TECHNICAL ARTICLE

An Introduction to Metal-Organic Frameworks

Examining the potential of MOFs and how surface area and porosity define performance, with expert insight from Dr. Mircea Dincă

Working with a classic technique on a new generation of materials

First synthesized around the turn of the century metal-organic frameworks (MOFs) continue to attract significant research investment as they transition to commercial use. Crystalline solids with controllable nano-scaled structure MOFs have the largest specific surface areas of any materials known [1]. This is a defining attraction, for applications ranging from gas storage and separation to catalysis and drug delivery.

The development of MOFs is directly dependent on detailed, accurate surface area and porosity data and classic gas adsorption techniques are a workhorse tool for researchers in this area. In this article we provide an introduction to MOFs and the use of gas adsorption in their characterization. Expert commentary from a leading researcher in the field, Dr. Mircea Dincă, Associate Professor at MIT adds unique insight on the potential of this exciting class of materials and the practicalities of development.

What are MOFs?

As the name suggests MOFs are organic-inorganic hybrids assembled from single metal ions or metal ion clusters which act as 'nodes', connected via organic struts or linkers. The periodic structures of MOFs self-assemble under closely controlled reaction conditions, typically in the presence of a solvent, though solvent-free processing routes have been commercialized [1]. Learning how to make structures rigid and stable was a defining step in the evolution of MOFs [2] but synthesis techniques have since become well-established. Chemists can now confidently stitch together a vast array of transition metals and organic ligands to make MOFs with relatively predictable structures, to address different applications.

MOFs offer unique structural diversity and unprecedented flexibility to produce the porosity profiles required to exert control at the molecular level. Furthermore, the tunability of MOFs extends well beyond surface area and porosity, additional functionality such as hydrophobicity or hydrophilicity is readily incorporated to enhance commercially interesting properties.

'Once MOFs could be made permanently porous people really began to recognize the potential not only to control porosity but to augment, for example, electrical, adsorptive or catalytic properties,' says Dr. Dincă. 'This tunability of MOFs is an important commercial factor because it offers considerable scope for the development of intellectual property. Investment is fueled by the recognition that there are important societal challenges that MOFs are uniquely well-placed to help with, where we are reaching the limits of performance with traditional materials'

The potential of MOFs

2016 saw the first commercial application of a MOF, in a fruit packaging system [3]. The MOF releases 1-methylcyclopropene which binds with ethylene receptors in the fruit to slow the ripening process. A MOF for storage of the toxic gases used as dopants in the semiconductor industry (e.g. arsine, phosphine, and boron trifluoride) is also now commercially available [4]. It facilitates storage under far lower pressures than are conventionally used, reducing safety concerns. These are relatively niche applications, with MOF costs, though reducing, still an issue for commodity applications.

'Reducing cost is important for the commercialization of MOFs but shifting certain misconceptions about what MOFs are and what they are not is also critical,' says Dr. Dincă. 'MOFs are not necessarily a replacement for zeolites, for example, rather they offer potential for applications where zeolites and other materials may not be suitable. And it's vital to recognize that not all MOFs are made the same.

MOFs are also not the answer for every application – no one class of materials is – but it is important that their value is not underestimated simply as a result of choosing a MOF with properties that are misaligned with the intended application.'

MOFs are interesting for the capture, separation or storage of gases and liquids since they can be uniquely tailored to retain specific molecules. The resulting potential to store large volumes of gas at low pressure, for example, or to separate gases with minimal energy input offers significant scope to reduce the energy consumption associated with gas processing. MOFs are already being demonstrated for catalysis and there are exciting applications on the horizon such as water harvesting – the extraction of water from air, driven by solar energy [1,5]

Quantifying surface area and porosity

The surface area and porosity of a MOF are performance-defining, making measurement essential; gas adsorption is the 'gold standard' technique.

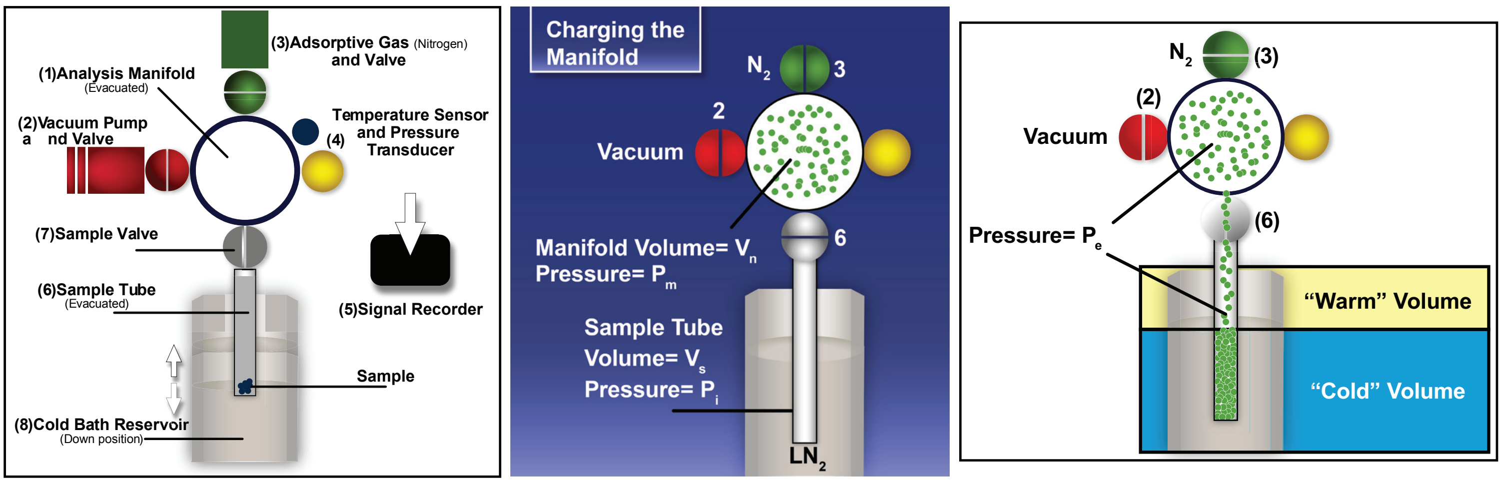

Figure 1: A simple schematic of a generic, volumetric gas adsorption analyzer showing, from left to right – degassing, charging of the manifold, and gas absorption onto the sample.

Figure 1 shows a generic volumetric gas adsorption apparatus. Measurement begins with sample preparation – degassing or outgassing – which is typically carried out at ambient or slightly elevated temperature. The manifold, of known volume, is then charged with adsorptive gas to a specified pressure; the number of moles or mass of gas present can be calculated from the gas law. Opening the manifold to the sample tube allows gas to adsorb into the sample, with the amount of gas adsorbed calculated by difference, using the gas law, once pressure has equilibrated. Repeating this process at progressively increasing pressures produces an adsorption isotherm for the material, a unique fingerprint of its textural characteristics. Figure 2 shows what is happening at the molecular level during the gas adsorption process.

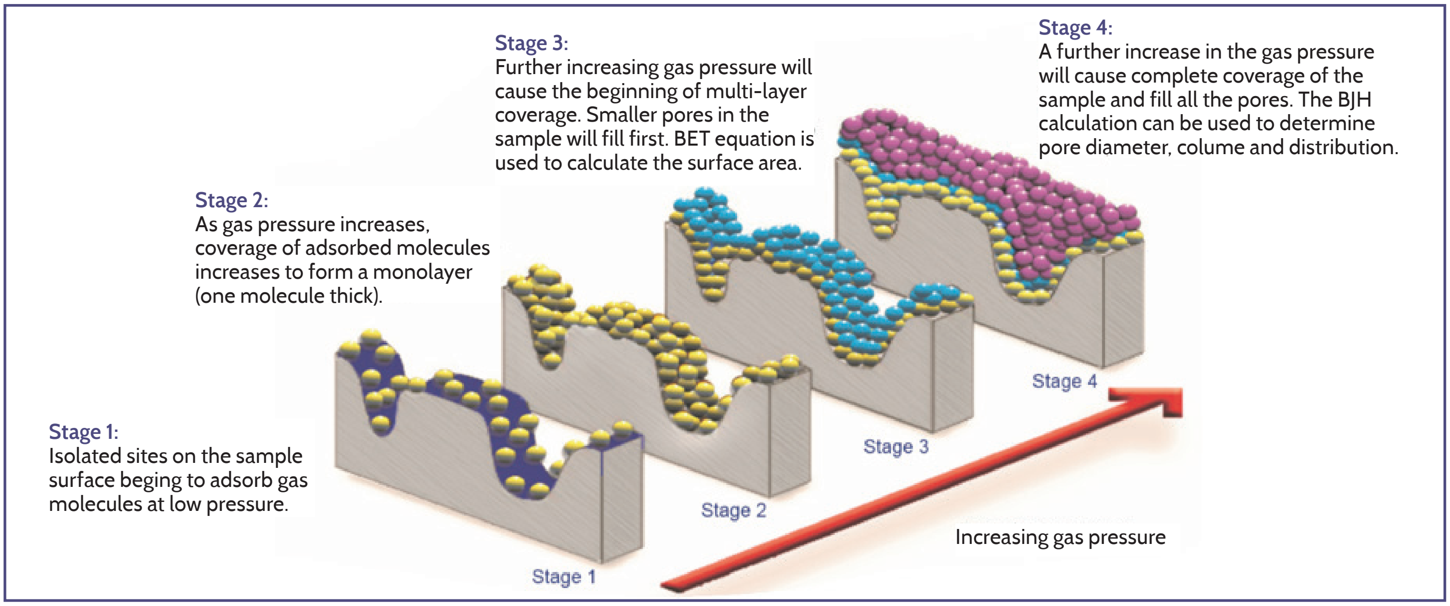

Figure 2: In a gas adsorption measurement the pores of the sample progressively fill with the adsorptive gas as pressure is increased.

Surface area and porosity can be calculated from an adsorption isotherm using appropriate mathematical theories. Brunauer, Emmett and Teller (BET) theory is the classic approach for surface area while pore size distributions are usually determined by the method of Barrett, Joyner and Halenda (BJH), using the Kelvin model of pore filling. The parameters generated include specific surface area – surface area per unit mass – total pore volume and pore volume distribution by pore size. The pore size range covered runs from the macropore down into the ultra-microporous region, from 300nm to 0.3 nm comfortably spanning the range of interest for MOFs.

'For MOFs surface area and porosity are defining characteristics so gas adsorption is essential both to characterize new materials and to check whether an existing material has been made reproducibly, essentially as a proxy for QC. I've been using gas adsorption systems from Micromeritics since graduate school and they deliver a level of dependability that is relatively rare in a research-grade tool. Our systems require minimal routine maintenance and incur very little in the way of downtime or repair costs.'

Optimizing gas adsorption for MOF applications

While physisorption is used to characterize the surface area and porosity of MOFs, advanced systems also enable the application of chemisorption. Chemisorption involves the use of an active adsorptive gas in place of one that is inert to quantify the level of active sites on the sample surface. The ability to switch between these two modes of measurement makes it possible to carry out more advanced MOF characterization, for example, to investigate adsorption enthalpy as a function of linker or ligand structure.

More generally, state-of-the-art systems enable the simultaneous utilization of more than one gas in a single analysis, to gain more detailed insight into adsorption site binding mechanisms. They also offer the precise gas management and temperature control needed for high resolution micropore and ultra-micropore measurements and accurate data collection at low pressures, to investigate behavior at low loadings. Coupled with software that is increasingly well-tailored to MOFs, these capabilities can substantially boost the contribution of gas adsorption to MOF optimization.

'An important strand of our research is MOFs that can be used in applications involving ammonia and water, including adsorbents for heat pumps and for gas masks, and the development of technology that can generate fresh water from air. Micromeritics has helped us to customize our gas adsorption systems so that we can use water and ammonia as the adsorptive gases to gain highly relevant information. The company's responsiveness and knowledge are really valuable when it comes to issues such as this and help us to get the best out of the excellent hardware.'

Looking ahead

MOFs have exciting potential to answer directly to societal challenges associated with energy consumption, pollution, transport and even water availability and healthcare. Accurate, detailed and precise characterization of the surface area and porosity of these fascinating materials is essential for progress. Analytical instrumentation that delivers such information reliably and efficiently therefore has a vital role to play in supporting the commercialization of MOFs.

References

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