

Calculation of hydrogen storage capacity of metal-organic and covalent-organic frameworks by spillover

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We have used accurate *ab initio* quantum chemistry calculations together with a simple model to study the hydrogen storage capacity of metal-organic and covalent-organic frameworks by spillover. Recent experiments by Tsao *et al.* [J. Am. Chem. Soc. **131**, 1404 (2009)] {based on an earlier work by Li and Yang [J. Am. Chem. Soc. **128**, 8136 (2006)]} have found that IRMOF-8 with bridged Pt catalysts can reversibly store up to 4.7 wt % of hydrogen at room temperature and 100 bar. We have calculated the binding energy for multiple H atoms on model molecules. By counting active storage sites, we predict a saturation excess storage density at room temperature of 5.0 wt % for IRMOF-8. We also predict storage densities of 4.5 wt % for IRMOF-1, 5.4 wt % for MOF-177, 4.5 wt % for COF-1, and 5.7 wt % for IRMOF-15 and IRMOF-16. This suggests that the current experimental H storage results for IRMOF-8 are well optimized. However, for other materials such as MOF-177 and COF-1, the experimental results are not yet optimized, and significantly more H can be stored on these materials. We also find that significant strain will result from shrinkage of the linker molecules as H atoms are loaded onto the crystals. © 2009 American Institute of Physics. [doi:10.1063/1.3257737]

I. INTRODUCTION

There is great interest in finding porous solid materials that can store hydrogen for use in fuel cell vehicles.¹ Ideally, these materials would adsorb large amounts of hydrogen gas reproducibly at room temperature and moderate pressure.

Remarkably, recent experiments have found exciting results for hydrogen storage by spillover at room temperature on high surface area materials.² Some of the most promising results utilized metal-organic frameworks (MOFs) (Ref. 3) and covalent-organic frameworks (COFs) (Ref. 4) as substrates. These materials are easy to fabricate, porous, lightweight, and have extremely high surface area. Hydrogen storage in MOF materials was recently reviewed by Murray *et al.*⁵

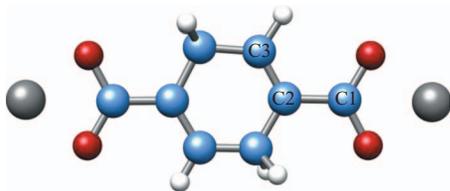
Li and Yang⁶ found that isoreticular metal-organic framework (IRMOF)-8 with bridged Pt catalysts can reversibly store 4 wt % of hydrogen at room temperature and 100 bar pressure by spillover. Ingeniously, they used commercial Pt catalysts, mounted on amorphous carbon substrates (Pt/AC). These were then mixed with IRMOF-8 crystals, and sucrose, and annealed to form amorphous carbon bridges between the Pt/AC and the IRMOF-8. Spillover works by distributing small metal catalysts in the material to dissociate hydrogen molecules into hydrogen atoms that then spillover and bind more strongly onto a large surface area substrate. This process operates at room temperature and is reversible. Tsao *et al.*⁷ have recently extended the IRMOF-8 result to 4.7 wt % in equilibrium at 70 bar. These promising results suggest that even higher storage capacities might be

achieved by higher surface area materials such as MOF-177. A serious limitation in these experiments is that the substrates do not survive multiple loading and unloading cycles. Wang and Yang² suggest that moisture resistant materials such as HKUST-1 (Ref. 8) or MIL-101 (Ref. 9) may be more durable.

There have been several theoretical studies of the spillover process. Li *et al.*¹⁰ published a study of the kinetics and mechanistics of this process on a MOF substrate. They used density functional theory (DFT) with a large test molecule to calculate the binding energies for individual H atoms added to different sites. They found a variety of energies of adsorption ranging from 3 kJ/mol on the Zn₄O corners (physisorption), to 50 kJ/mol (0.52 eV) at the C3 sites, and 40 kJ/mol at O2 sites, with only 8 kJ/mol at the C1 and 15 kJ/mol at C2 sites. Their conclusion was that H atoms could bind by spillover at all sites studied (producing 6.5 wt % storage), however, even within their theory, at room temperature, the low binding energy sites (corners and C1) would not be significantly occupied.

Cheng *et al.*¹¹ have studied the energetics and binding energies of hydrogen spillover on several graphitic materials using DFT calculations. They found an average binding energy of 0.92 eV for H relative to H₂ for a saturated Pt₉ cluster. However, the threshold energy to remove one H from the saturated cluster was 2.5 eV. They found that it cost 0.23 eV each (slightly exothermic) to transfer 2 H atoms from a saturated Pt₆ cluster onto a graphene sheet. They found an H adsorption energy of 0.82 eV on graphene. DFT calculations

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FIG. 1. BDC-Li₂ with two H added at C3 sites. Top view.

by Sha and Jackson¹² found an energy barrier to forming a C–H bond of approximately 0.2 eV when a H atom approaches a graphite surface.

Most recently, Miller *et al.*¹³ have studied the addition of multiple hydrogen atoms to BDC and naphthalene dicarboxylate (NDC) linkers using DFT. They present enthalpies of addition of dihydrogen at 298 K and 1 bar and find a range of values from +10 to –22 kcal/mol as pairs of H atoms are added to the BDC or NDC linkers. Typically, the first pair of H atoms were found to be endothermic, while most other pairs were found to be exothermic. They found that one can add up to 10 H to the naphthalene molecule.

II. COMPUTATIONAL METHODS

Second order Møller–Plesset perturbation theory (MP2) calculations were performed with the frozen core approximation, using restricted and unrestricted Hartree-Fock, using the Gaussian03 program.¹⁴ The DG-DZVP^{15,16} basis set was used for geometry optimization and energy calculations. Preliminary geometrical optimizations were also performed using the PC GAMESS (Ref. 17) program with the FACIO graphical interface.¹⁸ Images of the molecules were created using the Chimera program.¹⁹

III. RESULTS AND DISCUSSION

The first step is to estimate the binding energies for hydrogen atoms on the MOF and COF. We will do this by calculating the binding energy for incremental addition of hydrogen atoms to small model molecules.

For IRMOF-1, the framework consists of Zn₄O corners connected by benzene dicarboxylate (BDC) linkers. In this case we will use Li terminated BDC molecules for the calculation to mimic the electron transfer from the full IRMOF-1 framework.²⁰ Hydrogen atoms were added to the BDC-Li₂ molecules, and then the geometry was optimized using MP2 theory. The average relative energies $[E(\text{BDC} + \text{NH}) - E(\text{BDC})]/N - E(\text{H})$ for N atoms relative to atomic hydrogen are presented in Table I. We pin the four O and two Li atoms during the geometry optimization to mimic the environment of the linker in the real crystal (i.e., we constrain the length of the molecule to fit in the bulk crystal).

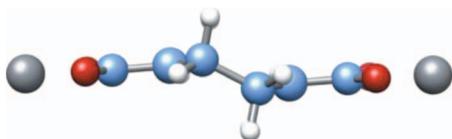
FIG. 2. BDC-Li₂ with four H added at C3 sites. Side view.

TABLE I. Average binding energies for one to six hydrogen atoms added to Li-BDC relative to atomic hydrogen.

Name	Sites	Binding Energy per H (eV)
BDC-Li ₂ +H	C3	–0.02
BDC-Li ₂ +2H	C3	1.78
BDC-Li ₂ +2H	C2	1.56
BDC-Li ₂ +4H	C3	1.66
BDC-Li ₂ +6H	C3 and O	1.81
BDC-Li ₂ +6H	C2 and C3	2.41

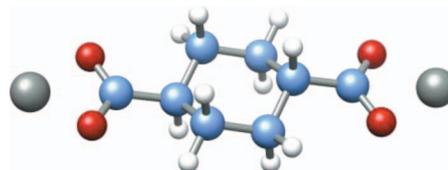
We show the optimized geometry for BDC-Li₂+2H at C3 sites in Fig. 1. We have labeled the C1, C2, and C3 sites in this figure. We find the binding energy of 1.78 eV per hydrogen for 2 H at the C3 sites. For BDC-Li₂+4H at C3 sites, we find an average binding energy of 1.66 eV and the geometry shown in Fig. 2.

We can also add two H at the O sites. We were unable to bind two H at a single O atom. We calculated BDC-Li₂+6H (with four H at C3 sites, two H at O sites, and one H per CO₂) to have average binding energy of 1.81 eV.

We tested configurations with four H at O sites, but without H added at the C1 sites, the CO₂ saturates with only one H per CO₂. We also tested adding two H at C1 sites, but found large structural rearrangement, and only metastable states. However, we believe that it will be possible to add two H at C1 sites together with four H at O sites. This should be a favorable saturated configuration of the CO₂, comparable to methanediol. So, although we have not calculated the binding energy for this configuration (due to time constraints), we will assume that this configuration binds 6H at C1 and O sites for the simple model below. These additional binding sites are needed to reach agreement with the experimental results of Tsao *et al.*⁷ and Li *et al.*⁶

We have also found favorable binding geometry for two H at C2 sites with binding energy of 1.56 eV. Therefore, one can also add six H to the benzene ring (similar to the liquid benzene-cyclohexane cycle²¹). The BDC-Li₂+6H result is shown in Fig. 3, and has a large average binding energy of 2.41 eV. As the benzene is converted to cyclohexane, we see that the molecule has a tendency to bend and shrink, and this will strain the lattice and lead to reduced lattice constant. Although our calculations use pinned atoms to produce consistent binding energies that correspond to low loading of the crystal, this shrinkage issue will become more important at high hydrogen loading and should be investigated separately.²²

One can also compare these binding energies to molecular hydrogen. For example, BDC-Li₂+6H (C2 and C3 sites)

FIG. 3. BDC-Li₂ with six H added at C2 and C3 sites.

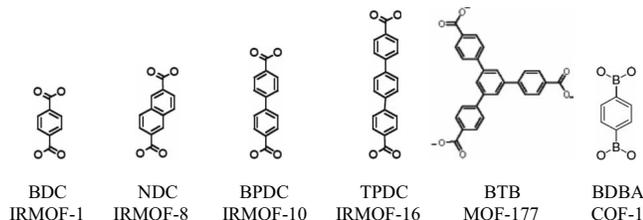


FIG. 4. Linkers for MOF and COF materials from Refs. 4, 22, and 23.

has average binding energy +0.4 eV relative to H_2 , while BDC- Li_2+4H (C3 sites) is -0.36 eV relative to H_2 . We see that the saturated configuration (6H on benzene) has strong binding.

To study H chemisorption on the Zn_4O corners of the MOF materials, we placed H atoms in chemisorption sites on an $Zn_4O(COOH)_6$ terminated corner structure. We tested one H on a three-fold symmetric site near the Zn atom, and three H located symmetrically above three Zn atoms, and also three H located above each of three Zn atoms and symmetric toward interior. We also tested one H in a threefold symmetric site above the central O atom. We also tested two H in symmetric positions above the O atom of the COOH group. We did not find any chemisorption binding sites on the Zn_4O corner structure. Therefore, we conclude that the Zn_4O corners will not play a significant role in H storage by spillover in the IRMOF materials.

To study H chemisorption on the B_3O_3 (boroxine) corners of the COF-1 material, we placed H atoms in potential chemisorption sites on a $B_3O_3H_3$ terminated corner structure (potential sites outside the B, outside the O, and above the molecule). We did not find any H chemisorption binding sites on the boroxine corners.

IV. SATURATION MODEL

We have built a simple model to estimate the saturation hydrogen storage density by spillover at room temperature and reasonable pressure for various metal-organic and COFs. We count chemisorption binding sites based on the above calculations. We place one H on each of the C1, C2, C3, C4, and O sites of each linker, and no H on the Zn_4O and boroxine corners. This is consistent with the work of Miller *et al.*,¹³ who showed that ten H atoms can be added to the NDC linker of IRMOF-8. The linkers for several MOF and COF materials are shown in Fig. 4. By counting these binding sites for these MOF and COF materials, we predict the saturation storage densities presented in Table II. Details of these calculations are given below.

For the BDC linker in IRMOF-1, we find six H binding locations on the benzene ring at C sites, and three H binding locations on the CO_2 . This corresponds to 36 H atoms per formula unit. For IRMOF-1, the model predicts a saturation value of 4.5 wt %, compared to the 3 wt % found experimentally at 100 bar, although the experiment is not yet saturated.⁶

For IRMOF-8, we have binding sites at C1, C2, C3, and O sites as above, but also two more C4 sites (one above, one below) at the interior of the naphthalene molecule. This corresponds to 48 H atoms per formula unit. The model predicts a saturation density of 5.0 wt % for IRMOF-8. This can be

TABLE II. Predicted hydrogen gravimetric storage density by spillover for various metal-organic and COF materials. Formula units from Refs. 4, 22, and 23. Experimental results from Refs. 6 and 7.

Material	Formula unit	Number of H/formula unit	Gravimetric storage density (%)	Experimental result (%)
IRMOF-1	$Zn_4O(BDC)_3$	36	4.5	3.0
IRMOF-8	$Zn_4O(NDC)_3$	48	5.0	4.7
IRMOF-10	$Zn_4O(BPDC)_3$	54	5.3	
IRMOF-15	$Zn_4O(TPDC)_3$	72	5.7	
IRMOF-16	$Zn_4O(TPDC)_3$	72	5.7	
MOF-177	$Zn_4O(BTB)_2$	66	5.4	1.5
COF-1	$C_6H_4B_2O_2$	6	4.5	0.7

compared to the unsaturated 4 wt % hydrogen storage at 100 bar experimental result of Li and Yang.⁶ We can also compare to the newer result by Tsao *et al.*⁷ of 4.7 wt % in equilibrium at 70 bar. This shows good agreement between experiment and theory for spillover on IRMOF-8. (We note that the experiments are based on a mixture of Pt/AC, sucrose, and IRMOF-8.)

Higher storage density is predicted for MOF-177, at 5.4 wt % (assuming six H per benzene ring and three H per CO_2). This system and variants are promising storage targets. Two experimental groups have already measured spillover onto MOF-177. Wang and Yang² found 1.5 wt % storage at 100 bar, using physical mixing of MOF-177 and Pt/AC catalysts with bridge building. However, the particle size of MOF-177 may have been too large, or the bridge building may not have been optimized fully. Proch *et al.* fabricated samples by Pt chemical vapor deposition, but were only able to reproducibly load small amounts of H. In this case, improved Pt catalyst fabrication may lead to better results.

Higher predicted storage density is also found for IRMOF-9 and IRMOF-10 with 5.3 wt %, and IRMOF-15 and IRMOF-16 with 5.7 wt %. IRMOF-9 and IRMOF-15 are catenated (with two interpenetrating lattices), and will have double the volumetric storage density. IRMOF-15 has a predicted volumetric storage density of 23 g/l, while IRMOF-9 has 35 g/l. These should be favorable candidates for storage by spillover.

The IRMOF materials that we have been discussing range from 80%–90% free volume, and therefore if one considers the total storage (as opposed to the excess storage we have been discussing), then additional hydrogen can be stored as H_2 in the free space.²³

For COF-1, we put one H on each C atom, but no H on the B_3O_3 corners, for a total of six H per unit cell. We therefore predict a saturation storage density of 4.5 wt % for COF-1.⁴ We expect that other COF materials, where H could bind on the corners, will have even higher storage densities. This suggests that the COF materials are attractive targets for hydrogen storage by spillover.

V. SUMMARY

We have seen that hydrogen storage by spillover onto IRMOF-1 and IRMOF-8 is able to store one H for every

linker atom, with no storage on the corners at room temperature. We have constructed a model based on favorable binding sites which predicts the saturation hydrogen storage capacity for several metal-organic and COF materials. We see that for crystalline materials, counting binding sites is preferable to comparing to surface area. For IRMOF-8, we predict 5.0 wt % storage, in good agreement with the new experimental results of Tsao *et al.*⁷ The model predicts that MOF-177 can store 5.4 wt % and COF-1 can store 4.5 wt %, much larger than the experimental results. This suggests that the experimental results for MOF-177 and COF-1 are not fully optimized, and that significantly larger storage can be obtained with these materials. We found that IRMOF-9 has the largest volumetric storage capacity of the materials studied with 35 g/l. We find that the linkers will shrink as H atoms are loaded. This will strain the lattice, and may damage the substrate during loading and unloading cycles. It should be possible to fabricate other metal-organic and covalent-organic materials with even higher hydrogen storage capacities.

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