Journal of Aerosol Science 105 (2017) 1–9

Contents lists available at ScienceDirect

Journal of Aerosol Science

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

Experimental evidence for the sintering of primary soot particles

Kiminori Ono[a,b,*], Kazuki Dewa[a], Yoshiya Matsukawa[a,b], Yasuhiro Saito[a], Yohsuke Matsushita[a], Hideyuki Aoki[a], Koki Era[a,c], Takayuki Aoki[c], Togo Yamaguchi[c]

[a] *Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Miyagi , Aoba-ku, Sendai 980-8579, Japan*

[b] *JSPS, Japan*

[c] *ASAHI CARBON CO., LTD., 2 Kamomejima-cho, Higashi-ku, Niigata 950-0883, Japan*

ARTICLE INFO

Keywords:
Soot
Sintering
Surface growth
Aggregate
Tandem differential mobility analysis
Aerosol

ABSTRACT

Sintering behavior and the contribution of soot produced in the absence of oxygen are experimentally investigated. A tandem differential mobility analyzer technique equipped with thermophoretic sampling was used to reveal the change in the mobility diameter of soot aggregates, which is proportional to the surface area. The mobility diameter decreased with an increase in reheating temperature. The decrease in mobility diameter clearly shows a decrease in the aggregate surface area. SEM images also clearly showed the decrease in the surface area and the simplification after heat treatment. These are experimental evidence that sintering of carbonaceous particle occurs in the absence of oxygen. Acetylene, which is considered to promote surface growth, is also added to size-selected soot particles before heat treatment to investigate the effect of surface growth on simplification of aggregate structure. The addition of acetylene, which is relevant to the surface growth via the hydrogen-abstraction/carbon-addition (HACA) mechanism, did not affect the mean mobility diameter at low temperature around 1200 K. These results showed that simplification of soot aggregates would not be affected by surface growth caused via the HACA mechanism.

1. Introduction

Soot is a nanoparticle produced via the formation of polycyclic aromatic hydrocarbons (PAHs), and ultrafine soot particles affects health since they can penetrate the respiratory system more deeply than larger particles (D'Anna, 2009). Although soot is required to be reduced, carbon black, soot produced industrially, has been widely used as an important material in automobile tires, battery electrodes, and pigments in toners for laser printers. When soot is used as a material, the control over morphological features such as primary particle diameter and aggregate structure is important. Nevertheless, the techniques used to control soot morphology are based on trial and error, and the fundamental aspects of these processes are not well understood (Xiong & Pratsinis, 1991). Therefore, to reduce soot formation and control the morphology of carbon black, the formation mechanism of soot needs to be comprehensively understood.

Although several soot formation mechanisms have been proposed (D'Anna, 2009; Frenklach, 2002a; Richter & Howard, 2000; Wang, 2011), there is considerable agreement on the general features of the processes involved; these processes are summarized as follows. PAHs are produced by pyrolysis of hydrocarbons, which are mainly produced by the incomplete combustion of fossil fuels.

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[*] Corresponding author at: Department of Chemical Engineering, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Miyagi , Aoba-ku, Sendai 980-8579, Japan. Fax: +81 22 795 6165.

E-mail address: kiminori@tranpo.che.tohoku.ac.jp (K. Ono).

http://dx.doi.org/10.1016/j.jaerosci.2016.11.013
Received 9 April 2016; Received in revised form 18 October 2016; Accepted 25 November 2016

The molecular precursors of soot particles are thought to be heavy PAHs with molecular weights of 500–1000 amu (Richter & Howard, 2000). The hydrogen-abstraction/carbon-addition (HACA) mechanism captures the essence of the thermodynamic and kinetic requirements for the formation of PAHs(Frenklach, 2002a). During the mass growth process, these particles collide to produce larger spherical particles, which then aggregate into the final carbon black clusters. The particles are converted into amorphous carbon and a progressively more graphitic material in the furnace. Our recent experimental studies revealed the morphological changes in carbon black that occur with changes in temperature, residence time, and feedstock composition (Ono et al., 2012, 2013). In addition, a detailed kinetic analysis of these experimental conditions indicated that the nuclei concentration and nucleation rate strongly affect the morphology of carbon black (Ono et al., 2014a, 2014b). Our experimental results showed that the aggregate structure becomes ~~simple~~ one with less surface asperity with increasing residence time (Ono et al., 2012). Surface growth has proposed as the main factor responsible for this simplification and increasing particle sphericity (Balthasar & Frenklach, 2005; Morgan et al., 2007). Morgan, Patterson, and Kraft (2008) claimed that sintering, which is important for inorganic materials, is unlikely to be relevant to soot formation. Some characteristic sintering time models for inorganic materials such as Cu (Chepkasov, Gafner, & Gafner, 2016), TiO_2 or SiO_2 (Goudeli, Eggersdorfer, & Pratsinis, 2015; Hao, Zhao, Xu, & Zheng, 2015) have been developed continuously, some sintering model for soot have been proposed (Chen, Totton, Akroyd, Mosbach, & Kraft, 2014; Chen et al., 2013; Shishido et al., 2007). In contrast to inorganic materials, no reports of experimental evidence for the sintering of soot primary particles are found in the literature, although recent models of soot formation have included sintering. In addition, the contribution of surface growth and sintering to the simplification of soot aggregates is still not well understood, either experimentally or theoretically.

Several studies on the experimental investigation of the sintering behavior of inorganic and metal nanoparticles have been reported previously. Tandem differential mobility analyzer (TDMA) is a powerful tool that has been used to investigate the sintering behavior and rate of silver (Shimada, Seto, & Okuyama, 1994), titania (Nakaso et al., 2001; Seto, Hirota, Fujimoto, Shimada, & Okuyama, 1997; Seto, Shimada, & Okuyama, 1995), silica (Seto et al., 1997), and gold (Nakaso, Shimada, Okuyama, & Deppert, 2002) nanoparticles. TDMA has also been employed to reveal the oxidation behavior of soot (Higgins, Jung, Kittelson, Roberts, & Zachariah, 2001; Ma, Zangmeister, & Zachariah, 2013). Ma et al. recently introduced a new tandem ion-mobility method (differential mobility analyzer-aerosol particle mass (DMA-APM) analyzer) to study the size-resolved oxidation kinetics of freshly generated flame soot (Ma et al., 2013).

Herein, sintering behavior and the contribution of soot produced in the absence of oxygen are experimentally investigated. Accordingly, we introduce size-selected soot particles produced by the pyrolysis of hydrocarbons in the first electric furnace in the absence of oxygen using DMA on the basis of a measurement of its equivalent mobility diameter to the second furnace, allowing the investigation of primary particle sintering from the differences in mobility diameter. In addition, acetylene, which is considered to play an important role in surface growth, is introduced to the gas including monodisperse soot aggregates.

2. Experimental

The experimental setup (Fig. 1) shows a laminar flow reactor equipped with an electric furnace, a probe sampling system equipped with the first DMA, a second electric furnace, a scanning mobility particle sizer (SMPS) consisting of the second DMA, and an ultrafine condensation particle counter (UCPC). Soot was generated by the thermal pyrolysis of ethylene or benzene in an alumina tube ($\phi = 11$ mm and length = 640 mm) that is heated using an electric furnace from 1500 to 1800 K. Liquid benzene was introduced via a syringe pump into the nitrogen flow (TAIYO NIPPON SANSO, 99.9999%) and subsequently into the reaction tube through mass flow controllers at a flow rate of 3.0 NL/min. The benzene concentration was 0.14 vol% to prevent the formation of coke in the tube. The ethylene concentration was 1.0 vol% and the flow rate was 2.0 NL/min. The condition is summarized in Table 1.

The gas, including soot particles, was drawn into a sampling probe that was horizontally connected to the end of the reactor. The

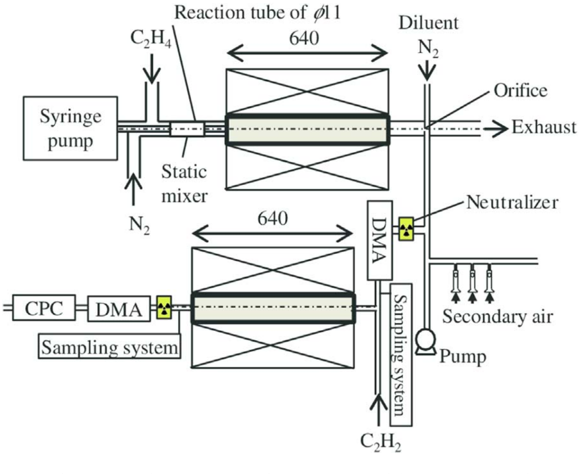

Fig. 1. Schematic diagram of the experimental apparatus used for sintering by the TDMA method.