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OXYGEN CHEMISORPTION ON MICROPOROUS CARBONS : AN ANALYSIS OF EXPERIMENTAL DATA

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Abstract—Chemisorption of oxygen on Spherocarb has been performed to determine the surface oxide formation and the initial adsorption rate of Spherocarb, at the temperature range of 360 K to 851 K and oxygen pressure range of 0.05 to 1 atmosphere respectively. The maximum amount of oxygen adsorbed is estimated to occupy 91.8 m^2/gC or 10% of the total surface area (TSA). The rate of chemisorption of oxygen on Spherocarb is very rapid in the beginning but it slows down with coverage. The initial oxygen chemisorption data can be linearized when plotted as amount adsorbed vs.ln (time). The data can be fitted to the integrated form of the Elovich equation, which is $q = 1/b^{*}\ln(1+abt)$ where q is the amount adsorbed and a and b are constants. This equation is applicable to the adsorption data for a wide variety of systems. A study of the variation of oxygen up-take with temperature during the first minutes of chemisorption for Spherocarb has suggested that chemisorption is the rate-controlling process initially while diffusion of oxygen and the desorption of oxidation products rapidly assume control of the oxidation rate. The experimental results show that oxygen chemisorption has an activation energy between 12 Kcal/mole and 25 Kcal/mole. It can be modeled using the Elovich equation and the initial amount chemisorbed increases in direct proportion to carbon conversion.

Key words: Chemisorption, Carbon-oxygen Surface Complex, Active Sites, Oxidation

INTRODUCTION

A carbon-oxygen surface complex is the principal reaction intermediate in the gasification of solid carbon, and because of its central role in the gasification reactions, a large number of studies have been undertaken to characterize the chemistry of this intermediate. The characterization of the complex has followed a number of distinct paths that include measurements of the oxygen chemisorption rate and the desorption rate of the surface complex; the correlation of reactivity with surface oxide concentration; and spectroscopic investigations of the complex. At present, our understanding of the chemistry of this intermediate species and its role in the gasification reactions is at best ambiguous; nonetheless, recent advances in the spectroscopic characterization of oxides together with our present understanding of the reaction kinetics for its formation and desorption could lead to further insights into the nature of this intermediate and its role in the gasification reactions of carbon.

A wide range of reactants can be used to form carbon-oxygen surface complexes. Of particular interest in carbon gasification are the complexes formed by reaction with O_2, CO_2, and H_2O. Relatively few kinetic studies have been reported for oxygen chemisorption from CO_2 and H_2O. However, in general, complex formation by CO_2 and H_2O occurs only at elevated temperatures, is apparently reversible, and results in the formation of only a few complexes on the carbon surface. On the other hand, the formation of surface complexes from oxygen takes place at relatively low temperatures (appreciable adsorption occurs at ambient temperature) and is dissociative and irreversible.

EXPERIMENTAL

Chemisorption measurements were obtained using a Stanton-Redcroft thermogravimetric analyzer. The unit is shown in Fig. 1. The instrument consists of an electronic balance and a water cooled microfurnace having a temperature limit of 1500°C and a heating rate capability of 50°C/min. A significant feature of the instrument is the small volume of the furnace (ca. 5 cc) which makes a rapid change in gas composition possible upon introduction of a reactant. At nominal gas flow rates of 1-3 standard cc/s, the transient time associated with a change in gas composition is a few seconds. Weight changes of less than 1 mg can be readily measured with this instrument, and with a sample weight of 10 mg, a sensitivity of ca. 100 ppm in weight is possible. The response time of the balance to a step change in weight is ~4 s.

Experiments were conducted with microporous chars, containing little or no ash and having minimal (S, N) heteroatom content. Char characteristics are summarized in Table 1. Most of the experiments reported here were made with Spherocarb that was preoxidized to 16% conversion. Preoxidation of the Spherocarb increased the chemisorption capacity of the carbon significantly. Additional experiments were conducted with a sucrose char, which was manufactured in our laboratory, to determine the effect of particle size on the chemisorption kinetics.

Gases used in experiments were Matheson UHP grades and were used as received. The oxygen content of the UHP nitrogen, which was determined by monitoring carbon weight loss at elevated temperatures, was 3 ppm (v/v). Gases were introduced at the bottom of the furnace and flowed upward past the sample pan. A dual analyzer, enclosed ion source, quadrupole mass spectrometer was used to measure gas compositions. Sample gases

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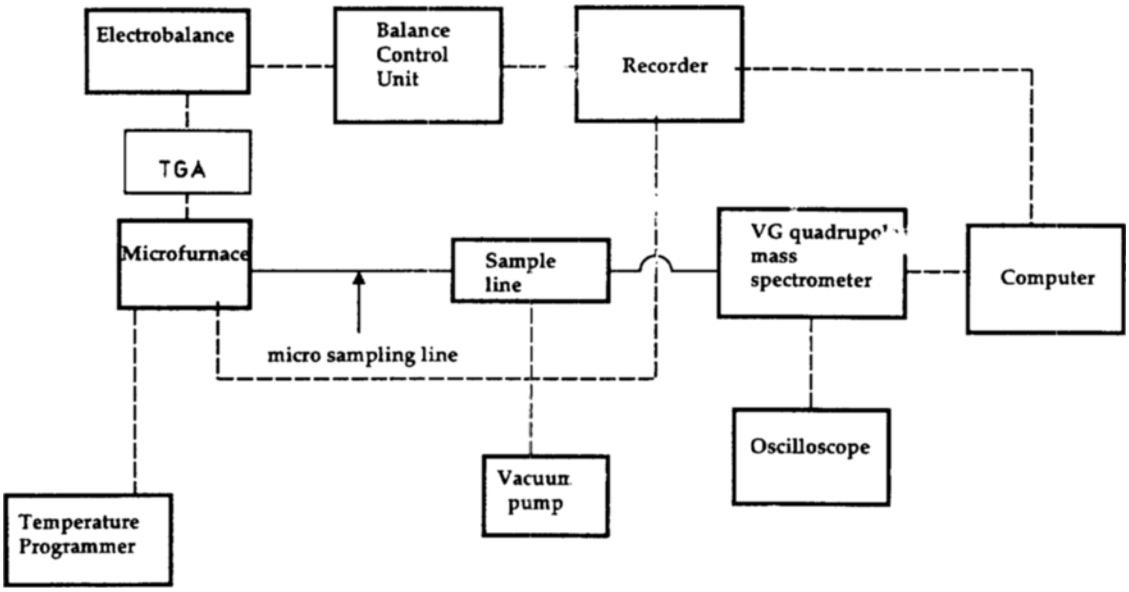

Fig. 1. Experimental block diagram.
— Gas line, --- Electric line

Table 1. Elemental analysis and surface area and porosity data for spherocarb and sucrose char

Elemental analysis	Spherocarb	Sucrose char
C (wt%)	96.8	95.95
H (wt%)	0.73	1.08
O (wt%)	2.43	3.02
ash (ppm)	200	
Physical properties	Sherocarb	Sucrose char
Surface area (m^2/g)	1020	282
Micropore volume (cm^3/g)	0.39	0.129
Pore radius (Å)	6.7	7.1

were withdrawn through a capillary sample probe located ~1.5 cm above the sample pan.

A typical run proceeded as follows: 5-10 mg of carbon were heated to 530℃ and reacted in 0.21 atm oxygen to 5% conversion. After reaction, the sample was heat treated under nitrogen (argon was used when gas analyses were made) at 780℃ for 10 min to remove all surface oxides. Outgassing resulted in additional carbon loss and brought the overall conversion to ~16%. The sample was then cooled to the chemisorption temperature and a run started by switching from nitrogen to a nitrogen/oxygen gas mixture. The elapsed time between the start of heat treatment and the start of a chemisorption run was typically 40 min and was approximately equally divided between heating and cool down times. This elapsed time was kept the same (but was not identical) from run to run. At the conclusion of a run, the char was again heated to 780℃ for 10 minutes to remove the surface oxides. About 15% more oxygen (as CO) was removed from the char upon heat treatment than was adsorbed during the chemisorption experiments. The difference is due in part to gasification by trace oxygen in the inert gas during the heat treatment cycle and to adsorption of the trace oxygen before the start of a run. Calculations indicate that 1/3 to 1/2 of the difference between the amount chemisorbed and the amount desorbed may be accounted for by these two factors. In addition, gas composition measurements made during chemisorption runs showed that gasification occurs con-currently with chemisorption. The CO and CO_2 concentrations in the gas were low so that it was not possible to obtain quantitative compositional data from the mass spectrometer data; however, the concentration levels remained essentially constant during a run, indicating a constant gasification rate during chemisorption. These three factors can account for most of the discrepancy between the amounts adsorbed and desorbed. Furthermore, the difference in the amount desorbed and adsorbed that is accounted for by these factors will change only the magnitude of the adsorption curves by a small degree but not the shape of the curves.

Each run was made with a fresh carbon sample so as to avoid possible effects of heat treatment cycles on chemisorption capacity

KINETICS OF OXYGEN GASIFICATION

It is assumed that the following mechanism represents the essential elementary steps of the oxidation reaction of carbon:

$$C + O_2 \rightarrow C(O_2) \quad (1)$$

$$C + C(O_2) \rightarrow 2C(O) \quad (2)$$

$$C(O) \rightarrow C(O)' \quad (3)$$

$$C(O) \rightarrow \text{products} \quad (4)$$

$$C(O)' \rightarrow \text{products} \quad (5)$$

It is assumed in this mechanism that the dissociative chemisorption of oxygen on the carbon is proceeded by a trapping of the oxygen molecule into a physisorbed or precursor state. Step (1) is rapid and presumably at equilibrium relative to the time scales of steps 2-5. Whereas steps 2-5 are all activated processes since they involve the formation or breakage of a chemical bond, step (1) should have no activation energy for formation (Measureable amounts of physisorbed oxygen are present on microporous carbons at temperatures below ~150℃). The chemisorption step, (2), is assumed to be dissociative and irreversible. It is this step that is the focus of this paper. Once chemisorption of oxygen has occurred, it is assumed that the surface oxide may be mobile. The mobility of the surface oxide has been proposed by a number of investigators based on microscopic studies of graphite oxidation. The desorption of the surface complex is given symbollically by reactions 4 and 5. The removal of a carbon oxide requires the breaking of least one and usually two carbon-carbon bonds in the solid. The formation of CO is presumably straightforward; however, the exact steps leading to CO_2 formation are, at this time, speculative. Since desorption of the surface complex involves the breaking of bonds different from those involved in the formation of the complex, the adsorption and desorption steps follow distinct chemical pathways. In other words, the adsorption and desorption reactions involve separate and distinct transition states. As a result, one would not necessarily expect to have any correlation between the activation energy for adsorption and the stability of the surface complex.

For microporous chars the situation is more complex. These chars presumably consist of small basal plane lamellae, present singly or in stacks of two or three turbostratic layers. The lamellae are apparently curved forming larger ultramicropores in the shape of a triangle and small ultra-micropores between adjacent curved lamella or stacks of lamellae. The average diameter of the lamellae is a function of the heat treatment temperature, the nature of the precursor, and presumably also the extent of carbon conversion. Based on this picture of microcrystalline carbons it is possible to obtain an estimate for the fraction of carbon atoms that are potential adsorption sites as follows. One first estimates the edge to total surface area of a microcrystallite, which will be a function of the initial lamellae size and the degree of carbon conversion, and the number of doubly bonded edge atoms in a crystallite to determine the ratio of edge to total carbon atoms. With experimental information on the total surface area, one can then estimate the edge to total carbon atom ratio. Obviously there a number of approximations in this calculation-most importantly the fraction of the carbon that is present in unorganized form as aliphatic cross-linking structures-but the calculation should yield a first order approximation for the fraction of carbon atoms that are potential adsorption sites. Edge carbon atoms are expected to be present in a wide range of irregular configurations in addition to the usual arm chair and zig-zag configurations. Most of these configurations will likely involve labile carbon atoms or a labile carbon atom acting as a linking structure. Some examples of possible edge structures are shown in Fig. 2. From this picture, it is apparent that both structure and chemistry will be important in the adsorption of oxygen and that one would expect adsorption to occur with a range of activation energies and the resulting complexes to have a range of desorption energies. It is probable that at some sites dissociative adsorption may occur in a single step, whereas at other sites adsorption may involve a complicated sequence of reaction steps. Clearly, the details of the reaction is speculative without further spectroscopic information on the nature of the bonding between atoms that form the carbon-oxygen complexes.

RESULTS AND DISCUSSION

1. Elovich Model

The Langmuir model for adsorption have been used to describe the reaction of carbon with oxygen. However, the Langmuir model for the rate of adsorption usually does not agree with experimental data because it has three important limitations. These are the following; first, the adsorption is energetically homogeneous surface and takes place only through collision of gas molecules with vacant sites, second, each site can accommodate only one adsorbed particles, and third, the energy of an adsorbed particle is the same at any site on the surface and is independent of the presence or absence of near by adsorbed molecules. The Langmuir equation is only obeyed the first condition during the initial stages of chemisorption on solids. The rate of adsorption is independent of the surface coverage. However, it probably applies to slower chemisorptions where a small activation energy is involved and it is for this type of system that experimental isotherms can normally be obtained. For chemisorption, the second condition may be obeyed. However, the third condition is rarely obeyed, since this condition requires that the surface is perfectly uniform and that forces of attraction and repulsion between adsorbed molecules are negligible.

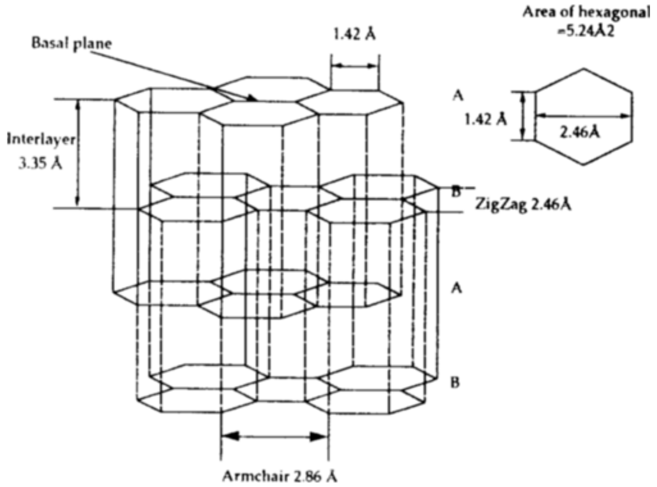

Fig. 2. Structure of the hexagonal form of graphite.
There are two kinds of sites (zigzag and arm chair)

The Langmuir model for the rate of adsorption usually does not agree with experimental data. The observed rates decrease so rapidly with increasing coverage θ. Also the condensation coefficient (σ) in Eq. (15) may vary with θ. These variations may be caused by surface heterogeneity; that is, the activity of the sites varies, so that different sites possess different value of condensation coefficient and activation energy. The most active sites would have the lowest activation energy and would be occupied first.

If we compare the Langmuir equation, $r_a = K^*P(1-q)$, with Elovich equation it is shown that K in the Langmuir equation is a function of surface coverage. However the reason the condensation coefficient (σ) and activation energy (E) are function of q is that the first two postulates of the Langmuir treatment are not satisfied experimentally; that is in real surface all sites do not have the same activity and interactions do exist.

The Elovich model is frequently assumed to be valid in kinetic model for adsorption and desorption that are better able to fit experimental data than the Langmuir model.

Conclusionly, the Elovich equation is usually expressed in terms of the amount of gas adsorbed or desorbed.

It is often found that adsorption and desorption of oxygen on carbon can be adequately modeled by the Elovich equation which may be written as:

$$\frac{dq}{dt}=a\ \exp(-bq)=a_0\ \exp(-E/RT)\ \exp(-bq) \qquad (6)$$

where q is the amount chemisorbed at time t, and a and b are constants. The constant a is usually assumed to have an Arrhenius temperature dependence and can be expressed in its temperature dependent form; $a_0\ \exp(-E/RT)$. This equation has wide applicability in representing rates of adsorption. It was first formulated to describe the kinetics of oxidation process and later developed for adsorption kinetics by Elovich et al.

If the Elovich equation is interpretated theoretically, it is based on an isothermal rate equation of the form as follows:

$$dq/dt=K(p)*n*\exp(-E/RT)$$

where, at constant temperature, K(p) is a pressure dependent constant comparing the collision frequency $[p/(2\pi mkT)^{0.5}]$ of the gaseous adsorbate molecules with unit area of adsorbent surface and a condensation coefficient; n is the number of sites available for adsorption and E is the activation energy for adsorption and is a function of q.

If applicable to an adsorption system, the Elovich equation has three main functions. First it provides a method of interpolating and graphing the data, second we can calculate the initial rates of adsorption from evaluation of "a" and third we can get a means of extrapolating the data at long adsorption times.

The integrated form of the Elovich equation is:

$$q=\left(\frac{1}{b}\right)\ln(ab)+\frac{1}{b}\ln\left[t+\left(\frac{1}{ab}\right)\right]=\left(\frac{1}{b}\right)\ln(abt+1) \qquad (7)$$

where the lower limits of integration is $q=0$ at $t=0$. For values of $t \gg 1/ab$, the plot of q against ln(t) is linear and values of "a" and "b" can be derived from its slope and intercept

at $t=0$

$$b=\frac{1}{\text{slope}}$$

$$a=\frac{1}{b}\exp(\text{intercept}*b)$$

For the case where $abt<1$, the initial estimates for a and b may be used to construct the plot of q against $\ln[t+(1/ab)]$.

One interpretation of the Elovich equation is based on the site number variation. Eq. (6) may be derived by assuming that the number of sites available for adsorption decreases exponentially with the number on which adsorption has already taken place, i.e., with extent of adsorption q:

$$n_q=n_0\ \exp(-bq) \qquad (8)$$

n_0 is the number of sites available at $t=0$ and b is a constant independent of T and p; n_q is the number of sites still free after an amount q of adsorbate has been adsorbed. To impart physical significance to this model, the differential form of Eq. (10) may be combined with Eq. (6)

$$dn_q/dt=-n_0b*\exp(-bq)*dq/dt=n_0\ ab[\exp(-bq)]^2. \qquad (9)$$

so that

$$dn_q/dt=(ab/n_0)n_q^2. \qquad (10)$$

Eq. (10) describes a second-order process, in which the rate of removal or destruction of bare sites as a function of the number presenting the surface.

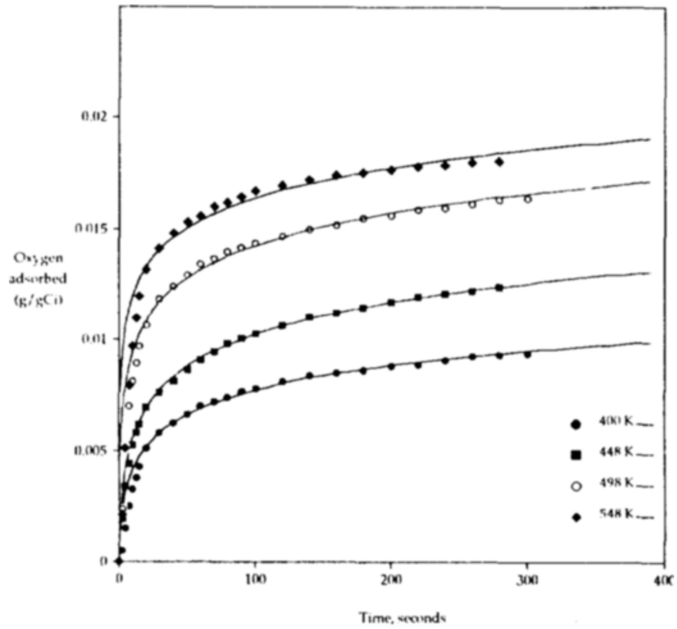

Fig. 3. Oxygen chemisorption; 0.21 atm; Spherocarb at 16% conversion (line→Elovich model).

Since adsorption eliminates more sites than by actual occupancy, bare sites are in short supply, and the rate of adsorption is therefore governed by the availability of sites.

2. Chemisorption Studies

The chemisorption of oxygen on Spherocarb has been studied over the temperature range of 360 to 575 K and oxygen partial pressures between 0.05 and 1 atmosphere using a thermogravimetric analyzer. Chemisorption measurements were determined on two bases. One is a adsorption base and the other is a desorption base. The amount of chemisorption which based on adsorption is calculated by the oxygen up-take and desorption based amount of chemisorption is calculated by the desorption weight which assumed that the CO is only the product gas in reaction.

The experimental measurements carried out the rate of oxygen chemisorption at different temperatures, pressures and particle size to get the quantitative values for changing in controlling step on the carbon surface. The temperature range which accurate measurements could be made was quite limited. At 575 K, carbon sample showed a weight gain when exposed to oxygen, however the weight decreased as products desorbed or takes place the gasification.

The effect of carbon particle size on the rate of adsorption is performed however it is still not clear.

A series of experiments was also performed on unreacted samples the purpose of which was to study the variation of the amount of oxygen adsorbed as a function of carbon conversion.

Various experiments carried out to measure the active surface area (ASA), which is generally assumed much less than the total surface area (TSA).

3. Effect of Temperature and Pressure on Oxygen Chemisorption

The rate of chemisorption of oxygen on Spherocarb at various temperatures in the range of 360 to 548 K are shown in Fig.

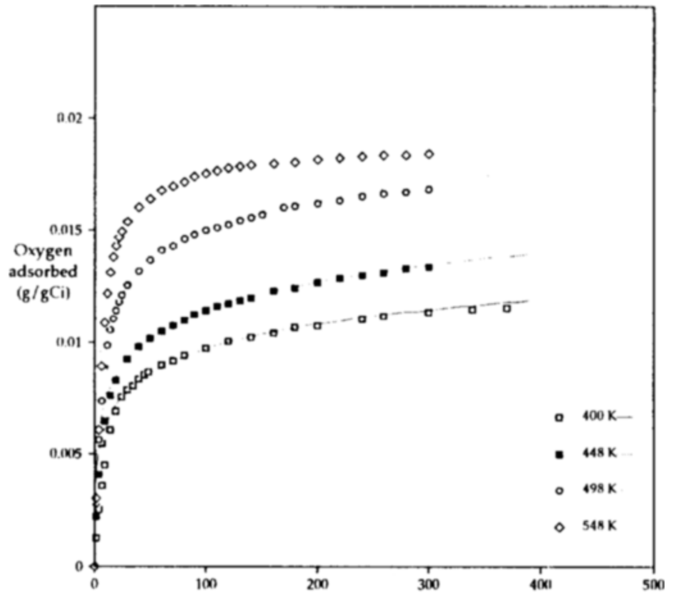

Fig. 4. Oxygen chemisorption; 0.5 atm; Spherocarb at 16% conversion (line→Elovich model).

3 and 4. From the Fig. 3 and 4 we can see that chemisorption rate is very rapid in the beginning (within the first 20 sec) but the rate slows down with increasing the coverage. In figures the y axes represent the amount of oxygen per carbon (Spherocarb) remaining weight after 16% carbon conversion and the x axes represent the chemisorption running time. Most of the experiments reported here were conducted with Spherocarb that preoxidized to 16% conversion to increase the chemisorption capacity of carbon. In Figs. the points indicate the experimental data and the line indicate the best fit of Elovich model. The results show that for low temperature, the rate and equilibrium oxygen uptake are influenced by peak chemisorption temperatures suggesting that at higher temperature, sites with a higher activation energy for adsorption are being occupied.

Generally we assume that each carbon atom represents an adsorption sites and desorption of an adsorbed oxygen atom removes the carbon atom to uncover a further adsorption site. If each new site is refilled immediately, implying a surplus of oxygen above the surface, the rate of adsorption is controlled by the adsorption or residence time of the adsorbed oxygen molecules. This value can be used to estimate rates of adsorption.

The results obtained in this study are in agreement with Khan [Khan, 1988] who investigated the influence of chemisorption temperature on oxygen uptake on char prepared from demineralized Pittsburgh No. 8 coal at 773 K and that the weight loss by gasification become significant over 400 minutes at 498 K. According to his results, equilibrium uptake is essentially complete after 15 hours of chemisorption at 473 K.

To determine the activation energies of chemisorption, the reaction rates must be expressed in a consistent way, because the chemisorption rates are not constant with time. As shown in Fig. 3 to 4, the chemisorption rates decrease with time. In present study we calculated the initial rates by the use of the best fit of the Elovich plot and it is shown in Table 2. The two constants in the equation obtained from the Elovich constants expressed in μg adsorbed oxygen per second per μg original carbon are plotted 1/T in Fig. 5. In Fig. 5 we are able to see there are some changes in slope. The changes in slope can be assumed due to a change in controlling mechanism on the surface or external mass transfer limitations.

Table 2. The temperature dependence of the Elovich constants at 16% conversion

Temperature (K)	Oxygen pressure (atm)	a (μg/μg-sec)	b (μg/μg)
360	0.21	0.00192	621
400	0.21	0.00256	469
448	0.21	0.00922	518
498	0.21	0.0171	469
548	0.21	0.0893	514
575	0.21	0.1473	543
400	0.5	0.00649	620
448	0.5	0.00785	530
498	0.5	0.0303	491
548	0.5	0.618	614
448	1.0	0.01232	438
498	1.0	0.02093	451
548	1.0	0.155	467

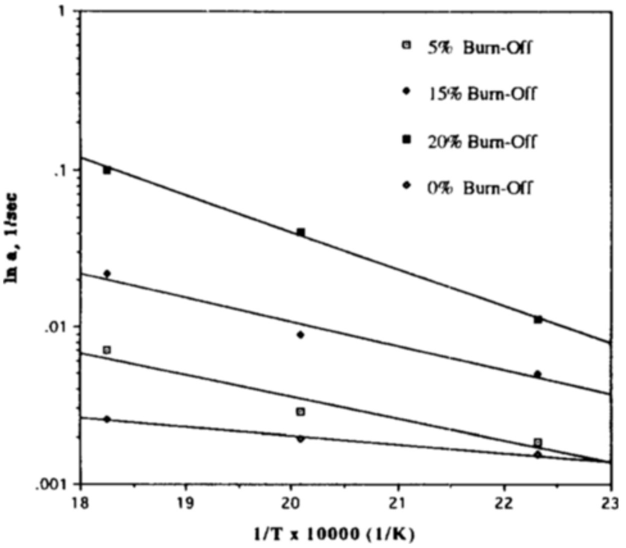

Fig. 5. Arrhenius plot of oxygen chemisorption for Spherocarb at different burn-off.

We can consider that the transition in Fig. 5, to a very lower slope is attributed to the limiting rate of diffusion of oxygen through the layer of gas at the top of the sample pan. The mass transfer in this space becomes controlling before diffusion in the very thin layer of sample becomes important. Second the pore diffusion limitations might be suggested for transition to a lower slope in Fig. 5 since the activation energy is low.

The activation energies which based on the Elovich constants "a" is 10.3 Kcal/mole in Fig. 5. Floess et al. [1989, 1991] calculated the activation energy using the site energy distribution model and it was 19-28.68 Kcal/mole. When Allardice [1966] calculated the activation energy using the value of the Elovich constant "a", an activation energy of 11.1 Kcal/mole was calculated from the Arrhenius plot slop. This was the apparent activation energy for the initial irreversible adsorption of oxygen on degassed brown coal char.

The value obtained for activation energy of the initial adsorption (5% burn-out, 7.2 Kcal/mole) is rather low for a chemical reaction. Sevenster [1961] has also obtained values of less than 20 Kcal/mole for chemisorption reactions on carbonaceous materials. We can assume that activation energies are generally attributed to rate control by some mass transport or diffusion phenomenon. Rate control by diffusion of oxygen through a surface film of inert gas or through the pores to adsorption sites is unlikely at the temperatures investigated.

It may be concluded that the adsorption in the initial stage can be represented by the Elovich equation and, consequently, that chemisorption is the only process operative during this initial stage of adsorption such a predominant rate-determining process that one may consider the adsorption to be a simple process at this initial stage.

When we compared the amount of chemisorption which based on adsorption with desorption based amount of chemisorption there are some weight differences (about 10%). If no gasification took place, the adsorption base oxygen uptake should be equal to the desorption base oxygen uptake.

The amount of complex calculated from the desorption base is a function of product composition and the results were obtained by assuming that CO was the only product gas during the desorption. Tucker and Mulcahy [1966] who also investigated oxygen chemisorption, noted that more than 90% of the products of decomposition of the complex was CO.

Oxygen irreversibly adsorbed on Spherocarb can be recovered in a different chemical form, as oxides of carbon such as CO, CO_2. The desorption of these oxides begins at temperatures range of 473-573 K however the oxygen cannot be recovered quantitatively below 1273 K. Thus the oxygen must undergo a chemical change during adsorption process.

As mentioned earlier, the Elovich constant "a" is actually the initial rate of the adsorption when $q=0$. The value of "a" was independent of pressure, in contrast, "a" shows a marked dependence on temperature (Table 2).

4. Effect of Mass Transfer on Oxygen Chemisorption Behavior

When the reaction rate is under mass transfer control, it is assumed that the chemical reaction rate is so fast that the concentration of oxygen at the external surface of the char particle is effectively zero and the particle can be treated as if it were nonporous. Thus, if the char particle is assumed to be spherical, its effective surface area would always be $4\pi r^2$. The burning particle would shrink progressively from its original diameter to the point where the particle became fragmented. The oxygen diffusion rate can be predicted assuming that Fick's law applies. Briefly, if we assume that Fick's law applies, we have for a spherical particle with a large excess of oxidant.

$$-q_r 4\pi r^2 = -q_x 4\pi x^2 = D(dC_x/dx)4\pi x^2$$

where q is the molar flux of oxidant to the solid surface. C is molar concentration and D is diffusion coefficient. Hence

$$-q_r = [D(C_x - C_r)]/[r(1-r/x)]$$

when $x \gg r$, $C_x \rightarrow C$ (the bulk concentration) and $r/x \rightarrow 0$, and since the mass transfer control $C_r=0$, we have $-q_r=(DP/RT)\ (f_r/r)$ where P is the system pressure and f_r the mole fraction of oxidant in the bulk phase. Equating $-q_r$ to the reaction rate R_{mt}, referring physical properties to standard conditions, and converting molar to mass units yields.

$$R_{mt} = 48D_0(f_m/d)\rho_0(T/T_0)^{0.75}/3$$

f_m is mass fraction of oxidant in the bulk phase, D is the diffusion coefficient, d is the particle diameter, r is the gas density and T is the reaction temperature and the subscript 0 denotes properties referred to standard conditions. Thus the rate is independent of system pressure and has a small temperature coefficient (0.75), and is inversely proportional to particle diameter.

If it is assumed that carbon-oxygen reaction at the particle surface produce CO and the subsequent burning of CO occurs far away from the particle surface, the char reaction rate per unit geometric are of external surface of the particle (R_{mt}) can be predicted as follows

$$R_{mt} = 0.75 h_d r_g f_m.$$

where h_d is the mass transfer coefficient, r_g is the density of gas and f_m is mass fraction of oxidant in the bulk phase. The mass transfer coefficient can be calculated; $h_d = S_h D d_p$, where S_h is the Sherwood number, D is the diffusion coefficient and d_p is the diameter of the particle.

The above equation does not take into account the convective flow of the gaseous medium taking place normal to the particle surface. This flow, known as the Stefan Flow, can arise in two ways; from the stoichiometry of the reaction at the particle surface and from the nature of the diffusing species. For example, the $C + 1/2\ O_2 \rightarrow CO$ reaction on a particle surface generates a net convective flow away from the particle and leads to a lower oxygen diffusion rate.

At low temperature, where the reactivity of the char is low, a molecule of oxygen entering a porous particle has a high probability of diffusing deeply into the pellet before finally reacting with the pore surface. In this temperature range, the concentration of the gaseous reactant is essentially uniform throughout the porous solid and equal to that in the bulk gas stream. The overall rate of reaction is independent of the particle size and is controlled by the rate of the intrinsic chemical reaction and the total pore surface area. The rate of the intrinsic chemical reaction per unit area of pore surface can be expressed as follows:

$$R_i = K_i P_0{}^m 2 = A_0 \exp(-E_i/RT) P_0{}^m 2$$

where K_i is the intrinsic rate constant, A_0 is the frequency factor, E_i is the activation energy and m is the order of the intrinsic reaction.

However, there are some difficulties to measure the intrinsic rate since the pore surface area may change with the burn-off of the particle. The chemical reaction rate of the char is usually presented on a basis of either the weight or the external surface area of the char particle.

The most probable explanation of the low activation energy is that the rate of chemisorption is controlled by the migration of a mobile physically adsorbed layer across the surface to activities where chemical interaction occurs.

5. Effect of Particle Size and ASA

It is known that the ASA (active surface area) contains both a reactive fraction and a relatively unreactive fraction. These were based on the observed initial weight gain during combustion at 723 to 773 K. The value for the active surface area can be calculated from the amount of oxygen adsorbed at equilibrium. The ASA

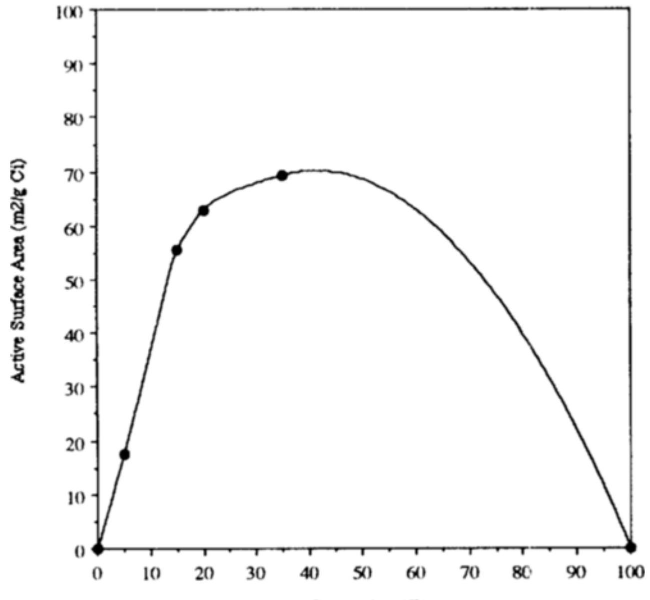

Fig. 6. Effect of burn-off on active surface area for Spherocarb: 498 K and 0.21 atm.

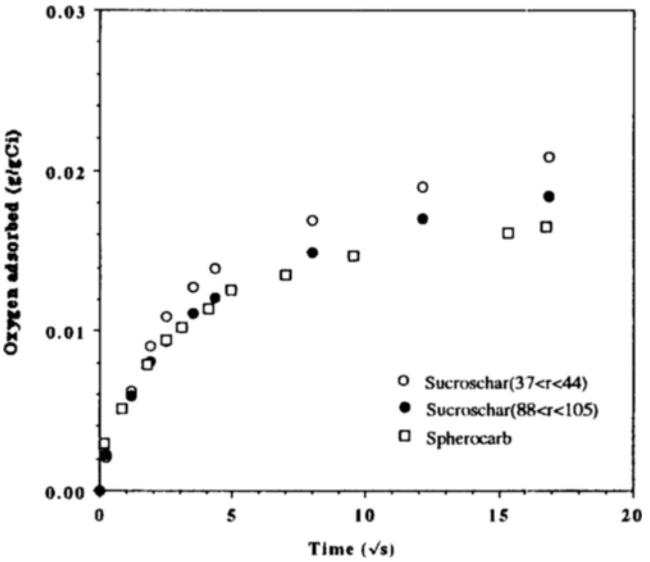

Fig. 7. Oxygen chemisorption on different size carbon; 498 K and 0.21 atm.

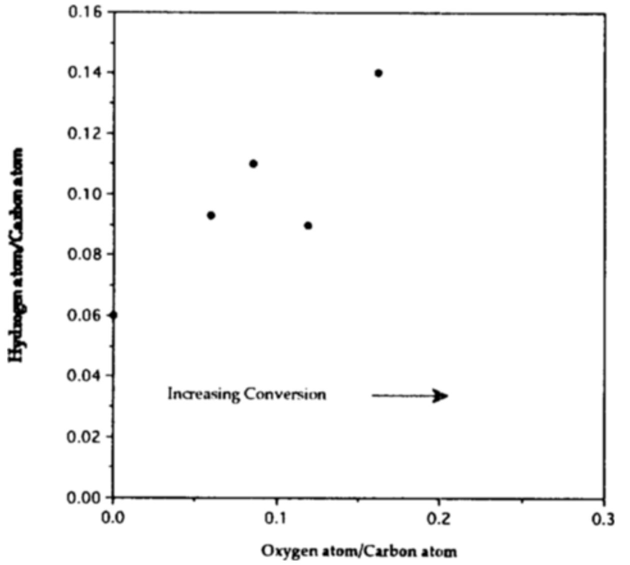

Fig. 8. H/C atom ratio vs. O/C atom ratio of Spherocarb (conversion range of 0 to 66%)

occupied by dissociatively chemisorbed oxygen atom can be determined assuming a value of 13.6×10^{-16} cm²/atom for the area occupied by each oxygen atom. The value for the surface area (m²/g) covered by oxygen chemisorbed at 498 K and 0.21 atm in Fig. 6 was calculated from the product of the number of molecules adsorbed at saturation and the surface area that each molecule occupied.

It is necessary to clean the carbon surface of oxygen complexes before the chemisorption tests because the surface impurities include not only catalytic materials but also some unknown inhibitors.

Fig. 7 shows the effect of particle size on chemisorption as reflected by the amount of oxygen chemisorbed by two different size sucrose char and Spherocarb. It is shown that there is no effect of particle size on the rate of chemisorption. For sucrose char samples the amount of chemisorbed oxygen increased with decreasing mean particle diameter. Sucrose char particles are largely devoid of macropores, and as a result, the particle size is a measure of the size of the microporous domains in the particle. Furimsky et al. [1988] also studied the effect of particle size on chemisorption as reflected by the amounts of oxygen chemisorbed by two fractions of FC coke and they showed a decrease in the diameter from 100 to 30 μm should more than double the amount of chemisorbed oxygen. For oil shale samples it is shown that the amount of chemisorbed oxygen increased with decreasing mean particle diameter as did the initial rate of chemisorption. So we can conclude that the overall particle effect is much less significant in the initial adsorption rate.

The chemical composition of mineral matter of the low carbon solids was similar, as was the structure of Kerogen. Carbon and hydrogen analysis was performed by the Huffman Laboratories in Colorado. The carbon conversion was correlated with structural parameters such as H/C ratio. These parameters are frequently used to identify structural differences in carbonaceous solids. A correlations were established between the carbon conversion and H/C ratio in Fig. 8. For solids containing the same amount of organic matter but differing in chemical structure, solids having a lower aromaticity (a higher H/C ratio) will chemisorb more O_2 than high aromaticity solids. These observations refer to solids having a similar mean particle diameter and very low surface area.

SUMMARY AND DISCUSSION

1. The analyses of a number of oxygen chemisorption studies provide evidence that oxygen adsorption on carbon occurs with a range of activation energies. The principal evidence that adsorption occurs on a number of distinct sites is the observation that oxygen chemisorption for different time, temperature, and oxygen pressure histories do not lead to the same oxygen loading; conse-

quently, a Langmuir adsorption model cannot correctly fit the experimental data. For a microcrystalline carbon, the activation energies for adsorption appear to vary approximately linearly with coverage and range from ~10 to ~30 kcal at oxygen coverages of 0.1 to 0.9 of maximum.

2. The surface oxygen concentration increases dramatically with carbon conversion relative to the amount adsorbed at reaction conditions where there is negligible gasification. Therefore, gasification results in the formation of additional surface complexes as well as in the formation of carbon oxides. The surface complexes on a carbon during gasification can be divided into three general classes: oxygen atoms that are strongly bound and thus remain on the surface during gasification; reactive complexes, or those that desorb at a rate characteristic of the gasification rate, and complexes that are formed and desorb to products in a single concerted reaction step. The relationship between these various surface oxides and the kinetics of their formation is at present not known.

3. Additional spectroscopic characterization of the surface complexes are clearly needed to further extend our understanding of the carbon-oxygen surface complexes.

NOMENCLATURE

a_m : cross-sectional area of the sample pan [cm^2]
E : activation energy [kcal/mole]
E_d : desorption activation energy [kcal/mole]
Θ : surface coverage
t : time
T : temperature [K]
D : diffusion coefficient
w : oxygen adsorbed weight [g]
Q : gas flow rate [scc/sec]
C_s : oxygen concentration at the surface [mole/cc]
C_b : oxygen concentration in the bulk gas [mole/cc]
k_m : mass transfer coefficient [cm/cc]
k_r : reaction rate constant [cm^3/cc]
w_i : initial weight of sample [mg]
q : amount chemisorbed [μg]
a : Elovich constant [μg/μg sec]
b : Elovich constant [μg/μg]
n_0 : number of sites available at time = 0
n_q : number of sites still free after adsorbed
r_a : the rate of adsorption
s : condensation coefficient
p : pressure [atm]
m : mass of a molecular
k : Boltzmann constant
C : molar concentration

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