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Ultra micropores in macromolecular structure of subbituminous coal vitrinite

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ABSTRACT

Pores in coal provide surface area and volume for coalbed methane storage. In this study, a 3 dimensions (3D) macromolecular structure of subbituminous coal vitrinite was constructed, which was demonstrated to be consistent with the experimental Nuclear Magnetic Resonance (NMR) data, density data and pore volume data, to study ultra micropores formed in the macromolecule. The results showed that both accessible pores and inaccessible pores existed in the macromolecular structure and that all pores were smaller than 0.62 nm. Most of the accessible pores were formed by aliphatic chains and most of the atoms that directly touched the pore surface were hydrogen atoms. The accessible pores showed obvious fractal features, and the fractal dimension of pores detected by probes smaller than 0.5 nm is 2.73. We also found that the volume of pores seen by helium is considerably larger than that of pores seen by methane. This would result in underestimation of methane adsorption capacity in a volumetric methane adsorption experiment, where the void volume is tested by helium. For the coal sample Y-1, the methane adsorption capacity would be underestimated by 2.7 cm^3/g at 10 MPa.

1. Introduction

As a clean energy, coalbed methane is of great significance to energy safety and environmental protection in the United States, Australia, China and other countries. Research on the pores of coal is very important for coalbed methane exploration, as pores provide surface area for adsorbed phase methane and volume for free gas [1–6]. Pores also serve as tunnels for gas diffusion and gas flow [7,8]. Currently, many methods have been employed to study pore structures in coal, such as high pressure mercury injection, nitrogen adsorption, carbon dioxide adsorption, scanning electron microscopy, and NMR among others [1,6,9–12], and significant achievements have been made regarding such factors as pore size distributions, shapes, fractal features, and effects on adsorption [5,8,13–16] Pore systems in coal are quite complex due to their heterogeneity and wide size distribution, from micropores (< 2 nm) to macropores (greater than50 nm) [1,15,17]. In the pore systems of coal, micropores occupy a large part and have a great influence on methane adsorption in coal as these micropores provide most of the total surface area [18]. Researchers have also observed that portions of the ultra micropores (smaller than 1 nm) are related to the coal macromolecular structure [19–23]. Faulon et al. [21] used computer-generated models studied ultra micropores, and found that many ultra micropores can be formed in the 3D coal models and these pores contributed to most of the micropores. Boursige et al., [20] and Zhou et al. [23] believed nanopores in shale were related to the molecular model and used the macro molecule to generate pores. Zhang et al. [24,25] used coal macromolecular structures to simulated methane adsorption in coal as coal macromolecular structures could provide pores for methane adsorption.

Based on the statistics of Dr. Mathews, more than 134 proposed molecular level models of coal had been presented by 2010 [26], and these molecular representations of coal have greatly facilitated the study of, for instance, coalification pathways, physical evaluations, pyrolysis process representation, and methane adsorption simulation [21,22,24,25,27–29]. Following the 1990s, computer technology was applied to build 3D models of coal, which made the study of pores in macromolecule possible [26,30]. Dr. Mathews and his group have done excellent work in presenting macromolecular models of coal and the utility of coal molecular models [21,31–35]. Most of the molecular models constructed of coal recently are large scale, in which there are more than 200 atoms [26,29,36,37]. The size of these macromolecules is usually larger than 2 nm. Several large-scale molecules even have

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more than 10,000 atoms. Conversely, calculated from CO_2 adsorption experimental data, there are many coal pores smaller than 1 nm or even smaller than 0.5 nm [1,18]. The macromolecular structure of coal is large enough to form these ultra micropores [20,21,23].

Although different methods have been used to study pores in coal, micropores in coal still warrant further study, especially ultra micropores (smaller than 1 nm). Ultra micropores are too small to be tested by scanning electron microscope (SEM) and some other visible methods. Gas injection methods are the most commonly used to study ultra micropores in coal. But it is difficult to study shapes, connectivity and other characteristics using only these methods. Moreover, different gas molecules can see different pores in coal. For example, methane can only see pores larger than 0.38 nm, helium can see pores larger than 0.26 nm, and CO_2 can see pores larger than 0.33 nm [38]. This has resulted in trouble accurately describing pore characteristics. Additionally, as we know, in volumetric methane adsorption experiments in coal, helium is usually used to test void volume, and this often caused underestimation of methane adsorption capacity, especially at high pressure [39].

Coal is a mixture that contains such macerals as vitrinite, inertinite, exinite. Among them, vitrinite accounts for the largest proportion. The proportion of vitrinite in Dalianhe formation subbituminous raw coal (Yilan open-pit mine in China) is more than 85%. What is more, the macromolecular structures of different types of macerals are different. To improve the representation accuracy of macromolecular structure, we used only vitrinite separated from coal as the experimental samples. In this study, a 3D macromolecular structure of subbituminous coal vitrinite has been constructed to study pore shapes, volume distribution and fractal characteristics. Using the 3D macromolecular structure, we studied the atoms on the surface of the pores, which is very important for gas adsorption in coal, as gas adsorption is due to the interaction forces between the gas and atoms on the pore surface of coal [40]. The differences in pores seen by methane and helium were also assessed in this study, and the underestimation in methane adsorption experiment is calculated.

2. Materials and methods

2.1. Samples

The coal vitrinite sample Y-1 was collected from the Yilan open-pit mine in Heilongjiang province, China. It is from the Dalianhe Formation of the Paleogene, and the raw coal of Y-1 is famous for high vitrinite content. We chose the vitrain part from the raw coal by hand, and the results showed that in the separated vitrinite samples Y-1, the vitrinite content was 95%. The ash content of the vitrinite samples was 1.8%, and the maximum reflectivity of vitrinite ($R_{o,max}$) was 0.5%.

2.2. Macromolecular structure construction

Before the 3D macromolecular structure was constructed, we represented the 2D chemical structure of the Y-1 vitrinite, primarily based on the ^{13}C NMR spectrum and element composition. FT-IR data was also used to provide information on oxygen functional groups. ^{13}C NMR spectrum has been demonstrated to be effective in representing 2D chemical structure [29,37]. The ACD/C NMR Predictor was used to calculate the ^{13}C NMR chemical shift of the macromolecular structure constructed. After hundreds of adjustments, the calculated ^{13}C NMR spectrum based on the macromolecule structure was able to match the experimental ^{13}C NMR spectrum of the Y-1 vitrinite samples (Fig. 1).

Materials Studio (Accelrys) was used for geometry optimization to construct a 3D macromolecular model. Considering that the Y-1 vitrinite sample is subbituminous vitrinite and that the structure order has not been formed [26,41], we used 16 building blocks together for geometry optimization. The universal forcefield was employed for the geometry optimization, in which the Van der Waals forces are

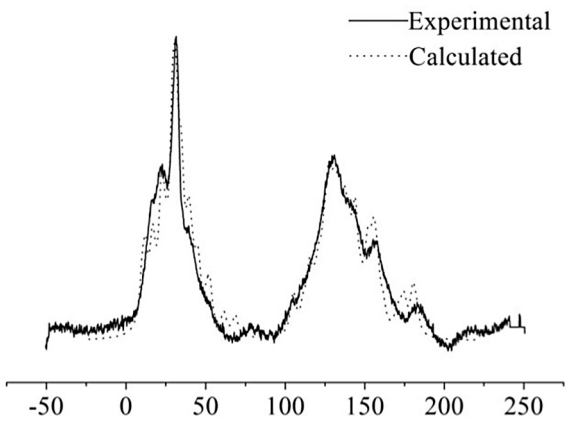

Fig. 1. Experimental and calculated ^{13}C NMR spectrum of Y-1 vitrinite sample.

calculated by the L-J 12-6 equation [42]. The density of the 3D macromolecular model is 1.30 g/cm^3, which is equal to the experimental true density (1.30 g/cm^3). In addition, accessible volume in the macromolecular model is 0.042 cm^3/g (probe radius = 0.165 nm), which is similar to the experimental micropore volume (0.041 cm^3/g) from the CO_2 adsorption experiment (Dubibin-Astakhov model).

Experimental data of ^{13}C NMR in Fig. 1 shows that the two highest peaks are from 27 to 34 ppm and 125 to 135 ppm, respectively. 27–34 ppm are the chemical shifts of methyl and methylene, and 125 to 135 ppm are the chemical shifts of protonated aromatic carbon and bridgehead aromatic carbon. As the sample is subbituminous coal vitrinite sample, many aliphatic chains still exist in these vitrinites, and the macromolecule has a low aromatic carbon rate. The aromatic rings are primarily benzene and naphthalene, and all nitrogen atoms exit in the pyridine (Fig. 2). The total number of atoms in the 3D molecular structure (Fig. 4a) is 2992 and the size of the 3D lattice is 3.37 nm × 3.37 nm × 3.37 nm.

2.3. Calculation methods for pores in the macromolecular structure

It is necessary to define pores in the macromolecular structure. As the fractal dimension of ultra pores is not an integer (3) [21], if we use different rulers to measure the same pores, the results are different. In addition, certain pores may be too small for gas molecules, such as methane and CO_2 to access. These pores are insignificant when we study methane adsorption and others. Thus, it is important to study pores that can be seen by a responding molecule. In this study, we used probes to calculate pore volume and surface area based on van der Waals forces (Fig. 3).

We calculated the pore space through finding out the van der Waals (vdW) surface of coal macromolecular structure (Fig. 3a, b, c). The vdW surface of the macromolecular is also the surface of ultra micropores. After we found out the surface of the pores, we can calculate volume, surface area and other information of these ultra micropores in macromolecular structure.

In the calculation, we moved the probes in all the parts of the coal macromolecular structure cube evenly (interval = 0.015) to find out the vdW surface of macromolecule. When we moved the probe, there are three situations (Fig. 3a).

Situation 1: the location has been occupied by the coal macromolecule (red probes).

Situation 2: the location is not occupied by coal macromolecule but space around this location has been occupied (white probes).

Situation 3: the location is not occupied by coal macromolecule and space around this location is also not occupied (green probes).

Then, we can find that the white probes could form the vdW surface of the macromolecule.

It should be noted that we did not use specific molecules to measure