

HYDROGEN ADSORPTION PROPERTIES OF METAL-ORGANIC FRAMEWORKS WITHIN THE DENSITY-FUNCTIONAL BASED TIGHT-BINDING APPROACH

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Practical methods for hydrogen storage are still a prime challenge in the realization of an energy economy based on Hydrogen. Metal organic frameworks (MOFs) are crystalline ultra-porous materials with ability to trap and store voluminous amounts of gas molecules. MOFs represent an encouraging storage method relying on their enormous surface area. However, MOFs show reduced hydrogen uptake at room temperature due to low adsorption energy of hydrogen. To increase the adsorption uptake of MOFs at room temperature, the adsorption energy must be increased. In this contribution, materials exhibiting higher adsorption energy and enhanced hydrogen adsorption, namely MIL-53 (Al) and MOF-74, have been investigated using molecular dynamics (MD) simulation. MD simulations were performed within the density functional based tight binding method (DC-SCC-DFTB). Our results demonstrate that DC-SCC-DFTB method predicts structural parameters, adsorption sites, adsorption energies and diffusion factors with a very good accuracy, making this method a very powerful tool to investigate various types of MOF. Moreover, results show that the adsorption energy can be increased by incorporation of transition metals in MOF structures.

Keywords: Hydrogen storage, Metal Organic Frameworks, Molecular dynamics, DFTB, adsorption energy.

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1. Introduction

Hydrogen storage in metal organic framework materials (MOFs) attracts significant attention because these materials have enormous specific surface area, low density and a crystalline structure that can be tailored and chemically functionalized to maximize the adsorption uptake. MOFs are constructed from metal oxides interconnected by different organic linkers. Thousands of MOFs have been synthesized (only some of them are stable and porous), categorized and carefully studied over the last decade [1,2]. Some MOFs showed exceptional gas storage capacity and selectivity [3–5]. The essential issues for hydrogen adsorption in MOFs are both the strength of adsorption interaction (adsorption energy), and the number and surface of adsorption sites. The former determines the operation temperature and pressure, and the latter determines the storage capacity. The hydrogen adsorption energies on MOFs are ranging from 3 to 5 kJ/mol [6,7]. This small adsorption energy is sufficient for H₂ adsorption below 80K, but not at room temperature because an extremely high pressure is needed to make the adsorption possible [8]. To store the hydrogen reversibly at room temperature and moderate pressures, the

adsorption energy should be about 0.3 – 0.4 eV/molecule (30 – 40 kJ/mol), according to the estimations of Li *et al.* [9]. According to the estimations of another authors, the adsorption energy should be about 0.15 eV/molecule (15 kJ/mol) [10] according to Myers *et al.* and 20 kJ/mol according to Snurr *et al.* [11].

Several strategies have been proposed in order to enhance the adsorption energy of hydrogen such as incorporation of transition metals, fullerene impregnation and lithium doping [12,13]. Another method to improve the storage capacity is reducing the framework density. This requires investigating the MOFs formed by light metal ions such as Li^+ , Mg^{2+} , and Al^{3+} . One expects that the large polarizing power of Al^{3+} should give rise to relatively strong coordination bonds [14]. From structural point of view, a large number of different Al-based MOFs have been synthesized and studied [15–17]. Some compounds are highly porous and promising for gas storage, separation and adsorption applications [18,19]. The MIL-53 [20,21] are porous materials synthesized by the group of Férey, first reported to store significant amount of hydrogen at 77 K [22]. These structures are made up of chains of corner-sharing metal octahedral (Al^{3+} , Cr^{3+}) interconnected by benzene dicarboxylate (BDC) groups, forming 1D diamond-shaped channels and a porous solid with pores of 8.5 Å (see Fig. 1).

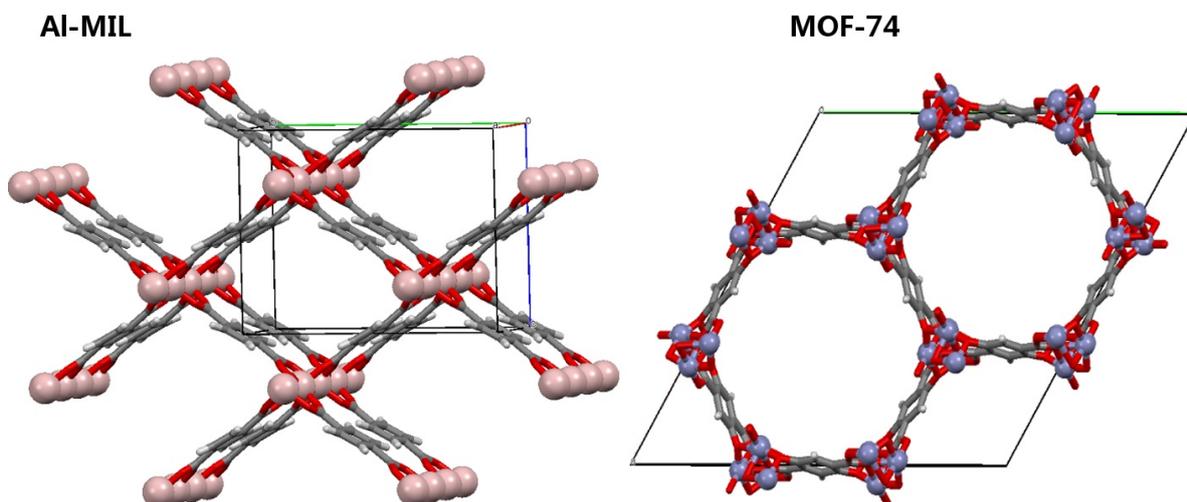


FIG. 1. Crystal structures of the MOFs studied in this work. (Zn, dark blue; O, red; C, gray; H, white; Al, pink). (For interpretation of the references to colour in this fig legend, the reader is referred to the web version of this article)

MOF-74 is constructed from rod-shaped secondary building units; the rod is constructed from 6-coordinated Zn^{2+} centers, where each Zn has three carboxyl and hydroxy groups to produce one-dimensional channels of section area $10.3 \times 5.5 \text{ \AA}^2$ (see Fig. 1). MOF-74 is especially interesting, because it shows the highest surface density for physisorbed hydrogen in framework structures [23], which leads to enhanced hydrogen capacity.

From a modeling point of view, hydrogen binding in MOFs has been extensively investigated in the last few years [24]. Most of studies focus on prediction of hydrogen storage properties of these compounds [25], and trying to optimize chemical structure, pore volume and surface area to enhance hydrogen uptake [26,27].

In this contribution, we report a comprehensive theoretical study comparing the H_2 adsorption in the MIL-53(Al) and MOF-74 materials. We performed molecular dynamics (DFTB MD) simulation on the full crystal structures with hydrogen molecules adsorbed in them. The adsorption sites and energies as well as the values for the hydrogen diffusion coefficients will be presented. The results are compared to experimental data in the literature.

2. Molecular dynamics simulation and calculations of H₂ binding energies

The pore surfaces of MOFs contain numerous distinct sites at which hydrogen might be adsorbed. To investigate the preferable sites for hydrogen adsorption, we performed MD simulations within the dispersion-corrected self-consistent density functional based tight binding method (DC-SCC-DFTB) [28–31], as implemented in the deMonNano program package [32]. DFTB is an approximate version of the DFT method that was later extended to account for the London dispersion energy. This technique showed exceptional performance and ability to study large biological and supramolecular systems [33, 34]. The DC-SCC-DFTB method was successfully used to study the structural, energetic, electronic, and mechanical properties of variety of MOF materials [35, 36]. Recently, DC-SCC-DFTB has been shown to describe the structural properties, formation energies and hydrogen adsorption sites of covalent organic frameworks (COFs) in rather good accuracy [37, 38].

Two sets of Slater-Koster parameters have been used: the standard SCC-DFTB parameter set optimized by Seifert *et al.* for MOF-74 [39], and for Al-MIL we have used materials science parameter set developed by Heine *et al.* [40].

Initially, the structures for Al-MIL and MOF-74 from X-ray diffraction data were optimized with the DC-SCC-DFTB method. In order to obtain the possible adsorption sites, up to 11 and 22 H₂ molecules (corresponding to 2.67 and 1.56 wt. %) were added randomly to the optimized Al-MIL and MOF-74 unit cells, respectively. First, the structures were equilibrated for 4 ps at 100 K. A 16 ps DFTB MD simulation was performed starting at temperatures of 100 K with a step size of 0.25 fs; the temperature was gradually decreased by simulated annealing down to 5 K. The DFTB MD trajectories were generated in the NVT ensemble using the Berendsen thermostat. Such procedure allows determination of the preferred adsorption sites in a rather unbiased manner, because the H₂ molecules were free to diffuse between the different sites, and by decreasing the temperature were first trapped in the strongest adsorption sites.

The H₂ binding energy at each of the revealed adsorption sites (EB) was calculated from the energy difference between the relaxed structure with adsorbed hydrogen and the same structure after specific hydrogen molecule was removed plus the free hydrogen molecule in the same but empty unit cell. i.e. The binding energy was calculated using:

$$EB = E(\text{MOF} + \text{H}_2) - E(\text{MOF}) - E(\text{H}_2). \quad (1)$$

The mean square displacements (MSDs) for the H₂ molecules were evaluated at 25 K, using the following equation where N corresponds to the number of H₂ molecules considered:

$$MSD(t) = \langle \Delta r_i^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N (r_i(t) - r_i(0))^2. \quad (2)$$

We note that MSDs present a reasonably linear profile after 2 ps simulation time and over a broad time domain. The self-diffusion coefficients (Ds) were then obtained by fitting the MSDs plots as a function of time in the region, 2 – 6 ps and assuming the well-known Einstein formula:

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{\langle \Delta r^2 \rangle}{t}, \quad (3)$$

where $\langle \Delta r^2 \rangle$ is the mean square displacement of the particles averaged on trajectories of duration t .

3. Results and discussion

The optimized structure of empty Al-MIL has a shape similar to that reported in the literature [21], the calculated lattice parameters: ($a = 6.76 \text{ \AA}$, $b = 16.91 \text{ \AA}$, $c = 12.59 \text{ \AA}$) are well comparable with those reported from experiment ($a = 6.6085 \text{ \AA}$, $b = 16.6750 \text{ \AA}$, $c = 12.8130 \text{ \AA}$) at 548 K [21]. The fact that the minimized structure at zero temperature is not exactly the same, but closely related to the experimental one is not surprising in light of the presence of thermal motion at 548 K.

The results of the DFTB MD simulation at $T = 25 \text{ K}$ for Al-MIL loaded with molecular hydrogen are shown in Fig. 2. The three sites with the largest adsorption energies are numbered 1 – 3 and listed in Table 1. Two of them with the highest adsorption energies (site 1 and 2) are near the AlO_6 clusters at the corners of the pore. Site 3 is located over to the benzene ring (the organic linker); site 3 has the lowest adsorption energy so it is the least preferred adsorption site for the hydrogen molecules. The average adsorption energy for 11 hydrogen molecules was found to be 6.35 kJ/mol, and this value was consistent with experimental results where the average heat of adsorption was found to be 5.6 kJ/mol [41]. The maximum total hydrogen uptake, i.e. when the three adsorption sites are fully occupied, was found to be 3.87 wt.%, which compared favorably with 3.8 and 3.1 wt.% measured at 77 K and 16 and 20 bar, respectively [22,41].

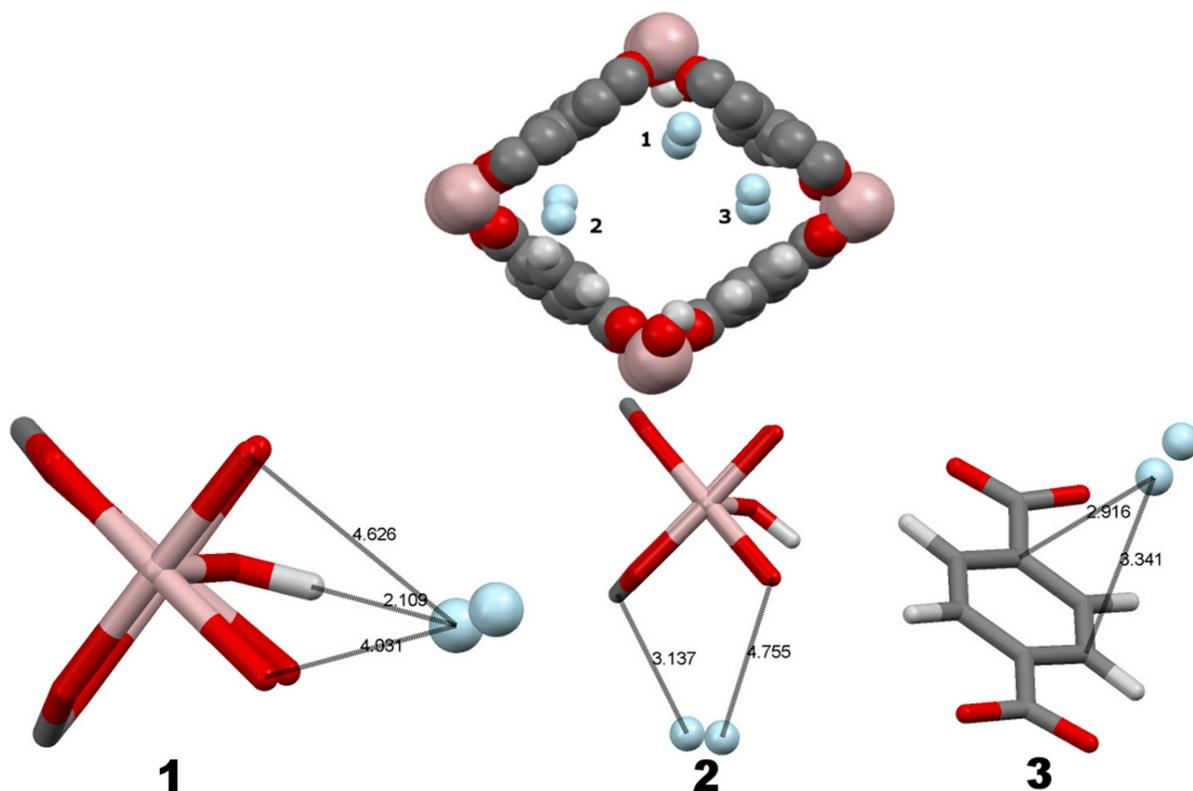


FIG. 2. The main three hydrogen adsorption sites in Al-MIL-53 obtained from DFTB MD simulations. White: hydrogen, dark gray: carbon, red: oxygen, pink: Aluminum. The Hydrogen molecule is plotted in light blue

The optimized structure of empty MOF-74 has a shape similar to that reported in the literature [23], the optimized ($a = 25.987 \text{ \AA}$, $b = 25.981 \text{ \AA}$, $c = 6.846 \text{ \AA}$) and the experimental ($a = b = 25.887 \text{ \AA}$, $c = 6.816 \text{ \AA}$) lattice parameters are in good agreement. The DFTB MD

TABLE 1. Adsorption energy per H₂ of different adsorption sites in MIL-53(Al) and MOF-74. Multiplicity indicates the number of available similar sites in the unit cell, the Max. wt.% indicates the maximum weight percentage reached when the site would be fully occupied.

Material	Adsorption site number	Adsorption energy (kJ/mol)	Multiplicity	Max. wt. %
Al-MIL-53	1	9.41	4	0.97
	2	5.88	4	0.97
	3	3.76	8	1.94
MOF-74	1	9.56	18	1.23
	2	6.13	18	1.23
	3	4.09	18	1.23

simulations of MOF-74 loaded with molecular hydrogen revealed three adsorption sites with the largest adsorption energies. The adsorption sites are presented in Fig. 3 and the corresponding adsorption energies are listed in Table 1. Site 1 is located directly above the Zn²⁺ ions with distance of ≈ 2.5 Å, site 2 is located above a triangle of oxygen atoms with distance of ≈ 3.1 Å, and site 3 is located vertically on the side of the benzene ring with a closest distance to the framework atoms of 2.7 Å.

The calculated adsorption sites are in very good agreement with the neutron diffraction results reported by Channing *et al.* [23], in which 4 adsorption sites were found. Three of them, with the highest adsorption energy are consistent with the calculated adsorption sites. The short distance between the unsaturated metal and H₂ molecules is not a surprising finding and has been observed in other framework structures, where the distance varied between 2.3 – 2.5 Å [42–44]. A recent theoretical calculation has also implicated such short distances [45]. This confirms that the DC-SCC-DFTB method used in this simulation is appropriate to investigate the adsorption of hydrogen in MOF materials. The inelastic neutron scattering (INS) experiments indicate that the H₂ adsorption energy for site 1 is ≈ 8.8 kJ/mol, for site 2 is ≈ 5 kJ/mol and it drops to ≈ 4 kJ/mol with increasing H₂ uptake. Such values are comparable to the calculated adsorption energy for the adsorption sites found from DFTB MD simulation (see Table 1).

The theoretical maximum total hydrogen uptakes, i.e. sites 1 – 3 are fully occupied, is found to be 3.69 wt.%, such value compares favorably with 3.6 wt.% achievable at $T \approx 30$ K and a very low pressure, i.e. with the complete population of the first three adsorption sites found experimentally [23]. Lower experimental H₂ adsorption capacities, ≈ 1.7 wt.% and ≈ 2.5 wt.% at 77 K and 1 and 30 bars respectively, have been reported in literature [45]. The higher maximum calculated capacity could be attributed to the fact that each site is assumed to be fully occupied, but actually, there may be steric hindrance from the different hydrogen molecules which may prevent all the sites from being occupied simultaneously. Another source of error may arise when one considers that the real material has nanoporous artifacts, while the DFTB MD simulations were carried out in under perfect crystal conditions, which can lead to a difference in hydrogen uptake.

Our theoretical calculations for the H₂ binding energies in MIL-53(Al) and MOF-74 demonstrate that such MOFs have at least one adsorption site, located next to the metal cluster with stronger H₂ binding energy than classical MOFs, due to the direct H₂-metal interaction.

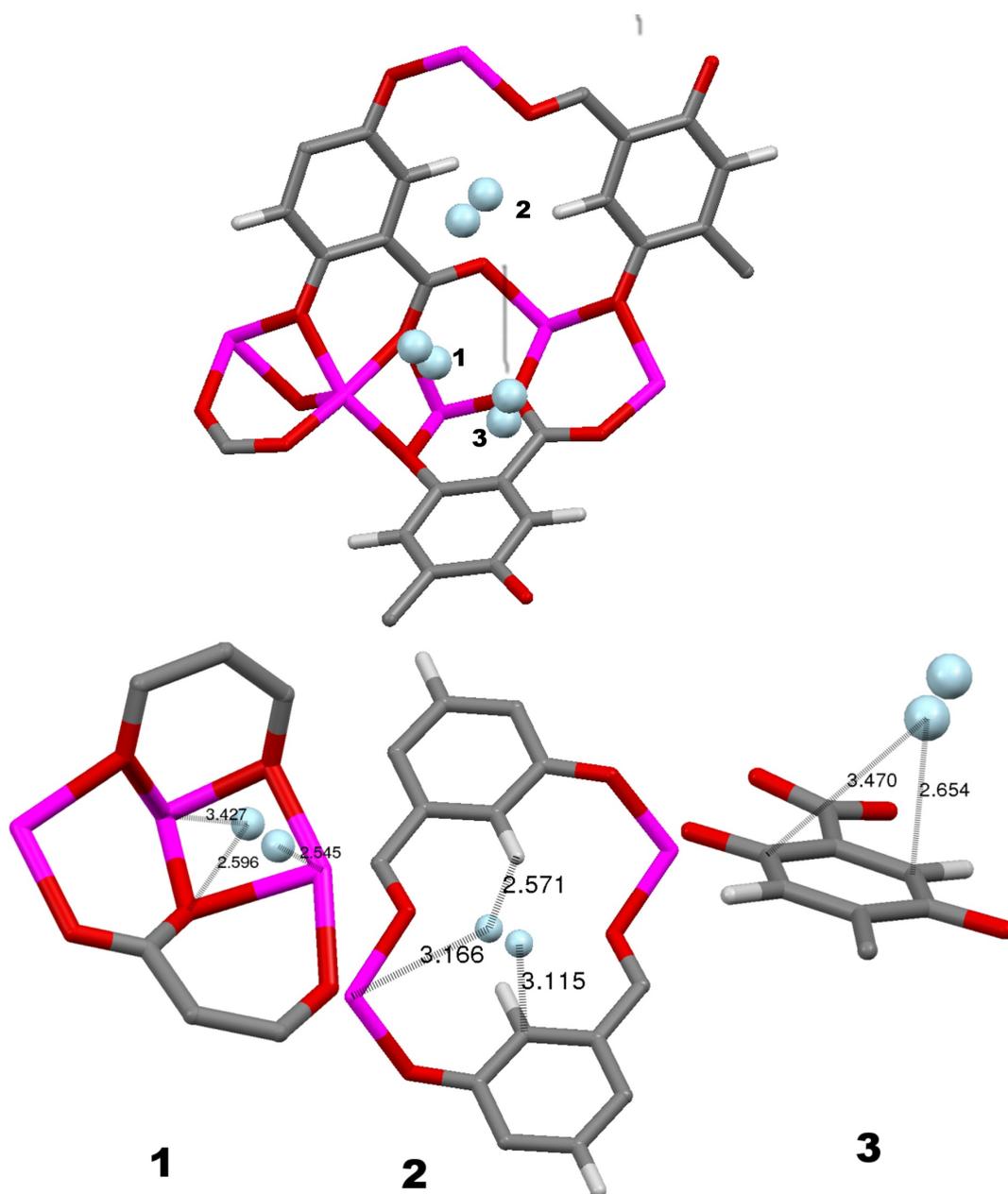


FIG. 3. The main three hydrogen adsorption sites in MOF-74 obtained from DFTB *metal clusters* simulations. The colours are like in Fig. 1.

From DFTB MD simulation at 25 K, the values of the diffusion coefficients can be obtained (Fig. 4). The simulation results for the self-diffusion coefficients of Al-MIL were found to be 4.36×10^{-10} m²/s. At 25 K, the values of the diffusion coefficients appear to be much smaller than those reported at 77 K for such MOF systems [46,47]. This indicates that at such a low temperature only a few H₂ molecules left the site in which they were adsorbed. Clearly, this will also depend on the loading of the sample with hydrogen. To compare our results with the other results in the literature, we have performed an extra 8 ps DFTB MD simulation for Al-MIL at 77 K. The diffusion coefficient at this temperature is calculated to be 5.2×10^{-9} m²/s. This value is also smaller than the values reported for other MOFs [46]. For instance, for Cr-MIL and MIL-47 loaded with 5 H₂ per unit cell the diffusion coefficient

is around 1.0×10^{-8} m²/s. This is due to the difference in the loading of the material with hydrogen, whereas in our simulations, the unit cell was loaded with 11 H₂ molecules. Apart from that, it appears that the order of magnitude of the diffusion coefficient is comparable to that found experimentally for hydrogen adsorbed onto nanostructured carbon, like nanotubes. For instance, at 38 K, a diffusion coefficient of 2.0×10^{-8} m²/s is reported [48]. However, the higher adsorption energy for MILs when compared to the nanocarbon does not limit the diffusion. Perhaps the reason for this is that the differences in adsorption energy between the different sites are not large, and the H₂ molecules can easily diffuse between the different sites in which they can be temporarily trapped.

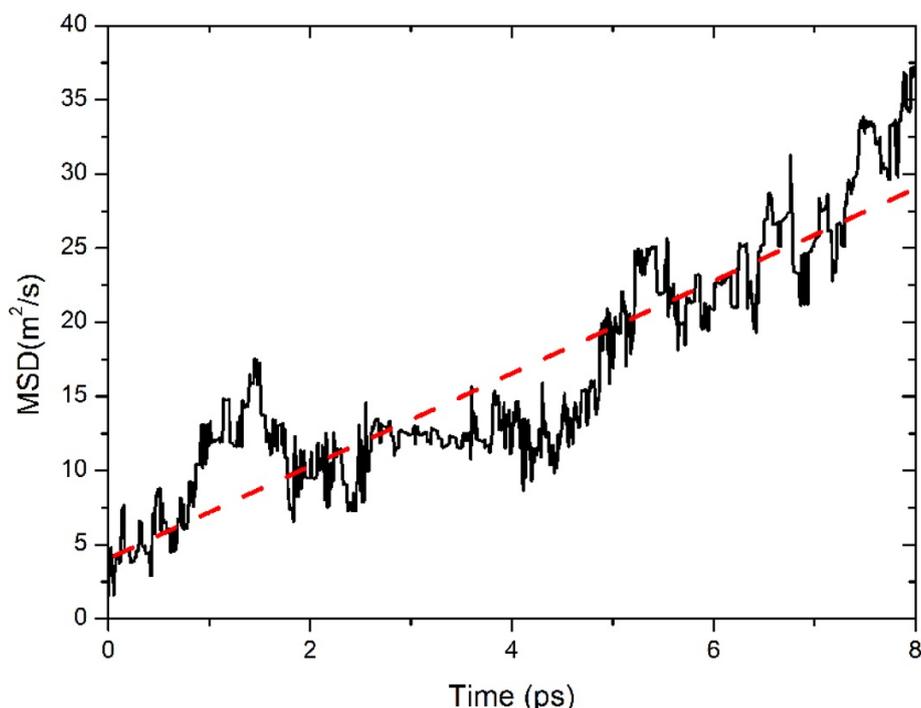


FIG. 4. Example of MSD fits of Al-MIL at 77 K. The simulated MSD curve is represented in thin black; the least square fits of the MSD curve are represented with thick dash red

4. Conclusion

Molecular dynamics (DFTB MD) simulations were used to investigate the hydrogen adsorption in MIL-53 (Al) and MOF-74. DFTB MD simulations were performed within the density functional based tight binding method (DC-SCC-DFTB). Our results demonstrate that DC-SCC-DFTB predicts structural parameters, adsorption sites, adsorption energies and diffusion factors with a very good accuracy, which makes this method a very powerful tool to investigate various types of MOFs. Moreover, the results show that the adsorption energy can be increased by the incorporation of transition metals into MOFs. However, further investigation is required to focus on the design of new MOFs with optimal metal coordination environment.

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