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# Abstract

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# Acknowledgements

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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 do 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 porous inorganic materials like zeolites take the form of pore window vibrations or counterion displacement.<sup>(1)</sup> 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<sup>(2)</sup>, crystal size<sup>(3,4)</sup>, external pressure<sup>(5,6)</sup>, structural defects<sup>(7)</sup> 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

## 5. *Exploring novel behaviours*

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.

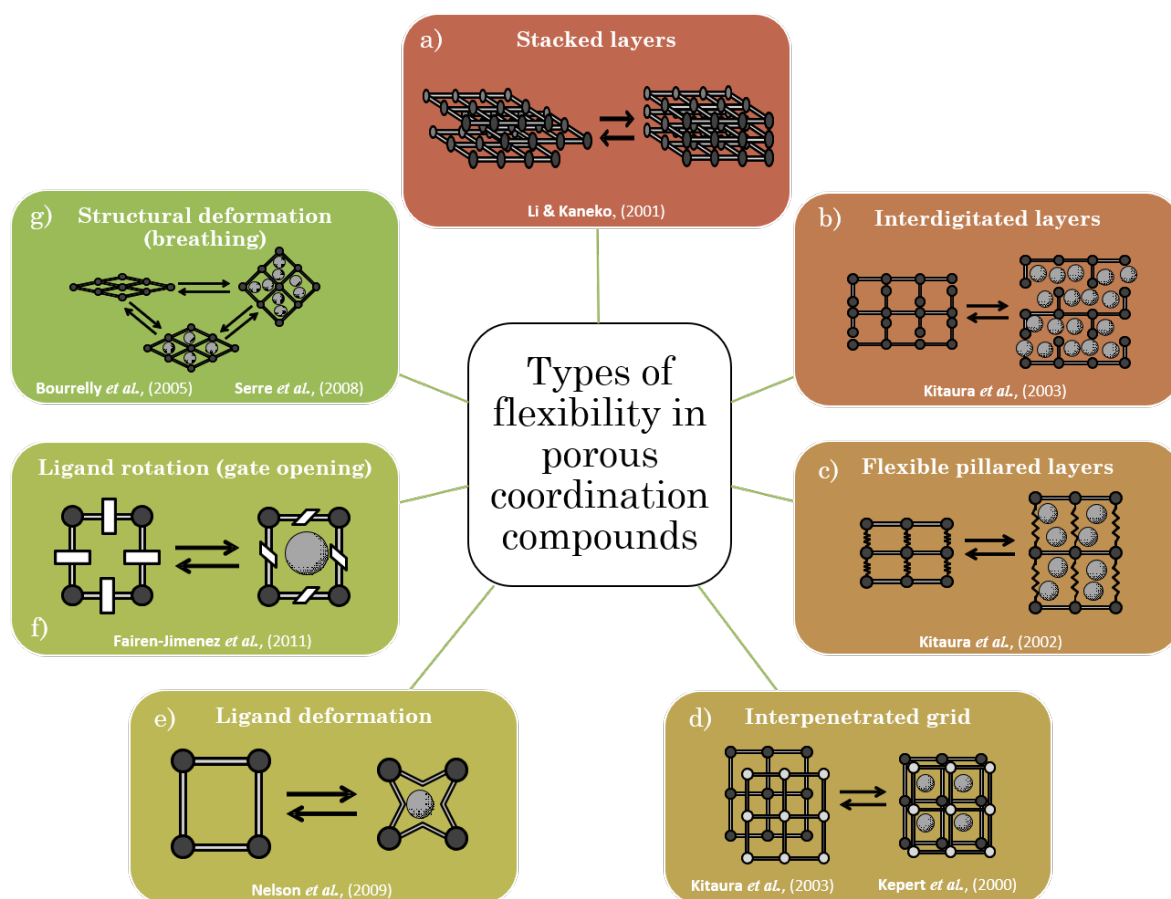
### **5.2. Context and scientific approach**

### **5.3. Materials and characterisation methods**

#### **5.3.1. title**

### **5.4. Results and discussion**

### **5.5. Conclusion**



**Figure 5.1.:** A visual summary of the types of flexibility which are documented in MOFs, as detailed in (a) Li and Kaneko<sup>(8)</sup> (b) Kitaura et al.<sup>(9)</sup> (c) Kitaura et al.<sup>(10)</sup> (d) Kitaura et al.<sup>(9)</sup>, Kepert et al.<sup>(11)</sup> (e) Nelson et al.<sup>(12)</sup> (f) Fairen-Jimenez et al.<sup>(13)</sup> (g) Bourrelly et al.<sup>(14)</sup>, Serre et al.<sup>(15)</sup>

## Bibliography

- [1] François-Xavier Coudert and Daniela Kohen. Molecular Insight into CO<sub>2</sub> “Trapdoor” Adsorption in Zeolite Na-RHO. *Chemistry of Materials*, 29(7):2724–2730, April 2017. ISSN 0897-4756, 1520-5002. doi: 10.1021/acs.chemmater.6b03837.
- [2] Yun Liu, Jae-Hyuk Her, Anne Dailly, Anibal J. Ramirez-Cuesta, Dan A. Neumann, and Craig M. Brown. Reversible Structural Transition in MIL-53 with Large Temperature Hysteresis. *Journal of the American Chemical Society*, 130(35):11813–11818, September 2008. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja803669w.
- [3] Chen Zhang, Jason A. Gee, David S. Sholl, and Ryan P. Lively. Crystal-Size-Dependent Structural Transitions in Nanoporous Crystals: Adsorption-Induced Transitions in ZIF-8. *The Journal of Physical Chemistry C*, 118(35):20727–20733, September 2014. ISSN 1932-7447, 1932-7455. doi: 10.1021/jp5081466.
- [4] Simon Krause, Volodymyr Bon, Irena Senkovska, Daniel M. Többs, Dirk Wallacher, Renjith S. Pillai, Guillaume Maurin, and Stefan Kaskel. The effect of crystallite size on pressure amplification in switchable porous solids. *Nature Communications*, 9(1), December 2018. ISSN 2041-1723. doi: 10.1038/s41467-018-03979-2.

## BIBLIOGRAPHY

- [5] Masashi Ito, Hiroto Nishihara, Kentaro Yamamoto, Hiroyuki Itoi, Hideki Tanaka, Akira Maki, Minoru T. Miyahara, Seung Jae Yang, Chong Rae Park, and Takashi Kyotani. Reversible Pore Size Control of Elastic Microporous Material by Mechanical Force. *Chemistry - A European Journal*, 19(39):13009–13016, September 2013. ISSN 09476539. doi: 10.1002/chem.201301806.
- [6] Nicolas Chanut. *Using External Factors to Improve Gas Adsorption in Nanoporous Materials: Control of Humidity and Mechanical Pressure*. PhD thesis, Aix-Marseille, December 2016.
- [7] Thomas D. Bennett, Anthony K. Cheetham, Alain H. Fuchs, and François-Xavier Coudert. Interplay between defects, disorder and flexibility in metal-organic frameworks. *Nature Chemistry*, 9(1):11–16, December 2016. ISSN 1755-4330. doi: 10.1038/nchem.2691.
- [8] Di Li and Katsumi Kaneko. Hydrogen bond-regulated microporous nature of copper complex-assembled microcrystals. *Chemical Physics Letters*, 335(1-2):50–56, February 2001. ISSN 00092614. doi: 10.1016/S0009-2614(00)01419-6.
- [9] Ryo Kitaura, Kenji Seki, George Akiyama, and Susumu Kitagawa. Porous Coordination-Polymer Crystals with Gated Channels Specific for Supercritical Gases. *Angewandte Chemie International Edition*, 42(4):428–431, January 2003. ISSN 14337851, 15213773. doi: 10.1002/anie.200390130.
- [10] Ryo Kitaura, Kentaro Fujimoto, Shin-ichiro Noro, Mitsuru Kondo, and Susumu Kitagawa. A Pillared-Layer Coordination Polymer Network Displaying Hysteretic Sorption: [Cu<sub>2</sub>(pzdc)<sub>2</sub>(dpyg)]<sub>n</sub> (pzdc= Pyrazine-2,3-dicarboxylate; dpyg=1,2-Di(4-pyridyl)glycol). *Angewandte Chemie*, 114(1):141–143, January 2002. ISSN 0044-8249, 1521-3757. doi: 10.1002/1521-3757(20020104)114:1<141::AID-ANGE141>3.0.CO;2-D.
- [11] C. J. Kepert, T. J. Prior, and M. J. Rosseinsky. A Versatile Family of Interconvertible Microporous Chiral Molecular Frameworks: The First Example of Ligand Control of Network Chirality. *Journal of the American Chemical Society*, 122(21):5158–5168, May 2000. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja993814s.
- [12] Andrew P. Nelson, Omar K. Farha, Karen L. Mulfort, and Joseph T. Hupp. Supercritical Processing as a Route to High Internal Surface Areas and Permanent Microporosity in Metal-Organic Framework Materials. *Journal of the American Chemical Society*, 131(2):458–460, January 2009. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja808853q.
- [13] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, and T. Düren. Opening the Gate: Framework Flexibility in ZIF-8 Explored by Experiments and Simulations. *Journal of the American Chemical Society*, 133(23):8900–8902, June 2011. ISSN 0002-7863, 1520-5126. doi: 10.1021/ja202154j.
- [14] Sandrine Bourrelly, Philip L. Llewellyn, Christian Serre, Franck Millange, Thierry Loiseau, and Gérard Férey. Different Adsorption Behaviors of Methane and Carbon Dioxide in the Isotypic Nanoporous Metal Terephthalates MIL-53 and MIL-47. *Journal of the American Chemical Society*, 127(39):13519–13521, October 2005. ISSN 0002-7863. doi: 10.1021/ja054668v.
- [15] C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, and G. Férey. An Explanation for the Very Large Breathing Effect of a Metal–Organic Framework during CO<sub>2</sub> Adsorption. *Advanced Materials*, 19(17):2246–2251, September 2007. ISSN 09359648, 15214095. doi: 10.1002/adma.200602645.

# 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 cm<sup>3</sup> min<sup>-1</sup>. 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 recorded using the volumetric method. A separate cell is used to condense the adsorptive throughout the measurement for accurate determination of its saturation pressure.

### **A.5. Vapour physisorption at 298 K**

Vapour adsorption isotherms throughout this work are measured using a MicrotracBEL BELSORP-max apparatus in vapour mode. Glass cells are first weighed and then filled with about 50 mg of sample. The vials are then heated under vacuum up to the activation

temperature of the material and re-weighed in order to measure the exact sample mass without adsorbed guests. The cells are then immersed in a mineral oil bath kept at 298 K. To ensure that the cold point of the system occurs in the material and to prevent condensation on cell walls, the reference volume, dead space and vapour source are temperature controlled through an insulated enclosure.

## A.6. Gravimetric isotherms

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

## A.7. High throughput isotherm measurement

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

## A.8. Powder X-ray diffraction

## A.9. Nuclear magnetic resonance

## Bibliography

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