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## Reaction pathway for nascent soot in ethylene pyrolysis

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## ABSTRACT

In this study, growth mechanisms of polycyclic aromatic hydrocarbons (PAHs) leading to soot formation were discussed. In addition, the effect of PAHs on soot nucleation was investigated by comparing the concentration of PAHs under sooting and non-sooting conditions. The feedstock ethylene was pyrolyzed in an isothermal laminar flow at 1150–1730 K with a residence time of 16–363 ms. Reaction pathways of PAH growth at each temperature were discussed using total ion chromatograms (TICs) of gas chromatography/mass spectrometry (GC/MS). These TICs suggest that the hydrogen-abstraction–carbon-addition (HACA) and methyl addition/cyclization (MAC) mechanisms are the main mechanisms for large PAHs at 1350 K and that phenyl addition/cyclization (PAC) also plays an important role at 1730 K. This paper was the identification of pathways previously rarely considered in soot models: the pathway via dimerization of acenaphthylene; the pathway from perylene to coronene; the pathway from tetraphene to benzo[k]tetraphene. Some significant peaks of aliphatic hydrocarbons were also detected in the TIC at 1730 K. The quantification of pyrolysates was examined by GC/MS with deuterides. At 1730 K, the number concentration of nascent soot increased along with the mole fraction of PAHs. Despite a relatively high mole fraction of PAHs with molecular masses of 200–300 u, no soot was observed at 1150 K. This indicates that such PAHs are not precursors of nascent soot.

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## 1. Introduction

Soot, which comprises nanoparticles formed from polycyclic aromatic hydrocarbons (PAHs) during combustion, has a harmful influence on our health because it can penetrate deeper than larger particles into the respiratory system [1–3]. PAHs, which exist on the soot surface, are also known to be carcinogenic, mutagenic, and teratogenic [4]. A better understanding of the formation mechanism of soot particles and PAHs may allow us to minimize emissions of these substances. In contrast, the soot called carbon black has been widely used as an important material for automobile tires, electrodes in batteries, and pigment in toners for laser printers. The morphology of carbon black, which strongly affects the performance of those applications, is controlled on the basis of trial-and-error. Our previous studies have experimentally revealed that the morphology changes with temperature, residence time, and the composition of feedstock [5,6] and have indicated that the nuclei concentration and nucleation rate strongly affect the morphology of carbon black with detailed kinetic analyses for those

experimental conditions [7,8]. The nucleation model for nascent soot particles, including carbon black, is of importance in the simulation of their exact morphology.

Soot formation models have been presented and revised by many researchers over the last few decades. Most of these models comprise chemical reaction of PAHs, nucleation, and physical coagulation of particles. The experimental photoionization mass spectroscopy of soot exhibits a periodicity with frequency around 500 u, suggesting that PAH stacks are indeed building blocks of nascent soot [9]. The nucleation model of nascent soot particles has been actively discussed. The majority of numerical studies performed have considered an irreversible dimerization of one or a very limited number of PAHs such as pyrene and coronene to be a soot inception model for the condensed phase [10–13]. However, several computational studies have evaluated the dimerization potentials of PAHs [14–16]. Molecular dynamics (MD) simulations to investigate the collision efficiency of PAHs of various sizes have shown that the particle inception cannot be caused through physical dimerization of species smaller than circumcoronene [16]. A model for the collision efficiency, defined as the ratio of successful collisions to the total number of collisions, has been introduced to capture the particle size distributions (PSDs) of the

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experimental results [17,18]. While they determined the collision efficiency by parameter-fitting to the experimental data, some researchers have attempted to obtain collision efficiencies for several PAHs by molecular dynamics simulation [16]. However, these theoretical works include significant estimation, and the soot inception mechanism is still not clearly understood experimentally.

Experimentally, the PSD probed by a scanning mobility particle sizer (SMPS) [19–25] or atomic force microscopy (AFM) [26] indeed displayed a bimodal distribution of particle mass growth, indicating that the dynamics of particle growth are governed not only by coagulation but also by particle nucleation and surface reaction. Results from an inclusive analysis of AFM, transmission electron microscopy (TEM), helium-ion microscopy (HIM), and infrared spectrometry coupled to a microscope (micro-FTIR) suggest that the particles are liquid-like at the time of impact on a substrate surface and that significant amounts of aliphatic compounds are present in the nascent soot formed by the ethylene–argon–oxygen flame [23,27–29].

The gas-phase chemical reaction for PAHs has been discussed using detailed kinetic models [11,30–36]. The detailed kinetic model by Appel et al. [11] includes PAH formation up to pyrene based on  $C_2$  and  $C_4$  additions, the so-called hydrogen-abstraction–carbon-addition (HACA) mechanism, which follows the model of Wang and Frenklach [30]. Richter et al. developed a kinetic model describing the growth of PAHs up to coronene and of  $C_{60}$  and  $C_{70}$  fullerenes [31,32] with consideration of  $C_2$  addition. These two models have been widely used and extended by many researchers [33–37]. Experimental in situ analysis with time-of-flight mass spectrometry (TOFMS) has been performed to probe additional reaction pathways for the formation of PAHs [38–47]. Shukla et al. detected mass spectra via an in situ sampling of the gas-phase hydrocarbons produced in a flow tube reactor at low pressure around 10 Torr and relatively low temperatures for soot formation (1136–1507 K) with a constant residence time of around 0.56 s [41–44,48]. The mass spectra with the signature sequence indicated pathway difference with a feedstock (i.e., phenyl addition/cyclization (PAC) and methyl addition/cyclization (MAC) in addition to well-known HACA mechanism). Although the in situ direct sampling technique gives us insight into PAH formation, the lack of possible isomers and the postulates to determine the attribution of isomers may cause misinterpretation. While some very recent approaches achieve the qualification of species with TOFMS analysis [38,45–47], sufficient accuracy of analysis for large PAHs has not been obtained.

Unlike the in situ direct sampling technique, the ex situ trap technique enables us to analyze possible intermediates and easily quantify those species. High-performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS) analysis for PAHs and soot formed in a premixed benzene/oxygen flame gave concentration profiles for the fullerenes  $C_{60}$ ,  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ , and  $C_{84}$ , and PAHs up to 300 u [49]. Ergut et al. [50–53] collected the volatile and semivolatile organic compounds from the combustion of ethylbenzene and ethyl alcohol on quartzwool and XAD-4 placed in a sampling probe coupled with the cooling jacket and these compounds extracted from the collected samples using an accelerated solvent extractor. The results showed quantification of PAHs up to 5-membered rings. Recent trap techniques for  $C_3$  and  $C_4$  hydrocarbon pyrolysis with HPLC with diode-array ultraviolet-visible absorbance detection has led to the identification of 80 PAHs with three to nine rings [54,55]. To improve capture rate of condensing products, two or three cold traps set at 195–276 K were used [56–58]. Although these works contribute to a better understanding of PAH formation, the residence time for soot formation or the kinetics of PAH formation is relatively long. Ergut et al. [53] investigated PAH formation in the sooting limit with an

equivalence ratio, but the effect of residence time on the sooting limit has not been clarified. Our recent experimental study indicated that the critical particle size of the soot formed by ethylene pyrolysis was affected by the reaction temperature and the residence time. In particular, the critical diameter at 1350 K was over 3 nm [59].

The present study attempts to clarify the reaction pathway for large PAHs and nascent soot in ethylene pyrolysis in an isothermal laminar-flow reactor at a wide range of temperatures (1150–1730 K) and residence times (16–363 ms). Because the condition was the same in our previous experiment with SMPS, the sooting appearances under each condition were judged from these PSDs [59]. The pyrolysates – including PAHs with 2–7 rings and the isomers – were analyzed in detail using GC/MS. The techniques for the extraction and condensation allowed for the detection of minor species, which have high boiling point, high melting point, low solubility, and low concentration, e.g. benzo[k]tetraphene and dibenzo[def,mno]chrysene. Because of difficulty to analyze the minor species, most of them have not been detected and previous studies. The information concerning minor species helped us to consider the reaction pathway for large PAHs and nascent soot in detail. Furthermore, the former compounds involved in the formation of nascent soot were discussed by comparing the species around sooting limit.

## 2. Experimental

The experimental setup shown in Fig. 1 comprises a laminar-flow reactor heated by an electric furnace, a probe sampling system, and either a scanning mobility particle sizer (SMPS) device or a sample-collecting system. Soot was generated by the thermal pyrolysis of ethylene in an alumina tube ( $\Phi=11$  mm, length=650 mm) over a temperature range of 1150–1730 K at atmospheric pressure. A mixture of ethylene (99.99%) and nitrogen (TAIYO NIPPON SANSO, 99.9999%) was supplied through mass flow controllers and a static mixer (Noritake, T3–21) into the reaction tube. The concentration of ethylene was 1 vol% at all pyrolysis conditions. The residence time was defined as the time during which the feedstock gas passed through the axial temperature area with a temperature greater than 90% maximum and was controlled by a carrier gas flow rate in a range of 0.5–7.0 NL/min. The gas including soot particles and species was drawn into a sampling probe connected horizontally at the end of the reactor and was immediately diluted in the probe by nitrogen at a flow rate of 1.0–3.0 NL/min. The setup for the dilution probe and the determination of the dilution ratio have been explained in detail in a previous publication [60]. The sampling from the center line allowed us to neglect the radial distribution of temperature and the residence time. The dilution ratio was controlled by a pump and a regulator.

The appearances of both the sooting and the sooting-limit were judged based on the PSDs in our previous study [59]. In this study, the sooting-limit was defined by minimal residence time when nascent soot was detected by SMPS. Only in the case of the non-sooting condition, we confirmed using SMPS that no soot particle was formed. The sooting appearances at each residence time and temperature are shown in Table 1.

The sample condensation was performed separately from the SMPS analysis. The condenser comprised three cold traps filled with glass beads set at 273, 258, and 193 K, respectively. The samples collected on beads and walls of traps were extracted by ultrasonic-assisted extraction with 600–1000 mL of toluene (Wako Pure Chemical Industries, for Pesticide Residue-PCB Analysis) at least twice for 10 min. The extracts were then concentrated in a rotary evaporator. Subsequently, the sample was condensed to approximately 1 mL under nitrogen. The extract was

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