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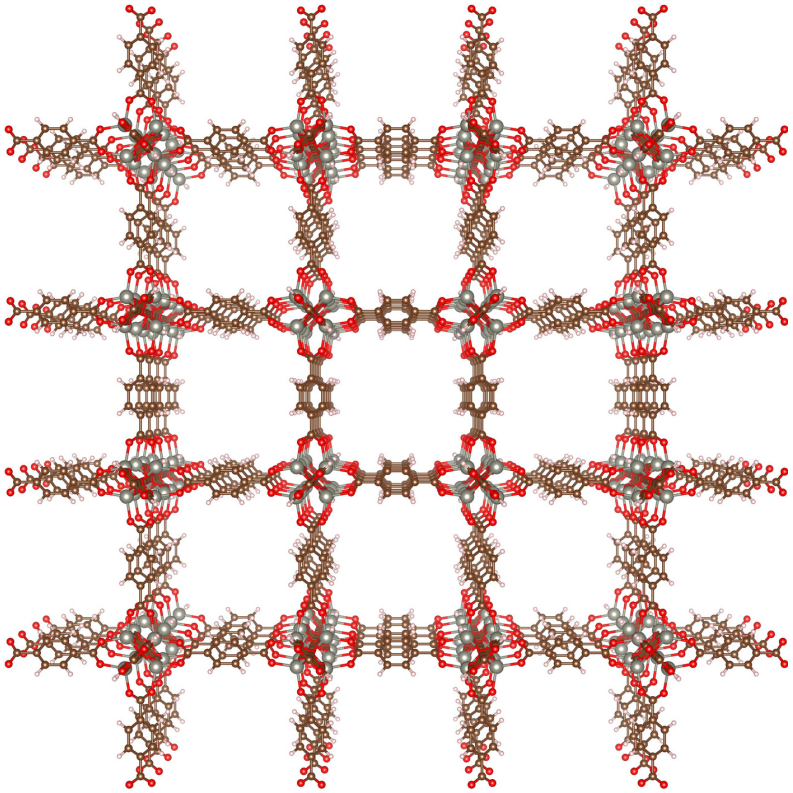

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Cover: Ball-and-stick model of MOF-5. © Roshani Sharma. Printed with permission.

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Himalayan Physics

Cluster modelling of MOF-5 and its application on gas storage

Research Article

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Abstract: MOF-5 exhibits unique characteristics for applications in gas storage particularly in the field of hydrogen storage. MOF-5 is a porous crystalline cubic structure formed by connecting a Zn_4O inorganic moiety to benzene-1, 4-dicarboxylate (BDC), a bidentate ligand where, the Zn_4O-cluster represents the central part of the structure. It can be an alternative to high pressure tanks and multistage compressor used in hydrogen storage. Using the cluster modelling approach, a thorough investigation of MOF-5 is provided. A density functional theory calculation was performed to examine the hydrogen storage potential in MOF-5. The geometry optimizations were carried out using the B3LYP functional together with the LanL2DZ/6-31G basis set. It is observed that the adsorption of hydrogen in MOF-5 cluster is physisorption and the hydrogen molecule is held in the core with the binding energy in the range 26-27 meV.

Keywords: Metal organic framework • Density functional theory • Cluster modeling • Hydrogen storage

I. Introduction

Metal Organic Frameworks (MOFs) are crystalline solids composed of a hybrid network of metal ions and organic molecules called linker all bounded to metal ions in well-organized fashion [1]. MOFs have large surface area, large surface to volume ratio and are highly porous and have structural flexibility.Researchers have synthesized MOFs that feature a surface area of more than 7800 square meters per gram [2]. To put this into context, if you could lay out the available surface area in a teaspoon of this material (around a gram of solid), it would cover an entire soccer field.Applications of MOF comprise drug delivery, non-linear optics, luminescence, separation, catalysis, gas adsorption and storage, sensing, molecular recognition, and catalysis [1]. Metal-organic frameworks (MOFs) with their exceptionally high surface area, low density and adjustable pore size and functionality are a class of promising materials for hydrogen storage [3]. They can also be employed as an alternative to multistage compressors and high pressure tanks for retaining hydrogen. But very few MOFs have

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shown good adsorptive capacities. Theoretical research has demonstrated that, among different MOFs, MOF-5 exhibits good adsorptive capacity [4].

MOF-5 is a highly crystalline microporous coordination polymer [5] (Fig. 1(c)). The Zn_4O cluster represents the central part of this structure (Fig. 1(b)). Oxygen atoms are located in the center of the tetrahedron coordinated by four zinc atoms that are positioned at the tetrahedral vertices. The edges of these tetrahedral are bridged by six carboxylate groups of the organic linker forming an octahedral node. The nodes are linked together with 1, 4-phenylene groups of the BDC linker resulting in a three dimensional cubic network [6]. It was found by Omar M.Yaghi [5].

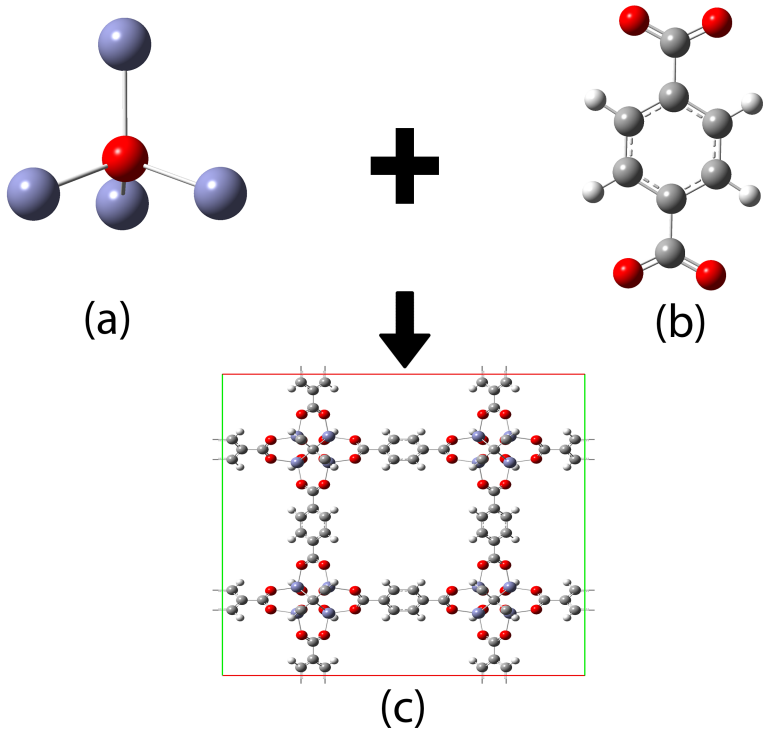

Figure 1: (a) Benzene 1,4 dicarboxylate, (b) Zn_4O cluster, and (c)MOF-5 crystal structure. Atom representations: red is oxygen, gray is carbon, white is hydrogen and blue is zinc atom.

Since, MOF-5 is the first in a line of isoreticular metal-organic frameworks where the BDC molecule is replaced out for a different spacer that maintains the topology of the net and allows us to modify both pore size and framework functioning, it is also known as IRMOF-1 [7]. It is expected that MOF-5 can be a good candidate for hydrogen storage.

In 2003, the first investigations of hydrogen storage in MOF-5 was reported [8]. Since then, it has been intensively investigated due to its high specific surface area as well as the simple and cheap chemical constituents of the material [9]. Understanding mechanism of loading and unloading gases in MOFs is important not only for practical purpose of designing and recommending new porous material but also for purpose of understanding fundamental physics and chemistry that happens at electronic structural level. Density Functional Theory (DFT), which is one of the most successful and popular quantum mechanical modelling method used in physics, chemistry and material science, focused upon the study of various electronic, mechanical and magnetic properties of matter. The fundamental concept of DFT was first introduced by Thomas[10] and Fermi in 1927. Later, the exchange and correlation terms were introduced by Dirac and the approximation is named as Thomas-Fermi Dirac (TFD) approximation[10, 11]. Determining the hydrogen storage capacity of MOF-5 and understanding how it stores hydrogen are the key goals of this investigation. Density functional theory (DFT) methods has been implemented for data collection, presentation and analysis in order to predict hydrogen storage capacity of MOF-5 using Gaussian09 software at Becke's 3-parameter hybrid method with the Lee, Yang, and Parr (B3LYP) and basis set (LANL2DZ) suites. The Gaussian09 is a more advanced version of the Gaussian which is used by Physicists, material scientists, chemical engineers, biochemists, and other scientists as the computational chemistry software program. It uses the basic laws of quantum mechanics to predict energy, molecular structure, spectroscopic data and many advanced calculations. It was initially released in 1970 by John Pople [12] and his research group at Carnegie-Mellon University as Gaussian 70 [13].

II. Computational Details

In principle, density functional theory (DFT)-based calculations provide a highly accurate description of the bond-breaking processes during hydrogen storage in MOF. However, these calculations remain a challenge because of the large number of atoms in the computational cell (106 atoms in the MOF-5 primitive cell and 424 atoms in the conventional cell). For this reason, cluster approximations or structural simplifications are commonly adopted to MOF structure formed by 1,4-benzenecarboxylate linkers and metal cation connectors to make the calculations tractable. The MOF-5 cif structure was obtained from Cambridge Crystallography Data centers (CCDC). The crystal structure was then cleaned by using Gauss View. The metal core consisting of six carbon atoms, six hydrogen atoms, thirteen oxygen atoms and four zinc atoms was extracted from the structure. Since, adsorption primarily occur on the metal core only, the metal core was taken for calculation. This saves our computational time.

The primary goal is to evaluate the connection between hydrogen uptake in MOF-5 and its energy change. In order to understand the hydrogen storage by MOF-5 and to determine its hydrogen storage capacity, we calculated the binding energy per hydrogen atom in the core and HOMO-LUMO gap using the DFT method.

Thus, the binding energy was calculated as:

$$B.E = E(X) + nE(H2) - E(Y) \tag{1}$$

Here n denotes the total number of hydrogen molecules adsorb in MOF-5 cluster. E(X) and E(Y) are the ground state energies of the bare MOF-5 cluster and the MOF-5 cluster with hydrogen.

Also, HOMO-LUMO gap is calculated as:

$$E(HOMO - LUMO) = E(LUMO) - E(HOMO) \tag{2}$$

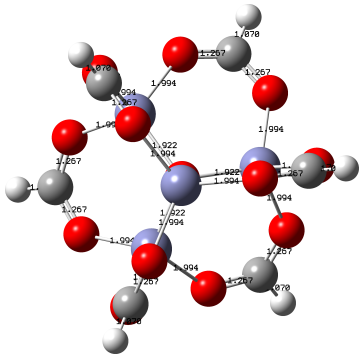

Figure 2: Bare MOF-5 core.

III. Results and Discussion

The energy of bare metal core of MOF-5 having six carbon atom, six hydrogen atom , thirteen oxygen and four zinc atom was calculated. The structure was optimized in B3LYP with basis sets LANL2DZ to calculate electronic properties i.e ground state energy, HOMO-LUMO gap. The ground state energy of bare MOF-5 metal core obtained after optimization in LanL2DZ basis set was -40081.93 meV (-1472.98 Hartree) and HOMO-LUMO gap was 26 meV. Optimization was performed after adsorption of one hydrogen molecule near one of a metals atom of metal core to compute ground state energy, HOMO LUMO Gap and binding energy per hydrogen molecules in core. Also the ground state energy of hydrogen has been computed and its value was found to be -31.95 meV (-1.17 Hartree).

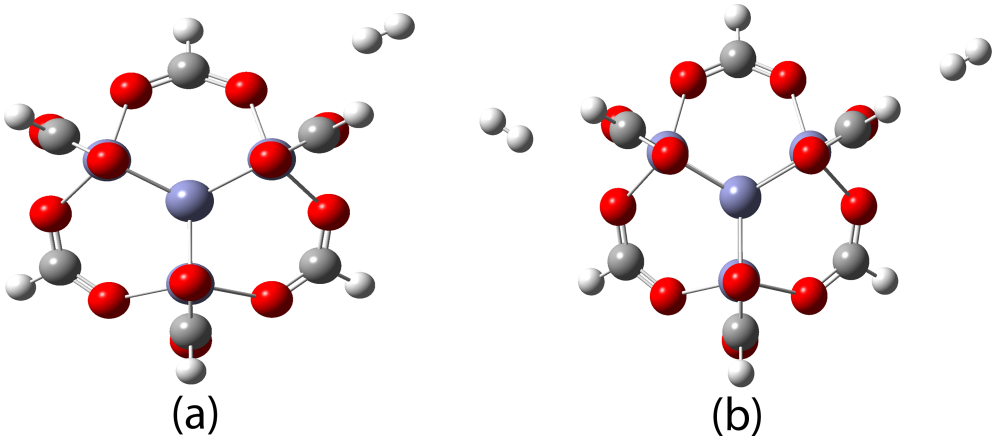

Figure 3: MOF-5 with hydrogen molecules (a) One (b) Two

Further, calculations and analysis were done for the MOF-5 core with another hydrogen molecule adsorbed near another metal of the core and binding energy and HOMO LUMO gap were computed and the process was repeated for all four metal atom each adsorbing one hydrogen molecule at a time. And similar computational work have been done for all these molecules.

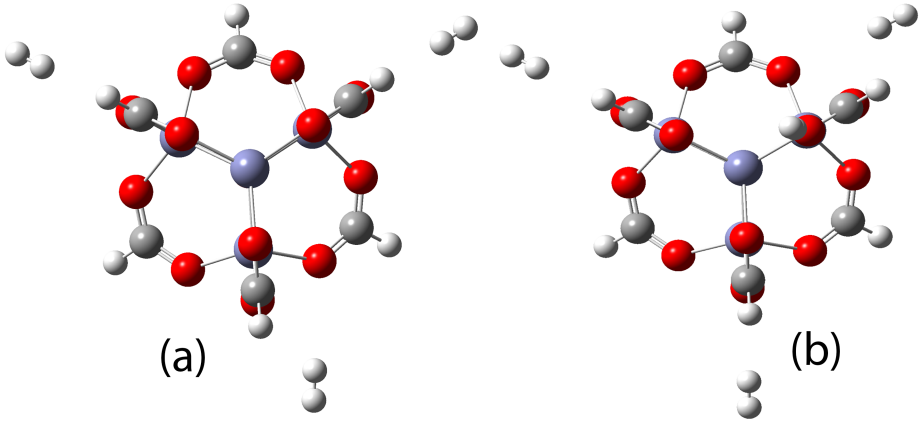

Figure 4: MOF-5 with hydrogen molecules (a) Three (b) Four

Binding energy per atom

The first column of the Table 1 shows the quantity of hydrogen molecules that adsorb in the metal core of MOF-5 while the second column shows the energy of the core of MOF-5 relative to the number of hydrogen molecules. And the binding energy of the MOF-5 core per hydrogen molecule is displayed in the third column. As seen in the above table,binding energy per atom marginally reduces as the number of molecules increases to two. However, on adding another molecule it rises. Further, it lowers again when we adsorb four molecules. The

value of binding energy per hydrogen atom present inside cluster keeps oscillating in range 25-27 meV .

Table 1: Calculated binding energy per atom values

No. of hydrogen adsorb	Energy of MOF-5 core with hydrogen (10^{-3} eV)	Binding energy per hydrogen (10^{-3} eV)
1	-40.11	26.67
2	-40.15	25.98
3	-40.18	26.81
4	-40.21	26.41

Again, as per our knowledge, binding energy of physisorption is about 10–300 meV and non-localized. Chemisorption usually forms bonding with energy of 1–10 eV and localized. From the table, we can visualize that the binding energy per hydrogen molecule fulfills the criteria and it suggests that adsorption of hydrogen molecule in metal core of MOF-5 is physiorption. It is caused by the intermolecular force that exists between adsorbates and adsorbents i.e Van der Waals force . Since physisorption is caused by intermolecular forces, the binding force is weak with low adsorption heat, and the rate of adsorption and desorption is fast. Also, it has been observed that the hydrogen molecules in the core possess slightly negative charge however, metal core possess slightly positive charge and the whole structure is neutral.

HOMO LUMO gap

The highest molecular orbital (HOMO) and lowest unoccupied orbit (LUMO) gap gives measure of their enegy state values also called “Band gap”. We have calculate the HOMO LUMO gap of metal core with and without hydrogen by optimization, using functional B3LYP with suitable basis set LanL2DZ. Its value for a bare metal core is calculated as 7.19 eV. Table 2 shows the HOMO LUMO gap of the MOF-5 core with a respective number of hydrogen molecules.

Table 2: Values of HOMO-LUMO gap

No of Hydrogen adsorb	HOMO-LUMO Gap(eV)
1	7.48
2	7.49
3	7.49
4	7.49

From the Table 2, the first row represent the number of hydrogen molecule adsorbed in metal core of MOF-5 and the second column represent the HOMO LUMO gap of core with hydrogen molecules store in it. We can easily visualize from the table that the value of HOMO LUMO gap increases on adding molecule inside core and it

has not changed on adding one, two,three or four molecule molecules. Increase in HOMO-LUMO gap on adding hydrogen to the core suggest that the MOF-5 likes hydrogen i.e. it becomes more stable after adsorbing hydrogen molecules.

IV. Conclusions

Different electronic properties of MOF-5 core has been studied along with the hydrogen molecule stored in it. Also, the detailed analysis and comparison for stability and geometry was performed. It suggests that, adsorption of hydrogen in MOF metal core is physisorption and hydrogen molecule is held in core by a weak Van der Waals force. It lead to the conclusion that the binding force of hydrogen molecule in the MOF-5 metal core is weak with less adsorption heat, which further suggests that the rate of adsorption and desorption of hydrogen in MOF core is fast. Morever, from the calculation of HOMO-LUMO gap; the upgrade in the value of HOMO-LUMO gap on adding one molecule of hydrogen and its value being constant for two, three and four molecules lead us to conclude that MOF-5 is fond of hydrogen. Furthermore, computations clearly indicates that MOF-5 core has room for at least four hydrogen molecules.

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