

## State of Tin in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Reforming Catalysts Investigated by TPR and Chemisorption

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The state of tin in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> was investigated by temperature-programmed reduction (TPR) and adsorption of H<sub>2</sub> and of O<sub>2</sub>. With both these independent methods a partial reduction of Sn<sup>IV</sup> to Sn<sup>0</sup> was detected. This Sn<sup>0</sup> is alloyed with Pt. The composition of the alloy only depends on the total tin content. The main part of Sn<sup>IV</sup> is reduced only to Sn<sup>II</sup>. The reduction of all the Sn<sup>IV</sup> is catalyzed by Pt. At higher temperatures (500°C) Pt and/or Sn species were found to become mobile. A model of the surface topography is proposed. © 1984 Academic Press, Inc.

### INTRODUCTION

Additions of tin to Pt/Al<sub>2</sub>O<sub>3</sub> reforming catalysts improve their activity in aromatization and their stability with respect to deactivation (1-5). In order to clarify the role of tin in reforming reactions several investigations about the state of tin on the surface of the activated catalyst have been performed. However, there are considerable contradictions in the results and interpretations of these investigations.

In some papers the formation of Pt-Sn "alloys" or bimetallic clusters has been proposed (6-11). In particular, Dautzenberg *et al.* (7) found substantial reduction of tin to the zero valent state and formation of Pt-Sn alloys. However, their catalysts were prepared from a sodium-neutralized, i.e. nonacidic, alumina. A further argument for an alloy formation could be derived from catalytic experiments. The typical tin effect in Pt/Al<sub>2</sub>O<sub>3</sub> reforming catalysts mentioned above could be observed with unsupported Pt-Sn alloys, too (12). Moreover, the products of temperature-programmed reaction gave a distinct hint on alloy formation (7).

On the other hand, in the recent paper of Muller *et al.* (13) the formation of zero valent tin and of alloys has been expressly denied. Only Sn<sup>II</sup> is held to coexist with Pt<sup>0</sup>

in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. Burch (14) did not find alloys, but nevertheless considered the possibility of an alloy formation to a small extent.

In order to investigate the state of tin in supported Pt-Sn catalysts some authors have used Mössbauer spectroscopy (8-11). Evaluating the spectra, the coexistence of all the states in question (Sn<sup>IV</sup>, Sn<sup>II</sup>, Sn<sup>0</sup>) in different ratios has been proposed. However, according to our experience (9) it is difficult to distinguish between Sn<sup>II</sup> species and Sn<sup>0</sup> alloyed with Pt by Mössbauer spectroscopy.

The aim of our work was to clarify the state of tin in real, bifunctional, highly dispersed Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. Moreover, the influence of tin on the surface chemistry of Pt/Al<sub>2</sub>O<sub>3</sub>, as described recently (15, 16), merited further investigation. The methods we used were temperature-programmed reduction (TPR) and chemisorption of oxygen and hydrogen.

### EXPERIMENTAL

*Catalysts.* For this study chloride-containing catalysts of the types Sn/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, and especially Pt-Sn/Al<sub>2</sub>O<sub>3</sub> were used. Tin contents of 0.3, 0.6, 1.2, and exceptionally 12 wt% were chosen. The Pt contents were 0.5 and 1.0 wt% Pt. As car-

rier Condea  $\gamma$ -alumina with a grain size of 0.5–0.8 mm was used.

The Pt/Al<sub>2</sub>O<sub>3</sub> or Sn/Al<sub>2</sub>O<sub>3</sub> samples were prepared by impregnating the carrier with a solution of H<sub>2</sub>PtCl<sub>6</sub> or SnCl<sub>2</sub>, respectively, in dilute hydrochloric acid, followed by drying at 120°C.

The Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared consecutively. Sn/Al<sub>2</sub>O<sub>3</sub> samples, prepared as described above, were calcined for 1 h at 500°C in air. The calcined samples were impregnated with a solution of H<sub>2</sub>PtCl<sub>6</sub> in dilute hydrochloric acid and dried at 120°C. Additionally we used a chloride-free (CF) Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst with 0.5 wt% Pt and 0.3 wt% Sn. This catalyst was prepared from  $\gamma$ -alumina, Sn<sup>II</sup> acetate, and the Pt- $\pi$ -methallyl complex according to Ryndin (17).

**TPR.** The TPR experiments were performed with the flow apparatus and the procedure already described (15), using a 5% H<sub>2</sub>/Ar mixture for reduction. The correction of the TPR peak intensity for amounts of adsorbed hydrogen, mentioned previously (15), was not necessary with Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts. Only negligible or no negative peaks, caused by hydrogen desorption, were observed.

**Hydrogen and oxygen adsorption.** The adsorption experiments were carried out with a dynamic pulse apparatus. The procedure for hydrogen adsorption has already

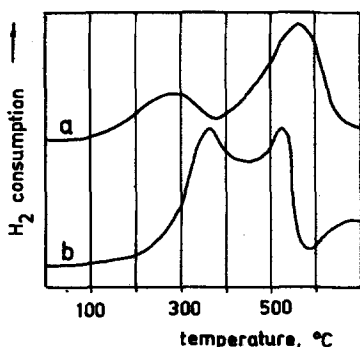


FIG. 1. TPR of Sn/Al<sub>2</sub>O<sub>3</sub>, calcined at 500°C in O<sub>2</sub>. (a) 1.2 wt% Sn; (b) 12 wt% Sn; the weight of the samples was 1.0 and 0.1 g, respectively.

TABLE 1

Tin Valence Change $\Delta V_{Sn}$ and Sn <sup>0</sup> Content of Pt-Sn/Al <sub>2</sub> O <sub>3</sub> , Calculated from TPR Intensities				
wt% Sn	wt% Pt	$\Delta V_{Sn}$	% Sn <sup>0</sup> /Sn	wt% Sn <sup>0</sup>
0.3	—	2.01	0	0
0.6	—	1.96	0	0
0.6	0.5	2.40	22	0.13
1.2	—	1.94	0	0
1.2	0.5	2.08	7	0.08
1.2	1.0	2.27	16	0.19

been described (15), and that for oxygen adsorption was analogous.

## RESULTS AND DISCUSSION

### Oxidation State of Sn in Sn/Al<sub>2</sub>O<sub>3</sub>

TPR curves of Sn/Al<sub>2</sub>O<sub>3</sub> samples, calcined in oxygen at 500°C, are shown in Fig. 1. Two distinct peaks were obtained with both samples. This indicates that the oxidized tin is fixed on the alumina in two different species. Samples with the usual small tin contents between 0.3 and 1.2 wt% gave the type of TPR curve shown in Fig. 1a, of course with corresponding intensities. Table 1 shows the change of the tin valence during the reduction as calculated from the TPR intensity. All samples gave values near 2.

Previously it was found that a calcination of supported tin results in the formation of Sn<sup>IV</sup> (e.g., Ref. 9). Thus the valence change of about 2 indicates that Sn<sup>II</sup> is the product of the reduction. It is well known that unsupported Sn<sup>IV</sup> is reduced to metallic tin. Therefore one must conclude that Sn<sup>II</sup> is stabilized by formation of a Sn<sup>II</sup>-alumina surface complex. This is supported by the observation that the samples with 0.3–1.2 wt% Sn did not adsorb oxygen at all at room temperature. Metallic tin adsorbs oxygen (7). Moreover, the color of the samples remained white.

The stabilizing capacity of the alumina should be exceeded if the ratio of Sn to Al<sub>2</sub>O<sub>3</sub> becomes large. This was observable with the sample containing as much as 10

wt% Sn. In this sample the amount of the strongly stabilized oxide, indicated by the higher reduction temperature of 550°C, was decreased in favor of the less stabilized one (Fig. 1b). Moreover, a small part of the oxide was obviously reduced to metallic tin. This was indicated by the grey color of the reduced sample and especially by a certain uptake of oxygen at room temperature, detectable directly by adsorption as well as by a small TPR signal.

This thesis of a more or less strong interaction between SnO and Al<sub>2</sub>O<sub>3</sub> can explain the contradictions in the literature. Recently Muller *et al.* (13) as well as Burch (14) reported that only Sn<sup>II</sup> is formed during the reduction, whereas Dautzenberg *et al.* (7) found metallic tin as the main product. Only the latter authors used sodium-neutralized, nonacidic alumina. Evidently on this modified alumina the stabilizing interaction with Sn<sup>II</sup> is excluded and therefore the normal reduction to metallic tin could proceed.

#### Oxidation State of Sn in Reduced Pt-Sn/Al<sub>2</sub>O<sub>3</sub>

As already mentioned, it is disputed whether the tin in reduced Pt-Sn/Al<sub>2</sub>O<sub>3</sub> exists as Sn<sup>0</sup> in bimetallic Pt-Sn clusters or in an oxidized state, especially as Sn<sup>II</sup>. As will be demonstrated below, in our catalysts prepared as real reforming catalysts, Sn<sup>0</sup> as well as Sn<sup>II</sup> occur: a minor part of the tin is reduced to Sn<sup>0</sup> and forms bimetallic clusters with Pt, but the main part of tin exists, as is the case with Sn/Al<sub>2</sub>O<sub>3</sub>, as carrier-stabilized Sn<sup>II</sup>. This could be proved independently by TPR and chemisorption of H<sub>2</sub> and O<sub>2</sub>.

As an example for Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 500°C, Fig. 2c shows the TPR curve of 0.5% Pt, 1.2% Sn on Al<sub>2</sub>O<sub>3</sub>. A single peak appears, just as is the case with the system Pt/Al<sub>2</sub>O<sub>3</sub> (Fig. 2a). In comparison with Pt/Al<sub>2</sub>O<sub>3</sub> the peak temperature is slightly increased and the peak intensity is strongly increased. Obviously the reduction of the strongly stabilized main part of tin, reducible at 550°C in the absence of Pt

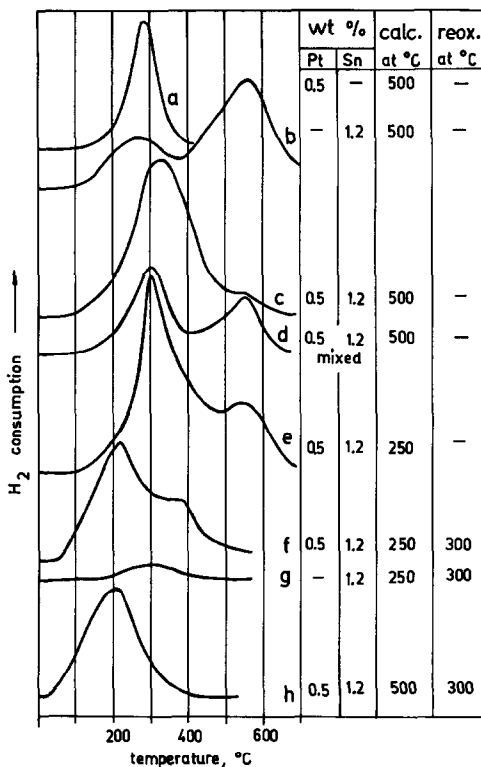


FIG. 2. TPR of Pt-Sn/Al<sub>2</sub>O<sub>3</sub>, calcined at the above temperatures, reduced at 500°C, reoxidized at the above temperatures; (d) mixture of 0.5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> and 1.2 wt% Sn/Al<sub>2</sub>O<sub>3</sub>.

(Figs. 1a and 2b), is catalyzed by Pt. This will be discussed in the next section.

On the understanding that Pt is reduced from the Pt<sup>IV</sup> state to Pt, as is the case with Pt/Al<sub>2</sub>O<sub>3</sub> (15), the change of the tin valence ( $\Delta V_{Sn}$ ) during TPR can be calculated from the intensity of this unitary peak. In Table 1 the  $\Delta V_{Sn}$  values of Sn- and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts are listed. Whereas with Pt-free catalysts values of about 2 were measured, which correspond to the formation of Sn<sup>II</sup>, with Pt-containing catalysts this value is distinctly exceeded. This indicates that a part of tin, also listed in Table 1, was reduced to the zero valent state. The tin content being constant, the  $\Delta V_{Sn}$  values and the portion of zero valent tin, respectively, increase with increasing Pt content. Only with the listed Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts could an acceptable reproducibility be reached; combining high Pt contents with low Sn contents, the mea-

surement of  $\Delta V_{\text{Sn}}$  values becomes unreliable.

The formation of zero valent tin leads to the question whether it is alloyed in bimetallic clusters with platinum or not. There are several arguments in favor of an "alloy" formation.

(i) Catalytic arguments. The typical effect of added tin is to be seen with Pt-Sn bulk alloys as well as with Pt-Sn/Al<sub>2</sub>O<sub>3</sub> carrier catalysts (7, 12). Moreover the observed inhibition of the cyclohexane dehydrogenation with Pt-Sn/Al<sub>2</sub>O<sub>3</sub> must be due to an interaction of Pt and Sn(19).

(ii) Thermodynamic arguments. In the absence of Pt no Sn<sup>0</sup> was formed during reduction. This was demonstrated above and was additionally checked with samples reduced in pure H<sub>2</sub> for 10 h at 500 or 700°C. Hence one should assume that the reduction of the Sn<sup>II</sup>-alumina surface complex is impossible for thermodynamic reasons. Thus an additional driving force would be necessary for the reduction Sn<sup>II</sup> → Sn<sup>0</sup>. This additional affinity should be provided by the alloy formation.

(iii) Adsorption of hydrogen. As shown in Fig. 3a, the adsorption of hydrogen strongly decreases with increasing tin content of the catalysts. This behavior is analogous to adsorption data on bulk alloys determined by Verbeek and Sachtler (18). They found that the adsorption of deuterium on Pt is strongly suppressed by an alloying with Sn. However, in the case of a supported catalyst a decrease of hydrogen adsorption also could be caused by a decrease of Pt dispersion. This possibility can be excluded. Methane is adsorbed on Pt/Al<sub>2</sub>O<sub>3</sub> (1 wt% Pt) and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> (1 wt% Pt; 0.15–1.2 wt% Sn) to nearly the same amount, indicating nearly the same dispersion (20). XRD gave no hint of a decreased dispersion (9). Electron microscopic examinations of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> showed no influence or even a promoting influence of added Sn on the dispersion (21). Considering these results the observed decrease of hydrogen adsorption can hardly be ex-

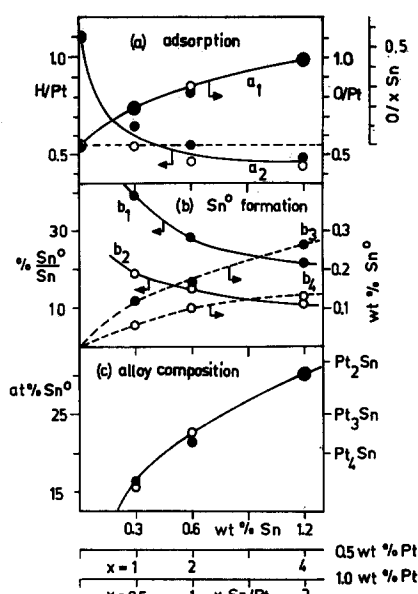


FIG. 3. Adsorption of H<sub>2</sub> and O<sub>2</sub> on Pt-Sn/Al<sub>2</sub>O<sub>3</sub> and alloy formation: (a) adsorption results: a<sub>1</sub> oxygen adsorption, a<sub>2</sub> hydrogen adsorption in dependence on the total tin content; (b) amount of zero valent tin; b<sub>1</sub> and b<sub>2</sub> ratio of Sn<sup>0</sup> to total tin content, b<sub>3</sub> and b<sub>4</sub> absolute percentage of Sn<sup>0</sup> in the catalyst; (c) composition of the formed Pt<sup>0</sup>-Sn<sup>0</sup> alloy; ○, 0.5 wt% Pt; ●, 1.0 wt% Pt

plained by a decreased dispersion and therefore indicates an alloy formation. It should be mentioned that Burch (14) concluded an increase of dispersion by Sn from high temperature hydrogen adsorption. However, we have previously shown that hydrogen adsorption is not a reasonable measure for the dispersion of Pt-Sn/Al<sub>2</sub>O<sub>3</sub> because Sn can decrease (0°C) or even slightly increase (300°C) hydrogen adsorption depending on the temperature of adsorption. Thus we are sceptical of the above conclusion of Burch.

The formation of Sn<sup>0</sup> in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts was checked by an independent method, namely the adsorption of oxygen. As shown above, oxygen is adsorbed on Sn<sup>0</sup>, but not on Sn<sup>II</sup>. Thus in a Pt-Sn<sup>II</sup> system oxygen should be adsorbed only on Pt, whereas the formation of Sn<sup>0</sup> should cause an additional adsorption. The results of the oxygen adsorption experiments are shown in Fig. 3a. Samples with 0.5 and 1.0 wt% Pt and with different amounts of Sn were

used. The oxygen adsorption, calculated as the atomic ratio O:Pt, clearly increases with increasing tin content. This is an independent, qualitative evidence of Sn<sup>0</sup> in Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts.

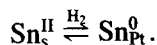
The excess adsorption of oxygen caused by tin was used to estimate the amount of zero valent tin and the composition of the bimetallic clusters. Two assumptions concerning the adsorption stoichiometry were made: (i) Tin adsorbs oxygen as SnO. Sn<sup>II</sup> could be stabilized again by the alumina, as mentioned above. Moreover, SnO has been found in the first adsorption layer on tin (22). (ii) The oxygen adsorption on Pt (O/Pt = 0.55) is not significantly changed by Sn, because oxygen is very strongly adsorbed on Pt. These assumptions are not proved exactly. However, using them, the estimated Sn<sup>0</sup> amounts are practically identical with those estimated from TPR experiments. The result of the calculation is shown in Fig. 3b. The curves b<sub>3</sub> and b<sub>4</sub> demonstrate the dependence of the percentage of zero valent tin on the total content of tin in catalysts containing 0.5 and 1.0 wt% Pt, respectively. The percentages of Sn<sup>0</sup> increase with increasing tin content. Doubling the Pt content leads to about double the Sn<sup>0</sup> content. Curves b<sub>1</sub> and b<sub>2</sub> describe the dependence of the relative amount of zerovalent tin (Sn<sup>0</sup>/Sn) on the total tin content. This relative amount decreases with increasing total content. Comparing the adsorption data with the TPR data (Table 1) one can see a remarkable accordance. The percentages of Sn<sup>0</sup>, calculated from TPR, are 7, 16, and 22%, whereas the corresponding data from the adsorption on the same three catalysts are 11, 22, and 15%. Despite the uncertainties of the two different methods they give practically the same estimation of the Sn<sup>0</sup> amount.

From the amounts of Sn<sup>0</sup> and of Pt an average composition for the bimetallic Pt-Sn clusters was calculated. This is represented in Fig. 3c. As is to be expected, the tin content in the alloys increases with increasing tin content of the catalysts. In de-

tail the alloy composition varies between about Pt<sub>4</sub>Sn and Pt<sub>2</sub>Sn. With Pt<sub>3</sub>Sn bulk alloy catalytic effects analogous to Pt-Sn/Al<sub>2</sub>O<sub>3</sub> were observed (7).

It is evident that the alloy compositions with 0.5% Pt and 1.0% Pt (Fig. 3c) practically coincide. The alloy composition does not depend on the Pt content in this range of Pt concentration. It depends only on the total tin content. This corresponds to the coincidence of the adsorption curves for the catalysts with 0.5 and 1.0% Pt in Fig. 3a, too. This simple but nevertheless surprising finding should be taken as a hint that there is a relatively even distribution of Sn<sup>0</sup> in Pt. All the Pt clusters seem to be diluted with Sn<sup>0</sup>. If there were a considerable amount of "free" Pt on the surface, it should depend on the Pt content, the total tin content being constant. This did not prove to be true. This conclusion conflicts with both Dautzenberg *et al.* (7) and Baccard *et al.* (11). The former authors assumed a part of the Pt to be "free", while the latter proposed the coexistence of "free" Pt and Sn-rich Pt-Sn alloys.

The dependence of the Sn<sup>0</sup> content of the alloy on the total tin content could be explained by a competition for the tin between alumina, able to stabilize tin as Sn<sup>II</sup>, and Pt clusters, able to stabilize tin as Sn<sup>0</sup> by alloy formation. In this way an equilibrium is established during reduction in hydrogen:



Provided that this equilibrium really exists, the Sn<sup>0</sup> content of the alloy should depend only on the Sn<sup>II</sup> concentration on the carrier, which is approximately equal to the total tin content, and should not depend on the Pt content:  $[\text{Sn}_{\text{Pt}}^0] = K[\text{Sn}_s^{\text{II}}]$ . Moreover, all Pt clusters should contain similar amounts of Sn<sup>0</sup>. These predictions are in accordance with the experimental data.

Titration of the reduced samples with oxygen, Muller *et al.* (13) also found an increased oxygen consumption with tin containing Pt/Al<sub>2</sub>O<sub>3</sub>. They have assumed a part of the Sn<sup>II</sup> to be modified by Pt in such a

way that it becomes able to adsorb additional hydrogen, which is responsible for an increased oxygen titration value. However, as has been shown in Fig. 3a, we found that tin causes no increase but even a strong decrease of hydrogen adsorption. Thus we are inclined to assume that the increased oxygen titration values of Muller *et al.* are not due to an increased hydrogen adsorption but to an increased oxygen adsorption, caused by zerovalent tin, just as with our catalysts.

#### *Effect of Pt on the Reduction Sn<sup>IV</sup> → Sn<sup>II</sup> and Surface Topography*

As already mentioned, the main part of Sn in a calcined Pt-free sample is reduced at about 550°C, whereas a small part is reduced already at 250°C (Fig. 2b). The TPR curve of a Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst (Fig. 2c) is quite different. The main peak of tin at 550°C is absent, and only one peak is observed at about 300°C. This peak is very close to the peak of the tin-free Pt catalyst (Fig. 2a). This indicates that all of the tin is reduced together with Pt; Pt catalyzes the reduction. The mechanism of this catalysis can be explained by two different models, depending on the surface topography: (i) Pt and Sn<sup>IV</sup> are in intimate contact, thus the hydrogen, activated by Pt, can reduce Sn<sup>IV</sup>, or (ii) Pt and Sn<sup>IV</sup> are located separately and the activated hydrogen is transported from Pt to Sn<sup>IV</sup> by spillover over long distances via the alumina.

We tried to prove a long distance spillover mechanism. A 0.5 wt% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was carefully milled with a 1.2 wt% Sn/Al<sub>2</sub>O<sub>3</sub> catalyst (weight ratio 1:2) in a mortar. The powder was pressed into pellets. The TPR curve of the crushed pellets, calcined at 500°C in O<sub>2</sub>, is shown in Fig. 2d. This curve is a simple superposition of the Pt/Al<sub>2</sub>O<sub>3</sub> and the Sn/Al<sub>2</sub>O<sub>3</sub> spectra (Figs. 2a and b); the reduction of tin was not catalyzed. This result fails to support the second model, where Pt and Sn<sup>IV</sup> are located separately, but is compatible with the first model.

A further argument against separated Pt and Sn species in calcined Pt-Sn/Al<sub>2</sub>O<sub>3</sub> was obtained from samples which were only weakly calcined at 250°C. The TPR curve (Fig. 2e) has two peaks, a large Pt-Sn peak and a smaller Sn peak at 550°C. Provided there is neighborhood of Pt and Sn one would expect only one peak, caused by the coreduction of Pt and Sn, and not, depending on the calcination temperature, an additional Sn peak. Consequently we assume that in the weakly calcined sample that part of the tin indicated by the rest of the 500°C peak is not in contact with Pt, whereas in samples calcined at 500°C, Pt and Sn are in rather complete contact.

After reduction and reoxidation of this sample at 300°C one obtains again a two-peak spectrum (Fig. 2f). The large peak is the Pt-Sn peak. The smaller one is interpreted as a tin peak. Such a peak was obtained after reoxidation of a Pt-free Sn/Al<sub>2</sub>O<sub>3</sub> sample at 300°C (Fig. 2g). Therefore we conclude that after reoxidation at 300°C a part of the tin still remains separated from the Pt.

This separation is only cancelled by an oxygen treatment at 500°C, either as a calcination (Figs. 2c and h, respectively) or as a reoxidation (Fig. 4d). In both cases single peak curves were obtained, indicating intimate neighborhood of Pt and Sn. This neighborhood can be developed only if at least one of the oxidized metal species becomes mobile at temperatures of about 500°C. Recently we showed that Pt on Al<sub>2</sub>O<sub>3</sub> forms a mobile surface species at these temperatures: [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]<sub>s</sub> (15).

Our conclusion that after calcination at 500°C an intimate contact between Pt and Sn is achieved is contrary to the proposal of Dautzenberg *et al.* (7) that at higher oxidation temperatures a segregation of Pt and Sn occurs. Burch (14), who did not find Sn<sup>0</sup> by TPR, did not mention the calcination of his Pt-Sn/Al<sub>2</sub>O<sub>3</sub> samples. His TPR curves are similar to ours from low-temperature calcined catalysts with an incomplete contact of Pt and Sn species. Moreover, in his

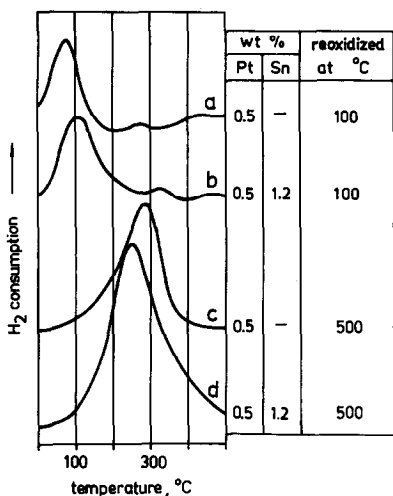


Fig. 4. TPR of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub>, calcined at 500°C, reduced at 500°C, reoxidized at the above temperatures.

samples the Pt dispersion is rather low. Alloying would be hindered by both the above described factors and therefore the detection of Sn<sup>0</sup> by TPR would become more difficult.

The failed spillover experiment and the occurrence of separated reduction of Pt and Sn with low-temperature calcined samples and with chloride-free catalysts (see the later section on influence of chloride) should rule out a reduction by a long distance hydrogen spillover from Pt to Sn. On the other hand, with the low metal contents of our catalysts the coverage of the support is not higher than a few percent. In the case of a uniform distribution of these few percent a long distance spillover would be necessary for a complete coreduction of Pt<sup>IV</sup> and Sn<sup>IV</sup>. However, this spillover is ruled out above. Hence one must assume a non-uniform distribution of Sn<sup>IV</sup>.

Our experiments can be explained by the following patch model: Sn<sup>IV</sup> and Pt<sup>IV</sup> species are concentrated and intimately mixed in small two-dimensional patches on the support surface. The reduction of such a patch starts with the formation of Pt<sup>0</sup> clusters from the Pt<sup>IV</sup> species inside the patch. These clusters activate hydrogen which re-

duces in the next step the Sn<sup>IV</sup> species in the patch. In this way the Sn<sup>IV</sup> reduction is catalyzed and the reduction behavior of tin is governed by Pt.

A minor part of the Sn is taken up by the Pt<sup>0</sup> clusters as Sn<sup>0</sup>. The main part of the Sn is only reduced to an alumina-stabilized Sn<sup>II</sup> species, forming the outer region of the reduced patch.

#### TPR of Reoxidized Pt-Sn/Al<sub>2</sub>O<sub>3</sub>

The formation of different oxidized Pt species during the reoxidation of reduced Pt/Al<sub>2</sub>O<sub>3</sub> can be found by TPR (15). Therefore it was interesting to investigate the influence of tin on the formation of these species.

In Fig. 4 TPR curves of Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> samples are shown in dependence on the temperature of reoxidation. The reoxidation at 100°C of a reduced Pt/Al<sub>2</sub>O<sub>3</sub> sample results in the partial formation of a chloride-free Pt oxide (15), which causes the peak at 100°C (Fig. 4a). The same pretreatment of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> sample gives a very similar curve with a somewhat increased intensity (Fig. 4b).

After reoxidation of Pt/Al<sub>2</sub>O<sub>3</sub> at 500°C a TPR peak appears at about 290°C (Fig. 4c) caused by [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]<sub>s</sub> (15). The corresponding TPR curve of the Pt-Sn/Al<sub>2</sub>O<sub>3</sub> sample is very similar (Fig. 4d), except that the peak temperature is a little lower. This may be due to deficient chloride, caused by tin. After HCl addition the peak temperature of the only once calcined catalyst (Fig. 2c) is reached again.

Not only after reoxidation but also after the first calcination at 500°C the TPR curves of the Pt/Al<sub>2</sub>O<sub>3</sub> and Pt-Sn/Al<sub>2</sub>O<sub>3</sub> samples are very similar (Figs. 2a and c).

This general analogy of the bimetallic samples with the monometallic Pt samples suggests the following explanation. The whole reduction process is governed by the reduction of Pt. On the metallic Pt the hydrogen is activated and reduces the tin species at once. Therefore, just at the reduc-

tion temperature of the Pt species the tin is reduced, too.

Table 2 contains  $\Delta V_{Pt}$  and  $\Delta V_{Sn}$  values of reoxidized Pt/Al<sub>2</sub>O<sub>3</sub>, Sn/Al<sub>2</sub>O<sub>3</sub>, and Pt-Sn/Al<sub>2</sub>O<sub>3</sub>. Calculating these values from the intensities of the TPR peaks (type of Fig. 4b for reoxidation at 100°C, type of Fig. 4d for 500°C) it was a prerequisite that the  $\Delta V_{Pt}$  values, measured with Pt/Al<sub>2</sub>O<sub>3</sub> (15), remain valid with Pt-Sn/Al<sub>2</sub>O<sub>3</sub>. On this understanding, Table 2 can be interpreted as follows: At 100°C only that part of the tin which is alloyed in bimetallic Pt-Sn clusters is oxidized. The residual Sn<sup>II</sup> on the alumina remains almost completely unoxidized, just as tin in Pt-free samples. Under the catalytic influence of Pt the alloyed tin is oxidized from Sn<sup>0</sup> to Sn<sup>IV</sup>. This assumption is in accordance with the observation that in the absence of Pt at 100°C the first traces of the reoxidation Sn<sup>II</sup> → Sn<sup>IV</sup> can be observed by TPR. During TPR Sn<sup>IV</sup> is reduced to Sn<sup>0</sup> again. Given this stoichiometry one can estimate percentages of zero valent tin from  $\Delta V_{Sn}$ . These values nearly coincide with those calculated from oxygen adsorption (Fig. 3b). In particular this consistency of our values, estimated from different experiments, should be regarded as evidence in favor of our model and of its simple prerequisites.

At 500°C all the Pt and all the Sn<sup>II</sup> are essentially reoxidized to the tetravalent state. The  $\Delta V_{Sn}$  values of Pt-Sn/Al<sub>2</sub>O<sub>3</sub>

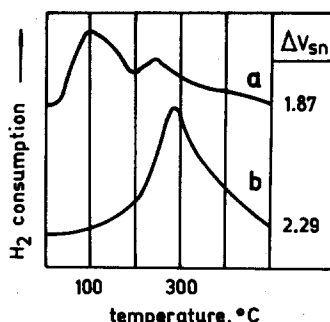


FIG. 5. TPR of chloride-free 0.5% Pt-0.3% Sn/Al<sub>2</sub>O<sub>3</sub>; (a) after reduction and reoxidation at 500°C; (b) after HCl addition and renewed reoxidation at 500°C.

nearly but not completely reach the values of the samples only once calcined (Table 1). It may be that during the several preceding experiments some crystalline Pt was formed, which cannot be easily reoxidized (15).

#### *Influence of Chloride on the Formation of Bimetallic Pt-Sn Clusters*

Chloride, which is an essential component of real reforming catalysts, has been found to have a crucial influence on the Pt/Al<sub>2</sub>O<sub>3</sub> surface chemistry (15, 16). Particularly the mobility of oxidized Pt is inseparably linked with the presence of chloride. One could assume that there are coherences between the mobility of Pt and/or Sn species and the degree of Pt-Sn cluster formation. Therefore the following experiments were made.

The chloride-free catalyst CF 0.5% Pt/0.3% Sn/Al<sub>2</sub>O<sub>3</sub> was used. The corresponding chloride-free Pt/Al<sub>2</sub>O<sub>3</sub> has the same high dispersion as the chloride-containing one, H/Pt = 1.1 (15).

The TPR spectrum of the reduced catalyst being reoxidized at 500°C in O<sub>2</sub> (Fig. 5a) shows two peaks. The low temperature peak corresponds to the reduction of  $\alpha$ -[PtO<sub>2</sub>]<sub>s</sub> (15), possibly containing small amounts of tin. The peak at 250°C indicates an oxidic tin species, reduced independently of Pt. No complete neighborhood of Pt and Sn species seems to be reached. Now the sample was wetted with the same

TABLE 2

Valence Changes of Sn and Pt in Reoxidized Pt-Sn/Al<sub>2</sub>O<sub>3</sub>

wt% Sn	wt% Pt	Reoxidation temperature				
		100°C			500°C	
		$\Delta V_{Pt}$	$\Delta V_{Sn}$	% Sn <sup>0</sup> /Sn	$\Delta V_{Pt}$	$\Delta V_{Sn}$
—	0.5	2.5 <sup>a</sup>	—	—	4.0 <sup>a</sup>	—
1.2	—	—	≈0	≈0	—	1.94
0.6	0.5	2.5	0.61	15	—	—
1.2	0.5	2.5	0.33	8	4.0	1.98
1.2	1.0	2.5	0.82	20	4.0	2.06

<sup>a</sup>  $\Delta V_{Pt}$  is assumed to reach the same value in tin-containing catalysts.



volume of 0.5 N HCl, dried, and reoxidized at 500°C in O<sub>2</sub> once more. The following TPR gave a single peak (Fig. 5b) identical with those of calcined chloride-containing Pt-Sn/Al<sub>2</sub>O<sub>3</sub> (Fig. 2c).

This transition from the chloride-free surface compounds to the typical surface compounds of chloride-containing Pt-Sn/Al<sub>2</sub>O<sub>3</sub> is analogous to the system Pt/Al<sub>2</sub>O<sub>3</sub> (15). In the monometallic system the less easily reducible [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]<sub>s</sub> was formed from the easily reducible chloride-free α-[PtO<sub>2</sub>]<sub>s</sub> by reaction with chloride at 500°C. This [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]<sub>s</sub> is mobile, contrary to the chloride-free platinum oxide. In the present TPR curves of the system Pt-Sn/Al<sub>2</sub>O<sub>3</sub> the HCl addition causes not only the shift from the α-[PtO<sub>2</sub>]<sub>s</sub> peak to the [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]<sub>s</sub> peak but also the disappearance of the separate tin peak. This disappearance indicates that Pt and all of the tin must now be located together. This implies that at least one of the species must have become mobile, e.g., the complex [Pt<sup>IV</sup>O<sub>x</sub>Cl<sub>y</sub>]<sub>s</sub>.

The transformation of separated tin into tin in the neighborhood of Pt should increase the content of zero valent tin, too. This could be proved by TPR. The ΔV<sub>Sn</sub> value increased from 1.87 before to 2.29 after the HCl treatment. The increased Sn<sup>0</sup> content is additionally confirmed by corresponding hydrogen and oxygen adsorption measurements after both the TPR measurements in Fig. 5. In Table 3 the adsorption of the chloride-free CF 0.5% Pt/0.3% Sn/Al<sub>2</sub>O<sub>3</sub> and of the chloride-containing 0.5% Pt/

0.3% Sn/Al<sub>2</sub>O<sub>3</sub> catalyst is compared. The chloride-free catalyst adsorbs more hydrogen than oxygen before, but less hydrogen than oxygen after the HCl treatment. The chloride-containing catalyst adsorbs before and after the HCl treatment less hydrogen than oxygen. After the HCl treatment the values for both the catalysts are practically equal.

From Fig. 3a it can be seen that Sn-free Pt adsorbs more hydrogen than oxygen, whereas with increasing tin content this ratio changes and more oxygen than hydrogen is adsorbed. By comparing with Fig. 3c one can see that decreasing hydrogen adsorption and increasing oxygen adsorption indicate increasing alloying. These relations enable us to interpret the adsorption data in Table 3. During HCl addition the ratio of adsorbed hydrogen and oxygen is changed in a way indicating an increased alloying of Pt and Sn.

Hence, both from the TPR and the adsorption results one can conclude that the amount of alloyed tin is increased by the chlorination. Chloride forms mobile Pt and/or Sn species. The mobility is a necessity for establishing sufficient neighborhood of Pt and Sn species and consequently for a higher degree of alloy formation.

## CONCLUSIONS

The reduction and the reduced state of highly dispersed chloride-containing Pt-Sn/Al<sub>2</sub>O<sub>3</sub> have been investigated by TPR and adsorption of oxygen and hydrogen.

(1) A minor part of the tin is reduced by hydrogen from the state Sn<sup>IV</sup> to the state Sn<sup>0</sup>. This part forms bimetallic "alloy" clusters with Pt.

(2) The amount of the alloyed tin increases with increasing total tin content and with increasing Pt content. The tin content of the alloy increases with increasing total tin content, too.

(3) The major part of the tin is only reduced to the state Sn<sup>II</sup>. This state Sn<sup>II</sup> is strongly stabilized by interaction with alumina.

TABLE 3

Influence of Chloride on Hydrogen and Oxygen Adsorption in Chloride-Free and Chloride Containing 0.5% Pt-0.3% Sn/Al<sub>2</sub>O<sub>3</sub>

Pretreatment	Chloride-free		Chloride containing	
	H/Pt	O/Pt	H/Pt	O/Pt
Reduced, reoxidized at 500°C, 1. TPR	0.75	0.56	0.54	0.74
HCl addition, reoxidized at 500°C once more, 2. TPR	0.38	0.59	0.42	0.57

(4) The reduction of all the Sn<sup>IV</sup> is catalyzed by Pt. There are strong arguments that this is caused by an intimate contact of Pt and Sn. This contact is formed during high temperature calcination by mobile Pt<sup>IV</sup> and/or Sn<sup>IV</sup> species. The result should be small two-dimensional patches on the alumina surface. By reduction these patches are converted to Pt<sup>0</sup>-Sn<sup>0</sup> alloy clusters, surrounded by surface stabilized Sn<sup>II</sup> species.

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