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Adsorption of Oxygen on Potassium-Covered Gold Surfaces

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Adsorption of oxygen was studied on potassium-covered polycrystalline gold surfaces around 100 K by means of thermal desorption combined with isotope tracer techniques. O_2 adsorbs rapidly on the K-covered surfaces. The amount at saturation is limited by the coverage of K, θ_k. The thermal desorption at $\theta_k < 1$ showed two peaks, one in the temperature range of 200–500 K and the other above 500 K. The former is due to the desorption of oxygen admolecules on KO_2 sites. The latter is assigned to the decomposition of several kinds of potassium oxides. © 1985 Academic Press, Inc.

1. INTRODUCTION

The interaction of oxygen with alkali metals deposited on transition metal surfaces has received considerable attention. Alkali metals and their oxides are important additives to transition metal catalysts and also to photocathodes or thermionic emitters. For example, alkali metal compounds (probably in the oxide form under working conditions) are used as additives for iron catalysts in both the ammonia (*1–3*) and the Fischer–Tropsch synthesis (*4*). Alkalis also enhance the adsorption of oxygen on silver (*5–7*), which is a key process in the C_2H_4O formation from C_2H_4 (*8, 9*). However, the chemical state of the alkali metals after oxygen adsorption is still vague, i.e., whether oxygen interacts directly with alkali or whether the interaction with the transition metal dominates.

Lambert and his co-workers observed the desorption of oxygen above 500 K on K/Ag(100) (*5*), Na/Ag(110) (*6*), and Rb/Ag(111) (*7*). This desorption was assigned to the decomposition of several kinds of alkali oxides as well as the desorption of absorbed oxygen. A similar conclusion was derived on K/Pt(111) by Garfunkel and Somorjai (*10*). Lambert *et al.* also observed a small desorption peak of oxygen below 500 K. The desorption of oxygen admolecules was concluded for this peak from isotope experiments (*5, 7*). A similar small peak was reported below 500 K on K/Pt(111) (*10*). On the other hand, Bonzel *et al.* (*11, 12*) concluded from XPS and UPS experiments that oxygen adsorption on K/Fe(111) did not lead to the formation of potassium oxide, as long as the K concentration did not exceed one monolayer. They also concluded that K/Pt(111) did not form a bulk like potassium oxide (K_2O), despite that shifts in binding energy of O(1*s*), K(2*p*) and K(3*p*) levels indicated some interaction between potassium and oxygen (*12*). The complexity of O_2 adsorption experiments cited above is partly caused by the superposition of the adsorption on alkali adatoms and substrate surfaces.

As the first step in analysis of the states of alkalis on transition metals, we have tried to study the adsorption only on potassium adatoms deposited. In this paper we will report the desorption of oxygen from K/Au(polycrystalline) surface and discuss the states of K after O_2 adsorption. On this surface only the adsorption on K sites can be studied, since Au surface itself shows no adsorption from gaseous O_2 (*13–15*). Two oxygen molecules can adsorb on a potassium adatom around 100 K. One of them desorbs below 500 K and preserves the integrity of the O–O bond. This is due to the

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desorption of oxygen admolecules. The other desorbs above 500 K, which is assigned to the decomposition of the oxides.

2. EXPERIMENTAL

The experimental apparatus was reported previously (*16*). Briefly, the apparatus consisted of a reaction chamber, an analyzer chamber, and a collimator. The following experiments were conducted in the reaction chamber. The chamber had LEED-AES optics, an Ar^+ gun, a K source, a mass spectrometer, a B-A gauge, and a gas handling system. Atomic potassium was deposited by heating a "Saes Getters" potassium source mounted approximately 5 cm from the sample. During evaporation of K, the getter was biased positively by 9 eV against the sample to monitor the deposition rate with the current due to K^+ ions.

The polycrystalline gold sample was a disk-shaped slice (10 mm diameter × 0.5 mm thickness, purity 99.99% from Furuchi Chemicals, Tokyo). Both faces were polished with standard metallographic techniques and treated briefly with aqua regia. The sample was mounted on a rotatable axis of the manipulator, in such a way as to face the first three attachments described above. The sample was argon ion bombarded at 860 K until it was clean as judged by AES. Before each adsorption experiment, the sample was flashed three times up to 1050 K to remove K and its oxide. At this stage, a trace amount of K and O was detected by AES. After these procedures, however, no desorption of oxygen was observed even after a large exposure at 100 K.

3. RESULTS

3.1. Coverage of Potassium

The coverage of potassium was estimated from the ion current due to depositing K^+ and the evaporation time. It is difficult to determine the coverage with AES, since the K 252-eV Auger peak is superimposed on the Au 255-eV Auger peak, as seen in Figs. 1a and b. At first the interval required to produce one monolayer should be determined at a fixed evaporation rate.

The intensity of the K Auger signal was followed as a function of the evaporation time, which is shown in Fig. 1d. No breakpoint, which would indicate the completion of the first monolayer, was found in this Auger signal time plot. Another approach (thermal desorption) was used in order to determine this completion. The thermal desorption (TD) was followed by monitoring the amount of K remaining on the surface after sequential heating. A special arrangement of the mass spectrometer is required against the sample, in order to obtain TD spectra of potassium, since desorbing K is deposited on the chamber wall and also a part of it is K^+ ion. Such experiments cannot be performed with the present apparatus. In TD spectra of potassium deposited on transition metals (*10, 17*), a sharp peak

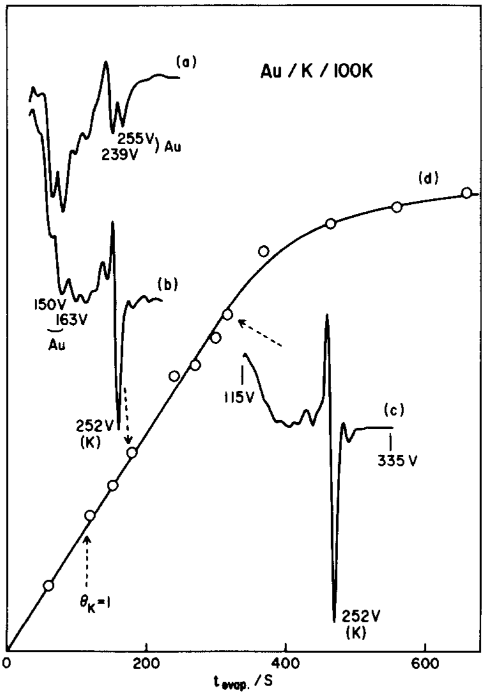

FIG. 1. Potassium Auger uptake curves on Au surfaces. Auger signals from 115 to 335 eV of (a) clean Au, (b) with 1.5 monolayer K, and (c) with about 3 monolayers K. (d) K (252 eV) peak intensity versus deposition time. The crystal was kept at 100 K.

is usually observed due to the desorption from a multilayer above the first layer. The desorption from the first layer yields a broad peak in the temperature range of 500–1200 K. It means that the completion of the first layer can be examined from a sharp decrease in the amount of K during sequential heating procedures.

Figure 2 shows the intensity of the K Auger signal as a function of the temperature to which the sample was heated. Potassium was first deposited around 100 K for an interval, t_{evap}, at a fixed evaporation rate. The sample was heated to the desired temperature, T_p, at a heating rate of about 5 K/s and cooled down around 100 K. The amount of potassium remaining was measured with AES. The signal intensity decreased sharply around 540 K when $t_{evap} > 180$ s. Above 540 K the intensity decreased almost linearly with the increasing T_p and followed the same line independent of t_{evap} when $t_{evap} > 120$ s. We conclude that the sharp decrease around 540 K is due to the desorption from the multilayer. The completion of the first layer was determined from the cross point of the vertical dashed-dotted line at 540 K and the curve of the Auger signal intensity above 540 K. The intensity level was shown as a horizontal dashed-dotted line. This level indicates 110 s as the interval for the first monolayer in Fig. 1. The absolute density of K atoms cannot be determined, since only a fraction of deposited K contributes to the ion current.

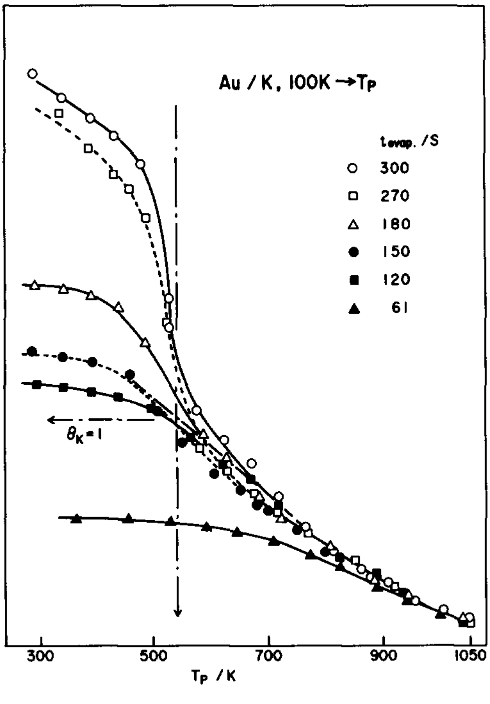

FIG. 2. Intensity of the K Auger signal at 252 eV as a function of heating temperature. The surface covered by K in various amounts was heated to T_p and the amount of K was measured after cooling. Such procedures were repeated to T_p = 1050 K.

This conclusion is supported by the following considerations. The Auger signals of Au at 150 and 163 eV were attenuated in the course of K deposition as seen in Fig. 1b, since the growing potassium layer scatters Auger electrons from Au atoms. The signals disappeared almost completely around $t_{evap} = 310$ s as shown in Fig. 1c, where θ_k was estimated to be 2.8. θ_k is defined as the evaporation time relative to 110 s. The thickness of two monolayers of potassium was estimated to be 7.2 Å, by assuming that the atoms form a crystal layer such as the bulk potassium metal (the lattice constant = 5.3 Å, and the minimum interatomic distance = 2.29 Å). A similar thickness of three monolayers was 9.9 Å. The mean free path of electrons with kinetic energy of 150–163 eV is 6–7 Å (*18*). This means that the Auger signals of Au should disappear at $\theta_k = 2–3$. It agrees well with the above value of $\theta_k = 2.8$.

3.2. *Oxygen Adsorption*

Oxygen can adsorb rapidly on the K covered surfaces, although no adsorption was detected on clean gold surfaces even when the sample was exposed to O_2 in large amounts (>10 L; L = Langmuir) at 100 K. The desorption of oxygen shows two peaks, one in the temperature range of 250–500 K and the other above 500 K (Figs. 3 and 4). The amount of O_2 desorbed after the large exposure was limited by θ_k. The ratio of the amount to θ_k was constant below θ_k

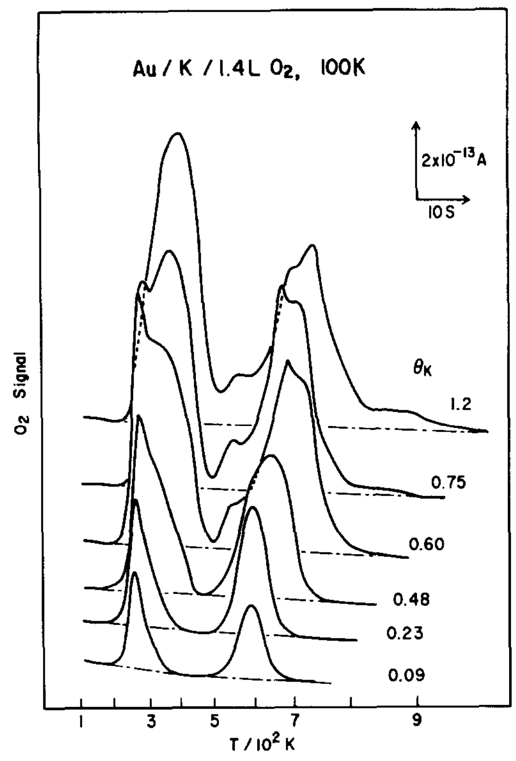

FIG. 3. Thermal desorption spectra of O_2 at small θ_k. The surface was kept at 100 K during K deposition and O_2 adsorption.

= 1 as shown in Fig. 5. This means that no spillover of oxygen occurs at least at adsorption temperatures, ~100 K. If it should occur, the amount of oxygen adsorption at saturation would increase irrespective of θ_k with the increasing O_2 exposure. This was not observed. Typical desorption spectra with 1.4 L O_2 (almost saturation) are reproduced in Figs. 3 and 4. The surface was first covered by potassium in various amounts around 100 K, and exposed to O_2 at 1.2×10^{-8} Torr. Then it was heated with a constant heating voltage. The temperature increased almost linearly with a rate of about 14 K/s below 700 K.

The peak in the low temperatures appeared at 250 K when $\theta_k < 1$, and shifted slightly to higher temperatures with the increase of θ_k. A shoulder around 350 K grew with the increasing θ_k. It became predominant in the low temperatures above $\theta_k = 0.75$. The former peak became a shoulder and disappeared when $\theta_k > 1$. The latter peak (i.e., the shoulder at $\theta_k < 0.75$) shifted from 400 to 500 K by increasing θ_k above $\theta_k = 1$. The peak area decreased greatly by increasing θ_k above $\theta_k = 1.2$.

The desorption in the high temperatures (>500 K) shows complicated behaviors. A small shoulder around 550 K was well reproduced with $\theta_k = 0.6$–1.2. The major peak was shifted from 600 to 800 K. This desorption consists of at least three components which peak at 600–700, 750, and 800 K. It is likely that such structures are due to the decomposition of several kinds of oxides, as discussed below.

The amount of oxygen desorbed after a large exposure in the low temperatures was equal to that in the high temperatures, when $\theta_k < 1$, as shown in Fig. 5. As de-

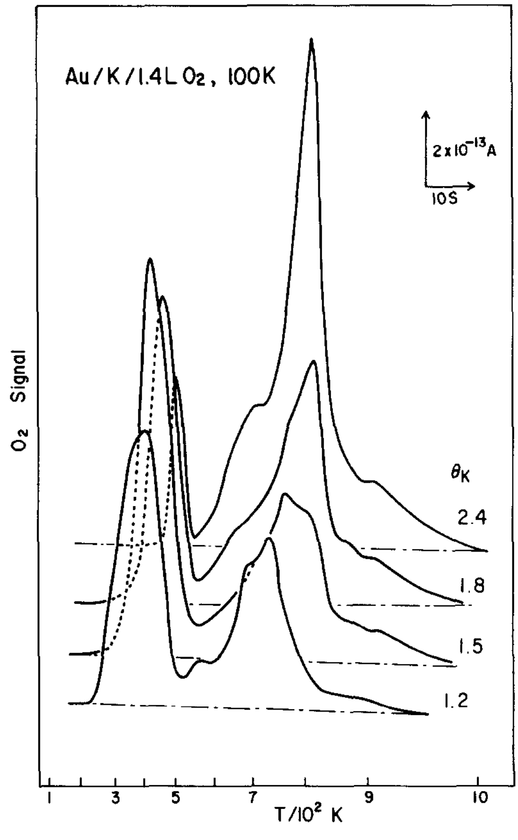

FIG. 4. Thermal desorption spectra of O_2 at large θ_k. The surface was held at 100 K during K deposition and O_2 adsorption. The spectrum at $\theta_k = 1.2$ was reproduced from Fig. 3 for comparison.

scribed in the next section, the low-temperature peak is due to the desorption from molecular adsorption state. Therefore, this equality indicates that one K adatom traps an even number of oxygen molecules (most likely two molecules). This equality did not hold when oxygen exposure was not large enough to saturate the adsorption capacity, or when $\theta_k > 1$. In the latter case, oxygen admolecules can be converted into the form desorbed in the high temperatures during heating procedures, since the latter can penetrate into the bulk potassium and produce the oxide layer (*19, 20*).

Three typical series of TD spectra at θ_k = 0.17, 0.46, and 1.2 are shown in Figs. 6, 7, and 8. When θ_k = 0.17, the desorption in the high temperatures was saturated with 0.71 L O_2. 3.0 L O_2 was dosed to saturate both states. The ratio of the peak area in the low temperatures to that in the high temperatures became unity above 3.0 L. Here, the

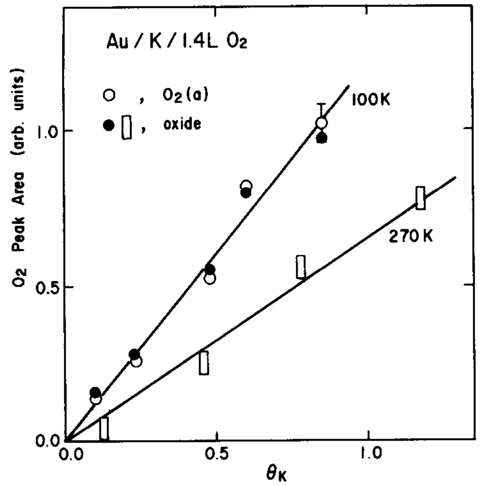

FIG. 5. Amount of O_2 desorption at saturation as a function of θ_k. K was first deposited on the surface at 100 K and then the surface was exposed to 1.4 L O_2 at 100 or 270 K. The amount of O_2 desorbed was determined from the peak area. O_2(a) and oxide mean oxygen desorbed below and above 500 K, respectively. Experimental details at 100 K given in Fig. 3.

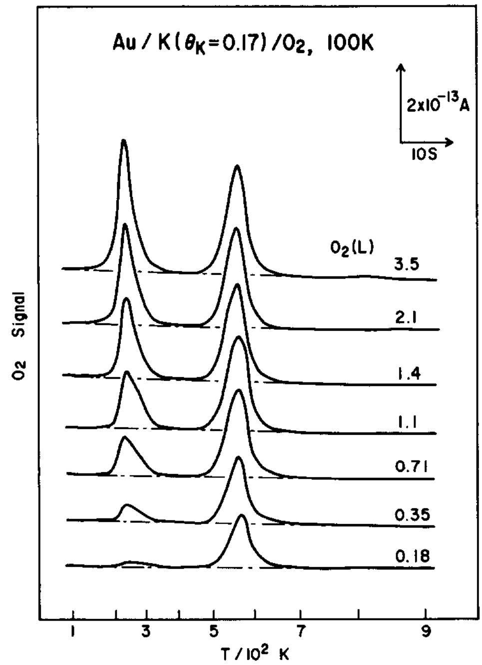

FIG. 6. Thermal desorption spectra of O_2 at θ_k = 0.17 with various O_2 exposures. The areas of both peaks became equal at large O_2 exposure.

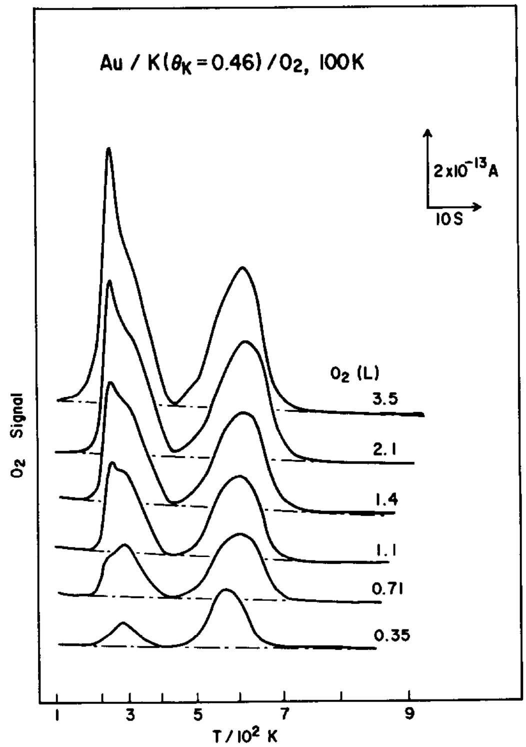

FIG. 7. O_2 desorption spectra at θ_k = 0.46 with various O_2 exposures. The ratio of the peak areas became unity at large exposures.

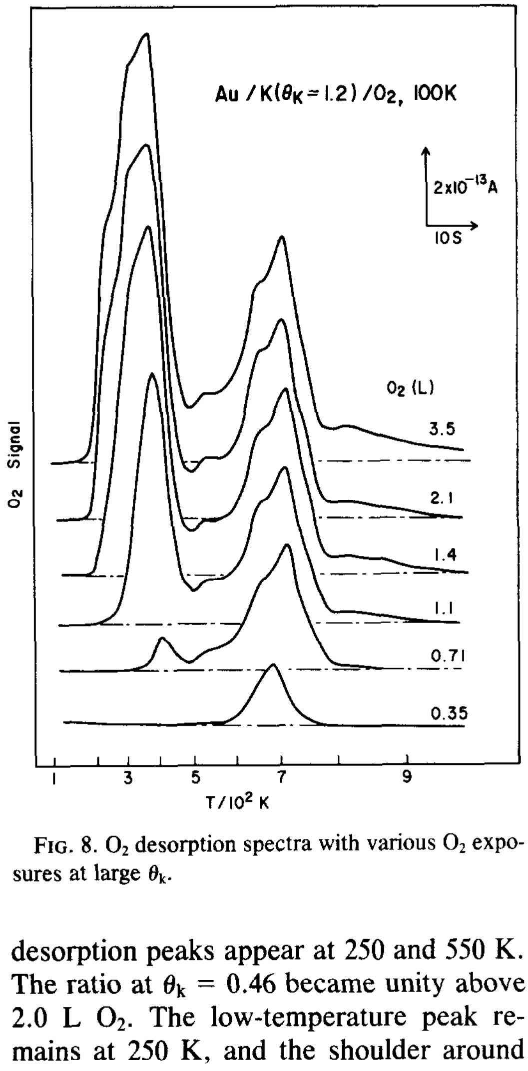

FIG. 8. O_2 desorption spectra with various O_2 exposures at large θ_k.

desorption peaks appear at 250 and 550 K. The ratio at $\theta_k = 0.46$ became unity above 2.0 L O_2. The low-temperature peak remains at 250 K, and the shoulder around 310 K was significant. The peak in the high temperatures was shifted from 570 to 620 K with the increasing O_2 exposure. When $\theta_k = 1.2$ the peaks were not well separated, however, the equality of the areas roughly held above 2.0 L, as shown in Fig. 8.

When the surface was kept at 270 K during O_2 exposure, the equality of the desorption areas did not hold, even with a small θ_k. The desorption below 500 K was always less than the other, since the desorption from the molecular adsorption state begins below 270 K. Here we can again examine whether oxygen adsorbed on the K sites makes the spillover to clean parts of Au surfaces. The amount of oxygen desorbed in the high temperatures was limited by θ_k and did not exceed the level at saturation at 100 K even when the adsorption temperature was increased to 400 K. The results at 270 K are shown in Fig. 5. Recently, Madix and his coworkers have shown that atomized oxygen can be adsorbed on Au surfaces (*15*). If spillover occurs and the resultant oxygen adatoms desorb as O_2, the desorption would peak in the narrow temperature range of 630–680 K (*15*). However, our experimental results show that the desorption in the high-temperature peaks in the temperature range from 550 to 800 K with increasing θ_k. Hence, it is unlikely that oxygen adatoms produced by the spillover is desorbed as O_2 in the high-temperature range.

3.3 Isotope Experiments

Isotope experiments showed clearly that the low-temperature peak is due to the desorption from the molecular adsorption state. Oxygen desorbed in the low temperatures did not involve $^{16}O^{18}O$ when the surface was exposed sequentially to $^{18}O_2$ and $^{16}O_2$.

Typical TD spectra of isotope oxygen with various θ_k are shown in Fig. 9. The surface was exposed to 0.35 L $^{18}O_2$ and then 1.1 L $^{16}O_2$ at 100 K. The resultant desorption involved $^{16}O_2$ and $^{18}O_2$ in the low temperatures even above 400 K when $\theta_k < 0.5$. No $^{16}O^{18}O$ was observed. On the other hand, when $\theta_k > 0.5$, the oxygen desorbed in the low temperatures showed a significant isotope mixing especially above 350 K. The amount of $^{16}O^{18}O$ was much less than the value which would be observed at a random mixing. This means that oxygen desorbed in the low temperatures is molecularly adsorbed irrespective of θ_k. K adatoms are isolated from each other when $\theta_k < 0.5$. Thus, no exchange of oxygen occurs. The exchange becomes possible by increasing θ_k, since the K adatoms are closely distributed. The mechanism of such exchange is not clear at present.

On the other hand, oxygen in the high temperatures always showed an almost ran-

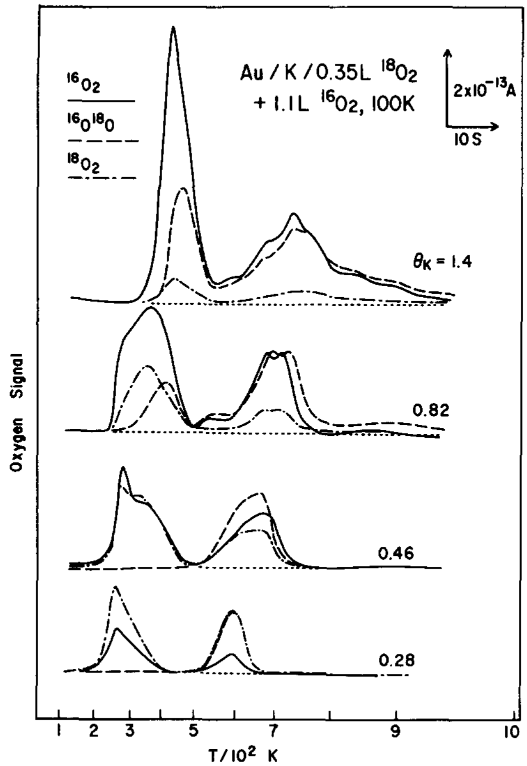

FIG. 9. Isotope scrambling by surface oxygen species. The surface was first exposed to $^{18}O_2$ and then $^{16}O_2$ at 100 K.

dom mixing of isotopes. It was independent of θ_K. The desorption of oxygen has frequently been reported in this temperature range on K-covered transition metals (*5, 7, 10*). In general, this oxygen is due to the decomposition of oxides in several forms. The detailed mechanism will be discussed in the next section.

4. DISCUSSION

Here we will briefly discuss the mechanism of the adsorption–desorption of oxygen on potassium-covered gold surfaces.

4.1. Molecular Adsorption State

We will first examine the results of isotope experiments to determine whether molecular oxygen is adsorbed on the potassium oxide. UPS and XPS data (*19*), and also adsorption measurements (*20*) in the literature show that potassium metal surfaces are oxidized by exposing to O_2 at 77 K. Oxygen admolecules have been confirmed on the oxidized surfaces below 250 K by UPS and XPS (*19*). Upon increasing the surface temperature, some admolecules are converted into the oxide even at 120 K. It is likely that K adatoms on gold surfaces are oxidized before oxygen is molecularly adsorbed.

From a comparison of the atomic fraction of predosed oxygen in both desorption peaks, it should be examined whether the predosed oxygen forms the oxides at the adsorption temperature. In the adsorption experiments, where the surface is first exposed to one isotope ($^{18}O_2$) and later to the other ($^{16}O_2$), the isotope dosed first should be enriched in the oxides when the admolecules are at least partially converted into the oxides at the adsorption temperature. In other words, the atomic fraction of oxygen predosed in the oxide would be higher than that in the molecular state. With these considerations, no exchange of oxygen is assumed between the admolecules and the oxides. On the other hand, the fraction of isotope oxygen will be equal in each state, when the oxygen molecules predosed are identical to those postdosed, and the oxidation occurs during the following heating procedures. Experimental results are summarized in Table 1. The experimental conditions are shown in Fig. 9. The fraction of ^{18}O predosed in the oxygen desorbed in low temperatures was equal to that in the high

TABLE 1

The Atomic Fraction of ^{18}O Predosed in Oxygen Desorbed, ^{18}X, in Low and High Temperatures[a]

θ_k	^{18}X	
	Low temp.	High temp.
0.28	0.67	0.65
0.46	0.45	0.45
0.82	0.36	0.35
1.4	0.22	0.28

[a] The experimental conditions are shown in Fig. 9.

temperatures within experimental errors, when $\theta_k < 1$. The fraction was determined from the peak areas. These data indicate that the probability of the desorption in low temperatures is independent of the sequence of adsorption. There are two possibilities: (1) at 100 K, K adatoms are not oxidized, two admolecules of oxygen on a K adatom are in identical chemical environments, thus, the oxidation occurs during the following heating procedures; (2) the first molecule is in the oxide form and can be replaced by the following admolecule before desorption in low temperatures begins. At present, it is difficult to differentiate the above mechanisms. As mentioned above, XPS and UPS experiments indicate that K metal surfaces are already oxidized at 77 K. This oxidation occurs only to a small extent. However, it proceeds rapidly with the increasing temperature (*19*). Mechanism (2) is also reasonable, since the crystal of KO_2 consists of O_2^- ions and K^+ ions. A K^+ adion may be surrounded by two O_2^- ions. In this case the desorption probability in low temperatures may be independent of the oxide formation. In either mechanism, the desorption in high temperatures is due to the decomposition of the oxides.

4.2. Decomposition of Oxides

The oxide first produced is probably KO_2 (superoxide), since isotope experiments suggest that the adsorption sites for molecular oxygen are isolated especially at small θ_k. This isolation is reasonable, since K adatoms are thought to be positively charged, as observed commonly in alkali adatoms on transition metals (*21*). K adatoms appear to have a tendency to be far from each other. When O_2 exposure is not large, O_2 is desorbed only in high temperatures. This means that the superoxide is not decomposed below 500 K. With large O_2 exposures, O_2 is molecularly adsorbed on this superoxide. The desorption of oxygen below 500 K occurs through the reaction

$$O_2(KO_2)(a) \rightarrow KO_2(a) + O_2(g) \quad (1)$$

The heat of adsorption of molecular oxygen was estimated at 15–25 kcal/mole from the desorption peak temperature. The superoxide molecule will decompose above 500 K, in such a way that isotopically mixed oxygen is evolved. It is unlikely that the superoxide is decomposed directly to K and O_2. No isotope exchange would occur. The heat of formation of KO_2 is large, 67.6 kcal/mole (*22*). The decomposition to KO and O_2 occurs more easily (*23*). Here two reaction pathways are possible. The first involves the O_2 desorption from oxygen adatoms, as follows,

$$KO_2(a) \rightarrow KO(a) + O(a) \quad (2)$$

$$KO(a) \rightarrow K(a) + O(a) \quad (3)$$

$$2O(a) \rightarrow O_2(g) \quad (4)$$

And the second involves bimolecular processes of potassium oxides

$$2KO_2(a) \rightarrow K_2O_2(a) + O_2(g) \quad (5)$$

$$2K_2O_2(a) \rightarrow 2K_2O(a) + O_2(g) \quad (6)$$

$$2K_2O(a) \rightarrow 4K(a) + O_2(g) \quad (7)$$

The amount of O_2 evolved through reaction (1) will be equal to the total oxygen produced through reactions (2)–(4) or (5)–(7), when K sites are saturated with oxygen and the oxides are decomposed on the surface to yield O_2. This agrees with the experimental results. Both pathways can yield isotopically mixed oxygen, as observed. If the first pathway is operative, the rate-determining process is either reaction (2) or reaction (3). Otherwise the spillover of oxygen would occur. At present the differentiation of above two pathways is impossible.

Oxygen evolution from alkali-covered transition metal surfaces above 500 K has typically been explained by the decomposition of several oxides (*5–7, 10, 24–27*). The K-covered gold surfaces show similar O_2 desorption phenomena which can be explained mostly by the decomposition of potassium oxides.

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