Prediction of hydrogen storage properties of Zr-based MOFs

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ABSTRACT

Porous materials have potential hydrogen storage properties. MOFs have been widely used because of porous, structural diversity, higher surface area and lower crystal density. Zr-based MOFs can be regarded as ideal hydrogen storage materials because of good thermal and chemical stability. Here we predicted the hydrogen storage properties of Zr-based MOFs (MOF-801, MOF-802, MOF-808, and MOF-841) at 77 K by means of GCMC method, mainly analyzed the adsorption isotherm and isosteric heat of H_2 in several Zr-based MOFs and explored the influence factors of hydrogen storage properties. The results showed that the isosteric heat was the factor of hydrogen storage at low pressures, while the surface area and porosity were the factors at high pressures. MOF-808 had a high mass and volume adsorption capacity both at low pressure and high pressure, which can be regarded as an ideal hydrogen storage material in the future.

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1. Introduction

As a new energy, which is safety, environmental protection, resource rich, high calorific value and no pollution, hydrogen energy has been widely concerned. However, hydrogen is easy to burn, which has the risk of fire and explosion. The problems of transportation and storage restrict the application of hydrogen energy, which has become a key factor in the development and utilization of hydrogen energy. Porous material is a very promising hydrogen storage material, which stores hydrogen in the form of molecules at low temperatures and compresses hydrogen into the hole effectively. This method has a higher volume storage density compared with the free gas under the same temperature and pressure condition.

MOFs are a kind of organic-inorganic hybrid crystals formed by the organic bridge connecting metal ions or clusters [1]. Because of their high surface areas, light skeleton densities and many gas adsorption sites, these materials are widely used in the field of gas adsorption and separation [2–7], exhibited exceptional H_2 storage capacities. There are many kinds of MOFs [8–18], many new MOFs materials are also synthesized every year [19–25]. The prototype of MOFs is $Zn_4O(bdc)$, in which bdc is terephthalic acid. It is often called MOF-5 or IRMOF-1. Although MOFs have many

advantages as hydrogen storage materials, they also have their own shortcomings, especially in terms of stability. The thermal stability of MOFs is much lower than that of molecular sieve materials. Most molecular sieve materials can be subjected to high temperatures of 600–800 °C, such as MCM-41 [26]. The structure remains stable at 897 °C after the ion exchange. While the crystal structure of many MOFs will collapse when the temperature higher than 350 °C [27,28]. The most important thing is that the stability of the MOFs framework is likely to be influenced by the moisture in the air when it is exposed to the air. It has the instability in the aqueous environment. But the Zr-based MOFs have recently found good stability [29]. The thermal decomposition temperature can reach 540 °C and can maintain the structural stability in the water, acetone, benzene, DMF and other organic solvents. So the Zr-based MOFs can be used as an ideal hydrogen storage material.

The experimental method has the disadvantages of long cycle and high cost in predicting the hydrogen storage properties of materials. The predicted results are also susceptible to the influence of experimental environment. However, the molecular simulation method can reduce the experimental repeatability and can explain the adsorption behavior of the materials from the microscopic view. Monte Carlo is a simulation method based on random process. Grand Canonical Monte Carlo (GCMC) method is widely used to describe the adsorption process of gas in porous materials [30–36]. The work of this paper is to exploit a highly efficient and stable hydrogen storage material by means of molecular simulation and provide a direction to explore for the experiment.

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2. Calculations

2.1. Models

We mainly compared hydrogen storage properties of several Zr-based MOFs materials, including UiO-66, UiO-67, MOF-801, MOF-802, MOF-808, and MOF-841. These materials were formed by Zr_6-$O_4(OH)_4(-CO_2)_n$ secondary building units (SBUs) and several different carboxylic acid organic linkers (Fig. 1).

The Materials Studio software, which was provided by Accelrys based on PC platform, was used in the simulation. The framework model was constructed according to the Cambridge Crystallographic database (CCDC). The L-J potential parameters of atoms in the framework derived from Dreiding force field [37]. The H_2 molecule was calculated based on the model proposed by Darkrim and Levesque (D–L model) [38], which regarded the H_2 molecule as a model with three atoms considering the Coulomb force. The bond length was fixed at 0.741 Å. Van Der Waals interactions were focused on the centroid position of hydrogen atoms with the LJ parameters of $\sigma = 2.958$ Å and $\varepsilon = 36.7$ K. H atoms were assigned charges to reproduce the quadrupole moment. The charges of central H atoms were $q_{CM} = -0.9382e$ and the other two H atoms were $q_H = 0.4664e$. The quantum effect of H_2 was obvious at low temperature due to the small molecular mass. It could be described by Feynman–Hibbs function. The LJ parameters of H_2 molecule at low temperature were proposed by Wenzel et al. [39] with $\sigma = 3.064$ Å and $\varepsilon = 30.104$ K.

Table 1 was the structure properties of Zr-based MOFs. The material density ρ and pore volume V_p were got by the crystal structure database. The surface area S_a and porosity were calculated by Atom Volumes & Surfaces tool in the Materials Studio.

2.2. Method

The interactions between the non-bonded atoms were calculated by L-J 12-6 potential energy. ε and σ were the potential parameters. They were calculated with the Lorntz–Berthelot mixing rules.

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] + \frac{q_i q_j}{r_{ij}} \tag{1}$$

The adsorption behavior of H_2 in MOFs materials was simulated by Grand Canonical Monte Carlo method. Volume, temperature and chemical potential were fixed in this ensemble. The simulation process was calculated by Sorption module. The interactions between gas molecules and framework materials were represented by Dreiding force field and periodic boundary conditions were considered. Van Der Waals interactions between H_2 molecules and the atoms in the MOFs framework were described by the L-J 12-6 potential, and the electrostatic interactions were estimated by the Ewald sum method. In the simulation process, try the following four kinds of movement types in every step, including deleting a molecule, inserting a molecular, molecular rotation and translation. There were a total of 2×10^7 steps in the simulation. The first 1×10^7 steps made the system reach equilibrium, and the after 1×10^7 steps for the statistical average.

The amount calculated by GCMC simulation is absolute adsorption N_{ab}, while directly measured by experiment is excess adsorption N_{ex}. The relationship between them is $N_{ex} = N_{ab} - \rho_b V_{pore}$. Where ρ_b is the gas density, V_{pore} is the pore volume.

In order to verify the accuracy of the simulation results, we calculated H_2 uptakes in UiO-66 and UiO-67 at 77 K and 0–80 bar and N_2 uptakes in MOF-801, MOF-802, MOF-808 and MOF-841 at 77 K and 0–1 bar, and then compared them with the experimental data of Chavan [40] and Furukawa [20] to prove this method was correct and persuasive (Fig. 2). The corresponding density maps of MOFs can be seen in Fig. 3. The left side is under the low pressure, the right side is under the high pressure in the map of each material. The gas density distribution under high pressure was significantly higher than that of the low pressure, which was consistent with the increase of the adsorption capacity with the increase of pressure. It is assumed that the structure is perfect crystal in the simulation, while actually the structure used for adsorption experiments usually has certain defects. At the same time, the deviation is inevitable for Van Der Waals interaction assessment. So there is a certain deviation between the amount of simulation and the experimental value, while all in the permitted range (5–13%). This shows that the calculation results are in good agreement with the experimental results.

3. Results and discussion

3.1. Adsorption isotherms

From the above analysis, the calculation method can reasonably predict the hydrogen storage properties of MOFs with similar chemical structure. In this paper, the hydrogen storage properties of Zr-based MOFs at 77 K were studied by means of the GCMC method.

As shown in Fig. 4, the mass adsorption isotherms of several different MOFs under different pressures at 77 K were compared. The absolute adsorption of H_2 was concerned. We investigated the hydrogen storage and the influence factors at high pressures (0–30 bar) and low pressures (0–1 bar). The hydrogen storage increased gradually with the increase of pressure. Under low pressures, hydrogen storage performance of MOF-808 and MOF-841 was the best. It can reach 2.79 wt% and 2.52 wt% at 1 bar. Since then, the hydrogen storage of MOF-808 increased rapidly, while the capacity of MOF-841 gradually saturated with the increase of pressure. It was much lower than that of MOF-808 under high pressures. The lower porosity and surface area of MOF-841 resulted in the smaller hydrogen storage. Under high pressures, the increase of hydrogen storage gradually leveled off and reached
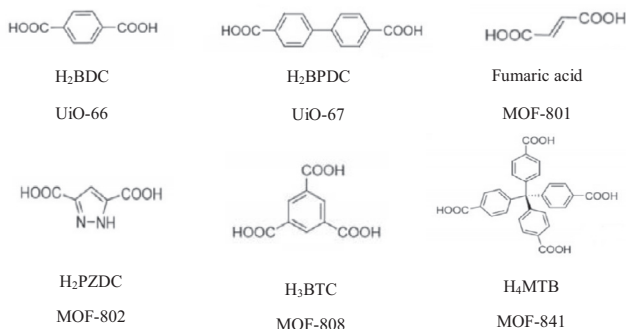

Fig. 1. Structures of organic linkers.

Table 1
Summary of the physical and pore structure properties of Zr-based MOFs.

Materials	ρ (g/cm³)	S_a (m²/g)	V_p (Å³)	Ratio of pore volume (%)
UiO-66	1.219	1301.20	4248.54	47.90
UiO-67	0.752	2313.61	11483.85	59.32
MOF-801	1.592	726.51	2363.65	41.67
MOF-802	1.736	17.33	6397.92	22.48
MOF-808	0.885	2242.77	26275.59	60.88
MOF-841	1.038	1403.77	2589.43	42.93