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Exchange and Isomerization of But-1-ene on Supported Pd, Ni, and Pd–Ni Alloys

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The catalytic reactions between but-1-ene and deuterium on five Pd–Ni alloy catalysts supported on silica were investigated at 23 and −85°C and compared to supported palladium and nickel catalysts. The hyperfine distribution of monodeuterated but-1-ene was shown to be a specific property of the metals: on palladium the primary vinylic hydrogen atoms are mainly exchanged with deuterium while on nickel the secondary vinylic hydrogen is involved in a proportion of more than 80%. In the alloys, down to 10 atom% palladium concentration, the catalytic properties of palladium are observed; the catalytic behavior of nickel is observed only with a 4 atom% palladium alloy. A surface study with AES and XPS, respectively, on a bulk and supported 4 atom% palladium alloy showed that the palladium surface concentration was near 50%, which is consistent with the catalytic results.

INTRODUCTION

In the past few years the introduction of sophisticated techniques such as microwave spectrometry has shed new light on the catalytic exchange and isomerization of *n*-butenes on transition metals. The classical Horiuti–Polanyi mechanism, which was almost universally considered in the past, proved to be only one among others, the importance of the various mechanisms depending on the metal and on the nature of sites. For example, the rupture of a vinylic carbon–hydrogen bond was found to be responsible for the exchange of but-1-ene on iron and nickel films (*2, 3*) while on palladium films (*4*) the same reaction involved an allylic carbon–hydrogen bond. The isomerization of but-1-ene without the introduction of a deuterium atom in the molecule can be explained by a 1–3 sigmatropic shift (*5*) on Fe (*6*), Ni (*7*), and Pd (*4*) films, and deuterated molecules are formed by a Horiuti–Polanyi mechanism that introduces one deuterium atom in the molecule. The relative importance of these different mechanisms has been related to surface heterogeneity (*8*).

The differences between the mechanisms of the exchange of but-1-ene on nickel and palladium led to large variations of the deuterium distributions. It was therefore tempting to study a mixture of both metals to see whether the result is just an additivity of the properties of the components or whether a different selectivity appears. In this paper we report on a comparison between 10% Pd, Ni, and Pd–Ni alloys supported on silica and a correlation has been made with the surface properties of these alloys.

EXPERIMENTAL

Catalysts. All catalysts were 10% in weight metal on silica Aerosil. In the following the percentages of Ni and Pd will be expressed in terms of total metallic atom content, i.e., without considering the silica. Ni, Pd, and five alloys with 1, 4, 10, 50, and 80 atom% Pd were prepared by impregnating the carrier with solutions of $NiCl_2 \cdot 6H_2O$ and/or $PdCl_2$, drying for 15 h at 70°C in an oven and reducing in a hydrogen flow

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for 15 h at high temperature (typically 950°C). Before each run, the catalyst was reduced overnight by hydrogen at 450°C and by deuterium for 90 min at the same temperature *in situ*. The quantity of catalyst varied very much, from 5 mg up to 1 g, but when small amounts were to be used, silica was added so that the total weight in the microreactor was not less than 200 mg. In a blank experiment, it was checked that silica treated under the same conditions was totally inactive up to 100°C.

The unsupported 4 atom% Pd–Ni alloy was prepared by melting at high temperature Johnson–Matthey specpure Pd and Ni wires in an induction oven followed by 72 h homogenization at 1000°C under argon atmosphere.

Materials. Puriss grade but-1-ene was purchased from Fluka. U-grade hydrogen and 99.4% deuterium from Air Liquide were dried on molecular sieves at 77 K before use.

Apparatus, procedure, and analysis for catalytic reactions. The catalytic reaction was carried out in an all-glass grease-free system including a reactor operating under differential conditions. A small amount of reactant (4 mg) was used for each run and was carried through the reactor at a constant partial pressure (5 Torr) by deuterium gas (755 Torr). The hydrocarbon reaction mixture was collected at 77 K and then analyzed and separated by gas–liquid chromatography. Each butene isomer was analyzed by mass spectrometry and for but-1-ene and *cis*-butene by microwave spectrometry.

All these analysis procedures are described elsewhere (*9*). The mass spectrometer used was a Varian Mat-CH7 and the rotational spectrum of butene was recorded on a conventional 50-kHz square-wave Stark spectrometer (University of Nancy) and a Hewlett-Packard 33-kHz spectrometer (University of Strasbourg).

Apparatus and analysis for surface studies. The surface composition of the unsupported alloy was studied by Auger electron spectroscopy (AES) in an ultra-high vacuum chamber with 4-grid optics and a cylindrical mirror analyzer as Auger detector. The energy of the incident electrons was 2 kV and the beam current 10 μA. Pure nickel and palladium were also inserted on the same sample holder. The transitions chosen for the calculation of the concentrations were the $M_{45}N_{45}N_{45}$ palladium peak at 327 eV and the $M_{23}VV$ and L_3VV nickel peaks at 61 and 848 eV.

X-ray photoelectron spectroscopy (XPS) was carried out in a Vacuum Generators ESCA 3 spectrometer. The analyzer was of the hemispheric type and the electron multiplier a channeltron. The K_α transition of Al at 1486.6 eV was used as photon source. The Pd 3d peaks at 335 and 340 eV and the Ni $2p^{3/2}$ transition at 855 eV were recorded.

Calculations of the surface composition were made in two ways. As a first approximation we have already shown (*10*) that, if I_{Pd} and I_{Ni} are the intensities of two chosen transitions of Pd and Ni in the Auger or XPS spectrum of the alloy, the concentration of Pd may be given by:

$$C_{\mathrm{Pd}} = I_{\mathrm{Pd}}/(I_{\mathrm{Pd}} + \alpha_{\mathrm{Pd,Ni}} I_{\mathrm{Ni}}) \quad (1)$$

where $\alpha_{\mathrm{Pd,Ni}}$ is the ratio of the same transitions in the Auger spectra of the pure elements recorded under the same experimental conditions. In a recent paper (*11*) we developed for Pt–Ni alloys a layer by layer calculation of the composition near the surface allowing us to obtain concentration profiles. This is based on the well-known exponential decrease of the Auger signal giving for an alloy:

$$I_{\mathrm{alloy}} = I_{\mathrm{pure}}(1 - e^{-1/\lambda}) \sum_{i=0}^{\infty} C_i e^{-i/\lambda} \quad (2)$$

where λ is the inelastic mean free path of the electrons and C_i the concentration in the ith layer. The calculations consist of a comparison by iteration of the experimental signal with a spectrum calculated theoretically: varying C_i allows one to find the best fit between the two approaches.

RESULTS

A. *Characterization of the Samples*

The composition and homogeneity of the supported catalysts and of the unsupported alloy were checked by X-ray diffraction. The concentrations calculated from the maximum of the peaks are shown in Table 1 and correspond well to nominal compositions. Diffraction line broadening was used to obtain the crystallite mean value diameter D_v. The values given in Table 1 are quite large, which is not surprising if one considers the high temperature of preparation. The choice of so drastic conditions was justified if one refers to a recent paper by Moss *et al.* (*12*) who could not homogenize Pd–Ni/SiO_2 completely at 500°C. In the present study, a comparison with the X-ray diffraction peaks of pure Pd and Ni prepared in the same conditions revealed a good homogeneity.

B. *Catalytic Results*

The reactions between but-1-ene and deuterium on five Pd–Ni alloy catalysts were investigated and compared to supported Pd and Ni catalysts. The reactions were studied at 23°C (Table 2) and −85°C (Table 3). Experimental conditions are indicated at the top of the tables—weight of catalyst (ω) and hydrocarbon flow rate (F). The percentages of reaction products, butane (α_h), but-2-ene (α_i), and deuterated but-1-ene (α_e), which correspond respectively to hydrogenation, isomerization, and exchange reactions are reported as well as the mass distribution of olefins and the microwave analysis of d_1 but-1-ene and in some experiments d_1 *cis*-butene.

1. Exchange, isomerization, hydrogenation: comparison between reaction rates. Though no kinetic study was made on these different catalysts, their activities can be roughly estimated by the comparison of the different values, α_i, α_h, α_e multiplied by the space velocity F/ω which are reported in Tables 2 and 3. The palladium catalyst was found to be more active than any alloy and nickel. However, it will be noted that nickel was very irreproducible from the point of view of activity. Nevertheless, concerning the selectivity between the different reactions which occurred, each catalyst had a very reproducible behavior: at 23°C, the conversions to hydrogenated, isomer, and exchanged products were nearly similar, except on pure nickel where hydrogenation was very fast by comparison with the other reactions. At −85°C, on palladium, the conversions, α_h, α_i, α_e were still similar but when palladium was alloyed, isomerization became the predominent reaction while on nickel, contrary to what happened at higher temperature, hydrogenation was similar to exchange conversion which was higher than isomerization.

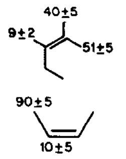
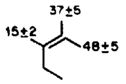
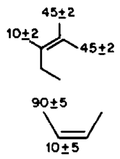
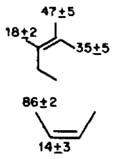
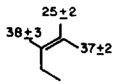
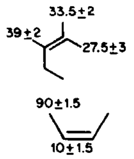
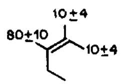
2. But-1-ene distributions. Very characteristic results were obtained from the hyperfine distribution of d_1 but-1-ene analyzed by microwave spectroscopy. First, no deuterium atom was found on C_3. At least, that

TABLE 1

Theoretical atomic composition	Reduction temperature (°C)	Reduction duration (h)	(111) D_v (Å)	Alloy composition by X-ray analysis from Végard's law
Pd_0–Ni_{100}	1148	15	947	0–100
Pd_1–Ni_{99}	950	15		1– 99
Pd_4–Ni_{96}	936	16		
Pd_{10}–Ni_{90}	1130	17	718	
Pd_{50}–Ni_{50}	1000	16	763	50– 50
Pd_{80}–Ni_{20}	950	15	463	80– 20
Pd_{100}–Ni_0	960	16	484	100– 0

TABLE 2

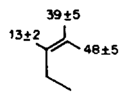
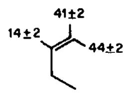
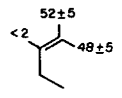
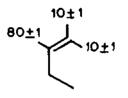
Deuterium–But-1-ene Reactions on Pd, Ni, and Pd–Ni Alloys Supported on Silica at 23°C

Catalyst[a]	Pd			$Pd_{80}Ni_{20}$			$Pd_{50}Ni_{50}$			$Pd_{10}Ni_{90}$			Pd_4Ni_{96}			Pd_1Ni_{99}			Ni		
Weight (ω) (mg)	5			10			20			100			100			13.4			300		
Butene flow rate (F) (μl/min)	5.75			2.7			1.6			1.2			6.6			1.25			0.9		
α_h ($\alpha_h \times F/\omega$)	5.3 (6.1)			24.4 (6.6)			23.9 (1.9)			19.4 (0.23)			38.6 (2.5)			10.2 (0.95)			78.6 (0.24)		
α_i ($\alpha_i \times F/\omega$)	8 (9.2)			20.1 (5.4)			24.5 (2)			19.2 (0.23)			44 (2.9)			7.2 (0.67)			9.3 (0.03)		
α_e ($\alpha_e \times F/\omega$)	6.9 (7.9)			24.1 (6.5)			22.9 (1.8)			13 (0.16)			27.8 (1.8)			4.7 (0.44)			6.6 (0.02)		
Products	1–B	*trans*	*cis*	1–B	*trans*	*cis*	1–B	*trans*	*cis*	1–B	*trans*	*cis*	1–B	*trans*	*cis*	1–B	*trans*	*cis*	1–B	*trans*	*cis*
Composition of olefins	92.0	4.0	4.0	79.9	11.9	8.2	75.5	12	12.5	80.8	10.4	8.8	56	31.6	12.4	92.8	4.8	2.4	90.7	5.7	3.6
d_0	93.1	45.1	49.3	75.9	41.4	33.7	77.1	40.7	43.3	87	49.5	47.4	72.2	23.3	23.2	95.3	39.5	35.6	93.4	64.0	64.6
d_1	5.9	34.9	33.8	18.0	35.9	37.5	17.5	33.3	32.7	9.7	30.7	32.2	20.1	40.7	40.3	3.9	41.4	43.4	5.1	18.2	17.4
d_2	0.9	12.3	9.9	5.0	13.3	16.2	4.6	15.6	14.9	1.9	10.6	10.8	6.1	20.3	20.6	0.7	12.4	13.2	0.8	7.7	6.7
d_3	0.1	5.0	4.5	0.7	6.3	8.7	0.5	6.8	6.2	1.2	5.2	5.9	1.3	10.1	10.4	0.1	4.5	5.4	0.3	4.2	4.0
d_4		1.5	1.4	0.2	1.8	2.4	0.2	2.1	1.7		1.9	1.9	0.2	3.3	3.4		1.4	1.6	0.2	2.9	3.4
d_5		0.7	0.5		0.6	0.8		0.7	0.6		0.9	0.8	0.1	1.2	1.0		0.5	0.5		1.6	2.1
d_6		0.3	0.4		0.3	0.4		0.3	0.3		0.5	0.6		0.5	0.5		0.2	0.2		0.8	0.9
d_7		0.2	0.2		0.2	0.3		0.2	0.1		0.4	0.4		0.4	0.3		0.1			0.4	0.5
d_8								0.1			0.3			0.2	0.1						0.2
$M = \sum_{i=0}^{8} id_i$		87.2	78.4		94.8	113.9		101.2	94.2		85.5	88.7		138.2	137.2		89.7	96.1		73.9	78.1
																					

[a] α_h = butane/butane + Σ butenes; α_i = but-2-enes/Σ butenes; $\alpha_e = \sum_{i=1}^{8} d_i$ but-1-ene.

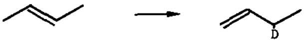
TABLE 3

Deuterium–But-1-ene Reactions on Pd, Ni, and Pd–Ni Alloys Supported on Silica at −85°C

Catalyst[a]	Pd			$Pd_{80}Ni_{20}$			$Pd_{50}Ni_{50}$			$Pd_{50}Ni_{50}$			$Pd_{10}Ni_{90}$			Ni		
Weight (ω) (mg)		55			100			200			150			500			1000	
Butene flow rate (F) (μl/min)		1			1.6			1.6			1.2			0.9			1.2	
α_h ($\alpha_h \times F/\omega$)		19.7 (0.36)			2.4 (0.04)			5 (0.04)			1.4 (0.01)			1.2 (2.2×10^{-3})			17.9 (0.02)	
α_i ($\alpha_i \times F/\omega$)		24.9 (0.45)			4.1 (0.07)			22 (0.18)			5.4 (0.04)			4.5 (8.1×10^{-3})			8 (0.01)	
α_e ($\alpha_e \times F/\omega$)		25.6 (0.47)			1.4 (0.02)			4 (0.03)			1.7 (0.01)			2.4 (4.3×10^{-3})			13.2 (0.015)	
Products	1-B	*trans*	*cis*	1-B	*trans*	*cis*	1-B	*trans*	*cis*	1-B	*trans*	*cis*	1-B	*trans*	*cis*	1-B	*trans*	*cis*
Composition of olefins	75.1	14.8	10.1	95.9	3.5	0.4	78	19.3	1.6	94.6	4.9	0.5	95.5	2.8	1.6	92	4.1	3.8
d_0	74.4	31.8	28.1	98.6	86.9	73.6	96.0	91.7	74.7	98.3	90.9	77.3	97.6	92.4	94.1	86.8	71	70.9
d_1	17.5	31.5	34.7	1.4	10.7	15.4	3.5	7.5	14.9	1.3	7.7	13.9	2.0	5.8	4.6	12.0	21.8	22.4
d_2	7.3	16.3	17.0		1.6	6.4	0.4	0.7	7.3	0.4	0.9	4.7	0.4	1.2	0.9	1.0	4.7	4.3
d_3	0.6	12.5	13.8		0.6	3.3		0.1	1.7		0.4	3.2		0.4	0.3	0.1	1.6	1.4
d_4	0.1	4.2	3.5		0.2	0.7			0.7			0.5		0.2			0.6	0.8
d_5		1.6	1.2			0.3			0.4			0.2					0.2	0.2
d_6		0.8	0.6			0.2			0.2									
d_7		0.7	0.5															
d_8		0.6	0.5															
$M = \sum_{i=0}^{8} i d_i$		141	140		16.5	43.6		9.2	40.6		10.7	36.4		9.4	7.4		39.4	38.4
																		

[a] α_h = butane/butane + Σ butenes; α_i = but-2-enes/Σ butenes; $\alpha_e = \sum_{i=1}^{8} d_i$ but-1-ene.

means no readsorption of but-2-ene isomers had to be considered. Effectively the double bond migration but-2-ene → but-1-ene in the presence of deuterium gas was shown to introduce the deuterium atom mainly in the allylic position (*13*).



Second, the deuterium atom was localized on C_1 and C_2 with percentages depending very much on the catalysts: on palladium, the deuterium atom was localized for 90% on C_1 and 10% on C_2; on nickel, opposite results were observed, 80% was localized on C_2 and 20% on C_1. On Pd–Ni alloys, down to 10% of palladium atom concentration, the localization of deuterium was identical to what was observed on "pure" palladium while on Pd_4Ni_{96} and Pd_1Ni_{99} the hyperfine distributions were different: 60% on C_1 and 40% on C_2. One can say that the results at +23 and −85°C are similar. There might be an exception on the $Pd_{10}Ni_{90}$ alloy. However, in this case the quantity of monodeuterated but-1-ene at −85°C was very small so that the uncertainty in microwave analysis was quite large.

3. But-2-ene distributions. At 23°C, the behaviors of palladium and that of palladium-rich alloys (down to 10% Pd) were still similar: the ratio *trans* to *cis* was near unity (1.2 ± 0.2) and *cis* and *trans* distributions were equivalent; d_0 was 45 ± 5, d_1 33 ± 3, and the rest consisted of decreasing multiple exchange, d_2 to d_8, while on Pd_4Ni_{96} and Pd_1Ni_{99}, the ratio *trans*/*cis* was higher (2.5 and 2, respectively) and d_0 was lower than d_1. On nickel, d_0 molecules were more important (64%) and in multiple exchange, d_2 to d_8, the average deuterium content (3.1) was higher than on other catalysts (2.7 ± 0.1).

At −85°C, it is interesting to note on $Pd_{80}Ni_{20}$ and $Pd_{50}Ni_{50}$ the definite predominance of *trans*-butene by comparison to *cis*-butene and the nonequivalent distributions of the two isomers: the deuterium content $\sum_{i=0}^{8} id_i$ in *trans*-butene was three or four times lower than in *cis*-butene. So it appears that the formation of the d_0 isomer, mainly *trans* isomer, became the predominent reaction on going from "pure" metals to the alloys at this low temperature.

C. Surface Studies

Except for double bond migration at low temperature it appeared that only Ni-rich alloys revealed a catalytic behavior where both Ni and Pd played a part. We therefore focussed our attention on the 4 atom% Pd–Ni alloy and to begin with we studied in Auger spectroscopy an unsupported alloy of this concentration.

As will be seen below, numerous theoretical estimations of the surface atom fractions in binary alloys have been attempted and the equations developed include in particular the equilibrium temperature of the surface. The lack of knowledge of this parameter has led in the past to numerous misleading conclusions.

In the present case the sample was prepared at a temperature much higher than the equilibrium one. However, in the cleaning procedure ion bombardment was extensively used resulting in a complete rearrangement of the surface and subsequent annealing was necessary to recover equilibrium. In Fig. 1 the surface palladium concentration, calculated using Eq. (1), has been plotted as a function of annealing times at different temperatures. It is seen that annealing at a temperature as high as 650°C is necessary to obtain a stable concentration within a reasonable period of time. During this procedure, attention must be paid to segregation of impurities, especially sulfur, which may be quite fast at these temperatures and results in a strong attenuation of the Pd MVV peak (but not the Ni one).

After 1 h at 650°C the surface palladium concentration was 29%. Ion bombardment led in all cases to a surface concentration of about 5%. This is due to the fact that the

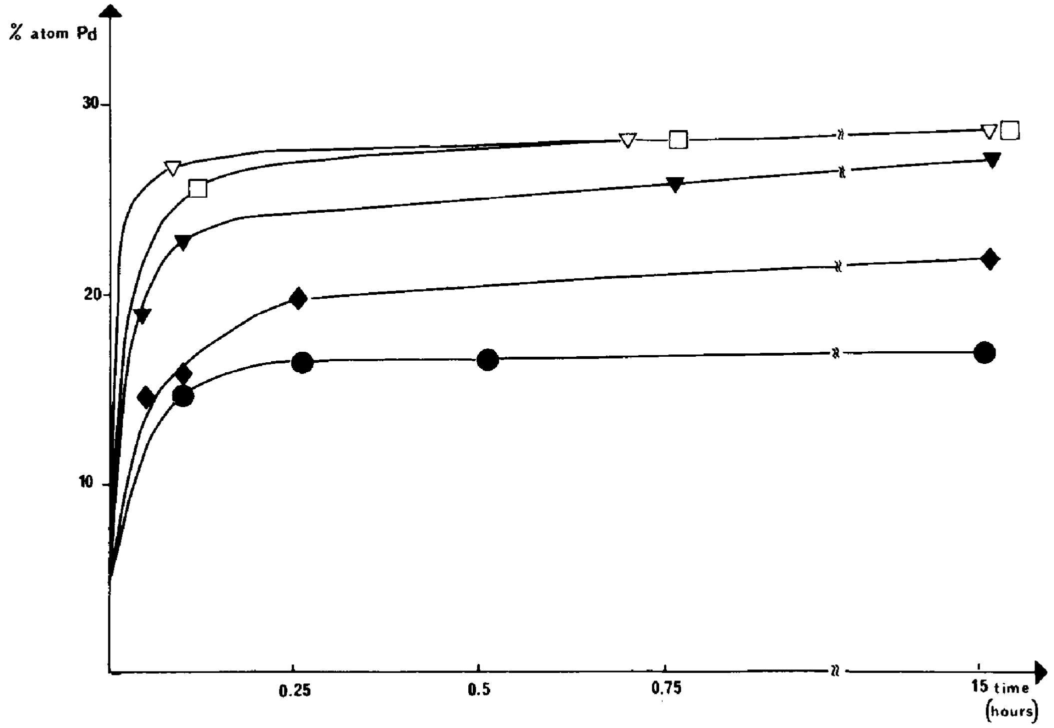


FIG. 1. Surface equilibration of the Pd_4Ni_{96} alloy: ●, at 350°C; ◆, at 450°C; ▼, at 550°C; □, at 650°C; ▽, at 750°C.

sputtering yield of palladium is higher than that of nickel (2.1 and 1.45 atom/ion, respectively, for 500 eV Ar^+ ions).

It must be emphasized that, as the energies of the Ni (61 eV) and Pd (327 eV) peaks used in this study are very low, it is expected from the well-known universal curve (*14*) that most of the signal recorded comes from the three or four first layers.

A brief study of the interaction of the equilibrated surface with oxygen was also made. Oxygen could be adsorbed at room temperature at low pressure (5.10^{-6} Torr) but modifications of the surface composition were detected at temperatures higher than 200°C. At 500°C and 1 Torr oxygen, no palladium was left on the surface.

Concentration profiles are given in Fig. 2a for an alloy just after ion bombardment and in Fig. 2b for an equilibrated surface. Figure 2a shows a very smooth variation from about 10% (first layer) to the nominal composition which was reached in the 7th or 8th layer. The surface after equilibration exhibited large variations. The bulk composition was reached in the 10th layer and the palladium concentration in the very first layer was 47%, to be compared with the value of 29% obtained using Eq. (1).

The supported alloy, with the same nominal composition, 4 atom% Pd, was studied in XPS. The spectra of the Pd 3d and Ni $2p^{3/2}$ transitions are given in Fig. 3. Both spectra were recorded under the same experimental conditions and if one considers that the ionization cross-sections for the Pd $3d^{5/2}$ and Ni $2p^{3/2}$ transitions are nearly identical, as checked on pure palladium and nickel samples, the Pd surface concentration, using Eq. (1), may be estimated as 52%. It must be noted that the binding energy of the Ni $2p^{3/2}$ transition, corrected for charging effects due to the nonconducting character of the sample, was 856.5 eV and the peak was followed by a shake-up satellite at 862.2 eV. It may therefore be con-

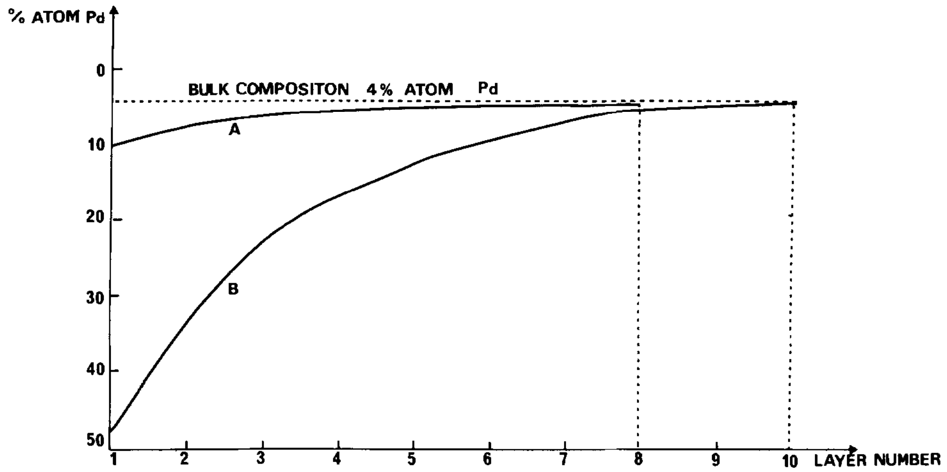


FIG. 2. Concentration profiles of the Pd_4Ni_{96} alloy: (A) after ion bombardment; (B) for equilibrated surface.

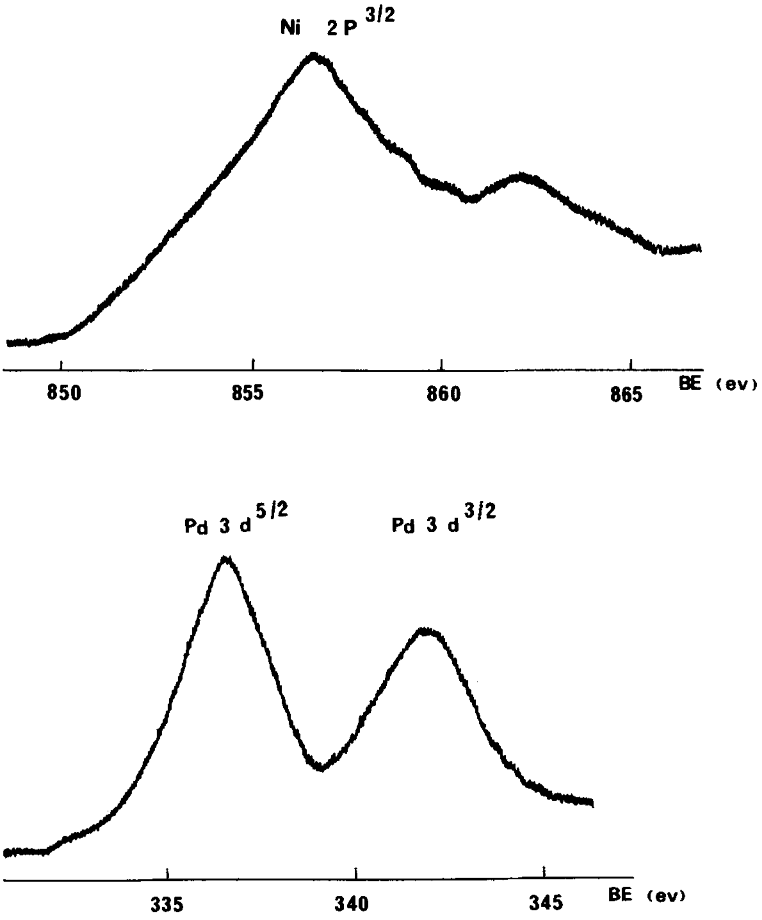


FIG. 3. Photoelectron spectra of Ni $2p^{3/2}$ and Pd 3d transitions in the Pd_4Ni_{96} alloy supported on silica.

cluded that Ni atoms were in an oxidized state in this sample.

DISCUSSION

The main results to be discussed are the following: (i) the palladium enrichment of the first layer in Pd_4Ni_{96} alloy found by XPS and AES; (ii) the correlation between this palladium enrichment and the catalytic behavior in exchange and isomerization of butene; (iii) the different results observed in the exchange reaction on palladium/silica and nickel/silica, respectively, for which some mechanisms will be proposed.

A. *Surface Compositions*

The heat of segregation ΔH_a of a solute A in a binary solution AB is related to the bulk and surface atom fractions $X_A{}^b, X_B{}^b, X_A{}^s, X_B{}^s$ in the following way:

$$X_A{}^s/X_B{}^s = (X_A{}^b/X_B{}^b)\exp(-\Delta H_a/RT)\exp(\Delta S_a/R)$$

where ΔS_a is the entropy of segregation and T the absolute temperature at equilibrium.

If one wishes to predict surface compositions it is necessary to determine a correct value for T. The problem has often been oversimplified in the past, leading to several misunderstandings. From Fig. 1 it is seen that equilibrium is reached quickly at 650°C for Pd–Ni. As our alloys were prepared at a higher temperature, Auger studies will give values of surface compositions consistent with those of our catalysts only if any treatment disturbing the surface (e.g., ion bombardment or oxidation) is followed with equilibration at this temperature.

The calculation of the heat of segregation ΔH_a has led to numerous speculations. After the development of the bond-breaking theory (*15*) involving the differences in the heats of vaporization of the constituents as the driving force for segregation, and the strain energy model (*16*) based on differences between atomic radii, a unified theory was proposed a few years ago by Wynblatt and Ku (*17*) taking into account both parameters. In the present case the heats of vaporization of palladium and nickel are 90 and 102.8 kcal/mole and the atomic radii are 1.37 and 1.24 Å, respectively. Both these differences are large enough to contribute to the heat of segregation. The heats of vaporization predict a surface segregation of palladium, which has the lower value, in the whole range of concentrations. On the other hand the equations developed by Wynblatt and Ku (*17*) show that the contribution of the size difference being a function of $(r_A - r_B)^2$ the element which is present in lower quantity will migrate to the surface, whether it is larger or not. Qualitatively in the case of Pd–Ni, we can therefore make the following predictions:

(1) In the Ni-rich region both effects will add and lead to a very important segregation of palladium.

(2) In the Pd-rich region both effects will offset or partly offset depending on their relative importance. Actually we may expect the size difference contribution to be weaker.

Stoddart *et al.* (*18*) studied with AES the surface composition of Pd–Ni alloys in the concentration range 20–100 atom% palladium. The alloys were films evaporated *in situ* at room temperature and not equilibrated. The authors found that the surface was covered with a layer of palladium from 60 atom% palladium (nominal composition) upward. However, this situation may be rather idealized since in a subsequent study Moss *et al.* (*12*) found catalytic results consistent with the presence of a small quantity of nickel atoms at the surface in the same range of concentration.

Equilibrium after ion bombardment of our unsupported 4 atom% Pd–Ni alloy at 650°C for 15 min gave a surface concentration, determined by AES and using Eq. (1) of 30 atom% palladium. This result is consistent with a study by Merwyn *et al.* (*19*) who found the same concentration with a 1 atom% Pd–Ni alloy using a method of calculation comparable to ours. However, our concentration profiles showed that the composition on the very first layer is still much more enriched in palladium, with a surface concentration of about 45%. Our XPS spectra of the supported alloy gave a palladium surface concentration which was still higher (52%) but in this case the difference in escape depths which correspond to the kinetic energies of the transitions studied may somewhat favor palladium.

We may summarize the comparison of our results with those of the literature in the following way: the contribution of nickel atoms to the surface composition is very small in a large domain of concentration and becomes important only for very Ni-rich alloys. Even in the latter case the nickel surface concentration is hardly higher than 50%.

Oxidation treatments at 500–600°C led to nickel surface segregation. This is not surprising since nickel is easier to oxidize than palladium. Our supported catalysts were treated with hydrogen in such drastic conditions that complete reduction is very much likely. However, the samples were left in open air before XPS analysis and we found nickel peaks characteristic of an oxide. The fact that no nickel segregation was found is not contradictory: the mobility of nickel in palladium is much too low at room temperature for chemisorption-induced segregation to occur.

B. Correlation between Surface Studies and Catalytic Behavior

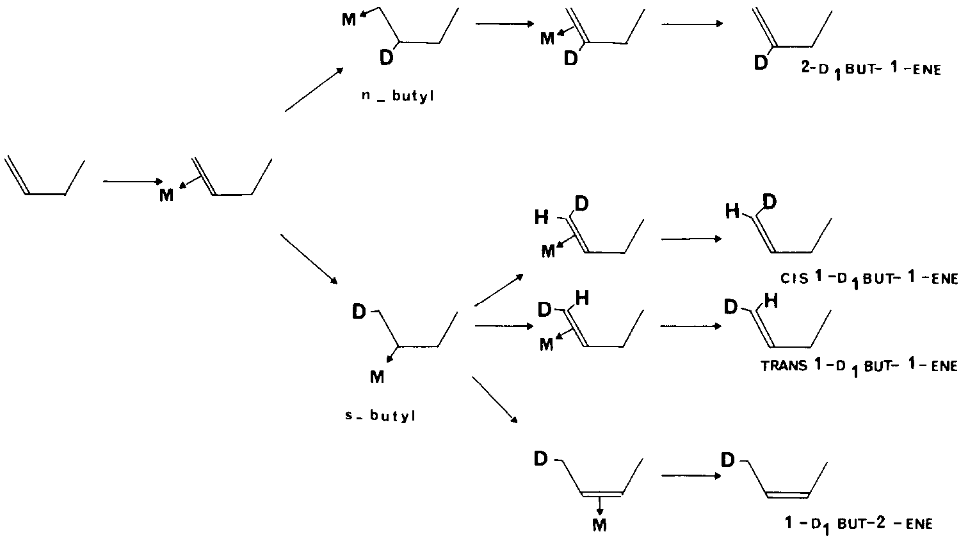
From the exchange reaction of but-1-ene, it can be concluded that down to 10% in palladium atom concentration, Pd–Ni alloys had the same catalytic behavior as "pure" palladium. Two different explanations can be given: either the surface was covered only by palladium or, if nickel was present, its activity was so low by comparison to palladium that nickel had no effect on the result. Let us examine the results of the Pd_4Ni_{96} alloy: if we assume additive properties of palladium and nickel in the exchange reaction, knowing the hyperfine distribution of d_1 but-1-ene given by the "pure" metals, the relative contributions of palladium and nickel can be deduced from the hyperfine distribution of d_1 but-1-ene given by the Pd_4Ni_{96} alloy. We found 60% of palladium and 40% of nickel. Such a result is in good accordance with the palladium enrichment given by the XPS and AES study. It would mean that, in this case, palladium and nickel would have nearly the same activity. From our studies on "pure" palladium and "pure" nickel such a conclusion could not be drawn because of the irreproducibility in the activity of "pure" nickel. However, this does not prove the above assumption to be incorrect: alloying seems to stabilize nickel since Ni-rich alloys, where nickel was shown to play a role in the catalytic reactions, exhibited a much more reproducible activity than pure nickel. Moss *et al.* (*20*) found the same conversions on nickel and palladium films in the hydrogenation of ethylene but they also showed that the activity of the alloys was higher, which is not true in the present case. In fact the activity of our alloys decreased regularly from palladium to nickel with the exception of Pd_{10}–Ni_{90}. In this case the accessibility of the metallic particles seemed to be surprisingly low: XPS spectra of this catalyst gave very weak intensities for the transitions of both Ni and Pd. However, one must emphasize that, regardless of the variations in activities, the microwave results remained very coherent.

Another interesting result was the increase of double bond migration without deuterium atom introduction which occurred at −85°C on Pd–Ni alloys. Such a reaction was already discussed and shown to take place by an intramolecular hydrogen shift while the double bond migration with deuterium introduction takes place by an associative Horiuti–Polanyi mechanism, to give rise to but-2-ene labeled on C_1 (*4, 7, 9*). It is thought that this effect of increase of intramolecular hydrogen shift is not due to an alloy effect but to a particular behavior of palladium, the exchange reaction showing that the upper layers contain mainly palladium atoms. In another work on Pd/pumice the same tendency was sometimes found (*13*).

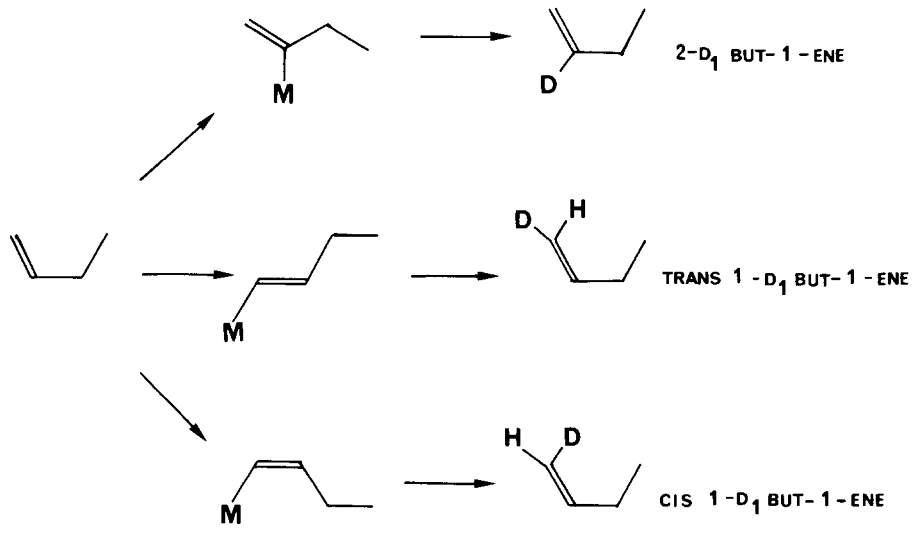
C. *Exchange Mechanism on Ni/Silica and Pd/Silica*

As no allylic hydrogen was exchanged by deuterium in but-1-ene, the allylic mechanism (*21*) has to be ruled out for the exchange reaction on Pd and Ni. Two mechanisms may then account for the exchange reaction, the associative mechanism (Scheme 1) and the vinylic type dissociative mechanism (Scheme 2).

A Horiuti–Polanyi mechanism (Scheme 1) common to isomerization and exchange reactions would lead to the same deuterated distributions (d_1 to d_8) in but-1-ene and but-



Scheme 1



Scheme 2

2-ene. However, if it is assumed that the adsorption–desorption step for but-2-ene is slower than for but-1-ene and in the same order as the interconversions betwen di- and mono-adsorbed species, the multiple exchange will be more important in but-2-ene than in but-1-ene as it was observed on any catalyst. If we take into account the label in the reaction products, d_1 but-1-ene and d_1 but-2-ene, the relative rates of formation of sec- and *n*-butyl intermediates could be calculated. It would be 15 on palladium and 0.94 on nickel at 23°C. On Ni/silica the hyperfine distribution of isomer which failed in the table was taken to be equal to 100% on C_1 in d_1 but-2-ene as was the case on Ni/pumice (*13*) which was found to have the same catalytic behavior as Ni/SiO_2 for this reaction.

The hyperfine distribution of d_1 but-1-ene could as well be explained by a dissociative mechanism (Scheme 2) if we assume that on palladium the 1-butenyl radical would be preferentially formed while the 2-butenyl radical would predominate on nickel. In this single study, no direct proof allows us to say whether the Horiuti–Polanyi mechanism, which is responsible for the isomerization, also leads to exchange or whether the dissociative mechanism plays the major part in the latter reaction. On iron (*2*) and nickel (*7*) film, and on iron supported on pumice (*9*) in the presence of perdeuteropropene as deuterating agent instead of deuterium, the 2-butenyl radical was shown to be formed from but-1-ene and to lead to exchange of but-1-ene with deuterium on C_2. It was also proved that such a radical was a precursor in the reaction mechanism leading to double bond migration from internal to external position in olefins (*22*) on iron film. For the main part of the distribution, our results obtained on nickel/silica are similar to those on nickel films and lead us to adopt the same dissociative mechanism with the preferential formation of the 2-butenyl radical. On palladium films in the presence of perdeuteropropene (*4*) an allylic mechanism was shown to play the main part in the exchange mechanism; however, the dissociative mechanism was also assumed to explain the observed dissymmetry of the label on C_1 in d_1 but-1-ene (*trans* 1-d_1 but-1-ene > *cis* 1-d_1 but-1-ene). Quite different results are observed on Pd/silica in the presence of deuterium since 90% of the deuterium is localized on C_1 with no significant dissymmetry. Further work is in progress to try to understand the mechanisms of these reactions on palladium.

In conclusion we have shown in this study that the reactions of but-1-ene on Pd–Ni/SiO_2 alloys differ very much from what would be expected in view of their nominal compositions. This behavior is related to a strong palladium enrichment. Mechanisms have been tentatively proposed but further work is needed to determine them unequivocally on Pd–Ni alloys as well as on Pd and Ni. It would also be interesting to study the effect of alloying Ni and Pd on other reactions such as skeletal rearrangments of saturated hydrocarbons.

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