Atmospheric Research 184 (2017) 139–148

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmosres

Smog chamber study on aging of combustion soot in isoprene/SO_2/NOx system: Changes of mass, size, effective density, morphology and mixing state

Kangwei Li, Linghong Chen *, Ke Han, Biao Lv, Kaiji Bao, Xuecheng Wu, Xiang Gao, Kefa Cen

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form 28 September 2016
Accepted 18 October 2016
Available online 19 October 2016

Keywords:
Smog chamber
Complex air pollution
Soot aging
SOA
Heterogeneous reaction

ABSTRACT

Atmospheric soot aging process is always accompanied by secondary particle formation, which is a comprehensive environmental issue that deserves great attention. On one hand, aging of primary soot could change its own physicochemical properties; on the other hand, complex air pollution caused by pollutant emission from various sources (e.g., vehicle exhausts, coal-fired flue gases and biogenic VOCs emission) may contribute to secondary particle formation onto primary particle surface. In this study, aging of combustion soot in isoprene/SO_2/NOx system was investigated under controlled laboratory conditions in several smog chamber experiments. During the evolution of soot, several physical properties such as mass, size, effective density, morphology and mixing state were determined simultaneously by an integrated aerosol analytical system of Scanning Mobility Particle Sizer (SMPS), Differential Mobility Analyzer-Aerosol Particle Mass Analyzer-Condensation Particle Counter (DMA-APM-CPC) and Transmission Electron Microscopy coupled with Energy-dispersive X-ray Spectrometry (TEM/EDX) techniques. Here, based on the experimental results of soot aging under different gas-phase composition and relative humidity (RH), we firstly proposed possible aging pathways of soot in isoprene/SO_2/NOx system. A synergetic effect was speculated to exist between SO_2 and isoprene on soot aging process, which led to more secondary particle formation. At the same time, TEM/EDX analysis showed that a competitive mechanism between H_2SO_4(g) and isoprene oxidation vapor may exist: H_2SO_4(g) firstly condensed onto fresh soot, then an acceleration of isoprene oxidation products formed onto H_2SO_4 pre-coated soot. In isoprene/SO_2/NOx system, high RH conditions could contribute to soot aging and new particle formation. The changes of effective density and dynamic shape factor of soot also indicated that high RH conditions could accelerate soot aging process, and led chain-like soot into more spherical morphology, which was further confirmed from the STEM image. Moreover, it was found that volume equivalent coating thickness (Δr_{ve}) could also be applied to normalized characterize soot aging parameters like diameter growth factor (*Gfd*) and mass growth factor (*Gfm*) in a complex reaction system like isoprene/SO_2/NOx. Our results revealed the dual mechanism (competitive effect&cooperative effect) of isoprene and SO_2 on photochemical aging of soot, which is of significance for improving understanding of complex air pollution in China.

1. Introduction

Soot is mainly produced through the incomplete combustion process of fossil fuels and open biomass (Bond et al. 2004; Mueller et al. 2015). Compared to other components of $PM_{2.5}$, soot also strongly absorbs sunlight besides decreasing visibility and weakening human health (Cho et al. 2009), which is able to produce positive radiative forcing of the atmosphere (Bond and Bergstrom 2006; Peng et al. 2016). Ramanathan and Carmichael (2008) have pointed out that soot is the second largest contributor to the greenhouse effect, inferior only to carbon dioxide. Fresh soot is generally a branched chain-like cluster composed of a large number of primary carbon particles, and the loose structure provides a greater surface area for heterogeneous reactions through adsorption and catalytic process in atmosphere. Previous studies (Lu et al. 2009; Pagels et al. 2009) have shown that some pollutants such as H_2SO_4(g) and semi-volatile organic compounds (SVOC) can be attached on the surface of soot by condensation, forming new coating compounds which can lead to the morphological reconstruction of soot. These coating matters alter mixing state of fresh soot from external mixture to internal mixture, then change its physical and chemical properties such as hygroscopicity and optical properties and make it possible for soot to become cloud condensation nuclei (CCN) (Wang et al. 2016; Zhang et al. 2008). Therefore, studies on soot aging are helpful in assessing its influence on environment, climate and health (Tong et al. 2016a; Zhang et al. 2015a).

---

* Corresponding author.
E-mail address: chenlh@zju.edu.cn (L. Chen).

http://dx.doi.org/10.1016/j.atmosres.2016.10.011

Volatile organic compounds (VOCs) in the atmosphere are emitted from anthropogenic and biogenic sources (Seinfeld and Pandis 2012). By reacting with oxidants such as OH, O_3, and NO_3, VOCs can generate organic species that contain one or several polar functional groups, including aldehydes, ketones, alcohols, nitrocellulose, and carboxylic acids (Hallquist et al. 2009; Seinfeld and Pankow 2003). These species can participate in physical and chemical processes like nucleation, condensation, gas/particle partition and heterogeneous reactions to form secondary organic aerosols (SOA). Isoprene is not only a typical representative of VOCs with high reactivity in the atmosphere, but is also a precursor for both ozone (O_3) and secondary organic aerosol (SOA) from atmospheric photooxidation processes (Lei et al. 2000; Zhang et al. 2002). Isoprene is mainly emitted by natural sources, with global emissions of 600 Tg per year (Guenther 2006), and it contributes significantly to SOA formation. SO_2 is mainly emitted by coal-fired flue gases, and can react with OH radicals to form $H_2SO_4(g)$ in atmosphere, which then participates in nucleation or condensation to form sulfate on the surface of primary particles (Guo et al. 2014).

In recent years, lots of big cities like Beijing and Shanghai in China are faced with serious haze issues (Tang et al. 2016; Tong et al. 2016b; Tong et al. 2016c; Zhang et al. 2016; Zhang et al. 2015b). Many studies (Guo et al. 2014; Huang et al. 2014; Wang et al. 2015) have shown that the haze pollution in China presents obvious complex characteristics, that is pollutants in the atmosphere from various sources interact and react complexly under different atmospheric conditions, including temperature and humidity, leading to the rapid formation of secondary particles containing sulfate, nitrate and organics. Under such a highly complex condition, studying the synergistic effects of SO_2 and isoprene on soot aging and secondary aerosol formation is crucial and helpful to understand the formation mechanism of severe haze pollution.

Previous chamber studies on soot aging in different reaction systems have been investigated extensively, which are summarized in Table 1. For example, when fresh soot is coated by VOCs oxidation products from α-pinene ozonolysis (Saathoff et al. 2003), isoprene-OH (Khalizov et al. 2013), toluene-OH (Qiu et al. 2012), or xylene-OH (Guo et al. 2016; Schnitzler et al. 2014), it was found that the size and mass of soot particles increased and their morphology and hygroscopicity significantly altered. On the other hand, when soot is coated by organic acid compounds such as glutaric acid (Xue et al. 2009), succinic acid (Xue et al. 2009), or oleic acid (Slowik et al. 2007), the morphology and hygroscopicity of fresh soot remain unchanged. This indicates that different coating materials may lead to different soot aging process. Although it has been well recognized that formation of coatings on soot particles from gas-phase pollutants condensation could significantly change particle size, mass, morphology, etc. There have been a few studies that investigated the synergistic effects of SO_2 and VOCs on secondary particle formation. According to some recent studies (Mauldin et al., 2012, Welz et al. 2012), alkenes can react with O_3 to form Criegee intermediates (CIs), and CIs can react with SO_2 quickly to produce sulfate, which means that it is possible to make the formation of sulfate and SOA more complicated when SO_2 and isoprene are mixed. Besides, some results of smog chamber experiments show that SO_2 can enhance the production of SOA from anthropogenic and biogenic sources VOCs (Edney et al. 2005; Jaoui et al. 2012; Kleindienst et al. 2006).

More recently, Guo et al. (2016) found that volume equivalent coating thickness (Δr_{ve}) could be used as a normalized parameter to characterize soot aging process in the xylene-OH system. However, soot aging when SO_2 and VOCs co-exist is far more complicated, and is also relatively poorly understood. First of all, further study is needed to verify whether Δr_{ve} could be extensively applied to complex reaction system like isoprene/SO_2/NOx. Secondly, the effects of SO_2 and VOCs on soot aging and secondary particle formation have rarely been investigated together. Our recognition of SO_2 oxidizing paths to form sulfate is still incomplete, and the formation mechanism of SOA as well as the influence of mixing SO_2 into VOCs-NOx system on soot aging are not well understood. What's more, there still exists a lot of uncertainty when considering the influence of the various environment conditions (e.g., RH) on its evolving characteristics. To our best knowledge, there is still no report concerning the influence of isoprene/SO_2/NOx complex system on chamber soot aging.

To study the complex air pollution by pollutants from vehicle exhausts, coal-fired power plants and biogenic VOCs, we introduced isoprene, NOx, SO_2 and soot particles into a 3 m^3 smog chamber. The design of experiments addresses the following three questions: 1. How does SO_2 and isoprene individually transform into sulfate and SOA? What influence do they have on soot aging when SO_2 and isoprene coexist? Does the isoprene/SO_2/NOx system have synergistic effect on the production of sulfate and SOA? 2. How does relative humidity affect the soot aging as well as the formation of secondary particles under the isoprene/SO_2/NOx system? 3. Could Δr_{ve} be extensively applied into complex reaction system, and normalized to characterize soot aging process in the isoprene/SO_2/NOx system?

Using isoprene/SO_2/NOx as the reaction system and addressing at soot aging as well as secondary particle formation, this study simulates the photochemical process of soot aging with VOC from natural sources and SO_2 to monitor the changes of gaseous pollutants (SO_2, NOx, O_3) concentration and particle size distribution, mass concentration, effective density, coating thickness and dynamic shape factor during experiments. Influence of different factors (gas-phase composition and relative humidity) on soot aging characteristics and formation of SOA are analyzed. This paper aims at assessing the interaction mechanism of SO_2 and isoprene on soot aging process, confirming the key factor of soot aging characteristics and secondary particle formation, and providing effective data for the complex atmospheric pollution.

2. Method

2.1. Smog chamber setup

The schematic diagram of CAPS-ZJU (Complex Air Pollution Study-Zhejiang University) smog chamber is shown in Fig. 1. The CAPS-ZJU chamber consists of an injection system, a reaction system and a

Table 1

Summary of chamber experiments in VOCs-NOx and VOCs-SO_2-NOx system.

System	Seed aerosol	T (°C)	RH %	Light source	Results	References
Isoprene/NOx	Soot	29–31	20 ± 4	UV lamp	Promote soot aging	(Khalizov et al. 2013)
Toluene/NOx	Soot	29-31	8	UV lamp	Promote soot aging	(Qiu et al. 2012)
Propylene/NOx	Soot	30	60	UV lamp	Soot reconstruction	(Lu et al. 2009)
Isoprene/NOx/O_3	Soot, AS[a]	23–25	45	dark	Soot reconstruction	(Saathoff et al. 2003)
Isoprene/SO_2/NOx	AS	NA[b]	NA	UV lamp	Promote SOA yields	(Edney et al. 2005)
Isoprene/SO_2/NOx α-Pinene/SO_2/NOx	AS	25	30	UV lamp	Promote SOA yields	(Kleindienst et al. 2006)
MBO/SO_2/NOx	AS	24–26	<3, 30	UV lamp	Promote SOA yields	(Jaoui et al. 2012)
α-Pinene/SO_2/NOx	Al_2O_3	30	12, 50	UV lamp	Promote sulfate formation	(Chu et al. 2015)

[a] AS represents $(NH_4)_2SO_4$, NA represents that data was not available.

[b] NA represents that data was not available.