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Formation of multilayered tin organometallic surface species. Preparation of new type of supported Sn–Pt catalysts

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Abstract

In this study, a new aspect of anchoring of tin organic moieties onto platinum is described and discussed. The new approach resulted in substantial increase of the Sn/Pt ratio in tin modified Pt/SiO_2 catalysts. In the earlier approach, adsorbed hydrogen was exclusively used for tin anchoring, resulting in a monolayer of tin organic moieties at the top of platinum. In the new approach, a large excess of either tin tetraethyl or hydrogen was used in the tin-anchoring reaction. The presence of coadsorbents, such as oxygen, also led to a substantial increase of the amount of tin anchored. When the primary formed $-SnR_3$ surface entities were partially decomposed, the coordinatively formed unsaturated $-SnR_2$ and –SnR surface species provided additional anchoring sites for the next layer of SnR_4. In the presence of adsorbed oxygen, additional new types of landing sites were created to anchor SnR_4 in the neighborhood of platinum. The above approach resulted in $Sn–Pt/SiO_2$ catalysts with exclusive tin–platinum interaction and an Sn/Pt ratio ca. 2. Results obtained in this study also reveal that the formation of surface organometallic moieties takes place in a stepwise way, e.g. the buildup of tin organic moieties occurs layer-by-layer. The supported Sn–Pt bimetallic entities formed showed both high activity and selectivity in the hydrogenation of crotonaldehyde to crotylalcohol. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Pt/SiO_2 catalyst; $Sn–Pt/SiO_2$ catalyst; Surface organometallic chemistry; Controlled surface reactions; Tin tetraethyl; Catalyst modification; Hydrogenation of crotonaldehyde; Formation of crotylalcohol

1. Introduction

1.1. *Surface organometallic chemistry of tin tetraalkyls*

Controlled surface reactions (CSRs) between hydrogen adsorbed on transition metals and tin tetraalkyls are widely used to prepare tin-modified skeletal or supported bimetallic catalysts [1–12]. In these catalysts, either a bimetallic alloy-type surface species had been evidenced [13] or poisoning of the first metal by small amount of tin was achieved [14–17]. These bimetallic catalysts appeared to be active and selective in different selective hydrogenation reactions [9,14,16,18] and in the reactions of fatty acid esters [8] and hydrocarbons [19,20].

Surface chemistry involved in the modification of supported and skeletal metal catalysts by tin tetraalkyls can be given using the following general equations [1,3,4]:

$$MH_{ads} + SnR_4 \rightarrow \underset{PSC}{M–SnR_{(4-x)}} + xRH \qquad (1)$$

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$$\mathrm{M{-}SnR_{(4\text{-}x)}} + (4\text{-}x)/2\mathrm{H_2} \rightarrow \underset{\mathrm{(SBS)}}{\mathrm{Sn{-}M}} + (4\text{-}x)\mathrm{RH} \qquad (2)$$

In reaction (1), hydrogen adsorbed on metals (M) reacts with tin tetraalkyls with the formation of an anchored primary surface complex (PSC), with general formula of $\mathrm{M{-}SnR_{(4\text{-}x)}}$. Reaction (1) is often called the tin anchoring step. The PSC formed in reaction (1) is decomposed in a hydrogen atmosphere to obtain supported bimetallic species (SBS). Depending on the conditions used in reaction (2), the obtained SBS can form either a bimetallic alloy [13] or a two-dimensional tin overlayer atop the first metal [14]. The decomposition of PSC at high temperature leads to the formation of alloy-type surface species [13,20].

As it emerges from earlier results, the exact separation of the anchoring and decomposition steps cannot always be achieved [2,6–9,12]; however, in our studies [1,3,4,11] a special attempt was made to separate surface reactions (1) and (2) as much as possible.

In addition, it should also be mentioned that an exclusive formation of tin–platinum interaction in reaction (1) requires special control to avoid (i) reactions with the involvement of surface OH groups and (ii) adsorption of tin tetraalkyls onto the support. In order to achieve a high degree of control in surface reaction (1), the rate of surface reaction (1) should be much higher than either the rate of adsorption of tin tetraalkyls onto the support or the rate of side reactions with the involvement of support OH groups.

In order to minimize the tin–support and to maximize the tin–metal (Pt, Ni) interaction in reaction (1), the following measures were taken:

1. use of relatively low concentration of tin tetraalkyls;
2. avoiding high reaction temperature;
3. use of short reaction times; and
4. strong separation of reaction (1) from reaction (2).

The above measures provided a definite guaranty both, for the exclusive introduction of tin onto platinum (or other metals) and the suppression of tin–support interaction. However, the disadvantage of the above strict approach was the strong limitation of the amount of tin introduced. In our approach [1,3,4,11], the amount of tin introduced was controlled by the chemical nature of PSC formed at the top of the first metal. Beyond a definite coverage level, the PSC formed created a specific 'shielding'. On account of the above shielding, the longer the length of the alkyl groups in PSC the lower the amount of tin anchored onto the first metal. As it emerges from our earlier results [1,3,4], upon using tin tetraethyl the maximum $\mathrm{Sn_{anch}/Pt_{surf}}$ ratio is ca. 0.4. The above result is supported by computer modelling made in this study. It should also be mentioned that, in studies where no attempt was made to separate the first and second steps of tin anchoring, relatively high $\mathrm{Sn_{anch}/M}$ ratios ($\mathrm{Sn_{anch}/M}>2$) were obtained [6–10,12].

The goal of this work was to find ways and means to increase the amount of tin anchored onto the platinum and maintain the overall control of tin anchoring, i.e. to suppress the amount of tin introduced onto the support. A further aim of this study is the extension of our approach to supported platinum catalysts with high platinum load as in our earlier studies platinum catalysts with 0.3–0.5 wt% Pt were modified [1,2,4]. In this study, an attempt was also made to show that anchoring of tin organic moieties onto supported platinum is a stepwise process leading to the formation of multilayered structures.

2. Experimental part

2.1. Computer modelling

The computer modelling was performed using the MSI: InsightII program package. The optimized geometries of the $\mathrm{-Sn(C_2H_5)_n}$ (n=2–4) and $\mathrm{-SnR_2(O)}$ species were determined by the Discover module, using the *esff* force field. For the $\mathrm{-Sn(C_2H_5)_3}$ and $\mathrm{-Sn(C_2H_5)_2}$ species the AMPAC/MOPAC module with the AM1 semi-empirical method was also used. The C–Sn–C bond angles varied between 99.30° (for $\mathrm{-SnR_2O}$) and 113.54° (for $\mathrm{-SnR_2}$). The relative orientation of species formed either in the first or the second layer and also the positions of the anchored species were set manually. Multifold sites on the plain surfaces (Pt(111) and Pt(100)) and the top of Pt on the kink and corner sites were used to anchor $\mathrm{-Sn(C_2H_5)_2}$ or $\mathrm{-Sn(C_2H_5)_3}$ moieties. The Sn–Pt distance was between 0.35 and 0.40 nm.

2.2. Catalyst preparation

The silica-gel prepared in the Boreskov Institute of Catalysis (Novosibirsk, Russian Federation) containing 0.02 wt% impurities was used as a support. Surface area (S=302 m^2/g), pore volume (V_p=0.95 cm^3/g) and mean pore diameter (d_p=12 nm) were determined by N_2 adsorption. The silica-supported monometallic catalyst containing 3 wt% Pt was obtained by the ion-exchange technique using $[Pt(NH_3)_4]Cl_2$ as precursor compound. The ion-exchange was carried out at 30–35°C for 1 h and a pH of 10 adjusted by ammonia solution. After filtration, the catalyst was washed free of chloride ions with demineralised water until pH of 7, and then dried in two steps at 60 and 120°C for 3 and 2 h, respectively, (heating rate=0.3°C/min). The catalyst was reduced under hydrogen for 4 h at 300°C (heating rate=1.5°C/min). The H/Pt ratio of the Pt/SiO_2 catalyst used was 0.52 measured by hydrogen chemisorption. The total amount of the overall hydrogen pool (H_{total}/Pt) determined by TPD was 2.3. The above amount includes both, chemisorbed and spilled over hydrogen.

2.3. *Study of the tin-anchoring step*

The catalyst was re-reduced in hydrogen prior to the tin anchoring step. The temperature of re-reduction was 300°C for 60 min. After re-reduction, the catalyst was cooled in a hydrogen atmosphere to room temperature, followed by purging with argon for 30 min to eliminate the amount of physisorbed hydrogen. The catalyst was transferred into a glass reactor and slurred with deoxygenated benzene either in an argon or a hydrogen atmosphere. Upon achieving the required reaction temperature, the tin-anchoring reaction was started by injecting tin tetraethyl. It should also be mentioned that, in the present study, the reaction time of surface reaction (1) was sufficiently enhanced as compared to those used in our earlier studies [1,3,4].

Reaction (1) was monitored by determining the amount of hydrocarbons formed by GC using a 3 m long Al_2O_3 column at 100°C. In selected experiments, the amount of $Sn(C_2H_5)_4$ in the reaction mixture was also determined by using a 1.5 m long silica column coated with 10% Silicon 410 and operated at 160°C. This analysis provided the sum of reacted and adsorbed tin tetraethyl. The amount of adsorbed tin tetraethyl was determined by analyzing the washing solution obtained after washing out the unreacted tin tetraalkyl from catalyst particles. After surface reaction (1), the catalyst was washed four times with benzene at 50°C, followed by washing twice with n-hexane at the same temperature. The catalysts were dried in vacuum (5 torr) at 50°C for 1 h.

2.4. *Decomposition of primary formed surface complex.*

The decomposition of PSC was carried out in a hydrogen atmosphere by thermal programmed reaction (TPR) technique using the following experimental parameters: heating rate=5°C/min, hydrogen flow rate=30 cm^3/min, amount of catalyst=0.4–0.6 g. The products of decomposition (C_2H_6 and C_2H_4) were analyzed by GC (see details in Section 2.3). After the decomposition the tin content of the modified catalysts was determined by AAS and was compared with the amount of tin calculated from the overall material balance of tin anchoring.

The TPR peaks obtained in the decomposition step were deconvoluted. First, the TPR curves obtained at low Sn_{anch}/Pt_s ratios were deconvoluted into three individual TPR peaks. The position and the half width of each peak (in the range of ±6 and 12°C, respectively) was fixed for the subsequent deconvolution. The stepwise appearance of the new decomposition peaks was used in the consecutive deconvolution procedure. The heights of the peaks were determined, and suggested a Gaussian form of the individual TPR peaks.

2.5. *Calculation of the overall material balance of tin anchoring.*

The material balance of tin anchoring was calculated, based on the determination of the amount of C_2 hydrocarbons formed in reactions (1) and (2). In reaction (1), a correction was made to take into account the amount of hydrocarbons (ethane or ethylene) dissolved in benzene. The material balance allowed to separately calculate the amount of alkyl groups reacted either in the first step of anchoring (n^I, mol/g_{cat}) or during the decomposition of PSC in the TPR experiment (n^{II}, mol/g_{cat}). The value of n^I contains the amount of both ethane and ethylene. In this way, the total amount of tin anchored could also be calculated. The amount of tin calculated in this way had a good agreement with the amount of tin determined by AAS (see data presented in Table 2).

The material balance allowed us to calculate the value of x (see reaction (1)). In this way, the stoichiometry of surface reaction (1) could be determined.

2.6. Hydrogenation experiments

The prepared Sn–Pt/SiO_2 catalysts were tested in the hydrogenation of crotonaldehyde (CA) in gas phase under atmospheric pressure in the 60–100°C range. Prior to the catalytic reaction the catalysts were pre-reduced in a hydrogen atmosphere at 180–340°C. Special care was taken not to contaminate the catalysts with oxygen prior to their use in the catalytic reaction.

In the gas phase, hydrogenation of CA over different modified platinum catalysts, fast ageing under time-on-stream condition, was observed. In order to overcome the ageing induced deactivation problem, the conventional continuous-flow reactor was used in a periodic mode by introducing the CA–hydrogen mixture in the form of a long pulse (pulse length=7 min, product analysis at the end of the pulse) followed by a long pulse of pure hydrogen (7 min). The use of long hydrogen pulse resulted in full or partial restoration of the catalytic activity. Upon using 15–20 consecutive pulses, a constant activity (and selectivity) period was achieved allowing to carry out kinetic experiments. Product analysis was done by the GC method using a 3-m long glass column (Chromosorb W AWDMCS coated with 10% Carbowax 20M). Starting at 60°C for 6 min, followed by heating with 10°C/min up to 90°C, it was kept at the above temperature for 5 min.

3. Results

3.1. Computer modelling of $-SnR_3$ and $-SnR_2$ moieties anchored onto the platinum cluster.

Three-dimensional platinum clusters with Pt (111) plain surface were used for modelling. The size of the cluster is as follows: nine platinum atoms in the diagonal of the lowest *hexagonal* surface and either two or three layers of platinum on top. The overall size of this hypothetical metal cluster was 2.2 nm. The calculated ratio of Pt_{surf}/Pt_{total} for the cluster having three layers of Pt is 0.56, i. e. very close to the H/Pt ratio found by hydrogen chemisorption (H/Pt=0.52). The corresponding two-layered structure resulted in a Pt_{surf}/Pt_{total} ratio equal to 0.68, a slightly higher value than the H/Pt ratio found experimentally.

We have calculated the amount of tin organic moieties with general formula of $-Sn(C_2H_5)_3$ or $-Sn(C_2H_5)_2$ at the top of the above Pt cluster by building up a monolayer of either $-Sn(C_2H_5)_3$ or $-Sn(C_2H_5)_2$. The modelling was based on earlier results, thus indicating that in the first step of tin anchoring reaction only one or two alkyl groups can be lost. The results of modelling using a Pt cluster made from three layers of Pt atoms are shown in Fig. 1(A and B). Fig. 1(A and B) shows the top view of anchored $-Sn(C_2H_5)_3$ and the side view of anchored $-Sn(C_2H_5)_2$, respectively. Further results of modelling are summarized in Table 1. These results indicate that the maximum Sn_{anch}/Pt_{surf} ratio is between 0.31–

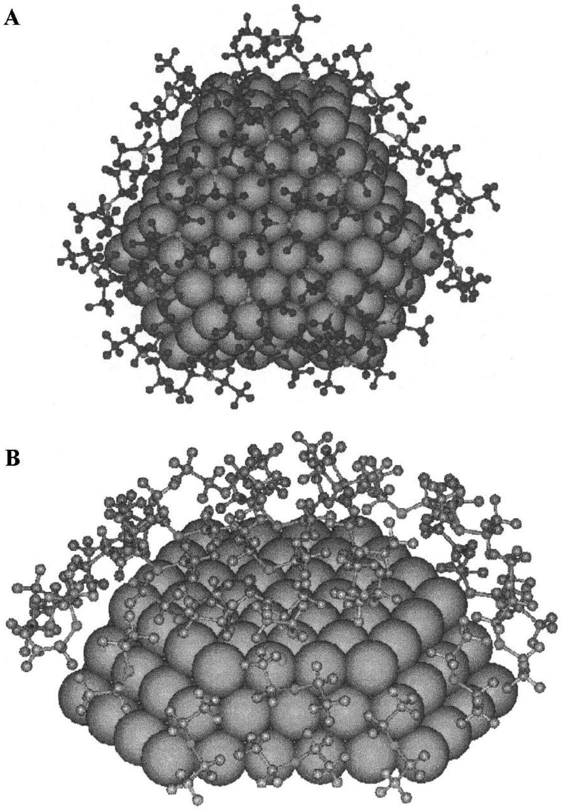

Fig. 1. Computer modelling of organometallic moities anchored onto the platinum cluster. A, anchoring of $-SnR_3$ (top view); B, anchoring of $-SnR_2$ (side view).

Table 1
Computer modelling of anchoring $-Sn(C_2H_5)_3$ and $-Sn(C_2H_5)_2$ moieties onto small Pt cluster [a]

Number of Pt layers	Pt_{surf}/Pt_{total}	Number of $-Sn(C_2H_5)_3$	Number of $-Sn(C_2H_5)_2$	Sn_{anch}/Pt_{surf} for $-Sn(C_2H_5)_3$	Sn_{anch}/Pt_{surf} for $-Sn(C_2H_5)_2$
Two	0.68	22	27	0.38	0.47
Three	0.57	25	30	0.31	0.37

[a] The size of the Pt cluster is 2.2 nm.

0.37 and 0.38–0.47 for $-Sn(C_2H_5)_3$ and $-Sn(C_2H_5)_2$ moieties, respectively.

3.2. *Controlled surface reaction in the presence of adsorbed hydrogen.*

3.2.1. *General pattern*

The general kinetic behaviour of surface reaction (1) at three different concentrations of $Sn(C_2H_5)_4$ is shown in Fig. 2(A–C). Fig. 2(A and C) shows the main differences in the formation of C_2 hydrocarbons at low and high concentration of $Sn(C_2H_5)_4$, respectively. The concentration difference covers more than two orders.

The above-mentioned kinetic curves show that in the first 30–60 min surface reaction (1) is selective, i.e. in this period the formation of ethane is exclusive. At low concentration of tin tetraethyl, i.e. up to 2.53×10^{-2} M, no ethylene formation was observed at all. In the experiment shown in Fig. 2(A), the formation of ethane is completely terminated after reaching a certain level due to the total consumption of tin tetraethyl. Total consumption implies the sum of the amount of tin tetraethyl reacted in surface reaction (1) and that of weakly adsorbed onto the support. It is noteworthy that the latter was completely removed by the washing procedure used.

At higher $[Sn]_o/Pt_{surf}$ ratios small amount of ethylene has been detected in reaction (1). However, on this Pt/SiO_2 catalyst under standard condition (i.e. in the concentration range of $[Sn(C_2H_5)_4]_o$ up to 8.10×10^{-2} M), the overall amount of ethylene formed does not exceed 15% of the sum of C_2 hydrocarbons. The appearance of ethylene, as the reaction proceeds, is an indication for the partial loss of control in surface reaction (1).

As seen from Fig. 2(c), the kinetic curves of ethane formation show two definite parts, a fast and a slow rate part. The fast rate part is maintained up to 35–45% of conversion. At low $Sn(C_2H_5)_4$ concentration, the second part cannot be seen as the reaction has been terminated. It is worth mentioning that the slow rate part in the kinetic curves shows a strong parallelism with the appearance of ethylene. This parallelism is

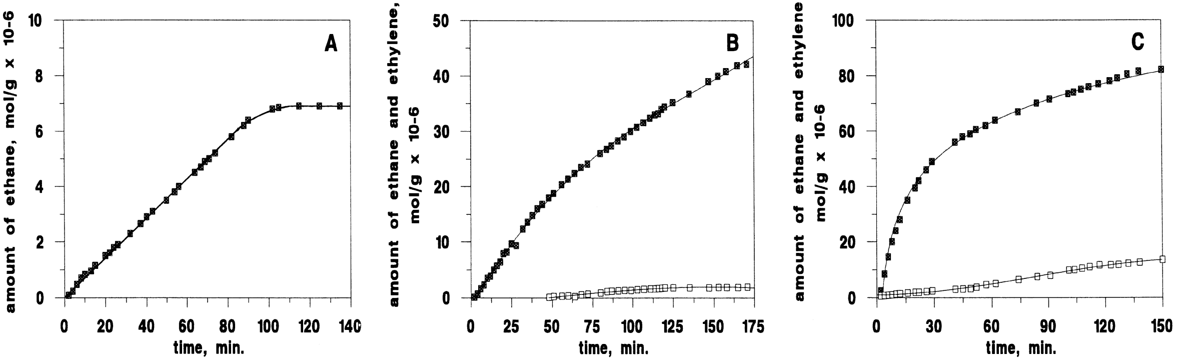

Fig. 2. Kinetic curves of the formation of ethane and ethylene in reaction (1). Reaction temperature: 50°C. A $-[Sn(C_2H_5)_4]_o=0.08\times10^{-2}$ M, $[Sn]_o/Pt_{surf}=0.09$. B – $[Sn(C_2H_5)_4]_o=1.27\times10^{-2}$ M, $[Sn]_o/Pt_{surf}=1.58$. C – $[Sn(C_2H_5)_4]_o=8.10\times10^{-2}$ M, $[Sn]_o/Pt_{surf}=9.83$. (■), ethane; and (□), ethylene.

Table 2
General data related to tin anchoring. Catalyst Pt/SiO_2.

Exp. No.	$[SnEt_4]_o$ $\times 10^{-2}$ (M)	$[Sn]_o/Pt_{surf}$	$W_o \times 10^{-6}$ (mol/g_{cat} min)	$n^I \times 10^{-6}$ (mol/g_{cat}) [a]	$C_2H_4 \times 10^{-6}$ (mol/g_{cat}) [b]	$n^{II} \times 10^{-6}$ (mol/g_{cat}) [c]	X	Sn_{anch}/Pt_{surf} (at/at) [d]	Sn_{anch}/Pt_{surf} (at/at)[e]
1	0.08	0.09	0.07	6.9	–	11.7	1.48	0.06	–
2	0.20	0.25	0.10	8.9	–	14.7	1.51	0.07	–
3	0.35	0.42	0.16	13.5	–	23.9	1.44	0.12	0.13
4	1.27	1.58	0.43	44.0	1.9	81.7	1.40	0.39	0.38
5	2.53	3.01	1.15	66.6	–	113.4	1.48	0.56	0.61
6	4.31	5.28	1.49	84.9	2.4	169.5	1.33	0.79	–
7	8.10	9.83	3.17	95.0	13.0	273.9	1.03	1.15	–
8	27.86	33.50	3.50	129.0	25.0	396.2	1.00	1.64	1.41

[a] Total amount of C_2 hydrocarbons formed in reation (1).
[b] Amount of ethylene in reaction (1).
[c] Amount of ethane formed in reaction (2).
[d] Sn_{anch}/Pt_{surf} ratio calculated from the overal material balance of tin anchoring.
[e] Sn_{anch}/Pt_{surf} ratio calculated from the tin content determined by AAS.

very pronounced at high $[Sn]_o/Pt_{surf}$ ratios (see Fig. 2C).

Results presented in Fig. 2 also show that upon increasing the initial concentration of tin tetraethyl both, the initial rate of surface reaction (1) and the amount of hydrocarbons formed increased. Further data related to the rate and material balance of surface reaction (1) obtained at different initial tin tetraethyl concentrations are summarized in Table 2.

While the increase of the initial concentration of tin tetraethyl did not result in a significant difference in the overall kinetic behaviour of surface reaction (1), surface reaction (2), i.e. the decomposition of PSC in a hydrogen atmosphere, showed marked differences depending on the $[Sn]_o/Pt_{surf}$ ratio as seen in Fig. 3(A–D). At low concentrations of tin tetraethyl, two major TPR peaks were detected ca. 30 and 50°C. The increase of the $[Sn]_o/Pt_{surf}$ ratio up to 1.5 resulted in a broadening of the TPR peak up to 150°C, without showing any further high temperature peaks. However, the broadening indicated that further peaks ca. 80 and 110°C should exist. If the concentration of tin tetraethyl increased to $[Sn]_o/Pt_{surf}$=9.8, two further TPR peaks were detected ca. 110 and 150°C (see Fig. 3(C)). Further increasing on the $[Sn]_o/Pt_{surf}$ ratio an additional new peak and a shoulder was always detected at ca. 200 and 260°C, respectively. The appearance of further new TPR peaks, as the $[Sn]_o/Pt_{surf}$ ratio increases, indicates that the increase of the $[Sn]_o/Pt_{surf}$ ratio leads to the formation of different types of surface species containing $-Sn(C_2H_5)_{(4\text{-}x)}$ moieties, probably with different extents of dealkylation and different environment.

3.2.2. Material balance

Results obtained in the first and second steps of tin anchoring allowed us to calculate the overall material balance of tin anchoring. These data are also included in Table 2. The calculated material balance for tin (see Sn_{anch}/Pt_{surf} ratios) was compared with the amount of tin determined by AAS. This comparison shows a very good agreement. This is a very important issue indicating that in our preparation procedures the amount of undetected alkyl groups is negligible.

Two important experimental parameters were calculated from the material balance: (i) value of x; and (ii) the Sn_{anch}/Pt_{surf} ratio. The value of x shows the amount of alkyl groups lost in the first step of anchoring (see reaction (1)). In other words, x reveals the stoichiometry of surface reaction (1). As seen from the data given in Table 2, this value is in the range of 1.5–1.0. In our previous studies, using Pt/Al_2O_3 catalysts with low Pt loading (0.3–0.6 wt%), the value of x was 1.0±0.1 [1,3]. The value 1.5 indicates that, at low concentrations of tin tetraethyl, the mean number of alkyl groups lost in the first anchoring step is ca. 1.5. It also means that in reaction (1), under the given experimental condition, different surface species, such as $-SnR_1$ (x=3), $-SnR_2$ (x=2) and $-SnR_3$ (x=1) anchored onto platinum can be formed. The decrease

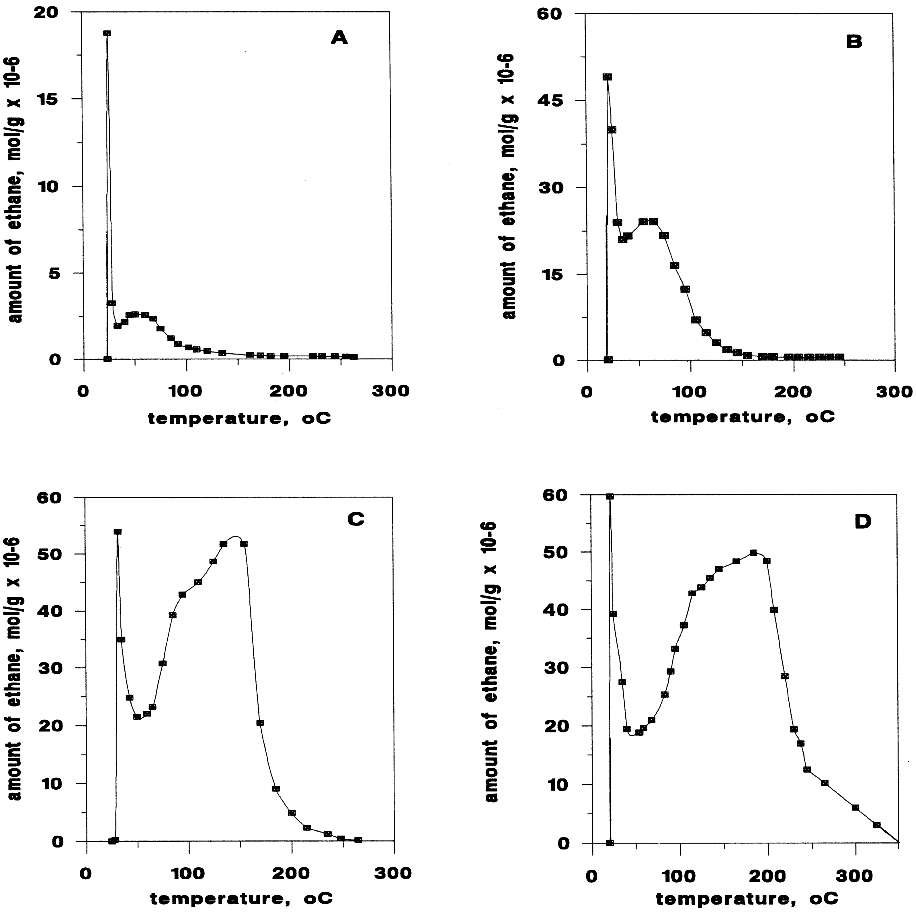

Fig. 3. Decompsition of the surface complexes by thermal programmed reaction technique. The influence of the $[Sn]_o/Pt_{surf}$ ratio on the decomposition pattern. A – $[Sn]_o/Pt_{surf}=0.09$; B – $[Sn]_o/Pt_{surf}=1.58$; C – $[Sn]_o/Pt_{surf}=9.83$; and D – $[Sn]_o/Pt_{surf}=33.49$.

of x observed at high concentration of tin tetraethyl suggests (see Table 2) that, in addition to the formation of the above forms of tin, organic moieties anchoring of SnR_4 species onto the first layer, i.e. the formation of a second anchored layer, can also take place.

The obtained Sn_{anch}/Pt_{surf} ratio shows a strong dependence on the initial tin concentration. The most important information is that the above-mentioned ratio exceeds the value of 0.4, characteristic for the monolayer formation of $–SnR_{(4-x)}$ obtained earlier [1,3,4]. The results obtained by computer modelling also show that the monolayer of $–SnR_2$, and $–SnR_3$ can give Sn_{anch}/Pt_{surf} ratios between 0.31 and 0.47 (see Table 1). However, as emerges from the data given in Table 2, the experimentally obtained highest Sn_{anch}/Pt_{surf} ratio reaches the value ca. 1.6. This high Sn_{anch}/Pt_{surf} value can be obtained if (i) 'naked' tin (SnR_o) and strongly dealkylated species, such as $–SnR$, $–SnR_2$, are also formed in the first anchored layer, and (ii) a second tin organic layer containing $–SnR_4$ and $–SnR_{(4-y)}$ is also formed at the top of the first one.

Table 2 shows also that the overall value of x is a function of Sn_{anch}/Pt_{surf}. In this respect, three distinct areas of Sn_{anch}/Pt_{surf} can be distinguished:

(i) x has a constant value ca. 1.46 up to $Sn_{anch}/Pt_{surf}=0.56$;

(ii) x is decreasing from 1.46 to 1.0 in the range of $Sn_{anch}/Pt_{surf}=0.56–1.15$; and

(iii) the value of x is constant and close to one when $Sn_{anch}/Pt_{surf}>1.15$.

These data show that, depending on the amount of tin anchored, the stoichiometry of the formed surface species is changing. At high Sn_{anch}/Pt_{surf} ratios the formation of surface species containing SnR_4 moieties increases.

The form of the TPR curves obtained at high Sn_{anch}/Pt_{surf} ratios (see Fig. 3(C and D)) indicates that in these curves the low temperature TPR peaks observed ca. 30, 50, and 80°C were maintained and new peaks ca. 110 and 150°C (see Fig. 3(C)) and 200 and 260°C (see Fig. 3(D)) appeared. The TPR pattern shown in Fig. 3 indicates that the anchoring of tin organic moieties is a stepwise buildup process.

Fig. 4 shows the deconvolution of the TPR peaks obtained at different Sn_{anch}/Pt_{surf} ratios. The deconvolution allowed us to calculate separately the amount of C_2 hydrocarbons formed up to 80°C and above. Both the material balance (see Table 2) and the form of TPR curves indicate that the monolayer formation of PSC can be reached if the Sn_{anch}/Pt_{surf} ratio is ca. 0.4–0.5. This value has been reached in experiment when $[Sn]_o/Pt_{surf}$ was 1.58 (exp. No. 4 in Table 2). The TPR pattern of the above experiment (see Fig. 3(B) and Fig. 4(B) indicates that the contribution of the high temperature peaks (above 110°C) to the overall

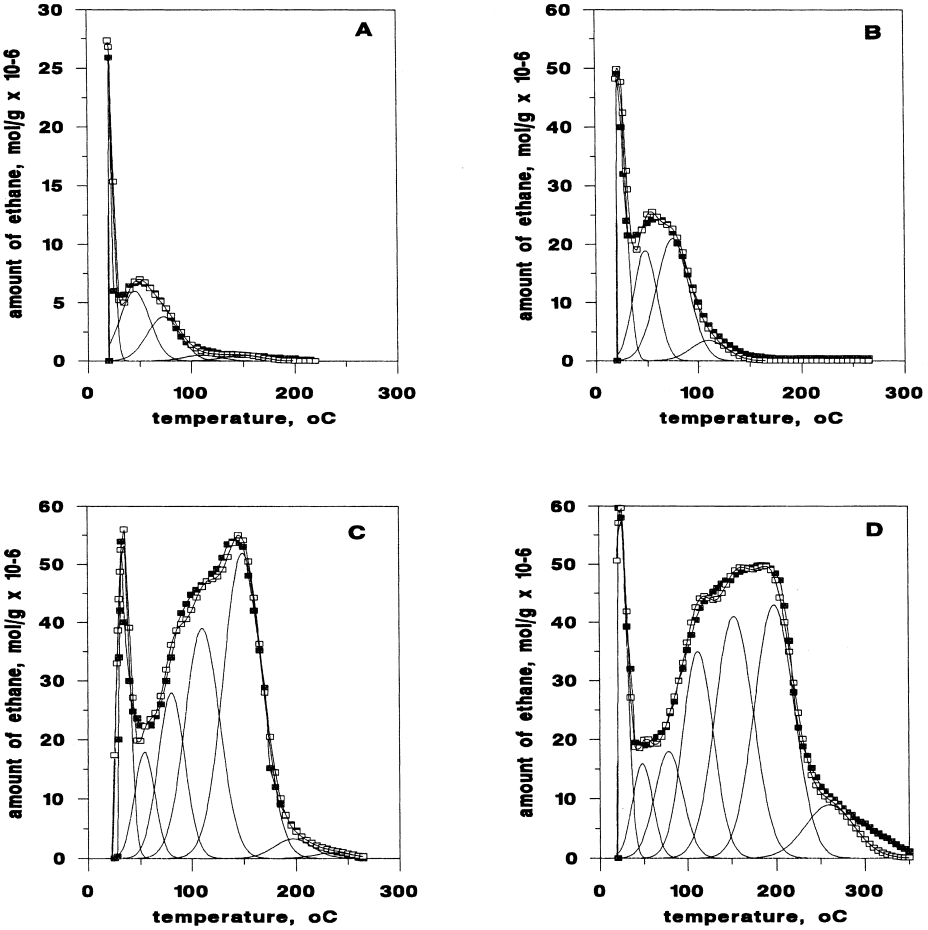

Fig. 4. Deconvolution of the TPR peaks. A – $[Sn]_o/Pt_{surf}=0.42$; B – $[Sn]_o/Pt_{surf}=1.58$; C – $[Sn]_o/Pt_{surf}=9.83$; and D – $[Sn]_o/Pt_{surf}=33.49$. (■), Measured; and (□), fitted.

Table 3
The influence of the reaction temperature of the tin-anchoring step [a]

Temperature (°C)	Initial rate ($\times 10^{-6}$, mol/$g_{cat}\times$ min)	Sn_{anch}/Pt_{surf} (at/at)	X
27.0	0.11	0.21	n.a. [b]
34.5	0.15	0.22	n.a. [b]
39.0	0.20	0.27	n.a. [b]
50.0	0.43	0.39	1.40
55.0	0.47	0.48	1.55
60.0	2.14	0.80	1.7

[a] Initial concentration of $Sn(C_2H_5)_4$=1.27×10^{-2} M, $[Sn]_o/Pt_{surf}$=1.58, amount of catalyst=1.0 g.

[b] Insofar as the washing of the adsorbed and unreacted tin tetraethyl was done at 50°C, x values could not be calulated accurately.

decomposition is negligible. Based on the above findings, the high temperature peaks at 110, 150 and 200°C were attributed to the new type of surface species, such as tin organic moieties in the second layer, with the general formula $-SnR_{(4-y)}$. The shoulder ca. 260°C was tentatively attributed to SnR_4 adsorbed onto SiO_2. It should be mentioned that the shoulder ca. 260°C was formed when extremely high concentrations of tin tetraethyl were used for tin anchoring (see Table 2, exp. 8).

3.2.3. *Influence of the reaction temperature of the tin-anchoring step*

The influence of the reaction temperature of surface reaction (1) was investigated in the 27–60°C range. The corresponding experimental data are given in Table 3 and Fig. 5, which show the TPR pattern of the decomposition of PSC formed at different temperatures.

The initial rate showed a good temperature dependence in the 27–55°C range. The calculated energy of activation was 42.6±1.9 kJ/mol. The experiment carried out at 60°C did not fit into the overall trend observed. In this experiment, both, the initial rate of reaction (1) and the amount of tin anchored was much higher than in other experiments. It means that, at 60°C, a new type of surface reaction was involved in the tin-anchoring process.

As seen from the data given in Table 3, the amount of tin anchored strongly depended on the reaction temperature. The obtained Sn_{anch}/Pt_{surf} ratios indicated that, in the 27–50°C range, the PSC forms a

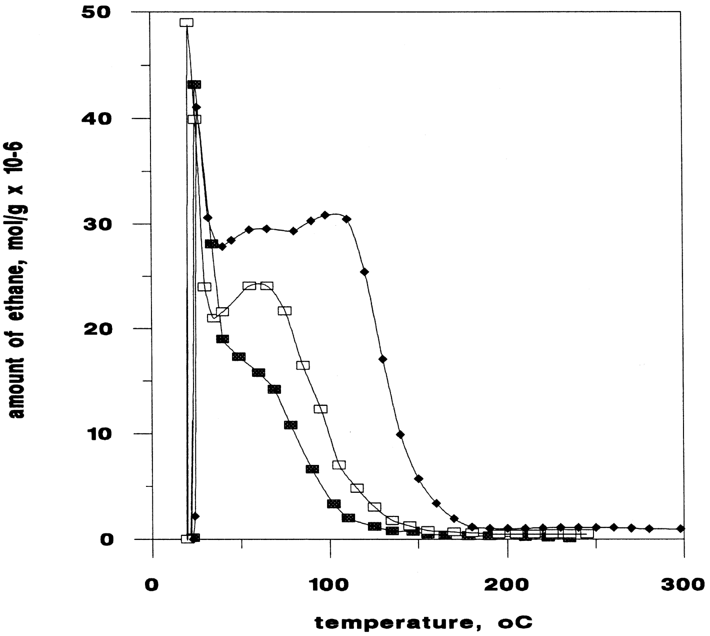

Fig. 5. TPR pattern of the decomposition of surface complexes formed at different reaction temperatures. (■), T_r=27°C; (□), T_r=50°C; (◆), T_r=60°C. $[Sn(C_2H_5)_4]_o$=1.27×10^{-2} M and $[Sn]_o/Pt_{surf}$=1.58.

monolayer of $-SnR_{(4-x)}$ while, at 60°C, the buildup of the second layer is already noticeable. This observation is further supported by TPR results presented in Fig. 5. The TPR pattern clearly shows the differences between surface organometallic species formed at 27, 50 and 60°C. The appearance of the new peak at 105–110°C is an indication for the formation of the second layer. Indeed, in the experiment at 60°C, the Sn_{anch}/Pt_{surf} was ca. 0.8, i.e. it was almost twice as much as the corresponding monolayer of $-SnR_{(4-x)}$.

These results imply that the overall amount of anchored tin can be increased by changing the temperature of tin anchoring. The variation of the reaction temperature in the above range did not result in any additional side reactions as no other products were detected in reaction (1).

3.2.4. *Influence of the reaction time*

The influence of the reaction time was studied by comparing results obtained in standard experiments (2–3 h reaction) with experiments carried out up to 7 h. In these experiments, a relatively high $[Sn]_o/Pt_{surf}$ ratio was used. The increase of the reaction time allowed us to reach the moment when the amount of ethane and ethylene showed no further increase. The increase of the reaction time from 2.5 to 7 h led to the increase of the Sn_{anch}/Pt_{surf} ratio from 1.15 to 2.35; however, no change in the x value was observed. The only difference in the TPR pattern is the increase and decrease of the TPR peaks at 200 and 110°C, respectively. These data indicate that, upon increasing the reaction time, the primary formed surface species loses additional alkyl groups and the buildup of the multilayered species continues further.

3.3. *Controlled surface reaction in the presence of added hydrogen.*

Insofar as the aim of this study was to increase the amount of tin anchored, it was interesting to study the influence of added hydrogen on the tin-anchoring process. The presence of hydrogen strongly increased the initial rate of reaction (1) as shown in Fig. 6. The TPR profile also showed significant changes compared to the experiment carried out in the absence of hydrogen (see Fig. 7). When surface reaction (1) was carried out in a hydrogen atmosphere, the contribution of the low temperature part of the TPR curve (i.e. peaks between 20 and 110°C) decreased considerably and an additional peak and a shoulder were observed ca. 190 and 220°C, respectively. The summary of experimental data is given in Table 4.

Results obtained in the above series of experiments indicate that, in the presence of hydrogen, the amount

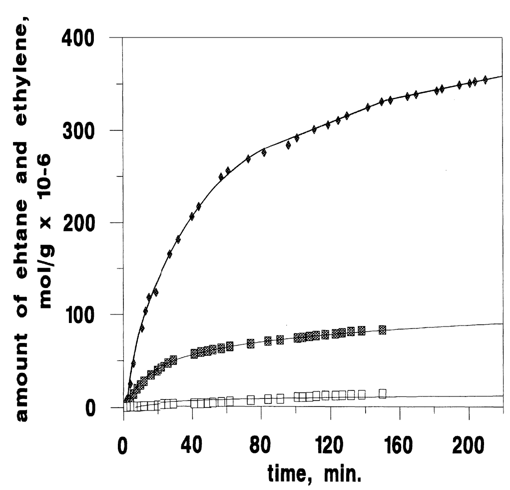

Fig. 6. The influence of added hydrogen on the kinetics of reaction (1). (■), Amount of ethane in the absence of hydrogen; (□), amount of ethylene in the absence of hydrogen; and (◆), amount of ethane in the presence of hydrogen. $[Sn(C_2H_5)_4]_o = 8.10\times10^{-2}$ M, and $[Sn]_o/Pt_{surf} = 9.83$; $T_r = 50°C$.

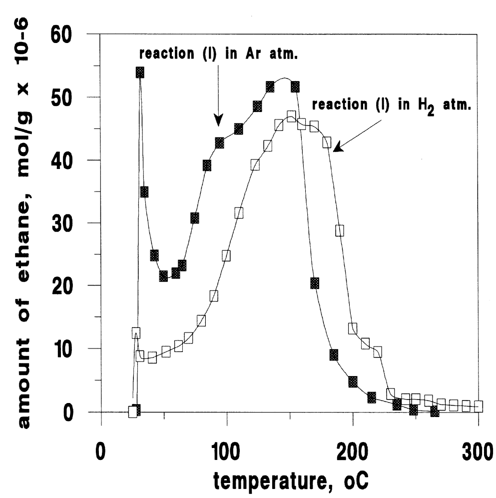

Fig. 7. TPR pattern of the decomposition of surface complexes formed in the presence, and absence, of hydrogen. $[Sn(C_2H_5)_4]_o = 8.10\times10^{-2}$ M, and $[Sn]_o/Pt_{surf} = 9.83$; $T_r = 50°C$.

Table 4
Comparision of the tin-anchoring process in the absence, and presence, of added hydrogen

Exp.	$[Sn]_o/Pt_{surf}$	$W_o \times 10^{-6}$ (mol/g_{cat} min)	$n^I \times 10^{-6}$ (mol/g_{cat})	$C_2H_4 10^{-6}$ (mol/g_{cat})[a]	$n^{II} \times 10^{-6}$ (mol/g_{cat})	x	Sn_{anch}/Pt_{surf} (at/at)
in Ar	9.8	3.2	95	13.0	274	1.0	1.2
in H_2	9.0	8.8	354	no C_2H_4	290	2.2	2.0

[a] Amount of ethylene formed in reaction (1).

of tin anchored can be significantly increased. The presence of hydrogen, consequently, strongly increases the value of x. In the presence of hydrogen, the extent of loss of the alkyl groups in the first step of anchoring is much higher than in its absence. The changes of the TPR profile indicate that the type of tin organic moieties, both in the first and second layers, is different from those formed in the absence of hydrogen. We suggest that, in the presence of added hydrogen, both the first and second layers of tin are dealkylated to a higher extent than in the absence of hydrogen.

3.4. *Controlled surface reaction using partially or fully oxidized samples.*

Our recent results indicated that, in the presence of either oxygen or unreduced forms of platinum, the character of surface reaction (1) is strongly altered [21]. For this reason, it was interesting to investigate the influence of oxygen on the fate of surface reaction (1). Results obtained in these experiments are summarized in Table 5. The Pt/SiO_2 catalyst was treated in an oxygen atmosphere for 1 h at 300°C and was introduced into the reactor without reduction and its reaction with tin tetraethyl was monitored. As seen from Fig. 8(A), in this experiment ethylene was the major reaction product, ethane formed only in small amounts. The formation of ethylene indicates that the ethyl group in tin tetraethyl was used either to reduce supported platinum oxide to metallic platinum or remove the strongly bound chemisorbed oxygen overlayer formed at the platinum surface. In other words, these results indicate that tin tetraethyl was involved in an oxidation–reduction-type reaction. The corresponding decomposition pattern of surface complexes formed on oxidized platinum is shown in Fig. 8(B). In Fig. 8(B), the decomposition pattern of surface complexes formed at the same $[Sn]_o/Pt_{surf}$ ratio on fully reduced platinum is also given for comparison. The appearance of TPR peaks ca. 160 and 210°C is attributed to the presence of oxygen. The oxygen treatment resulted in an increase of the Sn_{anch}/Pt_{surf} ratio up to 2.3 (see Table 5). Under similar condition

Table 5
Influence of added oxygen on the tin-anchoring process.

No.	Experimental condition	$[Sn]_o/Pt_{surf}$	$W_o \times 10^{-6}$ (mol/g_{cat} min)	$n^I \times 10^{-6}$ (mol/g_{cat}) [d]	$C_2H_4 \times 10^{-6}$ (mol/g_{cat}) [e]	$n^{II} \times 10^{-6}$ (mol/g_{cat}) [f]	X	Sn_{anch}/Pt_{surf} (at/at)
1	reduced sample	5.28	1.49	84.9	2.4	169.5	1.33	0.79
2	oxidized sample [a]	4.51	0.14	156.5	145.0	580.7	0.85	2.31
3	reduced sampe	1.58	0.43	44.0	1.9	81.7	1.40	0.39
4	addition of O_2 [b]	1.72	0.52	63.4	20.6	218.7	0.90	0.88
5	reduced sample	9.20	2.1	189.0	26.0	561.7	1.01	2.35
6	oxid. at 50°C [c]	8.79	0.63	131.2	85.2	770.6	0.60	2.82
7	addition of O_2^{**}	8.51	2.0	167.0	92.2	770.7	0.71	2.93

[a] Oxidation at 300°C.

[b] Addition of 20 cm^3/g_{cat} oxygen in the 50th minute of surface reaction (1).

[c] Oxidation at 50°C in the absence of solvent for 1 h.

[d] Total amount of C_2 hydrocarbons formed in reaction (1).

[e] Amount of ethylene in reaction (1).

[f] Amount of ethane formed in reaction (2).

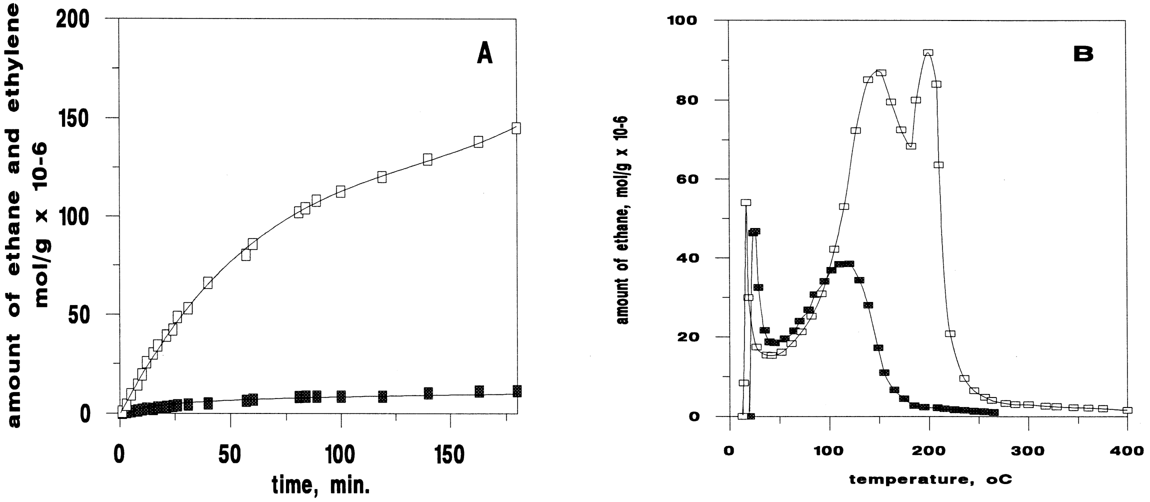

Fig. 8. Anchoring tin onto platinum oxidized at 300°C. A – First step of anchoring: (□), amount of ethylene, and (■), amount of ethane formed, respectively. $[Sn(C_2H_5)_4]_o=3.62\times10^{-2}$ M and $[Sn]_o/Pt_{surf}=4.51$. $T_r=50°C$. B – TPR pattern of the decomposition of surface complexes formed: (□), on oxidised platinum; and (■), on fully reduced platinum.

on fully reduced samples, the Sn_{anch}/Pt_{surf} ratio was 0.8. These results indicate that anchoring of tin tetraethyl onto oxidized platinum can lead to a significant increase in the amount of tin anchored. On the oxidized sample, the value of x was 0.85, while on fully reduced platinum the above value was 1.33 (see Table 5). From this comparison, it follows that on the oxidized platinum the contribution of the second layer, in the form of $-SnR_{(4-y)}$, is much higher than over fully reduced samples.

The role of added oxygen was studied in additional experiments. In one of these experiments, the catalyst was oxidized by purging the catalyst with oxygen at 50°C for 1 h in the absence of solvent. Surface reaction (1) was studied after the above mild oxidation. The kinetic curves of the formation of C_2 hydrocarbons are shown in Fig. 9(A), further details are given in Table 5 (exp. No. 6). In the above experiment, due to the mild oxidation the amount of ethane increased compared to the result given in Fig. 8(A). This treatment also resulted in high Sn_{anch}/Pt_{surf} ratio. However, the increase of the Sn_{anch}/Pt_{surf} ratio was not significant (compare exp. Nos. 5 and 6), probably due to the use of high $[Sn]_o/Pt_{surf}$ ratio and prolonged reaction time.

In another series of experiments, the influence of oxygen added to the reactor during surface reaction (1), i.e. in the tin anchoring step, was investigated. In these experiments, oxygen was introduced in the 50th minute and the reaction time was prolonged up to 7 h as shown in Fig. 9(B). As seen from Fig. 9(B), the addition of oxygen resulted in an instantaneous formation of ethylene and a strong decrease in the rate of formation of ethane. Within further 20–30 min, the ethane formation was completely stopped. In these experiments, the amount of ethylene depended on the $[Sn]_o/Pt_{surf}$ ratio used (see Table 5, compare exp. Nos. 4 and 7). The change in the Sn_{anch}/Pt_{surf} ratio, induced by oxygen addition, also showed a strong dependence of the $[Sn]_o/Pt_{surf}$ ratio (compare exp. No. 3 vs. No. 4, and No. 5 vs. No. 7). The increase was very pronounced at low $[Sn]_o/Pt_{surf}$ ratios, where the addition of oxygen doubled the amount of tin anchored. The addition of oxygen has altered the TPR pattern too. Fig. 10 shows the TPR pattern without oxidation, and when oxygen was added prior to or during surface reaction (1). The addition of oxygen resulted in a new TPR peak at 210°C and a shoulder at 250°C. The latter was observed only when the catalyst was oxidized prior to surface reaction (1) (Table 6).

3.5. *Reactions with the involvement of the support*

Silica treated in a hydrogen atmosphere at 300°C appeared to be almost inert. In the presence of

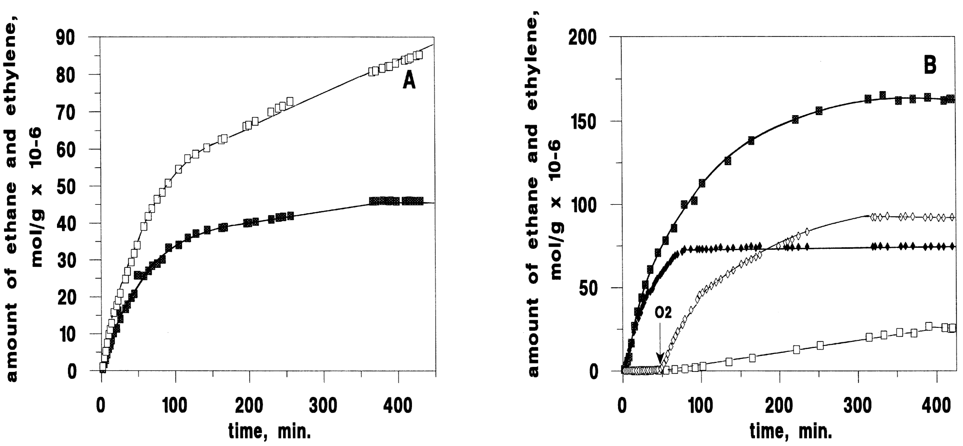

Fig. 9. Anchoring tin onto platinum oxidized at 50°C. $[Sn(C_2H_5)_4]_o$=6.33×10^{-2} M, and $[Sn]_o/Pt_{surf}$=8.8. A – Oxidation prior to the anchoring step: (□), amount of ethylene, and (■) amount of ethane formed, respectively. B – Oxidation during tin anchoring (20 cm^3/g_{cat} O_2 added in the 50th minute). (◆), amount of ethane, and (◇) amount of ethylene formed on platinum oxidized during tin anchoring, respectively; (■), amount of ethane, and (□), amount of ethylene formed on fully reduced platinum, respectively.

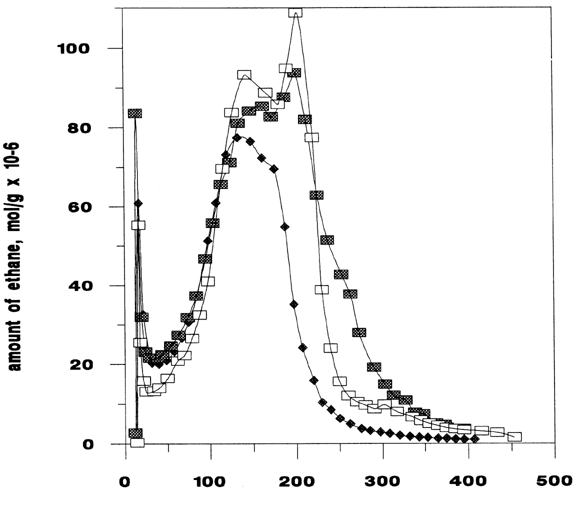

Fig. 10. TPR pattern of the decomposition of surface complexes formed on reduced and oxidized platinum samples. (◆), Fully reduced sample; (□), sample oxidized prior to the anchoring step; and (■), sample oxidized during tin anchoring. The formation of surface complexes is shown in Fig. 9.

4.3×10^{-2} M tin tetraethyl, the amount of ethane formed after 2 h was 3.4×10^{-6} mol/g_{cat}. Under identical tin tetraethyl concentrations, the Pt/SiO_2 catalyst resulted in 83×10^{-6} mol/g_{cat} ethane and 2.4×10^{-6} mol/g_{cat} ethylene. Upon increasing the concentration of tin tetraethyl up to 27.9×10^{-2} M, the amount of ethane formed was 20.9×10^{-6} mol/g_{cat}. The corresponding tin tetraethyl concentration over the Pt/SiO_2 catalyst resulted in 104×10^{-6} mol/g_{cat} ethane and 25×10^{-6} mol/g_{cat} ethylene.

Although the amount of C_2 hydrocarbons formed over SiO_2 at high concentration of tin tetraethyl cannot be neglected, it should be mentioned that in the above two experiments the initial rate of surface reactions

Table 6
Deconvolution of the TPR peaks [a]

Exp. No.	$[Sn]_o/Pt_s$	Sn_{anch}/Pt_s(at/at)	Amount of C_2H_6 formed in different TPR peaks, n^{II}_{ij}, $\times 10^{-6}$ mol/g_{cat} min						
			1st peak 22–34°C	2nd peak 48–54°C	3rd peak 75–80°C	4th peak 110–112°C	5th peak 149–153°C	6th peak 197–198°C	7th peak 260°C
1	0.42	0.12	9.55	7.50	5.31	0.75	0.79	—	—
2	1.58	0.39	19.75	**18.32**	28.50	5.13	—	—	—
3	3.01	0.56	17.54	**15.94**	**39.20**	33.06	4.22	1.41	2.03
4	5.28	0.79	23.19	**19.29**	**36.51**	**74.06**	10.58	3.17	2.70
5	9.83	1.15	34.79	**19.05**	**38.65**	**69.98**	**102.88**	6.53	1.98
6	23.84	1.60	40.16	**16.78**	**38.60**	**65.78**	**106.37**	**105.18**	12.43
7	33.50	1.64	46.46	**20.36**	**32.23**	**67.62**	**96.60**	**105.36**	27.57
mean values				19.2±1.65	937.04±2.88	69.36±3.57	101.95±4.95	105.27±0.13	—

[a] The values given in bold were used to caluclate the mean value of hydrocarbons formed.

with the involvement of surface OH group was still 20–60 times lower than on Pt/SiO_2 catalyst. These results indicate also that these extremely high initial concentrations of tin tetraethyl should be avoided as, under these conditions, the exclusive introduction of tin onto platinum cannot be guaranteed.

The corresponding TPR pattern is shown in Fig. 11. Parallel to the formation of ethane ethylene was also observed in the TPR experiment resulting in a peak at 340°C. The low temperature ethane peak at ca. 200°C was attributed to $-Sn(C_2H_5)_{(4-z)}$ anchored to the silica, while the high temperature peak at ca. 340°C was ascribed to the adsorbed form of tin tetraethyl. It should be mentioned that tin alkyls are very stable organometallic compounds, their decomposition requires extreme conditions. For instance, in the gas phase, tin tetraalkyl thermally decomposes at a measurable rate above 440°C [22]. There is one additional important remark: the TPR peak at 340°C was never observed over Pt/SiO_2 catalyst; thus, during tin anchoring and subsequent washing the adsorbed forms of tin tetraethyl were removed.

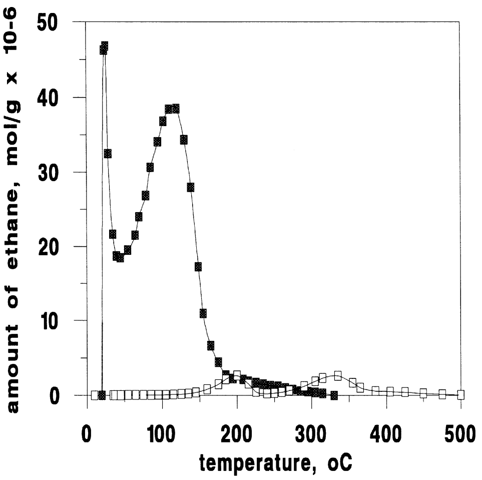

Fig. 11. Comparison of surface reaction (1) and reaction of $Sn(C_2H_5)_4$ with silica surface. (■), Surface reaction (1); (□), reaction of $Sn(C_2H_5)_4$ with silica surface. $[Sn(C_2H_5)_4]_o$= 4.31×10^{-2} M, and T_r =50°C.

3.6. *Testing of Sn–Pt/SiO$_2$ catalysts in a model reaction*

The $Sn-Pt/SiO_2$ catalyst (Sn_{anch}/Pt_{surf}=1.2) was investigated in the selective hydrogenation of crotonaldehyde (CA) to crotylalcohol. The steady state activities and selectivities measured at 5% conversion are summarized in Tables 7 and 8.

As seen from the data given in Table 7, the parent Pt/SiO_2 catalyst does not hydrogenate the aldehyde group at all. Over this catalyst, both the S_{UOL} and S_{SOL} selectivities are zero. The introduction of tin strongly increased both the overall activity of the catalyst and its selectivity towards the formation of crotylalcohol. The increase in the activity can be attributed either to the increase in the intrinsic catalytic properties or the decreased poisoning of the $Sn-Pt/SiO_2$ catalyst. Over $Sn-Pt/SiO_2$ catalyst, the selectivity of the formation of crotylalcohol (S_{UOL}) exceeded 70%.

The increase of the temperature of re-reduction resulted also in a strong influence on the catalyst activity and selectivity (see Table 8). The above

Table 7
Hydrogenation of crotonaldehyde over Sn–Pt/SiO$_2$ catalyst. Effect of the reaction temperature (Preactivation temperature=340°C; and C_0=0.64 mmol/dm^3)

Catalysts	Reaction temperature (°C)	W_{ini} [a] (μmol/g s)	Selectivity (%) [b] SAL [d]	SOL [e]	UOL [f]	HC[g]
Pt/SiO$_2$	80	2.7	97	0	0	3
	60	8.9	28	0	72	0
Sn–Pt/SiO$_2$ [c]	80	11.3	34	4	62	0
	100	15.3	53	6	40	1
	120	27.3	57	9	30	4

[a] Measured from the conversion–contact time dependences and extrapolated to zero conversion.
[b] Measured at 5% conversion.
[c] Sn$_{anch}$/Pt$_{surf}$=1.2.
[d] Butyraldehyde.
[e] Butylalcohol.
[f] Crotylalcohol
[g] Hydrocarbons.

Table 8
Hydrogenation of crotonaldehyde over Sn–Pt/SiO$_2$ catalyst. Effect of the temperature of preactivation (Reaction temperature=80°C; and C_0=0.64 mmol/dm^3)

Catalysts	Preactivation temperature (°C)	W$_{ini}$[a] (μmol/g s)	Selectivity (%)[b] SAL [d]	SOL [e]	UOL [f]	HC [g]
Pt/SiO$_2$	340	2.7	97	0	0	3
	180	9.3	48	7	45	0
Sn–Pt/SiO$_2$[c]	250	12.9	38	7	55	0
	340	11.3	34	4	62	0

[a] Measured from the conversion–contact time dependences and extrapolated to zero conversion.
[b] Measured at 5% conversion.
[c] Sn$_{anch}$/Pt$_{surf}$=1.2.
[d] Butyraldehyde.
[e] Butylalcohol.
[f] Crotylalcohol.
[g] Hydrocarbons.

activity and selectivity changes indicate that a reconstruction of the primary formed Sn–Pt bimetallic species takes place. Further results on catalytic experiments can be found elsewhere [23]. As seen from the results given in Ref. [23], the S_{UOL} selectivity of Sn–Pt bimetallic catalysts depends on the Sn$_{anch}$/Pt$_{surf}$ ratio and catalysts up to Sn$_{anch}$/Pt$_{surf}$=3 can be used to hydrogenate selectively crotonaldehyde to crotylalcohol.

Results obtained in the model reaction indicate that our new approach to anchor large amount of tin onto platinum can result in highly active and selective catalysts for selective hydrogenation of CA. The investigation of additional selective hydrogenation and other model reactions are in progress in our laboratory to discover the application potential of the new type of supported Sn–Pt catalysts.

4. Discussion

In this study new aspects of the tin anchoring process have been investigated. As it has already been shown in our previous studies [1,3,4], the above anchoring process is based on controlled surface reactions between hydrogen adsorbed on transition or noble metals and tin tetraalkyls (see reaction (1)). In this study, an attempt was made to find ways and means of increasing the amount of tin anchored. The focus was laid on the study of interactions involved in the buildup of different type of tin organic moieties at small platinum clusters supported on silica. From our results it is seen that the above buildup process takes place layer-by-layer.

In this work, the key steps of tin anchoring, i.e. the formation and the decomposition of surface complexes, were separated from one another in a way similar to that demonstrated in our earlier studies [1,3,4]. However, results obtained under different experimental conditions, such as (i) high $[Sn]_o/Pt_{surf}$ ratio, (ii) prolonged reaction time, (iii) presence of hydrogen, (iv) high reaction temperature, and (v) presence of oxygen, indicate that the formation and decomposition of surface complexes cannot always be separated, i.e. the decomposition of PSC takes place under condition of surface reaction (1).

Results of computer modelling indicate that the monolayer of tin organometallic species with general formula of $-Sn(C_2H_5)_3$ or $-Sn(C_2H_5)_2$ can result in Sn_{anch}/Pt_{surf} ratios between 0.31–0.47 (see Table 1 and Fig. 1). It also means that, in order to obtain high Sn_{anch}/Pt_{surf} ratios, new anchoring sites should be created. However, in order to avoid the introduction of tin onto the support the buildup of additional tin organic moieties, with the general formula $-SnR_{(4-y)}$, should take place at the top of the PSC, i.e. in the second layer. The key issue of the new approach is the creation of new anchoring sites at the top of the PSC, i.e. in the neighbourhood of the metal.

The new anchoring sites are created during surface reaction (1) by changing the condition of the tin anchoring process. The increase of the temperature of reaction (1), the use of either high $[Sn]_o/Pt_{surf}$ ratios or hydrogen in reaction (1) or the treatment of Pt in an oxygen atmosphere leads to the formation of new anchoring sites. All of the above measures leads to substantial increase of the Sn_{anch}/Pt_{surf} ratio.

In Ref. [8], by using computer modelling it was proposed that $-SnR_3$ moieties can be anchored onto 'naked' tin formed at the top of supported rhodium and the ratio of anchored $-SnR_3$ to naked tin was two. We believe that similar phenomenon can also take place on supported platinum. The higher the extent of dealkylation of PSC the higher the probability to form the second layer of tin organic moieties at the top of the PSC. In this work, the term surface complex in the second layer (SCSL) is used for the second layer of tin organic moieties. Depending on the experimental conditions, the second layer is also partially dealkylated, thus providing further sites for the formation of multilayered structures (MLS). It is very important to emphasize that the buildup of different layers has a stepwise character. The stepwise character is well manifested by the TPR pattern of the formed species (see Figs. 3 and 4). The deconvolution of the TPR peaks reveals that at least seven different forms of anchored tin organic moieties can be formed.

As follows from the general behaviour of solid-phase reactions studied by the TPR technique, the higher the temperature of formation of a given reaction product the higher the energy required for its formation. Let us discuss how this principle can be applied to surface reactions involved in the tin anchoring process, i.e. in the decomposition of different surface organometallic moieties.

The decomposition reactions involved in the tin anchoring process (see reaction (2) and decomposition of SCSL and MLS) require atomic hydrogen. The atomic hydrogen is provided by platinum not covered by PSC. Hydrogen can also be provided by the alkyl groups of $-Sn(C_2H_5)_{(4-x)}$. However, the latter surface reaction would lead to the formation of ethylene under condition of decomposition. We have never observed the formation of ethylene in the TPR experiments over our Pt/SiO_2 catalyst. A further specific feature of surface reactions involved in the decomposition of surface complexes formed is that all surface species decompose with the formation of ethane.

When $Sn_{anch}/Pt_{surf}<0.4–0.5$, the buildup of a monolayer of PSC takes place. If conditions of surface reaction (1) are chosen properly, the surface concentration of $-Sn(C_2H_5)_{(4-x)}$ can reach the monolayer coverage shown in Fig. 1(A and B). We suggest species involved in the formation of PSC in the form of monolayer should decompose below 80°C (see Figs. 3 and 4). Under monolayer coverage the Pt surface is covered by $-SnR$, $-SnR_2$ and $-SnR_3$ species, thus the value of x should be higher than one ($x>1$). Indeed we have found that under this experimental condition the mean value of x is ca. 1.5 (see experiments 1–4 in Table 2). The above value of x indicates that anchored $-SnR_2$ and $-SnR_3$ were formed in 1 : 1 ratio. However, as emerges from Fig. 1(A and B), even at monolayer coverage of $-SnR_2$ and $-SnR_3$ there is sufficient room on the Pt surface for further accommodation of the –SnR species. We suggest that tin organic moieties containing only one alkyl group should have the highest reactivity, i.e. the first TPR peak at 24–30°C is tentatively attributed to the coordinatively unsaturated $-\mathrm{Sn(C_2H_5)}$ moieties. Insofar as the TPR peaks up to 80°C resulted in $\mathrm{Sn_{anch}/Pt_{surf}}$ ratios below 0.5, the second and the third peaks around 48–54°C and 75–80°C, respectively, are attributed to the first layer of primary surface complexes with general formula of $-\mathrm{Sn(C_2H_5)_2}$ and $-\mathrm{Sn(C_2H_5)_3}$. Consequently, all of the high temperature peaks above 80°C are assigned to SCSL or MSL.

Let us discuss the surface reaction leading to the formation of the second layer. If the concentration of $\mathrm{Sn(C_2H_5)_4}$ in the liquid phase is high and the Pt surface is fully covered by $-\mathrm{SnR}_{(4\text{-}x)}$ moieties, with different extent of dealkylation, the probability to form SCSL is high. The formation of SCSL requires unsaturated sites in the PSC to anchor $\mathrm{SnR_4}$. The formation of SCSL can be written as follows:

$$\mathrm{Pt{-}SnR}_{(4\text{-}x)} + n\mathrm{SnR_4} \rightarrow \mathrm{Pt{-}}\underset{\mathrm{SCSL}}{\{\mathrm{SnR}_{(4\text{-}x)} - (\mathrm{SnR}_{4\text{-}y})_n\}} \tag{3}$$

Reaction (3) describes the general equation for the formation of the surface complex in the second layer (SCSL). In the first approximation, the first layer is considered to have partially dealkylated, coordinatively unsaturated species, while the second layer consists of anchored $\mathrm{SnR_4}$ moieties. We believe that this process takes place at high $[\mathrm{Sn}]_o/\mathrm{Pt_{surf}}$ ratios in the second part of the kinetic curve. The loss of alkyl group in SCSL leads to the formation of $\mathrm{Pt{-}\{SnR}_{(4\text{-}x)}\mathrm{{-}(SnR}_{(4\text{-}y)})_n\}$, where $y>0$. The high extent of dealkylation of PSC also means high extent of unsaturation, i.e. the ability of $-\mathrm{Sn(C_2H_5)}_{(4\text{-}x)}$ species to donate or accept electrons. We consider that coordinatively unsaturated tin organometallic moieties can be considered as donors, while $\mathrm{Sn(C_2H_5)_4}$ as an acceptor of electrons.

The increase of both x and y values has been evidenced under the following experimental conditions:

1. in the presence of added hydrogen;
2. when reaction (1) was carried out above 55°C; and
3. when the time of reaction (1) increased considerably.

We also suggest that the above experimental conditions are also favourable to increase the value of n in SCSL (see reaction (3)), when the extent of dealkylation of $-\mathrm{SnR}_{(4\text{-}y)}$ is high.

The formation of the second layer in the form of $-\mathrm{Sn(C_2H_5)_4}$ at the top of PSC containing surface species with general formula of $-\mathrm{Sn(C_2H_5)_3}$ and $-\mathrm{Sn(C_2H_5)_2}$ is shown in Fig. 12(A and B), respectively. The above figures show that the second layer of tin organic moieties can be formed both at the *top* and *side* sites of platinum. However, there is a strong difference between the above two forms. The second layer at the *top site* can interact with hydrogen formed on the platinum sites, while the second layer on the *side site* can also interact with spilled-over hydrogen available on the support.

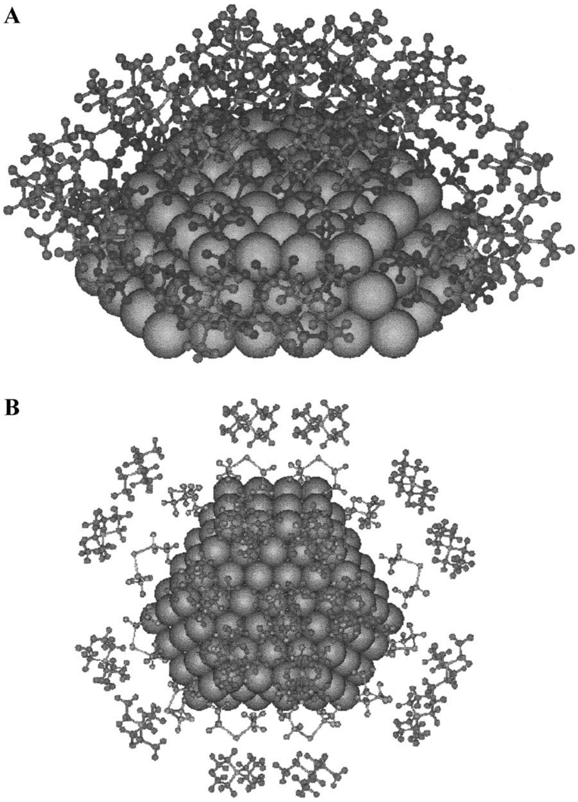

Fig. 12. Computer modelling of the formation of the second layer of tin organic complex. A – Anchoring $\mathrm{SnR_4}$ onto $-\mathrm{SnR_3}$ (side view); B – choring $\mathrm{SnR_4}$ onto $-\mathrm{SnR_2}$ (top view).

The increase of the reaction time in the first step of tin anchoring leads to the increase of both x and y values of SCSL (see reaction (3)), i.e. in this way, the extent of coordinative unsaturation of SCSL increases. The above coordinative unsaturation provides new sites to anchor additional $Sn(C_2H_5)_4$. This process leads to the formation of MLS with the general formula given below:

$$Pt–[\{SnR_{(4\text{-}x)} - (SnR_{(4\text{-}y)})_n\} - (SnR_4)_m]$$

The analysis of the deconvoluted TPR curves provided further evidences for the formation of different types of anchored tin organic moieties and allowed us to distinguish between PSC and SCSL. As emerges from Fig. 4(A–D), the deconvolution of TPR peaks resulted in almost similar peak positions in all experiments with Sn_{anch}/Pt_{surf} between 0.12 and 1.6. The only difference is that at low Sn_{anch}/Pt_{surf} ratios, only low temperature TPR peaks were detected. The amounts of ethane related to the area of each deconvoluted TPR peaks (see Fig. 4(A–D)) were calculated and are summarized in Table 6. Further data obtained in this series of experiment (see Table 2) are also included into Table 6.

As it has already been mentioned, we consider that the separate TPR peaks correspond to ethane formed from different tin organic moieties. At present it is difficult to give further assignment for TPR peaks above 80°C; however, the analysis of data given in Table 6 allows us to differentiate between surface species formed in different environments, i.e. to differentiate between PSC formed over platinum in the first layer and SCSL or MSL formed over PSC.

An analysis of the data given in Table 6 provides the following very important information. The first peak ca. 22–34°C increases in the whole range of Sn_{anch}/Pt_{surf}. It means that the surface concentration of the corresponding species increases in the whole interval of Sn_{anch}/Pt_{surf}. This is the only moiety, which shows this type of behaviour. Previously, we ascribed this peak to the decomposition of surface species –SnR.

The amount of ethane corresponding to the second peak ca. 48–54°C, with the exception of exp. No. 1, is constant. It should be emphasized that in exp. No. 1, the monolayer of PSC is not achieved yet ($Sn_{anch}/Pt_{surf}=0.12$). However, the constant values of the second TPR peak (see exp. Nos. 2–7 in Table 6) indicate that the corresponding surface species have reached a certain stationary value. The stationary value corresponds to the full coverage of the given surface species and can also be calculated from data given in Table 6. For the second TPR peak suggesting the formation of $–SnR_2$ species the stationary coverage corresponds to $Sn_{anch}/Pt_{surf}=0.11$. Analogous calculation was done for the third peak at 75–80°C. The stationary value is reached at $Sn_{anch}/Pt_{surf}=0.15$ or $Sn_{anch}/Pt_{surf}=0.23$ when $–SnR_3$ or $–SnR_2$ is used for the calculation.

Further calculations of the amount of ethane formed in the first three peaks up to 80°C resulted in $Sn_{anch}/Pt_{surf}=0.42$. These data indicate that the coverage of $–Sn(C_2H_5)_{(4\text{-}x)}$ ($x=1–3$) in the first layer found experimentally is very close to the value found by molecular modelling (see results given in Table 1).

A similar approach was followed for the fourth, fifth and sixth TPR peaks. The calculated stationary Sn_{anch}/Pt_{surf} ratios up to 110, 150 and 200°C are 0.68, 1.08, and 1.46, respectively. The incremental increase in the Sn_{anch}/Pt_{surf} ratios ($\Delta[Sn_{anch}/Pt_{surf}]_{ij}$, where i and j are the corresponding TPR peaks) were also calculated. These values are as follows:

$[Sn_{anch}/Pt_{surf}]_{3,4}=0.25$ (for peak No. 4, ca. 110°C);
$[Sn_{anch}/Pt_{surf}]_{4,5}=0.40$ (for peak No. 5, ca. 150°C);
$[Sn_{anch}/Pt_{surf}]_{5,6}=0.38$ (for peak No.6, up to 200°C).

The incremental value found for peak No. 4 indicates that SCSL formed first covers only a certain part of PSC as $\Delta[Sn_{anch}/Pt_{surf}]_{3,4}=0.25$. The exact assignment of peaks Nos. 4, 5 and 6 will require additional data; however, tentatively these peaks can be attributed to tin organic moieties, such as SCSL or MSC. The above calculations, although they did not allow us an exact assignment, provided information supporting our assumption about a stepwise character of the buildup process involved in the tin-anchoring process.

It has also been found that the formation of ethylene in reaction (1) is strongly correlated with the appearance of the second part in the kinetic curve. The appearance of ethylene is attributed to the disproportionation of $Sn(C_2H_5)_4$ taking place in the second layer. This reaction provides $–Sn(C_2H_5)_2$ moieties in one step as given below:

$$–Sn(C_2H_5)_4 \rightarrow –Sn(C_2H_5)_2 + C_2H_6 + C_2H_4 \qquad (4)$$

As far as the formation of ethylene was not observed either at low $[Sn]_o/Pt_{surf}$ ratios or at the very beginning of surface reaction (1), we suggest that reaction (4) should be related to the formation of SCSL or MLC.

At high $[Sn]_o/Pt_{surf}$ ratios and prolonged reaction time, the amount of ethane formed exceeded the amount of hydrogen adsorbed on the platinum sites. We suggest that, in this type of anchoring process, the overall hydrogen pool is involved. The overall hydrogen pool can be estimated from the hydrogen thermal programmed desorption (TPD) measurements. Prior to the TPD experiment the catalyst was treated in a hydrogen atmosphere in a similar way as before to the tin-anchoring process, i.e. the catalyst was cooled down in a hydrogen atmosphere. In the TPD measurement, the spilled-over hydrogen is also detected. The overall amount of hydrogen on our Pt/SiO_2 catalyst detected by TPD was 2.3 H/Pt_{surf}.

When oxygen treatment was used prior to the tin anchoring reaction, platinum becomes oxidized. The extent of oxidation of supported platinum depends on the temperature of oxygen treatment. In this case, the oxygen containing PtO_z species reacts with tin alkyl in the following surface reaction:

$$\begin{aligned}&PtO_z + zSn(C_2H_5)_4\\&\quad \rightarrow Pt\text{–}[Sn(C_2H_5)_2]_z + 2zC_2H_4 + zH_2O \qquad (5)\end{aligned}$$

The above reaction, i.e. exclusive formation of ethylene, was also evidenced when PtO_z was treated with $Sn(C_2H_5)_4$ in benzene solvent at 50°C. The formation of ethylene from tin tetraethyl indicates that the tin organic compound is involved in an oxidation–reduction type reaction. It should also be mentioned that tin tetraalkyls are good reducing agents [10]. Consequently, the formation of ethylene in reaction (5) can be considered as an evidence for the presence of unreduced platinum or adsorbed oxygen over the Pt sites.

The presence of oxygen during tin anchoring has also provided new anchoring sites for the formation of SCSL. In this case, either the chemisorbed oxygen formed on platinum sites is covered by $–SnR_{(4-x)}$ moieties or the oxidized PSC is considered as a new anchoring site. We suggest that coordinatively unsaturated $–SnR_{(4-x)}$ moieties, such as $–SnR_2$, –SnR and 'naked' Sn can very easily be oxidized with the formation of $–Sn(O)R_2$, –Sn(O)R or $–Sn(O)_2$ moieties, respectively. The lone pair of the oxygen in the above oxygen containing species is involved in the formation of the SCSL as shown in Fig. 13. This figure shows that the oxygen bridge between the first and second layers has a key role in the stabilization of SCSL. When SCSL is also oxidized, the oxygen bridge is also involved in the formation of MLC. The activity of surface tin organic moieties having an oxygen in its neighbourhood is probably lower than that formed in the absence of oxygen. This fact results in higher decomposition temperatures for $–Sn(O)R_2$, –Sn(O)R or $–Sn(O)_2$ moieties in comparison with that of formed in the absence of oxygen (see Fig. 8(B)). In this respect, there is an additional question: can the above species be fully reduced onto metallic tin or not? Further studies will be needed to elucidate the stability and reducibility of moieties, such as $–Sn(O)R_2$, –Sn(O)R or $–Sn(O)_2$ anchored onto platinum.

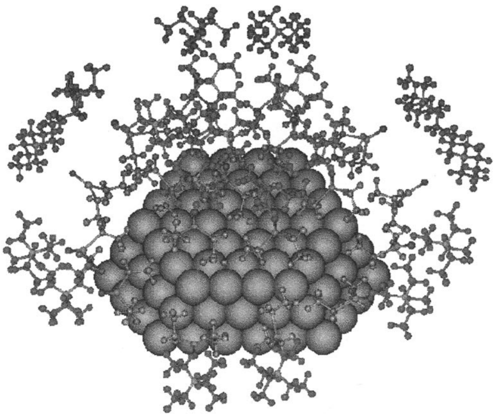

Fig. 13. Computer modelling of the formation of the second layer of tin organic complex on oxidized surface. Anchoring site: $–SnR_2(O)$.

The comparison of the reactivity of Pt/SiO_2 and SiO_2 indicates that, under conditions of surface reaction (1), direct anchoring of tin organic moieties onto the support can be neglected. However, extremely high initial concentration of tin tetraethyl in the solution should be avoided as, under this condition, strongly adsorbed forms of $Sn(C_2H_5)_4$ can be formed. This side reaction can take place when the initial concentration of $Sn(C_2H_5)_4$>16.2×10-2 M (see exp. Nos. 6 and 7 given in Table 6.).

The analysis of Figs. 12 and 13 indicates that the decomposition of tin organic moieties in the second and, probably, in the third layer can result in at least two different bimetallic tin–platinum species. In the first species, the tin–platinum interaction is not disturbed by any other interaction. These species were formed from organometallic moieties formed at the *top site* of platinum. The organometallic moieties formed at the *side site* of platinum upon increasing either the size or the number of layers can also interact with the platinum-support interface. In this case, the formed bimetallic surface species still have direct tin-platinum interaction, but this interaction is slightly disturbed either by the support or the support–metal interface. It is not excluded that the above interaction is reflected by one of the high temperature TPR peaks.

The possible formation of 'naked' tin in reaction (1) should also be mentioned. This form of tin can migrate to the bulk of platinum and form alloy type species even during surface reaction (1).

All of the above results indicate that at high Sn_{anch}/Pt_{surf} ratios, depending on the experimental conditions used, different type of surface species can be formed. Further works should be done to elucidate the character of interactions involved in silica supported Sn–Pt catalysts with high Sn_{anch}/Pt_{surf} ratio. These works are in progress in our laboratory.

As seen from catalytic experiments, tin-modified Pt/SiO_2 catalysts are very selective catalysts for the hydrogenation of crotonaldehyde to crotylalcohol. The parent Pt/SiO_2 catalyst showed no activity towards the hydrogenation of the carbonyl group. The selectivity of the Sn–Pt catalysts strongly depended on the temperature of the re-reduction. The above fact indicates that surface rearrangement might also play an important role in the formation of the working catalyst with high S_{CO} selectivity. Further results and discussions on the hydrogenation of crotonaldehyde over our tin-modified catalyst can be found elsewhere [23].

5. Conclusions

The results obtained in this study provided information about the character of anchoring of tin organic moieties onto silica-supported platinum. The exact material balance of the tin-anchoring process allowed us, for the first time, to obtain a real proof about the stepwise character of the tin-anchoring process. It was evidenced that the first species are anchored directly to the platinum, followed by the formation of the second layer and subsequent layers at the top of the first one. In the above stepwise buildup process, either the coordinative unsaturation of the $-SnR_{(4\text{-}x)}$ and $-SnR_{(4\text{-}y)}$ moieties formed in the first and second layer, respectively, or the oxygen bridge between different layers play the key role. Upon using this new approach $Sn–Pt/SiO_2$ catalysts with high Sn_{anch}/Pt_{surf} ratios were obtained. These catalysts showed high activity and selectivity in the selective hydrogenation of crotonaldehyde to crotylalcohol.

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