

## A Chemisorption and XPS Study of Bimetallic Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Catalysts

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Bimetallic Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts with nominally 1 wt% Pt and varying tin contents (0-3.25 wt%) prepared by coimpregnation of nonporous Degussa alumina were characterized by chemisorption of H<sub>2</sub>, O<sub>2</sub>, and CO at room temperature. The surface compositions and oxidation states of the reduced catalysts were tracked by XPS. Addition of tin to Pt resulted in significant differences in the gas uptake characteristics of the three adsorbates. Both H<sub>2</sub> and CO showed an initial increase in gas uptake with addition of small amounts of tin, and then the chemisorbed amount tended to drop off with further addition of tin. In the case of O<sub>2</sub> adsorption, there was a steady increase in gas uptake with increasing tin content. XPS of the reduced catalysts showed that in alumina-supported samples most of the tin was in a valence state of either Sn(II) or Sn(IV). On the other hand, large amounts of zero-valent tin were found in a SiO<sub>2</sub>-supported Pt-Sn catalyst which had been prepared from the same precursors and reduced under identical conditions. This supports the notion that interactions between the alumina support and tin prevent the complete reduction of tin. © 1991 Academic Press, Inc.

### INTRODUCTION

Bimetallic catalysts consisting of Pt as the primary metal and a second metal such as Re, Ir, or Sn dispersed on an alumina support are commonly used in reforming reactions in the petroleum industry. These catalysts help in achieving better activity maintenance and higher selectivity for catalyzing nondestructive hydrocarbon reactions as compared to the monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (1, 2). The oxidation state of the second metal after reduction and the possibility of alloy formation between the two dispersed metallic constituents is often a point of controversy and seems to depend on the catalyst preparation methods used (1). The nature of support used also can influence the extent of interaction between the two metallic components. An X-ray photoelectron spectroscopy (XPS) study of the state of Re in supported Re catalysts indicated that Re supported on SiO<sub>2</sub> is reduced to a greater extent than Re supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> probably due to greater interaction

effects between Re<sup>7+</sup> and the surface of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (3).

The Pt-Sn/Al<sub>2</sub>O<sub>3</sub> system has potential for use in catalyzing reforming reactions. In this system there is controversy as to the state of tin in these catalysts after reduction in hydrogen (4, 5). The solid solubility of Sn in Pt is limited to about 8.at.% while the solid solubility of Pt in Sn is negligible. The bulk phase diagram of the Pt-Sn system shows the existence of the following phases: Pt<sub>3</sub>Sn, PtSn, Pt<sub>2</sub>Sn<sub>3</sub>, PtSn<sub>2</sub>, and PtSn<sub>4</sub> (6). However, the interactions between Pt and Sn supported on alumina could be significantly different than in the bulk state mainly because of the presence of small metallic particles and due to interactions between tin and the support. Catalyst preparation techniques can also play a significant role in controlling the type of interactions that occur between tin and platinum and between tin and the support (7).

In this study, the effect of tin on the adsorptive behavior of platinum, and the oxidation state of the tin present on the surface

of the reduced catalysts, is explored for a series of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by conventional methods. The characterization tools used were room-temperature chemisorption of H<sub>2</sub>, O<sub>2</sub>, and CO, and X-ray photoelectron spectroscopy after *in situ* reduction treatment of the catalysts in a reactor directly attached to the spectrometer. A complementary study of the reaction behavior in *n*-hexane reactions and a detailed microstructural characterization by high resolution and analytical electron microscopy are published separately (8).

There have been some previous XPS studies on the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> system (9-14). Interestingly, two of the papers (9, 10) do not report any indication of Sn (0) from XPS after reduction of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts though the presence of small amounts of Sn (0) below the limit of detectability of XPS is not discounted. Four other publications (11-14) mention that XPS detected the presence of Sn (0) on reduction of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. It would be interesting to compare the pretreatment conditions and data obtained by these research groups to see if under certain conditions the reduction of tin to Sn (0) could be enhanced.

Sexton *et al.* (9) reduced their samples at 773 K under 0.5 atm of static hydrogen. They did not find Sn (0) in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts though on SiO<sub>2</sub>-supported Pt-Sn samples 25 to 48% of the tin was in zero-valent state after reduction. Adkins and Davis (10) performed their sample reduction under 1 atm of flowing hydrogen at 673 K. They too did not detect zero-valent tin in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. They also found from alcohol conversion reactions that a 10 wt% Sn/Al<sub>2</sub>O<sub>3</sub> catalyst did not act like a tin oxide containing catalyst though the XPS binding energy of the Sn 3*d* peaks matched that obtained for unsupported tin oxide. Hence they said that the tin in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst after reduction most likely forms a kind of tin-aluminate "egg-shell" structure which does not behave like tin oxide but influences the behavior of the Pt atoms in its vicinity leading to the different catalytic reaction behav-

ior characteristic of bimetallic catalysts as opposed to monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.

Li and Hsia (11) found that zero-valent tin could be detected by XPS on Pt-Sn/ $\eta$ -Al<sub>2</sub>O<sub>3</sub> catalysts prepared by using a Pt-Sn complex and by coimpregnation of the support by the traditional method, but in coprecipitated catalysts no Sn (0) was found suggesting a significant metal-support interaction between Sn (IV) and the alumina support which suppresses the reduction of tin (15). Baronetti *et al.* (12) used low loadings of metal in the bimetallic Pt-Sn catalysts with the Sn loading lying in the range 0.1-0.3 wt%. The catalyst samples were reduced before XPS data collection at 773 K under static hydrogen. They found no detectable Sn (0) in a 1.5 wt% Sn/Al<sub>2</sub>O<sub>3</sub> sample after H<sub>2</sub> treatment at 773 K. But in the bimetallic catalysts they found a significantly large shoulder on the Sn 3*d*<sub>5/2</sub> photoelectron peak. The main peak is due to Sn (II, IV) and the shoulder is attributed to Sn (0). But in their XPS plots, although there are distinct shoulders on the Sn 3*d*<sub>5/2</sub> peaks, there are no corresponding shoulders visible on the peaks shown in the spectra at higher binding energies, assuming that these belong to the Sn 3*d*<sub>3/2</sub> components of the spectra.

Davis and co-workers (13) used a 1.7-Pt-4.4 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst having a large loading of metal for their XPS experiments. The Pt-Sn catalyst was prepared by impregnating the support with a Pt-Sn complex in acetone. The samples were reduced *in situ* in the XPS reactor at a temperature of 648 K and a pressure of 2.5 bar. The researchers used spectral deconvolution to identify Sn (0) in the low-energy side of the large Sn 3*d*<sub>5/2</sub> peak and calculated that around 15% of Sn is present in the Sn (0) state in this catalyst in its reduced state and this Sn is probably in an alloyed form with Pt. A Pt-Sn complex instead of the traditional H<sub>2</sub>PtCl<sub>6</sub> and SnCl<sub>2</sub> precursors was used to impregnate the alumina. Pt-Sn complexes could lead to a closer interaction between Pt

and Sn during impregnation of the support and hence to some Sn(0) formation (12, 15, 16). Another possible reason for the formation of Sn (0) is that the pressure used for reducing the catalyst is 2.5 bar which is significantly larger than the pressures which other researchers have used for reducing their samples. This higher pressure could have led to complete reduction of some Sn to Sn (0).

Davis and co-workers (14), in their XPS study of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts reduced in flowing hydrogen (648 K, 2.5 bar, 2 h), found that there were large amounts of zero-valent tin in their samples (47–68% of the total amount of tin). They also found that this relatively large amount of zero-valent tin was present irrespective of the Pt/Sn atomic ratio. This could mean that as the Sn/Pt atomic ratio was increased, keeping the Pt loading constant at round 1 wt%, the amount of tin present in an alloy or solid solution with Pt increased. The authors also mention that the use of a cleaner system than earlier (10) was probably one of the reasons for observing zero-valent tin by XPS. Another reason could be that the higher than normal pressure used in the reduction process led to the formation of zero-valent tin. But it is clear from this work that under certain conditions significant amounts of zero-valent tin can be formed on reduced alumina-supported Pt-Sn catalysts.

#### EXPERIMENTAL

##### (a) Catalyst Preparation

The Pt-Sn catalysts were prepared by coimpregnation of Degussa nonporous fumed alumina having a BET surface area of 90 m<sup>2</sup>/g. Acetone was used as solvent for the precursors, H<sub>2</sub>PtCl<sub>6</sub> (Aldrich) and SnCl<sub>2</sub> (Aldrich). The nominal platinum loading was held constant at 1 wt%, and the tin loading was varied. In addition, a catalyst with significantly smaller chlorine content was prepared from the nonacidic precursors tetraamineplatinum (II) hydroxide hydrate (STREM) and tin (II) tartrate. After impregnation, the catalysts were dried at 393 K,

followed by calcination in air for 2 h at 773 K. After calcination, the catalysts were reduced for 5 h in flowing hydrogen at 673 K. The actual metal compositions and the chlorine contents of the catalysts before and after reduction were determined by neutron activation analysis. The samples were activated in the University of Michigan nuclear reactor and the radioactive decay counts were measured by using a Ge(Li) detector. A summary of the results of neutron activation is given in Table 1. The levels of chlorine found in the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from nonacidic, chlorine-free precursors can be attributed to the chlorine present in the alumina support. XPS analysis of the blank support (Table 3) showed that it contained a significant amount of chlorine.

##### (b) Chemisorption

Prior to chemisorption all samples were prereduced in a flow reactor in a stream of purified hydrogen at 673 K (15 ml/min). Then, 0.18 g of the prereduced samples were used for the chemisorption experiments which were performed in a static volumetric glass chemisorption system equipped with an oil diffusion pump and a mechanical pump to provide the necessary vacuum. Two liquid nitrogen traps were used to prevent backstreaming of pump oil into the vacuum system. Research grade gases were used for the static reduction and chemisorption. A Veeco ionization gauge was used for measuring gas pressures in the range of 10<sup>-3</sup> to 10<sup>-6</sup> Torr (1 Torr = 133.3 Pa) and on M.K.S. Baratron pressure gauge for the range of 0–1000 Torr. In the glass system, each sample was heated to 673 K under dynamic vacuum for outgassing purposes. Then 250 Torr of hydrogen was introduced into the sample loop at 673 K and the sample was reduced at this temperature for a total of 13 h under static hydrogen. After about 3 h of reduction, the sample loop was evacuated, and then a second dose of fresh hydrogen (250 Torr) was introduced for an additional 10 h of reduction at 673 K. After the

TABLE 1

Metal Loadings in the Pt-Sn Catalysts as Determined by Neutron Activation Analysis

Catalyst (nominal wt%)	Pretreatment	Component weight percent		
		Pt	Sn	Cl
1.0 Pt/Al <sub>2</sub> O <sub>3</sub>	Calcined	0.97	—	0.97
	Reduced	0.99	—	0.72
1.0 Pt-0.1 Sn/Al <sub>2</sub> O <sub>3</sub>	Calcined	0.96	0.13	1.35
	Reduced	0.96	0.14	0.97
1.0 Pt-0.5 Sn/Al <sub>2</sub> O <sub>3</sub>	Calcined	0.98	0.52	1.34
	Reduced	1.00	0.53	1.00
1.0 Pt-0.5 Sn/Al <sub>2</sub> O <sub>3</sub> (L.C.)	Calcined	0.85	0.54	0.35
	Reduced	0.92	0.58	0.38
1.0 Pt-1.0 Sn/Al <sub>2</sub> O <sub>3</sub>	Calcined	0.88	0.92	1.35
	Reduced	0.89	0.99	0.97
1.0 Pt-5.0 Sn/Al <sub>2</sub> O <sub>3</sub>	Calcined	0.90	3.26	1.93
	Reduced	0.94	3.25	0.48
2.0 Sn/Al <sub>2</sub> O <sub>3</sub>	Calcined	—	1.87	0.95
	Reduced	—	1.90	0.87

reduction the catalyst was evacuated at 693 K to remove adsorbed H<sub>2</sub>.

After the high-temperature evacuation the sample was cooled to room temperature under dynamic vacuum. Then chemisorption isotherms were collected using the following gases: hydrogen, oxygen, and CO. The advantages of using multiple adsorbates to probe the catalytic surface has been mentioned before (17). The chemisorption experiments for each gas consisted of measuring two isotherms. The first isotherm gave the total uptake of gas at room temperature. Subsequently, the sample was evacuated for 1 h at room temperature. A second isotherm was then obtained to determine the amount of weakly held gas removed from the surface during the evacuation. After collecting the two chemisorption isotherms for each adsorbate, the catalyst was reduced at 673 K and evacuated at 693 K.

Each isotherm consisted of seven data points. The equilibrium pressures were in the 0-12 Torr range. The technique of back-extrapolation of the linear portion of the isotherm to zero equilibrium pressure to determine the saturation uptake value was used. At the conclusion of the set of isotherms,

the dead space of the sample loop was measured by expanding a known amount of helium into the sample loop containing the catalyst. Chemisorption experiments were also conducted on the alumina support to assess the amount of H<sub>2</sub>, O<sub>2</sub>, and CO adsorbed on the blank support.

#### (c) X-ray Photoelectron Spectroscopy (XPS)

Before conducting the XPS analysis the samples were again reduced in an *in situ* reactor attached to the analysis chamber. Forks were used to insert and remove the sample holder containing the sample from the analysis chamber to the reaction chamber and vice versa so that the sample was not exposed to air at any time between the reduction and spectra collection. The samples were reduced *in situ* in flowing high purity carrier grade hydrogen at 673 K for 5 h at pressures close to 1 atm (1 atm = 1.013 × 10<sup>5</sup> Pa). A gas purifier (Oxisorb LP, M.G. Industries) was connected to the hydrogen line leading to the XPS reactor to further purify the hydrogen used for reduction. After the reduction, the samples were cooled to room temperature in flowing hy-

drogen. After room temperature was reached, the XPS reactor was evacuated with a turbomolecular pump, and the samples were removed from the reactor and reinserted into the analysis chamber.

Prior to detailed XPS studies a survey spectrum was collected in the range from 0 to 1200 eV. Then a detailed multiplex routine was run on all the regions of interest. We opted to use the Al anode instead of the Mg anode for the following reason: it was found that when the Mg anode was used, one of the satellites due to the O 1s peak (~531 eV) tended to fall close to where one would expect the Sn (0) 3d<sub>5/2</sub> peak (~484 eV). This satellite was of low intensity and if one were to use large loadings of tin in the samples, the peak would not play a significant role in the XPS spectrum. But if one were to use low loadings of tin, then this peak might be of significant intensity compared to the tin peak, causing error in the analysis of the Sn (0) peak.

We found that sample charging could shift the XPS peaks by 3 to 4 eV toward higher binding energies. To compensate for sample charging the charge neutralizer was turned on so that a stream of low-energy electrons would flood the sample. This had the effect of reducing the Al 2p binding energy to values closer to the reference binding energy though there was some sample charging still present (~1 eV) in some of the samples. Using low-energy electrons from an electron flood gun does not only allow correction of the peak positions for charging but gives the additional advantage of decreasing the peak broadening (18). It was found that in the case of the blank alumina the Al 2p peak was present at 74.6 eV after the charge neutralizer was turned on. It was decided to use this value as the reference binding energy to correct the XPS peak positions in all the other samples supported on alumina. Since the C 1s peak due to adventitious carbon in the samples can vary in position from 284.6 to 285.2 eV (19) it is probably more reliable to use the Al 2p peak for charge correction of photoelectron peak positions.

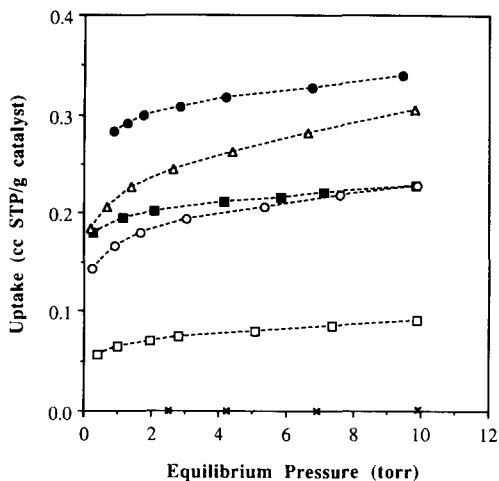


FIG. 1. Room-temperature hydrogen chemisorption isotherms for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series (total uptakes). (■) 1.0 Pt/Al<sub>2</sub>O<sub>3</sub>; (●) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>; (△) 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>; (○) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>; (□) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>; and (×) 2.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

The regions that were scanned in the multiplex routine were O 1s, Sn 3d, Pt 4d, C 1s, Cl 2p, Al 2s, and Al 2p. The primary Pt photoelectron peak the Pt 4f overlaps with the Al 2p peak (20), and hence we scanned for the Pt 4d and Al 2s to determine surface concentrations of Pt and Al, respectively, while the Al 2p was used to correct the peak positions for sample charging. High-resolution XPS data (0.1 eV/step, 17.90 eV pass energy) were collected on all the regions of interest for all the samples. The total collection time for all regions was 4 h. The take-off angle of the photoelectrons emitted from the sample was 45°. The pressure in the XPS spectrometer was better than 10<sup>-8</sup> Torr when collecting data (1 Torr = 133.3 Pa).

## RESULTS AND DISCUSSION

### (a) Chemisorption

Table 1 provides the information about the overall elemental composition of the catalysts as determined by neutron activation analysis. Figures 1, 2, and 3 show the isotherms obtained on the various catalysts at room temperature by using H<sub>2</sub>, O<sub>2</sub>, and CO, respectively, as adsorbate gases. A sum-

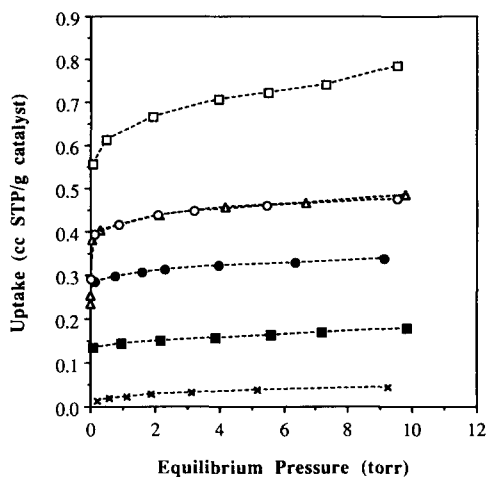


FIG. 2. Room-temperature oxygen chemisorption isotherms for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series (total uptakes). (■) 1.0 Pt-Al<sub>2</sub>O<sub>3</sub>; (●) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>; (△) 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>; (○) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>; (□) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>; and (×) 2.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

mary of the chemisorption results is provided in Table 2. We discuss the effect of tin on the adsorption of each adsorbate and compare how the behavior of each adsorbate is different from the other. Figure 4 shows the effect of tin on the uptake of H<sub>2</sub>, O<sub>2</sub>, and CO gas on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. The ordinate values are normalized in terms of H atoms or O atoms, or molecules of CO, respectively, adsorbed per atom of Pt in the catalyst as determined by neutron activation analysis. By doing this it is easier to observe the effect of tin on the adsorption uptake of the gases on the catalysts with varying tin contents. This does not however imply that tin cannot adsorb any of the gases at room temperature.

*1. Hydrogen.* From Fig. 1 and Table 2 it is seen that when small amounts of tin were added the hydrogen uptake increased from 0.200 cm<sup>3</sup> STP/g of catalyst for the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst to 0.300 cm<sup>3</sup> STP/g of catalyst for the 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. Further increase of the tin content caused a decline in the amount of adsorbed hydrogen. In the case of the 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, the total uptake fell to about

$\frac{1}{3}$  of that of the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The monometallic 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, in comparison with the 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, did not show significant hydrogen uptake. The larger hydrogen uptake of the two bimetallics with low tin loading (1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub> and 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>) as compared to the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst can be explained as follows: histograms derived from transmission electron microscopy indicated a preponderance of particles less than 1 nm in diameter in the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, while the monometallic Pt catalyst was dominated by 2-nm particles (8). This would indicate a higher Pt dispersion in the lower tin loading bimetallics as compared to the monometallic catalyst, and consequently justify a higher uptake of hydrogen. Whether or not small amounts of tin on the surface of these small Pt particles contribute to the enhanced hydrogen uptake cannot be determined. Although analytical microscopy indicated that these small particles with less than 1-nm

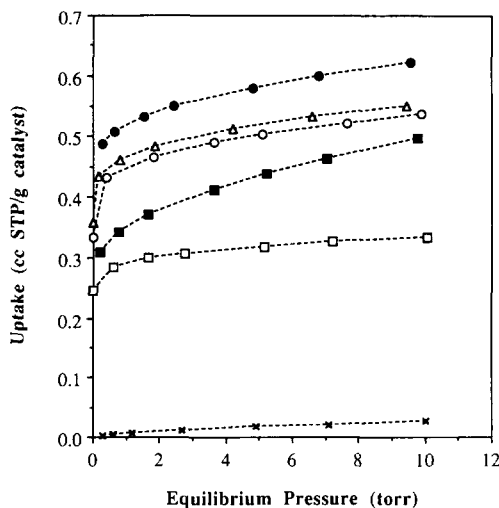


FIG. 3. Room-temperature CO chemisorption isotherms for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series (total uptakes). (■) 1.0 Pt-Al<sub>2</sub>O<sub>3</sub>; (●) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>; (△) 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub>; (○) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>; (□) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>; and (×) 2.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

TABLE 2  
 Catalyst Composition and Chemisorption Results

Catalyst Nominal wt%	Metal (wt%)	Sn (at.%)	Gas uptake (cc STP/g catalyst)					
			Hydrogen		Oxygen		CO	
			Total	%Weak	Total	%Weak	Total	%Weak
1.0 Pt	0.99	0	0.200	40	0.146	1	0.379	32
1.0 Pt-0.1 Sn	1.10	19	0.300	41	0.316	1	0.545	17
1.0 Pt-0.5 Sn	1.53	47	0.227	41	0.431	2	0.488	16
1.0 Pt-1.0 Sn	1.88	65	0.182	45	0.434	1	0.471	16
1.0 Pt-5.0 Sn	4.19	85	0.070	49	0.648	2	0.312	16
2.0 Sn	1.90	100			0.026	30	0.008	100
1.0 Pt-0.5 Sn (L.C.)	1.50	51	0.073	42	0.131	5	0.182	26

diameter consisted of either elemental Pt or both Pt and Sn, the exact nature of the Pt-Sn interaction could not be unequivocally determined (8). Tin could be forming bimetallic clusters with Pt, or form an alloy with Pt, or, as a third possibility, tin could be present in an ionic form stabilized by the alumina substrate in the immediate vicinity of Pt (8).

Upon adding more tin the total H<sub>2</sub> uptake tended to decrease with increasing tin content. Additionally, some decrease in hydrogen uptake could be caused by Sn enrichment to the surface of the catalyst because Sn, having a lower surface energy as compared to Pt, may tend to migrate to the surface of Pt-Sn ensembles and possibly cover the Pt surface, thereby decreasing the H<sub>2</sub> uptake. However, this hypothesis is not completely supported by the XPS data. No indication was found of surface enrichment of tin relative to platinum, except in case of the 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. Another possibility is that tin is firmly attached to the Al<sub>2</sub>O<sub>3</sub> support in form of Sn (II) ions and that Pt atoms are dispersed among the so-called tin-aluminate complex. One could envision a scenario where the distance between Pt atoms tends to increase as more tin is added. It is well known that hydrogen dissociately chemisorbs on Pt at room temperature requiring adjacent vacant surface

sites of Pt. With more and more tin being added fewer Pt ensembles capable to dissociate H<sub>2</sub> may be left. It is also possible that some Pt atoms may be covered by the tin-alumina matrix and are thereby rendered inaccessible for chemisorbing gases.

There have been contradictory results reported in literature concerning the effect of tin on the uptake of H<sub>2</sub> in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. In some cases, the uptake of H<sub>2</sub> has been used to calculate the dispersion of Pt

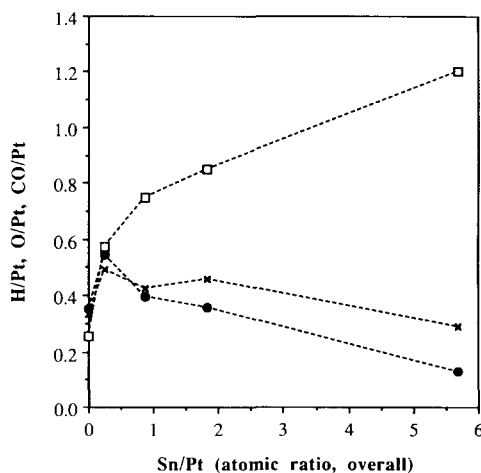


FIG. 4. Total gas uptake at room temperature versus overall tin content for catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series. (●) Hydrogen; (□) oxygen; and (×) CO.

in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, dispersion being defined to be equal to the  $H_a/Pt_t$  ratio. But it is our belief that one cannot obtain the dispersion of Pt in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts that simply, especially if tin modifies the Pt surface by either changing the chemisorption stoichiometry of an adsorbate on Pt, or by forming a Pt-Sn alloy which could chemisorb a gas in a different manner than pure Pt. Burch (21) found that tin increased the uptake of hydrogen in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. In this case, the uptake was measured as the amount of hydrogen adsorbed on cooling the catalyst from 960 K to 273 K in a 5% H<sub>2</sub>/Ar mixture. This increased uptake was attributed to the fact that tin did not allow small Pt particles to sinter. Burch determined by TPR experiments that the average oxidation state of tin was Sn (II). Muller *et al.* (22) titrated H<sub>2</sub> adsorbed at room temperature on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts with O<sub>2</sub> and came to the conclusion that with addition of tin there was more spillover of H<sub>2</sub> onto the Sn sites, resulting in larger O<sub>2</sub> uptake during the titration.

On the other hand, other researchers have found that there was a decrease in the uptake of hydrogen with increasing amounts of tin (23-25). Lieske and Völter (24) concluded that this decreased H<sub>2</sub> uptake with increasing tin content was due to alloy formation. This conclusion was reached because they found that the adsorption of methane was almost the same on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts and XRD and electron microscopy did not show any decrease in the dispersion of Pt with the addition of tin. As discussed later, in our XPS work we did not detect significant amounts of metallic tin on reduced Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts.

The amount of weakly adsorbed H<sub>2</sub> is summarized in Table 2. These values are in good agreement with the work of Palmer and Vannice (26) who reported that evacuation at 298K for 1 h can remove 40-50% of the hydrogen adsorbed on supported Pt. It was observed in our work that even after an addition of around 50 at.% tin in the metallic

component of the catalyst, the percentage H<sub>2</sub> weakly adsorbed remained almost the same. On further increase of the tin content, there was a small increase in the amount of weakly adsorbed H<sub>2</sub> but this change was not very significant. This indicates that the Pt-H bond is not significantly weakened by the addition of tin.

The comparison of the amount of hydrogen adsorbed on the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst prepared with nonacidic precursors as compared to the one prepared with acidic precursors is interesting. The amount of the H<sub>2</sub> uptake on the catalyst prepared with nonacidic precursors is about  $\frac{1}{3}$  of the one prepared with acidic precursors, despite similar particle structures and size distributions found in electron microscopy (8).

Based on total H<sub>2</sub> chemisorption, the metallic dispersion of the monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was close to 35%, corresponding to a chemisorption average particle size of 2.9 nm assuming a spherical particle geometry and the assumption that the average area occupied by one Pt surface atom was 0.089 nm (27). As mentioned before (17) one cannot calculate the average particle sizes of bimetallic particles from chemisorption especially when there is an uncertainty as to the interaction between the two metals. Even if the two metals are almost completely immiscible in the bulk, they could form bimetallic clusters where the second metal can have a significant influence on the chemisorption uptakes on the primary metallic component (28). In this case we are dealing with the Pt-Sn system which shows the formation of many different types of alloys in the bulk state and this makes the analysis more complicated.

The trends in  $H_a/Pt_t$  ratio seem to indicate that on addition of small amounts of tin the  $H_a/Pt_t$  value increases as compared to the value obtained for monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalysts. On addition of further tin the  $H_a/Pt_t$  value reaches a maximum and then drops with increasing tin content (Fig. 4). The presence of various regimes in correlating the  $H_a/Pt_t$  value with the tin content in



Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts has been noted before (29). Gault *et al.* (29) found that in the catalysts with low tin content (Pt/Sn ratio up to 7) tin formed tin-aluminate complexes which may be nucleation sites for Pt leading to increasing values of Pt dispersion and  $H_a/Pt_i$  values. For the regime Pt/Sn between 7 and 2.5 there was a significant lowering of  $H_a/Pt_i$  value, though Pt dispersion did not change much. On adding more tin, site blocking by tin became prominent. In their work on Pt-Te/Al<sub>2</sub>O<sub>3</sub> and Pt-Sb/Al<sub>2</sub>O<sub>3</sub> catalysts containing post-transition metals like Sn, Cheng *et al.* (30) found that on adding the second metal there was a dramatic decrease in the H/Pt and CO/Pt ratio. Though at low Te contents in the catalysts some electronic effects could be detected, for post-transition metal/Pt ratios larger than ~0.1 the main effect appeared to be geometric, causing the blocking of some of the Pt surface.

2. *Oxygen.* The O<sub>2</sub> uptake showed a very different trend as compared to that of hydrogen (Fig. 2). This highlights the effect of one metal on the adsorption behavior of another metal and also the difficulty of interpreting results under conditions where both metals are known to adsorb a gas. The  $O_a/Pt_i$  ratio increased with increasing Sn content (Fig. 4). In the case of the Pt-Au/SiO<sub>2</sub> catalyst system where the effect of gold on platinum has been observed to be mainly geometric in nature, it was determined that with increasing gold contents in the catalyst the amount of oxygen adsorbed tended to decrease in a fashion similar to the variations in the hydrogen and the carbon monoxide gas uptakes (17). But the analysis is much more complicated in the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> system, where the adsorption of oxygen and hydrogen show such a dramatic difference.

This increase in oxygen uptake with increasing tin content could be due to many factors. One reason could be that the chemisorption stoichiometry of oxygen adsorption on surface Pt atoms may be modified due to the addition of tin. This change in chemisorption stoichiometry could be due

to the electronic modification of Pt atoms in the close vicinity of the Sn (II) ions on the alumina substrate. Another reason could be that there is metallic tin present either independently or as Pt-Sn alloys. Metallic tin could chemisorb oxygen at room temperature, hence leading to a larger oxygen uptake as compared to the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. As the amount of tin was increased one could argue that more and more tin could go into the metallic tin state. But our XPS results, as detailed later on in this paper, do not indicate significant zero-valent tin formation in the reduced Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. It is also a possibility that some of the Sn (II) species could adsorb oxygen and get oxidized to Sn (IV), though it is conceivable that if the Sn (II) were anchored to the alumina in a tin-aluminate complex it may behave differently than if this metal-support interaction effect were not present and tin were just present as SnO.

Lieske and Völter (24) found similar results in their work on chemisorption on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. By assuming that the amount of oxygen chemisorbed on Pt sites was not affected by the addition of tin and that Sn (0) gets oxidized to Sn (II) on addition of oxygen, they came up with alloys of composition varying between Pt<sub>4</sub>Sn and Pt<sub>2</sub>Sn. Based on their calculations, their three bimetallic catalysts had 11, 22, and 15%, respectively, of Sn in the Sn (0) state. But there is the possibility that Sn could change the amount of oxygen adsorbed on Pt by a change in chemisorption stoichiometry. The other point to consider is that assuming Pt-Sn alloys are formed, the individual components in the alloy could conceivably chemisorb oxygen differently as compared to the chemisorption on the individual metal components if they were present in an unalloyed form.

The increasing uptake of oxygen with increasing tin content of the catalysts as observed in our work could be a result of spillover of oxygen from platinum to tin. Nishiyama *et al.* (31) found that bimetallic Rh-Sn/SiO<sub>2</sub> showed a greater oxygen up-

take at room temperature than the combined uptakes on the monometallic catalysts. This was attributed to the formation of Rh-Sn alloys where the tin atoms may behave like an "oxygen reservoir." It was proposed that such a close interaction between the two metals possibly leads to the spillover of oxygen from the Rh to the Sn sites and increases the oxygen uptake. In our case there could be the possibility of spillover of oxygen onto the "Sn-aluminate" complex from the nearby platinum atoms, explaining the greater uptake of oxygen with increasing tin content of the catalyst. This would also be consistent with the XPS data, detailed later in this paper, which indicate that in the reduced alumina-supported Pt-Sn catalysts most of the tin was in a Sn (II, IV) state.

The monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst gave an O<sub>a</sub>/H<sub>a</sub> ratio of 0.73. This shows that the extent of oxygen uptake at saturation is lower than that of hydrogen at saturation. A similar result was obtained in the case of the 1.0Pt/SiO<sub>2</sub> catalyst (17) and for other Pt/Al<sub>2</sub>O<sub>3</sub> catalysts (26). Boudart and co-workers (32) have made a detailed study of hydrogen and oxygen adsorption on unsupported Pt powder and found that the ratio of O<sub>a</sub>/H<sub>a</sub> was 0.65. Hence, an O<sub>a</sub>/H<sub>a</sub> ratio in this range appears to apply for both supported and unsupported samples. One reason given for the lower oxygen uptake is the relative immobility of the oxygen layer as compared to hydrogen (33). The monometallic 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> shows some uptake of oxygen but it is not a very significant amount in comparison to that observed in case of the 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. The amount of weakly adsorbed oxygen is around 1-2% for most of the Pt-containing catalysts. This shows that oxygen is much more strongly held than hydrogen at room temperature and that the addition of tin is not influencing the strength of the Pt-O bond. The sample prepared with non-chlorine-containing precursors shows a lower oxygen uptake as compared to the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, similar to the observation made during H<sub>2</sub> chemisorption. But the O<sub>2</sub> chemisorption/H<sub>2</sub> chemisorption

ratio for the two samples is not significantly different.

XPS results, as detailed later on in this paper, did not show the presence of detectable amounts of Sn (0) even in the higher tin loading catalysts. But as mentioned by Burch (21) even small amounts of tin could influence the Pt atoms on the surface electronically due to a possible inductive effect wherein tin behaves as an electron donor. This effect could be significant even at 5-10 at.% tin because of the tendency to surface segregation of tin in Pt-Sn clusters due to the lower surface free energy or heat of sublimation of Sn as compared to Pt. Such small amounts of Sn (0) on the surface may fall below the detectability limit of XPS.

3. *Carbon monoxide.* The trends in the CO uptake with increasing tin content are depicted in Figs. 3 and 4. Similar to the observations made in H<sub>2</sub> chemisorption, the CO<sub>a</sub>/Pt<sub>t</sub> ratio went through a maximum after which it tended to fall with further increase in tin content of the catalyst. However, there appear to be some subtle differences between CO and H<sub>2</sub> adsorption. For example, the 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample showed a larger CO<sub>a</sub>/Pt<sub>t</sub> ratio as compared to the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, in contrast to the trends observed for hydrogen (Fig. 4). The monometallic 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst showed some minute chemisorption uptake of CO (0.008 cc STP/g of catalyst) and almost all of this was weakly adsorbed. The trends in CO<sub>a</sub>/Pt<sub>t</sub> ratio as compared to H<sub>a</sub>/Pt<sub>t</sub> ratio tell us that for the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst and the bimetallic 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst the CO<sub>a</sub>/Pt<sub>t</sub> ratio is smaller than the H<sub>a</sub>/Pt<sub>t</sub> ratio but as the amount of Sn increases further the H<sub>a</sub>/Pt<sub>t</sub> ratio drops below the CO<sub>a</sub>/Pt<sub>t</sub> ratio. The 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> sample prepared with non-chloride-containing precursors shows a lower CO<sub>a</sub>/Pt<sub>t</sub> ratio as compared to the value for the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst with chloride-containing precursors. The trend is the same as observed with the other adsorbates. This implies that by using a different set of Pt and Sn precursors to impregnate the Al<sub>2</sub>O<sub>3</sub>

support, the number of exposed Pt sites has been decreased. This effect as mentioned previously may be due to the nature of the interaction of the ions with the alumina support during the impregnation process and subsequent pretreatments and may not necessarily be linked to the lesser amount of chlorine in the sample.

An important consideration is that bridge-bonded CO could be present on the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst. Infrared work on the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts would tell us more about the amount of bridge-bonded species. Dorling and Moss (34) found that on Pt/Silica catalysts CO chemisorption data in conjunction with XRD and electron microscopy showed that the ratio of Pt surface atoms/CO molecules adsorbed varied from ~1 to ~2 with increase in the Pt loading of the catalysts, which modified the size of the Pt particles. Hence some bridge bonding could lead to smaller CO<sub>a</sub>/Pt<sub>t</sub> values as compared to H<sub>a</sub>/Pt<sub>t</sub> values, assuming a H<sub>a</sub>/Pt<sub>t</sub> value of 1. The presence of bridge-bonded species on Pt supported on the same type of Al<sub>2</sub>O<sub>3</sub> as used by us has been observed before (35). The presence of tin can prevent CO bonding to multiple Pt sites due to a geometric effect as determined previously by infrared spectroscopy (25). The results also show that with addition of large amounts of tin like in the case of the 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample the CO<sub>a</sub>/Pt<sub>t</sub> and H<sub>a</sub>/Pt<sub>t</sub> values are lower than that of the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> sample, though the influence of tin on H<sub>a</sub>/Pt<sub>t</sub> value is much more dramatic as evident in the drop from 0.352 to 0.130, while the CO<sub>a</sub>/Pt<sub>t</sub> value drops from 0.333 to 0.289 (Fig. 4). Compared to H<sub>2</sub>, CO appears to be less sensitive to the Pt ensemble size and may represent a more suitable probe molecule for counting the actual number of exposed Pt surface atoms in bimetallic Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts as long as there are no chemisorption-induced surface segregation effects.

Chemisorption-induced surface segregation of one of the metals in a bimetallic system under certain gaseous environments has

been observed before. Bouwman (36), in his publication dealing with surface enrichment in alloys, has discussed the enrichment of Pt in Pt-Au alloys when exposed to CO. This enrichment would lead to increased Pt-CO bond formation which would lead to a lower surface energy as Au does not chemisorb CO to the extent that Pt does. The Pt-Sn alloy system has also shown this phenomenon under O<sub>2</sub> and H<sub>2</sub>. But to what extent this kind of phenomenon could exist in small bimetallic particles dispersed on a support is difficult to predict. De Jong *et al.* (37), in their infrared investigation of Pt-Ag alloy particles supported on silica, found that after reduction of the alloy particles and subsequent addition of CO, the infrared adsorption band which was formed due to CO adsorption on Pt sites tended to increase in intensity as a function of time by up to 30%. This could be due to enrichment of Pt induced by CO. If this phenomenon of surface enrichment was present it could change the nature of surface atoms in a bimetallic system depending on the type of gas adsorbed.

Another point of interest is that while 32% of the CO adsorbed on the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was weakly adsorbed and could be removed by evacuation for 1 h at room temperature, in the case of the bimetallic catalysts, except the one prepared with nonacidic precursors, the percentage of weakly adsorbed CO remained almost constant at around 16% and did not change significantly with addition of tin (Table 2). This result indicates that the addition of tin does not weaken the Pt-CO bond, but it does not agree with the result obtained by Palazov *et al.* (25). They found that the percentage of CO reversibly adsorbed increased with increasing tin content. The reason given for this was an electronic effect on the Pt surface leading to a decrease in strength of the  $\sigma$ -component of the metal-CO bond. The nature of catalyst preparation, loading of metal, catalyst pretreatment, and the type of support could play a part in the kind of electronic interac-

tions possible between the two metallic components in the catalyst. This could partially explain the conflicting results obtained by various researchers as to the nature of adsorption, and the oxidation states of Sn after reduction, in the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst system. Margitfalvi *et al.* (38) have conducted a detailed study of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by the method of controlled surface reactions. They found that the catalysts prepared in different ways showed very different catalytic reactivity because of variations in the metal-metal and metal-support interactions leading to ensemble and/or ligand effects on the Pt atoms and also influencing the support acidity.

The difference in the trends of the uptake of H<sub>2</sub> and CO with increasing tin can be attributed to the following reasons. Bridge bonding (or multiply bonding) sites for CO on Pt could be blocked by tin, forcing CO to adsorb in a linear manner in the bimetallic catalysts. CO adsorption on Pt is known to be associative, and consequently a single Pt site would suffice to accommodate an adsorbed CO molecule. Hydrogen, on the other hand, has to dissociatively adsorb on Pt, requiring adjacent Pt sites. Tin could lower the concentration of such adjacent Pt sites, and therefore hydrogen may not be able to adsorb to the same extent as CO on bimetallic Pt-Sn catalysts. A similar result was obtained by Verbeek and Sachtler (39) in their work on unsupported Pt-Sn alloys. They found that a lesser amount of deuterium was adsorbed on their Pt-Sn alloys as compared to CO and that the alloys adsorbed both adsorbates to a lesser extent than pure Pt. They mentioned two likely reasons for this observation. Dissociative adsorption of deuterium on two adjacent platinum atoms may be a nonactivated process. Separating the Pt atoms by introducing tin atoms between them may turn the dissociative adsorption of deuterium into an activated process. There is also the possibility of populating separate Pt atoms with deuterium atoms migrating from dual sites capable of dissociating molecular deuterium, but

this process would also be an activated one. Since CO adsorption is associative, the effect of tin addition may not be as dramatic. Second, there could be a decrease in the heat of adsorption of deuterium (or hydrogen) on Pt-Sn alloys as compared to pure Pt due to an electronic effect caused by the donation of electrons from tin to platinum.

#### (b) X-Ray Photoelectron Spectroscopy (XPS)

In view of the high oxygen affinity of Sn, it was decided to perform blank XPS studies on a Sn foil (Aldrich Chemical Company, 99+ % purity), going through treatment steps similar to the ones used on the supported catalyst samples. The air-exposed Sn foil showed only peaks due to tin oxides. Then the foil was sputtered with an argon ion beam for about 0.5 min and some of the oxide overlayer was removed and the spectrum shown in Fig. 5 was obtained. This spectrum shows a mixture of Sn oxides and metallic tin. The peak due to metallic tin is found at 484.3 eV and the peak due to tin oxides is present at 485.8 eV. From XPS one cannot tell the difference between Sn (II) oxide and Sn (IV) oxide (40), but it is obvious that if significant amounts of Sn (0) were present in a sample containing also Sn (II, IV) then XPS could be used to identify the presence of zero-valent tin. For the rest of the discussion whenever we refer to the Sn (II) species detected by XPS one must be aware that a mixture of Sn (IV) and Sn (II) species could be present. Other techniques like Mössbauer spectroscopy can be used to distinguish between Sn (IV) and lower-valency tin species (41). On further sputter treatment of the Sn foil one could remove all the Sn oxides and be left with only metallic tin, but on exposure of the foil to air Sn oxide is formed easily on the surface even at room temperature. Hence one must be careful in handling the supported Pt-Sn samples and make sure that the reduction and subsequent analysis is carried out without any possibility of the sample being exposed to even traces of air. Placing the sput-

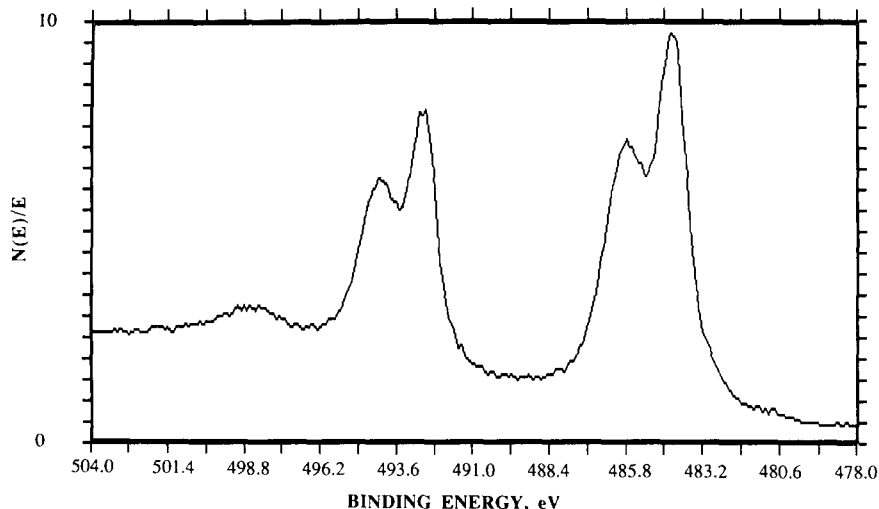


FIG. 5. XPS Sn 3d region of Sn foil.

tered Sn foil into the XPS reactor and treating it in a hydrogen stream retained the surface in the zero-valent state, confirming that the sample transfer from the reactor to the UHV chamber of the spectrometer did not expose the foil to even traces of oxygen. The zero-valent state of tin could be preserved in the UHV chamber throughout typical time periods required for XPS data acquisition. This confirms that the surface oxidation states of Sn as detected by XPS are attributable to the extent of reduction of Sn, rather than to an artifact due to accidental oxygen exposure during sample transfer and data acquisition.

Table 3 gives the position of all the main photoelectron peaks after referencing them to the Al 2*p* binding energy of 74.6 eV in case of alumina-supported samples or to the Si 2*p* peak of 103.4 eV for the silica-supported sample. It is evident that in all the tin-containing catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series the Sn 3*d*<sub>5/2</sub> peak lies in the range of 486–487 eV which tells us that the majority of the Sn is in the Sn (II,IV) state. On the other hand both Sn (II) and Sn (0) are found in case of the 1.0 Pt–1.0 Sn/SiO<sub>2</sub> catalyst which confirms the fact that Sn can readily be reduced to the Sn (0) state when using a silica support. Figures 6 and 7 show the XPS

Sn 3*d* region in the supported Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. The spectra have been displayed as obtained. They have not been shifted so as to reference the peaks to the primary photoelectron peak of the support.

The Pt 4*d*<sub>5/2</sub> peak lies at 314.9 eV in case of the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst though in the bimetallics it is found at a slightly higher binding energy. An exception is the catalyst 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) which was prepared with nonacidic precursors, for which the Pt peak was found at 314.5 eV (Table 3). The Pt in these catalysts is assumed to be in the zero-valent state after reduction (9). A previous XPS study on the Pt-Ge/Al<sub>2</sub>O<sub>3</sub> catalyst system, determined that after reduction the Pt 4*d*<sub>5/2</sub> peak is found at a larger binding energy in case of the bimetallic catalyst as compared to the monometallic Pt/Al<sub>2</sub>O<sub>3</sub> sample and this was attributed to Pt in the bimetallic sample being in a more electronegative state (20). In the Pt-Re/SiO<sub>2</sub> catalyst system the Pt 4*f*<sub>7/2</sub> peak in the bimetallic catalyst was at a slightly larger binding energy as compared to monometallic Pt/SiO<sub>2</sub> catalyst and this was said to be an effect of Pt-Re alloy formation leading to an electronic modification of the surface Pt sites (42).

The chlorine region in our samples was

TABLE 3  
XPS Binding Energies<sup>a</sup>

Sample	O 1s	Sn 3d5/2	Pt 4d5/2	C 1s	Cl 2p	Al 2s
Blank Al <sub>2</sub> O <sub>3</sub>	531.6	—	—	285.5	199.5	119.4
1.0 Pt/Al <sub>2</sub> O <sub>3</sub>	531.4	—	314.9	285.3	199.4	119.5
2.0 Sn/Al <sub>2</sub> O <sub>3</sub>	531.5	487.3	—	285.3	199.5	119.5
1.0 Pt-0.1 Sn/Al <sub>2</sub> O <sub>3</sub>	531.2	486.8	315.6	285.2	199.4	119.5
1.0 Pt-0.5 Sn/Al <sub>2</sub> O <sub>3</sub>	531.4	487.2	315.7	285.5	199.5	119.4
1.0 Pt-1.0 Sn/Al <sub>2</sub> O <sub>3</sub>	531.4	487.0	315.5	285.4	199.2	119.4
1.0 Pt-5.0 Sn/Al <sub>2</sub> O <sub>3</sub>	531.5	487.1	315.3	285.3	199.6	119.5
1.0 Pt-0.5 Sn/Al <sub>2</sub> O <sub>3</sub> (L.C.)	531.3	487.0	314.5	285.4	199.2	119.4
1.0 Pt-1.0 Sn/SiO <sub>2</sub>	532.8	486.8, 484.5	315.5	284.8	—	—

<sup>a</sup> In eV referenced to Al 2p = 74.6 eV or Si 2p = 103.4 eV.

scanned so as to determine how much chlorine lies on the surface of the catalysts as it is well known that chlorine plays an important part in reforming reactions. The chlorine peak was found close to 199 eV in all the alumina-supported samples. One could detect chlorine in even the sample prepared with nonacidic precursors and this chlorine must be present in the support even before impregnation as is evident from the chlorine peak found during analysis of the blank alumina. The C 1s peak in all the alumina-supported samples is found between 285.0 and

285.5 eV. The O 1s peak is found close to 531.5 eV for all the alumina-supported samples though it is found at a higher binding energy of 532.8 eV for the silica-supported one.

Gardner *et al.*(43), in their surface study of the Pt<sub>3</sub>Sn alloy before and after *in situ* reduction, found that although before reduction most of the Sn was in the tin oxide state, after reduction the tin was converted to mostly metallic state which was alloyed with Pt. They also detected migration of Pt from below the tin oxide layer to the surface to

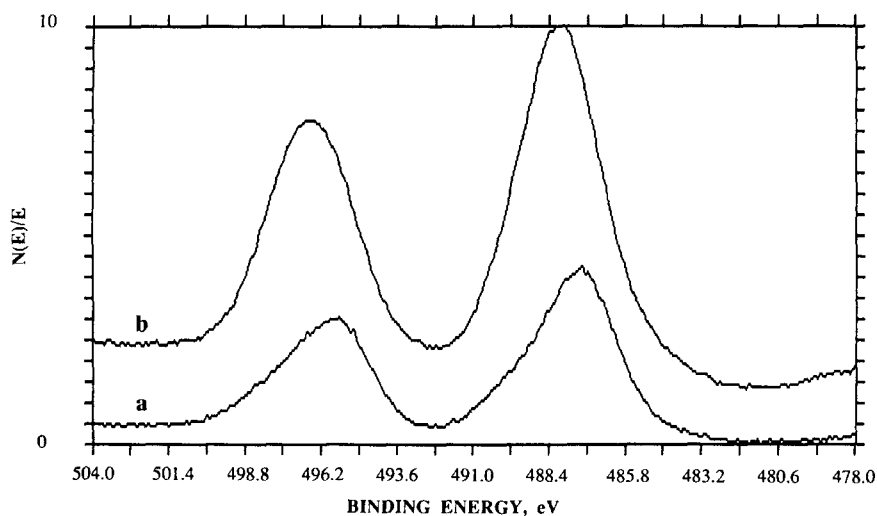


FIG. 6. XPS Sn 3d region of the following catalysts: (a) 2.0 Sn/Al<sub>2</sub>O<sub>3</sub>, and (b) 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

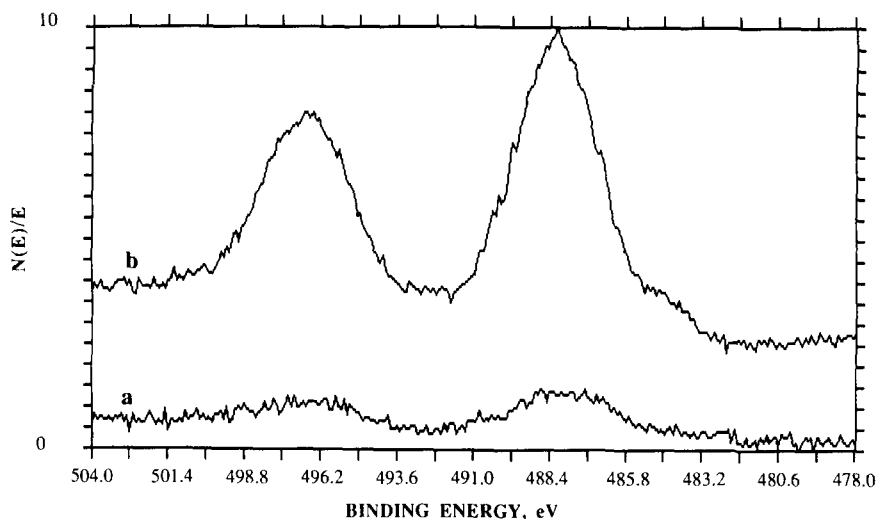


FIG. 7. XPS Sn 3d region of the following catalysts: (a) 1.0 Pt-0.1 Sn/Al<sub>2</sub>O<sub>3</sub>, and (b) 1.0 Pt-1.0 Sn/Al<sub>2</sub>O<sub>3</sub>.

form an alloy with tin. Their work is of significance as far as unsupported Pt-Sn systems are concerned but in Al<sub>2</sub>O<sub>3</sub>-supported systems the interaction between tin and alumina plays a major role in the behavior of the catalytic system and influences the Pt-Sn interaction. Complete reduction of tin in alumina-supported samples is said to be hindered due to the formation of a complex between the tin and the alumina support wherein a large portion of the tin is presumed to be in a state with a valency greater than zero.

After referencing to the Al 2p peak, the Sn 3d<sub>5/2</sub> peak in all the tin-containing Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts is located between 486 and 487 eV irrespective of the loading of tin and presence or absence of platinum. The peak position of the 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> sample is at 487.3 eV and the peak positions in case of the bimetallic Pt-Sn samples vary between 486.8 and 487.2 eV (Table 3). In case of the monometallic 2.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst there is no Pt present to assist in the reduction of Sn, hence the probability of forming zero-valent tin is very low, especially if there is any tin-aluminate complex formation. The XPS results imply that the major portion of Sn is in the Sn (II) state in all the alumina-

supported samples, although XPS spectra cannot tell the difference between Sn (II) and Sn (IV) species (40). Although Sn (II) is the major product after reduction of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst there is the possibility of small amounts of Sn (0) being present which may not be easily distinguishable by XPS. The Sn 3d peaks are broader with a larger FWHM in case of the supported samples as compared to the Sn foil and this also makes the differentiation of the Sn (0) peak from the Sn (II) peak more difficult. The Sn (II, IV) peak in the supported samples is at a higher binding energy as compared to its position in the sputtered tin foil. The possible reasons for this observation have been discussed before (44) and could indicate a kind of metal-support interaction where there could be electron transfer to the support from the metal atoms.

In case of the SiO<sub>2</sub>-supported catalyst, the Sn 3d<sub>5/2</sub> peak position and shape indicated the presence of a doublet. After curve fitting two peaks were obtained with peak positions at 486.8 and 484.5 eV (after referencing to the Si 2p peak at 103.4 eV) corresponding to Sn (II) and Sn (0), respectively (Table 3). The area of the Sn (0) peak was 45% of the total area of the Sn peak. Zero-valent tin has

been detected before on silica-supported Pt–Sn catalysts (9). XPS work indicated that in monometallic Sn/SiO<sub>2</sub> the tin was in a higher oxidation state than in bimetallic Rh–Sn/SiO<sub>2</sub> catalysts where the presence of Rh made it easier for Sn to get reduced (45). Our results show that unlike on alumina-supported samples, on silica-supported samples almost half of the tin can be reduced completely to a zero-valent state and this tin could be alloyed with Pt.

Another interesting observation is that the tin signal for the 1.0 Pt–1.0 Sn/SiO<sub>2</sub> catalyst is much weaker than the tin signal for the 1.0 Pt–1.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst meaning that there is a lesser amount of tin on the surface of the silica-supported sample as compared to the alumina-supported sample for the same nominal Pt and Sn loadings in the catalysts. This is confirmed by the atomic concentration calculations which indicated that whereas 0.42 at.% of tin were present in case of 1.0 Pt–1.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst after reduction, the 1.0 Pt–1.0 Sn/SiO<sub>2</sub> catalyst had only 0.11 at.% of tin. One reason for this is that in case of the alumina-supported sample an interaction between Sn (II) and alumina (conceivably forming a tin-aluminate complex) can lead to a spreading out of tin on the alumina support. In the case of the silica-supported sample this tin-support interaction effect either does not exist or is comparatively much weaker and hence, tin tends to form larger particles with a smaller fraction of metal exposed on the surface where XPS can probe it. As this anchoring effect of the support is not that evident in the case of the silica-supported sample, significant amounts of Sn can be reduced to the zero-valent state and also the Pt–Sn particles can grow to a larger size. A previous study found that X-ray diffraction could easily detect the presence of the Pt–Sn alloy in silica-supported samples after reduction at 623 K for 3 h while for the nonacidic Pt–Sn/Al<sub>2</sub>O<sub>3</sub> samples it was much more difficult to form the alloy, and the metallic dispersion was enhanced by using an alumina support (46).

But one cannot discount the possibility

that in our alumina-supported samples a small amount of Sn could be present as Sn (0), may be alloyed with Pt. This Sn (0) could be below the detection limits of XPS, or metallic Sn could be alloyed with Pt in the bulk of the Pt–Sn particles and Sn (0) in the interior of particles would not be detected by XPS. According to Sexton *et al.* (9) XPS would be able to positively identify Sn (0) provided that 5% or more of the total tin present in the surface layers were in the zero-valent state. According to Adkins and Davis (10), if Sn (0) were present to an extent of 15% or more of the amount of Sn (II, IV), XPS would be able to detect it. As pointed out by Burch (21), though to a large extent tin is reduced to Sn (II) on an Al<sub>2</sub>O<sub>3</sub> support and this Sn (II) is anchored on the support, it could influence the properties of Pt particles in close vicinity to it. Small amounts of Sn (0) in the form of an alloy or solid solution with platinum could have quite a large influence on the catalytic behavior because 15 at.% tin is sufficient to fill the holes in the Pt 5*d* band.

In assessing the extent of Sn reduction, the effect of temperature must be taken into consideration. In an XPS study of the closely related Pt–Ge/Al<sub>2</sub>O<sub>3</sub> system (20), the presence of Pt facilitated the reduction of Ge. However, a reduction at 923 K was necessary to form XPS detectable Ge (0) species, probably alloyed with platinum, along with Ge (II) species. After reduction at the lower temperature of 823 K, only Ge (IV) and Ge (II) species were found. Hence it is conceivable that for substantial amounts of Sn (0) to form in Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts the temperature of reduction may have to be much higher than 673 K. A recent study of Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts by means of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) showed that even after reduction of these catalysts at around 773 K under 1 atm of flowing hydrogen for close to 5 h, a large portion of the oxides and chlorides in the catalysts were not reduced though the dispersion was increased (47).

Atomic concentrations based on peak



area were calculated for all the elements present in our catalysts using the software provided by Perkin-Elmer. Atomic concentrations of the following elements were calculated: oxygen (O 1s), tin (Sn 3d<sub>5</sub>), platinum (Pt 4d<sub>5</sub>), carbon (C 1s), chlorine (Cl 2p), and aluminum (Al 2s). This software corrected the peak area for the sensitivity factors for each photoelectron line. One must be aware of the fact that there is always the possibility of some errors being present in the calculations of the XPS atomic concentrations but the values give us a good estimate as to the relative amounts of the different elements present on the surface. Another point to consider is that XPS is not as surface sensitive as chemisorption, since more than the uppermost atomic layers of the elements present may be detected by XPS. Hence if there is surface enrichment of a metallic component only in the uppermost atomic layers, then XPS might give very different values of surface composition compared to chemisorption (48). Chemisorption in supported Pt catalysts usually occurs only on the surface Pt atoms at room temperature. Hence one must be careful when comparing the results obtained by techniques having different surface sensitivity.

The variation of the Sn/Pt atomic ratio on the surface of the catalyst as obtained by XPS analysis with increasing overall Sn/Pt atomic ratio in the catalyst as obtained by neutron activation analysis is shown in Fig. 8. From the data we can infer that except for 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst, the other catalysts do not show much detectable enrichment of tin on the surface. The 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst shows significant surface enrichment which is understandable considering the large amounts of tin being present. Tin has a lower surface free energy than platinum and this could cause enrichment of tin in Pt-Sn particles. But from the peak position of the Sn 3d<sub>5/2</sub> peak (487.1 eV) in this catalyst the Sn is in the Sn (II) state even if there is an enrichment of tin on the surface. For all the other bimetallic Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts shown in the figure it

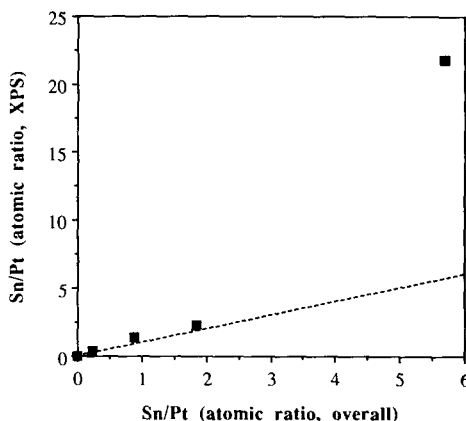


FIG. 8. XPS detected tin content versus overall tin content for the catalysts of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> series.

is obvious that the overall Sn/Pt ratio is very close to the XPS detectable Sn/Pt ratio. In case of the 1.0 Pt-5.0 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst this enrichment of Sn could at least partially explain the low chemisorption uptake values obtained as compared to the monometallic 1.0 Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

Another issue is the amount of chlorine in the sample and how much of it is on the surface, with chlorine being an important part of the reforming catalyst. Neutron activation analysis indicated that the amount of chlorine in these catalysts varied from 0.5 to 1 wt% (Table 1). In case of the catalyst prepared with non-chloride-containing precursors, the wt% of chlorine is around 0.38% as compared to 1 wt% for the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> prepared with chloride-containing catalysts. The chlorine in case of the 1.0 Pt-0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalyst is associated with the Al<sub>2</sub>O<sub>3</sub> support. XPS was able to detect some chlorine in the surface of these catalysts; the Cl 2p peak in the catalyst was in the region 199.2-199.6 eV. In case of the 1.0 Pt-1.0 Sn/SiO<sub>2</sub> catalyst, no peak due to chlorine could be detected. This could be due to the nature of the silica support which probably has less chlorine in the surface as compared to the alumina support.

Adkins and Davis (10), in their work on alumina- and carbon-supported Pt-Sn sam-

ples, found that on Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts the presence of surface chloride could not be detected by XPS after reduction, while it could be detected in Pt–Sn/C catalysts. But chemical analysis of these samples, after reduction and use of the catalysts in dehydrocyclization reactions, and XPS of unreduced samples showed that while alumina-supported samples retained a majority of their chloride even after reduction, the carbon-containing samples lost more than 90% of their initial chloride. Hence, the authors concluded that in the carbon-supported samples after reduction most of the chloride was present on the surface of the sample. In alumina-supported samples, the chloride from the impregnating mixture was incorporated into the bulk of the alumina during the reduction step and hence XPS could not detect chloride on the surface. In our case, XPS was able to detect chloride on the Al<sub>2</sub>O<sub>3</sub>-supported Pt–Sn samples even after reduction. This could be an effect of the nonporous nature of the support.

The comparison of the atomic concentrations obtained for the 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> and 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalyst is interesting. Neutron activation analysis of prerduced samples showed that while 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> and 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalysts had Pt and Sn contents which were very close to each other, the amount of chlorine was less than half in case of the 1 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalyst as compared to the 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst. This makes sense because the former sample was prepared using precursors which did not contain chloride. XPS atomic concentration calculations of the reduced catalysts show that after normalizing per atom of Al in the surface the 1.0 Pt–0.5 Sn catalyst has about double the number of surface Pt atoms/surface Al atom as compared to the 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalyst, while the surface Sn atom/surface Al atom ratios are not very much different for the two catalysts. This finding supports the chemisorption results, where the 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> catalyst had 3.1 times the hydro-

gen uptake and 2.7 times the CO uptake, respectively, compared to the 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalyst. This low uptake in the case of the 1.0 Pt–0.5 Sn/Al<sub>2</sub>O<sub>3</sub> (L.C.) catalyst could be due to the lesser number of Pt atoms on the surface. It appears that by changing the precursors to chlorine-free, nonacidic ones, the number of exposed Pt sites decreased while the number of exposed tin sites did not change significantly.

In conclusion, the chemisorption results indicate that as the tin content of the catalyst is increased, there is an increase in the oxygen uptake, and the trends in oxygen uptake do not track those for the hydrogen or the CO uptakes on these catalysts. XPS analysis of the reduced Pt–Sn/Al<sub>2</sub>O<sub>3</sub> catalysts show the presence of large amounts of tin in a valence state greater than zero. One cannot say for sure whether this Sn is in the form of either SnO or SnO<sub>2</sub>, or both, or whether a “Sn-aluminate” complex has been formed. The Pt in the reduced catalysts is assumed to be reduced to a zero-valent state. But there is a possibility of some of the platinum being in a Pt–O–Sn state, as proposed by Hoflund and co-workers (49, 50). XPS studies on platinum supported on tin oxide films (49) and on platinum–tin oxide films supported on alumina (50), showed that even after reduction at temperatures close to 773 K the Pt 4f XPS spectrum showed a peak at a higher binding energy than expected for metallic Pt leading to the hypothesis that some Pt might be present as Sn–O–Pt. It is conceivable that in our samples some Pt could be present in this form. This would be consistent with the XPS result showing that tin was to a large extent in the oxidized form. The reduced samples could contain a mixture of Sn-aluminate and tin in an oxidized state and XPS may not be able to tell the difference between them. The increasing oxygen uptake with increasing tin content could be due to spillover from the Pt sites to the tin sites which are probably in a tin-aluminate form. Assuming that most of the Sn is in a Sn (II) state in this complex, this spillover oxygen could lead to oxidation of

the tin to the Sn (IV) state at room temperature. In case of the monometallic Sn/Al<sub>2</sub>O<sub>3</sub> sample, since there is no source of atomic oxygen, the Sn, if present in the complex form with alumina, probably cannot get further oxidized, and there is no large oxygen uptake at room temperature.

Although XPS did not give direct evidence for the presence of zero-valent Sn, it is a possibility that very small amounts of Sn(0) could be present below the XPS detection limits. The addition of Sn to Pt altered the reactivity of the catalysts with low tin loading. For example, at about 10% overall conversion the dehydrocyclization selectivity was enhanced while the hydrocracking selectivity decreased (8). These trends are in good agreement with those reported by Klabunde and co-workers (51, 52) for Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by solvated metal atom dispersion (SMAD) leading to the formation of significant amounts of Sn (0), possibly in the form of Pt-Sn alloy. These authors mention that similar but less pronounced reactivity trends in conventionally prepared Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts could be attributed to the presence of small amounts of Sn (0) in close proximity to Pt (0), even though analytical methods might fail to prove the existence of zero-valent tin (52).

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#### REFERENCES

- Sinfelt, J. H., in "Catalysis Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, p. 257. Springer, Heidelberg, 1981.
- Sachtler, W. M. H., *Catal. Rev. Sci. Eng.* **14**(2), 193 (1976).
- Shapiro, E. S., Avaev, V. I., Antoshin, G. V., Ryashentseva, M. A., and Minachev, Kh. M., *J. Catal.* **55**, 402 (1978).
- Burch, R., and Garla, L. C., *J. Catal.* **71**, 360 (1981).
- Srinivasan, R., De Angelis, R. J., Davis, B. H., *J. Catal.* **106**, 449 (1987).
- Hanson, M., and Anderko, K., "Constitution of Binary Alloys," p. 1141. McGraw-Hill, New York, 1958.
- Margitfalvi, J. L., Hegedüs, M., and Tálás, E., *J. Mol. Catal.* **51**, 279 (1989).
- Sachdev, A., and Schwank, J., submitted for publication.
- Sexton, B. A., Hughes, A. E., and Foger, K., *J. Catal.* **88**, 466 (1984).
- Adkins, S. R., and Davis, B. H., *J. Catal.* **89**, 371 (1984).
- Li, Y.-X., and Hsia, Y.-F., *Hyperfine Interact.* **28**, 875 (1986).
- Baronetti, G. T., de Miguel, S. R., Scelza, O. A., and Castro, A. A., *Appl. Catal.* **24**, 109 (1986).
- Stencel, J. M., Goodman, J., and Davis, B. H., in "Proceedings 9th International Congress on Catalysis, Calgary" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1291. The Chemical Institute of Canada, 1988.
- Li, Y.-X., Stencel, J. M., and Davis, B. H., *React. Kinet. Catal. Lett.*, **37**(2), 273 (1988).
- Li, Y.-X., and Hsia, Y.-F., *Hyperfine Interact.* **28**, 879 (1986).
- De Miguel, S. R., Baronetti, G. T., Castro, A. A., and Scelza, O. A., *Appl. Catal.* **45**, 61 (1988).
- Balakrishnan, K., Sachdev, A., and Schwank, J., *J. Catal.* **121**, 441 (1990).
- Huchital, D. A., and McKeon, R. T., *Appl. Phys. Lett.* **20**(4), 158 (1972).
- Swift, P., Shuttleworth, D., and Seah, M. P., in "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy" (D. Riggs and M. P. Seah, Eds.), p. 437. Wiley, New York, 1983.
- Bouwman, R., and Biloen, P., *J. Catal.* **48**, 209 (1977).
- Burch, R., *J. Catal.* **71**, 348 (1981).
- Muller, A. C., Engelhard, P. A., and Weisang, J. E., *J. Catal.* **56**, 65 (1979).
- Völter, J., Lietz, G., Uhlemann, M., and Hermann, M., *J. Catal.* **68**, 42 (1981).
- Lieske, H., and Völter, J., *J. Catal.* **90**, 96 (1984).
- Palazov, A., Bonev, C. H., Shopov, D., Lietz, G., Sárkány, A., and Völter, J., *J. Catal.* **103**, 249 (1987).
- Palmer, Jr., M. B., and Vannice, M. A., *J. Chem. Tech. Biotechnol.* **30**, 205 (1980).
- Gruber, H. L., *J. Phys. Chem.* **66**, 48 (1962).
- Sinfelt, J. H., *J. Catal.* **29**, 308 (1973).
- Gault, F. G., Zahraa, O., Dartigues, J. M., Maire, G., Peyrot, M., Peyrot, E., Weisang, E., and Engelhardt, P. A., in "New Horizons in Catalysis, Proceedings of the 7th International Congress on Catalysis, Tokyo" (T. Seiyama and K. Tanabe, Eds.), Part A, p. 199. Elsevier, Amsterdam, 1980.
- Cheng, C. H., Dooley, K. M., and Price, G. L., *J. Catal.* **116**, 325 (1989).
- Nishiyama S., Yanagi, H., Nakayama, H., Tsuruya, S., and Masai, M., *Appl. Catal.* **47**, 25 (1989).

32. O'Rear, D. J., Loffler, R. C., and Boudart, M., *J. Catal.* **121**, 131 (1990).
33. Vannice, M. A., Benson, J. E., and Boudart, M., *J. Catal.* **16**, 348 (1970).
34. Dorling, T. A., and Moss, R. L., *J. Catal.* **7**, 378 (1967).
35. Barth, R., Pitchai, R., Anderson, R. L., and Verykios, X. E., *J. Catal.* **116**, 61 (1989).
36. Bouwman, R., *Gold Bull.* **11**(2), 81 (1978).
37. de Jong, K. P., Bongenaar-Schlenter, B. E., Meima, C. R., Verkerk, R. C., Lammers, M. J. J., and Geus, J. W., *J. Catal.* **81**, 67 (1983).
38. Margitfalvi, J., Hegedüs, M., Gobölös, S., Kern-Tálas, E., Szedlacsek, P., Szabó, S., and Nagy, F., in "8th International Congress on Catalysis, Berlin (West)" Vol. IV, p. 903. Verlag Chemie, Weinheim, 1984.
39. Verbeek, H., and Sachtler, W. M. H., *J. Catal.* **42**, 257 (1976).
40. Lau, C. L., and Wertheim, G. K., *J. Vac. Sci. Technol.* **15**(2), 622 (1978).
41. Kuznetsov, V. I., Belyi, A. S., Yurchenko, E. N., Smolikov, M. D., Protasova, M. T., Zatulokina, E. V., and Duplyakin, V. K., *J. Catal.* **99**, 159 (1986).
42. Biloen, P., Helle, J.N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63**, 112 (1980).
43. Gardner, S. D., Hoflund, G. B., and Schryer, D. R., *J. Catal.* **119**, 179 (1989).
44. Ross, P. N., Kinoshita, K., and Stonehart, P., *J. Catal.* **32**, 163 (1974).
45. Nishiyama, S., Yanagi, H., Nakayama, H., Tsuruya, S., and Masai, M., *Appl. Catal.* **47**, 25 (1989).
46. Dautzenberg, F. M., Helle, J. N., Biloen, P., and Sachtler, W. M. H., *J. Catal.* **63**, 119 (1980).
47. Li, Y-X., Chiu, N.-S., Lee, W. H., Bauer, S. H., and Davis, B. H., in "Characterization and Catalyst Development" (S. A. Bradley, M. J. Gattuso, and R. J. Bertolacini, Eds.), A.C.S. Symposium Series, Vol. 411, p. 328. American Chemical Society, Washington, DC, 1989.
48. Galvagno, S., and Parravano, G., *J. Catal.* **57**, 272 (1979).
49. Cox, D. F., Hoflund, G. B., and Laitinen, H. A., *Langmuir* **1**(3), 259 (1985).
50. Hoflund, G. B., Asbury, D. A., and Gilbert, R. E., *Thin Solid Films* **129**, 139 (1985).
51. Li, Y-X., and Klabunde, K. J., *Langmuir* **3**, 558 (1987).
52. Li, Y.-X., Zhang, Y-F., and Klabunde, K. J., *Langmuir* **4**, 385 (1988).