

ADSORPTION CAPACITY OF SAPO-34 AND ZSM-5 ZEOLITES DETERMINED BY
BREAKTHROUGH EXPERIMENTS

by

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

Masters of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

October 2016

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DEDICATION

This thesis is dedicated to Alisha, my soulmate and best friend. I love you forever and always.

ACKNOWLEDGMENTS

More than anyone else, I want to thank Alisha for helping me reach the end of this long journey. You have stood at my side and supported me incessantly and wholeheartedly for the last eight years even when it was less than easy. You have helped me become a better man and have introduced me to what is most important in life. And you have shown me love and given me hope when I needed it the most. Thank you for that and so much more.

The completion of this thesis wouldn't have been possible without my parents and all the love that they gave me. They escaped a war inflicted country, sacrificed everything familiar, and underwent countless tribulations with the sole purpose of providing me with the opportunity of building a happy and fulfilling life. I truly would have no chance of being here without them and will never be able to repay their kindness.

I also want to thank Aleksandar for cheering me on during this journey. I can say without any doubt or reservation that nobody on this planet has ever been fortunate enough to have a brother like you. Your compassion and thoughtfulness are traits that I can only hope to one day replicate.

Lastly, I am very grateful for all the support that Dr. Stephanie Wettstein provided during these last two years. Even when experiment results were less than great, she never failed to show kindness and unending optimism. Thank you for guiding me on this long road and ensuring that I was successful.

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ABSTRACT

Although it has been known for over 50 years that zeolite frameworks are flexible, it has been only of recent that a systematic investigation into this phenomenon has begun. An area that has not been significantly explored is the affect that zeolite flexibility may have on adsorption capacities. In order to explore this, a flow system was built and assembled, and the system performance was verified by replicating literature ZSM-5/isobutane, ZSM-5/n-hexane, and SAPO-34/methanol adsorption isotherms. Different packing schemes (powders, mixtures, pellets) were studied and corresponding adsorption capacities were evaluated for accuracy and precision. It was found that zeolite powder pressed into pellets led to the lowest deviation from literature values and that larger crystal sizes may also lead to more accurate values. While further investigation into packing methods is recommended, the relatively accurate adsorption capacities that were acquired suggests that the established flow system has been built and calibrated correctly, and that further adsorption experiments probing the flexibility of the zeolite structure can begin.

INTRODUCTION

1.1 Overview of Zeolite Science

The use of zeolites, which have high thermal and chemical stability, for industrial processes has become increasingly common primarily due to the excellent separation capabilities and catalytic properties that these microporous materials possess. The wide variety of zeolites allows for the ability to select and tune many material characteristics including polarity, pore size, surface area, and adsorption strength according to the particular application needs. While the majority of synthetic zeolites are used as detergent builders, in 2012, about 17% of total production volume was used for catalysis [29]. A large fraction of that volume was for oil and gas refining where the two main catalytic processes are fluid catalytic cracking (FCC) and hydrocracking, and for FCC alone, this volume equates to approximately 840,000 metric tons per year of catalyst [30-32]. Another 10% of zeolite consumption is used as adsorbents due to their unique adsorption capabilities and ability to make difficult gas separations [29], such as those between H_2/CH_4 [33], fructose/glucose [34], C_3H_8/C_3H_6 [35], CO_2/N_2 [36], ethanol/ H_2O [37], $n-C_4/i-C_4$ [34], and 1-butene/1,3-butadiene [38].

While adsorption-based methods, such as pressure swing adsorption [39], use zeolite pellets, great interest in the use of zeolite membranes has emerged, including that of membrane reactors [40, 41]. Membranes hold advantages over zeolite pellets including continuous operations, the ability to separate molecules by molecular sieving, and the

ability to maintain significantly different conditions (e.g., temperature, concentration, pressure) on either side of the membrane [42]. Although zeolite membranes are extensively being studied and could lead to substantial improvements in separation technology, at this time the only commercial application known is the dehydration of solvents with LTA membranes [43]. The lack of membrane usage is likely due to a combination of high synthesis cost, difficulty in reducing membrane defects that arise during synthesis, and the brittle nature of the zeolite, which makes it prone to cracking.

1.2 Zeolites in Industry Settings

Large-scale use of synthetic zeolites was primarily established in the petrochemical industry and has since grown to become a vital part of many refining processes. Former Union Carbide and Mobil companies were some of the first pioneers that, starting in the early 1960's, began aggressively pushing zeolite research, primarily as a response to government regulations of lead content in gasoline. These regulations eventually led to the commercialization of zeolite ZSM-5 (MFI) in 1988, a versatile zeolite that is now commonly used for many applications [44]. Since then, the oil and gas industry has continued to show great interest in zeolite science and has tasked numerous research groups to synthesize novel zeolites and study their unique properties. This effort has led to the extensive use of zeolites as thermally stable solid acid catalysts for a number of refining processes such as FCC, hydrocracking, residue hydro-processing, hydrotreating, dewaxing, reforming, isomerization, and alkylation [45].

Although zeolite research has exploded in the past decades and resulted in an ever-increasing availability of new synthetic zeolites, the implementation of new discoveries for industrial applications has proven to be a slow process. In fact only about 18 types of zeolites have been commercialized as of date [26], a disappointment that can be attributed to high risk and cost. If synthesis is not simple and relatively cheap, performance is not significantly better than the existing catalyst/adsorbent, and if the mechanical and physical properties of the zeolite cannot handle current infrastructure, then it is not likely for industry to invest resources and time for such an endeavor. Luckily, it is estimated that there are a total of 2.5 million hypothetical zeolites, making it very likely that a new structure with superior catalytic and/or adsorbent properties will eventually be discovered and thereby incentivize the industry to make the necessary financial investments for commercialization [46].

Regardless of the limited number of commercial operations that currently take advantage of zeolite technology, in those cases where zeolites have been optimized for industrial application, very large quantities are produced and used. In total, the value of the synthetic zeolite market is worth \$1.68 billion and is estimated to increase by 4.4% to \$1.76 billion by 2020 [44]. The characteristics that make zeolites so valuable for industrial applications, such as oil refining, include properties like easy acidity tuning, high temperature resistance, non-corrosiveness, non-toxicity, ability to be shaped (pellets, spheres, etc.), crystal size control, possibility of heteroatom integration, and the capability of designing the zeolite with carefully chosen framework features (channels,

pores, cages, etc.) [44]. Before a more in-depth discussion of such characteristics can be undertaken, a general knowledge of the zeolite structure is necessary and therefore is detailed in the next section.

1.3 Composition and Structure

Zeolites are porous, three-dimensional inorganic crystalline structures typically composed of aluminium, silicon and oxygen atoms. These three types of atoms arrange to form tetrahedral units (TO_4) that make up the primary building blocks of the zeolite structure (Figure 1.1a). These primary building units combine into secondary building units (SBUs; examples shown in Figure 1.1b) of which there are at least 23 types recognized [44]. The SBUs form a variety of unique zeolite frameworks with varying unit cell dimensions and pore sizes that result in the formation of individual framework types identified by three letter codes (e.g., MFI, LTA, CHA, RHO) [44, 47]. Each framework has a unique structure that contains 8, 10, or 12-member oxygen ring pores that lead to cavities and channels within the zeolite structure [48]. As of 2016, there are 231 unique variants of zeolite frameworks approved by the Structure of Commission of the International

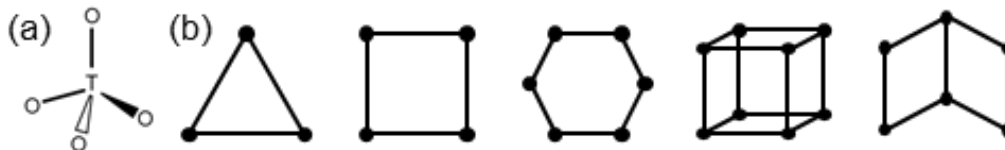


Figure 1.1. (a) Primary building unit of the zeolite framework ($T = \text{Al, Si}$) and (b) examples of secondary building units (SBUs) where the spheres at the vertices represent primary building units.

Zeolite Association (IZA-SC) [26]; however, millions of hypothetical zeolite structures have been predicted through computer simulation and modelling [46].

The zeolite structures can be made up of different T-atoms, crystal phases (e.g., monoclinic, orthorhombic or cubic), topological densities, and materials that result in different topologies. For example, there are 26 different zeolite topologies with the MFI framework structure, but all 26 topologies are characterized by the same channel system, which is defined by straight and sinusoidal channels [44]. Three of these topologies are: Silicalite-1, which contains only Si as T-atoms, ZSM-5, which has both Si and Al T-atoms, and B-ZSM-5, which has boron substituted for some of the Al, but all three topologies have the same MFI framework and approximately a 0.55 nm pore size, which determines what molecules can diffuse through the zeolite [44, 49]. It is known that pore sizes, typically determined by N₂ gas adsorption and/or calculated using the Saito-Foley model [50], fall within a range of values and can vary with temperature [51-55]. Pore flexibility likely occurs due to structural changes in the framework [56] and may have a significant effect on adsorption.

1.4 Adsorptive Properties of Zeolites

Adsorption is defined as an interaction between a chemical compound and a surface and is an important process in zeolite science. The type of interaction between the two materials is dependent on the adsorbate and adsorbent, and is categorized by either physisorption, identified by Van der Waals forces, or chemisorption, distinguished

by the exchange of electrons. This surface phenomenon is critical for many products such as detergent builders, spill kits, water filters, and extractor hoods, and also for many applications like catalysis, gas separations, and pollution control [57-61]. Zeolites are a particularly excellent class of adsorbent since they can be tailored for almost any kind of process and have a high surface area (ZSM-5: $385 - 1330 \text{ m}^2 \text{ g}^{-1}$) [62] for adsorption.

Many molecules adsorb to zeolite surfaces, ranging from hydrocarbons and alcohols to heavy metals and noble gases. To determine the adsorption capacity, an adsorption isotherm is measured and/or simulated [63, 64] and can take a variety of shapes, which gives insight into the mechanics of the adsorbent/adsorbate interaction. For example, the type I isotherm in Figure 1.2 is characteristic of adsorption on a microporous adsorbent while type II and III are respectively marked by strong and weak

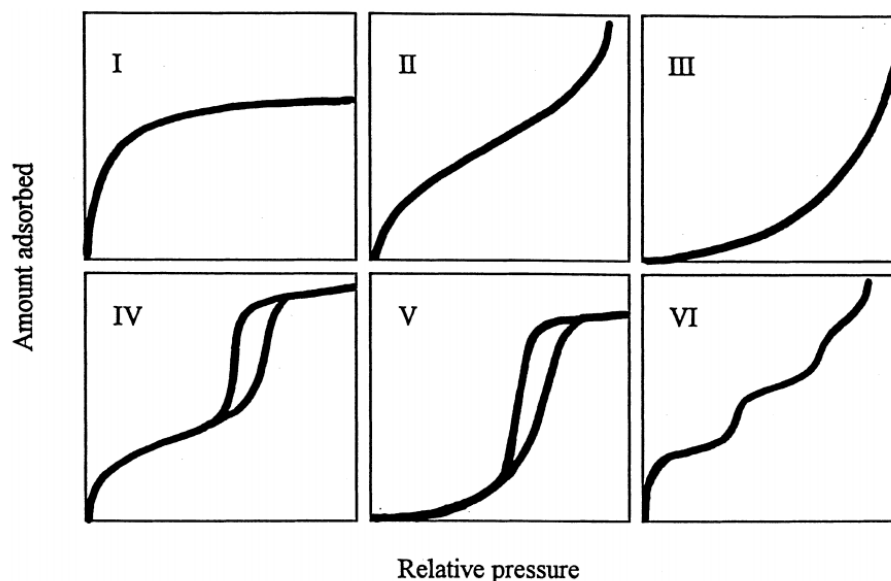


Figure 1.2. The IUPAC classification of adsorption isotherms for gas-solid equilibria. Image acquired from [2].

adsorption on a macroporous solid [2]. Also the isotherm shape can indicate the number of zeolite adsorption sites, where single-site adsorption is associated with the type I isotherm and the type IV curve is seen for dual-site adsorption such as for ZSM-5/isobutane adsorption [65]. The adsorption capacity (mmol adsorbate/g adsorbent) is also determined from the adsorption isotherm; for methanol/n-hexane and Silicalite-1, at room temperature and saturation pressures, 17 molecules of methanol adsorb to the Silicalite-1 (MFI) framework while only 8 molecules of n-hexane are adsorbed [5, 8]. As expected, adsorption capacities can differ greatly between individual zeolite frameworks. For 69 kPa CO₂ partial pressure, NaX (FAU) has an adsorption capacity of 5.4 mmol/g while H-ZSM-5 (MFI) adsorbs 1.6 mmol/g [66]. This variation of CO₂ adsorption results from fundamental differences between the two frameworks, likely the most important being the limiting free diameter and the percent of accessible pore volume. The FAU framework has a limiting free diameter of 7.5 Å and an accessible pore volume of 27.4%, while MFI has 9.81% of its pore volume accessible and a limiting free diameter of 5.5 Å [26, 67]. Not only does the NaX therefore have more available room to accommodate the CO₂ molecules ($k_d = 4.6$ Å) but, due to a larger limiting free diameter, intracrystalline self-diffusion of CO₂ is greater for FAU ($D_0 = 15 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) than MFI ($D_0 = 1.7 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) [67], and accordingly, CO₂ molecules can access adsorption sites more easily. These differences show, that while composed of the same materials, zeolites can differ greatly among themselves and can have distinctive properties.

Adsorption capacities can also change upon addition of extra-framework cations (EFC) since, unlike pure silicate materials (SiO_2) that have a zero overall charge, zeolites that have trivalent aluminum atoms as part of their framework require charge neutralization. Common EFCs found in natural zeolites include Na^+ , K^+ , Ca^{2+} , and Ba^{2+} while synthetic zeolites may have more complex cations such as quaternary ammonium ions [68]. These cations can be substituted by other cations (even in situ) thereby offering the possibility to modify various zeolite properties, like adsorption capacity, fairly quickly and easily. For instance, it was found that the identity of the EFC coordinated to the zeolite can have a noteworthy effect on CO_2 adsorption, where, as mentioned above, H-ZSM-5 adsorbed 1.6 mmol/g of CO_2 , but by exchanging the hydronium ions with Na^+ , the adsorption uptake increased to 1.9 mmol/g (69 kPa; 24 °C). This difference was hypothesized to be a result of a greater ion/induced-dipole interaction between the Na^+ and CO_2 [66].

Another, more recent, study observed a similar effect on both CO_2 and N_2 adsorption capacity for a different zeolite (BEA). Interestingly, the research showed that larger cations led to higher adsorption capacities (K-BEA: 12.4 m.u.c.; Li-BEA: 8.9 m.u.c.) and was hypothesized to be a result of the effective charge density of the cations inside the zeolite pores [18]. Investigations into CH_4 and N_2 adsorption onto cesium exchange-zeolite X found that the introduction of an EFC can affect the adsorption of individual compounds differently; in this case the nitrogen adsorption decreased with increasing Cs content, but concurrently lead to greater amounts of methane adsorption [69]. The

aforementioned studies highlight how nuanced adsorption capacities can be as EFCs are coordinated to a zeolite framework and how properties, such as Si/Al ratio [70], can be manipulated to change adsorption. The combination of altering a variety of such zeolite properties can therefore be used to precisely engineer the adsorption capacity and adsorbent/adsorbate interaction strength.

1.5 Zeolite Membranes

Growing zeolites as membranes allows them to be used to separate mixtures that, with traditional methods, are expensive or difficult to do. Membranes can be synthesized as individual zeolite layers, embedded zeolite crystals in polymer matrices, or as zeolite

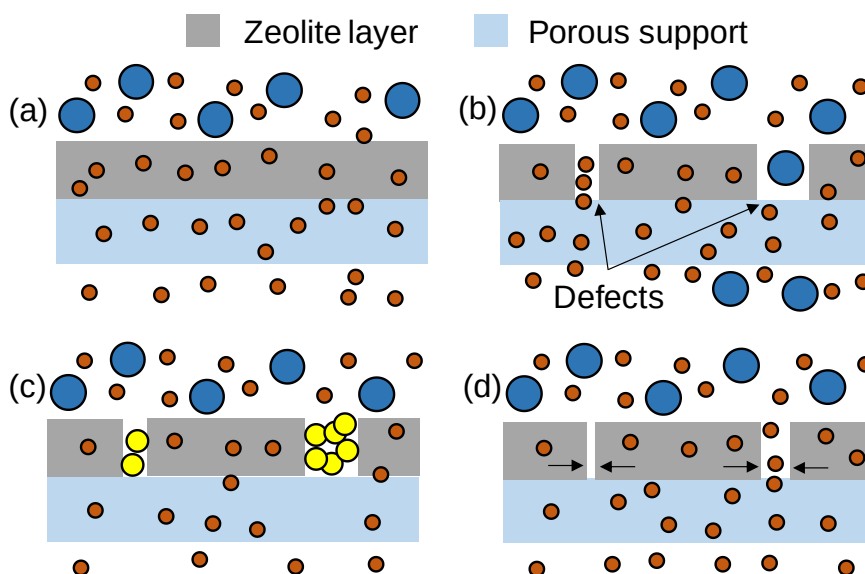


Figure 1.3. Representation of (a) an ideal membrane without defects that allows only the small molecule to permeate due to size exclusion; (b) a membrane containing defects, which allows the larger molecule to permeate; (c) defects blocked due to molecular condensation or atomic layer deposition; (d) defects shrunk due to thermal or adsorbate-induced expansion.

layers on porous supports, with the last method being the most reported on [71]. While zeolite membranes can be highly selective (Figure 1.3a), defects that form during synthesis lead to dramatic reductions in separation performance (Figure 1.3b). In order to minimize this negative effect, usually one of two paths are taken: (1) reducing the initial defect number/size by optimizing the synthesis process and (2) preventing permeation through defects by sealing them after they have already been synthesized [72]. The latter method can be achieved either by condensation [73] (Figure 1.3c), an after-synthesis treatment [74], or utilization of framework flexibility (Figure 1.3d) [75]. Framework flexibility due to an adsorbate or temperature change can lead to zeolite expansion, which can close off membrane defects and thus lead to much higher selectivity (Figure 1.4).

Identification of molecules that change the zeolite structure is important since, traditionally, characterization of zeolite membrane quality has been done with molecules such as i-butane, n-hexane, and SF₆. All of these compounds have recently been found to

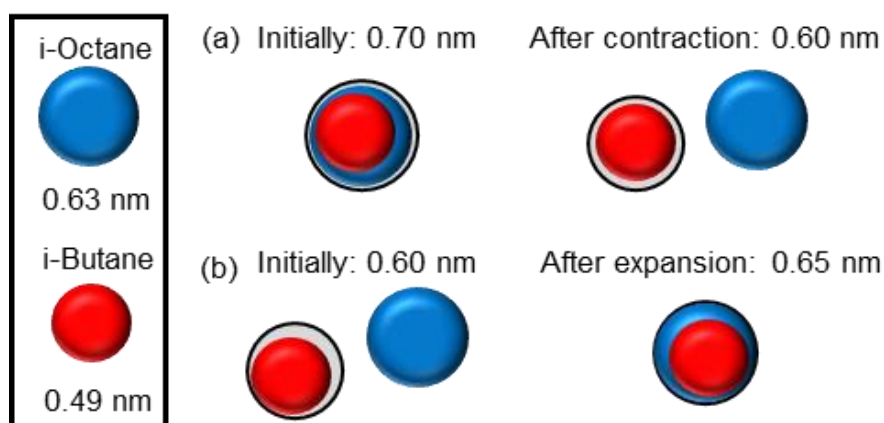


Figure 1.4. The effect of framework (a) expansion and (b) contraction on the ability for molecules to permeate through defects. The light grey circle represents a membrane defect.

expand or contract the zeolite framework, thereby leading to an inaccurate determination of membrane quality [18]. For example, if n-hexane, which expands MFI frameworks and thereby reduces the size and number of membrane defects, is used as a characterization molecule, the acquired data may show a lower permeation flux than if the membrane characterization had been done with benzene, a molecule that largely has no effect on zeolite structure. However, n-hexane and other molecules that expand and/or contract the zeolite can be used to help characterize the size and frequency of membrane defects [69]. Understanding framework flexibility and its effect on zeolite crystals may enable production of highly-selective membranes as well as lead to a better understanding of pore flexibility and its effect on molecular diffusion, which is important for both adsorption and catalytic purposes.

1.6 Research Objectives

The first synthetic zeolite, Levyne (LEV), was synthesized by Henry St. Claire Deville in 1862 [76] and by the early 1900's, commercial scale use of zeolites for ion-exchange of hard water had begun [77]. In the late 1930's it was observed that zeolite unit cell parameters could change due to cation exchange [78] and decades later, studies found that dehydration of the zeolite crystal and changes in temperature could also induce such effects [79-82]. Although initially noted nearly a century ago, it has not been until recently that researchers have started to discover the significance that this framework flexibility could have on separations and catalysis.

Consequently, since the workings of zeolite framework flexibility can still be better understood, the goal of this master's thesis was to build a flow system designed for gas/liquid permeation and permoporosimetry experiments (Figure 1.5), and to calibrate it by replicating literature adsorption isotherm data. These tasks were completed with the purpose of preparing the system for zeolite membrane experiments which could serve as a quick screening method for evaluating the effect of competing adsorbates on zeolite flexibility. Once a pair of adsorbates with interesting framework flexibility behavior are identified, binary breakthrough experiments would be run in order to see if changes within the adsorption isotherms occur. The results of these experiments would provide useful information about changes in adsorption capacities and about the molecular interactions between the compounds.

The remainder of this text will first provide the reader with a brief literature review of both adsorbate and temperature induced framework flexibility, and will then discuss the

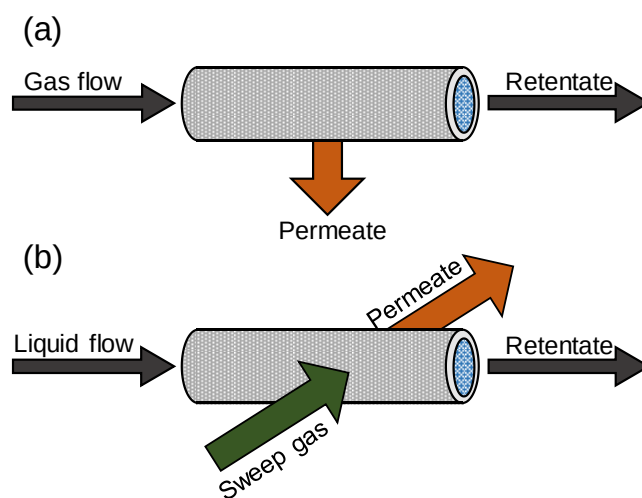


Figure 1.5. Sample flow diagrams for (a) pervaporation and (b) gas/vapor permeation.

implications of this flexibility. Next the design and construction of the flow system will be examined, followed by a discussion about the accuracy of the breakthrough experiments which were used to replicate literature adsorption isotherm curves. The conclusion of this document will compare the experimentally fabricated adsorption isotherms to literature curves and future steps for this project will ultimately be considered.

1.7 Literature Review: Adsorbate-Induced Flexibility

Adsorption of various chemical species has been observed to bring about changes in zeolite crystallogical dimensions causing as much as a 2.3% change in the unit cell volume [19]. In fact, computational methods have shown that all known existing zeolite frameworks are flexible, although some must be represented in their lowest symmetry form or include a heteroatom (e.g., Al, Ge, or B) in the framework in order to exhibit flexibility [83, 84]. This necessitates that TO_4 units adopt ideal O-T-O angles of approximately 109.47° and ideal T-O bond lengths (Si-O: 1.61 Å, Al-O: 1.75 Å) [85]. Distortion of these ideal angles/lengths results in a highly unfavorable energy cost [85], so much so that distortion of the tetrahedral units has an order of magnitude greater energy cost than distortion of the linkage angles [86]. These types of structural deformations can significantly impact membrane selectivity, and dependent on the adsorbate, the framework, and the orientation of the crystals.

Unit cell changes can occur differently for 2- and 3-dimensional frameworks since the geometric orientation of zeolite crystals (parallel or randomly oriented) within a

membrane can substantially affect defect size changes [87]. Less variation in flexibility effects has been seen for zeolites within the same framework family but with differing topologies. For example, n-hexane and i-butane saturation of B-ZSM-5 and Silicalite-1 crystals has not resulted in significant differences in expansion [5, 18]. Due to the considerable adsorbate effects on zeolite frameworks, the following two subsections will only summarize framework flexibility research for alkanes and alcohols, although considerable research on cyclic hydrocarbons, water, and other gases is also available.

1.7.1 Alkanes

The effect of alkane adsorption on zeolite frameworks is important to thoroughly explore since a variety of zeolites used in the petrochemical industry deform with alkane adsorption and these structural changes could potentially affect catalytic or sorption properties [88]. Additionally, understanding how adsorbates affect the unit cell could have far-reaching effects on implementing zeolite membranes in the petroleum industry.

Upon alkane adsorption (up to n-C₁₃), the MFI unit cell expands up to 1.53 vol% with the exception of i-C₄, which contracts the unit cell at low loadings [12]. n-Hexane has been extensively used as a characterization molecule for MFI membrane quality, but expands the unit cell by 1.19 vol% (Table 1.1) [5]. This expansion had a significant impact on membrane selectivity and single component fluxes. Single-component n-hexane pervaporation experiments showed that the n-hexane flux is orders of magnitude lower than the flux of single-component 2,2-dimethylbutane (DMB) pervaporation experiments [89]. While n-hexane permeates through both membrane defects and the MFI zeolite

Table 1.1. Unit cell changes due to alkane adsorption on MFI frameworks as determined using XRD (unless noted).

Topology	Temp (K)	Adsorbate	Loading (m.u.c.)	Unit cell (pm)			$\Delta\text{vol}\%$	Ref.
				Δa	Δb	Δc		
Silicalite-1	RT	i-C ₄	10	4.2	1.0	2.2	0.42	[5]
		n-C ₆	8	5.0	10.7	5.5	1.19	
	298 ^b	n-C ₄	10	-	-	3.29 ^a	-	[5]
		n-C ₆	8	-	-	4.99 ^a	-	
	180	n-C ₆	8	1.7	12.4	8.7	1.35	[5]
			8	13.5	13.6	9.5	2.3	[19]
B-ZSM-5	323	n-C ₆	8	8.3	9.5	5.3	1.29	[20]
	300	i-C ₄	3	-	-	-	-0.15	[18]
			8.5	1.2	1.6	3.9	0.42	
		n-C ₆	6.3	2.6	1.8	2.3	0.4	[18]
			8	-	-	-	1.14	

^a Based on a 13.142 Å c-parameter [26].

^b Determined using optical microscopy.

pores, DMB essentially does not permeate through MFI pores at the reaction conditions because of its large size. The lower n-hexane flux was attributed to the shrinking of defects due to framework expansion caused by adsorption of n-hexane in the unit cell. This effect was clearly seen when 0.2 mol% n-hexane was added to single-component DMB and 1,3,5-trimethylbenzene (TMB) pervaporation experiments and the DMB/TMB fluxes, which only permeate through defects at the reaction conditions, was reduced by 96% and 94%, respectively. The reduction in flux was attributed to the decrease in defect size due to framework expansion caused by the n-hexane [89]. When i-octane (0.70 nm) was used with n-hexane (1.4 wt%) in pervaporation experiments, the drop in i-octane flux was also pronounced, showing a decrease in the i-octane flux of 98.4% [12].

To confirm the hypothesis that crystal expansion was affecting the flow through defects, the percent volume and change in the c-direction of MFI crystals was measured

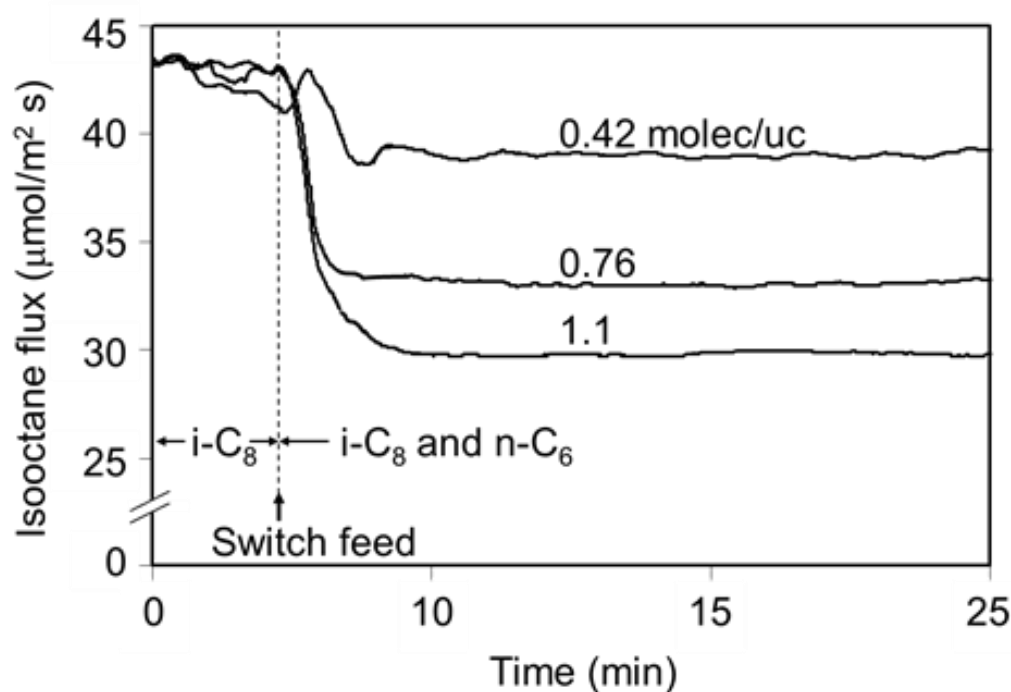


Figure 1.6. The effect of three different n-hexane loadings on the permeation flux of i-octane versus time for a MFI membrane at 473 K. Reprinted with permission from [5].

directly using multiple characterization techniques. Optical microscopy showed approximately 0.38% expansion in the *c*-direction when a Silicalite-1 crystal was saturated with n-hexane [5]. XRD measurements determined that the amount of unit cell expansion caused by n-hexane adsorption on B-ZSM-5 was strongly dependent on loading level [18]. A smaller degree of expansion (< 0.1 vol%) occurred at loadings below 4 m.u.c., at 6.3 m.u.c. there was a 0.4 vol% expansion, and at saturation, a 1.14 vol% increase was measured [18]; studies with magnetoelastic sensors have also detected framework expansion for MFI at n-hexane saturation levels [90]. The XRD data correspond to vapor permeation experiments that showed a decrease in the i-octane flow as the n-hexane loading increased (Figure 1.6), which is indicative of the crystal expansion closing off the

defects [5]. XRD and MAS NMR experiments at room temperature found that n-hexane molecules in a saturated Silicalite-1 framework were disordered and occupied all adsorption sites randomly resulting in substantial stress to the framework, which possibly explains why significant MFI framework expansion due to n-hexane adsorption was observed [19]. MAS NMR also showed that above 340 K this stress induced a symmetry phase transition from monoclinic (24 T sites/unit cell) to orthorhombic (12 T sites/unit cell) symmetry, which is a phenomenon known to be enabled by framework flexibility and is discussed further in section 1.7.

Apart from n-hexane, a variety of n-alkanes (C_3 - C_8) have also led to zeolite expansion [91]. Vapor permeation experiments using i-octane as the probe molecule, a compound too large to fit through MFI pores, and n- C_6 through n- C_{13} as the variable compound showed that the reduction in i-octane flux through two different Silicalite-1 membranes correlated with the percent volume expansion resulting from the n-alkane adsorption [12]. XRD experiments also showed that adsorption of these n-alkanes could expand unit cell parameters by as much as 11.2 pm (n- C_5 , *b*-direction) or as little as 1.1 pm (n- C_5 , *a*-direction) and that the changes in the lattice parameters were anisotropic. These types of distortions are more than enough to affect flow through MFI membranes and result in the observed i-octane flux reductions. For example, a 2.3 m.u.c. loading of n-octane, during n-octane/i-octane pervaporation (473 K) decreased i-octane flux by 93% [5]. Accompanying XRD measurements showed a strong correlation between the percent volume framework expansion and number of carbon atoms per unit cell, indicating an

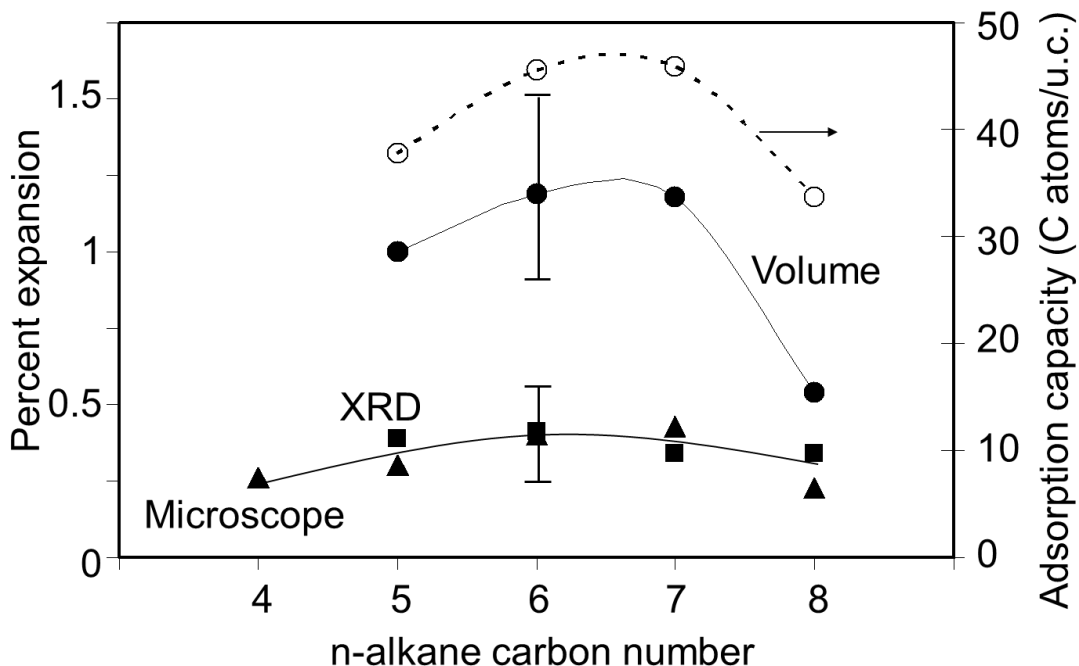


Figure 1.7. Percent expansion of the *c*-direction of Silicalite-1 crystals at 298 K (●) versus the number of carbon atoms in the linear alkane as measured by microscopy (▲) and by XRD (■). The percent volume increase of the unit cell of Silicalite-1 from XRD measurements is compared to the adsorption capacity of Silicalite-1 (○) from literature data [4]. Reprinted with permission from [5].

inverted parabola relationship where *n*-heptane expansion marked the apex of the parabola (Figure 1.7). The magnitude of the volumetric expansion appeared to be correlated with the adsorption capacity, where more carbon atoms resulted in greater expansions. This idea has been explained as a consequence of increased repulsive interactions between the *n*-alkanes and zeolite structure due to higher packing densities [12].

Unlike all other reported alkanes, *i*-butane contracted the MFI crystals at low loadings and expanded the framework at higher loadings (4.5 - 10 m.u.c.) [18, 91]. The change in flexibility effect coincides with a change in *i*-butane adsorption location, which,

depending on temperature, is seen by the appearance of an inflection point on the i-butane adsorption isotherm around 4 molecules per unit cell [92]. This inflection point is the point that i-butane has adsorbed in all of the channel intersection sites and then begins adsorbing in the channels themselves, a less energetically favorable adsorption location [93]. Simulations and infra-red microscopy find that the proximity of the i-butane molecules decreases once the MFI framework has a loading of more than 4 m.u.c. and that, at the same time, inter-molecular repulsions between i-butane molecules significantly increases as well [65]. The expansion of the zeolitic unit cell is likely a result of these repulsive interactions just as it was hypothesized to be for n-alkanes. The reasoning behind the initial contractive behavior at low loadings is not clear, but is likely related to the interaction between the i-butane molecules and the channel site oxygen atoms.

1.7.2 Alcohols

A variety of catalytic reactions that use alcohols as starting feeds, such as the methanol-to-olefin reaction, have the potential of being accomplished using zeolite catalysts [22]. Also, the dehydration of alcohols is an important but energy-intensive separation that can be completed with zeolite membranes in a more energy-efficient manner. Using zeolite for this purpose could result not only in improving product yield and purity, but also reduce process costs.

In general, the effect of alcohols on zeolite frameworks caused greater unit cell volume change than cyclic hydrocarbons, but less than alkanes (Table 1.2). For example,

Table 1.2. Unit cell changes due to alcohol adsorption effects on various zeolite materials as determined using XRD.

Framework	Topology	Temp (K)	Adsorbate	Loading (m.u.c.)	Unit cell (pm)			Δ vol%	Ref.
					Δ a	Δ b	Δ c		
MFI	Silicalite-1	RT	Methanol	7.7	0.1	0.4	0.13	0.04	[8]
				17.0	0.9	0.4	0.7	0.11	
		292	2-Propanol	11.6 ^a	7.1	5.0	4.7	0.96	[12]
CHA	SAPO-34	295	Ethanol	14.4 ^b	3.2	3.5	2.1	0.49	
				17.1	6.0	n/a	-7.0	0.65	[16]
		300	Methanol	17	-	n/a	-	0.41	[18]
LTA	NaA	723	Methanol	Saturation	1.5	n/a	22.7	1.74	[22]
		300		$a_m = 0.68$	-	n/a	n/a	0.43	[23]

^a Saturation loading found in [24].

^b Estimated from adsorption isotherms found in [27].

a_m = activity of methanol reported.

methanol adsorption contracted NaA zeolite at low activities (0.025-0.05), but expanded it at activities above 0.05 with a maximum expansion of 0.43 vol% at a methanol activity of 0.68 (300 K) [23]. Interestingly, SAPO-34 [16] and NaA [23] had similar percent volume expansion from methanol adsorption (0.50 vol% and 0.43 vol%, respectively), but Silicalite-1 [8] only expanded by 0.11 vol%. The average contact distance is longer for SAPO-34 [16] (2.92 – 3.52 Å) than Silicalite-1 [8] (3.41 – 3.81 Å) and implies that the interaction strength between methanol molecules and the different frameworks is not the same and may be the reason why Silicalite-1, which has a weaker methanol/framework interaction, does not expand as much as a framework with a stronger interaction, such as SAPO-34. Methanol adsorption into large void spaces of zeolite structures plays an important part in causing framework flexibility and made both the lower and upper limit of the zeolite flexibility window decrease [86, 94]. CHA and LTA have greater amounts of volume (CHA: 17.28 %; LTA: 23.09%) that can be occupied than compared to MFI (9.81%) [26], and the differences between these frameworks supports

the hypothesis that structures with larger void spaces may enable the zeolite to have a greater flexibility.

1.8 Literature Review: Overarching trends in packing density

The data at saturation loadings for MFI frameworks shows a general trend where the percent expansion increases with the number of carbons within the unit cell for alcohols, n-alkanes, and cyclic hydrocarbons (Figure 1.8). Alcohols result in the greatest extent of expansion, followed by n-alkanes, and then cyclic hydrocarbons. Alcohols may have stronger repulsive interactions with the framework as a result of their polarity,

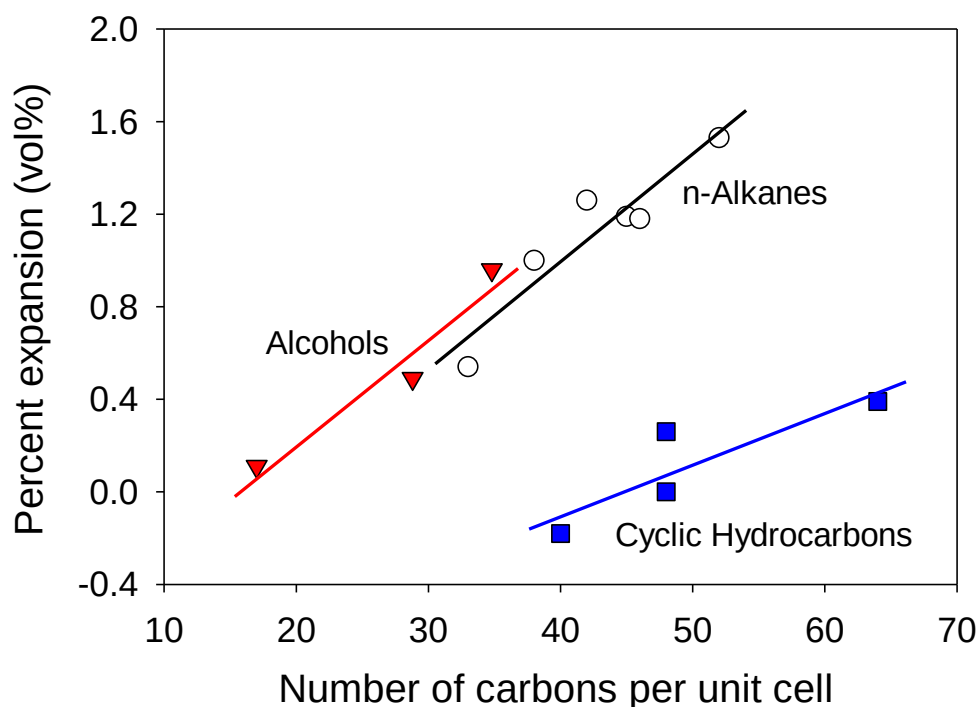


Figure 1.8. Percent expansion values for MFI zeolites at saturation loadings [4] of various adsorbates at room temperature for alcohols ($\blacktriangle$), n-alkanes ($\circ$), and cyclic hydrocarbons ($\blacksquare$). Lines have been added to guide the eye.

which would lead to greater unit cell expansion as compared to hydrocarbon adsorbates. Similar framework flexibility effects have been observed for MOFs; unit cell expansion was found to be strongly dependent on adsorbate identity and that synergistic effects could occur [95]. The cyclic hydrocarbons lead to less expansion than both the n-alkanes and alcohols (Figure 1.8) and may be the result of better molecular packing of the cyclic compounds within the MFI channels, which could lead to lower framework strain. Simulations with MFI zeolites have shown that cyclic compounds preferentially adsorb in intersections whereas linear hydrocarbons are more likely to adsorb in framework channels at saturation pressures [96, 97]. Since the dimensions of the framework intersections are larger than the channels, adsorption within these locations, as seen for cyclic hydrocarbons, may accommodate the molecules better and lead to lower adsorbate-framework repulsive interactions and hence less expansion. This shape selective packing has been found to be important not only for zeolites [98] but also MOFs [99] and aluminophosphate molecular sieves [100].

1.9 Literature Review: Temperature-Induced Flexibility

It is well-known that temperature can affect the geometric parameters of zeolite frameworks [101] and due to the wide range of industrial operating temperatures, it is important to understand the nature of such effects. Zeolites are often attached to membrane supports or binders in order to increase mechanical stability and make handling of the material easier. These support materials can have different thermal

Table 1.3. Thermal expansion coefficients for various zeolites.

Framework	Topology	Temp. range (K)	Thermal expansion coefficient (10^{-6} K^{-1})				Ref.
			α_a	α_b	α_c	β	
SiO ₂	α -quartz	298 - 838	26.5	-	15.5	69.5	[1]
FAU	NaX (hydrated)	323 - 423	48.43	-	-	145.29	[6]
LTA	NaA (hydrated)	298 - 373	-74.73	-	-	-224.19	[6]
MEL	Silicalite-2	298 - 773	-3.25	-	-6.44	-12.95	[17]
MFI	Silicalite-1 (dry)	323 - 723	-4.48	1.29	-1.72	-4.92	[6]
	H-ZSM-5	313 - 1113	-11.11	-5.82	-10.05	-9.0	[13]

expansion rates than the zeolites, so large temperature changes can lead to damage of the zeolite layer. For instance, during drying of α -Al₂O₃ supported-zeolite membranes, microcracking and delamination was observed with the most damage occurring for FAU and LTA frameworks [6]. The damage was attributed to large differences between the thermal expansion coefficients of the zeolite and support. A better understanding of the effect temperature has on the zeolite framework could lead to more robust zeolitic materials and provide insight into the general framework flexibility phenomena.

The linear thermal expansion coefficients of most zeolites have a non-linear relationship with temperature change, but it is possible to make linear approximations for α , the linear thermal expansion coefficient, and β , the volumetric thermal expansion coefficient [102]. However, care must be taken since the thermal expansion coefficients of zeolites is not necessarily constant throughout all temperatures. Not only can the value of the thermal coefficients vary at different temperatures, but it can also change signs, reflecting a change from expansion to contraction or vice versa. The linear thermal expansion coefficient is defined by:

$$\alpha = \frac{(L_2 - L_1)/L_0}{T_2 - T_1} = \frac{1}{L_0} \frac{\Delta L}{\Delta T} \quad (4)$$

and the volumetric thermal expansion coefficient is defined by:

$$\beta = \frac{(V_2 - V_1)/V_1}{T_2 - T_1} = \frac{1}{V_1} \frac{\Delta V}{\Delta T} \quad (5)$$

where L_0 is an initial length, L_1 and L_2 are lengths and V_1 and V_2 are volumes at T_1 and T_2 respectively [103]. The wide range of thermal expansion coefficients can be seen in Table 1.3, which excludes data recently published by Leardini et al. [104]. Equations 4 and 5 illustrate the relationship between temperature and length/volume, and can provide a starting point for finding compatible support materials.

For the majority of zeolites, temperature increases contract the unit cell, which is known as negative thermal expansion (NTE) [102] and this effect is seen in MWW, ITE, STT, IFR, MFI, LTA, RHO, and FER zeolites [20, 28]. Extensive tables of structural changes due to thermal treatment can be found in an article by Cruciani [101] along with data not previously summarized in Table 1.4. Contraction occurs over various temperature ranges depending on the type of framework; for example, both dry and hydrated MOR frameworks were observed to contract between 323-723 K while for hydrated NaX XRD measurements showed that the unit cell volume contracted 1.83% when heated through the same temperature range [6]. The general consensus is that temperature-induced contraction is primarily caused by flexibility of the Si-O-Si bond angle that connects zeolite tetrahedral units and not by changes in bond lengths [20, 105]. In fact, no materials have been reported to exhibit NTE because of decreased bond length [103]. XRD patterns confirmed this hypothesis to be true for Silicalite-1. The bridging Si-O-Si bond angles decrease by about 3% with increasing temperature (373-673 K) [106].

Table 1.4. Unit cell changes due to temperature for various zeolites.

Framework	Topology	Temp (K)	Unit cell (pm)			$\Delta\text{vol}\%$	Ref.
			Δa	Δb	Δc		
MFI	ZSM-5 (wet)	323 - 723	-2.6	0	-0.3	-0.15	[6]
	ZSM-5 (dry)	323 - 723	-1.6	0.5	-0.3	-0.07	
	H-ZSM-5	313 - 1113	-18.0	-9.5	-11.0	-2.23	[13]
	Silicalite-1	293 - 400	-0.82	3.4	2.1	0.29	[15]
		323 - 723	-4.1	0.7	-1.0	-0.24	[6]
LTA	NaA (wet)	298 - 723	-4.0	-	-	-0.49	[21]
		373 - 473	9.5	-	-	1.17	
MOR	(wet)	323 - 723	-5.0	-9.5	-1.0	-0.87	[6]
	(dry)	323 - 723	-3.5	-5.5	-1.0	-0.46	
RHO	Ca-RHO	298 - 723	-48.0	-	-	-9.63	[25]
	Na-RHO	100 - 600 ^a	-19.6	-	-	-3.97	[28]

^a Computational study.

Although most zeolites exhibit NTE behavior, there are certain zeolite that behave like the majority of common materials and display positive thermal expansion (PTE); one such zeolite is CIT-5 (CFI). The unusual behavior exhibited by this zeolite was hypothesized to be due to the presence of a one-dimensional channel system and a relatively high framework density [102]. Computational studies predicted that this behavior would occur for any one-dimensional channel zeolite, such as sodalite (SOD) and cancrinite (CAN), and explained the occurrence to be a result of greater structural stability and density resulting from the lack of a two or three-dimensional channel system [107]. Unlike NTE, which is caused by transverse movement of T-O-T connections, PTE has been attributed to the lengthening of interatomic bond lengths. The transverse vibrational modes need less energy than longitudinal modes to become excited and therefore, tend to control framework deformation at lower temperatures [103].

Anisotropic variations of lattice parameters caused by heating, which can be seen in Table 1.4, have been observed for most framework types [6, 13, 17]. For example, in

the case of Silicalite-1, XRD showed an initial slight expansion in the a and b unit cell parameters as the zeolite was heated (323 – 373 K) followed by contraction with increasing temperature (373 – 523 K) [20]. The c -direction shortened over the length of this whole temperature range (323 – 523 K). Interestingly, different XRD data showed that the Silicalite-1 c -parameter increased when heated from 298 K to 450 K by about 1.5 pm or 0.11% [108]. An explanation of the difference between these XRD measurements is not evident, although it may be related to the differences between the amounts of water adsorbed onto the zeolite samples. One experiment [20] was conducted in a reactor chamber and degassed with synthetic air while the other [108] was heated in air. Also, when Silicalite-1 is heated to higher temperatures (473 to 673 K) the unit cell dimensions decrease anisotropically, with the a -dimension contracting five times more than the b -direction and 2.6 times more than the c -direction [106]. This variation was hypothesized to result from the stacking of 2-dimensional zeolite layers along the a -direction of the zeolite unit cell. The layering led to higher densities in the b and c -directions making those directions more resistant to contraction compared to the a -direction. This emphasizes that flexibility deformations can significantly be affected by the manner in which the zeolite sample is synthesized. Simulations also showed that different regions of a framework may swell while simultaneous contraction can occur in other areas [109].

Commonly, during heating through a large temperature range, zeolites experience a rearrangement of their geometry symmetry (cubic, hexagonal, monoclinic, etc.) that coincides with volume contraction or expansion and changes in framework density [84,

110]. Zeolites with densities within the flexibility window, the range of possible structure densities, are with little distortion or steric strain while those with densities outside this range are expected to have distorted tetrahedral units and be geometrically stressed [111]. For this reason, many frameworks cannot cross the limits of the flexibility window range without undergoing a structural rearrangement [85, 111, 112]. When ZSM-5 was heated from 303 K to 333 K in NMR, the framework gradually expanded, but increasing the temperature further to 356 K caused an abrupt structural change where the zeolite converted from monoclinic symmetry to orthorhombic symmetry [113]; a transition occurred with volume contraction [13, 15]. Such symmetry phase transitions can, in many instances, lead to the thermal expansion coefficient of the material changing from a positive value to a negative (or vice-versa) since the organization of certain symmetries prevent rotation of the rigid tetrahedral units [103].

It is also possible for frameworks to undergo thermal collapse when heated too fast or too hot. For instance, Silicalite-1 goes through a symmetry transition at 373 K from monoclinic to orthorhombic symmetry, but as the temperature is elevated to 1123 K the Silicalite-1 structure undergoes thermal collapse and exhibits a single α -cristobalite phase [108]. Similarly, heating H-ZSM-5 to 1113 K and subsequent cooling to room temperature has not resulted in a reversion to original geometric parameters [13]. The final structure had decreased a , b and c crystallogical parameters and a smaller overall unit cell volume suggesting that a certain degree of irreversible thermal collapse likely had occurred. Other frameworks are also affected by thermal collapse. Between 623 - 673 K (depending on

the heating rate) H-zeolite-A (LTA) experienced thermal collapse identified by a concave down relationship between the temperature and percent change in zeolite length [114].

1.10 Implementation of Flexibility Effects

The nature of the flexibility of zeolite frameworks is far from well understood. The effects of both temperature and adsorbate-induced flexibility combined with the large variety of framework types and topologies ensures that more research is needed in order to have a better understanding of this phenomenon. With increasing usage of zeolite materials in a growing number of industries, the interest for such knowledge will undoubtedly be present. Research on framework flexibility is of particular interest for future zeolite membrane processes since expansion and contraction can have significant implications on selectivities. In the previous sections it was shown that large groups of adsorbates and wide ranges of temperatures and frameworks have been studied, but comprehensive insight on the effects induced by the compounds and temperatures within these zeolites have yet to be realized. Detailed relationships between framework deformations and adsorbate loading at various industry-pertinent temperatures could provide a critical understanding in order to commercialize zeolite membranes that “self-repair” defects using temperature and/or adsorbate-induced expansion. As a better understanding of zeolite flexibility is gained new opportunities will arise to take advantage of this phenomenon and use it to make current chemical process more effective and efficient, and, even more excitingly, to solve problems that have failed to be

answered through conventional methods. In order to contribute to the knowledge pool of zeolite framework flexibility and more specifically to evaluate the combined flexibility effects caused by mixed adsorbate feeds, the rest of the text describes the construction and calibration of a flow system that has the capacity of running such experiments.

EXPERIMENTAL

2.1 Overview

The majority of experiments were performed on a flow system with the primary goal of exploring the flex properties of different zeolite materials when subject to mixed and unmixed adsorbate fluxes. Adsorption capacities were measured by breakthrough experiments and compared to the literature. Data collection for flow experiments was acquired with a mass spectrometer (MS). Characterization of the ZSM-5 zeolite was carried out via powder x-ray diffraction (XRD), field emission scanning electron microscopy (FEM), and energy-dispersive x-ray spectrometry (EDS).

2.2 Zeolite Characterization

2.2.1 Powder X-ray Diffraction

To determine whether the starting ZSM-5 material was pure and if the material remained unchanged after breakthrough experiments, ZSM-5 samples were analyzed with X-ray powder diffraction at the Imaging and Chemical Analysis Laboratory (ICAL) at Montana State University. The XRD analyses were performed on a Scintag X1 Advanced diffraction system equipped with a monochromatic Cu K_{α} radiation source with $\lambda = 0.154056$ nm. The instrument was operated at a working voltage of 45 kV and a 40 mA current. A small amount of the sample (30 mg) was mounted on a glass microscope slide by means of a thin layer of Vaseline. The slide was clamped into the XRD instrument and

the diffraction pattern acquired over a Bragg angle (2θ) range of 5 to 80° using the Scintag DMSNT (version 1.37) software. The measurements were conducted over 30 min in which the scan mode was continuous, the step size was 0.02° , the time per step was 0.5 s, and the scan speed was $0.04^\circ/\text{min}$. The XRD patterns for the ZSM-5 samples were compared with reference patterns for H-ZSM-5 (#87-2275) acquired from the Powder Diffraction File published by the International Centre for Diffraction Data (ICDD) using the Scintag Powder Diffraction Database Search (version 1.06) software.

2.2.2 Scanning Electron Microscopy

Structural and physical changes in the ZSM-5 samples was established via field emission scanning electron microscopy. A Zeiss Supra 55VP FEM equipped with Si(Li) detector material, located at ICAL-MSU, captured the images that were analyzed with Zeiss SmartSEM software. Bulk compositional variations between ZSM-5 samples were determined using the attached energy-dispersive x-ray detector (Princeton Gamma-Tech), which was analyzed with PGT Spirit software.

2.3 Flow System

The basic setup of the flow system consists of four main sections: gas control area, liquid injection area, experiment area, and analysis area. A schematic of the flow system is shown in Figure 2.1 and photographs of the front and back of the flow system are presented in Figure 2.2 and Figure 2.3a respectively. The system consists of stainless steel tubing, valves, and other Swagelok components, all of which are attached to a 4'x26''

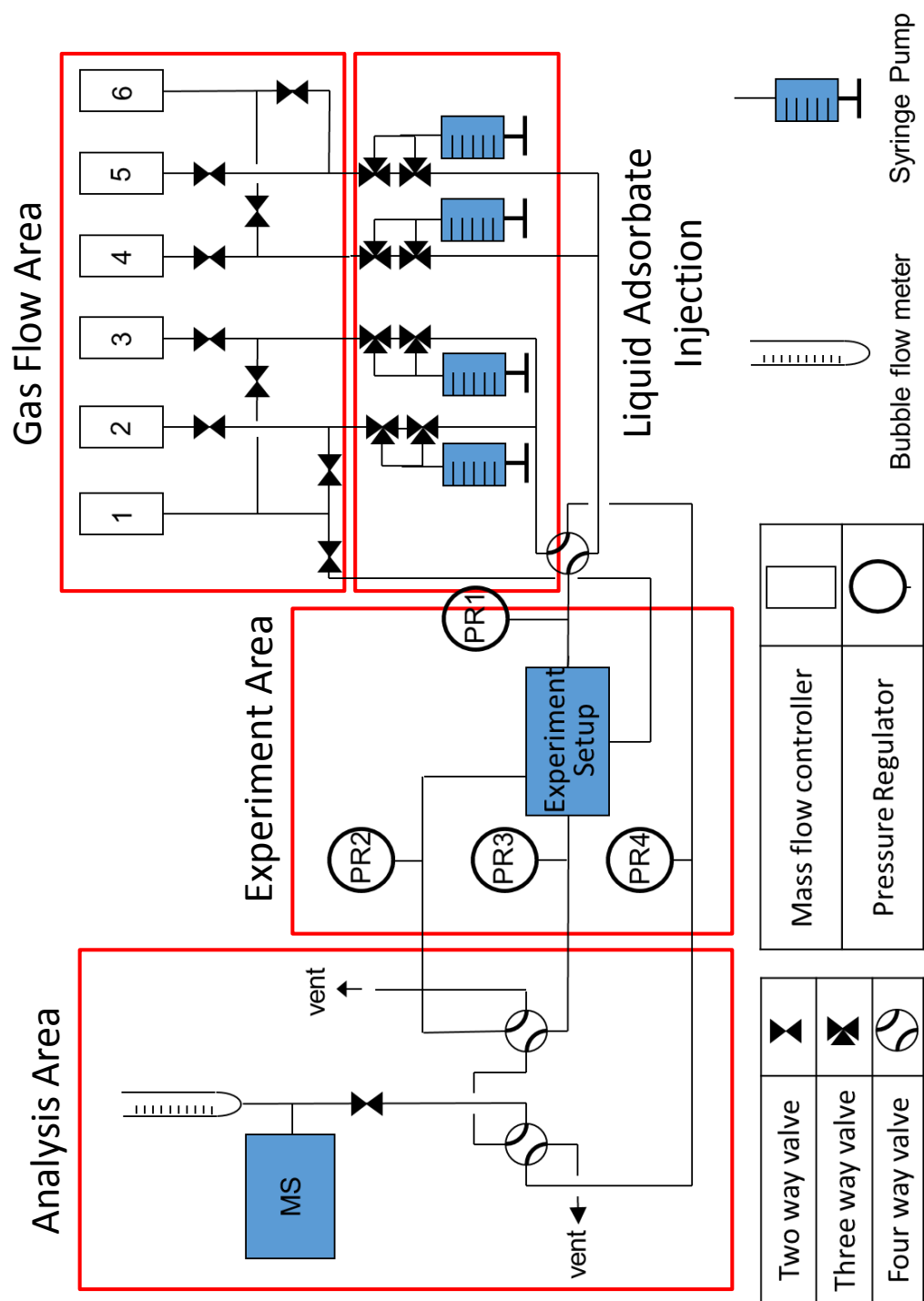


Figure 2.1. A schematic of the flow system with a general experiment setup. The four main sections of the system (gas flow area, liquid adsorbate injection area, experiment area, and analysis area) are highlighted.

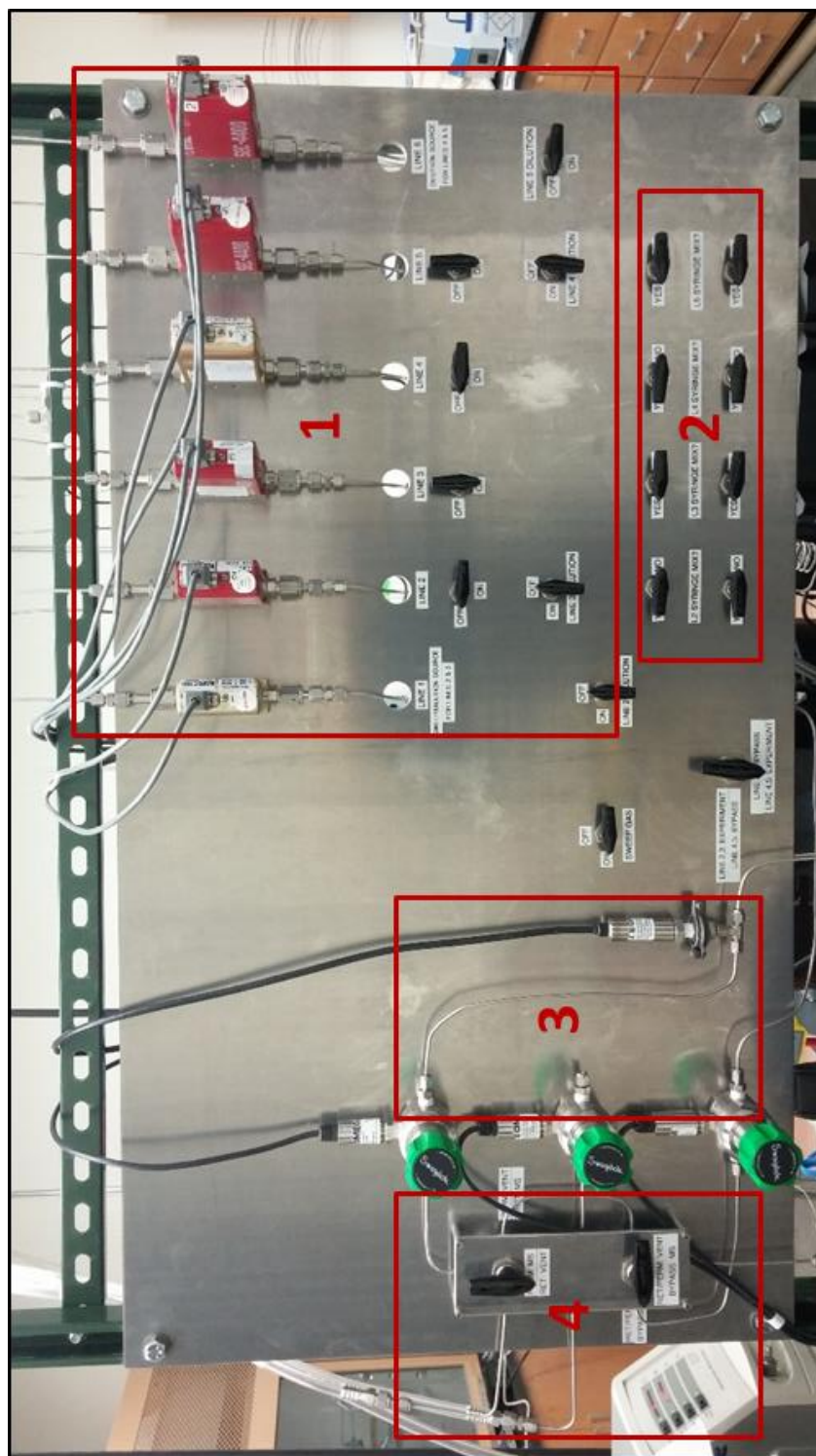


Figure 2.2. A front-side photograph of the flow system where the numbers represent different areas: (1) gas flow area, (2) liquid adsorbate injection area, (3) experiment area, and (4) analysis area.

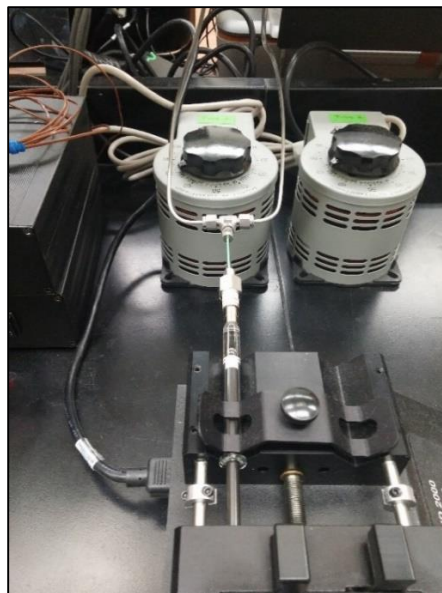
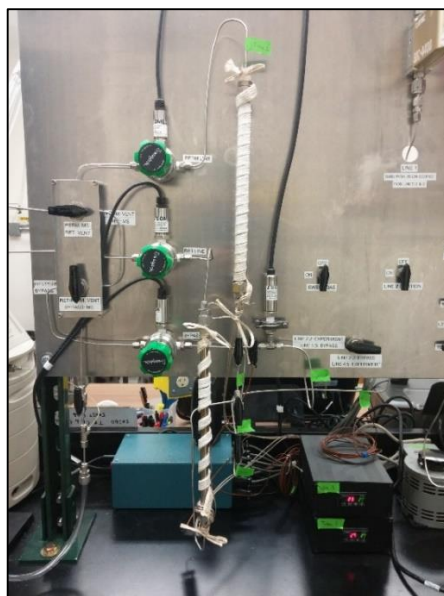
(a)**(b)****(c)**

Figure 2.3. Photographs of (a) the back-side of the flow system showing two-way valves that control which gases can flow into the system, (b) the general syringe pump connection, (c) the dual breakthrough experiment setup.

stainless steel plate. The plate was securely attached to McMaster-Carr struts that, in turn, were attached to a heavy table.

The gas entry area allows for flow of up to six different types of gases that enter through the top of the system by way of one of six custom LabVIEW program controlled mass flow controllers (MFC). The user has the ability to mix/dilute these gasses by adjusting a series of two-way and three-way valves. The liquid injection area, located directly below the MFCs and gas-control valves, allows for liquid compounds to be pumped into the flow system through one of four inlets and injected with syringes (2.5 mL Hamilton 81420 luer lock) which were controlled by syringe pumps (Harvard Apparatus PHD 2000 Infusion; Figure 2.3b).

The third section of the flow system is the experiment setup and is located to the left of the gas control area. While various experimental set-ups are possible in this section of the flow system, for the research presented only a breakthrough experiment setup was used (Figure 2.3c). The breakthrough experiment (adsorption isotherm) setup consisted of two flow pathways: 1) a bypass line that permitted the adsorbates to circumvent the experiment setup (i.e. the zeolite) and enabled a MS calibration signal to be measured and 2) an experimental zone containing two distinctive pathways through two zeolite packed stainless steel tubes (Figure 2.4). The stainless steel tubes (McMaster-Carr; $\frac{1}{2}$ " or $\frac{1}{4}$ " O.D.) were packed with zeolite held in place by quartz wool plugs on either side. The first plug of quartz wool would be packed into the tube and served as the support for the zeolite and the second quartz wool plug was lightly placed above the zeolite in order to

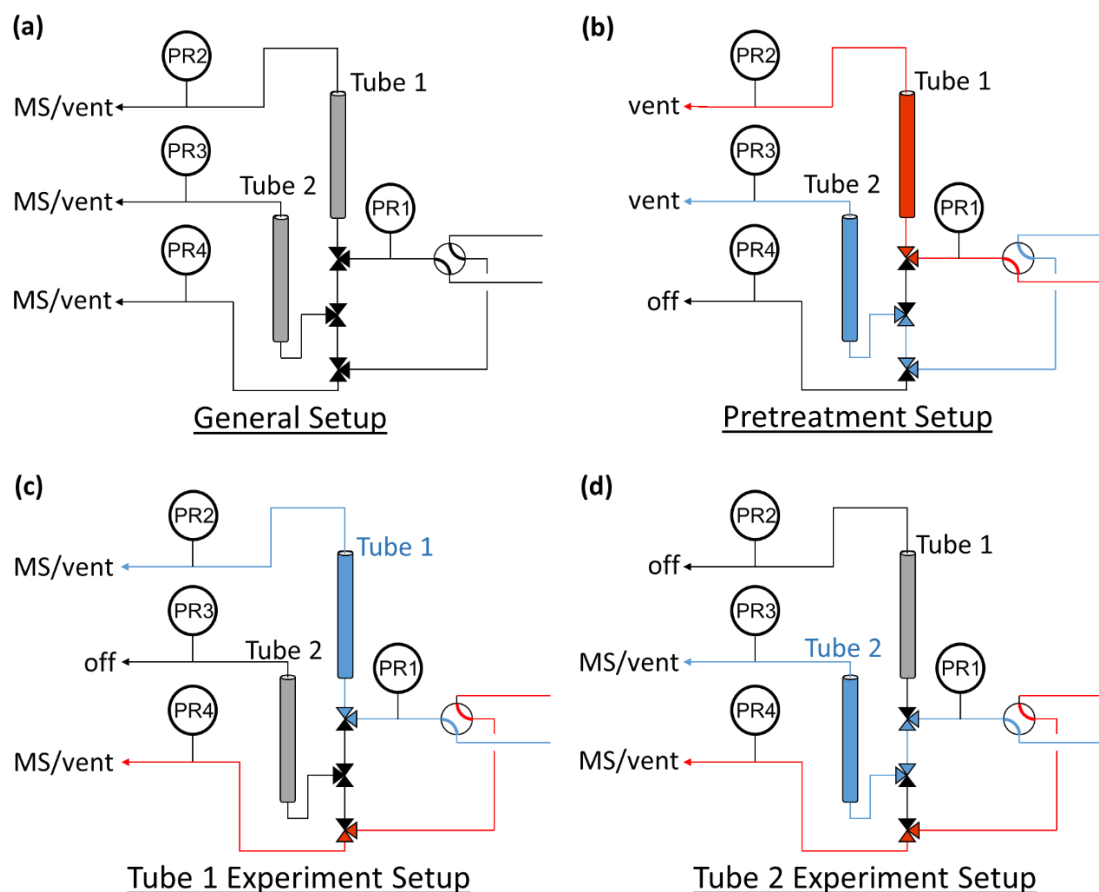


Figure 2.4. Schematics of the adsorption isotherm (breakthrough) experiment setup for a variety of flow modes: (a) general setup, (b) pretreatment flow, (c) tube 1 experiment flow and (d) tube 2 experiment flow. The red and blue lines show concurrent flow paths where, for (c) and (d), the bypass line is shown in red and the experiment line is in blue.

prevent zeolite from moving upstream. Two tubes were used in order to increase the experimental capacity. A back pressure regulator (Omega/PX409-205A5V) maintained the pressure, when required, and a pressure sensor (Omega/PX309-300A5V) relayed the system pressure to the LabView program. By manipulating valves, the gas flow could either go to the MS or be diverted to the hood.

The fourth and final section of the flow system is the analysis area where the composition of the bypass line or the non-adsorbed gases is analyzed with a mass spectrometer (Stanford Research Systems QMS Series gas analyzer). The fraction of the flow that is not routed to the MS passes through a bubble flow meter for flow rate measurement and then is vented to a fume hood. Excess gas and gas exiting from unanalyzed lines are also vented to a fume hood.

2.3.1 Breakthrough Experiments.

The breakthrough experiment setup was designed with the ability to run the system in three different modes: pretreatment (Figure 2.4b), tube 1 experiment (Figure 2.4c), and tube 2 experiment (Figure 2.4d) mode. For all of these operation modes the zeolite was packed inside the stainless steel tubes as previously described.

Powder Preparation. During breakthrough experiments with SAPO-34 (ACS Material), the zeolite was packed into the tubes as a powder as received. For experiments with ZSM-5 (Acros Organics), the tubes were packed in a variety of ways, one of which was as received. In other experiments, the powder was equally divided by weight, and layered with quartz wool in 2 layers. Additionally, adsorption isotherms were measured for a packing of ZSM-5 powder and silicon dioxide crystal shards (Aldrich) which was mixed, in the weight ratio stated for the experiment, outside of the tube prior to packing.

Pressed Powder Preparation. Experiments with pressed ZSM-5 powder were also conducted for which the ZSM-5 powder was compressed at a pressure of 12,000 psi with a manual hand powder press equipped with a $\frac{3}{4}$ " stainless steel die (located in EPS 248). The resulting zeolite disks were broken into smaller pieces with a spatula and sieved with a No. 7 mesh (2.83 mm). Depending on the experiment, 0.5 or 1 g of the resulting pieces were packed into the breakthrough tubes.

Pretreatment. The first step of carrying out the breakthrough experiments necessitated a pretreatment step in order to remove contaminants (Figure 2.4b). During this step the two breakthrough tubes with the packed zeolite were fully desorbed of any remnant adsorbates by flowing nitrogen gas through the tubes and heating them using a programmed temperature ramp up to a temperature of 300 °C in 2 h, holding at this temperature for 10 h, and then cooling to the experiment temperature (typically 27 °C). Each tube was wrapped with heating tape from bottom to top and then wrapped with insulation and aluminum foil. The heating tape was used to heat the tubes and were controlled by two pairs of Staco Energy Products Variac variable transformers and Omega CN7500 temperature controllers.

Experiment. The general experiment process involved flowing the adsorbate of interest through the flow system bypass line, waiting for the corresponding MS signal to reach an equilibrium, and then exposing the zeolite to the adsorbate until the adsorption isotherm equilibrium was established. Experiments were begun by first flowing pure

nitrogen gas through both the bypass and experiment lines and measuring the flow rates with a bubble flow meter (BFM) and a stop watch; the flow rates were adjusted with a LabVIEW program if necessary. After a steady N₂ flow was established, the experiment adsorbate was mixed with the N₂ either by directly combining the N₂ with the (gaseous) adsorbate or by pumping the (liquid) adsorbate into the N₂ flow path. In the case of gaseous compounds (isobutane: 99.95%, Matheson), a gas cylinder containing the adsorbate was connected to the system upstream of the MFCs (Figure 2.3a), diluted with nitrogen gas, and then directed to the bypass line using a series of valves. For liquid adsorbates (n-hexane: 99+%, Acros Organics; methanol: 99.9%, Fisher Scientific), a 2.5 mL syringe was filled with the particular compound, attached to the flow system via a Luer Lock connection, and then placed on a syringe pump (Figure 2.3a). During breakthrough experiments, 0.2 mL of the adsorbate was quickly (5 min) pumped into the system in order to shorten the time needed to reach steady state, and after, the adsorbate flow rate, syringe size, and maximum injection volume were set for the syringe pump.

At this point, in the case of both gaseous and liquid adsorbates, the combined flow rate of the adsorbate and nitrogen was calculated with the BFM. The flow rate (w) was determined with the following equation:

$$w = \frac{60V_b C_f}{t_{avg}} = \frac{60V_b P_{atm} T_{std}}{t_{avg} P_{std} T} \quad (6)$$

where V_b is the BFM measurement volume (mL), t_{avg} is the average time it took the soap bubble to travel up to the V_b mark, and C_f is a unitless correction factor that adjusts the flow rate (mL/min) to standard temperature and pressure. Once a stable bypass

equilibrium signal was detected on the MS, the adsorbate flow was rerouted (with a four-way valve) through the experiment tube, the flow rate measured again, and after a certain amount of time (0.5 – 25 h), dependent on the adsorbate partial pressure, a stable adsorption isotherm signal was reached. The adsorbate flow was then routed back to the bypass line while pure nitrogen was sent through the experiment tube. After the MS signal for the adsorbate (coming from the experiment tube) had reached zero, the MS was turned off and the flow rates through both the bypass and experiment lines were verified for consistency.

Analysis. The mass spectrometer data was visualized with RGA Windows (v. 3.213) software and used to determine the adsorption capacity of the packed zeolite. The zeolite adsorption capacities for particular adsorbate partial pressures were calculated by the two following ways: (1) by evaluating a difference of signal areas and (2) an equation using the time (t_{50}) it took to reach the half-way point of the adsorption isotherm (Figure 2.5). The first way that adsorption capacities were evaluated was by calculating the difference in the areas of the calibration and adsorption signal both multiplied over the experiment time span. The calibration signal was measured from adsorbate flow through the bypass line and the adsorption signal was measured from adsorbate flow through the experiment tube. The area difference (ΔA) was used to calculate the adsorbed volume (V_a) of the experiment gas:

$$V_a = \frac{\Delta A * \text{volume of adsorbate flowed}}{\text{signal area without adsorption}} \quad (7)$$

which was then used to determine the adsorption capacity (q):

$$q = \frac{1000V_a\rho_a}{MG} \quad (8)$$

where ρ_a is the density of the adsorbate (g/mL), M is the adsorbate molecular weight (g/mol), and G represents the weight of the adsorbent (g) in the breakthrough tube. This adsorption capacity could then be compared to those previous published in the literature.

The second method was calculated with the following equation:

$$a_g = \frac{t_{50}wMC_i}{24.1G} \quad (9)$$

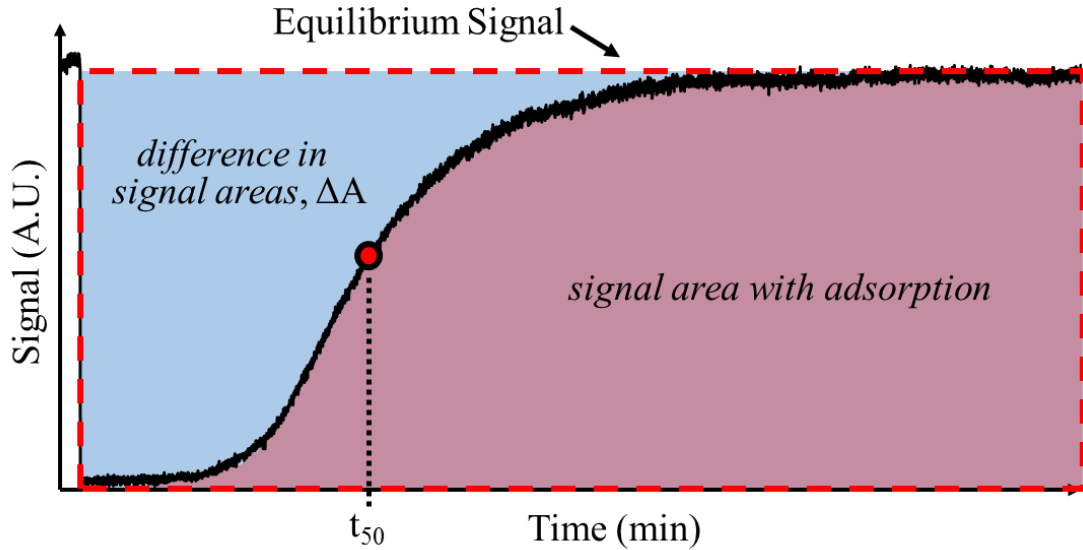


Figure 2.5. Example of an adsorption isotherm curve obtained during a general breakthrough experiment. The red dot represents the t_{50} point which is used to calculate the adsorption capacity. The top of the red, dashed square marks the equilibrium signal acquired when the experiment gas is flowed through the bypass line and the coinciding red, dashed square represents the signal area without adsorption. The red shape represents the signal area with adsorption while the blue shape represents the difference in signal areas, ΔA , which is also used in a calculation method for adsorption capacities.

where a_g is the grams of adsorbate per gram of adsorbent, w is the flow rate (L/min) of the adsorbate, and C_i is the volumetric fraction of the adsorbate [115]. The determined a_g value was converted to moles of adsorbate per kg of zeolite in order to make literature comparisons easier.

RESULTS & DISCUSSION

Framework flexibility leads to unit cell changes that can significantly impact zeolite membrane separations and may even influence what compounds have access to the interior structure, which was seen with other microporous materials [116]. For this reason, developing a method to modify unit cell size could potentially prove to be useful for controlling separations, catalysis, and gas storage properties. Before exploring such interactions experimentally, the flow system needed to be calibrated by replicating adsorption isotherms found in the literature.

3.1 Isobutane/ZSM-5 Breakthrough Experiments

Isobutane/ZSM-5 adsorption isotherm experiments conducted with 0.25 g of powder and an isobutane partial pressure of approximately 2200 Pa showed that the measured adsorption capacities were on average $30 \pm 8\%$ lower than literature values at 27 °C [3]. XRD, SEM, and EDS confirmed the ZSM-5 structure and that it was not contaminated or undergoing structural changes during experiments. Using XRD, the ZSM-5 sample spectra were compared to an H-ZSM-5 reference pattern (#97-003-429), no significant variation in crystal structure was observed (Figure 3.1). The post-experiment ZSM-5 sample peaks were slightly narrower, which indicated that a small amount of ZSM-5 particles aggregated. The increased particle size was confirmed by comparing SEM images of the pre-experiment ZSM-5 with the post-experiment sample (Figure 3.2). Before adsorption isotherm experiments, the zeolite powder appeared as a finely

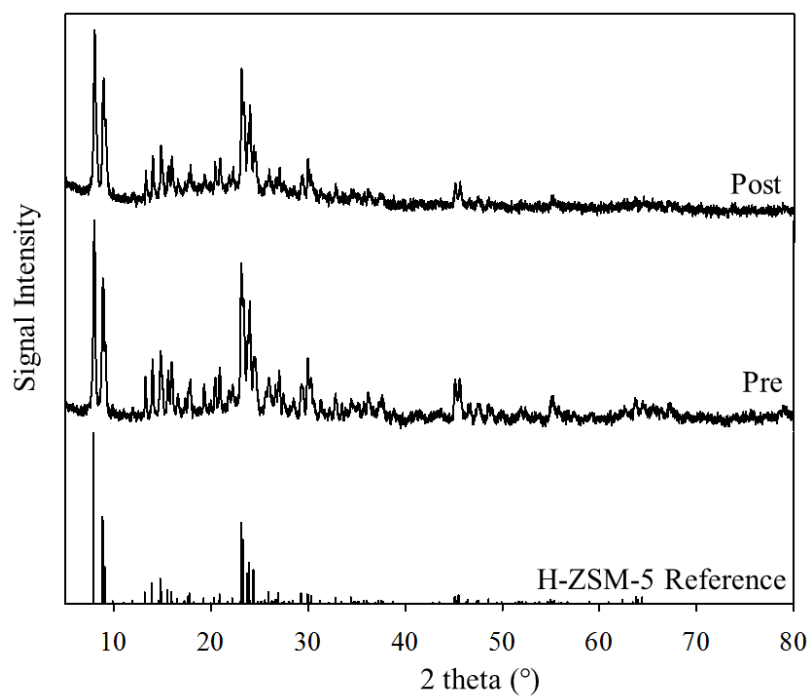


Figure 3.1. Comparison of XRD patterns for an H-ZSM-5 reference, pre-experiment ZSM-5 sample, and post-experiment ZSM-5 sample.

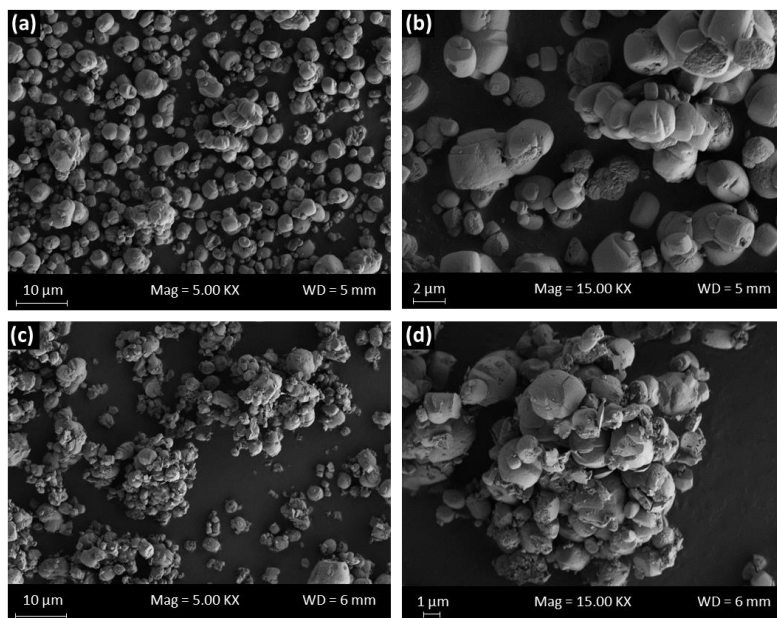


Figure 3.2. SEM images of (a-b) pre-experiment and (c-d) post-experiment ZSM-5 powder at 5 KX and 15 KX magnification.

Table 3.1. Elemental composition as determined by EDS for pre-experiment and post-experiment ZSM-5 powder.

ZSM-5 Sample	Element Weight Percent		
	O	Si	Al
Pre-Experiment	57	39	4
Post-Experiment	59	37	4
Percent Change	3.5	-5.1	0

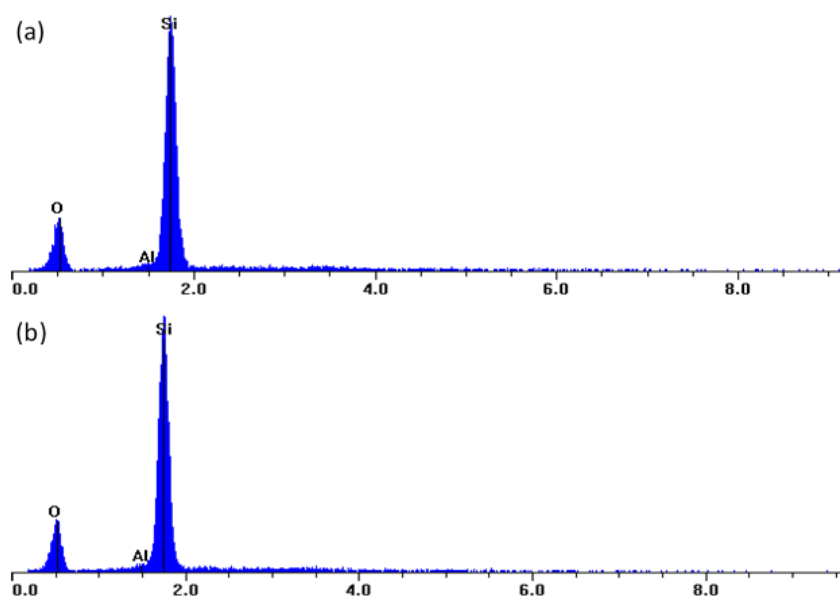


Figure 3.3. (a) EDS spectra of clean ZSM-5 powder and (b) post-experiment ZSM-5.

experiment, a significant amount of the powder aggregated into 10 μm particles (Figure 3.2d). Aggregation of crystals may lead to mass transfer limitations, which would have led to lower adsorption amounts, and therefore, may explain the lower values seen experimentally. On the other hand, since the post-experiment XRD patterns did not show any peak broadening, the aggregation seen with SEM is likely due to loose clumping and is not leading to mass transfer issues. Compositional analysis of the samples using EDS showed no major change in Si, Al, or O content before and after experiments (Table 3.1)

Table 3.2. Isobutane adsorption isotherm experiments with tubes packed with 0.25 g of ZSM-5 powder run at 27 °C. Expected loading at 2200 Pa is 1.05 mmol/g [3].

Partial Pressure (Pa)	Loading (mmol/g)	Literature Percent Difference	Pressure Drop (Psi)
2160	0.80	-24	13
2190	0.61	-42	9
2160	0.84	-20	14
2270	0.71	-33	9

and no other elements were detected (Figure 3.3). In combination, the XRD, SEM, and EDS characterization of the ZSM-5 samples showed that the zeolite was compositionally and structurally as expected, but that small clumps of powder were present post-experiment. These small clumps may have been caused by the pressure drop (~11 psi; Table 3.2) that occurred during the breakthrough experiments.

One potential cause of inaccurate adsorption amounts is isobutane pooling. To check this, the syringe pump delivering isobutane was stopped and then only nitrogen

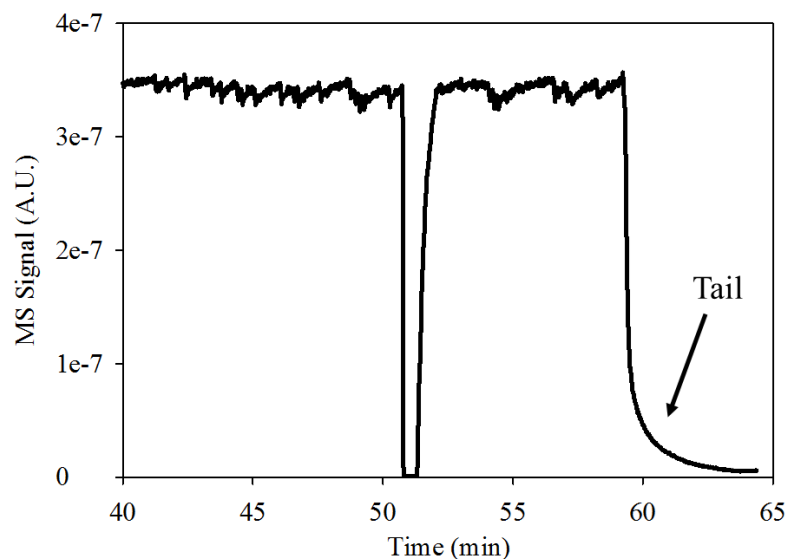


Figure 3.4. A plot of an adsorption isotherm experiment for ZSM-5/isobutane depicting a clear tail after isobutane flow stoppage.

flowed through the experimental tube. As seen in Figure 3.4, the isobutane signal dropped quickly when the isobutane flow was stopped ($t = 60$ min) and the tail that formed was likely due to desorption. Since the zeolite sample was determined to not be the cause of the literature deviations, it was decided that next possible source of error to be examined was the compound itself. To decide whether the literature deviations were specific to isobutane the adsorbate was changed to n-hexane.

3.2 n-Hexane/ZSM-5 Breakthrough Experiments

3.2.1 ZSM-5 Powder

Adsorption isotherm experiments with n-hexane and ZSM-5 powder (0.5 g) were carried out at 27 °C and at a variety of partial pressures between 370 and 9500 Pa. The average percent differences between the experiment and literature [9] adsorption

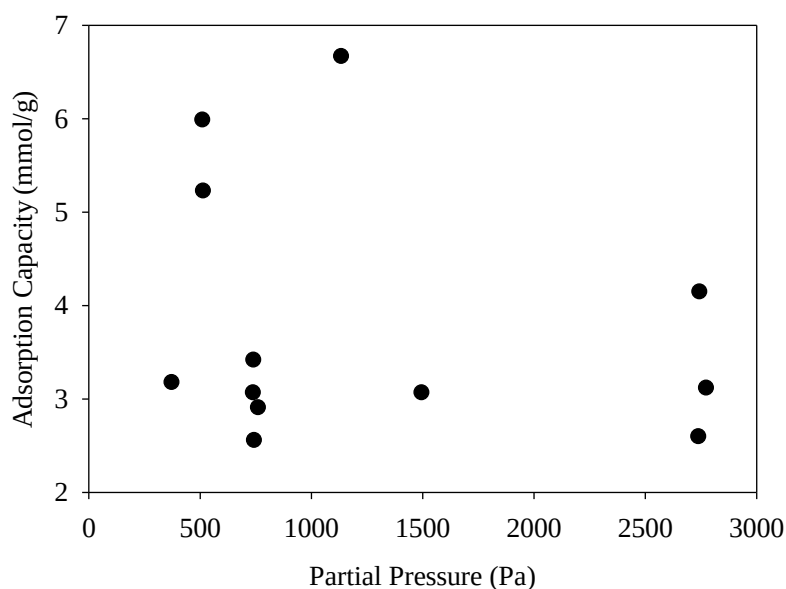


Figure 3.5. A comparison of partial pressures versus experimental adsorption capacities for adsorption isotherm experiments with ZSM-5 powder and n-hexane.

Table 3.3. n-Hexane adsorption isotherm experiment data for tubes packed with ZSM-5 powder (0.5 g) and run at 27 °C.

Partial Pressure (Pa)	Equilibrium Time (min)	Signal (A.U.)
10000	15	8.80 E-07
2700	25	2.56 E-07
1500	33	1.25 E-07
740	72	6.56 E-08
370	140	2.95 E-08

capacities was $158 \pm 78\%$ and was likely caused by the high average pressure drop (11.7 psi) across the breakthrough tubes. The wide variability in the adsorption capacities can be seen in Figure 3.5. The syringe pumps were cleaned, exchanged, and the dispensed volumes validated to ensure proper function. Elimination of other potential sources of adsorption occurred next and it was determined that the stainless steel experiment tubes and ~2 g of quartz wool packing material normally used in an experiment did not indicate n-hexane adsorption.

The chances of pooling are higher for n-hexane than isobutane due to vapor pressure differences and therefore changes in partial pressure were evaluated in order to ensure the system was not at saturation (Table 3.3). As the n-hexane partial pressure was raised, the corresponding MS signal increased and this linear behavior would not have occurred if n-hexane pools were present within the flow system tubing (Figure 3.6). Additionally, heating of the system tubing with a heat tape set to 150 °C, and a separate experiment that used a heat gun to heat the lines, did not increase the hexane signal, which would have occurred if pools of hexane vaporized. The results of these two final experiments determined that pooling was not the cause of the adsorption capacity

percent difference that had been seen for the ZSM-5 powder adsorption isotherm experiments. Instead, it is possible that the high pressure drop, due to the powder

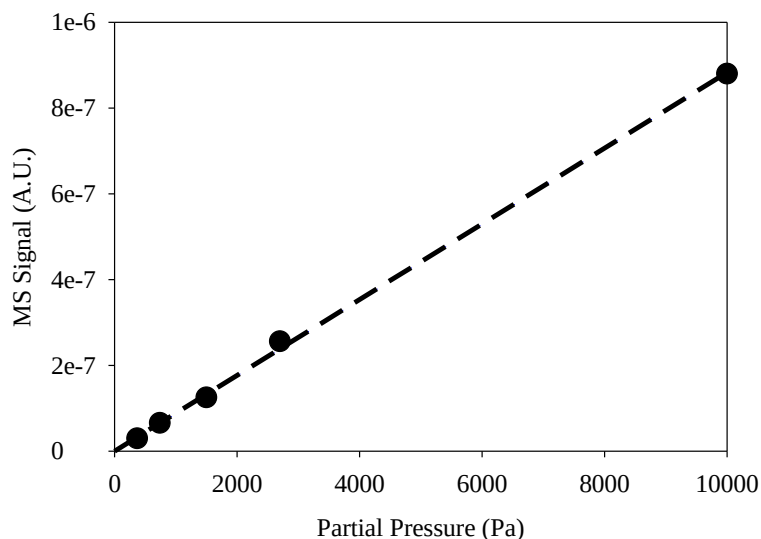


Figure 3.6. Partial pressure versus n-hexane MS signal data for tubes packed with ZSM-5 powder and run at 27 °C.

packing, resulted in a non-uniform pressure change across the zeolite bed.

3.2.2 ZSM-5 Layered Powder

In order to reduce the pressure drop across the powder, a layered packing scheme was chosen in which two equal weights (0.5 g) of ZSM-5 powder were layered between quartz wool plugs. After conducting a number of adsorption isotherm experiments (27 °C; 139 – 1160 Pa) the layered powder packing was found to result in an average adsorption capacity percent difference of $80 \pm 106\%$ (Figure 3.7) and an average pressure drop of 4.5 psi. Compared to the non-layered experiments, the pressure drop decreased 7.2 psi and the percent difference decreased 78%, but due to the variability in the data, there was no significant difference. These results indicated that the lower pressure drop improved the

accuracy of the adsorption measurement and that reducing the pressure drop further may improve the accuracy, and potentially the variability.

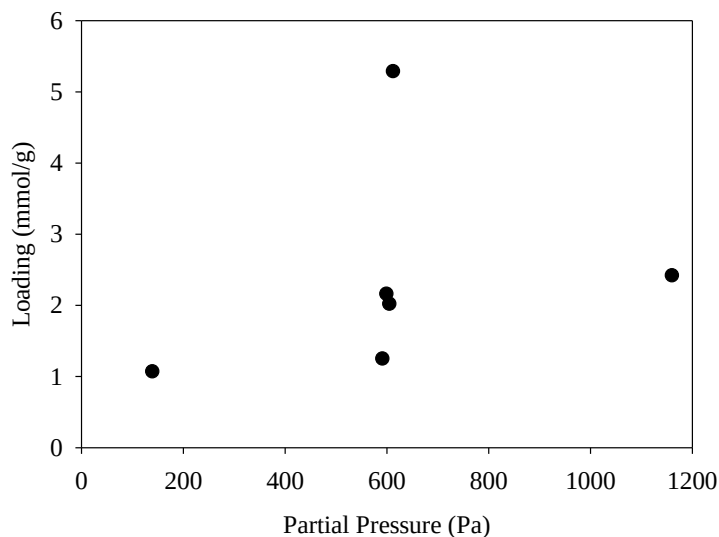


Figure 3.7. A comparison of partial pressures versus experimental loadings for adsorption isotherm experiments with layered ZSM-5 powder and n-hexane.

3.2.3 ZSM-5 Powder/Silica Shards Mixture

In order to prevent the powder from packing, which leads to a pressure drop, a 1:2 ratio of ZSM-5 powder (0.25 g):silica shard was used at 27 °C and 250 Pa n-hexane. There was no measurable pressure drop and the average adsorption percent difference was $-4 \pm 45\%$, which highlights the significance of eliminating pressure drop. Both the accuracy and variability improved significantly, although the standard deviation was still large. Only a small amount of powder, 0.25 g, was used in order to eliminate the pressure drop, but by increasing the amount of zeolite the variability would improve as long as the pressure drop remained close to zero. Therefore, a 1:2 powder (1 g):shard ratio was used

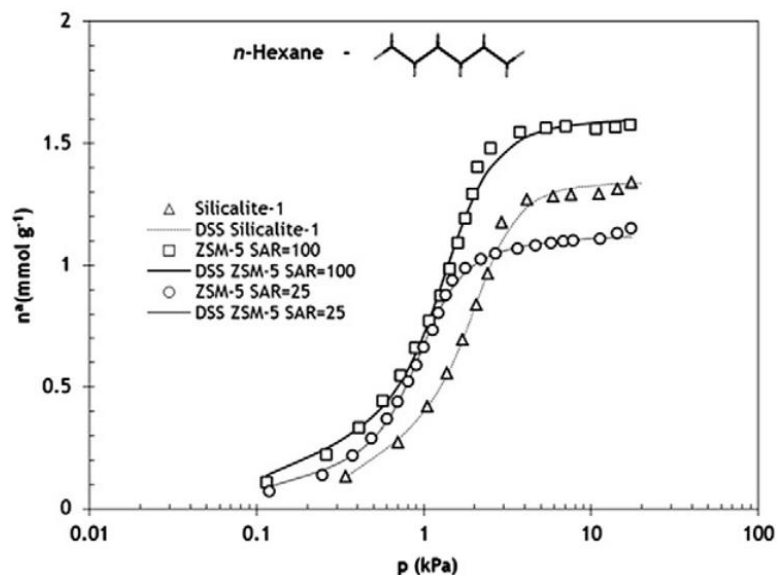


Figure 3.8. An adsorption isotherm of n-hexane on MFI at 20 °C where the Si/Al ratio are: (○) 25, (□) 100, and (Δ) ∞. The curves show the isotherm model fits by the dual-site sips model. This image was acquired from [10].

(27 °C; 250, 500 Pa) and the adsorption percent difference variation improved by a factor of two ($10 \pm 21\%$) while the pressure drop only slightly increased to 1.0 psi.

Adsorption isotherms follow power-law curves and therefore, exhibit little change at high partial pressures (Figure 3.8). Due to this relationship, in order to measure low n-hexane/ZSM-5 adsorption amounts, experiments at low n-hexane partial pressures were run. The previous tube packing and conditions (1:2 powder (1 g):shards; ZSM-5; 27 °C) were used to run breakthrough experiments at an n-hexane partial pressure of 50 Pa, which was the lower limit of the flow system. Although the precision was similar, the accuracy of the adsorption amounts decreased, resulting in a percent difference of $84 \pm 25\%$.

By increasing the experimental temperature, the partial pressure required to hit the same 50 Pa adsorption amount increases due to the flattening of the adsorption isotherm curve. For example, at 20 °C and at a partial pressure of 2000 Pa, the MFI framework adsorbs 63% of the n-hexane saturation capacity but, when heated to 150 °C (still at 2000 Pa), only 26% of the capacity is adsorbed [10, 11]. Therefore, by increasing the temperature, a greater region of the adsorption isotherm can be measured since reaching low partial pressures is no longer necessary. As hypothesized, when experiments at 150 °C were conducted with the flow system, lower standard deviations (15 – 53%) were realized, but the adsorption percent difference increased significantly to 350%.

Comparing adsorption amounts of 1:1, 1:2 powder:shards, and literature values, shows that the experiment adsorption error bars are low and that the adsorption capacities for the tube packed with a greater amount of silica shards (2 g) resulted in greater error from the literature values (Figure 3.9). This suggests that the shards may have adsorbed n-hexane and thereby increased the adsorption amount. Consequently, experiment tubes were packed with 2 g of silica shards and quartz wool plugs (500 Pa n-hexane at 27 °C) and were determined to have significantly adsorbed n-hexane (0.13 mmol/g shard; Figure 3.10). The adsorption amounts for experiments using silica shards were therefore, erroneously high. Although the adsorption on shards could be corrected for single adsorbate experiments, the long-term goal would be to run mixture experiments for which correction for the shards would be time consuming and difficult.

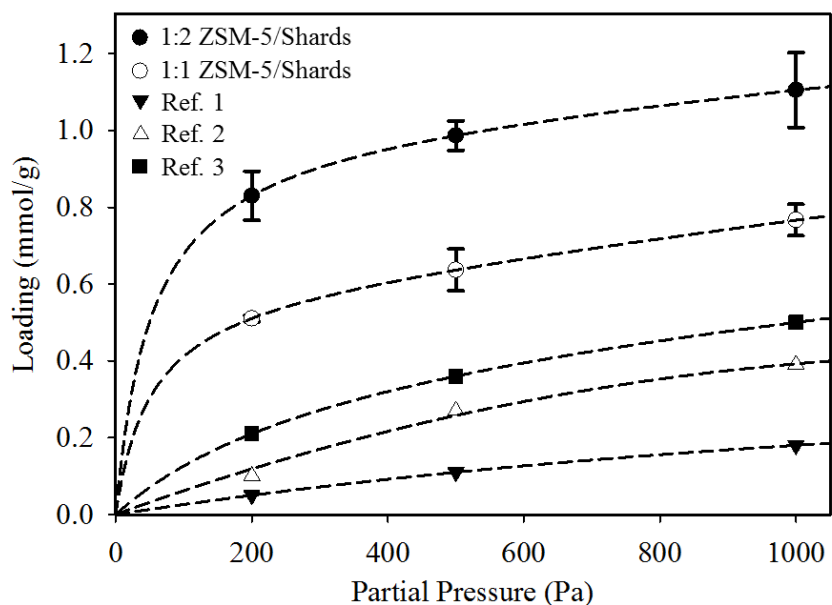


Figure 3.9. Partial pressure versus n-hexane loading for tubes packed with ZSM-5/SiO₂ shards and ran at 150 °C. Experimental data is compared to three different literature adsorption isotherms acquired from the following references: Ref. 1 = [7], Ref. 2 = [11], and Ref. 3 = [14].

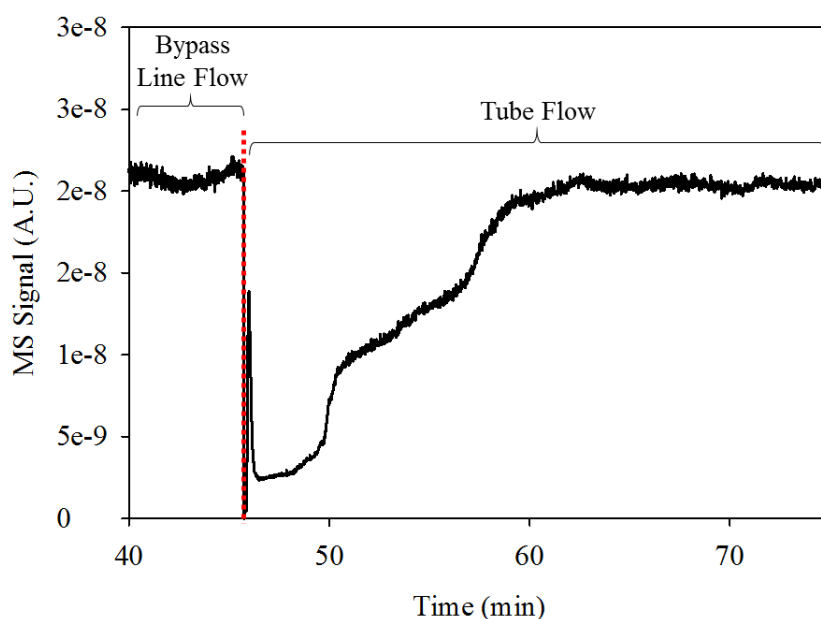


Figure 3.10 A plot showing adsorption of n-hexane onto silica shards at 500 Pa and 27 °C. The n-hexane flow was rerouted from the bypass line to the tube at the time marked by the dotted red line.

3.2.4 Pressed ZSM-5

In order to eliminate the use of packing materials, but also keep the pressure drop to a minimum, the ZSM-5 powder was pressed into disks, broken, sieved, and packed into the experiment tubes. Preliminary breakthrough experiment data (27 °C; 530 Pa) for the pressed ZSM-5 had no pressure drop, excellent precision, and improved accuracy for the adsorption percent difference ($15 \pm 0.5\%$). Further experiments should be run with the pressed ZSM-5 since the results are promising (Table 3.4).

Table 3.4. Effects of tube packing for ZSM-5/n-hexane adsorption isotherm experiments.

Packing Material	ZSM-5 Mass (g)	Temp (°C)	Partial Pressure (Pa)	Literature Percent Difference	Standard Deviation	ΔP (Psi)
Powder	0.5	27	> 370	158 ^a	78	11.7
Layered Powder	0.5	27	> 140	80 ^a	106	4.5
1:1 Powder/SiO ₂	1.0	27	> 235	5 ^a	25	-
	1.0	27	50	37 ^a	29	-
	1.0	150	> 200	198 ^b	93	-
1:2 Powder/SiO ₂	0.25	27	250	-4 ^a	45	-
	1.0	27	> 250	10 ^a	21	1
	1.0	27	50	84 ^a	25	1
	1.0	150	> 200	349 ^b	167	1
Pellets	0.5/1.0	27	> 525	15 ^a	0.5	-

^a Experiment adsorption capacities compared to literature adsorption capacities from [9].

^b Experiment adsorption capacities compared to the average literature adsorption capacities from [7], [11], and [14].

3.3 Methanol/SAPO-34 Breakthrough Experiments

Breakthrough experiments with SAPO-34 (CHA) were conducted to see whether lower pressure drops would arise from the larger crystal size and to determine whether adsorption differences between experiments and literature [117] would be different due to a different zeolite being used. No pressure drop occurred with 0.5 g SAPO-34 at 75 °C and a variety of partial pressures (480 – 2100 Pa), and the average adsorption percent difference was $6 \pm 41\%$ (Figure 3.11). This value was significantly lower than the ZSM-5 powder experiments likely due to the SAPO-34 crystals being larger than ZSM-5 crystals, as seen in SEM images (Figure 3.12), and thereby, preventing tight packing of the powder. The experiment results indicate that larger crystals of ZSM-5 should be evaluated and

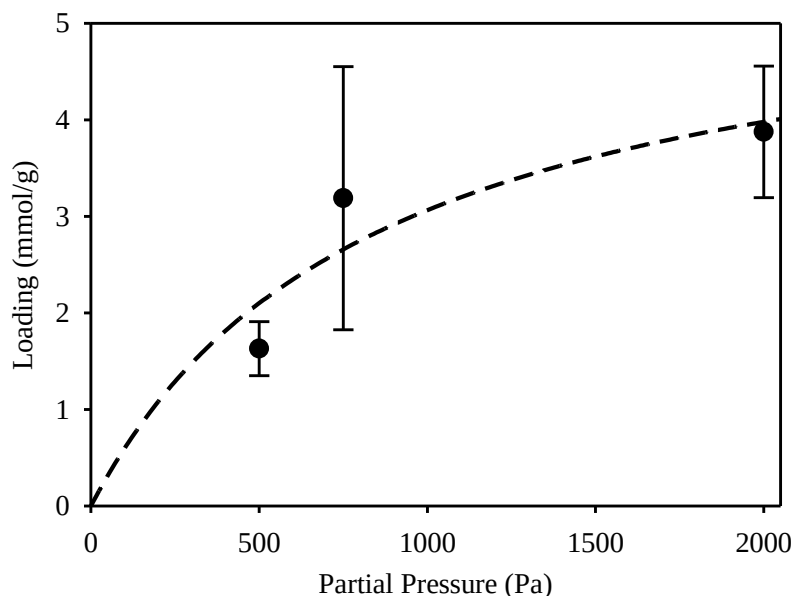


Figure 3.11. Partial pressure versus methanol loading for tubes packed with SAPO-34 powder and ran at 75°C.

that, for future experiments, SAPO-34 is a good candidate for testing the function of the flow system and recreating literature adsorption isotherms.

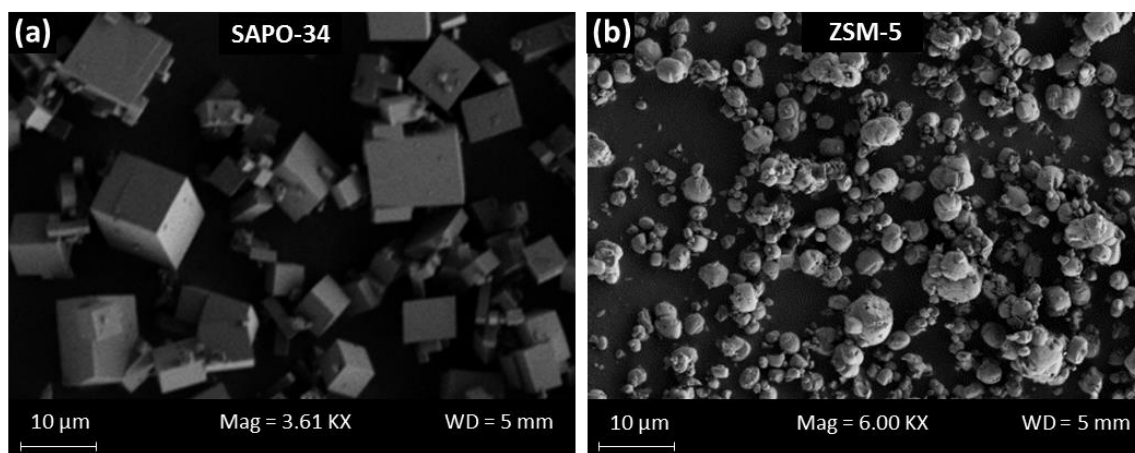


Figure 3.12. SEM images of (a) SAPO-34 and (b) ZSM-5 powder showing a large difference in crystal size.

CONCLUSION

A gas flow system was successfully constructed and a series of adsorption isotherm experiments that were compared to preexisting literature data were conducted. Initial experiments with pure powder ZSM-5 packing resulted in significant pressure drops across the experiment tube, ultimately leading to low adsorption capacity accuracy and precision. In subsequent experiments, where the packing material was changed to mixed ZSM-5/silica shards, the pressure drop was greatly reduced and more accurate adsorption capacities were measured, but the silica shards adsorbed significant amounts of n-hexane and therefore, mixture adsorption experiments would be difficult. Preliminary adsorption isotherm experiments with pressed ZSM-5 powder yielded promising results with elimination of pressure drop and experimental adsorption capacities only 15% different from literature values. An alternative to the pressed powders would be to use powders with increased crystal size such as SAPO-34 since experiments with these larger crystals did not exhibit a pressure drop and resulted in a difference of $6 \pm 41\%$ from the literature adsorption isotherms for methanol.

4.1 Future Work

Whatever packing material is chosen in the end, it is necessary that the resulting adsorption capacities closely replicate the literature and that standard deviation is low since flexibility-caused deformations can be slight and system sensitivity is therefore critical. Determining the effect of crystal size on accuracy would allow powders to be used

in their as-received form versus needing to press the powders into pellets. After single-adsorbate adsorption isotherms are accurately measured, the desorption signal upon heating would need to be evaluated to determine the lower threshold of the mass spectrometer (in terms of $\text{g/g}_{\text{zeolite}}$). If the desorption of a low number of molecules can be measured accurately, binary breakthrough experiments for various adsorbate partial pressures and mixture ratios could be performed. Once the binary measurements of isotherms existing in the literature are accurately measured, novel molecules could be used and evaluated with membranes. These experiments would provide greater insight into adsorbate-adsorbate interactions and point the future researcher towards an interesting compound combination that could be used for zeolite membrane experiments. Researching such adsorbate effects on membranes could prove to be very valuable since developing a fine control over zeolite unit cell dimensions could drastically improve current industrial separation processes by increasing adsorption capacities and lead to alternative separation methods for difficult-to-separate compounds.

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