

SURFACE CHARACTERIZATION OF O₂ AND CO₂ ADSORPTION ON CLEAN AND OXIDIZED GLASSY CARBON SURFACES

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Abstract

ESCA was used to characterize glassy carbon surfaces following exposure to O₂ and CO₂. Temperature-programmed Reaction Spectroscopy (TPRS) was used to monitor subsequent decomposition chemistry. The ability of O₂ and CO₂ to undergo dissociative chemisorption depends on the extent of prior oxidation. On initially clean surfaces, CO₂ and O₂ oxidation produced similar species characterized by a 531.0 (eV) O(1s) peak and a 285.8 (eV) C(1s) peak in the difference spectrum. The species decomposed above 700°C to produce gaseous CO. Additional exposure to CO₂ up to 700°C did not increase the oxygen surface coverage. O₂ generated additional oxygen with a 531.5 (eV) O(1s) and a 285.8 (eV) C(1s) peak in the difference spectrum. This oxygen species is associated with the production of CO near 600°C. O₂ is distinguished in its ability to dissociate on partially oxidized surfaces. The 285.8 (eV) C(1s) peak could not be interpreted in a straightforward way in terms of a carbonyl functionality. HNO₃ oxidation of glassy carbon was studied as a reference and favors the formation of carboxylic acid groups characterized by a 288.4 (eV) C(1s) peak and O(1s) peaks at 531.2 and 532.7 (eV).

Introduction

ESCA has been used to characterize the surfaces of a wide variety of different carbons which include glassy carbon(1-3), graphite(4,5) and carbon fibers.(6-11) Information has been gathered about the degree of surface oxidation and type of oxygen complexes formed after various oxidative treatments.(1-3, 5-11) The degree of oxidation can be monitored by the O(1s) intensity. In general a distinction about the kind of surface oxide is made based on the C(1s) emission which occurs at higher binding energies from the main (1s) line. Extensive ESCA studies of organic molecules and polymeric materials(12-16) have demonstrated that the magnitude of the C(1s) peak shift to higher binding energy is related to the number of carbon oxygen bonds and in the range of 1.5 eV ± 0.4 per bond. The result is significant because common functionalities can be grouped according to their C(1s) shift. The guidance from these simple additivity rules have been employed in the interpretation of results from carbon surfaces. For example ~1.5 eV shifts are associated with alcohols and ethers, ~3.0 eV shifts with carbonyl groups, ~4.5 eV shifts with acids and esters.(1-3, 6-16)

The O(1s) peak also contains functional group information. In esters singly and doubly bonded oxygen is separated by ~1.3 eV with the singly bonded oxygen at higher binding energies.(13-16) A distinction between carbonyl oxygen at 531.6 eV and ether oxygen at 533.1 eV was recently made on carbon fiber surfaces.(10)

We have previously used AES in a comparative study of the O₂ and CO₂ oxidation of glassy carbon surfaces.(17) As expected O₂ has a much higher reactivity. This was associated with a more facile gaseous dissociation step at high oxygen coverages which generated lower energy CO formation sites. The available ESCA results suggested that CO₂ and O₂ produced similar oxygen functionalities at 300°C having a 532 eV binding energy with the absence of carboxylic-like C(1s) features. These results are consistent with a carbonyl-type functionality, however, a definitive identification based on the C(1s) peak was not made. The object of the present work is to obtain high resolution C(1s) and O(1s) spectra produced under previously defined chemical conditions. The spectra should lead to functional group identification. This information coupled with TPRS results and previous kinetic data(18) will provide a good basis for further fundamental mechanistic work and interpretation of carbon oxidation and gasification processes.

Experimental

The glassy carbon starting material was obtained as plates from Atomergic Chemetals. Samples were made in the form of powders and chips. Both powders and chips were used in TPRS experiments while chips were used exclusively in ESCA experiments. 60-80 mesh powders were produced by grinding and sieving glassy carbon plates. Powders were found to have 5 m²/g specific surface area based on Kr chemisorption measurements. The powders were outgassed to 900°C prior to oxidation. O₂ and CO₂ oxidation were done in a Dupont model 951 thermogravimetric analyzer. 50 mg of material was normal sample size. The glassy carbon chips were cut from plates with a diamond saw to 1 cm x 1 cm x 1 mm dimensions. The chips were successively polished with Buehler Carbimet silicon carbide paper up to 600 grit number. The samples were further polished with Buehler Alumina paste down to 0.05 micron size.

The chips were washed with deionized water and then outgassed to ~1300°C in UHV prior to use. The specific surface area of the chips were 0.3 m²/gram based on Kr chemisorption measurements. Oxidative treatments could be given to samples in the TGA apparatus as with powdered samples. The chips were especially suited for use in a atmospheric pressure/UHV sample introduction system. Samples could be given reactive treatment up to 700°C in 1 atm gas and returned into a UHV apparatus for surface analysis without exposure to air. Glassy carbon chips as well as powdered samples which received oxidative treatments in the TGA apparatus and which were cooled to room temperature in the reactant gas mixture, could be transferred in atmosphere to respective holders for TPRS experimentation. Brief exposure to air at room temperature did not alter reactivity patterns observed in subsequent TPRS experiments. Nitric acid oxidation was accomplished by boiling the samples in HNO₃ under reflux conditions.

The TPRS apparatus used with powdered samples was specially constructed as an appendage to a UHV spectroscopy chamber which housed an EAI and an Extranuclear quadrupole mass spectrometer. The EAI unit had dual mass scanning capability during a TPRS experiment while the Extranuclear Spectrometer, interfaced to a PDP 11 data acquisition system, provided the capability to follow up to eleven masses during a TPRS experiment. The TPRS unit had a base pressure of 5×10^{-10} Torr pumped separately by a Balzers 300 l/s turbomolecular pump. 5-10 mg samples were accommodated in a ceramic vessel 9mm long x 3 mm diameter. A chromel-alumel thermocouple was inserted into the sample bed. The sample holder was resistively heated by tantalum elements and the sample temperature was controlled by a Micristar controller. The volume of the TPRS apparatus was approximately 100 cc.

ESCA Spectra were obtained from a Vacuum Generators ESCALAB equipped with a 150 degree Spherical Sector Analyser. The base pressure in the analysis chamber was less than 1×10^{-10} torr. Non-monochromatic Mg K α radiation was the excitation source. The x-ray source was operated at 300w (20ma, 15 kV). Glassy carbon and graphite samples did not experience charging problems during data acquisition. The work function of freshly cleaned Union Carbide XYA Monochromator Graphite was 4.2 eV and the carbon (1s) binding energy with respect to the vacuum level was 284.4 eV. The work function of Glassy carbon was also 4.2 eV. The binding energy of the C(1s) peak of clean Glassy carbon was 284.5 eV with respect to the vacuum level. Oxidation of Glassy by O $_2$ at 700°C increased the work function of the sample to 4.4 eV. The increase was smaller for milder oxidations while HNO $_3$ oxidation increased the value to 4.5 eV. The slight binding energy corrections due to the increase in work function upon oxidation, < 0.3 eV, were not made to the oxidized spectra. All N(E) spectra were obtained at 0.9 eV resolution. The signal from the C(1s) peak of graphite corresponded to 35,000 counts/sec. Typical counting times yielded spectra with 10^6 maximum counts. Data acquisition was by means of VGS 2000 software package using multi scan averaging.

Results

Following HNO $_3$ oxidation, glassy carbon samples were temperature programmed and the gaseous evolution recorded as a function of temperature. Figure 1 shows the results at two different heating rates. The gaseous production patterns shift to higher temperatures with increased heating rate. It was not possible to derive detailed energetics of the decomposition processes from the variation of the peak maximum with heating rate(19, 20) because of the extremely broad features from overlapping peaks. Nevertheless the evolution patterns are sufficiently distinct so as to be interpreted on a chemical basis. H $_2$ O is a major product below 200°C. CO $_2$ and CH $_4$ dominate the profile between 200 to 400°C. CO production increases over this interval while H $_2$ O declines to background levels. Above 500°C there is a fall off of CO $_2$ and CH $_4$ as CO becomes the major product.

ESCA was used to characterize the initial state of HNO $_3$ oxidized glassy carbon surfaces and as a function of heating in UHV. The heating schedule was approximately 1 degree per sec. to a maximum temperature then cooled in UHV for analysis. The C(1s) ESCA results are shown in Figure 2 in

the form of a difference spectrum. The spectrum of a "clean"(21) glassy carbon sample outgassed at 1300°C in UHV was used as the reference spectrum for subtraction from each oxidized spectrum. The y axis scales are different in each spectrum so as to highlight the relative changes. The absolute magnitude of the changes relative to the reference spectrum decreases with decreasing degrees of oxidation. The 600°C sample contains approximately 1/4 the oxygen as the 100°C case and the 600°C difference spectrum is on a four times more sensitive scale relative to the 100°C case. The magnitude of the change is clearly evident from the actual spectra, not shown. The large negative going peak in each spectrum is a result of decreased emission from the parent C(1s) signal upon oxidation. The positive going features are a result of oxidation and represent modified carbon forms. The 100°C spectrum has one prominent peak at 288.5 eV. The peak occurs 4.1 eV shifted from the parent carbon (1s) line. In additivity terms the peak can be related to carbon atoms triply coordinated to oxygen, as in the case of an acid functionality. The total amount of hydrogen produced as H₂O and CH₄ in TPRS experiments relative to the total oxygen produced as CO, CO₂, and H₂O is consistent with the 288.5 eV peak in the 100°C spectrum being primarily due to acid functionalities. There is another major peak at 285.2 eV which is shifted by 0.7 eV. The magnitude of the shift is consistent with it being a β peak, i.e., a shift of the carbon atom adjacent to the acid carbon.(22)

There is also a broad decrease in emission, representing a 50% absolute decrease centered at 290.5 (eV). We have observed a broad peak centered at this energy with clean glassy carbon samples. As in other aromatic systems the peak is due to π to π^* transitions.(23) UPS studies of glassy carbon(21) show substantial valance band emission within 2 (eV) of the Fermi level. This emission is derived from the π bonding structure and is associated with unsaturated carbon valencies. Upon oxidation this emission decreases. In the case of HNO₃ oxidation the emission within 4 eV is lost and the UPS valance band spectrum resembles that from insulating structure. It is not surprising that π to π^* emission intensity would decrease upon oxidation although we do not know what changes occur in the unoccupied states.

Between 100-525°C, during the stage of major CO₂ evolution, the 285.2 eV peak and the 288.5 eV peak simultaneously decline. There is an absolute 80% decline evident in the 288.5 eV peak from the N(E) spectra. The coupled decline further supports the contention that the 285.2 eV represents a β peak. At 600°C a peak near 286.0 eV becomes the major component and the subsequent gaseous evolution is mainly to CO. Note also the retention of a proportionate decline in the π to π^* intensity.

The initial oxygen (1s) spectrum is broad (FWHM 3.5 eV) and can be resolved into two peaks of equal intensity at 531.2 and 532.7 eV. Two peaks are anticipated for an acid structure with the doubly bonded oxygen at lower binding energy. As the sample is heated in stages the O(1s) incremental difference spectra between 100 to 300°C show a slight nonuniform decline in intensity toward the low binding energy side and H₂O is an important product. H₂O formation may result from acid decomposition and formation of lactone structures. Between 300° to 525°C there is a uniform decline in O(1s) intensity and CO₂ and CH₄ are major products. The O(1s) behavior indicates that the initial O(1s) spectrum may be composed of several different acid functionalities with individual two-peaked structures. Above 600°C the O(1s) signal can be resolved into two peaks at 531.0 eV and 533.2 eV. The 531.0 eV

peak declines at higher temperatures and there is CO evolution. The 533.2 eV peak corresponds to stable ring ether.

Clean glassy Carbon samples were oxidized in O₂ and CO₂ and characterized with ESCA and TPRS. Figure 3 show the O(1s) signal on the same intensity scale. Each sample was oxidized for 300 sec under specified conditions and cooled in the reactant gas. Negligible burn-off occurred below 300°C. The 700°C oxidations in O₂ and CO₂ corresponded to 20% and <0.1% burn-off respectively. The amount of surface oxidation that could be achieved with O₂ increased with temperature. A 531.0 eV peak is generated at 150°C with a shoulder at higher binding energies. The O(1s) intensity increases at 300°C and 700°C as higher binding peak components begin to contribute. In contrast there is a limited amount of oxidation with CO₂ and similar levels are achieved at 300°C and 700°C. This is consistent with previous AES studies.(17) Two main components occur at 531.0 eV and 533.0 eV. The 531.0 eV peak decreases with concomitant CO evolution upon heating above 700°C.(17) The 533.0 eV peak represents very strongly bound oxygen with small residuals stable at 1300°C (see Figure 6). The 533.0 eV peak is associated with ring ethers.

It is tempting to interpret the 531.0 eV O(1s) peak produced by CO₂ and O₂ with doubly coordinated oxygen as in a carbonyl functionality. Indeed we had previously taken an unresolved 532 eV peak as evidence for a carbonyl functionality. Current carbon (1s) difference spectra in Figure 4 seem to belie the presence of a simple carbonyl functionality. From simple additivity arguments we would expect a carbonyl oxygen to shift carbon by approximately 3.0 eV. There is little intensity in this region. The main carbon (1s) difference features look very similar for O₂ and CO₂. The large negative going peak represents lost parent C(1s) intensity upon oxidation. The main positive peak occurs at 285.8, shifted 1.3 eV from the main line. This would represent carbon singly coordinated to oxygen based on additivity reasoning. In the case of 700°C CO₂ and 300°C O₂ oxidation there is a decrease in emission centered near 290.5 eV reflective of lost π to π^* intensity. In the case of 700°C O₂ oxidation a small positive peak occurs at 288.7 eV along with added emission near 291 eV. The 288.7 eV can be rationalized by the presence of carbon triply coordinated to oxygen. Acidic properties have been reported following O₂ oxidation of carbon which have been supported with spectroscopic evidence.(28) It should be recognized the enormous amount of material on the atomic scale which must be removed to achieve 20% burn-off. The exact nature of the residual carbon may be different. We have observed UPS features from glassy carbon which tended more toward graphite after 1300°C cleaning following severe oxidation; specifically the appearance of a Γ_{3u} final state peak of graphite.(25) The fine luster of a polished surface was gone; the surface was dull and pitted. The selective oxidation of less refractory carbonaceous components in glassy carbon could change the π to π^* intensity contributions and account for the broad 291 eV peak. The other possibility is the presence of carbonate structures, however, this interpretation is less likely as the added emission at 291 eV persists upon heating to high temperature where carbonates should decompose.

As observed in previous systems(26), O₂ oxidation and quench procedures results in both CO and CO₂ evolution in subsequent TPRS experiments. Figure 5 shows the results with glassy carbon as well as for CO₂ oxidation. CO₂ oxidation produces surface species which only yield CO. O₂ generates

surface species which produce CO at much lower temperatures. This behavior has been detailed in previous work.(17) The small 288.7 eV C(1s) peak decreases along with the 285.8 eV peak concomitant with CO₂ and CO evolution between 400-600°C. Above 600°C CO is produced and the 285.8 eV peak decreases. A distinction between the species generated at high oxygen coverages with O₂, which produces CO near 600°C, and the species generated at low oxygen coverages with either O₂ or CO₂, which produces CO above 700°C cannot be made based on C(1s) spectra.

The O(1s) spectra, shown in Figure 6, produced a clear indication of a distinct electronic configuration at high oxygen coverages. A glassy carbon sample was heated for 300 sec in 1 atm O₂ at 700°C, cooled in the reactant gas and then incrementally heated in UHV. The initial oxygen spectrum at 100°C was previously described. The O(1s) signal decreases at each temperature interval. Previous AES results(17) mapped the oxygen stability profile at high oxygen coverages. We expect a step decrease in signal between 450-600°C. The O(1s) difference spectra shows a selective decrease in O(1s) signal over this interval characterized by a 531.5 eV peak (FWHM of 1.7 eV). At 600°C the O(1s) signal is a two-peaked structure and can be resolved into 531.0 eV and 533.0 eV components. A 531.0 eV peak can be produced by low temperature O₂ and CO₂ oxidation and yields CO between 700 and 900°C. The 533.0 eV peak represents oxygen more strongly bound, probably ring ether. A small peak remains after 1300°C heating. Similar structures remain above 900°C on potassium catalyzed glassy carbon surface following potassium loss. The relative amount of this type of oxygen depends on the prior sample treatment.(27) It is a minor component following 150°C O₂ oxidation as these conditions are not harsh enough to generate substantial oxygen incorporation into the ring structure. The relative amount of oxygen stable above 900°C tends to increase with increasing severity of prior oxidation. It is a significant component following O₂ oxidation at 700°C and HNO₃ oxidation of glassy carbon. The ability of O₂ and CO₂ to dissociatively adsorb on glassy carbon depends on the amount of oxygen already present. It is likely that this kind of very stable oxygen will also modify the ability of O₂ and CO₂ to dissociate on proximate carbon sites.

Discussion

The ability of O₂ and CO₂ to dissociatively adsorb on glassy carbon is dependent on the degree of surface oxidation. Similar kinds of species are produced by CO₂ and O₂ up to moderate oxygen coverages. O₂ is distinguished by its ability to dissociate on partially oxidized surfaces. It is apparently this property which enables O₂ chemisorption to be a useful surface area probe in gasification systems.(29) The nature of the CO₂ and O₂ dissociation products is a more complicated question. C(1s) deconvolution schemes based on the simple additivity relationship have been used in the interpretation of oxidized carbon surfaces (1-3, 6-16). In the study of carbon fiber surfaces Takahagi and Ishitani (7) use a 2.4 eV shifted peak for carbonyl groups. Proctor and Sherwood (8) use a 3.0 eV shifted peak; nevertheless, the same authors present evidence that carbonyl functional groups on extended aromatic ring systems may have smaller shifts than those found for similar functionalities in polymers. They suggest that the C(1s) shifts in extended aromatic carbonaceous systems are modified due to the presence of π -interactions. Kozlowski and Sherwood (9) have electrochemically oxidized

carbon fiber surfaces in nitric acid and show a distinct C(1s) peak shifted 2.1 eV and assigned to carbonyl type oxides. This is in addition to ester-type groups shifted ~4.0 eV. In later work (10) these authors suggest the 2.1 eV shifted peak is a result of a keto-enol type structure. In general, it is believed that the C(1s) position, for a carbonyl-like group on a carbon surface, does not depart significantly from the simple additivity relationship of ~3.0 eV. While a ~3.0 eV shifted peak has been used to represent a carbonyl-like species, only in one study has a spectrum been presented which shows this as the dominant surface species.(1) In this study glassy carbon was oxidized in an O₂ RF plasma. CO₂ and H₂O RF plasmas were ineffective in the production of carbonyl-type functionalities.(1) IR photothermal beam deflection spectroscopy has been used to study the O₂ oxidation of high temperature chars (28). Evidence of ether-like species appeared as a band centered near 1300 cm⁻¹. The presence of a band corresponding to carbonyl-like species was absent.

The presence of carboxylic acid functionalities following HNO₃ oxidation is supported by TPRS and ESCA results. The C(1s) peak at 288.5 eV could be interpreted in terms of simple additivity behavior. Extensive TPRS and thermal stability (17) studies of O₂ and CO₂ oxidation have defined conditions where species are produced which yield CO upon decomposition. The C(1s) peak at 285.8 eV in difference curves decreases concomitant with CO evolution. We cannot interpret this peak as a carbonyl functionality on the basis of the widely accepted additivity behavior of the C(1s) "shift" with carbon bond coordination. Either the chemical shift for this particular system is significantly different than in polymeric systems or a different species is involved in carbon oxidation. Within the framework of the additivity rules the 285.8 eV peak, shifted by ~1.3 eV, is consistent with carbon singly bonded to oxygen. We would expect this peak for ring ethers, however, it is not likely that this species is responsible for low temperature CO formation. The peak is also consistent with phenolic groups but subsequent O₂ and CO₂ oxidation chemistry which yields virtually no hydrogen containing products would necessitate that hydrogen would remain on the surface and thus participate in a quasi catalytic manner.

The carbon-carbon bonding situation on the glassy carbon surface may depart from a simple two dimensional picture. LEED results from the clean edge surface of graphite were not representative of bulk lattice terminations and suggested substantial surface reconstruction (30). The well ordered C (2 x 2/3) LEED pattern from the edge graphite surface was lost and only a diffuse background scattering was observed upon surface oxidation with O₂(31). The pattern was regenerated by heating above 800°C in vacuum. Similar kinds of perturbations away from two dimensional organic chemistry analogues may also occur with glassy carbon. The carbon (1s) peak shifted by ~1.3 (eV) may be a consequence of a surface ether-like species. It is currently not possible to distinguish whether a breakdown in additivity behavior or novel bonding configurations is responsible for the C(1s) spectrum of these systems. Future work using HREELS is under way to help clarify this dilemma by providing surface vibrational information.

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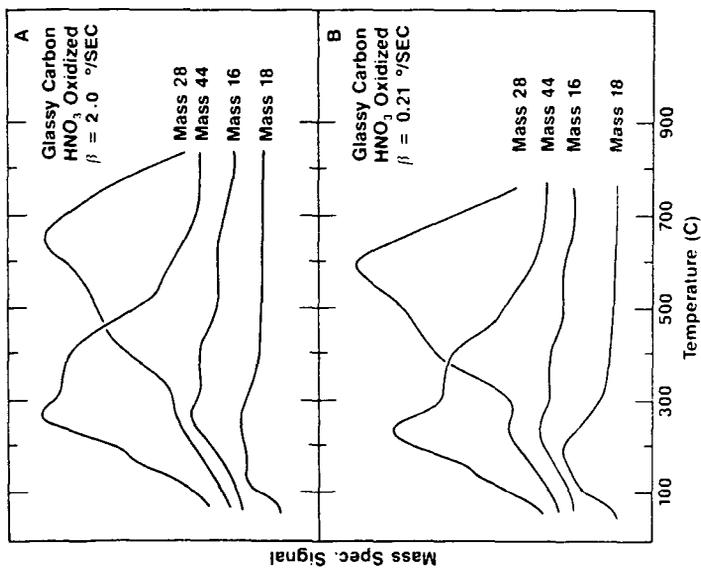


Fig. 1

TPRS after HNO₃ oxidation and subsequent heating in UHV.

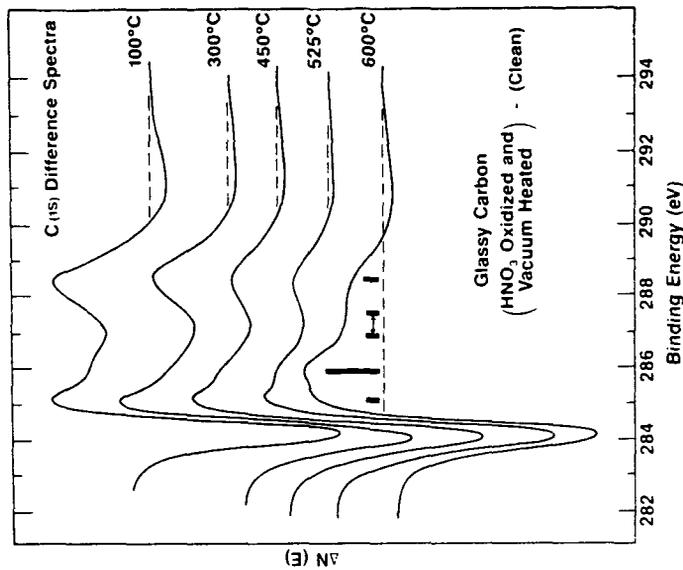


Fig. 2

C(1s) difference spectrum following HNO₃ oxidation and subsequent heating in UHV.

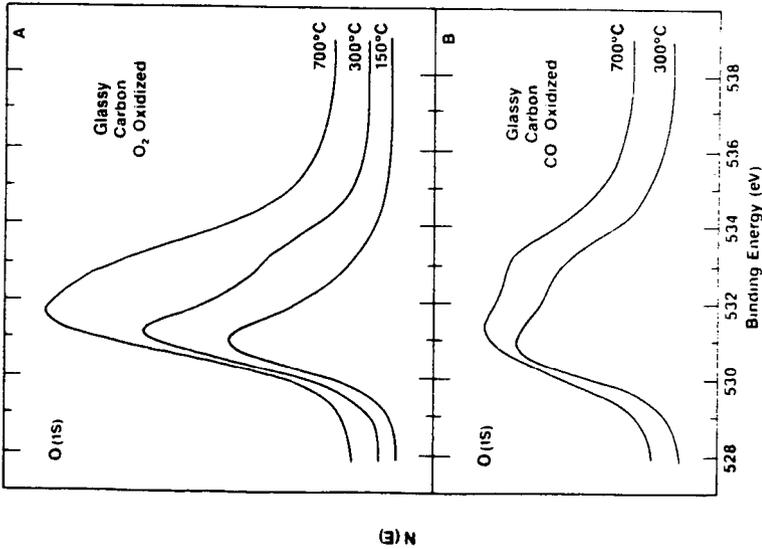


Fig. 3

- A) O(1s) spectrum for glassy carbon samples oxidized at different temperatures with O₂.
 B) O(1s) spectrum followed different CO₂ oxidations.

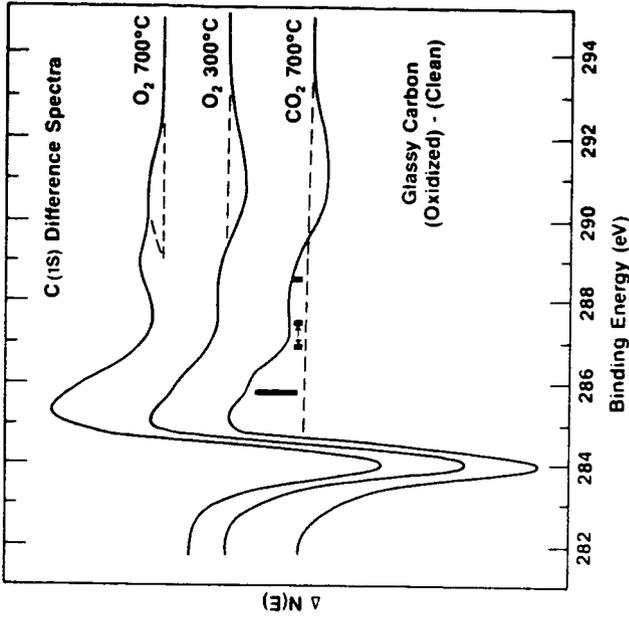


Fig. 4

- C(1s) difference spectrum following O₂ and CO₂ oxidations.

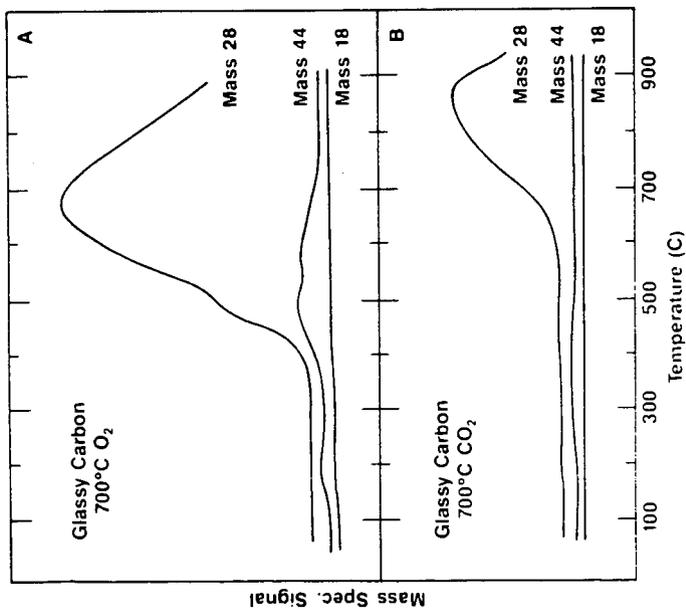


Fig. 5

- A) TPRS following 700°C O₂ oxidation.
 B) TPRS following 700°C CO₂ oxidation. The heating rate was 1.0 degrees per sec. in both experiments.

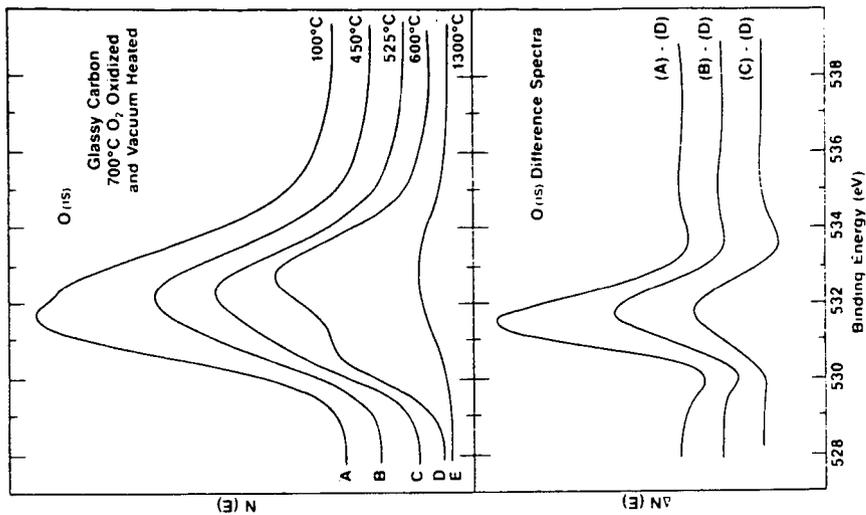


Fig. 6

- A) O(1s) spectrum following O₂ oxidation at 700°C and after heating in UHV to the indicated temperatures.