

Heat of Adsorption for Hydrogen in Microporous High-Surface-Area Materials

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The limited resources of fossil fuels will soon require a change to renewable energies. The ideal energy carrier for mobile applications is hydrogen, but the problem of an adequate and safe storage system is still unsolved. One of the possibilities for hydrogen storage is physisorption in porous materials. The big advantage of molecular hydrogen storage is that short refueling times can be realized due to the extremely fast kinetics. Additionally, no extra heat management is needed as the heat of adsorption is lower than for other storage processes, for example in metal hydrides. On the other hand, owing to this low heat of adsorption, a cryosystem is needed to reach high storage capacities.

Microporous materials possessing a high specific surface area (SSA), for example carbon nanotubes, activated carbon, zeolites, and coordination polymers or metal-organic frameworks (MOFs), show a high hydrogen uptake at low temperatures, typically 77 K.^[1–8] Characteristic for this cryo-adsorption in porous materials is that the maximum hydrogen uptake at high pressures depends linearly on the SSA of the material.^[9–11] At low pressures distinct differences in the hydrogen uptake exist for the different materials. Therefore, the pressure to reach, for example, 80% of the maximum storage capacity, differs strongly between the materials. For all materials the hydrogen uptake decreases with increasing temperature. The strength of this decrease as well as the hydrogen uptake at low pressures are governed by the heat of adsorption. Typically, the isosteric heat of adsorption is calculated from the adsorption isotherms measured at 77 K and 87 K since these temperatures can easily be realized by liquid nitrogen and liquid argon, respectively.^[12] This small temperature range leads to a very high uncertainty in the heat of adsorption. Only in a few publications is the isosteric heat of adsorption determined with higher accuracy from several isotherms measured at various temperatures.^[13]

Herein, we present hydrogen adsorption isotherms measured over a wide temperature (77–298 K) and pressure (0–20 bar) range. This allows the determination of the heat of adsorption for a wide range of surface coverage with very high accuracy. For the first time different microporous materials have been investigated systematically and their heats of adsorption are correlated to the structures of the materials.

Two activated carbon samples, Norit R0.8 and Takeda 4A, with BET SSAs of 1384 m² g^{−1} and 397 m² g^{−1} respectively, and four different metal-organic frameworks, MOF-5, Cu-BTC, MIL-53 and MIL-101, with SSAs between 902 m² g^{−1} and 3293 m² g^{−1} have been investigated. The hydrogen uptake was measured with an automated Sieverts' apparatus (PCTPro2000, HyEnergy, USA).

Figure 1 shows the dependence of the hydrogen uptake on the pressure as an example for Cu-BTC (for other materials, see the Supporting Information). For all materials the isotherms at

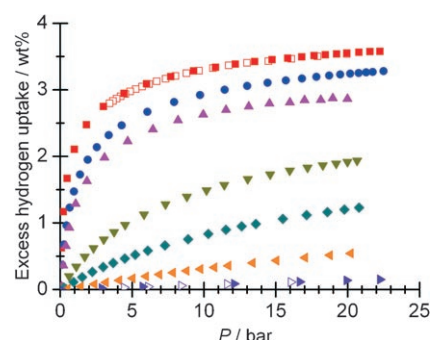


Figure 1. Excess hydrogen adsorption (full symbols) and desorption (open symbols) isotherms of Cu-BTC: 77 K (■), 87 K (●), 93 K (▲), 128 K (▼), 158 K (◆), 218 K (◀), and 296 K (▶).

77 K show a steep initial increase in the excess hydrogen uptake followed by a saturation plateau at elevated pressures. Furthermore, no hysteresis between adsorption and desorption is observed. Typically for physisorption systems, the isotherms in Figure 1 represent type I isotherms in the IUPAC classification. The slope of the initial increase as well as the maximum hydrogen uptake becomes smaller with increasing temperature. For all materials the shape of the isotherms at 77 K is similar, however, the maximum hydrogen uptake at 20 bar (Tab. 1) and the slope of the isotherm at low pressures depend on the type of material.

In Figure 2 the saturation hydrogen uptake at 77 K evaluated by using the Langmuir–Freundlich model is plotted versus the BET SSA for all materials. The hydrogen uptake increases linear-

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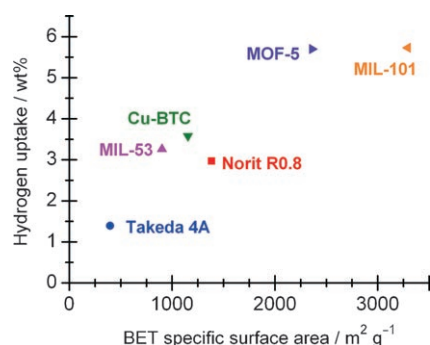
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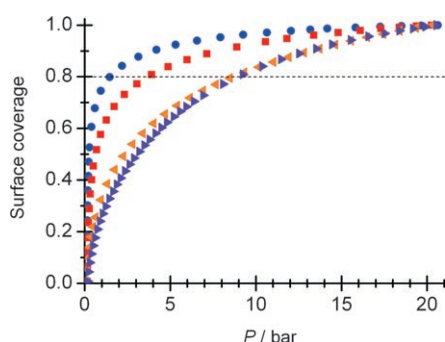
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Table 1. Characteristic data for all materials investigated.

Material	BET SSA	Chemical composition	Evacuation	He density	H ₂ uptake at 77 K at 20 bar	H ₂ uptake at RT at 20 bar
MOF-5	2360 m ² g ⁻¹	Zn ₄ O(BDC) ₃	0.5 h at 200 °C	1.71 g cm ⁻³	4.4 wt %	0.1 wt %
Cu-BTC	1154 m ² g ⁻¹	Cu ₃ (BTC) ₂ (H ₂ O) ₃	1 h at 200 °C	1.7 g cm ⁻³	3.6 wt %	0.15 wt %
MIL-53	902 m ² g ⁻¹	AlOH(BDC)	1 h at 200 °C	1.52 g cm ⁻³	3.1 wt %	0.15 wt %
MIL-101	3293 m ² g ⁻¹	Cr ₃ F(H ₂ O) ₂ O(BDC) ₃	0.5 h at 150 °C	1.52 g cm ⁻³	4.5 wt %	0.15 wt %
Norit R0.8	1384 m ² g ⁻¹	activated carbon	12 h at 120 °C	2.04 g cm ⁻³	2.9 wt %	0.15 wt %
Takeda 4A	397 m ² g ⁻¹	activated carbon	24 h at 110 °C and 4 h at 250 °C	1.85 g cm ⁻³	1.45 wt %	0.1 wt %


Figure 2. Saturation hydrogen uptake at 77 K obtained by a Langmuir-Freundlich fit as a function of the BET SSA.

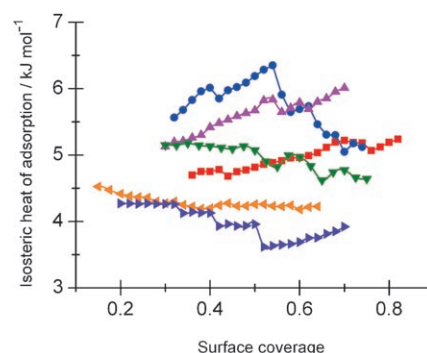
ly with the BET SSA with a slope of about 2×10^{-3} wt % m⁻² g, as shown before for various microporous materials.^[3,9-11] To compare the slope of the isotherms measured for the different materials, the uptake is normalized to the value at 20 bar and 77 K (Figure 3). A strong dependence on the material is observed; for example, the pressure to obtain 80% of the uptake at 20 bar varies between 1 and 9 bar.


Figure 3. Normalized hydrogen uptake at 77 K for Takeda 4A (●), Norit R0.8 (■), MIL-101 (◊), and MOF-5 (►).

From the isotherms measured at different temperatures the isosteric heat of adsorption can be determined for each material. The isosteric heat of adsorption in dependence of the surface coverage θ is given by Equation (1):^[14]

$$\Delta H = -R \left[\frac{\partial \ln(P)}{\partial (T^{-1})} \right]_{\theta} \quad (1)$$

where R is the gas constant, P the pressure and T the temperature. For each material at least four different isotherms measured up to high pressures have been used for the evaluation of the isosteric heat of adsorption resulting in a high accuracy (see the Supporting Information). The isosteric heats of adsorption for all materials are shown in Figure 4 as a function of the surface coverage. Owing to the wide temperature and pressure range, the isosteric heat of adsorption could be determined for coverages ranging from 10%


Figure 4. Isosteric heat of adsorption in dependence of the surface coverage: Takeda 4A (●), MIL-53 (▲), Cu-BTC (▼), Norit R0.8 (■), MIL-101 (◊), and MOF-5 (►).

to 90%. The variations in the isosteric heat of adsorption for different coverages might be caused by changes in interaction with the adsorbate and by different adsorption sites. Detailed interpretation of these spectra would require further measurements. The average isosteric heat of adsorption is given in Table 2. With 4 kJ mol⁻¹, MOF-5 shows the lowest isosteric heat of adsorption, Takeda 4A reaches more than 6 kJ mol⁻¹. A direct correlation between the pressure to reach 80% uptake at 77 K and the isosteric heat of adsorption is shown in Figure 5. This clearly indicates that a high isosteric heat of adsorption leads to a high hydrogen uptake at low pressures.

Furthermore, the temperature dependence of the hydrogen uptake is governed by the isosteric heat of adsorption. In

Table 2. Average isosteric heat of adsorption.

Material	Isosteric heat of adsorption
MOF-5	4.0 kJ mol ⁻¹
Cu-BTC	5.0 kJ mol ⁻¹
MIL-53	5.6 kJ mol ⁻¹
MIL-101	4.3 kJ mol ⁻¹
Norit R0.8	5.0 kJ mol ⁻¹
Takeda 4A	5.7 kJ mol ⁻¹

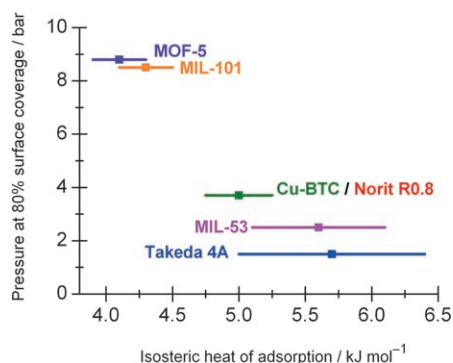


Figure 5. Pressure at which 80% of the surface coverage is reached as a function of the average isosteric heat of adsorption.

Figure 6 the hydrogen uptake of all materials at 20 bar is shown in dependence of the temperature. The slope of those isobars varies strongly with the isosteric heat of adsorption. A higher isosteric heat of adsorption means lower temperature dependence and therefore a higher relative uptake at elevated temperatures.

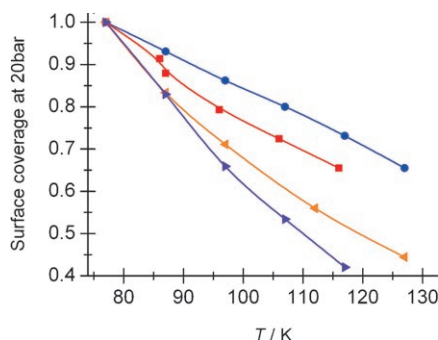


Figure 6. Isobars of hydrogen uptake at 20 bar for Takeda 4A (●), Norit R0.8 (■), MIL-101 (▲), and MOF-5 (▼).

Microporous materials possessing high SSAs ($> 2000 \text{ m}^2 \text{ g}^{-1}$) can be divided into two classes: carbons or aerogels typically showing disordered structures and MOFs, which have crystalline structures. In contrast to carbons, MOFs can be synthesised using different building units resulting in a huge variety with different chemical compositions. The open question is, which are the adsorption sites for hydrogen, and how can they influence the heat of adsorption? On the one hand, charges on the metal centres, especially at unsaturated metal sites, may polarize the hydrogen molecule and cause stronger binding. On the other hand, small pores with a high curvature of the surface lead to an overlap of the van der Waals forces of neighbouring atoms and may give rise to a stronger interaction. Presently there are experimental and theoretical indications for both mechanisms.

As one of the first, Spencer et al.^[15] used single-crystal neutron diffraction to determine the hydrogen adsorption sites within MOF-5 and showed that hydrogen is preferentially adsorbed on the metal centres. Forster et al.^[16] showed by hydrogen adsorption isotherms, temperature-programmed desorp-

tion, and inelastic neutron scattering spectroscopy that hydrogen in a MOF with unsaturated Ni^{II} sites is strongly adsorbed at the metal sites. Adsorption measurements for isostructural MOFs with exchanged metal ions by Dinca et al.^[17] showed a strong influence of the metal sites on the adsorption behaviour of the material. In general, these findings indicating metal centres as adsorption sites are mainly obtained for low hydrogen concentrations. If higher hydrogen concentrations are considered, the hydrogen uptake shows strong dependence on the pore size of the material. Jhung et al.^[18] showed experimentally for several nanoporous aluminiumphosphates that decreasing pore size leads to increased relative hydrogen uptake per unit cell and increased heat of adsorption. Chun et al.^[19] investigated the gas sorption properties of isomorphous MOFs and found increased hydrogen uptake for smaller pores. Recently, Klontzas et al.^[20] found an equal contribution of inorganic metal clusters and organic linkers to hydrogen physisorption in a multiscale theoretical study.

The present measurements of the heat of adsorption are in the range of 10% to 90% surface coverage, that is, at higher hydrogen concentrations. Therefore in Figure 7 the average

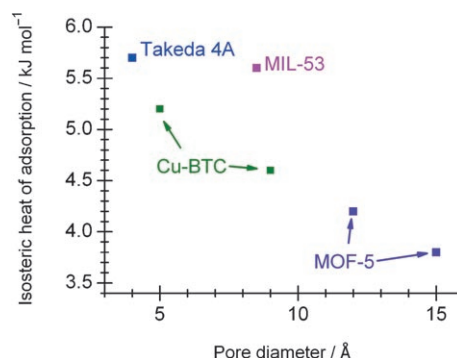


Figure 7. Pore size correlated to the isosteric heat of adsorption.

isosteric heat of adsorption (Table 2) is shown as a function of the pore size of the different materials. MIL-53 shows a single pore size with a diameter of 8.5 Å .^[21] For Takeda 4A a pore size distribution between 3 and 5 Å is reported.^[22] For Cu-BTC two different kind of pores with diameters of 5 and 9 Å need to be regarded.^[23]

As smaller pores lead to higher heats of adsorption, they should be filled first. Thus the isosteric heat of adsorption at lower coverage is correlated to the smaller pore and at higher coverage to the larger pore. MOF-5 has also two different pores sizes of 12 and 15 Å . This is caused by the orientation of the aromatic ring.^[24] MIL-101 has very large pores of 29 Å and 34 Å in diameter. It is not sure yet if adsorption would take place in such huge pores or rather in smaller voids of the material.^[4] This is why MIL-101 is not shown in Figure 7 even though the large pores as well as the small voids would be consistent with the other results.

Figure 7 clearly indicates a correlation between the pore size and heat of adsorption, that is, the heat of adsorption increases for materials possessing smaller pores. This indicates that in

the investigated range of surface coverage the pore size mainly determines the adsorption strength and that the chemical composition of the MOFs only has a minor influence. In addition, the activated carbon Takeda 4A fits well into the trend shown by all the measured materials.

A similar correlation of the isosteric heat of adsorption to the pore size of the material is also reported Panella et al.^[25] Thermal desorption spectroscopy experiments for hydrogen in various MOFs show a correlation between the desorption temperature and the pore size. Typically, desorption temperatures are directly correlated to the heats of adsorption.

In conclusion, for hydrogen, the heat of adsorption over a wide range of surface coverage was determined for several microporous high-SSA materials. A correlation to the structure of the materials indicates that materials with smaller pores show higher heats of adsorption. Furthermore, in the observed region of high hydrogen concentrations the influence of chemical composition, for example, metal sites or linkers seem to have only a minor or even negligible influence. For the future, the synthesis of materials with even smaller pores may be favourable for hydrogen storage applications as a higher heat of adsorption leads to a lower temperature dependence of the maximum hydrogen uptake and increases the hydrogen storage capacity at low pressures.

Experimental Section

The automated Sieverts apparatus PCTPro2000 was used with a Microdoser (MD) from HyEnergy, USA. This MD offers the possibility to measure the hydrogen uptake of very small amounts of material. Therefore the MD includes a 0.51 mL reservoir, a pressure sensor and minimizes the sample cell volume to 1.2 mL. The sample mass was between 99 mg and 400 mg and the samples have been activated in high vacuum according to Table 1. Adsorption isotherms (0–20 bar) were measured at liquid nitrogen, liquid argon and temperatures above 87 K. The latter was realized by heating the sample cell in a Dewar cooled by liquid nitrogen. The temperature was controlled to ± 1 K. For further details and sample preparation see the Supporting Information.

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Keywords: adsorption • hydrogen storage • metal–organic frameworks • microporous materials • physisorption

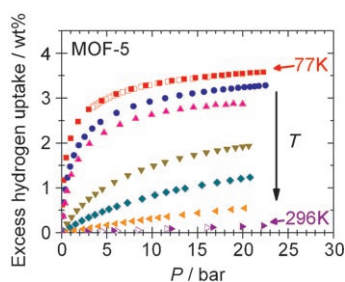
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COMMUNICATIONS

Pore size matters: The heat of adsorption for hydrogen is determined over a wide range of surface coverages for activated carbon and several metal–organic frameworks. Heat determination is based on hydrogen adsorption measurements performed at temperatures between 77 and 296 K (see figure, BTC=benzene-1,3,5-tricarboxylate). The materials with smaller cavities show a higher heat of adsorption for hydrogen.



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