



Research article

Exploration on the removal mechanism of sulfur ether model compounds for coal by microwave irradiation with peroxyacetic acid



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ABSTRACT

The removal mechanism of sulfoether in coal by microwave with peroxyacetic acid, was determined by evaluating changes in sulfur containing compounds after desulfurization by XANES and GC/MS. The highest occupied molecular orbital composition, the electrostatic potential distribution, and the sulfur containing bond dissociation energy (BDE) of model compounds molecules were also determined to support the experimental results. Results showed that sulfoether was easily oxidized to corresponding sulfoxide or sulfone in treated samples. Although benzyl sulfides were more readily oxidized than disulfides, the latter was easier to remove due to the higher breaking probability of the S–S bond. The sulfur atoms within sulfur ether in coal are the active sites for electrophilic reaction. As sulfur atoms were oxidized, the sulfur containing BDEs decreased considerably and the dipole moments of sulfoether molecules increased. These findings suggest that the removal efficiency of sulfoether in coal may be improved by moderate and selective oxidation under microwave treatment.

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1. Introduction

Coal has played an important role in China's energy landscape and economic development over the past several decades [1]. However, high quality coal reserves have been gradually depleted and the combustion of high sulfur coal has resulted in release of sulfur dioxide and environmental consequences [2].

Several pre-desulfurization methods have been developed to treat high-sulfur coal, including physical, chemical, and biological processes [3]. Coal desulfurization by microwave (MW) irradiation with accessory ingredients is a relatively new sulfur removal method in which desulfurization is achieved by harnessing the differences in MW response among the various sulfur components in coal [4–6].

Previous research in the coal MW desulfurization field has mainly focused on process optimization, variation among sulfur forms in coal, and the dielectric properties of coal [7–11]. Prior studies have found that coal desulfurization by MW irradiation acts to create fractures and allows for better contact between the leaching reagent and sulfur groups in coal [12,13]. The reaction of $\text{Fe}_3(\text{CO})_{12}$ with thiophene has been shown to be accelerated by microwaving, which results in the removal of sulfur from the ring structure [14]. Under MW, the organic

sulfur components in coal are more difficult to remove compared with inorganic sulfur [15–17]. One study showed that the desulfurization of aliphatic sulfur compounds could be effectively controlled by the electron transfer process with the metal ion Co^{2+} [18]. Study of model sulfur compounds (methionine and di-benzothiophene) revealed that the desulfurization reaction under the studied experimental conditions is primarily because of aliphatic sulfur compounds [19]. Another study demonstrated that organic sulfate, sulfones and sulfoxides have been noticed in the coal samples treated by microwave and 85–98% pyritic sulfur of coal was removed by MW irradiation with peroxyacetic acid (PAA), which was attributed to the dielectric characteristic of pyrite interacting efficiently with MW irradiation [20].

The selective oxidation pretreatment makes the sulfur component in the oxidized coal easier thermal decomposed by weakening of C–S bonds in the coal via the conversion of divalent sulfur species to sulfones, sulfoxides or sulfonic acids during the oxidative pretreatment [21], as the energy of the C–S bonds decreased when the sulfur species were oxidized to sulfones [22]. In comparison to past studies, the desulfurization mechanisms of sulfur ether in coal by MW with oxidation additives have received limited attention. The complexity of sulfur forms in coal makes it difficult to determine the desulfurization mechanism accurately, so sulfur model compounds of coal have been employed for coal desulfurization study instead of coal [16,19,23–25].

X-ray absorption near edge structure (XANES) can be used to identify and quantify sulfur functionalities in coal non-destructively [26,27], and is highly sensitive to the changes in the oxidation state of sulfur [28–30]. Bond dissociation energy (BDE) can be used to determine the

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strength of chemical bonds and provide a better understanding of reaction mechanisms [31,32]. The structures and energetics of different disulfide compounds have been calculated by a number of previous studies [22,33–35]. The C–S bonds were found to be reduced by an average of 5.2 kcal/mol for aliphatic sulfides and 11.8 kcal/mol for aromatic sulfides and thiophenes with the divalent sulfur species oxidized to the sulfones form [36].

The frontier molecular orbital theory stipulates that the highest occupied molecular orbital (HOMO) determines the ability to gain and lose electrons in a molecule [37]. The atom of maximum charge density in the HOMO is the most susceptible to attack by a nucleophile [38]. In addition, the closer the distance is between the atom and the minimum point of electrostatic potential (ESP) on the molecule surface, the more an electrophilic reaction will occur [39]. In order to analyze the desulfurization experimental results from the microscopic point of view and elucidate removal mechanisms, quantum chemistry calculations were utilized to study the properties of the model compounds.

The objective of this study was to identify the desulfurization mechanism of sulfoether model compounds in coal during MW treatment with peroxyacetic acid. The variation of sulfur forms in the product after desulfurization was determined by XANES and gas chromatography-mass spectrometry (GC/MS). To quantify the mechanism from the molecular level, the molecular properties of sulfur model compounds were computed, including the molecular orbital composition, the electrostatic potential distribution, the sulfur containing BDEs and the dipole moment.

2. Materials and experiment methods

2.1. Materials

Dibenzyl sulfide (DS) and diphenyl disulfide (DDS) were subjected as the sulfur ether model compound of coal [23–25]. Their geometric configurations are shown in Fig. 1. In order to simulate the coal environment, the model compounds were impregnated onto an activated charcoal by the incipient wetness method using acetone as the solvent. The activated charcoal is of low sulfur (0.1%) content. Briefly, the sulfur containing compound was placed into a beaker with acetone solution and thoroughly mixed. The resulting solution was poured into another beaker to which activated charcoal had been added. The contents of the beaker were stirred by ultrasonication for about 1 h in sealed condition, filtrated and washed with acetone, dried at room temperature for about 48 h in a vacuum oven, and then collected for further experiment [25, 40]. All reagents of analytical grade were purchased from Aladdin.

2.2. Microwave/PAA desulfurization procedure

Samples and the additive were put in the quartz flask. A mixture of PAA solvent (1:1, v/v) was chosen as the desulfurization additive, with

a ratio of coal sample to additive of 1:5 (g/mL). The irradiation was performed by a microwave oven (MAS-II) with 2.45 GHz frequency, and the microwave irradiation power was set at 400 W, with different irradiation times (30, 90, 150 and 210 s). After irradiation time, the reactor was cooled down and the residue solution was filtered, washed with hot distilled water and dried in a vacuum oven at 60 °C for 6 h. The sulfur content of products was determined by the sulfur determination analyzer.

2.3. XANES and GC/MS analysis

XANES measurements were carried out at 4B7A beam-line (medium X-ray beam-line 2100–6000 eV) using synchrotron radiation from Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences. The normalization of the spectra was performed at 2.50 keV where the variation of the absorption cross-section is small. All the data calculation above was performed in WinXas (3.0), and the spectra were fitted with the LSFITXAFS [41,42].

Under ultrasonic condition, the filtrate and solid products were extracted using *N,N*-Dimethylformamide (DMF) as the solvent. Then the extractions were analyzed by JOEL-Q1000 GC/MS.

2.4. Density functional theory calculation

The BMK (Boese–Martin for Kinetics)/6-31G (d)//BMK/6-311++G (2df, 2p) method was utilized to study the sulfur containing BDEs of model compounds in this research [43,44]. While the HOMO composition and the electrostatic potential distribution were computed with B3LYP/6-31G (d)//B3LYP/6-311++G (2df, 2p). All calculations were performed by the Gaussian 09 programs [45].

3. Results and discussion

3.1. Changes of sulfur forms

3.1.1. GC/MS analysis results

Results of the XANES analysis for solid products after desulfurization are shown in Fig. 2. In the XANES spectra, the peak value was observed to gradually shift to the right with reaction time, which indicated that the sulfur was gradually oxidized to a higher valence [46].

The distribution of different sulfur forms compared with total sulfur in samples is presented in Fig. 3. With increasing reaction time, the content of the two sulfur ether compounds in samples decreased rapidly. A small amount of sulfonate and sulfate was detected and the sulfur was mainly in the form of oxidation state as the reaction time over 90 s. These results suggest that these two model compounds were oxidized easily and that desulfurization was achieved through oxidation to the water-soluble sulfonate or sulfate in MW field.

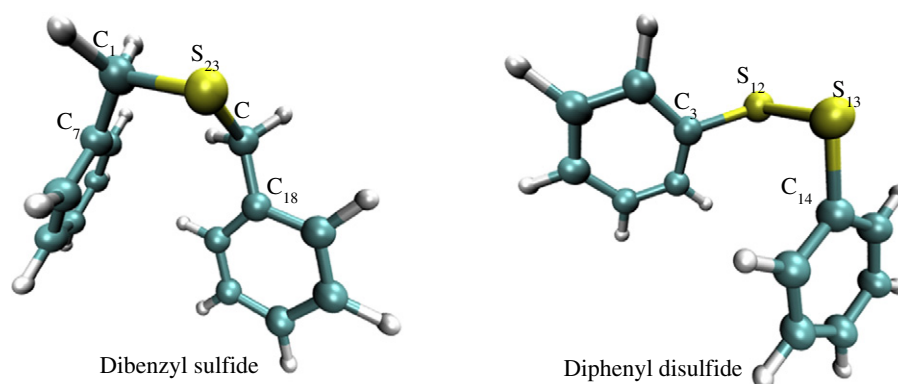


Fig. 1. Geometric configuration of the model compounds.

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