Increasing the Density of Adsorbed Hydrogen with Coordinatively Unsaturated Metal Centers in Metal−Organic Frameworks

Yun Liu,[†,‡] Houria Kabbour,[§] Craig M. Brown,[†] Dan A. Neumann,[†] and Channing C. Ahn*,[§]

*NIST Center for Neutron Research, National Institute of Standards and Technology, Maryland,
Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, and
Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California*

Storing molecular hydrogen in porous media is one of the promising avenues for mobile hydrogen storage. In order to achieve technologically relevant levels of gravimetric density, the density of adsorbed H_2 must be increased beyond levels attained for typical high surface area carbons. Here, we demonstrate a strong correlation between exposed and coordinatively unsaturated metal centers and enhanced *hydrogen surface density* in many framework structures. We show that the MOF-74 framework structure with open Zn^{2+} sites displays the highest surface density for physisorbed hydrogen in framework structures. Isotherm and neutron scattering methods are used to elucidate the strength of the guest−host interactions and atomic-scale bonding of hydrogen in this material. As a metric with which to compare adsorption density with other materials, we define a surface packing density and model the strength of the H_2-surface interaction required to decrease the H_2−H_2 distance and to estimate the largest possible surface packing density based on surface physisorption methods.

I. Introduction

Early neutron diffraction studies[1] of H_2/D_2 adsorbed onto graphene show that the minimum intermolecular H_2 (D_2) distances that can be achieved are 3.5 Å (3.4 Å) at 5 K with an adsorption enthalpy typically less than 6 kJ/mol.[2,3] This intermolecular distance is smaller than that in the bulk solid H_2 (D_2) of 3.8 Å (3.6 Å).[4] Given the observed intermolecular H_2 distance of 3.5 Å and assuming a hard sphere close-packed model for adsorbed molecular hydrogen, a single graphene sheet which has a surface area of 2630 m^2/g could accommodate a maximum of 8.2 wt % H_2. Consequently, in order to maximize the gravimetric uptake and achieve the Department of Energy (DOE) targets of hydrogen storage materials for a transportation infrastructure,[5] there is a drive to produce materials with ever higher specific surface areas.

While these efforts have made significant progress,[6,7] the low surface packing density (SPD) of many carbon materials at technically relevant temperatures has limited their adsorption capabilities. For example, activated carbons[8] and carbon aerogels[9] typically adsorb only ≈1 wt % H_2 for every 500 m^2/g surface area at 77 K rather than the 1.6 wt % expected for an isolated graphene sheet at 5 K. Many materials display Brunauer−Emmett−Teller (BET) surface areas that would be expected to

allow one to achieve the DOE gravimetric targets for hydrogen storage materials. However, these materials typically have even smaller SPDs. For example, if H_2 in MOF-177 (BET surface area of 4500 m^2/g)[10] had a similar *hydrogen surface density* to that of hydrogen in activated carbons, it would adsorb ≈9.0 wt % rather than 7.5 wt % at 77 K[6]. The DOE 2015 volumetric target of 81 g/L is also a considerable challenge and requires *an adsorption surface density* for a monolayer of H_2 to be close to or exceed the density of solid H_2 (86 g/L at 4.2 K and 0 Pa).[4]

In this paper, we report the first neutron scattering results from MOF-74,[11,12] which demonstrates the largest surface density of adsorbed H_2 at 77 K in any framework structure studied to date. Our results reveal the shortest intermolecular D_2−D_2 distance observed in a physisorption-based material, which we are aware of, without the application of pressure. We can attribute part of this high density to the presence of coordinatively unsaturated Zn^{2+} centers that promote intermolecular deuterium distances of about 2.85 Å at 4 K. This observation, along with results from other systems with coordinatively unsaturated metal centers (CUMCs) that exhibit large SPDs, presents an avenue to increase the surface density of adsorbed hydrogen in this class of materials. Quantum mechanical calculations for model systems are performed to estimate the shortest distance achievable between H_2 molecules thereby defining the surface area requirements for a material that can reach DOE targets based on surface adsorption.

II. Materials and Methods

Synthesis and Chemical Characterization. MOF-74 samples were synthesized using previously published procedures.[11,12] Typically, 1 g of $Zn(NO_3)_2 \cdot 6H_2O$ was mixed with 0.25 g of the organic linker (2,5-dihydroxyterephtalic acid) in 50 mL of dimethylformamide (DMF) and 2.5 mL of water. The mixture was stirred to dissolve the solid reactants, and the solution was sealed in a 100 mL autoclave and heated to 100 °C for 20 h. At the end of this heating cycle, the

* Corresponding author. E-mail: cca@caltech.edu.

† National Institute of Standards and Technology.

‡ University of Maryland.

§ California Institute of Technology.

(1) Nielsen, M.; Mctague, J. P.; Ellenson, W. *J. Phys.* **1977,** *C4,* 10−18.

(2) Gigras, A.; Bhatia, S. K.; Kumar, A. V. A.; Myers, A. L. *Carbon,* **2007,** 24, 1043−1050 and references therein.

(3) Bhatia, S. K.; Myers, A. L. *Langmuir* **2006,** *22,* 168.

(4) Silvera, I. F. *Rev. Mod. Phys.* **1980,** *52,* 393−452.

(5) U. S. Department of Energy. Energy Efficiency and Renewable Energy. http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/freedomcar_targets_explanations.pdf.

(6) Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006,** *128,* 3494−3495.

(7) Latroche, M.; Surblé, S.; Serre, C.; Mellot-Draznieks, C.; Llewellyn, P. L.; Lee, J. H.; Chang, J. S.; Jhung, S. H., Férey, G. *Angew. Chem., Int. Ed.* **2006,** *45,* 8227−8231.

(8) Chahine, R.; Benard, P. In *Advances in cryogenic engineering*; Kittel, P., Ed.; Plenum Press: New, York, 1998 Vol. 34, p 1257.

(9) Kabbour, H.; Baumann, T. F.; Satcher, J. H., Jr., Saulnier, A.; Ahn, C. C. *Chem. Mater.* **2006,** *18,* 6085−6087.

(10) Chae, H. K.; Sibero-Pérez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O' Keeffe, M.; Yaghi, O. M. *Nature* **2004,** *427,* 523−527.

(11) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O' Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005,** *127,* 1504−1518.

(12) Rowsell, J. L. C.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006,** *128,* 1304−1315.

mixture was allowed to cool to ≈40 °C and was opened in air. Yellow crystals of MOF-74 were formed on the autoclave walls and base. If the solution is allowed to cool to room temperature over several hours, large orange crystals of an unidentified phase are formed. To minimize the formation of this unwanted secondary phase, the solution is filtered while the solution temperature is still ≈40 °C.

After filtration, the remaining crystals were rinsed several times, first with DMF and then with methanol. In order to activate the MOF-74 crystals, the DMF guests within the porous structure must be exchanged with methanol molecules, which are more easily removed. This activation consists of immersing the crystals in methanol for approximately 5 to 6 days, over which time the methanol solution is changed two or three times. After this immersion step, the sample was filtered and washed with methanol and then heated to 200 °C under vacuum for at least 20 h to remove the remaining methanol from the pores. This procedure completed the activation process.

The powder product was characterized using X-ray powder diffraction. The experimental pattern was compared to a simulated pattern using a previously published structure, and the experimental data matched the theoretical patterns.

Sieverts Measurements. High-resolution hydrogen adsorption/desorption measurements were performed with a volumetric Sieverts apparatus[13] to pressures up to 30 bar. Samples were outgassed prior to measurements. A pretreatment was used that consisted of heating the sample under vacuum to 120 °C until outgassing was completed and a vacuum pressure of ≈10^{-4} Pa was attained. After this treatment, the sample reactor was immersed in liquid nitrogen or liquid argon for data acquisition.

The evolution of the isosteric heat of adsorption versus mass coverage was determined from the thermodynamic equation below, using two adsorption isotherms at temperatures of 77 and 87 K:

$$\bar{h} = R\left[\frac{\partial \ln P}{\partial (1/T)}\right]_n$$

In this equation $\bar{h}$ is the differential enthalpy of adsorption. The absolute value of $\bar{h}$ corresponds to the isosteric heat. The partial differentiation is performed at constant coverage n.

Neutron Powder Diffraction. Neutron powder diffraction experiments, identifying H_2 adsorption sites in MOF-74, were performed at the NIST Center for Neutron Research using the BT-1 diffractometer and neutrons of a wavelength of 2.0787 Å. Deuterium was used as an adsorption gas in order to minimize the large incoherent neutron scattering cross-section of hydrogen that contributes to signal background. Diffraction patterns were collected at D_2 gas loadings of 0.0, $^1/_3$, $^2/_3$, 1.0, 2.0, 3.0, and 4.2 D_2:Zn. (1.0 H_2:Zn corresponds to ≈1.2 wt % H_2 adsorption, see Supporting Information for more details.)

Calculations of $H_2−H_2$ Interaction Distance. Two H_2 molecules are put into a very wide square well potential defined as:

$$V_{sw}(r) = \begin{cases} 0, & \text{if } |r| < r_m \\ +\infty, & \text{if } |r| > r_m \end{cases}$$

where $r_m = 20$ Å. Harmonic potentials are then added to this square well potential:

$$V_h(r) = \begin{cases} \frac{1}{2}m\omega^2 r^2 - E_d & \text{if } \frac{1}{2}m\omega^2 r^2 < E_d \\ 0 & \text{if } \frac{1}{2}m\omega^2 r^2 > E_d \end{cases}$$

where m is the mass of a hydrogen molecule. There are two parameters determining the properties of this potential: the potential depth, E_d, and the quantized eigenenergy difference, $\hbar\omega$, with $\hbar$ the reduced Planck constant. This potential is used to simulate binding sites in

a real system. Two identical harmonic potentials with a distance, D, are added to simulate two different binding sites. Hence the external potential is

$$V_{ex}(r) = V_{sw}(r) + V_h(r + D/2) + V_h(r − D/2)$$

The $H_2−H_2$ interaction potential is taken from the well-established semiempirical isotropic interaction potential:[4]

$$V_{HH}(r) = \exp(\alpha − \beta r − \gamma r^2) + f(r)\left\{\sum_{i=6,8,10} C_i/r^i + C_9/r^9\right\}$$

with

$$f(R) = \begin{cases} \exp\left\{-\left[\left(1.28\frac{R_m}{R}\right) − 1\right]^2\right\} & \text{if } R < 1.28R_m \\ 1 & \text{if } R > 1.28R_m \end{cases}$$

where $\alpha = 1.713$, $\beta = 1.5671$, $\gamma = 0.00993$, $C_6 = −12.14$, $C_8 = −215.2$, $C_{10} = −4813.9$, and $C_9 = −4813.9$ due to many body effects (all parameters in atomic units), $R_m = 3.41$ Å. In our calculation, $C_9 = 0$ since we do not expect many body effects although it is important for solid hydrogen.[4] We have also ignored the anisotropic interaction between H_2 molecules. In most cases, this is a good approximation since H_2 is a very good quantum rotor due to its light mass. This isotropic potential between H_2 molecules has been shown to work very well for solid hydrogen at pressure up to 25 kbar.[4]

Given V_{ex} and V_{HH}, the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2}\right) + V_{ex}(r_1) + V_{ex}(r_2) + V_{HH}(r_1,r_2)\right]\psi(r_1,r_2) = E\psi(r_1,r_2)$$

can be solved numerically, where $\psi(r_1,r_2)$ is a normalized two-particle wave function with E its corresponding eigenenergy. The mean distance between H_2 molecules is then given by

$$r_{HH} = \int dr_1\, dr_2\, \psi_0^2(r_1,r_2)|r_1 − r_2|$$

where $\psi_0(r_1,r_2)$ is the wave function of the ground state. Using the above method, one can only calculate the value of r_{HH} at $T = 0$ K. In order to calculate r_{HH} at 77 K, wave functions with larger eigenenergies need to be considered.

III. Results and Discussions

In order to evaluate the hydrogen surface density properties of different adsorbents, we use the experimental surface packing density, which we define as

$$\text{SPD}(T) = \frac{\text{MassFraction}(T)}{S}$$

where MassFraction(T) is the excess mass adsorption of H_2 saturated at temperature T and S is the nitrogen BET surface area.[14] At 77 K, hydrogen molecules are typically adsorbed as a monolayer on the material surface.[15] Although the surface excess adsorption is the additional hydrogen adsorbed on the surface over what the real gas law would yield for the volume displaced by the adsorbate, given the low density of hydrogen in the gas phase, our definition of SPD at 77 K should be a good approximation to the monolayer surface density of adsorbed H_2.

(13) Bowman, R. C., Jr.; Luo, C. H.; Ahn, C. C.; Witham, C. K.; Fultz, B. *J. Alloys Compd.* **1995**, *217*, 185−192.

(14) If there are internal volumes with entrance ports too small to allow N_2 gas to pass through but yet H_2 can, the accessible surface for H_2 and N_2 becomes different, and the SPD defined in the text would need to be modified. However, in most metal−organic frameworks, all internal space is available for both H_2 and N_2 gas.

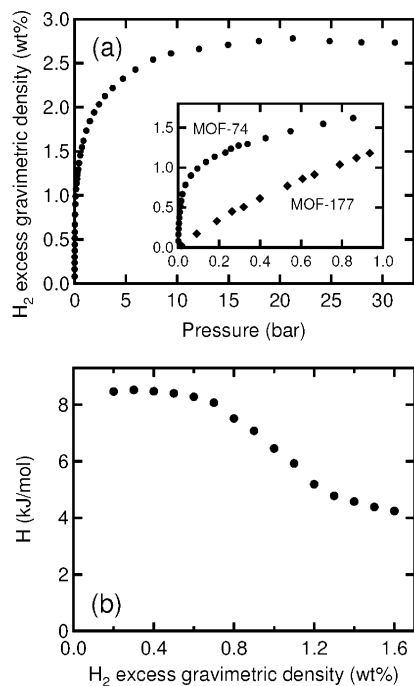(15) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353−358.

Figure 1. H_2 Isotherm measurements of MOF-74. (a) The H_2 adsorption/desorption isotherms at 77 K. The inset shows the comparison of H_2 adsorption isotherms for MOF-74 and MOF-177. (b) The H_2 adsorption enthalpy of MOF-74 is shown with the initial H_2 adsorption enthalpy of ≈ 8.8 kJ/mol.

Therefore, the SPD approximates the mass of hydrogen adsorbed per unit area, and is not a function of the mass of host materials. Thus, it is an indicator of surface adsorption properties. Because the maximum gravimetric adsorption is the product of SPD and *S*, ideally both quantities should be large. According to the above definition, the experimental surface packing density of activated carbons at 77 K, SPD_{AC}, is 2.0×10^{-5} g/m^2. By use of the nearest neighbor distance of solid H_2 (3.8 Å), the calculated surface packing density for triangular packing in a plane, SPD_{H_2}-(*Th*), is 2.8×10^{-5} g/m^2.

Figure 1a shows the H_2 adsorption/desorption isotherm of MOF-74 at 77 K up to 30 bar with a maximum surface excess value of about 2.8 wt %. The N_2 BET surface is 870 m^2/g. (See Supporting Information for details.) Thus the experimental SPD is 3.2×10^{-5} g/m^2, which is the largest value for framework structures studied to date and significantly larger than that of SPD_{H_2}(*Th*).

In order to understand the extremely dense packing of H_2 on MOF-74 and to develop a strategy for increasing the SPD in other carbon materials, neutron powder diffraction experiments were performed to identify the D_2 adsorptions sites (which closely reflect the adsorptions sites of H_2[16−20]). All diffraction data were obtained at 4 K and analyzed using standard Rietveld refinement techniques in conjunction with Fourier difference maps.[16−20] Figure 2a shows the superposition of the Fourier difference map and the crystal structure of MOF-74 with the red-yellow (gray-white) regions indicating the locations of D_2 sites 1 and 2. Figure 2b shows the projection of the four observed hydrogen adsorptions
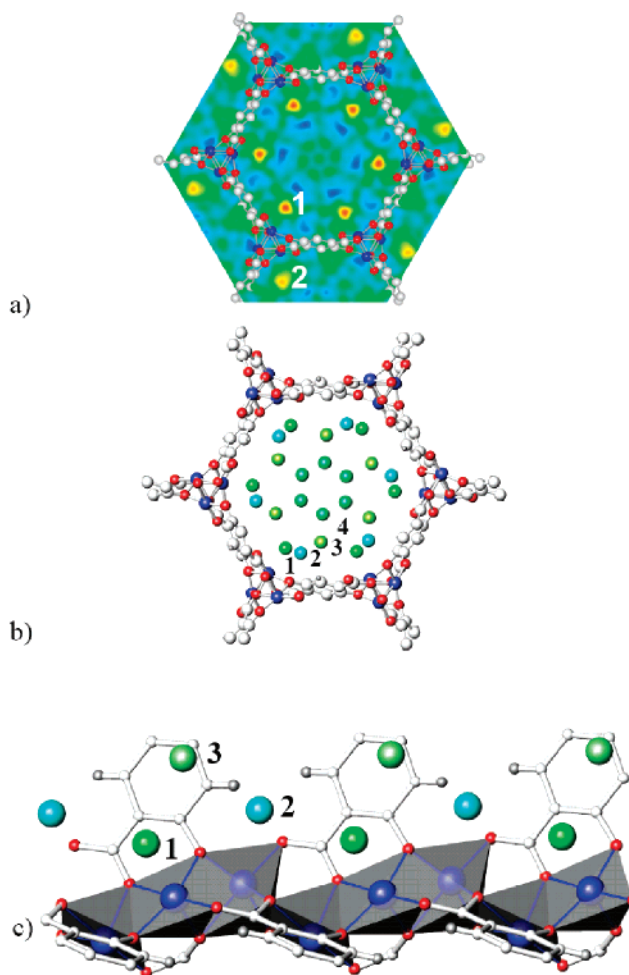
(16) Dincă, M.; Dailly, A.; Liu, Y.; Brown, C. M.; Neumann, D. A.; Long, J. R. *J. Am. Chem. Soc.* **2006**, *128*, 16876−16883.

(17) Dincă, M.; Han, W. S.; Liu, Y.; Dailly, A.; Brown, C. M.; Long, J. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 1419−1422.

(18) Peterson, V. K.; Liu, Y.; Brown, C. M.; Kepert, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 15578−15579.

(19) Yildirim, T.; Hartman, M. R. *Phys. Rev. Lett.* **2005**, *95*, 215504.

(20) Hartman, R. M.; Peterson, V. K.; Liu, Y.; Kaye, S. S.; Long, J. R. *Chem. Mater.* **2006**, *18*, 3221−3224.

Figure 2. D_2 adsorption sites in MOF-74 at 4.2 D_2:Zn. (a) Suppositions of Fourier difference map together with the crystal structure of MOF-74 projected down the *c* axis. The red-yellow regions (gray with white halo indicated by 1 and 2) indicate the high scattering regions of the first two adsorption sites. (b) The four D_2 adsorption sites identified by neutron powder diffraction (labeled 1−4, spheres of green (gray) and light blue (light gray)). (c) The first three D_2 adsorption sites are shown with the first site directly interacting with the Zn^{2+} ions (blue (dark gray) balls).

Table 1. Fractional Coordinates of D_2 Adsorption Sites in MOF-74 at the Loading of 4.2 D_2:Zn. The Values in the Parentheses for Coordinates Indicate the Estimated Standard Deviation in the Last Digit from the Rietveld Refinements

site	X	Y	Z
$D_2(1)$	0.2002(4)	−0.0104(5)	0.034(1)
$D_2(2)$	0.4924(6)	0.1174(7)	−0.017(3)
$D_2(3)$	0.7489(4)	0.2359(4)	0.169(1)
$D_2(4)$	0.6214(9)	0.2484(6)	0.041(1)

sites along the *c* axis. The adsorption sites are numbered 1−4, according to the order they are occupied. A decrease of binding strength results in adsorption sites that are further from the adsorbent surface. The first three adsorption sites can be fully occupied at T $\approx$ 30 K and zero pressure. By decreasing the temperature slowly to 15 K, the fourth site is fully populated. Table 1 gives the coordinates of the four adsorption sites at 4.2 D_2:Zn.[21]

Figure 2c shows more clearly that the first site is located directly above the Zn^{2+} ions with a center-to-center distance of

(21) In order to saturate all D_2 adsorptions sites in MOF-74, a final loading of 4.2 D_2:Zn was used. The Rietveld refinements show that there are about 4.0 D_2:Zn in the material, yet we did not observe obvious diffraction peaks from solid D_2. Refinement details are provided in the Supporting Information.

$\approx$2.6 Å. The direct interaction between H_2 and CUMCs has been observed in other framework structures with D_2−metal distances of 2.3, 2.5, and 2.4 Å in Mn-BTT,[16] Cu-BTT,[17] and HKUST-1,[18] respectively. There is, however, no simple correlation between these distances and the large initial H_2 adsorption enthalpies, ΔH, which are 10.1,[16] 9.5,[17] 6.6,[12] and 8.8 kJ/mol for Mn-BTT, Cu-BTT, HKUST-1, and MOF-74, respectively. Both the direct metal interaction and the van der Waals attraction from the other atoms of the framework contribute to the overall binding strength and affect the adsorption enthalpy. Since the typical van der Waals attraction is not negligible compared to the binding strength at each metal site, if there is a correlation with the interaction distance, it could only be obtained after removing the contributions from the typical van der Waals attraction.

The second adsorption site is located above a triangle of oxygen atoms with a closest sorbate−sorbent distance of $\approx$3.1 Å. The third site is near the benzene ring with a closest distance to the framework atoms of $\approx$3.3 Å. The larger distances suggest that the H_2 binding of sites 2 and 3 are likely dominated by dispersive interactions.

Although the diffraction measurements were performed at 4 K, the D_2−D_2 intermolecular spacings between the first three adsorption sites shed light on the relatively large SPD in MOF-74 at 77 K. The first three sites cover the entire surface without applying any vapor pressure at 30 K. Additional adsorbed D_2 begins to form a second layer below the condensation temperature. Comparing the maximum value of the surface excess adsorption of 2.8 wt % at 77 K to the maximum of 3.6 wt % H_2 achievable with the complete population of the first three adsorption sites, we should expect sites 1−3 to dominate the adsorption/desorption properties at 77 K. The sequence of adsorption site occupation shows that the first site has a relatively large binding energy due to the direct interaction of H_2 with the CUMCs. Temperature dependent inelastic neutron scattering (INS) experiments (see the Supporting Information) further indicate that this binding energy difference is very large and consistent with the sharp decrease of the adsorption enthalpy curve at around 1 wt % (Figure 1b). We may reasonably conclude that ΔH for site 1 is $\approx$8.8 kJ/mol and ΔH for site 2 is $\approx$5 kJ/mol. ΔH for site 3 cannot be estimated using our current data.

The D_2−D_2 intermolecular distances in the first layer vary from $\approx$2.85 to $\approx$4.2 Å with an average of $\approx$3.4 Å,[22] which is shorter than the 3.6 Å distance found for solid D_2. The shortest distance from the site 1 to site 3 is $\approx$2.85 Å and from site 1 to site 2 is $\approx$2.9 Å. These close distances between adsorption sites explain the large SPD of MOF-74 at 77 K. The two shortest distances occur from site 1, directly above the Zn^{2+} ion, to sites 2 and 3, respectively. Given the high density of Zn^{2+}, it is reasonable to conclude that the large SPD for hydrogen in MOF-74 is at least partly induced by the Zn^{2+} CUMCs though additional contributions may come from favorable geometrical considerations. The adsorbed D_2 molecules form a one-dimensional network as shown in Figure 3. The one-dimensional nanoscale tubelike structure of D_2/H_2 molecules may present a model system for studies of low-dimensional quantum objects.

In order to assess the value of this analysis more completely, the experimental SPD's of different framework structures,[23] including our results for MOF-74, are summarized as a function of BET surface area in Figure 4. While S measured by the N_2 BET method at 77 K is not a true surface area, a recent Monte
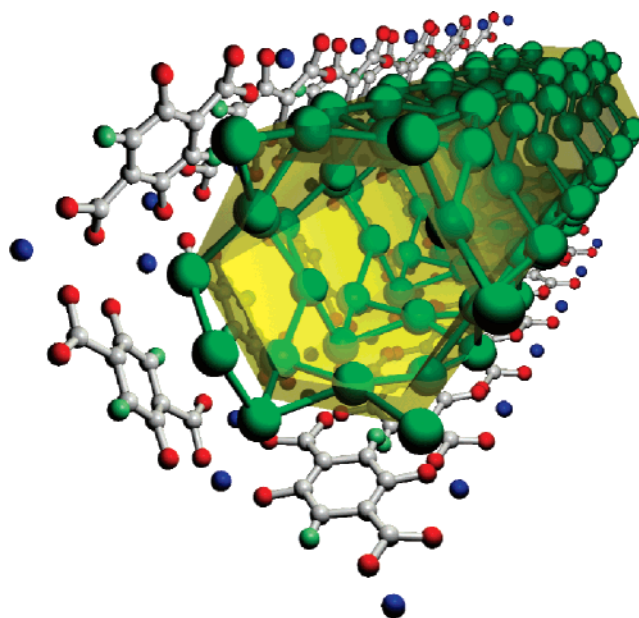

Figure 3. One-dimensional nanoscale tubelike structure formed from adsorbed D_2. D_2 molecules (large green (gray) balls) adsorbed in MOF-74 form a one-dimensional nanoscale tubelike structure. (Only the first three adsorption sites are shown.) Molecules of deuterium are connected if the distance between D_2 molecules is less than 3.65 Å.
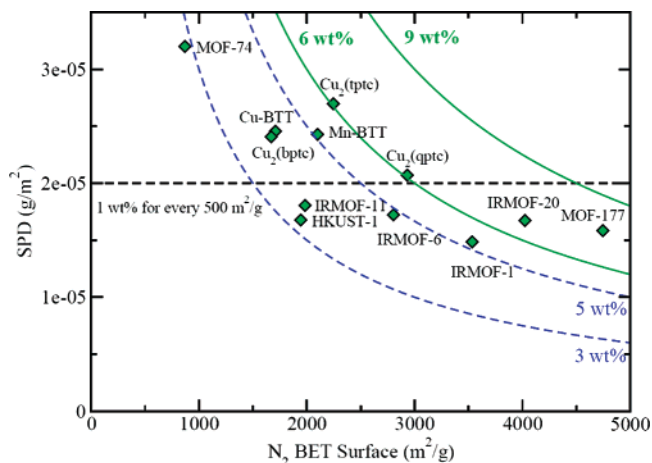

Figure 4. The H_2 surface packing density, SPD, as a function of N_2 BET surface, S. The MOFs with CUMCs, in general, show larger SPD compared to those without CUMCs. The horizontal dashed line shows the SPD for typical carbon material, where every 500 m²/g of N_2 BET surface area can adsorb 1 wt % of H_2. Solid green (gray) curves show the lines for gravimetric uptake of 6 wt % and 9 wt %, which is the product of SPD and S.

Carlo simulation has indicated that the BET surface is a good estimation of the real surface area for at least a few MOFs.[24] For many framework structures, hydrogen packs less efficiently than it does when adsorbed on typical carbons, while each of Mn-BTT, Cu-BTT, MOF-74, Cu_2(bptc), Cu_2(tptc), and Cu_2(qptc) has a larger experimental SPD than SPD_{AC}, with the present

(22) Due to interactions among D_2 molecules, the D_2−D_2 distances vary slightly depending upon the amount of loaded gas. The average distance among D_2 molecules for the first three adsorption sites are calculated based on the refined data of the 4.2 D_2:Zn case. The mean distance is calculated as the total average over the four nearest-neighbor distances of the first three adsorption sites.

(23) Except for the MOF-74 data presented here, data for other materials were taken from literature results. The data for IRMOF-1, MOF-177, IRMOF-20, IRMOF-11, IRMOF-6, and HKUST-1 are from ref 5. The data for Cu-BTT and Mn-BTT are from refs 16 and 17. The data for Cu_2(bptc), Cu_2(tptc), and Cu_2(qptc) are from ref 25. (Ligand nomenclature: HKUST-1, Cu_3(1,3,5-benzenetricrboxy-late)₂; BTT, 1,3,5-benzenetristetrazolate; Cu-BTT, HCu[(Cu_4Cl)₃(BTT)₈]·3.5HCl; Mn-BTT, Mn_3[(Mn_4Cl)₃(BTT)₈(CH_3OH)₁₀]₂; bptc, biphenyl-3,3′:5,5′-tetracar-boxylate; tptc, terphenyl-3,3′′:5,5′′-tetracarboxylate; qptc, quaterphenyl-3,3′′: 5,5′′′-tetracarboxylate.)

(24) Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, *129*, 8552−8556.

results for MOF-74 showing the highest SPD. Previous work has demonstrated that Mn-BTT and Cu-BTT have CUMCs that strongly bind H_2[16,17]. Similarly, the hydrogen adsorption sites in HKUST-1 have been carefully investigated by neutron powder diffraction[18] and the strongest binding site is found to be due to coordinatively unsaturated Cu^{2+}. While there are no reports of hydrogen adsorption sites yet in $Cu_2(bptc)$, $Cu_2(tptc)$, and Cu_2-(qptc), these three materials have Cu^{2+} sites with bound solvent molecules[25] before activation. Thus, it is likely that if the solvent molecules are removed by sample activation, the open Cu^{2+} centers would have high adsorption enthalpies for H_2 similar to HKUST-1. Therefore, all seven MOFs displaying a SPD larger than SPD_{AC} in Figure 4 have, or likely have, CUMCs.[26] This strong correlation between exposed CUMCs and the large SPD in framework structures shows that CUMCs not only enhance the H_2 binding energy but also increase the SPD. A plot of SPD as a function of Langmuir surface area demonstrates a similar correlation (see Supporting Information, Figure S1).

In order to understand how an attractive surface potential decreases the H_2-H_2 distance and to determine if sorbent−sorbate interactions can significantly increase the SPD beyond that in MOF-74, we have performed quantum mechanical calculations on the model described in the previous section. As shown in Figure 5a, two harmonic potentials separated by a distance D are used to simulate the effect of two neighboring surface binding sites. Two H_2 molecules are placed into the potential, and the mean distance between the two, r_{HH}, is calculated.

We have estimated how r_{HH} varies as the identical potential wells approach each other. Both potentials have the same potential depth, E_d, with variable inter-potential distance, D, as shown in Figure 5a. The results for $\hbar\omega = 10$ meV and $\hbar\omega = 15$ meV are summarized in Figure 5b, where $\hbar\omega$ is the quantized energy difference of the harmonic potential used in the calculations. In both cases, when $D = 4$ Å, r_{HH} is ≈4 Å as expected when each H_2 molecule is trapped in its own potential well. As D decreases, r_{HH} also decreases, although the repulsion between H_2 molecules forces r_{HH} to be somewhat larger than D. When D is smaller than some threshold value, r_{HH} increases rapidly because the repulsion between H_2 molecules is now so strong that the two potential wells cannot simultaneously bind both H_2 molecules. For $\hbar\omega = 10$ meV, the minimum r_{HH} is about 3.2 Å at $D \approx 2.4$ Å and $E_d = 20$ meV. Increasing E_d to 40 meV decreases the minimum r_{HH} to ≈3.0 Å for a very small D of approximately 1.8 Å. When $\hbar\omega = 15$ meV, the minimum r_{HH} is about the same as that compared to the previous case although the value of D for the minimum r_{HH} is different. Increasing E_d to 80 meV only slightly changes the minimum r_{HH} to about 2.8 Å with an extremely short D of 1.6 Å at $\hbar\omega = 15$ meV. Further increasing E_d to 160 meV does not decrease the minimum r_{HH} significantly. An estimate of r_{HH} for two hydrogen molecules at 77 K for the case of $\hbar\omega = 15$ meV and $E_d = 80$ meV shows that the smallest r_{HH} is still about 2.8 Å with $D = 1.8$ Å, indicating that r_{HH} can reach ≈3 Å at 77 K, if E_d is large enough.

While the anharmonicity of the potential and thermal population at higher temperature, such as 77 K, may cause r_{HH} to vary more smoothly with E_d and D than the present results suggest, these calculations indicate that it is unlikely that r_{HH} can be substantially
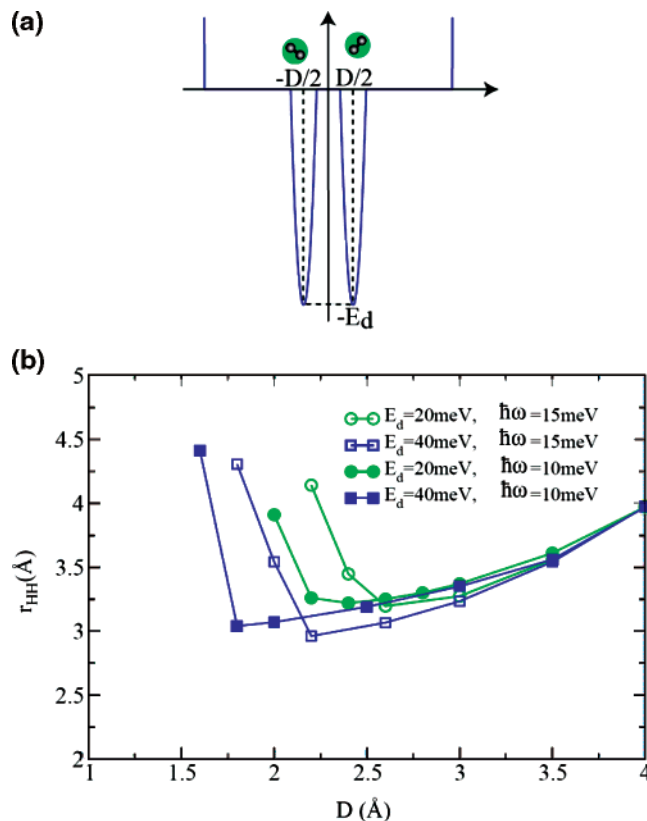
(25) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Angew. Chem.* **2006**, *118*, 1−7.

(26) It should be noted that HKUST-1 also has CUMCs, yet the SPD is only comparable to other MOFs without CUMCs. Detailed study of the H_2 adsorption sites (ref 18) shows that the volume of the small cage in HKUST-1 is not efficiently used because the small pore can accommodate only one H_2. The wasted volume in the small cage largely explains the low SPD.

Figure 5. The mean H_2-H_2 distance, r_{HH}, for different external potentials. (a) The external potentials shown here are used to calculate how close two H_2 molecules can approach each other. (b) The calculated mean intermolecular H_2-H_2 distance, r_{HH}, for different potential parameters. E_d is the depth of the potential and quantized eigenenergy difference, $\hbar\omega$, for harmonic potentials.

less than 3 Å with any physically reasonable choice of interactions. Although applying pressure would reduce the H_2-H_2 intermolecular distance, given the fact that a pressure of ≈25 kbar is needed to compress solid H_2/D_2 to a nearest-neighbor distance of 2.8 Å at ≈4 K[4], no significant improvement would be expected with a technically relevant pressure. Therefore, it is reasonable to assume that 3.0 Å is about the shortest distance between two hydrogen molecules physically absorbed on a surface. Assuming H_2 packs in a triangular lattice with $r_{HH} = 3$ Å, the theoretical SPD would be 4.3×10^{-5} g/m^2, which corresponds to 1 wt % H_2 for each 234 m^2/g of surface area. This is more than double the density one would expect for commensurately adsorbed molecular hydrogen on typical high surface area carbons (typically 2.0×10^{-5} g/m^2). Our estimate indicates a minimum surface area requirement of ≈1400 m^2/g (or ≈2100 m^2/g) for a material that can reach an excess adsorption of 6 wt % (or 9 wt %).

From the study of our model system, we see that larger binding energies are associated with shorter H_2-H_2 intermolecular distances, a requirement for a larger SPD. Since the existence of CUMCs in MOFs is usually associated with larger attraction potentials for H_2, our model system partially explains the reasons for larger SPD of these MOFs and the short distances between H_2 molecules in MOF-74. It is also interesting that only modest binding energies are necessary to decrease the H_2-H_2 distance to values less than that observed in solid H_2 at ≈4 K and zero pressure. This required surface interaction is certainly within the range of adsorption enthalpies already measured in carbon-based materials and framework structures.

In our study, we have demonstrated a strong correlation between exposed CUMCs in framework structures and larger associated SPDs. These observations provide an avenue to improve the gravimetric H$_2$ uptake by increasing the SPD. The study of MOF-74 with neutron powder diffraction alongside isotherm measurements show that H$_2$ adsorbed on the MOF-74 surface has a higher surface density at 77 K than that of solid H$_2$ at $\approx$4 K and zero pressure. In fact, the intermolecular hydrogen distances between sites 1 and 2 as well as between sites 1 and 3 in MOF-74 approach the expected minimum r_{HH}.[27] This offers the prospect that a material with a larger surface area can be synthesized with a similarly large SPD that meets engineering requirements for a hydrogen storage system. Our neutron powder diffraction results and model calculations indicate that the adsorption potentials for a hydrogen molecule in framework structures are large enough to induce a high SPD at 77 K. The SPD of 4.3×10^{-5} g/m^2 calculated with the estimated r_{HH} from our model systems is roughly the upper limit for the SPD of a physisorption system, which in turn sets a minimum surface area required for a working material based on surface physisorption methods.

Supporting Information Available: Additional information concerning BET analysis, hydrogen adsorption, the neutron powder diffraction, inelastic neutron scattering experiments, a full table of atomic parameters, tables of gas adsorption/desorption data, a plot of SPD as a function of Langmuir surface area, the inelastic neutron scattering spectra of H$_2$ in MOF-74, and the neutron powder diffraction pattern at 3.0 D$_2$:Zn is available. This material is available free of charge via the Internet at http://pubs.acs.org.

LA703864A

(27) Lokshin, K. A.; Zhao, Y.; He, D.; Mao, W. L.; Mao, H. K.; Hemley, R. J. *Phys. Rev. Lett.* **2004**, *93*, 125503. The D$_2$−D$_2$ distance in a clathrate hydrate cage is found to be 2.93 Å.