Influence Mechanism of Water-Soluble Sodium on Zhundong Coal Pyrolysis

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1. INTRODUCTION

The predicted reserves of the Zhundong coalfield are 390 billion tons, and the cumulative proven coal resource reserves are 213.6 billion tons. It is the largest packaged coalfield in China. Zhundong coal has the advantages of low ash content, easy ignition, and strong combustion stability and has a good application prospect. However, as a special kind of coal in China, the content of alkali metal elements (mainly sodium) in Zhundong coal is very high. Also, the mass fraction of Na2O in Zhundong coal ash composition analysis is no less than 5%, even higher than 10%, which is much higher than the normal sodium content level in typical Chinese coal, usually between 1 and 2%.1−3 This leads to serious slagging, scaling, and corrosion problems on the heating surface of the reactor in the process of direct combustion or coal chemical utilization.4,5 Also, as a necessary stage of coal combustion, gasification, and liquefaction, the pyrolysis of coal has a direct impact on the subsequent conversion and utilization of coal.6−8 Therefore, it is of great significance to study the influence of sodium on coal pyrolysis characteristics.

The effects of sodium compounds loaded in coal during pyrolysis have been widely investigated. Quyn et al.7 found that the pyrolysis conversion rate of Loy Yang lignite after loading NaCl using the impregnation method increased significantly, and when Na exists in the ionic state, it has a better catalytic effect, while when it exists in the form of NaCl compound, the catalytic ability decreases. Zhang et al.8 found that during the pyrolysis of Wyodak coal loaded with 3% Na2CO3, Na2CO3 can promote char condensation, decrease tar production, and promote the release of H2, but inhibits the release of CH4. Ding et al.9 observed the interactions of Na2CO3 with Shenhui bituminous coal and Zunyi anthracite coal by in situ heating stage microscope and found that H2 and CO are the main pyrolysis gas products of coal pyrolysis, and the yield of H2 and CO increases with the addition of Na2CO3 in a certain range. Murakami et al.10 found that after loading sodium, magnesium, calcium, barium, and nickel cations in Loy Yang brown coal by ion exchange or impregnation, the yield of char produced by pyrolysis is almost the same, but there are great differences in the specific surface area of char. Also, the surface area of char produced by coal loaded with sodium decreases significantly with the sodium content.

Most of the previous studies focused on the influences of water-soluble sodium compounds loaded in coal during pyrolysis and the effect of the amount of sodium compounds on the pyrolysis effect.11−13 These achievements provide great help for the development of industrial coal pyrolysis catalysis. However, the research on the effects of inherent water-soluble sodium in coal during the pyrolysis step is still rare. In this work, using crown ether, a kind of supramolecular compound, the inherent water-soluble sodium-loaded coal samples were prepared. The influences and mechanisms of inherent water-soluble sodium and water-soluble sodium compounds loaded...
in Zhundong coal during pyrolysis were compared and discussed. Moreover, the distributed activation energy model (DAEM) was used to determine the kinetic parameters of pyrolysis.

2. MATERIALS AND METHODS

2.1. Coal Samples. The raw Zhundong coal from the Dajing mining area was ground, and particles smaller than 90 μm (80 wt % passed through a 170-mesh screen) were used in this work. The characteristic analysis data of the samples are summarized in Table 1. Before the experiments, the coal sample was dried in an oven at 98 °C until no detailed change in mass, and then cooled in a dryer and sealed for standby.

The coal sample was successively extracted with deionized water and 1.0 mol L⁻¹ hydrochloric acid (HCl) at a temperature of 60 °C for 24 h. The solid-to-liquid ratio is the solid sample of 1 g to a solution of 25 mL. The solid residue was dried at 98 °C until no detailed change in mass, which was denoted as HC.

The procedures of the inherent water-soluble sodium-loaded coal sample preparation are as follows: the wastewater in which after washing, coal with deionized water was successively extracted with 20 mmol L⁻¹ dicyclohexyl-18-crown-6 (DCH18C6) solution and 10 mmol L⁻¹ DCH18C6 solution using chloroform as a diluent. The volume ratio of wastewater to DCH18C6 solution is 1:1. After the process of extraction separation, alkali metal ions and alkaline-earth metal ions in the wastewater were taken, except Na⁺. Then, a certain amount of HC was added to the wastewater, and this mixture was stirred with a magnetic stirrer at 60 °C until the liquid thickens. Finally, this thickened mass was dried at 98 °C in a vacuum oven until no detailed change in mass, which was denoted as IC.

The water-soluble sodium compound-loaded coal samples were prepared using the incipient wetness impregnation method (IWIM): a certain amount of NaCl, Na₂SO₄, NaHCO₃, and Na₂CO₃ powders was separately dissolved in 100 mL of deionized water to prepare the corresponding solutions. The rest of the process is similar to that for IC. It should be noted that HC coal with NaCl, Na₂SO₄, NaHCO₃, Na₂CO₃ additive were designated as NC1, NC2, NC3, NC4, respectively.

Before the pyrolysis experiments, the dried samples were ground, mixed uniformly and sieved to a particle size fraction of less than 90 μm. The theoretical weight percentage of sodium added in the coal samples was 10 wt % on a dry basis, respectively. For each run, the parallel experiment for blank reagents was carried out to ensure that there was no possible deviation caused by reagents.

2.2. Pyrolysis Experiments. The pyrolysis experiments of coal samples were carried out using a TA Instruments SDT Q50 thermogravimetric analyzer (TGA). To start the TGA test, about 15 mg of the coal sample was weighed and placed in a crucible. The reaction chamber was closed, and the sample was heated to 105 °C at a rate of 40 °C/min in a nitrogen flow of 60 mL/min. After 20 min of isothermal equilibration, the sample was continuously heated at a rate of 40 °C/min to the maximum pyrolysis temperature of 900 °C, and then, the sample was maintained at this temperature for another 10 min for isothermal equilibration.

2.3. Structure Tests of Samples. The specific surface area and the pore structure of coal samples were determined using an ASAP-2460 physical adsorption instrument. The microcrystalline structures of coal chars were determined using a Bruker D8 ADVANCE X-ray diffraction (XRD) instrument. The surface morphology characteristics of coal chars were observed using a S-4800 scanning electron microscopy (SEM) instrument at a working voltage of 5.0 kV. The distribution of sodium elements in coal samples was determined using an S-4800 SEM and a Quantax-400 energy spectrometer (EDS).

2.4. XRD Analysis. During the XRD analysis experiment, the coal char samples were prepared to the finest thickness and placed in a Bruker D8 ADVANCE X-ray powder diffractometer, and then, an appropriate magnification was selected to ensure that all samples were within the scanning range. Measurements were conducted using copper Cu Kα radiation (1.54060 and 1.54439 Å) operating at 40 kV/40 mA, with 2θ ranging from 5 to 90° with 0.01°/step.

The lateral size of the crystallite, Lc, and the stacking height of the crystallite, Lc, were obtained from the 100 and 002 diffraction peaks, respectively, using the Scherrer equation:

\[
L_c = \frac{1.84\lambda}{\beta_{100}\cos(\theta_{100})}
\]

\[
L_c = \frac{0.9\lambda}{\beta_{002}\cos(\theta_{002})}
\]

The interlayer spacing, d₀₀₂, was obtained using the Bragg equation:

\[
2d_{002}\sin(\theta_{002}) = \lambda
\]

where \(\lambda\) is the wavelength of the X-rays, the average value of \(\lambda\) is 1.5418 Å in this study; \(\theta_{100}\) and \(\theta_{002}\) are, respectively, the Bragg angle of the 100 diffraction peak and the 002 diffraction peak, (°); and \(\beta_{100}\) and \(\beta_{002}\) are, respectively, the peak width at half maximum intensity of the 100 diffraction peak and the 002 diffraction peak, (rad).

2.5. DAEM Method. The pyrolysis process of coal has been successfully described by the DAEM. To further analyze the pyrolysis kinetics of coal samples, this study assumed that the whole pyrolysis process of coal is composed of a set of irreversible single (first-order) reactions occurring successively. These reactions are numbered \(i = 1...n_i\) and the contribution of the \(i\)th reaction to the pyrolysis process is expressed by the first-order equation:

\[
\frac{da_i}{dt} = k_i(a_i^* - a_i)
\]
where $a_i$ is the weight loss mass fraction of the $i$th reaction, and $a_i^*$ is the total weight loss mass fraction of the $i$th reaction. Based on this, $(a_i^* - a_i)$ means the amount of unreacted volatile remaining at time $t$. $k_i$ is calculated by the Arrhenius formula.

In the DAEM, $d a^*$ is related to the distribution of activation energy $E$. Therefore, the total amount of volatile available for release from the coal is taken to be a distribution that is satisfactory.

$$
\int_0^\infty f(E)\,dE = 1
$$

Thus, the total amount of volatile material released up to time $t$ is given by

$$
\frac{a}{a^*} = \int_0^\infty \left(1 - e^{-\frac{a}{a^*} f(E)\,dE}ight)\,dE
$$

This formula is also the equation of the DAEM model and could be simplified using the Miura integration method:

$$
\ln\left(\frac{h}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT}
$$

where $h$ denotes the heating rate, ($^\circ\text{C}/\text{min}$); $T$ denotes the given temperature, ($^\circ\text{C}$).

### 3. RESULTS AND DISCUSSION

#### 3.1. Distribution Characteristics of Sodium

Figure 1 shows the EDS mapping photographs of sodium distribution in the coal samples; the yellow bright spot in the diagram represents the sodium element. It is shown that although the contents of sodium are the same, the distributions of sodium are different in different types of sodium compounds. Most of the inherent water-soluble sodium elements are distributed on the coal surface. However, the sodium distributions of the water-soluble sodium compound-loaded coal samples are not as concentrated as that in IC.

The main factors that affect the adhesion of sodium to coal particles are temperature, pressure, contact time and solution characteristics. The temperature, pressure, and contact time of the procedures of the inherent water-soluble sodium-loaded coal sample preparation and the water-soluble sodium compound-loaded coal sample preparation were the same, and three parallel control experiments were carried out to ensure the accuracy of the experiment, so the reason for different sodium distributions may be due to the characteristics of solution.

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**Figure 1.** EDS mapping photographs of the Na-loaded coal sample.
The type and content of the anions can affect the activity coefficient of the metal cations in the solution, and then, the adsorption and desorption of metal ions by an adsorbent are affected. The influence of anions on the adsorption characteristics of metal cations is mainly through three ways: (1) change in the ionic strength of the solution. The composition, structure, and chemical properties of anions vary with their species. Therefore, even at the same molar concentration, different kinds of anions have different effects on the ionic strength of the solution. The activity coefficients of metal cations that coexist with anions are also different, which in turn affect the adsorption of metal ions by the adsorbent. (2) Specific adsorption. The anions may have special adsorption with the adsorbent and react with the functional groups of the adsorbent surface. Furthermore, the adsorption capacity of the adsorbent to the metal cations in the solution is affected. (3) Formation of ion pairs. The ion pair theory holds that some anions and cations with opposite charges can form ion pairs through the action of Coulomb gravitation. The chemical properties of ion pairs are quite different from those of their constituent ions. Therefore, the adsorption characteristics of ion pairs have great changes compared with the constituent ions.

The type and content of anions coexisting with inherent water-soluble sodium in Zhundong coal were obtained by an ICS-2000 ion chromatograph, and the results are shown in Table 2. By calculating the number of anionic and cationic charges in Zhundong coal, it is found that the total charge of the cation is 0.1700 mmol/g, and the total charge of anions is 0.1629 mmol/g. According to the principle of conservation of charges in Zhundong coal, it is found that the total charge of anions and cations should be equal. Therefore, there are some anions that cannot be detected by instruments. Under the common action of these undetected anions, the adsorption of sodium ions by coal particles can be promoted. Therefore, the inherent water-soluble sodium has better affinity with coal particles and is more easily attached to coal particles.

The surface area and average pore diameter of coal samples are shown in Table 3. The data results fully show that sodium addition has a significant effect on the specific surface area of HC while it shows a weak effect on the porosity, which is similar to the results obtained by Ding et al. It is indicated that the inherent water-soluble sodium and the water-soluble sodium compounds can block some pore structures of the coal sample. It is noteworthy that the specific surface area of IC is the smallest in five kinds of Na-loaded coal samples, which further confirms the conclusion that the sodium elements in the IC mainly concentrate on the coal particles.

### Table 2. Contents of Water-Soluble Anions in Zhundong Coal (mg/g)

| Anion  | Cl\(^{-}\) | SO\(_4^{2-}\) | CO\(_3^{2-}\) | NO\(_2^{-}\) | NO\(_3^{-}\) | HCO\(_3^{-}\) | OH\(^{-}\) | PO\(_4^{3-}\) | HPO\(_4^{2-}\) | F\(^{-}\) |
|--------|-----------|------------|------------|----------|----------|-----------|--------|---------|-----------|--------|
| Value  | 2.26      | 2.51       | 0.13       |          |          | 1.96      |        |         |           |        |

### Table 3. Specific Surface Area and the Average Pore Diameter of Coal

| Sample | Surface Area (m²/g) | Average Pore Diameter (nm) |
|--------|---------------------|---------------------------|
| HC     | 2.03                | 12                        |
| NC1    | 1.41                | 12                        |
| NC2    | 1.39                | 11                        |
| NC3    | 1.27                | 13                        |
| NC4    | 1.24                | 10                        |
| IC     | 1.09                | 11                        |

Figure 2. TG/DTG curves of the pyrolysis of coal samples.

The pyrolysis process of all coal samples can be obviously divided into three stages: the drying degassing stage (100–350 °C); the primary devolatilization stage (350–550 °C); and the secondary devolatilization stage (550–900 °C).

The order of size of weight loss in the drying degassing stage is as follows: IC > NC4 > NC3 > NC2 > NC1 > HC. The weight loss and weight loss rate of Na-loaded coal samples are all greater than those of HC. It is likely that the presence of sodium increases the equilibrium moisture content in coal, and the water in coal is heated and evaporated at this stage. In addition, the presence of sodium may combine with some oxygen-containing functional groups (such as –COOH, –OCH\(_3\), –OH, >C=O, –O–) and promote the thermal decomposition of these oxygen-containing functional groups:

\[
(-\text{COO} - \text{Na}) + (-\text{CM}) = (\text{CM} - \text{Na}) + \text{CO}_2 \quad (9)
\]

The order of size of weight loss in the primary devolatilization stage is as follows: IC > NC4 > NC3 > NC2 > NC1 > HC. The weight loss and weight loss rate of Na-
loaded coal samples are all lower than that of HC. The experiment results clearly show that the loaded Na hindered the escape of some volatile constituents of coal samples and reduced the pyrolysis rate. The effects of alkali metal on coal pyrolysis have been widely investigated by scholars.25,26 The research of scholars shows that the escape of carbon dioxide during coal pyrolysis leads to more fracture of the bond between $-\text{COO}^-$–Na, while the disconnected $-\text{Na}$ continuously bonded to the coal/char matrix ($-\text{CM}$) and continuously acts as a virtual cross-linking point. This reaction further aggravates the difficulty of subsequent release of the tar fragments, hinders the formation of volatile matter, and prolongs the retention time of volatile matter in coal particles:

$$\text{(CM} - \text{Na}) + (-\text{CM}) = (-\text{CM}^*) + (\text{Na} - \text{CM})$$

(10)

The order of size of weight loss in the secondary devolatilization stage is the same as that in the drying degassing stage. This is probably due to the stability of the newly formed Na–CM bonds, which are not strong, and the increase in temperature leads to the fracture of the Na–CM bond again and the formation of new free radical sites. Finally, some aliphatic fragments escape in the form of gas, and some more aromatic units, especially the larger aromatic ring system, eventually become part of the char.

It is noteworthy that although the content of sodium in the Na-loaded coal samples is the same, the inherent water-soluble sodium has the strongest effect on the pyrolysis process of coal samples.

3.3. XRD Results. The influence of sodium on the microstructure of coal chars was discussed, and the carbonaceous structure of corresponding coal chars was analyzed by XRD to determine the effect of sodium. Figure 3 shows the XRD spectra of coal chars prepared at 40 °C/min to pyrolysis temperature 900 °C.

The 002 and 100 peak intensity of HC-char is relatively higher compared with Na-loaded coal chars. Table 4 presents the $2\theta_{002}$, $d_{002}$, $L_\alpha$, and $L_c$ calculated for the char samples. Under the same pyrolysis condition, the Na loading resulted in lower $2\theta_{002}$, $L_\alpha$, and $L_c$, but a higher $d_{002}$. These results fully show that the presence of Na probably inhibited the graphitization process in the process of coal pyrolysis and reduce the order of carbon microcrystalline structure. It is likely that sodium elements can enter the microcrystalline structure of coal char and distribute in the interlayer of microcrystalline structure, which inhibits the growth of the microcrystalline structural units and the condensation of the interlayer spacing of adjacent microcrystalline structural units, and promotes some aliphatic fragments to escape in a relatively large molecular weight form.25,27

The $2\theta_{002}$, $L_\alpha$, $L_c$, 002 peak intensity, and 100 peak intensity of IC char are the smallest compared with the other samples, while $d_{002}$ is the largest. It is indicated that inherent water-soluble sodium has stronger inhibition in the process of graphitization during coal pyrolysis compared with water-soluble sodium compounds. It is possible that the inherent water-soluble sodium elements are mainly distributed on the coal surface, and these sodium atoms are easier to enter the microcrystalline structure of coal char, resulting in the distortion of the coal char lattice.

Figure 4 shows the SEM photographs of several areas on the coal char surface. Typically, the surface of HC-char is smooth, with fewer cracks, pore structures, and floc. The chars formed...
by Na-loaded coal samples have a rough surface, with more cracks and pore structures. This phenomenon confirms that the existence of sodium elements inhibits the graphitization process in coal pyrolysis. In addition, the chars formed by Na-loaded coal samples have a large number of fragmentation. It is possible that sodium elements will block some pore structures of the coal sample (as in Table 3); the volatile components produced during the pyrolysis process cannot escape in time and accumulate in the interior of the coal particle, and the pressure can only be released by particle crushing.

### 3.4. Activation Energy from DAEM

The DAEM method can be used to describe the process of coal pyrolysis. This method assumes that the whole pyrolysis reaction process is composed of countless independent first-order reactions. The kinetic parameters were determined by the coal pyrolysis conversion degree under the reducing atmosphere or oxidizing atmosphere. Also, the calculation steps were as follows:

1. The weight loss curves of the pyrolysis process at different heating rates should be obtained.
2. The values of \((h/T^2)\) at the same carbon conversion rate values from the weight loss curves of the pyrolysis process at different heating rates should be calculated. Carbon conversion rate \(x\) is given by the following equation:
   \[
   x = \frac{m_0 - m}{m_0 - m_a} \tag{11}
   \]
3. \(\ln(h/T^2)\) vs \((1/T)\) at the same \(x\) value should be plotted, and the \(E\) (from the slope) and \(A\) (from the intercept) values should be obtained by using the relationship shown in eq 8, and then, the curve of the change of \(E\) with \(x\) in the process of pyrolysis can be obtained.

The parameters from the DAEM method for IC under nitrogen at different heating rates are illustrated in Figure 4. Other coal samples were calculated using similar methods, and the straight lines were no longer enumerated. The linear and

| sample   | \(\theta_{002}\) (°) | \(d_{002}\) (nm) | \(L_a\) (nm) | \(L_c\) (nm) |
|----------|-----------------|-----------------|-------------|-------------|
| HC-char  | 24.71           | 0.360287        | 2.984364    | 1.082310    |
| NC1-char | 24.23           | 0.367315        | 2.741875    | 0.998966    |
| NC2-char | 23.97           | 0.371240        | 2.660001    | 0.985169    |
| NC3-char | 23.64           | 0.376347        | 2.569419    | 0.968142    |
| NC4-char | 23.49           | 0.378716        | 2.504469    | 0.954230    |
| IC-char  | 23.10           | 0.385021        | 2.397565    | 0.938127    |

Figure 4. SEM photographs of chars.
parallel development for different $x$ from 0.1 to 0.9 at different heating rates shown in Figure 5 indicates that the process of coal pyrolysis under nitrogen can be described by a series of similar single reactions.

The relationship between the activation energy ($E$) and the carbon conversion rate ($x$) for the six kinds of coal samples is shown in Figure 6. It is shown that the activation energy increased as the carbon conversion rate increased, which coincided with the research results of Shen et al.28 and Vyazovkin et al.29 This phenomenon is an important characteristic of the multistep reaction, which fully illustrates the complexity of coal pyrolysis. The cause of this phenomenon is mainly due to the transition from the thermal decomposition stage to the thermal condensation stage as the carbon conversion rate increased, and the size of the aromatic ring structure in the coal char increases, and the condensation reaction becomes difficult, so the activation energy is also increased.

The distributions of the six kinds of coal sample activation energy cover a wide range, and the activation energy of the coal sample loaded of the sodium element is obviously lower than that of HC at the same carbon conversion rate, indicating that the activation energy in the process of pyrolysis was significantly reduced by the presence of sodium.

The activation energy distribution curve $f(E)$ of the six coal samples all show a single peak distribution, but do not follow the Gaussian function distribution, so the frequency factors are not a fixed value. The activation energy corresponding to the maximum value of the activation energy distribution curve of HC, NC1, NC2, NC3, NC4, and IC is 377.20, 288.92, 276.82, 261.99, 238.27, and 225.31 kJ/mol. It is indicated that the main distribution range of activation energy moves to the region where the activation energy is low after loaded sodium, and the interval of activation energy distribution also narrows.

The results of the DAEM model show that the distribution range of the activation energy of IC is the narrowest, and the activation energy corresponding to the maximum value of the activation energy distribution curve $f(E)$ of IC is the lowest. This confirms the previous result that inherent water-soluble sodium has a stronger catalytic effect than that on the coal pyrolysis process than additional water-soluble sodium compounds.

4. CONCLUSIONS

(1) In the case of the same contents of sodium-loaded, the inherent water-soluble sodium is mainly concentrated on coal particles. Therefore, it is easier to interact with coal particles in the pyrolysis process, which further aggravates the degree of pyrolysis reaction.

(2) The presence of sodium can promote the weight loss of coal samples at the initial stage of pyrolysis and the stage of thermal condensation and block the escape of volatile matter in the main pyrolysis stage.

(3) The coal sample loaded with sodium can increase the degree of char fragmentation and surface roughness, and the pore structure becomes more developed. The 002 and 100 peak intensity, the Bragg angle of the 002 diffraction peak, the lateral size, and the stacking height of the crystallite of chars prepared from Na-loaded coal samples are obviously reduced, while the interlayer spacing and the degree of disordering of the microcrystalline structure of char are obviously increased.

(4) The DAEM can describe the pyrolysis process of the Zhundong coal in a wide range of temperature and the effect of the existence of sodium elements on the coal pyrolysis. In the process of coal pyrolysis, the activation energy increases with the increase in the carbon conversion rate, and the presence of sodium can reduce
the activation energy under the same carbon conversion rate.

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**Notes**
The authors declare no competing financial interest. All data, models, and code generated or used during the study appear in the submitted article.

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