

Understanding Hydrogen Adsorption in Metal-Organic Frameworks with Open Metal Sites: A Computational Study

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Supporting Information

Density Functional Theory Calculations

To calculate the adsorption energies of hydrogen in MOF-505, density functional theory (DFT) calculations were carried out. Since DFT cannot give good results for weak Van der Waals interactions between hydrogen and the organic units, calculations were only performed for the adsorption energies of hydrogen with the inorganic clusters. In our calculations, the structural model of MOF-505 was constructed from the XRD data²⁰ using Materials Visualizer (Materials Studio, V3.1, Accelrys, Inc.). In weak Van der Waals complexes, because the binding is due to dynamical charge-charge correlations between two separated fragments, DFT calculations with local density approximation (LDA) usually fail to calculate these interactions accurately (Zhang et al., *J. Chem. Phys.* 1997, *107*, 7921-7925), while the generalized gradient approximation (GGA) retains the correct features of LDA and combines them with the inhomogeneity features, which are supposed to be the most energetically important. Many investigations, such as Wu et al. (*J. Chem. Phys.* 2001, *115*, 8748-8757) and Tran et al. (*J. Phys. Chem. B.* 2002, *106*, 8689-8696), have shown that the results of GGA depend strongly on the exchange-correlation functional used. They suggest that functionals obeyed the Lieb-Oxford bound, such as PBE developed by Perdew et al. (*Phys. Rev. Lett.* 1996, *77*, 3865) and PW91 by Perdew and Wang (*Phys. Rev. B.* 1992, *45*, 13244), are best functionals to model the weak interactions. Thus, in this work, PBE exchange-correlation functional coupled with the precise numerical basis set DNP (double numerical plus polarization) was used. In our calculations, MEDIUM quality mesh size was employed, and three-dimensional periodic boundary conditions were applied to the unit cell, which was described in rhombohedral space group R-3m with lattice length parameters $a=b=18.4826$ and $c=24.7130$ Å, angle parameters $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$. In the calculations, the atoms of the crystal lattice were assumed to be immobile. After the framework was built, a H₂ molecule was added to several positions around an inorganic unit Cu₂(CO₂)₄ and allowed to move during the optimizations. All of the calculations were performed using DMol³ as implemented in the Materials Studio package.¹⁹

Atomic partial charges calculations for MOF-505

In GCMC simulations, the atomic partial charges of MOF-505 are required as input parameters. They were calculated using the model cluster of MOF-505 shown in Figure S1. The terminations were saturated with methyl groups. In this work, the electrostatic charges were used as the atomic partial charges, and the ChelpG method, developed by Breneman and Wiberg (*J. Comp. Chem.* 1990, *11*, 361-373), was adopted in this work, which is recognized as the most popular and reliable

electrostatic charge calculation method (Heinz, H.; Suter, U. W. *J. Phys. Chem. B.* 2004, *108*, 18341-18352; Maciel, G. S.; Garcia, E. *Chem. Phys. Lett.* 2005, *409*, 29-33). Thus, based the ChelpG method, DFT calculations using the unrestricted B3LYP functional were carried out to compute the atomic partial charges, and two kinds of basis sets were adopted. The first one is using 6-31+G* for all the atoms in the cluster. This basis set has been used for calculating atomic partial charges for MOF-5.¹⁵ The other one is to use the LANL2DZ basis set for atom Cu and 6-31+G* for the rest atoms. For heavy atoms, effective core potential (ECP) is often choiced in ab initio calculations to reduce the amount of the necessary computation. LANL2DZ is a collection of double- ζ basis sets, which is one of the most common ECP basis sets for complexes involving transition metal elements (Davidson, E. R.; Clark, A. E. *J. Phys. Chem. A.* 2002, *106*, 7456-7461; Foguet-Albiol et al. *Angew. Chem. Int. Ed.* 2005, *44*, 897-901). All the calculations were carried out using GAUSSIAN 03 suite of programs (GAUSSIAN 03, 2003, Gaussian, Inc.). The calculated results are listed in Table S1. Since the two basis sets give similar results, those from the latter were adopted in this work.

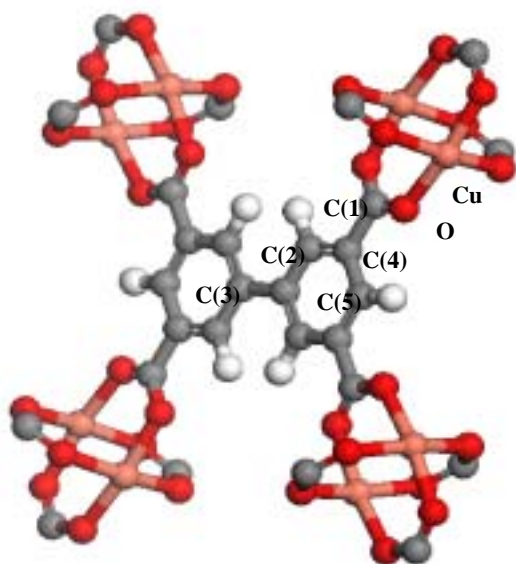


Figure S1. Model cluster of MOF-505 used for the calculation of atomic partial charges.

Table S1. Atomic Partial Charges in Cluster Based on DFT/B3LYP Level (unit of e)

Basis set	Cu	O	C(1)	C(2)	C(3)	C(4)	C(5)	H
6-31+G*	1.083	-0.645	0.724	-0.166	0.098	0.030	-0.134	0.118
6-31+G* + LANL2DZ	1.106	-0.656	0.733	-0.167	0.098	0.032	-0.136	0.120

GCMC Simulation

GCMC simulations were performed using standard algorithms. The simulation cell consists of $2 \times 2 \times 1$ unit cells of the MOF-505. The structure of the unit cell was constructed the same as that in our DFT calculations. The cutoff radius was set to 12 Å. Periodic boundary conditions were applied

in all three dimensions. For each state point, GCMC simulation consisted of 1×10^7 steps to guarantee equilibration followed by 1×10^7 steps to sample the desired thermodynamic properties. The program for GCMC simulations of adsorption of fluids in porous materials was developed by our group and has been verified in our previous work.¹⁸ The program was modified to be applicable to more complex materials such as MOF-505 in this work. To estimate the statistical uncertainty, the production phase of each state point was divided into 10 blocks and the standard deviation of the block average was calculated. The uncertainties on the final results, including the ensemble averages of the number of adsorbate molecules in the simulation cell and the total potential energy, were estimated to be within $\pm 2\%$.

Force Fields and the Parameters

Force fields play an important role in molecular simulations. In this work, an all-atom representation was adopted for both hydrogen and the atoms of the MOF-505 materials. Hydrogen was treated as a diatomic molecule modeled by a Lennard-Jones (LJ) core located at the center of mass of it and three partial charges with two ($q=0.468\ e$) located at H atoms and one ($q=-0.936\ e$) at the center between two H atoms. The LJ parameters for hydrogen molecule are $\sigma_{H_2}=0.2958\ \text{nm}$ and $\varepsilon_{H_2}/k=36.7\ \text{K}$ with hydrogen bond length of $0.074\ \text{nm}$ (Marx, D.; Nielaba, P. *Phys. Rev. A*. 1994, 45, 8968). Quadratic Feynman-Hibbs (FH) effective potential^{23, 24} was adopted to account for quantum effect on the hydrogen adsorption at low temperature. At this order in \hbar^2 (\hbar is the Planck constant), the quantum effect was applied to all the LJ interactions, with the contribution of the quadrupole interactions being negligible.²³ Above temperature of 20 K, this effective potential was demonstrated to well reproduce the results obtained by the path-integral formalism (Chakravarty et al. *J. Chem. Phys.* 1998, 109, 2123-2129), and it has also been successfully used to simulate the adsorption of hydrogen in carbon nanotubes²³ and carbon nanohorns,²⁴ and the results are in good agreement with the corresponding experimental data.

As to the interactions between hydrogen molecules and the atoms in MOF-505, various all-atom force fields have been considered, such as the all-atom universal force field (UFF) of Rappe et al. (*J. Am. Chem. Soc.* 1992, 114, 10024-10035), the all-atom DREIDING force field of Mayo et al. (*J. Phys. Chem.* 1990, 94, 8897-8909), and the all-atom OPLS force field (OPLS-AA) of Jorgensen et al.²⁵ Since the OPLS-AA force field can distinguish the types of atoms of the MOF materials in more details and has been used to model adsorption isotherms of Ar in MOFs by Vishnyakov et al. (*Nano Lett.*, 2003, 3, 713-718) and H₂ in MOFs in our previous work,¹⁸ it was also adopted here as the force field describing the interactions between hydrogen molecules and the atoms in MOF-505. Quadratic Feynman-Hibbs (FH) effective potential is also used for all the LJ interactions between H₂ molecules and MOF-505 framework. Since the parameters of the OPLS-AA force field were developed in conjunction with Monte Carlo simulations by computing thermodynamic and structural properties for pure organic liquids with the standard combining rules of $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$ and $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$, the existing parameters may not properly represent the interactions of the atoms of the solid MOF

materials with H₂. Therefore, the energy parameters of oxygen and copper were adjusted to give better representation of the experimental adsorption isotherm of hydrogen in MOF-505 at 77 K²⁰ as shown in Table S2.

Table S2. Potential parameters for the atoms in MOF-505.

Atom	OPLS-AA force field parameters	
	σ (nm)	ϵ/k (K)
Cu	0.311 ^a	95.76 ^b
O _{carboxyl}	0.296 ^c	63.41 ^b
C _{Carboxyl}	0.375 ^c	52.84 ^c
C _{Benzene}	0.355 ^c	35.23 ^c
H _{Benzene}	0.242 ^c	15.10 ^c

a Taken from the all-atom UFF force field.

b Obtained in this work (totally two).

c Taken from the OPLS-AA force field of Jorgensen et al.²⁵