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Nitric Oxide Adsorption and Decomposition on the (111) and (110) Surfaces of Iridium[1]

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Ultraviolet and X-ray photoelectron spectroscopies, UPS and XPS, have been used to study the adsorption states of NO on the Ir(111) and Ir(110) surfaces. Two states of approximately equal population are found on Ir(111), whereas one state predominates on Ir(110). The predominant state on Ir(110) decomposes thermally at a significantly higher temperature than the two states on Ir(111). Steady-state NO decomposition studies demonstrate that Ir is a better decomposition catalyst than a reduction catalyst, and the presence of CO is required to prevent poisoning by a surface oxide. The formation of a surface oxide of low chemical reactivity begins at a significantly lower temperature with NO as the oxidizing agent than with O_2.

1. INTRODUCTION

The importance of the catalytic decomposition of NO in automotive emission control as well as the relative simplicity of the process makes it well suited for fundamental research into its microscopic reaction dynamics (*1–3*). For this reason, a number of photoemission studies have appeared recently concerning the interaction of NO with the surfaces of single crystals of such metals as Pt, Pd, Ni, and Ru (*4–7*). However, in spite of the well-known similarities of the catalytic properties of these metals to those of Ir, very little has been published concerning the interaction of NO with single crystal surfaces of Ir (*8–10*). In a previous letter, we reported a preliminary study of the decomposition of NO on Ir(111) (*9*). The present studies are an extension of that work and increase the scope of our understanding of the microscopic surface processes.

2. EXPERIMENTAL

The data reported in this paper were obtained with a Vacuum Generators ESCA-3 spectrometer (*11, 12*). The instrument included AlKα and MgKα X-ray sources and a rare gas resonance lamp for HeI and HeII radiation. The base pressure of the chamber was $\leq 2 \times 10^{-10}$ Torr, and

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all clean surface spectra were recorded in this ultrahigh vacuum. For gas adsorption experiments, the system design permitted either discrete exposures or a continuous flow of the gas over the crystal surface during the recording of the photoelectron spectra. The spectra were obtained in a multiscan mode by an on-line PDP-8 minicomputer. For each of the steady-state experiments, the clean surface was exposed to NO and/or CO at the indicated temperature for at least 5 min before the spectrum was recorded in order to allow the concentration of adsorbed species to come to equilibrium. The flow of the gases was continued during the 20-min accumulation time of the spectrum to maintain equilibrium while keeping the background level of contaminating gases in the 10^{-10} Torr range. As expected, this procedure held the level of extraneous surface contamination below 5% of a monolayer, thus insuring that the spectra reflect the equilibrium surface conditions.

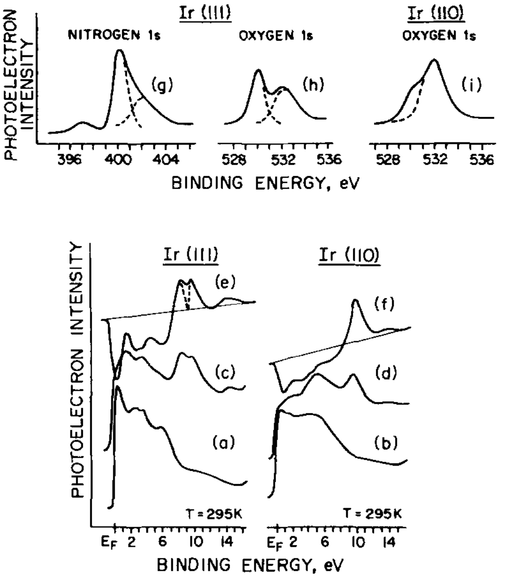

FIG. 1. HeII UPS data for (a) clean Ir(111) surface, (b) clean Ir(110) surface, (c) (111) surface saturated with NO, and (d) (110) surface saturated with NO. The difference spectra of (e), (c) minus (a), and (f), (d) minus (b), are also shown. XPS data for the NO saturated (111) surface are shown in (g) and (h) for the nitrogen 1*s* and oxygen 1*s* core levels. For the NO saturated (110) surface the oxygen 1*s* core level is shown in (i).

3. RESULTS AND DISCUSSION

The results presented in Fig. 1 establish the fundamental difference in the adsorption states between NO adsorbed on Ir(111) and on Ir(110). The spectra (a) and (b) are HeII ($h\nu$ = 40.8 eV) spectra of the clean Ir(111) and (110) surfaces. Spectra (c) and (d) are of these surfaces following exposure to a saturation coverage of NO at a surface temperature of 295 K. The difference spectra, obtained by subtracting the clean surface spectra from the corresponding NO + Ir spectra, are presented in (e) and (f), and they reflect the changes induced by the adsorption of NO. The different character of the NO adsorption between the two crystallographic orientations is immediately apparent from the large two-peak structure seen for Ir(111) and the single peak seen for Ir(110). In connection with this, it is interesting to note that two adsorption states have been found for NO chemisorbed on the close-packed surface of Ru by high-resolution electron energy loss spectroscopy (*13*). The X-ray photoelectron spectra ($h\nu$ = 1486.6 eV) for these surface conditions exhibit analogous structures. Spectrum (g), of the nitrogen 1*s* level, and (h), of the oxygen 1*s* level, show clear evidence of the existence of two adsorption states for NO on Ir(111). The oxygen 1*s* spectrum for NO on Ir(110), (i), also shows evidence for one predominant state with a shoulder at lower binding energy.

The results presented in Fig. 2 illustrate the sharply different behavior of NO on the (111) and (110) surfaces when the surface temperature is raised in steps in a constant flow of NO at 5×10^{-8} Torr. On Ir(111) at 223 K, the two adsorption states of NO are clearly observed in 2(a) and (b). As the temperature is raised to

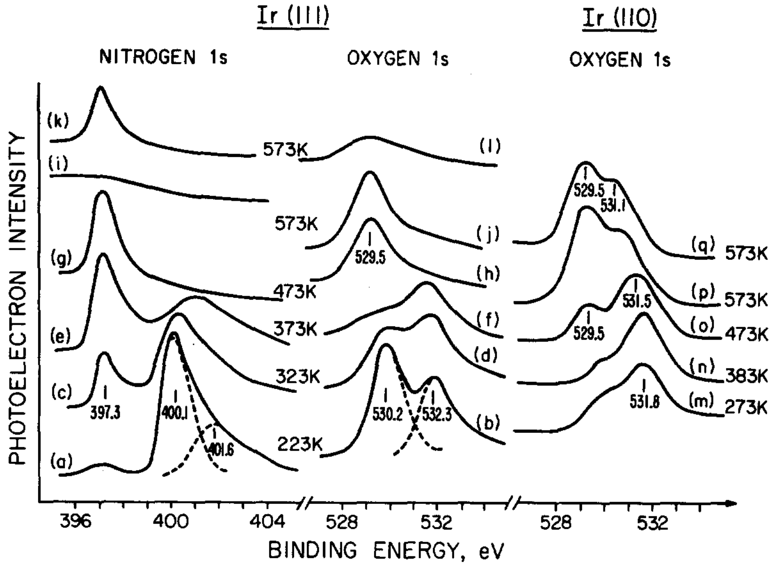

FIG. 2. XPS data for Ir(111) and Ir(110) in equilibrium with 5×10^{-8} Torr NO at the indicated surface temperatures. Spectra (a) through (j) and (m) through (p) were obtained during a continuous flow of pure NO. For spectra (k), (l), and (q), 5×10^{-8} Torr of CO was added to the NO.

323 K, 2(c) and (d), the NO state which produces peaks at 400.1 and 530.2 eV is diminished sharply due to dissociation, and a peak appears at 397.3 eV indicating the presence of adsorbed nitrogen atoms. Temperatures of 373 K, 2(e) and (f), and 473 K, 2(g) and (h), complete the removal of both states of adsorbed NO. The lack of a substantial atomic oxygen peak at 373 K in (f) implies that some mechanism is operating to remove this adstate, a mechanism which is at present unidentified. The only remaining adsorbates at 473 K are atomic nitrogen at 397.3 eV and atomic oxygen at 529.5 eV. At 573 K, 2(i) and (j), the nitrogen is desorbed from the coadsorbed overlayer consisting of atomic nitrogen and oxygen. This is clarified by admitting a partial pressure of CO equal to the NO partial pressure, 2(k) and (l). The oxygen concentration is considerably diminished by reaction with CO and the resulting cleaner surface permits an increased coverage by atomic nitrogen at 397.3 eV, i.e., the presence of oxygen decreases the binding energy of the nitrogen to the surface.

These characteristics on Ir(111) may be contrasted with the behavior of NO on Ir(110). The NO states on Ir(110) are practically unaffected by heating to 273 and 383 K as seen in 2(m) and (n). The NO state at 531.8 eV in Fig. 2(m) shifts slightly to 531.5 eV in Fig. 2(o) upon heating from 273 to 473 K. However, between 473 and 573 K in Fig. 2(p), this state disappears and is replaced by a peak at 531.1 eV. Such an oxygen state at 531.1 eV has been observed on Ir(110) following high temperature oxidation by O_2. Thus, we interpret the 531.1 eV peak as subsurface oxygen resulting from diffusion of oxygen at or near the surface into the subsurface region. Both of these states of atomic oxygen are quite unreactive with respect to CO. Fig. 2(q) differs from Fig. 2(p) in that a pressure of CO equal to that of NO was exposed to the surface. Clearly, there was little effect on the oxygen states. Finally, the data of Fig. 2 show that the formation of the state at 529.5 eV occurs at a higher temperature on Ir(110) than on Ir(111). This is seen by noting that the 529.5 eV peak increases in intensity from

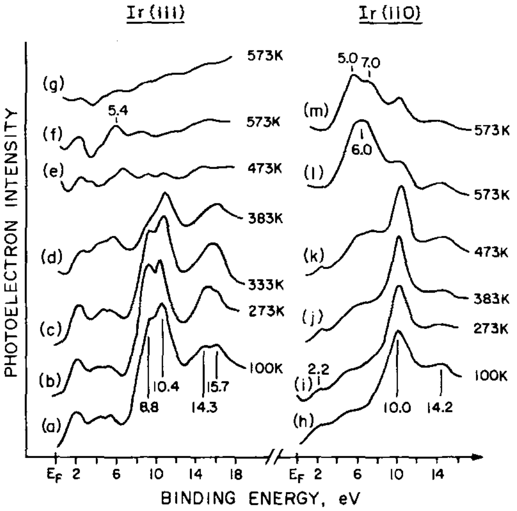

FIG. 3. HeII UPS data for Ir(111) and Ir(110) in equilibrium with 5×10^{-8} Torr of NO for the indicated surface temperature are presented in (a) through (f) and (h) through (l), respectively. In spectrum (g) and (m), 5×10^{-8} Torr CO was added to the NO. All spectra are difference spectra relative to the clean surface.

473 to 573 K on Ir(110), while on Ir(111) it has already reached to maximum intensity at 473 K. The differences in the formation temperature and in reactivity with respect to CO mean that the 529.5 eV state is substantially different on the two surfaces.

Figure 3 presents the HeII spectra of Ir(111) and (110) in a flow of NO at 5×10^{-8} Torr. The range of temperatures parallels that of Fig. 2. The data presented are difference spectra which reflect the spectra of the adsorbed species. The two sets of doublets on Ir(111) at 100 K, 3(a), again provide evidence of two adsorption states for NO. At higher temperatures, the adsorption state producing the peaks at 8.8 and 14.3 eV disappear first, as seen in 3(b), (c), and (d). At 473 K, 3(e), even the state with peaks at 10.4 and 15.7 eV has been removed. In 3(f) at 573 K, the peak at 5.4 eV is apparently a reflection of the atomic oxygen on the surface since it disappears in 3(g) when CO is admitted at the same partial pressure as NO. On most transition metals, atomic nitrogen yields a peak near that of atomic oxygen, but the width is greater so the maximum intensity is lower. On Ir(110), the behavior of NO is quite different. At 100 K, 3(h), one adsorption state of NO predominates. This state is substantially unaffected by heating to temperatures of 273, 383, and 473 K as seen in 3(i), (j), and (k). By 573 K, 3(l), the concentration of this state of NO is reduced, and additional structure at lower binding energy is apparent. This structure is due predominantly to the unreactive surface oxide discussed above. This is demonstrated in 3(m) where CO was admitted at a partial pressure equal to that of NO. This would have removed any reactive oxygen adatoms; yet the spectrum is altered only by a slight reduction at 6 eV to give peaks at 5 and 7 eV. This indicates the substantial concentration of unreactive oxide on the (110) surface.

Figure 4 presents two sets of data from which the plots of Fig. 5 are made. These data quantify the concentrations of the adsorbed species on Ir(111) during NO decomposition and reaction with CO. Fig. 4(a) is a set of nitrogen 1*s* and oxygen 1*s* spectra for heating Ir(111) in 3×10^{-8} Torr of NO. Figure 4(b) is the corresponding set for Ir(111) in NO and CO each at 3×10^{-8} Torr. The concentrations of the adsorbed species have been calibrated against spectra of oxygen on Ir(111) and CO on Ir(111) for which the coverage was known exactly from the LEED patterns (*9*). The surface coverage of CO in Fig. 5(e) was corrected for the intensity contribution at 532.3 eV due to NO [see Fig. 5(a)]. This correction was made by using the N 1*s* intensities in Fig. 4(b) to calculate the O 1*s* intensity that must be subtracted to correct the CO coverage. In Fig. 5(a) and (b), the NO state at 530.2 eV begins to desorb between 200 and 300 K, before any decomposition is evident. It is clear that between 300 and 350 K, molecular NO is decomposing and atomic

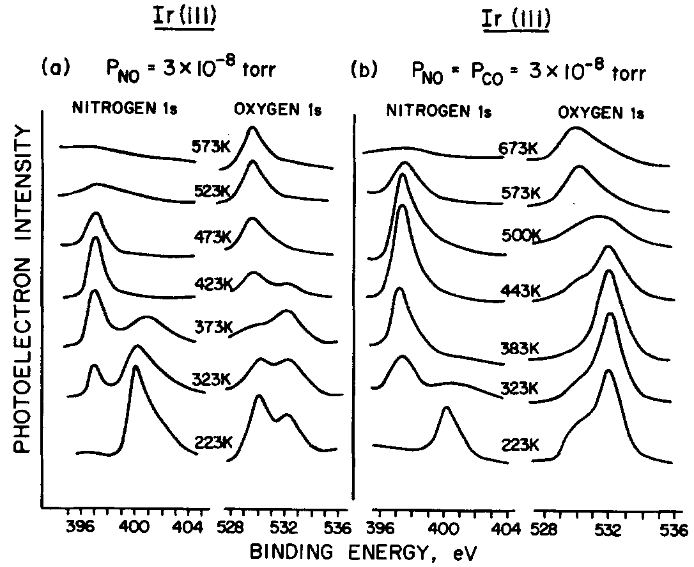

FIG. 4. XPS data for the Ir(111) surface in equilibrium with (a) 3×10^{-8} Torr NO, and (b) NO and CO each at 3×10^{-8} Torr, for a variety of surface temperatures.

nitrogen is appearing on the surface. However, the decrease in NO is not paralleled by an equal increase in atomic oxygen and nitrogen. Evidently some process is operating to remove the atomic oxygen, perhaps desorption of NO_2 although we have no independent verification of this desorption.

Above 420 K, the atomic nitrogen concentration decreases, probably because thermal desorption of N_2 is occurring due to a lowering in the binding energy of the nitrogen by the adsorbed oxygen. This is evidenced by the rapid decrease of atomic nitrogen and the simultaneous increase in

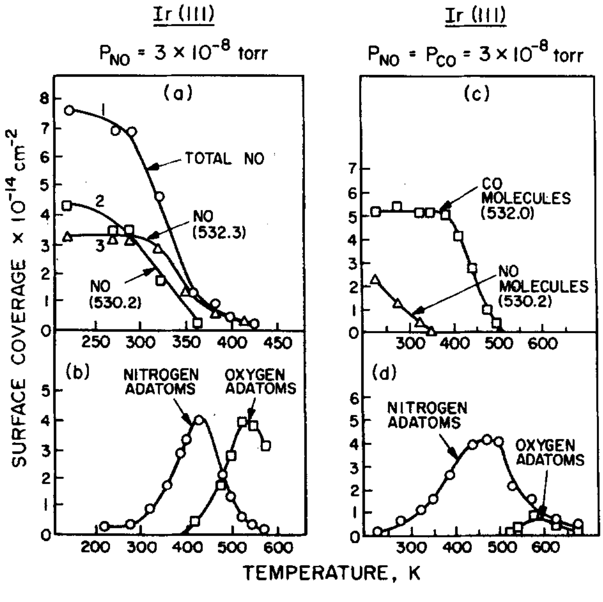

FIG. 5. Concentrations of the adsorbed species on Ir(111). (a) and (b): pure NO at 3×10^{-8} Torr; (c) and (d): NO and CO each at 3×10^{-8} Torr. The data are taken from Fig. 4.

atomic oxygen above 420 K. This means Ir is a better decomposition catalyst than a reduction catalyst for NO.

Clearly, different behavior is observed for the equal partial pressures of CO and NO in Figs. 4(b), 5(c), and 5(d). A large concentration of adsorbed CO is present on the surface until about 400 K. The concentration of molecular NO decreases at a somewhat lower temperature than for pure NO, and the concentration of atomic nitrogen is appreciable over a wider temperature range. The low concentration of atomic oxygen indicates that the presence of CO greatly inhibits the formation of any unreactive surface oxide. These results emphasize the crucial role played by CO in the reduction of NO on Ir(111). The desorption of N_2 is rapid at 450 K in the absence of CO, leaving a surface oxide which poisons further catalytic reduction. In the presence of CO, however, Ir becomes an excellent NO reduction catalyst since CO maintains the surface in its reduced (active) state.

The results of Figs. 4 and 5 may be outlined in the following processes. On Ir(111) in 5×10^{-8} Torr of NO, the reactions occurring are the following:

$$\underbrace{NO_{(ads)} + NO_{(ads)}}_{\text{2 states}} \overset{200\ K-300\ K}{\rightleftarrows} 2\,NO_{(g)},$$

with equilibrium shifting to the right with increasing temperature,

$$\underbrace{NO_{(ads)} + NO_{(ads)}}_{\text{2 states}} \xrightarrow{300\ K-350\ K} N_{(ads)} + O_{(ads)} + NO_{(ads)}$$

$$NO_{(ads)} \xrightarrow{T\ >\ 350\ K} N_{(ads)} + O_{(ads)} \rightarrow N_{2(g)} + O_{(ads)}$$

On Ir(111) in 5×10^{-8} Torr of NO and CO, the reactions occurring are the following:

$$NO_{(ads)} + CO_{(ads)} + CO_{(g)} \xrightarrow{200\text{–}350\ K} N_{(ads)} + CO_{2(g)} + CO_{(ads)}$$

$$NO_{(g)} \rightarrow N_{(ads)} + O_{(ads)} \xrightarrow[CO_{(g)}]{350\text{–}500\ K} N_{(ads)} + CO_{2(g)}$$

$$NO_{(g)} \rightarrow N_{(ads)} + O_{(ads)} \xrightarrow[CO_{(g)}]{500\text{–}600\ K} N_{2(g)} + CO_{2(g)}$$

Figure 6 provides considerably more insight into the oxidation of the Ir(111) surface. The data presented are the concentration of the unreactive surface oxide produced at various temperatures by exposing the surface to NO and O_2 (separately). The oxygen 1*s* spectra were obtained in the following manner. The clean Ir(111) surface was heated to the indicated temperature and then exposed to NO or O_2 at 10^{-6} Torr for 40 min. The NO or O_2 was then pumped out and the surface was exposed to 30×10^{-6} Torr-s of CO to remove any reactive surface oxygen. The surface was then heated in ultrahigh vacuum to 650 K to remove any adsorbed CO. The oxygen 1*s* spectrum was then recorded. The plots above the spectra are of the concentration of oxygen atoms in the unreactive surface oxide as a function of the temperature of formation. They indicate a significantly different temperature for the onset of oxidation for NO and O_2. For O_2, the onset is near 600 K, whereas for NO it is approximately 400 K. Similar behavior has been observed previously for Pd by Conrad *et al.* (*14*), and it is probably the result of the marked difference in the exothermicity of oxidation of Ir by NO and O_2. If this explanation is

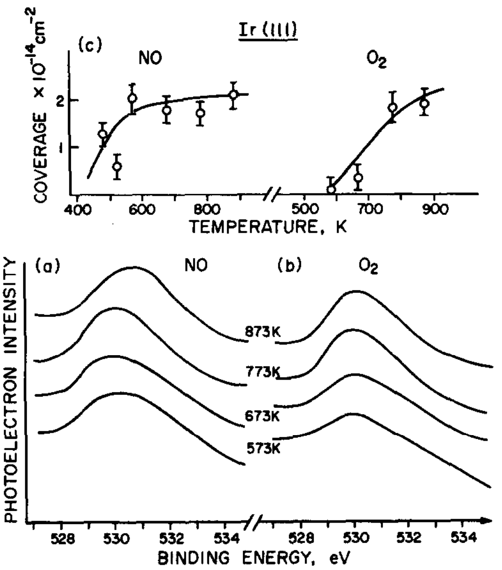

FIG. 6. XPS spectra of the unreactive surface oxide on Ir(111) formed by exposure to (a) NO and (b) O_2 at the indicated temperatures (see text). The coverage of the oxide as a function of the temperature at which it was formed is shown in (c).

correct, it implies that the oxidation by NO is a concerted process in which the formation of N_2 with its very large exothermicity helps drive the oxidation process.

4. CONCLUSIONS

Our major conclusions may be summarized as follows:

(1) Ultraviolet and X-ray photoemission show two adsorption states with comparable saturation concentrations for NO on Ir(111). On Ir(110), a single adsorption state predominates with a small concentration of a second state.

(2) The NO adsorption state on Ir(111) giving rise to the photoemission peaks with lower electron binding energy decomposes at a lower temperature than the state with the higher electron binding energies.

(3) The predominant NO adsorption state on Ir(110) decomposes only at a higher temperature than either state on Ir(111).

(4) Steady-state decomposition of NO over Ir(111) with and without the presence of CO establishes that Ir is a better decomposition catalyst than a reduction catalyst. The presence of CO to act as a reducing agent permits Ir to function as an excellent NO reduction catalyst by preventing the accumulation of a surface oxide (poison).

(5) The formation of an unreactive surface oxide on Ir(111) begins at 400 K in the presence of NO, but only at 600 K in the presence of O_2.

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