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Formation of Nitrogen-Containing Organic Aerosol during Combustion of High-Sulfur-Content Coal

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Supporting Information

ABSTRACT: Carbonaceous aerosols, including organic carbon aerosols and black carbon aerosols, are produced by the combustion of pulverized coal even under fuel-lean conditions. These carbonaceous aerosols can be particularly hazardous to human health. In this study, the chemical compositions and formation pathways of organic aerosols emitted during the combustion of high-sulfur-content coals were investigated. It was found that nitrogen-containing organic matter contains a significant proportion of organic aerosol mass from the combustion of high-sulfur-content coals, which is not the case for organic aerosols generated during the combustion of low-sulfur-content coals. The formation of organic aerosols was significantly enhanced when higher-sulfur-content coal was burned. A strong correlation between organic aerosol mass and the sulfate concentration was observed. It is proposed that acidic sulfate particles absorb the nitrogen-containing organic volatiles produced by coal pyrolysis onto the particle phase through acid−base neutralization reactions.

1. INTRODUCTION

Coal combustion is a primary source of electricity and heat generation in many parts of the world. It is also a major source of particulate matter in the atmosphere, particularly in developing countries.[1−3] The main component of the aerosols produced by a well-operated coal-fired boiler is inorganic ashes, such as SiO_2 and CaO.[4] However, organic matter can contribute a significant fraction of the aerosol mass, particularly when the coal combustor is poorly operated and is equipped with inefficient particle capture devices.[1] In many developing countries, such as China, coal combustion has been identified as one of the major sources of atmospheric organic aerosols.[3,5,6]

Organic aerosol (OA) comprises about 20−80% of the total fine particulate mass of atmospheric aerosols.[7] A significant fraction (up to 18%) of particulate organic matter is nitrogen-containing organic compounds (NOCs).[8,9] NOCs also account for a major fraction of the total nitrogen in atmospheric aerosols.[10,11] The deposition of nitrogen-containing organic aerosols is an essential part of the nitrogen cycle in the ecosystem.[12] One major identified source of nitrogen-containing compounds in OA is the burning of biomass.[13] Thus, it is possible that other types of combustion could also emit significant amounts of nitrogen-containing organic aerosols into the air.

Not many studies have focused on the characterization and formation pathways of organic aerosols from the combustion of pulverized coal. Zhang et al. measured the emission factors of particulate organic carbon and reported that they range from 0.3 to 17.1 mg (kg of coal)$^{-1}$.[2] Their characterization of organic aerosols showed that the main components are alkanes, aliphatic acids, aromatic acids, and polycyclic aromatic hydrocarbons (PAHs). Linak et al. reported thath the carbon content in coal fly ash particles was correlated with their toxicity.[14] Our previous study proposed that particulate organic matter originates from coal pyrolysis products.[15] These organics are mixed with inorganic particulate matter, which can protect the organics from complete oxidation even under fuel-lean combustion conditions.[1,16]

The combustion of high-sulfur-content coal usually produces larger amounts of air pollutants, including SO_2 and particulate matter.[17] However, such coals are still widely used in many developing countries. For instance, about 6.86% of the coal used in China has very high sulfur contents (>3% by mass).[18] Few studies have reported the formation of organic aerosols during the combustion of high-sulfur-content coals. In this work, using advanced aerosol mass spectrometry techniques, we characterized the emissions of nitrogen-containing organic aerosols during the combustion of coals with different sulfur contents. The formation mechanisms of these organic aerosols were also studied.

2. EXPERIMENTAL SECTION

2.1. Experimental Setup. Coal particles were combusted in a drop-tube furnace, which is widely used as a laboratory-scale coal combustor.[19,20] Figure 1 shows the experimental setup for coal combustion, which consisted of a Lindberg/Blue M model HTF55342C drop-tube furnace (Thermo Electron Corp., Waltham, MA) with a 5.72-cm-inner-diameter and 121.92-cm-long alumina tube connected to several aerosol instruments, including a high-resolution time-of-flight aerosol mass spectrometer (HR-Tof-AMS, Aerodyne Research, Billerica, MA) and a scanning mobility particle sizer (SMPS, TSI Inc., Shoreview, MN). Illinois No. 6 (ILL#6) coal and Powder River Basin (PRB) coal mixed with different ratios of elemental sulfur particles were separately combusted. The proximate and ultimate analyses of the ILL#6 coal and PRB coal used in this study are

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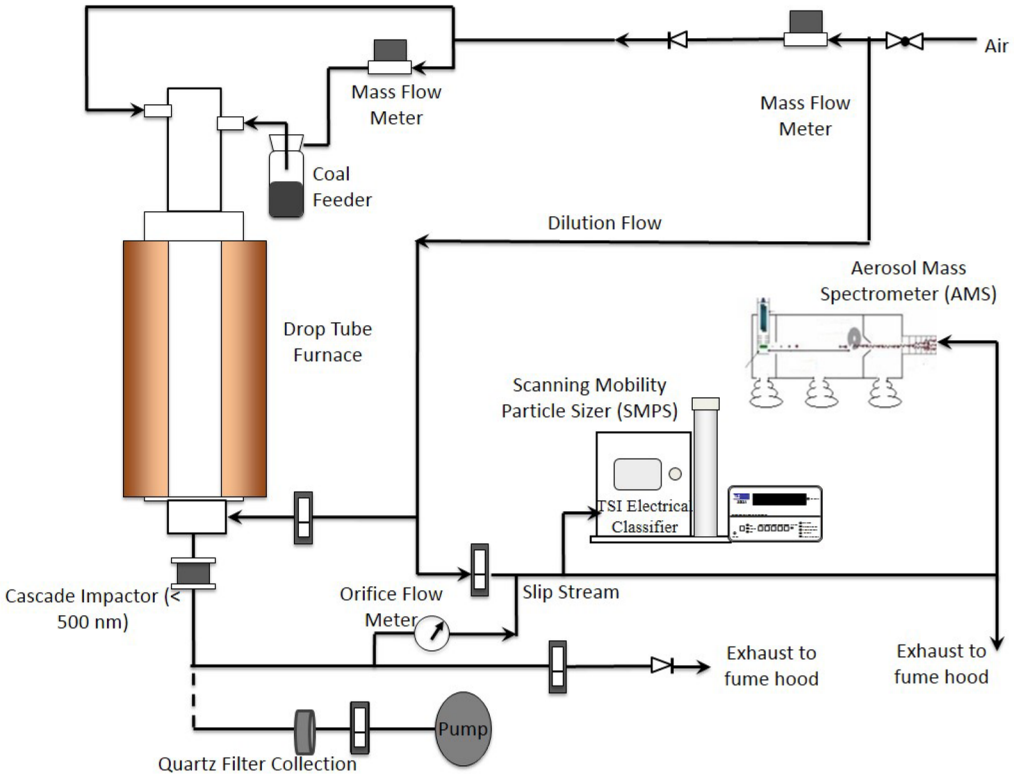

Figure 1. Schematic diagram of the experimental setup.

provided in Table 1. Pulverized coal particles (diameter < 50 μm) were introduced into the drop-tube furnace using a self-made coal feeder.[21]

Table 1. Proximate and Ultimate Analyses of Coals[41]

	ILL#6 coal	PRB coal
Proximate Analysis		
volatile matter[a] (wt %)	42	48.3
fixed carbon[a] (wt %)	48	42.9
ash[a] (wt %)	10	8.0
moisture[b] (wt %)	13.5	27.7
lower heating value[a] (MJ/kg)	29.6	28.0
Ultimate Analysis[a] (wt %)		
carbon	71	67.3
nitrogen	1.3	0.96
hydrogen	5	4.58
oxygen	9.13	19.9
sulfur	3.47	0.57
chlorine	0.11	0.01
fluorine		0.796

[a]Dry. [b]Air-dried.

The coal feed rate was fixed at 2.5 g/h. A total of 3 L/min (LPM) of air was fed into the furnace: 0.5 LPM of air went through the coal feeder to carry coal particles, and the remaining 2.5 LPM of air was directly fed into the drop-tube furnace. Thus, the fuel/air equivalence ratio was 0.083. The fuel/air equivalence ratio (ϕ) is defined as

$$\phi = \frac{m_{\text{fuel}}/m_{\text{oxidizer}}}{(m_{\text{fuel}}/m_{\text{oxidizer}})_{\text{st}}} \quad (1)$$

where m represents the mass and the subscript st indicates stoichiometric conditions. The temperature on the inside wall of the alumina tube was set at 1376 K. The adiabatic flame temperature for these combustion conditions is 1901 K. At the exit of the drop tube, the exhaust gas was diluted with 5 LPM of particle-free air. Then, the diluted exhaust gas was passed through a six-stage particle cascade impactor (Mark III, Pollution Control System Corp, Seattle, WA) to remove aerosol particles with diameters larger than 500 nm. After the impactor, a 0.5 LPM slipstream was mixed with a 3.8 LPM flow of particle-free air to achieve secondary dilution. The HR-Tof-AMS and SMPS were used to characterize chemical compositions and size distributions of fine particles in the diluted exhaust gas [dilution ratio = (8/3) × (4.3/0.5) = 23]. Assuming a particle density of 2 g/cm^3, mass concentrations were calculated based on the particle size distributions using the equation:

$$M = \rho V = \rho \int \frac{\pi}{6} D_p^{\,3} \frac{\mathrm{d}N}{\mathrm{d}(\log D_p)} \mathrm{d}D_p \quad (2)$$

where ρ is the particle density, V is the volume concentration of aerosol particles, and D_p is the particle diameter. $\mathrm{d}N/[\mathrm{d}(\log D_p)]$ is the particle size distribution, which is measured by the SMPS. Fine particles from coal combustion exhaust gas were also collected immediately after the impactor (dilution ratio = 2.7) for further offline analysis with (1) an ultraperformance liquid chromatograph coupled with an electrospray ion source and an ultrahigh-resolution time-of-flight mass spectrometer (UPLC/ESI-UHRTOFMS) and (2) an X-ray fluorescence (XRF) spectrometer (Epsilon 5 energy-dispersive XRF spectrometer, PANalytical, Almelo, The Netherlands).

2.2. High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-Tof-AMS). A detailed description of the HR-Tof-AMS instrument can be found elsewhere in the literature.[22−25] Briefly, aerosol particles pass through an aerodynamic focusing lens that makes most of the particles move in a narrow beam. The particle size can be obtained by measuring the velocity of the particles at the exit of the aerodynamic lens. The particles are then collected on a hot vaporizer (600 °C). Organic matter and some inorganic matter are evaporated and then immediately ionized by electron impact. The produced ions are introduced into a time-of-flight mass spectrometer, which can accurately determine the mass-to-charge ratios for these ions.

2.3. Analysis Using UPLC/ESI-UHR-TOFMS. Aerosol samples were collected on Teflon filters (47-mm diameter, 1.0-μm pore size, Teflo membrane, PALL Life Sciences). The filter samples, including a

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filter blank, were extracted in 5 mL of methanol by 40 min of sonication. The extract was blown dry under a gentle N_2 stream (without added heat) to 0.5 mL of solution, which was then analyzed on a high-performance liquid chromatograph (HPLC) coupled with an electrospray ion source (ESI) and an ultrahigh-resolution time-of-flight mass spectrometer (HPLC/ESI-UHR-TOFMS). The detailed HPLC operation procedure can be found in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Submicrometer Aerosol Emissions from the Combustion of a Low-Sulfur Content Coal and a High-Sulfur-Content Coal. PRB coal is a low-sulfur-content subbituminous coal (its sulfur content is 0.57%) that has commonly been used in the United States. Submicrometer aerosol emissions from the combustion of PRB coal were characterized in great detail in our previous works[1,15,26] and did not show the presence of significant amounts of nitrogen-containing organic species. However, there are significant differences between the aerosol emissions from the combustion of low-sulfur content coal and those from the combustion of high-sulfur-content coal. Figure 2A compares the particle size distributions of the aerosols from the combustion of PRB coal, a low-sulfur-content coal, and Illinois No. 6 (ILL#6) coal, a high-sulfur-content coal with a sulfur content of 3.47%. The combustion of ILL#6 coal produced a higher mass concentration (~478 $\mu g/m^3$) of submicrometer aerosols than the combustion of PRB coal (~246 $\mu g/m^3$). It was at least partly due to the formation of particulate sulfates or sulfuric acid. During the burning of coal, most of the sulfur in the coal is oxidized to SO_2. A small fraction of SO_2 is further oxidized to SO_3, which can condense on existing coal fly ash aerosols and react with metal oxide to form sulfate. Alternatively, it can react with water vapor and form droplets of sulfuric acid. Thus, the combustion of a higher-sulfur-content coal, such as ILL#6 coal, usually produces higher mass concentrations of submicrometer particles. An aerosol mass spectrometer was used to characterize the emissions of organic aerosols from the combustion of these two coals. Surprisingly, Figure 2B shows that the combustion of ILL#6 coal produced a much higher mass concentration of organic aerosols than the combustion of PRB coal. Moreover, the differences in the AMS spectra of these aerosols also showed that the organic aerosols emitted during the combustion of these two coals had very different chemical compositions. Notably, the main difference between ILL#6 coal and PRB coal is their sulfur content. Thus, it is likely that sulfur content could affect organic aerosol emissions from coal combustion, which needs to be further investigated.

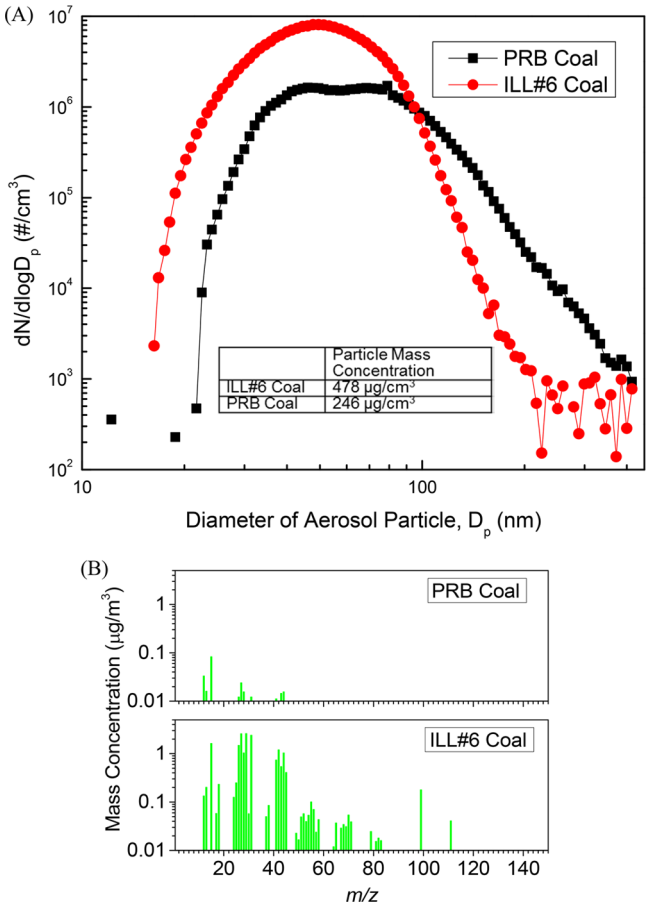

Figure 2. (A) Size distributions and calculated particle mass concentrations and (B) AMS organic mass spectra of submicrometer aerosols from the combustion of ILL#6 coal and PRB coal. For panel A, note that N is the particle number concentration and D_p is the particle diameter; thus, $dN/[d(\log D_p)]$ is the number size distribution of aerosol particles.

3.2. Characterization of Nitrogen-Containing Organic Aerosols from the Combustion of ILL#6 Coal. High-resolution AMS spectra can provide more detailed information on the chemical compositions of organic aerosols. Moreover, it is well accepted that aerosol mass spectrometry can measure organic mass quantitatively.[27] Figure 3A shows the high-resolution AMS organic mass spectrum for the fine particulate matter from the combustion of ILL#6 coal. A large fraction of the peaks, such as those at m/z 30, 42, 43, and 44, belong to CHN ($C_xH_yN_z^+$) groups, clearly demonstrating the presence of nitrogen-containing organic species. The low signal intensities at m/z 55 and 57 indicate low concentrations of hydrocarbon-like fragments. To verify the molecular formulas of these important peaks, the high-resolution peak patterns were analyzed (see Figure 3B). The unit mass resolution (UMR) peak at m/z 30 is actually composed of two peaks, corresponding to CH_2O^+ and CH_4N^+. $C_2H_6^+$ does not contribute much to this UMR peak, because $C_2H_6^+$ (m/z 30.047) is away from the center of the peak. The UMR peak at m/z 42 is composed of peaks for $C_2H_2O^+$, $C_2H_4N^+$, and $C_3H_6^+$. $C_2H_4N^+$ should contribute the largest fraction, because the exact mass of $C_2H_4N^+$ is located at the center of the UMR peak at m/z 42. Similarly, the UMR peak at m/z 43 is composed of peaks corresponding to $C_2H_3O^+$, $C_2H_5N^+$, and $C_3H_7^+$, where $C_2H_4N^+$ should be the main peak. The peak at m/z 44 is usually considered to represent CO_2^+, which is an indicator of oxygenated organic aerosol.[22] However, Figure 3B shows that m/z 44 corresponds to CO_2^+, $C_2H_4O^+$, $C_2H_6N^+$, and $C_3H_8^+$, among which $C_2H_6N^+$ is the dominant peak at m/z 44. CO_2^+ makes a much smaller contribution to this UMR peak. The contributions from $C_2H_4O^+$ and $C_3H_8^+$ are not significant, because both of these species are away from the centers of the two peaks at m/z 44. Elemental ratios are provided in Figure S1. The N/C ratio is about 0.048, which is even much higher than the corresponding value for the aerosols generated by burning biomass.[28]

3.3. Formation Mechanism of Nitrogen-Containing Organic Aerosols Produced during the Combustion of High-Sulfur-Content Coal. As mentioned previously, there were large differences between the aerosol emissions from the combustion of PRB coal, a low-sulfur-content coal, and from

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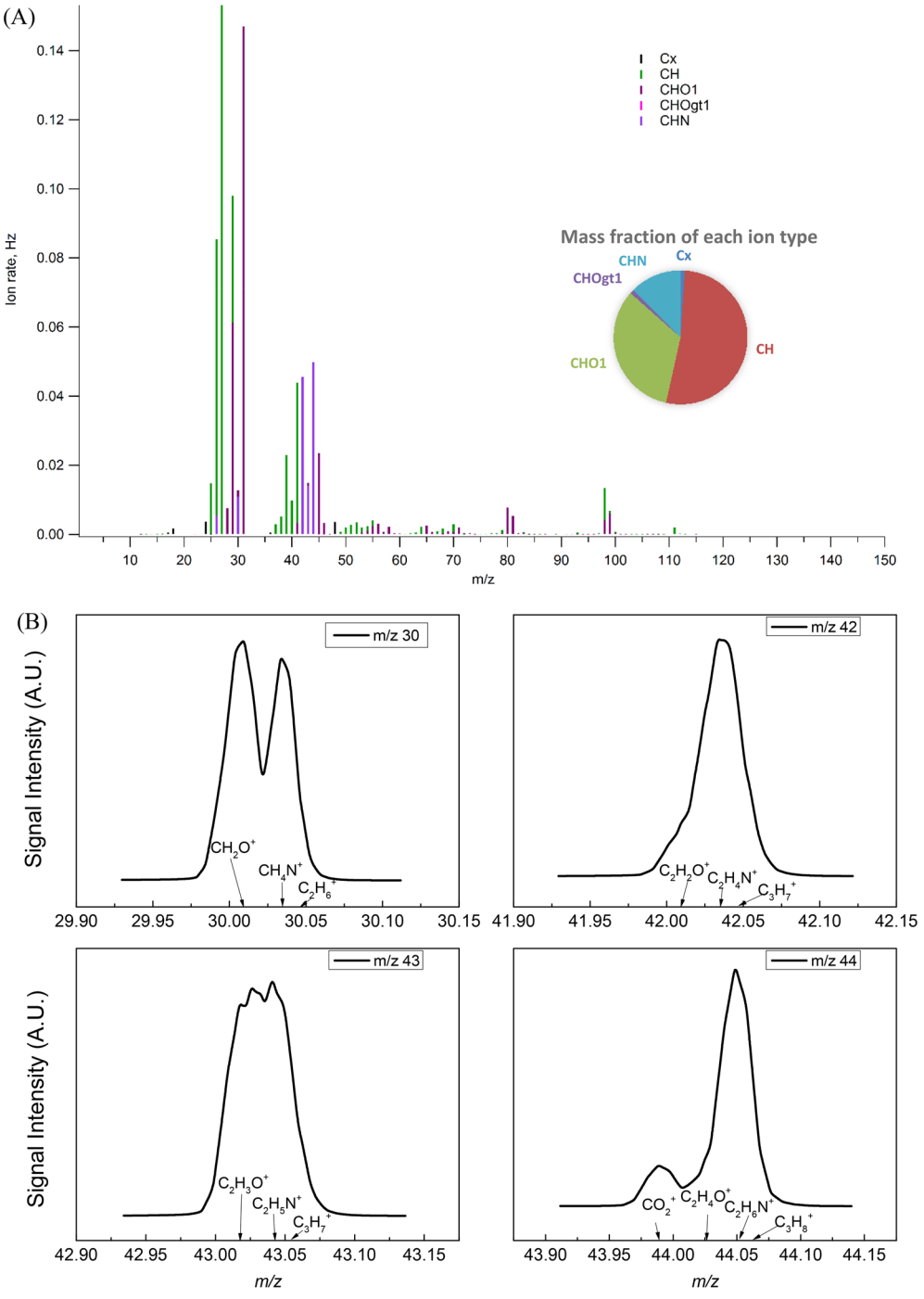

Figure 3. (A) AMS mass spectrum and (B) high-resolution peak patterns for fine organic particulate matter from the combustion of ILL#6 coal, a high-sulfur-content coal. In panel A, "gt" means "greater than", so that CHOgt1 represents a group of high-resolution ions, including CO_2^{2+}, CO_2^+, $^{13}CO_2^+$, $CH_2O_2^+$, $C_3O_2^+$, $C_8H_5O_3^+$, $C_8H_7O_4^+$, and $C_{16}H_{23}O_4^+$. The mass fractions of C_x, CH, CHO1, CHOgt1, and CHN are 1%, 52.5%, 32.5%, 1%, and 13% respecively. (Combustion coniditions: temperature, 1376 K; air flow rate, 3 LPM; fuel/air equivalence ratio, 0.083.)

the combustion of Illinois No. 6 (ILL#6) coal, a high-sulfur-content coal. The combustion of ILL#6 coal produced much higher mass concentrations of total submicrometer aerosols and organic aerosols than the combustion of PRB coal. In particular, the combustion of ILL#6 coal produced a significant fraction of nitrogen-containing organic aerosols, whereas that of PRB coal did not. Therefore, it is crucial to study the effects of the sulfur content of coals on the organic aerosol emissions. To change the sulfur content in the coal used in this work, elemental sulfur particles were mixed with PRB coal. Then, the coal mixtures were combusted in the drop-tube furnace. Notably, the natural forms of sulfur in coal are not elemental sulfur. The forms of sulfur present in coal include (1) pyrites (FeS_2), (2) organic sulfur and (3) some minor fraction of sulfate. It is generally considered that organic sulfur in coal is present in four forms: (1) mercaptan or thiol, (2) sulfide or thioether, (3) disulfide and (4) aromatic systems containing the thiophene ring. Gluskoter and Simon reported that the mean ratio of pyritic to organic sulfur is about 1.56 for all types of Illinois coal.[29] For

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Illinois #6 coal, the organic sulfur content ranges from 0.4% to 3% of the total coal mass.

During the burning of coal, most sulfur from various forms is oxidized to SO_2, some of which is then converted into sulfate particles. Thus, the forms of sulfur in coal might not be important to the formation of sulfate aerosol,[30] and the addition of elemental sulfur to coal should be an appropriate method for studying how the sulfur content in coal affects aerosol formation. Figure 4 shows the characteristics of the

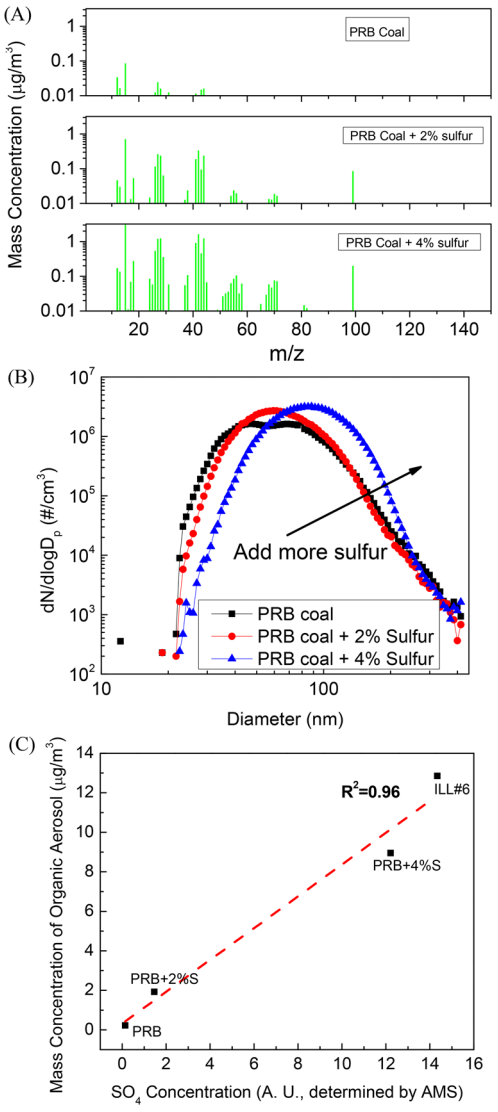

Figure 4. (A) AMS organic spectra, (B) size distributions, and (C) correlation between the concentrations of SO_4 (from sulfate) and organic matter of submicrometer particles from the combustion of PRB coals mixed with different contents of sulfur. (Combustion coniditions: temperature, 1376 K; air flow rate, 3 LPM; fuel/air equivalence ratio, 0.083.)

submicrometer particles generated by the combustion of PRB coals mixed with different mass contents of elemental sulfur (0%, 2%, and 4%). When more elemental sulfur was mixed with the PRB coal, the organic aerosol formation was significantly enhanced (Figure 4A), which suggests that sulfur content does play a role in organic aerosol formation. As for the combustion of ILL#6 coal, the high-resolution AMS spectrum of the aerosol from the combustion of PRB coal plus 4% sulfur also shows the presence of a large amount of nitrogen-containing organic peaks (Figure S2). This finding that the formation of nitrogen-containing organic aerosol is actually related to the sulfur content in coal is very surprising.

Figure 4B shows that higher concentrations of submicrometer particles were produced when the elemental sulfur content in coal was increased. The calculated particle mass concentration was increased from 246 to 679 $\mu g/m^3$ when the elemental sulfur content was increased from 0% to 4% (Figure S3A). Notably, the particle size distribution of the aerosol from ILL#6 coal (Figure 2A) peaked at smaller size than did that of the aerosol from PRB coal plus sulfur. The difference might due to the form of sulfur. In the ILL#6 coal, sulfur is in the organic form, whereas elemental sulfur particles (sulfur powder, Sigma-Aldrich Inc.) were mixed with the PRB coal. Thus, during combustion, organic sulfur might be released and oxidized much more rapidly than elemental sulfur. The fast formation of sulfuric acid might favor nucleation rather than condensation. XRF spectroscopy was used to analyze the elemental compositions of the submicrometer aerosols and showed that the submicrometer aerosols from the combustion of higher-sulfur-content coal also contained more sulfur (Figure S3B). Therefore, the combustion of higher-sulfur-content coal did produce a higher concentration of submicrometer aerosols, probably as a result of the enhanced formation of sulfate particles. A strong correlation, R^2 = 0.96, between the concentrations of organic aerosol and SO_4^+ (from sulfate) was found (Figure 4C). Figure S3C also shows a strong correlation between organic aerosol and particulate sulfur that was quantitatively determined by XRF spectroscopy. The correlation provides firm evidence that sulfates play a critical role in the formation of organic aerosols and that a large fraction of these particulate organic compounds are nitrogen-containing species.

In our previous study, we proposed a mechanism for the the formation of organic aerosol during coal combustion: Coal pyrolysis produces large amounts of organic volatiles, most of which are completely oxidized to CO_2 and H_2O. A small fraction of these organic volatiles can be trapped in inorganic particles, which can protect them from complete oxidation and finally form particulate organic emissions. All coals contain certain amounts of fuel nitrogen. For example, fuel nitrogen accounts for 1.0% and 1.3% of the total coal dry mass for PRB coal and ILL#6 coal, respectively. Nitrogen is mainly bound to organics in coal. It is well-known that those nitrogen atoms are connected to aromatic clusters in coal through C−N bonds.[31,32] Pyrrolic, pyridinic, and quaternary nitrogen species typically account for 50−80%, 20−40%, and 0−20%, respectively, of the total nitrogen mass in coal.[33,34] Aromatic amine might also contribute a small fraction of coal nitrogen. For ILL#6 coal, pyrrolic, pyridinic, and quaternary nitrogen species account for 62%, 26%, and 12%, respectively, of the total nitrogen.[35] During coal devolatilization, fuel nitrogen can either be released as organic volatiles or remain in char particles. The ratio of these two fates depends on the coal type and temperature.[36] Almost all of the nitrogen-containing organic volatiles are aromatic compounds.[37]

Therefore, coal pyrolysis can produce many nitrogen-containing organic volatiles.[38,39] The C−N group has basic properties, and some sulfate particles, such as iron sulfate, are acidic. These sulfate species in the aerosols from coal combustion might help trap nitrogen-containing organic volatiles through acid−base neutralization reactions. Therefore,

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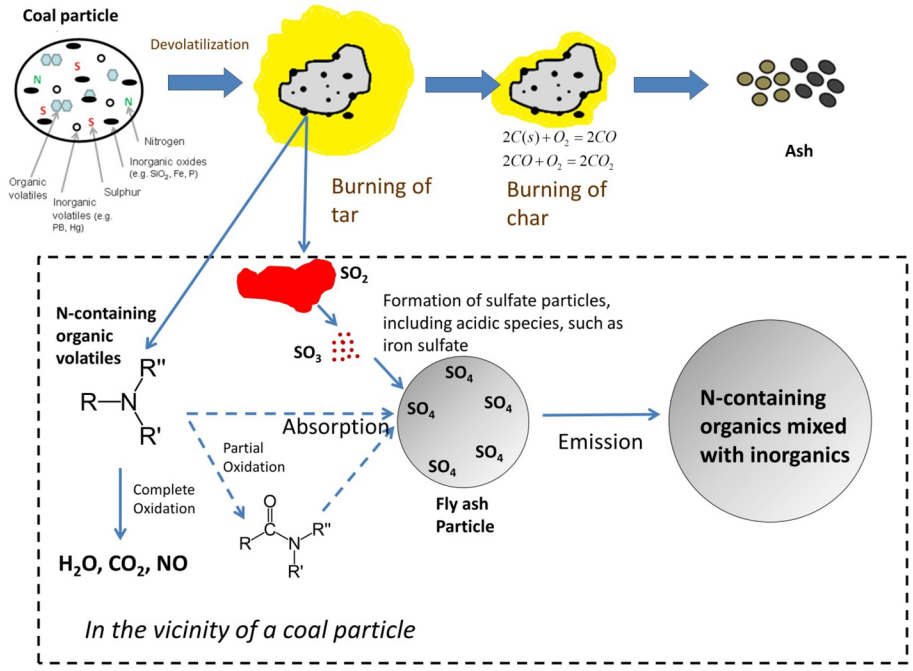

Figure 5. Formation mechanism of particulate nitrogen-containing organic matter during the combustion high-sulfur-content coal.

the nitrogen-containing organic compounds identified in this study are probably organic salts. Figure 5 summarizes the proposed mechanism for the formation of nitrogen-containing particulate organic compounds during the combustion of high-sulfur-content coal.

To identify the molecular formulas of the organic compounds, fine particulate matter from the combustion of PRB coal plus 4% elemental sulfur was collected on a Telfon filter and then extracted with methanol. The extract was analyzed by HPLC/ESI-UHR-TOFMS (see detailed procedures in the Supporting Information). Figure S4 shows the total ion chromatogram obtained in positive ESI mode. Most of signals came out after 40 min, indicating that the corresponding compounds are very hydrophobic. The major peaks in Figure S4 are listed in Table S1. Using accurate mass and isotopic patterns, the ion formula for each peak was calculated. All major peaks were identified as nitrogen-containing organic ions, thus confirming the findings from the AMS results. Most of these ions also contain O atoms, suggesting that they are oxygenated organic compounds. Notably, $C_{20}H_{30}N$ and $C_{27}H_{42}N$ were identified. These are amine species, as only C, H, and N are present in their molecular formulas, and their C/H ratios are very high, indicating the presence of aromatic rings in their structures. It is very possible these two compounds are aromatic amines.

3.4. Implications. This study reported a new source of nitrogen-containing organic aerosols: the combustion of high-sulfur-content coals. Nitrogen-containing organic matter was found to comprise a large fraction of total organic aerosol emissions from the combustion of high-sulfur-content coal. These organic species could be very toxic, given that some of their structures might be similar to those of aromatic amines, a type of known toxic substances.[40] Many developing countries are still using high-sulfur-content coals. For example, about 6.86% of the coal used in China has sulfur contents greater than 3%.[18] Therefore, the combustion of high-sulfur-content coals might produce a certain amount of these nitrogen-containing organic aerosols in the atmosphere. More studies will be needed to quantify the contribution of nitrogen-containing organic aerosols from the combustion of high-sulfur-content coal.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.7b02273.

More detailed information on the experimental setup and additional experimental data (PDF)

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Notes

The authors declare no competing financial interest.

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