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Reactions of Hydrocarbons on Palladium–Gold Alloys

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Hydrogenation of acetylene and reactions of hexane were studied on Pd and Pd–Au alloys. Alloying increases the selectivity for nondestructive reactions of hexane, and the activity in hydrogenation of acetylene as a function of alloy composition shows a maximum.

The present results and the comparison with results obtained on Ni–Cu alloys show that the changes in the population of the transition metal orbitals cannot alone be responsible for the variations in the kinetic parameters and product distributions.

INTRODUCTION

The use of alloys in fundamental catalytic research is no new subject, as can be seen for example, from the review by Bond (*1*). Recently, however, two new aspects have appeared in this work. The theory of alloys, which forms the theoretical background, has developed from the so-called rigid-band model (*2*) into the more sophisticated coherent potential approximation or virtual band model [see Ref. (23)]. Secondly, geometrical considerations have been included in the explanation of the experimental results on catalysis by alloys (*3–6, 27*).

In this paper we report the behavior of Pd–Au alloys in two reactions: (1) reforming of hexane; (2) hydrogenation of acetylene. The reasons for this choice were as follows. During our previous studies with Ni–Cu alloys (*3, 6*) it appeared that alloying a transition metal with a Group Ib metal increased the activity in hydrogenation and decreased strongly the activity in hydrocracking so that reactions not previously ascribed to Ni could operate, such as isomerization or dehydrocyclization. In this paper we again compare the catalytic activity of alloys toward the C–H and C–C bonds, but using alloys of palladium instead of nickel. The comparison of results on the two systems Ni–Cu and Pd–Au offers a very interesting possibility to check the role in catalysis of the number of "*d* holes." Their number remains constant in the Ni–Cu system but decreases in Pd–Au alloys with increasing content of the Group Ib metal.

Reactions of hexane were followed, as in our previous paper (*7*), in a steady-flow reactor, and the reactions of acetylene in a pulse reactor (*6*). The latter was mainly chosen because of its simplicity and efficiency in studies on the selectivity. *A posteriori*, this appeared to be a lucky choice because some transient phenomena which could not be observed in a static steady-flow reactor could be studied here.

EXPERIMENTAL METHOD

All experiments with hexane were performed in an open-flow apparatus described previously (*7*). The primary gas-chromatographic data were first converted into the molar concentrations C_i of various compounds (i denotes hydrocarbon with i carbon atoms) and the total conversion α, in percent was calculated as

$$\alpha = 100\left(\sum_{i=1}^{6}\sum_{j,j\neq k} iC_i^{(j)}\right) \times \left(\sum_{i=1}^{6}\sum_{j,j\neq k} iC_i^{(j)} + 6C_6^{(k)}\right)^{-1}. \quad (1)$$

Summation over j is performed over all detected compounds with i carbon atoms, and the subscript k denotes hexane. At low rates of reaction and high flow rates the conversion α is directly proportional to the total rate.

Selectivity S, for the nondestructive reactions, i.e., all reactions leading to the six-carbon atom compounds, is characterized by the parameter S:

$$S = 600\left(\sum_{j,j\neq k} C_6^{(j)}\right)\left(\sum_{j,j\neq k}\sum_{i=1}^{6} iC_i^{(j)}\right)^{-1}. \quad (2)$$

The chain splitting is characterized by a fission parameter M_f, defined as (*7*)

$$M_f = \left(\sum_{j}\sum_{i=2}^{5}(6-i)C_i^{(j)}\right)\Big/C_{\text{measured}}. \quad (3)$$

For single terminal splitting, M_f should be near unity, for multiple fission into methane directly, much lower than unity; and for statistically random fission, much higher than unity. Parameters S and M_f were compared under the same (or at least very similar) reaction conditions.

All results on acetylene hydrogenation were obtained in a pulse reactor as described previously (*6*). Product analysis was performed by means of a column 2.20 m long, 4-mm i.d., filled by Durapak-vinylisocyanate on poracil C 80–100 mesh.

The flow of hydrogen (which was the reacting component and simultaneously the carrier gas) was 48 ml/min. The peak areas were used to determine the concentration of gases, ethylene (1), ethane (2), and acetylene (3). The total conversion α (%) is defined as

$$\alpha\,(\%) = \frac{C_1 + C_2}{C_1 + C_2 + C_3}\cdot 100, \quad (4)$$

and the selectivity for ethylene formation S_E as

$$S_E\,(\%) = \frac{C_1}{C_1 + C_2}\cdot 100. \quad (5)$$

When necessary, corrections were made for polymerization. However, this correction was negligible at low temperatures. The reactions were performed with a pulse of 0.2 ml acetylene at atmospheric pressure.

At low conversions α (%) is proportional to the total rate, and the apparent activation energy can be calculated from the plot of log α vs $1/T$. The specific activity per unit total surface area was defined as

$$A_s = \log(\alpha/sw) \quad (6)$$

and evaluated for all alloys for $T = 193$ K, s being the total specific surface area and w the weight of the catalyst used. The surface areas of catalysts were determined by a Perkin-Elmer/Shell sorptometer.

Alloys were prepared without any carrier by the method described in Refs. (*8*, *9*). Solutions of metal chlorides were reduced by hydrazine. In order to obtain homogeneous alloys, the precipitated powder was further sintered at 400°C for 16 hr in a flow of hydrogen. The diffractograms showed rather sharp peaks after this treatment and no phase separation. The catalysts used are listed in Table 1. Before catalytic experiments the alloys were oxidized and then rereduced *in situ* at 350–400°C for at least 15 hr.

For acetylene hydrogenation 0.05–0.1 g of the catalyst was used in a fixed-bed reactor of about 1-cm^2 cross-sectional area. A layer about 1 mm thick was spread over a sintered glass bed. For hexane reforming,

TABLE 1

Pd-Au CATALYSTS USED

Au, at%	s,[a] m^2/g	Reactions studied[b]
0	0.15	1, 2, 3
39	0.12	1, 2, 3
48	0.28	1, 2, 3
70	0.82	1, 3
100	0.11	1, 3

[a] s = surface area.

[b] Reactions: 1—hydrogenation of acetylene; 2—reactions of hexane; 3—hydrogenation of cyclopropane.

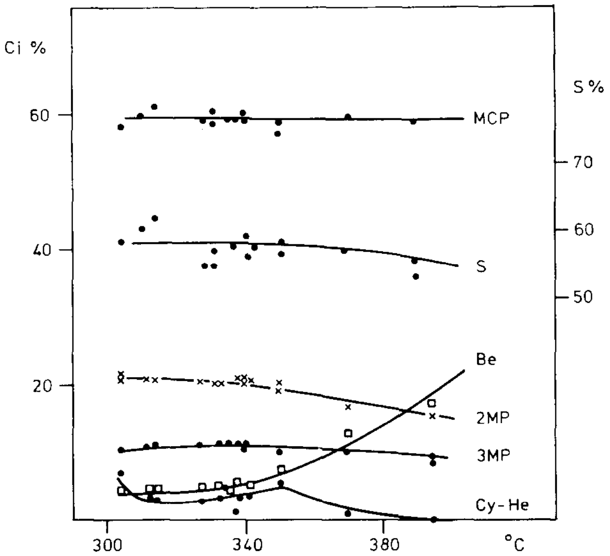

FIG. 1. Selectivity parameter S and molar concentrations C_i as a function of temperature (°C) for a 39% Au alloy. MCP = methylcyclopentane; 2-MP = 2-methylpentane; 3-MP = 3-methylpentane; Be = benzene; CyHe = cyclohexane; C_i = hydrocarbons with i C atoms.

about 1 g of the catalyst was used, spread over a cross-sectional area of about 2 cm^2. A rough estimate according to standard criteria for internal diffusion and external mass transfer shows that the measured rates are not influenced by these phenomena. Hexane reactions were investigated at 280–410°C, and hydrogenation of acetylene between −130 and +40°C.

Some preliminary results on cyclopropane hydrogenation are mentioned toward the end of the paper; these were obtained as in Ref. (*6*), using the pulse reactor.

EXPERIMENTAL RESULTS

Reactions of Hexane

These reactions are accompanied by a stronger self-poisoning than the analogous reactions on Ni–Cu alloys. The self-poisoning is more extensive at higher temperatures, and a real steady-state of the reaction has never been reached with Pd–Au alloys. This fact precluded determination of the activation energy and of other kinetic parameters. It can only be said that the detectable reaction sets in at lower temperatures with Pd than with alloys (by 30–50°C). Each increase in temperature is accompanied by increasing self-poisoning and conversion higher than 2% could not be reached. Most of the determinations were performed at $\alpha < 1\%$.

The poisoned catalyst could not be regenerated by hydrogen reduction at 300–400°C. However, considerable regeneration occurred when the poisoned catalysts were oxidized first and then reduced, e.g., at 300°C.

The selectivity pattern, however, was little influenced by self-poisoning, and reproducible results were obtained in this respect. The product composition was also rather independent of the temperature, as can be seen from Fig. 1 for 39% Au alloy. Similar results were obtained with other alloys and pure Pd as well.

The initial product distribution (IPD) for three catalysts is shown in Fig. 2. The S value for Pd is higher than for Ni, and it increases with alloying. The same was found for the fission parameter M_f. However, this parameter reached a maximum at the value of 2–2.5, while with Ni–Cu alloys, also, values up to 3–4 were found.

Reactions of Acetylene

The basic determination was the measurement of conversion α as a function of temperature at comparable conditions for

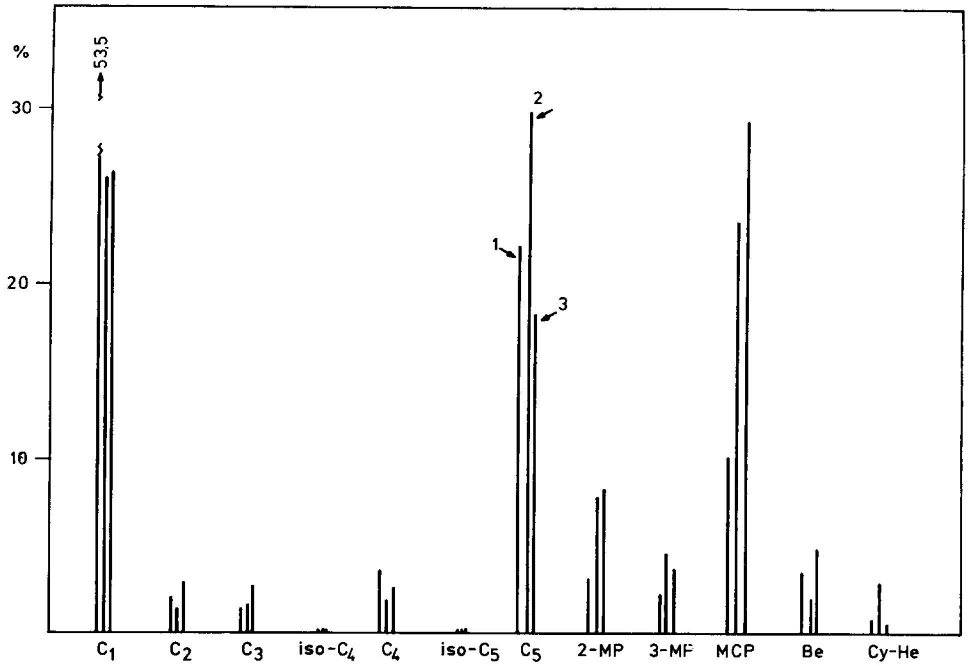

FIG. 2. Initial product distribution. Catalysts: 1—pure Pd; 2—39% Au; 3—48% Au. C_i = hydrocarbons with i C atoms. Other symbols as in Fig. 1.

all catalysts. A part (at low α's) of the $\alpha(T)$ function was measured in more detail in order to be able to evaluate the apparent activation energy E_a. At low temperatures the reaction was practically free from self-poisoning. When some self-poisoning occurred at measurements at higher temperatures, it was possible to regenerate the catalysts by the oxidation–reduction cycle.

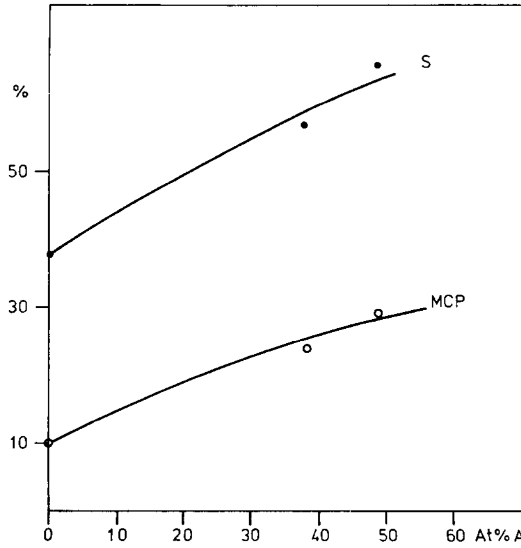

FIG. 3. Selectivity parameter S and the MCP content among products, at comparable conditions. Pd: conversion α = 1.02; 383°C. 39% Au: α = 0.7; 360°C. 48% Au: α = 0.6; 373°C.

The determinations of α and other parameters were complicated at lower temperatures by the appearance of two gas-chromatographic peaks with a retention time similar to that of ethane. One of these peaks, denoted as EA I, appeared at all temperatures of the reactor and always with the same retention time, which coincided very precisely with that of ethane in the calibrations. However, the second peak (EA II) appeared only at the lowest temperatures, and its retention time was dependent on the temperature of the reactor. The EA II peak was identified in the following way.

Pulses of acetylene were repeatedly injected, and from the effluents the fraction with the retention time of the EA II peak was collected by freezing out at liquid-nitrogen temperature. A sample collected in this way was then analyzed mass-spectrometrically and appeared to be pure ethane. When the temperature is increased, the EA II peak shifts to shorter retention times and finally merges into the EA I peak.

The relative production of the two ethane peaks, the ratio of peak areas (EA II/EA I), first increases for all catalysts with temperature; at about −50°C a maximum is reached, and then the ratio decreases again. All catalysts behaved in a similar way; only the maximum value of the ratio was higher for the 68% Au catalyst. No EA II peak was observed with Au, which is inactive at low temperatures.

If the logarithm of the apparent retention time of the EA II peak is plotted against $1/T$, an apparent heat of adsorption can be evaluated. It is a function of the Au content in the alloy and increases monotonically between 0.5 and 0.8 kcal/mol.

When ethylene is injected together with acetylene in one pulse, both the EA I and the EA II peak increased in size. However, when ethylene without acetylene was injected, the EA II ethane peak was never observed. When acetylene was injected together with carbon monoxide, no EA II peak appeared while the EA I ethane production was influenced only marginally. The ratio of EA II/EA I ethanes can be increased a little by shortening the contact time, i.e., by increasing the flow rate.

In the determination of the total conversion, α (%), and of the selectivity, S_E, etc., at low temperatures, the total ethane production (EA I + EA II) was always considered.

From the Arrhenius plot of the $\alpha(T)$ function the apparent activation energy E_a was evaluated for various catalysts used. The variation of E_a with the alloy composition is shown in Fig. 4. In the same figure the activity parameter A_s is plotted.

Figure 5 shows, as an example, the selectivity for partial hydrogenation, S_E, as a function of temperature for one alloy. The results for Pd and other alloys are qualitatively the same. Only on the decreasing part of the $S_E(T)$ curve are the values of S_E lower at corresponding temperatures when the Au content is higher. This is illustrated by Fig. 6, where the selectivity S_E, determined at the same total conversion but at different temperatures, is plotted as a function of alloy composition.

Besides ethane and ethylene, C_4- and C_6-hydrocarbons (mainly butane and *n*-hex-

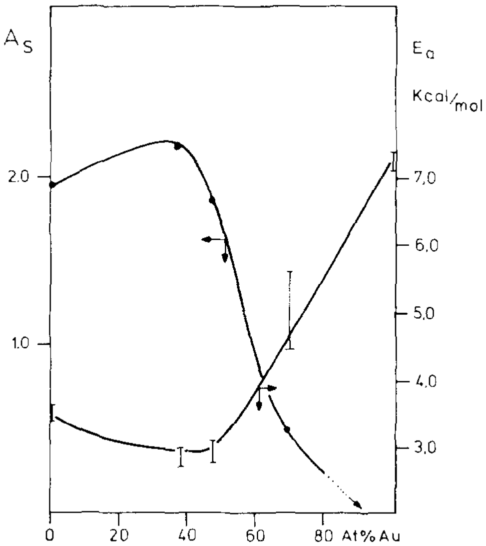

FIG. 4. Variation of the specific activity $A_s + 3$ and the activation energy E_a with the alloy composition. In the graph of E_a the limits of uncertainty of the determination of E_a are indicated. The corresponding value of $A_s + 3$ for Au is −3.5. For A_s, see Eq. (6).

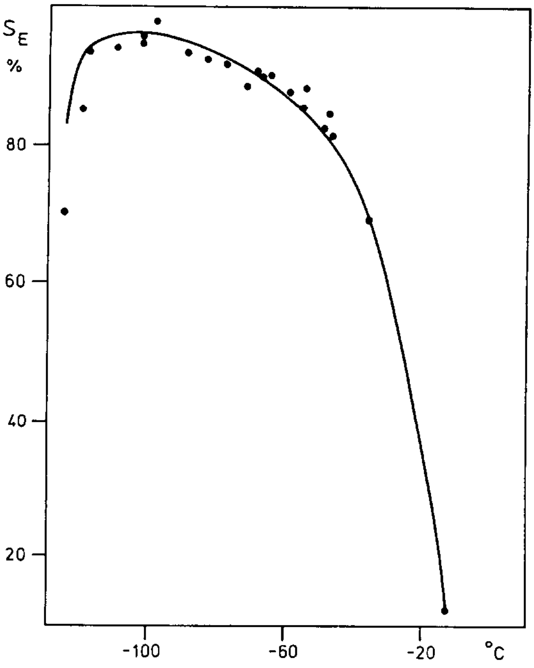

FIG. 5. Selectivity in ethylene formation, S_E, as a function of alloy composition. Alloy catalyst: 39% Au.

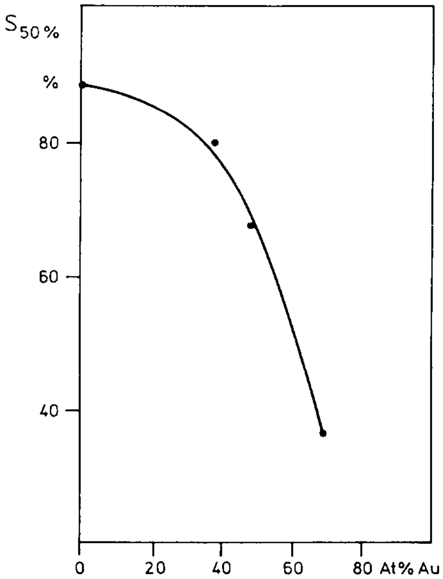

FIG. 6. Selectivity in ethylene formation at 50% conversion of acetylene, as a function of alloy composition.

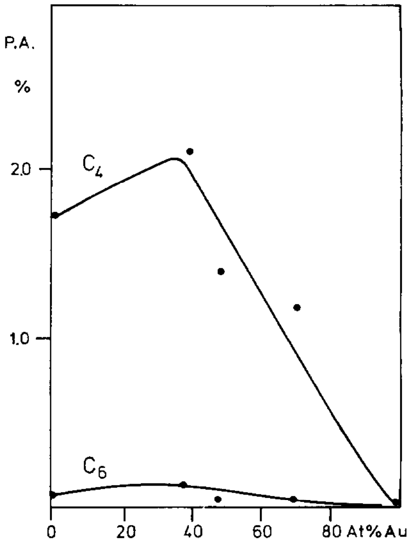

FIG. 7. Amount of acetylene (in percent of the total pulse of acetylene) polymerized (P.A.) into the respective hydrocarbons (C_4, C_6), as a function of alloy composition.

ane) are also formed at temperatures higher than 0°C. Polymerization activity is a function of the alloy composition, and this function has a similar shape to the curve of total activity vs composition (Fig. 7).

Some preliminary results on hydrogenation of cyclopropane were also obtained. In contrast to Ni catalysts, the reaction proceeds here as a pure hydrogenation. Only at temperatures higher than 300°C are methane and ethane formed. However, the main features of the effect of alloying on the catalytic activity are very similar for both Pd-Au and Ni-Cu alloys. The activity passes through a maximum and the activation energy decreases monotonically. These facts indicate that the increase of activity observed with the Ni–Cu system is not due only to suppressing the competition of hydrogenolysis.

DISCUSSION

The discussion will be subdivided into two sections, dealing, respectively, with the mechanism of acetylene hydrogenation and the effects of alloying.

Acetylene Hydrogenation

Numerous papers and reviews (*1*, *10*, *11*) are available on this subject. However, most of the results were obtained by experiments in a closed static apparatus and, therefore, transient phenomena such as the formation of the EA II-ethane could not be observed in the previous work.

The EA II-ethane can be formed from gaseous ethylene, but only if acetylene is also present in the gas phase. This EA II-ethane appears in the temperature range where the physical adsorption of acetylene is possible (sublimation point of acetylene is −83.6°C). The retention time of acetylene is not dependent on the temperature of the reactor, but the apparent retention time of EA II-ethane is temperature dependent. Ethylene can be displaced from the surface by acetylene or carbon monoxide (*12*). These are the relevant facts on the formation of EA II-ethane.

Before proceeding on this point we should mention that it is known for several reactions, such as hydrogen–deuterium exchange (*14–16*), ethylene and cyclopropane hydrogenations (*13*, *17*, *18*), and others, that at a given temperature a part of the layer formed by the chemisorption of the reaction components is unreactive and the reaction is limited to the "working surface," the extent of which is a function of temperature. It is therefore reasonable to expect that also in acetylene hydrogenation a part of the adsorbed acetylene species is effectively unreactive at low temperatures.

We have attempted to combine the phenomena mentioned in the last two paragraphs into the following picture.

At low temperatures three forms (at least) of the adsorbed acetylene exist—namely, reactive chemisorption, unreactive chemisorption (accompanied probably by dissociation of C–H bonds), and physical adsorption. Due to its more extensive physical adsorption, acetylene moves through the catalytic bed more slowly than ethane or ethylene. Part of the adsorbed species (these species may arise from either acetylene or ethylene) would not react at low temperature but can be activated for the reaction by the chemisorption of acetylene from the delayed physisorbed pool. This part appears as the EA II peak, because when the strongly adsorbed species do react, they react through to the formation of ethane. At higher temperatures less acetylene is physisorbed, the working surface is larger, the delay of acetylene behind other gases is less pronounced, and so the difference between the adsorbed species reacting directly and those reacting after activation by acetylene disappears. Then, only one ethane peak appears.

The selectivity S_E for ethylene formation passes through a maximum, as a function of temperature, for Pd, and all three alloys studied. The decrease on the low-temperature side coincides with the appearance of EA II-ethane, which is probably responsible for the decrease.

For many metals [Pt, Ru, Rh, Os, Ir (*1*, *10*, *11*)] the selectivity increases with increasing temperature in the range 20–200°C. However, for pure Pd a temperature-independent selectivity was found (*10*) at p_{H_2} = 200 Torr and $p_{C_2H_2}$ = 50 Torr. If we compare data at some other pressures [see Ref. (*30*), Fig. 5], we can also see a decrease of S_E (at given pressure) with increasing temperature. The apparent difference between Pd and other metals as far as the temperature dependence is concerned could indicate that the rate-determining steps are different, at low and high temperatures or with different metals.

The selectivity of Pd in the conversion of acetylene is high. In the most interesting temperature range in this paper it is always about 90%. It means that the complicating factors, such as the existence of two parallel or consecutive reactions leading to ethane and ethylene, respectively, and the appearance of the EA II-ethane, do not influence substantially the discussion on the effects of alloying in the activity of Pd–Au catalysts.

Catalytic Effects of Alloying

A comparison between the two systems (i) Ni–Cu and (ii) Pd–Ag or Pd–Au is essential for the discussion; therefore, the most important information on these systems will be summarized first.

(1) It is common for both systems that the metal more active for the reaction studied is diluted in a matrix of a much less active metal. Dilution in the surface is even stronger than in the bulk because of the accumulation of the component with a lower sublimation heat (surface energy) in the surface of the equilibrated alloys. With nickel at temperatures when two phases are in equilibrium, the copper-rich alloy forms the surface.

(2) It is common for both systems that alloying leads to a decrease of the heat of adsorption of gases—that is, most probably, to a decrease in the chemisorption bond strengths. This has been found experimentally for hydrogen and Ni–Cu (*19*) and carbon monoxide and Pd–Ag (*20*), but on the grounds of the Tanaka–Tamaru rules (*36*) it is reasonable to assume that this holds for other gases and bonds as well.

(3) Both systems differ, however, strongly in the way in which the population of Pd or Ni *d*-orbitals varies upon alloying. While *no* changes are observable in the Ni–Cu system (*21, 22*) in Pd alloys, Pd is forced by Au to redistribute its own *s* and *d* electrons and the alloy with about 50% Au has already Pd in its free atom structure ($4d^{10}5s^0$) (*23, 24*). Let us now see if this is also reflected by the catalytic behavior of alloys.

First, consider the reactions of hexane. We observe with Pd–Au alloys an increase in parameters S and M_f, the same phenomenon as with Ni–Cu alloys. There is only one remarkable difference—namely that, while with Ni alloys the selectivity S increased mainly due to isomerization to 2-methylpentane, with Pd alloys the formation of methylcyclopentane was also important for this increase. Otherwise, there are no signs of a special role played by the differences in the *occupation* of the Pd *d* orbitals in hexane conversion. However, it must be said immediately that the mere dilution of the active in the inactive component is also insufficient to explain all the data; also among Ni–Cu alloys which reveal the same number of active sites as determined by hydrogen adsorption, the parameters S and M_f vary.[1]

Secondly, let us compare in this paper the results obtained on acetylene hydrogenation with the results on several hydrogenations on Ni–Cu and Pd–Au alloys. It has been found for various reactions, such as hydrogenation of acetylene on Pd–Au alloys (this paper), hydrogenation of acetylene on Ni–Cu at higher temperatures (*25*), hydrogenation of methylacetylene on Ni–Cu alloys (*26*), hydrogenation of cyclopropane on Pd–Au alloys (this paper), and on Ni–Cu alloys (*6*), hydrogenation of cyclopentene on Pd–Ag (*32*), that the *activity* as a function of composition *passes through a maximum.* Hydrogenation of benzene seems to be more complicated. According to the method of preparation of the catalysts and the temperature of the measurements, either a monotonic decrease [Pd–Au (*35*), Ni–Cu (*31* (low T), *33*)] or a function with a shallow maximum [Pd–Au (*32*), Ni–Cu (*31* (high T), *34*)] is found. Hydrogenolysis of hexane (and of other hydrocarbons as well) is *always inhibited* by the *alloying* with a Group Ib metal. Again, similar results are obtained with both systems, Ni–Cu and Pd–Au, and also the contrast between H_2 addition and hydrogenolysis is common to both alloy systems.

Because these two systems are so similar in a number of important catalytic features, but substantially differing in the *occupation* of *d* orbitals, we conclude that the degree of occupation of orbitals alone cannot be responsible for the catalytic behavior of these alloys.

The absolute values of the apparent activation energy E_a as determined in previous papers by means of static apparatus or, in this paper, by a pulse reactor may be subject to criticism. Nevertheless, if we dare to make this step and we compare results for E_a on Ni–Cu and Pd–Au alloys, we

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[1] *Note Added in Proof:* Recent results obtained in our laboratory by Mrs. Stephan (will be published in *J. Catal.*) revealed that this variation could be due to the variations in the size of the ensembles of active sites, at almost constant total number of active sites.

observe the following interesting behavior. With Ni–Cu alloys the activation energy varies with composition, in spite of the number of *d* holes at Ni atoms remaining constant. With Pd–Au alloys the more pronounced variation in the apparent activation energy sets in when Pd *d* holes have already been filled (>40% Au). Also, these facts strengthen our belief in the statement put forward in the foregoing paragraph.

However, this statement does not exclude a role of the other electronic factor, the changes in *position* of the electronic energy levels (ligand effect). These changes are probably similar for both systems (Ni–Cu, Pd–Au), and we may expect that they will mainly manifest themselves in the bond strength of chemisorption. The theory is unable to predict exactly and in detail what consequence it should have for catalysis. However, some correlations between bond strength and activity are experimentally well established [see Ref. (*1*) for a review] for pure metals and they can be helpful with alloys as well.

As already mentioned in our previous papers (*3*, *6*, *7*), the bond strength of various chemisorption bonds decreases when a transition metal (Pd, Ni) is alloyed with a Group Ib metal. This may have different consequences for different reactions.

For example, if a C–C bond is to be broken (as in the reactions of hexane), two conditions must be fulfilled. First, by splitting off hydrogen from the molecule the C–C bond must be made accessible for the interaction with the metal. The surface must have a sufficient number of free sites for such dissociative adsorption to be able to bind all fragments and to "park" the hydrogen splitoff. Secondly, the bond strength of the metal–carbon bonds must be high enough to make the reaction thermodynamically possible. By alloying, both conditions are negatively influenced in both alloy systems in question. As we have already mentioned, active sites are diluted and the bond strengths decreased for both alloys.

However, the decrease in bond strengths may have a positive influence on other reactions, say, hydrogenation of acetylene or cyclopropane, as also found in this paper. Among the Group VI–VIIIc metals the activity in hydrogenation is inversely proportional to the bond strengths (*1*) and this tendency is likely to be responsible for the increase of activity before the maximum is reached (and in similar, other functions) in Fig. 4. This can be due either to the increase in the "intrinsic" hydrogenation activity or to the elimination or "softening" of the side reactions leading to self-poisoning.

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