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Catalytic effect of sodium components on the microstructure and steam gasification of demineralized Shengli lignite char

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ABSTRACT

The catalytic effect of sodium on the demineralized Shengli (SL^+) lignite char microstructure and the performance of steam gasification were studied. Various sodium compounds including $NaNO_3$, CH_3COONa, Na_2CO_3 and NaOH were loaded on the demineralized coal samples, respectively, and the steam gasification was tested on the fix-bed reactor. The char samples were characterized by X-ray diffraction (XRD), Raman, X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy. Experimental results showed that sodium hydroxide loaded samples exhibited the highest gasification reactivity among the coal samples prepared. With the increase of the alkalinity of sodium compounds, the carbon crystallite structure tended to be disordered. In the process of pyrolysis, the introduction of sodium species promoted the ring-opening and polycondensation process of the chemicals in the coal samples. The possible reaction mechanism might be inferred that the sodium ions may replace the hydrogen ions in the oxygen-containing functional groups to form sodium phenolate intermediate, which may be critical for the catalytic effect of sodium species during gasification. It was speculated that the ring-opening of the condensation aromatic nucleus was the rate-limiting step in the whole process of gasification.

Introduction

Low-rank coals, an abundant fossil resource on earth, become more and more important especially with the fast depletion of the high-rank coals. Unfortunately, low-rank coals suffer several disadvantages, such as high ash yield, high moisture content, and low calorific value. Therefore, utilizing the low-rank coals in clean and high value approaches is important to improve the utilization efficiency of this carbon resource. Gasification of low-rank coals has been considered as a promising technology in terms of its efficiency and clean utilization [1]. Catalytic gasification is a potential way due to its

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salient advantages of low operating temperature, low cost, high efficiency of energy conversion, and selective reaction pathways towards production of desired gases [2]. Up to now, extensive studies on the catalytic coal gasification with alkali and alkaline earth metals (AAEMs) [3–7] were conducted, because of their superior catalytic activity, low cost, and inherent presence in coals [8].

Although the inorganic matters take a very small proportion in the coal, they usually play a significant catalytic role in the gasification of the low-rank coals or their char. It has been proved that the AAEMs have obvious catalytic action in gasification [9–12,4,5]. Among various AAEMs, K, Ca, and Na are considered to be the most effective. Extensive studies have been reported in this field. Karimi and Gray [13] revealed that K_2CO_3 had a better catalytic activity than that of Na_2CO_3 for the steam gasification of bitumen coke. Zhang et al. [14] studied the steam gasification of tobacco stalk sample with potassium catalysts and found the addition of K_2CO_3 increased hydrogen yield and carbon conversion. Murakami et al. [15] investigated the catalytic effect of Ca catalysts prepared from $CaCO_3$ on the steam gasification of Indonesian subbituminous coal. The results confirmed that $CaCO_3$ is effective as a catalyst raw material in the steam gasification even at low catalyst loadings. Tang et al. [16] investigated the catalytic steam gasification of coal char with alkali carbonates and their synergic effects with calcium hydroxide. They found the addition of $Ca(OH)_2$ to the coal substantially increases the rate of char gasification for alkali carbonates. Kopyscinski et al. [17] confirmed that K_2CO_3 could increase the steam gasification rate, and decrease the activation energy during the steam gasification of the ash-free coal. Kong YJ et al. [18] found K_2CO_3 with ash-free coals can significantly enhance the gasification rate and H_2/CO ratio. Quyn et al. [19] studied the effect of different chemical forms of Na on catalytic gasification of char. Suzuki et al. [20] found that K_2CO_3, KCl, and Li_2CO_3 are the most effective additives for steam gasification of coal or char, and the presence of alkali additives allowed the catalytic gasification process to proceed at lower temperatures. What is well known is that some different calcium-bearing compounds, such as $CaCO_3$, $Ca(OH)_2$, $Ca(COO)_2$, are catalytically active for lignite gasification [21–23]. The catalytic activity of minerals in char gasification was studied by adding catalysts in the preparation stage. The results demonstrated that the gasification rates were improved, but the mechanism of the catalytic behavior of the inherent inorganic matters was still unclear.

Therefore, in this study, the catalytic effect of Na-containing compounds on the microstructure and steam gasification of demineralized Shengli lignite char was investigated in detail. The possible mechanism of the catalytic effect of the sodium species was proposed.

Experimental

Preparation of coal samples

The used lignite was collected from Shengli coalfield in Inner Mongolia of China, which was abbreviated as SL-Raw. The coal sample was dried at 105 °C for 4 h, and then ground and sieved to the particle sizes between 0.038 mm and 0.075 mm. The SL-Raw samples (0.038–0.075 mm) was mixed with HCl (18.5%) with a coal 1 g:10 ml, the mixture was maintained for 24 h. Then the coal samples were washed with deionized water to neutrality to obtain demineralized coal samples (SL^+). NaOH, Na_2CO_3, CH_3COONa and $NaNO_3$ were added, respectively, in 5% proportion of the mass of SL^+ samples by using the impregnation method. The suspension was stirred at 120 rpm using a motor stirrer at room temperature for 4 h. Then, the slurry evaporated in a vacuum oven at 105 °C without filtration until the sample was thoroughly desiccated. These samples was abbreviated as SL^+–NaOH, SL^+–Na_2CO_3, SL^+–CH_3COONa, and SL^+–$NaNO_3$, respectively. The samples were ground into powder (200–400 mesh) and analyzed for moisture, ash and elemental composition. The ultimate analyzes of the samples are summarized in Table 1. The metal ions in and their contents in the lignite samples were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 7000, PerkinElmer) on the basis of coal (Table 2).

Char gasification

The char gasification was performed in the fixed-bed gasification reactor. And the experimental process was as follows: a 0.15 g sample of coal was loaded into the reactor. Argon was used as a carrier gas, and the system pressure was maintained at 0.15 MPa. The reactor was heated from room temperature to 500 °C at 15 $°C\cdot min^{-1}$, then up to 900 °C at 2 $°C\cdot min^{-1}$. The deionized water was introduced into the vaporizer, and the vaporizer temperature was raised up 300 °C previously. The tar and steam in the carrier gas was separated in a cold trap, and finally the gas entered into the gas chromatograph (SP3420).

The major gaseous products H_2, CO, CH_4 and CO_2, were quantitatively determined online using a rapid gas chromatograph (TCD), and sampling time interval for 4 min. The reaction was stopped when the content of resulting syngas (H_2, CO, CH_4 and CO_2) at the largest relative rate was not more than 0.2%.

Analysis methods

X-ray diffraction analysis

The XRD profiles of the samples were measured using an X-ray diffractometer (Bruker D8) with Cu-K_α radiation (40 kV, 40 mA) by a step-scanning method over the angular range of 5°–70° (2θ). The broad hump in this region was fitted to two

Table 1 – Ultimate analyzes of the coals.

Samples	C	H	N	S	O[a]
SL^+	61.42	3.34	0.86	1.74	25.10
SL^+–$NaNO_3$	56.56	3.31	2.48	1.11	23.56
SL^+–CH_3COONa	56.80	3.49	0.83	1.18	22.21
SL^+–Na_2CO_3	56.27	3.11	0.91	1.52	21.73
SL^+–NaOH	53.54	3.03	1.07	1.08	22.76

ad, air-dried basis; d, dried basis.
[a] By difference.