Effect of Furnace Temperature on the Nucleation Behavior and Configurations of Carbon Nanoparticles

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ABSTRACT

The impact of nucleation behavior and particle size distribution on the morphology of carbon black is investigated using a fixed sectional approach by applying the detailed chemical kinetic reaction for our previous experimental work. The development rate of the particle size distribution increases with an increase in temperature and the size of small particles (size below 10 nm) decreases with an increase in residence time. To form the complex aggregate shapes, three requirements should be fulfilled: (i) large particle number concentration, (ii) high nucleation rate, and (iii) quench before small particles of size below10 nm collide with large particles consisting of a log-normal shape. The sensitivity of the furnace temperature on the particle size distribution and morphology of carbon black was further investigated by performing the calculation with the temperature being constant. With three requirements fulfilled, the aggregate shapes would become the most complex at 1850 K with a residence time of around 40 ms.

Keywords: carbon black, soot, particle size distribution, detailed chemical kinetic reaction; nucleation

1 INTRODUCTION

Carbon black, a carbon nanoparticle, is a type of soot that is produced industrially and is used for composite materials such as tires and electrode materials of batteries. The aggregate shape is one of the factors that affect the properties of composite materials. At present, because the technique used to control the aggregation of carbon black particles is basically a trial and error process, a theoretical solution is required to precisely control the aggregate shape.

Watanabe et al. [1] simulated aggregate formation in the furnace process using the cluster–cluster aggregation model. Their work indicated that particle number density contributes to the aggregate shape. In a recent study [2], to investigate the relationship between the formation mechanism and the configuration of carbon black and determine the factors controlling its configuration, carbon black was produced by the pyrolysis of benzene in an inert atmosphere. We concluded that the factors controlling the configurations of carbon black are nucleation, surface growth, and sintering of primary particles. However, these discussions lacked quantitative insights because chemical species and nuclei were neither measured nor simulated.

In contrast, in the research area of soot formation, numerous experimental and modeling studies have been conducted since two decades in an attempt to describe the formation mechanism of soot precursors and nuclei. Abid et al. [3] indicate that the particle size distribution functions (PSDFs) probed by a scanning mobility particle sizer demonstrate a persistent bimodality for an atmospheric-pressure ethylene–oxygen–argon flame. Although the nucleation behavior and the PSDFs has been investigated experimentally and numerically, little attention has been paid to control aggregate shapes of soot and carbon black.

The objective of the present study is to examine the impact of nucleation behavior and particle size distribution on the morphology of carbon black. We used a fixed sectional approach [4] by applying the detailed chemical kinetic reaction [5], and calculated for our previous experimental work [2]: the pyrolysis of benzene in an inert atmosphere. By comparing the numerical behavior of polycyclic aromatic hydrocarbons (PAHs) formation and nucleation with experimental configurations of carbon black, the impacts of behavior of PAHs formation and nucleation on configurations are discussed. The sensitivity to the different temperatures is explored and the effect of furnace temperature on the particle size distribution and morphology of carbon black was discussed.

2 METHOD

2.1 Gas phase kinetics and nucleation

The modeling of the gas phase chemistry and the formation and oxidation of carbon black particles is taken from Appel et al. (ABF model) [5]. The gas phase mechanism describes the oxidation of the fuel and the formation of PAHs. The PAHs chemistry is described up to pyrene, whereas further growth of the aromatic molecules is excluded from the present study. Particle inception is modeled by a nucleation reaction. Carbon black particles are formed by the nucleation reaction, which is modeled as dimerization of two pyrene molecules [5] in the present study. The surface growth sub-model described by the mass increase through the hydrogen-abstraction—carbon-addition (HACA) mechanism and the mass consumption

through the oxidation of OH and molecular O_2 was used in the ABF model [29].

2.2 Sectional method

A fixed sectional approach for soot particle dynamics proposed by Kumar and Ramkrishna [6] offers a combination of computational speed and accuracy, and was adopted to model agglomeration. The corresponding population balance equation (PBE), called the Smoluchowski equation, was designed to conserve two moments simultaneously. Kumar and Ramkrishna proposed a general discretization technique to preserve any two properties (e.g., mass and number density) of particle-size distribution. The proposed technique offers a general grid that can be effectively adapted to special situations including the ones that require a uniform grid in a certain size range and a nonuniform or geometric type grid elsewhere. The discretization of PBE is given as

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_{m_{i-1}\le(m_j+m_k)\le m_{i+1}}^{k\le j\le i} \left(1-\frac{\delta_{j,k}}{2}\right)\eta_{i,j,k}\beta_{j,k}n_j n_k - n_i \sum_{k=1}^{N_{\mathrm{BIN}}} \beta_{i,k}n_k \quad (1)$$

where n_i is the number concentration of size class i at time t, $\beta_{j,k}$ is the collision kernel at which particles of size class j attach with class k, and $\delta_{j,k}$ is the Kronecker delta. For a particle size class i, the first and second terms on the right-hand side correspond to birth and death due to aggregation. The parameter $\eta_{i,j,k}$ is the fraction of a newly created particle that the size class i will receive when two particles of sizes j and k are combined. We used the bins distributed geometrically as

$$m_{i+1} = f_s m_i \quad (2)$$

where f_s is a geometric spacing factor that was set to 2.0 in the present study.

2.3 Experimental method

The sectional method was applied to our previous experimental work [2] and the experimental procedure is described in detail elsewhere [2]. Carbon black was produced by the thermal pyrolysis of 1.2 vol% benzene entrained by a N_2 carrier flow. The reactor consists of an alumina tube and is heated by an electric furnace. The reaction tube used in the present study had an ID of 11 mm. The axial gas temperature in the reaction tube was measured using an R-type thermocouple in a preliminary experiment. The temperature distribution was used as input data. The flat temperature zone (length = 350 mm) was set to 1473, 1573, and 1673 K. Although the residence time was defined as the time during which the feedstock gas passes through the zone [2], in this study, the whole part (length = 1000 mm) was used in the calculations because the reaction may proceed owing to the increased temperature.

3 RESULTS AND DISCUSSION

The starting point of the discussion is the validation of the numerical model by comparing the particle size distribution obtained with the sectional model and image analysis of TEM pictures of the experimentally produced particles. In Figure 1, the computed particle size distribution is compared with the experimental measurements [2] at different temperatures. The numerical results at 1573 and 1673 K very well predict the experimental data, while the numerical result at 1473 K underpredict the experimental data. This difference could be due to the used detailed kinetic model described as the ABF model. [5]. The ABF model has been constructed based on a laminar premixed flame of ethane, ethylene, and acetylene, whose PAHs formation is mainly described by the HACA reaction. This study apparently suggests that the numerical concentrations agree well with the experimental values at higher maximum flame temperatures, while there is a difference between the numerical and experimental data owing to large lower maximum flame temperatures. Shukula and Koshi [6] carried out toluene pyrolysis in a flow reactor at temperatures between 1136 and 1507 K, and suggested that the role of aromatic radical-radical and radical-molecule reactions are dominant in the low and moderate temperature regions (< 1500 K) and that the HACA mechanisms are dominant in the high temperature region (> 1500 K) owing to the production of smaller species (especially acetylene) produced by toluene for the PAHs formation. These results confirm the underprediction of the result at 1473 K, particularly suggesting that a phenyl addition needs to be reconsidered to describe the pyrolysis behavior below 1500 K. Although the numerical results at 1573 and 1673 K are consistent with the experimental results, the peaks predicted by the numerical results are slightly larger than that seen in the experiments. This difference is caused by not considering depth effects in the TEM image and by fact that the numerical diameter was calculated using the particle volume. Considering that the PAHs formation above 1500 K is described as the HACA mechanism, the numerical results of the present study above 1500 K are sufficiently reasonable.

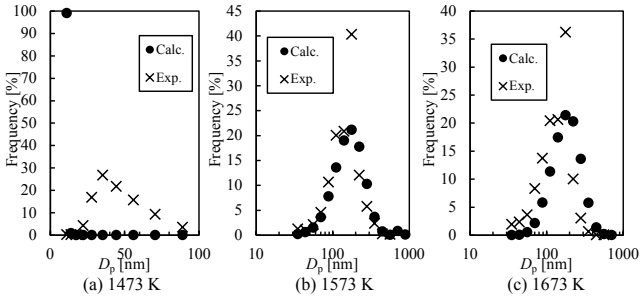


Figure 1: Comparison of experimental [2] and calculated particle size distributions in a reactor.

To examine the impact of the nucleation behavior and particle size distribution on the morphology of carbon black, the previously obtained experimental results of carbon black configurations [2] are now briefly described. Under these conditions (the reaction tube ID was 11 mm and feedstock flow rate was 3.0 L/min), the aggregate shapes became complex with an increase in furnace temperature. The variation between 1473 and 1573 K was particularly large, and the variation became small between 1573 and 1673 K. The carbon black structures formed in the reactor are largely dependent on the formation and concentration of solid particles. The features of the complicated structures are as follows: (i) the number of particles per aggregate is large and (ii) the specific surface area is large, which means that the primary particle diameter consisting of the aggregates is small. The complexity of the carbon black structures could be owing to the increase in the frequency of particle collisions because of an increase in the number of nuclei [2]. As shown in Figure 2, the computed nuclei mole fraction increased with an increase in furnace temperature, and hence these computed profiles strongly support above consideration. The variation in complexity between 1573 and 1673 K could be attributed to a decrease in the specific surface area of an aggregate by surface growth and collision of small particles formed later. Aggregate shapes produced at 1673 K are likely to become drastically more complex and then simple with an increase in residence time, while the shapes produced at 1573 K are likely to become gradually more complex.

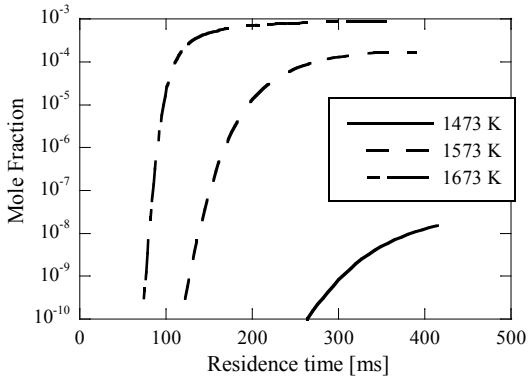
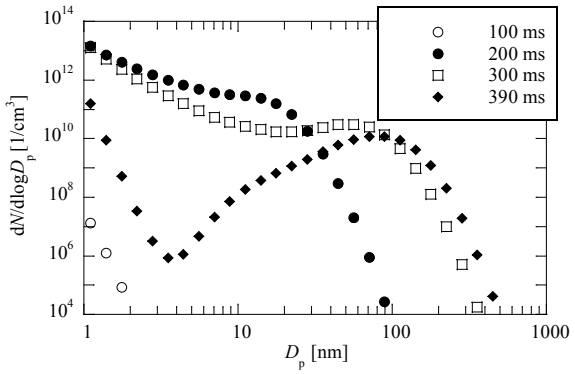
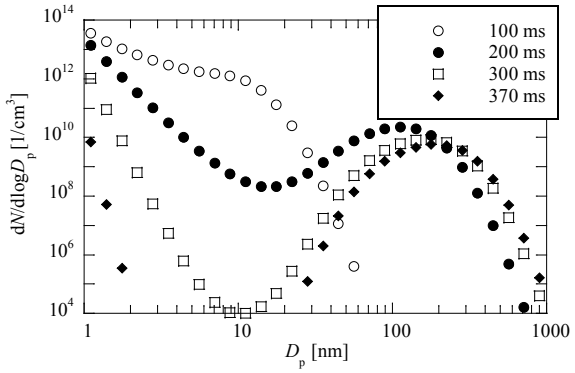


Figure 2: Variations in nuclei mole fractions.

Let us attempt to extend the above observation to the temporal change of the computed particle size distribution. Figures 3(a)–(b) show the variation of the computed particle size distribution at 1573–1673 K as a function of residence time. The calculated particle diameter, D_p, is described as the equivalent volume diameter of an aggregate and is not the primary particle diameter fundamentally. The particle size distribution above 1573 K initially shows bimodality, and gradually becomes unimodal with an increase in residence time: this is consistent with the results from other flame studies [7]. In experimental studies on the particle size distribution [7], because the critical level of the particle number density in the probe was about 10^5 cm^{-3}, we focus on the number density above 10^4 cm^{-3}. At 1573 K, very few particles were produced at a residence time of 100 ms, and the particle diameter increased gradually as the residence time increased. The particle size distribution remains clearly bimodal in shape at 390 ms (i.e., the furnace outlet point). At 1673 K, a second peak appeared at around 10 nm for the 100 ms residence time suggesting that the particle was produced quickly. The development rate of the particle size distribution at 1673 K is higher than at 1573 K. The bimodal shape matches the shape of the furnace outlet point at 1573 K at around 200–300 ms. Although the particles below 10 nm size remain, the log-normal shape appears clearly at 300 ms. As the residence time reaches 370 ms at the furnace outlet point, the small particles below 10 nm size are consumed and the particle diameter is increased maintaining the width of log-normal part constant. These results suggest that aggregate shapes would become complex when the obvious log-normal shape appears. The small particles below 10 nm that collide with large particles will increase the primary particle diameter and fill voids in the aggregates, leading to simplification of the aggregate shapes. Summarizing the above discussion, to form the complex aggregate shapes, three requirements should be fulfilled: (i) large particle number concentration, (ii) high nucleation rate, and (iii) quench before small particles of size below 10 nm collide with large particles consisting of the log-normal shape.



(a) 1573 K



(b) 1673 K

Figure 3: Variation of the particle size distribution in the reactors as a function of residence time.

To investigate fulfill three requirements, the impact of the furnace temperature on the particle size distribution and the morphology of carbon black was further investigated by implementing the calculation with the temperature being constant. The nucleation behavior to 100 ms (Figure 4) is discussed. The nucleation rate increases with an increase in temperature. Although the rate is nearly identical between 1850 and 2000 K, the behavior describes gradual curb below 1750 K. The mole fraction decreases with an increase in temperature: this is especially pronounced at 2000 K although the differences are small at temperatures below 1850 K. The two requirements, (i) large particle number concentration and (ii) high nucleation rate, are fulfilled when the temperature is 1850 K. This is consistent with the flame experiments conducted by Zhao [7], which suggested that the nucleation intensity in the soot mass growth region reduced in high-temperature flames above 1850 K. To examine the timing of quench before small particles of size below 10 nm collide with large particles consisting of the log-normal shape, particle size distributions at 1850 K is shown in Figure 5. At the onset of carbon black formation and growth of nuclei, the particle size distribution clearly appears as a power-law function around 1 ms. This suggests that the nuclei concentration instantly increases. The bimodal distribution is very obvious, and log-normal shapes clearly appear above 20–40 ms. Therefore, with three requirements fulfilled, the aggregate shapes would become the most complex at 1850 K with a residence time of 20–40 ms for the current benzene pyrolysis.

4 CONCLUSION

We used a fixed sectional approach by applying the detailed chemical kinetic reactions for our previous experimental work: the pyrolysis of benzene in an inert atmosphere. By comparing the numerical behavior of PAHs formation and nucleation with experimental configurations of carbon black, the impacts of the behavior of PAH formation and nucleation on the configurations are discussed. 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 carbon black was further investigated by implementing the calculation with the temperature being constant. Although the nucleation rate is nearly identical between 1850 and 2000 K, the behavior describes gradual curb below 1750 K. The mole fraction decreases with an increase in temperature, especially at 2000 K although the differences are small below 1850 K. To form complex aggregate shapes, three requirements need to be fulfilled: (i) large particle number concentration, (ii) high nucleation rate and (iii) quench before the small particles below 10 nm collide to large particles consisting of a log-normal shape. With these requirements fulfilled, the aggregate shapes would become the most complex at 1850 K with residence time of around 20–40 ms for the current benzene pyrolysis. Future work will comprise experimental confirmation of the above conditions for controlling the aggregate shape.

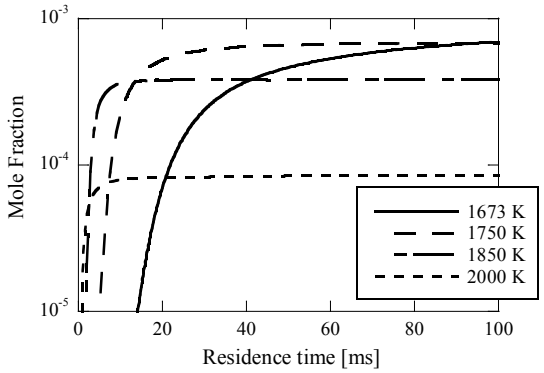


Figure 4: Nuclei mole fraction profiles computed at constant temperature.

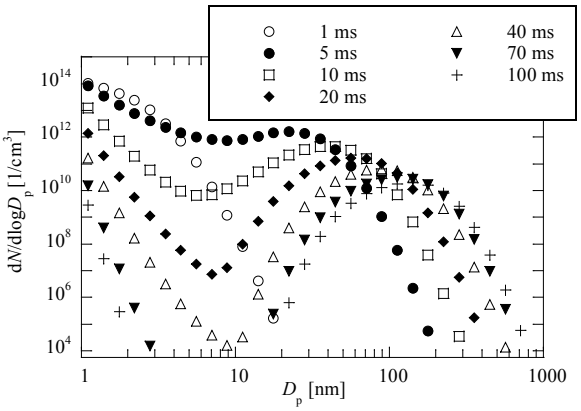


Figure 5: The particle size distributions at 1850 K

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