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Low-Loaded Pd–Pb/α-Al_2O_3 Catalysts: Effect of Alloying in the Hydrogenation of Buta-1,3-diene and Hydrogenation and Isomerization of Butenes

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Butadiene hydrogenation, butene isomerization, and hydrogenation reactions were studied on low-loaded Pd–Pb/α-Al_2O_3 catalysts and the results were compared with those previously obtained on Pd/α-Al_2O_3 catalysts (Goetz *et al., J. Catal.* 164, 369 (1996)). A deuterium tracer study was used to investigate the reaction mechanisms. The studied catalysts exhibited different catalytic properties which were related to physicochemical characteristics already described (Goetz *et al., J. Catal.* 167, 314 (1997)). Catalysts with a low metal content (bi-or monometallic) containing particles in strong interactions with the support promoted mainly the isomerization reaction, occurring by intramolecular hydrogen shift, with a rate proportional to the number of Pd surface atoms. The low hydrogenation activity observed on these particles was not affected by lead addition. In contrast, the addition of lead to Pd/α-Al_2O_3 with a high metal content, containing rugged particles noninteractive with the support, induced a decrease in hydrogenation and an increase in isomerization rates. These observations are well explained assuming a decrease in hydrogen coverage due to an alloying effect. The Pd–Pb alloy would also be responsible for the superior semi-hydrogenation selectivity observed at high conversion in butadiene hydrogenation. © 2001 Academic Press

Key Words: **Pd–Pb alloyed particles; butadiene hydrogenation; butene hydrogenation; isomerization–hydrogenation mechanisms; butene deuteration; bimetallic catalysts.**

INTRODUCTION

Although palladium is the most used catalyst for the semi-hydrogenation reaction of alkynes and dienes due to its outstanding intrinsic selectivity, its catalytic performances can be improved by the addition of a second metal. Several bimetallic supported catalysts have been reported to be more selective than the corresponding unmodified palladium catalysts (1–5). Even a slight increase in selectivity is considered a significant modification, since the demand in the purity of products is very high.

Bimetallic supported systems consisting of palladium and lead have been reported to be highly selective catalysts for the hydrogenation of triple or conjugated C=C bond compounds either in homogeneous (6–8) or in heterogeneous phase (9–12). However, the reason why lead improves the desired selectivity is not well understood. It is not clearly established whether the second metal plays a role in the catalytic process or if it merely modifies the catalyst surface. A controversy about the role of lead is reflected in several publications (13–15).

In previous studies (16–18), we have extensively characterized unmodified Pd/α-Al_2O_3 samples by transmission electronic microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and chemisorption of CO and H_2 and tested them for the hydrogenation of buta- 1,3-diene and but-1-ene as well as the isomerization of but-1-ene reactions. We have also characterized a series of Pd–Pb/α-Al_2O_3 catalysts by the same techniques (in addition to Fourier transform infrared spectroscopy (FTIR) of adsorbed CO (16, 19)); the physicochemical characteristics of the bimetallic particles were determined from these results. Taking into account this background, we have tested the Pd–Pb/α-Al_2O_3 system for the title reactions in order to make comparisons between mono and bimetallic catalysts and to attempt to determine the basic Pd–Pb structure favoring the selective hydrogenation, thus providing a background for the rational design of a selective hydrogenation catalyst.

The main physicochemical characteristics of these catalysts have been presented in previous publications (17–19). Two types of Pd catalysts supported on α-Al_2O_3 were prepared from $Pd(AcAc)_2$ (palladium *bis*-acetylacetonate) using solutions with different concentrations of the complex precursor. One catalyst, named A, was prepared from a low concentrated complex solution and contains Pd particles grown in epitaxy with the support; they are essentially composed of (111) faces. The second, named B, was prepared from a higher concentrated complex solution and is composed of Pd particles rich in stepped and kinked sites, showing no interaction with the support. The difference in

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the nature of particle–support interactions between A and B catalysts was evidenced by an increase in the binding energy of XPS core levels of samples A with respect to the corresponding binding energy of samples B. These morphological characteristics influence the catalytic pattern of Pd/α-Al_2O_3 catalysts for hydrogenation and isomerization reactions. High hydrogenation and low isomerization activities are observed on the B catalyst; in contrast, on the A catalyst, isomerization reactions are favored over hydrogenation reactions.

In order to obtain bimetallic catalysts, the introduction of lead was carried out by reaction of an organic solution of *n*-tetrabutyllead with the base monometallic catalysts. It was established that lead atoms are not located on the highly unsaturated surface Pd sites (kinks, corners, edges) but on the terraces, forming an alloy. For A samples, the formation of the alloy is restricted to the surface, since the interaction with the support prevents Pb penetration. In the case of B catalysts, lead penetrates more deeply inside the bulk of the particle giving a concentration gradient from the surface to the bulk. Thus, two types of bimetallic Pd–Pb crystals may be prepared, depending on the nature of the base monometallic catalysts. It was also determined that a certain amount of lead remains at the noble metal–alumina interphase as lead oxide. This species, inactive for hydrogenation reaction, will not be considered for the purpose of the present study.

In this work, the catalytic behavior of two bimetallic catalysts are studied: Pd (0.09 wt%)–Pb (0.05 wt%)/α-Al_2O_3 (named A_1) and Pd (0.30 wt%)–Pb (0.12 wt%)/α-Al_2O_3, (named B_1), prepared respectively from the base A and B monometallic catalysts previously characterized (19). All samples have low metal loadings in order to resemble industrial catalysts. They have been tested for the hydrogenation of buta-1,3-diene, and hydrogenation and isomerization of butenes. Both, the activity and selectivity were measured and compared with the corresponding base monometallic catalysts in order to determine how the introduction of lead modifies the catalytic pattern of palladium. We have tried to establish a relationship between the available model for the Pd–Pb/α-Al_2O_3 system and its catalytic behavior.

EXPERIMENTAL

Catalytic Tests

The title reactions were carried out in a stainless steel reactor operating under atmospheric pressure and at constant temperature, 273 K. Catalysts were pretreated at 573 K during 1 h and cooled down to the reaction temperature under a H_2/He (5/100) mixture. Subsequently, a partial pressure of hydrocarbon (7 torr) was carried over the catalyst by a H_2/He flow. The gas flow was controlled by a flowmeter and was adjusted by changing the pumping rate at the end of the flow line. The stability of the hydrocarbon partial pressure and the time on stream were controlled by two katharometers inserted before and after the reactor. The reaction products were drawn off the flow line and analyzed by gas–liquid chromatography (GLC). At the beginning of a run, a period of transient behavior was observed: the conversion decreased to reach a "steady state" value where data were obtained. Calculations using the Weisz–Prater criterion (20) for internal diffusion and the Anderson criterion (21) for heat transfer limitations showed that there was no influence of mass and heat transfer on reaction kinetics, even at high conversions. We conclude, therefore, that our experimental data correspond to intrinsic kinetics.

The activity and selectivity of all samples for hydrogenation and isomerization reactions were then measured. The mass of the catalyst (W) and the molar flow of the hydrocarbon (F) were adjusted in order to obtain low conversion values ($\alpha < 15\%$) in the steady state regime and to calculate the rate of a given reaction as moles of hydrocarbon converted per gram of palladium and per second ($\alpha F/W$). The turn over frequency (TOF), moles of hydrocarbon converted per second and per exposed Pd atom was calculated

TABLE 1

Activity for Pd–Pb (0.05–0.09 wt%) (A_1) and Pd–Pb (0.3–0.12 wt%) (B_1) and Their Corresponding Monometallic Catalysts in (a) buta-1,3-diene, but-1-ene, and but-2-enes Hydrogenation, and (b) but-1-ene and but-2-enes Isomerization

(a)	$Rate_h * 10^6$ (moles/s/gcata)		TOF_h (s^{-1})	
	A_1 : Pd–Pb	A : Pd	**A_1 : Pd–Pb ($D^a = 0.19$)**	A : Pd ($D = 0.54$)
buta-1,3-diene	**1.7**	1.6	**1.0**	0.35
but-1-ene	**1.0**	1.66	**0.62**	0.36
trans but-2-ene	**0.11**	0.10	**0.07**	0.02
cis but-2-ene	**0.66**	0.78	**0.41**	0.17
	B_1 : Pd–Pb	B : Pd	**B_1 : Pd–Pb ($D = 0.10$)**	B : Pd ($D = 0.26$)
buta-1,3-diene	**9.1**	32.8	**3.6**	4.5
but-1-ene	**4.7**	23.4	**1.9**	3.2
trans but-2-ene	**1.3**	6.6	**0.5**	0.9
cis but-2-ene	**1.9**	5.6	**0.75**	0.70

(b)	$Rate_i * 10^6$ (moles/s/gcata)		TOF_i (s^{-1})	
	A_1 : Pd–Pb	A : Pd	**A_1 : Pd–Pb ($D^a = 0.19$)**	A : Pd ($D = 0.54$)
but-1-ene	**44.0**	97	**27.4**	21.3
trans but-2-ene	**2.0**	11	**1.3**	2.4
cis but-2-ene	**8.2**	22.4	**5.1**	4.9
	B_1 : Pd–Pb	B : Pd	**B_1 : Pd–Pb ($D = 0.10$)**	B : Pd ($D = 0.26$)
but-1-ene	**20.0**	33.3	**7.9**	4.5
trans but-2-ene	**3.4**	4.8	**1.3**	0.7
cis but-2-ene	**1.9**	5.6	**3.3**	1.4

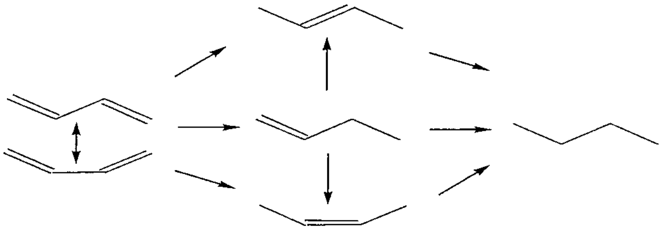
[a] D = fraction of surface Pd atoms measured by H_2 chemisorption $(H/Pd)_{irr}$.

using the H_2 chemisorption values shown in Table 1 (17, 19). For both the rate and the TOF, indexes h and i refer to hydrogenation and isomerization reactions, respectively. The selectivities toward olefins, S, were calculated as the ratio between the amount of semi-hydrogenation products (for butadiene hydrogenation) or butene isomers (for butene hydrogenation) and the total amount of products. The dependence of the selectivity S on conversion was also determined in order to compare the results at high conversion values; high conversions were obtained by decreasing the hydrocarbon flow rate.

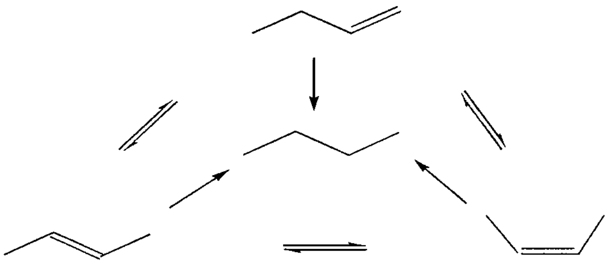
In an additional experiment, a deuterium tracer study was carried out. Rectangular pulses of but-1-ene carried by a purified D_2/He (5/100) mixture were admitted to the reactor. Products were analyzed by GLC and mass spectrometry according to the proper procedures described in detail elsewhere (18).

RESULTS AND DISCUSSION

The following schemes describe the reactions involved in the present study.



SCHEME 1. Buta-1,3-diene hydrogenation: overall reaction network according to (22).



SCHEME 2. Butene hydrogenation and isomerization.

In Table 1 we have reported the rates and TOF of mono and bimetallic catalysts for the reactions mentioned above.

First, we will present and discuss the results of hydrogenation reactions (Table 1a). We have reported the rate$_h$ for the hydrogenation of buta-1,3-diene, but-1-ene, and but-2-enes over Pd–Pb/α-Al_2O_3. For the sake of comparison, the activity of the base monometallic catalysts has also been presented (results taken from (18) for butadiene and but-1-ene reactions). It can be observed that the addition of lead to A catalyst does not alter significantly the rate$_h$ values (per unit mass of catalysts). The hydrogenation activities of Pd (0.09 wt%)/α-Al_2O_3 (A catalyst) and Pd–Pb (0.09–0.05 wt%)/α-Al_2O_3 (A_1 catalyst) are rather meagre compared to B-type catalysts. As proposed in the previous study (18) this fact is related to the low concentration of high unsaturated sites, ^2M (corners) and ^3M (kinks), on the metallic surface which are responsible for hydrogenation reactions; the (111) faces (^1M sites) are covered by spectator butadiene species when butadiene is the reactant or by butene molecules further transformed into isomers when butenes are the reactants. The invariance of the hydrogenation rate, r_h, suggests that the concentration of low coordinated active Pd sites is not modified upon lead addition. This situation arises because lead atoms are not located at the corners or edges of the Pd particles but mainly on the open surfaces performing a dilution of the noble metal surface. This is in agreement with the previous FTIR characterization results (19); we have shown that the CO adsorption spectra after the lead addition exhibit a strong attenuation of bridge bonded CO and an enhancement of linear CO which is shifted to a lower frequency due to adsorption on Pd atoms with a high coordination number. Regarding the TOF$_h$ values in Table 1, a two- to three fold increase is observed after addition of lead. This result is simply due to the change in the fraction of exposed Pd atoms; the replacement of Pd atoms by Pb on the open surfaces produces a dilution of inactive Pd sites. Consequently the intrinsic catalytic activity of low-coordinated Pd atoms is not modified. Regarding the other bimetallic catalyst, Pd–Pb (0.30–0.12 wt%)/α-Al_2O_3 (B_1), it is observed that it is considerably less active for the hydrogenation of C_4 hydrocarbons than the base monometallic catalyst (B). However as mentioned above, the r_h values are much higher than those of samples A and A_1. Sample B has been reported to be highly active for hydrogenation reactions due to its rugged surface (18). Despite the rather large Pd particle size, this sample contains a high number of ^2M and ^3M sites that promote hydrogen adsorption and dissociation. The roughness of this sample comes from the hydrogen treatments, which introduce cracks in the crystal network by successive formation and destruction of Pd hydride. Upon lead addition the activity is reduced by a factor of 3–5, depending on the reaction considered, which is close to the change in the fraction of exposed Pd atoms. Consequently the TOF$_h$ values are only slightly affected.

Turning the attention to the isomerization rates (Table 1b) one first observes that they are higher than hydrogenation rates for all C_4 hydrocarbons, on all samples. This is an expected result. The most active sample is A, and its behavior is assigned to the predominance of (111) surfaces (^1M sites) as already explained (18). When Pb is incorporated into this sample, the activity clearly decreases. The change in rate is approximately compensated by the reduction in the fraction of exposed Pd atoms which leads to

TABLE 2

Isomer and Semi-hydrogenation Selectivity in, Respectively, Butene and Butadiene Hydrogenation on Pd–Pb (0.05–0.09) (A_1) and Pd–Pb (0.3–0.12) (B_1) and Their Corresponding Monometallic Catalysts

	S (%)	
reactant	**A_1 : Pd–Pb**	A : Pd
but-1-ene	**98.3**	98.7
trans but-2-ene	**95.0**	99.0
cis but-2-ene	**92.5**	96.6
buta-1,3-diene	**99.6**	99.5
	B_1 : Pd–Pb	B :Pd
but-1-ene	**82.0**	59.0
trans but-2-ene	**73.3**	42.0
cis but-2-ene	**81.3**	65.0
buta-1,3-diene	**99.7**	99.4

similar TOF_i values. Here again the specific activity of Pd is not modified by Pb addition to sample A. On the Pd–Pb(0.30–0.12 wt%)/α-Al_2O_3 catalyst (sample B_1) the decrease in isomerization rate with the addition of lead is less marked. This moderate change in rate and the threefold decrease in the fraction of exposed Pd atoms are reflected in TOF_i values that are higher for the bimetallic sample. The TOF_i for sample B_1 is twice that of sample B.

The variations of the butene isomerization and hydrogenation rates on A- and B-type catalysts are clearly expressed by examining the isomer selectivity factor (Table 2), which is defined as follows: $S = (100^*$ isomer products)/(isomer + hydrogenated products). For samples A and A_1, the low hydrogenation rates are not modified by lead addition and the isomerization rates decrease but remain high; consequently, the selectivity exhibits very high values. On the other hand for sample B, lead addition decreases the rate of bu-1-ene hydrogenation by a factor of five, while for the isomerization reaction, only a 50% decrease is observed. The trend is similar for the other hydrocarbons, though to a lesser extent. Therefore, modifications in selectivity are expected when comparing mono and bimetallic samples: the selectivity to olefins for Pd–Pb (0.30–0.12 wt%)/α-Al_2O_3 is much higher than that of Pd (0.30%)/α-Al_2O_3. In this case it seems that a simple dilution effect could not be invoked to explain the results. Therefore, an electron interaction between Pd and Pb is proposed. At this point, considerations on butene hydrogenation and isomerization mechanisms must be taken into account to further explore the influence of the addition of lead to palladium on the different reaction rates. Consequently, we have performed tracer studies using deuterium instead of hydrogen gas.

Study of but-1-ene Deuteration on B-Type Catalysts

The but-1-ene-deuterium reactions were carried out over Pd–Pb (0.3–0.12 wt%)/α-Al_2O_3 and the results were compared with those obtained on the corresponding monometallic catalyst. The rates of deuteration and isomerization and the isomer selectivities are presented in Table 3. Upon the addition of lead, a decrease of both the rate of deuteration and the rate of isomerization was observed; the former reaction being more affected than the latter. Consequently, the isomer selectivity is higher on the bimetallic than on the monometallic as observed under H_2 flow. However, it could be noticed that on both mono- and bi-metallic catalysts, the selectivity is higher when D_2 is used instead of H_2.

TABLE 3

Rate of Isomerization and Deuteration of But-1-ene on Pd–Pb (0.3–0.12 wt%) (B_1) and Its Corresponding Monometallic Catalyst

	B_1 : Pd–Pb	B : Pd		**B_1 : Pd–Pb**	B : Pd
$Rate_d * 10^6$ (mol/s · gcata.) ($\alpha = 26\%$)	**0.43**	10	TOF_d (s^{-1})	**0.16**	1.36
$Rate_i * 10^6$ (mole/s · gcata.) ($\alpha = 25\%$)	**9**	31.7	TOF_i (s^{-1})	**3.35**	4.34
Isomer selectivity (%)	**95.4**	76.1			

The deuterium atom distributions in the reaction products, namely butane, *cis* and *trans* but-2-enes, and but-1-ene have been determined and are reported in Table 4

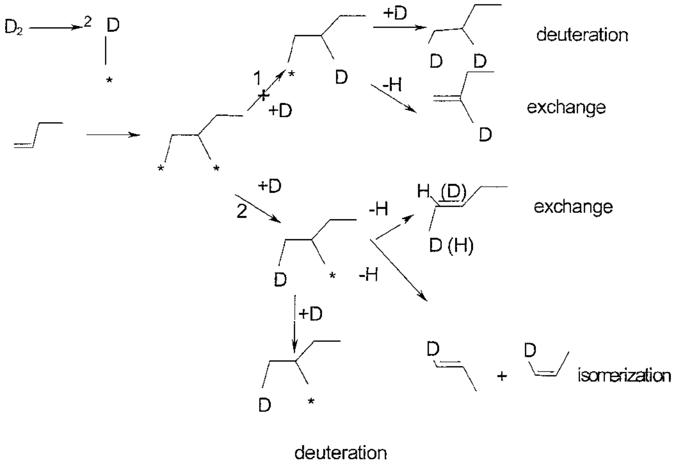
TABLE 4

Isotopic Distributions in Deuteration of But-1-ene on B_1 Catalyst

Hydrocarbon	Pd/α-Al_2O_3 conversion		Pd–Pb/α-Al_2O_3 conversion	
	51%	26%	40%	25%
Butane				
C_4H_{10}	35	37	64	66
C_4H_9D	40	39	28	24
$C_4H_8D_2$	25	24	8	7.5
$C_4H_7D_3$		1	1	1.5
$C_4H_6D_4$			<1	1
But-1-ene				
C_4H_8	88	97	98	99
C_4H_7D	10	3	2	1
$C_4H_6D_2$	2	<1	<1	
Trans but-2-ene				
C_4H_8	66	76	93	94
C_4H_7D	25	18	6	5
$C_4H_6D_2$	9	6	1	1
$C_4H_5D_3$			1	<1
Cis but-2-ene				
C_4H_8	64	69	91	92
C_4H_7D	26	21	7	7
$C_4H_6D_2$		7	1	1
$C_4H_5D_3$		3	<1	<1
$C_4H_4D_4$		<1		

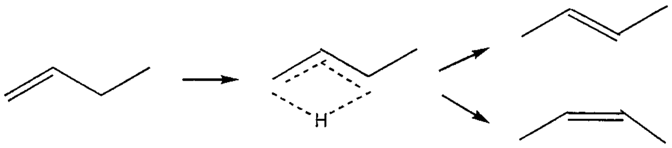
for two different conversion levels. It can be seen that, whatever the conversion (25 or 50%), the distributions are similar and the consecutive reactions can be omitted. In addition, a relatively high concentration of nondeuterated products (butane and but-2-ene) was found for mono and bimetallic catalysts. The concentration was always higher on the bimetallic sample. Taking into account that no hydrogen is available from the gas phase, one can postulate that the hydrocarbon molecules are the source of hydrogen. Besides, the quite low proportion of di-deuterated molecules shows that the direct addition of D_2 to the double bond does not occur, but the reaction proceeds essentially between the adsorbed hydrocarbon and adsorbed hydrogen and deuterium atoms. These results strongly suggest that isotopic dilution of the hydrogen and deuterium atoms takes place at the catalytic surface as already postulated by Burwell many years ago (23). This isotopic dilution is much more in favor of hydrogen on the bimetallic as on the monometallic catalyst. This suggests that the adsorption of deuterium atoms at the catalyst surface from the gas phase is in some way limited in the presence of lead.

Before discussing these results further, it is important to recall the mechanisms of the different reactions that but-1-ene accomplishes under D_2. The well-known Horiuti–Polanyi (HP) mechanism (Scheme 3) describes together the deuteration, the exchange, and the isomerization reactions.



SCHEME 3. Formal Horiuti–Polanyi scheme for the reactions of but-1-ene and D_2 (18).

But-1-ene isomerization may also occur due to an intramolecular hydrogen shift (IM) (Scheme 4). Smith and Swoap (24) were the first to propose such a reaction intermediate in hydrogen deuterium exchange of cyclohexene, which was later proposed to be involved in propene (25) and butene (26) double bond migration mechanism.



SCHEME 4. Intramolecular hydrogen shift mechanism (IM).

The HP mechanism involves the addition of one or two deuterium (hydrogen) atom(s) while no deuterium atom is involved in the IM mechanism. It is then reasonable to consider that a high deuterium (hydrogen) coverage will favor the HP mechanism and inversely the intramolecular hydrogen shift will take place on a surface free of deuterium (hydrogen) adsorbed species.

From the data of Table 4 it is possible to estimate the percentages of the different mechanisms involved in the deuteration–hydrogenation and isomerization reactions. These results are shown in Table 5 for mono and bimetallic samples (see (18) for more details). Assuming a statistical distribution of H and D atoms in the butane molecules formed by the HP mechanism, the isotopic dilution $(x = D/D + H)$ can be deduced from the d_0/d_1 butane ratio, $(1-x)^2/x(1-x)$. However, if one further calculates the statistical d_2 value $(=x^2)$ it is always found to be slightly smaller than the observed values. For this reason, we have considered an additional HP mechanism introducing 2 deuterium atoms $(D/(D+H)=1)$. However, it must be noted that the participation of this second HP mechanism is small. Neglecting this last HP mechanism, the isotopic dilution (x) can be further used to calculate the d_0/d_1 ratio, $(1-x)/x$, of isomer olefins (HP isomerization). The d_0 value estimated this way is far from the observed d_0 isomer value. The excess of nondeuterated isomer molecules is produced by the

TABLE 5

Percentage of Different Reactions Occurring over Pd and Pd–Pb/α-Al_2O_3 in But-1-ene-D_2 Reactions

Mechanism	%	TOF (s^{-1})
Pd/α-Al_2O_3		
HP hydrogenation		
$(D/D+H)= 0.35)$	20.6	1.17
$(D/(D+H)=1)$	3.3	0.19
HP isomerization		
$(D/D+H)=0.35)$	45.2	2.58
Intramolecular isomerization	30.9	1.76
Pd–Pb/α-Al_2O_3		
HP hydrogenation		
$(D/D+H)= 0.15)$	4.4	0.153
$(D/(D+H)=1)$	0.2	0.007
HP isomerization		
$(D/D+H)=0.15)$	36.2	1.28
Intramolecular isomerization	58.2	2.07

intramolecular hydrogen shift mechanism. For the bimetallic catalyst, it is important to note that only 15% of the deuterium atoms (D/D + H), coming from D_2 dissociation, are involved in the HP reactions depicted in Scheme 3. The rest, 85%, is represented by hydrogen atoms coming from the hydrocarbon molecules. Over the monometallic catalyst these proportions are quite different: 35% for deuterium and 65% for hydrogen. This result also suggests that the concentration of deuterium atoms at the metal surface is lower for the bi- than for the monometallic catalyst. Consequently, hydrogenation pathways are less probable in the bimetallic sample than in the unmodified catalyst and the intramolecular shift mechanism is much more important in the case of the modified catalyst (58.2%) than when the monometallic catalyst is used (30.9%). It can also be seen that the TOF_i values corresponding to the intramolecular isomerization, 1.76 and 2.07 for the base and modified catalysts respectively, are not very different due to the fact that deuterium atoms do not participate in the reaction mechanism. In contrast, TOF_i values corresponding to the HP isomerization, which involves the addition of one deuterium atom, vary more, 2.58 and 1.28, respectively, for Pd and Pd–Pb samples.

In summary, the low concentration of adsorbed deuterium atoms is responsible for the main differences between mono and bimetallic samples. Thus, we can postulate that the role of lead is to decrease the amount of chemisorbed hydrogen (deuterium) coming from H_2 (D_2) gas during the reaction. In other words, the formation of an alloy introduces strong Pd–Pb interactions, which renders the exposed metallic surface less reactive toward the adsorption of deuterium (or hydrogen). The effects of the addition of lead to palladium in hydrogen thermodesorption experiments were reported by Sandoval and Gigola (27), for catalysts similar to those studied in the present work, and by Paal *et al.* (28) for polycristalline palladium. In both studies, the authors concluded that lead influences the hydrogen chemisorption in such a way that the intensities of the desorption peaks observed at high temperature on the monometallic sample disappears on the bimetallic. In fact, in palladium, several adsorbed and absorbed atomic hydrogen species were evidenced by hydrogen thermodesorption experiments (29); however it is not clear which species are involved in the hydrogenation process (30). In this present study, an unusually large isotopic effect, TOF_H/TOF_D, was observed on the bimetallic catalyst (1.36/0.16) while, on the monometallic catalyst, a TOF_H/TOF_D value similar to those already reported (31) was found (3.2/1.9). Thus, the large isotopic effect observed upon the addition of lead reveals that the population of reactive deuterium atoms compared to equivalent hydrogen atoms, when D_2 is used instead of H_2, is much lower on the bimetallic catalyst than on monometallic catalyst. This could be interpreted assuming that the hydrogen (deuterium) atoms which participate in the hydrogenation process are localized at the subsurface region, as already postulated in the H_2 desorption mechanism (29). Eley and Pearson (32), comparing the hydrogen and the deuterium sorption, concluded that the rate of solution of deuterium, determined by its permeability constant, is less than that for hydrogen. Therefore, although palladium hydride is formed in both mono- and bimetallic catalysts, we could speculate that the penetration of deuterium through the surface, compared to hydrogen, is in some way restricted when lead is present. In this way, a strong isotopic effect arises on the bimetallic catalyst. To support this explanation it would be interesting to compare hydrogen and deuterium thermodesorption experiments.

Otherwise, it has been calculated that the electronic population at the Fermi level (33) is lower for Pd_3Pb than for Pd aggregates. If the same situation is present in our alloyed particles, different chemisorptive properties could be expected, that is, a decrease in the adsorption energy of hydrogen when palladium is alloyed with lead.

At this point, it is important to note that lead introduces modifications in the activity and selectivity for the title reactions on the Pd–Pb (0.30–0.12%) catalyst, while the catalytic pattern of the Pd–Pb (0.09–0.05%) sample is not influenced by alloy formation. This occurs because the promoted mechanism on this catalyst is the intramolecular hydrogen shift, which is not influenced by deuterium (hydrogen) atom coverage.

Selectivity in Butadiene Hydrogenation on B-Type Catalysts

The olefin selectivity values in butadiene hydrogenation, obtained for low butadiene conversion, are reported in Table 2. As expected on Pd catalysts, these selectivity values are very high and even higher on the bimetallic catalysts, although the increase is very small. Obviously, as high yields of products are desired, it is interesting to study the dependencies of selectivity as a function of conversion. Then, we have measured the selectivity at increasing conversion for the hydrogenation of buta-1,3-diene over the base A and B catalysts and the corresponding bimetallic systems (Fig. 1). We observed that up to a conversion limit, the selectivity is constant and then decreases. It is very interesting to note that this limit depends on the catalyst and reaches a higher value (>95%) on the bimetallic compared to monometallic catalysts. This good performance of bimetallic catalysts can be explained considering that they favor the isomerization of butene intermediates with regard to their hydrogenation. Taking into account the mechanisms described in Schemes 1–4 and the deactivation phenomenon it has been possible to advance a kinetic model with a series of parameters describing the selectivity in the whole range of conversions (22).

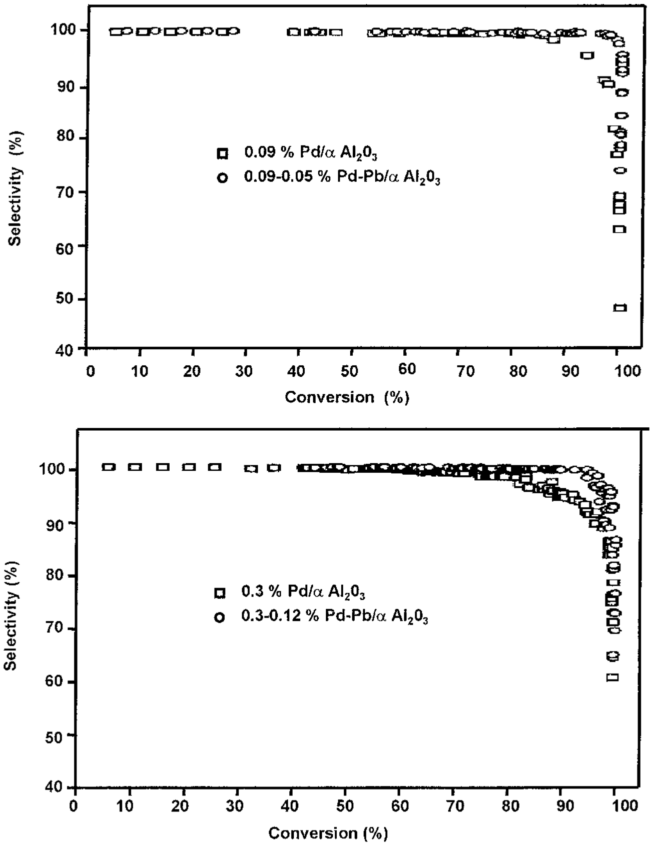


FIG. 1. Selectivity (%) as a function of conversion (%) in butadiene hydrogenation on (a) ☐ 0.09% Pd/α-Al_2O_3, ○ 0.09–0.05% Pd–Pb/α-Al_2O_3; (b) ☐ 0.3% Pd/α-Al_2O_3, ○ 0.3–0.12% Pd–Pb/α-Al_2O_3.

CONCLUSION

In this study, we have compared the reactivity of two Pd–Pb bimetallic catalysts with their corresponding Pd monometallic catalysts in hydrogenation of butadiene and isomerization–hydrogenation of butenes. We estimated the proportions and the reaction rates of the different mechanisms, the Horiuti–Polanyi (HP) type mechanism which is common for hydrogenation, isomerization and H,D exchange, and the intramolecular hydrogen shift mechanism (IM). It clearly appeared that the competition between these different mechanisms depends on the surface hydrogen coverage and then on the geometric and electronic structure of the metal particles. This reactivity study reinforces the model of the supported bimetallic particles which were deduced from different physical characterisation methods and reported in (19). The Pd particles, flat shaped, in interaction with alumina promote mainly the butene isomerization by the intramolecular hydrogen shift, a mechanism which does not require the participation of hydrogen from the gas phase. This mechanism is not influenced by any Pd–Pb alloying effect; only the reactivity decreases by dilution of the number of surface Pd atoms. In contrast, the rugged particles, loosely bonded to the support, favor the reactions occurring by HP mechanism. Their reactivity is largely affected when lead is added. The isomerized products are favored at the expense of the hydrogenated products or, in more explicit manner, the IM mechanism is favored at the expense of the HP mechanism. This reflects a decrease of the surface hydrogen coverage that originated from electronic interactions between Pd and Pb. It is worthwhile to emphasize that consequently the bimetallic catalysts, Pd–Pb/α-Al_2O_3, promote a higher selectivity at high conversion for butadiene hydrogenation, which is an important result from an industrial point of view.

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