Analyses on Forms of Sulfur in Chinese Yanzhou Coal and Their Transformation during Pyrolysis by X-ray Absorption Spectroscopy

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Abstract: In the process of pyrolysis, inherent and the added minerals are the main factors to affect the transformation and distribution of sulfur in coal. In order to cleanly and efficiently use the inferior coal with high-sulfur content, Yanzhou coal containing 5wt % sulfur was chosen as the sample to do pyrolysis experiments in a fixed-bed reactor. The effect of iron additive on the sulfur forms and their transformation during coal pyrolysis was studied in this paper. Fe and S forms in raw coal with (FC) and without (RC) iron additive and their chars from different temperature were determined by XANES, and the gaseous products and total sulfur in char were also considered. The results show that addition of Fe in coal can make more sulfur retained in the char. The transformation of sulfur exists in the entire coal pyrolysis process from 200 to 1000 °C, and more inorganic sulfur was produced during the FC pyrolysis at high temperature (700-1000 °C). FeS existing in the FC char from 1000 °C occupies about 62% of the total sulfur in char, but there is almost no FeS in the RC char at 1000 °C. The semi-quantitative analysis of XANES data by LCF fitting will also be discussed.

1. Introduction
The energy and environment undergo more and more serious tension with the rapid development of social economy and the mass consumption of coal resource in China. One of the main problems obstructed the effective and extensive utilization of coal is the sulfur existing in coal. Sulfur in coal can be generally divided into two categories, inorganic sulfur and organic sulfur. Understanding the sulfur forms and the transformation during coal pyrolysis plays a role in the theoretical direction for the removal of sulfur.

Pyrolysis, the initial stage of the coal conversion process, is one of main approaches to adjust and control the proportion and composition of coal gas, tar and char. In this process, there exist the release of sulfur from coal and the mutual transformation among different sulfur forms [1,2]. The transformation and distribution of sulfur are determined by coal properties and its pyrolysis conditions. The inherent minerals in coal, such as alkali, alkaline-earth and transition metal, have the ability to change the devolatilization reactions during coal pyrolysis and the transformation of sulfur [3-6]. Iron is the main inherent minerals in coal and the common catalyst for many chemical reactions, which has the efficient, cheap and multi-valent characters [7]. How the inherent and additional iron in coal affecting the transformation of sulfur during pyrolysis are our primary focus.
X-ray absorption spectroscopy (XAS) is a non-destructive technique that can be used to probe the chemical and electronic structure of various materials. S K-edge XAS to qualitatively and quantitatively determine the inorganic sulfur forms has previously applied [8], but the analyses of organic sulfur forms in coal are rarely reported. Based on the above analysis, the present work chose Yanzhou coal with high-sulfur content as the experimental samples, the sample loaded iron was prepared and their pyrolysis experiments were carried out in a fixed-bed reactor. The performance of sulfur transformation during coal pyrolysis and the effect of iron in coal on them were discussed based on the XANES spectra analyses.

2. Experimental

2.1 Samples preparation

Yanzhou raw coal (RC) used as the experiment sample was ground and sieved to the particle sizes of 0.154-0.258 mm. The proximate, ultimate analyses and sulfur forms of RC are given in Table 1. It can be seen that the total sulfur content in RC is 5.0%, which is a typical high-sulfur coal, the pyritic sulfur and organic sulfur have similar proportion and the sulfate sulfur is also significant.

| Proximate analysis /% | Ultimate analysis /% (daf) | Sulfur forms / % (daf) |
|-----------------------|----------------------------|-----------------------|
| M_d  | A_d  | V_daf | C  | H  | N  | S_t | S_p | S_o* |
| 2.3  | 13.6 | 43.4  | 81.5| 5.1| 1.3| 5.0 | 7.1 | 0.9  | 2.1  | 2.0  |

ad: air-dried basis; d: dry basis; daf: dry and ash-free basis. * by difference.
S_t: the total sulfur; S_p: the pyritic sulfur; S_o: the organic sulfur.

The coal added iron (FC) with 1% (wt) FeCl_3 was prepared by impregnation method according to the following procedures. 0.167 g FeCl_3·6H_2O was dissolved in deionized water and then 10 g raw coal was added into this precursor solution, fully blended for 30 min and placed 12 h in the atmosphere, then dried for 12 h at 60 °C in a vacuum drying oven.

2.2. Pyrolysis

About 0.5 g RC and FC samples are preset on the sintered plate in a fixed-bed quartz reactor (600 mm long and 28 mm ID) under pure argon atmosphere and pyrolyzed by temperature programmed-isothermal thermal evolution course with a gas flow rate of 600 mL/min. Each experiment was carried from room temperature to the preset levels (300, 400, 500, 600, 700, 800, 900 and 1000 °C) at a heating rate of 10 °C/min and then held for 40 minutes. The concentrations of H_2S and COS in outlet gas were determined by gas chromatograph of GC-950 with the FPD detector. The yield of sulfur in gases (Y_{s-gas}) is calculated by the ratio of the sum of H_2S and COS with the total sulfur in raw coal.

The total sulfur content in char from different temperature was measured using a HCS-140 carbon sulfur analyzer. The yield of sulfur retained in char (Y_{s-char}) is expressed according to the ratio of total sulfur in char with total sulfur in raw coal.

2.3. S K-edge XAS spectra

The iron and sulfur forms in coal sample and pyrolyzed chars were detected by the X-ray absorption spectroscopy at Canadian Light Source by using the soft X-ray Micro characterization Beam line (SXRM). Si (111) double crystal monochromator was used, giving an energy resolving power of 10,000 eV [9]. The experimental sample was placed in a vacuum chamber (base pressure of 1 x 10^{-8} torr), using a double-sided conduct carbon tape. The Fe and S K-edge XAS spectra were recorded in the bulk sensitive fluorescence yield (FLY) with a micro-channel plate detector. The energy scale was calibrated using the Ar K-edge in the ion chamber and a sulfate peak at 2481.6 eV. The accuracy of energies reported here is 0.2 eV.
3. Results and discussion

3.1. The formation of char and transformation of sulfur during coal pyrolysis

The effect of iron added on the formation of \( \text{H}_2\text{S} \) and COS during coal pyrolysis is shown in Figure 1. The addition of iron in coal decreased largely the release of gaseous sulfur \( \text{H}_2\text{S} \) and COS during pyrolysis below 650 °C and shifts the temperature of maximal \( \text{H}_2\text{S} \) and COS release to the low values, due to the possibility that the pyrite may be oxidized to ferrous sulfate and elemental sulfur by \( \text{FeCl}_3 \) solution [7]. However, the release of gaseous sulfur was promoted by iron above 650 °C, which was caused by the decomposition of iron sulfate from the oxidation of pyrite to form iron sulfide and the catalytic influence of the iron on the decomposition of the sulfates. And the restraining effect of iron added to coal during pyrolysis was further proven by the yields of gaseous sulfur in Figure 1.

Figure 2 shows the yields of char and total sulfur in chars during coal pyrolysis. The char yields of both RC and FC samples presented a general trend, decreasing with the increasing of temperature. But the addition of iron in RC changed the yield of char at different temperature. Below 450 °C, the char yield of RC was larger than FC, indicating that iron improved the volatilization of coal during low pyrolysis temperatures by catalyzing the breakage of unstable bonds. However, at 450 °C to 900 °C, the case is in reverse, which indicates that the combination of char with the volatile to form new species in char was improved by the iron. When the pyrolysis temperature is further risen to 1000 °C, their change of char yields performed the same shape, and then tended to be constant, for the volatiles have been entirely released.

![Figure 1. Release concentrations and yield of \( \text{H}_2\text{S} \) and COS during coal pyrolysis](image1)

![Figure 2. Yields of char and sulfur retained in char during coal pyrolysis](image2)

The sulphur retention in char of RC performed a sharp decrease below 600 °C, and then kept stable, owing to the mass decomposition of pyrite, unstable organic sulphur and sulphate in coal during pyrolysis. However, above 600 °C, the degree of decrease became slightly, which was resulted from the great difficulty of decomposition of the complicated sulfur species. Compared with the change of RC, the sulfur of FC was quite stable and the change of yield of sulphur in char was not obvious. The difference between RC and FC samples may be owing to the effect of iron added in coal by changing the decomposition behaviour of pyrite and the secondary reactions of sulfur species, such as formation of the complex organic sulphur or stable sulphide from \( \text{H}_2\text{S} \) and COS releasing during pyrolysis.

3.2. The transformation of iron during coal pyrolysis

Figure 3 shows the XANES spectra of Fe K edge in FC and the corresponding chars at different pyrolysis temperature. Compared with the XANES spectra of the serial Fe model compounds, it can be seen from the XANES spectra that FC and chars samples below 500 °C had obvious edge positions at 7124.0 eV, 7135.5 eV, indicating that there existed large amount of ferrous chloride (Fe\(^{2+}\)) and ferric sulfate and ferrous sulfate during FC coal samples pyrolysis below 500 °C, meanwhile, the high contents of ferrous chloride and ferrous sulfate in the FC were from the oxidation of pyrite by ferric chloride (Fe\(^{3+}\)) during the impregnation process of sample. However, the peak position at 7124.0 eV almost disappeared between 600-700 °C, illustrating that FeCl\(_2\) decomposed completely and transformed into the other sulfur-containing species.
There appeared obvious edge position edge at around 7131eV in the XANES spectra of the chars of FC above 400 °C, which is related to the characteristic peaks of Fe₂O₃ and FeO, implying that these iron oxides produced from the decomposition of iron sulfate. Subsequently these iron oxides reacted with the H₂S from the pyrolysis volatiles to form FeS retaining in char [10].

3.3. Effect of iron additive on the changes of sulfur forms during coal pyrolysis

Figure 4 shows the X-ray fluorescence spectra of FC samples at different pyrolysis temperatures. Based on the experiments of some sulfur-containing model compounds, it can be obtained the peak positions of these pure substances, such as FeS is at 2470.1 eV, pyrite at 2471.4 eV, CaS at 2477.7 eV, Fe₂(SO₄)₃ at 2481.6 eV, DBS sulfone at 2479.3 eV and 2,2'-Bithiophene at 2473.3 eV.

Figure 3. XANES results of the iron-containing modal compoundsand samples

Figure 4. X-ray Fluorescence yields of FC sample and chars from different temperature

It can be seen that the catastrophe point of the sulfur transformation during coal pyrolysis presents in the temperature range of 400-600 °C, from which the decomposition reactions of unstable sulphur-containing species had been already completed, and new sulphur species began to form. The X-ray Fluorescence spectra of RF indicated the presence of ferric sulphate, thiophene, and pyrite, which was characterized by the edge position at 2481.8 eV, 2473.0 eV, and 2471.3 eV, respectively. Above the temperature of 600 °C, ferric sulphate and pyrite in char decomposed completely to form FeS and other stable sulphide such as CaS (at 2478.0 eV) in char and the sulfur-containing gaseous products. With the increase of pyrolysis temperature, the peak position of thiophene rings began to move to the higher energy position, indicating that condensation reactions of thiophene rings happened to form the complex thiophene rings restraining in char.

The differential percentages of different sulfur species in chars at different pyrolysis temperatures from the results of X-ray Fluorescence spectroscopy are shown in Table 2. It can be seen that the addition of iron played an important role in the transformation of sulfur in coal during coal pyrolysis. The increase of sulfate on the surface of sample may be due to the oxidation on the surface of sample by air during the coal preparation. In the process of coal pyrolysis, the iron decreased the amount of organic sulfur and sulfate, while increased the inorganic sulfur contents in solid products, indicating that iron catalyzed the breakage of organic sulfur bond to form some sulfur-containing radicals, and then the sulfur-containing radicals pass through the pore channel to release. When the radicals encountered the iron on the surface of pore, reactions of forming inorganic sulfur occurred. From the data of CaS in char, the content of calcium sulfide between 600-800 °C increased by the addition of iron but decreased at above 800°C, indicating that the addition of iron affected the formation of CaS. FeS is the main residue of iron in the char, whose amount is far larger than that of CaS, so sulfur is more susceptible to combine with iron not calcium.

Table 2. The differential percentage of different sulfur species between FC and RC samples from the results of X-ray Fluorescence spectroscopy

| Sample | FeS | CaS | Pyrite | Sulfide | Thiophene | Sulfoxide | Sulfate |
|--------|-----|-----|--------|---------|-----------|-----------|---------|
|        |     |     |        |         |           |           |         |
4. Conclusion

(1) The pyrolysis temperature of 600°C is a catastrophe point for the sulfur behavior in coal during pyrolysis, where both organic sulfur and inorganic sulfur begins to distribute again.

(2) Iron changed the release of H$_2$S and COS in the gaseous products dramatically during pyrolysis. The H$_2$S from the decomposition of pyrite decreased largely, due to the intermediate sulfur combining with iron rather than the H radicals to form H$_2$S. Compared with raw coal, the release temperature zone of COS is in advance, for iron added improved the formation of volatile at low temperature.

(3) The addition of iron decreased the formation of organic sulfur and sulfates in char, and increased the formation of inorganic sulfur like FeS, indicating that iron played a catalytic role in breaking the organic sulfur and recombined with free sulfur to reform new sulfur-containing species in char.

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