

Abstract: CO chemisorption on Ir(111)*

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(Received 3 September 1975; in final form 2 October 1975)

PACS numbers: 82.65.M, 68.20.D

The adsorption of carbon monoxide on the (111) crystallographic orientation of iridium both at and below room temperature has been investigated using both low-energy electron diffraction (LEED) and thermal desorption mass spectrometry. At room temperature, CO adsorbs rapidly resulting in the appearance of a faint $(\sqrt{3}\times\sqrt{3})R 30^\circ$ LEED pattern after only approximately 1.3×10^{-6} Torr s (1.72×10^{-4} Pa s) exposure. Upon further exposure to CO, the intensity of the overlayer LEED beams initially increases, but then decreases passing through a maximum at an exposure of approximately 2.4×10^{-6} Torr s (3.2×10^{-4} Pa s). By an exposure of 10^{-5} Torr s (1.3×10^{-3} Pa s) each of the (rather dim and diffuse) overlayer beams has split into two beams. These beams then move toward the substrate beams with increasing CO surface coverage, until near saturation coverage the angle between the split overlayer beams subtended at the (00) beam is greater than 30° .

The $(\sqrt{3}\times\sqrt{3})R 30^\circ$ surface structure has also been found when Ir(111) is exposed to CO at a surface temperature between 150 and 300 K. However, for a surface temperature approximately between 150 and 250 K, an ordered $(2\sqrt{3}\times 2\sqrt{3})R 30^\circ$ LEED pattern is clearly evident at a saturation coverage of CO. If the surface on which this ordered overlayer is present is heated, the overlayer beams become rather weak and diffuse, but they are still faintly visible at room temperature. Indeed, it is possible to form the $(2\sqrt{3}\times 2\sqrt{3})R 30^\circ$ CO at room temperature with a quite large exposure of the surface to the CO.

Thermal desorption mass spectrometry has revealed the existence of two binding states of the CO at saturation coverage. At a low surface coverage, corresponding to a CO exposure of $\leq 2.5\times 10^{-6}$ Torr s (3.3×10^{-4} Pa s), the CO has been found to desorb in a single peak with the peak maximum shifting to a lower temperature as the surface coverage increases. This behavior could be due to the population of an unresolved substate of the initial binding state, or it could result from a surface-coverage-dependent binding energy. Such a (low) surface-coverage-dependent binding energy has been reported recently for the adsorption of CO on (111) Ni.¹

For carbon monoxide exposures greater than 2.5×10^{-6} Torr s (3.3×10^{-4} Pa s), a shoulder appears on the low temperature side of the initial peak as a second "binding state" of the CO begins to be populated. A comparison of the thermal desorption spectra with the LEED intensity versus exposure to CO profiles indicates that the appearance of the second binding state coincides with the onset of the decrease in the

$(\sqrt{3}\times\sqrt{3})R 30^\circ$ overlayer LEED beam intensity; i.e., the onset of the transformation from the $(\sqrt{3}\times\sqrt{3})R 30^\circ$ to the $(2\sqrt{3}\times 2\sqrt{3})R 30^\circ$ surface structure. If the rate at which the saturated iridium surface is heated is 9 K s^{-1} , the maximum temperatures in the thermal desorption spectrum are found to be 450 and 525 K. Since the heating rate of the crystal is approximately constant over the complete range of temperature in which the CO is desorbed, it is possible to determine the CO surface coverage as a function of exposure. The experimentally determined relationship between surface coverage and CO exposure has shown that the measured initial sticking probability of ~ 0.90 is nearly constant up to approximately 20%–25% of a monolayer coverage. At coverages greater than this, the sticking probability is found to decrease markedly.

A comparison of thermal desorption spectra following a saturation exposure of the Ir surface to CO both at 295 and at 150 K indicates that there is no significant increase in CO surface coverage at 150 as compared to 295 K. Moreover, the surface coverage at saturation was found to be approximately 75% greater than that coverage which corresponds to the maximum in the LEED intensity of the $(\sqrt{3}\times\sqrt{3})R 30^\circ$ overlayer beam. Since the optimum CO surface coverage for the $(\sqrt{3}\times\sqrt{3})R 30^\circ$ structure is a third of a monolayer, the surface evidently saturates at approximately 7/12 of a monolayer coverage. Rather similar behavior has been reported for the adsorption of CO on the (001) surface of ruthenium.²

The isosteric heat of adsorption corresponding to a constant surface coverage has been determined from the appropriate Clausius–Clapeyron equation using the intensity of the overlayer LEED beams as a measure of the CO coverage. The isosteric heat of adsorption was measured at a third of a monolayer coverage by monitoring the maximum intensity of the $(\sqrt{3}\times\sqrt{3})R 30^\circ$ overlayer LEED beam upon cooling the crystal in an ambient of various pressures of CO. In this determination, a low primary LEED beam energy ($E_p = 23\text{ eV}$) and a low primary beam current ($i_p < 10^{-7}\text{ A}$) were used to ensure negligible electron-beam-induced desorption and/or dissociation of the CO. The isosteric heat of adsorption was found to be $35\pm 1\text{ kcal mole}^{-1}$ for 1/3 monolayer coverage of the CO.

It is concluded that the sticking probability of CO on Ir(111) is constant at surface coverages less than 20%–25% of a monolayer, and its value is essentially unity. Moreover, the isosteric heat of adsorption at 1/3 of a monolayer coverage is 35 kcal mole^{-1} , and the value at lower coverages may be somewhat larger based

on the observed shift in thermal desorption peak temperatures with coverage at less than $1/3$ of a monolayer. Finally, it is concluded that the (111) surface of iridium is rather energetically homogeneous based on the small lowering of the desorption peak temperature for $7/12$ monolayer coverage of CO. At this higher coverage, the registry of the CO with the surface has been lost.

*Research supported via instrumentation grants from both the National Science Foundation (Grant No. GP-37186) and the Research Corporation. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

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