Hydrogen Storage

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Desorption Studies of Hydrogen in Metal–Organic Frameworks**

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The development of light materials that reversibly store and release large amounts of hydrogen is essential for the use of hydrogen as an energy carrier in mobile systems. One possible mechanism for hydrogen storage is physisorption by van der Waals interaction of H_2 molecules on porous materials. Besides the complete reversibility of the process, the great advantage of physisorption is the fast kinetics of adsorption and desorption. However, owing to the weak energies involved, high storage capacities are reached typically only at low temperatures of about 80 K. Furthermore, a great challenge is the design of new porous materials possessing strong adsorption sites which then enable the storage of large amounts of H_2 already at low pressures. Metal–organic frameworks (MOFs) possess a well-defined structure with a network consisting of ordered building blocks, metal oxide clusters and organic ligands, and a pore structure which can be tailored by chemical engineering.[1] Owing to these characteristics and to their extremely high specific surface area, MOFs are ideal materials to study the host–guest interaction with H_2 molecules. Therefore, many investigations, both experimental and theoretical, presently focus on the nature of the adsorption sites for hydrogen in metal–organic frameworks. However, different views exist about the possible sites concerning their strength of interaction. On the one hand, metal centers,[2,3] especially unsaturated coordination positions,[4,5] are proposed to be preferential adsorption sites for H_2 molecules. On the other hand, the pore size was shown to influence the hydrogen adsorption in porous materials like Prussian blue analogues[6] or aluminophosphates.[7] Furthermore, MOFs with small pores show a relatively high affinity for hydrogen.[8,9] The different views may arise from different H_2 concentrations applied in the individual studies. Some investigations show a preferential occupancy of metal sites at low hydrogen concentrations and a change to pore filling at higher concentrations.[10–12] However, further experiments are needed to clarify the adsorption mechanism of H_2 in MOFs.

Desorption studies of adsorbed hydrogen into a vacuum may reveal different adsorption sites which will show different desorption temperatures depending on the interaction energy. Owing to the weak interaction, the material has to be cooled down to very low temperatures, and therefore no systematic study is known so far. With a newly developed setup for thermal desorption spectroscopy (TDS) allowing temperatures down to 20 K, we have been able to identify different adsorption sites of hydrogen in various metal–organic frameworks (Cu-BTC, MIL-53, MOF-5, and IRMOF-8), and we have determined quantitatively the total amount of hydrogen which is desorbed.

Cu-BTC or HKUST-1 consists of dimeric Cu(II) paddle-wheel units with each Cu ion coordinated by four oxygen atoms of benzene-1,3,5-tricarboxylate ligands and by one H_2O molecule.[13] The resulting framework is a cubic structure with two types of pores,[14] larger pores with a square aperture of about 9×9 Å^2 and smaller side pockets which are accessible from the larger pores and possess a diameter of approximately 5 Å.[15]

MIL-53 is an Al-based MOF consisting of *trans* chains of corner-sharing $AlO_4(OH)_2$ octahedra interconnected by benzenedicarboxylate (BDC) linkers. The framework of MIL-53 possesses one-dimensional channels which, after removal of solvent and BDC molecules, have dimensions of 8.5×8.5 Å^2.[16]

MOF-5 is the metal–organic framework that has most attracted interest for hydrogen storage owing to its very high specific surface area and simple building units. MOF-5 possesses a cubic framework structure with Zn_4O clusters at each corner of a cube which are connected to each other by BDC ions. In MOF-5 the organic ligand is oriented alternately to the inside or to the outside of the network. The different orientation of the organic linker leads to the formation of two kind of pores with distinct diameter (15 Å and 12 Å).[17]

IRMOF-8 is part of the series of isoreticular metal–organic frameworks, like MOF-5, possessing the same cubic network topology. In this case the oxide-centered Zn_4O clusters are coordinated by naphthalene-2,6-dicarboxylate.[1] Owing to the length of the ligand and depending on the synthesis procedure,[18] catenation of the framework, that is, the growth of one framework into another, can occur in IRMOF-8. This intergrowth leads to the formation of smaller pores than expected for a purely cubic framework.[19]

The hydrogen adsorption isotherms measured at 77 K (Figure 1) show the different uptake properties of the metal–organic frameworks in different pressure ranges. It has been previously shown that the maximum hydrogen uptake (at high

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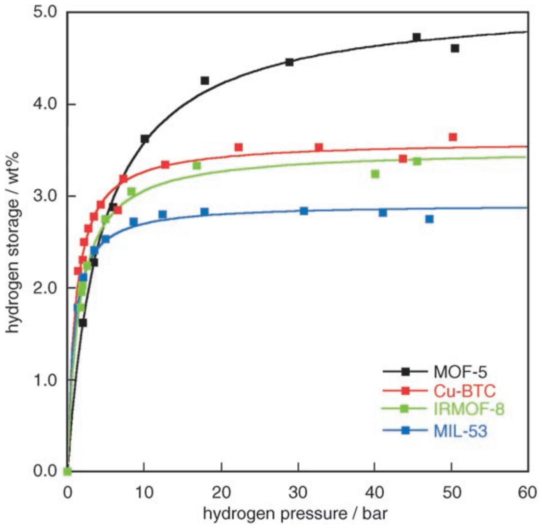

Figure 1. Hydrogen adsorption isotherms of MOFs at 77 K.

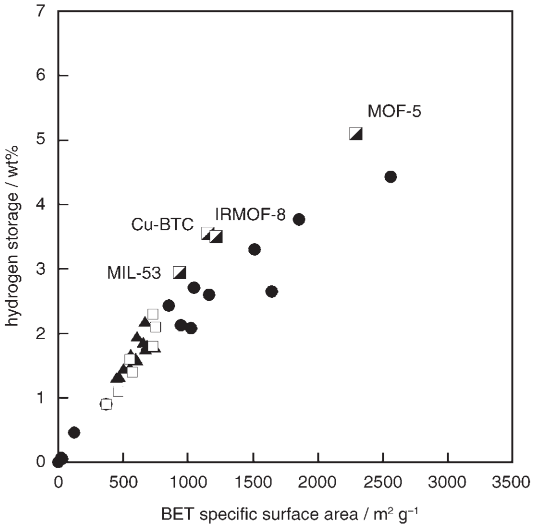

Figure 2. Maximum hydrogen storage of MOFs (half-filled squares), zeolites (triangles),[22] Prussian blue analogues (open squares),[24] and carbon materials (circles)[23] at 77 K correlated with their BET specific surface area.

Table 1: Langmuir and BET specific surface area, pore size, total amount of hydrogen desorbed (determined by TDS), and excess hydrogen uptake at 77 K determined volumetrically for the four different MOFs.

MOF	Langmuir/BET [$m^2 g^{-1}$]	Pore size [Å]	Desorb. H_2 [wt%]	Max. H_2 uptake (77 K) [wt%]
MOF-5	3840/2296	15, 12[17]	2.5 ± 0.2	5.1 ± 0.3
Cu-BTC	1958/1154	9, 5[15]	3.3 ± 0.2	3.6 ± 0.2
MIL-53	1779/933	8.5[16]	2.7 ± 0.2	2.9 ± 0.1
IRMOF-8	1922/1215	n.d.[a]	2.5 ± 0.5	3.5 ± 0.2

[a] Not determined.

pressures and 77 K) of MOFs correlates linearly with their specific surface area,[20,21] as is also the case for MOF-5, Cu-BTC, IRMOF-8, and MIL-53 (Table 1). Similar correlations have been reported as well for hydrogen storage in zeolites[22] and carbon materials.[23] A comparison between different classes of porous materials like MOFs, zeolites,[22] Prussian blue analogues,[24] and porous carbon samples[23] (Figure 2) shows that this correlation is valid even if materials with different composition and building blocks are considered. The scattering of the data in this graph can be attributed to the fact that the BET model does not appropriately describe the specific surface area of microporous samples, even if it is commonly reported in the literature. Nonetheless, the general trend of the maximum hydrogen uptake versus the specific surface area can be well recognized for the different materials, which indicates that at maximum hydrogen coverage the uptake does not at all depend on the composition of the material but only on the porosity of the material. However, at lower pressures the hydrogen-storage capacity mainly depends on the interaction strength between H_2 and the framework.[11] The existence of preferential adsorption sites which determine the uptake in the low-pressure region of the adsorption isotherms was observed, for example, by inelastic neutron scattering.[25] Especially at a very low H_2 loading (four H_2 molecules per formula unit) the authors could identify different binding sites in the MOF structures. However, a different influence of the framework on the interaction with hydrogen is expected at higher H_2 densities, at which, for example, the preferential sites are all occupied and more molecules are accommodated in the metal–organic framework.

To gain insight into the nature of the adsorption sites, thermal desorption spectra were recorded after cooling the sample in hydrogen atmosphere (25–80 mbar) to 20 K. Under this condition the surface coverage with hydrogen was similar to the coverage at 77 K and high pressures (Table 1), thus implying that these TDS spectra represent sites which are also occupied under technologically relevant conditions.

Figure 3 shows the H_2 desorption spectrum of Cu-BTC, MOF-5, IRMOF-8, and MIL-53 in the range between 20 K and 120 K, recorded with a heating rate of $0.1 \mathrm{K s^{-1}}$. After a careful calibration of the instrument it is possible to determine from the area under the desorption curve the total amount of desorbed hydrogen (Table 1).[26] All desorption spectra exhibit a hydrogen desorption peak at approximately 25 K, independent of the adsorbent material. Owing to the low temperature of desorption, which is close to the critical temperature of hydrogen, this desorption peak is assigned to liquid hydrogen or H_2 weakly adsorbed in multilayers (i.e., hydrogen adsorbed on another H_2 layer with an enthalpy close to the liquefaction enthalpy). In contrast to the other maxima in the TDS spectrum, the intensity of this peak can vary with cooling time and rate. Since this peak is independent of the investigated material and furthermore occurs at a low desorption temperature, it is unlikely that it corresponds to hydrogen adsorbed directly on the framework, and it was not further considered for identifying the adsorption sites of MOFs. Therefore, the amount given in Table 1 was obtained after subtracting the amount desorbed below 27 K.

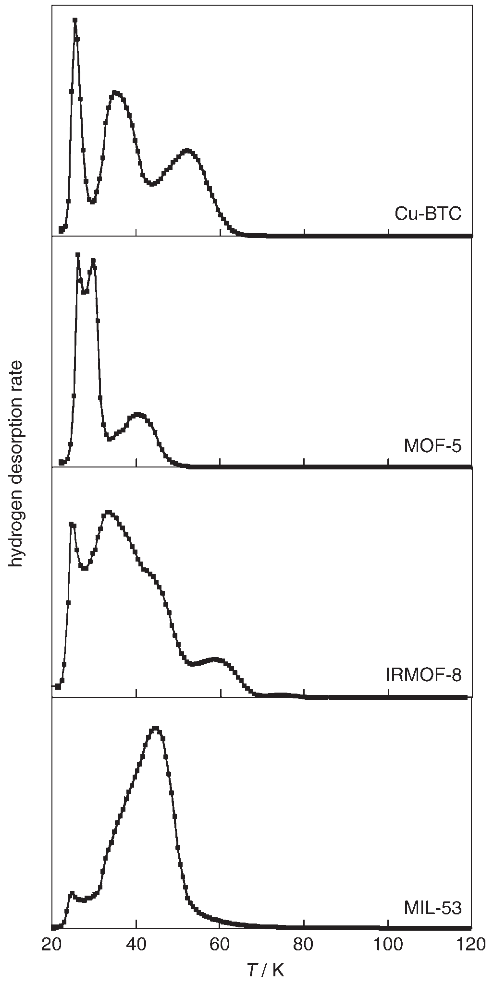

Figure 3. Spectra of H_2 thermal desorption (in arbitrary units) of Cu-BTC, MOF-5, IRMOF-8, and MIL-53 recorded with a heating rate of 0.1 K s^{-1}.

For all investigated metal–organic frameworks desorption of hydrogen mainly takes place at temperatures between 27 K and 80 K. At higher temperatures the amount of hydrogen desorbed is negligible (<0.02 wt %). The low temperatures of desorption indicate that hydrogen is reversibly stored in MOFs, which is characteristic for physisorption. This observation is in good agreement with the gravimetric measurements performed by Rowsell et al. on MOF-5, which show that at 77 K and under vacuum all hydrogen could be reversibly removed from the surface.[27] This result also shows that thermal desorption spectra recorded in vacuum at temperatures higher than 80 K[4] cannot provide quantitative information about the adsorption sites for H_2 in porous materials, since the amount of desorbed hydrogen measured under these conditions is very small.

The desorption spectra of the four MOFs differ strongly from each other. The hydrogen desorption curve of Cu-BTC shows two distinct peaks. The presence of two desorption maxima is strong evidence for the existence of at least two distinct adsorption sites for hydrogen with different enthalpies. Grand canonical Monte Carlo simulations for argon adsorption in Cu-BTC, combined with experimental adsorption isotherms, suggest that the two types of pores present in Cu-BTC are distinct adsorption places for argon.[15,28] From static-energy optimization, the authors[15] demonstrated that the small side pockets are preferential adsorption sites for argon, compared to the main channels which possess a less negative adsorption enthalpy. Similar conclusions can be drawn for hydrogen adsorbed in Cu-BTC: Hydrogen molecules, like argon atoms, are small enough to access the side pockets through the triangular windows of 3.5 Å in diameter. According to the studies of Ar adsorption, we can assume that the hydrogen desorption peak at higher temperatures, which is related to higher adsorption enthalpies, corresponds to H_2 adsorbed in the small tetrahedral pockets. In contrast, the desorption maximum at 35 K is assigned to hydrogen weakly adsorbed at the surface of the main pores. Similar conclusions were recently obtained from neutron powder diffraction studies of D_2 adsorbed in Cu-BTC.[12] At low deuterium loading the authors found that D_2 preferentially adsorbs at the metal sites. However, at higher loadings pore filling of the smaller pores takes place with subsequent occupancy of the larger pores. This result is in agreement with our thermal desorption spectrum performed at high hydrogen concentrations.

The H_2 desorption spectrum of MIL-53 exhibits only one broad desorption maximum at 45 K, indicating the existence of a single type of adsorption site for H_2. MIL-53 possesses uniform one-dimensional channels where hydrogen can be adsorbed. Owing to the very flexible structure of this MOF, the channels can be compressed to a certain extent, leading to a broad distribution of pores with similar diameter. Even though MIL-53 possesses both an organic and an inorganic moiety where hydrogen could be potentially adsorbed with different strengths, no multiple adsorption sites could be identified in the TDS spectrum. Therefore, the presence of a single maximum in the desorption curve can be related to the one-dimensional channels of MIL-53 whose size determines the interaction strength with H_2. The slightly asymmetric and broadened shape of the peak could be determined not only by the flexibility of the channel structure but also by the shape of the pores of MIL-53. The channels are rhombic in cross-section; therefore, the overlap of the van der Waals potential from the walls is more effective at the corners, where hydrogen might be adsorbed more strongly, while it is slightly weaker on the sides.

The thermal desorption spectrum of hydrogen adsorbed on MOF-5 reveals the low heat of adsorption of H_2 in this framework. In vacuum MOF-5 desorbs all hydrogen already at temperatures below 50 K, which is considerably lower than for the other metal–organic frameworks. The amount of hydrogen adsorbed on MOF-5 at 20 K (2.5 wt %) is considerably lower than the maximum excess adsorption value measured at 77 K and high pressure (5.1 wt %). This low value can be related to the low heat of adsorption of H_2 in MOF-5.[20] The interaction with hydrogen is so weak that a large amount of H_2 does not adhere to the surface of the MOF even at temperatures close to 20 K and is partially desorbed in vacuum before the TDS experiment is started. Compared to the other metal–organic frameworks, for MOF-5 higher hydrogen pressures are necessary to reach the maximum adsorption potential at 77 K (Figure 1), and lower temperatures than 20 K would be needed to avoid desorption of weakly adsorbed H_2 molecules in vacuum. In spite of the fact that some amount of hydrogen is desorbed before heating the sample, two desorption maxima can be observed for MOF-5 in the TDS spectrum. These maxima can be related to the two types of pores present in MOF-5. The larger pore possesses a diameter of 15 Å, which is more than five times the kinetic diameter of hydrogen (2.9 Å). The adsorption potential is therefore only weakly enhanced by the constraint of the pore; instead, hydrogen is mainly adsorbed on the pore surface. Owing to this weak interaction, hydrogen is desorbed at temperatures close to that of liquid hydrogen. The smaller pores of MOF-5 (12 Å) may slightly enhance the adsorption potential of the framework, and hydrogen is desorbed at higher temperature (40 K). Overall, the low temperatures of desorption are in good agreement with the low enthalpy of adsorption determined from the H_2 uptake isotherms of MOF-5.[20,29]

A similar hydrogen desorption spectrum as for MOF-5 would be expected for IRMOF-8 if it possessed an identical cubic structure. In contrast, IRMOF-8 exhibits a very complex desorption spectrum (Figure 2) with a peak at 35 K, a shoulder at 40 K, a maximum at 60 K, and a very small peak which accounts for less than 0.02 wt % at 74 K. At least four adsorption sites for H_2 corresponding to different desorption temperatures can be identified in this framework. The large number of adsorption sites available for hydrogen can be related to the fact that in IRMOF-8 interweaving (the minimal displacement of two catenated frameworks) occurs during the synthesis, providing a complex but well-defined framework structure. The effect of interweaving on the pore structure of MOFs was investigated by Rowsell and Yaghi.[30] They showed that an interwoven MOF possessing the same framework structure as IRMOF-8 (but a different ligand) exhibits two larger pores with slightly different pore dimensions and six smaller cavities defined by the four Zn_4OL_3 units, where L stands for the ligand.[30] Furthermore, it may also be possible that both frameworks, that is, a noncatenated and an interwoven framework, are present in the sample, which would lead to a smaller fraction of small pores than in a completely interwoven structure. The presence of several adsorption sites for hydrogen can therefore be related to cavities possessing different dimensions. The higher hydrogen desorption temperatures of IRMOF-8 are in good agreement with the higher heat of adsorption found for IRMOF-8 than for MOF-5.[29] Moreover, considering that both MOFs possess the same Zn_4O cluster, the higher desorption temperature of IRMOF-8 cannot be related to the metal sites. Instead, it may be attributed to the presence of smaller pores in the interconnected metal–organic framework.

All thermal desorption spectra could be consistently explained by assigning the H_2 adsorption sites to the different cavities in the structure. However, no evidence was found for any correlation of the adsorption on a specific building block. This result can be explained by the strong overlap of the van der Waals potential between the walls in small cavities, which influences the adsorption of the weakly polarizable H_2 molecule. Under the assumption that the interaction strength is determined by the pore size, it may be possible to correlate the desorption temperature with the diameter of the cavities in the MOFs (Figure 4). Here IRMOF-8 is not considered since the pore size for this interconnected structure is not known. With decreasing pore size the desorption temperature increases, indicating that MOFs with smaller cavities may possess a higher heat of adsorption.

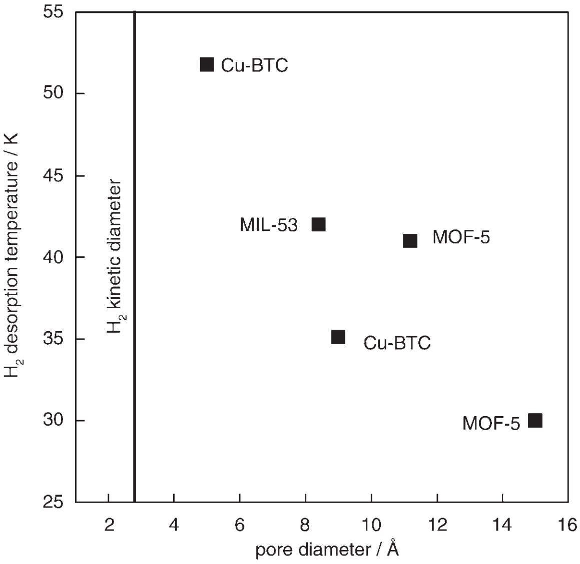

Figure 4. Thermal desorption temperatures of hydrogen in MOFs versus the diameter of their pores.

In conclusion, we studied the adsorption sites for hydrogen in different metal–organic frameworks by using low-temperature thermal desorption spectroscopy. The H_2 desorption spectra of these materials show that hydrogen adsorbed in cavities of different sizes is desorbed at different temperature. This result shows that at high hydrogen concentrations the heat of adsorption for hydrogen is influenced by the pore size and that the metal centers have minor importance at relevant hydrogen concentrations. Novel materials for hydrogen storage based on physisorption should therefore possess primarily a combination of high specific surface area and small pores.

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