# NOTE

## Ethane Hydrogenolysis over Nickel–Palladium Alloy Films

As part of a catalytic study of Group 8 metal pairs, ethylene hydrogenation rates (at $-100°C$) were measured over Ni–Pd alloy films, showing maximum activity at a bulk composition of $\sim45$ atom% Pd (1). In an associated analysis of surface composition by Auger electron spectroscopy (AES), it was deduced, from the relative intensities of low and high energy nickel Auger electrons, that the outermost surface approximated to a palladium monolayer when the bulk composition was $\sim65$ atom% Pd or more (2). Hence constant catalytic activity at bulk concentrations in the range 65 to 100 atom% Pd might have been expected; the observed decrease in activity beyond the maximum at $\sim45$ atom% Pd was ascribed, *inter alia*, to hydrogen absorption in Pd-rich alloys.

When ethylene hydrogenation is used as a test reaction, the variation of rate with composition is modest for Ni–Pd alloys, and in order to pursue the correspondence of activity and *surface* composition, a reaction was sought where alloying might be expected to cause larger changes in reaction rate. The specific activity of silica-supported metals for ethane hydrogenolysis shows enormous variation (3), seven to eight orders of magnitude at 205°C over the activity sequence: Os > Ru > Ni > Rh > Ir > Re > Co > Fe > Cu > Pt $\sim$ Pd. Alloying, or bimetallic catalyst formation, e.g., the addition of copper to nickel (4), causes a substantial decrease in the rate of ethane hydrogenolysis, and so this reaction was chosen for the present study of Ni–Pd alloys.

Nickel–palladium alloy films were prepared by simultaneous deposition from separate sources on to the inner surface of a spherical Pyrex glass reaction vessel maintained at 400°C. Then the film was annealed for 1 hr at 400°C in 5 Torr hydrogen and cooled to $-100°C$, and hydrogen was pumped off before admitting the reactant gases. Further information on alloy film preparation and the analysis of bulk composition by X-ray fluorescence and atomic absorption is given in Ref. (1), where the bulk structure of these alloy films is also described in detail. The reaction mixture was prepared from 99.98% pure ethane (Phillips Research Grade) and 99.9998% pure hydrogen (British Oxygen), which when expanded into the reaction vessel at $-100°C$ gave 8.5 Torr $C_2H_6$ ($2.0 \times 10^{20}$ molecules) + 15.5 Torr $H_2$ (1 Torr = 133.32 N m$^{-2}$). Gases of this composition remained after study of ethylene hydrogenation (1), and in preliminary experiments (see below), the ethane formed was then subjected to hydrogenolysis by raising the temperature. This gas composition and the procedure for gas admission were adopted in subsequent work with ethane + hydrogen mixtures. The reaction vessel was connected directly to a mass spectrometer and the progress of the reaction was monitored in terms of methane formation.

Figure 1 shows the rate of ethane hydrogenolysis to methane at 300°C as a function of *bulk* composition; most measurements were made by admitting the ethane + hydrogen mixture to the catalyst
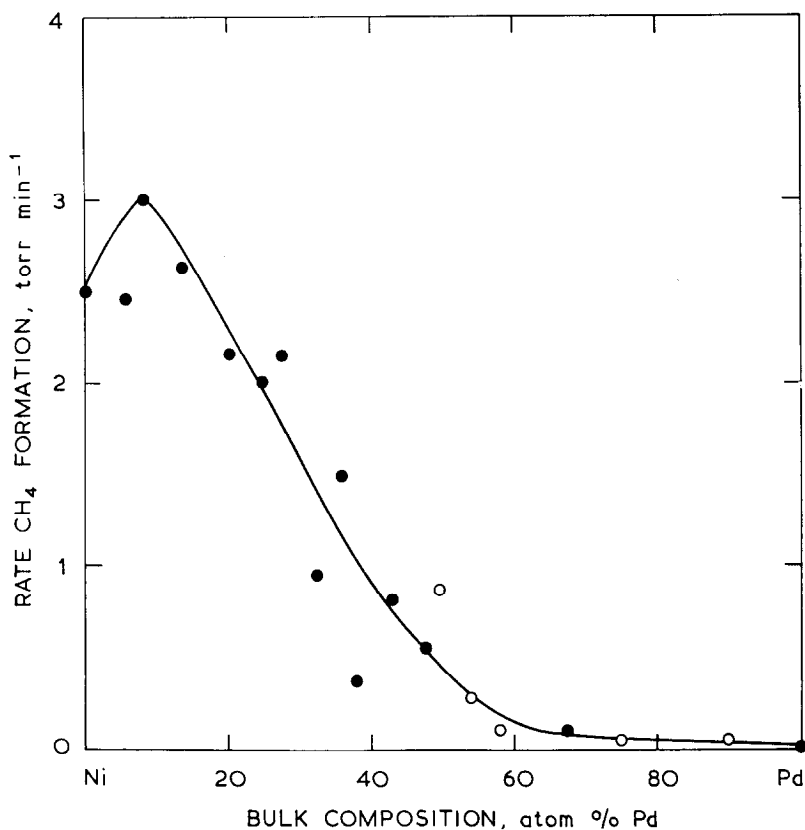
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Fig. 1. Rate of methane formation at 300°C over Ni–Pd alloys as a function of bulk composition.

(filled circles), but in a few cases the ethane had been formed by prior *in situ* ethylene hydrogenation (open circles). Instead of decreasing the rate, alloys with up to 20 atom% Pd were at least as active as pure nickel. Larger palladium additions decreased the rate to a low constant level in alloys with more than ~60 atom% Pd. It will be remembered that AES analysis indicated an extremely palladium-rich outermost surface layer at *bulk* compositions more than 65 atom% Pd (*2*), and the hydrogenolysis activity pattern corresponds in so far as the activity declined to a low value beyond ~60 atom% Pd. However, this low activity is still significantly greater than the activity of pure palladium. As an indication of relative activities, the rates of methane formation over pure nickel, alloys with >60

atom% Pd, and pure palladium were 2.5, ~0.05, and 0.0006 Torr min⁻¹, respectively.

Figure 2 shows the line of best fit through the experimental AES data reported in Ref. (*2*), plotted in terms of surface vs bulk composition. Also shown in the curve predicted from the theory of Williams and Nason (*5*), for a regular solution binary alloy, assuming an fcc (111) surface, $\Delta H_{sub} = 10\,RT$, $\Omega = -0.1\,kT$ and $\delta = +0.1$ [where $\Delta H_{sub}$ is the difference in the heats of vaporization of the pure elements; for definitions of other quantities see Ref. (*5*)]. For palladium–nickel alloys, $\Delta H_{sub} = 10\,RT$ implies an alloy equilibrium temperature of 370°C, sufficiently close, for our purposes, to the alloy preparation temperature used here. A reasonable fit of the experimental data was obtained, but of interest now is the small
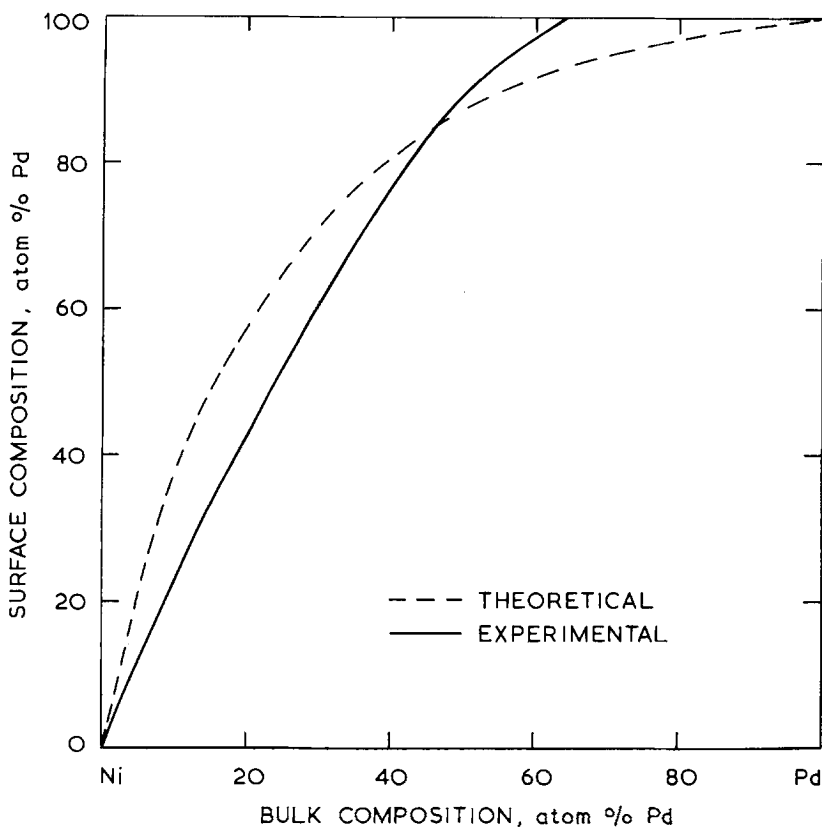
FIG. 2. Analysis of surface composition by AES from Ref. (*2*) compared with curve predicted from theory (*5*), plotted in terms of surface vs bulk composition.

but significant nickel content of the surface predicted in alloys with >65 atom% Pd. So qualitatively, at least, the marked difference in the activities of alloys with >65 atom% Pd and pure Pd might be explained.

Using the "theoretical" curve relating surface and bulk composition, the rates of methane formation are replotted in Fig. 3 against apparent *surface* composition. There is now a broad range of surface concentrations over which the activity changed little (0–50 atom% Pd) followed by a decline in activity between 50 and 100 atom% Pd. It is suggested (*4*) that a number (*n*) of adjacent metal atoms is required to bond the intermediates in hydrogenolysis, believed to be highly unsaturated dicarbon surface residues. [Re-

cent magnetic evidence suggests $n = 6$ for ethane adsorption on a nickel surface (*6*).] If *pure ensembles* containing only a number of nickel atoms are required, then activity should be greatly decreased by modest additions of the palladium "diluent." If, however, *mixed ensembles* are permissible, activity might be maintained up to larger surface palladium concentrations.

By way of illustration, an ensemble was envisaged with $n = 6$ containing a central nickel doublet, the other atoms being either nickel or palladium. Figure 4 shows part of a (111) surface containing *one* such mixed ensemble (i.e., the six atoms joined by lines). Starting with a grid representing 650 Pd-atom positions, increasing numbers of nickel atoms were "substituted" randomly and the number
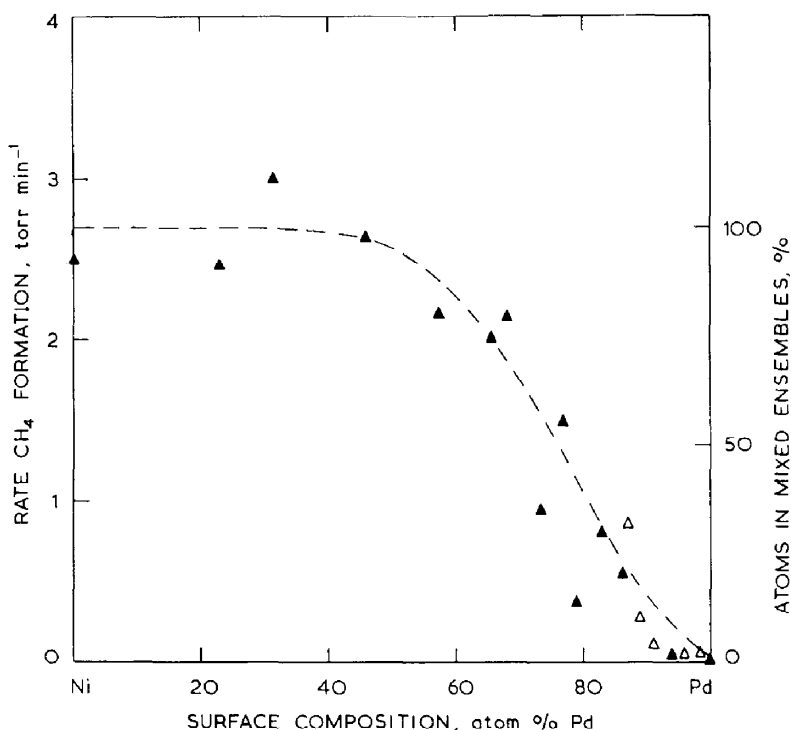
FIG. 3. Rate of methane formation at 300°C over Ni–Pd alloys replotted against apparent surface composition (symbols); percentage total surface atoms participating in mixed ensembles, (– – –).

of atoms participating in mixed ensembles was counted. Atoms "participate" either as part of the central nickel doublet or as one of the other four atoms (Ni or Pd) joined to the doublet, as shown in Fig. 4. Edge corrections were made by envisaging the sides of the grid and also the top and
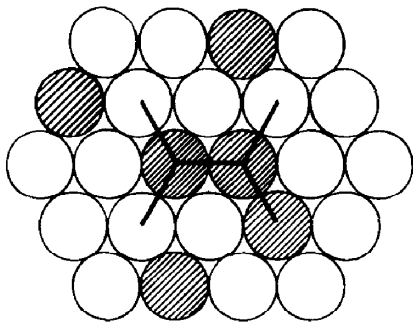


FIG. 4. Mixed nickel–palladium ensemble on (111) surface, $n = 6$ with central nickel doublet (nickel atoms shaded).

bottom as joined. The procedure seemed to provide a reasonable estimate for exploratory work of the percentage of atoms participating in this particular type of mixed ensemble as a function of surface composition. (Similar estimates for small pure ensembles had been checked by computer using larger grids.)

Results are plotted in Fig. 3 (broken line) and "fitted" to the experimental data by assuming that 100% participation of the surface atoms in mixed ensembles (right-hand scale) corresponds to constant activity. Looking first at the *palladium*-rich side of Fig. 3, the number of participating atoms (broken line) soon builds up, determined by the probability of nickel doublet formation. Eventually, in the 50–50 Ni–Pd alloy, most of the surface atoms (~95%) are involved in mixed ensembles. From this composition on to pure nickel, arguably only the composition of the en-

sembles changes, i.e., progressively more pure nickel ensembles are formed on the surface, replacing mixed ensembles, so that catalyst activity remains constant.

Alternatively, carbon deposition, which must be considered in any hydrocarbon reaction over nickel, may be an explanation of the approximately constant activity of nickel-rich alloys. For example, palladium may inhibit the formation of carbonaceous residues, tending to enhance activity in opposition to its deactivating role, i.e., the elimination of active nickel surface. However, there is only a minimal indication of enhancement, and the concept of mixed ensembles as illustrated above, or small nickel ensembles (e.g., doublets), with a restriction on their action at nickel-rich compositions, may provide an explanation of the activity vs surface composition relationship.

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