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Abstract

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5. Exploring novel behaviours

5.1. Introduction

Until this chapter, it has been assumed that the porous materials are static when adsorbing a gas. Differences in pore size, crystallinity or structure may exist, but these properties did not change as the host fluid enters the pores. In most cases this is a reasonable assumption. However, it is not universally applicable, as the forces and interactions exerted during adsorption may induce changes in solid itself.

Such effects in classic porous inorganic materials like zeolites, carbons and clays take the form of structural contraction and expansion, swelling or counterion displacement.⁽¹⁾ It is only recently that flexibility was discovered in coordination polymers, such as MOFs. A feature which arises from their comparatively weak coordination bonds or pliant organic components, it allows for a systematic deflection of bonds throughout the entire crystal lattice. As such, the term “soft porous crystals” defines porous solids that are both highly ordered and possess the ability to reversibly transform their structure upon external stimuli. Part of the so-called third generation of crystalline porous compounds, they represent some of the latest developments in the field of MOFs.

The unique properties of flexible materials can result in their application in fields such as sensing, micromechanical devices and highly efficient gas storage. It is these perspectives that make their synthesis and design a key research interest. However, their flexible nature introduces new challenges in their characterisation, as factors such as temperature and thermal history⁽²⁾, crystal size^(3,4), external pressure^(5,6), structural defects⁽⁷⁾ and even adsorption kinetics play a role in their compliance. This type of variability goes beyond what has been insofar discussed in this thesis and it is here where a combined characterisation approach becomes essential in understanding the fundamental physics governing flexibility and potential prediction of adsorption behaviour.

Summary

After a brief introduction of the background of soft porous materials, this chapter will present the characterization of a novel flexible MOF (DUT-49) and its analogues. This material undergoes a sudden collapse of its pore network into a closed form state upon adsorption, resulting in the expulsion of gas from its pores. This phenomena was coined “negative gas adsorption” (NGA). The text will focus on characterisation through calorimetric methods performed by Paul Iacomi, together with references of results obtained

by collaborating groups included in order obtain a complete story of the underlying mechanism behind NGA.

Contribution

The synthesis of all MOFs was performed by Simon Krause (TU Dresden), together with their initial characterization through nitrogen adsorption at 77 K. Ambient and low temperature calorimetry was carried out by Paul Iacomì. Computer simulations of adsorption isotherms are the result of work from Jack Evans and Prof. F.X Coudert. Mechanical compression experiments were performed in the group of Prof. Guillaume Maurin in Montpellier. Prof. Philip Llewellyn and Prof. Stefan Kaskel were instrumental in the analysis of the results obtained.

5.2. Compliance in porous crystals

5.2.1. Examining the assumption of an inert adsorbent

Adsorption induced changes in porous media have been known to occur for over 90 years⁽⁸⁾, with both clays, coals and polymers undergoing swelling during gas or vapour uptake.⁽⁹⁾ However, the effect upon the macroscopic properties of the material is often negligibly small and of little consequence to industrial adsorption processes. Studies of this aspect of porous adsorbents have therefore been scarce in the large part of the 20th century, likewise influenced by lack of sufficiently accurate methods for characterising and modelling such occurrences.

In recent years, the advent of reference materials, highly sensitive methods such as synchrotron-grade light sources and *in silico* computational techniques such as DFT has put at our disposal the tools required to study these transformations. Together with the discovery of their role in natural and industrial processes e.g. the swelling of shale during natural gas extraction, maturation of concrete and the perspectives afforded by novel porous materials, these factors have generated much scientific interest in material compliance. For example, the attractive option of combined carbon capture and methane recovery implemented through pumping of carbon dioxide into reservoirs is prohibited by swelling-induced loss of porosity and well blocking.⁽⁹⁾

In-depth studies⁽¹⁰⁾ have revealed that most porous materials possess some small degree of compliance, with *in-situ* dilatometry going so far as to obtain pore size distributions from accurate volume changes.⁽¹¹⁾ Most flexible processes can be likened to continuous order processes. It is, however, the discovery of large scale flexibility in MOFs such as MIL-53 and linker-controlled gate opening like in ZIF-8, where the transformation between the different framework states occurs suddenly at precise points in the loading curve, which has shown that compliance may also take the form of a first-order transition. Such types of transformations are desirable⁽¹²⁾ due to their highly specific response. The

possible dependence of flexibility on other stimuli, such as light, mechanical pressure, temperature, magnetic fields may allow for precise tuning of structural changes. As such, it is reasonable to state that the mobility of the solid phase can no longer be ignored.

5.2.2. Flexibility in metal organic frameworks

Since the highlight of compliance in porous coordination polymers in the report of Kitagawa et al.⁽¹²⁾, much progress has been made in the synthesis and understanding of this phenomenon. An exhaustive review of MOF flexibility is outside the scope of this thesis, with the field progressing rapidly enough to generate a wealth of critical literature.^(13–19) Some of the known types of structural flexibility encountered in MOFs will be briefly discussed, with a summary available in Figure 5.1.

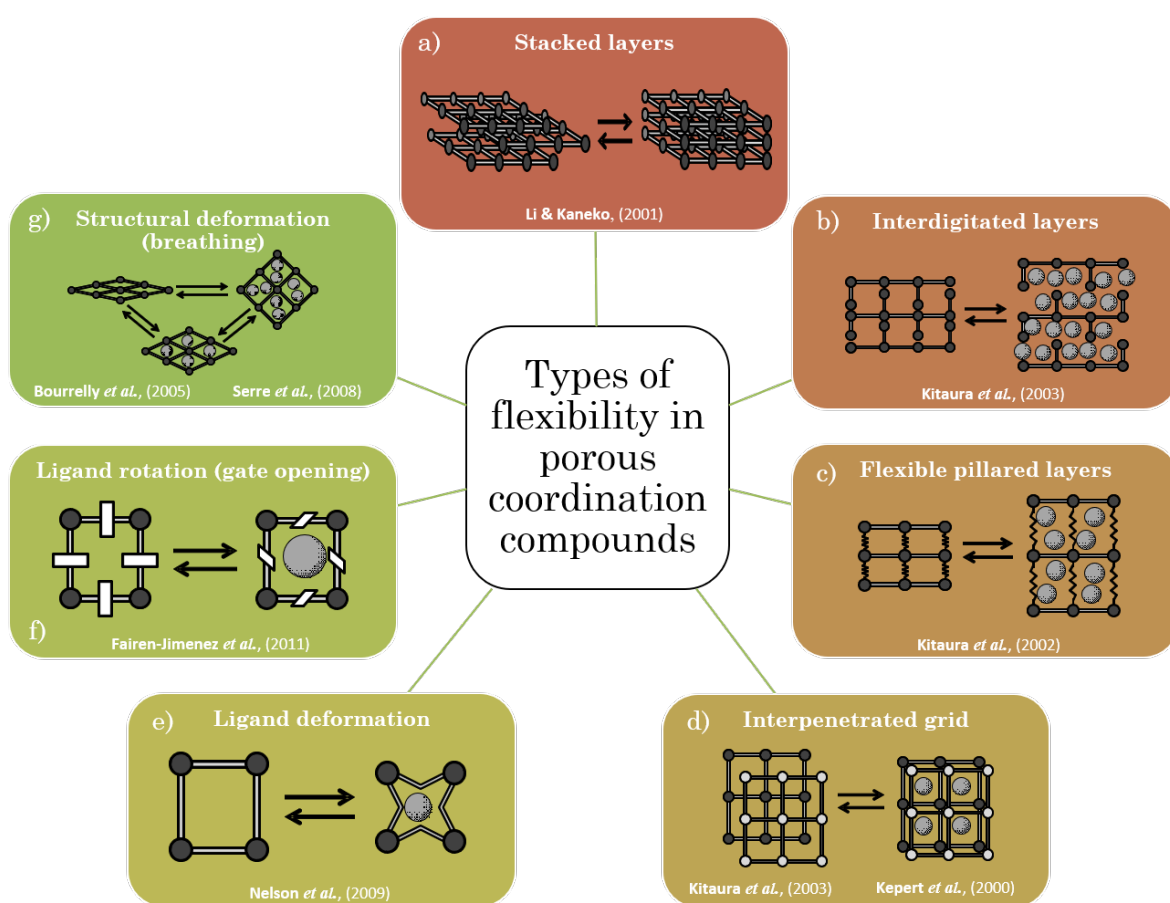


Figure 5.1.: A (non-exhaustive) visual summary of the types of flexibility documented in MOFs, as detailed in (a) Li and Kaneko⁽²⁰⁾ (b) Kitaura et al.⁽²¹⁾ (c) Kitaura et al.⁽²²⁾ (d) Kitaura et al.⁽²¹⁾, Kepert et al.⁽²³⁾ (e) Nelson et al.⁽²⁴⁾ (f) Fairen-Jimenez et al.⁽²⁵⁾ (g) Bourrelly et al.⁽²⁶⁾, Serre et al.⁽²⁷⁾

Since MOFs, like clays and graphite, can form discrete two-dimensional sheets, bound together by weak Van-der-Waals, $\pi-\pi$ interactions or hydrogen bonds, adsorbed molecules

may force these layers apart by intercalation. The concept is taken further in the pillared layer approach, where the sheets are connected by tertiary linkers instead of weak attractions. With the judicious choice of linker they can act as springs, allowing pore expansion while maintaining structural integrity.

As briefly mentioned in chapter 3, a large void space in the unit cells allows secondary networks to grow throughout the MOF, effectively creating an intercalated structure.^(21,23) These secondary grids are independent of the primary framework and are displaced upon guest adsorption.⁽²⁸⁾ This internal translation may also be associated with a tilting of the linker⁽²⁹⁾, combining intercalation with structural-deformation type flexibility.

The origin of flexibility may be purely due to the linker itself. Organic bonds are inherently labile, as seen in polymer chains, unsaturated connections in the linker may bend if the strain on the organic strut overcomes its tensile strength. Increasing the linker length often induces this type of flexibility, for example in the IRMOF isorecticular series of materials.⁽²⁴⁾ Even an unsaturated bond may be induced by a photon with a suitable energy to undergo an analogue of a *cis-trans* transition. The deformation may also lead to expansion and therefore of framework swelling, as encountered in MIL-88 and its derivatives.⁽³⁰⁾

MOFs can also have structural flexibility which does not require any volume changes in the unit cell. The rotation of linkers can act as gating for different guests, allowing entry of probes larger than the window size would suggest or preferential adsorption of a gas which has the right property to act as a “key” from a mixture.⁽³¹⁾ The former effect is common in zeolitic imidazole frameworks (ZIFs).⁽²⁵⁾

The discovery of the so-called “breathing” type of structural deformation^(26,27,32) in the MIL-53 family of materials has revealed step-like transformations in its unit cell size and metastable intermediaries with an open pore (**op**), closed pore (**cp**) and narrow/intermediate states (**np/ip**). No other family of flexible MOFs has, to date, generated more scientific interest. This is likely due to the relative stability of the material, combined with its ability to undergo massive and reversible structural deflections, while retaining its crystallinity. The relatively simple structure and large capability for functionalisation, either through ligand modification or exchange of the metal node (with variants of MIL-53 synthesised for Cr, Fe, Al, Sc, Ga or In), allowed for its use as an archetypal material for the study of flexible behaviour. More recently, similar materials, like DUT-8(M) (M=Ni, Co, Cu, Zn) which allow the the impact of the metal⁽³³⁾ on compliance to be evidenced have emerged.

5.2.3. Describing and inducing MOF compliance

The mechanistic phenomena during adsorption can be seen as an overlap⁽³⁴⁾ of several competing effects: a sub-monolayer contraction⁽³⁵⁾ resulting from micropore bridging or surface stresses, followed by a monotonic expansion with the gradual decrease of

5. Exploring novel behaviours

the solid-fluid interface energy also known as the Bangham effect.⁽³⁶⁾ Such behaviour is highly dependent of pore size, geometry and anisotropy, with condensation in macropores a further complex source of strain.^(37–39) The degree of adsorption induced changes in a framework is generally a function of its porosity, with very high surface area materials such as aerogels capable of undergoing up to 30% deformation.⁽⁴⁰⁾ In MOFs, the adsorption stresses are no different than in other materials. However, the ability of the porous network to undergo displacements is much higher, due to its low rigidity, in between that of “hard” adsorbents such as zeolites/silica and purely organic polymers (although porous covalent frameworks can also achieve self-support and porosity).

Finding a suitable model that would predict both the adsorption induced stress and the resulting structural changes from strain has so far remained a challenge. A thermodynamic-based method which has been successfully applied to breathing MOFs is that of Neimark et al.⁽⁴¹⁾ This model assumes that the deformation strain is fully determined due to surface stress, calculated from the grand thermodynamical of a rigid analogue of the pore. It has been used to explain the existence domains of MIL-53(Al)⁽⁴²⁾, in conjunction with an osmotic thermodynamic description of the framework itself.⁽⁴³⁾ For mesoporous materials, the stress-strain model has been extended by Gor and Neimark⁽³⁴⁾ through the Derjaguin–Broekhoff–de Boer (DBdB) theory⁽⁴⁴⁾ and applied to predict the resulting strain in mesoporous silica. Nevertheless a complete theory of adsorption-deformation which can fully predict the changes in the measured enthalpy of adsorption and the mechanistic behaviour of MOFs has remained elusive.

The most promising characteristics of flexible MOFs are the ability to control the compliance through external means which are detached from guest loading, which would dramatically expand their potential applications. Pure mechanical pressure on a flexible material is often enough to induce transitions. First observed on ZIFs, through pressure induced phase change^(45,46) and latter applied to breathing MOFs using mercury porosimetry^(47,48), it shows a direct relationship between the bulk modulus of a MOF and its flexible behaviour. Entropic control through temperature-induced switching has been shown to be possible in MIL-53 by Liu et al.⁽²⁾, explained as a change in the range of metastability of its pore forms.⁽⁴²⁾ More precise external control may be possible if molecules which have the ability to switch their state when exposed to suitable wavelengths are used as linkers. In this case light irradiation may be used to force the transition.⁽⁴⁹⁾ Magnetic field dependent switching can also be theorised, although has not been so far encountered. One of the least understood factors that changes the flexible behaviour of porous crystals is the effect of particle size. It is clear that the thermodynamical potential of the crystal surface has a profound influence on its compliance, as shown on the large shift of the gate-opening pressure of ZIF-8.⁽³⁾ However, a rigorous model of the contribution of the surface on breathing has yet to be developed in our knowledge. Finally, the presence of structural defects likely impacts the framework flexibility, as highlighted by Bennett et al.⁽⁷⁾ in a recent article, although currently few studies have focused on this subject.

5.2.4. Consequences and applications of flexible MOFs

The study of flexible MOFs is motivated from both a desire for fundamental understanding of compliance and from the potential applications of such systems. The use of soft porous crystals in sensing and gas storage and separation is evident, although applications in catalysis, electrochemistry and drug delivery have also been alluded to by recent studies.

The usefulness of adsorption induced flexibility for sensors or actuators has been recognised, initially by nature itself, with humidity induced swelling acting to open pine cones.⁽⁵⁰⁾ More recently, similar sensing devices based on adsorption strain in mesoporous silica have been developed such as a flexing silica-polymer membrane⁽⁵¹⁾ or deformation of a nano sized cantilever⁽⁵²⁾ which show promise for use in micromechanical systems.

From a gas storage and separation point of view, changes in the adsorbent structure may yield crucial process improvements. Pressure swing adsorption (PSA) is heavily dependent on the working capacity of the adsorbent used, or the difference between loading at the operation pressure and at the regeneration pressure. In this case, an S-shaped isotherm, with the vertical part of the slope in the aforementioned pressure range would lead to high process efficiency gains by eliminating material “dead volume adsorbed”.⁽¹³⁾ In a temperature swing process (TSA), where the regeneration is performed through heating of the adsorbent bed, the key parameter is the integral enthalpy of adsorption, a measure of the energy requirements for the process. As a part of the chemical potential of the adsorbed phase is used by the mechanical contraction of the material, flexible adsorbents have the potential of intrinsic thermal management, reducing the energy cost.⁽⁵³⁾ Both effects are equally applicable to the storage of pure gasses, increasing the storage capacity and minimizing the energetic requirement of recovery. Entrapment of guest molecules inside a gated pore might lend itself to temperature controlled storage and release of gasses⁽⁵⁴⁾, or “sealing” of a target gas inside the structure once adsorption has taken place. It is also possible that by using external mechanical pressure to control flexibility, the adsorption behaviour of porous materials may be tuned, as suggested by the work of Chanut⁽⁶⁾ on MIL-53.

Catalytic applications of flexible MOFs could be envisaged where the switching behaviour can bring into contact active sites or hold reactants in place until complete reaction has taken place. A recent study by Souto et al.⁽⁵⁵⁾, has shown that the redox potential of the sulphur bond in a tetrathiafulvalene breathing MOF is dependent on its dihedral angle in different pore states. This raises the possibility of tunability of the oxidation potential of flexible framework. Finally flexible MOFs constructed of biocompatible materials could be used as drug delivery methods^(56,57) if release of the encapsulated molecule is triggered through a structural transition.

5.2.5. Unique flexible behaviour of DUT-49

It is clear that one of the most desirable kinds of flexibility is one that can be likened to a Heaviside step function, with switching between two states or phases. However, not many MOFs synthesised to date follow this type of behaviour. It is why the surprising compliance of DUT-49, a highly porous MOF constructed with a super-molecular approach, has generated interest in the MOF community.

In the initial paper of Stoeck et al.⁽⁵⁸⁾, the synthesis of DUT-49 through a super-molecular approach is described, with the goal of generating a highly porous material. The MOF is built through the secondary building unit or SBU approach, where the crystallographic vertices of the structure are metal organic polyhedra (MOP), in this case 12-connected cuboctahedra based on copper paddlewheels, which are then connected by a tetratopic carboxylate linker. The resulting MOF forms a face centered cubic (**fcu**) net if the MOP are considered as nodes and a trimodal pore size distribution: the 12 Å MOP, a 18 Å tetrahedron and a very large 26 Å octahedron. The material has a high nitrogen accessible surface area (of more than 5000 m²/g) and accessible volume (84.7%).

In the original study, the MOF did not show any flexible behaviour. However, it was later found by Krause et al.⁽⁵⁹⁾ that when adsorbing CH₄ at 111 K, a sharp step occurs in the isotherm, corresponding to an **op**/**cp** transition. More interestingly, the step is accompanied by an expulsion of the adsorbed gas from the interior of the pores, increasing the pressure in the experiment cell. This type of pressure-amplifying transition has been coined negative gas adsorption (NGA) and was found to occur with other adsorbates at different temperatures such as C₄H₁₀ at 303 K or Xe at 195 K, which allowed study of the transition at ambient temperature and through ¹²⁹Xe NMR spectroscopy.⁽⁶⁰⁾

The origin of this phenomenon has been elucidated by Evans et al.⁽⁶¹⁾ where it has been shown to emerge due to a buckling of the central strut of the tetratopic linker under compressive stress induced by adsorption, similar to the failure of a metal column under critical load. The **op** and **cp** phase stability depends on the adsorbate loading of the material, with the **op** form being energetically favoured at zero and high loadings. At intermediate pore filling, the **cp** state is stabilized by the fluid molecules and becomes energetically favoured. At this point, the **op** phase is metastable and can contract if the energy barrier between the two states is overcome.

However, questions still remain about the driving forces behind the transition itself such as the contribution of guest-host interactions, as well as the temperature range and adsorbates where it is possible. The rational design of such materials is also put into question, where framework parameters such as linker length, functionalisation and composition may be used to tune the pressure and extent of NGA. It is here where the adsorption methodology introduced in chapter 1 combined with *in-situ* calorimetry as presented in chapter 2 can be used to shed light on the energetic background of NGA in DUT-49.

5.3. Materials and characterisation methods

5.3.1. Materials

The

Several DUT materials have been synthesised in order to study the effect of different parameters on the switching behaviour. From the point of view of the criterion of interest, the materials can be divided into the following categories:

- Series dedicated to studying the influence of isorecticular design through variation of linker length in the order of theoretical increasing porosity: DUT-48, DUT-46, DUT-49, DUT-50, DUT-151/DUT-152
- Series assessing the impact of steric hindrance of the central linker bond on NGA, in the order of connectivity: DUT-49, DUT-149, DUT-148, DUT-147
- Series investigating the effect of heterocycles on compliant behaviour, using thiofene as replacement for the benzene rings, in the order of increasing linker size: DUT-170, DUT-171, DUT-172, DUT-173
- Series aiming to possess a progressively more labile central strut, through the use of different degrees of saturation, in order of central bond hybridization: DUT-160, DUT-161, DUT-163
- Series of increasing crystallite size to study the effect of the crystal surface to volume ratio on NGA.

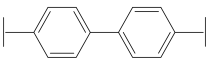
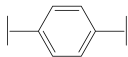
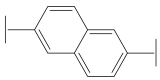
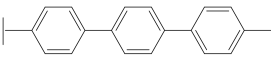
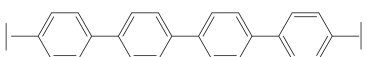
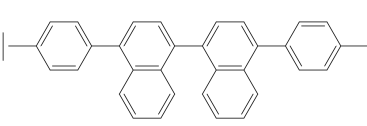
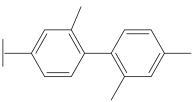
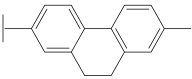
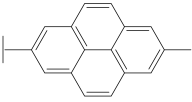
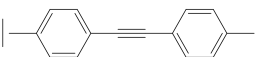
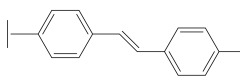
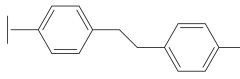
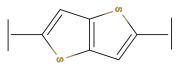
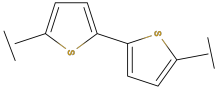
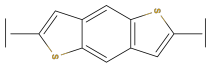
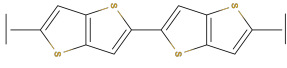
The material name, together with the central part of the linker, which was modified to change the flexible behaviour of the framework, is presented in Table 5.1.

5.4. Results and discussion

5.5. Conclusion

5. Exploring novel behaviours

Table 5.1.: Flexible materials analogous to DUT-49

Name	Linker center	Study	Observations
DUT-49		Original material	Multiple crystal sizes
DUT-48		Linker size	—
DUT-46		Linker size	—
DUT-50		Linker size	—
DUT-151		Linker size	Interpenetrated
DUT-152		Linker size	Interpenetrated
DUT-149		Functionalization	—
DUT-148		Functionalization	—
DUT-147		Functionalization	—
DUT-160		Strut saturation	—
DUT-161		Strut saturation	—
DUT-162		Strut saturation	—
DUT-170		Heterocycle	—
DUT-171		Heterocycle	—
DUT-172		Heterocycle	—
DUT-173		Heterocycle	—

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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 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 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 recoded 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

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