JOURNAL OF CATALYSIS **116,** 459–466 (1989)

Carbon–Chlorine Hydrogenolysis over PdRh and PdSn Bimetallic Catalysts

PEDRO BODNARIUK,[1] BERNARD COQ,[2] GERARDO FERRAT, AND FRANÇOIS FIGUERAS

Laboratoire de Chimie Organique Physique et Cinétique Chimique Appliquées, UA 418 du CNRS, ENSCM, 8 Rue de l'Ecole Normale, 34075 Montpellier, France

Received February 3, 1987; revised October 27, 1988

The conversion of chlorobenzene has been investigated over PdRh/Al_2O_3 and PdSn/Al_2O_3 bimetallic catalysts. In a previous study on supported palladium and rhodium (B. Coq, G. Ferrat, and F. Figueras, *J. Catal.* **101,** 434 (1986)) a reaction scheme was proposed in which there is considered to be a steady state between the chlorination of the metallic surface by chlorobenzene and hydrogen chloride and the reduction of the chlorine-covered metallic surface; palladium was found to be much more active than rhodium for this reaction. On PdRh and PdSn bimetallic catalysts, a marked decrease of C–Cl hydrogenolysis is observed, the factor being 10^2–10^3 upon rhodium addition, and larger than 10^6 when tin is added. This behavior is interpreted as follows. On the one hand there is a dilution of the palladium surface by the second metal; this geometric effect is enhanced by a surface enrichment of the modifier, the driving force for this segregation being the higher affinity of rhodium and tin for the chlorine produced in the reaction. Second, there is an electronic interaction between palladium and rhodium or tin, which decreases the reducibility of the chlorine-covered palladium surface by hydrogen. This modification, which is small in the case of rhodium, is noteable when tin is added since an increase of 125 kJ mol^{-1} is observed for the activation energy of the reaction.

INTRODUCTION

Chlorine removal from organic compounds is an important reaction in the manufacture of fine chemicals. It readily occurs on Group VIII metals such as Pd, Rh, or Pt. In a previous study (*1*) the conversion of chlorobenzene over Pd and Rh was taken as a simple model for this reaction. A mechanism closely similar to that widely accepted for the oxidation of hydrocarbons (*2*) was proposed, in which chlorobenzene reacts with a H-covered surface to form benzene and a surface chloride, whereas hydrogen reduced the surface to yield HCl and H-covered surface. This mechanism accounts for the inhibition effect of HCl in the process. A weak influence of particle size on the catalytic properties was noticed for both metals.

Little is known on the catalytic properties of alloys for such types of reaction. The addition of a second metal to palladium can have the two different effects (a) and (b) detailed below.

(a) Dilution of the palladium surface into ensembles of small size: In the case of the Pt-catalyzed conversion of hydrocarbons (*3*), it has been reported that widely different modifiers such as Au, Sn, S, and C all affect the platinum in a manner similar to dividing the surface into very small ensembles of Pt atoms. From this point of view, alloying Pd with Rh or Sn should be equivalent. For a catalytic reaction showing a particle size effect of 10, as observed previously on Pd (*1*), a decrease of the rate by a factor 10^2–10^3 may happen upon alloying (*4*).

(b) A modification of the density of states at the Fermi level, on the surface Pd atoms: If the rate determining step of the reaction involves an electron transfer, the electronic

---

[1] Present address: Plapiqui (UNS CONICET), 12 de Octubre 1842, Bahia Blanca, Argentina.

[2] To whom correspondence should be addressed.

0021-9517/89 $3.00

structure of the surface Pd atoms will determine the catalytic properties. From this point of view alloying Pd with Rh or Sn is not equivalent. Whereas the addition of Rh to Pd causes only marginal modifications in the *d*-band structure of Pd (*5*), addition of Sn shifts the XPS *d*-lines of Pd by several electron volts (*6*). Tin either donates electrons to Pd or induces a redistribution of the *d*-electrons, so as to reduce the density of states at the Fermi level. A lower density of states localized at the Pd atoms should result in a weaker alkene–Pd bond, in agreement with the results reported for deuterium exchange of hydrocarbons (*7*) and hydrogenation of dienes (*8*).

Chlorine is a strong inhibitor for the reaction and is known to act as an electron acceptor with respect to the metals, in the same way as oxygen or sulfur (*9*). In previous work it was reported that the thioresistance of palladium was remarkably increased by the addition of a small amount of rhodium (*10*), and it was therefore interesting to investigate the effect of alloying on the inhibiting effect of HCl. By analogy with thioresistance, a higher activity was expected on $PdRh/Al_2O_3$ than on Pd/Al_2O_3, and the comparison of PdRh with PdSn allows us to investigate the possible influence of the electronic modification of palladium on C–Cl hydrogenolysis.

The preparation of these $PdSn/Al_2O_3$ catalysts using the reaction of tetrabutyltin on a reduced Pd/Al_2O_3 has been described elsewhere (*8*). This procedure yields well-defined catalysts useful for the selective hydrogenation of isoprene to pentenes (*8*). The present work describes their catalytic properties for C–Cl hydrogenolysis.

EXPERIMENTAL

PdRh catalysts. The solids were prepared using the ion-exchange technique described previously (*10*). The support used was γ-alumina from Rhône–Poulenc (200 m^2 g^{-1}); the salts were $RhCl_3$, $3H_2O$, and $PdCl_2$ from Merck. The support was first acidified at pH 2 with hydrochloric acid (1 g/10 ml). After 1 h, the requisite quantities of the two solutions of salts were simultaneously added. The slurry was kept for 2 h under stirring, the solvent was then gently evaporated at 343 K, and the solid was oven-dried overnight at 383 K. In order to obtain similar dispersions for all the samples, the reduction temperature was gradually decreased from 773 K for Rh/Al_2O_3 to 673 K for Pd/Al_2O_3. At the same time the hydrogen flow rate was increased.

PdSn catalysts. The preparation of PdSn catalysts has been detailed elsewhere (*8*). The usual procedure followed to obtain PtSn bimetallic catalysts from chloride salts (*11*) failed in the case of PdSn samples from $PdCl_2$ and $SnCl_2$ precursors (*8*). The support was a α-alumina from Rhône–Poulenc (13 m^2 g^{-1}). Palladium was deposited first from Pd acetylacetonate (purity >98.5%, from Merck) in benzene medium. The solids were further dried at 393 K, calcined at 573 K, and reduced at 573 K. Thus a well-dispersed palladium catalyst (H/Pd = 0.54) was obtained, which was modified by tin addition.

Tin was introduced as $(n\text{-}C_4H_9)_4Sn$ (purity >95%, from Merck) dissolved in *n*-heptane, to a suspension of the reduced Pd/Al_2O_3 catalysts. The solids were further dried at 393 K and reduced in flowing hydrogen at 573 or 773 K.

Characterization. Hydrogen adsorption measurements were performed in a conventional volumetric apparatus. Prior to any determination the sample was reduced *in situ*. For PdRh samples the isotherm was determined in the range 0–1.3 kPa H_2 pressure. For PdSn the double isotherm technique proposed by Boudart and Hwang (*12*) was used. In this method a first isotherm is determined at room temperature for pressures up to 33.2 kPa; this isotherm includes both adsorption and hydride formation by absorption. The sample is evacuated at room temperature, which results in the reversible elimination of the hydride. A second H_2 absorption at room temperature restores the hydride. The difference between

TABLE 1

Characteristics of the Catalysts

Catalysts				
Designation	Metal loading (wt%)			H/Me
	Pd	Rh	Sn	
PdRh1.80(773)	—	1.80	—	0.27
PdRh1.53(773)	0.17	1.53	—	0.27
PdRh1.29(773)	0.41	1.29	—	0.38
PdRh0.97(773)	0.83	0.97	—	0.26
PdRh0.87(723)	1.36	0.87	—	0.19
PdRh0.51(673)	1.69	0.51	—	0.22
PdRh0.20(673)	1.80	0.20	—	0.09
PdRh0.10(673)	2.00	0.10	—	0.64
PdRh0.0(673)	2.00	—	—	0.47
PdSn0.0(573)	0.09	—	—	0.54
PdSn0.02(573)	0.09	—	0.02	0.34
PdSn0.06(573)	0.09	—	0.06	0.22
PdSn0.11(573)	0.09	—	0.11	0.17
PdSn0.0(773)	0.09	—	—	0.05
PdSn0.02(773)	0.09	—	0.02	0.07
PdSn0.06(773)	0.09	—	0.06	0.05
PdSn0.11(773)	0.09	—	0.11	0.05

Note. H/Me represents the degree of dispersion.

the two isotherms is due to adsorption of hydrogen at the Pd surface. The hydrogen used was high purity grade (99.9995%).

For some samples the results of chemisorption were checked by transmission electron microscopy. Generally the agreement is quite satisfying. Chemical analysis of the samples was performed by the wet method using analysis of the solution by atomic absorption.

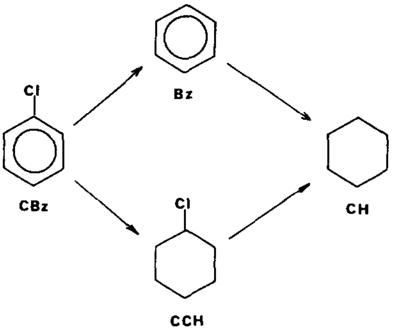
The main features of the catalysts are summarized in Table 1. In the nomenclature used, PdRh1.80(773), for instance, means that this metallic PdRh catalyst contains 1.80 wt% Rh and was reduced at 773 K. H/Me represents the ratio between adsorbed hydrogen (extrapolated at zero pressure value) and total metal atoms of Pd and Rh, for PdRh catalysts, and of Pd alone for PdSn catalysts.

Activity experiments. A conventional flow reactor was used in the differential mode. The reactants were chlorobenzene (CBz) from Carlo Erba (purity >99.99%) and hydrogen (purity >99.99%). Hydrogen was saturated with the vapor pressure of CBz at varying temperatures in order to obtain a CBz pressure ranging from 40 Pa to 3.3 kPa. In order to avoid any condensation of CBz in the feed lines, the connecting tubes were heated, and all the valves (control and sampling) were located in a "hot box" maintained at 353 K. Products and reactant were analyzed by on stream gas chromatography using a column (2 m × $\frac{1}{8}$ in.) packed with 10% Carbowax 20M on Gas-Chrom Q (120–140 mesh). The reaction temperatures ranged between 353 and 519 K. In these conditions, the reaction yields essentially benzene (Bz) and chlorocyclohexane (CCH), together with cyclohexane (CH) by a secondary reaction.

Depending on the reactivity of the solid, the catalyst amount for the reaction ranged from 0.02 to 0.2 g, and the H_2 flow rate from 0.33 to 20 ml s^{-1}.

RESULTS

As described previously (*1*), the conversion of chlorobenzene yields three products which correspond to the formal reaction in Scheme 1.



SCHEME 1

However, the selectivity to chlorocyclohexane is very low whatever the reaction conditions, in the range 1–7% for Rh and less than 0.1% for Pd. The ratio (Bz + CH)/CCH is constant in a wide range of conversions, and hence cyclohexane was considered to come from a secondary reaction of benzene.

In the conditions of the reaction, all the samples suffer some "self-poisoning" due to HCl produced in the reaction. With a partial pressure of chlorobenzene of 3.3 kPa a constant activity is reached after 24 h on stream; the steady state then reached is stable, since at the end of the kinetic study, the initial activity is recovered within 10% variation. A reversible self-inhibition of the surface by HCl also occurs, since the rate decreases when the conversion increases.

The kinetic data fit very well with a scheme formally identical with that proposed for the selective oxidation of hydrocarbons (*2*)

$$\text{Pd–H} + \text{C}_6\text{H}_5\text{Cl}_{(g)} \xrightarrow{k_1} \text{Pd–Cl} + \text{C}_6\text{H}_6$$

$$\text{Pd–H} + \text{HCl}_{(g)} \xrightarrow{k_2} \text{Pd–Cl} + \text{H}_2$$

$$\text{Pd–Cl} + \text{H}_2 \xrightarrow{k_\text{H}} \text{Pd–H} + \text{HCl}$$

from which the rate equation

$$r = \frac{k_1 k_\text{H} P_\text{CBz} P_{\text{H}_2}^{0.5}}{k_\text{H} P_{\text{H}_2}^{0.5} + k_1 P_\text{CBz} + k_2 P_\text{HCl}}$$

was proposed for Pd/Al_2O_3 and Rh/Al_2O_3 (*1*).

As in this previous work, a kinetic study was performed on the bimetallic PdRh and PdSn catalysts. Then k_1, k_2, and k_H were obtained by fitting the above equation using a least-squares method.

In order to compare the specific activities per surface metal atom, the rate constants expressed in mole per second per gram were converted to turnover frequencies (TOF), i.e., molecules converted per unit time and per surface metal atom, the latter being taken as Pd plus Rh in PdRh catalysts and Pd alone in PdSn catalysts. These specific constants are designated as k_1', k_2', and k_H'. Table 2 reports the values of these constants determined at 353 K for $PdRh/Al_2O_3$ catalysts. The most salient point is a small variation of k_1' and k_2' which remains within a factor of 10, whereas k_H' decreases by three orders of magnitude from pure Pd to pure Rh. The amount of HCl present in the reaction mixture can be changed by the conversion of the reactant. A comparison of the rates at 1 and 10% conversion is reported in Fig. 1. This shows that the turnover frequency decreases when the pressure of hydrogen chloride increases, but not the pattern of activity which decreases as a function of the catalyst composition. $PdSn/Al_2O_3$ catalysts exhibit large differences in reactivity and have been tested at temperatures ranging from 353 to 519 K. The values of the rate constants are reported in Table 3 for PdSn samples reduced at 773 K. It appears here also that the variations of k_H' with temperature are much larger than the variations of k_1' and k_2'. The comparison of these catalysts is made in Table 4, in which the values of the rate constants extrapolated to the temperature of 413 K are reported for the PdSn catalysts reduced at 773 K. The activation energies,

TABLE 2

Rate Constants at 353 K for the Chlorination and the Regeneration of the Metallic Particles of PdRh/Al_2O_3 Catalysts

Catalyst	Rate constant (mol s^{-1} g^{-1})			Turnover frequency (s^{-1})		
	$k_H \times 10^6$	$k_1 \times 10^2$	k_2	$k'_H \times 10^2$	$k'_1 \times 10^{-2}$	$k'_2 \times 10^{-4}$
PdRh1.80(773)	0.19	3.4	0.4	0.4	6	0.9
PdRh1.53(773)	1.1	10	3	2.5	23	6.8
PdRh1.29(773)	2.5	1.5	0.8	4	2.4	1.3
PdRh0.97(723)	14	0.8	1.2	31	1.8	2.7
PdRh0.87(723)	6	2.5	0.35	15	6.3	0.88
PdRh0.51(673)	13	4.5	0.35	28	9.8	0.76
PdRh0.20(673)	17	1.5	0.7	100	8.7	4.1
PdRh0.10(673)	180	2	5	140	1.6	3.9
PdRh0.0(673)	250	1	1	140	2.2	1.1

determined at 5% conversion for these catalysts, are reported in Table 5. Tables 4 and 5 show very large variations of the rate of reduction of the surface, which varies by 10^6, and of the overall activation energy, which is increased by 125 kJ mol^{-1}, upon addition of 0.11 wt% Sn on Pd/Al_2O_3.

The temperature of reduction of the PdSn catalysts exerts a notable influence on the catalytic properties. Thus, the samples re-

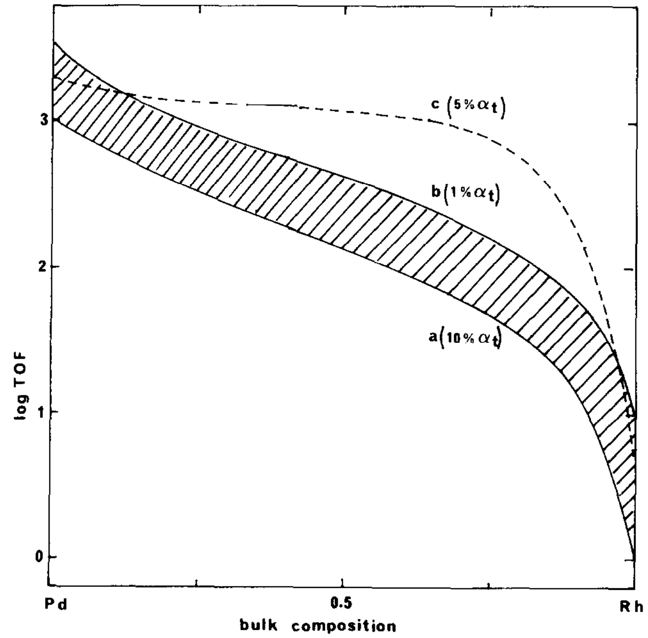


FIG. 1. Logarithm of the turnover frequency (TOF) as a function of the bulk composition of PdRh/Al_2O_3 catalysts. Curve a, at 10% overall conversion; curve b, at 1% overall conversion; curve c (dashed line), activity calculated assuming a surface composition identical to that observed on PdRh films (Ref. (*1*)). Reaction temperature, 353 K.

TABLE 3

Rate Constants at Different Reaction Temperatures for the Chlorination and the Regeneration of the Metallic Particles of PdSn/Al_2O_3 Catalysts Reduced at 773 K

Catalyst	Reaction temperature (K)	Rate constant (mol s^{-1} g^{-1})			Turnover frequency (s^{-1})		
		$k_H \times 10^5$	$k_1 \times 10^4$	$k_2 \times 10$	k'_H	$k'_1 \times 10^{-3}$	$k'_2 \times 10^{-5}$
PdSn0.0(773)	353	2	40	0.6	42	8.4	1.2
PdSn0.0(773)	383	3	30	1	63	6.3	2.1
PdSn0.02(773)	393	0.05	0.3	0.1	0.7	0.04	0.13
PdSn0.02(773)	413	0.25	0.8	0.2	3.5	0.10	0.26
PdSn0.02(773)	433	1	0.8	0.1	14	0.10	0.13
PdSn0.06(773)	453	0.15	2	1	3.1	0.42	2.1
PdSn0.06(773)	471	0.6	3.5	1.2	12.7	0.73	2.5
PdSn0.06(773)	491	3	6	1.2	63	1.3	2.5
PdSn0.11(773)	452	0.07	5	5	1.2	0.88	8.7
PdSn0.11(773)	471	0.3	10	8	5.1	1.75	14
PdSn0.11(773)	501	2.6	18	15	44	3.15	26

duced at 573 K suffer a rapid deactivation when the amount of Sn is higher than 0.05 wt%. The catalytic activities of these PdSn samples (reduced at 573 or 773 K) are reported in Fig. 2, at two partial pressures of HCl. It appears clearly that the inhibiting effect of tin is lowered by two orders of magnitude on the catalysts reduced at 573 K. The inhibition of activity by hydrogen chloride, evidenced by the lower rate of reaction when the conversion increases from 1 to 10%, is greater on the catalysts reduced at 773 K.

DISCUSSION

In previous work on the influence of particle size of alumina-supported Pd and Rh catalysts (*1*) modest changes of turnover frequencies for large variations of the particle size were reported. The large particles were found to be slightly more active per surface metal atom. Since palladium is the most active component of these bimetallic catalysts, a dilution of the palladium surface by a less active second metal (Sn or Rh), which results in a decrease of the number of surface Pd atoms and the formation of small Pd ensembles, should decrease the catalytic activity, too. Indeed this occurs in both cases. These activity falls reflect a lower rate of reduction of the chlorinated surface (k_H constant). By contrast, the rate of chlorination of the surface is less affected by alloying. However, the magni-

TABLE 4

Extrapolated Values (at 413 K) of the Rate Constants for the Chlorination and the Regeneration of the Metallic Particles of PdSn/Al_2O_3 Catalysts Reduced at 773 K

Rate constant (mol s^{-1} g^{-1})	Catalyst			
	PdSn0.0(773)	PdSn0.02(773)	PdSn0.06(773)	PdSn0.11(773)
$k_H \times 10^4$	160	0.03	5.6×10^{-4}	2.8×10^{-4}
$k_1 \times 10^4$	50	0.7	0.7	1.6
$k_2 \times 10^2$	10	1	7	20

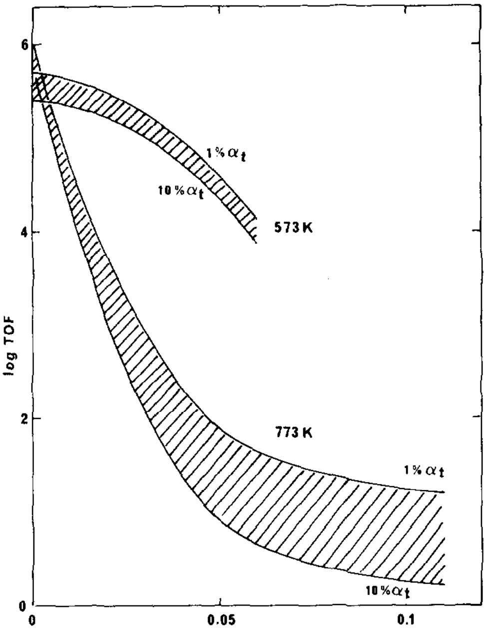


FIG. 2. Logarithm of the turnover frequency (TOF), at two different overall conversions α_t, as a function of the tin content of $PdSn/Al_2O_3$ catalysts reduced at 573 and 773 K. Reaction temperature, 413 K.

tude of the effect is quite different when alloying Pd either with Rh or with Sn.

The $PdRh/Al_2O_3$ catalysts have been previously studied in several other reactions (*1*). The main conclusion was that Pd segregates at the surface of the bimetallic particles in the same manner as that on PdRh films (*13*). Curve c of Fig. 1 then represents the specific activity expected assuming that the activities of Pd and Rh atoms are additive, and that the surface composition is the same as on films (*13*). The ratios of the experimental activities to these computed values are relatively small (<10) and can be explained by a decrease of the size of the Pd ensembles. Moreover, this dilution of the active surface by Rh may be enhanced by a modification of surface composition. It has been suggested (*14, 15*) that surface segregation of alloys can be modified by impurities or by reactive gas atmosphere. This is particularly true when the difference of affinity is high between the metals and the impurity or reactant. This is the case with HCl since $RhCl_3$ ($\Delta H^\circ_f = -234$ kJ mol^{-1}), or $SnCl_2$ ($\Delta H^\circ_f = -350$ kJ mol^{-1}), is more stable than $PdCl_2$ ($\Delta H^\circ_f = -190$ kJ mol^{-1}). Thus, a surface enrichment of these less active metals, Rh and Sn, is expected under HCl atmosphere. This last point could also explain the different behavior observed between $PdSn/Al_2O_3$ catalysts reduced at 573 or 773 K.

TABLE 5

Activation Energy for the Hydrodechlorination of Chlorobenzene Determined at 5% Conversion as a Function of the Tin Content for $PdSn/Al_2O_3$ Catalysts Reduced at 773 K

Catalyst	E_A (kJ mol^{-1})
PdSn0.0(773)	105
PdSn0.02(773)	134
PdSn0.06(773)	172
PdSn0.11(773)	230

It was concluded previously (*8*) that Sn is mainly localized at the surface in bimetallic particles of $PdSn/Al_2O_3$ reduced at 573 K and diffuses into the bulk after reduction at 773 K. Thus, the presence of HCl cannot noteably modify the surface composition of supported PdSn particles reduced at 573 K. By contrast, Sn atoms which had diffused into the bulk of the particles reduced at 773 K could be reextracted from the bulk to the surface, thereby decreasing the number of surface Pd atoms, and the apparent specific activity. In the course of hydrodechlorination, these modifications of the surface composition rationalize the differences of activity between $PdSn/Al_2O_3$ catalysts reduced at low or high temperature. However, geometric effects alone cannot explain the larger decrease of TOF on PdSn0.06(573) than that on PdRh0.97(723) on the one hand, and particularly the large increase of the activation energy from 105 to 230 kJ mol^{-1} on $PdSn/Al_2O_3$ catalysts reduced at 773 K. An electronic influence of Sn on the catalytic properties of Pd can be then envisaged.

In the bulk Pd and Sn can form definite intermetallic compounds, e.g., Pd_3Sn, Pd_3Sn_2, PdSn, $PdSn_2$, and $PdSn_3$ (*16*). Depending on the Pd/Sn ratio these different phases have been observed on $PdSn/SiO_2$ (*6*). On these solids, when the Pd/Sn ratio decreases, the XPS peak associated with Pd 4*d* states shifts by several electron volts toward higher binding energies. This shift has been interpreted by the formation of bonding orbitals (*17*). This behavior is quite different from that observed for NiCu or NiSn alloys, where the shape of the local density of states does not change significantly with the composition. Actually, the XPS spectrum of these Ni alloys is a mere addition of the peaks of each component. In the case of the PdSn alloys, it can be assumed that the filling of the *d*-band of palladium has been modified upon alloying. The weakening of the Pd–alkene bond has been interpreted by this effect (*7*). In the present case, a large effect of tin is noted only after reduction at 773 K, where the suppression of hydrogen dissolution into the bulk suggests the formation of alloys (*8*). A higher electron density at the Pd atom would stabilize the adsorption of an electrophilic element like chlorine, which then explains the lower reducibility of the surface reflected by the decrease of k_H. In the case of PdRh, the situation is basically the same, with the noteable difference that the shift is only a fraction of an electron volt (*18*), and therefore the effect of alloying is reduced to a simple dilution of palladium by rhodium.

In conclusion, alloying palladium by rhodium or tin induces a decrease of activity for C–Cl hydrogenolysis, which can be understood as a decrease of the reducibility of the surface by hydrogen. The surface composition of the catalyst is modified by the HCl produced in the reaction. The addition of rhodium decreases the turnover frequency by a factor of 10^2–10^3, interpreted in terms of dilution of the palladium surface by rhodium. On formation of PdSn alloys the turnover frequency decreases by 10^6, and the activation energy increases by 125 kJ mol^{-1}, which is interpreted in terms of an electronic interaction between palladium and tin.

ACKNOWLEDGMENT

The chemical analyses of the catalysts have been performed by the Service Central d'Analyses du CNRS, Solaize, France, whose help is warmly acknowledged.

REFERENCES

1. Coq, B., Ferrat, G., and Figueras, F., *J. Catal.* **101,** 434 (1986).
2. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci.* **3,** 41 (1954).
3. Dautzenberg, F. M., Helle, J. N., Biloen, P., and Sachtler, W. M. H., *J. Catal.* **63,** 119 (1980).
4. Boudart, M., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), Vol. 1, p. 1. The Chemical Society, London, 1976.
5. Ulmer, K., *in* "Band Structure of Metals and Alloys" (D. J. Fabian and L. M. Watson, Eds.), p. 521. Academic Press, London, 1973.
6. Masai, M., Honda, K., Kubota, A., Ohnaka, S., Nishikawa, Y., Nakahara, K., Kishi, K., and Ikeda, S., *J. Catal.* **50,** 419 (1977).
7. Clarke, J. K. A., and Taylor, J. F., *J. Chem. Soc. Faraday Trans 1* **72,** 917 (1976).
8. Aduriz, R., Bodnariuk, P., Coq, B., and Figueras, F., submitted for publication.
9. Halachev, T. D., and Ruckenstein, E., *J. Catal.* **73,** 171 (1982).
10. Del Angel, G. A., Coq, B., and Figueras, F., *J. Catal.* **95,** 167 (1985).
11. Bacaud, R., Bussière, P., and Figueras, F., *J. Catal.* **69,** 399 (1981).
12. Boudart, M., and Hwang, H. S., *J. Catal.* **39,** 44 (1975).
13. Moss, R. L., and Gibbens, H. R., *J. Catal.* **24,** 48 (1972).
14. Overbury, S. H., Bertrand, P. A., and Somorjai, G. A., *Chem. Rev.* **75,** 547 (1975).
15. Sachtler, W. M. H., and van Santen, R. A., *Adv. Catal.* **26,** 69 (1977).
16. Elliot, R. P., "Constitution of Binary Alloys, First Supplement," p. 732. McGraw-Hill, New York, 1965.
17. Tamura, K., Fukushima, J., Endo, H., Kishi, K., Ikeda, S., and Minomura, S., *J. Phys. Soc. Japan* **36,** 565 (1974).
18. Eggs, J., and Ulmer, K., *Z. Phys.* **213,** 293 (1968).