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Surface organometallic chemistry on metals in water Chemical modification of platinum catalyst surface by reaction with hydrosoluble organotin complexes: application to the selective dehydrogenation of isobutane to isobutene

F.Z. Bentahar[a], J.P. Candy[a,*], J.M. Basset[a], F. Le Peltier[b], B. Didillon[b]

[a] *LCOMS-CPE, 43 bd du 11 Novembre 1918, F-69616 Villeurbanne, France*

[b] *IFP, 1 et 4 av. de Bois Préau, F-92506 Rueil-Malmaison, France*

Abstract

Surface organo-metallic chemistry on metals can be a new route to generate supported bimetallic catalysts. According to previous works on Pt–Sn catalysts, the reaction of tetra *n*-butyl-tin on the reduced platinum surface leads to well-defined bimetallic catalysts which are very active and selective in the dehydrogenation of isobutane into isobutene. The presence of tin not only isolates the surface platinum atoms from each other (EXAFS) and thus prevents a fast deactivation by decreasing the processes of C–C bond cleavage but also favors the regeneration processes under air. So far the catalyst preparations were carried out either in the gas phase or in organic solution (e.g. heptane). However, in order to meet the industrial criteria of process simplicity, there is a need to carry out such catalyst preparation in water.

In this work, Pt–Sn/Al_2O_3 and Pt–Sn/SiO_2 catalysts was prepared by reacting tris *n*-butyl-tin hydroxide on the platinum surface, in water solution under atmospheric pressure of hydrogen. The kinetics of the reaction was followed by measuring the amount of butane evolved as a function of time. The solids obtained were characterized by CO, O_2 or H_2 chemisorption and electron microscopy (CTEM and EDAX). Clearly, the $(n\text{-Bu})_3Sn(OH)$ reacts selectively on the platinum surface and not with the support, with evolution of butane, leading to a bimetallic catalyst where the platinum atoms are isolated from each other by the tin atoms. Very high selectivities (>95%) and activities were obtained for the reaction of isobutane dehydrogenation into isobutene and it was concluded that surface organo-metallic chemistry on metal in water can be an alternative route to prepare well-defined supported bimetallic Pt–Sn catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metals; Platinum–tin catalysts; Dehydrogenation; Surface organometallic chemistry on metal

1. Introduction

Supported bimetallic platinum–tin catalysts are now widely used to dehydrogenate paraffins to olefins and particularly isobutane into isobutene as demonstrated by Box et al. [1], Olbrich et al. [2] or Wilhelm [3]. When compared to the monometallic platinum catalysts the platinum–tin systems are more selective, their lifetime is much higher and they are more stable toward oxidative regeneration. It has been proposed by Dautzenberg et al. [4], Caballero et al. [5] and Stagg et al. [6] that the tin atoms have several positive effects: they prevent the hydrogenolytic properties of the platinum toward C–C bonds, by reducing the size of Pt ensemble or by the so-called site isolation effect, leading to a better selectivity for the dehydrogenation

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[*] Corresponding author. Tel.: +33-72-43-17-94; fax: +33-72-43-17-95.
E-mail address: candy@mulliken.cpe.fr (J.P. Candy).

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process; they diminish the sintering process and then stabilize the size of the metallic particles; they diminish the rate of coke formation and thus increase the lifetime of the catalyst. It is expected that the selectivity and the stability of the catalysts will drastically depend on the distribution of the two metals on the support. It is evident that the presence of unmodified platinum particles (i.e. without tin) could drastically destroy the selectivity of the catalyst. In the same way, the presence of tin in excess either on the metal particle or on the support could modify or eventually destroy the activity of the catalyst by favoring the tin migration (in excess) onto the particles during the regeneration process. It is, therefore, interesting to find a way to prepare selectively bimetallic particles in such a way that the two metals are selectively located in the same particle.

Surface organo-metallic chemistry on metals is a new route to generate selectively supported bimetallic platinum–tin catalysts. According to previous works done by Humblot et al. [7,8], the reaction without solvent, under hydrogen of tetra *n*-butyl-tin on the reduced platinum surface leads to well-defined bimetallic catalysts which were found to be very active and selective in the dehydrogenation of isobutane into isobutene. The reaction between tetra *n*-butyl-tin and group VIII metallic surface was previously performed under atmospheric pressure of hydrogen in *n*-heptane solution by Travers et al. [9] or in benzene solution by Margitfalvi et al. [10]. However, in order to meet the industrial criteria of process simplicity and environmental friendly catalytic synthesis, there is a need to carry out such catalyst preparation in water.

In order to adapt the grafting process to this new solvent, we used Bu_3SnOH as a water-soluble precursor. Bu_3SnOH was obtained from $Bu_3SnCOOMe$ by exchange of the –OC(O)Me ligand by –OH group in $H_2O + KOH$ (pH 10) solution. The reaction of Bu_3SnOH on silica- and alumina-supported catalysts was studied under atmospheric pressure of hydrogen in $H_2O + KOH$ (pH 10) media. The reaction was followed by measuring the butane evolution. The solids obtained were characterized by elemental analysis, electron microscopy and adsorption of CO as probe molecules. The catalytic properties of the resulting bimetallic catalysts were tested the reaction of isobutane dehydrogenation. These results were then compared to that of $Pt–Sn_x$ catalysts prepared from Bu_4Sn in *n*-heptane.

2. Experimental

The monometallic Pt/SiO_2 starting material was prepared by the ion-exchange procedure proposed by Benesis et al. [11] from $Pt(NH_3)_4(OH)_2$. The support was a silica Aerosil 200 ($200\,m^2/g$) from Degussa. Prior to any study, it was treated at 450°C under flowing dry air in order to eliminate any traces of hydrocarbons. Ten grams of the silica support and 400 mg of platinum salt was stirred in ammonia solution (pH 10) during 24 h. The solid was then filtered and dried overnight at 80°C. It was then treated under flowing dry air at increasing temperature from 80 to 350°C, during 4 h, to form small particles of PtO/SiO_2. These particles were reduced at 350°C under flowing hydrogen during 4 h. After cooling down to room temperature, the sample was kept under air.

The monometallic $Pt/\gamma\text{-}Al_2O_3$ starting material was prepared by dry impregnation technique using a toluene solution of platinum acetylacetonate, following the procedure already described by Merlen et al. [12]. $\gamma\text{-}Al_2O_3$ with a surface area of $215\,m^2/g$ was used as support material.

2.1. Characterization of the catalysts

The dispersion (number of surface platinum atoms/number of total platinum atoms) of the sample is determined by chemisorption of hydrogen, oxygen and CO at 25°C in a volumetric apparatus already described by Candy et al. [13]. The stoichiometry of hydrogen, oxygen and CO adsorption (number of adsorbed hydrogen, oxygen atoms or CO molecules per surface platinum atom) are assumed to be equal to $1.8\ H/Pt_s$, $1\ O/Pt_s$ and $1\ CO/Pt_s$, respectively, as proposed by Jackson et al. [14] and Candy et al. [15]. Prior to the adsorption measurement, the samples are reduced under flowing hydrogen at 350°C for 3 h and then evacuated at the same temperature under vacuum (10^{-6} mbar) for 6 h.

The metal loading of monometallic and bimetallic samples is measured by elemental analysis. The metallic particle size is determined by electron microscopy (JEOL 100 CX). The average metallic particle size is correlated to the dispersion, assuming that the metallic particles have a cubo-octahedral shape, as suggested by Van Hardeveld and Hartog [16].

The tributyltinhydroxide (Bu_3SnOH) is synthesized from tributyltinacetate ($Bu_3SnCOOMe$) in potassium solution at pH 10 (Eq. (1))

$$\begin{aligned} &Bu_3SnOC(O)Me + OH^-K^+ + xH_2O \\ &\quad \rightarrow Bu_3SnOH + MeC(O)O^-K^+ + xH_2O \end{aligned} \tag{1}$$

The reaction between Bu_3SnOH and the monometallic catalysts is performed at room temperature in a closed glass reactor filled with the water solution at pH 10 in the presence of 1 atm of hydrogen following the procedure already described for supported rhodium catalysts by Ferretti et al. [17]. Prior to the reaction, the desired amount of catalyst (2 g) is reduced at 450°C under flowing dry hydrogen during 3 h. After cooling down to room temperature under hydrogen, the reduced catalyst is introduced under hydrogen into a Schlenk tube. Ten milliliters of freshly purified water (+KOH, pH 10) and a known amount of isobutane (namely 2 ml as internal standard) are introduced in the Schlenk tube which is then closed under 1 atm of hydrogen. After 30 min of stirring, the desired amount of Bu_3SnOH in solution in 10 ml of water (+KOH, pH 10) is added. The variation of the amount of butane evolved are then followed by gas chromatographic analysis of the gas phase, carried out after increasing times, t, of the reaction. Since the only gaseous product is butane, it has been checked that isobutane is never formed during the reaction of Bu_3SnOH with alumina-supported platinum and that the equilibrium of isobutane and butane in the gas and in the liquid phase is rapid. In this study, the hydrogen used for the reduction of samples and for the reaction in the closed reactor is fully deoxygenated and dehydrated by flowing through deoxo and zeolite traps. After reaction with Bu_3SnOH, the sample is extracted from the solution by filtering. Bu_3SnOH in excess is removed by washing with pure n-heptane. The sample is then treated under flowing hydrogen at increasing temperature (1°C/min) up to 550°C prior to elementary analysis and isobutane dehydrogenation reaction.

Isobutane dehydrogenation is performed in a dynamic reactor working under atmospheric pressure at 550°C with a ratio isobutane/hydrogen of 1/1 (mol/mol). The conditions of the reaction have been described by Humblot et al. [7]. If m is the amount of catalyst introduced (g), Pt the platinum loading of the sample (w/w) (%), $f(iC_4{}^i)$ the flow rate of isobutane (mol/s), and $[A]$ the sum of the products expressed as equivalent C_4, one can define

- $[A] = [iC_4{}^{=}] + [nC_4] + [nC_4{}^{=}] + \frac{3}{4}([C_3] + [C_3{}^{=}]) + \frac{1}{2}([C_2] + [C_2{}^{=}]) + \frac{1}{4}[C_1]$.
- Conversion: $\text{conv.}\,(\%) = 100 \times [A]/([A] + [iC_4])$.
- Selectivity for isobutene: $\text{sel.}\,(\%) = 100 \times [iC_4{}^{=}]/[A]$.
- Activity: $r\,(\text{mmol/s/g}_{\text{Pt}}) = \text{conv.}\,(\%) f(iC_4{}^i)/100 \times m/\text{Pt}$.

The flow rate of isobutane + hydrogen and the amount of catalyst are adjusted (in the range 40–200 ml/min and 20–50 mg) to obtain isobutane conversions in the range 5–10%.

3. Results

3.1. Characterization of the monometallic catalysts

Various alumina- and silica-supported platinum catalysts were prepared and characterized. The amount of hydrogen, oxygen and CO adsorbed at 25°C under 150, 50 and 50 mbar, respectively, on the various samples, and the corresponding dispersions (Pt/Pt_s) calculated assuming the following stoichiometries ($H/Pt_s = 1.8$; $O/Pt_s = 1$; $CO/Pt_s = 1$) are reported in Table 1.

A fairly good agreement between the three chemical methods is obtained. The average metallic particle size measured by electron microscopy and the corresponding dispersion of the samples, assuming a cubo-octahedral shape for the metallic particles are reported in Table 1. There is a also a fairly good agreement between the two (chemical and physical) methods.

3.2. Reaction of Bu_3SnOH with alumina- and silica-supported platinum catalysts

3.2.1. Reaction with the supports

The amount of tin fixed after 24 h of reaction of Bu_3SnOH in water (+KOH, pH 10) with the surface of alumina and silica, pretreated at 450°C under flowing dry hydrogen during 3 h is reported in Table 2. Clearly,

Table 1
Metal loading, amount of H_2, O_2 and CO adsorbed and average metallic particle diameter for the various catalysts[a]

Sample	Pt (wt.%)	H_2 adsorbed (μmol/g)	O_2 adsorbed (μmol/g)	CO adsorbed (μmol/g)	Electron microscopy (nm)	Average dispersion[b] (%)
Pt/Al-1	0.6	23 (0.82)	13 (0.84)	30 (0.97)	1.0 (0.90)	0.88
Pt/Al-2	3.2	52 (0.35)	36 (0.42)	74 (0.45)	2.3 (0.40)	0.41
Pt/Si-1	0.7	10 (0.50)	11 (0.51)	22 (0.47)	2.0 (0.50)	0.50

[a] For each value, the corresponding average dispersion is given in parentheses.
[b] It is the average value of dispersion from all the obtained values.

Table 2
Amount of Sn fixed on the supports after reaction at 25°C under hydrogen with Bu_3SnOH in water + KOH, pH 10 solution

Support	SiO_2	Al_2O_3
Sn introduced (wt.%)	1.9	1.9
Sn fixed (wt.%)	<0.006	0.064

there is no significant reaction between Bu_3SnOH and the two supports at pH 10.

3.2.2. Reaction of Bu_3SnOH with Pt/SiO_2 and Pt/Al_2O_3

The amount of tin fixed (Sn_f) after 24 h of reaction of Bu_3SnOH in water (+KOH, pH 10) with the alumina- and silica-supported Pt is reported in Table 3. Note that various amounts of Bu_3SnOH were introduced (Sn_i). The greatest amount of Sn introduced is 1.5 wt.% for Pt/Al-2 and $Sn_i/Pt_s = 1.5$. One should notice that the amount of tin fixed never exceeds the monolayer of platinum: this is a strong support for the selective reaction of the organotin complex with the platinum surface. Even when the amount of tin introduced is higher than the value corresponding to a platinum monolayer, one cannot reach values above 0.80 Sn/surface platinum atoms.

Table 3
Amount of tin fixed (Sn_f) as a function of the amount of tin introduced (Sn_i) after 24 h of reaction of Bu_3SnOH in water (+KOH, pH 10) with the surface of Pt/Si-1, Pt/Al-1 and Pt/Al-2 catalysts[a]

Catalyst	Pt/Si-1	Pt/Al-1	Pt/Al-2
Dispersion (%)	0.50	0.85	0.50
Sn_f/Pt_s for $Sn_i/Pt_s = 0.5$	0.58	0.55	0.50
Sn_f/Pt_s for $Sn_i/Pt_s = 1.0$	0.68	0.70	0.69
Sn_f/Pt_s for $Sn_i/Pt_s = 1.5$	0.73	0.79	0.80
C_4/Sn_f for $Sn_i/Pt_s = 1.5$	1.78	1.15	2.04

[a] Row 6 indicates the amount of butane evolved during the chemisorption process.

During the reaction of Bu_3SnOH on the platinum surface, the only one gas evolved is *n*-butane. The kinetics of *n*-butane evolution for Pt/Si-1 is reported in Fig. 1. There is almost no effect of the Bu_3SnOH concentration on the kinetics of the reaction.

The total amount of *n*-butane evolved reaches a plateau after about 10 h of reaction. The total amount of butane evolved after 24 h of reaction at 25°C on the three catalysts and for the amount of Bu_3SnOH introduced corresponding to $Sn_i/Pt_s = 1.5$ are reported in Table 3. Clearly, some butyl groups are remaining on the surface complexes, even after 24 h of reaction at 25°C. For Pt/Si-1 and Pt/Al-2 catalysts (dispersion = 0.5), the amount of remaining butyl groups is close to 1 Bu/Sn_f fixed, while for Pt/Al-1 catalyst (dispersion = 0.85), this value is close to 2 Bu/Sn_f. It is clear that the amount of remaining

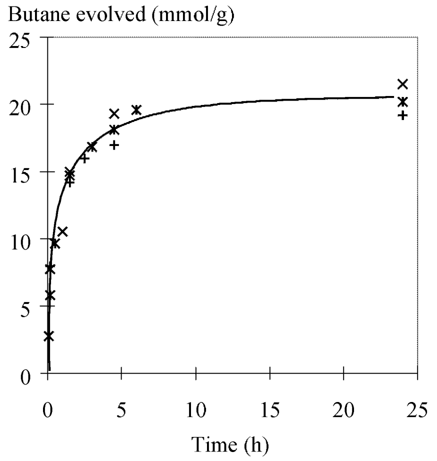

Fig. 1. Amount of butane evolved at 25°C on Pt/Si-1. Sn_i/Pt_s: 0.5 (+); 1 (∗); 1.5 (×).

butyl groups is greater on well-dispersed catalyst than on less-dispersed catalysts. These results are in good agreement with the results previously obtained in *n*-heptane solution, with Bu_4Sn by Bentahar et al. [18]. Large particles with high concentration of exposed planes give rise to higher hydrogenolysis of the grafted tin alkyl fragments.

After treatment under flowing hydrogen at 550°C of the samples, the total amount of butane evolved is always close to 3 Bu/Sn_f. At this stage, there is no remaining butyl groups on the catalysts.

3.3. Characterization of the bimetallic Pt–Sn catalysts

The chemisorption of carbon monoxide on the various samples was measured on the volumetric apparatus already described by Candy et al. [13]. Prior to carbon monoxide chemisorption, the various samples were treated under flowing hydrogen at 550°C during 3 h and then evacuated at the same temperature during 3 h. The average metallic particle size of the various samples, measured by electron microscopy and the various amounts of chemisorbed CO at 25°C and under 50 mbar are reported in Table 4.

Clearly, the average metallic particle size is greater for the bimetallic catalysts than for the monometallic starting materials. In contrary, the amount of chemisorbed CO is lower for the bimetallic catalysts than for the monometallic starting materials. These results are in perfect agreement with the previous results obtained with Bu_4Sn on Pt/SiO_2 catalysts by Humblot et al. [8]. It can be concluded that the tin atoms fixed on the supported platinum catalysts by reaction of Bu_3SnOH in water are randomly distributed on the surface of the metallic particles.

Table 4
Average metallic particle size of the various Pt and Pt–Sn samples, measured by electron microscopy and the corresponding amount of adsorbed CO at 25°C and 50 mbar

Samples	Sn/Pt_s	Average particle diameter (nm)	CO (μmol/g)
Pt/Si-1	0	2.0	22.0
$Pt–Sn_{0.7}/Si-1$	0.68	3.2	9.9
Pt/Al-1	0	1.0	30.0
$Pt–Sn_{0.7}/Al-1$	0.70	2.2	13.8
Pt/Al-2	0	2.3	74.0
$Pt–Sn_{0.7}/Al-2$	0.69	3.5	23.9

3.4. Dehydrogenation of isobutane into isobutene

The aim of this part of the work is to see whether or not bimetallic Pt–Sn catalysts obtained from the water-soluble complex Bu_3SnOH are as active and selective than the corresponding Pt–Sn catalysts obtained from Bu_4Sn in organic media.

In Fig. 2, we report the catalytic activity and selectivity for isobutene of the monometallic Pt/Si-1 and of the corresponding bimetallic catalysts prepared in water or organic media, as a function of time on

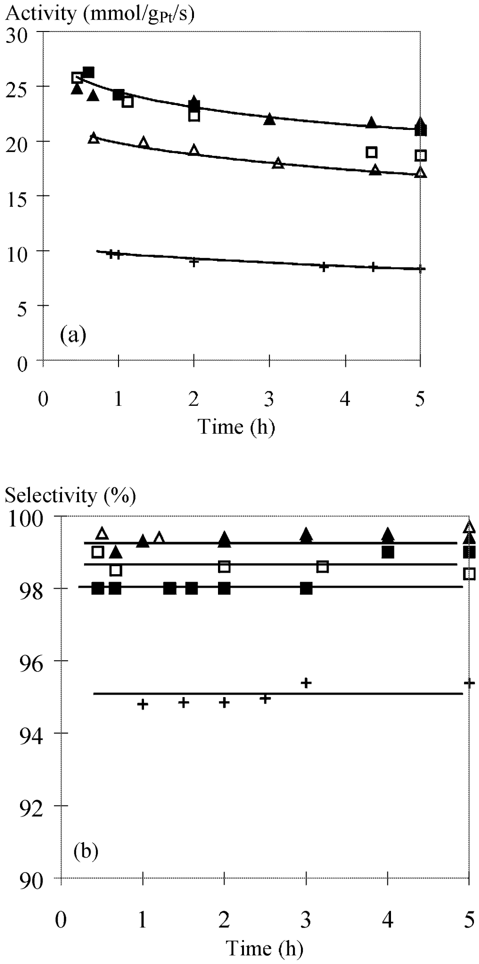

Fig. 2. (a) Activity for isobutane dehydrogenation and (b) selectivity for isobutene obtained at 550°C under 1 atm of H_2 + isobutene (H_2/isobutene = 1) and conv. < 10% with: (+) Pt/Si-1; (□) $Pt–Sn_{0.5}/Si-1$; (△) $Pt–Sn_{0.7}/Si-1$ (open symbols: catalysts prepared in *n*-heptane; filled symbols: catalysts prepared in water).

Table 5
Activities and selectivities measured at 550°C, after 5 h on stream of the various monometallic and bimetallic catalysts prepared in organic or water media

	Catalyst								
	Pt/Si-1			Pt/Al-1			Pt/Al-2		
Sn/Pt_s	0	0.7[a]	0.7[b]	0	0.7[a]	0.7[b]	0	0.7[a]	0.7[b]
Act. ($mmol/g_{Pt}/s$)	9	17	21	9	22	22	28.5	85	75
Sel. (%)	95.1	99.3	99.4	95.2	99.8	99.8	95.4	99.4	99.4

[a] Prepared in organic media.
[b] Prepared in water media.

stream. The activities and selectivities measured at 550°C, after 5 h on stream of the various monometallic and bimetallic catalysts prepared in organic or water media are reported in Table 5. Clearly, the catalytic activities and the selectivities for isobutene obtained for the bimetallic Pt–Sn catalysts prepared in water or in organic media are very close.

4. Conclusion

Pt–Sn/Al_2O_3 and Pt–Sn/SiO_2 catalysts was prepared by reaction of Bu_3SnOH on the platinum surface, in water solution under atmospheric pressure of hydrogen. The kinetics of the reaction was followed by measuring the amount of butane evolved. The solids obtained was characterized by CO, O_2 or H_2 chemisorption and electron microscopy. Clearly, Bu_3SnOH reacts selectively on the platinum surface, leading to bimetallic catalysts where the platinum atoms are isolated from each other by the tin atoms. These bimetallic catalysts exhibit activities and selectivities for isobutane dehydrogenation into isobutene as high as the corresponding Pt–Sn catalysts prepared from Bu_4Sn in organic media. It is then obvious that surface organo-metallic chemistry on metal carried out in water can be an alternative route to prepare well-defined bimetallic alumina- or silica-supported Pt–Sn catalysts. The structure, the activities and the selectivities are comparable.

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