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Screening of hypothetical metal-organic frameworks for H_2 storage

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A computational screening throughout a database containing ~138000 metal-organic frameworks (MOFs) has been performed to select candidate structures for hydrogen storage. A total of 231 structures (of which 79 contain paddle-wheel units) have been selected that meet the gravimetric and volumetric targets at 100 atm and 77 K. Grand Canonical Monte Carlo simulations have been performed to calculate the isotherms and select structures which meet the targets at 50 atm, and also to check the adsorption in the low pressure regime (1 atm). From this a reduced set of 18 structures has been analysed more in detail, regarding not only gravimetric and volumetric uptakes but also pore size distribution and pore volume. A few structures with 3 % gravimetric uptake at 1 atm and 77 K perform at the level of the best found so far.

1. Introduction

In the context of the development of new technologies which would enable us to use hydrogen as a sustainable energy vector for on-board applications, the production of H_2 and its gas storage has been broadly studied. Regarding the storage through physisorption[1,2], materials are required that adsorb 5.5 % (weight) and 40 g/L of H_2 at low pressures (1-100 atm) and 233-358 K, based on the current targets of the US Energy Department for onboard hydrogen storage for light-duty fuel cell vehicles[3]. Most of the literature, however, reports hydrogen adsorption in MOFs at 77 K[1,4], and hence for the sake of comparison we will use 77 K. Regarding the pressure selected for our study, we believe low pressure (~ 1 atm) gives the most reliable values rather than those at the upper range of target pressure (~ 100 atm) where adsorption is mainly due to simple occlusion. Adsorption at low pressure is mostly due to the interaction of hydrogen with the active sites, and this is one key parameter that should be improved to achieve targets. Adsorption data at 77 K and high pressure tends to favour structures with large pore volumes regardless the isosteric heat of adsorption, but hydrogen storage targets can only be achieved if a rather strong (~15-25 kJ/mol) physisorption enthalpy is achieved, and this depends on the specific surface and the density of adsorption sites.

Although certain frameworks with, temporarily, “record” hydrogen adsorption uptakes have appeared in the literature[5,6] two important aspects have to be taken into account: (i) high gravimetric uptake is not, alone, a substantial achievement because on-board (2017) targets require large gravimetric (5.5 %) and volumetric (40 g/L) uptakes; (ii) specific structures with high uptakes are one important thing, but it is also desirable to identify particular descriptors that structures have to meet in order to reach the commercial targets. Along these lines, a recent computational work[7] reported a covalent organic framework (COF-301 with Pd) with an exceptional volumetric uptake at 100 atm, achieving the ultimate target (60 g/L), with also a large excess gravimetric uptake (4.2 %), not far from the 2017 target (5.5 %). Although the target should include the system weight, an advantage of this study is that the adsorption indicated corresponds to 298 K instead of the usual 77 K. Hence, the values represent a considerable computational breakthrough, and hopefully consistent with future experimental synthesis and measurements. This achievement is mainly due to the presence of accessible Pd centres.

A recent study by Firlej et al.[8] highlights the importance of computational methods to understand the adsorption on porous materials at atomic level. Along the same lines, Goldsmith et al.[9] performed a screening along the Cambridge Structure Database (CBS) in order to find promising structures for hydrogen storage. The authors suggest that surface area alone is not the main descriptor to focus in order to find candidate structures, and also they point several overlooked structures where better tuning may lead to improved storage.

In this study we use structural and chemical descriptors that metal-organic frameworks have to fulfil in order to become candidates for hydrogen uptake. With these descriptors, we will explore a MOF database and will make a computational study applying the previous criteria in order to select the best structures and suggest structures for further improvements in hydrogen storage.

2. Methodology

The screening study was performed over the hypothetical MOFs database recently reported by Wilmer et al[10]. In order to identify the best candidates for H_2 adsorption, two independent screenings were applied (Figure 1). In the first one, three different conditions have been applied to all structures of the database, with a final selection of 10 structures (called 'Best-1') that matched the criteria.

In the second screening, a particular subset of the database, paddle-wheel structures, has been selected. After applying the target conditions, 8 structures have been obtained, called 'Best-2'. An analysis more in detail has been performed over these selected structures ('Best-1' and'Best-2'.

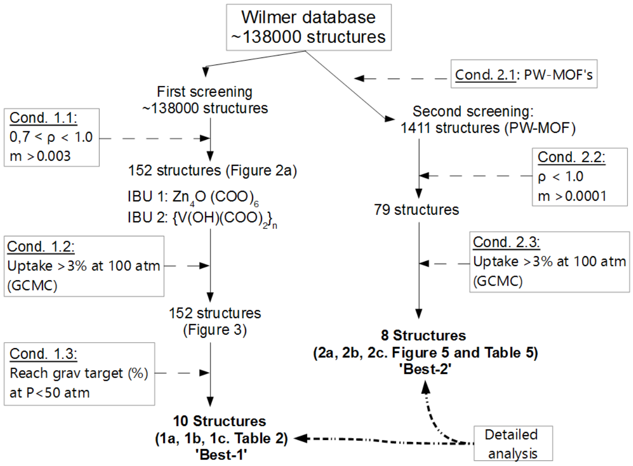

Figure 1. Scheme of the screening procedure to select suitable candidate MOF structures for H_2 storage.

2.1 First Screening

As a first screening, frameworks with appropriate physical properties for gravimetric and volumetric H_2 storage were selected. However, increasing simultaneously the gravimetric and volumetric targets is somehow contradictory: a large gravimetric uptake (grams of hydrogen adsorbed per mass of material+hydrogen) can benefit from a low dense structure. But then, too low framework density will result in low volumetric uptake (volume of hydrogen adsorbed per volume of material+hydrogen). In a recent work[11], we suggested that a material density between 0.7 and 1.0 g/cm^3 would be the optimum range to maximise both, volumetric and gravimetric targets. Hence, we include this condition (Table 1) in our search criteria across the database. Goldsmith et al.[9] find a similar conclusion pointing towards optimum densities as those > 0.5 g/cm^3 combined with appropriate surface area. A second condition, also based in the same previous study, refers to the density of adsorption centres in the material: the larger this number the higher the adsorption. Considering that the metal atoms are the main adsorption centres, the number of metal atoms per Å^3 ('m') can be easily calculated just from the stoichiometry and volume of the unit cell, and we have established a convenient threshold value (Table 1). Only with this data, and without any computational calculation, a rough estimation of the hydrogen gravimetric uptake, 'x', can be made by using equation (1)(11), where we introduce the parameter 'n' as the number of hydrogen molecules adsorbed per each metal site. Using previous computational studies, values of 'n' depend obviously on the topology and chemical composition, but a range 1-3 is a reasonable approximation. Using Condition 1.1, gravimetric uptakes close to 3 % can be expected according to equation (1).

$$x(\%)=\frac{m\cdot n}{m\cdot n+\frac{\rho_{MOF}}{3.343}}\cdot 100 \qquad (1)$$

By using these criteria (Condition 1.1 in Table 1), structural and physical factors are already taken into account, and this will give a reduced number of candidate structures. Hence, as a second test (Condition 1.2 in Table 1), Grand Canonical Monte Carlo (GCMC) simulations were performed in order to compute the adsorption isotherms for the selected candidates. Applying the 'Condition 1.1' over the 138000 elements of the database(10), a set of potential frameworks (152 structures) were identified. Monte Carlo simulations (Condition 1.2) were then run over these 152 structures. Another criteria (Conditon 1.3 in Table 1) was finally applied, that the obtained adsorption isotherms should reach the gravimetric 2017-target (5.5%) at pressures $\leq$ 50 atm. Finally, an analysis of the pore size has been performed over the selected structures in search of optimum pore sizes according to previous work[13,15], which deals with the contribution of confinement effects to hydrogen adsorption and establishes an optimum pore range to maximise this effect.

Table 1. Threshold values of physical properties used as criteria for the first screening. GCMC is Grand Canonical Monte Carlo simulation.

Properties	**Range**
Condition 1.1	
ρ, MOF density (g/cm³)	**0.7 < ρ < 1.0**
m, Metal atoms density (M-at./Å³)	**m > 0.003**
Condition 1.2	
Grav. uptake at 100 atm (%) using GCMC	**> 3 %**
Condition 1.3	
Reaching grav. 2017-target at < 50 atm	**> 5.5 % at 50 atm**

The effect of the pore size is a key factor directly related to the storage capacity, but also pore volume is important. Only increasing the pore volume does not provide better results[13] because a large pressure will be needed to reach saturation. A further problem is that large pore volumes are usually associated to low material densities and this decreases the volumetric uptake for a given gravimetric value. Regarding pore size, recent studies[13,15], suggested that the optimum pore size that maximise confinement effects was determined as 5.4-10.2 Å, and this range will be used in the present study. At such range of pore size, confinement effects contribute significantly to increase the heat of adsorption.

However, the estimation of pore size is not trivial. The pore size is not an individual value but rather a distribution of values whose calculation requires to include successive spheres of decreasing volume inside the pores. Hence the largest cavity diameter (LCD) only means the largest sphere that can be contained in the pore, but this is not the real volume of the pore when the pore is not spherical in shape. The estimation of percentage of pores in the optimum range (5.4-10.2 Å) to maximise confinement effects for hydrogen adsorption is, therefore, just a rough estimation whose value may depend on the algorithm employed. In our case we employed a home-made code used in a previous work[15] which inserts smaller and smaller spheres in the empty space of the microporous material, and continues down until all the empty spaces are filled. Finally, a summation of all spheric volumes gives the total pore volume of the structure. With the data obtained the pore size distribution and thus the percentage of pores in the range 5.4-10.2 Å has been estimated.

With the 152 structures obtained after 'Condition 1.1' and 'Condition 1.2' (Table 1) have been applied, a classification in groups according to gravimetric and volumetric performance will be made, and an analysis of pore size of the best structures will be performed trying to find structures meeting the condition of optimum pore size distribution. As a final result of this screening test described in Table 1, a small subset of candidates structures will be obtained. We will refer to this subset of structures as 'Best-1'.

2.2 Second Screening: MOFs containing open metal sites

Secondly, a parallel and independent screening over the database will also be considered, and the reason for that is that it has been reported in the literature[16-18] that open metal sites pose an interesting requirement which makes these structures as good candidates for hydrogen storage. Some of the highest gravimetric uptakes at low pressure and temperature (1 atm and 77 K) have been reported for Cu-paddle wheel (Cu-PW) containing MOFs, where accessible open metal sites at the surface, coupled with confinement effects[13,15], favour stronger interactions and larger adsorption enthalpies, close to the optimum value of 15-25 kJ/mol[19,20]. UTSA-20, Mepy, HKUST-1, PCN-12 and NOTT-103 show uptake values of 2.92[21], 3.07[21], 2.27[22], 3.05[23] and 2.63[12], respectively, at 77 K and 1 atm.

Taking into account that some open metal structures might not fulfil some of the previous criteria (such as 'Condition 1.1') defined in Table 1, it seemed convenient to establish a new screening, starting again from all the elements of the database. Criteria for the first screening should not be viewed as necessary but rather as sufficient, hence it is possible that a different set of criteria may also lead to suitable candidates for hydrogen storage. This is the reason for this second screening.

First of all, structures containing open metal sites (Cu/Zn-PW building unit) have been selected (Condition 2.1 in Figure 1) and then a second criterium based on density (Condition 2.2 in Table 4) has been applied to narrow the search.

From Condition 2.1, 1411 structures were selected (PW-MOFs). Then, Condition 2.2 yielded 79 structures whose isotherms have been calculated using Monte-Carlo simulations (Condition 2.3 in Table 4) in order to obtain the gravimetric and volumetric uptakes, from which the best structures will be selected. They will be called 'Best-2'.

2.3 Force Field performance

It has been suggested that Grand Canonical Monte Carlo (GCMC) simulations using general force fields such as DREIDING or UFF can be used to evaluate the hydrogen adsorption properties of MOFs with a reasonable, albeit not large, accuracy[24-26]. Recent reports[27,28] indicate that a simple Lennard-Jones is not able to capture the full behaviour of the Metal-H_2 and H_2-H_2 interactions which dominate at low (Metal-H_2) and high (H_2-H_2) pressure. Hence, some parts of the isotherm will necessarily be less accurate. More sophisticated functional forms including ab initio and quantum-mechanical density functional theory terms as input for the force fields have been proposed[26,29,30].

A different attempt has been made by trying to parametrise a Lennard-Jones force field for the MOF-H_2 interaction with data from ab-initio MP2 calculations[31,32]. In a similar way, Matanovic et. al.[33] perform rigorous quantum calculations to study the H_2 binding in porous materials with state of the art accuracy and show the intrinsic difficulties of the subsequent GCMC simulations to reproduce the potential energy surface.

The results reported for several materials indicate that DREIDING performs slightly better than UFF at low pressure[34]. In both cases, the uptake is overestimated[35] partly because the neglection of the quantum effects, essential at low temperature to capture the weak $H_2\cdots H_2$ interactions[36-38]. Being DREIDING and UFF force fields with Lennard-Jones terms, the considerations above also apply and hence regardless the accuracy of the ab-initio data, the functional form of the Lennard-Jones is a bottleneck which precludes to obtain more accurate results. In this study we have focused on the adsorption at low pressure where the dominant hydrogen-adsorbent interactions imply that the more difficult to quantify $H_2\cdots H_2$ interactions will be less important and hence this system can be simulated to a reasonable accuracy by simple potential expressions such as the common Lennard-Jones.

In materials with open metal sites, small $H_2\cdots$Metal distances are not topologically constrained, which means the potential energy lies in the region of high curvature and a fine tuning of the $H_2\cdots$Metal parameters was considered convenient. We tested previous forcefields for $H_2\cdots$Cu and $H_2\cdots$Zn[36-38] as well as a set of DFT-derived parameters from a previous study in our group[15] for $H_2\cdots$Cu, and finally we tested the recent parameters (including Cu, Zn, V) from Addicoat et. al.[39] combined with the classic approach for H_2 by Darkrim and Levesque[40], the latter of which has been extensively used among others by Garberoglio et al.[41] The rest of the parameters were taken from DREIDING as in previous work[15,42].

From the results of this test obtained in MOFs with and without open metal sites, not shown for the sake of brevity, we chose a combination of the potentials from Heine et al. for metals with that of Darkrim and Levesque for H_2, using the Lorentz-Berhelot rules to obtain the parameters for the metal$\cdots H_2$ interactions (ESI section S5). With this force field employed in the GCMC calculations, the adsorption isotherms were calculated using MUSIC[42] (see more details in ESI, section S6). The computational results in Table 2 tend to overestimate the adsorption of hydrogen, but this is within the intrinsic limitations of the simple approach chosen. However, this simple approach allows a fast screening over the database.

3. Results and Discussion

3.1 First Screening

By using as selection criteria the range of values of the physical properties presented in Table 1 (Condition 1.1 and Condition 1.2), a total of 152 frameworks were found. They comprise two types of inorganic building units (IBUs) (Figure 2a) and several organic linkers (Figure 2b).

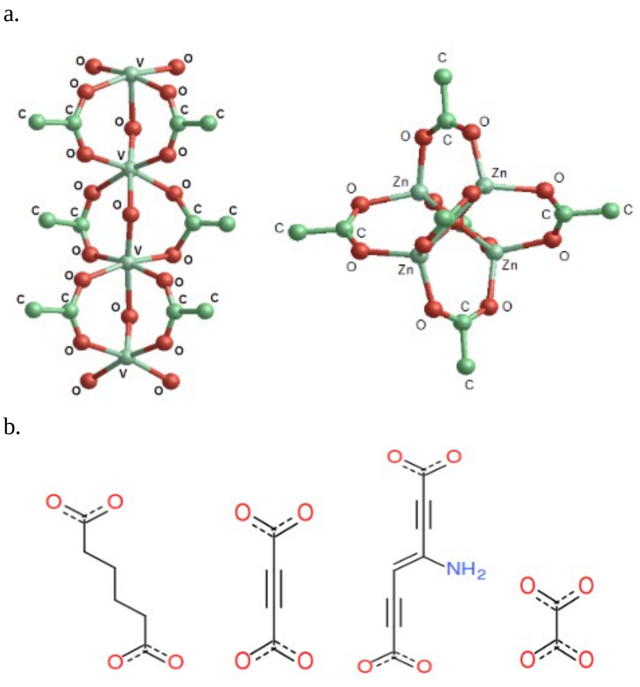

Figure 2. Inorganic building units present in 152 selected hypotetical MOFs. a) {V(OH)(COO)$_2$}n unit (left, 4 structures) and Zn$_4$O(COO)$_6$ (right, 148 structures). b) Some organic linkers (See ESI, section S2).

Then, GCMC simulations of these 152 MOF structures were performed. The analysis of the computed isotherms allows to classify this selection of MOFs into three groups (Figure 3).

Group-1 comprises hypothetical MOFs that reach the target at pressures < 50 atm. In Group-2 we found materials that reach the target between 50-100 atm. Finally, Group-3 comprises MOFs that do not reach the target[3] below 100 atm. Given that 100 atm is the maximum range of pressure indicated as target, structures in Group 3 are clearly outside any selection of candidate materials.

The fact that the selection criteria included an appropriate range of densities means that structures meeting the gravimetric target also reach the volumetric target, as can be seen in Figure 3. Groups 1 and 2 reach the volumetric targets at 50 and 100 atm respectively. Regarding Group 3, the fact that some of them reach the volumetric target at 100 atm (Figure 3, bottom) does not allow them to be included as appropriate materials as they do not reach the gravimetric target. Hence, only Group 1 (10 structures), also called 'Best-1', will be used for further analysis. The gravimetric and volumetric uptake of the 'Best-1' structures at low pressure (1 atm) and the percentage of pores in the optimum range (5.4-10.2 Å) is reported in Table 3. Figures and CIF files of these structures are included as ESI (section S1).

In Group 1-b, structures '5008433' (H), '5008453' (F) and '5008565' (NH$_2$) are isostructural with the substitutions indicated in parenthesis. Their pores in range are different but they also differ in their respective pore sizes giving the largest pore volume for the unsubstituted framework ('5008433') in spite of its smallest value of pores in range.

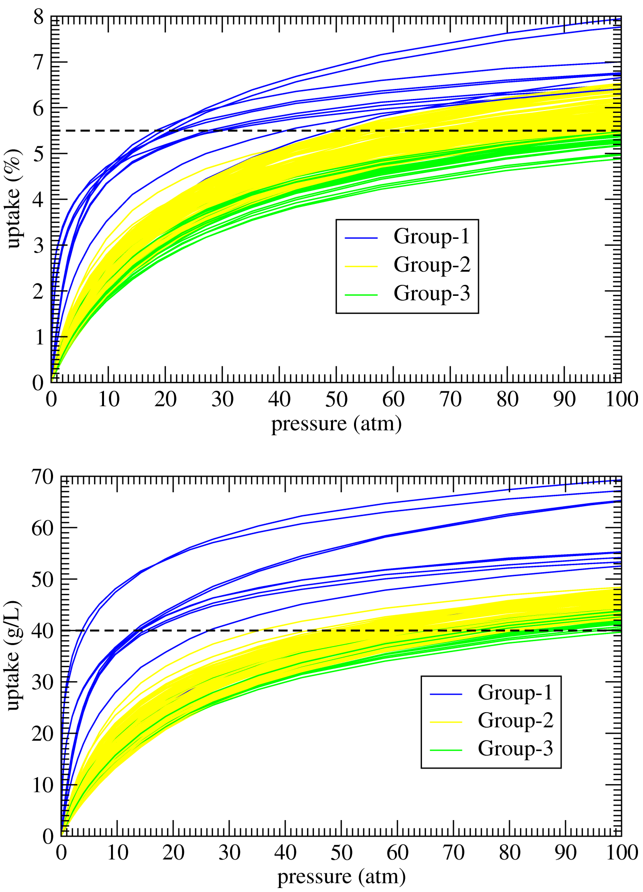

Figure 3. Absolute adsorption isotherms at 77 K computed over the 152 structures obtained from the first screening test using conditions 'Condition 1.1' and 'Condition 1.2' (Table 1). The dashed line represents the target for 2017.[3] Top) gravimetric uptake; bottom) volumetric uptake.

Table 2. Calculated gravimetric (%) and volumetric (g/L) uptakes at 1 atm and 77 K for the 'Best-1' materials (Group 1 in Figure 3). 'Group-1' is here subdivided into Groups 1-a, 1-b and 1-c. Ligand size has been measured as the distance between carboxylic carbons.

Group	**Structure code(1)**	**%**	**g/L**	**Pores in range (2)**	**Ligand size (Å)(3)**	**SSA (m^2/g)**	**w-capac. (4) (%)**	**Porosity/density(5)**
1-a	1001432	3.0	31.6	50.0	4.06/6.20	1764	2.9	0.59/0.99
	6000362	2.9	29.1	71.4	3.73/6.20	1319	3.4	0.61/0.96
	8702	2.4	18.6	33.3	1.51/6.20	3293	5.0	0.72/0.75
	8688	2.3	18.5	40.0	1.51/6.20	3228	4.8	0.71/0.78
1-b	5008565	1.0	8.2	80.0	6.91/9.17	3529	4.5	0.70/0.78
	5008433	1.0	7.7	77.7	6.91/9.17	3746	4.9	0.71/0.76
	5008453	0.9	7.7	90.0	6.91/9.17	3579	4.7	0.71/0.78
	5005539	0.9	7.0	100	6.91/9.64	4480	5.2	0.72/0.73
1-c	8627	0.7	6.1	40.0	1.51/5.60	2877	3.5	0.72/0.77
	5893	0.4	2.4	50.0	4.06/5.60	3357	6.0	0.76/0.67

(1) Codes from the Snurr-Wilmer database[10]. More details in ESI.

(2) % of pores within the optimum pore range size (5.4 -10.2 Å).

(3) Size of the two organic linkers of each structure.

(4) Working capacity: gravimetric uptake between 2-100 atm.

(5) Volume of pores/Unit cell Volume. Pore volume = porosity/density.

Regarding Group 1-a, the first two materials ('1001432' and '6000362') present a rod-type IBU (Figure 1a, left), composed by chains of vanadium and oxygen atoms combined with two different ligands (ESI, section S2). Although the percentage of pores in range in '1001432' is low compared to the other 'Best-

1' structures, the length of the ligands and the type of metal center leads to the highest gravimetric and volumetric uptakes (~3.0 % and 30 g/L respectively). The other two hypothetical frameworks of Group 1-a (‘8702’ and ‘8688’) contain the well known IBU of the IRMOF series (Figure 2a, right) linked by a short oxalate ligand of ~1.5 Å (Figure 2b).

Group 1-b is formed by catenated frameworks with the $Zn_4O(RCOO)_6$ IBU and slightly different organic ligands (see Figure 4 and ESI, section S2). These materials have a very large percentage (70-100 %) of pores in range for optimum H_2 uptake, but they show gravimetric and volumetric uptakes lower than those of the materials of Group 1-a. However, this is only at 1 atm, and at larger pressure, the isotherms become similar to those of ‘8702’ and ‘8688’, also IRMOFs. When the pressure is increased, the effect of adsorption by confinement effects plays a major role and then, between 50-100 atm, they show an excellent behaviour, exceeding the storage targets.

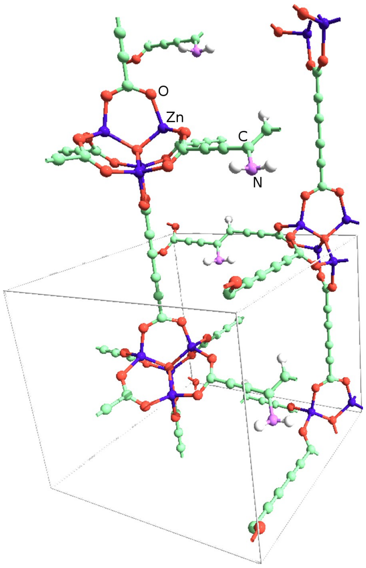

Figure 4 Structure of mof ‘5008565’ (from Group 1-b, Table 3).

Our analysis also reveals little effect on the storage properties of halogen-substitution in the linkers. Two MOFs in Table 3 contain F atoms in their organic linkers (‘5008453’ and ‘8688’). If we compare the same structures with linkers that do not contain F (‘5008433’ and ‘8702’) we notice small differences in gravimetric and volumetric uptake.

Finally, Group 1-c contains only two frameworks, ‘8627’ and ‘5893’. Structure ‘8627’ is topologically equivalent to MOF-5, but with the important difference that in the [100] direction it contains the short oxalate ligand (instead of benzo-dicarboxylate in MOF-5). This contributes to the presence of a more optimised pore distribution to maximise hydrogen storage (MOF-5 pore size distribution can be found in ESI, section 4). At low pressure, the weak interaction with the Zn centres provides the low adsorption reported in Table 3. But this structure improves considerably the storage as the pressure is increased, reaching the targets at pressure lower than 50 atm. Regarding structure ‘5893’, it shows the lowest gravimetric and volumetric uptake values in Table 3, slightly above the targets at 50 atm and hence also within the Best-1 selection. A reason for the lower performance of '5893' is that the size of its only pore in range is 9.0 Å, close to the upper edge (10.2 Å) of the optimum range, and far from the lower end (5.4 Å) where the confinement effects are more important.

In order to compare with recent landmarks, we performed calculations on IRMOF-62[43] (37.6 % of pores within optimum range), claiming a gravimetric uptake of 1.7 % at 77 K and 1 atm. We obtained values of 2.4 % and 17.3 g/L at 77 K and 1 atm, close to the values of Group 1-a. This means our search allows to identify good candidate MOFs. The uptakes values for IRMOF-62 differ from the experimental data but they show the same trends than those reported in Table 2.

3.2 Second Screening. Paddle-wheel-containing MOFs.

As explained above, the final selection of the first screening did not yield paddle-wheel (PW) structures which in fact are usually reported in the literature as good candidates for hydrogen storage[12,21-23]. For this reason, a specific screening was performed for all PW-structures of the database. Initially, a total of 1411 PW-containing MOFs were considered. Then, we used the selection criteria indicated in Table 4 in order to refine the structures. These selection criteria are similar to those in Table 1 but the threshold values have been adjusted to the specific characteristics of PW MOFs.

Previously to the screening, a benchmarking test was run in PW-MOFs such as HKUST-1, UTSA-20, Mepy, PCN-12 and NOTT-103 in order to validate our methodology (Table 3). The experimental values reported for HKUST-1 at 77 K are 2.27 and 3.6 % (at 1 and 10 atm, respectively)[22], which compare reasonably well to our calculated gravimetric uptakes at the same temperature (1.80 and 4.0 % at 1 atm and 10 atm respectively). The calculated values for the other PW-MOFs tend to overestimate the uptake and the reasons are the same than those indicated previously. With this methodology, the computed isotherms were fitted to the Langmuir equation and the results were used to estimate the uptakes at low pressure.

Table 3. Calculated and experimental excess gravimetric uptakes at 1 atm and 77 K for MOFs containing Cu-PW units.

Structure	**Calc.**	**Exp.**
UTSA-20	3.08	2.92[21]
[Cu-Me-4py-trz-ia][a]	3.77	3.07[21]
HKUST-1	1.82	2.27[22]
PCN-12	3.69	3.05[23]
NOTT-103	3.69	2.63[12]

[a] Me-4py-trz-ia=5-(3-methyl-5-(pyridin-4-yl)-4H-1,2,4-triazol-4-yl)-isophthalate

After the first selection (Condition 2.2 in Table 4), 79 structures were found that matched our criteria. From the corresponding isotherms (Condition 2.3 in Table 4), we selected 8 structures, which we call ‘Best-2’ (Figure 5). Figures and further details of the ‘Best-2’ structures can be found on ESI (section S3).

Table 4. Range of physical properties used as a selection criteria for the second screening, corresponding to 1411 structures of the database containing paddle-wheel units. Condition 2.1 (Figure 1) selected 1411 PW-MOFs from the database.

Properties	**Range**
Condition 2.2	
ρ (g/cm³)	**ρ < 1.0**
m, Metal atoms density (M-at./ Å³)	**m > 0.0001**
Condition 2.3	
Grav. uptake at 100 atm (%) using GCMC	**> 3 %**

Most of the isotherms (Figure 5) show large uptakes (> 7 %) at high pressure, except in one case (6 %). However, at low pressure the uptakes are considerably lower (Table 5).

Most 'Best-2' materials show an uptake close to 1 % at 1 atm, similarly to Groups 1-b and 1-c within the 'Best-1' materials (Table 3). The best performing materials within 'Best-2' ('2000000' and HKUST-1) show an uptake similar to the best performing materials within the 'Best-1' materials (Group 1-a). The 'Best-2' structures have been classified into three Groups (Table 5) according to the isotherms in Figure 5.

The first Group (2-a) comprises two structures, '2000132' and '2000149' (red lines in Figure 5) that show an exceptional gravimetric uptake, reaching the gravimetric target at 10 atm and the volumetric target at 35 atm. At 50 atm these structures reach a considerable 45 g/L and 12 % as volumetric and gravimetric uptakes. This is mainly due to their low density (0.33 g/cm^3) and hence large porosity (0.77) as shown in Table 5. However their performance at 1 atm is not so high, with gravimetric uptakes of 0.82 % ('2000132') and 0.87 % and '2000149'. We believe this is not the kind of candidate structures on which future prospects should be based.

The second Group (2-b) comprises five structures that reach the targets around 30 bar (blue lines in Figure 5). Finally, the Group 2-c (green lines in Figure 5) is formed by the structure '2000000' and also HKUST-1, both showing large uptake at 1 atm (~2 %) and reaching the volumetric target at pressures around 10 atm. In fact, '2000000' (Zn)[44] is isostructural to HKUST-1 (Cu), which means that our screening has been able to identify one of the best to date paddle-wheel based hydrogen adsorbers.

In Table 5, a large number of parameters related to adsorption have been gathered such as material density (ρ), density of metal centres (m), percentage of pores in the optimum range (5.4-10.2 Å), and porosity of the structure. We now analyse more in detail all the results shown in Table 5.

Structures in Group 2-a have low gravimetric uptakes at low pressure. However, at larger pressures they are far beyond the targets, owing to their large porosity, with the largest values (86 % and 85 %) among all 'Best-2' and 'Best-1' materials. Some of the best adsorbing 'Best-1' MOFs, '1001432' and '6000362', only have porosities of 59% and 61%, hence a large porosity is not needed to reach the targets. In fact, large porosities will severely penalise the adsorption at low pressure.

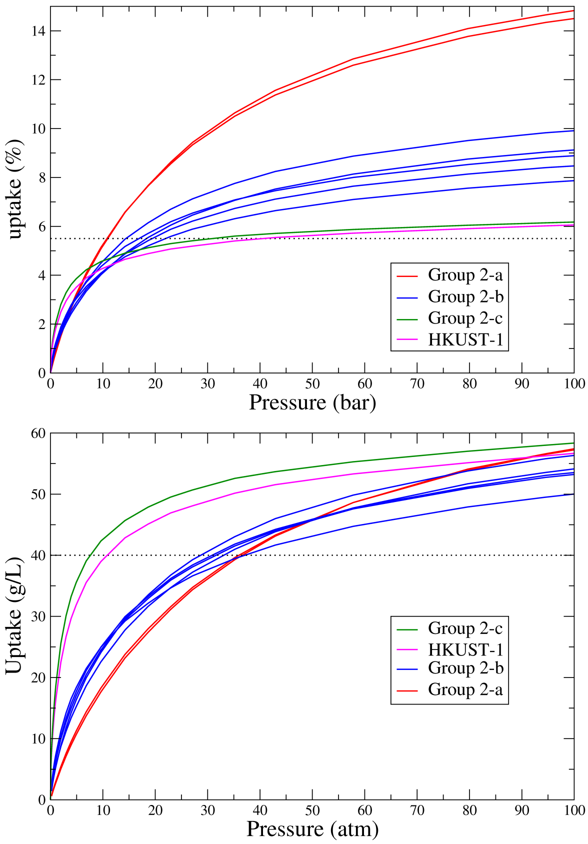

Figure 5. Absolute adsorption isotherms at 77 K computed for 'Best-2' structures. The dashed line represents the target for 2017.[3] Top) gravimetric uptake; bottom) volumetric uptake.

The isotherms of Group 2-a at higher pressures show that these structures have a higher storage capacity when compared to the other 'Best 2' structures. This leads to the largest working capacities throughout the database.

Group 2-b contains structures with a higher uptake at low pressure. This can be explained by looking at the number of pores within optimum range (~25 %), larger than those of Group 2-a (18-22 %). Structure '2000592' shows the highest uptake at 1 atm (1.23 %) within Group 2-b due to its high porosity (76 %) and higher density (0.58 g/cm^3), close to the optimum range (0.7-1.0 g/cm^3)[11]. This result is still far from that obtained for '2000000' and HKUST-1 (Group 2-c) showing a much more advantageous pore size distribution, with 50 % of pores within the optimum range, the largest values among all 'Best-2' MOFs, and also with a better value for the density (0.9 g/cm^3), the only case within the optimum range among the 'Best-2' materials.

Looking at the working capacities, the selection of 'Best-2' (specially '2-a' and '2-b', with values ~6-13 %)show better results than those of 'Best-1' (~3-6 %), however applying the excess correction, the upper range in Best-2 (13 %) will be particularly penalised. If isosteric heats of adsorption around 15 kJ/mol[19,20] are needed, clearly structures '2000132' and '2000149' will not be suitable candidates for hydrogen storage.

Table 5. Calculated gravimetric (%) and volumetric (g/L) uptakes at 1 bar and 77 K for the 'Best-2' materials (see also Figure 5).

Group	Structure code	%	g/L	Porosity (1)	ρ (g/cm³)	metal atoms density, m (M-at./Å³)	Pores in range (%)(2)	Smallest pore(4)	working capacity(6) (%)
2-a	2000132	0.82	2.72	0.86	0.33	0.0007	21.7	5.70	13.2
	2000149	0.87	2.97	0.85	0.33	0.0007	17.8	5.70	12.8
2-b	2000066	1.03	5.33	0.79	0.51	0.001	25.0	7.60	8.2
	2000082	1.18	6.57	0.76	0.55	0.001	27.2	7.40	7.0
	2000089	1.10	6.42	0.75	0.58	0.001	22.2	5.50	6.8
	2000108	1.02	5.56	0.78	0.55	0.001	26.6	5.50	7.5
	2000592	1.23	7.33	0.76	0.58	0.001	27.2	8.90	6.0
2-c	2000000	2.05	18.56	0.66	0.90	0.002	50.0(5)	4.60	3.4
	HKUST-1	1.82	16.29	0.69	0.89	0.002	50.0 5)	4.60	3.5

(1) Porosity is Volume of all accessible pores / Unit cell Volume. The 'pore volume' (cm^3/g) can be obtained as porosity/density.
(2) % of pores in the material in the optimum pore range size (5.4 -10.2 Å).
(3) The codes are named after the Snurr-Wilmer database. More details in ESI.
(4) Smallest pore diameter within the optimum pore range (5.4 -10.2 Å).
(5) Pores within the range 4.6-10.2 Å, where the low end of the optimum range has been extended from 5.4 to 4.6 Å.
(6) Gravimetric uptake between 2-100 atm

Hence, in HKUST-1 topology, several aspects explain the large uptakes: presence of open metal sites, appropriate pore size distribution and appropriate material density. The corresponding volumetric isotherm (Figure 5 bottom) shows the best behaviour and this is due to the near optimum density of HKUST-1, larger than any other among 'Best-2' structures, which contributes to a larger volumetric uptake for a given gravimetric value according to equation (2)[11]:

$$\rho_{H_2}(gH_2/L)=\frac{\rho_{MOF}(g/cm^3)\cdot x(\%)}{100-x(\%)}\cdot 1000 \qquad (2)$$

In comparison, the gravimetric uptake is not as good as in the other 'Best-2' materials, and in this case, the higher density of HKUST-1 contributes, according to equation (1), to a lower gravimetric uptake. As said above, among all PW-MOFs explored in the database, HKUST-1 seems the most valuable for hydrogen storage and its descriptors and results are within the best possible choice among open metal sites, this leading to a large isosteric heat of adsorption (high uptake at 1 atm), and combining optimum density and pore size distribution which favour hydrogen adsorption due to confinement effects[13,15]. All of this suggests that HKUST-1 is probably the best among the PW-MOF hydrogen absorbers.

A better performance than that of HKUST-1 has been found among the 'Best-1' materials, with '1001432' and '6000362' (both belonging to Group 1-a) showing ~3 % gravimetric uptake and ~30 g/L volumetric uptake at 1 atm and 77 K. The behaviour at larger pressures, up to 100 atm is better for these two materials than for HKUST-1, with similar volumetric uptakes but with better gravimetric uptakes for '1001432' and '6000362' with respect to HKUST-1 (see Figures 4 and 5). It can also be expected that further inspection including new inorganic building units will still improve these results, while it is unlikely that new PW-MOFs will lead to significantly better results than HKUST-1.

In spite of the presence of open metal sites, which provide a large adsorption enthalpy, the density of metal sites in PW-MOFs (see 'm' values in Table 5) is not large. Having up to 50% of small pores is a good contribution, but, overall, this is not sufficient to reach the targets.

Adsorption at high pressure in large pores (Groups 2-b and 2-c) will be badly affected by the 'excess' corrections, and hence this will affect more drastically to PW-MOFs than to the other topologies explored in the database (see ESI, section S7). For these reasons, 'Best-1' materials are better candidates than 'Best-2' (paddle-wheel), because the former tend to show a better pore size distribution, more pores in the optimum range (5.4-10.2 Å), and a larger density of metal sites. Hence, we do not expect PW-MOFs will ever reach the commercial targets for hydrogen adsorption. Ideally, if those advantages of 'Best-1' could be combined with the presence of open metal sites, a still better group of materials could be obtained. Catenated networks containing open metal sites could be an interesting possibility. Many more unexplored topologies could offer new possibilities to implement in future databases. This is a topic for further studies.

Mn-BTT is another among other well known MOFs containing open metal sites for which a considerably high hydrogen uptake has been reported[45], with 6.9 % and 60 g/L as gravimetric and volumetric at 77 K and 90 atm and an isosteric heat of adsorption of 10.1 kJ/mol. At 1 atm, 2.1 % gravimetric uptake is reported. A GCMC computational study[46] using an ideallised unit cell of composition $[Mn_4Cl]_3[BTT]_8$, where some of the Mn ions have been removed and the charges have been averaged, gives 1.7 % gravimetric uptake at 1 atm and 6.3 % at 60 atm. We have also calculated the isotherm, using the original composition of the material, $Mn_3[Mn_4Cl]_3[BTT]_8$ (without solvent molecules), giving 1.6 % (at 1 atm) and 6.8 % (at 60 atm); and volumetric values 12 and 54 g/L. At 100 atm gives 7.2 % and 58 g/L.

Recently, a screening of MOFs for hydrogen storage has been made using a database of 13383 structures[47]. The screening finds 17 kJ/mol as optimum isosteric heat of adsorption and 0.75 porosity as optimum for hydrogen storage in MOFs taking into account a maximisation of the working capacity at 243 K.

Conclusions

A selection of candidate MOF structures for hydrogen storage has been obtained from a database containing ~138000 structures. Since literature reports focus on results at 77 K, this temperature was selected for our study, even considering that commercial targets include a temperature range (233-358 K) far from 77 K. This indicates that MOFs are still far from commercial targets and much improvement is still needed. In order to partially compensate the unrealistic choice of 77 K to calculate uptakes, we have particularly focused on the adsorption at the lower end (1 atm) of the commercial pressure range (1-100 atm) where adsorption is mainly related to the strength of the active (metal) sites. But also, the adsorption in the full pressure range (1-100 atm) has been calculated in this study, together with working capacity and excess-corrected uptakes. With the results obtained, not only a selection of structures has been made, but also some trends for future prospects are suggested.

Given that many top-performing MOFs in the literature belong to paddle-wheel-containing MOFs, a specific screening on these PW-MOFs has been run, apart from the screening over the full database.

The first screening, over ~138000 frameworks, was constrained according to certain selection criteria based on our definitions of physico-chemical descriptors, and then volumetric and gravimetric uptakes were considered. From the outcome of 152 structures, isotherms and the resulting 10 best structures (‘Best-1’) were analysed more in detail.

Isotherms were calculated by means of GCMC simulations using a forcefield specific for MOFs. These 152 structures comprise two types of IBUs: one type is composed by chains of vanadium and oxygen atoms and the other one is composed by the well known IRMOF series ($Zn_4O(RCOO)_6$). The corresponding organic linkers were also discussed, and in particular regarding their contribution to porosity.

In a different set, structures of paddle-wheel containing MOFs have been also studied given their high gravimetric uptakes reported in the literature. Initially, 1411 structures were considered, and 79 matched the selection criteria. Finally, a total of 8 structures, called ‘Best-2’, were selected and discussed in detail.

Comparing the results of the two sets, 'Best-1' and 'Best-2' (10 and 8 structures), the ‘Best-1’ set shows slightly higher uptakes at low pressure (1 bar, 77 K) whilst ‘Best-2’ materials tend to give larger hydrogen uptakes at high pressure (ca. 100 bar) mainly due to their high porosity.

The argument of appropriate pore size where confinement effects contribute substantially to increase uptake has been brought up into the discussion in order to rationalise the results and to suggest that frameworks with pores in the range 5.4-10.2 Å are more appropiate than those having larger pores. However, the definition of this range is to some extent arbitrary and at the present moment we are not able to quantify whether all the range is equally appropriate. This is also matter of future work which is complicated by the fact that current definitions of pore size mostly rely on spherical pores and, for instance, confinement effects in elliptical pores is not properly accounted using these definitions.

Our results show several hypothetical structures giving similar uptake than that of IRMOF-62, recently reported as one of the best hydrogen adsorbers so far. Our screening also found that HKUST-1 (and its isostructural Zn derivative) is the best paddle-wheel based structures for hydrogen adsorption, in agreement with the general belief.

All of these results are still far from the commercial targets, due in part to the reduced set of topological IBUs in the database comprising only four different types. However, applying these analysis and methods to larger databases and other topologies would possibly allow to select new subfamilies of MOFs which could be better candidates to approach the commercial targets required.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Structural information about 'Best1' and 'Best-2' materials; detailed pore size distribution; details of force-field employed for the Metal-H_2 interaction, and CIF files of the corresponding structures]. See DOI: 10.1039/b000000x/

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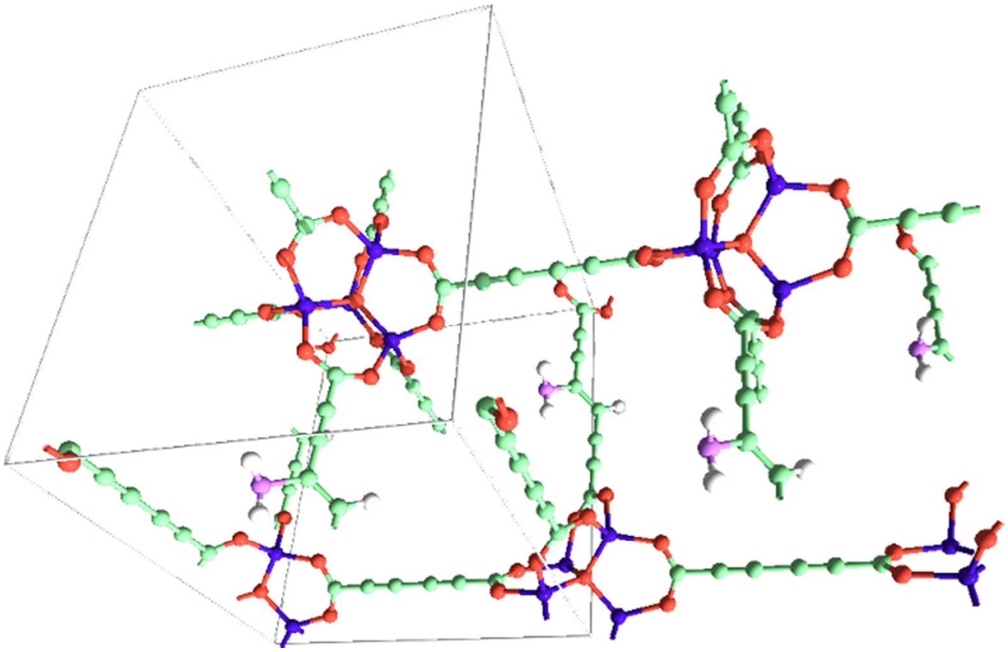

138000 MOFs from the Northwestern University database have been screened for hydrogen storage using specific physico-chemical descriptors