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The interaction of potassium with oxygen on graphite as studied by high-resolution electron energy loss spectroscopy and thermal desorption spectroscopy

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Abstract. High-resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS) are employed to study the interaction between oxygen and potassium on graphite in the coverage range up to 2.5 monolayers and in the temperature range 160–800 K. Annealing gives rise to a succession of different KO_x complexes, partially induced by surface segregation of intercalated potassium. A vibrational excitation at 39 meV is attributed to K_2O formation, in agreement with a recent interpretation of XPS and HREELS spectra of oxidized single-crystal potassium. Two vibrational excitations at 30–31 meV and 180 meV are tentatively attributed to either KO_2 or K_2O_2 . A high-temperature complex, which is an unidentified precursor to CO_2 formation/desorption, has a single electron energy loss at 27 meV.

1. Introduction

Co-adsorption of oxygen and potassium has previously been studied on metal [1–6], semiconductor [7, 8] and graphite surfaces [9–11]. The studies of these co-adsorption systems are related to the promoting effect of alkali metals and alkali metal compounds in heterogeneous catalysis [12], and to the catalytic effect of alkali metals in semiconductor oxidation [7, 13] and carbon gasification [14]. On a more fundamental level, the nature of the oxygen–alkali interaction has attracted considerable interest, partly because of the variety of ionic configurations that are displayed by these systems [15], and more recently due to the interesting electronic effects accompanying alkali adsorption and co-adsorption on surfaces [16–18].

It is well established that the reaction between oxygen and solid carbon, i.e. carbon oxidation, is effectively catalysed by the presence of alkali compounds [14, 19]. In a previous study [11], we observed a 10^4 -fold increase in the oxidation rate of clean evaporated carbon films when small amounts of potassium were added to the carbon substrate. In subsequent studies [9, 10], TDS and AES measurements of potassium and oxygen co-adsorption on graphite were performed in order to obtain information about the mechanism for the catalytic carbon oxidation.

The previously obtained TDS data indicated that potassium oxides, KO_x , of then undecided stoichiometries, were formed on the graphite surface at low temperatures [9–11]. Heating of the co-adsorption system (2.5 K s^{-1}) resulted in extensive K desorption

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around 600 K [9], which was attributed to decomposition of the potassium oxide, leaving a more oxygen-rich potassium compound on the surface. All the adsorbed oxygen was found to eventually form CO_2 , which desorbed simultaneously with the remaining K at around 800 K [11].

While the thermal stability properties of the reaction intermediates have now been fairly well characterized, there were hitherto no direct spectroscopic data providing information about their chemical identity.

The present work is, to our knowledge, the first HREELS study of co-adsorbed oxygen and metallic potassium on graphite. It complements our previous kinetic studies [9–11], with vibrational spectroscopy information about KO_x complexes, formed upon O_2+K co-adsorption on graphite. It also provides new information about reaction intermediates in potassium catalysed gasification of carbon. However, we emphasize the more general aspects of these results, in the contexts of alkali–oxygen interaction on surfaces and alkali promoted oxidation. Preliminary results were presented in [20].

2. Experimental details

The experimental system, graphite sample and potassium deposition are described in detail elsewhere [9]. Briefly, the experiments were performed in a UHV chamber with base pressure $< 2 \times 10^{-10}$ Torr. The potassium deposition on graphite was made at a sample temperature of 160 K by controlled heating of a SAES alkali–metal getter encased in a collimator tube. Most measurements were made at a potassium coverage of 2.5 ML. (All potassium, coverages in this paper will be given in fractions of ‘monolayer coverage ML’, where 1 ML is taken to be 5.2×10^{14} atoms cm^{-2} , which approximately corresponds to the surface density of a closed packed potassium layer, assuming potassium metallic radius $r_m = 2.26 \text{ \AA}$.) Additional measurements were also performed for four different lower potassium coverages. Absolute calibration of the potassium depositions was made using a quartz-crystal micro balance and by a comparison with obtained LEED and work function data. Some potassium intercalates into graphite at 160 K (the process is also coverage dependent), so the surface coverage is lower. Details on the coverage calibration and potassium intercalation will be reported elsewhere [21].

Oxygen exposures of the potassium covered surface were made at 160 K by backfilling the experimental chamber with O_2 in the 10^{-8} Torr range. The HREELS measurements (Leybold–Heraeus, ELS22) were performed with a primary electron energy of 15 eV in specular geometry. Thermal desorption spectroscopy was made with a linear heating rate of 2.5 K s^{-1} . The mass spectrometer (Balzers QMG311) was multiplexed so that multiple desorption products could be monitored simultaneously.

3. Results

Figure 1 shows HREELS spectra obtained after different oxygen exposures of potassium-precovered (~ 2.5 ML) graphite at 160 K. Spectrum (a) corresponds to the clean graphite surface, exhibiting a strong loss continuum typical for semimetals [22]. The deposition of potassium (spectrum (b)) results in dramatic changes of the HREEL spectra: the surface reflectivity drops $\sim 10^2$ times, as measured by the elastic peak intensity, and the characteristic graphite loss continuum disappears. The decrease in the surface reflectivity is believed to be primarily due to surface disorder introduced by the adsorbed potassium layer.

After a 3 L oxygen exposure of the K-covered surface (spectrum (c)) a distinct loss peak, centred at 32 meV is observed. HREEL spectra obtained after lower oxygen exposures (not shown) exhibit a broader and weaker peak at about the same loss energy. Additional exposures (8 L, spectrum (d)) cause the peak intensity to increase, but the loss energy remains the same. Still larger oxygen exposures result in broadening of the peak, and its maximum moves to higher loss energies, reaching 35 meV after 25 L (e). The width of the loss peak in spectrum (e) indicates that this peak is actually a superposition of the peak at 32 meV and a new one centred at around 38 meV.

The spectroscopic observations from the HREEL spectra, obtained after varying O₂ exposures of the K/graphite surface at 160 K are summarized in table 1.

Table 1. Observed loss peaks (K–O stretch) after oxygen adsorption on K/graphite at $T = 160$ K (vw—very weak, w—weak, b—broad).

Oxygen exposure (L)	Loss energy (meV)
0.2–1.2	31 (vw)
1.5–3.0	32 (w)
3.0–8.0	33
10–30	33–38 (b)

Although not shown in figure 1, all HREEL spectra were typically recorded to 300 meV loss energy. No additional peaks were observed at these higher loss energies. Specifically, no indications of O–O or C–O vibrations were found.

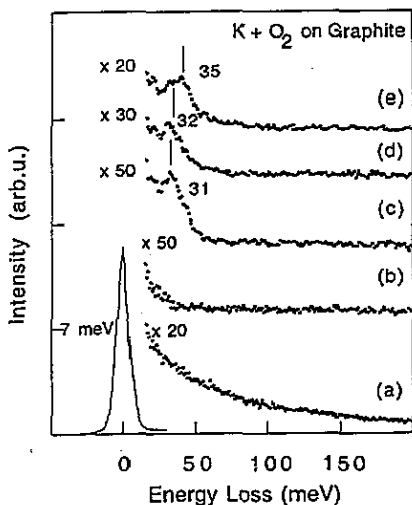


Figure 1. HREEL spectra for (a) clean graphite surface, (b) after 2.5 ML K deposition, and after (c) 3 L, (d) 8 L and (e) 25 L oxygen exposures on potassium precovered graphite at $T = 160$ K. Beam energy 15 eV, FWHM for the clean surface 7 meV, specular scattering.

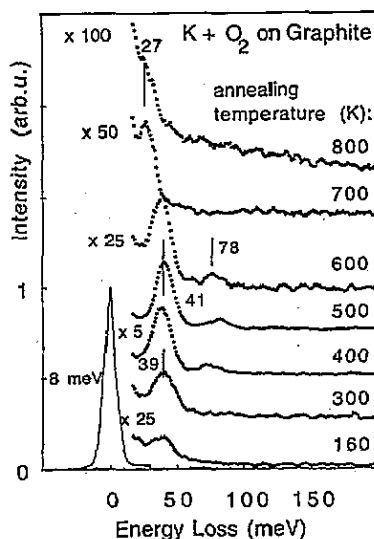


Figure 2. HREEL spectra after 25 L O₂ exposure of 2.5 ML potassium on graphite and after annealing the surface to the indicated temperatures in vacuum. All spectra are recorded at 160 K. Note scale factor variations. Experimental conditions as in figure 1.

Figure 2 shows HREEL spectra of the graphite-potassium-oxygen system after annealing (in vacuum) to the indicated temperatures. The initial system was prepared by deposition of potassium (~ 2.5 ML) and oxygen adsorption (25 L) at 160 K, i.e., it corresponds to spectrum (e) of figure 1. The annealing was done by applying a linear temperature ramp of 2.5 K s^{-1} on the sample. When the desired annealing temperature was reached, the substrate heating was abruptly stopped, and the sample was cooled again to 160 K as quickly as possible. All HREEL spectra were recorded at a temperature of 160 K. This annealing procedure was applied in order to permit direct comparison between the obtained HREEL spectra and the corresponding TDS spectra recorded at a heating of 2.5 K s^{-1} .

The intensity of the loss peak at 35 meV, obtained after 25 L O_2 exposure at 160 K, increases after annealing to 300 K and remains broad. The loss intensity increases further (more than five times) after annealing to 400 K, and the resulting strong, well defined peak is now centred at 39 meV and the double energy loss at ~ 80 meV (explicitly shown in figure 3, see below). Annealing to 500 K causes an additional energy shift to 41 meV, without any significant intensity changes. The energy shift is better revealed at the multiple losses (figure 3), also visible in the spectra. Further increase of the annealing temperature to 600 K results in a back shift to 39 meV accompanied by a substantial intensity drop.

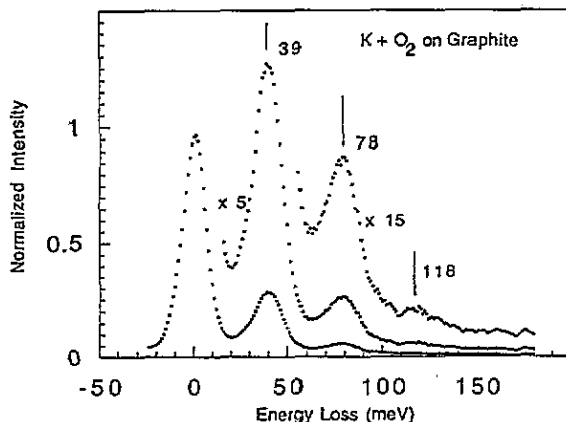


Figure 3. Electron energy loss spectrum of K_2O on graphite with multiple losses, characteristic for strong excitation of surface photons in ionic materials. Note the scale factors to obtain Poisson distribution of the multiple losses.

After heating to 700 K a new peak at 27 meV appears in the spectra. The 800 K spectrum displays no well resolved losses, but the continuum shape of the loss spectrum is clearly different from that of the clean graphite surface (compare with the spectrum in figure 1(a)), indicating that adsorbates are still present on the surface after annealing to 800 K. Final annealing to 1000 K gives back the spectrum of figure 1(a).

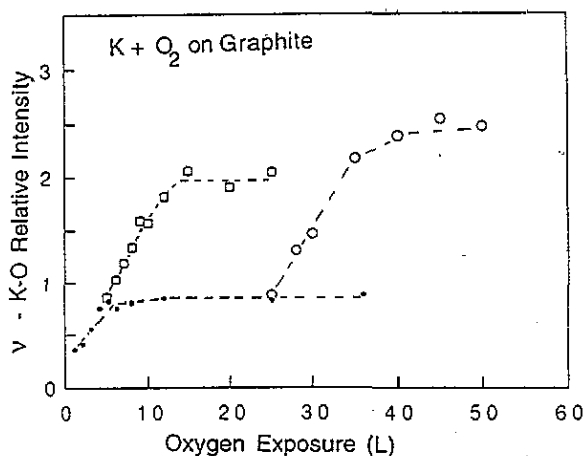
The spectroscopic observations from the annealing experiments obtained with two different initial oxygen coverages are summarized in table 2. The energies of the observed loss peaks are essentially the same for the two different oxygen coverages, while the temperature ranges in which they appear differ somewhat.

Multiple losses are clearly visible in the spectra. Figure 3 shows an HREEL spectrum obtained after 2.5 ML potassium coverage, and 25 L oxygen exposure at 160 K, followed by annealing to 400 K in vacuum. In this spectrum single (39 meV), double (78 meV), and triple (118 meV) losses are clearly observed. The intensities of the multiple losses follow the expected Poisson distribution [23].

Figure 4 shows the observed intensities of the K-O vibration (39 meV) as a function of oxygen exposure on K precovered graphite (2.5 ML), obtained by three different oxygen

Table 2. Observed loss peaks after annealing of the K-O co-adsorption layer to different temperatures (b—broad, s—strong, vs—very strong, w—weak, sh—shoulder, — absent).

Temperature (K)	Loss energy (meV)	
	Low oxygen coverages (1.0 L)	High oxygen coverages (25 L)
160	32	33–38 (b)
300	32–35 (b)	38 (s)
400	39 (s)	39 (vs)
500	41	42 (s)
600	27 (w)	40
700	~ 27 (sh)	27
800	—	~ 25 (sh)

**Figure 4.** Normalized K-O stretch loss intensity versus exposure from HREEL spectra recorded after different oxygen exposures at $T = 160$ K (solid circles) and at 400 K (open symbols). The predeposited potassium coverage was ~ 2.5 ML (see text).

exposure procedures. (i) The solid circles correspond to exposure at 160 K followed by annealing to 400 K in vacuum. The open symbols represent observed loss intensities after the K-covered graphite surface was initially exposed to 5 L (squares) and 25 L (circles), at 160 K, and then additionally exposed to oxygen at 400 K. (The broken curves are drawn to help the eye.) The indicated exposures are the total accumulated oxygen exposures, i.e. 5 and 25 L, plus the applied exposure at 400 K. It is evident that oxygen dosing at 400 K causes a further increase of the K-O loss intensity beyond the saturation value reached for exposures at 160 K.

Oxygen adsorption on the potassium covered graphite results in a substantial increase in the potassium desorption temperatures and in the number of thermodesorption states. The potassium TDS spectra ($m/e = 39$) shown in figure 5 were obtained after a K deposition of 2.5 ML at 160 K on graphite, and after the following pretreatments: (a) no O₂ exposure, (b) 25 L O₂ exposure at 160 K and subsequent annealing to 400 K in vacuum, and (c) after additional O₂ exposure (12 L) at 400 K. Spectra (b) and (c) represent TDS results from the experiments shown in figure 4. (For more extensive discussions on the TDS spectra see references [9] and [10]. Here they are primarily used to support the discussion of HREELS

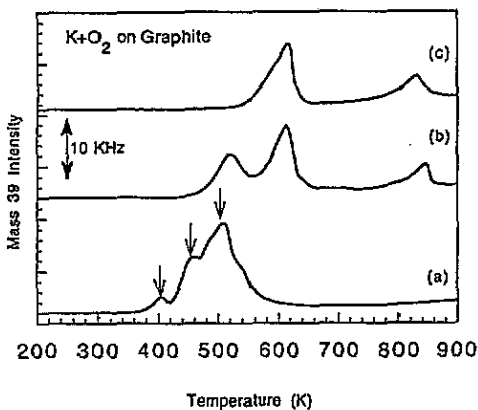


Figure 5. Thermal desorption spectra of potassium, $m/e = 39$. (a) After 2.5 ML K deposition at 160 K on graphite, (b) after 25 L oxygen exposure of the same predeposited K-coverage and after annealing the system at 400 K in UHV for 600 s, (c) the same experimental conditions as in (b) but after annealing the system at 600 K in oxygen (2×10^{-8} Torr for 10 min). The arrows mark desorption of intercalated potassium. For details see [21].

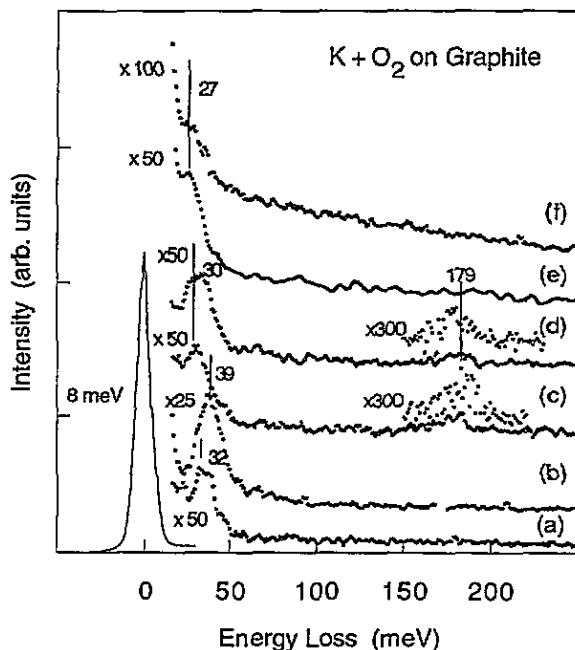


Figure 6. Electron energy loss spectra showing the effect of a large oxygen exposure at elevated temperature, and of subsequent annealing. All spectra were obtained with an initial K-deposition at 160 K. The following pretreatments preceded the spectra recording (at 160 K). (a) 1 L O_2 exposure at 160 K, (b) annealing of (a) to 400 K in vacuum, (c) an additional O_2 exposure of 10^4 L at 400 K, (d) annealing of (c) to 480 K, (e) and (f) additional annealing to 720 K and 800 K respectively.

data.)

For the case of clean potassium on graphite, the desorption starts at around room temperature (depending on the coverage), and is completed before ~ 600 K, exhibiting a broad feature with multiple peaks. These peaks are attributed [21] to a kinetic competition between intercalation of the adsorbed potassium into the graphite substrate, and thermal desorption. Low-temperature oxygen exposures split the potassium desorption into three separate peaks at ~ 500 , ~ 600 , and ~ 850 K. Annealing of the system in vacuum at 400 K did not induce any big changes in the K-desorption spectrum except for a small decrease in the amount of desorption in the peak at 500 K. The reduced K desorption in the 500 K peak is probably due to potassium desorption occurring while the system is kept at 400 K, before recording of the TDS spectra.

Oxygen exposures at 400 K result in complete removal of the 500 K potassium

desorption peak, redistributing its amount among the other two peaks at 600 and 850 K. Oxygen exposures of 5–7 L at 400 K are enough to remove the 500 K potassium desorption peak completely.

K desorption during annealing is likely to be responsible for the difference in the saturation HREEL-intensity values beyond ~30 L observed in the experiments presented in figure 4. In the data corresponding to an initial 5 L oxygen exposure at 160 K and subsequent exposures at 400 K, the indicated oxygen exposures are achieved after a longer accumulated annealing time at 400 K than for the data obtained after a 25 L oxygen exposure. More K desorption can thus have occurred in the 5 L case, resulting in a lower saturation value of the K–O loss at 39 meV.

Figure 6 presents the results of an experiment performed in order to explore the response of the system to very high oxygen exposures, which turned out to be vital for the interpretation (see below). Spectra (a) and (b) were recorded after an initial 1.0 L oxygen exposure of a potassium precovered surface (2.5 ML) at 160 K, and subsequent annealing to 400 K in vacuum respectively. Spectrum (c) was obtained after an additional 10⁴ L oxygen exposure (2×10^{-5} Torr \times 500 s) at 400 K. The latter spectrum is characterized by a relatively strong loss peak at 30 meV. A weaker peak at ~180 meV is also observed, indicating the presence of a species with O–O bonds on the surface. TDS examination of the system after 10⁴ L oxygen exposure at 400 K shows a small molecular oxygen desorption peak between 400 and 450 K. To check the origin of the 180 meV loss peak, spectrum (d) was recorded after annealing the sample to 480 K, beyond the observed molecular oxygen desorption peak. This treatment should also remove loosely bound contaminants, which are potentially adsorbed during the large oxygen exposure. The observed loss peak in the characteristic O–O stretching region (i.e. the peak at 180 meV) remains in the loss spectrum, showing that its origin is not related to the observed molecular oxygen desorption or to weakly bound contaminants. (The former probably originated from the manipulator parts, which is not unexpected after these large oxygen exposures.)

HREEL spectra obtained after further annealing of the system to 720 K and 800 K (spectra (e) and (f) respectively), show the same features as the corresponding spectra obtained for low oxygen exposures, i.e. a loss peak at 27 meV, which loses intensity upon annealing to 800 K.

The increase in the K–O vibration intensity upon O₂ exposure at 400 K, after initial exposure at 160 K, and the peak energy shift after a very large O₂ exposure of 10⁴ L at 400 K, are both indicative of changes in K–O stoichiometry, and structural changes. Potassium supply from the bulk (intercalated K) and oxygen addition both play a role in these changes. An additional piece of information for the interpretation (see below) was obtained as follows. A 2.5 ML potassium layer was exposed to 1.0 L of O₂ at 160 K, yielding a loss peak at 32 meV (similar to curve (d) in figure 1). 1 ML potassium was then deposited on top of this structure. The new, potassium-enriched layer showed an energy loss peak at 38 meV, i.e. essentially the same result as after annealing to 300–400 K in vacuum. This result demonstrates the equivalence of adding extra potassium to the oxygen-exposed K layer via deposition from the gas phase, and from the bulk by annealing. It also shows that the 38 meV loss corresponds to a more potassium rich structure than the 32 meV loss.

4. Discussion

The assignment of vibrational losses of surface KO_x complexes on metal and semiconductor surfaces has been and still is a subject of considerable interest. An unambiguous picture is

still not available and several conflicting interpretations exist [1, 3, 7]. An important guide in the assignment of various losses to KO_x structures (K_2O , K_2O_2 , KO_2) have been vibrational frequencies of matrix isolated KO_x [24–26]. One may, however, question such comparisons when extended complexes of KO_x are present, i.e. when more bulk-like than molecule-like structures are formed. The latter is likely even at submonolayer coverages on surfaces.

A complication in the interpretation of the presented data is that the vibrational loss appearing at different oxygen exposures or annealing temperatures, are likely to represent continuous transformations between different K:O stoichiometries, often containing mixtures of different KO_x complexes. This is particularly likely for unannealed structures.

The HREEL spectra show four different loss peaks which could possibly be associated with K–O stretch vibrations. (i) Initial oxygen exposures at 160 K result in a loss peak around 31 meV. (ii) Additional oxygen adsorption at 160 K and/or annealing in vacuum to 400 K produces a very strong peak at around 39 meV. (iii) Very large (10^4 L) oxygen exposures at 400 K result in a loss peak at 30 meV, which is accompanied by a peak at 180 meV, likely to be an O–O stretch vibration. (iv) Substrate annealing to 700 K results in a loss peak at 27 meV independent of the amount of initial oxygen adsorption.

In the following discussion we concentrate primarily on the interpretation of the two energy losses at around 31 meV (called the 31 meV peak) and at around 39 meV (called the 39 meV peak). Some guidance for the assignment of these losses might be obtained from the energies of matrix isolated K_2O , KO and KO_2 species. However, because of intermolecular interactions, the symmetry of a molecule is generally lower in the crystalline state than in the isolated state. Thus the vibrational spectra of crystals must be interpreted with caution, especially in the low-frequency region. In our case the surface KO_x complexes consist of several monomer units, as evident from the strong multiple losses (figure 3, see also [23]), i.e., they are more bulk-like than single monomers. It is well known and obvious from simple physical reasons that monomer frequencies generally differ from those of the corresponding bulk compounds.

A direct comparison between the observed loss peak at 39 meV and the vibrational energies in table 3 for matrix isolated species [27] might at a first glance suggest that this peak originates from a KO_2 -like surface oxide. Several observations contradict such an interpretation, however, and rather suggest that the 39 meV loss peak is due to K_2O and that instead the loss at 31 meV should be associated with KO_2 . Firstly, KO_2 is the most oxygen-rich structure and is also thermodynamically more stable than K_2O in oxygen excess. Thus one would expect high oxygen exposures and simultaneous annealing to be a likely condition for KO_2 formation. Exactly this experiment was performed (10^4 L O_2 at 400 K) and produces a loss peak at 30 meV (figure 6, spectrum (c)), which we thus tentatively attribute to the K–O stretch of clusters of KO_2 or possibly of K_2O_2 . The appearance of an O–O stretch in the latter spectrum supports this interpretation (O–O bonds exist in KO_2 and K_2O_2 but not in K_2O). Furthermore the fact that an oxygen exposed K layer at 160 K, with a vibrational loss at 32 meV, upon additional K deposition shifts the loss energy to 38 meV, contradicts the interpretation of the 38–39 meV peak as a KO_2 related loss.

Table 3. Vibrational energies of K–O stretching modes for matrix isolated potassium oxides.

Molecule	Vibrational energy (meV)
KO_2	38.2
KO	47.6
K_2O	62.2

The 39 meV peak is best developed after an oxygen exposure to saturation at 160 K, followed by annealing in vacuum at ~400 K. Under these conditions we know that some potassium is intercalated at 160 K [21], and moves to the surface upon heating. Thus we interpret the effect of annealing as an addition of potassium to the surface layer of KO_x. This is thus a potassium excess situation and is likely to produce the potassium-rich oxide K₂O.

Our assignment of the 39 meV loss peak to K₂O is further supported by recent results of Baddorf and Itchkawitz [28]. They studied the adsorption and reaction of O₂ on a single crystal potassium (110) surface using HREELS and XPS. The presented HREELS spectra show vibrational losses very similar to those observed in the present work. Initial oxygen adsorption at 88 K resulted in a single loss peak at 30 meV, while additional oxygen adsorption and/or annealing to 240 K produced a strong loss peak at 41 meV. Using the chemical shifts of O1s binding energies in XPS, these vibrational losses were attributed to dissociatively adsorbed oxygen (30 meV) and bulk K₂O oxide (41 meV). Together these observations provide strong support for the assignment of the loss peak at 39 meV to K₂O.

Yet another observation supports the K₂O interpretation of the 39 meV peak, and contradicts a KO₂ interpretation. In a previous study [10] the O₂ sticking on a potassium precovered surface was found to be consistent with a K:O ratio of 2:1 at saturation for the potassium coverages used in the present work, while KO₂ formation was incompatible with the sticking data.

In the analysis above we have been giving more weight to the spectra obtained under known oxygen and potassium excess conditions in combination with elevated temperatures (i.e. annealed structures), than to the low temperature spectra, where non-stoichiometric structures and/or mixtures of different structures, rich in defects, are likely to be present due to kinetic barriers.

The loss peak at 27 meV, appearing after annealing to 700 K, currently lacks an interpretation. The TDS spectra [9] show that this is a potassium deficient situation (K:O < 1:2). The surface complex associated with the 27 meV peak is a precursor to the CO₂ formation which occurs at around 800 K and is accompanied by desorption of the residual potassium. It would be tempting to associate the 27 meV loss with a surface carbonate species [29], but under no conditions have the spectra shown a C–O stretch frequency. This could of course be due to in-plane positioning of the C–O bond(s) but this is so far only speculation.

5. Summary and conclusions

HREEL spectra of mixed oxygen–potassium structures on graphite were recorded at 160 K. The evolution of these spectra upon oxygen exposure and annealing to different temperatures were followed by and correlated with TDS spectra of desorbing K and CO₂. A vibrational excitation of about 39 meV energy was fairly conclusively attributed to K₂O, in agreement with recent XPS and HREELS results [28] for single-crystal potassium, and XPS results for potassium interaction with solid oxygen [30]. Energy losses at about 31 meV and 180 meV were attributed to a more oxygen-rich structure, KO₂ or K₂O₂. A precursor to the final reaction product, CO₂, is formed after annealing to 700 K, with an energy loss of 27 meV. The composition of this reaction complex has not yet been identified.

Acknowledgments

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