

SOOT AND CARBON NANOPARTICLES FORMATION IN COMBUSTION

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Synthesis of carbon nanomaterials, such as the fullerenes, carbon nanotubes and graphene was carried out by evaporation of graphite arc – it is an expensive method that requires pure graphite and electrical energy. An alternative method is to get them into the burning mode sooting conditions.

The small size of structural components – typically up to 100 nm – determines the difference in the properties of nanomaterials from massive analogues. Flame is a self-sustaining system in which hydrocarbons can be precursors of carbon nanomaterials, and the heat released during combustion, is a parameter of the process control. The flame could be considered as a chemical reactor for the synthesis of the desired products. The main feature of the processes based on the combustion process is that the desired product is formed by reaction of combustion flowing spontaneously at elevated temperatures with a high speed without external energy input, i.e. by its own heat. With the development of nanotechnology there are new challenges for the synthesis of nanomaterials in the combustion mode.

The original results on development of carbon nano- materials of different functional application which were obtained at the Institute of Combustion Problems are presented in the article:

- Formation of soot and synthesis of fullerenes in flame;
- Formation of carbon nanotubes in flames;
- Formation of the hydrophobic soot in hydrocarbon flames;
- Formation of layered graphene films in the flames;
- Modeling of PAHs formation
- Full scheme of soot formation

The black (technological) carbon is used as a filler of elastometers (90% of the technological carbon is used for this purpose, and 2/3 of it — in the production of tires) and has a wide applications in printers. However, soot is a carcinogenic pollutant of the environment, formed as a result of the combustion of hydrocarbon fuels in power plants and engines. For example, diesel engines with direct fuel injection initially transform approximately 10–20% of the introduced fuel into the soot [1]. Coincidentally with the soot formation, fullerenes and nanotubes are formed by the mechanism competing with the mechanism of soot formation [2,3]. A knowledge of the conditions and mechanisms of formation of soot, fullerenes, and nanotubes in a flame allows one to change the combustion such that soot particles, fullerenes, or nanotubes are predominately formed.

At present a large number of experimental data on the processes of soot formation have been accumulated and different phenomenological models have been proposed [4, 5]. However, the mechanism of soot formation is imperfectly understood yet. This is explained by the fact that even in simple cases, such as the homogeneous pyrolysis of hydrocarbons, this process includes a large number of rapid simultaneous reactions leading to the formation of a new solid phase – soot particles (e.g., the time of transformation of methane with the molecular mass of 16 a.m.u into soot with the molecular mass more than 10^6 a.m.u makes up 10^{-4} – 10^{-2} s) [4].

Synthesis of fullerenes in flame

The structure of fullerene C_{60} proposed by R. Smalley resembles a football, so it is sometimes called footballene, and that of C_{70} resembles a rugby ball. Fullerenes C_{60} and C_{70} were identified in 1985 and prepared in macroscopic quantities in 1990, both by evaporation of graphite in an arc discharge [5]. In flames, fullerene ions were found in 1987, and in 1991, C_{60} and C_{70} were extracted in large quantities from laminar sooting flames of premixed mixtures of benzene and oxygen at low pressures and then spectroscopically identified [6].

The influence of gas discharge, the type of electrode, and the inter electrode spacing on the yield of fullerenes in combustion was studied.

The experimental conditions were as follows: C/O = 1, $p = 40$ torr, flow rate of benzene $250 \text{ cm}^3/\text{min}$, oxygen $758 \text{ cm}^3/\text{min}$, argon $101 \text{ cm}^3/\text{min}$, $v = 18.4 \text{ cm/s}$, $T = 1200 \text{ K}$, and $\delta = 0.5\text{--}0.8 \text{ cm}$; electrode systems are the needle-plane, plane-plane, and ring-plane with an inter electrode spacing of 4–21 cm; voltage $U = 0.5\text{--}20 \text{ kV}$. A premixed $C_6H_6/O_2/Ar$ flame under conditions corresponding to the maximum yield of fullerenes was studied [7].

Formation of carbon nanotubes in flames

The most promising way to produce carbon nanotubes is the flame method. In the synthesis of carbon nanoparticles using flames, part of the fuel is consumed in heating of the mixture, and part is used as a reactant, which makes this method more cost-effective than methods based on the use of electricity, pyrolysis of hydrocarbons or arc evaporation of graphite.

Results of a study of a flat diffusion propane–oxygen flame stabilized on an opposed-jet burner at atmospheric pressure are presented in [8]. Two opposed flows formed the flat flame. The flame was surrounded by an external nitrogen flow supplied from the burner matrices. A solution of catalyst [$Fe(CO)_5$] or an alcoholic solution of nickel nitrate] was sprayed by an ultrasonic nebulizer and delivered through a metal nozzle into the flame from the side of the fuel.

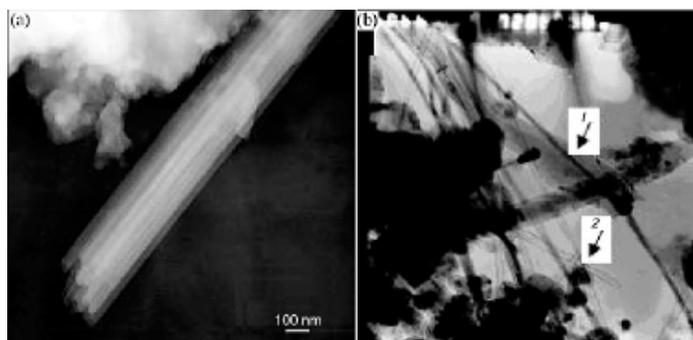


Fig. 1. Electron micrographs of samples: (1) carbon nanotube; (2) Ni in a carbon shell [8]

The resulting products were deposited on the walls of the reactor and collected in traps with liquid nitrogen. The temperature in the reactor was measured by a thermocouple, and in the flame by an Iron Ultrimax pyrometer. It is evident from Fig. 1 that the samples contain soot agglomerates, among which metal particles are encountered. It was found that under certain experimental conditions, well-ordered bundles of carbon nanotubes 20–30 nm in diameter formed.

Formation of hydrophobic soot in hydrocarbon flames

The formation of hydrophobic soot surface on silicon and nickel substrates during combustion of propane-oxygen flame was studied [9]. It is stated that the hydrophobic properties are due to the

presence of soot particles in the form nanobeads. Schematic diagram of the synthesis process and water droplets on superhydrophobic soot is shown in Fig. 2.

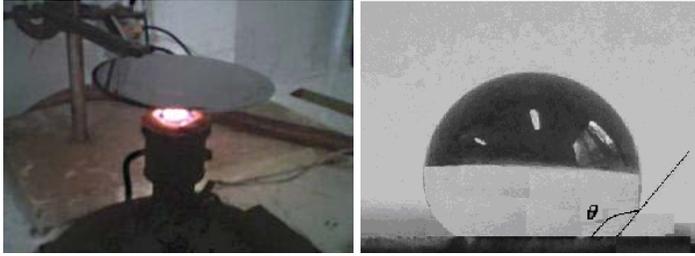


Fig. 2. Photo of schematic diagram of the synthesis process and water droplets on superhydrophobic soot [9]

Studies have shown that carbon deposits on the plates are differences in the morphological structure of deposited particles in different zones. In the central and middle zone formed long chains of individuals in the form nanobeads 15-30 nm without applying an electric field, and 40-50 nm when an electric field. In the outer zone, regardless of the conditions of combustion, there are coagulated aggregates of soot particles with sizes 30-50 nm.

The results for the exploration of the soot formation of hydrophobic surfaces on silicon substrates and nickel during combustion of propane oxygen flame are listed. The distance from the matrix burner and the substrate was varied, the exposure time and the influence of the electric field of different polarity and voltage. It is shown that at the exposure of more than 4 minutes the soot with hydrophobic properties is formed and a division of the soot surface area is occurred. The applying of an electric field narrows the soot deposition on the substrate and in diameter of 2.5-3 cm from the center, the soot super hydrophobic surface with a wetting angle of more than 170° is formed.

Synthesis of graphene in flame

The synthesis of graphene layers on a nickel substrate in a butane–benzene–oxygen premixed flame at a pressure of 40-100 Torr is studied. It is demonstrated that, the temperature of 900-950°C and exposure time of 0.5 min are sufficient for synthesizing graphene layers on a nickel substrate. It is shown that, at a pressure of 45-55 Torr, single-layer graphene is predominantly formed. It is found that, at a pressure of 90 Torr and an exposure time of 0.5 min, monolayer graphite can be produced, but with a lower yield as compared to that prepared at 45-55 Torr. It is demonstrated that the degree of defectiveness of graphenes decreases with the exposure time, reaching a minimum value of $I_D/I_G = 0.36$.

Graphene layers were synthesized at 40–100 Torr in a butane–benzene–oxygen premixed flame. For this purpose, the burner was placed in a quartz glass tube in which a low initial pressure, 5 Torr, was created. The experiments were performed at butane, oxygen, and benzene flow rates of 450, 740, and 70–120 cm³/min, respectively, which corresponds to C/O ratios of 0.8-0.9. The flame temperature in the graphene synthesis zone was 900-950°C, as measured by a Chromel–Alumel thermocouple. The substrate was a 0.2 mm thick (111) surface nickel plate pretreated in a 20% HNO₃ solution for 30 min.

It was shown [10] that, at low pressure, as at atmospheric pressure, graphene layers are formed in the presooting zone. Figure 1a shows Raman spectra typical of carbon structures formed on a nickel plate in zones 0, 1, 2, and 3 (Fig. 3b). In zones 0, 1, and 2 (Figs. 3a and 1b), amorphous carbon structures are formed, whereas in zone 3, graphene layers are synthesized. Note that, at low pressure, the width of the graphene formation zone (~5 mm at 40 Torr) is larger than that at atmospheric pressure. Above zone 3, a soot like structure is observed (Fig. 3b).

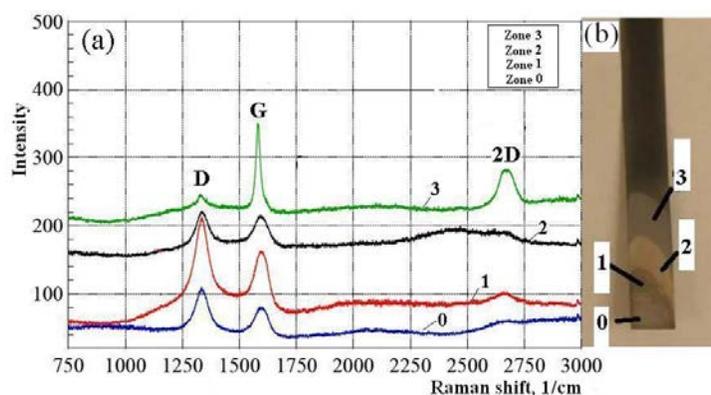


Fig. 3. The Raman-Spectra of carbon structures in accordance with (a) zones; and photo of nickel substrate (b) with an indication of formed carbon structure zones (P = 90 Torr, C/O = 0.8, T = 900 °C, t = 30 sec)

Analysis of the results showed that, at the pressure of 90 Torr, soot formation more strongly influences the process of graphene formation than it does at 45 Torr. In this case, typically 3 to 5 layers of graphene are formed. However, reducing the time of exposure of the substrate in the flame to 30 s makes it possible to obtain a graphene monolayer at the pressure of 90 Torr as well. The degree of imperfection of graphenes decreases and reaches a minimum value of $I_D/I_G = 0.36$, which brings them closer in quality to graphenes synthesized by the CVD method.

Modeling of PAHs formation

The formation of polycyclic aromatic molecules (PAHs) in flames is a key element in the process of soot formation. The reaction paths of formation of these precursors, primarily C_2H_2 , C_3H_3 , C_3H_4 , C_3H_5 , C_4H_2 , C_4H_4 , depend on the type of fuel and flame settings. Although the formation of polyaromatic molecules and soot in the combustion process fuels intensively studied, the final kinetic scheme has not worked out, it requires further refinement and optimization of kinetic parameters [11]. In work [12] has investigated the flames of acetylene, ethylene and propane to determine features of the formation of the first aromatic ring (benzene, C_6H_6) in flames saturated (C_3H_8) and unsaturated ($CH\equiv CH$, $CH_2=CH_2$) hydrocarbons.

On the basis of existing detailed kinetic schemes a general and consistent mechanism of the oxidation of hydrocarbons and the formation of higher hydrocarbons [11], were compiled for computational studies covering the characteristic properties of a wide range of combustion processes. Computed ignition delay times of hydrocarbon-oxygen mixtures (C_2H_2 [13], C_2H_4 [14], and C_3H_8 [14]) match the experimental values. The calculated absolute flame velocities of laminar premixed flames (C_2H_2 [15], C_2H_4 [16], and C_3H_8 [17]) and the dependence on mixture strength agree with the latest experimental investigations reported in the literature. With the same model concentration profiles for major and intermediate species in fuel-rich, sooting, premixed C_2H_2 , C_2H_4 and C_3H_8 air flames are predicted in good agreement with experimental data. An analysis of reaction pathways shows for C_2H_2 and C_3H_8 flames that benzene formation can be described by propargyl combination in high temperature.

The reaction pathway of benzene in flames C_2H_2 , C_2H_4 and C_3H_8 indicates that the formation of the first-aromatic benzene ring occurs at the same reactionary routes all flames, occurred after the decomposition of fuel and formation of aromatic precursors. The reaction pathways depend on the temperature. For low temperature $T < 1500$ K dominated pathway, which include the formation of C_2H_3 from C_2H_2 , and further C_4H_5 , which in reaction with C_2H_2 gives C_6H_6 . For high temperature at $T > 1500$ K dominated pathway to aromatic ring is H_2CCCH recombination [12].

The fullerenes formation is generally observed at pressures below 40 Torr [18], because for fullerenes formation is necessary an adherence of steric spatial factor, but in flames at

atmospheric pressure this factor is prevented by triple collisions. Therefore, the pressure coordinate can be introduced to the general scheme for soot formation. At low pressure the formation of fullerenes from polycyclic aromatic hydrocarbon (PAH) is occurred, but with pressure increase the polycyclic aromatic hydrocarbons (PAHs) are coagulates to soot particles. From (PAH) follows the graphene formation as intermediate product between PAH and soot particles, which is confirmed by the formation of multi-layered graphene films at atmospheric pressure and single-layered at the pressures below 60 Torr [19,20].

Full scheme of soot formation

To build a complete scheme for the rich fuel flames should be noted the work Jager [21] and Starik [22,23]. Jager noted in [21], nano- and subnanosize particles are formed by gas-phase condensation in asymptotic giant branched stars. Experiments were carried out at pressures of 0.1–2.6 and 7 mbar, close to the values of p in the astrophysical atmosphere at temperatures $T < 1\,700$ K, at which the formation of fullerenes was observed.

Kinetic model, which allows to determine the dynamics of the formation of polydisperse ensemble of charged particles from the birth of primary clusters should include both the kinetics of formation of heavy molecular components – the building material for the formation of these clusters. Also, the ions and electrons in the gas phase processes and the formation of these clusters, their growth surface, interaction with ions and electrons, and coagulation neutral charged particles and the ability of electron emission particles at high temperatures [22,23].

On the basis of the data on synthesis of fullerenes, carbon nanotubes, superhydrophobic soot and graphene in the flame it is possible to modify the general scheme proposed by H. Bockhorn [24] and Frenklach [25] for rich fuel flames, namely to make a pressure-coordinate, which allows the formation of fullerenes at low pressures, and soot at high pressures. In addition the scheme was completed by graphene formation as an intermediate product stage of graphene formation (Fig. 4) [26].

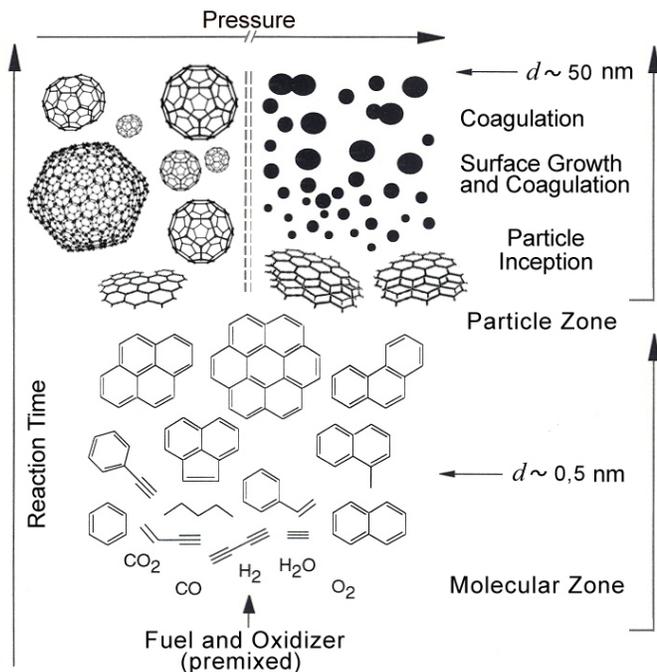


Fig. 4. Full scheme for soot, fullerenes and graphene formation in rich fuel flames

Conclusion

Fullerene formation developed diagram graphene and carbon black-rich hydrocarbon flames taking pressure, shows that the synthesis of fullerenes in flames, graphene and carbon nanotubes technology represents an alternative to existing methods of synthesis in the electric arc of graphite.

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