Hydrogenation of Ethylene on Induction-Evaporated Films of Nickel and Some Nickel Alloys*

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The effects of alloying Cu, Fe, or Pd with a thin Ni film used to catalyze the hydrogenation of C_2H_4 have been studied. To obtain homogeneous alloy films, these were vacuum-evaporated from alloy pellets. In the absence of deliberately preadsorbed hydrogen, alloying Ni with Cu (diamagnetic) or Fe (ferromagnetic) produced only small changes in catalyst activity, however, Pd (paramagnetic) promoted the activity sharply. Deliberately preadsorbed hydrogen considerably promoted the activity of the Cu-Ni and Fe-Ni films, but not that of the Pd-Ni films. The effect of hydrogen is discussed in terms of Types A and C adsorption. Apparent activation energies ranged from 6 to 10 kcal/mole. Although the Pd-Ni catalysts were in several respects unique for all catalysts the reaction order was fractional, being positive in H_2 but negative in C_2H_4.

INTRODUCTION

A study of alloy catalysts represents one of the more promising means of elucidating the catalytic properties of metals. Alloy catalysts in bulk or massive state have frequently been used. However, catalysts evaporated in the form of thin films offer the possibility of greater purity and surface cleanliness. Although evaporated metal alloy films have been prepared for other purposes, their catalytic properties appear to have been little studied. However, Gharpurey and Emmett (1) produced alloy film catalysts by successively depositing Ni and Cu from separate filaments, then annealing in hydrogen. These authors state, and preliminary experiments in the present study confirmed, that such filament-evaporated alloy films may vary in chemical composition and thickness throughout the extent of the film area. Because of this, alloy films in the present work were evaporated from preformed, homogeneous alloy pellets and subsequently annealed. Although con-

siderable fractionation occurred, especially during the evaporation of the Cu-Ni alloy pellet, chemical analysis on different areas of a film showed that the compositions of these areas differed by only small amounts.

The present study has inquired how the reaction rate at several temperatures, and the reaction order respond to changes in catalyst composition and pretreatment. It was not an object of the present work to study any binary alloy system thoroughly, but rather to explore the use of induction-evaporated films for the study of the catalytic effects of singly alloying with Ni several metals having different magnetic properties. The catalytic properties of induction-evaporated alloy films did not appear to have been studied previously. In an endeavor to simplify deductions, only alloys in which the component metals are mutually soluble to form unordered, fcc lattices have been employed. Although the alloy lattice parameter increases linearly with solute metal concentration, the saturation magnetization of Ni is varied in very different ways (2) in that it is increased by alloying Fe, is decreased by Cu, but is

substantially unchanged by Pd. Thus the alloys would appear to offer the opportunity for the electronic factor to exhibit itself if it is important and not masked in the catalytic system investigated. Because of the marked effect which preadsorbed hydrogen can exert in the catalytic hydrogenation of C_2H_4 (3), the catalytic activity of the films has been measured both in the presence and absence of such deliberately preadsorbed gas. The catalyst films were further characterized by BET surface area measurements and examination with an electron microscope.

EXPERIMENTAL

Unless otherwise stated, all temperatures are in degrees Centigrade, and all pressures are expressed as mm of Hg.

Materials. Film metals comprised spectrographically standardized Matthey Ni rod, purity better than 99.99%; Cu rod, purity exceeding 99.999%; Fe rod, purity at least 99.95%; and Pd sponge, purity 99.99%. The gases He and Kr used in the surface area measurements were research grade obtained in sealed glass bulbs, and were not further purified. For catalyst activity measurements "prepurified" tank H_2, and "chemically pure" tank C_2H_4 were each finally purified with a liquid Na-K alloy, prior to which the C_2H_4 was also repeatedly fractionated.

Apparatus. The catalyst films were produced and their catalytic activities measured in a conventional all-glass apparatus which included a two-stage Hg diffusion pump; cold traps; a dosage and measuring system containing two McLeod gauges, a Hg manometer, and calibrated volumes; and a reaction system which comprised the reaction vessel, a Hg manometer, and a cold trap to protect the catalyst film. No stopcocks were employed in the reaction system which could be completely isolated from other parts of the apparatus by means of Hg-actuated glass float valves. One of the McLeod gauges was of the Pfund type (4) which permitted pressures to be measured down to 1×10^{-7}. The reaction vessel, shown in Fig. 1, had a volume of about 400 cc without the sidearm. It was designed
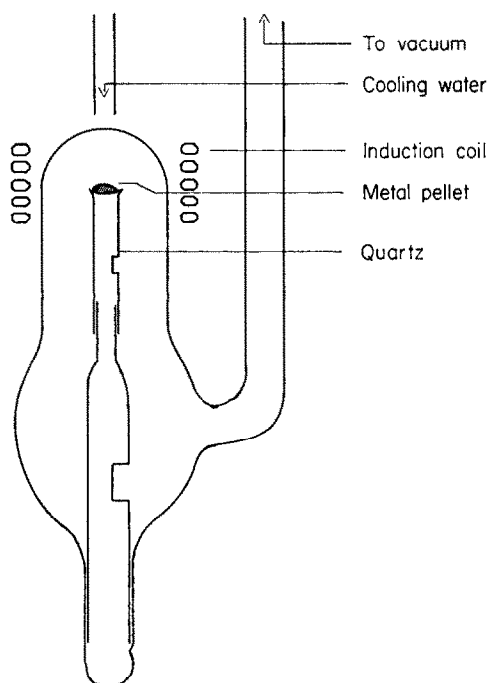

FIG. 1. Reaction vessel.

to minimize the intrusion of diffusion-controlled reaction, yet permit the deposition of a uniform catalyst film inside the upper hemispherical dome. The metal pellet was positioned in as small a quartz cup as possible, with its surface equidistant from the hemispheric top of the reaction vessel. Because of its close proximity to the molten pellet, any metal film (<10%) deposited on the quartz cup was severely sintered. Separate experiments showed that the cup film metal and the metal of the pellet itself could have made only a negligible contribution to the measured catalytic activity of the metal film deposited on the reaction vessel dome.

Preparation of catalyst films. An alloy pellet weighing about 4 g was formed by twice heating a weighed portion of the pure metals under H_2 in an alumina crucible. To ensure a well-stirred, uniform alloy, free from hydrogen, the pellet was then placed in a vessel similar to Fig. 1. After outgassing and baking at 450° for about 10 hr to yield a pressure of at least 1×10^{-6}, the pellet was induction-melted with a spark-

gap converter at its maximum power output of 2 kw so as to produce vigorous stirring in the pellet. From 3 to 10 mg of metal was thus evaporated. When cool, the pellet was examined and weighed.

For the formation of the catalyst film itself, the so prepared pellet was sealed in a clean reaction vessel. After baking and evacuating at 450° as in the premelt, the pellet was finally induction-evaporated at full power during 3 to 6 min, depending upon the alloy. During film evaporation the pressure was between 5×10^{-6} and 1×10^{-6}, and a fast flowing cold water curtain kept the reaction vessel cool. The catalyst film was then thoroughly annealed, further to homogenize and to stabilize the catalyst for the long series of activity measurements which was to follow. In the rigidly controlled annealing program the evacuated catalyst film required 40 min to rise from 400° just to 425°. Upon lowering the temperature to 335°, and admitting about 50 mm of H_2, annealing was continued for 11 hr.

Determination of film catalytic activity. Ordinarily reaction velocity measurements were made in sequences of three to eight runs, between which the catalyst film remained in H_2 protected by a cold trap. After each run, catalyst regeneration and pretreatment for the next run were carried out. Thus after evacuation at the prior run temperature, about 50 mm of H_2 was admitted and the catalyst heated to reach 335° asymptotically during 90 min, then evacuated if desired. If the next run were to be made with the catalyst containing deliberately preadsorbed hydrogen, the catalyst was cooled to run temperature in H_2, then evacuated to a residual pressure of 10^{-5}, thereby leaving some hydrogen adsorbed on the catalyst film. If the next run were to be made in the absence of preadsorbed hydrogen, evacuation was continued at 335° to a pressure below 10^{-5}. Upon cooling to the run temperature a few mm of He was temporarily admitted to equilibrate the catalyst thermally. Runs were made at $-28.5°$, $0.0°$, $28.5°$, $48.0°$, and $71.5°$ and these temperatures were maintained well within $\pm 0.5°$. The zero time

pressure for all equimolar doses of H_2 and C_2H_4 was close to 90 mm. The course of the reaction was followed manometrically, using a cathetometer, often until the rate finally became diffusion controlled. From 6 to 22 runs were made per catalyst film. For the Cu-Ni and Fe-Ni films the average change in catalytic activity was only about 0.5% per run. For the nickel film and the nickel film containing 5.5 atom % Pd, the comparable activity change was about 1.5%. However, for the nickel film containing 9.5 atom % Pd, the activity change averaged about 6% per run. The measured catalytic rates were corrected for such systematic changes in film activity.

Determination of film surface areas. Because of the large volume of the reaction vessel and the relatively small surface area of the metal film Kr adsorption at liquid N_2 temperature was used. No correction for thermal transpiration was needed above pressures of 0.3 mm, and corrections for deviations from ideal gas behavior were negligible. Using an extrapolated liquid vapor pressure for P_0, in the linear BET equation gave straight lines for relative pressures up to about 0.35 (5). The area of an adsorbed Kr atom was taken as 19.5 Å². In agreement with recent work (6), it has been assumed that Kr was not adsorbed on the glass directly underlying the metal film. However, the considerable amount of bare glass surface at liquid N_2 temperature adsorbed Kr. Having determined the roughness factor for this bare glass to be 2.1, its BET area was calculated and subtracted from a BET total area value to yield the surface area of the metal film alone. Surface area measurements were made upon completion of the reaction velocity runs on a film.

Chemical analysis of alloy films. In order to determine the uniformity of alloy composition, the dome portion of a reaction vessel with attached alloy film was carefully broken into pieces, after other measurements had been made. At least duplicate analyses were run on each of four different areas of an alloy film. The dome top yielded one area while three different portions of the cylindrical dome sides each

produced one other area. Because the amount of metal present in each area was small (0.3 to 1.5 mg), sensitive spectrophotometric methods were used. For Pd and Ni, chloroform solutions of dimethylglyoxime precipitates formed at pH 2 and 8 respectively, were used. For Cu a chloroform solution of the diethyldithiocarbamate complex, and for Fe a nitrobenzene solution of the salt of the tris-(1,10-phenanthroline)Fe(II) ion were used.

RESULTS AND DISCUSSION

1. Composition and Uniformity of Catalyst Films

The results of the chemical analyses on four different areas of an alloy film are shown in Table 1. The weight per cent of each alloying component B, is given along with its standard deviation s. From the latter, variances were calculated in the usual way to measure the precisions of the analytical methods. The average film compositions are shown in the fifth column, along with their standard deviations s_2, and variances s_2^2. A variance analysis indicated that the analytical methods were adequate to detect the small differences found in film area composition. Fluctuations in alloy area composition are seen to be small, ranging from 0.55% for the Fe-Ni alloy to 1.41% for (Pd-Ni)20. From the last two columns of Table 1 differences may be observed between the composition of the catalyst film and that of the original pel-

TABLE 1
PROPERTIES OF CATALYST FILMS

Catalyst film	Weight (mg)	BET surface (cm²)	Compn. different areas of a film (wt %B ± s)[a]	Av. compn. of film (wt %B)[b]	Compn. of evapn. pellet (atom %B)
(Ni)19	7.25	1070	—	—	
(Cu-Ni)17	11.88	900	56.51 ± 0.07 57.22 ± 0.14 56.14 ± 0.23 56.51 ± 0.16 $s_1^2 = 0.0257$	56.59 ± 0.64 $s_2^2 = 0.4135$ [54.6]	9.6
(Fe-Ni)22	12.42	1770	10.49 ± 0.07 10.27 ± 0.14 10.32 ± 0.02 9.94 ± 0.07 $s_1^2 = 0.0066$	10.26 ± 0.33 $s_2^2 = 0.1060$ [10.8]	11.0
(Pd-Ni)18	2.23	950	—	25.69 ± 0.65 [16.00]	
(Pd-Ni)20	3.86	810	15.92 ± 0.21 16.53 ± 0.27 15.12 ± 0.08 16.42 ± 0.07 $s_1^2 = 0.0521$	16.00 ± 0.96 $s_2^2 = 0.9212$ [9.5]	7.9
(Pd-Ni)21	2.72	1030	9.76 ± 0.02 9.22 ± 0.31 8.88 ± 0.47 10.08 ± 0.06 $s_1^2 = 0.0813$	9.49 ± 0.76 $s_2^2 = 0.5770$ [5.5]	3.8

[a] B represents either Cu, Fe, or Pd.
[b] Atom % in brackets.

let. This difference was negligible for the
Fe-Ni alloy but the Pd-Ni alloys showed
the films to be considerably richer in Pd,
while the Cu-Ni alloy film showed a very
large enrichment in Cu. These fractionation
effects would be qualitatively predicted
from the latent heats of sublimation of the
component metals. Even in the case of the
Cu-Ni pellet the evaporation of the premelt
film should have reduced the Cu in the
pellet by less than 0.1% prior to the evapo-
ration of the catalyst film itself. Evapora-
tion from a preformed alloy pellet is be-
lieved to yield a more uniform alloy film
than has been possible from filaments of
the single component metals.

2. Some Physical Properties of the Catalyst Films

Table 1 also summarizes other properties
of the catalyst films. Although the geomet-
rical area per film varied from only 60 to
80 cm², the BET areas varied about two-
fold. Even though the induction-evaporated
catalyst films had a brilliant, mirrorlike,
external appearance, electron microscopy
showed them to be an essentially continuous
array of crystallites. For the Cu-Ni film
the transmission picture showed the pres-
ence of holes which, in view of the small
specific surface area of this film, and its
high Cu content suggested that considerable
sintering of this film occurred during the
standard annealing procedure. Only the
(Pd-Ni)20 films yielded electron diffraction
patterns sharp enough for calculation of
lattice constants. The premelt and catalyst
films yielded fcc values for a_0 of 3.565 ±
0.010 and 3.577 ± 0.016 Å, respectively,
taking a_0 for Au as 4.0785_5 Å. Interpolation
between the lattice constants of very pure
Pd-Ni alloys (7) yielded values of 3.562 Å
and 3.569 Å respectively, in satisfactory
agreement with the foregoing film values.

3. Catalytic Activity of Films

Since straight lines could be drawn
through the first three to six experimental
points (taken at 30 sec intervals) of the
plots of total pressure vs. time, the slopes
of these lines gave the initial rates of hy-

drogenation. Experiments with H_2 alone
showed its adsorption to be manometrically
undetectable. Specific initial rates of hydro-
genation r_s, were calculated as millimoles of
C_2H_4 reacted per minute per square centi-
meter of film surface. To allow the activity
of the various films to be compared as
fairly as possible, such rates for the essen-
tially equimolar reaction mixtures have
been normalized to a zero-time total pres-
sure of 87 mm. The normalized rates r'_s
differ from the rates r_s by less than ±2.5%.

Because apparent first order behavior has
often been assumed for the catalytic hydro-
genation of C_2H_4, plots first order in H_2
were also made. For the equimolar reactant
mixtures, these plots fell into three groups.
A strictly linear plot was obtained only
when preadsorbed hydrogen was present
on the surface of the Cu-Ni film. On all
surfaces of the Ni and Fe-Ni films, the
plots were linear up to the diffusion-
controlled region, following a small initial
concavity. On all surfaces of the two active
Pd-Ni films, and on the outgassed surfaces
of the Cu-Ni film, the plots became truly
linear only in the latter half of a run. This
last type of plot has been reported by
others (8, 9) for this hydrogenation on
evaporated films conditioned with pread-
sorbed C_2H_4. Recent work with this hydro-
genation on Ni and on Fe films (10), has
emphasized that the reaction order and/or
mechanism may change during the course
of a single run in a static system. Because
of the uncertainties associated with choos-
ing the most characteristic rate constant in
measuring catalyst activity during a reac-
tion velocity run, in the present study
initial specific rates have been employed
throughout.

The catalytic activities of the various
films at 0° are shown in the third column
of Table 2. As is clear from the next col-
umn, alloying either Cu or Fe changed the
activity of Ni relatively little, but alloying
Pd increased the activity about 30-fold.
Whereas the presence of deliberately pread-
sorbed hydrogen changed the activities of
the Ni film and the Pd-Ni films, including
the poisoned one, but slightly, the Cu-Ni
and Fe-Ni films showed eightfold and two-

TABLE 2

SUMMARY OF FILM CATALYTIC ACTIVITIES, ARRHENIUS PARAMETERS AND REACTION ORDERS

Catalyst		Catalytic activity at 0° $(r'_s \times 10^t)$	Relative activity $(r'_s\text{ alloy}/r'_s\text{ nickel})$	Activation energy (kcal/mole)	$(E_{alloy} - E_{Ni})$[a]	$(\log A_{alloy} - \log A_{Ni})$	$r = k\,p_{H_2}^m \cdot p_{C_3H_4}^n$	
No.	Compn.						m	n
19	100% nickel	6.9	—	7.0	—	—	—	—
17	54.6 atom % Cu	7.2	1.04	8.9	2.3	1.9	0.9	−0.3
22	10.8 atom % Fe	8.2	1.19	8.9	2.3	1.9	0.8	−0.3
21	5.5 atom % Pd	219[b]	31.7	7.0	0.0	1.5	0.6[c]	−0.2[c]
18[d]	16.0 atom % Pd	0.014[b]	0.002	(9.8)	2.3	−0.8	—	—
		(H)[a]	$r'_s\text{ catalyst(H)}/r'_s\text{ catalyst}$		$(E_{catalyst(H)} - E_{catalyst})$	$(\log A_{catalyst(H)} - \log A_{catalyst})$		
19	100% nickel	8.5	1.23	7.0	0.0	0.05	0.9[f]	−0.5[f]
17	54.6 atom % Cu	63.6	8.8	8.9	0.0	0.9	0.8	−0.4
22	10.8 atom % Fe	24.6	3.0	6.5	−2.3	−1.3	0.9	−0.4
20	9.5 atom % Pd	487	—	6.6	—	—	0.6	−0.2
21[d]	5.5 atom % Pd	216[b]	0.99	—	—	—	—	—
18[d]	16.0 atom % Pd	0.016[b]	1.14	9.8	0.0	—	—	—
				6.8 Av. 9.1 Av.				

[a] Average values of E_a used.
[b] Calculated from adjacent reaction temperature using activation energy.
[c] Obtained on (Pd-Ni)20.
[d] Poisoned in preparation.
[e] Deliberately preadsorbed hydrogen present.
[f] Obtained on nickel film (Ni)11.

fold activity increases, respectively. For a less completely studied film, (Ni)16, preadsorbed hydrogen, however, caused a small poisoning effect. Poisoning effects have also been found by others (3, 14).

To assess the effect of the temperature at which hydrogen was deliberately preadsorbed, in one run on the Cu-Ni catalyst, hydrogen was preadsorbed at 0°, the run temperature, instead of temperatures up to 335°. As a result catalytic activity increased about 33%, but this was only about one-sixth of the activity produced by the higher temperature hydrogen preadsorption. Presumably because at the higher temperatures more preadsorbed hydrogen was more strongly bonded to the catalyst surface.

4. Determination of Reaction Orders

Reaction orders at 0°, except Pd-Ni at −28.5°, obtained from the slopes of the plots in Figs. 2 and 3 appear in the last two columns of Table 2. The pressure of one reactant gas was varied while the pressure of the other was adjusted to be constant at
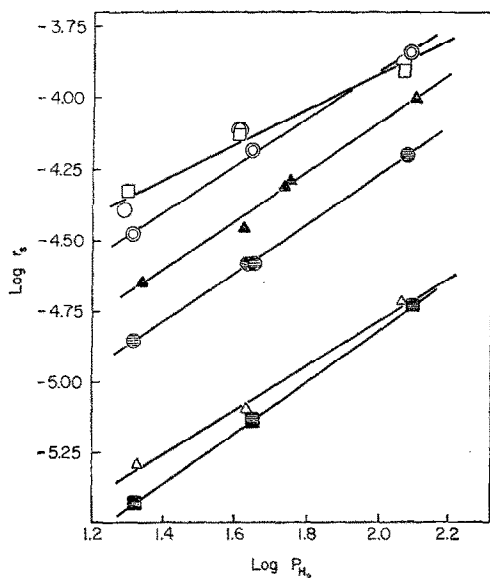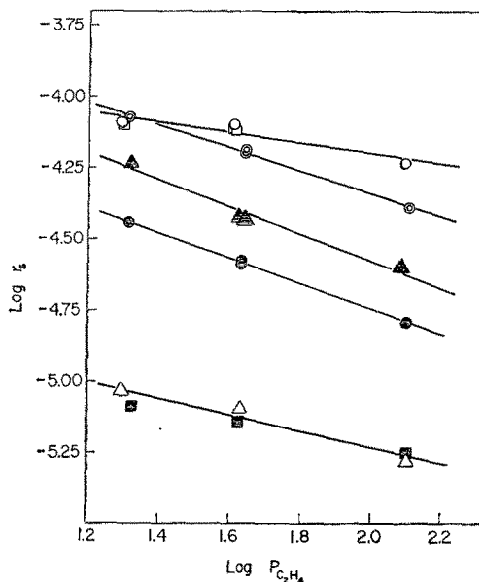

FIG. 3. Reaction order in ethylene at 0°, except the Pd-Ni catalyst at −28.5°; ○, (Pd-Ni)20(H); □, (Pd-Ni)20; ⊙, (Cu-Ni)17(H); ▲, (Ni)11(H); ●, (Fe-Ni)22(H); △, (Fe-Ni)22; ■, (Cu-Ni)17. Notation (H) means preadsorbed hydrogen present. $P_{H_2} = 43$ mm.

a pressure of 43 mm. On all films tested fractional orders were obtained which were positive in H_2 and negative in C_2H_4. Such order behavior for the hydrogenation of C_2H_4 has been reported by others for films of Ni or of Fe (10), for supported catalysts of the metals studied here (11), and for supported Pt (12). The present reaction orders appear to fall into two groups, regardless of whether the film surface was preconditioned with preadsorbed hydrogen. The Pd-Ni film was unique, showing values of 0.6 and −0.2 in H_2 and C_2H_4, respectively, while the other films yielded values averaging 0.8 and −0.4, respectively.

5. Activation Energy and Frequency Factor

Apparent activation energies E_a calculated from Arrhenius plots shown in Figs. 4 and 5 are tabulated in Table 2. These activation energies fall into two groups yielding average values of 6.8 and 9.1 kcal/mole, respectively. The use of average values, rather than individual values is preferred because of the limited number
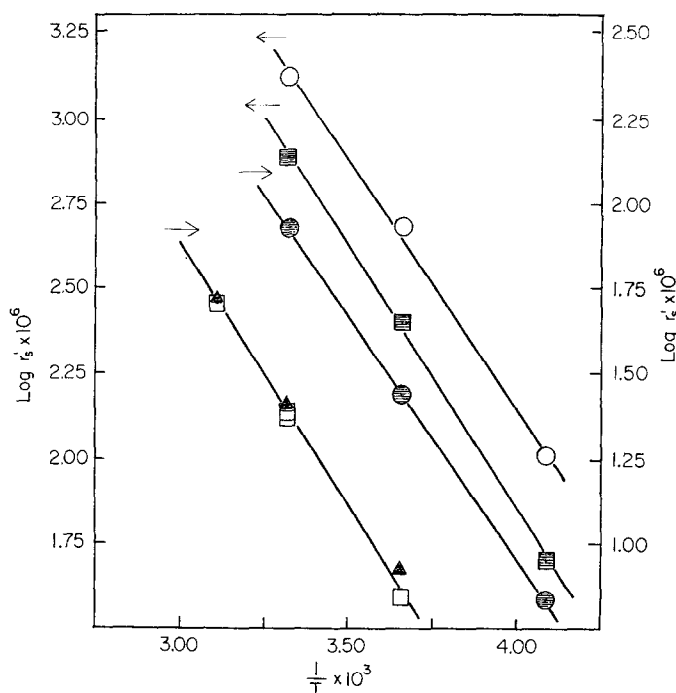

FIG. 2. Reaction order in hydrogen at 0°, except the Pd-Ni catalyst at −28.5°; ○, (Pd-Ni)20(H); □, (Pd-Ni)20; ⊙, (Cu-Ni)17(H); ▲, (Ni)11(H); ●, (Fe-Ni)22(H); △, (Fe-Ni)22; ■, (Cu-Ni)17. Notation (H) means preadsorbed hydrogen present. $P_{C_2H_4} = 43$ mm.

Fig. 4. Arrhenius plots yielding an average value of $E_a = 6.8$ kcal/mole; $\bigcirc$, (Pd-Ni)20(H); $\blacksquare$, (Pd-Ni)21; $\bullet$, (Fe-Ni)22(H); $\square$, (Ni)19; $\blacktriangle$, (Ni)19(H). Notation (H) means preadsorbed hydrogen present.

of different temperatures used in securing data for a given film. In general literature values of E_a for C_2H_4 hydrogenation on Ni films vary from about 6 to 11 kcal/mole, with a value of 6 to 8 reported for a Cu-Ni alloy film (1). It appears of interest that in accordance with a recent study (10) of this hydrogenation on Ni and on Fe films, our lower value of 6.8 would be identified with a Rideal mechanism and our higher value of 9.1 with a Langmuir-Hinshelwood mechanism. Pre-adsorbing hydrogen does not change the activation energy on a film except in the case of the Fe-Ni film. In the absence of deliberately preadsorbed hydrogen, alloying either Cu or Fe with Ni increases E_a.

Also shown in Table 2 are the changes in log A, the pre-exponential factor, caused by alloying Cu, Fe, or Pd with Ni, or by the presence of deliberately preadsorbed hydrogen. Since alloying Cu or Fe with Ni produced little change in the observed activity at $0°$, the large change in E_a is

almost exactly compensated by the increase in A. The large increase in activity caused by alloying Pd with Ni appears due only to an increase in A. Poisoning a Pd-Ni film appears to involve both an increase in E_a and a decrease in A. While the promoting effect of preadsorbed hydrogen on the Cu-Ni film appears due solely to increased A, for the Fe-Ni film promotion would be due to poor compensation in the decreases of E_a and A.

CONCLUSIONS

The facts that of the three different metals alloyed, only Pd does not much change the saturation magnetization of Ni, and only Pd markedly changes the catalytic activity of Ni, indicate that an electronic factor does not appear to be directly involved. Although Pd increases the size of the Ni lattice more than either Cu or Fe, it is probable that the unique affinity of Pd for hydrogen (13) is relatively the more important factor. The
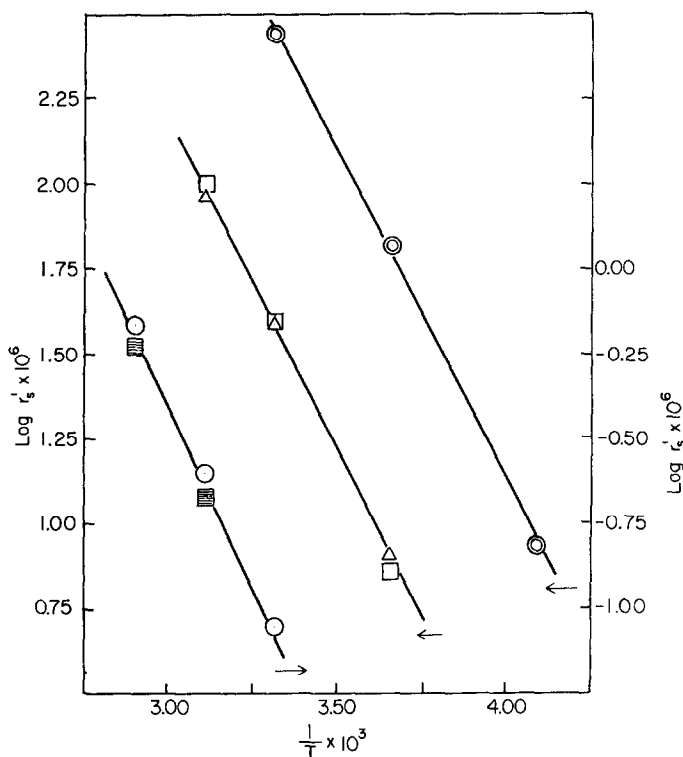
FIG. 5. Arrhenius plots yielding an average value of $E_a = 9.1$ kcal/mole. $\odot$, (Cu-Ni)17(H); $\triangle$, (Fe-Ni)22; $\square$, (Cu-Ni)17; $\bigcirc$, (Pd-Ni)18(H); $\blacksquare$, (Pd-Ni)18. Notation (H) means preadsorbed hydrogen present.

experiments with deliberately preadsorbed hydrogen support this viewpoint. However, the presence of alloyed Cu or Fe along with deliberately preadsorbed hydrogen was necessary to achieve a marked promoting effect on nickel. Also hydrogen preadsorbed at high temperatures was much more effective than when adsorbed at zero. In the experiments with deliberately preadsorbed hydrogen, the hydrogenation of C_2H_4 is believed limited to portions of the catalyst surface on which hydrogen was adsorbed reversibly at reaction temperature. As there appears to be no evidence that the deliberately preadsorbed hydrogen itself participated directly in the hydrogenation (3, 14).

There is much evidence that hydrogen can be adsorbed in at least two ways in a fcc lattice such as nickel. Strongly adsorbed hydrogen, sometimes called Type A, "first species," or negative (surface potential) is believed to be located in pits around surface atoms, preferably in A sites (15). More weakly or reversibly adsorbed hydrogen, sometimes called Type C, "second species," or positive (surface potential) is believed to exist on A–B sites perhaps as a stretched molecule, preferably on the (111) faces (15). The deliberately preadsorbed hydrogen is believed to have been Type A and this or a similar type of strongly held hydrogen from the feed gas mixture is thought to have existed on the Pd-Ni catalysts even when hydrogen was not deliberately preadsorbed. As Type A hydrogen adsorption coverage increased the amount of Type C hydrogen adsorption should increase inasmuch as its transition to Type A is slowed down due to an increased activation energy for this transition (16, 17). In terms of such a model the reversibly adsorbed Type C hydrogen possibly existing as

stretched molecules adsorbed on A–B sites (15), would be largely responsible for C_2H_4 hydrogenation. The activity of an adsorbed, stretched hydrogen molecule could be understood if a C_2H_4 molecule were thereby hydrogenated in a single successful encounter. Thus a surface containing Type A hydrogen, but having many single A sites vacant would be especially active. Whereas, only normal A and B sites may exist in a perfect (111) face of fcc pure nickel, the properties of some or all of these sites should be modified by the presence of foreign lattice atoms due to solid solution of metals such as Cu, Fe, or Pd. For example the promoting effect of preadsorbed hydrogen on the Cu-Ni catalyst would be attributed to modified A and B sites which permitted desorption of hydrogen not only from B sites, but also from many single A sites in preparing this surface for reaction with the H_2 and C_2H_4 mixture. The existence of such Type C hydrogen adsorption at higher temperatures can probably be attributed to the stability of BA_3 adsorption complexes stabilized by electrostatic attraction (15).

The present work appears to emphasize that the metallic properties of a catalyst surface may be of importance only indirectly and to the extent that they determine the nature and extent of adsorption complexes on the surface.

ACKNOWLEDGMENTS

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