Low-Loaded Pd/α-Al$_2$O$_3$ Catalysts: Influence of Metal Particle Morphology on Hydrogenation of Buta-1,3-diene and Hydrogenation and Isomerization of But-1-ene

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Buta-1,3-diene hydrogenation and but-1-ene hydrogenation and isomerization were studied on low-loaded Pd/α-Al$_2$O$_3$ catalysts (0.1–0.3 wt.%) prepared from palladium acetylacetonate (Pd(C$_5$H$_7$O$_2$)$_2$). Deuterium tracer study, hydrogen chemisorption, transmission electron microscopy, and X-ray photoelectron spectroscopy analysis were used to establish the relationships between metal–support interactions, particle shapes, and buta-1,3-diene and but-1-ene hydrogenation and isomerization mechanisms. It was found that the hydrogenation reaction rates (turnover frequencies) are similar for buta-1,3-diene and but-1-ene, but 10 times lower for the 0.1% Pd catalyst compared to the 0.3% Pd catalyst. However, the 0.1% Pd catalyst has a high activity for the isomerization reaction which leads to 98% selectivity in isomers for the but-1-ene reaction. This unusual specific activity is explained considering that the 0.1% Pd catalyst contains flat particles in strong interaction with the support, as was deduced from several characterization methods, while the 0.3% Pd catalyst has more rugged bulk type particles after H$_2$ treatments because they are not interacting with the support.

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INTRODUCTION

It is well known that Pd/Al$_2$O$_3$ catalysts present high activity and selectivity for the semihydrogenation of alkynes and alkadienes; this specificity is used in many industrial processes for the selective hydrogenation of acetylenic and diolefinic compounds in the presence of large amounts of olefins.

Palladium being a precious metal, high dispersion on the support is desired for the preparation of industrial catalysts. Boitiaux *et al.* (1), using palladium acetylacetonate (Pd(C$_5$H$_7$O$_2$)$_2$) as a catalyst precursor, were able to control the particle size by varying the reduction temperature; they obtained supported palladium catalysts with dispersions ranging from 9 to 100%. The activity of but-1-yne,

buta-1,3-diene, and isoprene hydrogenation, performed in the liquid phase, exhibited a clear dependence on the particle size. The catalytic activity decreased rapidly for particle diameters smaller than 3–5 nm (dispersion $\leq$20%). The authors proposed an intrinsic modification of the properties of the metallic sites, specifically a stronger adsorption of the unsaturated hydrocarbons on the smaller particles which leads to a decrease of the turnover frequency. Other authors obtained results which show the sensitivity of the hydrogenation reaction to the Pd particle size using the same type of alumina-supported palladium catalysts (2, 3) or other types of palladium catalysts (4, 5), studying either the same (3) or different alkadienes and alkynes (2, 4, 5). The core level binding energy of the palladium 3d electrons, examined by X-ray photoelectron spectroscopy, has been found to be higher for small particles supported on alumina (3), silica (6), and carbon (7), compared to bulk palladium, but it has been found to be lower when particles were supported on pumice (5). Except for Pd/pumice, in which Na ions could play an important role in electronic and then catalytic properties of small Pd particles, it has been suggested that the low density of states at the Fermi level for small particles would lead to a strong adsorption of the alkyne or diene which are electron-rich molecules and thus would give rise to a decrease of the hydrogenation rate (1, 3, 8, 9).

Pd/α-Al$_2$O$_3$ catalysts examined in this paper have been obtained by the procedure described by Boitiaux *et al.* (1). Their palladium contents are low (0.1–0.3 wt.%) and their dispersion varies from 54 to 23%. From a previous study (10), two types of catalysts emerge: one presenting particles with a strong interaction between metal and support, the other being less interactive. These catalysts have been tested for buta-1,3-diene hydrogenation and but-1-ene hydrogenation and isomerization. In addition the but-1-ene reactions have been followed by deuterium tracer study. This work concentrates on the relationships between metal–support interactions, particle shapes, and mechanisms of hydrogenation and isomerization reactions.

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METHODS

Catalyst Preparation

The catalysts were prepared by wet impregnation of α-Al$_2$O$_3$ (Rhône Poulenc, 10 m^2/g, precalcined at 773 K) with benzene solutions of palladium *bis*-acetylacetonate (Pd(C$_5$H$_7$O$_2$)$_2$), in accordance with the procedure described by Boitiaux *et al.* (1). Benzene solutions containing 0.7 and 3.33 g Pd/liter were used to obtain samples with Pd loadings of 0.09 and 0.30 wt.%, respectively, keeping the solution to support ratio constant. The resulting mixtures were maintained at room temperature in closed flasks for 72 h with occasional stirring. The samples were then filtered, dried overnight at 383 K, and calcined in air at 573 K for 2 h. Finally they were reduced in flowing hydrogen at the same temperature and for the same period of time. Subsequently, a certain amount of each catalyst was reduced at 773 K for 1 h in order to increase the Pd particle size by metal sintering. Metal loadings were determined by atomic absorption spectroscopy (AAS).

Transmission Electron Microscopy

The particle size distribution was determined by transmission electron microscopy (TEM) using a Jeol 100 CX instrument operated at 100 kV (Centro Regional de Investigaciones Basicas y Aplicaas de Bahia Blanca, Argentina). The Pd catalysts were ground and dispersed onto holey carbon-coated Cu grids for direct observation. Over 100 particles were examined on the TEM micrographs and the average particle size has been calculated as $d = \Sigma n_i d_i^3 / \Sigma n_i d_i^2$.

Sorption Measurements

The fraction of exposed palladium atoms was derived from hydrogen sorption measurements performed at room temperature in a static volumetric apparatus, following the double isotherm method proposed by Benson *et al.* (11). Prior to sorption measurements, the samples were treated in a stream of hydrogen at 573 K for 1 h and evacuated at the same temperature overnight. The first isotherm, measured in the 0 to 14-kPa pressure range, gave the total H$_2$ uptake. Subsequently, the catalysts were evacuated for 30 min and a second isotherm was obtained to determine the amount of absorbed and weakly adsorbed gas removed during the evacuation step. The linear portion of both isotherms was extrapolated to zero pressure to estimate the corresponding uptake values. The extent of irreversibly adsorbed gas was obtained by subtracting the contribution of the second isotherm from the total uptake. Assuming that the surface stoichiometry of the irreversibly adsorbed hydrogen is unity, the fraction of exposed palladium atoms is given by (H/Pd)$_{irr}$.

X-Ray Photoelectron Spectroscopy

The measurements were performed using a VG Esca III spectrometer with AlKα radiation (1486.6 eV) as incident beam without a monochromator, as described previously (10). Before conducting the X-ray photoelectron spectroscopy (XPS) analysis, the samples, already reduced at 573 K, were treated *in situ* at 573 or 773 K for 1 h under 1 atm of hydrogen (1 atm = 1.013×10^5 Pa) to avoid possible air contamination, which is known to influence the XPS palladium lines in supported palladium catalysts (12).

Due to charging effects on the α-Al$_2$O$_3$ samples, the XPS peaks were found to shift toward higher BE. Consequently, the Al 2s BE was used as a reference to correct the XPS peak position in all samples. It was fixed at 119.6 eV since Légaré and Fritsch (13) found this value referenced to the Fermi level of Pd obtained by metal vapor deposition on a single α-Al$_2$O$_3$ crystal. On this sample the Pd 3$d_{5/2}$ BE was found to be 335.2 eV.

It will be noted that using Al 2s at 119.6 eV to calibrate the binding energies, the C 1s BE was found at 285.6 eV whatever the sample; i.e., the charging correction using an internal element of the support, or contaminating carbon, leads to the same BE of Pd.

Catalytic Tests

Apparatus, procedure, and analysis of catalytic reactions. The catalytic reactions were carried out in a stainless steel reactor operating under differential conditions at atmospheric pressure. the total gas flow (H$_2$ + He + hydrocarbon), controlled by a flowmeter, was varied by changing the pumping rate at the end of the flow line. A known quantity of hydrocarbon was carried over the catalyst by the hydrogen flow at a constant hydrocarbon pressure: 6.7 Torr and 7.2 Torr for buta-1,3-diene and but-1-ene, respectively. The stability of the hydrocarbon pressure and the reaction time was controlled by two katharometers inserted upstream and downstream with respect to the reactor, enabling the hydrocarbon flow rate (mol s^{-1}) to be measured.

Rectangular pulses of hydrocarbon carried by H$_2$ (D$_2$)– He mixture (38/722 Torr), were used for each experiment. The H$_2$ (D$_2$)–He mixture was purified by passing through a tube containing Pt/Al$_2$O$_3$ powder heated at 543 K, followed by a cold trap at 196 K and a zeolite trap maintained at room temperature to remove the oxygen and water impurities.

The reaction products were drawn off the flow line at different time during the catalytic run and analyzed by gas–liquid chromatography (GLC, using a 2.5-m-long, 3.175×10^{-3}-m o.d. dimethyl sulfolane column operating at 273 K with a flame ionization detector).

Before each catalytic experiment, the catalyst was treated at 573 K during 1 h (heating rate: 10 K/min) and cooled to the reaction temperature (273 K) under H$_2$ (D$_2$)/He flow. At
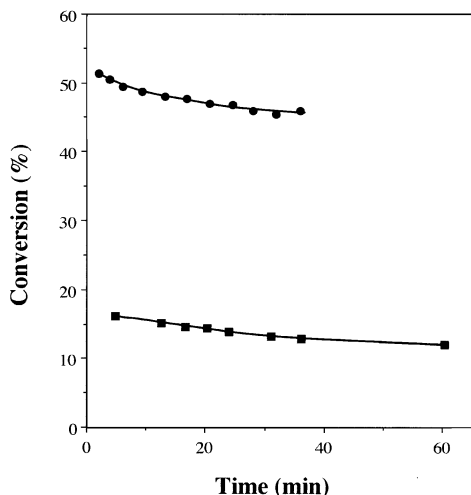
FIG. 1. Conversion as a function of time. (●) 0.30% Pd/α-alumina; (■) 0.09% Pd/α-alumina. Reduction temperature, 573 K; reaction temperature, 273 K. Partial pressures: but-1,3-diene, 6.7 Torr; hydrogen, 38 Torr; helium, 715.3 Torr.

the initial stage of the experiment the conversion decreases slightly to reach a steady state after 10–20 min (Fig. 1) and reproducible results are then obtained.

The conversion values (α) used for the rate calculation were taken in the range where the rate equation $k = (\alpha F/\omega)$ was verified, F being the hydrocarbon flow in mol/s, and ω the quantity of catalyst. If ω is given in grams of catalyst (metal + support), the reaction rate k is obtained in mol/s/catalyst g; if ω is given in term of surface metal atoms (measured by hydrogen chemisorption), then the catalytic activity is given by the turnover frequency (TOF). For these two values, the index "h" indicates the hydrogenation reaction and the index "i" indicates the isomerization reaction. The selectivity in but-1-ene toward but-2-enes is given by

$$B1/B2 = \frac{\text{but-1-ene}}{(\textit{trans}\text{-but-2-ene} + \textit{cis}\text{-but-2-ene})},$$

the selectivity in *trans*-but-2-ene toward *cis*-but-2-ene is

given by

$$T/C = (\textit{trans}\text{-but-2-ene})/(\textit{cis}\text{-but-2-ene}),$$

and the selectivity in olefins toward butane is given for the *buta*-1,3-diene reaction by

$$S = \frac{(\text{but-1-ene} + \textit{trans}\text{-but-2-ene} + \textit{cis}\text{-but-2-ene})}{(\text{but-1-ene} + \textit{trans}\text{-but-2-ene} + \textit{cis}\text{-but-2-ene} + \text{butane})},$$

and for the but-1-ene reaction by

$$S = \frac{(\textit{trans}\text{-but-2-ene} + \textit{cis}\text{-but-2-ene})}{(\textit{trans}\text{-but-2-ene} + \textit{cis}\text{-but-2-ene} + \text{butane})}.$$

When deuterium was used in the experiments, each hydrocarbon was separated by GLC and further analyzed by mass spectrometry (using a Varian type CH7 spectrometer) according to the proper procedures described in detail elsewhere (14).

RESULTS AND DISCUSSION

Table 1 summarizes the chemisorption and TEM data as well as XPS results for samples reduced at 573 and 773 K (10). Catalysts prepared with an impregnation solution containing 0.7 g Pd/liter will be designated A; these samples exhibit a 0.09 Pd wt.%. Catalysts B are prepared with an impregnation solution containing 3.33 g Pd/liter and exhibit a 0.30 Pd wt.%. The subscripts 1 and 2 are used for catalysts reduced at 573 K and 773 K, respectively.

An increase in reduction temperature leads to an increase in particle size, more important for the catalyst A_1 than for the catalyst B_1. It is worth noting that an increase in particle size does not affect the Pd $3d_{5/2}$ core level electron binding energy. This phenomenon has already been described in Ref. (10) and ascribed to an epitaxial growth of the particles of catalysts A in strong interaction with the support, developing (111) faces. Catalysts B, which have particles which interact less with the support, exhibit the binding energy of bulk palladium. As has been mentioned before

TABLE 1

Chemisorption, TEM, and XPS Characterization for Pd/α-Al₂O₃: Catalysts with Different Metal Loadings Reduced at 573 and 773 K [Ref. (10)]

Solution concentration (g Pd/liter)	Pd content (wt.%)	Name	Reduction temperature (K)	Surface Pd atoms (H/Pd)$_{\text{irr}}$	Particle size (TEM) (nm)	BE Pd $3d_{5/2}$ (eV)
0.70	0.09	A_1	573	0.54	2.8	336.1
0.70	0.09	A_2	773	0.25[a]	4.5	335.9
3.33	0.30	B_1	573	0.26	6.0	335.1
3.33	0.30	B_2	773	0.23	7.2	335.2

[a] Calculated from TEM results.

TABLE 2

Activity and Selectivity for the Buta-1,3-diene Hydrogenation and But-1-ene Hydrogenation and Isomerization

Catalysts	Reduction temperature (K)	$k_h \times 10^6$ (mol/s/g cat.)	$k_i \times 10^6$ (mol/s/g cat.)	TOF_h (s^{-1})	TOF_i (s^{-1})	Produced butenes		S (%)
						B_1/B_2	T/C	
		Buta-1,3-diene hydrogenation Reaction temperature: 273 K						
A_1	573	1.6		0.35		1.8	8.7	99.5
B_1	573	32.8		4.50		2.1	9.1	99.4
		Reaction temperature: 255 K						
A_1	573	0.95		0.21		1.8	8.7	99.5
A_2	773	0.22		0.10		1.2	6.4	99.5
		But-1-ene hydrogenation and isomerization Reaction temperature: 273 K						
A_1	573	1.65	99.0	0.36	21.3		2.9	98.7
B_1	573	23.40	33.3	3.2	4.5		1.6	59.6

Note. h, hydrogenation; i, isomerization.

(10), for these catalysts (A and B) the Pd $3d$ core level electron binding energy is not related with the particle size but with the concentration of $Pd(C_5H_7O_2)_2$ in the impregnation solution.

Table 2 presents, for catalysts A and B, the activity and selectivity for buta-1,3-diene hydrogenation and but-1-ene hydrogenation and isomerization. The reaction schemes are illustrated in Figs. 2 and 3, respectively.

Let us first analyze the results obtained for the buta-1,3-diene hydrogenation. Comparing the results obtained for catalysts A_1 and B_1, we observe that an increase in Pd content leads to an increase in hydrogenation rate, which is about 13-fold higher if one compares the activity per surface atom (TOF_h). It is noticeable that catalyst A_1 has a very low activity compared to catalyst B_1. In order to test the effect of particle size on the hydrogenation activity, let us consider the results obtained for catalyst A_1, reduced at 573 K and A_2, reduced at 773 K, having respectively a mean Pd particle diameter of 2.8 and 4.5 nm. At 255 K, both catalysts present a very low hydrogenation activity per gram of catalyst (k_h) as well as per surface atom (TOF_h). These
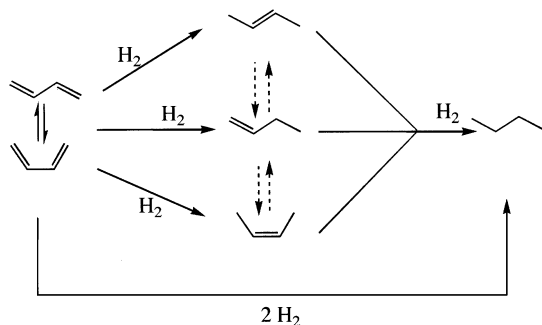
results indicate that the large difference observed in hydrogenation activity between A_1 and B_1 is not related to the difference in particle size.

Let us introduce here the results obtained for the but-1-ene reactions in which one discriminates between the hydrogenation and the isomerization rates. Comparing the hydrogenation activity for the buta-1,3-diene and but-1-ene, one observes that, for a given catalyst, both rates are very similar. Therefore, the hydrogenation rate does not depend on the hydrocarbon but depends on the catalyst.

For the isomerization reaction, it is worth noting that the catalyst showing the lowest hydrogenation rate (A_1) exhibits an isomerization activity, TOF_i, about five times higher than the catalyst which shows the highest hydrogenation activity (B_1). All these catalytic results suggest that the differences in physical characteristics, revealed mainly by the Pd $3d$ electron binding energy, determine the catalytic behavior:

—catalyst A_1 (Pd $3d_{5/2}$ BE = 336.1 eV) has a very low hydrogenation rate, both for buta-1,3-diene and for but-1-ene, but shows a high isomerization rate for but-1-ene reaction which leads, in but-1-ene reaction, to a high selectivity to but-2-enes toward butane (more than 98.5%);

—catalyst B_1 (Pd $3d_{5/2}$ BE = 335.1 eV) has hydrogenation and isomerization rates in the same range, and its
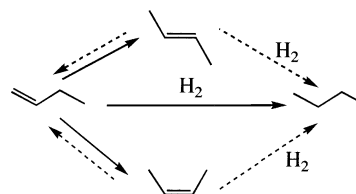

FIG. 2.   Buta-1,3-diene hydrogenation.

FIG. 3.   But-1-ene hydrogenation and isomerization.

TABLE 3

Isotopic Distribution for the But-1-ene Deuteration

Hydrocarbons	Catalysts			
	A$_1$		B$_1$	
Conversion (%):	67	54	51	26
Selectivity (%):	98.5	97.7	71.8	76.1
T/C:	2.8	2.7	1.8	2
Hydrocarbons	Percentages			
Butane				
C$_4$H$_{10}$	56	56	35	37
C$_4$H$_9$D	37	27	40	39
C$_4$H$_8$D$_2$	4	14	25	24
C$_4$H$_7$D$_3$	2	2		
C$_4$H$_6$D$_4$	1	1		
But-1-ene				
C$_4$H$_8$	99	99	88	97
C$_4$H$_7$D	1	1	10	3
C$_4$H$_6$D$_2$	<1		2	<1
trans-But-2-ene				
C$_4$H$_8$		97	66	76
C$_4$H$_7$D		3	25	18
C$_4$H$_6$D$_2$		<1	9	6
C$_4$H$_5$D$_3$		<1		
cis-But-2-ene				
C$_4$H$_8$		95	64	69
C$_4$H$_7$D		4	26	21
C$_4$H$_6$D$_2$		1	10	7
C$_4$H$_5$D$_3$				3
C$_4$H$_4$D$_4$				<1

Note. Reaction temperature, 273 K; reduction temperature, 573 K; deuterium partial pressure, 38 Torr; but-1-ene partial pressure, 7.2 Torr.

selectivity to but-2-enes is quite poor ($\approx$60%) for the but-1-ene reactions.

In order to clarify the reaction mechanism, a deuterium tracer study was performed on the two types of catalysts. It has been performed under a deuterium/helium flow (D$_2$–He/5–95%). The comparison of the deuterium atom distributions in the reaction products shows the relationships between deuteration, isomerization and exchange reactions.

Table 3 indicates the distribution of the reaction products for catalysts A$_1$ and B$_1$ at different conversions.

The butane distributions exhibit a high proportion of nondeuterated molecules (35 to 56%). These results indicate that hydrogen atoms are introduced in the products although the reaction is taking place under a deuterium/ helium flow. On the other hand, the rather low proportion (4 to 25%) of di-deuterated molecules indicates that the main process does not occur by a direct addition of the deuterium molecule to the olefin. These results clearly show that there is an isotopic dilution of the hydrogen and deuterium atoms at the catalytic surface and that the

catalytic reaction occurs between the hydrocarbon and one hydrogen or deuterium atom, both adsorbed at the catalytic surface.

Let us analyze the results obtained for these two catalysts at the same conversion level (ca. 50%): the A$_1$ catalysts, the most selective ($S = 97.7$%) and the most active for the isomerization reaction (TOF$_i = 21.3$ s^{-1}), produce the highest ratio of nondeuterated isomers (more than 95%), while the B$_1$ catalyst, which is less selective (71.8%) and less active for the isomerization reaction (TOF$_i = 4.5$ s^{-1}), produces only 65% of nondeuterated isomers. The latter catalyst, which is the most active for the hydrogenation reaction (TOF$_h = 3.2$ s^{-1}), produces the highest percentage of deuterated but-1-ene (exchange reaction) and the highest ratio of deuterated isomers. It happens as if on A$_1$ catalyst the hydrogen from the gas phase would have difficulties to react, then the hydrogenation, exchange, and isomerization with deuterium introduction would be limited, while the isomerization, which uses no hydrogen atom from the gas phase, would be favored.

To sum up, we can say that the number of deuterium atoms introduced in the reaction products is much lower for the A$_1$ catalyst than for the B$_1$. However, even for this latter catalyst, one introduces statistically less than one deuterium molecule per butane molecule ($\Sigma i \mathrm{d}_i = 0.9$; d$_i$, molecules containing i deuterium atoms).

Applied to but-1-ene, the well known Horiuti–Polanyi (HP) mechanism (15) describes together the addition reactions, the exchange of but-1-ene (H to be replaced by D), and the isomerization to deuterated products (see Fig. 4).

Analyzing the deuterium location in but-1-ene, it has been shown (16–18) that, on palladium, the deuterium is
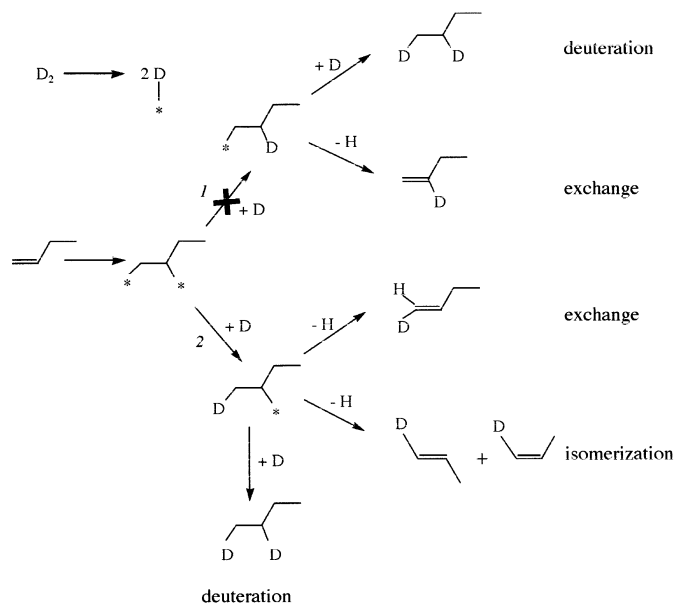

FIG. 4. Horiuti–Polanyi (HP) mechanism.

localized, for 90%, on carbon number 1. Hub (18) has determined that this specific place was due to the preferential formation of half-hydrogenated secondary butyl radicals; therefore the pathway number 1, described on the Horiuti–Polanyi mechanism (Fig. 4), is not favored on palladium.

On the other hand, to explain large amounts of d_0 and d_1 butane molecules, one must suppose an isotopic dilution of hydrogen and deuterium atoms at the catalytic surface when the addition reaction occurs (19). The difference between the number of hydrogen atoms involved in the addition process and the number of deuterium atoms substituted for the hydrogen atoms is actually positive. The hydrogen atoms lost by the molecules are, for a large part, involved in the hydrogenation process and are not balanced by the deuterium from the gas phase. Therefore, when the catalytic surface is covered with olefin, the equilibrium, $(D_2, HD, H_2)_{gaz} \rightleftharpoons (H, D)_{adsorbed}$, does not exist.

If one considers an isotopic dilution of the deuterium and hydrogen atoms on the catalytic surface and a mechanism taking place by the addition of two adsorbed atoms, H or D, the ratio of the different isotopes of butane can be calculated. If x is the percentage of deuterium atoms adsorbed at the catalytic surface, $(1 - x)$ is the percentage of hydrogen atoms on the same surface. The probabilities to obtain the different isotopes are given by

$$C_4H_{10}(d_0) = (1 - x)^2, \quad C_4H_9D(d_1) = 2x(1 - x),$$
$$C_4H_8D_2(d_2) = x^2.$$

Thus,
$$\frac{d_0}{d_1} = \frac{(1 - x)}{2x} \quad \text{or} \quad x = \frac{d_1}{(2d_0 + d_1)}.$$

Hence one obtains the calculated distribution in d_0, d_1, and d_2 indicated by $d_{0calc.}$, $d_{1calc.}$, and $d_{2calc.}$, given for a statistical distribution of deuterium and hydrogen atoms at the catalytic surface determined by x.

The results given in Table 4 indicate that the proportion of d_2 is underestimated by this calculation. This means that the estimated amount of deuterium at the catalytic surface, which is in accordance with the d_0/d_1 ratio, is too low to explain the formation of the quantity of d_2 butane actually observed ($d_{2exp.} = 24\%$ and $d_{2calc.} = 10\%$ for the catalyst B_1). The formation of an excess of d_2 butane can be explained if one supposes a nonhomogeneous isotopic distribution at the catalytic surface and, for several regions of this surface, a deuterium concentration of 100%. On such sites, only the deuteration reaction would occur, leading directly to the di-deuterated butane. This process would lead to 14% ($= 24 - 10$) of the d_2 production on the catalyst B_1 and to 11% ($= 14 - 3$) on the catalyst A_1.

To sum up, one can describe the nonhomogeneous isotopic dilution by the following scheme. For the A_1 catalyst, 89% of the hydrogenation reaction occurs on sites containing D/H atom ratio equal to 0.23, and 11% occurs on sites

TABLE 4

But-1-ene Hydrogenation: Comparison of Experimental and Calculated Distributions of Non-, Mono-, and Di-deuterated Products in Butane Taking into Account an Isotopic Dilution of Hydrogen and Deuterium Atoms at the Catalytic Surface ($x = D/(H + D)$)

	Catalysts			
	A_1		B_1	
Isotopes	Exp. (%)	Calc. (%)[a] $x = 0.19$	Exp. (%)	Calc. (%)[a] $x = 0.35$
d_0	56	56	37	37
d_1	27	27	39	39
d_2	14	3	24	10

[a] The calculated data are normalized taking into account the butane d_0, d_1.

covered by 100% of deuterium atoms; for the B_1 catalyst, 86% of the hydrogenation reaction occurs on sites containing D/H atom ratio equal to 0.54, and 14% occurs on sites covered by 100% of deuterium atoms.

If the hydrogenation and isomerization reactions occur on the same sites, by the Horiuti–Polanyi mechanism, one can suppose that the isotopic dilution (in hydrogen and deuterium) is the same for both reactions and it is possible to calculate the d_0 and d_1 isomerization ratio obtained by the Horiuti–Polanyi mechanism.

As the but-1-ene isomerization products are, for more than 90%, d_0 and d_1 molecules, one can neglect the participation of the polydeuterated molecules for the calculation of the product distributions. In the Horiuti–Polanyi mechanism, the formation of the half-hydrogenated radical occurs by addition of one deuterium or hydrogen atom, on carbon number 1, losing one hydrogen atom on carbon number 3. This mechanism leads to d_0 and d_1 molecules with the same distribution as the ratio of hydrogen and deuterium atoms present at the catalytic surface, and thus, $d_0/d_1 = D/H$.

Table 5 gives a comparison between experimental and calculated data, these latter being obtained by taking into account the isotopic dilution D/H at the catalytic surface. One obtains experimentally much more d_0 but-2-enes than is predicted by the statistical calculation based on the isotopic dilution at the catalytic surface applied to Horiuti–Polanyi mechanism. These results indicate that a part of the isomers has been produced without any hydrogen or deuterium atom insertion in the molecules, which means that an intramolecular hydrogen shift (IM) takes place in this reaction (Fig. 5). The part of this second mechanism is given by the difference between the but-2-enes values obtained experimentally and by calculation. Such a mechanism has already been proposed by Smith and Swoap (20) to explain the exchange reaction H, D in cyclohexene and has been demonstrated in the case of propene (21) and butene (22) reactions.

TABLE 5

But-1-ene Isomerization: Comparison of the Experimental Results and Calculated Data Taking into Account the Isotopic Dilution D/H

		Catalyst		
		A$_1$		B$_1$
		Calc. $x=0.19$		Calc. $x=0.35$
Isotopes	Exp.	D/H = 0.23	Exp.	H/D = 0.54
trans-but-2-ene				
d$_0$	97	13	81	35
		HP = 16		HP = 54
d$_1$	3	3	19	19
d$_{0\ exp.}$ − d$_{0\ calc.}$	$\Longrightarrow$	IM = 84	$\Longrightarrow$	IM = 46
cis-but-2-ene				
d$_0$	96	17	69	40
		HP = 21		HP = 61
d$_1$	4	4	21	21
d$_{0\ exp.}$ − d$_{0\ calc.}$	$\Longrightarrow$	IM = 78	$\Longrightarrow$	IM = 29

Note. HP, Horiuti–Polanyi; IM, intramolecular hydrogen shift.

Scheme I indicates the distributions obtained for the different mechanisms of hydrogenation and isomerization for A$_1$ and B$_1$ catalysts. While A$_1$ catalyst, in the total reaction, leads to 80% of intramolecular isomerization mechanism, B$_1$ catalyst leads only to 30% of this mechanism. On this latter catalyst, the Horiuti–Polanyi mechanism, which leads to both hydrogenation and isomerization reactions, represents the main part with 70%. The part of deuterium atoms which is inserted in the molecules, compared to the hydrogen atoms, on B$_1$ catalyst, is twice the quantity observed on the A$_1$ catalyst, even though the D/H ratio remains less than one.

The distribution between the two isomerization mechanisms, by intramolecular hydrogen shift or by Horiuti–Polanyi mechanism, is directly related to the relative hydrocarbon and hydrogen coverage at the catalytic surface. If the atomic hydrogen coverage is high, the Horiuti–Polanyi mechanism, in which a determining step is the formation of the half-hydrogenated radical, will be enhanced. If the atomic hydrogen coverage is low, the intramolecular hydrogen shift, which needs no other hydrogen atom than those present in the molecule, will be predominant.

In order to explain the competition between hydrogenation and isomerization reactions, several authors (23, 24)

a) **A$_1$ Catalyst**

mechanism	x = D/(D+H)	reaction	%	D/H
Horiuti-Polanyi	x = 1	hydrogenation	0.3	∞
	x = 0.19	hydrogenation isomerization	2 17 }	0.23
Intramolecular Hydrogen Shift		isomerization	80.7	0

b) **B$_1$ Catalyst**

mechanism	x = D/(D+H)	reaction	%	D/H
Horiuti-Polanyi	x = 1	hydrogenation	3.3	∞
	x = 0.35	hydrogenation isomerization	20.6 45.2 }	0.54
Intramolecular Hydrogen Shift		isomerization	30.9 ·	0

SCHEME I

proposed a classification of the surface metallic sites into corner, edge, or face sites, with respectively 3, 2, and 1 unsaturated degrees (called ^{3}M, ^{2}M, and ^{1}M). The hydrogenation, which leads to the reaction between one adsorbed olefin and two hydrogen atoms, would take place one the ^{3}M sites, the isomerization resulting from the Horiuti–Polanyi mechanism would take place on the ^{2}M sites, and the isomerization resulting from the intramolecular hydrogen shift would take place on the ^{1}M sites. Smith *et al.* (25) applied this concept to explain the modification of the isomerization//hydrogenation ratio observed in the apopinene (+) reaction on palladium catalysts. If we apply this concept to our catalysts, we could assume that the A$_1$ and A$_2$ catalysts present mainly ^{1}M sites (face atoms), while the B$_1$ catalyst would develop a large number of ^{2}M and ^{3}M sites (edge and corner atoms), which would be in good accordance with the characterization of the catalysts (10). The B catalysts contain rather larger particles which generally develop fewer corner and edge atoms than the smallest ones. However, for palladium particles, the situation might be different. The
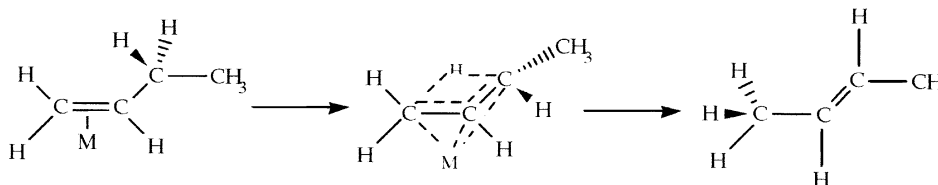
FIG. 5. Intramolecular hydrogen shift mechanism (IM).

catalysts studied here undergo hydrogen treatments which lead to successive hydride formation and destruction for the palladium particles. For particles less interactive with the support, these treatments would lead to cracks in the crystal network (26, 27) and thus to a rugged surface containing ^2M and ^3M sites. Such sites can adsorb the hydrocarbon and the hydrogen atoms. That is why the hydrogenation process is encouraged on this catalyst which gives high TOF_h (4.5 s^{-1} for buta-1,3-diene and 3.2 s^{-1} for but-1-ene). The low isomerization selectivity ($\leq 60\%$) in the but-1-ene reactions and the higher contents of deuterium atoms in the isomers are due to a higher quantity of hydrogen (deuterium) on the active sites. On the other hand, the A catalysts contain particles in strong interaction with the support and thus might develop particular morphology. In fact, several studies on palladium single crystals indicate that, in the buta-1,3-diene hydrogenation, the (111) face is less active than the (110) face. The TOF_h, given by the authors concerned (28–30) and standardized to our experimental conditions are of the same order of magnitude. The A particles might contain mainly (111) faces. These faces (^1M sites) would be covered by hydrocarbons and would have few sites able to dissociate hydrogen. These surfaces are very poor in ^3M sites which would be able to dissociate hydrogen in the presence of hydrocarbons. On such hydrocarbon-covered catalysts, the difficulties to dissociate hydrogen would explain the low TOF_h, both for the buta-1,3-diene (0.35 s^{-1} at 273 K) and for the but-1-ene (0.36 s^{-1} at 273 K). However, it is noticeable that the but-1-ene shows a high isomerization activity (21.3 s^{-1}), which indicates the presence of two different types of sites, one for the hydrogenation and isomerization by the Horiuti–Polanyi mechanism and the other for the isomerization which occurs mainly by intramolecular hydrogen shift (Fig. 6). The sites situated on the (111) faces would be able to promote the intramolecular hydrogen shift leading to butene isomerization reaction. When buta-1,3-diene is the reactant, these sites are no longer active for hydrogenation but they might be covered by species which
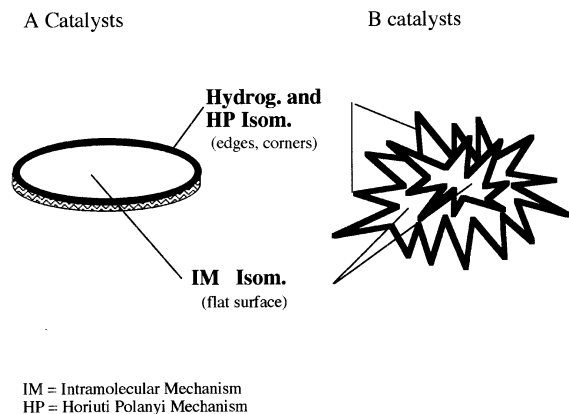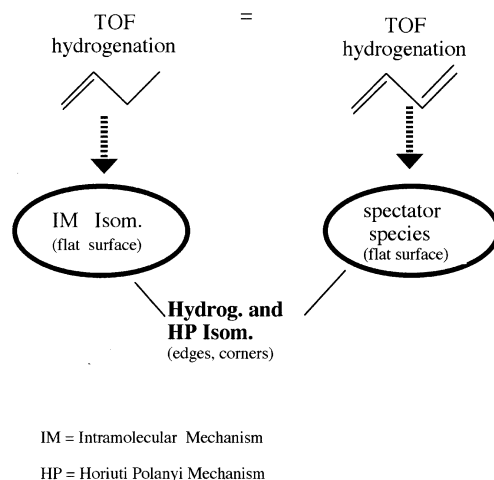

FIG. 7. But-1-ene hydrogenation and isomerization and buta-1,3-diene hydrogenation sites.

act only as spectators. The presence of spectator species in hydrogenation reactions has often been suggested and the structure has even been defined in ethyne, ethene, and butyne hydrogenation (31–33). It is reasonable to assume that this hypothesis is also applicable in butadiene hydrogenation; however, in this case the structure of the spectator species has still to be defined. With this interpretation, we are able to explain the similar rates obtained for the hydrogenation of buta-1,3-diene and but-1-ene, for the two types of catalysts: for both hydrocarbons, the hydrogenation reaction takes place on the corner or edge atoms, for the but-1-ene, the ^1M sites are very active in the isomerization reaction, while for the buta-1,3-diene they are covered by spectator species (Fig. 7). Thus, the number of sites involved in the hydrogenation reaction is the same whatever the hydrocarbon.

CONCLUSION

A coherent explanation concerning the reaction mechanism for the hydrogenation of buta-1,3-diene and the hydrogenation and isomerization of but-1-ene on Pd/α-Al$_2$O$_3$ catalysts emerges from the comparison of reaction rates and using deuterium for a tracer study, as well as chemisorption, TEM, and XPS data. Two types of catalyst, prepared from benzene solutions of Pd acetylacetonate with two different Pd concentrations, were used for this study. From the low concentration solution (0.7 g Pd/l) the particles obtained show a high BE for Pd $3d_{5/2}$, 336 eV, while from the high concentration solution (3.33 g Pd/liters) the Pd particle have 335 eV as their Pd $3d_{5/2}$ BE, similar to bulk Pd. These results were considered to originate not from a particle size effect but from a difference in the nature of the interactions between the metal and the support. In the first catalyst a strong interaction induces the formation of flat monocrystalline

FIG. 6. Hydrogenation and isomerization sites on A and B catalysts.

(111) particles, while the second catalyst contains less inter-active particles (10). The catalytic activity results support these interpretations. On interactive flat particles isomerization reactions would be favored while the noninteractive particles which might present rugged (rough) surfaces after hydrogen pretreatments would preferentially be active for the hydrogenation reaction. The deuterium tracer study shows that the isomerization reaction occurs by two different reaction mechanisms, the Horiuti–Polanyi mechanism with addition of adsorbed hydrogen (deuterium) atoms to form a half-hydrogenated (-deuterated) radical, and an intramolecular hydrogen shift which occurs without addition of hydrogen or deuterium atom; the first mechanism takes place on corner or edge atoms and the second on face atoms. Thus, palladium particles in strong interaction with alumina present high activity for isomerization of but-1-ene and low hydrogenation activity for buta-1,3-diene and but-1-ene, with an identical value for both hydrocarbons. The numerous (111) face atoms in this type of catalyst are fully covered by tightly adsorbed hydrocarbon molecules and accordingly have no places left for hydrogen dissociation; on these sites but-1-ene molecules are transformed into but-2-enes (IM isomerization) while butadiene molecules are standing as spectator molecules. On the other hand the catalyst with less interactive particles presents rough surfaces and permits high hydrogenation and comparatively lower isomerization rates.

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