PHYSICAL CHEMISTRY

G. G. FEDOROV, Yu. A. ZARIFYANTS, and V. F. KISELEV

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

G. G. FEDOROV, Yu. A. ZARIFYANTS, and V. F. KISELEV

CHEMICAL AND PHYSICAL ADSORPTION OF OXYGEN ON A FRESHLY CLEAVED GRAPHITE SURFACE

(Presented by Academician M. M. Dubinin, March 15, 1961)

When a solid is comminuted in a vacuum or in an inert gas, a surface is formed that contains a high concentration of broken chemical bonds. Such a surface will therefore possess high adsorption activity. It was shown earlier ([1]) that graphite, which is quite inert at ordinary temperatures, acquires pyrophoric properties after dispersion in liquid argon. Strong heating of graphite ground in a vibratory mill upon its contact with air was observed by Feigin ([2]). Investigations of the properties of the cleaved surface of a solid and of its interaction with molecules of various substances are of fundamental interest for studying the reactivity of the surface of a solid, and for finding ways to modify the surface in order to obtain more effective adsorbents and polymer fillers.

In the present work we investigated the physical and chemical adsorption of oxygen on highly dispersed graphite obtained by grinding the initial sample in a laboratory vibratory mill in an argon atmosphere. Two samples of natural graphite were used, one of which was subjected to special purification. After dispersion, the samples obtained, with specific surface areas of 275 and 400 m^2/g, were transferred without contact with air into a volumetric apparatus. The specific surface area was determined after a cycle of adsorption measurements with oxygen from the low-temperature adsorption of nitrogen by the BET method.

The results of measuring oxygen adsorption on the freshly cleaved surface of graphite at room temperature are given in Fig. 1. As can be seen from Fig. 1, the specific adsorption values for both samples fit well on a single isotherm, which indicates good reproducibility of the surface properties with the grinding method used. Some portion of the oxygen could have been sorbed on a fine iron powder which, in an amount of several tenths of a percent ([2]), is invariably present in graphite ground in a vibratory mill. Control experiments ([3]) carried out for this purpose showed that the magnitude of adsorption on iron did not exceed 0.5% of the magnitude of adsorption on graphite.

The observed interaction of oxygen with the freshly cleaved graphite surface at room temperature is a typical case of activated chemical adsorption ([4]). Physical adsorption of oxygen at these temperatures is negligibly small. In the initial

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

stage, adsorption equilibrium is established very rapidly, which indicates a low activation energy of the process. With a further increase in pressure, adsorption increases extremely slowly. The kinetics of equilibrium establishment in the region of the rectilinear portion of the isotherm is tens of times more prolonged than in its initial part. Apparently, the graphite surface is very heterogeneous and consists of regions with different adsorption activity. Saturation of the surface with chemically adsorbed oxygen is practically incomplete.

ends at a pressure close to atmospheric. Subsequent desorption measurements showed that practically all of the adsorbed oxygen had irreversibly bound to the graphite surface. Carrying out a cycle of secondary adsorption on the oxidized sample, as was to be expected, did not lead to any noticeable uptake of oxygen (Fig. 1).

In order to study the stability of the surface properties of a freshly split graphite surface, measurements were made of the chemical adsorption of oxygen on separate portions of one and the same sample of highly dispersed graphite ($S = 400$ m^2/g), which had been kept for 1, 10, and 30 days at room temperature in an argon atmosphere. No changes in adsorption activity were observed. In the case when one of the ampoules with unoxidized graphite was heated for 50 hours at 300°, a decrease in the specific adsorption by approximately 20% was observed (Fig. 1). This is probably connected with saturation of part of the surface by gas molecules released from the glass during its heating. When the graphite sample was calcined in a previously degassed quartz ampoule for 24 hours at 800°, a decrease in adsorption of only 10% was observed (Fig. 1). Such a high stability of free radicals on the graphite surface makes it possible to use it as a convenient object for studying the mechanism of elementary interactions of various molecules with radicals on the surface.

Fig. 1. Specific isotherms of the chemical adsorption of oxygen on the freshly split surface of samples of vibration-milled graphite with specific surface area 275 m^2/g (1), 400 m^2/g (2), on samples of unoxidized graphite ($S = 400$ m^2/g), heated for 50 hours at 300° (3), for 24 hours at 800° (4), and the isotherm on the oxidized sample ($S = 400$ m^2/g) (5). Black points indicate desorption.

Fig. 2. Isotherms of oxygen adsorption at a temperature of $-196°$ on samples of unoxidized (1) and oxidized (2) graphite ($S = 400$ m^2/g).

Studies (^{2}) of the structure of finely ground graphite show that, when it is dispersed in dry air, destruction of the crystals occurs along all crystallographic

Fig. 3

Figure 3: Fig. 3

directions. This produces a large surface containing a high concentration of broken π- and σ-bonds. Some of these unsaturated radicals remain on the surface, and they are the centers of chemical adsorption of oxygen. On the other hand, in the process of graphite crushing, possible deformations of the crystal lattice in the basal plane may lead to an increase in the activity of the π-electrons of the conjugated bond system (^{5}) and, consequently, to an increase in adsorption activity.

To clarify the nature of the interaction of oxygen with the graphite surface at low temperatures, oxygen adsorption isotherms were measured at a temperature of $-196°$ (Fig. 2). As can be seen from Fig. 2, the isotherm of primary adsorption is characterized by a very steep initial section. The monomolecular layer (a_m by BET) is reached at a pressure of several

millimeters of mercury. After completion of the adsorption cycle and holding the sample for 3 hours under a layer of liquid oxygen, the desorption isotherm was measured. It follows from Fig. 2 that over the entire pressure interval the desorption branch lies above the primary-adsorption isotherm. Because of the specifics of the volumetric method, we were unable, with our apparatus, to carry out desorption measurements in the region of very low pressures. In this connection, after measurement of the last desorption point at $P/P_s = 0.03$, the sample was pumped out for 6 hours at low temperature and then its temperature was slowly raised under continuous pumping. The subsequent measurements of the chemical adsorption of oxygen at room temperature gave values lying only 15% below the corresponding isotherm on the unoxidized sample (Fig. 1). It is possible that the small decrease in the amount of adsorption is connected with partial oxidation of the graphite as the temperature was raised. We observed a very slow kinetics of liberation of the residual amount of oxygen after desorption had been carried out. This experiment shows that no appreciable oxidation of the surface occurs in the low-temperature region. To verify this conclusion, after complete oxidation of graphite at room temperature an analogous cycle of adsorption-desorption measurements at $-196°$ was carried out. It is seen in Fig. 2 that the measurement results fit well the corresponding branches of the isotherms on the initial unoxidized sample. These data confirm the conclusion drawn about the absence of appreciable irreversible chemical adsorption of oxygen at low temperatures. The latter is in agreement with measurements on activated carbons considered in (4).

Fig. 3. Isotherms of low-temperature adsorption of oxygen (a, b) and nitrogen (c) on samples of unoxidized (1) and oxidized (2) graphite ($S = 400$ m^2/g). The dashed line denotes the desorption curve shown in Fig. 2.

As is seen from Fig. 2, the isotherms both on the initial and on the oxidized graphite samples have a hysteresis loop extending into the region of low relative pressures. It is difficult to assume that hysteresis in this pressure region is due to capillary condensation. It is more probable that the small excess of the desorption value over the adsorption curve in this pressure region is connected with some swelling of the sample, owing to the penetration of oxygen molecules into the interplanar spaces of graphite crystals, which were substantially destructured during grinding.* In the region of high relative pressures the hysteresis is evidently connected with capillary condensation in pores and gaps between particles. The desorption isotherm at $P/P_s = 0.25$ undergoes a break, probably connected with the freeing of part of the pores filled at high vapor elasticities. This break was not observed when adsorption-desorption cycles were carried out in the region of low pressures (Fig. 3, a, b). It should be noted that hysteresis phenomena both on the unoxidized (Fig. 3a) and on the oxidized (Fig. 3b) graphite samples are already observed in the initial part of the adsorption isotherm.

* It is known that when graphite oxide is formed the interplanar distances increase from 3.36 to 6.3 Å. During dispersion this distance also increases somewhat (3.6 Å) (2). Swelling of a graphite sample owing to the introduction of water molecules into the interplanar spaces was observed in work (6). The isotherms obtained by these authors are similar in form to those shown in Fig. 2.

Only after a number of adsorption and desorption cycles had been carried out (without evacuation) did the branches of the adsorption and desorption isotherms coincide both with each other and with the desorption isotherm (Fig. 2). However, the indicated difference in the course of the adsorption and desorption isotherms was invariably restored upon prolonged evacuation of the sample. On the nitrogen adsorption isotherm (Fig. 3b), in the same region of relative pressures, no hysteresis phenomena were observed. Apparently, this is connected with the greater penetrating ability (in comparison with nitrogen) of oxygen molecules at low temperatures.* In this connection, the specific surface area of highly dispersed graphite, calculated from low-temperature adsorption of nitrogen (Fig. 3b), may be somewhat underestimated in comparison with the surface accessible to oxygen molecules. This circumstance is of no fundamental significance for the conclusions drawn in the present work.

Moscow State University
named after M. V. Lomonosov

Received
13 III 1961

CITED LITERATURE

1. V. S. Veselovskii, G. L. Ormanskaya, *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 65.

2. L. A. Feigin, Candidate' s dissertation, Moscow, 1958.
3. Yu. A. Zarifyants, V. F. Kiselev, G. G. Fedorov, *ZhFKh*, **35**, No. 9 (1961).
4. M. M. Dubinin, *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 9.
5. I. Koutezký, H. Tomachék, *Phys. Rev.*, **120**, 1212 (1960).
6. I. H. De Boer, A. B. C. Van Doorn, *Prsc. Kon. Ned. Akad. Wet.*, B **61**, 242 (1958).

---

* In work (6) the authors indicated that, in contrast to water molecules, nitrogen molecules do not penetrate into the interplanar spaces of graphite oxide.

Note: Figure translations are in progress. See original paper for figures.