

Liquid-Phase Selective Hydrogenation of Hexa-1,5-diene and Hexa-1,3-diene on Palladium Catalysts. Effect of Tin and Silver Addition

Emerson Andrade Sales,* Mario de Jesus Mendes,† and François Bozon-Verduraz‡¹

**Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, 40170-290 Salvador, Bahia, Brazil;* †*Faculdade de Engenharia Química, Unicamp, C.P. 6066, 13083-970 Campinas, São Paulo, Brazil;* ‡*Laboratoire de Chimie des Matériaux Divisés et Catalyse, Université Paris 7-Denis Diderot, case 7090, 2, place Jussieu, 75251 Paris Cedex 05, France*

Received March 5, 2000; revised June 13, 2000; accepted June 13, 2000

The liquid-phase hydrogenation of hexa-1,5-diene and hexa-1,3-diene on alumina-supported palladium catalysts is investigated with special attention paid to the effects of tin or silver addition. All catalysts show a global selectivity near 100%; these high values persist at total conversion when the reactant is hexa-1,3-diene but decrease to about 70% in the case of hexa-1,5-diene. In the hexa-1,5-diene hydrogenation, monometallic palladium catalysts give mainly 1-hexene at conversions lower than 80% and E-hex-2-ene at higher conversions. The fractional selectivity to 1-hexene is significantly improved by tin or silver addition; however, significant yields are observed only on Pd–Sn catalysts with a low Sn/Pd atomic ratio (≈ 0.1) and when the intermetallic compound Pd₃Sn is present. On the other hand, in the hexa-1,3-diene hydrogenation, hex-1-ene is preferentially formed on monometallic catalysts with low dispersion; on bimetallic Pd–Sn or Pd–Ag catalysts, the selectivity to E-hex-3-ene is enhanced and this isomer is even predominant up to 100% conversion on the Pd–Sn catalysts containing the Pd₃Sn intermetallic compound. These results are explained by the geometric effect of dilution of Pd atoms, which delays the palladium double-bond isomerization ability. The proposed mechanism suggests that strongly adsorbed alkadienes react with dissolved hydrogen, following a zero-order kinetics. © 2000 Academic Press

Key Words: Pd catalysts; Pd–Sn catalysts; Pd–Ag catalysts; selective hydrogenation; hexa-1,5-diene; hexa-1,3-diene.

1. INTRODUCTION

For the selective hydrogenation of alkadienes and alkynes to alkenes, palladium catalysts have by far proved to be the most active and selective (1–3). Numerous studies have been performed to maximize the selectivity and stability of these catalytic systems, through (i) varying dispersion (4–11), (ii) adding carbon monoxide (8, 9, 12, 13, 16), (iii) changing the nature of the solvent (14, 15); (iv) adding organic bases (15) or sulphur compounds to

the reaction medium (16, 17), (v) controlling the support acidity (18–20), (vi) controlling the metal–support interactions (21–23), and finally (vii) adding a second metal such as silver (2, 24–26), chromium (27, 28), copper (8, 9), lead (29, 30), tin, germanium, and antimony (30).

For the *monometallic* catalysts, the activity was shown to decrease with the crystallite size (4–6, 11), below ca. 5 nm, which was explained by the very strong adsorption of alkadienes and alkynes on low coordination sites, whose proportion increases at high dispersion (5). An alternative explanation takes into account the geometric and electronic effects associated with the small size of palladium particles, e.g., those prepared by atomic beam deposition techniques (11). For the *bimetallic* catalysts, the activity was generally shown to decrease and the selectivity to increase with the second metal addition, which was explained by geometric (8, 9, 29) or electronic (2, 27, 28) effects.

Almost all these studies were realized in the gas phase, mostly for buta-1,3-diene and acetylene hydrogenation, and very few in the liquid phase (5, 23, 26), although some important industrial applications concern C₆₊ unsaturated hydrocarbons, such as the selective hydrogenation of undesirable C₁₁–C₁₃ alkadienes to the alkenes used in the linear alkylbenzene production process.

The aim of this work is to study the selective hydrogenation of hexa-1,3-diene and hexa-1,5-diene, *in the liquid phase*, as model reactions for the hydrogenation of C₁₁–C₁₃ alkadienes on palladium catalysts. Monometallic (Pd) and bimetallic (Pd–Sn and Pd–Ag) alumina-supported catalysts are compared to investigate the effects of tin and silver additives on both activity and selectivity. Previous works have concerned the hydrogenation of hexa-1,5-diene on monometallic palladium catalysts (1, 14).

The preparation of Pd, Pd–Sn, and Pd–Ag alumina-supported catalysts was described previously (31), in addition to the characterization of the solutions used for impregnation and of the solids during all stages of preparation. The characterization of the solid phases by Mössbauer

¹ To whom correspondence should be addressed. Fax: 33-1-44276137. E-mail: bozonver@ccr.jussieu.fr.

studies, temperature-programmed reduction (TPR), and IR spectroscopy of adsorbed CO is presented in Ref. (32). The present paper is devoted to the catalytic performances.

2. EXPERIMENTAL

2.1. Materials

The catalysts preparation and characterization are described elsewhere (31, 32). All catalysts were reduced in flowing hydrogen (30 ml min⁻¹) with a temperature rise of 10 K min⁻¹ up to 773 K. It is important to note that both supports used for impregnation were Alcoa aluminas A-1 (zero point charge = 8.4, pore volume = 0.9 cm³/g) and A-2 (zero point charge = 5.9; pore volume = 0.6 cm³/g) with relatively low surface areas (around 60 m²/g) to minimize undesirable reactions like cracking and skeletal isomerization. Table 1 summarizes the catalyst notation and metal loading.

For catalytic tests, high-purity hexa-1,5-diene, hexa-1,3-diene, predominantly *trans* (E), heptane, and pentane from Aldrich were used.

2.2. Methods

The catalytic tests were performed at 313 K, under 792 Torr of hydrogen pressure (1 Torr = 133.3 N m⁻²). The reactions were carried out in a 100-ml well-stirred slurry-type thermoregulated glass reactor, filled with 50 ml of a ≈2% w/w hexa-1,5-diene or hexa-1,3-diene in heptane solution. The mass of prerduced catalysts varied from 15 to 150 mg. These precautions guaranteed the absence of mass and heat transport limitations. The reaction products were analyzed by gas chromatography using *n*-pentane as an internal standard, with a Delsi Di200 gas chromatograph equipped with a 0.2 mm × 50 m HP-PONA capillary column and a flame ionization detector linked to a Delsi Enica 31 integrator.

TABLE 1

Catalysts Identification and Metal Loading (wt%)

Identification	%Pd	%Sn	%Ag	Sn/Pd or Ag/Pd atomic ratio
01. Pd _{5,0} /A1	5.05	—	—	—
02. Pd _{5,1} Sn _{3,8} /A1	5.14	3.79	—	0.66
03. Pd _{4,9} Sn _{5,0} Et/A1	4.89	4.96	—	0.91
04. Pd _{5,2} Sn _{0,8} /A1	5.17	0.77	—	0.13
05. Pd _{4,9} Ag _{5,1} /A1	4.93	—	5.13	1.03
06. Sn _{4,9} /A1	—	4.93	—	—
07. Pd _{4,6} /A2	4.55	—	—	—
08. Pd _{4,1} Sn _{4,5} /A2	4.12	4.50	—	0.98
09. Pd _{3,8} Ag _{5,2} /A2	3.77	—	5.24	1.37

2.3. Procedure for Hydrogenation

The prerduced catalysts (15–150 mg) were first outgassed for 1 h in the reactor, before treatment with 792 Torr of H₂ at 313 K for 1 h, and this procedure was repeated with a final outgassing before introduction of the reaction medium (50 ml), already saturated with hydrogen, containing the reagent (hexa-1,5-diene or hexa-1,3-diene, ca. 2 wt%), the internal standard (pentane, ca. 1 wt%), and the solvent (heptane). Then, hydrogen was charged up to the operating pressure, 792 Torr, and the first sample was immediately collected, before stirring was begun (2000 rpm).

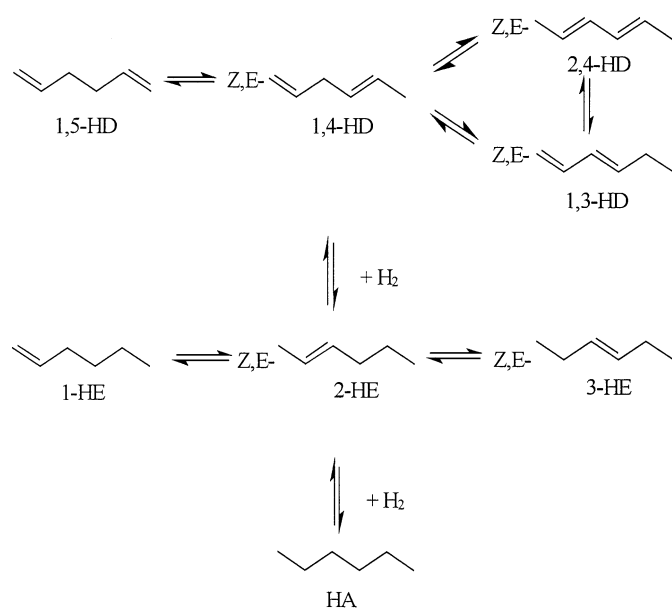
The reaction was carried out at constant pressure (792 Torr), hydrogen being supplied from two interconnected thermostatic vessels of known volumes (0.926 and 1.664 L), filled initially with 980 Torr of this gas. Depending on the rate of hydrogen uptake, one or both vessels were used. This rate was calculated by measuring and recording the vessel pressure fall by means of an ECA-323 absolute pressure sensor.

During the reaction, small samples (ca. 0.2 ml) were collected at regular intervals through a syringe valve equipped with a microfilter. These samples were kept in a freezer and analyzed by gas chromatography (see Section 2.2) to follow the changes of the reaction medium composition.

The catalytic activity was described by initial rate values and conversion versus time curves. Both results obtained from the hydrogen uptake curves and from composition (mol%) versus time curves agreed well. Selectivity values were expressed by the following: (i) the *global* selectivity (S_g), defined as the proportion of reactant (hexadiene) transformed into hexenes; (ii) the *fractional* selectivity (S_f) to a particular hexene (e.g., hex-1-ene, product chosen as a target), defined as *the proportion of this hexene among all hexenes*. The hydrogenation of hexa-1,5-diene (named hereafter 1,5-HD) or of hexa-1,3-diene (1,3-HD) represents a complex system of parallel and consecutive reactions. The main interest here is to observe the distribution of the semi-hydrogenated products, hex-1-ene (1-HE), Z- and E-hex-2-enes (Z2-HE and E2-HE), Z- and E-hex-3-enes (Z3-HE and E3-HE), and also their conversion to hexane (HA) (Scheme 1).

2.4. Thermodynamics of the Process and Transport Limitation Analysis

Mathematical simulations were realized minimizing the Gibbs free energy of theoretical mixtures involving all possible compounds using the Lagrange multipliers for helping convergence. They allow one to determine molar fractions at equilibrium. Upon variation of the temperature in the 313–323 K range (Table 2), the thermodynamic stability sequence of all alkene isomers was kept unchanged as follows: Z2-HE > E2-HE > E3-HE > Z3-HE > 1-HE. In the



SCHEME 1. Possible reactions between the C_6 compounds studied.

presence of the solvent (heptane), HA was the most stable and 1,5-HD the least stable C_6 compound.

To avoid mass transport limitations, some precautions were taken. The powder supports were ground down to the range of 37–44 μm before impregnation to minimize intraparticle transport limitations. Moreover, diluted solutions of the reagents (about 2 wt%), low catalysts loading (15–150 mg/50 ml), low temperatures (standard: 313 K), and high stirring rate (ca. 2000 rpm) were employed for the catalytic tests.

The absence of interphase and external mass transport limitations was checked by conventional tests, varying the stirring rate and the mass of catalyst, but the definitive test for the absence of mass transport limitations (even intraparticle) was realized according to the work of Madon and

Boudart (33), based on the Koros and Nowak criterion (34): catalytic tests were realized on a sample loaded with 5.05% Pd (mean particle size of 8.4 nm, measured by TEM) and for another one, containing 8.9% Pd, prepared by the polyol process (35) (mean particle size: 7.8 nm). Both catalysts were tested in the hexa-1,5-diene hydrogenation, at 313 K, using the same operating conditions. The initial turnover rates were very close, 10.9 s^{-1} for the latter and 11.4 s^{-1} for the former, with initial conversions ($1.88 \times 10^{-5}\text{ mol s}^{-1}$ for the latter and $1.07 \times 10^{-5}\text{ mol s}^{-1}$ for the former) proportional to the Pd loading, which confirmed the absence of mass transport limitations.

3. RESULTS AND DISCUSSION

3.1. Selective Hydrogenation of Hexa-1,5-diene

Table 3 gives, for each *mono-* or *bimetallic* catalyst, the values of (i) the reaction rate measured at the beginning of the reaction, expressed in $\text{mol s}^{-1}/\text{g}$ of Pd, (ii) the global selectivity in hexenes, S_g , measured at 90% and 70% conversion, and (iii) the fractional selectivity, S_f , to the different hexenes, determined at 90% and 70% conversion (see Section 2.3). These values were based on the following criteria: (a) S_g decreases only at high conversion levels; (b) the reaction suffers the influence of thermodynamics factors after ca. 70% of conversion, changing the S_f values.

3.1.1. Monometallic catalysts. Samples $\text{Pd}_{5.0}/\text{A1}$ and $\text{Pd}_{4.6}/\text{A2}$ exhibit high hydrogenation activities (initial reaction rates around $10^{-2}\text{ mol s}^{-1}\text{ g}_{\text{Pd}}^{-1}$; see Table 3) and very good global selectivity (S_g), that is, very low HA production up to about 90% conversion; for higher conversion values, S_g decreases, especially on the more acidic carrier ($\text{Pd}_{4.6}/\text{A2}$). Regarding the fractional selectivities, E2-HE is preferentially formed at high conversions, whereas 1-HE is predominant below ca. 70–80% conversion (Fig. 1). This means that 1-HE is isomerized at high conversion.

These results may be explained as follows: strongly adsorbed 1,5-HD is the predominant species up to high conversion levels; when the 1,5-HD surface coverage decreases, the alkenes formed may re-adsorb, which favor their isomerization or hydrogenation to HA. In such a situation thermodynamics factors prevail, E2-HE (and to a lesser extent Z2-HE) become predominant, and the less favored compounds 1-HE and Z3-HE tend to disappear.

Some experiments were also conducted to investigate the influence of the metal fraction exposed (MFE) on the turnover frequency (TOF); increasing values of the MFE were obtained by varying the temperature and duration of the reducing pretreatment of sample $\text{Pd}_{5.0}/\text{A1}$. As shown in Table 4 (together with $\text{Pd}_{4.6}/\text{A2}$ for comparison), the variations of TOF are not large enough to consider this reaction as structure sensitive; in addition, the selectivities do not differ significantly from one sample to another.

TABLE 2

Molar Fractions at Equilibrium for the Hexa-1,5-diene/
Hydrogen System

T (K):	313		323		333	
	Pure 1,5-HD	1,5-HD 2% in heptane	Pure 1,5-HD	1,5-HD 2% in heptane	Pure 1,5-HD	1,5-HD 2% in heptane
Z2-HE	0.3924	0.0269	0.3941	0.0284	0.3955	0.0300
E2-HE	0.3495	0.0224	0.3467	0.0233	0.3439	0.0244
E3-HE	0.2153	0.0132	0.2124	0.0137	0.2097	0.0146
Z3-HE	0.0279	0.0017	0.0296	0.0019	0.0313	0.0021
1-HE	0.0052	0.0003	0.0060	0.0004	0.0068	0.0004
HA	0.0048	0.1235	0.0056	0.1365	0.0064	0.1490
1,5-HD	0.0048	0	0.0056	0	0.0064	0

TABLE 3

 Catalytic Performances of *Mono-* and *Bimetallic* Samples in the Hexa-1,5-diene Selective Hydrogenation Reaction

Catalyst	Pd		Pd-Sn				Pd-Ag	
	01	07	02	03	04	08	05	09
	Pd _{5.0} /A1	Pd _{4.6} /A2	Pd _{5.1} Sn _{3.8} /A1	Pd _{4.9} Sn _{5.0} Et/A1	Pd _{5.2} Sn _{0.8} /A1	Pd _{4.1} Sn _{4.5} /A2	Pd _{4.9} Ag _{5.1} /A1	Pd _{3.8} Ag _{5.2} /A2
Initial reaction rate (mol · s ⁻¹ · g _{Pd} ⁻¹)	9.24 × 10 ⁻³	1.44 × 10 ⁻²	2.8 × 10 ⁻⁵	1.3 × 10 ⁻³	7.3 × 10 ⁻³	3.4 × 10 ⁻⁵	1.5 × 10 ⁻³	4.4 × 10 ⁻³
S _g ⁷⁰ (%)	98	97	^a	98	95	^a	92	94
S _g ⁹⁰ (%)	93	91	^a	92	91	^a	83	89
(1-HE) S _f ⁷⁰ (%)	37	33	~50	41	45	~50	54	46
S _f ⁹⁰ (%)	30	22		30	39		42	41
(E2-HE) S _f ⁷⁰ (%)	30	32		28	25		20	24
S _f ⁹⁰ (%)	37	38		38	32		29	29
(Z2-HE) S _f ⁷⁰ (%)	15	18		16	15		12	14
S _f ⁹⁰ (%)	19	21		20	18		17	18
(E3-HE) S _f ⁷⁰ (%)	10	10		9	8		7	9
S _f ⁹⁰ (%)	11	16		9	8		9	9
(Z3-HE) S _f ⁷⁰ (%)	8	7		6	7		7	7
S _f ⁹⁰ (%)	3	3		3	3		3	3

^aVery slow reaction: It didn't reach 90% conversion.

3.1.2. Bimetallic catalysts. All samples exhibit a high global selectivity but markedly lower activity, especially samples Pd_{5.1}Sn_{3.8}/A1 (atomic Sn/Pd ratio ≈ 2/3) and Pd_{4.1}Sn_{4.5}/A2 (Sn/Pd ≈ 1), both exhibiting initial reaction rates around 10⁻⁵ mol s⁻¹ g_{Pd}⁻¹ (Table 3). An exception is noted for sample Pd_{5.2}Sn_{0.8}/A1 (atomic Sn/Pd ratio ≈ 0.13, Fig. 2), which exhibits high activity and good 1-HE fractional selectivity up to high conversions (ca. 90%) as well. In opposition to the other Sn-rich samples, Pd_{5.1}Sn_{3.8}/A1 and Pd_{4.1}Sn_{4.5}/A2, the catalyst Pd_{4.9}Sn_{5.0}Et/A1 (Sn/Pd ≈ 1) shows good performance (Fig. 3); 1-HE is the predominant product up to about 85% conversion. Let us recall that the latter catalyst was prepared by tin impregnation in ethanol.

The bad performances of Pd_{5.1}Sn_{3.8}/A1 and Pd_{4.1}Sn_{4.5}/A2 may be explained by the composition of the active phases. The Pd₂Sn intermetallic compound is detected only on

these two catalysts, from the XRD patterns (31). From the Mössbauer findings (32), two types of Sn⁰ species were detected on both catalysts, one associated with Pd₂Sn and the other ascribed to a PdSn solid solution. However, the TPR profiles obtained for these two catalysts in the 298–773 K interval (32) are somewhat different because of the support effect. Whereas Pd_{5.1}Sn_{3.8}/A1 and Pd_{4.1}Sn_{4.5}/A2 contain the *Sn richer* species Pd₂Sn, the Pd₃Sn phase was identified on the other Pd–Sn catalysts (Pd_{5.2}Sn_{0.8}/A1 and Pd_{4.9}Sn_{5.0}Et/A1, Figs. 2 and 3) that show better performances. Moreover, according to FTIR spectroscopy of adsorbed CO (32), only end-on CO adsorption occurs on Pd_{5.1}Sn_{3.8}/A1, while bridged species were observed on Pd_{5.2}Sn_{0.8}/A1. Hence, it should be concluded that the Sn atoms dilute the Pd atoms, depending on the Sn/Pd ratio and on the catalyst preparation procedure, which determines the nature of the intermetallic species formed. This effect may be beneficial, changing the reaction pathway, as observed on Pd_{4.9}Sn_{5.0}Et/A1 and on Pd_{5.2}Sn_{0.8}/A1; but in some cases (Pd_{5.1}Sn_{3.8}/A1 and Pd_{4.1}Sn_{4.5}/A2, figures not shown, see Table 3), the Sn richer species Pd₂Sn apparently hinder the formation of multiple Pd adsorption sites, preventing the adsorption of both bridged CO species and of the reactant 1,5-HD.

Sample Pd_{5.2}Sn_{0.8}/A1, which showed the best performance, was selected to perform complementary tests, for instance, a long-term test with re-injections of the reagent, 1,5-HD. The results presented in Fig. 4 show three different stages of reaction. In the first one, a good selectivity to 1-HE is observed, as in the other tests. When the reagent is re-injected (second stage), S_f (1-HE) decreases, S_f (E2-HE)

TABLE 4

Particle Size Effect on the Initial Reaction Rate and Turnover Frequency for *Monometallic* Catalysts, in the Hexa-1,5-diene Selective Hydrogenation Reaction

Catalyst	d _p (nm) ^a	V _S ⁰ (mol · s ⁻¹ · g _{Pd} ⁻¹)	MFE ^b	TOF (s ⁻¹)
Pd _{5.0} /A1-a	2.9	2.22 × 10 ⁻²	0.39	6.1
Pd _{4.6} /A2	5.0	1.44 × 10 ⁻²	0.22	6.8
Pd _{5.0} /A1-b	8.4	1.43 × 10 ⁻²	0.13	11.4
Pd _{5.0} /A1	10.8	9.24 × 10 ⁻³	0.10	9.5
Pd _{5.0} /A1-c	12.5	1.30 × 10 ⁻³	0.09	6.7

^aMeasured by electronic microscopy (31).

^bEstimated by MFE = 1.12/d_p (nm) (31).

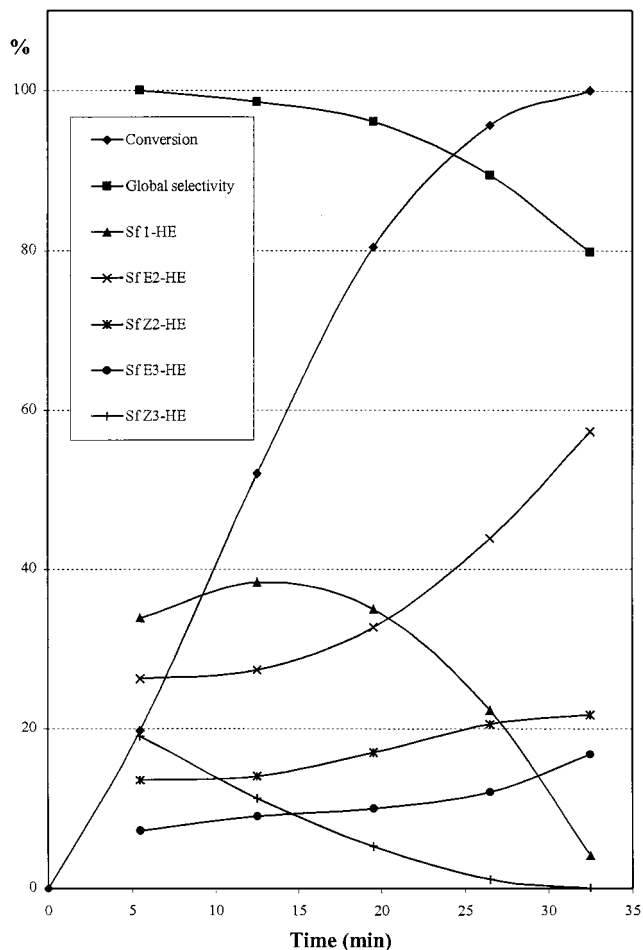


FIG. 1. Hydrogenation of hexa-1,5-diene on catalyst $\text{Pd}_{5,0}/\text{A1}$ at 313 K: variation of conversion and selectivities versus time. Catalyst mass, 15 mg. (See hydrocarbons symbols in Section 2.3.)

and $S_f(\text{Z2-HE})$ increase, and the global selectivity S_g diminishes slightly. Another injection (third stage) does not bring immediate marked changes. It appears that, at the beginning of each cycle, mechanistic factors are governed by the strong adsorption of the reagent 1,5-HD; at the end of each cycle, the decrease of 1,5-HD surface coverage favors the isomerization of alkenes. In such a situation, thermodynamics factors prevail, as already seen on monometallic catalysts. In addition, going from one cycle to the following, the liquid phase contains increasing proportions of the alkenes formed (together with HA) and this certainly will influence their adsorption and, consequently, the reaction pathway.

On the other hand, both Pd–Ag catalysts, $\text{Pd}_{4,9}\text{Ag}_{5,1}/\text{A1}$ (figure not shown) and $\text{Pd}_{3,8}\text{Ag}_{5,2}/\text{A2}$ (Fig. 5), with a Ag/Pd atomic ratio equal to 1.03 and 1.37, respectively, show very good 1-HE fractional selectivity and good global selectivity as well (Table 3), which may be ascribed to a dilution effect, the active phase being an Ag-enriched Pd–Ag solid solution (31, 32). Nevertheless, their activities are markedly lower

than that of the Pd–Sn catalyst $\text{Pd}_{5,2}\text{Sn}_{0,8}/\text{A1}$ (Table 3); this may be ascribed to the presence of a part of silver as shells on palladium cores, especially in the case of $\text{Pd}_{4,9}\text{Ag}_{5,1}/\text{A1}$ (32).

3.2. Selective Hydrogenation of Hexa-1,3-diene

The use of a reacting molecule with conjugated double bonds changes markedly the performance of all catalysts. Table 5 presents the results obtained on monometallic samples $\text{Pd}_{5,0}/\text{A1}$ ($\text{MFE} \approx 0.1$), $\text{Pd}_{5,0}/\text{A1-a}$ ($\text{MFE} \approx 0.4$), and $\text{Pd}_{4,6}/\text{A2}$ ($\text{MFE} \approx 0.2$) and on the bimetallic samples, $\text{Pd}_{5,2}\text{Sn}_{0,8}/\text{A1}$ and $\text{Pd}_{3,8}\text{Ag}_{5,2}/\text{A2}$. By comparison with the hydrogenation of hexa-1,5-diene, (i) the global selectivity S_g remains near 100%, even at conversions higher than 95% on monometallic and bimetallic samples; (ii) the fractional selectivity to 1-hexene is enhanced, up to 95% conversion, on the monometallic catalyst $\text{Pd}_{5,0}/\text{A1}$. However, on the monometallic catalysts $\text{Pd}_{5,0}/\text{A1-a}$ and $\text{Pd}_{4,6}/\text{A2}$, this performance is not observed. The absence of this effect may be related to the higher MFE in the former case and, for the

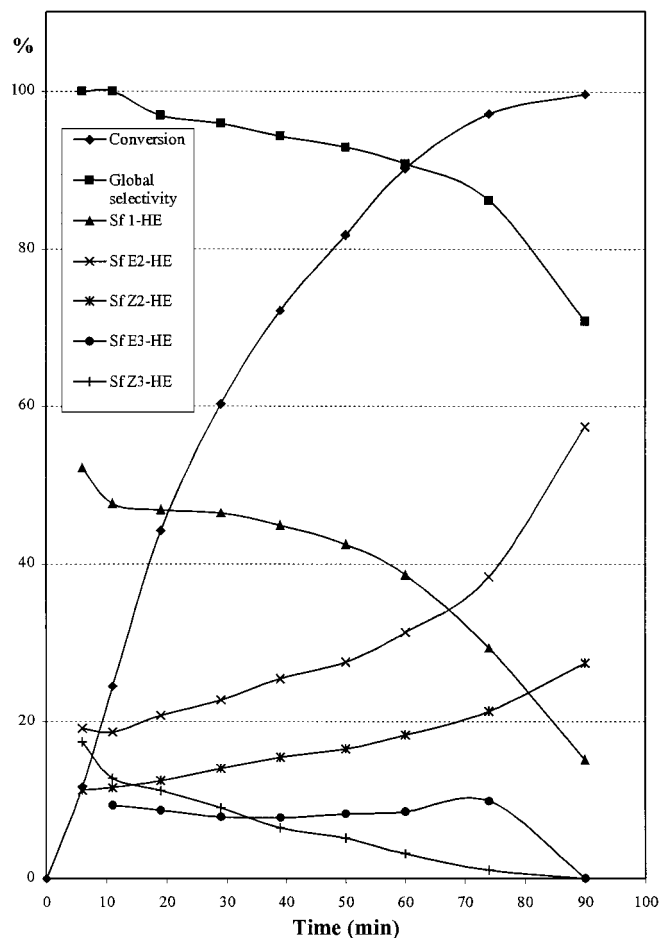


FIG. 2. Hydrogenation of hexa-1,5-diene on catalyst $\text{Pd}_{5,2}\text{Sn}_{0,8}/\text{A1}$ at 313 K: variation of conversion and selectivities versus time. Catalyst mass, 15 mg. (See hydrocarbons symbols in Section 2.3.)

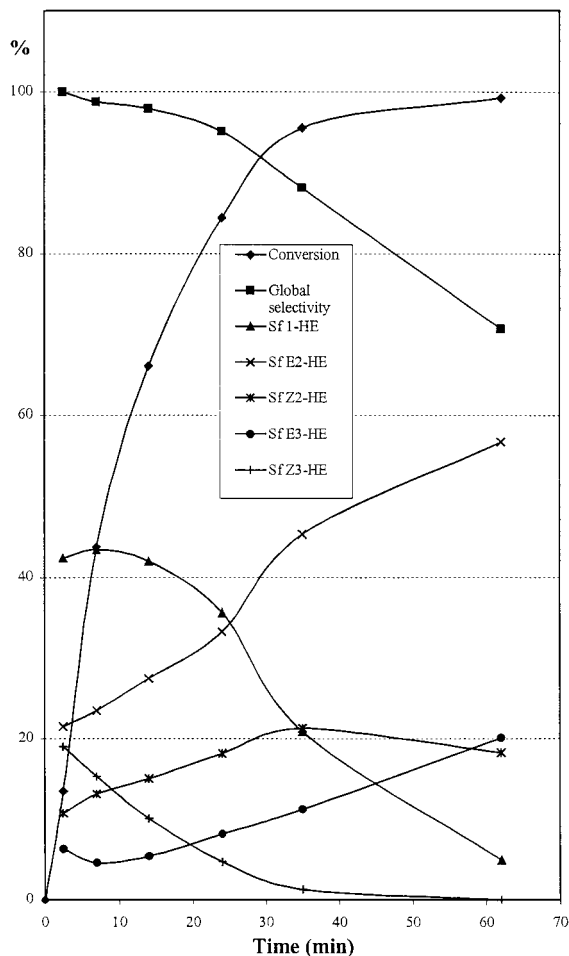


FIG. 3. Hydrogenation of hexa-1,5-diene on catalyst $\text{Pd}_{4.9}\text{Sn}_{5.0}\text{Et}/\text{A1}$ at 313 K: variation of conversion and selectivities versus time. Catalyst mass, 150 mg. (See hydrocarbons symbols in Section 2.3.)

latter sample, to the intermediate MFE (≈ 0.2) and to the acidity of the support (A-2), which may favor the isomerization, i.e., the formation of the most thermodynamically stable hexenes (e.g., 2-HE); (iii) on the bimetallic Pd-Sn cata-

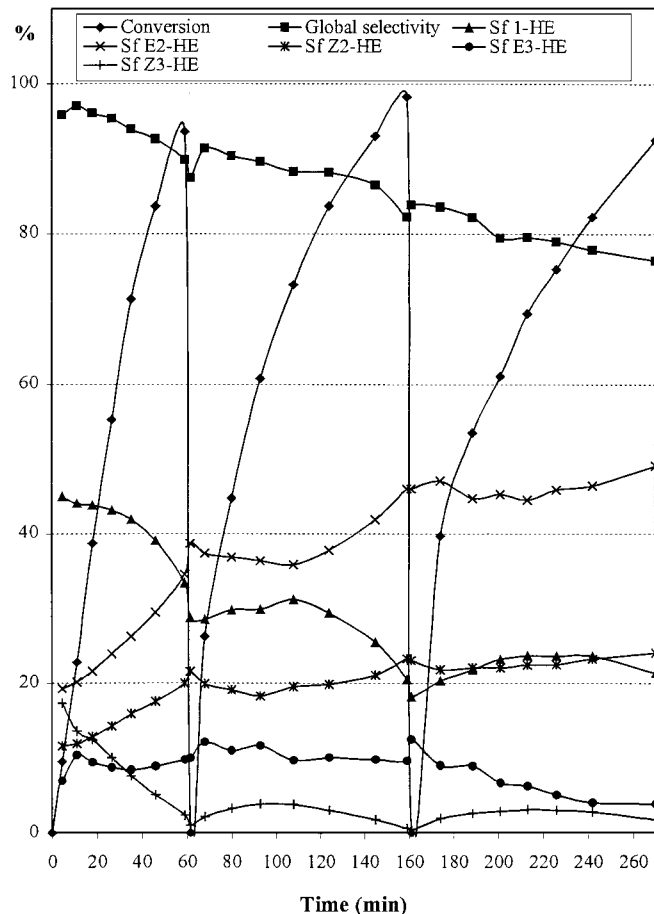


FIG. 4. Hydrogenation of hexa-1,5-diene on catalyst $\text{Pd}_{5.2}\text{Sn}_{0.8}/\text{A1}$ at 313 K: effect of readdition of 1,5-HD to the reaction medium. Catalyst mass, 15 mg. (See hydrocarbons symbols in Section 2.3.)

lyst $\text{Pd}_{5.2}\text{Sn}_{0.8}/\text{A1}$, the striking result is the predominance of E3-HE up to 100% conversion, 1-HE and E2-HE being less favored (Fig. 6, Table 5); on the bimetallic Pd-Ag catalyst $\text{Pd}_{3.8}\text{Ag}_{5.2}/\text{A2}$, E3-HE is only slightly predominant over 1-HE and E2-HE, but its selectivity is significantly higher than

TABLE 5

Catalytic Performances of Mono- and Bimetallic Samples in the Hexa-1,3-diene Selective Hydrogenation Reaction

Catalyst	$\text{Pd}_{5.0}/\text{A1}$	$\text{Pd}_{5.0}/\text{A1-a}$	$\text{Pd}_{4.6}/\text{A2}$	$\text{Pd}_{5.2}\text{Sn}_{0.8}/\text{A1}$	$\text{Pd}_{3.8}\text{Ag}_{5.2}/\text{A2}$
Initial reaction rate ($\text{mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Pd}}^{-1}$)	1.2×10^{-2}	1.8×10^{-2}	7.8×10^{-3}	1.3×10^{-3}	8.9×10^{-4}
S_g^{90} (%)	100	99	99	100	100
S_f^{90} (1-HE) (%)	42	30	29	27	27
S_f^{90} (E2-HE) (%)	28	36	38	27	31
S_f^{90} (Z2-HE) (%)	4	6	7	4	5
S_f^{90} (E3-HE) (%)	26	28	26	42	35
S_f^{90} (Z3-HE) (%)	0	0	0	0	0

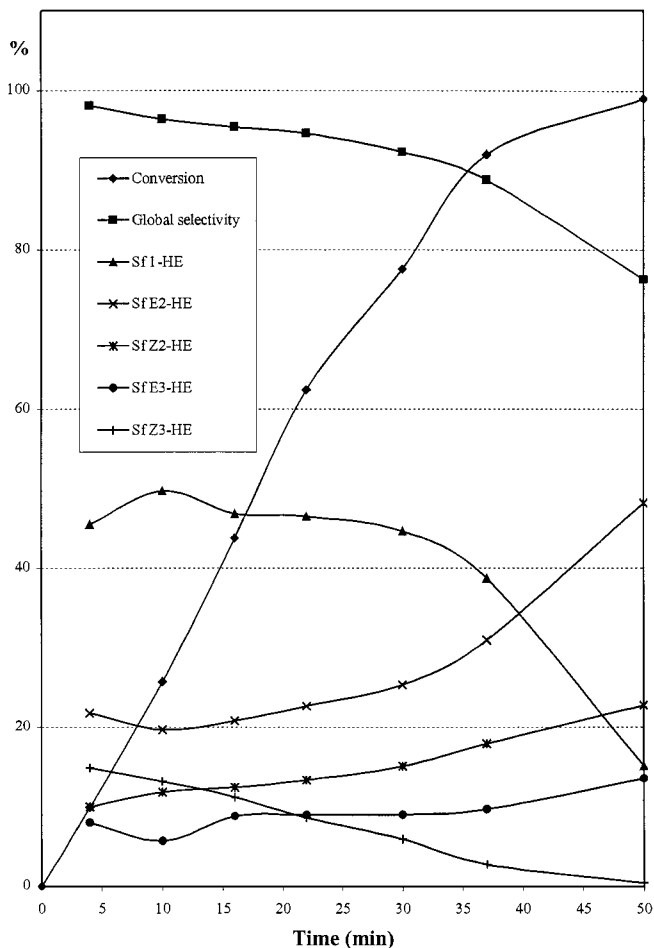


FIG. 5. Hydrogenation of hexa-1,5-diene on catalyst $\text{Pd}_{3.8}\text{Ag}_{5.2}/\text{A}2$ at 313 K: variation of conversion and selectivities versus time. Catalyst mass, 30 mg. (See hydrocarbons symbols in Section 2.3.)

that observed for the corresponding monometallic sample ($\text{Pd}_{4.6}/\text{A}2$, Table 5). On all samples, the production of Z3-HE is quite negligible.

The better global selectivity is explained by the adsorption strength of 1,3-HD, which is even greater than that of 1,5-HD, due to the additional stabilization of the adsorbed species provided by the conjugated bonds. This means that alkenes re-adsorption, and subsequent isomerization and/or hydrogenation to HA, will take place only at extremely low 1,3-HD liquid-phase concentrations.

3.3. General Discussion

A molecule with double bonds may theoretically adsorb with rupture of these bonds and formation of metal-carbon bonds or through interaction between the metal and the π electrons of these unsaturated bonds without rupture (36). Some authors recognize that these two adsorbed species may co-exist in equilibrium (37). In both cases, before hydrogenation, the double bonds may migrate into the ad-

sorbed species, leading to different isomers, including Z/E. Palladium, conversely to platinum, favors these isomerization reactions, especially double-bonds migration (38, 39).

Hence, the performances of monometallic and bimetallic catalysts in both 1,5-HD and 1,3-HD selective hydrogenation reactions should be understood in the following terms: in the case of 1,5-HD, the “independent” hydrogenation will give first 1-HE, which may either desorb or be converted to others isomers. Using bimetallic catalysts, the presence of either Sn or Ag apparently inhibits the Pd double-bond isomerization ability, by a geometric effect of dilution, hindering the formation of multiple adsorption sites required for this reaction. This justifies the high 1-HE selectivity observed. On monometallic catalysts, however, the migration of double bonds occurs freely, and the proportion of hex-2-enes, the most stable thermodynamically, increases.

On the other hand, the independent hydrogenation of double bonds in 1,3-HD cannot be taken into account as they are conjugated. If no isomerization occurs, the

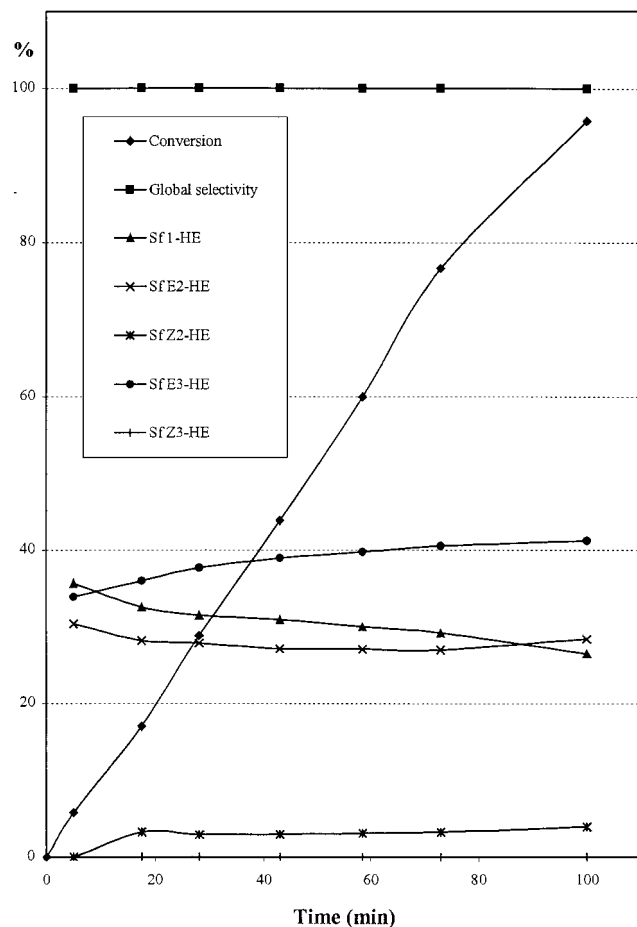


FIG. 6. Hydrogenation of hexa-1,3-diene on catalyst $\text{Pd}_{5.2}\text{Sn}_{0.8}/\text{A}1$ at 313 K: variation of conversion and selectivities versus time. Catalyst mass, 15 mg. (See hydrocarbons symbols in Section 2.3.)

formation of 1-HE, 3-HE, and also 2-HE is expected, and this was observed with bimetallic catalysts, which delay the catalytic isomerization of these compounds, leading to a broad distribution (Table 5); on monometallic catalysts, the product distribution appears to depend on MFE: on Pd_{5.0}/A1 (MFE ≈ 0.1, Table 5) 1-HE is predominant up to ca. 95% conversion, whereas on Pd_{5.0}/A1a (MFE ≈ 0.4) the proportion of 1-HE does not overcome that of 2-HE, even at low conversion. In other words, the particle size influences the fractional selectivities (in opposition to the 1,5-HD hydrogenation, see Section 3.1.1).

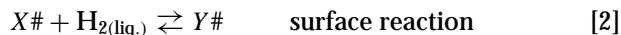
For the monometallic catalysts, the mean particle sizes observed by TEM were not very different from the values obtained from XRD measurements, indicating that the observed particles are single crystallites (31). It is known that Pd atoms in low Miller index planes may favor Z/E isomerization and double-bonds migration; Pd atoms on corners may perform the same reactions and also hydrogen exchange, and Pd atoms on crystal edges or at isolated sites (over the crystal planes) may catalyze π -species hydrogenation (40, 41). Moreover, the crystallite size determines the distribution of these various Pd sites (42). Hence, the differences observed in the fractional selectivities may arise from different Pd sites distribution in each catalyst.

In addition, comparing the catalytic tests of each catalyst in both 1,5-HD and 1,3-HD hydrogenation, a significant increase of E3-HE production is observed in the latter, using monometallic or bimetallic catalysts, but more marked on bimetallics, especially on Pd_{5.2}Sn_{0.8}/A1 (Table 5), as the migration of double bonds is inhibited by the geometric effect of dilution of the Pd atoms (see above). In fact, an increase in the hex-3-enes production is expected, as the probability of formation of these isomers is increased using 1,3-HD as the starting molecule. However, the formation of the Z3-HE isomer is not observed in this case. Using 1,5-HD as the starting molecule, both Z3-HE and E3-HE are detected on all catalytic tests (Figs. 1–5), but at the end of the reaction the Z3-HE disappears, and the production of the more stable E3-HE is increased. This should be explained by the random possibility of 1,5-HD adsorption, which may give both Z3- and E3-HE, after selective hydrogenation and double-bond migration to the C₃ position. When 1,3-HD is the reactant, as the initial solution contains almost exclusively E-1,3-HD (cf. Section 2.1), the adsorption will be restricted to this configuration because the E → Z isomerization is generally not possible near room temperature; hence, the main 3-ene hydrogenation product must be E3-HE, as skeletal isomerization needs a more acidic carrier or active phase. This was in fact observed, as no Z3-HE was detected in all 1,3-HD catalytic tests (Table 5).

3.4. Reaction Mechanism

We proposed a simple model, where the diene (1,5-HD or 1,3-HD, named hereafter *X*) adsorbs on the catalytic site

(#), reacts with the hydrogen dissolved in the liquid phase, and the partially hydrogenated product (named hereafter *Y*) desorbs and remains in the liquid phase. It was assumed that *X* adsorbs more strongly than *Y*; hence, *Y* may adsorb and suffer hydrogenation to hexane (named hereafter *Z*) only when the *X* concentration is low. The scheme proposed for the first reaction stages (neglecting further hydrogenation of *Y*) is



We assume that (2) is the rate-controlling step. Consequently, the adsorption and desorption steps reach equilibrium. Following a Langmuir–Hinshelwood treatment, we find

$$r_s = k_s K_X C_m [C_X C_{H_2} - (1/K) C_Y] / (1 + K_X C_X + K_Y C_Y + K_I C_I), \quad [5]$$

where r_s = surface (and overall) reaction rate, k_s = rate constant for the surface reaction step, K_X , K_Y , and K_I = adsorption equilibrium constants for *X*, *Y*, and inert compounds, respectively, C_X , C_{H_2} , and C_Y = liquid-phase concentrations, K = thermodynamic equilibrium constant for the overall reaction, and C_m = concentration of all adsorption sites = $C_\# + C_X + C_Y + C_I$, where $C_\#$ = vacant sites.

Using the data cited in Section 2.4, the overall equilibrium constant, K , in the reaction conditions is estimated to ca. 3.0×10^5 . Hence, neglecting the reverse reaction, Eq. [5] becomes

$$r_s = k_s K_X C_m (C_X C_{H_2}) / (1 + K_X C_X + K_Y C_Y + K_I C_I). \quad [6]$$

Moreover, we assume that the alkadienes adsorb much more strongly than all other species, that is, $K_X C_X \gg 1 + K_Y C_Y + K_I C_I$, leading to

$$r_s = k_s C_m C_{H_2}. \quad [7]$$

This means that the kinetics follows a zero order with respect to the 1,5-HD or 1,3-HD concentration (C_X), in agreement with the experimental data: the concentration versus time curves obtained from all catalytic tests performed in Sections 3.1 and 3.2 are straight lines up to high conversion levels.

We also observe straight lines in the hydrogen consumption curves, indicating a pseudo-zero-order kinetics. The reactions were carried out at constant hydrogen pressure and the hydrogen concentration was limited by its solubility in the solvent, heptane, estimated to be ca. 6.88×10^{-4} (molar

fraction) (43). Hence, in such conditions, C_{H_2} is kept unchanged, and the reaction rate equation simplifies to

$$r_s = k', \quad [8]$$

where $k' = k_s C_m C_{H_2}$ is the apparent zero-order rate constant.

In the low X concentration region (high conversion) this model cannot fit the data because Y hydrogenation takes place and Eq. [6] must be used instead, giving more complicated kinetics.

A k' value was obtained by linear regression from an Arrhenius plot in the 1,5-HD hydrogenation at 313, 323, and 333 K: $r_s = k' = 10^5 \exp(-5200/T)$ for the bimetallic catalyst $Pd_{5.2}Sn_{0.8}/A1$, r_s in $\text{mol s}^{-1} \text{g}_{Pd}^{-1}$, and T in K. From these values, the apparent activation energy is estimated to $E_a = 43 \text{ kJ mol}^{-1}$ whereas for the monometallic catalyst $Pd_{5.0}/A1$, $E_a = 56 \text{ kJ mol}^{-1}$; the presence of tin as Pd_3Sn (31, 32) decreases the activation energy and increases the fractional selectivity to 1-HE. It suggests that the presence of the second metal influences the bonding strength of 1,5-HD (Eq. [1]) and of the semihydrogenated species (Eqs. [2] and [3]) with the surface. As the catalysts containing the Pd_2Sn phase ($Pd_{5.1}Sn_{3.8}/A1$ and $Pd_{4.1}Sn_{4.5}/A2$) (32) are much less active, it appears that the above results may be accounted for by an ensemble effect, i.e., a geometric effect rather than the involvement of a ligand effect.

4. CONCLUSIONS

Supported palladium catalysts show high global selectivity to hexenes in the liquid-phase hydrogenation of hexadienes; at conversions approaching 100% these high selectivity values persist when the reactant is hexa-1,3-diene, but decrease to about 80% in the case of hexa-1,5-diene.

For hexa-1,5-diene hydrogenation, on monometallic Pd catalysts, 1-hexene is preferably formed up to ca. 75% conversion, while E-hex-2-ene is the main product at higher conversions. The addition of a second metal, either tin or silver, changes markedly the catalytic performances: the selectivity to 1-hexene is significantly improved but accompanied by an important loss of activity, except on the Pd-Sn catalyst with low Sn/Pd atomic ratio. These results are explained by a geometric effect of dilution, which inhibits the double-bond isomerization ability of palladium, hindering the formation of the multiple adsorption sites required for this reaction. The best performances are obtained on samples containing the Pd_3Sn compound whereas the presence of Pd_2Sn has a negative effect.

On the other hand, in the hexa-1,3-diene hydrogenation, hex-1-ene is preferentially formed on the monometallic catalysts with low metal fraction exposed (ca. 0.1); it may be ascribed to the influence of the sites distribution (faces, edges, corners) in the adsorption of this conjugated diene. On the bimetallic Pd-Sn or Pd-Ag samples, the selectivity

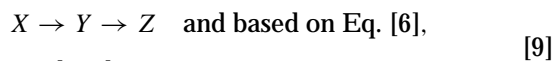
to E-hex-3-ene is enhanced, and this isomer is even predominant up to 100% conversion on the Pd-Sn catalyst with a low Sn/Pd atomic ratio. These results are still explained by the geometric effect of dilution of Pd atoms, which delays catalytic isomerization.

Hence, if the target is 1-hexene, the best catalyst is the Pd-rich bimetallic Pd-Sn catalyst when starting from hexa-1,5-diene and monometallic Pd samples, with low metal fraction exposed, if hexa-1,3-diene is the reactant. If the target is E-hex-3-ene, the best compromise is to use hexa-1,3-diene on the Pd-rich bimetallic Pd-Sn sample.

The proposed mechanism suggests that strongly adsorbed alkadienes react with dissolved hydrogen, following a zero-order kinetics. Better control of the yields of the different hexenes requires further studies, now in course, about the species involved in the adsorption of the hexadienes and especially the influence of particle size below about 3 nm.

APPENDIX

The adsorption constants ratio K_X/K_Y was also estimated from the experimental data to confirm the assumed hypothesis of strong 1,5-HD and 1,3-HD adsorption. From the simplified model used,



$$r_1 = -dX/dt = k_1 K_X C_X f(H_2)/(1 + \sum K_i C_i).$$

Assuming that Y hydrogenation obeys a similar kinetic model,

$$r_2 = dZ/dt = k_2 K_Y C_Y f(H_2)/(1 + \sum K_i C_i). \quad [10]$$

Hence, the Y accumulation rate will be $dY/dt = -dX/dt - dZ/dt$:

$$dY/dt = (k_1 K_X C_X - k_2 K_Y C_Y) f(H_2)/(1 + \sum K_i C_i). \quad [11]$$

Dividing Eq. [11] by Eq. [9],

$$dY/dX = -1 + (k_2 K_Y C_Y / k_1 K_X C_X) = -1 + K' C_Y / C_X, \quad [12]$$

where

$$K' = k_2 K_Y / k_1 K_X. \quad [13]$$

K' is in fact the "relative reactivity" of Y compared to X . The solution of Eq. [12] gives

$$C_Y = [1/(K' - 1)](C_X - C_X^{K'}) \quad [14]$$

and this expression will reach a maximum at

$$C_Y = K'^{K'/(1-K')} \quad [15]$$

Using now the experimental data from the above-mentioned tests, considering Y as the sum of all monohydrogenated isomers, it is found from Eq. [15] that $C_{Y,\max} = 0.82$ (molar fraction), giving a K' value of 0.06915. Moreover, the zero-order kinetic model leads to the rate constants values of $k_1 = 8.98 \text{ mol s}^{-1} \text{ g}_{\text{Pd}}^{-1}$ and $k_2 = 5.64 \text{ mol s}^{-1} \text{ g}_{\text{Pd}}^{-1}$. Introducing these values into Eq. [13] gives the desired ratio with respect to 1,5-HD:

$$K_X/K_Y = k_2/K'k_1 = 9.1,$$

which confirms the initial assumption of stronger alkadienes adsorption.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Carroll Bennett and Mr. Robert Weber for discussions on mass and heat transport limitations, to Mr. Guy Bugli for suggestions in the execution of the catalytic tests, and to Mrs. Roberta Brayner for her help in data processing. We also gratefully acknowledge the CNPq (Brazil) for financial support in this international cooperation and Engelhard-CLAL for palladium delivery.

REFERENCES

1. Stadler, K. H., Schneider, M., and Kochloeff, K., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 5, p. 229. Dechema, Frankfurt-am-Main, 1984.
2. Bond, G. C., Dowden, D. A., and Mackenzie, N., *Trans. Faraday Soc.* **54**, 1537 (1958).
3. Den Hartog, A. J., Deng, M., Jongerius, F., and Ponec, V., *J. Mol. Catal.* **60**, 99 (1990).
4. Gigola, C. E., Aduriz, H. R., and Bodnariuk, P., *Appl. Catal.* **27**, 133 (1986).
5. Boitiaux, J. P., Cosyns, J., and Vasudevan, S., *Appl. Catal.* **6**, 41 (1983).
6. Itoh, N., Xu, W. C., and Sathe, A. M., *Ind. Eng. Chem. Res.* **32**, 2614 (1993).
7. Otsuka, K., and Yagi, T., *J. Catal.* **145**, 289 (1994).
8. Weiss, A. H., LeViness, S., Nair, V., Guzzi, L., Sarkany, A., and Schay, Z., in "Proceedings of the 8th International Congress on Catalysis, Berlin, 1984," Vol. 5, p. 591. Dechema, Frankfurt-am-Main, 1984.
9. LeViness, S., Nair, V., Weiss, A. H., Schay, Z., and Guzzi, L., *J. Mol. Catal.* **25**, 131 (1984).
10. Tessier, D., Rakai, A., and Bozon-Verduraz, F., *Bull. Soc. Chim. Fr.* **133**, 1 (1996).
11. Tardy, B., Noupa, C., Leclercq, C., Bertolini, J. C., Hoareau, A., Treilleux, M., Faure, J. P., and Nihoul, G., *J. Catal.* **129**, 1 (1991).
12. Sarkany, A., Guzzi, L., and Weiss, A. H., *Appl. Catal.* **10**, 369 (1984).
13. Park, Y. H., and Price, G. L., *Ind. Eng. Chem. Res.* **30**, 1693 (1991).
14. Horner, L., and Grohmann, I., *Liebigs Ann. Chem. Bd.* **670**, 1 (1963).
15. Aramendia, M. A., Borau, V., Jimenez, C., Marinas, J. M., Sempere, M. E., and Urbano, E. J., *Appl. Catal.* **63**, 375 (1990).
16. Boitiaux, J. P., Cosyns, J., and Martino, G., in "Metal-Support and Metal-Additive Effects in Catalysis" (B. Imelik *et al.*, Eds.), p. 355. Elsevier, Amsterdam, 1982.
17. Barbier, J., Lamy-Pitara, E., Marécot, P., Boitiaux, J. P., Cosyns, J., and Verna, F., *Adv. Catal.* **37**, 279 (1990).
18. Contescu, C., Sivaraj, C., and Schwarz, J. A., *Appl. Catal.* **74**, 95 (1991).
19. Massardier, J., Bertolini, J. C., Ruiz, P., and Delichère, P., *J. Catal.* **112**, 21 (1988).
20. Park, Y. H., and Price, G. L., *Ind. Eng. Chem. Res.* **31**, 469 (1992).
21. Goetz, J., Volpe, M. A., and Touroude, R., *J. Catal.* **164**, 369 (1996).
22. Bensalem, A., and Bozon-Verduraz, F., *React. Kinet. Catal. Lett.* **60**(1), 71 (1997).
23. Liotta, L. F., Deganello, G., Delichere, P., Leclercq, C., and Martin, G. A., *J. Catal.* **164**, 334 (1996).
24. de Gouveia, V., Bellamy, B., Masson, A., and Che, M., *Stud. Surf. Sci. Catal.* **48**, 347 (1988).
25. Hightower, J. W., Furlan, B., Sarkany, A., and Guzzi, L., *Stud. Surf. Sci. Catal.* **75**, 2305 (1993).
26. Fragale, C., Gargano, M., Ravasio, N., Rossi, M., and Santo, I., *J. Mol. Catal.* **24**, 211 (1984).
27. Ouchaib, T., Moraweck, B., Massardier, J., and Renouprez, A., *Catal. Today* **7**, 191 (1990).
28. Borgna, A., Moraweck, B., Massardier, J., and Renouprez, A. J., *J. Catal.* **128**, 99 (1991).
29. Aduriz, H. R., Gigola, C. E., Sica, A. M., Volpe, M. A., and Touroude, R., *Catal. Today* **15**, 459 (1992).
30. Aduriz, H. R., Bodnariuk, P., Coq, B., and Figueras, F., *J. Catal.* **129**, 47 (1991).
31. Sales, E. A., Bugli, G., Ensuque, A., Mendes, M. J., and Bozon-Verduraz, F., *Phys. Chem. Chem. Phys.* **1**, 491 (1999).
32. Sales, E. A., Jove, J., Mendes, M. J., and Bozon-Verduraz, F., *J. Catal.* **195**, 88 (2000).
33. Madon, R. J., and Boudart, M., *Ind. Eng. Chem. Fundam.* **21**, 438 (1982).
34. Koros, R. M., and Nowak, E. J., *Chem. Eng. Sci.* **22**, 470 (1967).
35. Sales, E. A., Benhamida, B., Caizergues, V., Lagier, J.-P., FiÉvet, F., and Bozon-Verduraz, F., *Appl. Catal. A* **172**, 273 (1998).
36. Bond, G. C., and Wells, P. B., *Adv. Catal.* **15**, 91 (1964).
37. Karpinski, Z., *Adv. Catal.* **37**, 45 (1990).
38. Freifelder, M., "Practical Catalytic Hydrogenation—Techniques and Applications." Wiley-Interscience, New York, 1971.
39. Cerveny, L., Skala, P., and Ruzicka, V., *J. Mol. Catal.* **29**, 33 (1985).
40. Ledoux, M. J., *Nouv. J. Chim.* **2**, 9 (1978).
41. Ledoux, M. J., Gault, F. G., Bouchy, A., and Roussy, G., *J. Chem. Soc. Faraday Trans. I* **74**, 2652 (1978).
42. Van Hardeveld, R., and Hartog, F., *Surf. Sci.* **15**, 189 (1969).
43. Orentlicher, M., and Prausnitz, J. M., *Chem. Eng. Sci.* **19**, 775 (1964).