



Full Length Article

Investigations on interactions between sodium species and coal char by thermogravimetric analysis



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ABSTRACT

Sodium species in sodium-rich coals could be enriched in char residue after devolatilization. At high temperatures, there must exist some interactions between char and sodium species. It should be noted that the interactions have significantly affected the transformation of sodium species and gasification reactivity of char. Thus, the interactions were investigated in detailed by comparing TG-DTG curves of pure sodium species, char and graphite mixing with sodium species. Meanwhile, the properties of char samples after sodium temperature-programmed treatments were characterized by SEM, XRD, N₂ adsorption and CO₂ chemisorption. The results indicated that the interactions between them were closely associated with the occurrence modes of sodium. In the case of the transformation of sodium species, the presence of coal char significantly inhibited NaCl release; however, for CH₃COONa and Na₂CO₃, coal char exhibited the catalytic effect for Na₂CO₃ decomposition and reducibility for the following Na generation; for Na₂SO₄, only an intense reducibility was discovered. In the case of char gasification reactivity, sodium species, especially those oxygen-containing species, could remarkably increase char BET surface areas and amount of active sites after temperature-programmed treatment; furthermore, the increase of active sites significantly enhanced char gasification reactivity.

1. Introduction

Sodium-rich coals are extensively distributed around the world, such as Victorian (Australia), Montana (United States), Zhundong (China) and Donbas (Ukraine) [1–3]. Due to the great reserves and low-mining cost, those coals are currently regarded as a promising energy source [4]. Among the various utilization methods, coal gasification is considered to be a clean and efficient way to use coal reserves. However, as a result of high temperature required by coal gasification, the abundant sodium species in coal can partly release to gas phase, and inevitably cause a series of severe problems [5–6]. Taking fluidized-bed gasification as an example, the fouling deposit in syngas cooler, ash deposit in cyclone and the corrosion of refractory brick were frequently encountered [5,7]. Unfortunately, those problems have seriously restricted the wide utilization of sodium-rich coals [8].

To solve those sodium-related problems, some fundamental investigations have been conducted on release and transformation of sodium during gasification [2,9–12]. A literature review shows that the vast majority of researches are concentrated on two aspects: the influence of operating conditions and coal compositions [4,13–14]. For the former, the influence of operating temperature, atmosphere, pressure

and even reactor type has been investigated in detailed [9,13–15]. For instance, Zhang et al. [9] found that more sodium would be released to gas phase with the elevated gasification temperature. During combustion/gasification in a circulating fluidized bed, Song et al. [6] found that more sodium was released in combustion process. For the latter, the influence of internal mineral matters, minor element (Cl or S) and organic groups has been investigated as well [4,16–19]. For instance, under the steam atmosphere, Guo et al. [4] found that the inhibiting effect of Si-Al minerals played a dominant role on the sodium release, while the promoting effect of Cl was insignificant. The abundant organic groups in low-rank coals also exhibited an important effect on the transformation of sodium species. During gasification of a low-rank coal, Kosminski et al. [20] found that the loaded NaCl could react with some carboxylic acid groups, forming the active Na₂CO₃.

So far, the influence of operating conditions and coal compositions has been well investigated during gasification. However, it should be noticed that little work has been done with the interactions between sodium species and coal char. Our recent experiment found that the original sodium can be enriched in char residue after rapid heating treatment. Li et al. [11] also observed that sodium species were presented enrichment in residue particles during coal pyrolysis and char

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Nomenclature

SEM	scanning electron microscope
XRD	X-ray diffraction
MS	mass spectrometer
TG	thermogravimetry
DTG	differential thermogravimetry
CH	ash-free char
GR	graphite
/T	after temperature-programmed treatment
/W	after HCl-washing treatment

X	carbon conversion, %
R_s	gasification reactivity, h^{-1}
r	gasification rate, %/min
T_i	initial temperature of weight-loss, °C
T_m	temperature of maximum weight-loss rate, °C
T_f	finish temperature of weight-loss, °C
S_{BET}	BET surface area, m^2/g
C_{wea}	weak CO_2 chemisorption, $\text{mg-CO}_2/\text{g-char}$
C_{str}	strong CO_2 chemisorption, $\text{mg-CO}_2/\text{g-char}$
C_{tot}	total CO_2 chemisorption, $\text{mg-CO}_2/\text{g-char}$

gasification. This may be because coal devolatilization or char gasification was much more intense than the release of sodium. According to the previous studies, char gasification was the rate-controlled step in whole gasification process [21–22]. Thus, we believe that there must exist some interactions between char and sodium species at high temperatures, which play a vital role on the transformation of sodium species.

However, only a limited researchers have focused their interest on the interactions [23–25] up to now. In the field of catalytic gasification, Huhn et al. [23] investigated the behaviors of char mixed with alkali carbonate under inert atmosphere by using TGA coupled with the mass spectrometer. The results indicated that K_2CO_3 reacted with char carbon, transforming into K_2O or even elemental K. This meant that char carbon showed an intense reducibility to alkali metals at high temperatures. In turn, alkali metals also played an important role on char properties. Mckee [24] found that the molten alkali catalyst could cut channels on the surface of graphite. This indicated that both BET surface and the corresponding char gasification reactivity would increase significantly.

In this work, the effect of coal char on the transformation of several typical sodium species was investigated under a N_2 atmosphere by comparing TG-DTG curves of pure sodium species, char and graphite mixed with sodium species. After temperature programming, sodium crystal in residue were detected by XRD analysis. Sodium species retained in residue were removed by HCl-washing. Subsequently, gasification reactivity of sodium-free char was determined by TG analysis. Meanwhile, BET surface areas and corresponding CO_2 chemisorption of residues were determined by a specific surface analyzer and TGA, respectively. The objectives of this work is (1) to investigate the effect of char on the transformation of sodium species with the elevated temperature and the reasons for that; (2) to check whether sodium species can affect char properties and provide some useful information on the mechanism of char catalytic gasification.

2. Material and methods

2.1. Preparation of experimental samples

2.1.1. Coal sample

A typical sodium-rich Zhundong coal (ZD coal) from Xinjiang province, China was used in this work. The proximate and ultimate analysis of ZD coal were listed in Table 1. Before use, coal sample and the following char sample were dried at 110 °C, then pulverized and sieved to less than 74 μm .

2.1.2. Preparation of ash-free char

To eliminate the effect of minerals, coal sample was initially pre-treated to remove the original mineral matters. The specific dematerialized procedure can be found elsewhere [26]. Briefly, about 60 g sample was sequentially impregnated into 400 mL concentrated hydrochloric acid, hydrofluoric acid and 1:1 hydrochloric acid. The specific washing conditions were magnetic stirring at 60 °C for 2 h in an electric-heated thermostatic water bath. Subsequently, the

demineralized coal was filtered and washed by de-ionized water. According to GB/T 212-2008, ash content of demineralized sample was detected as low as 0.2 wt%. The ash-free sample was employed to prepare the high-temperature char. The simple procedure was as follows: ca. 1.00 g raw coal was pyrolyzed in a horizontal tube furnace at 1000 °C with a heating rate of over 500 °C/min. The residence time kept for 30 min. After that, the volatiles of char was considered to be released completely. The ash-free char (CH) was grinded and sieved to less than 74 μm .

2.1.3. Preparation of Na-mixed char and graphite

Several sodium species (NaCl , CH_3COONa , Na_2CO_3 , Na_2SO_4) were mechanically mixed with CH to prepare 20 wt% sodium species mixed samples and denoted as CH-1, CH-2, CH-3 and CH-4, respectively. Since graphite (GR) has the perfect stable carbon structure, thus it was employed as a comparison to determine the phenomenon resulting from stable carbon or active carbon in char. The corresponding Na-mixed GR samples were denoted as GR-1, GR-2, GR-3 and GR-4, respectively. A blank experiment was performed without mixing any sodium species and denoted as CH-0 and GR-0, respectively.

2.2. Thermogravimetric analysis

2.2.1. Temperature programmed experiment

A thermogravimetric analyzer (Setsys-HD, Setaram, France) coupled with a mass spectrometer was used to investigate the possible reactions between sodium species and coal char/graphite during temperature programmed experiment. In each experiment, about 20 mg sample was put in a platinum crucible and heated from 110 °C to 1000 °C at a rate of 5 °C/min under N_2 atmosphere. After reach the preset temperature, it was rapidly cooled to room temperature at a rate of 50 °C/min. The residues were denoted as “Sample/T” (For example, CH-1/T).

2.2.2. Char gasification

To explore the effect of sodium species on char property, the residues were washed by 1.0 mol/L HCl at a ratio of 1:500 to remove residual sodium. After leaching for 12 h, the filtered residues were washed by the plentiful deionized water to ensure sodium removal completely. Finally, residues were dried at 110 °C for 5 h and stored in a desiccator. The residues were denoted as “Sample/TW” (For example, CH-1/TW).

Isothermal gasification was performed on a TGA to investigate the variation of char gasification reactivity. In each trial, about 5 mg

Table 1
Proximate and ultimate analyses (wt.%) of ZD coal.

Sample	Proximate analysis			Ultimate analysis(daf)				
	M_{ad}	A_d	V_{daf}	C	H	O^a	N	S_t
Raw coal	3.93	8.17	39.67	75.88	4.87	18.02	0.91	0.32

ad, air-dried base; d, dry base; daf, dry and ash free base; ^a, by difference.

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