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Heat transfer and growth of nano- and submicron particles of black carbon in nonequilibrium gas mixture. Experiment and simulation

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ABSTRACT

It was shown experimentally and theoretically that heat transfer between carbon clusters and gas mixture substantially affects on growth of soot particles during ethylene pyrolysis in the shock tube. We used photoemission pyrometer for measuring of temperature of submicron carbon particles with microsecond temporal resolution, and bitmapped electron microscope for studying of geometrical parameters of primary carbon nanoparticles. Mathematical model of the nonisothermal carbon nanoparticles growth and results of its simulation is presented also.

1. Introduction

Black carbon (soot) particles are formed in various transformations of hydrocarbon fuels at relatively high temperature conditions. These conditions create some difficulties in experimental studies of black carbon formation. Nevertheless, there are a lot of works of experimental study and theoretical modeling of soot formation [1–6] and references therein. The main reason of such activity is that black carbon is widely used industrial product. It is now well established that black carbon particles affect the functioning of power plants and engines, on the climate changes, and human being health ([7–11] and references therein).

Kinetics of the formation of black carbon nanoparticles and their subsequent growth are challenging scientific problem at present. Unfortunately, the modern level of measurement technique does not meet all the requirements of such studies and cannot support theoretical researches. The basic problem for experimental studies is that primary soot particles are actually nanoparticles. Additionally, a short growth time of primary nanoparticles is a serious obstacle for experimental registration of parameters of heat and mass processes during the particles growth.

The deviation of the temperature of black carbon nanoparticles from the gas temperature during their formation and growth is the subject of growing interest of scientists, e.g. [12]. This deviation is the result of latent heat release of phase transition at condensation of carbon atoms. It also depends on a heat transfer rate of primary carbon nanoparticles with carrier gas in the nonequilibrium gas mixture. Obviously, the temperature of primary black carbon nanoparticles is a substantial parameter that affects many aspects of the growth and, no doubts, the pyrolysis of hydrocarbon vapor in its vicinity.

The aim of this work is to present results of our experimental and computational study of the interference of heat transfer and the growth of primary black carbon particles in supersaturated carbon vapor. In experiments this supersaturated carbon vapor has been formed due to ethylene pyrolysis in the shock tube. Some preliminary results have recently been published in [13]. It is worthy to note that in our experiments we used the photoemission pyrometer with microsecond temporal resolution [14,15].

The structure of the paper is the following. First, we describe out experimental setup. Then we analyze our experimental results about temperature of black carbon particles obtained in the shock tube during ethylene pyrolysis and condensation. Next, we discuss our simulation results on the formation of primary soot particles and calculation of temperature of black carbon nanoparticles. Some results of our simulations of the free molecular regime of the nonisothermal growth of primary nanoparticles are published in [16].

2. Experimental setup

Experimental study of black carbon formation was carried out on the setup based on the stainless steel shock tube with plane reflected wall. The tube diameter was 50 mm and its length was 7.1 m. The schematic of test section of shock tube is sketched in Fig. 1.

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Nomenclature

c	heat capacity per an atom, J/K
D	diameter of soot particle, m
g	number of atoms
k	Boltzmann coefficient, J/K
m	atomic mass, kg
m_c	particle mass, kg
N_c	number density of particles, m^{-3}
N_{dc}	number density of double particles, m^{-3}
n	numerical density of carbon vapor, m^{-3}
n_s	numerical density of the saturated carbon vapor, m^{-3}
p	pressure of gas, Pa
p_s	pressure of the saturated carbon vapor, Pa
R	radius of a particle, m
S	supersaturation of the carbon vapor
t	time, s
T	temperature of gas, K
v_a	volume per carbon atom in the condensed phase, m^3
v	mean thermal velocity of particle, m/s
U	latent heat of a phase transition per an atom, J

Greek symbols

ε	particle-to-circumscribed sphere volume ratio
λ	wavelength, m
ρ_c	carbon density, kg/m^3
σ	surface tension of the condensed carbon, N/m
σ_{SB}	Stefan–Boltzmann coefficient, $W/(m^2\,K^4)$
σ^*_{SB}	effective Stefan–Boltzmann coefficient, $W/(m^2\,K^4)$
Π	energy flux from the gas to a particle, $J/(m^2\,s)$

Subscripts

*	effective
5	behind the reflected shock wave
a	atom
c	carbon particle
car	carrier gas
max	maximum value
s	saturated
st	steady-state value

A prepared manometric ethylene–argon mixture (5% C_2H_4–95% Ar) was used for experiments. For monitoring pressure high-frequency pressure sensors were installed along the tube wall and in the reflected plane. To provide spectroscopic observations, two quartz rods 8 mm in diameter were mounted opposite to each other in the shock tube. Radiation impinged through one rod on a registering photomultiplier tube of the pulse photoemission pyrometer. The last registered the radiation of hot carbon particles to determine their temperature. The fundamentals of the photoemission method for temperature measurement were detailed in [16]. In particular, in our experiments the accelerating voltage of the pulse photoemission pyrometer was 1100 V and the retarding voltage realizing the separation of photoelectrons was −0.6 V.

Another rod was used to detect the radiation of C_2 radicals (transitions $A^3\Pi$–$X^3\Pi$) at the wavelength of λ = 516.5 nm and of hydrogen atoms (transitions H_α) at the wavelength of λ = 656.3 nm. For this purposes, two photomultipliers having narrowband interferometric filters with λ_{max} = 516.2 nm ($\Delta\lambda_{0.5}$ = 4.6 nm) and λ_{max} = 656.2 nm ($\Delta\lambda_{0.5}$ = 2.6 nm), respectively, were used.

Stainless steel plates were attached to the reflected wall to collect deposited soot produced in experiments. We examined the soot structure under a bitmapped electron microscope Carl Zeiss Supra 55.

The pyrolysis of the ethylene–argon mixture was studied behind the reflected shock wave at post-shock temperatures of 2000–3400 K. The gas pressure behind the reflected shock wave was 7.0–11.5 bars and the gas density was 1.61–1.63 kg/m^3. Post-shock gas parameters were calculated by the shock adiabatic curve, assuming the "frozen" chemistry, and by the temperature dependence of the heat capacity from shock wave velocity measurements at different locations along the tube.

The analysis of the experimental errors of our experiments showed that the measurement error of the incident shock wave velocity was of the order of 1%. When combined with the error associated with preparing a test mixture, this resulted in the 1.5% error in determining parameters behind a reflected shock wave. The temperature measurement error by the photoemission method did not exceed 5%. Registering the luminescence of C_2 radicals and hydrogen atoms allowed determining the induction time of a gas mixture that corresponded to the time interval between the arrival of the reflected shock wave and the 5% increasing of luminescence intensity with respect to its maximal value. Such a choice of a criterion for determination of the induction time could result in the 10% measurement error according to our estimates.

3. Experimental results

An advanced home-made photoemission pyrometer was used to measure a temperature of soot particles. Two series of experiments under the same initial conditions were carried out. In the first experiments, neutral color filters with the transmitting efficiency 3–70% were located in front of the pyrometer in order to detect carbon particle radiation without signal pining. Under the same conditions we then carried out experiments without neutral color filters (or using filters with higher transmitting efficiency) for exact temperature measurement at the initial detecting stage.

From the results of the first experimental series we observed that the temperature of black carbon particles initially was near the carrier gas temperature, but it dropped fast to the one that was lower than the gas temperature by 400–550 K and finally reached the steady-state. The rate of temperature change was about 10^6 K/s.

Results of the second series of experiments showed that at the initial detecting stage temperature of carbon particles was significantly higher then the carrier gas temperature. In different experiments the temperature difference between carrier gas and initial carbon particles temperature was about 550–900 K (Table 1). For lower temperature of pyrolysis (<2400 K) temperature of black carbon particles did not exceed gas temperature significantly.

Interesting experimental results are displayed in Fig. 2. For practically the same initial conditions we used a neutral color filter in front of the photoemission pyrometer in one experiment. We then registered experimental values without the use of this filter. Obtained results are presented in Fig. 2. As can be seen, the temperature of carbon particles is initially higher than the gas one but then due to fast cooling it has become lower than the gas temperature and, finally, reached its steady-state value.

As already mentioned above, the soot produced in experiments was collected and examined under a bitmapped electron microscope. The example of the obtained electron picture is shown in Fig. 3. By analyzing the electron pictures we found that the mean diameter, D, of primary carbon nanoparticles decreased from 55 to 27 nm if the pyrolysis temperature T_5 was varied from 2100 to 2800 K (Table 2). The standard deviation is about 6 nm.

Additionally, we detected the radiation of C_2 radicals (λ = 516.5 nm) and hydrogen atoms (λ = 656.3 nm) in the course of our experiments. We determined the induction time as a time difference between the arrival of reflected shock wave and the