Zeolite supported Sn–Pt catalysts prepared by surface reactions

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Abstract

A Pt/H–mordenite (Pt/H–MOR) catalyst has been modified with tin using the controlled surface reaction between tin tetraalklyls and hydrogen adsorbed on platinum. Experimental evidences show that upon modification of Pt/H-MOR catalyst with tin tetraalkyls, the surface chemistry established for Pt/SiO_2 and Pt/Al_2O_3 cannot be maintained, i.e., the formation of multilayered organometallic complexes (MLOC) is hindered. Consequently, the results indicate that the introduction of tin into platinum is possible if the Sn/Pt_s ratio is below 0.5. In this case, zeolite supported alloy type Sn–Pt nanoparticles are formed. At higher Sn/Pt_s ratios, in addition to the formation of alloy type Sn–Pt nanoparticles, ionic forms of tin anchored onto the zeolite are also formed. The reaction between tin tetraalkyls and surface OH groups of the zeolite is involved in the formation of ionic forms of tin stabilized on the zeolite surface. Upon applying Mössbauer spectroscopy, different tin containing surface species were identified including two SnPt alloy phases. Tin introduced in this way slightly decreases the H/Pt and CO/Pt ratios measured by chemisorption and changes the activity and selectivity of these catalysts in *n*-hexane isomerization at 275°C. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst modification; Modification with tin tetraalkyls; Pt/H–mordenite catalysts; Sn–Pt/mordenite catalysts; Tin tetramethyl; Tin tetraethyl

1. Introduction

Recently, we have described an approach to the preparation of new type of alumina and silica supported Sn–Pt catalysts with almost exclusive Sn–Pt interaction [1,2]. The basis of this new approach is the surface reaction between tin tetraalkyls and hydrogen adsorbed on platinum [3,4]. The new approach leads to the formation of multilayered organometallic complexes (MLOC) anchored onto supported platinum. The formed MLOC can be decomposed either in reductive or oxidative atmosphere with the formation of new type of supported Sn–Pt catalysts with high Sn/Pt_s ratios $((Sn/Pt_s)_{max} = 3)$ [2].

Tin tetraalkyls have also been used by other research groups to prepare different tin modified supported metal catalysts [5–10]. The common feature of these approaches is the control of surface reactions involved in the tin anchoring process. The exclusive formation of Sn–Pt, Sn–Rh and other bimetallic nanoclusters requires choosing experimental conditions not favourable for the reaction be-

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tween tin tetraalkyls and the surface OH groups of the support. In this respect, a pronounced difference between the reactivity of surface OH groups on silica and alumina has been reported [2], the latter appeared to be more reactive. Consequently, when zeolite supported Pt catalysts are modified with tin tetraalkyls, high initial concentration of tin tetraalkyls and high reaction temperatures should be avoided as, under these conditions the highly acidic surface OH groups of zeolite can react with tin tetraalkyls, hence exclusive introduction of tin onto platinum cannot be guaranteed and part of tin is introduced into the support.

Methods of surface organometallic chemistry have already been applied to modify zeolite supported metal catalysts by other research groups. NaY zeolite supported platinum [11,12] and rhodium [13] catalysts were modified by different tin tetraalkyls SnR_4 (R = Me or Et, Ph, respectively). According to Ref. [11], a definite part of tin in its oxidized form was deposited not to the platinum, but to the zeolite surface in the vicinity of Pt particles. As shown in Ref. [13], the presence of intrazeolitic protonic acidity promoted the formation of Sn^{2+} ions by reoxidation of zero-valent Sn phase in $Rh^0–Sn^0$ to $Rh–Sn^{\delta+}$ ($\delta \sim 2$). It has been suggested that in this oxidation reaction, the zeolitic proton is involved. However, in non-acidic metal-zeolite samples, the exclusive formation of bimetallic $Rh^0–Sn^0$ particles has been evidenced [13].

The characteristic feature of the approaches used in Refs. [11–13] is the fact that the added tin organic compound was decomposed in a hydrogen atmosphere without removal of unreacted tin tetraalkyls by a washing procedure. Thus, different types of surface reactions, i.e., surface reaction with involvement of hydrogen adsorbed on the metal and surface reaction with the engagement of surface hydroxyl groups were not differentiated.

In the present approach, a two-step procedure is used for anchoring tin into Pt/H–mordenite (Pt/H-MOR) catalyst. In this study, an intensive washing procedure is applied after the first anchoring step. Consequently, the present study provides a good possibility to (i) compare the advantage or disadvantage of different approaches used for tin anchoring and (ii) find favourable experimental conditions for the modification of zeolite supported platinum cata-

Table 1
Comparison of methods used for the modification of zeolite supported metal catalysts

Experimental variables	Earlier results [11,12]	Present study
Type of zeolite	NaY	Mordenite
Precursor compound	$SnMe_4$	$SnEt_4$, $SnMe_4$
Solvent	*n*-hexane	*n*-hexane
Atmosphere	Ar	Ar, H_2
Temperature (°C)	25	25–50
Duration of anchoring (h)	24	0.15; 2; 24
Washing procedure	–	4 times with hexane
Drying in vacuum for 2 h (°C)	200	50

lysts with tin. The main features of earlier and present methods used to modify zeolite supported metal catalysts with tin tetraalkyls are given in Table 1.
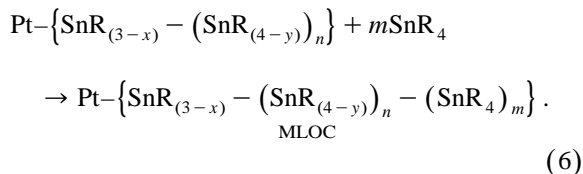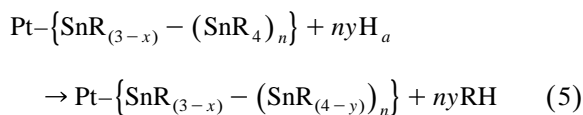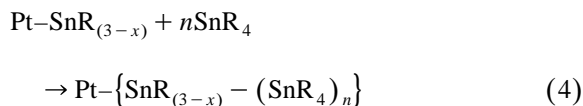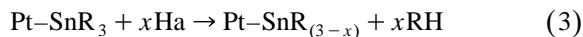
2. Surface chemistry

The reaction between tin tetraalkyls and adsorbed hydrogen has been first described in the early eighties [3]. This reaction provided direct tin–platinum interaction, which was maintained upon decomposition of the formed primary surface complex (PSC) in a hydrogen atmosphere [14]. The surface chemistry of the tin anchoring reaction can be written as follows [3]

$$PtH_{ads} + SnR_4 \rightarrow \underset{(PSC)}{Pt–SnR_3} + RH \tag{1}$$

$$Pt–SnR_3 + 1.5H_2 \rightarrow Pt–Sn + 3RH \tag{2}$$
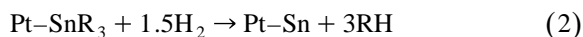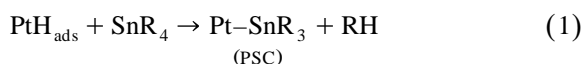
Upon using surface reaction (1) monolayer coverage of platinum by tin organometallic species can be achieved. Depending on the particle size of platinum and the size of the alkyl group the monolayer coverage resulted in Sn/Pt_s ratios around 0.3–0.6 [4].

Recently, we have demonstrated that upon modification of Pt/SiO_2 catalysts with tin tetraethyl high Sn/Pt_s ratios ($Sn/Pt_s = 3$) can be obtained without introduction of tin into the support [1]. The new results indicated that in the presence of large excess of tin tetraethyl in addition to the earlier proposed

CSR further anchoring-type reactions took place leading to the formation of MLOC. The formation of MLOC was strongly enhanced by excess hydrogen introduced and using a high initial concentration of tin tetraalkyl. The surface chemistry involved in the formation of MLOC can be described by the following surface reactions [1,2]

$$Pt\text{–}SnR_3 + xH_a \rightarrow Pt\text{–}SnR_{(3-x)} + xRH \qquad (3)$$

$$Pt\text{–}SnR_{(3-x)} + nSnR_4$$
$$\rightarrow Pt\text{–}\left\{SnR_{(3-x)} - (SnR_4)_n\right\} \qquad (4)$$

$$Pt\text{–}\left\{SnR_{(3-x)} - (SnR_4)_n\right\} + nyH_a$$
$$\rightarrow Pt\text{–}\left\{SnR_{(3-x)} - (SnR_{(4-y)})_n\right\} + nyRH \qquad (5)$$

$$Pt\text{–}\left\{SnR_{(3-x)} - (SnR_{(4-y)})_n\right\} + mSnR_4$$
$$\rightarrow \underset{\text{MLOC}}{Pt\text{–}\left\{SnR_{(3-x)} - (SnR_{(4-y)})_n - (SnR_4)_m\right\}}. \qquad (6)$$

Eq. (3) is related to the transformation of PSC to coordinatively unsaturated surface species, which interacts with tin tetraethyl used in large excess (see reaction (4)). In reaction (4), surface species in the second layer (SSSL) are formed similar to that suggested earlier for supported rhodium modified with tin tetrabutyl [15]. In the formation of SSSL, tin–tin dative bonds are involved. In the presence of excess hydrogen, SSSL can also be partially hydrogenolyzed resulting in coordinatively unsaturated species in the second layer (reaction 5), which can also interact with tin tetraethyl (reaction (6)). The net result is the formation of MLOC anchored to the platinum. It is suggested that MLOC anchored to the platinum have a slablike form. The length of these slabs can be different, however results obtained on Pt/SiO_2 indicate that they may contain up to three tin atoms. In this paper, reactions (1), (3)–(6), which take place in the presence of a solvent, will be referred as tin anchoring reactions.

CSRs with tin tetraalkyls can also be carried out to introduce tin organometallic moieties into the support. In this reaction, as it has already been mentioned earlier [2,11,16], surface OH groups and/or spilled over hydrogen are involved. This reaction can be written as follows

$$x|\text{–}OH + SnR_4 \rightarrow \underset{\text{OMSAS}}{|\text{–}O_x\text{–}\left\{SnR_{(4-x)}\right\}} + xRH. \qquad (7)$$
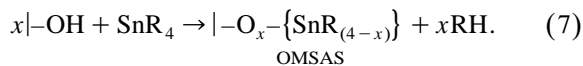
Surface reaction (7) leads to the formation of organometallic species anchored to the support (OMSAS). These species upon decomposition leads to the formation of ionic forms of tin stabilized on the support. In case of zeolites, due to their strong acidic character, the contribution of surface reaction (7) can be very pronounced.

In this study, if PSC, MLOC, and OMSAS cannot be differentiated from each other in this case a general term, surface organometallic complexes (SOMC) will be used.

The decomposition of MLOC has been carried out in the absence of solvent in a gas–solid reaction using temperature programmed reaction (TPR) technique. The decomposition pattern of MLOC in a hydrogen atmosphere clearly reflected the stepwise character of the anchoring process [1], i.e., the build-up of tin containing slabs step by step. The decomposition in a hydrogen atmosphere led to the formation of bimetallic surface entities with unique catalytic properties [1,2,17–19]. Recent Mössbauer spectroscopic results confirmed that in case of silica supported platinum catalysts even at $Sn/Pt_s = 2.5$ more than 90% of tin introduced was in the form of alloy [19].

Upon decomposition of PSC, MLOC and OMSAS TPR peaks appear at different temperatures. Experimental evidences indicated [1,2] that OMSAS has the highest (TPR) peak (above > 190–$200°C$ on silica or alumina), consequently the loss of control of surface reactions leading to the formation of supported Sn–Pt nanoclusters can be easily monitored by analysis of the TPR pattern of the decomposition of SOMC formed.

The analysis of the TPR pattern of SOMC formed indicated that traces of hydrocarbons left in the pores of the support can strongly alter the TPR behavior resulting in false TPR peaks in the temperature range above 230°C. In order to remove traces of *n*-hexane

heating at 50°C at 5 Torr vacuum for 1 h appeared to be sufficient both for alumina and silica. However, preliminary results on zeolites showed that due to their specific pore system, the complete removal of hydrocarbons from the pores is almost impossible.

3. Experimental

The 0.4 wt.% Pt/H-MOR catalyst was prepared by ion exchange using $[Pt(NH_3)_4](NO_3)_2$ as a precursor compound and H-MOR zeolite (UOP product designated as LZ-M8) with $Si/Al = 8.9$. Details of the preparation can be found elsewhere [20]. Prior to the modification with tin tetraalkyls the Pt/H-MOR sample was first dried at 150°C in flowing nitrogen for 1 h, and then heated up 400°C (heating rate 5°C/min) under vacuum (5 Torr) for 2 h to remove trace amounts of water. After drying hydrogen was introduced (30 ml/min), the catalyst was heated up in H_2 flow to 500°C (heating rate 10°C/min) and treated at this temperature for 2 h. After re-reduction, the catalyst was cooled in a hydrogen or argon atmosphere to room temperature followed by purging with argon for additional 30 min. All gases and solvents used were high purity and special care was taken to remove traces of oxygen and water. The re-reduced catalyst was transferred into a batch type glass reactor without any contact to air and was slurred with deoxygenated solvent either in an argon or a hydrogen atmosphere. Upon achieving the required reaction temperature, the tin anchoring (see reactions (1), (3)–(6)) was started by injection of tin tetraalkyls. In this work, tin tetraethyl and tin tetramethyl have been used as tin precursor compounds and dry and oxygen-free n-hexane was applied as a solvent. Samples for Mössbauer spectroscopic measurements were prepared using $^{119}Sn(CH_3)_4$.

The reaction temperature in the tin anchoring step was in the range of 20–50°C. The anchoring step was monitored by determining the amount of hydrocarbons formed using GC technique. Details on the analysis can be found elsewhere [1]. The duration of tin anchoring was 10–120 min, however in some experiments it was extended for 24 h. After tin anchoring, the solution was removed and the tin modified catalyst was washed four times with n-hexane at the temperature of tin anchoring. The catalyst was then dried in vacuum (at 5 Torr) at 50°C for 2 h to remove the solvent from the pores of the zeolite.

The decomposition of SOMCs formed was carried out in a hydrogen atmosphere by TPR technique using the following experimental parameters: heating rate = 5°C/min, hydrogen flow rate = 30 cm^3/min, amount of catalyst = 0.2–0.3 g. The products of decomposition (CH_4, C_2H_6 and C_2H_4) were analyzed by GC. The tin content of the modified catalysts was determined by AAS and was compared with the amount of anchored tin calculated from the overall material balance of tin anchoring. In a separate blank experiment it has been found that the solvent (n-hexane) cannot be fully removed from the pores of zeolite. n-Hexane left in the pores of zeolite upon its hydrocracking resulted in different hydrocarbons, including ethane and methane. Consequently, the TPR peaks of methane and ethane around 200°C were attributed to experimental artifacts, and were not taken into account when the material balance of tin anchoring was calculated.

The material balance allowed to calculate separately the amount of alkyl groups reacted in the first step of anchoring (n^I, mol/g$_{cat}$) and the amount of corresponding hydrocarbons formed in the decomposition of SOMC in the TPR experiment (n^{II}, mol/g$_{cat}$). In case of tin tetraethyl, the value of n^I contains the amount of both ethane and ethylene. The formation of ethylene has been observed under hydrogen deficient conditions and in the presence of oxygen contamination. More details on the ethylene formation can be found elsewhere [21]. In this way, the total amount of tin anchored could be calculated. The amount of tin calculated is in 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, which reflects the average number of alkyl groups reacted in the tin anchoring step.

Mössbauer spectra of tin modified samples were recorded at 80 K with a constant acceleration spectrometer using a $Ba^{119}SnO_3$ source. The catalyst samples were kept in a specially designed glass sample holder sealed under inert gas or vacuum and held at 80 K. Isotope enriched tin tetramethyl $^{119}Sn(CH_3)_4$ was used to prepare these samples. A

Table 2
Summary of results obtained upon varying the concentration of tin tetraethyl and the duration of tin anchoring

Experiment number	$[SnEt_4]_0$ $\times 10^{-3}$ (M)	$[Sn]_0/Pt_s$	Reaction time (min)	$W_0 \times 10^{-6}$ [a]	$n^I \times 10^{-6}$ [b]	$n^{II} \times 10^{-6}$ [c]	$HTP \times 10^{-6}$ [d]	Sn (%)[e]	Sn (%)[f]	Sn/Pt_s (at/at)[g]	X
1	0.17	0.31	40	0.25	8.2	6.8	44.2	0.05	–	0.23	2.2
2	0.68	0.56	70	0.50	21.5	14.7	45.7	0.11	0.10	0.55	2.4
3	1.18	0.90	15	0.79	16.6	14.6	19.6	0.09	–	0.48	2.1
4	5.06	3.51	10	3.10	30.9	35.6	11.9	0.20	0.20	1.01	1.9
5	5.06	3.35	120	2.91	63.4	55.6	7.1	0.35	–	1.81	2.1
6[h]	5.08	3.29	120	2.40	32.7	74.6	30.8	0.32	0.34	1.64	1.2
7[i]	5.08	3.34	120	4.00	56.0	67.6	2.8	0.37	–	1.88	1.8
8[j]	5.08	–	120	1.33	19.1	21.1	–	0.12	–	–	1.9
9[k]	5.06	–	120	0.60	11.5	15.5	–	0.08	–	–	1.6

Reduction at 500°C, cooling in an argon atmosphere, tin anchoring in the presence of hydrogen at 27°C.

[a] Initial rate of tin anchoring in 1st step of anchoring ($mol/g_{cat} \times min \times 10^{-6}$).

[b] Total amount of C_2 hydrocarbons formed in the 1st step ($mol/g_{cat} \times 10^{-6}$).

[c] Amount of ethane formed in the 2nd step up to 170°C ($mol/g_{cat} \times 10^{-6}$).

[d] Amount of ethane formed above 170°C ($mol/g_{cat} \times 10^{-6}$).

[e] Tin content calculated from the material balance of tin anchoring.

[f] Tin content determined by AAS.

[g] Amount of tin anchored per surface Pt atom.

[h] Cooling in a hydrogen atmosphere, tin anchoring in the absence of hydrogen, modification with $Sn(CH_3)_4$.

[i] Catalyst used in Mössbauer spectroscopy studies, modification with $^{119}Sn(CH_3)_4$.

[j] Tin anchoring onto H-MOR after treatment in a hydrogen atmosphere at 500°C using $^{119}Sn(CH_3)_4$.

[k] Tin anchoring onto H-MOR after treatment in a hydrogen atmosphere at 500°C using $Sn(C_2H_5)_4$.

standard least squares minimization routine was used to fit the spectra as a superposition of Lorentzian lines. All isomer shifts were referred to SnO_2.

The dispersion of selected Pt/H-MOR and Sn–Pt/H-MOR samples was determined by hydrogen and CO chemisorption using ASDI RXM-100 equipment (Advanced Scientific Designs). The dispersion of the parent Pt/H-MOR catalyst determined by hydrogen chemisorption was 89%. Some of the Sn–Pt/H-MOR samples were also tested in n-hexane reaction at 275°C in a continuous flow reactor operated in a periodic mode. Details on the reactor-setup and product analysis can be found elsewhere [22].

4. Results and discussion

4.1. Study of the tin anchoring step

In the tin anchoring step, the most important experimental variables are as follows: (i) concentration of the tin precursor compound, (ii) reaction temperature, (iii) the duration of the tin anchoring step, (iv) presence or absence of hydrogen during tin anchoring, (v) type of the tin precursor compound [1–3]. When alumina and silica supported catalysts were modified with tin tetraethyl or tetramethyl, a reaction temperature around 50°C appeared to be an optimum one, while the concentration of tin tetraethyl in the solution was in the range of $0.5–5 \times 10^{-3}$ M. It should be mentioned that the required concentration of tin tetraalkyls depended on the amount of tin to be anchored, i.e., on the Pt load and the Sn/Pt_s ratio aimed to be reached.

Selected kinetic curves of tin anchoring, i.e., the time dependence of ethane (or methane) formation in the first step of tin anchoring, are shown in Fig. 1A and B. As emerges from Fig. 1A and B, the kinetics of tin anchoring into Pt/H-MOR strongly resembles that of into Pt/SiO_2. The kinetic curves have two distinct parts. In the first 15–20 min, the formation of ethane (or methane) is fast, which is followed by a relatively slow part, which in most of the cases shows a zero order character.

Experimental results presented above show that the initial rate of tin anchoring depends on the reaction temperature, the chain length of tin tetraalkyl, and the presence or absence of hydrogen. As emerges from these results the addition of hydrogen strongly increases the rate of tin anchoring, and tin tetramethyl appeared to be more reactive than tin tetraethyl. Similar behavior has also been found for Pt/SiO_2 and Pt/Al_2O_3 catalysts [1–4]. It should also be noted that in tin anchoring shown in Fig. 1A and B the amount of ethylene was negligible, consequently the tin anchoring reaction appeared to be highly selective.
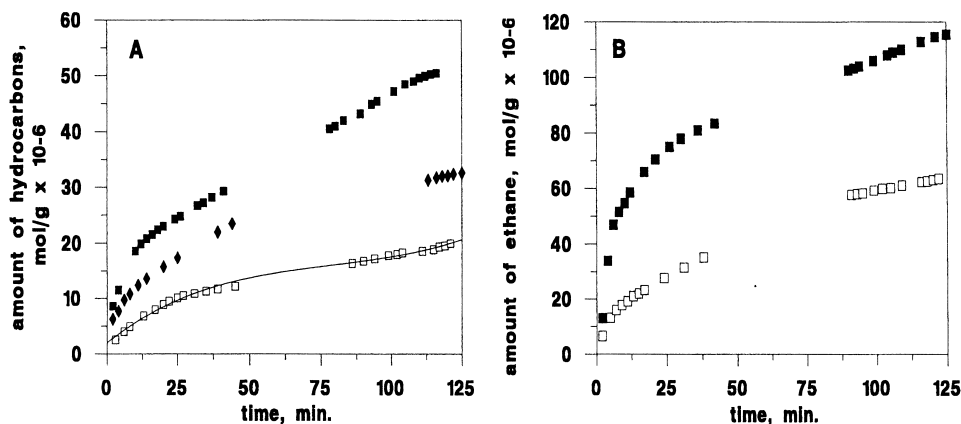

Fig. 1. Kinetic curves of ethane formation during tin anchoring. (A) tin anchoring in the absence of added hydrogen, □ — $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.28$, $T = 27$°C; ♦ — $[Sn(CH_3)_4]_0 = 5.08 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.29$, $T = 27$°C; ■ — $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.28$, $T = 50$°C; (B) tin anchoring in the presence of added hydrogen, □ — $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.35$, $T = 27$°C; ■ — $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.35$, $T = 50$°C.

Fig. 2 demonstrates the reproducibility of tin anchoring. Similarly good reproducibility was obtained when the reaction was carried out at higher temperature. This figure shows both ethane and ethylene formation. As emerges from Fig. 2, the extent of ethylene formation is very low, especially at the very beginning of the tin anchoring step.

Fig. 3 shows the kinetic curves in a series of experiments when the initial concentration of tin tetraethyl was systematically varied. High initial concentration of tin tetraethyl provides high rates of tin anchoring, however the increase of the concentration of tin tetraethyl has an upper limit, i.e., at high initial concentrations of tin tetraalkyls the latter interacts with the OH groups of zeolite. Due to this side reaction, the formation of alloy type Sn–Pt nanoparticles is not exclusive.

In separate blank experiments, the pure H-MOR support without platinum was used and the rate of tin anchoring was determined at 27°C. These experiments indicated that both tin tetraethyl and tin tetramethyl reacted with H-MOR, but the rate of this surface reaction was less than that of Pt/H-MOR. Results of these experiments are also included in Table 2. As emerges form data presented in Table 2 when tin tetraalkyls were anchored into pure H-MOR tin tetramethyl was about twice as active as tin tetraethyl (see Table 2, exp. nos. 8 and 9). It is also worth mentioning that under similar experimental condition, the silica support used in our earlier stud-
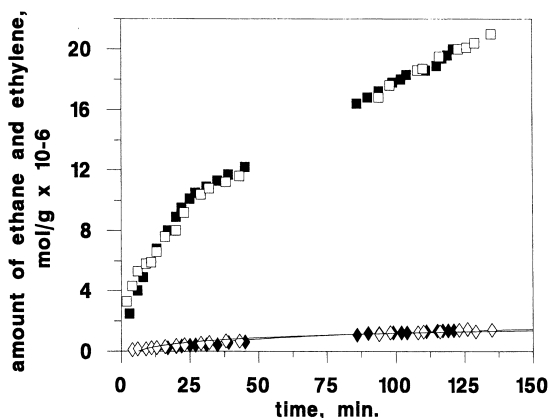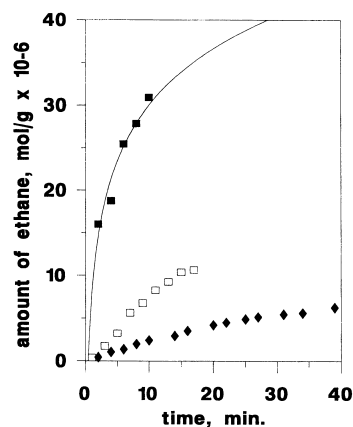

Fig. 3. The influence of the initial concentration of tin tetraethyl on the rate of the tin anchoring reaction. Tin anchoring in the presence of hydrogen at 27°C. $[Sn(C_2H_5)_4]_0$, 10^{-3} M =: ◆ — 0.17, □ — 0.68, ■ — 1.18. $[Sn]_0/Pt_s$: ◆ — 0.31, □ — 0.56, ■ — 0.90.

ies [1,2] was inactive in this surface reaction, i.e., no measurable ethane or methane formation was observed.

The comparison of results of tin anchoring onto Pt/H-MOR and H-MOR indicates that the rate of tin anchoring is about four and three times faster on Pt/H-MOR than on H-MOR for $Sn(C_2H_5)_4$ and $Sn(CH_3)_4$, respectively (see Table 2, exp. no. 5 vs. no. 9 and no. 7 vs. no. 8). These results clearly indicate that at high concentration of tin tetraalkyls, their anchoring into the zeolite support is unavoidable.

4.2. Study of the decomposition of SOMC formed

Typical TPR curves obtained upon decomposition of SOMC formed under various experimental condition are shown in Fig. 4A–C. Fig. 4A and B show the decomposition pattern when tin tetraethyl, while Fig. 4C when tin tetramethyl was used as a precursor compound. Fig. 4C shows the formation of both methane and ethane. In this case, methane is originated form SOMC, while ethane from the hydrocracking of the solvent (n-hexane) left in the zeolite pores after the tin anchoring step. The TPR curves were deconvoluted into several peaks. Peak maxima around 20°C, 40°C, 80°C, 110°C, 150°C, 175°C and 195°C were found in these experiments. The repro-

Fig. 2. Reproducibility of tin anchoring. $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.28$, $T = 27$°C; □, ■ — ethane, ◇, ◆ — ethylene. Tin anchoring in the absence of hydrogen.
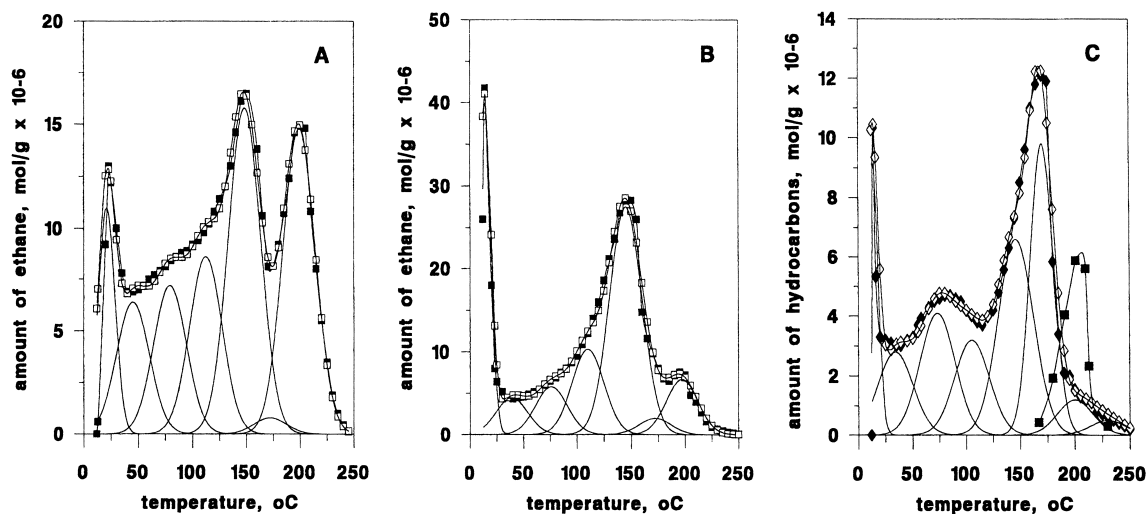
Fig. 4. Temperature programmed decomposition of anchored SOMC. Tin anchoring in the absence of hydrogen; ■, ◆ — measured, □, ◇ — fitted. ◇, ◆ — methane, ■, □ — ethane. Conditions of tin anchoring; (A) $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.28$, $T = 27°C$; duration of tin anchoring: 2 h, $[Sn]_{anch}/Pt_s = 1.69$; (B) $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.39$, $T = 27°C$; duration of tin anchoring: 24 h, $[Sn]_{anch}/Pt_s = 2.30$; (C) $[Sn(CH_3)_4]_0 = 5.08 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.29$, $T = 27°C$; duration of tin anchoring: 2 h, $[Sn]_{anch}/Pt_s = 1.64$. Tin anchoring in the absence of hydrogen.

ducibility of the temperature maxima of these TPR peaks was in the range of $\pm 3°C$. Similar treatment procedure has been applied when Pt/SiO_2 catalysts were modified with tin tetraethyl [1].

Let us discuss first the high temperature peaks (HTP) around 175°C and 195°C. The TPR peak at 195°C appeared in all experiments, while the peak at 175°C appeared only in experiments when the catalyst was cooled down in a hydrogen atmosphere prior to the tin anchoring step.

In a separate blank experiment, it has been shown that the TPR peaks around 175°C and (195°C) are originated from *n*-hexane and their appearance can be attributed to the hydrocracking of *n*-hexane by the Pt/H-MOR catalyst. It is interesting to note that the intensity of the ethane peak at 195°C is much higher than that of methane (see Fig. 4C). This fact is considered as an additional proof that the ethane peak at 195°C originated from the solvent.

The comparison of results shown in Fig. 4A and B show that the increase of the duration of tin anchoring strongly alters the contribution of peak at 195°C and peaks between 20°C and 145°C. Upon increasing the time of tin anchoring, the intensity of the peak at 195°C decreases, consequently the intro-

duced forms of tin decrease the hydrocracking activity of the Pt/H-MOR catalyst. Upon increasing the duration of tin anchoring, the probability for introducing tin into the zeolite support increases. This phenomenon is reflected by the substantial increase of the intensity of the peak around 150°C. Hence, the TPR peak around 150°C can be attributed to OMSAS, i.e., to surface species anchored to the zeolite. This assumption has been proved upon analysis of the TPR pattern of surface species obtained when pure H-MOR was reacted with tin tetramethyl and tin tetraethyl (see exp. nos. 8 and 9 in Table 2). The TPR pattern of these samples is similar, i.e., there is one intensive TPR peak around 155°C and 150°C for tin tetramethyl and tin tetraethyl, respectively. The appearance of these TPR peaks is due to the formation OMSAS on H-MOR. Based on these results, the TPR peak in the temperature range of 150°C was attributed to OMSAS formed on the zeolite.

TPR results shown in Fig. 5A and B provided further prove with respect to the assignments made above. These TPR curves represent samples when the tin anchoring process was carried out in the presence of hydrogen and the duration of the tin anchoring was increased from 15 min to 2 h. The
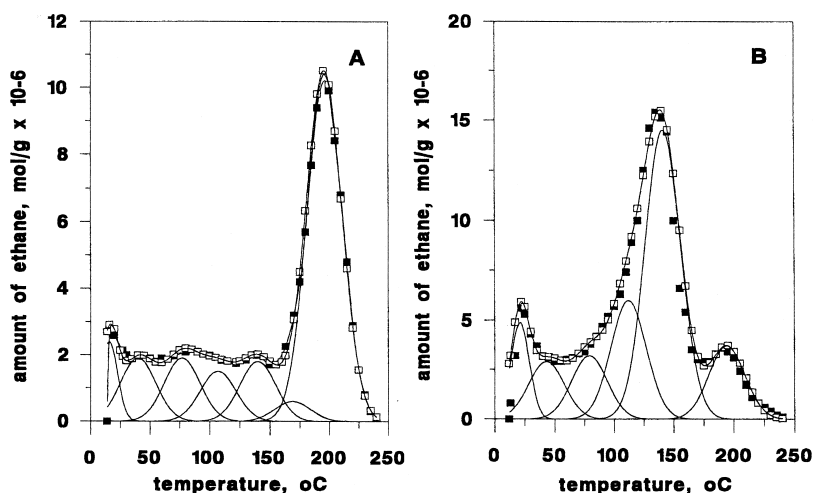
Fig. 5. Influence of the duration of tin anchoring on the TPR pattern. Tin anchoring in the presence of hydrogen; ■ — measured, □ — fitted. Conditions of tin anchoring: (A) $[Sn(C_2H_5)_4]_0 = 1.18 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 0.90$, $T = 27°C$; duration of tin anchoring: 15 min, $[Sn]_{anch}/Pt_s = 0.48$; (B) $[Sn(C_2H_5)_4]_0 = 5.06 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.35$, $T = 27°C$; duration of tin anchoring: 2 h, $[Sn]_{anch}/Pt_s = 1.81$.

prolonged anchoring time increased the intensity of the TPR peak around 150°C, while it decreased the intensity of the HTP at 195°C. Results shown in Fig. 5A indicate also that experimental conditions of tin anchoring applied in this experiment is very favourable for the introduction of tin into the platinum as the overall ratio of the TPR peak around 150°C is quite low.

In the experiment, shown in Fig. 5A a standard vacuum treatment (2 h) was applied after the tin anchoring process. The increase of the duration of vacuum treatment from 2 to 4 h decreased the intensity if the TPR peak at 195°C by a factor of 2.5, without substantial alteration of the intensity of other TPR peaks.

The analysis of the TPR pattern of tin modified Pt/H-MOR catalysts shows that this system is much more complex than tin modified Pt/SiO$_2$ or Pt/Al$_2$O$_3$ catalysts. The complexity is due to the high adsorption capacity of the zeolite and the high reactivity of the zeolitic protons towards tin tetraalkyls.

It has already been suggested in our previous study [1] that the deconvoluted TPR peaks correspond to different tin organometallic moieties anchored into different sites of Pt. This study shows that the TPR peak around 150–155°C can be attributed to the OMSAS, while peaks at 175 and 195

to hydrocracking products originated from the solvent. However, exact designation of the low temperature peaks between 20°C and 150°C is not possible. There is a general observation in surface organometallic chemistry: the higher the temperature of these TPR peaks the lower the reactivity of the given surface organometallic moiety. As far as the reactivity of these species strongly depends on the relative distance of the $-Sn(R)_z$ moiety form the Pt surface it has been concluded that the low temperature TPR peaks (i.e., peaks below 150°C should be related to the decomposition of PSC and MLOC, while TPR peaks at relatively higher temperatures (around 150°C) originated from the decomposition of OMSAS.

4.3. Material balance of tin anchoring

Material balance of tin anchoring is calculated from experimental data obtained in the anchoring step and in the TPR experiments. The HTP obtained above 170°C in the TPR experiments were not included into the calculation. These results are summarized in Table 2.

Results given in Table 2 indicate that the increase of the initial concentration of tin tetraethyl has a

strong influence on the amount of tin anchored. Upon variation of both the initial concentration of tin tetraethyl and the duration of tin anchoring the amount of tin introduced (in Sn/Pt_s (at/at)) is changed in a relatively broad range. In experiment nos. 1–3 a monolayer coverage of tin organometallic surface species on platinum can be suggested, while in experiment nos. 4–7 anchoring of tin onto the zeolite support takes also place (formation of OM-SAS).

With respect to the stoichiometry of anchored species, the analysis of X values given in Table 2 indicated that in a hydrogen atmosphere slightly more than two alkyl groups reacted in the tin anchoring step. However, in the absence of hydrogen the X value is close to one (see exp. no. 6 in Table 2). It is worth mentioning that anchoring of tin both to the platinum and the zeolite support results almost in the same stoichiometry.

4.4. Characteristic feature of tin anchoring onto Pt / H-MOR using tin tetraalkyls

As it has been described in Section 2 that the tin anchoring process leading to the formation of supported bimetallic entities has two main steps: (i) formation of PSC and (ii) formation of MLOC. The formation of MLOC allows obtaining supported alloy type Sn–Pt catalysts with high Sn/Pt_s ratio. When Pt/SiO_2 catalysts are modified with tin tetraalkyls, in this case the rate of reactions (3)–(6) leading to the formation of MLOC is much higher than that of reaction (7) resulting in OMSAS. Contrary to that, when Pt/H-MOR catalyst is modified with tin tetraalkyls, the rate of surface reaction (7) is much higher than the rate of reactions involved in the formation of MLOC. Consequently, in this case the build-up of MLOC is strongly hindered, and the excess tin tetraalkyl is anchored into the zeolite. The results indicate also that the reactivity of the H-MOR support towards tin tetraalkyls is higher in the presence of platinum than in its absence. This phenomenon can be attributed to the involvement of spillover hydrogen in the tin anchoring process. Consequently, the spillover hydrogen increases the amount of tin introduced onto the support. The net result is that over Pt/H-MOR catalysts, the build-up of the MLOC is strongly hindered and the excess tin tetraalkyl is anchored into the zeolite.

Based on results in Sections 4.1–4.3 with respect to anchoring of tin tetraalkyls onto Pt/H-MOR, the following main conclusions can be drawn.

- The initial rate of tin anchoring strongly depends on the initial concentration of tin tetraethyl, data shows that in the presence of hydrogen the tin anchoring reaction is first order with respect to the concentration of tin tetraethyl.
- The initial concentration of tin tetraalkyls appeared to be the key experimental variable to increase the amount of tin anchored.
- The amount of tin anchored (Sn/Pt_s) can be altered in a relatively broad region, however the amount of tin anchored into the platinum is relatively small, i.e., it is close to the monolayer coverage of anchored $-SnR_{(n-x)}$ moieties, that corresponds to $Sn/Pt_s \cong 0.5$.
- The presence of hydrogen increases the rate of tin anchoring, however at prolonged reaction time (2 h) it has only minor influence on the amount of tin anchored.
- In the presence of hydrogen the X value is higher than in its absence. This fact indicates that in the presence of hydrogen the extent of coordinative unsaturation of anchored organometallic species is higher than in its absence.
- Due to the high sorption capacity of the zeolite, the solvents used in the anchoring reactions cannot be fully removed, the adsorbed solvent leads to the formation of hydrocracking products in the TPR experiments.
- The presence of hydrogen in the anchoring step suppresses the amount of hydrocracking products originated from n-hexane.

4.5. Chemisorption properties of Sn–Pt / H-MOR

The chemisorption of CO and hydrogen has been measured on selected tin modified catalysts. These measurements were done after decomposition of SOMC either in a hydrogen or an oxygen atmosphere ((H) and (O) type samples, respectively).

Prior to the chemisorption measurements both types of samples were treated in a hydrogen atmosphere at 500°C for 90 min and cooled to room temperature and inert atmosphere. Results of these measurements are shown in Fig. 6A and B.

These results indicate that the introduction of tin strongly reduces the chemisorption of hydrogen both in (H) and (O) type of samples. However, the reduction of CO chemisorption especially in (O) type samples is less pronounced. The strong difference between hydrogen and CO chemisorption data is attributed to the difference in the mechanism of chemisorption of hydrogen and CO. The chemisorption of hydrogen is an activated process, due to the need to break the H−H bond prior to the chemisorption. In supported bimetallic Sn–Pt nanocluster, platinum is replaced by tin. In this case due to the dilution of platinum by tin, the activation of dihydrogen at the kink and corner sites is strongly hindered, hence the amount of chemisorbed hydrogen strongly decreases. Contrary to that, the introduction of tin into the platinum has no influence on the chemisorption of CO on the Pt sites. It reduces only the ratio of bridged/linear ratio due to the site isolation of Pt by tin [18].

The difference between (H) and (O) type catalysts can be attributed to the formation of carbonaceous residues on (H) type catalysts. The calcination of (H) type catalysts at 400°C and subsequent reduction at 500°C resulted in similar chemisorption values as that of the (O) type catalysts.

It is worth mentioning that a significant decrease in the chemisorption values takes place at relatively low Sn/Pt_s ratios, i.e., in the range of $Sn/Pt_s = 0.2$–0.5. Further increase of the Sn/Pt_s ratio only slightly decreases both the H/Pt and the CO/Pt values. These data indicate that in the range of $Sn/Pt_s = 0.2$–0.5, the anchoring process leads to the modification of platinum, while at $Sn/Pt_s = 0.5$–2.3, both the platinum sites and the support are modified by tin and the modification of the zeolite support is more pronounced. Consequently, these results support our earlier remark, i.e., the loss of control in the tin anchoring reaction at high Sn/Pt_s ratios. The chemisorption results provided further hint that the modification of the platinum sites in Pt/H-MOR catalysts can be controlled only up to the monolayer formation of $Pt–SnR_{(4-x)}$ species. These results indicate also that in Pt/H-MOR catalysts the formation of MLOC is strongly hindered due to the high activity of the acidic OH groups of the support.

4.6. Mössbauer spectroscopy results

In order to characterize the valence state of surface species, formed [119]Sn Mössbauer spectroscopy was applied. Due to limited sensitivity of the method only catalysts with $Sn/Pt_s > 1.8$ could be investigated. Based on results obtained in Section 4.1–4.3 it is known that this is the range of Sn/Pt_s ratio where the tin anchoring reaction is not selective, i.e., at this Sn/Pt_s ratio only minor part of tin is anchored into the platinum and the major part of tin is introduced into the zeolite support. Please note that samples used in Mössbauer spectroscopy studies were prepared from [119]$Sn(CH_3)_4$, the use of $Sn(CH_3)_4$
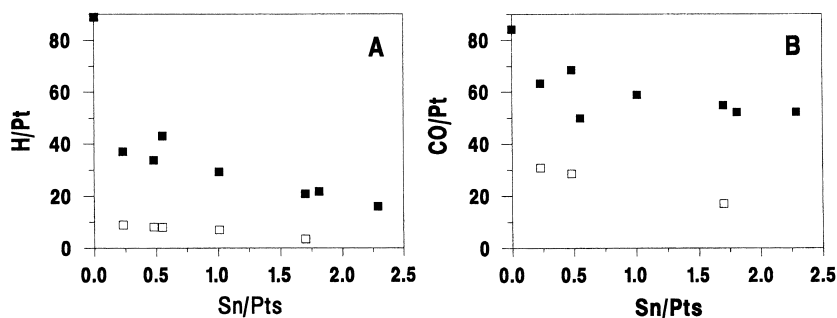

Fig. 6. Chemisorption properties of Sn–Pt/H-MOR catalysts. (A) hydrogen chemisorption, (B) CO chemisorption. ■ — (O) type catalysts; □ — (H) type catalysts.

increases further the probability of introducing more tin into the support then into the platinum.

Fig. 7 shows the Mössbauer spectra of pure H-MOR after tin anchoring (sample (A-I), SOMC as received), and after decomposition of SOMC in hydrogen at 350°C for 2 h (sample (A-II)). Mössbauer spectra of Pt/H-MOR samples after tin anchoring are given in Fig. 8. Different Sn–Pt/H-MOR samples were studied by Mössbauer spectroscopy: (B-I)-SOMC as received, (B-II)-Sn–Pt/H-MOR catalyst obtained after decomposition of SOMC in a hydrogen atmosphere ($T_{max} = 350$°C, (H) form of catalyst,), (B-III)-Sn–Pt/H-MOR catalyst obtained after decomposition of SOMC in an oxygen atmosphere ($T_{max} = 500$°C, (O) form of catalyst), and (B-IV)-sample B-III after reduction in a hydrogen atmosphere at 500°C for 8 h. The corresponding Mössbauer parameters are summarized in Table 3.

The Mössbauer spectrum of sample (A-I) (see Fig. 7a) has a doublet with isomer shift at 1.52 mm s^{-1} and high quadruple splitting (QS = 4.16 mm s^{-1}). This doublet can be attributed to $(|-O)_2-Sn^{4+}Me_2$ surface species interacting with two oxygen atoms of the zeolite. The anchoring of tin to the zeolite with more than one $-O-Sn$ bond may produce an anisotropy around the tin atom, consequently this type of species should have a very high quadruple splitting [23,24]. The formation of surface species $(|-O)_2-Sn^{4+}Me_2$ is also in a good agreement with the stoichiometry of tin anchoring on H-MOR ($x = 2$, see Table 2). Contrary to that in our earlier studies using silica support, based on the stoichiometry of tin anchoring reaction the formation of $-O-SnEt_3$ type surface species were suggested [1]. It is important to note that the rate of tin anchoring onto pure silica was extremely slow at 27°C and 50°C. The alteration of the stoichiometry of tin anchoring reaction onto the support can be attributed to the high acidity of H-MOR and its high reactivity towards tin tetraalkyls.

The Mössbauer spectrum of sample (A-2) shows a superposition of two doublets and one singlet (see Fig. 7b). The majority of tin is present in Sn^{2+} form, while very small amounts of unreacted $(|-O)_2-Sn^{4+}Me_2$ surface species can also be seen (7%). Based on the IS and QS parameters (3.50 and 1.28 mm^{-1}, respectively) one of the doublets can be related to the Sn(II) species on the surface of the
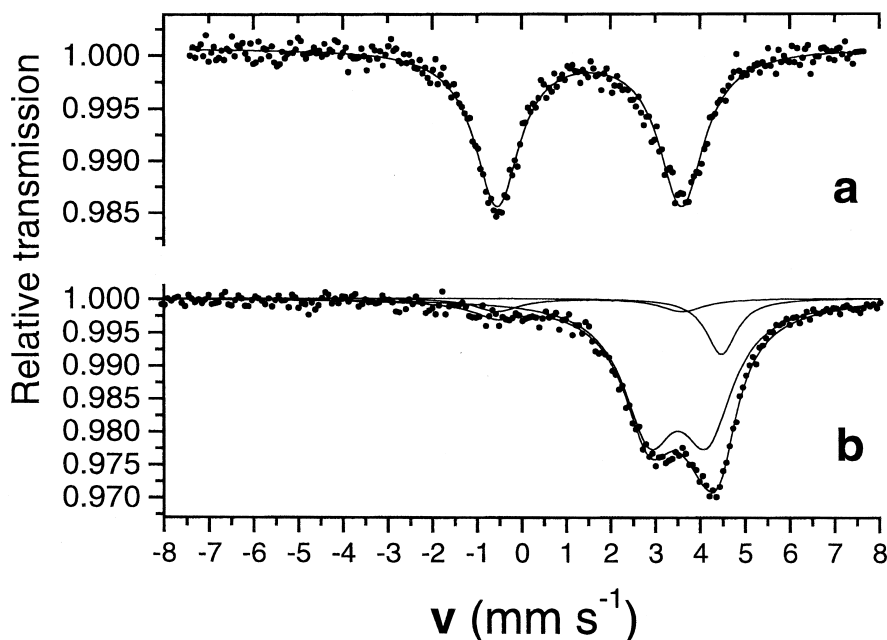

Fig. 7. Mössbauer spectra of tin modified H-MOR; (a) sample A-I; (b) sample A-II (see Table 3 for exact assignment of samples). $[^{119}Sn(CH_3)_4]_0 = 5.08 \times 10^{-3}$ M, $T = 27$°C, duration of tin anchoring: 2 h, anchoring in the presence of hydrogen.
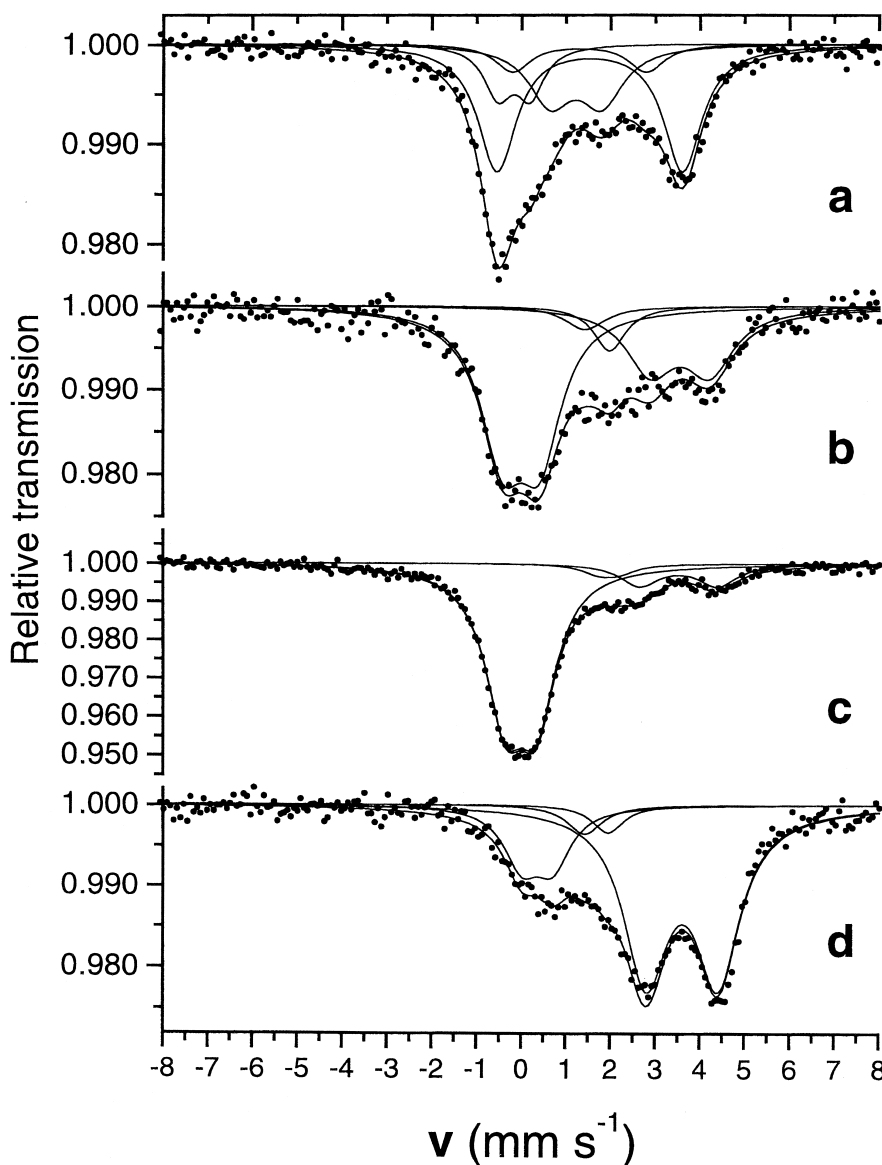
Fig. 8. Mössbauer spectra of tin modified Pt/H-MOR. $[^{119}Sn(CH_3)_4]_0 = 5.08 \times 10^{-3}$ M, $[Sn]_0/Pt_s = 3.34$, $T = 27°C$, duration of tin anchoring: 2 h, $[Sn]_0/Pt_s = 3.35$, anchoring in the presence of hydrogen; (a) sample B-I; (b) sample B-II; (c) B-III; (d) IV (see Table 3 for exact assignment of samples).

zeolite [25,26]. With respect to the singlet found at 4.47 mm s^{-1}, our result is also in a full agreement with literature data [26], hence this form of tin has been found in tin containing zeolites and was attributed to Sn(II) in the lattice of the zeolite.

The spectrum given in Fig. 8a (see sample (B-I)) indicates that the Sn–Pt/H-MOR sample after tin

anchoring contains several forms of tin with IS values characteristic for covalently bonded Sn^{4+} forms. The multiplicity of the signals suggests a mixture of species. The best fit of the spectrum was obtained with four doublets.

Around half of the tin is present in the form of $(|-O)_2-Sn^{4+}Me_2$, i.e., in tin containing surface

Table 3
Mössbauer parameters of modified catalyst samples

Catalyst sample	Catalyst sample (short form)	Species	IS (mm s^{-1})	QS (mm s^{-1})	RI (%)
(H)-MOR SOMC as received	A-I	$(|-O)_2-Sn^{4+}Me_2$	1.52	4.16	100
(H)-MOR SOMC after $T_{H_2} = 350°C$	A-II	$(|-O)_2-Sn^{4+}Me_2$	1.52	4.16	7
		$Sn(II)_{surf.}$	3.50	1.28	82
		$Sn(II)_{bulk}$	4.47	0	11
Pt/H-MOR SOMC as received	B-I	$(|-O)_2-Sn^{4+}Me_2$	1.53	4.16	51
		$Pt_x-Sn^{4+}Me_3$	1.29	3.00	10
		$Pt_x-Sn^{4+}Me_2$	1.21	1.16	25
		$Sn(IV)_{tetra}$	−0.18	0.73	14
Sn–Pt/H-MOR (H) type after $T_{H_2} = 300°C$	B-II	$Sn(II)_{surf.}$	3.55	1.33	30
		Pt–Sn(a)	1.43	–	5
		Pt–Sn(b)	1.98	–	7
		$Sn(IV)_{surf.}$	0.00	0.84	58
Sn–Pt/H-MOR (O) type	B-III	$Sn(II)_{surf.}$	3.53	1.73	13
		SnO–Pt	1.96	0.45	4
		$Sn(IV)_{surf.}$	0.00	0.72	83
Sn–Pt/H-MOR (O) type after $T_{H_2} = 500°C$	B-IV	$Sn(II)_{surf.}$	3.60	1.61	70
		Pt–Sn(a)	1.23	–	8
		Pt–Sn(b)	1.98	–	6
		$Sn(IV)_{surf.}$	0.27	0.67	16

species anchored to the zeolite (IS about 1.53 mm s^{-1} and QS 4.16 mm s^{-1}). Similar species were also formed on pure H-MOR (sample A-I). However, the species $Me_2Sn(-O)(-Pt)$, which can also be formed at the zeolite-Pt interface, would have rather similar IS and QS values. Nonetheless, in this spectrum it is impossible to distinguish between these two types of surface species. The second and third doublets (IS around 1.29 and 1.21 mm s^{-1}; QS = 3.00 and 1.16 mm s^{-1}, respectively) are in a good agreement with literature data [14,15]. The Mössbauer spectra indicate the formation of surface species $Pt_x–SnMe_3$ and $Pt_x–SnMe_2$, respectively. These results are also in agreement with the observed stoichiometry of the tin anchoring reaction (see X values in Table 2), i.e., when tin anchoring is carried out in a hydrogen atmosphere the extent of loss of the alkyl groups in the anchoring step is much higher than in the absence of hydrogen.

The fourth form of tin has a significant negative IS value (IS = −0.18). This IS value is close to those found in Ref. [25]. Based on this analogy, this form of tin can be assigned to Sn(IV) ions surrounded with oxygen atoms in tetrahedral symmetry.

The spectrum of sample (B-II) (see Fig. 8b), which was obtained after decomposition of SOMC hydrogen, show that after reduction several new types of tin containing species were formed. In this sample, tin is in 4 +, 2 + and 0 valance states. The majority of tin is in Sn^{4+} form (58%), while the remaining part of tin is present both in alloy and Sn^{2+} forms. Similar to our recent results [19], two forms of alloy could be distinguished. The Pt–Sn(a) phase with IS = 1.43 mm^{-1} was assigned to Pt_3Sn like phase, i.e., as a Pt rich alloy phase [19,26], while the Pt–Sn(b) phase with IS = 1.98 mm^{-1} was assigned to PtSn phase [26–29]. We suggest that the Sn^{4+} form can be identified as nonstoichiometric SnO_2 (IS = 0.0), while the Sn^{2+} form (IS = 3.55 and QS = 1.33 mm^{-1}) strongly resembles the surface species formed also on pure H-MOR (see sample A-II).

Results of Mössbauer spectroscopy indicate that the decomposition of SOMC formed on Pt/H-MOR catalyst in an oxygen atmosphere at 500°C leads to the exclusive formation of ionic tin (see Fig. 8c, sample (B-III)). The deconvolution of the spectrum resulted in three species. Two of these species have

already been assigned as they were also found in sample B-II. The most abundant component is $Sn(IV)_{surf.}$ (83%). The second major component is $Sn(II)_{surf.}$ (13%). The species with $IS = 1.96$ and $QS = 0.45$ mm^{-1} can be related either to a tin rich Sn–Pt alloy, or to SnO–Pt surface species formed at the metal-support interface [29]. We favour the formation of SnO–Pt surface species as their formation is much more probable in an oxidative atmosphere at high temperature. As far as the relative intensity of this species is very low (4%), it is difficult to give a more detailed assignment.

The spectrum of sample B-IV (see Fig. 8d) consists of two doublets and two singlets, similar to sample B-II (see Fig. 8b). The assignment is the same as for sample B-II, i.e., this sample contains $Sn(IV)_{surf.}$ (16%), $Sn(II)_{surf.}$ (70%) and two alloy phases, such as Pt_3Sn and PtSn. The main difference between samples B-IV and B-II is that the former has much more $Sn(II)_{surf.}$ species. Its formation is due to the prolonged treatment in the hydrogen atmosphere at 500°C.

The Mössbauer spectra of samples B-II and B-IV provided a solid evidence for the formation of zeolite supported Sn–Pt alloy phases. It is worth mentioning that the condition of tin anchoring applied for this Sn–Pt/H-MOR sample was not favourable for the exclusive formation of Sn–Pt alloy phases. In this sample, the Sn/Pt_s ratio is 1.88. It has already been mentioned that introduction of tin into platinum can be expected when the Sn/Pt_s ratio is in the range of 0.4–0.5. Consequently, in the Sn–Pt/H-MOR sample used for Mössbauer spectroscopy, the amount of excess tin is about four to five times higher than the optimum value, for this reason only one fifth of the amount of tin anchored can be expected to form the Sn–Pt alloy phase, however, the overall amount of Pt–Sn alloy phases is around 12–14%.

We suggest that the decrease of the overall amount of Sn–Pt alloy phases can be attributed to the involvement of acidic protons in the oxidation of the zeolite supported bimetallic Sn–Pt alloy phases. A similar behavior was also observed in Ref. [13] when zeolite supported rhodium catalysts were modified with tin tetraalkyls. As shown in Ref. [13], the presence of intrazeolitic protonic acidity promoted the formation of Sn^{2+} ions by reoxidation of zero valent Sn in the bimetallic Rh^0–Sn^0 nanocluster. It

has been suggested that in this oxidation reaction the zeolitic proton is involved. However, in non-acidic Rh–zeolite samples after modification with tin alkyls the formation of only bimetallic Rh^0–Sn^0 particles has been evidenced [13].

The oxidation reaction with the involvement of highly acidic protons can be written as follows

$$2H^+ + Sn^0 \rightarrow Sn^{2+} + H_2 \tag{8}$$
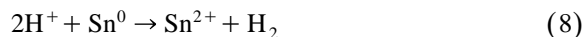
In reaction (8) metallic tin in the supported Sn–Pt alloy phase reacts with highly acidic protons. This reaction probably takes place at a temperature higher than the formation of supported Sn–Pt type bimetallic nanoclusters. Consequently, in order to stabilize the alloy type Sn–Pt nanoclusters supported on H-MOR the use of high temperature treatment procedures should be avoided.

The results of Mössbauer spectroscopy indicate also that tin containing surface species introduced into the zeolite support cannot be reduced to metallic state, however, the reduction of $Sn(IV)_{surf.}$ species to $Sn(II)_{surf.}$ has been evidenced.

4.7. Catalytic properties of Sn–Pt / H-MOR catalysts

It is known that Pt/H-MOR catalysts have high activity and selectivity in the isomerization of *n*-alkanes [30–33]. For this reason, selected tin modified catalysts were tested in *n*-hexane transformation at 275°C. Only products of isomerization and hydrocraking were detected. Isomerization products, such as 2-methylpentane (2MP), 3-methylpentane (3MP), 2,2-dimethylbutane (2,2DMB), and 2,3-dimethyl-butane (2,3DMB) were the main reaction products. The ratio of 2MP/3MP was around 2.1 at 5% conversion and 1.9 at 40% conversion in all catalysts, this ratio was independent of the amount of tin introduced. Kinetic experiments have shown that both 2MP and 3MP are primary products, while 2,2DMB is a secondary one both over Pt/H-MOR and Sn–Pt/H-MOR catalysts. Propane was the main hydrocracking product over all catalysts. The isomerization selectivity (S_i) was calculated as the sum of the selectivities of all isomerization products (2MP, 3MP, 2,2DMB and 2,3DMB).

The results obtained at low conversion are summarized in Table 4, while isomerization selectivity data measured around 30% conversion are shown in Fig. 9.

The introduction of tin resulted in always a decrease in the overall rate. However, the decrease of the rate on the Sn–Pt/H-MOR catalysts was proportional to the decrease of the CO chemisorption values measured. Results obtained at low conversion indicate that at low tin loading ($Sn/Pt_s = 0.44$–0.55) the introduction of tin has no measurable influence neither on the TOF data nor the isomerization selectivities extrapolated to zero conversion. It is worth mentioning that in these catalysts the modification of platinum sites has been suggested.

Contrary to the catalyst containing tin anchored both to the metal and the support the TOF value was much lower than in the parent catalyst and the $(S_i)_0$ value was also slightly altered.

Results measured at high conversion show similar trends. Upon changing the Sn/Pt_s ratio up to 0.55, the S_i values are constant, while further increase of the Sn/Pt_s ratio leads to the decrease of the S_i values.

These results indicate that when the platinum site is modified with tin the number of accessible metallic sites decreases, while the introduction of tin onto the zeolite support leads to the formation of new types of acidic sites. In both cases, the metal/acid balance of the Pt/H-MOR catalyst is altered.

When tin is introduced to the platinum, the overall conversion decreases due to the loss of available platinum sites at the surface of the supported nanocluster. This experimental finding indicate that at low conversion the number of metallic sites should
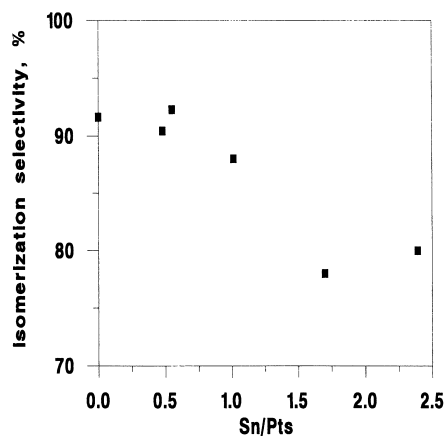

Fig. 9. The influence of the Sn/Pt_s ratio on the isomerization selectivity. Selectivity values measured at 30–32% conversion.

be considered as the key factor to control both the activity and the selectivity in *n*-alkane conversion.

With respect to the application of Pt/zeolite catalysts in *n*-alkane isomerization at low temperature, there is a general observation, i.e., the introduction of platinum into the zeolite strongly increases the rate of transformation of *n*-alkane. There are lots of disputes with respect to the role of Pt sites in the overall mechanism of *n*-alkane isomerization at low temperature. All of the research groups working in this field agree that the classical bifunctional mechanism developed in the fifties for bifunctional Pt/Cl–Al$_2$O$_3$ [30] cannot be applied when the isomerization reaction is carried at low temperature (below 300°C).

There are two general views with respect to the role of Pt in the isomerization of *n*-alkanes over Pt/zeolite catalysts:

(i) in the reaction mechanism, Pt is only spectator, its role is: (a) to hydrogenate the excess olefins formed and (b) to remove harmful coke precursors [31];

(ii) in the reaction mechanism, the "hybrid metal-proton" sites are involved, i.e., the supported metallic nanoclusters interact simultaneously with more than one proton to form a specific "ensemble site", this new site is involved in the isomerization reaction [32].

Our results indicate also that the number of metallic sites has a very important contribution to the mechanism of *n*-alkane isomerization. The overall

Table 4
Summary of catalytic measurements. Transformation of *n*-hexane

Catalysts	Sn/Pt_s	TOF $(h^{-1})^a$	S_i^a
Pt	–	83.2	97.1
Sn–Pt	0.48	78.4	96.9
Sn–Pt	0.55	81.7	96.7
Sn–Pt	1.01	71.2	93.3
Sn–Pt	2.30	47.6	91.6

$T = 275°C$, $P_{CH} = 123$ Torr, $H_2/CH = 6.2$, amount of catalyst: 0.05 g, flow rate 45 ml/min.
[a] Determined from initial rates extrapolated to zero conversion, relative error: ± 3.5 h^{-1}.

rate decreases after introduction of tin to platinum, however at low Sn/Pt_s ratios (Sn/Pt_s is around 0.5) the specific rate, measured at zero conversion and calculated as the TOF, is independent of the amount of tin introduced. These experimental findings indicate that the number of Pt sites controls the reaction rate, consequently our finding strongly supports the earlier suggestion that Pt is not a spectator in this reaction. It is more likely that in Pt/zeolite catalyst platinum is part of the "ensemble sites" where the isomerization of *n*-alkane takes place. Further studies will be needed to elucidate the character of these "ensemble sites" involved in the isomerization of *n*-alkanes.

5. Conclusions

The modification of Pt/H-MOR with tin tetraalkyls by applying controlled surface reactions resulted in two types of catalysts. At low Sn/Pt_s ratio the modification leads to the formation of alloy type Sn–Pt bimetallic catalysts. However, at Sn/Pt_s ratio higher than 0.5, the modification becomes nonselective and in addition to the formation of alloy type bimetallic Sn–Pt surface entities ionic forms of tin were formed on the zeolite support. These results indicate also that in Pt/H-MOR catalysts the formation of MLOC is strongly hindered due to the high affinity of the acidic OH groups of the support towards tin tetraalkyls. However, the use of the two step anchoring process allowed us to determine conditions favourable for the formation of alloy type SnPt nanoclusters supported on H-MOR. Results of Mössbauer spectroscopy indicated that at high Sn/Pt_s ratio various surface species can be formed and they can be transformed to new forms upon applying high temperature hydrogen or oxygen treatments. This study also demonstrated the limitation of the surface organometallic approach using tin tetraalkyls. One of the main conclusions is: if the anchoring process is aimed to create alloy type SnPt surface species on an acidic support the condition of the tin anchoring process should be altered and the anchoring type of surface reactions should be carried out at sub-ambient temperature. The catalytic results indicated that alloy type SnPt/zeolite catalysts can be used in low temperature *n*-alkane isomerization to elucidate the role of platinum in this reaction.

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