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論文内容要約

【Chapter 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. 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. 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. Nevertheless, the formation mechanism of soot and the evolution of morphology are not still understood. In this thesis, to overcome the above problem, experimental and numerical investigation are attempted. The abstract of each chapter are summarized as follows.

【Chapter 2: Effect of Furnace Temperature and Feedstock Composition on Morphology of Soot】To investigate relationship between the formation mechanism and the configuration of soot and clarify the factors controlling its configuration, soot was produced by the pyrolysis of benzene and benzene/acetylene in an inert atmosphere. With a high furnace temperature and short residence time, the mean primary particle diameter decreases and the aggregate shapes are complex. This result implies that chemical reactions are promoted and that there are more high-molecular-weight PAHs, which contribute to nucleation, than low-molecular-weight PAHs, which contribute to surface growth. As a result, the collision rate increases. With high furnace temperature and long residence time, the mean primary particle diameter increases and the aggregate shapes are relatively simple. However, the shapes remain mostly unchanged with increasing residence time. These results indicate that the sintering of primary particles, which contributes to the simplification of aggregate shapes, occurs at a high temperature and long residence time.

When the acetylene concentration is changed and the benzene concentration is made constant, aggregate shapes become complex as the acetylene concentration increases. However, in the case where the acetylene concentration is larger than the benzene concentration, the variations in the aggregate shapes are small with an increase in acetylene concentration, because surface growth occurs and the collision rate decreases owing to an increase in the mean primary particle diameter. In the case where there is a change in the furnace temperature, the flux of soot particles increases. Also, the mean primary particle diameter

decreases with an increase in furnace temperature because the rate coefficient for the reaction between benzene and acetylene increases. In addition, aggregate shapes become complex with an increase in furnace temperature. Therefore, from the observations we conclude that nucleation occurs and aggregate shapes become complicated when the ratio of the benzene and acetylene concentration is suitable (about 2:1 in this study), and the furnace temperature is high. However, in the case where benzene or acetylene concentration is large and the furnace temperature is low, the aggregate shapes are simplified because of the formation of small PAHs, which contributes to surface growth.

【Chapter 3: Optimum Condition for Complex Morphology of Soot using Detailed Kinetic Analysis】We used a fixed sectional approach by applying the detailed chemical kinetic reactions for our previous experimental work described in chapter 2. By comparing the numerical behavior of PAHs formation and nucleation with experimental configurations of soot, the impacts of the behavior of PAH formation and nucleation on the configurations are discussed. The comparison of numerical and experimental studies showed the validity of the present model above 1573 K. The log-normal component of the bimodal shape suggests that particles sufficiently collide, and it is possible that the aggregate shapes are complex in the log-normal component. Aggregate shapes produced at 1673 K are likely to become drastically complex and then simple with an increase in residence time, while the shapes produced at 1573 K are likely to become gradually more complex. The impact of furnace temperature on the particle size distribution and morphology of soot was further investigated by implementing the calculation with the temperature being constant. The aggregate shapes would become the most complex at 1850 K with residence time of around 40 ms for the current benzene pyrolysis.

The nuclei mole fraction increases with additive concentration, which strongly affects the complexity of the aggregate shape. Specifically, when the amount of benzene added to 3.0 vol% acetylene is increased to 5.0 vol% benzene, the particle number concentration of 30–80-nm-sized particles, which are considered as primary particles or spherical aggregates, increases. The increase in the number concentration of 30–80-nm-sized particles contributes to the simplification of the aggregate shapes. When acetylene is added to 1.0 vol% benzene, although the particle size distribution at 200 ms begins to shift to a bimodal shape with the addition of 0.5 vol% acetylene, a log-normal shape clearly appears at 200 ms with the addition of 5.0 vol% acetylene because the nuclei mole fraction reaches equilibrium at 200 ms. Thus, if the reaction is quenched before small particles (<10 nm in size) collide with larger particles with a log-normal shape, the complexity of the aggregate shape increases. The results for both of these cases indicate that the calculated nucleation behavior and the particle size distribution describe the aggregate shapes obtained experimentally.

【Chapter 4: Speed up and Validation of Cluster-Cluster Aggregation Method】

This study presents the validity and ability of an aggregate mean free path-cluster–cluster aggregation (AMP-CCA) model, which is a direct Monte Carlo simulation, to predict the aggregate morphology by comparing the particle size distributions (PSDs) with the results of the fixed sectional model associated with the stochastic approach. We introduce a new collision

detection method obtained by modifying the grid partitioning method, which employs spatial- and cell-partitioning, into the AMP-CCA model. This modification allows the AMP-CCA model to calculate the three-dimensional aggregate morphology and particle size distributions (PSDs) with computational efficiency. As compared with the previous model, the new model successfully calculates the morphology in 15% of the computational time. The PSDs calculated by the AMP-CCA model with the calculated aggregate as a coalesced spherical particle are in reasonable agreement with the results of the sectional model regardless of the number concentration of particles. The shape analysis using two methods, perimeter fractal dimension and the shape categories, has demonstrated that the aggregate structures become complex with increasing number concentration. The AMP-CCA model provides a useful tool to calculate the aggregate morphology and PSD with reasonable accuracy.

【Chapter 5: PAH Growth Mechanism and Nucleation Behavior】This chapter first attempts the clarification of the detailed reaction pathway for large PAHs and nascent soot in ethylene pyrolysis in an isothermal laminar-flow reactor in a wide range of temperature of 1200-1800 K and residence time of 16-363 ms. The condition of sooting limit, which includes none of nascent particle or a few nanometers, were determined by scanning mobility particle sizer (SMPS). The pyrolysates, including from 2-7 rings PAHs and the isomers were analyzed in detail using GC/MS. The technique for extraction and condensation allowed for detection of major species and intermediates, which have not been detected in previous studies, at an inception stage and consideration of reaction pathway for large PAHs and nascent soot in detail. Furthermore, the former of nascent soot was discussed by comparing the species around sooting limit.

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 the 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 of soot particles and a log-normal distribution compared with those of the soot produced by the pyrolysis of benzene and the PAH additives. At 1500 K, as shown in Figure, 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

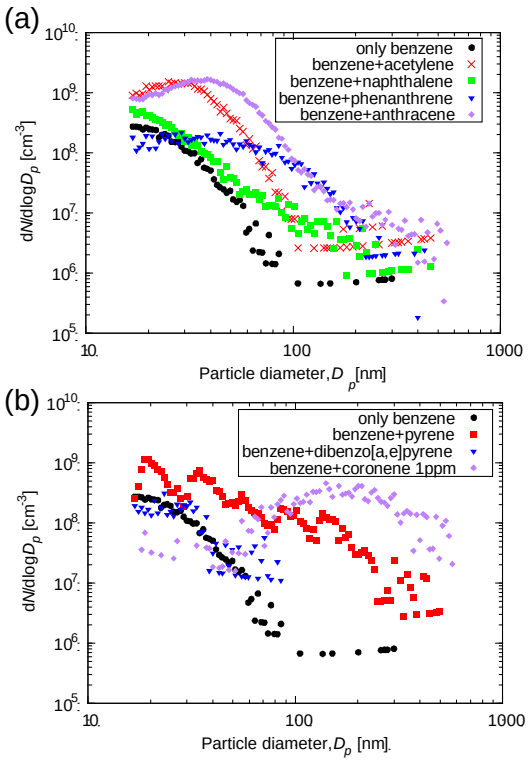

Figure PSDs of the soot formed by the 1500-K pyrolysis of (a) benzene or acetylene or 2–3-ring PAHs added to benzene and (b) benzene or the 4–7-ring PAHs added to benzene.

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.

【Chapter 6: Experimental Evidence for Sintering of Primary Particles of Soot】Herein, sintering behavior and the contribution of soot produced under no oxygen condition are experimentally investigated. Accordingly, we introduce size selected soot particles using DMA, which are produced by pyrolysis of hydrocarbons under no oxygen, on the basis of a measurement of its equivalent mobility diameter to second furnace, allowing for the investigation of sintering of primary particles by the difference of the mobility diameter. In addition, acetylene, which is considered to be an important role for surface growth, is introduced to the gas including soot aggregates with mono disperse. Mobility diameter decreased with reheating temperature. Considering the inert atmosphere, the decrease in mobility diameter clearly shows the decrease in surface area of an aggregate. Although possibility of oxidative sintering of soot and sintering of silica and titania nanoparticles have been reported, the present study indicate that sintering of carbon nanoparticles occur in spite of inert atmosphere.

【Chapter 7: Conclusion】This paper presents the study to clarify the formation mechanism of soot and the evolution of morphology experimentally and theoretically. This paper includes new knowledge about the PAH formation mechanisms, nucleation behavior, which strongly affects the morphology of soot, conditions to control the morphology.