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Abstract

Full Text

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ISOTOPIC EXCHANGE OF OXYGEN ON PLATINUM FILMS

The interaction of oxygen with the surface of platinum has been studied by various methods by many investigators ([1–9]). In a number of works the conclusion is drawn that different forms of bonding of oxygen with the surface are present ([1,2,6]).

In the present study an attempt was made to assess the nature of the change in the bond energy of adsorbed oxygen with the surface of platinum films by measuring the rate of isotopic exchange of gaseous oxygen with adsorbed oxygen, as well as the homomolecular isotopic exchange of oxygen. The kinetics of the exchange were studied by the static method in a vacuum apparatus, the scheme of which is shown in Fig. 1. The film was prepared directly in the reaction vessel by evaporation in vacuum of a platinum filament. Analysis of oxygen samples was carried out on an MI-1305 mass spectrometer.

The accuracy of the analysis was 1-1.5% (relative). The enriched oxygen used in the studies contained 38 at.% O_{18}.

Measurements were carried out in the following order. On the prepared films, adsorption of the initial heavy oxygen was carried out at 20° immediately after deposition, or at 250° after heating the freshly deposited film in vacuum for 3 hours at 250°. Films that had adsorbed oxygen at 20° were then heated in vacuum at 250° for 2.5-3 hours; after heating, additional adsorption of oxygen was carried out on them at 250°. On films prepared in this way, the isotopic exchange of gaseous oxygen with adsorbed oxygen was investigated.

Fig. 1. Scheme of the apparatus: *1* –reaction vessel; *2* –platinum filament; *3* –traps cooled with liquid nitrogen; *4* –sampler; *5* –McLeod manometer; *6* –burette; *7* –U-shaped manometer; *8* –reserve volume; *9* –stopcocks; *10* –LM-2 manometric lamp.

For this purpose the heavy oxygen was pumped out from the reaction volume at room temperature to high vacuum; then natural oxygen was admitted into it, and the reactor was placed in a furnace preheated to the experimental temperature. The moment when the reactor was placed in the furnace was taken as the beginning of the experiment. During the experiment, oxygen samples were periodically taken to determine the O_{18} content. The experiments were carried out at 200, 224, 250° and at an oxygen pressure of 0.5–0.56 mm Hg.

The final stage of the study was homomolecular exchange. Experiments on homomolecular exchange were carried out mainly at 200

and 250° in the pressure range 0.15–0.50 mm Hg. The reaction mixture was prepared by mixing equal amounts of the initial heavy oxygen and natural oxygen.

The surface area of the films was determined from krypton adsorption at the temperature of liquid nitrogen (^{10}). We give the surface areas of films subjected to various treatments.

Treatment to which the films were subjected before surface measurement	Freshly deposited film	Oxygen adsorption at 20° on a freshly deposited film	Heating at 250° of a freshly deposited film	Heating at 250° of a film that had adsorbed oxygen at 20°
Surface area, cm^2	2600	2300	200	800–1000

As can be seen from the data given, the reduction in surface area upon sintering of a film with adsorbed oxygen is considerably smaller than in the case of a freshly deposited film.

Oxygen adsorption. At first rapid adsorption of oxygen occurred, followed by very slow uptake. At 20° the rapid adsorption amounted to about half a monolayer. The monolayer value was calculated from the assumption that one platinum atom on the surface adsorbs one oxygen atom. The number of platinum atoms on 1 cm^2 of surface was taken to be $1.3 \cdot 10^{15}$. At 250° the rapid sorption exceeded the monolayer value.

The slow uptake of oxygen did not cease during the entire adsorption experiment and, apparently, continued during the subsequent experiments.

As established by T. V. Kallish and R. Kh. Burshtein (2), oxygen is capable of dissolving in the near-surface layers of platinum at 200–400° in amounts of tens of monolayers. Probably, in the present case as well, the slow sorption is due to diffusion of oxygen into the depth of the film. The total sorption of oxygen by the film before the exchange experiments amounted to 2–4 monolayers.

Homomolecular isotope exchange of oxygen. The specific exchange rate was determined by a first-order equation (11). Table 1 gives the specific exchange rates for different films. As can be seen from the data of Table 1, the exchange rates under identical conditions for films that underwent different oxygen treatments are close to one another.

The activation energy of the reaction is 16.5 ± 1.5 kcal/mol. The order with respect to the oxygen pressure is close to 0.5.

No noticeable change in the activity of the films with time was observed.

Table 1

T, °C	Preliminary treatment of the film with oxygen	P, mm Hg	K, mol/sec · cm^2
200	Adsorption at 250°	0.5	$6.1 \cdot 10^{-13}$
200	Adsorption at 20° → heating and adsorption at 250°	0.5	$5.2 \cdot 10^{-13}$
250	Adsorption at 250°	0.5	$2.8 \cdot 10^{-12}$
250	Adsorption at 20° → heating and adsorption at 250°	0.5	$3.3 \cdot 10^{-12}$

Isotopic exchange of adsorbed oxygen with oxygen of the gas phase. In Fig. 2 the curve of the increase in concentration in the gas phase is plotted. As can be seen from Fig. 2, the rate of increase of the O_{18} content in the gas phase rapidly decreases with time. At the same time the concentration of O_{18} in the gas phase throughout the entire experiment rema—

was insignificant in comparison with the concentration corresponding to isotopic equilibrium with the surface.

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

The rate of isotopic exchange decreases with time much more rapidly than it could in the case of a homogeneous surface. Indeed, eight hours after the start of the experiment the rate of isotopic exchange had decreased by more than two orders of magnitude, whereas in the case of a homogeneous surface this decrease would have amounted to about 15%. This indicates the heterogeneity of the adsorbed oxygen.

Fig. 2. Increase in the concentration of O_{18} in the gas phase ($P = 0.52$ mm Hg): 1—at 200°; 2—at 250°

The rate of exchange in the present case proved to be close to the rate of exchange in the case of the homomolecular exchange reaction only at the very initial moment of time. At $\tau = 8.6$ h, the reaction temperature was raised from 200 to 250° (Fig. 2), and from the change in the reaction rate the activation energy corresponding to this depth of exchange (about 0.15 of a monolayer) was calculated. It proved to be equal to 28 ± 3 kcal/mole.

Assuming substantial heterogeneity of the adsorbed oxygen, one can calculate the change in the activation energy of exchange ΔE with the exchange time τ from the equation (12,13):

$$\Delta E = 2.3\, RT\, \Delta \lg \tau. \tag{1}$$

Fig. 3. Change in the activation energy of exchange (desorption) with the degree of exchange: 1—dependence obtained directly from the experimental data; 2—dependence constructed with allowance for the change in the degree of coverage

Figure 3 (curve 1) presents the dependence, found by the indicated method, of the change in the activation energy of exchange ΔE on the degree of exchange X, defined as the fraction of a monolayer of adsorbed oxygen that has come into isotopic equilibrium with the gas phase. The dotted part of the curve corresponds to extrapolation to $X = 0$. In constructing curve 1, the same degree of coverage was assumed for sites with different E. Allowance for the decrease in the degree of coverage for sites with small E (curve 2) leads to an insignificant increase in the heterogeneity.

The results obtained make it possible to conclude that oxygen adsorbed on the surface of a platinum film is heterogeneous, and that the activation energy of its exchange increases by 6 kcal/mole within 25% of a monolayer.

It is of interest to compare the activation energies of homomolecular exchange (E_1) and isotopic exchange of adsorbed oxygen (E_2). We shall proceed from the assumption that both processes occur by an adsorption-desorption mechanism. The difference in the values found for the activation energies cannot be explained only by surface heterogeneity; extrapolation to zero degree of exchange from the data of Fig. 3 gives $E_2 = 28 - 5 = 23$ kcal/mole, whereas for E_1 the value 16.5 kcal/mole was found. This difference is due to the fact that E_2 was measured for sites with a degree of oxygen coverage close to unity. Under these conditions the observed activation energy ···

of isotopic exchange is equal to the activation energy of oxygen desorption:

$$E_2 = E + q, \tag{2}$$

where E is the activation energy of adsorption and q is the heat of adsorption. Homomolecular isotopic exchange, as was shown earlier[14], proceeds predominantly on sites with degrees of coverage close to α, where α is the fraction by which the change in the activation energy of oxygen adsorption differs from the heat of adsorption,

$$\Delta E = -\alpha \Delta q.$$

The reaction order found by us for homomolecular oxygen exchange with respect to the oxygen pressure, equal to 0.5, makes it possible to conclude that, for the process of oxygen adsorption, α is close to 0.5. The observed activation energy of homomolecular exchange in this case is equal to

$$E_1 = E + 0.5q. \tag{3}$$

Substituting into equations (3) and (4), on the basis of the experimental data, the values $E_1 = 16.5$ and $E_2 = 23$ kcal/mol, we find that the heat of adsorption of oxygen on sites with a degree of coverage close to 0.5, at a pressure of 0.5 mm Hg and a temperature of 200°, is about 13 kcal/mol and increases within the first 25% of the monolayer to 25 kcal/mol.

Fig. 4. 1 –plot of the function $\theta(q/RT)$, where θ is the degree of coverage. 2 – plot of the function $W/W_m(q/RT)$, where W is the exchange rate (adsorption, desorption); W_m is the exchange rate at $\theta = 0.5$.

In Fig. 4 are shown the calculated changes in the degree of surface coverage and in the exchange rate as a function of the heat of adsorption.

A comparison of Figs. 3 and 4 makes it possible to establish that the homomolecular exchange reaction proceeds predominantly on sites constituting about 3% of the entire surface.

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