



Effect of temperature on hydrogen and carbon dioxide adsorption hysteresis in an ultramicroporous MOF



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ABSTRACT

Different types of hysteresis commonly observed in gas adsorption isotherms of metal-organic frameworks (MOFs) and possible reasons are discussed. The temperature effect of hydrogen (H₂) and carbon dioxide (CO₂) adsorption/desorption hysteresis in an ultramicroporous MOF and a method to obtain accurate isosteric heats of adsorption in small-pore adsorbent materials are presented.

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1. Introduction

Microporous metal organic framework (MOF) materials have become a topic of intense interest over the past decade [1,2] due to their enormous potential for applications in sensing and detection [3–9], magnetism [10,11], catalysis [12–14], gas storage and separation [15–30], chiral recognition [31] and LEDs [32,33]. Among numerous useful features of microporous MOFs, gas storage and separation are by far the most intensively explored properties because of their broadly tuneable surface area, pore volume, pore size, and shape [34]. Extensive studies have been performed to investigate the adsorption–desorption mechanisms and thermodynamics in these materials by both experimental and computational methods [17,35–37]. However, the accuracy of experimental adsorption data, in particular in the ultralow pressure range depends strongly on the chosen experimental conditions. Key information derived from the adsorption data, such as isosteric heats of adsorption (Q_{st}), can be largely affected by these conditions,

especially when MOFs have very narrow pores or pores that are only accessible through very narrow windows, which cause significant diffusion restrictions particularly if adsorption experiments are performed at low temperatures [37]. One indication that data are not properly equilibrated due to the diffusion restriction is the occurrence of artificial adsorption hysteresis. On the other hand, interesting and genuine adsorption hysteresis phenomena have been observed, and their correct interpretation is crucial for assessing the potential that these materials have in the aforementioned gas storage and separation applications. In this work we have taken a closer look at the adsorption behavior of hydrogen and carbon dioxide in a highly flexible MOF consisting of very narrow micropores (e.g. ultramicropores with pore diameter < 7 Å). RPM3-Zn or [Zn₂(bpdc)₂(bpee)]·2DMF (**1**) (bpdc = 4,4'-biphenyl dicarboxylate, bpee = 1,2-bipyridylethene, DMF = N,N-dimethylformamide), is an ultramicroporous MOF structure embracing one-dimensional (1D) channels with a window size of ~5 × 7 Å (excluding the van der Waals radius of the carbon atom, 1.7 Å, see Fig. 1) [4].

Hysteresis has commonly been observed in gas adsorption/desorption isotherms on MOF materials; here we discuss some important aspects of this phenomenon. Genuine hysteresis can, of course, also be observed in the presence of mesopores where hysteresis is associated with pore condensation. This form of

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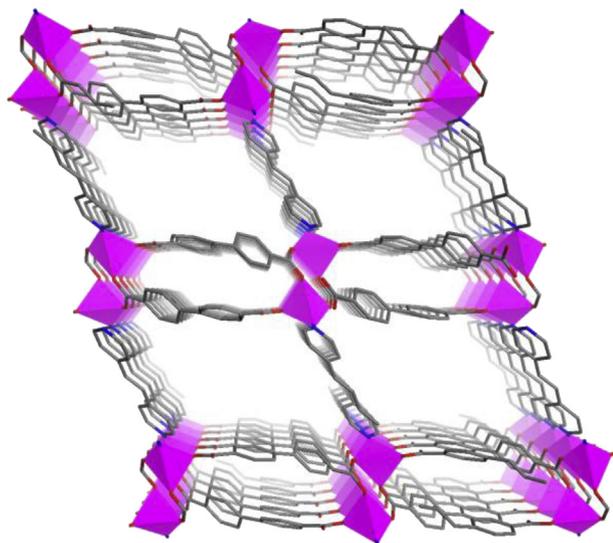


Fig. 1. View of the structure **1** embracing a 1D channel along the *b*-axis with window size of $\sim 5 \times 7$ Å. Color scheme: Zn: Magenta tetrahedron, N: Blue, O: Red, and C: Grey. H atoms and DMF are omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hysteresis can be attributed to adsorption metastability and/or network effects. For instance, genuine pore condensation hysteresis of nitrogen and argon adsorption at 77 K and 87 K, respectively, occurs in the range of relative pressure higher than 0.38 [38–40]. Physical adsorption isotherms are generally expected to be completely reversible in the monolayer, or micropore filling, range. However, for certain microporous systems (e.g., clays, coal, some activated carbons), low-pressure hysteresis is observed. This kind of hysteresis can occur when insufficient time is given for the system to attain equilibrium. Another source of error is the presence of impurities either in the gas phase or on the surface. These complications must be avoided or removed before the evidence for reproducible and genuine low pressure hysteresis can be considered. Genuine low-pressure hysteresis is often associated with structural expansion and contraction of the adsorbents, or irreversible entry of the adsorbate molecules into pores of molecular dimensions can produce inelastic distortion of the adsorbent structure. Related is the activated diffusion effect, which is associated with the very slow diffusion of molecules through narrow pore entrances [40]. Gas adsorption can also induce structural transformations of the adsorbent, which leads to associated low-pressure hysteresis. This phenomenon has been observed in zeolites, where well-defined hysteresis loops are found in a pressure range far below the range associated with capillary condensation. Similarly, hysteresis is also associated with deformation of flexible pore networks, such as “breathing”, also referred to as “gate opening/closing”, a common phenomenon observed in many small pore MOFs as a result of structural change during the course of gas adsorption and desorption [41–45]. One should note that for materials that undergo such structural changes, application of standard methods for the assessment of surface area and the analysis of pore size may lead to meaningless BET areas and pore size distributions. Non-genuine hysteresis due to slow adsorption kinetics is often observed in structures characteristic of ultramicropores with complex pore geometries (as indicated above) [43]. For example, the diffusion coefficient of methane in porous materials may vary up to 10 orders of magnitude [46]. Similarly, the H_2 diffusion coefficient may also vary substantially in MOF structures. Calculation shows that the H_2 diffusion coefficient in **1** is in the range of

$\sim(2-4) \times 10^{-5} s^{-1}$ at 77 K and $(2-11) \times 10^{-5} s^{-1}$ at 87 K, which is 10 times lower than those found for the IRMOF series (e.g. IRMOF-1, -8, and -18) [37]. This is because of the very small window size in the guest-free form of **1** (which is further reduced from 5×7 Å in the as-made structure upon removal of guest molecules). At low temperatures, pseudo-equilibration may be mistakenly recognized due to slow diffusion/transportation and instrument limit.

2. Results and discussion

2.1. Effect of temperature on hydrogen adsorption hysteresis

A typical supercritical hydrogen adsorption and desorption measurement was performed on **1** at 77 and 87 K at pressures ranging from 10^{-3} to 1 atm. Strong hysteresis was found at both temperatures and was clearly more severe at the lower temperature, of 77 K (see Fig. 2). Significantly longer equilibration time at each data point did not lead to the expected reversible hydrogen adsorption isotherms [37].

In order to examine the nature of such hysteresis and obtain accurate hydrogen Q_{st} values in this system, we carried out a series of adsorption–desorption isotherm experiments at higher temperatures. In Fig. 2, we show the isotherm data between 77 and 117 K in increments of 10 K. From these data it is clear that the hysteresis loop reduces as the temperature increases. The adsorption and desorption isotherms nearly overlap at 97 K, and the hysteresis loop is completely closed at 107 and 117 K. This clearly indicates the kinetic origin of supercritical hydrogen adsorption–desorption hysteresis at lower temperatures. Consequently, accurate heats of hydrogen adsorption were calculated using the fully reversible hydrogen isotherms collected at 97, 107 and 117 K, employing two fitting methods (Virial [47] and Polynomial [48]). The results are plotted in Fig. 3.

2.2. Effect of temperature on carbon dioxide adsorption hysteresis

In addition to the hydrogen adsorption study, we investigated the adsorption behavior of carbon dioxide in this material. Fig. 4a shows the adsorption/desorption isotherm of CO_2 on **1** collected at 195 K. It exhibits two characteristic steps (inflection points)

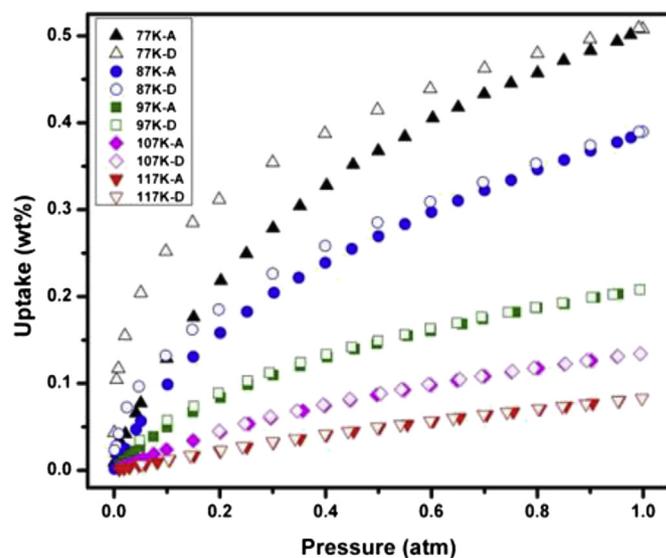


Fig. 2. H_2 adsorption–desorption isotherms at different temperatures from 77 to 117 K. Filled and open symbols represent adsorption (A) and desorption (D) branches, respectively.

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