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Theoretical design of Li-doped ILCOF-1 for high H_2 uptake at moderate temperature

Jing-Hua Guo

Laboratory of Advanced Materials Physics and Nanodevices, School of Physics and Technology, University of Jinan, Jinan, Shandong 250022, China

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ABSTRACT

In this paper, we designed a good hydrogen storage material of Li-doped ILCOF-1 in theory. The first-principles studies show that the Li-doped ILCOF-1 has a high hydrogen storage capacity (the gravimetric and volumetric uptake are 7.26 wt% and 27.2 g/L, respectively). The 2020 U.S. Department of Energy (DOE) gravimetric target can be achieved. The kinetic Monte Carlo simulations are performed to predict the optimal condition for hydrogen storage and release. Based on the DOE limits, the optimal condition for hydrogen storage is at 250 K and 12 bar, and for hydrogen release is at 350 K and 0.5 bar.

1. Introduction

Hydrogen is the cleanest energy in the world, as its product is only water after the combustion. Due to its special chemical and physical properties (e.g., hydrogen is inflammable, explosive, and highly diffusive.), the transportation and storage of hydrogen is the largest obstacle to realize the hydrogen economy. Numerous studies have paid special attentions to the pursuit of materials for hydrogen storage [1–8]. Covalent organic frameworks (COFs) are considered as promising materials for non-dissociative hydrogen adsorption. COFs are covalent porous crystalline polymers connected via covalent bonds, which exhibit great potential for hydrogen storage due to their relatively high H_2 uptake at low temperature (77 K) [2,5]. However, the hydrogen uptake will decrease drastically at room temperature (about 298 K). For example, COF-108 displays a hydrogen uptake of 10.2 wt% at 77 K while it is 0.88 wt% at room temperature [9]. Therefore, it is of vital importance to improve H_2 uptake at moderate temperature for practical applications.

The previous study has suggested that hydrogen molecules can be bound to a metal cation (e.g. Li^+ or Ni^+) with the binding energy of 0.18–0.50 eV [10,11]. It is a desirable binding strength that the hydrogen can desorb at near-ambient conditions. To use such an advantage, metal-doping (e.g., Li, Ca and Mg) on microporous materials was advanced to enhance the H_2 uptake [12–19]. Among all these metals, Li is considered as a suitable decorating candidate because Li atoms are lightweight and can polarize the hydrogen molecules. In addition, they are comparatively not likely to form clusters when they are dispersed on nanostructures. Sun et al. have theoretically predicted that coating of C_{60} fullerenes with 12 Li atoms can effectively store hydrogen with the gravimetric density of 9 wt% [20].

As a good porous material, the pores or channels inside of COFs provide good places for the deposition of Li atoms. The H_2 adsorption properties in Li-doped COFs, have been studied by several groups, and it reveals that the hydrogen adsorption properties can be improved a lot [13,21–23]. For example, Cao et al. predicted that the H_2 uptake of Li-doped COF-202 can reach 4.39 wt% at room temperature [23]. The Li atoms not only can be deposited on the top of the skeleton of COFs, but also can form ionic bonds with the organic linker. By introducing the —OLi groups into the COF-105, Froudakis et al. improved the storage capacity (>6.0 wt % at 300 K and 100 bar) of COF-105 [24]. In our previous work, we introduced the Li atoms in Pc-PBBA COF by constructing the —OLi groups, and it shows a high hydrogen uptake both in gravimetric (4.70 wt%) and volumetric (40.23 g/L) terms at 250 K and 100 bar [25].

Although the boroxine or boronate ester-linked COFs have been widely investigated, they are not stable to moisture, which limits their application in gas storage [26]. Recently, a new class of COFs (e.g., COF-300, COF-LZU1, COF-366 and ILCOF-1) was designed and synthesized in crystalline form linked by C=N bonds, named imine-linked COF [27–30]. This class material is highly stable in water and most organic solvents. This prompted us to explore the possibility of using Li-doping imine-linked COFs for hydrogen storage. The ILCOF-1 serves as the representative substrate, whose

E-mail address: sps_guojh@ujn.edu.cn

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synthetic scheme is shown in Fig. 1 [29]. ILCOF-1 has mesopores (pore dimensions ~28.0 × 24.3 Å and pore volume = 1.21 cm^3 g^{-1}) and high surface area (Langmuir surface areas = 3453 m^2 g^{-1}).

In this work, we first studied the Li doping sites in ILCOF-1, and following studied the hydrogen adsorption and diffusion properties in Li-doped ILCOF-1. At last, by performing kinetic Monte Carlo (KMC) simulations, we studied the hydrogen adsorption kinetics in Li-doped ILCOF-1 under different conditions. The KMC simulation is one of the practical methods for studying the exact dynamical evolution of a system from state to state, which allows us to explore time scales that are orders of magnitude longer than molecular dynamics (MD). Based on the U.S. Department of Energy (DOE) limits and the KMC results, we predicted the optimum condition for hydrogen storage and release.

2. Computational methods

2.1. The first-principles calculations

The density-functional theory (DFT) calculations were carried out using the VASP package [31] to study the distribution scheme of Li in ILCOF-1. The Perdew-Burke-Ernzerhof (PBE) functional [32] was used to calculate the exchange correlation potential, along with PAW (projector augmented-wave) method [33]. The energy cutoff was 500 eV. The energy and force convergence criterion was set to 10^{-5} eV and 0.03 eV/Å, respectively. The simulation cell in our calculations is shown in Fig. 2. Based on the Monkhorst-Pack scheme [34], the Brillouin zone was sampled by 1 × 1 × 2. The calculations were performed with full optimization of the geometry. Table 1 shows the lattice constants and some bond lengths of ILCOF-1. The values calculated in this work agree well with the experimental values [29], which confirms the accuracy of our results.

The binding energy (B.E.) per Li atom in ILCOF-1 was calculated using the formula:

$$B.E. = -[E(m\mathrm{Li}-\mathrm{COF}) - E(\mathrm{COF}) - mE(\mathrm{Li})]/m \quad (1)$$

where $E(m\mathrm{Li}\text{-COF})$ is the total energy of the geometry optimized Li decorated ILCOF-1, $E(\mathrm{COF})$ is the energy of the pure ILCOF-1, $E(\mathrm{Li})$ is the energy of one isolated Li atom and m represents the number of Li atoms.

Consequently, the H_2 adsorption energy ($\triangle E_n$) with zero point correction energy on Li-doped ILCOF-1 was calculated using the formula:

$$\Delta E_n = -\{E[\mathrm{Li}-\mathrm{COF}(H_2)_n] - E[\mathrm{Li}-\mathrm{COF}(H_2)_{n-1}] - E[H_2] + \Delta ZPE\} \quad (2)$$

where $E[\text{Li-COF}(H_2)_n]$ and $E(\text{Li-COF}(H_2)_{n-1})$ are the total energies of the Li doped ILCOF-1 with H_2 molecules adsorbed, $E(H_2)$ is the energy of the isolated H_2 molecule, and n corresponds to the number of H_2 molecules. ΔZPE is the zero point correction energy, which is calculated by

$$\Delta ZPE = ZPE[\mathrm{Li}-\mathrm{COF}(H_2)_n] - ZPE[\mathrm{Li}-\mathrm{COF}(H_2)_{n-1}] - ZPE[H_2] \quad (3)$$

The average adsorption energy per H_2 molecule calculated by

$$\overline{\Delta E} = n_{\max}^{-1}\sum_{i=1}^{n_{\max}}\Delta E_i \quad (4)$$

A positive binding energy in these equations corresponds to a stable system.

To establish the stability of Li-doped ILCOF-1 at higher temperature, the first-principles molecular dynamics (MD) simulations are performed in VASP. The MD simulations are carried out in the canonical NVT ensemble, and the temperature is controlled using the Nosè thermostat. In these simulations, we used G-point sampling with a time step of 0.5 fs for 5 ps.

2.2. Concept of the kinetic Monte Carlo scheme

To study the hydrogen adsorption kinetics in Li-doped ILCOF-1, we performed the KMC simulations under different conditions. In our work, we used the Bortz-Kalos-Lebowitz (BKL) KMC algorithm, which has been quite successful in simulating kinetic behavior in

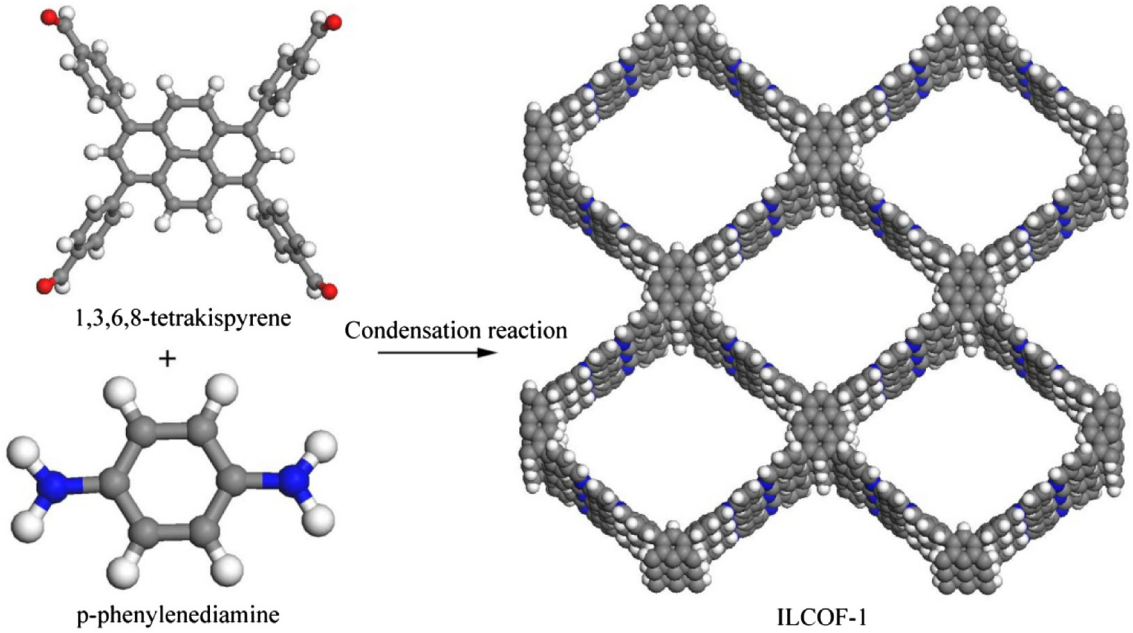

Fig. 1. Synthesis scheme of ILCOF-1 in the experiment, where gray, blue, red and white balls correspond to carbon, nitrogen, oxygen and hydrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)