Time dependence of tin anchoring to supported platinum

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Abstract

In this paper new kinetic results obtained in the two step tin anchoring process are summarized. In this tin anchoring process the key step is the controlled surface reaction (CSR) between tin tetraalkyl and hydrogen adsorbed over platinum. In this study the focus was laid on the influence of the duration of tin anchoring on the type of surface organometallic species formed. The results of temperature programmed decomposition (TPD) of surface organometallic species in a hydrogen atmosphere indicated that at the beginning of tin anchoring, i.e. at low tin coverage, one of the main surface species is $Sn(C_2H_5)_4$ strongly adsorbed into platinum. As the surface reaction proceeded the amount of tin anchored increased and the strongly adsorbed form of $Sn(C_2H_5)_4$ was transformed into surface species with general formula of $-Sn(C_2H_5)_{(4-x)}$, and $-\{Sn(C_2H_5)_{(4-x)}[Sn(C_2H_5)_4]\}$. This behavior has been well-demonstrated on different supported platinum catalysts at relatively low $[Sn]_o/Pt_s$ ratios ($[Sn]_o/Pt_s < 2$). Under this condition monolayer tin coverage can be achieved, i.e. the ratio of Sn_{anch}/Pt_s in the formed alloy type supported Sn-Pt catalysts is around 0.4–0.5.
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1. Introduction

1.1. Surface organometallic chemistry of tin tetraalkyls

Controlled surface reactions (CSRs) between hydrogen adsorbed on transition metals and tin tetraalkyls [1–10] or surface organometallic chemistry (SOMC) [11–27] are widely used to prepare tin modified supported bimetallic catalysts. Most of these studies were related to supported rhodium [11,14–18,25] and platinum catalysts [1–10,13, 20–33]. The bimetallic catalysts obtained after modification with tin appeared to be highly active and selective in different hydrogenation reactions [3,4, 12–17,19,23,26,29,31,32], in the hydrogenolysis of fatty acid esters [11,17], in hydrocarbon reactions and *n*-alkane reforming [5–8], in low temperature CO oxidation [9,10].

The use of tin tetraalkyls in CSRs gives a definite guaranty that both the amount and the location (landing site) of tin can be controlled [2,28,32]. The control of the environment of tin requires that the rate of adsorption of tin tetraalkyls onto the support has to be much less then that of the anchoring type surface reaction (1). For example, the use of $Sn(C_2H_5)_2Cl_2$ for modification of Pt/Al₂O₃ catalysts resulted in uncontrolled introduction of tin into the support, due to its high rate of adsorption [1]. The surface chemistry involved in the modification of supported platinum catalysts strongly depended on the $[Sn]_o/Pt_s$ ratio ($[Sn]_o$ is the initial amount of tin used in the tin anchoring

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step, Pt_s is the total number of surface Pt atoms). At relatively low $[Sn]_o/Pt_s$ ratios ($[Sn]_o/Pt_s < 2$) the anchoring reaction of tin tetraalkyls can be described by the following equation [1,2,28]:

$$Pt H_a + SnR_4 \rightarrow \underset{PSC}{Pt\text{-}SnR_{(4-x)}} + xRH \qquad (1)$$
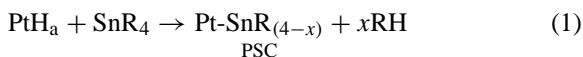
In reaction (1) hydrogen adsorbed on platinum (PtH_a) reacts with tin tetraalkyls resulting in the formation of a primary surface complexes (PSC).

At high $[Sn]_o/Pt_s$ ratio ($[Sn]_o/Pt_s > 2$) the surface chemistry is more complex leading to the formation of both coordinatively unsaturated surface species and to multilayered surface organometallic species (MLSOS) [7,8,29].

Under condition of tin anchoring parallel to the formation of ethane ethylene was also formed in very small amount [30,31]. The formation of ethylene was relatively more pronounced at high conversions, i.e. under condition of hydrogen deficiency. No ethylene has been formed in the presence of hydrogen added [29,32]. In the present study the formation of ethylene was around twenty times less than that of the ethane thus the formation of ethylene will not be discussed.

Surface reaction (1) is considered as the first step of the two-step tin anchoring process leading to the formation of alloy type supported Sn-Pt catalysts. The second step of this process is the temperature programmed decomposition (TPD) of PSC in a hydrogen atmosphere [1,2,28]. This reaction leading to the formation of alloy type Sn-Pt catalysts can be written as follows:

$$Pt\text{-}SnR_{(4-x)} + (4-x)H_2/2 \rightarrow Pt\text{-}Sn + (4-x)RH \qquad (2)$$
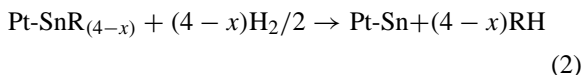
Upon comparing SiO_2 and Al_2O_3 supported Pt catalysts it has been observed that under identical experimental condition ($[Sn(C_2H_5)_4]_o = 25.3$ mM, solvent = benzene, reaction temperature $= 50\,°C$, reaction time = 2 h) the tin precursor compound reacts with the surface OH group of alumina [7,8], while no such side reaction was evidenced on silica [29]. However, it should be emphasized that the rate of this side reaction is much slower than that of the tin anchoring one [7,8,29]. Characteristic feature of this side reaction is the appearance of TPD peaks in the high temperature region, i.e. about 250 and $340\,°C$ for alumina [7,8] and silica [29], respectively. It should be mentioned

that experimental conditions used in our studies were not favorable for this side reaction, the initial concentration of tin tetraethyl was relatively low, it was in the range of 0.51–3.55 mM, and the duration of tin anchoring was short (less than 1 h).

It is necessary to mention that in the case of Sn-Rh/Al_2O_3 and Sn-Rh/SiO_2 catalysts prepared by SOMC [18] the formation of tin anchored onto the rhodium was also exclusive under identical experimental conditions ($[Sn(n\text{-}C_4H_9)_4]_o = 22.3$ and 50.2 mM for alumina and silica supported catalysts, respectively, solvent = n-heptane, reaction temperature $= 25\,°C$, reaction time = 20 h). The formation of detectable amount of $\equiv Si\text{-}O\text{-}Sn(n\text{-}C_4H_9)_3$ surface complex was observed only after 15 h of reaction at $90\,°C$ upon using high concentration of tin precursor compound (50.2 mM) [18].

In our earlier studies it has been demonstrated that the form of the TPD curves of PSC or MLSOS is completely different [29,32]. The characteristic feature of PSC is the lack of TPD peaks above $100\,°C$ as shown in Fig. 1. The TPD curves obtained at low Sn_{anch}/Pt_s ratios were deconvoluted into three major TPD peaks at 20, 40 and $75\,°C$ [32]. It should be emphasized that
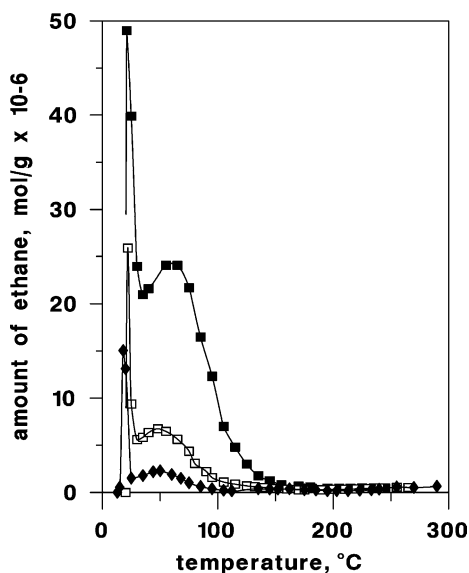

Fig. 1. The influence of the $[Sn]_o/Pt_s$ ratio on the decomposition of anchored tin organometallic complexes under monolayer coverage. Catalyst type Pt1. (◆) $[Sn]_o/Pt_s = 0.25$, $Sn_{anch}/Pt_s = 0.07$; (□) $[Sn]_o/Pt_s = 0.42$, $Sn_{anch}/Pt_s = 0.12$; (■) $[Sn]_o/Pt_s = 1.58$, $Sn_{anch}/Pt_s = 0.39$.

in all of our earlier studies [7–10,29–32] the duration of tin anchoring prior to the decomposition of PSC formed in a hydrogen atmosphere was about 2 h.

The aim of the present study is to characterize PSC formed at the very beginning of tin anchoring when the coverage of Pt by PSC is relatively low. We believe that this approach shall provide new information about the elementary steps involved in anchoring of tin tetraalkyls onto platinum.

2. Experimental part

In this study three different supported platinum catalysts were investigated. Characteristic features of these catalysts (Pt1, Pt2 and Pt3) are summarized in Table 1. Silica Pt1 (3.0 wt.% Pt) and alumina Pt2 (0.3 wt.% Pt; 1.0 wt.% Cl) supported catalysts were provided by Boreskov Institute of Catalysis (catalysts InCat Pt-1 and InCat Pt-3, respectively). More details about the preparation and some additional properties can be found elsewhere [7,8,29,31,32]. All these catalysts have been used in our earlier studies to obtain Sn-Pt/SiO$_2$ [29,31,32] and Sn-Pt/Al$_2$O$_3$ [7,8] catalysts with high Sn$_{anch}$/Pt$_s$ ratios.

The amount of tin anchored onto platinum (Sn$_{anch}$/Pt$_s$ ratio) was calculated using the H/Pt ratio determined by chemisorption. Prior to the tin anchoring step the alumina supported platinum catalysts were re-reduced in a hydrogen atmosphere at 500 °C for 2 h and cooled down to room temperature in hydrogen (flow rate = 30 cm^3/min) followed by purging with argon for 30 min. The silica supported catalyst was reduced at 300 °C for 1 h. The high purity argon (99.999 vol.%) (Linde) was purified further to remove traces of oxygen and water.

The tin anchoring process was monitored in two ways: (i) by determination of hydrocarbons formed (ethane and ethylene) both during the tin anchoring step and the decomposition of surface organometallic complexes [7,29,32], (ii) by analysis of the liquid phase for tin tetraethyl [33].

The first step of tin anchoring, i.e. the reaction of tin tetraethyl with hydrogen adsorbed on Pt (PtH$_a$) was investigated under argon atmosphere at 50 °C in deoxygenated tiophene-free benzene using a 75 cm^3 stirred glass reactor equipped with rubber septum to take samples both from gas and liquid phases. In the tin anchoring step the solvent volume was 10 ml and the amount of the parent supported Pt catalysts was 1 g. Reaction (1) was started by injection of tin tetraethyl and was monitored by determining the amount of hydrocarbons (ethane and ethylene) formed. The [Sn]$_o$/Pt$_s$ ratios were in the range of 0.1–1.9. The above conditions, as well as the short reaction time used are not favorable for surface reactions with the involvement of surface OH groups of the support. The amount of hydrocarbons formed was determined by GC using a 3 m long Al$_2$O$_3$ column at 100 °C. A correction was done for the amount of ethane and ethylene dissolved in the solvent used. The analysis of the liquid phase for tin tetraethyl during tin anchoring was accomplished by GC at 160 °C using a 4 m long Chromosorb WAW-DMCS column (inner diameter: 3 mm) coated with 10 wt.% Silicone DC 410. These results 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 [33].

In this studies different Sn-Pt/Al$_2$O$_3$ and Sn-Pt/SiO$_2$ catalysts have been prepared by varying the duration of the first step of tin anchoring in the range of 4 and 120 min.

Reaction (2) was studied by TPD technique (heating rate 5 °C/min). This techniques can also be considered as thermal programmed reaction (TPRe). However, we consider that TPD gives a better characterization of surface reaction (2), where decomposition of surface species takes place. The temperature range used in these experiments was 20–350 °C. The products of

Table 1
Characteristic properties of supported Pt catalysts

Catalyst	Support	Precursor	Pt (wt.%)	H/Pt	CO/Pt	References
Pt1	SiO$_2$	[Pt(NH$_3$)$_4$]Cl$_2$	3.0	0.52	n.a.	[29,32]
Pt2	Al$_2$O$_3$	H$_2$PtCl$_6$	0.3	0.34	0.36	[7]
Pt3	Al$_2$O$_3$	H$_2$PtCl$_6$	0.3	0.34	0.70	[7]

decomposition (C_2H_6 and C_2H_4) were analyzed by GC (see details above). In TPD experiments special care was taken (i) to use the same amount of sample in each series of experiments compared (~ 0.4 g), (ii) to prevent any contact of PSC formed with air or moisture, (iii) to decompose PSC immediately after the preparation.

The TPD peaks obtained in the decomposition step were integrated and deconvoluted. The position and the half width of each peak (in the range of ± 6 and $12\,^\circ$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 TPD peaks. The integrated values of TPD peaks were used to calculate the material balance of tin anchoring. No loss of tin was observed during the TPD experiment. However, if the washing procedure was omitted desorption of tin tetraethyl from the support was observed during the TPD experiment.

Before the TPD experiment the sample containing PSC was washed four times with purified, deoxygenated benzene and three times with *n*-hexane to remove tin tetraalkyl adsorbed onto support. It should be mentioned that under this condition full removal of all tin organic compound could be achieved both from Al_2O_3 and SiO_2. The absence of tin tetraalkyl in the last portion of washing solution was verified by GC. This washing procedure was followed by drying in vacuum (5 Torr) at $50\,^\circ$C for 1 h to remove adsorbed hydrocarbons from the catalyst. The above procedures used prior to the TPD experiment required 2 h.

The amount of C_2 hydrocarbons formed in reactions (1) and (2) (n^I, mol/g_{cat} and n^{II}, mol/g_{cat}, respectively) were determined using GC method allowing to obtain full material balance of tin anchoring. Based on the overall material balance the stoichiometry of surface reaction (1), i.e. the value of x ($x = 4n^I/(n^I + n^{II})$, and the amount of tin anchored was calculated. Good agreement was obtained between the tin content of Sn-Pt/Al_2O_3 and Sn-Pt/SiO_2 catalysts determined by AAS and from the material balance of tin anchoring. No loss of tin was observed during the TPD experiment. Further details on the preparation and analysis can be found elsewhere [7–10,29–32].

3. Results and discussions

As it has already been mentioned earlier the tin anchoring process is based on the surface reaction between hydrogen adsorbed on platinum or other noble metals and tin tetraethyl (see reaction (1)) [1,2,7,29]. Typical kinetic curves of tin anchoring are shown in Fig. 2. In all experiments the final tin coverage was below the monolayer. Upon increasing the initial concentration of $[Sn(C_2H_5)_4]_o$ the initial rate of tin anchoring increases significantly. At the very beginning the rate obeys zero order dependence. The lower the initial concentration of $[Sn(C_2H_5)_4]_o$ the longer is this period. The kinetic curves of ethane formation can be divided into three separate parts: (i) a region with relatively high rate, (ii) a part with intermediate rate, and (iii) a termination region.

At high initial concentration of tin precursor compound the fast rate is maintained up 30–40% of conversion, while at very low $[Sn(C_2H_5)_4]_o$ ($[Sn]_o/Pt_s < 0.5$) the second part cannot be seen as the reaction has been terminated relatively fast, due to the total consumption of tin tetraethyl. The total consumption indicates that the amount of tin tetraethyl reacted in surface reaction (1) plus the amount of tin tetraethyl weakly adsorbed onto the support is equal to the
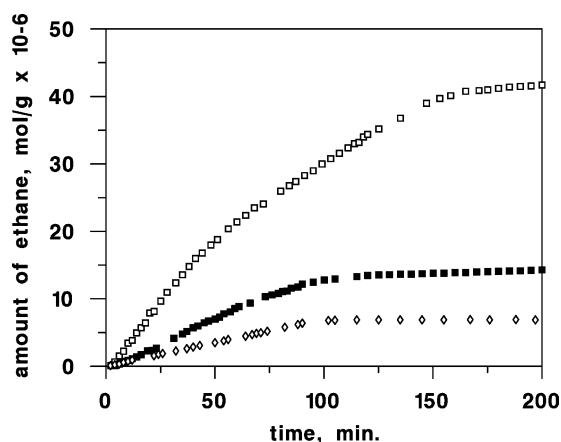

Fig. 2. Kinetic curves of the formation of ethane in the surface reaction (1). Influence of the $[Sn]_o/Pt_s$ ratios. Catalyst type Pt1. ($\diamondsuit$) $[Sn(C_2H_5)_4]_o = 0.76$ mM; $[Sn]_o/Pt_s = 0.09$ ($Sn_{anch}/Pt_s = 0.06$); ($\blacksquare$) $[Sn(C_2H_5)_4]_o = 3.55$ mM, $[Sn]_o/Pt_s = 0.42$ ($Sn_{anch}/Pt_s = 0.12$); ($\square$) $[Sn(C_2H_5)_4]_o = 12.66$ mM, $[Sn]_o/Pt_s = 1.58$ ($Sn_{anch}/Pt_s = 0.39$). T_r: $50\,^\circ$C; amount of catalyst: 1 g; solvent: benzene.

Table 2
Summary of results of tin anchoring onto different supported platinum catalysts

Experiment number	$[SnEt_4]_0$ (mM)	$[Sn]_o/Pt_s$	Reaction time (min)	W_o[a]	n^{Ib}	n^{IIc}	x	Sn_{anch}/Pt_s[d]
Pt1-1	0.76	0.09	120	0.07	6.9	11.7	1.48	0.06
Pt1-2	3.55	0.42	120	0.16	13.5	23.9	1.44	0.12
Pt1-3	12.66	1.58	120	0.43	44.0	81.7	1.40	0.39
Pt2-1	0.15	0.15	120	0.05	1.5	4.7	0.98	0.14
Pt2-2	0.51	0.46	100	0.19	4.0	10.7	1.08	0.33
Pt3-1	0.15	0.11	120	0.04	1.3	4.5	0.90	0.09
Pt3-2	0.51	0.37	90	0.13	4.2	14.8	0.88	0.31
Pt3-3	2.53	1.85	120	0.31	9.4	34.9	0.85	0.72

T_r: 50 °C, amount of catalyst: 1 g.

[a] Initial rate of tin anchoring reaction (1) (mol/g_{cat} × min × 10^{-6}).

[b] Total amount of C_2 hydrocarbons formed in surface reaction (1) (mol/g_{cat} × 10^{-6}).

[c] Amount of hydrocarbons formed in reaction (2) (mol/g_{cat} × 10^{-6}).

[d] Calculated from the overall material balance of tin anchoring.

amount of tin introduced. It should be mentioned that the adsorbed form of tin tetraethyl was completely removed by the washing procedure used. It should also be noted that under the same experimental condition on alumina supported catalysts the amount of adsorbed tin tetraethyl was more than twice as much as on the silica supported one.

Further data related to the reaction rates and material balance of tin anchoring using three different supported platinum catalysts are summarized in Table 2. It should be emphasized that similar to our previous studies [7–10,29–32] the duration of tin anchoring in experiments presented in Table 2 was between 90 and 120 min. As emerges from these results for each type of catalysts (Pt1, Pt2 and Pt3) both the rate of formation of PSC and the amount of tin anchored onto platinum (Sn_{anch}/Pt_s) is proportional to the $[Sn]_o/Pt_s$ ratio, however the stoichiometry of surface reaction (1) (see x values in Table 2) is in the range of 0.85–1.48 and depends on both the type of catalyst and the metal loading. However, these values, within a given type of catalyst, are almost independent of the $[Sn]_o/Pt_s$ ratio.

The value $x = 1.0$ indicates on the exclusive formation of $-Sn(C_2H_5)_3$ type surface species, while the value $x = 1.5$ suggests that Pt is covered by $-Sn(C_2H_5)_3$ ($x = 1$) and $-Sn(C_2H_5)_2$ ($x = 2$) species formed in 1:1 ratio [29]. The behavior of the two alumina supported catalysts (Pt2 and Pt3) in tin anchoring reaction is almost identical. Please note that the dispersions of Pt in these alumina supported catalysts determined from H/Pt ratio is also similar

(see Table 1). It is noteworthy that contrary to the alumina supported catalysts, the silica supported one (Pt1) showed lower activity in surface reaction (1). As emerges from Table 2 on catalyst Pt1 the monolayer tin coverage ($Sn_{anch}/Pt_s = 0.35–0.45$) was reached at $[Sn]_o/Pt_s = 1.58$, while on both alumina supported catalysts (Pt2 and Pt3) it was attained at $[Sn]_o/Pt_s = 0.4$ (compare experiments Pt1-3 with Pt2-2 and Pt3-2). In the case of alumina supported catalyst the use of almost identical initial concentration of tin tetraethyl ($[Sn]_o/Pt_s$ about 1.7, see experiments Pt3-3 and Pt1-3) resulted in much higher tin content than on silica supported catalyst (compare $Sn_{anch}/Pt_s = 0.72$ and 0.39, respectively).

In the next set of experiments upon using the same initial concentration of $Sn(C_2H_5)_4$ surface reaction (1) has been terminated after different reaction time. The TPD pattern ofeaction time. The TPD pattern of these samples was compared and the results are given in Fig. 3A–D. As emerges from Fig. 3A–D the TPD pattern of these samples showed marked differences depending on the duration of surface reaction (1). The sample obtained after 100 min of reaction (see Fig. 3D) strongly resembles earlier results, i.e. it contains no major TPD peaks in the temperature range above 100 °C.

Contrary to that short reaction times resulted in quite complex TPD profiles (see Figs. 3A and B). Samples obtained after 4 and 10 min after injection of tin organic compound contained two broad TPD peaks. After deconvolution the first broad peak, representing around 45% of the total amount of ethane formed,
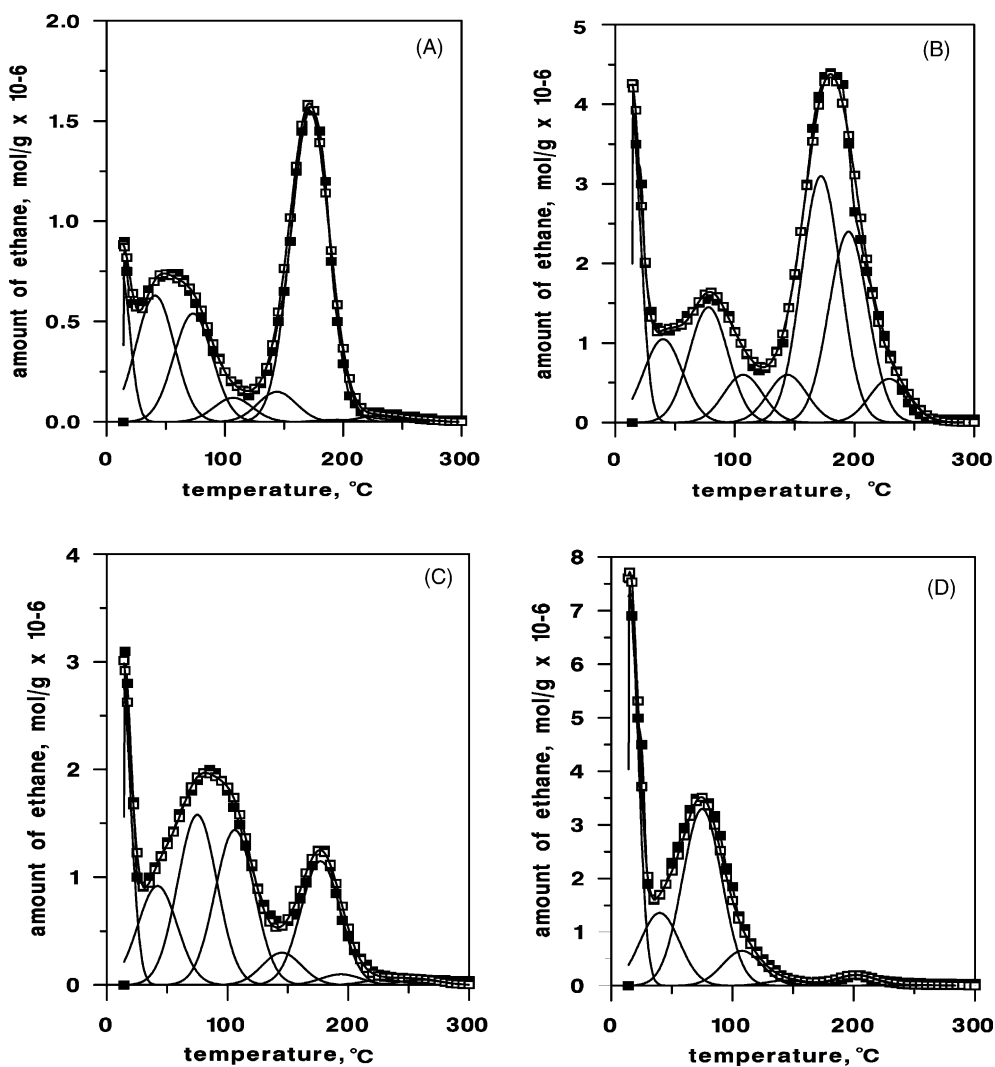
Fig. 3. The influence of the time of surface reaction (1) on the TPD pattern. Catalyst type Pt2; $[Sn(C_2H_5)_4]_o = 0.51\,mM$; $[Sn(C_2H_5)_4]_o/Pt_s = 0.46$. (A) Reaction time: 4 min ($Sn_{anch}/Pt_s = 0.14$); (B) 10 min ($Sn_{anch}/Pt_s = 0.37$); (C) 60 min ($Sn_{anch}/Pt_s = 0.33$) and (D) 100 min ($Sn_{anch}/Pt_s = 0.33$). (■) Measured and (□) fitted.

contained tree low temperature peaks around 20, 40, and 75 °C, while the high temperature peak consisted two major peaks around 170 and 200 °C and a small shoulder above 200 °C. In these samples the contribution of the peaks around 110 and 140 °C is small. The small shoulders above 200 °C detected around 230 and 260 °C accounted for less than 1.0% of the total amount of hydrocarbons formed. This fact confirm unambiguously that, based on literature data [7,8,29], under experimental condition used for tin anchoring

the amount of tin introduced into the support is negligible.

The results of deconvolution of the TPD peaks are summarized in Table 3. These results clearly show the time dependence of the formation of different surface entities. The obtained Sn_{anch}/Pt_s ratios indicate that conditions used for tin anchoring resulted in monolayer tin coverage as $Sn_{anch}/Pt_s < 0.4$. After 10 min of reaction the amount of tin anchored is constant within the experimental error. However, the stoichiometry of

Table 3
Deconvolution of the TPD peaks obtained on catalyst Pt2

Experiment number	Reaction time (min)	Sn_{anch}/Pt_s	x	Amount of C_2H_6 form in different TPR peaks, n_{ij}^{II}, $\times\ 10^{-6}$ mol/g_{cat} $\times$ min								
				First peak 15–22 °C	Second peak 39–44 °C	Third peak 72–78 °C	Fourth peak 102–108 °C	Fifth peak 141–148 °C	Sixth peak 172–180 °C	Seventh peak 194–199 °C	Eighth peak 230 °C	Ninth peak 260 °C
1	4	0.14	0.32	0.57	1.01	0.87	0.19	0.24	2.49	0.02	0.05	0.02
2	10	0.37	0.37	1.66	1.41	1.95	0.81	0.81	4.16	3.24	0.74	0.01
3	30	0.39	0.74	2.07	1.48	2.16	1.89	0.81	3.10	1.62	0.74	0.01
4	60	0.33	0.74	2.30	1.55	2.66	2.43	0.51	1.94	0.17	0.09	0.09
5	100	0.33	1.08	3.91	1.64	3.98	0.78	0.12	0.01	0.24	0.01	0.01

$[Sn(C_2H_5)_4]_o = 0.51$ mM; $[Sn(C_2H_5)_4]_o/Pt_s = 0.46$.

tin anchoring, i.e. the value of x shows a characteristic increase as the surface reaction (1) proceeds. This experimental finding is a very important one, as it provides further prove with respect to the formation of new species at the very beginning of tin anchoring.

The low value of x obtained after 4 and 10 min ($x = 0.32$ and 0.37, respectively) indicates that surface species formed should contain both -$Sn(C_2H_5)_4$ and -$Sn(C_2H_5)_3$ type surface species and the formation of -$Sn(C_2H_5)_4$ prevails. However, after 100 min of reaction time the value of x is close to one, i.e. this sample should contain only -$Sn(C_2H_5)_3$ type surface species. It should be emphasized that this sample resulted in only low temperature TPD peaks below 100 °C, i.e. it strongly resembles our earlier findings shown in Fig. 1.

Results given in Table 3 indicate that the intensity of all TPD peaks above 100 °C (peaks 4–9) passes through a maximum. However, after 100 min of reaction the intensity of these peaks decreases to a value close to the detection limit.

The nine TPD peaks were divided into the following four different regions: (i) low temperature region up to 80 °C (peaks no. 1–3), intermediate region between 110 and 140 °C (peaks no. 4 and 5), high temperature region between 170 and 200 °C (peaks no. 6 and 7) and region above 200 °C (peaks no. 8 and 9). The latter temperature range is characteristic for tin tetraethyl adsorbed into the support. We suggest that the above temperature regions of TPD peaks can represent at least four different types of surface entities (surface species A, B, C, and D, respectively).

The time dependence of the formation of these four different types of surface species exhibits a very interesting relationship as shown in Fig. 4.

Based on our earlier results [29,32] and discussions made above surface species A should represent -$Sn(C_2H_5)_3$ type surface species anchored to the platinum. Surface species D can be designated to $Sn(C_2H_5)_4$ adsorbed to the support [7,29]. The question is how to designate surface species B and C.

In our previous studies [29,32], the high temperature peaks around 170 and 200 °C were attributed to surface species, such as surface complexes in the second layer (SCSL), containing -{$Sn(C_2H_5)_{(4-x)}$-[$Sn(C_2H_5)_4$]} moieties. However, in the present case it is hardly to assume that a second layer of tin organic moieties at the top of the PSC can be formed immedi-
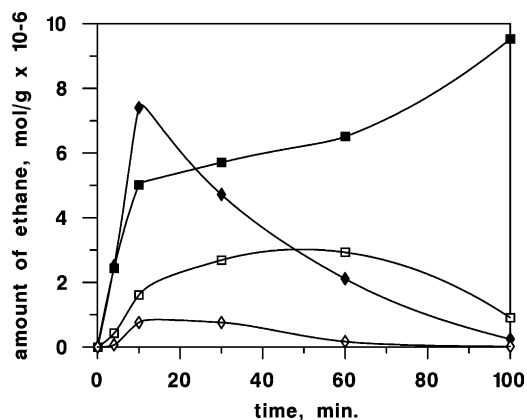

Fig. 4. Time dependence of the formation of different types surface species during tin anchoring. Results obtained from deconvoluted TPD peaks (see results given in Table 3). Catalyst type Pt2, [$Sn(C_2H_5)_4$]$_o$ = 0.51 mM, [Sn]$_o$/Pt$_s$ = 0.46. (■) Sum of the amount of ethane formed in the first three peaks up to 80 °C (peaks no. 1–3, surface species A); (□) sum of the amount of ethane formed in the fourth and fifth peaks (temperature region between 110 and 140 °C) (surface species B); (◆) sum of the amount of ethane formed in the sixth and seventh peaks (temperature region between 170 and 200 °C) (surface species C); (◇) sum of the amount of ethane formed above 200 °C (temperature region between 230 and 260 °C) (peaks no. 8–9, surface species D).

ately after introduction of tin tetraethyl. Consequently, the formation of surface species in the second layer with general formula -{$Sn(C_2H_5)_{(4-x)}$-[$Sn(C_2H_5)_4$]} can be excluded.

The low x values of samples obtained after 4 and 10 min ($x = 0.32$ and 0.37, respectively) indicates also that in all surface species formed in this period at the Pt sites -$Sn(C_2H_5)_4$ moiety is a dominating one.

The time dependence shown in Fig. 4 as well as data given in Table 3 show that surface reactions involved in tin anchoring under monolayer condition should have *consecutive character*. The time dependence clearly shows that at the very beginning of tin anchoring there are only two primary products, i.e. in this period only two classes of major surface entities are formed, namely surface species A and C. However, Fig. 4 clearly shows also that after 100 min of tin anchoring all major and minor species are transformed into surface species A. The character of kinetic curves indicates also that after 10 min of reaction surface species C starts to consume. The character of kinetic curves indicates that it can be transformed into surface species A and B. Surface
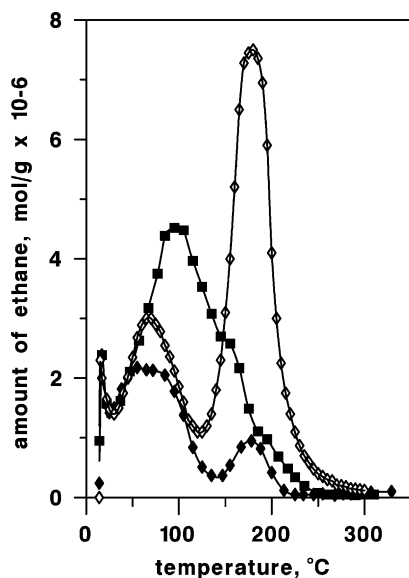
Fig. 5. The influence of the duration of surface reaction (1) on the TPD pattern of surface organometallic complexes formed. Catalyst Pt3. $[Sn(C_2H_5)_4]_o = 2.53$ mM; $[Sn(C_2H_5)_4]_o/Pt_s = 1.85$. Time of surface reaction (1): (◆) 4 min ($Sn_{anch}/Pt_s = 0.20$); (◇) 10 min ($Sn_{anch}/Pt_s = 0.55$); (■) 20 min ($Sn_{anch}/Pt_s = 0.56$).

species B appeared to be also unstable as after 60 min reaction it was transformed into A.

Similar results confirming the consecutive character of surface reactions involved in anchoring of tin tetraethyl onto supported platinum were also obtained on catalyst Pt3. These results are shown in Fig. 5 and Table 4. It is necessary to mention, that in these experiments the initial tin concentration was about five times as much as used in experiments shown in Fig. 3 (compare $[Sn(C_2H_5)_4]_o$ values given Tables 3 and 4). The TPD profiles shown in Fig. 5 strongly resemble the TPD patterns obtained on catalyst Pt2 (see Fig. 3A and B) when the duration of surface reaction (1) was also 4 and 10 min. The low value of the stoichiometry of tin anchoring ($x = 0.34$ and $x = 0.40$) indicates that -$Sn(C_2H_5)_4$ type surface species is the dominant one at short reaction time.

The decomposition pattern of the surface complexes formed after 20 min showed marked differences compared to surface complexes formed after short reaction time. The TPD pattern shows a slight increase in the intensity of peaks between 40 and 75 °C (surface species A) and pronounced increase for peaks between 110 and 140 °C (surface species B), but the

high temperature peaks between 170 and 200 °C (surface species C) strongly diminished and became a minor component. The notable increase of the value of x ($x = 0.75$, see Table 4) reflects also the considerable decrease of the contribution of surface species C. Consequently, the comparison of the TPD patterns obtained at short and prolonged tin anchoring (compare Figs. 3C and 5), shows that the higher the $[Sn]_o/Pt_s$ ratio used, the faster the transformation of strongly adsorbed -$Sn(C_2H_5)_4$ surface entities into surface species A and B. Accordingly, the increase of the $[Sn]_o/Pt_s$ ratio resulted in an increase of both the mobility and the reactivity of surface species C. We believe that all facts discussed above strongly indicate, that surface species C is located exclusively on supported metal nanoclusters.

In [34] by using infrared spectroscopy it has been shown, that in the presence of metallic Rh the hydrogenolysis of $Sn(n\text{-}C_4H_9)_4$ occurs exclusively on the metallic particles. At room temperature tin tetra-n-butyl was physisorbed on the silica surface, but the increase of the reaction temperature up to 50 °C resulted in fast migration and reaction with the Rh particles. We believe that similar behavior can also take place on supported platinum. In all of our experiments the reaction temperature was 50 °C, the rate of reaction was fast and all transformations proceeded selectively on platinum. Moreover in our previous studies it was shown that after 2 h of tin anchoring reaction even at 27 °C the organotin precursor was exclusively anchored onto platinum [29].

In order to study further transformation of surface species C resulting in high temperature TPD peaks between 170 and 200 °C the following experiment was performed. The tin anchoring reaction has been terminated after 10 min and the sample was divided into two parts. Sample I was treated as usual and was decomposed in a subsequent TPD run, while sample II was washed with benzene to remove all unreacted and adsorbed tin tetraethyl and the surface reaction was continued at 50 °C under argon atmosphere using new portion of benzene for another 150 min. These results are shown in Figs. 6 and 7.

Results presented in Fig. 6 show that the rate of tin anchoring is high, however all secondary transformations with the involvement of anchored surface species (see part of the kinetic curve after 10 min) proceed with much slower rate than surface reaction (1). The

Table 4
Deconvolution of the TPD peaks obtained on catalyst Pt3

Experiment number	Reaction time (min)	Sn_{anch}/Pt_s	x	Amount of C_2H_6 form in different TPR peaks, n_{ij}^{II}, $\times$ 10^{-6} mol/g_{cat} $\times$ min								
				First peak 15–22 °C	Second peak 39–44 °C	Third peak 72–78 °C	Fourth peak 102–108 °C	Fifth peak 141–148 °C	Sixth peak 172–180 °C	Seventh peak 194–199 °C	Eighth peak 230 °C	Ninth peak 260 °C
1	4	0.20	0.34	1.90	2.80	2.60	2.14	0.33	1.35	0.25	0.08	0.09
2	10	0.55	0.40	1.97	2.76	4.88	2.03	1.84	12.41	3.33	0.93	0.39
3	20	0.56	0.75	1.98	3.32	6.23	7.47	4.77	2.70	1.04	0.46	0.02
4	10 + 150[a]	0.40	0.86	1.45	3.08	5.26	4.90	2.72	0.85	0.91	0.18	0.02

$[Sn(C_2H_5)_4]_o = 2.53$ mM; $[Sn(C_2H_5)_4]_o/Pt_s = 1.85$.

[a] Surface reaction (1) in the presence (10 min) and absence of tin tetraethyl (150 min).
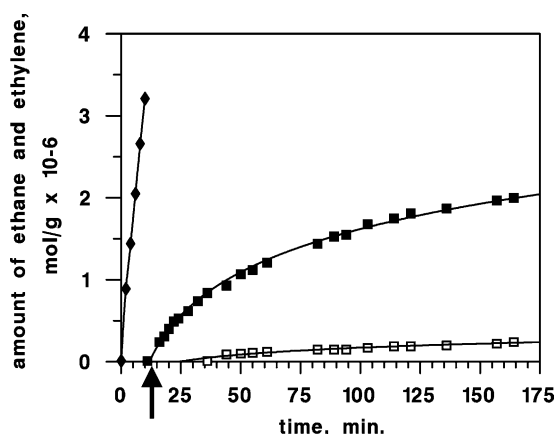
Fig. 6. Formation of ethane (◆) in the first 10 min of tin anchoring (sample I) and in the secondary transformation of anchored tin organic species (■) ethane, (□) ethylene) (sample II). The arrow shows the time of removal of unreacted tin tetraethyl and starting the secondary transformation of surface species anchored. Catalyst Pt3. Conditions of tin anchoring: $[Sn(C_2H_5)_4]_o = 2.53$ mM; $[Sn]_o/Pt_s = 1.85$; T_r: 50 °C; amount of catalyst: 1 g; solvent: benzene.

amount of C_2 hydrocarbons formed in both steps was almost identical, however in sample II the value of x was about twice as much as in sample I ($x = 0.86$ and 0.40, respectively; see value of x in Table 4). The TPD

pattern of these two samples (see Fig. 7A and B) was also completely different. In sample I the main TPD peak appeared around 170 °C as shown in Fig. 7A, while in sample II (see Fig. 7B) it is the minor component. Consequently, these results provided further prove for the consecutive character of surface reactions involved in tin anchoring. These results clearly confirm that surface species **C** (TPD peak around 170 °C) formed after 10 min of tin anchoring are transformed into species **A** and **B** (temperature regions between 20 and 80 °C and 110 and 140 °C, respectively) when the surface reaction was continued in the absence of $Sn(C_2H_5)_4$ for additional 150 min.

Results obtained on silica supported Pt1 catalyst are shown in Fig. 8. The trend is the same, i.e. the decrease of the reaction time increases the amount of high temperature TPD peaks between 170 and 200 °C. Upon increasing the reaction time the contribution of low temperature peaks below 110 °C increases with parallel decrease of the high temperature TPD peaks. Consequently, the observed phenomenon is general, i.e. it is independent of the support and the metal loading.

Based on the evidences given above it is suggested that under monolayer tin coverage surface reactions involved in tin anchoring can be written as follows:

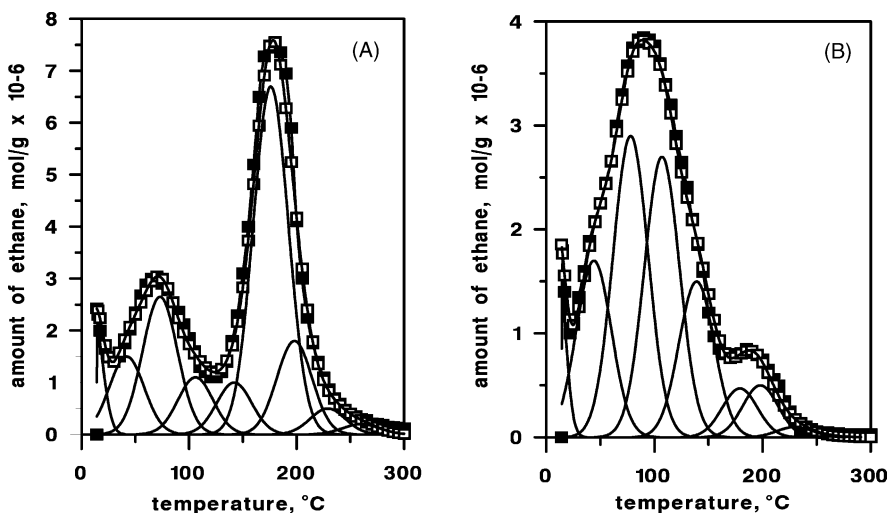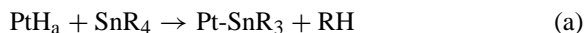$$PtH_a + SnR_4 \rightarrow Pt\text{-}SnR_3 + RH \qquad (a)$$

Fig. 7. Decomposition of surface species formed in samples (I) and (II) (see Fig. 6): (A) decomposition of surface species formed in the first 10 min of tin anchoring (sample I); (B) decomposition of surface species formed from sample I in secondary transformation performed in the absence of tin tetraethyl for additional 150 min (sample II). (■) Measured and (□) fitted.
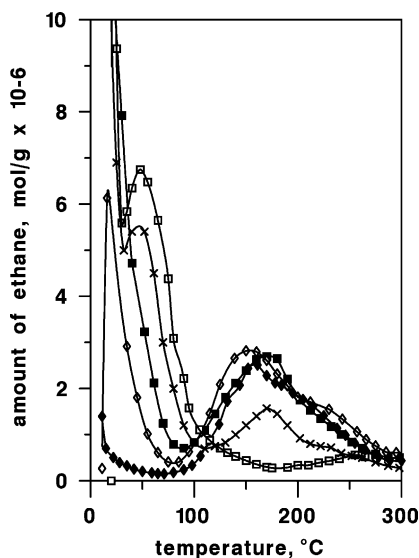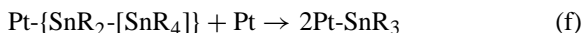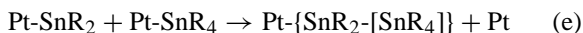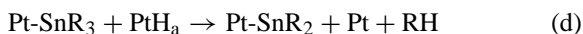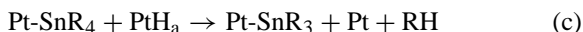
Fig. 8. Influence of the duration of the tin anchoring on the decomposition of surface organometallic complexes. Catalyst Pt1, $[Sn(C_2H_5)_4]_o = 3.55$ mM, $[Sn]_o/Pt_s = 0.42$. Time of surface reaction (1): (◆) 4 min ($Sn_{anch}/Pt_s = 0.04$); (◇) 10 min ($Sn_{anch}/Pt_s = 0.07$); (■) 60 min ($Sn_{anch}/Pt_s = 0.12$); (×) 90 min ($Sn_{anch}/Pt_s = 0.12$); (□) 120 min ($Sn_{anch}/Pt_s = 0.12$).

$$Pt + SnR_4 \leftrightarrow Pt\text{-}SnR_4 \quad (b)$$

$$Pt\text{-}SnR_4 + PtH_a \rightarrow Pt\text{-}SnR_3 + Pt + RH \quad (c)$$

$$Pt\text{-}SnR_3 + PtH_a \rightarrow Pt\text{-}SnR_2 + Pt + RH \quad (d)$$

$$Pt\text{-}SnR_2 + Pt\text{-}SnR_4 \rightarrow Pt\text{-}\{SnR_2\text{-}[SnR_4]\} + Pt \quad (e)$$

$$Pt\text{-}\{SnR_2\text{-}[SnR_4]\} + Pt \rightarrow 2Pt\text{-}SnR_3 \quad (f)$$

Reaction (a) corresponds to reaction (1) in our earlier scheme. This reaction leads to the formation of *A* type surface species with low temperature TPD peaks. Reaction (b) is an equilibrium reaction leading to the formation of surface species *C*, what can be considered as tin tetraethyl strongly bonded to the platinum. It has to be emphasized again that both surface species *A* and *C* have to be considered as primary products (see explanations given to Fig. 4). Due to the peculiarities of the given system, when the time of reaction (1) is very short, only surface organometallic moieties, such as Pt-SnR$_3$ and Pt-SnR$_4$, can be considered as primary products of tin anchoring onto platinum.

Due to coordinative saturation surface species *C* is much less reactive towards adsorbed hydrogen than *A*,

for this reason it should give a high temperature TPD peak. Fig. 4 shows also that this surface species reacts further with the formation of surface species *A* and *B* (reactions (c) and (e), respectively). Surface species *B* corresponds to TPD peaks between 110 and 140 °C. Consequently, surface species *B* should have an intermediate activity between surface species *A* and *C*.

As it emerges from Fig. 4 the formation of surface species *B* has a slight S-character, for this reason it is considered that *it cannot be a primary product*. In our earlier studies [29,32] these peaks have been attributed to surface complexes in the second layer.

In the presence of hydrogen adsorbed on Pt (PtH$_a$), surface species *A* can lose one more alkyl group leading to the formation of coordinatively unsaturated -SnR$_2$ surface species (reaction (d)). This reaction has been considered in our earlier scheme as one of the key reactions responsible for the formation of multilayered surface organometallic entities [29]. This type of surface species is highly reactive and will interact with surface species *C* in reaction (e) leading to the formation of surface complex in the second layer.

The kinetic curve of the formation of surface species *D* has also an S-character and passes through a maximum. This species is completely consumed after 60 min reaction time. This species decomposes above 200 °C, i.e. its decomposition requires the highest energy of activation. For this reason it should be formed on the support. However, its relatively fast consumption strongly indicates that it should be located close to the Pt sites. Consequently, we suggest that this surface species should be located at the metal-support interface and has similar stoichiometry as surface species *C*.

4. Summary

The first step of the tin anchoring reaction with the involvement of tin tetraethyl and hydrogen adsorbed on Pt sites has been investigated. The focus was laid on the variation of the duration of this surface reaction. Experimental evidences indicated that (i) below monolayer coverage of surface organometallic moieties, and (ii) under condition of short reaction time parallel to the formation of anchored -SnR$_3$ moieties new surface species are formed, such as anchored SnR$_4$ and

its derivatives. This finding has been supported by the following experimental evidences:

(i) Complete change of the TPR pattern of samples, as the reaction proceeded (see Fig. 3).
(ii) Alteration of the stoichiometry of tin anchoring (see data given in Tables 3 and 4).
(iii) Pronounced time dependence of the formation of different surface species (see Fig. 4).
(iv) Different decomposition pattern of primary surface species formed after 10 min of tin anchoring and species obtained after secondary transformation of primary surface species in the liquid phase in the absence of tin tetraethyl (compare decomposition pattern shown in Figs. 7A and B).

As the tin anchoring reaction proceeds the new surface entities are transformed into -SnR_3 moieties. The fact that the amount of tin anchored is almost independent after 10 min, but the position of peaks on the TPD curves is strongly altered is a strong indication for the transformation of surface organometallic moieties primary formed on supported metal nanoclusters.

Acknowledgements

References

[1] J. Margitfalvi, M. Hegedűs, S. Gőbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó, F. Nagy, in: Proceedings of the Eighth International Congress on Catalysis, vol. 4, Berlin (West), 2–6 July 1984, p. 903.
[2] J.L. Margitfalvi, E. Tálas, S. Gőbölös, Catal. Today 6 (1989) 73.
[3] J.L. Margitfalvi, H.P. Jalett, E. Tálas, A. Baiker, H.U. Blaser, Catal. Lett. 10 (1991) 325.
[4] J.L. Margitfalvi, A. Tompos, I. Kolosova, J. Valyon, J. Catal. 174 (1998) 246.
[5] J.L. Margitfalvi, E. Kern-Tálas, S. Gőbölös, M. Hegedűs, P. Szedlacsek, in: Proceedings of the Symposium on Advancement in Naphtha Reforming Division, Petroleum Chemicals, 194th ACS National Meeting, New Orleans, 30 August–4 September 1987, pp. 715–721.
[6] J.L. Margitfalvi, S. Gőbölös, E. Kern-Tálas, M. Hegedűs, P. Szedlacsek, in: B. Delmon, G.F. Froment (Eds.), Catalysts Deactivation IV, vol. 34, Elsevier, Amsterdam, Stud. Surf. Sci. Catal., 1987, p. 147.
[7] J.L. Margitfalvi, I. Borbáth, M. Hegedűs, S. Gőbölös, F. Lónyi, React. Kinet. Catal. Lett. 68 (1999) 133.
[8] J.L. Margitfalvi, I. Borbáth, M. Hegedűs, S. Gőbölös, A. Tompos, F. Lónyi, in: A. Corma, F.V. Melo, S. Mendioroz, J.L.G. Fierro (Eds.), Proceedings of the 12th International Congress Catalysis, Granada, 2000, 9–14 July, Stud. Surf. Sci. Catal., vol. 130, Part B, Elsevier, Amsterdam, 2000, p. 1025.
[9] J.L. Margitfalvi, I. Borbáth, K. Lázár, E. Tfirst, A. Szegedi, M. Hegedűs, S. Gőbölös, J. Catal. 203 (2001) 94.
[10] J.L. Margitfalvi, I. Borbáth, M. Hegedűs, A. Szegedi, K. Lázár, S. Gőbölös, S. Kristyán, Catal. Today 73 (2002) 343.
[11] C. Travers, J.P. Bournonville, G. Martino, in: Proceedings of the 8th International Congress on Catalysis, vol. 4, Berlin (West), 2–6 July 1984, p. 891.
[12] H.R. Aduriz, P. Bodnariuk, B. Coq, F. Figueras, J. Catal. 119 (1989) 97.
[13] B. Coq, A. Tijani, F. Figueras, J. Mol. Catal. 71 (1992) 317–333.
[14] O.A. Ferretti, J.P. Bournonville, G. Mabilon, G. Martino, J.P. Candy, J.M. Basset, J. Mol. Catal. 67 (1991) 283–294.
[15] B. Didillon, A.E. Mansour, J.P. Candy, J.P. Bournonville, J.M. Basset, in: M. Guisnet, et al. (Eds.), Heterogeneous Catalysis and Fine Chemicals II, Stud. Surf Sci. Catal., vol. 59, Elsevier, Amsterdam, 1991, p. 137.
[16] B. Didillon, J.P. Candy, F. Le Peletier, O.A. Ferretti, J.M. Basset, in: M. Guisnet, et al. (Eds.), Heterogeneous Catalysis and Fine Chemicals III, Stud. Surf Sci. Catal, vol. 78, Elsevier, Amsterdam, 1993, p. 147.
[17] J.P. Candy, B. Didillon, E.L. Smith, T.B. Shay, J.M. Basset, J. Mol. Catal. 86 (1994) 179.
[18] O.A. Ferretti, C. Lucas, J.P. Candy, J.-M. Basset, B. Didillon, F. Le Peletier, J. Mol. Catal. A: Chem. 103 (1995) 125–132.
[19] V.D. Stytsenko, Appl. Catal. 126 (1995) 1.
[20] E. Merlen, P. Beccat, J.C. Bertolini, P. Delichére, N. Zanier, B. Didillon, J. Catal. 159 (1996) 178.
[21] F. Humblot, B. Didillon, F. Le Peltier, J.P. Candy, J. Corker, O. Clause, F. Bayard, J.M. Basset, J. Am. Chem. Soc. 120 (1998) 137–146.
[22] F. Humblot, J.P. Candy, F. Le Peltier, B. Didillon, J.M. Basset, J. Catal. 179 (1998) 459–468.
[23] R. Psaro, S. Recchia, Catal. Today 41 (1998) 139–147.
[24] F.Z. Bentahar, F. Bayard, J.P. Candy, J.M. Basset, B. Didillon, in: J.P. Blitz, C.B. Little (Eds.), Proceedings of the Seventh International Symposium on Fundamental and Applied Aspects of Chemical Modified Surfaces, Evanston, USA, 24–28 June 1998, Spec. Publ. Roy. Soc. Chem., 1999, p. 235.
[25] E. Tena, J.P. Candy, M.F. Cornil, B. Jousseaume, M. Spagnol, J.M. Basset, J. Mol. Catal. A: Chem. 146 (1999) 53–64.
[26] G.F. Santori, M.L. Casella, G.J. Siri, H.R. Aduriz, O.A. Ferretti, Appl. Catal. A: Gen. 197 (2000) 141–149.
[27] L. Stievano, F.E. Wagner, S. Calogero, S. Recchia, D. Dossi, R. Psaro, in: A. Corma, et al. (Eds.), Stud. Surf. Sci. Catal., vol. 130, Elsevier, Amsterdam, 2000, p. 3903.

[28] Cs. Vértes, E. Tálas, I. Czakó-Nagy, J. Ryczkovski, S. Gőbölös, A. Vértes, J. Margitfalvi, Appl. Catal. 68 (1991) 149.

[29] J.L. Margitfalvi, I. Borbáth, E. Tfirst, A. Tompos, Catal. Today 43 (1998) 29.

[30] J.L. Margitfalvi, I. Kolosova, E. Tálas, S. Gőbölös, Appl. Catal. 154 (1997) 1.

[31] J.L. Margitfalvi, I. Borbáth, A. Tompos, in: B. Delmon P.A. Jacobs, R. Maggi, J.A. Martens, P. Grange, G. Poncelet (Eds.), Preparation of Catalysts VII, vol. 118, Stud. Surf. Sci. Catal., Elsevier, Amsterdam, 1998, p. 195.

[32] J.L. Margitfalvi, I. Borbáth, M. Hegedűs, A. Tompos, Appl. Catal. 229 (2002) 35.

[33] J.L. Margitfalvi, I. Borbáth, M. Hegedűs, S. Gőbölös, Appl. Catal. 219 (2001) 171.

[34] B. Didillon, C. Houtman, T. Shay, J.P. Candy, J.M. Basset, J. Am. Chem. Soc. 115 (1993) 9380.