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Effects of Chemical Forms of Alkali and Alkaline Earth Metallic Species on the Char Ignition Temperature of a Loy Yang Coal under O_2/N_2 Atmosphere

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ABSTRACT: Experiments were performed to determine the effects of alkali and alkaline earth metallic (AAEM) species on the ignition behavior of char under O_2/N_2 conditions. The char ignition temperatures of a Loy Yang brown coal were investigated using a wire-mesh reactor, where the secondary reactions of the evolved volatiles were minimized. Water, ammonium acetate, and sulfuric acid sequential extractions were employed to prepare the coal samples of different chemical forms of AAEM compounds from raw coal. In comparison to that of raw coal, the increases in the average char ignition temperature of 33 and 55 °C were observed for ammonium-acetate-extracted coal and sulfuric-acid-extracted coal (H-form coal), respectively, indicating the strong catalytic effects of various chemical forms of AAEM species on the char ignition behavior of brown coal. To find out which chemical form of sodium has a higher catalytic effect on the char ignition behavior, combustion experiments were also carried out for Na-exchanged coals and NaCl-loaded coals, which were prepared from H-form coal. The average char ignition temperature of 0.05 M Na-exchanged coal is 48 °C lower than that of 0.05 M NaCl-loaded coal in air, although those two samples have a close content but different chemical forms of sodium. It was found that sodium in char as carboxylates (−COONa) or NaCl can both improve the ignition characteristics of coal samples but carboxylates (−COONa) show a more significant catalytic effect on the average char ignition temperature in air combustion.

1. INTRODUCTION

The main alkali and alkaline earth metallic (AAEM) species in Victorian brown coal are sodium, magnesium, and calcium.[1] They exist in two main forms: as carboxylates and as soluble salts (mainly −COONa and NaCl).[1] The presence of AAEM species in low-rank coal is always an important consideration in the use of brown coal.[1−8] In the current pulverized-coal furnace, the high levels of inherent AAEM species present in low-rank coals cause operational problems, such as slagging, fouling, and particle agglomeration.[2] On the other hand, the AAEM species in low-rank coal can also act as excellent catalysts for the combustion and gasification reaction.[1,4−6] A large number of studies have been carried out for the catalytic effects of AAEM species on char reactivity during pyrolysis or gasification.[1−16] The catalytic activity of AAEM species in char depends upon its dispersion and chemical forms in the char.[1,5,10,11] For example, earlier studies reveal that sodium loaded into a Loy Yang brown coal substrate as NaCl and as sodium carboxylates (−COONa) can have very different catalytic effects on the char reactivity.[5]

Generally, coal ignition was always described as a continuous reaction process between the fuel and oxidizer, and coal flashing was generally used to identify ignition.[9,17] The pyrolysis of coal/char at low temperatures before ignition plays a significant role in its ignition behavior.[17] The volatilization of AAEM species in low-rank coal during the devolatilization stage determines the retention of AAEM species in the char, which act as the catalysts of char ignition or combustion.[5,10,18] The ignition behavior of coal/char has been studied over many years. Earlier studies[18,19] have provided some basic understanding about the catalytic effects of alkali chlorides and alkaline earth chlorides on the ignition properties of coal. It was

concluded that the catalytic activity of alkali and alkaline earth salts correlates well with the first ionization energy of the metal: the lower the first ionization energy, the higher the catalytic activity.[3,6] Our recent work[9] also clearly indicates that a 29 °C ignition delay was observed for H-form coal (0.1 M sulfuric acid) compared to that of Loy Yang raw coal and the AAEM species in the former as both carboxylates and soluble salts were removed. However, the catalytic effects of different chemical forms of AAEM species on the coal/char ignition temperature remain unclear. There are clearly needs to investigate if the effects of catalytic effects of various chemical forms of AAEM species on the char ignition behavior could be drawn directly from the majority of the conclusions on char reactivity in the past studies. Furthermore, some investigations into the volatilization of AAEM species during pyrolysis have been carried out in the past,[1,4−8,10−16] but the rate of AAEM species release during the various stages of coal combustion is not known; therefore, a further systematic study is required.[20,21] Specifically, the role of oxygen in release and retention of AAEM species in the stage of coal ignition remains unknown. Very little literature was reported for the retention of AAEM species in unburned char before ignition of the coal/char samples.

Coal particles can ignite either homogeneously or heterogeneously depending upon different reaction conditions, which

Table 1. Properties of the Loy Yang Raw Coal and H-Form Coal Samples Studied

	proximate analysis (wt %, db)			ultimate analysis (wt %, daf)				
coal	fixed carbon	volatile matter	ash	C	H	N	S	O (by difference)
raw coal	46.6	50.2	3.2	68.1	4.9	0.6	0.6	25.8
H-form coal	47.3	50.6	2.1	67.8	5.0	0.6	0.6	26.0

Table 2. Contents of AAEM Species in Loy Yang Coal Samples[a]

	Na (%, db)	Mg (%, db)	Ca (%, db)
sample 1	0.347	0.172	0.070
sample 2	0.268	0.128	0.053
sample 3	0.041	0.088	0.038
sample 4	0.016	0.001	0.012
sample 5	0.323	ND[b]	ND
sample 6	0.752	ND	ND
sample 7	1.479	ND	ND
sample 8	0.375	ND	ND
sample 9	1.191	ND	ND
sample 10	3.860	ND	ND

[a] Sample 1 was Loy Yang raw coal. Sample 2 was prepared by washing raw coal in ultrapure water. Sample 3 was prepared by sequential washing raw coal in ultrapure water and ammonium acetate. Sample 4 was also termed as H-form coal and prepared by sequential washing raw coal in ultrapure water, ammonium acetate, and sulfuric acid. Samples 5, 6, and 7 were prepared by adding the H-form coal sample into the 0.05, 0.1, and 0.5 M solutions of sodium acetate, respectively. Samples 8, 9, and 10 were prepared by adding the H-form coal sample into the 0.05, 0.1, and 0.5 M solutions of sodium chloride, respectively. [b] ND = not detected.

include particle size, heating rate, final temperature, gas pressure, etc.[22−25] In practice, a clear distinction between homogeneous and heterogeneous ignition is quite difficult or nearly impossible.[25] Thermogravimetric analysis (TGA) and drop-tube furnace are among the most common methods used to study coal ignition.[26] Although the TGA techniques have been widely employed to determine the ignition behavior of coal,[27,28] they operate under conditions (e.g., in terms of coal sample stacking and very slow heating rates) very different from those in industrial furnaces. On the other hand, it is not possible to determine or control the heating rate and particle temperature accurately in other bench-scale equipment, such as a drop-tube furnace, which are mainly based on the conventional measurement of the minimum gas temperature required for the ignition of coal/char particles.[22,23] In this work, the ignition temperatures of chars from a Loy Yang brown coal were investigated in a wire-mesh reactor (similar to that described by Gibbins and co-workers[29] and Li and co-workers[30,31]), which features a relatively accurate control of particle time−temperature history in the absence of significant secondary reactions of volatiles. As was explained in our earlier work,[9] the ignition temperature observed in a wire-mesh reactor is the ignition temperature of char rather than coal, which was unlikely affected to any great extent by the volatiles because the volatiles were rapidly quenched, diluted, and swept away from the vicinity of char particles. The ignition of (concentrated) volatiles would take place at a much lower temperature. For example, an ignition temperature of about 300 °C in air in a thermogravimetry (TG)−differential thermal analysis (DTA) system was reported for a similar Loy Yang raw coal as a result of the presence of the volatiles around the coal/char particles in the TGA,[32] while in a wire-mesh reactor system, the ignition temperature is about 440 °C.[9]

Therefore, the purpose of this study is to investigate the catalytic effects of chemical forms of AAEM species (particularly Na) on the ignition temperature of Loy Yang chars in a wire-mesh reactor. The sequential extractions of water, ammonium acetate, and sulfuric acid were employed to prepare the three coal samples with different chemical forms of AAEM compounds from raw coal. To gain a fundamental understanding of the catalytic effect of different chemical form, ignition experiments were carried out using particles of both Loy Yang raw coal and the three extracted coal samples. Moreover, the char ignition temperatures of Na-exchanged coal and NaCl-loaded coal samples were also observed, which prepared H-form coal (containing no AAEM species), in 0.05, 0.1, and 0.5 M solutions of sodium acetate and sodium chloride, respectively.

2. EXPERIMENTAL SECTION

2.1. Coal Preparation. Samples of Loy Yang brown coal with a particle size between 106 and 150 μm were used in this study. The coal

samples are hereafter termed as "raw coal", and the properties are listed in Table 1.

Experiments were carried out using both raw coal particles and extracted coal particles from the same brown coal. Because Loy Yang brown coal contains significant amounts of AAEM species as carboxylates and soluble salts (mainly −COONa and NaCl),[1] raw coal was sequentially extracted by water, ammonium acetate, and sulfuric acid to prepare three coal samples containing virtually different chemical forms of AAEM species.[4,5,8] Briefly, the raw coal (sample 1) was stirred in ultrapure water for 24 h, then filtered, and partially dried at low temperatures (<35 °C) to prepare the water-washed coal (sample 2). The fraction of AAEM species in the water-extracted solution was defined as a "water-soluble" AAEM species (mainly NaCl).[8] The water-washed coal sample was then extracted in 0.5 M ammonium acetate solution for 24 h and partially dried at low temperatures to obtain the ammonium-acetate-washed coal (sample 3). The extracted AAEM species by ammonium acetate solution was termed as "ion-exchangeable" AAEM species (mainly −COONa).[8] The ammonium-acetate-washed coal sample was finally washed in 0.1 M sulfuric acid for at least 16 h under nitrogen atmosphere, then washed with double-distilled water, and dried at low temperatures (<35 °C) to prepare the H-form coal (sample 4), containing virtually no AAEM species. To prevent a significant change in the coal substrate and ash structure, 0.1 M sulfuric acid rather than hydrofluoric acid or hydrogen nitrate was employed as the acid of extraction agents.[5] The fraction of AAEM species during sulfuric-acid-extracted solution was termed as "acid-soluble" AAEM species. The properties of H-form coal are also shown in Table 1. The ash yield of H-form coal does show some reduction after extraction by water, ammonium acetate, and sulfuric acid.

The Na-exchanged coals (samples 5, 6, and 7) and NaCl-loaded coals (samples 8, 9, and 10) were also prepared by adding H-form coal samples into the 0.05, 0.1, and 0.5 M solutions of sodium acetate and sodium chloride, respectively. The mixtures were stirred under nitrogen and then dried at low temperature (<35 °C) to prepare the coal samples. The procedures of these treatments have been detailed elsewhere.[5,15] The contents of AAEM species in these 10 coal samples were listed in Table 2. It can be seen that most of AAEM species in H-form coal were removed.
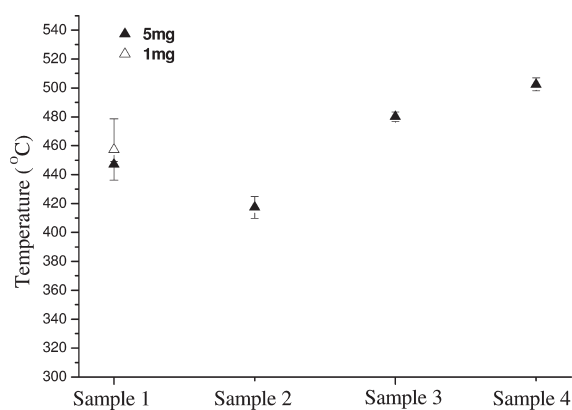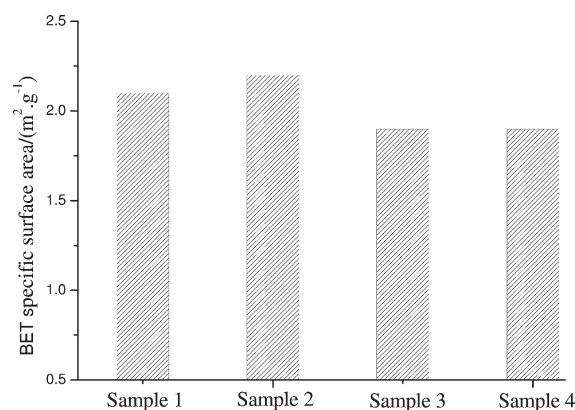
Figure 1. Average ignition temperatures of Loy Yang raw coal and three sequential extracted coal samples in air conditions. Sample 1 was Loy Yang raw coal. Sample 2 was prepared by washing raw coal in ultrapure water. Sample 3 was prepared by sequential washing raw coal in ultrapure water and ammonium acetate. Sample 4 was also termed as the H-form coal sample and prepared by sequential washing raw coal in ultrapure water, ammonium acetate, and sulfuric acid. The error bars indicate one standard deviation. Note that the scale of the *x* axis is not linear. The data point at 1 mg was taken from ref 9.

2.2. Ignition Temperature Determination in a Wire-Mesh Reactor.

The effect of the particle amount on the char ignition temperature of Loy Yang raw coal has been reported in our earlier studies.[9] The details of the experimental process can be found in our recent work.[9] In brief, about 5 mg of coal sample was distributed within a round working area of 20 mm in diameter between two layers of wire mesh. The distribution of coal particles approached almost that of "single particles"; the particles certainly existed as a single layer and did not come into significant contact with each other. The wire mesh was then heated at a rate 10 K s^{-1} to 700 °C, while a stream of O$_2$/N$_2$ mixture continually passed through the mesh at 4.0 L min^{-1} (0.1 m s^{-1}, measured under ambient conditions) to carry the evolved volatiles away. As soon as particles ignited, the heat released caused a sudden increase in the mesh temperature and a decrease in the thyristor control voltage (i.e., a decrease in electrical power input into the system). This temperature is considered to be the char ignition temperature. The particle ignition could also be observed visually. The detection of particle ignition by monitoring a sudden mesh temperature increase agreed well with the visual observation of particle ignition. Each ignition temperature shown hereafter represents the average of up to 10 repeats under each condition. The *t* tests were carried out to prove that the differences in the ignition temperature that we observed were statistically significant. It should be noted that a sample loading of 5 mg rather than 1 mg of coal particles was used in this work to decrease the possible variation in lithotype composition of coal/char, which can significantly affect the observed ignition temperature.[33]

2.3. Quantification of AAEM Species in Various Coal/Char Samples.

The AAEM species contents in the coal/char sample was quantitatively analyzed by inductively coupled plasma—atomic emission spectrometry (ICP—AES) after the sample had been dissolved in a hydrofluoric acid, fuming nitric acid, and boric acid solution.[8] The Italy Milestone's ETHOS microwave chemical reaction system was used in the digestion process.

2.4. Determination of the Brunauer—Emmett—Teller (BET) Surface Area of Coal Particles.

An instrument of Micromeritics ASAP 2020 with the single-point BET nitrogen adsorption method was used to determine the BET surface area of the samples. The widely used method[34] was applied in this study to determine the pore surface area of the coal particle from gas adsorption isotherms, which use N$_2$ at −196 °C as the adsorptive conditions.


Figure 2. BET specific surface area of Loy Yang raw coal and three sequential extracted coal samples. Sample 1 was Loy Yang raw coal. Sample 2 was prepared by washing raw coal in ultrapure water. Sample 3 was prepared by sequential washing raw coal in ultrapure water and ammonium acetate. Sample 4 was also termed as the H-form coal sample and prepared by sequential washing raw coal in ultrapure water, ammonium acetate, and sulfuric acid. The error bars indicate one standard deviation. Note that the scale of the *x* axis is not linear.

3. RESULTS AND DISCUSSION

3.1. Effects of Indigenous AAEM Species on the Char Ignition Temperature.

The char ignition temperatures from Loy Yang raw coal, water-washed coal, ammonium-acetate-washed coal, and H-form coal samples were shown in Figure 1. These four coal samples were termed as samples 1, 2, 3, and 4, respectively. As shown in Figure 1, raw coal (sample 1) has an average ignition temperature of 447 °C in air and the use of 5 mg of sample would reduce the ignition temperature about 10 °C compared to that for 1 mg of sample loading. An increase in the average particle temperatures of 33 and 55 °C was measured for the ammonium-acetate-washed coal (sample 3) and H-form coal (sample 4), respectively. In comparison to the presence of both "ion-exchangeable" (mainly sodium carboxylates) and "acid-soluble" AAEM species in sample 2 and only "acid-soluble" AAEM species in sample 3, sample 4 contains virtually no AAEM species. It was indicated that AAEM species in samples as both "ion-exchangeable" and "acid-soluble" have significant effects on char ignition temperatures of the coal samples. As we state above, a few studies have provided some basic understanding about the change of reactivity between raw coal and H-form coal, obtained by the analysis of Fourier transform (FT) Raman spectroscopy and TGA.[9,31] The char ignition temperatures of raw coal and H-form coal also confirm the similar conclusion on char reactivity. In the absence of a catalyst of H-from coal (sample 4), the reaction of char—O$_2$ was slow and took place on some specific (e. g., sp^3-rich or sp^2—sp^3 mixed) sites distributed throughout the char.[31]

An interesting observation arises from the comparison between raw coal and water-washed coal samples. The data in Figure 1 show that the average ignition temperatures of water-washed coal (sample 2) decrease about 30 °C compared to that of Loy Yang raw coal, although sample 2 has the lower content of AAEM species and no "water-soluble" AAEM species (mainly NaCl) compared to raw coal. The decrease in the ignition temperature was unlikely reflected because of the absence of NaCl, indicating that there would be other factors influencing the char ignition temperature. Some earlier literature has reported
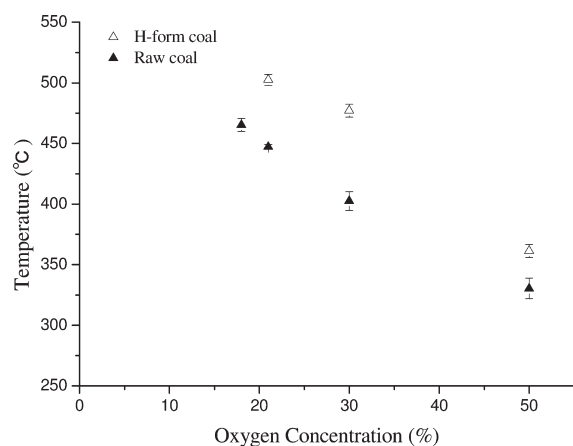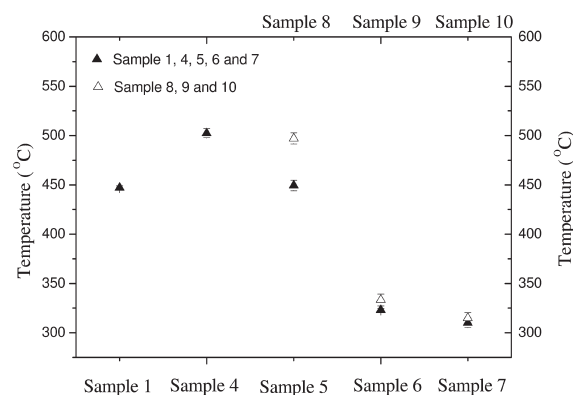
Figure 3. Average ignition temperatures of Loy Yang raw coal and H-form coal under O_2/N_2 combustion conditions. The error bars indicate one standard deviation.

Figure 4. Average ignition temperatures of Loy Yang brown coal samples of Na exchanged and NaCl loaded in air. Sample 1 was Loy Yang raw coal. Sample 4 was termed as the H-form coal sample and prepared by sequential washing raw coal in ultrapure water, ammonium acetate, and sulfuric acid. Samples 5, 6, and 7 were prepared by adding the H-form coal sample into the 0.05, 0.1, and 0.5 M solutions of sodium acetate, respectively. Samples 8, 9, and 10 were prepared by adding the H-form coal sample into the 0.05, 0.1, and 0.5 M solutions of sodium chloride, respectively. The error bars indicate one standard deviation. Note that the scale of the x axis is not linear.

that the properties of the char structure, including particle size, pore structures, and pore surface areas, can affect the ignition temperature of coal and char particles.[35] To gain a better understanding of lower ignition temperatures for water-washed coal, the BET surface area of four coal samples was measured and shown in Figure 2 as well. The BET surface area of water-washed coal (sample 2) shows a slight increase compared to that of raw coal. It was also estimated that some inorganic minerals in brown coal were removed, as well as water-soluble AAEM species, and the coal surface area was increased rather than decreased because of water leaching when raw coal was washed by ultrapure water.[34] A comparison of the data in Figures 1 and 2 reveals a close correspondence between the ignition temperature and the BET surface area ratios: the larger the pore surface areas of the char, the lower the char ignition temperature.[35] As shown in Figure 2, the coal samples 3 and 4 represent the equivalent value of the BET surface area but significantly different ignition temperatures were found (see Figure 1). This clearly indicates that the AAEM species as "acid-soluble" also play an important role on the char ignition of sample 3 particles.

3.2. Effect of the Oxygen Concentration on the Char Ignition Temperature. Figure 3 shows the average ignition temperature of Loy Yang raw coal and H-form coal as a function of the O_2 concentration during the combustion in O_2/N_2 mixtures. The average char ignition temperature of two coal samples decreases with an increasing O_2 concentration. Another very interesting observation takes place when H-form coal was employed to ignite in 18% O_2 + 82% N_2. The particles of H-form coal containing no AAEM species were found to gradually oxidize, but no obvious ignition was observed when heated at 10 K s^{-1} from ambient to 700 °C. However, particle ignition of raw coal in 18% O_2 + 82% N_2 could be observed visually and also measured by thermocouple readings. The average char ignition temperature of raw coal increased to 465 °C in 18% O_2 + 82% N_2 compared to 447 °C in air (21% O_2 + 79% N_2). As shown in Figures 1 and 3, the char ignition temperatures of H-form coal largely increased when AAEM species were removed from raw coal. It was found that AAEM species have a significant catalytic effect on the ignition behavior of brown coal mainly because of a significant amount of AAEM species,[36] while similar properties of both raw coal and H-form coal are listed in Table 1.

3.3. Effects of Sodium Acetate and Sodium Chloride on the Char Ignition Temperature. As was explained above, the

effects of NaCl on the char ignition behavior remain unclear. However, it is well-recognized that the gasification of chars with oxygen, carbon dioxide, and steam is catalyzed by small concentrations of alkali metals.[19] The mechanism of the catalytic behavior of AAEM species is generally postulated to consist of an oxidation–reduction cycle, in which oxygen is transferred to the carbon active sites via the catalytically active AAEM species.[21] There are two possible mechanisms for the significant release of solium chlorides during the devolatilization stage.[20] One is direct vaporization of NaCl from the coal particle, and another is suggested that the carboxylic acid group within the coal structure reacts with alkali chlorides to transform a relatively stable sodium species and release HCl.[1,20] It is clear that, the higher the temperature of the devolatilization process, the higher the proportion of NaCl is released from the coal substrate via direct evaporation rather than the reaction.[20,21] To gain a better understanding of the effect of sodium as carboxylates and as NaCl on the char ignition temperature, a set of Na-exchanged coals (samples 5, 6, and 7) and NaCl-loaded coals (samples 8, 9, and 10) were carried out for combustion experiments.

Figure 4 shows the average char ignition temperatures of Na-exchanged and NaCl-loaded coal samples in air conditions. It is clear that char ignition temperatures decrease with an increasing sodium content of coal samples. As shown in Table 2, the samples 5 and 8, prepared by 0.05 M solutions of sodium acetate and sodium chloride, respectively, have a close content of sodium but a different chemical form of sodium. The average char ignition temperature of Na-exchanged coal (sample 5) is 48 °C lower than that of NaCl-loaded coal (sample 8) in air. The experimental data indicate that the Na load into the H-from coal substrate as NaCl and as sodium carboxylates (−COONa) can have very different catalytic effects on the char ignition temperature. Sodium as carboxylates has a more significant effect on the ignition temperature of char particles than NaCl. This was further proven by 0.1 and 0.5 M Na-exchanged coals (samples 6 and 7), which have a much lower measured sodium content (see Table 2) but still slightly lower ignition temperature compared to those of 0.1 and
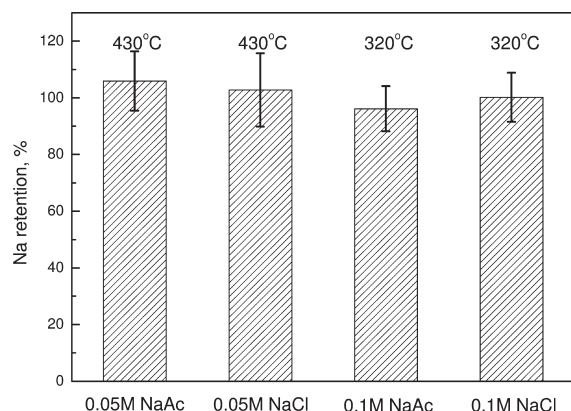
Figure 5. Na retention in unburned chars from NaCl-loaded coals and Na-exchanged coals. The samples of 0.05 M NaCl-loaded coal and 0.05 M Na-exchanged coal were heated in air at 10 K s^{-1} to 430 °C in a wire-mesh reactor before char ignition. The samples of 0.1 M NaCl-loaded coal and 0.1 M Na-exchanged coal were heated in air at 10 K s^{-1} to 320 °C in a wire-mesh reactor before char ignition. The error bars indicate one standard deviation. Note that the scale of the x axis is not linear.

0.5 M NaCl-loaded coals (samples 9 and 10), respectively. Alkali species in the form of carboxylates have proven to be less volatile than alkali chlorides in the stage of volatile release. For example, it was determined by kinetic simulation that approximately 33% NaCl is released in the volatile stage, whereas only a little amount of sodium as carboxylates is released during devolatilization of a similar Loy Yang brown coal.[20] For the Na-exchanged coal where sodium existed as sodium carboxylates, the devolatilization stage at low temperatures (e.g., 400−500 °C) results in a significant proportion of sodium being bonded to oxygen in the char matrix.[5]

A 5 °C decrease in the char ignition temperature of 0.05 M NaCl-loaded coal (sample 8) compared to that of H-form coal (sample 4) reveals that NaCl in 0.05 M NaCl-loaded coal has negligible catalytic effects on the ignition temperature of char, in which the sample was prepared H-from coal in 0.05 M NaCl solution. NaCl in coal/char was volatilized mainly as Na and Cl separately rather than as NaCl molecules.[1] Below 500 °C of the char ignition temperature of 0.05 M NaCl-loaded coal, Na in 0.05 M NaCl-loaded coal could not release completely.[1] The retention of Na in the char as whatever form is mostly not enough to transfer oxygen to the carbon active sites for the catalytic effect on the char ignition of 0.05 M NaCl-loaded coal. The lower the temperature, the less Na releases from the char.[1,20,21] The retention of Na in char from 0.1 M NaCl-loaded coal at about 330 °C should be much higher than that from 0.05 M NaCl-loaded coal at approximately 500 °C. To gain a better understanding of Na release from char before char ignition, the Na contents in unburned chars from NaCl-loaded coals and Na-exchanged coals were measured by ICP−AES. Figure 5 shows the retention of Na in unburned char, which was prepared by heating the two 0.05 M samples and two 0.1 M samples in air at 10 K s^{-1} to 430 and 320 °C, respectively, in a wire-mesh reactor. The negligible Na as both NaCl and carboxylates was released from char particles in air before char ignition at relatively low temperatures. The data in Figure 5 show that NaCl cannot directly evaporate from char during the devolatilization stage. However, a 150 °C decrease in the char ignition temperature of 0.1 M NaCl-loaded coal compared to that of 0.05 M NaCl-loaded coal indicates the remarkable catalytic effect of NaCl on the char

ignition temperature because the concentration of NaCl solution increased to 0.1 M. It is most likely proven by the presence of a minimum catalytic concentration of NaCl in char. NaCl can also act as excellent catalysts when the concentration of NaCl is high enough in coal/char. As impossible direct evaporation of NaCl from char at relatively low temperatures, the catalytic effects of NaCl are likely to react with the carboxylic acid groups within the coal structure, thus retaining Na and releasing HCl as follows:[20,37]

$$-(COOH) + NaCl \rightarrow -(COONa) + HCl \qquad (R1)$$

The lower char ignition temperature of 0.1 M NaCl-loaded coal compared to that of 0.05 M NaCl-loaded is most likely because of more −COONa species in char transformed from NaCl for 0.1 M NaCl-loaded coal.

Furthermore, an equivalent sodium content for 0.05 M Na-exchanged coal and raw coal was shown in Table 2, but the former only contained sodium carboxylates, while the latter mainly contained sodium, magnesium, and calcium. As mentioned above, sodium in raw coal as both carboxylates and "acid-soluble" can improve the char ignition. Because a low concentration of NaCl in raw coal does not significantly affect the char ignition temperature, a close char ignition temperature observed between 0.05 M Na-exchanged coal and raw coal indicates that sodium plays a more important catalytic effect on the char ignition behavior of Loy Yang brown coal than Ca and Mg.

4. CONCLUSION

The effects of chemical forms of AAEM species on the char ignition behavior of a Loy Yang brown coal were investigated in a wire-mesh reactor. The following main conclusions can be drawn: (1) AAEM species in Loy Yang raw coal as "ion-exchangeable" (mainly sodium as carboxylates) and as "acid-soluble" can both improve the char ignition temperature. In comparison to the average char ignition temperature of Loy Yang raw coal, the ignition temperature increases of 33 and 55 °C were observed for ammonium-acetate-washed coal (sample 3) and H-form coal (sample 4), respectively. (2) NaCl can also act as excellent catalysts when the concentration of NaCl is high enough in coal/char. A 150 °C decrease in the char ignition temperature of 0.1 M NaCl-loaded coal was measured in comparison to that of 0.05 M NaCl-loaded coal. (3) Sodium in coal as carboxylates (−COONa) and NaCl can both improve ignition characteristics of char samples, but carboxylates (−COONa) show a more significant catalytic effect on the average particle ignition temperature under our experimental conditions.

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