoos on our faces at Raider’s games.

0.3.1.2 Cultivation of a Remarkable Research Group

I’m not just grateful that Jeff is my advisor, I’m grateful that he is a chemist, and stepping back further, a person in the world. As the director of a large research group and simply as a person, Jeff is an incredible role model. His love of science runs so deep that it touches every person in the group in so many unique and thoughtful ways, and I see him tailor his supportive nature to each individual. His kind attention reaches so many people: He carefully brings people who love science into the lab regardless of gender or nationality, he chooses people who will also be kind colleagues, and this ripples out into the greater scientific community by both generating cutting edge science and creating positivity in the chemistry community. He is kind, generous, and fun, and this attitude is contagious whenever he’s around.

0.3.2 Professor Paul J. Fischer, Undergraduate Research Advisor

Writing about Paul Fischer has been the hardest part of this thesis and the piece that I have saved for last. My first memory of Paul is an email he sent out to my freshman chemistry class with the subject “Are you ready?”. The email asked if we were ready to understand the physical phenomena of the world like frost on windows and why food cooks faster in a pressure cooker. It was inspiring. About a year later, out of the blue, he summoned me to his lab via email. For me it was literally like when Dorothy opens her front door to see the land of Oz in color when her whole world had been black and white until that moment. The room was full of Schlenk lines and intricate glassware and a glovebox and a hundred other things I didn’t know existed. He said that he had researched me by talking to other faculty in the department and wanted to give me the opportunity to do research in his lab. I knew I loved chemistry, but I didn’t even know exactly what I loved or what I wanted to do with that excitement. He believed in me and saw things in me that I didn’t know could be seen in a person.

From that summer until now, Paul has been my rock. I loved working for him and it was so easy because he was so inspiring. At the beginning, he showed up every morning ready for new experiments for me and taught me diligence and rigor. He checked my lab notebook almost every day to the point of re-doing my stoichiometry because there was no room for error. The chemistry was so challenging and the expectations were so high and waking up every morning felt like a rush. I went on to make more compounds in 18 months than I made in all of graduate school. Outside of the science, Paul signed me up to give talks at ACS meetings, nominated me for awards, and writes recommendation letters for me constantly. I am now unbelievably lucky to get to count Paul as a friend, or really more like family.
0.3.3 Prof. Rajamani Krishna, Graduate Research Collaborator

Prof. Krishna gave me three significant opportunities during graduate school. The first was the day I met him, when he aggressively shot me down during a presentation I was giving because he didn’t believe the data I was presenting, that had been generated by other collaborators, was real. He asked for the raw data to do his own analysis and try to reproduce what I had shown, and a research relationship was born. He enhanced the quality of that project substantially and led to it generating two papers instead of one. It is very special to me that he cared enough about a stranger’s work, let alone a graduate student’s, to pay close enough attention to catch inconsistencies only a theorist would catch. After that, he had been brewing an idea independently for some time that he pitched to me and Jeff, which ended up being my most successful result in graduate school. Finally, during the co-authorship process of those three papers, he was so impressively detail-oriented and taught me to truly think about every clause in every sentence that I publish. I hope that someday my writing and thought processes will be as immaculate as his.

0.3.4 Mr. Howard Hill, High School Chemistry Teacher

Before I took Mr. Hill’s chemistry class in high school, I was uninspired and lost to the point where I even temporarily quit traditional high school to go to hippie art school. His careful pedagogy and enthusiasm gave me the window to see an academic pursuit I was truly excited about, and I think if I had a different teacher I may never had seen that. As I began to become more excited about chemistry, he upped his energy to match mine. He believed in me and saw that I was good at chemistry and brought me to life.

0.4 The Long Lab

My unique and brilliant colleagues in the Long group have inspired and supported me. Some people are those with whom I make and characterize metal organic frameworks all the time, like my epic co-authors Eric and Jarad, Miguel, and Jeff van Humbeck. Other people on my project like Dana and Dianne who always have a good idea right when I need it. My amazing friends who also happen to study magnetism are Katie and Lucy, and I have become very close with both of them over the years in different ways. I feel especially lucky to have stuck around long enough to get to know the young (grad-school-wise) Lucy, and I am so excited to see all the amazing science she does during her career. Michael Nippe helps me with science, helps me with professional development, and drives me home from Jeff’s holiday party at 6am. Working closely with Kaitlyn Weeber, a brilliant then-undergraduate and soon-to-be-doctor, taught me so much. I also feel priviledged to get to have worked with Mary Anne Manupil, now a graduate student at Stanford. Others in the lab who are always there to talk about science or make silly jokes are Mike Aubrey, Xiaowen Feng, Jordan Axelson, Matt Kapelewski. So many postdocs helped me along the way as well: Elizabeth Montalvo, Deanna D’Allessandro, Aude Demessence, Satoshi Horike, Hye Jin Choi.
0.4.1 The Long Lab Entering Class of 2008

When I started grad school with with Curtis Wray, Tom McDonald, and Brian Wiers I didn’t anticipate how close the experience would make us. Curtis and I took our qualifying exams one day apart and were partners throughout the entire process. Among other achievements we walked each other through, we perfected the windmill high five. He and I also started learning about green and sustainable chemistry together, a direction in which we are now both taking our careers.

Tom and Brian are now truly my family. Tom and I have sat five feet away from one another for four years and know every success and hardship one another has experienced and know how to make each other laugh. I smile every time I see him. Brian is uniquely brilliant and makes an effort every day to know me for who I am and be interested in making conversations with me that are memorable and thoughtful. I will be friends with both of them for life.

0.4.2 The Champion Longballs Softball Team: The Long Lab Circa 2009

When I started graduate school, the Long lab was a dynamic and magic group of people. Staff in the department still come up to me and talk about they halcyon days of 2008-2010 with Dave Harris, Danna Freedman, Jeff Rinehart, Kenji Sumida, Leslie Murray, and Joe Zadrozny. I’ll still always think of Dave as our coach who brought us to win the chemistry softball league championship, giving compelling speeches about playing like champions and leaving everything we had out on the field. Fulfilling his dream as a chemistry professor, he now lives according to that policy every day. Every time I work late in lab I remember playing “mummy and museum curator” with Jeff Rinehart, rolling each other around on carts for compressed gas cylinders and choosing when to come to life and scare each other. Danna was the first peer to take me seriously as a scientist, as she delegated responsibilities to me starting my first week in lab and told me she wasn’t going to hold my hand seeing them through. I am so grateful that she had the confidence in me to learn how to do things on my own. I remember following Leslie around with a notebook writing down every word he said and Kenji staying late many nights to teach me how to use instruments. Sometimes groups of people come together in a phenomenal way, and this was one of them.

0.5 Friends

0.5.1 Friends Outside of Berkeley

My close friends that supported me up until graduate school can’t go without mention. Laura Balanoff has thought I was cool since 1992. Mike Speilman thought I was lame since we met in 1999, until 2003 when we magically became best friends. Josh Stern has kept my mind sharp with his amazing ability to argue the details of any minutiae since high school. Karmela Anderson and Sophia Giebultowicz loved me though the awkward growing pains of becoming a near-adult during college. When I was scared to apply to Berkeley for grad school, Karmela said to me, “Don’t be silly.
Berkeley is for people just like you.” Her belief in me and her own personal strength have made me a stronger person.

0.5.2 Friends at Berkeley

My scientific career would be nothing without Jessica M. Smith, Erica E. Schultz, Michel T. Dedeo, Eric J. Sundstrom, Stephen J. Elkind, and Sophie Soltani. During my time at Berkeley they have been there for my exciting results and my frustrations. Erica was kind enough to live with me for four years, which came with hanging out later than we should have after work, blasting music, and hosting parties that I will look back on forever. And co-adopting the world’s best cat, Henrietta (aka Hank). Michel has cooked me more dinners than I have cooked for myself in Berkeley, and he knows me so well that he is the one who suggested writing my acknowledgements in outline form. Eric was my first friend in Berkeley and has been a quiet source of love and support since that day at Jupiter. Stephen exudes more joy and excitement and intelligence than I could ever imagine.

0.5.2.1 Friends at Berkeley who are Especially Strong Women and with whom I am Especially Close

Sophie and Jessica are the two strongest women I have met. Sophie has listened to me and laughed with me, and her endless wisdom and kindness make her the best role model I have ever had. I have cited many people above who have believed in me as a scientist, but Sophie was the first person who has really believed in me as a person. She sees me as the person I want to be.

I have shared essentially every thought and feeling I have had in Berkeley with Jessica and she has loved me unconditionally. We have had so much fun together, most of which she has planned, and we have supported each other with our whole hearts. She is brilliant, witty, thoughtful and principled. Every time I look at her I see so many things I want to be.

I don’t know how all of the other people out there get through life, let alone grad school, without those two.
Chapter 1: The Use of Metal-Organic Frameworks for Separating Industrially-Relevant Gas Mixtures

1.1 Introduction

The world is facing an energy crisis. Not only do we lack the resources to meet ever-increasing energy demands, but the processes for creating energy add carbon dioxide to the atmosphere. Identifying major avenues for curbing both the need for energy and the CO₂ emissions of energy production are major strategies in combatting these issues that plague human health and the environment. Figure 1.1 shows the International Energy Agency’s plan for reducing future CO₂ emissions below the current global output, which includes both CO₂ capture and increased global efficiency.¹ Carbon capture and storage, or CCS, involves capturing CO₂ from point sources such as power plants and sequestering it underground or chemically. Increased fuel and electricity efficiency can come from a variety of sources.

![Image](image1.png)

**Figure 1.1** The International Energy Agency’s suggested strategy for reducing global CO₂ emissions. Each wedge corresponds to a different tactic for combatting these emissions, and two of the largest are carbon dioxide capture and efficiency. Permitted reproduction of Reference 1.

Separation of mixtures accounts for approximately 15% of global energy use.¹ In the context of Figure 1.1, efficient separation of mixtures in the gas phase is highly relevant to both global energy efficiency and CO₂ capture. Separations are a mammoth component of the chemical industry and petroleum refining, and due to the large scales of the global industry even small increases in efficiency can save measurable and high-impact levels of energy.² In terms of capturing CO₂, separating CO₂ from flue gas mixtures can allow for it to be sequestered underground.
1.1.1 Mixture Separation Technologies

Despite the promise held by gas mixture separations, outstanding technological challenges have led to an industrial landscape with many opportunities for improvement. The four primary strategies for gas mixture separations – distillation, membrane separation, absorption and adsorption – are outlined in Table 1.1. Many large-scale separations, such as most of petroleum refining, are performed via distillation. Distillation requires cryogenic temperatures or heating, which both require extensive energy input. Membrane separations also come with a unique set of challenges. They often don’t have as high of separation performance and are subject to faults such as plasticization and clogging with dust particles.3

<table>
<thead>
<tr>
<th>Summary of Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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<tbody>
<tr>
<td>Distillation</td>
<td>Separate based on boiling point</td>
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</tr>
<tr>
<td>Membranes</td>
<td>Pressure-driven filtration⁴</td>
<td>Simple approach with potential for high efficiency⁵</td>
</tr>
<tr>
<td>Absorption</td>
<td>Reversible, selective absorption into solutions</td>
<td>Non-prohibitive cost⁷</td>
</tr>
<tr>
<td>Adsorption</td>
<td>Reversible, selective adsorption onto surfaces</td>
<td>Low cost, high density</td>
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<td>Zeolites</td>
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<td>Activated Carbons</td>
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<tr>
<td>Metal-Organic Frameworks</td>
<td>High tunability</td>
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Table 1.1 Summary of the concept, advantages, and disadvantages of the major technologies for gas separation.

Absorptive and adsorptive separations rely on exposing a mixture to a solvent or solid respectively, selectively removing one component, and then regenerating the material with heat or vacuum to prepare for another cycle. Absorptive separations are typically carried out with solutions of aqueous amines, and are limited by their regeneration energies and the corrosion the amines cause to their surrounding equipment.⁷ Sorptive separations, in which a solid or solution selectively and reversibly interacts with one component of a mixture so that the components can be separated
followed by regeneration of the sorbent, have many advantages when compared with
distillation and membranes. Adsorption can often be done at the starting temperature of
the mixture and therefore avoid any energy cost due to temperature regulation.
Adsorption also offers many more handles for separating individual components than
absorption; Differences in polarizability, size, reactivity, boiling point, shape, electron
affinity can all contribute to selectivity. By taking advantage of these properties,
regeneration can be tuned for a particular application and minimized.

Two of the most common adsorbents are activated carbons and zeolites. They are
both relatively inexpensive and are regularly used on industrial scales. Activated carbons
are generated through pyrolysis of natural matter followed by some type of activation
treatment, and zeolites are a class of naturally-occurring porous aluminosilicates that are
easily synthesized and modified. Many synthetic zeolites have been discovered, however
there are a finite number of possible structures. Activated carbons are also limited in
their structure and reactivity: Their porosity is irregular and modification of their surfaces
is limited. More recently, a class of materials called metal-organic frameworks have
received great attention because their properties allow for many improvements in
separation performance when compared to other adsorbents.

1.1.2 Metal-Organic Frameworks

Metal-organic frameworks are a relatively new class of porous, inorganic
materials that have wide-ranging applications in adsorptive separations. They are
constructed from metal cations or inorganic clusters, and these vertices are connected by
multitopic organic bridging ligands. The resulting structures are permanently porous and
crystalline in three dimensions. The nearly infinite number of organic ligands and metals
available makes these materials tunable, and therefore many separations that are
inefficient or even impossible with any of the technologies in section 1.1.1 have been
demonstrably effected in the pores of metal-organic frameworks. The synthetic and
physical chemistry of metal-organic frameworks is detailed in the next section, followed
by detailed treatments of two industry- and clean-energy-related classes of separations.

1.1.2.1 Structural Diversity

An illustrative example of the vast and often unintuitive structural properties of
metal-organic frameworks stems from the ligand benzene dicarboxylate ($\text{bdc}^2$). Four
different structural examples based on this ligand are presented in Figure 1.2. The
material that is commonly known to be the first metal-organic framework, MOF-5, was
synthesized with this ligand. When solvothermally reacted with $\text{Zn(NO}_3)_2$, the resulting
material is a cubic structure with the formula $\text{Zn}_4\text{O(bdc)}_3$. The vertices are a larger
tetrahedron composed of four smaller $\text{Zn}_4\text{O}$ tetrahedra which all share one central oxide.
The simplicity of the structure makes it very attractive for study, as well as the
straightforward synthetic conditions: Commercially available and relatively inexpensive
starting materials can yield millimeter-sized cubic crystals in 10 hours. Unfortunately,
the framework is very unstable to humidity, limiting its practical utility.

One avenue for modifying this structure type is to further functionalize $\text{bdc}^2$. By
elongating the linker or adding functional groups to the central benzene ring, many
isostructural materials can be generated with new surface potentials and porosity. These materials suffer the same stability issues as the parent framework because the Zn-O bonds are relatively constant throughout the large series of isostructures that have been reported. Figure 1.2 shows a modified structure where the central benzene ring has been replaced by pyrene.

![Figure 1.2](image_url)

**Figure 1.2** Illustration of the variety of structure types linked with benzene dicarboxylate where gray, red, green, blue, and purple atoms are carbon, oxygen, zinc, zirconium, and chromium, respectively. The top right is MOF-5, or Zn₄O(bdc)₃. The top left is an isostructure of Zn₄O(bdc)₃ wherein the benzene ring has been replaced by a pyrene. The bottom right is Zr₆O₄(OH)₄(bdc)₆, a material with remarkable stability due to the Zr–O bonds. The bottom left is Cr(OH)₄(bdc) in its closed-pore form, which can expand due to its flexibility.

Varying the metal cation can have drastic effects on structure and reactivity. When bdc²⁻ is reacted with Zr⁴⁺, the resulting structure is strikingly different from Zn₄O(bdc)₃, as are the properties. The framework with the formula Zr₆O₄(OH)₄(bdc)₆ known as “UiO-66” is extremely stable, not just to humidity but to water and other solvents. The harder Zr⁴⁺ cations form stronger bonds with the carboxylate anions, forming a much stronger scaffold.
In addition to imparting more stability to the framework structure, changing the metal can allow for flexibility in a metal-organic framework. The chromium(III) material with the formula Cr(OH)(bdc) flexes between two crystallographically distinct structures when exposed to guests which enter the pores. This accordion-like breathing is highly dependent on the identity of the metal bridging the bdc$^{2-}$.

The variety of metal-organic framework structures known can be illustrated by the point that not only are there more dicarboxylate-linked metal organic frameworks than those listed above, but there are dozens or hundreds of other linkers, and each linker holds the potential to generate its own family of structures. Rigid nitrogen- and oxygen-coordinating linkers are the most common, such as carboxylates, oxides, azolates, and amines. Stability, pore size, surface area, functional group accessibility, flexibility, and many other properties are accessible and can often be engineered, such as the above example of modifying the linker of Zn$_4$O(bdc)$_3$.

A feature of some metal-organic frameworks that has proven to be powerful in gas separations is the presence of coordinatively unsaturated metal centers. These sites are generated when one of the octahedral coordination sites of each metal is bound to a solvent molecule rather than to a ligand. With careful heating and evacuation this solvent can be removed, leaving behind a strongly polarizing site which can be used as a handle for separation.

Some metal-organic frameworks are encountered repeatedly in the gas separation studies performed to date, and a brief discussion of each is useful to inform the content of this chapter (Figure 1.3). The canonical Zn$_4$O(bdc)$_3$ is among the simpler structures. Lauded for its stability and structural similarity to zeolites, ZIF-8 contains Zn$^{2+}$ cations linked by 2-methylimidazolate (MeIM). The structure of ZIF-8 is somewhat flexible, and gate-opening effects can be seen for different adsorbates. The structure of Cu$_3$(btc)$_2$, consists of Cu$_2$(O$_2$CR)$_4$ paddlewheel units connected via 1,3,5-benzenetricarboxylate (btc$^{3-}$) linkers. Upon activation, the Cu$^{2+}$ centers each have an axial coordination site open and pointing into the pore, allowing rich reactivity at this Lewis acidic site. The structure of the frameworks M$_2$(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn; dobdc$^{4-}$ = 2,5-dioxido-1,4-benzenedicarboxylate) (Figure 1.3), sometimes referred to as M-MOF-74 or CPO-27-M, also contains coordinatively-unsaturated divalent metal cations. Here, the metal centers are exposed with an exceptionally high surface density of ~3 open metal sites per 100 Å$^2$, leading to particularly high separation abilities. The similar structures of MIL-47 and MIL-53 are both composed of bdc$^{2-}$ struts, with MIL-47 containing V, while MIL-53 can be based upon Al, Sc, Cr, Fe, Ga, or In. Although MIL-47 is relatively rigid, the MIL-53 materials are flexible frameworks that can open and close like an accordion in the presence or absence of different adsorbates.

**1.1.2.2 Methods of Characterization**

Crystallographic structural data is perhaps the most powerful tool for characterizing metal-organic frameworks. From structural data, many properties such as surface functionality, density, and surface area can be determined. Without these results, drawing conclusions about the origin of material behavior towards guest molecules is challenging. Due to the modular nature of metal-organic frameworks, often powder diffraction patterns are sufficient to confirm a new material is isostructural to a
previously documented structure. Other structural information is commonly determined using infrared spectroscopy, elemental analysis, thermogravimetry, and NMR spectroscopy of either acid-digested materials or of the intact solids.

Figure 1.3 Crystallographic structure, molecular formula, common name, BET surface area, and centroid-centroid pore diameters or distances for the structure types regularly encountered in gas separations. Surface areas are reported in references within this review with the exception of MIL-53, MIL-47, and Cu₃(btc)₂. Green, red, gray, yellow, purple, orange, dark red, and blue correspond to Zn, O, C, Cr, V, Fe, Cu, and N, respectively. Variations of these structures can include functional groups bound to the organic ligand such as the “IRMOF” series of MOF-5 or amino-MIL-53, which includes an amino group bound to the central benzene ring of the linker. Metal cations can also differ within the M₂(dobdc) and MIL-53 series, which in this figure contain Fe and Cr, respectively. MIL-53 is shown in the “narrow pore”, or closed, form, although this material can also expand to a structure very similar to MIL-47.

1.1.2.2.1 Gas Sorption

Gas sorption is used to characterize metal-organic frameworks in two ways: The determination of the surface area of the internal structure of the material, and the capacity and strength of adsorption for a variety of guests. Generally, surface area is measured with 77 K N₂ adsorption isotherms and those can be used to generate physically meaningful surface areas using the BET method.

Surface area measurements are particularly useful for establishing the purity of a metal-organic framework. Powder X-ray diffraction patterns only confirm the presence of an ordered phase, and the presence of amorphous dense phases is not confirmed or
denied. Elemental analyses and thermogravimetry are often complex to interpret in metal-organic frameworks due to the presence of solvent molecules in the pores. Purity can often be inferred from measurement of a surface area matching the predicted value from the structure or samples previously determined to be pure.

Storage and separation of gases is one of the most commonly discussed applications of metal-organic frameworks. Storage of gases like hydrogen and methane has direct relevance to emissions-free or low-emission transportation, while separation of mixtures like CO₂ and N₂ could result in materials that can simply be added to power plants to avoid CO₂ emissions into the atmosphere. Adsorption of these gases can be measured by volumetrically, and the strength of adsorption can be determined by fitting the Clausius-Clapeyron equation to isotherms at multiple temperatures.

1.2 CO₂/H₂ Separations in Metal-Organic Frameworks

Separating mixtures of CO₂ and H₂ is performed on enormous scales globally for the production of ammonia, and can be used to effect a specific kind of carbon dioxide known as “precombustion” capture. Figure 1.4 illustrates this process in which methane or coal is converted into H₂, which can then be either used as a reactant or combusted to produce electricity.

![Figure 1.4 Basic schematic of industrial CO₂/H₂ separation.](image)

1.2.1 Precombustion CO₂ Capture

Precombustion CO₂ capture is a process in which fuel is decarbonated prior to combustion, resulting in zero carbon dioxide production during the combustion step (see Figure 1.4 for a detailed schematic). Here, coal is gasified, generally at high temperature and pressure, to produce synthesis gas or “syn gas”, which is a mixture of mostly H₂, CO, CO₂, and H₂O (Table 1.2). This gas mixture is then run through the water-gas shift reaction to produce H₂ and CO₂ (“shifted syn gas”) at high pressure and slightly elevated temperature (5-40 bar and 40 °C, depending on the production plant). Pre-combustion CO₂ capture, which refers to the separation of CO₂ from H₂ within this gas mixture, can then be performed to afford pure H₂, which is subsequently combusted in a power plant to generate electricity.

1.2.1.1 Considerations for Precombustion Capture

Solid adsorbents, membrane materials, and liquid absorbers are currently under consideration as potential candidates for use in pre-combustion CO₂ capture. With regard to industrial applications, precombustion CO₂ capture systems based upon CO₂-absorbing
solvents are the closest to being realized, and a number of power plants incorporating such systems are being constructed.\textsuperscript{25} Furthermore, the use of solid adsorbents in pressure-swing adsorption-based processes is currently under intense investigation. Here, the high-pressure gas mixture is transported through a packed bed of a porous adsorbent incorporated into a PSA process. The CO\textsubscript{2} within the flue gas is selectively adsorbed along with other minor impurities of the mixture, such as CO, and following a series of concurrent and countercurrent pressurization and depressurization steps, the adsorbed gases can be removed, and the capture material can be regenerated for subsequent CO\textsubscript{2} capture cycles.\textsuperscript{26}

<table>
<thead>
<tr>
<th>Component</th>
<th>Approximate percentage (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2}</td>
<td>25-35</td>
</tr>
<tr>
<td>CO</td>
<td>0.5-0.7</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>30-50</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>0</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>15-40</td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>0.3-2.3</td>
</tr>
<tr>
<td>Ar</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*Table 1.2* Composition of Shifted Product of Coal Gasification.\textsuperscript{19}

1.2.1.2 Advantages of Precombustion Capture

In comparison to post-combustion CO\textsubscript{2} capture and oxy-fuel combustion-based processes, precombustion CO\textsubscript{2} capture carries a number of advantages that may be of benefit for its rapid industrial implementation. Perhaps most significantly, the gases are produced at high pressure, and the partial pressure of CO\textsubscript{2} in the mixture is high compared to post-combustion flue gas. As a result, regeneration of the loaded adsorbent can occur through a drop to atmospheric pressure, which is energetically favorable and is more practical compared to a temperature or vacuum swing-based process. Furthermore, the CO\textsubscript{2}/H\textsubscript{2} separation is inherently easier to perform than CO\textsubscript{2}/N\textsubscript{2} or O\textsubscript{2}/N\textsubscript{2} separations, owing to the greater differences in the polarizability and quadrupole moment of the molecules.\textsuperscript{15} Thus, for purely physisorption-based separations, a greater selectivity for CO\textsubscript{2} over H\textsubscript{2} can be anticipated, which may allow next-generation precombustion CO\textsubscript{2} capture materials to be more rapidly developed than new adsorbents for post-combustion CO\textsubscript{2} capture, or oxy-fuel combustion.
1.2.2 Hydrogen Purification

Pressure-swing adsorption separation of shifted syn gas is a mature technology because of its wide use in hydrogen purification. Hydrogen used for industrial applications is generally synthesized from methane reforming followed by the water gas shift reaction, which is very similar to coal gasification. The same processes as coal gasification are applied, although the composition of the final products differ in the partial pressures of the gases (Table 1.3) owing to the differences in carbon content between methane and coal. While liquid solvents such as Selexol are often used, PSA columns employing solid adsorbent beds are also common, and are responsible for the purification of millions of tons of hydrogen annually. This hydrogen is used for ammonia synthesis and large industrial-scale reactions such as the Fischer-Tropsch synthesis of hydrocarbons.

<table>
<thead>
<tr>
<th>Component</th>
<th>Approximate Percentage (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>70-80</td>
</tr>
<tr>
<td>CO₂</td>
<td>15-25</td>
</tr>
<tr>
<td>CO</td>
<td>1-3</td>
</tr>
<tr>
<td>CH₄</td>
<td>3-6</td>
</tr>
</tbody>
</table>

Table 1.3 Components of the Shifted Products of Steam-Methane Reformation.

In the context of Figure 1.1, the tremendous scale of H₂ purification (50 million tons of H₂ annually) suggests that even slight enhancements in the efficiency of this process would have significant benefits on global energy savings. For example, if the energy cost of purification (7.3 MWh per ton of H₂) can be reduced by 10%, the energy savings would represent the equivalent of shutting down 18 average-sized coal-fired power plants. Thus, the development of next-generation materials for precombustion CO₂ capture that exhibit improvements in energy efficiency over existing materials would also have a significant impact on the economic and environmental costs associated with H₂ production worldwide.

Zeolites and activated carbons remain the most well studied solid adsorbents for H₂ purification from steam-methane reforming. Zeolite 13X possesses a high selectivity for CO₂, CO, and CH₄ over H₂ compared with BPL activated carbon, although the capacity of activated carbons is generally greater than that of zeolites. Considering that these are the state of the art porous solid adsorbents used for hydrogen purification, we compare the performance of these materials with metal-organic frameworks in the following sections to evaluate the potential of the latter to become the materials of choice for this application.
1.2.3 Metrics for Evaluating Adsorbents

In pressure swing adsorption processes, the performance of adsorbents is evaluated using the selectivity for CO\textsubscript{2} over H\textsubscript{2}, sometimes in the presence of other gases such as CH\textsubscript{4}. In the example of a binary CO\textsubscript{2}/H\textsubscript{2} mixture, the selectivity is given by the expression:

$$S_{\text{CO}_2/\text{H}_2} = \frac{x_{\text{CO}_2} \cdot y_{\text{H}_2}}{y_{\text{CO}_2} \cdot x_{\text{H}_2}}$$  \hspace{1cm} (1)

where $x_i$ is the mole fraction of species $i$ in the adsorbed phase and $y_i$ is the mole fraction of species $i$ in the bulk gas phase.

Although the selectivity value is the most important factor for determining the purity of the respective gas phases following the separation process, another highly important metric for evaluating an adsorbent is the CO\textsubscript{2} working capacity. This parameter is evaluated by taking the difference between the quantity adsorbed at equilibrium and the quantity adsorbed at the lower purge pressure. A high working capacity is particularly favorable in that less adsorbent is needed to form the PSA bed that performs the separation, which in turn decreases initial capital costs, and more importantly, lowers the long-term energy requirements for adsorbent regeneration.

An increase in either the selectivity or the working capacity would decrease the cost of a pressure-swing adsorption-based CO\textsubscript{2} capture system and optimization of both of these parameters is essential for developing promising candidates for PSA processes.\textsuperscript{32,33}

1.2.4 Non-CO\textsubscript{2} Impurities in CO\textsubscript{2}/H\textsubscript{2} Streams

In both hydrogen purification and precombustion CO\textsubscript{2} capture applications, the two main gas components are CO\textsubscript{2} and H\textsubscript{2}. As can be seen in Tables 1.2 and 1.3, both product gases also contain CO, and in the case of steam-methane reformation CH\textsubscript{4} is also present. Thus, discovery of materials that selectively capture CO and CH\textsubscript{4} in the presence of H\textsubscript{2} is also of high importance, since the impurity gases adsorb onto surfaces less strongly than CO\textsubscript{2} and consequently break through the end of the column and contaminate the H\textsubscript{2}.\textsuperscript{34} Removing these impurities has additional relevance owing to the implications of CH\textsubscript{4} as a greenhouse gas\textsuperscript{35} and the high toxicity of CO. Other trace impurities, such as H\textsubscript{2}O and H\textsubscript{2}S, may also influence the performance of the material over time, and at the very least, and the materials should be robust towards these components. There is relatively little known regarding the effect of H\textsubscript{2}S on metal-organic frameworks, though initial studies have demonstrated strong (irreversible) adsorption within materials with exposed metal cation sites.

1.2.5 Metal-Organic Frameworks as Adsorbents for CO\textsubscript{2}/H\textsubscript{2} Separation

Metal-organic frameworks have recently been investigated as potential next-generation adsorbents for pressure-swing adsorption-based separation of CO\textsubscript{2} from H\textsubscript{2}. Their high surface areas afford enhanced gas adsorption capacities compared to the porous solids conventionally employed in multi-layer beds within current PSA systems.
namely activated carbons and zeolites, and their tunable surface chemistry is anticipated to facilitate further optimization of the material properties. Here, optimization refers to creating adsorption characteristics that are ideal for the CO\textsubscript{2}/H\textsubscript{2} separation with the aim of reducing the regeneration cost of the PSA adsorbent, while maintaining a high gas adsorption working capacity and selectivity for CO\textsubscript{2} over H\textsubscript{2}.\textsuperscript{36}

Despite the opportunity for the development of metal-organic frameworks as precombustion CO\textsubscript{2} capture adsorbents (and H\textsubscript{2} purification adsorbents), relatively few reports have emerged in this regard. Although evaluation of the performance of candidate frameworks can be well-approximated via the collection of high-pressure, single-component CO\textsubscript{2} and H\textsubscript{2} isotherms at near-ambient temperature, there are only a small number of examples where such experiments have been performed. In cases where they have been reported, the isotherms have seldom been discussed and analyzed in the context of precombustion capture. Note that in this section, we consider CO\textsubscript{2}/H\textsubscript{2} separations only in the context of pressure-swing adsorption-based processes in which the separation of the gases is achieved by a thermodynamic equilibrium that results from the bulk adsorptive properties of the material. An alternative strategy for achieving the separation would be to make use of the difference in the kinetic diameters or diffusion properties of the two molecules in a kinetic-based separation using metal-organic framework membranes. It should further be noted that, although the present discussion predominantly addresses CO\textsubscript{2}/H\textsubscript{2} separations, CO\textsubscript{2}/CO separation is also highly relevant to precombustion CO\textsubscript{2} capture and has been investigated in metal-organic frameworks.\textsuperscript{37,38} The separation of CH\textsubscript{4} and H\textsubscript{2} is also highly relevant to hydrogen purification and has been investigated in metal-organic frameworks in a number of studies.\textsuperscript{39,40,41,42}

In metal-organic frameworks there is often a trade-off between the working capacity and the selectivity since more selective materials will tend to have a steeper initial portion in the CO\textsubscript{2} isotherms ($P < 1$ bar). This leads to a lower working capacity due to the fact that the CO\textsubscript{2} adsorbed at the lowest pressures will not be removed at the purge pressure. Thus, since the working capacity is highly sensitive to the lower-pressure region of the adsorption isotherm, a single high-pressure CO\textsubscript{2} isotherm is not sufficient to evaluate a material for precombustion CO\textsubscript{2} capture.

1.2.5.1 Experimental CO\textsubscript{2}/H\textsubscript{2} Separations in Metal-Organic Frameworks

It can be expected that most metal-organic frameworks will exhibit some kind of selectivity, especially at high pressures, based simply on the polarizability of CO\textsubscript{2} compared to H\textsubscript{2} and the resulting interactions with the framework walls. This is illustrated in an otherwise non-selective carboxylate-linked ytterbium\textsuperscript{43} and indium\textsuperscript{44} frameworks.

One of the most promising avenues for CO\textsubscript{2}/H\textsubscript{2} separations is the introduction of charge polarization on metal-organic framework internal surfaces through the incorporation of coordinatively unsaturated metal centers. Chapter 2 will present the first directed, experimental study of CO\textsubscript{2}/H\textsubscript{2} separation in materials with unsaturated metal centers. Subsequent studies have shown higher strengths of adsorption for CO\textsubscript{2} than for H\textsubscript{2} in a material with unsaturated Ni\textsuperscript{2+} sites\textsuperscript{45} and Cu\textsuperscript{2+} sites\textsuperscript{46}.
As an alternative to open metal centers, two dimensional sheets of Cu-bipyridine grids pillared by SiF$_6^{2-}$ generate neutral frameworks with both high CO$_2$/H$_2$ selectivity and, because of the lack of charge separation, minimal loss of performance in the presence of water.$^{47}$ The material is interpenetrated and low surface area and the selectivity is attributed to interactions between CO$_2$ and the SiF$_6^{2-}$ pillars. A theoretical follow-up study substantiated this hypothesis.$^{48}$

1.2.5.2 Computational CO$_2$/H$_2$ Separations in Metal-Organic Frameworks

While the performance of metal-organic frameworks can be probed by collecting high-pressure CO$_2$ and H$_2$ isotherms, an alternative option for screening the vast number of materials is to simulate the adsorption of a precombustion gas mixture to predict the separation performance. This can be performed by using only the crystal structure of a porous material, making crystallography a very powerful tool in this regard. While such a methodology would allow a large number of structures to be rapidly screened, it should be noted that synthetic limitations, such as obtaining a perfectly activated sample, make theoretical results a best-case scenario that require experimental substantiation in the case of the most promising materials.

In a similar situation to the experimental studies discussed above, simulation-based investigations of CO$_2$/H$_2$ separations are also limited to a relatively small number of reports. One of the earliest reports involved a indium-based metal-organic framework, [In$_3$(abtc)$_{1.5}$(H$_2$O)$_3$](NO$_3$)$_3$3H$_2$O, consisting of 3,3',5,5'-azobenzene-tetracarboxylate (abtc) organic bridging units and charge-balancing nitrate anions in the pores.$^{49}$ The predicted selectivity for CO$_2$ over H$_2$ in a 15:80 CO$_2$/H$_2$ mixture introduced at 298 K increases from approximately 300 to 600 between 0 and 5 bar, and then gradually decreases to 450 up to 30 bar. While the authors did not report the CO$_2$ working capacity for this material, the high-pressure CO$_2$ adsorption of a 15:85 CO$_2$:H$_2$ mixture was reported and from this isotherm a maximum working capacity of 7 mmol/g can be approximated. If the nitrate anions are truly accessible to gas molecules in the experimentally prepared material, this compound would be very promising for precombustion CO$_2$ capture.

Quaternary and quinary mixtures were also simulated in this study. The quaternary mixture was composed of 15:75:5:5 CO$_2$/H$_2$/CO/CH$_4$ and the quinary mixture was 15:75:5:5:0.1 CO$_2$/H$_2$/CO/CH$_4$/H$_2$O. These were included to better model precombustion carbon capture mixtures. Both selectivity curves maintain the same shape as the binary mixture; however, the maximum selectivity drops by approximately 20 for the quaternary and another 30 for the quinary mixture. The selectivity continues to decline from 5 to 30 bar, and as such the quaternary mixture drops to approximately 375 and the quinary selectivity to 350. In the context of precombustion CO$_2$ capture, this work suggests that a modest amount of water in the gas mixture could significantly decrease the selectivity for CO$_2$ due to selective binding of H$_2$O over CO$_2$ due to its stronger polarizability. Interestingly, between 0 and 2 bar the highest selectivity was observed for the quinary mixture, which was attributed to bound water promoting the adsorption of CO$_2$.

The same 4- and 5-component mixtures were employed in evaluating a second cationic metal-organic framework with charge-balancing nitrate anions.$^{50}$ The copper-
based material, \((\text{Cu}_6\text{O}(\text{TZI})_3(\text{H}_2\text{O})_9(\text{NO}_3))\cdot15\text{H}_2\text{O}\) (TZI\(^{3-}\) = tetrazolylisophthalate), was shown to be much less selective for \(\text{CO}_2\) in both the quaternary and quinary mixtures, and the initial selectivity of ca. 42 drops to 40 at 1 bar, increases to 60 at 40 bar, and then approximately plateaus until 50 bar. The authors attributed this difference to the large pore volume.

Another tetracarboxylate-linked indium-based metal-organic framework was also investigated for \(\text{CO}_2/\text{H}_2\) separation.\(^{51}\) This anionic framework with formula \(\text{Li}_{0.5}(\text{H}_3\text{O})_{0.5}\text{[In(biphenyl-3,3',5,5'-tetracarboxylic acid)]}\) contains charge-balancing \(\text{Li}^+\) cations in the pores, which are shown to be the primary binding site for \(\text{CO}_2\). The selectivity for \(\text{CO}_2\) in a 15:85 \(\text{CO}_2/\text{H}_2\) mixture decreases from 1100 to 600 between 0.01 and 1 bar, increases up to 600 at 10 bar, and then decreases back down to 500 at 50 bar (Figure 1.5). These three regions are attributed to strong binding sites becoming unavailable with increasing \(\text{CO}_2\) loading, followed by cooperative \(\text{CO}_2-\text{CO}_2\) interactions becoming predominant, and lastly the entropic favorability of \(\text{H}_2\) binding at high pressures. This entropic effect has been observed previously for other porous materials.\(^{52}\)

![Figure 1.5 Selectivities calculated from simulations for a 15:85 CO\(_2\)/H\(_2\) mixture at 298 K in \(\text{Li}_{0.5}(\text{H}_3\text{O})_{0.5}\text{[In(C}_16\text{H}_6\text{O}_8])\) shown with (solid line) and without (dashed line) inclusion of electrostatic interactions. Reproduced with permission from Reference 51. Copyright 2011 American Chemical Society.](image)

Simulations for \(\text{CO}_2/\text{H}_2\) separations were further reported within the indium-based metal-organic framework, \(\text{In}_{48}(4,5\text{-imidazoledicarboxylate})_{96}\text{Na}_{48}(\text{C}_2\text{H}_5\text{OH})_{96}(\text{H}_2\text{O})_{192}\).\(^{53}\) This framework is anionic and contains charge-balancing \(\text{Na}^+\) cations in the pores which bind \(\text{CO}_2\) strongly and preferentially. Only at high pressures when the cations are completely solvated by \(\text{CO}_2\) does the \(\text{CO}_2\) begin to bind at other surfaces. This strong \(\text{Na}^+-\text{CO}_2\) interaction leads to an initial selectivity of 200 at 10 bar which remains steady until 30 bar for a 15:85 \(\text{CO}_2/\text{H}_2\) mixture. A maximum working capacity of 4 mmol/g can be estimated from the high-pressure \(\text{CO}_2\) adsorption of a 15:85 \(\text{CO}_2/\text{H}_2\) mixture. This is approximately half that of other metal-organic frameworks with exposed metal sites. Interestingly, the \(\text{Na}^+\) cations shift locations slightly with \(\text{CO}_2\) adsorption.
The effect of replacing the hydrogen atoms on benzenedicarboxylate in Zn₄O(bdc)₃ with O⁻⁻⁻Li⁺ groups was studied computationally. Upon exposure to a 20:80 CO₂/H₂ mixture, this structure reaches predicted CO₂/H₂ selectivities of 10,000 at infinite dilution, compared to approximately 10 for unmodified Zn₄O(bdc)₃. This was determined to be solely from electrostatic interactions by turning these forces off and examining the changes in selectivity.

The selectivity for CO₂ in a 50:50 CO₂/H₂ mixture in a material with coordinatively unsaturated Cu²⁺ sites, Cu₃(btc)₂ and Zn₄O(bdc)₃ (Figure 1.3) were compared via simulations. In Zn₄O(bdc)₃, the authors found that the selectivity slowly increases from less than 10 to approximately 30. A selectivity curve similar to In₄₈(4,5-imidazolodicarboxylate)₉₀Na₄₈(C₂H₅OH)₉₀(H₂O)₁₉₂ is seen in Cu₃(btc)₂, with an initial decrease from 100 to 80 by 1 bar, an increase to 150 by 15 bar, and then a decrease to 100 at 50 bar. The last decrease is ascribed to the favorable packing of the small hydrogen molecules when gas molecules are filling the pores, as opposed to physisorption onto the surface. This effect is not seen in Zn₄O(bdc)₃, because at 40 bar the pores are not fully occupied. The authors also compared these selectivities to those generated using IAST and found that for Zn₄O(bdc)₃ the prediction is reasonably accurate, but in Cu₃(btc)₂, IAST underestimates the selectivity with a drop from 100 at 0 bar to 70 at 50 bar. An additional insight was the composition-dependence of selectivity, which was shown to be minimal as the selectivity did not change more than 10% upon increasing the amount of CO₂ in the mixture from 10% to 90%.

A compound with a neutral framework structure, Co₂(adenine)₂(CO₂CH₃)₂⋅2DMF⋅0.5H₂O was studied theoretically for pure-component CO₂ and H₂ adsorption and a 15:85 CO₂/H₂ mixture. Radial distribution functions demonstrated that CO₂ binds at Lewis basic sites of the adenine linker, and not near the framework cobalt atoms. The selectivity of the gas mixture increases from 270 to 370 between 0 and 5 bar, then decreases to 220 at 30 bar. The addition of 0.1 mol% H₂O to the mixture had a negligible effect on the selectivity, in contrast to the results of the cationic materials discussed above.

Some researchers have focused on comparing groups of porous solids to extract meaningful trends in CO₂/H₂ separations. Simulated breakthrough curves of CH₄/H₂, CO₂/H₂, and CO₂/CH₄/H₂ mixtures of five metal-organic frameworks as well as a common zeolite were reported. A packed bed of metal-organic framework was simulated and both the composition of the gas mixture exiting the bed as a function of time and the amount of CO₂ adsorbed were evaluated. The metric τ break, the time at which a specified fraction of impurity (either CO₂ or CH₄) is present in the gas leaving the bed, was used to characterize the adsorbents. In terms of τ break and the amount of CO₂ adsorbed at τ break, a framework with coordinatively unsaturated Mg²⁺ sites was determined to be the best material of those studied (Figure 1.6). Note that this method provides an important means of ranking materials via a single metric, which takes into account both selectivity and working capacity.

The effect of interpenetration on CO₂/H₂ selectivity was examined computationally and it was found that catenated Zn₄O(bdc)₃ analogues are much more selective than the non-interpenetrated materials. Looking at five different mixture compositions (5:95, 30:70, 50:50, 70:30, and 95:5 CO₂/H₂), the interpenetrated metal-organic frameworks all displayed selectivities between approximately 40 and 110,
whereas the three non-interpenetrated materials were much lower (below 20). The shapes of the selectivity curves differed for the different compositions, with the three steps discussed above for Li$_{0.5}$(H$_3$O)$_{0.5}$[In(abtc)] becoming more apparent with more CO$_2$ in the mixture. This substantiates the attribution of CO$_2$-CO$_2$ interactions to the increase in selectivity after an initial decrease, as this increase is not apparent in the 5:95 CO$_2$/H$_2$ mixture. Furthermore, turning off electrostatic interactions between CO$_2$ molecules only resulted in the loss of this feature in the selectivity trace. The adsorption sites of the gas molecules of the mixture gas demonstrated that selective CO$_2$ adsorption happens in the small channels of the interpenetrated frameworks.

**Figure 1.6** Amount of CO$_2$ adsorbed as a function of breakthrough time ($\tau_{\text{break}}$), where the breakthrough concentration of CO$_2$ is 0.05% and the conditions are 313 K, 48 bar adsorption and 12 bar desorption pressures. Reproduced with permission from reference 34. Copyright 2011 American Chemical Society.

The CO$_2$/H$_2$ selectivity was compared between two Zn$^{2+}$-based imidazolate-bridged materials and of Zn$_4$O(bdc)$_3$ analogues. In a 10:90 mixture of CO$_2$/H$_2$, the imidazolate frameworks had selectivities in the 100-200 range, while the (bdc) frameworks varied between 7 and 12. The difference in selectivity between the two classes of frameworks was attributed to the smaller pore size in the imidazolate materials and confinement effects, which is a result of the higher degree of overlap of the van der Waals forces associated with opposing wall surfaces.

In a separate study, six metal-organic frameworks were compared to six covalent-organic frameworks (COFs). These are porous crystalline solids that consist of only covalent bonds and are typically assembled from the co-condensation of boronic acids. The six COFs studied are very similar with respect to their properties since they are composed of the aromatic units connected by boron oxide rings. These were compared to Zn$_4$O(bdc)$_3$ analogues and Cu$_3$(btc)$_2$. One of the COFs and Cu$_3$(btc)$_2$ were found to have substantially higher selectivities due to the presence of small pores and open Cu$^{2+}$ sites, respectively.
A compilation of previously published data obtained from configurational-bias Monte Carlo (CBMC) simulations compared metal-organic frameworks and zeolites. The results showed that based on both selectivity and capacity a material with open Mg$^{2+}$ sites that is discussed in detail in Chapter 2 is a clear frontrunner for CO$_2$/H$_2$ separations.

1.2.5.3 Conclusions and Outlook

Taking all of the simulation work published to date relating to metal-organic frameworks for precombustion CO$_2$ capture into consideration, open metal sites and small pores that take advantage of van der Waals overlap are the most promising avenues for study. Strategies for (1) maximizing open metal site-CO$_2$ interactions by changing the identity of the metal or the density of metal sites in the material, (2) optimizing pore size constraints, or (3) experimentally realizing some of the promising theoretical work are strong future directions for this research.

1.3 Hydrocarbon Separations in Metal-Organic Frameworks

Hydrocarbon mixtures are separated into various component fractions on enormous scales for the production of fuels and chemical feedstocks. Owing to the high energy costs associated with many of these critical separation processes, the development of metal-organic frameworks that could enable efficient adsorptive separations represents an exciting new direction of study. In this chapter, the goal is to be inclusive of all adsorbates composed of only carbon and hydrogen atoms, focusing exclusively on these adsorbates and reporting on all types of hydrocarbon mixtures. The use of metal-organic frameworks within membranes or as components in capillary columns is not treated.

Nearly all hydrocarbons are generated from petroleum or natural gas processing. Natural gas, which is primarily methane, also contains ethane, propane, and butanes. Petroleum can be composed of hundreds of thousands of chemicals, and varies in its composition between 50 and 97 wt % hydrocarbons. Petroleum is divided into fractions based upon boiling points: butanes and lighter, gasoline, naphtha, kerosene, gas oil, and residue. Compositions among these fractions vary widely. The liquids and gases discussed in this review mostly fall into the light gas, gasoline, or naphtha fractions, although adsorption of some longer alkane kerosene components have been reported and are included.

Improvements in separation efficiency and investigations of separations that have not yet been reported provide a strong motivation for studying the behavior of hydrocarbon molecules within porous materials. In particular, the extraordinary chemical tunability of the pore geometry and surface functionality within metal-organic frameworks can facilitate control over adsorption selectivity, while their high surface areas generally give rise to a large separation working capacity. Both the most fundamental separations, such as methane/ethane separations, and more esoteric separations have already been investigated to a considerable extent within metal-organic frameworks. While estimating a priority order for industrial relevance is challenging, the separation of essentially all hydrocarbons generated within the same petroleum fraction...
can be considered both industrially relevant and a tool for better understanding the separation abilities of metal-organic frameworks.

Here, we will focus on how the variations within such structures can lead to the facile separation of various important hydrocarbon mixtures. Concepts related to adsorptive separations such as distinctions among isotherm types,\textsuperscript{17} calculating enthalpy of adsorption,\textsuperscript{17} and ideal adsorbed solution theory (IAST)\textsuperscript{84} are explained in detail elsewhere. In addition, it should be noted that the physical properties of most of the adsorbates found in this review have been tabulated.\textsuperscript{65} Throughout the body of the text, all studies are experimental results unless otherwise specified.

1.3.1 Saturated Hydrocarbon Mixtures

Normal alkanes can be found in petroleum from trace levels to up to 50 wt % of the hydrocarbon content. Methane through \textit{n}-decane are relevant as gasoline components, while alkanes up to C20 are present in kerosene.\textsuperscript{85} Ethane is a feedstock for ethylene plants, while propane and butanes are feedstocks for chemicals or petroleum refining processes. Longer normal alkanes are further reacted either in catalytic reforming or isomerization because their low octane numbers make them of little value other than as niche feedstocks.\textsuperscript{82,86}

To explain the results presented for linear alkane separations within metal-organic frameworks, some broad theories are under development and investigation. In Zn$_4$O(bdc)$_3$ and PCN-6', a “clustering” phenomenon has theoretically been shown to occur below the critical temperature of an adsorbate, which strongly affects the selectivity of linear alkanes, especially when the temperature of separation is above the critical temperature of one adsorbate and below that of another.\textsuperscript{17} Further, a general trend is seen in which stronger adsorption is usually coupled to an entropic cost as it leads to a loss in degrees of freedom.\textsuperscript{87}

1.3.1.1 Short Normal Alkanes

Given its high surface area and thermal stability, Zn$_4$O(bdc)$_3$ (Figure 1.3) serves as an excellent platform for the adsorption of short chain hydrocarbons.\textsuperscript{88-92} A theoretical study demonstrated that the van der Waals interactions with the pore surfaces enforce a trend of both the enthalpy and entropy of adsorption becoming more negative with increasing chain length.\textsuperscript{93} An adsorption step in the isotherms is seen at increasing pressures for smaller alkanes, and these adsorbates boast a higher capacity as well. In a mixture, the more strongly adsorbing, longer alkanes are preferred until the selectivity reaches a maximum, when the entropic cost of ordering the long adsorbates overcame the enthalpic benefit to adsorption (Figure 1.7). Similar results were seen experimentally.\textsuperscript{87}

The separation of methane from \textit{n}-butane was also investigated computationally for five materials isostructural to Zn$_4$O(bdc)$_3$, wherein the bdc$^{2-}$ linker was replaced with multi-ring dicarboxylate ligands.\textsuperscript{94} Up to 40 bar, methane exhibits a typical Type I isotherm that does not saturate, while \textit{n}-butane isotherms all show a pronounced capillary condensation step that occurs at different pressures depending on the linker length. Generally, increasing the length of the linker leads to decreased selectivity. However, the framework containing 9,10-anthracene dicarboxylate, which has the same length as bdc$^{2-}$
but more aromatic surfaces lining the pores, was found to exhibit selectivities an order of magnitude higher than that of Zn₄O(bdc)₃.

The strength of adsorption is more than double for n-butane than for methane in both Zn₄O(bdc)₃ (–23.6 and –10.6 and kJ/mol, respectively) and Cu₃(btc)₂ (Figure 1.3) (–29.6 and –12.0 kJ/mol, respectively). Many theoretical alkane separation processes have also shown similar results Cu₃(btc)₂. 80-90,96-98

![Figure 1.7 Theoretically-determined adsorption isotherms of linear alkanes in Zn₄O(bdc)₃ at 300 K. Reprinted with permission from Reference 93. Copyright 2006 American Chemical Society.](image)

Adsorption strengths for methane, ethane, propane, and butane in MIL-47 (Figure 1.3) increase with chain length, and pairing theory with experiment suggests that no preferential binding sites exist within the pores at low loadings. At high loadings, methane and ethane prefer the μ₂-O groups while n-butane prefers the aromatic linkers. Propane and ethane were shown to rotate freely and have no preferred orientation, while n-butane is more confined.

Differences in adsorption behavior among linear alkanes is also seen on MIL-53(Cr) (Figure 1.3), where at 303 K a step is observed in the adsorption of n-propane through n-nonane, but not for methane or ethane. Powder diffraction data suggest that this step is associated with framework swelling. Structural transitions occur as a result of the relative affinities of any guest for the open or closed forms of the structure. Generally, alkane adsorption in the MIL-53 series, including amino-MIL-53, is highly temperature dependent due to the thermodynamics of the framework breathing. Interestingly, despite their isostructural nature the same steps seen in MIL-53(Cr) arise in MIL-53(Al) at different pressures.

Adsorption isotherms for C₁-C₄ gases in MIL-53(Fe) are much more complex than in the MIL-47 or MIL-53(Al, Cr) cases. At 303 K, MIL-53(Fe) has two intermediate phases in addition to the completely open or completely closed structures available in MIL-53. This difference leads to stepwise adsorption of all short alkanes as opposed to those with three carbons and higher.
Highly flexible materials outside of the MIL series can exhibit similar behavior to the MIL-53 frameworks. In the flexible framework material Zn$_2$(bpdc)$_2$(bpee) (bpdc$^{2-}$ = 4,4′-biphenyldicarboxylate; bpee = 1,2-bipyridylethylene), the gate opening pressure decreases with alkane size from n-butane to methane.$^{107}$

In ZIF-8 (Figure 1.3), the capacity hierarchy for short alkanes is methane > ethane > propane > n-butane.$^{108}$ In ZIF-7, which is built from benzimidazole in contrast to the 2-methylimidazole linkers of ZIF-8, ethane, propane, and n-butane show gate-opening pressures of 0.12, 0.012, and 0.008 bar, respectively, at 298 K.$^{109}$ This demonstrates that adsorption strength is inversely correlated with gate-opening pressure. The compound Ni$_{18}$(5-bbdc)$_6$(µ$_3$-OH)$_4$ (bbdc$^{2-}$ = 5-tert-butyl-1,3-benzenedicarboxylate) can also discriminate methane/ethane or ethane/propane mixtures based on gate-opening phenomena, and, by carefully controlling the temperature, it is possible to separate methane and ethane from propane and butane, or separate methane from ethane, propane, and butane.$^{110}$

To summarize, trends can be found among short normal alkane adsorption in metal-organic frameworks. Adsorption steps are often seen, either from a gate-opening step in the material or from capillary condensation within the pores. These steps occur at different pressures for different adsorbates. Additionally, the molar capacity is usually comparatively higher for shorter alkanes while the strength of adsorption is lower. The smaller size allows for more molecules to fit in the pores, but each adsorbate has less molecular surface area for van der Waals interactions. Due to the variety of adsorption step locations as well as the consistent thermodynamic behavior of adsorption, it can be assumed that metal-organic frameworks could be used to separate many more mixtures of linear alkanes than even the ones reviewed here.

1.3.1.2 Long Normal Alkanes

The same trends and behaviors seen for shorter normal alkanes extend to longer normal alkanes, as does the conclusion that most separations are possible using metal-organic frameworks. These studies of longer alkanes reported here are all at temperatures between 294 and 313 K in metal-organic frameworks with rigid structures.

The strength of adsorption between longer alkanes and the surfaces of metal-organic frameworks is generally correlated with the potential for van der Waals interactions. Accordingly, the reported strengths of adsorption followed the order n-pentane > propane > butane in Zn$_2$(bdc)$_2$(dabco) (dabco = 1,4-diazabicyclo[2.2.2]octane), which has a structure in which two-dimensional sheets of bdc$^{2-}$-linked zinc-paddlewheel units are pillared by dabco.$^{111}$ This trend can presumably explain the behavior of an analogous framework, Zn$_2$(bdc)$_2$(bpy) (bpy = 4,4′-bipyridine), which can separate n-pentane from n-hexane.$^{112}$ Similarly, a porphyrin-linked covalent polymer, PCPF-1, demonstrates linearly increasing adsorption capacities for C5-C8 linear hydrocarbons.$^{113}$

Comparisons among adsorbents rather than adsorbates also confirms the role of van der Waals forces in alkane separations. The adsorption of pentane, hexane, and heptane in Zn$_4$O(bdc)$_3$ is weaker than in Zn$_4$O(bdc)$_3$ isostructures with longer linkers owing to the fewer available van der Waals interactions with each individual linker.$^{88}$

Mechanisms other than thermodynamic selectivities have also been shown to separate long alkanes. As alkanes increase in length, pore size can begin to dictate
differences in adsorption. A metal-organic framework with cylindrical channels and small channel windows, \( \text{Cu}(\text{hfipbb})(\text{H}_2\text{hfipbb})_{0.5} \) (\( \text{H}_2\text{hfipbb} = 4,4'\)-hexafluoroisopropylidine)bis(benzoic acid)), can selectively sieve linear hydrocarbons longer than butane, as modeling shows that the corrugations along the channels creates pockets which can accommodate short alkanes but not \( n \)-pentane or higher.\(^{114}\)

While \( \text{Cu}(\text{hfipbb})(\text{H}_2\text{hfipbb})_{0.5} \) has uniform pores, separate types of pores within the same material can also dictate separation. The differences in adsorption of C5-C9 linear alkanes were explored in MIL-100(Cr) and MIL-101(Cr),\(^{115}\) and adsorbates exhibit a small adsorption step only apparent at low pressures. In MIL-100, this was attributed to the filling of the smaller of the two types of pores in the material based upon the percentage each contributed to the total volume. In both materials, \( n \)-nonane was adsorbed significantly less than the smaller alkanes due to entropic effects.

MIL-47, MIL-53(Cr), and a series of flexible MIL-88(Fe) structures have been investigated for longer alkane adsorption and separation. Increasing the alkane chain length leads to a decrease in the molar uptake capacity for MIL-47 and MIL-53.\(^{116,117,118}\) The MIL-53 isotherms show a distinct step that occurs at a lower pressure for \( n \)-nonane compared to \( n \)-hexane, and similar results were seen with the MIL-88(Fe) materials. Interestingly, simulations illustrate that shorter alkanes are more distorted from a traditional \textit{trans} conformation in MIL-47.\(^{119}\)

Changes in adsorption attributed to flexibility are not confined to the MIL-53 series. A flexible material TetZB constructed from zinc nodes, 4,4'‐bipyridine, and tetrakis[4-(carboxyphenyl)oxamethyl]methane is an open pore structure when evacuated and closes upon initial alkane adsorption.\(^{120}\) Comparing among normal alkanes, the adsorption step moves to higher pressures for longer hydrocarbons. This is in contrast to other stepwise adsorption behavior in metal-organic frameworks such as \( \text{Zn}_4\text{O(bdc)}_3 \),\(^{88}\) and industrially this reversal could render TetZB an ideal material for a specific set of separation conditions.

### 1.3.1.3 Cyclic Alkanes

Cyclic alkanes, often referred to as naphthenes, such as cyclohexane, decalin, and terpenes compose up to 60% of the hydrocarbon content in petroleum.\(^{82}\) They are produced as part of the cracking process. They have varying industrial utility, for example cyclohexane and cyclododecane are used industrially, while cyclopentane is not.

Generally, linear alkanes bind more strongly than their cyclic counterparts in metal-organic frameworks. Presumably, this is a result of linear alkanes maximizing van der Waals surface overlap, whereas cycloalkanes have geometric restrictions to adsorption. The strength of adsorption of \( n \)-hexane is significantly higher than that of cyclohexane in MIL-100(Fe) and MIL-100(Cr),\(^{121}\) MIL-47,\(^{116}\) \( \text{M(bdc)(ted)}_0.5 \) (\( \text{M} = \text{Zn}, \text{Cu} \)) (ted = triethylenediamine),\(^{122}\) and amino-MIL-53.\(^{104}\)

The large pore surfaces of \( \text{Zn}_3\text{O(bdc)}_3 \) only vaguely follow the above trend. Theoretically, \( \text{Zn}_3\text{O(bdc)}_3 \) adsorbs \( n \)-decane only approximately 10% more strongly than butylcyclohexane.\(^{82}\) Cyclohexane and \( n \)-hexane bind with the same adsorption strength, while the larger dipole moment of methylcyclohexane leads to a 10% stronger interaction. In contrast, lower-surface area isostructures of \( \text{Zn}_4\text{O(bdc)}_3 \) with more bulky
and longer linkers, show a strength of adsorption much higher for \(n\)-hexane than cyclohexane.\(^{87}\)

Capacities of linear and cyclic alkanes do not necessarily follow as predictable of a trend as adsorption strength: the capacity for cyclopentane and \(n\)-pentane are comparable in the porphyrin-linked covalently polymer PCPF-1, while the cyclohexane capacity is nearly 50% higher than the \(n\)-hexane capacity.\(^{113}\)

### 1.3.1.4 Branched Alkanes

The separation of branched and linear alkanes is highly relevant to gasoline production. Octane number, which is proportional to economic value, is higher for branched isomers than for linear alkanes. For \(C_5\), \(C_6\), and \(C_7\) hydrocarbons, the mixture from the distillation unit is fed into an isomerization reactor, which transforms the mixture into equilibrium ratios of the isomers. The less valuable linear isomers are removed by sieving and fed back into the isomerization unit, while the rest of the isomers are added to gasoline.\(^{123}\) \(n\)-Butane is used to generate isobutane, which is then used in alkylation reactions to generate higher-octane chains.\(^{124}\)

Separation of linear alkanes from their branched counterparts has been reported in metal-organic frameworks. Binary \(C_4\) and \(C_5\) isomer mixtures were investigated computationally in \(\text{Zn}_4\text{O}\text{(bdc)}_3\) and one of its isostructures with an amino group on the central benzene ring of the linker. The branched isomers exhibited higher uptake capacities than the linear isomers.\(^{125}\) Small differences in adsorption enthalpy between a linear and branched isomers are seen both experimentally and theoretically in \(\text{Cu}_3\text{(btc)}_2\) and \(\text{Zn}_4\text{O}\text{(bdc)}_3\) (Figure 1.3),\(^{93,95}\) and some metal-organic frameworks can sieve linear alkanes from their branched isomers.\(^{114,116}\)

The separation of linear from branched alkanes does not necessarily improve upon existing technology, as zeolites currently perform these separations with a sieving mechanism. Separation among the branched isomers, however, represents a new frontier in this (non-distillative) technology. Importantly, among non-linear alkanes, more branching is associated with a higher octane number and value. This type of separation is illustrated in Figure 1.8(b). Ideally, the separation will generate fractions according to branching, as seen in the schematic, but two fractions composed of the most valuable dibranched isomers and all of the lesser valuable isomers together is also an advance in this technology. The tunable pore surface geometries in metal-organic frameworks allow for shape selectivity and therefore advances in this separation.

Modeling studies demonstrate the promise of metal-organic frameworks for shape-selective isomer separations. Calculations show \(\text{Zn}_4\text{O}\text{(bdc)}_3\) to be capable of separating all three pentane isomers at 300 K.\(^{93}\) The linear isomers were found to adsorb near the vertices, while the branched ones were sterically hindered from doing so. Similarly, the isomers of butane and pentane were modeled in two pairs of comparable metal-organic frameworks.\(^{126}\) An isostructure to \(\text{Zn}_4\text{O}\text{(bdc)}_3\) with a pyrene-derived linker, IRMOF-14, and its catenated counterpart were one pair. The other pair was again catenated and non-catenated versions of the same material, here an isostructure to \(\text{Cu}_3\text{(btc)}_2\) with a triazine-tribenzoate linker. In the 20 total isotherms (five adsorbates in four materials), all showed stepwise adsorption. Contrary to previous results,\(^{96}\) the
Two-dimensional sheets composed of zinc paddlewheels pillared by nitrogen-donor ligands have been extensively studied for branched isomer separations. In a five-component breakthrough experiment in which a mixture of n-pentane, 2-methylbutane, 2,2-dimethylbutane, 2-methylpentane, and n-hexane was passed through a column of Zn$_2$(bdc)$_2$(bpy), only 2,2-dimethylbutane and 2-methylpentane showed any overlap.$^{112}$ A 13-component mixture of pentane, hexane, and heptane isomers was simulated in the pores of a similar material, Zn$_2$(bdc)$_2$(dabco).$^{127}$ With the exception of 2,3-dimethylpentane, the adsorbates followed a general trend of higher octane numbers achieving lower uptake capacity. This was explained with the concept that more flexible alkanes were able to “adapt” to the pore environment and utilize the available surface area more effectively. Experimentally, Zn$_2$(bdc)$_2$(dabco) has been shown to separate n-hexane, 3-methylpentane, and 2,2-dimethylbutane.$^{128}$

In addition to canonical materials such as Zn$_4$O(bdc)$_3$, Cu$_3$(btc)$_2$, and the group of pillared frameworks covered above, other metal-organic frameworks have been studied in isolation. Amino-MIL-53(Al) was demonstrated to separate pentane, hexane, and heptane isomers through a shape selective mechanism.$^{104}$ This conclusion was arrived at by examining the non-linearity of the relationship between vapor pressure and Henry’s constants, which has previously been demonstrated to correlate with shape selectivity. Additionally, single-component isotherms in Zn(IIbdc)(dmtrz)(dmtrz = 3,5-dimethyl-1H, 1, 2, 4-triazole) suggest that the material is selective for n-hexane and 3-methylpentane over 2,2-dimethylbutane.$^{129}$ A variety of hexane binary breakthrough experiments were performed at 398 K on ZIF-76, ZIF-8, and IM-22, a material designed specifically for alkane isomer separations.$^{130}$ Among these materials, the best performance was seen in IM-22 which achieved a modest separation of 3-methylpentane from 2,2-dimethylbutane.

The above examples illustrate the preferred elution order for branched alkane separations, where more branched alkanes elute first. This is because isolating the least adsorbed species is more straightforward than isolating the most adsorbed isomer. This order is not always observed, as seen in UiO-66.$^{131}$ Based on the pore size, the order of elution in a breakthrough column is n-hexane, followed by 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane. The separation is not complete, however. Modifications to this material can be made which effect its performance; Decorating the linker with functional groups changes the pore size and alters the order of elution.$^{132}$

The above examples illustrate marked improvements in alkane isomer separations over zeolites; however, none offer a complete separation of the considerably more valuable highly branched isomers from the less branched. In contrast, it has been shown experimentally that the five hexane isomers can be separated into useful fractions on a column of Fe$_2$(BDP)$_3$ (BDP$^{2-}$ = 1,4-benzenedipyrazolate), a metal-organic framework with triangular channels (Figure 1.3).$^{129}$ Chapter 5 details the promising experimental separation of pentane, hexane, and heptane isomers in Fe$_2$(BDP)$_3$.

Computationally, over 100 metal-organic frameworks have been examined for hexane and heptane isomer separation at 433 K.$^{133}$ By examining both the uptake capacity and selectivity for branched over linear isomers—metrics that are explained to be equally important to the engineering separation process—the authors were able to discover that ZIF-77, a rarely discussed metal-organic framework, is particularly well
suited for separating dibranched from monobranched from linear isomers. Potentially, these results could be verified experimentally and compared to those of Fe₂(BDP)₃.

The above examples all pertained to gasoline. Similarly, in diesel fuel longer alkanes such as cetanes (16 carbon chains) have variable worth in the final product.¹³⁴ *n*-Hexadecane is much more valuable than its isomer 2,2,4,4,6,8,8-heptamethylnonane (isocetane),¹³⁵ and these isomers can be separated by sieving in Zn₂(adc)₂(dabco) (adc²⁻ = 9.10-anthracenedicarboxylate).¹³⁶

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**Figure 1.8** (a) The breakthrough results of hexane isomers on a column of Fe₂(BDP)₃. (b) Schematic demonstrating the separation process possible when the separation generates fractions according to the degree of branching. (ON = octane number)."
1.3.2 Unsaturated Hydrocarbons

Although alkenes are generally not present in petroleum\textsuperscript{82} they can be found in distilled fractions as a result of the cracking that occurs during distillation. They are also synthesized from a variety of reagents and used as extremely important industrial precursors, mostly for making polymers. For example, nearly 25 trillion tons of ethylene are generated per year, and the vast majority of the cost of production is in separation from other hydrocarbons.\textsuperscript{137}

Below, the treatment of metal-organic frameworks for separations involving unsaturated hydrocarbons is subdivided into four categories. Some examinations do not fall neatly into one of these categories, such as the adsorption of propylene, isobutene, and propane in Cu\textsubscript{3}(btc)\textsubscript{2} (Figure 1.3)\textsuperscript{138-140} and MIL-100(Fe),\textsuperscript{141} the adsorption of methane, acetylene, ethylene, and propane in a novel covalent-organic framework\textsuperscript{142} and acetylene/ethylene separation in an enantiopure metal-organic framework.\textsuperscript{143}

Of metal-organic frameworks that boast impressive alkane/alkene separation abilities, two main strategies can be seen: sieving and adsorption onto unsaturated metal centers. Sieving materials such as ZIF-8 selectively adsorb the alkane, while unsaturated metal centers preferentially interact with the alkene or alkyne through interaction with the \(\pi\)-system.\textsuperscript{144,145} These unsaturated metal centers are found in the M\textsubscript{2}(dobdc) series, however other materials such as MIL-100(Fe)\textsuperscript{146} and Cu\textsubscript{2}L(H\textsubscript{2}O)\textsubscript{2} (L\textsuperscript{4-} = biphenyl-3,3',5,5'-tetracarboxylate)\textsuperscript{147} can also interact strongly with double bonds in a side-on fashion to generate strong selectivities. The identity of the metal center can alter the separation ability, and generally softer metals interact more strongly with double bonds.

In each of the sections below considering C1, C2, and C3 alkene/alkane separations, the remarkable separation results of Fe\textsubscript{2}(dobdc) are presented.\textsuperscript{148} Neutron diffraction studies of methane, acetylene, ethane, ethylene, propane, and propylene not only show verifiably the side-on binding of the double bond to the metal center, but also the short distances between the hydrogen atoms and the Fe\textsuperscript{2+} cations for the unsaturated adsorbates (Figure 1.9). Computational modeling has confirmed these results.\textsuperscript{149}

1.3.2.1 Methane/Acetylene

Acetylene is typically viewed as less industrially relevant than ethylene,\textsuperscript{150} and can be obtained as a byproduct of petroleum and natural gas processing.\textsuperscript{86} Additionally, a number of industrial processes exist for the oxidative and non-oxidative coupling of methane into ethane, ethylene, and acetylene, although many of these processes realize incomplete methane conversion. Thus, there is a clear benefit to recovering unreacted methane from these processes. Given the large differences in the physical properties of methane and C2 hydrocarbons, both size selective effects and metal-hydrocarbon interactions can be tuned to achieve a high selectivity within a metal-organic framework.

There have been a number of recent reports investigating methane/acetylene separations with metal-organic frameworks.\textsuperscript{151-164} The earliest was in Cu\textsubscript{3}(EBTC) (EBTC\textsuperscript{4-} = 1,1'-ethylenbenzene-3,3',5,5'-tetracarboxylate).\textsuperscript{151} This framework boasts a high surface area and open Cu\textsuperscript{2+} sites similar to those found in Cu\textsubscript{3}(btc)\textsubscript{2} (Figure 1.3), and an acetylene uptake capacity (252 cm\textsuperscript{3}/g) nearly ten times higher than that of methane at
295 K. The strength of acetylene adsorption in this material is substantially higher than in Cu₃(btc)₂ as well as another material with open Cu²⁺ binding sites MOF-505). This is likely a combined result of Cu²⁺-acetylene interactions, pore size and geometry, and a weak interaction between the carbon-carbon triple bond of EBTC⁴⁻ and acetylene.

A majority of the subsequent studies of methane/acetylene separations have involved low-surface area frameworks (< 700 m²/g BET), often materials exhibiting interpenetration. These materials typically suffer from capacity limitations. For example, Zn₅(bta)₆(tda)₂ (bta⁻ = 1,2,3-benzenetriazolate, tda⁻ = thiophene-2,5-dicarboxylate), displays a selectivity of 15.5 for an equimolar acetylene/methane mixture at 295 K, but an acetylene capacity of just 44 cm³/g at 1 bar.

In contrast, compounds of the type M₂(dobdc) couple selectivity for adsorption with high surface area and a high density of open metal sites. For example, Fe₂(dobdc) displays an acetylene/methane adsorption selectivity of approximately 700 at 1 bar and 318 K (from an equimolar mixture of methane, ethane, ethylene, and acetylene). This is a direct result of the large difference in the isosteric heat of adsorption between the two molecules (–42 kJ/mol vs. –20 kJ/mol). Additionally, both Mg₂(dobdc) and Co₂(dobdc) are well-suited for the separation of acetylene and methane. Both frameworks bind acetylene with more than twice the adsorption strength of methane. Calculations indicate that these frameworks will perform well in the separation of methane from an equimolar methane, ethane, ethylene, acetylene mixture at 296 K and 1 bar of total pressure. On a volumetric basis, they outperform nineteen other frameworks investigated, as well as materials with open Cu²⁺ sites such as MOF-505, Cu₃(btc)₂, and PCN-16.

1.3.2.2 Ethane/Ethylene

Ethylene is generated primarily by refining crude oil, and over 10⁸ tons of it were produced in 2005. After the cracking process, the series of separations to isolate ethylene from the dozens of other hydrocarbons present are incredibly complex. Ethane is an important feedstock for ethylene production, and as a result the separation of ethylene from ethane is of great industrial relevance.

Sieving in metal-organic frameworks can enable the discrimination of ethane and ethylene. The compounds ZIF-7 and ZIF-8 illustrate this concept. The adsorption isotherms for ethane and ethylene in ZIF-7 at 298 K are Type IV, with negligible uptake until a “gate-opening” event, after which uptake rapidly increases and quickly saturates at approximately 1.75 mmol/g. The three regions of the adsorption isotherm are explained as adsorption to the external surface of the particles, gate opening and adsorption in the cavities of the material, and, finally, filling of the cavities with adsorbate. The pore apertures in ZIF-7 of ~3Å are too small to allow adsorption of either molecule and significant structural flexing must take place for adsorption to occur. It has been postulated that the threefold symmetry of the methyl groups of ethane allows the molecule to interact favorably with the triangular pore windows of the framework. This allows ethane to adsorb at lower pressures than ethylene. Accordingly, ZIF-7 performed well in an actual separation process, producing pure ethylene from an equimolar mixture.
in a breakthrough experiment. Similarly, ZIF-8 selectively adsorbs ethane over ethylene.\textsuperscript{79,172,173}

Thermodynamic separations of ethane and ethylene can also be achieved in metal-organic frameworks. Ethane and ethylene are equally polarizable, lack a dipole moment, and have small quadrupole moments,\textsuperscript{65} and therefore metal-organic frameworks with exposed cation sites are one of the few attractive options for their efficient separation. Frameworks without this feature adsorb ethane and ethylene with nearly identical adsorption enthalpies, including Zn\textsubscript{4}O(bdc)\textsubscript{92} and amino-MIL-53,\textsuperscript{104} and an entire series of zinc carboxylate frameworks that have been extensively studied for this application.\textsuperscript{147,161,165-167}\textsuperscript{160}

The first investigation into metal-organic frameworks with open metal sites for ethane/ethylene separations was performed with Cu\textsubscript{3}(btc)\textsubscript{2},\textsuperscript{96} and has been followed up computationally.\textsuperscript{174,175} The noticeable difference in the shapes of the isotherms indicate ethylene selectivity. Subsequent calculations showed that ethylene binds stronger than ethane based on both hydrogen bonding interactions between the $-\text{CH}_2$ protons and the electronegative oxygen atoms in the Cu\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4} paddlewheel units, as well as some degree of $\pi$–backbonding from the copper cations to the alkene. Given its very limited backbonding capability, this framework displays a theoretical IAST selectivity of only approximately 2 for an equimolar ethylene/ethane mixture at 1 bar and 298 K.\textsuperscript{176}

The M\textsubscript{2}(dobdc) frameworks perform exceptionally well for the separation of ethane/ethylene mixtures. The first reports were of ethane and ethylene isotherms in Mg\textsubscript{2}(dobdc) at various temperatures.\textsuperscript{177} Although this framework displays similar saturation capacities for these two gases at a given temperature, the isosteric heat of adsorption of ethylene is much higher than that of ethane ($-43$ vs. $-27$ kJ/mol). Although the isosteric heat of ethane adsorption increases with increasing loading, likely a result of adsorbate-adsorbate interactions, the ethylene adsorption enthalpy remains higher over the entire loading range investigated. As expected, GCMC calculations indicate the primary adsorption site is the coordinatively-unsaturated Mg\textsuperscript{2+} cation.

With soft, high-spin Fe\textsuperscript{2+} cation sites exposed on its surface, Fe\textsubscript{2}(dobdc) performs even better for the separation of these molecules.\textsuperscript{148} Increased $\pi$–backbonding as compared to Mg\textsuperscript{2+} results in an increased selectivity for ethylene over ethane, which increases from 7 in Mg\textsubscript{2}(dobdc) to 18 in Fe\textsubscript{2}(dobdc). In breakthrough experiment, Fe\textsubscript{2}(dobdc) is capable of separating an equimolar ethane/ethylene mixture at 1 bar and 318 K into 99% and 99.5% pure components, respectively. Neutron powder diffraction experiments confirm that indeed the unsaturated metal cation is the strongest adsorption site, and ethylene adsorbs via the anticipated side-on binding mode (Figure 1.9). Other members of the M\textsubscript{2}(dobdc) family both theoretically and experimentally display high ethylene/ethane selectivity based on preferential coordination of the alkene to the metal cations in these frameworks.\textsuperscript{169,178} The selectivity follows the trend Fe\textsuperscript{2+} > Mn\textsuperscript{2+} > Ni\textsuperscript{2+} $\approx$ Co\textsuperscript{2+} > Mg\textsuperscript{2+} > Zn\textsuperscript{2+}, which is likely associated with the relative softness of the (high-spin) metal center, together with its ability to engage in $\pi$–backbonding.

### 1.3.2.3 Propane/Propylene

Like in ethane/ethylene separations, Cu\textsubscript{3}(btc)\textsubscript{2} was among the first metal-organic frameworks to be studied for propane/propylene separations,\textsuperscript{139,140} and since then
has been investigated extensively. Analogous to its performance in methane/acetylene and ethane/ethylene separations, this material preferentially binds propylene over propane (−41.8 vs. −28.5 kJ/mol at zero coverage) over a wide pressure range. GCMC simulations suggest that propane is adsorbed most strongly in the small octahedral pockets present in the framework, and that the strongest propylene binding sites in the framework are the Cu²⁺ sites. UV-vis spectroscopy confirms this as the primary propylene adsorption site as the d-d band associated with the cations centered at 540 nm shifts to a lower energy upon propylene coordination. Propane has little to no effect on the UV-vis spectrum, supporting the notion that the primary adsorption sites are likely the octahedral cages in the framework. The promising results of Cu₃(btc)₂ propane/propylene separations have sparked interest in the mechanical stability and performance of the material, and one of the first steps in using industrial adsorbents is to shape them into pellets. Research has shown that spheres of Cu₃(btc)₂ maintain the highest propylene capacity upon shaping, followed by tablets and lastly extrudates.

ZIFs also show selective propane/propylene adsorption behavior through a sieving mechanism, as evidenced by size exclusion studies in ZIF-8. Interestingly, ZIF-7 displays inverse selectivity at 373 K, preferentially adsorbing propane over propylene. This is thought to be a result of a gate opening effect in which propylene has a more favorable adsorption on the external surfaces of ZIF-7, delaying the pressure at which the framework opens.

Although a number of other metal-organic framework display moderate propylene/propane selectivity based on gate opening and kinetic effects, the most selective materials are typically those containing a higher density of coordinatively-unsaturated metal cation sites than Cu₃(btc)₂. Every M₂(dobdc) isostructure, with the exception of the newly synthesized copper analog, has been investigated for propane/propylene separation. In all cases M₂(dobdc) binds propylene over propane with selectivities between 3 and 20, assuming an equimolar mixture. All six materials show increasing selectivity with increasing pressure as adsorbate-adsorbate interactions become more important. At 318 K and 1 bar of total pressure, Fe₂(dobdc) is capable of separating an equimolar propane/propylene mixture into greater than 99% pure components. Another iron-based metal-organic framework, MIL-100(Fe), is capable of separating propane/propylene mixtures upon reduction of a portion of its Fe³⁺ centers. The presence of open Fe²⁺ sites leads to an increase in the isosteric heat of propylene adsorption from −30 to −70 kJ/mol.

1.3.2.4 Long Alkanes and Alkenes

Alkanes are the primary starting materials for alkene synthesis, and the products of these reactions are mixtures of alkenes and unreacted alkane which require separation for purification of various industrial feedstocks. While some alkenes such as cyclohexene are not industrially relevant, they are nonetheless informative from a fundamental perspective.

Separating longer alkenes from alkanes is more complex than shorter chains because of the distinct hydrophobic interactions of the long chains and interactions with
the π cloud of the double bond. Sieving has been shown to be possible, as in the example of isobutane separation from C2 and C3 alkanes and alkenes due to rational design of pore sizes in Zn-carboxylate metal organic frameworks. Additionally, hints of separation ability were reported in ZIF-7, where the saturation capacity of trans-2-butene is markedly lower than that of n-butane cis-2-butene and 1-butene.

As a result of greater molecular surface area and geometric flexibility in long alkanes, their adsorption is generally stronger than that of their corresponding alkenes. This trend is seen for n-octane and 1-octene in a suite of metal-organic frameworks without unsaturated metal centers. In a separate study, isostructures of Zn₄O(bdc)₃ were shown to bind n-hexane more strongly than 1-hexene. The strength of interaction was highest for Zn₄O(bdc)₃ and decreased with increasing carbon atoms per linker. Modeling shows n-pentane adsorption to be slightly stronger than that of 1-pentene in Zn₄O(bdc)₃.

As in shorter alkane/alkene separations, the most successful mechanisms rely on open metal sites that are selective for the alkene. This was shown by comparing metal-organic frameworks with and without these sites. Additionally, the open metal sites in Cu₃(btc)₂ have been studied in depth. The material shows an expected preference for 1-pentene over n-pentane. Isobutane and isobutene were also separated in this material, and the isosteric heats of adsorption were determined to be −42 and −46 kJ/mol, respectively. A breakthrough experiment at 303 K revealed excellent separation characteristics.

The above MIL-53 and MIL-125 examples serve to illustrate that selective adsorption of longer alkenes and alkanes is complex and does not always depend on the presence of open metal centers. Despite a lack of these sites, strengths of adsorption within amino-MIL-53(Al) are higher for the alkene in pairs of C2, C3, and C5 normal alkanes and 1-alkenes. n-Hexane and 1-hexene did not adhere to this pattern, and the binding was stronger to the alkanes. n-Butane also bound more strongly than 1-butene, however the experimental setup was reported to be non-ideal. This unexpected behavior is not limited to the MIL-53-type MIL materials, as isoprene was selectively adsorbed over 2-methylbutane in liquid-phase batch experiments in MIL-125 and amino-MIL-125.

1.3.2.5 Alkene Mixtures

Alkene/alkene separations primarily consist of cis/trans isomer separations. The four butene isomers are generated during the cracking process, and their large-scale commercial use has been hampered by the lack of separation technologies to isolate individual isomers. Distillative separations of all four isomers are not feasible due to their close boiling points. Therefore, over 70% of butene mixtures are used either directly in gasoline or alkylation reactions to form high-octane components of gasoline, however about 10% are able to be used for specialty chemical manufacture. Here the cis- and trans- isomers have varying reactivity and utility, and so improved separation technologies are an ongoing challenge.

The adsorption of butenes has been reported in many materials. The compound Cu(hfipbb)(H₂hfipbb)₀.₅ adsorbs 40% more of the trans isomer at 303 K, as it is more volatile. In ZIF-7, cis-2-butene fits into the pores better than the trans isomer.
Interestingly, neither butene isomer was appreciably adsorbed in MIL-53(Al) or MIL-47, although the pore apertures are large enough to accommodate them as guests.\textsuperscript{124}

In an \textit{n}-hexane solution, Cu\textsubscript{3}(btc)\textsubscript{2} selectively adsorbs 	extit{cis}-butene over the \textit{trans} isomer, with a modest separation factor of 1.9:1. The \textit{cis} isomer is often favored in zeolites due to \textpi-complexation with extraframework cations, and the open Cu\textsuperscript{2+} sites in Cu\textsubscript{3}(btc)\textsubscript{2} result in the same behavior. As four Cu\textsuperscript{2+} centers point into one pore, after the adsorption of one butene per four Cu\textsuperscript{2+} centers, the selectivity drops. These results represent a vast improvement over the current near-inability to separate these isomers industrially. This separation extends to longer hydrocarbon \textit{cis}/\textit{trans} isomer pairs, as high as methyl-9-octadecenoate. An aluminum-based framework with benzenetricarboxylate linkers, MIL-96, adsorbs more than double the amount of the slim \textit{trans}-piperyline compared to \textit{cis}-piperyline or isoprene.\textsuperscript{193} This is also reflected in the enthalpies of adsorption of \textminus54.6, \textminus53.0, and \textminus52.1 kJ/mol, respectively. A breakthrough column separated these alkenes as well.

\textbf{Figure 1.9} (Top) The structure of acetylene bound to the open Fe\textsuperscript{2+} sites in Fe\textsubscript{2}(dobdc), where orange, red, gray, and blue spheres represent Fe, O, C, and D atoms, respectively and (bottom) the first coordination spheres for the iron centers in the solid-state structures obtained upon dosing methane, ethane, propane, acetylene, ethylene, and propylene. Reproduced with permission from Reference 148.
In addition to cis/trans isomer separations, many other alkene mixture separations have been reported. In catalytic dehydrogenation processes, the location of double bonds in alkenes is random, and different alkene position isomers are feedstocks for specialty chemicals. In Cu₃(btc)₂, the preferential adsorption of butane position isomers follows cis-2-butene > 1-pentene > trans-2-pentene. In ZIF-7, the saturation capacity of 1-butene is nearly 25% lower than either 2-butene isomer at 338 K, although the capacity for trans-2-butene drops below the other butenes at 373 K. 

Alkenes with the double bond at the 1-position have the most industrial utility. They are synthesized in a variety of ways, but when produced from n-alkanes they are generated as a mixture of chain lengths. The separation of 1-alkenes ranging from ethene to hexene, was investigated in amino-MIL-53(Al). Adsorption enthalpy increased in magnitude approximately linearly with carbon number.

In a more esoteric type of alkene separation, a homochiral Cd²⁺-based framework theoretically achieved partial separation of enantiomers of 1,3-dimethyl-1,2-propadiene, 1,2-dimethylcyclobutane, and 1,2-dimethylcyclopropane.

### 1.3.3 Aromatics

Aromatics are present in all petroleum, and benzene is generally among the least represented molecules compared to others like substituted benzenes. As polymer precursors, 24.6 million tons of styrene are produced per year. Vinyl toluenes and cumene are also important precursor molecules that require separation. Xylenes and other substituted benzenes are almost exclusively generated as mixtures, and are important additives in gasoline. p-Xylene is used for industrial chemical processes much more value than other C8 alkyaromatics, leading to the necessity of separation. The close boiling points lead to highly difficult and inefficient distillative separation processes. Ideal separation materials preferentially bind p-xylene. Approximately 60% of p-xylene is currently separated using adsorptive strategies, however there is reported need for improvement in this technology. Once p-xylene is removed, the remaining products also have disparate industrial worth. Subsequently, materials are valuable that selectively adsorb m-xylene, the next most valuable isomer, from mixtures which include other aromatics except p-xylene.

C8 alkyaromatics, benzene, toluene, and polycyclic aromatic hydrocarbons dominate the body of work covering adsorptive separations of aromatic compounds in metal-organic frameworks. Some more esoteric separations have also been reported, such as separating fullerenes or industrially-relevant substituted naphthalenes.

Among the many materials that have been studied, only MIL-47 and MIL-53 have shown substantial separation among the most industrially-relevant mixtures. Specifically, MIL-47 demonstrated varying degrees of xylene separation ability among the many papers probing this adsorbent/adsorbate combination, including one including excellent separation of p-xylene from m- and o-xylene. Additionally, MIL-53 can separate p-xylene from other xylenes and aromatics, however this is through the non-ideal process of selectively adsorbing the para isomer. MIL-101(Cr) was shown theoretically to separate xylene isomers in the elution order p-xylene > m-xylene > o-xylene, and follow-up experimental studies could substantiate the promise of this material. Due to
the large body of work surrounding these materials and their exciting separation performance, they are treated in a separate section from the other materials.

Early work on metal-organic frameworks hinted at their ability to separate alkylaromatics, and over time interesting behavior has been observed between metal-organic frameworks and aromatics. One unique example is a material forms in the presence of certain xylene isomers but not others. Some materials have been reported to show almost no selectivity, but the examples below illustrate the promise of metal-organic frameworks for aromatic separations.

In Zn₄O(bdc)₃, the theoretical order of adsorption strength increases in the order $m$-xylene > ethylbenzene > toluene > benzene. Zn₄O(bdc)₃ can experimentally separate any xylene isomer from ethylbenzene in a breakthrough column, and in a quaternary mixture the three xylenes elute essentially together at 523 K. Similarly, Zn₂(bdc)₂(dabco) binds alkylaromatics preferentially, with the Henry’s constants following the order $o$-xylene > $m$-xylene > ethylbenzene > $p$-xylene; however, quaternary breakthrough experiments show little to no separation. The theoretical Zn₂(bdc)₂(dabco) selectivity for $o$-xylene over the other C8 aromatics lies between 1.3 and 1.9 at temperatures as high as 448 K.

Breakthrough separations of $o$- and $p$-xylene in ZIF-8, ZIF-76, Cu₃(btc)₂, Ni₂(dobdc), and RHO-ZMOF, a zeolitic imidazolate framework with extraframework In³⁺ cations, showed selectivity for the ortho isomer with the exception of ZIF-8. The reason for the selectivity in ZIF-8 was the required “saloon door”-style opening of the pore aperture, leading to sieving selectivity. Sieving is also seen in MIL-96, wherein triisopropylbenzene can be separated from $p$-xylene, $m$-xylene, and 1,3,5-trimethylbenzene.

Non-sieving chromatographic separations have also been achieved. Benzene, toluene, ethylbenzene, and naphthalene were separated on a packed column of MIL-100(Fe) at 298 K using methanol and water as the mobile phase. The framework Cd(4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole)₂ adsorbs only toluene and benzene in the presence of xylenes. When only xylenes are present, $o$- and $m$-xylene adsorb in equal amounts, while $p$-xylene is not adsorbed measurably. In MIL-101, the molecular cross sectional area is nearly linearly related to uptake capacity for alkylaromatic compounds, although a packed column of MIL-101(Cr) was not found to separate the corresponding liquid mixture.

Open-metal-sites in Cu₃(btc)₂ and Ni₂(dobdc) have been theoretically shown to be inaccessible for binding the π-system in alkylaromatics. Selectivity can still be seen in these frameworks, as Cu₃(btc)₂ can separate xylenes, benzene, toluene, and ethylbenzene chromatographically, and preferentially adsorb a mixture of aromatics in the order decalin, tetralin, 1,2,4-trimethylbenzene, $o$-xylene, $p$-xylene, $m$-xylene, ethylbenzene, toluene, and finally benzene. Modest adsorption selectivity has been observed in fibers coated with Cu₃(btc)₂, which adsorb more $p$-xylene than ethylbenzene, toluene, styrene, trimethylbenzene, or benzene. Despite similar single-component isotherms and only modest separation in a breakthrough, styrene and ethylbenzene were separated by a factor of 6 in batch experiments in Cu₃(btc)₂.

Perhaps the most promising material outside of the MIL family for aromatic separations is UiO-66. This material separates ethylbenzene and all three xylenes in a
breakthrough scenario, although the crucial separation between the \textit{para} and \textit{meta} isomers is only modest\textsuperscript{131,223}.

\subsection*{1.3.3.1 MIL-47 and MIL-53}

MIL-47 and MIL-53 have been studied extensively for aromatic hydrocarbon separations, both in tandem and individually. In these studies, theoretical models are highly useful, as C8 alkylaromatics in MIL-47 and MIL-53(Al) can be modeled with near-experimental accuracy.\textsuperscript{224} When comparing the xylene selectivities in these frameworks, those in MIL-47 are much higher.\textsuperscript{234} The strengths of adsorption of C8 alkylaromatics in MIL-47 are not substantially different, and coupling that observation with incongruent uptake capacities lead to the conclusion that entropic differences dominate the selectivities in this material, although enthalpic differences do enhance the separations. Rietveld refinement of powder diffraction data for MIL-47 crystallites loaded with the four C8 alkylaromatics confirmed this hypothesis, as shown in Figure 1.10. Styrene and ethylbenzene vapor separation in MIL-47 and MIL-53(Al) was also shown to be enthalpic for MIL-53(Al) and entropic for MIL-47, although the selectivity for styrene is higher in MIL-53(Al).\textsuperscript{225} Density functional theory calculations support the hypothesis that xylene isomer separation is primarily entropically-driven in MIL-47.\textsuperscript{226}

Despite different separation mechanisms and performance, similar strategies can be used to modify sorption within the pores of MIL-47 and MIL-53. When the \textit{bdc}\textsuperscript{2-} linker of MIL-47 or MIL-53(Al) is partially fluorinated, both \textit{o}- and \textit{p}-xylene are still adsorbed significantly, whereas water sorption is significantly less and the MIL-53(Al) fluorinated analog is extremely water resistant.\textsuperscript{227} This property is favorable because hydrolytic stability is crucial for industrial applications.

Due to its superior separation abilities, the mechanism of alkylaromatic adsorption in MIL-47 has been of great interest. Clear conclusions were extracted about the bonding of xylenes in MIL-47 using previous results and calorimetrically-derived adsorption enthalpies.\textsuperscript{200} The ethylbenzene heat of adsorption is derived primarily from the alkyl group interaction with the framework walls, while \textit{p}-xylene can overlap with another \textit{p}-xylene molecule and the walls of the framework ideally and \textit{m}-xylene requires some tilt to fit into the pores that decreases the strength of adsorption. Both entropic and enthalpic factors result in chromatographic separation of ethylbenzene, while enthalpic factors are primarily responsible for the \textit{para}/\textit{meta} separation. These observations held true at high and low loadings. Most other alkylaromatics fall along a linear trend of increasing adsorption enthalpy with molecular polarizability.\textsuperscript{228} Size exclusion generates small deviations from this trend, with mesitylene and \textit{o}- and \textit{m}-xylene being examples of lower enthalpy than expected based on their polarizability.

Breakthrough results vary drastically among different reports. This is often a byproduct of different experimental temperatures and total pressures. However, in a quaternary mixture at 338 K three separate fractions were observable: ethylbenzene eluted first, followed by a close combination of \textit{p}- and \textit{m}-xylene, and finally \textit{o}-xylene (Figure 1.11).\textsuperscript{229} In a separate study, MIL-47 showed selectivity for \textit{p}- over \textit{m}-xylene and almost complete separation of all three xylene isomers in a chromatographic column. This same sample could not separate ethyltoluene isomers.\textsuperscript{230} Activation conditions were shown to alter the selectivity only slightly.
Other alkylaromatics can also be separated in MIL-47. Longer alkyl chains have been shown to bind more strongly, as seen by comparing cumene vs. \(n\)-propylbenzene. The same trend is seen for the series spanning from ethylbenzene to \(n\)-octylbenzene.\(^{200}\)

The adsorption of alkylaromatics in MIL-53 compounds has also been studied extensively. Single-component isotherms of xylene and ethylbenzene in MIL-53(Al) show that an adsorption step present in all of these isotherms moves to higher pressures at higher temperatures.\(^{231}\) These single-component adsorption differences are reflected in the adsorption strengths of these different adsorbates, which follow the order ethylbenzene > \(o\)-xylene > \(m\)-xylene > \(p\)-xylene, and further increases with increasing coverage, ranging between \(-10\) and \(-20\) kJ/mol. The structures of MIL-53(Al) loaded with xylenes reflect the adsorption and breakthrough data. Both methyl groups of \(o\)-xylene can interact with the framework carboxylate groups, while only one \(m\)- and \(p\)-xylene each can have this interaction. The framework is most distorted upon adsorption of \(o\)-xylene and least for the \(para\) isomer. The entropy of adsorption is significantly less negative for \(o\)-xylene than for the other two isomers, which explains the discrepancy between the relative enthalpies and breakthrough elution order.\(^{231,232}\) The flexibility of MIL-53(Al) creates a separation environment that is highly dependent on total pressure as at 383 K the separation is poor at 0.0009 bar but improves at 0.056 bar.\(^{233}\)

![Figure 1.10](image)

Figure 1.10 The structures of (a) \(p\)-xylene, (b) \(o\)-xylene, (c) \(m\)-xylene, and (d) ethylbenzene in MIL-47, where gray, red, and pink represent C, O, and V atoms, respectively. Reproduced with permission from Reference 234. Copyright 2007 American Chemical Society.

Liquid and gas-phase separation of C8-C10 alkylaromatics have also been reported for MIL-53(Al).\(^{235}\) In batch experiments, the selectivity order is \(o\)-xylene > ethylbenzene > \(p\)-xylene \(\approx\) \(m\)-xylene. Similarly, \(p\)- and \(m\)-ethyltoluene were not separated from each other, but were baseline separated from \(o\)-ethyltoluene and \(o\)-cyomene. Similar behavior was seen for pelletized MIL-53(Al).\(^{236}\)

A study focusing on the structural transitions of MIL-53(Al) showed that all C8 alkylaromatics cause a distortion in the flexible framework structure;\(^{200}\) however, the distortion caused by the interaction of the xylene methyl groups with the carboxylates of
the framework is less disfavored than that caused by ethylbenzene. Both methyl groups in 
\( o \)-xylene can interact favorably with the framework, leading to the high strength of 
adsorption. This study reported that \( p \)-xylene has more possible adsorption sites, and 
therefore is entropically favored. These competing factors result in the difficulty of 
separation of xylene isomers in MIL-53(Al). In liquid chromatography separations, MIL- 
53(Al) outperformed a conventional LCMS column for toluene and ethylbenzene 
separation at 298 K,\(^{237} \) although different eluents have produced different results.\(^{238} \)

Excellent alkylaromatic separation in MIL-53 is not limited to the aluminum 
isostucture. In a variety of experiments, xylene isomers have been found to behave 
differently in the pores of MIL-53(Fe).\(^{239} \) The isotherm of \( o \)-xylene is essentially of Type 
I, while that of \( m \)-xylene shows one step and that of \( p \)-xylene shows two: one at the same 
pressure as \( m \)-xylene and one at a lower pressure. The \( o \)-xylene isomer is adsorbed with 
substantially higher uptake capacity than the other isomers, although \( m \)-xylene has the 
highest strength of adsorption. Crystal structures of MIL-53(Fe) loaded with xylenes 
show similar behavior between \( o \)- and \( m \)-xylenes, with \( \pi-\pi \) interactions between the 
xylene and the bdc\(^2- \) linker. This interaction is not found in \( p \)-xylene. Binary 
breakthrough experiments with the three xylene isomers show separation of \( para/ortho \) 
and \( para/meta \) mixtures. In addition to MIL-53(Fe), a Mn-based MIL-53 analogue with 
pyridine \( N \)-oxides as \( \mu_2-O \) substitutes, shows better \( \pi \) overlap with benzene than 
toluene.\(^{240} \)

![Figure 1.11](image.png)

**Figure 1.11** Results of a 4-component breakthrough experiment on MIL- 
47 at 383 K and 0.5 bar total hydrocarbon pressure. Reproduced with 
permission from Reference 229. Copyright 2008 American Chemical 
Society.

### 1.3.3.2 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons, or PAHs, are carcinogenic byproducts of 
incomplete combustion of organic matter such as fossil fuels.\(^{241} \) The emissions of PAHs 
totaled approximately 550,000 tons in 2004.\(^{242} \) The major source of PAHs in air, water, 
soil, and food are anthropogenic – either vehicular emissions or stationary sources such 
as petroleum cracking or residential heating.\(^{243,244} \) Their vapor pressures span a range of 
\( \sim 10^7 \), and they can be present in the gas phase (e.g. naphthalene) or as adsorbed solids
(organics with five rings and higher). Their separation is critical to obtaining an environmental profile of these pollutants. The current CGMS separation techniques for separation are far from optimized, as the uncertainties of quantitation are quite high. Metal-organic frameworks could serve as a new frontier in PAH separation for analysis. Additionally, preconcentration of these pollutants from air samples is under investigation, and adsorbents such as metal-organic frameworks could serve a dual purpose of preconcentration and analytical separation. This preconcentration inquiry is relatively new in metal-organic frameworks, but promising results have shown promise for extracting PAHs from water.

The wide range of sizes of PAH’s allows for size-exclusion separations. To this end, both Cu₃(btc)₂ and Zn₄O(bdc)₃ can sieve pyrene from phenanthrene, anthracene, naphthalene, and benzene, as well as benzene from a more complex mixture of PAH’s.

The strength of adsorption of polycyclic aromatic hydrocarbons at low loadings in metal-organic frameworks relatively strong, and therefore they can often be discriminated based on adsorption strength. These differences in adsorption strength were seen theoretically in Cu₃(btc)₂, Zn₄O(bdc)₃ isostructures, and MIL-53(Cr). Experimentally, PAH’s were separated on a reverse-phase liquid chromatography column packed with MIL-53(Al).

Strengths of adsorption were also used to separate PAH’s using a less conventional strategy: When exposed to an activated sample of Ni₂(μ₂-OH₂)(1,3-bdc)₂(tpcb), (tpcb = tetraakis(4-pyridyl)cyclobutane), naphthalene sublimes and is adsorbed selectively from a mixture of naphthalene and anthracene. The ability of naphthalene to align favorably within the pores was cited as the reason for this selectivity.

The separation of PAH’s is generally applied in identifying components of mixtures, and therefore the separation is not necessary if identification can be achieved without it, and different PAHs can be detected, albeit not separated, using creative techniques in metal-organic frameworks. For example, the magnetic susceptibility of the spin-crossover compound [Fe(dpe)][Pt(CN)₄] (dpe = trans-(1,2-di(4-pyridyl)-ethylene) changes drastically among guests phenazine, anthracene, and naphthalene.

1.3.3.3 Aromatic and Aliphatic Mixtures

The separation of aromatics from aliphatics is applicable to petroleum refining. These molecules all fractionate together and ultimately need to be separated for a variety of uses. Separation generally involves inefficient distillation or extraction, while sometimes π–complexation adsorbents are used. Some papers report single isotherms of hydrocarbons of interest, but without thermodynamic or separation data, little information about their separation ability can be deduced. Other studies report a lack of separation ability, as in the nearly identical strength of adsorption of benzene and cyclohexane in M(bdc)(ted)₀.₅ (M = Zn, Cu).

Generally, metal-organic frameworks can interact more strongly with alkylaromatics than small molecules or aliphatic hydrocarbons, as seen theoretically in Cu₃(btc)₂, Zn₄O(bdc)₃ isostructures, and MIL-53(Cr). Similarly, a series of metal-azolate frameworks can selectively adsorb specific aromatics in non-aromatic solvents.
Comparing aromatic rings with hydrocarbons of similar sizes, some metal-organic frameworks bind aliphatics more strongly than their aromatic counterparts. Decalin theoretically binds $\text{Zn}_4\text{O(bdc)}_3$ slightly more strongly than tetralin, an adsorbate with the same number of carbons but three unsaturated bonds. Benzene binds less strongly than $n$-hexane or 1-hexene in amino-MIL-53. Benzene is less strongly adsorbed than cyclohexane or $n$-hexane in MIL-47, which shows distinctive structural deformations upon adsorption of benzene, 1,4-cyclohexadiene, 1,3-cyclohexadiene, cyclohexene, and cyclohexane.

The majority of aromatic/aliphatic separation studies show preference for the aromatic adsorbate, presumably due to favorable interactions with the aromatic linkers. The strength of adsorption of toluene is much higher than that of $n$-hexane in MIL-101(Cr). Some novel materials separate benzene from cyclohexane very effectively. When exposed to a 1:1 mixture of benzene and cyclohexane, a disproportionate amount of benzene is adsorbed in the pores of NH$_4$[Cu$_3$(μ$_3$-OH)(μ$_3$-4-carboxypyrrozolato)$_3$]$_2$. Similarly, a pillared zinc carboxylate framework adsorbs essentially entirely benzene when exposed to a 1:1 benzene: cyclohexane mixture. Here, pore size was posited to be the source of the selectivity.

$\text{Zn}_4\text{O(bdc)}_3$ also binds aromatics more strongly than aliphatics. In an early study, $\text{Zn}_4\text{O(bdc)}_3$ was shown to adsorb cyclohexane slightly more strongly and with a modestly higher capacity than benzene. However, a later, more rigorous investigation showed contrasting results. Adsorption isotherms were reported for benzene, toluene, cyclohexane, methylcyclohexane, 1-hexene, and $n$-pentane through $n$-octane in $\text{Zn}_4\text{O(bdc)}_3$ and two isostructures. When comparing the same number of carbons, the aromatics bound more strongly than the cyclic aliphatics.

Open metal sites can allow for even more selective binding to aromatics. Through a comparison with MIL-53(Al), the open Cu$^{2+}$ sites in Cu$_3$(btc)$_2$ were shown to adsorb m-xylene in the presence of an alkane solvent. As the length of the alkane solvent decreased, less was adsorbed for each material. The capacity of m-xylene decreased to almost zero for MIL-53(Al) and plateaued near 4 wt % for Cu$_3$(btc)$_2$. The selectivity of Cu$_3$(btc)$_2$ for benzene or toluene over cyclohexane is preserved and potentially enhanced when polyoxometalates are present in the pores.

1.3.4 Conclusions and Outlook

Since the outset of hydrocarbon separation experiments in metal-organic frameworks approximately a decade ago, the ability to separate mixtures more efficiently – or even access previously impossible separations – has demonstrated the utility of this approach. The variety of normal alkanes studied has shown that for a given system, a metal-organic framework seemingly exists for separating any mixture of adsorbates. The pore shapes of metal-organic frameworks offer a novel platform for separating branched alkanes based on shape, as zeolites or other porous materials are constructed in ways that preclude features such as acute angles. As a result, valuable highly branched isomers that could only be isolated by distillation by can now be separated by adsorption. Additionally, coordinatively-unsaturated metal centers have been shown to be an excellent strategy for separating alkenes from alkanes. Finally, the separation of xylenes

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(and other aromatics) has been demonstrated in the MIL series of metal-organic frameworks, a separation which was also previously inaccessible.

The number of metal-organic frameworks is limited to only a fraction of the materials reported to date. New structure types or properties could improve upon the results seen here. Using the current canon of literature results to direct efforts towards new or overlooked metal-organic frameworks, specifically those that are stable to heat and impurities like water, could result in new discoveries. Petroleum technology, from which most hydrocarbons are derived, is highly mature, and therefore investigations of other porous materials like zeolites have been exhaustive, making metal-organic frameworks with novel properties particularly exciting. Experimentally, future directions could focus strongly on breakthrough data. These results are particularly useful in evaluating the practical ability of a material to separate hydrocarbons, either with new frameworks or materials that have been evaluated using adsorption or computer modeling. Advances in computational modeling have also begun to allow for screening of large databases of real and predicted metal-organic framework structures, and this strategy could continue to be used in partnership with experimental work. Modeling studies can also investigate dozens of adsorbates on a single promising material, potentially identifying materials that could be scaled up for use in a variety of processes.

1.4 References


(217) Fu, Y.-Y.; Yang, C.-X.; Yan, X.-P. J. Chromatogr. A 2013, 1274, 137.


Chapter 2: Metal-Organic Frameworks as Adsorbents for Hydrogen Purification and Pre-Combustion Carbon Dioxide Capture

2.1 Introduction

Coal is an abundant resource that is heavily relied upon for global energy, and therefore emission-free coal-fired power plants are a necessary near-term component of a clean energy future.\(^1\) Integrated gasification and combined cycle (IGCC) systems equipped with precombustion CO\(_2\) capture, wherein CO\(_2\) is separated from H\(_2\) and sequestered, are promising in this regard.\(^2\) The technology for separating H\(_2\) and CO\(_2\) is already well-developed due to the tremendous scale of H\(_2\) production (50 million tons per year worldwide), and is primarily accomplished using pressure-swing adsorption (PSA).\(^3\) Here, porous zeolites or activated carbons selectively and reversibly adsorb impurities in the presence of H\(_2\) at high pressures. Methods for altering the current PSA specifications to meet the needs of precombustion CO\(_2\) capture in an IGCC system are being explored,\(^4\) although vast improvements in CO\(_2)/H\(_2\) separations must be made to render this strategy economically viable.\(^2\) Regardless, optimizing the efficiency of adsorptive H\(_2\) purification in industry is also of crucial importance to minimizing energy usage,\(^5\) since at current production rates, which are steadily rising, a 10% increase in the efficiency of the process could save the energy output of approximately 18 average US coal-fired power plants.\(^6\)

Much of the energy input for a PSA system is used in mass transport of the gas and regeneration of the adsorbents, and as a result improving adsorbent selectivity and capacity for CO\(_2\) would increase efficiency.\(^3\) Extensive experimental\(^7\) and theoretical\(^8\) investigations suggest that further optimization of zeolites and activated carbons will yield only modest improvements in CO\(_2)/H\(_2\) separation performance. Thus, there is a need for new types of adsorbents with the potential for displaying significantly improved CO\(_2\) capacity and selectivity.

Microporous metal-organic frameworks have yet to be experimentally investigated for the separation of CO\(_2\) from H\(_2\). These materials exhibit record internal surface areas and, as a result, a tremendous CO\(_2\) storage capacity at the pressures relevant for a CO\(_2)/H\(_2\) separation (ca. 5-40 bar).\(^3\) Further, the high adsorbent surface area could enhance the selectivity for adsorption of CO\(_2\) over H\(_2\), since H\(_2\) packs more efficiently than CO\(_2\) due to its smaller size.\(^10\) Moreover, the ability to adjust the nature of the surfaces within these materials could potentially be exploited to increase the strength of the interaction with CO\(_2\),\(^11\) and has already spurred investigations into their uses in other industrially-relevant gas separations, such as CO\(_2)/N\(_2\),\(^12\) CO\(_2)/CH\(_4\),\(^12\) and O\(_2)/N\(_2\) separations.\(^14\)

Despite the recent interest in high-pressure, fixed-bed separation applications using metal-organic frameworks as the adsorbent,\(^12\) their study for CO\(_2)/H\(_2\) separations was only until recently limited to theoretical investigations, which have predicted excellent selectivities.\(^10\) Herein, we report the first experimental study of the utility of metal-organic frameworks for high-pressure CO\(_2)/H\(_2\) separation by PSA.\(^16\) We consider single-component CO\(_2\) and H\(_2\) adsorption isotherms as an initial indicator of effectiveness, and further adopt a complementary theoretical model for the prediction of the performance of each material under realistic mixed gas conditions.
2.2 Experimental Section

Dichloromethane was received from Aldrich and dried over activated 4 Å sieves prior to use. Ethanol was refluxed for 24 h over Mg turnings and I$_2$. All other reagents were obtained from commercial vendors and used without further purification. Powder X-ray diffraction patterns were obtained on a Bruker D8 Advance diffractometer with a Cu anode (λ = 1.5406 Å). Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 Optica FTIR spectrometer furnished with an attenuated total reflectance accessory (ATR). **Caution!** Beryllium compounds can pose a serious health risk through skin contact and inhalation. All manipulations of solid beryllium-containing materials should be performed in a fume hood or glove bag, taking care not to generate airborne dust in the open air under any circumstances.

**Synthesis of 1,3,5-triphenylbenzene** 1,3,5-triphenylbenzene was prepared according to literature procedure.$^{18}$

**Synthesis of 4,4',4''-benzene-1,3,5-triyltribenzoic acid (H$_3$BTB)** H$_3$BTB was synthesized from 1,3,5-triphenylbenzene and nitric acid according to literature procedure.$^{19}$

**Synthesis of MOF-177** MOF-177 was prepared according to literature procedure.$^{20}$

**Synthesis of Be$_{12}$(OH)$_{12}$(1,3,5-benzenetribenzoate)$_4$ (BeBTB)** The same sample characterized in Sumida et al. was used for this study.$^{21}$

**Synthesis of 1,4-benzenedi(4'-pyrazolyl) (H$_2$BDP)** H$_2$BDP was synthesized according to literature procedure.$^{22}$

**Synthesis of CoBDP** CoBDP was synthesized according to literature procedure.$^{22}$

**Synthesis of 1,3,5-tris(triazol-5-yl)benzene (H$_3$BTTri)** H$_3$BTTri was synthesized according to literature procedure.$^{12c}$

**Synthesis of CuBTTri** CuBTTri was synthesized according to literature procedure.$^{12c}$

**Synthesis of Mg$_2$(dobdc)** Mg$_2$(dobdc) was synthesized according to literature procedure.$^{23}$

**Activation of MOF-177** Activation of the sample was performed by transferring the collected product into a nitrogen-filled glove bag, where the solid was soaked in N,N-dimethylformamide (50 mL) for 24 h. The supernatant was decanted and replenished a further two times over two days. The solid was then soaked in dichloromethane (50 mL) for 24 h. The supernatant was decanted and replenished a further three times over three days, and after the final wash a gentle stream of nitrogen was passed over the sample so as to remove excess solvent. The product is hygroscopic and was therefore stored in a glove box under a dinitrogen atmosphere. The final degassing was performed on a vacuum manifold at 1 mTorr and 100 °C for 10 h. Surface area was determined by 77 K N$_2$ adsorption and confirmed with literature data.$^{25}$ Powder pattern was compared to the simulated pattern from the crystal structure.$^{26}$

**Activation of BeBTB.** BeBTB was activated according to literature procedure.$^{21}$

**Activation of CoBDP.** CoBDP was evacuated at ambient temperature at 1000 mTorr for 24 h and then transferred quickly to a Schlenk flask in a glovebag.
was then evacuated at 1 mTorr for two days and brought to 170 °C at a ramp rate of 5 °C per hour.

**Activation of CuBTTri** CuBTTri was activated according to literature procedure.\(^{12}\)

**Activation of Mg\(_2\)(dobdc)** Mg\(_2\)(dobdc) was activated using a strategy adapted from the literature procedure. The yellow microcrystalline material was combined and washed repeatedly with DMF and soaked in DMF for 24 h. The DMF was decanted, and freshly distilled methanol was added. The solid was then transferred to a nitrogen-filled glovebox. The methanol was decanted and the solid was soaked in DMF on a hotplate set at 100 °C for 18 h. The DMF was decanted and replaced, and the solid was soaked at 100 °C for 4 h. The DMF was decanted and replaced by methanol, which was decanted and replenished 6 times with a minimum of 6 hours between washes.

**Low-Pressure Gas Sorption Measurements** Low-pressure gas adsorption was used in two contexts in this study: to measure the surface area of the prepared metal-organic framework samples and to measure adsorption of CO\(_2\) onto Mg\(_2\)(dobdc) below 1 bar. Mg\(_2\)(dobdc) required this measurement due to the open Mg\(^{2+}\) sites which interact strongly with CO\(_2\). During these measurements, glass sample tubes of a known weight were loaded with approximately 200 mg of sample, and sealed using a TranSeal. Samples were degassed on a Micromeritics ASAP 2020 analyzer until the outgas rate was no more than 1 mTorr/min as described above. The degassed sample and sample tube were weighed precisely and then transferred back to the analyzer (with the TranSeal preventing exposure of the sample to the air after degassing). The outgas rate was again confirmed to be less than 1 mTorr/min. Adsorption isotherms were measured at 77 K in a liquid nitrogen bath for and N\(_2\) and 313 K in an isothermal water bath for CO\(_2\).

**High-Pressure Gas Sorption Measurements** In a typical measurement, at least 200 mg of sample was loaded in a sample holder in a glove box under an argon atmosphere. Hydrogen and carbon dioxide excess adsorption measurements were performed on an automated Sieverts’ apparatus (PCTPro-2000 from Hy-Energy Scientific Instruments LLC) over a pressure range of 0-50 bar. UHP-grade hydrogen, carbon dioxide and helium (99.999% purity) were used for all measurements. Total adsorption was calculated using NIST Thermochemical Properties of Fluid Systems: CO\(_2\) and H\(_2\) densities between 0 and 50 bar were fit using a sixth-order polynomial, then multiplied by the pore volume of each material.\(^{27}\)

**Interpolation of 313 K adsorption data for zeolite 13X** Belmabkhout et al.\(^{28}\) reported excess adsorption of CO\(_2\) and H\(_2\) on zeolite 13X at 303 K and 323 K. These were converted to total adsorption using a pore volume of 0.34 cm\(^3\)/g. Carbon dioxide uptake values and hydrogen uptake values were fit to dual- and single-site Langmuir Freundlich fits, respectively. The averages of these curves were taken at intervals of 0.1 bar from 0 to 14 bar, and then these averaged values were again fit to dual- and single-site Langmuir Freundlich fits for the interpolated CO\(_2\) and H\(_2\) data sets, respectively.

**Ideal Adsorbed Solution Theory calculations** The ideal adsorbed solution theory (IAST) was used to estimate the composition of the adsorbed phase from pure component isotherm data.\(^{29,30}\) Experimental absolute isotherm data were fit to the dual-site Langmuir-Freundlich isotherm for CO\(_2\) adsorption and the single-site Langmuir-Freundlich model for H\(_2\). H\(_2\) saturation capacities were allowed to refine between two and three times the saturation capacity for CO\(_2\), which was confirmed visually. The integrals
were computed numerically and the adsorbed phase composition that minimized the difference between the integrals of the two spreading pressures was found using Mathematica®. Selectivities were calculated according to equation 1, where $x_i$ is the mole fraction of component $i$ in the adsorbed phase and $y_i$ is the mole fraction of component $i$ in the bulk. Working capacities were calculated according to equation 2, where $n_t$ is the total number of adsorbed moles of gas per unit mass of adsorbent and $n_i^o$ is the number of moles of component $i$ in the adsorbed phase per unit mass of adsorbent.

\[
S = \frac{x_i y_j}{x_j y_i}
\]  

\[
\frac{1}{n_t} = \frac{x_i}{n_i^o} + \frac{1}{n_j^o} = \frac{x_i}{n_i^o} + \frac{x_j}{n_j^o}
\]

2.3 Results and Discussion

The compounds Zn$_4$O(BTB)$_2$ (MOF-177, BTB$^{3-} = 1,3,5$-benzenetribenzoate)$^{32}$ and Be$_{12}$(OH)$_{12}$(BTB)$_4$ (Be-BTB)$^{21}$ were chosen as representative of metal-organic frameworks exhibiting a high surface area and a rigid framework structure. As a flexible framework, Co(BDP) (BDP$^{2-} = 1,4$-benzenedipyrazolate) was selected owing to its high surface area relative to most compounds of this type.$^{22}$ Finally, H$_3$[(Cu$_3$Cl)$_3$(BTTri)$_8$] (Cu-BTTri, BTTri$^{3-} = 1,3,5$-benzenetristriazolate)$^{12c}$ and Mg$_2$(dobdc) (Mg-MOF-74, dobdc$^{4-} = 1,4$-dioxido-2,5-benzenedicarboxylate)$^{11a}$ were chosen as prototypical of the broad class of metal-organic frameworks that possess surfaces coated with exposed metal cations. All five compounds were synthesized and activated, and their BET and Langmuir surface areas (Figure 2.1) were determined from N$_2$ adsorption isotherms collected at 77 K. Cryogenic nitrogen adsorption isotherms were compared to literature values because optimized activation of each material is crucial for an accurate comparison of adsorption behavior. These comparisons can be found in Figure 2.1.

Figure 2.2 shows the single-component CO$_2$ and H$_2$ adsorption isotherms recorded at 313 K for MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg$_2$(dobdc). As might be expected, the CO$_2$ adsorption capacity scales roughly with surface area, and is much higher than the corresponding adsorption capacity for H$_2$ due to the higher polarizability and quadrupole moment of the CO$_2$ molecule. CO$_2$ adsorption capacity also scales qualitatively with the accessible pore volumes of 1.59, 0.93, 0.713 and 0.573 cm$^3$/g for MOF-177, Co(BDP), Cu-BTTri and Mg$_2$(dobdc), respectively. As in the surface area scenario, validation of experimental data lends greater confidence to any results. Figure 2.3 presents high pressure CO$_2$ adsorption on Mg$_2$(dobdc) from previously reported literature in comparison with the data from this study. The more complete activation achieved in this report is reflected in the similar adsorption results despite the literature data being collected at a lower temperature.
Figure 2.1. Adsorption isotherms for N\textsubscript{2} at 77 K in MOF-177 (top left), Be-BTB (top right), Co-BDP (middle left), Cu-BTTri (middle right), and Mg\textsubscript{2}(dobdc) (bottom). Black and red represent previously reported and experimental data, respectively.
Figure 2.2 Absolute adsorption isotherms for CO$_2$ (green triangles) and H$_2$ (blue circles) in MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg$_2$(dobdc) at 313 K. The Langmuir surface area (SA) obtained for each framework is given.
Figure 2.3 Gas adsorption isotherms for CO\textsubscript{2} on Mg\textsubscript{2}(dobdc). Green triangles represent the isotherms measured for this study at 313 K and black diamonds are data recorded at 303 K.\textsuperscript{12}\textsuperscript{d}

Notably, Cu-BTTri and Mg\textsubscript{2}(dobdc) exhibit high CO\textsubscript{2} adsorption (particularly at low pressures) relative to their surface areas due to the additional polarizing influence of the open metal cation sites decorating the framework surfaces. Contrasting with these results, the step-like features in the CO\textsubscript{2} isotherm for Co(BDP) are presumably associated with a gate-opening phenomenon arising from the flexibility of the framework structure.

In order to probe the performance of the materials under an 80:20 H\textsubscript{2}:CO\textsubscript{2} gas mixture relevant to H\textsubscript{2} purification,\textsuperscript{3} ideal adsorbed solution theory (IAST) was employed to estimate mixed-gas adsorption behavior.\textsuperscript{34} The accuracy of IAST for estimating component loadings for adsorption of a wide variety of binary mixtures in zeolites has been established with the aid of Configurational-Bias Monte Carlo (CBMC) simulations.\textsuperscript{35} Specifically, it has been previously been applied to the separation of CO\textsubscript{2} from H\textsubscript{2} within metal-organic frameworks\textsuperscript{15}\textsuperscript{a,c,c} and other porous solids.\textsuperscript{7}\textsuperscript{a,f,8}\textsuperscript{a,d}

Figure 2.3 shows the selectivities for CO\textsubscript{2} over H\textsubscript{2} calculated for the metal-organic frameworks using the single-component gas sorption isotherms. Significantly, the two frameworks with exposed metal cation sites, Cu-BTTri and Mg\textsubscript{2}(dobdc), display by far the highest selectivities, presumably owing to the greater polarizability of CO\textsubscript{2} versus H\textsubscript{2}. The selectivity seen can presumably be ascribed to these open metal site-CO\textsubscript{2} interaction because the enhanced interaction of guest gas molecules, specifically CO\textsubscript{2}, in porous materials with coordinatively unsaturated metal sites is well-established.\textsuperscript{9}\textsuperscript{a,b,11}\textsuperscript{a,13}\textsuperscript{d,36}

With a greater concentration of cationic sites exposed on its surfaces, Mg\textsubscript{2}(dobdc) shows the best performance, exhibiting a selectivity that gradually decreases from 859 at 5 bar to 305 at 40 bar. We note that this material has also previously been shown to exhibit a high CO\textsubscript{2}/N\textsubscript{2} selectivity under lower-pressure conditions.\textsuperscript{11}\textsuperscript{a}\textsuperscript{12}\textsuperscript{d}
Figure 2.4 313 K IAST CO$_2$/H$_2$ selectivities for a 80:20 H$_2$:CO$_2$ mixture, as calculated from gas sorption isotherms collected for the metal-organic frameworks MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg$_2$(dobdc), activated carbons BPL and JX101 and zeolites 5A and 13X.

The other metal-organic frameworks, MOF-177, Be-BTB, and Co(BDP), all show drastically lower selectivities of less than 10. The particularly poor performance of Be-BTB is likely associated with its unusually high H$_2$ uptake, as previously reported at 298 K and attributed to the dimensions of the rings comprising its structure.21 We note that although flexible frameworks such as Co(BDP) are sometimes touted as good separation materials based on single-component isotherms, cooperative effects, in which one gas can open the pores and facilitate admission of the other, may invalidate these claims (and additionally the application of IAST).

For comparison, CO$_2$ and H$_2$ isotherm data for common PSA adsorbents,$^{3a,c,f,6a}$ zeolite 5A$^{37}$ and two activated carbons,$^{35,38}$ were taken from the literature and treated similarly using IAST. Due to the variability in activated carbons, both JX101 and BPL35 were considered in an effort to broaden the scope of the comparison. Data for zeolite 13X$^{39}$ were also included, since this material has recently been shown to outperform zeolite 5A in terms of CO$_2$ capacity$^{40}$ and breakthrough measurements.$^{41}$ Zeolite 13X selectivity values are depicted in Figure 2.4 at 313 K (determined from interpolating literature adsorption data at 303 K and 323 K), and Mg$_2$(dobdc) outperforms zeolite 13X at all pressures. Selectivities for zeolite 5A at 303 K (which can be assumed to decrease at 313 K) are similar to those of Mg$_2$(dobdc), but with higher values at low pressures and slightly lower values at high pressures. Thus, in terms of selectivity,
Figure 2.5 IAST-calculated gravimetric (top) and volumetric (bottom) CO$_2$ working capacities for an 80:20 H$_2$:CO$_2$ mixture for the metal-organic frameworks MOF-177, Be-BTB, Co(BDP), Cu-BTTri, and Mg$_2$(dobdc) and the activated carbon JX101 at 313 K, and for zeolite 13X at 303 and 323 K.37
Mg\textsubscript{2}(dobdc) can be expected to perform the separation of CO\textsubscript{2} from H\textsubscript{2} at least as well as any known adsorbent under the conditions assessed.

Due to the nature of PSA purification, the working capacity—the difference between the capacity at the high intake pressure and at the lower purge pressure—is a critical metric for evaluating adsorbents.\textsuperscript{3,42} The CO\textsubscript{2} working capacities for the metal-organic frameworks under an 80:20 H\textsubscript{2}:CO\textsubscript{2} mixture and assuming a purge pressure of 1 bar were calculated using IAST and compared to the values obtained for the zeolites and activated carbons (Figure 2.5). While gravimetric capacities (moles of CO\textsubscript{2} adsorbed per kg of adsorbent) are normally reported when evaluating materials for a CO\textsubscript{2}/H\textsubscript{2} separation, the volumetric working capacities (moles of CO\textsubscript{2} adsorbed per L of adsorbent) were also calculated, since both factors are critical in designing a PSA separation process.\textsuperscript{6a} Here, the true advantage of utilizing metal-organic frameworks comes to the fore. Owing to its greater specific surface area and larger pore sizes, Mg\textsubscript{2}(dobdc) and outperforms the zeolites by a considerable margin, with working capacities climbing to values of 6.7 mol/kg and 6.2 mol/L at 40 bar. Thus, at higher pressures, use of Mg\textsubscript{2}(dobdc) in place of zeolite 13X could reduce the mass of adsorbent needed by a factor of 2.2 and the volume needed by a factor of 2.9.

2.4 Conclusions and Outlook

In this investigation, we have discovered that metal-organic frameworks containing strongly adsorbing sites are strong candidates for CO\textsubscript{2}/H\textsubscript{2} separations. Interestingly, the high surface areas and concomitant extraordinary CO\textsubscript{2} uptake of many metal-organic frameworks does not necessarily make them ideal for CO\textsubscript{2} separations. This conclusion could potentially apply to other separations within metal-organic frameworks as well. Industrially, adsorbents for this separation are tailored and optimized for each specific PSA system,\textsuperscript{3a} and therefore the equilibrium adsorption data presented here provide an initial step towards improving the efficiency of the process. In order to validate the efficacy of metal-organic frameworks, however, additional experiments are still needed, such as investigating CO\textsubscript{2} desorption by purge.\textsuperscript{43} This regeneration is not expected to stand in the way of their use, however, since the isosteric heats of CO\textsubscript{2} adsorption in Mg\textsubscript{2}(dobdc) (−42 kJ/mol)\textsuperscript{11a} and Cu-BTTri (−21 kJ/mol)\textsuperscript{12c} are quite similar to those of the currently employed zeolite 5A (−40 kJ/mol) and activated carbon (−23 kJ/mol).\textsuperscript{3f} Ultimately, the successful implementation of such new adsorbents could both reduce the substantial energy cost of hydrogen purification and eliminate CO\textsubscript{2} emissions in the generation of electricity from coal. Along these lines, future work will probe whether metal-organic frameworks with good thermal and hydrolytic stability might even be suitable for the \textit{in situ} separation of CO\textsubscript{2} from H\textsubscript{2} during sorption-enhanced water-gas shift reactions.\textsuperscript{44}

2.5 Acknowledgements

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2.6 References


(16) While high-pressure CO₂ and H₂ adsorption isotherms have been reported previously for various metal-organic frameworks, including some of the ones studied here, to our knowledge they have never been investigated in relation to a realistic H₂ purification separation. See for example: (a) Miller, S. R.; Wright, P. A.; Devic, T.; Serre, C.; Férey, G.; Llewellyn, P. L.; Denoyel, R.; Gaberova, L.


(20) Vajo, J.; Pinkerton, F.; Stetson, N. *Nanotechnology* 2009, 20, 204006.


(22) Vajo, J.; Pinkerton, F.; Stetson, N. *Nanotechnology* 2009, 20, 204006.


Chapter 3: \( \text{CO}_2/\text{CH}_4 \), \( \text{CH}_4/\text{H}_2 \), and \( \text{CO}_2/\text{CH}_4/\text{H}_2 \) Separations at High Pressures Using \( \text{Mg}_2(\text{dobdc}) \)

3.1 Introduction

The development of efficient new methods of separating gas mixtures into their component parts is urgently needed for two distinct reasons. First, many gas separations are performed on vast scales in numerous industrial processes and so improvements will lead to global energy savings.\(^1\) Additionally, carbon capture and storage is an exciting possibility for preventing the release of anthropogenic carbon dioxide into the atmosphere and hinges on gas separations at its core. Current gas separation processes are not sufficiently advanced to render carbon capture a viable addition to power plants.\(^2,3\) As a result, optimizing gas separations is a pragmatic approach to solving contemporary energy-related problems.

The adsorptive separation of gases, wherein one constituent interacts more strongly with the internal surfaces of a porous material, is a leading candidate in most gas separation applications.\(^4\) This cyclic process exposes a gas mixture to a bed filled with porous adsorbent, through which one component moves quickly to the other end. The other gas adsorbs to the internal surface of the adsorbent, and is removed by either dropping the pressure or increasing the temperature to regenerate the bed.\(^5\) Zeolites and activated carbons are common, established porous materials that offer the advantages of being inexpensive and already optimized for many existing gas separation processes.

The exceptional porosity and chemical tunability of metal-organic frameworks, a class of porous materials that has emerged relatively recently, render them exciting candidates to replace or augment the current suite of available adsorbents.\(^6\) Because these materials are composed of multifunctional organic molecules linked by metal cations, a nearly limitless number of combinations are available to form new structures, resulting in an immense versatility in the possible geometries and surface properties. Ideally, a metal-organic framework could be synthesized specifically for application in any given gas separation.\(^7\)

### High-pressure \( \text{CO}_2/\text{CH}_4 \), \( \text{CH}_4/\text{H}_2 \), and \( \text{CO}_2/\text{CH}_4/\text{H}_2 \) separations

Hydrogen purification is one industrial process for which optimized adsorbents are urgently needed. Over 50 million tons of \( \text{H}_2 \) are synthesized and purified annually,\(^8\) and the same process for generating hydrogen could potentially be a step in one method for reducing carbon dioxide emissions from power plants. In pre-combustion \( \text{CO}_2 \) capture, \( \text{H}_2 \) is isolated from the other gases present after its synthesis and prior to its combustion, rendering water as the only combustion product. Physisorptive separation using porous adsorbents, the strategy that is already performed in most \( \text{H}_2 \) purification plants,\(^9\) is attractive for both \( \text{H}_2 \) purification and pre-combustion \( \text{CO}_2 \) capture, because improvements to current processes will not require drastic engineering overhauls.

Hydrogen is commonly generated by steam-reforming of methane. This process generates \( \text{CO} \) and \( \text{H}_2 \). Using this \( \text{CO} \), the water-gas shift reaction generates \( \text{CO}_2 \) and more \( \text{H}_2 \). Some \( \text{CO} \) (ca. 1-3%) and \( \text{CH}_4 \) (ca. 3-6%) impurities remain in addition to the large fraction of \( \text{CO}_2 \) (ca. 15-25%).\(^10\) Because such a large proportion of the resulting gas mixture is \( \text{CO}_2 \), an ideal adsorbent will have a high capacity for \( \text{CO}_2 \). However, the separation of \( \text{CH}_4 \) from \( \text{H}_2 \) is equally or perhaps more important than \( \text{CO}_2/\text{H}_2 \) separation.
This is because in a packed bed of porous adsorbent the least adsorbing non-H$_2$ impurity will elute first and contaminate the product stream.\textsuperscript{11} The adsorbent must be regenerated when an impurity starts to elute, and regeneration is a critical factor in optimizing an H$_2$ purification system.\textsuperscript{12} In a CO$_2$/CH$_4$/CO/H$_2$ mixture, CH$_4$ adsorbs less strongly than CO because it has no quadrupole or dipole moment.\textsuperscript{13} Methane is also important to remove from a flue gas, since it is a potent greenhouse gas.\textsuperscript{14}

The separation of CH$_4$ from H$_2$ is also relevant to refinery off-gas processing.\textsuperscript{13-15} The gas mixture being separated is approximately 50\% H$_2$ at 5-10 bar.\textsuperscript{16,17} Here, the impurities are C1-C5 hydrocarbons. As in CO$_2$/CH$_4$/H$_2$ separation, the most difficult separation is the most important to optimize. Methane is the smallest of the impurities, making the van der Waals forces between it and the surface of a porous material the weakest.\textsuperscript{16} As a result, CH$_4$/H$_2$ separation is the most difficult separation to achieve in refinery off-gas separation.

Separation of CO$_2$ from CH$_4$ is a distinct separation from those described above. It is relevant to the purification of natural gas, which can have up to 92\% CO$_2$ impurity at its source.\textsuperscript{18} Removal of CO$_2$, which is most commonly accomplished using amines\textsuperscript{19} to reduce CO$_2$ levels to the required 2\% maximum, is conducted between 20 and 70 bar.\textsuperscript{20} Carbon dioxide removal is required for approximately 25\% of the natural gas reserves in the United States.\textsuperscript{18}

The metal-organic framework Mg$_2$(dobdc) Metal-organic frameworks are a class of porous materials that offer potential advantages over traditional adsorbents for all of the aforementioned gas separations. A number of these have already been studied for separations of CO$_2$/CH$_4$,\textsuperscript{21-26} CH$_4$/H$_2$,\textsuperscript{27-35} and CO$_2$/H$_2$\textsuperscript{11,13,31,32,36-45} Frameworks featuring coordinatively-unsaturated metal sites are especially promising for these gas separations. High-pressure adsorption isotherms of CO$_2$ and CH$_4$ have been calculated\textsuperscript{46,47} and measured\textsuperscript{48} together in metal-organic frameworks of this type. High-pressure CO$_2$, H$_2$ and CH$_4$ adsorption behavior have been studied in isolation in even more metal-organic frameworks with open metal sites.

We recently reported that metal-organic frameworks are promising candidates for effecting H$_2$ separation from CO$_2$ and, as a result, are possible alternatives to current adsorbents (zeolites and activated carbons) for H$_2$ purification or pre-combustion CO$_2$ capture.\textsuperscript{42} In particular, Mg$_2$(dobdc), a metal-organic framework with a high concentration of exposed Mg$^{2+}$ sites decorating its surface, displayed a much higher CO$_2$/H$_2$ selectivity than other frameworks, as well as zeolites and activated carbons. Additionally, its working capacity (the difference in the amount adsorbed at the high adsorption pressure and the lower purge pressure) is much higher than activated carbons, zeolites, and many other metal-organic frameworks. Computationally, Mg$_2$(dobdc) was shown to be outstanding in both selectivity and CO$_2$ capacity among an even larger group of zeolites, activated carbons and metal-organic frameworks when compared for both CO$_2$/H$_2$ and CH$_4$/H$_2$ separations.\textsuperscript{45} Experimentally, the material was investigated for the ambient-pressure separation of CO$_2$ and CH$_4$ in Mg$_2$(dobdc)\textsuperscript{26} and high-pressure adsorption isotherms of CO$_2$ and CH$_4$ were also measured.\textsuperscript{49} Both of these studies reported breakthrough curves for CO$_2$/CH$_4$ mixtures, but neither discussed the equilibrium mixture behavior.

In order to rigorously examine the applicability of Mg$_2$(dobdc) for CO$_2$/CH$_4$, CH$_4$/H$_2$, and CO$_2$/CH$_4$/H$_2$ separations, we now report pure-component CH$_4$ adsorption
behavior onto Mg\(_2\)(dobdc). These data are analyzed together with the previously reported high-pressure CO\(_2\) and H\(_2\) isotherms.[42] Low pressure (0-1 bar) CO\(_2\) and CH\(_4\) adsorption isotherms are also reported in order to improve the quality of the data set. The Ideal Adsorbed Solution Theory (IAST)\(^{50}\) is applied to pure component isotherms of CH\(_4\), H\(_2\) and CO\(_2\) in order to demonstrate the selectivity and working capacity for binary CO\(_2/\)CH\(_4\) and CH\(_4/\)H\(_2\), as well as ternary CH\(_4/\)H\(_2/\)CO\(_2\), mixtures. Breakthrough behavior for CO\(_2/\)CH\(_4\) and CO\(_2/\)H\(_2/\)CH\(_4\) mixtures are simulated. All of the isotherms were measured on samples of Mg\(_2\)(dobdc) generated in the same laboratory and confirmed to be of high quality via cryogenic N\(_2\) adsorption measurements, a technique that is very sensitive to the purity of the sample.

3.2 Experimental Section

**Synthesis and characterization of Mg\(_2\)(dobdc)** The compound Mg\(_2\)(dobdc) was synthesized as reported previously.[42] All reagents were obtained from commercial vendors and used without further purification. The material was activated using a strategy adapted from the literature procedure. The yellow microcrystalline solids were combined and washed five times with DMF and soaked in DMF for 24 h. The DMF was decanted, and freshly distilled methanol was added. The solid was then transferred to a nitrogen-filled glovebox. The methanol was decanted and the solid was soaked in anhydrous DMF on a hotplate set at 100 °C for 18 h. The DMF was decanted and replaced, and the solid was soaked at 100 °C for 4 h. The DMF was decanted and replaced by methanol, which was decanted and replenished 12 times with a minimum of 6 h between washes. Infrared spectroscopy was used to confirm the removal of all DMF by monitoring the C=O stretch at ca. 1650 cm\(^{-1}\). Infrared spectra were obtained on a Perkin-Elmer Spectrum 100 Optica FTIR spectrometer furnished with an attenuated total reflectance accessory (ATR).

**Low-pressure gas adsorption measurements** Gas adsorption isotherms for pressures in the range 0-1.1 bar were measured by a volumetric method using a Micromeritics ASAP2020 instrument. A sample was transferred in an N\(_2\)-filled glovebox to a pre-weighed analysis tube, which was capped with a transeal and evacuated by heating to 180 °C for under dynamic vacuum until the outgas rate was determined to be 4 \(\mu\)Torr/min. The evacuated analysis tube containing the degassed sample was then carefully transferred to an electronic balance and weighed again to determine the mass of sample. The tube was then transferred back to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity); N\(_2\) isotherms at 77 K were measured in liquid nitrogen using UHP-grade gas sources. Adsorption of CO\(_2\) and CH\(_4\) at 323 K was measured using a Julabo isothermal bath with UHP-grade gases. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

**High-pressure gas adsorption measurements** A sample of Mg\(_2\)(dobdc) (289.0 mg) was loaded in an air-free sample holder in a glove box under a nitrogen atmosphere. The stainless steel sample holder was weighed five times before adding the sample and three times afterwards in order to determine the precise mass of Mg\(_2\)(dobdc). Methane excess adsorption measurements were performed on an automated Sieverts’ apparatus.
(PCTPro-E&E from Setaram Instrumentation) over a pressure range of 1-50 bar. UHP grade 5.0 methane and helium (99.999% purity) were used. Total adsorption was calculated using NIST Thermochemical Properties of Fluid Systems. CH$_4$ densities between 0 and 50 bar were fit using a sixth-order polynomial, then multiplied by the previously reported pore volume of 0.57 cm$^3$/g. The Langmuir region of the 77 K N$_2$ adsorption isotherm was measured again after the high-pressure adsorption measurement to ensure sample contamination had not occurred.

**Ideal Adsorbed Solution Theory calculations** The Ideal Adsorbed Solution Theory (IAST) of Prausnitz and Myers was used to estimate the composition of the adsorbed phase from pure component isotherm data. A detailed explanation of the IAST calculations has been previously reported.

The pure component isotherm data for CO$_2$, CH$_4$, and H$_2$ in Mg$_2$(dobdc), after conversion to absolute loadings, were fitted with Langmuir-Freundlich isotherm models. For the cases of CO$_2$ and CH$_4$ dual-site isotherm models of the type shown in equation 1 were employed.

$$q_i = q_{i, A, sat} \frac{b_{i,A} P_i^{\nu_{i,A}}}{1 + b_{i,A} P_i^{\nu_{i,A}}} + q_{i, B, sat} \frac{b_{i,B} P_i^{\nu_{i,B}}}{1 + b_{i,B} P_i^{\nu_{i,B}}}$$  

Here, $q_i$ is the component molar loading of species $i$ (in mol/kg), $q_{i, sat}$ is the saturation loading of species $i$ and $p_i$ is the bulk gas pressure of species $i$ (in Pa). Subscripts A and B refer to the two different types of adsorption sites on the surface. The parameters $\nu_i$ are the dimensionless exponent in the Langmuir-Freundlich isotherms. For the case of H$_2$, the data were fit using a single-site isotherm model in which the second term in equation 1 is dropped.

**Zeolite 13X data treatment** The pure component isotherm data for CO$_2$, CH$_4$, and H$_2$ in zeolite 13X were obtained from previous reports. In cases where the excess loadings were reported, these were converted to absolute loadings using the reported pore volume data along with the Peng-Robinson equation of state for estimation of fluid densities in the pores. The reported data are for a variety of temperatures that unfortunately do not include 313 K. In these cases the Langmuir constants were fitted using equation 2.

$$b_{i,A} = b_{i,A0} \exp \left( \frac{E}{RT} \right)$$  

$$b_{i,B} = b_{i,B0} \exp \left( \frac{E}{RT} \right)$$  

Here, $b$ is the dual-site Langmuir-Freundlich constant for species $i$ and A and B represent the two adsorption sites on the surface. The heats of adsorption, $E$, for CO$_2$, CH$_4$, and H$_2$ were taken to be 35, 14, and 6 kJ/mol respectively.

### 3.3 Results and Discussion

**Pure-component CO$_2$, CH$_4$, and H$_2$ adsorption in Mg$_2$(dobdc)** Figure 3.1 shows the pure-component absolute adsorption isotherms for CH$_4$, H$_2$, and CO$_2$ in Mg$_2$(dobdc) at 313 K and pressures in the range 0-40 bar. These isotherms are in agreement with previously published data. At 35 bar, CO$_2$ has reached saturation
at 15 mmol/g, while CH\textsubscript{4} and H\textsubscript{2} have not, reaching ca. 10 and 3 mmol/g, respectively. The H\textsubscript{2} adsorption isotherm is linear in this pressure window, while CH\textsubscript{4} begins to approach saturation behavior.

![Figure 3.1](image.png)

**Figure 3.1** Absolute adsorption isotherms for CO\textsubscript{2} (green triangles), CH\textsubscript{4} (red squares) and H\textsubscript{2} (blue circles) in Mg\textsubscript{2}(dobdc) at 313 K.

These isotherms were fit with Langmuir-Freundlich models using a dual-site model for CO\textsubscript{2} and CH\textsubscript{4} and a single-site model for H\textsubscript{2}. The open-metal sites in Mg\textsubscript{2}(dobdc) create heterogeneity in the surface that requires this type of modeling; however, the small size and low adsorption enthalpy of H\textsubscript{2} led to a sufficiently good fit of the data using a single-site model.

**CO\textsubscript{2}/CH\textsubscript{4}, CH\textsubscript{4}/H\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4}/H\textsubscript{2} separations calculated with IAST** The remainder of this chapter discusses the mixed-gas adsorption behavior of CO\textsubscript{2}, CH\textsubscript{4}, and H\textsubscript{2} in Mg\textsubscript{2}(dobdc). Using the Ideal Adsorbed Solution Theory (IAST), 50 mixed-gas adsorption behavior was extracted from the pure-component isotherms. Such estimations are essential in practice because collecting experimental data on mixture adsorption is time consuming and extremely rare.\textsuperscript{55} IAST was used to calculate selectivity, working capacity and breakthrough performance.

The binary mixtures are calculated as a 50/50 composition. This composition was chosen because most reports of these mixtures employ a 50/50 mixture. Further, this ratio should mitigate some of the artifacts of IAST that can be observed when the less-adsorbed species is a large fraction of the gas mixture.\textsuperscript{44} The ternary mixture is 1:4:20 CH\textsubscript{4}:CO\textsubscript{2}:H\textsubscript{2} in an effort to model a realistic hydrogen purification composition.

The use of IAST with any adsorbent/adsorbate mixture system must be carefully considered due to the limitations of the theory.\textsuperscript{56} We have determined IAST to be appropriate for the gas mixtures evaluated here. The theory has been used to evaluate CH\textsubscript{4}/H\textsubscript{2}, 30 CO\textsubscript{2}/CH\textsubscript{4},\textsuperscript{25,63} and CO\textsubscript{2}/H\textsubscript{2} gas mixtures in metal-organic frameworks.
More valuable in evaluating the validity of IAST in these gas mixtures are comparisons of IAST and Grand Canonical Monte Carlo (GCMC) simulations. It has been shown that IAST compares well with GCMC simulations of CH$_4$/H$_2$ selectivity in MOF-5 and HKUST-1.32 The effectiveness of IAST has also been validated by this method for CH$_4$/H$_2$ separations in non-interpenetrated29,31,33,34 and interpenetrated35-64 metal-organic frameworks. GCMC simulations have further validated the use of IAST for the modeling of CO$_2$/CH$_4$ mixtures in metal-organic frameworks.64,65,66 Finally, the use of IAST for CO$_2$/H$_2$ separations has been validated in Mg$_2$(dobdc) specifically using configurational bias Monte Carlo simulations.67

**CO$_2$/CH$_4$, CH$_4$/H$_2$ and CO$_2$/CH$_4$/H$_2$ selectivity** Selectivity is an important metric for evaluating adsorbents and can be calculated using IAST.68,69 Selectivity for a binary gas mixture is defined as in equation 3, where $q_i$ is the mole fraction of component $i$ in the adsorbed phase and $p_i$ is the mole fraction of component $i$ in the bulk gas phase.

$$\text{Selectivity} = \frac{q_1 / q_2}{p_1 / p_2} \quad (3)$$

Figure 3.2 shows CO$_2$/CH$_4$, CH$_4$/H$_2$ and (CO$_2$ + CH$_4$)/H$_2$ selectivities for Mg$_2$(dobdc). CO$_2$/H$_2$ selectivity is also shown for comparison for an 80:20 mixture. As expected, the CO$_2$/CH$_4$ selectivity is higher than the CH$_4$/H$_2$ selectivity, and both are lower than the CO$_2$/H$_2$ selectivity, which ranges from 900-400 at these pressures.42 This can be rationalized using the quadrupole moments and polarizabilities of the three gases and are discussed individually below.

CO$_2$/CH$_4$ selectivity is high because CH$_4$ has no quadrupole moment, while CO$_2$ does. In contrast, CO$_2$/H$_2$ selectivity is higher than CO$_2$/CH$_4$ because CO$_2$ has a higher quadrupole moment and higher polarizability than H$_2$, while CO$_2$ and CH$_4$ have similar polarizabilities. The selectivity decreases drastically for the CO$_2$/CH$_4$ mixture up to 5 bar, which can be attributed to the strong CO$_2$ binding at low loadings evidenced by the steep rise in the pure-component isotherm at low pressures.38

CH$_4$/H$_2$ selectivity is the lowest selectivity examined here because while CH$_4$ is more polarizable than H$_2$ the quadrupole moment of H$_2$ is larger than that of CH$_4$. However, the difference in quadrupole moment between CH$_4$ and H$_2$ is larger (6.62 x 10$^{25}$ esu cm$^3$) than the difference in polarizability (17.888 x 10$^{25}$ cm$^3$). The selectivity for three-component CH$_4$/CO$_2$/H$_2$ mixtures relevant to hydrogen purification and pre-combustion CO$_2$ capture is also shown in Figure 3.2. In a 1:4:20 CH$_4$:CO$_2$:H$_2$ mixture, the selectivity for both CO$_2$ and CH$_4$ decreases from 1400 at 1 bar to 260 at 40 bar. This selectivity is slightly lower than the 20:80 CO$_2$:H$_2$ selectivity reported in an earlier work.42 This is expected, as compared to a 20:80 mixture a 4:16:80 CH$_4$:CO$_2$:H$_2$ mixture replaces a fraction of CO$_2$ with less-selective CH$_4$.

Because of the variability in gas mixture compositions in the shifted products of steam-methane reforming, refinery off-gas, and natural gas, investigating the performance under different compositions is an important indicator of a broadly useful material. Figure 3.3 shows the selectivity for CH$_4$ in a CH$_4$/H$_2$ mixture and mixture as a function of mole fraction of CH$_4$. Selectivity for CH$_4$ in a CH$_4$/H$_2$ mixture varies only slightly with composition at all pressures. This is expected because the selectivity shown in Figure 3.2 is only slightly pressure-dependent and therefore should not be dependent on the partial pressure of CH$_4$. 

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Figure 3.2 IAST selectivities obtained for Mg$_2$(dobdc) at 313 K for CO$_2$ and CH$_4$ in a 1:4:20 CH$_4$:CO$_2$:H$_2$ mixture (black diamonds), CO$_2$ in a 1:1 CO$_2$:CH$_4$ mixture (blue triangles), CH$_4$ in a 1:1 CH$_4$:H$_2$ mixture (red squares) and CO$_2$ in an 80:20 H$_2$:CO$_2$ mixture (green circles). Selectivities are calculated throughout the entire line trace, and symbols are only shown to distinguish the lines visually.

Figure 3.3 shows the selectivity for CO$_2$ in a CO$_2$/CH$_4$ as a function of mole fraction of CO$_2$. In contrast to CH$_4$/H$_2$ selectivity, which is strongly pressure-independent, CO$_2$/CH$_4$ selectivity decreases by half from 2 to 98% CO$_2$ in the case of a 5 bar mixture. This is expected because selectivity decreases with higher partial pressures of CO$_2$ due to the saturation of the strongly adsorbing sites on the surface of Mg$_2$(dobdc). At high mole fractions of CO$_2$, the selectivity asymptotically approaches ca. 57.

**CO$_2$/CH$_4$, CH$_4$/H$_2$ and CO$_2$/CH$_4$/H$_2$ working capacity** The working capacity of Mg$_2$(dobdc) for these same three mixtures can be seen in Figure 3.4. The working capacity is the difference between the amount adsorbed at high pressures and the amount adsorbed at the lower purge pressure, which is assumed here to be 1 bar. It has been previously reported that the working capacity is equally as important as selectivity in optimizing an adsorbent for pressure-swing adsorption. The working capacity of CO$_2$ is higher than for CH$_4$, but the difference is smaller than the difference in the pure-component isotherms. This is a result of the shallow rise in adsorption of CH$_4$ at lower pressures. The three-component mixture working capacity falls close to the binary mixture capacities but is lower at high pressures. This can be attributed to the difference in compositions of the three mixtures studied, as 80% of the mixture is comprised of H$_2$ in the three-component mixture.
Figure 3.3 |AST selectivities obtained for Mg₂(dobdc) at 313 K for CH₄ in a 1:1 CH₄:H₂ mixture (top) and CO₂ in a 1:1 CO₂:CH₄ (bottom) at 5 (blue circles), 10 (black vertical triangles), 20 (green squares), 30 (purple horizontal triangles) and 40 (orange diamonds) bar. Selectivities are calculated throughout the entire line trace, and symbols are only shown to distinguish the lines visually.
Figure 3.4 IAST-calculated gravimetric working capacities for Mg$_2$(dobdc) at 313 K assuming a purge pressure of 1 bar for CO$_2$ and CH$_4$ in a 1:4:20 CH$_4$:CO$_2$:H$_2$ mixture (black diamonds), CO$_2$ in a 1:1 CO$_2$:CH$_4$ mixture (blue triangles), and CH$_4$ in a 1:1 CH$_4$:H$_2$ mixture (red squares). Working capacities are calculated throughout the entire line trace, and symbols are only shown to distinguish the lines visually.

CO$_2$/CH$_4$, CH$_4$/H$_2$ and CO$_2$/CH$_4$/H$_2$ selectivity, working capacity and breakthrough performance in zeolite 13X compared to Mg$_2$(dobdc) Figure 3.5 displays the selectivity and working capacity of zeolite 13X using the same analysis scenarios described above for Mg$_2$(dobdc) and shown in Figures 3.2-3.4. This zeolite was chosen for comparison because it has an exceptionally high CO$_2$ capacity and breakthrough performance compared to other zeolites. High-pressure adsorption isotherms for CO$_2$, CH$_4$, and H$_2$ in zeolite 13X have been reported previously.

In every case, Mg$_2$(dobdc) outperforms zeolite 13X. The three selectivities shown resemble those in Figure 3.2, but are 75-50% lower. The three working capacity traces are approximately half of those of Mg$_2$(dobdc). The CH$_4$/H$_2$ selectivity displays a clear trend of decreasing selectivity between 10 and 6 from 2 to 98% CH$_4$. This can preliminarily be ascribed to a modestly higher pressure dependence in CH$_4$/H$_2$ selectivity for zeolite 13X compared to Mg$_2$(dobdc). The CO$_2$/CH$_4$ selectivity decreases with increasing CO$_2$ partial pressure, here approaching a value of 20 rather than 57.

The working capacity of zeolite 13X is approximately half that of Mg$_2$(dobdc) for all separations evaluated. In all three cases of breakthrough adsorption, Mg$_2$(dobdc) adsorbs approximately double the amount of gas as zeolite 13X with slightly higher breakthrough times. The difference in working capacity can explain this behavior.
Figure 3.5 All data are calculated using IAST for zeolite 13X at 313 K. Symbols are only shown to distinguish the continuous lines visually.

Top: Selectivities (right) and gravimetric working capacities (left) for CO₂ and CH₄ in a 1:4:20 CH₄:CO₂:H₂ mixture (black diamonds), CO₂ in a 1:1 CO₂:CH₄ mixture (blue triangles), CH₄ in a 1:1 CH₄:H₂ mixture (red squares) and CO₂ in an 80:20 H₂:CO₂ mixture (green circles).

Bottom: Selectivities for CH₄ in a 1:1 CH₄:H₂ mixture (right) and CO₂ in a 1:1 CO₂:CH₄ (left) at 5 (blue circles), 10 (black vertical triangles), 20 (green squares), 30 (purple horizontal triangles) and 40 (orange diamonds) bar.

3.4. Conclusions and Outlook

Here, we have presented the experimental single-component CH₄ adsorption behavior of Mg₂(dobdc). Together with previously reported CO₂ and H₂ isotherms, we experimentally evaluated this material for high-pressure gas separations performance. Binary CO₂/CH₄ and CH₄/H₂ as well as ternary CO₂/CH₄/H₂ mixtures were examined by applying the Ideal Adsorbed Solution Theory to these pure component isotherms. The selectivity and working capacity of Mg₂(dobdc) render this material promising for all of these high pressure separations, where it offers significant improvements over the competing material zeolite 13X.
Additionally, experimentally evaluating Mg₂(dobdc) for its performance under regeneration conditions is pertinent. We expect Mg₂(dobdc) to perform as well or better than zeolite 13X due to the isosteric heat of adsorption of CO₂ onto the two materials. Between 0 and 6 mmol/g, zeolite 13X decreases from approximately 50 to 37 kJ/mol, where Mg₂(dobdc) decreases from approximately 42 to 38 kJ/mol. More specifically, the strengths of the interaction at the assumed purge pressure of 1 bar are 46 and 41 kJ/mol for zeolite 13X and Mg₂(dobdc), respectively. At higher loadings, the heat of adsorption on Mg₂(dobdc) decreases even further after a steep drop in heat at 8 mmol/g where 1 CO₂ per Mg²⁺ site is achieved. Despite the promising regeneration capability these data suggest, laboratory regeneration experiments are necessary to determine the usefulness of this material in an industrial setting.

3.5 Acknowledgements

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3.6 References

(15) Voss, C. Adsorption 2005, 11, 527.


Chapter 4: CO$_2$/H$_2$ Separations in a Metal-Organic Framework with Exposed Mn$^{2+}$ Sites

4.1 Introduction

Metal-organic frameworks are a particularly interesting class of materials due to their modularity and tunability. These porous materials are crystalline scaffolds built from organic ligands bridging metal cations, and both metal and ligand can be systematically varied. This quality can provide general insight to fundamental chemistry and also be used to optimize materials for industrial uses. One specific feature of metal-organic frameworks that can be modified is the nature of coordinatively-unsaturated metal centers. These can be accessed when the self-assembled structure of a metal-organic framework results in one removable solvent molecule per metal vertex. Both the identity of the metal and the surrounding coordination environment can be modified to enhance certain features of the material by changing how polarizing these Lewis acid sites are towards guest molecules. Among the largest series of materials which has been compared is M$_2$(dobdc) (dobdc$^{4-}$ = 1,4-dioxido-2,5-benzenedicarboxylate). The material has been synthesized with Mg, Mn, Fe, Co, Ni, Cu, and Zn, and each has shown different properties.$^{1,2,3}$

![Figure 4.1](image)

**Figure 4.1** Crystallographic structure of Cu-BTTrri where gray, blue, orange, red, and yellow atoms correspond to C, N, Cl, Cu, and nonspecific removable solvent molecules, respectively.

Another interesting set of metal-organic frameworks with open metal sites is built from tetrazolate- or triazolate-based ligands. The general framework structure can be seen in Figure 4.1. The example shown is H$_3$[(Cu$_4$Cl)$_3$(BTTrri)$_8$] (Cu-BTTrri, BTTrri$^{3-}$ = 1,3,5-benzenetristriazolate), the open Cu$^{2+}$ sites of which have been shown to be promising for...
separating high pressure mixtures of CO$_2$ and H$_2$. This is based on the higher quadrupole moment of CO$_2$, which enables polarization from the open metal site to selectively interact with CO$_2$ over H$_2$.

This set of materials is versatile due to the potential of modifying both metal and bridging ligand. Ideally, Cu-BTTri could be improved upon to polarize CO$_2$ more strongly and therefore be a better industrial CO$_2$/H$_2$ separation material. Strategies for such an improvement can be taken from lessons from the previously-published, isostructural tetrazolate-based frameworks Cu-BTT \(^5\) (BTT$^{3-}$ = 1,3,5-benzenetristetrazolate) and Mn-BTT.\(^6\) Due to the higher Lewis acidity of the Mn$^{2+}$ centers compared to the softer Cu$^{2+}$ sites, Mn-BTT can polarize adsorbents better than Cu-BTT. Both of these materials are more polarizing than Cu-BTTri, however their lack of hydrolytic and thermal stability makes them less attractive candidates for industrial applications like CO$_2$/H$_2$ separations.\(^7\) Between tetrazoles and triazoles, the decrease in polarizing ability is due to the higher pK$_a$ (and therefore stronger electron donation) of triazole rings compared to tetrazole rings. This leads to more electron density at the metal center, which lowers the Lewis acidity. The benefit of this electron donation is that Cu-BTTri has stronger Cu–N bonds and therefore greater stability.

A useful target material would improve on the polarizing ability of Cu-BTTri while maintaining its stability (Table 4.1). Because of their isostructural nature, trends observed when comparing Mn-BTT and Cu-BTT can be applied. To that end, here we present the synthesis of a new triazole-based metal-organic framework with exposed Mn$^{2+}$ sites, Mn-BTTri, and report its improved CO$_2$/H$_2$ separation ability over Cu-BTTri.

<table>
<thead>
<tr>
<th>Less Polarizing</th>
<th>More Polarizing</th>
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</thead>
<tbody>
<tr>
<td>Cu-BTT</td>
<td>Mn-BTT</td>
</tr>
<tr>
<td>Cu-BTTri</td>
<td>Mn-BTTri</td>
</tr>
</tbody>
</table>

Table 4.1 Rationale for targeting Mn-BTTri as a CO$_2$/H$_2$ separation material.

4.2 Experimental Section

**General** Anhydrous methanol and DMF were obtained from Sigma Aldrich, used without further purification, and handled in a N$_2$-filled glovebag. Water was purified by a milli-Q purification system. All glassware was dried in an oven set to a temperature of 150 °C for 2h. All other reagents were obtained from commercial vendors and used without further purification.

**Physical measurements** Thermogravimetric analyses were carried out at a ramp rate of 1 °C/min under a 25 mL/min nitrogen flow with a TA Instruments TGA Q5000 V3.1 Build 246. Manganese content was determined by oxidizing pyrolysis (heating in air to 700 °C at 2 °C/min to transform into Mn$_2$O$_3$, as confirmed by powder X-ray diffraction). Infrared spectra were collected on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory (ATR). Powder X-ray diffraction data were collected using Cu Kα ($\lambda = 1.5406$ Å) radiation on a Bruker D8 Advance diffractometer. Elemental analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley. $^1$H NMR spectra were recorded at ambient
temperature on Bruker AV-300, AVQ-400, and AVB-400 spectrometers, and all chemical shifts are given in relation to residual solvent peaks.

**Unit Cell Determination** Mn-BTTri was ground with silicon powder as a slurry in methanol using an agate mortar and pestle. The resulting paste was pressed onto a powder mounting stage and the solvent allowed to evaporate. A 0.015 degrees 2θ step size was approximated on the continuous integration diffraction instrument with a theta-two theta geometry. A Reitveld refinement was performed on the Mn-BTTri powder data and the Mn-BTT-m cif file using the EXPGUI8 graphical user interface for the program GSAS26. A Le Bail fit was used because intensity data is expected to be different with different occupancies of heavy atoms, as in the case of Mn-BTT and Mn-BTTri. This approximation is valid when only unit cell parameters are being fit. The large manganese fluorescence background was fit graphically, and is unavoidable with a non-monochromated X-ray source.

**Low-Pressure Gas Adsorption Measurements** Gas adsorption isotherms for pressures in the range 0-1.2 bar were measured by a volumetric method using a Micromeritics ASAP2020 instrument. A sample of ca. 160 mg of Mn-BTTri-MeOH was transferred to a pre-weighed analysis tube, which was capped with a transeal and evacuated by heating at 170 °C under dynamic vacuum until an outgas rate of less than 2 mTorr/min (0.27 Pa/min) was achieved (ca. two days). The evacuated analysis tube containing the degassed sample of Mn-BTTri was then carefully transferred to an electronic balance and weighed again to determine the mass of sample (50.7 mg). The tube was then transferred back to the analysis port of the gas adsorption instrument. The outgas rate was again confirmed to be less than 2 mTorr/min (0.27 Pa/min). For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity); N2 and H2 isotherms at 77 and 87 K were measured in liquid nitrogen and liquid argon baths, respectively, using UHP-grade gas sources. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements. BET surface areas were determined from N2 adsorption data at 77K using the requirements described by Walton et al.9 Langmuir surface areas were output by Micromeritics software.

**Isosteric Heat of Adsorption (Qst) Calculations** Similarly to previous reports,6 a virial-type expression of the following form was used to fit the combined isotherm data for Mn-BTTri at 77 and 87K:

\[
\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i
\]

Here, \(P\) is the pressure expressed in Torr, \(N\) is the amount adsorbed in mmol/g, \(T\) is the temperature in K, \(a_i\) and \(b_i\) are virial coefficients, and \(m\) and \(n\) represent the number of coefficients required to adequately describe the isotherms. The equation was fit using the statistical software package included in Origin®; \(m\) and \(n\) were gradually increased until the contribution of extra added \(a\) and \(b\) coefficients was deemed to be erroneous. The values of the virial coefficients \(a_0\) and \(b_0\) were then used to calculate the isosteric heat of adsorption using the following expression:

\[
Q_{st} = -R \sum_{i=0}^{m} a_i N^i
\]
Here, $Q_v$ is the coverage-dependent isosteric heat of adsorption and $R$ is the universal gas constant.

**Synthesis of H$_3$BTTri** 1,3,5-triethynylbenzene was prepared as described in Demessence *et al.* Under a nitrogen atmosphere, trimethylsilyl azide (9.16 g, 79.5 mmol) was added to a solution of CuI (505 mg, 2.60 mmol) and 1,3,5-triethynylbenzene (2.65 g, 17.6 mmol) in a mixture consisting of 90 mL of DMF and 10 mL of methanol. The reaction mixture was stirred and heated at 100°C for 36 h. The hot mixture was filtered, washed three times with 30 mL of a hot 9:1 DMF:methanol mixture, and concentrated to a volume of ca. 10 mL under reduced pressure. Water (30 mL) was added to the filtrate to afford a pale green precipitate. The precipitate was filtered on Whatman 40 filter paper and then dissolved in 20 mL of a 1:2 H$_2$O:ethylene diamine solution. 3M HCl was added dropwise to afford a tan precipitate. The solid was collected by filtration, washed with diethylether, and this process was repeated two more times. The solid was dried in an oven at 150°C for 2h to yield 3.74 g (76%) of product. Filtration in hot chlorobenzene or sublimation did not increase purity as characterized by $^1$H NMR. Anal. Calc. for C$_{12}$H$_9$N$_9$: C 51.61, H 3.25, N 45.14. Found C 51.25, H 3.57, N 43.76.

[^1H NMR]: δ = 15.21 (s, 1 H), 8.52 (s, 1 H), 8.34 (s, 1 H) ppm. $^{13}$C NMR (400 MHz, (CD$_3$)$_2$SO): 132.10, 122.38, 71.72. EI$^+$/−MS: m/z = 279. IR (neat): ν = 3135, 2915, 2875, 2825, 2660, 1650, 1615, 1560, 1520, 1435, 1350, 1285, 1225, 1150, 1125, 1105, 1080, 1025, 975, 875, 810, 770, 685 cm$^{-1}$.

**[Mn(DMF)$_6$]$_3$[(Mn$_4$Cl)$_3$(BTTri)$_8$(CH$_3$OH)$_4$]$_2$·35HCl·25H$_2$O·9DMF (Mn-BTTri-DMF)** In a 125-mL vial, 437 mg (1.56 mmol) of H$_3$BTTri and 60 µL conc. HCl (0.726 mmol) was added to 76.2 mL anhydrous DMF in an N$_2$-filled glovebag. The yellow solution was sonicated 2h. In a 20-mL vial, 828 mg MnCl$_2$·4H$_2$O (4.18 mmol) was added to 17.2 mL of anhydrous methanol and sonicated for 10 minutes. 6.4 mL of the H$_3$BTTri solution and 1.6 mL of the MnCl$_2$·4H$_2$O solution were added to 10 20-mL vials via syringe filter. The vials were capped with Teflon caps and heated for 16h at 100°C. The off-white solid was collected via filtration and washed with hot DMF and diethyl ether to yield 0.454 g (70.9% by H$_3$BTTri) of product. Anal. Calc’d. for C$_{320}$H$_{173}$N$_{181}$Cl$_4$Mn$_{27}$O$_{42}$·C 34.64, H 4.27, N 22.92. Found C 34.28, H 4.7, N 23.27. IR (neat): ν = 3135, 2915, 2875, 2825, 2660, 1650, 1615, 1560, 1520, 1435, 1350, 1285, 1225, 1150, 1125, 1105, 1080, 1025, 975, 875, 810, 770, 685 cm$^{-1}$.

**Mn$_3$[(Mn$_4$Cl)$_3$(BTT)]$_8$·5HCl·7CH$_3$OH (Mn-BTTri-MeOH)** Soaking Mn-BTTri in 15 mL anhydrous methanol at 150 ºC for 24h, allowing to cool, decanting methanol and adding a fresh 15 mL to soak another 24h yielded 250 mg of off-white powder washed with diethyl ether. Mn-BTTri-m was heated to 100 ºC at a rate of 0.1 ºC/min for 1 week. This resulted in the 171 mg of tan, fully desolvated Mn-BTTri. Anal. Calc’d. for C$_{199}$H$_{129}$N$_{144}$Cl$_{11}$Mn$_{27}$O$_7$ 36.37, 1.98, 30.69. Found 36.60, 1.43, 30.17. IR 1614.14, 1445.92, 1356.37, 1306.52,1241.34, 1228.27, 1144.27, 1098.47, 1020.94, 882.79, 862.53, 775.67.

**High-Pressure Gas Sorption Measurements** In a typical measurement, at least 200 mg of sample was loaded in a sample holder in a glove box under an argon atmosphere. Hydrogen and carbon dioxide excess adsorption measurements were performed on an automated Sieverts’ apparatus (PCTPro-2000 from Hy-Energy Scientific Instruments LLC) over a pressure range of 0-50 bar. UHP-grade hydrogen, carbon dioxide, and helium (99.999% purity) were used for all measurements. Total
adsorption was calculated using NIST Thermochemical Properties of Fluid Systems: CO$_2$ and H$_2$ densities between 0 and 50 bar were fit using a sixth-order polynomial, then multiplied by the pore volume of each material.\textsuperscript{10}

**Ideal Adsorbed Solution Theory calculations** The ideal adsorbed solution theory (IAST) of Prausnitz and Myers was used to estimate the composition of the adsorbed phase from pure component isotherm data.\textsuperscript{11,12} Experimental absolute isotherm data were fit to the dual-site Langmuir-Freundlich isotherm for CO$_2$ adsorption and the single-site Langmuir-Freundlich model for H$_2$. H$_2$ saturation capacities were allowed to refine between two and three times the saturation capacity for CO$_2$, which was confirmed visually. The integrals were computed numerically and the adsorbed phase composition that minimized the difference between the integrals of the two spreading pressures was found using Mathematica\textsuperscript{8,13}. Selectivities were then calculated according to equation 3, where $x_i$ is the mole fraction of component $i$ in the adsorbed phase and $y_i$ is the mole fraction of component $i$ in the bulk. Working capacities were calculated according to equation 4, where $n_t$ is the total number of adsorbed moles of gas per unit mass of adsorbent and $n_i^0$ is the number of moles of component $i$ in the adsorbed phase per unit mass of adsorbent.

\begin{align*}
S &= \frac{x_i y_j}{x_j y_i} \quad (3) \\
\frac{1}{n_t} &= \frac{x_i}{n_i^0} + \frac{x_j}{n_j^0} = \frac{x_i}{n_i^0} + \frac{x_j}{n_j^0} \quad (4)
\end{align*}

4.3 Results and Discussion

High-throughput methods were implemented to determine reaction conditions to form the Mn(II) triazole framework. In a 96-well plate, variables such as pH and cosolvent were screened and the resulting powders were characterized by powder X-ray diffraction. Conditions that yielded crystalline materials were scaled to synthesize quantities. Reaction of 1,3,5-tris(triazol-5-yl)benzene (H$_3$BTTri) with MnCl$_2$·4H$_2$O and HCl in a 4:1 mixture of DMF:methanol at 100 °C afforded an off-white solid formulated as [Mn$_3$(DMF)$_{18}$][(Mn$_4$Cl)$_3$(BTTri)$_8$]:35 HCl·66 DMF (Mn-BTTri-DMF) based on elemental analysis and thermogravimetric experiments. The parent, base framework Mn-BTTri is isostructural to the manganese and copper tetrazole frameworks, Mn-BTT and Cu-BTT respectively, as determined by X-ray powder diffraction (Figure 4.2). Le Bail Reitveld refinement of the diffraction pattern revealed comparable unit cell dimensions for Mn-BTTri (19.2782(7) Å) and Mn-BTT (19.116 Å).

The characterization data of Mn-BTT and Cu-BTT were used to contextualize preliminary characterization of Mn-BTTri. The formula units for these frameworks have been determined to be Mn$_3$[(Mn$_4$Cl)$_3$(BTT)]$_3$(CH$_3$OH)$_{10}$]$_2$ and HCu[(Cu$_4$Cl)$_3$(BTT)$_8$] by X-ray powder diffraction. X-ray structural analysis revealed that these frameworks display cubic topologies, where M$_4$Cl clusters are coordinated by 8 tetrazolate groups. These desolvated structures yield an anionic framework that is charge-balanced by coordinatively unsaturated metal cations bridged by tetrazole nitrogens. When desolvated, two separate open metal sites lead to hydrogen binding enthalpies of 10.2
(Mn-BTT) and 9.5 (Cu-BTT) kJ/mol. As seen in the formula unit, not all methanol molecules could be removed from Mn-BTT. Attempts to remove this methanol resulted in framework collapse.

Mn-BTTRi was therefore an important target. As the partially-solvated Mn-BTT already displays a high hydrogen binding enthalpy, an analogous framework that retains its structural integrity upon complete methanol removal would be an promising material for hydrogen storage. Further, Cu-BTTRi, the copper framework incorporating H$_2$BTTRi, had been synthesized and shown to be more thermodynamically and hydrolytically stable than Cu-BTT. Indeed, Mn-BTTRi is stable in air for weeks while the tetrazolate frameworks begin to decompose in air within hours.

**Figure 4.2** Powder X-ray diffraction patterns of Mn-BTTRi (top) and Cu-BTTRi (bottom).

**Desolvation of Mn-BTTRi-MeOH** To obtain an optimal measurement of the gas storage capacity and adsorption enthalpy of hydrogen within this porous solid, all guest solvent molecules within the pores and coordinated to metal cations must be removed. To achieve this at temperatures lower than the decomposition temperature of the framework, low-boiling solvents such as methanol are employed to substitute the high-boiling solvents used in synthesis such as DMF. Soxhlet extraction, an improvement on past exchange methods of decanting and exchanging solvent, of as-synthesized Mn-BTTRi-DMF with methanol for six days left residual DMF in the pores. This was evidenced by the characteristic infrared carbonyl stretch at 1651 cm$^{-1}$. However, bound DMF was readily removed by taking advantage of the thermal stability of Mn-BTTRi and heating at 130 °C in freshly distilled methanol in a Teflon-lined steel autoclave. This resulted in the completely exchanged framework, Mn$_3$[(Mn$_2$Cl)$_3$(BTTRi)$_8$]:5HCl·7CH$_3$OH (Mn-BTTRi-MeOH). Employing this strategy for the desolvation of Cu-BTTRi allowed for the
removal of all guest methanol, as demonstrated by the loss of the IR spectra shoulder at 1651 cm\(^{-1}\).

Attempts to desolvate Mn-BTTr-MeOH were performed by heating under vacuum. Heating Mn-BTTr-MeOH at 6 mTorr and temperatures of up to 190 °C led to a 21.30% weight decrease. The IR spectrum of this material shows no DMF, but methanol coordinated to the metal ions is still present as evidenced by the absorption at 1018 cm\(^{-1}\). This methanol is posited to coordinate to extraframework cations. Extraframework Mn\(^{2+}\) coordinate two nitrogens on tetratolylate rings in Mn-BTT. Because of the different structural motif in triazolate frameworks, metal ions will potentially be singly-coordinated to the framework and thus are expected to have an extremely strong interaction with residual solvent.

**Charge Balancing Cation in Mn-BTTr**

Mn-BTTr was designed to be a robust framework in which the increased thermal stability permits complete removal of all solvent-occupied metal coordination sites. Not all azolate metal-organic frameworks contain extraframework metal cations, however. Rather than containing extra-framework copper, Cu-BTTr is proposed to be balanced by protons as \(\text{H}_3[(\text{Cu}_4\text{Cl})_3(\text{BTTri})_8]\). This motivated studies of the charge balancing cation in Mn-BTTr as the framework was designed with the hopes of incorporating extraframework Mn(II) ions capable of binding hydrogen. In the absence of a single crystal, and due to the highly paramagnetic nature of Mn-BTTr, experiments were designed to probe the species, either protons and/or metal cations, in the framework.

To ascertain the framework counter-cation in Mn-BTTr, we examined the IR spectrum of the desolvated compound to assign a particular vibrational mode to the triazole N–H stretch. The desolvated framework contains no stretches between 1610 cm\(^{-1}\) and 4000 cm\(^{-1}\), implying that metal cations rather than protons are incorporated into the material. We attempted to confirm this hypothesis by demonstrating that treatment of Mn-BTTr with a strong base, such as \(n\)-butyllithium, would result in no changes in the IR spectrum of the compound. This experiment was inconclusive, as excess methanol within the pores obscures the relevant region of the spectrum.

In lieu of direct spectroscopic evidence for N–H protons in the framework, we confirmed the content of manganese(II) ions by thermogravimetric analysis and inductively coupled plasma atomic absorption spectroscopy (ICP-AA). TGA under an oxygen atmosphere using a ramping rate of 1 °C/min to 600 °C and heated isothermally for 5h yielded Mn\(_2\)O\(_3\) as characterized by powder X-ray diffraction. A 17% manganese content in the as-synthesized framework was calculated by the resultant residual mass. This is within 1% agreement with a formula unit of \([\text{Mn}_3(\text{CH}_3\text{OH})][(\text{Mn}_4\text{Cl})_3(\text{BTTri})_8]\cdot84\text{CH}_3\text{OH}\) and is 4% higher than a proton-balanced formula. To avoid water coordination and obtain accurate Mn content of the desolvated Mn-BTTr, air-free ICP-AA experiments showed 20.6% Mn, a parameter that also fits with a Mn-balanced formula. In concert, these experiments lead to a provisional assignment of extraframework manganese cations in Mn-BTTr.

**Surface area and hydrogen uptake of Mn-BTTr**

At 77 K Mn-BTTr exhibits an almost identical hydrogen uptake as Mn-BTT of 11.5 mmol/g. This cannot, however, be explained by isostructural frameworks exhibiting analogous behavior. Nitrogen adsorption measurements carried out at 77 K show Mn-BTTr possesses a BET surface
area of 1625 m$^2$/g, which is significantly less than Mn-BTT (2100 m$^2$/g). This can possibly be explained by disorder at the surface of the microcrystals of Mn-BTTrri.

![Figure 4.3 Mn-BTTrri-m 77 K and 87 K adsorption and desorption isotherms.](image)

The zero-coverage isosteric heat of adsorption of H$_2$ on metal-organic frameworks reflects the average adsorption enthalpy experienced by one hydrogen molecule on the surface of the material. This value as a function of H$_2$ loading is generated from both 77 K and 87 K H$_2$ adsorption, which for Mn-BTTrri can be seen in Figure 4.3. While the hydrogen uptake capacity at 77K is the same for Mn-BTT and Mn-BTTrri, the zero-coverage isosteric heats of adsorption of 10.2 and 8.9 kJ/mol, respectively, reveal this to be incidental. These data can possibly be explained by the stronger electron donation of the triazolate ring when compared to the tetrazolate ring: A hydrogen molecule will on average encounter a lower energy interaction with the framework walls despite the presence of more desolvated extraframework manganese ions.

When compared with Cu-BTTrri, Mn-BTTrri adsorbs H$_2$ more strongly (Figure 4.4). This behavior is expected due to the stronger Lewis acidity of Mn$^{2+}$ compared to Cu$^{2+}$. At high pressures, the adsorption results are less straightforward (Figure 4.5). The H$_2$ adsorption is nearly identical for the two materials, while the capacity for CO$_2$ is greater in Cu-BTTrri. Based on earlier adsorption data points, however, Mn-BTTrri seems to adsorb CO$_2$ slightly more strongly based on a steeper initial portion of the isotherm. Together, these results can be viewed as self consistent: Mn-BTTrri has a lower surface area than Cu-BTTrri (1625 vs. 1900 m$^2$/g), however the adsorption is slightly stronger. This difference is less apparent in high pressure H$_2$ adsorption at 433 K due to the low uptake at this temperature.
Figure 4.4 Isosteric heat of adsorption of H$_2$ on Mn-BTTr (blue squares) and Cu-BTTr (orange circles). Squares and circles are included only to guide the eye.

Figure 4.5 High-pressure CO$_2$ (top) and H$_2$ (bottom) adsorption onto Cu-BTTr (orange circles) and Mn-BTTr (blue squares) at 433 K.
Figure 4.6 CO\textsubscript{2}/H\textsubscript{2} selectivity (top) and gravimetric working capacity for CO\textsubscript{2} (bottom) for Cu-BTTri (orange circles) and Mn-BTTri (blue squares) in an 80:20 mixture at 433 K generated from IAST treatment of high-pressure adsorption isotherms. Squares and circles are included only to guide the eye.
These results are also reflected in the mixture adsorption of CO$_2$ and H$_2$ as estimated by the Ideal Adsorbed Solution Theory (Figure 4.6). In an 80:20 CO$_2$/H$_2$ mixture, Mn-BTTr is more selective than Cu-BTTr below 15 bar, at which point Cu-BTTr becomes more selective. At all pressures, Cu-BTTr has a higher working capacity than Mn-BTTr, which is the difference between the adsorbed amount at a given pressure and the capacity at 1 bar, which is the assumed desorption temperature in an industrial setting. These results are again consistent with a less crystalline but more polarizing Mn-BTTr material. At higher pressures, the greater number of available Cu$^{2+}$ sites allows for greater selectivity, and at all pressures the higher surface area leads to higher working capacity.

4.4 Conclusions and Outlook

In an attempt to improve upon the promising CO$_2$/H$_2$ separation ability of Cu-BTTr, the metal-organic framework Mn-BTTr with exposed Mn$^{2+}$ sites was synthesized. This material was shown to be more selective for CO$_2$ in the presence of H$_2$ from the analysis of high-pressure single-component isotherms. The stronger polarizing ability of the harder Mn$^{2+}$ cation compared to Cu$^{2+}$ was cited as the reason for this stability. Future work will include optimizing the synthesis and activation of Mn-BTTr in order to obtain a surface area closer to that of Cu-BTTr, as well as comparing other metal cations such as Co$^{2+}$ or Ni$^{2+}$. This work serves as an example of the ability to rationally tune metal-organic frameworks for specific purposes.

4.5 Acknowledgments

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4.6 References

Chapter 5: Separation of Hexane Isomers in a Metal-Organic Framework with Triangular Channels

5.1 Introduction

Metal-organic frameworks constitute a large family of microporous solids exhibiting high surface areas, tunable pore dimensions, and adjustable surface functionality. Consequently, they are beginning to rival traditional solid adsorbents such as zeolites and activated carbons in terms of performance for some key gas storage and molecular separation applications. With regard to the latter, the possibility of creating pore characteristics that cannot readily be achieved in zeolites or carbons expands the opportunities for molecular recognition. In the presence of the right surface environment, inefficient separations currently carried out by cryogenic distillation could potentially be performed at higher temperatures with a significantly reduced energy cost. Relatedly, the efficient separation of alkane isomers by adsorption is especially challenging because the molecules are chemically inert and have similar polarizabilities, leaving shape as the main handle available for their differentiation. This separation is critical to the production of gasoline, which is composed of approximately ten percent pentanes and hexanes. Herein, we report a metal-organic framework featuring sharply-angled pore walls of a type not encountered in zeolites and is capable of fractionating alkane isomers according to the degree of branching.

Hexanes of formula C$_6$H$_{14}$ are generated at enormous scale through a catalytic isomerization reaction that results in a thermodynamically-controlled product stream composed of 10 to 30% of each of the five different isomers. The worth of a particular isomer as a component in the gasoline pool is related to its research octane number (RON), and is highest for the dibranched hexanes 2,3-dimethylbutane and 2,2-dimethylbutane, which have values of 105 and 94, respectively. The RONs for the monobranched isomers 2-methylpentane and 3-methylpentane are significantly lower, at 74 and 75, respectively, whereas the value for linear n-hexane is only 30. To achieve higher octane number blends, current processes sieve n-hexane using zeolites. This process generates a mixture of the other four isomers with a final RON of nearly 83 while returning n-hexane to the isomerization reactor. Additionally, some separation processes achieve higher-grade mixtures by subsequently distilling the monobranched isomers away from the valuable dimethylbutane products. Currently, approximately two million barrels of pentanes and hexanes are processed daily.

An improved hexane separation process would selectively isolate the most valuable products, 2,3-dimethylbutane and 2,2-dimethylbutane, while returning the less valuable monobranched isomers to the isomerization reactor along with n-hexane (Figure 5.1A). Performing this separation at or near the isomerization temperature would save a great deal of energy in the production of high-quality gasoline. Further, it would potentially benefit public health since it could reduce the usage of toxic aromatics, which are currently added to boost the octane number of gasoline. Numerous attempts have been made to identify solid adsorbents capable of effecting an efficient separation of hexane isomers according to octane number including zeolites, silicas, and, very recently, metal-organic frameworks. Although zeolite BETA facilitates the separation of 2,2-dimethylbutane from the monobranched isomers and some 2,3-dimethylbutane (the highest value isomer) elutes with it, these results are only seen at 0.01 bar and are therefore not useful for a separation. The many studies that have examined the adsorption or separation of some hexane isomers generally do not include the crucially important separation of the two dibranched isomers from the monobranched and linear isomers.
Figure 5.1 Illustrations of the proposed future hexane isomer separation processes. The individual RON of each isomer and the average research octane number (RON) of the final product are included. Current technology uses the small cross-sectional area of \(n\)-hexane and a zeolite sieving process to remove this low-RON isomer from the mixture and return it to the isomerization reactor. In some cases distillation is then used to further augment the RON of the final product. Given the adsorption selectivity that can be attained within a metal-organic framework (MOF), as demonstrated here for \(\text{Fe}_2(\text{BDP})_3\), it may now be viable to separate only the two valuable dibranched isomers from the other three. Schematic A would offer vast improvements over the current separation technology, and Schematic B would provide an even greater enhancement by optimizing the location of recycled hexanes.

5.2 Experimental Section

Synthesis of \(\text{Fe}_2(\text{BDP})_3\) \(\text{H}_2\text{BDP}\) was synthesized according to the literature.\(^{32}\) A 100 ml Schlenk flask was charged with 6.04 g (17.1 mmol) of \(\text{Fe(acac)}_3\), 1.20 g (5.71 mmol) of \(\text{H}_2\text{BDP}\) and a magnetic stir bar. 80 mL of dry, degassed N,N-dimethylformamide (DMF) was added to the Schlenk flask via cannula transfer. The reaction was refluxed under nitrogen for 18 hours. The black microcrystalline precipitate was collected on a Buchner funnel. This material was heated in dimethyl sulfoxide (DMSO) at 100 °C for 8 hours, and the DMSO was decanted. The material was then washed 5 more times with heated DMSO and similarly six more times with
DMF heated to 100 degrees C and six more times with methylene chloride heated to 70 °C. This washing procedure removes unreacted ligands, metal sources, polymerization products of DMF and solvents from previous washes. The material is then heated under 10 mTorr vacuum to 180 °C for 24 hours to remove guest solvent molecules. FT-IR: (solid, ATR): \( \nu_{\text{C=C}} 1576, \nu_{\text{C=N}} 1384, 1342 \text{ cm}^{-1} \). An aliquot of the activated sample was then soaked in DMSO, filtered, dried in air and then examined by TGA and CHN analysis. The 16% weight-loss observed at 150 °C was consistent with a formulation of \( \text{Fe}_2(\text{BDP})_3 \cdot 1.75 \text{DMSO} \) which was in agreement with CHN analysis. Anal. Calcd. for \( \text{Fe}_8\text{C}_{158}\text{H}_{138}\text{N}_4\text{S}_7\text{O}_7 \): C, 54.23; H, 4.18; N, 19.21. Found: C, 54.73; H, 3.82; N, 18.73.

Low pressure gas adsorption measurements For all gas adsorption measurements 200-225 mg of \( \text{Fe}_2(\text{BDP})_3 \cdot 1.75 \text{DMSO} \) was transferred to a pre-weighed glass sample tube under an atmosphere of nitrogen and capped with a Transeal. Samples were then transferred to Micromeritics ASAP 2020 gas adsorption analyzer and heated at a rate of 1 °C /min from room temperature to a final temperature of 180 °C. Samples were considered activated when the outgas rate at 150 °C was less than 2 \( \mu \text{bar/min} \), which occurred near 48 hours after the start of evacuation. Evacuated tubes containing degassed samples were then transferred to a balance and weighed to determine the mass of sample, typically 150-175 mg. The tube was transferred to the analysis port of the instrument where the outgas rate was again determined to be less than 2 \( \mu \text{bar/min} \) at 180 °C. 99.999% purity gas was used for nitrogen adsorption. All non-cryogenic measurements were performed using sand bath connected to an automated temperature controller. Liquid hexane isomers were obtained from Sigma Aldrich and were added to the ASAP 2020 vapor adsorption apparatus. The liquids were frozen. The pressure was monitored until it reached a low of 0.001 mbar, and then the headspace was evacuated for 5 minutes. The solid was melted and the freeze-pump thaw procedure was repeated two more times. The liquid was then distilled into a new sample tube three times, each time only collecting approximately 50% of the original volume.

Breakthrough measurements A column of 0.491 g of \( \text{Fe}_2(\text{BDP})_3 \) was packed into a glass u-tube with an internal diameter of 0.9525 cm. The height of the sample was 11.5 cm. Dry \( \text{N}_2 \) at a rate of 2.5 mL/min was bubbled through a mixture of hexane isomers according to the following volumes: 2.67 mL of 2,2-dimethylbutane, 3.50 mL of 2,3-dimethylbutane, 3.79 mL of 2-methylpentane, 4.22 mL of 3-methylpentane, and 5.82 mL of \( n \)-hexane. These volumes were determined through trial and error: The experiment was run without any sample and the vapor phase ratios were optimized to an equimolar final product. The effluent was passed through a VICI Valco 6-way sampling valve. Every minute, a 0.25 mL aliquot of gas was delivered to a Perkin Elmer Clarus 500 gas chromatograph fitted with a Supelco Equity-1 capillary GC column, 15 m long, with a 0.1 mm outside diameter and 0.10 \( \mu \text{m} \) poly(dimethyl sulfoxane) coating, submerged in an ice water bath. All five peaks were separated and easily integrated in the resulting GC trace.

Powder X-ray diffraction structure solution of \( \text{Fe}_2(\text{BDP})_3 \) Microcrystalline samples of solvated \( \text{Fe}_2(\text{BDP})_3 \) were gently ground and deposited in an aluminum sample holder equipped with a zero-background plate. Diffraction data was collected by means of an overnight scan in the \( 2\theta \) range of 5–105° with 0.02° steps using a Bruker AXS D8 Advance diffractometer equipped with Ni-filtered Cu- \( \alpha \) radiation (\( \lambda = 1.5418 \text{ Å} \)), a Lynxeye linear position-sensitive detector, and mounting the following optics: primary beam Soller slits (2.3°), fixed divergence slit (0.3°), receiving slit (8 mm). The nominal resolution for the set-up is 0.08° of \( 2\theta \) (FWHM of
the α₁ component) for the LaB₆ peak at about 2θ = 21.3°. The generator was set at 40 kV and 40 mA. In order to get higher resolution data, a powder pattern was also collected on a powder diffractometer of the Institute of Crystallography of the Italian CNR in Bari that is equipped with a primary beam Ge(111) monochromator, Cu-Kα radiation in Debye-Scherrer geometry (glass capillary diameter: 0.5 mm), and an INEL CPS-120 position sensitive detector covering a 120° 2θ range. (The courtesy of Giuseppe Chita, IC-CNR, is acknowledged for technical assistance).

A standard peak search followed by indexing through the Single Value Decomposition approach, as implemented in TOPAS-Academic, allowed the determination of approximate unit cell parameters. The space group was assigned as Fddd on the basis of systematic absences. The unit cell and space group were checked by a Le Bail refinement and confirmed by successful structure solution and Rietveld refinement. The structure solution of Fe₂(BDP)₃ was performed using the simulated annealing technique, as implemented in TOPAS. Initially, a rigid, idealized model was employed for the crystallographically independent portions of the BDP²⁻ moiety (one full and one half ligands). To build the rigid model describing BDP²⁻, the following bond distances and angles have been adopted: a) for the benzene ring: C–C = 1.39 Å; C–H = 0.95 Å; C–C–C, C–C–H = 120°; b) C–C, C–N, N–N = 1.36 Å; C–H = 0.95 Å; internal ring angles = 108°; C–C–H = 126°; Cbenzene–Cpyrazole = 1.45 Å. After the initial structure solution, the arene-pyrazole torsion angle was allowed to refine. Residual electron density in the channels was modeled as a disordered dimethylformamide (DMF) solvent molecule. The final refinement was performed using the Rietveld method, maintaining the rigid bodies introduced at the structure solution stage. The background was modeled by a polynomial function of the Chebyshev type. Peaks shapes were described by the Fundamental Parameters Approach. Anisotropic peak broadening was modeled using spherical harmonics to define the peak widths. A single refined isotropic thermal parameter was assigned to the Fe atom, and this was augmented by 2.0 Å² for the atoms of the BDP²⁻ ligand and by 4.0 Å² for the atoms of the DMF molecule. Note that in the final Rietveld refinements, both collected X-ray diffraction patterns were used as independent observations of different information content and were employed simultaneously during model refinement.

Crystal data for Fe₂(BDP)₃ at 298 K: Fe₂(C₁₂N₄H₂₀)₃(C₃H₇NO)₀.₅; orthorhombic, Fddd, a = 7.1046(2), b = 26.4943(5), c = 45.3489(9) Å, V = 8536.1(4) Å³, Rwp = 0.026; Rp = 0.017; RBragg = 0.012. Metrical data for the solid-state structure of Fe₂(BDP)₃ is available free of charge from the Cambridge Crystallographic Data Centre under reference number CCDC 915106.

The solvent accessible area was calculated using Platon crystallographic software with 0.2Å grid spacing 1.2 Å probe size. The atomic van der Waals radii were C 1.70 Å, H 1.20 Å, Fe 2.14 Å, N 1.55 Å. The calculated packing index (Calc K.P.I) was 49.5% and the total Potential Solvent Area 3275.2 Å³ per 8535.3³ Unit Cell Volume (38.4%).

**Fitting of pure component isotherms from experiments and IAST calculations**

The pure component isotherm data for adsorption of n-hexane (nC₆), 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (22DMB) and 2,3-dimethylbutane (23DMB) in Fe₂(BDP)₃ were experimentally determined for different temperatures.

The absolute loadings were fitted with the dual-Langmuir-Freundlich isotherm model

\[
q = q_{A, sat} \frac{b_A p^{v_A}}{1 + b_A p^{v_A}} + q_{B, sat} \frac{b_B p^{v_B}}{1 + b_B p^{v_B}}
\]

with T-dependent parameters bₐ and bₜ
The 5-component mixture adsorption equilibrium was determined using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz. At any specified pressure, the hierarchy of component loadings is \( nC6 > 2MP \approx 3MP > 22DMB \approx 23DMB \), indicating the possibility of separation of the hexanes isomers into three fractions depending on the degree of branching.

**Isosteric heat of adsorption calculations** The isosteric heats of adsorption, \( Q_{st} \), defined

\[
Q_{st} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_q
\]

were determined using the pure component isotherm fits. The dual-site Langmuir-Freundlich isotherm fits were differentiated with the Clausius-Clapeyron equation.

**CBMC calculations and packed bed adsorber breakthrough simulation methodology** The breakthrough simulation methodologies for step- and pulse- inputs are described in detail in earlier works.

### 5.3 Results and Discussion

In comparing the structures of zeolites to those possible in metal-organic frameworks, a prominent distinction lies in the angles that can be obtained for the internal pore walls. Whereas the pore contours defined by a zeolite scaffolding are necessarily obtuse owing to the O-Si-O and Si-O-Si angles of \(~109^\circ\) and \(>130^\circ\), respectively, the higher coordination numbers possible for the metal nodes within a metal-organic framework can give rise to flat pore surfaces that intersect at acute angles. An extreme example of this is apparent in the structure of the new metal-organic framework Fe\(_2\)(BDP)\(_3\) (Figure 5.2), which was obtained as a black microcrystalline solid upon reaction of Fe(acetylacetonate)\(_3\) and 1,4-benzenedipyrazole (H\(_2\)BDP) in \(N,N\)-dimethylformamide. Here, octahedral iron(III) centers are linked via \(\mu^2\)-pyrazolate units to form chains running along one crystal axis, where both nitrogens on one ring bind to different iron atoms. The rigid, nearly planar BDP\(^2\)-ligands define a corrugate triangular channel structure featuring sharply-angled crevices running along the triangle corners. The chains of octahedral iron(III) centers form the vertices of these triangles. One can readily envision how these crevices might provide strong van der Waals contacts for linear alkanes, whereas branched alkanes would be likely to wedge themselves within the corners. The framework of Fe\(_2\)(BDP)\(_3\) is directly analogous to the carboxylate-linked structure of Sc\(_2\)(BDC)\(_3\) (BDC\(^{2-}\) = 1,4-benzenedicarboxylate), but with a larger metal····metal triangle edge length of 13.25(2) Å as a result of the longer BDP\(^2\)-linker. The structure is also related to that of Co(BDP), wherein chains of tetrahedral cobalt(II) centers lead instead to square channels.

The strong iron(III)-pyrazolate bonds and highly-connected architecture of Fe\(_2\)(BDP)\(_3\) lend it exceptional chemical and thermal stability. The material can be boiled in aqueous solutions at pH 2-10 for two weeks (Figure 5.3). Heating the solvated, as-synthesized form of Fe\(_2\)(BDP)\(_3\) at 180 °C under dynamic vacuum afforded a completely-activated, microporous form of the compound exhibiting a Brunauer-Emmett-Teller surface area of 1230 m\(^2\)/g.
Figure 5.2 Depiction of the bridging ligand precursor H$_2$BDP (A), and portions of the structure of Fe$_2$(BDP)$_3$, as determined by analysis of powder x-ray diffraction data. Orange, blue, and gray spheres represent Fe, N, and C atoms, respectively; H atoms are omitted for clarity. The view in B is along the [001] direction in the orthorhombic crystal structure (space group Fddd); while C depicts a perpendicular view of the one-dimensional chains of pyrazolate-bridged Fe$^{III}$ octahedra. Selected interatomic distances (Å) and angles (deg): Fe-N1x 1.981(2), Fe-N2 2.04(1), Fe-N1 1.94(1); Fe···Fe (vertex to vertex) 13.255(1), Fe-Fe (nearest neighbor) 3.852(4); N1x-Fe-N2 96.698(1), N1x-Fe-N2’ 92.479(1), N1x-Fe-N1 81.236(1), N1x-Fe-N1’ 88.946(1), N1-Fe-N2 91.65(2); Fe-N1x-N1x 123.070(1), Fe-N2-N1 115.592(1), Fe-N1-N2 130.994(1). D shows the van der Waals surfaces associated with the corrugated triangular channels running through the structure. E provides snapshots of the hexane isomers within the channels of Fe$_2$(BDP)$_3$ for a loading of four molecules per unit cell at 160 °C, as observed in configurational-bias Monte Carlo simulations.
Figure 5.3 X-ray powder diffraction patterns of 20 mgs of Fe$_2$(BDP)$_3$ after 14 day soaking in 10 mL of pH 0 and pH 14 water at 298 K and pH 2 and pH 10 water at 398 K.

Pure-component equilibrium adsorption isotherms for the five different hexane isomers were measured for Fe$_2$(BDP)$_3$ at temperatures of 130, 160, and 200 °C (Figure 5.4) within the range of 100 to 200 °C relevant to the industrial separation. In contrast to zeolite 5A, which operates as a sieve for separating $n$-hexane, the dimensions of the channels in the evacuated structure of Fe$_2$(BDP)$_3$ are large enough to accommodate all five hexane isomers. At 130 °C, the isotherm data rise with varying degrees of steepness until reaching saturation. The decreasing degrees of steepness in the isotherms for linear vs. monobranched vs. dibranched isomers indicate a corresponding decrease in the adsorption strength. At 200 °C, the isotherms rise considerably less steeply and do not reach saturation. At 160 °C, $n$-hexane and the monobranched isomers exhibit the behavior expected of an interpolation between the 130 and 200 °C isotherms: saturation capacity is reached or nearly reached, but at pressures higher than those required at 130 °C. At approximately 100 mbar and 200 °C, Fe$_2$(BDP)$_3$ adsorbs 60% more $n$-hexane by volume and 100% more by weight than zeolite 5A. This enhancement, together with the adsorption selectivity discussed further below, renders Fe$_2$(BDP)$_3$ a more efficient adsorbent than zeolite 5A for the $n$-hexane separation presently carried out in industry.

At 160 °C the two dibranched hexane isomers display stepwise adsorption with an inflection point near 100 mbar. The stepwise uptake of alkanes has been observed previously with cyclohexane and $n$-hexane adsorption, and can be explained with entropic arguments as supported by calorimetric data. Here, the inflection point occurs near 0.5 moles of guest per mole of Fe$_2$(BDP)$_3$. As supported by the simulations discussed below, rearrangement occurs at this loading based upon packing around the structural ridge that is created along the triangular channel by two adjacent Fe$_2$(BDP)$_3$ subunits (Figure 5.2E). This behavior is not evident at 200 °C because a loading of 0.5 moles is not attained under the conditions measured. The step is not as prominent at 130 °C for two reasons: the entropic component of the Gibbs free energy is smaller at lower temperatures and the steepness of the isotherm obscures the feature.
Figure 5.4 Gas adsorption isotherms for (A) $n$-hexane, (B) 2-methylpentane, (C) 3-methylpentane, (D) 2,3-dimethylbutane, and (E) 2,2-dimethylbutane in Fe$_2$(BDP)$_3$ at 130 °C (squares), 160°C (circles), and 200 °C (diamonds). Lines represent dual-site Langmuir-Freundlich fits to these data. Isosteric heats of adsorption ($Q_{st}$) calculated from these isotherm data are plotted in F as a function of loading.
Figure 5.5 Separation of an equimolar mixture of 2,2-dimethylbutane (red), 2,3-dimethylbutane (orange), 3-methylpentane (green), 2-methylpentane (blue), and n-hexane (purple) running through a packed bed of Fe$_2$(BDP)$_3$ at 160 °C. Plot A shows experimental breakthrough data, together with the RON calculated for the eluted mixture at 1 bar; B shows the pulsed chromatogram calculated based on the isotherm data.

The enthalpy of adsorption of the five hexane isomers in Fe$_2$(BDP)$_3$ is indeed dependent on the degree of branching. Isosteric heats of adsorption (Figure 5.4F) were calculated by differentiation of the temperature-independent, combined dual-site Langmuir-Freundlich fits to the isotherm data obtained at 130, 160, and 200 °C. In order to report enthalpy values obtained without extrapolation, the results are only plotted up to the highest loading attained at the highest temperature. The linear n-hexane isomer has the strongest interaction with the framework,
because a greater fraction of its surface can interact with the triangular channel pore surface than the other isomers. Comparing methylpentane isomers, the zero-coverage isosteric heat is initially very similar, but as more guests enter the pores, the strength of interaction of the two isomers diverges. Here, the higher flexibility of the 2-methylpentane chain apparently allows a stronger adsorbate-adsorbent interaction to be maintained at higher loadings. The bulkier dimethylbutane isomers are not flexible enough to maximize van der Waals interactions with the pore surfaces and have the lowest enthalpies at all loadings. This trend in selectivity has occasionally been observed at very low loadings in zeolites as a result of different isomers residing in different parts of a heterogeneous pore structure, but at more substantial loadings it disappears. In contrast, for Fe$_2$(BDP)$_3$, the isomers are all interacting with the same, relatively homogeneous surface differently. This trend has also been observed in other metal-organic frameworks for a selected subset of hexane isomers, but never for all five isomers.

Taken together, the trends in the enthalpy and entropy of adsorption for the five hexane isomers conspire to generate a free energy hierarchy of linear > monobranched > dibranched isomer adsorption magnitude. The linear isomers bind more strongly and additionally do not require substantial reorganization at loadings above 0.5 molecules per unit cell. Though separate enthalpy and entropy trends of this type have been established previously, the combined contributions of both within Fe$_2$(BDP)$_3$ offers exceptional potential for separating the valuable dibranched hexanes from the other isomers.

The hexane isomer separation ability of Fe$_2$(BDP)$_3$ was evaluated with a breakthrough experiment in which an equimolar mixture of all five isomers in N$_2$ was passed over a bed of the material heated at 160 °C. As shown in Figure 5.5A, pure 2,2-dimethylbutane eluted from the bed, followed by 2,3-dimethylbutane. These dibranched isomers are the most desirable, owing to their high RON values. Monobranched 2-methylpentane eluted subsequently, immediately followed by 3-methylpentane, and then, much later, linear n-hexane. The RON of the product mixture leaving the column is also plotted in Figure 5.5A as a weighted average of the RONs of each component. During the beginning of the breakthrough experiment, the RON of the eluted mixture rises to greater than 90, significantly higher than the value of 83 that is typical for industrially-refined hexane blends.

The shape of the breakthrough curve for each isomer is informative with regard to the separation. The steepness of the dimethylbutane breakthrough events suggests that the separations for these isomers result from essentially equilibrium processes and are not diffusion controlled. As shown in Figure 5.4F, the enthalpy of adsorption for the two dimethylbutane isomers is essentially identical up to a loading of 0.6 mmol/g. If diffusion is not the primary cause of the separation and the material is saturated at the breakthrough event, the strength of adsorption of these isomers presumably diverges at higher loadings with 2,3-dimethylbutane adsorbing more strongly. The methylpentanes and n-hexane display more gradual breakthrough events, suggesting that diffusion is a contributory factor in their elution dynamics.

Pulse chromatography simulations were performed to further probe the separation properties of Fe$_2$(BDP)$_3$. The results, plotted in Figure 5.5B, indicate that the material can separate a mixture of hexane isomers into three fractions consisting of the two dimethylbutane isomers, the two methylpentane isomers, and, finally, pure n-hexane. These three fractions could potentially serve independent purposes: the dibranched isomers would be added to gasoline, the n-hexane would be reintroduced to the isomerization reactor, as it is presently, and additionally the monobranched isomers could be returned to the isomerization reactor at a downstream
location, allowing for better conversion (Figure 5.1B). It is expected that such a staged recycling scheme could significantly boost the efficiency of the isomerization process.

Configurational-bias Monte Carlo (CBMC) simulations illustrate and support the mechanism of hexane isomer fractionation in Fe$_2$(BDP)$_3$. The methodology employed has been described in detail. The results are presented in Figure 5.3E as snapshots of the locations and conformations of hexane isomers adsorbed within the triangular channels of the structure. The snapshots are obtained from arbitrary channel segments, and so although the simulated loading of four molecules per unit cell is the same overall for each isomer, the number of molecules in each channel differs among the images. The regularity of the 2,3-dimethylbutane and 2,2-dimethylbutane positions supports the hypothesis that these molecules have a preferred arrangement, one that requires energy input to overcome. The snapshots also validate the enthalpic argument that van der Waals overlap decreases with the degree of branching, a hypothesis previously put forth to explain the trends in the diffusion rates for pentane isomers in zeolite NaY. Generally, the hexane backbones align along the vertices of the triangular channels, which provide the maximum surface area for dispersion interactions. From the observed conformations, it is evident that the number of carbon atoms that can effectively interact with the pore wall decreases with the degree of branching. The dimethylbutane isomers are more compact and have the weakest van der Waals interactions with the framework surface.

Comparisons with published data and further CMBC simulations demonstrate the unique efficacy of Fe$_2$(BDP)$_3$ in separating hexane isomers according to the degree of branching. A realistic comparison of relevance to industrial operations is obtained by comparing the number of moles of 92 RON product that can be obtained per liter of adsorbent in a packed bed adsorber, taking account of diffusional limitations. These comparisons show that for Fe$_2$(BDP)$_3$ the 92 RON productivity is 0.54 mol/L, whereas the values obtained for other adsorbents are consistently lower.

Very recently, a series of four carboxylate-linked metal-organic frameworks with triangular channels was reported. Though these could potentially provide surrogates or even more efficient replacements for Fe$_2$(BDP)$_3$, our CMBC calculations suggest that the size of the channels in Fe$_2$(BDP)$_3$ are nearly optimal for a hexane isomer separation. The two materials with smaller triangular channels cannot accommodate the hexane isomers, the two materials with larger channels do not maximize the van der Waals contacts.

5.4 Conclusions and Outlook

This work has presented the unprecedented separation of hexane isomers. A metal-organic framework with triangular channels and remarkable stability can distinguish isomers by shape and both enthalpically and entropically result in separation by degree of branching. Calculations suggest that both smaller and larger triangular channels are less ideal for these types of separations. Future work will include investigation of other isomers such as alkenes.

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5.6 References