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Complete Scheme for Fullerene, Graphene, and Soot Formation in Flame

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Abstract

Soot formation processes have been studied for more than 100 years, they include empirical and phenomenological description of conversion of various fuels to soot particles. This article provides an overview of current state of soot formation foundations, including the chemistry of soot nucleation, nucleation, mass growth as well as size of soot particles. Consideration of this issue shows that a great progress has been made, but there is still a lot of ambiguity in many areas of our knowledge. This concerns the role of aromatic molecules and radicals in nucleation and subsequent growth mass in laminar pre-mixed flames. Along with environmental problems, in recent time there are considered soot particles as an environment for nanomaterial synthesis, such as fullerenes, carbon nanotubes and graphenes. In this regard, a complete scheme of nanomaterials formation in mode of soot formation has been developed.

1. Introduction

At the present time a large number of experimental data on soot formation processes have been accumulated and different phenomenological models have been proposed [1–6]. However, the mechanism of soot formation is imperfectly understood until now.

In accordance with general scheme, which was proposed previously by Frenklach [7] and Bockhorn [8] the precursor soot formation contributed to the formation of first aromatic ring, polycyclic aromatic hydrocarbons, as well as nucleation of soot particles growth (Fig. 1).

In pyrolysis of hydrocarbon fuel there are formed small species that containing two or four carbon atoms, also polycyclic aromatic hydrocarbons (PAHs) and polyacetylenes are presented there [9]. PAH and acetylene are formed during pyrolysis of aromatic fuel. The formation of acetylene through this process is based on Glassman and Yetter [10] and Ciajolo et al. [11] and Ahrens et al. [12]. There is some difference of opinion in details of soot precursors formation.

Different species such as polycyclic aromatic hydrocarbons, polyacetylenes, and ionic species have been proposed as soot particle precursors.

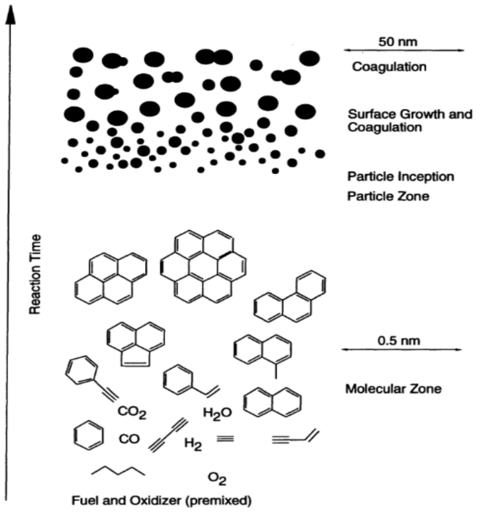

Fig. 1. A rough picture for soot formation in homogeneous mixtures (premixed flames) [8].

Frenklach and Wang [7] proposed that aromatic hydrocarbons once formed, aromatic rings grow by a sequential two-step process: H-abstraction which activates the aromatic molecules, and acetylene addition which propagates molecular growth and cyclization of PAH. This H-abstraction – C_2H_2-addition reaction sequence as HACA (Fig. 2). Following the Frenklach [13], it should be emphasized that PAH was assumed to be major precursor. It can

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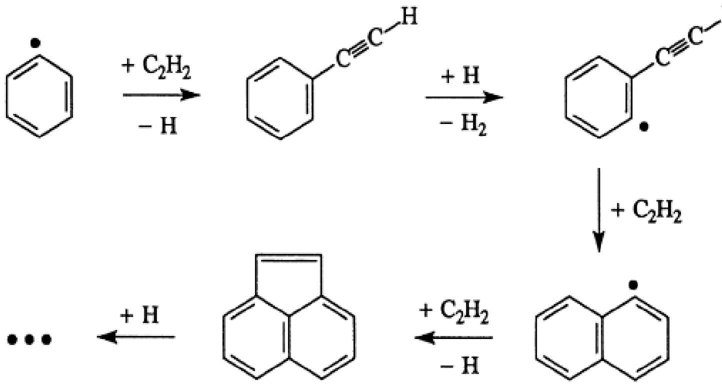

Fig. 2. H-abstraction-C_2H_2-addition reaction pathway of PAH growth.

be observed that PAH may represent the aromatic precursor in the phenomenological soot model.

As noted in [14], 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 $T < 1700$ K, at which the formation of fullerenes was observed.

The necessary condition for fullerene formation is a low pressure. As the pressure increases, i.e., with transition to atmospheric pressure or above, where triple collisions dominate, PAHs coagulate to form soot clusters. It has been shown [15] that the maximum of fullerene formation is shifted to the right relative to the maximum of soot formation. In a detailed study of fullerene formation from benzene flames, the second maximum at 70 mm from the burner matrix was detected [16]. These data have provided the basis for the development of an alternative method of producing fullerenes in the hydrocarbon combustion regime.

The main feature of technological combustion processes is that the desired product is produced by a combustion reaction which proceeds spontaneously at high temperatures, at a high rate, without energy expenditure from outside, i.e., due to its own heat release. Considerable interest of researchers and technical experts in methods of producing, structure and properties of nanoscale systems is due to the diversity and uniqueness of their practical applications. The small size of the structural components – usually up to 100 nm – determines the difference between the properties of nanomaterials and their analogs with larger particle sizes [17]. Soot particle formation is accompanied by formation of polycyclic aromatic hydrocarbons (PAHs), fullerenes and graphenes – (nanosized materials) each one can be obtained mainly under certain experimental conditions, so the regime of soot formation can be regarded as nanomaterials synthesis regime, which is the subject of the article.

Particle surface growth is the mass addition process to the surface of soot particle nuclei by chemical reaction with either small hydrocarbon species or larger aromatic molecules. The beginning of surface growth is not clearly distinguished from termination process of nucleation [18]. The relative contribution to particle growth of small hydrocarbon species and larger aromatic molecules depend on the process conditions. The process of particle growth by addition of PAHs is referred as PAH deposition. Frenklach [13], has considered that acetylene is the main growth element at the surface of soot particle.

The growth of soot particles by collision process is interpreted as "coagulation" when particles remain spherical, the term “agglomeration” is used when particles acquire a cluster structure. In both processes, the number of particles decreases, while the overall mass remains unchanged.

2. 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 [9]. In flames, fullerene ions were foundin 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.

In 1987, the fullerene ions such as C_{60} and C_{70} were discovered in flames and identified using mass-spectrometry method [19]. Howard [15] have obtained large amounts of C_{60} and C_{70} in laminar premixed flame using benzene and oxygen at low pressures. Despite graphite evaporation, the ratio of C_{70}/C_{60} is formed in flames and changed from 0.26 to 8.8 (in case of graphite evaporation, this ratio changes from 0.02 to 0.18).

Two ways of formation of fullerenes in flames were mainly discussed. Frenklach and Ebert [20] suggest that the number of the bent structures, i.e., PAHs containing five- and six-membered rings, increase successively, which leads to the formation of fullerenes. They believe that the "bent" PAHs are formed more rarely than the plane PAHs in flames, which is in agreement with measurements of the concentrations of the PAHs (including corannulene – a bent molecule) in the fullerene-forming flames [21].

Because fullerenes are formed at low pressures, the corresponding spatial orientation is important, which requires a consideration of the steric factor. For a molecule of C_{60} to form, a spatial orientation of two molecules of C_{30} is required. There are various models of formation of fullerenes C_{60}, one of which is the zip mechanism [12].

3. Formation of a layered graphene films in flames

The formation of layered graphene films was performed in the propane-oxygen flame using following conditions such as: propane flow rate is – 219.1 cm^3/min, oxygen flow is – 381.2 cm^3/min that corresponding to the ratio of C/O = 0.86. Two methods were used there, the first one with an addition of argon in benzene-oxygen mixture in an amount of 300–650 cm^3/min and the second one without argon. Catalytic substrates were made of copper and nickel and placed into the fire. Varied range of stay period of the substrate in the flame was: 5, 10, 20, 30, 40, 60 sec, 5 and 10 min, the angle varied in flame as follows: α = 0, 30, 45, 60, 85°. Flame temperature during experiments was in the range of 900–950°. The samples that formed at substrate were examined using Raman spectrometer "NTEGRA Spectra".

Investigations on synthesis of graphene layers in hydrocarbon flame at low pressure have shown that the formation of graphene layers is occurred in sooting zone as well as at atmospheric pressure, as was shown in [22–24]. Figure 3 shows the Raman spectra (a) that characterizing the carbon structures are formed on nickel plate in areas 0, 1, 2, 3 (b). In zones 0, 1 and 2 (Fig. 3a and b) the amorphous carbon structure is observed, but in zone 3 the graphene layers are synthesized.

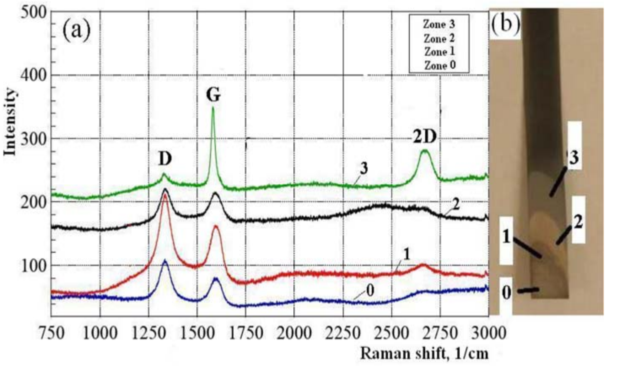

Fig. 3. The Raman-spectra of carbon structures in accordance with (a) zones; and photo of nickel substrate (b) with an indication of formed carbon structure zones (P = 90 Torr, C/O = 0.8, T = 900 °C, t = 30 sec) [23].

At that, an area of graphene formation at low pressure is more expanded than at atmospheric pressure. Above zone 3, there is soot structure is formed (Fig. 3b) [23, 24].

Analysis of the results of synthesis of graphene layers in the flame at low pressure and with addition of benzene showed that in the pressure range of 40–100 Torr one- to three-layer graphene sheets on nickel substrate are formed, which is characterized by the intensity ratio $I_G/I_{2D} \leq 1.3$. At a pressure of 55 Torr preferential formation of a single layer graphene is observed, its characteristic Raman spectra was shown in Fig. 4 [25].

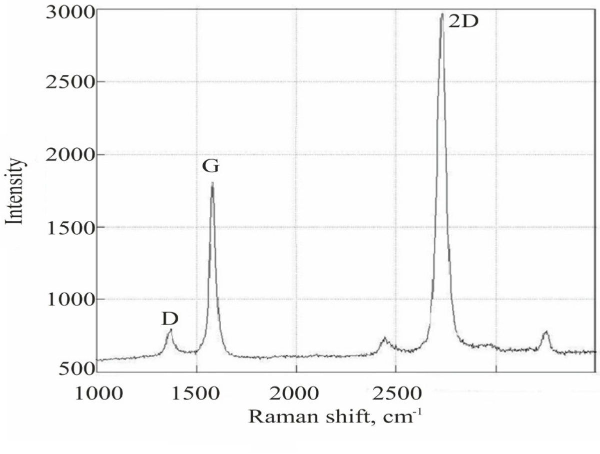

Fig. 4. Raman spectra of single-layer graphene samples obtained with the addition of benzene to C_3H_8/O_2 flame on a nickel substrate at a pressure of: 55 Torr (I_G/I_{2D} = 0.58)

4. Mechanism of soot formation in rich flames

Arad A. [26] has presented an article on soot formation modeling in diesel – biodiesel flames, where a classification of soot formation models was described. These models can be classified by three groups: empirical, detailed, and phenomenological.

It should be noted that over the last 40 years the studies on soot formation have mainly focused on environmental problems that associated with air pollution because of various fuels usage. It is known that soot affecting on atmospheric visibility, global climate and human health. However, due to development of nanoscience, the combustion is considered as a method for synthesis of nanomaterials.

The flame front structure of soot formation flames can be considered in close connection with mechanism of fuel conversion. A scheme that suggested by Bockhorn [8] in 1994 is known, where polycyclic aromatic hydrocarbon (PAH) are precursors of soot particles. According to the scheme of fuel-rich flames, hydrocarbon conversion takes place, initially forming small hydrocarbon molecules, in particular acetylene, which combines hydrocarbon radicals to form aromatic rings, first one aromatic ring, and then polycyclic aromatic hydrocarbons (PAH) up to coronene with further coagulation with the formation of three-dimensional soot particles, up to 50 nm in size at times of 10^{-3} and 10^{-2} sec.

Since then, in rich fuel flames the nanosized particles such as fullerenes and graphenesare found. The fullerene formation is generally observed at pressures below 60 Torr, 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 as general scheme for soot formation. At low pressure the formation of fullerenes as well as polycyclic aromatic hydrocarbon (PAH) is occurred, but with increased pressure the polycyclic aromatic hydrocarbons (PAHs) are coagulates to soot particles. It can be seen that graphene formation as intermediate product between PAH and soot particles, which is confirmed by the formation of multi-layered graphene films at atmospheric pressure, the single-layered graphene films are formed at the pressures below 60 Torr.

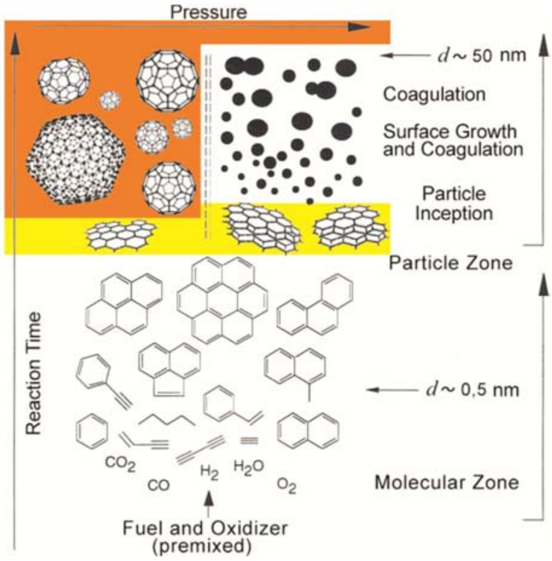

Fig. 5. Modified scheme for soot, fullerenes and graphene formation process in flame [27].

Based on these data the synthesis of fullerenes, carbon nanotubes, superhydrophobic soot and graphene in the flame it is possible to modify the general scheme which was proposed by H. Bockhorn [8] for rich fuel flames, in order to make a pressure-coordinate, which allows to form fullerenes and single graphenes at low pressures, few layers graphenes as well as soot at high pressures (Fig. 5) [27].

6. Conclusions

New phemonological soot formation model, including formation of nanoparticles, fullerenes, single and multilayered graphenes is proposed for fuel rich flames. It should be noted that formation of fullerenes and single graphene has occurred at low pressure. Due to this method it can be described the conversion of fuel to soot formation.

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