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The Thermal Desorption of Oxygen from Silver After Adsorption from 25 to 150°C

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The thermal desorption of oxygen from silver powder has been studied from 20 to 350°C by applying a nominal heating rate of 2°C/min and measuring the mass lost with a vacuum microbalance. The desorption was carried out after adsorbing oxygen on cleaned silver at temperatures ranging from 25 to 150°C. The temperature, where the maximum rate of desorption was reached for the first adsorbed state ranged from 63 to 75°C and depended on the adsorption temperature. Desorption was completed below 130°C. The data from the adsorbed state were found to be second order and could be fit by a Wigner-Polanyi desorption equation. The desorption parameters obtained from a computerized fit of each complete evolution curve ranged from $E = 16$ to 28 kcal/mol and from $\nu = 10^7$ to 10^{15} sec^{-1}. They depended upon the temperature of adsorption. The second-order desorption probably results from the scission of two molecularly adsorbed species with a yield of one gas-phase molecule and two adatoms.

INTRODUCTION

A number of explicit expressions (*1-8*) have been developed to account for the thermal desorption of a gas from a solid surface. The different expressions have been obtained to adapt them to one of several methods used for detecting the number of gaseous species desorbed and to the programmed heating schedule chosen. The basic equation assumed to describe the desorption process has been some form of the Wigner-Polanyi equation. When applied to the work in this paper, the rate of desorption of a single adsorbed state is

$$\frac{d\theta_s}{dT} = \left(\frac{\nu_n \theta_s n}{\beta}\right) \exp\left(\frac{-E}{kT}\right). \qquad (1)$$

The significance of considering the surface coverage θ_s as a single adsorbed state instead of the monolayer coverage θ has been discussed (*9*).

Nomenclature

θ_s	the fractional coverage of a single adsorbed state; it varies from 1 to 0 during desorption of the entire state
T	the temperature in degrees Kelvin
ν	the frequency factor
E	the activation energy for desorption
n	the order of the process
β	the heating rate in °K/min = $(T-T_0)/t$
T_0	a low temperature where $d\theta_s/dT$ is neglible and $\theta_s = \theta_{s0}$
θ_{s0}	the maximum coverage of the adsorbed state
m_1	mass of oxygen desorbed from a weakly chemisorbed state
m_2	mass of oxygen desorbed from a strongly chemisorbed state
T_p	the temperature at which $d\theta_s/dT$ is a maximum

The direct measurement of a loss in mass during desorption with a microbalance (*7*) has not been used widely (*10*) even though it offers a number of advantages (*7*) for obtaining quantitative values of E and ν (*9*). The microgravimetric method requires a large amount of prior work (*7*) to establish that the desorption might be interpreted as a single adsorbed state with ν and E essentially independent of θ_s and T as

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assumed in the simplest form of Eq. (1). In this paper, the thermal desorption of oxygen from a silver surface has been studied to determine n, E, and ν from Eq. (1) and to compare the values of E and ν obtained from a computerized fit of the entire evolution curve with those obtained from equations developed by Redhead (*3*).

EXPERIMENTAL

For measuring the thermal desorption of oxygen from silver powder, an aliquot was suspended from a vacuum microbalance (*11*) and prepared for study by a cyclic thermochemical process (*12*), e.g., OAOR cycling at 350°C to produce reproducible chemisorptive behavior and a cleaned surface. The sample was exposed to 10 Torr of oxygen at a series of temperatures ranging from 25 to 150°C. In each case, the sample was cooled at 25°C in oxygen, evacuated to 2×10^{-6} Torr and then subjected to a nominal (*13*) temperature increase of 2°K/min. Detailed descriptions of the microbalance and vacuum system (*11*), the preparation of the powder for reproducible chemisorption studies (*12*), the purity of the materials used (*12, 13*), the surface area and chemisorptive behavior of the silver (*12*), the determination of the sample temperature (*13*), and the procedures used for chemisorption and thermal desorption (*13, 14*), have been reported. The data obtained consisted of the mass of oxygen desorbed as a function of sample temperature from which θ_{s0}, θ_s, and $d\theta_s/dT$ were calculated.

ANALYSIS

The data were analyzed to determine the order of the process as described by Kollen and Czanderna (*15*). Then, the experimental curves were fit by calculating evolution curves from the values deduced for E and ν from Redhead's equations (*3*), as modified for the microbalance data (*15*), and from values obtained by a computerized least squares fit of the entire evolution curve (*16*).

RESULTS

The thermal desorption of oxygen was carried out after adsorbing oxygen at temperatures of 35, 40, 50, 60, 72, 84, 97, 112, 127, 144, and 150°C. The measurement at each temperature was repeated two or three times to establish the reproducibility of the desorption process and to decrease the statistical fluctuations of the experimental results. The evolution curves obtained from recording the mass lost during thermal desorption up to 350°C were used first to confirm the existence of two adsorbed states (*17*). Desorption of oxygen from the first state occurred from 25 to 130°C and of the second state from 175 to 285°C. The mass lost from each state is listed in Table 1 for the various temperatures of adsorption. As the temperature of adsorption increases, it is seen that the amount of oxygen adsorbed into the first state increases up to 72°C and remains approximately constant up to 144°C. The increase in the amount obtained in the second state at increased adsorption temperatures is similar to that obtained previously (*14, 16*). The peak rate and temperature range of desorption of the second state are the same as reported recently by Kollen and Czanderna (*15*).

For this paper, the results obtained for the first state are of interest. By varying

TABLE 1

MASS LOST FROM TWO CHEMISORBED STATES AFTER ADSORPTION AT DIFFERENT TEMPERATURES

T_{ads}(°C)	m_1(μg/g)[a]	m_2(μg/g)[a]
40	13.5	6.0
50	12.7	8.2
60	13.5	8.4
72	16.8	10.5
84	16.2	11.1
97	16.7	13.2
112	17.5	15.4
127	15.0	18.9
144	15.0	21.4
150	13.9	20.2

[a] BET surface area: 0.09 m²/g. The masses m_1 and m_2 were obtained from desorption that occurs from 25 to 130°C (state 1) and 175 to 285°C (state 2) (*15, 17*).

the partial surface coverages of oxygen adsorbed at 35°C, it was found that T_p is a function of the surface coverage and it was possible to show that the desorption of the first state is second order.

The maximum mass of oxygen, m_1 in Table 1, adsorbed into the first state is the mass of oxygen corresponding to $\theta_{s0} = 1$ for each temperature. These values of θ_{s0} were used with the corresponding mass evolution curves to construct plots of θ_s versus T for analysis. Four representative evolution curves, after oxygen adsorption at temperatures of 40, 72, 112, and 144°C, are plotted as solid lines in Figs. 1 to 4. The ordinate in these figures is the fraction of the weakly chemisorbed state remaining on the silver surface. The dots in the figures are values calculated for a second-order process from the parameter, E and ν, obtained from a computerized least-squares best fit to the experimental data. The open circles were calculated from Redhead's equations (*3*), as modified for the microgravimetric application (*15*), by using the experimental data for T_p, $d\theta_s/dT$ at T_p and β to determine E and ν. The values of E and ν, obtained from the computerized curve fitting and those calculated from Redhead's equations, are listed in Table 2. The apparent anomalous behavior of the values of E and ν at 84, 97, and 127°C for the values obtained from the computer probably results from the relative insensitivity of the least square errors method

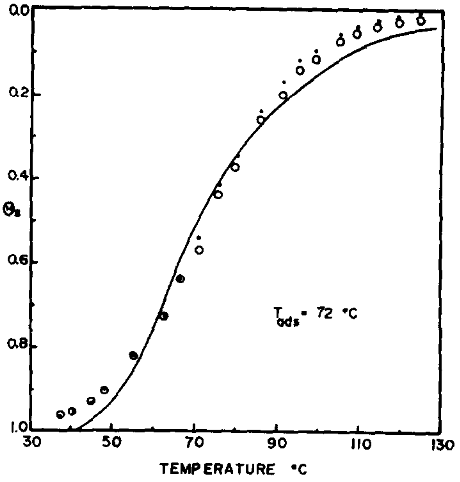

Fig. 2. The thermal desorption of oxygen from silver powder after adsorption at 72°C. The solid line is the average of three experimental runs. The open circles and solid circles were calculated from E and ν from the least squares fit and Redhead's equations, respectively.

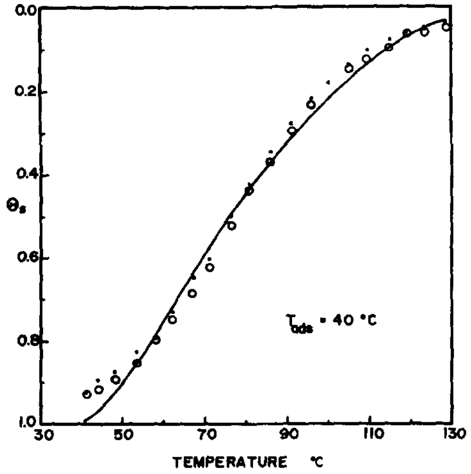

Fig. 1. The thermal desorption of oxygen from silver powder after adsorption at 40°C. The solid line is the average of three experimental runs. The open circles and solid circles were calculated from E and ν from the least squares fit and Redhead's equations, respectively.

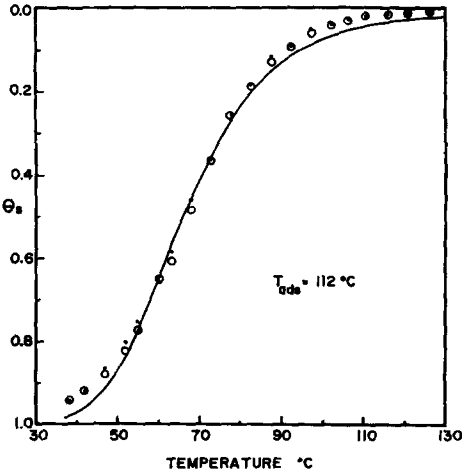

Fig. 3. The thermal desorption of oxygen from silver powder after adsorption at 112°C. The solid line is the average of three experimental runs. The open circles and solid circles were calculated from E and ν from the least squares fit and Redhead's equations, respectively.

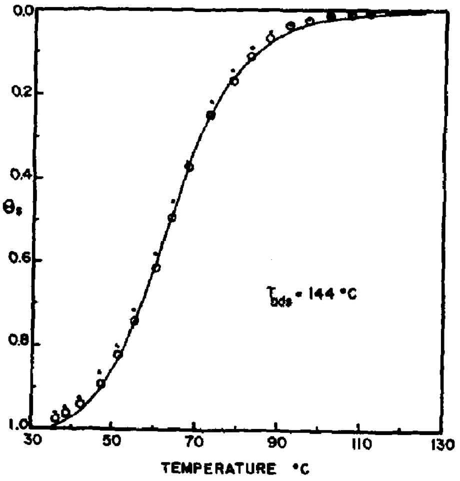

FIG. 4. The thermal desorption of oxygen from silver powder after adsorption at 144°C. The solid line is the average of three experimental runs. The open circles and solid circles were calculated from E and ν from the least squares fit and Redhead's equations, respectively.

to random fluctuations in the process of curve fitting.

DISCUSSION

Examination of Figs. 1 through 4 shows that for oxygen adsorbed at a temperature of 144°C, the theoretical fit was nearly perfect but became progressively poorer at lower temperatures. The differences between the experimental and calculated curves most likely results from the adsorption of oxygen into a distribution of states at the different temperatures. It is not likely that readsorption causes the differences seen in Figs. 1–4. Only one sample was used in this study; the time of the thermal desorption was the same, the same processing of the sample was followed, the same pumping speed was employed, the same system pressures were obtained during desorption, etc., but yet at 144°C the fit was perfect while at 40°C it was relatively poor.

The curves obtained at the lower temperatures have a wider temperature range for desorption than those obtained at the highest adsorption temperatures. It has been shown that a broadening of the evolution curve occurs when a distribution of activation energies is present (*9*). Thus, instead of a single adsorbed state, it is more likely that there is a distribution of the activation energies of desorption.

It is seen in Table 1 that there is a steep rise in the amount of the second adsorbed state of oxygen at about 100°C. Over the temperature range, 97 to 150°C, the calculated fit is good to excellent. The good fits probably arise because oxygen adatoms

TABLE 2
VALUES OF E AND ν AT DIFFERENT ADSORPTION TEMPERATURES OBTAINED BY TWO DIFFERENT METHODS

T_{ads} (°C)	E^a (cal/mol)	ν^a (sec^{-1})	T_p (°C)	$10^2 \times \frac{d\theta_s}{dT}$ (°C^{-1})^b	E (cal/mol)^c	ν (sec^{-1})^c
40	16,000	2.1×10^7	75	1.65	15,900	2.1×10^7
50	17,000	1.1×10^8	75	1.76	16,900	1.1×10^8
60	20,000	1.2×10^{10}	73	2.10	20,000	1.2×10^{10}
72	20,000	1.2×10^{10}	72	2.21	20,900	5.0×10^{10}
84	19,000	3.6×10^9	70	2.33	21,800	2.3×10^{11}
97	17,000	2.4×10^8	65	2.35	21,300	1.8×10^{11}
112	22,000	4.5×10^{11}	66	2.40	21,900	4.0×10^{11}
127	18,000	9.5×10^8	67	2.54	23,300	3.2×10^{12}
144	27,000	1.3×10^{15}	64	2.98	26,900	1.0×10^{15}
150	28,000	6.2×10^{15}	63	3.00	26,900	1.2×10^{15}

[a] Values from a computerized least squares fit of the entire evolution curve.

[b] $d\theta_s/dT$ at $T = T_p$.

[c] Values from Redhead's equations using the experimentally determined values listed for T_p and $d\theta_s/dT$ at T_p.

adsorbed from 97 to 150°C can distribute themselves uniformly by diffusion over the silver surface. Thus, the layer of mobile oxygen adatoms can be "ordered" and the oxygen adsorbed on top of this layer would more likely yield a "single state."

The fit, which is poorer at 84°C and below, could be corrected by introducing an appropriate distribution of activation energies. This was not done because either a value for the frequency factor or the distribution of activation energies would have to be assumed. It is evident from previous work that at these temperatures the first layer of adsorbed oxygen is immobile and can not "order" itself. Therefore, a surface with a broader distribution of activation energies for adsorption is presented and as a result, the weakly chemisorbed state of oxygen will adsorb with a "distribution of states" that has a mean value close to the activation energy obtained for a uniformly covered surface.

In Table 2, the values for E and ν, calculated from Redhead's equations, have similar trends as those obtained from curve fitting and, quantitatively, they are very close. This shows that the results obtained from the two above-mentioned methods correspond to the same physical reality.

The usual explanation of the meaning of a second-order desorption process is that adatoms recombine before desorption. It is to be noted that a second-order process is an empirical result and does not always guarantee a molecular interpretation. It could be suggested that the "weakly chemisorbed state" consists of adatoms adsorbed at a different displacement from the surface and in a layer over the initial oxygen coverage. However, the low energy involved is easier to accept on a physical basis as a molecular adsorption of oxygen ions. The repulsion between the tightly bound state (m_2) and the weaker state (m_1) would keep the molecule ions at a greater displacement than the adions. A mechanism of desorption that would be second order could involve the scission of the O–O bonds in two molecules "on-end" and the formation of one free molecule and two oxygen adatoms, thus yielding the association of two different species. The atoms released could recombine with adatoms in the tightly bound state to complete the desorption of the species adsorbed in state m_1.

The weaker state observed, adsorbed as a "2nd" layer of adatoms on oxygen covered silver, would also lead to the second-order desorption process observed but it is more difficult to accept on a physical basis.

The energy for desorption above 100°C (22–28 kcal/mol) is considerably less than that for the state existing at lower coverages and which yields a desorption energy of 35–42 kcal/mol *(15)*. Thus, this species would more likely be active in the catalytic oxidation reactions on silver such as ethylene oxide *(18)* and carbon monoxide to carbon dioxide *(19)*. At temperatures where the catalytic reaction is normally carried out (250°–300°C) both of these states can be desorbed in a vacuum. However, the oxygen coverage at 250°–300° at pressures of 100–300 Torr is sufficient *(14)* to populate the surface with both states as long as the oxygen pressure is maintained.

CONCLUSIONS

The thermal desorption of oxygen from silver after adsorption between 25 and 150°C yields two adsorbed states.

The first state desorbs between 25 and 130°C with a maximum rate of desorption between 63 and 75°C depending on the adsorption temperature. The evolution data from this adsorbed state obey second-order kinetics and could be fit by a Wigner-Polanyi desorption equation. The activation energies and the frequency factors, which depended on the adsorption temperature, ranged from 16 to 28 kcal/mol and, from 10^7 to 10^{15} sec^{-1}, respectively. At temperatures of 25 to 84°C, it is likely that there is a distribution of the activation energies of desorption, probably resulting from immobility of some of the chemisorbed species. The second-order desorption probably results from the scission of two molecularly adsorbed species with a yield of one gas-phase molecule and two adatoms.

The second state, which desorbs between

175 and 285°C, has the same properties as that for oxygen adsorbed at about 150°C, as previously reported by Kollen and Czanderna (*15*).

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