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Properties of Supported Pd–Ni Catalysts Prepared by Coexchange and Organometallic Chemistry

II. Correlation between the Reactivity for Butadiene Hydrogenation and the Surface Properties Studied by XPS and LEIS

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The preparation and bulk characterization of a series of silica-supported Pd–Ni catalysts obtained either by coexchange or by organometallic chemistry have been described in Part I (J. F. Faudon, F. Senocq, G. Bergeret, B. Moraweck, G. Clugnet, C. Nicot, and A. Renouprez, *J. Catal.* **144, 460 (1993)). The present work describes their catalytic activity in the hydrogenation of 1,3-butadiene, in which palladium is one order of magnitude more active than nickel, in relation with their surface composition measured by LEIS, a powerful physical method, still seldom applied to study the surface of real catalysts. Both types of Pd–Ni catalysts exhibit an activity increasing monotonically with the palladium concentration,** *without any synergy effect***. A more rapid increase of initial activity with the concentration is, however, observed for the catalysts with organometallic precursors than for those prepared by exchange. This difference is explained by the migration of palladium from the bulk to the surface of the particles, shown by XPS and LEIS measurements, which is more pronounced on the large particles of the catalysts prepared by organometallic chemistry. Indeed, the theoretical predictions for bulk alloys, based on thermodynamic calculations but corrected for the effect of particle size, are in agreement with the LEIS results and do conclude to more enrichment on large particles. Compared to nickel, the Pd–Ni alloys undergo less deactivation. A larger proportion of 1-butene and** *trans***-2-butene is formed on the alloys than on pure nickel. This variation of selectivity is explained by the presence on nickel of a** *strongly adsorbed* **di-σ metallocyclobutene intermediate coexisting with the di-π adsorbed form of the diene normally present on palladium. This strongly adsorbed species can also explain the low activity of nickel and its large deactivation.**

INTRODUCTION

In the previous paper (1), the preparation and bulk characterization of two types of silica supported Pd–Ni catalysts were described. The first type was obtained by reacting nickelocene with a prereduced Pd supported on silica; they will be considered below as being obtained by an organometallic route. The second family was prepared by coexchange with nickel nitrate and tetramminepalladium hydroxide. The present work tries to establish a correlation between the reactivity of these catalysts in a simple test reaction, the hydrogenation of 1,3-butadiene (in which palladium is one order of magnitude more active than nickel), and their composition.

In many cases, the variation of reactivity with the composition of bimetallic catalysts is not a simple additivity of the reactivities of the two elements. For example, in the case of alumina supported Pt–Ni catalysts (2), a synergy between the two metals occurs for well-defined compositions, leading to an exaltation of reactivity for the isomerization of neopentane. It was concluded on the basis of a Pt $L_{\mathrm{II}}/L_{\mathrm{III}}$ edges study that a modification of the electronic structure of platinum had occurred, promoting the adsorption of neopentane. On our Pd–Ni catalysts, an XPS study of the core levels binding energies was thus carried out for both elements, in order to establish a possible correlation between the activity variations and shifts of the binding energies.

Undoubtedly, a clear conclusion can only be drawn if the composition of the surface has also been determined. In a previous work on the same bimetallic system (3), but which was equilibrated at high temperature, 1200 K, it was shown that in the exchange and isomerization of 1-butene, the signature of palladium was observed down to a concentration of 10%. Only for an atomic Pd concentration as low as 4%, did the selectivity approach that of nickel. It was concluded from XPS studies that a strong surface segregation of palladium could explain the reactivity of these catalysts. In the present case, the composition of the surface has been determined both by XPS and low energy ion scattering (LEIS), this last technique being specially well adapted to determine the composition of the topmost surface layer.

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EXPERIMENTAL

Materials

The preparation and characterization of these two types of catalysts was extensively described in Ref. (1). To obtain the catalysts by the organometallic way, a silica (Aerosil 200) supported monometallic Pd catalyst was first prepared by exchange of $Pd(NH_3)_4(OH)_2$ in an ammonia solution. The catalyst was dried at 370 K, calcined at 740 K, and reduced in flowing hydrogen at 510 K. A solution of biscyclopentadienyl-nickel (nickelocene) in amylacetate was then added to this Pd catalyst. A grafting reaction by exchange between the C_5H_5 ligands and H atoms adsorbed at the surface of the Pd particles was then carried out. It was easily achieved by flowing hydrogen at 390 K during 4 h in the suspension. Analytical microscopy showed that the nickel complex is almost entirely fixed on the Pd particles. It was also shown by X-ray diffraction that homogeneous alloys are obtained by heating these bimetallic samples at 720 K in flowing hydrogen.

The second family of catalysts was prepared by coexchange on the same silica, starting from an ammonia solution of the same Pd precursor and of nickel nitrate. The activation steps include a drying at 370 K, a calcination at 740 K, and a reduction at 840 K.

Analytical microscopy showed that the bimetallic particles of the samples prepared by grafting the nickel on palladium have a more uniform composition than those obtained by exchange but have a larger diameter. All the characteristics of these catalysts are gathered in Table 1.

TABLE 1

Description of the Catalysts Prepared Either by Coexchange or from Organometallic Precursors

Preparation mode and Pd at.% concentration	Reduction temperature (K)	Mean diameter (nm)	Dispersion[a] (%)
Ni/SiO_2	870	3.4[b]	31
Coexchanged 7%	840	3.5[b]	30
Coexchanged 13%	840	2.8[b]	37
Coexchanged 21%	840	2.8[b]	37
Coexchanged 53%	840	1.9[b]	56
Coexchanged 71%	840	3.1[b]	35
Organometallic 9%	820	8[c]	14
Organometallic 21%	820	7[c]	16
Organometallic 41%	820	7[c]	16
Organometallic 58%	820	6[c]	20
Organometallic 79%	820	6[c]	20
Organometallic 88%	820	7[c]	16
Pd/SiO_2	670	1.9[b]	58

[a] Calculated for spherical particles of fcc structure assuming equal proportions of the (100), (110), and (111) planes on the surface.

[b] Measured by SAXS.

[c] Measured from the (111) diffraction linewidth.

The total metal concentration lies between 2.5 and 5.1 wt%.

Catalytic Activity

The study of the hydrogenation of 1,3-butadiene was carried out at low conversion (10%), which is well suited for kinetic studies. It was performed in a gas flow microreactor between 270 and 300 K, at atmospheric pressure and followed by gas chromatography using a flame ionization detector. The column (1/8 in., stainless steel) is made of 0.19% picric acid on graphpac. The flows were controlled with a Brooks flow gauge. The hydrogen pressure was limited to 3 kPa, the hydrocarbon pressure to 1.5 kPa, and the total flow rate was varied between 5 and 10 liters/h. It was checked that the reaction was not controlled by mass or heat transfer since the conversion was always proportional to the mass of the catalyst or to the inverse of the flow. The initial rate of butadiene conversion, A_0, is not easy to determine. In this work, it was obtained by extrapolating to zero time the first 10 activity determinations (performed every 15 min) adjusted to a third or fourth degree polynomial. The activity after stabilization, A_S, was measured after 5 h. Three selectivities are defined: S_0, the total butenes selectivity, S_1, the fraction of 1-butene among the butenes, and S_2, the fraction of *trans*-2-butene among the 2-butenes. Before the catalytic studies, the catalysts were retreated in the reactor in flowing hydrogen at 720 K for 2 h. It should be mentioned that high purity reactants have to be used; traces of oxygen during the pretreatment considerably modify the reactivity, probably by inducing a migration of the nickel to the surface. A study at 50% conversion was also performed to mimic practical conditions and to follow the catalysts deactivation. In this case the pressure of hydrogen was increased to 13.5 kPa (butadiene 5.5 kPa, helium carrier 85 kPa, total flow rate 2 to 5 liters/h) and the temperature of reaction varied between 300 and 340 K.

Low Energy Ion Scattering and XPS

The X-ray photoelectron spectroscopy (XPS) and LEIS experiments were performed with an ESCALAB 200R (Fisons Instruments) with a base pressure lower than 3×10^{-10} mbar. The samples were pretreated at 820 and 920 K under flowing hydrogen in a reaction chamber and transferred via a UHV case to the spectrometer. The XPS analysis was performed with an Al X-ray source ($K\alpha = 1486.6$ eV). The bandpass energy of the hemispherical analyzer was 50 eV, and the collection angle of the photoelectrons with respect to the plane of the surface was 90°. The binding energies were calibrated with respect to the SiO_2 support as standard (Si 2*p* at 103.4 eV). The concentration ratio of two elements A and B in the first layers is given by the classical expression

$$X_A/X_B = (A_A/A_B)\,(\sigma_B/\sigma_A)\,(T_B/T_A)\,(\lambda_B/\lambda_A), \qquad [1]$$

where A is the photoemission peak area, σ is the Scofield photoemission cross section, T is the transmission coefficient of the analyzer, and λ is the mean free path of the photoelectrons.

LEIS is known to be sensitive to the outermost layer (4). The principle of the method is based on the energy analysis of impinging rare gas ions (of energy E_0) which undergo collisions on the atoms of the surface. The energy E_1 of the back-scattered ions measured at the scattering angle θ leads to the determination of the mass of the target atoms. The LEIS experiments were performed with 1 keV ^{4}He ions. A compensation for charge effects on the support was achieved by a flood gun. A useful signal is obtained before 1% of the top layer has been removed by the inevitable sputtering. The ratio of the energies of the scattered and incident ions, E_1/E_0, is related to γ, the ratio of the mass of the surface atoms and incident ions, and to the scattering angle θ, in the present case 142°:

$$(E_1/E_0)^{1/2} = [\cos\theta + (\gamma^2 - \sin^2\theta)^{1/2}]/(1+\gamma). \quad [2]$$

The surface atoms can thus be identified. For a quantitative analysis of the surface composition, one has to take into account the cross-sections of the various surface atoms. A calibration with Pd(100) and Ni(100) single crystal faces, which have a known number of atoms per surface area, was thus carried out (5). A sensitivity factor $S_{\mathrm{Pd/Ni}} = 2.3$ was derived and the concentration ratio can be expressed with respect to the areas A of the peaks located at 775 and 865 eV, corresponding respectively to Ni and Pd:

$$C_{\mathrm{Ni}}/C_{\mathrm{Pd}} = (A_{\mathrm{Ni}}/A_{\mathrm{Pd}})\, S_{\mathrm{Pd/Ni}}. \quad [3]$$

To avoid the possible sputtering of the atoms of the first layer by the He ions *during the measurement*, the beam flux was set to a low value, 50 nA/mm^2, which is sufficient to reach a good statistics ($N^{1/2}/N \approx 10\%$), within 1 min. At the beginning of the analysis both signals can increase by elimination of a pollution layer. One can obtain qualitative information on the composition of underlying layers by ion etching upon increasing the time of measurement. Their accuracy is limited by disrupting effects such as recoil implantations and cascade mixing occurring simultaneously with the sputtering on the time scale of a few picoseconds.

Thermodynamic Predictions of the Surface Composition

Many theoretical studies have been devoted in recent years to the prediction of segregation in binary alloys. A good review of the recent methods and results can be found in the book by Dowben and Miller (6). When only a knowledge of the surface composition is needed, macroscopic models based on simple thermodynamic considerations generally lead to a good agreement with the experiments.

One of these approaches, the "broken bond model" has been well described by Williams and Nason (7) for example. In this model, the energy of the system is written as a sum of pair interactions between nearest neighbors and the composition of several surface layers are allowed to differ from that of the bulk. The determination of the surface concentration in the first layers is based on the minimization of the total free energy of the system. But this approach has some serious weaknesses. First of all, the bond energies are calculated for a fixed bulk concentration and are not reevaluated when changes in concentration occur in the surface layers. Secondly, when bonds are removed in the outermost layer, it is well known that the remaining bonds are reinforced. This is not taken into account in the model described above or at the very best only empirically. So, to obtain more reliable predictions, mainly for systems undergoing large surface segregation, we have developed a model using the concept of equivalent medium approximation (EMA) which allows us to calculate *concentration-dependent* pair interaction (8). Bond strength modifications at surfaces are taken into account through an empirically modified tight binding scheme in the second moment approximation (MTB) (9, 10), using the thermodynamic data of pure metals and alloys. We have been able to predict semiquantitatively the composition of the five topmost layers of a series of palladium based alloys, by minimizing the total free energy of the system $G = H - TS$ (8–10). A set of differential equations,

$$(\partial G_{\mathrm{Surf.}}/\partial X_i) - (\partial G_{\mathrm{Bulk}}/\partial X_{\mathrm{Bulk}}) = 0, \quad [4]$$

is resolved, where X_i is the actual concentration of the ith layer.

These calculations are valid for bulk alloys. For small particles, which have a large fraction of the atoms at the surface, the reservoir of diffusing atoms is limited by the total concentration of palladium. One has thus to correct the surface concentration determined above, by the mass balance conservation expression

$$X_{\mathrm{N}} = DX_{\mathrm{S}} + (1-D)\, X_{\mathrm{B}}, \quad [5]$$

where X_{S} and X_{B} are the unknown surface and bulk concentrations. X_{N} is the nominal concentration measured by chemical analysis, and D is the dispersion determined by the physical methods. For a given set of X_{N} and D, the actual X_{S} is determined as shown in Fig. 5, at the intersection of the straight line corresponding to Eq. [5], $X_{\mathrm{S}} = X_{\mathrm{N}}/D + [(D-1)/D]X_{\mathrm{B}}$, with the theoretical curve representing the surface composition of a bulk alloy as a function of its nominal composition determined by chemical analysis.

RESULTS

Reactivity of the Catalysts Prepared by Coexchange

The initial activity of pure palladium at 10% conversion is one order of magnitude larger than that of nickel and the

TABLE 2

Reactivity at 10% Conversion of the Bimetallic Catalysts Prepared by Coexchange (Reaction Temperature 270–300 K)

Reduction temperature (K)	Pd concentration (at.%)		TOF (s^{-1})	A_0/A_S	S_0 (%)	S_1 (%)	S_2 (%)
	Nominal[a]	Surface[b]					
870	0	0	0.55	15	25	30	55
840	7	28	0.40	5.0	40	45	70
840	13	34	0.60	3.0	60	43	73
840	21	53	1.0	1.8	80	41	72
840	53	76	2.7	1.8	88	40	75
840	71	91	5.6	2.7	84	35	72
720	100	100	5.4	3.4	90	44	72

Note. A_0/A_S, ratio of the initial rate of butadiene conversion to the rate after stabilization. S_0, total butenes selectivity; S_1, fraction of 1-butene among the butenes; S_2, fraction of *trans*-2-butenes among the 2-butenes.

[a] From chemical analysis by atomic absorption.

[b] Predicted by theory for a temperature of equilibration of 820 K.

deactivation is also less pronounced as shown by the ratio A_0/A_S (Table 2). For palladium, the selectivity for butenes formation is higher and equal amounts of 1- and 2-butenes are produced (S_1 is close to 50%). These supported catalysts have an activity per unit of surface area comparable with those of Ni and Pd single crystal faces. But if the Ni(111) face is 10 times less active than the Pd(111), like the supported catalysts, they are both 100% selective for the formation of butenes and, moreover, undergo little deactivation (11).

The results of the activity measurements concerning all the catalysts prepared by coexchange are gathered in Table 2. On these alloys, like on pure nickel, the deactivation also takes place, but with a considerably reduced amplitude, whatever their composition. Another point is the increase of the selectivity for butenes and of the proportion of 1-butene (shown by S_1) as soon as Pd is alloyed with Ni. This difference of selectivity on Ni on one side and on Pd and the alloys on the other side is a first indication that the reactivity of the alloys is mainly governed by palladium.

At 50% conversion, on pure Ni, as can be seen in Fig. 1a, the TOF for the conversion of butadiene decreases steeply with time. Simultaneously, the proportion of butenes among the products increases from 25 to 100%. Comparatively, the deactivation is much slower on the alloy containing 53 at.% Pd as shown in Fig. 1b.

Reactivity of the Catalysts Prepared by Organometallic Chemistry

As already mentioned (1), these catalysts are composed of larger particles than those prepared by coexchange but with a more uniform composition. Homogeneous alloys are observed after reduction at 720 K in hydrogen. Surprisingly, after the reduction, these catalysts appeared to be totally inactive. This can be attributed either to a contamination by the amylacetate solvent used to dissolve the nickelocene or to remaining organic residues arising from an incomplete decomposition of the Ni precursor. It was thus necessary to calcine these samples in oxygen for 2 h at 720 K to clean their surfaces. As can be seen in Fig. 2a (solid line), after this treatment, only NiO and PdO are identified on the diffraction diagram. A further reduction in H_2 at 620 K reduces the oxides (Fig. 2a, dashed line). A final treatment at 770 K under H_2 (Fig. 2b, solid line), leads to an alloy with Bragg lines which have a width and a position identical to those of the starting material. It was also verified by analytical electron microscopy that none of the two metals has migrated onto the support. The remarkable point is that no substantial particle diameter increase has occurred during these treatments.

To determine the influence of the reduction temperature on the reactivity, measurements have also been performed on samples reduced at 820 and 920 K. The position of the Bragg lines of the diffraction patterns shows that the bulk composition undergoes minor modifications but heating may induce a modification of the surface composition. Figure 2b (dashed line), corresponding to the sample heated at 920 K, shows a slight narrowing of the diffraction lines compared to those of the sample heated at 770 K (Fig. 2b, solid line). As electron microscopy did not reveal

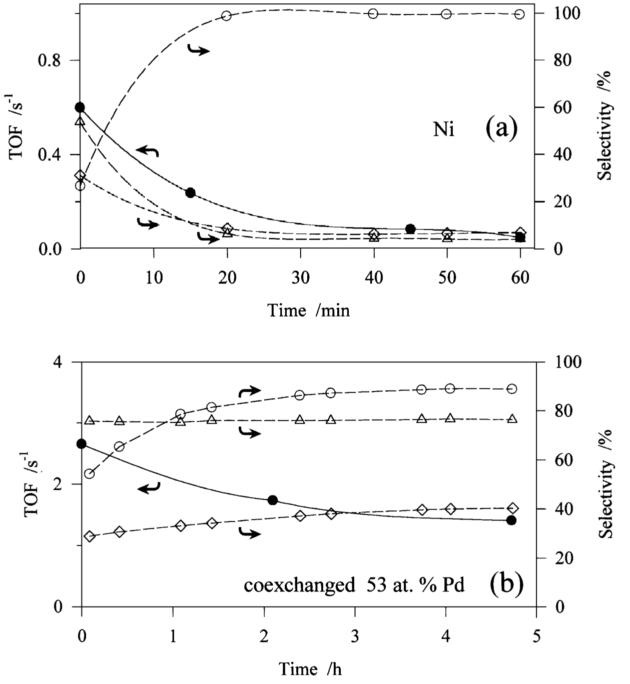

FIG. 1. Variation of the activity (solid circles) and of the selectivities (open symbols: ○, S_0; ◇, S_1; and Δ, S_2) with the time of reaction measured at 50% initial conversion (reaction temperature 300–340 K): (a) for the pure Ni and (b) for the 53 at.% Pd coexchanged catalysts.

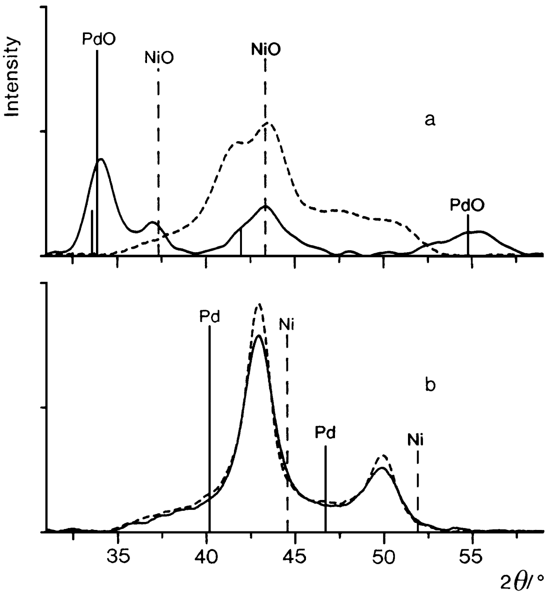

FIG. 2. X-ray patterns observed during the cleaning procedure for the organometallic 41 at.% Pd catalyst: (a) after flowing with O_2 at 720 K (solid line) and after treatment under H_2 at 620 K (dashed line); (b) patterns measured after treatments under H_2 at 770 K (solid line) and 920 K (dashed line).

any particle growth, this decrease of width is attributed to an homogenization of the alloy.

As the samples obtained by exchange, these catalysts have a reactivity globally governed by a strong deactivation. Table 3 shows that the *samples reduced at only 770 K* have an activity at 10% conversion comparable to that of pure Ni and little dependent on the composition. After a further treatment of 4 h at 820 K in H_2, the activity increases. As in the case of the samples of the first family, the selectivities S_0 for the formation of butene and S_1 for the fraction of 1-butene are greatly increased by alloying nickel with 10% palladium. In all cases, the samples reduced at 920 K have the highest activity, substantially larger than that of the catalysts obtained by coexchange, for the same mean composition except for high Pd concentration. The successive augmentations of activity upon increasing the reduction temperature are well illustrated by the behavior of the sample containing 41 at.% Pd, whose activity increases 50 times from 0.05 s^{-1} at 770 K to 0.5 at 820 K and 2.3 at 920 K. This suggests that indeed *the surface palladium concentration has been increased by the thermal treatments*. It is thus important to try to establish a correlation between the reactivity and the actual composition of the first layers.

Surface Composition

As explained in Part I (1), X-ray diffraction has shown that alloys are formed when the samples have been heated at 720 K. However, no substantial shifts of the diffraction lines are observed for higher treatment temperatures. Similarly, EXAFS experiments, which were performed above the edges of both elements on the organometallic catalysts, led to the same coordination numbers (CN) around Pd and Ni, ≈10.7. If an appreciable migration of palladium at the surface had taken place, lower CN around this element would have been expected, since surface atoms of dense faces have a CN varying between 7 and 9, compared to 12 for atoms in the bulk. Actually, the precision in the determination of CN is not better than 10% and taking into account the dispersion (16% of the atoms are located at the surface), only a small fraction of the Pd atoms can be concerned by this reduction of CN. Thus *XRD and EXAFS are probably not sensitive enough* to detect a surface enrichment for particles of this diameter. For this reason, XPS and especially LEIS have been used.

The XPS results gathered in Table 4 show that the Pd concentration is larger than the nominal value determined by chemical analysis (CA) for both types of samples. Considering the mean free path of the electrons for the Pd 3*d* and Ni 2*p* levels (respectively, 1.8 and 1.2 nm), and the particle diameters of the sample prepared by coexchange, only 2.8 nm, XPS indicates unexpectedly a high Pd concentration on the surface of the particles compared to the bulk.

TABLE 3

Reactivity at 10% Conversion of the Catalysts Prepared by Organometallic Chemistry (Reaction Temperature 270–300 K)

Reduction temperature (K)	Pd concentration (at.%)		TOF (s^{-1})	A_0/A_S	S_0 (%)	S_1 (%)	S_2 (%)
	Nominal[a]	Surface[b]					
870	0	0	0.55	15	25	30	55
770			0.30		80	53	64
820	9	54	0.45		90	52	82
920			1.0	5.0	92	56	77
770			0.40		99	55	63
820	21	71	0.55		100	60	83
920			1.6	4.0	100	60	78
770			0.05		94	39	63
820	41	80	0.50		93	52	82
920			2.3	1.8	99	51	79
820	58	87	1.3	2.0	99	60	86
920			2.8				
770			0.30		90	50	80
820	79	96	1.0		93	52	82
920			4.3	3.0	99	57	86
820	88	98	1.2		91	53	83
920			4.6	4.0	100	59	86
720	100	100	5.4	3.4	90	44	72

Note. A_0/A_S, ratio of the initial rate of butadiene conversion to the rate after stabilization. S_0, total butenes selectivity; S_1, fraction of 1-butene among the butenes; S_2, fraction of *trans*-2-butenes among the 2-butenes.

[a] From chemical analysis by atomic absorption.

[b] Predicted by the theory for a temperature of equilibration of 820 K.

TABLE 4

Surface Composition and Binding Energies of Pd $3d_{3/2}$ and Ni $2p_{3/2}$ Transitions Measured by XPS

Preparation mode	Reduction temperature (K)	Pd concentration (at.%) Nominal[a]	Pd concentration (at.%) Surface[b]	Binding energies[c] (eV) Pd $3d_{5/2}$	Binding energies[c] (eV) Ni $2p_{3/2}$
Ni foil		0	0		852.8
Coexchanged	820	21	26	335.1	852.4
Organometallic	820	9	25	335.8	852.3
	920	9	27	335.6	852.3
Organometallic	820	21	35	335.3	852.4
Organometallic	820	58	70	335.6	852.6
	920	58	70	335.2	852.6
Pd foil		100	100	335.3	

[a] From chemical analysis by atomic absorption.
[b] Measured by XPS.
[c] Calibration with respect to Si $2p$ binding energy at 103.4 eV.

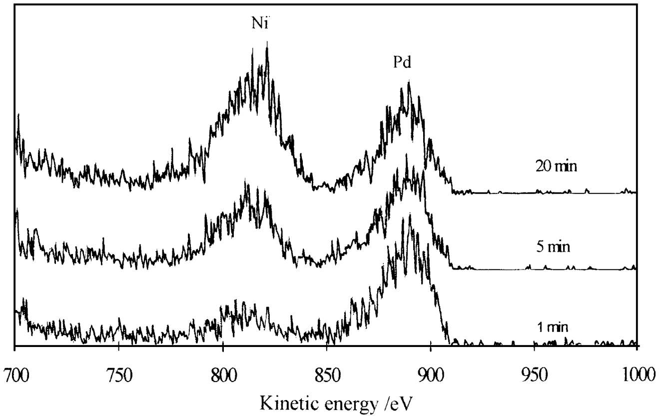

FIG. 3. Typical LEIS spectra measured on the organometallic catalysts (9 at.% Pd) showing the variation of intensities of the peaks corresponding to the two elements, as a function of the time of analysis.

The difference with the CA is amplified in the case of the organometallic samples, either because for particles of a larger diameter, 6–8 nm, the observed photoelectrons are not coming from the core of the particles or because of the mass balance effect which, as explained above, allows a greater increase of the Pd concentration in the first layers for samples composed of large particles.

The core level binding energies for the catalyst obtained by coexchange with 21 at.% Pd and for the organometallic samples with 9, 21, and 58 at.% Pd can be compared in Table 4 with those of the reference materials. Shifts of the order of 0.5 eV to higher energy are observed for the Pd $3d$ level for the organometallic with 9 at.% Pd, in which the largest effect is expected because of large dilution of this metal. Also the Ni $2p_{3/2}$ is shifted by 0.2 to 0.4 eV to lower energy. Thus, even if the structure of the valence bands was not studied here, an effect of the modification of the electronic structure of the metals upon alloying cannot be discarded.

To determine the composition of the first layer, *LEIS experiments* have also been performed. For dense faces, as well as for less compact-like (110) faces, studies on single crystals have shown that this analysis is only sensitive to the first layer. The typical LEIS spectra shown in Fig. 3 for the organometallic 9 at.% Pd sample exhibit strong modifications as a function of the time of analysis. An increase of the signal of both elements, attributed to the elimination of the pollution layer, can be observed during the first minute of analysis. This phenomenon is no longer observed for the sample evacuated in UHV at 800 K during 3 h. When the ion bombardment is carried out up to 30 min, the ratio of the two concentrations is progressively modified by sputtering of the first layers. A comparison between the 9 and 58 at.% Pd catalysts is shown in Fig. 4a and Table 5. The decrease of the Pd concentration after 30 min of analysis is more pronounced for the 9 at.% Pd, indicating that only one or two layers are concerned by the migration of Pd. On the contrary, on the 58 at.% Pd, the Pd-rich layer is certainly thicker since the decrease of the Pd concentration measured by LEIS is only 5% after 30 min.

The effect of the temperature on the kinetics of equilibration of the surface composition is illustrated in Fig. 4b for the 58 at.% Pd sample treated at 820 or 920 K. Not only is the Pd concentration measured in the first moments larger for a treatment at 920 K, but for long etching times, although decreasing, it remains larger than for the catalyst heated at 820 K. The limit reached after a period of ion bombardment of 30 min is still 1.5 to 2 times the concentration determined by chemical analysis (Table 5).

The segregation of palladium measured on these catalysts has indeed also been observed on polycrystalline bulk alloys. Miegge *et al.* (5), studying Pd_5Ni_{95} and Pd_1Ni_{99} polycrystalline alloys by LEIS, found that the Pd concentration in the first layer are, respectively, 50 and 20%. An angular

TABLE 5

Comparison of the Surface Pd Concentration Measured by LEIS and XPS with the Theoretical Predictions for the Catalysts Prepared by the Organometallic Route

Pd at.% (chemical analysis)	Reduction temperature (K)	XPS	LEIS[a] 1 min	LEIS[a] 30 min	Theory
9	820	25	55	20	54
	920	27	60	19	51
21	820[b]	35	63	44	71
58	820	70	79	74	87
	920	70	89	82	84

[a] Measured after 1 and 30 min of sputtering.
[b] 870 K for LEIS measurements.

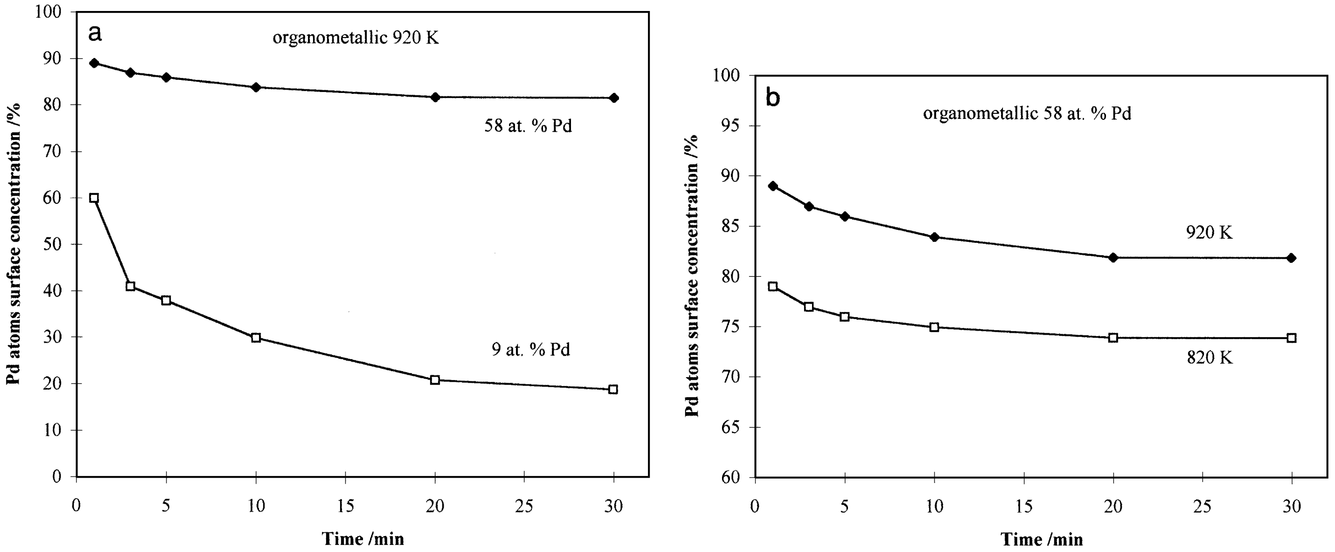

FIG. 4. Palladium surface concentration measured by LEIS as a function of the sputtering time. (a) Organometallic catalysts treated at 920 K: 9 at.% Pd (open squares) and 58 at.% Pd (filled diamonds); (b) comparison between the surface compositions of the 58 at.% Pd treated at 820 K (open squares) and 920 K (filled diamonds).

profile analysis (by modifying the angle of analysis), performed by XPS, states that three layers are concerned by this segregation with still 20 at.% Pd in the second layer, for the Pd_5Ni_{95} alloy. On the Pd_1Ni_{99} diluted alloy, Mervyn *et al.* (12) have found a Pd concentration of 25% in the surface layer. This type of alloy has actually a monotone concentration profile, in contrast with those which form ordered compounds, like Pt–Ni, where oscillating profiles extending over four layers has been observed (13).

To determine the composition of the first layers of the bulk sample of Pd_5Ni_{95} nominal composition, Rousset *et al.* (8) implemented the thermodynamic calculations described above with an optimization of the composition of the five topmost layers. One obtains at 840 K a concentration of 50 and 17%, respectively, for the first and the second layer, the fifth layer reaching the bulk composition. At important point is the temperature dependence of this segregation.

Actually, the surface concentration at equilibrium should vary with the temperature in proportion of $\exp(-\Delta G_{\text{seg}}/RT)$. For a free enthalpy of segregation $\Delta G_{\text{seg}} = -32$ kJ/mol, the increase of surface Pd concentration should be of the order of 10% for equilibration temperatures lowered from 1000 to 800 K. However, a limitation to the migration of palladium is its diffusivity which decreases exponentially with T. This kinetic factor would prevent the equilibrium to be reached below 800 K within several days. This effect explains probably why for a Pd nominal concentration of 58%, the Pd surface concentration is *increasing* between the treatments performed at 820 and 920 K (Fig. 4b and Table 5). A representation of the Pd concentration on the surface of bulk alloys as a function of the nominal concentration is shown in Fig. 5 (continuous curve) for the (111) exposed face and a temperature of equilibration of 820 K.

It is worthwhile to check how these predictions agree with the surface composition determined by ion scattering. In the case of agreement, the surface composition of the

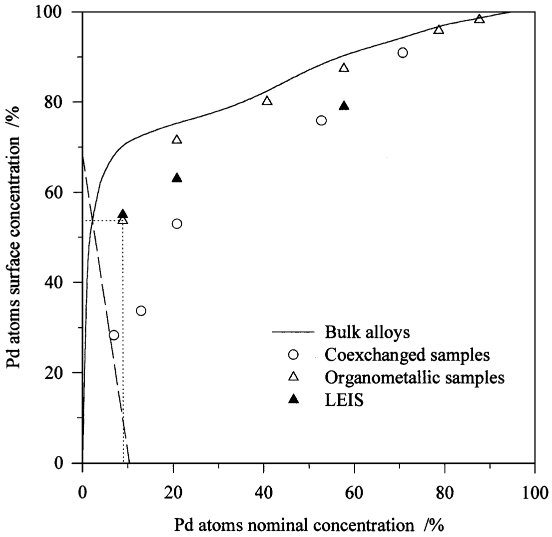

FIG. 5. Theoretical predictions for the palladium surface concentration vs palladium nominal concentration; continuous curve, bulk alloys with a (111) orientation; ○, organometallic catalysts; Δ, coexchanged catalysts. The filled triangles correspond to the experimental points measured by LEIS on the organometallic catalysts. The predicted surface composition for both types of catalysts takes into account the particle size effect. The predicted value, 54 at.% Pd, compared to 9 at.% Pd by CA, is determined by the intersect of the dashed straight line representing Eq. [5] with the continuous curve corresponding to the bulk alloy.

coexchanged catalysts which have not been studied by LEIS can be reasonably predicted. These calculated surface compositions for both series of samples are shown in Fig. 5 (open symbols) where they can be compared with those calculated for the bulk alloy (continuous curve). One can notice that as expected from Eq. [5], *the effect of particle size limits the Pd enrichment of the surface*, especially for the catalysts prepared by coexchange and at low nominal Pd concentration. Figure 5 shows how the actual predicted surface composition for the organometallic with 9 at.% Pd is determined at the intersect of the straight line corresponding to Eq. [5] with the theoretical curve predicting the composition of the surface of the (111) single crystal face. This figure shows that the experimental values of the surface compositions determined by LEIS on the organometallic catalysts (filled triangles) are close to the predicted values. Thus, the predictions for the coexchanged catalysts can be considered as reliable. A final point is that XPS which probes several layers leads to Pd concentrations lower than LEIS (Table 5).

DISCUSSION

The question is to what extent the catalytic activity can be explained by the surface properties described above. The TOF of the two sets of catalysts, reported in Tables 2 and 3, are to be compared both with the nominal and the measured or predicted surface compositions. The major point is that *no synergy effect on the reactivity between the two metals* is observed, the rate increasing regularly with the Pd concentration. This is illustrated by Fig. 6, which shows the initial activities plotted against the *surface* composition. The experimental points are well represented by a third degree polynomial, adjusted to the data points by linear regression. This leads to the idea that, in first approximation, the activity can be proportional to small ensembles of ≈2–3 Pd atoms. A second important feature is the simultaneous increase of the proportion of butenes and the decrease of the deactivation phenomenon with the augmentation of the Pd concentration.

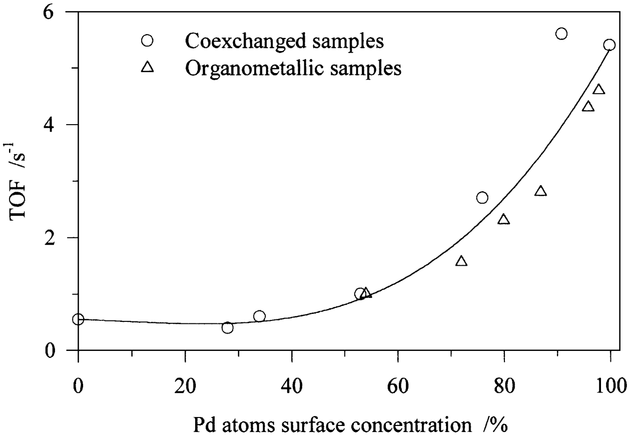

FIG. 6. Initial activities measured at 10% conversion as a function of the Pd surface concentration (reaction temperature 270–300 K).

Concerning the variation of activity with the time of reaction, a large decrease of the deactivation is noted upon increasing the Pd concentration. The ratio A_0/A_S varies from 15 on Ni to 5 on the 7 at.% Pd coexchanged catalyst and 1.8 on 53%. This phenomenon of increase of selectivity and decrease of deactivation is probably related to the preferential migration of Pd atoms on well-defined sites. The same behavior of the Pd–Cu system in this reaction has been recently reported by Furlong *et al.* (14). The authors attribute this effect to a decrease of hydrogen adsorption.

Indeed, the macroscopic method described above to predict the surface concentration cannot describe the *detailed arrangement* of the atoms on the different sites of the surface and the size of the ensembles. For structured surfaces exhibiting steps or for small particles, Monte Carlo methods such as that used by Strohl and King (15) for the Pt–(Cu, Ag, Au) alloys, should be applied. For the Pd–Ni couple, however, the enthalpy of mixing is negligible which *a priori* discards a tendency to clustering of nickel atoms. The ordering of the atoms and the size of the ensembles are thus expected to be simply a function of their probability of presence. The only indication is that the segregating element should exhibit a strong tendency to *first occupy the corner and edge sites which have the lowest coordination numbers*. In the case of the coexchanged catalysts which are typically formed of particles of ≈500 atoms, 40% of the surface atoms are located on the edges or on the corners. So an explanation to the variation of activity with the time of reaction could be the disappearing of "hot" Ni sites replaced by Pd atoms. The carbonaceous layer which is at the origin of the deactivation would be preferentially initiated on these low coordination sites when they are occupied by Ni atoms.

The initial activity of the organometallic catalysts increases more rapidly with the Pd nominal concentration than that of the samples of the second family. This is well explained by their higher Pd surface concentration, for comparable mean concentrations, *because of the particle size effect* mentioned above. This concentration reaches for example already 54 at.% for a Pd nominal concentration of 9 at.% compared to 28 at.% calculated for coexchanged with 7 at.% Pd nominal concentration. One thus understands why the activity of the organometallic with 9 at.% Pd is already comparable to that of the coexchanged containing 21 at.% Pd.

Even if no preferential Pd migration at low coordination sites occurs, the same explanation holds for the selectivity toward butenes which is 90% for organometallic containing 9 at.% Pd, compared to only 40% for the coexchanged with 7 at.% Pd: indeed, for the first sample, palladium covers 54% of the surface whereas only 13% of the superficial atoms are in low coordination positions. Conversely, for the second sample, the predicted Pd surface concentration is 28% with 28% of the surface atoms on corners or edges.

One can now compare the initial activity of these catalysts with the results of Hermann *et al.* (16) who studied a sample prepared by vapor deposition of 0.25 to 3 layers of palladium on a Ni(111) single crystal face. These authors found that, as prepared, without any thermal treatment, one monolayer of Pd is already more active than a Pd(111) face. After annealing at 475 K, the deposit becomes 20 times more active than the Pd(111) surface and 4 times more than the Pd(110). The activity of this layer is close to that of the polycrystalline Pd_5Ni_{95} alloy studied by Miegge *et al.* (5), which contains 50 at.% Pd in the first layer. An important point is also the very mild deactivation of these samples along the successive reaction experiments. Their explanation for the increased activity of the Pd layer on Ni and of the polycrystalline alloy is based on the observation by XPS of a 0.8 eV upward shift of the Pd 3*d* core levels and on extended Hückel calculations. A modification of the electronic structure of palladium by the surrounding Ni atoms would result in a modification of the adsorption strength for the diene. More precisely, electrons located in the d_{z^2} orbital (perpendicular to the metal surface) would be transferred to *s–p* orbitals. This can lead to a modification of energy of the di-π bonding of the diene. The thermal treatment would produce an insertion of the Pd atoms in the first Ni layer and an increase of the coordination of the Pd atoms by Ni first neighbors, increasing the electronic interaction between the two elements. The authors, however, do not explain why a modification of adsorption energy of the hydrocarbon would necessarily increase the reaction rate.

Although the organometallic catalysts also show a shift of the Pd 3*d* levels (0.5 eV for 9 at.% Pd catalyst) compared to pure metal, *none of the alloys has an activity greater than that of palladium*. The variation of the initial activity exhibits an increase with the Pd surface concentration compatible with a di-π bonded butadiene molecule requiring two or three adjacent sites (17).

However, one should keep in mind that in this reaction the rate is of the first order with respect to hydrogen and *of zero order with respect to the hydrocarbon*. This is probably the indication of a large coverage of the surface by butadiene, which has an adsorption energy of 36 kcal/mol (17) compared to 20 kcal/mol for hydrogen. As shown recently by neutron inelastic scattering (18), the reactive form of hydrogen is adsorbed in apical position, these on-top sites being populated at rather high pressure, with a weakly bonded hydrogen. Thus, the rate would not be limited by the chemisorption of the hydrocarbon. Thus, either an increase of the sticking coefficient of hydrogen or preferentially *of its diffusion constant* would readily lead to an increased activity. Thus, we believe that the main difference between the supported samples and the flat surfaces could be attributed to transport phenomena and especially to an easier diffusion of hydrogen on flat surfaces. This effect of modification of the height of the barrier of diffusion for hydrogen on bimetallic compared to pure metal surfaces was indeed predicted by Rochefort *et al.* (19), who used the LGCTO theoretical method.

Concerning the selectivities, Ni-rich like pure Ni-supported catalysts have a poor initial selectivity S_0 for the formation of butenes. Also, more 2-butenes are observed on this catalyst than on Pd or on the alloys, since an increase of S_1 from 25 to 45–50%, as soon as Pd is present on the surface is observed. Indeed, a di-π form which is normally accepted on palladium (17) should clearly lead to a mixture of 1- and 2-butenes. The larger formation of 2-butenes on nickel can be the indication of the presence of a different adsorption intermediate, like a metallocyclobutene.

CONCLUSION

The presence of a large concentration of palladium at the surface of the Pd–Ni alloys, especially, for the large particles of the catalysts prepared by grafting nickel over palladium particles, adequately accounts for the variation of their reactivity with the composition. The limited electronic structure modifications observed by XPS seem to have no influence on the reactivity.

The experimental determination of the surface composition of supported Pd–Ni catalysts confirms the predictions based on simple thermodynamic concepts of palladium migration to the surface. For particles in the 2 to 8 nm diameter range, no size effect on the reactivity has been evidenced, except that due to the limited amount of diffusion element which regulates the composition of the surface.

The deactivation phenomenon takes place more readily on nickel; on alloys, a milder deactivation is well explained by a preferential migration of Pd atoms on low coordination sites, strong sites for the butadiene adsorption when occupied by Ni atoms.

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