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Highly Porous and Stable Coordination Polymers as Water Sorption Materials

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Three MIL-100-type porous coordination polymers were synthesized using different types of anions and their water sorption properties were investigated. All of the compounds adsorbed huge amounts of water ($0.6\,g\,g^{-1}$) at a moderate humidity ($P/P_0 < 0.6$), and one of the compounds showed the same adsorption property even after two thousand replicate water sorption tests. In addition, the pressure of water adsorption was found to be controlled by counter anions incorporated in the structure, which was attributed to the hydration energy of the anions.

Porous compounds have been widely investigated not only for scientific interests but also for potential applications such as gas storage, gas separation, molecular catalysis, etc.[1] In particular, the applications of heat transformation utilizing water adsorption, such as thermally driven adsorption heat pumps (AHP) and desiccant cooling systems (DCS), have attracted attention as promising energy-saving materials for efficient air conditioning.[2,3] The energy efficiency and working humidity range of AHP and DCS strongly depend on the properties of the water adsorbent.[4,5] Therefore, it is important to prepare adsorbents showing large amounts of water adsorption and to control their adsorption pressure.[6,7] Currently, silica gels or zeolites are used as adsorbents for AHP and DCS; however, further development of adsorbents is required for effective systems. Recently, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) composed of metal ions and various organic ligands have been extensively studied as a new class of microporous compounds, and many unique porous properties, such as extremely large specific surface area and highly selective gas adsorption, have been found for this class of compounds.[8,9] One of the most attractive features of PCPs is the high ability to design pore structures and properties. The metrics and surface properties of pores are finely tuned by choosing structural components such as organic ligands, metal cations, and counter anions. In this work, we focused on PCPs as water adsorbents that show high capacity for water adsorption and high durability through replicate water sorption and on tuning the water sorption pressure.

We synthesized new MIL-100-type PCPs using several counter anions and investigated their water adsorption properties. MIL-100 ($Cr_3FO[C_6H_3(CO_2)_3]_2\cdot nH_2O$ ($n \approx 28$)) (hereafter denoted as **1**•(F)), which was discovered by Férey et al., is constructed from Cr^{3+} ions, trimesic acid (benzene-1,3,5-tricarboxylate (BTC)), and fluoride anion.[10] The **1**•(F) has two types of giant cages with inner diameter sizes of 25 and 29 Å and an extremely large specific surface area (the Langmuir surface area = ca. $3100\,m^2\,g^{-1}$) estimated by nitrogen adsorption. Interestingly, the free counter anions are accommodated in the pores; therefore, they can be replaced with other counter anions using different inorganic acids in the synthesis instead of hydrofluoric acid.

We prepared three types of MIL-100-type compounds denoted as **1**•(F), **1**•(Cl) (=($Cr_3ClO[C_6H_3(CO_2)_3]_2$)) and **1**•($SO_4$) (=($Cr_3[(SO_4)_{1/2}]O[C_6H_3(CO_2)_3]_2$)), using hydrofluoric acid, hydrochloric acid, and sulfuric acid, respectively. For use in AHP and DCS, it is important that adsorbed water molecules can be desorbed from the adsorbent at relatively low temperatures, e.g., below 373 K, because waste heat from plants or solar heat used in industrial processes is unlikely to supply high temperatures for heating. To examine the water release temperature and the thermal stability, thermogravimetric (TG) analyses of **1**•(F), **1**•(Cl), and **1**•(SO_4) were carried out (Figure S1).[11] The TG curves for all of the compounds showed release of guest water molecules at ca. 353 K, which is a sufficiently low temperature for the desorption requirement for successful use in AHP and DCS.

Figure 1 shows a simulated XRPD pattern obtained from reported structure data and experimental XRPD patterns of as-synthesized **1**•(F), **1**•(Cl), and **1**•(SO_4). Each pattern of **1**•(F), **1**•(Cl), and **1**•(SO_4) is in good agreement with the simulation, indicating they have similar structures to the reported MIL-100. Nitrogen (N_2) adsorption isotherms of **1**•(F), **1**•(Cl), and **1**•(SO_4) were measured at 77 K (Figure S2).[11] All samples were evacuated at 398 K before the measurements. The adsorption isotherms show typical Type I curves in the IUPAC classification, indicative of the presence of permanent micropores. The Brunauer–Emmett–Teller (BET) specific surface areas of **1**•(F), **1**•(Cl), and **1**•(SO_4) were calculated from these isotherms to be

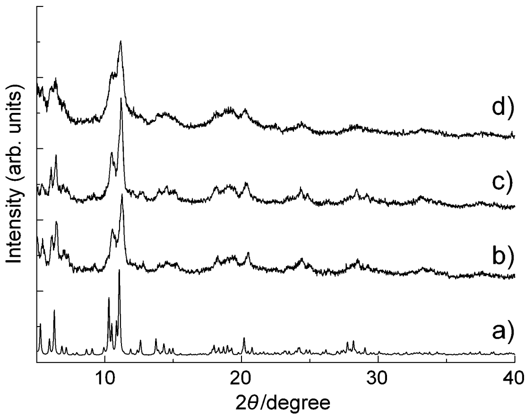

Figure 1. XRPD patterns of a) simulation of MIL-100, b) **1**•(F), c) **1**•(Cl), and d) **1**•(SO_4), respectively. All measurements were carried out at 293(5) K with Cu Kα radiation.

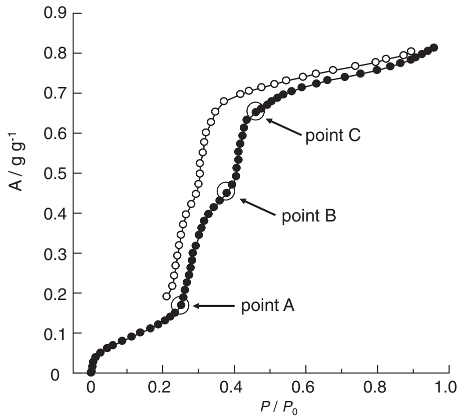

Figure 2. Water adsorption and desorption isotherms at 298 K for desolvated **1**•(F). P/P_0 is the relative pressure of water where saturation vapor pressure (P_0) is 3.16 kPa. A is the amount adsorbed (g g^{-1}).

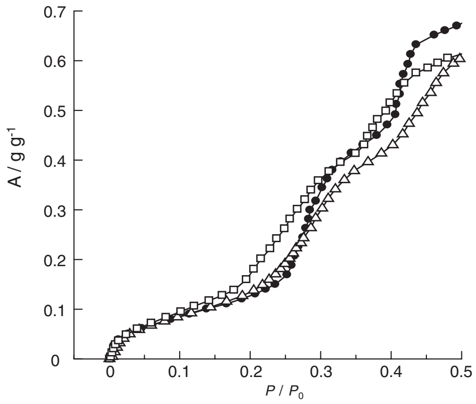

Figure 3. Water adsorption isotherms at 298 K for desolvated **1**•F (●), **1**•(Cl) (△), and **1**•(SO_4) (□). P/P_0 is the relative pressure of water where saturation vapor pressure (P_0) is 3.16 kPa. A is the amount adsorbed (g g^{-1}).

1517, 1522, and 1456 m^2•g^{-1}, respectively. The adsorption isotherm of water on **1**•(F) measured at 298 K is shown in Figure 2. Interestingly, the isotherm shows several distinct steps. The mechanism of this stepwise water sorption isotherm is assumed to be as follows: First, a small number of water molecules is strongly adsorbed on the open metal sites (OMSs) of chromium ions via coordination bonds below a relative pressure (P/P_0) of 0.2. Then, a large number of water molecules are suddenly adsorbed into the smaller cages of 25 Å diameter from point A to point B. Another steep increase is then found from point B to point C, attributed to water uptake into the larger cages of 29 Å diameter.

It is worth noting that an exceptionally large amount of water (over 0.5 g g^{-1}) can be adsorbed and desorbed on **1**•(F) in the middle relative pressure range from 0.22 to 0.58. We carried out a durability test by recycling the water adsorption and desorption processes. Surprisingly, the amount of adsorption does not change even after two thousand cycles of the ad/desorption test (Figure S3).[11] These results indicate that **1**•(F) is quite stable for use in AHP and DCS.

For use in AHP and DCS, it is also important to carefully regulate the water uptake pressure of adsorbents. To determine the counter anion effect on water adsorption, we carried out water adsorption measurements of **1**•(Cl) and **1**•(SO_4). Marked differences were found among the sorption isotherms of **1**•(F), **1**•(Cl), and **1**•(SO_4), as shown in Figure 3. The amount adsorbed and the pressure region attributed to the adsorption on the OMSs are almost the same for all of the compounds; however, the values of P/P_0 for the steps are different. The steps in the isotherm of **1**•(SO_4) moved to lower P/P_0 values compared with those of the other compounds. On the other hand, the steps of **1**•(Cl) moved to higher P/P_0 values. We assume that these differences can be attributed to differences in the hydration energy of the counter anion in the pore. The hydration energies, ΔG_h, for fluoride, chloride, and sulfate ion have been reported as -472, -347, and -1090 kJ mol^{-1}, respectively.[12] Isosteric heats of adsorption (q_{st}) for the all isotherms were estimated from Dubinin–Radushkevich (DR) analysis (Figure S4)[13] and are summarized in Table S1.[11] Two different values of q_{st} for each isotherm were obtained, which was attributed to the steps in the isotherms. Interestingly, the both two of q_{st} for **1**•(SO_4) shows the largest values, and those for **1**•(Cl) shows the smallest ones, which the is same tendency of the hydration energies. According to the hydration energy and isosteric heat of adsorption, the interaction between water and sulfate anion is stronger than that between water and chloride anion. As a result, the adsorption for **1**•(SO_4) begins at a lower pressure than for **1**•(Cl).

In conclusion, we have investigated the water sorption properties of three MIL-100-type PCPs. They have shown exceptionally high water adsorption in the moderate humidity range. In addition, the sorption profile, especially for the guest uptake pressure, can be tuned by the counter anions incorporated in the structure, although adsorption properties of PCPs are usually changed by the pore size or organic ligands of the frameworks. The results of this work will lead to the development of new water adsorption materials for applications in AHP and DCS using PCPs.

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