Independent verification of the saturation hydrogen uptake in MOF-177 and establishment of a benchmark for hydrogen adsorption in metal–organic frameworks†‡

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Hydrogen isotherms for MOF-177, Zn_4O(1,3,5-benzenetribenzoate)$_2$, crystals were independently measured by volumetric and gravimetric methods at 77 K to confirm its hydrogen uptake capacity and to establish the importance of calibrating gas adsorption instrumentation prior to evaluating H_2 storage capacities. Reproducibility of hydrogen adsorption experiments is important because non-systematic errors in measurements can easily occur leading to erroneous reports of capacities. The surface excess weight percentage of hydrogen uptake in MOF-177 samples is 7.5 wt% at 70 bar, which corresponds to an absolute adsorbed amount of 11 wt%. These values are in agreement with our previous report and with those found independently by Southwest Research Institute. Considering its well-known structure and its significant H_2 uptake properties, we believe MOF-177 is an excellent material to serve as a benchmark adsorber.

Introduction

The discovery of hydrogen adsorption in porous metal–organic frameworks (MOFs) and subsequent related studies has firmly established these materials as interesting candidates for hydrogen storage applications.[1–8] This is due to the availability of a large number of well-characterized MOFs and to the flexibility with which their organic and inorganic components can be varied.[9] In a recent review[10] we delineated numerous strategies that can be used in MOF chemistry for achieving the targets for on-board hydrogen storage systems set by the US Department of Energy (DOE) for use of hydrogen as a fuel. The gravimetric (6.0 wt%) and volumetric (45 g L^{-1}) densities to be achieved by 2010[11] are important in the context of the present report as many research groups are aiming to achieve these targets.

Recently, under a DOE-funded program, we showed that MOF-177 (Fig. 1) can store 7.5 wt% hydrogen with a volumetric capacity of 32 g L^{-1} at 77 K and 70 bar.[4] Another MOF was found to store 5.1 wt% with a volumetric capacity of 43 g L^{-1} at 77 K and 45 bar.[5] These results are exciting as these MOFs exhibit the highest hydrogen uptake of any porous materials and clearly show that in principle the DOE targets can be achieved at 77 K. In light of these developments and the extensive work being done on MOFs we propose the establishment of MOF-177[12] as a benchmark material for researchers in the field. This is important as the field of hydrogen storage has often suffered from reports of high hydrogen uptake which were later found to be erroneous.[13] Accordingly, our DOE program officers have advised that independent measurements of hydrogen uptake should be performed at a DOE-approved facility (Southwest Research Institute®; SwRI) to independently verify hydrogen uptake measurements reported for MOF-177. Here we report jointly on the results of the verification tests, point out some of the intricacies of hydrogen measurements, and suggest a standard for reporting results of hydrogen adsorption.

We remark that MOF-177 is an ideal material to use as a benchmark for hydrogen adsorption measurements on MOF materials due to the following facts: (1) it has high gravimetric and volumetric uptake capacity[4] that is 3–5 times higher than in well-studied commercial materials, such as activated carbons or zeolites,[14] leading to ease of high accuracy measurements; (2) its synthesis is simple and highly reproducible;[15]

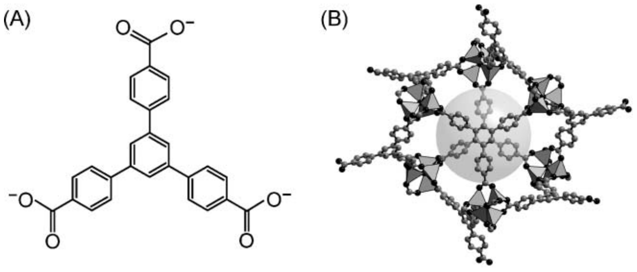

Fig. 1 (A) Molecular structure of the BTB link and (B) crystal structure of MOF-177. An approximately spherical pore is shown as the large sphere with a 17 Å diameter.

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and (3) it has a crystalline structure that is well-characterized in terms of atomic connectivity and chemical composition.

In this study, independent investigations were undertaken to assess the H_2 saturation uptake on MOF-177 samples using volumetric and gravimetric instruments located at the University of Michigan, UCLA and SwRI. We demonstrate the validity of MOF-177 as a benchmark material based on the agreement between volumetric (7.5 wt% at SwRI) and gravimetric (7.3 wt% at UCLA) H_2 adsorption measurements at 77 K, which are in agreement with our original report[4] (volumetric data at UM, 7.5 wt%).

Experimental

Synthesis of MOF-177

N,*N*-Diethylformamide (DEF, BASF) was treated by addition of charcoal carbon (*ca.* 0.5 g, Acros, CAS No.: 7440-44-0) into 1 L and stirred for 12 h at room temperature. The black suspension solution was filtered through a silica-gel column (*ca.* 350 g, Silica gel 60, 230–400 mesh, EMD Chemicals) to remove carbon powder. Pure MOF-177 was prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ (0.187 g, 0.63 mmol, Aldrich) and 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid‡ (H_3BTB, 0.0395 g, 0.090 mmol) in DEF (10 mL) in a 20 mL vial. The vial was capped tightly and placed in an oven at 85 °C for two days to yield clear block crystals. After cooling, the yellow solution was decanted, and the crystals were washed with 3 × 20 mL *N*,*N*-dimethylformamide (reagent-grade, Fisher). The product was then immersed in chloroform (20 mL, pentene stabilized, reagent-grade, Fisher) for three days, during which time the activation solvent was decanted and freshly replenished three times. The crystals were transferred to a glass tube (7 mm i.d. × 300 mm length) as a chloroform suspension by using a glass pipette to prevent exposure to air. The material was evacuated to 10^{-3} Torr at room temperature for 2 h, heated at a constant rate (1 °C min^{-1}) to 120 °C for 6 h, then cooled at a constant rate of 1 °C min^{-1} to room temperature. Powder X-ray diffraction patterns for as-synthesized and activated materials were coincident and in agreement with the simulated pattern, indicating the bulk purity of MOF-177 samples. Although MOF-177 will not be decomposed even if the samples are quickly transferred to a gas sorption cell in the air, activated MOF-177 samples were handled using standard techniques to avoid exposure to air or moisture.

Low-pressure gas adsorption measurements

Low-pressure N_2 and H_2 adsorption measurements (up to 1 bar) were performed on an Autosorb-1 (Quantachrome) volumetric analyzer at 77 K using a liquid nitrogen (LN_2) bath.[16] H_2 isotherms were collected at 87 K using a liquid argon bath. The analysis station of the volumetric adsorption apparatus was equipped, in addition to the standard pressure transducers in the dosing volume (manifold) of the apparatus, with high-precision pressure transducers (Baratron MKS) dedicated to read the pressure in the sample cell alone. Hence, isolation of the sample cell during equilibration ensured a very small effective dead volume and, therefore, a highly accurate determination of the amount of gas adsorbed. To provide high accuracy and precision in the determination of P/P_0, the saturation pressure P_0 was measured throughout the entire analysis by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. It should be noted that H_2 adsorption data should not be displayed as P/P_0 because there is no saturation pressure defined for supercritical H_2. An ultra-high purity (UHP, 99.999% purity) grade of N_2, H_2 and He gases was used throughout the adsorption experiments.

Volumetric high-pressure gas adsorption measurements at Southwest Research Institute

Low-temperature hydrogen adsorption isotherms were independently measured (SwRI) from the same synthetic batch of MOF-177 as in ref. 4 (see Table 1). Approximately 210 mg of MOF-177 sample was transferred to a high-pressure sample vessel constructed from 316L stainless-steel tubing (4.6 mm i.d. × 45 mm length). A polished stainless-steel dowel was used to lightly compact the sample in the vessel, thereby minimizing the intergranular free volume. The remaining free volume above the sample was minimized by inserting segments of polished stainless-steel rod, precisely milled to be slightly smaller than the inner diameter of the vessel, and accommodating a center bore for the transfer of gas. A high-pressure Sieverts-type volumetric analyzer (Hy-Energy Scientific Instruments, Model PCTPro2000) was used to quantify the isothermal Gibbs excess for H_2 adsorption in the MOF-177 sample at 77 K.[16] Prior to analysis, the total free volume of the sample and vessel was determined from the expansion of low-pressure helium (<5 bar) while maintaining isothermal conditions. A typical free volume determined for this system was 9.50 ± 0.03 cm^3. The assumption that helium does not interact adsorptively with MOF-177 was independently confirmed by measuring the helium-derived free volume of pure silicon granules (99.999%, Aesar) at low pressures (<5 bar), using a mass of silicon equivalent in volume to the helium-derived volume previously determined for the sample. The difference between the two free volume measurements was in fact not measurable.

Table 1 Summary of high-pressure H_2 adsorption measurements for MOF-177

		Surface excess amount			Absolute adsorbed amount			
Investigator	Surface area[a]/m^2 g^{-1}	mg g^{-1}	g L^{-1}	(pressure/bar)	mg g^{-1}	g L^{-1}	(pressure/bar)	Method
SwRI #1	5640 (4750)	76	32	(66)	112	48	(72)	Volumetric
SwRI #2	5640 (4750)	74	32	(57)	115	49	(72)	Volumetric
UCLA	5250 (4630)	73	31	(52)	111	48	(75)	Gravimetric
UM[b]	5640 (4750)	75	32	(69)	114	49	(78)	Volumetric

[a] Langmuir model (BET model). [b] Data from ref. 4.

After re-evacuating the sample vessel, low-temperature isotherms were achieved by immersing the sample vessel in a LN_2 bath, then allowing the vessel and sample to equilibrate at 77 K for 2 h before commencing the experiments. The liquid level of LN_2 was *carefully* adjusted to a predefined mark on the sample vessel above the sample position so as to mitigate density fluctuations of gas in the column above the vessel, which are reflected as pressure fluctuations by the pressure transducers of the instrument. H_2 adsorption isotherms were constructed in replicate by dosing the initially evacuated sample in a step-wise fashion, allowing sufficient time for equilibration between each pressure increment in the profile such that the variance in the time course profile for H_2 uptake was less than 0.001 wt%.

To account for the temperature gradient that arises between the calibrated dosing volume (304 K) and the sample vessel (77 K), a linear correction factor (C_f) was derived by calibrating the effect of this gradient on the gas density in this segment of the instrument. Experimental determination of C_f was achieved by replacing the sample with high purity silicon granules and measuring the adsorption isotherm (77 K) over the requisite pressure regime.

Hydrogen gas concentrations were corrected for non-ideal behavior by computing the pressure dependence of the compressibility factor derived semi-empirically from *PVT* tables.[17] The adsorbed concentrations of H_2 (excess mass) were then computed using the previously measured free-volume and thermal-gradient correction factor (C_f).

The accessible volume was calculated in the Void Space routine in Cerius^2 using the default settings (1.3 Å probe radius which is half of the kinetic diameter of helium), which was used for the estimation of absolute adsorbed amount (*i.e.*, V_{pore} = 1.56 cm^3 g^{-1}).[18] In the unit conversion (mg g^{-1} → g L^{-1}), the bulk density of MOF-177 (d = 0.427 g cm^{-3}) was applied to the amount of H_2 uptake (*i.e.*, 10 mg g^{-1} = 4.27 g L^{-1}).

Gravimetric high-pressure gas adsorption measurements at UCLA

Gravimetric H_2 sorption isotherms were measured by use of a GHP-300 (Gravimetric High Pressure analyzer) from the VTI Corporation.[16] A Rubotherm magnetic suspension balance MC-5 was used to measure the change in mass of samples suspended within a tube (22 mm i.d.) constructed from Inconel 625 under a chosen atmosphere. Prior to admittance of the analyte gas, the entire chamber and manifold were evacuated at room temperature, and the weight of the Al sample bucket (12 mm i.d. × 21 mm length) was measured. After loading the MOF-177 sample (*ca.* 200 mg) the system was purged at room temperature with hydrogen and helium, and the sample was outgassed, using a turbomolecular drag pump (Pfeiffer, TSH 071 E), until a constant mass was attained. When H_2 gas was used, water and other condensable impurities were removed with a LN_2 trap. Pressure was measured with a MKS Baratron transducer 120AA (0 to 1000 Torr) and an electronic Bourdon gauge-type transducer (Mensor, up to 1500 psi). The adsorbate was added incrementally, and data points were recorded when no further change in mass was observed. The temperature in the Inconel tube was also monitored with a platinum resistance thermometer.

To obtain the excess adsorption isotherm, all data points were corrected for buoyancy and the thermal gradient that arises between the balance (313 K) and the sample bucket (77 K). Buoyancy and thermal-gradient effects exhibited by the bucket and the components associated with the magnetic suspension balance were corrected on the basis of the change in mass of the empty bucket within the analyte gas at 77 K. The weight loss due to the buoyancy of the adsorbent was determined by multiplying the volume of the MOF-177 framework skeleton by the density of H_2[20] (*i.e.*, corrected mass for buoyancy is $V_{skeleton} \times \rho_{bulk}$). The volume of the MOF-177 framework skeleton was determined from the helium (<15 bar) buoyancy curve at 298 K using the same gravimetric system.[19] The absolute amount of gas adsorbed was calculated from the density of the framework skeleton (inverse of the skeleton volume) and the crystallographic density (d = 0.427 g cm^{-3}), leading to an accessible pore volume (V_{pore} = 1.69 cm^3 g^{-1}) for MOF-177.[18]

Estimation of absolute adsorbed amount

There are two components of gas adsorption: namely, the surface excess and the absolute adsorption.[21] Fig. 2 illustrates these components based on the definition of the Gibbs dividing surface.[22] When an adsorbent is exposed to gas molecules, some of the gas molecules are physisorbed on the surface. However, since this process is an equilibrium between adsorption and desorption, the bulk density (*i.e.*, the amount not adsorbed but present in the free volume) of the adsorbate is usually not zero. Therefore, the observed mass change in the sample is represented by the difference between the total adsorbed amount and the bulk density of the adsorbate. Experimental measurements are reported as a surface excess amount.[21] To estimate the absolute amount of gas adsorbed, the thickness of the adsorbed layer must be known. However, this variable, and its spatial profile, cannot be measured experimentally. Instead, the absolute adsorption can only be estimated theoretically using, for example, Monte Carlo simulations.[23]

Although the surface excess mass is a useful concept, from the viewpoint of hydrogen storage, the total amount that a material can store is more relevant to use for hydrogen as a fuel. However, at high temperatures and pressures (*i.e.*, above the critical temperature and pressure of hydrogen), the density profile of the adsorbed phase becomes more diffused and, therefore, it is not possible to distinguish between the adsorbed and bulk phases with the present techniques. In this situation the surface excess is the only experimentally accessible quantity, and there is not a reliable method to estimate the absolute adsorbed amount with high accuracy, although many efforts have been devoted to resolve this issue.[24] Therefore, we estimate the absolute amount of hydrogen adsorbed using a simple equation:[25,26]

$$N_{abs} = N_{ex} + \rho_{bulk} V_{pore} \qquad (1)$$

where N_{abs} is the absolute adsorbed amount, N_{ex} is the surface excess amount, ρ_{bulk} is the bulk density of H_2,[19] and V_{pore} is the pore volume for MOF-177.

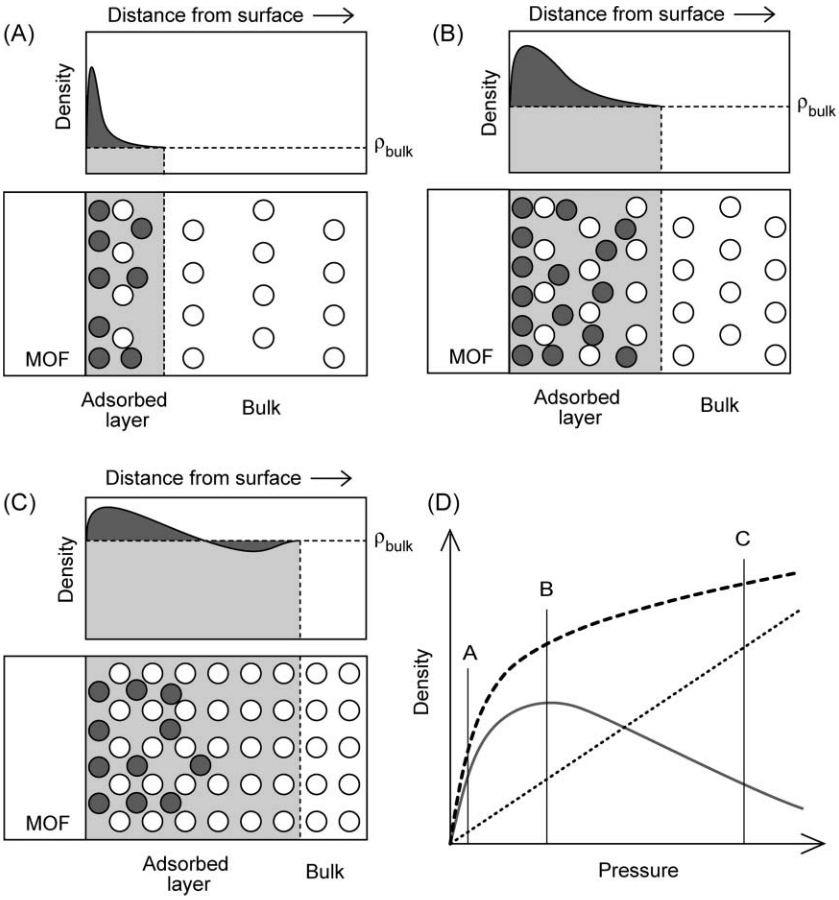

Fig. 2 (A–C) Schematic representation of the relation between the surface excess mass and absolute adsorbed amount. Dark gray regions in the top diagrams represent the surface excess mass. Since absolute adsorbed amounts should include all gas molecules (dark gray and white circles in the bottom boxes) in the adsorbed layer, summation of the dark gray and light gray areas in the diagrams corresponds to the absolute adsorbed amount. The density of excess mass is not necessarily higher than the bulk fluid density at all locations, and negative excess mass can be obtained under large bulk density. (D) The surface excess amount (solid curve) possesses a maximum value because the excess mass can be decreased in the high-pressure region, while total gas uptake (dashed curve) should increase monotonically with an increase in the pressure because of the contribution from the large bulk density (dotted curve, ρ_{bulk}) of the adsorbate.

Results and discussion

Low-pressure gas adsorption

MOF-177 samples showed significant N_2 uptake at low pressures, whose profile can be classified as a Type I isotherm (Fig. 3). The N_2 uptake (1200 cm^3 g^{-1} at P/P_0 = 0.25) corresponds to an *apparent* surface area of 5250 m^2 g^{-1} using the Langmuir model (4630 m^2 g^{-1} for the BET model[27] using the adsorption branch of the N_2 isotherm over $0.03 < P/P_0 < 0.07$).

Low-pressure H_2 isotherms of MOF-177 were measured at 77 and 87 K, respectively, and are shown in Fig. 4. Under these conditions, H_2 adsorption isotherms are not saturated, because these temperatures are above the critical temperature (33 K for hydrogen). The rapid pressure equilibration (*ca.* 5 min per step) and absence of hysteresis indicate that H_2 molecules are reversibly physisorbed by MOF-177. The maximum uptake at 800 Torr for 77 and 87 K was 142 and 82 cm^3 g^{-1}, respectively. The isotherm measured at 77 K shows good agreement with previously reported gravimetric data (12.45 mg g^{-1} at 751 Torr, see secondary axis for adsorbed amount of H_2 in Fig. 4) in Ref. 2.

In general, when gas molecules are adsorbed on the pore surface, heat is released, indicating that the adsorbed amount should be influenced by the measurement temperature.

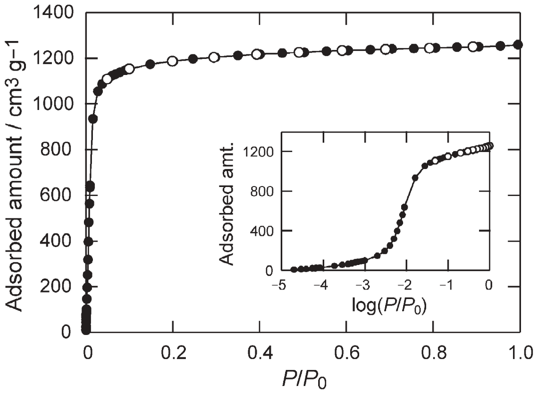

Fig. 3 N_2 isotherm for MOF-177 measured at 77 K. Filled and open circles represent adsorption and desorption branches respectively. (Inset) Logarithmic relative pressure expression of N_2 isotherm for MOF-177.

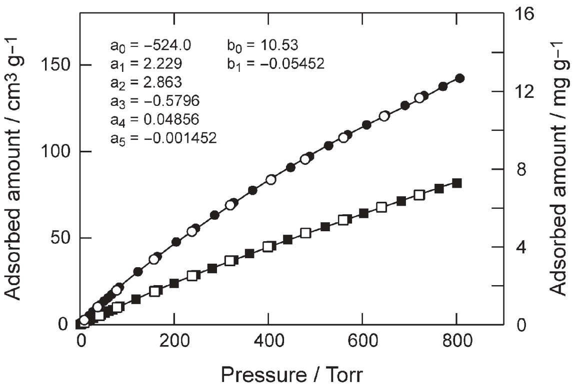

Fig. 4 H_2 isotherms measured at 77 K (circles) and 87 K (squares) for MOF-177. Filled and open symbols represent adsorption and desorption branches respectively. These symbols are traced by fitting curves from eqn (2) with the presented parameters.

Therefore, the temperature dependence of H_2 uptake provides useful information regarding H_2–adsorbent interactions. In particular, estimation of the coverage-dependent isosteric heat of adsorption (Q_{st}), which may allow estimation of the number of strong binding sites per unit cell, is a useful diagnosis. For the calculation of the isosteric heat of adsorption, an empirical equation (for instance, the Langmuir–Freundlich model) is applied,[28] so, in most cases, the differential enthalpy derived at low coverage is suspect because the model fits were poor (see Fig. 5), even though the low-coverage region is mechanistically more interesting than at high coverage. To estimate reliable isosteric heats of adsorption, a virial-type expansion comprising the temperature-independent parameters a_i and b_i should be used and was applied:[3,5,29]

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (2)$$

where P is pressure, N is the adsorbed amount,[30] T is temperature, and m and n represent the number of coefficients required to adequately describe the isotherms. From these results, the isosteric heat of adsorption is calculated from

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad (3)$$

where R is the universal gas constant.

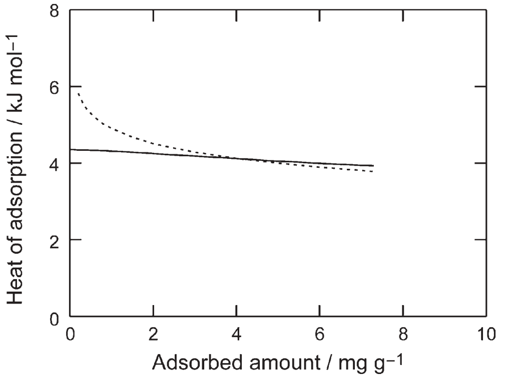

Fig. 5 Coverage dependence of the isosteric heat of adsorption for H_2 in MOF-177 calculated from fits of its 77 and 87 K isotherms (solid curve). For comparison, the isosteric heat of adsorption was also estimated based on the Langmuir–Freundlich model (broken curve). The obtained Q_{st} value is apparently overestimated at low coverage region due to poor fitting. Although the virial-type expansion fits better than the Langmuir–Freundlich model, it is reasonable to apply three or more temperatures for the Q_{st} calculation with high accuracy.

The initial value of the isosteric heat of adsorption for MOF-177 is estimated to be 4.4 kJ mol^{-1}, which decreases slightly with an increase in the surface coverage of hydrogen (Fig. 5). The profile is quite similar to that of IRMOF-1,[3] aside from the slightly lower adsorption enthalpy compared to IRMOF-1. It should be noted that the nearly constant Q_{st} value is attributed to the linear shape of the H_2 isotherms in the low-pressure region. Although the results indicate that MOF-177 does not have a strong hydrogen binding site, as indicated by the low Q_{st} value, the constant Q_{st} value for the isotherms in accordance with Henry's law is a desirable property for H_2 storage materials.[32] In such a scenario, H_2 storage capacity is not influenced by surface coverage, leading to a large amount of available H_2 as the low-pressure limit of the delivery system is approached.

High-pressure H_2 adsorption

High-pressure hydrogen uptake properties for MOF-177 were evaluated by use of volumetric and gravimetric techniques. Isotherms acquired volumetrically are illustrated in Fig. 6A. These isotherms saturate at near 60 bar with maximum surface excess amounts of 75 mg g^{-1}. The profiles are similar to the data which we have reported previously (Fig. 6C).[4] Gravimetric measurement provides a similar profile as the volumetric isotherm measured at 77 K (Fig. 6B). The reversible isotherm indicates that H_2 is physisorbed even in the high-pressure region. After buoyancy correction the uptake (surface excess amount) is 73 mg g^{-1} at a saturation pressure of approximately 50 bar. We presume that the small difference between volumetric and gravimetric uptake is attributed to the difference in the apparent surface area of MOF-177 samples (see inset of Fig. 6). It should be noted that the saturation pressure for gravimetric measurements is slightly lower than that determined by volumetric measurements. This may be attributed to small inaccuracies in the He buoyancy correction, because the total volume of adsorbents (*i.e.*, MOF-177 sample and adsorbed H_2 molecules) can be slightly increased when gas molecules are adsorbed on the surface of adsorbents, while we assume that no He molecule is adsorbed on the MOF-177 surface. Consequently buoyancy attributed to the volume of adsorbed H_2 cannot be corrected, leading to an underestimation of H_2 uptake in the high-pressure region. In principle, it is possible to compensate for these differences, however, we will address this issue in future work.[33]

Absolute adsorbed amounts at 70 bar are estimated to be 113 mg g^{-1} from the measurements, which corresponds to 48.3 g L^{-1}. Since the absolute adsorbed amount cannot be measured experimentally, it is not possible to confirm whether or not this value is reasonable. Therefore, we compared the absolute H_2 uptake with N_2 adsorption data which were taken at 77 K (Table 2).[34] In contrast to the difference in gravimetric uptake, the volumes of adsorbed gases between N_2 and H_2

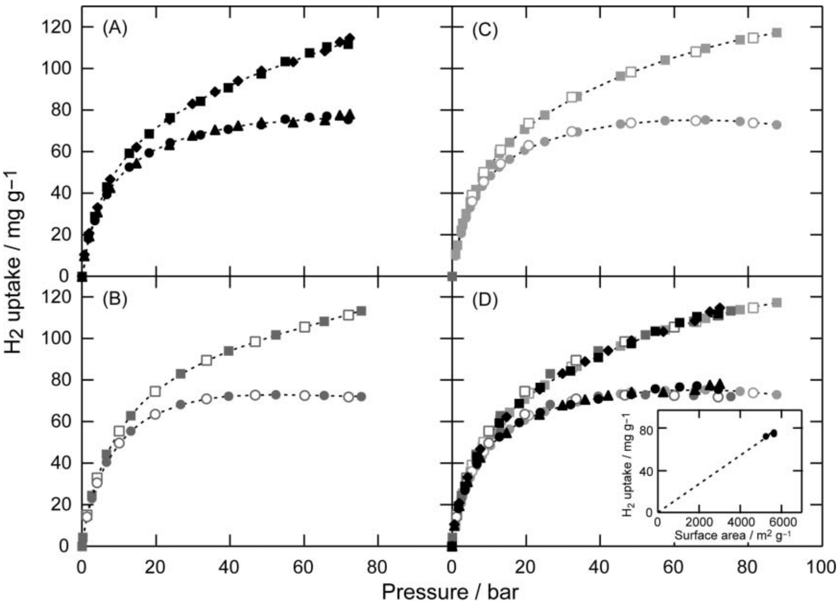

Fig. 6 High-pressure H_2 isotherms for MOF-177 taken by volumetric (A) and gravimetric (B) methods (circles and triangles). As a reference, volumetric data in ref. 4 are shown in (C) and all plots are overlaid in (D). Filled and open symbols represent adsorption and desorption branches, respectively. Square and diamond symbols which are absolute adsorbed amounts are obtained from eqn (1). Connecting traces are guides for eyes. Inset: surface area dependence of H_2 uptake.

(*i.e.*, $cm^3\ g^{-1}$) are quite similar. Consequently, the number of adsorbed N_2 and H_2 molecules in the formula unit is almost the same. This clearly demonstrates that the micropores in MOF-177 are in large part occupied by H_2 molecules in the high-pressure region. This observation can be supported by the ratio between the absolute adsorbed amount for H_2 and the liquid density of H_2 (*ca.* 68%, see Table 2). Thus it is presumed that H_2 adsorption under these conditions can be explained by a micropore filling model, in contrast to a monolayer coverage model which might otherwise be widely assumed on the basis of weak adsorbent–dihydrogen interactions. Indeed, the idea that the H_2 storage capacity strongly depends on the pore volume of the adsorbent is consistent with Monte Carlo simulations for various MOFs.[23] In light of the fact that the molecular diameter of H_2 is small and that the isotherm for the absolute adsorbed amount is not saturated, the DOE 2010 volumetric target of 45 g L^{-1} could probably be met if a high-pressure H_2 container is engineered for operation at cryogenic temperatures. However, as predicted,[32] higher binding energies of adsorption (Q_{st}) than exhibited by unmodified MOFs are required for room temperature H_2 storage in addition to the high surface-areas afforded by these materials.

Table 2 H_2 and N_2 adsorption data for MOF-177

Guest	Adsorbed amount[a] $cm^3\ g^{-1}$	$mg\ g^{-1}$	$g\ L^{-1}$	No. of guests per f.u.[b]	Ratio[c] (%)
H_2	1270	113	48.3	65	68
N_2	1200	1500	641	61	79

[a] The absolute adsorbed amount at 77 K and 70 bar for H_2; low-pressure data at 77 K for N_2. [b] Formula unit (f.u.) is $Zn_4O(BTB)_2$. [c] Comparison with corresponding liquid densities (71 g L^{-1} for H_2, 806 g L^{-1} for N_2).

Under more practical conditions, such as actual gas cylinders, it is important to realize that the discharge pressure of a cylinder needs to be at least 1.5 bar.[32] In other words, a large isosteric heat of adsorption may reduce the amount of H_2 available for use. In order to consider this issue, absolute H_2 amounts for MOF-177 were plotted. As shown in Fig. 7, the amount of H_2 delivered for MOF-177 is 40 g L^{-1} when the pressure ranges from 1.5 to 70 bar. Therefore, we propose that an alternative metric for achieving the DOE target should be defined on the basis of the total amount of delivered H_2 (*e.g.*, an absolute adsorbed amount ranging from 1.5 to 100 bar),[32] instead of a simple surface excess mass of H_2.

Conclusions

The utility of MOF-177 as a benchmark material for high-pressure and low temperature H_2 adsorption was demonstrated by verification of its uptake capacity [surface excess

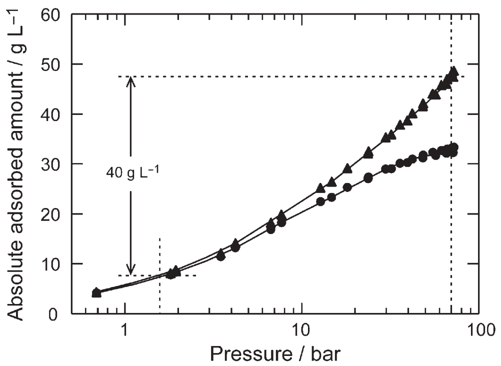

Fig. 7 Absolute adsorbed amount (triangles) and surface excess amount (circles) for MOF-177 expressed on a log scale.

weight uptake of 75 mg $g^{-1}$and total (absolute) H_2 uptake of 110 mg g^{-1} (47 g L^{-1}) at 70 bar, 77 K]. The theoretical H_2 uptake capacity depends on the pore volume of the adsorbent rather than the enthalpy of adsorption, especially at high pressures and low temperature. However large binding energy (15–20 kJ mol^{-1}) is required for viable room temperature storage.[32] Adsorbents possessing large binding energy and high density of binding sites need to be developed to confine large amounts of H_2 molecules for use as a fuel in automotive applications.

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