Communication

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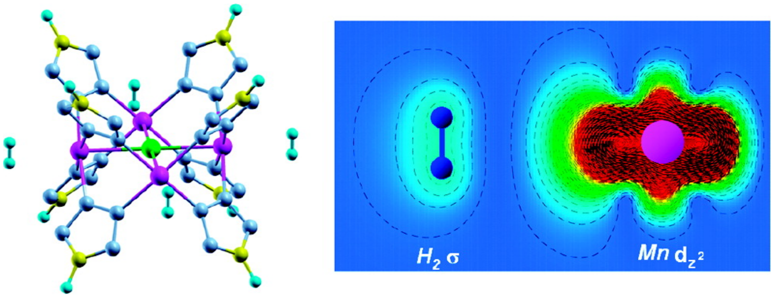

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Effect of Spin State on the Dihydrogen Binding Strength to Transition Metal Centers in Metal-Organic Frameworks

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A safe, compact, lightweight, and cost-effective way to store hydrogen fuel is critical to realizing the future hydrogen economy. Developing new materials to meet the DOE 2010 system target (6 wt % and 45 g/L) is currently a focus of research on hydrogen storage.[1] Materials that bind molecular hydrogen stronger than pure physisorption and weaker than typical chemisorption are desired so that enhanced storage capacity at near-ambient conditions and easy uptake and release of hydrogen fuel can be balanced.

Recently, there have been intensive experimental studies on the metal-organic framework (MOF) systems, which have shown promise for hydrogen storage based on their high porosity, tunable binding strength to H_2, and low-cost synthesis.[2−5] To date, up to 6.9 wt % hydrogen storage at 77 K and 90 bar has been experimentally measured in these systems.[5] It has been found that the exposed transition metal (TM) sites give the largest binding to H_2 by about 10 kJ/mol.[3−5] The measured separations, 2.3−2.5 Å between the adsorbed H_2 and the TM centers such as Mn and Cu, are much shorter than those resulting from van der Waals interactions (3.26−3.66 Å).[5] Both the binding energies and the shorter separations are indications that chemical bonding takes place between H_2 and the TM centers. However, such a weak binding energy does not fall in any known regime of chemical bonds. Intuitively, this bonding could be assigned to Kubas interaction, which is a three-center bonding between an H_2 and a TM center similar to the current scenario.[6] Yet, this is not obvious because the typical binding energy in a TM−dihydrogen complex is greater than 50 kJ/mol.[7] In this communication, we use the Mn−MOF system[5] to demonstrate that the splitting and occupation of the spin orbitals account for this weak binding.

We performed ab initio calculations based on the density functional theory (DFT) with the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional[8] using the VASP code.[9] A molecular model, as shown in Figure 1a, was used to simulate the MOF system (see Supporting Information for calculation details). Four H_2 molecules were symmetrically put on the four Mn atoms in Figure 1a in the side-on configuration. We found that the minimum energy configurations have the total magnetic moment of 13 μ_B (i.e., 3.25 μ_B/Mn) before and after H_2 adsorption. Detailed electronic structure analysis shows that the spin-up levels for each Mn are occupied by 4 electrons and the spin-down by 0.75 electrons, while almost no s electrons were found for Mn. In other words, each Mn is oxidized by 2.25 electrons. The binding energy to H_2 was calculated to be 8.4 kJ/mol with a separation of 2.42 Å between Mn and the center of H_2. Similar calculations for the Cu−MOF system give 4.4 kJ/mol for the binding energy and 2.69 Å for the Cu−H_2 separation. Note that the PBE functional systematically underestimates the binding energy for the van der Waals interactions. For some hydrogen storage systems, the DFT-PBE calculations simply give no binding.[10]

To understand the unexpected small binding energy, we analyzed the local density of states (LDOS) on Mn d and H s orbitals before and after H_2 adsorption, as shown in Figure 2a. It is evident that significant orbital interactions take place between the H_2 σ and Mn d levels. The sharp H_2 σ peak before adsorption is considerably pushed to lower energy and splits into several small peaks after H_2 adsorption. Only a couple of Mn d levels are pushed to higher energy significantly, whereas others just shift up slightly. By analyzing the symmetry of the Mn d orbitals, it is found that the significantly shifted d levels always have the d_{z^2} symmetry. These levels can be identified as the antibonding states resulting from the coupling between H_2 σ and Mn d_{z^2}, as shown in Figure 1b. It is also clear that the protrusion of the d_{z^2} orbital toward the H_2 σ orbital makes it the most responsive orbital to the approaching H_2 (see Supporting Information).

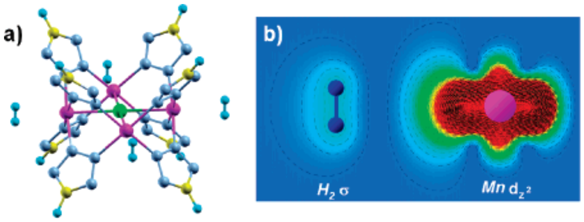

Figure 1. (a) Simulative model for Mn-based MOF systems. The magenta, gray, yellow, green, and cyan balls represent Mn, N, C, Cl, and H atoms, respectively. Four H_2 molecules are adsorbed on the four Mn centers in the side-on configuration. (b) Electron density plot of an antibonding state between the H_2 σ and Mn d_{z^2} orbitals.

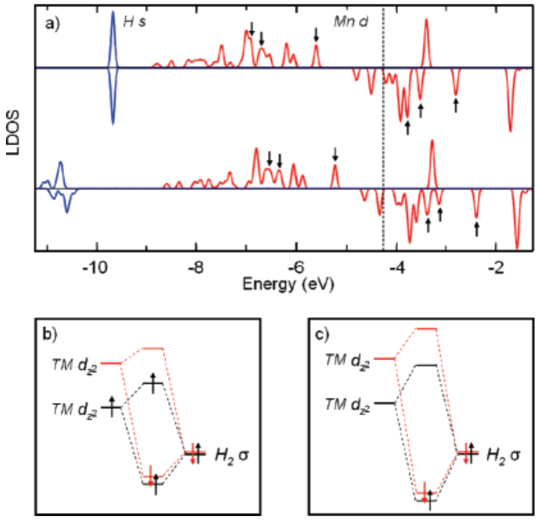

Figure 2. (a) Local spin density of states on Mn d and H s before (upper) and after (lower) H_2 adsorption. The arrows label the positions of the four d_{z^2} orbitals of the four Mn. Both the spin-up and spin-down d_{z^2} levels at the highest energy are twofold degenerate. The dashed line separates the occupied and unoccupied states. (b) Schematic diagram illustrating the orbital interactions between TM d_{z^2} and H_2 σ in the Mn− and Cr−MOFs. Spin-up orbitals are denoted by black color and spin-down by red. (c) Similar diagram for the Sc−, Ti−, and V−MOFs.

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Table 1. Binding Energies per H_2 Molecule (E_b in kJ/mol), Magnetic Moments per TM Atom (m in μ_B), and Separation (d in Å) between the TM Center and H_2 in the MOF Systems

	Sc	Ti	V	Cr	Mn
E_b	21.9	34.6	46.5	10.4	8.4
m	0.75	1.75	2.75	3.75	3.25
d	2.35	2.07	1.93	2.32	2.42

The most striking feature in Figure 2a is that *both* the spin-up and spin-down Mn d_{z^2} levels are pushed to higher energies. Because the spin-up levels are occupied, the upshift of these levels will raise the total energy of the system. Therefore, two competing mechanisms exist in this system. One is the energy-gaining mechanism caused by the down-shift of bonding levels, and the other is the energy-costing mechanism resulting from the upshift of antibonding levels if they are *occupied*. This argument explains the weak binding to H_2 in the Mn−MOF system.

As a comparison, we studied the $Mn(\eta^2\text{-}H_2)Cl(CO)_4$ complex,[11] in which the Mn center has similar local symmetry as in Mn−MOF, but a different oxidation state (i.e., Mn^+). On the basis of our calculation, the Mn center in this complex is non-spin-polarized. The Mn d_{z^2} orbital is also found to be the most responsive to the dihydrogen. However, in contrast to the Mn−MOF system, the d_{z^2} orbital is now unoccupied. Thus, the energy-costing mechanism is not present in this system, and a higher binding energy is expected. Our calculations give a binding energy of 113.6 kJ/mol. This binding is much stronger than that in the Mn−MOF system but is typical for the TM−dihydrogen complexes.[7]

On the basis of the argument above, if replacing Mn with early TMs in MOF, one can expect stronger binding to H_2. Because of the nearly square-pyramidal local symmetry of the Mn centers, the crystal field splitting of the Mn d orbitals renders the d_{z^2} orbital the fourth highest in energy, which is lower than only the $d_{x^2-y^2}$ orbitals.[12] This can be seen in Figure 2a, in which the peaks at the highest energy for each spin are the $d_{x^2-y^2}$ orbitals. Because early TM elements have a smaller number of valence electrons, replacing Mn with these elements could deplete the occupied spin-up d_{z^2} orbitals, and the energy-costing mechanism can be avoided. We list the calculated binding energy to H_2 in Sc−, Ti−, V−, Cr−, and Mn−MOF systems in Table 1 and draw the corresponding schematic energy level diagrams in Figure 2b and 2c (see Supporting Information for detailed electronic structures). It can be seen that, for Sc, Ti, and V, considerably higher binding energies are obtained. This is consistent with our electronic structure analysis on these systems in which both spin-up and spin-down d_{z^2} levels are found unoccupied. From Sc to V, the binding energy increases. As the atomic number increases, the d levels are lowered and the energy difference between the H_2 σ level and the TM d_{z^2} levels becomes smaller, which enhances the orbital interactions between them based on the second-order perturbation theory. This trend, however, stops at Cr as the spin-polarization argument enters here. For the Cr−MOF, a similar but slightly higher binding energy than Mn was obtained. This is because the spin-up Cr d_{z^2} orbital is occupied by only 0.75 electrons, whereas in the Mn−MOF, it is fully occupied by 1 electron. In the case of Cu−MOF, both spin-up and spin-down d_{z^2} orbitals are occupied, resulting in smaller binding energy of 4.4 kJ/mol.

From Table 1, it can be seen that the binding energy to H_2 can be tuned from about 10 to 50 kJ/mol by using different TMs in the MOF systems. This is the desired range for hydrogen storage at near-ambient conditions. Currently, the Mn-based MOF system achieves the best performance only at the liquid nitrogen temperature. On the basis of the larger binding energies in the Sc-, Ti-, and V-based MOF systems, we expect they could work at higher temperatures. The stability of these MOFs was also studied in terms of substituting the Mn centers in Mn−MOF by Sc, Ti, V, and Cr atoms. It is found that the Mn substitutions are thermodynamically favorable (see Supporting Information).

We summarize the four key factors that affect the orbital interactions between a TM center and an approaching dihydrogen as follows: (1) the separation of the H_2 σ level and the TM d levels which decreases when the atomic number increases; (2) the splitting of the spin-up and spin-down d levels which is reflected by the magnetic moment of the TM center; (3) the position of the most responsive d levels to the approaching H_2 which is determined by the crystal field splitting of the d orbitals according to the local symmetry of the TM center; and (4) the occupancy of the responsive d levels which is determined by the number of valence electrons and the oxidation states.

In conclusion, based on the argument of spin-polarization, we have given an explanation to the abnormally small H_2 binding energy experimentally measured in the Mn-based MOF systems. By using this argument, the trend on the calculated H_2 binding energies in different TM-based MOF systems becomes clear. It is also found that the binding energy of the TM center in MOF to H_2 can be tuned in a range of about 10 to 50 kJ/mol.

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Supporting Information Available: Structure of the Mn−MOF (Figure S1), calculation details, charge density plots of the d_{z^2} and $d_{x^2-y^2}$ orbitals (Figure S2), LDOS plots (Figures S3−S7), and the stability of the five early TM MOF systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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