JOURNAL OF CATALYSIS 129, 47–57 (1991)

Alumina-Supported Bimetallics of Palladium Alloyed with Germanium, Tin, Lead, or Antimony from Organometallic Precursors

II. Gas-Phase Hydrogenation of 2-Methyl-1-Buten-3-yne (Valylene) and 2-Methyl-1,3-Butadiene (Isoprene)

HUGO R. ADURIZ,* PEDRO BODNARIUK,* BERNARD COQ,†,[1]
AND FRANÇOIS FIGUERAS†

**Plapiqui (UNS-CONICET), 12 de Octubre 1842, 8000 Bahia Blanca, Argentina; and †Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquées, UA 418 du CNRS, ENSCM, 8, Rue de L'Ecole Normale, 34053 Montpellier Cedex, France*

Received November 10, 1989; revised October 1, 1990

A series of PdGe, PdSb, PdSn, and PdPb/α-Al_2O_3 catalysts, prepared by the controlled surface reaction (CSR) technique from organometallic precursors have been tested in the gas-phase hydrogenation of 2-methyl-1-buten-3-yne (valylene) and 2-methyl-1,3-butadiene (isoprene). On catalysts reduced at 573 K, the turnover frequencies for valylene (TON_V) and isoprene (TON_I) hydrogenation were not modified by addition to the 0.09 wt% Pd/α-Al_2O_3 base catalyst of Ge, Sb, Sn, or Pb, up to 0.1 wt% (at 293 K: $TON_V = 20\ s^{-1}$ and $TON_I = 33\ s^{-1}$). Pd/α-Al_2O_3 reduced at 773 K was severely sintered (d_{TEM} increased from 2.8 nm to 12.4 nm) and TON_V and TON_I at 293 K increased to 190 and 283 s^{-1}, respectively, as a result of an apparent crystal size effect: the reactants adsorb more strongly on the smaller Pd particles. Upon alloying with Ge, Sb, Sn, or Pb and a subsequent reduction at 773 K, a modest decrease of both TON_V (by a factor of 2) and TON_I (by a factor of 2–5) was observed. At high conversion, both the selectivity to isoprene (S_I) in valylene hydrogenation, and to olefins (S_O) in isoprene hydrogenation on Pd/α-Al_2O_3 were improved upon alloying with Sb, Sn, or Pb (Ge had no effect). In addition, the isomerization of 2-methyl-1-butene and 3-methyl-1-butene (double bond migration reaction) during isoprene hydrogenation was partially suppressed on PdSn and PdPb/α-Al_2O_3. The improvement in selectivities was interpreted in terms of a change in the relative adsorption strength of the reactants and intermediate products over the new bimetallic sites.

INTRODUCTION

The catalytic hydrogenation of unsaturated hydrocarbons on metals of Group VIII has been investigated extensively (*1*, *2*). It is well known that Pd presents high activity and selectivity for the semihydrogenation of alkynes and alkadienes. Modern industrial processes use selective hydrogenation over supported Pd catalysts for the purification of many petrochemical products obtained by steam cracking, for example C_2H_2 in the C_2H_4 cut and butadiene in the 1-butene-rich cut. Nevertheless, the use of Pd involves several drawbacks, some of which might be summarized as follows. The thermodynamic factor (competitive adsorption between the alkyne and olefin), which appears to govern the selectivity, fails at a relatively low alkyne or alkadiene conversion, leading to the hydrogenation of the corresponding olefin. Also, both the high activity of Pd and the exothermicity of the reactions make the control of the reactor difficult, particularly in gas-phase hydrogenations, resulting in a nonisothermal operation with a subsequent decrease in selectivity. The new technologies have attempted to improve the selectivity either by operating in the liquid phase or by using bimetallic Pd catalysts (*3*, *4*).

---

[1] To whom correspondence should be addressed.

0021-9517/91 $3.00

Recently we have initiated a series of investigations aimed to design improved Pd-based supported bimetallic catalysts for the hydrogenation of alkynes and/or alkadienes. The objective of this study was to modify supported Pd catalysts by alloying with a second metal (modifier) in order to achieve at high conversion both higher selectivity to the semihydrogenation and stability.

It is well known that better selectivities for many selective hydrogenations have been obtained by partial poisoning of Pd/$CaCO_3$ with Pb or Zn (Lindlar catalysts) (*5*). For selective hydrogenation of alkynes and alkadienes on Pd/Al_2O_3 Boitiaux *et al.* (*6*) have reviewed the effects of addition to the reactant mixture of CO, pyridine, SH_2, thiophene, Cl_2, N_2O, etc.

Palczewska *et al.* (*7, 8*) reported that the high selectivity of Pd for the semihydrogenation of acetylenic bonds could be improved by alloying with Pb. Cerveny *et al.* (*9*) found higher selectivities for the competitive hydrogenations in the liquid phase of 2,5-dimethyl-2,4-hexadiene with 1-heptene, and 2-octyne with 1-heptene, on Pd black modified with an ad-layer of Pb or Tl.

Boitiaux *et al.* (*3*) reported that the performance of Pd catalysts could be enhanced by the incorporation of a second metal. Their results were interpreted in terms of a ligand effect, i.e., a change of the electronic properties of Pd upon alloying. At variance with this, Maier and co-workers (*11, 12*) suggested that the deposition of Pb by the Lindlar treatment over the Pd particles has no effect on the selectivity for the semihydrogenation of 2-hexyne. It was concluded that the selectivity enhancing action seems to be merely a morphological rearrangement of the catalyst surface, namely an increase of terrace Pd atoms (selective sites) relative to Pd atoms at steps and kinks (nonselective sites).

New techniques are now available for the preparation of true supported bimetallic particles. These methods, as reported by Travers *et al.* (*13*) and Margitfalvi *et al.* (*14, 15*), are the controlled surface reactions (CSR) between organometallic compounds and transition metal-supported catalysts. These techniques were applied for the preparation of PdGe, PdSb, PdSn, and PdPb bimetallic particles supported on a low area α-Al_2O_3 (*16*). It was shown that true bimetallic aggregates could be prepared, and that surface composition could be regulated by reducing the catalysts at different temperatures.

Valylene (2-methyl-1-buten-3-yne) hydrogenation is not well documented. This reactant has been chosen by considering its characteristic of possessing a triple bond and a double bond tagged with a methyl group. Recently Ryndin *et al.* (*17*) studied the gas-phase hydrogenation of a parent hydrocarbon, namely vinylacetylene. It was found that the specific activity decreased on the highly dispersed Pd catalysts, in agreement with recent literature data on the influence of Pd dispersion on the hydrogenation of acetylenic hydrocarbons (*18–22*). The selective hydrogenation of vinylacetylene to butadiene remains a challenge for purification of butadiene cuts. Moreover, this hydrocarbon adsorbs strongly on Pd catalysts, and may extract the metal from the carrier by a ligand effect (*3*). Many papers have been devoted to isoprene (2-methyl-1,3-butadiene) hydrogenation in the liquid phase by using batch reactors. In fact, high activity and selectivity to olefins have been reported in an early paper by Lebed'ev and Yabubchik (*23*) on Pd black and recently by Vasudevan (*18*) and Boitiaux *et al.* (*19*) on Pd/α-Al_2O_3, and by Frolov *et al.* (*24*), over alumina-supported Pd complexes. Vasudevan and co-workers (*18, 19*) also reported, for the liquid-phase isoprene hydrogenation, a decrease of the specific activity (per Pd surface atom) and of the selectivity to olefins with increasing Pd dispersion.

Few studies concerning the gas-phase isoprene hydrogenation on bimetallic Pd catalysts have been carried out. The kinetics on PdPb catalysts was studied by Kiperman (*25*). More recently, Aduriz *et al.* (*26*) compared the specific activity and selectivity of $PdSn/\alpha-Al_2O_3$ prepared either from chlorides or organometallic precursors.

The present work reports the effects of Ge, Sb, Sn, or Pb addition by the CSR technique on the activity and selectivity of $Pd/\alpha-Al_2O_3$ in the gas-phase hydrogenation of valylene and isoprene. The influence of the reduction temperature of the catalysts (573 and 773 K) was investigated also.

EXPERIMENTAL

A complete description of the preparation procedures and characterization techniques of the catalysts used in this study has already been reported (*16, 20*). The methods employed are summarized here as follows.

Catalyst Preparation

The base catalyst, 0.09 wt% $Pd/\alpha-Al_2O_3$, was prepared by wet impregnation of Rhône Poulenc $\alpha-Al_2O_3$ SCS9 with a solution of Pd acetylacetonate ($Pd(C_5H_7O_2)_2$) in benzene. It was dried in He at 393 K, calcined in air at 573 K and reduced at 573 K. The bimetallic catalysts (PdGe, PdSb, PdSn, and $PdPb/\alpha-Al_2O_3$) were prepared by the so-called controlled surface reaction technique initially proposed in the literature for the preparation of supported RhSn (*13*) and PtSn (*15*) catalysts. The base catalyst $Pd/\alpha-Al_2O_3$ was prereduced at 573 K, cooled in flowing H_2 and purged with N_2. It was then maintained in contact (72 h at 363 K) with solutions of $(n-C_4H_9)_4Ge$, $(n-C_4H_9)_3Sb$, $(n-C_4H_9)_4Sn$, and $(n-C_4H_9)_4Pb$ in *n*-heptane. The samples were then dried at 393 K and reduced at 573 K (Series I). A second group of catalysts (Series II) was obtained by reducing again Series I samples at 773 K.

Catalyst Characterization

The Pd percentage exposed was determined by hydrogen adsorption at 298 K using the dual-isotherm technique proposed by Boudart and Hwang (*27*). Measurements were carried out in a low dead volume glass apparatus connected to a capacitance electronic manometer (MKS Baratron). The chemisorption measurements were checked by transmission electron microscopy.

Activity Measurements

Activity measurements were carried out at atmospheric pressure in a flow reactor which consisted of a preconditioner coil (2 m × 1 mm i.d.) and two stainless-steel microreactors (dead volume of $\frac{1}{8}$-in. Swagelok unions) connected with a heat exchanger tube (2 m × 1 mm i.d.). This configuration was intended to optimize the removal of the heat of reaction. 2-Methyl-1-buten-3-yne (purity > 98%) was supplied by Lancaster Synthesis and 2-methyl-1,3-butadiene (purity > 98%) by Merck. Hydrogen (Air Liquide, 99.99%), previously purified over 5A molecular sieves and by MnO/Al_2O_3 traps, was saturated with valylene or isoprene at 253 K and 405 kPa. The experimental molar feed ratios were H_2/valylene = 16 and H_2/isoprene = 35. An adsorption tube packed with $\gamma-Al_2O_3$ and connected in series with the saturator was used to eliminate the isoprene stabilizer (4-tert-butylcatechol) from the feed. Small catalyst charges (0.001–0.01 g) ground to 80 mesh were used. They were diluted to 0.015 g with the $\alpha-Al_2O_3$ used as support and placed between porous stainless-steel disks. Catalytic tests were performed in the 278–323 K temperature range. The space velocity varied from 66 to 660 $cm^3_{STP}\,g\,cat^{-1}s^{-1}$ maintaining a constant gas-flow rate of 40 $cm^3_{STP}\,min^{-1}$. Specific activities and apparent activation energies were measured at differential conversions by slowly increasing and decreasing the temperature. Prior to catalytic measurements the samples were dried in flowing ultrahigh purity He at 393 K for 0.5 h. The reaction mixture, e.g., H_2/isoprene = 35, was then fed through the catalytic bed at 283 K and 40 $cm^3_{STP}\,min^{-1}$ flow rate. During this activation period of 2 h the conversion increased slowly up to a steady state. By using this procedure of catalyst conditioning no deactivation was observed and very reproducible results were obtained. The effluents were sampled on line to a gas chromatograph (Girdel 30, FID model) coupled with a data processor (Shimadzu CR3A). Two packed columns in series were used: 10% squalane on Chromosorb Q (3 m × 2 mm i.d.)) and 20% Carbowax 20 M on chromosorb Q (4 m × 2 mm i.d.) at 313 K, with N_2 carrier at 25 cm^3 min^{-1} flow rate.

For valylene (VL) hydrogenation the products were isoprene (IP), 2-methyl-1-butene (2M1B), 3-methyl-1-butene (3M1B), and 2-methyl-2-butene (2M2B). The molar selectivity to isoprene S_I was evaluated as

$$S_I(\%) = \frac{\text{mol IP}}{\text{mol VL converted}} \times 100.$$

For isoprene hydrogenation the products were 2M1B, 3M1B, 2M2B, and 2-methylbutane (2MB). The molar selectivity to olefins S_0 was defined as

$$S_0(\%) = \frac{\text{mol 2M1B} + \text{mol 3M1B} + \text{mol 2M2B}}{\text{mol IP converted}} \times 100.$$

The specific activity (turnover number) for hydrogenating valylene (TON_V), or isoprene (TON_I), is defined as the number of reactant molecules converted per surface Pd atom and per unit time.

RESULTS

Catalyst Characterization

Listed in Table 1 are some important characteristics of the catalysts used in this work (from Ref. (*16*)). The sample denoted PdSb0.02(573), for instance, refers to the PdSb/α-Al_2O_3 containing 0.02 wt% Sb and reduced at 573 K. The strongly adsorbed hydrogen (H/Pd, column 2) determined by the dual-isotherm technique at 298 K was used to calculate the specific activities by assuming a H/Pd_S stoichiometry equal to unity. Column 3 reports the average diameters in nanometers determined by TEM for both pure and bimetallic Pd catalysts (with the highest modifier loading).

TABLE 1

Catalyst Characterization (From Ref. (*16*))

Catalyst	(H/Pd)[a]	d_{TEM} (nm)[b]
Pd(573)	0.56	2.8
Pd(773)	0.05	12.4
Pd0.02Ge(573)	0.26	—
Pd0.02Ge(773)	0.05	—
Pd0.03Ge(573)	0.25	—
Pd0.03Ge(773)	0.05	—
Pd0.05Ge(573)	0.24	3.5
Pd0.05Ge(773)	0.04	8.4
Pd0.02Sb(573)	0.26	—
Pd0.02Sb(773)	0.05	—
Pd0.05Sb(573)	0.24	—
Pd0.05Sb(773)	0.05	—
Pd0.12Sb(573)	0.15	3.4
Pd0.12Sb(773)	0.05	11.8
Pd0.02Sn(573)	0.34	—
Pd0.02Sn(773)	0.07	—
Pd0.06Sn(573)	0.22	—
Pd0.06Sn(773)	0.06	—
Pd0.11Sn(573)	0.17	3.3
Pd0.11Sn(773)	0.06	12.0
Pd0.02Pb(573)	0.37	—
Pd0.02Pb(773)	0.04	—
Pd0.05Pb(573)	0.19	—
Pd0.05Pb(773)	0.04	—
Pd0.07Pb(573)	0.13	3.6
Pd0.07Pb(773)	0.04	15.6

[a] Strongly adsorbed hydrogen determined by the double isotherm technique; (H/Pd) = $(H/Pd)_{total}$ − $(H/Pd)_w$.

[b] Average particle size from TEM.

Let us recall briefly the results obtained in the first part of this study (*16*):

(1) low loading catalysts with true bimetallic particles (PdGe, PdSb, PdSn, and PdPb) supported on α-Al_2O_3 could be prepared by the controlled surface reaction technique;

(2) for catalysts reduced at 573 K, the second metal stands mainly as an ad-layer on the Pd particles;

(3) for catalysts reduced at 773 K, the Pd tends to migrate onto the surface under the reductive atmosphere, whereas part of the second metal diffuses into the bulk. Large bimetallic aggregates were formed and the extent of hydrogen absorption in the β-PdH phase was strongly suppressed.

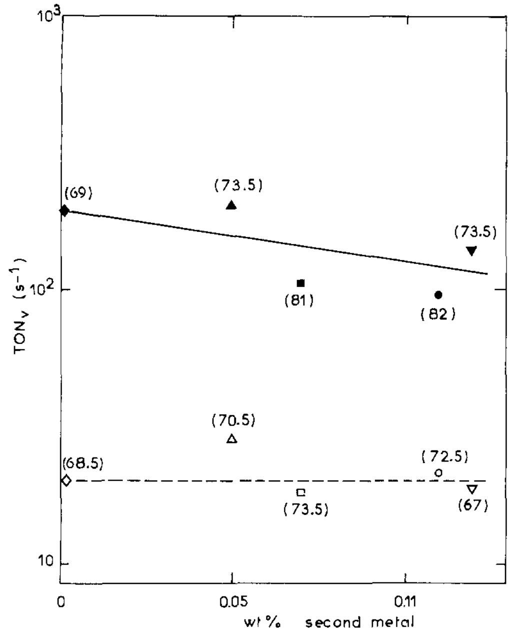

FIG. 1. Specific activities TON$_V$ (s^{-1}) at 293 K for valylene hydrogenation on alumina-supported Pd (◇, ◆), PdGe (△, ▲), PdSb (▽, ▼), PdSn (○, ●), and PdPb (□, ■) catalysts reduced at 573 K (dashed line) and at 773 K (solid line) versus the percentage loading of the second metal. Conditions: 101 kPa, 40 cm$^3_{STP}$ feed min^{-1}, W$_{cat}$ = 0.001–0.01 g, molar feed ratio: H_2/valylene = 16. The apparent activation energies in kJ mol^{-1} are shown in parentheses.

Valylene Hydrogenation

Activity. Valylene hydrogenation was carried out over all the samples prepared with the highest modifier loading. The results are illustrated in Fig. 1. The specific activity TON$_V$ at 293 K of catalysts reduced at 573 K was found to be approximately constant at 20 s^{-1}, irrespective of the modifier added. These data confirm the idea that, for catalysts reduced at 573 K, the modifier remained on the surface of Pd particles and partially blocked the active sites. On the other hand, the TON$_V$ of Pd(773) increased to 190 s^{-1}. This observation, i.e., a decrease of the specific activity as Pd dispersion increases, is in accordance with previous work on the hydrogenation of acetylenic hydrocarbons (*17–21*). The average apparent activation energies for valylene hydrogenation, shown in parentheses in Fig. 1, were 70.5 ± 3 kJ mol^{-1} for catalysts reduced at 573 K and 75.5 ± 6.5 kJ mol^{-1} for those reduced at 773 K. The similarity in the activation energy values indicates that the same reaction mechanism is operating on these catalysts.

Selectivity. The selectivity to isoprene S_I at different conversions for the different catalysts, is shown in Table 2. These results can be summarized as follows.

(1) A significant decrease in S_I on pure Pd/Al_2O_3 with increasing valylene conversion is observed. Indeed, S_I decreased from 84 to 25% on Pd(573) and from 88 to 38% on Pd(773) when increasing the valylene conversion from 20 to 80%. It might be related in part to the failure of the thermodynamic factor: valylene concentration was too low to prevent isoprene adsorption and its subsequent hydrogenation. Moreover, at high conversion nonisothermal surface condi-

TABLE 2

Selectivity to Isoprene (S_I) for Valylene Hydrogenation on Pd, PdGe, PdSb, PdSn, and PdPb/α–Al_2O_3 Catalysts Reduced at 573 K (I) and 773 K (II)

Catalyst	Conversion (%)	S_I (%)	
		I	II
Pd	15	84	88
	50	67	75
	80	25	38
PdGe0.05	15	84	88
	50	69	75
	80	25	38
PdSb0.12	15	90	95
	50	73	89
	80	38	52
PdSn0.11	15	93	96
	50	86	88
	80	43	64
PdPb0.07	15	93	98
	50	87	93
	80	58	78

tions can be suspected which alter the selectivity, as the use of different reactor configurations indicated (*26*). Finally, some diffusional limitation in these test conditions cannot be ruled out. In other respects, the S_I of pure Pd catalysts appeared to depend on particle size: the less dispersed Pd catalyst Pd(773) exhibited higher selectivity when compared with the other Pd catalysts at the same conversion, in agreement with the results of vinylacetylene hydrogenation (*17*).

(2) The data showed that S_I was improved, particularly at high valylene conversion, upon alloying Pd with Pb, Sn, or Sb for both series of catalysts (Ge has no effect). It is important to note that the differences in selectivity between bimetallic and monometallic Pd catalysts of each series were nearly the same, particularly at high conversion.

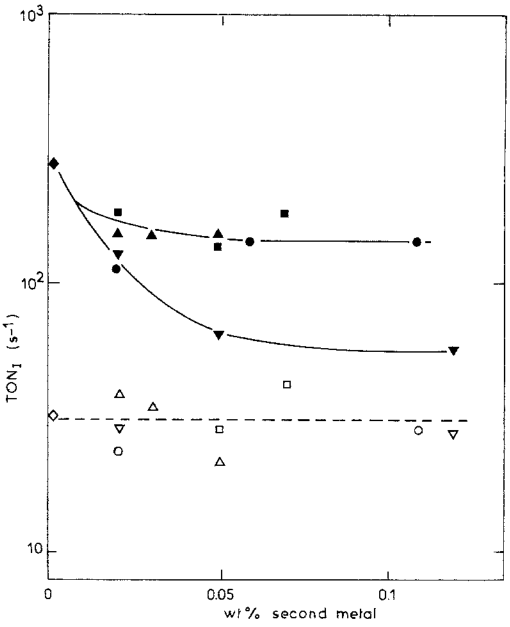

FIG. 2. Specific activities TON_I (s^{-1}) at 293 K for isoprene hydrogenation on alumina-supported Pd (◇, ◆), PdGe (△, ▲), PdSb (▽, ▼), PdSn (○, ●), and PdPb (□, ■) catalysts reduced at 573 K (dashed line) and at 773 K (solid line) versus the percentage loading of the second metal. Conditions: 101 kPa, 40 cm^3_{STP} feed min^{-1}, W_{cat} = 0.001–0.01 g, molar feed ratio: H_2/isoprene = 35.

Isoprene Hydrogenation

Activity. The dependence of the specific activity, TON_I, for isoprene hydrogenation at 293 K on Ge, Sb, Sn, and Pb percentage loading is shown in Fig. 2. The apparent activation energies for the formation of 2M2B, 3M1B, and 2M2B over the various samples were 54.5 ± 8 kJ mol^{-1}. Several trends are evident from these data. First, the specific activities TON_I at 293 K for catalysts reduced at 573 K were found to be nearly constant at 33 s^{-1} irrespective of both modifier and loading. From these results it was concluded that the main effect of Ge, Sb, Sn, or Pb addition to Pd/Al_2O_3 by the CSR technique, and subsequent reduction at 573 K, is a blockage of the Pd active sites. Second, the TON_I at 293 K for Pd/Al_2O_3 reduced at 773 K increased approximately to 380 s^{-1}, in agreement with previous studies dealing with the influence of Pd particle size (*18, 19*) on isoprene hydrogenation in the liquid phase. The orders of reaction determined in the temperature range 278–308 K, for Pd(573) and Pd(773), were zero with respect to isoprene and 0.7 with respect to hydrogen, respectively. These values confirmed that isoprene was the more strongly adsorbed reactant.

With regard to bimetallic catalysts reduced at 773 K, the inclusion of the first amounts of Ge, Sb, Sn, or Pb caused a sharp decrease (by a factor of 2–5) of specific activity. After that, the TON_I was less affected by the successive additions of modifiers up to 0.1 wt%. Finally, the close agreement between activation energies for 2M1B, 3M1B, and 2M2B formation over Pd, PdGe, PdSb, PdSn, and $PdPb/Al_2O_3$ (54 ± 8 kJ mol^{-1}), suggests that the respective mechanisms of the reactions were altered neither by the addition of Ge, Sb, Sn, or Pb nor by the reduction temperature.

Selectivity. The products, 2M1B and 3M1B, were produced by 1–2 addition of hydrogen to the isoprene, whereas 2M2B was formed, at low conversion (< 20%) by 1–4 addition. It was assumed that 2MB was produced mostly by the 2M1B and 3M1B hydrogenation. At higher conversion (> 20%) the isomerization of 2M1B and 3M1B (double bond migration reaction) was also responsible for 2M2B formation. The selectivity to olefins S_0, the ratio (2M1B + 3M1B)/2M2B representing 1–2 addition versus 1–4 addition, and the ratio 2MB/2M2B (hydrogenation versus isomerization) at different conversions for catalysts of Table 1 are given in Table 3. The results for Pd(573) and Pd(773) can be summarized as follows.

TABLE 3

Selectivity to Olefins S_0 (%), (2M1B + 3M1B)/2M2B and 2MB/2M2B Ratios for Isoprene Hydrogenation on Pd, PdGe, PdSb, PdSn, and PdPb/α–Al_2O_3 Catalysts Reduced at 573 K (I) and 773 K (II)

Catalyst	Conversion (%)	S_0 (%)		(2M1B + 3M1B)/2M2B		2MB/2M2B	
		I	II	I	II	I	II
Pd	20	95.2	97.2	1.12	0.92	0.11	0.06
	50	93.4	96.2	0.61	0.78	0.11	0.07
	70	91.6	94.6	0.30	0.54	0.11	0.09
PdGe0.02	20	95.4	96.2	0.52	0.61	0.07	0.06
	50	94.8	95.5	0.33	0.54	0.07	0.07
	70	94.2	93.6	0.25	0.43	0.08	0.09
PdGe0.05	20	95.7	95.4	0.61	0.69	0.07	0.08
	50	94.0	95.0	0.33	0.54	0.08	0.08
	70	93.2	94.3	0.30	0.45	0.09	0.09
PdSb0.02	20	97.5	98.1	0.82	0.72	0.05	0.03
	50	95.7	97.7	0.54	0.54	0.07	0.04
	70	94.1	96.5	0.41	0.43	0.09	0.05
PdSb0.05	20	97.4	97.6	0.75	0.67	0.05	0.04
	50	96.0	97.0	0.56	0.49	0.06	0.05
	70	94.3	96.6	0.41	0.39	0.08	0.05
PdSn0.02	20	98.5	98.6	1.00	1.04	0.03	0.03
	50	98.2	98.2	0.92	0.85	0.04	0.03
	70	98.2	97.4	0.75	0.67	0.03	0.04
PdSn0.06	20	98.2	99.0	0.96	0.96	0.04	0.02
	50	97.8	98.2	0.82	0.82	0.04	0.03
	70	97.4	97.9	0.69	0.64	0.04	0.03
PdPb0.02	20	99.0	98.6	0.96	1.04	0.02	0.03
	50	98.8	98.2	0.82	0.79	0.02	0.03
	70	98.5	97.4	0.61	0.61	0.02	0.04
PdPb0.03	20	99.8	99.0	1.13	1.13	0.004	0.02
	50	99.2	98.4	0.89	0.92	0.01	0.03
	70	98.7	98.0	0.79	0.67	0.02	0.03

(1) The selectivity S_0 was found to be high but it diminished as isoprene conversion increased. The change was from 95.2 to 91.6% for Pd(573) and from 97.2% to 94.6% for Pd(773) as the conversion was varied from 20 to 70%, due to the same reasons as proposed above for valylene hydrogenation. Moreover, at a given isoprene conversion, S_0 seemed to depend on the particle size: it increased with decreasing Pd dispersion, in line with previous observations (*18, 19*).

(2) The olefin distributions at 20% conversion, in close agreement with previous reports (*22, 23*), were 25% 2M1B, 28% 3M1B, and 47% 2M2B for Pd(573), and 22% 2M1B, 26% 3M1B, and 52% 2M2B for Pd(773). At higher isoprene conversion, 2M1B and 3M1B diminished whereas 2M2B increased (i.e., lower (2M1B + 3M1B)/2M2B)) due to the isomerization of 2M1B and 3M1B. However, the decrease of this ratio was influenced by particle size. The small Pd particles exhibited higher activity for 2M1B and 3M1B isomerization: (2M1B + 3M1B)/2M2B at 70% conversion was 0.30 for Pd(573) and 0.54 for Pd(773).

(3) The 2MB/2M2B ratio was found to be rather low and nearly independent of conversion: 0.11 for Pd(573) and 0.06–0.09 for Pd(773) in the 20–70% conversion range. Furthermore, the Pd particle size had only a marginal effect on 2MB/2M2B, particularly at high isoprene conversion.

The data for PdMe(573) and PdMe(773) from Table 3 (Me = Ge, Sb, Sn or Pb) can be collated in the following way.

(1) The high selectivity to olefins S_0 of Pd(573) was still improved, particularly at high isoprene conversion, on PdMe whatever the second metal, whereas the S_0 of Pd(773) was improved only upon alloying with Sb, Sn, or Pb. The differences in S_0 between PdMe(573) and PdMe(773) were insignificant as compared with the corresponding differences between Pd(573) and

Pd(773). It is to be noted that the decrease in S_0 in both the PdSn and PdPb series with isoprene conversion was rather small. In addition, the selectivity patterns of the bimetallic catalysts appeared to be marginally changed with increasing modifier loading.

(2) The values of the (2M1B + 3M1B)/2M2B ratio (1–2 addition vs 1–4 addition) at 20% conversion for PdSn and PdPb were close to those for Pd. On the other hand, it appears that PdGe, and to a lesser extent PdSb, enhanced the 1–4 addition. With increasing isoprene conversion, the rate of decrease of the (2M1B + 3M1B)/2M2B ratio was lowered on PdSn and PdPb/α-Al_2O_3. These data suggest that isomerization of 2M1B and 3M1B was partially suppressed on both catalysts.

(3) The values of the 2MB/2M2B ratio on PdMe were lower than those on Pd and were also practically independent of conversion. The marked decrease of 2MB/2M2B for PdSn and PdPb is related to the lower 2MB production (i.e., higher S_0) in comparison with the restricted formation of 2M2B via 2M1B and 3M1B isomerization.

DISCUSSION

The interaction of $(n\text{-}C_4H_9)_4Ge$, $(n\text{-}C_4H_9)_3Sb$, $(n\text{-}C_4H_9)_4Sn$, and $(n\text{-}C_4H_9)_4Pb$ with Pd/α-Al_2O_3, in the presence of adsorbed hydrogen, and a subsequent reduction treatment gave a series of bimetallic PdGe, PdSb, PdSn, and PdPb catalysts with true supported bimetallic particles. The results on the preparation and characterization of catalysts of Table 1 were discussed previously (*16*).

Activity of Monometallic Pd Catalysts

The results showing the decrease of the specific activity of Pd for the gas-phase hydrogenation of valylene and isoprene with increasing Pd dispersion are consistent with previous studies on the hydrogenation of alkynes and alkadienes, namely the hydrogenation of vinylacetylene (*17*), acetylene (*20*), and 1-butyne (*21, 22*) in the gas phase, and of 1-butyne, 1,3-butadiene, and isoprene (*18, 19*) in the liquid phase. Boitiaux *et al.* (*28, 29*) found, for the liquid-phase hydrogenation of 1-butyne on Pd, Pt, and Rh catalysts, that the apparent order with respect to 1-butyne concentration was nearly zero for the poorly dispersed catalysts, whereas it took negative values with increasing metal dispersion. A kinetic model was proposed which supported these data. The rate law provided evidence that the decrease of the TON when increasing the metallic dispersion came from a higher strength of adsorption of butadiene and isoprene on the small metallic particles compared to the larger ones. This phenomenon was confirmed by calorimetric studies on the enthalpy of adsorption of propyne and propene over Pd/Al_2O_3 catalysts (*30*). It was concluded that 1-butyne formed a strong complex with the.small metal particles. In addition, Hub *et al.* (*21*) and Ryndin *et al.* (*17a*) reported in their studies with XPS that the small Pd particles might be considered electron deficient. In fact, these authors observed an increase of the binding energy for the 3*d* core level of Pd on the highly dispersed catalysts. It was concluded that electron-donating compounds (1-butyne, vinylacetylene) could be more strongly adsorbed on the electron deficient small Pd particles. In accordance with the above mentioned results, recent data from our group for C_2H_2 hydrogenation (*20*) showed that the apparent zero order with respect to C_2H_2 for a poorly dispersed Pd catalyst (H/Pd = 0.18) changed to −0.5 for a catalyst with higher dispersion (H/Pd = 0.63). Consequently, it seemed reasonable to suggest that the low activity of the highly dispersed Pd catalysts for valylene and isoprene hydrogenation might also be related to a variation of the adsorption strength of the hydrocarbons. The fact that the apparent order with respect to isoprene was zero for both large and small Pd particles might be ascribed to the reduced range of hydrocarbon concentrations used here.

Selectivity in the Semihydrogenation on Monometallic Pd Catalysts

It appeared that the selectivities S_I and S_0 for the gas-phase hydrogenation of valylene and isoprene decreased, at a given conversion, on the less dispersed Pd catalyst. The difference in selectivity, clearly observed even at 20% conversion, increased at high hydrocarbon conversion. Our results are in agreement with those reported by Vasudevan (*18*) and Boitiaux *et al.* (*19*) for the liquid-phase hydrogenation of 1-butyne, 1,3-butadiene, and isoprene. Ryndin *et al.* (*17*) reported that the selectivity for the gas-phase hydrogenation of vinylacetylene was nearly independent of Pd dispersion. Nevertheless, a careful inspection of their data revealed that the selectivity decreased as Pd dispersion increased, even at a conversion less than 10%. In contrast, Hub *et al.* (*21*) in their study of 1-butyne hydrogenation in the gas phase reported similar selectivity values (approx. 98%) for Pd catalysts with 26 and 97% dispersion, up to 50% conversion. For higher conversion values, it was shown that the selectivity for the small particles was higher than that for the larger ones. In our opinion the discrepancy between the literature data might be ascribed to the different experimental conditions adopted, particularly the catalyst pretreatment. As previously mentioned, the samples in the present work were activated *in situ* by the reaction mixture at low conversion. While catalysts were slowly reduced by the hydrogen of the reaction mixture the catalytic activity increased until a steady state was reached. On the other hand, we found that conditioning the samples by reduction at 573 K, purging with He at 573 K, and cooling to 283 K was inadequate. In fact, the reduced catalyts presented such a high activity that they readily deactivated with a subsequent breakdown in selectivity. It must be noted that this effect was observed for both highly and poorly dispersed Pd catalysts.

Concerning the decrease in selectivity with increasing Pd dispersion it appeared that the onset of isoprene and olefin (2M1B, 3M1B, and 2M2B) readsorption depends on Pd particle size. Alternatively, it cannot be excluded that the reactants could be adsorbed on Pd in different forms and that their ratio might alter the selectivity control at high conversion. Hence it is likely that the crystal size will favor the formation of a certain adsorption complex on Pd particles at high conversion. In addition, the observed decrease in selectivity with increasing Pd dispersion might also be ascribed, at least in part, to a heat transfer effect. If the apparent order with respect to the hydrocarbon changed to more negative values it is conceivable that at high conversion the rate of heat transfer might not be high enough to preserve the isothermicity of the catalyst bed (*10, 20a*). Certainly a more in-depth research is needed to gain information on the reaction mechanisms.

Activity and Selectivity of Bimetallic Pd Catalysts

It has been shown that TON_I, TON_V, and S_I, S_0 (at low conversion) values of Pd/α-Al_2O_3 remained nearly constant upon addition of Ge, Sb, Sn, or Pb up to 0.1 wt% for catalysts reduced at 573 K. It is obvious that the intrinsic high selectivity of Pd at low conversion obscured the modifier effects. Nevertheless, improved S_0 and S_I values at high conversion resulted with PdSb, PdSn, and PdPb in the order PdSb < PdSn < PdPb. The higher selectivities of bimetallic catalysts reduced at 573 K (small particles) might be ascribed in part to a dilution effect of the Pd sites. The isolation of the active sites upon alloying probably produced a significant improvement in the dissipation of the heat of reaction. Another possibility is that the modifiers selectively blocked the sites which would be responsible for the unselective behavior. This interpretation was put forward to explain the improved selectivity in semihydrogenation of acetylene, when alloying Pd with Cu (*31*). Formation of multiply adsorbed ethylidyne species, responsible for the direct hydrogenation of C_2H_2 to C_2H_6, was prevented by dilution of the Pd surface with Cu, the ensemble size effect (*31, 32*). Nevertheless, the observed selectivity pattern indicated that some other effect might be playing a role. We suggest that the presence of modifiers (Sb, Sn, or Pb) as an ad-layer on the Pd surface upon reduction at 573 K produced a change of the relative adsorption strength of the reactants and intermediate products over the bimetallic sites, in accordance with the results of Palczewska *et al.* (*7*) and Cerveny *et al.* (*9*). Palczewska *et al.* (*7*) reported an improved selectivity for the C_2H_2 hydrogenation on Pb/Pd(111). It was observed that the molecular C_2H_4 adsorption, the dissociative adsorption of hydrogen and the strongly adsorbed C_2H_2 were nearly suppressed. In addition, Cerveny *et al.* (*9*) found that the selectivities for the competitive hydrogenations of 2,5-dimethyl-2,4-hexadiene with 1-heptene, and 2-octyne with 1-heptene, increased on Pd covered by Pb. The authors suggested that the ability to form π-bonds with the reactants decreased on Pd covered by Pb and this fact influenced to a relatively larger degree the interactions of alkenes rather than the interactions of alkadienes or alkynes. On the other hand, it is well known that the possibility of discrimination between geometric and electronic effects of alloying may be achieved by studying the IR spectra of adsorbed CO. For Pt catalysts Bastein *et al.* (*33*) using the isotopic dilution method reported a shift of the IR band of adsorbed CO to a lower wavenumber upon alloying with Pb or Sn. This shift was attributed in part to a ligand effect. We suggest that the same effects would most likely be operative with PdPb and PdSn catalysts.

For PdMe catalysts reduced at 773 K (large particles), a moderate decrease of TON_V and TON_I (at low conversion) was observed, whereas S_I and S_0 at high conversion increased on PdSb, PdSn, PdPb. Upon reduction at 773 K, Pd tends to migrate toward the surface, whereas the modifiers diffused into the bulk of the particles (*16*). Most probably intermetallic compounds of Sb, Sn, or Pb have formed on the surface, namely Pd_3Sb, Pd_3Sn, and Pd_3Pb. We speculate that the presence of these compounds on the surface might also alter the chemisorption strength of the hydrocarbons, in agreement with results by Palczewska *et al.* (*8*) who reported improved selectivities with $Pd_3Pb/CaCO_3$ catalysts for the hydrogenation of C_2H_2 and 2-butyne.

Finally, with respect to the isomerization of 2M1B and 3M1B (double bond migration reaction) in the isoprene hydrogenation the more important result is the partial suppression of this reaction over PdSn and PdPb/α-Al_2O_3.

CONCLUSIONS

(1) On the PdMe/α-Al_2O_3 catalysts reduced at 573 K the turnover frequencies for the hydrogenation of valylene and isoprene were not modified by Ge, Sb, Sn, or Pb addition.

(2) On Pd/α-Al_2O_3 reduced at 773 K, the turnover frequencies increased due to an apparent crystal size effect.

(3) The specific activities for hydrogenating the two reactants on the bimetallics PdGe, PdSb, PdSn, and PdPb/α-Al_2O_3 reduced at 773 K decreased by a factor of 2–5 upon addition of Ge, Sb, Sn, or Pb up to 0.1 wt%.

(4) Selectivities S_I and S_0 at high conversion were improved upon alloying in the order Sb $<$ Sn $<$ Pb, while Ge had no effect. These results were interpreted in part by a change in the relative adsorption strength of reactants and intermediate products.

(5) The isomerization of 2M1B and 3M1B during isoprene hydrogenation was partially suppressed on PdSn and PdPb/α-Al_2O_3.

REFERENCES

1. Bond, G. C., "Catalysis by metals." Academic Press, London/New York, 1962.
2. Bond, G. C., and Wells, P. B., "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 15, p. 91. Academic Press, New York, 1964.

3. Boitiaux, J. P., Cosyns, J., Derrien, M., and Leger, G., *Hydrocarbon Process.* **64,** 51 (1985).
4. Derrien, M., *in* "Catalytic hydrogenation" (L. Cerveny, Ed.), p. 613. Elsevier, Amsterdam, 1986.
5. Lindlar, H., *Helv. Chim. Acta* **35,** 446 (1952).
6. 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.
7. Palczewska, W., Ratajczykowa, I., Szymerska, I., and Krawczyk, M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 173. Dechema, Frankfurt-am-Main, 1984.
8. Palczewska, W., Jablonski, A., Kaszkur, Z., Zuba, G., and Wernish, J., *J. Mol. Catal.* **25,** 307 (1984).
9. Cerveny, L., Paseka, I., Surma, K., Thanh, N. T., and Ruzicka, V., *Collect. Czech. Chem. Commun.* **50,** 61 (1985).
10. Aduriz, H. R., Bodnariuk, P., Dennehy, M., and Gigola, C. E., *in* "Proceedings, 38th Canadian Chemical Engineering Conference, Edmonton, 1988."
11. Ulan, J. G., Kuo, E., Maier, W. F., Rai, R. S., and Thomas, G., *J. Org. Chem.* **52,** 3126 (1987).
12. Ulan, J. G., Maier, W. F., and Smith, D. A., *J. Org. Chem.* **52,** 3132 (1987).
13. Travers, Ch., Bournonville, J. P., and Martino, G., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 891. Dechema, Frankfurt-am-Main, 1984.
14. Margitfalvi, J., Hegedus, M., Gobolos, S., Kern-Talas, E., Szedlacsek, P., Szabo, S., and Nagy, F., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. IV, p. 903. Dechema, Frankfurt-am-Main, 1984.
15. Margitfalvi, J., Szabo, S., and Nagy, F., *in* "Catalytic Hydrogenation" (L. Cerveny, Ed.), p. 373. Elsevier, Amsterdam, 1986.
16. Aduriz, H. R., Bodnariuk, P., Coq, B., and Figueras, F., *J. Catal.* **119,** 97 (1989).
17. (a) Ryndin, Yu. A., Nosova, L. V., Boronin, A. I., and Chuvilin, A. L., *Appl. Catal.* **42,** 131 (1988). (b) Ryndin, Yu. A., Stenin, M. V., Boronin, A. I., Bukhtiyarov, V. I., and Zaikovskii, V. I., *Appl. Catal.* **54,** 277 (1989).
18. Vasudevan, S., Ph.D. thesis, I.F.P. (Technip. Ed.), Paris, 1982.
19. Boitiaux, J. P., Cosyns, J., and Vasudevan, S., *Appl. Catal.* **6,** 41 (1983).
20. (a) Gigola, C. E., Aduriz, H. R., and Bodnariuk, P., *Appl. Catal.* **27,** 133 (1986). (b) Aduriz, H. R., Bodnariuk, P., Dennehy, M., and Gigola, C. E., *Appl. Catal.* **58,** 227 (1990).
21. Hub, S., Hilaire, L.,and Touroude, R., *Appl. Catal.* **36,** 307 (1988).
22. Hub, S., and Touroude, R., *J. Catal.* **114,** 411 (1988).
23. Lebed'ev, S. V., and Yabubchik, A. O., *J. Chem. Soc.*, 823 (1928).
24. Frolov, V. M., Parenago, O. P., Novikova, A. V., and Kovaleva, L. S., *React. Kinet. Catal. Lett.* **25,** 319 (1984).
25. Kiperman, S. L., *in* "Catalytic hydrogenation" (L. Cerveny, Ed.), p. 1. Elsevier, Amsterdam, 1986.
26. Aduriz, H. R., Bodnariuk, P., Coq, B., and Figueras, F., *in* "Proceedings, 10th Iberoamerican Symposium on Catalysis, Merida," p. 438, 1986.
27. Boudart, M., and Hwang, H. S., *J. Catal.* **39,** 44 (1975).
28. Boitiaux, J. P., Cosyns, J., and Robert, E., *Appl. Catal.* **32,** 145 (1987).
29. Boitiaux, J. P., Cosyns, J., and Robert, E., *Appl. Catal.* **32,** 169 (1987).
30. Guerrero, A., Reading, M., Grillet, Y., Rouquerol, J., Boitiaux, J. P., and Cosyns, J., *Z. Phys. D.: At. Mol. Clusters* **12,** 583 (1989).
31. Leviness, S., Nair, V., Weiss, A. H., Schay, Z., and Guczi, L., *J. Mol. Catal.* **25,** 131 (1984).
32. Sarkany, A., Weiss, A. H., and Guczi, L., *J. Catal.* **98,** 550 (1986).
33. Bastein, A. G. T. M., Toolenaar, F. J. C. M., and Ponec, V., *J. Catal.* **90,** 88 (1984).