



Full Length Article

Exploration on the action mechanism of microwave with peroxyacetic acid in the process of coal desulfurization

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ABSTRACT

To clarify the action mechanisms of microwave field with peroxyacetic acid in the process of sulfur removal from coal, this study was carried out on the molecular level and diphenyl sulfide was selected as the sulfur model compound of coal. Its oxidation reaction path was determined utilizing XANES and GC/MS. The transmission reflection method was adopted to analyze the dielectric property of the substances detected before. Their C–S bond dissociation energies (BDEs), bond dissociation times (BDTs) and the intrinsic reaction coordinate of desulfurization reactions were calculated under various extra electric fields to support the experimental results. Results showed that most of diphenyl sulfide was oxidized to the corresponding sulfoxide and sulfone, resulting in a desulfurization degree of 22.37% after microwaving treatment at 500 W for 120 s combined with peroxyacetic acid. With the oxidation degree deepening, the absorption efficiency of microwave energy for sulfur groups increased and their C–S BDEs decreased, resulting in the reducing of their C–S BDTs. In addition, the C–S BDTs and the barrier of desulfurization reactions were reduced under the extra electric field. These findings confirmed that the sulfur-containing bonds cleavage and desulfurization reactions of sulfur groups were promoted under the extra microwave field with peroxyacetic acid, which is conducive to the effective removal of sulfur groups from coal.

1. Introduction

In China, coal is a primary source of energy and has played an important role in economic development over the past several decades. Coal is still utilized in large numbers for the foreseeable future [1]. Nevertheless, sulfur in coal is a major factor inhibiting the use of coal due to the release of sulfur dioxide.

Among the primary coal desulfurization methods, including physical, physico-chemical, chemical and microbial desulfurization, chemical-related desulfurization is considered to be the most effective methods for both inorganic and organic sulfur of coal. In addition, the effective desulfurization technologies were achieved by combining various desulfurization methods [2]. Coal desulfurization by microwave irradiation is a relatively new sulfur removal method and obtains developments in recent decades [3,4], which harnesses the differences of microwave response for the various components in coal [5,6].

The sulfur forms in raw coals and chars were analyzed using sulfur K-edge X-ray absorption spectroscopy, finding that the sulfur forms in

different coals were different and they behaved differently during desulfurization [7,8]. The organic sulfur in coal of low metamorphic degree are mainly composed of aliphatic sulfides, and those in coal of medium and high metamorphic degree are mainly composed of thiophenes [9].

It was found that the imaginary part of the complex permeability (ϵ'') of pyrite in coal was much larger than that of coal (excluding minerals), and the heating rate of the former was about 9 times of the latter [10,11]. Compared with external heating pyrolysis, the microwave method improved the desulfurization efficiency obviously. Pyrite in coal was dissociated to pyrrhotite and troilite by microwave radiation under a nitrogen flow stream [12]. It was observed that hydrogen could promote the desulfurization rate considerably and more than 65% of sulfur could be removed in the hydrolysis process of high-sulfur coal [13]. The decomposition temperatures of sulfur model compounds of coal were lower during pyrolysis under an oxidative atmosphere than that under inert or hydrogen atmospheres, indicating that oxygen could break C–S bonds more easily [14].

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The inorganic and organic sulfur of coal were removed without destructing coal organic matrix by combination of microwave irradiation and peroxyacetic acid (PAA) washing, obtaining pyrite and the organic sulfur reductions of about 84% and 49%, respectively [15]. The removal of organic sulfur was more difficult than that of inorganic sulfur in coal by microwave [16]. Sulfate, sulfone and sulfoxide were all detected in the treated samples after microwave treatment [17]. In addition, the microwave treatment resulted in changes of physical characteristics for coal [18]. Thiophene sulfur of coal tar pitch was effectively oxidized to the oxidized organosulfur compounds using ureahydrogen peroxide complex with a carboxylic anhydride in tetrahydrofuran [19]. 73% organic sulfur was removed after the coal was treated by combining atmospheric oxidation and chemical cleaning with alkali solutions at temperature around 363 K [20]. The organic sulfur was effectively removed from coal using peroxyacetic acid (PAA) and molten sodium hydrate combined with microwave, whose reaction mechanism is that the microwave response characteristics of sulfur groups were improved after mixing with PAA or sodium hydrate [21–23]. Microwave-ultrasonic irradiation combined with oxidants [24], organic solvents [25] or chemical leaching [26] was an effective method for coal desulfurization, and their desulfurization rates could be above 50% [27].

Sulfur model compounds studies revealed that the desulfurization process was effective for aliphatic type compounds by electron-transfer process, while thiophene and condensed thiophene-type compounds remained unaffected due to their higher stability [28–31]. The sulfur removal efficiency of coal was apparently enhanced by the selective oxidation pretreatment with PAA [32]. In our previous studies, the effective desulfurization of sulfoether in coal was realized by oxidation under microwave treatment [33]. The main reaction mechanism in the low-temp oxidation of the sulfur ether model compound was that the sulfur ether generated the corresponding sulfoxide and sulfone, producing a small amount of free radicals [34]. With the aid of microwave field, selective heating and special function of polarizable molecules could be realized [5,6] and some difficult reactions could be promoted to carry out [35,36].

In comparison to past studies, the effect of microwave field with PAA on the removal of sulfur in the process of coal desulfurization has received limited attention. In order to reveal the mechanism of coal desulfurization by microwave and the effects of microwave on the properties of sulfur-containing groups, desulfurization reactions need to study from a molecular level.

Bond dissociation energy (BDE) reflected the strength of chemical bonds, which was the basis of understanding the reaction mechanism [37–40]. As the divalent sulfur species were oxidized to the sulfones, the C–S bonds of aliphatic sulfides and aromatic sulfides or thiophenes were found to be reduced by the average of 5.2 kcal/mol and 11.8 kcal/mol, respectively [41]. In addition, carbon-sulfur bond dissociation times (C–S BDTs) was used to quantitatively analyze the dissociation regularity of C–S in sulfur model compounds of coal, which was computed according to the results of the dielectric test and carbon-sulfur bond dissociation enthalpies [6]. So the quantum chemistry calculation was used to explore the mechanism of coal desulfurization by microwave from the microscopic point of view according to the experimental results.

The objective of this paper was to study the effect mechanisms of microwave field on the removal of sulfur from coal. Diphenyl sulfide was selected as the model compound of sulfur in coal. In order to determine the oxidation reaction path, the treated samples were analyzed by XANES and GC/MS. The dielectric properties of reactants and detected products were analyze utilizing the transmission reflection method. For quantitatively analyzing the effect of the external microwave field on the C–S bonds, the variations of BDEs and BDTs for C–S bonds under the different extra electric field intensity were calculated with Gaussian 09. The calculation of intrinsic reaction coordinate (IRC) was also carried out to investigate the effect of the extra microwave

Table 1
Ultimate analyses of the activated charcoal.

C	H	O	N	S
<i>Ultimate analysis (wt% dry ash free basis)</i>				
80.76	2.82	15.61	0.78	0.03

field on the desulfurization reactions.

2. Materials and experiment methods

2.1. Materials

Considering the limits of computing power, diphenyl sulfide was selected as the sulfur model compound of coal [14,42–44]. In order to simulate the coal environment, the model compound was impregnated onto an activated charcoal by the incipient wetness method using acetone as the solvent. The activated charcoal is of low sulfur content as indicated by the ultimate analyses shown in Table 1. 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 coal had been added. The contents of the beaker were stirred by ultrasonic for about 1 h in sealed condition, dried at room temperature for about 48 h, and then collected for further experiment [14,33]. Total sulfur content of the obtained initial samples was 2.28 wt %. All reagents of analytical grade were purchased from Tokyo Chemical Industry.

2.2. Microwave/HAc-H₂O₂ desulfurization procedure

A mixture of HAc-H₂O₂ 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 500 W, with different irradiation times (10, 20, 30, 60, 90 and 120 s). After the set irradiation time, the reactor was cooled down and the residue solution was filtered. Solid products and filtrate were collected respectively. The desulfurized sample was washed with hot distilled water, dried in an vacuum oven at 60 °C for 6 h. Sulfur content of dried products were determined by using the sulfur analyzer.

2.3. XANES and GC/MS analysis

For studying sulfur forms, the X-ray absorption near edge structure analysis (XANES) of samples was performed at 4W1B endstation, Beijing synchrotron Radiation Facility, which ran 2.5 GeV electron with current from 150 mA to 250 mA. The XANES data of the standard samples (diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, sodium diphenylamine sulfonate, methyl para-toluene sulfonate, Zinc sulfate) and model samples were processed by interpolating and normalizing, and then fitted by the Athena software [45].

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

2.4. Dielectric properties measurement

In this study, the transmission reflection method was used to measure the dielectric properties [46]. All samples were uniformly mixed with dissolved paraffin at a weight ratio of 3:4 and die-pressed into a toroidal shape with 7 ± 0.2 mm length, 3.04 mm inner diameter and approximately 2.0 mm thickness. The scattering parameters of samples were measured in the 100 MHz–6.5 GHz frequency range by a vector network analyzer (E5071C Agilent). Then the complex dielectric constant (ϵ_r) of the sample were calculated out [47].

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