

Article

Effective Thermal Conductivity of MOF-5 Powder under a Hydrogen Atmosphere

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Academic Editors: Qinjun Kang and Li Chen

Received: 8 September 2015 / Accepted: 3 November 2015 / Published: 6 November 2015

Abstract: Effective thermal conductivity is an important thermophysical property in the design of metal-organic framework-5 (MOF-5)-based hydrogen storage tanks. A modified thermal conductivity model is built by coupling a theoretical model with the grand canonical Monte Carlo simulation (GCMC) to predict the effect of the H₂ adsorption process on the effective thermal conductivity of a MOF-5 powder bed at pressures ranging from 0.01 MPa to 50 MPa and temperatures ranging from 273.15 K to 368.15 K. Results show that the mean pore diameter of the MOF-5 crystal decreases with an increase in pressure and increases with an increase in temperature. The thermal conductivity of the adsorbed H₂ increases with an increased amount of H₂ adsorption. The effective thermal conductivity of the MOF-5 crystal is significantly enhanced by the H₂ adsorption at high pressure and low temperature. The effective thermal conductivity of the MOF-5 powder bed increases with an increase in pressure and remains nearly unchanged with an increase in temperature. The thermal conductivity of the MOF-5 powder bed increases linearly with the decreased porosity and increased thermal conductivity of the skeleton of the MOF-5 crystal. The variation in the effective thermal conductivities of the MOF-5 crystals and bed mainly results from the thermal conductivities of the gaseous and adsorption phases.

Keywords: GCMC; effective thermal conductivity; H₂ adsorption; MOF-5 powder bed; gaseous thermal conductivity

1. Introduction

As a type of clean energy, hydrogen is expected to be used in hydrogen vehicles, but hydrogen-based energy cycles require hydrogen storage as the key technology. A promising hydrogen storage material is the metal-organic framework-5 (MOF-5) which features high surface area and permanent porosity; specifically, this material can absorb up to 7.1 wt% hydrogen at 77 K and 40 bar [1]. MOF-5 is composed of 1,4-benzenedicarboxylate organic linkers and Zn₄O tetrahedral clusters treated as secondary building units [2]. However, the process of H₂ adsorption is an exothermic reaction, with the heat of H₂ adsorption ranging from 2 kJ/mol to 5 kJ/mol [3], and the amount of H₂ adsorption decreases rapidly with an increase in temperature. Heat release should be timely to avoid heat accumulation. Effective thermal conductivity is an important criterion to judge how fast the heat of adsorption is dissipated and to determine how to maintain a low temperature in a fuel storage tank during hydrogenation.

The effective thermal conductivity of MOFs has attracted the attention of many researchers. Huang *et al.* [4,5] studied the thermal conductivity of a MOF-5 crystal and found it to be 0.32 W/m K at a temperature of 300 K in a vacuum; they also found a very weak relation between the thermal conductivity of the MOF-5 crystal and temperature, particularly when the temperature is above 100 K. In fact, MOF-5 powders in a tank are very loose and consist of small crystallites. The effective thermal conductivity of MOF-5 powders is less than the single-crystal value because of their large pore sizes and high free volumes. Purewal *et al.* [6,7] adopted two representative ways to increase the effective thermal conductivity of MOF-5 powders in a storage tank. The first method is powder densification, which can yield a 350% increase in volumetric H₂ density compared with powders with a density of 0.5 g/cm³. However, mechanical compaction causes the pores of MOF-5 crystals to collapse easily and thus results in the low porosity of these crystals because of the small surface area of the compression process [8]. These phenomena, which depend on compression by storage pressure under high pressure, can be avoided by directly placing MOF-5 powders as adsorbents in fuel storage tanks. The second method is synthesizing MOF-5 with natural graphite (ENG). MOF-5 with ENG can improve the effective thermal conductivity of MOF-5 powders. However, this method slightly degrades the H₂ adsorption capacity. MOF-5 powders directly placed as adsorbents in fuel storage tanks can generally avoid these issues. Nevertheless, the varying effective thermal conductivities of the MOF-5 powder bed and crystals should be comprehensively investigated.

Effective thermal conductivity is related to adsorbate uptake, temperature, and pressure [9]. The amount of adsorption can be predicted with the grand canonical Monte Carlo (GCMC) simulation, which only requires macroscopic variables, such as temperature and pressure. Walton *et al.* [10] used GCMC simulation to simulate CO₂ adsorption in MOF-5 and reported that a step phenomenon occurs during the adsorption process. Zhang *et al.* [11] simulated H₂ adsorption in MOF-5 at 77 K at different pressures (0–1.0 bar) and obtained results that fit well with the experimental data; they then performed computer tomography on the MOF-5 at a molecular level. Yang *et al.* [12] combined GCMC simulation

and density functional theory in their study of hydrogen adsorption in MOF-505; they found that metal oxygen clusters are preferential adsorption sites for hydrogen.

The aforementioned studies mainly focus on improving the effective thermal conductivity of MOF-5 powders, measuring the thermal conductivity of MOF-5 crystals at different temperatures, and simulating the adsorption properties of MOF-5. In the process, these studies neglect the varying effective thermal conductivities of the MOF-5 powder bed and crystals during H₂ adsorption. Moreover, no model has been designed to predict the effective thermal conductivity of the H₂ adsorption bed. In the present work, a thermal conductivity model coupled with GCMC simulation is employed to predict the effective thermal conductivities of the MOF-5 crystals and powder bed at different pressures and temperatures under the H₂ atmosphere. The key factors of thermal conductivity and different gases are also studied.

2. Theoretical Modeling

2.1. Effective Thermal Conductivity

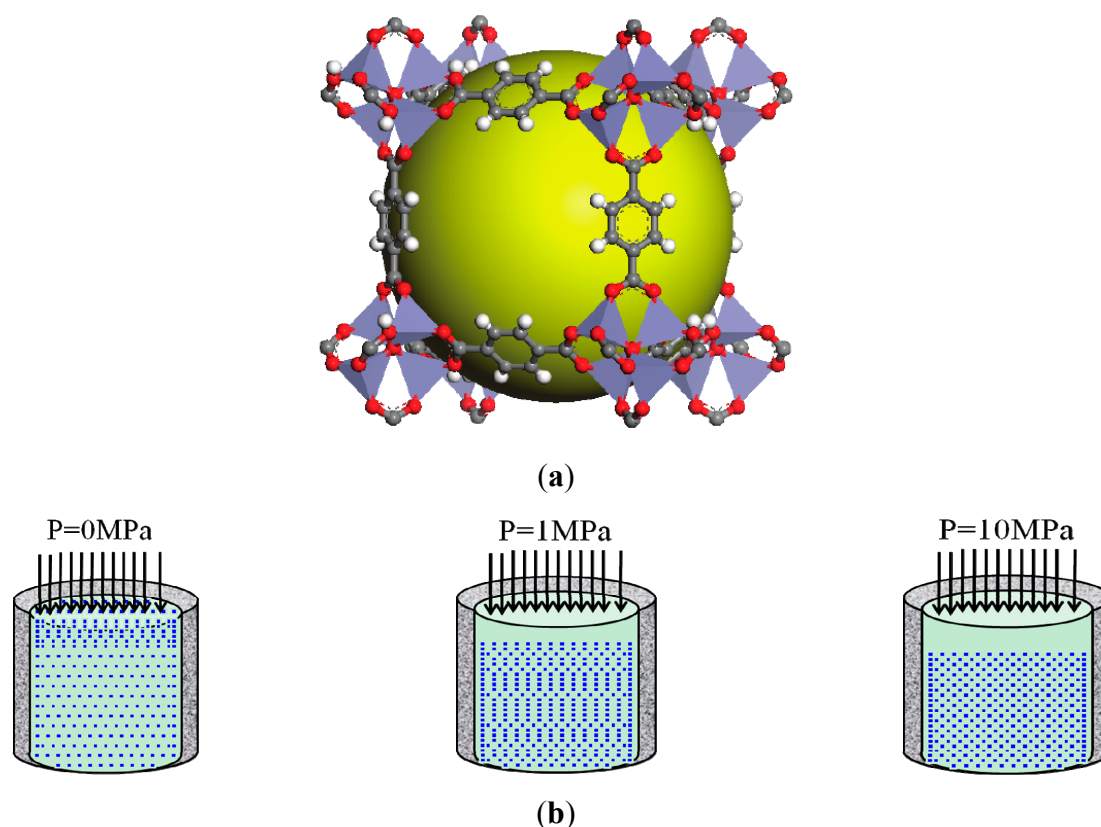


Figure 1. Structure of MOF-5 crystal and varying porosity at different pressures. (a) Structure of MOF-5 and its topology (ZnO₄ tetrahedral: blue polyhedra; benzene dicarboxylate linkers: O, red and C, black; pore: yellow sphere); (b) Varying bed porosity at different pressures.

The MOF-5 powder bed is composed of many cubic crystallites and a gaseous phase, as shown in Figure 1a. The porosity of the MOF-5 powder bed will decrease with an increase in pressure, as shown in Figure 1b. In this work, the following assumptions are made: the pore in the crystal does not experience

the collapse phenomenon at the study pressure range (0.01–50 MPa), and the relation between density and pressure is linear [7]. This relationship is expressed as

$$\rho = 0.13 + 0.006P \quad (1a)$$

$$\varepsilon = 1 - \frac{0.13 + 0.006P}{0.605} \quad (1b)$$

Where ρ is the density of the adsorption bed, P is the pressure in the adsorption bed, and ε is the porosity among the particles. Although MOF-5 features a regular crystal structure, many MOF-5 crystals are randomly distributed in the adsorption bed. Thus, the effective medium theory model is adopted [13].

$$(1 - \varepsilon) \frac{\lambda_{seff} - \lambda_{eff}}{\lambda_{seff} + 2\lambda_{eff}} + \varepsilon \frac{\lambda_g - \lambda_{eff}}{\lambda_g + 2\lambda_{eff}} = 0 \quad (2a)$$

Which can be solved as

$$\lambda_{eff} = \frac{\lambda_{seff}}{2} - \frac{\lambda_g}{4} + \frac{3\varepsilon\lambda_g}{4} - \frac{3\varepsilon\lambda_{seff}}{4} + \frac{(9\varepsilon^2\lambda_g^2 - 18\varepsilon^2\lambda_g\lambda_{seff} + 9\varepsilon^2\lambda_{seff}^2 - 6\varepsilon\lambda_g^2 + 18\varepsilon\lambda_g\lambda_{seff} - 12\varepsilon\lambda_{seff}^2 + \lambda_g^2 + 4\lambda_g\lambda_{seff} + 4\lambda_{seff}^2)^{\frac{1}{2}}}{4} \quad (2b)$$

Where λ_{eff} is the effective thermal conductivity of the adsorption bed, λ_g is the thermal conductivity of the gaseous phase, and λ_{seff} is the effective thermal conductivity of the MOF-5 crystal. The MOF-5 crystal comprises the skeleton of the MOF-5 and gaseous phase, and the MOF-5 crystal features a pore diameter of 1.12 nm [2]. A model of the effective thermal conductivities of MOF-5 crystals is used in [14] but without consideration of radiation.

$$\lambda_{eff} = \lambda_s + \lambda_g = \frac{\lambda_{g0}}{1 + 2\beta Kn} + \frac{\lambda_{MOF-5} \sqrt[3]{(1 - \varphi)}}{\mu} \quad (3)$$

Where λ_s is the thermal conductivity of solid MOF-5, λ_g is the gaseous thermal conductivity, and λ_{g0} is the gaseous thermal conductivity at 0.1 MPa and 298.15 K; then λ_{MOF-5} is the thermal conductivity of the MOF-5 skeleton, φ is the porosity of Cu-BTC crystal [6], μ is the tortuosity factor, β is the correction coefficient, and Kn is the Knudsen number. When the effect of adsorption is considered, the model can be corrected similarly to the model for water adsorption in zeolite [15]. This condition can be explained as follows. First, the condition of gas adsorption in MOF-5 is similar to that of water adsorption in a zeolite, with both conditions being physical adsorption. Second, the state of adsorption is assumed to be the boiling point in both the zeolite and the MOF-5. The effective thermal conductivity of a MOF-5 crystal is expressed as

$$\lambda_{seff} = \frac{\lambda_{g0}}{1 + 2\beta Kn} + \frac{\lambda_{MOF-5} \sqrt[3]{(1 - \varphi)}}{\mu} + \frac{\lambda_L \sqrt[3]{N(1 - \varphi) \frac{\rho_{skMOF-5}}{\rho}}}{\mu} \quad (4)$$

Where λ_L is the thermal conductivity of the adsorbed gas, which is assumed to be equal to the thermal condition at the boiling point at 0.1 MPa [16], and N is the amount of adsorption, which can be obtained from the results of the GCMC simulation. The GCMC calculation is performed in a static state, in which the adsorption heat is assumed to be completely released. Hence, we do not consider the chemical potential caused by changes in vibrational entropy, as mentioned in [11,12]. Then β is defined as

$$\beta = 2k(2 - \gamma) / [\gamma(k + 1)] \quad (5)$$

Where k is the ratio of the heat capacities of the gases and γ is the effectiveness of energy transfer between the gas molecule and the MOF-5 skeleton, respectively. Then Kn is defined as

$$Kn = \Lambda / d \quad (6a)$$

Where d is the mean pore diameter of the adsorbed MOF-5 structure, which can be obtained as follows [16]:

$$d = d_e \left[1 - \sqrt[3]{\frac{N \rho_{skMOF-5} (1 - \varphi)}{\rho_L \varphi}} \right] \quad (6b)$$

Where ρ_L is the density of the adsorbed phase, which is assumed to be equal to the density at the boiling point at 0.1 MPa; $\rho_{skMOF-5}$ is the density of the MOF-5 skeleton; d_e is the mean pore diameter of the MOF-5 structure as expressed in zeolite [15]; and Λ is the mean free path of the molecule, which is defined as

$$\Lambda = \Lambda_0 \frac{p_0}{p} \frac{T}{T_0} \quad (6c)$$

Where p_0 and T_0 refer to 0.1 MPa and 298.15 K, respectively; Λ_0 is the mean free path of gas under this reference condition. The final effective thermal conductivity of the MOF-5 crystal is expressed as

$$\lambda_{eff} = \frac{\lambda_{g_0}}{1 + 4k(2 - r)\Lambda_0 p_0 T / \left[r(k + 1) p T_0 d_e \left[1 - \sqrt[3]{\frac{N \rho_{skMOF-5} (1 - \varphi)}{\rho_L \varphi}} \right] \right]} + \frac{\lambda_{MOF-5} \sqrt[3]{(1 - \varphi)}}{\mu} + \frac{\lambda_L \sqrt[3]{N(1 - \varphi) \frac{\rho_{skMOF-5}}{\rho}}}{\mu} \quad (7)$$

The values of the main parameters are shown in Table 1.

Table 1. Constant parameters (the missed parameters of density and thermal conductivity in the reference are from REFPROP 4.0).

Parameter	Value	Unit	Reference
ρ_{N_2}	808.60	kg·m ⁻³	[16]
ρ_{H_2}	71.26	kg·m ⁻³	-
ρ_{CO_2}	1227.78	kg·m ⁻³	[16]
$\rho_{skMOF-5}$	2030	kg·m ⁻³	[6]
λ_{LN_2}	0.14429	W·m ⁻¹ ·K ⁻¹	-
λ_{LH_2}	0.10329	W·m ⁻¹ ·K ⁻¹	-
λ_{LCO_2}	0.21815	W·m ⁻¹ ·K ⁻¹	-
$\lambda_{g_0H_2}$	0.18488	W·m ⁻¹ ·K ⁻¹	-
$\lambda_{g_0N_2}$	0.025835	W·m ⁻¹ ·K ⁻¹	-
$\lambda_{g_0CO_2}$	0.01642	W·m ⁻¹ ·K ⁻¹	[17]
Λ_{wv0H_2}	1.278×10^{-7}	m	[18]

Table 1. Cont.

Parameter	Value	Unit	Reference
Λ_{wv0N_2}	6.28×10^{-8}	m	-
Λ_{wv0CO_2}	6.29×10^{-8}	m	-
φ	0.702	-	[6]
γ_{N_2}	1.92	-	-
γ_{H_2}	1.95	-	-
γ_{CO_2}	1.95	-	-
μ	1.57	-	-
k_{N_2}	1.4	-	-
k_{H_2}	1.4	-	-
k_{CO_2}	1.35	-	-
λ_{MOF-5}	0.75	$W \cdot m^{-1} \cdot K^{-1}$	-
d_e	1.12×10^{-9}	m	[2]

2.2. GCMC Models

2.2.1. Simulation Model

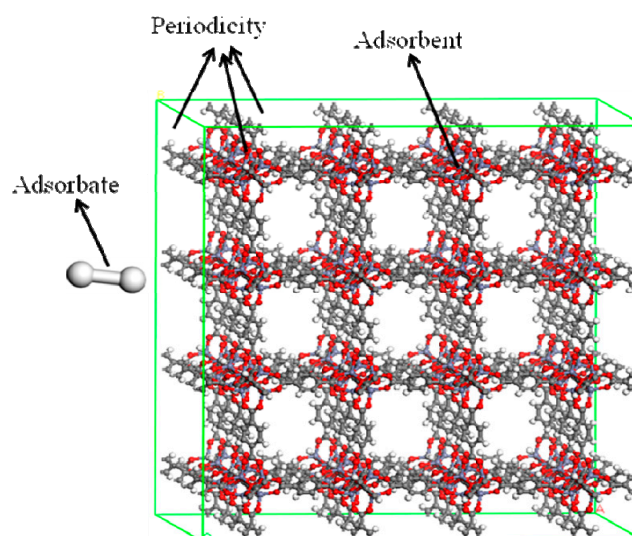


Figure 2. Computed physical model.

The amount of adsorption is numerically simulated using the GCMC method with constant chemical potential (μ), simulation box volume (V), and temperature (T). The temperature and pressure are treated as input parameters. Figure 2 shows the simulation box that includes eight unit cells. The size of the simulation box is $5.1788 \text{ nm} \times 5.1788 \text{ nm} \times 5.1788 \text{ nm}$. The MOF-5 adsorbent, which is treated as a rigid structure with atoms fixed at their crystallographic positions, is located inside the simulation box with a periodic boundary condition. The adsorbate H_2 is treated as a rigid single molecule. The MOF-5 and H_2 structures are built and optimized in the Materials studio packages [19] to satisfy the real material properties. The potential energy (U_{ij}) between atoms in the configurations is considered to calculate the interactions between two H_2 molecules or between the MOF-5 framework and the H_2 molecule; i and j

represent the interacting MOF-5 atoms or H₂ molecules. When i represents H₂ atoms, j can represent MOF-5 or H₂ atoms. The values of the Lennard–Jones (LJ) potential parameters of MOF-5 are adopted from the all-atom optimized potentials for liquid simulations (OPLS-AA) force field [20] and from the work of Yang *et al.* [21]. The detailed values are shown in Figure 3 and Table 2. The detailed potential parameters of H₂ are shown in Table 3. The potential parameters of N₂ and CO₂ are also shown in Table 3.

U_{ij} has two contributions: the LJ potential (U_{LJ}) and the electrostatic potential (U_{Eq}), which refers to the coulomb potential. Potential energy U_{ij} is calculated using Equation (8).

$$U_{ij} = U_{LJ} + U_{Eq} = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (8)$$

Where r_{ij} is the distance between atoms i and j ; ϵ_{ij} and σ_{ij} are the LJ depth and diameter, respectively; q_i and q_j are the partial charges of the interacting atoms; and ϵ_0 is the dielectric constant (8.85×10^{-12} F/m). Electrostatic interaction is conducted using the Ewald summation technique. The cutoff radius is set to 1.3 nm for the LJ interactions. All the LJ cross-interaction parameters are determined using the Lorentz–Berthelot mixing rules.

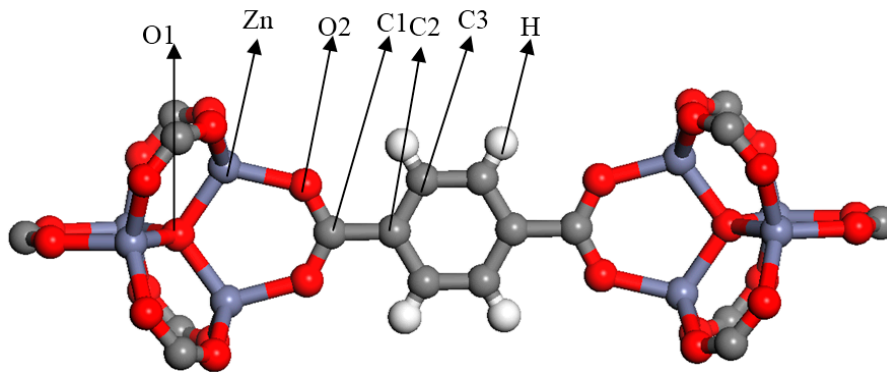


Figure 3. Model clusters for different atoms.

Table 2. New LJ parameters for MOF-5 atoms.

Atom Type	$\sigma(\text{\AA})$	$\epsilon/k_B (K)$		$q(e)$
		Hydrogen/Nitrogen	Carbon Dioxide	
C1	3.75 ^a	52.84 ^a	52.84 ^a	0.667 ^b
C2	3.55 ^a	35.23 ^a	28.18 ^b	0.072 ^b
C3	3.55 ^a	35.23 ^a	28.18 ^b	−0.132 ^b
O1	2.96 ^a	73.98 ^b	63.41 ^b	−1.846 ^b
O2	2.96 ^a	73.98 ^b	63.41 ^b	−0.724 ^b
H	2.42 ^a	15.10 ^a	15.10 ^a	0.140 ^b
Zn	2.46 ^c	62.40 ^c	62.40 ^c	1.501 ^b

^a Adopted from the OPLS-AA force field of Jorgensen *et al.* [20]; ^b Adopted from Yang *et al.* [21];

^c Adopted from the all-atom universal force field (UFF) force field (missing in the OPLS-AA force field) [22].

Table 3. LJ parameters and partial atomic charges for N₂, H₂, and CO₂ atoms.

Species	Atom	$\sigma(\text{\AA})$	$\epsilon/k_B (K)$	$q(e)$	Ref.
N ₂	N	2.598	36.7		[23]
H ₂	H	3.73	148		[24,25]
CO ₂	C	2.80	27.0	0.70	[26]
	O	3.05	79.0	−0.35	

2.2.2. Simulation Method

The GCMC method started with an initial configuration. The initial configuration is the state at which the size of the simulation box and the initial number of adsorbates are known and determined. The number of adsorbates and potential energy in the initial configuration (m) are N_m and U_m , respectively. The initial configuration is further updated with simultaneous procedures of random move, insertion, and deletion for the adsorbate molecule selected at the same probability of one of three. The detailed solution process can be found in [27]. The move, insertion, and deletion steps are repeated for 1×10^7 steps until the chemical potentials in the adsorbed and bulk phases are identical. Another 1×10^7 steps similar to the previous process are used to obtain the converged number of adsorbates and potential energy by means of averaging. After all the iterations converge, the final number of adsorbate molecules (N_{am}), adsorbate-adsorbate potential energy (U_{ff}), and adsorbate-adsorbent potential energy (U_{fs}) are obtained.

The adsorbate molecule only refers to the number of adsorption molecules in the simulation box. This number should be converted to the excess adsorption amount (N), which can be compared with the experimental data based on [28].

$$N = 1000 \left(\frac{N_{am} M_a}{N_a} - \rho_g V_{free} N_A \right) / (M_s M_a) \quad (9)$$

Where M_s , M_a , V_{free} , N_a , and N_A are the substance amounts of a single crystal cell (6159), relative molecular masses of adsorbates (2 for H₂, 14 for N₂, and 44 for CO₂), free volume of the single crystal cell ($1.37 \times 10^{-26} \text{ m}^3$), number of structure cells (eight), and Avogadro's constant (6.022×10^{23}), respectively; ρ_g is the gaseous density.

3. Results and Discussions

3.1. Model Validation

Figure 4a shows the simulated adsorption isotherm of the H₂ adsorption in MOF-5 at 298 K compared with the experimental data [29]. The simulated adsorption isotherm fits well with the experimental data at different pressures, with the standard deviation being less than 6.57%. The GCMC model in the present work is precise enough to let us learn further the H₂ adsorption behavior of MOF-5.

Figure 4b shows the simulated effective thermal conductivity of the MOF-5 powder under the N₂ atmosphere compared with the experimental data by Purewal *et al.* [6]. The calculated theoretical porosity of the adsorption bed is 0.43. However, the mechanical compaction leads the pores in the crystals to collapse slightly, which in turn leads to the decreased porosity of the MOF-5 crystal; hence,

the porosity in the powder bed is in fact higher than the theoretical calculation [6]. When the porosity is set to 0.63, the standard deviation is only 8.4%. The model in this work can be further used to study H_2 adsorption beds to a certain extent.

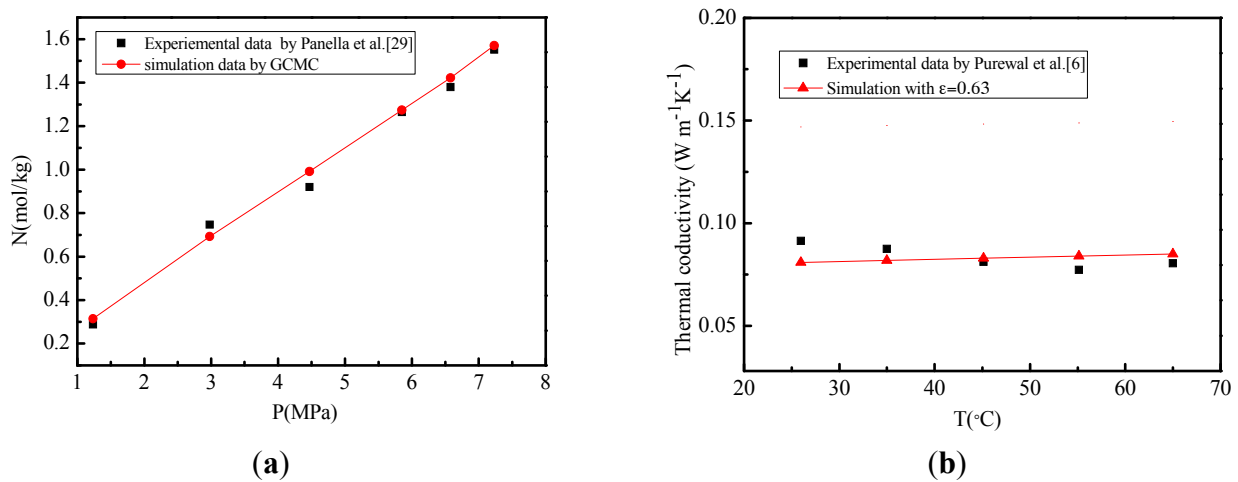


Figure 4. Comparison of simulated results and experimental data. (a) Comparison of simulated and experimental adsorption isotherm of H_2 in MOF-5 at 298 K; (b) Comparison of simulated and experimental thermal conductivity at different temperatures.

3.2. Effect of Amount of Adsorption on Pore Width

Figure 5 shows the mean pore diameter and the amount of adsorption in the MOF-5 crystal against hydrogen pressures ranging from 0.01 MPa to 50 MPa at 298.15 K. The plots indicate that the mean pore diameter is dependent on the hydrogen pressure. With an increase in pressure, the amount of H_2 adsorption increases and occupies the free volume. As a result, the mean pore diameter of the adsorbed MOF-5 crystal decreases. Figure 6 shows the varying mean pore diameter and the amount of adsorption in the MOF-5 crystal at temperatures ranging from 273.15 K to 368.15 K at 10 MPa. With an increase in temperature, the mean pore diameter increases, and the amount of adsorption decreases linearly. Accordingly, the mean pore diameter increases linearly.

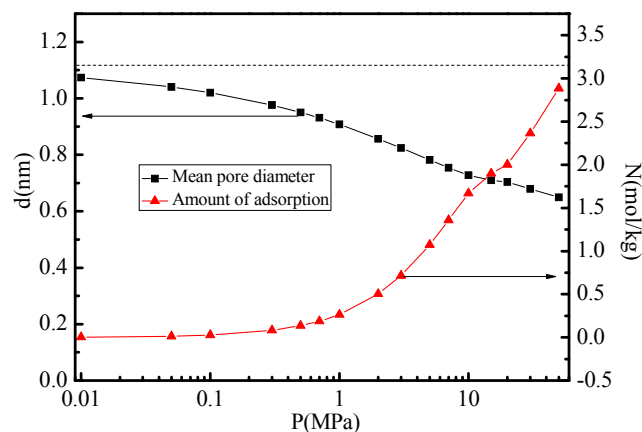


Figure 5. Varying mean pore diameter and amount of H_2 adsorption at different pressures and 298.15 K.

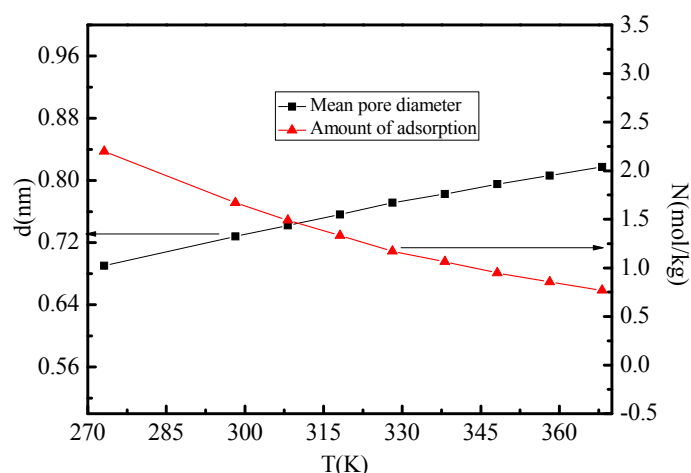


Figure 6. Varying mean pore diameter and amount of H₂ adsorption at different temperatures and 10 MPa.

3.3. Effect of Pressure

Figure 7 shows the effective thermal conductivities of the adsorbed MOF-5 crystals and bed at different pressures (0.01–50 MPa) and 298.15 K. The effective thermal conductivity of the MOF-5 crystals at the H₂ atmosphere increases in an “S” shape, as confirmed by the experimental data on zeolite K under the H₂ atmosphere [9]. The effective thermal conductivity of the MOF-5 crystals with consideration of the adsorbed phase is slightly higher than that without such consideration. The difference is evident with an increase in pressure because of the thermal conductivity of the adsorbed phase. Given that the thermal conductivity of the adsorbed phase increases, the amount of H₂ adsorption increases with an increase in pressure. The change in the effective thermal conductivity is determined by the adsorbed and gaseous phases in the MOF-5 crystal. At region I (0.01–0.1 MPa), the amount of H₂ adsorption is significantly small enough that the thermal conductivity of the adsorbed phase can be ignored. The varying effective thermal conductivity of the MOF-5 crystal mainly results from the gaseous phase because the mean free path of the molecule decreases with an increase in pressure. At region II (0.1–2 MPa), the change is mainly determined by the adsorbed and gaseous phases. The amount of adsorption increases rapidly at this region; hence, the thermal conductivity of the adsorbed phase increases obviously. The mean free path of the molecule and the mean pore diameter of the crystal all decrease with an increase in pressure. This condition results in a competition in the thermal conductivity of the gaseous phase. The effect of the varying mean free path of the molecule performs an important function in the gaseous phase compared with the effect involving the consideration and non-consideration of adsorption. The increased thermal conductivity of the adsorbed phase is similar to the decreased thermal conductivity induced by the mean pore diameter of the crystal in the gaseous phase because the effective thermal conductivity of the MOF-5 crystal is similar regardless of the consideration of adsorption. At region III (2–50 MPa), the variation is mainly due to the adsorbed phase. The mean free path of the molecule and the mean pore diameter of the crystal all decrease with an increase in pressure. However, the Knudsen number remains constant, which in turn leads the thermal conductivity of the gaseous phase to be constant. Therefore, the variation of the effective thermal conductivity of the MOF-5 crystal mainly results from the thermal conductivity of the adsorbed phase.

This phenomenon is the main reason for the effective thermal conductivity of the MOF-5 crystal being higher in the condition that considers adsorption than in the condition that does not consider adsorption. The pressure ranges above indicate that the variation in the effective thermal conductivity of the MOF-5 crystal is due to the Knudsen number, as explained by Shim *et al.* [6], and to the amount of H₂ adsorption.

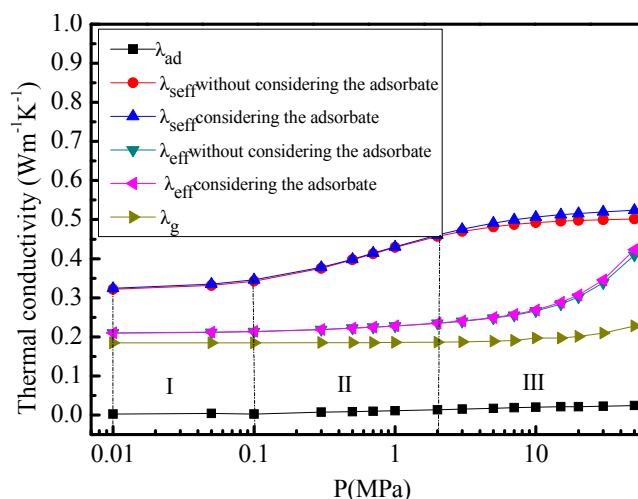


Figure 7. Varying thermal conductivity at different pressures and 298.15 K.

The effective thermal conductivity of the MOF-5 powder bed initially remains constant (pressure ranging from 0.01 MPa to 2 MPa) and then increases rapidly at a high pressure range (2–50 MPa). The gaseous thermal conductivity between the crystals is kept constant with an increase in pressure. The effective thermal conductivity of the MOF-5 powder bed with consideration of the adsorbed phase is higher than that without consideration of the adsorbed phase at a high pressure range of 2–50 MPa (Figure 7). The reasons are as follows. The porosity in the powder tank is high at low pressures (regions I and II). The gaseous thermal conductivity performs an important function. With an increase in pressure, the MOF-5 powder is compressed rapidly such that the porosity among the particles becomes low at region III. The thermal conductivity of the crystal gradually performs a lead function in the ratio of the increased effective thermal conductivity of the MOF-5 bed. The variation in the effective thermal conductivity results from the variation of the crystal and the porosity of the powder in the MOF-5 bed.

3.4. Effect of Temperature

Figure 8 shows the effective thermal conductivity of the adsorbed MOF-5 crystal and bed at different temperatures (273.15–368.15 K) and at 10 MPa. The effective thermal conductivity of the MOF-5 crystal with consideration of the adsorbed phase is slightly higher than that without such consideration because the adsorbed phase has thermal conductivity and the adsorbed H₂ molecule can reduce the mean pore diameter of the crystal. This phenomenon contributes to the change in the thermal conductivity of the gaseous phase in the MOF-5 crystal. The difference between the two models is relatively small with an increase in temperature because the amount of H₂ adsorption decreases with an increase in temperature. The reasons are as follows. For the MOF-5 crystal without consideration of the adsorbed phase, the thermal conductivity of the gas phase decreases with an increase in temperature because the Knudsen number increases with an increase in temperature. For the MOF-5 crystal with consideration of

the adsorbed phase, the decrease in effective thermal conductivity is faster than that without consideration of the adsorbed phase because the thermal conductivity of the adsorbed phase decreases. However, the mean pore diameter increases with an increase in temperature, and this condition helps improve the thermal conductivity of the gaseous phase. The adsorbed phase plays only a small role in the overall effective thermal conductivity of the MOF-5 crystal.

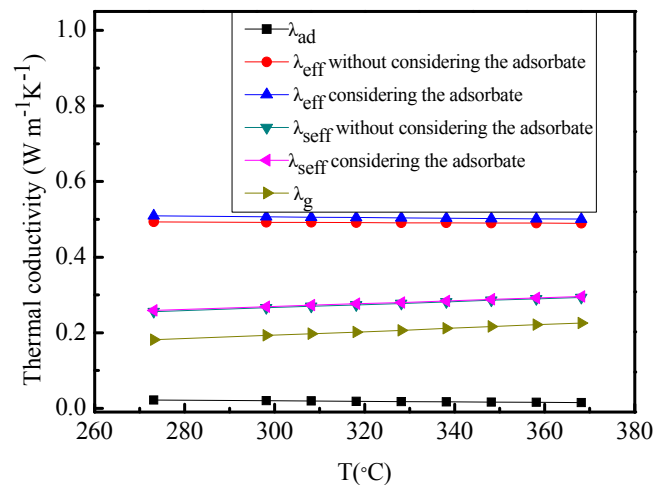


Figure 8. Varying thermal conductivity at different temperatures and 10 MPa.

The effective thermal conductivity of the MOF-5 bed with consideration of the adsorbed phase is similar to that without consideration of the adsorbed phase, as shown in Figure 8. The reasons are as follows. The porosity of the MOF-5 adsorption bed at this condition is 0.686, which indicates that the gaseous phase in the powder bed has a dominant function in the conductivity of the MOF-5. The effective thermal conductivity of the MOF-5 bed increases with an increase in temperature because the gaseous thermal conductivity among the crystals increases with an increase in temperature.

3.5. Effect of Main Parameter on Effective Thermal Conductivity

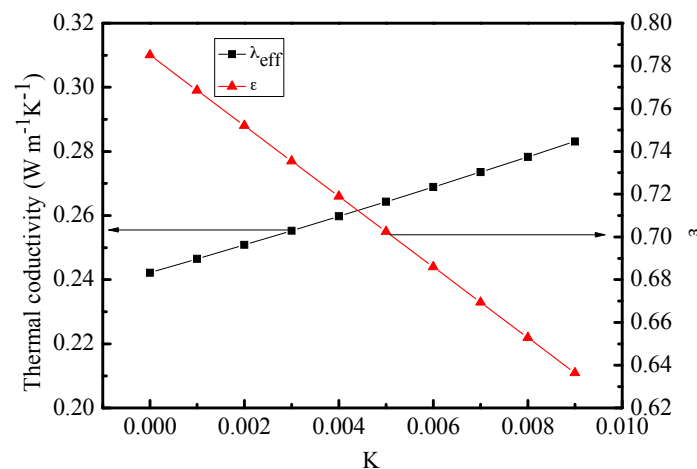


Figure 9. Varying porosity and thermal conductivity at different slopes.

Figure 9 shows the varying effective thermal conductivity of the MOF-5 bed and porosities at different slopes of functions between density and a pressure range (0–0.009) at 298.15 K and 10 MPa. The increase in the speed of compression apparently enhances the effective thermal conductivity of the MOF-5 bed by decreasing the amount of interstitial voids between the crystals in the bed. Figure 10 shows the effect of the varying thermal conductivity of the MOF-5 skeleton on the thermal conductivities of the crystal and bed. The effective thermal conductivities of the MOF-5 crystals and adsorption bed increase with an increase in the thermal conductivity of the MOF-5 skeleton. Notably, this relationship is linear, which means that the thermal conductivity of the MOF-5 skeleton does not influence the rules at different pressures and temperatures.

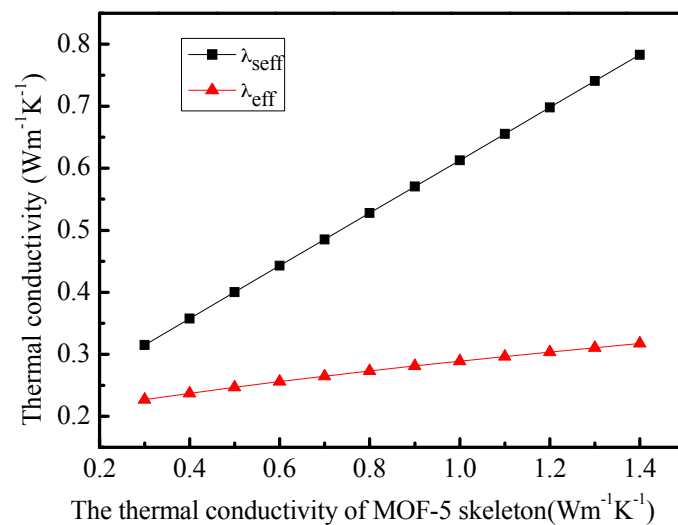


Figure 10. Varying porosity and thermal conductivity at different solid thermal conductivity values.

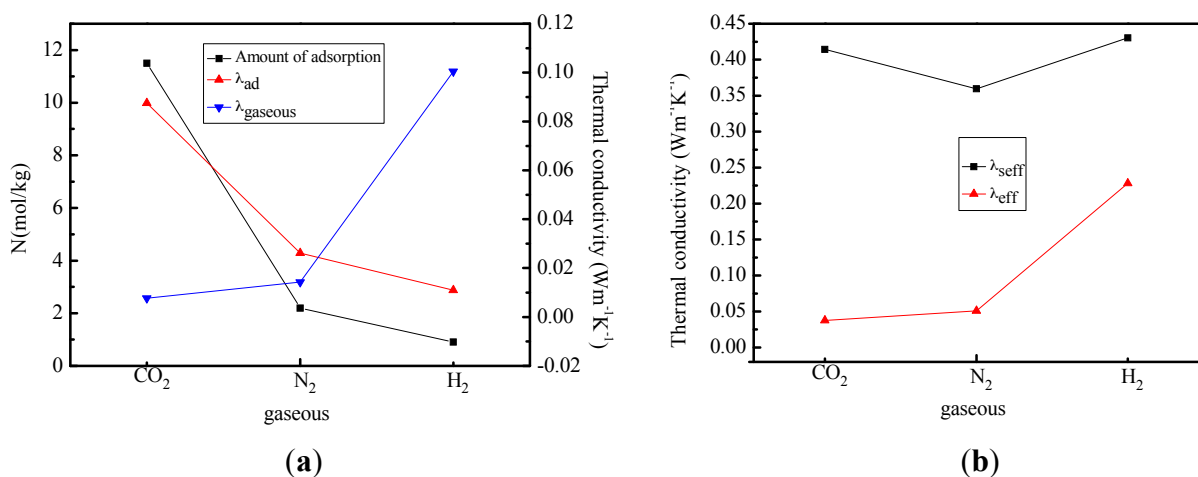


Figure 11. Amount of adsorption and thermal conductivity at 1.0 MPa and 298.15 K.

(a) Amount of adsorption and thermal conductivity at 1.0 MPa and 298.15 K; (b) Effective thermal conductivity at 1.0 MPa and 298.15 K.

Figure 11a,b show the amount of adsorption and the effective thermal conductivity of the MOF-5 crystal and adsorption bed under the CO₂, N₂, and H₂ atmosphere at 1.0 MPa and 298.15 K. Given that the amount of CO₂ adsorption is the largest, the thermal conductivity of the CO₂ adsorbate is also the

largest, as shown in Figure 11a. The thermal conductivity of the CO₂ adsorbed phase is higher than that of the gaseous phase in the MOF-5 crystal. This result indicates that the amount of adsorption contributes to the effective thermal conductivity of the MOF-5 crystal. Figure 11b shows the effective thermal conductivities of the MOF-5 crystal and adsorption bed at the CO₂, N₂, and H₂ atmosphere. The thermal conductivities of the MOF-5 crystal and bed at the H₂ atmosphere are higher than those at the CO₂ and N₂ atmosphere. The difference results from the thermal conductivity of the gaseous and adsorption phases.

4. Conclusions

A modified thermal conductivity model is built by coupling a theoretical model with the GCMC simulation to predict the effect of the H₂ adsorption process on the effective thermal conductivity of a MOF-5 powder bed at pressures ranging from 0.01 MPa to 50 MPa and temperatures ranging from 273.15 K to 368.15 K. The results show that the mean pore diameter of the MOF-5 powder crystal decreases with an increase in pressure and increases with an increase in temperature as the H₂ adsorption occurs. The effective thermal conductivity of the MOF-5 powder bed increases with an increase in pressure. The main reasons are as follows. The porosity of the adsorption bed decreases with an increase in pressure because the MOF-5 powder compacts and the thermal conductivity of the adsorbed phase increases with an increased amount of H₂ adsorption. With an increase in temperature, the effective thermal conductivity of the MOF-5 powder bed remains nearly unchanged because of the high porosity. The thermal conductivity of the MOF-5 powder bed increases linearly with a decrease in porosity and an increase in the thermal conductivity of the skeleton of the MOF-5 crystals. The main variation in the effective thermal conductivities of the crystal and bed results from the thermal conductivities of the gaseous and adsorption phases.

Acknowledgments

This work was financially sponsored by the National Natural Science Foundation of China (No. 51322604, 51176149), the National Key Projects of Fundamental R/D of China (973 Project: 2011CB610306), the Fundamental Research Funds for the Central Universities (No. xjj2012102), and the Open Funding Project of the National Key Laboratory of Human Factors Engineering (Grant No. HF2013-K-05).

Author Contributions

Hui Wang did the simulation; Wen Zhang analyzed the data; Zhiguo Qu discussed the results of simulation; Hui Wang, Zhiguo Qu, Wen Zhang wrote the paper; Wenquan Tao revised the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

References

1. Kaye, S.S.; Dailly, A.; Yaghi, O.M.; Long, J.R. Impact of preparation and handling on the hydrogen storage properties of $\text{Zn}_4\text{O}(\text{1,4-benzenedicarboxylate})_3$ (MOF-5). *J. Am. Chem. Soc.* **2007**, *129*, 14176–14177.
2. Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O.M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276–279.
3. Schmit, B.; Müller, U.; Trukhan, N.; Schubert, M.; Fe’rey, G.; Hirscher, M. Heat of adsorption for hydrogen in microporous high-surface-area materials. *ChemPhysChem* **2008**, *9*, 2181–2184.
4. Huang, B.L.; McGaughey, A.J.H.; Kaviani, M. Thermal conductivity of metal-organic framework (MOF-5): Part I. molecular dynamics simulations. *Int. J. Heat Mass Transf.* **2007**, *50*, 393–404.
5. Huang, B.L.; Ni, Z.; Millward, A.; McGaughey, A.J.H.; Kaviani, M.; Yaghi, O.M. Thermal conductivity of a metal-organic framework (MOF-5): Part II measurement. *Int. J. Heat Mass Transf.* **2007**, *50*, 405–411.
6. Purewal, J.J.; Liu, D.; Yang, J.; Sudik, A.; Siegel, D.J.; Maurer, S.; Müller, U. Increased volumetric hydrogen uptake of MOF-5 by powder densification. *Int. J. Hydrog. Energy* **2012**, *37*, 2723–2727.
7. Liu, D.; Purewal, J.J.; Yang, J.; Sudik, A.; Maurer, S.; Mueller, U.; Ni, J.; Siegel, D.J. MOF-5 composites exhibiting improved thermal conductivity. *Int. J. Hydrog. Energy* **2012**, *37*, 6109–6117.
8. Hu, Y.H.; Zhang, L. Amorphization of metal-organic framework MOF-5 at unusually low applied pressure. *Phys. Rev. B* **2010**, *81*, 174103.
9. Griesinger, A.; Spindler, K.; Hahne, E. Measurements and theoretical modeling of the effective thermal conductivity of zeolites. *Int. J. Heat Mass Transf.* **1999**, *42*, 4363–4374.
10. Walton, K.S.; Millward, A.R.; Dubbeldam, D.; Frost, H.; Low, J.J.; Yaghi, O.M.; Snurr, R.Q. Understanding inflections and steps in carbon dioxide adsorption isotherms in metal-organic frameworks. *J. Am. Chem. Soc.* **2008**, *130*, 406–407.
11. Zhang, L.; Wang, Q.; Liu, Y.C. Design for hydrogen storage materials via observation of adsorption sites by computer tomography. *J. Phys. Chem. B* **2007**, *111*, 4291–4295.
12. Yang, Q.Y.; Zhong, C.L. Understanding hydrogen adsorption in metal-organic framework with open metal sites: A computational study. *J. Phys. Chem. B* **2006**, *110*, 655–658.
13. Wang, J.F.; Carson, J.K.; North, M.F.; Cleland, D.J. A new approach to modeling the effective thermal conductivity of heterogeneous materials. *Int. J. Heat Mass Transf.* **2006**, *49*, 3075–3083.
14. Lu, X.; Caps, R.; Fricke, J.; Alviso, C.T.; Pekala, R.W. Correlation between structure and thermal-conductivity of organic aerogels. *J. Non-Cryst. Solid* **1995**, *188*, 226–234.
15. Dawoud, B.; Soheli, M.I.; Freni, A.; Vasta, S.; Restuccia, G. On the effective thermal conductivity of wetted zeolite under the working conditions of an adsorption chiller. *Appl. Therm. Eng.* **2011**, *31*, 2241–2246.
16. Dreisbach, F.; Staudt, R.; Keller, J.U. High pressure adsorption data of methane, nitrogen, carbon dioxide and their binary and ternary mixtures on active carbon. *Adsorption* **1999**, *5*, 215–227.
17. Yang, S.M.; Tao, W.Q. *Heat Transfer*, 3rd ed.; Higher Education Press: Beijing, China, 2006.
18. Zhao, X.B.; Rodil, S.V.; Fletcher, A.J.; Thomas, K.M. Kinetic isotope effect for H_2 and D_2 quantum molecular sieving in adsorption/desorption on porous carbon materials. *J. Phys. Chem. B* **2006**, *110*, 9947–9955.

19. *Materials Studio v 6.0*; Accelrys Software Inc: San Diego, CA, USA, 2010.
20. Jorgensen, W.L.; Maxwell, D.S.; Tirado-Rives, J. Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
21. Yang, Q.Y.; Zhong, C.L. Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks. *J. Phys. Chem. B* **2006**, *110*, 17776–17783.
22. Martin, M.G.; Siepmann, J.I. Transferable potentials for phase equilibria. 1. united-atom description of n-alkanes. *J. Phys. Chem. B* **1998**, *102*, 2569–2577.
23. Liu, Y.; Liu, H.L.; Hu, Y.; Jiang, J.W. Density functional theory for adsorption of gas mixtures in metal-organic frameworks. *J. Phys. Chem. B* **2010**, *114*, 2820–2827.
24. Greathouse, J.A.; Kinniburgh, T.L.; Allendorf, M.D. Adsorption and separation of noble gases by IRMOF-1: Grand canonical Monte Carlo simulations. *Ind. Eng. Chem. Res.* **2009**, *48*, 3425–3431.
25. Skoulidas, A.I.; Sholl, D.S. Self-diffusion and transport diffusion of light gases in metal-organic framework materials assessed using molecular dynamics simulations. *J. Phys. Chem. B* **2005**, *109*, 15760–15768.
26. Potoff, J.J.; Siepmann, J.I. Vapor-liquid equilibria of mixtures containing alkanes, carbon dioxide and nitrogen. *AIChE J.* **2001**, *47*, 1676–1682.
27. Frenkel, D.; Smit, B. *Understanding Molecular Simulation From Algorithms To Applications*; Academic press: New York, NY, USA, 2002.
28. Kowalczyk, P.; Tanaka, H.; Kaneko, K.; Terzyk, A.P.; Do, D.D. Grand canonical Monte Carlo simulation study of methane adsorption at an open graphite surface and in slit like carbon pores at 273 K. *Langmuir* **2005**, *21*, 5639–5646.
29. Panella, B.; Hirscher, M.; Putter, H.; Muller, U. Hydrogen adsorption in metal-organic frameworks: Cu-MOFs and Zn-MOFs compared. *Adv. Funct. Mater.* **2006**, *16*, 520–524.