Molecular Simulation of Adsorption and Diffusion of Hydrogen in Metal-Organic Frameworks

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Supporting Information

GCMC Simulation

GCMC simulations are performed using standard algorithms. The simulation cell is cubic consisting of 2×2×2 elementary cells of the IRMOF crystal lattice and the structural model of a unit cell of IRMOF was constructed from XRD data[16] using Materials Visualizer (Materials Studio, V3.1, Accelrys, Inc.). The unit cells of IRMOFs concerned are all composed of eight formula units, and the side lengths of which are 25.832, 30.092 and 25.614 Å for IRMOFs-1, -8 and –18, respectively. The cutoff radius is set to half of side length of the corresponding unit cell. Periodic boundary conditions are applied in all three dimensions. For each state point, GCMC simulation consists of 1×10^7 steps to guarantee equilibration followed by 1×10^7 steps to sample the desired thermodynamic properties. To estimate the statistical uncertainty, the production phase of each state point is divided into 10 blocks and the standard deviation of the block average is calculated. The statistical uncertainties for simulations of hydrogen adsorption in IRMOF-1 are shown in Figure S1. The program for GCMC simulations of adsorption of fluids in porous materials is developed by our group and has been verified in our previous work.[18] To further validate it for adsorption in IRMOFs, it was used to repeat the adsorption isotherm of methane in IRMOF-1 using the same force fields and the parameters as adopted by Düren et al.,[12] and very good agreement was obtained between our simulations and theirs.

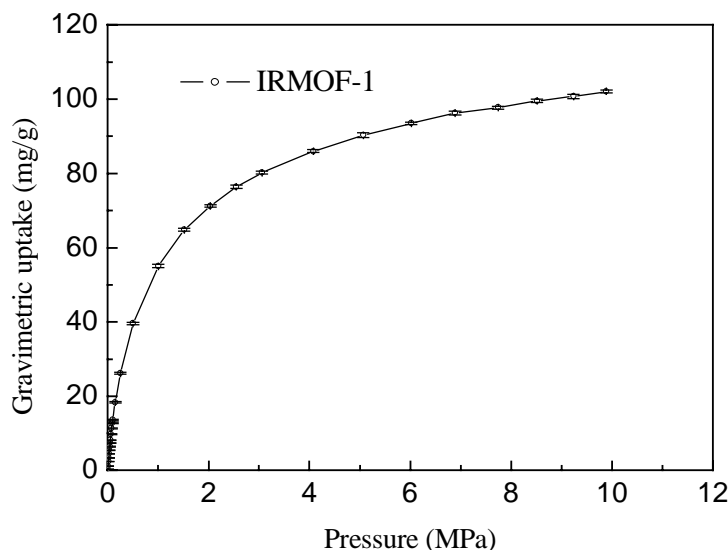Figure S1. The simulated isotherm for hydrogen in IRMOF-1 at 77 K and P=0-10MPa. (Error bars indicate the statistical uncertainties).

Force Fields and the Parameters

Force field plays an important role in molecular simulations. In this work, an all-atom representation was adopted for both hydrogen and the atoms of the IRMOF materials. Hydrogen was

modeled as a two-site LJ fluid. Although Cracknell (*Phys. Chem. Chem. Phys.* 2001, *3*, 2091-2097) has proposed a pair of two-site LJ parameters for hydrogen, the energy parameter was determined to give the same isosteric heat of adsorption on a graphite surface as the single-site model of Buch (*J. Chem. Phys.* 1994, *100*, 7610-7615), and thus the parameters may not be suitable for describing the adsorption of hydrogen in IRMOFs. Therefore, we refitted the two-site LJ parameters for hydrogen based on fitting the PVT curve of bulk hydrogen (Vargaftik, N.B. *Tables of Thermophysical Properties of Liquids and Gases*, John Wiley & Sons: New York, 1975). The LJ parameters obtained are σ_{HH} =0.272 nm and ε_{HH}/k =10.00 K with hydrogen bond length of 0.074 nm. The experimental values together with the simulated results using the new pair of parameters and that of the two-site parameters of Cracknell, and the single-site LJ parameters of Buch are shown in Figure S2. Obviously, the new two-site LJ parameters give improved reproduction of the experimental data. Since we will also simulate the diffusivity of hydrogen in IRMOFs, it is useful to validate if the pair of parameters obtained in this work can reproduce the self-diffusion coefficients of bulk hydrogen well. The experimental self-diffusion coefficient data and the simulated results using the new pair of parameters and that of Cracknell, and Buch are reported in Table S1. Evidently, the new LJ parameters can predict the self-diffusion coefficients of bulk hydrogen much better than the existing LJ parameters. As a result, the new two-site LJ parameters can be used for simulating both adsorption and diffusivity of hydrogen in IRMOFs.
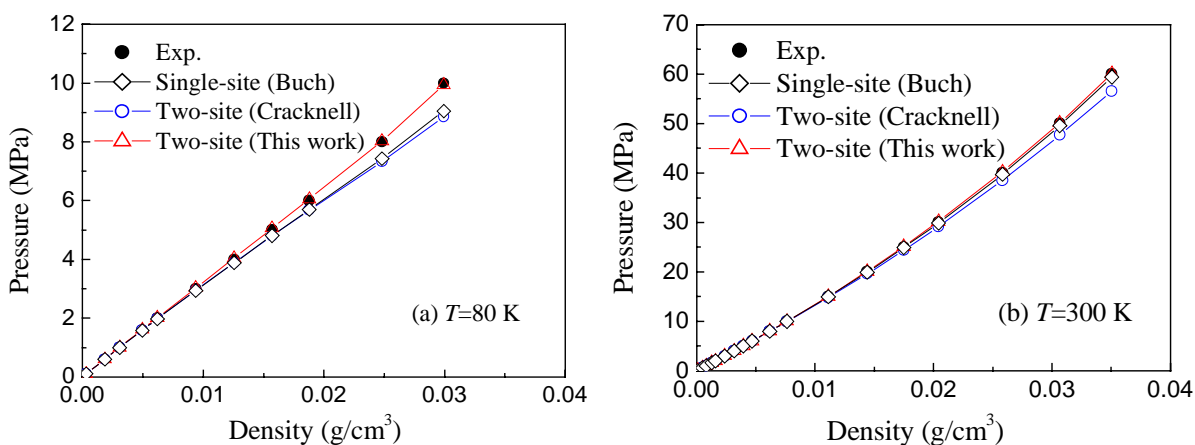

Figure S2. Experimental and simulated dependency of pressure on the density of bulk hydrogen obtained with different potential parameters.

Table S1. Experimental and simulated self-diffusion coefficient D_s (in unit of 10^{-4} m^2/s) of bulk hydrogen at ambient pressure.

T (K)	D_s (exp.) [a]	Single-site (Buch)		Two-site (Cracknell)		Two-site (This work)	
		D_s	AAD%[b]	D_s	AAD%	D_s	AAD%
77.5	0.133	0.141	6.0	0.153	15.0	0.142	6.8
85.0	0.172	0.160	7.0	0.188	9.3	0.171	0.6
90.3	0.192	0.176	8.3	0.226	17.7	0.195	1.6
273.0	1.285	1.208	6.0	1.340	4.2	1.307	1.7
293.2	1.400	1.291	7.8	1.455	3.9	1.371	2.1
average			7.0		10.0		2.6

a   For T=77.5 and 85 K, data from *J. Chem. Phys.* 1962, *36*, 1235-1237; for other temperatures, data from the book of Vargaftik.

b $AAD\% = \left| D_{simu.} - D_{exp.} \right| / D_{exp.} \times 100$

As to the interactions between hydrogen molecules and the atoms of the solids, 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.[19] Since the OPLS-AA force field can distinguish the types of atoms of the IRMOF materials in more details and has been used to model adsorption isotherms of Ar in MOFs by Vishnyakov et al.,[11] it was adopted as the force field describing the interactions between hydrogen molecules and the atoms of the solid materials. However, 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 $\sigma_{ij} = \left(\sigma_i \sigma_j \right)^{1/2}$ and $\varepsilon_{ij} = \left(\varepsilon_i \varepsilon_j \right)^{1/2}$, the existing parameters may not properly represent the interactions of the atoms of the solid MOF materials with H$_2$. Therefore, the energy parameters of oxygen and methyl hydrogen and carbon were adjusted to give better representation of the experimental adsorption isotherms of hydrogen in IRMOFs-1 and -18,[7] as shown in Table S2.

Table S2. Parameters of the atoms of the IRMOF materials.

Atom	OPLS-AA force field parameters	
	σ (nm)	ε/k (K)
O	0.296[a]	126.82[b]
$C_{Carboxyl}$	0.375[a]	52.84[a]
$C_{Benzene}$	0.355[a]	35.23[a]
C_{Alkane}	0.350[a]	20.03[b]
$H_{Benzene}$	0.242[a]	15.10[a]
H_{Alkane}	0.250[a]	7.25[b]
Zn	0.246[c]	62.40[c]

a Taken from the OPLS-AA force field of Jorgensen et al.[19]

b Obtained in this work (totally three).

c Taken from the all-atom UFF force field.

MD Simulation

In this work, a constant temperature MD by momentum scaling method was used to investigate the self-diffusivity of H_2 in the three IRMOF materials. The simulation cell consists of 2×2×2 to 4×4×4 elementary cells of the IRMOF crystal lattice to ensure at least fifty hydrogen molecules are accommodated in the cell, and the structural model was constructed using the experimental XRD data as done in our GCMC simulations. Periodic boundary conditions were applied in all three dimensions. The six-value second-order and five-value first-order Gear predictor-corrector algorithms were applied to solve the center of mass translational motion and the angular rotational motion in quaternion, respectively. The adsorbed hydrogen densities obtained in our previous GCMC simulations were used in MD simulations. Since we started from a random configuration of fluid molecules in the porous materials, some of them may overlap with each other or with the atoms in IRMOFs, which may exert extremely large forces and leads to a breakdown of the integration algorithms. To avoid this problem, the initial configuration was allowed to relax through a Monte Carlo method. The finally obtained configuration was then used as initial configuration of a MD run under the same temperature and overall density. MD simulation consists of $2×10^5$ steps to guarantee the equilibration for the system followed by $2×10^6$ steps to sample the diffusion properties of interest. The time-step is taken as 2 fs. The self-diffusion coefficient D_s was calculated by the mean square particle displacement (MSD) method. For each state point, the average diffusivity D_s and its uncertainty are calculated from the results of 10 independent simulation runs with different initial configurations. The simulated diffusivities D_s and their statistical uncertainties for hydrogen in IRMOF-1 are shown in Figure S3. To calculate the activation energy of self-diffusion at infinite dilution, MD simulations were performed at T=77, 120 and 160 K to calculate three D_s, then the activation energy was calculated using Arrhenius equation.
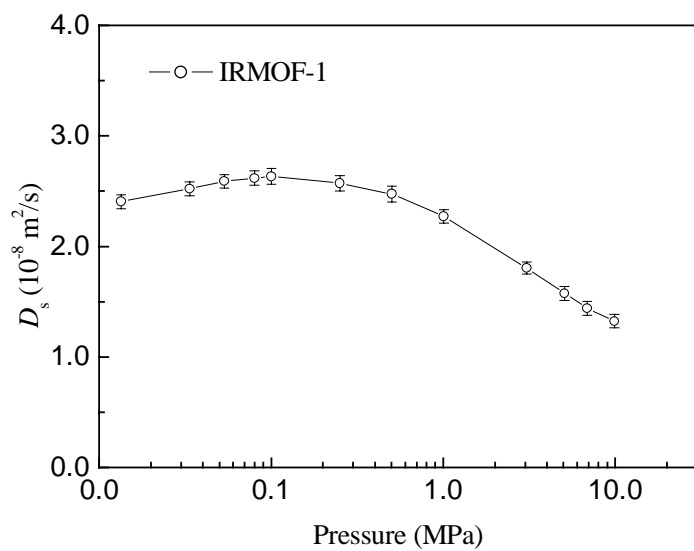
Figure S3. The dependence of self-diffusivity of hydrogen in IRMOF-1 on pressure at T=77 K. (Error bars indicate the statistical uncertainties)