

# Physical Adsorption Characterization of MOFs

## 1. Introduction

Despite the fact that hybrid porous materials such as MOFs, ZIFs, etc. are crystalline, various factors can contribute to deviations from perfect crystalline structure. For example, reduced pore volumes can be due to nonvolatile reactants in the pores, partial collapse, and/or other activation related problems. Hence, an advanced physical adsorption characterization is crucial for accurately assessing the effective pore sizes, pore size distribution, pore volumes and apparent surface areas of MOFs, ZIFs, COFs, and related materials.

## 2. Sample Pre-Treatment - Outgassing the Adsorbent

For physical adsorption experiments it is mandatory to remove all physically adsorbed material from the adsorbent surface while avoiding irreversible changes to the surface prior to the adsorption analysis. This may be achieved by outgassing, i.e. exposure of the surface to a high vacuum (for microporous materials, pressures  $< 1$  Pa are desirable) usually at elevated temperature. To obtain reproducible isotherms, it is necessary to control the outgassing conditions (the heating program, the change in pressure over the adsorbent and the residual pressure) to within limits which depend on the nature of the adsorbent [1 -3]. With sensitive samples a pressure controlled procedure together with a dedicated heating program is recommended. Outgassing of hydrophilic microporous samples is particularly challenging because it is difficult to remove the pre-adsorbed water from narrow micropores. High temperatures (e.g. up to 400 °C) and long outgassing periods (often no less than 8 hours) are required. Due to their heterogeneous nature in composition and structure, pre-treatment conditions for MOFs and related materials often need to be customized on a case by case basis in order to avoid potential structural damage of the sample.

## 3. Choice of Adsorptive

The proper choice of adsorptive is crucial for an accurate and comprehensive pore structural analysis. For many years, nitrogen adsorption at 77 K has been generally accepted as the standard method for both micropore and mesopore size analysis, but for several reasons it is now evident that nitrogen is not an entirely satisfactory adsorptive for assessing the micropore size distribution because the interpretation of the isotherm data is not always straightforward. Argon adsorption at 87 K is considered to be more reliable and is now recommended - particularly for micropore size analysis [3,4]. It is well known that the quadrupole of the nitrogen molecule is largely responsible for specific interactions with a variety of surface functional groups and exposed ions. This not only affects the orientation of the adsorbed nitrogen molecule on the adsorbent surface, but it also strongly affects the micropore filling pressure. For example, for many zeolites and MOFs, the initial stage of physisorption is shifted to extremely low relative pressures (to  $P/P_0 \sim 10^{-7}$ ) where the rate of diffusion is exceptionally slow, making it difficult to measure equilibrated adsorption isotherms. These specific interactions with surface functional

groups also cause the problem that the pore filling pressure is not correlated with the pore size in a straightforward way.

In contrast, argon at 87 K (liquid argon temperature) does not exhibit specific interactions with surface functional groups. As a consequence of this and the slightly higher temperature, argon at 87 K fills micropores of dimensions 0.5-1 nm at significantly higher relative pressures compared to nitrogen at 77 K, leading to accelerated diffusion and faster equilibration time. The pore filling pressure of argon (87 K) is often shifted 1-1.5 decades in relative pressure as compared to nitrogen.

Despite the advantages which argon adsorption at 87 K offers, there still exists the well-known problem of restricted diffusion, which prevents both nitrogen and argon molecules from entering the narrowest micropores, i.e. pores of width  $< 0.45$  nm. In order to overcome this problem, the use of CO<sub>2</sub> (kinetic diameter of 0.33 nm) at temperatures close to room temperature (e.g., 273K) has been suggested as an adsorptive. At 273 K, the saturation vapor pressure of CO<sub>2</sub> is very high ( $\sim 35$  bar) and, hence, the pressures required for micropore size analysis are in the moderate range ( $\sim 1$  mbar – 1 bar). Because of these relatively high temperatures and pressures, diffusion problems are considerably reduced and pores as small as 0.4 nm can be accessed. On the other hand for typical low pressure adsorption equipment with a maximum achievable pressure of 1 bar, the maximum relative pressure for measurements with CO<sub>2</sub> at 273 K is  $P/P_0 \sim 3 \times 10^{-2}$  (corresponds to ambient pressure) and only pores  $< ca. 1$  nm can be explored. While CO<sub>2</sub> adsorption at 273 K has become an accepted method for the pore size analysis of nanoporous carbons, it cannot be recommended for the pore size determination of MOFs and other materials with polar surface groups since the quadrupole moment of CO<sub>2</sub> is even larger than that of N<sub>2</sub>, making it difficult to correlate the CO<sub>2</sub> pore filling pressure with the pore size [1-3]. However, CO<sub>2</sub> adsorption at 273 K can still be useful for assessing the pore volume and porosity of MOFs exhibiting ultramicropores.

#### **4. Determination of BET Area**

The BET equation is applicable for surface area analysis of nonporous materials as well as for nanoporous materials consisting of wider meso- and macropores, i.e. under certain carefully controlled conditions, the BET area of a non-porous, macroporous, or mesoporous solid (i.e. leading to a well-defined Type II or a Type IVa isotherm) can be regarded as the ‘probe accessible area (the effective area that is available for the adsorption of the specified adsorptive) [1-3]. This is, in a strict sense, not applicable in the presence of micropores or narrow mesopores ( $< ca. 5$  nm) because it is difficult to separate the processes of mono- and multilayer adsorption from pore filling [1-3]. In the presence of micropores, the linear range of the BET plot may be very difficult to locate. This problem can be overcome by applying a useful procedure [5]. The application of this procedure avoids any subjectivity in determining the linear BET range and improves the reproducibility of the method; however, it does not confirm the validity of the BET monolayer capacity [3, 5, 6]. Hence, the BET area derived from a microporous material must not be treated as a realistic probe accessible surface area, but reflects an apparent surface area, which can be regarded as a useful adsorbent ‘fingerprint’ [3].

## 5. Pore Size/Volume Analysis

### 5.1. Determination of Pore Volume

If the physisorption isotherm exhibits a virtually horizontal plateau, the limiting uptake may be taken as a simple measure of the total pore volume. For example, in the case of a Type I isotherm, the total pore volume would correspond to the micropore volume. To convert the adsorbed amount at the plateau into the pore volume it is usually assumed that the pores are filled with the condensed adsorptive in the normal bulk liquid state (Gurvich rule [1,2]). However, in the absence of a plateau, the Gurvich rule cannot be applied to determine the total pore volume or the micropore volume.

A number of different methods have been proposed for the pore volume analysis of physisorption isotherms obtained on microporous solids. They can be divided into classical, macroscopic procedures and those based on statistical mechanics (e.g. molecular simulation or density functional theory). For a routine assessment of micropore volume, macroscopic procedures such as the comparison plot methods (e.g. t- and alpha-s methods or methods based on Dubinin's approach) are applied. However, it must be kept in mind that these classical methods are not based on the assumption of a realistic density profile of the adsorbed phase. This problem has been addressed in methods based on molecular simulation (MC) and density functional theory (DFT).

### 5.2 Pore Size Analysis

Classical, macroscopic thermodynamic methods for calculating pore size distribution such as Dubinin-Raduskevich and related methods, Horvath-Kawazoe (HK), Saito-Foley (SF) and Kelvin equation based methods (e.g. BJH), assume that pores are filled with a liquid adsorptive with bulk-like properties. However, this is not the case for a fluid confined to narrow meso- and micropores. This and other problems associated with the classical methods have been addressed in modern approaches based on density functional theory (DFT) and molecular simulation. These modern theoretical and computational methods, which are based on the statistical mechanics of nanophases, describe (contrary to the classical, macroscopic, thermodynamic methods) the configuration of adsorbed fluid (i.e. the adsorbate) on a molecular level. It has been shown that the application of these advanced methods allows one to obtain (in contrast to the classical methods) reliable pore size distributions over the complete range of micro- and mesopores. Methods for pore size analysis based on DFT are now widely used and are commercially available for many important adsorptive/adsorbent systems. MOFs have very specific surface properties which have hampered the development of DFT based methods dedicated to certain MOF systems, which could be applied on a routine basis for the pore size analysis of a certain MOF types. Despite this, it has been shown that if certain conditions are fulfilled, the application of available DFT methods may produce a useful and reliable pore size analysis of a MOF [7,8].

## 6. Comments on Flexible MOFs

Major problems are associated with the characterization of soft materials where the adsorbent undergoes a phase or structural change during the adsorption process. In fact, the methods discussed above for surface area and pore size analysis are based on the assumption that the

adsorbent properties do not change in the process of adsorption and the shape of the adsorption isotherm is entirely associated with the adsorption and phase behavior of the adsorbate. The adsorption behavior of flexible MOFs requires the development of new theoretical approaches [9]. By applying the standard methods of pore size analysis, the steps in the isotherms caused by structural transformation of the adsorbent would be associated with pore filling giving rise to artificial peaks in the pore size distributions.

## 7. References

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