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## Understanding Hydrogen Adsorption in MIL-47-M (M = V and Fe) through Density Functional Theory

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The present paper aims to investigate the role of open metal site metal-organic frameworks (MOFs) on hydrogen adsorptivity using periodic boundary condition (PBC) density functional theory (DFT). Hence, MIL-47-M (M = V and Fe) were selected and one hydrogen molecule adsorptivity was calculated in different orientations on them. Four different chemical sites were identified in every cluster section of these MOFs, and molecular hydrogen adsorption was studied in these sites. In these MOFs, V has fewer electrons than Fe in its valence layer. Results demonstrated that when dihedral angle of M-O-H-H is  $0^\circ$ , the binding energy of hydrogen adsorption is higher than that in other orientations in both MILs (-26.16 and -19.73 kJ mol<sup>-1</sup> for V and Fe, respectively). In this orientation, hydrogen molecule has a head-to-head interaction with O in M-O-M. Also, hydrogen desorption in various orientations in MIL-Fe was found, and minimum distances between the hydrogen molecule and one atom of MILs were calculated in all the orientations. It was revealed that there are not significant differences in all orientations and the best adsorptivity condition is hydrogen molecule in a head-to-head orientation with O, (M-O-M), which is 2.419 and 2.338 Å for V and Fe, respectively. According to PBC-DFT results, hydrogen adsorption on MIL-V is energetically more stable than that on MIL-Fe. Findings indicate that MOFs with an open metal site are more proper candidates for hydrogen adsorptions.

**Keywords:** MOFs, Hydrogen molecule adsorption on MIL-47-M (M = V, Fe)

### INTRODUCTION

Hydrogen storage has been a target for a great deal of numerous ambient projects whose main goal is finding alternative renewable clean energy carriers [1-3]. In comparison with other fuels, such as diesel and petroleum, hydrogen fuel is lightweight, has the highest energy density, produces no pollutant compounds and is extremely friendly with the environment [4-6]. Various ways have been considered for hydrogen storage as of now [4-8]. Due to some characteristics of hydrogen such as being a volatile gas under normal conditions, multifarious investigations have been conducted to find the best materials with an

effective hydrogen storage capacity [9,10]. In particular, based on 2017 Department of Energy (DoE) objective-which determined 5.5 wt% (kg H<sub>2</sub>/kg) as gravimetric and 4.0 vol% (kg H<sub>2</sub>/L) as volumetric capacities [9] -to utilize such materials in transportation industry as fuel, it is necessary to find new materials, with sufficient surface area, light weight and suitable adsorption/desorption traits [9,11]. Metal-organic framework (MOF) compounds are attractive candidates for gas storage. MOFs have a well-defined crystalline structure with extended networks consisting of organic linkers and metal ions, as two basic elements [3,10, 12-15]. One of the advantages of using MOFs is that their structure related to chemical component can be tuned to achieve an effective internal surface area and pore volume. Moreover, their kinetic adsorption and desorption behavior

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are fast [10,13,15]. Over the last decade, due to the unique structure of MOFs, various experimental and theoretical attempts have been made to find new MOFs for hydrogen storage in ambient temperature and pressure because the range of temperature and pressure is an effective factor on hydrogen storage capacity.

In recent years, experimental studies have investigated the hydrogen storage capacity of some MOFs using different practical methods [16-20]. To enhance the capacity of hydrogen storage in MOFs, varied investigations have theoretically focused on microscopic and electronic structures, and have mainly examined metal ions and organic linkers with dispersive and repulsive interactions between gas guest molecules and atoms of framework in physisorption progress [1,13-15].

Numerous molecular modeling studies using density functional theory (DFT) methods and molecular simulations have been conducted on hydrogen adsorption capacity of MOFs. DFT and molecular simulations are well-established tools to explore sorption properties and are a means of obtaining details about structures and dynamics of MOFs, particularly when guest molecular gases exist [9,21,22].

In this paper, a systematic and efficient methodology is presented to explore how the open-metal sites (OMSs) can improve the hydrogen storage capacities of MOFs with the same organic linkers. Hence, in the present study, first, MIL-47(V) is selected, and then V is substituted with Fe. Subsequently, one hydrogen molecule adsorption in different orientations is calculated using DFT to investigate the metals' role on hydrogen adsorption in MIL-M (M = V and Fe). It should be noted that MIL-47(V) is  $V^{(IV)}(O)(BDC)$  [ $V^{(IV)}$  = vanadium (4+), and BDC is ligand = the benzene diacboxyle ( $O_2C-C_6H_4-CO_2$ )]. Also, in MIL-47(V), V has six-coordination bonds with O to form  $VO_6$ . Therefore, V is almost an OMS in terms of molecular orbitals (MOs). In comparison with V ( $[Ar]3d^34s^2$ ), Fe ( $[Ar]3d^64s^2$ ) has half-filled  $d$  orbitals and substitution of V with Fe, and creation of  $FeO_6$  with the same organic linker and same stereochemistry, can produce a theoretical MIL that makes comparison of the role of  $d$  orbitals in hydrogen adsorption possible. In this study, the adsorption energy and adsorption distances are investigated to clarify the role of open metal orbitals in hydrogen adsorption.

## Methodology

PBC-DFT was applied to perform structural optimization using Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA), which considers exchange-correlation functions [23]. DZP basis set was utilized to obtain reliable geometries with the SIESTA package [24,25]. The energy cutoff was set to 680 eV, and a  $3 \times 1 \times 2$  Monkhorst-Pack grid was used for  $k$ -point sampling of the Brillouin zone to obtain an optimum distance and energy between a hydrogen molecule and MILs. However, for all calculations, the basis set superposition error (BSSE) was corrected by means of the counterpoise method. The BSSE-corrected binding energies (BEs) of single hydrogen molecules obtained from 16 orientations (4 sites and 2 orientations for each metal) for MIL-47-M (M = V and Fe) are shown in Fig. 1A.

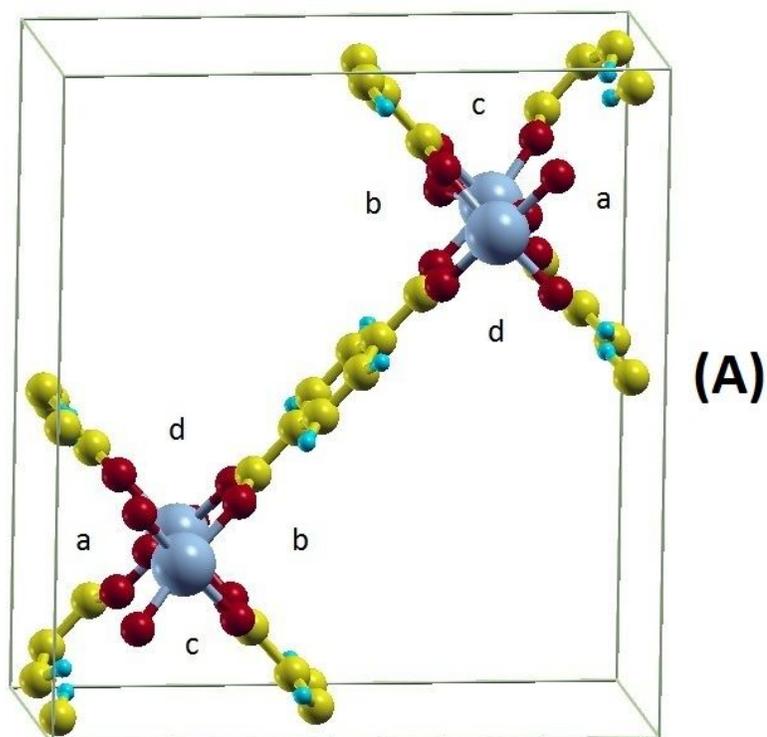
At the equilibrium geometries of a complex ( $H_2$ +MOF), the BEs per adsorbed molecule (here  $H_2$ ) were calculated according to

$$\Delta E = E_{H_2+MOF} - (E_{MOFx} + E_{H_2x}) \quad (1)$$

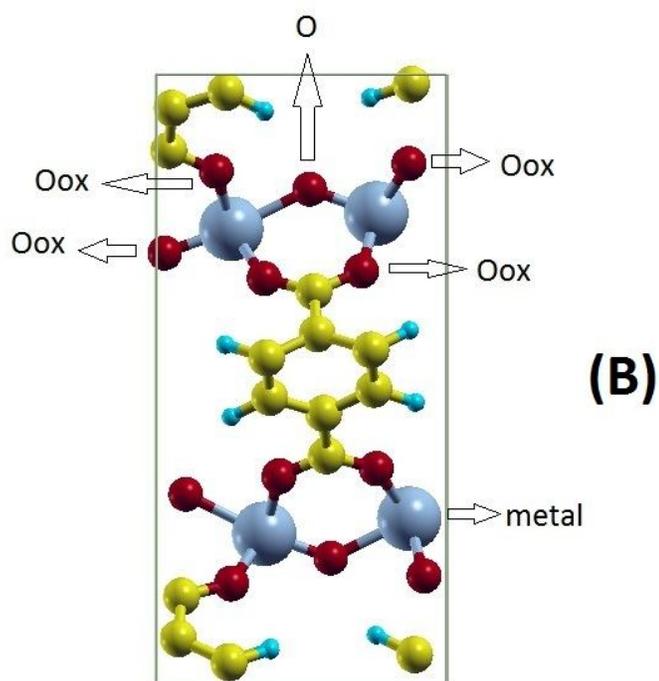
where  $\Delta E$ ,  $E_{H_2+MOF}$ ,  $E_{MOFx}$  and  $E_{H_2x}$  represent BE, energy of complex, energy of complex when MIL atoms are just ghost atoms and energy of complex when  $H_2$  atoms are ghosts, respectively.

## RESULTS AND DISCUSSION

This study investigates the impact of hydrogen adsorption in four sites of a MIL-M (M = V and Fe) with periodic simulation cell, while the hydrogen molecules were considered in two different orientations: 2i) when dihedral angle of M-O-H-H is  $0^\circ$  (where O is an oxygen between two metals: M-O-M, and  $H_2$  is in a head-to-head orientation with respect to O), and 2ii) when dihedral angle of O-M-H-H is  $0^\circ$  (where  $H_2$  is in a head-to-head orientation with respect to M). It is noteworthy that there are two different oxygens in the chemical structure of MILs. One of them is bonded between two metals (M-O-M) and the other is bonded between one metal and carbon of phthalic acid (M-O-C), which is named "Oox" here. Figure 1B shows oxygens of MILs.



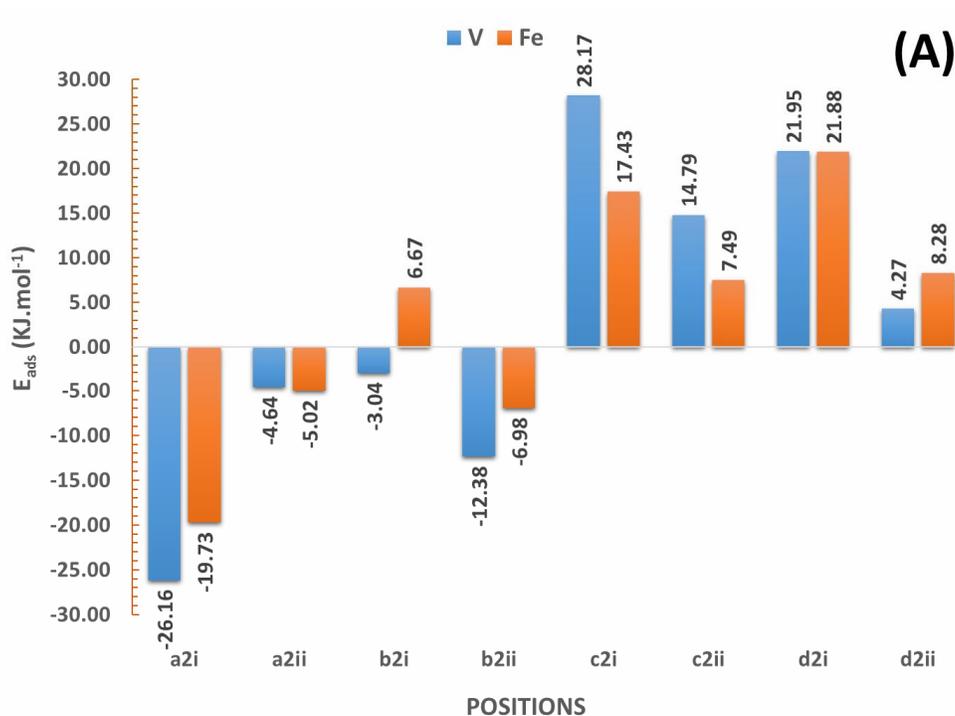
**Fig. 1A.** Four sites of each MIL series considered in this work.



**Fig. 1B.** Oxygens of MILs.

In all orientations, PBC-DFT optimization was carried out, while the initial distances between the nearest atom of MIL and one H from the hydrogen molecules were set at 2.5 Å. DFT runs were performed to obtain the optimized ground state and electronic structural properties including four sites of MIL and two orientations of hydrogen molecules corresponding to the two metals. After any DFT calculation, the orientation of hydrogen molecules would be significantly changed and optimal electronic structures would be achieved.

Figure 2 shows the BEs obtained for hydrogen molecules in MIL-M (M = V and Fe). The BEs reported here are considered with the BSSE correction for H<sub>2</sub>-MOF complexes in kJ mol<sup>-1</sup>. The values of BSSE vary between 4.16 to 7.54 kJ mol<sup>-1</sup> and they do not change the ranking of BEs shown in Fig. 2. It is illustrated that c2i, c2ii, d2i and d2ii sites are not proper hydrogen adsorption sites in MILs and their BEs are positive numerically. They are shown in gray color in Table 1. Table 1 presents the minimum distances between the hydrogen molecule and one atom of



**Fig. 2.** The binding energy of hydrogen adsorption in MILs.

**Table 1.** The Minimum Distances between One Hydrogen Molecule and Atoms of MILs Calculated from PBE-GGA Procedure. The Gray Color are Desorption Sites and the BEs have Positive Values There

	a2i	a2ii	b2i	b2ii	c2i	c2ii	d2i	d2ii
V	2.419 <sup>a</sup>	2.711	2.821	2.654	2.871	2.671	2.698	2.627
Fe	2.338	2.629	2.961	2.657	3.097	2.665	2.680	2.613

<sup>a</sup>The unit is Å.

MILs. Here, the hydrogen molecules are just distant from MILs and these sites are not adsorption sites.

In addition, in b2ii site, the BE for MIL-V is almost two times as large as the BE for MIL-Fe (Fig. 2), while the minimum distances of the hydrogen molecule in both MIL-

V and -Fe are identical. Furthermore, present results show that the hydrogen molecule with its one H-atom has interacted with three “Oox”s in almost equal distances, simultaneously, in both MIL-V and -Fe. Figure 3 displays interaction sites of hydrogen molecules in both MIL-V and

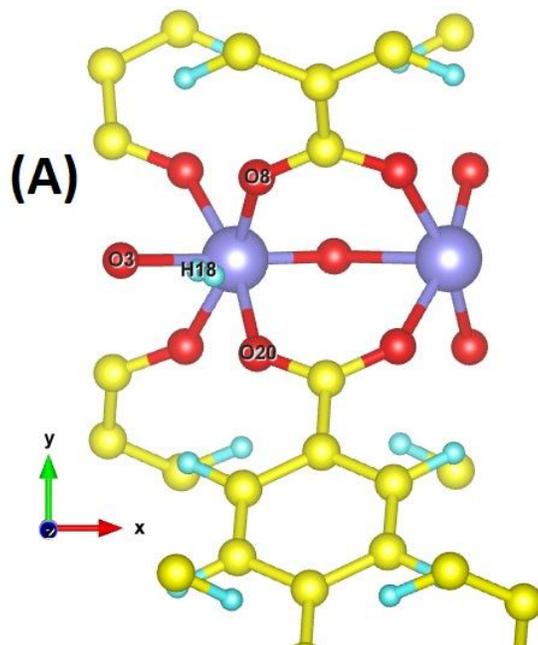


Fig. 3A. The hydrogen molecule interaction in MIL-V in b2ii site.

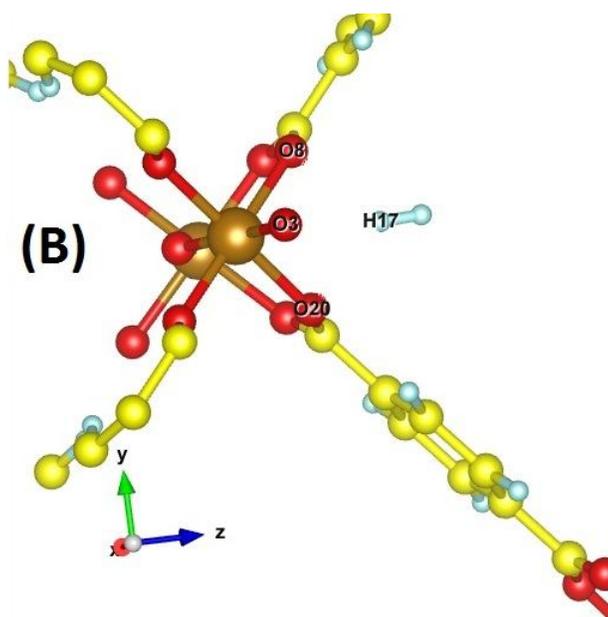
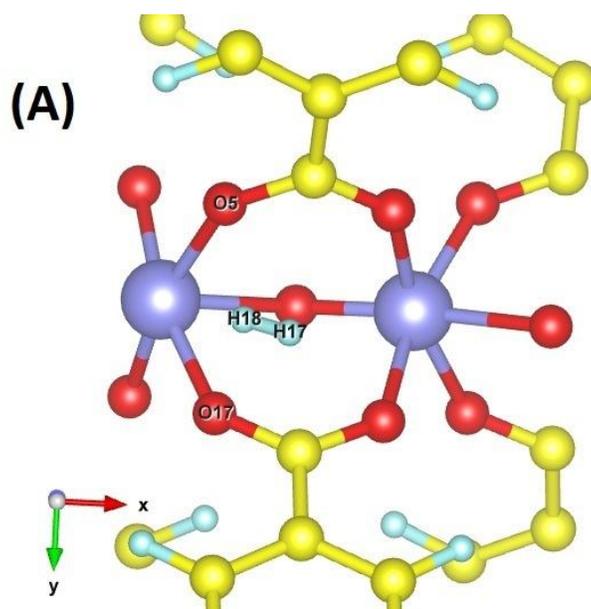


Fig. 3B. The hydrogen molecule interaction in MIL-Fe in b2ii site.

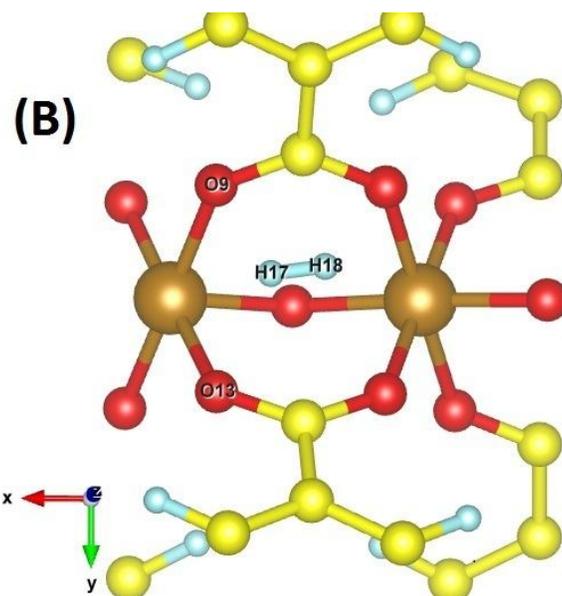
**Table 2.** The Minimum Distances between H and Atoms of MILs in b2ii Site

V	O3				O8				O20				Fe2			
	H18	2.738 <sup>a</sup>	2.654	2.759	3.492	H17	2.738 <sup>a</sup>	2.654	2.759	3.492	H18	2.738 <sup>a</sup>	2.654	2.759	3.492	
Fe	O3				O8				O20				V2			
	H17	2.867	2.657	2.744	3.307	H18	2.867	2.657	2.744	3.307	H17	2.867	2.657	2.744	3.307	

<sup>a</sup>The unit is Å.



**Fig. 4A.** The hydrogen molecule interaction in MIL-V in b2i site.

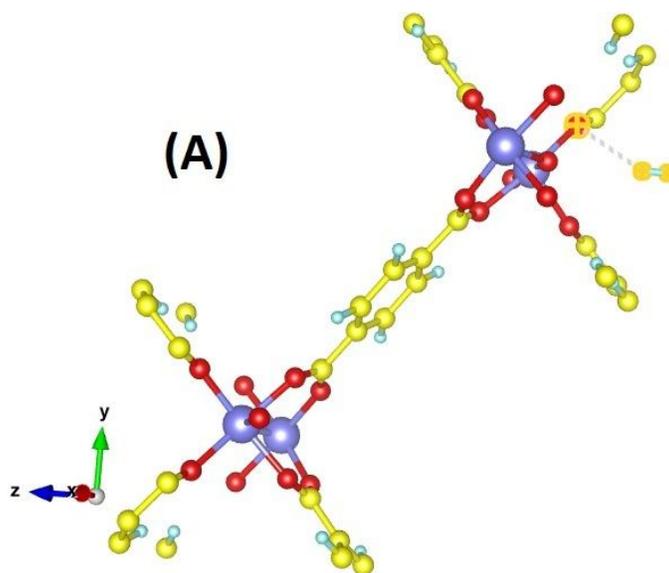


**Fig. 4B.** The hydrogen molecule interaction in MIL-Fe in b2i site.

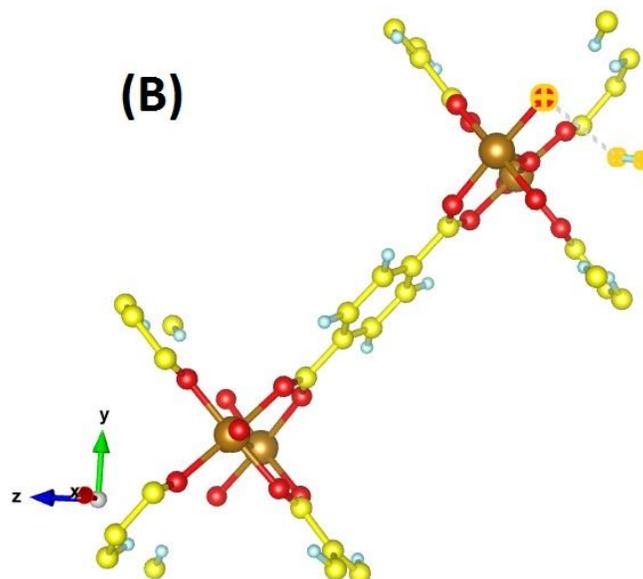
Fe in b2ii site. Also, Table 2 indicates the minimum distances of H from three “Oox”s of MILs. Hence, in both MILs, the minimum distances and the orientation of interactions are identical, though with different BEs. In fact, the hydrogen molecule with one of its H atoms senses three “Oox”s in both MILs.

Also, Fig. 2 indicates that in b2i site, the closest

distances between the hydrogen molecule and MIL atoms are 2.821 Å for MIL-V (between H18 and O5 [see Fig. 4]) and 2.961 Å for MIL-Fe (between H17 and O13 [see Fig. 4]). The corresponding BEs illustrate that for MIL-V, it is an adsorption case, while it is a desorption case for MIL-Fe. For more description, Fig. 4 plots the orientation of the hydrogen molecule in MIL-V and Fe. According to Fig.



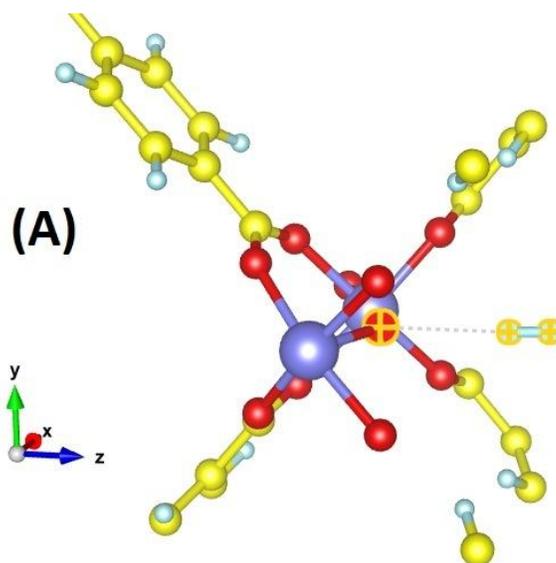
**Fig. 5A.** The hydrogen molecule interaction in MIL-V in a2ii site.



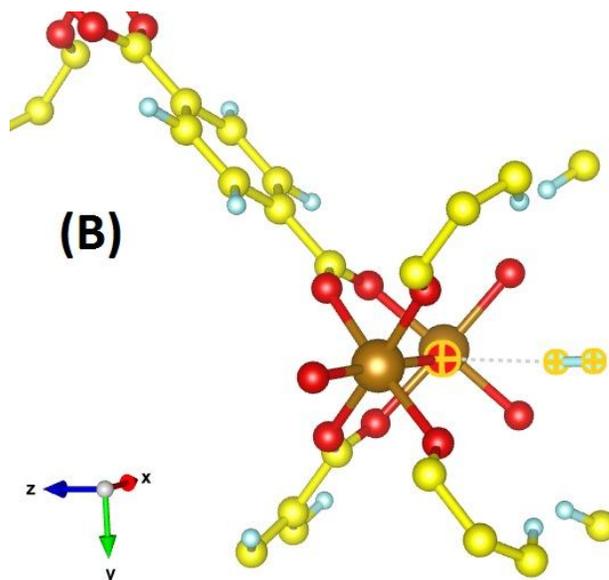
**Fig. 5B.** The hydrogen molecule interaction in MIL-Fe in a2ii site.

4, the hydrogen molecule in b2i site is in a head-to-head interaction with MIL-V atoms, while its orientation changes in MIL-Fe to horizontal without any orientation with atoms of MIL-Fe. In fact, the interactions of hydrogen with “Oox” (“Oox” = O5 in MIL-V) atom in MIL-V are angled at  $139.42^\circ$  ( $\angle H17-H18-O5$ ), while the angle is  $105.03^\circ$  ( $\angle H18-H17-O13$ ) in the case of MIL-Fe (“Oox” = O13 in

MIL-Fe). It should be noted that the larger angles (*i.e.*,  $\angle H-H-atom$  (*atom of MIL*)) resulted in better interactions; thus, the smaller ones in MIL-Fe caused the positive BE of hydrogen adsorption in MIL-Fe and desorption of hydrogen molecules. On the other hand, the hydrogen molecule was in an almost head-to-head orientation in MIL-V, which is energetically more stable.



**Fig. 6A.** The hydrogen molecule interaction in MIL-V in a2i site.



**Fig. 6B.** The hydrogen molecule interaction in MIL-Fe in a2i site.

This result emphasizes that the best orientation in the case of hydrogen adsorption in MILs (with the highest probability in all MOFs) takes place when the hydrogen molecule interacts in a head-to-head direction.

As seen in Fig. 2, the BE for both metals is approximately equal (the difference between the BEs in  $\text{kJ mol}^{-1}$  is 8.12%) in a2ii sites. As shown in Table 1, the minimum distance of the hydrogen molecule in both of them is 3.12% in angstrom unit, which is small and ignorable. Also, Fig. 5, clearly indicates that both orientations between hydrogen and MILs are the same, with angles of interaction being  $128.4^\circ$  and  $133.5^\circ$  for MIL-V and -Fe, respectively. Here, the angle of interaction of hydrogen in MIL-Fe is slightly larger than that of MIL-V, and it was expected that the BE related to MIL-Fe is higher than the BE related to MIL-V as displayed in Fig. 2.

According to Fig. 2, the site of a2i for both metals has the highest amount of energy ( $-26.16$  and  $-19.73 \text{ kJ mol}^{-1}$  for V and Fe, respectively). Based on Table 1, the minimum distances ( $2.419$  and  $2.338 \text{ \AA}$  for both metals) in a2i site, have just a 3.3% difference in angstrom unit and can be ignored. At this site, the hydrogen molecule tends to have a head-to-head interaction (the angles are  $174.4^\circ$  and  $175.0^\circ$  for MIL-V and Fe, respectively) with the central oxygen (O in M-O-M) in both MIL-V and -Fe (see Fig. 6).

Therefore, it can be concluded that some parameters such as the orientation of hydrogen, the larger angle, the minimum distances of interactions and the highest amount of energy play important role in hydrogen adsorption on MOFs, and on the other hand, a MOF including an open metal orbital in its cluster part, is more capable to adsorb hydrogen molecules.

## CONCLUSIONS

In this paper, the PBC-DFT is applied to investigate the role of open metal site MOFs on hydrogen adsorptivity. Therefore, MIL-47-M ( $M = \text{V}$  and  $\text{Fe}$ ) were chosen and one hydrogen molecule adsorption was computed in 8 orientations for each metal. It was found that there exist two sites in each site; the site near the metal and the other near oxygen. In selected MOFs, V has fewer electrons than Fe in its valence layer. The obtained results emphasize that the BEs of hydrogen adsorption, when the dihedral angle of M-

O-H-H is  $0^\circ$  (a2i site), is more than those in other orientations in both MILs, where BEs are  $-26.16$  and  $-19.73 \text{ kJ mol}^{-1}$  for V and Fe, respectively. Hence, the BEs of MIL-V are more than those in all orientations where hydrogen desorption occurs in different orientations in MIL-Fe. In a2i orientation, the hydrogen molecule has a head-to-head orientation with O (M-O-M). It is also shown that the best hydrogen adsorptivities take place in MIL-V more energetically stable than MIL-Fe, and this is while hydrogen has a head-to-head orientation with O (M-O-M). Moreover, it can be concluded that there are not significant differences between minimum distances of the hydrogen molecule in both MILs ( $2.419$  and  $2.338 \text{ \AA}$  for V and Fe, respectively). It was found that in MIL-V, the interaction angles of the hydrogen molecule are a little more than those of MIL-Fe. Consequently, MOFs with open metal site are suitable for hydrogen adsorption.

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