On the Universality of Capillary Condensation and Adsorption Hysteresis Phenomena in Ordered and Crystalline Mesoporous Materials

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Using adsorption experiments for argon over a wide range of temperatures from above the triple point (i.e., 87 K) down to 65 K, coupled with advanced molecular simulation studies, the underlying mechanism of capillary condensation and hysteresis in a mesoporous metal-organic framework (MOF), MIL-101(Cr) is explored. The results obtained on the mesoporous MOFs are compared with the experimental and molecular simulation studies of argon adsorption and phase behavior in mesoporous molecular sieves (e.g., MCM-41 silica) of similar pore size and over the same temperature range (65–87 K). The studies provide insights into the nature of confinement effects on the adsorption and phase behavior of fluids in mesoporous MOFs. The obtained results suggest that certain features of adsorption, capillary condensation, and associated hysteresis phenomena in mesoporous MOFs and in mesoporous molecular sieves are governed by the same underlying physics, despite the striking differences in pore structure and chemical composition. Hence, the findings are of importance for advancing characterization methodologies based on gas adsorption, but also for predicting the behavior of mesoporous MOFs in various potential applications.

Over the last 20 years, substantial progress has been made in understanding adsorption phenomena and confined fluid phase behavior in porous materials. This is associated with two concurrent developments. On one hand, molecular simulation and theoretical approaches, such as classical density functional theories, evolved to provide a detailed picture of the adsorption phenomena on the atomistic scale. On the other hand, several families of mesoporous materials have been recently discovered with pores of regular shape and well-controlled size, such as M4IS and SBA series of materials, several new classes of activated carbons, and mesoporous zeolites. Availability of these materials made it possible for the first time to directly compare theoretical predictions for simplified pore geometries with the experimental observations. This proved to be invaluable in accessing the accuracy and scope of classical, macroscopic, thermodynamic characterization methods, such as the Barrett–Joiner–Halenda method for obtaining pore size distributions. These reference mesoporous materials have been also instrumental in calibrating and advancing modern structural characterization methods based on density functional theory and molecular simulations.

Several new classes of materials have also emerged over the last 20 years. In particular, metal-organic frameworks (MOFs) are crystalline structures, which can be viewed as a system of vertices, formed by metal-organic clusters, and struts, based on organic molecules. A rich arsenal of organic chemistry implies essentially infinite number of possible MOFs and indeed many thousands of these structures have already been reported. Many of these materials feature truly remarkable properties, such as record high surface areas and record low crystalline densities. Although the first structures reported were predominantly microporous materials, since then MOFs have been synthesized with pores of 3 nm and larger. This suggests two important avenues of research. First, MOFs are very promising materials for adsorption separations, gas storage, catalysis, sensing, and other applications. Developing robust methods for accurate characterization of these materials becomes vital for further implementation of the technologies based on MOFs. Second, mesoporous MOFs can provide yet another set of reference materials with well-defined pores to probe and evaluate currently available physical adsorption characterization methods.

It is therefore crucial to explore capillary condensation and adsorption phenomena in these mesoporous MOF structures. Recently, Cho et al., used argon at 87 K, carbon dioxide at 194 K, and nitrogen at 77 K adsorption measurements...
in combination with the X-ray crystallography to obtain an unprecedentedly detailed picture of the adsorbed phase during different stages of adsorption in several mesoporous MOFs (e.g., PCN-224, ZIF-412, IRMOF-74-V-hex). Indeed, it was possible to visualize the state of the pore before the capillary condensation step, featuring a film on the surface of the pore, and after the capillary condensation. This is clearly a powerful approach to understand adsorption phenomena on a molecular level. For practical applications, physical adsorption using argon or nitrogen at cryogenic temperatures will remain the key characterization technique for the foreseeable future. Correct interpretation of the adsorption data in terms of pore structure is vital for the real industrial application of MOF samples and as has been recently demonstrated by Dantas et al., for microporous MOFs, it can be challenging and defying our intuition. Here, we focus on developing further understanding of the adsorption phenomena in mesoporous MOFs by exploring capillary condensation and adsorption hysteresis in these structures.

For this, we employ experiments and computer simulations to investigate argon adsorption in a mesoporous MOF over a wide range of temperatures from above the triple point (i.e., 87 K) down to 65 K. Argon was chosen because, contrary to nitrogen and carbon dioxide, argon does not possess a quadrupole moment, and hence does not exhibit specific interactions with surface functional groups. Hence, argon adsorption at 87 K allows a much more straightforward correlation to be obtained between the pore filling pressure and the confinement effect (depending on pore width and shape). This is particularly important for materials with polar surface functionality such as zeolitic materials, MOFs. For these reasons IUPAC recommends argon as the standard adsorptive for adsorption and characterization of microporous materials.

Comparison of the results for this MOF to those for a MCM-41 material with pores of similar size reveals certain features of capillary condensation and adsorption hysteresis phenomena that seem to be universal for all mesoporous materials, regardless of their chemical nature.

We begin our analysis by first reflecting on the structure of the materials under consideration by using experimental adsorption data and computational structure analysis. Argon adsorption isotherms at 87 K for two samples of MCM-41 are shown in Figure 1A. Pore size distributions obtained using the NLDFT method and the desorption branch of the isotherms are shown in Figure 1B. MCM-41 materials feature straight cylindrical pores and, according to the PSD analysis, these pores are of 3.6 nm and 4.3 nm in diameter for the two materials, respectively.

The mesoporous MOF in the study is MIL-101(Cr) and to justify this choice it is important to briefly review the key properties of this material. MIL-100 and -101 reported by Ferey and co-workers in 2004 and 2005, respectively are the early examples of so called super-MOFs, MOFs with very large pore volumes and surface areas. Indeed, the cell volume of MIL-101(Cr) is enormous (~702 000 Å³) while its BET surface area was reported at ~4000 m²g⁻¹. Although computational structure characterization tools suggest a more realistic value of 2716 m² g⁻¹, it is still a very high surface area compared to the conventional crystalline materials, such as zeolites. The structure of MIL-101(Cr) closely follows MTN zeotype architecture and can be viewed as a system of cages of 2.7 nm and 3.5 nm in diameter connected by windows of 1.3 nm in diameter, as reported using Poreblazer (v3.0.8) (Figure 1D). Figure 2 also shows the structure of MIL-101(Cr) as a system of cages of two sizes. Windows exist between smaller cages, larger cages, and also between small and large cages, and therefore no pore connectivity effects, such as pore blocking or cavitation, should be expected in the system. The larger cage in MIL-101(Cr) is of essentially the same diameter as the cylindrical pore in one of the MCM-41 materials, making this MOF an interesting case for comparison.

Figure 3 presents argon adsorption isotherms at three different temperatures for the MCM-41 material with the pore diameter of 4.3 nm and MIL-101 (Cr). Let us first focus on the MCM-41 results in Figures 1A and 3A,B as they allow us to reflect on the current understanding of the adsorption phenomena in mesopores of well-defined geometry. All three isotherms exhibit capillary condensation and adsorption hysteresis of Type H1, according to the IUPAC classification. In general, confinement in a porous structure shifts condensation of a fluid toward lower pressures, compared to bulk. Stronger confinement (smaller pores) shifts this transition further toward lower pressures until capillary transition disappears altogether, which would correspond to the capillary filling regime. This trend is clearly seen in Figure 1A, with the capillary condensation occurring at a relative pressure of about 0.3 and 0.4 for 3.6 and 4.3 nm pores, respectively. A complete phase diagram collected for a cylindrical pore of a particular diameter will have a shape similar to the bulk phase diagram, but with lower values of the critical temperature and shifted to higher densities. A series of isotherms corresponding to different temperatures within the two phase region of the confined phase diagram will feature hysteresis loops associated with the metastability of the confined fluid. These hysteresis loops become smaller in size as the temperature increases and the system approaches the confined fluid critical point. This is the trend observed for MCM-41 in Figure 3A,B, with the hysteresis loops becoming progressively smaller for higher temperature isotherms. This, however, also implies that, given the same temperature, fluid in a smaller pore is closer to the critical point of the confined phase diagram, and as a result, the capillary phase transition in addition to being shifted to a lower relative pressure should also feature a smaller hysteresis loop, or no hysteresis at all. Again, the variation in the width of hysteresis loops as a function of pore size can be clearly seen in Figure 1A.

Consider now adsorption isotherms for argon in MIL-101(Cr) measured at the same temperatures (Figure 3C,D). Notably all isotherms feature two transitions, the first corresponding to the filling of the smaller of two cages, whereas the second transition at higher pressures is associated with condensation in the larger of the cages. We also note that the size of the steps in density diminishes with temperature, and they become less sharp. The additional panel on the right in Figure 3D also shows hysteresis loops associated with the capillary condensation in the larger of the pores at 65 K. At higher temperatures this hysteresis loop disappears.

A more detailed picture of the capillary condensation in MIL-101(Cr) can be obtained using molecular simulations.
Prior to discussing the actual results, it is important to briefly reflect on how the simulated results should be compared with the experimental data. Here, we employ an off-the-shelf force field for the MOF (universal force field [UFF] [21]) and standard parameters for argon [22] and it is unrealistic to expect quantitative agreement with experiments, and in fact this is not an objective of this study.

Therefore, here we consider two simulated adsorption isotherms at 97 K and 107 K. In reduced units, this corresponds to $T/T_c = 0.62$ and 0.68, respectively, where $T_c$ is the critical temperature of the employed model of argon (obtained from the Lennard-Jones EOS [23]). This can be compared to the equivalent dimensionless temperatures for the experiments 0.43, 0.51, and 0.58 for 65, 77, and 87 K and given the

Figure 1. Argon at 87 K physisorption isotherms and corresponding pore size distribution A,B) MCM-41 ordered mesoporous silica samples exhibiting two different pore sizes; the pore size distribution for MCM-41 is obtained using NLDFT method and the desorption branch of the isotherm [23] and C,D) MIL-101(Cr) metal organic framework sample; for MIL-101(Cr) the pore size distribution is obtained using Poreblazer analysis on the crystal structure [20].
critical temperature of the real argon (150.86 K). Importantly, the conditions in molecular simulations correspond to the similar conditions on the confined phase diagram as in the experiments, giving rise to qualitatively comparable adsorption and hysteresis effects. Similarly, for the pressure scale, the pressure must be reduced using the vapor pressure of the model argon at a particular temperature for more consistent comparison. More details on the properties of the models used to generate the results below are provided in the Supporting Information.

Figure 4A shows an adsorption isotherm for argon at 95 K and 105 K (\(T/T_c = 0.62\) and 0.68) from grand canonical molecular simulations. In agreement with the experiments, the isotherm exhibits two transitions, with the second transition at a higher pressure exhibiting adsorption hysteresis. The simulated adsorption isotherm overestimates the adsorption capacity for argon (about \(\approx 1430–1490\) cm\(^3\) (STP) g\(^{-1}\) compared to the experimental values \(1270–1450\) cm\(^3\) (STP) g\(^{-1}\)). In agreement with the experiments, the second step on the isotherm features adsorption hysteresis, which disappears as we increase the temperature. There are also some differences between the experiments and simulations. In the simulations, the first transition is smoother and the densities in the second transition are closer to each other. These differences could be associated with both the model employed and the relative temperature of the adsorption process.

Figure 4B, in addition to the adsorption isotherm, also shows snapshots of fluid confined within individual cages during the process. The visualization at the lowest relative pressure point corresponds to the state of the smaller cage preceding the first transition. The smaller cage (purple) features a layer of adsorbed argon (1.5–2 atom thick), leaving a cavity inside (shown in light green) of about 1.5 nm. At the end of the first transition, the smaller cage is completely filled with argon (next visualization on the isotherm).

Again, prior to the second transition the larger cavity features a layer of argon (2–2.5 atom thick) and a sparser gas-like region (cyan sphere in the third snapshot) of about 1.7 nm. Filling this space with argon corresponds to the second transition at higher relative pressures.

These visualizations of the states of the pores before and after condensation are in agreement with X-ray data of adsorption states in mesoporous MOFs by Cho et al.\(^{[16]}\) These computer visualizations also illustrate that in a state before the condensation, the pores are formed not only by organic struts but also by argon atoms adsorbed on the structural elements of MIL-101(Cr).
and occupying the windows between the pores. This explains why the chemical nature of the structural elements forming the mesopore may not necessarily substantially influence the position of the capillary condensation, as this process is best characterized as occurring within the pore with the walls formed by argon atoms (in other words, essentially forming an argon film which acts as a kind of pore wall for subsequent adsorption and pore condensation process). Layering of argon also to a significant extent masks the actual shape or organization of the pores, making them effectively spherical in the case of MIL-101(Cr) cages.

Given substantial differences in the properties of the materials, the observations of this study suggest that capillary condensation and hysteresis phenomena in various mesoporous
materials are united by the same underlying physics and that confinement effects play an important role, even for the adsorption and phase behavior of fluids in mesoporous MOFs despite their open pore structure.

Experimental Section

Physical Adsorption Experiments: Samples of MIL-101 (Cr) were provided by Prof. Jong-San Chang, Korea Research Institute of Chemical Technology (KRICT). Samples of MCM-41 were provided by Prof. Michael Fröba, University of Hamburg. Argon adsorption isotherms were measured using a Quantachrome Instruments Autosorb-iQ XR. 65 K isotherms were measured using a Quantachrome Instruments CryoCooler coupled to the Autosorb-iQ XR. MIL-101 (Cr) was outgassed at 150 °C for 12 h under turbomolecular pump vacuum. MCM-41 silica was outgassed at 120 °C for 12 h under turbomolecular pump vacuum.

Molecular Simulations: All simulations in this study were carried out using the energy biased grand canonical Monte Carlo method (GCMC), as implemented in the Music simulation package.[24] Further details of the GCMC simulation protocol adopted in this work, including the number of Monte Carlo moves per adsorption point, type and weight of Monte Carlo moves and other parameters, are provided in the Supporting Information.

For MIL-101(Cr) we adopted the UFF interaction parameters,[21] summarized in the SI file. For argon, the classical Lennard–Jones (LJ) parameters were employed.[25] The LJ cross-species interactions were calculated using the standard Lorentz–Berthelot mixing rules. All LJ interactions were truncated at the cut-off distance of 12.8 Å with no long-tail corrections applied. Adsorbent MIL-101(Cr) was treated as rigid. All solid-fluid interactions were pre-calculated using a cubic lattice with 0.2 Å resolution and stored as potential maps prior to the adsorption simulations. Saturation pressure of argon was calculated using the revised LJ equation of state.[23]

Structural characteristics of the systems, including surface area, pore volume, pore size distribution were obtained with the Poreblazer v3.0.8 simulation suite, using the methods summarized in a previous publication.[20]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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Figure 4. On the left: Argon at 97 K ($T/T_c = 0.62$, blue symbols, black line) and 105 K (0.68, green triangles, black line) physisorption isotherm in MIL-101 (Cr) from molecular simulations. On the right: Computer visualizations depicting states of the individual pores during the argon adsorption process in MIL-101 (Cr) at 97 K.
