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Effect of iron on Shenfu coal char structure and its influence on gasification reactivity

Xuejun Qi, Xin Guo*, Lucheng Xue, Chuguang Zheng

State Key Laboratory of Coal Combustion Huazhong University of Science & Technology, Wuhan 430074, Hubei, PR China

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ABSTRACT

The influence of iron on Shenfu coal char structure and its gasification reactivity was studied in the present paper. Acid-washing coal samples were loaded with different content of iron catalyst and then pyrolyzed at 1123 K. X-ray diffraction apparatus and Raman spectra apparatus were used to characterize the structure of coal char. The char gasified with CO_2 in a thermogravimetric analyzer to study the effect of iron loading on the gasification reactivity. Iron catalyzed steam gasification of char was carried out in a fluidized-bed reactor to investigate the impact of iron loading on the release characteristics of gas products. The results of XRD suggested that iron particle effectively hinders the trend of carbon graphitization in the process of pyrolysis. The intensity of (0 0 2) and (1 0 0) peaks of char decreased with the rise of iron loading. With the increase of iron loading, L_c and L_a reduced from 12.48 Å and 41.40 Å to 11.50 Å and 35.70 Å, respectively. Raman spectra analysis showed that iron inhibits the growth of large aromatic ring structure and increases the amount of amorphous carbon structure in char. Comparison of the reactivity of char loaded with various concentrations of iron catalyst, the char with 2 wt% iron exhibited highest gasification reactivity. It was found that iron catalytic gasification reaction generates much more product gas than that of un-catalyzed. In particular, the presence of iron promotes the direct interaction between carbon and water.

1. Introduction

Shenfu coal field is one of the biggest fields in China, which has more than 23 billion tons of coal reserves and accounting for 15% of the nation's explored reserves. Shenfu coal belongs to low rank coal, which is characterized by coal seam stability, buried shallow, easy mining, low ash, low sulfur and high reactivity. Converting coal into clean gas fuels through gasification process has attracted numerous researcher's attentions in recent years [1,2]. As China demand for energy rapidly increases, the need to convert coal into clean energy becomes much more urgent. Catalytic gasification is one of the promising technologies for the utilization of low rank coal in the future, as it can produce synthetic natural gas, hydrogen, green power energy and control the emission of CO_2. Iron is potentially popular as catalysts for low rank coal gasification in industrial application due to its lower price, abundance in raw materials and high catalytic activity at low temperature [3]. Moreover, iron is an important inherent element in raw coal, and it influences the char gasification reactivity and characterization of coal ash. Hence, understanding the effect of iron on the pyrolysis and gasification of Shenfu coal is important to the gasifier design and operation.

The process of coal gasification includes two steps: release of volatiles and gasification of char particles. In the actual gasification reaction, the gasification of char is usually a slow process compared with the release of volatiles. So, Char reactivity is very important to the efficiency of gasification. In the process of char formation, a lot of changes containing intraparticle pore structure, decrease of active surface area of coal chars and loss of functional groups on the carbon surface occurs, which have great impact on the subsequent char gasification reaction. Char gasification reactivity depends not only on the concentration, the chemical forms and the distribution of catalyst, but also on the physico-chemical structure of char [4,5]. However, in terms of the impact of iron on the char reactivity, previous research mainly focused on iron catalyst precursor and catalyst loading method [6–9], and concerned little about the effect of iron on char structure.

The aim of this paper is to investigate the effect of iron on the structure of Shenfu coal char and its influence on gasification reactivity. Acid-washing coal samples are impregnated with various content of iron catalyst, and then the coal samples are pyrolyzed under N_2 atmosphere on a fixed-bed reactor. The transformation of carbon crystallite structure parameters of coal char are analyzed

* Corresponding author. Tel.: +86 27 87545526; fax: +86 27 87545526.
E-mail address: guoxin@mail.hust.edu.cn (X. Guo).

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Table 1
Proximate and ultimate analyses of Shenfu coal samples.

Proximate analysis (wt% ad)	
Moisture (M_{ad})	8.53
Ash (A_{ad})	2.82
Fixed (FC_{ad})	55.25
Volatile matter (V_{ad})	33.4
Ultimate analysis (wt% daf)	
Carbon	68.61
Hydrogen	4.93
Nitrogen	1.02
Sulfur	0.37
Oxygen	24.84

by XRD, BET and Raman spectroscopy apparatus, and the effect of iron loading on the gasification reactivity is measured by a thermogravimetric analyzer. In addition, the impact of iron on the release characteristics of gas products during steam gasification was performed using a fluidized-bed reactor.

2. Experimental

2.1. Coal samples and catalyst loading

Shenfu coal was used in this study. The raw coal was partially dried at low temperature (<323 K), then pulverized and sieved to obtain a fraction sample of particle sizes between 100 and 150 μm. The proximate and ultimate analyses for this coal are listed in Table 1.

The raw coal was demineralized with acid washing for the purpose of study the influences of iron on the structure of coal char. Briefly, raw coal was washed with 1 mol/L HCl for 24 h, and then rinsed with deionized water over filter paper. Consecutively, aqueous (40%) HF was added to HCl-washed coal and this slurry was stirred for 24 h. The mixture was washed by deionized water. After washing, demineralized coal was dried in an oven at 378 K. Iron loading in the coal varies from 1 to 3 wt% to study the effect of catalyst loading on the structure of char. The catalyst loading was varied by changing the concentration of the catalysts in the solution. The iron loading is referred to the weight percent of the iron atom in the total amount of coal sample. For impregnation, acid washing coal sample (about 10 g) was immersed in an aqueous solution of $Fe(NO_3)_3$ and stirred for 6 h. Then the mixture was placed in an oven at 378 K and allowed to dry for several hours.

2.2. Char preparation

All the pyrolysis experiments were carried out in a constant flow rate of 1 L/min N_2 gas. The flow rate of N_2 was controlled by mass flow meters. About 2.0 g sample was placed in an alumina crucible. When the temperature reached to 1123 K, the coal sample was promptly placed into the central part of the reactor and held at that temperature for 15 min, and then cooled down to room temperature under the N_2 atmosphere.

2.3. Char characterization

The carbon crystal structure of the char was analyzed by Bruker D8 Advance X-ray diffraction with Cu-$K\alpha$ radiation. The sample was scanned in a step-scan mode over the range of 10–90° (2θ) with 0.02° step and using a counting time of 1 s per point. The Brunauer–Emmett–Teller (BET) specific surface area analysis was investigated by an ASAP 2020 physical adsorption instrument, with liquid N_2 adsorption at 77.40 K. The amounts of iron in the char sample were determined by Spectro arcos inductively coupled plasma–atomic emission spectrometry (ICP–AES). Laser Raman spectra analysis of char samples was performed on a LabRAM HR800 spectrometer. The exciting laser wavelength was 532 nm, and the spectra was recorded in the wave number range of 800–1800 cm^{-1} covering the first-order bands.

2.4. Char reactivity measurements

Char gasification reactivity was measured using a thermogravimetric analyzer (TGA). About 7 mg char sample was placed in an alumina crucible and heated at the rate of 25 K/min in each experiment. The reactor was heated to 1123 K in high purity N_2 atmosphere (75 ml/min). When the temperature reached to 1123 K, N_2 was switched to CO_2 (75 ml/min) for isothermal gasification. During the CO_2–char gasification, the weight of the sample was continuously recorded by a computer.

In this paper, the carbon conversion rate (X) and reactivity index R_s [10] are calculated by the following expressions:

$$X = \frac{W_0 - W_t}{W_0 - W_{cat}} \tag{1}$$

$$R_s = \frac{0.5}{\tau_{0.5}} \tag{2}$$

where W_0 is the initial mass of char sample, W_t is the instantaneous char sample mass at any time, and W_{cat} is the mass of iron catalyst in char sample. $\tau_{0.5}$ is the gasification time (min) taken to reach a carbon conversion of 50%.

2.5. Steam gasification of char in fluidized-bed reactor

About 0.3 g char sample was used in each experiment. The experimental procedure is described briefly as follows: The fluidized-bed reactor was heated to the predetermined temperature at 1123 K under high purity N_2 atmosphere. The mass flow meters was used to control the flow rate of high purity N_2 (0.85 L/min). The steam which was required for gasification reaction was produced inside the reactor through a pump. The water quickly converts into steam at high temperature and mixed with the N_2. The concentration of steam was always 15 vol%. Product gas stream from the outlet of the reactor passed through ice-water cooled condenser to remove tar and water vapor before it was sent to the online gas analyzer.

3. Results and discussion

3.1. The result of iron loading in char

The amounts of iron in the char samples as determined by ICP-AES are shown in Table 2. From the table, it can be seen that the content of iron in the char samples is higher than that in the precursor coal sample. This is ascribed to the decrease in mass of the coal samples as they loose volatile components during pyrolysis to form the char.

3.2. The BET results of char

The measured results of BET surface areas by N_2 adsorption method are given in Table 3. As can be seen from the table, the value of BET surface area of un-catalyzed char is 35.17 m^2/g. The catalyzed char obtained from the coal with 1 wt% iron drastically

Table 2
Contents of iron in coal char.

Sample	Contents of iron in char (wt%)
Coal + 1% Fe	1.58
Coal + 2% Fe	2.61
Coal + 3% Fe	3.96