

Adsorption of Oxygen on Polycrystalline Rhodium at Low Temperatures

TATSUO MATSUSHIMA

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

Received March 1, 1983; revised August 4, 1983

The adsorption and desorption of oxygen was studied on well-polished polycrystalline rhodium surfaces over the temperature range 120 to 1350 K by means of thermal desorption, isotope tracer, and Auger electron spectroscopy. Isotope-exchange experiments indicate that the low temperature desorption peak (~160 K) results from molecular adsorption, while the high temperature peak (600-1200 K) results from atomic adsorption. At 120 K oxygen molecules are partially dissociated to adatoms.

INTRODUCTION

Oxygen is known to adsorb molecularly and dissociatively on platinum (1-3). The vibrational modes of these adsorbed species have recently been analyzed on Pt(111) and stepped surfaces by using electron energy-loss spectroscopy (4-9). A similar analysis of the molecular adsorption has been reported on Ag(111) (10) and Pd(100) (11). From the vibrational frequencies it has been concluded that the double bond in free O₂ is reduced to a single bond in the adsorbed state. The O-O bond of the O₂ admolecule seems to be very weak (3, 5, 7, 10, 11). The admolecule may have high reactivity to other coadsorbed species. In fact the reaction with coadsorbed CO to produce CO₂ was observed around 160 K on Pt(111) (12). Previous authors (13) have expected only a few noble metals to be able to adsorb oxygen molecularly. Therefore, it is interesting to investigate the molecular adsorption of oxygen on the other metals.

The adsorption and desorption of oxygen on Rh(111) at low temperatures has been extensively studied by Thiel *et al.* (14). They have concluded that oxygen adsorbs in a disordered state at 100 K and orders irreversibly into a (2 × 2) structure upon heating to T ≥ 150 K. This behavior is quite similar to that of oxygen on Pt(111), where

oxygen admolecules are dissociated around this temperature (2, 4, 7). Very recently Fisher and Schmieg have studied oxygen adsorption on Rh(100) at low temperatures (15). They found the presence of a molecular state. In the present work the state of molecular oxygen adsorbed on polycrystalline rhodium has been extensively studied by monitoring the isotope exchange.

EXPERIMENTAL

The experimental apparatus and procedures were essentially the same as those reported previously (12). Briefly, the apparatus consisted of three chambers; a reaction chamber, a collimator and an analyzer chamber. They were separately pumped by ion pumps. The first had optics for AES, an Ar⁺ gun, and a mass spectrometer. The thermal desorption spectra were mainly recorded with this mass spectrometer. The signal (denoted angle-integrated) involves the contribution from the side of the sample crystal as well as the well-polished surfaces. A mass spectrometer in the analyzer chamber was used to confirm that the desorption signal recorded with the other mass spectrometer is truly due to the Rh crystal, and not to the crystal supports. The angular distribution of the desorption of oxygen will be published elsewhere.

The crystal was a disk-shaped slice

(diameter 10 mm × thickness 0.8 mm) of polycrystalline Rh. It was well polished with standard metallurgical techniques. It was cleaned by prolonged heating in 1×10^{-7} Torr oxygen at 1000 K and Ar⁺ bombardment. The crystal was annealed to 1350 K before each thermal desorption run. The temperature of the crystal was monitored by using a chromel–alumel thermocouple spot-welded to the side. A “clean surface” Auger spectrum is shown in Fig. 1. This still shows weak signals around 140 and 170 eV which may be due to impurities. These could not be eliminated by further Ar⁺ bombardment, or heating in O₂. Probably these impurities were uniformly distributed throughout the sample. These signals can always be found in the “clean surface” Auger spectra of Rh reported so far (16–18).

RESULTS AND DISCUSSION

A general overview of the present adsorption system will be summarized in the first section. The other sections will deal in

detail with the adsorption and desorption of oxygen, and also the isotope experiments.

General Features

Typical thermal desorption spectra of oxygen are shown in Fig. 2. The crystal was exposed to O₂ of 1.2×10^{-8} Torr at 125 K and heated with a constant current to 1350 K. The temperature increased almost linearly at a rate of ~ 45 K/s below 800 K. The rate decreased above this level, as shown in the figure. Two desorption features are observed; a sharp peak around 160 K and a broad peak in the temperature range 600–1200 K. Two similar peaks on Pt(1, 2, 7–9) and Ag(10) have been identified as desorbing molecular oxygen from adsorbed molecular and atomic oxygen, respectively. In order to investigate the identification on Rh, isotope exchange, $^{16}\text{O}_2 + ^{18}\text{O}_2 \rightarrow 2 ^{16}\text{O}^{18}\text{O}$, was examined. The crystal was exposed to 0.7 L (Langmuir) $^{16}\text{O}_2$ and further to 1.2 L $^{18}\text{O}_2$ at 125 K. Resultant thermal desorption spectra of $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$ are shown in Fig. 3. No exchange was observed in the low temperature peak, indi-

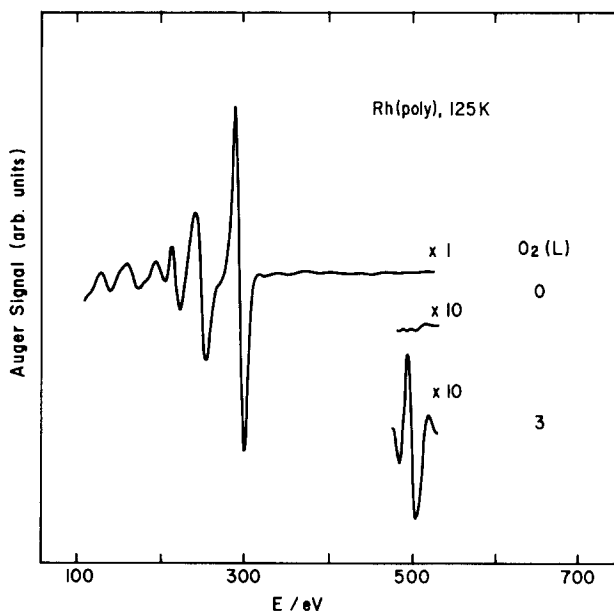


FIG. 1. Auger spectra of a clean surface (upper two curves) and a surface exposed to 3 L O₂ (bottom) at 125 K. Primary beam 5 μA at 2200 eV. Modulation 5 eV.

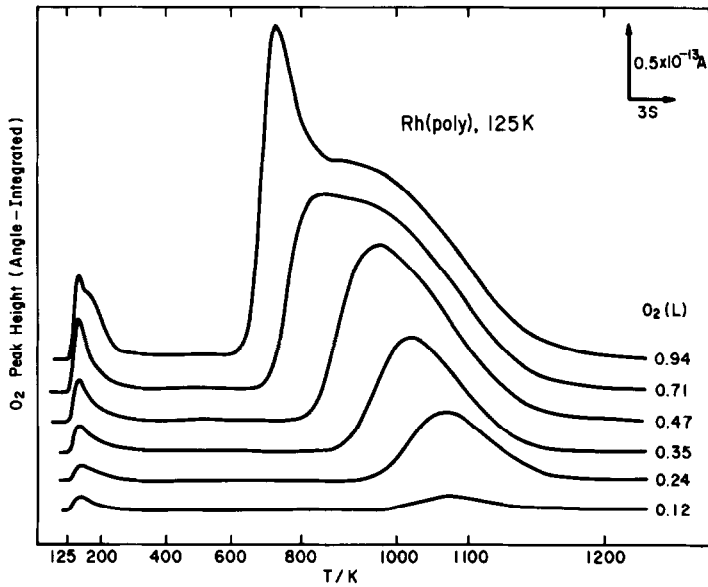


FIG. 2. Thermal desorption of O_2 from Rh exposed to various amounts of O_2 at 125 K.

cating molecular adsorption. On the other hand, complete exchange was confirmed in the high temperature peak, indicating desorption from atomic oxygen. Similar experiments have very recently been reported on Rh(100) (15).

Adsorption and Desorption of Oxygen

The shape of thermal desorption spectra

due to the desorption from oxygen adatoms is severely distorted due to the nonlinear heating rate above 800 K. The discussion, therefore, will be limited to their qualitative features. The features of the high temperature peak are similar to desorption spectra for oxygen adsorbed on polycrystalline Rh wire at room temperature reported by Campbell *et al.* (19). A higher desorption

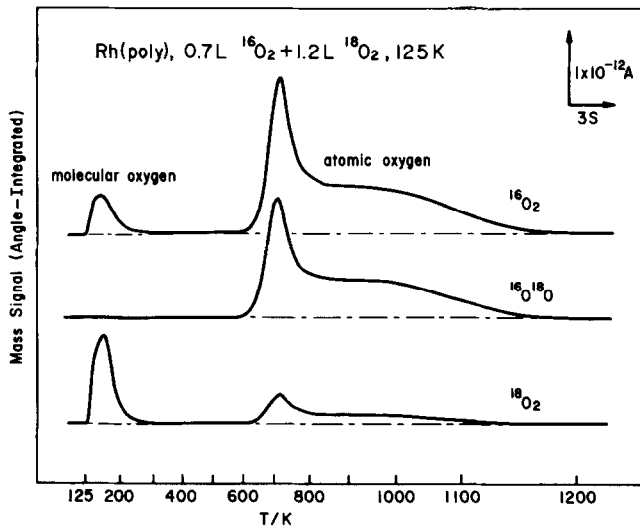


FIG. 3. Thermal desorption spectra after exposure to 0.7 L $^{16}O_2$ followed by 1.2 L $^{18}O_2$ at 125 K.

temperature has been reported on Rh(100) (15). The difference cannot be explained at present. Neither CO nor CO₂ was observed above 600 K (20). A large shift of the peak temperature with an increase in O₂ exposure suggests a second-order desorption as expected. Figure 4 summarizes the amount of oxygen desorbed from the atomic and molecular adsorption states. The peak area of both desorptions is plotted against O₂ exposure as the value relative to the maximum total peak area of O₂ desorption. The desorption from the molecular state increases sharply around 1 L, where the desorption from the atomic state reaches almost the maximum value. Extrapolation of the total amount of O₂ desorbed does not cross the point of zero. Some oxygen is missed during thermal desorption. In order to confirm this fact, the peak-to-peak height of the differentiated oxygen Auger signal at 510 eV (shown in Fig. 1) was monitored as a function of O₂ exposure. The relative value is plotted in Fig. 4. It increases linearly from the value of zero with O₂ exposure below 0.8 L. Assuming the saturation atomic oxygen concentration 3.9×10^{14} atoms/cm² (14), the initial sticking coefficient was estimated to be roughly 0.9. The comparison of the Auger data with thermal de-

sorption peak areas shows clearly that at small oxygen exposures, an appreciable amount of oxygen disappears upon heating. This disappearance has been discussed for Rh(111) by Thiel *et al.* (14). They concluded that dissolution of oxygen into the crystal bulk is the predominant depletion process of adatoms at low coverages. The amount of dissolved oxygen they found (~40% of the maximum coverage) is much larger than that reported in the present work (~10%). This large discrepancy may be caused by the difference in the estimation of the background level during the final stages of heating. In their case the background was rising with an increase in the sample temperature. In our spectra we have never observed such rising background. Recent work by Fisher and Schmieg focuses on this point. They have repeated Thiel's experiments and found a large effect of an Auger gun which produced a CO beam onto oxygen-covered surfaces. Some oxygen was removed as CO₂, but not as O₂ during heating. In our case, a small amount of CO could adsorb from the background ambient during O₂ exposure. About 5% of the maximum oxygen adatoms was removed through CO₂ formation below 500 K (20). This process plays a major role in yielding the difference

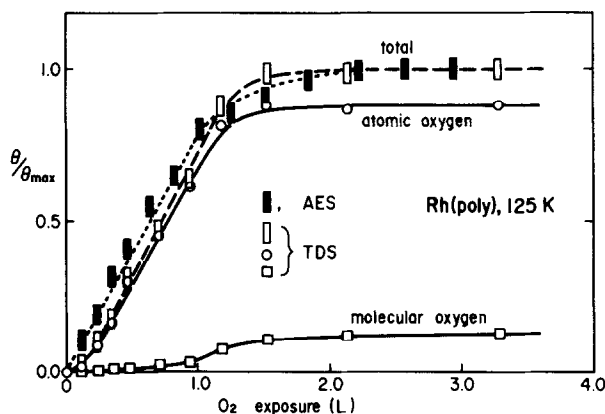


FIG. 4. Oxygen thermal desorption peak area of the low (from molecular oxygen) and high (from atomic oxygen) temperature peaks, and oxygen Auger peak intensities as a function of O₂ exposure at 125 K. The Auger signals were normalized to the asymptotic value at high exposures. The amounts of oxygen thermally desorbed are represented as values relative to the maximum total oxygen peak area.

between AES and TDS data. No appreciable diffusion into the bulk was observed. This conclusion is consistent with the results reported by Fisher and Schmiegl (15).

Thiel *et al.* (14) also observed a small, sharp, first-order O_2 desorption peak at 158 K. They could not conclude whether it was due to adsorption on the Ta wires as crystal supports or to desorption from molecularly adsorbed oxygen on the Rh(111) crystal. This low temperature peak could be reproduced with the mass spectrometer in the analyzer chamber. Fisher and Schmiegl (15) observed this desorption using a mass spectrometer with a slit in front of the ionizer. The desorption of O_2 at low temperatures truly comes from the Rh surface. The maximum amount of desorption directly from the molecular state is about 12% of the total desorption. This is extremely small, as compared to O_2 desorption on Pt(111) (7, 12). The values plotted as molecular oxygen in Fig. 4 do not necessarily represent the amount of molecular oxygen actually existing on the surface. Actual values should be larger than those, since a part of the adsorbed molecular oxygen can be dissociated during thermal desorption, as will be shown later.

Isotope Exchange

The presence of oxygen admolecule was verified by sequential isotope adsorption experiments. The surface was first exposed to various amounts of $^{16}O_2$ and then saturated with $^{18}O_2$. Typical thermal desorption spectra with 0.7 L $^{16}O_2$ followed by $^{18}O_2$ are shown in Fig. 3. No $^{16}O^{18}O$ was found in the low temperature peaks, whereas the isotope was randomly distributed in $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ desorbed in the high temperature peak. The product $(^{16}O^{18}O)^2 / (^{16}O_2)(^{18}O_2)$, was equal to 4 within experimental errors, where $(^{16}O_2)$ are the mole fractions of $^{16}O_2$, etc. in O_2 desorbed in the high temperature peak. The low temperature peak results from molecular adsorption, while the high temperature peak results from atomic adsorption. A large difference in the atomic fraction of ^{18}O between the low and high temperature peaks can be seen in Fig. 3. The ^{18}O fraction observed in the low temperature peak determined from the peak areas is about 0.7, whereas that in the other is about 0.3. The atomic fraction of ^{18}O in both peaks is plotted against the precoverage of ^{16}O in Fig. 5. The precovered of ^{16}O was determined from the relation between the oxygen Au-

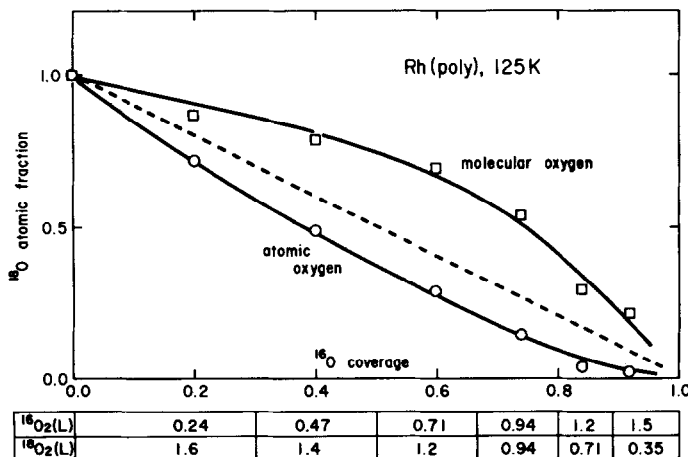


FIG. 5. The atomic fraction of ^{18}O in the low (from the molecular state) and high (from the atomic state) temperature desorption peaks. The surface was heated after exposure to various amounts of $^{16}O_2$ followed by saturation with $^{18}O_2$ at 125 K. Each exposure of $^{16}O_2$ and $^{18}O_2$ is listed in the bottom.

ger signal and O₂ exposure in Fig. 4. The amounts of sequential exposure of the isotopes are listed in the bottom of Fig. 5. The total exposure was kept above 1.8 L. This is large enough to saturate the surface with oxygen as can be seen in Fig. 4. The atomic fraction of ¹⁸O in oxygen desorbed would decrease linearly with an increase in the precoverage of ¹⁶O, if the probability of the dissociation of oxygen admolecules to adatoms is independent of the sequence of the adsorption. In this case the atomic fraction of ¹⁸O would follow the dashed line in Fig. 5. However, experimental results show a nonuniform distribution of ¹⁸O in the low and high temperature peaks. The atomic fraction in the former is always above the dashed line, whereas the fraction in the latter falls below the dashed line. The desorption when ¹⁸O₂ is postexposed is enriched in adsorbed molecular oxygen. Such a non-uniform distribution of ¹⁸O in adsorbed

atomic and molecular oxygen is quite different from the results on Pt(111). Similar isotope experiments on Pt(111) indicated uniform distribution of the oxygen isotope (2, 21). The results suggest that oxygen adsorbs molecularly on Pt(111) at 100 K, since predosed oxygen (¹⁶O₂) which might dissociate on initial adsorption should be enriched in ¹⁶O-containing molecules relative to the ¹⁶O₂ desorbed from the molecular state. On the other hand on Rh, oxygen which is preexposed is more easily dissociated to adatoms. These phenomena are clearly shown in Fig. 6. The ratio of the amount of ¹⁶O involved in the low temperature peak to that in the high temperature peak is plotted against ¹⁶O₂ preexposure. It was calculated from desorption peak areas. Experimental conditions are listed in Fig. 5. The same ratio for ¹⁸O and also the ratio obtained for only ¹⁶O₂ exposure are plotted in the same figure. The molecular/atomic

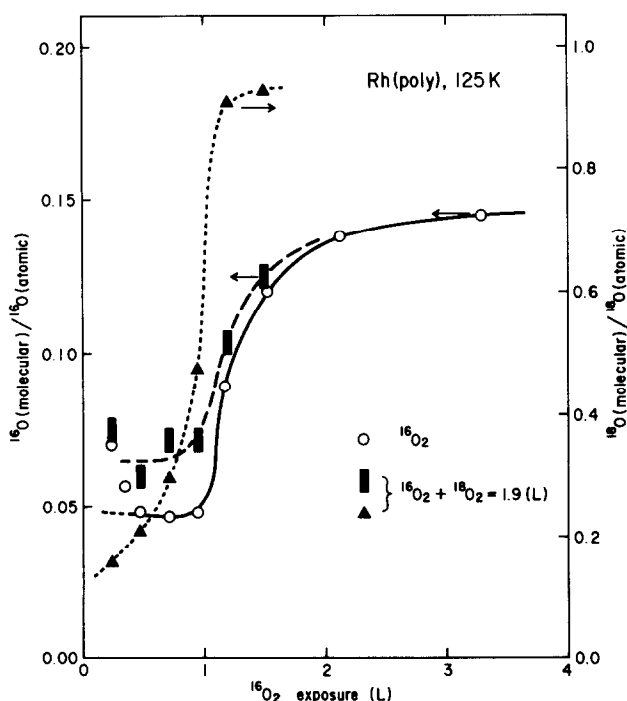


FIG. 6. The ratio of oxygen desorbed from the molecular state to that from the atomic state as a function of ¹⁶O₂ preexposure. ○, Ratio of the amount of ¹⁶O desorbed in the low temperature peak to that in the high temperature peak. ■, ▲, Same ratios for ¹⁶O and ¹⁸O from surfaces saturated with ¹⁶O₂ and ¹⁸O₂. Exposure amounts of ¹⁶O₂ and following ¹⁸O₂ are listed in Fig. 5.

oxygen ratio for postdosed ^{18}O is always much higher than that for predosed ^{16}O . The value for ^{18}O obtained with a 1.5-L pre-exposure of $^{16}\text{O}_2$, ~ 0.93 , is about seven times larger than that for ^{16}O . The latter is about 0.13. It is still much larger than the value for ^{16}O with a 0.5-L pre-exposure of $^{16}\text{O}_2$. The data are rather scattered below 0.3L pre-exposure of $^{16}\text{O}_2$. These results show clearly that oxygen molecules adsorbed on highly precovered surfaces have a relatively large probability of desorption directly from the molecular state, without being dissociated. Such heterogeneity in the dissociation of adsorbed molecular oxygen may be induced by partial dissociation of admolecules to adatoms at the adsorption temperatures used here. In fact, a weak (2×2) LEED pattern due to the super structure of oxygen adatoms appears after the adsorption on Rh(111) and (100) surfaces at 100 K (14, 15). This pattern is good evidence of dissociation of (at least a part of) oxygen at this temperature. In this case the probability of the dissociation of remaining or postdosed oxygen molecules should decrease with an increase in the coverage of adatoms, as observed. An appreciable difference can be seen in the ratio of ^{16}O (molecular) to ^{16}O (atomic) between the ($^{16}\text{O}_2 + ^{18}\text{O}_2$) and $^{16}\text{O}_2$ systems, as drawn in Fig. 6. The ratio in the former case is always above that in the latter. This means that the dissociation of predosed $^{16}\text{O}_2$ is retarded by saturation with $^{18}\text{O}_2$. In other words some fraction of the oxygen admolecules are also dissociated during thermal desorption.

SUMMARY

The adsorption of oxygen on polycrystalline rhodium was studied around 120 K, by means of TDS, AES, and isotope tracer. The results obtained are summarized as follows;

(1) The initial sticking probability of oxygen is close to unity.

(2) No appreciable diffusion of oxygen into the bulk was observed.

(3) Two types of surface oxygen were found. One is in a molecular state and the other is an atomic form. The maximum amount of the former desorbed is about 12% of the total adsorbed oxygen.

(4) A fraction of oxygen admolecules is already dissociated at the low temperatures used.

ACKNOWLEDGMENT

This work was supported in part by Grant-in-Aid 554060 for Scientific Research from the Ministry of Education.

REFERENCES

1. Peng, Y. K., and Dawson, P. T., *Canad. J. Chem.* **52**, 3507 (1974).
2. Gland, J. L., *Surf. Sci.* **93**, 487 (1980).
3. Norton, P. R., *Surf. Sci.* **47**, 98 (1975).
4. Gland, J. L., Sexton, B. A., and Fisher, G. B., *Surf. Sci.* **95**, 587 (1980).
5. Ibach, H., *J. Vac. Sci. Technol.* **20**, 574 (1982).
6. Lehwald, S., Ibach, H., and Steininger, H., *Surf. Sci.* **117**, 342 (1982).
7. Steininger, H., Lehwald, S., and Ibach, H., *Surf. Sci.* **123**, 1 (1982).
8. Avery, N. R., *Chem. Phys. Lett.* **96**, 371 (1983).
9. McClellan, M. R., McFeely, F. R., and Gland, J. L., *Surf. Sci.* **123**, 188 (1983).
10. Backx, C., De Groot, C. P. M., and Biloen, P., *Surf. Sci.* **104**, 300 (1981).
11. Nyberg, C., and Tengstal, C. G., *Surf. Sci.* **126**, 163 (1983).
12. Matsushima, T., *Surf. Sci.* **123**, L663 (1982); **127**, 403 (1983).
13. Rao, C. N. R., Vishnu Kamath, P., and Yashonath, S., *Chem. Phys. Lett.* **88**, 13 (1982).
14. Thiel, P. A., Yates, J. T., Jr., and Weinberg, W. H., *Surf. Sci.* **82**, 22 (1979).
15. Fisher, G. B., and Schmiege, S. J., *J. Vac. Sci. Technol. A* **1**, 1064 (1983).
16. Marbrow, P. A., and Lambert, R. M., *Surf. Sci.* **67**, 489 (1977).
17. Castner, D. G., Sexton, B. A., and Somorjai, G. A., *Surf. Sci.* **107**, 439 (1981).
18. Koestner, R. J., Van Hove, M. A., and Somorjai, G. A., *Surf. Sci.* **107**, 439 (1981).
19. Campbell, C. T., Shi, S-K, and White, J. M., *Appl. Surf. Sci.* **2**, 382 (1979).
20. Matsushima, T., *J. Catal.* **83**, 446 (1983).
21. Matsushima, T., unpublished data.