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Abstract

Full Text

Physical Chemistry

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Kinetics of the Growth of a Carbon Surface during the Thermal Decomposition of Methane in the Temperature Range 1400–1700°C

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The formation of carbon during the thermal decomposition of hydrocarbons has recently acquired great practical importance. At temperatures up to 1000–1200°, the kinetics of the process has been studied by a number of authors (1-5). Characteristic features of the kinetics of this process are: first order with respect to hydrocarbon concentration, sharp inhibition of the rate by hydrogen, and a high temperature coefficient of the rate. In work (6) it was shown that the activation energy of this process decreases with increasing temperature. The kinetics of the growth of a carbon surface at temperatures of 1600–2100° was studied by Brown and Watt (7). However, the reaction rates and activation energies obtained by these authors are distorted by diffusion. The present work is devoted to measuring the rate of growth of a carbon surface during the thermal decomposition of methane at 1400–1700°C.

Fig. 1. Schematic arrangement of the graphite rod inside the reaction space of a high-temperature furnace:
1 –gas-inlet tube, 2 –graphite reaction tube, 3 –graphite rod, 4 –gas-outlet tube

The experimental method consisted in determining the growth rate of a carbon film forming on a graphite rod. Such a rod (diameter 12 mm, length 500 mm) was placed in the reaction space of a high-temperature furnace equipped with a profiled graphite heater. The arrangement of the rod is shown in Fig. 1. A mixture of methane with hydrogen was passed through the annular space between the rod and the walls of the reaction tube. The experiments were carried out at methane concentrations of 2-10% and gas flow rates of 4-10 l/min. Higher methane concentrations caused soot formation, while at lower concentrations gasification of the graphite was observed.

Experiments in which nitrogen or helium was used instead of hydrogen to dilute the methane showed substantially different results. Even at a temperature of 1500°, at methane concentrations above 1%, soot formation was observed, and it was impossible to study the thickness of the carbon film being formed.

The thickness of the carbon film was determined by measuring the diameters of the rods along their entire length with a lever micrometer to an accuracy of $±$0.01 mm. Measurement of the temperature in the body of the graphite heater was carried out using high-temperature tungsten-rhenium thermocouples (ˆ8). Preliminary experiments showed that the difference between the temperatures of the rods and the heater body did not exceed 20-30°. As a result of each experiment, a curve was obtained for the dependence of the growth rate of the carbon layer on temperature, determined by the temperature field of the furnace. Figure 2 shows a typical pattern of such a dependence for various initial methane concentrations.

and gas flow rates at 1600° in the center of the furnace. The reaction rate constants α were found from the first-order equation:

$$\alpha = \frac{\gamma\, dr/dt}{C_x}, \tag{1}$$

where dr/dt is the film growth rate, cm/sec; γ is the film density, g/cm^3; C_x is the methane concentration in the given cross section of the reaction space, g/cm^3.

The methane concentration was found from its total consumption for the formation of the carbon film. The latter was determined by graphical integration of the curves of change in the film growth rate along the length of the rod.

The density of the carbon film formed under the experimental conditions at different temperatures was determined experimentally. For this purpose, a carbon film was obtained on the surface of an alumina rod. Owing to the difference in the temperature coefficients of expansion of the carbon film and alumina, such a film is readily detached after cooling. The density was measured by the method of equilibration in heavy liquids. The results obtained are shown in Fig. 3, where, in addition, literature data are also given.

Fig. 2. Change in the growth rate of a carbon film along the length of the rod at 1600° in the center of the furnace. **A**—methane concentration at the inlet 10%, **B**—methane concentration at the inlet 5.3%, **C**—temperature field of the furnace at 1600°. **I**—gas flow rate 3.6 l/min, **II**—gas flow rate 10 l/min.

All values of α found from formula (1) for different flow rates and methane concentrations at each temperature were treated by the correlation method.

Fig. 3. Dependence of the density of carbon films on the temperature of their formation: 1 —our data, 2 —according to (7), 3 —according to (4), 4 —according to (5)

Figure 2: Fig. 3. Dependence of the density of carbon films on the temperature of their formation: 1 —our data, 2 —according to (7), 3 —according to (4), 4 —according to (5)

Figure 4 shows the dependence of the reaction rate constants on temperature in Arrhenius coordinates, with the correlation points plotted on the graph.

The activation energy of the methane decomposition reaction corresponding to the straight line in Fig. 4 is 36 kcal/mole. The dependence of the reaction rate on temperature can be expressed by the formula:

$$K_s = 2042 C e^{-18200/T}. \tag{2}$$

Here the methane concentration C is expressed in g/cm^3, and the reaction rate K_s in g/cm^2·sec. The values found for the rate constants made it possible to determine activation energies at different temperatures from the equation:

$$N_a = N_0 e^{-E/RT}, \tag{3}$$

where N_a is the number of molecules that reacted, N_0 is the total number of molecular impacts on the surface, and E is the activation energy. The corresponding values of E are given in Table 1.

An estimate of the degree of distortion of the obtained constants by diffusion was made both computationally and experimentally. Under stationary conditions:

$$K_s = \beta (C_x - C_s), \tag{4}$$

where β is the rate coefficient of diffusion of methane in hydrogen, cm/sec; C_s is the concentration of methane at the surface of the rod, g/cm^3; C_x is the concentration of methane along the flow axis, g/cm^3.

The diffusion rate coefficient was found from formula (9), $\beta = \mathrm{Nu}\, D/d$, where Nu is the Nusselt criterion, D is the diffusion coefficient of methane in hydrogen, and d is the equivalent diameter. At 1900° the diffusion coefficient is $3.8 \cdot 10^{-3}$ m^2/sec. In calculating this coefficient, a temperature coefficient of 1.75 was adopted ([10]). The equivalent diameter is $6 \cdot 10^{-3}$ m. The Nusselt criterion for the experimental conditions is 3.66 ([11]).

Fig. 3. Dependence of the density of carbon films on the temperature of their formation:
1 —our data, 2 —according to ([7]), 3 —according to ([4]), 4 —according to ([5])

Fig. 4. Dependence of the rate constants α of the methane decomposition reaction at the surface on temperature

Figure 3: Fig. 4. Dependence of the rate constants α of the methane decomposition reaction at the surface on temperature

Fig. 4. Dependence of the rate constants α of the methane decomposition reaction at the surface on temperature

On the basis of the data presented, the value of β from formula (5) is 230 cm/sec. The difference between the methane concentrations along the flow axis and at the surface for that cross section of the reaction space where the reaction rate at 1900° is $2.8 \cdot 10^{-5}$ g/cm^2 • sec is $1.2 \cdot 10^{-7}$ g/cm^3.

Comparison of this value with the methane concentration along the flow axis, equal for the same cross section to $5 \cdot 10^{-5}$ g/cm^3, shows that the decrease in concentration is about 0.4%. From this it may be concluded that diffusion does not limit the reaction rate, and that the latter is determined practically only by chemical kinetics.

The experimental check of the influence of diffusion on the reaction rate consisted in comparing the kinetic constants found with constants obtained in the decomposition of methane on the surface of corundum powder particles of size 0–2 μ. The powder, together with the gas stream, was passed through the reaction space under the same conditions as in the experiments with rods.

On the basis of determination of the carbon content in the powder and of its specific surface area, the increases in the particle radii and the growth rates of the carbon film were calculated. Comparison of the results obtained with the data for the experiments with rods showed that in both cases close rates of film growth were obtained. This indicates the absence of noticeable diffusion complications, since methane decomposition on the surface of particles comparable with the mean free path of the molecules may be regarded as independent of the diffusion rate.

The main significance of the results obtained is that the reaction rate constants found are not distorted by diffusion and make it possible to calculate the absolute rate of the process of growth of a carbon layer in the range 1400–1700° at methane concentrations in hydrogen up to 10%.

Qualitative experiments with methane diluted with nitrogen and helium showed a considerably higher rate of film growth in comparison with experiments in which methane was diluted with hydrogen. In the experiments that were—

carried out by Brown and Watt (7) under vacuum with undiluted methane, the growth rates of the films, at the same partial pressures of methane and temperatures, despite the influence of diffusion, proved to be 3–4 times higher than in our experiments. This shows that in the temperature range studied, as also at considerably lower temperatures (2), the rate of decomposition of hydrocarbon molecules on the surface is substantially retarded by hydrogen. The observed retardation is apparently explained by activated adsorption of hydrogen on the carbon surface.

Table 1

Activation energies of the methane-decomposition reaction on the film surface at various temperatures

Temp., °C	Reaction-rate constant, cm/sec $\cdot 10^2$	Fraction of reacting molecules, $e^{-E/RT} \cdot 10^5$	Activation energy according to equation (3), kcal/mole
1400	3.9	0.56	40.0
1500	7.2	1.40	39.2
1600	12.0	2.29	39.7
1700	20.0	4.09	39.6

Of note is the close agreement between the activation-energy values calculated from the slope of the straight line in Arrhenius coordinates and from equation (3). This result shows that the value of the steric factor in this equation is indeed equal to unity (6, 12) and that the formation of the carbon surface is limited by molecular impacts with the surface and is, as at lower temperature (2), probably a purely molecular process. It is also interesting that the activation energy of the process in the range 1400–1700° remains constant, whereas in the temperature interval 800–1300° (6) it decreases by approximately 20 kcal/mole.

A comparison of our data on the density of carbon films with literature data (Fig. 3) shows a sharply pronounced minimum at a temperature of about 1700°, which may be explained as follows.

At temperatures up to 1300° the high density of carbon is explained by the low rate of the film-growth process. In this case the molecules react with the most active atoms of the carbon surface and a very dense structure is formed. As the temperature is raised, the rate of film growth increases and the degree of its ordering decreases. When the temperature is raised above 1700°, despite the continuing increase in the film-growth rate, the rate of structural ordering increases rapidly, as a result of which at 2100° the density reaches 2.2 g/cm^3, i.e., approaches the density of graphite. The significantly larger absolute value of the film densities in our experiments is probably explained by the retarding action of hydrogen, since the literature data refer to methane not diluted with hydrogen.

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