JOURNAL OF CATALYSIS 8, 162–172 (1967)

The Oxidation of Ethylene over Evaporated Palladium-Silver Alloy Films

II. Variation of Activity with Catalyst Composition

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Received December 12, 1966; revised March 7, 1967

The oxidation of ethylene in a static system using evaporated films as catalysts (without promoters), gave yields of ethylene oxide at 240°C which were highest over pure silver, decreasing to zero over alloy films with $>40\%$ palladium. The faster rate of CO_2 formation decreased slowly before increasing again—sharply above 90% Pd/Ag—to a substantial maximum over pure palladium. The alloy catalysts required reactivation by hydrogen between rate measurements to determine activation energies; pretreatment of silver films with oxygen, ethylene oxide, etc., confirmed the association of ethylene oxide with the deactivation of silver catalysts.

The high activity of palladium compared with silver for the complete oxidation to CO_2 is correlated with a lower heat of oxygen chemisorption. Most of the reported decrease in adsorption heat occurs near pure palladium, which is reflected in the present catalytic properties. The activation energy for CO_2 formation increased from $\sim$14 to $\sim$30 kcal/mole between $\sim$40 and $\sim$60% Pd, compensated by an increase in frequency factor. The extent to which silver enrichment at the surface, and hydrogen solubility in the lattice, may superimpose on a pattern of activity related to the electronic structure of the bulk is discussed. The reported rate of hydrogen-oxygen combination also falls rapidly when silver is added to palladium so that hydrogen dissolution in the lattice (see Part I, preceding paper) competes with its desorption as water. An explanation for the decrease in ethylene oxide formation with increasing palladium content was sought in variations between the modes of oxygen chemisorption. This variation may arise from changes in bulk electronic properties or surface structure; unchanged reaction rates over a 19% Pd/Ag film, prepared with the palladium-rich structure, suggest the former.

INTRODUCTION

The mechanism of ethylene oxidation over metals and oxides has been extensively studied (*1*, *2*) but the unique property of silver-based catalysts to form ethylene oxide, in addition to carbon dioxide and water, is still remarkable. Twigg (*3*, *4*) considered that the mechanism over silver involves the chemisorption of oxygen as atoms followed by the reaction of gaseous or weakly adsorbed ethylene, either with one oxygen atom to form ethylene oxide, or with two oxygen atoms to form species which are oxidized further to carbon dioxide. In addition, the ethylene oxide may isomerize to acetaldehyde which is oxidized rapidly to carbon dioxide and water. The mechanism by which carbon dioxide is formed has been debated particularly (*5*) but Margolis and Roginskii (*6*), using a mixture of ^{14}C-labeled ethylene and unlabeled ethylene oxide, found that 80% of the initial carbon dioxide was formed directly from ethylene. When mixtures with added formaldehyde or acetaldehyde were oxidized, more ethylene oxide and less carbon dioxide were formed than with ethylene alone, indicating that aldehydes cannot be important intermediates in the formation of carbon dioxide. The oxidation of ethylene therefore appears to be an attractive choice for studies on the effect of geometric and electronic factors on *selectivity* in catalytic oxidation reactions, observing the relative rates of ethylene oxide and carbon dioxide formation.

On the basis that the spatial separation of the chemisorbed oxygen atoms is important in determining the ratio of ethylene oxide to carbon dioxide in the product, Kummer (*7*) studied the reaction over the (211), (110), and (111) faces of single crystals of silver but found that the rates and selectivity were almost unaffected. Similarly, no marked differences in activity or selectivity were found for silver films (*8*) in which the crystallites were initially either randomly oriented or had the (110) plane parallel to the glass substrate, probably because under reaction conditions the oriented films recrystallized. When the nature of the metal was varied (*9*) it was found that, for the complete oxidation to carbon dioxide, the strength of the metal-oxygen bond is an important factor governing the relative activity observed over palladium, platinum, rhodium, and tungsten films. A detailed examination has also been made of the kinetics of ethylene oxidation over palladium films (*10*) where trace amounts of acetic anhydride and acetic acid, which progressively poisoned the reaction, were detected.

The present work is concerned with the activity and selectivity for ethylene oxidation of palladium-silver alloy films where the electronic structure of the catalyst varies with alloy composition. The area of these films was sufficient to permit the reaction to be studied at typical temperatures.

EXPERIMENTAL

The reaction mixture was prepared from "spectrographically pure" oxygen (British Oxygen Co., Ltd.) and 99.9+% ethylene, with ethane as the impurity (Phillips Petroleum Co., Ltd.) and when expanded through a trap at −78°C into the reaction vessel at ice temperature gave 25 mm oxygen + 10 mm (or 1.35×10^{20} molecules) of ethylene. The reaction was studied in a "static" system with the reaction vessel connected directly to the ion source of a mass spectrometer by means of a fine glass capillary leak. Less than 2% of the gas mixture was removed from the reaction system per hour. The mass spectrometric analyses were made with 70-V electrons to ionize the molecules, recording relevant peaks in the range *m/e* 12–44 and monitoring *m/e* 45–70 every 8–10 min. The amount of ethylene in the reacting mixture was measured using peak *m/e* 26 since carbon dioxide gave a large fragment at mass 28 and there is also the uncertainty of the contribution of residual gases at this mass number. Peak *m/e* 29 was the largest entity in the mass spectrum of ethylene oxide and, after correction for the isotopic contribution from ethylene, was used to determine ethylene oxide. To determine carbon dioxide from peak *m/e* 44, the peak height was first corrected for the parent ion of ethylene oxide. Although this is ~70% of mass 29, because the amount of ethylene oxide formed was small compared with carbon dioxide, this correction was not substantial. The sensitivities of carbon dioxide, ethylene oxide, and oxygen relative to ethylene were found from calibrations on suitable mixtures of these gases. In particular, the effect of variation in the amount of oxygen present on the relative sensitivities was examined. These results indicate that as the reactants are converted, the relative sensitivities should remain reasonably constant. Peak heights at reaction temperature, adjusted for relative sensitivities, were then brought to their corresponding values at 0°C. A fluidized sand bath was used to bring the catalytic vessel rapidly up to temperature, limiting "heating-up" corrections to about the first 5 min and thus reducing the error in observing initial rates. The absolute sensitivity of the mass spectrometer was determined from the ethylene peak height at 0°C before each experiment and hence results could be expressed in terms of pressure, millimeters at 0°C.

Results and Discussion

Reaction Rates and Products

Figures 1 and 2 show typical results for the oxidation of ethylene at 240°C over silver or silver-rich alloys and palladium or palladium-rich alloys, respectively, for films deposited and annealed at 400°C. The progress of the reaction was followed in terms of the variation with time of the par-

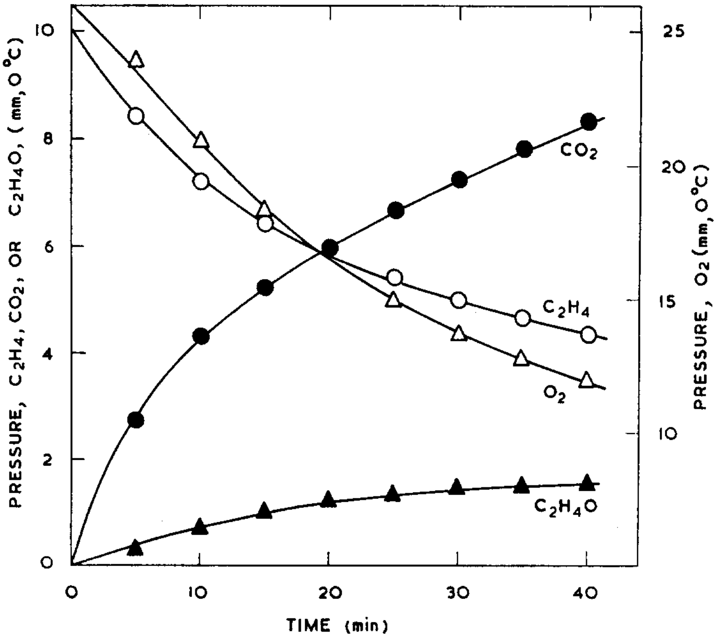

Fig. 1. Oxidation of ethylene at 240°C over a 24.5-mg alloy film of composition 12.6% Pd/Ag.

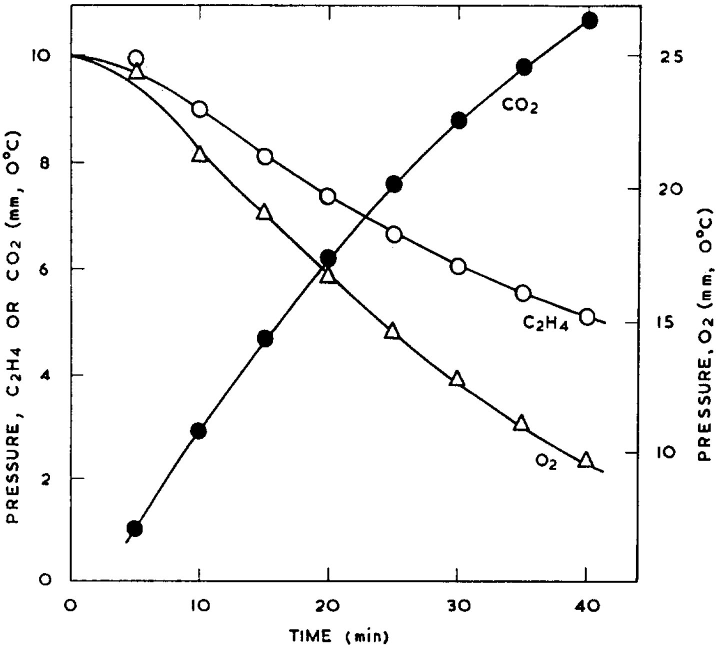

Fig. 2. Oxidation of ethylene at 240°C over a 20.7-mg alloy film of composition 76% Pd/Ag.

tial pressures (mm, 0°C) of ethylene, oxygen, carbon dioxide, and, where formed, ethylene oxide. A satisfactory carbon balance was obtained.

Over silver and silver-rich alloy films (Fig. 1), the formation of carbon dioxide was at least four to five times faster than the formation of ethylene oxide, both rates falling off markedly with time (a promoter for improving the selectivity to ethylene oxide was not, of course, used). Carbon dioxide and water were the only products formed at 240°C over palladium and palladium-rich alloys (Fig. 2), but now the rate of carbon dioxide production decreased only slowly as the reactants were converted. Reaction rates reported are *initial* rates and refer to product formation over the first 10–15 min. A careful search of the mass range 12–80 revealed only occasional very small peaks at *m/e* 55–60, which could not be accounted for.

Catalyst Reactivation and Pretreatment

The method of preparation does not readily repeat a given alloy composition just when required and, of course, the composition is not known until the reaction vessel has been dismantled. Hence for the determination of activation energies, it is desirable to extract the necessary information from each alloy film prepared. However, as Film No. 1, Table 1, shows, when the first reaction mixture was pumped out of the catalytic vessel and a second mixture admitted without any reactivation treatment, a substantially lower activity was observed. Therefore, various methods of reactivating the films were examined (summarized in Table 1).

It had been found previously (*11*) that heating in hydrogen would restore the activity of silver-rich Pd-Ag alloy films used for CO oxidation. In the present work, a similar treatment restored ethylene oxide and, to a large extent, CO_2 formation over a silver-rich film (Film No. 2). The activity of a palladium-rich film (Film No. 3) which had fallen to a low value after evacuating at 350°C and admitting a second gas mixture, could also be restored (Film No. 3, Test No. 3), and retained over many subsequent experiments by hydrogen reactivation.

After hydrogen reduction, the vessel was evacuated while still at 240°C to avoid hydrogen sorption in palladium-rich alloys which could alter the activity. In Film No. 3, the restored activity was approximately equal to the initial activity immediately after preparation and before the film had ever been exposed to hydrogen. The

TABLE 1
REACTIVATION AND PRETREATMENT OF CATALYSTS

Film No.	Weight/composition (mg)	(atom %)	Preparation and reactivation or pretreatment	Test No.	Catalytic activity (240°C) (mm/min) CO_2	C_2H_4O
1	7.6	pure Ag	Deposited and annealed at 400°C	1	0.25	0.05
			Evacuated at 0°C after 1st reaction	2	0.03	0.003
			50 mm H_2, 230°C, 60 min; evacuated, 0°C	3	0.05	0.006
2	31.5	11% Pd	Deposited, 400°C; annealed in H_2 400°C	1	0.46	0.08
			Evacuated, 240°C; 50 mm H_2 240°C 90 min and evacuated, 240°C	2	0.34	0.08
3	27.4	62% Pd	Deposited and annealed at 400°C	1	0.32	—
			Evacuated, 350°C, 60 min	2	0.04	—
			Evacuated, 240°C; 50 mm H_2 240°C 30 min and evacuated, 240°C	3	0.29	—
4	12.0	pure Ag	Deposited at 0°C; reaction stopped after 10 min	1	0.73	0.098
			Evacuated, cooled to 0°C, fresh reaction mixture	2	0.37	0.024
5	11.3	pure Ag	Deposited at 0°C; 25 mm O_2 240°C 15 min	1	0.50	0.12
6	7.8	pure Ag	Deposited at 0°C; 10 mm C_2H_4O 240°C 5 min	1	0.37	0.025

association of ethylene oxide with silver catalysts is known to give rise to a carbonaceous deposit which could be burned off in oxygen (*4*). However a moderate treatment of this type (50 mm oxygen for 60 min at 240°C) did not restore the activity of pure silver films used to catalyze the formation of ethylene oxide.

The bottom part of Table 1 reports some experiments on the deactivation of silver films, deposited at 0°C and possessing a slightly higher initial activity than films deposited and annealed at 400°C. A short period of reaction, i.e., 10 min at 240°C, was sufficient to reduce the activity when a second reaction mixture was admitted (Film No. 4). Pretreating with oxygen, while reducing the rate of carbon dioxide production, left the production of ethylene oxide apparently unaffected (Film No. 5). The role of ethylene oxide in deactivation is confirmed by the marked fall-off in ethylene oxide production after a brief pretreatment at the standard reaction temperature (Film No. 6).

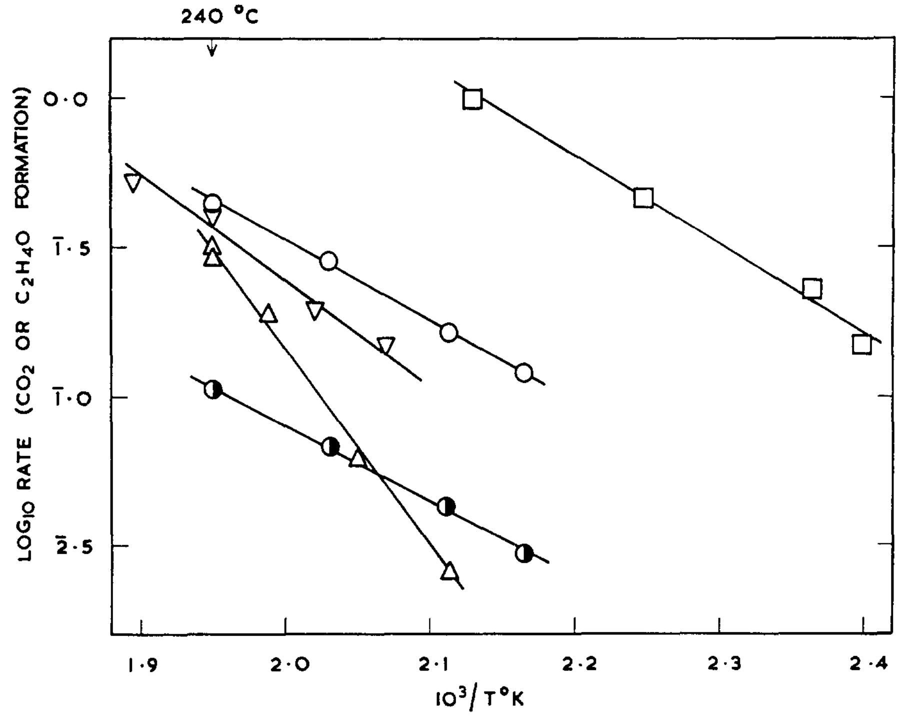

FIG. 3. Arrhenius plots for the formation of ethylene oxide over silver films, ◑ ; CO_2 over silver, ○; palladium, □; 11% Pd/Ag, ▽; and 62% Pd/Ag, △, films.

Activation Energies

Apparent activation energies for the production of carbon dioxide and where possible ethylene oxide were determined from reactions over palladium, silver, and some alloy films. For the pure metals, a number of films of approximately the same weight and annealed at 400°C were prepared and each film was used for a rate measurement at one temperature. For the alloys, the same film was used and reactivated with hydrogen between rate determinations at various temperatures, on the basis of the information reported in Table 1. In some cases an approximate activation energy was measured from rates at a few temperatures using only the first reaction mixture, because the mass spectrometer makes possible the observation of very slow rates with little conversion of reactants.

TABLE 2
ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR CO_2 FORMATION

Film composition	Ag	11% Pd	26% Pd	43.5% Pd	62% Pd	100% Pd
Activation energy (kcal/mole)	12.5	16.4	(18.5)	(13.9)	30.2	13.6
Log_{10} frequency factor (mm CO_2/min/cm^2 apparent area)	2.64	4.19	(5.29)	(3.21)	10.01	4.03

Figure 3 shows some Arrhenius plots obtained using each gas mixture at one temperature only, for the formation of CO_2 and ethylene oxide over silver films and CO_2 over silver-rich and palladium-rich alloy films and pure palladium films. Table 2 summarizes activation energies (kcal/mole) and frequency factors (mm/min cm^2 apparent surface) for CO_2 production. An activation energy for ethylene oxide formation could only be observed satisfactorily over pure silver films, yielding $E = 11.7$ kcal/mole and $\log_{10} A = 1.67$. The rates observed over the alloy films shown in Fig. 3 when the film was used for the first time (at 240°C), were reproducible after reactivation. It was found, however, that with alloy films of 26% and 43.5% Pd/Ag, reactivation approximately doubled the observed rate (determined initially at 190°C). Values of E and $\log_{10} A$ for these two alloy films are less certain and are recorded in parentheses in Table 2. It was noted, however, that the approximate activation energies from the first gas mixture were in fair agreement although the Arrhenius plots were displaced.

Apparent activation energies previously reported for a variety of silver catalysts are variable; for chemically deposited silver films, 12 and 15 kcal/mole were found for ethylene oxide and CO_2 production, respectively (*12*). Pure palladium films used for the complete oxidation (*10*) approach more closely the structure of the present catalysts. The absolute initial rate, r_0, expressed as molecules of ethylene reacting per second per cm^2 apparent surface was given by

$$r_0 = 10^{22.3\pm0.5} \exp [(-14300 \pm 600)/RT]$$

The present activation energy, 13.6 kcal/mole, agrees closely and converting the frequency factor to the same units, the slightly lower value found, $10^{21.1}$, might be expected for the more highly sintered films used in the present work.

Activity for CO_2 Formation vs. Composition

The first consideration is the selection of a method of expressing activity which is necessarily somewhat arbitrary when both the activation energy and frequency factor are variable. The order of activity is not unique when Arrhenius plots intersect, whether the criterion is the rate at a fixed temperature or the temperature for a chosen rate of reaction. However, reference to Fig. 3 shows that within the temperature range permitting observation of rates, the Arrhenius plots for CO_2 formation, open symbols, do not intersect (the half-filled circles refer, of course, to ethylene oxide production). Since ethylene oxide production could only properly be measured at 240°C over a number of alloy films, this temperature was also chosen for comparing rates of CO_2 formation (Fig. 4).

Further reference to Fig. 3 shows that this choice diminishes the effect of composition on activity for CO_2 formation, i.e., at a lower temperature the rate decreases more markedly with increasing palladium content (up to almost pure palladium). Nevertheless, the main feature of the results shown in Fig. 4 is unaffected by the choice of temperature for comparing rates, viz., the high activity of pure palladium films for CO_2 formation with the rate building up over alloy films containing only a small percentage of silver. The relationship between surface area and film weight is unknown but in these highly sintered films, little internal pore structure is expected (see Part I, Fig. 1). Further, the

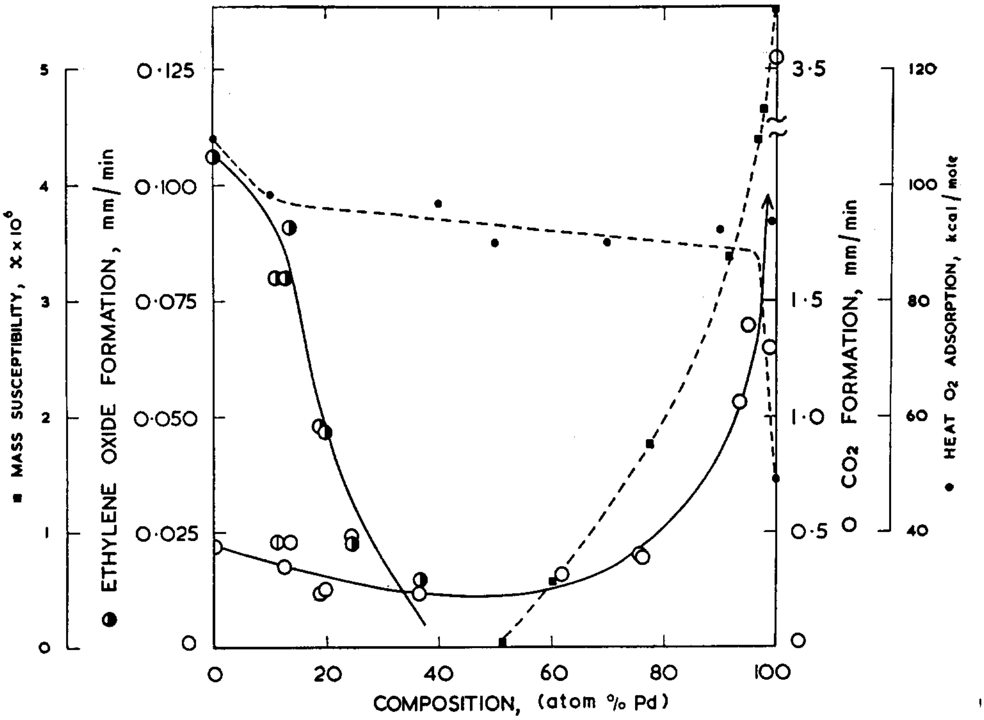

FIG. 4. Rates of formation, mm (0°C) per minute at 240°C, of ethylene oxide, ◑, and CO_2, ○, as a function of alloy film composition. Rate of CO_2 formation over film annealed in H_2 (see Table 1), ⦶. Magnetic susceptibility from J. E. Hoare *et al.*, *Proc. Roy. Soc.* (*London*) **A216**, **502** (1953), --■--; and heats of oxygen chemisorption from Bortner and Parravano, ref. (*15*), --●--.

results shown in Fig. 4 were measured over films of approximately the same weight, at least 20 mg, so that the sharp rise at very high palladium contents is unlikely to arise from an increase in surface area.

The activity of pure silver compared with pure palladium is discussed first. Observed rates for the complete combustion of various olefins, including ethylene, have been correlated (*9*) with the strength of oxygen chemisorption, i.e., the highest activity was found over platinum and palladium, the metals which adsorbed oxygen least strongly (silver was not studied). The heat of adsorption of oxygen on evaporated palladium films has been measured calorimetrically (*13*); a residual pressure was observed after one oxygen dose and the uptake following the admission of a second dose was very small and of negligible heat. The mean integral heat of adsorption was 67 kcal/mole and only 74% of the palladium surface was readily covered with oxygen. From the dissociation equilibria of water vapor over powders in the temperature range 200–300°C, Parravano and co-workers (*14, 15*) found 49 kcal/mole oxygen for palladium and 108 kcal/mole oxygen for silver, both values at very low coverages. Recent calorimetric measurements with porous silver (*16*) gave an initial heat of 120 kcal/mole oxygen, remaining high to beyond half-coverage (80–90 kcal/mole at $\theta = 0.5$).

The high activity of palladium for the complete oxidation of ethylene to carbon dioxide is therefore seen in terms of the moderate heat of oxygen adsorption which may not support full oxygen coverage. Ethylene may be chemisorbed directly onto the remainder of the metal. The estimated initial heat over palladium films is ~50 kcal/mole (*17*) but the variation with coverage is unknown. However, the general conclusion from previous kinetic studies (*10*) is that the rate-determining step involves chemisorbed oxygen and an ethylene molecule which is held on top of an oxygen-covered surface. Strong evidence is the absence of any negative dependence of the rate on oxygen pressure. Ethylene is not chemisorbed on clean silver surfaces at temperatures between 0° and 300°C and at a pressure of 7 mm, whereas in the presence of oxygen both gases are adsorbed at 95°C (*18*). Different types of chemisorbed oxygen exist on silver (see next section), but the same mechanism for the complete oxidation is envisaged and the lower activity of silver is associated with the higher heat of oxygen adsorption.

The activity of the alloy films for the complete oxidation to carbon dioxide is examined next. Figure 4 shows, in addition to the variation of activity with composition, heats of oxygen chemisorption for palladium-silver alloy powders determined by Bortner and Parravano (*15*). A large increase in the heat occurred when palladium was alloyed with only 1% silver; thereafter the heat of adsorption increased rather slowly with increasing silver content. The inverse correlation is again apparent between activity for complete oxidation and the heat of oxygen chemisorption, with the activity decreasing sharply on addition of a few percent of silver to palladium, then remaining relatively constant as the silver content increases.

The variation in activity does not arise from a simple variation in activation energy or frequency factor. The sharp decrease in activity between pure palladium and alloys with low silver content corresponds with a substantial increase in activation energy, 13.6 and 30.2 kcal/mole over pure palladium and the 62% Pd/Ag alloy, respectively, but somewhat compensated by an increase in frequency factor (Table 2). As the concentration of *d*-band vacancies falls to zero, the activation energy again decreases (13.9 kcal/mole at 43.5% Pd) and remains at low values. A compensation effect occurs in the range 0–62% Pd and the activity is relatively constant.

At this point it must be recognized that two other factors, reported in Part I (*30*), may be superimposed on a pattern of activity related to the electronic properties of the bulk, viz., silver enrichment at the surface and hydrogen solubility in the bulk. It was shown in Part I that a gross effect could be obtained by heating palladium-rich alloys in pure oxygen at a typical reaction temperature for ethylene oxidation, resulting in some obvious "de-alloying." The modification of the surface by a small amount of silver, whether concentrated at the surface or not, also determines the dissolution of hydrogen in the bulk. It was shown in Part I that alloys containing 65–99% palladium after catalyzing ethylene oxidation have apparently become charged with hydrogen. In contrast, pure palladium used as a catalyst remained uncharged with hydrogen.

The C–C bond may be broken first when ethylene undergoes complete oxidation or there may be stepwise removal of hydrogen atoms before the C–C bond is broken. In either case, the desorption of hydrogen as water molecules competes with the dissolution of hydrogen in the bulk. It has been suggested (*10*) that the formation of water over pure palladium films can occur easily once the hydrogen atoms have been removed from the ethylene and experiments have shown that hydrogen is much more rapidly oxidized than ethylene. Therefore it is not surprising that after ethylene oxidation, palladium films show no evidence of dissolved hydrogen. Further Kowaka (*19*) found, using ribbons, that activity for the hydrogen–oxygen combination falls rapidly between pure palladium and 20% silver/palladium. In these circumstances, i.e., on palladium-rich alloys, the bulk solution processes can compete with the desorption of hydrogen as water. The hydrogen dissolution process is also enhanced (see Part I) when the oxygen content of the system is reduced, viz., towards the end of the reaction using the standard mixture or by starting with a low oxygen/ethylene ratio. The measurement of *initial* rates of carbon dioxide production may not be affected.

If real, both complicating factors lead to the same result. Silver enrichment at the surface causes a more rapid filling of *d*-band vacancies than bulk composition would indicate (see magnetic susceptibility data in Fig. 4). The *d*-band vacancies in the palladium-rich alloys may also be filled by electrons from dissolved hydrogen [shown previously to alter the activation energy for the parahydrogen conversion over palladium wires (*20*)]. Hence the change away from the adsorptive and catalytic properties of pure palladium might be more rapid than expected from the bulk composition.

Some idea of what might be expected can be obtained by examining the oxidation of carbon monoxide over palladium-gold alloys (*21*). In this system there is no hydrogen dissolution and surface enrichment by gold seems unlikely. The initial rates in molecules/sec cm^2 at 150°C over 100%, 90%, and 70% Pd catalysts were 2.7×10^{15}, 5.6×10^{13}, and 1.1×10^{13}, respectively. Here again a substantial decrease in activity occurred on addition of the first 10% of the Group IB metal. A rapid change in adsorptive and catalytic properties by the addition of silver to palladium therefore seems plausible. However, the addition of only 1% Ag changed the adsorption heat substantially (*15*) and in the present work modified the reaction rates so that, unlike pure palladium, the 1% Ag/Pd alloy dissolved hydrogen (see Part I, Fig. 2) during reaction. In these extreme cases, the surface may well have contained rather more than 1% of silver.

Activity for C_2H_4O Formation vs. Composition

The previous considerations about selecting a method of expressing activity quantitatively again apply, but qualitatively the pattern of activity is clear. When palladium was alloyed with silver, the yields of ethylene oxide obtained with pure silver (240°C) could not be achieved and above 40% palladium no ethylene oxide was apparently formed (Fig. 4). It also seems less likely that the results over these silver-rich alloys would be affected by (a) a greater silver content at the surface compared with the bulk and (b) hydrogen solubility, since the expected lattice constants were observed after reaction (Part I Fig. 2) and previous work suggests essentially zero solubility between 0% and 30% or 40% Pd.

It is tempting to associate directly the absence of ethylene oxide over catalysts with more than 40% palladium with the appearance of holes in the *d* band. It could be assumed that ethylene is chemisorbed above this composition and rapidly decomposed on the bare metal, but this mechanism is inconsistent with the proposed mechanism for CO_2 formation over palladium (see previous section).

Electron micrographs of these alloy films [Part I (*30*), Fig. 1] show that the changing composition is associated with a change in structure. Thus silver-rich films had large "smooth" crystallites indicative of high mobility during preparation leading to extensive coalescence, particularly during annealing; (110) and other low integer planes were parallel to the substrate. Palladium-rich films consisted of a compact mass of smaller crystallites with random orientation. Hence a general explanation for the decreasing formation of ethylene oxide as palladium was added (Fig. 4) is sought in the relation between the modes of oxygen chemisorption and either the surface structure or alternatively the overall decrease in the Fermi level.

Mechanisms for the catalytic oxidation of ethylene have invoked atomic oxygen (*4*), and O^- or O_2^- ions (*2, 22*). Silver can also catalyze the formation of organic hydroperoxides (*23*) where undissociated oxygen seems the more likely active species. Many oxygen adsorption studies have been made on silver, not the alloys, but the extent to which they provide evidence for the existence of oxygen species important during ethylene oxidation where carbon and hydrogen are also involved is uncertain. Various criticisms can be put forward, e.g., hydrogen chemisorbed at high temperatures decreases the activation energy for oxygen adsorption (*24*). It seems generally accepted that the rate of oxygen adsorption on silver is initially rapid around 200°C on diverse catalysts [i.e., reduced silver oxide, evaporated silver films (*25*), and technical catalysts prepared from Ag-Ca alloys (*26*)] but slows down markedly at ~50% coverage. Recent ultramicrobalance studies (*27*) of oxygen adsorption on silver powders (typical pressure, 10 mm) identified various fractions, viz., (a) oxygen which would desorb rapidly at 200–250°C, (b) strongly adsorbed oxygen, which may be widely spaced or buried partially in the lattice and slowly desorbed at 350°C, and (c) very tightly bound oxygen, removed only by CO reduction.

Experiments specifically designed to show the presence of some of the proposed oxygen species do not provide much confirmation. Thus, oxygen chemisorbed at room temperature on carefully prepared silver powders did not accelerate the parahydrogen conversion (*28*) which would be expected from the existence of paramagnetic O_2^- ions. Early isotopic exchange experiments (*2, 25*) were interpreted as showing that one mode of oxygen adsorption is nondissociative but have not been confirmed by recent work (*29*). After prolonged pumping at 500°C, up to 2.5 equivalent monolayers of oxygen remain "occluded" in silver, of which up to one monolayer was in immediate isotopic equilibrium with oxygen adsorbing at 200°C (*24*).

The description which emerges of oxygen chemisorption on silver at 200°C and above shows at least two states of binding without identifying species such as O_2^-, etc. The stronger binding [(b) and (c) above] may refer partly to oxygen embedded in the lattice, which has often been reported. The heats of oxygen adsorption on silver and silver-palladium alloys at very low coverages found by Bortner and Parravano (*15*) probably accurately describe this strong oxygen binding. Determined in the presence of hydrogen at 200–400°C, they seem relevant to ethylene oxidation conditions.

It is suggested that adsorbed fragments from ethylene combine with strongly bound oxygen, removing it as carbon dioxide and thereby reducing its stationary concentration. It would appear that the slow step is not the final oxidation to and desorption of CO_2 over silver and silver-rich alloys. Evaporated alloy films, 0–20% Pd/Ag, prepared under identical conditions, formed CO_2 much more rapidly from CO than the present alloy films produced CO_2 from ethylene using the same partial pressure of oxygen (*11*).

The less strongly adsorbed oxygen [(a) above], now apparently dissociated, is believed to oxidize ethylene to ethylene oxide. The question then arises whether the decreasing rate with increasing palladium content (Fig. 4) is due to an effect of film structure, e.g., defects, grain boundaries, etc., rather than the apparent changes in electronic properties, on the proportion of less strongly bound oxygen. The electron micrograph shown in Part I, Fig. 1(f) is pertinent. This 19% Pd/Ag alloy film was deposited at 400°C as usual but not subsequently annealed. Making some allowance for its weight, it appears similar to high palladium content films [Part I, Fig. 1(e)] and most unlike films with 0–40% Pd [see Part I, Figs. 1(a) and (b)]. However, the yields of CO_2 and ethylene oxide over this film, 0.32 and 0.048 mm min^{-1}, respectively, were exactly as expected both as relative and absolute rates (cf. Fig. 4).

CONCLUDING REMARKS

Ethylene oxidation would be a novel addition to the repertoire of reactions, such as CO oxidation and formic acid decomposition, used to study "electronic factors" in catalysis. Selectivity towards ethylene oxide formation may be studied in the composition range 0–40% Pd/Ag, perhaps as a function of the position of the Fermi level. The activation energy for carbon dioxide formation increased sharply between 40% and 60% palladium (with a compensation effect) when *d*-band vacancies appeared. However, initial rates of carbon dioxide formation changed most between 90% and 100% palladium and the possibility was recognized that vacancies were filled by electrons from dissolved hydrogen. The rate of CO_2 formation was correlated empirically with the heat of oxygen chemisorption over the complete composition range. The observations that hydrogen absorbed into palladium-rich alloys but not into pure palladium during reaction could also be understood.

Palladium-silver and palladium-gold alloys approach the ideal catalyst system for studying electronic factors; in some ways the former has the advantage that silver has more "normal" catalytic activity than gold. Unlike the copper-nickel system, phase separation is not expected, but enrichment of the surface by silver in the environment of an oxidation reaction must be considered. Further mechanism studies are required before activity and selectivity in ethylene oxidation can be fully explained in terms of the electronic properties of the palladium-silver system. The emphasis of the present work has been to examine how far the inherent "electronic factors" in such catalysts have structural complications superimposed on them. In addition to their other advantages, evaporated alloy films may help to elucidate the role of lattice defects at various compositions, since thin films are particularly amenable to study by electron microscopy.

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