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Understanding the mechanism of hydrogen adsorption into metal organic frameworks

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Abstract

Hydrogen adsorption mechanism into MOF-5, a porous metal-organic framework (MOF) has been studied by density functional theory calculation. The selected functionals for the prediction of interaction energies between hydrogen and potential adsorption sites of MOF-5 were utilized after the evaluation with the various functionals for interaction energy of $H_2 \cdots C_6H_6$ model system. The adsorption energy of hydrogen molecule into MOF-5 was investigated with the consideration of the favorable adsorption sites and the orientations. We also calculated the second favorable adsorption sites by geometry optimization using every combination of two first adsorbed hydrogen molecules. Based on the calculation of the first and the second adsorption sites and energies, it has been suggested that the hydrogen adsorption into MOF-5 follows a cooperative mechanism in which the metal sites initiate the propagation of the hydrogen adsorption on the whole frameworks. In addition, the interaction mode between the simple benzene ring with hydrogen is significantly changed when the benzene ring has been incorporated into the framework of MOF-5.

Keywords: Metal-organic frameworks; MOFs; Hydrogen adsorption; Density functional theory

1. Introduction

Microporous metal-organic frameworks (MOFs) are crystalline compounds formed through the self-assembly of metal-ions or metal-clusters and various bridging organic ligands [1]. Yaghi et al. claimed that a series of isoreticular MOFs (IRMOFs) having zinc oxo acetate clusters and aromatic organic linkers could uptake hydrogen significantly at both low and room temperature [2]. They showed also that Zn ions were the primary adsorption sites and organic linkers also could contribute to the additional hydrogen adsorption, which was supported by inelastic neutron scattering experiments. Since then various MOFs have been investigated and their design strategies have been suggested toward promising hydrogen storage materials to meet the economic capabilities in the DOE standards [3]. However, the key structural features of MOFs to enhance adsorption amount of hydrogen are not found until now except that the presence of the aromatic rings of the organic linkers is seemingly favorable [4–11]. Consequently, the understanding of the mechanism of hydrogen adsorption into MOFs including interactions between adsorbed hydrogen molecules is highly required.

Previous theoretical works have been directed at investigating adsorption energy of hydrogen into the host frameworks. For example, Okamoto et al. found the non-repulsive intermolecular distance between two hydrogen molecules and showed the way of adsorption energy estimation using the vertical orientation of hydrogen molecule on graphene plane based on the Møller-Plesset (MP2) methodology [12]. But in this work the binding energy for hydrogen adsorption was overestimated as it was not calibrated by basis set superposition error (BSSE) correction. Later, Hübner et al. considered the BSSE correction for the adsorption energy of hydrogen on benzene with the calibrated value of −0.93 kcal/mol [13]. Furthermore they investigated the influence of the functional groups of benzene ring on hydrogen adsorption by setting up a

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model system of lithium terephthalates. However, this approach to mimic the environment of MOFs seems to be insufficient to investigate fully the geometric and electronic perturbation of MOFs for hydrogen adsorption. Recently, Ceder et al. reported elegant results on the hydrogen adsorption into MOFs by density functional theory (DFT) calculation [14]. They investigated adsorption sites of hydrogen on MOF-5 and found the stability of adsorption depends on the adsorption sites, but did not consider the functional dependency and the interaction between adsorbed hydrogen molecules.

The inelastic neutron scattering (INS) method has been used to characterize the adsorption of inert gases [15] or hydrogen [16] on MOFs. For the considered adsorbates, the observed adsorption sites were similar to each other, and the relative binding strength was measured.

We carried out DFT calculations on the system consisting of hydrogen molecules and benzene or MOF-5 as the adsorbents. The functional dependency and the interaction between adsorbed hydrogen molecules were also considered in our calculation. The main aims of this study are as follows. (1) The screening of the appropriate functionals and their validation to study the adsorption of hydrogen into MOF-5. (2) Characterization of hydrogen binding sites in MOF-5. (3) Comparison of hydrogen adsorption on benzene with that on MOF-5. (4) Understanding hydrogen adsorption mechanism into MOFs including interaction between adsorbed hydrogen molecules.

2. Methods

Our calculation of hydrogen adsorption into MOFs was focused on MOF-5, one of the most widely studied MOFs with relatively simple structures. In order to investigate the hydrogen adsorption into MOF-5 using DFT calculation, we considered three computational aspects carefully. First, the adequate functionals should be selected to represent the interaction between the adsorbate and adsorbent properly. Second, the model structure mimicking the real adsorption system should be constructed effectively and adequately. Finally, the pair of the first and the second hydrogen molecules adsorbed should be allocated and optimized systematically on the MOF-5 framework surface.

All of the theoretical calculations were performed by DMol^3 program in the MS Modeling 3.1^{TM} package [17], which is the quantum mechanical code using density functional theory (DFT). The double numeric polarization basis set [18] was used and any pseudopotential representation for the special treatment of core electrons was not used in our calculations.

2.1. Choice of adequate functional for hydrogen

To determine the adequate functionals and to validate their reliability, eight kinds of generalized gradient approximation (GGA) level density functionals (BP, BOP, BLYP, PBE, RPBE, VWN-BP, PW91 and HCTH [19–26]) were examined by calculating the interaction energy between hydrogen and benzene molecules. After comparison of our results with the data from MP2 level calculation on the interaction of hydrogen with benzene [27], the three functionals (HCTH, PW91 and PBE) were chosen and utilized for the investigation on the adsorption of hydrogen molecules into MOF-5.

2.2. Model buildup for hydrogen adsorption

The unit cell of MOF-5 (Fig. 1A) contains eight $Zn_4O(BDC)_3$ (BDC = benzenedicarboxylate) formula units which is too large for the calculation of every possible configuration of the first and second adsorbed hydrogen pairs. To save computation time we constructed the simplified cluster model (Fig. 1B), which is a side of the crystal structure of MOF-5 with 10 BDCs replaced by acetate groups, $(CH_3COO)_5Zn_4O(BDC)Zn_4O(CH_3COO)_5$. Our approach to construct the model is similar with the previous work [28], but our model could present a seamless representation including metal center and organic linker for tracing all of the possible adsorption positions using single model structure. All possible adsorption sites in our model were classified as metal site, carboxylato site and ring site as shown in Fig. 1B.

2.3. Assessment of first adsorption energy for hydrogen

The initial configuration was constructed using one randomly oriented hydrogen molecule. The number of the initial structure was more than 10 independent hydrogen-MOF-5 complexes per each site (metal site, carboxylato site and ring site). Local density approximation (LDA) level functional was adopted for the initial optimization of geometry to reduce the computational cost. When the duplicated configurations and the unstable binding ones were found, they were excluded for further calculation. These processes resulted in 14 distinct and stable structures that were regarded

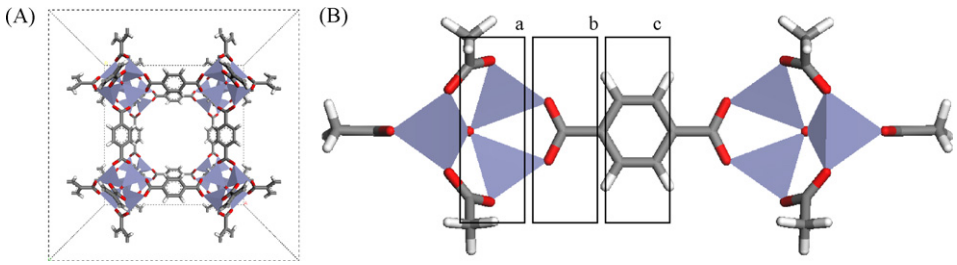

Fig. 1. The structures for MOF-5. (A) The unit cell of MOF-5 which consists of metal-clusters and organic linkers is represented as eight Zn_4OL_3 (L = organic linker) formula units. (B) Adsorption positions are classified into three positions: (a) metal site, (b) carboxylato site and (c) ring site.