KINETICS OF CHEMISORPTION OF OXYGEN ON DIAMOND

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Abstract—The rate of chemisorption of oxygen on diamond powder of 20 m\(^2\)g\(^{-1}\) 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 \(10^{-5}\) 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 \(5 \times 10^{18}\) 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 micro-
crystalline carbons and graphites has been
studied in detail during the last several
decades. However, a few data exist on the
corresponding diamond adsorbents. Lambert
[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 pres-
sure 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

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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
$-78$–$141^\circ$C and in the pressure range
$11$–$100$ mTorr

2. EXPERIMENTAL

Materials

The solid used was finely divided, pul-
verized 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 $1000^\circ$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$^2$g$^{-1}$. Electron microscope exami-
nation showed the sample to consist of flat
wedges of $0.5$ $\mu$m 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
$1000^\circ$C for $10$–$12$ hr until the residual gas
pressure was $10^{-8}$ Torr. The sample was
then cooled in vacuum to the required tem-
perature. A known volume of O$_2$ was allowed
to expand into the reactor, and the adsorp-
tion 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 signi-
ficant drop in adsorption rates.

Analysis of the gas using the mass spectro-
meter, at different stages of adsorption at
$85$ and $141^\circ$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
$-78^\circ$C was largely physical in nature. This
was established by outgassing the sample at
$-78^\circ$C in vacuum after the adsorption exper-
iment. This treatment would result in the
removal of any physically adsorbed oxygen
whereas the chemisorbed oxygen would
remain unaffected. The adsorption experi-
ment was once again repeated on the out-
gassed sample. It was found that $6.3 \times 10^{18}$
molecules of oxygen per gram were re-
adsorbed in the first $10$ min after which
additional adsorption was negligible. The
readsoorbed oxygen is, by definition, physi-
ically adsorbed. Since the measured rates of
adsorption at $-78^\circ$C could not be attributable
to just chemisorption, plots of results taken
at $-78^\circ$C are not included in this paper. The
adsorption of oxygen at all other tempera-
tures 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 CO₂.

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 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

\[
\frac{dq}{dt} = a \exp(-\alpha q)
\]  

or in the integrated form as

\[
q = \frac{2.3}{\alpha} \log \left( \frac{t + t_0}{t_0} \right)
\]

or

\[
q = \frac{2.3}{\alpha} \left( \log \left( t + t_0 \right) / t_0 \right)
\]

where \( a \) and \( \alpha \) are constants and \( t_0 = 1/\alpha a \). \( t_0 \) 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 \( \alpha \) is calculated from the slope of the linear Elovich plots. Substitution of \( \alpha \) in equation (2) gives the value of \( a \). The values of rate parameters \( a \) and \( \alpha \) for plots at different temperatures and pressures are summarized in Table 1. It is seen that while \( a \) is dependent on temperature, \( \alpha \) changes only slightly with the adsorption temperature. However, in experiments at different pressures \( \alpha \) 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
in Fig 4. It is seen that a straight line relationship is obtained, indicating that activation energy increases linearly with amount adsorbed.

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 rhombohedral face (110), and the cubic face (100). In an ideal, undistorted structure, each carbon atom would occupy 6·36, 4·50, and 5·51 Å² 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

<table>
<thead>
<tr>
<th>Face</th>
<th>Surface bonds per surface atom</th>
<th>Area per face atom (Å²)</th>
<th>Frequency of face (%)</th>
<th>Surface atoms of diamond cm⁻² × 10⁻¹⁸</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>2</td>
<td>6.36</td>
<td>10.4</td>
<td>0.15</td>
</tr>
<tr>
<td>(110)</td>
<td>1</td>
<td>4.50</td>
<td>23.5</td>
<td>0.75</td>
</tr>
<tr>
<td>(111)</td>
<td>1</td>
<td>5.51</td>
<td>56.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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 $1.03 \times 10^{15}$ atoms cm⁻² — or $206 \times 10^{18}$ atoms g⁻¹ of diamond used in this study. In fact, Sappok and Boehm were able to chemisorb a maximum of $216 \times 10^{18}$ atoms g⁻¹ on this material upon exposure to O₂ 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 O₂ pressure, $27 \times 10^{18}$ atoms g⁻¹ chemisorbed on diamond in 10 min; whereas, only $1.3 \times 10^{18}$ 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 $26.3 \times 10^{18}$ 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 $59 \times 10^{18}$ 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), $100 \times 10^{18}$ 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 ($140 \times 10^{18}$ 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 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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REFERENCES