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Interaction of Oxygen and of Ethylene Dichloride with Silver Surfaces

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Adsorption equilibria and rates for oxygen on silver powder were measured at 200°C. The rate of adsorption of oxygen on silver is markedly decreased by surface impurities; the rate was decreased more than tenfold by approximately one-quarter of a monolayer of chemisorbed chlorine. Controlled amounts of chemisorbed chlorine can be emplaced on the silver surface by making use of the fact that ethylene dichloride adsorbs strongly on a silver surface at room temperature; the adsorbed material decomposes slowly at room temperature, and rapidly at 100°C, to liberate ethylene and chemisorbed chlorine. A silver surface thus contaminated with chlorine adsorbs ethylene at room temperature.

INTRODUCTION

Silver is a uniquely effective catalyst for the oxidation of ethylene with oxygen to ethylene oxide (*1–3*); carbon dioxide and water are formed as additional products, apparently by a parallel reaction or series of reactions. Oxygen has long been known to chemisorb strongly by an activated process on silver (*4, 5*) whereas ethylene does not. The adsorption of oxygen is rapid at the usual reaction temperatures (200–300°C). On the basis of these facts, kinetic studies and other experiments with a silver-plated glass wool catalyst, Twigg (*6*) proposed that the initial step in the catalytic reaction occurs between chemisorbed oxygen and either weakly adsorbed or gas phase ethylene. Most subsequent studies by other authors have confirmed this general proposal, though there is disagreement with some details of Twigg's mechanism.

The steady state coverage of the surface by oxygen during the reaction will be determined by the competition between the rate of adsorption of oxygen and the rate of reaction with ethylene. For this reason a number of students of the catalytic reaction have investigated the kinetics and equilibria in the adsorption of oxygen on silver. The purpose of the present paper is to present some observations on the effects of surface contamination on the adsorption of oxygen on silver.

Part of the motivation for this study was the important discovery, made 20 years ago by Law and Chetwood (*7*), that the yield of ethylene oxide at a given conversion could be appreciably improved by the addition of traces of halogenated organic compounds to the ethylene feed; in particular, ethylene dichloride was effective for this purpose. This discovery has been confirmed by others (*8, 9*) who showed that an excess of ethylene dichloride poisons the catalyst completely and by Kummer (*10*) who showed that the presence of either chlorine or sulfur on the surface of a single crystal of silver decreased the activity of the catalyst but increased its selectivity for the formation of ethylene oxide. More recently it has been claimed (*11*) that similar effects are produced by sulfur, selenium, and tellurium on the silver surface.

As pointed out in a recent comprehensive review (*12*), no satisfactory explanation of these effects of surface contaminants on the selectivity of the ethylene oxide synthesis over silver has yet been offered.

EXPERIMENTAL

Adsorption was measured on 5 to 10 g of catalyst by following changes in pressure in a constant-volume system with a volume of 110 ml. Initial pressures varied between 0.1 to 15 mm Hg. Pressures were measured with a small multirange McLeod gauge. With the sample chamber at —196°C, the same apparatus was used to determine the surface area of the catalyst sample by the BET method from measurements of the adsorption of krypton; a molecule of krypton was assumed to occupy an area of 19.5 Å² on the surface.

Effect of Cleaning a Contaminated Surface

A sample of unsupported silver powder was made by the reduction of silver oxide with hydrogen. The oxide was precipitated from solutions of silver nitrate and potassium hydroxide, washed thoroughly with distilled water, dried at 120°C, and pelleted. The pellets were broken to granules, 10–20 mesh; these were reduced to silver by treatment with a purified stream of 10%*M* hydrogen in nitrogen. The temperature was increased gradually from 170° to 210°C during this reduction.*

An 8.2 g sample of this catalyst was sealed into the adsorption apparatus and swept with purified hydrogen at 200°C and 1 atm for 1 hr. After evacuation at 250°C for 0.5 hr, the sample was cooled to —196°C and its surface area was found to be 0.29 m²/g. The catalyst was then exposed to a series of cleaning treatments comprising sweeping with hydrogen at 1 atm and 225°C for 0.5 hr, evacuation at 250°C for 0.5 hr, exposure to air at 1 atm and 225°C for 1 hr, evacuation at 200°C for 10 min, sweeping with hydrogen at 200°C for 0.5 hr, and evacuation at 250°C for 0.5 hr. After one such cycle, the surface area was decreased to 0.244 m²/g; after three cycles, to 0.238 m²/g. Further repetition of the cycle gave no measurable additional loss of surface area. The fact that sintering of this sample did not continue at an appreciable rate with further repetitions of this cycle suggests that its surface still carried some sort of contamination.

Adsorption isotherms were measured on this sample at 200° and 250°C. The adsorption isotherm for oxygen on silver in this temperature range has previously been shown to follow a Temkin equation over a wide range of oxygen pressure (*13*) but can be represented adequately by a Langmuir-type isotherm over the range shown in Fig. 1. The solid curves were computed from

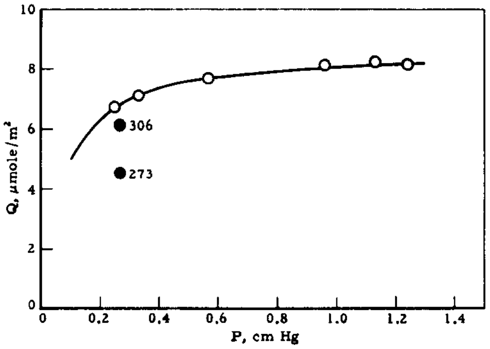

FIG. 1. Adsorption isotherm O_2 on Ag.

$$Q_e = ap/(1 + bp)$$

where Q_e represents micromoles adsorbed per square meter. The constants at 200° and 251°C, respectively, are $a = 112.(3)$, $84.(1)$ (cm Hg)$^{-1}$; $b = 12.85$, 10.07 (cm Hg)$^{-1}$. Agreement with the Langmuir isotherm ($a = b$) for the fractional coverage, θ, requires $\theta = Q/8.75$ for the 200°C data and $Q/8.35$ for the 251°C data. On this basis the maximum coverage of the surface attained at 1.2 cm Hg and 200°C is 0.93. Considerably higher pressures of oxygen appear to have been necessary to give comparable coverage on the promoted silver catalysts studied by Smelzer *et al.* (*14*).

Attempts were made to cover the surface more completely by equilibrating the silver sample with oxygen at 1.20 cm Hg and 250°C, and cooling the sample to successively lower temperatures. At each temperature the pressure was followed until it became constant. The maximum adsorption achieved was 9.12 micromoles/m² at 145°, 155°, and 165°C at pressures around 0.9 cm Hg. If this is assumed to be $\theta = 1$, then $\theta = Q/9.1$. This corresponds to 18.2 Å² per

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* The authors are indebted to H. H. Voge and L. T. Atkins of these laboratories for the preparation of the catalysts studied in this investigation.

molecule of oxygen; this is equal to the area occupied by two silver atoms on the (100) face of silver. The apparent relation between Q and θ depends, of course, on the area assumed to be occupied by an atom of krypton in the measurements of surface area. The adsorption data do appear, however, to be consistent with fairly complete coverage of the silver surface and, hence, with a relatively clean surface.

Figure 1 compares this adsorption isotherm at 200°C to single adsorption measurements on two samples of similar catalysts which had not been cleaned by repeated cycles of oxidation and reduction, but had simply been swept with hydrogen at 200°C before the adsorption measurement. The lower extent of adsorption is presumably associated with a less clean surface. Silver catalysts prepared as described above, even with care, are known to contain enough impurity to contaminate their relatively small surface to a significant extent (*15*).

Rates of adsorption were measured on these two catalysts at 200°C by treating them with hydrogen at 200°C, evacuating the system, admitting oxygen at an initial pressure of 3.5 mm Hg and following the change in pressure for about 3 hr until equilibrium was closely approached. This procedure is experimentally simple but suffers from the disadvantage that adsorption does not occur at constant pressure. The total change in pressure, however, was in no case greater than 25% of the initial pressure, and it proved to be possible to represent the later stages of the adsorption kinetics by an equation of the Langmuir type,

$$\ln Q_e/(Q_e - Q) = Kt$$

where Q_e is the final equilibrium amount adsorbed. For a Langmuir isotherm, $K = k_a p/\theta_e$, where k_a is the rate constant for the adsorption process, θ_e is the fractional coverage of the surface in equilibrium with p, and p is the average partial pressure of oxygen during the linear part of the curve. Rates of adsorption are plotted in accordance with this equation in Fig. 2. The linear region extended in both cases well beyond the limits shown; the curvature in the initial portion of the curves is due only in part to the fact that the pressure was changing during the experiment. The major cause of the curvature is the fact that the oxygen initially adsorbed inhibits the adsorption of more oxygen; the same effect presumably gives rise to the Temkin isotherm (*13*).

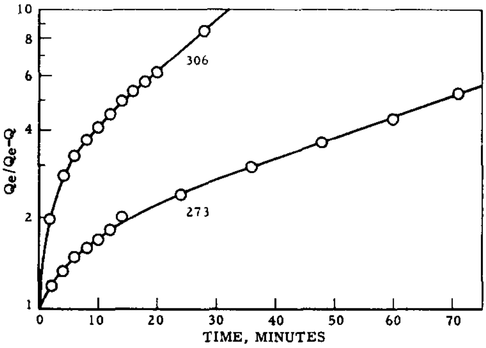

FIG. 2. Rate of adsorption O_2 on Ag.

The essential fact that is demonstrated by Fig. 2 is that surface contamination very strongly decreases the rate of adsorption of oxygen on silver. Unfortunately, neither the amount nor the nature of the contaminant on these samples is known.

Though measurements of rates of adsorption were made on the cleaned sample at low oxygen pressures, none were made under the same conditions as those used to obtain Fig. 2; the procedure for measuring rates of adsorption at higher pressure was introduced after the cleaned sample had been lost. A rough estimate of the rate constant for adsorption on the cleaned sample was made on the basis of the low-pressure measurements and is given in the last row of Table 1; it appears to be somewhat larger than the rate constant derived from the higher-pressure measurements for the relatively clean sample, No. 307.

Even on the cleanest samples studied, the rates of adsorption were much lower than those reported for the very fast chemisorption of hydrogen on nickel and other transition metals. This is a consequence of the fact that adsorption of oxygen on silver is an activated process (*5, 13*); indeed, at room temperature or below, the rate of

TABLE 1

RATES OF ADSORPTION OF OXYGEN ON SILVER POWDER AT 200°C

Sample No.	S (m²/gm)	Final p_{O_2} (mm Hg)	Equilibrium O_2/ coverage θ_e		Linear range[b] in θ	k_a [min^{-1} (cm Hg)$^{-1}$][c]
			Obs.	Calc.[a]		
307	0.36	2.72	0.67	0.74	0.48–0.67	0.22
458	0.31	1.54	0.46	0.64	0.35–0.46	0.17
306	0.34	2.76	0.67	0.75	0.50–0.67	0.096
273	0.29	2.73	0.50	0.75	0.36–0.50	0.027
458 + Cl	—	2.67	0.25[d]	—	—	≤ 0.004
273, cleaned	—	—	—	—	—	Probably >0.25[e]

[a] Calculated from isotherm measured for sample 273, cleaned by repeated oxidation and reduction.

[b] Range in θ over which approximate Langmuir rate plot was linear.

[c] Rate constant for adsorption of oxygen, assuming Langmuir kinetics.

[d] Assuming surface area of sample not changed by treatment with $C_2H_4Cl_2$.

[e] Estimated by extrapolation from rate measurements made at much lower pressures.

adsorption of oxygen on silver becomes quite slow.

INTERACTION OF SILVER WITH ETHYLENE DICHLORIDE

In the hope of finding a method to emplace known amounts of halogen on the silver surface, a study was made of the interaction of ethylene chloride with a silver surface. In these studies, pressures were measured in the range 0.001 to 0.3 mm Hg by means of a thermocouple gauge. It was found that the vapor of ethylene dichloride adsorbs rapidly on silver at room temperature and then decomposes slowly with the evolution of ethylene. The rate of decomposition increases rapidly with increasing temperature. For example, when 0.45 micromole of ethylene dichloride was exposed at room temperature and an initial pressure of 0.093 mm Hg to 6.50 g of silver with specific surface of 0.29 m²/g, the pressure dropped within 3 min to 0.0019 mm Hg, corresponding to adsorption of 98% of the initial charge. Whether the residual pressure was due to ethylene chloride or ethylene was not determined. The pressure was observed to increase very slowly during the next hour, at a rate corresponding to the evolution of about 0.012 micromole of ethylene per hour, or to decomposition of 2.8%/hr of the adsorbed ethylene dichloride. When the sample was warmed to 100°C, the pressure rapidly increased to a value corresponding to essentially complete decomposition of the adsorbed material (observed pressure, corrected to room temperature, 0.09 mm Hg). The gas evolved was identified mass-spectrometrically in a similar but separate experiment as essentially pure ethylene.

These observations provide a convenient means for putting known amounts of chlorine on a silver surface. A 15.8 g sample of silver powder with an area of 4.95 m² was swept with hydrogen at 200°C for 1 hr and evacuated at 250°C. Measurements of the rate of adsorption of oxygen were then made in a constant-volume system at room temperature and an initial pressure of 3.1 mm Hg; the pressure during the usable part of the rate measurement ranged from 1.8 to 1.6 mm. The sample was evacuated at 250°C, swept with hydrogen at 250°C for 2 hr, and evacuated.

Approximately 9 micromoles of ethylene chloride were decomposed on the surface of this sample of silver. If we assign a radius of 1.8 Å to the chlorine atom on the surface, which corresponds to a close-packed area of 11.2 Å² per chlorine atom, the amount of chlorine added to the sample was sufficient to cover 25% of the surface. Measurements of the rate of adsorption of oxygen on the chlorided surface were made at room temperature and an initial pressure of 2.94 mm Hg which declined to 1.74 mm during the measurement. The observations are compared in Fig. 3.

The decrease in rate of adsorption of oxygen is striking. In terms of the previously employed rate equation, the constant

K on the original surface was 3.7×10^{-2} min^{-1}; on the chlorided surface it is approximately fiftyfold smaller. This large effect of an electronegative surface contaminant on the rate of adsorption of oxygen on silver slows down markedly in the vicinity of 50% coverage. Thus the effect of adsorbed chlorine on the adsorption of oxygen is similar to, but larger than, the effect of adsorbed oxygen on its own further adsorption. Our data on rates of adsorption of oxygen on silver are summarized in Table 1.

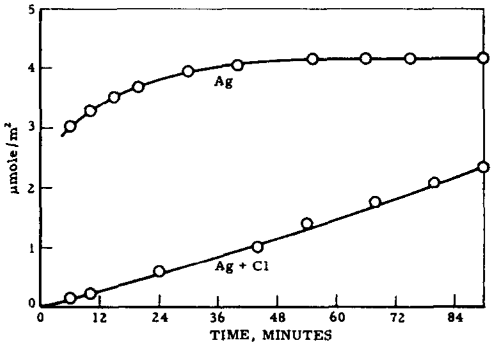

FIG. 3. Comparison of adsorption rates on chlorided and nonchlorided silver.

A remark may be in order here about the adsorption of ethylene on silver. In studying the decomposition of adsorbed ethylene dichloride on silver we observed that when the sample cell was cooled from 100°C back to room temperature, a large fraction of the ethylene that had been emitted was readsorbed. Even after the surface of the silver was treated with hydrogen, however, ethylene was still adsorbed about as strongly (0.1 to 0.2 micromoles/m^2 at a pressure of the order of 0.005 mm Hg) at room temperature, though adsorption was not detected at 200°C.

We have shown that ethylene dichloride adsorbs strongly on silver and decomposes readily to leave halogen on the silver. The chlorine on the surface at moderately high surface concentrations inhibits the rate of adsorption of oxygen. There may very well be other effects of adsorbed halogen on the individual steps in the catalytic oxidation of ethylene, but these remain to be demonstrated.

It would obviously be desirable to study both rates and equilibria in the adsorption of both ethylene and oxygen on silver surfaces contaminated with less than 25% of a monolayer of halogen. In view of the small surface usually attainable with silver samples, such measurements will require the use of very clean high vacuum technique. Our own data indicate that the effect of adsorbed chloride on the rate of adsorption of oxygen diminishes rapidly as the amount of adsorbed chlorine decreases below 15% of a monolayer, but the data are not sufficiently reproducible to warrant presentation here.

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