

Adsorption of water on three-dimensional pillared-layer metal organic frameworks

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Abstract

We showed water adsorption isotherms at 303 K on water-resistant three-dimensional (3-D) pillared-layer metal organic frameworks (MOFs) with 1-D semi-rectangular pores, of which size depends on the length of ligand. The shapes of all three adsorption isotherms are type I by IUPAC classification showing strong water–MOFs interaction. The adsorbed amount of water molecules on the hydrophilic site of carboxylic group in 2-D sheets coincided with the crystal water amount. The adsorption on the hydrophilic sites occurs at similar relative pressure even if the used ligand is different.

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1. Introduction

Recently, metal organic frameworks (MOFs) have attracted much attention, because they have the possibility of novel functional materials such as gas adsorbents, sensors, catalysts, and photoactive materials. MOFs can be designed by selecting adhesive metal, ligand, and counter anion, and we can control the pore geometry [1–7]. Moreover, the growth from building units to MOF proceeds by self-assembly mechanism, therefore the handling to get MOF samples is simple. These points are additional merits of MOFs for future applications.

Gas sorptivity of many MOFs has been energetically researched [7–20] and some reports showed an excellent gas sorption ability which is comparable with or exceeds that of carbon materials or zeolite [20–25]. For example, Yaghi et al. reported zeolite-like MOFs that have high surface area (over 3000 m² g⁻¹) and porosity [20,21]. Authors showed that highly flexible Cu-based MOF can adsorb predominant amount of methane and carbon dioxide with an unusual lattice expansion mechanism [22,26].

The high surface area and porosity would be allowed by the architecture of molecular-based linker instead of continuous atomic wall such as graphene sheet or zeolite. For the technological applications of MOFs, the stability of MOFs in an ambient condition is essentially important. Hence study on the stability of MOFs on water adsorption is desirable. Although there are many reports about MOFs with open architecture [7–26], water sorption studies are quite a few [27–30]. The reason is that many MOFs vary their structures on water sorption and furthermore many MOFs are unstable in the presence of water. Actually Greathouse and Allendorf more recently reported the interaction of water with MOF-5, showing the weakness of the secondary building unit against to water and the decrease of the surface area by the collapse of frameworks [31].

In this article, we report almost reversible adsorption and desorption characteristics of the desolvated samples of three-dimensional (3-D) MOFs {[Cu₂(pzdc)₂(pyz)]·2H₂O} (1), {[Cu₂(pzdc)₂(bpy)]·4H₂O} (2), and {[Cu₂(pzdc)₂(bpe)]·5H₂O} (3) (pzdc = 2,3-pyrazinedicarboxylate, pyz = pyrazine, bpy = 4,4'-bipyridine, and bpe = *trans*-1,2-bis(4-pyridyl)ethylene) with 1-D semi-rectangular pores, of which size depends on the length of the ligands [32].

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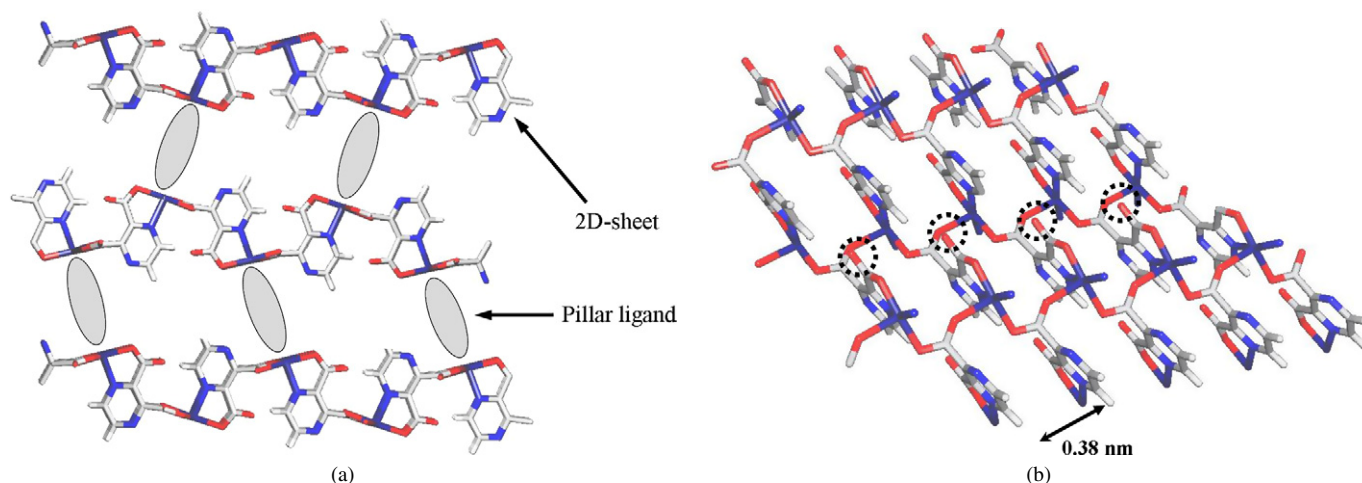


Fig. 1. Schematic representation of [Cu₂(pzdc)₂(PL)] (a) (PL = pillar ligand, pyz in **1**, bpy in **2**, bpe in **3**), and 2-D sheets of [Cu₂(pzdc)₂]_n (b). Dotted circle shows the terminal oxygen atom of carboxylic group (copper, dark blue; carbon, gray; nitrogen, blue; oxygen, red; and hydrogen, white). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Water adsorption measurement

The adsorption measurements of H₂O at 303 K were carried out on the laboratory designed gravimetric line with a quartz spring. Prior to the adsorption measurement in order to remove adsorbed molecules, the sample was treated under the vacuum of $<10^{-2}$ Pa at 373 K, until no further weight loss was observed. Thus-treated samples lose guest water molecules and the corresponding samples after the drying treatment of **1**, **2**, and **3** are noted **1a**, **2a**, and **3a**. The samples that were characterized in the previous report were used [32,33].

3. Results and discussion

3.1. Crystal structure

Three Cu complex samples consist of 2-D sheets of [Cu₂(pzdc)₂]_n and pillar ligands bridging neighboring sheets, and possess 3-D structure with 1-D semi-rectangular channels [32, 33], as shown in Fig. 1. The 2-D sheet [Cu₂(pzdc)₂] has no large pores through which water molecules can pass (calcd; 0.04 nm) [34] and terminal oxygen atom of carboxylic group as a hydrophilic site. Pore sizes depend on the size of the used ligand and are 0.6×0.4 nm² in **1**, 0.6×0.9 nm² in **2**, and 0.6×1.1 nm² in **3**, respectively. The compounds have crystal water molecules in pore spaces and the framework structures are presented after the removal of water molecules [32,33]. Thus, they have the permanence for water.

3.2. Water adsorption on **1a**

The H₂O adsorption isotherms measured at 303 K on **1a** are shown in Fig. 2. The compound **1a** gives the reproducible H₂O adsorption isotherm, indicating that the structure of **1a** is resistive against water. The shape of adsorption isotherm is categorized to type I by IUPAC classification. The type I adsorption

isotherm indicates the strong interaction between **1a** and H₂O molecules. The adsorption and desorption branches are almost similar to each other, leading to no hysteresis loop in Fig. 2a. However, the desorption isotherm shifts upward slightly in the low pressure region as shown in Fig. 2b. This indicates that a part of adsorbed water molecules are strongly bound in the **1a** crystals. The adsorption uptake in the low relative pressure region is not so marked compared with that of the nitrogen adsorption isotherm [32]. The adsorbed amount increases gradually in the low pressure region and reaches the plateau region around $P/P_0 = 0.08$, accompanying with the further increase at higher relative pressure. The adsorbed amount of H₂O at $P/P_0 = 0.08$ just coincides with the amount of crystal water molecules in **1** (66.2 mg g^{-1}). This result strongly suggests that guest water molecules are reproducibly bound to the crystal frame structures.

3.3. Water adsorption on **2a** and **3a**

The H₂O adsorption isotherms of **2a** and **3a** at 303 K are shown in Figs. 3 and 4, respectively. The shape of the isotherms is similar to that of the isotherm of **1a**. Both isotherms have no evident hysteresis, indicating the stable frameworks of **2a** and **3a** against water. Strictly speaking, the desorption branch shifts upward slightly in the high relative pressure region. Then the adsorption equilibration is not necessarily enough for determination of the correct adsorption branch in the case of compounds **2a** and **3a**. As the ligand as a pillar become longer, the adsorption amount is larger (up to 270 mg g^{-1}), and in the case of **3a** it is twice as large as that of **1a** (Fig. 5). Interestingly, the explicit step shown in the isotherm on **1a** is not observed in both isotherms. For compounds **2a** and **3a**, limited number of water molecules should be firstly adsorbed on the hydrophilic specific sites, and then water molecules are absorbed on the pre-adsorbed water molecules because of the presence of free space in the pores. Water molecules are adsorbed after the adsorption of limited number of water molecules which results the gradual increase of adsorption amount in middle pressure region. Ad-

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