XPS and XAS study of oxygen coadsorbed with a dispersed phase of K on graphite

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Abstract

The adsorption of O₂ onto a dispersed (low coverage) phase of K on graphite has been characterized by X-ray photoemission and X-ray absorption spectroscopy. We identify two oxygen adsorption phases before physisorbed oxygen appears. The first species dominates at low O₂ exposures whereas the second one, which is probably due to oxygen adsorbed in a superoxo-like configuration (O₂²⁻, δ ≤ 1), is dominant at higher oxygen coverage. As a function of increasing oxygen dose, we confirm that the charge, initially donated by the potassium adlayer to the graphite, is gradually withdrawn from the substrate. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The characterization of the adsorption of potassium on graphite and of oxygen coadsorbed with potassium on graphite have been the subject of many studies [1–10]. These systems have often been considered as model adsorption systems. In particular, they offer the opportunity to monitor in detail the electronic structure changes of the substrate and of the adsorbate upon the adsorption process.

The alkali/graphite system has been well characterized [1–6,11]. When potassium is dosed onto graphite a dispersed phase with a characteristic very large K–K distance (about 60 Å) is formed at low coverages [4,5]. In this alkali coverage range it is known that significant charge redistribution between the alkali and the graphite occurs [4–6]. Increasing the potassium coverage, the K–K spacing is continuously compressed until, for a coverage of 0.1 monolayer (ML) the dispersed potassium forms a (7 × 7) adsorption phase, with a K–K distance of about 14 Å [4]. Increasing the K coverage, (2 × 2) close-packed islands nucleate within the dispersed phase. At 0.25 ML a metallic (2 × 2) alkali overlayer covers the whole surface.

Study of the adsorption of oxygen on the alkali/graphite systems has indicated that the alkali-donated charge is withdrawn from the substrate, and a redistribution of charge within the adsorbed
overlayer occurs. An X-ray photoemission spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) study of oxygen dosed onto a (2 × 2) phase of potassium on graphite has shown that, depending on the oxygen coverage, atomic, peroxide (O\textsubscript{2}δ+, 1 < δ ≤ 2), and superoxide (O\textsubscript{2}δ−, δ ≤ 1) species are present on the surface [10]. Furthermore, a phase transformation from metal to insulator was observed within the potassium overlayer as the oxygen coverage increased. A previous electron energy loss spectroscopy (EELS) study of the coadsorption of oxygen with a dispersed potassium phase on graphite reported the presence of a superoxide species and of physisorbed molecular oxygen on the surface [2]. That study also found that the charge initially donated to the substrate is gradually withdrawn and redistributed within the adsorbate overlayer.

In this paper, we present an XPS and XAS study of oxygen adsorbed on a dispersed phase of potassium on graphite. As a function of increasing oxygen exposure, our data reveal the existence of two different oxygen adsorption phases before physisorbed oxygen appears on the surface. The characterization of the oxygen adsorption phase which dominates for low molecular coverage has not been conclusive due to the low intensity in the XAS spectra. The higher coverage phase could instead be identified as being due to a superoxide configuration of molecular oxygen (O\textsubscript{2}), in agreement with the earlier EELS work of Hock et al. [2]. A comparison of the XAS data of the superoxide phase with those of O\textsubscript{2}/(2 × 2)K/graphite [10] indicates that more charge is transferred to the oxygen 1π\textsubscript{g} orbital when oxygen is adsorbed onto a dispersed potassium phase on graphite. The withdrawal of charge from the substrate and its redistribution between potassium and oxygen gives clear spectral signatures.

2. Experimental

The O1s XPS data have been recorded at Uppsala University in an ultra high vacuum (UHV) system consisting of a preparation and an analysis chamber with base pressures of 1 × 10\textsuperscript{-10} and 8 × 10\textsuperscript{-11} Torr, respectively. The photoemission spectrometer consists of an AlK\textsubscript{α} (1486.7 eV) X-ray source with a water-cooled rotating anode and a monochromator on a Rowland circle arrangement. The photoelectrons are analyzed in a hemispherical electrostatic analyzer with 36 cm mean radius and are detected by a multichannel detector system. The angle of the incoming light and outgoing electrons in the presented experiments were both about 45° from the surface normal. The overall resolution in the present O1s XPS spectra was 0.5 eV. The calibration of the binding energies (referred to the Fermi level) was done by measuring the Fermi level region on a Pt crystal in electrical contact with the substrate.

The substrate, highly oriented pyrolytic graphite (HOPG), was mounted on a copper block in direct contact with the cold finger of a cryostat. This allowed us to maintain a sample temperature of 25 K. All data shown in this paper were taken at 25 K. The sample was cleaned by resistive heating, running a high current through the crystal perpendicular to the graphite planes. The temperature was measured by a chromel–alumel thermocouple fixed to the front of the sample holder.

Potassium from a well-outgassed SAES getter source was evaporated onto the graphite at a temperature of about 90 K in order to allow for sufficient adatom mobility [1]. After evaporation the sample was quickly cooled down to liquid He temperature in order to avoid intercalation of K into the substrate. The potassium dose was calibrated using the line profiles of the K 3p and C1s lines [6]. The oxygen coverages reported here are denoted by exposure in Langmuir (L) (1 L = 1 × 10\textsuperscript{-6} Torr s).

The C1s XPS and the XAS experiments were performed at beamline 22 at the MAX synchrotron radiation facility in Lund [12]. The beamline consists of a planar grating monochromator of modified SX-700 type and a hemispherical electron energy analyzer of modified Scienta type with a 20 cm mean radius [12]. The resolution of the C1s line, taken with a photon energy of 350 eV, was about 0.3 eV. The photoemission data were taken at normal emission of the photoelectrons. The photon energy resolution in the XAS measurements was 0.5 eV. For these data, the secondary electrons were collected by a pulse-counting
channeltron detector in partial yield mode, with a threshold selected to emphasise the oxygen Auger signal.

3. Results and discussion

In Fig. 1 we present the XPS spectra for different oxygen doses on a dispersed phase of potassium adsorbed on graphite together with the corresponding data for oxygen adsorbed on a (2 × 2)K/graphite substrate [10]. For low coverages, two O 1s features which indicate the existence of two different oxygen species adsorbed on the dispersed K/graphite substrate are clearly seen. For the lowest oxygen coverage (0.05 L) the higher-intensity peak is centred at about 531.4 eV, and the lower-intensity peak, at about 534.2 eV. When increasing the oxygen exposure (0.1 L), the peak at higher binding energy increases in intensity indicating an increased coverage of the corresponding oxygen phase. We define saturation coverage as the coverage of oxygen which gives rise to these two adsorption phases before the condensed or physisorbed oxygen appears, i.e., 0.1 L. The same convention is used when we compare our data with the previous study of oxygen adsorbed on a (2 × 2) phase of K/graphite [10], for which the saturation coverage corresponds to an oxygen dose of 5 L. Fig. 1 shows, for oxygen on dispersed K/graphite, that higher oxygen exposure (1 L), produces condensed molecular oxygen. This is indicated by the doublet at a binding energy (538 eV) and with a line profile previously found for physisorbed oxygen on clean graphite [13,14].

The peak centred at 531.4 eV represents the phase which is dominant on the surface for low oxygen coverage. In the same figure we show a comparison between the O 1s spectra on dispersed K/graphite with the data for oxygen adsorbed on the (2 × 2)K/graphite system. The low coverage oxygen phase for the latter system has been identified as a peroxide species (O$_2^-$) [10]. As far as the identification of the dominant species at low coverages for the dispersed K/graphite substrate is concerned, it is tempting to assign it to a peroxide species, since the O 1s binding energy coincides with that of the low coverage oxygen phase on the (2 × 2)K/graphite [8]. The similarity of the O 1s binding energies is not conclusive, however, since it results from both initial and final state effects and the screening of the core hole could be significantly different in the two cases. Moreover, one should keep in mind that for a potassium-covered surface the dissociation barrier for O$_2$ is much smaller than on clean graphite as shown by in a theoretical study [15]. Unfortunately, it is impossible to use X-ray absorption to identify this low coverage phase of O$_2$ on dispersed K/graphite because the intensity of the oxygen signal is too low.

Our data therefore clearly indicate the existence of two different adsorption species prior to the appearance of the condensed (or physisorbed) oxygen (Fig. 1). This is in contradiction to the previous EELS work, where only superoxide and physisorbed oxygen were reported [2]. It is likely that the absence of the first oxygen phase in this EELS study is due to the low sensitivity of this technique for very low molecular coverages.

![Fig. 1. Comparison between O 1s photoemission spectra for O$_2$/dispersed K/graphite (with the related oxygen exposures) and O$_2$/(2 × 2)K/graphite [10].](image-url)
From Fig. 1 it is clear that the O 1s XP binding energies of the saturation phases for the two compared systems are slightly different. The molecular phase which dominates the XP spectrum for higher oxygen coverage for O$_2$/dispersed K/graphite is characterized by a spectral feature at about 534.2 eV. The identification of this phase is aided by examining the XAS data for the saturation phase (0.1 L) in Fig. 2. The normal incidence spectrum is very noisy due to the low coverage and low intensity that we obtained for this experimental set-up. The spectrum is a result of spectra taken after different preparations in order to avoid contamination of the very reactive surface. For this reason we do not attempt to interpret the small structures in the data, such as the peak at about 532.5 eV, but merely note the overall trends (reduction of the $\pi^*$ and $\sigma^*$ intensity for normal incidence) which are also reflected in the data for the (2 x 2) overlayer. In the spectrum taken at grazing incidence we can see three distinct features centred at 529.2, 531.5 and 534.3 eV respectively. For a comparison we have plotted in the same figure the O 1s XAS data corresponding to a saturation coverage of oxygen on a (2 x 2) potassium layer on graphite [10]. For the latter system, superoxo-configuration (O$_2^-$) has been identified for the oxygen saturation coverage by means of XPS, ultra violet photoemission spectroscopy (UPS), XAS and autoionization data [10]. XAS data for the present system taken at grazing incidence reveal strong features at 528.9 eV and at about 534.6 eV which can related to the so-called $\pi^*$- and $\sigma^*$-resonances of the oxygen molecule. These resonances in the XA spectrum are due to the excitation of a 1s electron to the partially-empty molecular 1$\pi_g$ and to the empty 3$\sigma_u$ molecular orbitals, respectively. It has been shown [10,16,17] that the energy of the $\sigma^*$-resonance is related to the molecular electronic configuration, i.e., superoxide (O$_2^{2-}$, $\delta \leq 1$) or peroxide (O$_2^{2+}$, 1 $< \delta \leq 2$) oxygen species. Charge transfer to the partially-unoccupied oxygen antibonding 1$\pi_g$ orbital produces a lengthening of the molecular bond, which is reflected in the energy of the XA $\sigma^*$-resonance. Furthermore, the increased population of the 1$\pi_g$ orbital is confirmed by the decreased intensity of the $\pi^*$ resonance in the XA spectrum. The XAS data in Fig. 2 show less intensity of the $\pi^*$ resonance and a shift to lower photon energy of the $\sigma^*$ resonance indicating a greater charge transfer to the molecules for O$_2$/dispersed K/graphite in comparison with the O$_2$/ (2 x 2)K/graphite [10]. From the $\sigma^*$ resonance position it is possible to conclude that the oxygen molecule adsorbs in a superoxo-like configuration, in agreement with calculations [13] and EELS experiments [2] for O$_2$/dispersed K/graphite.

C 1s XP data (Fig. 3) also reveal a higher degree of the oxygen-induced charge withdrawal from the graphite substrate for the dispersed phase relative to the (2 x 2)K/graphite, confirming the XAS results. The C 1s line of clean graphite, characterized by a binding energy of 284.4 eV with a full width at half maximum (fwhm) of about 0.4 eV, becomes broader and shifts to higher binding energy upon the adsorption of the potassium overlayer in agreement with EELS [4,5] and more recent XPS studies [6]. This is due to the charge transfer from the alkali adatoms to the substrate and the shift in the C 1s line clearly matches that of the valence
band, as it can be simply described by the so-called rigid band model [6]. The coadsorption of oxygen, on the other hand, results in a shift to lower binding energy and, at increasing oxygen coverage, a decreasing fwhm which we interpret as indicating that the substrate is progressively approaching the charge state of clean graphite. These effects have already been observed for oxygen adsorbed on the (2 × 2)K/graphite substrate [10], but the recovering of the initial fwhm for the C1s line and the shift to lower binding energy (only 0.1 eV higher binding energy with respect to the clean graphite) confirm that the coadsorption of oxygen withdraws more charge initially donated to the substrate in the dispersed potassium phase than in the (2 × 2) phase. This is a striking confirmation of the higher charge transfer from the potassium towards the oxygen molecules for the dispersed K/graphite system, as deduced from the oxygen core level spectra. We therefore conclude that the interaction between the oxygen molecules and the dispersed alkali adatoms is stronger than in the case of the metallic (2 × 2) K overlayer. We speculate that oxygen and potassium build strong ionic K–O complexes. This is likely related to the fact that in this system, the potassium adatoms are further away from each other whereas in the (2 × 2) phase the alkali atoms form a more cohesive metallic overlayer.

4. Conclusions

The adsorption of oxygen on a dispersed phase of potassium on graphite has been studied by XPS and XAS. The data confirm that the charge initially donated by the potassium adatoms to the graphite is almost completely withdrawn and redistributed to the oxygen in agreement with previous studies [2]. Three different adsorption phases have been observed for the molecular overlayer. Our XPS data indicate that physisorbed oxygen appears on the surface only after saturation of the surface with two other phases. The identification of the oxygen phase which is dominant for low coverage has not been possible in this study but for the higher coverage (up to a oxygen surface saturation dose) the phase has been identified as due to a superoxo-like configuration (O2−) of the oxygen molecule, which agrees with previous EELS study [2]. A comparison with the data for O2/(2 × 2)K/graphite reveals that more charge is transferred to the adsorbed oxygen molecules in the higher coverage phase (0.1 L) for dispersed K/graphite substrate.

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References