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Research article

Investigation on solubility of multicomponents from semi-anthracite coal and its effect on coal structure by Fourier transform infrared spectroscopy and X-ray diffraction

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ABSTRACT

As a sedimentary rock composed of organic carbonaceous matters with different molecular sizes and inorganic minerals, coal can be extracted by organic solvents and dissolved by acids to make chemical compositions and structures changed, thus influencing on the occurrence and migration of coalbed methane (CBM). For the purpose of investigating the impacts of different solvents on coal structure, semi-anthracite coal samples from Huoerxinhe coalmine in the central part of Qinshui Basin were treated by four single solvents (tetrahydrofuran (THF), carbon disulfide (CS_2), hydrochloric acid (HCl) and chlorine dioxide (ClO_2)), and by combined solvents (an organic solvent and an inorganic solvent with different treatment orders). Then the solubility behaviors of the organic compounds or inorganic matters from coal were investigated and the changes of the functional groups and the microcrystalline structure in coal were addressed using Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The results show the extraction yields of organic solvents are significantly greater than the dissolution yields of inorganic solvents, and the solubility of HCl is relatively higher than that of ClO_2. Specifically, main functional groups in coal, including aliphatic, aromatic and oxygen-containing functional groups, have a decline tendency to different degrees under the treatment of organic solvents. Further, main microcrystalline structure parameters increase in vertical direction but reduce in parallel direction of the aromatic carbon network layer with the swelling effect, regardless of an organic solvent or inorganic solvent treatment. Only by the organic solvent treatment, do the d_{002} values of the basic structure unit of coal appear dramatically enlarged characteristics. Whereas, main functional groups and microcrystalline structure in coal show relatively complex features within the combined solvents treatment because of the phenomenon of pore-blockade, pore-expansion or slight solvent retention. Based on the change characteristics and mechanisms, the chemical structure model of semi-anthracite coal is put forward for providing a reference for the further study of coal structure.

1. Introduction

The growing interest in unconventional gas has been boomed with the increasing demands of clear energy in global nowadays, especially in China, where unconventional gas is widely and abundantly distributed [1]. As a kind of unconventional gas, coalbed methane (CBM) trapped within the coal seam, is also paid more attention with the increasing pressure for supplying conventional gas and reducing greenhouse effect. Generally coal with its unique nature, is deem to form the special occurrence space for CBM. Therefore, under the background of CBM development and utilization, studying the nature of coal itself has been of great concern. Whereas the heterogeneous and complex nature in coal make its composition and structure characteristics challenging [2].

Coal is viewed as a complicated mixture of polyfunctional, high-molecular organic matters, low molecular organic compounds and various inorganic minerals [3,4]. Its organic components are not only composed of the complex macromolecular network with fused aromatic and hydroaromatic ring clusters, but also consisted of aliphatic and heteroatom side chains and low molecular compounds [5–8]. So it is difficult to utilize a single method or technique to explore the chemical structure of coal, and thus widely techniques are highly necessary to provide the greatest -advantage into the coal research. Now solvent treatment as an effective way, is extensively applied into the research of

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the composition and structure characteristics on coal [9–12]. Numerous researches have discussed treatments on coal using solvents such as supercritical solvents [13,14], mixed or single organic solvents [15–18] under the help of microwave, high temperature or some favorable conditions. Further by means of testing techniques, such as solid state ^{13}C nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), obtaining the significant information on coal could contribute to seek more complex composition and structure. Solid state ^{13}C NMR is a powerful technique for acquiring coal carbon structural parameters effectively, mainly composed of aromatic (f_a) and aliphatic (f_{al}) parameters in the NMR spectrum [19–22]. FTIR, combined with curve-fitting methods, offers quantitatively valuable information of functional groups (−CH_2, −CH_3, C═C, C−O, −OH, et al.) about the chemical composition and structure of coal [23–25]. Microcrystalline structural parameters obtained from XRD, such as crystallite sizes (L_a, L_c), inter layer spacing of carbon stacking structure (d_{002}), and aromaticity ratio, can be used to comprehend three-dimensional carbon packing structure of coal better [26,27].

In the process of coalification, different chemical characteristics are performed in coals with different coal rank, due to the constantly changing geological conditions. So far, a large number studies involving the extraction of brown and sub-bituminous coals with some organic solvents have been reported. In early years, Larsen et al. [28] tried to gain further understanding about coal macromolecular structure using a sub-bituminous coal and a lignite swollen in both polar and nonpolar solvents. Murata et al. [21] analyzed the distribution of oxygen-functional groups in four brown coals, including phenol, alcohol, carbonyl, carboxyl, and ether groups, to investigate various oxygen-containing groups in low rank coal. Miura et al. [29] had proposed a new method to clean up mineral matters and most of sulfur in sub-bituminous and brown coal samples for providing an effective way to improve a large number of clean fuels from low rank coals. Li et al. [30] found that acid-treated low rank coals transforms metal carboxylate groups in coal into carboxyl groups with forming released hydrogen bonds more easily, then high extraction yields of low rank coals with polar solvent NMP were obtained at the conditions of shorter extraction times and lower extraction temperatures. Recently Shui et al. [31] have achieved a higher extraction yield in different mixed solvents at different temperatures with respect to some Chinese sub-bituminous coal, and further carry out more concrete organic matters in low rank coal (such as heteroatom compositions and hydrocarbons). Later Yan et al. [32] found that carboxyl groups and C−O bonds begin to decompose at 150 and 200 °C, respectively, meanwhile the aliphatic, phenolic groups and aromatic structures remain steady below 300 °C, within dewatering and upgrading of Yunnan brown coal. So the composition and structure of low rank coal have been investigated extensively. These could be widely proved that the composition and structure characteristics of coal under solvent treatments occurs differences [4,33–35].

But to date few works have been tried to choose varied solvents with different properties to study composition and structure of semi-anthracite coal in detail. In this work, our study is focused on the effect on major functional groups and microcrystalline structure under the solubility of multicomponents from semi-anthracite coal, through different single solvent treatments (tetrahydrofuran (THF), carbon disulfide (CS_2), hydrochloric acid (HCl) and chlorine dioxide (ClO_2)) and combined solvents treatments (an organic solvent and an inorganic solvent with different treatment orders). Then we explored the differences in the change characteristics and treatment mechanisms with two independent techniques, namely Fourier transform infrared spectroscopy (FTIR) for identification of functional groups and X-ray diffraction (XRD) for determination of microcrystalline structure. These methods and analysis could facilitate to understand the chemical structure in semi-anthracite coal, and further give a novel treatment way to study the composition and structure of coal better.

Table 1
The proximate and ultimate analyses results of raw coal.

Sample	Ultimate analysis (wt%)				Proximate analysis (wt%)			
	C	H	O	N	Moisture	Ash	Volatile matter	Fixed carbon
Raw coal	91.2	4.0	2.9	1.5	1.1	10.0	12.5	77.9

2. Material and methods

2.1. Coal samples and solvent treatment experiments

The semi-anthracite coal samples were collected from Huoerxiner coalmine in the central part of Qinshui Basin, Shanxi Province, China, with a vitrinite reflectance ($R_{o,max}$) of 2.23%. The proximate and ultimate analyses results of raw coal are referred to Table 1. Meanwhile the content of clay and carbonate minerals is up to 70% of total minerals in raw coal. Coal samples were crushed and selected using standard sifters (0.18 mm–0.15 mm), and next dried in the drying oven at 70 °C. Meanwhile each sample was carried out every 12 h for weighting until the change of adjacent weight was less than 0.001 g, and then cooled and restored in the dryer to ensure accuracy. In this paper, four solvents (two organic solvents and two inorganic solvents) were used in the single solvent and combined solvents treatment experiments, and the combined solvents were defined as an organic solvent and an inorganic solvent with different treatment orders, which can be expressed as “organic + inorganic” or “inorganic + organic”. According to solvent properties and coal components, the solvents selected were as follows: tetrahydrofuran (THF) and carbon disulfide (CS_2) as organic solvents, 20% hydrochloric acid (HCl) and 20% chlorine dioxide (ClO_2) as inorganic solvents. The experimental procedure is shown in Fig. 1.

Each treatment experiment was carried out in an erlenmeyer flask of 250 mL. And that was charged with 20 g of coal samples and 200 mL of solvent in a 1 g:10 mL ratio at room temperature and atmosphere. The procedure of organic solvent treatment was continued about 12 h by means of a magnetic stirrer. In order to ensure the reaction completely, the inorganic solvent and coal samples were mixed with 72 h. In the following, the process of centrifuge, filtration, evaporation were conducted in turn. Finally partly dry residues were preserved in small brown bottles for the next tests.

Subsequently, other residues were used in the further treatment (phase II) for achieving the combined solvents experiment. In addition, it is worth noting that the further treatment can be achieved accurately on the basis of same experimental procedures with the single solvent treatment (phase I). For the purpose of expressing the samples easily, raw coal is expressed by “I”, residues are expressed by molecular formula or abbreviation, such as “I-HCl” and “I-HCl + THF” represented that coal treated by a single solvent and combined solvents respectively.

2.2. XRD measurements

XRD measurements were carried out by a Bruker D8 Advance diffractometer in Germany, employing Cu target, K_α radiation (λ = 0.154056 nm). The X-ray generator voltage is held at 35 kV. Scan range is adjusted from 2 to 90° in 2θ range with 0.1° step size and 8 s/step scanning speed. The data processing takes quadratic polynomial least square fitting method to smooth curves. In addition, raw coal and residues didn't remove minerals with the weight of 5.0 g to the experiment. Then four microcrystalline structure parameters, including inter-layer spacing (d_{002}), stacking height (L_c), crystallite diameter (L_a) and the average number of aromatic layers per carbon crystallite (N), are acquired through XRD measurements. Detailed calculation formulas [36–39] are seen as follows.