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PAPER

Effect of NH₂ and CF₃ functionalization on the hydrogen sorption properties of MOFs†

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The hydrogen adsorption capacity and heat of adsorption at 77 K have been evaluated for several porous metal terephthalate MOFs (MIL-53(Fe), MIL-125(Ti) and UiO-66(Zr)), as well as in their –NH₂ and –(CF₃)₂ functionalized isoreticular structures. The capacity of hydrogen is basically related to the textural properties of the solids and not to their composition. The heats of adsorption at low coverage are on the whole close to those usually reported for MOFs (6–7 kJ mol^{-1}), except for the UiO-66(Zr) and MIL-53(Fe)-(CF₃)₂ analogues, whereas the presence of Lewis acid sites and/or a confinement effect enhances significantly the strength of interaction with hydrogen.

The current research interest towards hybrid porous solids, such as porous metal–organic frameworks (MOFs), lies in their high chemical versatility and control of their metric dimensions.[1,2] MOFs result from the reaction between organic and inorganic species in order to build up three-dimensional crystalline frameworks with high and controlled porosity. They are characterized by low densities, high specific surface areas, and uniformly sized pores and channels. The potential applications of MOFs concern catalysis, gas adsorption/separation/storage and drug delivery.[1,3]

MOFs are currently studied to store hydrogen, which is foreseen as an efficient and clean energy carrier.[4–6] Hydrogen capacity at 77 K strongly depends on textural properties such as specific surface area and microporous volume. The physisorption of H_2 in porous MOFs is usually reported at 77 K due to the low adsorption heat of the process (5–8 kJ mol^{-1}). A higher adsorption heat is required for a hydrogen storage system working at room temperature (15–20 kJ mol^{-1}).[6] Therefore, optimal hydrogen storage performance depends on tuneable porosity with a favourable size and shape, and the suitable chemical composition of internal and external surfaces.

Methods currently employed for enhancing H_2 sorption properties include (i) the generation of unsaturated metal sites,[4,7]

(ii) the doping of MOFs with noble metal nanoparticles in order to increase their H_2 capacity at room temperature *via* a spillover mechanism,[8,9] (iii) the insertion of alkali cations within the pores through redox or acid–base reactions[10,11] and (iv) covalent modification of the organic linkers.[12–17] The introduction of organic functional groups during (*in situ*)[15,16,18] or after (post-synthesis) the formation of crystalline MOFs[12–16] is indeed one of the most common strategies employed to modulate their physical and chemical properties, and thus may afford unique opportunities to improve the design of future hydrogen stores.

In this context, the hydrogen sorption properties at 77 K of several porous metal terephthalate (BDC) MOFs based on tri- and tetravalent cations (Fe^{III}(BDC)OH or MIL53(Fe),[19] Ti₈O₈(OH)₄(BDC)₆ or MIL-125(Ti),[20] Zr₆O₆(OH)₄(BDC)₆ or UiO-66(Zr)[21]) have been investigated. Whereas UiO-66(Zr) possesses a porous rigid structure with unsaturated metal sites (CUS),[21] MIL-125(Ti) (rigid structure) and MIL-53(Fe) (flexible structure) have no CUS but have bridging oxo or hydroxo groups. The influence of organic functionalization on hydrogen binding and capacity was also studied. Thus, the hydrogen adsorption of isoreticular porous MOFs based on the 2-amino or 2,5-diperfluoromethyl terephthalate linker (MIL-125(Ti)-NH₂, UiO-66(Zr)-NH₂, MIL-53(Fe)-(CF₃)₂ and UiO-66(Zr)-(CF₃)₂) was investigated and compared with their pristine forms. The hydrogen excess capacity and enthalpy of adsorption at 77 K, and low coverage are reported and discussed in relation to their crystalline and textural properties, as well as the nature of the grafted functional groups.

MIL-53(Fe),[19] MIL-125(Ti)[20] and MIL-53(Fe)-(CF₃)₂[18] were prepared from the corresponding BDCH₂ derivatives using published procedures. UiO-66(Zr),[21] UiO-66(Zr)-NH₂,[22] MIL-125(Ti)-NH₂ and UiO-66(Zr)-(CF₃)₂ were synthesized using similar conditions (see the ESI for details†). Direct synthesis from the

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† Electronic supplementary information (ESI) available: Synthesis conditions and characterisation of the MOFs, experimental sorption and calorimetric details. See DOI: 10.1039/c1dt10115c

functionalized linkers allows a total and homogeneous modified framework to be obtained.

Textural and hydrogen sorption properties, such as hydrogen excess capacity at 77 K and 4 MPa, and the enthalpy of hydrogen adsorption at 77 K at low coverage, of pristine and modified MOFs are listed in Table 1. The hydrogen adsorption isotherms at 77 K and the coverage dependence of the enthalpy of H_2 adsorption at 77 K for all the solids are plotted in Fig. 1 and Fig. 2, respectively.
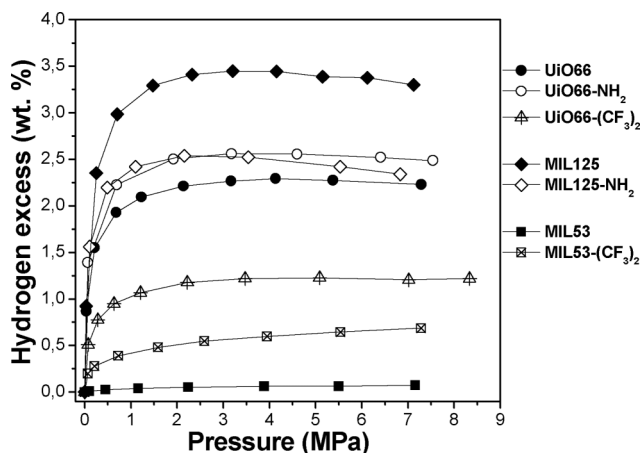

Fig. 1 Pressure–composition H_2 adsorption isotherms at 77 K. Full, empty and crossed symbols represent unmodified, –NH_2 and –CF_3 modified MOFs, respectively.

MIL-53(Al, Cr, Fe) exhibits a flexible 3D framework with a flexible 1D porosity, which is dependent on the nature of the metal.[23] Whereas the dehydrated forms of MIL-53(Al, Cr) present open pores and a permanent porosity, the iron analogue exhibits closed pores and thus no accessible porosity for N_2 at 77 K. As a consequence, dehydrated MIL-53(Cr, Al) can absorb a noticeable amount of H_2 at 77 K (up to 3.8 wt% under 1.6 MPa),[24] whereas this uptake is negligible for MIL-53(Fe) under similar conditions. On the other hand, the dehydrated form of MIL-53(Fe)-$(CF_3)_2$ presents a mixture of open ($\varphi \approx 6$ Å) and closed ($\varphi \approx 3$–4 Å) pores, in addition to a small but permanent porosity relative to N_2 ($S_{BET} = 100$ m^2 g^{-1}).[18] In contrast to pristine MIL-53(Fe), modified MIL-53(Fe)-$(CF_3)_2$ thus absorbs a small but significant amount of H_2 (0.6 wt% of H_2 at 77 K and 4 MPa). This value is quite important considering the small BET surface area (see Fig. S1 in the ESI†). Assuming that at low coverage, hydrogen is adsorbed preferentially by the narrow pores form, this would suggest a confinement effect within the small hydrophobic 1D pore system. The enthalpy of H_2 adsorption (Fig. 2) of MIL-53(Fe)-$(CF_3)_2$ reaches 11 kJ mol^{-1},
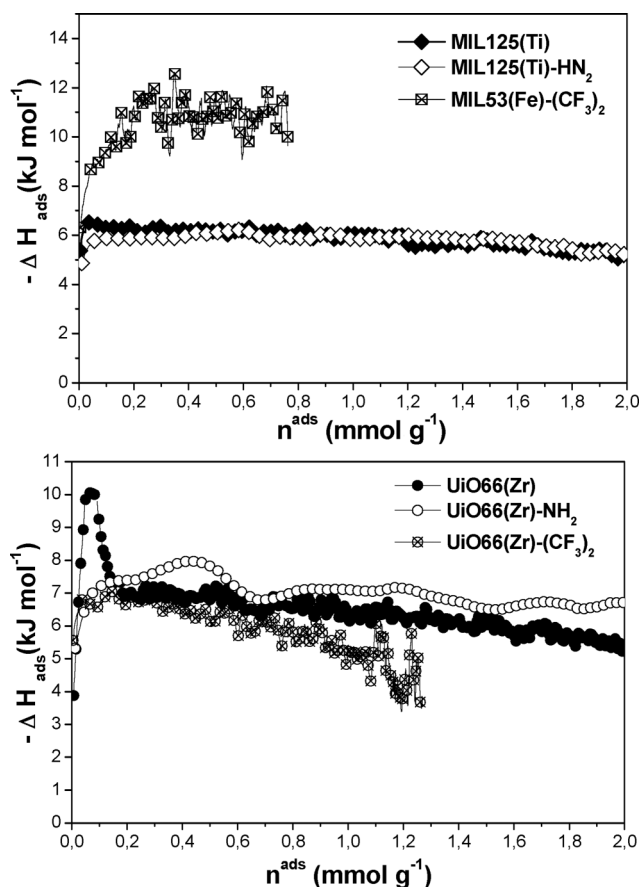

Fig. 2 Coverage dependence of the enthalpy of H_2 adsorption at 77 K for MOFs. Full, empty and crossed symbols represent unmodified, –NH_2 and –CF_3 modified MOFs, respectively.

which is indeed among the highest reported so far,[4] in agreement with the presence of a strong confinement effect, even if one cannot exclude an effect due to the perfluoromethyl groups.

MIL-125(Ti) has a rigid 3D interconnected porosity with two types of micropores (6 and 12.5 Å).[20] Modified MIL-125(Ti)-NH_2 is isostructural to the pristine solid. However, the presence of the amine group reduces the pore size and surface area, though its position and direction are not yet clearly identified. The H_2 capacity is, respectively, 3.4 and 2.5 wt% at 77 K and 4 MPa for MIL-125(Ti) and MIL-125(Ti)-NH_2. Although significant amounts, these values are far away from the best H_2 capacity reported for MOFs (up to 7.5 wt%), in agreement with the much smaller BET surface areas for these samples with regard to very

Table 1 Textural properties (S_{BET}/m^2 g^{-1}) (±20), hydrogen excess capacity at 77 K and 4 MPa (wt%) (±0.1), and hydrogen adsorption enthalpy at low coverage (kJ mol^{-1}) (±0.5) at 77 K for unmodified and modified MOFs. The BET surface area in grams per unmodified MOF is given in brackets

Sample	Organic linker	S_{BET}/m^2 g^{-1}	H_2 capacity at 77 K and 4 MPa (wt%)	$-\Delta H_{ads}$ at 77 K/kJ mol^{-1}
MIL53(Fe)	BDC	<20	<0.1	—
MIL53(Fe)-$(CF_3)_2$	BDC-$(CF_3)_2$	100	0.6	11
MIL-125(Ti)	BDC	1360	3.4	6.5
MIL125(Ti)-NH_2	BDC-NH_2	1130 (1203)	2.5	6
UiO-66(Zr)	BDC	880	2.3	10
UiO-66(Zr)-NH_2	BDC-NH_2	1206 (1280)	2.5	7.0
UiO-66(Zr)-$(CF_3)_2$	BDC-$(CF_3)_2$	540 (809)	1.2	6.5

large pore MOFs.[25] The lower capacity for the amino-modified MIL-125(Ti) at high pressure is consistent with the decrease in BET surface area. At low pressure, both MIL-125(Ti) and MIL-125(Ti)-NH$_2$ present a similar enthalpy of adsorption of about 6 kJ mol^{-1}. The interaction of H$_2$ and the framework is thus almost unaffected by the presence of the relatively weak amino groups from the organic linker, in agreement with previous studies on MOF-5 and MOF-5-NH$_2$.[16]

UiO-66(Zr) solid exhibits a 3D porous structure with two systems of microporous cages (7.5 and 12 Å) and unsaturated metal sites upon controlled dehydroxylation.[21] The surface area and pore volume of the isostructural modified solids UiO-66(Zr)-NH$_2$ and -(CF$_3$)$_2$ are comparable and smaller, respectively, as a consequence of the bulkiness and weight impact of the perfluoromethyl group (Table 1). Thus, a similar trend was also observed for the H$_2$ capacities at 77 K at high pressure, which are higher for unmodified UiO-66(Zr) and UiO-66-NH$_2$ (2.3 and 2.5 wt%, respectively) than for UiO-66(Zr)-(CF$_3$)$_2$ (1.2 wt%). At very low coverage, the enthalpy of adsorption of UiO-66(Zr) reaches 10 kJ mol^{-1} but rapidly decreases to 7 kJ mol^{-1}. This might indicate the presence of a small amount of strong binding sites, most probably the CUS. In the opposite sense, both UiO-66(Zr)-NH$_2$ and -(CF$_3$)$_2$ present enthalpies of adsorption of 7 and 6.5 kJ mol^{-1}, respectively, even at very low coverage. This might indicate either that the presence of –NH$_2$ and –(CF$_3$)$_2$ groups decreases the strength of the binding sites or most probably that they sterically shield access to the CUS. For further H$_2$ adsorption, the enthalpy decreases linearly, with a stronger drop in the case of UiO-66(Zr)-(CF$_3$)$_2$. A similar trend of enthalpy of adsorption has been observed for N$_2$ adsorption at 77 K in these solids. No difference in the heat of adsorption between the amino and perfluoromethyl terephthalate forms was observed, confirming the absence of any significant enhancement by the perfluoromethyl groups.

To summarize, organic functionalization of the linker influences the H$_2$ storage capacity, essentially by subsequent modification of the textural properties. Thus, in the MIL-125(Ti) and UiO-66(Zr) solids, the H$_2$ capacity decreases as the volume of the functional group increases (NH$_2$ < (CF$_3$)$_2$). Furthermore, –NH$_2$ and –CF$_3$ group inclusion in tetravalent-based UiO-66(Zr) or MIL-125(Ti) does not increase the enthalpy of H$_2$ adsorption at 77 K compared to pristine solids. In addition, no significant increase in the heat of adsorption is observed for tetravalent Ti and Zr MOFs, while the increase of valence might be considered a way to increase the polarity of the inorganic sub-units. An effect is clearly present for the non-modified UiO-66 sample, probably due to the presence of Lewis acid sites, as observed previously for di- or trivalent metal-based MOFs with CUS.[4,7]

The modification of the organic linker in MIL-53(Fe)-(CF$_3$)$_2$ also alters the porosity. However, in this case, perfluoromethyl groups block the total contraction of the pores of MIL-53(Fe), thus allowing access to an important amount of H$_2$ (0.6 wt%), considering its low surface area (100 m^2 g^{-1}). Moreover, a significant enthalpy of adsorption close to 11 kJ mol^{-1} is observed at low coverage for the MIL-53(Fe)-(CF$_3$)$_2$ solid as a consequence of a stronger confinement effect due to the smaller 1D porosity. In this particular case, CF$_3$ grafting within flexible MOFs seems to be a promising way of increasing the H$_2$ capacity and enthalpy of adsorption, while the use of a tetravalent metal (Ti, Zr) within porous rigid carboxylate-based MOFs, organically functionalised or not, does not enhance the adsorption of H$_2$.

Acknowledgements

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