



Effect of coal particle size on distribution and thermal behavior of pyrite during pyrolysis



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HIGHLIGHTS

- The evolution of gaseous sulfur is promoted by the reduction of coal particle size.
- Small coal particles facilitate the formation of low-sulfur Fe–S phases in chars.
- The possible mechanism for the effect of coal particle size on pyrite decomposition is proposed.

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ABSTRACT

Transformation of pyrite in a demineralized subbituminous coal with various coal particle size distributions (PSD) during pyrolysis was investigated using a thermogravimetric analyzer coupled with mass spectrometer (TGA-MS). The residues from pyrolysis were examined by X-ray diffraction (XRD) and scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS). It is found that the pyrite content is higher in coal with smaller particle size. The reduction of coal particle size is beneficial to the evolution of gaseous sulfur at 350–650 °C. The results from XRD and SEM-EDS analyses show that during pyrolysis small coal particles facilitate the formation of low-sulfur Fe–S phases and even elemental iron in char. The isolated pyrite crystals or the aggregates of pyrite are rich in coal with smaller particle size than in larger ones, and this is beneficial to the pyrite conversion and the formation of low-sulfur Fe–S phases in the finer char particles.

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1. Introduction

Coke is one of the most important feedstock in iron-making process. The sulfur in coke, which is an undesirable impurity, is directly related to the coke quality and the efficiency of metallurgy process. With the decrease in low-sulfur coking coal resources and the development of coke and metallurgical industry, the addition of high-sulfur coking coal in coking process will be inevitable. However, high sulfur coal will lead to the increase of sulfur content in coke and thus is not conducive to the production of qualified coke. Therefore, the sulfur removal is of great importance during coking process. According to the literature [1], sulfur forms in coal occur to be organic and inorganic sulfur as well as small amount of elemental sulfur. Pyrite (FeS₂), as the primary inorganic source of sulfur naturally occurring in coal, has attracted great attention in coking field. Prevalent methods of desulfurization adopted by

coking enterprises are physical washing and flotation, both of which can remove part of excluded pyritic sulfur, while be invalid for embedded one [2]. On the other hand, general chemical ways can be effective but often have some negative influence on coal matrix. For example, the caking property of coal is diminished under high temperature and high pressure or in the presence of chemical reagents, and thus the treated coal can no longer be used for coke-making [3,4].

Pyrolysis, the essential process in coke making, has been vastly investigated for sulfur removal to improve coke quality [5]. During pyrolysis, a portion of inorganic sulfur and volatile organic sulfur pass into the tar or gas, while sulfur compounds remaining in the coke are mainly stable organic sulfur and products of inorganic sulfur [6,7]. FeS₂ can be transformed into ferrous sulfide (FeS) and very active sulfur above 350 °C during pyrolysis. And the active sulfur can be captured by functional groups in coal matrix to form hydrogen sulfide (H₂S), carbon disulfide (CS₂) and sulfur dioxide (SO₂), or to convert to new organic sulfur species left in char or tar [7–10]. During pyrolysis of coal, the decomposition of pyrite

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is influenced by numerous factors such as other forms of sulfur, coal rank and reaction conditions [5–7,11]. Previous works examined interactions between pyritic sulfur and various organic species, sulfur distribution in coke, intermediates of the secondary reactions, effect of pyrite on sulfur retention and thermal decomposition of Fe–S compounds formed after pyrolysis [2,10,12–15]. Based on these work, it remains difficult to remove all of pyrite which is finely disseminated in coal matrix. Extra efforts need to be made to remove the stable Fe–S compounds within coke structures, so feasible and convenient desulfurization ways prior to pyrolysis may be considered.

Grain size classification and control will be a method of great feasibility and operability, since the efficiency of coal pyrolysis and desulfurization could be influenced by changing the particle size of feed coal or blending coal [7,16–21]. Experiments on sulfur reduction by controlling the particle size distributions (PSD) are valuable for coking industry. Weng [16] and Shyu et al. [17] found that smaller particle size of both the pyrite and coal sample was beneficial to improve desulfurization efficiencies under oxygen atmosphere due to a larger external surface area [18]. Besides, smaller grains of pyrite were found to be decomposed at lower temperature than larger ones in hydrogen atmosphere [20,21]. Most of the results above were concentrated on the oxidation or reduction of mineral pyrite, while ignored the decomposition of inherent pyrite during coal pyrolysis. Furthermore, previous work explained the effect of particle size on decomposition of pyrite from the viewpoint of thermodynamics and dynamics, and attributed this effect largely to the values of thermal diffusivity and total surface area. However, it is still incomplete and vague whether and how these factors work on the pyrite transformation during pyrolysis of coal with different particle size, especially under inert atmosphere similarly in coking process.

The purpose of this work is to extend the knowledge on thermal behavior of inherent pyrite in coal with different PSD during pyrolysis. A subbituminous coal with high pyrite content, which is often used for coal blending in coking process, was divided into three groups based on particle size. The thermal behavior of demineralized coals, the evolution of sulfur-containing gases as well as mineral forms and associations of coals and chars were examined to understand the effect of coal grain size on the sulfur behavior, especially pyrite transformation, during coal pyrolysis.

2. Experimental

2.1. Samples and preparation

The subbituminous coal in this work was from Yanzhou, Shandong province, China, designated as YZ. The coals were dried and ground to <0.2 mm. The proximate analysis, ultimate analysis and sulfur forms are listed in Table 1, which shows pyritic sulfur and organic sulfur are the primary sulfur forms in the sample.

Three particle ranges, 150–180, 75–150 and <75 μm , were chosen to section YZ coal and marked as YZ-L, YZ-M and YZ-S, respectively. The selection of coal particle sizes is considered as follows.

Particles less than 200 μm are available for proximate analysis and sulfur forms analysis and particles of <75 μm are always required for analysis reasons, such as X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). Coal samples with a size fraction of <150 μm or around 150 μm were selected in order to find some common or remarkable characters during coal pyrolysis as earlier works did [12,22,23].

To eliminate the influence of minerals, especially sulfate, in coal on thermal characteristic of pyrite, coal samples were treated by acid leaching [12,23]. The raw coal and the size-selected ones were treated with 5 M HCl, 33.3 M HF and 12 M HCl at 60 °C sequentially for 1 h. The suspension was filtered and washed with boiled double-distilled water until no chloride ion was detected from filtrate. The remaining solids then were dried at 105–110 °C for at least 24 h and denoted as YZ-Dem, YZ-DemL, YZ-DemM and YZ-DemS for YZ, YZ-L, YZ-M and YZ-S, respectively. Then the residue of YZ-Dem coal was also boiled in 2 M HNO₃ and filtered until no Fe³⁺ was detected from filtrate, and the dry sample was named as YZ-Demp. YZ-Demp (pyrite-free) was employed to confirm the pyrite decomposition in coal by comparing with pyrite-containing demineralized YZ coal samples during pyrolysis. The properties of sectioned YZ-Dem coals (YZ-DemL, YZ-DemM and YZ-DemS) as well as YZ-Demp are also shown in Table 1. Water- and acid-soluble inorganic minerals, such as clay, carbonates and certain silicate materials, were removed during the above process.

2.2. Pyrolysis experiments

Pyrolysis experiments were conducted using a SETSYS Evolution thermogravimetric analyzer (TGA) (SETARAM, France) coupled to a mass spectrometer (MS) (Omnistar, Switzerland) aiming at exploring the thermal decomposition behavior of pyrite and determining the composition of gaseous products evolved. The mass spectra ranged from 1 to 300 atomic mass unit (amu). A sample of about 10 mg was used in each TGA run. Coal sample was heated from room temperature to 1050 °C at 10 °C min⁻¹ in 100 mL min⁻¹ high purity (>99.9%) argon.

Pyrolysis was also performed in a horizontal fixed bed quartz reactor to collect amounts of coal char for subsequent analyses. All selected samples were subjected to temperature-programmed decomposition (TPD) and then followed by temperature-programmed reduction (TPR) processes. Coal sample was loaded into the constant temperature zone at room temperature and heated to 1050 °C at 10 °C min⁻¹ under 100 mL min⁻¹ N₂ atmosphere. Then the reactor was cooled to room temperature in a continuing nitrogen flow. Part of the residue was collected from the reactor for subsequent analysis, and the rest was subjected to TPR experiment under 100 mL min⁻¹ H₂ atmosphere from room temperature to 1050 °C at 10 °C min⁻¹ and then was cooled by N₂ purging. The char was collected for further analyses.

In order to prevent the influence of moisture in carrier gas on the decomposition of FeS₂, FeS₂ of 99.9% purity (<100 mesh powder, from Alfa Aesar) was decomposed under high purity (>99.999%) dry helium during TGA-MS and TPD runs.

Table 1
Proximate and ultimate analyses of YZ coal.

Sample	Proximate analysis (db) (wt%)		Ultimate analysis (daf) (wt%)				Sulfur forms (db) (wt%)			
	A	V	C	H	N	O ^a	S _t	S _p	S _s	S _o ^a
YZ	13.5	37.0	73.80	5.12	1.42	16.08	3.10	1.51	0.46	1.13
YZ-Demp	3.3	38.4	70.71	4.31	4.26	19.15	1.51	0.06	n.d.	1.45
YZ-DemS	4.5	26.8	73.45	4.87	1.35	15.59	4.52	3.24	0.17	1.11
YZ-DemM	5.0	35.3	74.02	5.00	1.34	14.99	4.41	2.96	0.11	1.34
YZ-DemL	7.3	28.9	72.56	5.08	1.81	16.89	3.39	2.18	n.d.	1.21

^a By difference; db, dry basis; daf, dry-ash-free; S_t, total sulfur; S_p, pyrite sulfur; S_s, sulfate sulfur; S_o, organic sulfur; n.d., not detected.

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