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Ethylene Hydrogenation over Supported Nickel–Palladium Catalysts

Although the adsorptive and catalytic properties of alloys can be conveniently studied using evaporated alloy films (*1*) it is both instructive and of possible benefit to attempt to reproduce certain observations using supported alloy catalysts. For example, we have studied the selective oxidation of ethylene over silver–palladium films (*2, 3*) and shown that a similar pattern of selectivity variation with composition could be obtained with silica-supported silver–palladium alloys (*4*). In contrast, apparently well-homogenized alloys on alumina, with as little as 5–10% Pd in the silver, produced only small amounts of ethylene oxide, possibly due to destructive oxidation by undetected "free" palladium.

Subsequently an investigation of Group 8 metal pairs was started using nickel–palladium alloy films (*5*) which were shown to be more active for ethylene hydrogenation than either pure metal, with maximum activity at a bulk composition of ~45 atom% Pd. In an associated study of the surface composition of nickel–palladium films by Auger electron spectroscopy (*6*), it was deduced that the outer surface layer was palladium-enriched and all palladium when the bulk composition was ~65 atom% Pd or more. However, calculation of the surface composition from the theory of Williams and Nason (*7*) suggested that the surface retained a small amount of nickel. Recent results for ethane hydrogenolysis (*8*) over nickel–palladium films, where there was a substantial activity difference between alloys with >60 atom% Pd and pure palladium itself, supported this view.

The work reported here was concerned with attempts to prepare silica-supported nickel–palladium alloy catalysts and the comparison of the activity of these preparations for ethylene hydrogenation with results obtained previously using nickel–palladium alloy films.

Catalysts were prepared from a solution of nickel nitrate hexahydrate ("Analar") and tetramminepalladous nitrate (Johnson Matthey "Specpure"), using sufficient volume to form a slurry with the silica support. The impregnated silica was then evaporated to dryness with stirring on a water bath and left overnight in an air oven at 110°C. Catalysts were reduced, calcined etc., as described below in attempts to produce good alloying, purging with nitrogen where necessary, e.g., between reduction and (air) calcination treatments. As the palladium salt decomposes vigorously, the temperature was raised slowly between 80 and 150°C when calcination was the initial treatment. The "standard" support was Davison "70" silica (used as received, unless otherwise stated); other silicas were a series of "Porasils" (Pechiney-Saint-Gobain from Waters Associates).

Ethylene hydrogenation rates were measured in an atmospheric pressure flow system incorporating a narrow U-tube glass reactor (6 mm o.d.) fitted with a side-arm for the exit gas so that a thermocouple through a glass joint could be inserted directly into a small bed of catalyst (~0.1 g). Ethylene (Phillips, Research grade) flowing at 2 ml/min was mixed with hydrogen (purified by diffusion) at 100 ml/min before the reactor. Before testing, the catalyst sample was purged with nitrogen, then hydrogen was passed at room temperature and at 450°C for 2 hr, the catalyst was

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cooled below −100°C and the ethylene flow was started.

The nickel–palladium system has been examined previously by X-ray diffraction, metallographic, electrical, and magnetic methods and is regarded as a continuous series of solid solutions. Although the heat of mixing is endothermic for nickel-rich alloys (*9*) the magnitude of $T\Delta S$ at normal alloying temperatures, say, >400°C, is sufficient to ensure that ΔG becomes negative. In fact, alloy films annealed in hydrogen at 400°C, although generally yielding the expected lattice constants, on the evidence of X-ray profile breadth and symmetry, appeared to contain some inhomogeneities when the bulk composition was in the range 20–60 atom% Pd (*5*). Hence the first approach to preparing supported alloys was to reduce the impregnating salts deposited on silica at 500°C and above.

TABLE 1

Crystallite Sizes of Ni and Pd on Various Silicas

Support	A	70	B	C	D	E	F	70S
Area (m^2/g)	430	296	225	83	39	24	4	3
Crystallite size (Å)								
Ni	59	51	53	58	134	145	227	500+
Pd	95	159	180	190	250	390	451	500+

Initially a series of crystallite size measurements was made by X-ray line-broadening on pure nickel and palladium to determine how much aggregation could be expected on silicas of different surface area (Table 1). The silicas used were Porasils A to F and Davison "70," the latter either used as received or after sintering at 900°C (designated 70S). The metal loading was 10% and reduction was carried out at 500°C for 5 hr. Table 1 shows the increase in crystallite size as supports of lower surface area were used, with crystallite growth becoming very extensive when the support area was below ~80 m^2/g. It is then of interest to discover if nickel–palladium alloys are better homogenized on low or high area silicas, i.e., whether or not it is useful to encourage crystallite growth.

Table 2 shows results, (i)–(vi), for catalysts with ~50% Pd supported on Porasil F (4 m^2/g), Porasil B (225 m^2/g) and Davison

TABLE 2

Alloying under Reduction Conditions

Number	Support	Nominal loading (wt%)	Reduction temperature[a] (°C)	Alloy composition	
				Actual (atom% Pd)	Calculated from lattice constant (atom% Pd)
(i)	Porasil "F"	5	500	51	82
(ii)	Porasil "F"	10	500	52	79
(iii)	Porasil "B"	5	500	54	67
(iv)	Porasil "B"	10	500	52	84
(v)	Davison "70"	5	500	57	64
(vi)	Davison "70"	15	500	54	64
(vii)	Davison "70"	15	500[b]	52	55
(viii)	Davison "70"	5	600[b]	63	69
(ix)	Davison "70"	5	600[b]	36	60
(x)	Davison "70"	5	700[b]	36	52

[a] For 5 hr.

[b] Preexposed to H_2 at room temperature for 2 hr.

"70" used as received (296 m^2/g). The extent of homogenization can be assessed by comparing the actual composition (column 5) with the apparent composition calculated from the lattice constant (column 6). Alloying was poor on Porasil F, at both 5 and 10% loadings, and on Porasil B at 10% loading but improved at 5% loading where there appeared to be the smallest crystallites. Both 5 and 15% loadings on Davison "70" were also moderately well alloyed, again suggesting some benefit from limiting crystallite growth by control of the metal loading per unit area of support surface (since an adequate homogenizing temperature is still required). Davison "70" *as received,* was used as the support in subsequent work.

In result (vii) of Table 2, it is seen that preexposure to hydrogen at room temperature for 2 hr (before reduction at 500°C, 5 hr) made a further improvement and this procedure was adopted in results (viii)–(x), where conditions for treating compositions with 63 and 36% Pd are given. The composition with 63% Pd was reasonably homogenized after reduction at 600°C for 5 hr but the composition with 36% Pd was still unsatisfactory after reduction at 600 and even 700°C.

A second general approach to preparing supported nickel–palladium alloys was the introduction of a high-temperature calcination stage, but this met with varying success. For example, silica with a 15% metal loading containing 52% Pd was initially calcined in air at 800°C for 3 hr and then reduced in hydrogen at 450°C for 2 hr, yielding a lattice constant corresponding to 84% Pd. In contrast, if the support impregnated with the nickel and palladium salts was first exposed to hydrogen at 200°C for 21 hr and calcined and reduced as before, the apparent composition was then 57% Pd.

On the basis of the above studies and other attempts, not described, it was concluded that it was difficult to produce really well homogenized nickel-palladium alloys (supported on silica), especially nickel-rich alloys. Nevertheless, the Ni–Pd system seemed of sufficient interest to justify a limited examination of its catalytic properties. Two series of catalysts (with 10% metal loadings) were prepared on Davison "70" silica, either by reduction alone (H_2, room temperture, 2 hr + H_2, 600°C, 5 hr) or by the method involving calcination (H_2, 200°C, 16 hr + air, 800°C, 3 hr + H_2, 450°C, 2 hr), and ethylene hydrogenation rates were measured. Figure 1 shows lattice constants determined on catalysts discharged from the reactor using both the position of the X-ray profile peak (triangles) and its centroid (circles). The vertical separation of the "peak" and "centroid" lattice constants indicates the asymmetry of the X-ray profile, due to incomplete alloying, and the separation increased with nickel content for each series of catalysts. The divergence of the observed lattice constants from reported values for annealed powder (*10*) also increased with the nickel content of the alloy. The pure nickel (on silica) catalysts prepared by the method involving calcination contained traces of nickel oxide despite the subsequent reduction treatments.

The mean crystallite size determined by X-ray line-broadening for pure nickel and pure palladium (supported) catalysts prepared by reduction only was 70 and ~165 Å, respectively, or when prepared by calcination + reduction, 77 and 161 Å, respectively. Some estimate of the crystallite size in alloy catalysts is also required in order to compare their activities with the activities of the pure metals. Crystallite sizes determined for alloy samples by X-ray line-broadening are only *minimum* sizes because of the extra broadening caused by inhomogeneities. For the 70% Pd catalysts prepared by reduction only or by calcination + reduction, the apparent crystallite sizes were 98 and 110 Å, respectively. Electron micrographs of ultramicrotome sections of catalyst samples set in resin (11) showed that the crystallite sizes in alloys prepared by calcination + reduction were intermediate between the sizes observed in

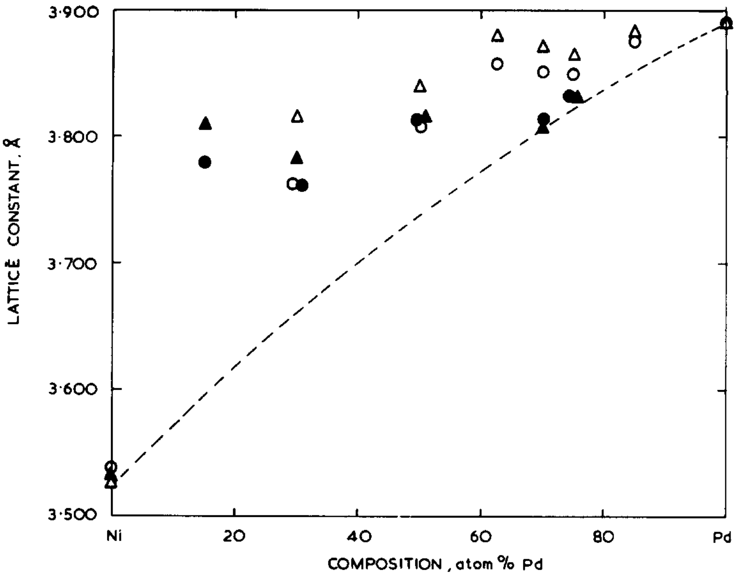

FIG. 1. Lattice constants for Ni–Pd on silica catalysts, prepared by hydrogen reduction; room temperature, 2 hr + 600°C, 5 hr (●, ▲) or by reduction and calcination; H_2, 200°C, 16 hr + air, 800°C, 3 hr + H_2, 450°C, 2 hr (○, △), using both centroid (circles) and peak (triangle) positions. [Some superimposing values at 30, 50, and 75% Pd slightly off-set.] Lattice constants reported (*9*) for annealed Ni–Pd powders (----).

pure nickel (40–140 Å) and pure palladium (60–300 Å) samples, with the exception of the 15% Pd sample (30–100 Å), but there was no consistent variation of size with alloy composition. For the 70% Pd sample (which showed maximum activity in the

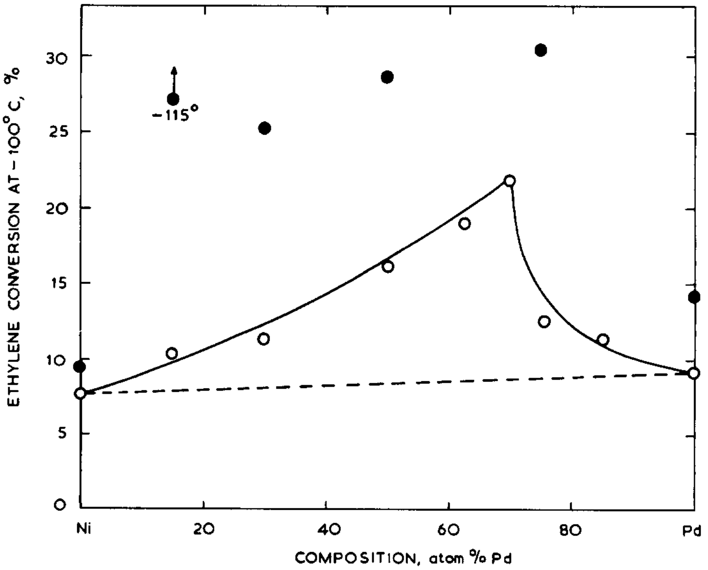

FIG. 2. Ethylene hydrogenation rates (percentage converted at −100°C over 0.1 g catalyst) as a function of (bulk) composition for two series of Ni–Pd on silica catalysts, prepared as Fig. 1, by reduction only (●) or by calcination and reduction (○).

calcination + reduction series, see below) the size range was 40–200 Å.

Catalyst activities were compared in terms of the percentage of ethylene hydrogenated at −100°C, taking the values from Arrhenius plots which were obtained starting at the lowest temperatures first. Activities for the two series of catalysts are shown in Fig. 2, viz, catalysts prepared by reduction only (filled circles) and by combination of calcination and reduction (open circles). The important result obtained for both series is that supported nickel–palladium catalysts of all compositions were more active than the corresponding pure metals, as found previously for nickel–palladium films (*5*). However, the position of maximum activity was not clear for supported catalysts prepared by *reduction only* (filled circles); the 15% Pd catalyst was particularly active but its X-ray pattern was very weak and it may have been highly dispersed. The catalysts prepared by reduction only were more active than the corresponding catalysts prepared by calcination + reduction. Pure palladium, and to a lesser extent pure nickel, also showed this effect of preparation on activity, although each method gave the same dispersion when applied to the pure supported metals (see "X-ray" crystallite sizes above).

The activity of nickel–palladium catalysts prepared by *calcination + reduction* (unbroken line, Fig. 2) varied systematically with (bulk) composition, with maximum activity at 70% Pd. This variation is itself interesting in view of the rather limited change of lattice constant (Fig. 1) with the (bulk) composition of the alloys. The enhancement in activity of these alloys compared with pure nickel does not seem to be the result of improved dispersion, e.g., the 70% Pd catalyst has larger crystallites than the pure nickel catalyst (see above). However, the pure palladium catalyst appeared to have still larger crystallites and the shape of the *specific* activity vs composition curve might show more of a plateau in the Pd-rich region up to and including pure Pd, as indicated by Auger (AES) measurements (*6*). Of course, there is a substantial difference between the conditions under which the AES measurements were made and those employed in the preparation and testing of the present catalysts.

In considering the activity maximum observed with nickel–palladium films (*5*), a review of the evidence tended to favor the idea that there was some involvement of dissolved hydrogen which was poisoning the catalysts once the outermost layer of the palladium-enriched surface was entirely palladium. (The decrease from maximum activity could also be considered as the dissolution of hydrogen to form the Pd–Ni hydride, if the surface layer contained both palladium and nickel). Subsequently an activity maximum was found with other nickel-based alloy films which did not contain palladium (*12*). Eventually the role of the second metal component in nickel-based alloys may be elucidated, but if supported alloys are to be used, it seems essential to find methods which will provide better homogenized crystallites. Nevertheless, the present activity measurements have demonstrated that the enhancement reported for Ni–Pd films (*5*) was not just a specific effect arising from the use of thin film catalysts.

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R. L. Moss
D. Pope
B. J. Davis

Warren Spring Laboratory
Stevenage
Hertfordshire
England

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