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Abstract

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3. Exploring the impact of synthesis and defects on adsorption measurements

3.1. Introduction

Ideality is a rarely encountered phenomenon in nature. In fact, experience has shown that deliberate and concerted efforts must be made in order to obtain states of matter that have all the properties described by an “ideal state”. Often the divergence from ideality is small and can be approximated away, as is the case when assuming the ideal gas behaviour of noble gasses or ascribing the thermal radiation emitted by an object to a black-body spectrum. It is, however, in non-ideality where the fascinating complexity of the world asserts itself and where advances in our understanding can be made.

When considering crystals, the ideal description of an infinite periodic repetition of building blocks in three dimensional space is not applicable in the real world. From the necessary existence of crystal boundaries to the possible presence of other structural irregularities, these so called crystal “defects” can have varying effects on the bulk properties of the material. Their presence is not necessarily a fault as they often impart the material with beneficial characteristics on multiple length scales. An understanding of the interplay of defects in the lattices of alloys is an art in itself. Crystal grain size and presence of additives such as carbon and nickel can completely change the hardness, ductility, tensile strength and corrosion resistance of steel.⁽¹⁾ Various other forms of disorder can introduce completely new behaviours altogether. The insertion of foreign elements into the crystal structure of semiconductor materials such as silicon can alter its electronic properties and is responsible for the ubiquitousness of computing devices based on the transistor.⁽²⁾ This application of defects can be said to have ushered in the modern digital age, just as the creation of steel led to the industrial revolution. Other such emergent properties exist such as high temperature superconductivity⁽³⁾ or thermoelectric behaviour⁽⁴⁾ which are influenced by defect-related spin effects or defect-mediated charge transfer. As such, the kind of heterogeneity afforded by defects is a key attribute in condensed matter physics and is a target for material design. The scientific foray in their control, either through generation or by inhibition can be termed “defect engineering” and is another degree of freedom for material science.

As porous coordination polymers (PCPs) and their subclasses metal organic frameworks (MOFs) and covalent organic frameworks (COFs) became prominent topics of study in the field of porous materials, the presence and desirability of defects in their

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ordered crystal structures has been put into question. Investigation of the propensity of these compounds to form defects has suggested potential benefits in the fields of catalysis⁽⁵⁾, gas storage and separation⁽⁶⁻⁸⁾, and has even alluded to applications in sensing and optoelectronics.⁽⁹⁾ Furthermore, MOFs such as UiO-66 and similar oxo-Zr coordination compounds have been shown to have intrinsically defective structures, where clustering and correlation of defects is in fact energetically favoured.⁽¹⁰⁾ The engineering of defects in PCPs is currently the focus of many initiatives as it is seen as a highly desirable method of tuning their properties through judicious design .^(5,11,12)

From the point of view of describing adsorption in such materials, the presence of defects introduces a conundrum. If a MOF can be defective, and is often intrinsically so, a slight change in synthesis conditions can introduce a large variability in its properties, and obtaining a “standard” isotherm may be a challenge. A large scale meta analysis of the correlation between material structure and its adsorption performance cannot be achieved unless the contribution of defects is assessed for each material.

Should I mention DEFNET?

maybe put in overall intro?

Chapter summary

In this chapter we explore the kind of changes in adsorption behaviour introduced through defect engineering with the high throughput processing tools presented in chapter 1. First, the range of crystal defects that can be found in MOFs is presented. A summary of the known methods for controlling defects in such materials is discussed, as well as the known impact on different properties. Particular focus is placed on the zirconium variant of UiO-66, due to its aforementioned remarkable stability to the presence of defects. An alternative approach to defect generation in this MOF is explored, through induced leaching of linkers in a solvent solution of monotopic acids which have been shown to induce defect formation when present during synthesis. The influence on defect type and preponderence of the acid, its concentration and the solvent itself is investigated, through the changes in adsorption behaviour.

Contributions

This work was in done in collaboration with the DEFNET project partner at the Centre for Surface Chemistry and Catalysis in KU Leuven. The study was designed by Paul Iacomi and João Marreiros during the secondment undertaken in COK as part of this project. Two PWI master students, Giel Arnauts and Wouter Arts helped with the synthesis, leaching and characterisation of the first trial batch. João Marreiros conducted the synthesis, leaching, XRD and NMR of further batches in Leuven. Paul Iacomi performed characterisation through TGA and all physisorption measurements in Marseille. Prof. Philip Llewellyn and Prof. Rob Ameloot provided critical input in the direction of the study and the significance of the results.

3.2. The defective nature of MOFs

3.2.1. Types of crystal defects and their analogues in MOFs

From a crystallographic point of view, defects can be described as features which suspend the order of components in an ideally regular lattice. The building blocks in the case of MOFs can be either individual atoms, molecules or other higher order structural building units (SBUs). Any change with leads to local breaking of symmetry with respect to the original structure can be viewed as a defect.

With respect to dimensionality, defects can be described as point defects, line defects (such as edge dislocations), plane defects (such as grain boundaries or stacking faults) and bulk defects (macroscopic voids, phase coexistence). When it comes to point defects, we can broadly refer to several types: **substitutional defects**, where an existing building unit is replaced or transformed into another, **inclusion** or **interstitial defects**, where a foreign component or building block is included in the framework and **vacancy defects** where one of the lattice sites is unoccupied. In the context of MOFs, the same general categories of defects apply. However, due to the higher degrees of freedom available in these compounds, a greater variety of potential crystal defects can exist.

Vacancy defects are encountered through missing linker and missing cluster defects. These analogues of Schottky defects arise from the removal of one or several topological nodes or vertices. In most cases, the charge neutrality of the framework is maintained through coordination of available counterions or solvent molecules through changes in the oxidation state of the metal atoms may also occur.

Substitution point defects are also highly common in MOFs, as the usual requirement for framework connectivity is the existence of “click groups” on metal nodes and linkers. Any piece which fulfils the connection and size requirements may be used, a property which has been exploited through the topological approach to creating new MOFs.^(13–15) It also allows for MOFs in which nodes or vertices are partly replaced with analogues to be created. This strategy has been successfully employed to create mixed-linker or mixed-metal structures.^(16,17) It should be noted that if the distribution of the substitutions takes a homogenous pattern throughout the lattice, the structure no longer falls under the definition of a defect.

A special case of substitutional defects which are present in MOFs are mixed valence defects. When metals with multiple stable oxidation states, such as Cu (I–II), Fe (II–III) etc. are part of the framework, a change in their oxidation state can occur. This has been shown to be an integral part of copper paddlewheel and iron trimesate containing MOFs⁽¹⁸⁾ and can even be seen with the naked eye, as such defects have been shown to give HKUST-1 its common blue colour.⁽¹⁹⁾

Inclusion-type point defects are loosely applied to MOFs. As the definition describes an interstitial defect to be an atom occupying an usually vacant space, all foreign bodies occupying the available porosity of the MOF, including aforementioned counterions and solvents could be considered as defects in the traditional crystallographic sense. Introduction of nanoparticles such as metals or metal oxides inside the pores has also been

3. Exploring the impact of synthesis and defects on adsorption measurements

studied, with beneficial effects in catalytical applications.⁽²⁰⁾

A common feature of structured high porosity compounds is interpenetration. While not a defect in the classical sense, it has important effects on their properties.⁽²¹⁾ With a large enough pore size, a secondary lattice can form in the pore voids of the primary one. This imposes a limit on the common design strategy of isoreticular synthesis, but can introduce new features such as better adsorption through confinement, increase in active site count and even flexibility.

Finally, the surface of the MOF can also be regarded as a boundary or plane defect. The nature of the surface plays a role in intra-particle interactions, important when considering the agglomeration behaviour or inclusion of crystals in a membrane.⁽²²⁾ The surface properties are also crucial in MOF films^(23,24), where the layers are better defined by interfacial characteristics than through bulk properties. Crystal size effects can also be through of as a consequence of surface characteristics, more specifically, of surface-to-volume ratio. When considering soft materials^(25,26), it has been shown that their flexible behaviour is highly influenced by the entropy barriers introduced by the surface.

fig -
defect
types

3.2.2. Consequences of defects

The introduction of defects in the regular crystal lattice of metal organic frameworks can have a dramatic impact on their properties. In general, the following may occur:

- the porosity of the structured is altered, increasing in the case of vacancy defects and decreasing when bulky substitutions or inclusions are made;
- interactions with adsorbed molecules change, through the different pore environment encountered or through the generation of coordinatively unsaturated sites (CUS);
- the stability of the resulting structure is lower than that of the parent MOF, influencing bulk mechanical and thermal properties.
- electronic properties can be changed which may affect the optical electric or magnetic behaviour of the material.

From a purely geometric point of view, the introduction of missing linker or missing cluster defects leads to more voids in the structure, increasing its porosity. It often results in a larger specific surface area and pore volume and thus useful for applications such as gas storage which depend only on the available surface or capacity. Macro-scale void networks can also be desirable, as the better developed pore network has a large impact on the transport properties of the compound, leading to increased diffusion rates.

The inclusion of defects also changes the landscape of the pore walls leading to different interactions with adsorbed molecules. Charge balancing counterions, molecules capping defect sites or functionalizations of substituted linkers or CUS can change the chemistry

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3. Exploring the impact of synthesis and defects on adsorption measurements

of the pore, with specific interactions towards certain adsorbates.⁽²⁷⁾ For example, adsorption of water on oxo-Zr MOFs, has been seen to be dominated by the percentage of defects. The pore filling step can shift from high partial pressure ($0.6\ p/p_0$) to much lower pressures as seen in UiO-66⁽⁷⁾ and MOF-801.⁽⁶⁾ Defect site adsorbed molecules can also lead to cooperative phenomena, such as the beneficial effect of defect-adsorbed water on the catalysis of Fischer esterification.⁽²⁸⁾ or the CO₂ capture on amine-grafted metal centers.⁽²⁹⁾ Another example can be seen in MOFs containing Fe trimers, such as MIL-127(Fe) or MIL-100(Fe) where heating or acid treatment can induce a reduction of one of the iron atoms, generating additional Lewis sites⁽¹⁸⁾ or providing CUS for cooperative binding of carbon monoxide through a spin transition mechanism.⁽³⁰⁾

Of course, defects are also problematic. Most metal organic frameworks synthesised to date suffer from poor stability. Even if the stability of the component parts is not an issue, the framework may not have enough structural stability to be able to sustain itself when fully evacuated. The activation process itself can lead to framework collapse, due to the forces encountered in guest removal, necessitating complex activation processes, such as supercritical drying or preliminary solvent exchange. After activation, the metal-ligand bond is susceptible to attack by adsorbed species. Here, defects in the framework have been shown to play a major role in its stability (or lack thereof).⁽³¹⁾ Copper paddlewheel containing structures are particularly vulnerable to such attack.⁽³²⁾

Finally, several completely different phenomena may emerge through the introduction of defects. Optical properties such as colour centers and induced luminescence⁽¹⁹⁾, changes in thermal conductivity or induced magnetic properties such as ferromagnetism⁽³³⁾ have been shown to be a consequence of the presence of defects.

3.2.3. Defect engineering of MOFs

Since defects introduce another degree of freedom for controlling the properties of metal organic frameworks, the study of their formation can lead to new methods of tuning a material towards a desired application. There are two major pathways of introducing defects, through control of the structure during synthesis or through post-synthetic methods.⁽³⁴⁾

For defect generation during synthesis, the so called “solid solution” approach is to mix several types of building blocks together, be it multiple linkers or metallic nodes. Mixing functionalised versions of linkers leads to the creation of partly-substituted MOFs. Mixed valency frameworks can also be synthesised through this method, as can be seen in the replacement of up to 32% of the linker in the framework in the ruthenium HKUST-1 analogue with a defect-generating linker.⁽³⁵⁾ The commonly used method of improving crystallinity and particle size of modulator-assisted synthesis⁽³⁶⁾ has been shown by Shearer et al. to be a reliable method of introducing defects.⁽³⁷⁾ The modulators act as capping agents and occupy metal coordination sites.

Post-synthetic methods are also widely employed for defect generation. Through acid treatment of the previously mentioned MIL-100(Fe), cleavage of one of the Fe–O bonds can be induced, with a protonation of the carboxylic linker and the generation of a CUS.⁽³⁸⁾ Thermal treatment can achieve the same results, with weakly coordinated

3. Exploring the impact of synthesis and defects on adsorption measurements

molecules removed to expose metal CUS or even *in situ* linker decomposition.⁽³⁹⁾ Ligand exchange has also been shown to be achievable post-synthetically,⁽⁴⁰⁾ through the replacement of existing linkers, capping agents or even induce structural “healing”. Finally, the linkers are still available for organic reactions which can transform a part of them into functionalised versions, as seen in the nitration of the terephthalate linker in MIL-101.⁽⁴¹⁾

3.2.4. The propensity of UiO-66(Zr) for defect generation

The UiO-66(Zr) MOF and its derivatives are well known due to their thermal and chemical stability.⁽⁴²⁾ It is composed of $[\text{Zr}_6\text{O}_4(\text{OH})_4]^{12+}$ clusters (seen in Figure 3.1a) which are connected with benzene dicarboxilate (BDC) linkers to form a face-centered cubic framework. Due to its exceptional stability among MOFs, it has been the focus of many studies, where it has shown promise⁽⁴³⁾ in use for gas adsorption and catalytic applications.

The synthesis of many functional derivatives of UiO-66, through the use of different struts of nodes has been a stepping stone towards obtaining mixed-linker and mixed-metal materials, either thorough the solid solution or post-synthesis modification approach.⁽⁴⁴⁾ It has also been used for a support for nanoparticles, such as palladium⁽⁴⁵⁾ or platinum.⁽⁴⁶⁾

However, UiO-66 is particularly adept is in its ability to support vacancy defects. Due to the stability of the Zr-O bond, and the high linker to metal ratio, the UiO family of MOFs can tolerate a high defectivity in their structure, which manifests through either missing linker (Figure 3.1b) or missing cluster (Figure 3.1c) defects. Ever since the discovery of a number of defects in the pristine material through neutron powder diffraction methods⁽⁴⁷⁾ and the theoretical basis laid down by Cliffe et al. for the existence of correlated defective nanodomains where the existence of a vacancy induces defect formation in neighbouring sites , this MOF became a prototypical framework for the study of these defects. The modulated synthesis approach, initially used as a means of creating novel topologies and controlling crystal size⁽⁴⁸⁾ has been remarkably successful in obtaining defective versions of UiO-66(Zr).⁽³⁷⁾ Post-synthetic methods such as ligand exchange⁽⁴⁰⁾, temperature-induced dehydroxilation of the zirconium cluster⁽⁴⁹⁾ and thermal removal of one of the linkers in a mixed-linker variant⁽¹⁶⁾ have been similarly adept in obtaining voids in the structure. More recently, the interplay between the defective nature of UiO-66 and the mechanism of post-synthesis linker exchange⁽⁵⁰⁾ has been put into the limelight.

In these defects, the metal sites are almost always capped, with monoacids such as formate and acetate, water, hydroxyl groups or other counterions being able to assume the role of capping agent. It has been shown by Thornton et al. that the influence of these defects on the adsorption properties depend not only on their position, but also on these capping agents.⁽⁵¹⁾

Such vacancy defects prove to be useful for generating Lewis sites for catalytic application, as can be seen in the 4-fold increase in conversion in citronellar cyclization or the increase in 4-tert-butylcyclohexanone reduction from 5–7% to almost 90%.⁽⁵²⁾ They are

3. Exploring the impact of synthesis and defects on adsorption measurements

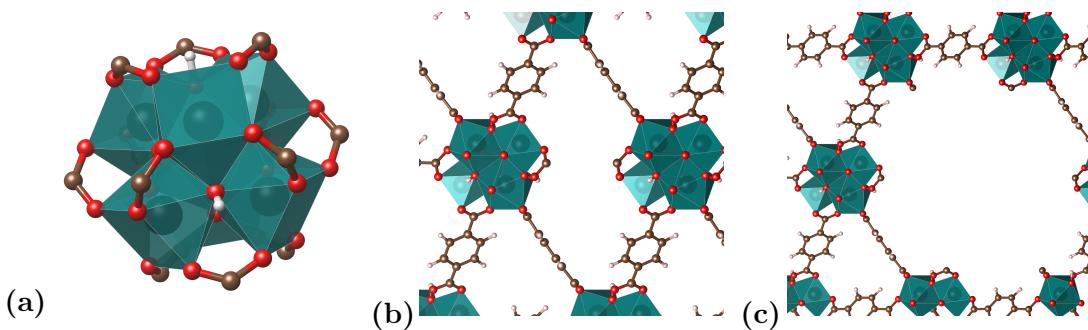


Figure 3.1.: (a) The 12-coordinated Zr cluster in UiO-66(Zr) which connects with benzene dicarboxilate (BDC) linkers. Two prototypical defect types are shown (b) a missing linker defect and (c) a missing cluster defect. Zirconium octahedra are represented in turquoise, oxygen in red, carbon in brown and hydrogen in white.

also useful for gas separation, as they can increase the interaction towards a component of the mixture as seen on CO₂ / N₂ separation.⁽⁵¹⁾

It can therefore be concluded that such defects are a fundamental characteristic of this MOF, with wide-ranging effects in its properties. As such, it is desirable to have methods to generate and control them. In the following pages, we examine a tertiary method for vacancy defect generation: leaching in solvent solution, a method which has been previously shown to be applicable to other MOFs.⁽⁵³⁾

3.3. Materials and methods

3.3.1. Materials

The UiO-66(Zr) MOF used in this study was synthesised according to the procedure described in section B.4. This particular method was chosen to ensure that a structure with a minimal number of intrinsic defects would be obtained.

The material was then gestated in a solvent solution of modulator through.

To generate a comprehensive map of all of the potential influence of different variables on defect concentration, a number of leaching conditions have been selected. In order to verify the contribution of the solvent in the leaching process dimethyl formamide (DMF), water, ethanol and dimethyl sulfoxide (DMSO) were used. The same monotopic acids which have been successfully used as modulators in the synthesis of defective UiO-66 (formic acid (FA), acetic acid (AA), trifluoroacetic acid (TFA) and benzoic acid (BA)) were used in various concentration ranges, from 1 to 100 equivalents with respect to the BDC linker. The DMF dataset does not include any trifluoroacetic acid leached samples, as it was only used in latter sample sets. Furthermore, no benzoic acid samples could be generated when using water as a solvent, due to its poor capability of dissolving the chemical in significant amounts. Finally, at high acid concentrations, several of the samples were completely dissolved at leaching conditions. A summary of all generated

3. Exploring the impact of synthesis and defects on adsorption measurements

materials can be found in Table 3.1.

3.3.2. Methods for quantifying defects

Determining the abundance of defects and characterising their distribution is a major challenge.

One of the most accessible way of assessing the defectivity of a MOF is thermogravimetry (TGA). Since through heating in an oxygen-rich atmosphere, the MOF is normally reduced to its metal oxide, a stoichiometric analysis of the TGA curve can allow for the percentage of missing linkers to be determined. TGA curves for this study were measured under an air atmosphere using the method described in section A.1. A heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ was used, as it is assumed to be low enough for the sample to be in permanent thermal equilibrium with the furnace. The curves are then normalized with respect to the weight at $600\text{ }^{\circ}\text{C}$, which is assumed to correspond to pure ZrO_2 . The maximum possible mass loss of a solvent-free structure is calculated from the ratio of the fully-substituted metallic cluster $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{C}_6\text{H}_4(\text{COO})_2)_6$. The plateau of the TGA curve between $400\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$, in the range where it is assumed that the molecules included in the framework are completely evacuated, is used as a measure of the number of BDC linkers which are missing.

If the distribution of defects can introduce changes in the long-range order and topology of their parent framework, such as by the introduction of phase changes, additional peaks can be observed through regular powder diffraction techniques. As Cliffe et al. has shown⁽¹⁰⁾, the UiO-66 defect-free face-centered unit (**fcu**) net can be transformed through missing cluster defects into a (**reo**) net. Short-range correlations of such domains form nanoregions inside the parent structure and generate diffuse scattering peaks observable at low angles in powder X-ray (pXRD) diffraction patterns, corresponding to “forbidden” reflections in a primitive cubic superstructure. As such, these pXRD peaks can be used to verify the existence of missing cluster defects, but only when their abundance allows for nanodomains of (**reo**) nets to be formed. In this study, pXRD measurements were performed as described in section A.8.

In order to check for the inclusion of a modulator in the framework, the MOF can be digested with the help of a hydrofluoric acid and the resulting solution can be analysed through proton nuclear magnetic resonance (^1H NMR) or high performance liquid chromatography (HPLC). In this study, ^1H NMR was used through the procedure detailed in section A.9 to qualitatively and quantitatively assess the presence of the capping agents in the UiO-66(Zr) samples.

Finally, both nitrogen adsorption at 77 K and CO_2 adsorption at 303 K can be used to describe the surface characteristics and porosity of the samples. The methods for obtaining the isotherms are presented in detail in section A.4 and section A.7 for N_2 and CO_2 respectively.

method

3. Exploring the impact of synthesis and defects on adsorption measurements

Table 3.1.: Samples used in the UiO-66(Zr) linker leaching study

Sample name	Solvent	Modulator	Concentration	Observations
PWI-C	None	None	None	Parent material
FA1	DMF	FA	1:1	—
FA5	DMF	FA	1:5	—
FA10	DMF	FA	1:10	—
FA20	DMF	FA	1:20	—
FA100	DMF	FA	1:100	—
AA1	DMF	AA	1:1	—
AA5	DMF	AA	1:5	—
AA10	DMF	AA	1:10	—
AA20	DMF	AA	1:20	—
AA100	DMF	AA	1:100	—
BA1	DMF	BA	1:1	—
BA5	DMF	BA	1:5	—
BA10	DMF	BA	1:10	—
BA20	DMF	BA	1:20	—
BA100	DMF	BA	1:100	Completely dissolved
JM237	None	None	None	Parent material
JM328	H ₂ O	FA	1:10	—
JM329	H ₂ O	FA	1:100	—
JM330	H ₂ O	AA	1:10	—
JM331	H ₂ O	AA	1:100	—
JM332	H ₂ O	BA	1:10	—
JM333	H ₂ O	BA	1:100	—
JM334	H ₂ O	TFA	1:10	—
JM335	H ₂ O	TFA	1:100	—
JM351	MeOH	FA	1:10	—
JM352	MeOH	FA	1:100	—
JM353	MeOH	AA	1:10	—
JM354	MeOH	AA	1:100	—
JM355	MeOH	BA	1:10	—
JM356	MeOH	BA	1:100	—
JM357	MeOH	TFA	1:10	—
JM358	MeOH	TFA	1:100	—
JM359	MeOH	None	0	Control
JM360	DMSO	FA	1:10	—
JM361	DMSO	FA	1:100	—
JM362	DMSO	AA	1:10	—
JM363	DMSO	AA	1:100	—
JM364	DMSO	BA	1:10	—
JM365	DMSO	BA	1:100	—
JM366	DMSO	TFA	1:10	—
JM367	DMSO	TFA	1:100	Completely dissolved
JM368	DMSO	None	0	Control

3.4. Results and discussion

3.4.1. Crystallinity of leached samples

The crystallinity of the leached samples is verified through XRD. The results in section D.1 confirm that all resulting materials retain the same peaks in their powder diffraction patterns.

A closer look at the low angle scattering (Figure 3.2) reveals the appearance of diffuse peaks, corresponding to forbidden reflections of the (**reo**) phase. They confirm that the leached samples begin to exhibit phase coexistence of the original UiO-66(Zr) unit cell and the missing cluster (**reo**) net.

3.4.2. Thermogravimetry results

A typical TGA curve, as measured on a pristine material is characterised by three main mass losses: a loss at low temperature, usually until 100 °C, which is indicative of adsorbed water from the environment; a secondary mass loss in the 100 °C to 200 °C range, corresponding to the evacuation of residual solvent from the pores and finally, a large step which is a sign of sample degradation as the linker is oxidized.

A selection of TGA curves measured on the leached samples can be seen in Figure 3.3. The complete set of data can be found in Appendix D, section D.2.

There are four types of differences that can arise between curves on different samples:

- the aforementioned change in overall height, which indicates the presence of missing linker defects;
- differences in the solvent removal step, as they have different boiling points and interactions with the framework;
- in case the defects are capped by an agent such as the modulator molecule used, it may introduce a new mass loss step between solvent removal and complete structure breakdown;
- finally, a highly defective structure loses part of its thermal resistance altering both the onset of mass loss and the final decomposition temperature.

From the TGA curve of the pristine UiO-66 material, it is immediately obvious that there are some defects already present in the sample. By using the normalized mass at 420 °C a linker-to-cluster ratio of around 11.6:1 can be calculated. This shows that there

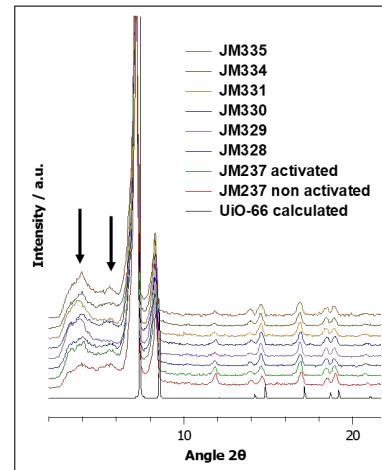


Figure 3.2.: Diffuse scattering peaks in the H₂O leached samples.

3. Exploring the impact of synthesis and defects on adsorption measurements

are still intrinsic defects in the as-synthesised structure. These defects are most likely capped by formate moieties, which have been generated during the solvothermal synthesis in DMF through solvent self-hydrolysis (through Equation 3.1), as commercially available DMF has a small percentage of residual water.⁽³⁷⁾



It follows that the mass loss step around 250 °C is the evacuation of formate capping agents from the structure, to generate an open metal site. The same step can be found in the samples which have been leached with formic acid.

In leached samples where other acids were used, it is likely that the original formate capping the defects has been replaced with an acid molecule from solution, either because it is thermodynamically favourable, or through kinetic means due to the large excess present. As evidenced in Figure 3.3, the mass loss corresponding to the formate is reduced, or no longer present. Acetic acid (Figure 3.3d) leaves the structure at a higher temperature, as a new peak is present at 390 °C. Strongly bound capping agents at defect sites have been shown to require a higher activation temperature to fully remove.⁽⁵⁴⁾ Benzoic acid (Figure 3.3c) introduces a progressive mass loss near the total decomposition temperature of 550 °C. As it is similar to the btc linker, its higher stability is not surprising. Finally, the samples leached with TFA have a more complicated curve, with two or even three peaks in the first derivative with respect to temperature. This kind of degradation suggests the existence of different types of capping sites, some more strongly bound than others. A slight difference is also observed in thermal stability, with all TFA samples having a 20 °C to 30 °C increase in decomposition temperature. Since defects normally have a negative impact on the thermal and mechanical resistance of a MOF, high resolution TGA experiments were carried out to eliminate possible influences of heating rate. The resulting curves (Figure D.6) still display the same behaviour. The effect is likely due to the electron-withdrawing effect of the TFA molecule on the Zr node, which induces a stronger Zr-carboxilate bond. A similar increase in mechanical stability has been shown by Van de Voorde et al. on TFA modulated defective UiO-66 materials.⁽⁵⁵⁾

The solvent used can be removed in all cases before 200 °C. DMSO has the highest preponderence in the leached samples (Figure 3.3d) and is the most difficult to remove, likely due to its high boiling point.

It is also clearly visible that the leaching procedure has, without doubt, led to the generation of defects. The curves of the leached samples fall below that of the original material in normalized weight, indicative of a lower linker-to-node ratio. These trends are analysed in subsection 3.4.4.

3.4.3. Nitrogen sorption at 77K

Isotherms have been recorded on samples activated at both 200 °C and 320 °C. It is important to note that, as seen from the TGA curves, not all capping agents leave the

3. Exploring the impact of synthesis and defects on adsorption measurements

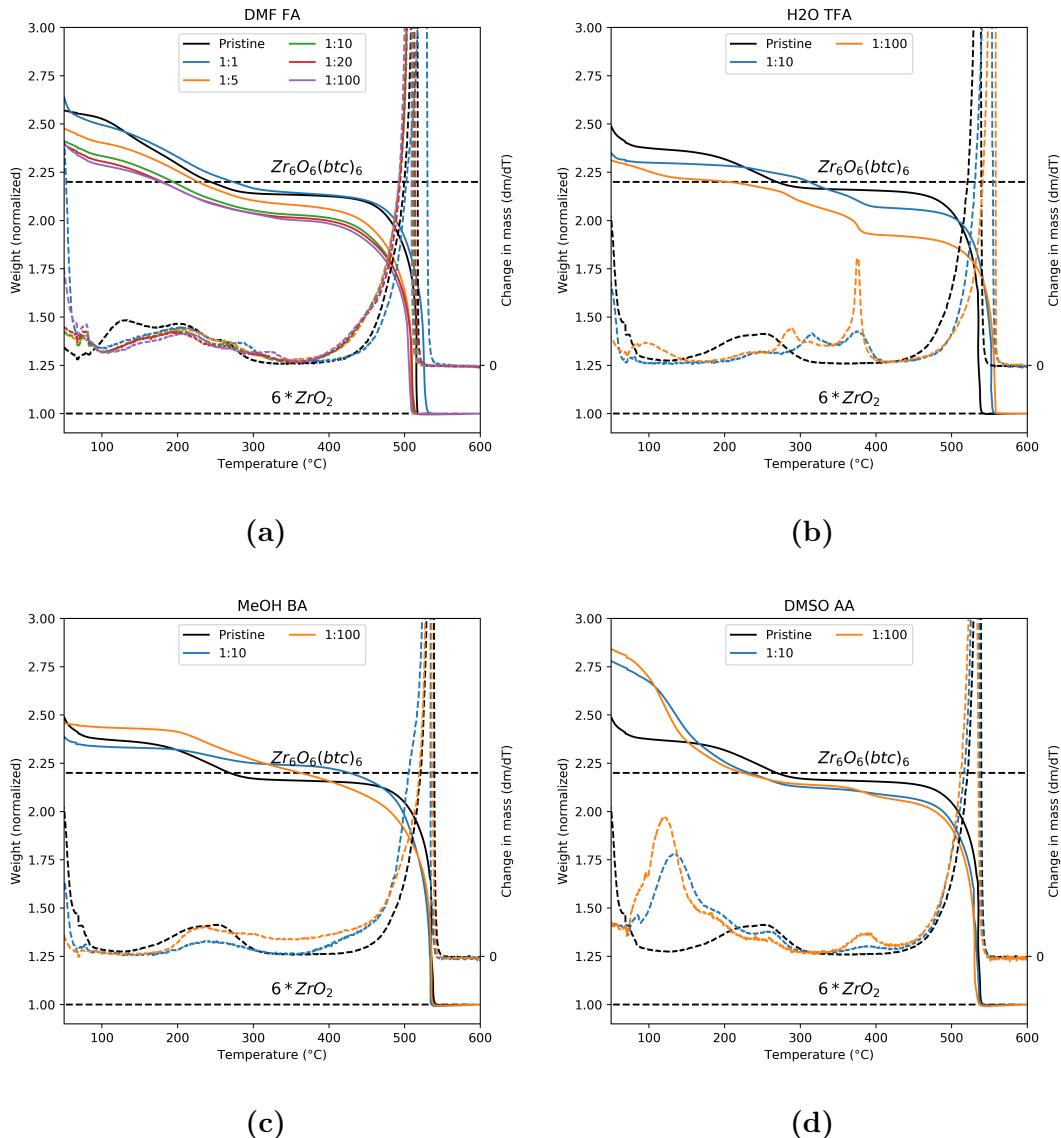


Figure 3.3.: A selection of the TGA curves as measured on the leached samples: (a) formic acid in DMF, (b) trifluoroacetic acid in water, (c) benzoic acid in methanol and (d) acetic acid in DMSO. The curve for the parent material is in black. Dotted lines correspond to the secondary y axis as a semilogarithm of the first derivative of mass loss with respect to temperature.

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structure when thermal treating at a lower temperature. The modulator which is still present within the pore surface will likely influence the adsorption behaviour. Several example isotherms can be found in Figure 3.4, with the complete dataset present in Appendix D, section D.3.

There are a few isotherm features which can be analysed to assess the type of modifications introduced in the structure and their preponderence.

- The slope of the isotherm at low p/p_0 is representative of the first interactions with the pore surface, which can be quantified using the initial Henry constant. It will be influenced by any changes in pore environment such as functionalised defect sites.
- Missing linker defects will lead to an increase of the apparent surface area and perhaps lead to a more extensive pore network.
- The pore size distribution and total pore volume give indications on the presence of missing cluster defects and/or of the formation of mesoporous voids within the structure.
- A steep step at high p/p_0 is indicative of intercrystal condensation and suggests particle aggregation due to lower average crystal size.

It is immediately apparent that the leaching process had an influence on the adsorption characteristics of UiO-66. Isotherms of acid treated samples diverge from the parent material, at often at different pressures. In general, the total molar capacity at full loading is seen to increase, a telltale sign of an increase in pore volume through defect generation. On the other hand, other particularities exist, such as the benzoic acid samples in methanol and DMSO where the low and high concentration has opposite effect on the total loading. Predictors of defects and trends will be analysed in the following section.

3.4.4. Characterisation of trends

The graphs in Figure 3.5 summarize the trends in missing linker defects as calculated through the TGA plateau at 420 °C. The DMF leached samples, due to the multiple datapoints with different acid concentrations show the clearest influence of this variable on defect generation. Even small amounts of modulator leads to the decrease of the linker-to-node ratio, but the increase in concentration stops having an effect at around 20:1 equivalents. It is likely that the trends are similar with other solvents, even if less datapoints are available.

For the nitrogen adsorption dataset, the predictors described in the previous section have been calculated using the pyGAPS framework (chapter 1). The Henry constant is determined through the initial slope method, with a linear section found below $10^{-4} p/p_0$. Pore volume is taken as the liquid density of the amount adsorbed at 0.8 p/p_0 , assuming that the nitrogen is in a liquid-like state in the MOF pores. The pore size distribution

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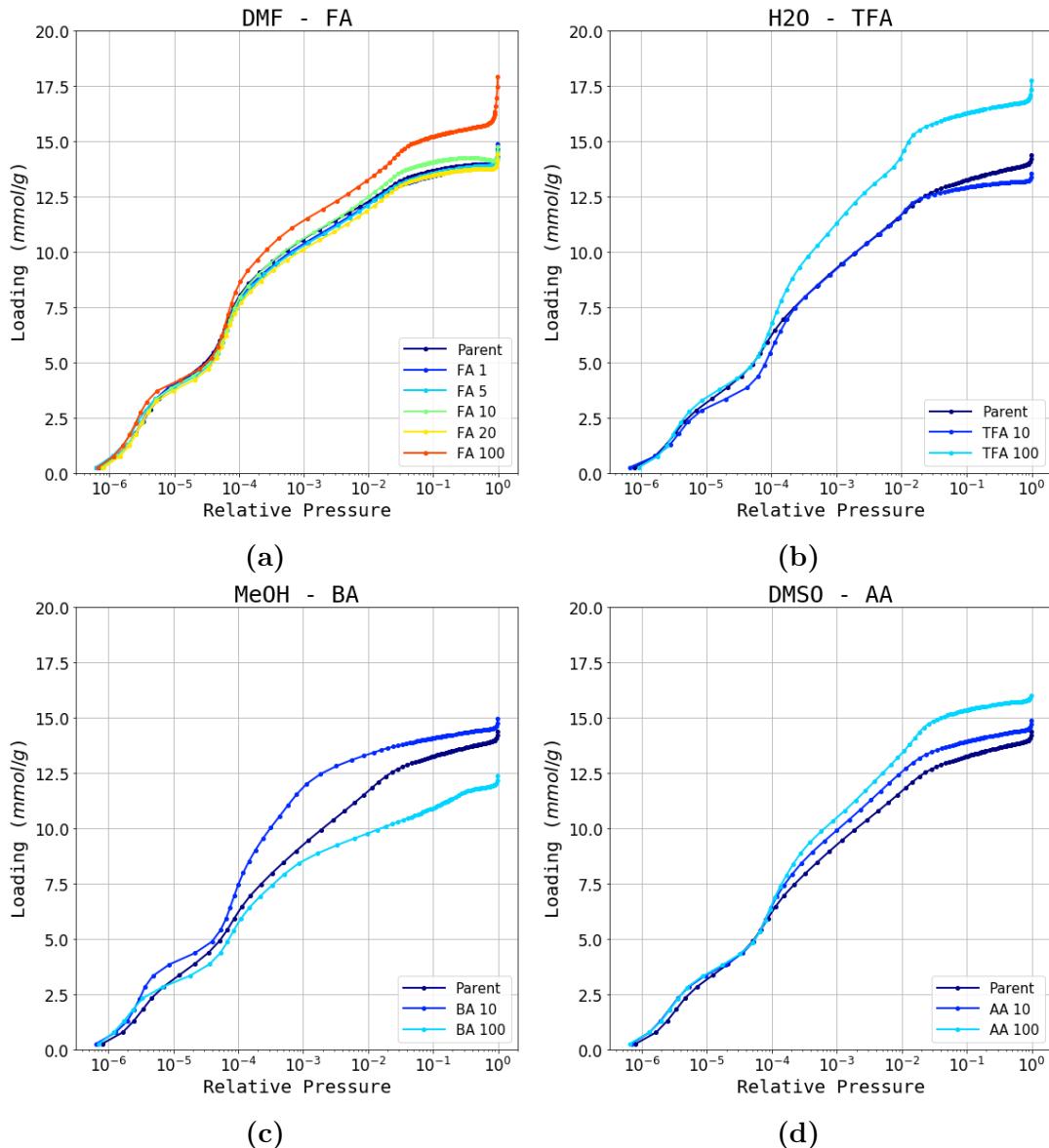


Figure 3.4.: A selection of nitrogen sorption isotherms as measured on the leached samples: (a) formic acid in DMF, (b) trifluoroacetic acid in water, (c) benzoic acid in methanol and (d) acetic acid in DMSO. The curve for the parent material is in dark blue. The x axis is logarithmic for clarity of low pressure points.

3. Exploring the impact of synthesis and defects on adsorption measurements

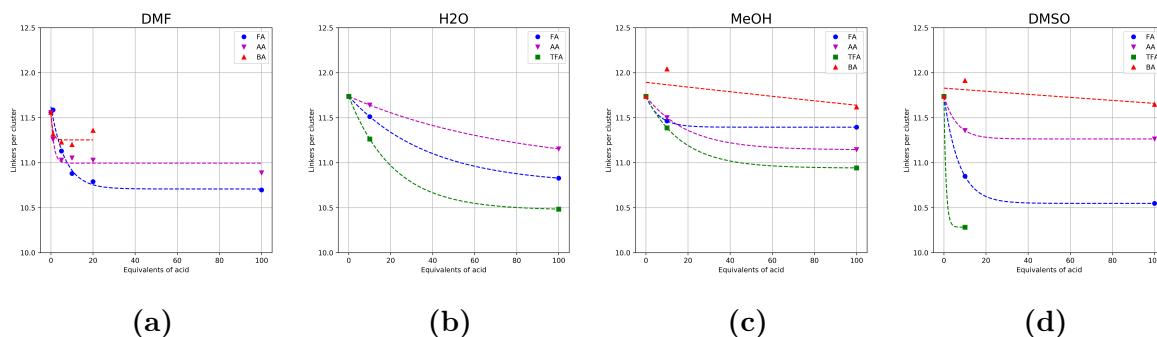


Figure 3.5.: Calculated linker-to-node ratio from the TGA curve normalized mass at 420 °C for (a) DMF (b) H₂O, (c) MeOH and (d) DMSO leached samples. A ratio of 12 to 1 corresponds to a completely defect-free structure. An exponential decay trendline is fitted to each set of points.

was calculated through the Horvatz-Kawazoe method for micropores, the Dollimore-Heal method for mesopores and DFT kernel fitting for a multiscale distribution. While the applicability of these methods for determination of absolute pore size may be questioned, they can be readily used to compare between different samples of the same material. In general, the leaching process has a positive effect on both surface area and pore volume, both of which increase with a higher concentration of acid used. The strength of the initial interaction of the nitrogen probe with the pore walls is changed as well, with more defective samples likely to have a more pronounced interaction, either through the introduction of CUS or modification of pore environment.

The influence of the modulator on the linker-to-node ratio appears to be constant throughout the solvents used, with an overall trend of TFA > FA > AA > BA for generation of defects. The order is similar to the acidic character of the modulators, except for benzoic acid which has a lower pKa (4.2) than acetic acid (4.7). When examining the influence of the solvent, another trend appears to emerge, with samples leached in DMSO having the largest propensity for defect generation, followed by DMF, water and methanol. The contribution of the solvent is not as easy to determine due to the complex interplay of multiple factors. The polarity of the solvent molecule has been linked to defect generation during modulated synthesis in the seminal report by Shearer et al.. The leaching results do not, however, conform to the same trend, as water with a relative polarity of 1.0 introduces more defects than methanol (relative polarity of 0.7) and DMF (0.38) is less effective than DMSO (0.44). The solubility of terephthalic acid in the solvent of choice is likely a limiting factor in the

In this case, the plateau might not be an accurate indication of the number of defects since the comparatively large molecule, high boiling point and similarity to the terephthalate linker make the removal of benzoic acid capping open metal sites harder. The nitrogen

The calculated pore sizes with both the HK method and the DFT method show two sharp peaks corresponding to the octahedral and tetrahedral pores in the UiO-66 structure. In Figure 3.8, the pore size distribution for the DMSO dataset is depicted.

check
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new
results

table
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3. Exploring the impact of synthesis and defects on adsorption measurements

The appearance of a tertiary pore is visible in the leached samples with formic, acetic and trifluoroacetic acid. This pore size likely corresponds to the increased pore volume introduced by missing linker-type defects. The calculated diameter of this tertiary pore is inversely proportional to the molecular size of the leaching compound used, which is a clear indication of the presence of the acid molecules in the structure as capping agents. On the samples which have been activated at 320 °C, the pore width shifts to a single value as the coordinated acids are evacuated.

The pore size distribution calculated in the benzoic acid leached samples shows the disappearance of peaks larger than around 1 nm, as the compound replaces formate as the capping agent for the initial defects in the structure. Due to the similarity of the terephthalate linker with benzoate, the structure becomes more “ideal” than the pristine material. At high concentrations of benzoic acid, an overall decrease in porosity may be seen, as two benzoate molecules may act as capping agents in adjacent sites as depicted in Figure 3.7, effectively lowering the available pore volume. The effect is corroborated by trends in the linker-to-node ratio, surface area and total pore volume in both methanol, DMSO and to a lesser extent DMF.

At very high concentrations of TFA and BA, a fourth pore size begins to appear in the DFT calculated pore distribution. This is likely evidence that missing cluster defects can be introduced at these concentrations. It should be noted that if such large-scale modifications of the structure are possible, complete structural breakdown is not far away. Indeed, samples with higher concentrations of acid could not be obtained with TFA in DMSO, with sample subjected to these conditions ending up completely dissolved.

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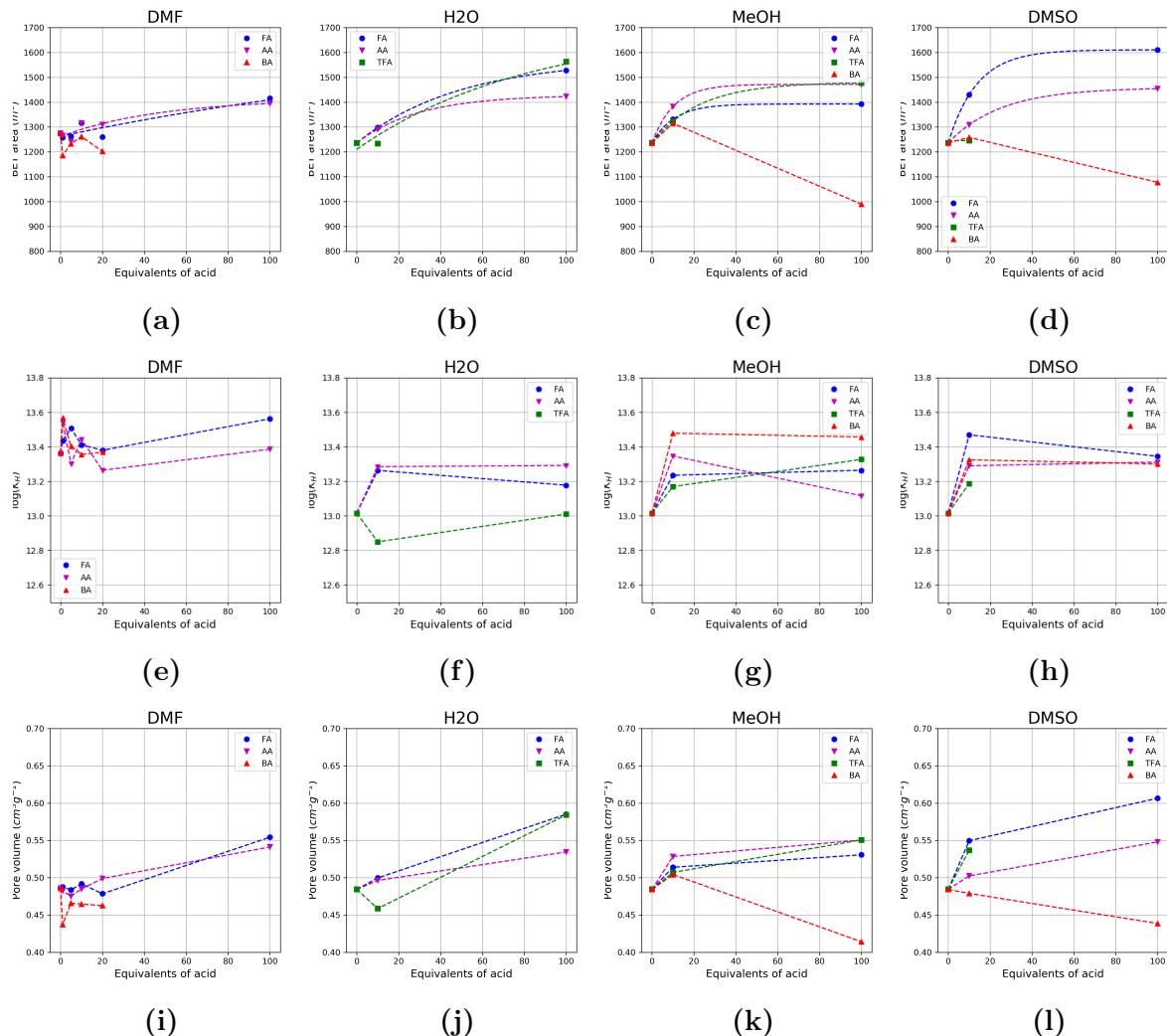


Figure 3.6.: Characterisation of all samples through predictors obtained through processing of the nitrogen physisorption data. The figure shows BET surface area (a-d), the logarithm or the initial Henry constant (e-h), the calculated pore volume (i-l) for DMF, H_2O , MeOH and DMSO leached materials, respectively.

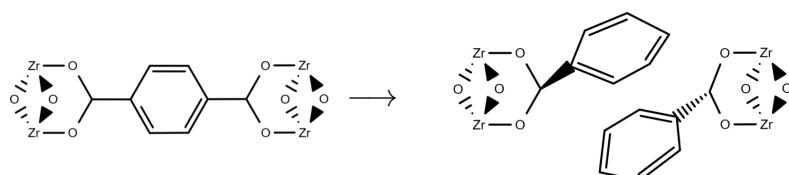


Figure 3.7.: A defect site created through benzoic acid.

3. Exploring the impact of synthesis and defects on adsorption measurements

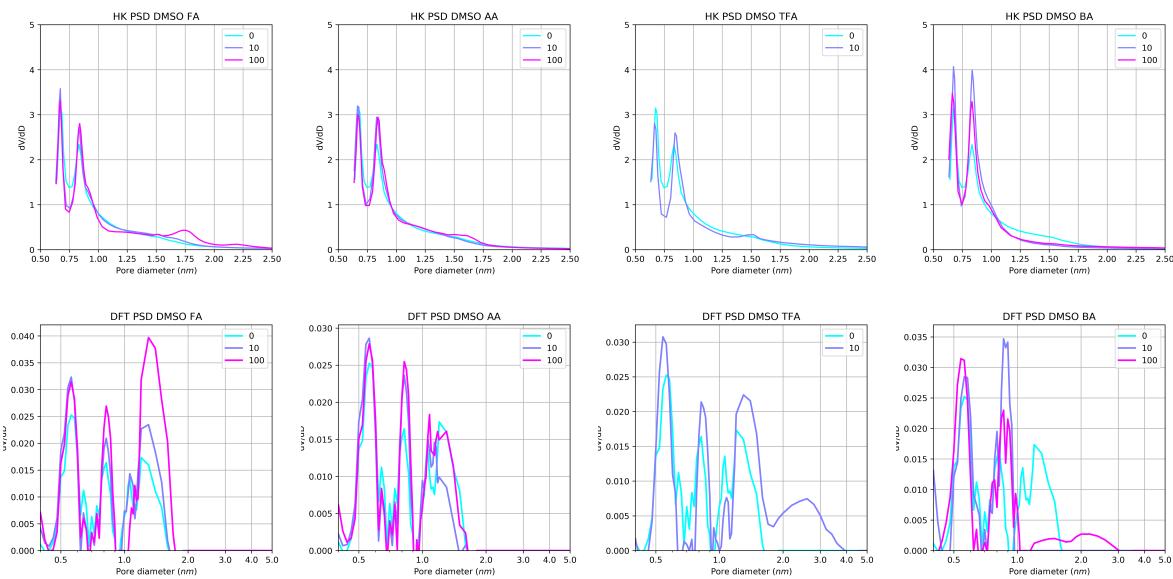


Figure 3.8.: Calculated pore size distribution for the DMSO-leached samples with the HK (a-d) and DFT (e-h) methods.

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3.5. Conclusion

In summary, a new method of generating missing linker and missing cluster type defects in a UiO-66(Zr) framework has been presented. This type of post-synthetic modification is an alternative to modulated synthesis, and can be useful when crystal growth is not desirable. It also introduces new possibilities of framework functionalisation, through sequential rounds of leaching and defect healing.

A few trends emerge in regards to the capacity of different solvents and acids to induce defect formation.

- The impact of the monotopic acid is mainly due to its acidity, with pKa a being a good predictor of the resulting defectivity.
- Bulky modulators suffer from kinetic effects, as seen with benzoic acid being the least effective in inducing defect formation.
- As the acid replaces the terephthalate linker in an 2:1 ratio, a critical concentration exists after which no further leaching of BDC happens. In solvents where the solubility of the linker is low, higher amount of modulator are needed to shift the equilibrium.
- High concentrations of acids may also induce complete structural breakdown through attack at the crystal surface.
- The resulting defective structures may have different bulk properties such as thermal and mechanical resistance due to the influence of the defect capping agents.
- The capping

These results also show the vast influence that defects have on the adsorption properties of MOFs. From different interactions with the material surface to vastly different capacities and, in some cases, even changing the sizes of pores or introducing new porosity. When transitioning a material from a lab-scale to an application it is important to consider that

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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 $40 \text{ cm}^3 \text{ min}^{-1}$. 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. Common characterisation techniques

A.3. Skeletal density determination

True density or skeletal density is determined through gas pycnometry in a Microtrac-BEL 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.

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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

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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 characterization

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,

B. Synthesis method of referenced materials

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 1h. 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

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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.

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D. Appendix for chapter 3

D.1. Powder diffraction patterns

D. Appendix for chapter 3

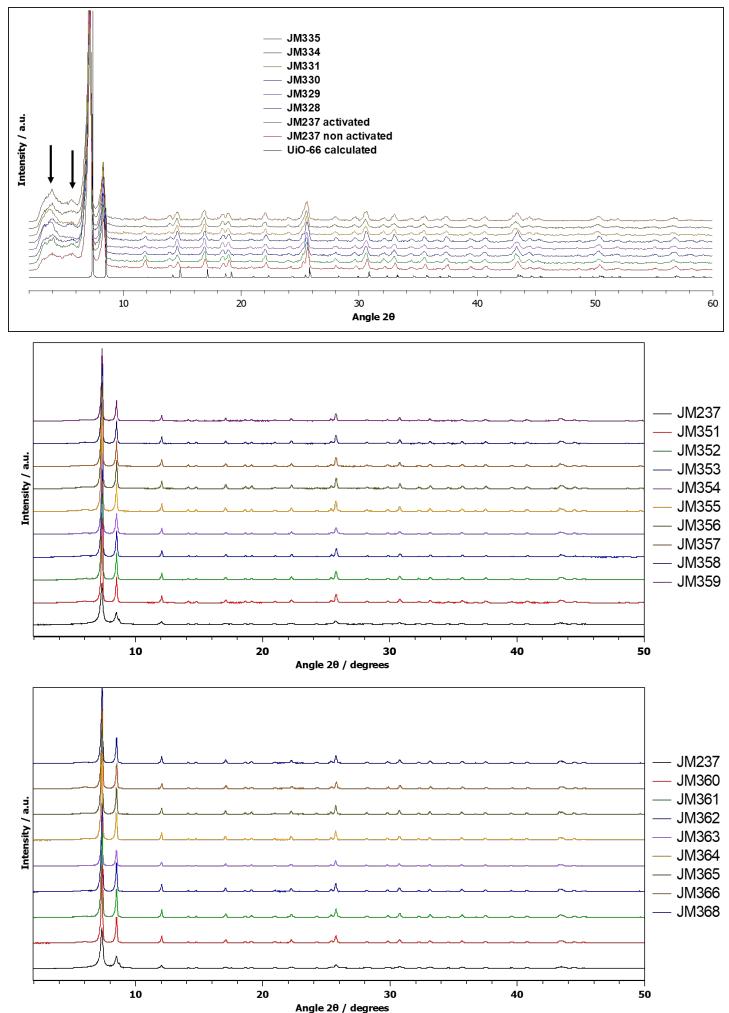


Figure D.1.: PXRD patterns for all samples

D.2. TGA curves

D.2.1. DMF leached samples

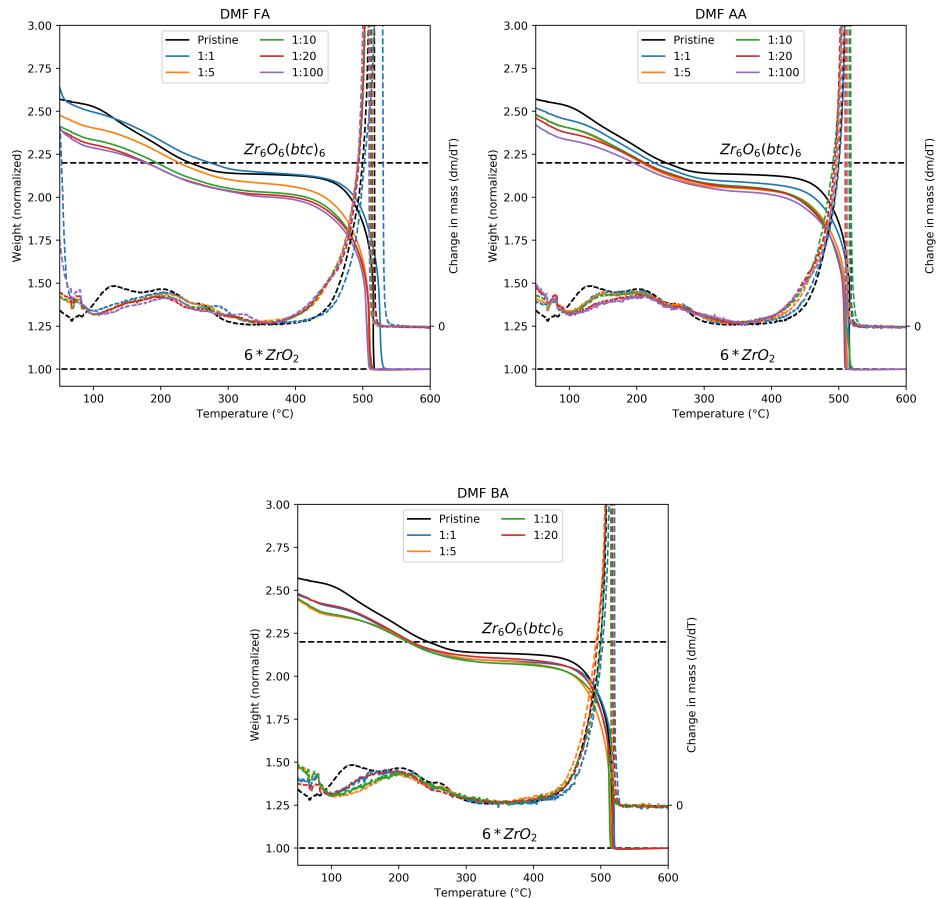


Figure D.2.: TGA curves for samples leached in DMF

D.2.2. Water leached samples

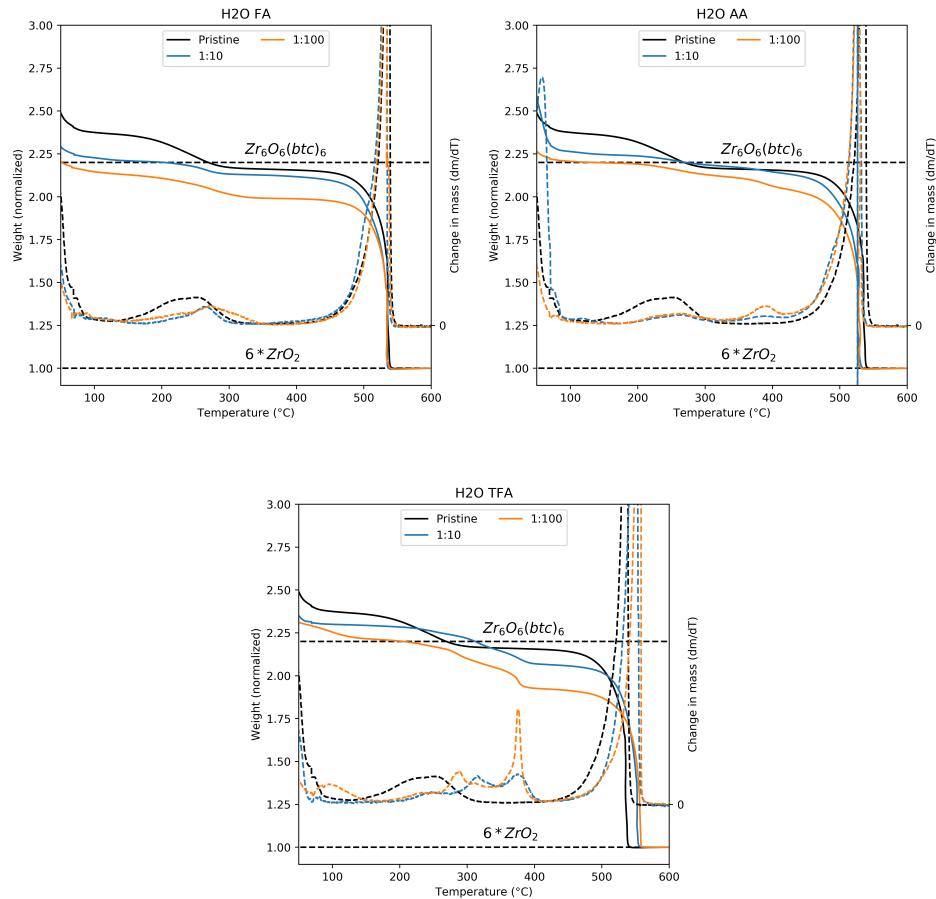


Figure D.3.: TGA curves for samples leached in H₂O

D.2.3. Methanol leached samples

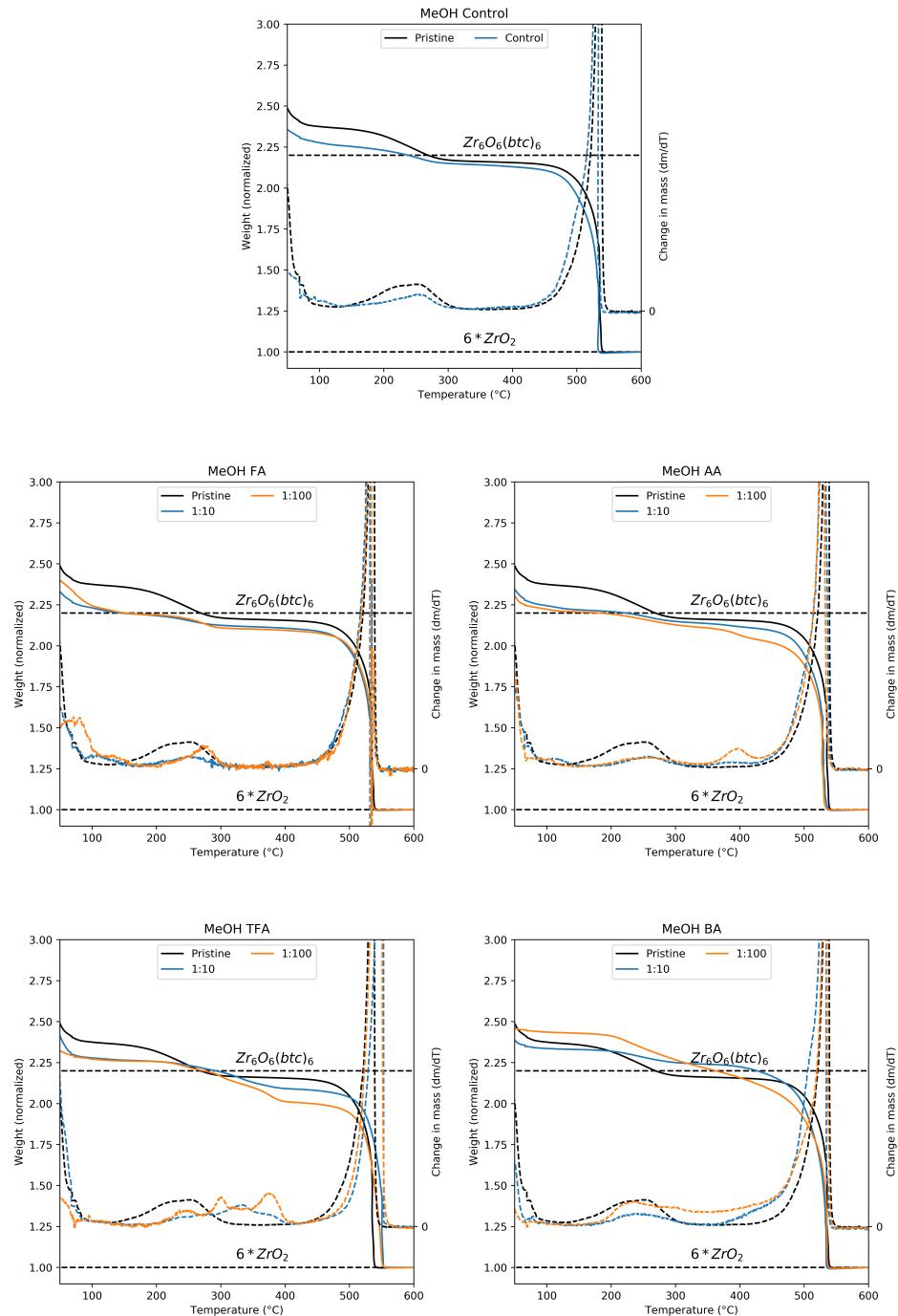


Figure D.4.: TGA curves for samples leached in MeOH

D.2.4. DMSO leached samples

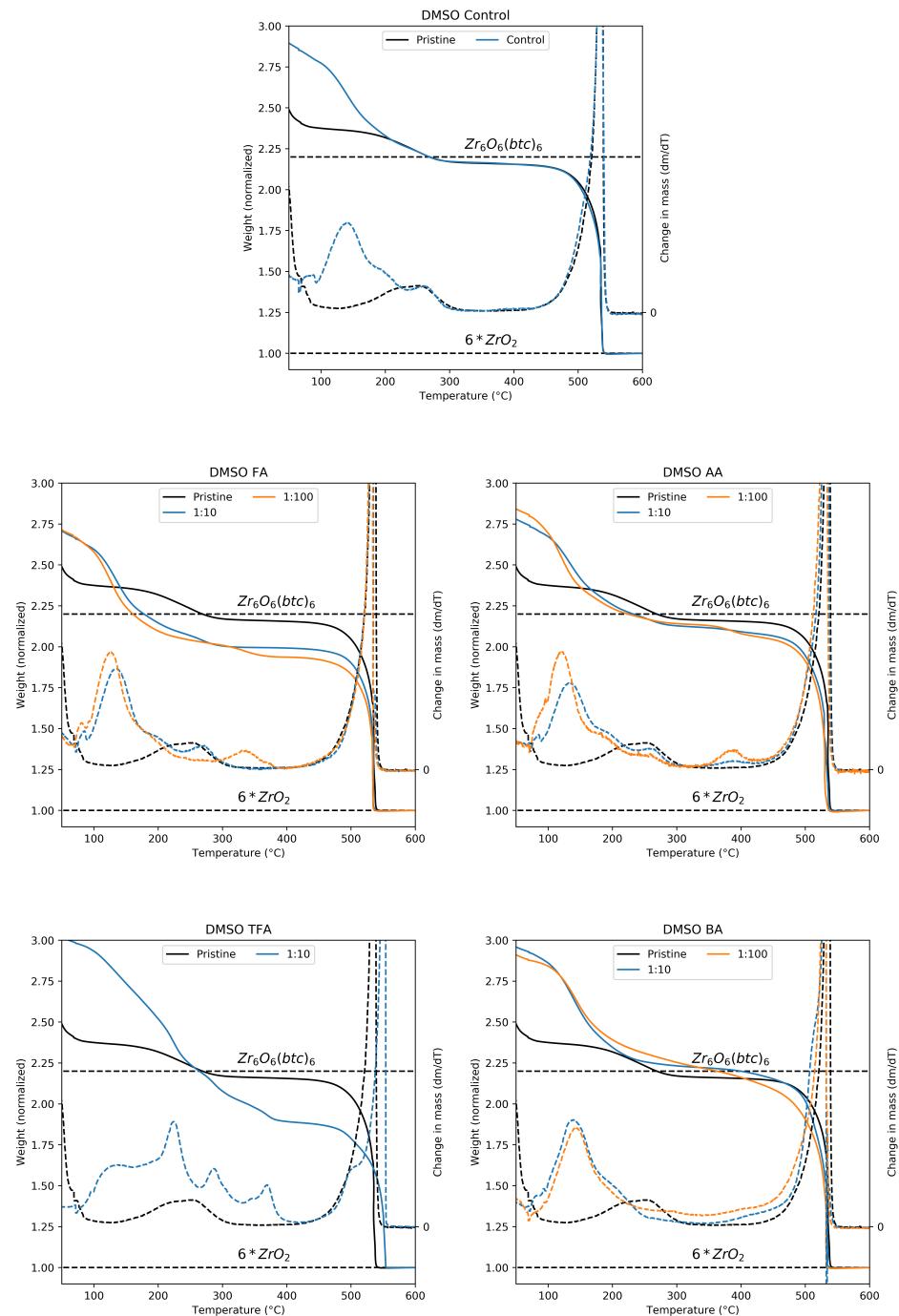


Figure D.5.: TGA curves for samples leached in DMSO

D.2.5. High resolution curves

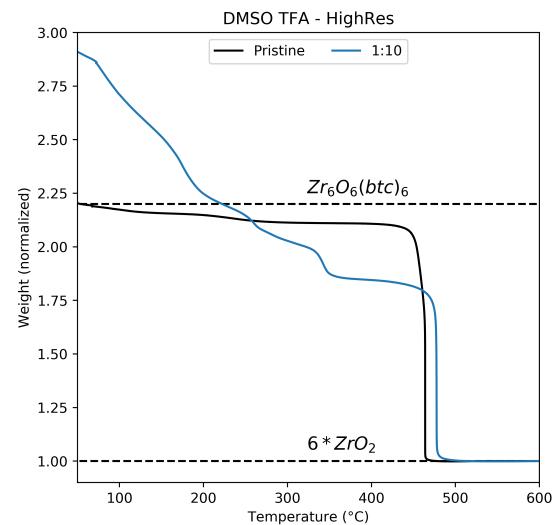


Figure D.6.: High resolution TGA curves for a DMSO/TFA leached sample

D.3. Nitrogen sorption isotherms

D.3.1. DMF leached samples

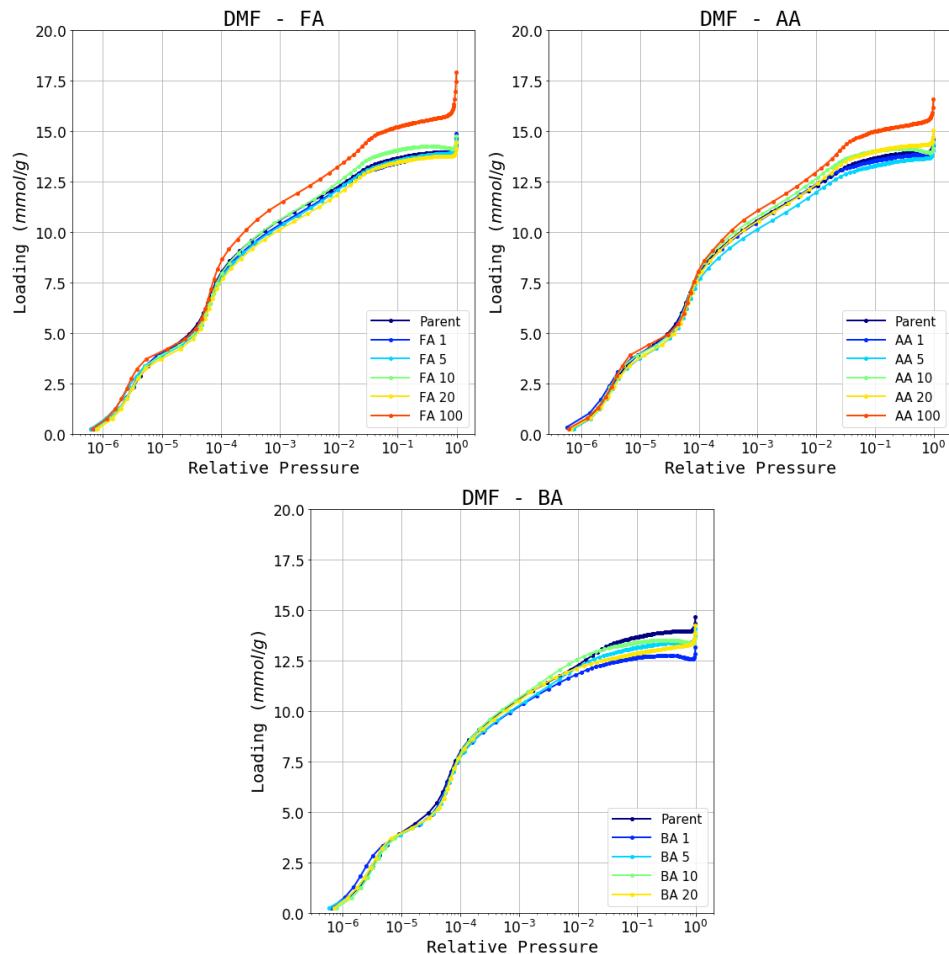


Figure D.7.: DMF isotherm dataset activated at 200 °C

D.3.2. H₂O leached samples

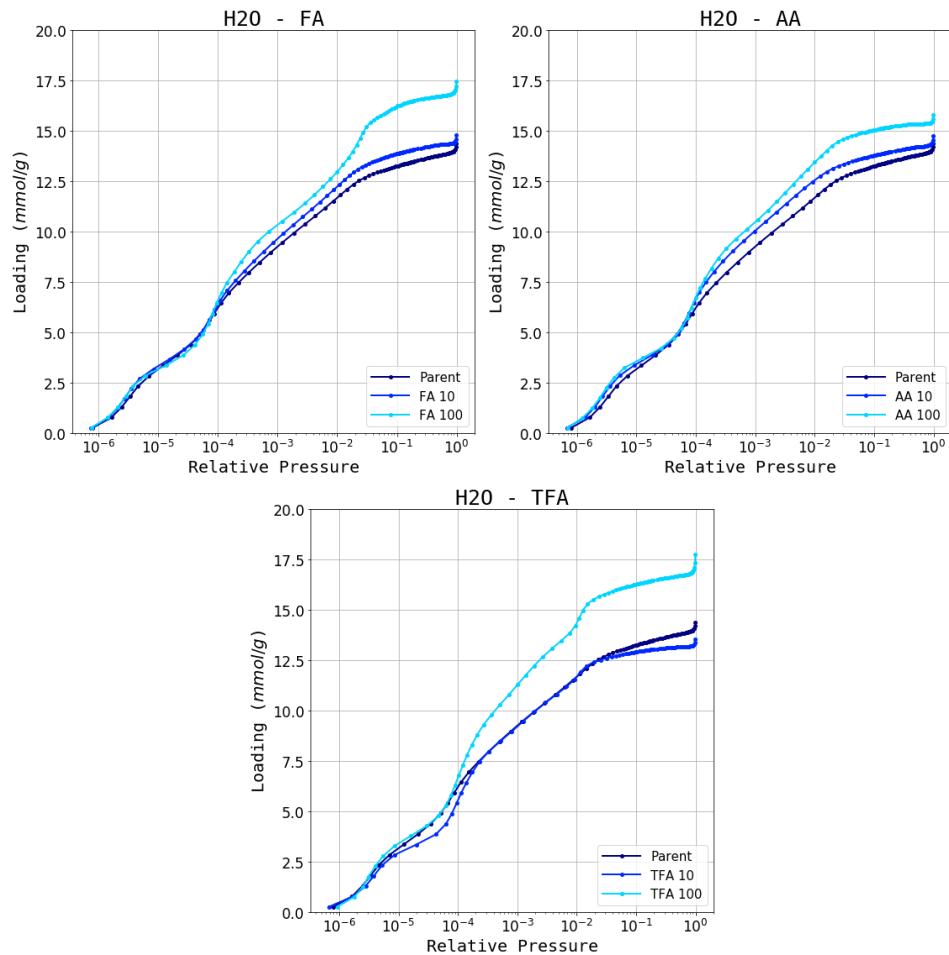


Figure D.7.: H₂O isotherm dataset activated at 200 °C

D.3.3. MeOH leached samples

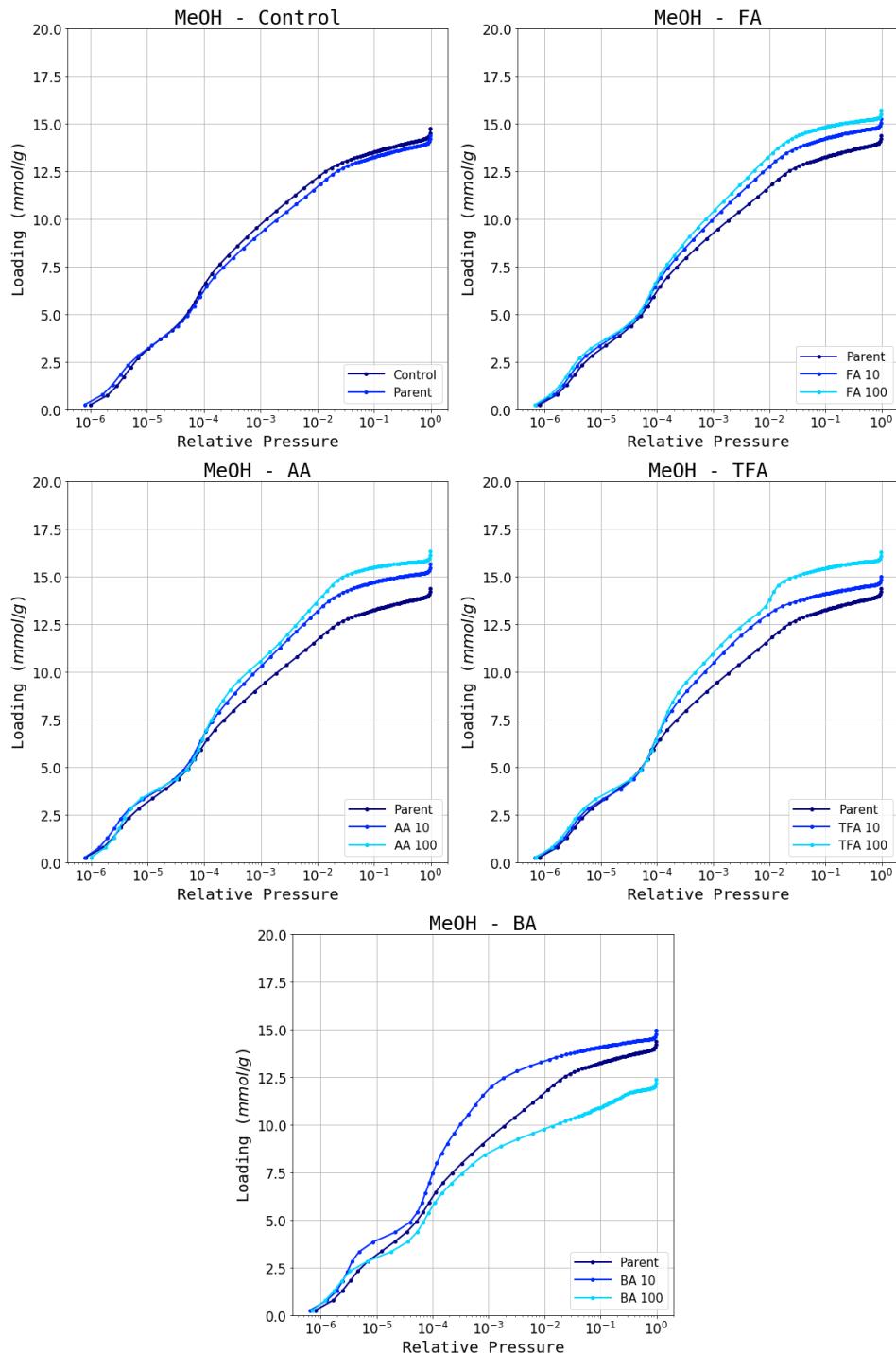


Figure D.8.: MeOH isotherm dataset activated at 200 °C

D.3.4. DMSO leached samples

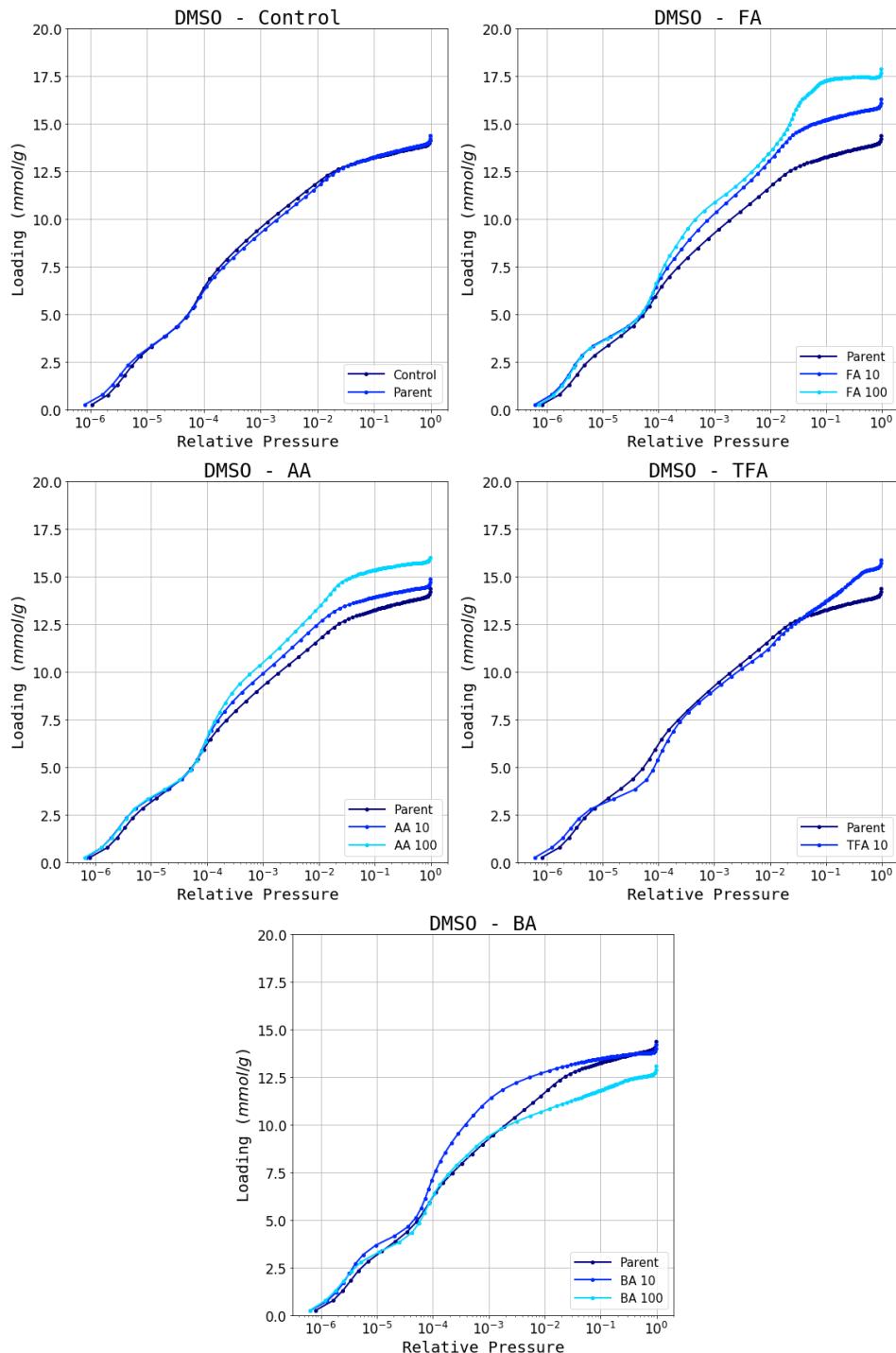
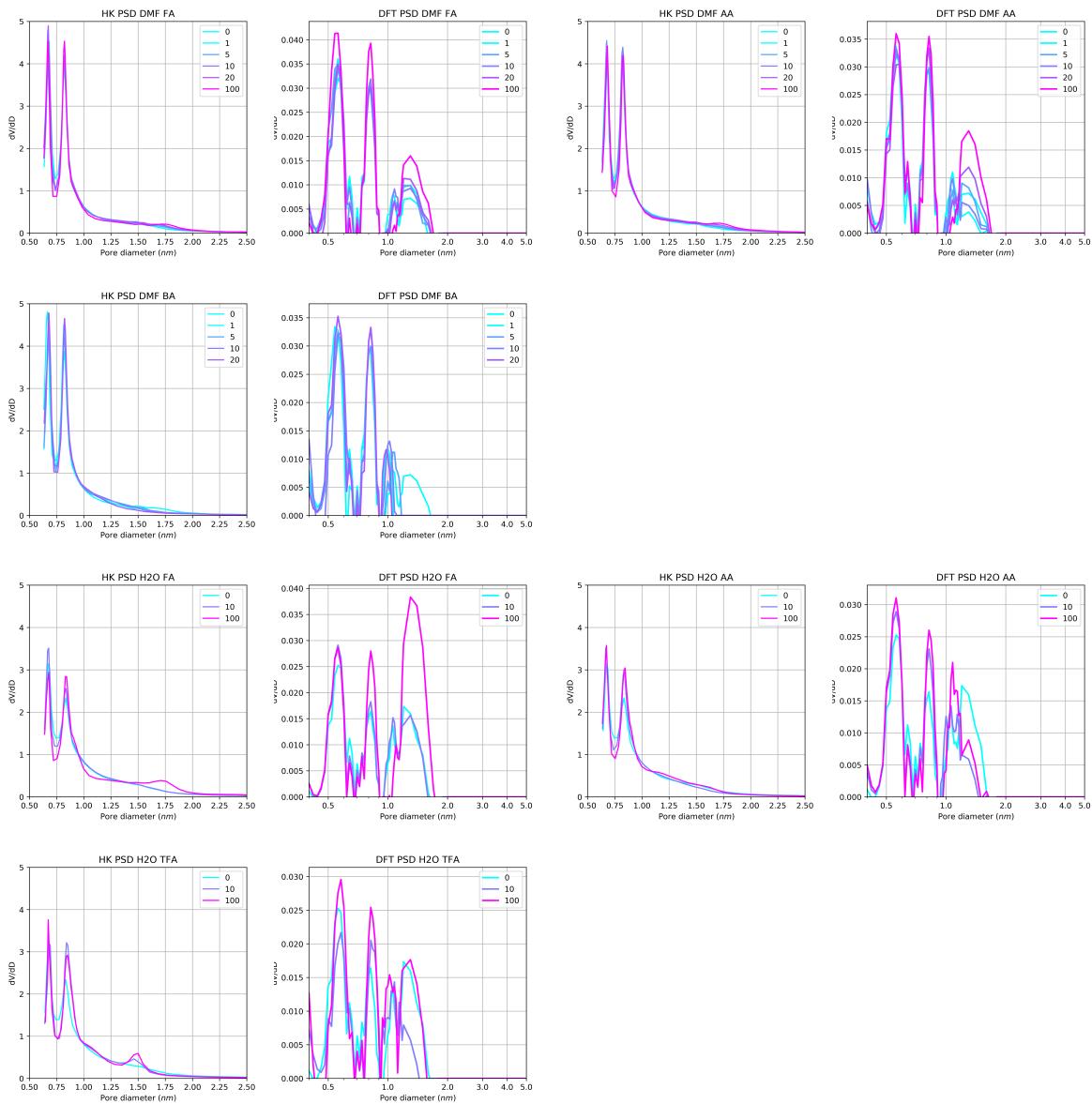


Figure D.9.: DMSO isotherm dataset activated at 200 °C

D. Appendix for chapter 3

D.4. Characterisation



D. Appendix for chapter 3

