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Metal–organic frameworks with high working capacities and cyclic hydrothermal stabilities for fresh water production

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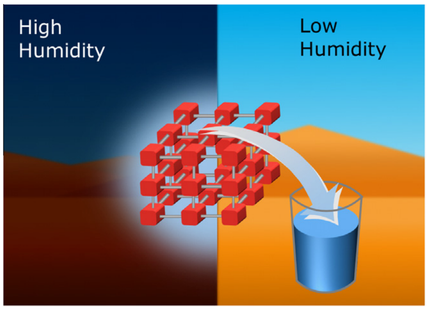
HIGHLIGHTS

- For medium humidity, MIL-100(M) MOFs show high working capacities.
- For high humidity, MIL-101(Cr) exhibits a significantly high working capacity.
- All the MOFs consisted of only M^{III} sites show good cyclic water adsorption.
- MIL-101(Cr) and MIL-100(M) MOFs are promising for fresh water production.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we evaluated the working capacities of eight hydrothermally stable metal–organic frameworks (MOFs) for water adsorption under typical humidity conditions in three representative dry regions. Remarkably, three MIL-100(M) materials (M = Cr, Al, and Fe) and MIL-101(Cr) exhibited very high working capacities for medium and high humidity conditions due to their large surface areas. All of the MOFs consisting of only M^{III} sites (MIL-101(Cr), MIL-100(Cr), and MIL-100(Al)) showed good cyclic water adsorption/desorption performances and good hydrothermal stabilities. Due to the presence of Fe^{II} sites formed during activation at 250 °C, MIL-100(Fe) showed a considerable decrease in its water adsorption isotherm during the 2nd cycle although almost unchanged water uptakes were observed in the following cycles. When MIL-100(Fe) was activated at 150 °C (MIL-100(Fe)_150) to prevent formation of Fe^{II} sites, the sample showed good cyclic adsorption/desorption performance and good hydrothermal stability. Considering the high working capacities, cyclic adsorption/desorption behaviors, and good hydrothermal stabilities, MIL-101(Cr), MIL-100(Cr), MIL-100(Al) and MIL-100(Fe)_150 are promising adsorbents for producing drinking water in dry regions with medium or high humidity conditions during the night.

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1. Introduction

The water sorption behaviors of porous materials have been investigated for various applications, such as desiccant dehumidification [1–3], fresh water production in extremely dry regions [4–6], and heat-transformation processes [7–10]. For these applications, adsorbents with high water uptake capacities at desirable relative pressures and good cyclic adsorption/desorption performances are required. Until now, commercial adsorbents, such as activated alumina, silica gel, and zeolites have been used for these applications. However, those porous adsorbents have limited water uptake capacities and/or poor cyclic performances due to their moderate surface areas and strong interactions between water and the adsorbents.

Recently, metal–organic frameworks (MOFs), which are synthesized by self-assembly of inorganic metal clusters and organic linkers, have emerged as a new class of porous materials [11–13]. MOFs have been vigorously studied as promising adsorbents for various applications, such as gas storage [14–18], separations [19–21], sensing [22,23] and catalysis [24] because of their extremely high surface areas, tunable pore sizes and adjustable internal surface properties [25]. As a result of these attractive features, MOFs may be considered as an alternative for water sorption applications. However, several issues related to the stability and reproducibility of MOFs remain because many MOFs have been found to be easily degradable under moist conditions. Because the water molecule has naturally strong nucleophilic sites, metal–ligand bonds in MOFs can be attacked by water molecules [26]. Fortunately, some types of MOFs, such as MIL-101(Cr) [27,28], MIL-100(M) (M = Cr, Fe, and Al) [9,28,29] and UiO-66(Zr) [30–32] have been found to be remarkably stable under humid conditions due to their strong metal–ligand bonds and other structural features [26]. Recently, several MOFs with reasonable hydrothermal stabilities have been studied for dehumidification [28,33,34], water purification [35,36], adsorption heat-transformation [7,9,10] and fresh water production [28,37].

Yaghi and co-workers [37] evaluated the water adsorption performances of 23 materials, including 20 MOFs based on the following three criteria: (1) condensation pressure of water in the pores, (2) high water uptake capacity, and (3) good cycling performance and water stability. By considering all three criteria, they suggested that two zirconium-based MOFs, MOF-801-P and MOF-841, performed the best. Because MOF-801-P adsorbed a large amount of water at $P/P_0 = 0.1$, they argued that this MOF was a good candidate for advanced thermal batteries. Because MOF-841 exhibited high water uptake at $P/P_0 = 0.3$, they suggested that MOF-841 has the potential to be used to produce fresh water in remote desert areas.

Most studies concerning water adsorption of MOFs have highlighted on the *storage capacity* at high humidity conditions, but for practical applications, the adsorbed amount at the discharge humidity condition should also be considered. The *working capacity* is defined by the difference in the adsorbed amount under adsorption conditions and the adsorbed amount under discharge conditions [38]. Therefore, the working capacity is more feasible for identifying the applicability of MOFs rather than the storage capacity. In the case of fresh water production in extremely dry areas, the concept of working capacity is well suited for the needed application. Based on the high working capacity of MOF-841 between $P/P_0 = 0.05–0.35$, Yaghi and co-workers argued that MOF-841 is a good candidate to produce fresh water in desert areas, such as the city of Tabuk in Saudi Arabia where the typical RH conditions during the day and night are 5% and 35%, respectively [37]. In fact, RH conditions vary depending on the region and season of the year. For Pampas de La Joya located in southern Peru, the relative humidity (RH) during the day is approximately 0%, while the typical RH at night is 45% [39]. For the Mojave Desert in California, typical RHs in the afternoon and night are 30% and 55%, respectively, during the winter [40]. Therefore, investigating the correlation between the working capacities of MOFs and various RH conditions that resemble possible climatic conditions is necessary.

In this work, we synthesized eight representative MOFs that are known to be hydrothermally stable [26]: UiO-66(Zr) [30–32] and its three derivatives (UiO-66(Zr)-NH_2 [32,41], UiO-66(Zr)-OH [32], and UiO-66(Zr)-$(OH)_2$ [32]), MIL-101(Cr) [27,28], and MIL-100-M (M = Fe, Cr, Al) [9,28,29]. Although some of these MOFs have been extensively studied for water adsorption, the water working capacities of these MOFs in terms of reliance on varied humidity conditions have not been fully unveiled so far. Therefore, we measured the water adsorption isotherms of the eight MOFs and evaluated their working capacities under three different RH conditions that were all representative of real humidity conditions. For MOFs with high working capacities, we measured the cyclic water adsorption/desorption isotherms to examine if the working capacities were maintained even after repeated uses. Especially for MIL-100(Fe), we investigated the effect of the activation temperature on the cyclic water adsorption behaviors. Moreover, we compared the powder X-ray diffraction (PXRD) patterns of the as-synthesized samples and the used samples after cyclic adsorption/desorption to investigate the hydrothermal stabilities. For the comparisons, MOF-801-P and MOF-841, which have been reported to have good water adsorption properties, were also employed in this study [37].

2. Experimental

UiO-66(Zr) and its derivatives (UiO-66(Zr)-NH_2, UiO-66(Zr)-OH, and UiO-66(Zr)-$(OH)_2$) [32], MIL-101(Cr) [42], MIL-100(Fe) [43], MIL-100(Cr) [44], and MIL-100(Al) [28] were synthesized according to previous protocols in the literature.

PXRD (powder X-ray diffraction) patterns were recorded with a Rigaku Miniflex (Rigaku Co., Japan) using nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å) from $2° < 2\theta < 40°$ in 0.02° steps at 1 s per step. PXRD patterns of the as-synthesized samples were measured to verify the purity of the crystalline phases. For selected MOFs, the PXRD patterns of the water-exposed samples were obtained to investigate changes in the crystalline structures after cyclic water adsorption.

The BET surface areas of MOFs were calculated from N_2 adsorption isotherms at 77 K, which were obtained by the Autosorb iQ system (Quantachrome Instruments, USA). For each measurement, approximately 50 mg of sample was used. Before determining the isotherms, as-synthesized UiO-66 and its derivatives were degassed under vacuum ($<10^{-4}$ mbar) at 90 °C for 1 h followed by 150 °C for 3 h. MIL-101(Cr) and a series of MIL-100(M) (M = Fe, Cr, Al) were degassed under vacuum ($<10^{-4}$ mbar) at 250 °C for 6 h. After measuring the N_2 isotherms, BET surface areas were calculated in the linear range determined using the consistency criteria [45–47]: UiO-66(Zr): $0.003 < P/P_0 < 0.068$; UiO-66-NH_2: $0.003 < P/P_0 < 0.070$; UiO-66-OH: $0.002 < P/P_0 < 0.050$; UiO-66-$(OH)_2$: $0.003 < P/P_0 < 0.071$; MIL-101(Cr): $0.007 < P/P_0 < 0.198$; MIL-100(Fe): $0.007 < P/P_0 < 0.196$; MIL-100(Cr): $0.007 < P/P_0 < 0.202$; MIL-100(Al): $0.005 < P/P_0 < 0.097$.

The adsorption isotherms of water in the MOFs at 298 K were measured using an Autosorb iQ system (Quantachrome Instruments) with a specially designed water circulation system to maintain constant temperature. The water adsorption isotherms were measured up to a relative humidity of 0.8. For the best-performing MOFs, the repeated water adsorption/desorption isotherms at 298 K were obtained for five cycles. Between each cycle,