JOURNAL OF CATALYSIS **128**, 1–12 (1991)

Alloy Formation in Supported Pt–Sn Catalysts: Mössbauer Studies

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Received March 2, 1990; revised August 8, 1990

A series of materials that contained 1 wt% Pt and Pt : Sn atomic ratios varying from 1 : 1 to 1 : 8 were prepared. These metals were supported on alumina (100 or 250 m^2/g) or silica (700 m^2/g). For both alumina supports, the fraction of Pt that was present in an alloy increased with increasing tin content; the data are consistent with, but do not require, an alloy with a composition of PtSn. For these materials, zero valent tin is more easily obtained following reduction in hydrogen when silica is used as the support. Mössbauer data alone indicate that an alloy richer in Sn than PtSn is present on the silica support; however, Mössbauer data combined with XRD data indicate that a PtSn alloy is formed with additional tin being in a "metallic" state.

INTRODUCTION

The introduction of the Pt–Re–alumina bimetallic catalyst (*1*) revolutionized naphtha reforming much as the introduction of Pt–alumina had done about 25 years earlier (*2*). The bimetallic catalyst was exceptional in its aging resistance. Several roles for the second metal were introduced (*3*). A widely accepted view was that the two metals were present as an alloy. While Pt–Re was the metal combination that received the initial widespread industrial acceptance, other combinations were used. Pt–Sn was introduced soon after Pt–Re but did not receive widespread attention until recently, when continuous regeneration processes were introduced for naphtha reforming. This lower pressure, continuous regeneration process demands that it be possible to introduce the regenerated catalyst into the reaction zone without special pretreatment. Thus, the Pt–Sn combination is now receiving renewed attention for use in commercial units.

The Pt–Sn combination was widely studied even though it was not initially the catalyst of choice for commercial application. Early work using temperature-programmed reduction (TPR) was inconclusive; for example, some contended that tin was not reduced to the zero valent state (*4, 5*) while others contended that Sn^0 was formed and that it alloyed with Pt (*6–8*).

TPR is an indirect method for examining the state of Sn in a catalytic material. Techniques are available to examine the surface region directly. Initial studies using electron spectroscopy for chemical analysis (ESCA, XPS) provided data to support the view that tin was present only in an oxidized state (*9–11*); however, later work by one of these groups showed that Sn^0 was observed in an instrument with an oxygen environment lower than that in the earlier instrument (*12, 13*). Hoflund and co-workers have utilized XPS, ion-scattering spectroscopy (ISS), and angle-resolved Auger electron spectroscopy (ARAES) to examine the effect of reduction and annealing conditions upon the state of tin in unsupported alloys and for platinum on tin oxide (for example, (*14–16*). These results were consistent with the formation of zero valent tin and the formation of platinum–tin alloy following reduction. While the XPS technique permits one to examine the system directly, the approach is a surface sensitive technique.

Pt–Sn catalysts have also been examined

0021-9517/91 $3.00

by techniques that represent a diagnostic of the bulk structure. NEXAFS and EXAFS have been used to study (*17, 18*) alumina and silica supported catalysts, each containing 1 wt% Pt but with variable tin content to range from Pt : Sn ratios of 1 : 1 to 1 : 9. The studies clearly revealed differences between the two supports for the Pt atoms, but less so for tin. A radial distribution peak could be assigned to Pt–Sn scattering, but this by itself is not sufficient to demonstrate the development of alloy clusters upon reduction. These catalysts were prepared by impregnation from an acetone solution to minimize hydrolysis of the tin compound.

Meitzner *et al.* (*6*) utilized EXAFS to study a Pt–Sn–SiO_2 catalyst prepared by impregnation and a Pt–Sn–Al_2O_3 catalyst. The Pt–Sn–Al_2O_3 material was obtained by first preparing an alumina hydrogel so that a small amount of tin was uniformly dispersed throughout the material; platinum was then added by impregnation with chloroplatinic acid. According to these authors, Pt is more highly dispersed on the Sn containing support than on alumina alone even though hydrogen chemisorption indicated that essentially all Pt atoms in both catalysts were surface atoms. Furthermore, Pt in Pt–Sn–Al_2O_3 is more electron deficient than Pt in Pt–SiO_2 or Pt–Sn–SiO_2. To these authors, it was most reasonable to conclude that the EXAFS data indicated that the catalyst is essentially one with platinum clusters on alumina containing Sn^{2+} at the surface.

Another bulk characterization technique is X-ray diffraction. The *in situ* technique has been utilized to examine Pt–Sn–Al_2O_3 catalysts (*7*). For catalysts prepared from the complex $[Pt_3Sn_8Cl_{20}[^{2-}$, a Pt : Sn = 1 : 1 alloy, and no other alloy, was observed for catalysts containing either 0.6 or 5 wt% Pt. In another XRD study (*8*), it was observed that only one form of Pt could be detected in a series of catalysts containing 1 wt% Pt and increasing amounts of Sn to give Pt : Sn ratios from 1 : 1 to 1 : 10; in all of these samples the alloyed Pt was present as Pt : Sn = 1 : 1.

^{119}Sn Mössbauer data also provide a bulk diagnostic and this method has been utilized in a number of studies (for example, (*19–34*). Direct evidence for PtSn alloy formation has been obtained from Mössbauer studies (e.g., (*22, 29, 30, 33, 34*); however, many of these studies were at high metal loadings and even then such a complex spectrum was obtained that there was some uncertainty in assigning Sn^0 to the exclusion of tin oxide phases. Mössbauer results clearly show changes upon reduction in hydrogen but the width of the peaks for the reduced sample prevents, in general, a specific assignment for some states of tin. This is exemplified by the results of Kuznetsov *et al.* (*29*), who reported that for samples prepared by conventional impregnation techniques Pt–Sn–γ-Al_2O_3 catalysts are multicomponent; that is, they have highly dispersed species that are a result of chemical interactions of Sn^{4+}, Sn^{2+}, and Sn^0 with both support surface and Pt. Pt, according to these authors, forms nearly all possible alloys with Sn.

In view of the inability to define the Pt–Sn–Al_2O_3 catalyst using any single experimental approach, we have utilized Mössbauer spectroscopy to examine a series of supported Pt–Sn catalysts that have been characterized using other techniques (*7, 11, 12, 17, 18*).

EXPERIMENTAL

1. *Catalyst*

The supports chosen for the preparation of the catalysts were United Catalyst Inc. (UCI) Al_2O_3 with a surface area of 250 M^2/g, Degussa Aluminum Oxide C with a surface area of 110 m^2/g, and Davison SiO_2 with a surface area of 700 m^2/g. Each 5 g of the support was impregnated with 20 ml acetone solution which contained the amount of H_2PtCl_6 and $SnCl_2 \cdot 2H_2O$ required to produce a material containing 1 wt% Pt and the desired Pt : Sn ratio. During the preparation, the slurry was continuously stirred. The impregnated catalyst was dried at room temperature for 2 hr, then at 120°C overnight.

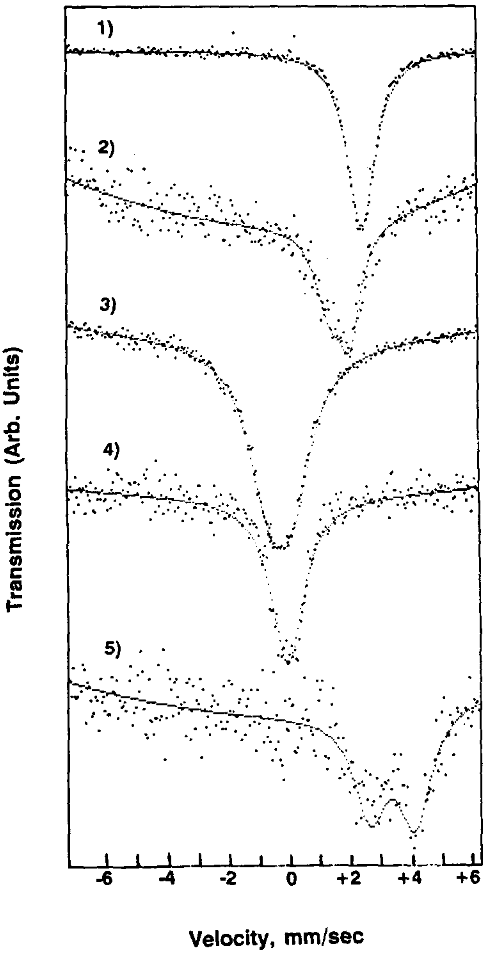

FIG. 1. ^{119}Sn Mössbauer spectra recorded at room temperature for some standard materials: (1) Sn metal, (2) PtSn alloy, (3) SnO_2, (4) $SnCl_4 \cdot 5H_2O$, and (5) $SnCl_2 \cdot 2H_2O$.

For reference, Mössbauer spectra of some standards (SnO_2, $SnCl_4 \cdot 5H_2O$, $SnCl_2 \cdot 2H_2O$, Sn metal, and a PtSn alloy; hydrate compositions are given but it is realized that they are approximate) were also obtained. For other tin compounds considered below, published parameters were utilized (*23, 30, 35, 36*).

RESULTS AND DISCUSSION

1. Spectra of Standards

TABLE 2

Mössbauer Parameters of Standards

Sample	Isomer shift (IS)[a] (mm/sec)	Quadrupole splitting (QS) (mm/sec)	FWHM (W) (mm/sec)
Sn metal	2.55	0	0.57
PtSn alloy	1.84	0.68	0.59
SnO_2	0.03	0.73	0.81
$SnCl_4 \cdot 5H_2O$[b]	0.16	0.11	0.62
$SnCl_2 \cdot 2H_2O$[b]	3.41	1.40	0.68

[a] With respect to Ca $^{119}SnO_3$.

[b] Ground together with alumina.

Mössbauer spectra obtained at room temperature for standards are shown in Fig. 1, and their Mössbauer parameters are listed in Table 2. It is observed that it is easy to distinguish, using these spectra, among the standards we examined by using the isomer shift (IS), quadrupole splitting (QS), and full width at half-maximum (FWHM) linewidth (W). Generally, the IS values for Sn^{4+} species, including the oxide and chloride, are less than 1.0 mm/sec; values for Sn^{2+} species, including the oxide and chloride, are in the range of 3.0–3.8 mm/sec. The IS value for metal is about 2.55 mm/sec and the IS values for Pt/Sn alloys are less than 2.55 mm/sec but larger than 1.0 mm/sec. Thus, the IS is a very important Mössbauer parameter for clearly identifying the valence state of Sn even if it is not possible to identify a specific compound. Other features were observed; that is, the doublets both for the PtSn alloy and for $SnCl_2$ have peaks of unequal intensities. The ratio of the two peaks is about 0.88 and 0.95 for these two compounds, respectively. Usually the peak located at the lower velocity is smaller. SnO_2 and $SnCl_4 \cdot 5H_2O$ have quite different QS and W (Fig. 1). SnO_2 has a QS of 0.73 mm/sec and a W of 0.81 mm/sec, but the QS of $SnCl_4$ is only 0.11 mm/sec and its W is 0.62 mm/sec.

The tin chloride "standards" were obtained by mixing either $SnCl_2 \cdot 2H_2O$ or $SnCl_4 \cdot 5H_2O$ with calcined alumina (ca. 1 : 3 weight ratio) and grinding the two together using a mortar and pestle. It is realized that these specific compounds will most likely not be present on the support catalysts; however, it is anticipated that there should

TABLE 1

Identification of the Catalysts Used in this Study

Catalyst	Support	Pt : Sn mole ratio
HA-1	Al_2O_3 (250 m^2/g)	1 : 1
HA-2.7		1 : 2.7
HA-5		1 : 5
HA-8		1 : 8
LA-1	Al_2O_3 (110 m^2/g)	1 : 1
LA-2.7		1 : 2.7
LA-5		1 : 5
LA-8		1 : 8
Si-1	SiO_2 (700 m^2/g)	1 : 1
Si-2.7		1 : 2.7
Si-5		1 : 5
CP-1	Al_2O_3 (250 m^2/g)	1 : 1.7

Note. All catalysts were obtained by H_2PtCl_6-$SnCl_2 \cdot 2H_2O$ impregnation except catalyst CP-1, which was obtained by impregnation with H_2PtCl_6. All materials contained 1 wt% Pt.

The dried material exhibited a bright red or dark red color, indicative of Pt–Sn–Cl complexes. Calcination of the catalyst in air was carried out at 500°C for at least 4 hr. The reduced catalysts were obtained under flowing H_2 (flow rate: 120 ml/min) at 500°C for 4 hr.

For all catalysts, the Pt loading was 1 wt%. Samples with a range of Pt : Sn ratios were prepared for this Mössbauer study: 1 : 1, 1 : 2.7, 1 : 5, and 1 : 8 (mole ratio of Pt : Sn). The catalysts used in this study are listed in Table 1. For comparison, a Pt–Sn–Al_2O_3 catalyst was also prepared by a coprecipitation method (1 wt% Pt and 1 wt% Sn). Aluminum and tin were precipitated as the hydroxide, washed, dried, and calcined at 550°C, and then impregnated with aqueous chloroplatinic acid (CP-1 in Table 1).

2. *Mössbauer Measurement*

The Mössbauer measurements utilized a Ranger MS-1200 spectrometer. The source was 10 mCi $Ca^{119}SnO_3$ (Amarsham). A laser device was used for velocity calibration. An IBM PC/XT was used to control the spectrometer and to store the data. The spectrum analysis was also performed on the PC using a modified version of a program provided by Ranger Scientific Inc.

All Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. For each peak, or multiplet of peaks, the parameters (IS, QS, and FWHM) of appropriate compounds, selected from Table 1 and the literature (*23, 30, 35, 36*) on the basis of potential match of isomer shift, were input. The program uses the input parameters as a first approximation to fit the experimental curve; successive iterations adjust the input parameters to provide a better fit to the experimentally generated data. The data in Tables 3–7 are the parameters that correspond to a good fit of the calculated curve (solid line in the figures) to the experimental data (points in the figures). Deconvolution of the calculated curves provides a measure of the relative areas corresponding to each chemical species of tin; the relative area is related to the fraction of each chemical species.

The reader should realize that it is not possible to make a positive identification of all of the chemical species in a material as complex as a Pt–Sn–Al_2O_3 catalyst. In the tables of data we have made an assignment for the tin chemical species on the basis of input data; thus, we list, for example, $SnCl_4$, even though the input data correspond to the hydrated compound $SnCl_4 \cdot 5H_2O$. Under Results and Discussion we refer to specific compounds and realize that the tin species is present in a state that resembles the particular compound, but may not have that precise chemical structure.

For the reduced sample, an argon-filled sealed holder containing a 450 mg sample was mounted on the instrument. Reduction was effected in flowing hydrogen at 500°C for 4 hr or more. Sample transfer was carried out in a glove box. To decrease X rays from the source, a piece of Pd foil, 0.05 mm thick, was placed in front of the sample.

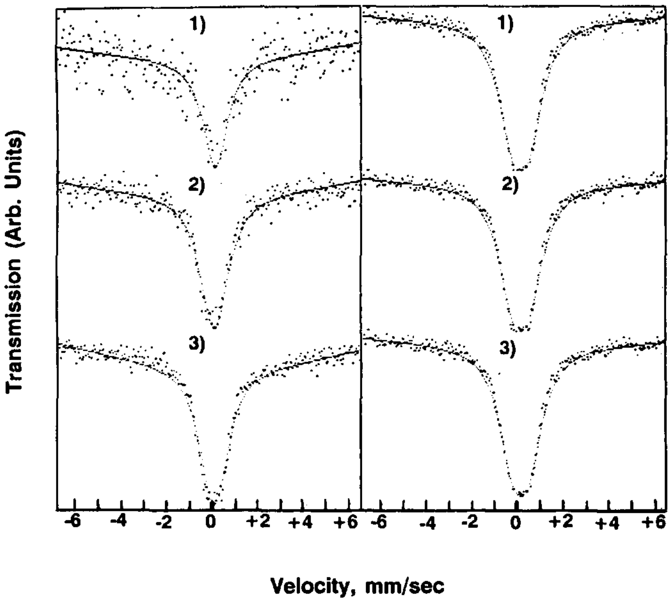

FIG. 2. ^{119}Sn Mössbauer spectra for materials after drying (left) and calcination (right): (top) catalyst HA-5, (middle) catalyst LA-5, and (bottom) catalyst Si-5.

be reasonable qualitative agreement between a spectrum corresponding to the physical mixture and that of the compound in a catalyst. The difference in IS for Sn metal (β phase) and PtSn alloy is obvious. Input of the Mössbauer parameters for these standards and literature data, fitting the spectral data for the catalysts used in this study, was accomplished.

2. *Dried, Calcined Catalysts*

Representative spectra for Pt–Sn–Al_2O_3 (250 m^2/g), Pt–Sn–Al_2O_3 (110 m^2/g), and Pt–Sn–SiO_2 (700 m^2/g) are shown in Fig. 2 and the calculated Mössbauer parameters are listed in Table 3. With the alumina support, tin oxides form during the drying step. It appears that the ease of tin oxide formation increases with increasing surface area. For SiO_2 as the support, the Sn is present as tin chlorides.

Following calcination, the Sn is mostly converted to tin oxides for both support materials; representative spectra for the calcined materials are also shown in Fig. 2, and Mössbauer parameters are also listed in Table 3. Compared with the spectra of the dried samples, the full width half-maximum of each calcined material is much broader. For the higher surface area alumina support some Sn is present as tin chloride even following calcination at 500°C in air. However, after calcination of catalyst CP-1 (prepared by coprecipitation), Sn is present only as the oxide. Here and elsewhere, we relate specific compounds to Mössbauer peak positions; however, it should be kept in mind that we are referring to compound-like materials; e.g., for SnO_2 we really mean SnO_2-like compound.

3. *Reduced Catalysts*

Figure 3 shows representative ^{119}Sn Mössbauer spectra for reduced Pt–Sn catalysts prepared by using an H_2PtCl_6–$SnCl_2 \cdot 2H_2O$ complex in acetone. The spectra show that several species are present in the catalysts; these include Sn^{4+}, Sn^{2+}, and Sn^0 chemical states. For the alumina support, SnO_2-like species are still present even after reduction at 500°C. The parameters obtained by computer fitting to the spectral

TABLE 3

Mössbauer Parameters for Different Catalysts After Drying and Calcination

Sample	Preparation stage	IS (mm/sec)	QS (mm/sec)	*W* (mm/sec)	Peak area (%)	Species[a] assigned
HA-5	Dried	0.03	0.76	0.73	54	SnO_2
		0.08	0.16	0.62	46	$SnCl_4$
LA-5	Dried	0.02	0.65	0.70	38	SnO_2
		0.04	0.11	0.65	62	$SnCl_4$
Si-5	Dried	0.04	0.10	0.62	100	$SnCl_4$
HA-5	Calcined	0.02	0.84	0.73	81	SnO_2
		0.05	0.27	0.62	19	$SnCl_4$
LA-5	Calcined	0.03	0.85	0.73	75	SnO_2
		0.04	0.25	0.62	25	$SnCl_4$
Si-5	Calcined	0.03	0.83	0.72	70	SnO_2
		0.05	0.27	0.63	30	$SnCl_4$
CP-1.7	Co precipitated	0.01	0.51	0.70	100	SnO_2

[a] Here and elsewhere, the specific compound is given. However, it is to be understood that, for example, SnO_2 is to be considered to be SnO_2-like and not necessarily the specific compound.

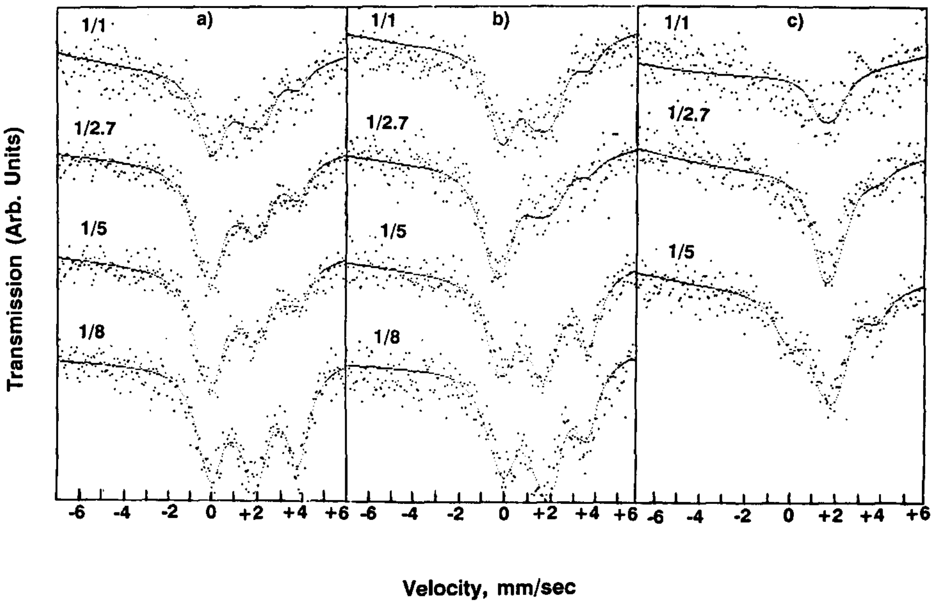

FIG. 3. ^{119}Sn Mössbauer spectra for reduced Pt–Sn catalysts: (a) Pt–Sn–Al_2O_3 (250 m^2/g), (b) Pt–Sn–Al_2O_3 (110 m^2/g), and (c) Pt–Sn–SiO_2 (700 m^2/g). (Pt : Sn mole ratios are indicated by the numbers shown in the figure.)

TABLE 4

Mössbauer Parameters for the Reduced Pt–Sn–Al_2O_3 (250 m_2/g) Catalysts

Sample	Parameter			Area (%)	Species[a] assigned
	IS (mm/sec)	QS (mm/sec)	*W* (mm/sec)		
HA-1	0.27	0.68	0.70	26	SnO_2
	0.27	0.14	0.62	25	$SnCl_4$
	1.95	0.51	0.62	24	PtSn
	2.58	0.00	0.54	5	Sn^0
	3.36	1.46	0.57	20	SnO or $SnCl_2$
HA-2.7	0.03	0.68	0.70	30	SnO_2
	0.21	0.11	0.62	24	$SnCl_4$
	1.83	0.62	0.62	16	PtSn
	2.56	0.00	0.51	2	Sn^0
	3.32	1.67	0.62	28	SnO or $SnCl_2$
HA-5	0.04	0.60	0.70	29	SnO_2
	0.27	0.10	0.62	24	$SnCl_4$
	1.80	0.68	0.62	15	PtSn
	2.58	0.00	0.51	4	Sn^0
	3.34	1.70	0.60	28	SnO or $SnCl_2$
HA-8	0.17	0.46	0.70	18	SnO_2
	0.27	0.08	0.62	16	$SnCl_4$
	1.75	0.68	0.62	8	PtSn
	2.57	0.00	0.51	2	Sn^0
	3.10	1.89	0.62	56	SnO or $SnCl_2$

[a] See footnote to Table 3.

data are listed in Tables 4, 5, and 6. An interesting observation is the presence of a doublet at IS = 1.75–1.95 mm/sec with QS = 0.51–0.78 mm/sec; it appears that for the Pt–Sn bimetallic catalysts prepared using the H_2PtCl_6–$SnCl_2 \cdot 2H_2O$–acetone complex, the PtSn alloy is readily formed. The presence of a PtSn alloy with the impregnated catalyst agrees with conclusions based on reported XRD results (*7, 8*). The Mössbauer spectra obtained for a coprecipitated Pt–Sn–Al_2O_3 catalyst after reduction show evidence for some alloy formation (Fig. 4 and Table 6). However, the portion of the peak that may be assigned to the alloy for the coprecipitated Pt–Sn–Al_2O_3 catalyst is located at IS = 1.25 mm/sec; this is much smaller value than is expected for a PtSn alloy. A similar peak position has been assigned to Pt_3Sn or $Pt_{85}Sn_{15}$ alloy (*16*). If this assignment of the 1.25-mm/sec IS peak is correct, the atom ratio in the alloy in a coprecipitated Pt–Sn–Al_2O_3 catalyst is different from that in the other Pt–Sn–alumina catalysts. In any event, the extent of alloy formation, if it does form, appears to be less for the coprecipitated catalyst than for the impregnated materials.

It is observed (Tables 4, 5, and 6) that the relative areas of the peaks depend on the support and the Pt : Sn ratio. Usually, the relative area of Sn present as the PtSn doublet decreases with an increase of the mole ratio of Sn : Pt. This is an apparent decrease in the amount of alloy. The amount of Pt is the same in all catalysts; hence, as the amount of Sn is increased it is possible for the amount of alloy to increase with increas-

TABLE 5

Mössbauer Parameters for the Reduced Pt-Sn-Al_2O_3 (110 m^2/g) Catalysts

Sample	Parameter			Area (%)	Species[a] assigned
	IS (mm/sec)	QS (mm/sec)	*W* (mm/sec)		
LA-1	0.23	0.76	0.70	24	SnO_2
	0.25	0.11	0.62	22	$SnCl_4$
	1.85	0.59	0.62	34	PtSn
	2.58	0.00	0.54	3	Sn^0
	3.37	1.46	0.57	17	SnO or $SnCl_2$
LA-2.7	0.41	0.78	0.70	38	SnO_2
	0.51	0.11	0.62	26	$SnCl_4$
	1.89	0.51	0.62	20	PtSn
	2.58	0.00	0.54	3	Sn^0
	3.40	1.38	0.57	12	SnO or $SnCl_2$
LA-5	0.31	0.78	0.70	18	SnO_2
	0.35	0.11	0.62	16	$SnCl_4$
	1.75	0.51	0.62	16	PtSn
	2.58	0.00	0.51	3	Sn^0
	3.32	1.38	0.62	47	SnO or $SnCl_2$
LA-8	0.32	0.81	0.70	19	SnO_2
	0.40	0.11	0.62	16	$SnCl_4$
	1.86	0.51	0.62	21	PtSn
	2.55	0.00	0.51	4	Sn^0
	3.23	1.59	0.62	40	SnO or $SnCl_2$

[a] See footnote to Table 3.

ing tin loading even though the fraction of Sn present as an alloy decreases. Using the fractional amount of Sn as the alloy, the total amount of tin present, and the Pt : Sn atomic ratio in the catalyst, we can calculate the percentage of tin that exhibits an IS = ca. 1.8 mm/sec, which has been assigned to the Pt : Sn = 1 : 1 alloy. The results for the two alumina supports, expressed as amount of PtSn alloy, are very similar (Fig. 5). The highest tin loading with the 110 m^2/g surface area deviates from this trend since it corresponds to ca. 168% PtSn, or an alloy of $PtSn_{1.68}$. It seems most likely that the deviation is caused by interactions of some of the tin with the low surface area alumina support to produce tin in a variety of species that appear in the background noise; any undetected tin will have the effect of making the calculated percentage of PtSn too high. For similar samples on the UCI high surface area alumina, we have observed only Pt : Sn = 1 : 1 alloy, and have not detected metallic tin by XRD (*8*).

The results of the silica support differ dramatically from those of the alumina supported materials. Essentially all of the tin appears in the doublet peak with an IS = ca. 1.75–1.95 mm/sec. For the lowest ratio of Pt : Sn, essentially all of the tin is detected only as a PtSn alloy. At higher Sn loadings on the silica support, half or more of the tin is present in an alloy form. The materials with the two higher tin loadings correspond, on the basis of the tin species distribution, to ca. 220% of PtSn; obviously a part of the

TABLE 6

Mössbauer Parameters for the Reduced Pt–Sn–SiO_2 and Coprecipitated Pt–Sn–Al_2O_3 Catalysts

Sample	Parameter			Area (%)	Species[a] assigned
	IS (mm/sec)	QS (mm/sec)	W (mm/sec)		
Si-1	1.85	0.68	0.62	100	PtSn
Si-2.7	1.81	0.54	0.62	82	PtSn
	2.56	0.00	0.54	4	Sn^0
	3.42	1.51	0.62	14	SnO or $SnCl_2$
Si-5	0.03	0.65	0.70	14	SnO_2
	0.21	0.11	0.62	9	$SnCl_4$
	1.76	0.59	0.62	44	PtSn
	2.56	0.00	0.54	9	Sn^0
	3.22	1.81	0.62	24	SnO or $SnCl_2$
CP-1.7	0.01	0.49	0.65	70	SnO_2
	1.11	0.78	0.65	19	Pt_xSn_y
	2.58	0.00	0.59	11	Sn^0

[a] See footnote to Table 3.

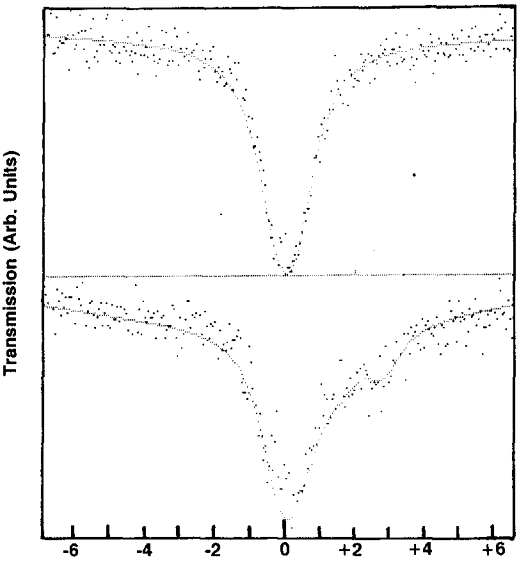

FIG. 4. ^{119}Sn Mössbauer spectrum (room temperature) for a coprecipitated Sn–Al_2O_3 impregnated with chloroplatinic acid following oxidation (top) and reduction (bottom).

tin must be present in a form other than as PtSn alloy for these higher tin loadings.

Bacaud *et al.* (*20*) report an IS at ca. 1.8 mm/sec for the α phase of tin and a value of ca. 2.6 mm/sec for β-Sn. The IS for tin in the Pt–Sn–SiO_2 catalyst is 2.55 mm/sec. Bacaud *et al.* (*20*) report that the IS of tin becomes more positive as the PtSn alloy phase becomes richer in tin. Thus, if an alloy with Pt : Sn = 1 : 2.2 is present on the Pt–Sn–SiO_2 catalyst, the Mössbauer peak is expected to be located at about IS = 2.15 mm/sec (*23*), not at an IS of 1.75–1.95 mm/sec as we obtained.

We have detected metallic tin in the materials with the higher (Pt/Sn = 1 : 12) tin loadings (*37*) and Pt : Sn = 1 : 1 alloy by XRD, but no alloy with Pt : Sn = 1 : 2.2 was detected. Therefore, the Mössbauer spectra and XRD both indicate that such an alloy with Pt : Sn = 1 : 2.2, i.e., 220% of SnPt, is not possible on the silica supported Pt–Sn catalyst. The tin species with IS = 1.75–1.95 mm/sec is not all in the PtSn (1 : 1)

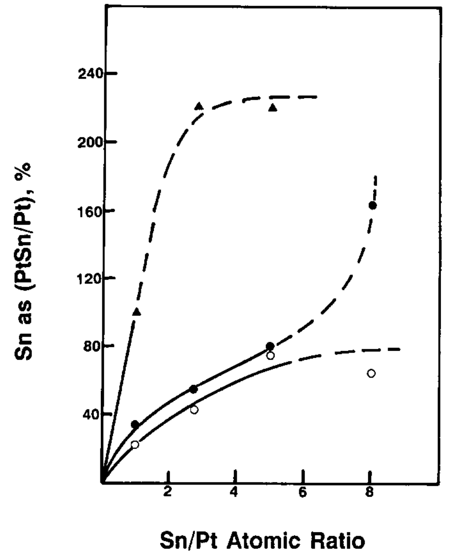

FIG. 5. Amount of tin calculated to be present as PtSn alloy versus tin : Pt ratio: ▲, silica support; ●, low surface area alumina support; ○, high surface area alumina support.

alloy, portions of such tin is in other environments. For metallic tin, with a melting point of ca. 230°C, to be retained in the catalyst bed at 500°C in flowing hydrogen, the metal must be retained in the small pores of the silica, which means there is a strong interaction between Sn metal and support silica or the Sn metal atom has a very different environment, and the Sn metal atoms could donate electrons to the support or to some groups on the support, which causes the IS to be decreased and overlap with peaks at 1.75–1.95 mm/sec.

Chloride, added in the compounds used in the impregnation step, is retained by all samples. It appears that following drying the relative fraction of tin present as a chloride is of the order high surface area alumina < low surface area alumina < high surface area silica. The fraction of tin present as chloride appears to be similar in a calcined catalyst and in the corresponding reduced catalyst. It is tempting to conclude that the alloy is formed from a tin oxide-like species with the tin chloride species undergoing little change during the reduction step; however, the data are insufficient to prove this point.

The data in Table 7 and Fig. 6 indicate that the PtSn alloy, once formed, is not readily oxidized at mild conditions. Thus, for samples that have been exposed to air at room temperature for ca. 24 hr there is little difference in the distribution of tin species from that of the corresponding reduced sample. Hence, bulk oxidation of the PtSn alloy appears to be reasonably slow at room temperature, as has been reported in several previous studies, even though our XPS data (*11–13*) indicate that surface reoxidation is rapid.

CONCLUSIONS

The present results are consistent with tin being present in both an alloy form and

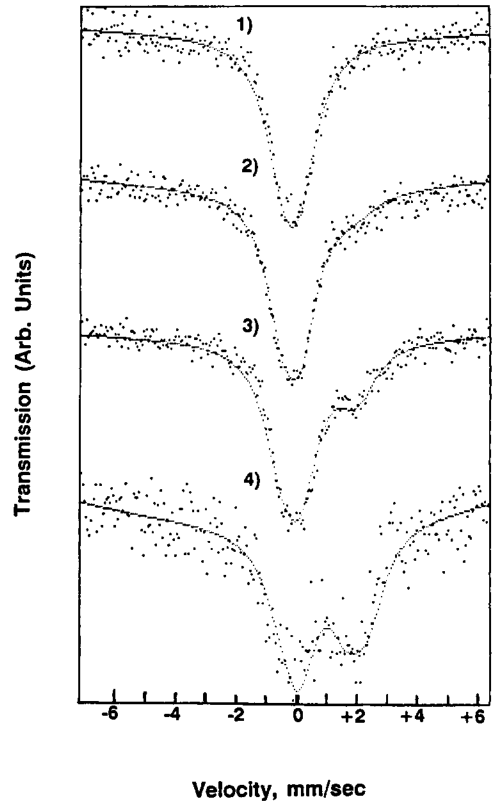

FIG. 6. The ^{119}Sn Mössbauer spectra for catalysts after reoxidation of reduced catalysts: (1) catalyst CP-1, (2) catalyst HA-5, (3) catalyst LA-5, and (4) catalyst Si-5.

TABLE 7

Mössbauer Parameters for the Representative Catalysts After Reoxidation in Air at Room Temperature

Sample	Parameter			Area (%)	Species[a] assigned
	IS (mm/sec)	QS (mm/sec)	W (mm/sec)		
CP-1.7	0.01	0.51	0.70	100	Sn^{4+} Oxides
HA-5	0.02	0.59	0.66	84	SnO_2
	0.17	0.11	0.62	8	$SnCl_4$
	1.87	0.59	0.62	8	PtSn
LA-5	0.03	0.70	0.70	65	SnO_2
	0.14	0.16	0.62	18	$SnCl_4$
	1.98	0.38	0.62	17	PtSn
Si-5	0.03	0.68	0.70	31	SnO_2
	0.17	0.11	0.62	24	$SnCl_4$
	1.90	0.57	0.62	38	PtSn
	2.57	0.00	0.54	7	Sn^0

[a] See footnote to Table 3.

oxidized forms when alumina is used as a support. For lower Sn : Pt ratios (5 or less) little difference is observed in the extent of alloy formation and the distribution of the oxidized species for a low and high surface area alumina support. In this respect, there is general agreement with data observed in the earlier Mössbauer studies described in the Introduction. The current data combined with XRD data for similar materials (*7, 8, 37*) lead us to conclude that the only significant alloy phase present is Pt : Sn = 1 : 1. Furthermore, both XRD and Mössbauer studies show a similar trend in the extent of alloy formation for the alumina supported materials; the fraction of Pt present in an alloy phase increases with increasing tin concentration and only approaches 100% alloy formation at Sn : Pt > ca. 5.

Pt–Sn supported on silica exhibits much different behavior than when it is supported on alumina. As has been observed by others (for example, Ref (*6*)) we find that it is much easier to reduce tin to the zero valent state when silica is used as the support. The XRD data (*37*) indicate that the only significant alloy is Pt : Sn = 1 and that at higher tin loadings β-tin is present. Mössbauer data indicate that a PtSn alloy is formed as well as a form of tin that has a very different environment than tin in pure metal.

For a coprecipitated tin oxide–alumina catalyst, we agree with an earlier report (*6*) that alloy formation occurs to a much smaller extent than it does on a material prepared by impregnation with the chloride complexes.

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