**Title and Subtitle**
Phosphine Chemistry on Mo(110) and Oxidized Mo(110)

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**Abstract**
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Phosphine Chemistry on Mo(110) and Oxidized Mo(110)


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The adsorption and desorption of phosphine and the oxidation of phosphorus on Mo(110) and oxidized Mo(110) have been studied by using Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), and low-energy electron diffraction (LEED). Both molecular desorption and dissociative processes were observed on Mo(110), leaving adsorbed P(1s) species in a c(4X1) overlayer structure. The P(1s) species do not undergo diffusion into the bulk below 1000 K. On the oxidized Mo(110) surface, the phosphine adsorption and dissociation process was inhibited significantly. Phosphorus on the Mo(110) surface could be oxidized to produce PO(g) and PO3(g) species near 900 K, as detected by line-of-sight mass spectrometry; neither P2O5(g) nor P2O3(g) was observed.

I. Introduction

Certain phosphorus compounds used in pesticides, herbicides, and chemical agents are extremely hazardous materials. Degradation of these chemicals into less harmful substances using heterogeneous catalytic methods is therefore of great importance. The surface chemistry of phosphine and organophosphorus compounds has been studied on both single-crystal metals and semiconductors and on supported metal catalysts and oxides. The decomposition and oxidation of the organophosphorus compound dimethyl methylphosphonate on certain single-crystal surfaces, Ni(111), Pd(111), Mo(110), and Pt(111), have also been investigated. Studies on Mo(110) and Pd(111) showed that the rate-limiting surface process to establish a continuous oxidation reaction was the regeneration of catalytically active sites which were free of chemisorbed phosphorus. Phosphorus is removed by the production of volatile phosphorus oxides. On this basis, we have selected the catalytic oxidation of elemental phosphorus as a key issue for study. The oxidation of phosphine has also been studied recently on a supported MoO3 catalyst. Here, infrared spectroscopy was used to observe surface intermediates present in the oxidation process, and a final stage of phosphorus oxide desorption was observed at about 800 K.

As part of the continuing systematic comparative study of phosphorus oxidation on a variety of transition metals and oxides, this paper reports the study of the oxidation of elemental phosphorus on a Mo(110) single crystal and also on MoO3 thin films prepared by adsorbing oxygen on Mo(110) at high temperature. A related study of the surface chemistry of phosphine on Mo(110) is also presented here.

II. Experimental Section

The experiments were performed in a stainless steel ultrahigh-vacuum system described in detail previously. The typical system base pressure was less than 1 X 10^-10 mbar. The ultrahigh-vacuum chamber is equipped with a differentially pumped and digitized quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), a cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), low-energy electron diffraction (microchannel plate amplifier, LEED), and two calibrated and collimated capillary array dosers. The QMS was located in a differentially pumped shield containing a 1.6-mm-diameter aperture. This arrangement permits study of temperature-programmed desorption from the front face of the Mo(110) crystal by line-of-sight detection using the mass spectrometer. The initial crystal cleaning procedure is described elsewhere. Each day the crystal was cleaned by cycles of oxygen treatment at 1100 K (carbon removed) and Ar+ sputtering (1 keV, 1100 K) (O, P, and S removed) followed by annealing to 1200 K in vacuum.

These procedures produced a clean Mo(110) surface within the detection limit of AES, and a sharp (1 X 1) LEED pattern was obtained after these procedures. The Auger spectrum of the clean Mo(110) is shown in Figure 1. The surface was considered to be free of sulfur when the [Mo + S] (151 eV)/Mo(187 eV) ratio reached a steady value of 0.16 and was considered to be free of phosphorus when the [Mo + P] (120 eV)/Mo(187 eV) ratio reached a steady value of 0.21. The values of the P(120 eV)/Mo(187 eV) ratio reported in this paper were obtained from the
difference between the measured [Mo + P](120 eV)/Mo(187 eV) value and 0.21.

Phosphine and deuterium gas were dosed to the crystal surface through a calibrated microcapillary array collimated beam doser. The doser axis was oriented normal to the surface and delivered a flux of $3.19 \times 10^{17}$ cm$^{-2}$ s$^{-1}$ to the surface when the gas line pressure was 0.5 Torr. At the crystal position 12 mm from the doser, a geometrical interception factor of 0.3 was employed to calculate the flux received by the crystal. In the phosphorus oxidation experiment, oxygen was delivered to the system through a leak valve to a steady system pressure in the 10$^{-6}$–10$^{-5}$ mbar range while the crystal was positioned and heated in front of the QMS.

Phosphine was obtained from Matheson Gas Products (99.9% pure). Three freeze–pump–thaw cycles were performed before it was used. Deuterium was obtained from Cambridge Isotope Laboratories (D, 99.8% pure).

III. Results

Auger Spectroscopy Studies of P/Mo(110). Figure 1 shows the Auger spectrum of a clean Mo(110) single crystal. Also shown are the P(LMAO) peak after phosphine decomposition and the O(KLL) peak of MoOx (OK20 eV)/Mo(187 eV) ratio $y = 0.3$. It was found from P/Mo Auger ratios that the surface phosphorus did not diffuse into the Mo(110) crystal in the temperature range 600–1000 K. This result differs from studies on P/Pt(111)$^{34}$ where surface phosphorus diffused into the bulk at 600–900 K. An analysis of the Auger intensity ratios suggests that an atom ratio P/Mo of about 0.4 exists in the depth of Auger sampling for the PH$_3$ saturated surface. In addition, it was found that electron irradiation (3.0 keV, 8 $\times$ 10$^{17}$ e/cm$^2$) did not result in perceptible loss of surface phosphorus by electron-stimulated desorption, indicating that Auger spectroscopy was not a perturbing probe for measurements of phosphorus surface coverage.

Adsorption and Desorption of PH$_3$. A series of TPD experiments were performed for different PH$_3$ exposures at 80 K. Adsorbed phosphine was partially desorbed, and partially desorbed, producing P(a) and H(a). H(a) desorbed as H$_2$, and phosphorus was left on the surface of the crystal after heating. Figure 2 shows phosphine TPD spectra from the Mo(110) surface for increasing exposure to phosphine. At low exposures, there was no phosphine desorption. All of the phosphine decomposed completely either upon adsorption at 80 K or upon heating. At intermediate exposures, only one phosphine desorption state was detected. This desorption state was due to the first layer of chemisorbed phosphine. At higher exposures, a low-temperature shoulder (85 K) developed; it originates from multilayer physisorbed phosphine.

Figure 3 shows a set of hydrogen desorption spectra from the TPD of dissociatively adsorbed PH$_3$ on Mo(110) for increasing PH$_3$ exposure. At low PH$_3$ exposures, the hydrogen desorption behavior was similar to that for hydrogen desorption from clean Mo(110). As the PH$_3$ exposure was increased, two other low-temperature H$_2$ desorption states developed. When the lowest-temperature H$_2$ desorption state reached saturation, the maximum amount of phosphorus on the surface ($\theta_{PH}=1$) was obtained. Figure 3 also indicates that at higher coverages phosphine began to dissociate at a temperature of 120 K or lower, yielding hydrogen. The saturated hydrogen desorption yield from PH$_3$ adsorption was 1.77 $\pm$ 0.06 times greater than for pure hydrogen desorption from a hydrogen monolayer on clean Mo(110).

The effect of preadsorbed phosphorus on hydrogen adsorption on Mo(110) was studied at monolayer P coverage. Only the highest-temperature H$_2$ desorption state was detected and amounted to 5% of the saturated coverage of hydrogen from PH$_3$.

Figure 4 shows the desorption yield of H$_2$ and PH$_3$ as a function of PH$_3$ exposure. In addition, the buildup of the phosphorus
molecules. recombines with experiment indicates clearly that neither P(a) nor PH3, the isotopically
PHD2
For phaephine desorption, only PH3 was detected. Neither PH2D, crystal at the possible deuterium isotope-exchange products were monitored. denum oxide layers were produced phosphine coadsorption experiment is displayed in Figure 5. Temperature-programmed desorption was carried out after the mixed
same partial pressure were mixed in the gas line. Adsorption of saturated PH3 at
upon adsorption or heating. When the phosphine exposure increased, the dissociation of PH3 reached saturation (at an exposure of about 4 \times 10^{-14} \text{PH}_3 \text{ cm}^{-2}), and additional adsorbed PH3 desorbs nondissociatively as PH3. The three measurements conform to each other. Both the H2 desorption yield and the P/Mo Auger ratio reached saturation at an exposure to PH3 of about 4 \times 10^{-14} \text{PH}_3 \text{ cm}^{-2}, and a little below this saturation exposure, phosphine began to desorb.

Isotopic Exchange Studies. To better understand phosphine adsorption and desorption on Mo(110), an isotope-exchange experiment was performed. Deuterium and phosphine at the same partial pressure were mixed in the gas line. Temperature-programmed desorption was carried out after the mixed gas was adsorbed on Mo(110) at 80 K. The result of this deuterium and phosphine coadsorption experiment is displayed in Figure 5. All the possible deuterium isotope-exchange products were monitored. For phosphine desorption, only PH3 was detected. Neither PH3D, PHD3, nor PD3 was produced. For hydrogen desorption, all of the isotopically labeled hydrogen molecules were observed. This experiment indicates clearly that neither P(a) nor PH3(a) recombines with D(a) to produce isotopically labeled phosphine molecules.

A comparison of phosphine desorption from PH3/Mo(110) and from PH3/D2/Mo(110) was made, and the result is shown in Figure 6. Coadsorbed deuterium had no effect on the phosphine desorption kinetics. In addition, the preadsorption of deuterium does not diminish the retention of P(a) from PH3 decomposition on Mo(110).

LEED Studies of P/Mo(110). LEED experiments were also performed. Adsorption of saturated PH3 at 80 K produced no extra LEED beams. After heating the crystal with saturated PH3 to 600-1000 K to leave only P(a) on the crystal, a c(4x1) LEED pattern was observed. This indicates that phosphorus is ordered on Mo(110). Figure 7 shows the LEED patterns observed in these experiments and the phosphorus overlayer structure. A c(4x1) structure corresponds to a coverage of 0.5 P atom/Mo atom.

Adsorption and Desorption of Phosphine on MoO2. Molybdenum oxide layers were produced by exposing the Mo(110) crystal at 1000 K to O2(g). Auger spectroscopy was used to measure the surface composition. One monolayer of molybdenum oxide was produced when the O/Mo(110) ratio was 0.3 (y = 0.3). An oriented oxide layer was produced when the O(520 eV)/Mo(187 eV) Auger ratio was 0.6 (y = 0.6). A much thicker molybdenum oxide layer (y = 4.0) was also prepared.

Temperature-programmed desorption spectra for PH3 on various MoO2 thin films. The y values, [O/Mo], are O(520 eV)/Mo(187 eV) Auger peak-to-peak ratio.

Figure 5. Temperature-programmed desorption spectra following deuterium and phosphine coadsorption on Mo(110). A mixture of deuterium and phosphine at the same gas line partial pressure was used.

Figure 6. Comparison of PH3 TPD spectra from PH3/Mo(110) and from PH3/D2/Mo(110).

Figure 7. (a) LEED pattern of clean Mo(110). (b) LEED pattern of P/Mo(110). (c) c(4x1) P overlayer structure compared to the unreconstructed Mo(110) surface. The P overlayer was produced from a saturated PH3 layer.

Figure 8. Temperature-programmed desorption spectra of PH3 on various MoO2 thin films. The y values, [O/Mo], are O(520 eV)/Mo(187 eV) Auger peak-to-peak ratio.
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On all the MoO₃ layers, the phosphine decomposition was inhibited as was observed for phosphine on iron oxide. On one monolayer of MoO₃ (θ = 0.3), the phosphine decomposition is only 20% of that on Mo(110) as measured by the P/Mo Auger ratio taken after heating. In this case (θ = 0.3), besides phosphine, some hydrogen desorption was also detected. Only phosphine desorption was detected for the thicker molybdenum oxide layer. The chemisorbed PH₃ desorption maximum was shifted to higher temperatures (as the molybdenum oxide layer thickness increased) compared to phosphine desorption from Mo(110). The phosphine desorption kinetics were different on the different oxide layers as displayed in Figure 8.

The adsorption of phosphine on the oriented MoO₃ films (θ = 0.6 and θ = 4.0) was further investigated by Auger electron spectroscopy. Figure 9 shows the AES of Mo(110) and MoO₃ (θ = 0.6) taken before phosphine adsorption and after phosphine thermal desorption. After phosphine desorption, the phosphorus retained on the MoO₃ film was only 1–5% of that retained on Mo(110). This indicates that phosphine decomposition on the oriented molybdenum oxide layers was inhibited extensively below 600 K.

The desorption of H₂O from PH₃/MoO₃ layers was not detected by line-of-sight mass spectrometry.

Phosphorus Oxidation on Mo(110) and MoO₃ (θ = 0.3).

Phosphorus oxidation experiments were performed by programmed heating of the crystal, containing a saturated phosphorus layer, in an oxygen background pressure while monitoring desorbed species from the surface by line-of-sight mass spectrometer measurements. Different oxygen pressures (1 × 10⁻⁴ to 1 × 10⁻¹ mbar) were used. MoO⁺, P₂⁺, P₃⁺ and several kinds of phosphorus oxides were monitored. Only PO⁺ and PO₂⁺ were detected near 1050 K as shown in Figure 10. Because PO₂⁺, P₂O₃⁺, and P₂O₅⁺ were not detected, the desorption species could only be PO and/or PO₂ according to the phosphorus oxides’ cracking patterns. The desorption products are designated as PO₃.

A detailed study of phosphorus oxidation was carried out at various oxygen pressures. Phosphorus on the surface was converted to volatile oxides by temperature programming, and the desorption spectra yielding PO⁺ in the mass spectrometer are shown in Figure 11. From the spectra, a trend could be seen indicating that phosphorus on Mo(110) could be removed from the surface completely by oxidation if the surface temperature was high enough. During the experiments the Mo(110) crystal was heated up to 1210 K, and at oxygen pressures higher than 5 × 10⁻⁷ mbar, phosphorus was removed completely. Auger spectra indicated that there was no phosphorus left on the surface after these oxidation procedures. The phosphorus oxide yields (monitored as PO⁺) as a function of steady-state oxygen pressure are plotted in Figure 12. Here two PO₃ desorption measurements at lower oxygen pressures are incomplete, as indicated by arrows, since some PO₃ species desorb above 1210 K.

The TPD spectra in Figure 11 indicate that there are two PO₃ desorption processes. Both processes shift to lower temperature when the O₂ pressure is increased from 1 × 10⁻⁴ to 1 × 10⁻¹ mbar. The lowest onset temperature for PO₃ desorption from the Mo(110) single crystal was 900 K in 1 × 10⁻⁴ mbar of oxygen.
IV. Discussion

Phosphine Adsorption on Mo(110): Coverage Estimations. The basis for an estimation of the absolute saturation phosphine coverage on Mo(110) is related to the measured yield of hydrogen from the decomposed PH$_3$. Estimations of the saturation coverage of pure hydrogen on Mo(110) range from 0.86 \times 10^{13} to 1.73 \times 10^{13} cm$^{-2}$. It is noted that this upper limit for hydrogen absolute coverage corresponds to 1.2 H/Mo and is probably unrealistic.

We measured that the ratio of hydrogen evolution from a saturated PH$_3$ layer to pure hydrogen (saturated) is 1.77 \pm 0.06. This implies that the PH$_3$ saturation coverage is in the range 0.51 \times 10^{13} to 1.02 \times 10^{13} cm$^{-2}$. Therefore, based on the hydrogen yield from saturated PH$_3$, the phosphorus coverage ranges from 0.36 P/Mo to 0.73 P/Mo, using a Mo atom surface density of 1.4 \times 10^{13} cm$^{-2}$ in the unreconstructed Mo(110) surface.

The c(4\times1) LEED pattern obtained for the P overlayer produced from the saturated PH$_3$ corresponds to 0.5 P/Mo, well within the large range of the saturated absolute P coverage, based on H$_2$ yield measurements.

From Figure 4, it may be seen that an exposure of about 4 \times 10^4 PH$_3$/cm$^2$ leads to PH$_3$ saturation as judged by the yield of the hydrogen. This agrees fairly well with the lower estimate of the PH$_3$ saturation coverage (about 5 \times 10^{14} PH$_3$ cm$^{-2}$) and is consistent with the lower estimate of the saturation coverage of pure hydrogen on Mo(110)$^{12,22}$ and also approximately with the LEED measurement (0.7 \times 10^{15} P/cm$^2$).

Phosphine Bonding to Mo(110). The bond between phosphine and a metal can be compared to that between CO and a metal. The phosphorus lone pair electrons act as an electron pair donor to Mo acceptor atoms, enabling the phosphorus atom in PH$_3$ to adopt a pseudotetrahedral configuration on atop Mo sites. In addition to acting as a σ donor, however, phosphine can act as an π electron acceptor when vacant 3d orbitals of phosphorus interact with nonbonding orbitals of a transition metal, thus increasing the metal-P bond strength. By analogy to PH$_3$ bonding in organometallic compounds, PH$_3$ bonding to Mo(110) sites is assumed. The above argument is traditional for PH$_3$ bonding to a transition metal. It has been suggested recently that P-H σ and π orbitals participate in the π acceptor process for PH$_3$ bonding.$^{24}$

Phosphine Desorption on Mo(110). An analysis of the desorption kinetics of the high-temperature PH$_3$ desorption state with peak maximum at 148 K (Figure 2) yields an extremely low activation energy and preexponential factor which is unrealistic for first-order desorption kinetics for PH$_3$ with a coverage-independent heat of adsorption. A large half-width (about 44 K) for the PH$_3$ desorption process is observed. In contrast, the sharp desorption feature at 84 K exhibits more normal desorption kinetics as judged by its small half-width, although the desorption kinetic order (zero or first order) cannot be determined from these data.

The unrealistic desorption kinetic behavior seen for the 148 K PH$_3$ desorption process may be due to repulsive PH$_3$-PH$_3$ interactions in the overlayer, causing a significant coverage-dependent shift in the activation energy for desorption. Similar effects, due to repulsive dipole-dipole interactions, have been observed for NH$_3$ on Ru(001).$^{13}$

From the D(a) + PH$_3$(a) coadsorption experiment, coadsorbed deuterium had no effect on PH$_3$ desorption, as shown in Figure 6, nor on the coverage of P(a) produced by PH$_3$(a) decomposition. This suggests that deuterium adsorbs on different sites from PH$_3$. Hydrogen is assumed to adsorb in the Mo(110) hollow sites, whereas PH$_3$ is adsorbed on terminal sites of Mo(110). Also, from the deuterium isotope exchange experiment (Figure 5), we found that molecular phosphine desorption (about 148 K) did not occur via a recombination process, again suggesting that PH$_3$- (a) and H(a) behave independently on Mo(110).

PH$_3$ Adsorption on MoO$_x$. A comparison between the thermal desorption results for PH$_3$ on Mo(110) and PH$_3$ on MoO$_x$ (Figures 2 and 8) indicates that MoO$_x$ surfaces result in the desorption of PH$_3$ at higher temperatures than observed on Mo(110). Thus, the decomposition of PH$_3$ is retarded by surface oxygen and/or the bond between PH$_3$ and the surface is strengthened in the presence of surface oxygen. Figure 8 indicates that the bonding energy of PH$_3$ to MoO$_x$ increases somewhat as x increases, ultimately leading to a broad PH$_3$ desorption state with the TPD peak maximum near 350 K.

V. Summary and Conclusions

The interaction of PH$_3$ with Mo(110) and MoO$_x$ films on Mo(110) has been studied in the temperature range 80–1210 K. The following results have been found.

1. PH$_3$ adsorption on Mo(110) results in H$_2$ desorption at temperatures near 120 K at the highest PH$_3$ coverages. Thus, phosphine decomposition begins near or below 120 K on Mo(110), producing adsorbed P or PH$_3$ species.

2. At high PH$_3$ exposures, the presence of undecomposed chemisorbed PH$_3$ was found on the basis of PH$_3$ thermal desorption in two low-temperature PH$_3$ desorption processes. Isotopic studies with D(a) + PH$_3$(a) indicate that neither exchange nor recombination reactions to produce PH$_3$(g) occur. In addition, adsorbed deuterium does not diminish the capacity of Mo(110) to chemisorb PH$_3$.

3. No evidence for diffusion of adsorbed P into the Mo(110) bulk was obtained in the temperature range 600–1000 K.

4. The hydrogen thermal desorption was measured for various PH$_3$ exposures. Higher PH$_3$ coverages produce H$_2$ desorption at temperatures below that for pure H$_2$ desorption from Mo(110) as a result of a P(a)-H(a) repulsive interaction.

5. LEED studies of P/Mo(110) produced from the decomposition of a saturated PH$_3$ layer show the production of a c(4\times1) overlayer, corresponding to 0.5 P/Mo. Studies of H$_2$ desorption from PH$_3$ and of the P/Mo Auger intensity indicate a saturation coverage range of PH$_3$ corresponding to 0.36–0.73 P/Mo, where only the decomposed PH$_3$ is measured in this case.

6. Phosphine dissociation on MoO$_x$ films was inhibited compared to dissociation on the clean Mo(110). For a three-
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dimensional MoO₃ layer, only 1–5% of the P/Mo Auger ratio could be obtained by monolayer PH₃ decomposition compared to clean Mo(110). MoO₃ layers retain undissociated PH₃ up to 350 K, whereas PH₃ desorption from Mo(110) is completed below 200 K.

7. Both PO⁺ and PO₂⁺ mass spectral cracking products were observed near 900 K during phosphorus oxidation over Mo(110) in O₂(g). Neither P₂O₅ nor PO₃ products are produced under the condition of this ultrahigh-vacuum experiment.

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References and Notes