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Platinum–Tin Reforming Catalysts

I. The Oxidation State of Tin and the Interaction between Platinum and Tin

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Two series of bimetallic Pt–Sn/alumina catalysts have been prepared by impregnation of samples of industrial Pt/alumina reforming catalysts with solutions of Sn(IV) chloride in acetone. The Pt content was constant at 0.3 wt% and the tin content was varied over the range 0.3 to 5.0 wt%. The reducibility of the catalysts was determined by temperature-programmed reduction, and by reduction in flowing hydrogen, followed by reoxidation in oxygen. The results show that the Pt catalyses the reduction of the tin. However, the average oxidation state of the tin after reduction is Sn(II), and no further reduction occurs even when Pt is present, or when reduction is continued for long times. The average oxidation state of the tin is independent of the concentration of tin on the catalyst over the whole range from 0.3 to 5.0 wt%. The dispersion of the Pt has been determined, as a function of tin content, by measuring the amount of hydrogen chemisorbed. The chemisorption experiments show that the amount of hydrogen adsorbed by Pt is increased when tin is present, which indicates that tin increases the dispersion of the Pt. It is concluded that tin is stabilised in the Sn(II) state by interaction with the support and, consequently, that no proper Pt–Sn alloys are formed in these catalysts. The role of tin cannot be to divide up the surface into small ensembles of Pt atoms. It is proposed that the special properties of the catalysts are due to a change in the electronic properties of small Pt particles either by interaction with Sn(II) ions on the support surface, or by incorporation into the Pt of a few percent metallic tin as a solid solution.

INTRODUCTION

The discovery of bimetallic catalysts has been one of the major technical developments in heterogeneous catalysis in recent years. A number of bimetallic reforming catalysts have been patented (*1*) and Pt–Re catalysts are used commercially. A most important property of bimetallic catalysts is their improved stability, believed to arise from a change in selectivity, with coke-forming reactions being suppressed as compared with reforming reactions. With Pt–Re catalysts it seems probable that the rhenium is in the zero-valent state and forms an alloy, or at least a solid solution, with platinum.

The role of other additives is less clear, although it has been suggested recently (*2*) that widely different modifiers (Au, Sn, S, C) all affect the platinum in a similar way by dividing the surface into very small ensembles of Pt atoms. This is rather surprising in the case of tin because it is well established that small traces of metallic tin will poison a Pt surface. Equally, however, there is ample evidence (*1*) that Pt–Sn/Al_2O_3 catalysts are much more stable than the corresponding monometallic catalysts. This raises the possibility that the tin exists in a different form in each case: when present in the metallic state it is a poison, when present in a nonmetallic state it acts as a promoter.

There is confusion regarding the reducibility of tin oxide supported on alumina. In a recent paper Dautzenberg *et al.* (*3*) have determined the oxygen consumed in the reoxidation of previously reduced tin oxide on alumina and concluded that the tin is fully reduced to the zero-valent state. They also report, however, that the first 0.6 wt% Sn is not reducible because of being chemically complexed by the alumina. In fact, it is also possible to draw a line from the

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origin through their first data points having a slope corresponding to the reduction of Sn(IV) to Sn(II). This would suggest that there is partial reduction of *all* the tin up to about 1.7 wt% (i.e., Sn(IV) to Sn(II)), and complete reduction of any additional tin (i.e., Sn(IV) to Sn(0)). This alternative interpretation would be consistent with the data of Muller *et al.* (*4*) who found using thermogravimetric and electron microdiffraction methods that *all* the tin was partially reduced (to Sn(II)) irrespective of the Pt or the Sn content. They also confirmed the presence of metallic platinum, but no metallic tin or Pt–Sn alloy could be detected. Bacaud *et al.* (*5*) have stated that although the formation of Pt–Sn alloys is believed to occur at high metal loadings, their reduction data are consistent with the formation of Sn(II) on alumina at low Pt loadings (i.e., 0.35 wt%, such as is used in a commercial catalyst).

In the related Pt–Ge/Al_2O_3 system Bouwman and Biloen (*6*) have investigated the valence state of the elements by XPS and found that even at high metal loadings (3.8 wt% Pt, 2.5 wt% Ge) the catalyst contained Ge^{4+} and Ge^{2+} after reduction at 823 K, and only after reduction at 923 K were alloys formed. In the Pt–Sn system Dautzenberg *et al.* (*3*) also detect Pt–Sn alloy formation after prolonged reduction at high temperatures, but find no direct evidence for alloy formation after reduction at lower temperatures.

Mössbauer spectra measurements have also been made, but the interpretation is again ambiguous. Bacaud *et al.* (*7*) find evidence of alloy formation at high metal loadings. Berndt *et al.* (*8*) find evidence of an interaction between platinum and tin, but cannot distinguish between species of Pt–Sn and Pt–SnO type. They do report, however, a sharp decrease in the capacity of the Pt to adsorb hydrogen when tin is present, and this would be consistent with the formation of a Pt–Sn alloy. Thus, Verbeek and Sachtler (*9*) have found for pure, unsupported Pt–Sn alloys that even with the Pt_3Sn alloy hydrogen adsorption is greatly reduced, and with the PtSn and $PtSn_2$ alloys no hydrogen adsorption occurs at all. This is to be expected since Auger (*10*) and XPS (*11*) data show that there is surface enrichment of Pt–Sn alloys with Sn atoms. For example, the Pt_3Sn alloy contains about 50% Sn atoms in the surface layer.

It is to be expected that where Pt–Sn alloys are formed hydrogen adsorption should be greatly diminished. It is interesting, therefore, that Bacaud and Figueras (*12*) find high H/Pt ratios in Pt–Sn catalysts, and indeed some evidence that the H/Pt ratio increases as the tin content is increased.

Finally, Pakhomov *et al.* (*13*) have recently shown by X-ray and Mössbauer spectroscopy that various Pt–Sn alloys can be formed on spinel supports. However, they also find that any alloy containing more than 25% Sn (e.g., PtSn, $PtSn_2$) is inactive as a catalyst. They conclude that the active catalyst contains only a small amount of tin, either as a solid solution of Sn in Pt, or possibly as the Pt_3Sn alloy.

The purpose of our work was to determine the reducibility of tin, and to investigate whether alloys of Pt and Sn are formed in alumina-supported catalysts. All our results have been obtained by using samples of commercial Pt/Al_2O_3 reforming catalysts as starting materials.

EXPERIMENTAL

1. Materials

(*a*) *Pt catalysts.* The Pt/γ-alumina catalysts used in this work were obtained from catalyst manufacturers and were standard reforming catalysts. Two different catalysts, series A and B, were used. The catalysts were received in the form of extrudate and this was crushed and sieved with the 30–60 mesh portion being retained for use. The catalysts contained 0.3 wt% Pt and about 0.6 wt% Cl.

(*b*) *Pt–Sn catalysts.* Two series of Pt–Sn catalysts were prepared in the following way using the commercial Pt catalysts as a base material: 2 g of the crushed and sieved Pt/alumina catalyst was placed in a 100-cm^3 round-bottomed flask, and 30 cm^3 of an acetone solution containing the appropriate amount of tin(IV) chloride hydrate ($SnCl_4 \cdot 5H_2O$) was added. The mixture was shaken and then allowed to stand for 1 h. It was observed with the series A catalysts that the acetone solution gradually became coloured yellowish-brown. Repeat experiments using only acetone showed no such effect. No coloration was observed with the series B preparations. Acetone was removed within about 0.5 h by heating the flask with a hot-air blower, while shaking continuously. When the catalyst powder appeared dry (free flowing) the flask was placed in an oven and the catalyst was dried overnight at 390 K. Samples were then either examined in this uncalcined form, or after calcination in air. The materials were either calcined by placing the samples for 2 h in a furnace already heated to 770 K, or by placing in a cold furnace and raising the temperature at 10 K min^{-1} to 770 K and holding for 2 h. A few samples were calcined from cold at a maximum temperature of 620 K. Only the final temperature was found to affect the properties of the catalysts.

The catalysts prepared with Pt/alumina catalyst A contained 0.3, 0.6, 0.9, 1.2, and 5.0 wt% Sn. These are referred to subsequently as A0.3Sn, etc. With Pt/alumina catalyst B the samples prepared contained 0.3, 0.6, 0.9, and 1.2 wt% Sn, referred to as B0.3Sn, etc.

(*c*) *Sn catalysts.* Catalysts containing 5 wt% Sn were prepared using acetone solutions of tin chloride as before, on different aluminas. One was a commercial alumina (Akzo Chemie B.V.), referred to as AHS, containing about 0.6 wt% sulphate. Since this alumina produces a signal during temperature-programmed reduction due to reduction of sulphate ions, two other catalysts were prepared. The supports used were a low-sulphate alumina (Akzo Chemie B.V., less than 100 ppm sulphate), referred to as ALS, and a homemade alumina prepared by precipitation of aluminium hydroxide from a solution of aluminium nitrate with ammonia. This aluminium hydroxide was dried and calcined at 770 K in the normal way. It is referred to as ANS.

To confirm that no loss of tin occurs during handling of the catalysts (drying and calcination)—a problem could arise since tin chloride is volatile—several batches of catalyst were prepared containing some of the radioactive isotope ^{113}Sn. Each batch was divided into two equal portions, one of which was stored as a reference. The other portion was given the standard catalyst pretreatment. Measurements of the activity after each stage of treatment and comparison with the reference samples confirmed that virtually no tin was lost from the alumina-supported catalysts.

Silica-supported catalysts were prepared also to observe if the support had any influence on the stability and/or reducibility of the tin. The preparative procedure was as before; the support was Davison silica, type 57, surface area 290 m^2 g^{-1}.

2. *Temperature-Programmed Reduction*

The temperature-programmed reduction (TPR) apparatus consisted of a quartz microreactor containing a sintered glass disc on which the sample (0.4 g) was supported. The microreactor was coupled to the remainder of the apparatus by ball and socket joints, using silicone-rubber O rings to make gas-tight seals. The gas used for reduction was 5% hydrogen in argon. It was supplied from a gas cylinder and the flow was controlled with a Negretti and Zambra flow controller (5 or 10 cm^3 min^{-1} was used). The hydrogen content of the gas was determined with a thermal conductivity detector by first passing the gas through the reference side of the detector, then down through the sample, through a cold trap (195 K) to remove water vapour, and back through the sample side of the detector.

The signal from the detector was displayed on a recorder. The sensitivity of the detector was calibrated both by injecting measured quantities of hydrogen into the hydrogen/argon stream, and by reducing known weights of Analar copper(II) oxide. The sensitivity was 8.000×10^5 mV s (mmol $H_2)^{-1}$. Samples were heated with a linear temperature programmer-controlled electric furnace at 6.9 K min^{-1}. Temperatures were measured with a thermocouple situated in a thermowell adjacent to the sample.

3. *Hydrogen Adsorption*

The amount of hydrogen adsorbed by the reduced samples was determined using the TPR apparatus at the end of the reduction period by quenching the sample to 273 K by removing the furnace and surrounding the microreactor with an ice bath.

4. *Reduction in Pure Hydrogen and Reoxidation in Oxygen*

The gas mixture, heating profile, etc., used in TPR do not reproduce the conditions normally used in the pretreatment of a sample before testing as a catalyst. To check whether further, more complete, reduction could occur during catalyst pretreatment than is observed during TPR, some experiments were performed in which catalysts were reduced in pure hydrogen at atmospheric pressure for 16 h at 770 K, and then reoxidized in oxygen at 770 K. The experiments were performed in a conventional glass volumetric apparatus consisting of a dosing volume (35.19 cm^3) and a sample volume (12.95 cm^3). Pressures were measured with diaphragm transducers (Bell and Howell) with a sensitivity of 30 N m^{-2}. The catalyst was contained in a Pyrex glass U-tube reactor coupled to the gas and vacuum lines by ball and socket joints. The procedure was as follows. The sample (0.5 g) was placed in the reactor, the apparatus was evacuated, and the sample volume isolated. A quantity of hydrogen was admitted to the dosing volume and its pressure and temperature were recorded. This hydrogen was then admitted to the sample volume and the new pressure noted. The sample was heated at 25 K min^{-1} to 770 K. The change in pressure with time was noted. Within about 1 h the pressure was constant. After 3 h the apparatus was filled with hydrogen and "reduction" at 770 K in flowing hydrogen was continued for a further 16 h. The apparatus was then closed and evacuated, and the sample cooled to 600 K. The sample was isolated, a dose of oxygen was introduced into the dosing volume, its pressure and temperature were noted, and then it was admitted to the sample volume. The sample was reheated to 770 K and the reoxidation followed by noting the pressure change over a period of 10 h. The quantities of hydrogen and oxygen consumed in reduction and reoxidation, respectively, were calculated in the normal way.

RESULTS

1. *Radiotracer Experiments*

The purpose of the reduction experiments described in this work is to determine the extent of reduction of Sn(IV) supported on alumina. Therefore, it is important to show that no loss of Sn occurs during pretreatment. Table 1 summarises data for one catalyst which had been doped with a small amount of ^{113}Sn. Very similar results were obtained with other catalysts. The results show that there is only a small loss of tin even when calcination involves rapid heating to the calcination temperature, as in this case. At most, 7% of the tin

TABLE 1

Radioactivity of ^{113}Sn in Catalyst 5.0 wt% ^{113}Sn

Pretreatment	Relative radioactivity[a]
None	1.000
Dry 390 K/24 h	0.995
Calcine 770 K/2 h	0.933

[a] Ratio of activity of treated sample to activity of untreated reference sample.

is lost during this pretreatment. This must indicate that there is a strong interaction between the tin ions and the alumina surface because in the absence of alumina Sn(IV) chloride hydrate volatilises completely. Furthermore, with silica-supported catalysts (see the TPR results below) there is a substantial loss of tin during pretreatment. Indeed, even after drying at 390 K there is a marked difference between alumina- and silica-supported tin catalysts. The silica catalyst was black, possibly indicating decomposition of the tin chloride into a slightly nonstoichiometric oxide, whereas the alumina catalyst was white, presumably because the tin is stabilised as a surface monolayer rather than as a bulk compound.

Further evidence of a strong surface interaction between alumina and tin chloride comes from the observation that when a commercial Pt/alumina catalyst is contacted with a solution of tin chloride in acetone much of the Pt compound used to impregnate the alumina is displaced from the alumina surface and the acetone solution becomes coloured yellowish-brown. No such coloration is observed with acetone in the absence of the tin compound. We conclude that the alumina stabilises the tin(IV) on the surface and prevents any substantial loss during pretreatment. Very similar effects are found with many other metal ions (such as Ge, Mo, W, Co, Ni). Moreover, it is a common feature of these interactions that the first fraction of the ions to interact with the alumina surface does so with the most active surface sites, and this is essentially an irreversible process. Therefore, it is probable that at low loadings of tin, such as the 0.3 wt% used in Pt–Sn catalysts, *all* the tin will interact strongly with the alumina and no loss will occur during pretreatment. Even at loadings of 5 wt% Sn our results show a loss of less than 7% of the original tin.

2. *TPR of Tin Catalysts*

Figure 1 shows the TPR profiles for a variety of catalysts. Curve 1 shows the profile for alumina AHS (0.6 wt% sulphate) alone and curve 2 the corresponding profile for catalyst AHS5.0Sn. The large peak at 900 K is due to reduction of sulphate ions. A separate sulphate peak is not observed when tin is present, although the larger area under curve 2 suggests that sulphate reduction is occurring but at a lower temperature. There could be a number of reasons for this, but we take it as further evidence of strong interaction between the tin and the surface of the alumina. Curve 2 shows that the tin is reducible and that for calcined samples the reduction occurs in two separate stages with peaks at about 680 and 850 K, indicating that two different forms of tin are present. This is not unusual and even Pt can exist in different forms on alumina, each with its own distinctive reduction peak. Curves 3 (catalyst ALS5.0Sn) and 4 (catalyst ANS5.0Sn) show that the double-peak reduction curve is reproducible and, apart from small variations in the relative intensities of the two peaks, is not greatly affected by the nature or origin of the alumina.

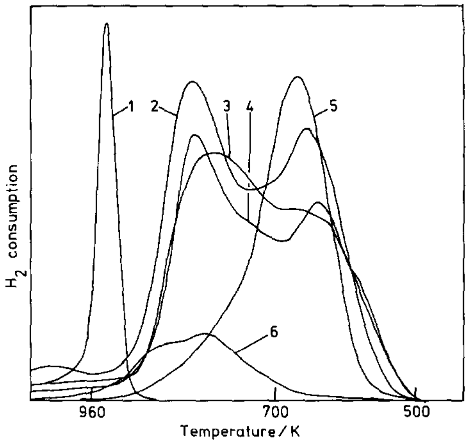

FIG. 1. TPR profiles for tin catalysts. 1, Alumina AHS; 2, AHS5.0Sn; 3, ALS5.0Sn; 4, ANS5.0Sn; 5, uncalcined ANS5.0Sn; 6, $SiO_2$5.0Sn.

The hydrogen consumed in reduction can be calculated from the areas under the curves. Assuming Sn(IV) reduces to Sn(0) the values for curves 2, 3, and 4 correspond, respectively, to 51, 43, and 53% reduction. (For curve 2 it is assumed that the same amount of hydrogen is consumed in reducing the support in catalyst AHS5.0Sn as for the support itself.) These results show that, even in the absence of Pt, the tin is reducible; that is, it is not essential to have Pt present to catalyse the reduction. However, the reduction does not proceed below an average oxidation state of Sn(II).

The effect of calcination can be seen by comparing curves 4 and 5 in Fig. 1. The uncalcined sample shows only a single reduction peak at 700 K, indicating that only a single type of tin is present. This presumably corresponds to some type of bulk oxide, or a weakly stabilised surface species, in which case the peak at 850 K in the calcined samples would correspond to a strongly stabilised tin species. Once again it is noticeable that the total amount of hydrogen consumed is much less than would be required to produce metallic tin.

The extent of loss of tin from a calcined silica-supported catalyst is illustrated by curve 6 in Fig. 1. The area corresponds to only 18% reduction. The radiotracer results described earlier have confirmed that tin is not lost from calcined alumina catalysts. We conclude that monometallic Sn/Al_2O_3 catalysts cannot be reduced below an average oxidation state of Sn(II) even at temperatures as high as 960 K, and that this is due to stabilisation of the tin by interaction with the alumina. This interaction is already present to some extent after impregnation, but is increased by calcination.

3. *TPR of Pt Catalyst A*

Figure 2 gives the TPR profiles for commercial catalyst A (using a gas flow of 10 $cm^3 min^{-1}$), and shows the complexity of the reduction of even monometallic Pt/alumina catalysts. The figure also shows the changes brought about by drying or calcining this catalyst. For a sample dried at 390 K overnight the small peak at 460 K disappears and the peak at 650 K moves up to 680 K. The total area decreases from the equivalent of 153% reduction for the "as-received" sample to 146% for the dried sample. The excess reduction observed for these samples may be due to the consumption of hydrogen by reaction with surface chloride ligands to give HCl. This may also be the reason for the anomalous curve obtained with a catalyst calcined very gently at 620 K for 1 h (curve 4, Fig. 2). This shows the expected reduction peak at 510 K, but at 650 K the curve suddenly increases rapidly to give a large peak at 730 K, which then decreases even more rapidly to give a large negative peak. We think the reduction peak at 650 K is associated with the loss of chlorine from the surface and the negative peak arises because HCl passes through the cold trap and is detected by the thermal conductivity detector. During these experiments it was noticed that the effluent gas had a slightly pungent odor.

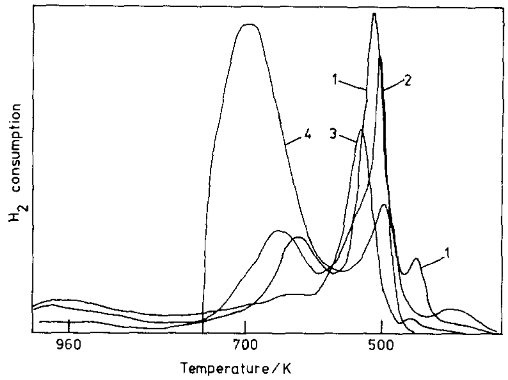

FIG. 2. TPR profiles for platinum catalyst A. 1, As received; 2, dried; 3, calcined 770 K/2 h; 4, calcined 620 K/1 h.

The pattern of events during drying and calcination seems to be as follows. After impregnation there is some interaction of the chloro–platinum precursors with the alumina to give an adsorbed species of approximate formula $PtOCl_2$ with the other two chloro-ligands from the Pt being adsorbed on the alumina. "Reduction" involves reduction of Pt(IV) to Pt(0) and conversion of the chloro-ligands into HCl. After drying at 390 K some of the adsorbed chloro-ligands are lost, and the hydrogen consumption decreases from 153 to 146%. Calcination at 770 K converts all the Pt to PtO_2 and removes all the reactive chloro-ligands from the alumina, so the hydrogen consumption is equivalent to 99% reduction of Pt(IV) to Pt(0). Calcination at 620 K presumably converts the Pt into PtO_2 but does not remove the chloro-ligands from the alumina, so during reduction there is a large chloro-peak at 700 K.

These results show that measurements of the reducibility of alumina-supported metals may be susceptible to error if the support itself contains reducible ions such as chloride or sulphate. It is possible, therefore, that reports that the reducibility of tin or alumina decreases after calcination (5) may be inaccurate. Our results (see Fig. 1) indicate a higher degree of reduction in calcined samples.

4. *TPR of Pt–Sn Catalysts*

(*i*) *Series A.* Figure 3 shows the TPR profiles for the series A catalysts. As the tin content is increased the main peak moves to slightly higher temperatures and becomes relatively much larger than the second peak. At high tin loadings a new peak begins to develop with a maximum at about 850 K. Comparison with Fig. 1 shows that this high-temperature peak corresponds to the high-temperature peak in monometallic tin catalysts, and that the peak at 700 K (catalyst A0.3Sn, Fig. 3) corresponds to the low-temperature peak in the monometallic tin catalysts. Figures 1 and 3 also show that the reduction of tin is catalysed in the presence of Pt. In the absence of Pt the tin has its first reduction peak at 680 K, whereas when Pt is present the first peak occurs at 600 K. However, since it is mainly the high-temperature peak in the reduction profile for tin which disappears, we conclude that the reduction of one form of tin is more strongly catalysed than the other. We have suggested earlier that the tin which gives the high-temperature peak, and whose reduction is catalysed by Pt, is tin stabilised by the support.

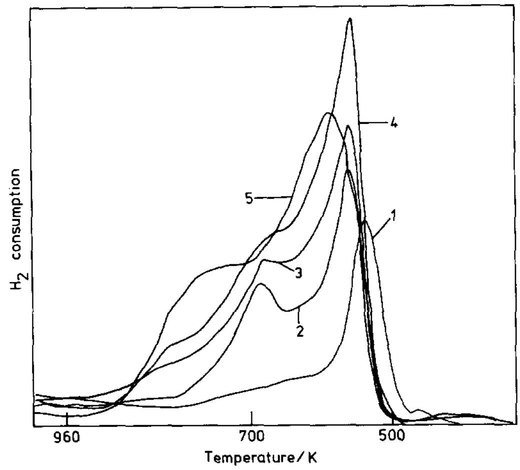

FIG. 3. TPR profiles of Pt–Sn catalysts, series A. 1, Catalyst A; 2, A0.3Sn; 3, A0.6Sn; 4, A0.9Sn; 5, A5.0Sn × 0.25.

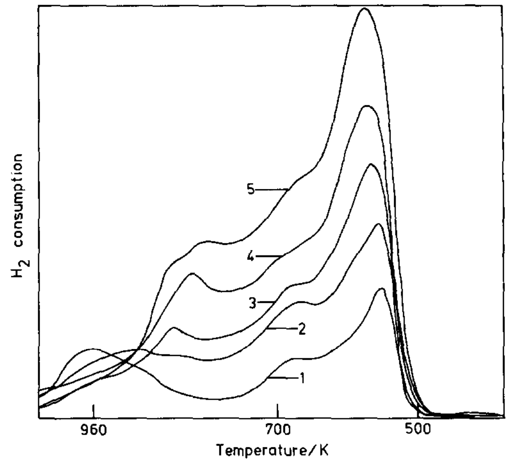

FIG. 4. TPR profiles for Pt–Sn catalysts, series B. 1, Catalyst B; 2, B0.3Sn; 3, B0.6Sn; 4, B0.9Sn; 5, B1.2Sn.

(*ii*) *Series B.* Figure 4 shows the TPR results for the series B catalysts. (The broad peak at 950 K is a sulphate reduction peak.) The curves are similar to those shown in Fig. 3 and illustrate that consistent and reproducible results are obtained using quite different commercial catalysts as starting materials. This is important because as we have pointed out above with the series A catalysts the tin, even at a concentration of only 0.3%, displaces the Pt from the alumina. In effect the series A samples are prepared by co-impregnation of Pt and Sn, whereas with the series B catalysts the tin is added after the Pt. Various workers have commented on the necessity of using a particular method of preparation (*1*, *3*, *5*). Our results show that the reducibility of the tin is the same irrespective of whether the Pt is added before or at the same time as the tin. The intermediate calcination step would seem to eliminate any substantial differences which might originally have existed between the two series of catalysts.

5. *Oxidation State of Sn in Pt–Sn Catalysts*

It was shown earlier that in monometallic Sn catalysts the average oxidation state after reduction was close to Sn(II). Since in Pt–Sn catalysts we find that Pt catalyses the reduction of Sn it might be anticipated that the average oxidation state of the Sn would be lower. In fact, as Table 2 shows, the average oxidation state of tin is very close to Sn(II) in all the catalysts whether they contain about equal amounts of Pt and Sn or a large excess of Sn. This is true for both series of catalysts. The data shown in Table 2 represent the average of many repeat experiments, sometimes on different batches of catalyst. The error in the hydrogen consumption was small (±2%), and no effect due to reduction of nonmetallic ions was observed, since reoxidation and rereduction experiments gave similar results. Under TPR conditions, although the reduction of Sn is catalysed by Pt, all that happens is that the rate of reduction is enhanced. The final state is not affected. There appears to be a thermodynamic barrier rather than a kinetic barrier to the reduction of tin to the metallic state. Of course, the reduction of catalysts generally involves heating in hydrogen at fairly high temperatures for quite long times, so it is possible that the TPR experiments underestimate the extent of reduction of tin which could occur in an actual catalytic experiment. The following results prove that this is not the case.

TABLE 2

Degree of Reduction of Sn(IV) in Pt–Sn/Alumina Catalysts[a]

	Sn (wt%)	Reduction[b] (%)
Series A	0.3	47
	0.6	48
	0.9	47
	1.2	50
	5.0	50
Series B	0.3	47
	0.6	46
	0.9	46
	1.2	54

[a] Degree of reduction of Sn calculated as difference between the hydrogen consumed in reducing Pt–Sn catalysts and the hydrogen consumed in reducing the corresponding Pt catalyst.

[b] Based on the reaction $Sn^{4+} + 2H_2 = Sn^0 + 4H^+$.

6. *Static Reduction and Reoxidation*

(*a*) *Reduction in pure hydrogen.* Figure 5a shows the change in pressure with time when catalysts containing 5 wt% Sn, with or without 0.3 wt% Pt are heated at 770 K in static hydrogen at a starting pressure of 1 bar. The Sn catalyst reaches a constant pressure within about 1.5 h, the Pt–Sn catalyst within about 0.5 h. Once again this shows the influence of Pt in catalysing the reduction of Sn. However, the hydrogen consumed in this reduction is only 50% of that required for complete reduction of Sn(IV) to Sn(0), just as in the TPR experiments.

The catalysts were now reduced for a further 16 h in flowing hydrogen at 770 K.

(*b*) *Reoxidation of reduced catalysts.* Figure 5b shows the change in pressure during reoxidation of the above catalysts at 770 K. The pressure decreases rapidly and becomes constant after about 1 h, and then remains constant during a further 10 h. The

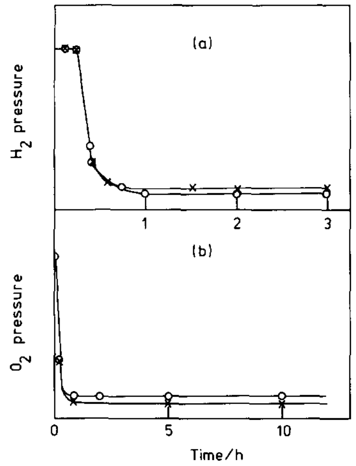

FIG. 5. (a) Change in pressure with time for the reduction of catalysts at 770 K. ○, Catalyst ANS5.0Sn; ×, catalyst A5.0Sn. (b) Change in pressure with time for the reoxidation of catalysts at 770 K. ○, Catalyst ANS5.0Sn; ×, catalyst A5.0Sn.

total oxygen consumption in the reoxidation corresponds to the oxidation of Pt(0) to Pt(IV) and of Sn(II) to Sn(IV). Thus, even an extended reduction in pure hydrogen does not lower the average oxidation state of the Sn below Sn(II). This shows that the TPR data accurately reflect the degree of reduction which is possible with these catalysts under normal conditions. Our catalytic results (see Part II (*14*)) show that identical catalytic properties in reforming reactions are obtained with either short or long reduction times, so the novel features of Pt–Sn catalysts must be due to the presence of partially reduced tin with an average oxidation state of Sn(II).

7. *Adsorption of Hydrogen by Reduced Catalysts*

To gain further insight into the role of the tin we have determined the amount of hydrogen adsorbed by the catalysts on cooling from the top TPR temperature (960 K) to 273 K. The data cannot be taken as an accurate measure of the surface area since the catalysts do not desorb all their hydrogen into a 5% H_2/Ar mixture even at 960 K. However, the trend in the amount of hydrogen adsorbed is reliable. Table 3 shows the amount of hydrogen adsorbed by the Pt as a function of Sn content (Sn alone does not adsorb hydrogen). The Pt surface area increases with Sn content for both series of catalysts. The role of the tin seems to be to improve the dispersion of the Pt, possibly by preventing sintering of the initial very small Pt particles.

TABLE 3

Adsorption of hydrogen by Pt–Sn/alumina catalysts

	Sn (%)	H_2 adsorbed (mol)	Pt surface area (m^2 g^{-1})	Pt dispersion
Series A	0.0	1.06	50	25
	0.9	1.63	77	39
	1.2	2.02	95	48
	5.0	3.79	179	90
Series B	0.0	0.96	60	30
	0.3	1.27	79	40
	0.6	1.38	87	43
	0.9	1.90	119	60
	1.2	2.47	155	77

The surface area determined for the monometallic Pt catalysts is lower than expected so the possibility exists that the "high" surface area in the presence of Sn is an artefact due to to the method of measurement. Therefore, some further experiments were performed in which great care was taken to ensure that the samples were rigorously dried, etc., and the results are given in Table 4. These results show that high Pt dispersions can be obtained as originally anticipated. It is still apparent that even higher dispersions are indicated when Sn is present.

TABLE 4

Hydrogen Adsorption by Predried Pt Catalysts

Sn (%)	Pt surface area (m^2 g^{-1})	Pt dispersion (%)
0.0	134	67
0.3	170	85
5.0	216	100

Our hydrogen adsorption data could be criticized because they are obtained in a dynamic system, and during cooling some activated processes, such as hydrogen spillover to the support, could occur which would not occur in conventional adsorption experiments. While we cannot exclude the possibility that hydrogen spillover contributes to the total uptake of hydrogen during adsorption our results suggest that this is not a significant factor. Thus, when the adsorbed hydrogen is subsequently desorbed into the 5% H_2/Ar in two stages, first by heating to 823 K, then by heating to 960 K, it is found that for *all* the catalysts the hydrogen retained at 823 K and then desorbed at 960 K constitutes about 50% of the total. This suggests that in all cases the hydrogen is adsorbed in the same form. It does not seem likely that hydrogen adsorbed on the support would be retained sufficiently strongly to adsorb only at high temperatures. The hydrogen which desorbs above 823 K must be very strongly chemisorbed and all the evidence is that in our catalysts this could only occur on the Pt. We think our results indicate that Sn increases the dispersion of the Pt; we think it less likely that the retention of hydrogen by Sn(II) ions in the surface of the alumina could account for the increased amount of hydrogen adsorption as suggested by Muller *et al.* (*4*). Bacaud and Figueras (*12*) have found that the adsorption of hydrogen by Pt in Pt–Sn/alumina catalysts is not decreased by the presence of Sn and, indeed, in agreement with our results they report some evidence that the amount of adsorbed hydrogen increases with Sn content. Since the work of Verbeek and Sachtler (*9*) shows that for *any* intermetallic Pt–Sn alloy the amount of adsorbed hydrogen is very small our chemisorption results are further strong evidence that intermetallic alloys are *not* formed in our catalysts.

DISCUSSION

The reduction experiments described in this work show that the lowest *average* oxidation state obtained after reduction at 770 K is Sn(II). This is the case even when Pt is present to catalyse the reduction, and even when samples are reduced for long periods. The degree of reduction is independent of the tin content throughout the range 0.3 to 5.0 wt% Sn. The hydrogen adsorption experiments show that the amount of hydrogen adsorbed by Pt is increased when Sn is present.

We conclude that *no* Pt–Sn alloys, such as Pt_3Sn, PtSn, etc., are formed during reduction and, therefore, that the special properties of these catalysts (see Part II (*14*)) cannot be due to alloy formation. Our measurements of the degree of reduction are not sufficiently accurate to exclude the possibility that a very small amount of the tin is reduced to the zero-valent state and forms a solid solution with the Pt, as suggested by Pakhomov *et al.* (*13*). However, if this does occur we can place an upper limit on the amount of tin reduced at less than 5% of the tin present. We think it is unlikely that even this much tin is reduced to the metal because if some complete reduction is possible the fraction of tin reduced should be related to the tin content. This is not the case. Moreover, the pattern of reduction, namely, rapid reduction for about 1 h, but with no further reduction even after prolonged heating in hydrogen, argues against complete reduction of any tin because if the heat of formation of a PtSn solid solution could overcome the thermodynamic barrier to reduction of Sn(II) we would expect to see a progressive increase with time of the total amount of zero-valent tin formed.

The possibility that, say, 50% of the tin is reduced completely to the metal rather than all the tin being only partially reduced can be discounted for two reasons. First, Mössbauer spectra measurements (*7*, *8*) show that at low loadings of Pt and Sn all the Sn(IV) species are absent after reduction. Second, our hydrogen adsorption data are not consistent with any substantial amount of Sn being combined with the Pt.

Model of Pt–Sn/Alumina Catalyst

The only interactions between Pt and Sn which are consistent with our data and other published data are either the formation of a solid solution of Sn in Pt, or an interaction between Pt crystallites and Sn(II) ions attached to the alumina surface. We do not think the formation of a solid solution is likely for the reasons given above. However, even if this turns out to be the correct model the fraction of the surface covered by Sn atoms must be small. Consequently, the observed changes in catalytic properties cannot be due to a geometric effect (*3*). An electronic effect could be responsible providing it is accepted that a single surface Sn atom can affect several surface Pt atoms. In bulk Pt–Sn alloys each tin atom has the effect of donating four electrons to the electron bands of Pt (*15*). This probably occurs as a result of an inductive effect (no electrons are actually transferred, but the end result is the same). Therefore, at a Sn content of 15 at.% the holes in the 5*d*-band of the Pt will be filled. Since there is a strong tendency for enrichment of Pt–Sn surfaces with Sn, this degree of band filling in the Pt states at the surface probably occurs at lower Sn contents, say 5–10%. Therefore, a few percent Sn dissolved in Pt could alter the electronic properties of the surface Pt atoms and this could change the catalytic properties. However, if there is an effective electron donation to Pt it might be expected that there would be a large decrease in activity as well as a change in selectivity, whereas the data show that there is only a small loss of activity.

Nevertheless, it is possible for a small amount of a second metal, present as a solid solution, to affect markedly the catalytic properties of a Group VIII metal. For example, we have found (*16*) that the presence of 2–3% Mo in Ni decreases the hydrogenolysis activity by nearly two orders of magnitude. This cannot be a geometric effect, so an electronic effect is indicated (*17, 18*). Whether such an effect is present in Pt–Sn catalysts is not yet clear.

The second model proposed above suggests an interaction between small Pt particles and Sn(II) ions trapped on the alumina surface. This model is consistent with our reduction data, and with the hydrogen adsorption data. The ability of each Pt atom to adsorb hydrogen would hardly be affected, but the increased total adsorption could be due to stabilisation of small Pt particles against sintering. The special catalytic properties of Pt–Sn/alumina would then be due to a change in the electronic properties of the Pt, presumably via electron withdrawal by the Sn(II) ions. There is evidence that even on alumina Pt is electron deficient (*19*). Results for Pt–Mo catalysts also indicate that the Pt is positively charged (*20*).

A further point concerning the role of tin relates to the observation by Bacaud *et al.* (*7*) that when tin is added to alumina strong acid sites are destroyed. This suggests that tin ions are adsorbed at strongly acid sites. Therefore, it is possible that the tin has a dual role. As well as stabilising and modifying the Pt it may affect the overall acidity of the support. Since reforming reactions are mostly bifunctional this would also lead to a change in product selectivity. It could also account for some of the results obtained by Dautzenberg *et al.* (*3*) who found a greater degree of reduction of Sn at high loadings than we observed. They used a nonacidic alumina. It is possible that the number of strongly acidic sites was very small, so some bulk tin oxide could be present, and this could be completely reducible. However, we emphasise that even though alloy formation would then be possible all the evidence is that this is not beneficial since Pt–Sn alloys are inactive.

CONCLUSIONS

The conclusions from this work are as follows.

1. Sn on alumina is stabilised by the alumina, but some reduction can occur.

2. Pt catalyses the reduction of Sn, but the lowest oxidation state is Sn(II).

3. Pt adsorbs more hydrogen when Sn is present.

4. No proper alloys of Pt and Sn are formed, so this cannot account for changes in catalytic properties.

5. The special properties of Pt–Sn catalysts cannot be due to a geometric effect in which Sn atoms divide the surface up into very small clusters of Pt atoms.

6. The special properties of Pt–Sn catalysts must be due to a change in the electronic properties of small Pt crystallites either by interaction with a Sn(II) ion stabilised on the alumina to give electron-deficient Pt, or by incorporation of a few percent metallic Sn as a solid solution in Pt to give electron-rich Pt.

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