



# Calcium-promoted catalytic activity of potassium carbonate for steam gasification of coal char: Transformations of sulfur



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## HIGHLIGHTS

- ▶ A high-sulfur bituminous coal char was gasified with  $K_2CO_3$  by pre-addition of  $Ca(OH)_2$  to coal.
- ▶ Sulfur XANES was used to determine sulfur transformations associated with coal pyrolysis and gasification.
- ▶ The calcium additive facilitated the decomposition of both inorganic and organic sulfur during coal pyrolysis.
- ▶ The calcium additive allowed more sulfur to be retained in the ash as  $K_2SO_4$  after gasification.

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## ABSTRACT

$K_2CO_3$ -catalyzed char gasification with steam was carried out on a laboratory fix-bed reactor and it featured in the preparation of char from a high-sulfur coal by the prior addition of  $Ca(OH)_2$  to the coal. This work was focused on the clarification of sulfur transformations during the coal pyrolysis and the char gasification. Sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy was employed to determine quantitatively the forms of sulfur in coal and their changes in process. Results showed that the addition of  $Ca(OH)_2$  to coal promoted the decomposition of both pyrite and organic sulfur during the charring. In the  $K_2CO_3$ -catalyzed char gasification, the calcium additive enabled more sulfur to be retained eventually as  $K_2SO_4$  rather than  $CaSO_4$ . The formation of  $K_2SO_4$  would be conducive to the recycled use of potassium catalyst.

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## 1. Introduction

In previous papers, we reported the  $K_2CO_3$ -catalyzed steam gasification of coal for production of hydrogen-rich gas [1] and the promoted catalytic activity of potassium carbonate for char gasification by addition of different calcium species to different coals [2,3]. This work is extended to investigate the behavior of sulfur in the process of pyrolysis and catalytic gasification. Sulfur, even as a minor impurity in coal, has monstrous impacts on coal processing and utilization. In combustion, sulfur in coal is converted to sulfur oxides which share an important cause of acid rain. In pyrolysis and gasification, although sulfur is not directly discharged as an environmental pollutant, the presence of sulfur in gas is harmful whether the gas is used as a fuel or a synthesis gas, or for production of hydrogen. From viewpoints of environ-

mental protection and process development, therefore, it is essential to gain intimate knowledge of the sulfur transformations associated with various coal pyrolysis and gasification processes. The pyrolytic behaviors of sulfur in coal have long been the subject of a large number of studies [4–12], but only a few studies are concerned with the influence of calcium additive [9] and the sulfur transformations in coal gasification [5,13,14].

Sulfur in coal is broadly divided into inorganic and organic sulfur. High-sulfur coal usually contains pyrite as a principal sulfur mineral, with minor sulfate and other sulfur minerals. The organic sulfur is bound in the heterocyclic structures (thiophene, aryl sulfide, etc.) and the functional groups (mercaptan, aliphatic sulfide, etc.). The organic sulfur is much more complex and difficult to analyze than the inorganic sulfur [15]. Sulfur K-edge X-ray absorption near edge structure (XANES) spectroscopy is a direct, nondestructive and powerful instrumental method for differentiating between different forms of sulfur in coal [16–21], pyrolysis char [21,22], and other materials [17,23,24]. Encouragingly, this technique offers a

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quantitative determination of all major forms of sulfur in coal. There are two approaches to quantify an original XANES spectrum. One is by the least squares fit using Gaussian or Lorentzian functions plus one or two arctangent function(s) [16,19,22]; another is also by the least squares fit but using a linear combination of XANES of sulfur-containing model compounds [23–25]. The latter may be preferred to the former when the model compounds are enough to be representative of all forms of sulfur in sample, because the former is easily subject to error from the multiple absorption peaks of some sulfur components.

In this paper, our interest is centered on the calcium-influenced transformations of the sulfur forms during pyrolysis and catalytic gasification. XANES is used for quantitative determination of the major forms of sulfur in both coal and char, and it is especially valuable to reveal the transformations of various sulfur forms.

## 2. Experimental

### 2.1. Coal pyrolysis and char gasification

A Chinese high-sulfur bituminous coal (YST coal) was used in this study. The coal sample was ground and sieved to the particle size of less than 0.15 mm. The proximate analysis showed that the coal sample used (air-dried) had 0.69% moisture, 32.2% volatile matter and 13.0% ash. The ultimate analysis showed that the coal (daf. basis) comprised of 84.41% C, 5.46% H, 0.65% N, 3.83% S and 5.64% O (by difference). X-ray fluorescence analysis of the ash composition showed that the coal (dry basis) contained 0.06% Na, 0.06% Mg, 2.01% Al, 0.08% K, 0.28% Ca, 2.78% Si and 1.77% Fe.

Experiments of pyrolysis and gasification were carried out on a corundum tubular fixed-bed reactor (i.d, 12 mm). The reactor was vertically mounted and heated by a temperature-programmed electric furnace. Ceramic pellets were packed in the lower part of the reactor to support the sample. In each pyrolysis experiment, a 2 g sample of coal was heated from room to the predetermined temperature at 15 °C/min in a stream of nitrogen at atmospheric pressure. The gas flowed from the bottom of the reactor to the top with a flow rate of 200 ml/min, which was controlled by the mass flow meter. The tar derived from coal pyrolysis was condensed in two ice/water traps, and the moisture in the gas was removed using a silica gel column. The dried gas was collected in gas bags at a temperature interval of 50 °C, and then used for gas analysis. The char was collected after the reactor was cooled down, and stored in a sealed bottle for the sample of char analysis and gasification. Two types of coal samples, raw coal and Ca(OH)<sub>2</sub>-added coal, were used. The latter was prepared by blending raw coal proportionally with powdery Ca(OH)<sub>2</sub> (particle size, 0.05–0.07 mm) in an agate mortar for 15 min. For simplicity, the Ca(OH)<sub>2</sub>-added coal is abbreviated to CH coal, and the chars prepared from the raw coal and CH coal are abbreviated to R char and CH char, respectively. The calcium additive loadings used in this study were 5%, 10% and 15%, in weight percentage, based on the initial mixture of coal/calcium additive.

In each gasification experiment, a 0.3 g sample of R char or CH char mixed with 10% K<sub>2</sub>CO<sub>3</sub> (mixture basis) was heated up to 750 °C in a stream of nitrogen. Then, the gasification started by switching the nitrogen stream to the nitrogen/steam gas (partial pressure of steam, 0.5; nitrogen flow rate, 200 ml/min), and maintained isothermally for 60 min. The steam in the off-gas was removed through an ice/water condenser followed by a silica gel column. The gas was collected in gas bags at a time interval of 5 min and then used for analysis. After gasification, the ash or residue was collected for analysis.

### 2.2. Analysis methods

The major gases (CO, CH<sub>4</sub> and CO<sub>2</sub>) were determined on a Microwave 3000 gas chromatograph (GC) equipped with thermal conductivity detector (TCD) and a molecular sieve column plus a Porapak Q column, using helium as a carrier gas. H<sub>2</sub> was determined on an Agilent-6820 GC equipped with TCD and a Unibeads C 80/100 packed column, using argon as a carrier gas. The sulfur-containing gases (H<sub>2</sub>S, COS and SO<sub>2</sub>) were determined by a Haixin GC equipped with flame photometric detector (FPD) and a capillary column. Elemental analysis (C, H and N) was carried out on an elemental analyzer (Elementar Vario EL III). Sulfur analysis was accomplished on a Coulomb sulfur analyzer (CLS-2). Forms of sulfur in coal were determined according to the standard method ASTM D 2492-02. X-ray diffraction (XRD) was performed on an X-ray diffractometer (Rigaku D/max 2550Vb/PC).

Most experiments of the K-edge XANES were conducted on a beamline 4B7A at Beijing Synchrotron Radiation Facility. Some experiments of the K-edge XANES were conducted on a soft X-ray micro-characterization beamline (SXRMB) at Canadian Light Source. Both beamlines were operated in a vacuum (10<sup>-7</sup> Torr) for sample measurement. The XANES spectra of all coal, char, and ash samples were measured using the fluorescence yield mode (FY mode) with a silicon draft detector (SDD), unless stated otherwise, while those of the reference samples were measured using total electron yield mode (TEY mode) with a 300 V bias voltage. This selection in the detection modes was because FY mode was more penetrating into the bulk sample than TEY mode and thus less sensitive to the surface assemblages, while its application for the reference sample would lead to the spectral distortion. The X-ray energy was scanned from 2431.0 to 2601.0 eV and calibrated by reference to the white line of calcium sulfate (2481.8 eV). The spectra were recorded at a step width of 0.2 eV and then normalized using Athena program package [26]. All reference inorganic and organic sulfur-containing compounds used in the study were chemical reagents, including iron sulfide (FeS), pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>), pyrite (FeS<sub>2</sub>), calcium sulfide (CaS), calcium sulfate (CaSO<sub>4</sub>), potassium sulfate (K<sub>2</sub>SO<sub>4</sub>), elemental sulfur, disulfide (dibenzyl disulfide), sulfide (benzylthio benzene), thiophene (dibenzothio-phenone), sulfoxide (DL-methionine sulfoxide), sulfone (saccharin), and sulfonate (sodium methanesulfonate). For conciseness, the spectra of these compounds are not separately presented in this paper.

## 3. Results and discussion

### 3.1. Sulfur speciation of raw coal

ASTM analysis showed that YST coal had total sulfur content of 3.84% including 1.11% pyrite, 0.40% sulfate, and 2.33% organic sulfur (by difference), so the inorganic sulfur accounted for 39% of the total sulfur in coal. XRD analysis revealed that the major crystalline minerals present in YST coal were kaolinite, quartz, pyrite, calcite, and melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O). The presence of hydrated iron sulfate in bituminous coal is well recognized as an indication of coal weathering in storage. Hydrated iron sulfate is formed by the oxidation of pyrite, so it is normally concentrated on the surface of pyrite grains.

Fig. 1 displays the XANES spectrum of YST coal and the fitting result obtained by the least squares linear combination of the reference spectra. It was seen that the major forms of inorganic sulfur in the coal were pyrites and sulfate, consistent with the XRD characterizations; the major forms of organic sulfur were thiophene and sulfide. These two forms of sulfur were also found in Argonne premium coals as the dominant forms of organic sulfur [17].

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