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Hydrogen Sorption in Functionalized Metal−Organic Frameworks

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Reticular synthesis (logical construction of networks from molecular building blocks) has yielded a new class of crystalline porous materials commonly referred to as metal−organic frameworks (MOFs) in which metal ions and clusters are linked by organic units.[1] The ability to prepare MOFs in high yield and with adjustable pore size, shape, and functionality has led to their study as gas sorption materials.[2−4] We have demonstrated that systematic variation of the organic component in isoreticular metal−organic frameworks (IRMOFs) has a marked effect on their capacities for methane.[3] More recently, we discovered that IRMOFs are also capable of storing significant amounts of H_2,[4] and inelastic neutron-scattering studies of molecular hydrogen adsorbed in IRMOF-1 pointed to the organic unit as one of the important adsorption sites. Thus, there is an acute need to collect and analyze more hydrogen uptake measurements on these materials to establish the favorable factors for its storage. In this study, we report such measurements on a set of MOF materials in which the $Zn_4O(CO_2)_6$ cluster is linked by chemically diverse organic units. With these results, we consider the impact of internal surface area and the number of rings in the organic link on storage capacity.

Five materials were prepared from the carboxylate links shown in Figure 1. These include IRMOFs-1, -8, and -11,[3] the recently described MOF-177,[5] and the new compound IRMOF-18; the structures of these have been determined by single crystal X-ray diffraction analyses. Crystalline samples of these materials were synthesized in large quantities (typically 1−2 g) by solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ or ZnO with the respective organic carboxylic acid by previously described methods.[3,5,6a] Activation of the porous materials was achieved by exchanging the included solvent molecules with chloroform and then removing this labile guest by evacuation ($<10^{-3}$ Torr) in a microgravimetric sorption apparatus until mass equilibration. The N_2 sorption isotherm was measured gravimetrically for each of the samples to confirm their porosity, followed by measurement of H_2 uptake at 77 K (see Table 1). Independent measurements were performed on the same samples by a volumetric method to confirm these observations.[6b] The crystalline phase purity of each sample was confirmed by powder X-ray diffraction (PXRD) both before and after the sorption measurements.

This subset of materials was chosen for their large surface areas and subtle chemical diversity. Each framework is constructed by octahedrally linking $Zn_4O(CO_2)_6$ clusters with organic units. As a result, the surface sites on the inorganic component should be identical in each case,[7] and any differences in hydrogen capacity can be attributed to differences in the organic units. Minor variances exist between the structures of these frameworks, and these are not expected to alter the interaction with hydrogen since large voids are defined in all cases. IRMOFs-1, -8, and -18 each exhibit a simple cubic topology (that is also described more rigorously as the B net in CaB_6),[3] while IRMOF-11 contains two catenated frameworks of this type. The topology of the net underlying MOF-177 has mixed (3,6)-connectivity due to the tritopic linkage of BTB.[5]

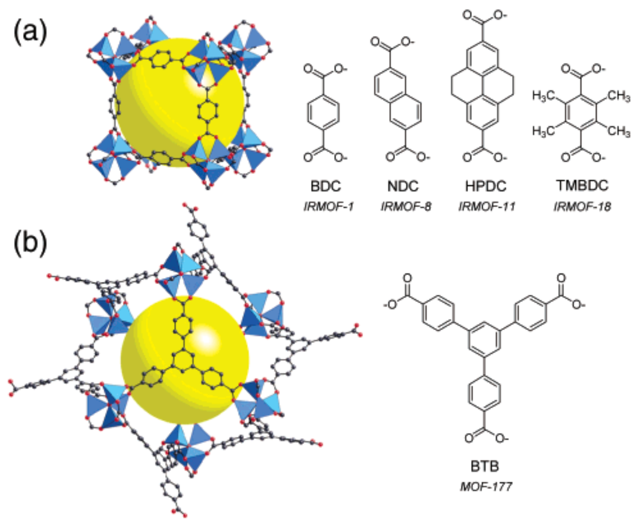

Figure 1. (a) Isoreticular (having the same underlying topology) metal−organic frameworks, $Zn_4O(\mathbf{L})_3$, are constructed by linking zinc oxide clusters with linear carboxylates **L** such as those shown. (b) The structure of MOF-177, $Zn_4O(BTB)_2$, is formed by linking the same clusters with a trigonal carboxylate. The large void regions are illustrated by yellow spheres with diameters equal to the distance of separation between the frameworks' van der Waals surfaces.

Table 1. Sorption Data for Metal−Organic Frameworks Measured Gravimetrically at 77 K

material	N_2 (mg/g)	A_{surf}[a] (m^2/g)	H_2[b] (mg/g)	H_2 per f.u.[b]
IRMOF-1	965	3362	13.2	5.0
IRMOF-8	421	1466	15.0	6.9
IRMOF-11	548	1911	16.2	9.3
IRMOF-18	431	1501	8.9	4.2
MOF-177	1300	4526	12.5	7.1

[a] Calculated assuming a monolayer coverage of close-packed N_2 with a cross-sectional area of 16.2 Å^2/molecule. [b] At 1 atm, f.u. = $Zn_4O\mathbf{L}_x$ formula unit.

The chemical differences of the organic units manifest themselves in the hydrogen sorption behavior. The isotherms in Figure 2 each display distinct initial slopes and curvatures. These differences become more apparent when the isotherms are normalized to each formula unit. At the highest pressure achieved in these experiments the maximum uptake varies considerably, from 4.2 molecules of H_2 per formula unit in IRMOF-18 to more than twice this value in IRMOF-11 (Table 1). Qualitatively, the maximum uptake scales with the number of organic rings per formula unit. The similar capacities of IRMOFs-1 and -18 also demonstrate a potential lack of dependence on the pendant groups adorning the phenylene spacer. Although they differ in gravimetric capacity of H_2, this is mainly due to their difference in density. Notable is the large value of the initial slopes of the IRMOF-8 and -11 isotherms, indicating higher affinity for molecular hydrogen. To further contrast the uptake by these compounds, the H_2-accessible volume fraction of each

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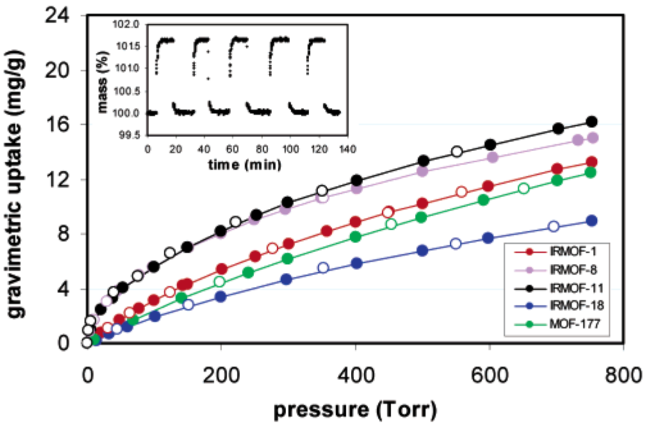

Figure 2. Hydrogen isotherms for the activated materials measured gravimetrically at 77 K (adsorption, ●; desorption, ○). The inset shows the time-dependent cycling of IRMOF-11 between 0 and 1 atm of H_2.

structure was calculated along with the volume occupied by sorbed hydrogen at 1 atm (see Supporting Information). These revealed an approximately inverse relationship between the accessible volume fraction and the percentage of these pores occupied by hydrogen.

Since the condensation pressure of hydrogen is substantial at 77 K, only a small part of the complete isotherm is measured in each case, and the absence of plateaus indicates that surface saturation is not achieved. For compounds of this class, sorption isotherms of heavier gases are of type I,[3,5,8] as expected for microporous materials. The shape of these isotherms is more physically reasonable, yet smaller in magnitude than that of IRMOF-1 recorded in the initial study, possibly due to a small amount of gaseous contamination sorbed during the first dosing. The consistencies within the present sample set and between the volumetric measurements attest to their accuracy; furthermore, they are similar to those recently reported for other MOFs.[9] Facile desorption without hysteresis has also been demonstrated by all compounds, confirming the interaction is one of physisorption. Complete uptake and release can be achieved in a matter of minutes at this temperature, as shown by the cycling curve for IRMOF-11 in Figure 1c (inset). This behavior is typical for all MOFs analyzed, and the reproducibility of equilibrated masses demonstrates that uptake and release is nondestructive, as expected for this weak interaction.

Surface areas (A_{surf}) were calculated[10] from the measured nitrogen sorption isotherms and are listed in Table 1 along with the maximum measured gravimetric uptake of hydrogen by each compound. The samples exhibit a large range of surface area, even among highly related structures, and we have recognized that the nitrogen uptake is highly dependent on the activation procedure (note the increased surface area of IRMOF-1 from that previously reported[8]). It is possible that some pore blockage (by resilient guest species) or collapse occurs within crystallites that is not distinguished by PXRD. There is the lack of correlation between the apparent surface areas and hydrogen uptake, but it must be remembered that saturation of the surfaces by hydrogen is not accomplished at this pressure; therefore, the maximum uptake of each compound is unknown at this time. Attempts to fit these isotherms to the Langmuir expression revealed strong deviations, especially at low pressure, which is not unexpected for microporous materials. Regardless, the diverse behavior of these MOFs is in stark contrast to porous carbons, where the uptake scales with the surface area independent of morphology.[11] Our previous inelastic neutron-scattering experiments revealed a stronger interaction of molecular hydrogen with the framework of IRMOF-1 compared to porous carbons, and it is now becoming clear that this attraction can be further increased by altering the chemical nature of the organic component.

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Supporting Information Available: Volumetrically measured hydrogen isotherms for all materials, calculations of the accessible and hydrogen-occupied crystal volumes, and details of the synthesis and characterization of IRMOF-18, including single-crystal X-ray analysis (CIF and PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) (a) A typical synthesis of these materials is exemplified by that of IRMOF-18: 2,3,5,6-tetramethylbenzene-1,4-dicarboxylic acid (1.2 g, Chem Service) and zinc nitrate hexahydrate (12 g, Aldrich) dissolved in *N,N*-diethylformamide (600 mL, BASF) and heated for 48 h at 70 °C. Details are provided in the Supporting Information. (b) A Cahn C-1000 microgravimetric balance was operated within a gas manifold system in contact with a liquid nitrogen bath (vacuum level $<10^{-3}$ Torr) to measure the nitrogen and hydrogen isotherms from 0 to 1 atm. Volumetric measurements were performed using a Micromeritics Co. sorption apparatus (model 2010). Experimental details are described in ref 2a and the Supporting Information.

(7) An exception occurs for IRMOF-18, where the sterics of the TMBDC methyl groups orient the phenylene planes perpendicular to the carboxylate planes, exposing alternate faces of the Zn_4O clusters.

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