



Full Length Article

Transformation mechanism of sodium during pyrolysis of Zhundong coal

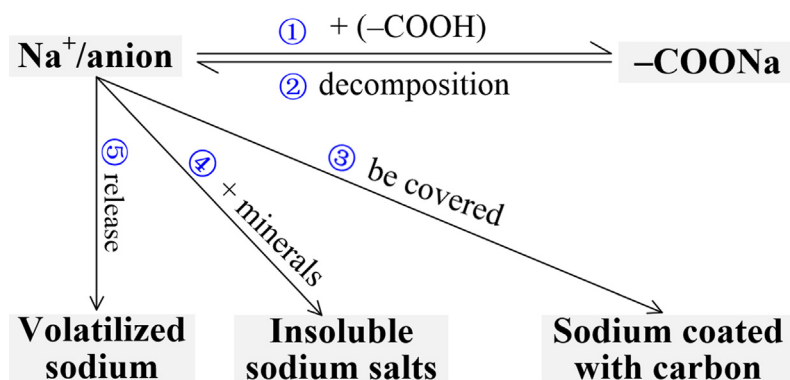
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GRAPHICAL ABSTRACT

Transformation routes and mechanisms of Na during pyrolysis of Zhundong coal are proposed. H_2O -soluble sodium can react with $-\text{COOH}$ to form $\text{CH}_3\text{COONH}_4$ -soluble sodium below 400°C . The decomposition of $\text{CH}_3\text{COONH}_4$ -soluble sodium occurred at temperatures lower than 600°C . H_2O -soluble sodium may combine with minerals or be coated by the carbon matrix to form insoluble sodium above 600°C . Na that volatilized above 600°C was mainly in the H_2O -soluble form.



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ABSTRACT

The modes in which Na occurs play an important role in its release and catalytic effects during thermal utilization of Zhundong coal. The modes of Na transform with increasing temperature during pyrolysis, but the transformation mechanism remains unclear. In this study, an acid-washed coal was used as a substrate to eliminate the influence of Na inherently present in the raw coal. Na_2SO_4 , NaCl , NaHCO_3 , and sodium carboxylate were loaded onto the acid-washed coal by impregnation or ion exchange. Pyrolysis of the sodium-loaded coals was conducted in a fixed-bed reactor. Transformation of Na in chars was studied over the temperature range $300\text{--}900^\circ\text{C}$. Interconversion of H_2O - and $\text{CH}_3\text{COONH}_4$ -soluble sodium occurred below 400°C . $\text{CH}_3\text{COONH}_4$ -soluble sodium mainly transformed to H_2O -soluble sodium at $400\text{--}600^\circ\text{C}$. The transformation of Na from the H_2O -soluble to insoluble form occurred above 600°C . The transformation of Na related to its initial form in the coal. Transformation routes and mechanisms of Na are proposed. H_2O -soluble sodium can react with $-\text{COOH}$ to form $\text{CH}_3\text{COONH}_4$ -soluble sodium below 400°C . The decomposition of $\text{CH}_3\text{COONH}_4$ -soluble sodium occurred at temperatures lower than 600°C . H_2O -soluble sodium may combine with minerals or be coated by the carbon matrix to form insoluble sodium above 600°C . Na that volatilized above 600°C was mainly in the H_2O -soluble form.

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1. Introduction

The Zhundong coalfield in Xinjiang province is capturing increasing attention owing to its large estimated reserves, i.e., 1.64×10^{11} t [1]. Its high volatiles, and low sulfur and ash contents make it a promising energy source for coal combustion and gasification; however, severe fouling, slagging, and ash deposition problems have occurred during its thermal utilization, which may be caused by volatilization of alkali and alkaline-earth metals (AAEM), particularly sodium species [2]. Sodium in raw coal can, however, also act as an efficient catalyst for its pyrolysis [3,4], gasification [5,6], and liquefaction [7].

Both the release and catalytic effects of Na relate to its occurrence modes in the coal. By sequential chemical extraction with H_2O , CH_3COONH_4 (NH_4Ac) solution, and HCl solution [8,9], sodium in Zhundong coals can be classified into four main types: H_2O -soluble form (e.g., Na_2SO_4 and NaCl), NH_4Ac -soluble form (e.g., sodium carboxylates), HCl-soluble form, and insoluble form. H_2O -soluble sodium contributes most to the release of Na in any combustion stage [10]. During pyrolysis, sodium in the form of NaCl (H_2O -soluble sodium) volatilizes more easily than that in the form of carboxylate (NH_4Ac -soluble sodium) [11]. Oil generation during liquefaction of Zhundong coal can be severely inhibited by NH_4Ac -soluble sodium [7]. Xu et al. [12] reported that removal of NH_4Ac - and HCl-soluble AAEM increased the average char ignition temperatures by 33 and 55 °C, respectively. A study by Li et al. [13] showed that Na present in the coal as NaCl and $-COONa$ (sodium carboxylates) exhibited very different catalytic abilities in char gasification. Occurrence modes of Na in the coal play an important role in both the release and catalytic effects of Na; however, these modes change with increasing temperature during pyrolysis. It was also stated that the chemical form of Na in char—not that in the coal—governed the catalytic ability of Na [13]. It is of importance to understand the transformation of Na for large-scale and high-efficiency utilization of Zhundong coal.

Pyrolysis is the first process of coal utilization. A few investigations on the transformation of Na during pyrolysis have been carried out. Wang et al. [2] studied the transformation of Na during pyrolysis of Zhundong raw coal in a horizontal fixed-bed reactor at 400–1100 °C. They found that most H_2O -soluble sodium was released from the coal and the remainder was partly converted into an insoluble form. H_2O - and NH_4Ac -soluble sodium showed a monotonous decrease during pyrolysis of lignite between 700 and 900 °C [14]. Xu et al. studied the conversion of Na during torrefaction of kitchen waste between 200 and 300 °C [9]. Transformation of Na from the H_2O - to the NH_4Ac -soluble form and the reverse conversion were found. Understanding of the transformation of Na during pyrolysis of coal is, however, still lacking: firstly, few studies have examined the conversion of Na during pre-treatment of coal at lower temperatures; secondly, the route and mechanism of its transformation remain unclear because Na occurs in various forms in the raw coal.

In this study, an acid-washed coal was used as the substrate to eliminate the influence of Na present in the raw coal. Based on our previous study [15], the major chemical forms of H_2O -soluble sodium in the raw coal are Na_2SO_4 , NaCl, and $NaHCO_3$. These three sodium salts were loaded onto the substrate to study the transformation of H_2O -soluble sodium. Sodium carboxylate was loaded on the substrate by ion exchange to study the transformation of NH_4Ac -soluble sodium. Transformations of Na in the char were studied over a wide temperature range (300–900 °C). The effect of sodium species was also discussed. Routes and mechanisms of Na transformation are proposed.

2. Experimental

2.1. Sample preparation

The Zhundong coal investigated in this study was the same as that in our previous study [15]. After being ground, air-dried, and sieved to a

Table 1

Proximate and ultimate analyses of Zhundong coal (wt%).

sample	proximate analysis (d)			ultimate analysis (daf)				
	A	FC	V	C	H	O ^a	N	S
Raw coal	3.57	64.21	32.22	73.52	6.55	18.51	0.91	0.51
H-form coal	0.95	67.22	31.83	81.84	3.69	13.24	0.68	0.55

^a By difference.

particle size of 109–180 μm , the coal was dried at 105 °C for 2 h and then labelled as raw coal. The content of Na in the raw coal was 0.27 wt % on a dry basis (db). An acid-washed coal (H-form coal) was obtained after demineralization of raw coal with dilute sulfuric acid (0.1 mol/L) [16]. The proximate and ultimate analyses of the raw and H-form coals are given in Table 1. Some organic molecules dissolved in the dilute sulfuric acid after acid-washing, most of which were volatile precursors, so the H-form coal showed a lower volatile yield than the raw coal. Ash analyses of the coals are shown in Table S1. The ash content of H-form coal was much less than that of raw coal. The Na content of the H-form coal was less than 0.01 wt% (db).

Almost all Na in the raw coal was removed by acid-washing (Fig. S1). Three sodium salts (Na_2SO_4 , NaCl, and $NaHCO_3$) were then loaded onto the H-form coal by impregnation (Fig. 1): each sodium salt was first mixed with a H-form coal water slurry, followed by dehydration of this slurry at 35 °C. NaCl loaded in this method was expected to occur in a similar form to the NaCl inherently exist in the raw coal [17], as were Na_2SO_4 and $NaHCO_3$. For convenience of comparison, the sodium contents in the three samples (Na_2SO_4 -, NaCl-, and $NaHCO_3$ -loaded coals) were set at equal values (0.5 wt%); the corresponding sodium salts were added at 1.54, 1.27, and 1.83 wt% (db), respectively.

Na-form coal was obtained after ion exchange of H-form coal with CH_3COONa solution at pH 8.3 for 20 h. All carboxyl groups in the H-form coal were converted to carboxylates during this process [18]. The Na content of the Na-form coal was 2.07 wt% (db), which was much higher than that of three other sodium-loaded coals.

2.2. Char preparation

A horizontal fixed-bed reactor, as shown in Fig. 2, was used for the pyrolysis of coal. Argon (1 L/min) was used to supply an inert atmosphere. The furnace was first heated to the target temperature. An alumina boat, loaded with about 1.0 g of dry coal sample, was then quickly introduced to the reactor. After 20 min, the boat was moved to the water-cooled zone. Chars prepared at 600 °C from the H-form, Na_2SO_4 -loaded, and Na-form coals were labeled as H-char-600, Na_2SO_4 -char-600, and Na-char-600, respectively. Similar labelling was used for other chars.

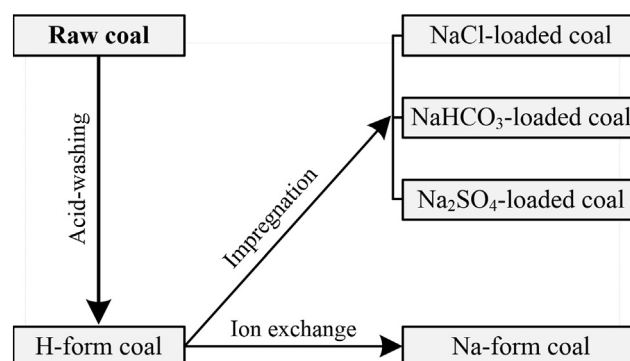


Fig. 1. Preparation of sodium-loaded coals.

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