

AIX-MARSEILLE UNIVERSITY

DOCTORAL SCHOOL: Physics and Material Science

PARTENAIRES DE RECHERCHE

Laboratoire MADIREL

Submitted with the view of obtaining the degree of doctor

Discipline: Material Science

Specialty: Characterisation of porous materials

Paul A. Iacomì

Titre de la thèse: sous-titre de la thèse

Defended on JJ/MM/AAAA in front of the following jury:

Prénom NOM	Affiliation	Rapporteur
Prénom NOM	Affiliation	Rapporteur
Prénom NOM	Affiliation	Examineur
Prénom NOM	Affiliation	Examineur
Prénom NOM	Affiliation	Examineur
Prénom NOM	Affiliation	Directeur de thèse

National thesis number: 2017AIXM0001/001ED62



This work falls under the conditions of the Creative Commons Attribution License - No commercial use - No modification 4.0 International.

Abstract

Abstract is here.

Acknowledgements

Acknowledgements go here

Contents

Abstract	iii
Acknowledgements	iv
1. Building a framework for adsorption data processing	1
1.1. Introduction	1
1.2. pyGAPS overview	2
1.2.1. Intended use cases	2
1.2.2. Core structure	2
1.2.3. Creation of an Isotherm	3
1.2.4. Workflow	4
1.2.5. Units	5
1.3. Isotherm characterisation and fitting	5
1.3.1. Mathematical descriptions of isotherms	5
1.3.2. Specific surface area and pore volume calculations	13
1.3.3. Assessing porosity	20
1.3.4. Predicting multicomponent adsorption	27
1.4. A case study of high throughput processing on a large dataset	29
1.4.1. The NIST ISOD dataset	29
1.4.2. A comparison between surface area determination methods	31
1.4.3. Observed reliability of results	32
1.5. Conclusion	33
Bibliography	34
2. Extending bulk analysis of porous compounds through calorimetry	34
2.1. Introduction	34
2.2. Literature	34
2.3. Method	35
2.4. Results and discussion	35
2.4.1. Routine characterization of a MOF sample	35
2.4.2. Analysis of a carbon sample for gas separation applications	37
2.5. Conclusion	37
Bibliography	38
3. Exploring the impact of synthesis and defects on adsorption measurements	39
3.1. Introduction	39

Contents

3.2.	The defective nature of MOFs	41
3.2.1.	Types of crystal defects and their analogues in MOFs	41
3.2.2.	Consequences of defects	43
3.2.3.	Defect engineering of MOFs	44
3.2.4.	The propensity of UiO-66(Zr) for defect generation	44
3.3.	Materials and methods	46
3.3.1.	Materials	46
3.3.2.	Methods for quantifying defects	48
3.4.	Results and discussion	49
3.4.1.	Crystallinity of leached samples	49
3.4.2.	NMR	49
3.4.3.	Thermogravimetry results	49
3.4.4.	Nitrogen sorption at 77K	52
3.4.5.	Characterisation of trends	52
3.4.6.	Carbon dioxide isotherms	58
3.5.	Conclusion	59
	Bibliography	60
4.	Exploring the impact of material form on adsorption measurements	68
4.1.	Introduction	68
4.2.	Shaping in context	69
4.3.	Materials, shaping and characterisation methods	71
4.3.1.	Materials	71
4.3.2.	Shaping Procedure	72
4.3.3.	Characterisation of powders and pellets	72
4.3.4.	Sample activation for adsorption	73
4.4.	Results and discussion	73
4.4.1.	Thermal stability	73
4.4.2.	Adsorption isotherms at 77K and room temperature	73
4.4.3.	Room temperature gas adsorption and microcalorimetry	76
4.4.4.	Vapour adsorption	82
4.5.	Conclusion	89
	Bibliography	90
5.	Exploring novel behaviours	94
5.1.	Introduction	94
5.2.	Literature	94
5.3.	Method	94
5.4.	Results and discussion	94
5.5.	Conclusion	94
	Bibliography	95
A.	Common characterisation techniques	96
A.1.	Thermogravimetry	96

Contents

A.2. Bulk density determination	96
A.3. Skeletal density determination	97
A.4. Nitrogen physisorption at 77 K	97
A.5. Vapour physisorption at 298 K	97
A.6. Gravimetric isotherms	98
A.7. High throughput isotherm measurement	98
A.8. Powder X-ray diffraction	98
A.9. Nuclear magnetic resonance	98
Bibliography	98
B. Synthesis method of referenced materials	99
B.1. Takeda 5A reference carbon	99
B.2. MCM-41 controlled pore glass	99
B.3. Zr fumarate MOF	99
B.4. UiO-66(Zr) for defect study	99
B.5. UiO-66(Zr) for shaping study	100
B.6. MIL-100(Fe) for shaping study	100
B.7. MIL-127(Fe) for shaping study	100
Bibliography	101
C. Appendix for chapter 4	102
C.1. Calorimetry dataset UiO-66(Zr)	102
C.2. Calorimetry MIL-100(Fe)	103
C.3. Calorimetry MIL-127(Fe)	106
Bibliography	106
D. Appendix for chapter 3	108
D.1. Acid and solvent properties	108
D.2. Powder diffraction patterns	109
D.3. TGA curves	109
D.3.1. DMF leached samples	109
D.3.2. Water leached samples	110
D.3.3. Methanol leached samples	111
D.3.4. DMSO leached samples	112
D.3.5. High resolution curves	113
D.4. Nitrogen sorption isotherms	114
D.4.1. DMF leached samples	114
D.4.2. H ₂ O leached samples	115
D.4.3. MeOH leached samples	116
D.4.4. DMSO leached samples	117
D.5. Characterisation	118
Bibliography	119

1. Building a framework for adsorption data processing

1.1. Introduction

Historically, the processing of isotherms was done by hand, with large worksheets being used for the calculations. As an example, we point out that one of the initial limitations of the BJH method was that each point had to be determined with an approximation of critical pore radius, due to the tedious work involved in the calculation.⁽¹⁾

The advent of computers meant that the calculations could be performed quickly and reliably and led to the introduction of more complex methods for isotherm processing, such as the DFT method for pore size distribution.^(2,3) Commercial adsorption equipment which offers the users a complete software solution for any isotherm calculations is now commonplace and makes obtaining reports of desired properties for measured materials a matter of minutes.

Given the current ubiquitousness of adsorption as a characterisation method, particularly for investigating surfaces and porous compounds, there is a large pool of data published in the scientific community. Key performance indicators such as specific surface area, working capacity and pore volume are commonly reported in scientific literature and used as benchmarking tools for comparing performance.

Recent efforts have also focused on building a database of adsorption isotherms⁽⁴⁾, to offer a searchable pool of standardised behaviours on different materials. This serves as both a useful reference for comparing synthesised compounds, as well as a method for quickly finding suitable materials which have the desired properties for a particular application.

Chapter summary

In this chapter an open-source software package is presented, which is released under an MIT licence and written in Python, intended to be used for manipulation, storage, visualisation and processing of adsorption isotherms. Developed internally at the MADIREL Laboratory in Marseilles, the software is aimed to give users a powerful yet easy to use package that can perform the kind of processing usually offered by commercial software, but using large datasets of hundreds or thousands of isotherms.

Contribution

Paul Iacomi wrote the python code for the pyGAPS framework and is responsible for its publication and maintenance as an open source package. The IAST functionality is a modified version of the pyIAST code, published by Cory Simon. The data used in this chapter is available from the NIST Adsorption Database, maintained by Dan Siderius.

1.2. pyGAPS overview

1.2.1. Intended use cases

The software was imagined for use in two types of scenario. First, as a command line interface, in environments such as `IPython` and `Jupyter`. The typical user working in these environments is likely to be processing a small batch of results at one time, and is interested in obtaining the results in graphical form. For this type of application, the framework should provide an unobtrusive way of importing the user data, as well as present an API which does not require extensive knowledge of processing methods. Finally, a graphing environment is required which will allow the user to visualise their dataset and results.

The second envisaged application is related to bulk data processing. Requirements here shift towards parameter control, scripting and extensibility. The framework API should offer the option to change implicit parameters, select calculation limits and return the results in a numerical form for further processing. This type of application is also likely to require storage of isotherms in a database or under other types of data files.

1.2.2. Core structure

In order to offer a clear structuring of functionality, `pyGAPS` introduces several classes which abstract data and functionality for facile interaction. The classes are intuitively named: `Isotherm`, `Sample` and `Adsorbent`.

The Isotherm class

The `Isotherm` class is a representation of an adsorption isotherm i.e. a function of the amount adsorbed, or loading, with pressure at a fixed temperature. The class also contains other information relating to the isotherm, such as the material name and batch it describes, the adsorbate used and other user-defined properties.

Because the aforementioned relationship can be either a physical measurement defined by individual pressure-loading pairs or a model, describing the relationship as a function rather than discrete data, the `Isotherm` class is used as a parent class for two subclasses: `PointIsotherm`, describing datapoints and `ModelIsotherm` containing a model such as Henry, Langmuir etc., which encapsulate the respective functionality. The two classes are interchangeable as they share most methods and properties. Once an instance of

an **Isotherm** class is created, it can then be used for the processing, conversion and graphing capabilities of **pyGAPS**.

The Sample class

The isotherm classes contain the name and batch of the sample they are measured on in a string format. The user might want to specify other information about the material, such as the date of synthesis or the material's density, as well as store this information in the database. For this case, **pyGAPS** provides the **Sample** class. The framework uses the string values in the isotherm to connect an **Isotherm** instance to a specific **Sample**.

The Adsorbate class

Finally, in order for many of the calculations included in **pyGAPS** to be performed, properties of the adsorbate used are needed e.g. liquid density, vapour pressure etc. The **Adsorbate** class is provided for this purpose, which is connected to an **Isotherm** class similarly to a **Sample**. The physical properties are either calculated in the background through an equation of state, either the open source CoolProp library⁽⁵⁾ or the NIST-made REFPROP.⁽⁶⁾ The properties can also be retrieved from the internal database or specified by the user.

1.2.3. Creation of an Isotherm

An **Isotherm** can be created either from the command line directly or through an import from a supported format. For the direct creation, the code takes two kinds of inputs: the data itself, in the form of a **pandas.DataFrame**, and the isotherm parameters describing it. Only four parameters are strictly required: the material name, the material batch, the adsorbate used and the experimental temperature. Other parameters can be passed as well and will be stored in the isotherm class.

Listing 1.1: Creating the DataFrame

```

1 isotherm_data = pandas.DataFrame({
2     'pressure' : [1, 2, 3, 4, 5, 3, 2],
3     'loading'  : [1, 2, 3, 4, 5, 3, 2],
4     'enthalpy' : [15, 15, 15, 15, 15, 15, 15],
5     'xrd_peak_1' : [0, 0, 1, 2, 2, 1, 0],
6 })

```

The **DataFrame** must contain a column containing the pressure points and one containing the corresponding loading points of the isotherm. Other columns can also be passed, when secondary data such as enthalpy of adsorption is present at each measurement point. These columns will be saved in the case of the **PointIsotherm** class and can be plotted afterwards.

If no unit data is specified in the constructor, the framework will assume that the isotherm is in units of mmol g^{-1} loading as a function of bar. Both the units and the basis can be specified, as it is explained in a latter section.

Listing 1.2: Creating the PointIsotherm

```

1 point_isotherm = pygaps.PointIsotherm(
2
3     # First the pandas.DataFrame with the points
4     # and the keys to what the columns represent.
5
6     isotherm_data,
7
8     loading_key='loading',           # The loading column
9     pressure_key='pressure',         # The pressure column
10    other_keys=['enthalpy',
11               'xrd_peak_1'],        # The columns containing other data
12
13    # Some of the unit parameters can be
14    # specified if desired.
15
16    pressure_mode='absolute',         # absolute pressure
17    pressure_unit='bar',              # with units of bar
18    adsorbent_basis='mass',          # adsorbent mass basis
19    adsorbent_unit='kg',              # with units of kg
20    loading_basis='mass',             # loading mass basis
21    loading_unit='g',                # with units of g
22
23    # Finally the isotherm description
24    # parameters are passed.
25
26    'sample_name' : 'carbon',         # Required
27    'sample_batch' : 'X1',            # Required
28    'adsorbate' : 'nitrogen',         # Required
29    't_exp' : 77,                     # Required
30    't_act' : 150,                    # Recognised / named
31    'user' : 'Username',              # Recognised / named
32    'DOI' : '10.000/mydoi',           # Unknown / user specific
33 )

```

Finally, the data is saved in the newly created class or used to generate parameters for a model such as BET, Langmuir, etc., in the case of a `PointIsotherm` and `ModelIsotherm` respectively. It should be noted that the creation of `Sample` and `Adsorbate` instances is similar.

Alternatively, the isotherm can be imported from a file containing a format that is recognised by pyGAPS. Parsing from suitably structured JSON, CSV and Excel files is supported.

1.2.4. Workflow

Once an isotherm object is created, it will be used for all further processing. The class contains methods which can be used to inspect the data visually, or retrieve parts of the isotherm such as the adsorption or desorption branches with user-chosen limits or

units. Singular values of pressure or loading can be calculated, either through interpolation in the case of a `PointIsotherm` or by evaluation of the internal model in the `ModelIsotherm`. For an isotherm with datapoints, these can also be converted into different units or modes.

Characterisation functions take a single isotherm object as their first parameter. This is the case for the BET area, Langmuir area, t-plot, α_s plot, and pore size distribution methods. These characterisation functions attempt to automate as much of the process as possible. For example, the BET area limits are automatically calculated using the Rouquerol⁽⁷⁾ method, with all the checks implemented into the code. In another example the straight line sections of the t-plot are determined automatically through a calculation of the second derivative of the transformed isotherm. For detailed control, there is an option to specify options for each individual method, such as manual BET limits, different thickness functions for the t-plot or Kelvin-based mesoporous pore distribution methods, custom parameters for the Horvath-Kawazoe microporous pore distribution, custom DFT or NLDFIT kernels and more. The results are returned in a dictionary or can be directly graphed if the `verbose` parameter is passed.

1.2.5. Units

When computers work with physical data, units are often a matter that introduces confusion. Here we explain how `pyGAPS` handles units and other physical world concepts such as relative pressure and mass or volume basis.

The following dimensions can be specified for an `Isotherm`: the measurement *pressure*, the quantity of guest adsorbed or *loading* and the amount of adsorbent material the loading is reported on, or *adsorbent*.

Pressure can be reported either in an absolute value, in several common units such as bar, torr, Pa, or as *relative pressure*, the pressure divided by the saturation vapour pressure of the adsorbate at the respective measurement temperature. Conversions between the two modes are automatic and handled internally.

Both the *loading* and *adsorbent* can be reported in three different bases: a molar basis, a mass basis or a volume basis. Within each basis different units are recognised and can be easily converted. The conversions between bases can also easily be performed if the required conversion factors (i.e. molar mass and density) are available. For *loading*, these factors are automatically calculated internally, while for the *adsorbent* they should be provided by the user in the respective `Sample` class.

1.3. Isotherm characterisation and fitting

1.3.1. Mathematical descriptions of isotherms

A lot of effort was put into attempting to describe the phenomenon of adsorption using a simple model. Through a mathematical understanding, the underlying mechanisms of adsorption can be understood. Unfortunately, the plethora of isotherm features and

shapes can only be truly recreated by molecular simulation, which requires an exact knowledge of the adsorbent structure and its interaction with the adsorbed gas. Nevertheless, great strides have been taken to obtain several models which can be useful when fitted to measured isotherms for obtaining simple parameters which are representative of physical factors such as guest-host interaction, surface area, pore size, total pore volume and others. More importantly, it allows us to numerically compare measured isotherms.

A page of figures for different models with several values of their parameter can be seen in Figure 1.1.

The Henry model

The simplest method of describing adsorption on a surface is Henry's law. It assumes only interactions with the adsorbate surface and is described by a linear dependence of adsorbed amount with increasing pressure.

$$n_a(p) = K_H p \quad (1.1)$$

It is derived from the Gibbs equation, by substituting a two dimensional analogue to the ideal gas law. From a physical standpoint, Henry's law is unrealistic as adsorption sites will saturate at higher pressures. However, the constant K_H , or Henry's constant, can be thought of as a measure of the strength of the interaction of the probe gas with the surface. At very low concentrations of gas there is a theoretical requirement for the applicability of Henry's law. Therefore, most models reduce to Equation 1.1 as $\lim_{p \rightarrow 0} n(p)$.

Langmuir and multi-site Langmuir model

The Langmuir theory^(?), proposed at the start of the 20th century, states that adsorption takes place on specific sites on a surface, until all sites are occupied. It is derived from a kinetic model of gas adsorption and is based on several assumptions:

- All sites are equivalent and have the same chance of being occupied.
- Each adsorbate molecule can occupy one adsorption site.
- There are no interactions between adsorbed molecules.
- The rates of adsorption and desorption are proportional to the number of sites currently free and currently occupied, respectively.
- Adsorption is complete when all sites are filled.

Using these assumptions we can define rates for both adsorption and desorption. The adsorption rate (Equation 1.2) will be proportional to the number of sites available on the surface, as well as the number of molecules in the gas, which is given by pressure. The

1. Building a framework for adsorption data processing

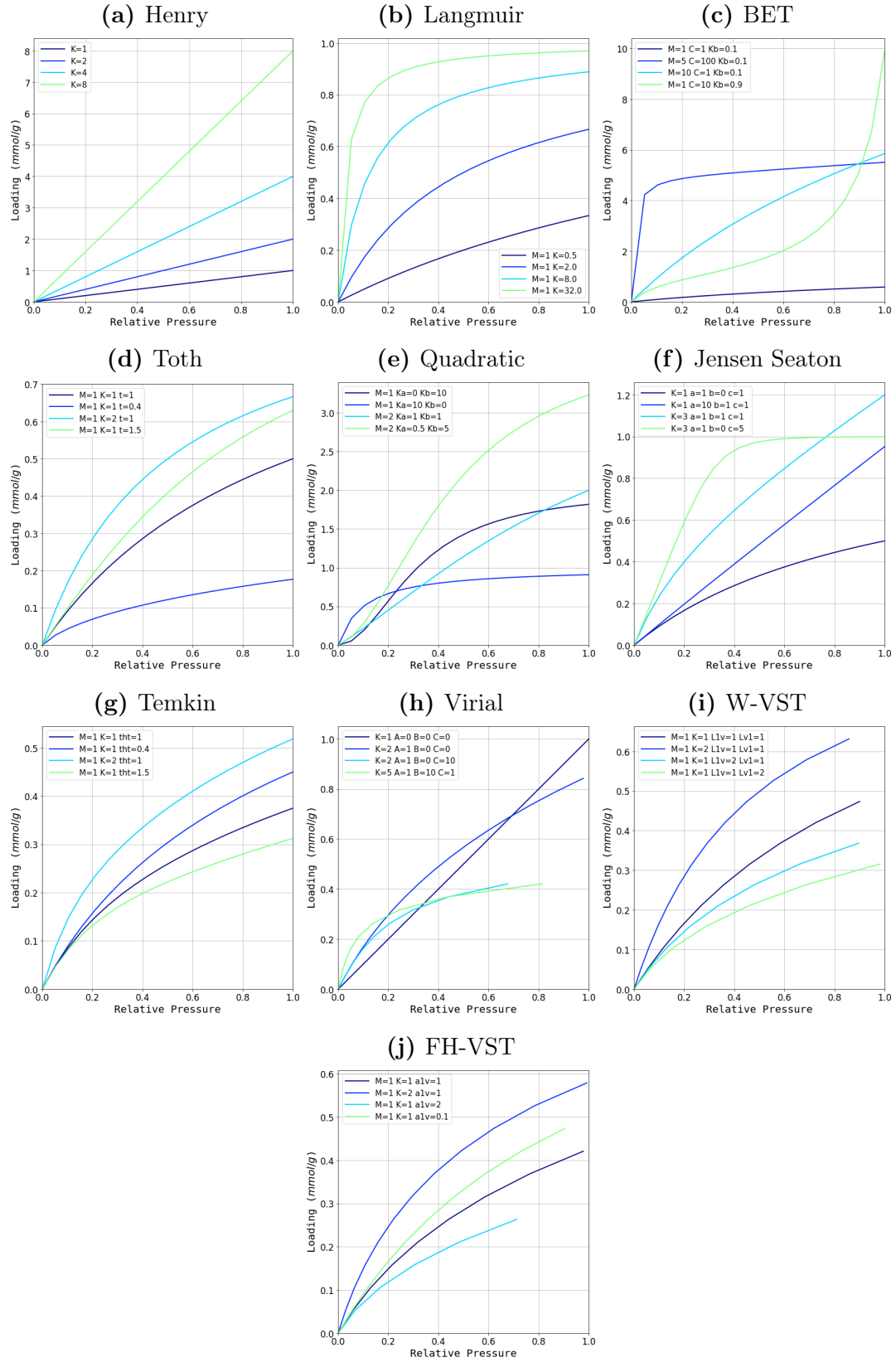


Figure 1.1.: Examples of models

1. Building a framework for adsorption data processing

desorption rate, on the other hand, will be proportional to the number of occupied sites and the energy of adsorption (Equation 1.3). It is also useful to define $\theta = n_a/n_a^m$ as the surface coverage, the number of sites occupied divided by the total sites. At equilibrium, the rate of adsorption and the rate of desorption are equal, therefore the two equations can be combined. The equation can then be arranged to obtain an expression for the loading called the Langmuir model (Equation 1.6).

$$v_a = k_a p(1 - \theta) \quad (1.2)$$

$$v_d = k_d \theta \exp\left(-\frac{E}{RT}\right) \quad (1.3)$$

$$v_a = v_d \quad (1.4)$$

$$k_a p(1 - \theta) = k_d \theta \exp\left(-\frac{E}{RT}\right) \quad (1.5)$$

$$n_a(p) = n_a^m \frac{Kp}{1 + Kp} \quad (1.6)$$

The Langmuir constant K is the product of the individual desorption and adsorption constants k_a and k_d and exponentially related to the energy of adsorption $\exp(-E/RT)$.

A common extension to the Langmuir model is to consider the experimental isotherm to be the sum of several Langmuir-type isotherms, each with specific maximum coverage and affinities. The underlying assumption is that the adsorbent has several distinct types of homogeneous adsorption sites and a Langmuir equation is used for each. This is particularly applicable in cases where the structure of the adsorbent suggests that different types of sites are present, such as in crystalline materials of variable chemistry like zeolites and MOFs. The resulting isotherm equation is:

$$n_a(p) = \sum_i n_{a,i}^m \frac{K_i p}{1 + K_i p} \quad (1.7)$$

In practice, only up to three adsorption sites are usually considered.

BET model

The BET model⁽⁸⁾ assumes that adsorption takes place on the surface of the material in incremental layers according to several assumptions:

- The adsorption sites are equivalent, and therefore the surface is heterogeneous.
- There are no lateral interactions between adsorbed molecules.
- The adsorption takes place in layers, with adsorbed molecules acting as sites for the next layer.

1. Building a framework for adsorption data processing

A particular surface percentage θ_x is occupied with x layers. For each layer at equilibrium, the adsorption and desorption rates must be equal. We can then apply the Langmuir theory for each layer as presented in Table Table 1.1. We can assume that the adsorption energy of a molecule on the second and higher layers is just the condensation energy of the adsorbent $E_{i>1} = E_L$. Since we are assuming that all layers beside the first have the same properties, we can also define $g = k_{d2}k_{a2} = k_{d3}k_{a3} = \dots$.

Table 1.1.: Derivation of the BET method applied for, each adsorbed layer

All layers	Re-arranged
$k_{a1}p\theta_0 = k_{d1}\theta_1 \exp\left(-\frac{E_1}{RT}\right)$	$p\theta_0 = \frac{k_{d1}}{k_{a1}}\theta_1 \exp\left(-\frac{E_1}{RT}\right)$
$k_{a2}p\theta_1 = k_{d2}\theta_2 \exp\left(-\frac{E_2}{RT}\right)$	$p\theta_1 = g\theta_2 \exp\left(-\frac{E_L}{RT}\right)$
$k_{a2}p\theta_2 = k_{d3}\theta_3 \exp\left(-\frac{E_3}{RT}\right)$	$p\theta_2 = g\theta_3 \exp\left(-\frac{E_L}{RT}\right)$
\vdots	\vdots
$k_{a_i}p\theta_{i-1} = k_{d_i}\theta_i \exp\left(-\frac{E_i}{RT}\right)$	$p\theta_{i-1} = g\theta_i \exp\left(-\frac{E_L}{RT}\right)$

The coverage for each layer θ can now be expressed in terms of θ_0 .

$$\theta_i = \left[p \frac{k_{a1}}{k_{d1}} \exp\left(-\frac{E_1}{RT}\right) \right] x^{i-1} \theta_0 \quad (1.8)$$

where

$$x = \frac{p}{g} \exp\left(-\frac{E_L}{RT}\right) \quad (1.9)$$

A constant C may be defined such that:

$$C = \frac{k_{a1}}{k_{d1}} g \exp\left(\frac{E_1 - E_L}{RT}\right) \quad (1.10)$$

$$\theta_i = C x^i \theta_0 \quad (1.11)$$

For all the layers, the equations can be summed:

$$\frac{n}{n_m} = \sum_{i=1}^{\infty} i \theta^i = C \sum_{i=1}^{\infty} i x^i \theta_0 \quad (1.12)$$

and since

$$\theta_0 = 1 - \sum_1^{\infty} \theta_i \sum_{i=1}^{\infty} ix^i = \frac{x}{(1-x)^2} \quad (1.13)$$

Then we obtain the BET equation:

$$n_a(p) = n_a^m \frac{C(p/p_0)}{(1 - p/p_0)[1 - (p/p_0) + C(p/p_0)]} \quad (1.14)$$

The BET constant C is a measure of the interaction with the adsorption surface and can be seen to influence the “knee” a BET-type isotherm has at low pressure, before the statistical monolayer formation.

Toth model

The Toth model is an empirical modification to the Langmuir equation (Equation 1.6) which introduces a power parameter for the denominator leading to the following formula:

$$n_a(p) = n_a^m \frac{Kp}{[1 + (Kp)^t]^{1/t}} \quad (1.15)$$

The parameter t is a measure of the system heterogeneity. Thanks to this additional parameter, the Toth equation can accurately describe a large number of adsorbent/adsorbate systems and, due to its correct behaviour in both the low and high pressure limits, is recommended as the fitting isotherms of many adsorbents such as hydrocarbons, carbon oxides, hydrogen sulphide and alcohols on activated carbons and zeolites.

Temkin model

The Temkin adsorption isotherm⁽⁹⁾, like the Langmuir model, considers a surface with n_a^m identical adsorption sites, but takes into account adsorbate-adsorbate interactions by assuming that the heat of adsorption is a linear function of the coverage. This expression for the Temkin isotherm is derived using a mean-field argument and uses an asymptotic approximation to obtain an explicit equation for the loading.⁽¹⁰⁾

$$n_a(p) = n_a^m \frac{Kp}{1 + Kp} + n_a^m \theta \left(\frac{Kp}{1 + Kp} \right)^2 \left(\frac{Kp}{1 + Kp} - 1 \right) \quad (1.16)$$

Here, n_a^m and K have the same physical meaning as in the Langmuir model. The additional parameter θ describes the strength of the adsorbate-adsorbate interactions ($\theta < 0$ for attractions).

Jensen-Seaton model

When modelling adsorption in micropores, a requirement was highlighted by Jensen and Seaton in 1996⁽¹¹⁾ that at sufficiently high pressures the adsorption isotherm should not reach a horizontal plateau corresponding to saturation but that this asymptote should continue to rise due to the compression of the adsorbate in the pores. They developed a semi-empirical equation to describe this phenomenon based on a function that interpolates between two asymptotes: the Henry's law asymptote at low pressure and an asymptote reflecting the compressibility of the adsorbate at high pressure.

$$n(p) = K_H p \left(1 + \frac{K_H p}{[a(1+bp)]^c} \right)^{(-1/c)} \quad (1.17)$$

Here K_H is the Henry constant, b is the compressibility of the adsorbed phase and c an empirical constant.

The equation can be used to model both absolute and excess adsorption as the pore volume can be incorporated into the definition of b , although this can lead to negative adsorption slopes for the compressibility asymptote. This equation has been found to provide a better fit for experimental data from microporous solids than the Langmuir or Toth equation, in particular for adsorbent/adsorbate systems with high Henry's constants where the amount adsorbed increases rapidly at relatively low pressures and then slows down dramatically.

Quadratic model

The quadratic adsorption isotherm⁽¹²⁾ exhibits an inflection point. The loading is convex at low pressures but changes concavity as it saturates, yielding an S-shape. The S-shape can be explained by adsorbate-adsorbate attractive forces; the initial convexity is due to a cooperative effect of adsorbate-adsorbate attractions aiding in the recruitment of additional adsorbate molecules.

$$n(p) = n_a^m \frac{(K_a + 2K_b p)p}{1 + K_a p + K_b^2 p^2} \quad (1.18)$$

The parameter K_a can be interpreted as the Langmuir constant; the strength of the adsorbate-adsorbate attractive forces is embedded in K_b .

Virial model

A virial isotherm model attempts to fit the measured data to a factorized exponent relationship between loading and pressure.⁽¹³⁾

$$p = n \exp(K_1 n^0 + K_2 n^1 + K_3 n^2 + K_4 n^3 + \dots + K_i n^{i-1}) \quad (1.19)$$

1. Building a framework for adsorption data processing

It has been applied with success to describe the behaviour of standard as well as supercritical isotherms. The factors are usually empirical, although some relationship with physical properties can be determined: the first constant is related to the Henry constant at zero loading, while the second constant is a measure of the interaction strength with the surface.

$$K_1 = -\ln K_{H,0} \quad (1.20)$$

In practice, besides the first constant, only 2-3 factors are used.

Vacancy solution theory models

As a part of the Vacancy Solution Theory (VST) family of models, it is based on concept of a “vacancy” species, denoted v , and assumes that the system consists of a mixture of these vacancies and the adsorbate.

The VST model is defined as follows:

- A vacancy is an imaginary entity defined as a vacuum space which acts as the solvent in both the gas and adsorbed phases.
- The properties of the adsorbed phase are defined as excess properties in relation to a dividing surface.
- The entire system including the adsorbent are in thermal equilibrium however only the gas and adsorbed phases are in thermodynamic equilibrium.
- The equilibrium of the system is maintained by the spreading pressure which arises from a potential field at the surface

It is possible to derive expressions for the vacancy chemical potential in both the adsorbed phase and the gas phase, which when equated give the following equation of state for the adsorbed phase:

$$\pi = -\frac{R_g T}{\sigma_v} \ln y_v x_v \quad (1.21)$$

where y_v is the activity coefficient and x_v is the mole fraction of the vacancy in the adsorbed phase. This can then be introduced into the Gibbs equation to give a general isotherm equation for the Vacancy Solution Theory where K_H is the Henry's constant and $f(\theta)$ is a function that describes the non-ideality of the system based on activity coefficients:

$$p = \frac{n_{ads}}{K_H} \frac{\theta}{1-\theta} f(\theta) \quad (1.22)$$

1. Building a framework for adsorption data processing

The general VST equation requires an expression for the activity coefficients. The Wilson⁽¹⁴⁾ equation can be used, which expresses the activity coefficient in terms of the mole fractions of the two species (adsorbate and vacancy) and two constants Λ_{1v} and Λ_{v1} . The equation becomes:

$$p = \left(\frac{n_{ads}}{K_H} \frac{\theta}{1 - \theta} \right) \left(\Lambda_{1v} \frac{1 - (1 - \Lambda_{v1})\theta}{\Lambda_{1v} + (1 - \Lambda_{1v})\theta} \right) \exp \left(- \frac{\Lambda_{v1}(1 - \Lambda_{v1})\theta}{1 - (1 - \Lambda_{v1})\theta} - \frac{(1 - \Lambda_{1v})\theta}{\Lambda_{1v} + (1 - \Lambda_{1v})\theta} \right) \quad (1.23)$$

Cochran⁽¹⁵⁾ developed a simpler, three parameter equation based on the Flory–Huggins equation for the activity coefficient. The equation for then becomes:

$$p = \left(\frac{n_{ads}}{K_H} \frac{\theta}{1 - \theta} \right) \exp \frac{\alpha_{1v}^2 \theta}{1 + \alpha_{1v} \theta} \quad \text{where} \quad \alpha_{1v} = \frac{\alpha_1}{\alpha_v} - 1 \quad (1.24)$$

Here α_1 and α_v are the molar areas of the adsorbate and the vacancy respectively.

1.3.2. Specific surface area and pore volume calculations

As adsorption takes place on the surface, isotherms measured on porous materials are uniquely suited for the determination of the accessible area of the void space present inside the material structure or external area of fine powders. **pyGAPS** comes with several common methods used to determine surface area, some with theoretical basis like the IUPAC-recommended BET method and some empirical, such as the t-plot method.

BET surface area

The BET method⁽⁸⁾ for determining surface area is the recommended IUPAC method⁽¹⁶⁾ to calculate the surface area of a porous material. It is generally applied on isotherms obtained through N₂ adsorption at 77 K, although other adsorbates (Ar at 77 K or 87 K, Kr at 77 K, CO₂ at 293 K) have been used. In principle, any probe with an adsorption behaviour which can be described through the BET equation in the low pressure regime can be used.

As previously mentioned, the method assumes that adsorption takes place in incremental layers according to the BET model (section 1.3.1). Even if the adsorbent is porous, the initial amount adsorbed (usually between 0.05–0.4 p/p_0) can be described through the equation written in its linear form:

$$\frac{p/p_0}{n_{ads}(1 - p/p_0)} = \frac{1}{n_m C} + \frac{C - 1}{n_m C} (p/p_0) \quad (1.25)$$

If we plot the isotherm points as $(p/p_0)/n_{ads}(1 - p/p_0)$ versus p/p_0 , a linear region can usually be found. The slope and intercept of this line can then be used to calculate n_m , the amount adsorbed at the statistical monolayer, as well as C , the BET constant.

1. Building a framework for adsorption data processing

$$n_m = \frac{1}{s + i} \quad C = \frac{s}{i} + 1 \quad (1.26)$$

From the BET monolayer capacity, the specific surface area can be calculated if the area taken up by one of the adsorbate molecules on the surface is known. The calculation uses the following equation together with Avogadro's number:

$$a_{BET} = n_m A_N \sigma \quad (1.27)$$

While commonly used for surface area determination, the BET area should be used with care, as the assumptions made in its calculation may not hold. To augment the validity of the BET method, Rouquerol⁽⁷⁾ proposed several checks to ensure that the selected BET region is valid:

- The BET (C) obtained should be positive;
- In the corresponding Rouquerol plot where $n_{ads}(1 - p/p_0)$ is plotted with respect to p/p_0 , the points chosen for BET analysis should be strictly increasing;
- The loading at the statistical monolayer should be situated within the limits of the BET region.

All these checks are implemented in **pyGAPS**. Regardless, the BET surface area should still be interpreted carefully. Since adsorption takes place on the pore surface, microporous materials which have pores of similar or smaller size as the probe molecule used will not give a realistic surface area since in the micropore range it is difficult to separate pore condensation behaviour from multilayer adsorption. Furthermore, the cross-sectional area of the molecule on the surface cannot be guaranteed. For example, nitrogen has been known to adopt a different conformation on the surface of some materials due to inter-molecular forces, which effectively lowers its cross-sectional area.⁽⁷⁾

In **pyGAPS**, starting from an isotherm object, it is easy to calculate the BET area by using the code in Listing 1.3. The framework automatically applies the Rouquerol rules to find the optimum pressure range and returns the results as a dictionary. The `verbose=True` option prints a short text with all the calculation variables as well as graphing the BET and Rouquerol plots (Figure 1.2). The user can override automatic pressure range selection by using the range parameter (`limits=(0.05, 0.3)`).

Listing 1.3: Calculating a BET area

```
1 area_dict = pygaps.area_BET(isotherm, verbose=True)
```

```
BET surface area: a = 1277 m2/g
Minimum pressure point chosen is 0.005 and maximum is 0.034
The slope of the BET fit:      s = 76.344
The intercept of the BET fit:  i = 0.052
BET constant:                  C = 1463
Amount for a monolayer:       n = 0.01309 mol/g
```

1. Building a framework for adsorption data processing

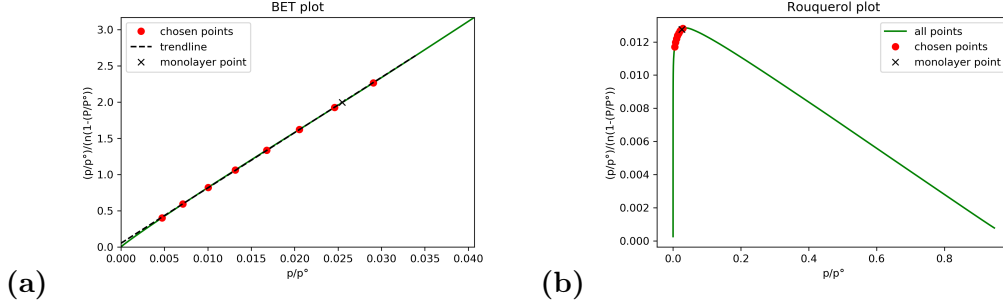


Figure 1.2.: Output from the BET area function (a) the BET plot showing the selected points for fitting the equation, as well as the location of the statistical monolayer and (b) the Rouquerol plot for this calculation.

Langmuir surface area

The Langmuir equation (Equation 1.6) can be also be expressed in a linear form by rearranging it as:

$$\frac{p}{n} = \frac{1}{Kn_m} + \frac{p}{n_m} \quad (1.28)$$

Assuming the data can be fitted with a Langmuir model, by plotting p/n against pressure, a straight line will be obtained. The slope and intercept of this line can then be used to calculate n_m , the amount adsorbed at the monolayer, as well as K , the Langmuir constant.

$$n_m = \frac{1}{s} \quad K = \frac{1}{i * n_m} \quad (1.29)$$

The surface area can then be calculated by using the monolayer capacity in a manner analogous to the BET surface area method.

$$a_{Langmuir} = n_m A_N \sigma \quad (1.30)$$

The Langmuir method for determining surface area assumes that adsorption takes place until all active sites on the material surface are occupied, or until monolayer formation in the case of complete surface coverage. As most adsorption processes (except chemisorption) don't follow this behaviour, it is important to regard the Langmuir surface area as an estimate.

As with the BET area, the Langmuir area is calculated by using the code in Listing 1.4. The framework will alert the user if the correlation is not linear in the selected range. Here the `verbose=True` option prints a short text with all the calculation variables and the graphs the Langmuir plot as seen in Figure 1.3a. If desired the user can override automatic pressure range selection as seen in the second example in Listing 1.4.

Listing 1.4: Calculating a Langmuir area

```
1 area_dict = pygaps.area_langmuir(isotherm, verbose=True)
```

```
| WARNING The correlation is not linear!
```

```
1 area_dict = pygaps.area_langmuir(isotherm,
2                                 limits=(0.05, 0.3),
3                                 verbose=True)
```

```
| Langmuir surface area:  a = 415 m2/g
| Minimum pressure point chosen is 0.0 and maximum is 0.194
| The slope of the Langmuir line:      s = 234.968
| The intercept of the Langmuir line:  i = 1.607
| The Langmuir constant is:           K = 146
| Amount for a monolayer:             n = 0.00426 mol/g
```

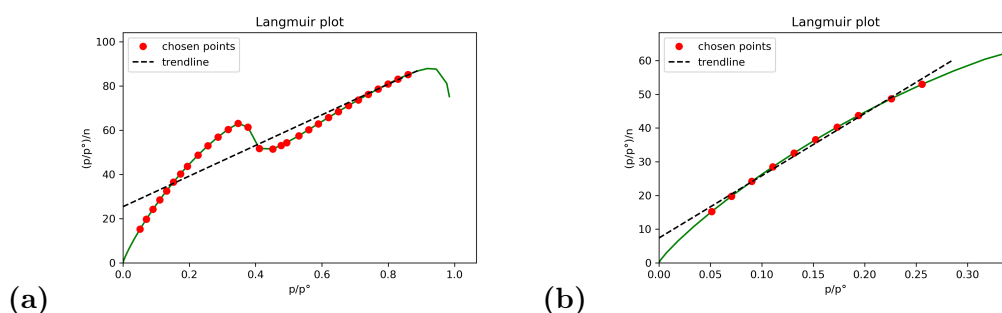


Figure 1.3.: Output from the Langmuir area function (a) the Langmuir plot showing the automatic fitting attempt which generates a warning and (b) a manually selected pressure range for the Langmuir plot.

Ideal isotherms or thickness functions

The initial part of an isotherm (the Henry regime) can be seen to be very dependent on the interactions between the adsorbate and the surface. However, the subsequent layers are less influenced by the material and can often be assumed, like in the BET model, to have an energy of adsorption identical to the enthalpy of liquefaction of the bulk liquid and therefore, their formation depends essentially only on the partial pressure.

With this assumption, several studies have been focused on obtaining an “ideal” isotherm of adsorption on a non-porous material which can then, if the cross-sectional area of the molecule is known, be transformed in a function capable of predicting the multilayer thickness as a function of pressure. This kind of empirical function, also referred to as a *thickness function* or *t-curve*, can then be used as an alternative method for surface area determination, as explained in the next section. These curves are also used in the classical methods for calculating mesoporous size distributions. It is important to clarify that the function is only applicable for a single adsorbent and a single temperature.

Several common thickness functions have been implemented in **pyGAPS**, applicable for nitrogen at 77 K such as the Halsey⁽¹⁷⁾ (Equation 1.31) and the Harkins and Jura^(?) (Equation 1.32) curve.

$$t_{Halsey} = 0.354 \left(\frac{-5}{\log(p/p_0)} \right)^{1/3} \quad (1.31)$$

$$t_{Harkins\&Jura} = \left(\frac{0.1399}{0.034 - \log_{10}(p/p_0)} \right)^{1/2} \quad (1.32)$$

check
equa-
tions

These t-curves are selected by name as parameters in the functions that use them. The user can also define their own t-curve as a function and pass it as a parameter. An example is shown in Listing 1.5 in the t-plot section.

t-plot Method

The t-plot method is an empirical method, developed as a tool to determine the surface area of porous materials, which can also be used for other calculations, such as external pore area and micropore volume calculations.⁽¹⁸⁾ A plot is constructed, where the isotherm loading data is plotted versus the ideal thickness of the adsorbate layer, obtained through the a t-curve (section 1.3.2). It stands to reason that, in the case when the experimentally measured loading follows the model, a straight line will be obtained with its intercept through the origin. However, since in most cases there are differences between adsorption in the pores and ideal surface adsorption, the t-plot will deviate and form features which can be analysed to describe the material characteristics.

- A sharp vertical deviation will indicate condensation in a type of mesopore structure.
- A gradual slope will indicate adsorption on a specific surface.

The slope of the linear section can be used to calculate the area where adsorption is taking place. If the linear region occurs at low loadings, it will represent the total surface area of the material. If at the end of the curve, it will instead represent adsorption on the external surface area of the sample. The formula to calculate the area is presented in Equation 1.33, where ρ_l is the liquid density of the adsorbate at experimental conditions.

$$a_{surface} = \frac{sM_m}{\rho_l} \quad (1.33)$$

If the region selected is after a vertical deviation, the intercept of the line will no longer pass through the origin. This intercept can be used to calculate the volume of the filled pore through the following equation:

$$V_{ads} = \frac{iM_m}{\rho_l} \quad (1.34)$$

1. Building a framework for adsorption data processing

Since the t-plot method is comparing the experimental isotherm with an ideal model, care must be taken to ensure that the t-curve is an accurate representation of the thickness of the adsorbate multilayers on the surface of the adsorbent. Since there is no such thing as a universal thickness curve, care must be taken when selecting a thickness model to ensure that it is applicable to both the material and the adsorbate. Also, features on the t-plot found at loadings lower than the monolayer thickness do not have any physical meaning.

In pyGAPS, when the function is called without any parameters except an isotherm, the framework will attempt to find plateaus in the data and automatically fit them with a straight line, returning a dictionary with the slope, intercept and calculated pore volume and specific area for each linear region found. As an example, the first function in Listing 1.5 will generate the graph in Figure 1.4a. The isotherm in this example is measured on a sample of MCM-41.

Listing 1.5: Generating a t-plot

```
1 # using automatic region detection
2 pygaps.t_plot(isotherm, verbose=True)
3
4 # specifying a manual region
5 pygaps.t_plot(isotherm, limits=(0.3,0.44), verbose=True)
6
7 # using the Halsey thickness curve
8 pygaps.t_plot(isotherm, thickness_model='Halsey', verbose=True)
9
10 # defining a custom t-curve to use in the t-plot
11 def carbon_model(relative_p):
12     return 0.88*(relative_p**2) + 6.45*relative_p + 2.98
13
14 pygaps.t_plot(isotherm, thickness_model=carbon_model, verbose=True)
```

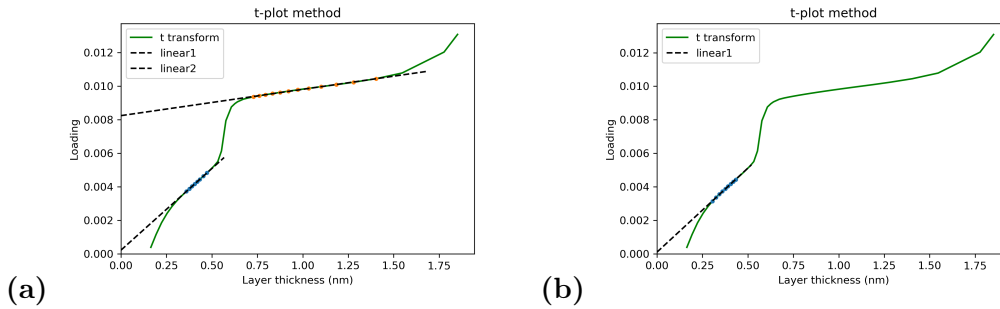


Figure 1.4.: Output from the t-plot method function (a) an automatically obtained t-plot with the calculated fit regions and (b) a manually selected range for the t-plot.

The first linear region in Figure 1.4a can be attributed to adsorption on the mesopore surface, while the second one represents adsorption on the available surface after meso-

pore filling. Therefore, the surface area values calculated for the first and second region correspond to the area of the mesopores and the external particle area, respectively. As only one pore filling event occurs, the pore volume calculated for the second region gives us the mesopore volume. We can obtain a more accurate result for the surface area by fitting the first linear region to a zero intercept through manual region selection, as shown in the second example in Listing 1.5.

Finally, the framework allows for the thickness model to be substituted with an user-provided function which will be used for the t-plot, as mentioned before in section 1.3.2. Usage of a carbon black-type thickness curve is presented in the last example in Listing 1.5.

α_s Method

In order to extend the t-plot analysis with other adsorbents and non-standard thickness curves, the α_s method was devised.⁽¹⁹⁾ Instead of attempting to find an ideal isotherm that describes the thickness of the adsorbed layer, a reference isotherm is used. This isotherm is measured on a non-porous version of the same material, assumed to have identical surface characteristics. The dimensionless α_s values are obtained from this isotherm by dividing the loading values by the amount adsorbed at a specific relative pressure, usually taken as $p/p_0 = 0.4$ since nitrogen hysteresis loops theoretically close at this point.

$$\alpha_s = \frac{n_a}{n_{0.4}} \quad (1.35)$$

The analysis then proceeds as in the t-plot method, with the same explanation for observed features. The only difference is that the surface area calculation from linear regions observed uses the known specific area of the reference material.

$$A = \frac{sA_{ref}}{(n_{ref})_{0.4}} \quad (1.36)$$

The reference isotherm chosen for the α_s method must be a description of the adsorption on a completely non-porous sample of the same material. It is often impossible to obtain such non-porous versions, therefore care must be taken how the reference isotherm is measured.

To generate an α_s -plot in `pyGAPS`, both an analysis isotherm and a reference isotherm must be supplied as shown in Listing 1.6. In this example, the reference isotherm is measured on non-porous silica. The reference material area can be specified by using the `reference_area` parameter. If not specified, it is automatically calculated by applying the BET method on the reference isotherm.

Listing 1.6: Generating an α_s -plot

```
1 pygaps.alpha_s(isotherm,
2               reference_isotherm=isotherm_r,
3               verbose=True)
```

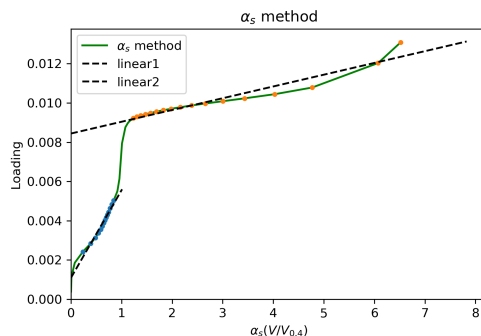


Figure 1.5.: Output from the α_s -plot function showing two automatically fit regions.

1.3.3. Assessing porosity

Characterization of pore sizes and their distribution in porous materials is often the main goal when performing adsorption experiments. It is therefore important that **pyGAPS** includes several robust methods for determining pore distribution from isotherm data.

When it comes to porous materials, three kinds of pore sizes have been defined, based on their lengthscales: micropores (<2 nm), mesopores (2 nm to 50 nm), and macropores (>50 nm).

Macropores are generally unable to be characterised through adsorption, with methods such as mercury intrusion porosimetry as the standard for pore size distributions at this lengthscale, although other alternatives have been suggested⁽²⁰⁾ due to the high toxicity of mercury. These methods are therefore outside the scope of this framework.

In the mesopore range, the “*classical*” methods are usually applied, which are based on the application of Kelvin’s equation pertaining to capillary condensation. This equation calculates the critical pressure at which the fluid completely files a pore of a specific diameter. This equation, applicable to a range of geometries is used in multiple approaches such as the Barrett-Joyner-Halenda (BJH) method or the Dollimore-Heal (DH) method.

For microporous materials, the Kelvin equation, with its assumption of continuous fluid properties and comparable density of the adsorbed state to bulk liquid density breaks down. An atomistic approach is required here, to address the interaction between solid-fluid and fluid-fluid through potential functions. The Horvath-Kawazoe or HK method is often used, and it is implemented in **pyGAPS**.

Finally, methods based on density functional theory (DFT) and derivations such as non-local DFT (NLDF) and quenched solid state DFT (QSDFT) should be mentioned, as they can be used for multiscale (micropore and mesopore) characterisation. These methods rely on *in-silico* simulation of isotherms on a range of pore sizes, which can then be collated in a so-called *DFT kernel*, able to be used in decomposition of a experimental isotherm to obtain a pore size distribution. While the generation of DFT kernels is outside the scope of the **pyGAPS** framework, it is able to use user-provided kernels to fit adsorption isotherms, and comes with a basic kernel for N_2 adsorption at 77 K on carbon slit pores.

It should be noted that all methods here described require knowledge of the pore

geometry and depend on the material having pores which conform to a well-defined shape. Real adsorbents usually have interconnected networks of irregular pores, which the ideal pores used in these models merely approximate.

Mesoporous size distribution

The Kelvin equation Since the Kelvin equation is the basis of both the BJH and DH methods its theory and its implementation will be described here. The original form of the equation (Equation 1.37) gives the dependence of pressure on the radius of curvature of a meniscus in a pore r by means of surface tension γ , molar liquid volume, here expressed as $v_l = M_m/\rho_l$ and the fluid contact angle with the surface θ . The fluid is often assumed to be fully wetting, with $\theta = 0$ and $\cos \theta = 1$.

$$\ln \left(\frac{p}{p_0} \right) = - \frac{\gamma M_m}{\rho_l R T} \frac{2 \cos \theta}{r} \quad (1.37)$$

To apply the Kelvin equation to different types of pore systems, the generalized form presented in Equation 1.38 is used. It replaces the meniscus radius by a mean radius of curvature r_m .

$$\ln \left(\frac{p}{p_0} \right) = - \frac{\gamma M_m}{\rho_l R T} \frac{2}{r_m} \quad (1.38)$$

The mean radius of curvature is defined through the two principal radii of the curved interface.

$$\frac{1}{r_m} = \frac{1}{2} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (1.39)$$

The relationship of the kelvin radius r_m to the actual pore radius is more subtle, as it depends on pore geometry and the filling state of the pore.⁽²¹⁾ If considering a cylindrical pore open at both ends, the radius reduces to the original Kelvin equation during the desorption phase, and takes other values with different combinations of parameters as can be seen in Table 1.2.

Table 1.2.: Relationship between pore geometry, pore filling and meniscus geometry

Pore geometry	Pore filling	
	Adsorption	Desorption
slit	cylindrical	concave
cylinder	cylindrical	spherical
sphere	spherical	spherical

According to Rouquerol⁽⁷⁾, in adopting this approach, it is assumed that:

1. Building a framework for adsorption data processing

- The Kelvin equation is applicable over the pore range (mesopores). Therefore in pores which are below a certain size (around 2.5 nm), the granularity of the liquid-vapour interface becomes too large for classical bulk methods to be applied.
- The meniscus curvature is controlled by the pore size and shape. Ideal shapes for the curvature are assumed.
- Pores are rigid and of well defined shape. Their geometry considered to be invariant across the entire adsorbate.
- The filling/emptying of each pore does not depend on its location.
- Adsorption on the pore walls is not different from surface adsorption.

The Barrett, Joyner and Halenda (BJH) method The BJH method for calculating pore size distribution is based on a classical description of the adsorbate behaviour in the adsorbent pores.⁽¹⁾ Under this method, the adsorbate is adsorbing on the pore walls in a predictable way, and decreasing the apparent pore volume until condensation takes place, filling the entire pore. The critical radius is a sum of two radii, the adsorbed layer thickness, which can be modelled by a thickness model (such as Halsey, Harkins & Jura or similar as presented in section 1.3.2) and a critical radius model for condensation/evaporation, based on a form of the Kelvin equation.

$$r_p = t + r_k \quad (1.40)$$

The original model uses the desorption curve as a basis for calculating pore size distribution. Between two points of the curve, the volume desorbed can be described as the volume contribution from pore evaporation and the volume from layer thickness decrease as per Equation 1.40. The computation is done cumulatively, starting from the filled pores and calculating for each point the volume adsorbed in a pore from the following equation:

$$V_p = \left(\frac{\bar{r}_p}{\bar{r}_k + \Delta t_n} \right)^2 \left(\Delta V_n - \Delta t_n \sum_{i=1}^{n-1} \Delta A_p + \Delta t_n \bar{t}_n \sum_{i=1}^{n-1} \frac{\Delta A_p}{\bar{r}_p} \right) \quad (1.41)$$

where

$$A = 2\Delta V_p / r_p \quad (1.42)$$

here

- ΔA_p is the area of the pores
- ΔV_p is the adsorbed volume change between two points

1. Building a framework for adsorption data processing

- \bar{r}_p is the average pore radius calculated as a sum of the kelvin radius and layer thickness of the pores at pressure p between two measurement points
- \bar{r}_k is the average kelvin radius between two measurement points
- \bar{t}_n is the average layer thickness between two measurement points
- Δt_n is the average change in layer thickness between two measurement points

Then, by plotting $\Delta V/(2 * \Delta r_p)$ versus the width of the pores calculated for each point, the pore size distribution can be obtained.

In order to calculate the

Listing 1.7: PSD using the BJH method

```
1 result_dict = pygaps.mesopore_size_distribution(
2     charact_iso,
3     psd_model='BJH',
4     verbose=True
5 )
```

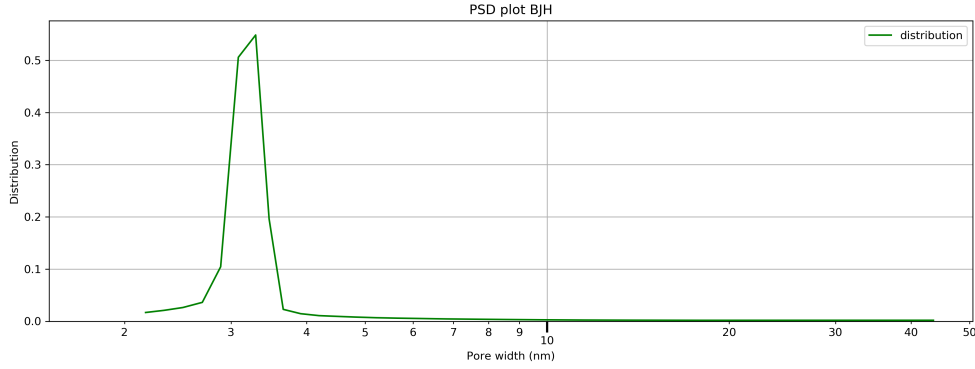


Figure 1.6.: BJH pore size distribution

The Dollimore-Heal (DH) method The DH or Dollimore-Heal method⁽²²⁾ of calculating pore size distribution is an extension of the BJH method which takes into account the geometry of the pores by introducing a length component.

Like the BJH method, it is based on a classical description of the adsorbate behaviour in the adsorbent pores.

$$V_p = \left(\frac{\bar{r}_p}{\bar{r}_k + \Delta t_n} \right)^2 \left(\Delta V_n - \Delta t_n \sum_{i=1}^{n-1} \Delta A_p + 2\pi \Delta t_n \bar{t}_n \sum_{i=1}^{n-1} L_p \right) \quad (1.43)$$

$$A = 2\Delta V_p / r_p \quad (1.44)$$

$$L = \Delta A_p / 2\pi r_p \quad (1.45)$$

Where:

1. Building a framework for adsorption data processing

- ΔA_p is the area of the pores
- ΔV_p is the adsorbed volume change between two points
- \bar{r}_p is the average pore radius calculated as a sum of the kelvin radius and layer thickness of the pores at pressure p between two measurement points
- \bar{r}_k is the average kelvin radius between two measurement points
- \bar{t}_n is the average layer thickness between two measurement points
- Δt_n is the average change in layer thickness between two measurement points

Then, by plotting $\Delta V/(2 * \Delta r_p)$ versus the width of the pores calculated for each point, the pore size distribution can be obtained.

Microporous size distribution

When it comes to micropores (width < 2 nm), classical fluid methods stop being viable. Adsorption of molecules in these pores of comparable scale is highly dependent on the surface properties and on guest-host interaction and leads to adsorbate densities often very different than those in the bulk liquid state. In order to model adsorption in such pores, a good description of both solid-fluid and fluid-fluid potential functions is required.

The Horvath-Kawazoe (HK) method The H-K method attempts to describe the adsorption within pores by calculation of the average potential energy for a pore.⁽²³⁾ The method starts by assuming the relationship between the gas phase as being:

$$R_g T \ln\left(\frac{p}{p_0}\right) = U_0 + P_a \quad (1.46)$$

Here U_0 is the potential function describing the surface to adsorbent interactions and P_a is the potential function describing the adsorbate-adsorbate interactions. This equation is derived from the equation of the free energy of adsorption at constant temperature where the term $T\Delta S^{tr}(w/w_\infty)$ is assumed to be negligible.

If it is assumed that a Lennard-Jones potential function can describe the interactions between adsorbate and surface molecules, then the two contributions to the total potential can be replaced by the extended function in Equation 1.47.

$$RT \ln(p/p_0) = N_A \frac{n_a A_a + n_A A_A}{2\sigma^4(l-d)} \times \int_{d/2}^{1-d/2} \left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^{10} - \left(\frac{\sigma}{l-r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10} \right] dx \quad (1.47)$$

where l is the width of the pore, d defined as $d = d_a + d_A$ is the sum of the diameters of the adsorbate and adsorbent molecules, n_a is number of molecules of adsorbent and A_a

1. Building a framework for adsorption data processing

and A_A the Lennard-Jones potential constant of the fluid molecule and solid molecule respectively which are defined as

$$A_a = \frac{6mc^2\alpha_a\alpha_A}{\alpha_a/\chi_a + \alpha_A/\chi_A} \quad (1.48)$$

and

$$A_a = \frac{3mc^2\alpha_A\chi_A}{2} \quad (1.49)$$

Here m is the mass of an electron, α_a and α_A are the polarizability of the adsorbate and adsorbate molecule and χ_a and χ_A the magnetic susceptibility of the adsorbate molecule and adsorbent molecule, respectively.

The HK method is applicable to slit pores, and it can be modified to be extended to cylindrical and spherical pores. It is worth noting that there are several assumptions which limit its applicability:

- The HK method is reliant on knowledge of the properties of the surface atoms. This assumption is true only if the material surface is homogenous. Furthermore, longer range interactions with multiple surface layers are not considered.
- Each pore is modelled as uniform and of infinite length. Materials with varying pore shapes or highly interconnected networks may not give realistic results.
- Only dispersive forces are accounted for. If the adsorbate-adsorbent interactions have other specific contributions, the Lennard-Jones potential function will not be an accurate description of pore environment.
- It does not have a description of capillary condensation. This means that the pore size distribution can only be considered accurate up to a maximum of 5 nm.

The `pyGAPS` framework contains the required physical properties for the most commonly used adsorbates in its database, as well as properties from literature for several materials: the original parameters developed by Horvath and Kawazoe for a carbon surface ⁽²³⁾ and the oxide surface parameters published by Saito and Foley. ⁽²⁴⁾ The user can provide custom dictionary of these parameters when calling the function as can be seen in the second example in Listing 1.8.

Multiscale computational methods

DFT theory emerged as a rigorous description of molecular adsorption in pores. ⁽²⁾ It calculates the properties of the fluid directly from the forces acting between constituent molecules through a statistical mechanical approach. Latter developments, like non-local DFT (NLDF) ⁽³⁾, which makes an account for short range molecule correlation and therefore for the changes in the density profile around the pore walls, and quenched solid

Listing 1.8: Using the HK method for PSD

```

1 # Calling the HK micropore method with the
2 # Saito-Foley oxide surface parameters
3 result_dict = pygaps.micropore_size_distribution(
4     isotherm,
5     psd_model='HK',
6     adsorbent_model='OxideIon(SF)',
7     verbose=True
8 )
9 # Defining a custom adsorbate parameter dictionary
10 # and using it in the HK method
11 adsorbate_params = {
12     'magnetic_susceptibility': 3.6e-35,
13     'molecular_diameter': 0.3,
14     'polarizability': 1.76e-30,
15     'surface_density': 6.71e+18
16 }
17 result_dict = pygaps.micropore_size_distribution(
18     isotherm,
19     psd_model='HK',
20     adsorbent_model='OxideIon(SF)',
21     adsorbate_model=adsorbate_params,
22     verbose=True
23 )

```

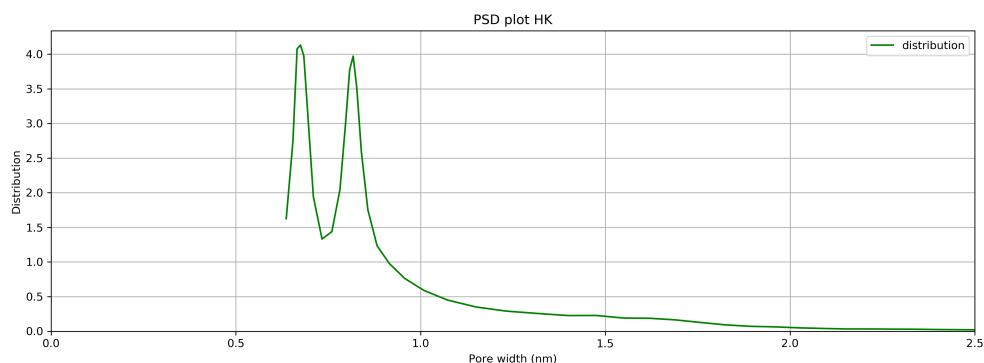


Figure 1.7.: Pore size distribution calculated through the Horvath-Kawazoe method on the UIO-66(Zr) sample

state DFT (QSDFT)⁽²⁵⁾, which allows for heterogeneity of pore walls to be incorporated in the model, have improved the accuracy of the method.

The density functional theory approach can therefore simulate adsorption isotherms on pores of different geometries and sizes. By defining a pore geometry and running the simulation with a range of pore radii, a collection of isotherms is obtained. If an experimental isotherm is thought of as a sum of adsorption isotherms in different material pores, then it stands to reason that the preponderance of those pores can be calculated

through deconvolution.

As the DFT method can model adsorbate condensation behaviour, as well as micropore filling and multilayer adsorption, it can be used for multiscale pore size distribution. The downside is that DFT kernels are temperature, probe, pore-geometry and adsorbent specific and as such are not universally applicable.

The `pyGAPS` framework can perform isotherm fitting to DFT kernels through the `dft_size_distribution` function. The function takes an `Isotherm` object, then then load the DFT kernel either from disk or from memory and apply a minimization function on the sum of squared differences of the sum of all individual kernel isotherms to generate the contribution of each as per the following equation:

$$f(x) = \sum_{p=p_0}^{p=p_x} \left(n_{p,exp} - \sum_{w=w_0}^{w=w_y} n_{p,kernel} X_w \right)^2 \quad (1.50)$$

The user can specify their own kernel in a CSV format, which will be used for the isotherm fitting. Alternatively, a common DFT kernel is included with the framework, which is applicable on nitrogen adsorption on a carbon slit-like pores in the range of 0.4 nm to 10 nm.

Listing 1.9: DFT size distribution in pyGAPS

```
1 result_dict = pygaps.dft_size_distribution(
2     charact_iso,
3     'internal',
4     verbose=True
5 )
```

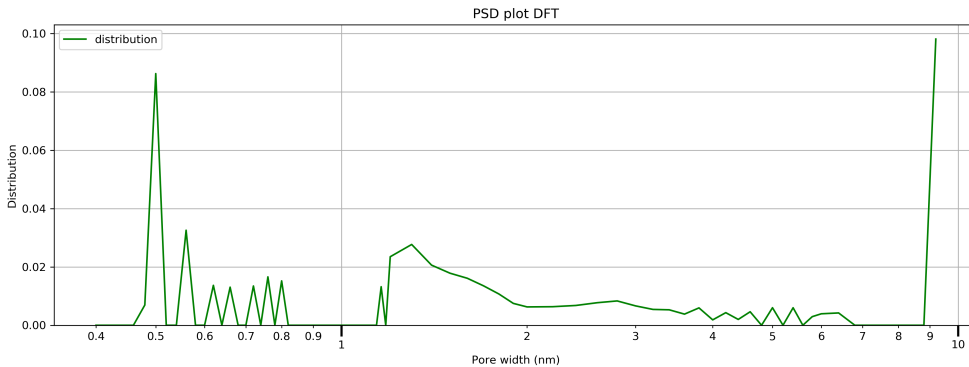


Figure 1.8.: Pore size distribution calculated through the DFT fitting on the Takeda 5A carbon

1.3.4. Predicting multicomponent adsorption

Until now, we have only referred to isotherms pertaining to the adsorption of a single adsorbate. However, besides gas storage, most if not all industrial applications of

adsorbents involve multiple chemical species undergoing competitive adsorption. Experiments involving several adsorbents are generally difficult and time consuming. There is therefore a requirement to predict such multicomponent systems in order to rapidly screen for potentially interesting separations starting from pure component data.

To this end, the several methods have been devised, with perhaps the most common approach as considering the adsorbed phase as an analogue to a fluid mixture. This method, also known as the ideal adsorbed solution theory (IAST), has been implemented in pyGAPS and will be presented here. Other multicomponent theories such as real adsorbed solution theory (RAST) or the Nitta model exist but usually require more information about specific surface binary activity coefficients to be well suited to a general high throughput approach.

Ideal adsorbed solution theory

The pyGAPS framework includes a modified version of the pyIAST code⁽²⁶⁾ which has been adapted to work with the `Isotherm` classes. Both model isotherms and real data can be used for IAST, with spreading pressure being calculated through the underlying isotherm model or through interpolation, respectively.

In this case, we fit the experimental data to the available models in pyGAPS which have been presented in subsection 1.3.1, then use the resulting model isotherms for IAST simulations. In order to get a ‘best-fit’ model isotherm, we use the function in Listing 1.10, which fits all available models and selects the one with the lowest residuals between the fitted function and the real data. The isotherms and their best-fitting model is displayed in Figure 1.9a for the CO₂-N₂ pair and in Figure 1.10a for the C₃H₈-C₃H₆ pair.

Listing 1.10: Guessing the best model

```
1 model = pygaps.ModelIsotherm.from_pointisotherm(iso, guess_model=True)

| Attempting to model using Henry
| Model Henry success, rmse is 7.42
| Attempting to model using Jensen-Seaton
| Modelling using Jensen-Seaton failed
| .....
| Best model fit is Quadratic
```

For the carbon dioxide separation, we simulate all equilibrium points for the adsorbed and gaseous phases at different concentrations of the two gases at 1 bar. To do this we use the `pygaps.iast_vle()` function which produces an analogue of a vapour-liquid equilibrium at a specified pressure for a binary mixture. The resulting graph of this function can be seen in Figure 1.10b. As expected, the predicted adsorbed mixture is rich in carbon dioxide. Selectivity can also be calculated in a single point, with the value at 15% CO₂ and 1 bar being 16.5.

For the propane-propylene separation, we simulate the selectivity for propane within a pressure range for a 50% mixture of the two gases. It can be seen that there is little

1. Building a framework for adsorption data processing

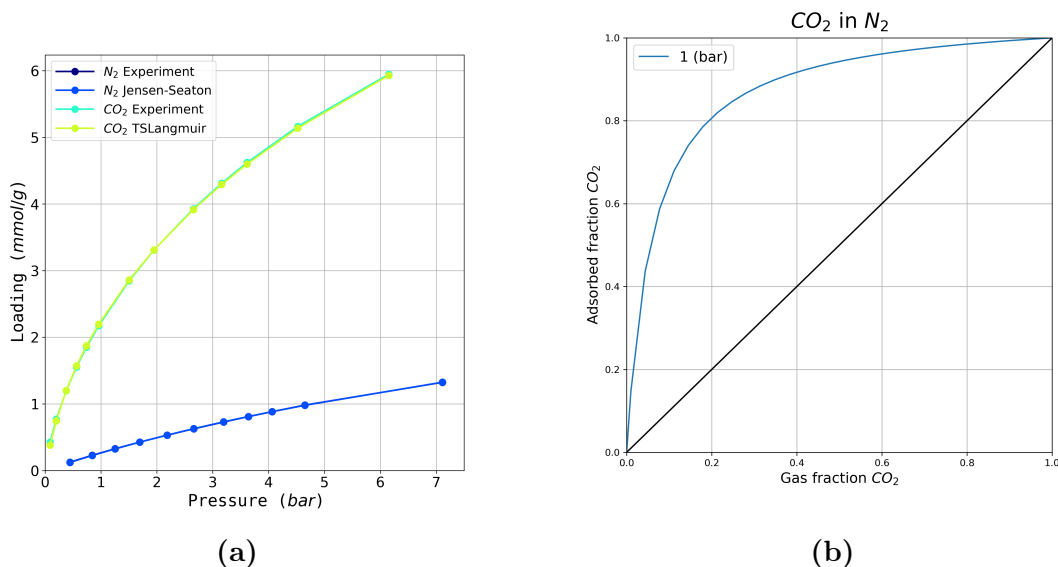


Figure 1.9.: Modelling binary adsorption of CO_2 and N_2 : (a) the pure component isotherms and their best fit models and (b) the predicted composition of the gaseous and adsorbed phase for different fractions of CO_2 at 1 bar

or no preference for the unsaturated molecule, though the selectivity increases slightly at pressures above 1 bar.

1.4. A case study of high throughput processing on a large dataset

1.4.1. The NIST ISOD dataset

The NIST/ARPA-E database of adsorbent materials (ISODB) is a comprehensive set of adsorption isotherms which have been systematically collected from peer-reviewed literature. The data includes measurements on a wide range of materials, from carbon, zeolite, and silica to MOFs and other such PCPs. This resource is a useful tool for reference purposes, as it contains isotherms on many reported porous materials. Furthermore, due to the availability of an application programming interface (API), isotherm data can be easily accessed. As such, this database is a great source of data for the kind of large-scale processing which pyGAPS is designed for.

The entire dataset in the NIST adsorption database was downloaded using the publicly available API. This yielded ≈ 26000 isotherms. In order to narrow down the dataset and ensure comparable starting values some sorting was performed.

- Isotherms which could not be converted to mmol g^{-1} were discarded outright. This includes data reported in a on a volume basis of material (as the material density

1. Building a framework for adsorption data processing

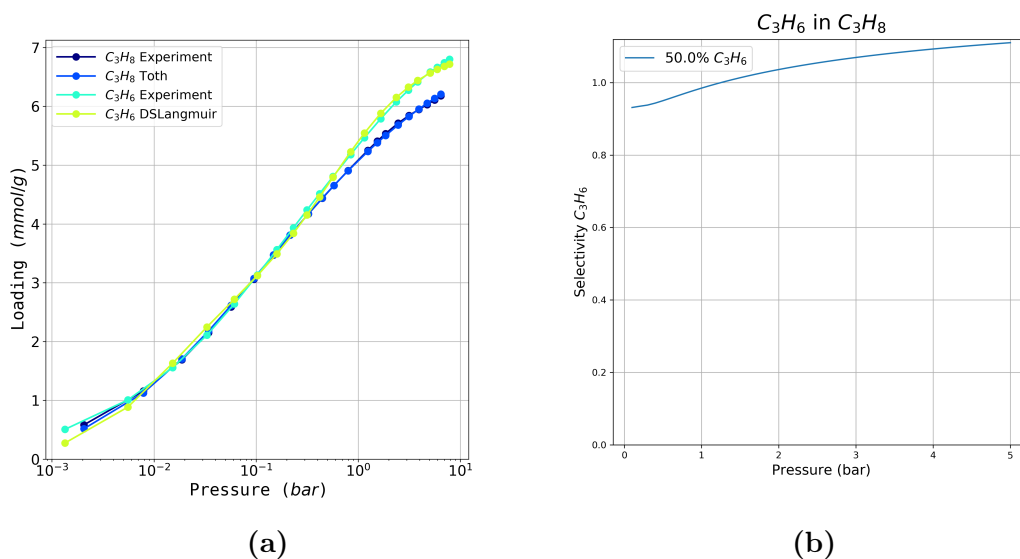


Figure 1.10.: Modelling binary adsorption of a propane-propylene mixture: (a) the pure-component isotherms and their best fit models and (b) the predicted selectivity of propane adsorption of a 50-50% mixture in a range of pressure from 0.1 to 7 bar

is unknown), simulation data which is reported in units such as molecules per unit cage and fractional coverage isotherms.

- No isotherms with less than 6 measurement points were considered, as sufficient datapoints are needed for characterisation.
- Isotherms were then converted into mmol g^{-1} , to ensure a consistent unit set.
- Possible outliers were removed from the data by selecting only isotherms recorded under 100 bar, with maximum capacities under 100 mmol and with a temperature of under 443 K. Any such isotherms are likely errors in the data collection process and have little to no physical meaning.

The process of data collation reduced the number of isotherms to ≈ 15800 . A distribution of the isotherms as a function of adsorbate and temperature can be found in Figure 1.11a. We can see that most isotherms are recorded at either 77 K, 273 K or 298 K as these are temperatures are readily available through immersion in liquid nitrogen, water-ice mixture, or a thermally controlled water bath.

To apply the high throughput data processing with pyGAPS, only isotherms recorded with nitrogen at 77 K were selected. These make up ≈ 3500 datapoints, recorded on more than 2200 materials. The BET surface area was then computed for each isotherm, with a distribution as seen in Figure 1.11b. Unfortunately, as many isotherms do not have enough points in the low pressure region, computing a well-defined BET surface

1. Building a framework for adsorption data processing

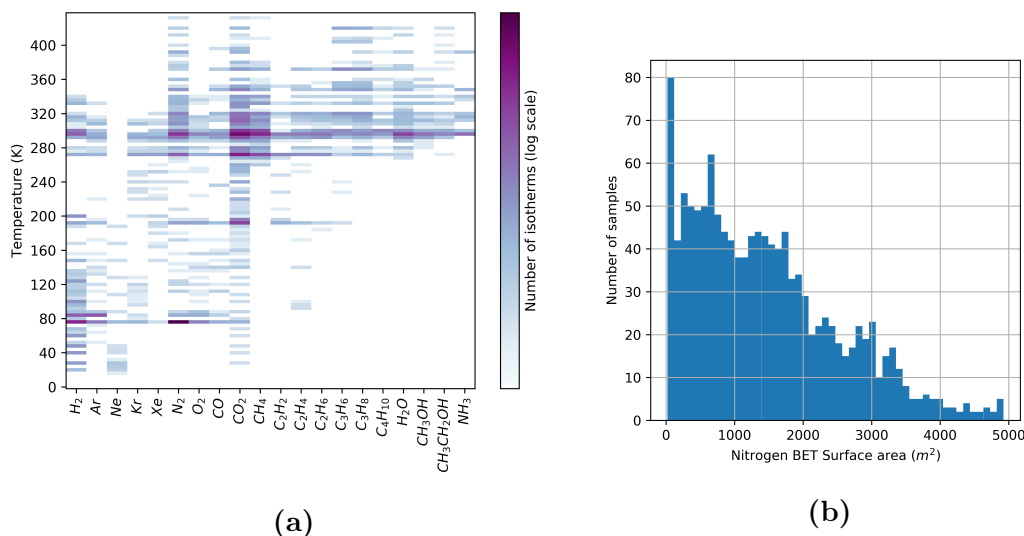


Figure 1.11.: A graphical description of the NIST ISODB dataset. (a) The selected 15800 isotherms presented per adsorbate used and temperature at which the measurement took place. (b) Calculated BET surface area with nitrogen at 77 K for all available isotherms.

area is impossible. In total, only around a third of the isotherms had enough data for this purpose.

Quite a few materials are seen to be essentially non-porous with a more than 80 isotherms with a BET area of less than 100 m².

1.4.2. A comparison between surface area determination methods

It is also useful to observe the differences between the Langmuir-calculated and the BET-calculated surface areas. If the Langmuir area is calculated with implicit parameters, by taking the entire available isotherm for the fitting routine, the correlation between the surface areas calculated through the two methods is presented in Figure 1.12a. The Langmuir surface area is generally higher than the BET surface area for the same isotherm. This is a consequence of the

If the partial pressure range is narrowed, by only using points up to 0.2 p/p_0 , the correlation improves dramatically, with near-overlap when the area is below 200 m². The better ,

It should also be noted that the, as shown by Walton and Snurr ⁽²⁷⁾ when attempting to compare nitrogen surface areas with BET-calculated surface areas for MOFs and microporous materials.

To go one step further into uncovering trends for

1. Building a framework for adsorption data processing

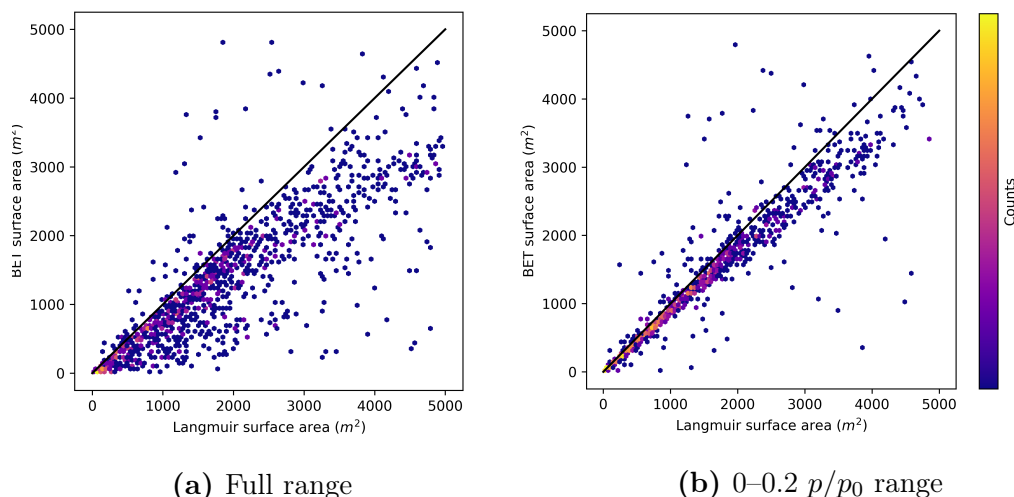


Figure 1.12.: Correlation between Langmuir-calculated and BET-calculated surface areas. The black line is a guide for the eye at $S_{\text{Langmuir}} = S_{\text{BET}}$.

1.4.3. Observed reliability of results

Recently, Sholl and co-workers⁽²⁸⁾ have published a report putting into question the reproducibility of adsorption isotherms, using CO₂ adsorption data from the NIST ISODB. Their findings highlight a large variability inherent to reported isotherms as on average “one in five CO₂ isotherms [...] cannot be used to provide information that is qualitatively reliable about the properties of the material”. In this paper no reasons behind the origin of such large variations in reproducibility are explored. Similar concerns have been raised for H₂⁽²⁹⁾ and CO₂⁽³⁰⁾ measurements.

The underlying cause for the poor reproducibility of adsorption isotherms, particularly those measured on metal organic frameworks is not easy to pinpoint. A large contribution to this divergence is likely accounted for through the variation introduced by the sample preparation method and adsorption apparatus. For example, a recent NIST interlaboratory study in which CO₂ isotherms were recorded on a reference material⁽³¹⁾, had six out of thirteen initial datasets outside the uncertainty range. Errors were determined to arise from sample mass measurement, insufficient activation conditions or improper choice of an equation of state. Other method-specific sources of error exist, such as the lack of a buoyancy correction when using a gravimetric system or a void volume correction when using a volumetric system, both of which can be made if an accurate determination of sample skeletal density is performed. Finally, small differences in thermal gradients, pressure transducer readings, and even the altitude at which the measurement takes place (if a phase change bath is used to control temperature) can also impact the final isotherm.

Such variation is likely minimised when using state-of-the-art adsorption equipment, which eliminates many of the concerns associated with adsorption methodology. *In situ* activation, internal consistency checks for pressure transducers, automatic measurement

1. Building a framework for adsorption data processing

of skeletal density and associated corrections, reference cells for saturation pressure determination and many other sanity checks are implemented in these machines.

However, it is often the case that the most important factor in the repeatability MOF and porous material adsorption isotherms is not the measurement procedure, but rather the material itself.

1.5. Conclusion

Bibliography

- [1] Elliott P. Barrett, Leslie G. Joyner, and Paul P. Halenda. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society*, 73(1):373–380, January 1951. ISSN 0002-7863. doi: 10.1021/ja01145a126.
- [2] N.A. Seaton, J.P.R.B. Walton, and N. Quirke. A new analysis method for the determination of the pore size distribution of porous carbons from nitrogen adsorption measurements. *Carbon*, 27(6):853–861, 1989. ISSN 00086223. doi: 10.1016/0008-6223(89)90035-3.
- [3] P. Tarazona, U. Marini Bettolo Marconi, and R. Evans. Phase equilibria of fluid interfaces and confined fluids: Non-local versus local density functionals. *Molecular Physics*, 60(3):573–595, February 1987. ISSN 0026-8976, 1362-3028. doi: 10.1080/00268978700100381.
- [4] Dan Siderius, Vincent Shen, and Russell Johnson. NIST / ARPA-E Database of Novel and Emerging Adsorbent Materials, NIST Standard Reference Database 205, 2015.
- [5] Ian H. Bell, Jorrit Wronski, Sylvain Quoilin, and Vincent Lemort. Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp. *Industrial & Engineering Chemistry Research*, 53(6):2498–2508, February 2014. ISSN 0888-5885, 1520-5045. doi: 10.1021/ie4033999.
- [6] Eric Lemmon. NIST Reference Fluid Thermodynamic and Transport Properties Database: Version 9.0, NIST Standard Reference Database 23, 1989.
- [7] Jean Rouquerol, Françoise Rouquerol, Philip L. Llewellyn, Guillaume Maurin, and Kenneth Sing. *Adsorption by Powders and Porous Solids : Principles, Methodology and Applications*. 2013. ISBN 978-0-08-097035-6.
- [8] Stephen Brunauer, P. H. Emmett, and Edward Teller. Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60(2):309–319, February 1938. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja01269a023.
- [9] Mikhail Temkin. Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Phys. Chim. USSR*, 12:327–356, 1940.
- [10] Cory M. Simon, Jihan Kim, Li-Chiang Lin, Richard L. Martin, Maciej Haranczyk, and Berend Smit. Optimizing nanoporous materials for gas storage. *Physical Chemistry Chemical Physics*, 16(12):5499, 2014. ISSN 1463-9076, 1463-9084. doi: 10.1039/c3cp55039g.
- [11] C. R. C. Jensen and N. A. Seaton. An isotherm equation for adsorption to high pressures in microporous adsorbents. *Langmuir*, 12(11):2866–2867, 1996.

BIBLIOGRAPHY

- [12] Terrell L. Hill. *An Introduction to Statistical Thermodynamics*. Dover Publications, New York, 1986. ISBN 978-0-486-65242-9.
- [13] Alan L. Myers. Thermodynamics of adsorption in porous materials. *AIChE Journal*, 48(1):145–160, January 2002. ISSN 00011541. doi: 10.1002/aic.690480115.
- [14] Solot Suwanayuen and Ronald P. Danner. A gas adsorption isotherm equation based on vacancy solution theory. *AIChE Journal*, 26(1):68–76, January 1980. ISSN 00011541. doi: 10.1002/aic.690260112.
- [15] T. W. Cochran, R. L. Kabel, and R. P. Danner. Vacancy solution theory of adsorption using Flory-Huggins activity coefficient equations. *AIChE Journal*, 31(2): 268–277, February 1985. ISSN 0001-1541, 1547-5905. doi: 10.1002/aic.690310214.
- [16] Matthias Thommes, Katsumi Kaneko, Alexander V. Neimark, James P. Olivier, Francisco Rodriguez-Reinoso, Jean Rouquerol, and Kenneth S W Sing. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, 87(9-10): 1051–1069, 2015. ISSN 13653075. doi: 10.1515/pac-2014-1117.
- [17] George Halsey. Physical Adsorption on Non-Uniform Surfaces. *The Journal of Chemical Physics*, 16(10):931–937, October 1948. ISSN 0021-9606, 1089-7690. doi: 10.1063/1.1746689.
- [18] B Lippens. Studies on pore systems in catalysts V. The t method. *Journal of Catalysis*, 4(3):319–323, June 1965. ISSN 00219517. doi: 10.1016/0021-9517(65)90307-6.
- [19] D. Atkinson, A.I. McLeod, and K. S. W. Sing. Adsorptive properties of microporous carbons: Primary and secondary micropore filling. *Journal de Chimie Physique*, 81: 791–794, 1984. ISSN 0021-7689. doi: 10.1051/jcp/1984810791.
- [20] Jean Rouquerol, Gino V. Baron, Renaud Denoyel, Herbert Giesche, Johan Groen, Peter Klobes, Pierre Levitz, Alexander V. Neimark, Sean Rigby, Romas Skudas, Kenneth Sing, Matthias Thommes, and Klaus Unger. The characterization of macroporous solids: An overview of the methodology. *Microporous and Mesoporous Materials*, 154:2–6, May 2012. ISSN 13871811. doi: 10.1016/j.micromeso.2011.09.031.
- [21] Duong D Do. *Adsorption Analysis: Equilibria and Kinetics: (With CD Containing Computer Matlab Programs)*, volume 2 of *Series on Chemical Engineering*. Imperial College Press, September 1998. ISBN 978-1-86094-130-6 978-1-78326-224-3. doi: 10.1142/p111.
- [22] D. Dollimore and G.R R. Heal. Pore-size distribution in typical adsorbent systems. *Journal of Colloid and Interface Science*, 33(4):508–519, August 1970. ISSN 00219797. doi: 10.1016/0021-9797(70)90002-0.

BIBLIOGRAPHY

- [23] Geza Horvath and Kunitaro Kawazoe. Method for the calculation of effective pore size distribution in molecular sieve carbon. *Journal of Chemical Engineering of Japan*, 16(6):470–475, 1983. ISSN 1881-1299. doi: 10.1252/jcej.16.470.
- [24] A. Saito and H. C. Foley. Curvature and parametric sensitivity in models for adsorption in micropores. *AIChE Journal*, 37(3):429–436, March 1991. ISSN 0001-1541. doi: 10.1002/aic.690370312.
- [25] Alexander V. Neimark, Yangzheng Lin, Peter I. Ravikovitch, and Matthias Thommes. Quenched solid density functional theory and pore size analysis of micro-mesoporous carbons. *Carbon*, 47(7):1617–1628, June 2009. ISSN 00086223. doi: 10.1016/j.carbon.2009.01.050.
- [26] Cory M. Simon, Berend Smit, and Maciej Haranczyk. PyIAST: Ideal adsorbed solution theory (IAST) Python package. *Computer Physics Communications*, 200: 364–380, 2016. ISSN 00104655. doi: 10.1016/j.cpc.2015.11.016.
- [27] Krista S. Walton and Randall Q. Snurr. Applicability of the BET Method for Determining Surface Areas of Microporous Metal-Organic Frameworks. *Journal of the American Chemical Society*, 129(27):8552–8556, July 2007. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja071174k.
- [28] Jongwoo Park, Joshua D. Howe, and David S. Sholl. How Reproducible Are Isotherm Measurements in Metal–Organic Frameworks? *Chemistry of Materials*, 29(24):10487–10495, December 2017. ISSN 0897-4756, 1520-5002. doi: 10.1021/acs.chemmater.7b04287.
- [29] D. P. Broom and M. Hirscher. Irreproducibility in hydrogen storage material research. *Energy & Environmental Science*, 9(11):3368–3380, 2016. ISSN 1754-5692, 1754-5706. doi: 10.1039/C6EE01435F.
- [30] Laura Espinal, Dianne L. Poster, Winnie Wong-Ng, Andrew J. Allen, and Martin L. Green. Measurement, Standards, and Data Needs for CO₂ Capture Materials: A Critical Review. *Environmental Science & Technology*, 47(21):11960–11975, November 2013. ISSN 0013-936X, 1520-5851. doi: 10.1021/es402622q.
- [31] H. G. T. Nguyen, L. Espinal, R. D. van Zee, M. Thommes, B. Toman, M. S. L. Hudson, E. Mangano, S. Brandani, D. P. Broom, M. J. Benham, K. Cychosz, P. Bertier, F. Yang, B. M. Krooss, R. L. Siegelman, M. Hakuman, K. Nakai, A. D. Ebner, L. Erden, J. A. Ritter, A. Moran, O. Talu, Y. Huang, K. S. Walton, P. Billemon, and G. De Weireld. A reference high-pressure CO₂ adsorption isotherm for ammonium ZSM-5 zeolite: Results of an interlaboratory study. *Adsorption*, July 2018. ISSN 0929-5607, 1572-8757. doi: 10.1007/s10450-018-9958-x.

A. Common characterisation techniques

pictures?

A.1. Thermogravimetry

Thermogravimetry (TGA) is a standard laboratory technique where the weight of a sample is monitored while ambient temperature is controlled. Changes in sample mass can be correlated to physical events, such as adsorption, desorption, sample decomposition or oxidation, depending on temperature and its rate of change.

TGA experiments are carried out on approximately 15 mg of sample with a TA Instruments Q500 up to 800 °C. The sample is placed on a platinum crucible and sealed in a temperature controlled oven, under gas flow of 40 cm³ min⁻¹. Experiments can use a blanket of either air or argon. The temperature ramp can be specified directly and should be chosen to ensure that the sample is in equilibrium with the oven temperature and no thermal conductivity effects come into play. Alternatively, a dynamic “Hi-Res” mode can be used which allows for automatic cessation of heating rate while the sample undergoes mass loss.

The main purpose of thermogravimetry as used in this thesis is the determination of sample decomposition temperature, to ensure that thermal activation prior to adsorption is complete and that all guest molecules have been removed without loss of structure. To this end, experiments are performed under an inert atmosphere (argon), and the sample activation temperature is chosen as 50 °C to 100 °C lower than the sample decomposition temperature.

A.2. Bulk density determination

Bulk density is a useful metric for the industrial use of adsorbent materials, as their volume plays a critical role in equipment sizing.

Bulk density is determined by weighing 1.5 ml empty glass vessels and settling the MOFs inside. Powder materials are then added in small increments and settled through vibration between each addition. The full vessel is finally weighed, which allowed the bulk density to be determined. The same cell is used in all experiments, with cleaning through sonication between each experiment.

A.3. Skeletal density determination

True density or skeletal density is determined through gas pycnometry in a MicrotracBEL BELSORP-max apparatus. Helium is chosen as the fluid of choice as it is assumed to be non-adsorbing.

The volume of a glass sample cell (V_c) is precisely measured through dosing of the reference volume with helium up to (p_1), then opening the valve connecting the two and allowing the gas to expand up to (p_2). Afterwards approximately 50 mg of sample are weighed and inserted in a glass sample cell. After sample activation using the supplied electric heater to ensure no solvent residue is left in the pores, the same procedure is repeated to determine the volume of the cell and the adsorbent. With the volume of the sample determined, the density can be calculated by.

$$V_s = V_c + \frac{V_r}{1 - \frac{p_1}{p_2}} \quad (\text{A.1})$$

A.4. Nitrogen physisorption at 77 K

Nitrogen adsorption experiments are carried out on a Micromeritics Triflex apparatus. Approximately 60 mg of sample are used for each measurement. Empty glass cells are weighed and filled with the samples, which are then activated in a Micromeritics Smart VacPrep up to their respective activation temperature under vacuum and then back-filled with an inert atmosphere. After sample activation, the cells are re-weighed to determine the precise sample mass. The cells are covered with a porous mantle which allows for a constant temperature gradient during measurement by wicking liquid nitrogen around the cell. Finally, the cells are immersed in a liquid nitrogen bath and the adsorption isotherm is recorded using the volumetric method. A separate cell is used to condense the adsorptive throughout the measurement for accurate determination of its saturation pressure.

A.5. Vapour physisorption at 298 K

Vapour adsorption isotherms throughout this work are measured using a MicrotracBEL BELSORP-max apparatus in vapour mode. Glass cells are first weighed and then filled with about 50 mg of sample. The vials are then heated under vacuum up to the activation temperature of the material and re-weighed in order to measure the exact sample mass without adsorbed guests. The cells are then immersed in a mineral oil bath kept at 298 K. To ensure that the cold point of the system occurs in the material and to prevent condensation on cell walls, the reference volume, dead space and vapour source are temperature controlled through an insulated enclosure.

A.6. Gravimetric isotherms

The gravimetric isotherms in this thesis are obtained using a commercial Rubotherm GmbH balance. Approximately 1 g of dried sample is used for these experiments. Samples are activated in situ by heating under vacuum. The gas is introduced using a step-by-step method, and equilibrium is assumed to have been reached when the variation of weight remained below 30 μg over a 15 min interval. The volume of the sample is determined from a blank experiment with helium as the non-adsorbing gas and used in combination with the gas density measured by the Rubotherm balance to compensate for buoyancy.

A.7. High throughput isotherm measurement

A high-throughput gas adsorption apparatus is presented for the evaluation of adsorbents of interest in gas storage and separation applications. This instrument is capable of measuring complete adsorption isotherms up to 50 bar on six samples in parallel using as little as 60 mg of material. Multiple adsorption cycles can be carried out and four gases can be used sequentially, giving as many as 24 adsorption isotherms in 24 h.⁽¹⁾

A.8. Powder X-ray diffraction

A.9. Nuclear magnetic resonance

Bibliography

- [1] Andrew D. Wiersum, Christophe Giovannangeli, Dominique Vincent, Emily Bloch, Helge Reinsch, Norbert Stock, Ji Sun Lee, Jong-San Chang, and Philip L. Llewellyn. Experimental Screening of Porous Materials for High Pressure Gas Adsorption and Evaluation in Gas Separations: Application to MOFs (MIL-100 and CAU-10). *ACS Combinatorial Science*, 15(2):111–119, February 2013. ISSN 2156-8952. doi: 10.1021/co300128w.

B. Synthesis method of referenced materials

B.1. Takeda 5A reference carbon

The Takeda 5A carbon was purchased directly from the Takeda corporation. The sample was activated at 250 °C under secondary vacuum (5 mbar) before any measurements.

full
char-
acteri-
zation

B.2. MCM-41 controlled pore glass

MCM-41 (Mobil Composition of Matter No. 41) is a mesoporous silica (SiO_2) material with a narrow pore distribution. First synthesised by the Mobil Oil Corporation, it is produced through templated synthesis using mycelle-forming surfactants. The material referenced in this thesis was purchased from Sigma-Aldrich. The activation procedure consists of heating at 250 °C under secondary vacuum (5 mbar).

B.3. Zr fumarate MOF

The synthesis of the Zr fumarate was performed in Peter Behren's group in Hannover, through modulated synthesis. This MOF can only be synthesised through the addition of a modulator, in this case fumaric acid, to the ongoing reactor, as detailed in the original publication.⁽¹⁾

The procedure goes as follows: ZrCl_4 (0.517 mmol, 1 eq) and fumaric acid (1.550 mmol, 3 eq) are dissolved in 20 mL N,N-dimethylformamide (DMF) and placed in a 100 mL glass flask at room temperature. 20 equivalents of formic acid were added. The glass flasks were Teflon-capped and heated in an oven at 120 °C for 24 h. After cooling, the white precipitate was washed with 10 mL DMF and 10 mL ethanol, respectively. The washing process was carried out by centrifugation and redispersion of the white powder, which was then dried at room temperature over night

B.4. UiO-66(Zr) for defect study

The UiO-66(Zr) sample preparation was adapted from Shearer et al.⁽²⁾ as follows: ZrCl_4 (1.55 g, 6.65 mmol), an excess of terephthalic acid (BDC) (1.68 g, 10.11 mmol), HCl 37 % solution (0.2 mL, 3.25 mmol) and N,N'-dimethylformamide (DMF) (200 mL,

2.58 mol) were added to a 250 mL pressure resistant Schott bottle. The mixture was stirred for 10 min, followed by incubation in a convection oven at 130 °C for 24 h. The resulting white precipitate was washed with fresh DMF (3× 50 mL) followed by ethanol (3× 50 mL) over the course of 48 h and dried at 60 °C. After drying, the sample was activated on a vacuum oven by heating at 200 °C under vacuum for 12 h. The yield was 78 % white microcrystalline powder. Before the experiment, the sample was calcined at 200 °C under vacuum (5 mbar) to remove any residual solvents from the framework.

B.5. UiO-66(Zr) for shaping study

The scaled-up synthesis of UiO-66(Zr) was carried out in a 5 L glass reactor (Reactor Master, Syrris, equipped with a reflux condenser and a Teflon-lined mechanical stirrer) according to a previously reported method.⁽³⁾ In short, 462 g (2.8 mol) of H₂BDC (98%) was initially dissolved in 2.5 L of dimethyl formamide (DMF, 2.36 kg, 32.3 mol) at room temperature. Then, 896 g (2.8 mol) of ZrOCl₂ · 8H₂O (98%) and 465 mL of 37% HCl (548 g, 15 mol) were added to the mixture. The molar ratio of the final ZrOCl₂ · 8H₂O/H₂BDC/DMF/HCl mixture was 1 : 1 : 11.6 : 5.4. The reaction mixture was vigorously stirred to obtain a homogeneous gel. The mixture was then heated to 423 K at a rate of 1 K min⁻¹ and maintained at this temperature for 6 h in the reactor without stirring, leading to a crystalline UiO-66(Zr) solid. The resulting product (510 g) was recovered from the slurry by filtration, redispersed in 7 L of DMF at 333 K for 6 h under stirring, and recovered by filtration. The same procedure was repeated twice, using methanol (MeOH) instead of DMF. The solid product was finally dried at 373 K overnight.

B.6. MIL-100(Fe) for shaping study

The synthesis of the MOF for the shaping study was done at the KRICT institute using a previously published method.⁽⁴⁾ To synthesise the MIL-100(Fe) material Fe(NO₃)₃ was completely dissolved in water. Then, trimesic acid (BTC) was added to the solution; the resulting mixture was stirred at room temperature for 1 h. The final composition was Fe(NO₃)₃ · 9 H₂O:0.67 BTC:*n* H₂O (*x*= 55–280). The reactant mixture was heated at 433 K for 12 h using a Teflon-lined pressure vessel. The synthesized solid was filtered and washed with deionized (DI) water. Further washing was carried out with DI water and ethanol at 343 K for 3 h and purified with a 38 mM NH₄F solution at 343 K for 3 h. The solid was finally dried overnight at less than 373 K in air.

B.7. MIL-127(Fe) for shaping study

MIL-127(Fe) was synthesized by reaction of Fe(ClO₄)₃ · 6 H₂O (3.27 g, 9.2 mmol) and C₁₆N₂O₈H₆ (3.3 g) in DMF (415 mL) and hydrofluoric acid (5 M, 2.7 mL) at 423 K in a Teflon flask. The obtained orange crystals were placed in DMF (100 mL) and

stirred at ambient temperature for 5 h. The final product was kept at 375 K overnight. MIL-127(Fe) was synthesized by reaction of $\text{Fe}(\text{ClO}_4)_3 \cdot 6 \text{H}_2\text{O}$ (3.27 g, 9.2 mmol) and $\text{C}_{16}\text{N}_2\text{O}_8\text{H}_6$ (3.3 g) in DMF (415 mL) and hydrofluoric acid (5 M, 2.7 mL) at 423 K in a Teflon flask. The obtained orange crystals were placed in DMF (100 mL) and stirred at ambient temperature for 5 h. The final product was kept at 375 K overnight.

Bibliography

- [1] Gesa Wißmann, Andreas Schaate, Sebastian Lilienthal, Imke Bremer, Andreas M. Schneider, and Peter Behrens. Modulated synthesis of Zr-fumarate MOF. *Micro-porous and Mesoporous Materials*, 152:64–70, April 2012. ISSN 13871811. doi: 10.1016/j.micromeso.2011.12.010.
- [2] Greig C. Shearer, Sachin Chavan, Jayashree Ethiraj, Jenny G. Vitillo, Stian Svelle, Unni Olsbye, Carlo Lamberti, Silvia Bordiga, and Karl Petter Lillerud. Tuned to Perfection: Ironing Out the Defects in Metal–Organic Framework UiO-66. *Chemistry of Materials*, 26(14):4068–4071, July 2014. ISSN 0897-4756, 1520-5002. doi: 10.1021/cm501859p.
- [3] Florence Ragon, Patricia Horcajada, Hubert Chevreau, Young Kyu Hwang, U-Hwang Lee, Stuart R. Miller, Thomas Devic, Jong-San Chang, and Christian Serre. In Situ Energy-Dispersive X-ray Diffraction for the Synthesis Optimization and Scale-up of the Porous Zirconium Terephthalate UiO-66. *Inorganic Chemistry*, 53(5):2491–2500, March 2014. ISSN 0020-1669, 1520-510X. doi: 10.1021/ic402514n.
- [4] Felix Jeremias, Stefan K. Henninger, and Christoph Janiak. Ambient pressure synthesis of MIL-100(Fe) MOF from homogeneous solution using a redox pathway. *Dalton Transactions*, 45(20):8637–8644, 2016. ISSN 1477-9226, 1477-9234. doi: 10.1039/C6DT01179A.