

Key Factor Identification for PM_{2.5} Formation in China: The Role of NH₃ in Atmospheric New Particle Formation

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Abstract—PM_{2.5} (particulate matters with aerodynamic diameter smaller than 2.5 μm) pollutions with adverse effect on human health and global climate has occurred frequently and caused widely concern in China. The main chemical compositions in PM_{2.5}, *i.e.*, SO₄²⁻, NO₃⁻, NH₄⁺ and organic compounds, are converted from SO₂, NO_x, NH₃ and volatile organic compounds (VOCs), respectively. In order to find out the key factor for PM_{2.5} generations to help to relieve the air pollution, formation characteristics of PM_{2.5} is investigated. A property of electric neutrality of PM_{2.5} is proposed according to the least-energy principle and verified through electricity-charge calculation in this paper. As the only cation in the main chemical compositions of PM_{2.5}, NH₄⁺ is vital for anions (such as SO₄²⁻ and NO₃⁻) to aggregate together and is a key factor for PM_{2.5} formations. The major source of PM_{2.5} is secondary new particulate formations (NPF) in atmosphere. Herein, to identify the role of NH₃ in atmospheric NPF, a new kinetic model, combining the oxidation of SO₂/NO₂ in SO₂/NO₂/NH₃/H₂O/air system and the aggregation of clusters in H₂SO₄/HNO₃/NH₃/VOC system, is established based on gas-kinetic theory. From the modeling analysis, it is found that NH₃ can enhance PM_{2.5} formations not only by facilitating conversions of SO₂ and NO₂ indirectly, but also by promoting aggregations of H₂SO₄, HNO₃, NH₃ and VOCs directly. And the enhancement of conversion fractions for SO₂ and NO₂ during oxidation processes is the major effect of NH₃ on PM_{2.5} formations. In addition, the presence of NH₃ can particularly promote the contribution of HNO₃ in NPF process. Therefore, in order to relieve PM_{2.5} pollutions in China, the control strategies for NH₃ as current restrictions on SO₂ and NO_x are suggested to be enhanced by government, such as decreasing the amount of nitrogenous fertilizer utilization, or changing the fertilizing environment from dry condition to wet condition.

Keywords—PM_{2.5}, NH₃, new particle formation, modeling studies, haze mitigation

I. INTRODUCTION

Severe haze pollutions featured by long-lasting time, extensive coverage, and high particle concentration occurs frequently in China [1,2]. As the dominant pollutant, particulate matters smaller than 2.5 μm (PM_{2.5}) has been extensively reported to adversely affect human health and global climate [3]. The major source of PM_{2.5} is secondary new particulate formations (NPF) with main precursors, SO₂, NO₂, NH₃ and OC [4,5,6].

In addition to heavy emissions of SO₂, NO₂ and OC due to rapid industrial developments and urbanizations in China, NH₃ emissions mainly coming from agriculture are also non-negligible. China is one of the largest agriculture country in the world, whose NH₃ emissions have been increased since 1978 and reached about 10-16 Tg yr⁻¹ in 2012, occupying 23% of global NH₃ budget [7,8,9]. It is found that fertilizer application and livestock manure are the two main sources, counting 80-90% of total NH₃ emissions in China [7,9]. The massive emission of NH₃ leads to a much higher NH₃ concentration in China than the typical level in troposphere (0.1-10 ppb) [10]. For example, the NH₃ level in urban sites of China, *e.g.*, Beijing and Xi'an, is in the range of 0.7-85.1 ppb, with an annual average of about 20 ppb, in 2008-2009 [11,12]. Moreover, NH₃ is the only alkaline inorganic gas with high reactive ability and solubility in the four major precursors of PM_{2.5}, playing a key role in aerosol particulates by neutralizing H₂SO₄ and HNO₃ [9,11]. Thus, it is urgent to understand the role of NH₃ in NPF for effective haze mitigations, especially in China with serious haze pollutions and high NH₃ levels in atmosphere.

In general, NPF occurs in two distinct stages, *i.e.*, nucleation to form a critical nucleus, and subsequent growth to a larger size (>2~3nm) [13]. During the NPF process, H₂SO₄ has been identified as the most prominent atmospheric nucleation

agent, and H₂O/H₂SO₄ binary nucleation theory has been widely used [2,13,14]. Previous studies suggest that the presence of NH₃ increases the nucleation rate significantly in H₂O/H₂SO₄ binary system. Theoretically, it was found that the interaction of NH₃ and H₂SO₄ considerably decreases the vapor pressure of H₂SO₄, and facilitates the formation of ammonium sulfate or bisulfate salts [14]. Experimentally, Benson et al. (2011) showed that NH₃ enhances atmospheric H₂SO₄ aerosol nucleation by 1-10 times under relevant atmospheric concentrations, *i.e.*, H₂SO₄ at 10⁶–10⁷ cm⁻³ and NH₃ at 0.08–20 ppb [15]. Kirkby et al. (2011) found atmospheric NH₃ at ppt level sufficiently contributes to nuclei formation by accelerating the nucleation of sulfuric acid particles [16]. In addition, Benner et al. (1992) investigated the effect of NH₃ on oxidation of SO₂ in SO₂/H₂O, suggesting the significant enhancement of the conversion of SO₂ from 1-3% to 81% with RH of 60% when NH₃ ranging from 0 to 1ppm [17].

The previous studies show the enhancing effect of NH₃ on NPF in H₂O/H₂SO₄ binary system and lay the foundation for further researches. However, for the recent haze occurrence in China, PM_{2.5} is formed under complicated multi-pollutant atmosphere. Measurements show that SO₄²⁻, NO₃⁻, NH₄⁺ and OC are the main components (total mass proportion >90%) in PM_{2.5}, due to the high levels of precursors [1,18]. According to a field measurement launched by the Program of Regional Integrated Experiments on Air Quality over Pearl River Delta of China 2004 (PRIDE-PRD2004), the concentrations of O₃, SO₂, NO₂ and NH₃ are respectively 68 (179), 37 (187), 44 (144) and 13 (49) [mean value (maximum value), ppb] [18], which are much higher than in other places around the world, *e.g.*, 10 and 6 ppb as mean concentrations for SO₂ and NH₃ in New York of U.S.A, and 2, 5 and 12 ppb as mean concentrations of SO₂, NO₂ and NH₃ in Rampur of India [19]. Therefore, due to the strongly-oxidizing and multi-pollutant atmosphere, NPF mechanism is hard to be explained by the conventional H₂O/H₂SO₄ binary, H₂O/H₂SO₄/NH₃ ternary, or even ion-induced nucleation theories [19], which hinders the understanding of the role of NH₃ in NPF.

Herein, to address this gap, the charge characteristics of PM_{2.5} was analysis and the role of NH₃ in NPF with multi-pollutants is discussed. According to the least-energy principle, a property of electric neutrality of PM_{2.5} was proposed and verified. A kinetic model combining the oxidation of SO₂/NO₂ in SO₂/NO₂/NH₃/H₂O/air system and the aggregations of H₂SO₄, HNO₃, NH₃ and OC in H₂SO₄/HNO₃/NH₃/OC system is established based on gas-kinetic theory. Model calculations with precursor concentrations at atmospheric level in China are carried out to investigate the effect of NH₃ on NPF quantitatively, including the contributions of NH₃ to oxidation of SO₂/NO₂ and to nucleation rate/concentration. And implications for haze mitigations in China are accordingly provided.

II. CHARGE ANALYSIS OF PM_{2.5}

According to the least-energy principle, all systems in nature would transfer from a high energy state to a low energy state in order to maintain their relative stability. By regarding the atmospheric space as a system, the high energy state is the situation with free pollutant precursors SO₂, NO_x, NH₃, and

VOCs, and the low energy state is that of aggregated particulate consisting of SO₄²⁻, NO₃⁻, NH₄⁺ and OC. In order to get relative stable, these free precursors would try to get a lower energy state by moving and aggregating together to form PM_{2.5}. Thereby, the positive and negative charges are neutralized, that is to say, the number of positive and negative charges would be equal, indicating PM_{2.5} would be electrical neutrality. To confirm that PM_{2.5} is in electrical neutrality, the mole concentration of positive and negative charges in PM_{2.5} was calculated. The Positive Charge Microequivalents (PCM) and Negative Charge Microequivalents (NCM) can be expressed as follows:

$$PCM = \sum \frac{Z^+ \cdot m(j)}{M(j)} \quad (1)$$

$$NCM = \sum \frac{Z^- \cdot m(k)}{M(k)} \quad (2)$$

Where, PCM and NCM are the mole concentration (mol/m³) of positive and negative charges in PM_{2.5}, respectively; m and M refer to mass concentration (g/m³) and relative molar mass (g/mol) of each ion, respectively; j and k represent the cations and anions in PM_{2.5}, respectively; z⁺ and z⁻ are the number of positive and negative charges in PM_{2.5}, respectively.

III. KINETIC MODEL FOR PM_{2.5} FORMATION

The major source of PM_{2.5} is secondary new particulate formations (NPF) in atmosphere. To investigate the NPF mechanism, some minor factors have been neglected and the general simplifications are adopted here. NPF occurs through homogeneous nucleation and subsequent growth (depositions are not considered) under steady atmospheric conditions [13]. As shown in Fig.1, NPF is dominated by two sequential steps: 1) oxidations from SO₂ to H₂SO₄, and NO₂ to HNO₃ in SO₂/NO₂/NH₃/H₂O/air system (oxidation stage); 2) aggregations of H₂SO₄, HNO₃, NH₃ and OC in H₂SO₄/HNO₃/NH₃/OC system (aggregation stage).

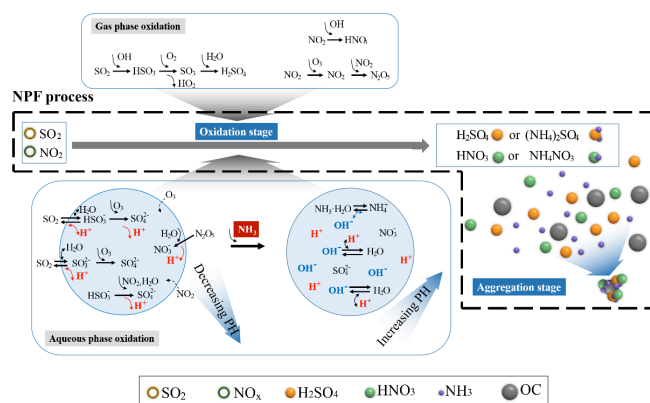


Fig.1 The schematic of NPF process. NPF is dominated by two sequential steps, *i.e.*, oxidation from SO₂ to H₂SO₄, and NO₂ to HNO₃ (oxidation stage), then aggregation of H₂SO₄, HNO₃, NH₃ and OC (aggregation stage).

For oxidation stage, the oxidation rate is determined by two pathways, the gas phase oxidation and the aqueous phase oxidation [11], as expressed by equations:

$$J_s = J_{s,g} + (J_{s,a}^O + J_{s,a}^N) \quad (3)$$

$$= k_{s,g} \cdot [N_1][N_2] + (k_{s,a}^O \cdot [M_1][M_2] + k_{s,a}^N \cdot [M_1][M_2])$$

$$J_n = J_{n,g} + J_{n,a} \quad (4)$$

$$= k_{n,g} \cdot [N_1][N_2] + k_{n,a} \cdot [M_1][M_2]$$

where, N_1 , N_2 and M_1 , M_2 are the concentrations of gaseous and aqueous reactants, respectively. J_s is the total generation rate of SO_4^{2-} . $J_{s,g}$ is the gas phase oxidation rate of SO_2 with the rate coefficient, $k_{s,g}$. $J_{s,a}^O$ and $J_{s,a}^N$ are the aqueous phase oxidation of dissolved SO_2 (i.e., S(IV)) by O_3 and NO_2 with rate coefficients, $k_{s,a}^O$ and $k_{s,a}^N$, respectively. Similarly, J_n is the total generation rate of NO_3^- . $J_{n,g}$ is the gas phase oxidation rate of NO_2 with the rate coefficient, $k_{n,g}$. $J_{n,a}$ is the aqueous phase oxidation of dissolved NO_2 with the rate coefficient, $k_{n,a}$. The main reactions along with corresponding rate coefficients are listed in Table 1.

Table.1 Main reactions in atmospheric oxidations of SO_2 and NO_2 . Here, K1-K12 represent the rate coefficient for the reaction 1 to reaction 12 unless otherwise stated.

Type	Product	Reaction	Rate coefficient (298K)
Gas phase oxidation	SO_4^{2-}	$SO_2 + OH \xrightarrow{1} HSO_3$	$K_1=2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$
		$HSO_3 + O_3 \xrightarrow{2} SO_3 + HO_2$	$K_2=4.5 \times 10^{-13} \text{ cm}^3\text{s}^{-1}$
		$SO_3 + H_2O \xrightarrow{3} H_2SO_4$	$K_3=6 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$
Aqueous phase oxidation	NO_3^-	$NO_2 + OH \xrightarrow{4} HNO_3$	$K_4=8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$
		$SO_2 + H_2O \xrightleftharpoons{5} SO_2 \cdot H_2O$	$K_5=1.23 \text{ mol L}^{-1} \text{ atm}^{-1}$ (equilibrium constant,
		$SO_2 \cdot H_2O + H^+ \rightleftharpoons HSO_3^-$	i.e., Henry law constant)
		$H^+ + HSO_3^- \rightleftharpoons 2H^+ + SO_3^{2-}$	
		$3HSO_3^- + O_3 \xrightarrow{6} 3H^+ + 3SO_4^{2-}$	
		$3SO_3^{2-} + O_3 \xrightarrow{7} 3SO_4^{2-}$	$K_6=4.0 \times 10^{-17} \text{ cm}^3\text{s}^{-1}$
		$HSO_3^- + 2NO_2 + H_2O \xrightarrow{8} 3H^+ + SO_4^{2-} + 2NO_2^-$	$K_7=6.1 \times 10^{-16} \text{ cm}^3\text{s}^{-1}$
		(Synergistic effect of NO_2 and SO_2)	$K_8=1.9 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$
		$NO_2 + O_3 \xrightarrow{9} NO_3 + O_2$	$K_9=6.5 \times 10^{-17} \text{ cm}^3\text{s}^{-1}$
		$NO_2 + NO_3 \xrightarrow{10} N_2O_5$	$K_{10}=1.9 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$
		$N_2O_5 + H_2O \xrightarrow{11} 2HNO_3$	$K_{11}=2.5 \times 10^{-22} \text{ cm}^3\text{s}^{-1}$
		NH ₃ hydrolysis	OH ⁻

Since H^+ are always generated during the aqueous phase oxidation process of S(IV) (Fig.1), the pH decreases as the reaction processes, which hinders the oxidation reactions [21]. Thus, the coefficient rate of the aqueous phase oxidation process, $k_{a,x}$, should be modified as:

$$k'_{a,x} = \alpha_{pH} \cdot k_{a,x}$$

where $k'_{a,x}$ is the modified value as the result of the value of $k_{a,x}$ at pH=7.0 multiplying a modification variation as a function of pH, α_{pH} . Previous studies have shown that the reaction in aqueous is favorable under the condition of high pH [20], which is consistent with the result of Wang et al. (2016) showing Henry's constant of SO_2 decreases by two orders of magnitude as pH reduces from 6.0 to 4.0 [2]. Therefore, it can be judged that α_{pH} decreases with pH decrease, and is close to 0 with pH below 4.0, rendering a possible expression as:

$$\alpha_{pH} = A + \frac{B}{1 + \exp(\frac{pH}{C})} \quad (5)$$

where, A, B and C are constants that can be determined with available data in literatures. Take reaction 8 (Table 1) as an example: $k_8 = 1.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at pH =5.8, and $k_8 \geq 2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ at pH=6.4 [21]. The value of pH as a function of mole concentration of H^+ can be expressed as:

$$pH = -\lg[H^+]$$

After the oxidation stage of SO_2 and NO_2 , the products, H_2SO_4 and HNO_3 , get into the aggregation stage with NH_3 and OC. Here, homogeneous nucleation for NPF, a continuous collision aggregation of molecules, is considered in the $H_2SO_4/HNO_3/NH_3/OC$ system. Aggregations are supposed to occur between H_2SO_4 and NH_3 , HNO_3 and NH_3 , H_2SO_4 and OC, HNO_3 and OC, NH_3 and OC, OC and OC, resulting neutral and stable clusters [22]. Thus, the evaporation and dissociation of cluster could be neglected and the nucleation rate of cluster containing i molecules ($i > 2$), $J_{nuc}^{C_i}$, is written as:

$$J_{nuc}^{C_i} = \sum_{j=1}^{i-1} \left(K_{j,i-j}^{S,H} \cdot \frac{1}{2} [C_j^S] \cdot \frac{1}{3} [C_{i-j}^H] + K_{j,i-j}^{S,O} \cdot \frac{1}{2} [C_j^S] \cdot \frac{1}{5} [C_{i-j}^O] \right) + K_{j,i-j}^{N,H} \cdot \frac{1}{2} [C_j^N] \cdot \frac{1}{3} [C_{i-j}^H] + K_{j,i-j}^{N,O} \cdot \frac{1}{2} [C_j^N] \cdot \frac{1}{5} [C_{i-j}^O] + K_{j,i-j}^{H,O} \cdot \frac{1}{3} [C_j^H] \cdot \frac{1}{5} [C_{i-j}^O] + K_{j,i-j}^{O,O} \cdot \frac{1}{5} [C_j^O] \cdot \frac{1}{5} [C_{i-j}^O]$$

where, the superscript, S, N, H and O, represent H_2SO_4 , HNO_3 , NH_3 and OC, respectively. C_j^S , C_j^N , C_j^H and C_j^O are the clusters with single surface molecules of H_2SO_4 , HNO_3 , NH_3 and OC, respectively. $K_{j,i-j}^{S,H}$ is the rate coefficient for the collision between C_j^S and C_{i-j}^H , which can be expressed based on the gas kinetic theory:

$$K_{j,i-j}^{S,H} = \alpha_{j,i-j}^{S,H} \cdot \pi \cdot (r_j + r_{i-j})^2 \cdot \left(\frac{8kT(m_j + m_{i-j})}{\pi(m_j \cdot m_{i-j})} \right)^{\frac{1}{2}} = \eta^{S,H} \cdot \gamma_{j,i-j} \cdot \beta_{j,i-j} \cdot \pi \cdot (r_j + r_{i-j})^2 \cdot \left(\frac{8kT(m_j + m_{i-j})}{\pi(m_j \cdot m_{i-j})} \right)^{\frac{1}{2}} \quad (7)$$

where $\alpha_{j,i-j}^{S,H}$ is sticking coefficient which is the product of energy factor $\beta_{j,i-j}$, steric factor $\gamma_{j,i-j}$, and correction factor for potential interactions between molecules $\eta^{S,H}$, respectively. $\beta_{j,i-j}$ is given as Eq.(10). ΔE represents the formation energy of cluster which could be determined by previous studies [25]. $\gamma_{j,i-j}$ is supposed to increase logarithmically from 0 to 1 with the rising size of colliding clusters. $\eta^{S,H}$ is related to the interaction force between two clusters [26]. Moreover, m_j , m_{i-j} , and r_j , r_{i-j} refer to the mass and the radii of colliding cluster C_j^S and C_{i-j}^H , respectively. Considering that all molecules and clusters are regarded as hard sphere, r_j could be expressed as Eq. (11). And ρ is the density of cluster usually in the range of 1-2 g cm⁻³ [27].

$$\beta_{j,i-j} = \exp\left(-\frac{\Delta E}{kT}\right) \quad (8)$$

$$r_j = \left(\frac{3m_j}{4\pi\rho}\right)^{\frac{1}{3}} \quad (9)$$

IV. RESULTS AND DISCUSSION

4.1 Electric-charge characteristics identification

Three different typical regions which are urban, industrial and rural areas, were selected to analyze the characteristic of PM_{2.5}. The urban areas are modern cities with multitudinous people and roads, and the pollutants mainly come from vehicle emissions. The industrial areas have a number of factories, and pollutant emission is mainly from industrial activities. In addition, the rural areas have less people and fewer modern manufacturers, and pollutants mainly come from agriculture or nature sources. Table 2 shows the related parameters of PM_{2.5} that including chemical components and their concentrations in these regions, and data were collected from the former researches and monitoring of the relevant departments [28-42].

Table 2. The components and concentrations of PM_{2.5} in different areas in China (μg/m³)

Areas	Mass concentration (μg/m ³)										Reference
	PM _{2.5}	SO ₂	NO ₂	F ⁻	Cl ⁻	NH ₄ ⁺	K ⁺	Ca ²⁺	Na ⁺	Mg ²⁺	
Urban	219.96	21.32	13.78	0.32	5.53	10.00	4.62	1.88	0.96	0.25	[28]
	106.94	10.55	7.83	0.00	0.00	5.46	1.44	0.00	0.00	0.13	[29]
	\	27.11	10.19	0.22	1.59	13.28	1.32	0.83	0.85	0.12	[30]
	\	64.27	19.22	0.21	3.18	28.01	4.62	0.29	2.12	0.03	
	\	30.99	11.69	0.15	1.44	15.13	1.44	0.23	1.04	0.01	
	\	42.84	21.77	0.61	8.75	29.19	3.07	1.41	1.34	0.22	
	60.62	7.01	4.10	0.13	1.62	3.30	0.61	0.94	0.54	0.13	[31]
	73.90	12.20	14.60	0.00	3.00	8.20	1.30	1.30	0.20	0.10	[32]
	\	27.80	4.31	0.00	0.55	12.10	2.59	0.49	0.46	0.69	[33]
	292.50	41.84	42.27	1.03	10.90	24.46	6.58	6.94	3.72	0.59	[34]
Industrial	\	22.34	3.03	\	0.89	3.81	\	5.29	\	0.60	[35]
	104.00	12.20	9.22	\	3.74	7.09	1.09	0.44	2.03	0.05	[36]
	125.00	14.70	12.80	\	3.47	8.52	1.10	0.42	1.96	0.04	
	49.70	11.60	1.89	\	0.24	2.56	0.48	0.56	1.00	0.06	
	51.40	9.33	3.14	\	0.91	2.83	0.39	0.48	0.57	0.04	
	111.00	13.10	9.44	\	2.39	7.23	0.81	0.37	0.47	0.06	
	105.00	11.10	6.92	\	3.64	6.29	0.93	0.34	0.49	0.06	
	48.50	11.20	2.61	\	0.50	2.78	0.38	0.66	2.77	0.06	
	58.70	9.75	4.42	\	2.17	3.68	0.48	0.53	2.45	0.05	
	211.00	22.30	17.30	1.10	10.00	17.40	2.90	3.30	1.40	0.40	[37]
186.00	35.20	23.30	0.90	7.10	15.40	2.80	3.00	1.20	0.40		
122.00	32.00	11.10	0.20	1.40	15.70	1.40	1.30	0.90	0.20		
181.00	26.50	16.80	0.50	2.70	11.60	1.70	3.70	1.20	0.40		
Rural	45.40	12.40	3.00	\	0.20	4.90	0.60	0.80	0.20	0.20	[38], [39]
	34.10	9.90	1.50	\	0.20	4.10	0.40	0.20	0.10	0.00	
	41.60	11.70	4.70	\	0.30	5.00	0.60	0.90	0.20	0.10	
	66.00	16.70	9.60	\	0.40	7.50	0.90	1.30	0.40	0.20	
	31.30	9.10	1.80	\	0.20	3.40	0.60	\	0.50	\	[40]
	36.80	9.50	1.60	\	0.20	3.70	0.70	\	0.50	\	
	67.10	17.80	1.40	\	0.20	7.60	0.80	\	0.60	\	
	40.80	12.60	2.90	\	0.30	5.80	0.70	\	0.50	\	
	104.89	14.22	0.62	0.11	0.35	3.39	0.99	1.62	0.29	0.15	[41]
	20.55	3.37	0.04	0.01	0.20	1.02	0.12	0.19	0.09	0.02	
29.19	6.79	0.27	0.15	0.85	1.84	0.42	0.51	0.30	0.06		
72.42	10.84	1.32	0.26	0.84	4.18	0.71	0.41	0.98	0.28		

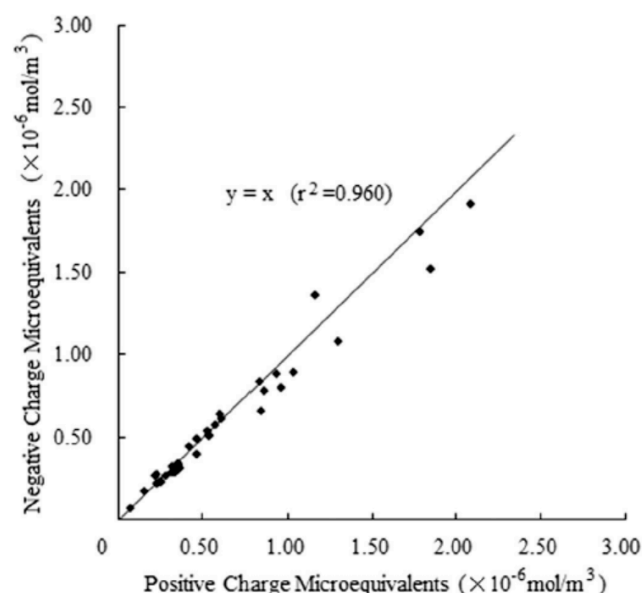


Fig.2 Relationship between PCM and NCM in PM_{2.5}.

According to Equations (1) and (2), the PCM and NCM values of different areas could be obtained and shown in Fig. 2. From Fig. 2, relationship between PCM and NCM in these study areas was fitting as a straight line, and the slope of this linear fitting equation was about 1. Although values of PCM and NCM may be not on the line strictly, they are around the fitting straight line. It indicated that PM_{2.5} was in an electrical neutrality condition. Since NH₄⁺ is the only cation in the main chemical compositions of PM_{2.5}, it would be vital for anions (such as SO₄²⁻ and NO₃⁻) to aggregate together and is a key factor for PM_{2.5} formations.

4.2 Mechanism for the role of NH₃ in promoting NPF

In the oxidation stage of NPF, SO₂ and NO₂, which are mostly emitted into atmosphere from anthropogenic sources, e.g., industry and traffic [2], are oxidized in series of pathways in gaseous and aqueous phases to transform into SO₄²⁻ and NO₃⁻ respectively, as shown in Fig.1 and Table 1.

It is noteworthy that H⁺ generated from those oxidation reactions decreases the pH of aqueous phase, hindering the proceeding of reactions. While the presence of NH₃, which can easily dissolve in water and produce OH⁻ by hydrolysis, results in the increasing of pH and alkalinity, then promotes the water solubility and oxidation reactions of SO₂ and NO₂.

In the aggregation stage of NPF, NH₃ is the only inorganic base species in H₂SO₄/HNO₃/NH₃/OC system, and could neutralize the charged particle. Therefore, it is a key factor for the aggregation of clusters according to the least-energy principle. The detail analysis was carried out in our earlier work [22].

Generally, the mechanism for the effect of NH₃ on enhancing NPF are embodied from two aspects: 1) NH₃ plays a catalysis role in enhancing NPF indirectly, i.e., promoting oxidation of SO₂ to SO₄²⁻ and NO₂ to NO₃⁻ by

mediating the PH in aqueous. 2) NH_3 plays a neutralizing role in facilitating the aggregation of SO_4^{2-} and NO_3^- , enhancing NPF directly.

4.3 Significant contribution of NH_3 on oxidation of SO_2 and NO_2

The impacts of NH_3 concentration on the conversion fraction (CF) for SO_2 and NO_2 in $\text{SO}_2/\text{NO}_2/\text{NH}_3/\text{H}_2\text{O}/\text{air}$ system are shown in Fig.3. Here, CF refers to the ratio of number concentration for converted SO_4^{2-} and NO_3^- to that for total SO_2 and NO_2 , respectively. The initial conditions of the model calculation are also displayed in Fig.3. A closed atmospheric system with SO_2 and NO_2 at 20 ppb, O_3 at 200 ppb, OH radical at $5 \times 10^6 \text{ cm}^{-3}$, and temperature at 298K, which is comparable to the real atmospheric condition in most cities of China [23].

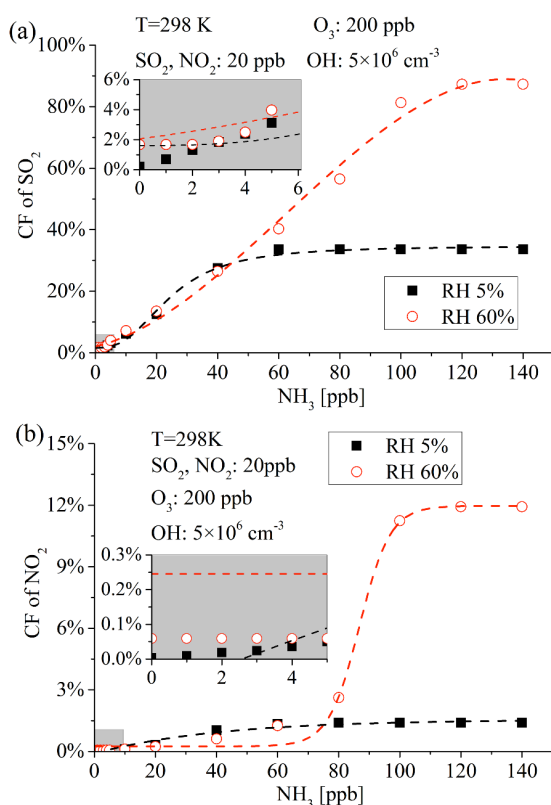


Fig.3 (a) and (b): the variation of CF for SO_2 and NO_2 with NH_3 levels at RH of 5% and 60%, respectively. Here, CF, i.e., conversion fraction, refers to the ratio of number concentration for converted SO_4^{2-} and NO_3^- to total SO_2 and NO_2 , respectively.

Figure.3 (a) shows the variation of CF for SO_2 with NH_3 levels at relative humidity (RH) of 5% and 60%, respectively. In the absence of NH_3 , CF for SO_2 is only around 0.02% with RH 5 % and 1.6% with RH 60%. Whereas, in presence of NH_3 , the CF for SO_2 increases with increasing NH_3 (ranging from 0 to 140 ppb), and ends up at around 30% with RH 5 % and 90% with RH 60%. The

results indicate that ppb level of NH_3 can lead to a remarkable increase in CF for SO_2 with atmospheric concentration. Figure.3 (b) shows the variation of CF for NO_2 with NH_3 levels at RH of 5% and 60%, respectively. Similarly, the presence of NH_3 (ranging from 0 to 140 ppb) promotes CF for NO_2 from 0.004% to 1.4% with RH 5%, and from 0.06% to 11.9% with RH 60%. Furthermore, the CF is much lower for NO_2 than for SO_2 . The obvious enhancement of CF for NO_2 appears at a higher NH_3 than that for SO_2 . These results indicate the oxidation of NO_2 is weaker than SO_2 by inorganic compounds. That is, NH_3 prefers SO_2 than NO_2 in the $\text{SO}_2/\text{NO}_2/\text{NH}_3/\text{H}_2\text{O}$ system, which agrees with previous studies [10]. For both oxidations of SO_2 and NO_2 , it's noteworthy that the CF reaches a greater steady value in wet condition (RH: 60%) than in dry condition (RH: 5%), implying a synergistic effect of NH_3 and H_2O on promoting oxidation of SO_2 and NO_2 . The similarly dramatically increase of CF for SO_2 affected by NH_3 was previously observed [17]. The reason is that the presence of NH_3 increases the alkalinity by producing OH^- from hydrolysis, leading to an enhancing effect of oxidation of SO_2 and NO_2 by aqueous reactions.

However, the CF for SO_2 and NO_2 in dry conditions are the same or even slightly greater compared with those in wet conditions when NH_3 level is in the range of 10-40 ppb, as shown in Fig.3 (a) and (b). This indicates that the dominant factor for oxidation of SO_2 and NO_2 in that condition is NH_3 rather than RH. Interestingly, the range of 10-40 ppb is almost the NH_3 level in Beijing, China [11, 12]. This may be the reason why PM2.5 pollution occurs quirkily in Beijing even in dry conditions.

4.4 Enhancing effect of NH_3 on nucleation rate and nuclei concentration

The effect of NH_3 levels on the nucleation rate and nuclei concentration in $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{NH}_3/\text{OC}$ system are shown in Fig.4. Here, the critical nuclei are in the range of 2-3nm, in terms of the previous findings that the size of critical nuclei is usually sub-3 nm [13]. The initial conditions of model calculation are displayed in Fig.3. A closed atmospheric system with temperature at 298K and total number concentration (TNC) of H_2SO_4 , HNO_3 and OC (as one of the typical organic compounds in atmosphere, the isoprene is used to present OC in this kinetic model) at $2 \times 10^8 \text{ cm}^{-3}$ (condition 1), $5 \times 10^8 \text{ cm}^{-3}$ (condition 2), and $1 \times 10^9 \text{ cm}^{-3}$ (condition 3) respectively, which are comparable with real atmospheric conditions [13].

Figure.4 (a) shows the variation of mean nucleation rate with NH_3 levels in three conditions. In the absence of NH_3 , the nucleation rate is about $20 \text{ cm}^{-3} \text{ s}^{-1}$, $40 \text{ cm}^{-3} \text{ s}^{-1}$ and $100 \text{ cm}^{-3} \text{ s}^{-1}$ under conditions 1, 2 and 3, respectively. Whereas, in presence of NH_3 (ranging from 0 to 50 ppt), the nucleation rate in the three conditions increases and then reaches a plateau at NH_3 levels of 5, 20 and 30 ppt, respectively. The ultimate nucleation rate in those three conditions with NH_3 presence is about 60, 140 and $280 \text{ cm}^{-3} \text{ s}^{-1}$.

s^{-1} respectively, which is 2-4 times higher than that in absence of NH_3 . Similarly, as shown in Fig.4 (b), the ultimate nuclei concentration in presence of NH_3 (ranging from 0 to 50 ppt) are 4-8 times higher than those in absence of NH_3 . Unlike the several magnitudes increase in nucleation rate or nuclei concentration due to the presence of NH_3 in H_2O/H_2SO_4 binary system [16], the results in this paper exemplify that adding NH_3 to $H_2SO_4/HNO_3/OC$ system leads to a modest increase. The modest enhancing effect of NH_3 on nucleation rate and nuclei concentration may due to the existence of OC (e.g., amine) which also acts as basic species [24]. Moreover, Fig. 5 shows that the nucleation rate and nuclei concentration both approach to ultimate values with NH_3 concentration in the range of 5-10, 20-30 and 30-40 ppt in condition 1, 2, and 3, respectively. That is, with H_2SO_4 , HNO_3 and OC at atmospheric concentration, the NH_3 concentration higher than about 40 ppt level would not influence the nucleation rate and nuclei concentration in $H_2SO_4/HNO_3/NH_3/OC$ system. Therefore, considering the ppb level of atmospheric NH_3 concentration in China, around 6 ppb in rural sites and 20 ppb in urban sites [12] the major increasing effect of NH_3 on NPF is the enhancement of CF for SO_2 and NO_2 in oxidation process.

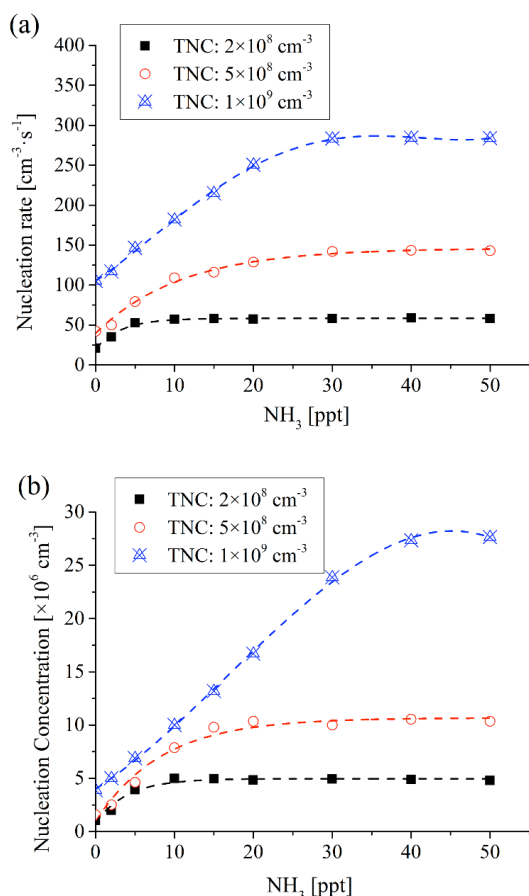


Fig.4 (a) and (b) the variation of mean nucleation rate and nuclei concentration with NH_3 levels in three conditions,

respectively. TNC is the total molecule number concentration of H_2SO_4 , HNO_3 and OC.

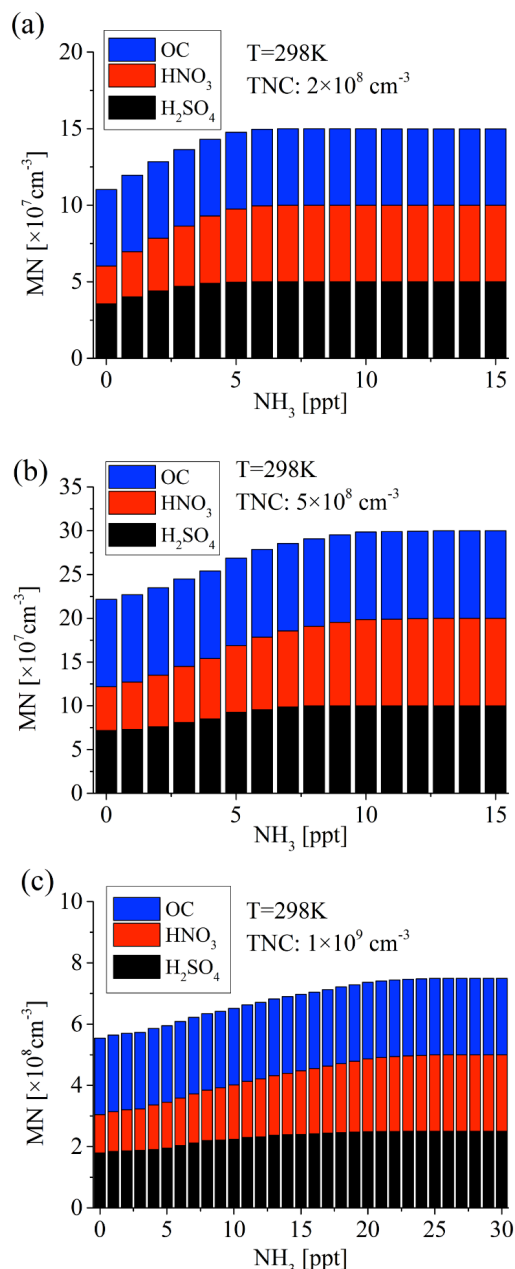


Fig.5 (a)-(c): the variation of MN for H_2SO_4 , HNO_3 and OC with NH_3 levels in condition 1, 2 and 3, respectively. MN represents the number concentration of molecules for different species in newly formed particles.

In addition, the impact of NH_3 on the role for HNO_3 in NPF has also been investigated, as shown in Fig.5. Here, molecule number (MN) refers to the number concentration of molecules for different species (H_2SO_4 , HNO_3 , and OC) in newly formed particles. The initial condition of model

calculation is also displayed in Fig.5, which is the same as in Fig.4.

Figure.5 (a) shows the variation of MN for different species with NH_3 levels in condition 1. In the absence of NH_3 , MN for H_2SO_4 , HNO_3 and OC are around $3.5 \times 10^7 \text{ cm}^{-3}$, $2.4 \times 10^7 \text{ cm}^{-3}$, and $5 \times 10^7 \text{ cm}^{-3}$, respectively. However, in presence of NH_3 (from 0 to 50 ppt), MN for H_2SO_4 and HNO_3 first increase, then both reach a plateau at around $5 \times 10^7 \text{ cm}^{-3}$. The similar variation is also found in Fig.5 (b) and (c), in which the MN for HNO_3 increases from $5 \times 10^7 \text{ cm}^{-3}$ to $1 \times 10^8 \text{ cm}^{-3}$, and $1.2 \times 10^8 \text{ cm}^{-3}$ to $2.5 \times 10^8 \text{ cm}^{-3}$. The results show the MN for HNO_3 increases about 50% due to the presence of NH_3 , which is the most notable in those three species, indicating that NH_3 enhances the positive effect of HNO_3 on NPF. The reason would be that NH_3 preferentially reacts with H_2SO_4 and only excess NH_3 is available for HNO_3 [10, 22]. Thus, in absence or low level presence of NH_3 , NPF is dominated by H_2SO_4 and minor affected by HNO_3 . Nevertheless, with the increase of NH_3 level, HNO_3 would also be a key factor as H_2SO_4 in NPF.

4.5 Implications for haze pollution in China

In order to mitigate haze pollution in China, strict pollution controls have been stressed during the latest five years, e.g., traffic restriction, desulfurization and denitrification in industry, and even temporary suspensions of operations for coating, printing, petrochemical and furniture industry. Those measures have made a transitory achievement and led to a clean atmosphere during special periods, e.g., during 2014 Asia-Pacific Economic Cooperation summit in Beijing and 2015 China Victory Day Parade. However, when the pollution control was relaxed, the haze pollution occurred continuously [23].

The reason may be that almost all the pollution control aims to reduce the emissions of SO_2 , NO_2 and volatile OC, but little for NH_3 . On the contrary, as one of the major sources of NH_3 , the nitrogenous fertilizer application still increased, and led to the increase of NH_3 emission. Due to the high level of NH_3 concentration in atmosphere, SO_2 and NO_2 could be quickly oxidized and to form particulates, causing serious haze pollution.

In addition, because of the enhanced positive effect of HNO_3 on NPF due to the presence of NH_3 , haze pollutions are difficult to be mitigated if only SO_2 emission has been limited. For example, the recent serious haze pollution ($\text{PM}_{2.5}$ maximums are over $500 \mu\text{g}/\text{m}^3$) in Beijing during 16-21, Dec., 2016, with a SO_2 level under 20 ppb but a NO_x level higher than 100 ppb, has been thought to be dominated by NO_x [23]. However, the deep reason may be the high level of NH_3 in Beijing atmosphere which facilitates the formation of particulate nitrate.

Therefore, for efficiently haze mitigation in China, NH_3 emission control should be stressed in addition to SO_2 and NO_x , e.g., optimizing the application approach for

nitrogenous fertilizer in order to reduce the volatilization of NH_3 .

V. CONCLUSIONS

In this paper, a property of electric neutrality of $\text{PM}_{2.5}$ was proposed under the least-energy principle and verified through electricity-charge calculation. Since NH_4^+ is the only cation in the main chemical compositions of $\text{PM}_{2.5}$, it would be vital for anions (such as SO_4^{2-} and NO_3^-) to aggregate together and is a key factor for $\text{PM}_{2.5}$ formations.

The mechanism for enhancing effect of NH_3 on NPF are embodied from two aspects: 1) in the oxidation stage, NH_3 enhances NPF indirectly with a catalysis role, i.e., mediating the pH to promote oxidation of SO_2 to SO_4^{2-} and NO_2 to NO_3^- . 2) in the aggregation stage, NH_3 enhances NPF directly with a neutralizing role, i.e., facilitating aggregation of H_2SO_4 and HNO_3 to form particulates.

For oxidation of SO_2 and NO_2 in $\text{SO}_2/\text{NO}_2/\text{NH}_3/\text{H}_2\text{O}/\text{air}$ system, with the increasing NH_3 level from 0 to 140 ppb, CF of SO_2 increases from 1.6% to 90% and CF of NO_2 increases from 0.06% to 11.9% in wet condition (RH at 60%), while CF of SO_2 increases from 0.02% to 30% and CF of NO_2 increases from 0.004% to 1.4% in dry condition (RH at 5%). The higher ultimate CF value in wet conditions implies a synergistic enhancing effect of NH_3 and H_2O on oxidation of SO_2 and NO_2 . Further, NH_3 plays dominant role in SO_2 and NO_2 oxidation when NH_3 level is lower than 40 ppb.

For aggregation in $\text{NH}_3/\text{H}_2\text{SO}_4/\text{HNO}_3/\text{OC}$ system, with the increasing NH_3 levels from 0 to 50 ppt, nucleation rate and nuclei concentration increase by 2-4 times and 4-8 times, respectively. Nucleation rate and nuclei concentration stop to increase when NH_3 surpasses 40 ppt. Therefore, considering the ppb level of atmospheric NH_3 concentration in China, the major influence of NH_3 on NPF is the enhancement of CF for SO_2 and NO_2 in oxidation processes. In addition, MN for HNO_3 increases about 50% due to the presence of NH_3 , indicating that NH_3 leads to a significant positive contribution for HNO_3 to NPF.

In China, with high levels of NH_3 in atmosphere, around 6 ppb in rural sites and 20 ppb in urban sites, the reasonable mitigation measure for haze pollution is to control the emission of NH_3 strictly as current restrictions on SO_2 and NO_x , e.g. limiting and optimizing the application for nitrogenous fertilizer.

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