

Đánh giá khả năng hấp phụ khí H_2 và CO_2 trong MIL-88A-Fe bằng phương pháp mô phỏng Monte Carlo chính tắc lớn

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TÓM TẮT

Hai trong những vấn đề mang tính toàn cầu đó là tìm ra nguồn năng lượng mới, sạch thay thế cho nhiên liệu hóa thạch ngày càng cạn kiệt và khắc phục vấn đề ô nhiễm môi trường, biến đổi khí hậu ngày càng trầm trọng. Để góp phần khắc phục những vấn đề trên, trong những năm gần đây, lớp vật liệu khung hữu cơ kim loại được chú ý cho ứng dụng lưu trữ năng lượng như khí H_2 và bắt giữ khí thải như CO_2 dựa trên cơ chế hấp phụ. Trong lớp vật liệu khung hữu cơ kim loại, MIL-88A-Fe được đánh giá là rất bền trong môi trường ẩm và có tính giãn nở và tính xốp cao. Chính vì những lý do đó, chúng tôi quan tâm đánh giá khả năng lưu trữ khí H_2 và bắt giữ khí CO_2 của MIL-88A-Fe bằng phương pháp mô phỏng Monte Carlo chính tắc lớn ở nhiệt độ 77 K và 298 K với vùng áp suất dưới 100 bar. Kết quả cho thấy cách thông số hóa trường một phần bằng cách kết hợp tính điện tích riêng phần bằng phương pháp DDEC cho tương tác tĩnh điện và chọn thông số trường lực phổ quát cho tương tác Lennard-Jones có thể giúp đánh giá nhanh và đáng tin cậy cho khả năng bắt giữ và lưu trữ khí của họ vật liệu xốp. Kết quả cũng cho thấy khả năng lưu trữ H_2 và bắt giữ CO_2 của MIL-88A-Fe theo dung lượng chưa cao lắm nhưng theo dung tích được đánh giá cao. Khí H_2 hấp phụ mạnh ở vị trí hốc của các O và Fe, trong khi đó CO_2 phân bố đều hơn trong chất hấp phụ.

Từ khóa: MIL-88A-Fe, phương pháp Monte Carlo, lưu trữ hydrogen, bắt giữ CO_2 , hấp phụ đẳng nhiệt.

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Evaluation of H₂ and CO₂ adsorption into MIL-88A-Fe by Grand canonical Monte Carlo simulation

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ABSTRACT

Two of the global issues are finding new, clean energy sources to replace increasingly exhausting fossil fuels and overcoming the problem of environmental pollution and climate change. In recent years, organic-metal framework series has been considered as a great candidate for H₂ storage and CO₂ capture to provide clean energy and reduce environmental pollution. Among them, MIL-88A-Fe has a stable and flexible structure in moist environments and high porosity. Therefore, in this research, hydrogen (H₂) storage and carbon dioxide (CO₂) capture capacities in MIL-88A-Fe were assessed quantitatively. By the grand canonical Monte Carlo simulation, the adsorption capacities of MIL-88A were elucidated via the adsorption isotherms, heats of adsorption at finite temperatures of 77 K and 298 K and pressures up to 100 bar. The results show that parameterizing force fields by combining DDEC method to calculate atomic partial charges for electrostatic interactions and the universal force field parameters for the Lennard-Jones interactions provide a quick and reliable method to evaluate gas capture and storage capacities of porous materials. The results also indicate that the abilities of H₂ storage and CO₂ capture of MIL-88A-Fe in gravimetric capacities were not very high; however, they were noticeable in volumetric uptakes. The hydrogen molecule is strongly adsorbed in the hollow positions of O and Fe atoms, while the CO₂ molecule is more evenly distributed in the sorbent.

1. INTRODUCTION

As known, hydrogen gas (H₂) is an abundant, potential and clean energy source. Hydrogen storage is the key to the development of fuel cell technology to reach the DOE gravimetric and volumetric targets. Besides, the globally rapid industrial development has resulted in an increasing amount of toxic gases released into the environment; in which, CO₂ is the main ingredient causing the greenhouse effect and affecting global warming. Therefore, reducing the amount of toxic gas and developing hydrogen

storage technology to provide a clean energy source are two very urgent issues.

In recent years, the technology of gas storage, capture and separation based on the adsorption mechanism of porous materials, especially the metal organic-framework (MOF) materials have gained considerable attention. MOF series is a porous crystalline composed of two main components: (1) inorganic connectors such as metal ions, metal clusters and (2) organic linkers.^{1,2} Therefore, MOFs have many outstanding features that are extremely high

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specific surface areas, tunable functionalities, large pore sizes, and reversible gas adsorption-desorption. So far, thousands of MOF structures have been successfully synthesized; however, at ambient temperatures and pressures under 100 bar, a few MOFs have been evaluated for H₂ storage and CO₂ capture.

In many MOFs that have not yet been evaluated for H₂ storage and CO₂ capture, we pay attention to MIL-88A-Fe³ (MIL = **M**aterials from **I**nstitut **L**avoisier) for the following reasons: (1) MOFs must be stable to avoid breaking down the structure in a humid environment. Compared to other MOFs, MIL-88A has strong durability and flexibility, swelling up to 85% of its original volume in solvents;⁴ (2) MIL-88A-Fe contains unsaturated metal sites that is one of the most effective strategies to improve gas storage and capture at room temperature;⁵⁻⁷ (3) Iron (Fe) is a common metal in nature, leading the low cost of this MOF compared to others.

2. CALCULATION METHODS

In order to evaluate the gas storage or capture capacity in porous materials, the grand canonical Monte Carlo (GCMC) technique was performed. This method allows the number of gas molecules entering freely to the rigid MOF during the simulation by the random insertion, deletion, translation, and rotation steps until the equilibrium system. In this work, the GCMC simulation was used to calculate the uptakes of H₂ and CO₂ adsorbed in MIL-88A-Fe through the RASPA simulation software package developed by Snurr group and published in 2014.⁸ This software package supports for simulating adsorption and diffusion of molecules in flexible nanoporous materials. It used the newest algorithm for MD and MC simulations with many outstanding features that are: easy to use, simple inputs, diverse output with many different measurements and units to meet the needs of users; surveying the flexibility of the material according to the temperature and pressure. This software package can calculate the Coulomb

interaction by the Ewald summation method for non-orthorhombic unit cells. For these reasons, we use RASPA in this research.

GCMC simulations were performed under the constant condition for volume (*V*), temperature (*T*) and chemical potential (*μ*) (ie. *μVT* ensemble). The chosen temperatures are 77 K and room temperature (298 K) and pressure up to 100 bar. The simulation steps are 10⁵ for equilibrium and 3×10⁵ for MC cycles. The simulation box was repeated 3×3×2 times the primary unit cell (3×3×2×68 atoms = 1224 atoms). The interaction between the gas (H₂, CO₂) and MIL-88A-Fe for a pair of the unlike atoms *i* and *j* at distance *r_{ij}* was presented as follows:

$$U(r_{ij}) = U_{LJ}(r_{ij}) + U_{CL}(r_{ij}), \quad (1)$$

where, the first term in the equation is the Lennard-Jones (LJ) interaction

$$U_{CL}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \quad (2)$$

describes the electrostatic interaction between pairs of the *i*th and *j*th atoms, in which *q_i* is the *i*th atomic charge (Fe, O, C, H), calculated based on the DDEC (**D**ensity **D**erived **E**lectrostatic and **C**hemical net atomic charge) algorithm by DFT calculation (DFT stands for the density functional theory). This parameterization of the force field improves the accuracy of the Coulomb interaction between the gas and MOF. The electrostatic potential was computed according to the Ewald method with a cut radius of 12 Å. And the second term describes the Lennard-Jones (LJ) interaction.

$$U_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

The parameters *ε_{ij}* and *σ_{ij}* correspond to the LJ potential depth and diameter for each pair of atoms. These parameters were calculated by the Lorentz-Berthelot mixing rule:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}; \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j), \quad (4)$$

where the parameters *σ_i* and *ε_i* for atoms of M-MIL-88A were taken from universal force

fields in the RASPA software, listed in Table 1. The cut-off radius of 12 Å was used for the LJ interactions.

A single LJ interaction site model at the center of mass (H_{COM}) was used for the hydrogen molecule. Here, the LJ parameters were taken from the TraPPE force field⁹ with $\sigma_{H_{COM}} = 2.96 \text{ Å}$, $\varepsilon_{H_{COM}} / k_B = 36.70$ and the $H-H_{COM}$ bond length of 0.37 Å. The CO_2 molecule was utilized by the EPM2 model.¹⁰ This force field parameterization above gives the results with high reliability.¹¹

Table 1. LJ parameters and the DDEC partial atomic charges of the MIL-88A-Fe.

Atom	ε/k_B (K)	σ (Å)	Atomic charge (e)
Fe	6.54	2.59	1.22
C1	47.86	3.47	0.73
C2			-0.18
O1	48.16	3.03	-0.57
O2			-0.87
H	7.65	2.85	0.12

The atom types in Table 1 are classified based on their links to the other atoms in the MIL-88A-Fe unit cell consisting of 12 H atoms, 12 C1 atoms, 12 C2 atoms, 24 O1 atoms, 2 O2 atoms at the μ_3 -O-centered trimer of Fe metals, and 6 Fe atoms. Figure 1 shows cut from the MIL-88A-Fe unit cell which the partial charges on the MOF calculated using the DDEC algorithm.

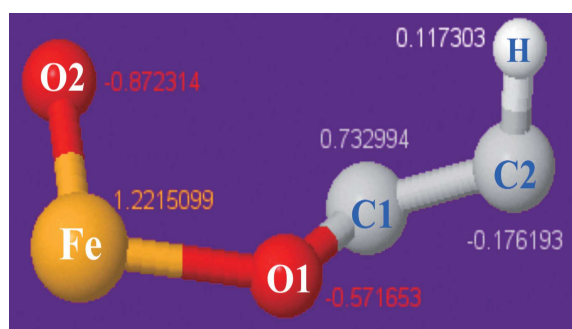


Figure 1. The partial atomic charges calculated using the DDEC method based on the density function theory.

3. RESULTS AND DISCUSSION

3.1. Optimization for MIL-88A-Fe structure

MIL-88A-Fe topology is shown in Figure 2. The unit cell of MIL-88A-Fe with the lattice constants of $a = b \neq c$ and the angles of $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ is in the rhombus frame. After the unit cell was designed based on experimental data,³ we relaxed all ions and volume of the MOF by using the van der Waals-density functional of Langreth group.¹²

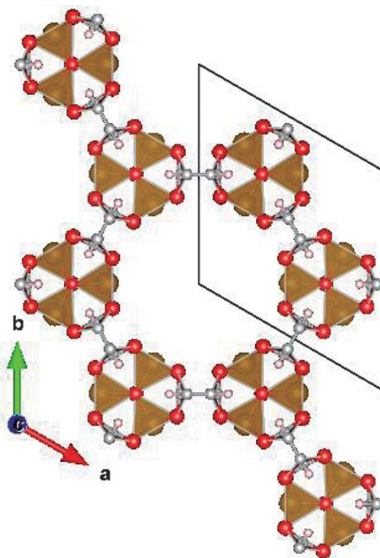


Figure 2. MIL-88A-Fe structure. The section in the frame is a primary unit cell. Brown, red, grey, white pink-coloured balls correspond to Fe, O, C and H atoms.

The unit cell was optimized based on the Murnaghan's equation of state¹³ from the total energies calculated by DFT calculations. This approach was indicated in detail in our previous research¹¹ by changing various lattice constants. The result of fitting the lattice constants versus the total energy is listed in Table 2. From these minimum points of total energy, the values of c/a and a versus the energy is fitted again by Murnaghan method, we find the optimal value pair (c/a , a) for the unit cell that is $a = b = 11.22 \text{ Å}$ and $c = 14.86 \text{ Å}$, leading to the volume of 1619 Å³. This result is quite suitable with the experimental data³ corresponding to the lattice parameters $a = b = 11.04 \text{ Å}$ and $c = 14.80 \text{ Å}$ as well as the volume size of 1562 Å³.

Table 2. The lattice constants and the minimum energy fitted based on the Murnaghan's equation of state corresponding to the determined values of c/a .

c/a ratio	Lattice constant, a (Å)	Minimum energy (eV)
1.25	11.46	-366.86
1.27	11.39	-367.41
1.29	11.32	-367.70
1.31	11.26	-367.88
1.33	11.19	-367.87
1.35	11.13	-367.76
1.37	11.08	-367.45
1.39	11.02	-367.02

3.2. H_2 storage capacity of MIL-88A-Fe

To quantitatively assess gravimetric and volumetric H_2 storage capability in MIL-88A-Fe, we determine the absolute and excess adsorption isotherms at two common temperatures of 77 K and 298 K according to the increasing pressure up to 100 bar. The results are shown in Figure 3 for gravimetric loadings (left y-axis) and volumetric loadings (right y-axis).

At 77 K (Figure 3a), both absolute and excess isotherms increase strongly at low pressure (below 5 bar) and then increase slowly with increasing pressure. The excess adsorption quickly reaches its saturation value of 4.06 wt% at 15 bar, then decrease slightly. Meanwhile, the total uptake still increases slightly, reaching 4.66 wt% at 100 bar. Remarkably, the total and excess volumetric H_2 adsorption capacities are very high, obtaining 44.32 g/L (at 15 bar) and 50.69 g/L (at 100 bar), respectively. At room temperature (Figure 3b), the H_2 adsorption capacity of MIL-88A-Fe increases almost linearly with pressure up to 100 bar, especially for the absolute uptake. The obtained results at 100 bar of total and excess storage capacities are 0.22 wt% and 0.63 wt% for gravimetric uptakes; 2.49 g/L and 6.97 g/L for volumetric uptakes. The above results show the noteworthy of the volumetric H_2 storage capacity of MIL-88A-Fe compared to the experimental results as well as other calculations.¹⁴ The most noticeable MOF is the Be-BTB material¹⁵ with the chemical

$Be_{12}(OH)_{12}(\text{benzene-1,3,5-tribenzoate})_4$, which obtained 2.3 wt.% for and 1.01 wt.% for absolute and excess uptakes, while the total and excess volumetric capacities reached 44 g/L at (77 K, 100 bar) and 11 g/L at (298 K, 100 bar).

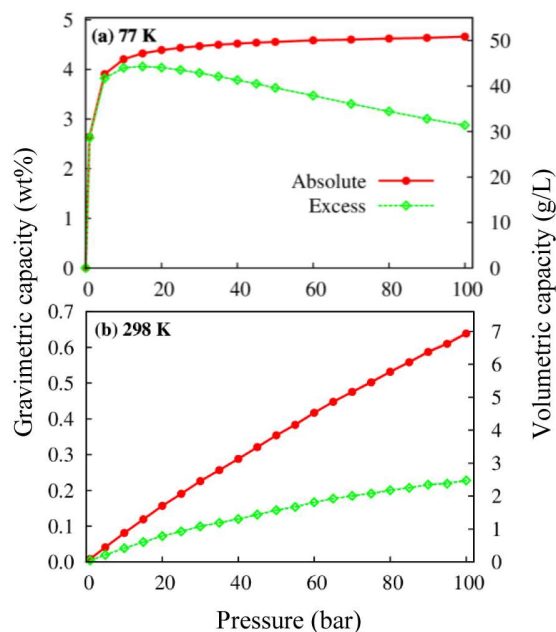


Figure 3. The absolute and excess H_2 adsorption isotherms in MIL-88A-Fe at 77 K (a) và 298 K (b), and the pressures up to 100 bar.

Deeper insights into the interaction strength between H_2 and MIL-88A-Fe were indicated via the heat adsorption (Q_{st}) of H_2 in MIL-88A-Fe at 77 K (Figure 4a) and 298 K (Figure 4b). The average value was calculated at the low-pressure area below 10 mbar with the obtained values of 7.38 kJ/mol at 77 K and 8.78 kJ/mol at 298 K.

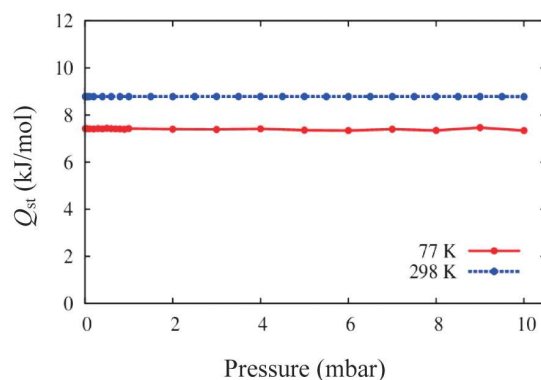


Figure 4. Isothermic heat of adsorption of H_2 in MIL-88A-Fe at temperatures 77 K and 298 K, the pressure below 10 mbar.

Figure 5 shows the visualization of the H_2 adsorption in MIL-88A-Fe. The figure indicates that H_2 molecules are preferable in the hollow than other sites of MIL-88A-Fe such as organic linkers or metal sites at both 77 K (Figure 5a) and 298 K (Figure 5b). Besides, the results show that, at low temperature, H_2 adsorption is much stronger. These conclusions are consistent with H_2 adsorption in MIL-88A-Co elucidated by electronic structure calculations.¹⁶

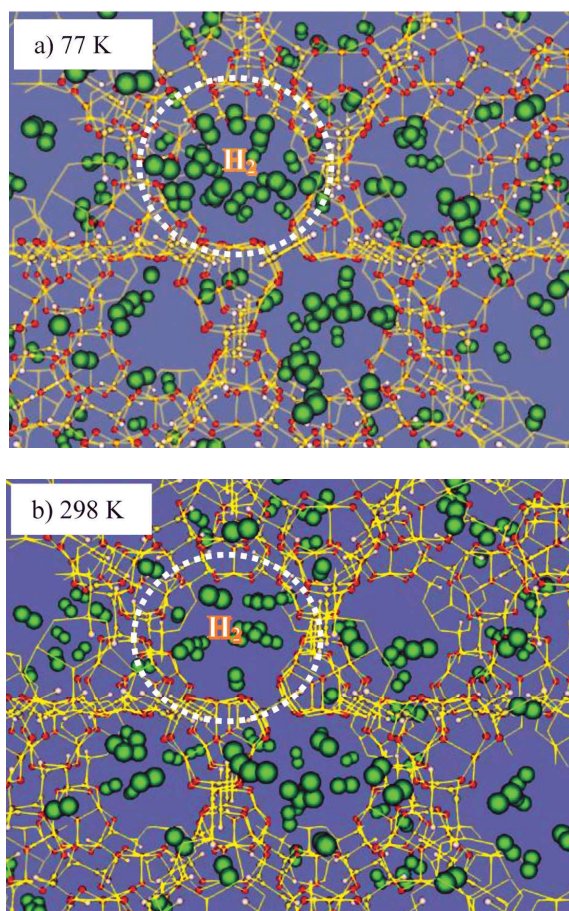


Figure 5. Visualization of H_2 adsorption in MIL-88A-Fe at 77 K (a) and 298 K (b) and the pressure of 1 bar. The H_2 molecule consists of two green balls.

3.3. CO_2 capture capacity of MIL-88A-Fe

For evaluating the CO_2 capture in MIL-88A-Fe, the reliability of the force field parameters was tested. The results showed that, at room temperature and pressure of 1 bar, the excess adsorption capacity of CO_2 in MIL-88A-Fe is 3.42 mmol/g. Meanwhile, at the same condition of pressure and temperature, the Chalati group's

experimental results showed the value of 4.95 mmol/g.¹⁷ The above results presented that the simulation accuracy was approximately 70% compared to the experimental data. The difference between the results is due to the influence of experimental factors such as water vapour and impurities affecting the adsorption capacity compared to the simulation. However, this calculation is enough reliable to predict the CO_2 capture capacity of MIL-88A-Fe and new materials.

We also assessed the CO_2 capture capability of MIL-88A-Fe at room temperature via the adsorption isotherms (Figure 6).

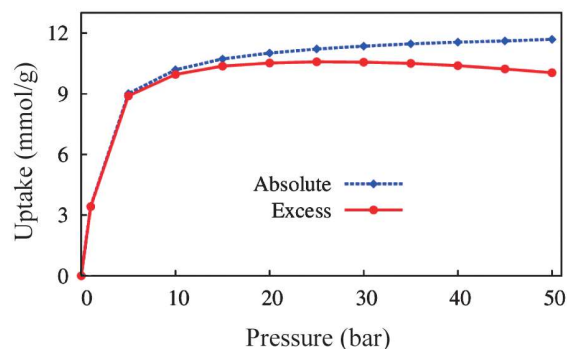


Figure 6. The absolute and excess CO_2 adsorption isotherms in MIL-88A-Fe at 298 K and pressures up to 50 bar.

For the investigated pressure below 50 bar, the maximum absolute and excess CO_2 uptakes of MIL-88A-Fe are 514.45 mg/g (11.69 mmol/g) at 50 bar and 465.61 mg/g (10.58 mmol/g) at 25 bar, respectively. The absolute and excess CO_2 amount adsorbed per unit volume of MIL-88A-Fe correspond to 280.57 và 256.83 $cm^3(STP)/cm^3$. The calculation shows that the CO_2 capture capacity is not higher than the highly appreciated MOF structures until now (such as MOF-200, MOF-210, MOF-205, MOF-177 and MOF-5).¹⁸ However, the CO_2 volumetric uptakes are remarkable. To date, the MOF materials with the highest CO_2 capture capacity are MOF-200 and MOF-210 with 2400 mg/g and 2396 mg/g at 298 K and 50 bar¹⁸ because of their high saturation pressures compared to other sorbents. MOF-117 was also evaluated for the high CO_2

capture capacity with 33.5 mmol/g and 320 cm³(SPT)/cm³ at 298 K and 35 bar. Details of the MOFs with high CO₂ uptakes are listed in the review journal.¹⁹

The visualization of CO₂ adsorption capacity in MIL-88A-Fe is also shown in Figure 7. The picture shows CO₂ concentrate more evenly in the adsorbent, *ie.* they concentrate on the hollow sites, organic linkers, and metal sites.

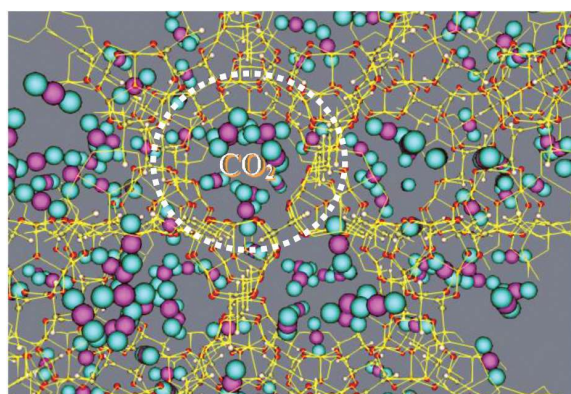


Figure 7. Visualization of CO₂ adsorption in MIL-88A-Fe at 298 K and 1 bar. The CO₂ molecule consists of two turquoise-coloured balls (O atoms) linked to a pink-coloured ball (C atom).

4. CONCLUSIONS

The force field parameterization that combines the DDEC partial atomic charge calculation and the LJ parameters taken in the universal force field leads to reliable results.

The results show that the volumetric capacity of H₂ storage and CO₂ capture in MIL-88A-Fe are noteworthy. These gases are favourable in the hollow sites of MIL-88A-Fe surrounded by O atoms and Fe atoms compared to other positions, especially for H₂ gas.

In the next research, based on the density functional theory, we will clarify and explain the preferred adsorption positions of H₂ and CO₂ in MIL-88A-Fe in more detail.

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