Metal-organic frameworks for hydrogen storage

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Abstract

Physiosorption of hydrogen in porous materials at cryogenic conditions is a viable mechanism for hydrogen storage in mobile applications. This storage mechanism has the advantage of possessing fast kinetics, low heat of adsorption and being completely reversible. Among all porous materials, metal-organic frameworks (MOFs) are the best candidates for H$_2$-adsorption, since they consist of light atoms, are highly porous and their pore dimensions can be tailored by chemical engineering. Additionally, MOFs show the highest storage capacity of any other porous material. Different properties of the material, like specific surface area, composition and pore size can influence the storage capacity. Therefore, an understanding about the correlation between adsorption properties and structure of MOFs is necessary to specifically improve these materials for hydrogen storage. Our main achievements in the investigation of H$_2$ storage in MOFs are discussed and compared to results reported in literature.

1. Introduction

Global warming and limited oil reserves will require a change from fossil fuels to cleaner and renewable energy sources in the near future. Presently, for mobile applications two main technologies are considered as energy storage: batteries for electrical vehicles and hydrogen for internal combustion engines or fuel cells. Batteries are considered as very promising since they do not require the additional production of a synthetic fuel. However, besides the long recharging time and the low cycling stability both the heavy weight and the large volume occupied by these batteries are large drawbacks [1]. Another possibility could be the use of hydrogen as energy carrier produced from clean energy sources. But the lack of an efficient storage system for hydrogen is the major bottleneck for the development of fuel cell driven vehicles. The commercially available hydrogen storage technologies for mobile applications are presently compressed gas in tanks at pressures up to 70 MPa and liquid hydrogen in cryogenic vessels at temperatures of approximately 20 K. These technologies have severe disadvantages and limitations. On the one hand, compressed hydrogen occupies large volumes, possesses low gravimetric densities and the high pressures find low consumer acceptance. On the other hand, the liquefaction process of hydrogen which occurs at very low temperature, has the drawback of consuming 30–40% of the energy content of H$_2$ and the storage at 20 K additionally implies a heavy insulation system to limit the boil-off of the liquid. Therefore, alternative possibilities for hydrogen storage have to be considered. One strategy to increase the stored hydrogen density is to exploit the interaction between H$_2$ and a solid material as e.g. by physisorption (i.e. molecular adsorption) of hydrogen on porous materials. The mechanism of physisorption possesses several advantages like being completely reversible and possessing very fast kinetics of adsorption and desorption. Additionally, due to the small enthalpy of adsorption for molecular H$_2$ storage, only a small amount of heat is produced during onboard refuelling which is a great advantage compared to chemical hydrides. Among all porous materials metal-organic frameworks (MOFs) show very large storage capacities due to their extremely high internal porosity [2–5]. This paper summarises the main achievements in the fundamental understanding of hydrogen adsorption in metal-organic frameworks.

2. Storage capacity and specific surface area

Fig. 1 shows as a typical example for metal-organic frameworks the hydrogen adsorption isotherm of MOF-5 at different temperatures. At 77 K the isotherm shows a typical type I isotherm according to the IUPAC classification with an initial steep increase in the hydrogen uptake, followed by the saturation at higher pressures. At 2 MPa saturation is not reached and a slightly lower hydrogen uptake (4.5 wt%) than the maximum storage capacity is obtained [6,7]. These results were independently confirmed by three other groups [3,8,9] all showing a similar maximum hydrogen uptake of 5 wt% for MOF-5 at 77 K. Owing to the small heat of adsorption of H$_2$ on porous materials, at higher temperatures both the initial slope of the isotherm and the maximum achievable hydrogen uptake decrease, reaching a storage capacity of only 0.1 wt% at room...
temperature and 2 MPa. Physisorption of hydrogen in metal-organic frameworks like for other porous materials is therefore presently limited to cryogenic conditions, i.e. at the temperature of liquid nitrogen (77 K).

The hydrogen adsorption in a variety of metal-organic frameworks with different building blocks and possessing a high porosity like e.g. Cu-BTC, IRMOF-8, MIL-53 was investigated. For different metal-organic frameworks it was shown that the maximum hydrogen storage capacity at 77 K depends linearly on the specific surface area (SSA) and is independent of the composition and the structure [7]. This indicates that for MOFs a high specific surface area is a necessary prerequisite for reaching a high storage capacity. A similar correlation between the SSA and the hydrogen uptake was previously obtained for other microporous materials like carbon nanostructures [10], zeolites [11] and Prussian blue analogues [12] as shown in Fig. 2 [4].

The scatter in the data is due to the fact that the commonly used N$_2$-BET specific surface area applied in the classical pressure range ($0.05 < p/p_0 < 0.3$) is often not an appropriate model for microporous materials [13]. Nevertheless, a clear trend for all these microporous materials can be recognized. Among these materials MOFs possess the highest specific surface area and are therefore presently the best candidates for hydrogen storage by physisorption.

### 3. Adsorption sites

At low hydrogen pressures the SSA is not the main property which influences the hydrogen uptake in MOFs. Indeed, if the adsorption isotherms of MOF-5 and Cu-BTC are compared, two different pressure regions can be distinguished (Fig. 3). At pressures above 0.6 MPa MOF-5 possesses a higher storage capacity due to the larger SSA, while at lower pressures a crossover in the adsorption isotherms is observed and Cu-BTC stores more hydrogen. Responsible for this crossover in the hydrogen uptake of the two MOFs are the higher heat of adsorption of Cu-BTC, which determines the storage capacity at low pressures and the larger SSA of MOF-5, which is responsible for the maximum storage capacity at high H$_2$ pressures. Therefore, a MOF structure possessing a large SSA together with a high heat of adsorption would allow to reach high storage capacities already at low pressures. Different opinions exist about the influence of the MOF structure and composition on the heat of adsorption for hydrogen storage. Metal-centres, especially with unsaturated coordination positions, were shown to be preferential adsorption sites for hydrogen at very low coverage. As an example for the influence of metal sites Rowsell et al. showed by inelastic neutron scattering that hydrogen molecules in MOF-5 first adsorb at the metal-oxide units since they interact more strongly with H$_2$ than the organic parts of the framework [14]. Additional experiments indicate that also the pore size in the MOFs has an influence on the heat of adsorption of hydrogen. By thermal desorption spectroscopy of H$_2$ adsorbed in several metal-organic frameworks it was possible to identify different adsorption sites in these materials [15]. With this technique hydrogen is first adsorbed on the metal-organic framework at room temperature and then cooled down to 20 K. At this low temperature it is possible to remove the free hydrogen molecules in the gas phase by applying a high vacuum ($10^{-5}$ Pa), while the adsorbed H$_2$ molecules stick on the surface of the framework. The amount of hydrogen adsorbed under these conditions corresponds to a storage

![Fig. 1. Hydrogen adsorption (full symbols) and desorption (open symbols) isotherms of MOF-5 at 77 K (liquid N$_2$), 87 K (liquid Ar), 97 K, 107 K, 117 K, 296 K.](image1)

![Fig. 2. Maximum hydrogen storage capacity versus BET SSA of different porous materials: MOFs (open squares) [7], filled squares [3], carbon materials (triangles) [10], zeolites (crosses) [11], Prussian blue analogues (circles) [12]. Reprinted from Hirscher et al. [4], Copyright (2007), with permission from Elsevier.](image2)

![Fig. 3. Hydrogen uptake of MOF-5 (squares) and Cu-BTC (triangles) at 77 K.](image3)
capacity close to the maximum value at 77 K. When the temperature is increased with a constant heating rate the desorbed hydrogen molecules are detected with a mass spectrometer. Since the hydrogen, which is adsorbed in sites possessing different energy, is released at different temperatures, the resulting desorption spectrum reflects the number of adsorption sites in the metal-organic frameworks. For Cu-BTC, MOF-5, MIL-53 and IRMOF-8 the hydrogen desorption spectra can be well correlated to the pore structure of their framework. As an example the thermal desorption spectrum of hydrogen on Cu-BTC is shown in Fig. 4 which presents three maxima at distinct temperatures. The maximum at very low temperature, which is not material specific, can be assigned to some liquid hydrogen or hydrogen adsorbed in multilayers. The two additional maxima are characteristic for the material and can be assigned to hydrogen adsorbed in the smaller cavities of Cu-BTC which is released at higher temperatures (approx. 52 K) and to H2 adsorbed in the large central pore which is released already at ~35 K. Hence, for the investigated MOFs the desorption temperature, which at a constant heating rate depends on the interaction energy with H2, can be directly correlated with the size of the pores present in the framework, i.e. hydrogen adsorbed in larger pores is released at lower temperatures and H2 molecules more strongly adsorbed in smaller pores are desorbed at higher temperatures (Fig. 5). These results indicate that at high hydrogen concentrations, i.e. when the metal-centres are already saturated with H2 and further molecules are introduced in the framework, the pore size mainly determines the interaction between hydrogen and the metal-organic frameworks. This is due to the fact that in smaller pores the van der Waals potential from the wall surface can more strongly overlap than in larger pore enhancing the interaction between the framework and the H2 molecules.

4. Heat of adsorption

The temperature and pressure dependence of the adsorption isotherms (fig. 1) are governed by the heat of adsorption. Measurements over a wide temperature and pressure range allow to determine very accurately the isosteric heat of adsorption ($\Delta H$) applying the Clausius–Clapeyron equation at different temperatures and in a large range of surface coverage up to 90% [6]. In Fig. 6 the isosteric heat of adsorption versus the surface coverage is shown for various MOFs. The values for the different materials range between 3.5 kJ/mol and 7 kJ/mol. The decrease of the isosteric heat of adsorption with increasing coverage is on the one hand due to the existence of different adsorption sites in these porous materials where the strongest binding sites are occupied at lower coverage, while those possessing a lower adsorption enthalpy are occupied only at higher hydrogen concentrations. On the other hand repulsive interaction between the adsorbed hydrogen molecules might appear at higher loadings which then decrease the heat of adsorption. The mean values of the isosteric heat of adsorption for each porous material can be correlated to the pore size in an analogous way as for the desorption temperature in thermal desorption spectroscopy which depends on $\Delta H$. Similarly, the higher heat of adsorption values at lower coverage are correlated to smaller pores since these are occupied first while the smaller values of $\Delta H$ obtained at high coverage are assigned to adsorption in the larger pores. Fig. 7 indicates an increase of the heat of adsorption with decreasing pore size.
5. Discussion

Results from literature and ours are compared to achieve a comprehensive picture on the nature of hydrogen adsorption in MOFs. In Fig. 8 the isosteric heat of adsorption for MOF-5 is compared to the heat of adsorption found by Dinca et al. [16] and Zhou et al. [17]. Dinca et al. used low pressure adsorption isotherms up to 0.1 MPa at 77 K and 87 K to determine the isosteric heat of adsorption. At low hydrogen concentrations they found a strong initial decrease in the isosteric heat of adsorption with increasing uptake, i.e. from an initial value of 6.5 kJ/mol to 4.5 kJ/mol at a storage capacity of 1 wt%. These results are in good agreement with our measurements. Measurements on other MOFs possessing open metal sites, i.e. unsaturated coordination positions, show even higher heat of adsorption at very low coverage and attribute these to adsorption sites at the metal centres [18]. Zhou et al. calculated the isosteric heat of adsorption in MOF-5 from isotherms at temperatures between 30 K and 300 K and pressures up to 6.5 MPa [17]. Therefore these measurements provide very precise isosteric heat of adsorption values at higher coverage. They found only a small decrease in the isosteric heat of adsorption of about 1 kJ/mol when the uptake increases from 1 wt% to 4.5 wt% compared to the low coverage region. This shows that few very strong adsorption sites exist which are occupied at low hydrogen uptake (<1 wt%) and the main hydrogen adsorption takes place at almost equally strong binding sites.

While MOF-5 does not possess metal sites with unsaturated coordination positions, in Cu-BTC, after removal of a water solvent, open metal sites are accessible to H₂ molecules. In Fig. 9 the isosteric heat of adsorption for Cu-BTC is compared to measurements from Lee et al. [19]. The isosteric heat of adsorption of Cu-BTC is determined from hydrogen adsorption data in the low pressure region up to 0.1 MPa at 77 K and 87 K, is lower than the initial value of 6.5 kJ/mol slightly higher. However, at higher coverage the ΔH decreases to less than 6 kJ/mol at 1 wt% which is in good agreement with our measurements. Again, a few stronger adsorption sites are occupied at low coverage and with increasing coverage the isosteric heat is decreasing slowly. These results can be compared to neutron powder diffraction data reported by Peterson et al. [20] who found that at a storage capacity of 0.5 wt% the hydrogen is adsorbed close to the metal centres of Cu-BTC. This is followed by adsorption at sites located in the small pore of Cu-BTC and finally at an uptake above 2 wt%, hydrogen is adsorbed in the larger pore. These results are consistent with the idea that hydrogen adsorption is governed by metal centres only at very low uptake but when increasing the H₂ concentration to technologically relevant amounts the pore dimension determine the interaction with hydrogen. Since the storage capacity at low pressures, i.e. the initial steep increase in the isotherm, depends on the heat of adsorption, small pores are responsible for large uptake values at pressures below saturation conditions.

6. Conclusion

The hydrogen storage properties have been studied for a variety of metal-organic frameworks possessing different structures and compositions. At high pressure the maximum hydrogen uptake in MOFs is determined by the specific surface area. Therefore, a high SSA is the first prerequisite for the application of MOFs in cryoadsorption systems for hydrogen storage. Furthermore, both thermal desorption studies and temperature-dependent measurements of the adsorption isotherms indicate clearly that at techno-
logically relevant hydrogen concentrations the pore size of the cavities in the framework determines the heat of adsorption and therefore the hydrogen uptake at low pressure. Only at very low hydrogen concentrations, H₂ is preferentially adsorbed on metal centres. Therefore, the use of MOFs for hydrogen storage requires a combination of small pores, which enable a lower pressure for storage, and a larger specific surface area, which is needed for a high storage capacity. However, the presently existing MOFs with the highest surface area possess relatively large pores (e.g. 11–34 Å [2,3]) and the frameworks with very small cavities show a low SSA [21]. For the future the great challenge will be the synthesis of new frameworks consisting of a network of small accessible pores and possessing still a large specific surface area.

Acknowledgment

Partial funding by the European Commission DG Research (contract SES6-2006-518271/NESSHY) is gratefully acknowledged.

References