The Adsorption of Oxygen on Evaporated Gold Films

While early work by Trapnell (*1*) indicated that evaporated gold films did not adsorb oxygen at room temperature, more recent studies on wires (*2*), foils (*3*), and powders (*4*) have found that oxygen may be adsorbed at temperatures in the range 25–120°C. Incorporation of oxygen into the bulk has been suggested at temperatures above 200°C (*2*). It may be noted that only the study by Wise *et al.* (*3*) on foils has been made under the ultrahigh-vacuum conditions necessary to ensure clean metal surfaces.

The present work is a preliminary determination of the conditions where oxygen is adsorbed on evaporated gold films prepared under ultrahigh-vacuum conditions. The experiments were made using a bakable glass system capable of attaining a pressure of 5×10^{-10} Torr. The gold film was evaporated onto the wall of a cylindrical reaction vessel from a gold wire wound on an electrically heated clean tungsten filament. The rate of evaporation was controlled so that the pressure did not exceed 5×10^{-8} Torr. Following evaporation, the pressure decreased to between 8×10^{-10} and 1×10^{-9} Torr. The pressure was measured on an ionization gauge, which was isolated from the reaction system during adsorption measuerments. Attempts to use the ionization gauge to measure oxygen adsorption on gold at low pressures were unsuccessful; it was found that the gauge itself adsorbed oxygen, leading to anomalous results. In an experiment, a measured dose of oxygen was admitted to the reaction vessel, and the decrease in pressure with time was measured using a Pirani gauge calibrated for oxygen. Runs were made on freshly prepared films at temperatures in the range 25–405°C and initial pressures from 10 to 20 μ. The volume of gas admitted was equivalent to between one and three surface monolayers. Initial pressures determined by extrapolation of pressure-time curves to zero time and by calculation from the pressure of gas admitted from a known volume were in good agreement. The surface areas of the films were taken as their geometric areas (i.e., fully sintered) (*1*), and were in the range 90–120 cm^2. The films were of sufficient thickness to be fully opaque and had a typically gold appearance. A reaction vessel with no evaporated film showed no adsorption of oxygen at temperatures up to 405°C.

The results of a typical experiment, at 405°C, are shown in Fig. 1. Oxygen was admitted to the film at an initial pressure of 14.5 μ. The pressure decreased with time until, after 20 min, a constant pressure of 10.4 μ was attained. Admission of a second dose of oxygen after 60 min at an initial pressure of 19.8 μ possibly resulted in a further small uptake. The reaction vessel was evacuated at 405°C for 15 min, after which oxygen was admitted to the film at an initial pressure of 11.8 μ. No decrease in pressure was observed over a period of 30 min. Calculation indicates a surface coverage, θ, of 0.7 at an equilibrium pressure of 10.4 μ, assuming diassociative chemisorption; the number of gold-surface sites is calculated to be 1.2×10^{15} cm^{-2}, assuming equal exposure of 100, 110 and 111 planes. It may be noted that for dissociative adsorption on adjacent sites, at high coverages there will be left a number of unfilled single sites which are not available for chemisorption; this number is approximately 9.15% (*5*). The initial rate of adsorption of oxygen at 405°C and 14.5 μ was 3×10^{11} molecules cm^{-2} sec^{-1}, in good agreement with the same value obtained by Wise *et al.* for foils at 427°C and 10^{-7} Torr oxygen (*3*).

In similar experiments, in the temperature range (295–341°C) oxygen adsorption was observed, with low coverages in the

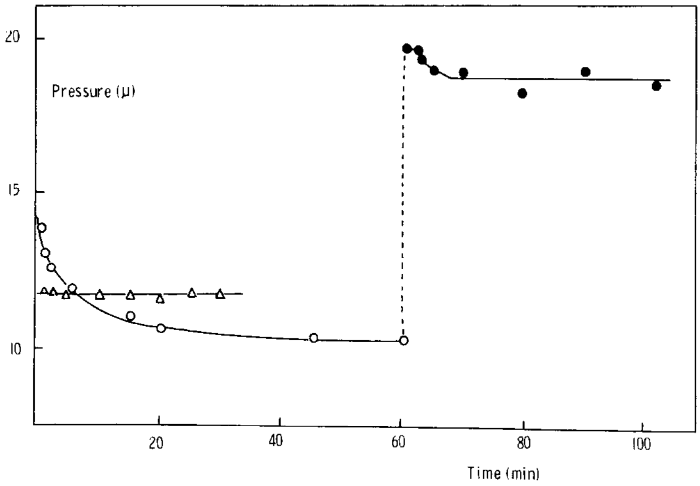

FIG. 1. Adsorption of oxygen at 405°C: ○, first admission of oxygen; ●, second admission of oxygen, and △, third admission of oxygen, after evacuation at 405°C for 15 min.

range $\theta = 0.1$–0.3. In these cases there was no further adsorption on addition of a second dose of oxygen, nor was oxygen desorbed on evacuation. A run at 250°C indicated the possibility of a very small amount of adsorption, but the extent was such that no meaningful conclusions could be made.

At 25, 133, and 229°C no adsorption was observed. The pressure in the system remained constant at the initial pressure over periods up to 60 min. The limits of accuracy of the experiments place any adsorption at these temperatures below 2% of a monolayer coverage. These results support and extend Trapnell's findings for evaporated films at room temperature (*1*). They are, however, in disagreement with the results on wires (*2*), and powders (*4*), although these studies were made at somewhat higher pressures. This anomaly is difficult to explain, but may result from the different surface treatment and vacuum techniques used. It may be noted that the present work and that of Wise *et al.* (*3*) on foils cannot easily be compared due to the very different pressures used. Thus Wise *et al.* found that the coverage increased with temperature to a maximum at 427°C at a pressure of 10^{-7} Torr; their data give a maximum value of approximately 0.03 for θ, assuming dissociative adsorption. The variation of surface coverage with temperature observed for evaporated films and for foils, suggest that oxygen adsorption on gold is an activated process, as noted by Wise *et al.* In the present case the oxygen was irreversibly chemisorbed and could not be desorbed on evacuation. There was no evidence of any significant incorporation of oxygen into the bulk of the gold; such a process would regenerate surface sites for further chemisorption and the amount adsorbed would continue to increase with time.

The adsorption of oxygen on gold is of interest in the understanding of heterogeneous catalytic reactions on the metal. For example, the decomposition of nitrous oxide (*6*) and the oxidation of carbon monoxide (*7*) have been investigated on gold catalysts; the mechanisms of these reactions are considered to involve adsorbed oxygen species. Following Trapnell's conclusion that oxygen was not adsorbed on gold, Daglish and Eley (*7*) suggested that in carbon monoxide oxidation at 200–400°C, CO adsorbs on normal gold-surface sites while oxygen is adsorbed at dislocations or impurity atoms, with the adsorption of oxygen being rate determining. The present study suggests that adsorption of oxygen at dislocations or impurity atoms is not necessary, and that the reaction proceeds on normal surface-gold sites. The slow and activated adsorption observed is in accordance with the suggestion that oxygen adsorption is the rate-determining step in carbon monoxide oxidation.

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Chemisorption of Carbon Monoxide on Ferric Oxide

A Test for the Active Site on the Transition Metal Oxides

It has been shown that the transition metal oxides such as Co_3O_4, NiO, Cr_2O_3 are active catalysts for the isotopic mixing in hydrogen (*1*) and ethylene (*2*), and the hydrogenation of ethylene (*3*). The twin peak pattern of the activity change (*1*) introduced by Dowden, Mackenzie, and Trapnell is well known, and a crystal field interpretation of this pattern has been proposed (*4*). On the other hand, it has been shown that the catalytic activities of these oxides for the isotopic mixing in ethylene is developed by dehydration of the oxide surface brought about by evacuation at higher temperatures above 200°C (*2*). The active sites thus formed on the oxide surface are admittedly oxygen vacant because of the removal of a water molecule from the hydroxylated surface. Accordingly, it seems that the oxygen vacancy is an essential condition for the active oxide catalyst.

As previously reported (*2*), the active sites on these oxides are effectively blocked by carbon monoxide and also by water. The fatal amounts of carbon monoxide that prevent the isotopic mixing in ethylene are generally small as follows: Co_3O_4:2.4, NiO:0.4, Cr_2O_3: <0.3 10^{14} molecules/cm^2, where oxides were pre-evacuated at 500°C. These figures give the approximate number of active sites. Thus one can estimate the number of active sites by the chemisorption of carbon monoxide at low pressure on these oxides.

In this respect it is interesting to study the chemisorption of carbon monoxide on ferric oxide which is known to be inactive for the isotopic mixing (*1–2*). However no data relevant to this problem is available. Thus it was decided to study the nature of the active site by the chemisorption of carbon monoxide on ferric oxide at low pressure.

EXPERIMENTAL

The ferric oxide sample was prepared by decomposition (550°C, 6 hr, in air) of ferric hydroxide, which was prepared by precipitation from ferric nitrate with ammonia. BET area of the sample was 20 m^2/g. Adsorption measurements were carried out at room temperature following pressure change by means of a rotating McLeod gauge. The dead space in the adsorption