Preparation of Pd–Pb/α-Al_2O_3 catalysts for selective hydrogenation using $PbBu_4$: the role of metal–support boundary atoms and the formation of a stable surface complex

Maria A. Volpe, Patricia Rodriguez and Carlos E. Gigola

Planta Piloto de Ing. Química, Camino La Carrindanga Km 7, 8000 Bahia Blanca, Argentina

Received 21 January 1999; accepted 9 June 1999

Pd–Pb/α-Al_2O_3 catalysts were prepared by reacting $PbBu_4$ with supported palladium samples derived from $Pd(AcAc)_2$, both in the presence and absence of hydrogen. The amount of lead fixed depends mainly on the concentration of palladium on the metal–support boundary. In the presence of hydrogen, all butyl groups are released during the anchoring process. When the Pd/α-Al_2O_3 was reduced and then purged with nitrogen, two butyl groups remained attached to the lead atom and a stable surface complex was formed. The analysis of gaseous products evolved during the $PbBu_4$–Pd/α-Al_2O_3 interaction and subsequent temperature-programmed reaction experiments indicate that a $(]\text{-L})_2\text{–Pb(Bu)}_2$ complex was obtained. Upon reduction at 573 K, the Pd–Pb/α-Al_2O_3 catalysts became very selective for the hydrogenation of acetylene in the presence of ethylene.

Keywords: palladium catalysts, bimetallic catalysts, organometallic precursors, surface complex, acetylene hydrogenation

1. Introduction

Many industrial processes employ supported palladium catalysts for the semihydrogenation of alkynes and dienes in the presence of large amounts of olefins. The objective is the selective hydrogenation of triple and double–double bonds to ppm levels without the hydrogenation of diolefinic hydrocarbons. Much effort has been devoted to empirical modification of Pd-based catalysts to improve their intrinsic selectivity. In this sense palladium bimetallic catalysts have been introduced [1].

There are several indications in the literature that surface organometallic chemistry provides an excellent tool for preparing bimetallic catalysts. The preparation method involves, basically, the reaction of organometallic compounds of metals of Group IVa with supported transition metals [2–4]. This synthetic route leads to bimetallic particles, without the formation of a segregated monometallic phase. For example, Ferretti et al. [5,6] prepared Rh–Sn/SiO_2 and Ni–Sn/SiO_2 by reaction of tetrabutyltin dissolved in n-heptane with nickel or rhodium supported catalysts. The characterization of the samples performed by FTIR, TEM, magnetic measurements and chemisorption of CO and H_2 showed that bimetallic particles are formed and the presence of an alloy is suggested. Examining the results of these studies one finds that Rh_s/Sn and Ni_s/Sn ratios lower than one have been obtained. Consequently, a fraction of $Sn(\text{–}C_4H_9)_4$ seems to react with sites that are not located on the metal particles. Margitfalvi et al. [7] have shown that a Pt_x–Sn alloy supported in γ-Al_2O_3 could be obtained by a similar procedure. Here again the Pt_s/Sn ratio was less than one.

More recently [8], a bimetallic catalyst containing 0.27% of Pb was obtained by reaction of an organic solution of tetrabutyllead (from now on, $PbBu_4$) with a highly dispersed Pd(0.19 wt%)/α-Al_2O_3 catalyst. It was established that this organometallic compound does not react with alumina, at least when the reaction is performed at room temperature and the concentration of lead is lower than 0.65 g Pb/l. Characterization of the sample by FTIR and XPS showed that this preparation method yielded metal particles where palladium and lead were closely associated. In spite of a strong interaction between both metals, here again a certain amount of the second metal seems to be retained by sites other than surface palladium atoms, since the Pd_s/Pb (Pd_s = surface palladium) ratio was lower than unity. Mallat et al. [9] reported similar Pd_s/Pb values when Pb^{2+} ions from an aqueous solution were deposited on a Pd/C catalyst. They have shown that in the presence of hydrogen, migration of Pb, Cd and Ge into the bulk of palladium takes place at room temperature. For Pb, a fast adsorption process characterized by a large uptake, followed by a rather slow dissolution process, was observed. The surface mobility of adsorbed atoms was considered to be a relevant variable to explain this behaviour. Consequently, we suspect that the metal–support boundary could be responsible for the large Pb uptake. Since the ratio of metal–support boundary atoms to the number of surface atoms increases as the particle size decreases, it was considered of interest to study the effect of palladium dispersion on the amount of lead fixed. The objective is to try to throw some light on the nature of the anchoring sites in the base monometallic catalyst. In this spirit, we have prepared and characterized seven bimetallic catalysts of varying palladium loading and metal dispersion. The beneficial effect of lead on the selectivity of Pd–Pb/α-Al_2O_3 catalysts for acetylene hydrogenation in the presence of a large excess of ethylene has been demonstrated.

In addition we have examined again [8] the quality and quantity of hydrocarbons evolved during the room temperature reaction between $PbBu_4$ and Pd/α-Al_2O_3 in the presence and absence of adsorbed hydrogen, and performed a subsequent temperature-programmed reaction experiment to follow the decomposition of surface precursors. In this way, the basic reactions that are responsible for the formation of Pd–Pb particles are proposed.

2. Experimental

A series of monometallic palladium catalysts was prepared by reaction of a benzene solution of $Pd(AcAc)_2$ with α-alumina particles (spheralite 512, from Rhône-Poulenc, BET area = 10 m^2/g) sieved to 16/20 mesh particle size. Further details of this preparation procedure may be found in [8]. Two other Pd/α-Al_2O_3 samples were prepared by impregnation using an aqueous solution of $Pd(NH_3)_4(NO_3)_2$. In order to estimate the metal dispersion, hydrogen sorption and back sorption isotherms were measured in a volumetric apparatus at 298 K. Assuming that the surface stoichiometry $(H/Pd_s)_{irr}$ is unity, the calculated $(H/Pd)_{irr}$ values give the metal dispersion (D). Palladium and lead contents were determined by AA.

Prior to reaction with $PbBu_4$, two different pretreatments were performed on the monometallic catalysts. In pretreament A, the monometallic sample was reduced in flowing H_2 for 2 h at 573 K and then cooled to room temperature in the same atmosphere. In this way palladium particles with chemisorbed hydrogen were obtained. In pretreatment B, the samples were reduced at 573 K under similar conditions and then purged in Ar at 573 K for 1 h. Finally, the catalysts were cooled to room temperature in the inert gas. Thus, a reduced sample without chemisorbed hydrogen was obtained.

In a typical experiment, 0.4 g of Pd/α-Al_2O_3 were transferred to a glass vial filled with 2 cm^3 of solution of $PbBu_4$ in n-heptane. In order to follow the surface reaction between $PbBu_4$ and palladium with or without adsorbed hydrogen, we measured the evolution of gaseous products in the liquid phase. Aliquots of the solution were extracted at 4 min intervals and the concentration of C_4 hydrocarbons was measured by GC analysis.

When a final state concentration was obtained, the catalyst precursor was filtered, washed with fresh solvent and dried under Ar flow for 20 h at room temperature. The temperature-programmed reaction (TPR) technique was then used to study the decomposition of the surface complexes formed in the surface reaction. The precursor was reduced from 25 to 250 °C in an Ar–H_2 (5%) mixture at 10 K/min. The temperature profile of the hydrogen consumption was recorded with a thermal conductivity cell. The exhaust of the reactor was connected to a gas chromatograph, equipped with a FID detector and a Poropack Q column, to identify the reaction products.

A bimetallic Pd–Pb/α-Al_2O_3 sample and the correspondent Pd/α-Al_2O_3 sample were tested for the hydrogenation of acetylene in the presence of a large amount of ethylene and hydrogen. Catalyst charges of approximately 0.01 g were placed in a two-stage SS reactor with intermediate cooling to minimize thermal effects. The feed composition was 0.90% C_2H_2, 11.71% CH_4, 77.48% C_2H_4 and 9.90% H_2. Catalytic tests were performed at 1111 kPa, with a flow rate of 60 cm^3/min (STP) in the 270–430 K temperature range. The feed mixture and the reaction products were analyzed by GC using a Carbosieve S-II column ($1/8'' \times 80$ cm) held at 393 K. Prior to catalytic experiments, the prereduced samples were pretreated under the reaction mixture at 273 K for 2 h. Conversion measurements at constant space velocity were carried out at increasing temperatures up to the point where the hydrogenation of ethylene was observed.

3. Results and discussion

3.1. Dependence of the amount of fixed lead on the concentration of palladium–support boundary atoms

The main characteristics of monometallic and bimetallic catalysts are presented in table 1. The palladium loading and metal dispersion of Pd/α-Al_2O_3 catalysts are listed in the first two columns of table 1. It is seen that samples of varying metal loading and dispersion have been obtained. We have also reported the Pb content for the Pd–Pb/α-Al_2O_3 catalysts derived from monometallic palladium samples pretreated with methods A and B. Both pretreatments give a similar concentration of lead. So no distinction between pretreaments will be done in this section.

The last column in table 1 shows the Pd_s/Pb (Pd_s = surface palladium) atomic ratios. For most of the samples, the values are lower than unity. First, it is important to state that the affinity between the organometallic compound and the support is null. In addition, no correlation was found between lead loading and the concentration of surface palladium, as shown in figure 1. Consequently, the fixation

Table 1
Catalysts composition and palladium dispersion.

Sample	Pd (wt%)	D $(H/Pd)_{irr}$[a]	Pb (wt%) Pretreat. A	Pb (wt%) Pretreat. B	Pd_s/Pb (at. ratio)
I	0.11	0.75	0.30	0.33	0.5
II	0.19	0.52 (0.07)	0.25	0.27	0.7
III	0.20	0.39	0.15	0.18	0.8
IV	0.30	0.26	0.15	0.12	1.2
V	0.20	0.19	0.08	0.08	0.9
VI[b]	0.06	0.54		0.10	0.6
VII[b]	0.24	0.33		0.08	1.9

[a] The $(H/Pd)_{irr}$ value in parentheses was measured after lead addition.
[b] Samples prepared from $Pd(NH_3)_4(NO_3)_2$.

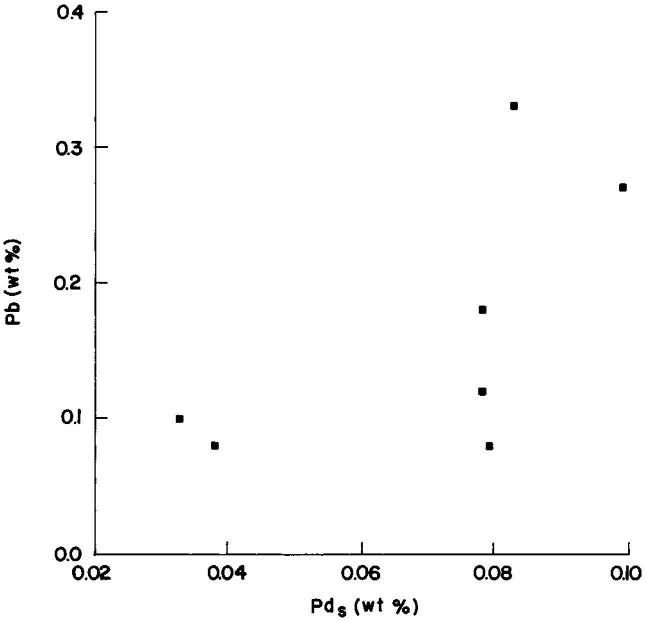

Figure 1. Dependence of the lead uptake on the concentration of surface palladium atoms.

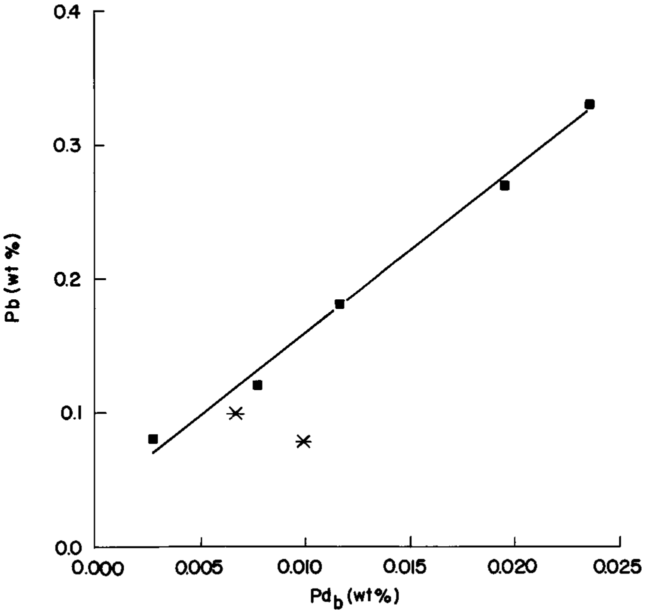

Figure 2. Dependence of the lead uptake on the concentration of palladium–support boundary atoms. Samples prepared from $Pd(AcAc)_2$ (■) and $Pd(NH_3)_4(NO_3)_2$ (∗).

of the second metal may occur at sites other than surface palladium atoms.

One possibility is the penetration of lead into the bulk of palladium to form an alloy. We have ruled out this hypothesis due to: (i) a lack of correlation between the lead uptake and the total concentration of palladium; (ii) the fixation of lead was in our case a fast process both in the presence or absence of hydrogen. According to Mallat et al. [9], the migration of lead into the bulk of palladium is a slow process mainly due to the high atomic radius of lead. In addition, it was suggested that the rate of penetration is faster in the presence of hydrogen due to hydride formation. Thus, if bulk diffusion occurs, different lead uptakes could be expected for pretreatments A and B.

These observations lead us to propose that Pd atoms located at the metal–support boundary are responsible for the fixation of $PbBu_4$. In order to explore this possibility, it is necessary to relate the amount of Pd at the palladium–support boundary, $[Pd]_b$, to the metal dispersion and the total Pd loading $[Pd]_t$. The corresponding equation is

$$[\mathrm{Pd}]_\mathrm{b}\ (\mathrm{wt\%}) = 0.38D^2[\mathrm{Pd}]_\mathrm{t}\ (\mathrm{wt\%}). \qquad (1)$$

The derivation of equation (1) is presented in the appendix. Using the data in table 1 the $[Pd]_b$ values were calculated for all samples. A linear dependence of the lead loading on the amount of boundary Pd atoms is shown in figure 2, for samples prepared from $Pd(AcAc)_2$. The fact that the straight line does not pass through the origin indicates that a small amount of lead is fixed on the metal surface. The correlation seems to fail for samples derived from $Pd(NH_3)_4(NO_3)_2$. This may be due to differences in particle morphology or the nature of the metal–support boundary. On $Pd/\alpha\text{-}Al_2O_3$ catalysts prepared from $Pd(AcAc)_2$ [10], the metal particles are characterized by a close interaction with the alumina support.

The previous results suggest that our $Pd/\alpha\text{-}Al_2O_3$ catalysts present two kinds of anchoring sites for the organolead compound: sites located at the metal–support boundary region and sites on the palladium surface particles. In this spirit, the following equation may be introduced:

$$[\mathrm{Pb}]\ (\mathrm{wt\%}) = K_\mathrm{s}[\mathrm{Pd}]_\mathrm{t}D\ (\mathrm{wt\%}) + K_\mathrm{b}[\mathrm{Pd}]_\mathrm{b}\ (\mathrm{wt\%}), \qquad (2)$$

where D (= $[Pd_s]/[Pd_t]$) is the metal dispersion, and K_s and K_b are constants associated to the surface of the particle and to the boundary region, respectively.

With the aim of finding the values of K_s and K_b, equation (2) may be written as

$$[\mathrm{Pb}]/\big(D[\mathrm{Pd}]_\mathrm{t}\big) = K_\mathrm{s} + 0.38K_\mathrm{b}D. \qquad (3)$$

Using the data in table 1, values of 0.9 and 10 for K_s and K_b, respectively, were obtained. For example, sample II, with a high metal dispersion, fixed 0.19 wt% of lead in the boundary region and only 0.08 wt% onto the palladium surface. The high value for K_s indicates that the interaction of $PbBu_4$ with Pd atoms in the metal–support region predominates and, consequently, should not be considered a surface-controlled reaction. Nonetheless, this undesirable characteristic of the method of preparation seems to be overcome during the activation of the catalyst precursor in hydrogen. Upon hydrogen treatment at 573 K, lead atoms located in the boundary region became a source for the formation of true bimetallic particles by a surface migration and diffusion mechanism. It is observed in table 1 that reduction produces a marked decrease in the hydrogen uptake which, in turn, affects the catalytic activity, as shown below. The existence of a Pd–Pb alloy in sample II has been demonstrated on the basis of XPS and FTIR studies [11].

It is difficult to explain why the boundary palladium atoms are more reactive towards tetrabutyllead as compared with surface atoms. Our results seem to be in disagreement with those from previous studies where surface reactions between metal alkyls and nickel, platinum and rhodium particles are claimed to be involved in the preparation of bimetallic catalysts [4,12]. At this point it is relevant to mention that the contribution of boundary atoms in a catalytic reaction, the hydrogenolysis of MCP to n-hexane, has been demonstrated for platinum on silica catalysts [13].

3.2. Interaction between $PbBu_4$ and Pd/α-Al_2O_3. Analysis of gaseous products and decomposition of surface precursors

During the reaction between $PbBu_4$ and Pd/α-Al_2O_3, decomposition of the organometallic compound occurs with the elimination of C_4 hydrocarbons (butane, 1-butene, *cis*- and *trans*-2-butene) and formation of a metastable surface complex, described as Pd–Pb(Bu)$_x$.

With regard to the gaseous products, figure 3 presents the variation of the concentration of C_4 hydrocarbons in the liquid phase with time for the reaction of $PbBu_4$ with sample II (Pd(0.19 wt%)/α-Al_2O_3) for both pretreatments A and B (data taken from [8]). In about 30 min, 80% of the total amount of C_4 hydrocarbons has evolved and a final state concentration is reached in 80 min.

Clearly, the amount of hydrocarbons produced with pretreatment A is higher than that obtained with pretreatment B. However, the amount of saturated hydrocarbons was the same, about 1.2–1.4×10^{-6} mol. In other words, the main difference is in the amount of butane. Pretreatment A produces 66% butane versus 8% under pretreatment B. In addition, it was found that the amount of lead fixed was not dependent on the pretreatment procedure, as shown in table 1. These results suggest that the anchoring sites are the same for both pretreatments despite the fact that different hydrocarbons are produced. In order to explain this behaviour, the following equation is proposed for the initial interaction of Pb(Bu)$_4$ with palladium atoms:

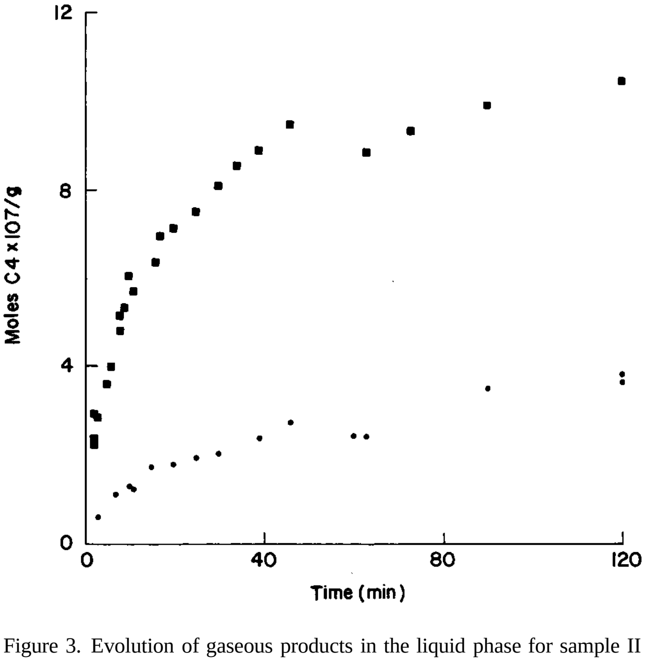

Figure 3. Evolution of gaseous products in the liquid phase for sample II (Pd(0.19 wt%)/α-Al_2O_3).

$$PbBu_4 + 2]\text{-}L \rightarrow (]\text{-}L)_2\text{–}PbBu_2 + 2C_4H_8 + 2H^*. \quad (4)$$

The nature of the anchoring ligand (]-L) cannot be specified, but based on the conclusion of the previous section, we consider that it is located on the metal–support region.

The formation of butenes may be explained by a classical β-abstraction mechanism. The other reaction products, (]-L)$_2$–PbBu$_2$ and H*, may remain on the surface or undergo further changes, depending on the pretreatment. In the absence of adsorbed hydrogen (pretreatment B), (]-L)$_2$–PbBu$_2$ became a stable surface intermediate, as demonstrated by subsequent TPR experiments (see below), while the hydrogen atoms are bound to the Pd surface. Upon pretreatment A, the situation is different because hydrogen produced by the β-abstraction reaction cannot be adsorbed on the saturated Pd surface. Consequently, it may undergo further reaction with the surface complex (]-L)$_2$–PbBu$_2$ leading to butane formation:

$$(]\text{-}L)_2\text{–}PbBu_2 + 2H^* \rightarrow (]\text{-}L)_2\text{–}Pb + 2C_4H_{10}. \quad (5)$$

Combining equations (4) and (5) we obtain

$$PbBu_4 + 2]\text{-}L \xrightarrow{\text{Pd–H}} (]\text{-}L)_2\text{–}Pb + 2C_4H_8 + 2C_4H_{10}. \quad (6)$$

Based on this interpretation, similar amounts of butenes and butane are expected in the liquid phase when pretreatment A is used. Our data shows that the amount of butane was higher, about 66%, presumably due to some butene hydrogenation. Consequently, Pd–PbBu$_x$ surface species should not be formed.

In order to support the interpretation given above, the decomposition of surface precursors has been followed by TPR. For pretreatment A, no hydrocarbon was detected during the TPR experiments, in accordance with reaction (6).

On the other hand, TPR experiments performed on samples pretreated with method B showed that the surface complex (]-L)$_2$–PbBu$_2$ is quite stable. The TPR profiles for samples I–III are shown in figure 4. The main feature is a hydrogen consumption peak at about 120 °C, equivalent to the release of two butyl groups per mole of lead fixed. Gas chromatography analysis of the hydrocarbons evolved indicated that butane is the main product. Consequently, these results support the stoichiometry proposed for the surface complex that is formed upon pretreatment B.

This stable surface complex, where the Pb atom is coordinated to hydrocarbon ligands and to boundary metal atoms, may have a potential application as a new catalytic material. The reactivity of several surface organometallic complexes for important catalytic reactions has been reviewed by Basset et al. [14,15].

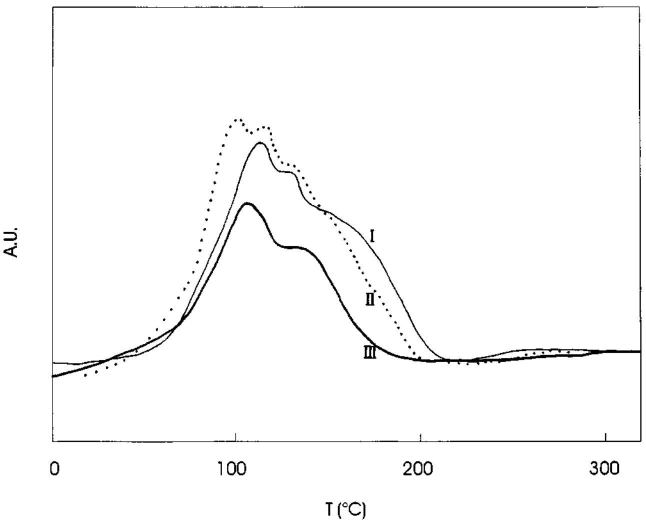

Figure 4. TPR profiles of surface complexes formed with pretreatment B: (I) Pd(0.11 wt%)/α-Al$_2$O$_3$; (II) Pd(0.19 wt%)/α-Al$_2$O$_3$; (III) Pd(0.20 wt%)/α-Al$_2$O$_3$.

It has been shown that equations (4) and (6) are in agreement with the quality of gaseous reaction products found in the liquid phase and eluted from the solid samples during the TPR experiments. However, according to these equations each mole of Pb fixed to the monometallic catalyst pretreated with method A or B should release for 4 or 2 moles of hydrocarbon to the solvent, respectively. In this way, the C_4 concentration in the liquid phase should be 0.003 and 0.001 mol C_4/g. As can be observed in figure 3, the liquid-phase concentration was four times lower. In order to explain the disagreement, it is important to mention that hydrocarbons may become trapped in the alumina pores, and butenes may also be adsorbed on the palladium surface. An experimental fact that is in accordance with this interpretation is that, upon solvent elimination and drying, a large amount of C_4 is briefly and suddenly detected [8].

3.3. The effect of Pb in the selective hydrogenation of acetylene over Pd/α-Al$_2$O$_3$ catalysts

Figure 5(a) shows the dependence of acetylene conversion on temperature for sample II before and after lead addition. Figure 5(b) presents the effect of temperature on ethylene concentration. It is important to recall that these catalysts were reduced at 573 K in hydrogen prior to reaction. The Pd/α-Al$_2$O$_3$ sample exhibits a dramatic increase in acetylene conversion in a very narrow temperature range (273–298 K). At low temperature, when the acetylene conversion is below 20%, the very high concentration of ethylene remains unaltered, an indication of good selectivity. As the conversion of acetylene increases over 20% there is a sharp decrease in ethylene concentration owing to hydrogenation. In other words, a breakdown in selectivity is observed. The addition of lead introduces a pronounced change in the activity and selectivity of Pd/α-Al$_2$O$_3$. It is shown in figure 5 (a) and (b) that the Pd–Pb/α-Al$_2$O$_3$ catalyst is less active but more selective. It exhibits a steady increase in acetylene conversion up to high values in the 298–393 K temperature range. In addition, ethylene hydrogenation was not observed up to 60% acetylene conversion. In fact, a small ethylene gain at about 323 K was noted, indicating the selective hydrogenation of acetylene to ethylene. At very high acetylene conversion values, ethylene losses that are lower than those reported for Pd/α-Al$_2$O$_3$ are observed. Consequently, the presence of lead suppresses the undesirable hydrogenation of ethylene improving the selectivity of palladium catalysts for acetylene hydrogenation in the presence of a large excess of ethylene.

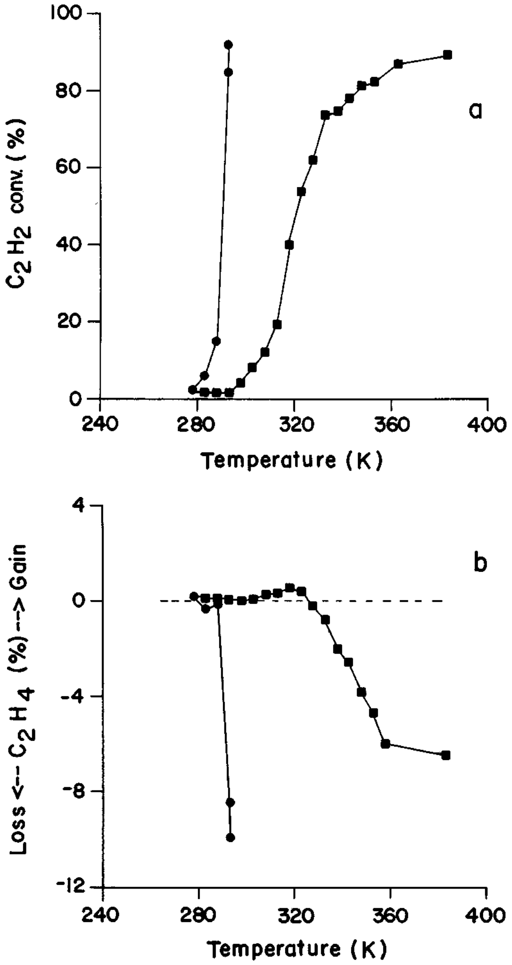

Figure 5. Catalytic activity and selectivity of sample II before and after lead addition. (a) Acetylene conversion (%) versus T (K) at constant space velocity. (b) Ethylene gain or losses (%) versus T (K).

4. Conclusion

The anchoring sites of PbBu$_4$ on Pd/α-Al$_2$O$_3$ catalysts prepared from Pd(AcAc)$_2$ takes place mainly on palladium atoms located in the metal–support boundary. The interaction of PbBu$_4$ with surface palladium atoms is almost null. Therefore, the reaction between the organometallic lead compound and Pd/α-Al$_2$O$_3$ should not be considered a true surface-controlled reaction. The presence of preadsorbed hydrogen does not alter the amount of lead fixed nor the type of anchoring sites. However, it affects the quality and quantity of hydrocarbons released. In the absence of hydrogen, a stable surface complex containing two butyl ligands is obtained. Consequently, the precursor of Pd–Pb catalysts may be described as Pd–$Pb(Bu)_2/\alpha$-Al_2O_3. Decomposition of these species in hydrogen at 573 K leads to Pd–Pb/α-Al_2O_3 catalysts that are very selective for acetylene hydrogenation in the presence of ethylene.

Appendix

Assuming hemispherical Pd particles with an average diameter d, the perimeter of N particles per gram of catalyst, P, is

$$P = N\pi d. \tag{7}$$

The number of particles N is given by the following equation:

$$N = V_\mathrm{t}/V_\mathrm{p} = 12[\mathrm{Pd}]V_\mathrm{at}/\left(\pi d^3\right), \tag{8}$$

where V_p is the particle volume, V_t is the total metal volume per gram of catalyst, V_at is the volume per metal atom in the bulk, and [Pd] is the number of Pd atoms per gram of catalyst.

In addition, the average particle diameter d is related to the metal dispersion, D, by the well known relation [16]

$$d = 6V_\mathrm{at}/(DA_\mathrm{t}), \tag{9}$$

A_at being the effective average area occupied by a Pd atom.

By substitution of equations (8) and (9) into equation (7), the following relation for P is obtained:

$$P = (1/3)\left\{D^2(A_\mathrm{at})^2[\mathrm{Pd}]/V_\mathrm{at}\right\}. \tag{10}$$

Therefore the perimeter P depends on the metal dispersion and the total number of Pd atoms. In order to calculate the number of perimetral or boundary metal atoms per gram of catalyst, equation (10) is divided by $d_\mathrm{at} = 1.5V_\mathrm{at}/A_\mathrm{at}$, where d_at is the atomic diameter, to obtain

$$[\mathrm{Pd}]_\mathrm{b} = (1/6)\left\{D^2(A_\mathrm{at})^3[\mathrm{Pd}]/V_\mathrm{at}^2\right\}.$$

Using values of 0.0789 nm^2/at and 0.0147 nm^3/at for A_t and V_t, respectively, and introducing the Pd content in weight percent, we arrived at the following formula for the concentration of boundary palladium atoms:

$$[\mathrm{Pd}]_\mathrm{b}\ (\mathrm{wt\%}) = 0.38D^2[\mathrm{Pd}]_\mathrm{t}\ (\mathrm{wt\%}). \tag{11}$$

References

[1] J.P. Boitiaux, J. Cosyns, M. Derrien and G. Léger, Hydrocarbon Process. 64 (1985) 51.

[2] J. Margitfalvi, S. Hegedüs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó and F. Nagy, in: *Proc. 8th Int. Congr. Catal.*, Vol. 4 (Verlag-Chemie, Berlin, 1984) p. 903.

[3] C. Travers, J.P. Bournonville and G. Martino, in: *Proc. 8th Int. Congr. Catal.*, Vol. 4 (Verlag-Chemie, Berlin, 1984) p. 891.

[4] J. Margitfalvi, S. Szabó and F. Nagy, in: *Catalytic Hydrogenation*, Stud. Surf. Sci. Catal., Vol. 27, ed. L. Cerveny (Elsevier, Amsterdam, 1986) ch. 11.

[5] J.P. Candy, O.A. Ferretti, G. Mabilon, J.P. Bournonville, A. El Mansour, J.M. Basset, J.P. Basset and G. Martino, J. Catal. 112 (1988) 210.

[6] M. Agnelli, J.P. Candy, J.M. Basset, J.P. Bournonville and O.A. Ferretti, J. Catal. 121 (1990) 236.

[7] Cs. Vértes, E. Tálas, I. Czakó-Nagy, J. Ryczkowski, S. Gobolos, A. Vértes and J. Margitfalvi, Appl. Catal. 68 (1991) 149.

[8] H.R. Aduriz, C.E. Gigola, A.M. Sica, A.M. Volpe and R. Touroude, Catal. Today 15 (1992) 454.

[9] T. Mallat, Zs. Bodnar, S. Szabó and J. Petró, Appl. Catal. 69 (1991) 85.

[10] J. Goetz, M.A. Volpe, A.M. Sica, C.E. Gigola and R. Touroude, J. Catal. 153 (1995) 86.

[11] J. Goetz, M.A. Volpe, A.M. Sica, C.E. Gigola and R. Touroude, J. Catal. 167 (1997) 314.

[12] M. Agnelli, P. Louessard, P.A. El Mansour, J.P. Candy, J.P. Bournonville and J.M. Basset, Catal. Today 6 (1989) 63.

[13] R. Kramer and J. Zuegg, J. Catal. 80 (1983) 446.

[14] S. Scott and J.M. Basset, J. Mol. Catal. 86 (1994) 5.

[15] J.P. Candy, B. Didillion, E.L. Smith, T.B. Shay and J.P. Basset, J. Mol. Catal. 86 (1994) 179.

[16] J.R. Anderson and K.C. Pratt, in: *Introduction to Characterization and Testing of Catalysts* (Academic Press, New York, 1985).