Computer simulation studies of structure characteristics of ordered mesoporous carbons and its naphthalene adsorption performance

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Abstract:

We could draw some valuable conclusions about adsorption capacity, adsorption isotherm, adsorption kinetics, adsorption thermodynamics by naphthalene adsorption experiments, but the experiments could not tell us directly what the adsorption location and adsorption state are exactly on the surface of OMCs. Actually, we still don't know the microscopic structure of OMCs very well because of the restriction of characterization technology, human factor and experimental conditions. However, molecular simulation technology could make up the disadvantages. In the work, Grand Canonical Monte Carlo method was performed for the first time to simulate the naphthalene adsorption behavior in OMCs structure model. The atomic structure model of OMCs was built firstly by using molecular modeling technique and was characterized by calculating the accessible solvent surface area, total pore volume, and small-angle X-ray diffraction patterns. The calculated results showed that the structure model of OMCs was reasonable and the structure characteristic was in agreement with experimental data. The adsorption isotherm curve is of type Langmuir IV, which was typical characteristic of ordered mesoporous materials. Also, adsorption isotherm curve revealed that the adsorption capacity of naphthalene on OMCs increased to a balance gradually, and the maximum adsorption capacity of naphthalene was 105.4 mg g^{-1}. Additionally, the adsorption state of naphthalene were observed that from monolayer to multilayer in the mesopores with the increasing of number of naphthalene molecules.

This work deepened the understanding of the adsorption state of naphthalene for OMCs on mesoscopic level. It also demonstrated that the GCMC method is effective for studying the adsorption process and gives useful guidance on research of structure-activity relationship and

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performance prediction of the carbon material.

Keywords: Grand Canonical Monte Carlo; Ordered mesoporous carbons; Adsorption; Naphthalene.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), known as one of the persistent organic pollutants, which have threatened people health and atmospheric environment seriously (International Agency for Research on Cancer, 1983; Carcinogen Assessment Group, 1985; Ministry of Environment and Energy, 1997). PAHs typically disperse from urban and suburban non-point sources through road run-off, sewage, and atmospheric circulation and subsequent deposition of particulate air pollution due to their volatility and reactivity (Lee *et al*., 1993; Sloss *et al*., 1995; Mastral *et al*., 1999; Hylland *et al*., 2006). Therefore, adsorption is one of the most important methods to remove PAHs effectively (Gerde *et al*., 1989; Hart *et al*., 1994; Dachs *et al*., 2000; Cheng *et al*., 2008).

Ordered mesoporous carbons (OMCs) have attracted great attention because of their interesting applications in many fields recently, especially in adsorption, catalysis, separation, and energy storage/conversion devices (Galo *et al*., 2002; Schrüth *et al*., 2003; Guo *et al*., 2005; Minchev *et al*., 2005; Taguchi *et al*., 2005; Lee *et al*., 2006; Li *et al*., 2006; Lu *et al*., 2006; Wang *et al*., 2013).Their utility for these applications could be attributed to ordered cubic or hexagonal frameworks, regulated pore sizes, narrow mesopore size distributions, high specific surface areas and large pore volumes. Therefore, the adsorption performance of OMCs for gaseous molecules is very well. However, most research focused on the adsorption capacity, adsorption isotherm, adsorption kinetics and adsorption thermodynamics(Zhou *et al*., 2005; Saha *et al*., 2010; Saini *et al*., 2010; Wang *et al*., 2013), and the experimental results could not tell us directly what the adsorption location and adsorption state are exactly on the surface of OMCs. Actually, we still don't know the microscopic structure of OMCs very well because of the restriction of characterization technology, human factor and experimental conditions.

Based on precise theoretical models for accurate theoretical calculation, the molecular simulation technique could be helpful for tackling the problem mentioned above. Grand

Canonical Monte Carlo (GCMC) method has been applied successfully in many fields, such as environment, material, adsorption and separation. The simulation results were proved that the GCMC method was a powerful and effective approach to probe the molecular adsorption action in mesoporous materials (Chen *et al*., 2000; Sun *et al*., 2009; Zhang *et al*., 2012) and could be the necessary complement for the experimental approach.

In the work, GCMC method was performed for the first time to simulate the naphthalene adsorption behavior in OMCs. The atomic structure model of OMCs was built firstly by utilizing molecular modeling technique and was characterized by calculating the accessible solvent surface area, total mesopore volume and small-angle X-ray diffraction pattern. Additionally, the adsorption capacity and the adsorption state of naphthalene in OMCs were simulated. This work could deepen the understanding of the adsorption performance of naphthalene in OMCs on mesoscopic level, and the results could provide some valuable information for further research on structure-activity relationship, performance prediction of the carbon material and the removal of PAHs effectively.

COMPUTATIONAL DETAILS

The commercial software package Materials Studio (MS), developed by Accelrys in the USA, was applied in the simulations.

OMCs Structure Model

The atomic structure model of OMCs was built by utilizing Materials Visualizer module of MS, and the process was summaried as follows: Firstly, OMCs were consisted of amorphous carbon, so the unit cell of amorphous carbon was imported from the database of MS, and a 5×3×2 supercell (10.7nm×6.4nm×4.2nm) was built by the unit cell, the mesoporous size (diameter=4nm) of OMCs was determined based on the experimental results obtained by Wang *et al*. (Wang *et al*., 2012), for which the adsorption performance was the best under the experimental condition. The carbon atoms，which were inside the selected 4nm mesoporous pore diameter of the supercell, were removed, then the produced vacant bonds were not saturated with hydrogen atoms because the influence could be neglected after theoretical calculation. Finally, the atomic structure model of OMCs was built by applying P1 symmetry of the periodical boundary conditions, and the

synthesis process diagram was showed in Fig.1.

Molecular dynamic (MD) simulation

The Forcite module of MS was applied in the MD simulations. The geometry optimization of the OMCs structure model was performed firstly using periodical boundary conditions to avoid any arbitrary boundary effects in the simulation process. The COMPASS Force Field was employed and the charges in the electrostatic scalar potential format can be assigned to the calculated values during the geometry optimization process, and the structure of OMCs was equilibrated to obtain the minimum energy configuration at 298 K and NVT ensemble. A step size of 1 fs and total simulation time of 20 ps were chosen, respectively. Then, the entire structure model was equilibrated for 120 ps in NVE dynamics and frame output every 100 steps.

Grand Canonical Monte Carlo (GCMC) simulation

For predicting the phase equilibrium of adsorption, the GCMC simulation could be one of the most common techniques (Allen *et al*., 1980; Fan *et al*., 2017). It was applied usually to simulate the equilibrium of collection of adsorbate in a pore structure at constant chemical potential, volume, and temperature (or pressure). Because the chemical potential will get equilibrium under a reaction condition, we could simulate the adsorption characterization of naphthalene in OMCs in this work. The GCMC simulations of naphthalene adsorption in OMCs were carried out by the Sorption module of MS package applying for Metropolis method. The Metropolis algorithm, COMPASS force field and basis set were applied to research the adsorption performance of naphthalene after MD simulation with periodical boundary condition. In this work, the adsorption system was equilibrated for 1×10^5 GCMC steps at 393K under the relative pressure range from 0 to 1 during the calculation. The electrostatic summation method was Ewald & Group, cutoff distance was 1.5nm, and the simulation data were collected for another 1×10^5 GCMC steps during the calculation to get the final adsorption structure, adsorption state and the adsorption capacity.

RESULTS AND DISCUSSION

Structure details

The structure model of OMCs after geometry optimization was showed in Fig. 2A, which was showed in ball and stick model, and the mesopore size was 4 nm and the lattice parameters were 10.7nm×6.4nm×4.2nm, respectively. The 3×3×1 supercell structure of OMCs was given in Fig. 2B. It revealed that the supercell structure obtained exhibited well ordered 2D-hexagonal structures, and the structures observed from parallel direction of channel were similar with the images of OMCs viewed along the (110) direction by TEM, which suggested that the simulation results were in good agreement with the experimental results (Wang *et al*., 2012).

The atom volume and surface tools of MS were applied to calculate the accessible solvent surface area of the OMCs model, and the simulation results were showed in Fig. 3. This figure presented that the wall thickness, total mesopore volume and surface area were 2.3nm, 0.15cm^3/g and 334m^2/g, respectively. Additionally, the pore structure parameters of OMCs obtained by structure model are compared with the experimental data (Wang *et al*., 2012), which were listed in the Table 1. It indicated that the mesopore sizes of them were same. However, the wall thickness, the accessible solvent surface area and the total mesopore volume were less than those of the experimental data. The decrease was probably because that structure units of OMCs were assumed perfect crystal during the process of simulation calculation. However, for realistic structure of OMCs, there are still some structural defects, impurity, surface coarseness, or pore wall thickness, which result in the simulation results are not in accord with the real structure fully. Additionally, there were a lot of pores, which sizes were less than 4nm, produced during the experimental preparation process of OMCs, the pore sizes distribution of experimental samples were concentrated in a relatively wider sizes range than simulation results. So these results mentioned above indicated that the model structure of OMCs still need further modification or optimization for the purpose of obtaining more accurate simulation results in subsequent research. Actually, it was normal and permitted that there were some difference between simulation results and experiment results, and the difference did not affect the simulation results reliability of the OMCs structure. Therefore, the simulation results demonstrated that structure model kept the typical structure characteristics of OMCs, and the structure model was reasonable and reliable.

X-ray diffraction (XRD) analysis

In order to investigate the structure characteristic of OMCs clearly, the Reflex module of MS was performed to simulate the small-angle XRD, and the XRD pattern was illustrated in Fig. 4. The Figure revealed three well resolved peaks, which were indexed to the (100), (110), and (200) diffraction peaks of a space group P6mm hexagonal structure (Liu *et al*., 2006; Wang *et al*., 2012). The values of interplanar spacing (d) were 5.48nm, 3.19nm and 2.74nm, respectively. Their ratios corresponded to 1: $(1/\sqrt{3})$: (l/2) (Trick *et al*., 1995), which indicated that the OMCs had well-ordered 2D hexagonal structure. It suggested that the simulation results fit the experimental results very well (Wang *et al*., 2012).

Naphthalene adsorption

The adsorption isotherm indicated the partition of adsorbate between gas and adsorbent at equilibrium. To study the adsorption capacity of OMCs at 393 K, the adsorption isotherm for naphthalene in the structure model of OMCs was calculated by GCMC, and the simulated result was showed in Fig. 5. The adsorption isotherm curve illustrated that the adsorption capacity of OMCs increased to a balance gradually when the relative pressure is increasing, and the maximum adsorption capacity was shown to reach up to105.4mg/g. Additionally, the adsorption isotherm is of type Langmuir IV, which was the characteristic adsorption curve of mesoporous materials (Febrianto *et al*., 2009; Zeng *et al*., 2016), and the adsorption isotherm revealed that it was monolayer adsorption at lower pressure region ($p/p_0<0.4$) and was multilayer adsorption at higher pressure region ($p/p_0>0.4$).

After 5×10^5 GCMC steps were performed, structures and density distribution of naphthalene in OMCs were recorded and showed at relative pressure level of 0, 0.2, 0.6 and 1.0 in Fig. 6. The simulation results showed that there was almost not any naphthalene molecule was adsorbed in the OMCs under the relative pressure of 0 (Fig. 6(a)). Then, there were much more naphthalene molecules were adsorbed with the increase of relative pressure from 0.2 to 0.6, and the adsorption was from monolayer adsorption to multilayer adsorption gradually. Finally, the mesopore was filled fully with naphthalene molecules (Fig. 6(d)).

Additionally, the adsorption process could still was observed directly and clearly in Fig.7. The adsorption state of naphthalene were simulated that from monolayer to multilayer in the

mesopores with the increasing of number of naphthalene molecules, which corresponded with the simulation results in Fig. 6.

CONCLUSIONS

In the work, GCMC method was performed for the first time to simulate the naphthalene adsorption behavior in the OMCs. The structure model of OMCs on atomistic level was built firstly by using molecular modeling technique. Additionally, the total mesopore volume, surface area and small-angle XRD are calculated to analyze the structural characterization of the OMCs atomic model. The calculated results showed that the structure model of OMCs was reasonable and reliable, and the structure characteristic was corresponded with experimental results. The adsorption isotherm curve is of type Langmuir IV, which was considered as typical adsorption characteristic isotherm of mesoporous material. Also, the adsorption isotherm curve revealed that the adsorption capacity of naphthalene on OMCs increased to a balance gradually when the relative pressure increased from 0 to 1.0, and the maximum adsorption capacity is shown to reach up to105.4mg/g. Additionally, the adsorption state of naphthalene were observed that from monolayer to multilayer in the mesopores with the increasing of number of naphthalene molecules. However, there is still some difference between experimental results and simulation results, which could be illustrated that the OMCs structure model were assumed as perfect crystal, and structural defects, impurity, surface coarseness, pore size and pore wall thickness are ignored during the simulation calculation. According, the simulation results did not correspond with the real structure of OMCs exactly, and the model structure of OMCs still need further modification or optimization for the purpose of obtaining more accurate simulation results in subsequent research. This work deepened the understanding of the adsorption state of naphthalene for OMCs on mesoscopic level. It also demonstrated that the GCMC method is effective for studying the adsorption process and gives useful guidance on research of structure-activity relationship and performance prediction of the carbon material.

ACKNOWLEDGMENTS

This work was financially supported by Science and Technology Planning Project of Guang

Dong Province of China (No. 2014A020216052) and Science and Technology Innovation Fund of Foshan City of of Guang Dong Province of China (No. 2015AG100242).

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CO_2. *Chem. Phys. Lett.* 413: 6-9.

Table. 1 Structure parameter of OMCs

OMCs	Mesopore size (nm)	Wall (nm)	S_{BET} (m^2/g)	V_{meso} (cm^3/g)
Simulation	**4.0**	**2.3**	**334**	**0.15**
Experiment	**4.0**	**3**	**558**	**0.26**

FIGURE CAPTIONS

Fig. 1. Schematic diagram of modelling process

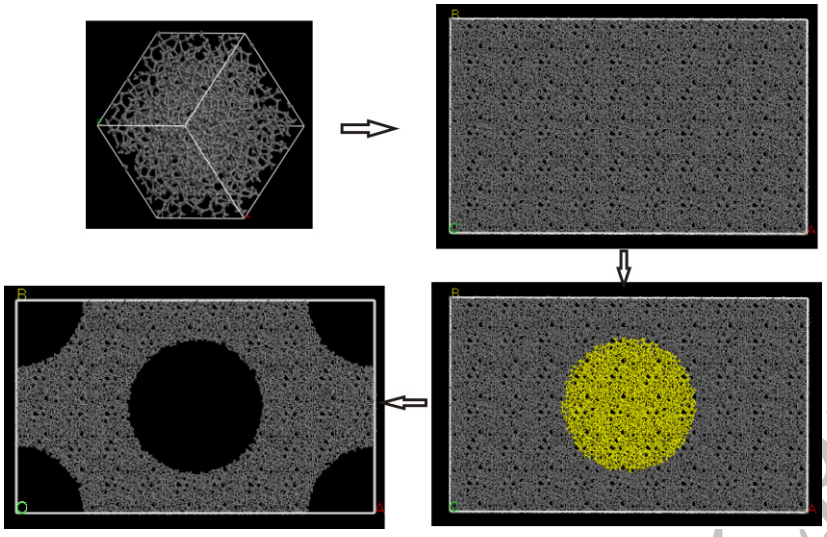


FIGURE 1

Fig. 2. Structure model of OMCs after geometry optimization (A)structure model, (B)3×3×1 supercell

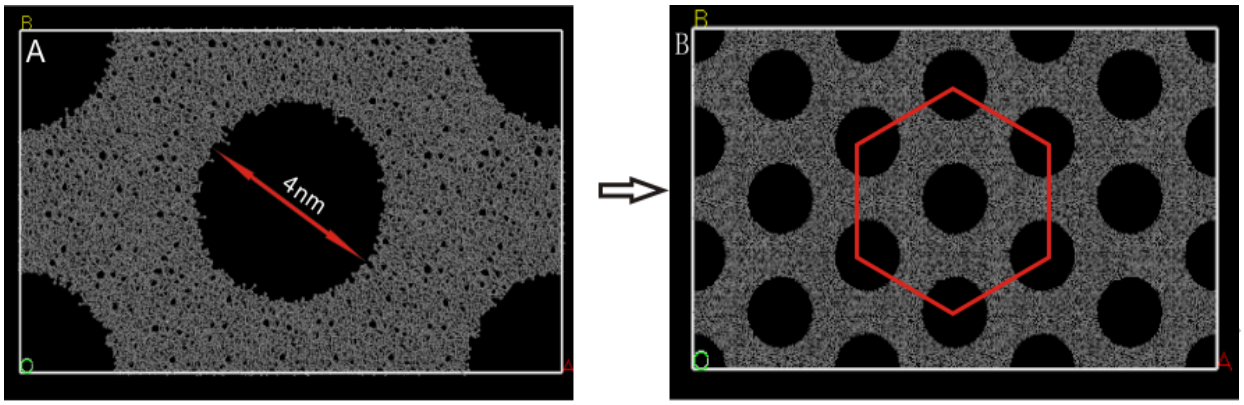


FIGURE 2

Fig. 3. Accessible solvent surface area of OMCs structure model

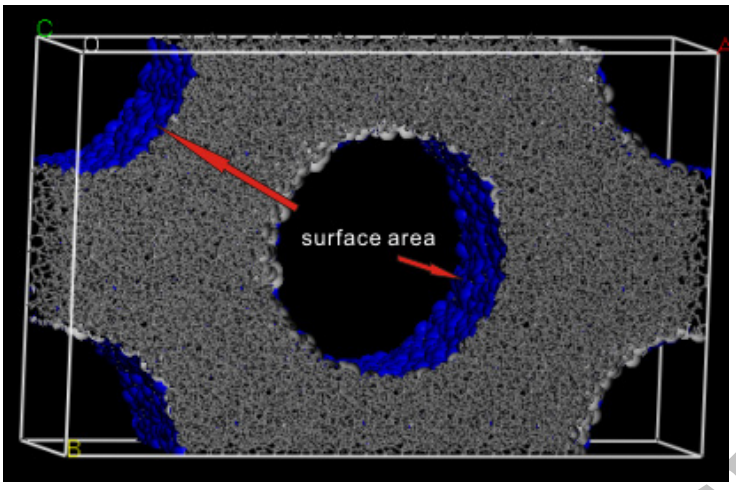


FIGURE 3

Fig. 4. Simulated small-angle X-ray diffraction pattern of OMCs

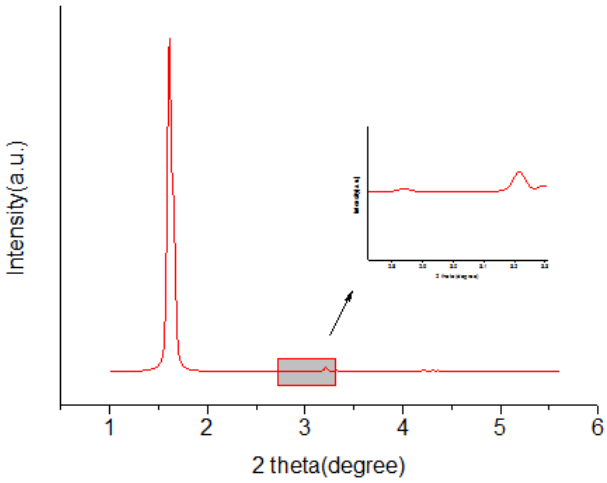
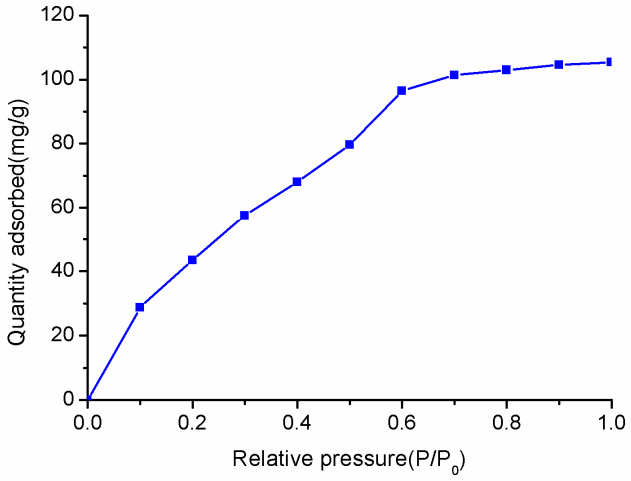


FIGURE 4

446 Fig. 5. Adsorption isotherm of naphthalene in OMCs model



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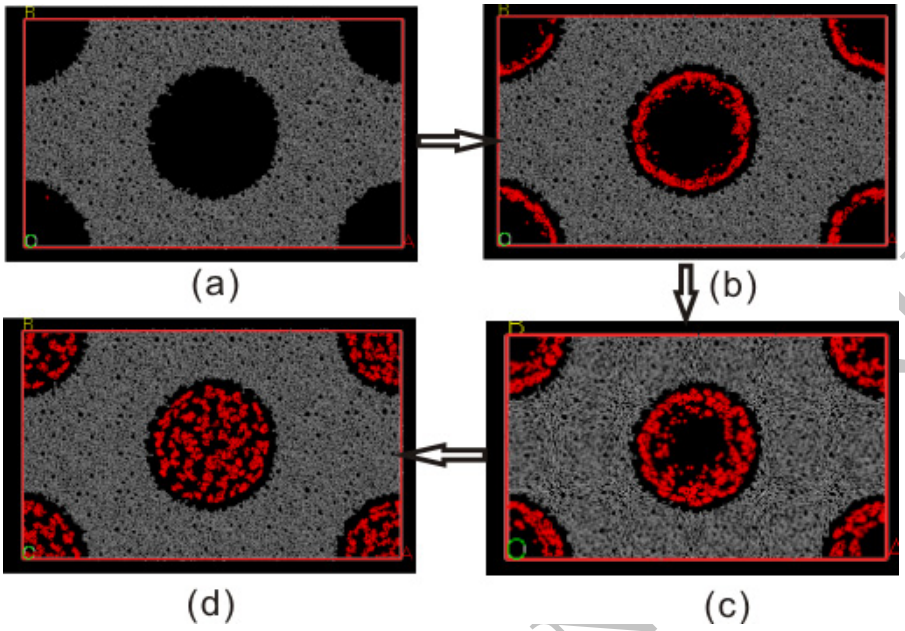
462 Fig. 6. Density distribution of naphthalene molecules in the OMCs model at different relative

463 pressure: (a) p/p_0=0, (b) p/p_0=0.2, (c) p/p_0=0.6, (d) p/p_0=1.0



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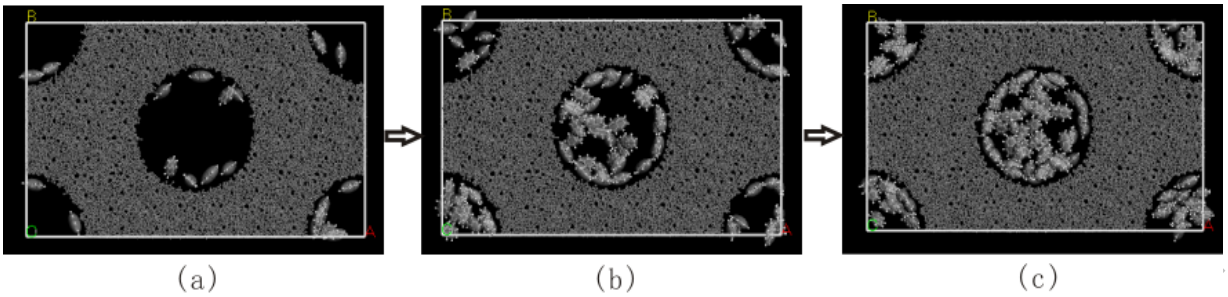
477 Fig. 7. Adsorption state of naphthalene molecules in OMCs model



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479 FIGURE 7