Hydrogen adsorption in Metal-Organic Frameworks Cu-BTC and Fe-BTC: A comparative theoretical study.

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Abstract. In order to obtain a hydrogen storage system that is cost-effective, safe and energy-viable, in this work we studied the adsorption process of different sites and configurations of the hydrogen molecule in both MOF HKUST-1 and FeBTC structure. For the computational study was used the Ab initio simulation package from Vienna (VASP) with the GGA PBE functional in an SBU of 672 atoms. The exposed metal sites were found to be the best interaction site for the hydrogen molecule. In this work showed adsorption energy of -0.114 eV and -0.93 eV for HKUST-1 and FeBTC, respectively. This work also evidences the modifications of the atomic positions when the hydrogen molecule interacts with the MOF and the network energy.

Keywords: VASP, MOF, adsorption, hydrogen

1. Introduction
The pollution caused by the continuous energy demands makes hydrogen an attractive alternative energy vector, especially if it is produced from renewable resources. However, besides the difficulties related to its production, high-capacity storage is still to be developed. Hydrogen can be stored in containers of compressed or liquefied H₂, in metal hydrides, or by gas-on-solid adsorption. Gas-on-solid adsorption is an inherently safe and potentially high energy density hydrogen storage method that could be more energy efficient than chemical or metal hydrides and compressed gas storage. Great efforts have been made to store hydrogen in solid materials¹ -³. However, the D.O.E. indicated that energy density goals for vehicular hydrogen storage call for systems capable of storing hydrogen at 6.5 wt % H₂ and 62 kg H₂/m³. So that, such compounds to be suitable for applications, must have high adsorption capacity, good reversibility, fast reactivity, and sustainability. In solid materials, the hydrogen storage may involve molecular hydrogen binding through weak Van der Waals forces (physisorption) or the hydrogen molecule is dissociated, and H atoms form chemical bonds with the solid (chemisorption).
Metal-organic frameworks (MOFs) have become a field important of research and a promising candidate as hydrogen storage materials due to their exceptionally high porosity and surface area, uniform but tuneable pore size and well-defined hydrogen occupation sites. They have received great attention as hydrogen storage materials since after the pioneer work of Yaghi and co-workers in 2003 that reported hydrogen adsorption on porous MOFs. For example, MOF-5 with large cubic cavities, adsorbs up to 4.7 wt % under 60 bar at 77 K.

Several research groups have performed calculations using DFT simulations in VASP (Vienna ab initio simulation package). With this method has been possible to conclude that the most favourable interaction sites for MOFs are exposed metal sites, unlike the organic part. Dixit and collaborators have demonstrated that the preferential adsorption sites in the MOF-5 determinated DFT, with MP2/cc-pVTZ and VASP can’t reproduce the weak interactions since this depends on electronic correlations.

Computational simulations using MP2/QZVPP were able to demonstrate for different types of IRMOF with the same organic ligand (BDC) and metal coordination and identical metallic cluster shape but different type of metal, finding that substitution of Zn metal sites, Mg made the hydrogen bonding energy stronger. And in the other hand, Chen et al. investigated the adsorption of methane in the HKUST-1, this research group was able to identify the sites of greatest interaction (metal sites exposed), simulate the adsorption capacity and obtain adsorption systems of this gas. They worked with the methods DFT / ab initio, DFT / CC and VASP and conclude that ab initio is not capable of predicting the adsorption isotherms. Therefore, they used GCMC to obtain a good result of it leads them to discover that the classical force fields are not able to describe the interactions in this material.

It has been shown that the fundamental electronic state of the SBU isolated from the HKUST-1 is a singlet state (anti-ferromagnetic), which can’t be described by a Slater determinant and which, consequently, is not accessible to DFT Kohn-Sham, instead, the triplet with energy very close describes correctly the structure and electronic density of the system, and also adsorption properties according to experiment.

It has been well demonstrated that the GGA functionals don’t have good interactions in the dispersions; therefore, it is necessary to complement it with modifications that allow having a better approximation to the models. Therefore, was shown that DFT / CC theory predicts very good the interaction of the water molecules in the metallic cluster of HKUST-1 with respect to the theoretical reference and other functional models, therefore, this model could also be well used to describe force fields for classical simulations. Grajciar, and coworkers studied the interchange-correlation functions to describe the process of adsorption of different gases in HKUST-1. After obtaining a very good approximation with the B2PLYP-D model, the results with PBE-D2 and PBE-D3 are reasonably good; also, they concluded that the accuracy method is not transferable to other systems. Therefore, the most practical and accurate approach is to find a suitable semi-local functional GGA and add the dispersion correction term. In such a way that the most accurate results can be obtained with DFT / CC because it tries to correct the DFT error including the dispersion.

DFT allows to determinate electronic structures and dynamic properties in HKUST-1, starting from DFT and B3LYP, added by means of DFT-GGA calculations. With these techniques, Lukose et al. obtained the distances of the CO bonds (1.42 and 1.22 Å for the single and double bond, respectively), typical carbon C=C with sp² hybridization (1.46 Å), verified the growth of the light smear cell by the presence unit from 27.283 to 27.323 Å. They also found that the adsorption energies of water and CO in the metal are 40 and 16.5 kJ / mol, respectively.
The procedures to determine the way in which the hydrogen molecule is adsorbed in the MOF using DFT in VASP, flat wave models GGA-PW91 and LDA have shown that one of the possibilities of optimal interaction is in the SBU perpendicular to the position of the copper atoms at a distance of approximately 2.47 Å and with energies of 0.33 eV (in excellent agreement with experimental results).

The FeBTC is a MOF very little studied experimentally, and no theoretical work has been reported so far. In this work, we will model its structure and emphasize one strategy for understanding through theoretical calculations using VASP computational package. Hydrogen storage performance of two different metal–organic frameworks with the same organic linker, but distinct metallic cluster.

2. Method and computational details

The structure of HKUST-1 was obtained from the experimental data of PXDR²⁰, the structure of FeBTC was obtained from the structure of HKUST-1 only changing the Cu atoms for Fe atoms. In both MOFs the water molecules were removed and it was optimized structurally and energetically with the VASP methodology using the PBE functional with different functional exchange correlations (PBE, PBE-D3, PBEsol) which predicts the structures in equilibrium very in accordance with the experimental ones and the most precise ones available at present, in specific PBEsol in addition to PBE-D2 and PBE-D3²¹,²²,²³.

2.1. Construction of the unit cell

With the help of the Molecular Prosersing Package Software (MAPS), once obtained the experimental atomic positions of the crystal, the water molecules were removed, obtaining thus a cubic structure type sodalite of 96 H atoms, 192 O atoms, 48 metal atoms (Fe for FeBTC and Cu for HKUST-1) and 288 C atoms for a total of 624 atoms like the Figure 1, with 3 functional PBE, PBEsol and PBE D3.

![Figure 1 Model for the unit cell for the HKUST-1 and FeBTC](image)

We worked with two different configurations to make a detailed study of the structure in the MOF cluster in interaction with the hydrogen molecules (Fig 2).
2.2. Computational details

The configuration of the spin was taken as open-singlet layer (anti-ferromagnetic state) for Cu (II) (3d⁹) the same case for Fe, although it could also be triplet (ferromagnetic) and closed-layer singlet. A sampling point-k of the Brillouin area was used for each of the frameworks, which is sufficient considering its large dimensions in real space. A flat wave cutoff point was found at 300 and 400 eV.

The cells were optimized using four steps;

I. Modify the positions of the atoms without to changing the size of the cell using a low calculation level with low cutoff of 300 eV and low precision.

II. Refinement of the first step with normal precision and cutoff of 400 eV.

III. Modify the network parameters without changing the atomic positions with a cutoff of 300 eV and normal precision.

IV. Optimize the atomic positions without modifying the network parameter (step II).

Once the empty cells were optimized, the hydrogen molecules were placed. Two types of sites were tested, one of them with two configurations; interaction of metallic ion and hydrogen molecule parallel (II) and perpendicular (T) to the surface (Figure 3). After finding the most stable site, different amounts of hydrogen molecules were placed (1, 2, 4, 12, 16, 24, 48 atoms)
Figure 3 Different sites and orientations of the hydrogen molecule.

The adsorption energy ($E_{\text{ads}}$) was calculated with the following equation:

$$E_{\text{ads}} = \frac{[E_{\text{MOF-H2}} - (E_{\text{MOF}} + nE_{\text{H2}})]}{n}$$

Where: $E_{\text{MOF-H2}}$, $E_{\text{MOF}}$, and $E_{\text{H2}}$ are the energy of the MOF and hydrogen system, the empty MOF system energy and hydrogen energy respectively, and $n$ is the number of hydrogen molecules adsorbed.

3. Results and Discussion

Table 1 Network parameter and system energy results for the HKUST-1 and the FeBTC optimized with the 3 functionals

| METHOD | $A=B=C_{\text{HKUST}}$ (Å) | $E_{\text{HKUST}}$ (EV) | $A=B=C_{\text{FeBTC}}$ (Å) | $E_{\text{FeBTC}}$ (EV) | $A=B=\Gamma$ (°) |
|--------|-----------------------------|-------------------------|-----------------------------|------------------------|------------------|
| PBE    | 26.3800                     | -4375.35                | 26.32932                    | -4639.35              | 90               |
| PBE-D3 | 26.3726                     | -4396.58                | 26.37817                    | -4660.19              | 90               |
| PBEsol | 26.3042                     | -4558.26                | 26.32932                    | -4834.83              | 90               |

The results of optimization of the HKUST-1 and Fe-BTC system show that the PBEsol method (table 1) describes best the dimensions of the unit cell (with the most favourable energy. For the case of the HKUST-1 (26.3046 Å$^2$) the results obtained are according to the literature.

Table 2 Energy of the MOF network with the adsorption of a hydrogen molecule in its two configurations

| CONFIGURATION | $E_{\text{H2-HKUST-1}}$ (EV) | $E_{\text{H2-FeBTC}}$ (EV) |
|---------------|-------------------------------|-----------------------------|
| T             | -4403.32                      | -4667.36                    |
| II            | -4382.46                      | -4667.04                    |

We can see in Table 2 how the configuration T) is more stable than the II), consistent with the values found in the literature for the HKUST-1. The values are much more evident for the HKUST-1. Although the FeBTC presents the same results than that HKUST-1, it has very similar values, which could indicate that the hydrogen molecule could be accommodated in any configuration for FeBTC.

To try to obtain a value closer to the real one, it was decided to make the unit cell interact with a greater quantity of hydrogen molecules, to observe how the characteristics of the unit cell vary with respect to the number of aggregated molecules. Table 4 shows H$_2$-MOF distance and adsorption energies for both MOFs. Is possible observed how the energy of the system begins to decrease as expected, because when adding atoms, we add electrons and therefore this energy has to increase in negative numbers.
On the other hand, the growth of the network parameter has reference to the ability of the MOF to expand and contract its cavities and thus adjust to a minimum energy in the interaction with other structures or molecules within its pores, results that are consistent with Peterson’s experimental reports in his neutron diffraction study.\textsuperscript{26}

The calculations of the adsorption energies for different amounts of molecules to show a more real information of a spontaneous adsorption process. We can observe how the values for 4 hydrogen molecules onwards start to change from sign to negative (endothermic process), when reaching half of the occupied metal sites exposed the energy starts to be constant (~ 0.114 eV for the HKUST-1) much more approximate to that obtained with a molecule and similar to what is reported in the literature for the HKUST-1.\textsuperscript{27}

On the other hand, we can observe that the value -0.114 eV for the D3 method, although it estimates the real value of the experimental reports, could be due to an ideal value considering that the total exclusion of the water molecules was achieved (the overestimation can due to the fact that part of the metal sites are occupied by other water molecules or synthetic solvents in the experimental calculations) is a better approach than the rest of the functions, therefore, we can affirm that PBE-D3 reproduces with greater precision the energy values of adsorption in HKUST-1.

\textbf{Table 3} Energy of the MOF network with the adsorption of different number of hydrogen molecules in perpendicular configurations.

| METHOD   | $A_{\text{H}_2\text{-HKUST-1}}$ (Å) | $E_{\text{H}_2\text{-HKUST-1}}$ (EV) | $A_{\text{H}_2\text{-FEBTC}}$ (Å) | $E_{\text{H}_2\text{-FEBTC}}$ (EV) |
|----------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| H$_2$-PBE-D3 | 26.3746                           | -4403.32                          | 26.3553                           | -4673.85                          |
| 2H$_2$-PBE-D3 | 26.3732                           | -4410.04                          | 26.3534                           | -4683.05                          |
| 4H$_2$-PBE-D3 | 26.3721                           | -4423.87                          | 26.3574                           | -4714.96                          |
| 12H$_2$-PBE-D3 | 26.382                            | -4478.99                          | 26.3581                           | -4742.37                          |
| 24H$_2$-PBE-D3 | 26.3779                           | -4561.56                          | 26.3831                           | -4787.87                          |
| 36H$_2$-PBE-D3 | 26.3801                           | -4644.02                          | 26.3831                           | -4870.14                          |
| 48H$_2$-PBE-D3 | 26.3831                           | -4726.39                          | 26.3637                           | -4989.12                          |
An important effect that occurs in the SBU structure of the HKUST-1 is the modification of the atomic positions when they are free, when they have one and when they have two hydrogen molecules. The Copper-Copper Ions begin to move away when they interact at one end with a hydrogen molecule and even more when at the two ends the molecule is adsorbed (Fig 4). Analogously Cu-H₂ distances increase when one more molecule is incorporated on the same SBU in the other copper. This local effect can be seen globally in the parameters of the unit cell of HKUST-1, and the variation between each will depend on whether the two ends of the SBU are occupied, one end or none.

Although a better adsorption value is obtained for HKUST-1 than FeBTC for in interaction with the metal cluster, in experimental terms HKUST-1 has a higher adsorption capacity (practically double), this can be explained by observing the physical advantages of HKUST-1, such as: greater porosity, specific area of more than double and pore size more akin to the kinetic diameter of the hydrogen molecule 28.

4. Conclusion

Through the VASP parcel, theoretical structures were obtained for Fe-BTC and HKUST-1 that agrees with those reported in the literature.

Since the functional GGA PBE-D3 contemplates the dispersion of the atoms, this yields values of conformational energy for the MOFs after the four steps of the protocol is a good approximation, -4660.1862 eV for the FeBTC which is lower compared to the HKUS-1 (Cu-BTC) whose energy value is -4396.5876 eV and with respect to the network parameter (26.38 Å), that of the Fe-BTC MOF (26.36 Å) is slightly higher.

It was determined that the optimal H₂ adsorption site is in the metal cluster so that the diatomic molecule is placed perpendicular (T) to the metal atoms of the metal cluster, and that a better approximation of the adsorption energy takes place when saturating the exposed metal sites of the MOF.
It was observed as the distances between the ions and between the copper ion molecules, this refers to the capacity that the MOF has to expand and contract its cavities, the data of the adsorption energy found with the PBE-D3 method are very close to that reported in the literature (with other types of methods and is close to the experimentally reported in specific when you have half of the metal sites occupied in the T configuration), this could give us information on the degree of hydration of the MOF.

5. References

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