Physical Adsorption Characterization of Mesoporous Materials: Comments on Hysteresis Scanning, Part 1

Abstract

In recent years, much progress has been achieved in the understanding of the adsorption and phase behavior of fluids in highly ordered mesoporous materials with simple pore geometries (e.g., M41S materials). This has led to major advances in the structural characterization by physical gas adsorption, mainly because of the development and availability of advanced theoretical approaches based on statistical mechanics (e.g., non local density functional theory (NLDFT) and molecular simulation) (for recent reviews see [1-4] and references therein). However, there are still open questions concerning the structural characterization of more complex micro-mesoporous materials which exhibit interesting pore condensation and hysteresis behavior.

Pore condensation hysteresis introduces a considerable complication for pore size analysis, but, if interpreted correctly provides important information about the pore structure/network. Within this context, so-called hysteresis scanning experiments [5, 8-12] allow one to identify the underlying mechanisms of hysteresis which are not only crucial for obtaining an accurate pore size distribution, but can also provide complimentary information about the texture of complex porous materials. In this whitepaper we address the background/concept of hysteresis scanning.

Pore Condensation and Hysteresis

An empirical classification of hysteresis loops, given by IUPAC (1985), correlates the hysteresis loops (types H1 – H4) with the texture of the adsorbent. Figure 1 shows schematics of hysteresis types H1 and H2. Type H1 hysteresis had been associated with porous materials exhibiting a narrow distribution of relatively uniform (cylindrical pores), whereas materials that give rise to H2 hysteresis contain more complex pore networks consisting of pores with ill-defined shape and wide pore size distribution.

It is now understood that the shape of the hysteresis loop reflects the underlying pore condensation-evaporation mechanism which can indeed be similar even in systems which consist of different pore topologies. For instance, perfect type H1 hysteresis has been observed in MCM-41 (e.g. [1] and references therein) where the mesopores are completely independent, but also in MCM-48 and KIT-6 silica which consist of three-dimensional networks of uniform pores [6].

Hysteresis observed in these systems can be considered to be an intrinsic property of a vapor-liquid phase transition in a finite volume system. In such systems the vapor-liquid transition is delayed due to the existence of metastable adsorption films and hindered nucleation of liquid bridges which occur only on the adsorption branch. Pore evaporation (desorption branch) is not affected by such metastabilities. Indeed, in an open pore filled by liquid-like condensate, the liquid-vapor interface is already present, and evaporation occurs without nucleation.

Meanwhile, modern, microscopic approaches such as non-local density functional theory (NLDFT) are capable of quantitatively predicting (i) the positions of equilibrium vapor-liquid transition which is associated with the desorption branch of the isotherm in a cylindrical pore of given size and geometry; (ii) the pressure where capillary condensation occurs by taking into account delayed condensation due to the metastability associated with the nucleation of...
In contrast to pore blocking, in this case the position of the desorption branch is empties, but the neck remains filled [1, 3, 7]. In occurs through cavitation, i.e. the large pore [6]), the evaporation from the main pore/cavity associated with the neck size. On the other hand, the position of the desorption branch is given pressure leading to a steep vapor pressure of desorption from the pore body depends on the neck size and network connectivity, as well as, on the state of the neighboring pores. The onset of evaporation from the pore network is associated with the percolation threshold and the formation of a continuous cluster of pores open to the external surface. The percolation mechanism is observed in the pore networks with sufficiently large neck. As a consequence, all pore liquid evaporates at a given pressure leading to a steep desorption/evaporation step and therefore to classical type H2 hysteresis as shown in Figure 1.

In the case of classical pore blocking/percolation, the position of the desorption branch is associated with the neck size. On the other hand, if the neck size (connecting) pore is below a certain critical width (ca. 5 - 6nm for N2/77K, [6]), the evaporation from the main pore/cavity occurs through cavitation, i.e. the large pore empties, but the neck remains filled [1, 3, 7]. In this case the position of the desorption branch is, in contrast to pore blocking, not associated with the neck size. However, in both cases (pore blocking and cavitation) type H2 hysteresis may be observed, and the pore (main cavity) distribution has to be determined (as indicated above) from the adsorption branch by applying a proper NLDFT adsorption branch kernel (which for a given pore geometry correctly takes into account delay in condensation due to metastable pore fluid)

**Hysteresis Scanning**

It follows from the previous sections that a proper pore size analysis is only possible if one identifies the underlying mechanism of hysteresis, and this is sometimes quite difficult for complex micro-mesoporous materials where the type of hysteresis loops cannot be identified in a straightforward way. In such cases more detailed information about the underlying mechanisms associated with the filling and emptying of the pores can be obtained if one scans the hysteresis loop [4, 8-12]: After the measurement of the initial hysteretic adsorption/desorption curve (the so-called boundary adsorption/desorption isotherms) one measures in subsequent adsorption/desorption cycles the adsorption and desorption isotherm only in the relative pressure range where hysteresis occurs. For instance, after one has obtained the initial adsorption/desorption isotherm one re-measures the adsorption branch only up to a relative pressure which is smaller than the saturation pressure. Consequently only a portion of the pore system of the porous material has been filled with pore liquid before one starts with the desorption isotherm. This procedure is called desorption scanning; on the other hand adsorption scanning is performed by increasing pressure from the desorption branch into the hysteresis loop [8 -12].

In the case that hysteresis is only due to metastable pore fluid associated with condensation/adsorption (see previous section), which would give rise to type H1 hysteresis for the initial boundary adsorption/desorption isotherms, one would expect that the primary desorption scanning curve will coincide with the desorption branch of the initial desorption isotherm (so-called boundary ads/des isotherm) in a way as shown schematically in Fig.1 for type H1 hysteresis, i.e., the scanning hysteresis loop will have a similar shape as the original hysteresis loop. In fact, the capillary evaporation pressure for a given adsorbed amount does not depend on whether or not the pore system had been completely filled during capillary (the scanning curves cross from adsorption to desorption branch for a given adsorbed amount); in other words the shape of the hysteresis loop does not depend on the degree of pore filling.
We tested these assumptions in the case of an SBA-15 silica by performing scanning hysteresis experiments with a Quantachrome Autosorb iQ analyzer (for more details see http://www.quantachrome.com/gassorption/autosorb_iq.html; the associated ASiQWin software version 1.11 contains pre-installed user files for performing scanning experiments as depicted in Figure 2a). The chosen SBA-15 sample consists of quasi-independent cylindrical mesopores, which are connected by micropore channels, but all mesopores are freely accessible.

As can be seen from Figure 2a the hysteresis loop is of type H1 and the shape of the subsequent scanning curves (desorption and subsequent adsorption scanning) do essentially resemble (with small deviations for the second desorption/adsorption scanning hysteresis loop) the initial adsorption/desorption boundary curves (i.e. they are all of type H1). This indicates that indeed the majority of SBA-15 mesopores do empty independently from each other, and pore/blocking and percolation phenomena do not play a role for capillary condensation/hysteresis in SBA-15 silica. This is in agreement with the NLDFT pore size distribution curves obtained from adsorption from adsorption (by applying the metastable adsorption branch kernel) and desorption branches (equilibrium transition kernel); the obtained pore size distribution curves agree very well indicating that hysteresis here is essentially caused by the existence of metastable pore fluid during adsorption/condensation (see earlier).

On the other hand, if the porous material consists of a disordered and inhomogeneous pore system which could result for instance in type H2 hysteresis quite different scanning behavior is expected to be observed (see Fig.1, schematics for type H2 hysteresis). As explained in section 1, type H2 hysteresis is observed if in addition to delayed condensation, pore blocking/percolation effects are present. In this case the desorption scanning curves do not follow the original/initial desorption branch of the hysteretic isotherm, because if the pore system is only partially filled with liquid, pore blocking and percolation effects are suppressed, i.e. mesopores have access to the bulk vapor phase and can empty quasi-independently from each other. In fact the capillary evaporation pressure for a given adsorbed amount does here depend on whether the pore system had been completely filled during capillary condensation or not.

Fig.2 (a) Nitrogen (77.4 K) sorption isotherms in SBA-15 silica and corresponding hysteresis scanning isotherms; (b) NLDFT pore size distribution (cylindrical pore model) from adsorption by applying the so-called metastable adsorption branch kernel and desorption (by applying an equilibrium transition kernel).
Fig. 3 (a) Nitrogen (77.4 K) sorption isotherms and corresponding desorption/adsorption scanning isotherms in porous vycor glass. (b) NLDFT pore size distribution (cylindrical pore model) from adsorption by applying the so-called metastable adsorption branch kernel and from desorption by applying an equilibrium transition kernel.

An example for such a scenario is given in Fig. 3, which shows nitrogen (77.4K) adsorption-desorption in porous vycor glass. Porous vycor glass consists of a disordered mesopore network, and gives rise to type H2 hysteresis. Subsequent primary desorption scanning as well as sub-loops (adsorption and secondary desorption scanning), were again obtained by using Quantachrome’s Autosorb iQ instrument. After measuring the initial adsorption-desorption hysteresis, adsorption was only measured in a subsequent experiment up to a relative pressure of ca. 0.8 where many, but not all, mesopores have been filled with condensate. Desorption was then started from this pressure, and the primary desorption scanning curve obtained in this way clearly shows that (contrary to the desorption/evaporation from porous vycor glass completely filled with condensate) pore blocking /evaporation now plays a less important role. This is illustrated by the fact that the shape of the primary desorption scanning loop and the shape of the sub-loops are now resembling more a type H1 loop. The scanning hysteresis results are consistent with the NLDFT pore size distribution curves shown in Figure 3b. In fact, the disagreement between the pore size distributions curves obtained from adsorption and desorption branches indicates that in case of type H2 hysteresis pores cannot empty independently from each other. The pore size distribution has to be determined from the adsorption branch (again by applying a method which takes delay in condensation due to metastable pore fluid), whereas the pore size distribution curve from desorption branch is associated with the distribution of pore entrances.

Conclusions

Summarizing, it can be said that measuring sorption scanning curves helps to identify the underlying mechanism of hysteresis, which is crucial for obtaining an accurate and comprehensive pore size analysis of mesoporous and micro-mesoporous materials. The interpretation of scanning hysteresis loops allows one, in principle, to obtain additional detailed information about the pore structure and pore network. However, more experimental work using materials with well-defined pore systems (and pore networks) is needed to arrive at a quantitative description of hysteresis scanning curves. Most of the work which utilized scanning hysteresis had been performed on disordered pore networks, but very recently has been expanded to mesoporous molecular sieves with various pore geometries and hierarchically structured porous materials; in a forthcoming note we will discuss scanning curves obtained in such materials.
References