

FORMATION OF DIVIDED PARTICLES FROM CARBON VAPOR
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Introduction. In previous work, the mechanism of finely divided carbons in hydrocarbon pyrolysis has been established (1). In particular, it has been shown, that the chemical processes occurring during the pyrolysis are based on the transformation of the starting hydrocarbon, methane or benzene, into polyaromatic hydrocarbons with molecular weights of several hundred units (2). Those hydrocarbons are then condensed into liquid droplets (phase change) which are transformed into solid particles mainly through dehydrogenation. The chemical reactions taking place during the phase change, gas to liquid, are very complex and thus hinder a better understanding of the physical processes involved. Therefore, we investigated a system of particles formation rather simple from a chemical stand point, i.e. the vaporization of graphite and the subsequent condensation of the carbon vapor. Depending on the experimental conditions of the vapor condensation, carbon films or carbon particles may be produced (3). When the condensation of carbon takes place in an atmosphere of inert gas, fine carbon particles can be obtained.

In the present study, we investigated mainly the size of the produced carbon particle as a function of the experimental conditions (evaporation rate, pressure of inert gas). A mechanism for the particle formation has been suggested.

Experimental. Carbon vapor is produced by electrically heating (10-14 V ; 100-140 A) of a spectroscopically pure graphite rod (length 20 mm, diameter 3 mm) placed in a cylindrical Pyrex vessel (80 mm diameter). The graphite rod is outgassed for five hours at 20°C under 10^{-5} torr and then for 15 min. at 2000°C. After cooling in vacuum the inert gas (argon) is introduced to a known pressure. The evaporation takes place during 2 min. heating cycles followed by cooling periods of about 20 min.

The weight loss of graphite rod is determined accurately and the evaporation rate is calculated by dividing the weight loss by the total evaporation time.

The carbon deposits may be recovered from the pyrex walls or from metallic supports set at known distances from the source. Grids for electron microscopy covered with a thin film of carbon are also used. The temperature of the carbon source is measured with an optical pyrometer. Thermocouples shielded with a refractory cap to prevent radiation disturbance from the source are used to measure the temperature at different points inside the evaporation chamber.

Thermal profiles (temperature as a function to the distance from the source) determined after 1 mm of evaporation do not show any marked variation with changes in experimental conditions (evaporation rate, argon pressure).

The carbon particles are observed under a Jeol 100B microscope. Their size is measured with a particle analyzer TG23 Zeiss. The carbon samples are characterized by the most frequent diameter D_f of their size distribution.

Results. The morphology of the carbon deposits has been studied as a function of the three following parameters in these ranges :

- P_A : pressure of argon (10^{-3} to 30 torrs)
- V_e : evaporation rate of carbon (0.5 to 4.5 mg/min)
- z : distance from the source (10 to 40 mm).

It appears that for $P_A < 1$ torr, the carbon deposits is mainly a film which may be smooth or rough. For $1 < P_A < 5$ torrs, particles appear at distances between 30 and 10 mm for evaporation rate higher than 1 mg/min.

Finally, when $P_A \geq 5$ torrs, particles are formed at any evaporation rate between 0.5 and 4.5 mg/min. This experimental range $5 \leq P_A \leq 30$ torrs has been especially investigated. The particles diameters (D_f) versus distance from the source (z) are indicated on figure 1 for different conditions. It is seen that for a given P_A , D_f increases with the evaporation rate V_e . Also, for given V_e and P_A values, D_f increases when $z < 20$ mm and remains constant for $z > 20$ mm.

Discussion. The results indicate clearly that the particles are formed in the gas phase. The shape of the particles, the presence of aggregates, the increase of the particle diameter with distance and the independence of the particle size of the nature of their support are strong indications of a gas phase formation of the particles.

Therefore the following mechanism may be postulated : the carbon species migrate from the source to the walls and collide with each other in the gas phase. The collision frequency is proportional to the residence time of the carbon species in the gas phase. It increases with the argon pressure and with the evaporation rate of carbon.

Estimations of the radius of the critical nucleus show no significant differences for film or particles formation. Moreover, a tremendously high thermal gradient ($\sim 10^7$ K/m) exists on our system and therefore classical nucleation thermodynamics involving equilibrium may not be applicable. We consider another approach based on collisions between two carbon species yielding a single one.

Assuming for simplification that the carbon vapor is composed only of C_3 , we postulate a stepwise growth mechanism.

The first step is $C_3 + C_3 \rightarrow C_6$ and the p^{th} step :
 $C_{3 \times 2^{p-1}} + C_{3 \times 2^{p-1}} \rightarrow C_{3 \times 2^p}$ (1)

At the end of each step, the number of particles is divided by two and the distance z_p is calculated after which the p^{th} step is terminated. The diameter of $C_{3 \times 2^p}$ may be determined assuming a spherical shape and a density of 1.9 g/cm³.

Kinetic theory of gases show that the number of particle N per unit volume may be calculated as a function of z by the equation

$$\frac{dN}{dz} = - \frac{c\sqrt{\pi}}{v} D^2 N^2 \left(\frac{4kT}{m}\right)^{1/2} \quad (2)$$

D : diameter of the particle

m : mass of the particle

v : migration velocity of the particles in the z direction

c : efficiency factor $\ll 1$

The number of C_3 per unit volume at the source may be calculated knowing the partial pressure of C_3 , $(P_{C_3})_s$. From the evaporation rates in vacuum and in argon atmosphere, it is possible to compute the $(P_{C_3})_s$ values.

Assuming that the migration along the z axis is generated by a thermophoresis mechanism, the velocity is given by

$$v \approx 3.1 \cdot 10^{-4} \frac{\Gamma T}{P_A}^{1/2} \quad (3) \quad (\text{SI units}).$$

Γ is the thermal gradient, experimentally determined.

Substituting (3) into (2), it is possible to calculate, after integration, the particle diameter. The theoretical curves fit the experimental points well when taking $c = 10^{-2}$ for $3 < 20$ mm and $c = 0$ for $3 > 20$ mm (figure 1). Indeed for particles large

enough, collisions do not lead to single particles but to the aggregation of two individual spheres and thus there is no more growth.

The assumptions are obviously over simplified, the efficiency factor c depending certainly on the particle size and the temperature. Nevertheless, it should be pointed out that a unique value allows a fit for all sets of experiments. Thus, the satisfactory agreement between theory and experimental values supports strongly the irreversible association of carbon species as being the fundamental process in formation of the carbon particles in our system. A generalization of the proposed mechanism may be found by investigating metal vaporization.

References.

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Figure 1 : Particle diameter as function of distance to carbon source.

