KINETICS OF OXYGEN CHEMISORPTION ON CHAR

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Introduction

Carbon gasification by oxygen involves a still poorly understood sequence of chemisorption and desorption processes. Low temperature chemisorption of oxygen is often utilized to draw inferences about the numbers of reactive gasification sites on the surface[1]. There have been many applications of the this method; normally, results are treated as though they involve a titration of active sites. Yet, it has been shown that the results obtained are sensitive to the conditions utilized for performing the chemisorption, since the chemisorption is a kinetically-controlled phenomenon[2,3]. It has long been thought that there exist sites with differing chemisorption reactivities, and that these determine the observed kinetics of the process. One study suggested "steps" corresponding to filling of different types of sites[4]. More typically, the chemisorption process is observed to follow the so-called Elovich kinetic law:

$$r_c = dq/dt = b \cdot exp(-a \cdot q) \qquad (1)$$

where r_c is the rate of oxygen chemisorption, q is the uptake of oxygen on the surface, t is time and a and b are constants. The common explanation for this form of kinetic law involves a variation of the energetics of chemisorption with the extent of surface coverage though a kinetic model based upon two-site chemisorption has also been advanced[5]. The possibility that physical, especially diffusional, limitations might lead to similarly shaped uptake curves has also been explored[6-9]. The general conclusion from these latter studies has been that there is a good possibility of fitting data that are well-described by the Elovich law with a diffusional law as well. The objective here is to explore further the kinetics of oxygen chemisorption, to help further elucidate the nature of the processes involved.
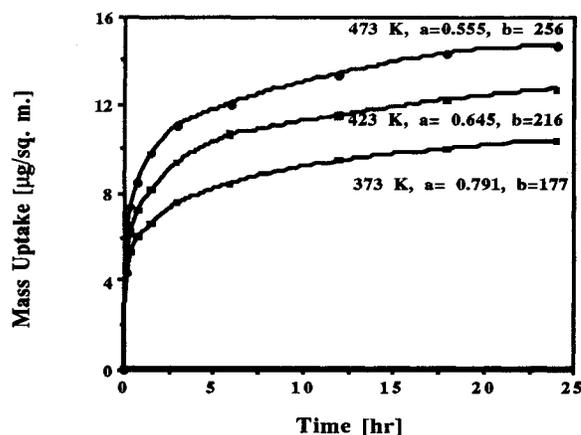
Experimental

A standard thermogravimetric analyzer (TGA) was used for the present study. Experiments were performed in a static system in an O_2/He mixture at 101 kPa total pressure. The vessel volume was large enough to ensure that under any reaction conditions the consumption of O_2 was insignificant. High purity chars were derived from phenol-formaldehyde resins synthesized in-house[10]. The chars were prepared by pyrolysis of the resin in helium at 1273 to 1323K for 2 hours, then ground and sieved to the desired particle size (100-300 μm). The surface of the char was cleaned of oxides prior to O_2 chemisorption experiments by heating the sample to 1223 K in helium for at least 2 hours. Specific surface areas of the samples were determined by the N_2 BET method at 77 K. Oxygen chemisorption experiments were performed immediately after surface cleaning. The sample temperature was quickly lowered from 1223 K to the desired chemisorption temperature, and then the desired O_2/He mixture was quickly introduced. Mass uptake and gas evolution were monitored.

Results

Typical results are seen in Fig. 1, obtained with 1323 K char under 10.1 kPa of O_2 pressure.

Figure 1

Since chemisorption behavior can depend upon burnoff[11], all chars used for these experiments have similar extents of oxygen burnoff. from 18-20% (the surface areas of these chars are about 690 m^2/g). Under the temperatures studied here, desorption during chemisorption was negligible[10]. It can be seen from Fig. 1 that, as usual, chemisorption is initially fast, and slows down markedly with increasing surface coverage. This behavior is described by the Elovich law, and the values of the constants are shown. After a long period of chemisorption, the rate of chemisorption becomes very low and the total amount of mass uptake varies little with time, although there is never a very distinct "endpoint" to the chemisorption, even at much longer times.

The parameter b represents the zero coverage rate. It is seen to increase with increasing temperature, and does so with an apparent activation energy of 5.5 kJ/mol. The value of "a" is a decreasing function of chemisorption temperature in oxygen. This has been earlier reported by others[12,13]. A decreasing value of a with increasing chemisorption temperature implies an increasing apparent activation energy for chemisorption with increasing extent of surface coverage, as may be seen from the following:

$$E_c/R = -[\partial \ln(r_c)/\partial (1/T)]_q = -d(\ln b)/d(1/T) +$$
$$[da/d(1/T)] \cdot q$$
$$= 650 + 418 \cdot q, \qquad (2)$$

For a typical range of coverages from q=0 to q=10 μ g/m^2, as

590

in Fig. 1, the activation energy rises from about 5.5 kJ/mol to about 41 kJ/mol. Such values are in the range typically reported for chemisorption.

Surface species formed during oxygen chemisorption at different temperatures were studied by TPD. The yield of CO_2-forming complexes is more weakly dependent on chemisorption temperature than the yield of CO-forming complexes.

Use of explicit activation energy distribution models (as opposed to the Elovich law) has been made by several workers in recent years[14-16]. We have applied such a technique earlier elsewhere to describing the desorption of oxygen complexes, and will not repeat details here[17]. The basic model assumes that the rate of chemisorption is governed by a distribution of activation energies, f(E), of any unrestricted form. The chemisorption is assumed to be first order in unfilled sites, and the different isothermal chemisorption curves are integrated assuming only that the same distribution governs all behavior, and that all three distributions are characterized by the same constant pre-exponential factor. For the conditions of Fig. 1, the pre-exponential that is determined from the fit is $5 \cdot 10^3$ $(hr)^{-1}$ The resulting distribution function is shown in Fig. 2, in which M_0 is the total chemisorption site inventory.

Figure 2
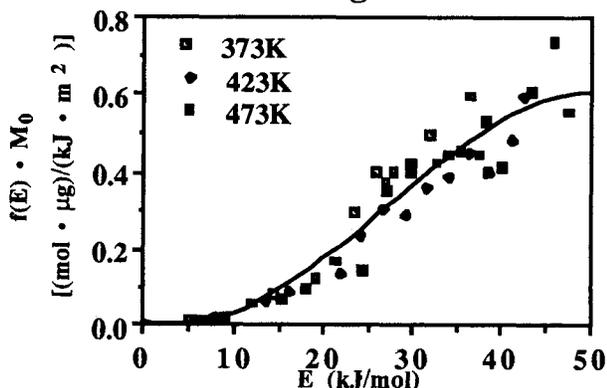
The activation energy for O_2 chemisorption on the char ranges from a low value of about 5 kJ/mol to 50 kJ/mol, in fair agreement with the activation energy range determined from the use of the Elovich equation. This is not surprising, since both approaches must fit the same data. The second approach, however, places no arbitrary restrictions on f(E) as were implied in (2), i.e., the strictly linear relationship between E and q implied if a and b are functions of temperature only. In fact, the almost linear variation of f(E) with E implies more like a quadratic variation of E with q. Examining f(E) suggests that there are parts of the distribution which are relatively "flat", giving weak support to the stepwise behavior suggested by others[4].

Additional experiments were performed in which chemisorption was carried out to a particular extent of surface coverage, the sample temperature was abruptly changed to a new value, and the effect on chemisorption rate then measured. In this way, the activation energy at a particular extent of coverage could be directly determined. Results are seen in Table 1.

Table 1. Results of Temperature Jump Experiments

Fractional Coverage = 0 to 0.2			
ΔT (K)	423->498	498->523	
E (kJ/mol)	0	8	
Fractional Coverage = 0.4 to 0.6			
ΔT (K)	398->423	423->448	448->398
E (kJ/mol)	11	41	28
Fractional Coverage = 0.3			
ΔT (K)	423->448	448->473	473->498
E (kJ/mol)	42	36	37

These results show activation energies to be in the same range as obtained from the isothermal chemisorption experiments. At low coverage, activation energies are quite low, but rise quickly to values near 40 kJ/mol. A very low activation energy emerged from temperature jump experiments involving low temperatures (398 K), even at moderate coverage. The reasons for this are still under investigation.

In conclusion, we doubt that a purely diffusion-controlled process governs oxygen chemisorption under most ordinary test conditions. This is based upon the fact that a distributed activation energy system is revealed by different methods in these experiments, and the activation energies are too high for ordinary diffusion control. The magnitudes of activation energies obtained could indicate an activated diffusion-controlled process, but the observed timescales for chemisorption were far greater than those for diffusion of N_2 during the BET surface area determinations at liquid N_2 temperatures, so we are dubious about a diffusional limitation on this basis as well.

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