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# Photoelectron Spectroscopic Evidence for the Oxidation of Ir(111)

In this note, we report the influence of CO on the incorporation of oxygen into the (111) surface of Ir, henceforth termed surface oxidation or near-surface oxidation. Oxidation of the Ir(111) surface has been investigated previously (*1–4*), but one aspect that has been neglected is the effect of the presence of CO on the surface oxidation reaction. We have found that the presence of CO affects the oxidation reaction markedly, and the results are presented below.

The work reported here was conducted in a VG-ESCA III photoelectron spectrometer with a base pressure of $1 \times 10^{-10}$ Torr. The Ir(111) crystal was cut, polished, and cleaned by standard procedures and mounted so that gases can flow continuously over it while the photoelectron spectra are being recorded. We have published details concerning this technique previously (*5*). The ultraviolet photoelectron spectra (UPS) were recorded with a He discharge lamp, optimized for the production of He II ($h\nu = 40.6$ eV) radiation. The sample was mounted so that photoelectrons were collected 50° from the surface normal.

The He II UPS data are presented in Fig. 1. The spectrum of the clean surface is shown in spectrum (a). Figure 1b is the spectrum after exposure at 375°K for several minutes to CO and $O_2$ each at $7 \times 10^{-8}$ Torr. The main peaks in the spectrum are identified according to the molecular orbitals of CO to which they correspond (*6*). Clearly, CO is the principal adsorbed species. Upon raising the crystal temperature to 575°K, Fig. 1c, the CO is substantially desorbed, and the spectrum is rather similar to that of the clean surface. When the crystal temperature is raised to 775°K (Fig. 1d) the mixture of CO and $O_2$ begins to oxidize the surface. The intensity increase in the 4 to 7 eV region reflects this onset of surface oxidation.

Following the spectrum in Fig. 1d, the CO leak valve was closed, allowing the CO pressure to drop to $2 \times 10^{-10}$ Torr. Immediately following this pressure drop, but still at 775°K and in $7 \times 10^{-8}$ Torr of $O_2$, the spectrum in Fig. 1e was recorded. The marked change in this spectrum indicates extensive oxidation of the surface. This oxidation reaction is retarded greatly by the presence of CO. Evidently, in the presence of CO, oxygen adatoms resulting from the dissociation of $O_2$ are removed by reaction with CO before they can react further to form a surface oxide.

Figure 1f demonstrates the relatively unreactive character of this surface oxide. In

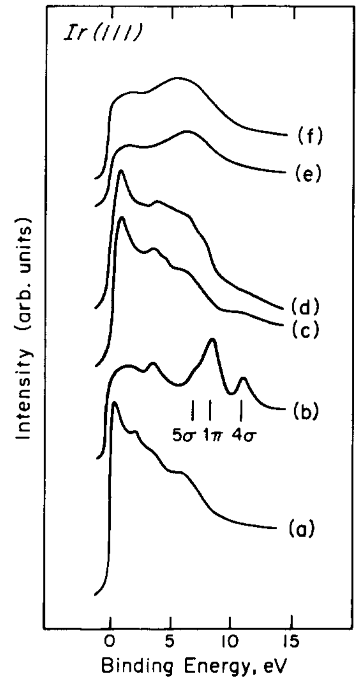

FIG. 1. The He II UPS data which illustrate the oxidation of the Ir(111) surface. Spectrum (a) is of the clean surface; (b) is during exposure to CO and $O_2$ each at $7 \times 10^{-8}$ Torr with the crystal at 375°K; (c) is as in (b) except that the crystal is at 575°K; (d) is as in (b) except that the crystal is at 775°K; (e) is in $7 \times 10^{-8}$ Torr $O_2$ after pumping out the CO with the crystal at 775°K; and (f) is under the same conditions as (b) except after the formation of the surface oxide.

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Fig. 1f, the temperature was lowered to 375°K, and CO was readmitted at a pressure of $7 \times 10^{-8}$ Torr. At this temperature and pressure, oxygen adatoms are quickly removed via a Langmuir–Hinshelwood reaction mechanism on a reduced surface (*1*), yet the spectrum is unchanged from that of Fig. 1e. Clearly, the surface oxide has a much lower reactivity compared to the oxygen adatoms which are an intermediate in the formation of the oxide, and CO does not chemisorb on the oxide at 375°K.

In conclusion, we have found that the presence of CO retards greatly the formation of a surface oxide when Ir(111) is exposed at high temperature to $O_2$. The reason for this is that oxygen adatoms which are an intermediate in the oxidation reaction can easily be removed by reaction with CO.

## ACKNOWLEDGMENT

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P. A. ZHDAN
A. P. SCHEPELIN
A. I. BORONIN
G. K. BORESKOV

*Institute of Catalysis*
*Novosibirsk, USSR 630090*

W. H. WEINBERG[1]
W. F. EGELHOFF, JR.[2]

*Division of Chemistry and Chemical Engineering*
*California Institute of Technology*
*Pasadena, California 91125*

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[1] Camille and Henry Dreyfus Foundation Teacher-Scholar.

[2] Present address: National Bureau of Standards, Washington, D.C. 20234.