A COMPARISON OF CO_2 AND O_2 GASIFICATION OF GLASSY CARBON

S. R. Kelemen
H. Freund
Exxon Research and Engineering Company
Clinton Township
Route 22 East
Annandale, New Jersey 08801

Abstract

O_2 is known to be much more reactive then CO_2 toward carbon. We have separated and studied with surface spectroscopies the dissociative adsorption step from the CO formation step in the O_2 and CO_2 gasification of glassy carbon. The reactive adsorption probabilities decreased with increased coverage. At high coverage the derived activation energy for O_2 dissociation was 33 kcal/mole and 50-60 kcal/mole for CO_2. The CO formation energy decreased from 90 kcal/mole at very low coverage to 70 kcal/mole at high coverages. The steady state oxygen coverage during CO_2 gasification corresponded to these high coverages with a measured activation energy of 67 kcal/mole. CO formation energetics limit the rate of CO_2 gasification. The increased gasification activity for O_2 is associated with a more facile gaseous dissociation step causing higher oxygen coverages which in turn generates lower energy CO formation sites.

I. INTRODUCTION

It is widely recognized that O_2 has a much higher reactivity than CO_2 toward carbon; this difference has been kinetically quantified to be 10^5 greater at 800K and 0.1 atm pressure (1). Despite this large reactivity difference the responsible elementary processes on the carbon surface are not well understood. Oxidation and gasification reactions of carbon are a class of very difficult reactions to characterize and quantify. Gasification reactions are sensitive to the type of carbon being gasified (2). A better understanding of these systems could be achieved by detailed physical characterization of the external surface of a given carbon coupled to adsorption and reactivity studies of the reactant gases (2-4). The application of surface sensitive probes to this area is an essential component to approach the problem. These results are used to interpret observations of steady state reactivity.

II. EXPERIMENTAL

Experiments were performed in an ultra-high-vacuum spectroscopy chamber with a base pressure lower than 2×10^{-10} Torr. Auger electron spectroscopy (AES) was performed with a double-pass cylindrical mirror analyzer using a 2.2 keV primary beam energy and 2V peak to peak voltage modulation.

The amount of oxygen was determined using AES. The overall amplitude of the dN(E)/dE oxygen (510 eV) to carbon (272 eV) was taken as the measure of oxygen surface concentration. A linear absolute coverage scale which corresponds to the AES O/C ratios was previously estimated and used in other studies on carbon surfaces (5-7). A coverage of one oxygen per surface carbon atom $\Theta_{oxygen} = \Theta = 1$ gives a AES O/C value of 0.25. We will self consistently apply this same coverage scale throughout the course of this study.

The glassy carbon samples were cut from plates obtained from Atomergic Chemetals and were outgassed at 1300°C in UHV prior to use. The presence of small amounts of very strongly bound oxygen could be reduced further by heating to higher temperatures, but this did not significantly effect the CO_2 and O_2 chemistry at high oxygen coverages. Further details of the characterization of the glassy carbon substrates can be found elsewhere (6). This procedure removed oxygen which was the principal contaminant measured by AES. The initial AES carbon to oxygen ratio was near 0.01. This represents a small amount of very strongly bound oxygen.

III. RESULTS

We have characterized the glassy carbon surface using ultraviolet photoemission spectroscopy following oxygen uptake from O_2 and CO_2 at 300°C. Previous UPS studies of atomically clean glassy carbon surfaces show enhanced electron emission near the Fermi level (6). This is associated with the presence of unsaturated surface carbon valences, "dangling bonds". These levels are removed upon chemically bonding to oxygen. Emission within 3 eV of the Fermi level decreases on glassy carbon as these levels become involved in bonding to oxygen (6). The emission from oxygen 2p levels was found between -4 and -11 eV following exposure to either O_2 or CO_2. Features which could be identified with molecularly adsorbed O_2 or CO_2 were absent. The similarity between O_2 and CO_2 suggest that the dissociation of CO_2 gives rise to surface oxygen and gaseous CO at 300°C. UPS thus gives us an indication that O_2 and CO_2 dissociation predominates under our conditions in these adsorption systems. This agrees with the conclusion reached for O_2 adsorption on graphon based on thermal desorption and isotope labeling studies (8).

XPS was also used to characterize the oxidized carbon surface. The O(1s) XPS signals following 300°C oxidation by O_2 and CO_2 showed a peak at 532 eV binding energy. The carbon (1s) peak for clean glassy carbon occurred at 284.2 eV. Following oxygen uptake from either O_2 or CO_2, there was a slight increase in emission at lower binding energies. The carbon (1s) peak did not, however, possess a 288.5 eV binding energy component which is associated with carbon coordinated to multiple oxygen atoms as in a carboxylic functionality (9-12). These results also indicate that similar oxygen functionalities were produced by CO_2 and O_2 at 300°C, and these are likely to be surface carbon atoms coordinated to one oxygen.

We have measured the increase in the oxygen AES signal following CO_2 and O_2 exposures at 300°C. We used a maximum temperature of 300°C in order to achieve high oxygen surface coverages but also to limit complications introduced by in situ gasification of carbon (13). The maximum oxygen coverages generated from O_2 and CO_2 corresponded to θ_o = 0.85 and 0.45 respectively. The adsorption processes were placed in quantitative terms. The efficiency of reactive adsorption as a function of the amount of oxygen already present was obtained from the incremental changes of oxygen coverage with the interval of exposure to either CO_2 or O_2 at 300°C. The efficiencies were calculated for increasing intervals of one decade of exposure. Figure 1 shows these results on glassy carbon as a function of oxgyen coverage. The adsorption process is characterized by relatively rapid initial uptake on the order of 10^{-4} efficiency for both gases up to approximately θ_o = 0.1 oxygen coverage. Above this coverage, there is a rapid decrease to 10^{-10}. Further exposure to O_2 will increase the oxygen coverage. The adsorption coefficient declines with coverage from 10^{-10} to 10^{-12} from θ_o = 0.25 to θ_o = 0.85. At higher coverages the behavior of O_2 and CO_2 begin to depart. CO_2 was limited in the amount of oxygen which could be deposited under these conditions. The decline in the coefficient for CO_2 was more rapid with coverage and decreased to below 10^{-14} near half monolayer coverage. Presumably, the coefficient declines further for CO_2 at higher coverages, but we were unable to measure slower processes.

The AES oxygen thermal stability profile was measured on glassy carbon following O_2 and CO_2 oxidation at 300°C. Figure 2 shows that the surface oxygen concentration remains nearly constant up to 600°C in both cases. Between 600 - 700°C, the surface oxygen coverage begins to decrease for the O_2 oxidized surface, yet for CO_2 the coverage still remains almost constant. Above 600°C CO was the dominant desorption product. Above 800°C there were similar reductions in oxygen coverage in both cases. CO evolves from the surface over a very wide range of temperature.

The CO formation energies were determined from the rate of change of oxygen coverage with time during heating in UHV by assuming first order kinetics and a frequency factor of 10^{13}. This formalism provides a framework to estimate the desorption energy. The results are shown in Figure 3. They are plotted as a function of oxygen coverage based on the common AES coverage scale as previously defined. The oxygen coverage dependency of the formation energy is similar for the surface oxgyen derived from O_2 and CO_2 adsorption. At low oxygen coverages, θ_o = 0.25, the energy decreases from 95 to 80 kcal/mole. The formation energy exhibited much smaller changes with coverage at the higher coverages. O_2 adsorption produced higher oxygen coverages. The energy ranged between 80 - 70 kcal/mole between θ_o = 0.25 to 0.85. CO_2 coverage was limited to θ_o = 0.4 but between θ_o = 0.25 , and 0.4 the energies were similar as with O_2. The CO formation energy decreases with increasing oxygen coverage.

IV. DISCUSSION

The adsorption of O_2, and CO_2 on glassy carbon surfaces were examined using AES. The study was restricted to carbon surfaces that had been previously outgassed in UHV at elevated temperature and characterized with surface sensitive techniques. In this way we were able to directly compare two gases which have widely different gasification activities.

There have been few adsorption studies on well-characterized, clean carbon surfaces. Original studies of oxygen adsorption on clean "paracrystalline" carbon (15) and sputter-damaged graphite surfaces (16) have shown complex adsorption behavior. The rate of uptake was characterized by coverage regions having a linear dependence with the log of exposure. This was interpreted as evidence for many discrete types of adsorption sites. It is believed that different oxygen adsorption sites exist on carbons with different thermal stabilities (2). Unfortunately these early studies did not relate adsorption to subsequent reactivity. A more recent study of O_2 on the edge surface of graphite has shown a strong oxygen coverage dependence on the reactive adsorption efficiency (7) similar to these original studies even though the edge surface of graphite has a limited amount of site heterogenity (14). Corrolated thermal stability studies of oxygen enabled estimates of the energetics of product formation. The values that were obtained on the edge graphite surface were dependent on the oxygen coverage (10). The thermal stability of oxygen on carbon for a given site is then sensitive to the amount of nearby oxygen already present. In this study we have compared the rate of oxygen uptake from O_2 and CO_2 at 300°C on glassy carbon and have measured the thermal stabilities of the resultant oxidized surfaces.

The maximum oxygen uptake from O_2 at 300°C on glassy carbon represented adsorption over a majority of the surface. A high absolute oxygen coverage was achieved. We observed a similar pattern of oxygen uptake on the edge surface of graphite 300°C (7) as on the glassy carbon samples. The similarity of the high coverage oxygen chemisorption results on the edge surface of graphite and glassy carbon is an indication that the sites on the less ordered carbon surface are actually chemically very close to those on the edge graphite surface. Although physically these surfaces are very different, microscopically their behavior is much the same.

Differences exist between O_2 and CO_2 uptake at 300°C. Under our conditions the absolute oxygen coverage reached nearly a monolayer using O_2 at 300°C. Exposure to CO_2 under the same conditions resulted in oxygen uptake only to one half monolayer coverage. Herein lies a significant difference between O_2 and CO_2 reactive chemisorption at 300°C. After saturation of the small number of very active sites, the adsorption efficiency of CO_2 and O_2 is approximately 10^{-10}. O_2 is able to sustain this efficiency to high coverages. The efficiency drops to 10^{-14} for CO_2 before a half monolayer oxygen coverage can be achieved. The adsorption efficiency must drop many more orders of magnitude for CO_2 at higher oxygen coverage.

The thermal stability studies in UHV for the resultant 300°C oxidized surfaces yielded estimates for the energetics of product formation. The energetics are related to the absolute oxygen surface coverage. The energies are similar at constant absolute oxygen coverage for oxygen generated from either O_2 or CO_2. The energies increase with decreasing oxygen coverage going from 75 kcal/mole at $\theta_0 = 0.4$ to 95 kcal/mole at $\theta_0 = 0.05$ coverage. Under our conditions, O_2 is capable of generating higher oxygen coverages, and the CO formation energy decreases to 70 kcal/mole at the highest coverage.

The adsorbed oxygen species are strongly bound. The observation of large heats of adsorption and low adsorption efficiencies (10^{-10} -10^{-14}) imply a substantial energy barrier for adsorption. We can estimate the barriers for adsorption for CO_2 and O_2 at several oxygen coverages by assuming a Boltzman energy distribution and the temperature of the gas equal to the surface temperature. At $\Theta_0 = 0.1$ this yields a barrier height of 13 and 15 kcal/mole for O_2 and CO_2 respectively. At $\Theta_0 = 0.4$ we find that the barrier increases to 25 kcal/mole for O_2 and 35 kcal/mole for CO_2. At $\Theta_0 = 0.9$ the value increases to 33 kcal/mole for O_2. The value for CO_2 must be substantially greater at this high oxygen coverage. Estimates based on adsorption efficiencies at higher surface temperatures of CO_2 exposure as well as extrapolation of the efficiencies at 300°C to $\Theta_0 = 0.9$ yield barriers in the range of 50 - 60 kcal/mole. Marsh has used an energy-reaction coordinate diagram to help illustrate the kinetics of adsorption and CO formation (2). We have been able to quantify parts of this diagram which we just described and are also illustrated in Figure 5 for the reaction of glassy carbon with CO_2 and O_2 to form CO.

Higher oxygen concentrations can be developed (13) by oxidation of carbon with O_2 above 400°C but this leads to <u>in situ</u> gasification and complicates the reaction-energy coordinate diagram. We have observed CO and CO_2 as gaseous products during thermal desorption of glassy carbon oxidized above 400°C in O_2. There are several possible origins for CO_2 production. Some carboxylic groups may be produced by O_2 at very high oxygen coverages. Studies (17) of nitric acid oxidized glassy carbon indicate that CO_2 can be produced from decomposition of carboxylic oxygen functionalities. The decomposition of surface carboxylic groups to form CO_2 will complicate the O_2 reaction with carbon. Another possible route at high oxygen coverages is the formation of CO with consecutive oxidation by surface oxygen to CO_2. Indications are that formation energy for CO declines further below 70 kcal/mole at very high oxygen coverages (7) but CO_2 eventually becomes a competitive reaction route. We have minimized the complications of CO_2 formation from O_2 oxidation in our studies by limiting the concentration of surface oxygen.

Activation energy for the O_2 adsorption step has been estimated at higher temperatures and presumably higher coverages and tends to higher values. Lussow et al. (13) report an activation energy of 29 kcal/mole for O_2 adsorption between 450°C and 675°C. In carbon gasification studies a value near 38 kcal/mole has been reported for the O_2 adsorption step.[18,19] Our

results at lower coverages show that the barrier for adsorption is greater for CO_2 than for O_2 at a given oxygen surface coverage and that the barrier increases for both gases as the oxygen coverage increases. The values reported for O_2 at high temperatures are of the same order that we find at high oxygen coverages in our studies.

The differences in adsorption behavior of CO_2 and O_2 at high oxygen coverages must be related to the much greater gasification activity for O_2. Our data suggest that CO_2 and O_2 produce similar kinds of adsorbed oxygen species at low and medium coverages. This is most likely carbonyl type oxygen functionality, carbon which is coordinated to one oxygen. The stability of this kind of oxygen is dependent on the amount already present. This can be interpreted as oxygen bound to one carbon having the ability to modify the energetics of the interaction of neighboring free carbon sites with oxygen and CO_2. At higher coverages, there are pronounced differences between CO_2 and O_2. The adsorption barrier for CO_2 relative to O_2 increases with increasing oxygen coverage, while the stability of the adsorbate decreases and gasification to CO becomes more facile. The observations suggest that the energy barrier for oxygen adsorption from O_2 is much lower than for CO_2 for sites which have lower subsequent CO formation energetics. At high oxygen coverages, the magnitude of the adsorption barrier increases while the energetics of gaseous product formation declines. For both CO_2 and O_2 at a given reaction temperature a steady state situation will develop. At higher temperatures the reaction coordinate energy diagram is thought to be one with a greater barrier for gas dissociation but a lower barrier for gaseous formation. The kinetics of CO_2 gasification of glassy carbon has been measured near atmospheric pressure above 650°C. The activation energy for CO_2 gasification was 67 kcal/mole (20). There is a correspondence between this value and the CO formation energetics that we observe at high oxygen coverages. In addition the oxygen coverages determined by AES following CO_2 gasification are also comparable. These results imply that the steady state surface situation during CO_2 gasification is close to that found for the highest oxygen coverages in this study. On the other hand greater oxygen concentration are developed with O_2. The energetics of CO_2 and O_2 dissociation under gasification conditions will be different and from our estimates it will be substantially lower for O_2. The increased gasification activity for O_2 is associated with a more facile gaseous dissociation step at high oxygen coverages which generates lower CO formation energy sites.

V. REFERENCES

1. P. L. Walker, Jr., F. Rusnko, L. G. Austin, Adv. Catalysis 11 (1959) 133.
2. H. Marsh, Spec. Publ.-Chem. Soc. 1977 32 (Oxygen Met. Gaseous Fuel Ind.) 133.
3. N. M. Laurendeau, Prog. Energy Combust. Sci. 4 (1978) 221 and references therein.
4. J. B. Donnet, Carbon 20 (1982) 267.
5. S. R. Kelemen and C. A. Mims, Surface Science 133(1983) 71.
6. S. R. Kelemen, H. Freund and C. A. Mims, J. of Vac. Sci. and Technol. A 2(2) (1984) 987.
7. S. R. Kelemen and H. Freund, submitted to Carbon.
8. P. L. Walker, Jr., F. J. Vastola and P. J. Hart, Fundamentals of Gas-Surface Interactions p. 307 (Academic Press, New York, 1967).
9. D. T. Clark in: Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy (Heyden, London, 1978).
10. R. Schlogl and H. P. Boehm, Carbon 21 (1983), 345.
11. A. Ashitani, Carbon 19 (1981) 269.
12. T. Takalagi and A. Ashitani, Carbon 22 (1984) 43.
13. R. O. Lussow, F. J. Vastola dn P. L. Walker, Jr. Carbon 5 (1967) 591.
14. S. R. Kelemen and C. A. Mims, Surface Science, 136 (1984) L35.
15. P. J. Hart, F. J. Vastola and P. L. Walker Jr., J. Colloid Interface Sci. 32 (1970) 187.
16. M. Barber, E. L. Evans and J. M. Thomas, Chem. Phys. Letl. 18 (1973) 423.
17. S. R. Kelemen and H. Freund, unpublished results
18. P. L. Walker Jr., Carbon 18 (1980) 447.
19. P. F. Lewis and G. A. Simons, Combustion Sci. Tech. 20 (1979) 117.
20. H. Freund, submitted to Fuel.

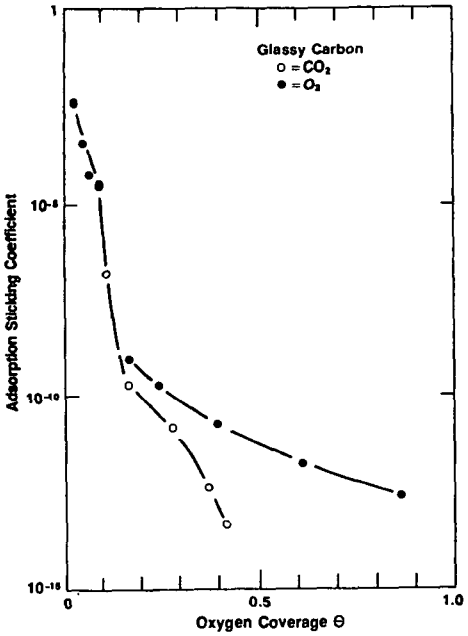

Figure 1: Reactive adsorption efficiency for O_2 and CO_2 as a function of the amount of oxygen already present on the glassy carbon surface held at 300°C.

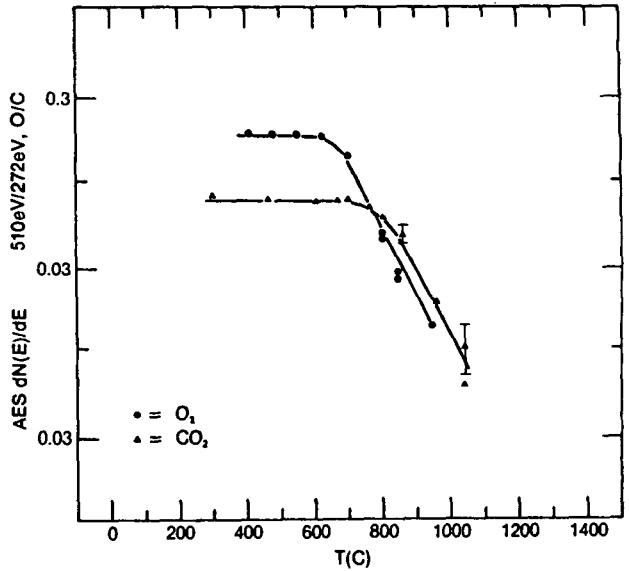

Figure 2: Oxygen AES signal after O_2 and CO_2 oxidation at 300°C and following heating in UHV for 300 sec at each data point.

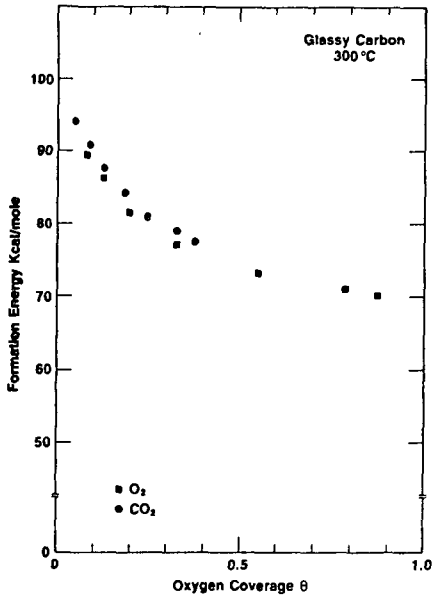

Figure 3: Formation energy of gaseous CO product as a function of oxygen coverage after O_2 and CO_2 oxidation at 300°C.

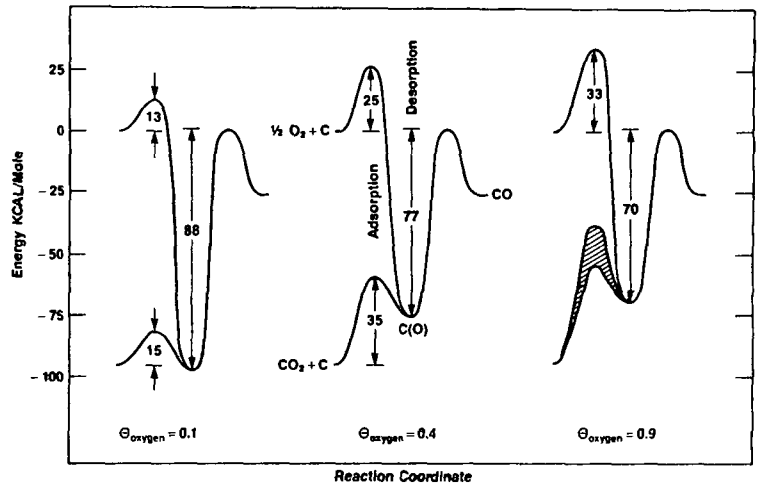

Figure 4: Energy - reaction coordinate diagram at different oxygen surface coverages in the reaction of CO_2 and O_2 with glassy carbon to form CO.