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The Oxidation of Ethylene over Evaporated Palladium–Rhodium Alloy Films

II. Variation of Activity with Film Composition and Structure

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Rates of CO_2 formation when ethylene was completely oxidized in a static system over evaporated Pd–Rh alloy films showed a complex variation with alloy composition. This activity pattern generally reflected the variations in activation energy, E, with composition; values of E and log (frequency factor) fell on a linear plot, indicating a compensation effect, with the exception of pure Rh which is discussed. The activity pattern can be interpreted in terms of the film structure and properties occurring in the three composition ranges distinguished as follows: *0–30% Rh;* increased activity compared with pure Pd, expected from bulk electronic properties and previous results with Pd–Ag alloy films, was not observed. Instead the activity passes through a minimum at 10–15% Rh. It is believed that at this composition the alloy has a reasonable capacity to dissolve hydrogen (from C_2H_4) which would reduce the activity by filling *d*-band holes, combined with a decreased ability to effect H_2–O_2 combination. An alternative explanation, based on the onset of phase-separation at the surface at lower Rh contents than expected, was tested by CO oxidation. *30–80% Rh;* the activity decreased continuously with increasing Rh content in alloys composed of two "phases," the Rh-rich Phase II is believed to form the kernel of the crystallites, surrounded by a variable-composition Phase I. The activity results were re-plotted assuming that the surface composition can be equated with the composition of Phase I given by X-ray data in Part I. Apparently anomalous results fitted into place and a maximum in activity below 30% Rh, which would occur in the absence of hydrogen solubility, was indicated. *80–100% Rh;* some enrichment of the surface by Pd may occur; the decrease in activity between 98% and pure Rh is discussed, as well as its very low absolute activity.

INTRODUCTION

Over silver and Pd–Ag alloy films with more than 60% Ag, partial oxidation of ethylene to ethylene oxide occurs together with the formation of substantial amounts of CO_2 (*1*). Trace amounts of acetic anhydride and acetic acid form over Pd films (*2*) but, under more favorable reaction conditions, these products together with acetaldehyde constitute 30–40% of the yield over Pd sponge (*3*). In addition to the continuing challenge of selective oxidation, there has recently been interest in the total oxidation of hydrocarbons to CO_2 at low temperatures.

Some of the transition metals which resist bulk oxidation at moderate temperatures are very active for the oxidation of olefins. From a general study (*4*) of the oxidation of ethylene, propylene, and methyl-substituted ethylenes, etc., the order of catalytic activity observed, $Pt > Pd > Rh \gg W$, was correlated with the strength of the metal–oxygen bond. The highest activity occurs with the metal which chemisorbs oxygen least strongly; the activity of Ag for CO_2 production compared with Pd can also be fitted into this correlation (*1*) but perhaps, as in the case of Au, an alternative explanation should be sought (*4*). However, the sharp increase in activity for CO_2 formation from ethylene oxidation and the sharp decrease in the heat of oxygen chemisorption (*5*) as the composition is varied from Pd–Ag alloys with a small Ag content to pure Pd itself is another example of this correlation.

Therefore two reasons prompted the choice of the Pd–Rh system for preparation as binary alloy films of a pair of Group VIII metals. While phase-separation was expected, and demonstrated in Ref. (*6*), Rh has a limited solubility in Pd. The magnetic susceptibility (*7, 8*) and electronic specific heat coefficient (*7*) increase from low values at ~60% Ag–Pd through pure Pd and reach a maximum at ~5% Rh–Pd. Hence, although information on the heat of oxygen chemisorption is apparently not available for Pd–Rh alloys, the rate of CO_2 formation from ethylene oxidation might be expected to increase when small amounts of Rh are added to Pd. However, it was also recognized that the Pd–Rh system might offer a further opportunity to study the complications, such as hydrogen solubility, surface enrichment and phase-separation, which superimpose on the pattern of activity in alloys expected from bulk electronic properties.

EXPERIMENTAL METHODS

Rates of ethylene oxidation were measured in a static system. The reaction vessel was connected to the ion-source of a mass-spectrometer by means of a fine glass capillary leak; $<2\%$ of the gas mixture was removed per hour. The reaction mixture was prepared from "spectrographically pure" oxygen (British Oxygen Co., Ltd.) and 99.9+% ethylene (Phillips Petroleum Co., Ltd.) and when expanded through a trap at −78°C into the reaction vessel at ice temperature gave 25 torr O_2 + 10 torr (or 1.35×10^{20} molecules) of C_2H_4 (1 torr = 133.32 N/m^2).

The amount of C_2H_4 in the reacting mixture was measured using peak *m/e* 26 since CO_2 gave a large fragment at mass 28 and there is also the uncertainty of the contribution of residual gases at this mass number. Oxygen and carbon dioxide analyses were made using peaks at *m/e* 32 and 44, respectively without further correction. Reaction rates were calculated from the increase of the carbon dioxide peak with time (see below) adjusting to the corresponding peak height at 0°C and for the relative sensitivity compared to oxygen. Frequent calibrations were made of the relative sensitivities of O_2 and CO_2 throughout the work and showed a variation of not more than ±10% about the mean value. The absolute sensitivity of the mass-spectrometer was determined from the oxygen peak height at 0°C before each experiment and hence results could be expressed in terms of pressure (at 0°C) of CO_2 formed per minute.

RESULTS AND DISCUSSION

Reaction Rates

At the temperatures used in the present work, complete oxidation to carbon dioxide and water occurred, and no partial oxidation products were observed. In a typical experiment, the rate of CO_2 formation and C_2H_4 and O_2 removal was followed for 15–20 minutes at 150°C, then the temperature was raised to 170°C and finally 190°C, if possible, for somewhat shorter times sufficient to obtain measurable reaction rates. Although substantial quantities of the reactants were converted, almost linear plots of CO_2 formation with time were observed at all film compositions.

Reaction rates, calculated in terms of the rate CO_2 formation, were not adjusted for variation in the surface area of the films used for the following reasons. The main point of interest is the effect of alloy composition on catalytic activity and if the film areas are reasonably constant, then the necessary results are available from the unadjusted rates. The film area may vary as a consequence of variations in either film composition or film weight. Electron micrographs of alloy films of closely similar weights but widely different Rh contents appearing as Fig. 5 in Ref. (*6*) showed that the films were extensively sintered and that the crystallites were approximately the same size.

The method of alloy film preparation does not provide films with exactly the desired composition and so the relationship between surface area or catalytic activity and film weight cannot be found. However, the effect of film weight on activity was examined for pure Pd films deposited and sintered at 400°C, as usual, and weighing between ~4 and ~40 mg. Care was taken to ensure that the pure Pd films were not "contaminated" by traces of Rh which sharply reduce the activity (see below); the reaction system was cleaned thoroughly and the first Pd film deposited was rejected. Over pure Pd films weighing 4.1, 17.3, 35.0, and 39.3, the rates of CO_2 formation (torr/min) at 150°C were 0.32, 0.30, 0.34, 0.29, respectively, showing reasonable reproducibility and no discernible trend due to increasing film weight.

It has been found previously for sintered Ni films (*9*) that the surface area, *a*, is related to the film weight, *w*, by the expression:

$$a = B + Dw,$$

but the constant D ($B = 490\ \mathrm{cm^2}$) for films sintered at 400°C is only 3.3 $\mathrm{cm^2/mg}$; the relationship does not hold for light films, <5 mg. Therefore in the present work it seemed advisable to restrict the weight range of the films prepared and to avoid using light films; accordingly the results reported below refer (with the exceptions indicated) to alloy films weighing between ~15 and ~30 mg.

E and log A Values

Activation energies were obtained from rates observed using the same reaction mixture at three, sometimes four, temperatures because the mass-spectrometer makes possible the accurate observation of very slow rates with little conversion of reactants. Over some alloy films the Arrhenius plots were unsatisfactory showing a small, usually upwards, curvature but, as Fig. 1 shows, good linear plots were also found.

Figure 2 shows activation energies, *E*, calculated from acceptable Arrhenius plots, except for the film containing 6.6% Rh for which the value is probably less accurate. Results for a few films are not strictly relevant to later data on the effect of composition on activity, because their weights are outside the limits set, but they do provide satisfactory values for the activation energy at these compositions.

When small amounts of Rh were added to Pd, *E* increased from initial values of 12–14 kcal/mole to a maximum beyond 10% Rh of more than 20 kcal/mole. Beyond 60% Rh, *E* again increased rapidly from a minimum to ~25 kcal/mole at 97.7% Rh but was ~5 kcal/mole *less* when the reaction was carried out over pure Rh.

Values of the pre-exponential term, *A*, in the Arrhenius equation, calculated in terms of the number of CO_2 molecules formed per second per $\mathrm{cm^2}$ apparent sur-

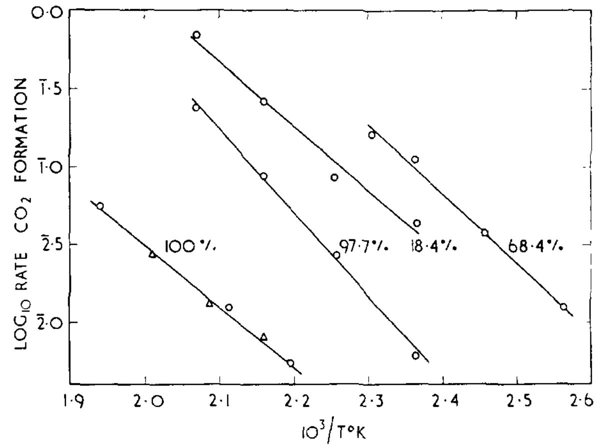

FIG. 1. Arrhenius plots for the formation of CO_2 over films with the Rh content indicated; results for two separate pure Rh films are shown.

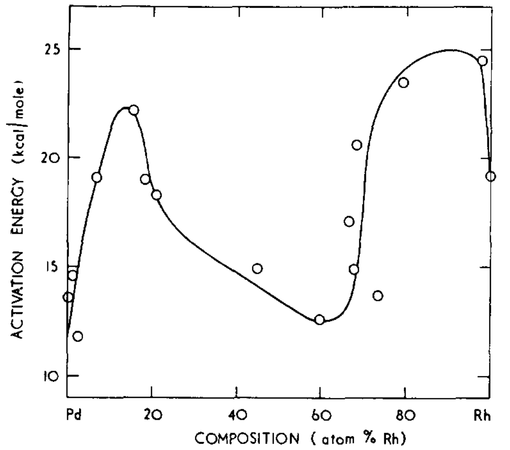

FIG. 2. Variation of activation energy (kcal/mole) with alloy film composition (at. %).

face, are shown plotted as $\log_{10} A$ vs E in Fig. 3 (circles). For comparison, a similar plot is given for ethylene oxidation over Pd–Ag films prepared in the same way, converting $\log_{10} A$ values in Ref. (*1*) appropriately (triangles).

The points for Ag and Ag–Pd alloys lie on the same straight line, a "compensation effect," except for the pure Pd point lying above the Ag–Pd line. The point for pure Pd lies on the line for Pd–Rh alloys, although reaction rates at a fixed temperature (see below) decrease, increase, and decrease again with a 65-fold variation in activity between the least active and most active alloy catalyst. In this case, the other pure metal in the series, i.e., rhodium, is anomalous and the point for pure Rh falls well below the Pd–Rh line.

Examination of the many compensation effect plots given in Ref. (*10*) shows that often one or other of the pure metals in a series of catalysts consisting of two metals and their alloys falls off the plot. Examples include CO oxidation and formic acid decomposition over Pd–Au catalysts, parahydrogen conversion (Pt–Cu) and the hydrogenation of acetylene (Cu–Ni, Co–Ni), ethylene (Pt–Cu) and benzene (Cu–Ni). In some cases, where alloy catalysts containing only a small addition of the second component have been studied, then such catalysts are also found to be anomalous, like the pure metal to which they approximate in composition.

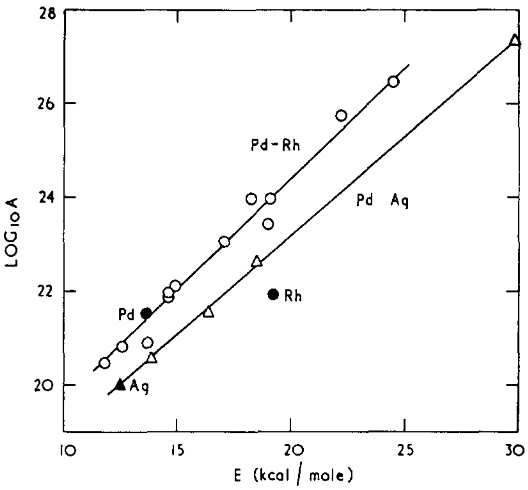

FIG. 3. Compensation effect plots for ethylene oxidation over Pd–Rh alloys, ○; and Pd–Ag alloys, △; positions of pure Pd, Rh, and Ag specially indicated by solid symbols.

Anomalous points for pure or nearly-pure metals in compensation effect plots for metal-alloy series of catalysts are often accompanied by sharp changes in catalytic activity. In the present work, pure Rh is 6 times less active than the Pd–Rh alloys with ~98% Rh, although the activation energy is 5 kcal/mole lower. Because pure Rh is relatively inactive compared with pure Pd (~300 times less active), the observed activities might be regarded as arising from active Pd centers in an inert Rh matrix. Palladium and its alloys with Rh might constitute a coherent series of catalysts, for which values of E and $\log A$ fall on the same compensation effect plot, while pure Rh may "belong" to some other series of catalysts.

Activity vs. Composition

Figure 4 shows the variation of activity (rate CO_2 formation at 150°C) with alloy film composition. Over many of the alloy films, rates were measured at 150°C as the first temperature for observations using the fresh reaction mixture. Comparison with Fig. 2 shows that the pattern of activity (apart from the anomaly of pure Rh discussed above) across the composition range follows in general the variations in apparent activation energy, although changes in

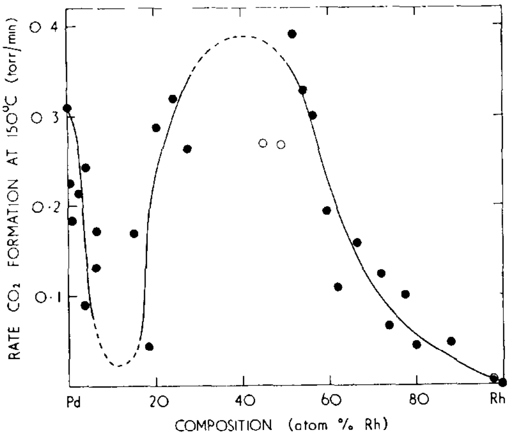

FIG. 4. Variation of rate of CO_2 formation at 150°C with the (bulk) composition of the alloy film.

activity are a consequence of variation in both A and E. Thus the minimum in activity at ~10–15% Rh reflects the maximum in E at these Rh contents and the steady fall in activity beyond 50% Rh follows the rise in E up to ~98% Rh.

As a preliminary to discussing the activity pattern shown in Fig. 4, some observation might be made on the pattern expected for *homogeneous* Pd–Rh alloys. Both the magnetic susceptibility and the electronic heat coefficient pass through a small maximum at ~5% Rh, thereafter decreasing smoothly to pure Rh (*7*, *8*). The present catalytic results for ethylene oxidation over pure Pd, and pure Rh agree with previous observations that Pd is more active than Rh (*4*). Assuming the relevance of bulk electronic properties to the catalytic activity of surface atoms, the activity pattern might be expected to show a continuous variation with composition, perhaps passing through a maximum at some favored electronic structure, as previously observed with binary alloys of Group VIII metals and surveyed in Ref. (*11*). Instead, the complex activity pattern shown in Fig. 4 was found but it can largely be explained in terms of the structure of the alloy films in the various composition ranges distinguished in Ref. (*6*).

Composition range 0–30% Rh. In this composition range the alloys appear to be reasonably homogeneous but the solubility of hydrogen in alloys with 0–30% Rh varies markedly [see Ref. (*6*)]. Even when the reaction was stopped before total oxygen consumption, the X-ray line profiles showed evidence of dissolved hydrogen in alloys with up to 10% Rh. The main feature of the observed activity variation is the decrease produced by small additions of Rh to give a minimum activity at ~10–15% Rh followed by an increase in activity to the pure Pd level beyond 20% Rh.

The obvious association of the minimum in activity within this 0–30% Rh composition range with the hydrogen solubility raises some problems, athough a reduction in activity as a consequence of filling *d*-band vacancies by electrons from dissolved hydrogen parallels the observed decrease in the rate of ethylene oxidation when the additive was a Group IB metal (*1*). The least active catalyst contains ~18% Rh whereas Fig. 1 in Ref. (*6*) shows that the hydrogen solubility is a maximum at ~5% Rh. However, the surface composition may be slightly Pd-rich and capable of greater hydrogen solubility; this view would be generally in accord with ideas expressed (*6*) about the occurrence of Pd–Rh crystallites consisting of a Rh-rich kernel and a Pd-rich exterior.

A more serious problem is the high activity of pure Pd itself despite its near maximum capacity to dissolve hydrogen, i.e., the plot (Fig. 4) shows an 8-fold decrease in activity *from* pure Pd whereas (H/Me) ratios only increase from 0.70 (pure Pd) to 0.83 (5% Rh). It has been suggested (*2*) that the formation of water over pure Pd 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 seems necessary to postulate that small additions of Rh, like small additions of Ag (*12*), decrease activity for H_2–O_2 combination so that hydrogen dissolution in the bulk of the alloy film can compete with its desorption as water. Minimum activity for ethylene oxidation would then occur at an alloy composition where a reasonable capacity to dissolve hydrogen is combined with this decreased ability to effect H_2–O_2 combination.

Figure 1 in Ref. (*6*) also shows that the solubility of Rh in Pd at an alloy film preparation temperature of 400°C is likely to be very limited, perhaps ~10% Rh. As discussed, the method of preparation produces apparently homogeneous but metastable alloys up to ~30% Rh. Under reaction conditions, equilibrium may be established at the catalyst surface and hence the initial decrease in activity (Fig. 4) from pure Pd may represent the true behavior of a dilute solution of Rh in Pd, and the subsequent increase in activity beyond 10–15% Rh may be a consequence of phase-separation at the surface.

In view of these alternative explanations for the activity pattern in the 0–30% Rh range, i.e., hydrogen solubility or phase-separation at the surface, it seemed useful to make measurements of the rate of CO oxidation over similar Pd–Rh alloy films, thereby eliminating the possible effect of dissolved hydrogen. Table 1 shows rates of CO_2 formation in a mixture of 50 torr of CO + 25 torr of O_2 at 240°C over the alloy composition range of interest.

TABLE 1
Rates of CO Oxidation

Composition (at. %)	Film wt (mg)	Rate, 240°C (torr/min)
0	25.6	0.57
1.45	32.4	1.04
3.6	45.5	1.19
13.9	22.7	1.56
36.9	28.7	1.26

The activity pattern is entirely different from that observed in ethylene oxidation, i.e., the rate of CO oxidation increased initially and then remained approximately constant through the critical composition range. (For the reasons discussed above, the variation in film weight is not likely to affect this pattern significantly.) Now it must be recognized that pure Rh is very much more active than pure Pd for CO oxidation, whereas the opposite is true for ethylene oxidation. Therefore an increase in activity for CO oxidation as Rh is added to Pd is not unexpected but the sharp variations in activity observed for ethylene oxidation over this composition range are absent. This provides some support for the idea that hydrogen solubility in alloys in the 0–30% Rh range determines the observed activity pattern for ethylene oxidation.

Composition range 30–80% Rh. The X-ray diffraction results presented in Ref. (*6*) show the occurrence of a two-phase system in this composition range; Phase I varies in composition and Phase II contains 88 ± 5% Rh. It was proposed that these results can be explained by the preferential nucleation of Rh leading to a model where the crystallites consist of a Phase II kernel surrounded by an outer shell (Phase I), the Rh content of which increases with an overall increase in the Rh content of the alloy film. Note the essential difference to recent work with Cu–Ni alloy films (*13–15*) where complete separation into two phases of fixed equilibrium composition is envisaged and over a wide composition range the crystallite surfaces have the same composition.

It is clear from the change in activity over this composition range that the surface composition of the crystallites varies and, as expected, the direction of change indicates an increasing Rh surface content. The maximum in activity at 52% Rh (rate ~0.4 torr/min), while an apparently satisfactory result, was not supported by results at slightly smaller Rh contents (open circles, Fig. 4). The film containing ~45% Rh weighed only ~9 mg, falling below the accepted weight range, which might explain its relatively low activity, but the film with 49% weighed 27.6 mg, close to the weight of the 52% Rh film with maximum activity. These anomalous results (open circles) are explained in the following treatment of the data.

Because of the uniformity of film composition achieved over the reaction vessel surface, samples for X-ray diffraction usually do not differ by more than a few percent from the mean film composition to which the catalytic results are referred. Therefore the X-ray data in Ref. (*6*), Fig. 4, were used to provide the *surface* com-

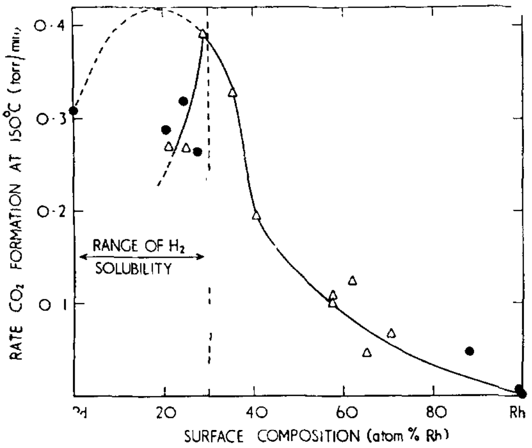

FIG. 5. Variation of rate of CO_2 formation at 150°C with alloy surface composition in region of phase-separation, △; observed rates over pure Pd and Rh and over homogeneous alloys, ●.

position, i.e., the surface composition is equated with the composition corresponding to the observed lattice constant of Phase I. In Fig. 5 the catalytic activity of alloys in the 30–80% Rh range is plotted against surface composition obtained as described (open triangles). Results shown by open circles in Fig. 4 are also included, again obtaining the surface composition of the 49% Rh film from X-ray data and estimating the surface composition of the 45% Rh film as 4% less. For comparison results on alloys with pure Pd and 20–30% Rh or >80% Rh (filled circles) are included, where in this case, the equivalence of surface and bulk composition is assumed, since the latter alloys are apparently reasonably homogeneous.

Figure 5 shows that, moving from pure Rh, the activity increases until a surface Rh content of ~30% is reached; at this point the surface composition is entering the range where the effects of hydrogen solubility become important (see above discussion of 0–30% Rh range). Now the apparently anomalous points (open circles, Fig. 4) fall into place with results for alloys with ~20–30% Rh (filled circles), which are at the tail end of the range where hydrogen solubility occurs and the activity is depressed.

It is a matter of speculation as to whether or not the activity would pass through a significant maximum at a surface composition between 0 and 30% Rh as discussed in the "Introduction." Certainly, the maximum activity recorded in Fig. 5 at ~30% Rh, is little more than the activity of pure Pd. The possibility of an activity maximum with films of surface compositions between 0 and 30% Rh is also interesting because activity maxima have also been reported for bulk and supported alloys of Group VIII metal pairs. For example, in the liquid-phase hydrogenation of nitrobenzene (*16*) maximum activity occurs at 25% Ru–Pt, 25% Ru–Pd, 15% Ir–Pt, and at 25% Rh–Pd.

Composition range 80–100% Rh. Evidence from the shape of the X-ray diffraction profile [Ref. (*6*), Fig. 3] suggests that the alloy with ~90% Rh (X-ray sample 90.3% Rh, mean composition 88.1% Rh) was homogeneous. However, it was pointed out that, while preferential Rh nucleation was again likely in the 80–100% Rh range, the difference between the Phase II kernel and the Phase I outer layers of the crystallites would be difficult to detect. The catalytic results re-plotted in Fig. 5 suggest that the surface of the 88.1% Rh film was indeed a little richer in Pd. It may be significant that the uncertainty in determining the lattice constant of this alloy was rather larger than normal [Ref. (*6*), Fig. 4].

Neither Figs. 4 or 5 show clearly the drop in activity between alloys with 97.7 or 97.9% Rh (0.006 torr CO_2/min at 150°C) and pure Rh (0.001), but the factor of 6 must be kept in perspective. If the activity produced by adding 30% Pd to Rh is 0.05 torr/min, from Fig. 5, then the observed activity for a nominal 98% Rh film with (say) 97% Rh in the surface should be 0.005 (due to 3% Pd) + 0.001 (due to Rh matrix), which is the observed value. Of course, the departure from linearity shown by Fig. 5 at higher Pd surface concentrations rules out any simple ideas about ascribing activity across the composition range to the activity of Pd atoms in an inert Rh matrix.

The very low activity of Rh compared

with Pd (a factor of 300 times less) in the present work might also be considered. Patterson and Kemball (*4*) reported an observation on the rate of ethylene oxidation over a pure Rh film at 155°C which converts to a rate of 4.4×10^{13} molecules oxidized/sec cm^2 geometric area compared with 1.0×10^{15} from an extensive study over Pd films (*2*), (i.e., a factor of 23). These films were deposited at 0°C but were considered to sinter on the admission of the reaction mixture. The observed rate of CO_2 formation over Pd films in the present work was 3.9×10^{14} at 155°C and the lower activity, by a factor of 2.5, is consistent with the more highly sintered films used (deposited and annealed at 400°C). The reaction was found to be zero order with respect to oxygen and from zero to first order in ethylene depending on the pressure (*2*). In contrast, the rate over pure Rh observed in this work was only 1.3×10^{12} at 155°C, a factor of 34 less.

Apart from the obvious ease with which Rh catalysts, which are rather inactive in this reaction could be "promoted" by a more active metal such as Pd and the different reaction mixtures used, differences in crystallite orientation [cf. Ref. (*6*), Table 2] might be an explanation of the lower activity of Rh observed in the present work.

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