NON-IDEAL BEHAVIOR IN GAS MIXTURE ADSORPTION ON TAILORED ADSORBENTS

A Dissertation
Presented to
The Academic Faculty

by

Danny Shade

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the
School of Chemical and Biomolecular Engineering

Georgia Institute of Technology
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NON-IDEAL BEHAVIOR IN GAS MIXTURE ADSORPTION ON TAILORED ADSORBENTS

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“The universe... what a concept”

-Dr. Jimes Tooper
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NOMENCLATURE

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<th>Description</th>
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<tr>
<td>” ”</td>
<td>denotes inch (length unit)</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius (temperature unit)</td>
</tr>
<tr>
<td>µ2</td>
<td>Denotes bridging ligand in which two metal atoms bond to one ligand atom</td>
</tr>
<tr>
<td>µL</td>
<td>microliter (volume unit)</td>
</tr>
<tr>
<td>µm</td>
<td>micrometer (length unit)</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom (length unit)</td>
</tr>
<tr>
<td>ARPA-E</td>
<td>Advanced Research Projects Agency–Energy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BISON-20</td>
<td>Binary adsorption ISOtherm ExperimeNtal 2020</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>Ethane</td>
</tr>
<tr>
<td>CAU</td>
<td>Christian-Albrechts-Universität</td>
</tr>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>cif</td>
<td>crystallographic information file</td>
</tr>
<tr>
<td>cm</td>
<td>centimeter (length unit)</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CPC</td>
<td>Concentration pulse chromatography</td>
</tr>
<tr>
<td>CV</td>
<td>Closed volumetric</td>
</tr>
<tr>
<td>DCB</td>
<td>Dynamic Column Breakthrough</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DSLF</td>
<td>Dual-Site Langmuir-Freundlich</td>
</tr>
<tr>
<td>g</td>
<td>gram (mass unit)</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>GCMC</td>
<td>Grand Canonical Monte Carlo</td>
</tr>
<tr>
<td>h</td>
<td>hour (time unit)</td>
</tr>
<tr>
<td>HKUST</td>
<td>Hong Kong University of Science and Technology</td>
</tr>
<tr>
<td>IAST</td>
<td>Ideal Adsorbed Solution Theory</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin (temperature unit)</td>
</tr>
<tr>
<td>kV</td>
<td>kilovolt (potential unit)</td>
</tr>
<tr>
<td>Kα1</td>
<td>Denotes K-alpha1 radiation, in this work x-rays with wavelength 1.5418 Å</td>
</tr>
<tr>
<td>m</td>
<td>meter (length unit)</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>mbar</td>
<td>millibar (pressure unit)</td>
</tr>
<tr>
<td>MC GAS</td>
<td>Multi-Component Gas Adsorption System</td>
</tr>
<tr>
<td>mg</td>
<td>milligram (mass unit)</td>
</tr>
<tr>
<td>MIL</td>
<td>Matériaux de l'Institut Lavoisier</td>
</tr>
<tr>
<td>min</td>
<td>minute (time unit)</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter (volume unit)</td>
</tr>
<tr>
<td>mm</td>
<td>millimeter (length unit)</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-Organic Framework</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometer</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>n-Butane</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer (length unit)</td>
</tr>
<tr>
<td>OD</td>
<td>Outer Diameter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>OMS</td>
<td>Open Metal Site</td>
</tr>
<tr>
<td>OV</td>
<td>Open volumetric</td>
</tr>
<tr>
<td>PID</td>
<td>proportional–integral–derivative (controller type)</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure Swing Adsorption</td>
</tr>
<tr>
<td>psia</td>
<td>pounds per square inch absolute (pressure unit)</td>
</tr>
<tr>
<td>psig</td>
<td>pounds per square inch gauge (pressure unit)</td>
</tr>
<tr>
<td>PVT</td>
<td>pressure, volume, and temperature data for use in equation of state</td>
</tr>
<tr>
<td>PXRD</td>
<td>Powder X-Ray Diffraction</td>
</tr>
<tr>
<td>pydc</td>
<td>Pyridinedicarboxylic acid</td>
</tr>
<tr>
<td>Q\textsubscript{st}</td>
<td>Isosteric heat of adsorption</td>
</tr>
<tr>
<td>RAPID</td>
<td>Rapid Advancement in Process Intensification Deployment</td>
</tr>
<tr>
<td>RCPSA</td>
<td>Rapid-Cycle Pressure Swing Adsorption</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary Building Unit</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal Conductivity Detector</td>
</tr>
<tr>
<td>TDC</td>
<td>2,5-thiophenedicarboxylic acid</td>
</tr>
<tr>
<td>TSA</td>
<td>Temperature Swing Adsorption</td>
</tr>
<tr>
<td>UiO</td>
<td>Universitetet i Oslo</td>
</tr>
<tr>
<td>VBA</td>
<td>Visual Basic for Applications</td>
</tr>
<tr>
<td>VSA</td>
<td>Vacuum Swing Adsorption</td>
</tr>
<tr>
<td>x</td>
<td>adsorbed phase mole fraction</td>
</tr>
<tr>
<td>y</td>
<td>gas phase mole fraction</td>
</tr>
<tr>
<td>ZSM</td>
<td>Zeolite Socony Mobil</td>
</tr>
<tr>
<td>(\delta_{ij})</td>
<td>Binary interaction parameter</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>wavelength (Å)</td>
</tr>
</tbody>
</table>
This dissertation describes investigations of non-ideal behavior arising in adsorption of gas mixtures on tailored metal-organic framework (MOF) adsorbents. Chapter 1 describes motivation for study of gas mixture adsorption as a more energy-efficient alternative to legacy separations methods. Adsorption processes offer potential for enormous energy savings over legacy methods, but inability to predict and model equilibrium adsorption of mixtures has represented a persistent obstacle to implementation of adsorption separations processes for decades. This work improves understanding of limitations of the preeminent mixing theory, the Ideal Adsorbed Solution Theory (IAST), for predicting equilibrium mixture adsorption on MOF adsorbents. Additionally, this work lowers barriers to the study of adsorption separations by facilitating construction of instrumentation for measurement of mixed gas adsorption.

Chapter 2 describes the adsorbent materials used in this work and the experimental methods used to characterize these materials. Chapter 3 serves as an illustrative example of many advantages MOFs pose over previous generations of adsorbent materials by highlighting structure-property relationships and adsorption behavior for carbon dioxide, methane, and nitrogen on several structurally similar aluminum-based MOFs. The work in this chapter demonstrates successful synthesis of four MOFs using the same basic synthesis procedure, and shows the impact on adsorption properties resulting from an isoreticular synthesis approach to introduce a variety of pore chemistries into CAU-10 frameworks. This work also shows that the orientation of a functional group in the pore space of the CAU-10 framework can enhance adsorption properties, including at least one case in which
a change in orientation can turn a nearly nonporous material into one of the best carbon
dioxide adsorbents tested in this work. Finally, in addition to the work in this area which
appears in the journal Adsorption, adsorption of a carbon dioxide/methane mixture is tested
at pressures up to 10 bar.

Chapter 4 delves deeper into the area of gas mixture adsorption, focusing on the
design, construction, and validation of a custom, automated instrument designed for
measurement of gas mixture adsorption at elevated pressures. This Multi-Component Gas
Adsorption System (MC GAS) was validated by comparison to published and in-house
measurements of adsorption of pure ethane and methane as well as mixed ethane/methane
on BPL carbon adsorbent. This chapter goes into technical detail sufficient to allow for the
replication of this instrument, which we hope will facilitate separations studies at other
research institutions.

Chapter 5 addresses questions central to this dissertation. In this chapter, three MOF
adsorbents (UiO-66 (Zr), UiO-66-NH₂ (Zr), and HKUST-1 (Cu)) are tested for pure
component adsorption of four gases (methane, ethane, n-butane, and carbon dioxide) and
four binary gas mixtures. Here we focus on pushing the assumptions made by IAST of
energetically homogeneous adsorbent surfaces and ideal interactions between molecules in
adsorbed phases to better understand when IAST provides reasonably accurate predictions
of mixed gas adsorption. Results show that anticipating when IAST provides accurate
predictions of mixed gas adsorption is difficult, and that characteristics of individual
adsorbent/mixture systems must be considered when evaluating the likelihood that IAST
will accurately describe mixture adsorption behavior.
Finally, chapter 6 gives conclusions and recommendations as to what paths may be taken in the future of the study of mixed gas adsorption. This chapter is based on parts of a review manuscript and describes the landscape of available experimental methods for measurement of mixed gas adsorption while seeking to make recommendations to investigators who may be interested in using these experimental techniques to study adsorption separations.
CHAPTER 1.  INTRODUCTION

1.1 Chemical separations and adsorption

The United States is the worldwide leader in the manufacture of chemical products, with an estimated chemical output value of over $200 billion projected for 2021.\(^1\) The amount of energy consumed by the chemical process industry is large and growing every year. Chemical separations are a critical but energy intensive component of these processes, consuming 10%-15% of all the energy in the US annually.\(^2\) Adsorption processes offer more energy-efficient alternatives to some existing legacy separation systems. To replace legacy separation systems, separation materials are needed whose adsorption behavior in complex chemical environments is well understood. A recent report from the National Academies of Sciences, Engineering, and Medicine states that the ability to understand and design separation systems for complex mixtures under various realistic conditions will be a turning point for the separations community and is a key to transforming separation science.\(^3\)

While promising adsorbent materials exist for a variety of separations, our understanding of how these materials behave in complex chemical environments is limited. Accurate modeling of the behavior of multi-component adsorption systems is essential for implementation of adsorption separations systems, and adoption of adsorption separations in industry has been hindered by challenges in predicting and modeling adsorption of mixed gases. Adsorption has been studied as a more efficient approach to myriad industrially relevant separations, including alkene/alkane separation, acid gas removal from flue gas and natural gas, and air separation.
1.1.1 Legacy gas separations

Contemporary methods for gas separations, or ‘legacy separations’ can present different disadvantages in comparison to adsorption methods. In general, legacy separations tend to be less energy-efficient but simpler to operate and with lower capital costs compared to adsorption methods. Cryogenic distillation and amine scrubbing are two widely used legacy separations which have great potential in many cases to be replaced by adsorption processes.

Cryogenic distillation is used in separation of ethane/ethylene mixtures and propane/propylene mixtures, among other separations. These enormously important separations are instrumental in the production of polyethylene and polypropylene, two of the most widely used plastics in the world. During the production of ethylene through steam cracking, other byproducts are created, including ethane. Highly pure ethylene (>99.9%) is required to produce high-quality polyethylene. The separation of ethane from ethylene is necessary to achieve such high purity, and remains one of the most challenging industrially relevant separations due to the similar physical properties of ethane and ethylene. Cryogenic distillation for this separation takes place in large-diameter pressurized columns which can hold in excess of 100 trays. Worldwide production of monomer-grade ethylene exceeds 1 billion pounds per year, and much of the cost of this ethylene is derived from the high cost of energy used to cool cryogenic distillation towers.

Amine scrubbing is the contemporary method of choice for removal of acid gases from a number of gas streams, including flue gas and recently natural gas as well. Acid gases are those gas species which produce acidic solutions when mixed with water.
Common acid gases and the corresponding acids they produce are carbon dioxide (which forms carbonic acid in water), nitrogen dioxide (nitrous and nitric acids), and hydrogen sulfide and sulfur dioxide (sulfurous and sulfuric acids). These species represent corrosive threats to process equipment as well as public health hazards when their release leads to the formation of acid rain. Removal of these species by bubbling gas mixtures through aqueous solutions containing ethanolamine species is an effective but energy-intensive route to cleaner flue gas emissions and adsorption processes offer enticing energy saving potential in this application.\textsuperscript{6}

Existing legacy separations are difficult to replace due to the relatively high capital costs associated with separations materials used in next-generation separations methods like adsorption or membrane processes. To invest in processes like adsorption in which adsorbent materials can be costly, investors must have confidence that these systems will perform as intended under a variety of operating conditions. This necessitates the ability to understand and model adsorption systems, which can be more complex than cryogenic distillation or amine scrubbing systems.

\subsection{1.1.2 Adsorption fundamentals}

Adsorption is the phenomenon of molecules from a bulk phase localizing to an interface. In this work, adsorption of molecules from a bulk gas phase onto a solid-gas interface is pertinent, but adsorption is of central importance in many liquid-solid or liquid-liquid systems.\textsuperscript{7-9} While cryogenic distillation for separation of ethane and ethylene requires modelling of three two-body interactions (ethane/ethane, ethane/ethylene, and ethylene/ethylene), adsorption processes to separate the same mixture introduce a third
body: the adsorbent. Thus, many more types of interactions can be present in an adsorption system. The use of energetically heterogeneous adsorbents adds complexity as different adsorption sites must be treated separately. However, it is most productive to discuss adsorption fundamentals beginning from a more general overview.

Adsorption can be broadly divided into chemisorption and physisorption. Chemisorption is the family of adsorption processes in which chemical bonds form between adsorbate and adsorbent. This is associated with high strengths of interaction and irreversible adsorption. Physisorption, meanwhile, does not involve the formation of chemical bonds. Physisorption is typically driven by relatively weaker interactions like van der Waals forces and electrostatics and is associated with reversible adsorption and facile regeneration of adsorbents. Adsorption of gases is thermodynamically more favoured at high pressures and low temperatures. This is evident in isotherm plots, some of the most common adsorption measurements. In gas adsorption isotherm measurements, an adsorbent is held at constant temperature while pressure is increased. Pressure decay or gravimetric analysis are among the most common methods used to measure adsorption isotherms.

Once gases are adsorbed, it is often useful to desorb these species to regenerate the adsorbent for repeated use. Regeneration of adsorbents can be accomplished by reducing pressure over the adsorbent or raising the temperature of the adsorbent. Cyclic adsorption separations like pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and temperature swing adsorption (TSA) take advantage of thermodynamic effects to enable separations. In these cases, adsorption is allowed to proceed to equilibrium where thermodynamically selective adsorption of one species occurs. Adsorption separations can
take advantage of chemical differences between species even when physical properties are similar, like the case of ethane and ethylene separation. Adsorbents can be designed to contain binding sites which preferentially adsorb one species in a mixture.\textsuperscript{10, 11} This preferential adsorption, or selectivity, enables the use of adsorption for separations.

However, adsorption separations are not limited to thermodynamically-controlled processes. Separations like rapid-cycle pressure swing adsorption (RCPSA) use kinetic effects to accomplish separations. One example of a kinetically-controlled adsorption separation under investigation is propane/propylene separation, which can use zeolite or carbon molecular sieve adsorbents which take up propylene more quickly than propane.\textsuperscript{12} This process is also used in air separation.\textsuperscript{13}

Pore windows and pore size distribution of adsorbents are closely associated with molecular sieving effects. Pore sizes are generally categorized as belonging to micropores (width < 2 nm), mesopores (2 nm < width < 50 nm), and macropores (50 nm < width).\textsuperscript{14} Very small pores may allow for exclusion of large molecules entirely, and very large pores are often associated with large adsorption capacities at high pressures. Some classes of amorphous adsorbents, like activated carbons, may have broad pore size distributions. Others, like carbon molecular sieves and zeolites, have much more tightly defined pore size distributions owing to long-range order in crystalline structures.

In addition to pore size distribution, surface area and pore volume are important characteristics of adsorbents and are associated with adsorption capacity at low and high pressures, respectively. Surface areas of adsorbents are typically measured in square meters per gram of adsorbent mass, and many classes of adsorbents can far exceed 1,000 m$^2$/g in
surface area. Pore volume is a measure of the internal free space in an adsorbent, and this is usually measured in cm$^3$/g. Carbon adsorbents have been reported containing pore volumes in excess of 10 cm$^3$/g, while crystalline adsorbents have been identified whose pore volumes exceed 5 cm$^3$/g.$^{15,16}$

While much research in the field of adsorption has aimed to create advanced adsorbent materials, the understanding of how these materials interact with gas mixtures has lagged behind, slowing progress towards widespread adsorption separations. This is due in part to the fact that adsorption experiments for gas mixtures are more difficult than adsorption experiments for pure gases, which has resulted in a shortage of mixture adsorption data and reliance on thermodynamic methods to predict mixture adsorption from only pure component adsorption data.

1.1.3 Ideal Adsorbed Solution Theory

Much contemporary academic study of adsorption separations relies on single-component adsorption behavior coupled with the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz to predict how an adsorbent might separate a mixture.$^{17-26}$ IAST is a popular thermodynamic theory used as a predictive method to estimate adsorption of mixed gases based only on adsorption behavior of each pure component of the mixture. This circumvents the need to actually expose an adsorbent to a gas mixture while still making claims about the promise of that adsorbent for separating that mixture. IAST has been the benchmark theory for over 50 years for predicting mixture adsorption behavior using only single-component adsorption data.$^{27}$
However, IAST has not been thoroughly experimentally evaluated due to experimental difficulty in measuring mixture adsorption, and a corresponding lack of the mixture adsorption data necessary to evaluate IAST. Relatively few studies exist in the literature that report mixture adsorption data, particularly for mixtures with more than two components. IAST requires three main assumptions: 1) all adsorbate molecules have equal access to the surface of the adsorbent 2) the adsorbent is energetically homogeneous, meaning that each adsorbent molecule has equal binding affinity for all sites on the adsorbent surface, and 3) the adsorbed phase behaves as an ideal solution- interactions between adsorbed molecules are of equal strength for all molecules.

At least one of these three assumptions of IAST are often not satisfied in studies that use it to predict mixture adsorption behavior. Many studies investigating energetically heterogeneous adsorbents use IAST to make claims about the efficacy of these adsorbents for various separations. Energetic heterogeneity refers to local variations in the strength of interactions between adsorbate molecules and the adsorbent surface. For example, 13X zeolite is energetically heterogeneous for adsorption of polar or quadrupolar species because it contains cation sites which can interact strongly with polar or quadrupolar molecules while other surface sites in this zeolite do not have such strong interactions with these species. In addition to zeolites, other families of adsorbents may also violate the assumption of energetic homogeneity. Energetic heterogeneity can arise in metal-organic frameworks (MOFs) from interactions of an adsorbate with functional groups included on connecting ligands, open metal sites (OMS), non-metal site secondary building unit (SBU) interactions, or impregnation with metal ions, polymers, or small molecules. This work will focus on adsorbents which have not been impregnated with other
molecules. Understanding which kinds of adsorbents lend themselves to good IAST predictions is valuable for determining when to trust IAST predictions of mixture adsorption, and when more difficult mixture adsorption experiments might be required to understand mixture adsorption on a certain adsorbent.

A second assumption required for IAST is that the adsorbed phase behaves as an ideal solution—interactions between adsorbed molecules are of equal strength for all molecules.\textsuperscript{20} Again there exist many studies which have applied IAST for mixtures containing non-ideal adsorbed phases, some noting that IAST fails to make accurate predictions about mixture adsorption. For example, this failure has been attributed in some cases due to hydrogen bonding in adsorbed water but no other adsorbed species, or dipole-dipole interactions in adsorbed sulfur dioxide while other species do not participate in these interactions.\textsuperscript{44-47} Much available research foregoes mixture adsorption measurements in favor of single component isotherms and IAST to predict selectivity for adsorption of one gas species from a mixture. Understanding which kinds of adsorbates lend themselves to good IAST predictions is valuable for determining when to trust IAST predictions of mixture adsorption, and when more difficult mixture adsorption experiments might be required to understand mixture adsorption for mixtures containing a certain component.

Despite the flaws of IAST, the research community continues to use IAST predictions as benchmarks to show which adsorbents are most promising for certain separations. Because it is still so widely used, IAST is obviously assigned some value in predicting mixture adsorption even when all assumptions for its application are not met. Understanding when IAST is likely to provide good predictions of mixture adsorption is
potentially very valuable, since experiments needed to make an IAST prediction of mixture adsorption are much simpler than measuring mixture adsorption directly.

1.2 Tailored adsorbents

Adsorbents can be designed for selective adsorption of one or more components from a mixture. This is often done by ‘tailoring’ or tuning the pore properties of the adsorbent material. Many families of adsorbent materials exist, and each come with their own opportunities to customize and control pore chemistry with the goal of increasing capacity or selectivity for adsorption of a target molecule.

1.2.1 Carbon adsorbents

Perhaps the simplest form of tailorable adsorbent is activated carbon. Activated carbon adsorbents are derived from a variety of carbonaceous materials including many forms of biomass. These adsorbents can be produced with thermal activation by first pyrolyzing carbonaceous material followed by activation at high temperature under a steam or carbon dioxide atmosphere. Alternatively, the precursor material may be impregnated with a chemical activation agent prior to pyrolysis to combine the pyrolysis and activation steps into a chemical activation process. Pyrolysis and activation conditions offer some control over pore size distribution and oxygen functional group content of the adsorbent. Postsynthetic treatment in reducing or oxidizing environment also offers options to impart nitrogen- or oxygen-containing functional groups, respectively, to the adsorbent. Many other carbonaceous adsorbents exist offering other opportunity for tailoring, including
carbide-derived carbons, which may contain residual metal nanoparticles, and carbon molecular sieves whose pore size distribution may be tightly controlled.49, 50

1.2.2 Aluminosilicate adsorbents

Activated carbon adsorbents offer relatively little opportunity for control over pore chemistry and pore size distribution compared to crystalline porous materials. Porous aluminosilicate materials known as zeolites have received much attention for use as adsorbents and catalysts. Zeolites may be naturally occurring or produced synthetically, and over 200 zeolite structures have been synthesized to date.51 The crystal structure of these materials creates a well-defined pore size distribution, which can allow for sieving effects and thereby kinetic separations. Aluminosilicate materials are derived from SiO$_4$ tetrahedra where some silicon ions are exchanged for aluminum ions. Of course, the exchange of a Si$^{4+}$ ion for an Al$^{3+}$ ion requires charge balancing to retain neutral charge on the zeolite structure. This is achieved through the inclusion of extra-framework cations. These cations are usually monovalent or divalent ions, including Na$^+$, K$^+$, Ag$^+$, Ca$^{2+}$, Mg$^{2+}$, and others. Cations can be exchanged in a contact solution to tune properties of the frameworks in which they are held. Extra-framework cations tend to interact strongly with polar or quadrupolar adsorbates, leading to the use of zeolites as adsorbents for capture of water vapor and carbon dioxide.52, 53 The heat of adsorption of water can be in excess of 44 kilojoules per mole in ZSM-5, and tends to be greater in more aluminum-rich zeolites.

1.2.3 Metal-organic frameworks as a platform for fundamental study of adsorption

While zeolites offer more control over pore size distribution than activated carbon adsorbents along with some control of pore chemistry through cation exchange, metal-
organic frameworks are in a class of their own with regard to potential for tuning and customization. These crystalline porous materials are composed of metal nodes connected by bridging ligands as shown in Figure 1.1. Opportunity for tailoring of MOF adsorbents includes ligand substitution or functionalization, metal center exchange, chemical impregnation, and introduction of structural defects.

![Figure 1.1: Popular adsorbents and their features which may violate the IAST assumption of surface homogeneity.](image)

(a) An activated carbon, showing amorphous structure with oxygen-containing functional groups. (b) A zeolite (in this case, ZSM-5) structure, showing possible locations of monovalent cations. (c) A MOF showing functionalized ligands, exchanged metal ions, a missing linker defect, and an open metal site.

1.2.4 MOFs & energetic heterogeneity

MOFs can display energetic heterogeneity due to a number of structural features. These can include pendant functional groups tagged to organic ligands, as well as open metal sites in the framework. MOFs contain one or more organic ligands connecting metal centers in a crystalline framework. These ligands are most commonly simple bidentate ligands like terephthalic acid, though ligands of much greater complexity have also been
incorporated into MOF structures. Some of these are pictured in Figure 1.2. MOFs make use of dozens of metals and hundreds of ligands combined in ever-diversifying synthesis methods to culminate in over 80,000 MOF structures. These are compiled in the Cambridge Structural Database, and represent hundreds of times more structures than all known synthetically accessible zeolite structures.\textsuperscript{56}
Figure 1.2: Ligands incorporated in metal-organic frameworks. Reproduced from Yaghi et al.\textsuperscript{57}
While these ligands represent a small fraction of the diversity of those represented in MOFs, a key approach of interest in study of adsorption fundamentals is the approach of isoreticular synthesis. The isoreticular synthesis approach aims to create isostructural frameworks using ligands which may vary in length or pendant functional groups. One example of materials synthesized in an isoreticular approach to vary pore size are the well-known UiO-66, UiO-67, and UiO-68 frameworks. These frameworks use linear ditopic ligands and zirconium metal nodes in isostructural FCU topology.

![UiO-66, UiO-67, UiO-68](image)

**Figure 1.3: Isoreticular series of UiO MOFs. Reproduced from Yuan et al.**

Isoreticular synthesis can also refer to MOFs synthesized from ligands of the same length which incorporate different pendant functional groups into the pore space of the MOF and impart different adsorption properties. This approach has been used to improve loading and selectivity for desired adsorbates and to improve chemical stability of MOFs. This approach to synthesis allows for the introduction of energetic heterogeneity in controlled ways to the surface of MOF adsorbents. This makes MOFs a powerful tool for interrogation of the effects of energetic heterogeneity on adsorption behavior for pure components and for mixtures.
Open metal site MOFs contain another potential source of energetic heterogeneity in the form of coordinatively unsaturated metal ions which may interact strongly with polar or quadrupolar adsorbates.\textsuperscript{61, 62} These sites have also been investigated for preferential binding of olefins in olefin/paraffin separations.\textsuperscript{63, 64} In this work we investigate the open metal site MOF HKUST-1 whose copper paddle wheel motifs offer opportunity for adsorbates to interact with unsaturated copper ions.

Other potential sources of energetic heterogeneity are numerous and not investigated in the scope of this work. These include, but are not limited to, mixed-ligand MOFs,\textsuperscript{65} mixed-metal MOFs,\textsuperscript{66} and MOFs containing structural defects.\textsuperscript{67} Many of these phenomena are still poorly understood and offer opportunity for further study in the area of separations. For example, short-range order of mixed ligands,\textsuperscript{68, 69} mixed metals,\textsuperscript{70} are under investigation but remain poorly understood.

1.2.5 Limitations of MOFs

While MOFs are extremely promising materials in a number of applications due to their enormous amenability to customization, their chemical and thermal stability often compares unfavorably to other porous materials like silicas, carbons, and zeolites. But, the number of materials falling under the label of MOF is approaching 100,000 and among these there are many instances of relatively stable materials. Meta-analysis and machine learning approaches to understand and improve stability under humid or corrosive conditions have shown promise.\textsuperscript{71, 72} Similarly, meta-analysis of thermal stability has shown some progress towards better ability to predict thermal stability and engineer MOFs with improved thermal stability.\textsuperscript{73}
Understanding of gas mixture adsorption behavior on MOFs, like understanding of chemical and thermal stability, is a challenge in part due to the breadth of existing MOF materials. In this work, understanding gas mixture adsorption relies on comparison of the foremost predictive method (IAST) with direct experimental measurement of mixed gas adsorption. The experimental challenges associated with measuring adsorption of mixed gases have led to a relative scarcity of mixed gas adsorption data in the open literature, which in turn has represented a persistent barrier to improved understanding and ultimately implementation of more efficient adsorption separations.

### 1.3 Measurement of mixed gas adsorption

Adsorption of pure gases can be measured easily using commercially available instrumentation from various sources, including 3P, Anton Paar, Hiden Isochema, Micromeritics, Microtrac, Quantachrome, and others. But, only recently have commercial options become available for measurement of adsorption of gas mixtures, and these have as yet seen only sporadic use in the open literature.\(^74\)-\(^77\) This has led to a long-standing conception that mixture adsorption data are rare. Indeed, until our recent work, published efforts to compile mixture adsorption measurements had resulted in collections of fewer than 50 isotherm measurements.\(^78\),\(^79\) In at least one case however, a large but unpublished dataset of mixed gas adsorption measurements exists but has not come into widespread use.\(^80\) Our Binary adsorption ISOtherm ExperimeNtal 2020 (BISON-20) dataset is the largest published dataset by far and includes more than 900 mixed gas adsorption isotherm measurements, challenging the assumption that mixture adsorption data are as scarce as
previously thought.\textsuperscript{28} However, even the BISON-20 dataset pales in comparison to the size of the NIST/ARPA-E adsorption database containing over 30,000 pure component adsorption isotherm measurements.\textsuperscript{81} The difficulty of mixed gas adsorption measurements is further highlighted by the existence of at least 18 unique experimental methods to this end. Scientists and engineers have applied their ingenuity and creativity to develop gravimetric, volumetric, chromatographic, spectroscopic, and other methods to study adsorption of gas mixtures. In some cases one method may hold unique advantages over others for a specific adsorbent or adsorbate mixture, but the diversity of extant methods serves to highlight that there is no one technique which is facile enough to have become the sole method for characterizing adsorbents for gas separations.

While computational methods and mixing theories to predict adsorption of mixtures have become more sophisticated in recent years, there are many cases in which experimental measurements of mixture adsorption are not easily explained by simulation results or mixing theory.\textsuperscript{28, 78} Experimental measurements of mixture adsorption remain essential to improved ability to understand and predict behavior of adsorption separations systems. The success of adsorption process design in any given separation depends strongly on the ability to predict the adsorption behavior of the adsorbent-mixture system under process conditions. This prediction is essential not only for selecting an adsorbent material for use in a separation but also for choosing the process conditions under which to perform the separation.

For decades, adsorption researchers have worked to improve mathematical models for predicting mixture adsorption. While prediction of mixture adsorption behavior from pure-component adsorption data has seen some success, non-ideal behavior remains
difficult to predict without mixture adsorption experiments. The need for greater availability of experimental mixture adsorption data, especially for non-ideal systems, has been reiterated for nearly as long as the study of mixture adsorption has existed.\textsuperscript{3, 27, 29, 82, 83} Many problems identified in a 1998 paper by Talu on the status of binary gas mixture adsorption experiments persist.\textsuperscript{29} This report noted that direct measurement of binary mixture equilibria is complicated and time consuming, while the advent of commercial systems have made measurement of pure-component adsorption much simpler and faster. The report also states that the Ideal Adsorbed Solution Theory (IAST) is widely used to predict mixture adsorption but that it cannot give information on deviations from ideal behavior. Both of these problems persist today. Many methods for measuring mixture adsorption have been reported, each with their own pros and cons.\textsuperscript{84} A summary and comparison of some methods for measuring mixture adsorption was published in 1999, but the landscape of the field has since changed.\textsuperscript{85} In this dissertation, an original instrument capable of automated measurements of mixed gas adsorption is described in sufficient technical detail to allow for replication and thereby lower barriers to mixture adsorption measurements.

1.4 Dissertation scope

Adsorption of gas mixtures on tailored adsorbents is a complex problem with layered intricacies. This dissertation addresses fundamental questions at the heart of understanding limitations of IAST in predicting mixed gas adsorption on tailored adsorbents through three major aims. These aims are to (1) assess the efficacy of IAST for predicting adsorption
from the gas phase onto energetically heterogeneous surfaces, especially for (2) non-ideal mixtures, using (3) automated instrumentation custom-built for this work while facilitating the use of mixture adsorption instrumentation by others. Our experimental approach has used original instruments, including a custom automated Multi-Component Gas Adsorption System (MC GAS), to probe properties of both adsorbents and adsorbate mixtures to investigate factors giving rise to non-ideal adsorption behavior. This work has resulted in intellectual contributions of improved understanding of adsorption of both pure components and mixtures in metal-organic framework materials and better accessibility by the scientific community of experimental methods for measuring mixture adsorption. Society benefits from this work as the separations community moves a step closer to widespread implementation of energy-efficient adsorption separation processes through better understanding of gas mixture adsorption and facilitation of worldwide experimental capacity for measurement of mixture adsorption.

This dissertation uses MOFs as a platform from which to investigate adsorption of gas mixtures. Pendant functional groups added to ligands in MOF structures can contribute to energetic heterogeneity of adsorbent surfaces, and give some adsorbents greater affinity for certain adsorbates. Chapter 3 describes a study of isoreticular synthesis and structure-property relationships of a family of aluminum CAU-10 MOFs. This work demonstrates that nature and geometric placement of pendant functional groups in a small-pore MOF can impact adsorption of several molecules and IAST selectivity for carbon dioxide from binary mixtures with methane and nitrogen, which are of interest for applications in gas sweetening and flue gas treatment.
An overarching theme in this work is that a lack of access to mixture adsorption data has hindered the study of adsorption separations for nearly as long as adsorption separations have been investigated. Therefore, aim 3 of this work is to decrease barriers to measurement of mixed gas adsorption. We seek to do this in Chapter 4, where our own custom, automated instrument for measurement of mixed gas adsorption (MC GAS) is described in sufficient detail to allow for replication. Additionally, Chapter 6 draws from work in our review of the contemporary landscape of measurement techniques for mixed gas adsorption. Here, we seek to make recommendations for which methods may best suit investigators aiming to make their own measurements of mixed gas adsorption.

Energetically heterogeneous adsorbent surfaces offer tremendous potential for thermodynamically selective adsorption separations. But, IAST struggles to predict adsorption on energetically heterogeneous surfaces. In some cases, IAST can give errors in excess of 100% in predicted selectivity for energetically heterogeneous surfaces while in other cases this error is less than 15%.78 The factors that give rise (or don’t) to these deviations from IAST behavior are poorly understood, but are systematically addressed in Chapter 5 for the MOFs UiO-66, UiO-66-NH$_2$, and HKUST-1. Each of these MOFs contain different potential sources of energetic heterogeneity, and this study focuses on low-pressure adsorption of two gas mixtures (carbon dioxide/methane and ethane/carbon dioxide) where, at low surface coverage, departures from ideal behavior may be attributed to adsorbent-adsorbate interactions. Here we demonstrate that while HKUST-1 is more energetically heterogeneous than the UiO-66 MOFs studied, non-ideal behavior occurs for at least one mixture on all three surfaces. Non-ideal interactions between adsorbed molecules can also lead to non-ideal adsorption behavior, even for energetically
homogeneous surfaces. Chapter 5 also deals with adsorption of two heavier binary mixtures including a relatively ideal mixture (n-butane/ethane) and a relatively non-ideal mixtures (n-butane/carbon dioxide). Due to higher adsorbed concentrations, departures from ideal behavior are in these cases more easily explained by non-ideal interactions between adsorbates. However, this chapter also demonstrates that deconvolution of effects from non-ideal adsorbent-adsorbate interactions and effects from non-ideal adsorbate-adsorbate interactions is difficult, which is why parts of aim 2 and all of aim 3 of this dissertation are addressed together here. We show here that breaking the IAST assumption of equal accessibility to all parts of the adsorbent surface may give rise to non-ideal behavior even when other assumptions are met.
1.5 References


15. Hönicke, I. M.; Senkovska, I.; Bon, V.; Baburin, I. A.; Bönisch, N.; Raschke, S.; Evans, J. D.; Kaskel, S., Balancing Mechanical Stability and Ultrahigh Porosity in


CHAPTER 2. MATERIALS AND METHODS

The adsorbent materials and experimental setups used in his dissertation are described in this chapter. The MOFs investigated as adsorbents in this work were synthesized via solvothermal approach, while experimental setups used include both commercially available and lab-built equipment. MOFs investigated in this work include CAU-10, MIL-53-TDC, MIL-160, MFM-300 (Al), UiO-66 (Zr), and HKUST-1. An activated carbon adsorbent known as BPL carbon was also used for instrument validation measurements. This chapter describes the structure of each adsorbent while synthesis procedures for each are listed in the experimental sections of later chapters. In addition, the principles behind gravimetric and volumetric adsorption measurements for pure gases are detailed here. Finally, this chapter also describes a custom flow system used in this work for measurement of mixed gas adsorption at low pressures (≤1 bar). More detail surrounding a custom volumetric system for adsorption of gas mixtures at higher pressures (≤10 bar) is available in chapter 4.

2.1 CAU-10

CAU-10 (Christian-Albrechts-Universität) is an aluminum isophthalate MOF with relatively small one-dimensional pores. This MOF contains cis-connected chains of corner-sharing AlO$_6$ octahedra connected by isophthalate ligands. The one-dimensional pores exhibit a maximum diameter of roughly 7 Å, and the framework has BET surface area of roughly 600 m$^2$/g with pore volume of approximately 0.43 cm$^3$/g.$^{1}$ The CAU-10 framework is shown in Figure 2.1 as viewed down the crystallographic c axis. CAU-10 has received attention for adsorption cooling and water vapor harvesting applications.$^{2,3}$
2.2 MIL-53-TDC

MIL-53 (Matériaux de l'Institut Lavoisier) is a commonly studied MOF which may be synthesized from a number of M$^{3+}$ species including V, Cr, Al, Fe, In, Co, Ga, Mn, Sc, and Ni. MIL-53 (Al) is known to exhibit gate-opening, or “breathing” behavior whereby the shape of the framework changes upon adsorption or desorption of guest species. When the terephthalate ligand used to synthesize MIL-53 (Al) is replaced with 2,5-thiophenedicarboxylic acid, the structure loses its flexibility and is known as MIL-53-TDC. MIL-53-TDC shows BET surface area of approximately 1150 m$^2$/g and pore volume of 0.48 cm$^3$/g.$^4$ Like CAU-10, the MIL-53-TDC structure contains chains of corner-sharing AlO$_6$ octahedra, though in the MIL-53-TDC framework these octahedra are trans-
connected, as shown in Figure 2.2. This MOF has also received attention for adsorption cooling applications.\textsuperscript{5}

![MIL-53-TDC structure](image)

**Figure 2.2**: MIL-53-TDC structure. Gray: carbon; red: oxygen; yellow: sulfur; pink: aluminum. Hydrogen atoms are omitted for clarity.

### 2.3 MIL-160

MIL-160 is another MOF which has received attention for adsorption cooling applications. This material shares the chains of cis-connected AlO\textsubscript{6} octahedra of the CAU-10 framework and likewise has relatively narrow one-dimensional pores.\textsuperscript{6} However, the ligand used in this framework is 2,5-furandicarboxylate rather than isophthalate used in CAU-10. MIL-160 has one-dimensional pores roughly 5 Å in diameter, and shows BET surface area of approximately 1070 m\textsuperscript{2}/g with pore volume of 0.4 cm\textsuperscript{3}/g.\textsuperscript{7} The larger
surface area compared to CAU-10 means that this MOF tends to adsorb molecules in greater quantities at low pressures. Figure 2.3 illustrates the structure of MIL-160.

![Figure 2.3: MIL-160 structure. Gray: carbon; red: oxygen; pink: aluminum. Hydrogen atoms are omitted for clarity.](image)

2.4 MFM-300 (Al)

MFM-300 (Al), also known as NOTT-300 (University of Nottingham) is an aluminum-based MOF containing the tetratopic ligand biphenyl-3,30,5,50-tetracarboxylic acid. This material is isostructural to NOTT-400, which replaces the aluminum ions for scandium ions. This material has been investigated for olefin/paraffin separation and acid gas capture. The structure of MFM-300 as viewed down the crystallographic c axis is
shown in Figure 2.4. MFM-300 has a surface area of 1370 m$^2$/g as calculated by DFT and Monte Carlo methods with a pore volume of 0.375 cm$^3$/g and an average pore size of 5.7 Å.$^9$

![Figure 2.4: MFM-300 (Al) structure. Gray: carbon; red: oxygen; pink: aluminum. Hydrogen atoms are omitted for clarity.](image)

2.5 UiO-66

UiO-66 (Universitetet i Oslo) is a highly stable zirconium (or hafnium) terephthalate MOF whose metal nodes are cuboctahedral metal oxide clusters allowing for 12 points at which terephthalate ligands may coordinate.$^{11}$ This 12-connected structure shown in Figure 2.5
lends the framework good chemical and thermal stability. Moreover, UiO-66 may be synthesized with the inclusion of monodentate “modulator” ligands which are later removed from the framework by heating under vacuum. This introduces defects via missing ligands or missing metal clusters. Defect engineering in UiO-66 can alter adsorption and catalysis properties. A defect-free UiO-66 structure contains two different pores: a tetrahedral cage approximately 7.5 Å in diameter and a larger octahedral cage with diameter 12 Å. The BET surface area of UiO-66 is roughly 1100 m²/g and the theoretical pore volume is 0.77 cm³/g. UiO-66 is one of the most widely studied MOFs, with only ZIF-8 (zeolitic imidazolate framework) and MIL-101 listed more frequently as paper topics in Web of Science prior to 2020.

Figure 2.5: UiO-66 structure. Gray: carbon; red: oxygen; blue: zirconium; white: hydrogen.
HKUST-1 (Hong Kong University of Science & Technology), also known as Cu-BTC, is a copper trimesate MOF with high surface area (in excess of 1500 m$^2$/g) and pore volume (in excess of 0.5 cm$^3$/g).\textsuperscript{14} This MOF contains coordinatively unsaturated metal sites, or open metal sites in the form of copper paddle wheels in which two adjacent copper atoms are each coordinated to one side of four carboxylate groups from four trimesate ligands. These open metal sites offer opportunity for inclusion of capping ligands in the framework and can serve as relatively high affinity binding sites for polar or quadrupolar molecules. The HKUST-1 framework contains three differently structured pores, including two roughly 14 Å in diameter and a smaller pore of approximately 10 Å. The structure of HKUST-1 is shown in Figure 2.6.

![HKUST-1 Structure](image)

**Figure 2.6: HKUST-1 structure.** Gray: carbon; red: oxygen; orange: copper; white: hydrogen.
2.7 BPL Carbon

While MOFs represent interesting opportunity to study adsorption due to their amenability to tuning and customization, sometimes different syntheses of what is ostensibly the same material may lead to products with different adsorption properties. The subject of reproducibility in adsorption measurements on MOFs has received attention largely due to this difficulty.\textsuperscript{15, 16} BPL carbon is a less tunable adsorbent, but is less prone to difficulty reproducing adsorption measurements. In this work we have chosen BPL carbon as an adsorbent material for validation measurements of mixed gas adsorption on new instrumentation.

2.8 Gravimetric Adsorption Principles

Perhaps the most conceptually straightforward way to measure adsorption of pure gases is the gravimetric adsorption technique. Gravimetric methods are generally considered more reliable at high pressure than volumetric methods and they often allow for comparable precision with much lower adsorbent mass. While volumetric methods seek to measure the molar quantity adsorbed by determining the moles that are ‘missing’ from the gas phase, gravimetric methods measure the change in the weight of the sample as gas molecules adsorb on it.

In a gravimetric experiment, a small quantity of the adsorbent is loaded on a sensitive microbalance. As little as 1 mg may be required for single component adsorption measurements.\textsuperscript{17} The cell containing this sample is pressurized with adsorbing gas, and the weight of the sample increases as gas adsorbs. Some complexity is introduced by the need
to correct for the buoyant forces acting on the adsorbent, the adsorbed phase, and the microbalance itself. The weight change in the sample is attributed to adsorption; this change determines the total mass adsorbed on the sample. Figure 2.7 shows an experimental setup for gravimetric measurement of pure gas adsorption.

![Gravimetric adsorption apparatus](image)

**Figure 2.7: Gravimetric adsorption apparatus.**

For a single component system, this weight change is sufficient to determine the quantity of a pure gas adsorbed on the sample. For mixtures, another method must be paired with the gravimetric system to determine the composition of the adsorbed phase and/or the composition of the gas phase. However, this type of measurement is not used in this work.

The need to correct for the buoyant effects in pure component adsorption measurements with gravimetry is well-known.\(^{18, 19}\) This correction is relatively simple for adsorption of pure gases, but more complex in the case of mixtures as the density of the gas phase depends not only on pressure and temperature but also on gas composition. An equation of state can be used to determine the density of the gas phase, or this density can be measured directly as in the gravimetric-densimetric method. Further precision may be gained by accounting for the density of the adsorbed phase, which is not easily measurable.
The potential theory developed by Polányi\textsuperscript{20, 21} and the pore-filling model of Dubinin\textsuperscript{22, 23} have been adapted to suit this application for mixture adsorption.\textsuperscript{24}

2.9 Volumetric Adsorption Principles

Volumetric measurements are extremely popular for single component adsorption measurement, especially at pressures below one bar. The volumetric method relies on careful measurement of the internal volumes of the instrument along with pressure and temperature measurements of the gas inside. All of this information allows for the use of an equation of state to calculate the molar quantity of gas in each internal volume of the volumetric system. It could be argued that the name ‘manometric’ is more appropriate than ‘volumetric’ as the change being measured is a pressure change and not a volume change. This terminology is used occasionally in the literature, but volumetric is the more widely used term.

Typically, a volumetric system used for single-component adsorption measurements consists of a reference cell, which is empty, and an adsorption cell or sample cell, which contains a known mass of adsorbent. This is illustrated in Figure 2.8. The experimental procedure involves pressurizing the reference cell with the adsorbate while the adsorbent is activated under heating and vacuum. The temperature and pressure in the reference cell are recorded, which allows calculation of the molar quantity of gas in the reference cell. Once the adsorbent has reached the desired temperature, a valve is briefly opened to connect the reference cell to the adsorption loop, dosing gas into the loop. As gas adsorbs on the adsorbent sample, the pressure in the adsorption loop drops. When equilibrium has been reached, the pressure should remain constant as the system is isothermal. Pressure
and temperature measurements of the reference cell at this point allow calculation of the molar quantity of gas dosed to the adsorption loop. Adsorption loadings are then calculated by subtracting the final number of moles remaining in the gas phase from the initial number of moles dosed into the adsorption loop. For pure gases, this measurement process gives complete equilibrium information: the temperature, pressure, and loading of the adsorbent. However, the process is more complicated for mixtures and requires a gas chromatograph (GC) or other analytical method to determine the composition of the gas phase.

**Figure 2.8: Volumetric adsorption apparatus.**

The principles of volumetric measurement may be paired with a number of techniques to assess mixture adsorption. Volumetric measurements of mixture adsorption work well for many systems, including mixtures with more than two components. Volumetric methods have even been used to study mixture adsorption in slurries and fluidized beds. Generally, volumetric methods rely on an equation of state to predict the compressibility factor of the gas being studied.
2.10 Breakthrough Adsorption System

Dynamic column breakthrough (DCB) adsorption measurements are a popular contemporary method to measure adsorption capacities, especially for mixed gases. This increasingly popular measurement technique already appears in over one-third of the 263 references reporting mixture adsorption data collected by Cai et al.\textsuperscript{27} DCB is a chromatographic method in which a flow of mixed gas is introduced to a clean adsorbent bed. The concentration of each component in the effluent is monitored over time until each component ‘breaks through’ the fixed bed. The flow rate of each component into and out of the bed are integrated until the flow rate out is equal to the flow rate in. In a typical dynamic column breakthrough, the volumetric flow rate of the effluent is assumed to be equal to the feed, while the more sophisticated open volumetric method requires measurement of the volumetric flow rate of the effluent stream. A simple integral of the difference in inlet and outlet molar flow rate of each component as a function of time is used to determine the adsorption of each component.

DCB measurements are extremely flexible. Often, a non-adsorbing inert carrier gas is included in the flow of mixed gas. Inclusion of a carrier gas can allow for use with vapors at very low partial pressures. The use of a back-pressure regulator enables measurements at high pressures. This method can be used with less than a gram of adsorbent and is easily adapted for mixtures of different compositions or single component adsorption measurements.

The simplicity and ease of use of DCB sets it apart from other methods used for measurement of mixed gas adsorption. Several automated instruments for measurement of breakthrough curves are available. While some kinetic information can be gleaned from
the shape of the breakthrough curves, the focus of the work in this dissertation is on measurement of equilibria and this dissertation will not delve into details of kinetic measurements. The largest critique of breakthrough methods is that, in the vast majority of publications using a breakthrough method, each breakthrough curve gives one equilibrium data point before the sample must be reactivated, making breakthrough measurements relatively tedious and unsuitable for the collection of large data sets. This is consistent with the low number of data points per reference observed in the BISON-20 database for references using breakthrough methods.

Since the study of adsorption is currently driven by advances in porous materials, often the ability to make just a few measurements is valuable to understanding the performance of a new material in ‘benchmark’ testing conditions. Often, large data sets are not required to understand whether an adsorbent shows some promise for a given separation. Breakthrough measurements are frequently used to make just a few measurements to establish a single-point selectivity measurement for novel adsorbents.

DCB measurements for mixed gas adsorption saw early use by Kenney and Eshaya in 1960. However, this method was used for liquid mixtures before it was applied to gases. The name ‘inverse gas chromatography’ has also been used to describe DCB experiments, and commonly the name ‘breakthrough’ is applied to this method, though the open volumetric method is also a breakthrough method. DCB may be paired with gravimetric measurement, though this combination is not common. A typical DCB setup is shown in Figure 2.9.
The breakthrough group is the most popular for mixture adsorption measurements, appearing in nearly twice as many papers as any other method for mixed gas adsorption measurement since 2010. Over 80% of these papers use DCB. Each DCB measurement begins with a fixed bed of adsorbent that has been activated by heating in a flow of inert, non-adsorbing gas. A feed flow of mixed gas is introduced at known composition and flow rate. Commonly, the composition of this gas is controlled using a different mass flow controller (MFC) for each adsorbing component and typically one MFC for a non-adsorbing carrier gas. As this feed flows through the bed and adsorption occurs, the composition of the effluent is monitored until the effluent and feed are identical in composition. The difference in the inlet and outlet molar flow rate of each component are integrated over time to find the amount of each component that has been adsorbed in the bed. This simple mole balance to determine how much of each component is ‘missing’ from the gas phase is shared by many other measurement techniques. A back pressure regulator is often used to control the total pressure during adsorption. Furthermore, measurements can be made using vapors introduced by a carrier gas, and a tracer gas may be included to facilitate measuring effluent flow rate. However, the inclusion of these gases in DCB measurements can affect the adsorption of components of interest.
DCB measurements are heavily dependent on accurate dead volume measurement, which may be done with sand or glass beads prior to adsorption measurements. Further, as with other fixed-bed methods, care must be taken to ensure uniform temperature distribution in the adsorbent bed. Attention should be paid to repeatable packing of fixed beds and ensuring that wall channeling is mitigated with appropriate particle size and bed diameter. Furthermore, users should be aware of the roll-up phenomenon and take care to handle this appropriately when making measurements. Finally, experiments must be run until every component breaks through to avoid mistakes related to the ‘order of addition’ phenomenon in which a strongly adsorbing component is sequestered to the entrance of the packed bed while another component passes by and adsorbs along the rest of the bed.

Many detectors can be used to measure the composition of the effluent gas including the common mass spectrometer (MS) and gas chromatograph (GC). High time resolution for composition measurement is desirable, especially for mixtures containing strongly adsorbing species with sharp breakthrough profiles. This makes the MS the most popular choice, though other sensors like infrared or hydrogen analyzers have also been used.

DCB is presently the most popular method of mixture adsorption measurement because it is inexpensive, flexible, and relatively simple. DCB experiments offer the ability to control the composition and pressure of the gas phase at equilibrium. Small quantities of adsorbent may be used; DCB measurements can be made using less than 200 mg of sample. However, DCB is not without drawbacks. The issue of changes in the effluent flow rate represents a challenge to DCB measurements, but the inclusion of an inert carrier gas to normalize signals from the detector can help address this issue. Additionally,
most DCB experiments only gather one equilibrium data point before the adsorbent must be reactivated, so collection of extensive data sets can be time-consuming.

2.11 References


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CHAPTER 3. RETICULAR CHEMISTRY

APPROACH TO TUNING PORE SPACE AND ADSORPTION PROPERTIES OF CAU-10

This chapter is an adaptation of the article “Structural similarity, synthesis, and adsorption properties of aluminum-based metal-organic frameworks” which appears in the 27th volume of the journal Adsorption, pages 227-236. This chapter contains work from this article which is reproduced with permission from the publisher. In this work, a general procedure has been developed for synthesizing four MOFs sharing similar chains of AlO₆ octahedra (CAU-10, NOTT-300, MIL-53-TDC, and MIL-160). CAU-10 has been synthesized with eight differently substituted ligands to impart different characteristics into the pore space. Isotherms of carbon dioxide, methane, and nitrogen were measured on all MOFs synthesized in this work to assess the effects of functional group and surface area on adsorption behavior. At low pressure (100 mbar), structures incorporating polar functional groups have the highest adsorption of carbon dioxide, while the structures with the highest surface areas have the highest adsorption of carbon dioxide at higher pressure (1000 mbar). The heterocyclic and amine-substituted structures show the greatest carbon dioxide adsorption and Henry’s law selectivity among all CAU-10 structures in this work. Comparison of CAU-10 MOFs substituted with a nitro group at different positions on the ligand (carbon 4 vs 5) showed that positioning the nitro group at the side of the pore rather than the center resulted in increased loading of all adsorbates over the studied pressure range up to 1 bar.
3.1 Introduction

Metal-organic frameworks (MOFs) have been the subject of recent study for applications including separations, gas storage, catalysis, and pharmaceuticals.\textsuperscript{2-4} These materials offer tremendous potential in a number of applications due to the modular nature of their construction.\textsuperscript{5, 6} By using different combinations of organic ligands and inorganic secondary building units (SBUs), many thousands of MOFs have been synthesized.\textsuperscript{7} Ligands substituted with different functional groups in conjunction with the same inorganic SBU can be used to synthesize isostructural MOFs which exhibit different adsorption properties.\textsuperscript{8} This isoreticular chemistry approach can be used to retain favorable properties of a parent MOF, like stability in humid environments, while introducing other favorable properties, like affinity for desired adsorbates.\textsuperscript{9, 10} For example, the MOFs UiO-66, CAU-10, and MIL-53 have been studied to some extent using this approach.\textsuperscript{11-13}

UiO-66 and MIL-53 incorporate the linear, ditopic ligand 1,4-benzene dicarboxylic acid (terephthalic acid). In UiO-66, the terephthalic acid ligands bridge 12-connected Zr\textsubscript{6}O\textsubscript{4}(OH)\textsubscript{4} SBUs.\textsuperscript{14} MIL-53 consists of trans-connected corner-sharing chains of M(III)O\textsubscript{4}(OH)\textsubscript{2} octahedra conjoined via \(\mu_2\)-OH groups.\textsuperscript{15} The octahedra in these chains are bridged by terephthalic acid ligands to create one-dimensional rhombohedral channels. The terephthalic acid ligand shared by these materials offers opportunity for functionalization at carbons 2, 3, 5, and 6. However, these carbon atoms are not geometrically unique within the MOF structure.

Like MIL-53, CAU-10 includes chains of corner-sharing AlO\textsubscript{6} octahedra.\textsuperscript{12} However, while the octahedra in MIL-53 are trans-connected, the octahedra in CAU-10 are cis-connected. In CAU-10, these octahedra are bridged by the bent ligand 1,3-benzene
dicarboxylic acid (isophthalic acid). This ligand offers the chance to add functional groups at carbons 2, 4 and 5, where the position of carbon 5 is unique compared to carbons 2 and 4. While prior isoreticular chemistry approaches to the study of CAU-10 have focused exclusively on functionalization at the 5 position, there is also the opportunity to synthesize CAU-10-X materials functionalized at the 4 position. This may provide some insight into how placing the same functional group at different geometric positions in the pore space may affect adsorption properties.

**Figure 3.1: Comparison of the CAU-10 channels with those in NOTT-300, MIL-53-TDC, and MIL-160.**

The infinite chains of cis-connected, corner-sharing AlO$_6$ polyhedra that make up the inorganic units of CAU-10 are shared by NOTT-300 and MIL-160 albeit in slightly stretched geometries, as shown in Figure 3.1. The organic ligand in NOTT-300 (also termed MFM-300 (Al)) is tetratopic biphenyl-3,3',5,5'-tetracarboxylic acid rather than ditopic isophthalic acid. This ligand bears a resemblance to two coplanar isophthalic acid ligands bridged by a bond between carbon 5 on the aromatic ring on each isophthalic acid.
The MOF MIL-53-TDC also contains infinite chains of aluminum octahedra. However, unlike the other three MOFs in this work, the chains of aluminum octahedra in MIL-53-TDC are trans-connected rather than cis-connected. We have selected to focus on MIL-53-TDC in this work rather than MIL-53, because MIL-53-TDC incorporates the bent ligand 2,5-thiophenedicarboxylic acid rather than the linear ligand terephthalic acid, making it more amenable to direct comparison with CAU-10 and MIL-160. The atom positions used to create the MIL-53-TDC structure in Figure 3.1 were reported by Tschense et al., while the other structures were drawn from cif files.\textsuperscript{12, 17, 19, 20}

CAU-10 has notable advantages for chemical separations relative to many other commonly studied MOFs. Foremost, CAU-10 is stable in water vapor, which is nearly ubiquitous in gas separations applications.\textsuperscript{21-23} This is in contrast to many other MOFs; one of the chief criticisms of MOFs for adsorption separations is their limited stability in the presence of water vapor. Secondly, CAU-10 is synthesized from aluminum salts and isophthalic acid, which are cheap and nontoxic relative to the requisite materials for synthesis of some other MOFs. We were inspired by the structural similarity of these MOFs (chains of aluminum octahedra connected by bent dicarboxylate ligands) to apply the relatively fast and low-temperature synthesis methods of CAU-10 to other frameworks.

In this work, we use the principles of isoreticular chemistry to synthesize a number of similarly structured CAU-10 MOFs using the same synthetic approach. Eight isoreticular CAU-10-X materials were successfully synthesized using this approach, including novel materials substituted at both the 4-position and 5-position in the aromatic ring of the isophthalic acid ligand. We also report, to the best of our knowledge, the first instance of a solvothermal synthesis of NOTT-300 excluding piperazine and nitric acid,
and at much lower temperature and shorter time than has been previously reported. MIL-160 is isostructural to CAU-10 save for the replacement of the isophthalic acid ligand in CAU-10 for 2,5-furandicarboxylic acid in MIL-160. MIL-53-TDC and MIL-160 were also synthesized using the same method. The various ligands employed in the syntheses are shown in Figure 3.2. We are particularly interested in the impact of functional group type and placement on resulting adsorption properties and present a detailed study of carbon dioxide, methane, and nitrogen adsorption in each material. The reported water stability of these materials and the variety of functional groups that can be added to the ligand make them attractive candidates for gas separations applications in humid environments.

3.2 Materials and Methods

3.2.1 Chemicals

Aluminum salts (Al₂(SO₄)₃, Al₂(SO₄)₃*18H₂O, AlCl₃*6H₂O, and Al(NO₃)₃*9H₂O) and isophthalic acid derivatives (isophthalic acid, 5-methylisophthalic acid, 5-aminoisophthalic acid, 5-hydroxyisophthalic acid, 5-fluoroisophthalic acid, 5-nitroisophthalic acid, 4-nitroisophthalic acid, 2,4-pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid, biphenyl-3,3’,5,5’-tetracarboxylic acid, 2,5-furandicarboxylic acid, and 2,5-thiophenedicarboxylic acid), methanol, and N,N-dimethylformamide (DMF) were procured from commercial sources (Sigma-Aldrich, Combi-Blocks, Alfa Aesar, and Acros Organics) and used without further purification.
3.2.2 Materials synthesis

For brevity, materials were synthesized with the ligands shown in Figure 3.2. CAU-10-5-H (1) was synthesized from a mixture of 856.3 mg Al$_2$(SO$_4$)$_3$ (2.50 mmol), 832.8 mg isophthalic acid (5.01 mmol), 5 g DMF, and 20 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 47 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air. The synthesis of the other CAU-10-X, MIL-53-TDC, and MIL-160 materials was performed analogously, and these syntheses are detailed in the supporting information.

NOTT-300 (10) was synthesized from a mixture of 228.4 mg Al(NO$_3$)$_3$·9H$_2$O (0.61 mmol), 49.9 mg biphenyl-3,3’,5,5’-tetracarboxylic acid (0.15 mmol), 1.00 g DMF, and 4.01 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.
3.2.3 Materials activation

After synthesis, the dried samples were collected into centrifuge tubes. They were solvent-exchanged by dispersing in methanol and soaking for 1 day, then they were centrifuged. After centrifugation, the methanol was decanted and replaced with fresh methanol. This soak-centrifuge process was repeated three times.

3.2.4 Experimental methods

3.2.4.1 Powder x-ray diffraction
Initial characterization by means of powder x-ray diffraction (PXRD) was done on a Malvern PANalytical Alpha-1 with X’Celerator detector using Cu Kα1 radiation (λ = 1.5418 Å). These scans were done at room temperature in ambient air. The diffraction patterns measured were compared to simulated patterns where available, as well as patterns in the literature where available to confirm the expected materials were present.

3.2.4.2 Surface area analysis

Adsorption isotherms for N\textsubscript{2} were measured at 77 K using a volumetric instrument (Quadrasorb by Quantachrome). Brunauer-Emmett-Teller (BET) surface areas were calculated over a range of 0.007 < P/P\textsubscript{0} < 0.035, as appropriate for ultramicroporous materials such as these.\textsuperscript{25} Prior to adsorption measurements, the samples were outgassed for 16 h under vacuum at 150 °C using a Quantachrome FloVac Degasser.

3.2.4.3 Pure component adsorption isotherms

Pure-component isotherms for carbon dioxide, methane, and nitrogen were measured at 298 K a volumetric instrument (3Flex by Micromeritics). All gases used for adsorption measurements were purchased from Airgas at Ultra-High Purity grade. Prior to adsorption measurements, the samples were outgassed for 16 h under vacuum at 150 °C using a Micromeritics Smart VacPrep.

3.2.4.4 Scanning electron microscopy

Scanning Electron Microscopy (SEM) images were collected on a Zeiss Ultra 60 FE-SEM instrument with a high-efficiency in-lens secondary electron detector at a working distance of 7-9 mm and accelerating voltage of 1.1-2.0 kV to mitigate charging of the
materials. Prior to SEM analysis, samples were applied to conductive carbon tape and treated with pressurized air to remove loosely attached particles to prevent damage to the SEM instrument.

3.3 Results and Discussion

3.3.1 Powder x-ray diffraction

PXRD was performed as an initial analysis to confirm similarity of the CAU-10 materials 1-9 to the previously reported PXRD patterns of the parent MOF CAU-10 (1), as well as to compare material 10 to the reported NOTT-300 PXRD pattern, material 11 to the reported MIL-53-TDC PXRD pattern, and finally material 12 to the reported MIL-160 PXRD pattern. Figure 3.2(a) shows powder diffraction patterns for all materials 1-5, as well as a simulated pattern from the reported cif for CAU-10 including water molecules. Each of these patterns show strong peaks at 8.3 and 15.0 degrees, closely matching the most prominent peaks in the simulated pattern. Where available, these materials show agreement with diffraction patterns measured by other authors.\textsuperscript{12,26,27} These materials have all been reported before, with the exception of CAU-10-5-F. However, Krüger et al. reported a mixed-linker version of CAU-10-5-H/F incorporating both isophthalic acid and 5-fluoroisophthalic acid ligands.\textsuperscript{28} All of these patterns appear to share some similarities to the hydrated CAU-10 pattern simulated from the available cif.\textsuperscript{22}
Figure 3.3: Powder X-ray diffraction patterns of all materials synthesized in this work, compared with patterns simulated from cif files where possible, including (a) materials 1-5, CAU-10 structures functionalized at carbon 5, (b) materials 6-9, CAU-10 structures functionalized with a nitro group at either carbon 5 or carbon 4, and heterocyclic CAU-10 structures, (c) NOTT-300 synthesized in the "CAU-style" reported in this work, and in the "piperazine" synthesis, and (d) MIL-53-10C and MIL-160 structures.

Figure 3.3(b) shows the powder diffraction patterns for materials 6-9, as well as a simulated pattern from the reported cif for CAU-10. To the best of our knowledge, this is the first report of materials 7 and 8, and the first example of a CAU-10 MOF functionalized at a position other than the 5-position on the isophthalic acid ligand. The diffraction pattern for material 6 shows more peak broadening than the other patterns. These patterns show peaks at 8.3 and 15.0 degrees, which match the most prominent
peaks simulated from the parent CAU-10 cif. The CAU-10 analogs synthesized with pyridine ligands show perhaps the most interesting powder diffraction patterns. While material 9 has a diffraction pattern similar to that of the parent MOF CAU-10, the other pyridine ligand material 8 has several notable differences from the diffraction pattern of the parent MOF. There is an absence of the peak at 8.2 degrees in material 8, and the appearance of a strong peak at 17.8 degrees. Material 9 has been synthesized before. Our powder diffraction pattern closely matches the one reported by Cadiau et al. (comparison in Figure A.7.

NOTT-300 synthesized in the manner reported by Yang et al. (labeled here as “piperazine”) yielded a powder diffraction pattern similar to that simulated from the reported cif, but with the inclusion of several extra peaks, especially those at 7.6 and 14.5 degrees. However, the CAU-10 style synthesis of NOTT-300 yielded a material with a closer match to the pattern simulated from the reported cif. Compared to the synthesis reported by Yang et al. (120 °C for 12 h vs 210 °C for 72 h), the “CAU-style” synthesis was conducted under milder conditions in shorter time and without the use of nitric acid or piperazine.

MIL-53-TDC synthesized by our approach shows a powder diffraction pattern which is, upon first inspection, not obviously similar to the pattern simulated from previously reported atomic positions. However, this pattern is similar to experimental measurements made by Tannert, as well as other authors. MIL-160 synthesized in the CAU-10 style has a very similar, although not totally identical diffraction pattern to the pattern simulated from the MIL-160 cif. It is possible that the extra peaks measured at 12°
and 12.5° are due to the water included in this structure, as the simulated pattern is generated from a sample devoid of water.

### 3.3.2 BET surface area

The surface areas calculated for each material using the BET method are shown in Error! Reference source not found.. CAU-10-5-H has a surface area consistent with what has been previously found (570 to 656 m²/g). Generally, bulkier ligands may give lower surface areas, though notable exceptions to this trend include 2 and 3, which have low BET areas due to measurement difficulty from slow equilibration. Materials 4 and 9 also incorporate relatively small ligands, but neither has measurable adsorption of nitrogen at 77 K, as shown in Figure 3.4. Materials 2-4 are those whose surface areas are difficult to measure at 77 K due to slow adsorption kinetics, which is consistent with previous reports\textsuperscript{12} although material 2 exhibits uptake of nitrogen near saturation pressure. Interestingly, material 9 has a higher BET surface area than the parent MOF CAU-10 despite incorporating a ligand which is of similar size to isophthalic acid. The reason for this is not readily apparent, and more detailed structural information may be needed to determine the cause for this relatively high surface area. However, it is possible that material 9 forms a structure with aluminum octahedra chains with spacing that falls between that of CAU-10 (10.165 Å, shown in Figure 3.1) and MIL-160 (10.647 Å). These otherwise similar MOFs show a large difference in surface area (632 vs 1129 m²/g).
Table 3-1: BET surface area of aluminum MOFs studied in chapter 3 calculated from nitrogen physisorption at 77 K.

<table>
<thead>
<tr>
<th>Number</th>
<th>MOF</th>
<th>BET Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CAU-10-5-H</td>
<td>632</td>
</tr>
<tr>
<td>2</td>
<td>CAU-10-5-CH₃</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>CAU-10-5-NH₂</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td>CAU-10-5-OH</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>CAU-10-5-F</td>
<td>590</td>
</tr>
<tr>
<td>6</td>
<td>CAU-10-5-NO₂</td>
<td>426</td>
</tr>
<tr>
<td>7</td>
<td>CAU-10-4-NO₂</td>
<td>493</td>
</tr>
<tr>
<td>8</td>
<td>CAU-10-2,4-pydc</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>CAU-10-3,5-pydc</td>
<td>844</td>
</tr>
<tr>
<td>10</td>
<td>NOTT-300</td>
<td>1172</td>
</tr>
<tr>
<td>11</td>
<td>MIL-53-TDC</td>
<td>1147</td>
</tr>
<tr>
<td>12</td>
<td>MIL-160</td>
<td>1129</td>
</tr>
</tbody>
</table>

Figure 3.4: Nitrogen physisorption at 77 K measured on select materials synthesized in this work with lines to guide the eye.
3.3.3  Pure-component adsorption isotherms

Adsorption isotherms for carbon dioxide, methane, and nitrogen measured at 298 K are shown in Fig. 5. In the region of 0-100 mbar shown in Figure 3.5(a), it is evident that the MOFs with heterocyclic ligands or polar functional groups tend to have the highest carbon dioxide adsorption. This is consistent with the idea that at very low pressures, adsorption behavior is dominated by guest-host interactions, which for carbon dioxide we expect to be strong for hosts with polar features. Ligand functionalization has been shown to dominate adsorption behavior in MOFs at low pressure, while surface area dictates loadings at higher pressure.\textsuperscript{11, 31} In the ultramicroporous frameworks studied here, this low pressure regime seems to be restricted to pressures even lower than other larger pore frameworks, and surface area becomes the dominant factor in explaining carbon dioxide adsorption behavior over 100 mbar. At low pressure (100 mbar) we find the highest carbon dioxide uptake in materials \textsuperscript{12, 11, 3}. These include the CAU-10 materials containing the amine functionalized ligand (3), as well as the MOFs containing heterocyclic ligands 2,5-thiophenedicarboxylic acid (11) and 2,5-furandicarboxylic acid (12). Our findings are consistent with the hypothesis that polar moieties lead to higher carbon dioxide adsorption at very low pressures.

While functional groups are the dominant factor in determining adsorption of carbon dioxide at lower pressures, surface area of these MOFs appear to be the dominant factor in determining the adsorption of carbon dioxide at higher pressures. Materials \textsuperscript{6} and \textsuperscript{10} form an illustrative example of a pair of adsorbents whose carbon dioxide loading is nearly identical below 100 mbar, but at 1000 mbar, the loading of \textsuperscript{10} is double that of \textsuperscript{6}. The increased loading of \textsuperscript{10} relative to \textsuperscript{6} at high pressure can be attributed to the greater
surface area of 10. Pore volume typically dictates adsorption behavior at saturation, but the isotherms for each of these sorbate/adsorbent pairs show that saturation has not been reached at the pressure ranges examined. The materials with the highest BET areas also have the highest carbon dioxide uptake at 1000 mbar. These include materials 1 and 12, which contain ligands without polar features which might typically be associated with increased adsorption of carbon dioxide. With the above we can clearly see that over the pressure range 100—1000 mbar, the adsorption capacity mirrors the surface area rather than chemical composition of the ligands with polar groups.

Figure 3.5: Pure component adsorption measured on select materials synthesized in this work at 298 K (a) Carbon dioxide adsorption from 0-100 mbar, (b) Carbon dioxide adsorption from 0-1000 mbar, (c) Methane adsorption from 0-100 mbar, and (d) Nitrogen adsorption from 0-1000 mbar, with lines included to guide the eye.
The shapes of the carbon dioxide isotherms for 1 and 10 are less sharp than the other materials, which is likely due to a combination of the two factors discussed to this point: first, neither contains a polar functionality to introduce high affinity at low pressure, and second, both have high surface areas. Meanwhile, the sharpest carbon dioxide isotherm predictably belongs to 3, whose amine group introduces high affinity for carbon dioxide at low pressure, but fills a fraction of the already small pore volume at high pressure. These factors result in higher carbon dioxide loading at low pressure, but lower carbon dioxide loading at high pressure, compared to the parent material CAU-10.

Unlike carbon dioxide adsorption, methane adsorption behavior is not a strong function of the BET surface area. Though there is no easily discernable relationship between functional group identity and methane adsorption, the materials with the highest methane adsorption across most of the pressure range tested are 1 and 2. This is consistent with the idea that a lack of large, polar functional groups may be conducive to increased methane adsorption. Instead, functional groups that are both nonpolar and small give rise to favorable van der Waals interactions with methane which dominate adsorption behavior at low pressure. Since these groups are not bulky, a relatively high surface area is maintained and leads to higher adsorption loadings at pressures approaching 1 bar. The trends observed for methane adsorption largely carry over to nitrogen adsorption. Again, the highest adsorption loading occurs in materials 1 and 2. Adsorption of nitrogen at 298 K presents a small measurement difficulty: slow equilibration of adsorption at pressures less than 100 mbar may have contributed to the appearance of a slight inflection around 100 mbar in nitrogen isotherms.
We hypothesized that substituting a functional group on carbon 4 rather than carbon 5 could render the already small pore of CAU-10 slightly more accessible to adsorbates. This proved to be true in the case of nitro-functionalized CAU-10 MOFs, as shown in Fig. 6. When compared to CAU-10-5-NO$_2$ (6), CAU-10-4-NO$_2$ (7) showed significantly higher loading of both carbon dioxide and methane across all pressures at 298 K that cannot be explained by BET surface area differences alone (493 m$^2$/g compared to 426 m$^2$/g). We believe that this difference can be attributed to greater accessibility of the pore volume in 7, where the bulky nitro group is directed towards the side of the pore rather than the center of the pore as it is in 6.

![Figure 3.6: Pure component adsorption at 298 K on pairs of materials synthesized with the same functionality at different positions in the frameworks, (a) Carbon dioxide adsorption from 0 to 1000 mbar, (b) Methane adsorption from 0 to 1000 mbar](image)

However, placing a heteroatom at a different position in the ligand did not give the same result. Materials 8 and 9, synthesized with 2,4-pyridinedicarboxylic acid and 3,5-pyridinedicarboxylic acid respectively, showed an unanticipated but much greater difference in adsorption behavior than the pair 6/7. The use of 2,4-pyridinedicarboxylic acid...
acid in this synthesis resulted in a product (8) with nearly zero adsorption of any species at 298 K. The combination of differences in the diffraction pattern and adsorption measurements indicate that material 8 may form a nonporous structure, or a structure whose pores are not fully accessible to adsorbates at 298 K.

Henry’s law selectivity was calculated from isotherms measured at 298 K. Isotherms were fit with the Langmuir isotherm model and the slope as pressure approaches zero was calculated to give Henry’s constants. Ratios of Henry’s constants are summarized in Table 3-2.

Table 3-2: Henry’s law selectivity for adsorption on aluminum MOFs studied in chapter 3 at 298 K.

<table>
<thead>
<tr>
<th>Number</th>
<th>MOF</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt;/CH&lt;sub&gt;4&lt;/sub&gt;</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt;/N&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CAU-10-5-H</td>
<td>4.6</td>
<td>27.8</td>
<td>6.0</td>
</tr>
<tr>
<td>2</td>
<td>CAU-10-5-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.0</td>
<td>14.6</td>
<td>4.8</td>
</tr>
<tr>
<td>3</td>
<td>CAU-10-5-NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.8</td>
<td>38.8</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>CAU-10-5-OH</td>
<td>4.3</td>
<td>20.2</td>
<td>4.7</td>
</tr>
<tr>
<td>5</td>
<td>CAU-10-5-F</td>
<td>2.8</td>
<td>8.5</td>
<td>3.1</td>
</tr>
<tr>
<td>6</td>
<td>CAU-10-5-NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.7</td>
<td>31.1</td>
<td>5.5</td>
</tr>
<tr>
<td>7</td>
<td>CAU-10-4-NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.2</td>
<td>38.3</td>
<td>6.2</td>
</tr>
<tr>
<td>9</td>
<td>CAU-10-3,5-pydc</td>
<td>9.5</td>
<td>53.3</td>
<td>5.6</td>
</tr>
<tr>
<td>10</td>
<td>NOTT-300</td>
<td>7.1</td>
<td>33.2</td>
<td>4.7</td>
</tr>
<tr>
<td>11</td>
<td>MIL-53-TDC</td>
<td>10.3</td>
<td>55.6</td>
<td>5.3</td>
</tr>
<tr>
<td>12</td>
<td>MIL-160</td>
<td>10.5</td>
<td>44.1</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Because material 8 had extremely low loadings of all adsorbate species in the Henry’s law region, measurement of adsorption at very low pressures did not yield data suitable for Henry’s constant calculation. Thus, material 8 is omitted from the table. The materials which showed the highest Henry’s law selectivity for carbon dioxide over methane are 12, 11, and 9, which all contain heterocyclic ligands. Interestingly, the amine
functionalized material 3 has only the fifth-highest selectivity for carbon dioxide over methane, and the fourth-highest selectivity for carbon dioxide over nitrogen. The same three materials showed the highest Henry’s law selectivity for carbon dioxide over nitrogen. It is apparent that the MOFs containing heterocyclic ligands show higher Henry’s constant selectivity for carbon dioxide than do the MOFs containing polar groups (-NH₂, -OH, -NO₂) substituted onto isophthalic acid. While the selectivities for carbon dioxide over other species are in some cases relatively high, the carbon dioxide capacities observed up to 1 bar are not particularly high.

3.4 Mixture adsorption

Adsorption behavior of a carbon dioxide/methane mixture on the MOF CAU-10 was investigated using the MC GAS instrument described in detail in Chapter 4 of this work. The results of carbon dioxide/methane mixture adsorption experiments conducted on CAU-10 are listed in Table 3-3. All quantities adsorbed q are listed in values of mmol/g. As expected, CAU-10 selectively adsorbs carbon dioxide over methane. The observed selectivities range from 7 to 14. While low capacities for carbon dioxide may prevent CAU-10 from being useful in capturing large quantities of carbon dioxide from concentrated streams, these data show that carbon dioxide selectivity exists even for the parent framework, let alone any of the functionalized MOFs described in this chapter. Obvious future extensions of this work could include screening of other aluminum MOFs in this chapter for aptitude in removal of carbon dioxide from relevant streams, especially at low pressure where the small pore volume of these MOFs may be a boon rather than a hindrance as we observe at high pressure.
### Table 3-3: Mixture adsorption loadings and compositions for adsorption of carbon dioxide and methane on CAU-10 at 298 K.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>P (bar)</th>
<th>y CO₂</th>
<th>x CO₂</th>
<th>q CO₂</th>
<th>q CH₄</th>
<th>q Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.06</td>
<td>0.070</td>
<td>0.348</td>
<td>0.664</td>
<td>1.245</td>
<td>1.909</td>
</tr>
<tr>
<td></td>
<td>4.41</td>
<td>0.060</td>
<td>0.475</td>
<td>1.416</td>
<td>1.568</td>
<td>2.985</td>
</tr>
<tr>
<td></td>
<td>7.18</td>
<td>0.080</td>
<td>0.482</td>
<td>1.737</td>
<td>1.869</td>
<td>3.606</td>
</tr>
<tr>
<td></td>
<td>10.08</td>
<td>0.091</td>
<td>0.490</td>
<td>1.985</td>
<td>2.069</td>
<td>4.054</td>
</tr>
</tbody>
</table>

### 3.5 Conclusions

This investigation shows that four structurally similar aluminum-based MOFs can be synthesized according to the same procedure by varying only the organic ligand and aluminum source. In one case, this allows the synthesis to complete in one third the time and at a temperature 90 °C lower than has been previously reported. The addition of functionalized isophthalic acid ligands to the synthesis led to the formation of three novel CAU-10 MOFs, using an isoreticular synthesis approach. We have evaluated adsorption behavior of all of the MOFs synthesized in this work and found that at very low pressures, the MOFs with heterocyclic ligands have the greatest Henry’s constant selectivity for carbon dioxide over methane and nitrogen, followed by MOFs with polar functional groups. At higher pressures, carbon dioxide loadings were strongly associated with the BET surface area. Comparison of CAU-10 MOFs substituted with a nitro group at different positions on the ligand showed that positioning the nitro group at the side of the pore rather than the center resulted in increased loading of all adsorbates over the studied pressure range up to 1 bar.
3.6 References


CHAPTER 4. MULTI-COMPONENT GAS ADSORPTION SYSTEM (MC GAS)

This chapter is an adaptation of the article “An automated multi-component gas adsorption system (MC GAS)” which appears in the 92nd volume of the journal *Review of Scientific Instruments*, beginning on page 054102. This material is reproduced with permission from the publisher. The knowledge gap on adsorption of complex mixtures in the literature relative to single component data represents a persistent obstacle to developing accurate process models for adsorption separations. The collection of mixed gas adsorption data is an imminent need for improved understanding of the behavior of adsorbent systems in these diverse adsorption applications. Current approaches to understanding mixture adsorption using predictive theories based on pure component adsorption experiments often fail to capture the behavior of more complex, non-ideal systems. In this work, we present an automated volumetric instrument for the measurement of mixed gas adsorption isotherms. This instrument was validated by comparison to other in-house instruments and data available in the literature, and the binary adsorption measurements were found to be thermodynamically consistent. The automation of this instrument allows for rapid collection of high-quality mixture adsorption data.

4.1 Introduction

All adsorption separations processes involve the adsorption of a mixture of gases, including carbon capture, gas sweetening, oxygen concentration, olefin/paraffin
separation, among others. However, adsorption of mixtures is poorly understood. A recent report on separations science from the National Academies of Sciences, Engineering, and Medicine identifies understanding behavior of complex systems as the biggest challenge in separation science. For adsorption separations, this challenge is apparent as adsorbent materials rarely perform as desired in the presence of multicomponent mixtures, especially when components span a wide range of compositions, or highly dilute or highly concentrated species. Though great advances have been made in increasing the adsorption capacity for a target species, the ability to predict adsorption behavior in complex systems remains an outstanding requirement to implement robust adsorption separations processes. This sentiment has been echoed for decades by researchers across the field of adsorption science.

Currently the study of adsorbents for gas separations is dominated by the use of pure component adsorption data to predict how a mixture might be adsorbed by an adsorbent. A number of theories and predictive methods have been developed to predict adsorption equilibrium of mixtures from single component adsorption data, most notably the Ideal Adsorbed Solution Theory (IAST). IAST is becoming more widely used every year, as evidenced by the rapidly increasing number of citations of Myers and Prausnitz’s 1965 work. In spite of its utility, IAST is not a perfect predictor of how gas mixtures will be adsorbed. A compilation of several dozen works using mixture adsorption experiments to assess IAST predictions showed that IAST is not always accurate, and in many cases results in errors greater than 100% in predicting selectivity for adsorption of one component from a mixture. This is consistent with findings by other authors that IAST tends to provide poor predictions of mixture adsorption for adsorbents with heterogeneous
surfaces and for mixtures of molecules whose sizes, polarities, and polarizabilities vary greatly.\textsuperscript{18, 19}

Increased experimental capacity for multicomponent adsorption measurements will allow for faster identification of adsorbents which are selective for desired components even in mixtures whose composition varies widely. Furthermore, greater experimental capacity brings with it the opportunity to improve understanding of the fundamental phenomena that drive behaviors of multicomponent adsorbent systems. An obvious benefit of a better fundamental understanding of multicomponent adsorption is the opportunity to validate new predictive models for multicomponent adsorption, especially for systems which have not yet been well studied.\textsuperscript{13}

The current state of the art in the study of gas adsorption is strong in development of novel materials with high capacities for target adsorbates, but weaker in the study of mixture adsorption and especially lacking in high-quality experimental measurement of mixture adsorption. Experimental measurement of mixture adsorption is nontrivial, and has represented a challenge for decades in the study of adsorption separations.\textsuperscript{20} Myriad measurement techniques using different principles have been used by groups spread throughout the world, with no consensus method emerging. Most methods of measurement are labor-intensive and difficult to automate. Moreover, no commercially available instrument has gained widespread popularity. The vast majority of measurements are made using home-built instrumentation, which can be costly as well as time-consuming to build and validate.
There are two broad categories of experimental systems: open systems and closed systems.\textsuperscript{14} Open systems generally involve flowing a gas mixture through a bed of adsorbent while monitoring the composition and flow rate of the feed and effluent streams. The system is considered “open” because gas moves in and out of the system during the measurement. The breakthrough method is the most popular open system used to study mixture adsorption.\textsuperscript{21-27} Open systems also include concentration pulse chromatography,\textsuperscript{28-33} zero-length column,\textsuperscript{34-36} differential column method,\textsuperscript{37} and others.\textsuperscript{38-40} Open systems require careful determination of dead volume or holdup time, and at times require more involved analysis of experimental data to determine equilibrium loadings during an adsorption experiment.

Closed systems do not allow gas to enter or leave the system during adsorption experiments. Gas is discretely dosed into this closed system and allowed to contact the adsorbent. There are many types of closed systems. The most popular is the volumetric-chromatographic system, which evolved from volumetric systems introduced as early as 1917.\textsuperscript{41-49} Other closed systems make use of the gravimetric method,\textsuperscript{50-54} densimetric method,\textsuperscript{55-58} isotope exchange technique,\textsuperscript{59, 60} and more.\textsuperscript{61-63} Closed systems present a different set of challenges from open systems, but a perhaps underappreciated challenge is slow measurement equilibration in the absence of a pump to circulate gas through the adsorption loop. Adsorption equilibration can take days or weeks in the absence of a circulation pump like the one included in the system described in this work. In addition, slow and labor-intensive operation of most closed systems mean that this group of techniques can be extremely time-consuming to operate manually. One of the principal advantages of the system described in this work is that it is automated in full; after the
adsorbent is activated, LabVIEW code allows the measurement to run completely automatically.

The variety of techniques that exist to study mixture adsorption reflects the fact that this measurement is inherently difficult. Many approaches have been tried without any one emerging as the clear favorite of the adsorption community. This is in large part because automation of any of these methods tends to be difficult, limiting each to slow, manual collection of data. A key opportunity for innovation in mixture adsorption measurement is the development and adoption of truly automated experimental systems. Much of the lack of existing experimental mixture adsorption data may be attributed to the labor-intensive nature of data collection for most existing instruments. Public availability of technical detail and validation processes for original mixture adsorption instruments is limited at best, and this lack of information in the literature contributes to a high barrier to entry in measuring adsorption of mixed gases. In this work, we aim to describe, in detail sufficient to facilitate replication, an automated instrument designed to measure adsorption of gas mixtures. We anticipate that this will reduce barriers to the construction and use of similar instruments to gather mixture adsorption data to address a decades-old deficit in the study of adsorption.

4.2 Experimental

4.2.1 Instrument setup

4.2.1.1 Manifold
A schematic of the Multi-Component Gas Adsorption System (MC GAS) instrument developed in this work is illustrated in Figure 4.1. The bulk of this instrument consists of a stainless steel manifold composed of Swagelok tubing, valves, and fittings. The operation of this manifold and other parts of this system are automated through LabVIEW. The manifold is centered on a reference cell and adsorption loop, which are separated by a needle valve (Swagelok SS-ORS2) and ball valve (Swagelok SS-41GS1). The needle valve is left only slightly open so as to restrict the rate of flow between the reference cell and adsorption loop when the ball valve is open. The reference cell is an empty stainless steel cell (Swagelok 316L-HDF4-150). The adsorption loop contains an identical empty cell for the purpose of increasing the free volume of the adsorption loop. In addition to the empty cell, the adsorption loop also contains a smaller stainless steel sample cell (Swagelok 304L-HDF2-40) which can be filled with adsorbent pellets. This sample cell is connected to the adsorption loop on either end by VCR fittings, which contain 20 µm fritted gaskets (Swagelok SS-4-VCR-2-20M) to ensure the solid adsorbent material does not leave the sample cell during the adsorption measurement. All three of these steel cells (reference cell, empty cell, and sample cell) are submerged in a water bath. The total internal volume of the reference cell is 154.48 cm$^3$, while that of the adsorption loop devoid of adsorbent is 200.48 cm$^3$. Where possible, all tubing outside of the thermostatic bath is of 1/16” (1.588 mm) outer diameter to minimize the volume of the reference cell and adsorption loop which is outside of this bath. The flexibility of this tubing allows the sample cell to be shifted from the water bath to the activation stage without disconnecting the sample cell from the adsorption loop.
4.2.1.2 Pressure transducers and thermocouples

Connected to the reference cell is a pressure transducer (Omega PX01K1-1KGI) capable of measuring 0 to 1,000 psig (1 to 70 bar) accurate to ± 0.05%. The adsorption loop also contains a pressure transducer (Omega PX 409-USBH) capable of measuring 0 to 750 psia (0 to 52 bar) accurate to ± 0.08%. The temperature in the water bath is monitored by two type J thermocouples (Omega and PolyScience). The Polyscience thermocouple provides feedback to the water bath controller, while the Omega thermocouple provides data to LabVIEW which will later be used in equation of state calculations.

4.2.1.3 Temperature control
During adsorption measurements, all three steel cells are submerged in a water bath whose temperature is controlled by a heated/refrigerated recirculator (PolyScience AD07R-40-A11B) and varies less than ±0.1 K during a 24 hour period. During adsorbent activation, the sample cell holding the adsorbent pellets is removed from the water bath and clamped in place on an activation stage. This cell, along with a third type J thermocouple, is then wrapped in heating tape (Omega) and an insulation jacket. The cell is heated with heating tape, while the thermocouple provides feedback to a virtual PID controller in LabVIEW. The temperature varied less than ±0.5 K from the set point during the 12 hour activation periods at 473 K used in this work.

4.2.1.4 Pneumatic actuators

All ball valves in the system are driven by pneumatic actuators (Whitey Co. 151SR), which are controlled through LabVIEW using solenoid valves (SMC SQ1131NY-5-C4-Q). This is conducive to automation of the system.

4.2.1.5 Circulation pump

A circulation pump (Eldex Optos 3HM) is included to recirculate gas through the adsorption loop and reduce time necessary to reach equilibration in mixture adsorption experiments. This pump can be turned on and off through LabVIEW. Typical mixture adsorption experiments use a flow rate of 10 mL/min and an equilibration time in excess of two hours. The pump operates on a positive displacement, reciprocating piston principle. The seal around the reciprocating piston is a possible source of leaks, and this concern could be avoided by using a welded metal bellows pump instead, though this may reduce the operating pressure of the instrument as the bellows can be limiting. If a reciprocating
piston pump is chosen by future investigators, care should be taken to check this seal regularly for leaks and the user should be prepared to replace the seal as a consumable item. While the volume of displacement by the piston is small relative to the volume of the adsorption loop (0.41 cm$^3$ vs ~200 cm$^3$), this reciprocation gives rise to small but measurable pressure fluctuations in the system. These fluctuations must be addressed in order to ensure collected data are of the highest accuracy for use in equation of state calculations. To address this problem, pressure data are averaged over two minutes (many cycles of piston reciprocation) before use in equation of state calculations so as to ensure this 0.41 cm$^3$ piston displacement change in volume does not impact calculations.

4.2.1.6 Vacuum pump

An Edwards RV3 rotary vane pump is used to evacuate the system. This pump is capable of evacuating the system down to approximately 0.1 mbar total pressure.

4.2.1.7 Gas chromatograph

Built into the adsorption loop is a small sample loop with volume approximately 20 µL. The contents of this sample loop can be injected to a gas chromatograph (GC), model Shimadzu GC-2014 for composition analysis. The detector is a thermal conductivity detector (TCD) (Shimadzu TCD-2014). The chromatograph is equipped with a 6-port sampling valve (Valco 14N-0179V) controlled with electronic actuator (Valco) which allows for automation of composition sampling. For the experiments in this work, the chromatography column used was 2 m in length with 2 mm inner diameter and packed with carbon molecular sieve (Restek ShinCarbon ST 80/100 2m 2mmid). During the experiments in this work, the column was kept at 408 K while the TCD was kept at 418 K.
4.2.1.8 Automation

Automation of the instrument is done primarily using LabVIEW code and National Instruments hardware as shown in Figure 4.2. LabVIEW is used to record temperature data (through National Instruments NI-9211) and pressure data (National Instruments NI-9203), control valve positions (National Instruments NI-9375), operate virtual proportional–integral–derivative (PID) controller for heat tape, and trigger Windows scripts to operate Shimadzu software. LabVIEW also monitors pressure to determine when equilibration has been reached in the adsorption loop after gas has been dosed to the adsorbent.

Figure 4.2: Schematic of how input and output are measured and controlled through LabVIEW.

Windows scripting is done through AutoHotKey, and functions to operate the Shimadzu LabSolutions software which controls the GC. When equilibrium is reached in the adsorption loop, LabVIEW calls a simple Windows script which opens LabSolutions.
and runs a pre-set injection program which allows for automated checking of the composition of gas in the adsorption loop.

The LabVIEW software operating MC GAS steps through a list of instructions during each experiment. Instructions controlling valve positions, temperature, and GC sampling are among those included in this list. A typical experiment can include thousands to tens of thousands of instructions. The list of instructions dictating the steps in each experiment is generated using Visual Basic for Applications (VBA) code based on a simple list of input variables like activation time and temperature, minimum equilibration time, and others. VBA code is used again after temperature, pressure, and composition data have been collected to iteratively solve the Peng-Robinson equation of state for mixtures to solve the molar volume of the gas mixture in the adsorption loop to determine the number of moles of each component in the gas phase and in the adsorbed phase.

4.2.1.9 Range of operation

The operating ranges and conditions for MC GAS are summarized in Table 4-1. This instrument has been optimized for use with adsorbent samples approximately 5 g in mass, though larger sample masses may be required for testing adsorption of weakly adsorbing components, especially at low partial pressures. The volume of the 40 cm³ sample cell limits the maximum amount of sample that can be used, while the minimum sample mass is limited by the sensitivity of the GC and the adsorption affinity for each species as discussed in Section B.4 Calculation S3: MC GAS Sample Mass Requirement.
Table 4-1: Range of operating conditions available on MC GAS as described in chapter 4.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Operating Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure during activation</td>
<td>&lt; 0.0001 bar</td>
</tr>
<tr>
<td>Pressure during adsorption</td>
<td>0.1 – 20 bar</td>
</tr>
<tr>
<td>Temperature during activation</td>
<td>Tested up to 523 K</td>
</tr>
<tr>
<td>Temperature stability during activation</td>
<td>±0.5 K</td>
</tr>
<tr>
<td>Temperature during adsorption</td>
<td>253-333 K</td>
</tr>
<tr>
<td>Temperature stability during activation</td>
<td>±0.1 K</td>
</tr>
<tr>
<td>Adsorption loading of each component</td>
<td>≥ 0.01 mmol/g</td>
</tr>
<tr>
<td>Adsorbent mass</td>
<td>~5 g</td>
</tr>
</tbody>
</table>

4.3 Calibration

Calibration measurements must be made to ensure that the internal volume of the system is well known and the GC is properly calibrated to measure the composition of the mixture to be used in adsorption experiments.

4.3.1.1 Free volume measurement

The free volume of the reference cell and the adsorption loop must be known very precisely so as to be able to calculate the number of moles of gas present in each of these volumes during adsorption experiments. This can be done by evacuating both the reference cell and the adsorption loop, then filling the reference cell to a known pressure with a non-adsorbing gas, such as helium. Both volumes are held at 298 K in the water bath during this measurement, and no adsorbent is loaded into the adsorption loop. It is reasonable to assume that helium does not adsorb on the internal surfaces in the instrument at 298 K.\(^{44}\)\(^{46}\) Once the reference cell has been filled and the adsorption loop remains evacuated, the pressure in the reference cell is recorded. Then the reference cell is opened to the adsorption
loop and the pressure is recorded again. This measurement gives the ratio of the volume of the reference cell to that of the reference cell plus the adsorption loop. This measurement is repeated several times.

Assuming ideal gas behavior, we find that charging the reference cell with helium to $P_0$ and then opening the reference cell to the adsorption loop will result in final pressure $P_1$. With the additional assumption that the number of moles of helium gas does not change, we can write equation 1. This equation can be rearranged to equation 2, which gives the ratio of the volume of the reference cell to that of the reference cell plus the adsorption loop. All variables are defined in Table B-1.

$$P_0V_{RC} = n_0RT = P_1(V_{RC} + V_{AL}) \quad (1)$$

$$\frac{V_{RC}}{V_{RC} + V_{AL}} = \frac{P_1}{P_0} \quad (2)$$

After expanding helium from the reference cell into the empty and evacuated adsorption loop, the adsorption loop is packed with glass beads of known volume, and the helium expansion is repeated. This measurement gives the ratio of the volume of the reference cell to that of the adsorption loop filled with a known volume of glass beads. This gives two equations (2 and 4) with two unknowns ($V_{RC}$ and $V_{AL}$) which can be solved simultaneously to determine the volume of both the reference cell and the adsorption loop.

$$P_2V_{RC} = n_1RT = P_3(V_{RC} + V_{AL} - V_{beads}) \quad (3)$$
\[
\frac{V_{RC}}{V_{RC} + V_{AL} - V_{beads}} = \frac{P_3}{P_2}
\]  

(4)

Once the volume of the reference cell is known, this experiment can be repeated with adsorbent loaded into the adsorption loop to give the free volume in the adsorption loop.

\[
P_4 V_{RC} = n_2 RT = P_5 (V_{RC} + V_{AL} - V_{adsorbent})
\]  

(5)

\[
\frac{V_{RC}}{V_{RC} + V_{AL} - V_{adsorbent}} = \frac{P_5}{P_4}
\]  

(6)

4.3.1.2 GC Calibration

Before this system can be used to measure the adsorption of gas mixtures, it must be capable of determining the composition of gas in the head space of the adsorption loop. This is done using a GC. This GC is calibrated using mass flow controllers (MKS PFC-50 \( \pi \)MFC) to generate mixed streams of gases which are collected in a tube and then injected into the GC. The stated accuracy of these mass flow controllers is ±0.2% of full scale for the flow rates used in calibration (<20% full scale). The GC peaks associated with each species are integrated for a variety of gas compositions, and the ratio of these GC peak areas is plotted against the molar composition of the gas from the mass flow controllers to form a calibration curve. The mass flow controllers used to generate the calibration mixtures are checked for accuracy by sampling their output with a mass spectrometer (Hiden DSMS HAL 201) and comparing main MS peak intensities for each species \((m/z = 16 \text{ for methane and } m/z = 28 \text{ for ethane})\).
4.4 Single component adsorption measurement

A typical single component adsorption measurement includes many of the steps necessary for a mixture adsorption measurement, so it is helpful to start with an understanding of this simpler process before moving on to the procedure for a mixture adsorption measurement. Each experiment can be broken into four steps: sample activation, free volume measurement, isotherm measurement, and finally use of an equation of state to convert pressure, volume, and temperature data (so-called “PVT” data) into excess amounts adsorbed.

4.4.1.1 Activation

Although the sample can be activated in situ, it is not possible to determine the dry mass of the sample in situ. To determine the dry mass of adsorbent used, approximately 5 grams of adsorbent pellets are first activated by heating under vacuum in a vacuum oven (Fisherbrand Isotemp 280A) for 24 hours and then weighed to determine their dry mass. Once the dry mass has been determined, the adsorbent is loaded into the sample cell of the instrument described in this work. The sample cell is clamped to the activation stage, where the sample cell and a thermocouple are wrapped in heating tape and then covered with an insulating jacket. The sample is then activated in situ under heat and vacuum. A typical activation might run for 12 hours at 473 K.

4.4.1.2 Free volume measurement

After activation, the free volume in the adsorption loop must be measured to ensure collection of high quality PVT data. This is done using the same helium expansion method
outlined above. The reference cell is charged with helium, which is then expanded into the adsorption loop. This is repeated ten times to ensure precision.

4.4.1.3 Isotherm measurement

Single component adsorption is measured according to the well-known pressure decay principle. First, gas is dosed to pressure $P_0$ into the reference cell, which has volume $V_{RC}$. The volume of this cell is well-known, and the pressure and temperature of this gas are recorded. This allows the use of the Peng-Robinson equation to calculate the number of moles of gas in the reference cell. The reference cell is then briefly opened to the adsorption loop before being closed again. As time passes, gas adsorbs on the adsorbent in the adsorption loop, and the pressure is observed to decay from its initial maximum. The system is allowed to equilibrate for a minimum of one hour, and for sufficient time that the pressure has stopped changing (rate of decrease less than 10 mbar/h). At this point, PVT data are recorded for both the reference cell and the adsorption loop. This allows calculation of number of moles of gas in both volumes. The number of moles adsorbed at the pressure in the adsorption loop can be taken to be the number of moles that is “missing” from the gas phase. This is the first point of the isotherm. Then, the reference cell is charged to a higher pressure and the process is repeated several times to gather points for the rest of the isotherm.

Beginning with the step of filling the reference cell to pressure $P_0$, one can use the Peng-Robinson equation in conjunction with a mole balance for each step of dosing gas to the adsorption loop and allowing time for equilibration. First, the Peng-Robinson equation
is iteratively solved for $V_{m0}$, the molar volume of gas in the reference cell.\textsuperscript{65} This equation is chosen for its mathematical simplicity.

$$P_0 = \frac{RT}{V_{m0} - b} - \frac{a}{V_{m0}(V_{m0} + b) + b(V_{m0} - b)}$$  \hspace{1cm} (7)

Here, $a$ and $b$ are empirical constants specific to the adsorbate gas and differ in value for each gas used in this work:

$$a = 0.45724\left(\frac{R^2T^2_c}{P_c}\right)\alpha$$  \hspace{1cm} (8)

$$b = 0.07780\left(\frac{RT_c}{P_c}\right)$$  \hspace{1cm} (9)

Where

$$\alpha = (1 + m(1 - T_r^{1/2}))^2$$  \hspace{1cm} (10)

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2$$  \hspace{1cm} (11)

Where $\omega$ is defined as

$$\omega = -\log_{10}(P_r^*) - 1, \text{ at } T_r = 0.7$$  \hspace{1cm} (12)

Dividing the molar volume by the volume of the reference cell gives the number of moles in the reference cell, $n_0$.

$$n_0 = \frac{V_{RC}}{V_{m,RC,0}}$$  \hspace{1cm} (13)
This gives the initial number of moles charged into the reference cell. After the reference cell is opened to the adsorption loop and the system is allowed to equilibrate, some moles of gas remain in the reference cell, some move to the adsorption loop, and some are adsorbed onto the adsorbent. This mole balance is as follows:

\[
    n_1 = \frac{V_{RC}}{V_{m,RC,1}} + \frac{V_{AL}}{V_{m,AL,1}} + n_{ads}
\]  

(14)

There is no reaction in the system, so the number of moles of adsorbate remains constant, and it can be stated that:

\[
    \frac{V_{RC}}{V_{m,RC,0}} = \frac{V_{RC}}{V_{m,RC,1}} + \frac{V_{AL}}{V_{m,AL,1}} + n_{ads}
\]  

(15)

The Peng-Robinson equation can be solved for \( V_{m0} \), \( V_{m1} \), and \( V_{m2} \) using pressure and temperature data. The volumes \( V_{RC} \) and \( V_{AL} \) are known from the free space measurement. Therefore, equation 15 allows for the solution of the number of moles adsorbed the first time adsorbate is dosed to the adsorbent. For subsequent dosing of more adsorbate to collect more isotherm points, this equation may be modified to include the differential number of moles in each volume:

\[
    \left( \frac{V_{RC}}{V_{m,RC,0}} - \frac{V_{RC}}{V_{m,RC,1}} \right) = \left( \frac{V_{AL}}{V_{m,AL,1}} - \frac{V_{AL}}{V_{m,AL,0}} \right) + \left( n_{ads,1} - n_{ads,0} \right)
\]  

(16)

Equation 16 reduces to equation 15 in the case that \( V_{m,AL,0} \) approaches infinity and \( n_{ads,0} \) approaches zero, which is true when the adsorption loop is evacuated and the adsorbent is clean. Equation 16 is solved for \( n_{ads,1} \) for each point in the isotherm.
4.5 Binary adsorption measurement

The procedure for measurement of binary mixture adsorption is very similar to that for single component adsorption. However, additional complexity arises from the needs to circulate gas over the adsorbent to achieve equilibration, sample the composition of the gas in the adsorption loop, and use a mixture equation of state for PVT calculations rather than a pure component equation of state.

The same sample activation and free volume measurement procedure are used for single component and binary adsorption measurements. Following the free volume measurement, the reference cell is charged with pure gas A. The PVT data for pure A in the reference cell are recorded, and then the reference cell is briefly opened to the adsorption loop. The number of moles of A adsorbed is calculated according to the same methodology used for single component adsorption. Then, the reference cell is evacuated and charged with pure gas B. Again, the reference cell is briefly opened to the adsorption loop. It is assumed that no gas flows back from the adsorption loop into the reference cell. This is reasonable as the pressure in the reference cell is always at least one bar higher than the adsorption loop when the two are connected, and the connection is made for a period of less than five seconds through a narrowly open needle valve in line with 1/16” (1.588 mm) outer diameter (OD) tubing. The system is left to equilibrate while the circulation pump circulates gas through the adsorption loop. After at least three hours, or such time that the pressure in the adsorption loop is no longer decreasing, the composition of the gas in the adsorption loop is checked using the GC.
In addition to the temperature, pressure, and volume of the adsorption loop, the composition of the gas completes all of the data that are needed to use the Peng-Robinson equation of state for mixtures to calculate the number of moles each of A and B that are present in the gas phase in the adsorption loop. The difference between the number of moles of A and B dosed into the adsorption loop and the number of moles of each component remaining in the gas phase after equilibration is the quantity of each component that remains in the adsorbed phase. This is the first equilibrium mixture adsorption data point. It is assumed that this 20 µL sample of gas is sufficiently small so as not to affect the adsorption measurement (See Calculation S1). Thus, more points can be collected without re-activating the sample by simply charging more component B into the reference cell and then repeating the process of opening the reference cell to the adsorption loop and sampling the gas composition after equilibration has been reached.

After all pressure, temperature, volume, and gas composition data (“PVTy” data) have been collected, they are used to calculate the number of moles of A and B in the reference cell and in the adsorption loop during each measurement step. The same process used to track the moles of gas in each volume for single component adsorption measurements is applied to each gas for the binary adsorption measurement.

The experiment begins with a clean adsorbent and evacuated adsorption loop. The reference cell is charged to pressure $P_0$ with pure component A, so that the number of moles of A in the reference cell can be solved using the molar volume of A in the reference cell using the following expressions:
\[ n_{A,0} = \frac{V_{RC}}{V_{m,ARC,0}} \] (17)

Notice this is equation 13 rewritten for component A alone. When opening the reference cell to the adsorption loop to allow component A to adsorb, this same approach follows with modifying equation 14 for component A:

\[ n_{A,1} = \frac{V_{RC}}{V_{m,ARC,1}} + \frac{V_{AL}}{V_{m,AL,1}} + n_{A,ads} \] (18)

After allowing the system to equilibrate, the reference cell is evacuated and charged to \( P_2 \) with component B.

\[ n_{B,2} = \frac{V_{RC}}{V_{m,B,RC,2}} \] (19)

The reference cell is then opened to the adsorption loop again to allow component B to mix with the gas in the head space of the adsorption loop. This creates a gas mixture of A and B. After allowing sufficient time for equilibration, we can write independent mole balances for each A and B in the style of equation 15:

\[ \left( \frac{V_{RC}}{V_{m,A,RC,0}} - \frac{V_{RC}}{V_{m,A,RC,1}} \right) = \left( \frac{V_{AL}}{V_{m,AL,1}} - \frac{V_{AL}}{V_{m,SL,0}} \right) + (n_{A,ads,1} - n_{A,ads,0}) \] (20)

\[ \left( \frac{V_{RC}}{V_{m,B,RC,0}} - \frac{V_{RC}}{V_{m,B,RC,1}} \right) = \left( \frac{V_{AL}}{V_{m,B,AL,1}} - \frac{V_{AL}}{V_{m,B,AL,0}} \right) + (n_{B,ads,1} - n_{B,ads,0}) \] (21)
These equations can be used to solve the number of moles of A and B in the adsorbed phase at each step of a mixture adsorption measurement. However, some additional complexity arises in calculating the molar volume of the mixed gas. In this case, the van der Waals mixing rules are applied to the Peng-Robinson equation for each pair of species i and j in the gas phase:

\[
\begin{align*}
    a &= \sum_i \sum_j y_i y_j (1 - \delta_{ij}) (a_i a_j)^{1/2} \\
    b &= \sum_i y_i b_i
\end{align*}
\]

(22) \hspace{1cm} (23)

The binary interaction parameter \(\delta_{ij}\) in this work was taken from Fateen et al.,\(^6\) and used in calculating mole balances for each component (equation 20-21) which give the adsorption loading at all equilibrium points in mixture adsorption experiments.

4.6 Validation experiments and results

Construction of a new instrument requires some validation of the measurement capabilities thereof. Though the measurement of gas mixture adsorption is frequently done using home-built apparatuses, this step is often omitted. In this work, validation is done twofold: once for measurement of pure component isotherms and separately for validation of binary mixture adsorption measurement. The strategy chosen was to compare single component isotherm measurements on the instrument constructed in this work both to measurements reported in the literature, and to measurements made on other trusted
instruments in the lab. For multicomponent measurements, comparison was made to published results.

Choosing a system for validation was not trivial. Many systems use adsorbents synthesized in-house, and this adds a level of difficulty in first reproducing the adsorbent material. Many metal-organic frameworks are either subject to this difficulty, or to added difficulty from instability under humid conditions. Zeolites are a class of materials less subject to these challenges, but bring challenges of their own- activation conditions can require very high temperatures to remove adsorbed water molecules, which can have strong effects on adsorption properties. For this work, BPL carbon was chosen as the adsorbent for validation. This material has been available from Calgon for decades, is stable under humid conditions, and easily activated. The system chosen for this work was the adsorption of a methane/ethane mixture on BPL carbon. We have chosen to validate our instrument against the measurements made by He et al. This work was chosen for several reasons beyond simply the fact that these authors studied BPL carbon. These authors applied a number of thermodynamic consistency tests to their data. Moreover, they were successful in validating the single-component measurement capability of their instrument. We are confident that the data reported in this study are of the highest quality, and are suitable for use in the validation of the instrument constructed in this work.

4.6.1 Materials

BPL carbon, 4x6 mesh, was generously supplied by Calgon corporation. All gases used were purchased from AirGas in the following purities: nitrogen- 99.999%, helium-99.999%, methane- 99.99%, ethane- 99.99%.
4.6.2 Pure component adsorption

The BPL carbon used in this work had BET surface area of 1135 m$^2$/g and average pore size of 10.9 Å, measured by nitrogen physisorption at 77 K on a Quadrasorb by Quantachrome. BET area was calculated using adsorption in the linear range of the BET plot where 0.01 < $P/P_0$ < 0.2. Pore size distribution was calculated using the density functional theory (DFT) method. These values are very similar to those reported by He et al, which were 1061 m$^2$/g BET surface area and 10.2 Å average pore size. The BPL carbon used in this work is, by initial inspection, similar to that used by He et al.

The first step in validating the instrument built in this work was measurement of pure component isotherms for methane and ethane for comparison with in-house instruments (Hiden Isochema IGA-003 and Micromeritics 3Flex) and measurements by He et al also using BPL carbon from Calgon. These measurements are shown in Figure 4.3.
Figure 4.3: Single component adsorption of methane and ethane compared to measurements on IGA-003 and by He et al. 2004. (a) Methane adsorption isotherms on BPL carbon at 301.4 K. (b) Ethane adsorption isotherms on BPL carbon at 301.4 K. (c) Difference in methane loading of three measurements compared to loading measured by MC GAS. (d) Difference in ethane loading of three measurements compared to loading measured by MC GAS.

Measurements from the instrument built in this work agree with measurements made on IGA-003. Loadings are slightly higher in both instruments compared to that reported by He et al., but the difference is not large. This difference could be attributed in part to the higher surface area of the BPL carbon used in this work (1135 m²/g) compared to that used by He et al. (1061 m²/g). These results validate the capability of the instrument built in this work to measure single component adsorption.
4.6.3 Binary mixture adsorption

The problem of validating mixture adsorption capabilities offers several challenges beyond those of validating single component adsorption capabilities. The nature of the volumetric apparatus for mixture adsorption means that it is impossible to directly control the pressure and composition of the gas phase at equilibrium. Thus, it is difficult to precisely replicate mixture adsorption points reported in other works. However, because the volume of the adsorption loop in this work and the loading of the adsorbent in the reference work are known, it should be possible to replicate points to some extent. Knowledge of the volume of the adsorption loop allows calculation of the number of moles of each component that should be in the gas phase at equilibrium to match the partial pressure of each component at equilibrium in the reference work. If we assume that the loadings of each component are likely to be similar to the reference work, we can also estimate the number of moles of each component that will be present in the adsorbed phase. By precisely dosing the number of moles of each component that sums to satisfy both the partial pressure of that component in the gas phase and the loading of that component in the adsorbed phase at equilibrium, we can ensure that the system can reach an equilibrium very close to any data point reported in another work.

This of course does not ensure the same equilibrium will be reached, merely that those conditions could be reached. Efforts to replicate measurements of binary mixture adsorption reported by He et al. for adsorption of methane and ethane on BPL carbon have been successful considering this inherent difficulty. These results of He et al. are presented in Table 4-2, while the replication of these results using MC GAS is shown in Table 4-3.
Adsorption loadings are shown in Figure 4.4(a) and Figure 4.4(b) while selectivity values are shown in Figure 4.4(c) and Figure 4.4(d).

**Table 4-2: Mixture adsorption loadings and compositions for adsorption of methane and ethane on BPL carbon at 301.4 K, measured by He et al.**

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>y ethane&lt;sup&gt;a&lt;/sup&gt;</th>
<th>x ethane&lt;sup&gt;b&lt;/sup&gt;</th>
<th>q ethane&lt;sup&gt;c&lt;/sup&gt; (mmol/g)</th>
<th>q methane&lt;sup&gt;c&lt;/sup&gt; (mmol/g)</th>
<th>ethane/methane Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.96</td>
<td>0.97</td>
<td>0.996</td>
<td>3.61</td>
<td>0.01</td>
<td>8.4</td>
</tr>
<tr>
<td>1.97</td>
<td>0.73</td>
<td>0.972</td>
<td>3.25</td>
<td>0.09</td>
<td>12.7</td>
</tr>
<tr>
<td>1.96</td>
<td>0.51</td>
<td>0.930</td>
<td>2.78</td>
<td>0.21</td>
<td>12.7</td>
</tr>
<tr>
<td>1.97</td>
<td>0.28</td>
<td>0.861</td>
<td>2.15</td>
<td>0.35</td>
<td>15.6</td>
</tr>
<tr>
<td>6.84</td>
<td>0.97</td>
<td>0.996</td>
<td>4.97</td>
<td>0.02</td>
<td>7.4</td>
</tr>
<tr>
<td>6.83</td>
<td>0.73</td>
<td>0.965</td>
<td>4.53</td>
<td>0.17</td>
<td>9.9</td>
</tr>
<tr>
<td>6.84</td>
<td>0.51</td>
<td>0.918</td>
<td>4.04</td>
<td>0.36</td>
<td>10.8</td>
</tr>
<tr>
<td>6.83</td>
<td>0.28</td>
<td>0.826</td>
<td>3.19</td>
<td>0.67</td>
<td>12.0</td>
</tr>
<tr>
<td>6.84</td>
<td>0.09</td>
<td>0.571</td>
<td>1.75</td>
<td>1.32</td>
<td>12.8</td>
</tr>
<tr>
<td>6.85</td>
<td>0.03</td>
<td>0.308</td>
<td>0.81</td>
<td>1.82</td>
<td>14.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> y = gas phase mole fraction  <sup>b</sup> x = adsorbed phase mole fraction  <sup>c</sup> q = adsorption loading

**Table 4-3: Mixture adsorption loadings and compositions for adsorption of methane and ethane on BPL carbon at 301.4 K, measured in chapter 4 of this work.**

<table>
<thead>
<tr>
<th>P (bar)</th>
<th>y ethane&lt;sup&gt;a&lt;/sup&gt;</th>
<th>x ethane&lt;sup&gt;b&lt;/sup&gt;</th>
<th>q ethane&lt;sup&gt;c&lt;/sup&gt; (mmol/g)</th>
<th>q methane&lt;sup&gt;c&lt;/sup&gt; (mmol/g)</th>
<th>ethane/methane Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.93</td>
<td>0.94</td>
<td>0.992</td>
<td>3.68</td>
<td>0.03</td>
<td>7.8</td>
</tr>
<tr>
<td>1.94</td>
<td>0.72</td>
<td>0.963</td>
<td>3.38</td>
<td>0.13</td>
<td>10.1</td>
</tr>
<tr>
<td>1.97</td>
<td>0.59</td>
<td>0.947</td>
<td>3.01</td>
<td>0.17</td>
<td>12.4</td>
</tr>
<tr>
<td>2.04</td>
<td>0.35</td>
<td>0.906</td>
<td>2.40</td>
<td>0.25</td>
<td>17.7</td>
</tr>
<tr>
<td>1.98</td>
<td>0.04</td>
<td>0.412</td>
<td>0.57</td>
<td>0.81</td>
<td>16.8</td>
</tr>
<tr>
<td>7.02</td>
<td>0.72</td>
<td>0.960</td>
<td>5.10</td>
<td>0.21</td>
<td>9.6</td>
</tr>
<tr>
<td>6.92</td>
<td>0.49</td>
<td>0.915</td>
<td>4.56</td>
<td>0.42</td>
<td>11.2</td>
</tr>
<tr>
<td>6.77</td>
<td>0.14</td>
<td>0.698</td>
<td>2.63</td>
<td>1.14</td>
<td>14.0</td>
</tr>
<tr>
<td>6.74</td>
<td>0.11</td>
<td>0.669</td>
<td>2.33</td>
<td>1.15</td>
<td>15.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> y = gas phase mole fraction  <sup>b</sup> x = adsorbed phase mole fraction  <sup>c</sup> q = adsorption loading

Efforts to replicate mixture adsorption reported by He et al. show a relatively small difficulty in replicating equilibrium pressure, and a larger difficulty in replicating gas phase composition. This is reflective of the nature of closed volumetric adsorption instruments.
However, despite this difficulty there is good agreement in amounts adsorbed for each species at similar pressures and gas phase compositions. Furthermore, in rows 1 and 5 of Table 4-3, it is apparent that the amounts adsorbed of each species approaches the pure component loading as the gas phase composition approaches its endpoints. As can be seen in Figure 4.4, the experimental data cross the thermodynamically consistent IAST model at least once across measurements at both pressures.

![Figure 4.4](image)

**Figure 4.4**: Binary adsorption measurements of methane/ethane mixtures on BPL carbon at 301.4 K. (a) Amounts adsorbed at 1.98 ± 0.06 bar. (b) Amounts adsorbed at 6.98 ± 0.13 bar. (c) Selectivity for ethane at 1.98 ± 0.06 bar. (d) Selectivity for ethane at 6.89 ± 0.13 bar.
There is generally good agreement between IAST and experiment for loading of each component, as shown in Figure 4.4 (a-b). This is consistent with the findings of He et al. However, small differences between IAST and experiment are amplified in the calculation for selectivity. It has been noted by other authors that small uncertainties in amounts adsorbed lead to large uncertainties in selectivity.\textsuperscript{15} Error bars in selectivity are calculated by propagation of experimental uncertainty as shown in Calculation S2.\textsuperscript{70} Nearly all of this uncertainty comes from uncertainty in the loading of methane, the more weakly adsorbed component. Uncertainty in selectivity is most noticeable when the amount of methane adsorbed is very low. This is especially evident in Figure 4.4(c) where the rightmost data point measured in this work has large uncertainty as the adsorbed phase for this measurement contains very little methane. Furthermore, measurement at lower pressures is generally more difficult than at higher pressures because amounts adsorbed are lower at lower pressures. This can likely explain the relatively larger scatter of the selectivities measured in this work and those measured by He et al shown in Figure 4.4 (c).

The problem of high fractional uncertainty in loading of the more weakly adsorbed component is not unique to the instrument used in this work. This problem is not easily solved in other mixture adsorption measurement techniques, and can be especially evident when calculating selectivity for very selective adsorption, as can be the case in carbon dioxide capture applications.\textsuperscript{71}

Mixture adsorption equilibrium measurements are extremely difficult and prone to many more sources of error than single component adsorption measurements. Thermodynamic consistency tests for binary mixture adsorption have been developed by Talu et al.\textsuperscript{10,72} to ensure internal consistency among a set of single component and mixture
adsorption data. While these tests do not assure the accuracy of the data collected, consistency within a data set increases confidence that the data are accurate. There are numerous ways to assess the consistency of mixture adsorption equilibrium data, and we have employed the following tests:

1. At fixed temperature and pressure, the total amount adsorbed must equal the single component values at the composition end points. (Table 4-2 and Table 4-3).
2. At fixed temperature and pressure, the x-y and selectivity curves of all thermodynamically consistent models must cross the experimental curves at least once (Figure 4.4).

These binary adsorption data meet these thermodynamic consistency criteria. While this does not in itself prove that these data are correct, the combination of agreement with the high quality data of He et al. and the satisfaction of these two thermodynamic consistency criteria validate this instrument as capable of measuring binary adsorption equilibria for light gases. Further validation measurements could be necessary for experiments with heavier components like water vapor. The instrument MC GAS developed in this work is fully automated and capable of repeatable, high-throughput measurements of binary mixture adsorption. The full automation of this instrument vastly increases the speed of data collection and available operating time relative to comparable manually operated systems.

While the strength of this instrument lies in its automation, the process of automation is not totally without drawbacks. By its nature, the closed volumetric system in this work does not give the user control over the equilibrium pressure at each adsorption
measurement point. This problem has been solved by others who have used manostats, or carefully calibrated pistons, to adjust the internal volume of the instrument during measurements to allow equilibration at a pre-determined pressure.Automation of a manostat is certainly possible and could be implemented as a future improvement to this instrument or others like it. In addition, the circulation pump used in this work could be replaced with a bellows pump to reduce potential for leaks during experiments. This instrument could also benefit from a single temperature control device. While the use of heating tape during sample activation and a water bath during adsorption measurements was sufficient to reach high activation temperatures and also hold temperature very stable during adsorption measurements, a single temperature control mechanism like an oil bath could achieve both of these goals and eliminate the need for two temperature controllers.

4.7 Conclusions

We have developed and validated an automated volumetric instrument for the measurement of binary gas mixture adsorption. The validation of this instrument has been completed by comparison of single component and binary adsorption measurements with data available in the literature, as well as single component adsorption measurements made in-house on commercially available instruments. We expect that the level of technical description here will allow for replication of this type of instrument, which will more widely enable the study of binary mixture adsorption and thereby address a major weakness in the study of adsorption separations.
4.8 References


57. Belmabkhout, Y.; Sayari, A., Adsorption of CO\textsubscript{2} from dry gases on MCM-41 silica at ambient temperature and high pressure. 2: Adsorption of CO\textsubscript{2}/N\textsubscript{2}, CO\textsubscript{2}/CH\textsubscript{4} and CO\textsubscript{2}/H\textsubscript{2} binary mixtures. *Chemical Engineering Science* **2009**, *64* (17), 3729-3735.


CHAPTER 5.  NON-IDEAL BEHAVIOR IN ADSORPTION OF GAS MIXTURES ON METAL-ORGANIC FRAMEWORKS

This chapter is an adaptation of the article “IAST Prediction and Experimental Measurement of Gas Mixture Adsorption on Three Metal-Organic Frameworks” for which experimental work has concluded. Ideal Adsorbed Solution Theory predictions of binary mixed gas adsorption on three metal-organic frameworks were assessed by breakthrough measurements for binary mixtures of n-butane, ethane, and carbon dioxide. Results show near-quantitative matching between IAST and experiment for some mixture-adsorbent pairs, but great differences for others. A lack of clear trends in IAST prediction performance based on characteristics of the adsorbent or adsorbate mixture reveals difficulty in prediction of IAST efficacy and shows that IAST prediction of mixture adsorption is not an adequate replacement for experimental measurement.

5.1 Introduction

Adsorption separations offer the potential for enormous energy savings over legacy separations systems.\textsuperscript{1} The ability to successfully model and predict the behavior of adsorption separations systems is critical to their successful implementation and operation. Adsorption separations are under investigation for medical oxygen concentration,\textsuperscript{2-5} flue gas treatment,\textsuperscript{6-9} and direct air capture of carbon dioxide,\textsuperscript{10-12} among other applications.\textsuperscript{13} A primary challenge in developing successful adsorption separations is the choice of
adsorbent material. The adsorbent must exhibit good selectivity and capacity for the target species, along with excellent stability under process conditions.

While adsorbents like activated carbons and zeolites continue to see widespread investigation, metal-organic frameworks (MOFs) are an intense area of focus in separations at present. MOFs are ordered porous materials composed of organic ligands connecting inorganic secondary building units. The modular character of these structures has led to the synthesis of thousands of MOFs. The addition of a pendant functional group to the ligand used in an existing parent MOF structure can create a different MOF exhibiting different adsorption properties than the parent framework. This approach can introduce desired properties to a structure, like affinity for an adsorbate of interest, while retaining other properties of the parent MOF like mechanical or chemical stability.

Two MOFs which have been the subject of much attention are UiO-66 and HKUST-1. UiO-66 exhibits excellent thermal, chemical, and mechanical stability, while HKUST-1 shows high capacity and selectivity for a number of adsorbates. The UiO-66 structure consists of ditopic terephthalate ligands connecting Zr₆O₈ nodes, and is readily amenable to ligand substitution with functionalized terephthalate ligands. HKUST-1 is made up of tritopic trimesate ligands bridging copper paddle wheel nodes. When activated by heating under vacuum or flow of inert, solvent molecules coordinated to the copper ions in the HKUST-1 structure are removed from the framework, leaving behind coordinatively unsaturated sites, also known as open metal sites. Pendant functional groups on UiO-66 analogs like UiO-66-NH₂ and open metal sites in HKUST-1 introduce favorable binding sites for adsorbates of interest. As such, functionalized MOFs and open metal site MOFs have become commonly studied classes of MOFs for adsorption separations.
While great progress has been made in the search for novel and promising adsorbent materials, further development and adoption of efficient adsorption separations systems is hindered by a lacking ability to predict adsorption of gas mixtures. The Ideal Adsorbed Solution Theory (IAST) is the predominant model used to predict the adsorption of mixtures, which it does using only pure-component adsorption data. IAST requires the assumption that the adsorbed phase is an ideal solution; the interactions between adsorbed molecules are of equal strength independent of species. Two more assumptions used in the development of IAST are that the adsorbent is energetically homogeneous and all adsorbate species have equal access to all parts of the surface of the adsorbent. However, these assumptions are not essential for IAST.

In many cases, mixture adsorption predictions by IAST have been compared to experimental measurement of mixture adsorption. A notable collection from 2016 includes a compilation of IAST predictions and experimental measurement for 44 adsorbent-adsorbate mixture pairs constituting 114 binary adsorption systems from 29 references. The authors of this collection found that IAST-predicted adsorption selectivity differed from experimentally measured selectivity in most cases by at least 15% and by at least 40% in nearly one-third of cases. A 2012 study comparing IAST predictions of selectivity to selectivity calculated from Grand Canonical Monte Carlo (GCMC) simulations found that while IAST gave similar predictions to GCMC in many cases, IAST had the worst agreement with simulations for cases where adsorbates differed in size. These authors noted that competition by different-sized adsorbates for adsorption sites in MOFs with adsorbate-scale heterogeneity led to departure from assumptions required for IAST and was associated with disagreement between IAST and GCMC. Other studies using GCMC
have identified challenges IAST faces in predicting mixture adsorption in MOFs with gate-
opening behavior\textsuperscript{34} or adsorption sites inaccessible to one adsorbate.\textsuperscript{35}

Adsorption of the mixtures studied in this work has in some cases been examined
with mixed success in using IAST to predict mixture adsorption where applied.\textsuperscript{36-38} However, this work is the first instance of experimental measurement of adsorption of these
mixtures in MOF adsorbents. In this work, pure component and competitive adsorption of
carbon dioxide, ethane, and n-butane were measured on the MOFs UiO-66, UiO-66-NH\textsubscript{2},
and HKUST-1 to assess the efficacy of IAST in MOF adsorbents, including a
representative MOF incorporating pendant functional groups and another incorporating
open metal sites. The purpose of this study was to further the understanding of the influence
of surface heterogeneities arising from common MOF motifs (pendant functional groups
and open metal sites) and adsorbed phase non-idealities (differing adsorbate quadrupole
moment or kinetic diameter) on accuracy of IAST prediction of mixed gas adsorption in
MOFs.

5.2 Experimental and theoretical methods

5.2.1 Chemicals

Gases used in this study were procured from AirGas in the following purities: carbon
dioxide (CO\textsubscript{2}) 99.9\%, ethane (C\textsubscript{2}H\textsubscript{6}) 99.99\%, n-butane (n-C\textsubscript{4}H\textsubscript{10}) 99.99\%, methane (CH\textsubscript{4})
99.99\%, nitrogen (N\textsubscript{2}) 99.999, and helium (He) 99.999\%. All other chemicals used in this
study were procured from commercial sources as follows and used without further
purification. Zirconium(IV) chloride (ZrCl\textsubscript{4}), copper(II) nitrate trihydrate
(Cu(NO\textsubscript{3})\textsubscript{2}\cdot3H\textsubscript{2}O), 1,4-benzenedicarboxylic acid (terephthalic acid), 2-aminobenzene-1,4-
dicarboxylic acid (2-aminoterephthalic acid) 1,3,5-benzenetricarboxylic acid (trimesic acid) were procured from Sigma Aldrich. Methanol, ethanol, and \(N,N\)-dimethylformamide (DMF) were procured from VWR.

5.2.2 Materials synthesis

UiO-66 was synthesized according to the procedures reported by Cavka et al.\(^{21}\) Uio-66-NH\(_2\) was synthesized using the same procedure replacing terephthalic acid with 2-aminoterephthalic acid as done by Garibay & Cohen.\(^{39}\) HKUST-1 was synthesized as described by Al-Janabi et al.\(^{40}\)

After synthesis, the resulting powders were filtered and collected into centrifuge tubes. At this point, the UiO-66 and UiO-66-NH\(_2\) were washed several times with DMF before being solvent exchanged with methanol. The HKUST-1 sample was likewise washed several times with a 50/50 V/V mix of ethanol and water before solvent exchange with methanol. All samples were solvent-exchanged by dispersion in methanol and soaking for 1 day, then they were centrifuged. After centrifugation, the solvent was decanted and replaced with fresh methanol. This soak-centrifuge process was repeated three times for each sample. Samples were stored for a period of approximately 90 days between synthesis and adsorption experiments due to pandemic-related shutdown of research facilities. Samples were then pelletized without the use of a binder at 10,000 psig as described by Peterson et al.\(^{24}\) before being crushed and sieved to 20x40 mesh size (0.318-0.635 mm particle diameter) for use in adsorption measurements. After pelletization, particles less than 0.318 mm diameter were saved and used for powder x-ray diffraction measurements.
5.2.3  Powder x-ray diffraction

Powder x-ray diffraction (PXRD) measurements were made with a Malvern PANalytical Alpha-1 with X’Celerator detector using Cu Kα1 radiation (λ = 1.5418 Å). All diffraction measurements were done at room temperature in ambient air. The diffraction patterns measured were compared to simulated patterns from available cif files to confirm the presence of the expected frameworks.41-43

5.2.4  Nitrogen physisorption

Nitrogen physisorption isotherms were measured at 77 K using a volumetric instrument (Quadrasorb by Quantachrome). Prior to adsorption measurements, samples were outgassed for 16 h under vacuum at 423 K using a Quantachrome FloVac Degasser. Brunauer-Emmett-Teller (BET) surface areas were calculated over a range of 0.007 < P/P0 < 0.035, as appropriate for the microporous materials used in this work.44,45 Pore volumes were calculated using adsorption capacity at P/P0 = 0.99.

5.2.5  Gravimetric pure component adsorption isotherms

Pure-component isotherms for carbon dioxide and ethane were measured using an Intelligent Gravimetric Analyzer (IGA-003) instrument (Hiden Analytical). Approximately 25-50 mg of adsorbent were used for each measurement. Prior to adsorption measurements, the samples were outgassed in-situ for 16 h under vacuum at 423 K.

5.2.6  Volumetric pure component adsorption isotherms

Pure-component isotherms for n-butane were measured with a volumetric instrument (3Flex by Micromeritics). Approximately 25-50 mg of adsorbent were used for
each measurement. Prior to adsorption measurements, the samples were outgassed for 16 h under vacuum at 423 K using a Micromeritics Smart VacPrep activation stage. Gibbs excess adsorption data measured experimentally through both gravimetric and volumetric methods were converted to absolute adsorption by the methods suggested by Brandani et al.\textsuperscript{46} Absolute adsorption was used in all isosteric heat of adsorption and IAST calculations.

5.2.7 Breakthrough mixture adsorption measurements

Two-component breakthrough curves were measured at 298 K using a home-built breakthrough apparatus. Approximately 200 mg of adsorbent was packed into a stainless-steel tube with length of 51 mm and an inner diameter of 4.50 mm. Gas mixtures were created using Omega mass flow controllers with static in-line mixing to ensure spatially homogeneous feed composition. For all experiments, the total pressure was 1 bar and the total flow rate of feed was 15 mL/min. Dry helium flow of 5 mL/min was included in all experiments as a carrier gas with the assumption that no helium was adsorbed.\textsuperscript{46} Experiments were carried out in duplicate for each combination of adsorbent, mixture species, and mixture composition. Outlet gas composition was recorded using a Hiden Isochema quadrupole mass spectrometer.

Prior to adsorption measurement, samples were degassed for 12 hours at 423 K in 5 mL/min helium flow. For the first adsorption experiment on each newly loaded sample, the sample was allowed to cool at this point before the stainless-steel fixed bed was removed from the breakthrough apparatus and weighed on a microbalance. The tare weight of the stainless-steel tubing was subtracted to give the weight of the clean adsorbent. The fixed bed was then returned to the breakthrough apparatus and degassed a further 12 hours at 423 K in 5 mL/min helium flow. Subsequent experiments on the same sample omitted
the weighing step and corresponding re-activation after weighing. Dead volumes were determined using the same procedure detailed above with a fixed bed packed with sand of the same particle size.

5.2.8 Ideal adsorbed solution theory

IAST calculations were performed in IAST++. Experimental excess adsorption data from isotherm measurements were converted to absolute adsorption data before isotherm model fitting and subsequent IAST and $Q_{st}$ calculations as recommended by Krishna and detailed by Brandani et al. Void fraction of HKUST-1 used to convert to absolute adsorption was taken from Qiao et al., who reported void fraction for HKUST-1 calculated from crystal structure data. Void fractions of UiO-66 and UiO-66-NH$_2$ were taken from Yot et al., who likewise used crystal structure data to calculate void fraction. Gas concentration was calculated using the Peng-Robinson equation of state. Absolute adsorption isotherms for carbon dioxide and ethane were fit with the Dual-Site Langmuir-Freundlich isotherm model (Equation 24).

$$q = \frac{q_{sat,1}(k_1 P)^{n_1}}{1 + (k_1 P)^{n_1}} + \frac{q_{sat,2}(k_2 P)^{n_2}}{1 + (k_2 P)^{n_2}}$$ (24)

Isotherm data for n-butane were fit using the interpolation function in IAST++, as we were unable to find an isotherm model to adequately fit the experimental data. Absolute adsorption data were used for all IAST and $Q_{st}$ calculations.

IAST relates the partial pressure of each component in the gas phase to the spreading pressure of the same component in the adsorbed phase, similar to the Raoult’s law relation for partial pressure of a component in the gas phase to vapor pressure for that
component in the liquid phase. The fugacity of a given component, \( i \), in an ideal adsorbed phase is related to the fugacity of the same component in the gas phase by the following:

\[
\bar{f}_i = f_i^0 (\pi)x_i
\]  

(25)

The fugacity of component \( i \) in the bulk gas phase is given by \( \bar{f}_i \) while \( f_i^0 \) represents the fugacity of component \( i \) in the adsorbed phase. Adsorbed phase fugacity of component \( i, f_i^0, \) is a function of spreading pressure, \( \pi \), of component \( i \) in the adsorbed phase. The mole fraction of component \( i \) in the adsorbed phase is represented by \( x_i \). The integrated isotherm model relates \( f_i^0 \) and \( \pi \) for each component as follows:

\[
\frac{\pi A}{RT} = \int_0^{f_i^0} q_i \, d \ln f_i
\]  

(26)

Here, \( q_i \) is the quantity of component \( i \) adsorbed from pure gas-phase \( i \) at fugacity \( f_i \) (partial pressure \( P_i \) is assumed equal to fugacity in this work) and temperature \( T \). \( A \) represents the surface area of the adsorbent, and \( R \) is the universal gas constant. Equation 26 requires the use of a continuous function (isotherm model) to describe single component isotherm data. A number of isotherm models can be used, but the model of choice should give a good fit to the experimental data, especially at low pressures. In this work, the dual-site Langmuir-Freundlich (DLSF) model was used as this more closely fit experimental data than other models including Langmuir, dual-site Langmuir, Sips, and Tóth models. At equilibrium, each component in the adsorbed phase has the same spreading pressure:

\[
\pi = \pi_i = \pi_j \forall i, j
\]  

(27)

The sum of the mole fractions of all components in the adsorbed phase is equal to unity, so equation 25 can be rearranged as the following:
\[
\sum \frac{\bar{f}_i}{f_i^0(\pi)} - 1 = 0
\]  

(28)

This expression can be solved for a given \(\bar{f}_i\) to obtain the value of \(f_i^0\) for component \(i\). Then the adsorbed phase composition \(x_i\) can be calculated from equation 25. The total number of moles adsorbed from the gas phase, \(n_t\), is predicted using:

\[
\frac{1}{q_t} = \sum \frac{x_i}{q_i^0}
\]  

(29)

Finally, the amount adsorbed of each component is given simply by:

\[
q_i = x_i q_t
\]  

(30)

Selectivity is a useful metric to describe the tendency of an adsorbent to adsorb one component over another. This quantity can be calculated from experimental data or IAST predictions of adsorption. Selectivity is defined as follows:

\[
S_{A/B} = \frac{x_A y_B}{x_B y_A}
\]  

(31)

Again, \(x_A\) represents the adsorbed phase mole fraction of component A while \(y_A\) represents the gas phase mole fraction of component A.

5.2.9 Isosteric heat of adsorption

Isosteric heat of adsorption was calculated using the Clausius-Clapeyron equation with isotherms measured at 288, 298, and 308 K. Absolute adsorption isotherms were used for heat of adsorption calculations as advocated by Nuhn and Janiak.\textsuperscript{52}
\[ Q_{st} = -R \left[ \frac{d(\ln P)}{d \left( \frac{1}{T} \right)} \right]_q \]  

(32)

Here, \( Q_{st} \) is the isosteric heat of adsorption, \( R \) is the universal gas constant, and \( q \) is the absolute amount adsorbed at pressure \( P \) and temperature \( T \). For each loading, the slope of the best fit line for a plot of \( \ln P \) vs \( 1/T \) was used for three values of \( 1/T \) to calculate the isosteric heat of adsorption.

5.3 Results and discussion

5.3.1 Materials characterization

Powder X-ray diffraction shows good matching between patterns measured in this work and patterns simulated from available cif files. The relative intensities of peaks at 9.5° and 13° in the measured HKUST-1 diffraction pattern are lower than the corresponding peaks in the simulated pattern, but all peak positions match well, as seen in Figure 5.1. Additionally, the intensities of peaks at 7.5° and 8.5° in the measured pattern for UiO-66-NH\(_2\) are low relative to peaks at higher 2θ. This could indicate some mechanical degradation as a result of pelletization, as noted by Peterson et al.\(^{24}\) However, these patterns suggest the pelletized samples used in this work share their crystal structures with the ideal structures described in the cif files.
Nitrogen physisorption measurement reveals surface area and pore volume for all MOFs in this work to be consistent with values reported by other authors as shown in Figure 2 and Table 1.\textsuperscript{53, 54} HKUST-1 shows larger surface area and pore volume than either Uio-66 framework. Slightly decreased surface area of Uio-66-NH\textsubscript{2} relative to Uio-66 is another indicator, along with PXRD measurement, that the Uio-66-NH\textsubscript{2} sample could have suffered some mechanical degradation upon pelletization. However, the BET surface area
of the UiO-66-NH$_2$ used in this work remains consistent with the value reported for the same MOF by Luu et al.,$^{54}$ who did not pelletize their sample. The surface area and pore volume of all MOFs used in this work are within reasonable agreement of prior reported values.

Figure 5.2: Nitrogen physisorption isotherms for each MOF studied in this chapter. Closed symbols denote adsorption, while open symbols denote desorption.
Table 5-1: BET surface area and pore volumes of MOFs studied in chapter 5 from N$_2$ physisorption at 77 K.

<table>
<thead>
<tr>
<th>MOF</th>
<th>BET Area (m$^2$/g)</th>
<th>Pore Volume$^a$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UiO-66</td>
<td>1083</td>
<td>0.56</td>
</tr>
<tr>
<td>UiO-66-NH$_2$</td>
<td>885</td>
<td>0.58</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1762</td>
<td>0.79</td>
</tr>
</tbody>
</table>

$^a$Pore volumes obtained from the Dubinin-Astakhov model.

5.3.2 Pure component adsorption

Pure component adsorption isotherms (absolute adsorption) are shown in Figure 5.3. These measurements show that HKUST-1 has the greatest adsorption capacity for all species through the entire pressure range tested, which is explained by its larger surface area and pore volume than the other MOFs in this work. UiO-66-NH$_2$ shows a lightly lower adsorption capacity than UiO-66 for both alkanes tested, which could be explained in part by the lower BET surface area measured for UiO-66-NH$_2$. UiO-66-NH$_2$ shows slightly greater capacity than UiO-66 for carbon dioxide, which is consistent with the inclusion of the polar amine functional group. Ethane adsorption isotherms on all adsorbents are slightly sharper than those for carbon dioxide. Isotherms measured for n-butane show extremely sharp curves, especially for adsorption on HKUST-1. Fits of n-butane isotherms with theoretical models were unsatisfactory for IAST calculations, which require good fits of experimental adsorption data. Instead, we used the interpolation function in IAST++ to perform these fits. All other isotherm data are plotted along with DSLF fit curves.
Figure 5.3: Pure component isotherms measured at 298 K for carbon dioxide (a), ethane (b), and n-butane (c) on each MOF studied in this work.
Isosteric heat of adsorption ($Q_{st}$) values are shown in Figure 4 with the same axis bounds for ease of comparison. Uncertainty bars are estimated from instrumental uncertainty in pure component adsorption measurement. Uncertainty in heat of adsorption values is relatively high at low loading values, especially for n-butane as these isotherm curves are extremely sharp. The heat of adsorption curve for carbon dioxide on HKUST-1 shows decreasing $Q_{st}$ with increasing loading, consistent with the idea that carbon dioxide first adsorbs onto high energy sites in the HKUST-1 framework. This phenomenon present but less pronounced for the UiO-66 MOFs, indicating that all three of these MOFs are somewhat energetically heterogeneous with regard to carbon dioxide adsorption. The heat of adsorption curves for ethane show somewhat unusual behavior with relatively flat curves at low and intermediate loadings before increasing, then decreasing at high loadings. An increase in heat of adsorption in this loading range could be indicative of adsorbate-adsorbate interactions causing increasing $Q_{st}$ as pore space is filled. The downturn at highest loadings in these curves could be attributed to overfitting of experimental data or simply measurement error.

Heat of adsorption curves for n-butane show higher uncertainty than those for carbon dioxide or ethane. This is due to the sharper shape of the isotherms from which isosteric heat of adsorption is calculated. Heat of adsorption for n-butane is generally much larger than for the other adsorbates tested, and shows “u-shaped” curves for all adsorbents. The decreasing slope at low loadings could correspond to high energy adsorption sites being filled, while the increasing slope at higher loadings is attributed to favorable interactions between adsorbed n-butane molecules.
Figure 5.4: Isosteric heat of adsorption for carbon dioxide (a), ethane (b), and n-butane (c) on each MOF studied in this work. The Clausius–Clapeyron equation was used to calculate isosteric heat of adsorption.
5.3.3 Mixture adsorption and IAST

Binary mixture adsorption was measured using the breakthrough method. Adsorption of ethane/carbon dioxide mixtures showed that IAST was reasonably accurate in predicting adsorption of carbon dioxide from these mixtures, but was unable to accurately predict adsorption of ethane. Strong negative deviations from IAST in ethane adsorption could be indicative of competition by ethane and carbon dioxide for the same adsorption sites in these MOFs, especially in the UiO-66 frameworks. These deviations could also indicate the presence of unfavorable interactions between adsorbed ethane and carbon dioxide molecules due to the quadrupole moment of carbon dioxide and corresponding lack of quadrupole moment for ethane. Negative deviations from IAST have been attributed to energetic heterogeneity of the adsorbent surface—something all three of these MOFs exhibit for adsorption of carbon dioxide, as evidenced by decreasing $Q_{st}$ with increasing loading in Figure 4. Interestingly, the best match between IAST prediction and experimental measurement is found for HKUST-1, the adsorbent whose surface has the greatest energetic heterogeneity. This unexpected result could be explained by a lack of competition for the same adsorption sites. The HKUST-1 structure includes pores of three different diameters as well as coordinatively unsaturated copper atoms. It is possible that at low coverages like those in these breakthrough measurements, the carbon dioxide molecules adsorb near the open metal sites while the ethane molecules adsorb elsewhere, mitigating competition for the same adsorption sites.

Interestingly, adsorption of n-butane/carbon dioxide mixtures shows even better agreement between IAST and experiment than do ethane/carbon dioxide mixtures. This result was unanticipated as IAST is not historically adept at predicting adsorption of
molecules whose molecules differ greatly in size. IAST is able to nearly quantitatively predict adsorption of n-butane/carbon dioxide mixtures on UiO-66. Experiments show positive deviations from IAST prediction of carbon dioxide loading for n-butane/carbon dioxide mixture adsorption on HKUST-1, but only for mixtures where $y_{\text{CO}_2}$ is greater than 0.25. Because this positive deviation in carbon dioxide adsorption is not met with a corresponding negative deviation in n-butane adsorption, it is possible that this adsorbed carbon dioxide is located at adsorption sites which are not used by n-butane.

Adsorption of n-butane/ethane mixtures on UiO-66 shows small negative deviations from IAST prediction for loading of both components at low gas phase mole fractions of n-butane, but the IAST predictions are more accurate for gas phases of at least 0.5 $y_{\text{n-C}_4\text{H}_{10}}$. Though negative deviations from IAST are often attributed to unfavorable interactions between adsorbed components, this is unlikely for two alkane species. Breakthrough measurements of n-butane/ethane adsorption on HKUST-1 reveal large positive deviations from IAST predictions of ethane adsorption, especially at low $y_{\text{n-C}_4\text{H}_{10}}$. Interestingly, both n-butane mixtures tested in HKUST-1 reveal large positive deviation from IAST prediction in loading of the lighter component as shown in Figure 4(j) and 4(k). The similar nature of these deviations even with different coadsorbates suggest that such deviations may be caused by the interaction of n-butane with the HKUST-1 framework rather than interaction of n-butane with the other adsorbate.

Interestingly, adsorption of carbon dioxide/methane mixtures shows large negative deviation from IAST behavior in the amount of carbon dioxide adsorbed, but little deviation in methane adsorption. This invites comparison to mixture adsorption of ethane/carbon dioxide mixtures where negative deviation from IAST is also observed in
the more strongly adsorbing component. It is possible that a small amount adsorbed of the weakly adsorbing component is in some cases sufficient to disrupt interactions between molecules of the strongly adsorbing component and in turn decrease the capacity for the strongly adsorbing component.

From the plots in Figure 5.5, it is apparent that many different deviations from IAST behavior can exist, even for a group of just three MOFs and three adsorbate mixtures. Deviation from IAST can be quantified in several different ways, including deviation in loading of either component or experimental deviation from predicted selectivity. It is evident from Figure 5.5 that the best predictions appear to be for adsorption of n-butane/carbon dioxide mixtures on UiO-66, but the adsorption of ethane/carbon dioxide mixtures on UiO-66 appears to differ greatly from IAST predictions. While a mixture of n-butane/ethane might be expected to be more ideal than a mixture of n-butane/carbon dioxide, IAST is able to predict adsorption of n-butane/carbon dioxide mixtures at least as well as n-butane/ethane mixtures. This shows the difficulty in using heuristics to predict when IAST will perform well. IAST is largely unable to predict adsorption of ethane/carbon dioxide mixtures on both UiO-66 MOFs, and for n-butane mixtures adsorbed on HKUST-1. However, IAST predictions for adsorption of n-butane mixtures adsorbed on UiO-66 are fairly accurate, as are predictions of ethane/carbon dioxide mixtures on HKUST-1. Experimental results can deviate from IAST prediction for many reasons, and finding a single variable to explain these deviations is difficult. Differences in size of adsorbate molecules could explain deviations for n-butane mixture adsorption on HKUST-1, but not the UiO-66 frameworks. Pure component heat of adsorption measurements, gas phase mole fraction of heavy component, presence of a quadrupolar
molecule, and other variables do not readily explain deviation from IAST-predicted selectivity.
Figure 5.5: Binary mixture adsorption equilibrium from breakthrough adsorption measurements. (a)-(d) show adsorption on UiO-66, (e)-(h) show adsorption on UiO-66-NH₂, and (i)-(l) show adsorption on HKUST-1.

Roll-up is a phenomenon sometimes observed in mixture breakthrough measurements. Roll-up can be observed when the outlet concentration of the more weakly adsorbed component exceeds the inlet concentration shortly before the more strongly adsorbed component breaks through the packed bed. Roll-up occurs when a more strongly adsorbed component displaces a more weakly adsorbed component and can indicate that components compete for some adsorption sites. Figure 5.6 shows examples of mixture breakthrough plots with and without roll-up. Table C-5 indicates which breakthrough
measurements showed evidence of roll-up. All mixture/adsorbate pairings measurements showed some evidence of roll-up except for n-butane/ethane mixtures, indicating that competition for adsorption sites by n-butane and ethane may not be as strong as competition for carbon dioxide mixtures with ethane or n-butane.

Figure 5.6: Observation of roll-up in some breakthrough curves. (a) Roll-up is present in ethane/carbon dioxide breakthrough at $y_{\text{CO}_2} = 0.5$. (b) Roll-up is not observed in ethane/carbon dioxide breakthrough at $y_{\text{CO}_2} = 0.25$.

5.4 High-Pressure Mixture Adsorption with MC GAS

After revelation of mostly negative deviations from IAST prediction in the uptake of both components from binary mixtures at low pressures, a study was conducted using the MC GAS instrument discussed in Chapter 2. In low-pressure breakthrough studies, we observed less adsorption than IAST predicted for the more strongly adsorbing component from binary mixtures of carbon dioxide/methane and ethane/carbon dioxide. Here, carbon dioxide was the more strongly adsorbed component when mixed with methane but the less strongly adsorbing component when mixed with ethane. We hypothesized that when coadsorbing with methane at higher pressures, we might observe less negative deviation in
adsorption of carbon dioxide, which would match more closely to the trends we observed in adsorption of ethane/carbon dioxide mixtures at lower pressures. Essentially, we hypothesized that if we were to increase the loading of the alkane methane to levels approaching that achieved by ethane in our breakthrough experiments, we might find behavior in carbon dioxide/methane mixtures at high pressure which is qualitatively similar to behavior in ethane/carbon dioxide mixtures at low pressures. While the low-pressure breakthrough experiments were conducted at a total pressure of 1 bar including 0.33 bar partial pressure of helium, the high-pressure adsorption experiments conducted on MC GAS reached pressures in excess of 10 bar. The results of carbon dioxide/methane mixture adsorption experiments conducted on UiO-66 are listed in Table 5-2. All quantities adsorbed q are listed in values of mmol/g.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>IAST Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (bar)</td>
<td>y CO₂</td>
</tr>
<tr>
<td>2.17</td>
<td>0.108</td>
</tr>
<tr>
<td>4.58</td>
<td>0.079</td>
</tr>
<tr>
<td>7.31</td>
<td>0.090</td>
</tr>
<tr>
<td>10.14</td>
<td>0.095</td>
</tr>
</tbody>
</table>

In the UiO-66 framework, we observe negative deviation in total adsorption loading across all data points. We find that the adsorbed quantities of methane are in worse agreement with IAST predictions than they are in the breakthrough experiments, however, especially at the highest pressure point observed. This is consistent with the hypothesis that the presence of more of both the alkane and carbon dioxide in the pores may disrupt favorable interactions between molecules of like species (i.e., favorable carbon dioxide-carbon dioxide or favorable methane-methane interactions). Table 5-3 lists the results of
high-pressure mixture adsorption experiments for carbon dioxide/methane mixtures on HKUST-1. All quantities adsorbed \( q \) are listed in values of mmol/g.

**Table 5-3: Mixture adsorption loadings and compositions for adsorption of carbon dioxide and methane on HKUST-1 at 298 K.**

<table>
<thead>
<tr>
<th>( P ) (bar)</th>
<th>( y_{CO_2} )</th>
<th>Experiment</th>
<th>IAST Prediction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( x_{CO_2} )</td>
<td>( q_{CO_2} )</td>
</tr>
<tr>
<td>2.01</td>
<td>0.104</td>
<td>0.260</td>
<td>0.241</td>
</tr>
<tr>
<td>4.48</td>
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<tr>
<td>12.93</td>
<td>0.095</td>
<td>0.633</td>
<td>1.285</td>
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</table>

Like higher pressure measurements of mixture adsorption in the UiO-66 framework, these measurements in the HKUST-1 framework show negative deviations from IAST in the loading of both components at all pressures investigated. Interestingly, however, the adsorbed phase mole fraction observed in experiments departs from the trends predicted by IAST, but only at low pressure. At a pressure of 2.01 bar, for example, the adsorbed phase mole fraction of carbon dioxide \( x_{CO_2} \) is about half that predicted by IAST. But at a higher pressure of 12.93 bar, the adsorbed phase mole fraction of carbon dioxide \( x_{CO_2} \) is in good agreement with that predicted by IAST (0.633 vs 0.614). While this data set is limited to gas phases with low concentrations of carbon dioxide \( y_{CO_2} < 0.11 \), this observation may suggest that IAST struggles more at low pressure than at higher pressure for this mixture-adsorbent pair.
5.5 Conclusions

This investigation of the performance of IAST in predicting gas mixture adsorption on three MOFs revealed mixed results. In some cases, IAST was able to give near-quantitative prediction of experimental gas mixture adsorption measurement, but in other cases experimental results deviated greatly from IAST prediction. All MOFs in this study showed some degree of energetic heterogeneity as evidenced by variation in isosteric heat of adsorption with loading of all three adsorbates. This was especially true for n-butane and carbon dioxide. However, accuracy of IAST prediction was not strongly associated with adsorbent surface heterogeneity, nor with the more ideal mixture of n-butane/ethane compared to the less ideal mixture of n-butane/carbon dioxide. IAST gave the best predictions for adsorption of n-butane/carbon dioxide adsorption on UiO-66, but the worst predictions were found for adsorption of ethane/carbon dioxide on the same MOF. IAST was able to accurately predict adsorption of what was expected to be a relatively non-ideal mixture (n-butane/carbon dioxide) on HKUST-1 but not UiO-66 or UiO-66-NH$_2$. Additionally, experiments with carbon dioxide/methane mixtures revealed different deviations from IAST when adsorption was tested at higher pressures in excess of 10 bar.

It is difficult to draw correlations between IAST performance and any characteristic of the adsorbent or adsorbate mixture tested; rather it is critical to consider the adsorbent and adsorbate mixture together. IAST is not a replacement for experimental measurement and caution should be exercised in using IAST-predicted selectivities in ranking the promise of adsorbent materials for achieving any given separation. Examination of IAST efficacy for three mixtures on three MOFs revealed no obvious association with adsorbent
heterogeneity or pairings of adsorbate molecules. Adsorbent, adsorbate mixture, and pressure are important in determining efficacy of IAST in predicting mixture adsorption.

5.6 References


35. Van Heest, T.; Teich-Mcgoldrick, S. L.; Greathouse, J. A.; Allendorf, M. D.; Sholl, D. S., Identification of Metal–Organic Framework Materials for Adsorption Separation of Rare Gases: Applicability of Ideal Adsorbed Solution Theory (IAST) and


CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The work described in this dissertation is focused on understanding limitations of IAST in predicting mixed gas adsorption on tailored adsorbents. MOFs were used as a platform material throughout this work. The effects of pore chemistry on adsorption properties in the CAU-10 and UiO-66 families of MOFs were explored, and an original volumetric instrument was constructed and automated for use in the study of mixed gas adsorption. Adsorption of four gas mixtures in various compositions was studied on three MOFs and revealed difficulty in predicting when IAST predictions of mixture adsorption were accurate.

6.1.1 Reticular chemistry approach to tuning adsorption in aluminum MOFs

The work described in chapter 3 highlights several pendant functional groups inserted for the first time into the CAU-10 framework. This chapter also describes a synthesis of MFM-300 (Al) without piperazine nor nitric acid. The description of different adsorption properties for frameworks containing the same functional groups in different positions shows that differing functional group position on ligands may have small effects on adsorption properties as seen with 4-nitroisophthalic acid vs 5-nitroisophthalic acid. These effects may in some cases be much more pronounced, as is the case with 2,4-pyridinedicarboxylic acid vs 3,5-pyridinedicarboxylic acid and 4-hydroxyisophthalic acid vs 5-hydroxyisophthalic acid. This opportunity may be leveraged further to tune adsorption
properties in MOFs with ligands like isophthalic acid which offer this geometric opportunity to place pendant functional groups in different positions.

6.1.2 Multi-Component Gas Adsorption System MC GAS

Chapter 4 describes an original instrument created in this work to perform automated measurements of mixed gas adsorption at elevated pressures. This chapter describes the instrument in fine technical detail, which we hope will allow for replication of this instrument and in turn lowered barriers to measurement of mixture adsorption. The validation of this instrument by comparison to published and original pure component adsorption measurements, as well as published mixture adsorption measurements, is a major focus of this chapter. Design considerations and potential improvements are also discussed here.

6.1.3 Efficacy of IAST predictions in MOFs

Chapter 5 describes studies of efficacy of IAST in predicting adsorption of several gas mixtures on three MOFs chosen to represent several types of MOFs prevalent in the separations literature. We use here UiO-66, one of the most stable and well-studied MOF adsorbents, as well as an amine-functionalized version of the same framework. We also use HKUST-1, a likewise well-known adsorbent, which contains open metal sites. Open metal sites and pendant functional groups are known to introduce energetic heterogeneity to the adsorbent surface, and by studying these materials we gain insight into the difficulty in anticipating non-ideal interactions between adsorbents and adsorbates. Furthermore, in this chapter we have studied adsorption of four binary mixtures: three including an alkane species and carbon dioxide, and one including two alkane species. This work reveals not
only difficulty in categorically predicting which adsorbents or mixtures might more closely
match IAST behavior, but shows that behavior in specific adsorbent-mixture pairs can be
very individual to the specific pair in question. This further validates the often-cited need
for increased quantity of mixture adsorption experiments to better understand and
characterize materials for adsorption separations.

6.2 Recommendations

6.2.1 Deepening understanding of IAST limitations

This work further confirms that limitations of IAST in predicting mixed gas
adsorption are difficult to paint in broad strokes across classes of adsorbents or even for
specific gas mixtures. While open metal sites or pendant functional groups may be linked
to deviation from IAST-predicted selectivity or loading in some cases, this work shows
that this is not always the case— even for mixtures whose constituents appear to have similar
properties. Similar mixtures may behave quite differently in the same framework. Broader
characterization of adsorbent-mixture systems via experimental measurement is essential
to improved understanding and ability to model real, complex adsorption separation
systems. The work in this dissertation only scratches the surface of all possible adsorbent-
mixture systems, which should be expected to behave in unique ways. One obvious
extension of this work which is narrow enough in scope to be reasonably achievable is to
branch out from carbon dioxide/ alkane mixtures to other relevant mixtures which are
interesting from a fundamental perspective. Many important separations involve removing
polar molecules from nonpolar mixtures, for example, which is a category of separation
not touched upon in this work. This is relevant for gas sweetening, flue gas treatment, and water harvesting applications.

6.2.2 Use of MOFs as adsorbents for industrially relevant separations

While approximately 20 out of 200 existing zeolites have found industrial use as catalysts or adsorbents,\(^1\) the same cannot be said for MOFs. Over 80,000 MOFs have been synthesized and yet none are used on large scale in industry. At the time of writing this dissertation, a Web of Science search returns 101,000 results for “zeolite” and 69,000 results for “metal-organic framework” and “metal organic framework”. This supports the idea that MOFs are no longer new materials, and are now comparable to zeolites in the size of the bodies of research into each class of material. Many would argue that at least one application of MOFs is needed to justify the cost of research into this class of porous materials. To more quickly approach such a goal, a narrowing of the scope of research would be beneficial. Rather than developing thousands of new MOFs every year, the scientific community might better serve itself and the populations that fund its research efforts by increasing focus on applications-driven research and expending less effort on materials searching.

Real steps towards this goal may be taken by identifying MOFs which share some characteristics of the most broadly used industrial adsorbents: thermal and chemical stability with some affinity for target molecules. The MOF community tends to place great import on affinity for target molecules while putting less emphasis on adsorbent stability. Of the materials in this work, only HKUST-1 shares this problem of low chemical stability in water vapour. The aluminum isophthalate family of CAU-10 MOFs offers relatively low
cost among MOF adsorbents and shows superior stability in water vapour. We recommend further study of the 3,5-pyridinedicarboxylic acid CAU-10 analog for equilibrium separations of polar and nonpolar molecules, especially for streams containing water vapour.

6.2.3 Future landscape of mixture adsorption measurement

Widespread implementation of more energy-efficient adsorption separations to augment or replace legacy separations depends on the ability of scientists and engineers to better characterize the behavior of real adsorption systems. To date, most study of mixed gas adsorption focuses on binary mixtures which mimic more complex real streams. For example, 15% carbon dioxide in balance methane is often used as an analog for natural gas, while 15% carbon dioxide in balance nitrogen is used as an analog for flue gas. These simplified analog streams omit important components from both real mixtures, most notably water vapor and various acidic species. These species tend to adsorb strongly and may change behavior or stability of adsorbents studied for these applications. If adsorption separations systems are to have a future in the realm of industry, they must first be better studied under real conditions. This means measurement capacity for complex mixture adsorption must improve. By examining the BISON-20 database containing experimental gas mixture adsorption data, we can look into the future of said measurements and make recommendations as to which measurement methods might be most useful for engineers interested in studying mixture adsorption.

By examining only BISON-20 entries published since 2010, several trends become clear. First, the breakthrough method has greatly increased in popularity relative to all other
methods. Before 2010, only 21% of BISON-20 references used breakthrough methods. Since 2010, this jumps to 55% reflecting a huge rise in popularity of breakthrough methods. This is reflective of the current materials-driven nature of the study of mixture adsorption. Breakthrough measurements are a convenient way to evaluate a specific separation by measuring a small number of data points and thus have been used extensively as a way to show a few experimental measurements of selectivity for adsorption of a mixture on a novel adsorbent. Breakthrough experiments have typically not been used for collection of larger data sets. Accordingly, references using breakthrough measurements tend to report fewer mixture adsorption data points than do references using closed volumetric instruments (17 vs 54 points per reference). As breakthrough methods become more popular, a related trend in the database becomes clear: recent references report fewer mixture adsorption data points than older sources. References reporting mixture adsorption before 2010 contain on average 50 mixture adsorption data points. This number decreased to 21 data points per reference among all references in the database published since 2010. This suggests that as research has become more materials focused the drive to quickly evaluate mixture adsorption on a large number of adsorbents has led to an overall decrease in the number of measurements per material.

A third finding is that many techniques have seen only sparing use in the last decade. Half of the techniques described in this work were not used to collect any of the data points in BISON-20 since 2010. Desorption and specialty methods in particular were used much less since 2010 than were the other groups of methods, falling almost entirely out of favor. This trend is a healthy sign that the mixture adsorption community is innovating and moving towards faster or less costly methods as they become available. One obvious
example of such innovation is the infrared (IR) spectroscopy method, which was introduced as applied to mixed gas adsorption shortly before 2010 but has become the 4th-most widely used method since.

The study of mixture adsorption presently relies to great extent on home-built systems. Though the most popular methods are DCB and the open volumetric (OV) and closed volumetric (CV) techniques, a wide variety of other methods have been developed. Many of these have risen in popularity even as DCB systems have become more widespread. This trend suggests that there will not be a lone method that will emerge as the preferred technique for all future measurements of mixture adsorption. Rather, a small group of methods, each with their own advantages, is likely to make up the bulk of mixture adsorption measurements in the future.

If the future of mixture adsorption measurement follows a similar path to pure gas adsorption measurement, use of commercial instruments will overtake that of home-built systems as they become more accessible. Nevertheless, at present the home-built systems still represent the vast majority of published mixture adsorption measurements. Among the various techniques presented in this paper, there are three which merit further discussion as part of the future of mixture adsorption measurement: concentration pulse chromatography (CPC), IR spectroscopy, and DCB.

Despite its relatively low throughput, DCB is currently the most widespread method for measuring mixture adsorption and is likely to account for the majority of such measurements in the next decade. The simplicity of the equipment required for this technique is among the greatest of any method presented in this work. DCB has found great
favor among those developing novel adsorbent materials, who might have small adsorbent samples and require a single measurement of selectivity for a component in a representative mixture for benchmark testing. These single-point selectivity measurements do not provide information on how the system responds to different gas compositions or pressures. However, there is a simple possibility to address this weakness. The OV and DCT systems use much of the same equipment as DCB systems with the addition of effluent flow rate measurement. Experimentalists who perform routine DCB measurements can adapt DCB systems to perform OV or DCT measurements. Adaptation offers the possibility to measure multiple equilibrium points per activation of the adsorbent, greatly increasing throughput. This adaptation is likely not trivial, but may be less daunting than building an OV or DCT system from the ground up.

While DCB has been widely used, CPC has not found such popularity. Researchers have lamented that the treatment of experimental data to calculate equilibrium loadings is not trivial.\(^2\) A variety of data treatment methods exist, which are becoming better able to handle highly selective adsorption at the cost of increasing complexity.\(^3\) This method, like DCB, uses relatively simple equipment and offers higher throughput than DCB. The introduction of robust software for the data fitting methods required to use CPC would make this technique more broadly accessible.

The use of IR spectroscopy to directly probe the composition of the adsorbed phase offers unique advantages when this method can be applied. \textit{In-situ} measurement of adsorbate composition allows high sensitivity and removes the need for careful material balances on the gas phase of the system. If this technique can be applied to adsorbents beyond zeolites and silica gels, IR spectroscopy could see widespread use in the near
future. This technique faces some challenges as it has yet to be applied to any MOF adsorbents, which are becoming a widely studied class of adsorbents.

We close by highlighting several issues that are relevant to producing and reporting high quality mixture adsorption data. Systematic meta-analysis of experimental replicates of single component adsorption have suggested that ~20% of reported single component isotherms are inconsistent with other reported data. Fewer experimental replicates are available for mixture adsorption, but analysis by Cai et al. of the BISON-20 data set also suggested that differences between measurements with nominally equivalent materials are not uncommon. This situation is exacerbated by the observation that in studies focused on materials discovery, it is common for materials to appear just once in the literature with no subsequent instances of the same material being synthesized. When aiming to produce high quality mixture adsorption data, it is highly advisable to first provide data showing the ability to reproduce single component isotherms that are known with a high degree of reliability. For carbon dioxide and methane adsorption, multi-laboratory studies have established isotherms of this kind with readily available reference zeolites, and additional examples with multiple replicates are available for carbon dioxide and alcohols. For mixture adsorption, the BISON-20 data set presents a comprehensive collection of extant mixture data including examples for which replicates have been reported, so careful comparisons to data from this source should be made in any new study of mixture adsorption. In addition, standard practices to enhance data reproducibility and reuse such as reporting experimental uncertainties and tabulating numerical data in readily available ways should always be followed when reporting mixture adsorption data.
While the study of mixture adsorption has seen tremendous innovation in its history, some central problems remain unsolved. Several challenges were identified in Talu’s 1998 examination of the state of the art of mixture adsorption experiments, and many of these challenges remain unsolved more than two decades later. Direct measurement of mixture adsorption equilibria is still complicated and time consuming, and researchers remain heavily reliant on IAST to predict mixture adsorption in the absence of a robust, accessible, high-throughput method for measurements. Though DCB has emerged as the closest candidate to this vision, many other methods maintain advantages for certain applications such as the ability of IR to directly monitor adsorbate concentrations albeit in only a fraction of adsorbents. Interest in complex mixture adsorption is currently enjoying a renaissance in the separations field, and this renewed interest will no doubt lead to new innovations in measurement and theory.

6.3 References


APPENDIX A. SUPPORTING INFORMATION FOR CHAPTER 3

A.1 Additional synthesis methods

CAU-10-5-CH₃ (2) was synthesized from a mixture of 171.5 mg AlCl₃*6H₂O (0.71 mmol), 152.9 mg 5-methylisophthalic acid (0.85 mmol), 1.04 g DMF, and 4.05 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

CAU-10-5-NH₂ (3) was synthesized from a mixture of 171.4 mg Al₂(SO₄)₃ (0.50 mmol), 182.7 mg 5-aminoisophthalic acid (1.01 mmol), 1.02 g DMF, and 4.02 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

CAU-10-5-OH (4) was synthesized from a mixture of 171.2 mg Al₂(SO₄)₃ (0.50 mmol), 183.0 mg 5-hydroxyisophthalic acid (1.00 mmol), 1.01 g DMF, and 4.00 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.
CAU-10-5-F (5) was synthesized from a mixture of 171.2 mg Al$_2$(SO$_4$)$_3$ (0.50 mmol), 183.5 mg 5-fluoroisophthalic acid (1.00 mmol), 1.01 g DMF, and 4.01 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

CAU-10-5-NO$_2$ (6) was synthesized from a mixture of 749.6 mg Al(NO$_3$)$_3$*9H$_2$O (2.00 mmol), 211.4 mg 5-nitroisophthalic acid (1.00 mmol), 0.99 g DMF, and 4.01 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

CAU-10-4-NO$_2$ (7) was synthesized from a mixture of 375.9 mg Al(NO$_3$)$_3$*9H$_2$O (1.00 mmol), 213.6 mg 4-nitroisophthalic acid (1.01 mmol), 1.00 g DMF, and 4.05 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

CAU-10-2,4-pydc (8) was synthesized from a mixture of 562.4 mg Al(NO$_3$)$_3$*9H$_2$O (1.50 mmol), 250.7 mg 2,4-pyridinedicarboxylic acid (1.50 mmol), 10.0 g DMF, and 40.7 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 100 mL Teflon autoclave liner,
which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

CAU-10-3,5-pydc (9) was synthesized from a mixture of 1879.1 mg Al(NO$_3$)$_3$*9H$_2$O (5.01 mmol), 936.2 mg 3,5-pyridinedicarboxylic acid (5.60 mmol), 10.00 g DMF, and 40.04 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 100 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

MIL-53-TDC (11) was synthesized from a mixture of 1666.8 mg Al$_2$(SO$_4$)$_3$*18H$_2$O (2.5 mmol), 430.4 mg 2,5-thiophenedicarboxylic acid (2.5 mmol), 4.00 g DMF, and 20.10 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 47 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.

MIL-160 (12) was synthesized from a mixture of 1666.2 mg Al$_2$(SO$_4$)$_3$*18H$_2$O (2.5 mmol), 390.2 mg 2,5-furandicarboxylic acid (2.5 mmol), 4.00 g DMF, and 20.05 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 47 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air.
The authors attempted unsuccessfully to synthesize a porous structure from aluminum and 4-hydroxyisophthalic acid. This material, termed “CAU-10-4-OH”, was synthesized from a mixture of 171.6 mg $\text{Al}_2(\text{SO}_4)_3$ (0.50 mmol), 213.6 mg 4-hydroxyisophthalic acid (1.01 mmol), 1.03 g DMF, and 4.05 g water. The aluminum salt was dissolved in the water, and the organic ligand was dissolved in the DMF. These solutions were dosed into a 20 mL Teflon autoclave liner, which was sealed in a steel autoclave. This autoclave was then placed in an oven for 12 h at 120 °C. After cooling to room temperature, the product was filtered and dried in air. PXRD pattern and CO$_2$, CH$_4$, and N$_2$ isotherms at 298 K are included below.

### A.2 Additional diffraction, SEM images, and adsorption data

![CAU-10-4-OH Powder X-Ray Diffraction](image)

**Figure A.1:** CAU-10-4-OH Powder X-Ray Diffraction.
This pattern appears to share some peaks with the simulated pattern for CAU-10, but also has prominent additional peaks at 7° and 27°, suggesting the presence of another crystalline phase may be a possibility.

![Figure A.2: CAU-10-4-OH Adsorption Isotherms at 298 K](image-url)
Figure A.3: SEM images of some of the materials analyzed in this work. A) CAU-10-5-OH B) CAU-10-5-NH$_2$ C) CAU-10-5-NO$_2$ D) CAU-10-3,5-pydc E) NOTT-300, synthesized in the “CAU-style” synthesis
Figure A.4: Nitrogen physisorption isotherms (materials 1-4), 77K.
Figure A.5: Nitrogen physisorption isotherms (materials 5-8), 77K
Figure A.6: Nitrogen physisorption isotherms (materials 9-12), 77K

Figure A.7: CAU-10-pydc-3,5 PXRD. A) reproduced from Cadiau et al.\textsuperscript{1} B) Our own work.
Figure A.8: All adsorption isotherms in chapter 3 measured at 298 K.
A.4 References

APPENDIX B. SUPPORTING INFORMATION FOR CHAPTER 4

B.1 Symbols & additional adsorption data

Table B-1: List of symbols used in Chapter 4.

<table>
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<tr>
<th>Variable</th>
<th>Description</th>
<th>Unit</th>
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<td>Pressure</td>
<td>Bar</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>P₀</td>
<td>Pressure at step 0</td>
<td>Bar</td>
</tr>
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<td>Volume of reference cell</td>
<td>mL</td>
</tr>
<tr>
<td>n₀</td>
<td>Number of moles at step 0</td>
<td>mmol</td>
</tr>
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<td>R</td>
<td>Gas constant</td>
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<td>mmol</td>
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<tr>
<td>P&lt;sub&gt;r&lt;/sub&gt;</td>
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<td>Molar volume of gas in the reference cell at step 1</td>
<td>mL·mol&lt;sup&gt;-1&lt;/sup&gt;</td>
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<tr>
<td>V&lt;sub&gt;m,AL,1&lt;/sub&gt;</td>
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<td>mL·mol&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td>mmol</td>
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<tr>
<td>V&lt;sub&gt;m,AL,0&lt;/sub&gt;</td>
<td>Molar volume of gas in the adsorption loop at step 0</td>
<td>mL·mol&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>n&lt;sub&gt;ads,0&lt;/sub&gt;</td>
<td>Number of adsorbed moles at step 0</td>
<td>mmol</td>
</tr>
<tr>
<td>n&lt;sub&gt;ads,1&lt;/sub&gt;</td>
<td>Number of adsorbed moles at step 1</td>
<td>mmol</td>
</tr>
<tr>
<td>n&lt;sub&gt;A,0&lt;/sub&gt;</td>
<td>Number of moles of component A at step 0</td>
<td>mmol</td>
</tr>
<tr>
<td>V&lt;sub&gt;m,A,RC,0&lt;/sub&gt;</td>
<td>Molar volume of component A in the reference cell at step 0</td>
<td>mL·mol&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>( n_{A,1} )</td>
<td>Number of moles of component A at step 1</td>
<td>mmol</td>
</tr>
<tr>
<td>( V_{m,A,RC,1} )</td>
<td>Molar volume of component A in the reference cell at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( V_{m,A,AL,1} )</td>
<td>Molar volume of component A in the adsorption loop at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( n_{A,ads} )</td>
<td>Number of adsorbed moles of component A</td>
<td>mmol</td>
</tr>
<tr>
<td>( n_{B,2} )</td>
<td>Number of moles of component B at step 2</td>
<td>mmol</td>
</tr>
<tr>
<td>( V_{m,B,RC,2} )</td>
<td>Molar volume of component B in the reference cell at step 2</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( n_{A,ads,0} )</td>
<td>Number of adsorbed moles of component A at step 0</td>
<td>mmol</td>
</tr>
<tr>
<td>( n_{A,ads,1} )</td>
<td>Number of adsorbed moles of component A at step 1</td>
<td>mmol</td>
</tr>
<tr>
<td>( V_{m,B,RC,1} )</td>
<td>Molar volume of component B in the reference cell at step 1</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( V_{m,B,RC,0} )</td>
<td>Molar volume of component B in the reference cell at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( V_{m,B,AL,1} )</td>
<td>Molar volume of component B in the adsorption loop at step 1</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( V_{m,B,AL,0} )</td>
<td>Molar volume of component B in the adsorption loop at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( n_{B,ads,0} )</td>
<td>Number of adsorbed moles of component B at step 0</td>
<td>mmol</td>
</tr>
<tr>
<td>( n_{B,ads,1} )</td>
<td>Number of adsorbed moles of component B at step 1</td>
<td>mmol</td>
</tr>
<tr>
<td>( \delta_{ij} )</td>
<td>Binary interaction parameter</td>
<td>-</td>
</tr>
<tr>
<td>( y_i )</td>
<td>Gas phase mole fraction species i</td>
<td>-</td>
</tr>
<tr>
<td>( y_j )</td>
<td>Gas phase mole fraction species j</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta n_{A,ads} )</td>
<td>Change in moles of species A adsorbed</td>
<td>mmol</td>
</tr>
<tr>
<td>( \text{srHS,2} )</td>
<td>Uncertainty in right side of equation 2</td>
<td>-</td>
</tr>
<tr>
<td>( s_{P1} )</td>
<td>Uncertainty in pressure at step 1</td>
<td>bar</td>
</tr>
<tr>
<td>( s_{P0} )</td>
<td>Uncertainty in pressure at step 0</td>
<td>bar</td>
</tr>
<tr>
<td>( \text{srHS,S3} )</td>
<td>Uncertainty in right side of equation S3</td>
<td>mL</td>
</tr>
<tr>
<td>( s_{Vbeads} )</td>
<td>Uncertainty in volume of glass beads</td>
<td>mL</td>
</tr>
<tr>
<td>( s_{P1}/P0 )</td>
<td>Uncertainty in P1/P0</td>
<td>-</td>
</tr>
<tr>
<td>( s_{P3}/P2 )</td>
<td>Uncertainty in P3/P2</td>
<td>-</td>
</tr>
<tr>
<td>( s_{VRC} )</td>
<td>Uncertainty in volume of reference cell</td>
<td>mL</td>
</tr>
<tr>
<td>( s_{VAL} )</td>
<td>Uncertainty in volume of adsorption loop</td>
<td>mL</td>
</tr>
<tr>
<td>( s_T )</td>
<td>Uncertainty in temperature</td>
<td>K</td>
</tr>
<tr>
<td>( s_{Vm0} )</td>
<td>Uncertainty in molar volume of gas at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( V_{m,A} )</td>
<td>Molar volume of species A at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( y_A )</td>
<td>Gas phase mole fraction of species A</td>
<td>-</td>
</tr>
<tr>
<td>( s_{Vm,A} )</td>
<td>Uncertainty in molar volume of species A at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( s_{Vm} )</td>
<td>Uncertainty in molar volume of gas</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>( s_{y_A} )</td>
<td>Uncertainty in gas phase mole fraction of component A</td>
<td>-</td>
</tr>
<tr>
<td>( s_{\Delta n_{A,ads}} )</td>
<td>Uncertainty in change in moles of species A adsorbed</td>
<td>mmol</td>
</tr>
<tr>
<td>( s_{Vm,A,RC,0} )</td>
<td>Uncertainty in molar volume of component A in the reference cell at step 0</td>
<td>mL*mol(^{-1})</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>SI Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>---------</td>
</tr>
<tr>
<td>$S_{vm,A,RC,1}$</td>
<td>Uncertainty in molar volume of component A in the reference cell at step 1</td>
<td>mL*mol$^{-1}$</td>
</tr>
<tr>
<td>$S_{vm,A,AL,0}$</td>
<td>Uncertainty in molar volume of component A in the adsorption loop at step 0</td>
<td>mL*mol$^{-1}$</td>
</tr>
<tr>
<td>$S_{vm,A,AL,1}$</td>
<td>Uncertainty in molar volume of component A in the adsorption loop at step 1</td>
<td>mL*mol$^{-1}$</td>
</tr>
<tr>
<td>$q_A$</td>
<td>Amount of species A adsorbed per gram of adsorbent</td>
<td>mmol*g$^{-1}$</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of adsorbent</td>
<td>g</td>
</tr>
<tr>
<td>$x_A$</td>
<td>Adsorbed phase mole fraction of species A</td>
<td>-</td>
</tr>
<tr>
<td>$q_B$</td>
<td>Amount of species B adsorbed per gram of adsorbent</td>
<td>mmol*g$^{-1}$</td>
</tr>
<tr>
<td>$x_B$</td>
<td>Adsorbed phase mole fraction of species B</td>
<td>-</td>
</tr>
<tr>
<td>$S_{B,A}$</td>
<td>Selectivity for species B over species A</td>
<td>-</td>
</tr>
<tr>
<td>$y_B$</td>
<td>Gas phase mole fraction of species B</td>
<td>-</td>
</tr>
<tr>
<td>$s_{yB}$</td>
<td>Uncertainty in gas phase mole fraction of component B</td>
<td></td>
</tr>
<tr>
<td>$s_{xA}$</td>
<td>Uncertainty in adsorbed phase mole fraction of component A</td>
<td></td>
</tr>
<tr>
<td>$s_{xB}$</td>
<td>Uncertainty in adsorbed phase mole fraction of component B</td>
<td></td>
</tr>
</tbody>
</table>

Figure B.1: Methane adsorption isotherms on BPL carbon at 301.4 K on MC GAS
Each set of points represents an isotherm run on a different sample of the carbon. I.e., each sample was activated, weighed, and run separately.

**Figure B.2: Ethane adsorption isotherms on BPL carbon at 301.4 K on MC GAS.**

Each set of points represents an isotherm run on a different sample of the carbon. I.e., each sample was activated, weighed, and run separately.

**B.2 Calculation S1: Volume of gas sample for composition analysis**

In the course of each mixture adsorption equilibrium measurement, the composition of the gas in the head space of the adsorption loop must be measured. Along with the readings from pressure transducers and thermocouples, this allows the calculation of the number of moles of each species in the gas phase after adsorption. To measure the
composition of the gas, 20 µL of gas from the adsorption loop is sent to the gas chromatograph. It is reasonable to assume that the removal of this volume from the adsorption loop does not affect the adsorption measurement, due to the small volume of this gas sample relative to the volume of the adsorption loop in the instrument (200 mL).

Each measurement relies on the calculation of the number of moles removed from the gas phase by adsorption. So, in assuming this 20 uL sample is small enough not to affect the measurement, we must compare this quantity of gas to the quantity that is adsorbed at each step of the measurement. Fortunately, removing this sample of gas does not change the composition of gas in the head space of the adsorption loop, as the gas is well-mixed by the circulation pump. Removing this sample of gas slightly reduces the pressure in the head space, however.

In order to assess the impact of removing this sample, it is important to remember that we are interested in the number of moles that are removed from the gas phase via adsorption, so the moles removed for composition analysis should be small relative to the amount that are removed via adsorption.

The process of measuring adsorption starts with dosing each pure gas into the adsorption loop, where they are mixed and allowed to adsorb on the adsorbent. The head space of the adsorption loop has a total volume of approximately 200 mL. At 298 K and a pressure of 1 bar, this volume contains 8.07 mmol of an ideal gas. If the adsorption loop starts in an evacuated state and then 0.5 bar (4.03 mmol) of each gas is dosed into the loop, we would expect that if no adsorption occurs, the final pressure will be 1 bar. The difference
in the measured final pressure and the final pressure in the absence of adsorption represents the amount of gas that has been adsorbed.

For a mixture of two weakly adsorbing gases, the amounts adsorbed of each component at 1 bar from an equimolar mixture might be, for example, 0.1 mmol/g of each component. At least 5 g of adsorbent is used in typical experiments on the instrument described in this work. So, the number of moles removed from the gas phase, even for this example using weakly adsorbing components at relatively low pressure, is 0.5 mmol of each component. This means that in this example, 1 mmol of gas is removed from the gas phase by adsorption. So, the moles of gas used for composition analysis must be much smaller than 1 mmol in order to assume that measuring the composition does not affect the measurement. In this example, 1 bar of ideal gas, or 8.07 mmol, was dosed to the adsorption loop. We supposed that 1 mmol was adsorbed, corresponding to a loading of 0.1 mmol/g of each component. This leaves 7.07 mmol in the head space of the adsorption loop. So, the pressure in the adsorption loop after equilibration should be about 7/8 of the original pressure that was dosed in. The original pressure was 1 bar, so we expect approximately 875 mbar after equilibration. To measure the composition of this gas, a 20 µL sample is sent to the gas chromatograph. For an ideal gas at 298 K and 875 mbar, a 20 µL sample contains 0.8 µmol, which is very small relative to the adsorbed amount of 1 mmol. Therefore, in this case it is safe to assume that the amount of gas removed to measure the gas composition is very small relative to the amount that is adsorbed, and accordingly it is safe to assume the amount of gas that is removed for composition measurement is sufficiently small so as not to affect the measurement.
In the case that the adsorbent has higher affinity for the adsorbates, the adsorbed amount is even larger. The volume of the gas sample removed for composition analysis stays the same throughout all measurements, so this example represents a “worst case” scenario in which the adsorbed amount is very low. Even in this “worst case”, the gas sample removed for composition analysis is sufficiently small so as not to be a principal cause of error in these measurements.

B.3 Calculation S2: Propagation of Uncertainty in Mixture Adsorption Measurement

Measurement of mixed gas adsorption is vulnerable to uncertainties arising from many sources. Very precise measurements of gas composition, free volume, pressure, temperature, and adsorbent mass are required for collection of high-quality measurements. The most basic quantity of interest in a mixture adsorption measurement is the number of moles of each component adsorbed at a given gas composition, pressure, and temperature.

The uncertainty in the mass of adsorbent loaded in the instrument is simply the measurement error in the balance used to weigh the activated adsorbent, which is stated as 0.1 mg.

In the operation of this instrument, this quantity is calculated by subtracting the number of moles of each gas remaining in the gas phase after equilibration from the number of moles of each gas dosed into the adsorption loop initially. From equation 20, we can see the mole balance for component A before and after adsorption occurs.
\[
\left( \frac{V_{RC}}{V_{m,A,RC,0}} - \frac{V_{RC}}{V_{m,A,RC,1}} \right) = \left( \frac{V_{AL}}{V_{m,A,AL,1}} - \frac{V_{AL}}{V_{m,A,AL,0}} \right) + \left( n_{A,ads,1} - n_{A,ads,0} \right) \tag{20}
\]

This equation can be rewritten to define a new quantity, \( \Delta n_{A,ads} = n_{A,ads,1} - n_{A,ads,0} \)

the change in amount of component A adsorbed during a step in the measurement.

\[
\Delta n_{A,ads} = \left( \frac{V_{RC}}{V_{m,A,RC,0}} - \frac{V_{RC}}{V_{m,A,RC,1}} \right) - \left( \frac{V_{AL}}{V_{m,A,AL,1}} - \frac{V_{AL}}{V_{m,A,AL,0}} \right) \tag{33}
\]

The quantities on the right side of this equation are the volume of the reference cell, \( V_{RC} \), volume of the adsorption loop \( V_{AL} \), molar volumes of component A before and after equilibration in both the reference cell and adsorption loop. The volume of the reference cell and adsorption loop are calculated from a helium expansion measurement, while the molar volume of the gas is calculated from the composition, temperature, and pressure of the gas.

The volume of the reference cell and adsorption loop are calculated from simultaneous solution of two equations:

\[
\frac{V_{RC}}{V_{RC} + V_{AL}} = \frac{P_1}{P_0} \tag{2}
\]

\[
\frac{V_{RC}}{V_{RC} + V_{AL} - V_{beads}} = \frac{P_3}{P_2} \tag{4}
\]

These equations make the assumption that the gas used in the expansion (helium) behaves as an ideal gas, and that the process is isothermal. The quantities measured for this calculation are the pressure before and after each expansion, as well as the volume of glass.
beads used for the expansion measurement. From equation 2, it is evident that the standard
deviation of the right side of the equation is equal to

\[
s_{RHS,2} = \sqrt{\left(\frac{1}{s_{P_0}}\right)^2 s_{P_1}^2 + \left(\frac{-P_1}{P_0^2}\right)^2 s_{P_0}^2} \tag{34}
\]

The standard deviation of \(P_0\) and \(P_1\) are identical at 0.08% of the measured value of
pressure, so \(s_{P_0} = 0.08 \times P_0\) and \(s_{P_1} = 0.08 \times P_1\). In these measurements, \(P_0\) was approximately
5 bar, while \(P_1\) was approximately 2.2 bar. This means \(s_{RHS,2} = 0.0005\). A similar
calculation for the right side of equation 4 shows that \(s_{RHS,4} = 0.0006\). The volume of the
glass beads was determined using a graduated pipet, with measurement error of 0.1 mL.
Equations 2 and 4 can be combined to show that:

\[
V_{RC} + V_{AL} = \frac{V_{beads} P_2}{\frac{1}{P_0} \left(1 - \frac{P_1 P_2}{P_0 P_3}\right)} \tag{35}
\]

Now, the uncertainty of every quantity on the right side of the equation is known.
This can be calculated as:

\[
s_{RHS,s3} = \sqrt{\left(\frac{1}{1 - \frac{P_1 P_2}{P_0 P_3}}\right)^2 s_{V_{beads}}^2 + \left(\frac{V_{beads} P_2 P_3}{P_0^2} \frac{P_2}{P_0 P_3} \right)^2 s_{P_2}^2 + \left(\frac{-V_{beads} P_1 P_3}{P_0^2} \frac{1}{P_0 - P_3} \right)^2 s_{P_0}^2} \tag{36}
\]

This calculation yields \(s_{RHS,s3} = 0.8\) mL. Now that the uncertainty in the sum \(V_{RC} + V_{AL}\) is known, the uncertainty in \(V_{RC}\) and \(V_{AL}\) can be equated and calculated as follows.
\[ s_{V_{RC}+V_{AL}} = 0.8 \text{ mL} = \sqrt{s_{V_{RC}}^2 + s_{V_{AL}}^2} \]  \hspace{1cm} (37)

\[ s_{V_{RC}} = s_{V_{AL}} = 0.57 \text{ mL} \]  \hspace{1cm} (38)

Now that the uncertainty in the free volumes of the system have been calculated, all that remains to calculate the amount adsorbed of each component is the uncertainty in the molar volumes of each component. The molar volume of the mixture as a whole is calculated from the Peng-Robinson equation.

\[ P_0 = \frac{RT}{V_{m0} - b} - \frac{a}{V_{m0}(V_{m0} + b) + b(V_{m0} - b)} \]  \hspace{1cm} (7)

This is an implicit function of \( V_{m0} \), which cannot be solved explicitly. However, the uncertainty in \( V_{m0} \) can be estimated by using the propagation of error formula:

\[ s_{V_{m0}} = \sqrt{\left( \frac{R}{V_{m0} - b} \right)^2 s_T^2 + \left( \frac{2a(b + V_{m0})}{(b(V_{m0} - b) + V_{m0}(b - V_{m0}))^2} - \frac{RT}{(V_{m0} - b)^2} \right)^2 s_{V_{m0}}^2} \]  \hspace{1cm} (39)

At this point it is helpful to choose an illustrative example. One such case could be a 10/90 mixture of A (methane) and B (ethane) at a pressure of 5 bar and 298 K. Here, \( s_{P0} = 0.004 \text{ bar} \), \( s_T = 1 \text{ K} \), \( a = 5532858 \text{ mL}^2 \text{ bar/mol}^2 \), and \( b = 39.03 \text{ mL/mol} \). This gives \( V_{m0} = 5206 \text{ mL/mol} \). Equation 43 can be solved using these example values to find that in this case, \( s_{V_{m0}} = 42 \text{ mL/mol} \). Further, the molar volume of each component can be calculated as follows:
\[ V_{m,A} = \frac{V_m}{y_A} \]  

(40)

The strong dependence of \( V_{m,A} \) on the mole fraction of \( A \) in the gas phase places strong emphasis on \( y_A \) as a source of experimental error, indeed the measurement of \( y_A \) is by far the largest source of experimental error in the measurement of mixture adsorption by the instrument described in this work.

\[
s_{V_{m,A}} = \sqrt{\left(\frac{1}{y_A}\right)^2 s_{V_m}^2 + \left(\frac{-V_m}{y_A^2}\right)^2 s_{y_A}^2} \]  

(41)

The uncertainty in \( y_A \) comes from uncertainty in the gas chromatograph measurement. This error is approximately 0.2\%, as estimated from repeated measurements of gas of identical composition. From this example calculation, we can see that the uncertainty in \( V_{m,A} \) is equal to 1052 mL/mol. Similarly, the uncertainty in \( V_{m,B} \) is 47 mL/mol using the same expression. The uncertainty associated with all terms on the right side of equation 34 is now known. This allows the use of the same error propagation formula to solve the uncertainty associated with the adsorbed amount of each component in this example.
Using the numbers from this example case, \( s_{\Delta n_{A,ads}} = 0.03 \) mmol while \( s_{\Delta n_{B,ads}} = 0.11 \) mmol. The loading of each component is simply calculated by dividing the total amount adsorbed by the mass of adsorbent (assumed to be 5 g):

\[
q_A = \frac{n_{A,ads}}{m} 
\]

Because the uncertainty in sample mass is very small, it can be written that the uncertainty in \( q_A \) is as follows:

\[
s_{q_A} = \frac{s_{q_A}}{m} 
\]

Therefore, the uncertainty in \( q_A \), \( s_{q_A} = 0.006 \) mmol/g and \( s_{q_B} = 0.02 \) mmol/g. For components A and B which behave like the methane and ethane used in this study, the amounts adsorbed under these conditions may be in the realm of \( q_A = 0.09 \) mmol/g and \( q_B = 4.8 \) mmol/g. The adsorbed phase mole fraction is calculated as:

\[
x_A = \frac{q_A}{q_A + q_B} 
\]
With corresponding uncertainty

\[
S_{x_A} = \sqrt{\left(\frac{q_B}{(q_A + q_B)^2}\right)^2 s_{q_A}^2 + \left(\frac{-q_A}{(q_A + q_B)^2}\right)^2 s_{q_B}^2}
\]  

(46)

The experimental uncertainty in the loading of the more weakly adsorbed component A, which results primarily from uncertainty in gas phase composition measurement, causes in turn large uncertainty in the adsorbed phase mole fraction of each component. This uncertainty dominates over the calculation for uncertainty in selectivity for the more strongly adsorbing component B. In this example, \(s_{x_A} = 0.004\), and \(s_{x_B} = 0.007\).

The selectivity is calculated as follows:

\[
S_{B,A} = \frac{x_b y_a}{x_a y_b}
\]  

(47)

Continuing with this example, we have \(S_{B,A} = 5.9\). It then follows that the uncertainty in selectivity can be calculated as:

\[
S_{S_{B,A}} = \sqrt{\left(\frac{x_b}{x_a y_b}\right)^2 s_{y_A}^2 + \left(\frac{y_a}{x_a y_b}\right)^2 s_{x_B}^2 + \left(\frac{-y_a x_b}{x_a^2 y_b}\right)^2 s_{x_A}^2 + \left(\frac{-y_a x_b}{x_a y_b^2}\right)^2 s_{y_B}^2}
\]  

(48)

Using the numbers from the example above, it follows that \(S_{S_{B,A}} = 1.3\). It is important to note that nearly all uncertainty associated with this selectivity calculation comes from the third term in the sum under the radical in equation Error! Reference source not found.. High uncertainty in adsorbed phase mole fraction of a weakly adsorbing
component causes very high uncertainty in selectivity. As shown by Talu, relatively small values of experimental uncertainty in gas mixture adsorption measurement can lead to extremely high uncertainties in selectivity.¹

**Table B-2: Estimates of uncertainty in quantities directly measured by MC GAS**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Measured By</th>
<th>Uncertainty Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference cell pressure</td>
<td>Digital transducer</td>
<td>±0.05%</td>
</tr>
<tr>
<td>Adsorption loop pressure</td>
<td>Digital transducer</td>
<td>±0.08%</td>
</tr>
<tr>
<td>Temperature</td>
<td>Thermocouple</td>
<td>±2.2 °C or 0.75% above 0 °C</td>
</tr>
<tr>
<td>Sample mass</td>
<td>Microbalance</td>
<td>±&lt;0.1 mg</td>
</tr>
<tr>
<td>Gas composition</td>
<td>GC</td>
<td>±0.2%</td>
</tr>
<tr>
<td>Reference cell volume</td>
<td>Helium expansion</td>
<td>±0.8 mL</td>
</tr>
<tr>
<td>Adsorption loop volume</td>
<td>Helium expansion</td>
<td>±0.7 mL</td>
</tr>
</tbody>
</table>

**B.4 Calculation S3: MC GAS Sample Mass Requirement**

The sample mass used in experiments in this work is approximately 5 g. However, the minimum sample mass which can be used to achieve acceptable measurement sensitivity depends on the adsorption of each component at the operating conditions of the instrument (pressure, temperature) during the measurement. The minimum sample mass is directly related to the maximum uncertainty in component loadings that is acceptable for the measurement.

The crucial quantity tracked through each measurement is the number of moles of each component in the gas phase, which is calculated in this work using the Peng-Robinson equation of state for mixtures, though other equations of state may be used. To understand the limiting sample mass, it is helpful to consider the mole balance used to calculate the number of moles adsorbed on the sample at each step in the measurement.
The mole balance begins with the Peng-Robinson equation of state, which is used to calculate the molar volume of each component in the gas phase in the head space over the adsorbent. This equation takes three inputs: pressure, temperature, and gas composition (determined from GC).

\[
P_0 = \frac{RT}{V_{m_0} - b} - \frac{a}{V_{m_0}(V_{m_0} + b) + b(V_{m_0} - b)}
\]  

(7)

For mixed gases, the constants \(a\) and \(b\) corresponding to mixtures of species A and B are calculated as follows. Indices \(i\) and \(j\) iterate over all pairs of interactions present in the mixture, ie \(ij = AA, ij = AB, ij = BA, ij = BB\).

\[
a = \sum_i \sum_j y_i y_j (1 - \delta_{ij})(a_i a_j)^{1/2}
\]

(22)

\[
b = \sum_i y_i b_i
\]

(23)

Then, the mole balance for each component is used to calculate the amount adsorbed of each component:

\[
\left(\frac{V_{RC}}{V_{m,A,RC,0}} - \frac{V_{RC}}{V_{m,A,RC,1}}\right) = \left(\frac{V_{AL}}{V_{m,A,AL,1}} - \frac{V_{AL}}{V_{m,S,SL,0}}\right) + \left(n_{A,ads,1} - n_{A,ads,0}\right)
\]

(20)

\[
\left(\frac{V_{RC}}{V_{m,B,RC,0}} - \frac{V_{RC}}{V_{m,B,RC,1}}\right) = \left(\frac{V_{AL}}{V_{m,B,AL,1}} - \frac{V_{AL}}{V_{m,B,AL,0}}\right) + \left(n_{B,ads,1} - n_{B,ads,0}\right)
\]

(21)
The uncertainty in the amount adsorbed of component A from equation 20 is calculated using equation Error! Reference source not found.. The volumes of the reference cell (V_{RC}) and adsorption loop (V_{AL}) are known with high precision, so the molar volume of each component in the gas phase is the primary source of measurement uncertainty. This measurement uncertainty comes primarily from uncertainty in gas composition measurement as discussed in Calculation S2.

\[
s_{\Delta n_{A,ads}} = \left[ \left( \frac{1}{V_{m,A,RC,0}} - \frac{1}{V_{m,A,RC,1}} \right)^2 s_{V_{RC}}^2 + \left( \frac{-1}{V_{m,A,AL,1}} + \frac{1}{V_{m,A,AL,0}} \right)^2 s_{V_{SL}}^2 \right. \\
+ \left. \left( \frac{-V_{RC}}{V_{m,A,RC,0}} \right)^2 s_{V_{m,A,RC,0}}^2 + \left( \frac{-V_{RC}}{V_{m,A,RC,1}} \right)^2 s_{V_{m,A,RC,1}}^2 \right]^{1/2}
\]

(42)

The uncertainty in quantity adsorbed of each component, \( s_{\Delta n_{A,ads}} \) and \( s_{\Delta n_{B,ads}} \), described in equation 42, comes from uncertainty in molar volume which in turn comes primarily from uncertainty in the gas composition measurement. These numbers may vary greatly for different adsorbent-adsorbate mixture combinations, so it is helpful to return to the example values used in Calculation S2 to understand the impact of sample mass on uncertainty in component loadings. Remember, the uncertainty in quantity adsorbed (in mmol) is calculated in equation 42 before the sample mass is taken into account to convert to a more usable uncertainty in quantity adsorbed per adsorbent mass (mmol/g).

Using the numbers from this example case, Calculation S2 used a 10/90 mixture of A and B where it was determined that \( s_{\Delta n_{A,ads}} = 0.03 \) mmol while \( s_{\Delta n_{B,ads}} = 0.11 \) mmol. The
loading of each component is simply calculated by dividing the total amount adsorbed by the mass of adsorbent as in equation 43 with uncertainty given in equation 44.

\[ q_A = \frac{n_{A,ads}}{m} \]  
\[ s_{q_A} = \frac{s_{q_A}}{m} \]  

In Calculation S2, a sample mass of 5 g was used. The resulting uncertainty in \( q_A \), \( s_{q_A} = 0.006 \text{ mmol/g} \) and \( s_{q_B} = 0.02 \text{ mmol/g} \). For components A and B which behave like the methane and ethane used in this study, the amounts adsorbed under these conditions may be in the realm of \( q_A = 0.09 \text{ mmol/g} \) and \( q_B = 4.8 \text{ mmol/g} \). Therefore the relative uncertainties for amounts adsorbed in this example are 7% for the weakly adsorbing component A and 0.4% for the more strongly adsorbing component B. If a sample mass of 1 g had been used, this would have resulted in uncertainties of 0.03 mmol/g (or 35%) in \( q_A \) and 0.11 mmol/g (or 2.3%) in \( q_B \). While an uncertainty of 7% for a weakly adsorbing component like methane is acceptable, an uncertainty of 35% is generally not desirable. The sample mass required is strongly related to the adsorption loading of the weaker component at the conditions tested.

While the cutoff for what uncertainty is acceptable can be debated, we chose to use a sample mass of 5 g in this work to balance the need to keep uncertainties in loading relatively low while setting a precedent for the use of manageable sample masses in future work, which may use adsorbents for which large samples are not easily available. A more sensitive gas composition measurement or use of a gas mixture whose weakly adsorbed component is adsorbed in greater quantities could reduce the required sample mass.
The maximum sample mass is limited in theory only by the size of the sample cell used and the packing density of the adsorbent. For example, the 40 cm$^3$ sample cell in this work held up to 16 g of BPL carbon adsorbent, but a larger sample cell might hold more. This could be of interest for testing adsorption of weakly adsorbing mixtures or testing adsorption at particularly low pressures or high temperatures.

APPENDIX C. SUPPORTING INFORMATION FOR CHAPTER 5

C.1 Symbols & additional adsorption data

Table C-1: List of symbols used in chapter 5.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Adsorbent surface area</td>
<td>m²/g</td>
</tr>
<tr>
<td>( f_i )</td>
<td>Fugacity of component i from isotherm measurement (in this work assumed equal to pressure)</td>
<td>bar</td>
</tr>
<tr>
<td>( \tilde{f}_i )</td>
<td>Fugacity of component i in the bulk gas phase</td>
<td>bar</td>
</tr>
<tr>
<td>( f_i^0 )</td>
<td>Fugacity of component i in the adsorbed phase</td>
<td>bar</td>
</tr>
<tr>
<td>( k_i )</td>
<td>DLSF parameter</td>
<td>bar⁻¹</td>
</tr>
<tr>
<td>( n_i )</td>
<td>DLSF parameter</td>
<td>-</td>
</tr>
<tr>
<td>( P )</td>
<td>Pressure</td>
<td>bar</td>
</tr>
<tr>
<td>( P_0 )</td>
<td>Saturation pressure</td>
<td>bar</td>
</tr>
<tr>
<td>( q_i )</td>
<td>Amount adsorbed of component i</td>
<td>mmol·g⁻¹</td>
</tr>
<tr>
<td>( q_t )</td>
<td>Total amount adsorbed of all components</td>
<td>mmol·g⁻¹</td>
</tr>
<tr>
<td>( q_{\text{sat},i} )</td>
<td>DLSF parameter</td>
<td>mmol·g⁻¹</td>
</tr>
<tr>
<td>( Q_{st} )</td>
<td>Isosteric heat of adsorption</td>
<td>kJ·mol⁻¹</td>
</tr>
<tr>
<td>( R )</td>
<td>Gas constant</td>
<td>mL·bar·K⁻¹·mmol⁻¹</td>
</tr>
<tr>
<td>( S_{ij} )</td>
<td>Adsorption selectivity for component i over component j</td>
<td>-</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>( x_i )</td>
<td>Adsorbed phase mole fraction of component i</td>
<td>-</td>
</tr>
<tr>
<td>( y_i )</td>
<td>Gas phase mole fraction of component i</td>
<td>-</td>
</tr>
<tr>
<td>( \pi_i )</td>
<td>Spreading pressure of component i</td>
<td>g·s⁻²</td>
</tr>
</tbody>
</table>
Table C-2: Dual-site Langmuir-Freundlich isotherm model fit parameters for carbon dioxide and ethane adsorption on MOF studied in chapter 5.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Adsorbent</th>
<th>T [K]</th>
<th>$q_{sat,1}$ [mmol/g]</th>
<th>$n_1$</th>
<th>$k_1$ [bar$^{-1}$]</th>
<th>$q_{sat,2}$ [mmol/g]</th>
<th>$n_2$</th>
<th>$k_2$ [bar$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>UiO-66</td>
<td>288</td>
<td>7.49613</td>
<td>0.85194</td>
<td>0.07855</td>
<td>3.68525</td>
<td>0.92704</td>
<td>0.77798</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>UiO-66</td>
<td>298</td>
<td>6.32608</td>
<td>0.92645</td>
<td>0.04625</td>
<td>4.72961</td>
<td>0.90766</td>
<td>0.46513</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>UiO-66</td>
<td>308</td>
<td>7.84244</td>
<td>0.88826</td>
<td>0.03438</td>
<td>4.03097</td>
<td>0.94346</td>
<td>0.38757</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>UiO-66-NH$_2$</td>
<td>288</td>
<td>8.5034</td>
<td>0.75503</td>
<td>0.34134</td>
<td>12.7981</td>
<td>1.12849</td>
<td>0.00977</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>UiO-66-NH$_2$</td>
<td>298</td>
<td>11.8901</td>
<td>0.6891</td>
<td>0.07547</td>
<td>0.8518</td>
<td>1.38022</td>
<td>1.58047</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>UiO-66-NH$_2$</td>
<td>308</td>
<td>3.41524</td>
<td>0.94899</td>
<td>0.51468</td>
<td>14.0803</td>
<td>0.62504</td>
<td>0.01162</td>
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<tr>
<td>Carbon dioxide</td>
<td>HKUST-1</td>
<td>288</td>
<td>12.3241</td>
<td>0.95172</td>
<td>0.66201</td>
<td>1.75593</td>
<td>2.20684</td>
<td>0.64017</td>
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<tr>
<td>Carbon dioxide</td>
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<td>0.64053</td>
<td>12.3757</td>
<td>1.02699</td>
<td>0.49785</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>HKUST-1</td>
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<td>1.21865</td>
<td>0.4699</td>
<td>7.83076</td>
<td>0.78273</td>
<td>0.00468</td>
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<td>Ethane</td>
<td>UiO-66</td>
<td>288</td>
<td>6.53295</td>
<td>0.434</td>
<td>0.28047</td>
<td>0.82269</td>
<td>1.47954</td>
<td>1.07902</td>
</tr>
<tr>
<td>Ethane</td>
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<td>1.62184</td>
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<td>5.95337</td>
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</tr>
<tr>
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<td>0.88994</td>
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<td>4.88281</td>
<td>0.32392</td>
<td>0.04016</td>
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<td>Ethane</td>
<td>UiO-66-NH$_2$</td>
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<td>2.77611</td>
<td>0.64574</td>
<td>5.81899</td>
<td>0.56102</td>
<td>0.4787</td>
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<td>Ethane</td>
<td>UiO-66-NH$_2$</td>
<td>308</td>
<td>5.06518</td>
<td>0.62782</td>
<td>0.2591</td>
<td>0.85272</td>
<td>0.59172</td>
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<td>HKUST-1</td>
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<td>11.7828</td>
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<td>1.44524</td>
<td>7.32585</td>
<td>0.63023</td>
<td>0.36837</td>
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</table>
Table C-3: Nitrogen physisorption isotherms at 77 K on MOFs studied in chapter 5.

<table>
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<tr>
<th>P/P₀</th>
<th>q (cc STP/g)</th>
<th>P/P₀</th>
<th>q (cc STP/g)</th>
<th>P/P₀</th>
<th>q (cc STP/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00123</td>
<td>215.9766</td>
<td>0.00154</td>
<td>152.1169</td>
<td>0.00829</td>
<td>406.1305</td>
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<td>0.00288</td>
<td>224.2278</td>
<td>0.00438</td>
<td>165.4195</td>
<td>0.0088</td>
<td>406.4069</td>
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<tr>
<td>0.0056</td>
<td>233.0786</td>
<td>0.00501</td>
<td>167.9735</td>
<td>0.01005</td>
<td>407.4476</td>
</tr>
<tr>
<td>0.0099</td>
<td>240.4216</td>
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<td>174.5958</td>
<td>0.01905</td>
<td>412.1565</td>
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<td>0.0094</td>
<td>240.5486</td>
<td>0.0088</td>
<td>179.2415</td>
<td>0.02925</td>
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<td>0.01877</td>
<td>248.1165</td>
<td>0.01003</td>
<td>182.5885</td>
<td>0.03921</td>
<td>421.5779</td>
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<td>0.02956</td>
<td>252.6915</td>
<td>0.01889</td>
<td>195.5613</td>
<td>0.04972</td>
<td>426.3711</td>
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<td>0.04258</td>
<td>255.6062</td>
<td>0.02929</td>
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<td>437.5749</td>
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<td>215.7814</td>
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<td>267.1798</td>
<td>0.19919</td>
<td>218.727</td>
<td>0.35071</td>
<td>462.1786</td>
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<td>268.4825</td>
<td>0.24978</td>
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<td>0.40075</td>
<td>464.7516</td>
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<td>269.5477</td>
<td>0.29937</td>
<td>223.6428</td>
<td>0.44879</td>
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<td>478.6435</td>
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<td>0.65015</td>
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<td>0.79935</td>
<td>480.4831</td>
</tr>
<tr>
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<td>481.9034</td>
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0.98886 373.161
Table C-4: Binary breakthrough equilibrium adsorption measurements used in chapter 5 (Gibbs excess adsorption).

<table>
<thead>
<tr>
<th>Adsorbate 1</th>
<th>Adsorbate 2</th>
<th>Adsorbent</th>
<th>Trial 1</th>
<th>Trial 2</th>
<th>Trial 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>Carbon dioxide</td>
<td>UiO-66</td>
<td>0.25</td>
<td>0.50</td>
<td>0.75</td>
</tr>
<tr>
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<td>Carbon dioxide</td>
<td>UiO-66</td>
<td>0.17</td>
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</tr>
<tr>
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<td>Carbon dioxide</td>
<td>UiO-66-NH₂</td>
<td>0.67</td>
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<tr>
<td>Ethane</td>
<td>Carbon dioxide</td>
<td>UiO-66-NH₂</td>
<td>0.17</td>
<td>0.62</td>
<td>0.07</td>
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<tr>
<td>Ethane</td>
<td>Carbon dioxide</td>
<td>HKUST-1</td>
<td>0.62</td>
<td>0.27</td>
<td>0.07</td>
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<tr>
<td>Ethane</td>
<td>Carbon dioxide</td>
<td>HKUST-1</td>
<td>0.62</td>
<td>0.27</td>
<td>0.07</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Carbon dioxide</td>
<td>UiO-66</td>
<td>0.50</td>
<td>0.41</td>
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<td>0.50</td>
<td>0.75</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Ethane</td>
<td>UiO-66</td>
<td>0.50</td>
<td>0.50</td>
<td>0.75</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Ethane</td>
<td>UiO-66-NH₂</td>
<td>0.50</td>
<td>0.50</td>
<td>0.75</td>
</tr>
<tr>
<td>n-Butane</td>
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<td>HKUST-1</td>
<td>0.50</td>
<td>0.50</td>
<td>0.75</td>
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<tr>
<td>n-Butane</td>
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<td>HKUST-1</td>
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</table>
All breakthroughs were measured at 1 bar total pressure with 0.333 bar helium and a temperature of 298 K. Partial pressure of adsorbing molecules summed to 0.667 bar. Adsorption loadings \( q_i \) are tabulated in mmol/g.
Table C-5: Observation of roll-up in breakthrough experiments conducted in chapter 5.

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<thead>
<tr>
<th>Adsorbate 1</th>
<th>Adsorbate 2</th>
<th>Adsorbent</th>
<th>(y_1)</th>
<th>Roll-up?</th>
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<td>HKUST-1</td>
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