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The Interaction of KOH with Clean and Oxidized Carbon Surfaces

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The interaction of KOH with oxidized edge graphite and glassy carbon surfaces was studied with Auger electron spectroscopy (AES), ultraviolet photoemission spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS). These results are compared to those from pure KOH deposited on the oxygen free basal and edge surfaces of graphite. Submonolayer concentrations of a potassium–oxygen surface species, which are stable to 800°C under vacuum, are formed from KOH on preoxidized edge graphite and glassy carbon surfaces. Similar properties are found on glassy carbon surfaces after potassium-catalyzed gasification in CO_2. XPS from these surfaces show two O(1*s*) peak envelopes centered near 531 and 533 eV. The higher binding energy peak is characteristic of oxygen strongly bound to carbon. Heating to 950°C results in the loss of potassium and the lower binding energy oxygen peak associated with potassium. The presence of an oxidized carbon surface enables development of stable potassium–oxygen surface species from KOH. Pure KOH interacts reversibly with the oxygen-free edge graphite surface and does not produce a form of potassium which is stable above 500°C under vacuum. Our results show the presence of strongly bound potassium surface intermediates in inert environments. As a consequence, a catalytic cycle can be postulated which does not involve bulk-like K_2O or K_2CO_3. © 1986 Academic Press, Inc.

I. INTRODUCTION

The reaction of solid carbons with H_2O and CO_2 is catalyzed by the addition of alkali salts such as KOH and K_2CO_3 (*1–7*). The chemical state of the alkali metal during the course of reaction is still subject of debate (*8*) and has been the focus of many current research efforts (*6–25*). The active form of the catalyst is thought to operate by way of an oxygen transference mechanism. Central to all proposed mechanisms is the issue of thermal stability of alkali intermediates. A definition of the chemical state of the catalytically active alkali species and composition of the carbon surface will lead to a better mechanistic description of the catalyzed reaction. For these reasons, the interaction of alkali salts such as KOH, with well-defined carbon substrates, is of fundamental interest.

Previous work has shown that the edge surface of highly orientated pyrolytic graphite (*26*) and glassy carbon substrates (*27, 28*) can be prepared which are suitable for surface spectroscopic analysis. The edge surface of graphite exhibited a reactivity toward oxidation by O_2 nearly the same as that found on para-crystalline glassy carbon substrates (*29, 30*). The clean edge surface of graphite showed evidence of domains having long-range order by the appearance of a $C(2 \times \frac{2}{3})$ LEED pattern (*26*), but the surface is polycrystalline and exhibits evidence of the structural disorder as well. The glassy carbon samples, on the other hand, showed only diffuse scattering in LEED experiments. The similarity of the O_2 oxidation chemistry on the edge graphite and glassy carbon samples indicates that the local surface carbon site environment is very close despite the differences in long-range order. These previous studies provide a foundation for the present surface studies.

It is known that KOH and K_2CO_3 are especially active precursors to catalytically active states on the carbon surface (*10, 11, 31, 32*). The initial oxygen content of carbon may be important in relation to the cat-

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alysts formation from KOH and K_2CO_3. Oxygen necessary for site formation can either be supplied from the reactant gas during approach to gasification conditions or be initially present on the carbon. This is the motivation to characterize the addition of KOH to oxidized edge graphite and glassy carbon surfaces. The clean oxygen-free edge surface of graphite was also studied under ultrahigh vacuum conditions in order to isolate the pure interaction of KOH with potentially "active" free edge 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.

II. EXPERIMENTAL

Experiments were performed in a standard ultrahigh vacuum spectroscopy chamber equipped with a double-pass cylindrical mirror analyzer (Physical Electronics) which was used for AES, XPS, and UPS measurements. Auger electron spectroscopy was performed using a 2.2-keV primary beam energy at grazing incidence. A 2-eV peak to peak modulation voltage was used in the $dN(E)/dE$ mode. The graphite used was a ZYA monochromator grade obtained from the Carbon Products Division of the Union Carbide Corporation. The details of the sample preparation and characterization of the oxygen-free edge surface of graphite can be found in a previous communication (*26*). The glassy carbon samples were cut from plates obtained from Atomergic Chemetals and were outgased at 1300°C in UHV prior to use. This procedure removed the oxygen which was the principal contaminant measured by AES. 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, as well as the methods of coverage determination using AES, appear elsewhere (*33*). 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°C in an isolated high-pressure preparation section. The oxidation kinetics by O_2 of the edge graphite surface and glassy carbon have been previously quantified (*29*) and conditions chosen which produced a substantial amount of surface oxidation. Nitric acid oxidation of the glassy carbon samples was accomplished by boiling the samples for 4 h in HNO_3 under reflux conditions. The HNO_3 treatment also produced heavily oxidized glassy carbon surfaces and no nitrogen-containing species were found on the surface in agreement with recent findings on carbon fiber surfaces (*34*). KOH was added to the oxidized carbon surfaces in laboratory air by physically contacting the carbon surface with a moist KOH pellet. This formed a liquid coating across the entire carbon surface. The procedure was accomplished within 1 min and the sample was returned to the UHV environment by use of the rapid introduction sample holder.

III. RESULTS

A. KOH on Basal Graphite With H_2O and O_2

The surfaces of pure KOH films took up H_2O and O_2 at room temperature. The AES oxygen signal increases following H_2O and O_2 exposure. The UPS spectra following gaseous exposure also provides evidence for rapid adsorption. Figure 1 shows UPS spectra obtained at $h\nu$ = 40.8 eV for the clean basal surface of graphite (curve A) and following the evaporation of multilayers of pure KOH (curve B). The clean carbon surface shows the expected emission originating predominantly from the π and σ bands of graphite (*35, 36*) and are labeled in Fig. 1. The KOH overlayer is thin with respect to surface charging, but sufficiently thick to attenuate the emission from carbon. We observe the typical emission from the 1π and 3σ levels of the hydroxyl near -6 and -10 eV, respectively, as well as a

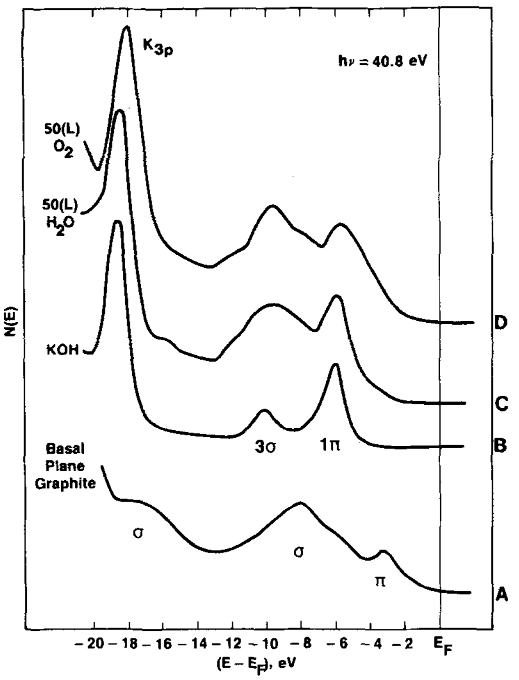

FIG. 1. Helium II UPS $N(E)$ curves for: the clean basal graphite surface (curve A), after evaporation of multilayers of KOH (curve B), after 50(L) H_2O exposure to pure KOH multilayers held at 30°C (curve C), and after 50(L) O_2 exposure to pure KOH multilayers held at 30°C (curve D).

large potassium $3p$ signal at -18.6 eV (*33*). The UPS spectra changes after exposure of pure KOH films to either 50(L) of H_2O (curve C) or 50(L) of O_2 (curve D). The changes then appear to saturate with further exposure. The potassium $3p$ peak shifts closer to the Fermi level by 0.2 eV with H_2O and 0.6 eV with O_2. At higher energies the UPS spectra become complicated. The changes in the UPS spectra are attributed primarily to oxygen $2p$ emission from the oxygenated species derived from H_2O and O_2. On both of these spectra we can identify two major emission peaks at energies which correspond to reminants or pure hydroxyl 1π and 3σ emission. These results show that pure KOH films are very active for uptake of H_2O and O_2.

The addition of KOH to carbon in air is expected to always introduce oxygen-containing gases into the system. Basal graphite surfaces which have been contacted by KOH in air have UPS spectral features similar to the H_2O- and O_2-exposed KOH films. The KOH multilayer films exposed to H_2O and O_2 on the basal graphite surface had thermal stabilities toward desorption in UHV comparable to those found for pure multilayer KOH films, 300–500°C. The vapor pressure of pure KOH is substantial above 300°C. Similar behavior was found on basal 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. Although prolonged atmospheric exposure of KOH leads to the uptake of CO_2 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.

B. 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 under vacuum. We will report our AES results in the $dN(E)/dE$ mode normalized to the carbon substrate which circumvents problems associated with absolute intensity calibrations. These results are shown in Fig. 2 and are compared to the results obtained on the basal surface in a previous investigation (*33*). On the basal surface of graphite a K/C ratio ~0.4 corresponded to a surface with a coverage of one KOH per eight carbon atoms and a 1 : 1 O : K stoichiometry was maintained during room-temperature deposition and subsequent heating under vacuum. KOH on the edge surface behaves in a similar manner.

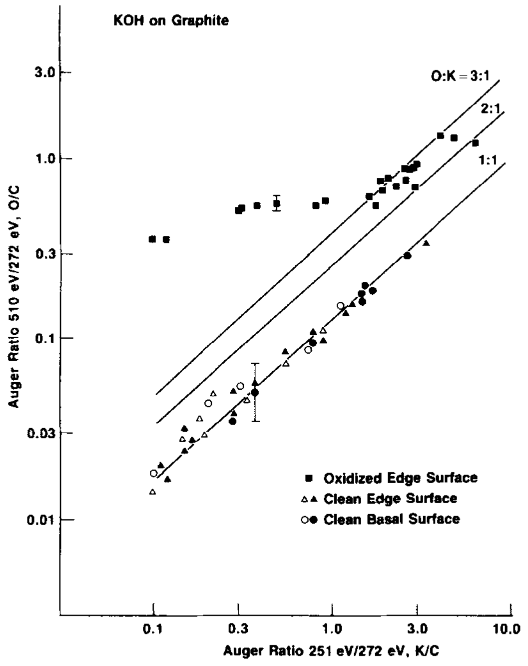

FIG. 2. Potassium and oxygen AES signals normalized to carbon. Solid triangles are obtained from the prism surface following KOH deposition at room temperature. Open triangles are a result of heating a KOH overlayer on the prism surface. Solid circles are obtained from the basal surface following KOH 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.

The coverage of KOH was monitored by AES following heating the edge surface of graphite to a given temperature for 300 s in UHV. Figure 3 contains these results. 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 and 500°C. Above 300°C the vapor pressure of KOH is substantial and this is one likely mode of multilayer loss at these temperatures. We have found that diffusion of KOH from the regions of multilayers across carbon surfaces to potassium-free carbon regions is important even at temperatures as low as 200°C. This is identified as another mode which will cause a decrease in the potassium AES signal. Submonolayer coverages of KOH persist in the range of 400°C. The presence of submonolayer concentrations of adsorbate at these moderate temperatures is attributed to a stabilizing interaction with the carbon substrate, which was also observed for pure KOH on the basal surface of graphite (*33*). KOH interacts with the oxygen-free edge graphite surface in a manner which does not produce strongly bound potassium–oxygen surface complexes.

C. KOH on Oxidized Edge Graphite

The thermal stability of the potassium-containing species after KOH addition in air to an O_2-oxidized edge surface of graphite was monitored in UHV. The results after heating for 300 s at each indicated temperature are presented in Fig. 3. The initial overlayer coverage is slightly in excess of a monolayer. The state of the carbon surface has a dramatic effect on the thermal stability of the potassium species in the thin multilayer and submonolayer regimes. Thin multilayer structures are stabilized to

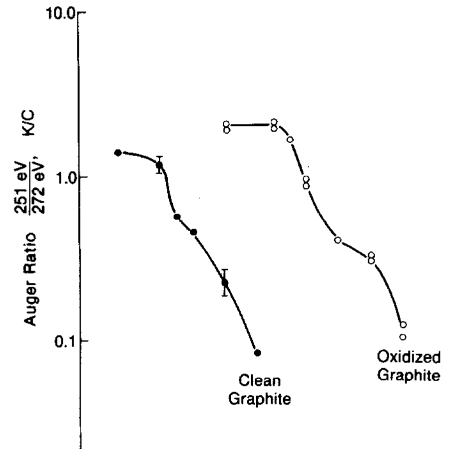

FIG. 3. A comparison of the decrease in the K/C Auger ratio as a function of temperature after KOH addition to a clean and to an oxidized edge graphite surface.

500°C. The potassium AES signal decreases upon heating to higher temperatures and the thin multilayer film is lost between 500 and 600°C. The single layer coverage range, AES K/C ≲ 0.4, persists between 700 and 800°C. All potassium is ultimately lost at higher temperatures.

The surface composition changes with temperature. Figure 2 shows the oxygen and potassium AES signals relative to the carbon substrate signal for the oxidized edge graphite surface contacted with KOH. The solid lines in Fig. 2 represent integral oxygen to potassium stoichiometric values. In the high coverage multilayer regime the KOH overlayer has between 2 and 3 times the oxygen content of 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 H_2O. Upon heating the sample in UHV the overlayer coverage decreases and the potassium content decreases. Figure 2 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 which corresponds to several times the 1 : 1 stoichiometry. A substantial fraction of this oxygen is associated with the carbon substrate introduced during the initial oxidation in O_2. This has a profound effect on the vacuum stability of the potassium species which forms in the submonolayer coverage range. Oxygen appears to be associated with the potassium species since there is a corresponding loss of a portion of the oxygen with the loss of potassium.

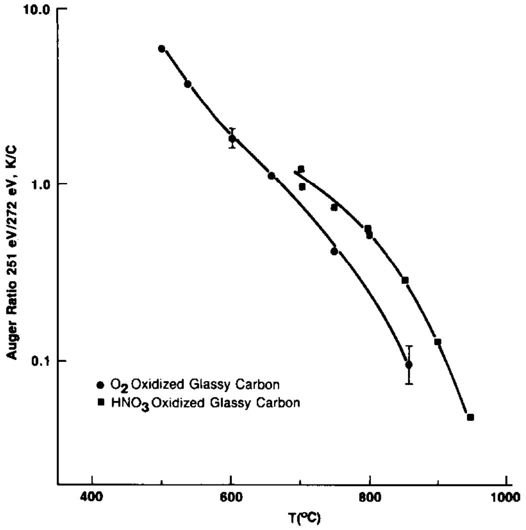

FIG. 4. A comparison of the decrease in the K/C Auger ratio as a function of temperature after KOH addition to glassy carbon surfaces oxidized by O_2 at 300°C and by HNO_3.

D. KOH On Oxidized Glassy Carbon

The vacuum thermal stability of the potassium species at high temperature and the elemental composition of the carbon surface were monitored in detail with AES. We will compare the results for glassy carbon samples which were oxidized in O_2 at 300°C to those oxidized by HNO_3 which produced a surface oxidized to a greater extent. Figure 4 contains the results of the thermal stability experiments following heating for 300 s in UHV at each temperature. In both cases a coverage of KOH greater than a monolayer was deposited and subsequently heated in UHV. The multilayer coverages were lost in the range 500–600°C on the O_2 oxidized substrate. This is similar to the results on the HNO_3 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 HNO_3-oxidized sample than for the O_2 case at any given temperature. There are differences in the surface elemental composition of these samples. Figure 5 shows the oxygen and potassium AES signals relative to the carbon substrate signal for the two samples. The solid lines in Fig. 5 represent integral oxygen-to-potassium stoichiometric values as defined from the previous results contained in Fig. 2 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

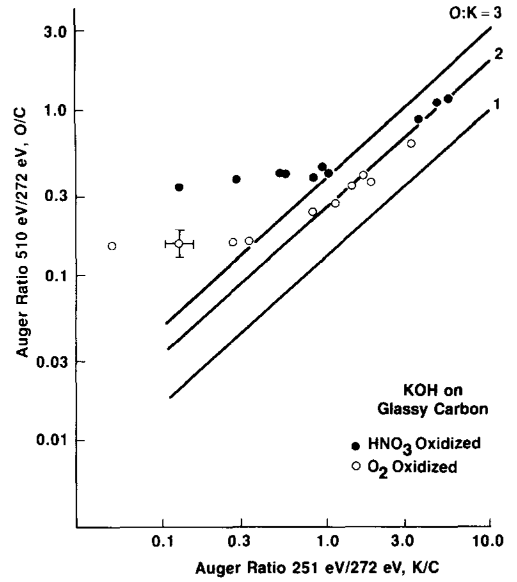

FIG. 5. Change in the potassium and oxygen AES signals normalized to carbon following KOH addition to oxidized glassy carbon surfaces.

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 5 shows that as the potassium coverages decrease into a submonolayer regime, AES K/C $\lesssim$ 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 concentration of the potassium species remaining at any given temperature is greater on the more oxidized surface. The degree of initial carbon surface oxidation is related to the subsequent concentration of potassium species exhibiting enhanced high-temperature stability.

We have used XPS in order to characterize the electronic structure of the oxidized glassy carbon surfaces after KOH addition and thermal treatment under vacuum. KOH was added to an HNO_3-oxidized glassy carbon samples. The O(1*s*) XPS spectra was recorded following 5 min heating to the temperatures shown in Fig. 6. 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 bulk KOH (*37*). We know that the KOH overlayer contains more than the stoichiometric amount of oxygen, and subsequent UPS measurements which probe the valence band region are perturbed from pure KOH, yet, we are unable to resolve

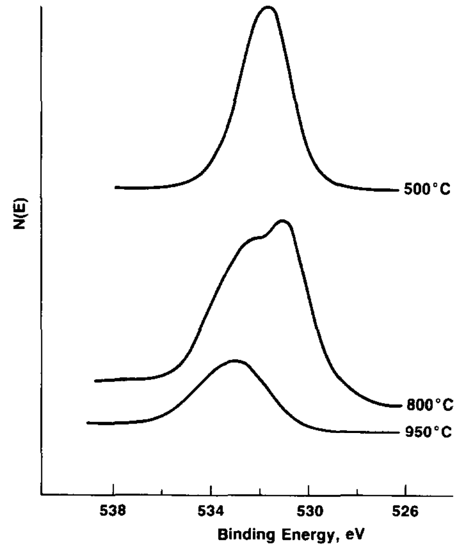

FIG. 6. O(1*s*) XPS signal after KOH addition to a HNO_3-oxidized glassy carbon sample and heating for 300 s in UHV at each temperature.

different oxygen (1*s*) peaks. Upon heating to 800°C the overlayer concentration was decreased into the monolayer regime. The 800°C XPS spectrum shows a broad (O(1*s*) signal, FWHM—4.5 eV. There appear to be two O(1*s*) peak envelopes which comprise the signal, one centered near 531 eV, the other at 533 eV. Heating to 950°C results in the loss of potassium. The O(1*s*) peak centered near 533 eV remains and this value is associated with oxygen strongly bound to glassy carbon. The 531-eV O(1*s*) peak occurs in the presence of submonolayer concentrations of the potassium species. 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 increase the work function to 4.4 eV, and on a heavily oxidized HNO_3 the value increased to 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 (1*s*) peaks with respect to the vacuum level we find there is almost a 3-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 can be found on the potassium-free surface.

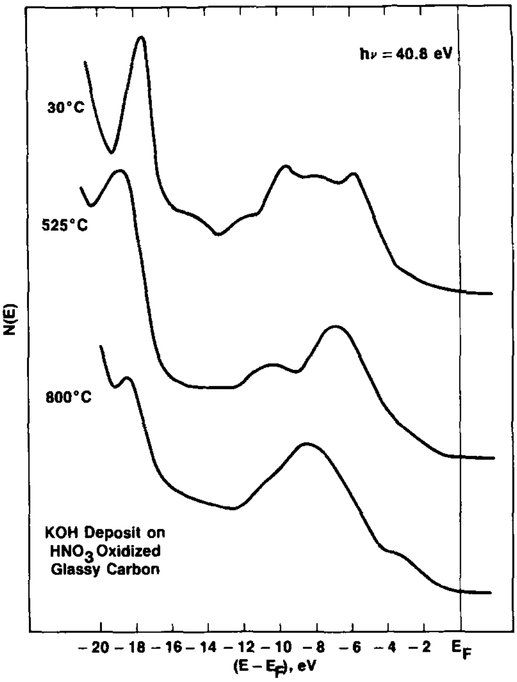

FIG. 7. He II UPS spectra after KOH addition to an O_2-oxidized glassy carbon sample and heating for 300 s in UHV at each temperature.

Ultraviolet photoemission spectroscopy was also used to characterize the electronic structure of the glassy carbon surfaces. The results at $h\nu = 40.8$ eV are shown in Fig. 7 following addition of KOH on an O_2-oxidized surface and after heating for 5 min in UHV to the indicated temperature. The 30°C spectrum corresponds to multilayers of KOH. KOH was shown to be sensitive to contamination from O_2 and especially H_2O. We therefore expect a complicated UPS spectrum. The largest peak at -17.5 eV corresponds to emission from the potassium 3*p* level. Features closer to the Fermi level corresponds to oxygen 2*p* emission from the mixture of oxygen species. At least five peaks can be found which are near -6, -8, -10, -12, and -15 eV. The peaks near -6 and -10 eV are reminiscent of the OH 1π and 3σ levels expected from KOH. The peaks near -8, -12, and -15 eV also appear for H_2O-exposed KOH multilayers on the basal surface of graphite. These peaks provide evidence for a KOH overlayer undoubtedly contaminated by H_2O. This conclusion is supported by the observation that H_2O is liberated to the gas phase and is the dominant species when the sample is heated to 525°C in UHV. The multilayer film thickness decreases to ~5 Å upon heating to 525°C as estimated from the attenuation of the carbon AES signal. The UPS spectra at 525°C has three peaks. The elemental composition from AES shows that there is still oxygen in excess of the stoichiometric KOH compound. There is a 1-eV shift to lower energy of the potassium 3*p* peak to a value of −18.5 eV. The work function is 4.0 eV and is not changed from the measured value of the overlayer at 30°C. There are two peaks at −6.9 and −10.5 eV. The overlayer does not have a well-defined elemental composition. At first glance the UPS spectrum resembles that of pure KOH which is the precursor salt but there are important differences. The potassium 3*p* peak and the two higher energy peaks are broader and the relative separation of the peaks is different. There is an 8.5-eV separation between the K_{3p} and OH 3σ peak in the pure KOH compound while only 8.0 eV separates the K_{3p} and the next peak higher in energy. There is a 4.0-eV separation between the 3σ and 1π levels of the pure compound but only a 3.1-eV separation for the two peaks in the same energy range for the 525°C heated overlayer. At 525°C an approximately 5-Å-thick potassium hydroxide-like film containing excessive oxygen coats the oxidized carbon surface.

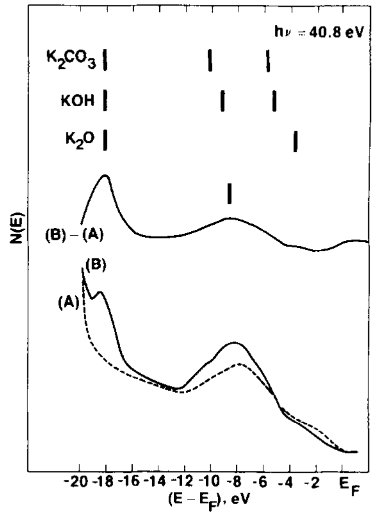

FIG. 8. He II UPS *N*(*E*) curves of a clean glassy carbon surface (curve A) and after KOH addition to an O_2-oxidized sample and heating to 800°C in UHV. Included above is the difference curve and a comparison of the separation between the K_{3p} peak and the major O_{2p} derived levels for various potassium salts. The energy scales are shifted to align the K_{3p} peak in each case.

Upon heating to 800°C the concentration of potassium species declines to submonolayer concentrations and we expect contributions from the carbon substrate in the UPS spectrum. There is a substantial decrease in the intensity of the potassium 3*p* signal which occurs at −18.2 eV. A large broad peak, which appears at lower energies, is predominantly emission from σ levels of the carbon substrate. AES and XPS results indicate that there is oxygen bound to the carbon as well as oxygen associated with potassium. Their presence will contribute to emission between −5 and −12 eV. This aspect can be seen in Fig. 8 by the comparison of the UPS spectra from the initial clean glassy carbon surface and after formation of the complex at 800°C. The observation is also aided by a difference representation of the data shown above. Oxidation of glassy carbon surfaces by HNO_3 and O_2 both result in emission increases between −5 and −12 eV with peaks at −5.5 and −9.5 eV. These are a result of oxygen 2*p* derived levels and also the changes in the carbon σ valence structure due to bonding with oxygen. The oxygen 2*p* derived levels from oxygen bound to carbon is expected to contribute to the spectrum containing the potassium species. We do find an increase in the relative emission between −5 and −12 eV. The maximum increase occurs at −8.7 eV. The emission increase is partially a consequence of oxygen bound to carbon but we also expect to find evidence of the potassium species. The potassium 3*p* peak is a prominent feature and occurs at −18.2 eV. The XPS results indicate that there is oxygen associated with this potassium complex. The oxygen 2*p* derived levels associated with the complex are expected in the same energy range as oxygen for the oxidized carbon surface.

This is an already complicated spectral region and it is difficult to assign with any great certainty an emission unique to the oxygen associated with potassium. A broad peak at −8.7 eV is not found on oxidized carbon surfaces (*27–29*) in the absence of potassium.

We can compare the measured emission maximum from the oxygen 2*p* derived peaks relative to the potassium 3*p* signal for several bulk potassium salts to that found in the presence of the potassium complex on glassy carbon. Figure 8 contains the comparison. Both KOH and K_2CO_3 (*38*) possess two sharp peaks at high energies. In each case the highest energy peak corresponds to essentially nonbonding oxygen 2*p* levels while the lower energy peak corresponds to oxygen 2*p* electrons involved in hydroxyl and carbonate bonding, respectively. There is no simple correspondence between the bulk KOH and K_2CO_3 features and the potassium species on the glassy carbon surface. A K_2O-like film formed on potassium metal (*39*) also gives different valence electronic emission features. In this case there is only a single sharp peak which occurs at much higher energies. We conclude that the stable high-temperature potassium species formed on the oxidized glassy carbon surface does not have valence electronic features characteristic of bulk-like KOH, K_2CO_3, or K_2O.

The presence of the potassium species changes the electronic structure of the oxidized carbon surface close to the Fermi level. Initial oxidation of carbon decreases emission from the carbon substrate at energies close to the Fermi level as these carbon levels become involved in the chemical bonding to oxygen (*27*). On heavily oxidized surfaces, the valence band changes from a semimetal to a more insulating structure. In the presence of the potassium complex, emission within 4 eV of E_F is not as severely suppressed even though the surface is oxidized. There is, however, a substantial surface concentration of potassium species, and their presence appears to modify the anticipated loss of emission near the Fermi level. This may be a consequence of charge donation from the potassium species into the valence band of graphite.

IV. DISCUSSION

We have studied the interaction of KOH with a variety of characterized carbon surfaces. The interaction of KOH and the clean edge surface of graphite was studied in order to isolate the pure interaction of KOH on "active" carbon surface sites. AES results show that a constant 1 : 1 oxygen to potassium stoichiometry is maintained throughout deposition on the clean edge graphite surface held at 30°C independent of coverage as well as after heating in UHV to produce submonolayer coverages. Previous results (*33*) on the basal surface of graphite showed that submonolayer coverages of KOH were thermally stable above the melting point of solid KOH where the KOH vapor pressure is substantial. Likewise, the present results on the edge surface show an increased stability for the adsorbate at low concentration. Submonolayer concentrations of KOH 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. The pure KOH overlayer on the clean edge graphite surface does not react to form stable adsorption intermediates above 500°C, and consequently, is not identified with the production of the catalytic potassium species.

The interaction of H_2O and O_2 with the pure KOH overlayer on the basal surface of graphite emphasize direct salt–gas interactions. The KOH surface was very active toward H_2O and O_2 at 30°C. The interaction of KOH with H_2O or O_2 on a "passive" basal graphite surface is not sufficient to produce potassium species which are stabilized with respect to vacuum at high temperatures, and therefore, catalytic species are not produced.

Oxygen already present in carbon is an important element in determining the formation of stable potassium species. Submonolayer forms of a potassium species remained above 700°C on KOH added to preoxidized edge graphite on glassy carbon surfaces. The concentration of these species increased with the extent of carbon preoxidation. The potassium form exists on a carbon surface that is heavily oxidized. This environment and the vacuum stability pattern is similar to those found on glassy carbon samples analyzed after extensive steady-state potassium-catalyzed CO_2 gasification of carbon (*41*). The carbon surface with the potassium complex shows oxygen in two different electronic environments. One is associated with potassium in an electropositive environment. The other is in a more electronegative environment which can also be observed on the potassium-free surface. Our UPS results show that the valence electronic structure of the carbon surface containing the potassium species does not possess bulk-like K_2CO_3, K_2O, or KOH features. The work function of the surface is 0.6 eV lower than clean or oxidized glassy carbon surfaces but is still 1.3 eV above metallic potassium (*42*). These results show that potassium is modified from a metallic state. The presence of reasonably strong emission close to the Fermi level suggests that there is some partial charge donation from the potassium species to the valence states of the oxidized carbon surface.

Discussions concerning the "active" chemical state of the potassium catalyst fall into three broad categories, namely intercalates, bulk-like surface salts, and oxidic surface species. Central to all proposed mechanisms is the issue of the thermal stability of alkali intermediates. Catalytic gasification activity can be regained after subjecting the solid carbon with catalyst to inert gaseous environments at reaction temperature (*13, 40, 41*), generally $T \geq 700°C$. Intercalates have been implicated in catalytic gasification (*6, 43, 44*), but seem to be the least likely candidates. Although it is well known that alkali metals form intercalation compounds with graphite, their vacuum thermal stabilities do not exceed 500°C (*45, 46*).

A reaction sequence on the carbon surface has been proposed based on a bulk-like reaction cycle (*10, 19, 20, 32, 47*)

$$K_2CO_3 + 2C = 2K + 3CO$$

$$2K + 2H_2O = 2KOH + H_2$$

$$2KOH + CO = K_2CO_3 + H_2$$

This reaction sequence has been invoked to explain the gasification reaction on a variety of different carbon systems. The physical forms of the potassium species are not specifically stipulated, i.e. (bulk-line salt or molecular adsorbate, etc.), but the cycle is feasible based on bulk thermodynamic values. Bulk potassium metal and potassium hydroxide are not stable with respect to vaporization at gasification temperatures under vacuum. On the other hand, bulk K_2CO_3 is stable and it has been suggested that the decomposition of a K_2CO_3-like species on carbon is the rate-determining step (*10, 19, 40, 47*). Furthermore, it has been suggested that these equations represent elementary steps in the reaction sequence (*10, 19, 40, 47*). In a related sequence for CO_2 gasification potassium metal is thought to react with CO_2 to form K_2O and CO (*10, 19, 40*).

$$K_2CO_3 + 2C = 2K + 3CO$$

$$2K + CO_2 = K_2O + CO$$

$$K_2O + CO_2 = K_2CO_3$$

The initial step, the reduction of K_2CO_3 by carbon to produce potassium vapor, is well documented (*48*). Recent temperature-programmed desorption (*9*), results with isotopically labeled K_2CO_3, confirm that K_2 CO_3 decomposes on carbon below the bulk decomposition temperature (*13, 15*). The resultant "active" potassium species does not reform K_2CO_3 upon cooling in CO_2 (*9*). The results of the present study also indicate the existence of a stable potassium surface species distinct from KOH-like, K_2CO_3-like, or K_2O-like forms. A catalytic mechanism based on a reformation of K_2CO_3 as a bulk-like salt or molecular adsorbate is not supported by our studies.

Recent studies of alkali metal carbonate–carbon interactions indicate that a discrete chemical compound is formed different from the carbonate, hydroxide, or oxide (*18*). They suggest that a substoichiometric oxide of potassium may form a liquid film distributed over the carbon surface. The composition of the film is determined by the reducing process at the carbon interface and the oxidizing process at the film surface in contact with gaseous CO_2 or H_2O. The potassium species at the carbon interface is not specified.

Surface species of potassium and oxygen are considered to be likely chemical forms of the potassium catalyst (*13, 14, 23, 24, 40*), and this picture is also supported by the present work. The presence of a surface species containing C—O—K bonds was determined by subsequent methylation of the carbon surface with CH_3I to produce C—O—CH_3 (*13, 14*). The existence of surface potassium species associated with oxygen has implications in the catalyzed gasification mechanism. A catalytic cycle can be postulated which does not involve the formation of bulk-like K_2O or K_2CO_3. We have recently obtained quantitative results which demonstrate that the submonolayer potassium surface species generated from KOH and characterized in the present work facilitates CO_2 dissociative adsorption under reaction conditions (*41*). These findings will be reported in more detail in a separate communication. The catalytic action can then be interpreted in terms of the oxygen transference mechanism, where the potassium catalyst promotes the oxidation of proximate carbon sites.

V. SUMMARY

The catalytic form of potassium in carbon gasification systems exhibits stability in inert gaseous environments at reaction temperatures. AES, UPS, and XPS results show that the addition of KOH to oxidized carbon surfaces produces a potassium species which shows thermal stability in UHV above 700°C. AES gave the elemental surface composition and concentration levels while UPS and XPS yielded chemical information about the potassium species and the carbon substrate. This information gives the following picture for the surface system: (1) the potassium species exists at submonolayer concentrations; (2) oxygen is associated with potassium as well as the carbon surface; (3) the potassium species does not correspond to bulk-like KOH, K_2CO_3, or K_2O salts; and (4) the presence of the potassium species modifies surface electronic properties in a manner consistent with partial charge donation to the carbon surface.

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