

Abstract: Chemisorption of carbon monoxide on the (110) surface of iridium

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The chemisorption of carbon monoxide on well-characterized clean and oxidized¹ Ir(110) surfaces has been studied in an ultrahigh vacuum environment. On both surfaces, adsorption occurs via a mobile precursor state. At surface temperatures of 90 and 300 K, the adsorption kinetics are independent of whether the surface is clean or oxidized. LEED and thermal desorption data indicate that saturation coverage is approximately 10^{15} molecules/cm² or one monolayer under all conditions. No evidence for physical adsorption of CO exists, even at 90 K. The sticking probability at that temperature is nearly unity until saturation coverage is reached. At 300 K, the sticking probability is unity at low coverages but decreases drastically at 0.8 of saturation coverage. This decrease is attributed to intermolecular repulsions. A kinetic model suggests a repulsive interaction of 2 kcal/mol exists between CO molecules at that coverage.¹ This result is in good agreement with the repulsion expected from a two-dimensional Lennard-Jones model for CO.

In the thermal desorption spectrum from clean Ir(110) saturated with CO, three peaks appear. The intensity ratio for these peaks is 1:2:1 in going from the lowest- to the highest-temperature feature. The completion of the highest-temperature thermal desorption peak is associated with a $p(2 \times 2)$ LEED pattern and a coverage of 0.25 monolayer; the completion of the two other peaks, with a (4×2) pattern and a coverage of a monolayer. For a heating rate of 36 K/s, the features have maxima near 400, 500, and 600 K. Assuming a preexponential factor of 10^{13} s⁻¹ for the desorption rate coefficient, these peaks are associated with desorption energies of 23, 29, and 34 kcal/mol. However, this simple assumption is not valid in this case.

A novel technique has been employed to measure accurately the preexponential factor and the desorption energy in a first-order Arrhenius model as the CO coverage varies.¹ If the coverage dependence of these quantities is ignored, desorption appears to proceed by a higher-order mechanism. The desorption energy is 35 kcal/mol at low coverages and drops to 26 kcal/mol at 0.25 monolayer. This quantity remains constant up to 0.7 monolayer where it decreases once again. The preexponential factor follows a similar decreasing trend. At low coverages, it is 10^{13} s⁻¹. Between 0.25 and 0.7 monolayer, it is 3×10^{10} s⁻¹. The decrease in the preexponential

factor with coverage may be rationalized in terms of activated complex theory. Either the concentration of the activated complex increases with coverage or the CO molecules become more mobile as coverage increases.

The contact potential difference (CPD) on Ir(110) was measured as a function of CO exposure for the clean and oxidized surfaces at 90 and 300 K. Topping plots were constructed from these data. The adsorption kinetics at 90 K were inferred from these plots by assuming that the initial sticking probability is unity. From the topping plots, the permanent dipole moment of a CO molecule is 0.57 debye on the clean surface and 0.74 debye on the oxidized surface. Unlike the case of oxygen adsorption on Ir(110), topping plots for CO adsorption have no discontinuities which may be attributed to changes in binding sites.¹ Hence, the two LEED patterns on clean Ir(110) do not result from the drastic changes in binding sites but are produced by a continuous compression of the adlayer. This is in keeping with ideas used to explain CO adsorption on other Group VIII metal surfaces. On oxidized Ir(110), a $p1g1$ (2×1) LEED pattern is observed for all CO coverages. The similarity between CO adsorption on the clean and oxidized surfaces indicates that compression must occur on the oxide.

On clean Ir(110), a monolayer of CO produces three features in the *KLL* Auger transition of carbon. From the previously mentioned results, these features cannot be interpreted as resulting from different binding sites. Instead, these are attributed to energy differences in the *KLL* transitions that involve the 3σ , $4\sigma + 1\pi$, and 5σ hole states. Auger spectroscopy was used to infer that thermal cracking of CO on Ir(110) is negligible in the temperature range 90–1000 K since the *KLL* feature of chemisorbed carbon is a single, broad transition.

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