



The role of sticking efficiencies in hydrogen gas adsorption on metal organic frameworks



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ABSTRACT

In this study, the adsorption of hydrogen gas on 17 MOFs was compared. The majority of the MOFs contained carboxylate type linkers and metal centers such as Cu and Zn. A new parameter denoted sticking efficiency was used to compare the adsorption behaviors of the 17 MOFs. Results showed that a better correlation exists between sticking efficiency and hydrogen adsorption capacity than between surface area and adsorption capacity. However, when only MOFs containing similar types of linkers were included in the comparison, the surface area correlated somewhat better with adsorption capacity than did sticking efficiency. Since a direct correlation was also found between the sticking efficiency and the adsorption enthalpy it appears that sticking efficiency is a measure of the binding energies of the MOFs.

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1. Introduction

There is great interest in materials that can adsorb and store hydrogen for a variety of practical applications. Metal organic frameworks (MOFs) have attracted considerable attention because many of them possess large surface areas with the potential to adsorb significant amounts of hydrogen gas [1–3]. MOFs are constructed of metal centers that are linked together through organic ligands, generally referred to as linkers. These MOFs may contain a variety of ligands but one of the most studied classes of MOFs has been those containing carboxylate ligands [4,5]. Some of the carboxylate ligands include: 1,4-benzenedicarboxylate (BDC), 1,3,5-benzenetricarboxylate (BTC), and 2,6-naphthalenedicarboxylate (NDC). These ligands can form a bond with certain metals to form well-ordered, crystalline MOFs [6]. Examples of some of the most common carboxylate-containing MOFs include $Zn_4O(BDC)_3$ also known as MOF-5. This material is considered to be one of the best hydrogen storage materials [7,8]. $Zn_4O(NDC)_3$ known as IRMOF-8 is also a good prospect for hydrogen storage [9–11]. $Cu_3(BTC)_2$, also known as HKUST-1, was one of the first MOFs shown to bind hydrogen at metal sites at low temperatures [12]. It has also been shown to be a good prospect for hydrogen storage [13,14]. Some other interesting MOFs with carboxylate linkers include CUK-1 and CUK-2 [15], in which CUK = Cambridge University – KRICT. CUK-1 has the formula: $[Co_3(2,4-pdc)_2(\mu_3-OH)_2]9H_2O$ whereas

CUK-2 has the formula: $[Co_2(6-mna)_2]3H_2O$. Both of these are porous cobalt (II) MOFs which have carboxylate containing linkers. Another interesting material is TUDMOF-1 [16], where TUDMOF-1 = Technical University of Dresden metal organic framework No. 1. This is a porous MOF whose formula is $Mo_3(BTC)_2$. There is also a whole series of MOFs that belong to the PCN (Porous Coordinate Network) series [17–19]. These are all carboxylate-based MOFs in which PCN-10, PCN-11, PCN-12 and PCN-12' contain Cu metal sites. PCN-17 is another member of the series but it contains a Yb metal center. Another interesting carboxylate containing MOF is IRMOF-18 [20]. This is an isorectangular MOF that contains a Zn metal center. UMCM-150 [21] termed University of Michigan crystalline material is a carboxylate based MOF that contains both a binuclear Cu(II) paddlewheel cluster and a trinuclear Cu(II) cluster. It shows relatively high excess gravimetric and volumetric H_2 uptake. Cu-BTT [22] contains a BTT (1,3,5-benzenetristetrazolate) linker and a Cu metal center. As with other Cu-containing MOFs, it has a high density of expose metal sites @ the surfaces. MOF-74 [23] is yet another carboxylate based MOF with a Zn metal center. It has been found to bind hydrogen very well in the low pressure region. The linkers and metal clusters contained in all of the MOFs mentioned here have been tabulated in the [supplementary materials Table S1](#).

It is well known that physisorption correlates with surface area and that greater gas uptake is favored by higher surface area [5]. However, it is also known that the way in which hydrogen interacts with the surfaces (binding energy) may also affect adsorption [24–26]. The interaction of hydrogen with the surface may be affected by factors such as the nature of metal sites and nature

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of the linkers [6]. Since surface area may or may not correlate well with adsorption capacity in MOFs containing different types of linkers and/or metal sites, the aim of this work was to determine if other parameters might correlate well with weight percent in those instances.

2. Experimental procedures

The following five MOFs were prepared or purchased for this work: $\text{Zn}_4\text{O}(\text{BDC})_3$, $\text{Zn}_4\text{O}(\text{NDC})_3$, $\text{Cu}_3(\text{BTC})_2$, $\text{Fe}_3(\text{BTC})_2$ and Zn-Mim (where Mim is 2-Methylimidazole). The $\text{Zn}_4\text{O}(\text{BDC})_3$ and $\text{Zn}_4\text{O}(\text{NDC})_3$ were prepared by a rapid solvothermal process developed by Orefuwa et al. [10,11]. For the $\text{Zn}_4\text{O}(\text{BDC})_3$ synthesis, 1.89 g of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was reacted with 0.33 g of terephthalic acid (H_2BDC), and mixed into a solution with 40 ml of anhydrous N,N-Dimethylformamide, 99.8% bought from Sigma–Aldrich. Reactants were heated at 443 K for 2 h. The product was filtered and purified three (3) times with 5 ml of anhydrous chloroform containing amylenes as stabilizer $\geq 99\%$, also obtained for Sigma–Aldrich, and put under vacuum overnight. The product was further degassed at 523 K for 10 h, and the BET and Langmuir surface areas were obtained using nitrogen adsorption. The procedure used to prepare $\text{Zn}_4\text{O}(\text{NDC})_3$ is given in detail elsewhere [10]. The $\text{Cu}_3(\text{BTC})_2$ was prepared by a mechanochemical synthesis method described in detail by Yang et al. [14]. The $\text{Fe}_3(\text{BTC})_2$ and Zn-Mim were obtained commercially from Sigma Aldrich U.S.A. BET surface areas and pore volumes were determined for all the MOFs using a Micromeritics ASAP 2020 sorptometer. Low and high pressure H_2 adsorption capacities were determined using the Micromeritics ASAP 2020 sorptometer and a High Pressure Volumetric Analyzer (HPVA-100).

3. Results and discussion

In addition to the five MOFs that were prepared or purchased for this work, data for 12 others were obtained from the literature. These MOFs contain a variety of linkers and metal clusters. With the additional data from the literature, it should be possible to make meaningful comparisons among the MOFs to determine what correlations exist in their properties. It is of particular interest to determine what effect factors such as the nature of the linkers and metal clusters may have on the hydrogen adsorption capacities of these MOFs.

3.1. Surface areas and pore volume

Surface areas and pore volumes were determined volumetrically from N_2 adsorption–desorption isotherms at 77 K, for the five MOFs that were prepared or purchased for this work. Fig. 1 contains BET isotherms that were used to calculate surface areas and pore volumes for these MOFs. The values are listed in Table 1 along with data for the 12 additional MOFs that were obtained from the

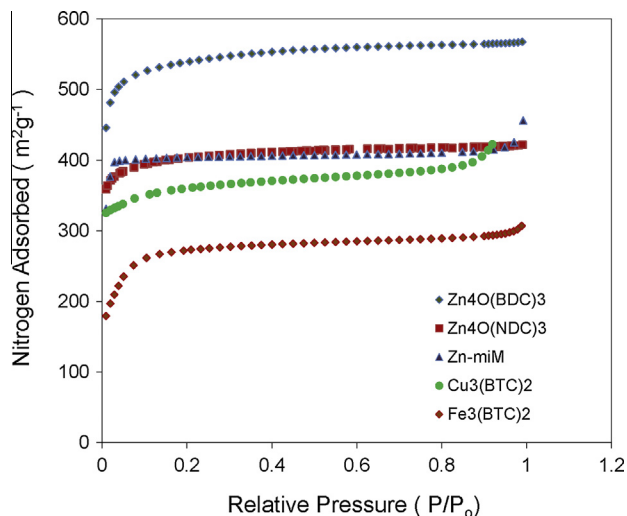


Fig. 1. BET isotherms for various MOFs at 77 K.

literature. There is a wide range of surface areas from a high of 2300 for UMCM-150 to a low of 420 $\text{m}^2 \text{g}^{-1}$ for CUK-2. As expected, the MOFs with high surface areas also have high pore volumes. There does not seem to be any relationship between linker size and surface area. For example, MOF-5 has just one benzene ring in its linker and it has a relatively high surface area of 2163 $\text{m}^2 \text{g}^{-1}$ whereas CuK-1 and CuK-2 also have one benzene ring with relatively low surface areas. PCN-17 has a relatively large linker with 4 benzene rings but it has a surface area of only 820 $\text{m}^2 \text{g}^{-1}$. There also does not seem to be a relationship between the nature of the metal cluster and surface area. For example, the Zn-containing MOFs have surface areas ranging from 2163 to 783 $\text{m}^2 \text{g}^{-1}$.

3.2. Adsorption Isotherms

An effort was also made to examine the hydrogen adsorption behavior of the various MOFs at 77 K. Fig. 2 contains adsorption isotherms for the five MOFs prepared or purchased for this study. For each isotherm, the weight percentage of hydrogen adsorbed at a pressure of 1 atmosphere was determined. The results are given in Table 1 along with data for the 12 MOFs that were selected from the literature.

It is apparent that the MOFs have a wide range of adsorption capacities ranging from a high of 3.05 wt% for PCN-12 to a low of 0.88 wt% for IRMOF-18 at 77 K and 1 bar. A plot of wt% versus surface area was made in order to determine if any correlation exists between these two parameters. The plot is shown in Fig. 3a. The plot shows that a correlation exists but that there is a fairly large amount of scatter in the data points. A correlation coefficient (R^2) was used to represent the degree of scatter in the data points. A value of $R^2 = 1$ would represent perfect correlation whereas $R^2 = 0$ would represent no correlation. In this case R^2 was 0.5388. A possible reason for the relatively low correlation coefficient may be the fact that the surfaces in these MOFs are not uniform. They contain a variety of different linkers, metal sites and structures. The different affinities of hydrogen for each of these surfaces may be responsible for the scatter.

3.3. Sticking efficiency

It was mentioned earlier that the way in which hydrogen interacts with the surfaces (binding energy) may also affect adsorption [24–26]. Therefore a new parameter denoted the sticking factor (θ) was developed with the hope that it would correlate better with the wt% hydrogen adsorbed than surface area. The sticking factor (defined as the percent gas adsorbed per m^2 of surface area per gram of material) was calculated for each gas based on the following equation:

$$\theta = \frac{Q_{\text{ads}}}{S_{\text{SA}}} \times \frac{N_A}{M_{\text{mm}}} \quad (1)$$

where Q_{ads} is the weight percentage of gas adsorbed, S_{SA} is the surface area of the MOF in m^2/g , N_A is Avogadro's number and M_{mm} is the molar mass of the adsorbed gas. Since the sticking factor is the percentage of hydrogen gas adsorbed per unit area of surface, it actually represents the efficiency in which the molecules are able to bind to the surface. If a material has a large surface area but, due to the nature of the binding sites, has low sticking efficiency, then it is possible that it will adsorb a relatively small amount of hydrogen.

The sticking factors calculated from Eq. (1) are given in Table 1 for all of the MOFs included in this work. Fig. 3b contains a plot of sticking factor versus the weight percentage of hydrogen on the surface. The results show that there is a reasonably good correlation, with $R^2 = 0.7486$. This is significantly better than the 0.5388 that was obtained when surface area was plotted versus wt% using

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