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The optimal binding sites of CH_4 and CO_2 molecules on the metal-organic framework MOF-5: ONIOM calculations

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Abstract

Optimal binding sites and its corresponding binding energies between MOF-5 clusters and small guest molecules, CH_4 and CO_2, were investigated using the ONIOM method with different levels of quantum chemical calculations. The clusters were validated using three different sizes of the MOF-5 clusters, SINGLE, DOUBLE and TRIPLE consisting of $(Zn_4O)_2(COOCH_3)_{10}(COO)_2C_6H_4$, $(Zn_4O)_3(COOCH_3)_{14}(COO)_4(C_6H_4)_2$ and $(Zn_4O)_4(COOCH_3)_{18}(COO)_6(C_6H_4)_3$ units, respectively. Guest molecules were assigned to lie in the configurations parallel (||) and perpendicular (⊥) to linker (LINK) and corner (CORN) domains of the clusters. The ONIOM(MP2/6-31G**:HF/6-31G**) with the corrections due to the basis set superposition errors was found to be the optimal choice for the investigation of these systems. Strong effects of cluster size were found for the CO_2/MOF-5 complexes, i.e., the SINGLE cluster is sufficient to represent interactions with CH_4, but the interaction with CO_2 requires the TRIPLE model. The optimal binding sites of guest molecules as well as their orientations in the cavity of the MOF-5 are CORN⊥ for both CH_4 and CO_2 with the corresponding binding energies of -3.64 and -9.27 kJ/mol, respectively.

Keywords: Metal-organic frameworks; MOF-5; Quantum calculations; ONIOM; Methane; Carbon dioxide

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1. Introduction

Metal-organic frameworks (MOFs) are a new class of porous materials which becomes a promising target for gas adsorption, storage and separation [1–3]. Attempts to use alternative fuels such as hydrogen and methane instead of the conventional fuels such as gasoline and diesel have raised the studies of storage applications for such MOFs [4]. Moreover, MOFs have been utilized for separation and purification of gas mixtures ($H_2/CO_2/CH_4$). Yaghi and his group introduced the first stable crystal structure of the MOF-5 and generated series of the iso-reticular metal-organic frameworks (IRMOFs) [5–8]. The structure of the IRMOFs composes of basic zinc acetate unit ($Zn_4O(CO_2)_6$) and linking units (LINK) which are rigid linear dicarboxylate groups. Both units are strongly bonded providing a well-defined structure in which different linking units are possible. In view of an advantage of the modification of such linking units, the MOFs are considered to be the most powerful targets for new storage media in the near future. The understanding of guest–host interactions as well as related properties at molecular level is the key of

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success to design and discover new class of materials and becomes the main goal of this study.

Some attempts have been made using quantum chemical calculations to study H_2–MOF-5 interaction. Sagara et al. [9,10] calculated the binding energy based on the second-order Møller–Plesset perturbation theory (MP2) with some models of linker and corner sites. The results show that the binding energy at the corner site (~6–7 kJ/mol) is a little bit stronger than once at the linker site (~4–5 kJ/mol). In addition, the investigation of Lee et al. [11] using density functional theory (DFT) shows that the interaction between the simple benzene ring with H_2 is significantly changed when the benzene ring has been incorporated into the framework of MOF-5. Moreover, molecular dynamics simulations have been performed for predicting the adsorption sites of the H_2 [12,13] on the MOF-5 structure. The results again, indicate that hydrogen adsorbs rather strongly at the sites near the zinc acetate cluster and less strongly at the sites near the 1,4-benzenedicarboxylate linker. Yang and Zhong [14] also found that the selectivity of gas absorption is almost pressure-independent. These above results clearly show that the calculated results depend significantly on method and model employed.

To our knowledge, no experimental results are available on the position of preferential CH_4 and CO_2 sites, only neutron spectroscopic techniques proposes at least two different adsorption sites with considerably strong interaction [1]. In this study, different levels of the ONIOM method were applied to investigate the interaction between MOF-5 and small guest molecules, CH_4 and CO_2, aimed to understand their preferential binding site in the cavity of the MOF-5. The investigations were also extended to seek for the optimal method used, optimal cluster size of the MOF and the effect of the unbalance of the basis set.

2. Computational details

2.1. Initial structure of the MOF-5

A column consisting of two corners connected by a linker, $(Zn_4O)_2(COOCH_3)_{10}(COO)_2C_6H_4$, was generated (Fig. 1a). It was, then, used to build up the whole MOF-5 unit cell (Fig. 1b). Aimed to get reliable geometries of the MOF-5 relative to experimental data [5], the two fragments were fully optimized using various quantum mechanical methods (semi-empirical, HF, DFT) and basis sets. All optimization and energy calculation were performed using Gaussian03 [15].

2.2. The models

Seeking for an optimal compromise between fragment size vs. the required computer time, different quantum mechanical methods and fragment sizes were examined. The MOF-5 was represented by the three models shown in Fig. 2a. The fragments consisting of 1, 2 and 3 columns were named, for simplicity, as SINGLE, DOUBLE and TRIPLE, respectively.

For interaction with the linker (LINK), guest molecules were generated to move along the vector perpendicular to the molecular plane of the benzene ring at the Cg (see Fig. 1a for definition). For the DOUBLE and TRIPLE models, calculations were carried out only for one wing of the fragments. Here, two possible orientations of guest

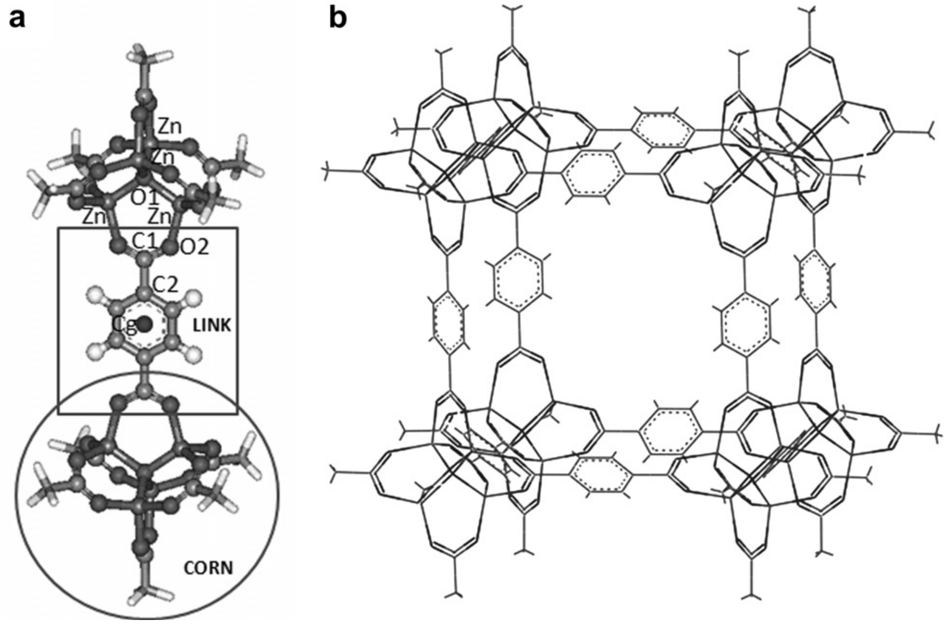

Fig. 1. (a) A single fragment of the MOF-5 consisting of two corners and one linker and (b) the whole MOF-5 unit cell which were generated as initial structures to be used in this study where Cg denotes center of mass of the benzene ring.