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Formation mechanisms of soot from high-molecular-weight polycyclic aromatic hydrocarbons

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ABSTRACT

The feedstocks, including benzene, acetylene, and benzene with acetylene or 2–7 ring PAH, were pyrolyzed in an isothermal laminar flow at 1400–1650 K. The particle size distributions (PSDs) of soot and nascent soot were analyzed using a scanning mobility particle sizer (SMPS). The morphology of particles with the same mobility particle diameter was examined using a scanning electron microscope (SEM), where the grid was sampled via thermophoretic sampling assisted by a differential mobility analyzer (DMA). The soot produced by the pyrolysis of acetylene at 1400 K exhibited the highest number concentration and a log-normal distribution compared with those of the soot produced by the pyrolysis of benzene and the PAH additives. At 1500 K, the pyrolysis of PAHs with three or more rings with zigzag sites significantly increased the number concentration, although the added carbon concentration was smaller than that of acetylene. The addition of dibenzo[a,e]pyrene, which possesses three armchair sites, inhibited soot formation, suggesting that the bay site is easily formed and that the formation of anisotropic PAHs inhibits dimerization. The morphology of the soot formed by the addition of dibenzo[a,e]pyrene exhibited a primary particle diameter of 10 nm and similar primary particles, whereas the morphology of the soot formed by the addition of PAHs with zigzag sites clearly indicated a structure with a primary particle diameter of 20–40 nm. These observations indicate that the incipient soot is formed by the formation of dimers or small clusters of large PAHs via the mechanisms of aromatic molecule addition to aromatic radicals referred to as the PAH–addition cyclization (PAH–AC) mechanism at high temperatures, whereas moderate-sized PAHs developed via the hydrogen-abstraction–carbon-addition (HACA) mechanism form clusters and incipient soot at relatively low temperatures.

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1. Introduction

Soot is composed of nanoparticles of polycyclic aromatic hydrocarbons (PAHs), and ultrafine soot particles play a particularly important role in health since they can penetrate the respiratory system deeper than larger particles [1]. PAHs, especially benzo[a]-pyrene, which has recently been determined to be a human carcinogen on the basis of a wealth of experimental data [2], condense on the soot surface in ambient air. Minimizing the emissions of the nascent particles and PAHs require a good understanding of the formation mechanism of these materials. Although soot and PAHs are associated with human diseases, soot, also called carbon black, has been widely used as an important material for automobile tires, as battery electrodes, and as a pigment in toners for laser printers. More recent applications include the use of carbon black or carbon nanoparticles as a cathode catalyst in dye-sensitized solar cells, and as a catalyst support in direct methanol and other fuel cells [3]. Although the morphology of carbon black is controlled on a trial-and-error basis, control of the morphology of carbon black used in the aforementioned applications is nonetheless important. Our recent experimental studies have revealed morphological changes of carbon black that occur with changes in temperature, residence time, and the composition of the feedstock [4,5]. In addition, detailed kinetic analysis for these experimental conditions has indicated that the nuclei concentration and the nucleation rate strongly affect the morphology of carbon black [6,7]. A nucleation model for nascent soot particles, including carbon black, is important for simulating the exact morphology.

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These issues have been theoretically and experimentally addressed. The majority of the numerical studies performed with detailed soot formation models invoke irreversible dimerization of pyrene as a soot inception model for the condensed phase [8–11]. Several computational results, however, have shown that particle inception cannot occur through the physical dimerization of species smaller than circumcoronene [12–14]. The alternative method is a model for collision efficiency, defined as the ratio of successful collisions to the total number of collisions, and has been introduced to capture the particle size distributions (PSDs) of the experimental results [15,16]. However, these theoretical studies include substantial hypothesization, and the soot inception mechanism remains experimentally unclear. Experimental evidence for PAH coalescence, such as the formation of dimers, trimers, and clusters of PAHs, has been provided by a laser-ionization mass spectrometric study [17]. The mass spectra exhibited a periodicity with frequency around 500 amu, suggesting that PAH stacks are indeed the building block of nascent soot [3,18]. Miller et al. [19,20] suggested that the observed Raman signals for soot generated from for nitrogen-diluted, ethylene/air flame were attributable to particulate with crystallite of 1.0–1.2 nm, consistent with a molecular mass range of 500–1000 Da. Sirignano et al. [21] determined structural properties of the carbon particulate from particles inception to their maturation as a function of fuel identity in terms of H/C ratio and UV–Visible absorption. In addition, Russo et al. [22] detected the 200–10^{11} μ molecular weight range of the carbonaceous species size exclusion chromatography coupled with on-line UV–Visible spectroscopy. The chemistry of PAH formation has been partially elucidated by detailed kinetic models [9,23–28]. The ABF model [9] that includes PAH formation up to pyrene and is based on the hydrogen-abstraction–carbon-addition (HACA) mechanism, which was following model of Wang and Frenklach [23], has been widely used and extended. Richter developed a kinetic model describing the growth of PAH up to coronene and of C_{60} and C_{70} fullerenes [24]. Recent proposed models include hydrogen atom migration, possible free radical addition schemes, methyl substitution/acetylene addition pathways, a cyclopentadienyl moiety involved in aromatic ring formation, and naphthalene formation via fulvenallenyl radicals [25–29]. A kinetic Monte Carlo–aromatic site (KMC–ARS) model can describe the further growth of PAH as a PAH molecule in terms of the number of reactive sites present along its outer edge [30–32]. The mechanisms of aromatic molecule addition to aromatic radicals leading to the formation of aromatic–aliphatic linked biphenyl-like hydrocarbons were considered to describe further PAHs growth [33–35]. This reaction sequence is considered to be favored by the presence of a high concentration of five-member ring PAHs in the PAH inventory. These compounds are exceptional intermediates, as they grow rapidly, forming resonantly stabilized radical intermediates. Experimentally, *in situ* analysis using a time-of-flight mass spectrometer (TOFMS) has been conducted to elucidate new reaction pathways for the formation of PAHs [36–45]. Shukla collected mass spectra via an *in situ* sampling of the gas-phase reaction products of several hydrocarbons produced in a flow tube reactor at a low pressure of approximately 10 Torr, at relatively low temperatures for soot formation (1136–1507 K) and with a constant residence time of approximately 0.56 s, which is relatively long for soot formation [36–40]. The mass spectra showed an interesting sequence with respect to the feedstock, indicating a variation of the pathway depending on the feedstock (i.e., the phenyl addition cyclization (PAC) and the methyl addition cyclization (MAC) mechanisms, in addition to the well-known HACA mechanism). In particular, the HACA process is too slow to compete with the very fast PAH and soot formation processes because it only increases the mass of the product species by 24 amu in each step [46,47]. Alternatively, the *in situ* TOFMS analysis indicated that the collaboration of the PAC and the HACA mechanisms was important to meet the fastness of the soot formation process [48].

A scanning mobility particle sizer (SMPS) is a powerful tool for the analysis of the PSDs of aerosol particles, including soot, and offers a wealth of information about the formation and growth processes of incipient soot. Zhao et al. developed a reliable sampling technique that can effectively and systematically eliminate particle–particle coagulation and diffusive wall loss in the sample probe [49]. SMPS analysis of a laminar premixed ethylene–argon–oxygen flame revealed that the PSD followed a power-law dependence with respect to particle diameter at the onset of soot inception and that the PSDs subsequently became bimodal and remained bimodal throughout the flame [50]. The PSDs in the flame transitioned from an apparent unimodal PSD to a bimodal PSD at approximately 1800 K [51]. An SMPS has also been used to analyze soot formation dynamics during ethylene combustion in a configuration comprising a well-stirred reactor followed by a plug flow reactor [52]. Echavarria et al. [53,54] measured the evolution of the PSDs of soot in benzene, ethylene, ethylene/air, and ethylene/benzene/air flat flames. In agreement with the experimental data, the model, which was a detailed kinetic scheme with a discrete-sectional approach, also predicted the decrease of nucleation-sized particles in the postflame region for ethylene flames doped with benzene.

Although PAHs have been widely accepted as the soot inception reactants, ethylene, which is structurally far from being a PAH, has been used as a feedstock in most previous studies [49–52,55–59]. Several studies have attempted acetylene pyrolysis, which is widely accepted as an important role in the HACA mechanism, in a burner [60,61] or flow reactor [62,63]. Although these investigations have provided detailed knowledge about soot formation based mainly on the HACA mechanism, more complex species need to be used to clarify the soot inception process. Some studies on the analysis of PAHs formed by the pyrolysis of benzene [24,48,64], toluene [36,37], the addition of C_2 species to C_6 aromatics [39], ethylbenzene, and ethyl alcohol [65,66] have been reported. In addition, studies of the combustion and *n*- and *i*-butanol [67], and the addition of naphthalene to methanol [68] have provided information about the evolution of the size distribution of nascent soot. However, to our knowledge, no study has attempted the pyrolysis of pyrene, coronene, and other PAHs, which are considered the species involved in nascent soot formation.

The aim of this article is to study the formation mechanism of incipient soot by the pyrolysis of benzene and PAHs with 2–7 rings, including naphthalene, phenanthrene, anthracene, pyrene, dibenzo[a,e]pyrene, and coronene, solved into benzene. The PSDs of soot and nascent soot pyrolyzed from the feedstocks in a flow reactor at 1400–1650 K were analyzed using SMPS. The effect of PAHs could be directly investigated because additives were present at sufficiently high concentrations compared with the concentration of PAHs under the investigated combustion conditions. To study the reactivity of armchair sites, acetylene was added to phenanthrene or dibenzo[a,e]pyrene, which has the armchair sites. PSDs obtained using each feedstock and temperature led to an experimental evidence for the possibility of the mechanisms of aromatic molecule addition to aromatic radicals referred to as the PAH–addition cyclization (PAH–AC) mechanism. In addition, thermophoretic sampling, combined with a differential mobility analyzer (DMA), allowed detailed consideration of soot morphology, which was observed using a scanning electron microscope (SEM).

2. Experimental

The experimental setup shown in Fig. 1 includes a laminar-flow reactor equipped with an electric furnace, a probe sampling

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