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Mössbauer Spectra Investigation of the Role of Tin in Platinum–Tin Reforming Catalysts

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The state of $Pt–Sn/Al_2O_3$ catalysts with Pt and Sn contents (wt%) 0.47–0.47, 0.95–0.5, and 0.5–0.2 was studied by tin Mössbauer spectroscopy pointing out the special features of the spectra of some highly dispersed species. The reduction by hydrogen of these three catalysts resulted in different amounts and compositions of Pt–Sn alloys, Sn(IV) and Sn(II) ionic species, and relatively high contents of platinum which seem to be not alloyed with tin. Alloying accounts for the decrease in the catalytic activity related to platinum, and the catalytic activity of the probably nonalloyed part of this metal is also inhibited. Tin ions poison the strong acidic sites of alumina. Evidence for the participation of the latter in catalytic reactions involving hydrogen is given by the oxidation of tin induced by desorption. Sequences of chlorination and hydrogenation modify the catalysts depending on their platinum and tin contents.

INTRODUCTION

Composite $Pt–Sn/Al_2O_3$ catalysts have been the subject of numerous patents (*1–7*), but little fundamental work has been published on this system. An interesting point is to determine how tin, which has long been considered as a poison for platinum, can promote the catalytic activity of Pt/Al_2O_3. Karpinsky and Clarke (*8*) reported the catalytic properties of Pt–Sn alloy films; the comparison of their results with those obtained with supported catalysts can give some insight into the role of tin in the latter. However, the tin in the supported catalysts could exist in another state than in films due to the reduction process and dispersion. From experiments of oxidation by oxygen and of adsorption of hydrogen and oxygen, Muller, Engelhard, and Weisang (*9*) described these solids as $Pt^0–Sn^{II}/Al_2O_3$.

Though a number or physical and chemical methods fail in giving a good picture of the state of tin in these catalysts, we used Mössbauer spectroscopy for achieving this characterization. A preliminary study (*10,11*) resulted in evidence for different degrees of reduction and alloying at different compositions and supported the hypothesis of interactions of Sn metal with platinum and of ionic tin with alumina. Therefore this research was extended by using improved technical conditions and other platinum and tin contents, and by making an examination of the desorption of hydrogen and of chlorination effects. Some features and conclusions of this work were already briefly reported (*12*). Here we present and discuss all the results of these investigations, also paying attention to those of Gray and Fahra (*13*) and Berndt, Mehner, Völter, and Meisel (*14*) on some supported Pt–Sn catalysts.

EXPERIMENTAL METHODS

1. Catalysts

Nonporous commercial alumina Degussa

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110 C (Surface area 300 m^2/g) was used as the support. Catalysts were prepared by impregnation of alumina from solution following the procedure patented by Compagnie Française de Raffinage (*1*): tin was introduced first and the dried solid was calcined in air at 400°C, then platinum was added as chloroplatinic acid, and the catalyst was dried at 110°C. The samples denoted C were calcined in air at 400°C after adding platinum, and others, denoted NC, were not so calcined. Temperature-programmed reduction has been performed as described below on the set of catalysts used in the adsorption and reaction work of the previous study (*11, 15*) and the determination of their platinum surface area has been published elsewhere (*15*). The reduction of the samples used in Mössbauer experiments was achieved in flowing hydrogen under atmospheric pressure by raising the temperature for 30 min up to 500°C and maintaining it at this value for 1 h.

Chemical analysis was carried out after the samples were dissolved in an HCl–HNO_3 medium; tin was determined by atomic absorption spectrometry using a N_2O–C_2H_2 flame, and platinum by visible spectrometry of the complex formed with $SnCl_2$. These procedures were successfully checked against some results of pure instrumental neutron radioactivation analysis.

Three catalysts were studied by Mössbauer spectroscopy: No. 1 had a platinum content 0.47% by weight and tin 0.47% by weight (designated hereafter as Pt 0.47–Sn 0.47). Correspondingly, No. 2 was Pt 0.95–Sn 0.55 and No. 3 Pt 0.5–Sn 0.2.

2. *Temperature-Programmed Reduction (TPR)*

Hydrogen consumption of 100-mg powder samples was measured at low constant pressure, about 10 Pa, in a volumetric apparatus equipped with a Pirani gauge. Pressure was maintained constant during a linear temperature increase by introducing measured quantities of hydrogen and trapping the evolved water and hydrogen chloride. In order to avoid the uncertainties related with the unknown hydrogen coverage of platinum at the final temperature of the experiments, the sample was allowed to return to room temperature, at which the total hydrogen consumption was measured.

3. *Mössbauer (Nuclear Gamma Resonance, NGR) Spectroscopy*

This was performed on ^{119}Sn-enriched catalysts. NGR absorption spectra were obtained using a constant-acceleration driving unit (Numelec), operated in the triangular mode, slaved to a 800-channel analyser (Intertechnique). γ-Rays from a 25-mCi $Ca^{119}SnO_3$ source (Amersham), with a linewidth 0.40 mm s^{-1}, were detected by a 0.1-mm thick NaI(Tl) scintillation probe (Harshaw). Velocity calibration was obtained from the spectrum of Fe metal. After computer folding, the decomposition of the spectra, all having over 10^6 counts per channel, and determination of the Mössbauer parameters were achieved using the program MOSFIT, assuming a Lorentzian shape of the lines, built up by F. Varret (University of Le Mans, France). Isomer shifts *IS* in this paper refer to SnO_2 and are given with a precision greater than 0.03 mm s^{-1}. Quadrupole splitting *QS* and experimental linewidth *W* were accurate within 0.05 and 0.03 mm s^{-1}, respectively. Due to the tin 119 content of the samples, the latter cannot be smaller than 0.80 mm s^{-1}, a value which very pure and perfect components of any spectrum cannot greatly exceed.

Because of the frequent asymmetry of doublets, due to anisotropy of the Lamb–Mössbauer factor (Karyagin–Goldanskii Effect, KGE) which may occur in particular near a surface, and hence very important at high dispersion, each spectrum was considered as made up from a number of single lines. The starting values for this number and NGR parameters were chosen according to the shape of experimental spectra. Only the results of the best fits, giving values of χ^2 per degree of freedom smaller than or equal to 1, were taken into account and are reported in the tables hereafter. Their interpretation, in particular the assessment of the occurrence of some doublet, was established by taking into account chemical and physical features of the systems (for instance, the compositions should not result in more platinum than is introduced in the catalysts).

Isomer shifts and quadrupole splittings of the possible Sn compounds were gathered from the literature (*13, 14, 16, 17*), with special attention to Pt–Sn alloys (*18–20*). The isomer shifts of the latter were reported as linearly dependent on tin atomic content, from 1.20 mm s^{-1} for the smallest values to 2.56 for β-Sn, and the linewidths are large, which in some cases is accounted for by a small quadrupole splitting. The ratio $A/A(SnO_2)$ of the total absorption area to that of the same catalyst in the nonreduced state was taken into account for achieving the characterizations.

The thermal treatments in hydrogen, argon–CCl_4 mixtures or *in vacuo* with subsequent NGR spectroscopy at room temperature without sample removal were performed using a furnace, designed by J. Moulin in the Grenoble Nuclear Center and equipped with two beryllium windows (Kawecki Berylco Industries, Inc.), which gave no measurable Sn resonant absorption. The samples were introduced as pellets, about 100 mg cm^{-2} thick, made by pressing the powders at 2×10^6 Pa.

RESULTS

1. Activation of the Catalysts

The volume of hydrogen consumed by the reduction was measured during a linear increase of temperature, and the results are given in Fig. 1. Pt/Al_2O_3 gives a one-step reduction, completed at 350°C and followed by hydrogen desorption from the platinum surface. The kinetics of reduction of $Pt-Sn/Al_2O_3$ samples are more complex and depend on tin content. However, it appears that hydrogen consumption at 500°C exceeds the quantity needed to reduce platinum alone, and therefore some reduction of tin occurs. The degree of reduction can be calculated from the hydrogen consumption, assuming that:

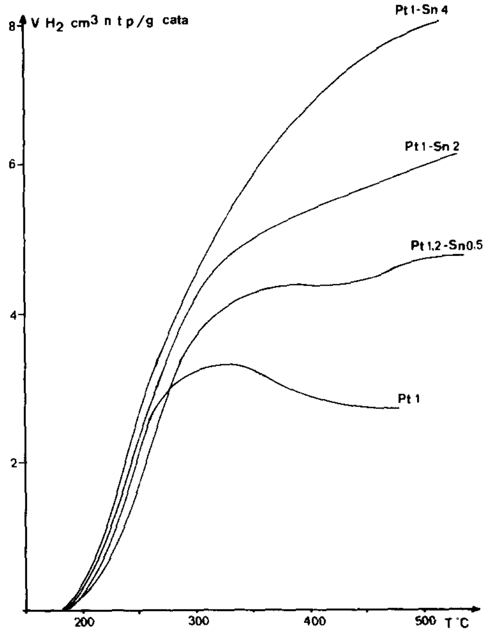

FIG. 1. Temperature-programmed-reduction curves for some noncalcined $Pt-Sn/Al_2O_3$ catalysts.

(a) the reduction of platinum is not greatly modified by tin and that the stoichiometry of the reaction is:

$$Pt^{4+} + \tfrac{5}{2}H_2 \rightarrow PtH + 4H^+$$

as is found for Pt/Al_2O_3, and

(b) tin is reduced to the metallic state.

This calculation was used for several catalysts and the results are shown in Table 1. They suffer a somewhat poor accuracy in the range of small metal content. Nevertheless it appears clearly that the degree of reduction of tin increases with the Pt/Sn ratio on both calcined and noncalcined samples, and that calcination of the catalyst seems to decrease the final reduction of tin. Sn/Al_2O_3 alone is hardly reducible (degree of reduction: 17%).

For the catalysts studied by Mössbauer spectroscopy, the spectra before reduction of the starting products, calcined or not, are quite identical to those of bulk SnO_2: *IS* =

TABLE 1

Final Degree of Reduction of Tin Calculated from Volumetric Measurements

Noncalcined catalysts			Calcined catalysts			Comparable catalysts of this study
% Pt	% Sn	% reduction	% Pt	% Sn	% reduction	
0.31	0.5	45	0.31	0.5	20	No. 1
0.68	0.5	65	0.65	0.5	40	
0.86	0.5	100	0.87	0.5	20	No. 2
0.52	0.2	100	0.4	0.2	10	No. 3
			0.6	0.2	50	
1.15	0.5	100	1	0.2	40	
1	2	65	2	0.2	100	
1	4	65	1.0	0.5	30	
			0	0.2	17	

0.00, QS = 0.59, and W = 1.0, close to the expected value. The spectra after reduction by hydrogen are reported in Figs. 2a (No. 1), 4a and 5a (No. 2), and 6a (No. 3). Their fits resulted in the lines characterized in Table 2 together with the values of $A/A(SnO_2)$.

Catalyst No. 1. The spectrum can be fitted to a sum of four lines. A high value of $A/A(SnO_2)$ indicates that all the tin element is represented and lie in states involving high recoilless fractions. This rules out the presence of a significant amount of β-Sn because of its small Lamb–Mössbauer factor (*19*). The degree of reduction of tin of about 50%, reported in Table 1 for noncalcined catalysts of similar composition, ensures that it was not totally reduced to the metallic state. As the NGR lines cannot account for only Sn^{2+}, the spectrum must show Sn^0 necessarily alloyed to platinum. Hence the main features of the possible characterization are the attribution of the line at 0.58 mm s^{-1} to H_2SnCl_6 or similar chlorinated Sn^{4+} species, and that of the line at 2.34 mm s^{-1} to $PtSn_4$. Due to the overall composition of the solid, the presence of only part of the tin in this alloy implies that a rather large amount of platinum exists as free metal. The two weak lines could be coupled, resulting in a small quantity of a highly dispersed (large QS) PtSn, or associated with small parts of the strong lines, indicating small amounts of a second Sn^{4+} and of Sn^{2+}.

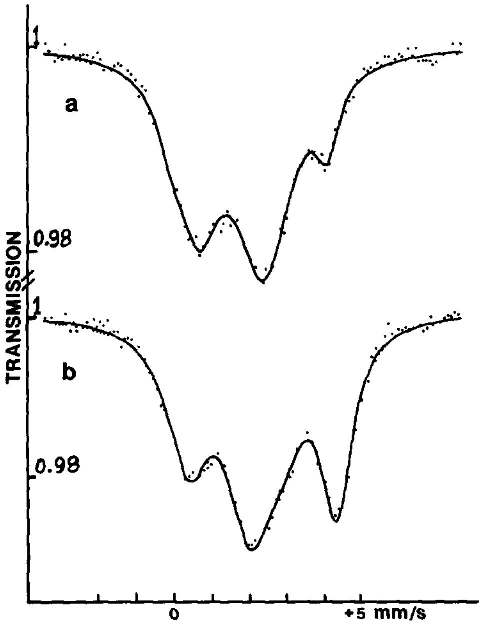

FIG. 2. Mössbauer spectra of Pt 0.47–Sn 0.47/Al_2O_3: (a) reduced, (b) desorbed.

Some samples exhibited spectra with somewhat different shapes but their interpretation leads to the same main conclusions, namely, that about one-third of their area is attributed to Sn^{4+} chlorides, one-third to $PtSn_4$, and the last third to oxygen-

TABLE 2

Mössbauer Parameters and Composition of the Reduced Catalysts

Catalyst No.	Composition (wt%)		Figure	Lines			$A/A(SnO_2)$	Main Sn species	Area of spectrum (%)
	Pt	Sn		*IS* (mm s^{-1})	*W* (mm s^{-1})	Area of spectrum (%)			
1	0.47	0.47	2a	−0.16	0.7	4			
				0.58	1.4	31	0.76	H_2SnCl_6	30
				2.34	1.8	58		$PtSn_4$	60
				4.06	0.75	7		PtSn	10
2	0.95	0.55	5a	1.04	1.0	12.5		Pt : Sn 85 : 15	30
				1.77	1.4	55	0.63	PtSn	70
				2.07	1.4	32.5			
2			4a	−0.16	1.2	7		PtSn	20
				1.53	1.2	40	0.65	PtSn	40
				2.22	1.2	23		SnO or $Sn(OH)_2$	40
				4.10	0.9	30			
3	0.50	0.20	6a	0.32	1.5	65	0.20	$SnCl_4 \cdot n\ H_2O$	65
				2.30	1.4	35		$PtSn_4$	35

ated, chlorinated or not, compounds of Sn^{2+}. About one-half of the platinum is thought to remain as free metal.

When the solid was calcined before its reduction by hydrogen similar spectra and composition were obtained.

Catalyst No. 2. For a noncalcined similar catalyst the reduction appeared total, as seen in Table 1. Table 2 shows that the spectrum of Fig. 5a is the association of the line at 1.04 mm s^{-1} with a part of that at 1.77 mm s^{-1} giving a doublet with $IS = 1.40$ mm s^{-1} and $QS = 0.73$ mm s^{-1}, which corresponds to an alloy containing about 15 at.% Sn. The association of the remaining part of the line at 1.77 mm s^{-1} with that at 2.07 mm s^{-1} gives a doublet with $IS = 1.90$ mm s^{-1} and $QS = 0.30$ mm s^{-1}, characteristic of PtSn. The asymmetry which at least one, more likely both, of these doublets shows can arise only from KGE due to a rather high dispersion. Taking into account that absorption factors are certainly somewhat different for the two alloys, it appears that they are the only metallic components of this solid whose the atomic ratio Pt : Sn is close to 1 : 1. This assessment is also supported by the value of $A/A(SnO_2)$, which is consistent with the Lamb–Mössbauer factor of the Pt–Sn alloys, of the order of half that of SnO_2 (*16*).

The reproducibility of the preparation is illustrated by the spectrum of Figure 4a, whose interpretation accepts the occurrence of Sn^{2+}, 20 to 30% of all tin, and highly dispersed (large *QS*) PtSn. A calcined sample gave a spectrum close to the latter.

Finally, in this catalyst no Sn^{4+} and no free platinum occur.

Catalyst No. 3. (spectrum 6a, Table 2). A degree of reduction of about 100% for a noncalcined similar catalyst (Table 1) suggests that no significant amount of ionic tin can be expected. Such a situation requires the association of the two lines of the spectrum, resulting in the assignment of such a wide and asymmetric doublet to a platinum-rich solid solution involving a small amount of tin. The major part of the latter, not seen in the spectrum, could only be β-Sn. These features could explain the low value of $A/A(SnO_2)$, but the existence of β-Sn is questionable because of the temperature of reduction which implies a liquid state, and therefore easier diffusion and alloying.

A second possibility, the only one we accept, is offered by the lack of precision in calculating the degree of reduction for so small a mass of tin as stated above in reporting the TPR results, therefore accepting even a rather large part of tin as ionic species. Then the line at 0.32 mm s^{-1} is attributed to hydrated Sn^{4+} chloride and the other to $PtSn_4$. The low value of $A/A(SnO_2)$ could be accounted for by that of $SnCl_4 \cdot n\ H_2O$ as appeared in chlorination of this catalyst (see Section 3).

The major part of the platinum is free.

2. *Desorption of Hydrogen and Subsequent Adsorption of Oxygen and Hydrogen*

Catalyst No. 1 (Fig. 2a) and No. 2 (Fig. 4a) were treated for 1 h at 500°C at a pressure lower than 10^{-3} Pa. Their spectra were taken under vacuum on returning to room temperature (Figs. 2b and 4b, respectively), interpreted according to the Mössbauer lines, and the resulting compositions are given in Table 3. No significant change occurred when a quantity of oxygen, corresponding to one atom for one Sn atom, was introduced at room temperature after this desorption. The spectra remained identical after pumping off oxygen gas and introducing hydrogen at 1 atm at room temperature.

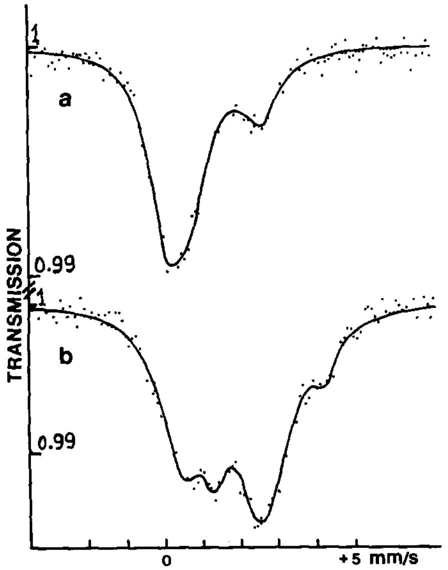

FIG. 3. Mössbauer spectra of Pt 0.47–Sn 0.47/Al_2O_3: (a) chlorinated, (b) rehydrogenated.

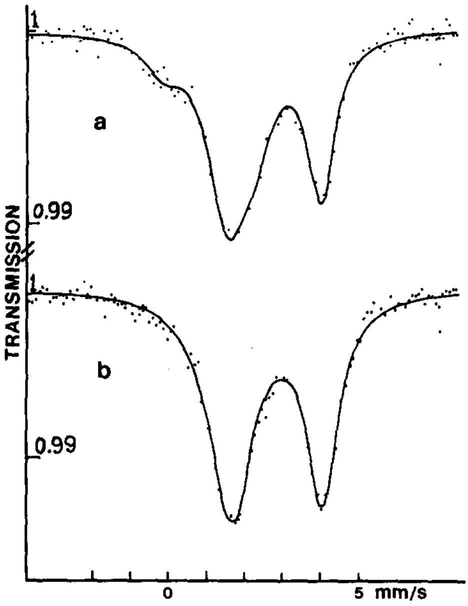

FIG. 4. Mössbauer spectra of Pt 0.95–Sn 0.55/Al_2O_3: (a) reduced, (b) desorbed.

Catalyst No. 1. The main result is the oxidation of all the highly dispersed or superficial PtSn and a part of $PtSn_4$ to a Sn^{2+} oxychlorinated species that appears together with an increase in $A/A(SnO_2)$. As the number of atoms of any component is proportional to this quantity and its fractional area, and inversely proportional to its linewidth, for a constant value of the Lamb–Mössbauer factor, the corresponding quantities in spectra 2a and 2b enable one to estimate the oxidized fraction of $PtSn_4$ to be about 0.50. This could represent its dispersion if only surface atoms underwent oxidation. The remaining particles of this alloy are small enough to exhibit a resolved quadrupole splitting.

Catalyst No. 2. Here also all the highly dispersed or surface PtSn is oxidized and a part of the less dispersed as well. This part, which may be the dispersion of the corresponding alloy, is about 0.60, with the same calculation and assumptions as in the case of catalyst No. 1. However, this value must be compared with that of 0.30 obtained from spectrum 4a in Section 1, and therefore tin atoms lying under the surface monolayer could have been oxidized.

TABLE 3

Mössbauer Parameters and Composition of Catalysts No. 1 and No. 2 after Desorption of Hydrogen

Catalyst No.	Figure	Lines			$A/A(SnO_2)$	Main Sn species	Area of spectrum (%)
		IS (mm s^{-1})	W (mm s^{-1})	Area of spectrum (%)			
1	2b	0.32	1.40	25		$SnCl_4 \cdot n\ H_2O$	30
		1.91	1.40	33	0.90	$PtSn_4$	25
		2.76	1.40	16			
		4.26	1.05	26		Sn(OH, Cl)$_2$	45
2	4b	1.70	1.10	31			
		1.85	2.15	32	0.85	PtSn	30
		4.18	1.00	37		SnO	70

3. *Chlorination and Rehydrogenation*

After the reduction by hydrogen as usual, the catalysts were cooled to room temperature and a flow of argon containing 15 vol% CCl_4 was established. The temperature was then raised to 200°C and maintained at this value for 1 h. After this treatment, CCl_4 was removed by purging with argon while cooling to room temperature, at which point the NGR spectra were recorded (Figures 3a, 5b, and 6b). The resulting characterizations are reported in Table 4.

It appears that all three catalysts underwent almost total oxidation to Sn(IV). The attribution of the lines to different species was achieved by considering the values of $A/A(SnO_2)$, chiefly that of catalyst No. 3 which clearly shows a low Lamb–Mössbauer factor for $SnCl_4 \cdot n\ H_2O$.

The catalysts were then reduced in the same conditions as for their preparation. The resulting spectra in hydrogen at room temperature are those of Figures 3b, 5c, and 6c, and their interpretation is given in Table 5. The comparison with the corresponding states of the catalysts before chlorination (see Table 2) results in some small changes, as follows.

Catalyst No. 1. From the composition of the spectra and the low value of the Lamb–Mössbauer factor of $SnCl_4 \cdot n\ H_2O$ (see above, this section), it can be concluded that the amount of Sn(IV) did not vary significantly. A small quantity of Sn(II) appeared. The composition of the recovered alloy differs slightly from that of

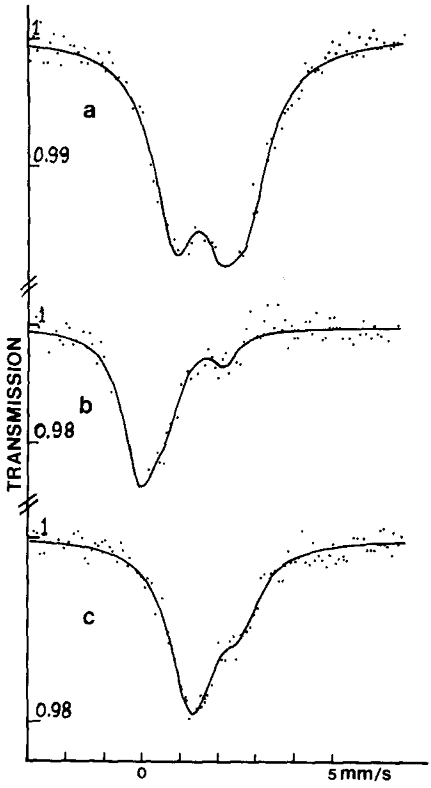

FIG. 5. Mössbauer spectra of Pt 0.95–Sn 0.55/Al_2O_3: (a) reduced, (b) chlorinated, (c) rehydrogenated.

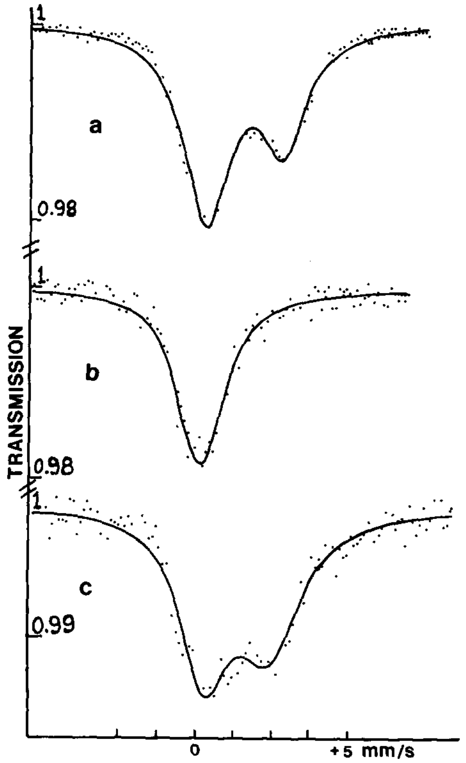

FIG. 6. Mössbauer spectra of Pt 0.5–Sn 0.2/Al_2O_3: (a) reduced, (b) chlorinated, (c) rehydrogenated.

$PtSn_4$, and PtSn disappeared, implying a release of free platinum.

Catalyst No. 2. The occurrence of Pt_3Sn and $PtSn_2$ instead of Pt : Sn 85 : 15 and PtSn implies that a significant amount of platinum was released.

Catalyst No. 3. This shows the reverse effect, since the degree of reduction and the concentration of platinum in the recovered alloy were increased.

DISCUSSION

1. NGR Parameters and Dispersion of the Components

The Lamb–Mössbauer factor of SnO_2, the only tin compound present in the solids before reduction, was found to be of the same order as that for bulk tin dioxide. As revealed by the values of $A/A(SnO_2)$, those of the alloys and ionic species, even highly dispersed, appear close to their bulk values also. This means that the corresponding solid particles were strongly bound to alumina (*22*). The Lamb–Mössbauer factor at room temperature of $SnCl_4 \cdot n\ H_2O$ in these catalysts, calculated from spectrum 6b and the result of its fit (Table 4), is about 0.28 that of SnO_2.

Quadrupole splittings are increased by dispersion, as can be seen in several cases here: PtSn in reduced catalysts (spectra 2a and 4a), $PtSn_4$ remaining after oxidation induced by desorption (2b), SnO in reduced (4a) or desorbed (4b) catalyst. As also evidenced in (*14*), an anisotropy of the Lamb–Mössbauer factor near surfaces (Karyagin–Goldanskii Effect, KGE) appears for highly dispersed phases. The most striking case is that of the reduced catalyst No. 2 (5a),

TABLE 4

Mössbauer Parameters and Composition of the Chlorinated Catalysts

Catalyst No.	Figure	Lines			$A/A(SnO_2)$	Main Sn species	Area of spectrum (%)
		IS (mm s^{-1})	*W* (mm s^{-1})	Area of spectrum (%)			
1	3a	0.09	1.00	34	0.14	$SnCl_4 \cdot n\ H_2O$	85
		0.53	1.40	48			
		2.46	1.20	18		Pt : Sn 10 : 90	15
2	5b	0.03	1.05	59	0.73	SnO_2	60
		0.69	1.10	33		H_2SnCl_6	30
		2.30	0.70	8		$PtSn_4$	10
3	6b	0.25	1.50	100	0.14	$SnCl_4 \cdot n\ H_2O$	100

TABLE 5

Mössbauer Parameters and Composition of the Rehydrogenated Catalysts

Catalyst No.	Figure	Lines			$A/A(SnO_2)$	Main Sn species	Area of spectrum (%)
		IS (mm s^{-1})	*W* (mm s^{-1})	Area of spectrum (%)			
1	3b	0.33	1.40	30	0.52	$SnCl_4 \cdot n\ H_2O$	30
		1.16	0.80	9		$Sn(OH, Cl)_2$	15
		2.45	1.80	57		Pt : Sn 10 : 90	55
		4.17	0.80	4			
2	5c	1.48	1.40	75	0.62	Pt_3Sn	60
		2.70	1.30	25		$PtSn_2$	40
3	6c	0.35	1.50	47	0.20	$SnCl_4 \cdot n\ H_2O$	47
		2.01	2.00	53		Pt_2Sn_3	53

where the two alloys exhibit rather large KGE, therefore existing as very small particles.

2. *Reduced Catalysts*

The three reduced catalysts (see Table 2) contain platinum–tin alloys. Several features of the system clearly depend on the platinum and tin concentrations, namely, the amount of free platinum, composition, dispersion and amount of the alloys, and the nature and oxidation state of the other tin compounds.

As for the latter it can be seen that at platinum content 0.5% some Sn(IV) chlorinated species remain, involving the major part of tin atoms of catalyst No. 3 and together with Sn(II) in some cases for catalyst No. 1. At 1% Pt and 0.5% Sn, only Sn(II) appears when ionic species is present.

Taking into account the Lamb–Mössbauer factors of the alloys (*19, 20*), SnO (*21*), and $SnCl_4 \cdot n\ H_2O$ (from the spectrum 6b), it is possible to calculate the degrees of reduction of tin. For catalyst No. 1 it is 75% (spectrum 2a) or 50% (some others), for No. 2 100% (5a) or 70% (4a), and for No. 3 40%. There are some discrepancies with the values obtained by volumetric measurements (Table 1). The most important is that the NGR spectra of calcined samples of catalysts No. 1 and 2 gave the same results as the corresponding noncalcined ones, contrary to the lower degrees of reduction found in volumetric measurements, mainly for catalyst No. 2. All these results lead to the statement that reduction is not very reproducible and that a water effect can be expected if this product is not rather quickly extracted.

3. *Desorption of Hydrogen and Subsequent Adsorptions of Oxygen and Hydrogen*

The oxidation of Sn that appeared when hydrogen was desorbed should be compared with the behavior of Fe/MgO (*23, 24*), Fe/Al_2O_3, and the latter modified by K, Mo, or Mn (*25*). The occurrence of a redox equilibrium, as indicated by NGR, magnetism, infrared, and thermodesorption results, now appears as more general when an oxidizable metal Me is used. It can be written:

$$Me + n\ H^+ \rightleftarrows Me^{n+} + \frac{n}{2}\ H_2$$

and explained by a complex mechanism involving basic sites of the support.

Two main inferences can be drawn from this effect. (I) Alumina is modified by the interaction of hydrogen with the catalysts, and the protons which it retains could be active species in the catalytic reaction of hydrocarbons with hydrogen. (II) The studies of this system in which a desorption of hydrogen is carried out probably suffer some error where the oxidation state of tin is concerned (*9*).

At least for catalyst No. 2 many more than surface Sn^0 atoms underwent oxidation during the desorption of hydrogen and sheltered the underlying ones, since an introduction of hydrogen at room temperature after this treatment did not recover Sn^0. Therefore in adsorption at room temperature of oxygen or hydrogen after desorbing the latter, only platinum atoms are involved and the conclusions concerning the behaviour of platinum proposed from such studies remain quite valid (*15*).

4. *Comparison between the Composition of the Reduced Catalysts and Their Activity in Hydrogenation of Benzene and Conversion of n-Heptane*

The activities of these solids in reactions of hydrocarbons with hydrogen were studied in a wider range of platinum and tin contents (*11*).

For benzene hydrogenation at 100°C, representative of the activity of platinum, the turn-over numbers were calculated using measurements of platinum dispersion (*15*). In the case of platinum alone at concentrations from 0.2 to 2% they range from 900 to 1100 (mole/atom Pt) h^{-1}. Any tin content results in a decrease, down to a value close to 150 in most cases, such as for the composition of the present catalysts No. 2 and 3, and about zero for a composition Pt 0.68–Sn 0.5 near that of the present catalyst No. 1. This means that the platinum atoms which alloyed with tin probably lost activity. As seen from the isomer shifts of alloys, the 5*s* electrons of tin are partly given to the platinum 5*d* band. An adsorption of hydrogen is still possible but not that of benzene or of both reagents in a configuration suitable for achieving hydrogenation. Besides, such low values of the turn-over number associated with rather high amounts of probably nonalloyed platinum ensure that the latter is not fully available for the reaction. It cannot be excluded either that a small part of the tin contributes a dilute solid solution in platinum, or that some amount of tin is alloyed to platinum inside very small particles having a low Lamb–Mössbauer factor. However, it is also possible that tin ions induce some electronic change in neighbouring platinum atoms, as recently stated from ESCA studies (*26*, *27*).

The conversion of *n*-heptane was studied at 500 and 400°C. At the higher temperature the differences between Pt and Pt–Sn catalysts, for any composition, were a decrease of cracking, by a factor of about 2 and an increase of isomerization and cyclization by some tens of percent. As only small changes of the activities were recorded when the platinum surface area showed a threefold increase, the reaction is bifunctionally catalyzed and the acidic function controls the overall process. At 400°C, a temperature at which cyclization proceeds partly on the metal and partly on the support, cracking decreased and all the activity of the support and part of that of platinum for cyclization were cancelled by some addition of tin. Furthermore, the ESR signal of perylene cations on the Pt–Sn catalysts did not appear. These effects are consistent with a poisoning of the strong acidic sites of alumina by tin ionic species, whose amounts and oxidation states are shown here by the Mössbauer spectra. The activities were restored at 500°C as an effect of the role of weaker acidic sites.

The diminution of cracking, probably as a consequence of alloying, accounts for the resistance of these catalysts to deactivation.

5. *Chlorination and Rehydrogenation Runs*

As presented in Section 3 of Results, these treatments induced some changes in the compositions of the three catalysts, with respect to amounts and compositions of alloys, amounts of free platinum, and amounts and nature of ionic species. Each of these modifications can contribute to changes in catalytic activity to some extent, as results from the discussion in the preceding section.

CONCLUSION

The quantitative analysis of the Mössbauer spectra appears to be an efficient means for a good characterization of all the tin species, taking into account the special features of NGR parameters arising from the small particle size. The use of several platinum and tin concentrations enabled us to understand the structure and reactivity of the Pt–Sn/Al_2O_3 system better than the study of only one catalyst would have allowed, although it would be convenient to extend this work to a wider range of compositions.

In their activated state, the three catalysts, two of which have platinum and tin contents close to those of industrial catalysts, exhibited rather large amounts of Pt–Sn alloys, Sn(IV) and Sn(II) ionic species, and rather high contents of probably nonalloyed platinum. Insofar as the compositions do not vary significantly during reactions, they explain the behavior of these catalysts rather well. Alloying accounts for the decrease in catalytic activity related to platinum. If a part of the platinum is not alloyed, its activity is also inhibited, probably due to an electronic effect of tin ions. In particular, such effects on cracking can explain the resistance of these solids to deactivation. Tin ions poison the strong acidic sites of alumina, thus inhibiting the reactions which the latter catalyze. The corresponding activity is recovered at higher temperature, where weaker acidic sites of the support can be used.

Evidence for the participation of alumina in the mechanism of reactions involving hydrogen is given by the oxidation of tin induced by its desorption. Moreover, this effect must be taken into acount in studies of subsequent adsorptions or reactions.

Sequences of chlorination and hydrogenation modify the compositions of the catalysts in different ways depending on the platinum and tin contents.

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