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Mechanisms on the size partitioning of sodium in particulate matter from pulverized coal combustion

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ABSTRACT

Particulate matter (PM) generated from pulverized coal combustion is influenced by a process of vaporization, nucleation and condensation/reaction of semi-volatile minerals. The objective of the work is to identify the controlling mechanism of the enrichment of volatile sodium (Na). Three representative kinds of coal with different rank and mineral content, Zhundong lignite, Hami lignite and high-ash-fusion (HAF) bituminous, were burned in a 25 kW self-sustained pulverized coal combustor. Zhundong lignite, possessing medium rank among the three coal samples, exhibits the highest formation ability of ultrafine $PM_{0.2}$, indicating a prominent effect of mineral content over that of coal rank on PM formation. The size partitioning behavior of sodium is affected by the molar ratio $Na_2O/(SiO_2+Al_2O_3)$ instead of the absolute Na content. With this ratio increasing from 0.27 (HAF bituminous) to 20 (Zhundong lignite), the gas-to-particle conversion of Na transits from a surface-reaction controlled process to a nucleation-condensation/coagulation dominated pathway. The Na partitioning behavior of Zhundong lignite is then quantitatively interpreted by a population-balance-based theoretical approach. The model reveals the details on the competing processes of homogeneous nucleation and vapor condensation, resulting in that the simulated final particle mass size distribution exhibits reasonable agreement with the experimental result. The model has also successfully reproduced the d_p^0 dependence of Na fraction in the ultrafine size regime from a process of homogeneous nucleation under the decreasing gas temperature from 1420 to 1270 K.

1. Introduction

The airborne particulate matter (PM) arises as an urgent environmental issue which attracts intensive attention in developing countries such as China and India, and pulverized coal combustion is one of the major source contributions [1–4]. The inhalable particulates become even more hazardous because of the toxic metals enriched in PMs [5]. Dozens of works have been dedicated to the formation of carbonaceous/mineral PMs and toxic matter enrichment processes during pulverized coal combustion [5–17]. In the high-temperature combustion environment, a process of vaporization, nucleation, condensation (known as heterogeneous nucleation) and reaction of minerals has been recognized to play a significant role in the formation of ultrafine particulates as well as the concentration of semi-volatile species in PMs [5–14].

The vaporization and nucleation process, which is more prevalent in the submicron range, causes a size-dependent partitioning of semi-volatile species across the whole particle size distribution (PSD) of PMs. It has been reported that the mass fraction of semi-volatile species in the fine PM exhibits d_p^{-1}, d_p^{-2} or even d_p^0 dependence, respectively, because of the different mechanisms of gas-to-particle conversion [5,18]. For instance, as far as the easily volatilized arsenic (As), selenium (Se) and antimony (Sb) are concerned, the d_p^{-1} dependence was usually found in the literature [10–12,18], which can be explicable by a surface-reaction controlled mechanism. However, an exception with a d_p^{-2} dependence was also reported for As and Se [12,13], implying a process of direct vapor condensation. These diverse behaviors may be related to coal properties, combustion conditions, etc. Therefore, further fundamental studies are needed to cover different ranks of coal samples.

The dynamic behavior of sodium (Na), among the semi-volatile elements from coal, is consistently a special concern, particularly for the reason that the use of low-rank coal is inevitably increased in recent years [19]. During coal combustion sodium is vaporized in devolatilization stage as well as in char burning-out stage [20–24]. The subsequent gas-to-particle conversion of the released sodium significantly contributes to ultrafine PM

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Nomenclature

D	diffusion coefficient of gas monomer, m^2/s
d_p	particle diameter, m
g^*	number of monomers in nascent particles, #
I_{cur}	particle current, #/(m^3•s)
$I(V_p^*)$	homogeneous nucleation rate of nascent particle with critical volume V_p^*, #/(m^3•s)
Kn	Knudsen number
K_p	chemical equilibrium constant
kx_s	reaction flux at the particle surface, #/(m^2•s)
m_1	mass of one gas monomer, kg
N_1	number concentration of gas monomer, #/m^3
N_{1s}	saturated surface number concentration of gas monomer, #/m^3
t	residence time in the furnace, s
V_p	particle volume, m^3
x_s	surface mole fraction of semi-volatile species
Y_1	mass fraction of Na species in gas monomer
Y_i	mass fraction of species i in particles
$\delta(V_p - V_p^*)$	delta function
ρ_p	particle density, kg/m^3

formation and fouling aggravation problems [14,25–27]. Previous studies usually reported a d_p^{-2} dependence of Na [18,28–30], which indicated a heterogeneous-condensation-dominated conversion pathway. Moreover, Takuwa et al. found a d_p^0 dependence in the ultrafine PMs (e.g., smaller than $PM_{0.3}$) from the combustion of a sodium rich coal [30]. More recently, it was further approved that the sodium-rich Zhundong lignite exhibits a much larger formation ability of $PM_{0.1}$ with highly enriched Na content, in contrast to normal bituminous coals [31]. These experimental findings suggest that, under certain combustion circumstances, the gaseous Na species should go through a pathway of homogeneous nucleation followed by coagulation growth. A justification of the proposed mechanism, which initiates from qualitative observations in the preliminary studies, calls for more extended PSD data on the ultrafine mode PM, as well as a detailed dynamic modeling of this complicated process.

When theoretical approaches are concerned, it is noteworthy that the nucleation–coagulation mechanism of ultrafine PM is quite similar to that existing in flame synthesis of nanoparticles [32,33]. Therefore, the *population balance model* (PBM) can be helpful to quantitatively interpret the size partitioning of Na during the combustion of low-rank coals. This method has been applied to simulate soot formation and char particle evolution during coal combustion [34–36]. Different from nanoaerosol synthesis system, significant amount of micron-sized ash particle is also formed *via* mineral coalescence and fragmentation during pulverized coal combustion [16,17]. The coarse PMs provide a large number of sites for gas–solid surface reaction and vapor condensation, leading to the aforementioned d_p^{-1} and d_p^{-2} dependences. Hence, a model based on the PBM framework, covering much broader particle size range and multiple compositions, is expected to reveal the crucial details on the Na conversion process as well as its effect on PM evolution. Such evolution systems containing alkali–sulfur–chlorine have been investigated in the PBM model and further validated by bench-scale experiments [37,38]. The applicability of nucleation theory and the formation of sulphate aerosols are drawn from these studies, with further kinetic details revealed in [39,40]. However, it is still challenging to apply the PBM theories to match or interpret the field data of Na partitioning in coal combustion.

The objective of the work is to divulge the controlling mechanism of the enrichment of volatile sodium (Na), during the combustion of coal samples with variations in rank and mineral content. We investigated the high-ash-fusion (HAF) bituminous, the Zhundong lignite, and a lower-rank Hami lignite in the 25 kW self-sustained combustor. We compared the PM formation abilities and Na partitioning behaviors among the several coal samples. We identified the key factor, molar ratio of $Na_2O/(SiO_2+Al_2O_3)$, in determining the Na conversion mechanisms. Inspired by the experimental results, we further investigated the case of Zhundong lignite, in which homogeneous nucleation of Na was thoroughly described by a multi-compositional PBM model.

Table 1
Proximate and ultimate analyses of the coal samples.

	Zhundong lignite	Hami lignite	HAF bituminous
Proximate analysis (wt%, dry basis)			
Volatile matter	30.58	33.00	24.10
Ash	5.88	26.60	20.30
Fixed carbon	63.54	40.40	55.50
HHV (MJ/kg, dry basis)	28.83	20.74	25.20
Ultimate analysis (wt%, dry and ash free basis)			
C	71.60	60.28	82.50
H	3.16	2.55	4.39
N	0.78	1.08	0.89
S_{total}	0.52	0.41	0.93
Cl	0.06	0.12	0.02
O (by difference)	23.85	35.52	11.27

Table 2
Ash compositions of the coal samples.

Ash composition (wt%)	Zhundong lignite	Hami lignite	HAF bituminous
SiO_2	28.53	57.04	56.80
Al_2O_3	3.27	14.12	26.10
Fe_2O_3	4.01	4.80	6.98
CaO	32.78	5.60	2.68
MgO	2.88	0.91	0.70
SO_3	21.47	3.61	2.10
K_2O	0.57	1.79	1.02
Na_2O	6.19	1.92	0.20
P_2O_5	ND[a]	0.34	0.48
TiO_2	0.30	1.01	1.20

[a] ND – Not Detected.

Table 3
The water soluble and organically-bounded portions of mineral elements.

wt%	Zhundong lignite	Hami lignite	HAF bituminous
Na	93.3	65.2	18.5
Ca	69	65.3	81.2
Mg	80.8	77.4	69.8
Fe	0.01	0	0
K	24.2	6.2	1.5
S	27.3	16.3	9.7
Si	0.6	0.3	0.1

2. Experimental

2.1. Coal properties

Three coal samples, Zhundong lignite, Hami lignite and HAF bituminous, were investigated. The coal properties are listed in Tables 1 and 2. The chemical fractionation results are listed in Table 3. In Zhundong lignite, more than 90% of Na are either water soluble or organically-bounded, as compared to 18.5% in HAF bituminous. The several coal samples also exhibit distinct differences in coal rank, as shown in the coalification diagram Fig. 1a. Considering the vast differences in mineral contents and occurrence modes, the coal samples are chosen in such a manner aiming at