

Ethylene Hydrogenation over Nickel-Palladium Alloy Films

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Ethylene hydrogenation rates at -100°C were measured over two series of evaporated Ni-Pd alloy films, either deposited on glass and annealed in hydrogen at 400°C or deposited at -196°C . Characterization of the bulk structure of annealed films by X-ray diffraction in terms of lattice constant, peak symmetry and breadth showed some inhomogeneities in alloys with 20-60 atom% Pd. The analysis of surface composition in Ni-Pd alloy films by Auger electron spectroscopy (described elsewhere) is summarized and related to present work on bulk structure; the outermost surface was a completed palladium monolayer when the bulk composition contained ~ 65 atom% Pd or more. For both series of Ni-Pd films, rates of ethylene hydrogenation were greater over the alloys compared with either pure metal, reaching maximum activity in alloys containing ~ 45 atom% Pd. Possible explanations of the activity maximum are considered: these are, respectively, that alloying increases surface area and hence activity, that the inhomogeneities detected in the bulk structure are responsible, and thirdly that the "true" activity of palladium is more closely approached when a palladium monolayer is present on a Ni-Pd base, whereas hydrogen absorption occurred at higher (bulk) Pd contents, inhibiting activity.

INTRODUCTION

In recent years there has been renewed interest in the study of alloy catalysis (1, 2) stimulated by various factors including the development of technical bimetallic catalysts and the advent of surface analytical methods such as Auger electron spectroscopy. In a number of studies of adsorption and catalysis, the alloys were prepared as evaporated thin films on glass, which provides surfaces of reproducible behavior and moderate surface area. Techniques for alloy film preparation and characterization have been reviewed (3). Most studies have involved Group 8-1B metal pairs and it was the intention of the present work to study combinations of Group 8 metal pairs where the component metals are themselves active catalysts for

hydrogenation, hydrogenolysis and related reactions.

The choice of metals for catalytic hydrogenation is often made from one of three elements, viz, nickel, palladium and platinum (4, 5). The present work examines the activity of nickel-palladium alloys prepared as evaporated thin films, for ethylene hydrogenation. It has been reported previously (6) that nickel films containing 5-10 atom% Pd were more active than pure nickel for this reaction. In the work reported here for a full range of Ni-Pd alloys, particular attention was paid to the characterization of the alloy films in terms of bulk structure. The analysis of surface composition in Ni-Pd films by Auger electron spectroscopy made in connection with this work is published in detail elsewhere (7).

EXPERIMENTAL METHODS

Two apparently distinct techniques were employed for the preparation of the alloy films discussed in the present work.

i. The component metals were deposited simultaneously on the inner surface of the spherical reaction vessel maintained at 400°C; then the film was annealed for 1 hr at 400°C in 5 Torr hydrogen, cooled to -100°C and hydrogen pumped off before admitting the reactant gases. (The description of this procedure is abbreviated to "prepared at 400°C"). It might be expected that such films would have a low surface area, approaching the geometric area of the reaction vessel surface (8).

ii. The component metals were deposited simultaneously on the inner surface of the reaction vessel cooled to -196°C. After film deposition, a cold bath at -100°C was substituted and the film exposed to 5 Torr hydrogen for 5 min before pumping out hydrogen and admitting the reactant gases. (This procedure is referred to as "deposited at -196°C"). Films deposited at -196°C will be porous and consequently should have an actual surface area well in excess of the geometric area. (It is known that nickel and palladium films deposited at 0°C have surface areas 5-10 times larger than geometric areas (9).

In the first method, annealing was carried out in hydrogen to minimize surface contamination and hydrogen was also employed in method (ii) at the appropriate stage to be consistent (i.e., to pre-expose the film to hydrogen before admitting the reactant gases) and to help cool the evaporation sources.

The evaporation sources were short concentric spirals of 0.5 mm diameter nickel and palladium wire (Johnson, Matthey and Co. Ltd "spectrographically standardized"). Before use for alloy film preparation, the wires were outgassed in a separate apparatus and some metal was

evaporated; the wires were then weighed and transferred to the reaction vessel where they were again outgassed with the vessel hot (400°C). The reaction vessel (Pyrex-glass) was attached to a stainless steel vacuum system incorporating sorption and ion-pumps, metal valves, etc. Alloy films were evaporated in a vacuum of 10^{-8} - 5×10^{-7} Torr (1 Torr = 133.32 N m⁻²).

Samples for analysis of bulk composition were obtained by cutting up the reaction vessel at the end of the catalytic rate measurements into 6 or 12 representative parts. The composition of individual samples was determined by X-ray fluorescence analysis. As a cross-check, the samples were then combined, the alloy films dissolved from their glass supports and the solutions were analyzed by using atomic absorption. All compositions are expressed in atom percentages. The total film weight was found from the combined weight loss from the evaporation sources. Attention to the geometry and positioning of the evaporation sources ensured that the alloy films were quite uniform in composition over the 220 cm² area of the reaction vessel.

The sample for X-ray diffraction was usually a small flat glass square placed at the bottom of the reaction vessel. A problem arises from the poor thermal contact which it makes with the inner curved surface of the vessel. Ideally, a fragment of the alloy film detached from the vessel surface should be examined but stripping was not achieved without change in composition. Diffraction results from curved portions of the vessel were not satisfactorily reproducible but showed that the glass squares probably gave representative results for films prepared at 400°C. Samples on glass squares during film deposition at -196°C were not representative of the film on the vessel surface.

The reaction mixture was prepared from Research grade ethylene (Phillips) and 99.9998% pure hydrogen (British Oxygen) and when expanded into the reaction vessel

at -100°C gave 8.5 Torr C_2H_4 (1.66×10^{20} molecules) + 24 Torr H_2 . The reaction vessel was connected to the ion source of a mass spectrometer by means of a fine capillary leak. The absolute sensitivity of the mass spectrometer to ethylene was determined before each rate measurement and the relative sensitivities of ethylene and ethane from time to time. Rates are expressed as C_2H_6 formed, Torr per minute at -100°C .

RESULTS AND DISCUSSION

Results are presented first on the characterization of Ni-Pd alloy films with respect to bulk structure and these are given in detail for alloys prepared at 400°C . Our purpose in using a heated support is the belief that, in so doing, atom mobility will be enhanced and that equilibrium will be reached; thus any inhomogeneities which have developed due to preferential nucleation, uneven evaporation, etc. are eliminated.

BULK STRUCTURE

The relevant thermodynamic properties have been determined in the temperature range 700 – 1200°C (10). The heats of

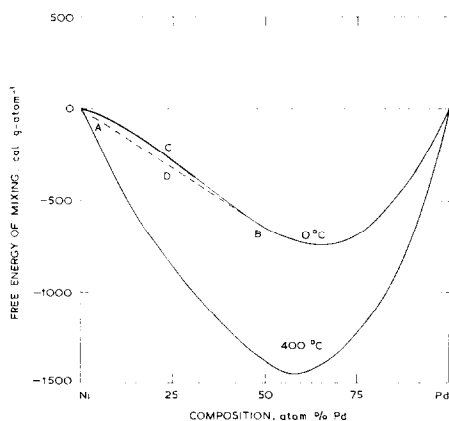


Fig. 1. Variation of the free energy of mixing calculated from thermodynamic data in (10) as a function of composition for Ni-Pd alloys equilibrated at temperatures indicated.

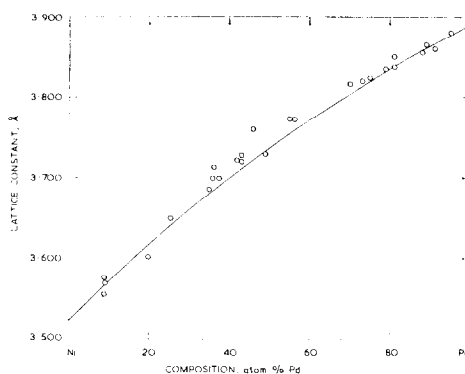


Fig. 2. Lattice constants for Ni-Pd alloy films prepared at 400°C , derived from the position of the X-ray diffraction peak maximum (O) and reported values (—) for annealed powders (12).

mixing are small and are endothermic for nickel-rich and exothermic for palladium-rich alloys; the entropies of mixing are positive at all compositions. Figure 1 shows the variation of ΔG as a function of composition at 0 and 400°C , calculated from the high-temperature thermodynamic data assuming the temperature-independence of ΔH and ΔS . The magnitude of $T\Delta S$ is sufficient to ensure that ΔG becomes negative at an equilibration temperature of 400°C . A small upward curvature is apparent in the curve for alloys equilibrated at 0°C in the nickel-rich region. (This temperature was chosen as illustrative of the effect of low-temperature equilibration, if achievable). The common tangent AB represents the free energy of unmixed solutions with compositions of a few percent Pd and $\sim 50\%$ Pd. In this composition range, the stable configuration corresponding to some intermediate composition C will be these two solid solutions. The intermediate composition C in that part of the curve which is convex upwards will be unstable relative to a point D on the tangent.

The nickel-palladium system has been the subject of a number of X-ray diffraction, metallographic, electrical and magnetic studies (11). Recent evidence (12)

favors the absence of a miscibility gap for vacuum-melted alloy ingots, annealed at 1000°C. The thermodynamic data are consistent with these observations but also suggest that equilibration at much lower temperatures could lead to the detection of phase-separation in the Ni-Pd alloys prepared. If the assumptions made in calculated ΔG are correct, then films prepared at 400°C should be single-phase alloys but perhaps single-phase alloy formation in nickel-rich films should be regarded as borderline. Accordingly, the bulk homogeneity of Ni-Pd films was carefully examined using three criteria which are believed to be necessary for an adequate appraisal of the X-ray diffraction data:

a. The lattice constant of the Ni-Pd alloy film was compared with the value expected for the well-annealed bulk Ni-Pd alloy (12).

b. The symmetry of the X-ray profile was assessed by both visual observation and measurements based on the positions of peak maximum and centroid.

c. X-Ray peak broadening in the alloy films was compared with broadening in the component metals, similarly prepared.

a. *Lattice constant.* Figure 2 records lattice constants measured in a series of Ni-Pd films prepared at 400°C and based on the position of the X-ray diffraction peak maximum. The curve represents lattice constants for well-annealed powder specimens (12). There is general agreement between observed values for Ni-Pd alloy films and expected values, but a more critical examination of the data shows that modest deviations from expected values are more common in the composition range 25–60% Pd.

b. *Peak symmetry.* It is believed that asymmetry of the X-ray diffraction peak, obtained from the counter-diffractometer recording, is a sensitive indicator of the occurrence of a range of lattice constants, indicating inhomogeneity. The converse is

not necessarily true, i.e., that a symmetrical peak indicates a homogeneous alloy, because a peak may be spread symmetrically by a range of lattice constants. However, a narrow symmetrical profile cannot contain substantial quantities of material with different lattice constants. (The X-ray diffraction peaks can additionally be broadened by the presence of strain or very small crystallites.)

A selection was made of X-ray diffraction profiles from Ni-Pd films prepared at 400°C; each example is representative of alloys of similar composition (Fig. 3). The alloy with 55% Pd as well as alloys with higher palladium contents, e.g., 70 and 89% Pd, yield symmetrical profiles. Alloys with 25 and 35% are somewhat asymmetrical but note also their angular breadth compared with pure nickel. To gain some perspective on the extent of the inhomogeneity indicated as well as an indication of the sensitivity available, the spread of the

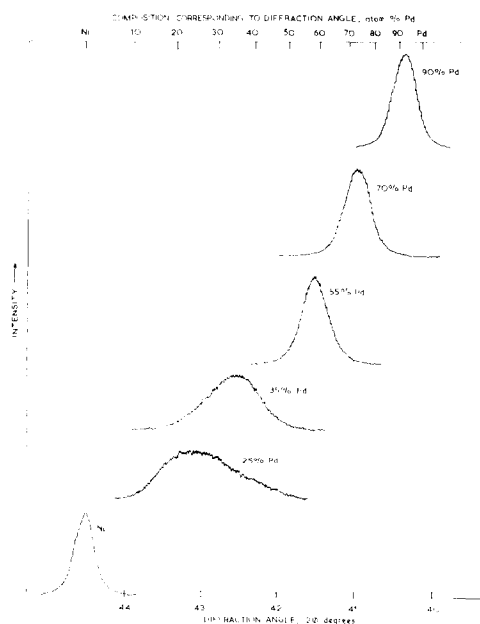


FIG. 3. X-Ray diffraction profiles from (111) planes in selected Ni-Pd films prepared at 400°C with compositions (atom% Pd) indicated, showing some examples of asymmetry and also peak broadening in alloys compared with pure Ni.

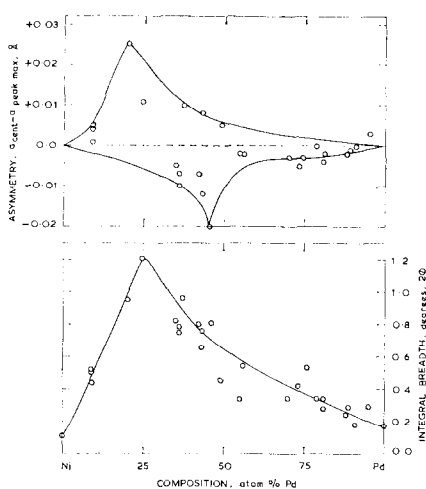


FIG. 4. Variation of the difference in lattice constants from peak centroid and maximum positions, $a_{\text{cent}} - a_{\text{max}}$ (upper) and peak breadth (lower) as a function of composition for Ni-Pd films prepared at 400°C.

35% Pd alloy (compared with pure nickel) is about $\pm 10\%$.

If the X-ray line profile is symmetrical then the lattice constants derived from the positions of the peak maximum and peak centroid will agree. Therefore, it would appear that the difference between these lattice constants, i.e., $a(\text{centroid}) - a(\text{peak maximum})$ constitutes a useful means of "quantifying" the visual impression of peak shape discussed above. Values of $a(\text{centroid}) - a(\text{peak maximum})$ for the pure metals were zero (within experimental error) and values >0 measure the degree of asymmetry (and hence the inhomogeneity) of the alloys (Fig. 4, top). Both positive and negative values of $a(\text{centroid}) - a(\text{peak maximum})$ were found and their limits are shown by the envelopes drawn in Fig. 4 (top). Values of $a(\text{centroid}) - a(\text{peak maximum})$ were greatest for alloys containing about 20–60% Pd.

c. Peak broadening. Reference to Fig. 3 shows that the X-ray profiles from the alloys were also substantially greater in angular breadth in comparison with the

profile from pure nickel. Often X-ray "line"-broadening is associated with the occurrence of small crystallite size and is often observed when supported metal catalysts are examined. In the present work, a further cause of X-ray line-broadening can arise from the occurrence of a range of alloy compositions within the X-irradiated area. A significant variation of composition on a macroscale can be dismissed because the alloy films were uniform in composition over the reaction vessel surface but localized inhomogeneity within or between crystallites is envisaged as a possible explanation. Figure 4 (bottom) shows the integral breadth measured in films of Ni-Pd and the pure component metals. Values of integral breadth were greatest in the composition range 20–60% Pd but, in general, the maximum at 25% Pd was approached smoothly from both the low pure metal values. The integral breadth of this alloy (25% Pd) converts to an *apparent* crystallite size of 78 Å which seems unrealistically small for metal film crystallites deposited and annealed at 400°C, thus supporting an explanation based on inhomogeneity.

These observations on the bulk structure of Ni-Pd alloy films prepared at 400°C may be summarized by stating that the three strict criteria adopted for analyzing the diffraction data agree that alloys with approximately 20–60% Pd contained some inhomogeneities although, as expected, no clear evidence of phase-separation was detected.

-196°C Films

In this alternative method, the mixed metal vapor is condensed on glass cooled at -196°C and if it could be immobilized by rapid quenching, the randomness of the condensing vapor would be preserved. In practice, it is not clear what bulk structure will result from using a glass support as heat sink, nor is it clear what value to

assume for the equilibration temperature. However, the alloy films prepared by deposition at -196°C were very much more active catalysts. Their bulk structure, determined from the deposit on the glass sample squares included in the reaction vessels, was remarkably similar to that observed for alloys prepared at 400°C with respect to both lattice constant, peak symmetry and breadth. However, as noted in Experimental Methods section, the samples on glass squares were thought to be unrepresentative. Alloys deposited on the vessel surface only yielded very weak and broadened X-ray diffraction peaks, indicating the presence of smaller crystallites and/or greater inhomogeneity than found in films prepared at 400°C .

SURFACE COMPOSITION

Methods for predicting the surface composition of binary alloys from bulk thermodynamic properties have been described, e.g., Williams and Nason (13) calculated surface layer compositions corresponding to the free energy minimum obtained from the heats of vaporization of the pure metals and the bulk alloy solution activity coefficients. In general, surface enrichment of the surface layer by the component with the lower heat of vaporization is expected when they are significantly different. The heats of vaporization (at 298°K) of nickel and palladium are 102,800 and 90,000 cal/mole, respectively, i.e., $\Delta H_{\text{sub}} = 12,800$ cal/mole and so the present Ni-Pd alloy films might consist of crystallites with a palladium-rich surface layer.

Therefore, an attempt was made to measure surface enrichment by transferring Ni-Pd film samples prepared in the catalytic reaction vessel to an Auger electron spectrometer for analysis of surface composition. A thin Pyrex-glass square was included in the reaction vessel and, after film deposition, removed under vacuum to a sidearm which was subsequently sealed off. The samples were

inevitably exposed to the atmosphere in the transfer process to the Auger electron spectrometer. After AES analysis, the bulk structure of the alloys was determined by X-ray diffraction and the bulk composition by X-ray fluorescence.

The surface composition of these transferred Ni-Pd alloys determined using high energy Auger electrons agreed closely with the bulk composition. However, it is estimated that the characteristic thickness contributing to AES for Pd 330 eV and Ni 848 eV Auger electrons is about 3 and 5 atom layers, respectively. The lower energy Ni 61 eV peak, which is necessary for the detection of surface enrichment in the outermost layer, was broadened and split in these air-transferred samples and could not be used. Accordingly, a separate investigation was made of the surface composition of Ni-Pd alloy films, prepared inside the Auger electron spectrometer, when both low and high energy Auger electron spectra could be used in the analysis. This work has been reported in detail elsewhere (7) but the main conclusions can usefully be summarized here and related to the work on bulk structure described in the previous sections.

i. Surface enrichment by palladium was indeed detected in Ni-Pd films from the relative intensity of the low energy Ni 61 eV Auger electrons, which "sense" the first one to three atom layers.

ii. It was deduced from the relative intensities of the low and high energy nickel Auger electrons that the palladium concentration was higher in the first atom layer than in the second and third layers. *The outermost surface was a completed palladium monolayer when the bulk composition contained 65 atom% Pd or more.*

iii. Within the bulk composition range 0-65 atom% Pd, a complete range of surface (first layer) compositions is available to provide a suitable alloy system for catalytic study.

The first atom layer composition values determined by AES in a series of Ni-Pd films were fitted to a curve relating them to bulk composition using the theory of Williams and Nason and assuming, *inter alia* (13), that $\Delta H_{\text{sub}} = 10 \text{ RT}$. This implies that the alloy films were equilibrated at a temperature of 640°K (367°C) although deposited with the support initially at room temperature. Now, it has already been mentioned that the bulk structure of Ni-Pd films on a flat glass square resting inside a spherical vessel maintained at -196°C closely resembled the structure of films prepared at 400°C because the glass square was a poor heat sink for the latent heat of condensation of the metal vapor and radiation from the sources. It seems entirely consistent with this observation that the effective support temperature of the *in situ* AES films should approach 400°C . It is also convenient that the AES results then relate more closely to films prepared for catalytic measurements.

CATALYTIC MEASUREMENTS

Two series of results are presented with respect to ethylene hydrogenation, viz, measurements of rates over sintered Ni-Pd

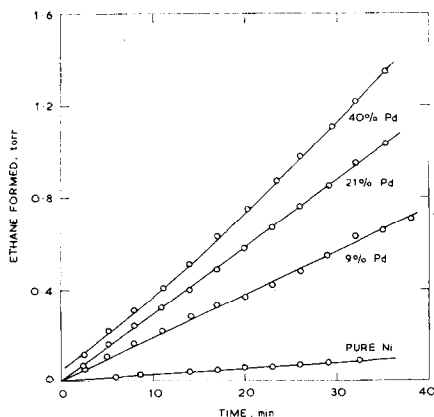


FIG. 5. Ethane formation with time at -100°C over Ni and Ni-Pd films prepared at 400°C , showing characteristic linear plots for Ni and Ni-rich alloys, i.e., up to $\sim 40\%$ Pd.

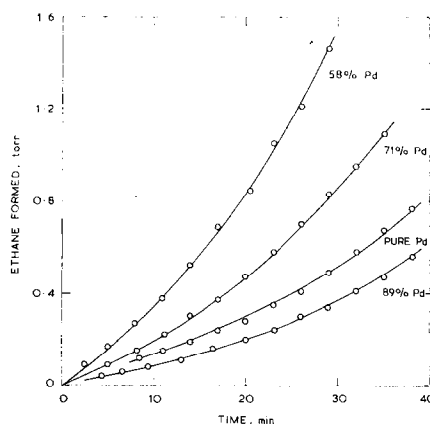


FIG. 6. Ethane formation with time at -100°C over Pd and Ni-Pd films prepared at 400°C , showing characteristic accelerating plots for Pd and Pd-rich alloys.

alloy films (deposited and annealed at 400°C) and over unsintered Ni-Pd films (deposited at -196°C).

Sintered Ni-Pd Alloys

Figures 5 and 6 show a selection of rate measurements over Ni-Pd alloys prepared at 400°C . The catalysts were very active and, together with the sensitivity of analysis available, reaction rates could be measured at -100°C . A characteristic

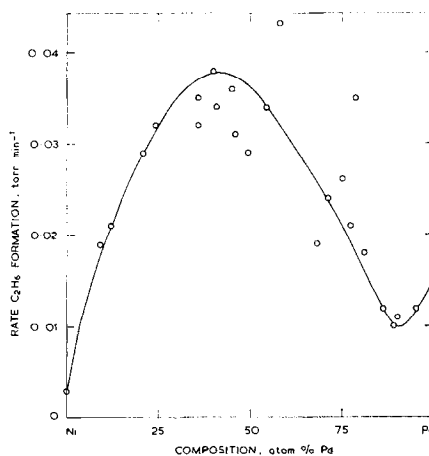


FIG. 7. Variation of the rate of C_2H_4 formation (Torr at $-100^\circ\text{C}/\text{min}$) as a function of composition for Ni-Pd films prepared at 400°C .

feature of these results is the linearity of plots, C₂H₆ formed vs time, for nickel and Ni-rich alloys up to alloy compositions of ~40% Pd (Fig. 5). In contrast, plots of C₂H₆ formed vs time for Pd-rich alloys and pure Pd (Fig. 6) show definite acceleration. Reaction rate measurements were based on the amount of C₂H₆ formed after 20 min.

It is believed that the sintered Ni-Pd alloys prepared were nonporous and that the surface area approximated to the geometric surface area of the reaction vessel with perhaps a small roughness factor. In support of this view, tests with varying weights of pure nickel and palladium showed that activity was independent of film weight. Accordingly, rates of C₂H₆ formation over the alloys were not adjusted for variation in film weight when presenting data on the variation of rate as a function of (bulk) alloy composition (Fig. 7). The rate of C₂H₆ formation passed through a maximum at ~45% Pd. The position of the maximum was reasonably clearly located as a consequence of the large number of alloy films used, although a few alloys had activities above the line drawn through the experimental data. Alloys with a few percent *nickel* were a little less active than pure palladium.

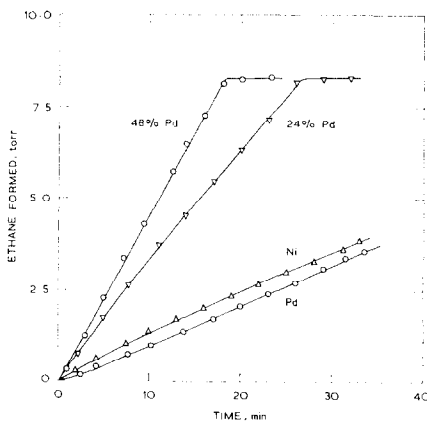


FIG. 8. Ethane formation with time at -100°C over Ni, Pd and Ni-Pd alloy films deposited at -196°C .

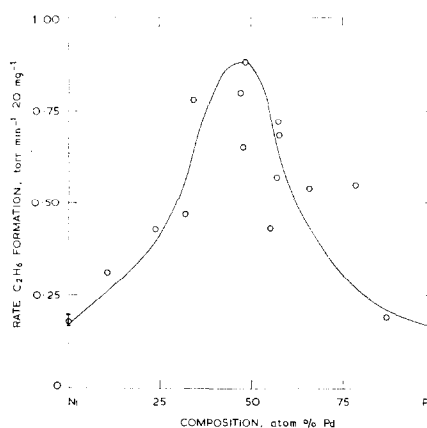


FIG. 9. Variation of the rate of C₂H₆ formation (Torr at -100°C / min / 20 mg catalyst) as a function of composition for Ni-Pd films deposited at -196°C .

Unsintered Ni-Pd Alloys

Rates of ethane formation were also measured over the series of Ni-Pd alloy films deposited at -196°C , which were extremely active catalysts. In contrast to sintered alloys, the plots of C₂H₆ formed vs time were linear for all alloy compositions (Fig. 8). It might be noted that the final conversions obtained after 30–40 min over the sintered alloys (Fig. 6) were reached within a few minutes over the unsintered alloys (Fig. 8). Over the most active unsintered alloy, ethylene conversion was complete after 18 min.

It is believed that the unsintered alloys have much larger surface areas than the near geometric areas of sintered alloys. In this case, tests of the weight-dependence of catalytic activity using pure nickel and palladium films deposited at -196°C showed a linear relationship up to ~25 mg. Consequently observed rates of ethane formation were adjusted to a common basis of 20 mg, which was the average weight of the series of alloy films prepared at -196°C , and expressed as C₂H₆ formed, Torr/min/20 mg. Figure 9 shows the variation of catalytic activity as a function of (bulk) alloy composition. Again the activity passed through a well-defined

maximum at $\sim 45\%$ Pd. The activities of the pure metals were carefully determined as the mean of a number of measurements (Ni, 4; Pd, 7) using separate films. Comparison of Figs. 7 and 9 shows that maximum activity is greater by a factor of about 20 times in unsintered compared with sintered catalysts. Nevertheless, the enhanced activity of Ni-Pd alloys over pure nickel and palladium is a feature common to both activity vs composition plots.

Interpretation

The main feature of the catalytic results is the enhancement of ethylene hydrogenation rate over Ni-Pd alloys, with a maximum at $\sim 45\%$ Pd, compared with the pure component metals. Possible explanations are considered primarily in terms of the information presented on bulk structure and surface composition.

i. The surface area may be greater in the alloys compared with the pure metals because alloying inhibits crystallite growth. If the increased X-ray line-broadening in alloys (Fig. 4, bottom) is due to smaller crystallite size rather than inhomogeneity, there could be a corresponding increase in surface area and activity. Presumably such enhanced surface area would mean that the sintered films prepared at 400°C would now be porous, unlike the pure metals, and their activity would respond to variation in film weight. Examination of the actual weights of alloy films of closely similar composition shows that activity was still independent of film weight. For example, alloy films with 40% Pd (Fig. 7) weighed 9.3 and 20.8 mg but their activities differed little, i.e., 0.038 and 0.034 Torr/min, respectively. Films with 45% Pd weighed 4.8 and 16.8 mg, whereas their activities were 0.036 and 0.031 Torr/min, respectively, again appearing to contradict the idea that enhanced activity was due to an increase in surface area.

ii. The enhanced activity may be correlated with the inhomogeneity detected in the bulk structure of Ni-Pd alloys of intermediate composition prepared at 400°C . The information on the bulk structure of these sintered films defines the region of maximum inhomogeneity as 20–60% Pd and it seems significant that the maximum of catalytic activity is within this range. Nevertheless, it is difficult to explain the cause of the enhancement, e.g., in terms of active sites thus created, and the correlation is not easily tested. Perhaps it is rather coincidental that the enhancement can arise in both sintered and unsintered films, the latter poorly crystalline at intermediate compositions.

iii. The enhancement in activity reaching a maximum at $\sim 45\%$ Pd may be correlated with the observation by Auger electron spectroscopy that the outermost layer in Ni-Pd alloys (prepared *in situ*) was complete (100% Pd) when the bulk composition was 65% Pd or more. There is some difference between the critical compositions, $\sim 45\%$ Pd (catalysis) and 65% Pd (AES) but at 40% Pd (bulk composition) the first atom layer contained $\sim 80\%$ Pd according to AES analysis. Alternatively, the electronic structure or other properties of the surface layer may be at their most favorable before the surface composition reached 100% Pd. The problem with this explanation is the lower activity of pure Pd and Pd-rich alloys, whereas constant activity beyond $\sim 45\%$ Pd might have been expected once the first surface layers consisted of palladium atoms.

In the case of sintered Ni-Pd alloys, rates of ethylene hydrogenation accelerated over Pd-rich alloys (with $\sim 40\%$ Pd or more), Fig. 6, and this is ascribed to the adjustment of the hydrogen content under reaction conditions. These sintered alloys had been annealed in hydrogen at 400°C , then cooled to -100°C before evacuation.

In contrast, the unsintered alloys were only pre-exposed to hydrogen at -100°C , and plots of C₂H₆ formation vs time (Fig. 8) for all compositions were linear. The slightly lower activity of alloys prepared at 400°C with a few percent nickel, compared with pure palladium, may be related to the time required to adjust the absorbed hydrogen content. The larger size of the crystallites in the films prepared at 400°C compared with the semicrystalline alloys deposited at -196°C would also be less favorable for hydride decomposition (14). Nevertheless, the calculation of rates using a later portion of the accelerating plots would not alter the occurrence of a maximum in activity but move its position to beyond 45% Pd.

These observations seem to suggest that hydrogen absorption into the catalyst surface can also provide an explanation of the decrease in activity beyond $\sim 45\%$ Pd. The poisoning effect of dissolving hydrogen in palladium on olefin hydrogenation and other reactions has been reviewed (14). It can be envisaged that the capacity of the surface layers for hydrogen absorption increased (and activity decreased) as the second and third layers, as well as the first, became increasingly close to being pure palladium (i.e., beyond a certain bulk composition, $\sim 65\%$ Pd according to AES analysis). Thus the "true" activity of palladium is more closely approached by a

palladium monolayer on a Ni-Pd base rather than by pure palladium itself.

ACKNOWLEDGMENT

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