Pd₁Ni₉₉ and Pd₅Ni₉₅: Pd Surface Segregation and Reactivity for the Hydrogenation of 1,3-Butadiene

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The combined use of low-energy ion-scattering and angular X-ray photoemission spectroscopy experiments permitted determination of the surface concentration and the concentration depth profile of Pd₁Ni₉₉ and Pd₅Ni₉₅ alloys equilibrated at 870 K. There was evidence that the outermost surface is largely enriched in Pd: the Pd surface compositions of Pd₁Ni₉₉ and Pd₅Ni₉₅ were found to be as large as 20 and 50 at.%, respectively. Such results fit well with the predictions based on a recently developed thermodynamic model. Reactivity of both alloys towards 1,3-butadiene hydrogenation was also measured (at 300 K and under an excess of hydrogen pressure). The activity of Pd₁Ni₉₉ (5×10^{15} molecules cm^{-2} s^{-1}) was found to be of the same order of magnitude as for (111) and (110) Pd single-crystal faces. Furthermore, a strong exaltation was observed for Pd₅Ni₉₅ (30×10^{15} molecules cm^{-2}s^{-1}), the selectivity in butenes being always about unity. The results are discussed in terms of geometric and/or electronic effects. A definition of the "active site" is proposed: the active site may involve a group of Pd atoms (probably two or a little more), but not mixed sites constituted of Pd and Ni atoms. These Pd atoms are found to be electronically modified by surrounding Ni atoms. © 1994 Academic Press, Inc.

I. INTRODUCTION

Bimetallic catalysts are of great interest for a variety of commercial processes. An understanding of the physical and chemical properties of the surfaces of such materials is needed to determine the "active site" for catalytic reactions. It implies a good knowledge of the surface composition and structure, both at the very top layer and in the underlayers near the surface since properties of the outermost surface may be changed by the chemical nature of the elements located just below (1–3).

Surface segregation of bimetallic alloys opens the way to a new generation of catalysts with "tuned" surfaces, highly concentrated in the active component for a given reaction, even for low concentration bulk alloys. This segregation effect can be at first qualitatively predicted using simple thermodynamic considerations concerning the surface tensions, the enthalpy of mixing, and the atomic radii of both components. In Pd$_x$Ni$_{1-x}$ dilute alloys, Pd, which has a lower surface tension than Ni as well as a larger atomic radius, will tend to be expelled out of the Ni matrix leading to a strong Pd surface segregation (4, 5). Such an effect has been observed on PdFe alloys (6, 7), for which we proposed an approach describing rather well the concentration equilibrium between the first and second layers. We are now developing a more sophisticated thermodynamic segregation model based on the broken bond theory and taking into account the variation of composition in several layers. It appears to be applicable to a large number of binary alloys, even nondilute ones (8).

Pd and Pt are known to be good catalysts for many hydrogenation reactions. In the case of the 1,3-butadiene hydrogenation, which is an important example of industrial catalysis, the practical problem is to purify the C₄-olefin fraction containing 0.5–1% residual butadiene. The C₄-olefin yield (1-butene + 2-butenes) must be close to 100%. In fact, a very good selectivity for the partially hydrogenated product is obtained with the Pd catalyst, while a Pt catalyst gives a higher amount of completely saturated molecules (9, 10).

The aim of associating Pd with a transition metal such as Ni may be not only to concentrate (by segregation effect) the noble and costly metal of catalytic interest at the surface, but also to improve the catalytic properties with respect to those of the pure metal (11) for the studied reaction (by a modification of the electronic environment of Pd, geometric or diluting effects, and so on).

In this paper, Section II deals with the methods and equipment used for the surface characterization and the reactivity measurements. Section III refers to the experimental determination of the surface composition of two Pd$_x$Ni$_{1-x}$ polycrystalline dilute samples ($x = 1$ and 5 at.%), equilibrated at 870 K, by low-energy ion scattering spectroscopy (LEIS or ISS) and X-ray photoemission spectroscopy (XPS). LEIS was expected to give precise informa-

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tion on the concentration at the top layer only. Combining LEIS and XPS measurements (performed at different angles with respect to the surface) allows us to deduce a possible depth profile. In this section the reactivity tests performed on both samples for the 1,3-butadiene hydrogenation reaction are also collected. From the study of both the catalytic reactivity and the electronic properties (measured by XPS) of the annealed alloys, a definition of the "active site" is proposed in Section IV. It should be noted that, throughout the paper, mainly the figures concerning Pd_1Ni_{99} will be exhibited, unless it seems necessary for a better understanding to display those dealing with Pd_5Ni_{95}.

II. EXPERIMENTAL

Pd_1Ni_{99} and Pd_5Ni_{95} binary alloys have been prepared by melting the high purity components (99.99 + %) in a cold crucible heated in an inert atmosphere in an induction furnace. This yielded cylindrical bars 9 mm in diameter. The nominal compositions, as checked by chemical analysis, were respectively 1 and 5 ± 0.02 Pd at.%. The bars were cut into disc-shaped samples of about 1 mm thickness and then they were mechanically polished up to 1 μm.

The experiments were performed in two separate UHV instruments. The clean surface was obtained by repeated cycles of Ar^+ ion bombardment (4 keV energy) and heating at 870 K.

The LEIS and XPS experiments were carried out in an ESCALAB 200R machine from Fisons Instruments, including a hemispherical analyzer, with a working pressure less than 3 × 10^{-10} mbar. The catalytic tests were achieved in a homemade UHV system equipped with an Auger electron spectrometer, for the checking of the surface, coupled with a static reactor working up to near atmospheric pressure.

LEIS analyses were performed with 1 keV $^4He^+$ ions. The scattering angle was 142°. The primary beam intensity was 5 nA, focused to an impact spot of about 1 mm in diameter. Reference samples used for the calibration of the LEIS signals were Pd and Ni single crystals of (100) orientation; they exhibit atomic densities in the first layer of 1.32 and 1.61 × 10^{15} atoms cm^{-2}, respectively. The spectra did not reveal the presence of any impurity. The relative sensitivity factor for Pd to Ni, S_{Pd}/S_{Ni}, deduced from the areas of the LEIS peaks, was found to be 2.3.

XPS measurements were performed using the Al–Mg dual anode. The Al anode was used for the quantitative analysis. The pass energy of the electron analyzer was 50 eV and the angle of the photoelectrons with respect to the plane of the surface, Θ, was varied from 25 to 90°. In addition, the Mg anode and a pass energy of 20 eV were chosen for the study of the electronic properties of the annealed alloys. In this latter case, the resolution of the spectrometer was better than 0.1 eV.

For both LEIS and XPS measurements, the entrance angle of the spectrometer was limited to 15° (except for quantitative angular XPS measurements: 10°).

The catalytic measurements were performed in a separate UHV system fully described in Ref. (12). The samples were cleaned by successive cycles of Ar^+ ion bombardment followed by annealing at 870 K; their surfaces were checked by Auger electron spectroscopy. The samples could be transferred into the 73 cm^3 reactor under UHV conditions. The 1,3-butadiene hydrogenation reaction was performed at room temperature in static conditions, with a large excess of hydrogen. The reaction mixture was prepared separately in a large volume cell and introduced through a valve; the composition of the reaction mixture was analyzed by mass spectroscopy with periodic sampling through a leak valve.

III. RESULTS

III.1. LEIS Data for the Characterization of the Top Layer

The main advantage of the LEIS technique is that it gives a quantitative information on the first layer only. Hence the Pd concentration of the outermost surface of the considered alloys can be determined if one assumes that:

(i) the chemical environment does not affect the sensitivity factor of the two considered elements, as is generally assumed (13).

(ii) the surface is sufficiently close packed and randomly oriented with respect to the direction of the incident and analyzed beams to imply that the second layer does not contribute to the signal. This was checked by small angle X-ray diffraction experiments, which revealed no preferential orientation of both samples in the surface region (14).

(iii) the sputtering effects are negligible. Indeed, the spectra were recorded within a few seconds and with a very low incident ion current density (5 nA/mm^2).

Figure 1 displays a typical LEIS spectrum of Pd_1Ni_{99} equilibrated at 870 K. Two peaks are observed at 783 and 874 eV, corresponding to ions backscattered by Ni and Pd surface atoms, respectively. No impurities were detected other than very slight amounts of O and S expected at 401 and 638 eV, respectively. The low background level at low kinetic energy also attested to the cleanliness of the sample. The simple comparison of the LEIS peaks measured on both the alloy surface before and after annealing implied a striking Pd enrichment in the outer layer of the alloys due to the thermal treatment. Indeed, taking into account the higher sensitivity factor for Pd to Ni (S_{Pd}/S_{Ni} = 2.3), the Pd concentration was found to reach 20 and 50 at.% for the Pd_1Ni_{99} and Pd_5Ni_{95} alloys, respectively. These results corroborate the studies of Mervyn *et al.* on Pd_1Ni_{99}(15)(see
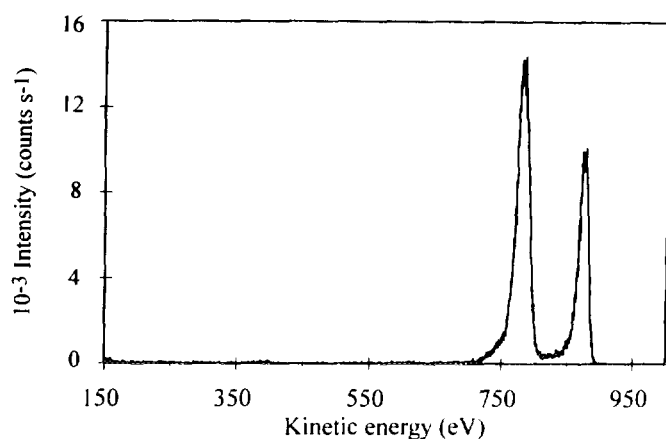
FIG. 1. LEIS spectrum of Pd_1Ni_{99} equilibrated at 870 K. The primary ions were $^4He^+$ with 1 keV kinetic energy. The incident current was 5 nA over about 1 mm².

also Ref (16) for a compilation of experimental binary alloy surface segregation studies).

III.2. XPS Data

III.2.a. Quantitative analysis. Figure 2 displays XPS spectra of Ni $2p$ and Pd $3d$ core levels corresponding to the Pd_1Ni_{99} sample. The peak areas were calculated after a nonlinear background subtraction by integrating the signal between 880 and 845 eV for the Ni $2p$ core level photoemission peak (respectively, between 350 and 330 eV for the Pd $3d$ one) on the binding energy scale. The Shirley-type background (17) is also represented in Fig. 2.

The determination of the surface concentrations of the alloys by XPS needs a good knowledge of certain factors. Among these is the transmission factor of the spectrometer which depends on several experimental variables besides the kinetic energy of the electrons (E_k) and the pass energy used (E_p) (18). In order to obtain an accurate value of this parameter in our experimental conditions and for the characteristic peaks of Pd and Ni, we used pure Pd and pure Ni as standard materials. These standards were available as they were necessary for LEIS quantification. Indeed, the ratio of the transmission factors of Pd $3d$ and Ni $2p$ photoemission peaks was deduced from the quantitative analysis of the standards (Pd and Ni of (100) orientation) as

$$\frac{A_{Pd(100)}}{A_{Ni(100)}} = \frac{N_{Pd(100)} \cdot \sigma_{Pd3d} \cdot T_{Pd3d}}{N_{Ni(100)} \cdot \sigma_{Ni2p} \cdot T_{Ni2p}}$$

$$\times \frac{\sum\limits_{n=0}^{\infty} \exp(-n \cdot d_{Pd(100)}/\lambda_{Pd3d} \cdot \sin \theta))}{\sum\limits_{n=0}^{\infty} \exp(-n \cdot d_{Ni(100)}/\lambda_{Ni2p} \cdot \sin \theta))}, \quad [1]$$

where $A_{Pd(100)}$ and $A_{Ni(100)}$ are the photoemission peak areas of Pd $3d$ and Ni $2p$ core levels of Pd(100) and Ni(100), respectively. $N_{Pd(100)}$ and $N_{Ni(100)}$ are the surface atomic densities of both standards, σ and T, the Scofield photoemission cross-section (19) and the transmission factor of the analyzer, respectively. λ represents the inelastic mean free path and d represents the interplanar distance. The exit angle, Θ, was chosen equal to 90°.

Equation [1] leads to

$$\frac{\sigma_{Ni2p} \cdot T_{Ni2p}}{\sigma_{Pd3d} \cdot T_{Pd3d}} = \frac{A_{Ni(100)} \cdot N_{Pd(100)}}{A_{Pd(100)} \cdot N_{Ni(100)}}$$

$$\times \frac{1 - \exp(-d_{Ni(100)}/\lambda_{Ni2p})}{1 - \exp(-d_{Pd(100)}/\lambda_{Pd3d})} \quad [2]$$

Taking into account that $\lambda_{Pd3d} = 18$ Å, $\lambda_{Ni2p} = 11$ Å (20), $N_{Pd(100)} = 1.32 \times 10^{15}$ atoms cm^{-2}, $N_{Ni(100)} = 1.61 \times 10^{15}$ atoms cm^{-2}, we found a "$\sigma \cdot T$" ratio: $\frac{\sigma_{Ni2p} \cdot T_{Ni2p}}{\sigma_{Pd3d} \cdot T_{Pd3d}} = 2.16$. This leads to a transmission factor ratio T_{Pd3d}/T_{Ni2p} of 0.64 considering the Scofield photoemission cross-sections ($\sigma_{Pd3d} = 16.04$ barns, $\sigma_{Ni2p} = 22.18$ barns (19)).
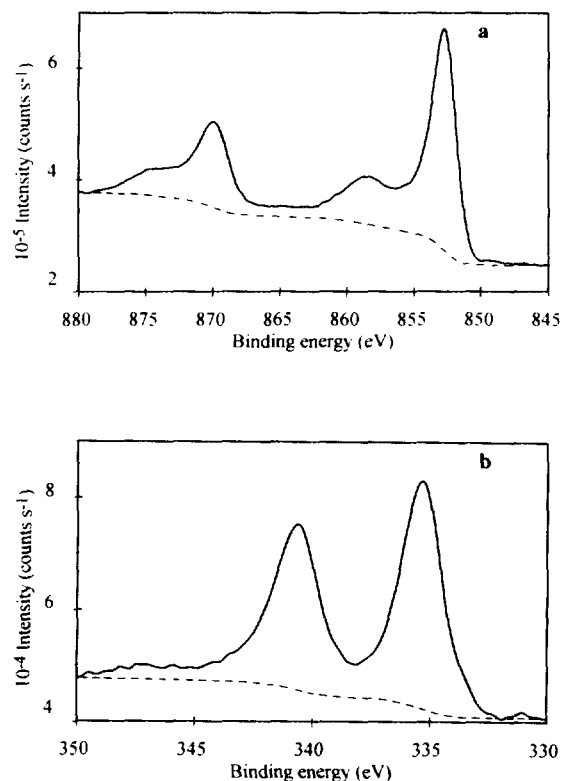

FIG. 2. XPS spectra of (a) Ni $2p$ and (b) Pd $3d$ for Pd_1Ni_{99} after annealing, at an exit angle with respect to the surface $\Theta = 25°$. The photon energy was 1486.6 eV (Al$K\alpha$ line) and the entrance angle of the spectrometer was 10°. The dashed lines represent the nonlinear background subtracted for area calculation (17).
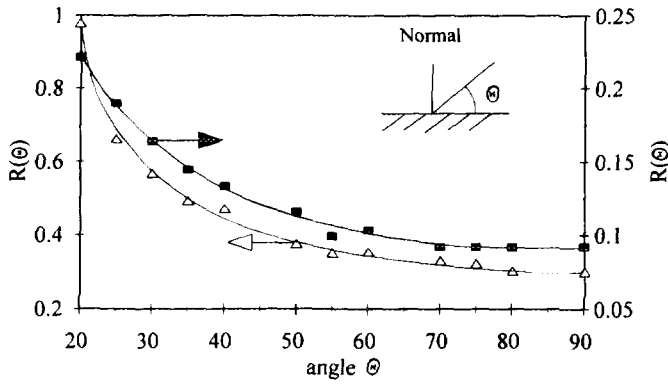
FIG. 3. $R(\Theta)$ ratio as defined by Eq. [3], after XPS measurements, at different exit angles Θ. Experimental results for (■) Pd_1Ni_{99} and for (△) Pd_5Ni_{95}. (—) Best fit deduced from matching $R(\Theta)$ with R_1/R_2, as described in Section III.2.a.

XPS data analyses of both samples at an exit angle of 90° give a mean Pd concentration on several layers. With a $\sigma \cdot T$ ratio of 2.16, it was found 3 and 9 at.% in the surface region for Pd_1Ni_{99} and Pd_5Ni_{95}, respectively.

Now looking at the angular variation of the $R(\Theta)$ ratio defined as

$$R(\Theta) = \frac{A_{Pd3d}}{A_{Ni2p}} \times \frac{\sigma_{Ni2p} \cdot T_{Ni2p}}{\sigma_{Pd3d} \cdot T_{Pd3d}} \qquad [3]$$

and reported in Fig. 3 for both samples, one can clearly see that $R(\theta)$ increases when θ decreases. This indicates again that Pd segregates to the surface.

In order to obtain a quantitative depth profile, we try to fit the XPS results with a very simple model, whose variables are X_1, X_2, and X_3, concentrations in the first, second, and third layers supposed equidistant ($d_{12} = d_{23} = 2$ Å), and a k coefficient which represents a depth variation of the concentration when starting from X_3 to reach the nominal bulk concentration X_b. As just mentioned, the results are put in the $R(\theta)$ form and we try to match $R(\Theta)$ with the R_1/R_2 ratio defined as

$$\frac{R_1}{R_2} = \frac{\displaystyle\int_0^2 X_1 \cdot \exp(-z/A)dz + \int_2^4 X_2 \cdot \exp(-z/A)dz + \int_4^6 X_3 \cdot \exp(-z/A)dz + \int_6^\infty X \cdot exp(-z/A)dz}{\displaystyle\int_0^2 (1 - X_1) \cdot \exp(-z/B)dz + \int_2^4 (1 - X_2) \cdot \exp(-z/B)dz + \int_4^6 (1 - X_3) \cdot \exp(-z/B)dz + \int_6^\infty (1 - X) \cdot \exp(-z/B)dz}$$

[4]

with $A = \lambda_{Pd} \cdot \sin \Theta$, $B = \lambda_{Ni} \cdot \sin \Theta$, and $X = X_b + (X_3 - X_b) \cdot \exp(-k(z - 6))$.

Because of the rather large values of λ, even at low exit angles, the depth resolution is not sufficient to allow one possible profile only. On the contrary, different triplets (X_1, X_2, X_3) give satisfactory fits. In Fig. 4, for each sample, two types of profile giving the best fits are displayed. It can be concluded that a great Pd enrichment is observed, either in the first plane only or in the first two planes. This enrichment does not seem to extend beyond the second layer. The profiles represented in white in Fig. 4 lead to concentration values in the outer layers quite similar to those measured by LEIS; however, it appears that the steepest profiles (shaded in Fig. 4) correspond to too high values of X_1.

It is now interesting to compare the profiles deduced from LEIS and XPS data for both samples with those calculated with the theoretical model we have recently developed (8). Figure 5 exhibits the Pd theoretical concentration of the first plane versus the Pd bulk concentration, at a temperature $T = 800$ K, for two types of faces: (111) and (100). One can clearly see that a strong segregation of Pd is expected on PdNi alloys, especially for low Pd

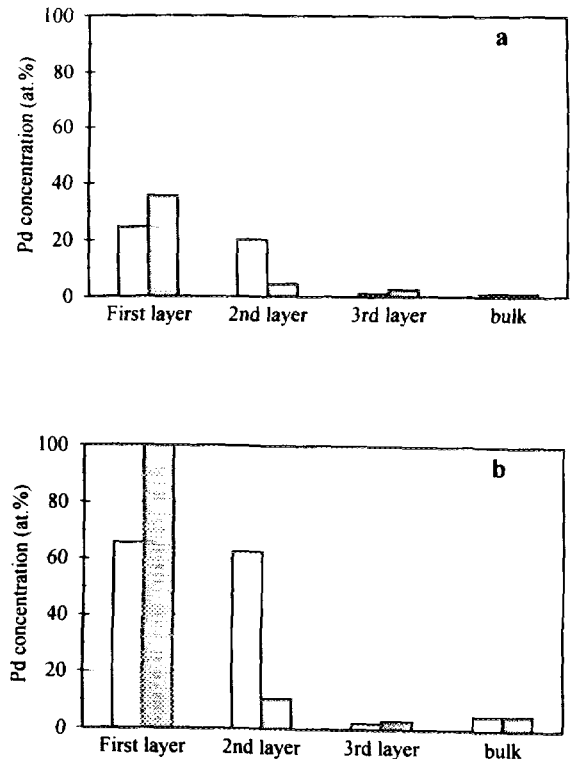FIG. 4. Depth profiles corresponding to the $R(\Theta)$ fitting curves shown in Fig. 3 in the case of the (a) Pd_1Ni_{99} and (b) Pd_5Ni_{95} alloys. Depth is given with respect to the surface. Distances between adjacent layers are taken equal to 2 Å. In white and shaded areas: two extreme fits among the best fits.
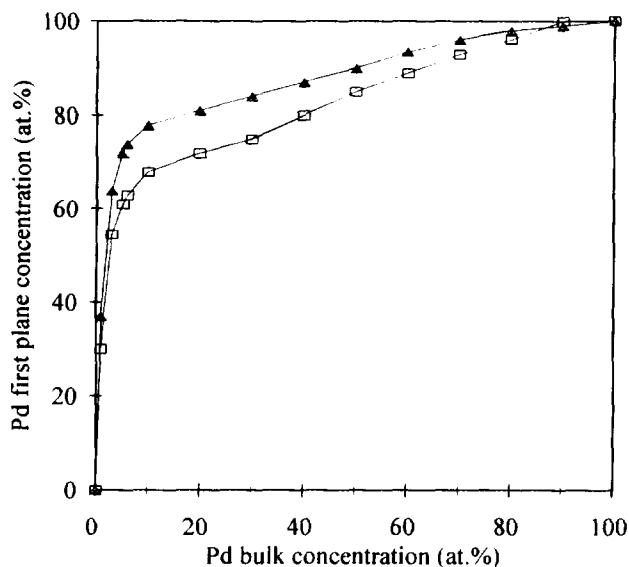
FIG. 5. First plane Pd theoretical concentration versus Pd bulk concentration for Pd_xNi_{1-x} alloys (□) (111) and (▲) (100) oriented, at 800 K, obtained with a recently developed thermodynamic model (8).

contents. This result is in agreement with the experimental values deduced from LEIS measurements. The calculated Pd concentration in the first plane will be enhanced if we pull down the temperature. Hence it is important to know exactly the quenching temperature of the samples. The surface equilibration by annealing needs a temperature high enough to allow the diffusion of atoms: segregation is first governed by the kinetics. When diffusion is allowed, atoms rearrange themselves in the surface according to the thermodynamics. For $T = 870$ K, surface equilibration arises in a rather short time since many experiments, performed for several lengths of time of annealing (2, 5, and 10 min), always gave the same first layer concentration value. Therefore, the quenching temperature of the samples must be situated below 870 K. However, since the cooling is relatively rapid during our experiments and since the diffusion becomes difficult with decreasing temperature, it seems reasonable to assume a quenching temperature of the alloys above 700 K. In order to calculate depth profiles, we took into account in our calculations a five-layered surface. For both samples, the profiles at 800 K were found to be gradually diminishing to finally reach the nominal concentration in the fifth layer (8). The agreement seems rather satisfactory between the experimental and theoretical approaches. Nevertheless, one can note that the in-depth resolution is within the limits of the XPS technique for a precise determination of the layer-by-layer composition.

III.2.b. Electronic properties. In order to focus attention on the chemical shift of the core levels related to the

Pd surface atoms, we analyzed carefully the energetic positions and line shapes of the Pd $3d_{5/2}$ signals recorded using the $MgK\alpha$ line and a low pass energy for the analyzer (i.e., with a high resolution). The results relative to the Pd_1Ni_{99} sample are reported in Fig. 6. We did not report the data relative to the Ni $2p$ core level because the shifts are nearly equal to zero. Indeed, in the surface region Ni is always strongly preponderant. As the measurements integrate many subsurface layers, it was not possible to extract the Ni surface contribution.

A precise analysis of the shape of the Pd $3d_{5/2}$ line of the annealed alloy (see Fig. 6a) revealed a larger full width at half maximum (FWHM) than that observed on pure Pd. This feature can be associated either:

(i) to an increase of the asymmetry of the line, due to the alloying effect, or (ii) to the presence of two
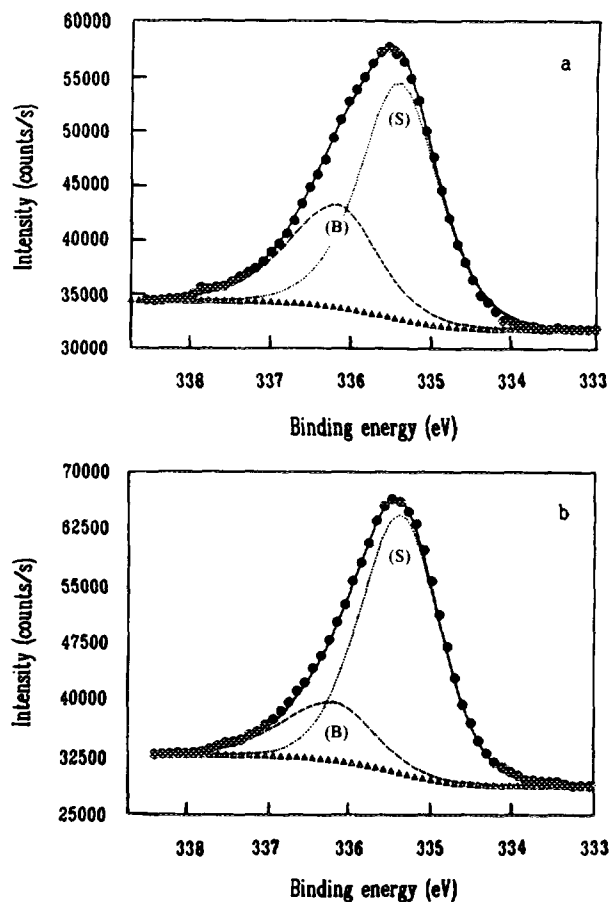

FIG. 6. XPS spectra of the Pd $3d_{5/2}$ core level for the Pd_1Ni_{99} sample after equilibration at 870 K at two exit angles Θ: (a) 90° and (b) 30°. The peaks are split up into two contributions: one for bulk (B) (—) and one for surface (S) (···). The photon energy was 1253.6 eV ($MgK\alpha$ line) and the entrance angle was 15°. The nonlinear background is also represented (▲).

335.3 eV
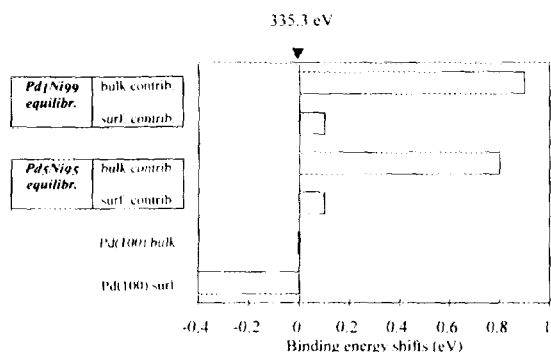

FIG. 7. Pd $3d_{5/2}$ XPS binding energy shifts with respect to the energy for pure bulk Pd. The shift of the surface Pd(100) results from the study of Andersen *et al.* (26). The Pd $3d_{5/2}$ line of the alloys, equilibrated at 870 K, was split up into two contributions (see text), one for *surface* and one for *bulk*. The shifts corresponding to the bulk contribution were also obtained by the direct XPS study of the samples before annealing.

ion of the following two effects: first, in our equilibrated systems, the Pd surface concentration is far above the bulk one; second, core levels of Pd atoms located at the surface are expected to shift with respect to the bulk Pd atom ones. Both effects lead to a lower binding energy for the core levels of the Pd atoms concentrated at the surface (21–25).

The same considerations suit the Pd_5Ni_{95} alloy sample; the core level energy shift values are given in Fig. 7. For reference, we report the surface versus bulk core level shift for pure Pd(100), i.e., 0.4 eV (26).

Referring to the energy of pure bulk Pd (335.3 eV), the upwards shifts found for bulk Pd atoms of Pd_1Ni_{99} and Pd_5Ni_{95} alloys, 0.9 ± 0.1 eV and 0.8 ± 0.1 eV, respectively, are in good agreement with values calculated by Steiner and Hüfner on the basis of a Born–Haber scheme (21).

contributions in the line: the first one is relative to *bulk* Pd atoms (very diluted in the Ni matrix and therefore making a weak contribution to the XPS Pd signal) and the second one is relative to *surface* atoms (making an important contribution since segregation is very strong). It has to be noticed that for pure Pd the bulk contribution always largely stands out in the XPS spectrum.

In fact, we are inclined to interpret our results with the second explanation for the following two reasons:

(i) the line shape of the Pd $3d_{5/2}$ peak of a sputtered Pd_1Ni_{99} alloy (exhibiting no segregation) is almost the same as the one recorded on pure Pd. The alloying effect only induces a 0.9-eV upward shift.

(ii) the FWHM of the Pd $3d_{5/2}$ peak of the segregated alloy decreases when the analysis is performed at more grazing angle, i.e., when the signal associated with the Pd *bulk* atoms decreases with respect to the signal of Pd *surface* atoms (see Figs. 6a and 6b). In any case, for the segregated alloys, the contribution of *surface* atoms is always largely dominating the Pd $3d_{5/2}$ photoemission peak.

As a matter of fact, we split this peak into the two just-mentioned contributions, assuming that the depth concentration profile of the annealed alloys is quite steep as described in Section III.2.a. As we can see from Fig. 6, there is a "surface contribution" (S) largely dominating at 335.4 eV, whereas the less important "bulk contribution" (B) is located about 0.8 eV upwards (value close to that measured for the nonequilibrated alloy with low Pd content). The shift observed between surface and bulk contributions is due to the superposit-

FIG. 8. Partial pressure variations of (□) 1,3-butadiene, (▲) butenes, and (×) butane versus time in the case of: (a) Pd_1Ni_{99} and (b) Pd_5Ni_{95} alloys after equilibration at 870 K. Experimental conditions: (a) Hydrogen pressure = 35 Torr; 1,3-butadiene pressure = 3.5 Torr; T = 300 K. (b) Hydrogen pressure = 18 Torr; 1,3-butadiene pressure = 3.6 Torr; T = 300 K. The areas of both samples are about 0.64 cm^2.

TABLE 1

Catalytic Reactivity for the 1,3-Butadiene Hydrogenation of Pd_1Ni_{99} and Pd_5Ni_{95} after Equilibration at 870 K, as Compared to Pure Pd(111), Pd(100), and Ni(111)

Sample	Pd at.% at Surface	Activity ($\times 10^{15}$ molecules cm^{-2} s^{-1})	Selectivity into butenes
Pd_1Ni_{99}	20	5.0	1
Pd_1Ni_{95}	50	30	1
Pd(111)	100	1.5	1
Pd(110)	100	7.1	1
Ni(111)	0	0.3	1

Note. The values are given for $T = 300$ K, $P_{H_2} = 35$ Torr, $P_{H_2}/P_{HC} \approx 10$, assuming a first order with respect to hydrogen and a zero order with respect to butadiene.
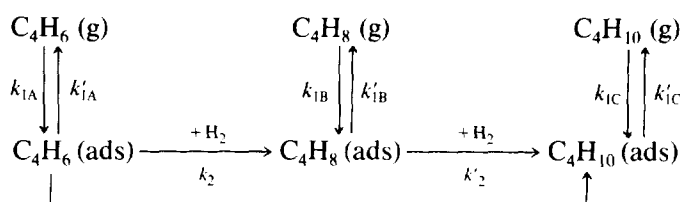
III.3. Reactivity

In Figs. 8a and 8b the variations of the 1,3-butadiene, butenes, and butane partial pressures, versus time, for the 1,3-butadiene hydrogenation reaction over the annealed Pd_1Ni_{99} and Pd_5Ni_{95} samples are reported. One has to specify that the reaction on the Pd_5Ni_{95} sample has been performed with a mixture poorer in hydrogen (18 Torr instead of 35 Torr); indeed, the activity of this last sample is so large that the conversion of butadiene into butenes was too rapid under 35 Torr H_2 and 3.5 Torr hydrocarbon to allow a relevant mesurement of the rate of the reaction. For both alloys it was found that, up to a quasi-complete conversion of butadiene, only butenes were formed. However, the detection by mass spectrometry did not allow the determination of the proportions of C_4H_8 isomers. It is clear from Figs. 8a and 8b that the decrease of the diene pressure (or the increase of the butenes pressure) is linear versus time. This agrees with a zero order with respect to the butadiene pressure. The activities of both alloys for the conversion of 1,3-butadiene into butenes (first reaction) are summarized in Table 1 and compared with those of pure Pd(111), Pd(110), and Ni(111). It is to be noted that reactions on pure Pd single crystals were performed at a lower hydrogen pressure (5 Torr) in order to avoid the formation of hydrides which would destroy their structure (9, 27). Ni(111) is only slightly active, whereas pure Pd exhibits a strong activity, especially the (110) face (9). For both studied alloys, a first order with respect to hydrogen has been assumed, as in the case of pure Pd (28, 29). One can clearly see a strong similarity between activities of the Pd_1Ni_{99} system and pure Pd, whereas the Pd_5Ni_{95} system is found to be largely more active. An important fact to be underlined is that the activity of both alloys is not proportional to the surface Pd concentration if we compare it to pure Pd.

Whatever the sample, Pd_1Ni_{99} or Pd_5Ni_{95}, the second hydrogenation (butenes → butane) was proceeding with a velocity quite similar to that of the primary reaction (1,3-butadiene → butenes), see Figs. 8a and 8b. On pure Pd, it was already found that the rate for consecutive hydrogenation of butenes was of the same order of magnitude as the "selective" (i.e., first) hydrogenation (9, 28). This leads us to conclude that the rate for the transformation of butenes into butane is higher on the Pd_5Ni_{95} alloy surface as compared with pure Pd. This behaviour will be discussed in the following section.

IV. DISCUSSION

We will now try to understand why the activity of Pd (the active metal) is improved when associated with Ni (the less active metal), the selectivity in butenes remaining always about unity up to a quasi-complete 1,3-butadiene conversion. As has been generally demonstrated (10, 30–32), this reaction proceeds according to a "rake" scheme, involving the following successive steps:

$$C_4H_6 \text{ (g)} \qquad\qquad C_4H_8 \text{ (g)} \qquad\qquad C_4H_{10} \text{ (g)}$$

$$\big\downarrow k_{1A} \big\uparrow k'_{1A} \qquad \big\downarrow k_{1B} \big\uparrow k'_{1B} \qquad \big\downarrow k_{1C} \big\uparrow k'_{1C}$$

$$C_4H_6 \text{ (ads)} \xrightarrow[k_2]{+H_2} C_4H_8 \text{ (ads)} \xrightarrow[k'_2]{+H_2} C_4H_{10} \text{ (ads)}$$

Here k_{1A} (k'_{1A}), k_{1B} (k'_{1B}), and k_{1C} (k'_{1C}) are the adsorption (desorption) constants of the butadiene, butenes and butane, respectively. k_2 and k'_2 are the hydrogenation rate constants of butadiene and butenes, respectively. k_{1C} is generally found to be close to zero and the direct hydrogenation of butadiene into butane is also generally considered to be negligible (32, 33).

As we said previously and according to this mechanism, a rough analysis of the curves in Fig. 8 shows that k_2 has the same order of magnitude as k'_2. Therefore, the very good selectivity in butenes would be the consequence of the difference between the adsorption coefficients of butadiene and butenes, as demonstrated in Ref. (9) (k_{1A}/k'_{1A}) $\gg$ (k_{1B}/k'_{1B}). This has been explained by the fact that, on Pd, the butadiene is thought to be adsorbed via the two double bonds, while butene adsorption would involve only its one double bond (34). Hence butadiene should be more strongly adsorbed (about twice as strong) than butenes. This is not the case for some other metals, such as Pt, for which the selectivity into butenes is less (10). In view of this, we will further consider a butadiene bonding implying two centers.

How can we explain the synergetic effect of Pd and Ni on the activity? In these conditions of pressure and temperature (low temperature = 300 K and low hydrogen

pressure), the adsorption of the hydrocarbon should be strong (order zero with respect to the butadiene) and the hydrogen coverage (supposed completely dissociated) would be low (order one with respect to H_2).

How does (if it does!) the association of Pd with Ni affect the adsorption of the reagents?

First, no different in the isosteric heats of adsorption of H_2 on Pd(111) (35) and Ni(111) (36) has been found (similar adsorption energies and sticking coefficients). One can think, in a first step, that adsorption of hydrogen is not responsible for the activity increase.

Considering that the adsorption of butadiene takes place on two adjacent atoms (34), three basic assumptions can be proposed regarding the chemical nature of atoms included in the active site:

(i) Ni atoms only.
(ii) Both Pd and Ni atoms.
(iii) Pd atoms only.

Let us investigate the three possibilities.

(i) Ni is only very slightly active towards 1,3-butadiene hydrogenation, as compared to Pd (see Table 1). Therefore, the sites involving only Ni surface atoms should not play a major role. Consequently, the "active site" would inevitably involve Pd surface atoms.

(ii) The possible action of mixed sites is clarified by the statistical counting of Pd–Pd and Pd–Ni bonds at the surface of completely disordered systems. Indeed, in the quasi-chemical approach (37), it is found that the number of Pd–Ni bonds is multiplied by a factor 1.56 when increasing the Pd coverage at the outermost surface from 20 to 50 at.%. Having in mind the fact that the activity increases by a factor 6 between both considered surface concentrations, such mixed sites seem very unlikely. We will therefore consider sites consisting of Pd pairs.

(iii) With the assumption of a random distribution of Pd and Ni atoms at the surface, and a coupling of butadiene with two adjacent Pd surface atoms, one can expect an increase of Pd pairs (i.e., of active sites) more rapid than a linear variation with the Pd concentration; in fact, the number of Pd–Pd bonds is multiplied by 6.25 when the Pd surface coverage increases from 20 to 50 at.%, a value which has to be compared to the increase of the activity by a factor 6.

However, such a consideration is not sufficient to explain the larger activity of the Pd_5Ni_{95} system with respect to pure Pd. Consequently, one has to consider in addition that the adsorption site would be made up of Pd pairs modified by surrounding Ni atoms. The presence of some facets with peculiar orientations, at the surface of the polycrystalline alloys and/or an induced corrugation of the surface due, for example, to strains appearing when

the Pd enriched alloy is formed, could explain the higher activity of some PdNi alloys. However, it has been shown that on a two-dimensional PdNi alloy (produced by a 0.5 monolayer Pd deposit on Ni(111) followed by a moderate heating), exhibiting a (1 × 1) LEED pattern, the activity increase for the considered reaction with respect to pure Pd is about the same as the one measured on the Pd_5Ni_{95} sample (38). We are inclined to think that purely geometric perturbations are not sufficient to justify this activity increase.

An alternative way to explain the higher activity of the Pd_5Ni_{95} alloy surface with respect to that of pure Pd is to consider a "positive" electronic influence of the surrounding Ni atoms on the Pd pairs with constitute the active site at the surface. Such an electronic influence is shown in Fig. 7, which displays the binding energy shifts of the Pd $3d_{5/2}$ line calibrated with respect to the Fermi level. Indeed, an upward shift of about 0.5 eV of the core level of *alloyed* Pd surface atoms with respect to *pure* Pd surface atoms is measured. A possible justification of the increase in the binding energy by alloying could be a charge transfer from Pd towards. However, this hypothesis seems to be very simplistic. Moreover, it does not agree with calculations of Baetzold (39), nor with the respective positions of the Fermi levels of Pd (−5.3 eV) and Ni (−4.9 eV) extrapolated from Ref. (40) assuming rectangular *d*-bands, nor with the work functions determined by the photoelectric experiments of Demuth (41) for Pd(111) (5.6 eV) and Baker *et al.* (42) for Ni(111) (5.35 eV), nor with the electronegativities of Pauling (2.2 for Pd and 1.8 for Ni). The following approach, as suggested in Refs (43) and (44), appears more realistic: an electronic conversion from localized 4d states to diffuse 5s states of Pd would lead to a decrease of the repulsive Coulomb interaction between core and valence electrons, and consequently to an increase of the Pd core level binding energies. Following this idea, the role of Ni could be to redistribute the *s* or *d* electrons of Pd close to the Fermi level. (Electronic modifications of Ni, even if they exist, are not visible on XPS spectra because of the large proportion of Ni atoms seen by this technique, both in the first plane and in many planes deeper.) Such electronic modifications of Pd atoms alloyed with Ni are not surprising since it has been shown by Chouteau (45) that for PdNi alloys above 2.2 at.% Ni, giant moment ferromagnetism appears, which would be the consequence of an increase of the density of states of Pd near the Fermi level.

This would probably imply a modification of the bond strength between the Pd and the diene, which would be responsible for the observed increase of activity. Such a modification could also be invoked to explain the same increase of activity observed for the hydrogenation of butenes. Indeed, if di–π bonding for 1,3-butadiene and π bonding for butenes are accepted, as already proposed

for pure Pd (34), one expects about the same behaviour for the conversion of either butadiene into butenes or butenes into butane. Complementary techniques, such as TDS, vibrational HREELS, or IR, are now needed to determine with precision the mode of adsorption of each type of molecule on these surfaces.

According to this discussion, it is proposed that two effects are associated in the case of the PdNi system: a *diluting* and an *electronic* effect. The active site would consist of Pd pairs (or of small groups of Pd atoms); their number increases more rapidly than the Pd coverage, the Ni atoms acting as "diluting agents"; these pairs are electronically modified in such a way that the catalyst becomes better performing for the 1,3-butadiene hydrogenation reaction.

CONCLUSION

Pd was found to segregate to a large extent on Pd_1Ni_{99} and Pd_5Ni_{95} alloys. After annealing and stabilizing at 870 K, the external Pd concentration reaches values as large as 20 and 50 at.%, respectively. On both solids, the Pd segregation was found to display quite steep concentration profiles, as concluded from angular XPS measurements. The study of activities towards 1,3-butadiene hydrogenation revealed that the alloys are either equivalent or more active than pure Pd, the selectivities in butenes always remaining very close to unity.

The catalytic behaviour of the alloys inclines us to propose an "active site" made up of small ensembles of Pd atoms (two or a little more Pd surface atoms), electronically modified by the surrounding Ni atoms. Indeed, XPS measurements revealed upwards shifts for the annealed alloys with respect to pure Pd, probably resulting from a modification of the hybridization of Pd and Ni valence levels. This electronic modification would act in such a way that the active site be largely more active than the same site located in a pure Pd matrix.

Other additional experimental and theoretical studies have to be performed to confirm our definition of the active site. More precisely, a better knowledge of the local order, of the empty electronic states, and of the adsorption modes of hydrocarbons, seems to be necessary.

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