I. L. MARYASIN, P. A. TESNER

1965

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Abstract

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PHYSICAL CHEMISTRY

I. L. MARYASIN, P. A. TESNER

RATE OF INTERACTION OF CARBON WITH CARBON DIOXIDE AND OXYGEN

(Presented by Academician M. M. Dubinin, February 3, 1965)

Despite the large number of studies on the combustion and gasification of carbon, we do not have reliable data on the rate of interaction of carbon with oxygen and carbon dioxide, since the data of different authors differ considerably from one another (⁀1). This is explained, on the one hand, by the difficulty in separating, in these processes, the rate of the chemical process from the rate of diffusion and, on the other hand, by the variety of structures of carbon materials and by the possible change in this structure during the course of the process.

In the present work, carbon black graphitized at 2800° was used as the object of study. The structural features and surface properties of this material have been investigated in a number of works (⁀2, ⁀3). Owing to the high structural uniformity of this carbon black, its interaction with oxygen or carbon dioxide does not lead to the appearance of significant porosity. This made it possible to develop an experimental procedure in which diffusion of the reacting molecules to the surface of the carbon being gasified was excluded. As a result, the rate of chemical interaction of carbon with carbon dioxide was measured in the temperature range 1000-1400° and with oxygen in the range 600-800°.

The essence of the measurement procedure consisted in passing the reaction gas through a 1 cm layer of carbon black. Because of the small size of the carbon-black particles (about 2000 Å), the concentration gradient of the reacting gas in the channels between the particles proves negligible, and its diffusion to the surface does not limit the gasification process. The amount of carbon black burned off during an experiment was determined from the difference in the weights of the sample before and after the experiment and, in addition, was checked from the amount of carbon oxides formed. The temperature was measured with a platinum-rhodium-platinum thermocouple placed in the layer of the carbon-black charge. Constancy of the temperature was maintained automatically with an accuracy of $±$2°.

Table 1

Temp., °C	Degree of combustion, %	S_{ads}, m^2/g	S_{calc}, m^2/g	$K_{\text{sh}} = S_{\text{ads}}/S_{\text{calc}}$
1000–1300°	10	19.0	16.0	1.19
1000–1300°	20	22.5	16.7	1.35
1000–1300°	50	32.5	19.5	1.67
1400°	10	16.5	16.0	1.03
1400°	20	17.0	16.7	1.02
1400°	50	19.0	19.5	0.98

The specific surface area of the carbon black before and after the experiments was determined by the BET method from benzene adsorption. To estimate the porosity arising during gasification of the carbon black, its specific surface area found by the indicated method (S_{ads}) was compared with the calculated value of the specific surface area (S_{calc}), which is obtained on the assumption that the carbon-black particles retain a spherical shape.

Table 1 gives the results of such a comparison for the case of gasification with carbon dioxide. It was found that at temperatures of 1000–1300° the roughness coefficient, although small in absolute magnitude, increases with increasing degree of burnoff. At 1400° the coef-

roughness coefficient is close to unity and does not depend on the degree of burnout.

The processing of the results consisted in calculating the gasification rate constants with allowance for the change in the concentration of the reacting gas over the height of the soot layer. The calculations are based on the assumption that the reactions are first order with respect to the concentration of carbon dioxide and oxygen and that the total surface of the soot does not change during gasification. The validity of the latter assumption is due to the fact that the burnout of part of the material observed in the experiments is compensated by an increase in its specific surface area, as a result of which the total surface of the soot changes only slightly during the experiment. For the calculation, the average value of the total surface over the experiment was taken. In order to minimize inhibition of the process due to diffusion of the reacting gas into the pores arising during gasification, only those experiments were treated in which the degree of burnout did not exceed 10% in the case of interaction with carbon dioxide and 30% in the case of combustion. Therefore, the surface roughness coefficients did not exceed values of 1.1–1.4.

Fig. 1. Dependence of the rate constants of the reactions of graphitized soot with oxygen and carbon dioxide. $[K] = \text{mol/cm}^2 \cdot \text{sec}$

Table 2

Rate constants for combustion of graphitized soot in oxygen

(sample 1 g, initial specific surface 12 m^2/g)

Temp., °C	O_2 concentration, %	Gas flow rate, l/min	Degree of soot burnout, %	Soot surface after experiment, specific m^2/g	Soot surface after experiment, total m^2	Rate constant* of the reaction (100% CO_2 concentration), mol/cm^2 · sec · 10^{10}	Rate constant* of the reaction (100% CO_2 concentration), Å/sec · 10^2	E**, kcal/mol
600	21.0	0.40	7.0	17.5	16.3	0.18	0.9	40.7
650	21.0	0.40	6.4	16.6	15.6	0.62	3.1	40.3
650	21.0	0.40	16.2	18.2	15.3			
700	7.6	0.44	6.5	12.0	11.2	2.90	14.5	40.2
700	7.6	0.44	12.4	16.1	14.1			
750	7.6	0.44	7.8	16.4	14.5	10.30	51.5	39.2
750	7.6	0.44	16.8	17.6	14.7			
800	7.6	0.44	13.8	13.8	11.9	24.8	124.0	38.4
800	7.6	0.44	29.4	13.7	9.7			

* The density of carbon was taken as 2.0 g/cm^3.
** Calculated in accordance with the theory of active collisions: number of active collisions/number of total collisions = $e^{-E/RT}$.

The main results are given in Tables 2 and 3 and in Fig. 1.

The activation energies for the interaction of carbon with oxygen and carbon dioxide, from the slopes of the straight lines in Fig. 1, are 52 and 62 kcal/mol, respectively, and the rates of these processes at temperatures of 600–800° and 1000–1400° are expressed by the following equations:

$$G_{O_2} = 130 \cdot 10^6 e^{-52000/RT} CS \quad \text{g/sec}, \tag{1}$$

$$G_{CO_2} = 1.17 \cdot 10^5 e^{-62000/RT} CS \quad \text{g/sec}, \tag{2}$$

Here C is the concentration of the reacting gas, mol/cm^3; S is the specific surface of the soot, cm^2/g. It may be assumed that the results obtained give the rate of the true chemical reaction and are not distorted by diffusion, owing to the insignificant increase in the porosity of the soot. The calculated ratio of the rate constants of the reactions, obtained by extrapolating dependences (1, 2) to temperatures of 1000-2000°, is approximately 4 orders of magnitude. The results obtained refer to the surface of graphitized soot, which is composed of basal graphite planes. Therefore the values found···

···changes in the interaction rate are, apparently, minimal. For any other carbon surfaces the interaction is accompanied by the development of porosity and proceeds faster. Comparison of the indicated values of the activation energy with the results of calculating this quantity from the fraction of active collisions (Tables 2 and 3) shows the following. For the inter—

Table 3

Rate constants for the gasification of graphitized soot by carbon dioxide
(soot charge 1 g, initial specific surface 15.5 m^2/g, CO_2 concentration 99%, degree of soot burnoff 10%)

T, °C	Gas flow rate, l/min	Soot surface after the experiment, specific m^2/g	Soot surface after the experiment, total m^2	Reaction rate at CO_2 concentration 100%, $mol/cm^2 \cdot s \cdot 10^{10}$	Reaction rate at CO_2 concentration 100%, $Å/s \cdot 10^3$	Energy E^{**}, kcal/mol
1000	0.06	19.0	17.1	0.20	1.2	57.9
1100	0.2	19.0	17.1	1.34	8.0	57.0
1200	0.2	19.0	17.1	5.40	32.0	57.0
1300	0.2	19.0	17.1	16.1	96.0	57.0
1400	0.2	16.5	14.8	37.0	221.0	58.1

* The density of carbon was taken as 2.0 g/cm^3.
** Calculated in accordance with the theory of active collisions: N active collisions/N total collisions $= e^{E/RT}$.

action $C + CO_2$, the values calculated by both methods practically coincide (62 and 57 kcal/mol, respectively); for the interaction $C + O_2$, the activation energy calculated from the fraction of active collisions is lower than that calculated from the temperature dependence of the rate constant and shows a tendency to decrease as the temperature is lowered [4].

For comparison of the data obtained with the literature data, among the numerous works those were selected which characterize the chemical kinetics of the interaction of a carbon surface with oxidizing agents. Since such data for high temperatures are very scarce, the comparison was made only for 900 and 600°, respectively, for the interaction with carbon dioxide and oxygen. Extrapolation of the data to the indicated temperatures was carried out on the basis of the activation-energy values found by the authors. Recalculation to a 100% concentration of the reacting gas was performed in accordance with first-order kinetics.

Table 4

Literature data on the rates of interaction of carbon with carbon dioxide (900°) and oxygen (600°)

Source	Material	Interaction rates, mol/cm^2 • s CO_2	Interaction rates, mol/cm^2 • s O_2
Armington [5]	Graphite powder	$0.5 \cdot 10^{-11}$	$4 \cdot 10^{-11}$
Armington [5]	Graphitized soot	$0.06 \cdot 10^{-11}$	$1 \cdot 10^{-11}$
Snegireva [6]	Acetylene soot	–	$1 \cdot 10^{-11}$
Austin [7]	Electrode carbon	$5 \cdot 10^{-11}$	–
Lee [8]	Channel black	–	$150 \cdot 10^{-11}$
Our data	Graphitized soot	$0.25 \cdot 10^{-11}$	$1.8 \cdot 10^{-11}$

As is evident from the data of Table 4, the burnoff rates for graphitized materials of similar properties are close to one another. This is explained by the fact that the experimental results are not distorted by diffusion and characterize the rate of the chemical interaction.

Received
22 I 1965

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