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Lithium doping on covalent organic framework-320 for enhancing hydrogen storage at ambient temperature

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ABSTRACT

Density Functional Theory (DFT) combines with grand canonical Monte Carlo (GCMC) simulations are performed to explore the effect of Li doping on the hydrogen storage capability of COF-320. The results show that the interaction energy between the H_2 and the Li-doped COF-320 is about three times higher than that of pristine COF-320. GCMC simulations are employed to study the hydrogen uptake of Li-doped COF-320 at ambient temperature, further confirm that the lithium doping can improve the hydrogen uptake at ambient temperature. Our results demonstrate that Li-doped COFs have good potential in the field of hydrogen storage.

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1. Introduction

Since entering 21 centuries, the environmental problems such as the massive use of fossil fuels and greenhouse gas emissions have become increasingly prominent, which greatly stimulate and promote the development of renewable energy. Hydrogen is an ideal fuel due to its high energy density and clean-burning characteristics [1], but the problems with the storage of hydrogen limit its applications in vehicles and portable electronics. The US Department of Energy's (DOE) H_2 storage targets is 5.5 wt% by 2017 [2]. However, the technical performance of the existing hydrogen storage materials cannot meet the application requirements of vehicle hydrogen fuel cells as well as the carrier of renewable energy, which needs to make a breakthrough. In numerous porous materials, covalent organic frameworks (COFs) are considered to be one of the promising molecular hydrogen storage materials. A new family of nanoporous materials, which are called COFs, have been proposed and synthesized by Yaghi and co-workers [3]. COFs are composed of lighter elements in the periodic table, such as C, H, O, B, this kind of material is connected by the organic groups through strong covalent bonds, and has regular crystal structure. According to the dimension of composition unit, COFs can be divided into two-dimensional (2D-COFs) [3] and three-dimensional (3D-COFs) [4]. Since the structure do not contain metallic elements, COFs have low density, for instance, the density of COF-108 as low as 0.17 g/cm^3, which is the lowest density in the reported porous materials.

Yaghi et al. [5] reported the hydrogen uptake in COFs, at 77 K and 35 bar, the hydrogen adsorption amount in the COF-102 can reach 7.16 wt%. Tylianakis and coworkers [6] explored the hydrogen adsorption capacity in COFs, experimental and theoretical studies have proven that COFs have comparable or better hydrogen storage abilities than other competitive materials, especially 3D-COFs have a superior performance of hydrogen storage at 77 K.

Though recent studies have shown that COFs have good hydrogen adsorption performance at low temperature, but at room temperature, it is difficult to reach the practical application standards published by the United States department of energy (DOE). Experimental and theoretical studies have shown that the hydrogen adsorption ability of COFs can be improved greatly through doping metal atom [7–10] and functionalize organic groups [11–13].

Cao et al. [9] suggested that the hydrogen adsorption amount of Li doped COF-105 and COF-108 reaches 6.84 wt% and 6.73 wt% at T = 298 K and p = 100 bar, respectively. This value exceeded the standards set by the U.S. department of energy (DOE). Lan [10] studied the hydrogen storage capacity of COF-202 and Li-COF-202 at T = 298 K and P = 100 bar. Simulation results show that the gravimetric uptakes of H_2 in COF-202 and Li-COF-202 are 1.52 wt% and 4.39 wt%, respectively. We can see that the insertion of Li atoms in COF-202 will increase the hydrogen storage capacity.

Recently, a new porous covalent organic framework (named as COF-320) was recently synthesized by Yaghi [14]. COF-320 has the

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characteristics of good chemical and thermal stability. Therefore, in this paper, the effect of lithium-doped in COF-320 on hydrogen adsorption is studied. At first, cluster model is used to study Li binding sites at the surface of COF-320. Then we explore the hydrogen adsorption properties in Li doped COF-320, including the adsorption energy, interaction mechanism between hydrogen and doped Li atom. Finally, the pressure dependence of hydrogen adsorption behavior in Li doped COF-320 at ambient temperature is studied by GCMC simulations.

2. Computational details

All calculations are performed using Material Studio software. The structure file of COF-320 is downloaded from the Cambridge Crystallographic Data Center (CCDC) [14], as seen in Fig. 1a. All the cluster calculations are performed using density functional theory (DFT), within the generalized gradient approximation (GGA) [15,16] using the Dmol3 code. The Perdew-Wang 1991 (PW91) [17] is adopted for the electronic exchange correlation functional. All electron calculations employed with the double numerical plus polarization (DNP) basis set [18] are used for all the atoms. We starts geometry optimization without symmetry constraints and smearing of "0.005 Ha". The electronic density convergence criterion is set to 1×10^{-6} e/Å^3. The convergence criteria for the energy, force and maximum displacement is set to 10^{-5} Ha, 2×10^{-3} Ha/Å, and 0.005 Å, respectively.

Because of the large size of the unit cell of COF-320, cluster model is adopted to represent the real structure to reduce the computational costs, as shown in Fig. 1. After optimization, Li atoms are introduced to COF-320 structures, for a single Li atom, the spin of Li atom is included in the calculation process. The average binding energy between the doped Li atoms and COF-320 is calculated by the following formula (1):

$$BE=\left[E(\text{cluster}) + nE(\text{Li}) - E(\text{cluster: nLi})\right]/n \tag{1}$$

where E(cluster: nLi), E(cluster) and E(Li) are the total energies of nLi decorated COF-320, COF-320, an Li atom respectively, the variable of n denotes the number of Li atoms doped on the host material. The average adsorption energy of H_2 on Li decorated COF-320 is defined as formula (2):

$$\Delta E = [E(\text{cluster: nLi}) + nE(H_2) - E(\text{cluster: nLi}+nH_2)]/n \tag{2}$$

where E(cluster: nLi+nH_2) and E(H_2) are the total energies of nH_2 molecules adsorbed on nLi decorated COF-320 and the total energy of a free H_2 molecule, respectively.

In the GCMC simulations, The Li-doped COF-320 is constructed based on its parent COF-320, and is treated as rigid frameworks. The simulated unit cell is composed of $1\times1\times4$ unit cells. The Dreiding force field [19] is employed to describe the interatomic interactions. For Li atom, the universal force field is adopted here. Hydrogen molecule is treated as a diatomic molecule, charge distribution in two H atoms (q_H=0.468 e) and one intermediate atom ($q_{CM}=-0.9382$e). Van Der Waals interactions are described by the L-J 12-6 potential, while the long-range electrostatic interactions are simulated using Ewald simulation technique. The LJ parameters for hydrogen molecule are σ=2.958 Å, ε=36.7 K. The cutoff radius is set to 13 Å. Periodic boundary conditions are applied in all three dimensions. The number of operations for each state point is 2×10^7, each step contains the following four disturbances, that is, insert, delete, translation and rotation, the former $l\times10^7$ step make the system to achieve balance, and the after $l\times10^7$ step for sampling. The GCMC simulation method has been verified to be reliable in our previous studies [11].

3. Results and discussion

At first, the structure is optimized without any geometrical constrains. Then one hydrogen molecule is added into the COF-320 structure to calculate the adsorption energy of H_2 over pure system. The results show that the adsorption energy between H_2 and bare COF-320 is so weak (just 0.07 eV) that we need to take measures to strengthen the binding energy. Then we investigates the doping of a single and multiple Li atoms in cluster. All possible sites have been investigated. After optimization, only three stable adsorption sites for a single Li atom are obtained. These represent as sites A, B, C in Fig. 1b.

Fig. 2 indicates the optimized structures of COF-320 fragments with adsorbed Li atoms, the charges loaded by the adsorbed Li atoms and the distances between Li atom and cluster are also presented. Fig. 2a, b, c show that a single Li atom can be stably located at the top of the center of the hydrocarbon ring (A, C site) and open hollow site (B site). Among them, B site is the most favorable position for Li atom on cluster. The Li binding energy of the B site is found to be 2.69 eV, whereas 2.21 and 2.45 eV for the A and C site. Our calculations show that when a Li atom is placed on the N-C bridge, it will migrates to the neighboring open hollow site after geometry optimizations, as shown in Fig. 2b. Subsequently, we further investigates the doping of two Li atoms on COF-320, and equilibrium geometries are shown in Fig. 2d–f. We find that the most stable geometry is that one located at the hydrocarbon ring (A site), and the other located at the open hollow site (C site), as shown in Fig. 2d, in this case, the calculated average binding energy is 2.18 eV, whereas the coadsorption energies of other two forms are found to be 1.92 (see Fig. 2e) and 1.96 eV (see Fig. 2f), respectively. Due to the average binding energies of Li onto the substrate are larger than the cohesive energies of Li (1.63 eV),

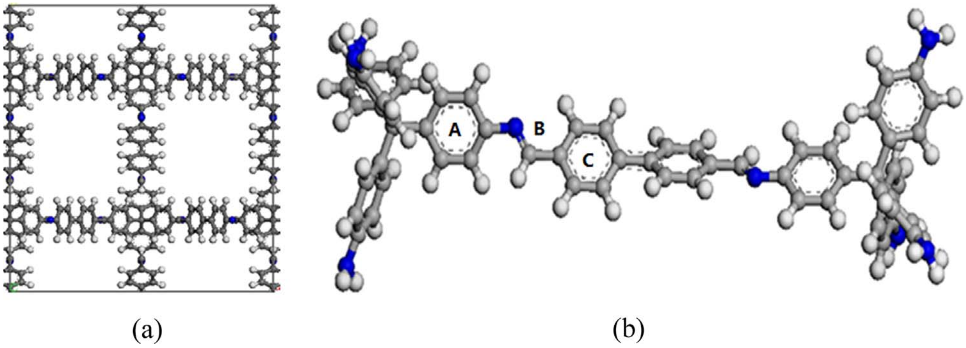

Fig. 1. (a) Configuration of COF-320 unit cell. (b) The optimized cluster model used here to represent the COF-320 and possible adsorption sites (A, B, C) for adsorption of metals in the COF-320. The dangling bonds are terminated by H atoms. C, H, and N atoms are shown as gray, white, and blue colors, respectively.

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