Hole-Mediated Hydrogen Spillover Mechanism in Metal-Organic Frameworks

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Hydrogen spillover on carbon-based systems has been proposed as a viable alternative for room-temperature storage. Given the strength of the C-H bonds, however, it is unclear if spillover indeed takes place in such materials. We performed a first-principles study of H spillover on IRMOF-1. Spillover becomes thermodynamically stable only at high H coverage with a calculated Gibbs free energy of -14 kJ/mol at ambient condition. In general, however, spillover may not proceed due to high-energy states at lower H coverage. We propose that hole doping can substantially lower the energies as well as barriers to enable spillover at ambient conditions.

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By virtue of their exceptionally high porosity, metal-organic frameworks (MOFs) are excellent materials for hydrogen (H) storage, as well as for the storage of other gas molecules [1,2]. The simple archetypal MOF, namely, IRMOF-1, can take dihydrogen molecules (H_2) up to 1.3 wt % at 77 K and 1 atm [3,4]. At room temperature (RT), however, the H storage capacity drops precipitately to below 0.4 wt % even at 100 atm [5], because the H_2 binds to IRMOF-1 by weak physisorption. Recently, a significant increase of the H sorption at RT, e.g., 3 wt % in IRMOF-1 at 298 K and 10 MPa, has been reported [6,7] via the so-called H spillover mechanism. Spillover refers to H_2 adsorption and dissociation on catalyst nanoparticles and subsequent diffusion of the atomic H to a receptor material to be stored [8]. In terms of the bonding characters, the stored H is similar to that in metal hydrides [9,10], rather than to the physisorbed H_2, but with more desirable binding strength and diffusion kinetics according to the report.

There are two important issues that potentially prevent the spillover from taking place at near ambient conditions: First, the binding of H to the carbon materials is not thermodynamically favorable. Second, the diffusion of H has a large energy barrier. Most of the theoretical studies focused on graphene or cluster model [11–17]. To explain the thermodynamic stability of hydrogenated MOFs, nucleation of chemisorbed atomic H into "magic" clusters was proposed [13,14] which takes place when the size of the clusters exceeds $N = 18$. However, a more reliable estimate of the critical size requires the inclusion of zero-point energy and entropy of H_2 in the gas phase at ambient conditions, which would place a fully hydrogenated graphene sheet (i.e., graphane [18]) as slightly less stable than pristine graphene plus H_2 gas. Even a rather unconventional physisorbed process was proposed [11,12] to account for the relatively fast kinetics. After all, based on the graphene model study, no definitive conclusion could be drawn for spillover in MOFs so far.

In this Letter we focus instead on the exact real system IRMOF-1. We found that, unlike graphene, hydrogenated IRMOF-1 becomes thermodynamically stable when more than four H atoms are attached per benzene-dicarboxylate (BDC) linker. However, spillover is still not feasible at RT due to the energy cost of breaking carbon π bonds in the linkers, as well as due to the high diffusion barrier of H from one carbon site to another. We found that electron holes (positive charges) inside the MOFs can completely alter the energetics and reaction pathways, by eliminating the electrons in the carbon dangling bonds during the reactions. In particular, even the addition of the first H to the BDC linker becomes exothermic. The H diffusion barrier is also substantially reduced to enable RT diffusion. Since holes do not actually participate in the final product of the spillover, only a minute amount of holes is sufficient. Our calculation suggests that Zn vacancies in IRMOFs could be a possible source for such holes. In a recent experiment [7], Tsao and co-workers reported that structural imperfections play an important role in H spillover on MOF.

The enthalpy of adsorption per H_2 is defined as

$$\Delta H = [H(n\mathrm{H@IRMOF\text{-}1}) - nH(\mathrm{H_2})/2 - H(\mathrm{IRMOF\text{-}1})](2/n), \quad (1)$$

where $H(\mathrm{IRMOF\text{-}1})$, $H(\mathrm{H_2})$, and $H(n\mathrm{H@IRMOF\text{-}1})$ are the enthalpy of the IRMOF-1, a H_2 in gas phase [19], and IRMOF-1 with nH atoms chemisorbed, respectively. A negative ΔH corresponds to exothermic adsorption. We decompose ΔH into three parts, i.e., adsorption energy ΔE, zero-point energy ΔZPE, and thermal energy. For total energy (E) and activation energy barrier calculations at the zero temperature we used VASP (Vienna *ab initio* simulation package) [20] with a plane wave basis set,

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Perdew-Burke-Ernserhof (PBE) exchange-correlation functional [21], and all-electron like projector augmented-wave (PAW) method [22] for core electrons and ionic potentials. The Brillouin zone was sampled at Γ point. All calculations are spin polarized. We used a plane-wave energy cutoff of 500 eV. The nudged elastic band (NEB) method [23,24] is used for the determination of activation energy barrier. In contrast to previous cluster model studies of H binding on IRMOF-1 [15,16] where lattice strain effects are missing, in our study we used a periodic model in a trigonal unit cell containing 106 atoms (Fig. 1) and lattice strain is correctly included. The calculated lattice constant for the conventional cubic cell is 18.462 Å, which is in good agreement with experiment [25] to within 1%. We simultaneously optimized the lattice vectors and the atomic positions in the cell by the variable cell dynamics [26]. The atomic positions are relaxed until forces are smaller than 0.03 eV/Å. For all key structures we have relaxed the atoms further until the forces are smaller than 0.01 eV/Å. The energies are converged to within 1–2 kJ/mol. The zero-point energies (ZPEs) and thermal energies are calculated within the harmonic approximation [27] at the standard temperature and pressure for lithium terminated BDC linker by using GAUSSIAN03 [28] at the B3LYP/6-311$+G(d, p)$ level. For H binding to O and Zn sites, which are very weak physisorption according to our calculation, the ZPE corrections were neglected.

Table I and Fig. 2 summarize our results for H adsorption. H binding sites are labeled in Fig. 1(b). Besides 1 H (termed 1H), we also considered all the possible configurations for multiple H addition (namely, 2H, 3H, etc.). For completeness we also considered H binding to the Zn sites on the Zn_4O cluster. With no exception, H always prefers to bind with unsaturated C atoms on the benzene ring of the BDC. The lowest-energy adsorption site for 1H is the C3 site (equivalently the C3′, C4, and C4′) with an enthalpy of adsorption of 194 kJ/mol. This turns out to be the most difficult step for hydrogenation of the IRMOF-1 and has the highest enthalpy of adsorption. The reason is that the added H atom leaves an unpaired dangling bond by breaking a resonating partial double bond and the aromaticity of the benzene ring. However, the addition of a second H passivates the dangling bond, thereby stabilizing the 2H state relative to the 1H state. Except for one new configuration (C12) in Table I, these results are in good agreement with the results of previous nonperiodic molecular model calculation [16]. The C12 configuration is important not only because it has the lowest energy for H pairs (e.g., 3 and 7 kJ/mol lower than C34 and C33′, respectively) but also because it leads to a broken bond. The C12 accommodates two H atoms not by saturating any partial double bond but by breaking a C-C single bond. This result suggests that H can potentially destroy the crystal structure of IRMOF-1. As it turns out, however, the presence of holes can eliminate such instability as will be detailed below.

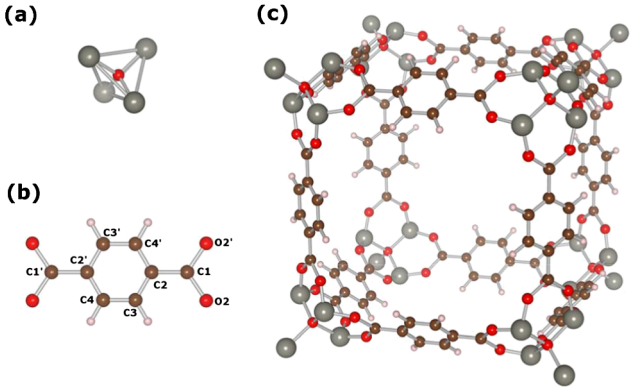

FIG. 1 (color online). (a) Zn_4O cluster and (b) benzenedicarboxylate (BDC) linker. They are joined together in (c) to form the periodic IRMOF-1 crystal.

The enthalpy of adsorption for 2H in Fig. 2 (e.g., 20 kJ/mol) is considerably lower than that for the first H (194 kJ/mol). It is a general trend that the odd numbered H state is higher in energy than adjacent even numbered H states, and is due to the negative-U effect [29] of covalent bonds. The odd numbered H states thus act as bottlenecks to one-by-one consecutive hydrogenation. We note that the C1-O2 bond in the carboxylate in Fig. 1(b) is also a resonating partial double bond that can be saturated by two H as in the case of benzene ring in the linker. However, the C1O2 configuration with saturated C1-O2 double bond is found to be energetically unfavorable because it forces the O2 to be threefold coordinated. According to our calculation, further H additions only take place at the carbon sites of the benzene ring, not at any of the oxygen or zinc sites (see Table I). The hydrogenation of the benzene ring of a BDC is expected to severely distort the originally flat BDC structure and results in the contraction of the MOF lattice due to the transformation of the planar sp^2 network into tetragonal sp^3 network. The same process, however, also increases the C-C bond length because in the linker a single bond (1.545 Å) is ~9% longer than the partial double bond (1.421 Å). It turns out that these two competing factors cancel out each other so the net effect is negligible. The IRMOF-1 lattice expands by less than 0.5% when all the six-BDC linkers are fully hydrogenated.

So far we have shown that the 1H state has a very high enthalpy of adsorption (+194 kJ/mol) that blocks the spillover from very beginning. Not only does this make the hydrogenation process thermodynamically unfavorable, but also the diffusion barrier of the atomic H could be an issue. Table II shows the diffusion barriers for a single H hopping from C2 to C3, from C3 to C4, and from C3 to C2 calculated by the NEB method. It can be seen that spillover requires overcoming the 1.50 eV barrier, which cannot be done at near RT. An important observation in our calcu-

TABLE I. Calculated enthalpies of adsorption (ΔH, in kJ/mol unit) of H in IRMOF-1. There are six (multi)-H states (1H, 2H, etc.) each may contain multiple configurations. Negative enthalpy implies exothermic reaction.

1H Configuration	ΔH	2H Configuration	ΔH	3H, 4H, 5H, 6H Configuration	ΔH
C1	458	C12	20	C234	25
C2	250	C23	48	C233′	38
C3	194	C34	27	C343′	49
O1	440	C33′	23	C2342′	−19
O2	298	C34′	195	C2343′	82
Zn	440	C24	231	C2344′	−34
		C1O2	70	C343′4′	69
		O2Zn	Do not bind	C2343′4′	−12
				C2342′3′4′	−55

lations is that the odd numbered H states are always associated with a singly occupied dangling bond level (DBL) inside the band gap, as shown in the inset in Fig. 2. In particular, the DBL is 2.02 eV above the valence band maximum (VBM) and 0.82 eV below the bottom of the conduction band minimum (CBM). This raises the question if one could alter the energetics depicted in Fig. 2 by changing the occupation of the DBL. By introducing an electron hole into the system, for example, one might be able to lower the energy of the odd numbered H states by dropping the electron in the DBL to a level near the VBM. The calculated results with one hole at the VBM are shown in Fig. 2 also. Several positive effects are seen simultaneously: first, the high-energy odd numbered H states are no longer bottlenecks for H spillover. As a matter of fact, in most cases their energies are now lower than those of the adjacent even numbered H states. The fact that the hole has little effect on the even numbered H states is easily understood because they do not possess any DBL. Second, the enthalpies of adsorption all become negative, implying that the reactions are all exothermic. Third, a breaking of the linkers at the 2H state (C12) no longer holds. In other words, the lowest-energy configuration (C33′) is no longer destructive to the IRMOF-1 lattice. Calculations on H binding to other possible sites in the presence of a hole also show no bond breaking, indicating reasonable structural stability of IRMOF-1 in such an environment. Fourth, a hole also substantially lowers the atomic H diffusion barriers. Table II shows that, in the presence of the hole, the barriers are reduced to only one-third of the original ones. The highest barrier now stands at 0.52 eV, so diffusion can be readily activated at near RT. While the effects of the holes are very significant, one might also wonder what would be the role of free electrons. We found that although free electrons can lower the enthalpies of adsorption for the odd numbered H states, similar to holes, the magnitudes are smaller. Because dropping an electron from the DBL to the VBM lowers the enthalpy by 2.02 eV but dropping an electron from the CBM to the DBL lowers the enthalpy by only 0.82 eV.

Because of the negative-U behavior, none of the even numbered H states, in particular, the final fully hydrogenated 6H state, takes any hole from the VBM. A hole is recovered after the hydrogenation of an odd numbered H state and can be reused repeatedly. Thus, even a small concentration of free holes is enough to mediate the H spillover. In the hydrogenation of lithium nitride/imide [30] mobile ions have a similar catalytic role. As possible candidates for the minute amount of holes in IRMOF-1, we have investigated oxygen-related defects (such as the addition or replacement of H by the hydroxyl group, addition of an ozone on the benzene ring of BDC), H defects (such as H addition to C), vacancies (such as the BDC vacancy or

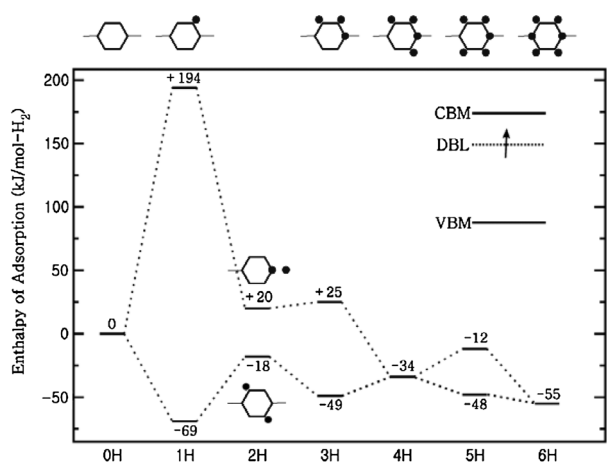

FIG. 2. Enthalpy of adsorption for consecutive hydrogenation of IRMOF-1. The upper line shows the results without hole participation and the lower line with holes. The most stable configurations are shown at the top of the figure except for 2H, where the presence of holes stabilizes IRMOF-1. The inset shows schematically the position of the dangling bond level (DBL) inside the band gap. Holes at the top of the valence band (VBM) facilitate the removal of the electron at the DBL during spillover, thereby lowering the enthalpy of adsorption.

TABLE II. Energy barriers (in eV unit) for H diffusion on a BDC linker without (first row) and with (second row) a hole. Note that C2 to C3, C2′ to C3′, C2 to C4′, and C2′ to C4 are all equivalent cases. C3 to C4 and C3′ to C4′ are equivalent, too. C3 to C2 is the reverse process of C2 to C3 and thus has also four equivalent cases.

Path	C2 to C3	C3 to C4	C3 to C2
Normal	1.21	1.15	1.50
Hole mediated	0.33	0.41	0.52

Zn vacancy), and Cu substitution to Zn. We found that Zn vacancy creates a shallow acceptor level near the VBM. One may increase the Zn vacancy (and hence hole) concentration by growing the MOFs in a zinc poor growth condition.

The maximum storage capacity would be 2.4 wt % when all the H atoms are stored in the carbon ring of the BDC linker. Including the 0.4 wt % physisorption of H_2 at the experimental condition (298 K and 10 MPa) [6], the reversible capacity would be 2.8 wt %. These may be compared with the experiment of about 3 wt % [6]. The corresponding calculated volumetric capacity is 17 g/L. To determine the stability of the spillover system, we need to calculate the Gibbs free energy. By using the expression $\Delta G = \Delta H - T\Delta S$, we obtain $\Delta G = -14$ kJ/mol for the case of full loading ($\Delta H = -55$ kJ/mol). We take $T\Delta S$ to be the entropy of the H_2 gas at the ambient condition, 39 kJ/mol [31], because the entropies of chemisorbed H and the IRMOFs are negligible. To the best of our knowledge, this is the first time that theory predicts MOF-based spillover systems can be made thermodynamically stable.

In summary, we showed that the spillover in IRMOF-1 is essentially the hydrogenation of the unsaturated benzene rings of the BDC linkers. However, H spillover cannot proceed at near ambient conditions in the usual manner as in the traditional spillover system [32] due to the high-energy odd numbered H states. Our calculation predicts that these high-energy bottlenecks are eliminated by the presence of holes. Meanwhile, the kinetic barriers for H diffusion are also substantially lowered by the holes. Zinc vacancy inside IRMOF-1 is a likely source for the holes.

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