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PHOTOELECTRON SPECTROSCOPIC STUDY OF SO_2 ADSORPTION ON MgO*

W. Siekhaus, A. B. Harker, N. L. Craig and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract:

SO_4^{2-} and SO_3 were identified by XPS-ESCA as the main reaction products formed by SO_2 adsorbed at STP on polycrystalline MgO and adsorbed under UHV conditions on the 100 face of single crystal MgO.

I. Introduction

A better understanding of the surface interactions of sulfur dioxide with metal oxides is of importance both as a problem in surface chemistry and as a problem intimately connected with the chemistry of aerosols in atmospheric pollution. Nevertheless, relatively little is known about such systems; in particular, there is a lack of information about the nature of the chemical species produced by SO_2 on metal oxide surfaces. For example, Schoonheydt and Lunsford[1] performed an infrared spectroscopic investigation of the adsorption and reactions of SO_2 on polycrystalline activated MgO. At room temperature no assignment to specific sulfur species was made by these authors. After heating in vacuum at 300°C the adsorbed species were found to transform to two forms of SO_3^{2-}.

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The technique of x-ray photoelectron spectroscopy (XPS) has been successfully employed recently in this laboratory to study the interaction of SO_2 with a clean Pt surface[2]. Because of this demonstrated usefulness of the XPS technique for surface chemistry, we have chosen this method to study the adsorption and desorption of sulfur species in the MgO-SO_2 system. In this paper we describe studies of the 100 face of single crystal MgO with monolayer coverage, and of polycrystalline MgO Powder with heavier SO_2 coverage.

II. Experimental

The photoelectron measurements were performed with an AEI ES200 spectrometer operating at a pressure of $<10^{-9}$ torr. The spectrometer is equipped with an U.H.V. sample holder heatable to 1200°C by electron bombardment. The MgO (100) face of the single crystal sample was prepared by cleaving a larger single crystal and mounting the crystal on a platinum plate attached to the sample holder. The crystal was heated in the spectrometer vacuum at a temperature of 800°C for about 45 minutes, in an atmosphere of $\approx 1 \times 10^{-6}$ torr O_2, until no trace of carbon was detectable (by ESCA) on the sample surface. Thereafter the MgO crystal surface was allowed to cool, and exposed to 3×10^{-6} torr-sec of SO_2 at room temperature; the chamber pressure during the subsequent measurement was below 1×10^{-9} torr.

The studies of sulfur species produced in the adsorption of SO_2 on polycrystalline MgO were done on degassed and dehydrated powder. The MgO powder was heated in vacuo at temperatures of 400 to 500°C after which an atmosphere of SO_2 was introduced. The exposure times usually used were

about 10 minutes. After the exposure to the adsorbate the samples were prepared by pressing the powder into the openings of a fine metallic mesh. The samples were then transferred to the spectrometer with only a brief exposure to air.

All binding energies quoted in this paper have been corrected for charging effects in such a way that direct comparison with reported binding energies of sulfur compounds is possible. These values are referred to a hydrocarbon C 1s binding energy of 285.0 eV.

II. Results

In Figure 1 the sulfur S(2p) and oxygen O(1s) spectra are shown for the MgO single crystal exposed to SO_2 at room temperature. In the sulfur spectrum two distinct peaks are seen at binding energies of 169.8 and 168.3 eV. The peak at 169.8 eV can be assigned immediately to the sulfur of sulfate ion. The peak at 168.3 eV corresponds to a lower oxidation state, such as S^{4+}. There is at best only an indication of a sulfide peak at a binding energy around 162 eV.

The oxygen 1s spectrum shows a dominant peak at a binding energy of 530.8 eV, corresponding to the oxide oxygen and a small peak at a higher binding energy of 532.8 eV. The O(1s) photoelectron line obtained with the same crystal before SO_2 was adsorbed is also shown in Figure 1. It is clear that the 532.8 eV peak arises from the adsorbed sulfate and/or sulfite. The binding energy of the $SO_4^{=}$ oxygen is known to be about 532.5 eV[4], which agrees with our value within experimental errors.

The MgO oxygen 1s peak intensity is not appreciably attenuated by the surface sulfate + sulfite layer, through which the O 1s electrons are penetrating. This information together with the ratio of the (sulfate +

sulfite) -oxygen photoelectron peak intensity to the oxide-oxygen peak intensity (≈0.1) can in principle be used to obtain an estimate of the thickness of the adsorbed layer. This is unfortunately complicated by the fact that the mean escape depth of photoelectrons of about 1000 eV is not known for MgO. The mean escape depth of 1400 eV electrons in Al_2O_3 has been recently determined to be 13 Å[3]. If a similar escape depth applies in the case of MgO, the sulfate + sulfite oxygen electrons originate from a depth of about one tenth of the mean escape depth of the oxide-oxygen electrons, or about 1.3 Å. This indicates that in the MgO single crystal case we are dealing with true surface species.

The sulfur 2p spectra of the MgO powder exposed to SO_2 are shown in Figure 2. The spectrum in the uppermost part of the Figure was measured at room temperature immediately after the insertion of the sample into the spectrometer. The other spectra in Figure 2 are of the same sample measured subsequently at elevated temperatures of 100, 200 and 300°C. Three sulfur binding energies are clearly recognizable: 171.0, 169.7 and 167.9 eV. The peak at 169.7 eV is assigned to the sulfate sulfur. Its intensity remains unchanged upon heating. In contrast, the intensities of the other two peaks decrease markedly with increasing temperature. They represent loosely bound physisorbed surface species. The binding energy value of 168.3 eV has been reported for (presumably) frozen SO_2[4]. This value is in agreement with the desorbable peak at 167.9 eV. The second desorbable peak at 171.0 eV is at a higher binding energy than the sulfate peak and hence has a more positive net charge. This peak most likely corresponds to SO_3. The expected position of the sulfite sulfur is also indicated in the figure. No prominent sulfite peak is visible, although its presence in the spectra taken at

200 and 300°C can not be excluded with certainty.

With this information we can definitely assign the peak at 168.3 eV binding energy in the single crystal experiment to SO_2. The expected SO_3 position is indicated in Figure 1. The statistics of the measured points are not adequate, however, to establish the presence of SO_3 on the MgO single crystal surface.

III. Discussion

The dominant species produced in the surface reactions of SO_2 with MgO are the sulfate ions and loosely bound SO_3, in addition to physisorbed SO_2. Trace amounts of sulfide may exist in both single crystal and powdered oxide cases. At elevated temperatures small amounts of sulfite ions may also be present.

A comparison of the results obtained from the single crystal with monolayer coverage and the MgO powder with a much heavier coverage, shows that in both cases the situation is qualitatively similar. The most obvious difference is in the relative concentration of the surface SO_2 which is considerably higher in the case of high coverage. It is therefore likely that the first layer (or layers) of SO_2 interacts with MgO producing the surface sulfate onto which the subsequent SO_2 layers are deposited.

The single crystal experiment, in particular, clearly shows that sulfite and sulfide do not play an important role in the conversion of SO_2 to $SO_4^=$. Therefore mechanisms involving sulfite formation with its subsequent disproportionation into sulfate and sulfide ($4MgSO_3 \rightarrow 3MgSO + MgS$) are not relevant for the surface reactions at low temperatures. If

this mechanism were indeed taking place, the sulfate to sulfide peak ratio should be 3:1, which is obviously not the case. (The expected sulfide peak height is indicated in Figures 1 and 2.) Therefore we must conclude that the conversion of SO_2 to SO_4^{2-} occurs primarily by engaging the MgO lattice oxygen, possibly through SO_3, produced by surface oxidation of SO_2, as an intermediary state.

At elevated temperatures the main observation is the fairly rapid desorption of SO_2 and SO_3. At 300°C there is an indication of the appearance of the sulfite peak (Fig. 2). This is in agreement with the findings of Schoonheydt and Lunsford[1].

Conclusions

The adsorption of SO_2 on MgO at room temperature results in the formation of $SO_4^{=}$ ions and loosely bound SO_3. Only a trace of sulfide is formed, and virtually no sulfite was detected. The SO_2 molecules are physisorbed at the surface. At elevated temperatures desorption of SO_2 and SO_3 was observed.

Acknowledgment

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References

1. R. A. Schoonheydt and J. H. Lunsford, J. Catal. 26, 261 (1972)
2. W. Siekhaus and T. Novakov, submitted to Surface Sci. (1973)
3. M. Klasson, J. Hedman, A. Berndtsson, R. Nilsson, C. Nordling and P. Melnik, Physica Scripta 5, 93 (1973)
4. B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling and K. Siegbahn, Physica Scripta 1, 286 (1970)

Figure Captions

Figure 1. Sulfur 2p and oxygen 1s x-ray photoelectron spectra of the (100) face of MgO single crystal exposed to SO_2 at room temperature. Identified sulfur species are $SO_4^=$ and SO_2. The expected positions of $SO_3^=$ and $S^=$ are indicated. The large oxygen peak is that of MgO oxygen while the smaller one is associated wtih $SO_4^=$ and SO_2 oxygens. The oxygen 1s line shape for the MgO crystal prior to SO_2 exposure is shown by smaller dots.

Figure 2. Sulfur 2p spectra of polycrystalline MgO exposed to SO_2 at STP. The uppermost spectrum was taken at room temperature immediately after insertion of the sample in the spectrometer. The other spectra were obtained with the same sample at elevated temperatures. The $SO_4^=$ peak stays constant upon heating while the SO_2 and SO_3 peaks decrease with temperature. The expected positions of $SO_3^=$ and $S^=$ are indicated.

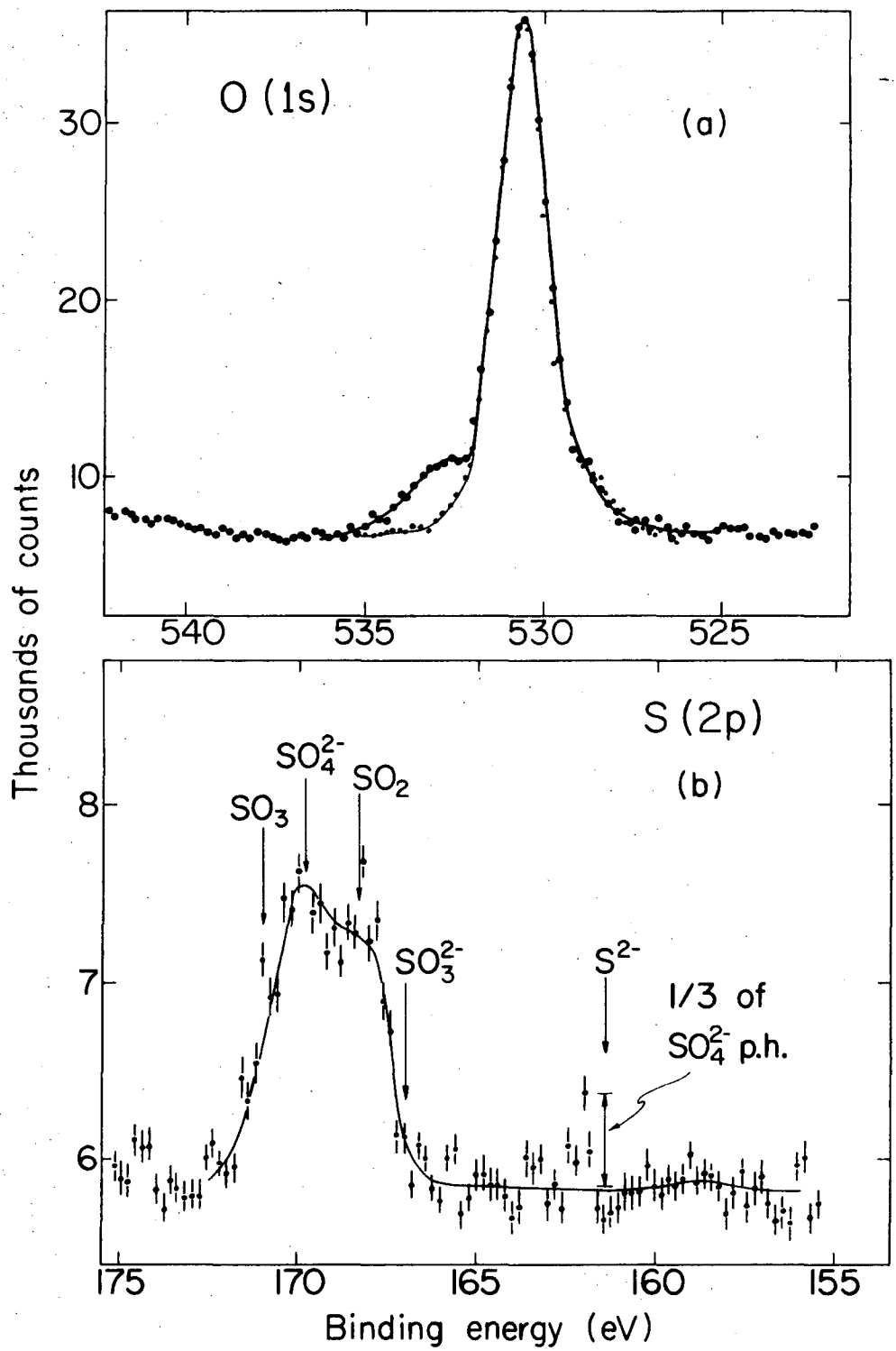

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Fig. 1

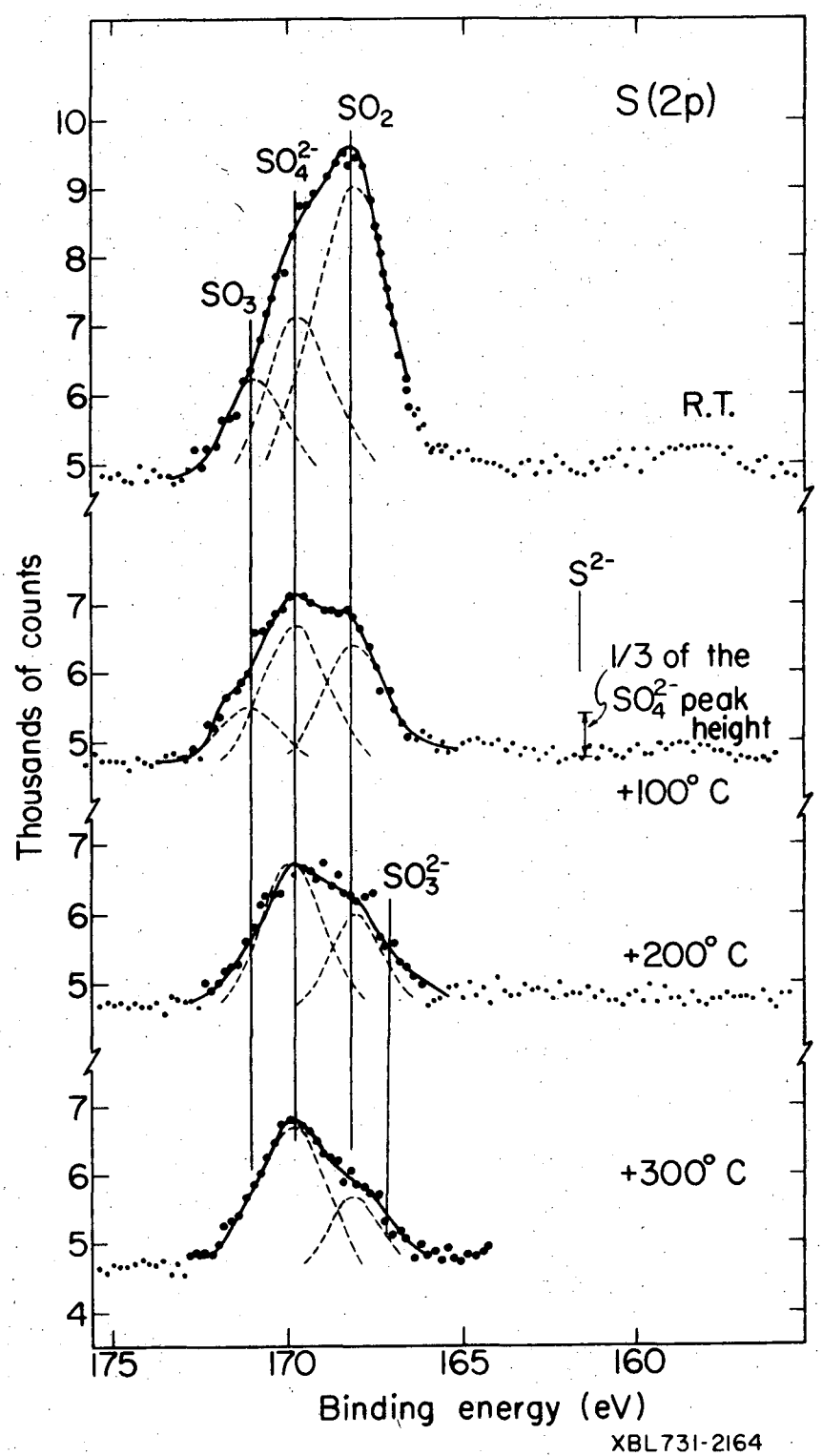
S(2p)
SO2
SO4 2-
SO3
R.T.
S2-
1/3 of the
SO4 2- peak
height
+100° C
SO3 2-
+200° C
+300° C
Thousands of counts
Binding energy (eV)
175
170
165
160
XBL731-2164

Fig. 2

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