

An X-Ray Photoelectron Spectroscopic (XPS) Investigation of the Decomposition of NO on the Ir(111) Surface

In response to major industrial efforts to develop a useful NO reduction catalyst (1-6), several studies have been carried out in recent years with the aim of ascertaining the properties of NO adsorption on single crystal surfaces of such metals as Pt, Pd, Ni, and Ru (7-11). However, very little work has been done to investigate NO adsorption on single crystal surfaces of other Group VIII metals in spite of many similarities in their catalytic properties (12). The present work consists of a study by X-ray photoelectron spectroscopy (XPS) of the adsorption of NO and its interaction with CO on the Ir(111) surface. To our knowledge, this is the first study of the adsorption of NO on an Ir single crystal surface. In addition to a determination of the details of the reduction of NO per se, this type of investigation is of considerable value in elucidating the reversible oxidation-reduction of the Ir surface during the course of the chemical reaction. The properties of Group VIII transition metal catalysts in their working state depend critically on the effective oxidation state of the surface (13, 14).

The data presented in this Note were all obtained in a Vacuum Generators ESCA-3 photoelectron spectrometer which had both ultrahigh vacuum (UHV) capability (i.e., base pressure $\lesssim 2 \times 10^{-10}$ Torr) and a means for exposing the surface continuously to the desired gases while the XPS spectrum is being recorded. The instrument and our general experimental techniques have been described fully in previous publications (14, 15).

In Fig. 1, we present XPS data for the nitrogen 1s and oxygen 1s binding energy region of the spectrum for various conditions of the Ir(111) surface. Spectra (a) and (b) correspond to the cleanest Ir surface which we were routinely able to obtain. The broad peak of low intensity with a binding energy (with respect to E_F) near 530 eV in the oxygen region [spectrum (b)] is due to oxygen dissolved in the Ir lattice. In a previous study, we demonstrated that this peak is due neither to an impurity atom nor to an intrinsic Ir emission line (14). Furthermore, in this state oxygen is extremely unreactive toward either CO or H₂ even at high temperatures, e.g., 1100°K (14). In contrast, oxygen adsorbed on the Ir(111) surface at $T \gtrsim 500^\circ\text{K}$ reacts with incident CO molecules with a reaction probability of essentially unity (16). The intensity of the peak in spectrum (b) could be routinely obtained by heating the crystal to 1600°K for several seconds. However, further heating did not reduce its intensity. In all subsequent spectra shown in Fig. 1, the smoothed "clean" surface spectrum has been included as a baseline.

In Fig. 1c and d, we show the spectra of the Ir(111) crystal at 170°K in equilibrium with 6×10^{-8} Torr of NO. The peaks in spectra (c) and (d) at 400.2 and 530.5 eV are due to nitrogen and oxygen present on the surface as adsorbed molecular NO. The shoulder in spectrum (d) at approximately 532 eV is due to background CO which adsorbed on the crystal either during cooling (prior to exposure to NO at 170°K)

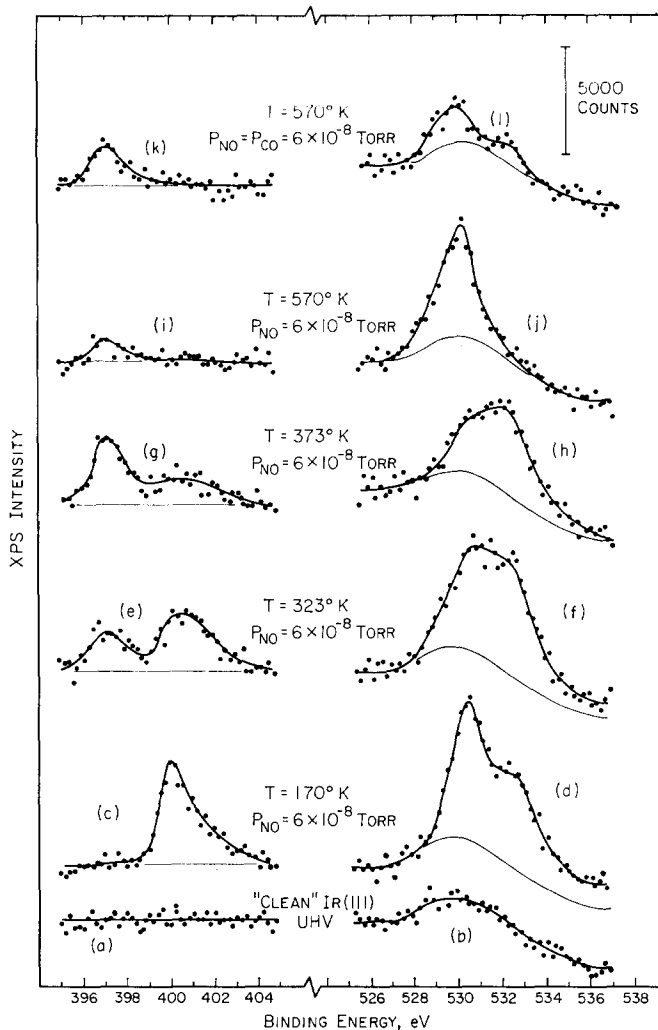


FIG. 1. The XPS data for the nitrogen 1s (on the left) and the oxygen 1s (on the right) region of the spectrum. Spectra (a) and (b) are of the cleanest surface routinely obtainable. Spectra (c)–(j) illustrate the changes occurring when the surface is in equilibrium with 6×10^{-8} Torr NO at the indicated crystal temperatures. Spectra (k) and (l) illustrate the changes occurring when the surface is in equilibrium with equal partial pressures of CO and NO at a crystal temperature of 570°K .

or while the spectrum was being recorded. By limiting both the time for cooling and for recording the spectrum to a minimum (approximately 20 min), the intensity of the CO contribution to the spectrum was limited to that shown in Fig. 1d.

In Fig. 1e–h, we illustrate the changes which occur in the spectra as the crystal is heated from 170 to 323 and 373°K in

6×10^{-8} Torr NO. After each temperature was attained, several minutes elapsed before recording the spectrum in order to ensure equilibrium was established. These spectra exhibit a decrease in the concentration of the molecularly bound NO. This decrease is due in part to desorption of molecular NO but is also partially due to decomposition of surface NO as ev-

idenced by the appearance of adsorbed atomic nitrogen with a binding energy of 397.2 eV. This assignment of atomic and molecular levels is made by the established principle that the core level binding energies are greater for molecular adsorbates than for those bound atomically (17, 18). The absence of molecular complexes such as NCO on the surface was verified by inspecting the valence band density of states using ultraviolet photoelectron spectroscopy (19). Apparently, the atomic oxygen peak in spectrum (h) is not very pronounced due to surface oxygen removal by reaction with adsorbed CO. These results indicate that the dissociation of adsorbed NO is an activated process on Ir(111).

In Fig. 1i and j, we present the spectra of the Ir(111) surface at 570°K in equilibrium with 6×10^{-8} Torr NO. At this temperature, the desorption both of NO and its decomposition product N₂ is probably rapid. For example, on Pt(111) it has been found that the desorption peaks of NO, N₂, and O₂ are observed at 490, 513, and 920°K, respectively, independent of the initial room temperature NO surface coverage (20). Thus, analogously, in spectra (i) and (j) at 570°K we observe a small concentration of adsorbed atomic nitrogen with a binding energy of 397.2 eV and an appreciable concentration of adsorbed atomic oxygen with a binding energy of 529.8 eV. In spectrum (j), the adsorbed CO concentration is quite small, and the background pressure of CO is sufficiently low to allow adsorbed atomic oxygen to accumulate on the surface. Based on our previous work concerning the adsorption of oxygen on Ir(111), we can estimate that the peak in spectrum (j) corresponds to a surface coverage of approximately 4×10^{14} atoms/cm² (14, 15). This is approximately half the value of the saturation coverage of oxygen on Ir(111) at room temperature.

Since spectrum (j) indicated an appreciable oxygen concentration on the surface, it was felt that the accumulation of adsorbed oxygen might be blocking sites for the decomposition of NO. To test this hypothesis, 6×10^{-8} Torr CO was admitted into the vacuum chamber, and spectra (k) and (l) were recorded with equal partial pressures of CO and NO over the crystal. In spectrum (k), an increase in the intensity of the atomic nitrogen peak was observed, and in spectrum (l) a decrease in the intensity of the atomic oxygen peak was observed. The decrease in the atomic oxygen peak was not at all unexpected since adsorbed oxygen reacts with essentially unit probability with incident CO molecules in this temperature regime (16). The more important result is the observed increase in the intensity of the atomic nitrogen peak between spectra (i) and (k). Evidently, adsorbed oxygen blocks sites which could otherwise catalyze the NO decomposition reaction. The increase in the concentration of adsorbed nitrogen is consistent with an increased rate of NO decomposition since, at a constant temperature, the rate of N₂ desorption should increase with nitrogen coverage.

There is an alternate explanation of these results which, although less likely intuitively, may not be discounted *a priori*. The increased surface nitrogen concentration in spectrum (k) compared to that in spectrum (i) could be a reflection of an increased activation energy for desorption of N₂ as the surface oxygen concentration decreases. An increase in the activation energy for N₂ desorption might allow the surface nitrogen concentration to increase without an increase in the rate of N₂ desorption. We consider this not to be a likely explanation of our results for the following reasons. The rate of removal of nitrogen atoms from the surface by N₂ desorption must balance the rate at which

nitrogen atoms adsorb (via the dissociative chemisorption of NO) in our steady-state experiment. If the rate of N₂ desorption does not increase, then, of necessity, the rate at which NO decomposition produces nitrogen adatoms does not increase. However, this would imply that an NO molecule incident on a rather clean Ir(111) surface has no greater probability of adsorbing and subsequently decomposing than an NO molecule incident on an Ir(111) surface with an appreciable oxygen adatom concentration. This unlikely eventuality causes us to interpret the increase in surface nitrogen concentration [compare spectra (i) and (k)] in terms of an enhanced N₂ desorption rate.

Inhibition in the rate of decomposition of NO by adsorbed oxygen has been reported previously in studies carried out over supported Pt, Cu, and Ir catalysts (21-23). However, a different type of inhibition of the NO decomposition can also occur on supported catalysts if a sufficient excess of CO is present (4). Presumably, this occurs by adsorbed CO blocking the adsorption of NO. Thus, optimization of the rate of decomposition (reduction) of NO requires the proper ratio of CO to NO partial pressures.

In conclusion, we have demonstrated that XPS can play a very useful role in understanding the mechanism of surface reactions by giving direct information concerning the concentrations of adsorbed reacting species and/or poisons likely present on the real catalyst surface *during the course of the catalytic reaction*.

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