Exceptional H2 Saturation Uptake in Microporous Metal−Organic Frameworks

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Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressures as a gas or very low temperatures as a liquid.[1] The desire to store hydrogen with sufficient efficiency to allow its use in stationary and mobile fueling applications is spurring a worldwide effort in new materials development.[2] The Department of Energy, in its Year 2010 guidelines, has set performance targets for on-board automobile storage systems to have densities of 60 mg H_2/g (gravimetric) and 45 g H_2/L (volumetric).[3] Given that these are system goals, a practical material will need to have higher capacity when the weight of the tank and associated cooling or regeneration system is considered. The size and weight of these components will vary substantially depending on whether the material operates by a chemisorption or physisorption mechanism. In the latter case, metal−organic frameworks (MOFs) have recently been identified as promising adsorbents for H_2 storage, although little data are available for their sorption behavior at saturation,[4] a critical parameter for gauging the practicality of any material. Herein we report sorption data collected for seven MOF materials at 77 K which leads to saturation at pressures between 25 and 80 bar with uptakes from 2.0 to 7.5 wt %. In this study, we show that H_2 saturation uptake in MOFs correlates well with surface area, and contrary to a widely held belief, viable volumetric densities in highly porous structures can indeed be achieved.

Figure 1 illustrates the metal oxide secondary building units (SBUs) and the organic carboxylate links of the MOFs investigated here. The isoreticular (IRMOF) series, IRMOF-1, -6, -11, and -20, is derived from linking the basic zinc acetate unit, $Zn_4O(CO_2)_6$, with linear ditopic carboxylates.[5] MOF-177 is constructed from this same SBU and the tritopic link BTB.[6] MOF-74 is constructed from infinite 3_1 (or 3_2) helical rods of composition $Zn_3[(O)_3(CO_2)_3]$,[7] and HKUST-1 is composed of the $Cu_2(CO_2)_4$ paddlewheel SBU linked by benzene-1,3,5-tricarboxylate.[8]

The MOFs chosen represent a subset of well characterized materials that exhibit some of the highest surface areas experimentally determined to date (Figure 1). These materials vary in chemical functionality, metrics of the link, and the nature of the SBU. Their structures are derived from noninterpenetrated nets, with the exception of the doubly interpenetrated IRMOF-11, and three distinct SBUs. Crystalline samples of all the MOFs were prepared and activated prior to sorption measurements according to recently optimized procedures.[9] Prior to H_2 sorption studies, apparent surface areas of the activated materials were calculated from the adsorption branches of the N_2 isotherms obtained at 77 K with the assumption of monolayer coverage of N_2 on the surface.[10]

Figure 2 shows the resulting H_2 sorption isotherms up to 90 bar at 77 K,[11] where saturation binding of H_2 is achieved. The isotherms do not show significant hysteresis, consistent with physisorption of supercritical H_2.[12] The saturation uptakes vary widely; for MOF-
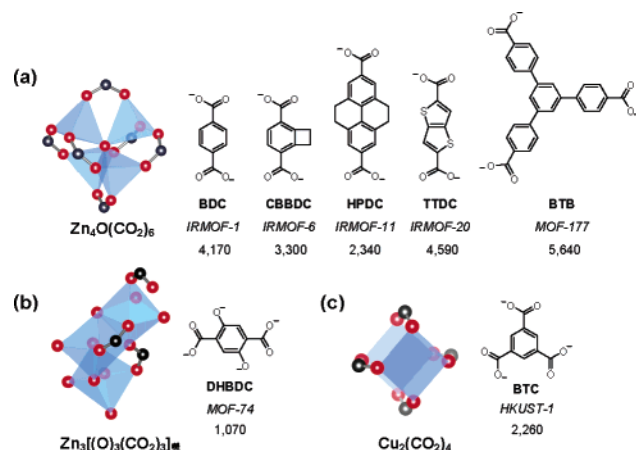
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Figure 1. (a) $Zn_4O(CO_2)_6$-based MOFs in italics derived from the link in parentheses: *IRMOF-1* (BDC), *IRMOF*-6 (CBBDC), *IRMOF-11* (HPDC), *IRMOF-20* (TTDC), and *MOF-177* (BTB). (b) *MOF-74*, based on $\{Zn_3[(O)_3(CO_2)_3]\}_\infty$ 3_1 helices and DHBDC. (c) *HKUST-1*, based on $Cu_2(CO_2)_4$ paddlewheels and BTC. Langmuir surface areas (m^2/g) are given below each link for the corresponding MOF.
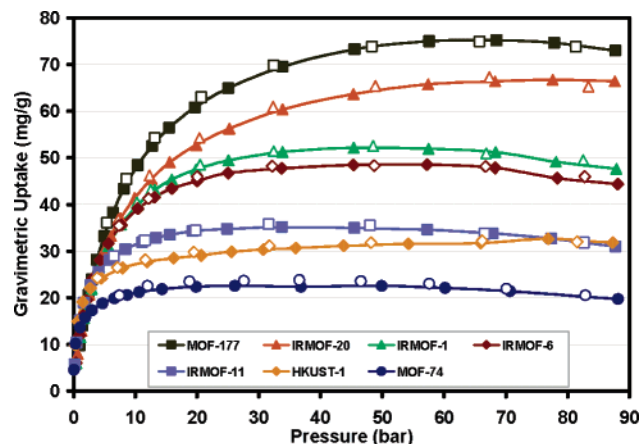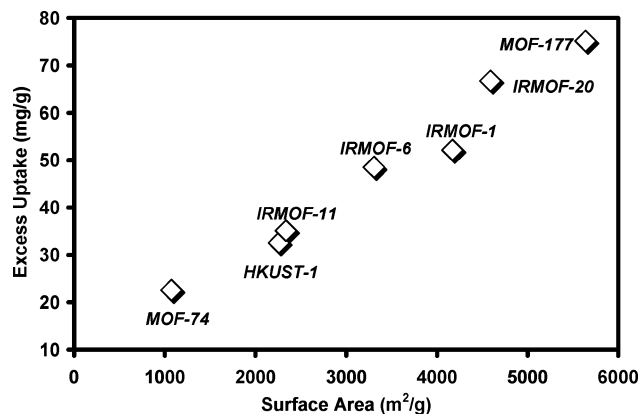

Figure 2. High-pressure H_2 isotherms for activated materials at 77 K in gravimetric units (mg/g) representing surface excess adsorption, that is, the amount of H_2 in excess of what would occupy the same free volume if the adsorbent was absent. Filled markers represent adsorption, open markers denote desorption.

74, the uptake at saturation (26 bar) is 2.3 wt % and 3.5 wt % for IRMOF-11 (34 bar), whereas for MOF-177 and IRMOF-20, saturation is reached between approximately 70 and 80 bar, giving H_2 uptakes of 7.5 and 6.7 wt %, respectively. A plot of gravimetric uptake as a function of apparent surface area reveals a nearly linear correspondence (Figure 3). This result stands in stark contrast to those obtained at low pressures where MOF-74, HKUST-1, and IRMOF-11, the three lowest surface area materials, showed maximal uptake.[5c] This difference may arise from binding to relatively higher affinity open-metal sites (present in MOF-74 and HKUST-1) or to constricted pores in IRMOF-11. Such behavior is important in the

Figure 3. Saturation H$_2$ uptake plotted against Langmuir surface area.
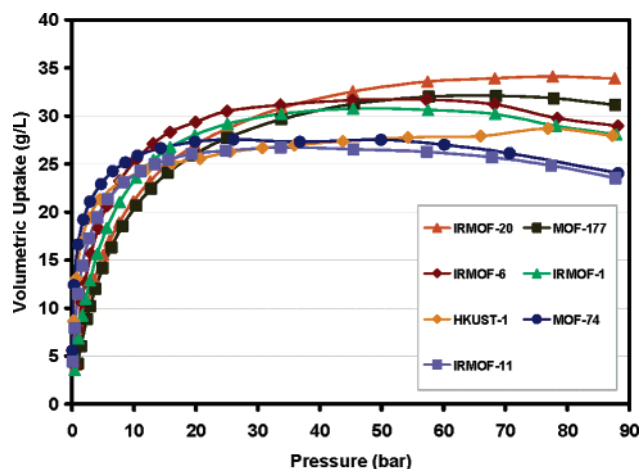

Figure 4. High-pressure H$_2$ isotherms for activated materials measured at 77 K in volumetric units (g/L).

area of separations. These structural attributes, when incorporated into higher surface area materials, should lead to an ideal combination of high affinity and capacity.

Although gravimetric capacity is often a major target for research in H$_2$ storage materials, there are practical limits associated with the tank volume required to house the sorbent which makes volumetric capacity just as critical a parameter to consider. Accordingly, the gravimetric data have been converted to volumetric units (g H$_2$/L) using the crystallographic densities of each MOF (Figure 4). By this metric, the MOF materials are much more similar in their sorption capacities due to canceling effects derived from the different densities of the materials. It should be noted that bulk packing densities will vary somewhat between materials and decrease the practical volumetric capacity in a storage system.

IRMOF-20 and MOF-177 show the best uptake on a volumetric basis due to a combination of substantial H$_2$ uptake and moderate densities. The values of 34 g/L for IRMOF-20 and 32 g/L for MOF-177 are well within the realm of the 2010 DOE target of 45 g/L,[3a] which demonstrates that the volumetric capacity of MOFs is feasible as a storage medium and dispels the misconception that porous materials will inherently have poor volumetric storage capacity. This is because highly porous materials can have small pores. MOF-74 has the highest density of any of the MOFs examined here (1.22 g/cm^3 compared to 0.477 g/cm^3 for MOF-177 which is the lowest) and thus shows a volumetric uptake of 28 g/L, which is better

performance than the gravimetric results taken alone imply. Although the density of IRMOF-11 is approximately 50% greater than that of MOF-177, it is still the lowest performing material on a volumetric basis.

The gravimetric and volumetric storage densities of H$_2$ in MOFs are approaching the limits of practical utility. Surface area values show the best correlation with gravimetric uptake. These results demonstrate the critical role of the organic linker and are clearly inconsistent with models where the metal oxide units dominate sorption behavior; indeed, the MOFs with the highest uptake, IRMOF-20 and MOF-177, have a relatively low proportion of metal oxide to organic link. Another key finding is that volumetric storage density, even in materials with extremely high porosity, can be excellent. The highest uptake by this metric is realized in IRMOF-20 because this structure combines extremely high surface area with moderate density.

Supporting Information Available: Hydrogen isotherms for all materials and details of measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Within the limits of applying the Langmuir and BET models to Type I isotherms, surface areas derived from both methods are reported (see Supporting Information). In general, these values are higher than the previously reported gravimetric data due to better thermal contact with the sample.

(11) H$_2$ sorption isotherms were measured by the static volumetric method at 77 K using a customized HPVA-100 instrument from the VTI Corporation. The implicit assumption is that He binding to the MOFs is negligible. As pointed out by one reviewer, this assumption may lead to underestimation of the hydrogen excess uptake. Details of the instrument and treatment of the data are given in the Supporting Information.

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