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Organic and inorganic sulphur compounds releases from high-pyrite coal pyrolysis in H_2, N_2 and CO_2: Test case Chinese LZ coal

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HIGHLIGHTS

- A high-pyrite coal was chosen to study the thermal effect of N_2, H_2 and CO_2 atmospheres.
- Different gases resulted in specific decompositions/changes of both organic and inorganic sulphur.
- The effect of CO_2 atmosphere on sulphur compound formation was evaluated in more details.

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ABSTRACT

The effects of different atmospheres on the distribution of organic and inorganic sulphur compounds during high-pyrite coal pyrolysis were investigated. Sulphur compound releases were determined by atmospheric pressure-temperature programmed reduction (AP-TPR) “on-line” coupled with MS and AP-TPR “off-line” coupled with TD-GC/MS, which is a reliable technique for coal sulphur characterization. The results show that the decomposition of both organic and inorganic sulphur is different in the three applied atmospheres: H_2, N_2 and CO_2. In H_2, most sulphur from LZ coal is hydrogenated/reduced to H_2S, decomposition of inorganic sulphur (pyrite and sulphates) has a great effect on the formation of H_2S. It not only enhances the intensity of its m/z 34 signal but also shifts the peak maximum of its profile to a higher temperature, even without a returning to the base line. In inert N_2 gas, as expected, hydrogenation of some sulphur compounds such as less-reactive di-aryl sulphur species and simple thiophenic structures are highly limited. The dominant peak of m/z 34 can also be related to the reduction of pyrite. In CO_2, coal sulphur is mainly converted into SO_2/SO, because CO_2 is a more reactive gas and rather acts as an oxidizing agent. Decomposition of organic sulphonic acids occurs before 500 °C and of sulphonics/sulphoxides after 500 °C. The decomposition of sulphates and pyrite is better detectable in CO_2 than in inert gas atmosphere. After 800 °C char gasification in CO_2 results in further decomposition of sulphur compounds and lower sulphur retention.

1. Introduction

Coal is an important energy source used in many countries, because it is cheap and the supply is stable [1]. However in the past years, the pollution from coal combustion has brought many problems [2], due to the emission of SO_X, NO_X, CO_2, particle matter and heavy metals. Especially the emission of SO_2 has caused serious harm to both environmental and health problems in many areas [3,4]. It is urgent to understand the mechanism of coal sulphur formation during combustion in order to decrease this pollution.

Coal sulphur consists of organic sulphur and inorganic sulphur. Organic sulphur is generally regarded as sulphur bound in hydrocarbon [5], including aliphatic and aromatic sulphur related compounds, such as disulphides, thiophenes, and benzothiophenes. Organic sulphur compound composition is different in every coal, due to coal history and geographic location, which leads to a complex and heterogeneous coal structure. Relatively, lignite coal has more aliphatic sulphur compounds, while anthracite coal has a higher content of aromatic sulphur compounds, which are more difficult to decompose. Inorganic sulphur includes pyritic and sulphate sulphur, present in coal as mineral matter. Some pyrites and sulphates also decompose to SO_2 in certain reactions, as some organic sulphur compounds do. Several methods have been

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studied to reduce coal sulphur amounts before combustion, such as physical, chemical and biological removal methods [6–9].

Oxy-fuel combustion is a promising technology to decrease CO_2 emission during coal combustion, which has been studied world widely [1,10–14]. Flue gas, which is mainly CO_2 and steam, is recycled back into the furnace for two reasons: one is to maintain the temperature and the other is to take place of the N_2 which is separated from air at the beginning [1,10,13]. Comparing to air combustion, SO_2 emission decreases in oxy-fuel combustion [7,14,15]. Unlike inert gas, CO_2 not only has a different effect on coal devolatilization, but also plays a significant role in char gasification above 800 °C. Some aliphatic and even aromatic sulphur compounds react with CO_2 forming new sulphur compounds due to its oxidation and better reactiveness than inert gas. During the process in CO_2, COS [16–18] and SO_3 are found in considerably high amounts compared to those sulphur compounds released in inert gas. There are only a few papers studying the impact of CO_2 on inorganic sulphur behaviour in coal [19,20]. It is found that in CO_2 pyrite decomposes faster than in inert gas, because the activation energy of the decomposition reaction is smaller in CO_2 [21]. Many studies show the effect of CO_2 on sulphur compounds formation, but an in-depth investigation on the effect of CO_2 with every organic sulphur compound is still lacking.

AP-TPR/MS is a reliable method for sulphur group characterization in coal, which has already been successfully applied for sulphur functionality determination during coal pyrolysis in a reducing or inert flow [22–32]. The AP-TPR method is based on experimental findings that a specific sulphur functional group is maximal hydrogenated/reduced at a specific temperature range. In previous studies, most researchers have been focusing on organic sulphur form determination/changes in coal in a reducing atmosphere or inert gases. In our previous report [33], for the first time organic sulphur evolution in CO_2 was quantitatively determined. It was found that CO_2 as reaction atmosphere results in changes of organic sulphur changes/evolutions. In this paper, a high-pyrite coal was chosen, in order to study also the effect of CO_2 on pyrite decomposition and inorganic sulphur form evolutions, which was determined using this AP-TPR method.

The purpose of this study is to evaluate sulphur compound releases during high-pyrite coal pyrolysis in H_2, N_2 and CO_2, especially the effect of CO_2 on the releases of organic and inorganic sulphur compounds. AP-TPR/MS was used to determine the presence of different sulphur species. AP-TPR "off-line" coupled with TD-GC/MS was used to quantify other volatile organic sulphur compound than H_2S. A C, N, H, S Elemental Analyser was used for quantitative sulphur determination in residual char and tar from an AP-TPR/MS experiment. This makes analyses of obtained H_2S profiles, not only qualitatively but also quantitatively possible.

2. Experimental

2.1. Fuel preparation

Chinese LZ coal was used for its high sulphur content, especially with high pyrite amount, in order to study the effect of CO_2 on organic sulphur and inorganic sulphur releases. LZ Coal is also a very typical Chinese coal, which has been widely used in research and industry in China. Raw coal was dried and ground to particle size below 200 μm.

2.2. AP-TPR/MS experiments

AP-TPR/MS is described in previous paper in more details [32]. In H_2 atmosphere, the detection of the mass/charge ratio range was between 10 and 150. In N_2 the ratio range was between 30 and 150, to avoid the strong signal of N_2 in the background as m/z of N_2 is 28. In CO_2 the mass/charge ratio range was also between 10 and 150. Although m/z of CO_2 is 44, m/z range 10–150 was chosen in CO_2 experiments. Otherwise m/z 34 would be lost if the range 45–150 was selected, making a comparative study with the other used gases impossible. The other option was to work in the m/z range of 10–43 but then all the aliphatic and aromatic fragment signals would be lost, being important in view of the impact of the CO_2 atmosphere during the thermal treatment on the coal matrix as on the sulphur form assignments. Additionally, a temperature correction for all AP-TPR/MS experiments is needed, the knowledge of the evolution temperatures of these aliphatic and aromatic fragment signals are therefore crucial.

In each experiment a mixture of 40 mg coal and 25 mg silica (to prevent clothing) was used and the heating rate was 5 °C/min in the three different atmospheres (pure H_2, N_2 and CO_2 respectively). The flow rate of N_2 was 50 ml/min, flow rate of H_2 and CO_2 was 100 ml/min. Each experiment was done at least two times, the repeated tests provide reliable measurements and error control. After pyrolysis sulphur captured in tar/char residue was determined by Elemental Analyser.

For the quantitatively comparison of different experimental conditions, all the AP-TPR-MS data of H_2S, SO_2 and SO have been normalized. The method of normalization can be found in Supplementary data.

2.3. AP-TPR-TD-GC/MS experiments

AP-TPR/MS is not able to quantify other volatile organic sulphur compound fragments, as they are also related to other CH-fragments. Therefore AP-TPR-TD-GC/MS experiments were performed, with dedicated adsorption tubes, to solve this problem.

Volatile organic sulphur compounds released from pyrolysis in $H_2/N_2/CO_2$ respectively were qualitatively and quantitatively determined by AP-TPR-TD-GC/MS. All the settings of temperature, heating rate and operation were the same as in the AP-TPR/MS experiments. The first adsorption tube was applied from room temperature to 300 °C during coal pyrolysis, then a temperature interval of 100 °C is applied for subsequent adsorption tubes. The adsorption tubes were silco steel coated and filled with Tenax/Carbpack B/Carbosieve SIII (Markes) adsorbing selectively all kinds of volatile sulphur compounds during pyrolysis experiments, except H_2S. Based on earlier findings it is believed that also SO and COS were not adsorbed at all. All tubes were ice cooled during the whole process. TD-GC/MS chromatograms were quantitatively interpreted by spiking the selective sorbents with 3 μg thiophene-d4. Different volatile sulphur compounds were quantitatively desorbed and determined by TD-GC/MS. NIST library spectra are used for peak identification of sulphur compounds [22]. More information can be found in Supplementary data.

3. Results and discussion

3.1. Coal sample characterization

The standard analysis includes proximate and ultimate analysis of coal LZ given in Table 1. Table 2 gives the major sulphur forms presence, pyrite and sulphate sulphur was determined according to ASTM D2492-02 [34], organic sulphur was determined by difference. The mineral composition of coal was determined by XRF shown in Table 3.

3.2. In H_2 atmosphere

Fig. 1 shows the H_2S kinetogram in H_2 atmosphere. As m/z 34 (H_2S^+) and m/z 33 (HS^+) reveal the same evolution profiles and