

CHARACTERIZATION OF POTASSIUM CATALYSTS ADDED AS KOH TO CARBON SURFACES

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ABSTRACT

Potassium catalysts active toward gasification of carbon by H_2O and CO_2 can be generated by addition of KOH to carbon. We have characterized the controlled addition of KOH to the edge surface of graphite and the surface of a glassy carbon using AES, XPS and UPS. Submonolayer concentrations of potassium-oxygen surface species are formed from KOH on pre-oxidized edge graphite and glassy carbon surfaces which are stabilized to $800^\circ C$ in vacuum. These surfaces have two O(1S) peak envelopes centered near 531 eV and 533 eV. The higher binding energy peak is characteristic of oxygen strongly bound to carbon. Heating to $950^\circ C$ results in the loss of potassium and the lower binding energy oxygen peak associated with the potassium catalyst. In contrast the interaction of KOH with the atomically clean edge graphite surface does not produce the active potassium form. The initial oxygen content of the carbon surface is important in catalyst preparation from KOH.

INTRODUCTION

Additions of alkali metal salts to carbon are known to produce catalytic effects toward gasification by CO_2 or H_2O (1-7). KOH and K_2CO_3 are especially active precursors to catalytically active states on the carbon surface (8). The catalytic form can be prepared by heating a mixture of the sample and the salt in the reactive gaseous environment. In kinetic studies this is usually a temperature greater than the maximum in the range used for the kinetics. The potassium catalyst when in an active form is believed to be mobile on the carbon surface yet stable to vaporization under gasification conditions. The catalyst's stability is demonstrated by the retention of potassium following prolonged heating in an inert environment at the reaction temperature of $700^\circ C$ subsequent to gasification (9). The active potassium form is found to be associated with surface bound oxygen based on akylation studies (9,10). A better understanding of potassium catalyzed carbon gasification will come from more knowledge of the details of the potassium complex and the carbon surface composition. For this reason the initial interaction of alkali salts such as KOH with well defined carbon substrates are of fundamental interest.

The importance of the oxygen content in relation to the catalytic gasification activity of KOH and K_2CO_3 toward various carbons has been recently emphasized (11,12). The clean oxygen free edge surface of graphite was studied under ultra high vacuum conditions in order to isolate the pure interaction of KOH with active carbon surface sites. The interaction of KOH films contaminated by exposure to H_2O or O_2 was studied on the "passive" basal

surface of graphite to determine the influence of direct KOH oxidant interaction in the absence of "active" carbon sites. In this way the chemistry of KOH with pre-oxidized carbon surfaces could be differentiated.

EXPERIMENTAL

Experiments were performed in a standard ultra-high vacuum spectroscopy chamber. A double-pass cylindrical mirror analyzer (Physical Electronics) was used for AES, XPS and UPS measurements. The details of the sample preparation and characterization of the oxygen-free edge surface of graphite and glassy carbon can be found in previous communications (13,14). Two different sample holders were used in the study. One was a standard UHV manipulator which could access a KOH evaporation source. The details of the KOH evaporation source used in the UHV studies appear elsewhere (15). The other holder was a Leybold Heraeus design which allowed rapid introduction of samples from atmospheric pressure to the UHV environment. The carbon samples were oxidized in O_2 at $300^\circ C$ in an isolated high pressure preparation section. The oxidation kinetics by O_2 of the edge graphite surface and glassy carbon have been examined and conditions chosen which produced substantial amount of surface oxidation.

Nitric acid oxidation of the glassy carbon samples was accomplished by boiling the samples for 4 hours in HNO_3 under reflux conditions. KOH was added to carbon surfaces in laboratory air by physically contacting the carbon surface in air with a moist KOH pellet. This formed a liquid coating across the entire carbon surface. The procedure was accomplished within one minute and the sample was returned to the UHV environment by use of the rapid introduction sample holder.

RESULTS

I. KOH on Basal Graphite With H_2O and O_2

When KOH is used as the precursor in gasification catalysis it is usually added from solution or directly added in atmospheric conditions. Furthermore, the carbon surfaces with the salt precursor are exposed to the oxidizing reactant gaseous environment prior to reaction. These are potential sources for chemical modification of parent KOH. In order to examine the effect of direct KOH gas interactions we have performed model experiments on the basal plane of graphite. The basal surface of pyrolytic graphite contains a preponderance of "inactive" carbon sites and provides a suitable surface to examine direct KOH gas interactions. We have found that the surfaces of pure KOH films evaporated in-situ in the UHV chamber will rapidly take up oxygen from exposure to H_2O and O_2 at room temperature.

The KOH films exposed to H_2O and O_2 on the basal graphite surface had only slightly greater thermal stabilities toward desorption in UHV than those found for pure KOH films. The vapor pressure of pure KOH is substantial above $300^\circ C$. This is also true for surfaces with KOH added in atmosphere. Following KOH addition in air H_2O was the major gaseous species produced along with KOH upon heating in UHV. Clean basal graphite surfaces were recovered upon heating to $500^\circ C$ in vacuum.

Addition of KOH to carbon in air will therefore always introduce oxygen containing gases into the system. Basal graphite surfaces which have been contacted by KOH in air have similar thermal stabilities to the H₂O and O₂ exposed pure KOH films. Although prolonged atmospheric exposure of KOH leads to the uptake of CO₂ and formation of potassium carbonate, our exposures to air were short. Potassium carbonate formation should show itself by increased thermal stability of the potassium species since bulk potassium carbonate decomposes at much higher temperature. We could not find any evidence for appreciable carbonate formation.

II. KOH On Clean Edge Graphite

We have studied the interaction of KOH on the clean edge graphite surface to determine if stable potassium states are formed on an "active" carbon surface in the absence of oxygen. The potassium, oxygen and carbon AES signals were monitored as a function of coverage following KOH deposition on the oxygen free edge surface of graphite held at room temperature and following heating in vacuum. We will report our AES results in the dN(E)/dE mode normalized to the carbon substrate signal which circumvents problems associated with absolute intensity calibrations. These results are shown in Figure 1 and are compared to the results obtained on the basal surface in a previous investigation (15).

The studies on the basal graphite surface established that a 1:1 O:K stoichiometry was maintained during room temperature deposition and subsequent heating in vacuum. On the basal surface of graphite an AES K/C ratio ~0.4 corresponded to a surface with a coverage of one KOH per eight carbon atoms. On this basis the present AES results for KOH on the edge surface indicate that a 1:1 O:K stoichiometry exists at multilayer as well as submonolayer coverages during the deposition near room temperature and after heating in ultra high vacuum to temperatures where the loss of potassium and oxygen occurs.

The coverage of KOH was monitored by AES following heating to a given temperature for 300 sec in UHV. The initial coverage corresponded to a K/C ratio near 2.0 and represents an amount in excess of a monolayer. The KOH coverage remains almost constant as the surface temperature neared 200°C. The potassium signal decreased between 200-500°C. Above 300°C the vapor pressure of KOH is substantial and this is one likely mode of multilayer loss at these temperatures. Submonolayer coverages of KOH persist in the range of 400°C. The presence of submonolayer concentrations of adsorbate at these higher temperatures is attributed to a stabilizing interaction with the carbon substrate. The same type of behavior was observed for pure KOH on the basal surface of graphite. KOH interacts with the oxygen free edge graphite surface in a manner which does not produce strongly bound potassium-oxygen surface complexes.

III. KOH on Oxidized Edge Graphite

We have determined the surface elemental composition and the thermal stability of the potassium containing species on the oxidized edge surface of graphite prepared by adding KOH external to the vacuum system in air. The edge surface of graphite was first oxidized in pure O₂ at 300°C near atmospheric pressure and then the KOH was added. This method of preparation of the

KOH overlayer has a dramatic effect on the thermal stability of the potassium complex. The single layer coverage range, AES K/C ~ 0.4 , persists between 700-800°C. The potassium is ultimately lost at temperatures above 800°C. The stability of potassium is very different on the oxidized edge graphite surface. There are also major compositional changes in the KOH overlayer as well as in the carbon surface. Figure 1 shows the oxygen and potassium AES signals relative to the carbon substrate signal for the oxidized sample contacted with KOH. The solid lines in Figure 1 represent integral oxygen to potassium stoichiometric values as defined from the previous results. In the high coverage multilayer regime the KOH overlayer has between 2 and 3 times the oxygen content as the stoichiometric KOH compound. This is evidence that the KOH layers have taken up and retained substantial quantities of oxygen species from atmospheric gases, predominantly H₂O. Upon heating the sample in UHV the overlayer coverage decreases and the potassium content decreases. Figure 1 shows that as the potassium coverages decrease into a submonolayer regime, AES K/C ~ 0.4 , there is a substantial amount of oxygen present as measured by AES several times the 1:1 stoichiometry. A good portion of this oxygen is associated with the carbon substrate. The carbon surface is heavily oxidized. This has a profound effect on the vacuum stability of the potassium species in the submonolayer coverage range. Oxygen appears to be associated with the species since there is a corresponding loss of a portion of the oxygen.

IV. KOH On Oxidized Glassy Carbon

The method of KOH addition to oxidized glassy carbon surface was the same as on the oxidized edge surface. This method of preparation was also used to add KOH to glassy carbon samples which were found to be catalytically active toward CO₂ carbon gasification (16).

We will compare the results for glassy carbon samples which were oxidized differently. One method was oxidation in O₂ at 300°C which was the same method previously used, the other was oxidation by HNO₃ and produced a surface which was oxidized to a greater extent. Figure 2 contains the results of the thermal stability experiments following heating for 300 sec in UHV at each temperature. In both cases a coverage greater than a monolayer was deposited and subsequently heated in UHV. The multilayer coverages were lost in the 500-600°C range on the O₂ oxidized substrate. This is similar to the results on the HNO₃ oxidized sample which are not shown. In both cases the potassium Auger signal persists to much higher temperatures. The potassium levels are approximately three times greater for the HNO₃ oxidized sample for the O₂ case at any given temperature. There are differences in the surface elemental composition of these samples. Figure 3 shows the oxygen and potassium AES signals relative to the carbon substrate signal for the two samples. The solid lines in Figure 3 represent integral oxygen to potassium stoichiometric values as defined from the previous results contained in Figure 1 based on 1:1 oxygen to potassium KOH stoichiometry. In the high coverage multilayer regime the KOH overlayer has between 2 and 3 times the oxygen content as the stoichiometric KOH compound independent of the method of glassy carbon preoxidation. This is again evidence that the KOH layers have taken up substantial quantities of oxygen containing gases from the air. Upon heating the sample in UHV the overlayer coverage decreases and the potassium content decreases. Figure 3 shows that as the potassium coverages decrease into a submonolayer regime, AES K/C ~ 0.4 , there is a substantial amount of oxygen present which is greater than a 1:1 stoichiometry as measured by AES. We see

that as the amount of potassium decreases in the low coverage regime there is a corresponding loss of a fraction of the oxygen present. As in the case with the edge graphite substrate oxygen appears to be associated with the potassium species. In both glassy carbon samples the carbon surface remains heavily oxidized following the loss of potassium. The oxygen Auger signal for the HNO_3 oxidized sample is slightly more than double that of the sample oxidized in O_2 . This reflects the different extents of initial oxidation. The vacuum stability of the potassium species is enhanced on the more oxidized surface. The degree of carbon surface oxidation is related to the stability of the potassium species generated from KOH.

We have used XPS in order to characterize the electronic structure of the oxidized glassy carbon surfaces after KOH addition and thermal treatment in vacuum. KOH was added to an HNO_3 oxidized glassy carbon sample. The O(1S) XPS spectra was recorded following 5 min heating to the temperature shown in Figure 4. As previously determined by AES the 500°C spectrum corresponds to multilayers of the potassium containing overlayer. The 500°C spectrum has a FWHM of 2.4 eV and a B.E. of 531.7 eV with respect to the Fermi level. This is close to the value reported for KOH (17). We know that the KOH overlayer contains more than the stoichiometric amount of oxygen yet we are unable to resolve different oxygen(1S) peaks. Upon heating to 800°C the overlayer concentration was decreased into the monolayer regime. The 800°C XPS spectrum shows a broad O(1S) signal, FWHM - 4.5 eV. There appears to be two O(1S) peak envelopes, one centered near 531 eV, the other at 533 eV. Heating to 950°C results in the loss of potassium. A O(1S) peak centered near 533 eV remains and this value is associated with oxygen strongly bound to glassy carbon. The 531 eV O(1S) peak occurs in the presence submonolayer concentrations of potassium. The work function of the different glassy carbon surfaces were determined from photoelectron spectroscopy. The clean glassy carbon surface had a work function of 4.2 eV. Oxidation by O_2 increases the work function to 4.4 eV and increases further on a heavily oxidized HNO_3 sample to a value of 4.5 eV. The oxidized glassy carbon surface with the potassium complex corresponding to the 800°C XPS spectrum showed a work function decrease to 3.6 eV. If these values are used to estimate binding energies of the oxygen (1S) peaks with respect to the vacuum level we find almost a three eV binding energy difference between the oxygen associated with the potassium species and oxygen bound to carbon. Lower binding energies of a given element are generally identified with more electropositive electronic environments. The carbon surface with the potassium complex therefore shows oxygen in two generally different electronic environments: one associated with potassium and in an electropositive environment; the other in a more electronegative environment which is typically observed on the potassium-free surface.

DISCUSSION

We have studied the interaction of KOH on clean graphite surfaces in order to isolate the pure interaction of KOH and carbon. AES results show that a constant 1:1 oxygen to potassium stoichiometry is maintained throughout deposition with the edge graphite surface held at 30°C independent of coverage as well as after heating in vacuum to produce submonolayer coverages. On the basal surface of graphite submonolayer coverages of KOH were thermally stable above the melting point of solid KOH where the KOH vapor pressure is substantial. Likewise the results on the edge surface show an increased stability

for the adsorbate a low concentration. Submonolayer concentrations of potassium species persist up to 500°C. Our results are consistent with the picture that KOH interacts reversibly with the edge surface of graphite. The adsorbate is stabilized with respect to solid KOH by the interaction with the carbon substrate. Pure KOH overlayers on the edge graphite surface do not form stable adsorption states above 500°C.

The interaction of H₂O and O₂ with a pure KOH overlayer on the basal surface of graphite emphasize direct salt gas interactions. The KOH surface was very active toward H₂O and O₂ at 30°C. Their presence does not directly lead to a significantly different interaction with the carbon surface. Essentially clean basal graphite surfaces are recovered upon heating in UHV to 500°C. The interaction of KOH with H₂O or O₂ on a passive basal graphite surface is not sufficient to produce potassium species which are stabilized with respect to vacuum at high temperatures.

The interaction of H₂O and KOH with the "passive" basal graphite surface or KOH alone on an "active" edge graphite surface does not generate potassium species which are stable above 500°C. Oxygen already bound to carbon is an important element in determining the formation of stable potassium species. Catalytic precursor alkali salts are generally added to carbons under oxidizing conditions of the gaseous environment or the carbon surface. The edge graphite and glassy carbon surfaces were preoxidized to introduced oxygen strongly bound to carbon. The interaction of KOH with these surface produces potassium containing overlayers with enhanced thermal stability. Only submonolayer concentration of a potassium complex remained above 700°C. The concentration of these species was increased with the extent of carbon preoxidation. The potassium form exists on a carbon surface that is heavily oxidized. The carbon surface with the potassium complex shows oxygen in two different electronic environments. One is associated with potassium is in an electropositive environment. The other is in a more electronegative environment which is typically observed on the potassium-free surface. We cannot distinguish from these results if potassium is bound to oxygen which is on the carbon surface from potassium which interacts with carbon and promotes the formation of oxygen in a more electropositive configuration bound to carbon. In the latter case this form of oxygen might exist on the carbon surface alone or promoted by materials other than potassium. Species where potassium binds to the surface through oxygen, C-O-K have been postulated to exist on catalyzed carbon surfaces (10,12,18). In the other interpretation potassium would be considered an adsorbate which interacts with an oxidized carbon site. In either case it is the initial oxidation of carbon which leads to their formation from KOH.

It is generally agreed that no single mechanism can be used to interpret all of the many different manifestations of catalytic carbon gasification. The oxygen transference mechanism has been widely used to explain alkali catalyzed carbon gasification (1,19). The action of the catalyst is to form intermediates in the oxidizing gaseous environment which decompose to oxidize carbon in the proximity. In doing this the catalyst returns to its original state and the action continues (20). Within the class of alkali gasification catalysts for the reaction of carbon with either H₂O or CO₂ and even for the single element potassium there are a variety of different intermediates postulated for the mechanism (21). Microscopic studies suggest that gasification activity may not be restricted to a single physical form as

catalytic gasification is observed for systems in the presence (22) and absence of discrete particles (23). The mechanisms and intermediates involved in alkali catalyzed carbon gasification by H₂O and CO₂ are still open issues.

We have found in the study of CO₂ and O₂ interaction with the edge surface of graphite and glassy carbon samples that the surface can possess considerable amounts of oxygen which is strongly bound and much less active for CO formation. The CO formation energy decreases as the total oxygen surface concentration increases (24). The efficiency for producing the needed high oxygen coverages from either CO₂ or H₂O is extremely low, <10⁻¹⁴ (24). The surface potassium complex is thought to be the active center for gas dissociation whereby CO or H₂ is formed and oxygen transferred to the carbon surface. This increases the carbon surface oxygen concentration in the vicinity of the complex and thus we would expect this to lower the CO formation energy. The action of the catalyst would be to increase the local oxygen coverage in a carbon domain and thereby increase the number of domains having lower CO formation energetics. For glassy carbon these are in the 60-70 kcal/mole range (24). This mechanism would effectively increase the number of sites found in the uncatalyzed reaction.

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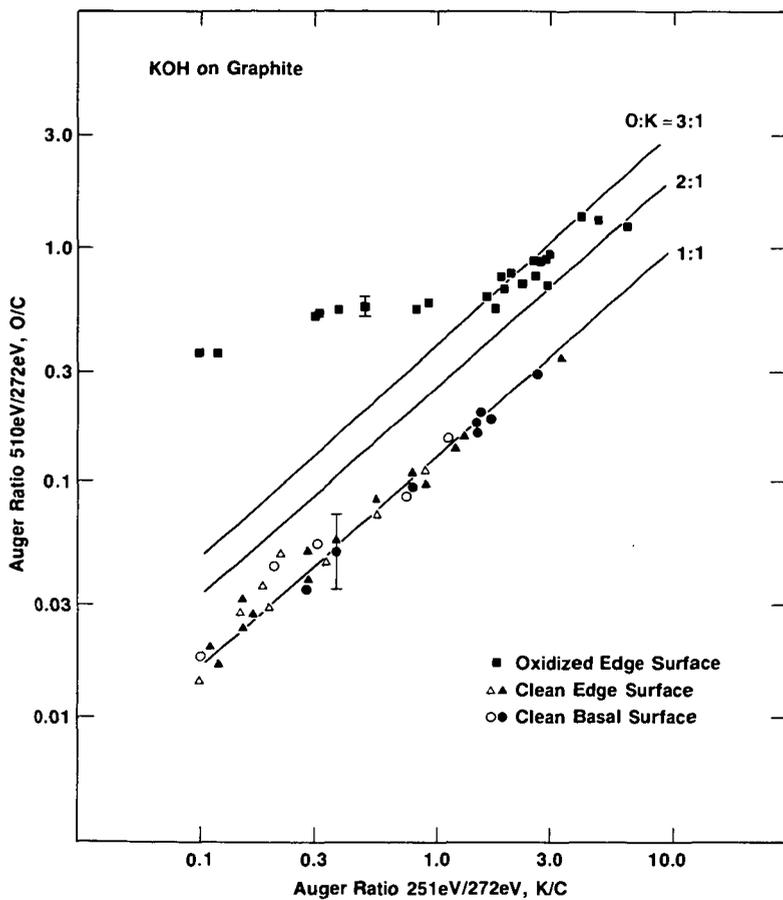


Figure 1: Solid triangles are obtained from the prism surface following KOH deposition at room temperature. Open triangles are a result of heating a KOH overlayer on the prism surface. Solid circles are obtained from the basal surface following KOH deposition at room temperature. Open circles are a result of heating the KOH overlayer on the basal surface. Solid squares are a result of heating KOH added to an oxidized edge graphite surface.

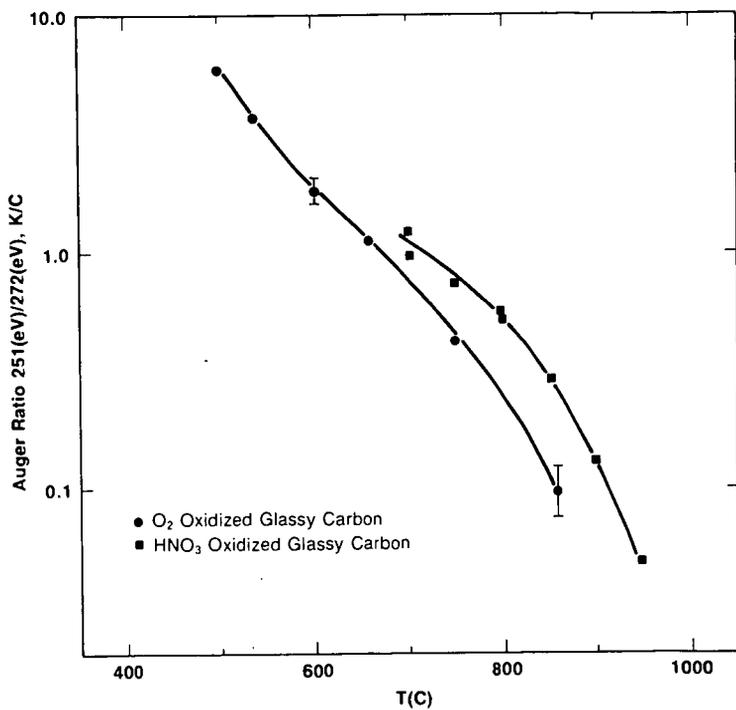


Figure 2: A comparison of the decrease in the K/C Auger ratio as a function of temperature after KOH addition to glassy carbon surfaces oxidized by O₂ at 300°C and by HNO₃.

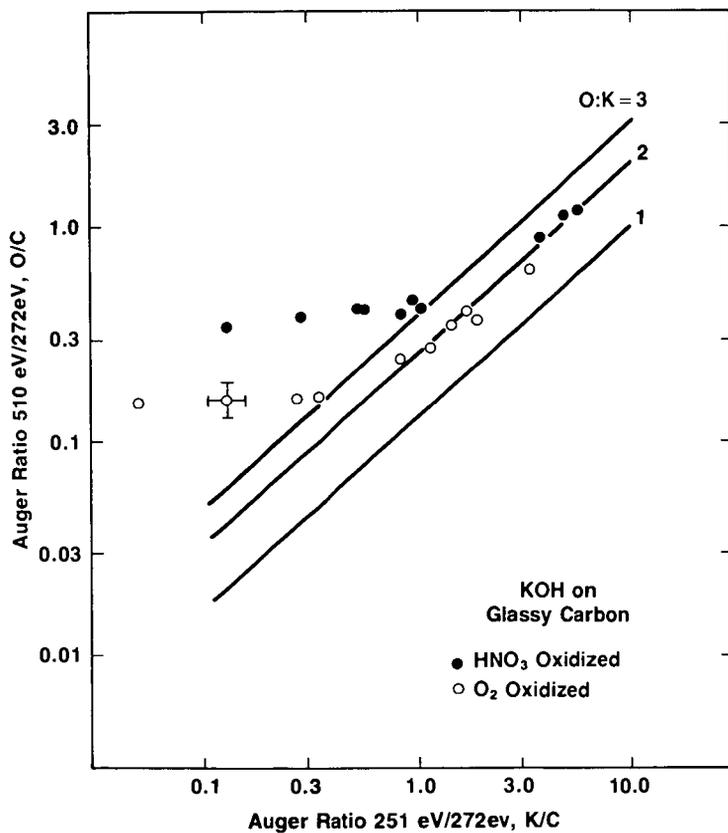


Figure 3: Change in the potassium and oxygen AES signals normalized to carbon following KOH addition to oxidized glassy carbon surfaces and subsequent heating in UHV.

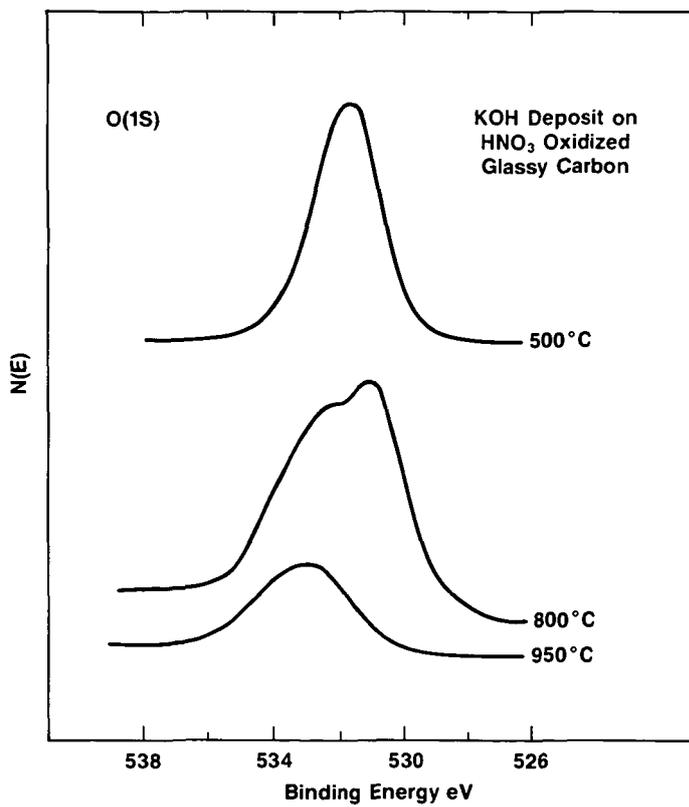


Figure 4: O(1S) XPS signal after KOH addition to a HNO₃ oxidized glassy carbon sample and heating for 300 sec in UHV at each temperature.