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Interaction of Cobalt with Oxygen, Water Vapor, and Carbon Monoxide

X-Ray and Ultraviolet Photoemission Studies[1]

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The interaction of oxygen, water vapor, and carbon monoxide with cobalt has been studied by combined *in situ* X-ray and uv photoelectron spectroscopy. Oxygen interaction gave rise to CoO at 295 K at low pressure (5×10^{-8} Torr) but to Co_3O_4 at high pressure (0.25 Torr). This was deduced by studies of the bulk oxides CoO and Co_3O_4. O(1s) binding energies were not useful in distinguishing between the two oxides but the shake-up satellites associated with the Co(2p) spectra were diagnostic. Co_3O_4 could be converted to CoO by heating to 700 K *in vacuo* which is in agreement with thermodynamic calculations. Water vapor was less reactive than $O_2(g)$ at 295 K and gave rise to a hydroxylated surface. Carbon monoxide adsorbed molecularly at both 80 and 295 K showing both core-level and valence-level spectra characteristic of the associative state. This is in accord with predictions based on the known heat of chemisorption.

INTRODUCTION

The study of cobalt and its interaction with oxygen and carbon monoxide by electron spectroscopy arose for a number of reasons. In the first instance we were interested in the nature of the oxide formed during exposure of an initially clean surface to oxygen and, in particular, whether it can be related to one of the stable bulk oxides of cobalt (CoO or Co_3O_4); this led naturally to a study of the bulk oxides themselves. Secondly, recent studies of the adsorption of carbon monoxide on metals showed a correlation between the O(1s) binding energy and the heat of adsorption (*1*). Furthermore, by studying simultaneously whether CO-like orbitals were present in the uv-induced spectra it was possible to decide whether carbon monoxide was either in the molecular or dissociated state. For heats of adsorption greater than about 300 kJ mol^{-1} the molecule was shown to be dissociated with an O(1s) binding energy value close to 530 eV, a value typical of chemisorbed oxygen. The reported (*2*) heat of adsorption of carbon monoxide on cobalt is about 200 kJ mol^{-1}; it was therefore of interest to explore whether the correlation (*1*) applied also to the cobalt + carbon monoxide system. The results have a more general significance in that they are relevant to a better understanding of both the bonding of carbon monoxide to metals and the catalytic activity of cobalt and its oxides. No previous electron spectroscopic studies of the adsorption of CO or oxygen on cobalt have been reported.

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Both Novakov (*3*) and Schön (*4*) recognized that shake-up satellites were frequently observed in the X-ray induced spectra of transition metal oxides, and in the case of copper oxide Schön suggested that there was a possible relationship between stoichiometry and the occurrence or otherwise of satellite peaks. In fact, Evans *et al.* (*5*) studied the oxidation of copper by examining the shake-up satellite structure, drawing on the more definitive evidence that had emerged regarding the origin of the satellites from studies of transition metal compounds. When this investigation was initiated, a study of CoO by X-ray photoelectron spectroscopy had been reported by Frost *et al.* (*6*), but during the course of our work papers were published which included studies of both bulk CoO and Co_3O_4 (*7–9*). A number of general points arose relevant to the present study of which the most important was that paramagnetic Co(II) species were expected to exhibit intense satellites associated with the Co(2p) lines while with Co(III) ions no satellites would be anticipated. There was, however, a general difficulty of ascertaining whether the surfaces of the solids studied were contaminated or showed deviations in stoichiometry from that of the bulk; furthermore, complete spectral information was not reported. We have therefore investigated the oxides and the influence of heat treatment on the spectroscopic data. Both X-ray- and uv-induced spectra were determined for bulk CoO, Co_3O_4, and the interaction of oxygen and carbon monoxide with atomically clean cobalt; no previous uv spectra have been reported for any of these systems. Although data have been reported (*9, 10*) ostensibly for Co_2O_3, there is some doubt as to whether this oxide exists as such.

EXPERIMENTAL

The details of the Vacuum Generators ultrahigh vacuum electron spectrometer (ESCA-3) have been described (*8*). This enabled X-ray- and uv-induced spectra to be determined of surfaces prepared *in situ.* Atomically clean cobalt surfaces were prepared by either evaporation from a 0.5-mm spec-pure filament on to the spectrometer probe maintained at room temperature or by pretreatment of cobalt foil (0.1 mm thick) with hydrogen and oxygen at 600 K. The foil was obtained from Goodfellow Metals. The films were evaporated at a pressure of about 10^{-8} Torr which decreased to about 10^{-9} Torr immediately after evaporation had ceased. The surfaces were transferred immediately from the preparation chamber to the electron spectrometer chamber where the background pressure was $\sim 4 \times 10^{-10}$ Torr. Co_3O_4, obtained from Johnson, Matthey & Co. Ltd. was spectrographically standardized and CoO, prepared by decomposing $CoCO_3$, was characterized by X-ray powder photography. The oxides were in the form of discs pressed on to the gold support. During the determination of the He(II) spectra the pressure of helium was about 2×10^{-9} Torr. Spec-pure gases (H_2, CO, and O_2) were obtained from British Oxygen Co. Ltd., and were passed through a liquid nitrogen cooled trap before being admitted to the surface under investigation. Data obtained with both cobalt in the form of "cleaned" foil and as an evaporated film were identical. All spectra are calibrated with respect to the Au($4f_{7/2}$) line at 83.8 eV and are referred to the Fermi level.

RESULTS AND DISCUSSION

Cobalt Oxide

In order to interpret the photoelectron spectra of the interaction of oxygen with cobalt surfaces there are distinct advantages in first studying bulk Co_3O_4 and CoO. In Fig. 1a are shown the X-ray-induced $2p_{\frac{3}{2}}$ spectral regions of atomically clean cobalt, Co_3O_4, and CoO. The data are

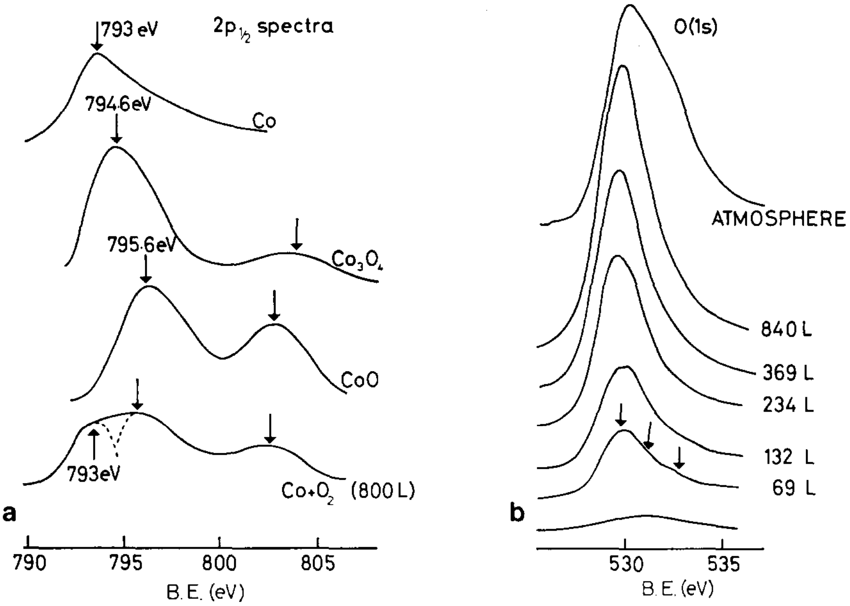

FIG. 1 (a) CO($2p_{1/2}$) spectra for atomically clean cobalt metal, Co_3O_4, CoO, CoO, and Co after exposure to oxygen (800 L, 5×10^{-8} Torr at 295 K). Arrows indicate approximate peak positions. (b) O(1s) spectra during controlled exposure of cobalt to oxygen at 295 K ($P_{O_2} \simeq 10^{-7}$ Torr) and finally to the "atmosphere" followed by evacuation. B. E., Binding energy with respect to Fermi level.

summarized and compared with other published results in Table 1; we draw particular attention to the following:

(a) The Co($2p_{3/2}$) and Co($2p_{1/2}$) values observed with cobalt metal at 778 and 793 eV are shifted with Co_3O_4 to about 779 and 794 eV, respectively.

(b) In the case of CoO the $2p_{3/2}$ and $2p_{1/2}$ values are at about 780 and 796 eV, respectively. It should be noted, however,

TABLE 1

Electron Binding Energies (eV) for Cobalt Oxides and "Oxidized" Cobalt Metal

Material and reference	O(1s) (a)	O(1s) (b)	Co($2p_{3/2}$) (c)	Satellite (d)	Intensity ratio (d):(c)	Co($2p_{1/2}$) (e)	Satellite (f)	Intensity ratio (f):(e)
Co_3O_4 (Present work)	529	531	779.5	788	—	794.6	803	0.2
Co_3O_4 (*7*)[a]	—	—	778.6	786.7	0.18	793.6	802.5	0.3
Co_2O_3 (*9*)	—	530	780	—	—	—	—	—
CoO (Present work)	529	531	779.6	785.6	0.67	795.6	802	0.81
CoO (*6*)	529.8	—	780	789.2	—	795	803	—
CoO (*8*)	529.5	531.3	780	786.3	0.13	795.8	802.5	0.27
CoO (*7*)	—	—	780.6	786.6	0.6	796	803	0.87
CoO (*9*)	529.6	—	780	—	—	—	—	—
Co + O_2(g) (P_{O_2} = 0.25 Torr, 295 K) (present work)	529.5	531	780	788	0.2	795	803.5	0.2
Co + O_2(g) (P_{O_2} = 5×10^{-8} Torr, 800 L, 295 K) (present work)	529.5	531	779	—	—	795	803	0.6
Co + O_2(g) high exposure, 295 K, heat *in vacuo* to 700 K (present work)	530	531	780.7	786.7	0.66	796.6	803.3	0.7
Co (Present work)	—	—	778	—	—	793	—	—

[a] We have subtracted (arbitrarily) 7.5 eV from all the binding energies quoted in their paper; satellite intensity ratios indicate the presence of Co_3O_4 at the surface.

that the "as prepared" CoO had present a surface layer of Co_3O_4. This was removed by heating *in vacuo* [see (d) below].

(c) The intensities of the shake-up satellites associated with the Co(2p$_{\frac{3}{2}}$) peaks of the two oxides are very different. With Co_3O_4 the satellite intensity is about 20% of the main Co(2p) lines while with CoO it is between 70 and 80%.

(d) When Co_3O_4 is heated to about 700 K *in vacuo* it is converted to CoO (Fig. 1); we use the satellite peak intensity for distinguishing between the two oxides. This conclusion agrees with thermodynamic calculations which indicate that for the equilibrium $Co_3O_{4(s)} \leftrightarrow 3CoO_{(s)} + \frac{1}{2}O_{2(g)}$ the oxygen pressure is about 10^{-8} Torr at 700 K.

(e) All the "as prepared" oxide samples showed evidence of contamination by surface hydroxide and adsorbed water. This conclusion is based on the presence of two distinct O(1s) peaks, one centered at 529.5 eV and the other, a much broader peak, at 531.5 eV. The higher binding energy peak diminished substantially on heating *in vacuo* to 700 K. We did not attempt to "clean the surface" by argon-ion bombardment since there was the possibility of producing a highly defective surface oxide. The assignments of these peaks are discussed later.

There were always present two O(1s) peaks, the major one centered at a binding energy of about 529.5 eV and a second which usually appeared only as a shoulder between 530.5 and 531 eV. The two oxides therefore showed very similar O(1s) spectra and could not be distinguished by them (Table 1). It is therefore clear that the only unambiguous criterion for distinguishing between the two oxides CoO and Co_3O_4 is the ratio of the satellite intensities to the main 2p peaks. The binding energies of the 2p levels are less useful since, although differing from the values characteristic of the metal (Co 2p$_{\frac{3}{2}}$ = 778 eV; Co 2p$_{\frac{1}{2}}$ = 743 eV) by about 1 eV, they are both very similar to each other. It is clear that although the present data for CoO and Co_3O_4 are in general agreement with the published results summarized in Table 1, the latter are less complete in that not all the relevant spectral features are reported. There has also been considerable discussion (*7*, *8*) of the "two O(1s) peaks," 529.5 and 531 eV, in terms of the "different" oxygens present in Co_3O_4 and CoO and therefore the possibility of the two oxides being present, one inadvertently, in any given oxide sample. We, however, take a different view based on data observed with the controlled exposure of clean cobalt to oxygen and water vapor. This is discussed below.

Oxygen Interaction with Cobalt

Figures 1b and 2a show the O(1s) and Co(2p$_{\frac{3}{2}}$) spectra for different oxygen exposures at 195 K; the main O(1s) peak is centered at 529.5 eV, but a small shoulder at about 531 eV is also present as well as evidence for a small peak at about 533 eV. These peaks are marked on the spectrum observed after an oxygen exposure of 69 L[3] (Fig. 1b). We assign the 531 eV "peak" to surface OH groups and the 533 eV "peak" to adsorbed water. The latter is now well characterized (*12*), and also there is good evidence for the OH surface species to be characterized by an O(1s) value of about 531 eV (*13*). It would appear that oxidized cobalt is very reactive to traces of water vapor present inadvertently in the purified oxygen gas. The assignments are discussed further in connection with our water vapor results. The relationship between the O(1s) intensity at 529.5 eV and the oxygen exposure in Langmuirs at 295 K conformed to Eq. (1):

$$I_{O(1s)} = 14.77(1 - e^{-0.0034 L}). \qquad (1)$$

The Co(2p$_{\frac{3}{2}}$) peak, originally at a binding energy of 778 eV with the clean metal,

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[3] 1 L (Langmuir) ≡ 10^{-6} Torr sec.

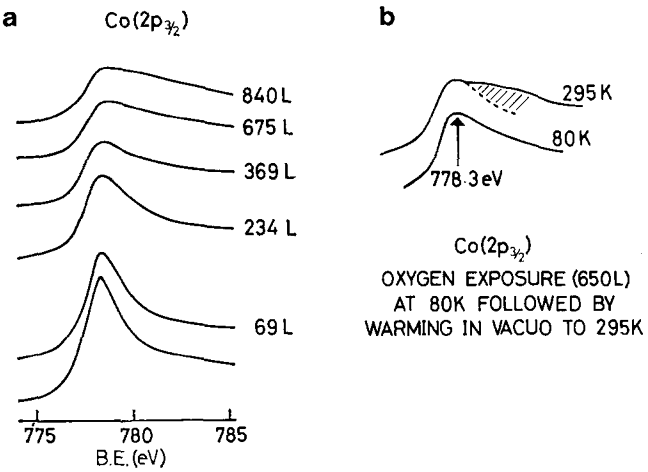
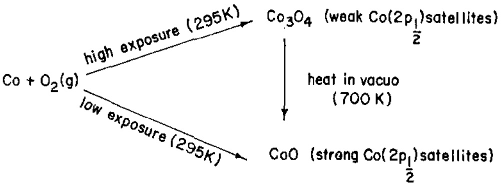


FIG. 2. (a) $\mathrm{Co}(2p_{3/2})$ spectra during exposure of cobalt to oxygen at 295 K. (b) $\mathrm{Co}(2p_{3/2})$ spectra after exposure of cobalt to oxygen (650 L) at 80 K followed by warming *in vacuo* to 295 K.

decreases in intensity and broadens to higher binding energy with increasing exposure to oxygen. After completing the controlled oxygen exposure experiments at 295 K, the surface was exposed to the atmosphere when the O(1s) peak broadened appreciably and further contributions to the peak profile could be observed at about 531 and 533 eV (Fig. 1b).

We consider next whether it is possible to decide on the basis of the core-level spectra as to which oxide is formed during exposure of the metal to oxygen at low pressure at 295 K. It is obvious that neither the $\mathrm{Co}(2p_{3/2})$ nor the O(1s) binding energies are diagnostic. However, when we compare the shake-up satellite intensities associated with the Co(2p) spectra, it is obvious that when cobalt is exposed (800 L) to oxygen at 5×10^{-8} Torr at 295 K CoO is formed rather than $\mathrm{Co_3O_4}$ (Fig. 1a, Table 1). With CoO the ratio of the shake-up satellite intensity to the main 2p peak is between 0.7 and 0.8 which compares with the experimentally observed value of about 0.6 and a ratio of about 0.2 with $\mathrm{Co_3O_4}$ (Table 1). For high oxygen exposures (0.5 Torr, 295 K) the ratio was 0.2 (Table 1), providing good evidence for $\mathrm{Co_3O_4}$; when this was heated *in vacuo* to 700 K the satellite intensity ratio increased to 0.7. We can therefore summarize our conclusions as follows:



Scheme 1

At 80 and 210 K the spectra were virtually identical to those observed at 295 K, the only noticeable difference being that the intensity of the O(1s) peak at 529.5 eV increased rather more steeply with oxygen exposure than at 295 K. This indicates that the sticking probability is appreciably greater at these lower temperatures, in keeping with a number of other chemisorption systems. The only change on warming the adlayer to 295 K was a broadening of the $\mathrm{Co}(2p_{3/2})$ peak (Fig. 2b). We interpret this as the development of the CoO oxide phase, a process of low activation energy characterized by a $\mathrm{Co}(2p_{3/2})$ peak at about 780 eV compared with 778 eV for the clean metal. That oxygen interaction leads to substantial oxide growth is also evident from the oxygen adsorption work of Rudham and Stone (*14*) and Brennan and Graham (*21*) who reported "nearly six monolayers" at 298 K.

The He(II) spectra observed at various oxygen exposures are shown in Fig. 3; up to an exposure of about 100 L the only new feature is a peak at about 5 eV. At higher exposures there is a new small peak at 10 eV, but the major change is a broad and intense feature between 2 and 8 eV below the Fermi level. The peak at 5 eV is attributed to the O(2p) orbital, while the spectrum after 800 L is close to that of the bulk CoO oxide. It should be noted, however, that the He spectra of both bulk CoO and Co_3O_4 are almost indistinguishable.

Figure 4 shows the O(1s) spectral region after the interaction of water vapor with cobalt at 80 K, followed by warming the adlayer to 290 K and further exposure to water vapor. At 80 K the O(1s) peak is centered at 532.5 eV, but asymmetry of the peak and the relatively large FWHM value suggest the presence of other components at about 530.5 and 534 eV. After warming to 290 K, the main peak at 532.5 eV has disappeared and the 530.5 eV peak is now dominant. Further exposure to water vapor (900 L, 5×10^{-6} Torr) resulted in little or no adsorption at 290 K. It should be noted that with water vapor we have no firm evidence for the O(1s) peak at 529.5 eV; this was the main peak observed during oxygen interaction with cobalt (Fig. 1). The O(1s):Co($2p_{3/2}$) ratios (by area) at 80 K, after warming to 290 K and further interaction with water vapor (Fig. 4), were 0.08, 0.01, and 0.02, respectively. The O(1s) peaks observed with water vapor are assigned to hydroxly groups (530.5 eV), strongly adsorbed water (532.5 eV), and multilayers of weakly held molecular water (534 eV). We discuss later evidence that the O(1s):Co($2p_{3/2}$) ratio

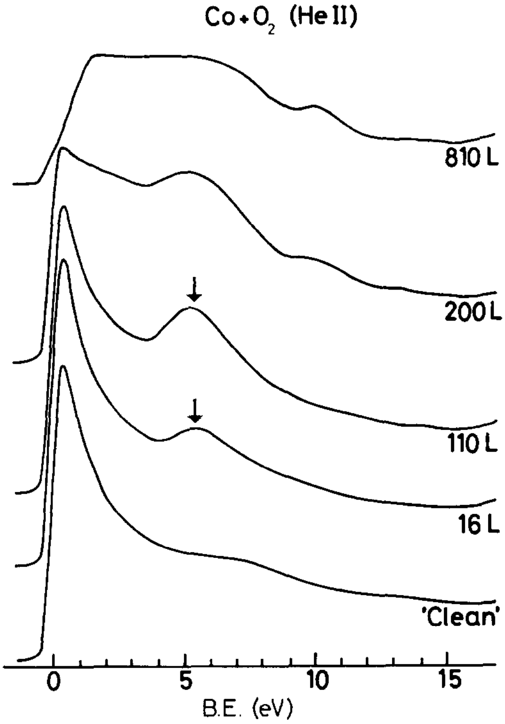


FIG. 3. He(II) spectra during exposure of cobalt to oxygen at 295 K.

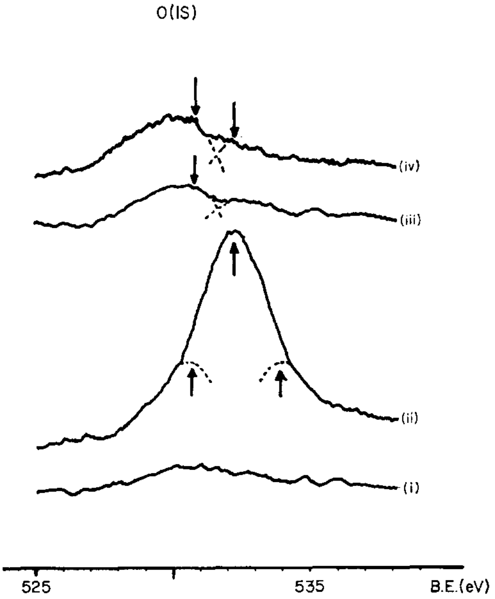


FIG. 4. O(1s) spectral region for (i) cobalt, (ii) cobalt after exposure to 200 L of water vapor at 80 K, (iii) the effect of warming (ii) to 295 K, and (iv) after further exposure (700 L) of the surface to water vapor at 295 K.

of 0.02 corresponds to about "half-a-monolayer" of surface hydroxyl groups.

The initial interaction of water vapor at 80 K is therefore dissociative, leading to surface hydroxyls characterized by an O(1s) value of about 530.5 eV followed by molecular adsorption of water. The molecularly adsorbed water is almost completely desorbed on warming to 290 K, leaving the OH peak as the major one. Since further exposure at 290 K to water vapor made little difference to the spectra the hydroxylated surface was clearly unreactive. For a similar exposure to oxygen at 290 K the O(1s) peak at 529.5 eV (Fig. 1) was nearly ten times the O(1s) intensity observed with H_2O vapor at the same temperature. The He(II) spectra support the above interpretation in that the peaks typical of multilayers of water at 6.4, 8.5, and 12 eV were observed at 80 K. These peaks were absent at 295 K.

Adsorption of Carbon Monoxide on Cobalt

Figure 5a shows the He(II) spectra of "clean" cobalt after exposure to carbon monoxide at 80 K, followed by warming *in vacuo* ($\sim 5 \times 10^{-10}$ Torr) to 295 K and further exposure to carbon monoxide at 295 K (curves i–iv). There are two distinct peaks centered at about 7 and 10 eV below E_F. The intensities of the peaks are somewhat greater at 80 K than after warming to 295 K but further exposure to carbon monoxide at 295 K restored the intensities to those observed at 80 K. After heating the adlayer to 450 K (Fig. 5a, curve V), these two peaks are replaced by a single but broader peak at about 4.5 eV below E_F. On cooling to 295 K no peaks reappeared at 7 and 10 eV on further exposure to carbon monoxide. The surface was obviously inactive at this stage to CO adsorption. The 7 and 10 eV peaks are similar to those observed in previous studies of the adsorption of carbon monoxide on iron (*15*), nickel (*16*), platinum (*17*), copper (*18*), and molybdenum (*19*) (at 80 K only) and are assigned to the 5σ and 1π orbitals (7 eV) and 4σ orbital (10 eV). There is now considerable evidence for this assignment; furthermore, the case for dissociation (when it occurs) of CO is unambiguous as is clear from the recent review by Umbach *et al.* (20).

The X-ray-induced C(1s) and O(1s) spectra for CO adsorbed at 80 K, after warming to 295 K and heating the adlayer to 450 K, are shown in Fig. 5(b). At 295 K the O(1s) and C(1s) peaks are at 531 and 284.5 eV, respectively, and their intensity ratio is about 2.5:1. This is the ratio expected for molecularly adsorbed carbon monoxide and therefore compatible with the uv-induced spectra (Fig. 5a) at this temperature. There was little change in the O(1s) and C(1s) spectra up to 400 K, but at 450 K there was a substantial increase in the intensity of the carbon peak. The O(1s):C(1s) intensity ratio decreased from that typical of molecularly adsorbed CO and the peaks at about 7 and 10 eV in the He(II) spectra are replaced by a broad peak at about 4.5 eV below the Fermi level.

These results are interpreted as reflecting the molecular adsorption of carbon monoxide at 85 K and partial desorption on warming to 295 K under dynamic vacuum conditions with further adsorption of carbon monoxide on exposure to CO at 295 K. At 450 K there is no evidence for molecularly adsorbed CO but both the uv and X-ray spectra indicate surface carbide. We can, however, not rule out the possibility that in addition to the dissociation of CO carbon segregation from the bulk to the surface has occurred. That carbon diffusion can occur under these conditions was established by other experiments where initially clean cobalt films were heated to 450 K *in vacuo* (5×10^{-10} Torr). Substantial C(1s) peaks were observed to develop very rapidly which could not be

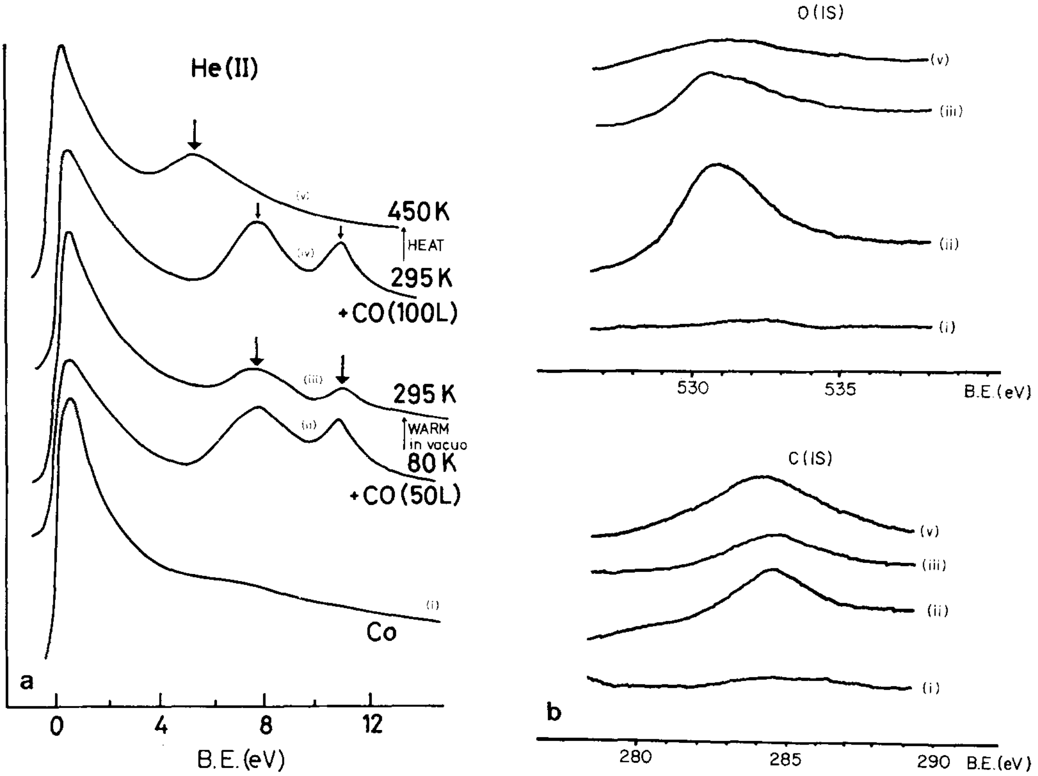


FIG. 5. (a) He(II) spectra for (i) cobalt, (ii) after CO adsorption at 80 K, (iii) after warming the adlayer from 80 K to 295 K *in vacuo*, (iv) after further exposure of the surface in (iii) to CO, (v) after heating the adlayer at 295 K to 450 K *in vacuo*. (b) X-ray-induced spectra. Numbered curves as in (a) above, but with (iv) not recorded.

accounted for by the dissociation of CO(g) present at a partial pressure of about 3×10^{-10} Torr.

The conclusion that carbon monoxide is adsorbed in the molecular form is in agreement with the prediction that only for heats of chemisorption of about 300 kJ mol^{-1} or greater does dissociation occur at 295 K. By using the O(1s) versus ΔH relationship (*1*), we estimate the heat of adsorption on cobalt to be about 250 kJ mol^{-1} which compares with a calorimetric value of about 200 kJ mol^{-1}.

Finally, we draw attention to the O(1s):Co($2p_{3/2}$) intensity ratio of 0.025 for CO adsorption (saturation) at 295 K. If we consider the CO to be bridge-bonded, then this ratio corresponds to effectively half a monolayer of "oxygen." We therefore estimate that the surface coverage of hydroxyl groups after exposure of cobalt to water vapor (700 L, 5×10^{-6} Torr) at 295 K is about half a monolayer. This would then imply about five "oxide layers" after oxygen interaction at 295 K. Since the CO adsorption data suggested that a monolayer of oxygen, based on the O(1s) intensity, was formed after an exposure of 80 L of oxygen at 295 K, then by comparing Eq. (1) with $I = I_\infty(1 - e^{-d/\lambda})$ it is possible to determine d knowing λ. I is the intensity from an adsorbate layer of thickness d and λ is the electron escape depth. Taking $\lambda = 10$ Å for the O(1s) photoelectron, for which there is good evidence, gives a value of 2.7 Å for d at the monolayer. This is close to the O^{2-}

diameter (2.8 Å), providing general support for the model.

CONCLUSIONS

Oxygen interaction at 295 K and low pressure (10^{-7} Torr) with cobalt leads to the formation of CoO, while higher oxygen pressure (0.25 Torr, 295 K) give Co_3O_4. This conclusion is based on a comparison of the Co(2p) satellite spectra observed with those characteristic of bulk Co_3O_4 and CoO. The O(1s) spectra are, in this context, not helpful. Although oxygen interaction with cobalt is extensive, even at 80 K, evidence from the Co(2p$_{3/2}$) spectra indicate that nucleation of the CoO phase is activated. The activation energy of the process is clearly small ($\lesssim$50 kJ mol^{-1}) since it occurs in the range 80 to 295 K. Oxidation of cobalt by water vapor is limited to the formation of an hydroxylated surface, estimated to be about half a monolayer at 295 K. This surface is passive to further water interaction, whereas cobalt reacts with O_2(g) to give an oxide some five "layers" thick.

Carbon monoxide adsorbs molecularly on cobalt at both 80 and 295 K. This agrees with our general model for CO adsorption on metals where correlations have been found between O(1s) binding energies in adsorbed carbon monoxide, the heat of adsorption, and the occurrence (or otherwise) of discrete peaks in the He spectra which can be associated with molecular CO (*1*). The predicted heat of adsorption is in good agreement with the experimental data of Brennan and Hayes (*2*).

ACKNOWLEDGMENTS

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REFERENCES

1. Joyner, R. W., and Roberts, M. W., *Chem. Phys. Lett.* **29**, 447 (1974).

2. Brennan, D., and Hayes, F. H., *Phil. Trans. Roy. Soc. A* **258**, 347 (1965).

3. Novakov, T., *Phys. Rev.* **B3**, 2693 (1971).

4. Schön, G., *Surf. Sci.* **35**, 96 (1973).

5. Evans, S., Evans, E. L., Parry, D. E., Tricker, M. J., Walters, M. J., and Thomas, J. M., *Faraday Disc. Chem. Soc.* **58**, 97 (1974).

6. Frost, D. C., McDowell, C. A., and Woolsey, I. S., *Molec. Phys.* **27**, 1473 (1974).

7. Bonnelle, J. P., Grimblot, J., and Huysser, A. D., *J. Electron Spectrosc.* **7**, 151 (1975).

8. Kim, K. S., *Phys. Rev.* **B11**, 2177 (1975).

9. McIntyre, N. S., and Cook, M. G., *Anal. Chem.* **47**, 2208 (1975).

10. Hirokawa, K., Honda, F., and Iku, M., *J. Electron Spectrosc.* **6**, 333 (1975).

11. Brundle, C. R., Roberts, M. W., Latham, D., and Yates, K., *J. Electron. Spectrosc.* **3**, 241 (1974).

12. Atkinson, S. J., Brundle, C. R., and Roberts, M. W., *Faraday Disc. Chem. Soc.* **58**, 62 (1974).

13. Kishi, K., and Roberts, M. W., *J. Chem. Soc. Faraday Trans. I* **71**, 1721 (1975).

14. Rudham, R., and Stone, F. S., *Trans. Faraday Soc.* **54**, 420 (1958).

15. Kishi, K., and Roberts, M. W., *J. Chem. Soc. Faraday Trans. I* **71**, 1715 (1975).

16. Joyner, R. W., and Roberts, M. W., *J. Chem. Soc. Faraday Trans. I* **70**, 1819 (1974); Page, P. J., and Williams, P. M., *Faraday Disc. Chem. Soc.* **58**, 80 (1974).

17. Clarke, T. A., Gay, I. D., Law, B., and Mason, R., *Chem. Phys. Lett.* **31**, 29 (1975).

18. Brundle, C. R., *J. Electron Spectrosc.* **7**, 484 (1975).

19. Atkinson, S. J., Brundle, C. R., and Roberts, M. W., *Chem. Phys. Lett.* **24**, 175 (1974).

20. Umbach, E., Fuggle, J. C., and Menzel, D., *J. Electron Spectrosc.* **10**, 15 (1977).

21. Brennan, D., and Graham, M. J., *Disc. Faraday Soc.* **41**, 95 (1966).