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Paul A. Iacomì

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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

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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 X-rays and computer-aided 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 perspectives afforded by novel porous materials, these factors have generated renewed scientific interest in material compliance.

The driving process behind the phenomenon is stress-induced framework strain. 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, with 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 Kitaura et al.⁽¹³⁾, much progress has been made in the synthesis and understanding of this phenomena. 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.^(14–19) Some of the known types of structural flexibility encountered in MOFs will be briefly discussed, with a summary evident in Figure 5.1.

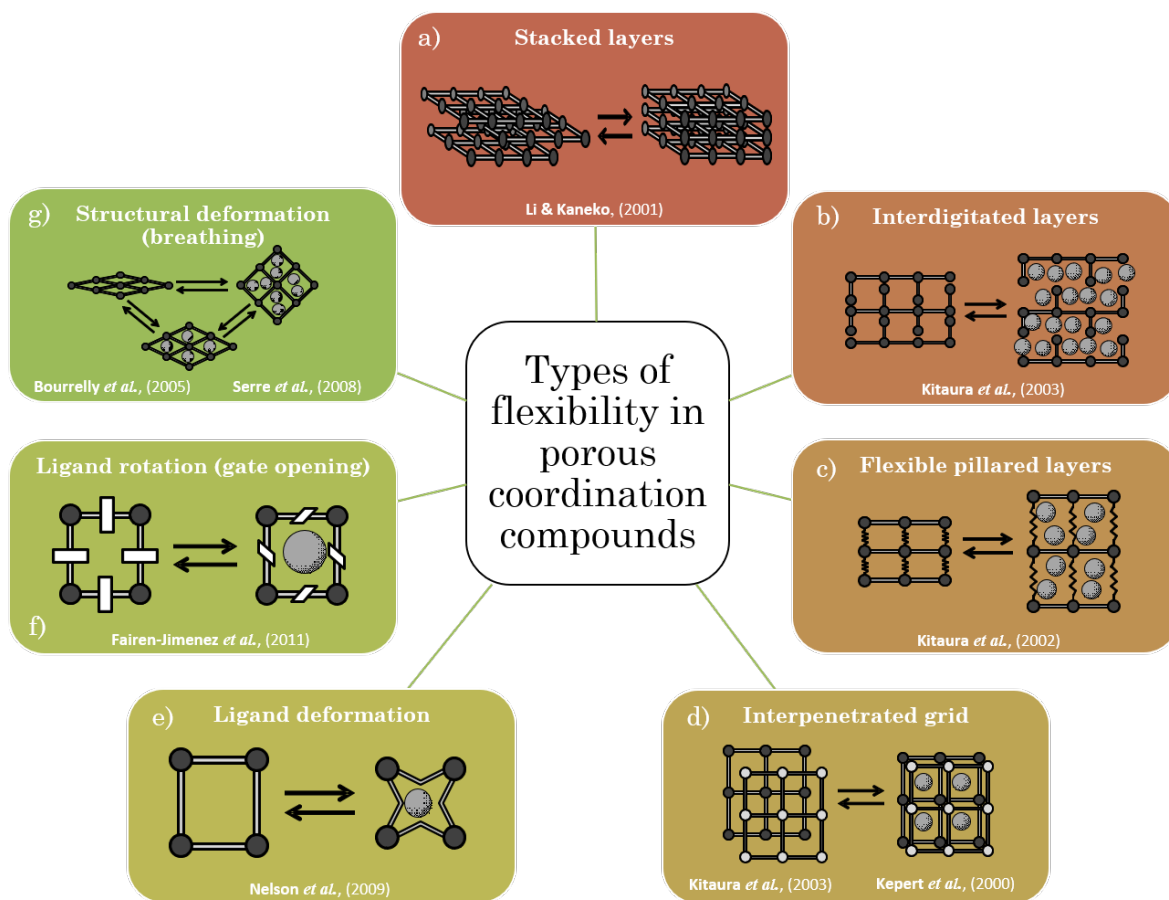


Figure 5.1.: A visual summary of the types of flexibility which are documented in MOFs, as detailed in (a) Li and Kaneko⁽²⁰⁾ (b) Kitaura et al.⁽¹³⁾ (c) Kitaura et al.⁽²¹⁾ (d) Kitaura et al.⁽¹³⁾, Kepert et al.⁽²²⁾ (e) Nelson et al.⁽²³⁾ (f) Fairen-Jimenez et al.⁽²⁴⁾ (g) Bourrelly et al.⁽²⁵⁾, Serre et al.⁽²⁶⁾

Layer separation, as is the case in interdigitated

Finally, MOFs can lead to 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.⁽²⁷⁾ The former effect might lend itself to temperature controlled storage and release of gasses⁽²⁸⁾ and is common in zeolitic imidazole frameworks (ZIFs).⁽²⁴⁾

, as they have been shown to undergo massive and reversible structural deflections, while retaining their crystallinity

The discovery of the so-called “breathing” type of structural deformation in the MIL-53 family of materials has shown that

5.2.3. Describing adsorbate compliance

The induced mechanistic phenomena are a result of several competing effects, a sub-monolayer contraction⁽²⁹⁾ resulting from micropore bridging or surface stresses, followed by a monotonic expansion with the gradual decrease of the solid-fluid interface energy also known as the Bangham effect.⁽³⁰⁾ Such behaviour is highly dependent of pore size, geometry and anisotropy, with condensation in macropores a further complex source of strain.^(31–33) The degree of adsorption induced changes in a structure is generally a function of its porosity, with very high surface area materials such as aerogels capable of undergoing up to 30% deformation.⁽³⁴⁾

The type of swelling, contraction and expansion usually follows a second order transition.

Finding a suitable model that would predict such structural changes has remained a challenge. A successful model for⁽³⁵⁾⁽³⁶⁾ Nevertheless a complete theory of adsorption-deformation which can fully predict the changes in the measured enthalpy of adsorption and the mechanistic behaviour of theoretical structures has remained elusive.

However, the most promising perspective for such materials come from

5.2.4. Consequences and applications of compliance

The usefulness of such phenomena have been long recognised as potential sensors or actuators, initially by nature itself, with humidity induced swelling acting to open pine cones.⁽³⁷⁾ More recently similar sensing devices based on adsorption induced strain in mesoporous silica have been developed^(38,39) which show promise for use in micromechanical systems. From a gas storage and separation point of view, changes in the adsorbent structure may be crucial for process improvement. 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”.⁽¹⁴⁾ In a temperature swing process (TSA), where the regeneration is per-

5. *Exploring novel behaviours*

formed 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.⁽⁴⁰⁾ Both effects are equally applicable to the storage of pure gasses, increasing the storage capacity and work required to desorb the gas. Finally, swelling of clays upon gas adsorption is quickly becoming a research interest as extraction of shale deposits is becoming common. In particular, the attractive option of combined carbon capture and methane recovery implemented through pumping of carbon dioxide into reservoirs leads to swelling-induced loss of porosity and well blocking due to the increased strain by CO₂ in comparison to methane.

5.3. Materials and characterisation methods

5.3.1. Material

DUT-49 is a MOF built on the secondary building unit or SBU approach where the metal nodes are substituted by a

5.4. Results and discussion

5.5. Conclusion

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A. Common characterisation techniques

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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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