UC Riverside
UCR Honors Capstones 2022-2023

Title
CRYSTAL ENGINEERING POROUS MATERIALS FOR PROPANE/PROPYLENE SEPARATION

Permalink
https://escholarship.org/uc/item/8tf371dx

Author
Kusumoputro, Emily

Publication Date
2023-02-24

Data Availability
The data associated with this publication are not available for this reason: N/A

CRYSTAL ENGINEERING POROUS MATERIALS FOR PROPANE/PROPYLENE

SEPARATION

By

Emily Kusumoputro

A capstone project submitted for Graduation with University Honors

February 24, 2023

University Honors
University of California, Riverside

APPROVED

Dr. Pingyun Feng
Department of Chemistry

Dr. Richard Cardullo, Howard H Hays Jr. Chair
University Honors

ABSTRACT

Metal-organic frameworks (MOFs) is a class of crystalline porous material composed of metal nodes and organic ligands. The vast compositional permutations allow MOFs to have unique properties and functionalities suited for industrial gas separations. One example is propane/propylene (C_3H_8/C_3H_6) separation. Propylene is a crucial organic building block, whose production results in propane impurities that must be removed through energy-intensive procedures. The objective of this project is developing effective MOF-based adsorbents as alternatives to C_3H_8/C_3H_6 separation. The first step of this project is designing and synthesizing new MOFs. The *pacs* (partitioned-*acs*) platform is chosen for this purpose as tailored structural features of specific *pacs* structures have resulted in several benchmark uptakes and separation performances. The *pacs* platform has a general formula: [(M1$_2$M2)(O/OH)L1$_3$L2], where metal trimers (M1$_2$M2)(O/OH) coordinate with L1 linkers to form 3D architecture with 1D hexagonal channels that are further divided by L2 linkers. Combinations of L1 and L2 of different lengths and functionalities will be systematically investigated to create material that excel in both uptake capacity and selectivity. Subsequently, various analytical software/instruments will be used to confirm phase purity, test thermal stability, measure pore size/surface area, and test gas separation. Overall, this project may lead to advancements in hydrocarbon gas-selective MOFs that will begin an era of environmentally-friendly and energy-efficient gas separation.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

INTRODUCTION

Metal-organic frameworks (MOFs) are a type of crystalline porous material constructed by combining metals or clusters of metals with organic ligands to create extended systems. MOFs have a wide array of compositional permutations, which allow them to have unique properties and functions suited for many potential industrial applications such as gas storage and separation, catalysis, conduction, and drug delivery. Some of these outstanding characteristics include remarkably high porosity (up to 90% free volume) and vast internal surface areas exceeding 6,000 m^2/g. These exceptional qualities, combined with the vast variability of their organic and inorganic components, make MOFs a promising candidate for clean energy applications. They are particularly appealing for storing gases, such as hydrogen and methane and acting as high-capacity adsorbents for various separation requirements (Zhou et al., 2012).

MOFs possess several unique characteristics, including their structural flexibility, that set them apart from traditional porous solids, contributing to their appeal in this rapidly developing research field. While inorganic porous solids, such as zeolites and metal oxides typically have rigid framework lattices and apertures, there are some exceptions that exhibit structural flexibility during phase transition under higher temperature or pressure. However, due to the presence of rigid covalent bonds, the change in lattice and aperture in these materials is usually minimal. On the other hand, MOFs are constructed by coordination bonds which are not as strong, leading to the possibility of lattice flexibility even under mild conditions. Developments over the years have highlighted how the lattice flexibility in MOFs can lead to a number of unique properties. The regularity in structure of MOFs enables convenient examination of the connection between structure and diverse properties. This, in turn, may assist in the development

and creation of new and enhanced MOFs. It has been shown that MOFs can display selective adsorption towards various gases at different gate-opening pressures, which is determined by the characteristics of the gas molecules. Such materials offer the potential for gas separation using a single adsorbent. Specifically, the even distribution of pore sizes in a MOF has a direct impact on various adsorption phenomena. Furthermore, molecules constrained in a uniform, limited area exhibit distinctive traits that are not observed in their bulk state. As a result, the uniform pore space can serve as a molecular reactor to facilitate reactions or stabilize reaction intermediates (Li et al., 2012).

More specifically, the focus of this research will be on the separation of propylene (C_3H_6) and propane (C_3H_8) gases. Propylene is a resourceful compound that is commonly used to produce medical tools, containers, and thermal clothing as well as a fuel for chemical and plastic industries. In order to produce propylene, it must be purified and separated from propane, which requires energy-intensive operations, such as cryogenic distillation (Hong et al., 2021). In addition, it is difficult to separate propylene from propane since both gases possess similar physical attributes and chemical properties. Due to the significant detrimental global impacts from the current methods of separation, the need for a new alternative that requires less energy consumption becomes more urgent and must be designed to produce positive economical and environmental long term effects.

Separation techniques are crucial in both industrial and everyday settings and serve three primary purposes: concentration, fractionation, and purification. The methods used for these processes include distillation, crystallization, extraction, absorption, adsorption, and membrane separation

with distillation accounting for the majority of all chemical industry processes. However, distillation may not always be feasible due to limitations such as the high temperatures required for some materials, which can cause them to decompose. As an alternative, adsorption and membrane-based separation techniques require a porous material to support the process (Li et al., 2012).

The performance of MOFs depends significantly on the size and shape of its pores, making it the primary consideration in selecting a suitable material for a specific separation. These two factors determine not only the precise size and shape exclusion but also the molecular diffusion dynamics, which are critical to the separation process. The industrial separation process utilizes kinetic separation based on variations in the diffusion of molecules in a porous material. For example, carbon molecular sieves are used in air separation by the pressure swing adsorption process. (Li et al., 2012). MOFs have a considerable advantage over traditional zeolites and other inorganic molecular sieves due to their easily controllable synthesis and modification. This characteristic increases their potential for variant designs of pore size and shape.

Propylene separation through MOF adsorbents is an advantageous alternative and should be considered for future usage. With special structural features and facile synthetic tuning, MOFs have the ability to become excellent adsorbents for gas separation. Currently, most porous materials that are used for propane and propylene separation are propylene-selective as propylene has a larger molecular size. However, this method is more complex and time consuming because it requires multiple steps to separate the two gases.

Propane-selective materials would simplify the separation process and greatly reduce energy consumption, which could eventually be implemented into industrial use (Yang, L. et al., 2020). With the aim of developing MOFs for propane selective gas separation, the concept of pore-space partitioning (PSP) will be put into practice. In 2013, our group pioneered the PSP strategy to divide large cage or channel space into smaller units with the purpose to alter host-guest interactions and to increase the density of interacting sites (Zhai et al., 2017). In particular, there will be a focus on the *pacs* (partitioned *acs*) platform. The *pacs* platform has a general formula: $[(M1_2M2)(O/OH)L1_3L2]$, where metal trimers $(M1_2M2)(O/OH)$ coordinates with L1 linkers to form 3D architecture with 1D hexagonal channels that are further divided by L2 linkers.

Our group's previous research on the separation of ethane and ethylene demonstrated that the *pacs* structure allowed for a tremendous increase in uptake capacity of ethane (similar to propane). The materials of the structure were also remarkably stable and very competent in ethane-selective gas separation (Yang, H. et al., 2020). With this recent discovery, it can be inferred that the *pacs* structure could have implications in processing to propane and propylene separation. The main purpose of carrying out this research is to lengthen dicarboxylate and tripyridyl ligands in order to obtain the optimal window size and volume of the metal-organic frameworks. Various combinations of L1 and L2 ligands of different lengths and functionalities will be systematically investigated to create material that excel in both uptake capacity and selectivity. Because larger pores will increase uptake capacity and reduce diffusion barriers, it can then be hypothesized that enlargement of pore aperture and size will construct optimal *pacs* for more efficient propylene and propane gas separation.
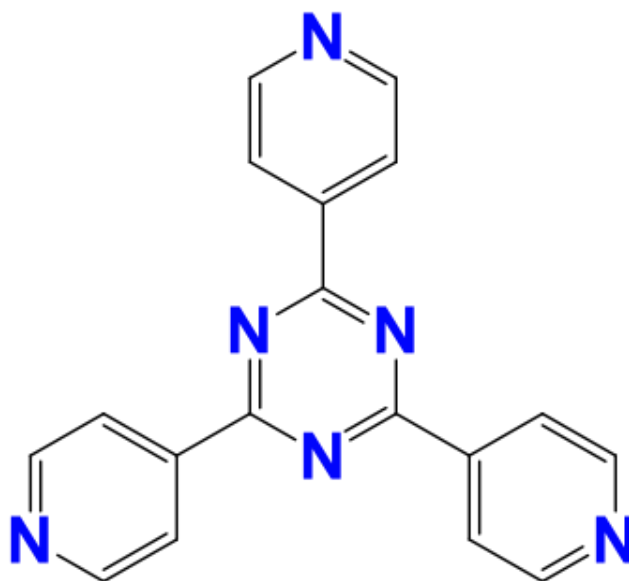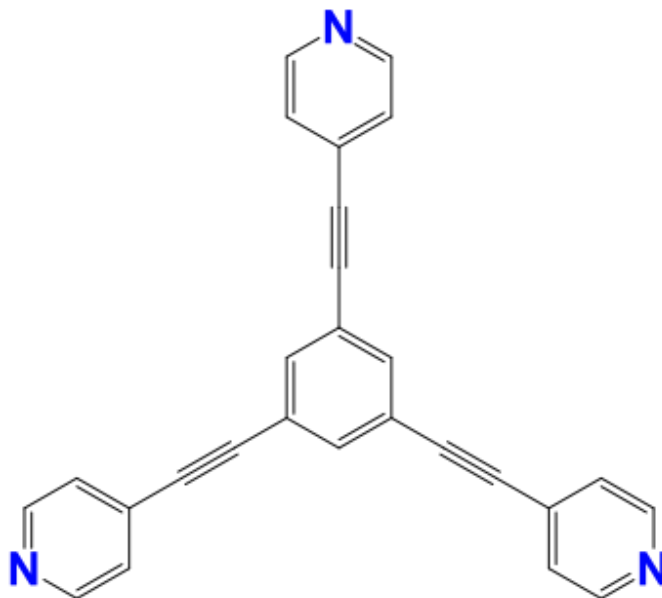
DESIGN AND METHODS

Designing MOF Materials

In the experiments carried out for this project, there were three main steps. The first step involved designing the MOF materials, based on our group's previous research on ethane/ethylene gas separation along with the current benchmark adsorbents. The ligand linker, also referred to as L1, was 2,6-napthalenedicarboxylic acid (2,6-ndc) (Figure 1). This structure was chosen because it is a longer L1 ligand compared to the terephthalate (bdc) ligand utilized in research on ethane/ethylene gas separation (Yang, H. et al., 2020). The bdc ligand has a length of 6.9 Å between oxygen atoms while 2,6-ndc is much longer and has a length of 9.1 Å. The next component added was the partitioning ligand (referred to as L2), in which there were two types of ligands: 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt) and 1,3,5-tris(pyridin-4-ylethynyl) benzene (tpab). Each L2 ligand was chosen based on structural and adsorption characteristics to optimize pore window and functionality that would help attract propane over propylene. tpt has many nitrogen atoms, which constitutes more weak nitrogen-hydrogen interactions. tpab has 3 triple bonds connecting aromatic rings, so it will be able to have strong pi-hydrogen interactions. These properties help increase the interactions between the gas molecules and our synthesized structures. Because propane has more hydrogen atoms than propylene, propane will have stronger interactions with materials containing these partitioning ligands.
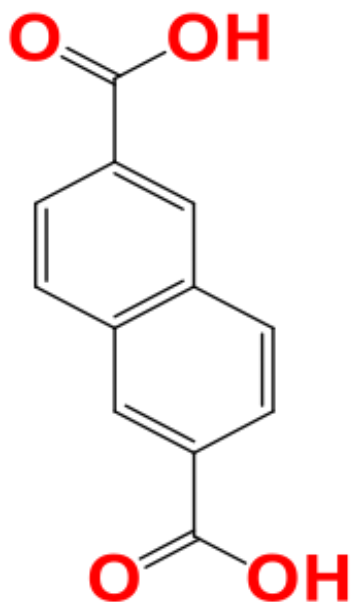
Figure 1. 2-dimensional structure of 2,6-napthalenedicarboxylic acid (2,6-ndc).

Figure 2. 2-dimensional structure of 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt).

Figure 3. 2-dimensional structure of 1,3,5-tris(pyridin-4-ylethynyl) benzene (tpab).

Synthesizing MOF Materials

Designing was then followed by the next step of synthesizing the materials. In order to determine the specific components and methods of synthesis, various conditions were tested, such as different metal salts, temperatures, and molar concentrations to avoid deviations that lead to unstable structures or possible byproducts. To create the MOF material, two types of metals were used, which were cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and vanadium chloride (VCl_3). This metal trimer combination was chosen based on ethane/ethylene separation results that achieved high paraffin uptake and were hydrothermally stable (Yang, H. et al., 2020). The selected partitioning ligands were used to create different adsorbent structures: $Co_2V(OH)(2,6\text{-ndc})_3$tpt and $Co_2V(OH)(2,6\text{-ndc})_3$tpab (Figure 2, Figure 3). The metals and ligands were then dissolved in amide solution and after stirring for 2 hours, it was placed in a

120°C oven for 5 days. The resulting hexagonal, crystalline structures were isolated by sonication and filtration.

Vanadium (III) chloride (VCl$_3$ was obtained and supplied from ACROS Organics. Cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), N,N-dimethylacetamide (DMA), dichloromethane (CH$_2$Cl$_2$), and Hydrochloric acid 38 wt % (HCl) were purchased from Fischer Scientific Co. N-methylformamide (NMF), 2,6-naphthalene dicarboxylic acid (2,6-ndc), 2,4,6-tri(4-pyridinyl)-1,3,5-triazine (tpt), and 1,3,5-tris(pyridin-4-ylethynyl) benzene (tpab) were purchased from TCIAmerica. All reagents were used without further modification or purification.

Analysis of the Structures

The last step was software and instrumental analysis of the synthesized structures. The composition of these crystalline materials were confirmed by single X-ray diffraction characterization with a Bruker diffractometer using graphite monochromated MoKα (λ= 0.71073 Å) radiation at room temperature. The diffraction data was processed using the "multi-scan" method with the Bruker APEX software, including integration and scaling. The crystal structure was determined through direct methods and further improved through refinement using SHELXTL. The PLATON software package was utilized with its SQUEEZE routine to occupy the solvent in the lattice pores. Next, the Accelerated Surface Area and Porosimetry System (ASAP 2020 Plus) was used for gas sorption tests, which measured the pore size and surface area of the crystalline framework. Each sample that was synthesized, was washed with dimethylformamide (DMF) several times, sonicated to remove impurities, and underwent solvent

exchange with dichloromethane (DCM). Subsequently, the sample was soaked in DCM and the solvent was replaced daily for five consecutive days. Afterward, the sample was transferred to a gas sorption tube and dried using a continuous flow of N_2 gas for 15 minutes. To finish, the degassing process was conducted at 60°C for a duration of 12 hours.

RESULTS

***Pacs* Framework System**

Two adsorbent structures were made, which were $Co_2V(OH)(2,6\text{-ndc})_3tpt$ and $Co_2V(OH)(2,6\text{-ndc})_3tpab$. In order to achieve the *pacs* structure, the strategy of pore-space partitioning must be used on the *acs* net structure, MIL-88, which is the nonpartitioned framework that is composed of L1 ditopic linkers. The *pacs* frameworks are constructed by having metal trimers coordinate with L1 dicarboxylate linkers into 3D architecture with 1D hexagonal channels (Figure 4). A second C_3 partitioning agent (L2) is then employed to break these channels into smaller segments, creating a *pacs* framework represented by $[(M1_2M2)(O/OH)L1_3L2]$. To ensure that unsaturated propylene molecules do not interact with open-metal sites (OMS), all OMS are eliminated. Additionally, the abundant aromatic surface enhances van der Waals interactions with larger propane molecules, making the *pacs* family an excellent platform for studying effective propane-selective adsorbents (Hong et al., 2021). Specifically, the metal trimer employed in this experiment is cobalt-vanadium, which coordinated with 2,6-ndc as the L1 ligand linker as well as tpt and tpab as the L2 partitioning ligands.
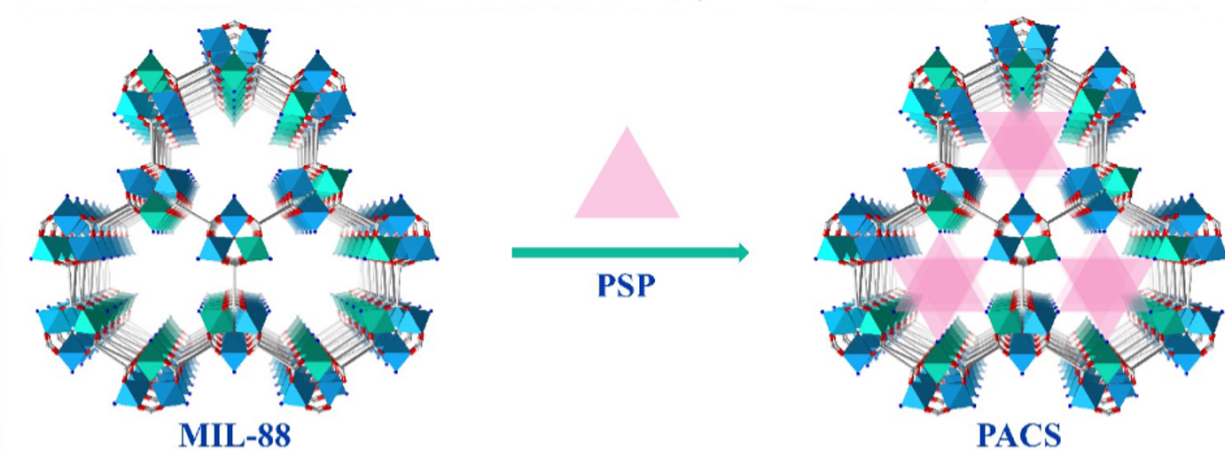
Figure 4. Diagram of the *acs* net structure, ML-88, that employs pore-space partitioning (PSP) to form the partitioned *acs* (*pacs*) platform. Adapted from "Pore-Space Partition and Optimization for Propane-Selective High-Performance Propane/Propylene Separation," by A. N. Hong, et al., 2021, *ACS Applied Materials & Interfaces, 13*, p. 52160-52166.

Stability and Porosity

When looking at the differences between the two structures, the c/a ratio is an important comparison factor. The c/a ratio is the unit cell of a structure and a lower value is optimal for better gas separation because this indicates a more compressed structure, which is optimal for higher gas uptake. $Co_2V(OH)(2,6-ndc)_3tpt$ has a c/a ratio of 1.23 and the length between nitrogen atoms in the structure is around 9.16 Å. $Co_2V(OH)(2,6-ndc)_3tpab$ has a much lower c/a ratio of 0.68 and its length between nitrogen atoms is 14.2 Å, denoting that tpab is significantly longer than tpt. The comparison of these values indicates that tpab is even more compressed than tpt, which allows for more compressed cylindrical pockets to increase host-guest interactions. As such, tpab has a higher likelihood that it has a larger capacity to uptake propane. Both L2 ligands

were tested for this study to demonstrate the effects of these structural differences in gas separation and phase purity was confirmed by powder X-ray diffraction.
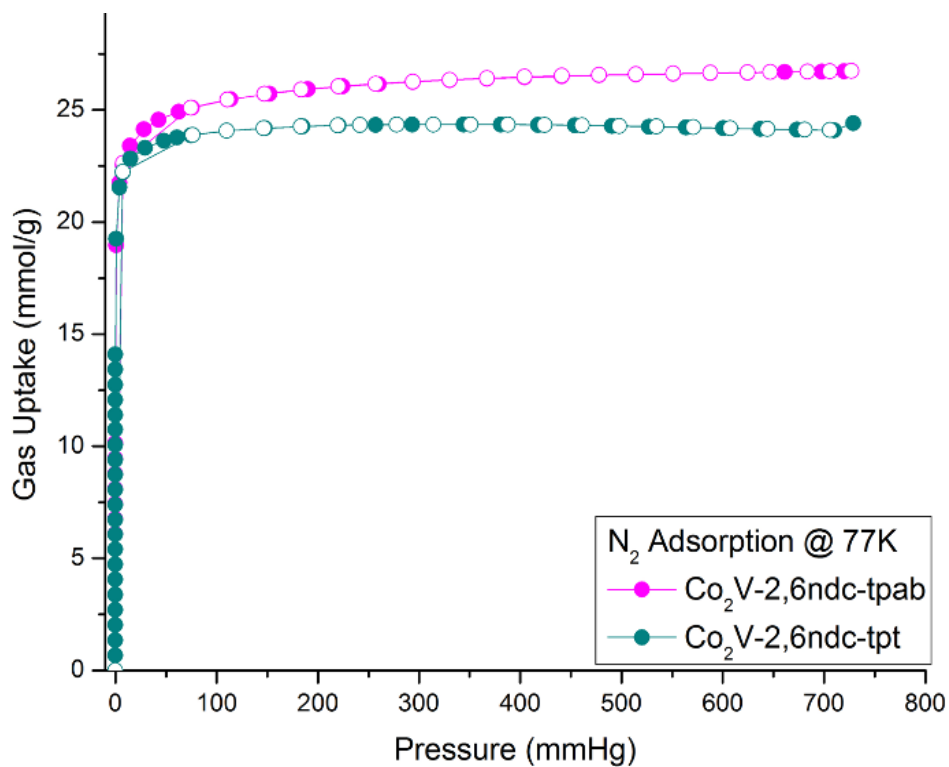
Figure 5. Comparison of N_2 adsorption at 77 K for $Co_2V(OH)(2,6\text{-ndc})_3tpt$ and $Co_2V(OH)(2,6\text{-ndc})_3tpab$ adsorbent structures.
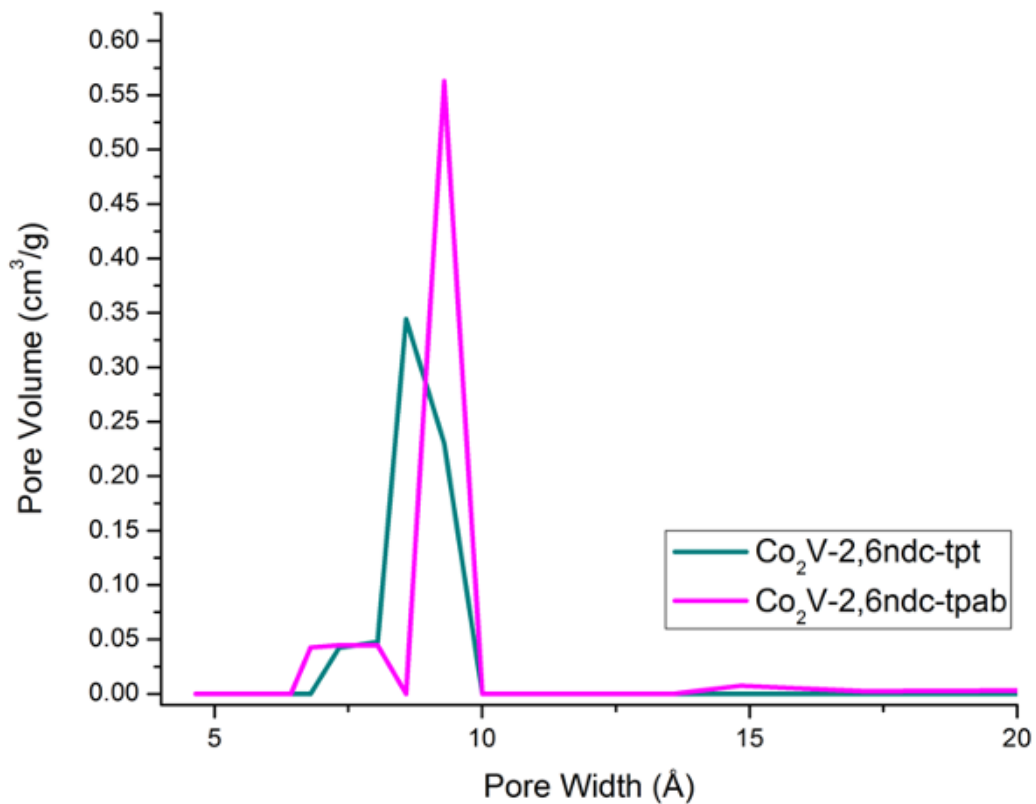
Figure 6. Comparison of pore volume and pore width of $Co_2V(OH)(2,6\text{-}ndc)_3tpt$ and $Co_2V(OH)(2,6\text{-}ndc)_3tpab$ MOF adsorbents based on N_2 adsorption.

Nitrogen Adsorption and Pore Volume

Figure 5 and Figure 6 depict the nitrogen adsorption in the tpab and tpt structures. The purpose of nitrogen adsorption is to obtain a specific pore size and volume. It can be seen that the tpab adsorbent had greater nitrogen uptake of 26.7 mmol/g compared to the tpt adsorbent which only had an uptake of 24.4 mmol/g. Figure 5 shows the pore volume and pore width of the MOF adsorbents. The tpab adsorbent has the greatest volume and width at 0.56 cm³/g and 9.29 Å while tpt had a maximum pore volume of 0.34 cm³/g at around 8.58 Å. Thus, tpab is confirmed to have

larger pores and greater pore distribution as a result of being a longer and more compressed ligand.
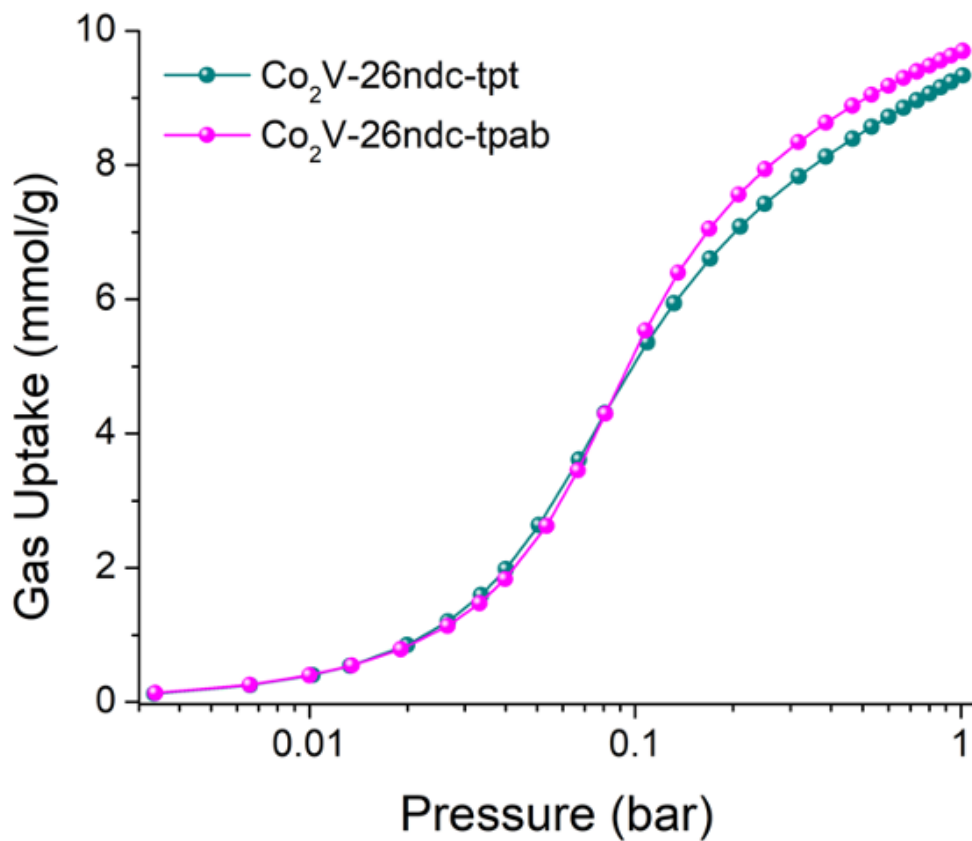
Figure 7. Gas sorption of propylene (C_3H_6) uptake at 298 K for $Co_2V(OH)(2,6\text{-ndc})_3$tpt and $Co_2V(OH)(2,6\text{-ndc})_3$tpab MOF adsorbents.
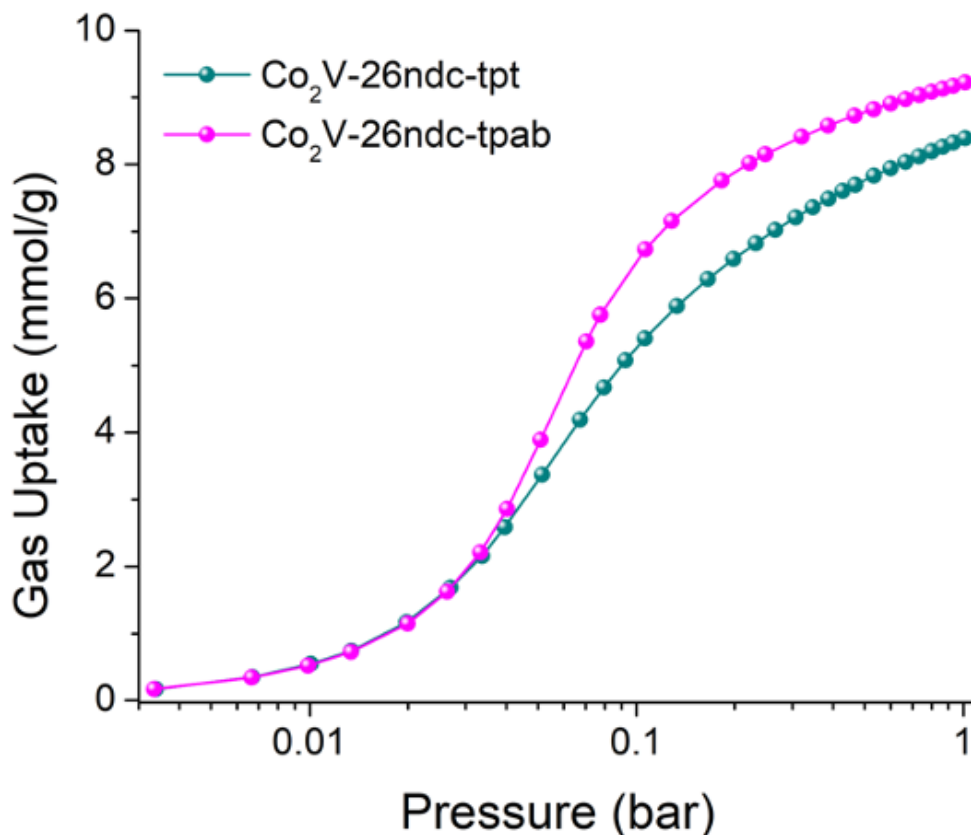
Figure 8. Gas sorption of propane (C_3H_8) uptake at 298 K for $Co_2V(OH)(2,6\text{-ndc})_3tpt$ and $Co_2V(OH)(2,6\text{-ndc})_3tpab$ MOF adsorbents.
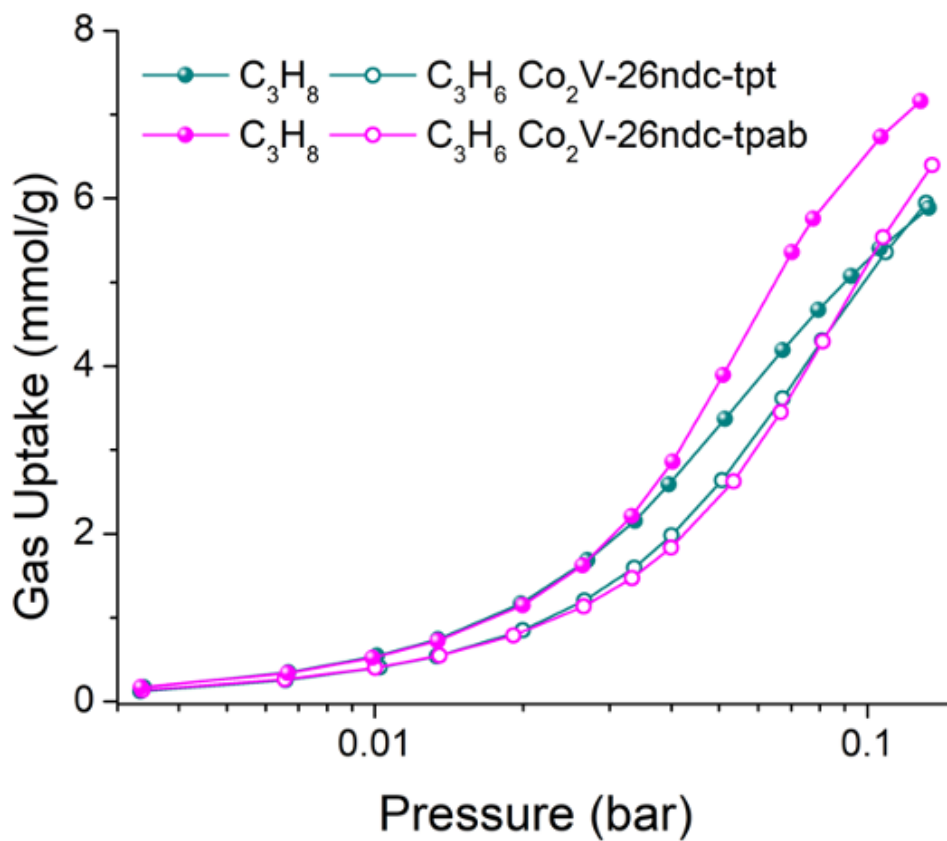
Gas Sorption and Uptake Capacity

Figure 7 and Figure 8 depict the gas uptake capacity of propane and propylene at different pressures with both MOF materials demonstrating preferential propane-selective uptake. Figure 7 shows the gas sorption and uptake of propylene where both the tpt and tpab adsorbents have relatively similar uptake, especially in the low pressure region. Figure 8 shows the uptake of propane gas and it is clear that the tpab structure has a much higher propane uptake than that of the tpt structure.

18

Figure 9. Comparison of gas sorption for C_3H_6/C_3H_8 uptake of $Co_2V(OH)(2,6\text{-}ndc)_3tpt$ and $Co_2V(OH)(2,6\text{-}ndc)_3tpab$ MOF adsorbents at 298 K.
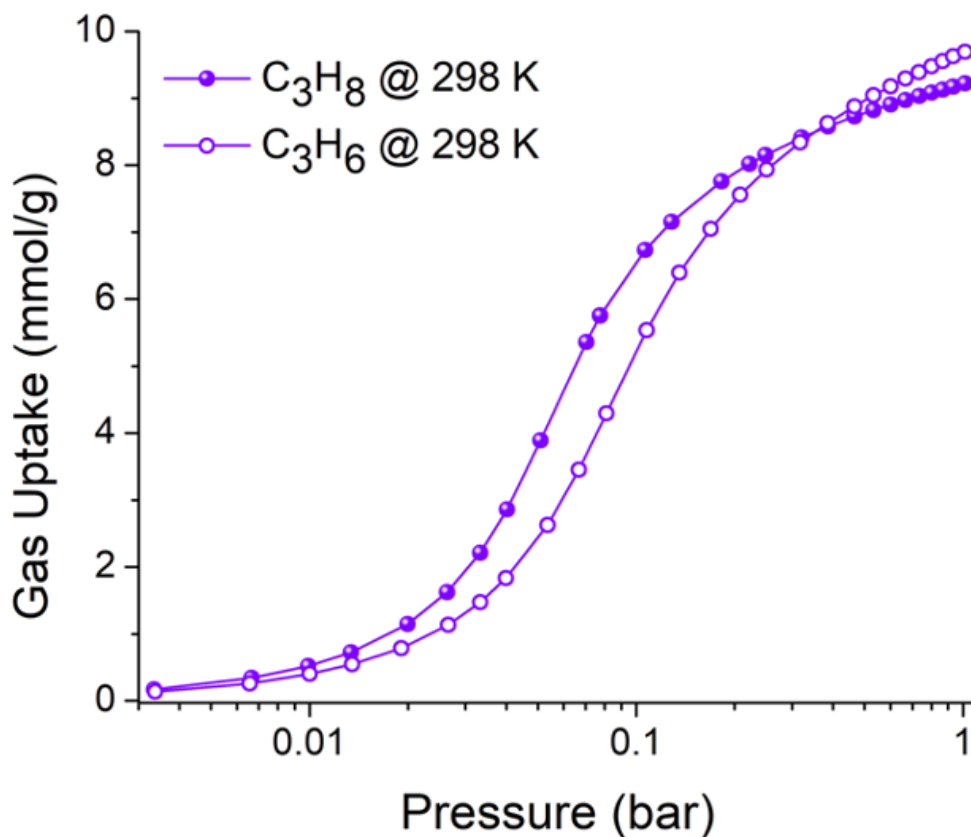
Figure 10. Gas sorption for C_3H_6/C_3H_8 uptake of the $Co_2V(OH)(2,6\text{-ndc})_3$tpab MOF adsorbent at 298 K.

Higher Uptake Capacity of $Co_2V(OH)(2,6\text{-ndc})_3$tpab

Propylene is the desired product in the currently used separation process due to its larger molecular size. Consequently, because of this characteristic of propylene, propylene-selective adsorbents require one or more adsorption–desorption cycles to obtain the purified gas. In comparison, propane-selective adsorbents could ideally allow for high quality propylene to be obtained in just one step, which further simplifies the separation process and reduces energy consumption. Figure 9 shows the combined gas sorption graphs from Figure 7 and 8. There is a

dramatic increase in propane uptake for the tpab adsorbent and it demonstrates that tpab also has the higher propane uptake overall. For the tpt adsorbent, there is only a small difference between the propane and propylene uptake, which is indicative of lower selectivity. On the other hand, there is a much larger difference between the propane and propylene uptake for tpab, which demonstrates that tpab has higher selectivity as well. This can be attributed to the pi-hydrogen interactions with the triple bonds in tpab's structure.

DISCUSSION AND FUTURE PERSPECTIVES

This research paper sought to discuss the specifics of designing MOFs that would optimize the separation of propylene and propane gas. Current methods use a complex system that requires several steps to separate propylene from propane. Additionally, the current methods are propylene-selective, which results in higher energy consumption and more waste generation. As a result, the aim of this research study is to develop a propane-selective method of separating the two gases, which would result in conserving energy and making the gas separation process more efficient. The results indicate that tpab is the preferred ligand over tpt in regards to propane uptake and tpab demonstrated higher selectivity. These characteristics of tpab underscores its potential to be used in propane and propylene gas separation and streamline this process, while also increasing its accuracy.

Future Directions

Based on current results, the MOF adsorbents still require fine tuning and other modifications in order to achieve the optimal balance between propane gas uptake capacity as well as selectivity.

One way to do this is employing new ligands with different sizes and functionalities. Substituting a new L1 ligand, such as 4-(1*H*-Tetrazol-5-yl)benzoic acid (tba) would help increase hydrogen interactions since it contains more nitrogen atoms than that of 2,6-ndc. In addition, tba also contains a tetrazole structure and contains an overall negative two charge due to resonance. The overall charge of the structure contributes to stability as well, so different counter ions should also be incorporated into future experiments. 4-(p-carboxyphenyl)-1,2,4-triazole (cpt) is another type of L1 ligand that contains a triazole with three nitrogen atoms, which gives the structure an overall negative one charge that could lead to a more stable structure. This type of varying counter ion structure could be implemented in future trials in an attempt to synthesize a more stable structure.

Exploring different types of metal ions is another important future step. In addition to coordination of the metal trimers with organic ligands, chemical stability also plays a significant role in porous materials for industrial applications. For instance, Ni^{2+} is an ion that has properties that may increase water stability. In comparison to the Co^{2+} used in this project's experiments, the nickel ion contains a smaller ionic radius along with a larger crystal field stabilization energy that contributes to stronger coordination and overall greater stability (Hong et al., 2023). Thus, utilizing different metal ions based on chemical properties could lead to enhanced stability and performance of MOF adsorbents. There are a wide range of possible combinations of varying metal ions and organic linkers under different conditions that can be conducted in future trials.

As another prime example, one research study investigated the use of a new L2 partitioning ligand, *N,N′,N″*-tri(4-pyridinyl)-1,3,5-benzenetri-carboxamide (tpbtc). The selectivity of

$Co_2V(OH)(2,6-ndc)_3tpbtc$ for propane has been evaluated through experiments involving C_3H_6/C_3H_8 breakthrough experiments to measure separation potential and has demonstrated excellent propane uptake capacity. $Co_2V(OH)(2,6-ndc)_3tpbtc$ has a c/a ratio of 0.77 and the length between nitrogen atoms is 13.7 Å, which lies in the middle in terms of length and potential uptake capacity compared to tpt and tpab adsorbents. The results show that propylene was detected first, while propane was trapped in the adsorbent. It was also observed that high-quality polymer-grade propylene could be collected from the C_3H_6/C_3H_8 mixture after a short period of separation (Hong et al., 2021).

Subsequently, multiple breakthrough cycles were performed on $Co_2V(OH)(2,6-ndc)_3tpbtc$ to further test its performance, and it was found that the separation performance was maintained even after multiple cycles, confirming the reusability and recyclability of the adsorbent (Hong et al., 2021). As a result, these new ligands have the potential to help strengthen the adsorbent structures and improve overall separation performance, and warrant further investigation by other research studies.

A significant issue in the preparation of MOFs is the acquisition of phase-pure products, as a single polymorph is necessary for accurate structural determination and full characterization. However, achieving this can be difficult in certain cases, such as with frameworks that have varying degrees of interpenetration, which are challenging to separate. Additionally, obtaining uniform, empty pores through complete sample activation is crucial for realizing the full potential of these porous materials, but it can be particularly challenging for highly porous MOFs (Li et al., 2012). As such, another important area to explore would be different types of solvent

exchange, such as reflux and Soxhlet exchange methods when removing impurities from the synthesized MOF materials. Reflux would involve utilizing condensation and distillation, which heats a solution at a constant temperature. The purity of the overhead products is increased through refluxing as the condensation of the heavier fraction prevents them from being carried along with the vapor stream that exits. On the other hand, Soxhlet exchange involves the extraction and isolation of water-insoluble and slightly water-soluble organic compounds. This would allow for a lower amount of consumed solvent and raw materials in solvent exchange, so it can purify greater amounts of MOF materials without losing as much of the product. Furthermore, other synthetic conditions with different types of solvents can be employed based on boiling point. A solvent with a lower boiling point will allow for adsorbent structures to be more stable and remain intact at higher temperatures, which will contribute to greater thermal stability. As such, the solvent can contribute to the overall stability of the structure undergoing various procedures of gas separation and gas sorption.

Limitations

The practical application of MOFs, including their use in separations, is directly linked to their stability. To better understand this relationship, MOF stability can be divided into three categories: framework stability, thermal stability, and chemical stability. Framework stability pertains to whether the open lattice structure remains intact after removing guest molecules or experiencing changes in the environment or external stimuli, and is closely related to thermal and chemical stabilities. In gas-phase adsorptive separations and membrane separations, the ability of the framework to maintain its structure after removing guest molecules from its pores is essential. However, there is usually a tradeoff with increased pore volume or size leading to

decreased stability. Many hybrid framework materials, including MOFs, face a major limitation in their thermal stability. Although a few MOFs can withstand temperatures of 400°C or higher while maintaining their framework integrity, the majority of them become unstable above 200°C (Li et al., 2012). Conversely, while the chemical stability of MOFs has not been extensively researched, it may pose a challenge in some separation applications as the coordination bonds between metal nodes and organic ligands are easily broken by reactive chemicals, including water.

Furthermore, studies in the future can perform a deeper examination of the effect of MOFs on the environment. While the current study focused on the comparison of propane gas uptake capacity between tpab and tpt, it is limited in that it did not elucidate specific information on their effects on the environment. Though it is promising that the current results show that propane-selective separation using tpab indicates that energy will be conserved and can potentially have positive effects on the environment than that of the current methods, detailed characteristics regarding how tpab can be more beneficial for the environment should be researched before the materials can be used in industrial applications. Further studies can measure environmental metrics including carbon emissions, energy consumption, and generation of waste in regards to the gas separation process. By examining these metrics, researchers can assess the overall sustainability of using MOFs for gas separation and determine whether they are a viable alternative to existing separation methods. Additionally, further research can investigate the potential long-term effects of MOF usage on the environment, including any potential hazards or risks associated with the materials. It is also essential to consider the economic feasibility of using MOFs in industrial applications. While MOFs have shown

promising results in laboratory studies, their production costs and scalability remain a significant concern. Further research should focus on developing cost-effective and efficient production methods for MOFs that can be used at an industrial scale.

In summary, this project serves as an initial presentation of the potential usefulness of tpab in propylene and propane gas separation. Its higher selectivity and increased propane uptake provides promising implications for gas separation processes in the future and applications for use in the industry. While the current study provides a promising outlook for using MOFs in gas separation processes, there is a need for further research to fully assess their environmental impact, economic feasibility, and potential long-term effects. By conducting comprehensive studies on these topics, researchers can develop a deeper understanding of MOFs' potential as a sustainable alternative to existing separation methods. As such, this project opens the doors to more advancements in effective hydrocarbon gas-selective MOFs that will lead to more environmentally-friendly and energy-efficient production of industrial materials.

REFERENCES

Hong, A. N.; Wang, Y.; Chen, Y.; Yang, H.; Kusumoputro, E.; Bu, X.; Feng, P. (2023).

    Concurrent Enhancement of Acetylene Uptake Capacity and Selectivity by Progressive

    Core Expansion and Extra-Framework Anions in Pore-Space-Partitioned Metal-Organic

    Frameworks. *Chem. Eur. J. 29*(13), e202203547.

    https://doi.org/10.1002/chem.202203547

Hong, A. N.; Yang, H.; Li, T.; Wang, Y.; Wang, Y. X.; Jia, X.; Zhou, A.; Kusumoputro, E.; Li, J.;

    Bu, X.; Feng, P. (2021). Pore-Space Partition and Optimization for Propane-Selective

    High-Performance Propane/Propylene Separation. *ACS Appl. Mater. Interfaces. 13*(44),

    52160-52166. https://doi.org/10.1021/acsami.1c10391

Liang, B.; Zhang, X.; Xie, Y.; Lin, R.; Krishna, R.; Cui, H.; Li, Z.; Shi, Y.; Wu, H.; Zhou, W.;

    Chen, B. (2020). An Ultramicroporous Metal-Organic Framework for High Sieving

    Separation of Propylene from Propane. *J. Am. Chem. Soc.* 142, 17795-17801.

    https://doi.org/10.1021/jacs.0c09466

Li, J. R.; Sculley, J.; Zhou, H. C. (2012). Metal-Organic Frameworks for Separations. Chemical

    Reviews, 112, 869-932. https://doi.org/10.1021/cr200190s

Yang, H.; Wang, Y.; Krishna, R.; Jia, X.; Wang, Y.; Hong, A. H.; Dang, C.; Castillo, H. E.; Bu,

    X.; Feng, P. (2020). Pore-Space-Partition-Enabled Exceptional Ethane Uptake and

    Ethane-Selective Ethane-Ethylene Separation. *J. Am. Chem. Soc. 142*(5), 2222.

    https://doi.org/10.1021/jacs.9b12924

Zhai, Q.; Bu, X.; Zhao, X.; Li, D.; Feng, P. (2017). Pore Space Partition in Metal-Organic

    Frameworks. *Acc. Chem. Res. 50*(2), 407-417.

    https://doi.org/10.1021/acs.accounts.6b00526

Zhao, X.; Bu, X.; Nguyen, E.; Zhai, Q.; Mao, C.; Feng, P. (2016). Multivariable Modular Design of Pore Space Partition. *J. Am. Chem. Soc.* 138, 15102-15105. https://doi.org/10.1021/jacs.6b07901

Zhou, H.; Long, R.; Yaghi O. (2012). Introduction to Metal-Organic Frameworks. *Chem. Rev. 112*(2), 673-674. https://doi.org/10.1021/cr300014x