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

I. Preparation and Characterization

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Bimetallic PdSn, PdSb, PdPb, and PdGe on alumina catalysts with a low metal content have been prepared using either chloride or organometallic precursors. For the catalysts obtained from chloride precursors no interaction was observed between the two metals, and the catalysts behaved like pure Pd/Al_2O_3. In contrast, the reactions of $(C_4H_9)_4Sn$, $(C_4H_9)_4Pb$, $(C_4H_9)_4Ge$, or $(C_4H_9)_3Sb$ in *n*-heptane solution with reduced Pd/Al_2O_3 catalyst yielded a supported alloy. The interaction between metallic palladium and the organic modifier is highly selective and leads to the formation of a well-tailored bimetallic catalyst. When these final solids are reduced at 573 or 773 K, the second metal locates preferentially at the outer layer of the bimetallic aggregates. After reduction at 773 K large metallic aggregates are obtained (particle size ≅ 15 nm), and the formation of β-palladium hydride, which can be formed with pure palladium catalysts, is suppressed by the addition of a small amount of the second metal. The specific activity of the palladium surface atoms for isoprene hydrogenation is then lowered, and the selectivity increased. © 1989 Academic Press, Inc.

INTRODUCTION

The addition of a second metal to a metallic catalyst is a well-known method for modifying its selectivity. In order to understand such selectivity changes, at least two questions must be answered: (i) where is the second metal located and are the two metals together in the same aggregates, and if so (ii), what is the surface composition? Answers to these questions are needed to interpret catalytic results within the framework of the ensemble or the ligand theory of alloys (*1*). The first question is of great importance since the beneficial effect on selectivity can arise, in part, from the presence of the two metals as separated entities on the carrier. This is the case for PtRe or PtSn reforming catalysts, for which the increased stability against coke poisoning may be partly explained by the presence on the alumina support of ionic tin or rhenium species, which prevent coke formation (*2*, *3*). Actually, it is difficult with supported bimetallic catalysts to ascertain the existence of a pure alloying effect which would not be altered by the phenomenon described above. The nature and composition of the supported particles strongly depend on the way in which the catalysts are prepared.

Various routes exist for the preparation of bimetallic catalysts (*4*). Most commonly, metals are introduced by co-impregnation or successive impregnations, or by exchange, of the carrier with solutions of the metallic salts. The formation of bimetallic particles then needs the migration of at least one of the components over the oxide surface. This process is greatly affected by thermal treatment of the solid, and the results observed reflect the averaged behavior of particles of very different compo-

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sitions. Another method of preparing such catalysts involves the deposition of molecular bimetallic clusters. However, the use of this method is limited by the availability of high nuclearity clusters and by the narrow choice of metallic couples. Finally, a new route which appears fruitful, but which has so far received less attention, is the addition of the second metal as an organometallic compound to a prereduced monometallic catalyst. This addition can proceed via the gaseous phase (*5*, *6*) or the liquid phase for rhodium, nickel, and platinum catalysts modified by tin (*7–9*). A characteristic feature of this method is the very selective metal–organometallic interaction which is achieved, for instance, in the case of RhSn catalysts. When tin is deposited on reduced Rh/Al_2O_3 as tetra-*n*-butyl tin no trace of tin can be detected on the alumina carrier (*8*).

From these considerations it appeared of great interest to extend the relevance of these concepts to other metals and organometallic compounds. In the work to be described we have studied the modifications of palladium catalysts by tin, antimony, lead, and germanium organometallics. The second metal is introduced from the liquid phase as tri- or tetra-*n*-butyl compounds. The choice of palladium arises from the great importance of this metal in selective hydrogenation of unsaturated hydrocarbons. The remarkable selectivity of palladium for partial hydrogenation of dienes and of alkynes can be improved by modification with certain metallic additives (*10*). The use of the procedure described above is particularly attractive with palladium because it opens up better possibilities for obtaining a well-dispersed bimetallic system, since a well-dispersed monometallic palladium as a starting material can be prepared.

EXPERIMENTAL

Catalyst Preparation

Pd, PdSn, PdPb, PdSb, and PdGe from organometallic precursors. The support used was α-alumina from Rhône-Poulenc (ref. SCS9, surface area = 13 $m^2\ g^{-1}$, pore volume = 0.47 $cm^3\ g^{-1}$, average pore size = 100 nm, particle size range = 0.15–0.5 mm). The support was first calcined at 773 K overnight and palladium was then introduced as Pd-acetylacetonate (Merck, purity >98%) in a benzene solution (7.10^{-4} g ml^{-1}) following the procedure described by Vasudevan *et al.* (*11*). In this procedure the fixation of the Pd complex occurs either by means of a ligand exchange with surface hydroxyl groups (*11*) or by direct insertion (anchoring) of the Pd into any vacant aluminium site on the carrier surface (*12*). The respective part of the two processes may depend on the nature of the alumina. The alumina was contacted for 72 h at room temperature with the Pd solution at the liquid/solid ratio of 5/1. The filtered solid was then dried overnight at 383 K, calcined at 573 K for 4 h, cooled to room temperature under N_2, and further reduced at 573 K in a flow of high purity hydrogen (>99.99%). The resulting solid contained 0.09 wt% Pd (Pd(573)) and constituted the parent material for the catalysts (monometallic or bimetallic) prepared from organometallic precursors.

Starting from the procedure described by Travers *et al.* (*8*), tin, lead, antimony, and germanium were deposited on the reduced Pd/Al_2O_3 as organometallic compounds. Tetra-*n*-butyl tin (Merck, purity >95%), tetra-*n*-butyl lead (Ventron, >98%), tri-*n*-butyl antimony (Alfa), and tetra-*n*-butyl germanium (Alfa) were dissolved in *n*-heptane (Fluka, >99%) at concentrations ranging from 10^{-4} to 10^{-3} g ml^{-1}, depending on the desired amount of Groups IVA and VA elements in the catalyst. The deposition was performed in a sealed tube at 363 K with a contact time ranging from 0.25 to 48 h. The filtered solid was then dried overnight at 383 K.

All samples were subsequently subjected to sintering under flowing H_2 at different temperatures. A catalyst prepared by this procedure, containing 0.11 wt% Sn and reduced at 573 K, will be designated PdSn0.11(573).

PdSn from chloride salt precursors. The α-alumina described above was used as the support. Pd was introduced first as $PdCl_2$ in acidic medium, dried at 393 K, calcined at 573 K, and reduced at 573 K. Tin was then added as $SnCl_2$ at room temperature and the solid was dried at 393 K and reduced at 573 K. More sintered samples were obtained by further reductions at higher temperatures.

For both series of catalysts chemical analyses were performed by the wet method, including dissolution of the solid and analysis by atomic absorption spectrometry.

Catalyst Characterization

Sorption measurements. Hydrogen sorption measurements were carried out in a conventional volumetric apparatus in the pressure range 0–50 kPa. The hydrogen used was of a high purity grade (>99.995) and was purified further by diffusion through a palladium thimble. Before the sorption measurements the samples were dried at 393 K under N_2, reduced at 573 K under H_2 for 2 h, and outgassed overnight to 10^{-2} Pa at the same temperature. The double isotherm method proposed by Benson *et al.* (*13*) was used to measure the amount of hydrogen chemisorbed on the palladium surface as well as that absorbed to form the bulk β-palladium hydride phase. The first isotherm consists of both adsorbed and absorbed hydrogen; outgassing at room temperature for 30 min removes the absorbed hydrogen and completely destroys the β-palladium hydride phase. Then a second (back-sorption) isotherm is performed which represents the amount of hydrogen absorbed into bulk palladium since hydrogen chemisorbed on the palladium surface has not been removed by evacuation at room temperature (*13*). The difference between the two curves represents the isotherm of adsorption of hydrogen. The extrapolated value at zero pressure was taken as the amount of irreversibly adsorbed hydrogen.

Provided the surface stoichiometry of irreversibly adsorbed hydrogen is unity, we have the metal dispersion given by $D_M = (H/Pd)_{Irr}$.

Temperature-programmed desorption (TPD). TPD analysis of a sample saturated with hydrogen enables one to obtain some experimental evidence for the strength of the Pd–H interaction and particularly to determine whether the β-palladium hydride phase is formed or not.

The apparatus used was very similar to that described by Robertson *et al.* (*14*). The solids were first reduced at 573 K and then cooled to 273 K under the reduction mixture of the TPD experiments, i.e., 5% H_2 in argon (Matheson, ultrahigh purity grade). The heating rate was 15 K min^{-1}, the sample weight 0.5 g, and the gas flow rate 10 cm^3 min^{-1}.

Transmission electron microscopy (TEM). A Jeol 100 CX instrument with side entry goniometer was used to determine the average particle diameter. The resolution at 100 kV acceleration voltage was 0.3 nm. The average particle diameter and the particle size distribution for each sample were obtained by taking bright field images from different areas. The average particle size has been calculated by the equation $\bar{d}_{VS} = \sum_i n_i d_i^3 / \sum_i n_i d_i^2$, where n_i is the number of particles with size d_i.

Catalytic Tests

Gas phase hydrogenation of isoprene was carried out in a flow reactor, operating in the differential mode. Isoprene (Merck, purity >98%) was purified over high-surface-area alumina to eliminate the stabilizing agent (4-*t*-butylpyrocatechol). The reactant pressure was 2.7 kPa in all experiments. Hydrogen (>99.99%) was passed through a MnO cell to trap trace impurities of oxygen and dried over molecular sieve. The samples tested in these experiments were the PdSn catalysts prepared according to the routes described above.

RESULTS

Adsorption of Germanium, Tin, Lead, and Antimony Organometallics on Pd/Al_2O_3

The adsorption of tetrabutyl germanium, lead, or tin, and tributyl antimony in *n*-heptane solution on Pd/Al_2O_3 catalysts has been studied at 363 K. UV spectroscopy and gas chromatography have been used to follow the concentration of organometallic compounds in *n*-heptane. Travers *et al.* (*8*) reported previously that $(C_4H_9)_4Sn$ does not adsorb on a γ-alumina support. We have checked that the same holds for the α-alumina used in this work. $(C_4H_9)_4Sn$ and $(C_4H_9)_4Ge$ do not adsorb on α-Al_2O_3, whereas $(C_4H_9)_4Pb$ and especially $(C_4H_9)_3Sb$ show adsorption. For the latter a solution containing 8.6×10^{-4} g Sb cm^{-3} leaves 3.7×10^{-3} g Sb (g $Al_2O_3)^{-1}$ on the support, for a liquid/solid ratio of 5. However, $(C_4H_9)_3Sb$ is weakly bound to the support and most of it disappears during the thermal treatment.

Figure 1 shows the adsorption of $(C_4H_9)_4Sn$ as a function of time on a Pd/Al_2O_3 catalyst having a metallic dispersion, D_M, of 0.54. The ratio between Sn and Pd surface atoms reaches a maximum value of 1.7 after 4 h contact time. At the temperature investigated the adsorption of $(C_4H_9)_4Sn$ is slow. Diffusional retardation of the transport of the reactant in the porous medium is thereby avoided, and inhomogeneity of tin distribution is prevented.

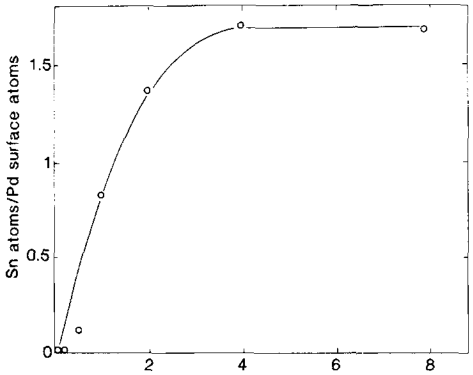

FIG. 1. Adsorption vs time for $(C_4H_9)_4Sn$ on 0.09 wt% Pd/α-Al_2O_3. $D_M = 0.54$; catalyst weight = 0.5 g; 10 ml of solution containing 1.35×10^{-2} g Sn; temperature = 363 K.

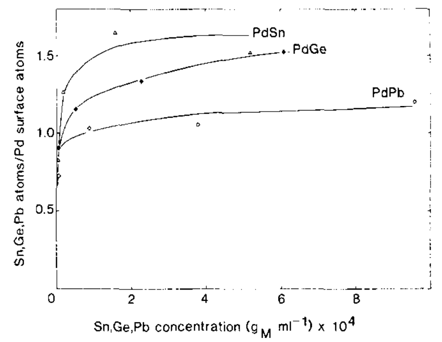

FIG. 2. Adsorption isotherms of $(C_4H_9)_4Sn$, $(C_4H_9)_4Ge$, and $(C_4H_9)_4Pb$ on 0.09 wt% Pd/α-Al_2O_3. $D_M = 0.54$; catalyst weight = 0.1 g; volume of solution = 0.5 cm^3; temperature = 363 K.

Figure 2 shows the adsorption isotherms at 363 K of tin, germanium, and lead organometallics on Pd/Al_2O_3. Where saturation of the surface is reached at low concentration, the interaction between the organometallic and the palladium surface is strong and selective. A second interesting point is that maximum coverage of the palladium surface by the second metal is reached at between 1.2 and 1.6 atom per Pd surface atom, the lower value corresponding to the larger molecule, namely $(C_4H_9)_4Pb$. It is relevant to enquire whether the maximum coverages depend on the Pd particle size. Table 1 shows that the Sn/Pd surface ratio remains constant whatever the

TABLE 1

Stoichiometry of $(C_4H_9)_4Sn$ Adsorption on Palladium as a Function of the Pd Dispersion, D_M, Calculated from $(H/Pd)_{irr}$

D_M	0.70	0.54	0.31	0.05
$\frac{\text{Sn(adsorbed)}}{\text{Pd(surface)}}$	1.5	1.75	1.75	1.8

Note. $T = 363$ K.

dispersion of palladium in the range of particle diameters from 1.5 to 20 nm. The slight increase, from 1.5 to 1.8, of this surface ratio with Pd particle size is not considered significant.

After the adsorption of the organometallic compounds on the Pd surface, various experiments were carried out with $(C_4H_9)_4Ge$ as a model compound in order to obtain information on the decomposition of the adsorbed species. The following observations were made:

(i) the α-alumina used in this work neither adsorbs nor decomposes $(C_4H_9)_4Ge$ at temperatures lower than 473 K, either in the liquid or the gaseous phase.

(ii) no butane can be detected in the gas phase when $(C_4H_9)_4Ge$ is adsorbed from a solution in *n*-heptane at 363 K.

(iii) after drying the solid in contact with air, treatment in hydrogen releases an amount of butane which represents only about 10% of the maximum possible value, assuming a surface stoichiometry Ge/Pd of 1.5. This suggests that the major part of the $(C_4H_9)_4Ge$ decomposes when exposed to air. This hypothesis seems to be confirmed by experiments in which gaseous $(C_4H_9)_4Ge$ in nitrogen has been led over a prereduced Pd/Al_2O_3 sample. Under these conditions amounts of butane and butene corresponding to the quantitative decomposition of $(C_4H_9)_4Ge$ over Pd have been detected in the effluents. Adsorbed hydrogen therefore acts as a reservoir for *n*-butane formation. This behavior appears to be different from that observed in the deposition of tin on Pt/Al_2O_3 as $(C_2H_5)_4Sn$ (*9*) where a hydrogen atmosphere seems to be necessary for the decomposition of organometallic tin. However, in both cases the reaction is:

$$M\text{–}H_{ad} + R_4M' \rightarrow M\text{–}M'R_{4-x} + xRH,$$

where M stands for Pt or Pd and M' for the second metal.

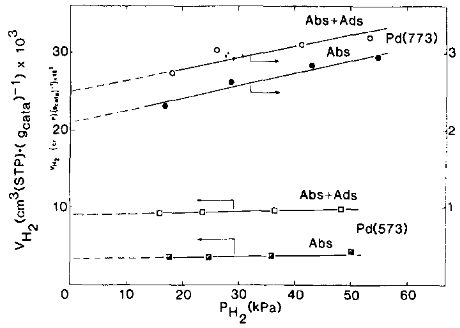

FIG. 3. Typical sorption and back-sorption isotherms at 293 K on Pd(773) and Pd(573) catalysts.

TABLE 2

Ratios of the Number of Tin, Lead, and Germanium Atoms to the Number of Palladium Atoms

	Samples (M'/Pd)		
	PdSn	PdPb	PdGe
$R1$	0.93	0.82	0.60
$R2$	0.96	0.72	0.70

Note. $R1$: after adsorption of the organometallic compounds. $R2$: in the final catalyst.

Finally, after the thermal treatments of the $PdM'(C_4H_9)_{4-x}/Al_2O_3$ samples, a near quantitative recovery of the second metal is achieved (Table 2).

Catalyst Characterization

Typical sorption isotherms are shown in Fig. 3 for catalysts reduced at 573 and 773 K. In Fig. 4 histograms of particle size distribution are reported for the catalysts prepared from organometallic precursors. Tables 3 and 4 report the main characteristics of the samples. The amount of strongly adsorbed hydrogen $(H/Pd)_{Irr}$ gives the metallic dispersion, D_M, which was used to calculate the turnover frequency for isoprene hydrogenation. $(H/Pd)_w$ corresponds either to hydrogen weakly chemisorbed at 298 K on small particles ($D_M > 0.5$) or to hydrogen contained as palladium hydride inside the large Pd particles (*15–17*); the dissolved hydrogen may also be present in small par-

TABLE 3

Main Characteristics of Catalysts Prepared from Organometallic Precursors

Catalyst	xPd	$(H/Pd)_{Irr}$	$(H/Pd)_{w}$	$x\mathrm{Pd}_s$	Particle size from TEM (nm)
Pd(573)	1	0.54	0.31	1	2.8
Pd(773)	1	0.05	0.20	1	12.4
PdGe0.02(573)	0.77	0.25	0.28	—	—
PdGe0.02(773)	0.77	0.05	0.19	—	—
PdGe0.03(573)	0.69	0.24	0.27	—	—
PdGe0.03(773)	0.69	0.05	0.12	—	—
PdGe0.05(573)	0.56	0.24	0.27	0.38	3.5
PdGe0.05(773)	0.56	0.05	0.06	0.15	8.4
PdSb0.02(573)	0.84	0.26	0.28	—	—
PdSb0.02(773)	0.84	0.05	0.11	—	—
PdSb0.05(573)	0.78	0.24	0.22	—	—
PdSb0.05(773)	0.78	0.04	0.06	—	—
PdSb0.12(573)	0.47	0.16	0.14	0.20	3.4
PdSb0.12(773)	0.47	0.03	0.02	0.18	11.8
PdSn0.02(573)	0.84	0.34	0.28	—	—
PdSn0.02(773)	0.84	0.07	0.05	—	—
PdSn0.06(573)	0.64	0.22	0.10	—	—
PdSn0.06(773)	0.64	0.05	0.03	—	—
PdSn0.11(573)	0.50	0.17	0.06	0.18	3.3
PdSn0.11(773)	0.50	0.05	0.03	0.23	12.0
PdPb0.02(573)	0.91	0.37	0.26	—	—
PdPb0.02(773)	0.91	0.04	0.14	—	—
PdPb0.03(573)	0.86	0.19	0.18	—	—
PdPb0.03(773)	0.86	0.04	0.10	—	—
PdPb0.07(573)	0.73	0.13	0.10	0.23	3.6
PdPb0.07(773)	0.73	0.04	0.02	0.30	15.6

ticles (*17*). A rough estimation of the Pd surface composition could be made from chemisorption and transmission electron microscopy data (Table 3). Although the crystallography of bimetallic particles is unknown, it was assumed that the density of surface atoms was not substantially altered by addition of the second metal. The atomic surface Pd fraction can then be estimated by the relation:

$$x\mathrm{Pd}_s = \frac{(\text{Pd surface area})}{(\text{bimetallic surface area})}$$
$$= 7.45 \times 10^{-2}\, D_M d x_{\mathrm{Pd}} \rho,$$

in which ρ is the bulk average density of bimetallic particles in g cm^{-3}, d the average diameter in nm determined by TEM, and x_{Pd} the atomic bulk Pd fraction. The Pd surface area was calculated from D_M considering an atomic area of Pd of 7.9×10^{-2} nm^2 per Pd atom. The surface area of the bimetallic particles was evaluated assuming that the particles were spheres with an average diameter d.

TABLE 4

Metallic Dispersion, D_M, of Palladium in PdSn/Al_2O_3 Catalysts Prepared from Chloride Precursors

Reduction temperature (K)	Tin content (wt%)			
	0.0	0.02	0.06	0.011
573	0.29	0.32	0.30	0.27
773	0.05	0.06	0.04	0.04

Note. Palladium content: 0.11 wt%.

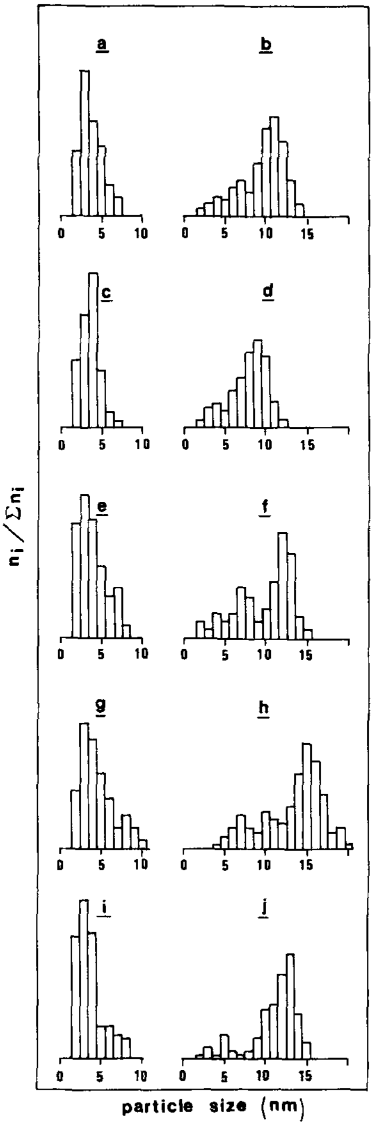

FIG. 4. Size distribution of the metallic particles for different samples: (a) Pd(573); (b) Pd(773); (c) PdGe0.05(573); (d) PdGe0.05(773); (e) PdSn0.11(573); (f) PdSn0.11(773); (g) PdPb0.07(573); (h) PdPb0.07 (773); (i) PdSb0.12(573); (j) PdSb0.12(773).

The general tendency is a strong sintering of the samples reduced at 773 K as evidenced by microscopy and hydrogen chemisorption. On the samples reduced at 573 K the addition of Ge, Sb, Sn, or Pb decreases the adsorption of hydrogen. The magnitude of this effect increases from Ge to Pb and with the amount of the second metal. However the addition of the second metal does not induce a further modification of the particle size. Indeed, sintering at 773 K is slightly slowed according to the sequence PdGe < PdSn, PdSb < PdPb as TEM indicates. Based on simple geometrical considerations it appears that the increase of the mean particle size from 2.8 nm (Pd(573)) to 3.4 nm (bimetallic aggregates) corresponds to an addition of an atomic monolayer of the second metal (*18*). An aggregate of 2.8 nm contains around 500–550 atoms and an overlayer adds about 400 atoms. Then, taking into account the changes of hydrogen chemisorption, it follows that most of the atoms of the second metal stay on the surface, i.e., 60–70% Sb and up to 90–100% Pb. However, the case of germanium does not enter into this simple scheme.

The value of $(H/Pd)_w = 0.20$ obtained on sintered Pd(773) sample indicates that some β-palladium hydride phase could be formed. In contrast the very low $(H/Pd)_w$ ratios obtained with PdSb, PdSn, and PdPb suggest that the formation of the β-hydride phase was inhibited by the addition of Sb, Sn, or Pb.

The findings described above are in good agreement with the TPD data (Fig. 5). The hydrogen desorption curves provide evi-

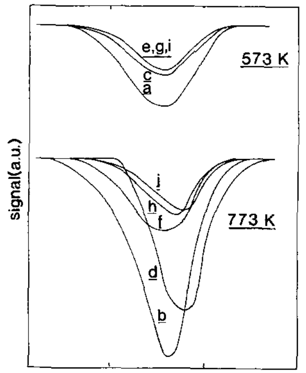

FIG. 5. Temperature-programmed desorption profiles for H_2 on different catalysts reduced at 573 and 773 K: same catalysts as in Fig. 4.

TABLE 5

Specific Activities for Hydrogenation of Isoprene, Expressed as Turnover Frequencies (s^{-1}), of PdSn/Al_2O_3 Catalysts Prepared from Chloride Precursors, as a Function of the Tin Content and the Reduction Temperature

Reduction temperature (K)	Tin content (wt%)			
	0.0	0.02	0.06	0.011
573	69	58	87	76
773	645	545	630	730

Note. Palladium content: 0.11 wt%; reaction temperature: 293 K.

dence for different behaviours. On the samples reduced at 773 K a small addition of the second metal modifies deeply the amount of desorbed hydrogen, except in the case of Ge. The hydrogen species which is suppressed is mainly the weakly absorbed form dissolved in the bulk of large particles (*17*). This constitutes a strong argument for the suppression of β-hydride formation by small amounts of tin, lead, or antimony. The inhibition of the β-phase by the presence of a second metal in bimetallic Pd aggregates was envisaged also in the PdCu catalysts for acetylene hydrogenation (*19*, *20*).

By contrast, when tin is added as a chloride precursor it does not influence the chemisorptive behaviour of Pd, whatever reduction temperature is used (Table 4).

Hydrogenation of Isoprene

During the course of isoprene hydrogenation no deactivation of the catalysts was observed. Such a deactivation is usually caused by the adsorption of oligomers produced either at the metallic surface or at the acidic sites of the carrier. The use of α-alumina as carrier and of a high hydrogen/isoprene ratio circumvented the occurrence of these phenomena, as previously observed (*15*, *21*). As shown in Table 5, for catalysts reduced at the same temperature the addition of tin via the chloride precursor has little effect on the turnover frequency (TOF) in isoprene hydrogenation. The higher specific activity per Pd surface atom for large metallic particles is in close agreement with previous work on the gas phase and liquid phase hydrogenation of dienes (*21*, *22*). By contrast, the incorporation of tin by tetra-*n*-butyl tin exerts a clear influence on the catalytic behaviour of palladium (Table 6). However, this influence depends on the reduction conditions of the sample. On catalysts reduced at low temperature (573 K), the specific activity does not change with the tin content, but after reduction at 773 K, tin lowers the catalytic activity of the large Pd particles. As previously reported for the hydrogenation of 1,3-butadiene in the liquid phase (*21*) the selectivity for the half-hydrogenation of isoprene to pentenes decreases when the dispersion increases. This behaviour differs from that

TABLE 6

Catalytic Properties in the Hydrogenation of Isoprene of PdSn/Al_2O_3 Catalysts Prepared from Organometallic Precursors as a Function of the Tin Content and the Reduction Temperature

Tin content (wt%)	0		0.02		0.06		0.11	
Reduction temperature (K)	573	773	573	773	573	773	573	773
TOF(s^{-1})	33	380	30	130	32	160	33	160
Selectivity to isopentane at 70% isoprene conversion	8.5	5.5	2	3	2.5	2.5	2	2

Note. Reaction temperature: 293 K.

observed during the hydrogenation of acetylene (*14, 23, 24*) where the selectivity for ethane formation is higher on large Pd particles.

DISCUSSION

The addition of tin (Tables 4 and 5) in the form of a chloride precursor influences neither the hydrogen adsorption nor the catalytic activity of palladium. Hence it may be postulated that most of this tin is not alloyed with palladium, and interacts mainly with alumina. Analogies may be found with properties of PtSn-reforming catalysts. On these latter the extent of reduction of tin decreases when a calcination step is performed prior to reduction and when the platinum content is low (*25, 26*). For a sample containing 1 wt% Pt all the tin is reduced and alloyed with platinum, but when the platinum content is lowered to 0.4 wt% and the catalyst previously calcined, only 20% of tin is reduced. In this last case tin remains as Sn^{2+} species on the carrier. It is therefore not surprising that the same effect occurs with the $PdSn/Al_2O_3$ catalyst used in this work, which contained only 0.09 wt% Pd.

In the case of $PdSn/Al_2O_3$ catalysts obtained from organometallic precursors, a clear influence of tin, lead, germanium, and antimony is observed. On the one hand, for the samples reduced at 573 K, the turnover frequencies for isoprene hydrogenation do not change, although the hydrogen uptake is always lowered by addition of the second metal. On the other hand, the samples reduced at 773 K exhibit the same behaviour with respect to hydrogen chemisorption, but the catalytic activities are modified by the addition of the second metal. It is reasonable to conclude that palladium and the second metal form an alloy. This conclusion is supported by the highly specific interaction between reduced palladium and the organometallics of the Group IVA metals, since the uptake of the second metal species by the carrier is negligible for α-alumina. Travers *et al.* found the same behaviour for $RhSn/Al_2O_3$ catalysts prepared in the same way (*8*). At variance with this, Margitfalvi *et al.* (*9*) consider that at high Sn/Pt ratios some -$Sn(C_2H_5)_x$ moieties interact directly with the alumina. No evidence of this could be observed with our support, which is a low-surface-area α-alumina. The discrepancy probably has to be attributed to the acidic properties of the support used by Margitfalvi *et al.* (*9*).

The $PdSn/Al_2O_3$-supported catalysts prepared via the organometallic procedure appear to be more useful models for studying pure alloying effects than $PdSn/Al_2O_3$ prepared via chloride precursors.

The saturation of the palladium surface by organometallics is reached after a few hours of contact. Whatever the nature of the second metal (M') and the palladium dispersion, the ratio of the number of second metal atoms to the number of surface palladium atoms stands between 1.2 and 1.6. We notice that with the bulkier molecule, $(C_4H_9)_4Pb$, the lowest value of this ratio resulted.

From the data of chemisorption, TEM, and TPD, one can postulate that on samples reduced at 573 or 773 K a fraction of Sb, Sn, or Pb tends to penetrate into the bulk.

The higher activity observed for the hydrogenation of isoprene on large Pd particles is in close agreement with previous studies on the hydrogenation of dienes and alkynes (*15, 20–24, 27*). The observation of a particle size effect by various authors, using different reaction conditions, implies that this is a real effect, and is not due to an artifact resulting from poisoning of the small particles by an impurity contained in the support or in the reactants. The interpretation of the phenomenon still remains a matter of discussion. Some authors (*15, 21*) ascribe the low activity observed on small particles to their electron-deficient character: the surface atoms of small particles would coordinate highly unsaturated hydrocarbons more strongly, since they are electron donors. Other authors (*15, 20, 23, 24*) ascribe the high activity observed on the large particles to the β-hydride. The β-hydride modifies the electronic properties of Pd, decreasing the strength of adsorption of the hydrocarbon, and acts as a hydrogen reservoir (*23*). The importance of β-hydride formation is clearly evidenced with PdSn/Al_2O_3 reduced at 773 K: its disappearance upon tin addition is followed by a decrease in activity, which was also observed after Cu addition (*19, 20*). The incorporation of tin has a clear positive effect on selectivity by reducing noticeably the total hydrogenation to isopentane. According to the authors mentioned above, the presence of the β-hydride phase on the one hand, and the occurrence of multiply bound species on the other hand would be responsible for the direct hydrogenation to alkanes. The presence of the second metal both in the bulk (suppression of the β-hydride formation) and on the surface (dilution of the active site (*19, 28*)) will then improve the selectivity to half-hydrogenation. The changes in catalytic properties after incorporation of the various second metals will be discussed in detail in a forthcoming paper dealing with the hydrogenation of highly unsaturated hydrocarbons (*29*).

The important point which emerges in this work is that the physics and chemistry of small alloy particles obtained by reduction at 573 K is different from that of large alloy particles obtained at 773 K: both activity and selectivity are affected in a different way by Sn addition, and H_2 absorption is also different. The fundamental interpretation of this effect is still unclear because the surface compositions appear to be relatively similar.

In conclusion, true bimetallic aggregates of palladium with tin, lead, antimony, or germanium can be obtained more easily from organometallic precursors when a relatively low amount of the second metal is needed. This is due to the highly selective interaction between the metallic palladium in Pd/Al_2O_3 and, for instance, $(C_4H_9)_4Sn$. Therefore, well-defined palladium/second-metal ratios can be obtained with this procedure. Finally, the catalytic properties of the clusters for diene hydrogenation are very sensitive to the reduction temperature in the final step of alloy preparation.

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