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Synthesis and Functional Analysis of Oxygen Complexes on the Surface of a Fresh Cleavage of Graphite

(Presented by Academician M. M. Dubinin, 20 XII 1961)

Surface chemical compounds play an important role in the phenomena of adsorption and catalysis on the surface of carbons and carbon blacks ([1], [2]). The chemical nature of the surface of these materials has a substantial influence on the technical properties of carbons, for example in the process of solvent recovery, and on the properties of carbon blacks in the processes of vulcanization, aging, and oxidation of rubbers ([1–4]). Although the formation of oxides on the surface of carbons as a result of the chemical adsorption of oxygen has been the subject of a number of studies and, first of all, of the work of N. A. Shilov and his students ([1], [5], [6]), the identification of functional groups on the surface of carbons and carbon blacks still remains a difficult problem. Thus, for example, in the case of carbon blacks it is possible to identify only groups containing 20–26% of the bound oxygen ([3], [7–9]). The reason for these difficulties is connected with the variety of ways in which oxygen can attach to the carbon surface, with the complex topography during its chemisorption in the high-temperature processes of formation of carbon blacks and carbons. In addition, analysis of the functional groups is complicated by the screening action of large reagent molecules on groups located close to one another on the surface, and by the low transparency of graphite bodies, which hinders spectroscopic investigations.

In the present work we set ourselves, in principle, the reverse problem: starting from the surface of a fresh cleavage of graphite, to synthesize on it a certain amount of oxygen complexes, carrying out quantitative measurements of chemical adsorption, and then, with the aid of existing chemical methods ([3], [7], [9]), to identify the functional groupings formed. Chemical adsorption occurring on the surface of graphite at room temperature ([10], [11]) is not complicated by the chemisorption that takes place during high-temperature oxidation of carbon ([1]).

It could therefore be expected that the set of oxygen groups formed on the surface would be less diverse than in the case of carbons and carbon blacks.

In the work a highly disperse preparation of natural graphite was used, obtained, as in ([10], [11]), by vibratory milling of the initial sample in an argon atmosphere. The specific surface area of the powder obtained was 380 m^2/g*. Adsorption measurements were carried out by the gravimetric method. For this purpose special adsorption quartz balances were constructed, into which the graphite powder was poured without its coming into contact with air.

The results of measuring the chemical adsorption of oxygen on the surface of a fresh cleavage agree well with the adsorption isotherm reported earlier. After adsorption had been carried out, the sample was held for 24 hours in oxygen at a pressure of 800 mm Hg and desorbed; the graphite irreversibly adsorbed 4.1 $\mu mol/m^2$ of oxygen, which coincides with the value determined earlier ([10], [11]) and indicates good reproducibility of the surface state in different grindings. The observed magnitude of irreversible oxygen adsorption is more than an order of magnitude higher than the limiting values of chemically adsorbed oxygen on carbons previously evacuated at high temperatures ([1]).

After carrying out the adsorption–desorption cycle with oxygen, the graphite sample was pumped for a long time to a vacuum of 10^{-5} mm Hg. Measurements show that secondary adsorption of oxygen on the oxidized sample is small. However, with respect to water vapor such a surface exhibits considerable activity, associated with hydration of surface complexes. Since chemical analysis of functional groups is carried out in an aqueous medium, it was of interest to determine the amount of irreversibly adsorbed water on the surface of oxidized graphite. For this purpose, a pumped graphite sample (without its contact with air) was connected with water vapor. The results of measuring the adsorption of water vapor are given in Fig. 1.

As follows from Fig. 1, the isotherm of the first adsorption–desorption cycle is characterized by hysteresis extending into the region of low relative pressures, which, apparently, as in the case of physical adsorption of oxygen ([10]), is connected with swelling of the sample.* After desorption and pumping of the sample to a vacuum of $5 \cdot 10^{-5}$ mm Hg, the latter irreversibly adsorbed 0.4 $\mu mole/m^2$ of water, which corresponds to 0.8 $\mu eq/m^2$ of hydrogen. It is of interest to note that after pumping a sharp shrinkage of the powder was observed in the pan of the adsorption balance. The isotherm of secondary adsorption also coincides in its initial part with the desorption curve

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* Measurements of the specific surface area were carried out by low-temperature adsorption of nitrogen after completion of the entire cycle of adsorption measurements.

Fig. 1. Isotherm of primary adsorption (1, 3) (independent series of measurements) and secondary adsorption (2) of water vapor on a sample of oxidized graphite. Black points—desorption.

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Table 1

Distribution of oxygen and hydrogen among functional groups on the surface of oxidized and hydrated graphite

Functional group	Content in µeq/m^2: oxygen	Content in µeq/m^2: hydrogen
–C(=O)OH (carboxyl)	0.96	0.48
–C–OH (acid hydroxyl)	0.16	0.16
–C–O–OH (hydroperoxide)	0.08	0.04*
>C=O (carbonyl, excluding carboxyl)	0.07	–
Sum . . .	**1.27**	**0.68**

* Possibly somewhat less, if allowance is made for the probability of the presence of peroxides in radical form.

(Fig. 1), which indicates that mainly only physical adsorption takes place on the surface. Some discrepancy in the isotherms at high relative pressures is probably connected with a change in the packing of the particles after the first adsorption cycle.

* A similar course of the isotherms in the adsorption of water by graphite oxide was noted ([12]). Possibly, the phenomena considered play some role in the swelling of graphite destructured by powerful neutron radiation in nuclear reactors ([13]).

After the adsorption of oxygen and then water vapor had been carried out, the sample was subjected to chemical analysis. Hydrated oxides—peroxide, hydroxyl (phenols), and carboxyl groups—were determined ([7,8]) separately; peroxides, iodometrically in aqueous isopropanol; protonogenic groups, by reaction

Figure 2

Figure 2: Figure 2

with NaOH; carboxyls, by reaction with Na_2CO_3; acidic hydroxyls, from the difference (protonogenic groups minus carboxyls). Carbonyls were determined by reaction with magnesium bromide-bromophenol*. The results are summarized in Table 1.

Fig. 2. Composition of the gas phase, in mole percent, over oxidized nonhydrated graphite at different calcination temperatures: 1 $-CO_2$, 2 $-CO$, 3 $-O_2$.

To determine the thermal stability of the oxygen groups formed on the graphite surface, after oxygen adsorption part of the oxidized sample was heated at each of the specified temperatures for 4-6 h, until a constant pressure of the evolved gases was established. After this, the gas phase was analyzed for O_2, CO, and CO_2. The results are shown in Fig. 2. The first traces of gas upon heating were detected at 100°. As follows from Fig. 2, with increasing calcination temperature a decrease is observed in the percentage content of the evolved O_2 and CO_2. At 250°, oxygen evolution practically ceases. The percentage content of CO in the mixture increases with increasing calcination temperature**.

At the initial stage of oxygen adsorption, some of the σ- and π-bonds broken in the process of graphite destruction chemically bind oxygen, with the formation of groups and radicals of the type

$$> C - O - O\cdot, \quad -O\overset{O}{\|}$$

and others. As follows from Table 1, the total amount of oxygen in the identified groups amounts to only 29% of the total amount of oxygen irreversibly adsorbed during its chemisorption and then water ($4.5\ \mu E/m^2$). Part of the bound oxygen may be present in the form of radicals not hydrolyzed during water adsorption, neutral and basic*** hydroxyls, or in oxygen bridges in the interplanar spaces of graphite ([15]). In addition, part of the oxygen that was not removed by pumping at room temperature could have been strongly adsorbed in molecular form on surface radicals (quasi-chemical bond ([16])) or on deformed regions of the surface in the basal plane which, according to ([17]), possess increased activity of π-electrons. Apparently, this oxygen is removed first upon heating of the sample (Fig. 2). In addition, with increasing temperature, the appearance of oxygen may be connected with decomposition of part of the peroxide radicals ([18]). At present it would be premature to give any well-founded mechanism for the formation of functional groups on the surface of freshly cleaved graphite. Very promising in this respect are our studies now being carried out on differential heats and electron paramagnetic resonance in graphite.

* The method was proposed by A. P. Terentev.

** We limited ourselves to low calcination temperatures, since, according to (^{14}), at higher temperatures iron impurities present in graphite (^{11}) catalyze the conversion of CO_2 to CO, and the analytical data no longer characterize the mechanism of decomposition of oxides on the surface.

*** Determination of basic hydroxyls was complicated by the presence of iron impurities in the graphite sample (^{11}).

As was stated, upon contact with water vapor some of the oxygen groups are hydrated, for example: $> C—O—O\cdot + H_2O \rightarrow > C—OOH + HO\cdot$. As is seen from Table 1, the total amount of hydrogen in these groups is somewhat lower than the equivalent amount of hydrogen in irreversibly adsorbed water ($0.8\,\mu$eq/m^2). Some part of the hydrogen ($0.12\,\mu$eq/m^2) is probably contained in neutral and basic hydroxyl groups.

The oxygen groupings formed on the surface are centers of physical adsorption of water vapor (^{1}). Adsorption of water on oxidized carbon surfaces is well described by the Dubinin and Serpinsky equation (^{19}), which makes it possible to estimate the number of primary adsorption centers a_0. A calculation carried out from the secondary-adsorption isotherm (Fig. 1) gives the value $a_0 = 5\,\mu$mol/m^2, which is considerably higher than the concentration of the identified groupings and close to the total amount of irreversibly adsorbed oxygen ($4.5\,\mu$eq/m^2). The adsorption centers may be nonacidic hydroxyls, oxygen-containing radicals, and also oxygen molecules firmly bound to the graphite surface and not removed by evacuation at room temperature.

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CITED LITERATURE

1. M. M. Dubinin, *Surface Chemical Compounds and Their Role in Adsorption Phenomena*, Moscow, 1957, p. 9.
2. N. N. Lezhnev, A. S. Kuzminsky, DAN, **119**, No. 1, 108 (1956).
3. M. L. Studebaker, Rubber Age, **80**, No. 4, 661 (1957).
4. J. R. Shelton, W. T. Wienham, Jr., Ind. and Eng. Chem., **49**, 1277 (1957).
5. N. A. Schilow, K. I. Tschmutow, Zs. Phys. Chem., A **148**, 233 (1930).

6. L. K. Lepin, Usp. Khim., **9**, 533 (1940).
7. D. S. Villars, J. Am. Chem. Soc., **70**, 3655 (1948).
8. L. Blom, L. Edelhausen, D. N. van Krevelen, Fuel, **36**, No. 2, 135 (1957).
9. N. N. Lezhnev, A. P. Terent’ ev, I. S. Novikova, T. A. Kozlova, *Natural Rubber*, No. 12 (1961).
10. G. G. Fedorov, Yu. A. Zarifyants, V. F. Kiselev, DAN, **139**, 1166 (1961).
11. Iu. A. Zarifianz, V. F. Kiselev, G. G. Fedorov, Proc. of the 5th Intern. Sympos. on Free Radicals, University of Upsala, Sweden, 1961.
12. J. H. DeBoer, A. B. C. van Doorn, Proc. Koninkl. Akad. Wet., B **61** (4), 242 (1958).
13. W. K. Woods, L. P. Bupp, J. F. Fletcher, *Materials of the International Conference on the Peaceful Uses of Atomic Energy*, Geneva, **7**, 1955, p. 554.
14. F. J. Vastola, P. L. Walker, Jr., Proc. of the 10th Symposium on Grafit, Paris, 1960.
15. S. Levina, A. Frumkin, A. Lunew, Acta Physicochim. URSS, **3**, 397 (1935).
16. D. Ingram, *Electron Paramagnetic Resonance in Free Radicals*, IL, 1961, p. 280.
17. J. Koutezky, H. Tomachek, Phys. Rev., **120**, 1212 (1960).
18. O. D. Tsvetkov, Yu. N. Molin, V. V. Voevodsky, *Vysokomolek. soed.*, **1**, 1634 (1959).
19. M. M. Dubinin, V. V. Serpinsky, DAN, **99**, No. 6, 1033 (1954).

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