Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 89, Number 2, April 1980, pp. 145-151.

X-ray photoelectron spectra and Auger studies of the surface oxidation of cobalt[†]

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MS received 7 February 1980

Abstract. Surface oxidation of Co has been investigated at different temperatures in the 300–600 K range at oxygen exposures upto 10^6 L by XPES and AES techniques. In the XPES, both the valence band and core level bands have been employed to monitor the oxidation while in the AES, metal Auger intensity ratios as well as $O(KLL)/Co(L_{23}M_{45}M_{45})$ ratios have been examined. Only CoO is formed on the surface at high oxygen exposures at and above 500 K.

Keywords. X-ray photoelectron spectroscopy; Auger electron spectroscopy; surface oxidation; Auger ratio; oxidation state.

1. Introduction

X-ray photoelectron spectra (XPES) of CoO and Co_3O_4 have shown the characteristic features of these oxides in the valence bands and core levels (Rao *et al* 1979; Haber and Ungier 1977, Oku and Hirokawa 1976; Bonnelle *et al* 1975). Thus, the $2p_{3/2}$ binding energy of Co^{2+} in CoO is 780·5 eV while that of Co^{3+} in Co_3O_4 is 779·5 eV. CoO shows a strong satellite around 6·3 eV after the $2p_{3/2}$ band whereas in Co_3O_4 a weak satellite is observed around 9 eV. Surface oxidation of Co has been investigated by Moyes and Roberts (1977), Chuang *et al* (1976) and Brundle *et al* (1976) mainly to determine the nature of the oxide formed on the surface at 300 K. We have carried out a systematic study of the surface oxidation of cobalt at 300, 400, 500 and 600 K by employing the valence band and core levels of Co as well as the oxygen (1s) band in the x-ray photoelectron spectra. We have also followed the surface oxidation by a novel technique recently proposed by Rao *et al* (1980) wherein the cobalt Auger line intensity ratios are employed to monitor the oxidation.

[†] Communication No. 62 from the Solid State and Structural Chemistry Unit.

2. Experimental methods

CoO, Co_3O_4 and $SrCoO_{2\cdot5}$ were prepared by standard methods as reported earlier (Rao *et al* 1979). X-ray photoelectron and Auger electron spectra were recorded using an ESCA-3 Mark II spectrometer of V. G. Scientific Limited, U. K. Pure (99·99%) polycrystalline Co plate has been used for surface oxidation studies. Co metal surface was cleaned by etching it with an Ar ion beam. Surface cleanliness was tested in terms of $Co(2p_{3/2})/O\,(1s)$ intensity ratio which was better than 100. The spectrometer was calibrated with reference to the binding energy of $Au(4f_{7/2})$ line at 83·7 eV. Oxdidation of Co has been carried out at 300, 400, 500 and 600 K by exposing it to oxygen gas in the preparation chamber. The oxygen exposure is expressed in Langmuir ($1L = 10^{-6}$ torr. sec.). Peak-to-peak height has been taken to be proportional to the intensity of Auger line in $N'(E)$ vs E spectrum.

3. Results and discussion

3.1. *XPES studies*

The variation of the valence band as a function of oxygen exposure at 600 K is shown in figure 1a. The temperature variation of the valence band of Co at an oxygen exposure of 10^4 L is shown in figure 1b. The temperature variation of

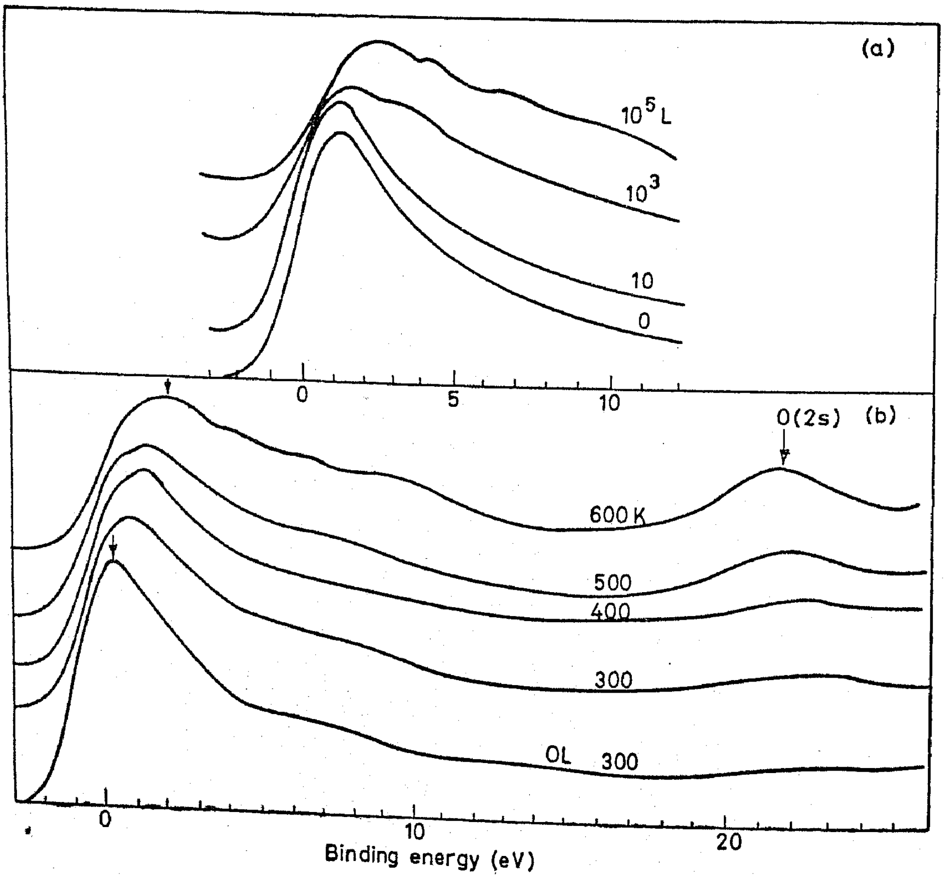

Figure 1. Valence band regions in the Al K_α x-ray photoelectron spectra of clean cobalt and cobalt subjected to different oxygen exposures at different temperatures. (a) change in valence band as a function of oxygen exposure at 600 K; (b) temperature variation of valence band at 10^4 L exposure.

the Co($2p_{3/2}$) band at 10^4 L oxygen exposure is shown in figure 2. A plot of the oxygen uptake as a function of oxygen exposure is shown in figure 3 in terms of the ratio of intensity of O (1s) to Co($2p_{3/2}$) peaks. From figure 3, we see that the oxygen uptake is less significant upto 50 L at all the temperature studied. From figure 1 we see that at lower temperatures, the changes in the valence band are not significant. At 600 K and 10^4 L, however, the valence band nearly resembles that of CoO (Rao *et al* 1979, Chuang *et al* 1976). We can readily see (from figure 1a) the continuous development of the CoO valence band from Co with a gradual shift of the peak position from 0·8 eV to 1·9 eV with reference to E_F. We also find that the intensity of the valence band decreases with the oxygen exposure.

An examination of the variation of Co($2p_{3/2}$) band with temperature at 10^4 L oxygen exposure confirms our observations based on the changes in the valence band. At 300 and 400 K, only Co metal peak is predominant and there are no significant peaks due to Co^{2+} or Co^{3+}. At 400 K, a small satellite similar to that of CoO becomes apparent; at 500 K, the characteristic satellite akin to that of CoO becomes evident in addition to the Co^{2+} peak at 780·5 eV. At 600 K, the $2p$ band fully resembles that of CoO.

Temperature variation of the O (1s) peak at 10^4 L oxygen exposure is shown in figure 4. There are clearly two peaks, one at 529·5 eV due to cobalt oxides (CoO or/and Co_3O_4) and another at 530·8 eV which was attributed to Co(OH_2) by earlier workers (Brundle *et al* 1976; Moyes and Roberts 1977). At 600 K there is only a

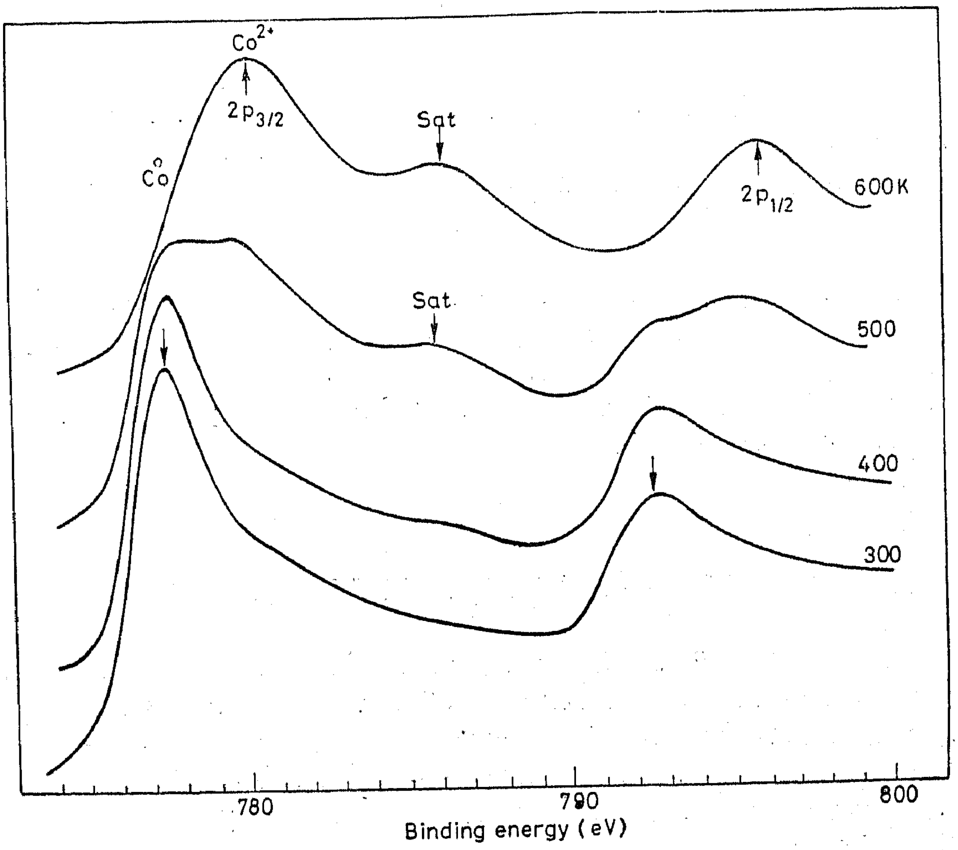

Figure 2. $2p_{3/2,\ 1/2}$ bands of Co subjected to 10^4 L oxygen exposure at different temperatures (sat = satellite).

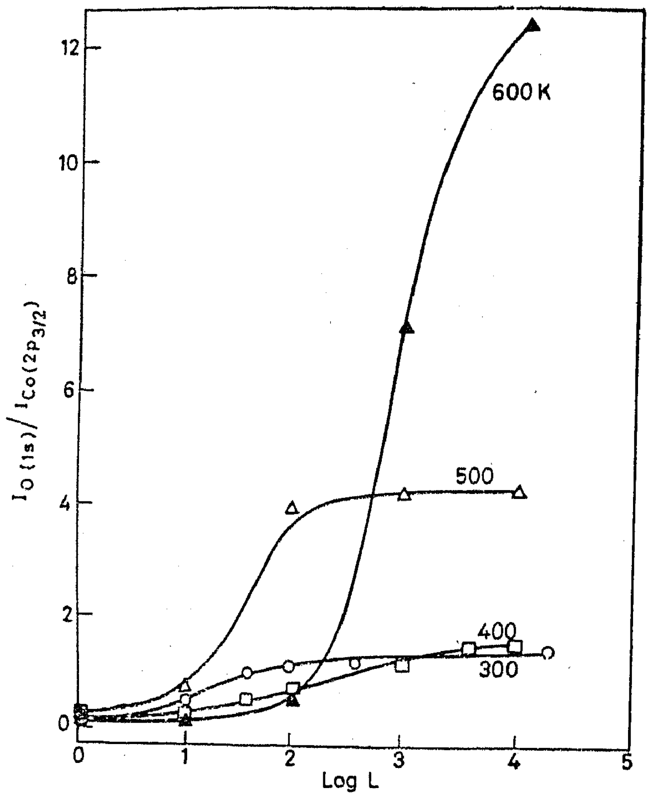

Figure 3. Dependence of the relative oxygen pick-up in terms of O(1s)/Co($2p_{3/2}$) peak intensity ratio on the oxygen exposure.

single O (1s) peak at 529·5 eV corresponding to CoO as we would expect from our studies of the valence and Co($2p_{3/2}$) bands; accordingly, the half-width of the O (1s) peak at this temperature is only 2·1 eV (identifiable with a single oxide). The half-widths of O(1s) peaks at 300 K as well as at 400 K are, however, 3·9 eV while it is 2·7 eV at 500 K indicating thereby the presence of more than one species. Since we have used dry oxygen in our studies and the relative pick-up of both the peaks is similar at 300 K and 400 K upto oxygen exposures of 10^6 L, it is possible that the O(1s) peak at 530·8 eV at lower temperatures arises from a disordered oxide layer (similar to CoO) rather than $Co(OH)_2$. The peak at 529·5 eV is certainly due to ordered CoO.

3.2. *AES studies*

The $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ and $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{45}$ Auger line intensity ratios of cobalt in Co metal, CoO, Co_3O_4 and $SrCoO_{2.5}$ are plotted against the formal oxidation state of Co in figure 5. In accordance with our earlier Auger study of the surface oxidation states and oxidation of transition metals (Rao *et al* 1980), the Auger line intensity ratios of Co decrease with the increase in the oxidation state of the metal. We thus see that different oxidation states of cobalt are readily distinguished from the Auger line intensity ratios thereby providing a means of studying surface oxidation.

In figure 6, the $I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{23})$ and $I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{45})$ Auger intensity ratios are plotted against oxygen exposure at 500 and 600 K. The

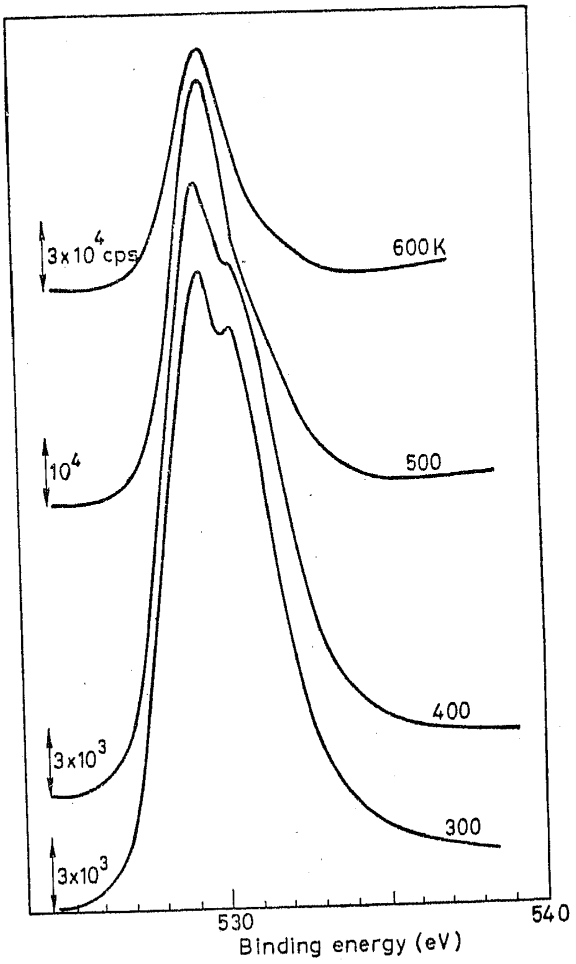

Figure 4. O(ls) band during the surface oxidation of Co (at 10^4 L) at different temperatures.

continuous decrease in $I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{23})$ from 2·50 to 1·92 at 600 K clearly shows that the metal goes from Co to CoO (also see figure 5). $I(L_{23}M_{45}M_{45})/I(L_{23}M_{23}M_{45})$ also shows a similar behaviour. At 500 K, the ratios do not approach the values corresponding to CoO indicating that the metal is still present at the surface under these conditions. This was also evident from the presence of the Co^0 $(2p_{3/2})$ peak at 500 K in figure 2. At 300 and 400 K, the $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ Auger intensity ratio decreases from 2·5 (pure Co value) to 2·35 and 2·30 respectively. Such a small change in the Auger ratio is an indication of chemisorption of oxygen on the surface; this is also clear from the valence and $(2p_{3/2,1/2})$ bands shown in figures 1 and 2 as also from the oxygen pick-up curves in figure 3. The large decrease of the Auger intensity ratios at 500 and 600 K indicates the large number of oxide layers formed on the surface. The above conclusions also find support from the O(KLL)/Co(LVV) Auger intensity ratios plotted in figure 7.

From figures 3 and 7, we are able to distinguish three regions of oxidation (Rao *et al* 1980, Srinivasan *et al* 1979).

(i) a chemisorption region below 50 L where oxygen pick-up is low; (ii) rapid oxygen pick-up between 50–10^4 L and (iii) saturation of oxygen pick-up beyond

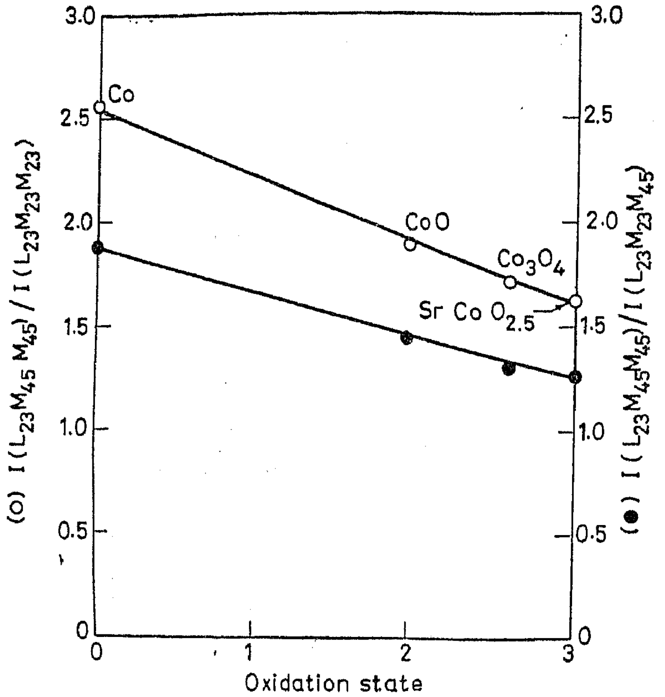

Figure 5. Plots of $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ and $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{45}$ metal Auger intensity ratios against oxidation state of Co.

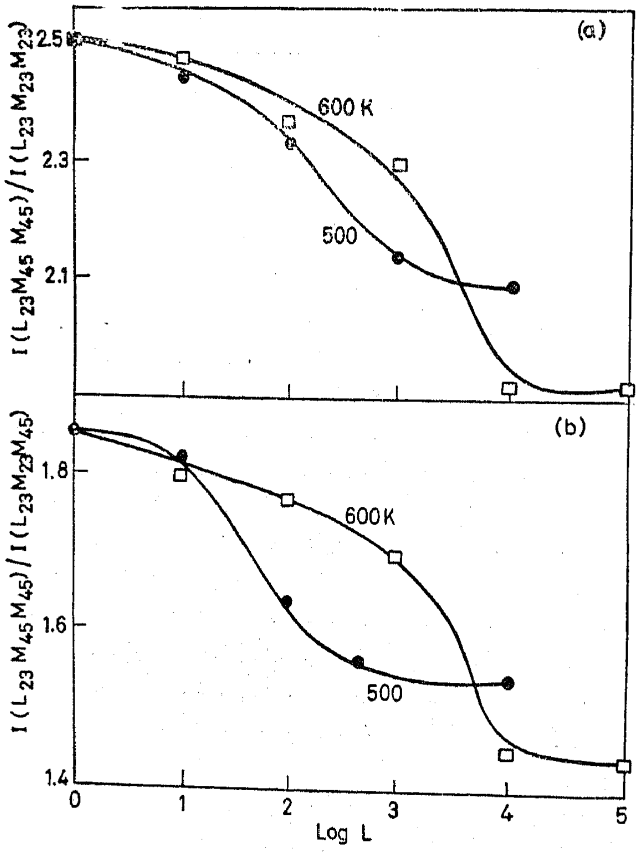

Figure 6. Plots of (a) $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{23}$ and, (b) $L_{23}M_{45}M_{45}/L_{23}M_{23}M_{45}$ cobalt Auger intensity ratios against log *L* at 500 and 600 K.

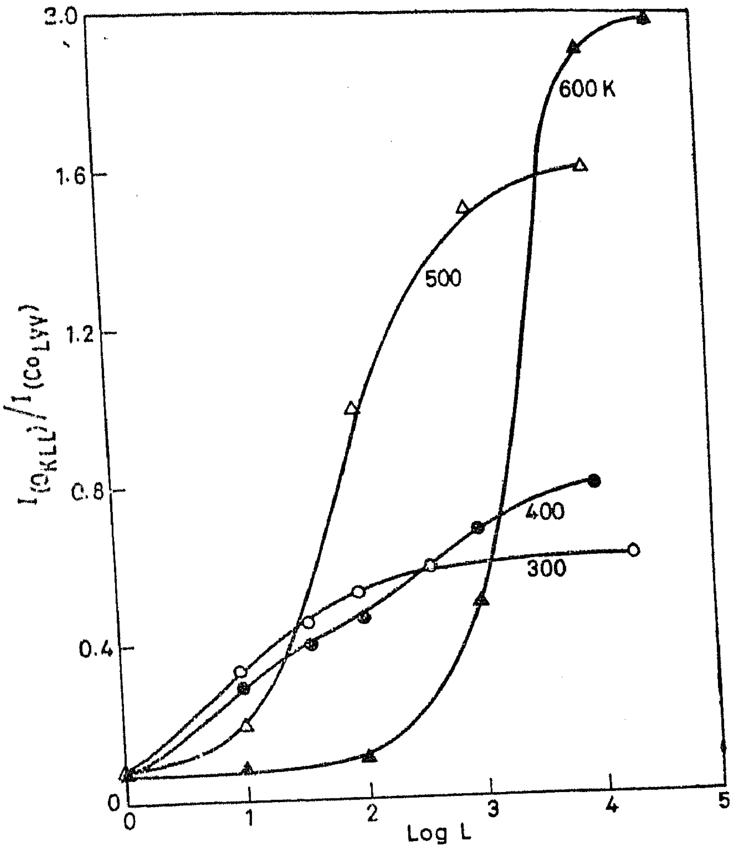

Figure 7. Plots of O (KLL)/Co ($L_{23}M_{45}M_{45}$) Auger intensity ratio against log *L* at different temperatures.

10^4 L. These observations are also supported by the metal Auger line intensity ratios shown in figure 6. It is also evident that the metal Auger line intensity ratios depend on the occupancy of the valence electrons in cobalt.

Acknowledgements

The authors are thankful to Professor C N R Rao for useful discussions. Financial support for this work from the Department of Science and Technology, Government of India, is gratefully acknowledged.

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