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KINETICS OF CHEMISORPTION OF OXYGEN ON DIAMOND

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Abstract—The rate of chemisorption of oxygen on diamond powder of 20 m^2g^{-1} total surface area has been studied. Adsorption conditions ranged from 28 to 141°C at 100 mTorr O_2 pressure. Also at 28°C rates were measured over the O_2 pressure range 11–100 mTorr. Prior to adsorption measurements, the sample was outgassed at 1000°C for 10–12 hr at a residual gas pressure of 10^{-8} Torr. Adsorption was followed up to 24 hr. Plots of amount of oxygen adsorbed vs. log of time were linear and showed no breaks. The activation energy for chemisorption increased linearly from 1·5 to 14·1 kcal $mole^{-1}$ with increasing oxygen coverage up to 53×10^{18} atoms g^{-1}. It is concluded that under the conditions used, chemisorption was occurring predominantly on the (111) surface of diamond. Chemisorption at least on the (100) surface is expected to occur primarily at higher adsorption temperatures.

1. INTRODUCTION

Chemisorption of oxygen on microcrystalline carbons and graphites has been studied in detail during the last several decades. However, a few data exist on the corresponding diamond adsorbents. Lambart [1] studied the kinetics of the oxidation of diamond in the temperature range 250–500°C and observed that the diamond is oxidized to CO_2 by direct impact of oxygen molecules on the carbon surface. The energy of activation for the reaction was 27 kcal $mole^{-1}$.

Barrer [2] carried out a series of low pressure adsorption and reaction rate studies of the diamond-O_2 and diamond-CO_2 systems in the temperature range −78 to 370°C. He found the adsorption to be predominantly physical at −78°C and purely chemical in nature between 0 and 244°C. The activation energy increased from 4 to 24 kcal $mole^{-1}$ as the fraction of the surface covered increased. A primary interaction between either gaseous or physically adsorbed oxygen and the bare carbon surface, giving CO_2, occurred in the temperature range 244–370°C. At still higher temperatures the decomposition of the oxide film into CO_2, and possibly simultaneous reduction to CO, took place.

Sappok and Boehm [3, 4] studied the conditions of formation, as well as the properties and the structure, of surface oxides of diamond using natural diamond powder. They found that surface oxides were always formed when diamond is brought into contact with O_2 after outgassing at higher temperatures. The amount of the surface oxide layer increased with increase in chemisorption temperature. After oxidation at 420°C the quantity of oxygen on the surface agreed well with the number of 'dangling bonds' estimated from the surface area of low index crystal faces. The presence of carboxyl, alcohol, carbonyl and ether groups has been suggested by these workers.

The present authors [5, 6], while studying the kinetics of chemisorption of oxygen on Graphon surfaces, observed that the chemisorption of the gas takes place on different types of sites. These different types of sites are presented by the existence of different carbon–carbon spacings on the Graphon sur-

face Since the diamond surface has carbon–carbon distances which are different from those present in Graphon, it should be of interest to make a kinetic study with diamond as the solid material.

The kinetics of oxygen chemisorption have been studied in the temperature range −78–141°C and in the pressure range 11–100 mTorr

2. EXPERIMENTAL

Materials

The solid used was finely divided, pulverized natural diamond obtained from West Africa. The sample was supplied by Boehm and is from the batch used in the studies of Sappok and Boehm [3, 4]. The diamond sample was treated with hydrofluoric and sulphuric acids. It was heated in high vacuum at 1000°C before use. This treatment resulted in eliminating the chemisorbed impurities. The spectral analysis gave the impurity content as follows: 0·2–0·3% Si, 0·02–0·15% Al, 0·01–0·02% Ca, 0·01–0·02% Cu, 0·007–0·01% Fe, 0·006% B, and 0·001–0·004% Mg. Ba, Zn, Ag and Pt were qualitatively detected. The BET (N_2) surface area of the sample was $20 \pm 2\ m^2g^{-1}$. Electron microscope examination showed the sample to consist of flat wedges of 0·5 μm dia.

Apparatus and procedure

The apparatus and procedure have been described in detail [5, 6]. The apparatus is a combination of an ultra high vacuum system and an ultra sensitive measuring unit. Briefly, the vacuum unit has a Vacion pump followed by an oil diffusion and a mechanical pump and is capable of giving a vacuum of the order of 10^{-9} Torr. The measuring unit has a Baratron differential manometer, a CEC mass spectrometer and a Cahn RG vacuum microsorption balance.

The diamond sample (*ca* 0·05 g) was held in a quartz boat suspended by means of a quartz fiber. It was degassed in vacuum at 1000°C for 10–12 hr until the residual gas pressure was 10^{-8} Torr The sample was then cooled in vacuum to the required temperature A known volume of O_2 was allowed to expand into the reactor, and the adsorption was followed continuously by monitoring the gas pressure with the Baratron or the mass spectrometer. In order to minimize the change in O_2 pressure, larger volumes were introduced into the reactor systems, specially for experiments at lower pressures. These volumes were so arranged that the drop in pressure of the gas due to adsorption was large enough to be accurately measured but sufficiently small so as not to cause a significant drop in adsorption rates.

Analysis of the gas using the mass spectrometer, at different stages of adsorption at 85 and 141°C, showed the presence of small amounts of CO_2. However, as the bulk of the CO_2 was formed in the first few minutes of the reaction, its formation did not interfere significantly with measurements of the rates of chemisorption.

3. RESULTS

The adsorption of oxygen on diamond at −78°C was largely physical in nature This was established by outgassing the sample at −78°C in vacuum after the adsorption experiment. This treatment would result in the removal of any physically adsorbed oxygen whereas the chemisorbed oxygen would remain unaffected. The adsorption experiment was once again repeated on the outgassed sample. It was found that $6{\cdot}3 \times 10^{18}$ molecules of oxygen per gram were readsorbed in the first 10 min after which additional adsorption was negligible. The readsorbed oxygen is, by definition, physically adsorbed. Since the measured rates of adsorption at −78°C could not be attributable to just chemisorption, plots of results taken at −78°C are not included in this paper The adsorption of oxygen at all other temperatures studied was chemical, as no part of it could be removed by outgassing at the adsorption temperature; and when it was

removed at elevated temperatures it came off as CO and CO_2.

The amounts of oxygen chemisorbed on diamond powder at temperatures between 28 and 141°C and also at pressures between 11–100 mTorr are shown in Fig. 1. It is seen

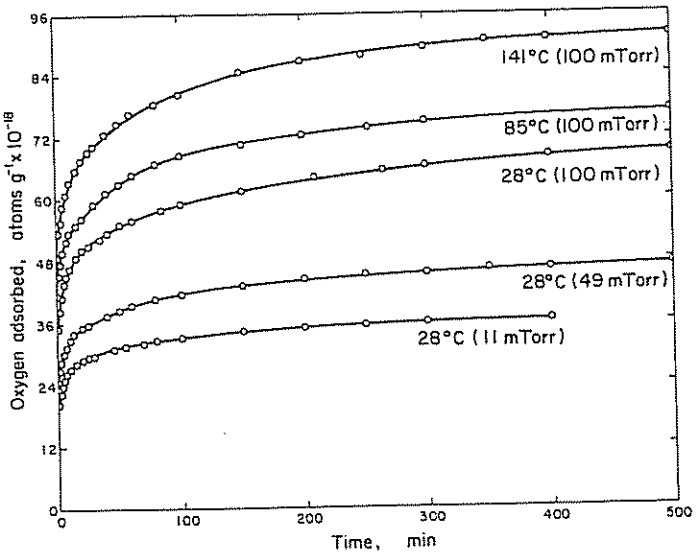

Fig. 1. Chemisorption of oxygen on diamond at different temperatures and pressures.

that the rate of adsorption is fast in the beginning and then slows down, indicating a decrease in the number of available sites as adsorption proceeds. The rate of adsorption increases with increase in temperature and pressure. It was found that the rates of adsorption after a period of 24 hr were very low Thus adsorption measurements were not carried out beyond this period. Amounts adsorbed have been plotted in Fig 1 only up to 500 min for clarity

It has been found that the data, when plotted as q (amounts adsorbed) vs. log t, give straight lines. This type of relationship is generally known as an Elovich plot. The Elovich equation is an empirical relationship which has been widely used in studies relating to chemisorption kinetics. The present authors have also used this relationship to satisfactorily explain their results for the chemisorption of oxygen on Graphon [5, 6]. The equation can be expressed as

$$dq/dt = a \exp(-\alpha q) \quad (1)$$

or in the integrated form as

$$q = \frac{2{\cdot}3}{\alpha}\{\log[(t+t_0)/t_0]\} \quad (2)$$

or

$$q = \frac{2{\cdot}3}{\alpha}\{\log[(t+t_0)/t_0]\} \quad (3)$$

where a and α are constants and $t_0 = 1/a\alpha$. t_0 is an adjustable constant which is chosen arbitrarily to give a linear q against log $(t+t_0)$ plot. However, in the present study this was not necessary since plots of q against log t are linear.

The Elovich plots of the chemisorption data at different temperatures and at different pressures are shown in Figs. 2 and 3. The plots are linear over the entire time period studied. The rate parameter α is calculated from the slope of the linear Elovich plots. Substitution of α in equation (2) gives the value of a. The values of rate parameters a and α for plots at different temperatures and pressures are summarized in Table 1. It is seen that while a is dependent on temperature, α changes only slightly with the adsorption temperature. However, in experiments at different pressures α varied significantly, whereas a is almost independent of the pressure. The high value of a at 11 mTorr is not understood.

It is seen from the Elovich equation that the rate parameter a is the initial rate when

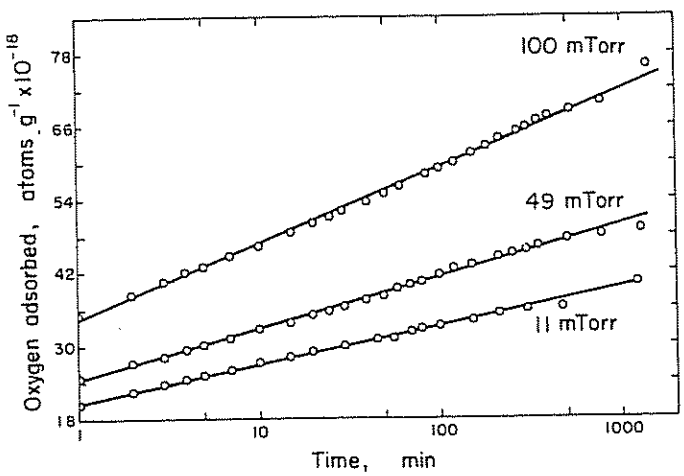

Fig. 2. Elovich plots for the chemisorption of oxygen on diamond at different pressures at 28°C.

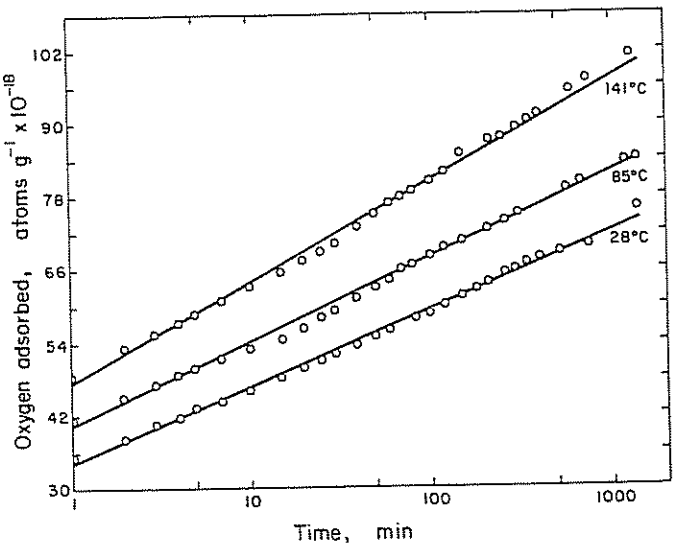

Fig. 3. Elovich plots for the chemisorption of oxygen on diamond at different temperatures at an O_2 pressure of 100 m Torr.

Table 1. Parameters in the Elovich equation for chemisorption of oxygen on diamond at different temperatures and pressures

Temperature or pressure	α (atoms^{-1} g $\times 10^{18}$)	a (atoms g^{-1} min^{-1} $\times 10^{-18}$)
	100 mTorr	
28°C	0·17	2320
85°C	0·16	4136
141°C	0·15	4476
	28°C	
100 mTorr	0·17	2320
49 mTorr	0·27	2267
11 mTorr	0·37	6302

q is zero. From an Arrhenius plot of log (a) vs. $1/T$, an activation energy of 1·5 kcal mole^{-1} is calculated for the initial adsorption of oxygen on diamond. In order to examine the variation of activation energy with surface coverage, instantaneous rates of adsorption at different values of q were calculated by substituting the values of a and α into the Elovich equation. The Arrhenius plots were not parallel, indicating that activation energy varies with surface coverage. The activation energies, as calculated from these plots, are plotted against amount of oxygen adsorbed in Fig 4. It is seen that a straight line relationship is obtained, indicating that activation energy increases linearly with amount adsorbed.

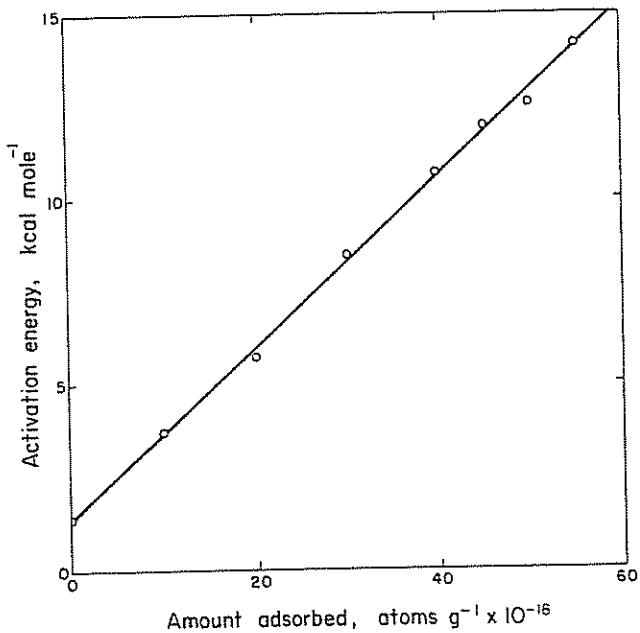

Fig. 4. Variation of activation energy for oxygen chemisorption on diamond with surface coverage.

4. DISCUSSION

As discussed by Sappok and Boehm [3], the surface of pulverized diamond powder should consist predominantly of three faces: the octahedral face (111), the rhomboduodecahedral face (110), and the cubic face (100). In an ideal, undistorted structure, each carbon atom would occupy 6·36, 4·50, and 5·51 A^2 in the (100), (110), and (111) faces, respectively. The number of surface bonds per surface carbon atom would be two for the (100) face and one for the (111) and (110) faces [3]. An estimate of the frequency of each face can then be made assuming that the specific surface energy is proportional to the number of free valencies per unit area and that there is an exponential relationship of exposed surface area and specific surface energy [7]. Table 2 summarizes the results of these calculations.

Sappok and Boehm [4] concluded that oxygen chemisorbs on the (111) and (110)

Table 2. Suggested make-up of diamond surface

Face	Surface bonds per surface atom	Area per face atom (A^2)	Frequency of face (%)	Surface atoms of diamond $cm^{-2} \times 10^{-15}$
(100)	2	6·36	10·4	0·15
(110)	1	4·50	33·5	0·75
(111)	1	5·51	56·1	1·0

faces with an ether structure (C—O—C) and on the (100) face with a carbonyl structure (C=O). They have identified both of these structures from infrared studies. On this basis, the maximum amount of oxygen which should be able to chemisorb on diamond is $1{\cdot}03 \times 10^{15}$ atoms cm^{-2} — or 206×10^{18} atoms g^{-1} of diamond used in this study. In fact, Sappok and Boehm were able to chemisorb a maximum of 216×10^{18} atoms g^{-1} on this material upon exposure to O_2 at 429°C. Thus, the entire surface of diamond is capable of chemisorbing oxygen. By contrast, the fraction of the surface of graphitic carbons on which oxygen can chemisorb is small. It is limited at most to the prismatic faces, as seen from studies on high purity natural graphite of known particle size and shape [8]; and, indeed, in the case of carbons of small crystallite size (like polyvinylidene chloride carbon) chemisorption appears limited to only a fraction of the prismatic area [9].

Chemisorption of substantial amounts of oxygen on the diamond sample used in this research is also much more rapid than was chemisorption on the graphitic carbon black, Graphon, previously studied [6]. For example, at room temperature and 100 mTorr O_2 pressure, 27×10^{18} atoms g^{-1} chemisorbed on diamond in 10 min; whereas, only $1{\cdot}3 \times 10^{18}$ atoms g^{-1} chemisorbed on Graphon, which was previously activated to 16·6 per cent wt. loss. Of the total active area, 12·5 and 4·9 per cent, for diamond and Graphon respectively, were covered with chemisorbed oxygen in 10 min More rapid chemisorption on the diamond surface may be attributable, in part, to its higher impurity content catalyzing chemisorption Thermal treatment of diamond at elevated temperatures in order to produce a very high purity material is not possible because of its significant rate of transformation to graphite above about 1500°C [10].

It is also interesting to note from Fig. 1 the effect of pressure on the magnitudes of the amount of oxygen chemisorbed. For example, at 49 mTorr and 28°C it takes approximately 500 min to chemisorb the same amount of oxygen that chemisorbs in 10 min at 28°C and 100 mTorr. This indicates that the initial rate of reaction has an effect on the magnitude of the amount of oxygen that is chemisorbed during the 'fast' portion of the Elovich isotherm. This pressure dependency is also found, although to a lesser extent, in oxygen chemisorption on Graphon [5].

In addition to the rates of chemisorption on diamond and Graphon being significantly different, so is the character of the Elovich plots. For Graphon, five distinct chemisorption stages were identifiable Abrupt changes in slope of the plots demarcated going from one stage to the next. As coverage proceeded within each stage, the activation energy of chemisorption changed little; however, an abrupt change occurred between stages. By contrast, for all the runs made on diamond, there were no abrupt changes in slope of the Elovich plots with time or at particular values of coverage Adsorption in only one stage was evident. Further, for diamond there was a linear increase in activation energy with coverage in the one stage. For Graphon, there was an over-all increase in activation energy (in discontinuous jumps) from 3·1 to 12·4 kcal $mole^{-1}$ as oxygen coverage increased from nil to $26{\cdot}3 \times 10^{18}$ atoms g^{-1}. For diamond, there was an overall increase in activation energy (in a linear manner) from 1·5 to

14·1 kcal mole^{-1} as coverage increased from nil to 53×10^{18} atoms g^{-1}. Barrer also found the activation energy for chemisorption of oxygen on diamond up to 244°C to increase with coverage; a maximum value of 24·4 kcal mole^{-1} being reported.

The fact that there were no breaks in the Elovich plots for oxygen adsorption on diamond, under the conditions used, appears reasonable. At the most extreme conditions of temperature, pressure, and time used in this study (that is, 141°C, 100 mTorr, and 1440 min), 100×10^{18} atoms of oxygen g^{-1} were chemisorbed. This represents only 46 per cent of the total oxygen which can be chemisorbed [4]. Indeed, the amount we report to be chemisorbed at 141°C agrees closely with that reported by Sappok and Boehm [4]. We suggest that we were following chemisorption primarily on the (111) surface of diamond, which has been estimated to occupy roughly 56 per cent of the total surface area for several reasons. First, Marsh and Farnsworth find from LEED studies that chemisorption of oxygen on the (111) surface of diamond is much more rapid than on the (100) surface [11]. Evans and Phaal [12] substantiate these findings. Second, Sappok and Boehm report that maximum chemisorption of hydrogen on diamond at 800–900°C (140×10^{18} atoms g^{-1}) produces a surface which is relatively resistant to chemisorption of oxygen. At 170°C, there was still no oxygen chemisorption. Marsh and Farnsworth [11] and Lander and Morrison [13] report that hydrogen chemisorbs on the (111) surface of diamond. It is suggested then that even though the chemisorbed hydrogen only covered 65 per cent of the diamond surface, little oxygen chemisorption occurred below 170°C because: (i) the (111) sites were covered with hydrogen and (ii) oxygen chemisorption on bare (110) and (100) sites was negligible below this temperature. If oxygen chemisorption were conducted at more elevated temperatures, it is possible that distinct breaks in the Elovich plots could be observed.

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