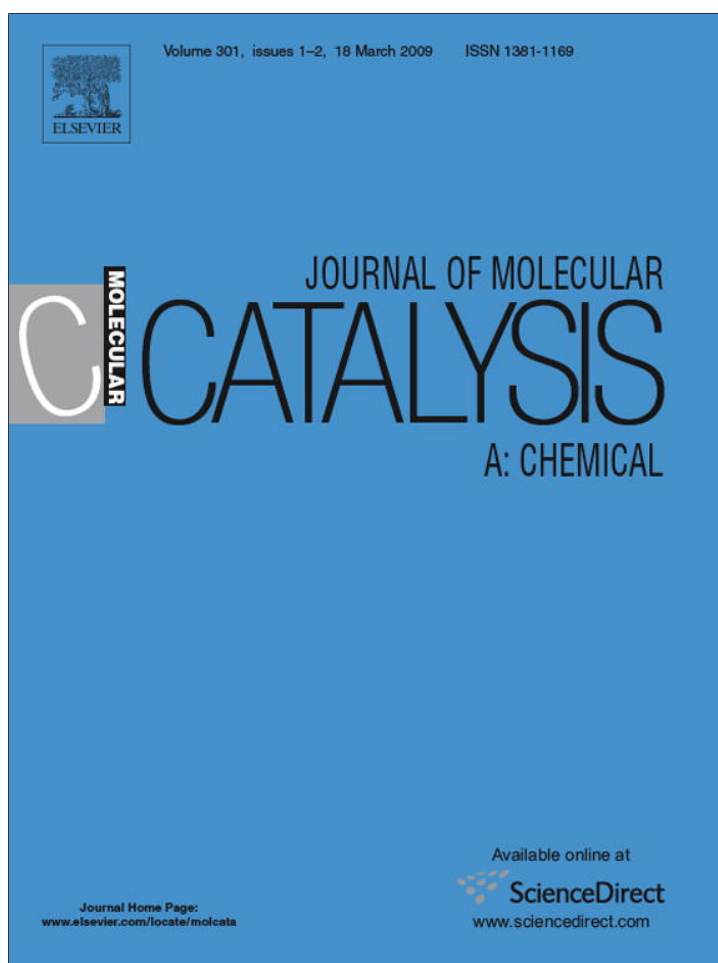


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Behavior of bimetallic PtSn/Al₂O₃ catalysts prepared by controlled surface reactions in the selective dehydrogenation of butane

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ABSTRACT

The “one-pot” circulation reactor system was used for the modification of Pt/Al₂O₃ catalyst using Controlled Surface Reactions (CSRs) with the involvement of tetraethyltin. At 40 °C the tin anchoring reaction resulted in exclusive formation of alloy type Pt–Sn/Al₂O₃ catalyst, while at higher temperatures tin was also introduced onto the alumina support. The bimetallic catalysts were characterized by Temperature Programmed Reduction (TPR), H₂ and CO chemisorption, XPS and test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis). It has been demonstrated that the decomposition of surface organometallic species of Sn in the presence of oxygen leads to the formation of Lewis-acid type active sites in the close vicinity of platinum. The formation Sn–Pt alloy phase together with oxidized Sn species has been evidenced by methods of characterization applied. The presence of these species in Pt–Sn/Al₂O₃ catalysts favors the catalytic behavior in n-butane dehydrogenation, thus increasing the n-butane conversion and the selectivity to olefins, and decreasing the coke deposition.

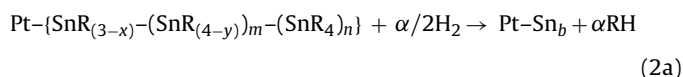
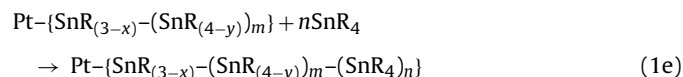
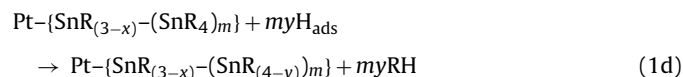
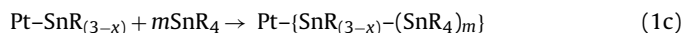
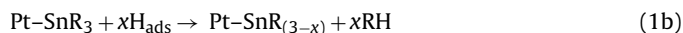
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1. Introduction

In the preparation of supported bimetallic catalysts the key issue is (i) how to create an intimate contact between the two metals, and (ii) how to control surface reactions responsible for the formation of bimetallic surface entities. Supported bifunctional catalysts containing tin and platinum have obtained great industrial importance in the field of refinery technologies [1,2], dehydrogenation processes [3–5] and fine chemistry [6]. The key factor in designing bimetallic supported metal catalysts is the knowledge about the reaction mechanisms and the information about the role of different types of active sites in a given elementary step of the catalytic reaction.

It has been proposed that tin atoms have several positive effects [7–11]: (i) they modify the electronic properties of the active metals (i.e., Pt); (ii) they prevent C–C bond hydrogenolysis by reducing the size of active metal ensemble or by the so-called site isolation (geometric or ensemble) effect; (iii) they diminish the sintering process and stabilize the size of the well-dispersed phase of the active component and (iv) they decrease the rate of coke formation and thus increase the lifetime of the catalyst.

We have developed a two step method to introduce tin onto supported platinum catalysts by using Controlled Surface Reactions (CSRs) [12]. The two main steps are as follows: (i) tin anchoring (step I), and (ii) decomposition of tin containing surface organometallic species (SOMS) formed in hydrogen or oxygen atmosphere (step II). The basic surface chemistry involved in the modification of monometallic supported Pt catalysts by SnR₄ can be given by the following equations:



Eq. (1a) is related to the formation of primary surface complex (Pt–SnR₃) with direct tin–platinum interaction. Upon using surface reaction (1a) monolayer coverage of platinum by SOMS can be achieved. Further studies revealed [12] that in the presence of high

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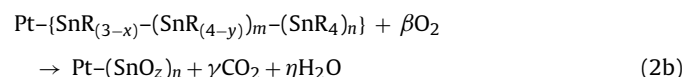
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excess of SnR_4 in the solution, in addition to the earlier proposed reaction (1a), further anchoring-type reactions took place leading to the formation of multilayered SOMS. In reaction (1b) the key issue is to obtain coordinative unsaturation of SOMS in the first layer. This surface species reacts with SnR_4 used in large excess (reaction (1c)) resulting in SOMS in the second layer. It has been shown, that in the presence of hydrogen, the extent of dealkylation of SOMS can be increased further (reaction (1d)) leading to the formation of coordinatively unsaturated SOMS in the second layer. These surface species are considered as the new landing sites for additional SnR_4 (see reaction (1e)). Reaction (1e) provides the multilayered tin coverage on platinum. In this paper, reactions (1a)–(1e), which take place in the presence of a solvent, are referred as “tin anchoring step I”.

The decomposition of SOMS in a hydrogen atmosphere (see reaction (2a)) leads to the formation of alloy type bimetallic nanoclusters supported either on SiO_2 [13] or Al_2O_3 [14] ((H)-type Pt–Sn catalysts).

It has been demonstrated [12] that the monolayer Sn/Pt_5 ratio can be increased substantially under following experimental conditions: (i) high initial concentration of SnR_4 ($[\text{Sn}]_0/\text{Pt}_5$ ratio); (ii) increased reaction temperature (T_r); (iii) use of excess of gas-phase hydrogen. Results of Mössbauer spectroscopy showed that upon modifying a Pt/ SiO_2 catalyst with $\text{Sn}(\text{C}_2\text{H}_5)_4$ the decomposition of multilayered SOMS in a hydrogen atmosphere leads to exclusive formation of Sn–Pt alloys even at $\text{Sn}/\text{Pt}_5 = 2.1$ [15]. It has been shown that the formation of alloy type Pt–Sn surface species resulted in: (i) decrease of hydrogen and CO chemisorption; (ii) decreased chemisorption of hydrocarbons; and (iii) high affinity towards oxygen [16].

It has been demonstrated that step II, i.e., the decomposition of SOMS can also be performed in oxygen (or air). The decomposition of SOMS in O_2 resulted in the formation of supported platinum covered and surrounded by finely dispersed tin-oxide with Lewis-acid character [15] ((O)-type Pt–Sn catalysts). The decomposition of multilayered SOMS in the presence of oxygen can be written as follows:

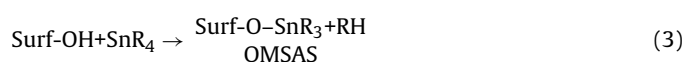


In this case the formation of “metal ion–metal nanocluster ensemble sites” has been suggested. The formation of new Lewis-acid sites was confirmed by adsorption of pyridine [17]. The atomic closeness of Pt and SnO_2 sites provided unique catalytic properties to the (O)-type supported Pt–Sn catalysts [18,19].

Consequently, this approach allowed us to design various bimetallic catalysts for different types of reactions performed both in reductive and oxidative atmosphere.

It has already been evidenced earlier both in our [18,19] and other studies [20–22], that SnR_4 can also be used to introduce organometallic tin moieties onto the support. It was demonstrated that the interaction between alumina and tetraalkyl tin proceeds via: (i) reactions with the involvement of surface OH groups and (ii) adsorption of SnR_4 onto surface oxygen or aluminium ions of the Al_2O_3 support.

Surface reaction (3) between the SnR_4 and the surface OH groups of alumina support at $T_r = 50^\circ\text{C}$ can be written as follows [18]:



Surface reaction (3) leads to the formation of Organometallic Species Anchored to the Support (OMSAS). Prior to the reaction, the support has to be dehydroxylated to various extents to control both the amount of the anchored/granted species. Reaction (3) is quite pronounced in case of alumina and zeolite supports, while silica is

relatively inert [23]. OMSAS can be decomposed either in hydrogen or oxygen atmosphere with formation of ionic forms of tin (SnO_2) anchored onto the support. In this work, no special attempt was done to suppress the formation of OMSAS, although its formation can be suppressed by: (i) using low concentration of SnR_4 ; (ii) using low temperature of tin anchoring [12]; and (iii) addition of small amount of water during the tin anchoring step I [24].

The use of a circulation reactor for the modification of Pt/ Al_2O_3 catalyst with $\text{Sn}(\text{C}_2\text{H}_5)_4$ has been reported in our earlier studies [25]. This technical innovation resulted in a scale-up of the modification procedure up to 250 g. The use of the “one-pot” circulation reactor system has advantages with respect to the conventional method: (i) all of the elementary steps of the modification are done in the same reactor; (ii) the presence of fixed bed catalyst suppresses the crashing of the catalyst during the anchoring process; (iii) the use of high rate of circulation and low $[\text{Sn}]_0$ in the liquid phase provides better conditions to eliminate mass and heat transfer related problems; (iv) it provides better conditions for the removal of unreacted tetraethyltin; and (v) good reproducibility of anchoring process can be achieved.

In this paper, results obtained in the modification of Pt/ Al_2O_3 catalyst with tetraethyltin by CSRs using a “one pot” circulation type reactor set-up are presented. The catalysts were characterized by Temperature Programmed Reduction (TPR), H_2 and CO chemisorption, XPS and test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis), and evaluated in n-butane dehydrogenation. The objective of this work is to correlate the preparation method of bimetallic catalysts with their physicochemical characteristics and their catalytic performance in dehydrogenation of light paraffins.

2. Experimental

2.1. Catalysts preparation

The parent 0.3 wt% Pt/ Al_2O_3 catalyst was prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ spheres using H_2PtCl_6 in 1 M HCl as described in our recent study [19]. The value of specific surface area (S) was measured by N_2 adsorption, while mercury porosimetry was used for the determination of total pore volume (V_s) and average pore radius (R) of the support. Their average values are as follows: $S = 135 \text{ m}^2 \text{ g}^{-1}$; $V_s = 0.66 \text{ cm}^3 \text{ g}^{-1}$ and $R = 8.4 \text{ nm}$. The chlorine content of the catalyst was 1.0 wt%.

In this study the circulation type fix-bed liquid phase reactor was used. Further details and the scheme of the circulation reactor set-up can be found elsewhere [25]. Prior to the tin anchoring step I, the parent Pt/ Al_2O_3 catalyst was reduced in flowing hydrogen at 500°C for 4 h followed by cooling in a hydrogen atmosphere to the temperature of modification. Hydrogen gas stream saturated with solvent vapour was passed through the catalyst bed with rate 200 ml/min for 2 h.

After conditioning the catalyst bed was wetted with the solvent and hydrogen babbled through the reactor for additional 0.5 h. Desulfurated low octane number naphtha (with composition in wt%: n-paraffins = 25.34, iso-paraffins = 32.47, naphthenes = 31.44, aromatics = 10.75; boiling range: 55–180 $^\circ\text{C}$, density = 0.7466 g ml^{-1} , mean molecular weight = 120) was used as a solvent (Hungarian Oil Company). The solvent volume was 540 ml and the amount of the parent supported Pt catalysts was 120 g. The modification started by injection of appropriate amount of $\text{Sn}(\text{C}_2\text{H}_5)_4$ into the solvent circulated by a pump (the rate of liquid circulation was about 150 ml min^{-1}). Duration of tin anchoring step I was 250 min.

It is necessary to mention that the result of blank experiment with parent monometallic Pt/ Al_2O_3 catalyst using standard preparation procedure and highest reaction temperature (65 $^\circ\text{C}$)

but without injecting the tin precursor compound unambiguously confirmed the lack of any sintering of the Pt particles during the modification.

The tin anchoring process (step I) was monitored by measuring the amount of ethane formed as well as by determining the decrease of the concentration of $\text{Sn}(\text{C}_2\text{H}_5)_4$ in the solution. The formation of ethane was exclusive. It should be noted that the decrease of the concentration of $\text{Sn}(\text{C}_2\text{H}_5)_4$ in the solution is due to both the tin anchoring reactions and the adsorption of tetraethyltin onto the support. Adsorbed tetraethyltin has been removed by washing procedure.

The amount of anchored tin calculated from the concentration change of $\text{Sn}(\text{C}_2\text{H}_5)_4$ in the liquid phase was defined as $\text{Sn}_{\text{anch}} = (N \times \text{Sn}_0) - (\text{Sn}_{\text{final}}) - (\text{Sn}_{\text{ads}})$, where Sn_0 is the amount of $\text{Sn}(\text{C}_2\text{H}_5)_4$ introduced per one injection, N is number of injections, Sn_{final} is the amount of $\text{Sn}(\text{C}_2\text{H}_5)_4$ measured in the liquid phase at $t = 250$ min after anchoring reaction, and Sn_{ads} is the amount of adsorbed $\text{Sn}(\text{C}_2\text{H}_5)_4$ determined from the washing solutions. The amount of adsorbed tetraethyltin has been determined from the washing solutions collected after the first and second washing cycles with an aromatic solvent. In the subsequent washing with *n*-hexane the amount of tetraethyltin in the solution was below the detection limit.

The analysis of gas and liquid phases has been carried out as described elsewhere [25]. The tin content was calculated from the overall material balance of tin anchoring and also determined by Atomic Absorption Spectroscopy (AAS). The experimental error of the AAS measurements was 3%. Further details on the tin anchoring, decomposition, washing, drying and analysis can be found elsewhere [25].

The decomposition of SOMS (step II) is accomplished by using Temperature Programmed Decomposition (TPD) technique using both reductive (hydrogen) and oxidative (air or oxygen) atmospheres [18,19,25]. The temperature range used in TPD experiments was 25–350 °C and the heating rate was 5 °C min⁻¹.

A small portion of SOMS formed (about 0.4 g) was decomposed in a hydrogen atmosphere aimed to calculate the overall material balance of tin anchoring, whereas the main portion of samples used for characterization and catalytic measurements in *n*-butane dehydrogenation was decomposed in oxygen ((O) type Pt–Sn catalysts). The use of both reductive and oxidative atmosphere in the decomposition of SOMS formed has been described in our earlier studies [18,19,25].

2.2. Catalysts characterization

The characteristic features of (O) type of bimetallic catalysts were determined by H₂ and CO chemisorptions, Temperature Programmed Reduction (TPR), X-ray photoelectron spectroscopy (XPS) and two test reactions of the metallic phase: cyclohexane dehydrogenation and cyclopentane hydrogenolysis.

Hydrogen and CO chemisorption measurements were carried out in conventional equipment (ASDI RXM 100 equipment (Advanced Scientific Designs Inc.)). Samples were previously reduced at 500 °C under flowing H₂ for 2 h, evacuated at 7×10^{-3} Pa and finally cooled down to room temperature.

The double isotherm method has been used in chemisorption studies. The hydrogen and CO adsorption isotherms were measured at room temperature between 0 and 4 kPa, and extrapolation to zero pressure was used to determine the uptake of hydrogen and CO, respectively. The values of experimental error of H₂ and CO chemisorption measurements are similar and equal to 7–8%.

TPR experiments were performed in a quartz flow reactor. A thermal conductivity detector was adopted to monitor the H₂ consumption during a TPR run. The profiles were automatically recorded with a computer and the area under the TPR curve was

integrated. The quantity of H₂ consumption was defined by calibrating the detector with a well-known volume and concentration of hydrogen containing gas mixture. The samples were heated at 6 °C min⁻¹ from room temperature up to about 800 °C. The reductive mixture (5 (v/v%) H₂–N₂) was fed to the reactor with a flow rate of 10 mL min⁻¹. Catalysts were previously calcined “in situ” at 350 °C for 2 h.

XPS spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg K α 300 W ($h\nu = 1253.6$ eV, $1 \text{ eV} = 1.6302 \times 10^{-19}$ J) 300 W X-ray source. The powder samples were pressed into small Inox cylinders and then mounted on a sample rod placed in a pre-treatment chamber and reduced in H₂ for 2 h at 530 °C before being transferred to the analysis chamber. Before recording the spectra, the sample was maintained in the analysis chamber until a residual pressure of 5×10^{-8} Pa was reached. The spectra were collected at a pass energy of 50 eV. Binding energies (BE) were referred to the C 1s peak at 284.9 eV. The intensities were estimated by calculating the integral of each peak, after subtraction of the S-shaped background, and by fitting the experimental curve to a combination of Lorentzian (30%) and Gaussian (70%) lines. Taking into account the intensity ratios of the XPS peaks corresponding to Sn and Pt, the Sn/Pt surface atomic ratios were determined. The experimental error for the XPS measurements was 5%.

Dehydrogenation of cyclohexane (CH) and hydrogenolysis of cyclopentane (CP) were carried out in a differential flow reactor. Prior to these reactions, samples were reduced “in situ” with H₂ at 500 °C. In both reactions the H₂/hydrocarbon molar ratio was 26. The reaction temperatures were 300 °C for dehydrogenation of CH and 500 °C for hydrogenolysis of CP.

2.3. Catalytic test in the *n*-butane dehydrogenation reaction

The *n*-butane dehydrogenation test was carried out in a continuous flow reactor at 530 °C for 2 h. The reactor (with a catalyst weight of 0.200 g) was fed with 18 mL min⁻¹ of the reactive mixture (*n*-butane + hydrogen, H₂/*n*-C₄H₁₀ molar ratio = 1.25). The reactive mixture was prepared “in situ” by using mass flow controllers. All gases, *n*-butane, N₂ (used for purge), and H₂ (used for the previous reduction of catalysts and for the reaction) were high purity ones (>99.99%). Prior to the reaction, catalysts were reduced “in situ” at 530 °C under flowing H₂ for 3 h. The reactor effluent was analyzed in a GC using a packed chromatographic column at 50 °C (1/8" \times 6 m, 20% BMEA on Chromosorb P-AW 60/80). The amounts of methane, ethane, ethylene, propane, propylene, *n*-butane, 1-butene, *cis*-2-butene, *trans*-2-butene and 1,3 butadiene were measured allowing to calculate both *n*-butane conversion and the selectivity to different reaction products. No homogeneous reaction was observed under these conditions.

After reaction, the used catalysts were characterized by Temperature Programmed Oxidation (TPO) by using air with a flow rate of 50 mL min⁻¹ and a heating rate of 15 K min⁻¹, in order to determine the coke content. The experiments were carried out in a Mettler Toledo equipment, model TGA/SDTA851^e.

3. Results and discussion

3.1. Modification of Pt/Al₂O₃ with Sn(C₂H₅)₄ in a circulation reactor

The preparation of catalysts with high tin content requires high excess of tetraethyltin in the solution. However, the use of high concentration of Sn(C₂H₅)₄ should be avoided as it can result in a concentration gradient of anchored tin along the catalyst bed [25]. For this reason the calculated amount of Sn(C₂H₅)₄ used for anchoring was divided into equal portions and injected into the

Table 1Summary of results obtained in the modification of parent 0.3 wt% Pt/Al₂O₃ catalyst with Sn(C₂H₅)₄ in a circulation reactor.

Exp. no.	T _r (°C)	Sn ₀ (mmol ^a)	n ^I × 10 ⁻⁶ b	n ^{II} _{total} × 10 ⁻⁶ c	n ^{II} _{C₂H₄} × 10 ⁻⁶ d	X ^e	Sn (wt% ^f)	Sn (wt% ^f)	Sn/Pt _s ^g
1	40	3.8	26.0	41.4	1.7	1.54	0.20	0.20	1.28
2	50	3.8	32.6	87.4	12.2	1.09	0.36	0.35	2.26
3	50	7.6	42.0	128.6	26.0	0.99	0.51	0.49	3.14
4	65	3.8	56.7	168.7	39.6	1.01	0.67	0.66	4.23

Amount of catalysts: 120 g; atmosphere of tin anchoring step I: hydrogen; solvent: naphtha; number of Sn(C₂H₅)₄ injections: 3; overall reaction time: 250 min.^a Amount of Sn(C₂H₅)₄ introduced per one injection.^b Amount of ethane formed in step I (mol g_{cat}⁻¹).^c Total amount of hydrocarbons formed in step II (mol g_{cat}⁻¹).^d Amount of ethylene formed in step II (mol g_{cat}⁻¹).^e The stoichiometry of tin anchoring step I X (X = 4n^I/(n^I + n^{II})).^f Calculated from the overall material balance of tin anchoring and AAS data, respectively.^g Amount of Sn anchored per surface Pt atom calculated from AAS data and the CO/Pt ratio of the parent catalyst.

reactor during equal periods of time in the 0th, 60th and 120th minute.

In our earlier studies [12,16,18] it has been shown that similar experimental conditions are favored for surface reactions (1c)–(1e) and (3), i.e., high initial concentration of Sn(C₂H₅)₄, increased T_r and use of excess of gas-phase H₂. However, in this study no special attempt was done to suppress the formation of OMSAS via surface reaction (3).

Table 1 shows the summary of tin anchoring in the series of experiments carried out at three different temperatures. Entries nos. 2 and 3 in Table 1 illustrates results obtained upon varying the amount of Sn(C₂H₅)₄ introduced per one injection (Sn₀). Upon increasing both reaction temperature and the total amount of Sn(C₂H₅)₄ introduced the amount of ethane, formed during tin anchoring step I (n^I), increased (see Table 1). As far as tin anchoring step I was carried out in the presence of gas-phase hydrogen therefore no ethylene was detected.

The Temperature Programmed Decomposition patterns of SOMS formed at three different temperatures are given in Fig. 1A–C. These figures show the formation of ethane and ethylene in the presence of hydrogen. The shape of the TPD curves of SOMS formed at different temperatures is quite similar. Fig. 1A–C show that upon increasing the temperature of tin anchoring from 40 to 65 °C the maximum of TPD ethane peaks is shifted from 170 to 200 °C. Parallel to the shift in the peak position the intensities of the TPD peaks in the temperature interval between 110 and 200 °C increased also.

In our earlier studies it has been demonstrated [12,16] that in the presence of hydrogen the decomposition of SOMS of Sn anchored to Pt gives only ethane. However, the decomposition of OMSAS formed in reaction (3) can give both ethane and ethylene [18]. The formation of ethylene provides indirect evidence for the formation of OMSAS upon modifying a Pt/Al₂O₃ catalyst with Sn(C₂H₅)₄.

Results given in Fig. 1A indicate that at T_r = 40 °C the introduction of tin to platinum is exclusive. As emerges from results given in Table 1 and Fig. 1B and C the increase of the temperature of

tin anchoring up to 65 °C resulted in an increase of both the total amount of hydrocarbons (n^{II}_{total}) and amount of ethylene (n^{II}_{C₂H₄}) formed in step II. These results indicate that the increase of the reaction temperature result in the increase of the contribution of surface reaction (3) with the involvement of surface OH groups of alumina.

In our earlier studies it has been unambiguously demonstrated [19,26] that at T_r = 50 °C upon using pure Al₂O₃ support the rate of surface reaction (3) is comparable with the rate of surface reactions (1a)–(1e) only at relatively high initial concentration of Sn(C₂H₅)₄ ([Sn]₀ = 25.3 mM). In this study the use of high concentration of Sn(C₂H₅)₄ was avoided as the total amount of Sn(C₂H₅)₄ used for anchoring reaction was divided into three equal portions and injected into the reactor during equal periods of time. These results indicate that in the presence of Pt the reactivity of OH groups of the Al₂O₃ support towards Sn(C₂H₅)₄ is higher than in the absence of Pt. This phenomenon can be attributed to the involvement of spill-over hydrogen in the tin anchoring process. Consequently, the spill-over hydrogen increases the amount of tin introduced both onto the Pt-support interface and the Al₂O₃ support.

According to our previous results of blank experiments upon modifying γ-Al₂O₃ support with Sn(C₂H₅)₄ [19] two ethane and one ethylene TPD peaks were observed. The first ethane TPD peak around 180–190 °C was attributed to the decomposition of tin surface species anchored to alumina (–O–Sn(C₂H₅)₃), while the high temperature ethane and ethylene peaks around 250–270 °C and 310–330 °C, respectively, were ascribed to the decomposition of tetraethyltin adsorbed onto surface oxygen or aluminum ions of alumina support. It has to be emphasized that the high temperature ethylene peak in these experiments was observed only upon decomposition of OMSAS containing high amount of anchored tin.

However, Fig. 1B and C show the lack of any ethane and ethylene TPD peaks above 200 °C. In the presence of Pt the temperature of the decomposition of tin containing OMSAS was shifted to the lower temperature region and the maxima of the TPD ethane and

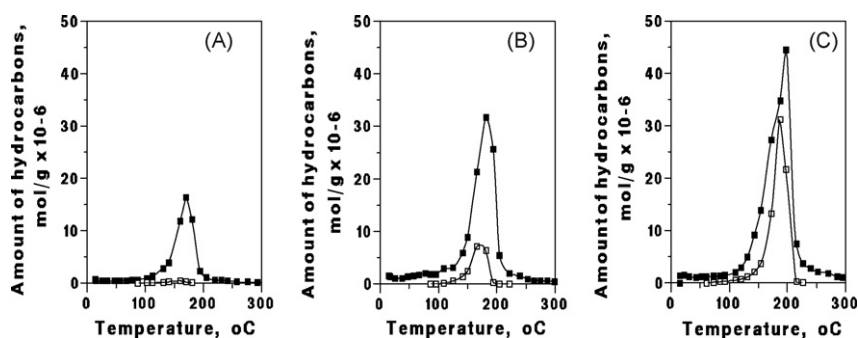


Fig. 1. Temperature Programmed Decomposition (TPD) of SOMS formed. Investigation of the influence of the reaction temperature on the decomposition pattern. A: T_r = 40 °C (Sn/Pt_s = 1.28); B: 50 °C (Sn/Pt_s = 2.26); C: 65 °C (Sn/Pt_s = 4.23); (■), Ethane and (□), ethylene.

ethylene peaks were observed around 170–200 °C and 170–185 °C, respectively (see Fig. 1B and C). Consequently, we propose that tin containing OMSAS are located in the close vicinity of Pt particles, i.e., on the platinum-support interface.

These results show that the modification of Pt/Al₂O₃ catalysts with Sn(C₂H₅)₄ results in Pt–Sn bimetallic catalysts in which two forms of tin can be distinguished: (i) tin anchored onto the platinum and (ii) tin anchored onto the support. In the latter case both the Pt-support interface and the bulk alumina support can be considered as anchoring site. As emerges from results given in Table 1 and Fig. 1A, the formation of tin anchored onto the platinum is exclusive up to Sn/Pt_s = 1.3.

The analysis of *X* values given in Table 1 can provide information with respect to the stoichiometry of anchored SOMS, i.e. the amount of alkyl groups reacted per one tin atom in the anchoring step I. In experiment no. 1 the *X* value was 1.54, it is an indication that in a hydrogen atmosphere at *T*_r = 40 °C more than one alkyl group per one tin atom is lost in the step I. In our earlier studies it has been shown [12,16] that the use of excess gas-phase hydrogen during tin anchoring resulted in high extent of dealkylation of SOMS in both the first and the second layer. In these type surface species the average number of alkyl groups per one tin atom is lower than in corresponding coordinatively saturated SOMS (compare, for example, Pt–SnR_(3–x) with Pt–SnR₃, or Pt–{SnR_(3–x)–(SnR_(4–y))_m} with Pt–{SnR_(3–x)–(SnR₄)_m}). The formation of SOMS with high extent of dealkylation (see Eqs. (1b) and (1d)) reflect the increase of the *X* value.

As emerges from results given in Table 1, the increase of both the reaction temperature (see experiments nos. 2 and 4) and the amount of Sn(C₂H₅)₄ introduced per one injection (compare experiments nos. 2 and 3) resulted in the increase of the Sn/Pt_s ratios, but the values of *X* were close to 1. It has been mentioned that under these experimental conditions surface reactions (1c)–(1e) and (3) are favored, i.e., the formation of multilayered SOMC on platinum and OMSAS can take place.

In our earlier studies it has been shown [12,16] that the coordinatively unsaturated SOMS with high extent of dealkylation are considered as new anchoring sites, which are involved to anchor additional amount of Sn(C₂H₅)₄. Upon increasing of the reaction temperature and/or the amount of Sn₀ introduced the reactivity of this unsaturated SOMS to form corresponding second or multilayer complexes of tin (Pt–{SnR_(3–x)–(SnR₄)} and Pt–{SnR_(3–x)–(SnR_(4–y))_m–(SnR₄)_n}, respectively) also increases. In these multilayered SOMS the R/Sn ratio is higher compared to the coordinatively unsaturated one. The surface chemistry described in reactions (1c) and (1e) indicates that the increase of the amount of anchored tin (the increase of the Sn/Pt_s ratio) should result in a decrease of the value of *X* [16]. Consequently, the observed difference in the values of *X* reflects the difference in the degree of coordinative unsaturation of SOMS formed in the first and subsequent layers.

Moreover, in blank experiments using pure Al₂O₃ it has been also demonstrated [18,19] that Sn(C₂H₅)₄ reacts with surface hydroxyl groups resulting in the release of only one ethyl group per grafted tin (*X* = 1.0) (see reaction (3)). Consequently, results given in Table 1 indicate that anchoring of tin both onto the alumina support and onto the platinum in a form of multilayers results in almost the same values of *X*.

The increase of the amount of Sn(C₂H₅)₄ introduced per one injection (compare experiment nos. 2 and 3 in Table 1) favoured both reactions (1c)–(1e) and (3). However, as far as the amount of tetraethyltin introduced per one injection in experiment no. 3 was still not really high, we proposed that the contribution of the surface reactions that provide the multilayered tin coverage on platinum was higher than the contribution of the surface reaction (3) involved in the modification of the support with tin.

Table 2

Chemisorption properties of parent Pt/Al₂O₃ and PtSn/Al₂O₃ bimetallic catalysts prepared by CSRs.

Catalyst	Sn (wt% ^a)	Sn/Pt _s ^b	H/Pt ^c	CO/Pt ^c
Pt/Al ₂ O ₃	–	–	0.76	0.82
PtSn (0.20 wt%)/Al ₂ O ₃	0.20	1.28	0.17	0.44
PtSn (0.35 wt%)/Al ₂ O ₃	0.35	2.26	0.14	0.39
PtSn (0.49 wt%)/Al ₂ O ₃	0.49	3.14	0.12	0.29
PtSn (0.66 wt%)/Al ₂ O ₃	0.66	4.23	0.09	0.27

^a Calculated from the AAS data.

^b Amount of Sn anchored per surface Pt atom calculated from the CO/Pt ratio of the parent catalyst.

^c Measured on (O) type of catalysts after hydrogen treatment at 500 °C.

The amount of C₂ hydrocarbons formed in steps I and II (*n*^I and *n*^{II}_{total}, respectively) allowed us to calculate the overall material balance of tin anchoring. These data are also included in Table 1. The calculated material balance for tin was compared with the amount of tin determined by AAS. This comparison shows a very good agreement.

3.2. Catalysts characterization

Table 2 displays the values corresponding to H₂ and CO chemisorption experiments. The addition of tin to parent Pt/Al₂O₃ catalyst decreases both H/Pt and CO/Pt ratios. The decrease of hydrogen chemisorption induced by tin is more pronounced than that of the CO. On parent Pt/Al₂O₃ catalyst the ratio CO_{chem}/H_{chem} ([CO/Pt]/[H/Pt]) was around one, while on tin modified catalysts this ratio was in the range 2.4–3.0. These results show that the addition of tin strongly diminishes the number of Pt sites involved in the activation of H₂ molecule. Hence, the drastic diminution of the H₂ chemisorption can be attributed to geometric effects (dilution and blocking) in addition to electronic ones. With respect to CO adsorption (which requires only one Pt site), the addition of tin to Pt inhibits the adsorption of this molecule but in a lower extent, due to side blocking or electronic effect. It is worth mentioning that pronounced decrease of the H/Pt and CO/Pt values takes place at relatively low Sn content, i.e., for PtSn (0.2wt%)/Al₂O₃ catalyst. Further increase of the Sn content resulted in much smaller decrease of both the H/Pt and the CO/Pt values.

Table 3 shows the results corresponding to initial reaction rates (*R*_{CH}) and activation energies (*E*_{CH}) measured in the dehydrogenation of CH and initial reaction rates (*R*_{CP}) of CP hydrogenolysis.

Dehydrogenation of CH is a structure-insensitive reaction [27], which is an indirect measurement of exposed surface Pt atoms (accessible to CH molecules). Benzene was the only product observed for all catalysts, and no deactivation was detected. The monometallic Pt/Al₂O₃ catalyst is very active in this reaction. The addition of tin to Pt decreases the dehydrogenation activity, and the diminution of the initial reaction rate is higher when the amount of tin added to Pt/Al₂O₃ increases. The results of activation energies for this reaction show higher values for bimetallic catalysts (25–27 kcal mol^{–1}) than for the monometallic one (17 kcal mol^{–1}). The significant increase of the activation energies over bimetallic

Table 3

Initial reaction rate (*R*_{CH}) and activation energies (*E*_{CH}) of cyclohexane dehydrogenation at 350 °C and initial reaction rate (*R*_{CP}) of cyclopentane hydrogenolysis at 500 °C for Pt/Al₂O₃ and PtSn/Al₂O₃ catalysts.

Catalysts	<i>R</i> _{CH} (mol h ^{–1} g Pt ^{–1})	<i>E</i> _{CH} (kcal mol ^{–1})	<i>R</i> _{CP} (mol h ^{–1} g Pt ^{–1})
Pt (0.3 wt%)/Al ₂ O ₃	123	17	4.9
PtSn (0.20 wt%)/Al ₂ O ₃	22	25	1.8
PtSn (0.35 wt%)/Al ₂ O ₃	12	27	1.0
PtSn (0.66 wt%)/Al ₂ O ₃	6	27	0.7

catalysts clearly indicates an electronic modification of the Pt phase, what can be related to the alloy formation. Besides, a blocking effect of Pt by Sn can be responsible for the decrease in the dehydrogenation activities. These results are in accordance with results obtained in hydrogen chemisorption.

The behavior of the catalysts in the cyclopentane hydrogenolysis reaction, which is a structure-sensitive one [28], displays that the monometallic Pt/Al₂O₃ catalyst is active for this reaction (Table 3). The addition of Sn to Pt produces an important diminution of the hydrogenolytic ensembles, since the activities of PtSn/Al₂O₃ catalysts are lower than that of the monometallic catalyst and the activity decreases with the increase of the tin content. These results can be interpreted taking into account that there is a decrease of the number of large Pt ensembles by addition of tin. Consequently, tin addition modifies geometrically the metallic phase and results in dilution of the surface Pt atoms.

In conclusion, results obtained in chemisorption study and test reactions clearly indicate that in catalysts prepared by CSRs, an important fraction of Sn strongly interacts with Pt, probably forming alloys, producing dilution and site blocking effects, while another fraction is introduced either onto the support or the Pt-support interface.

Fig. 2 shows TPR profiles of parent Pt/Al₂O₃ and PtSn/Al₂O₃ bimetallic catalysts, previously treated in oxygen at 350 °C for 2 h ((O) type of catalysts). TPR data can be used to determine the amount of H₂ required to reduce the sample and to evaluate the temperature of maximum consumption of hydrogen.

In parent Pt/Al₂O₃ catalyst the main reduction peak is located at 240 °C, whereas a small shoulder at 110 °C is also detected. Literature data indicate that there are two types of Pt oxides in monometallic catalyst, one in weak and the other in strong interaction with the support [3].

The TPR patterns of both tin modified catalysts contain peaks that appear at low temperature (in the interval between 100 and 250 °C) corresponding to the reduction of unalloyed Pt species. The medium temperature region of the TPR patterns, in the interval between 250 and 360 °C with temperature of maximum consumption of hydrogen at about 300–310 °C, can be probably attributed to the reduction of SnO₂ species in close proximity to metallic Pt or PtO_x. This form upon reduction in hydrogen results in Pt–Sn alloy type species. The twin peaks in the temperature interval between

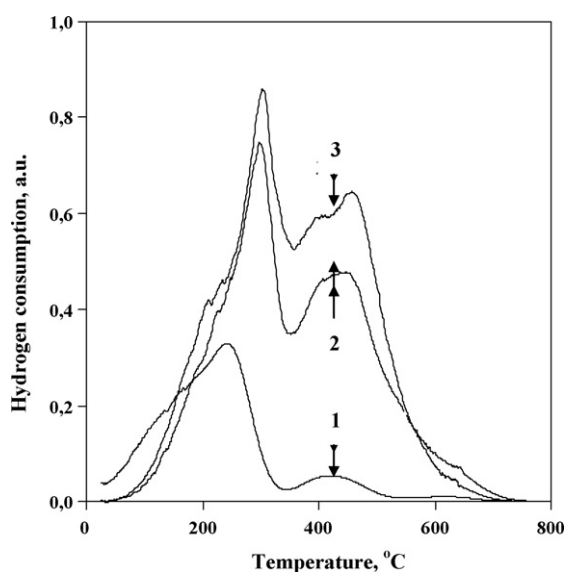


Fig. 2. Temperature Programmed Reduction (TPR) profiles of parent Pt/Al₂O₃ (1) and PtSn/Al₂O₃ bimetallic catalysts with lowest (2, PtSn(0.20 wt%)/Al₂O₃) and highest tin content (3, PtSn(0.66 wt%)/Al₂O₃), previously oxidized at 350 °C for 2 h.

360 and 700 °C probably corresponds to the reduction of separate SnO₂ species with strong interaction with the support. Armendáriz et al. [3] have pointed out that the position of the reduction peaks of the Pt–Sn alloy phases strongly depends on the tin concentration, and with increasing the Sn content in the Pt–Sn alloy, the shift to higher temperature (from 350 to 420 °C) can be expected. Therefore, we can also associate the peak around 405 °C to the reduction of highly dispersed tin oxide at the Pt-support interface and also forming Pt–Sn alloy nanoclusters. The other peaks centered at 450 and 460 °C for PtSn/Al₂O₃ bimetallic catalysts with lowest and highest tin contents, respectively can be attributed to the formation of separate oxidized tin oxide phases in the catalyst. It is worth for mentioning that the TPR peak of monometallic Sn/Al₂O₃ appears also at high temperatures (about 500 °C) as it was previously reported [29,30].

Our calculations, based on the hydrogen consumption up to 800 °C, indicate that Pt oxide is completely reduced and most part of Sn⁴⁺ is also reduced to Sn₀ (98% and 70% in PtSn(0.20 wt%)/Al₂O₃ and PtSn(0.66 wt%)/Al₂O₃ catalysts, respectively).

In TPR experiments the range of the intermediate TPR zone can be considered as an indication for bimetallic interaction. The shift of the first TPR peaks to higher temperatures (to 300–310 °C) and the broadening of these peaks indicate that the degree of Pt–Sn co-reduction in both bimetallic catalysts is high. These results confirm the strong Pt–Sn interaction, previously detected by chemisorption and test reaction results.

XPS spectra of the Pt 4f level for the PtSn(0.49 wt%)/Al₂O₃ and PtSn(0.66 wt%)/Al₂O₃ catalysts, reduced “in situ” at 500 °C, are shown in Fig. 3 and they displayed that the Pt 4f peaks overlaps with the Al 2p peaks of the alumina. Taking into account this fact, a curve synthesis procedure was performed assuming an intensity ratio of Pt 4f_{7/2} to Pt 4f_{5/2} of 1:0.75, obtaining in this way the Pt 4f_{7/2} binding energies corresponding to both bimetallic catalysts. The binding energies of Pt 4f_{7/2} and Pt 4f_{5/2} (71.6–75.0 eV for the

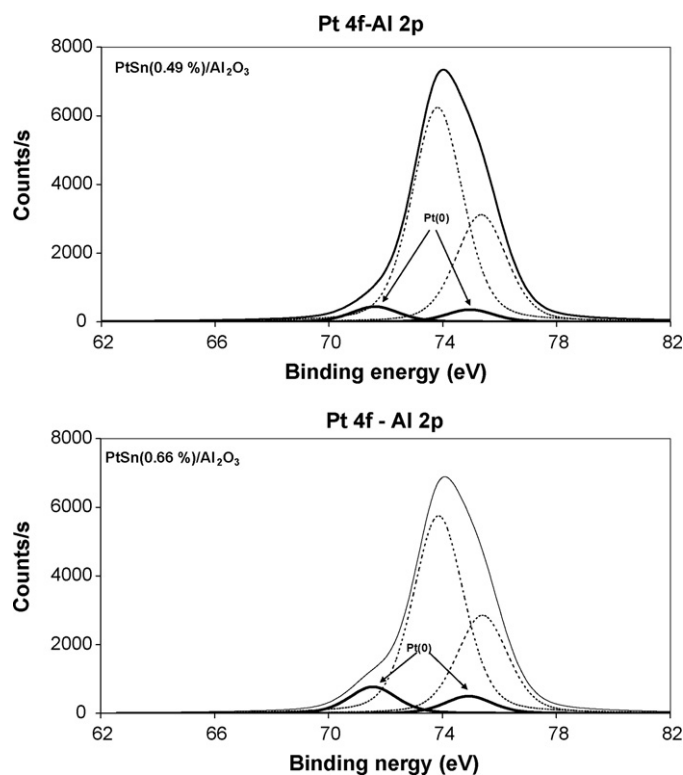


Fig. 3. XPS spectra corresponding to Pt 4f and Al 2p signals of PtSn(0.49 wt%)/Al₂O₃ and PtSn(0.66 wt%)/Al₂O₃ catalysts reduced at 500 °C.

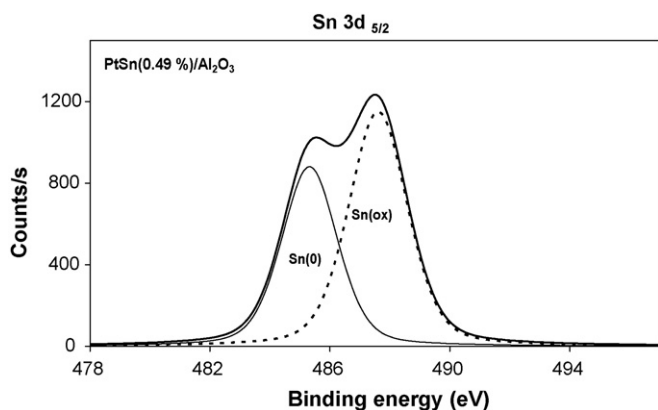


Fig. 4. XPS spectra corresponding to Sn $3d_{5/2}$ signals of PtSn (0.49 wt%)/Al₂O₃ catalyst reduced at 500 °C.

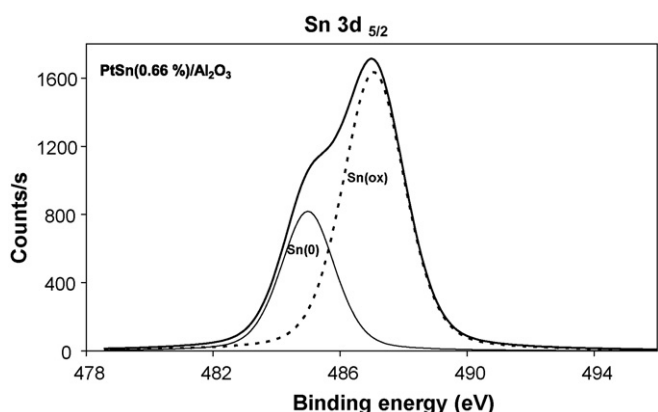


Fig. 5. XPS spectra corresponding to Sn $3d_{5/2}$ signals of PtSn (0.66 wt%)/Al₂O₃ catalyst reduced at 500 °C.

former and 71.6–74.9 eV for the latter) indicate in all cases the presence of metallic platinum [31].

Figs. 4 and 5 show the XPS spectra corresponding to the Sn $3d_{5/2}$ level of PtSn (0.49 wt%)/Al₂O₃ and PtSn (0.66 wt%)/Al₂O₃ catalysts, respectively after “in situ” reduction at 500 °C. From the deconvolution of both spectra presented in Figs. 4 and 5, two peaks were obtained at 485.3 and 487.6 eV, and 485.0 and 487.1 eV, respectively. The first peak would correspond to zerovalent Sn, in agreement with results found by several authors [32–34]. It must be noted that Homs et al. [5] attributed the peaks at 483.6 eV and 485 eV to Sn⁰ and Sn in a PtSn alloy (Sn⁰_{al}), respectively. The other peak appearing at 487.1–487.6 eV would correspond to oxidized Sn species. According to literature data, the line corresponding to Sn $3d_{5/2}$ for SnO has a BE at 486.5–486.9 eV, while the Sn $3d_{5/2}$ line for SnO₂ has a BE at 486.5 eV [5,33–35]. In consequence, the second peak in our catalysts will be assigned to supported Sn²⁺/Sn⁴⁺ oxides.

Table 4 shows data obtained by XPS, such as binding energies corresponding to Sn $3d_{5/2}$ and Sn/Pt surface atomic ratios. The

Table 4
Characterization of PtSn/Al₂O₃ catalysts by XPS.

Catalysts	BE Sn $3d_{5/2}$ (eV) ^a	Sn/Pt ^b
PtSn (0.49 wt%)/Al ₂ O ₃	485.3 (42%)	3.13 (2.68)
	487.6 (58%)	
PtSn (0.66 wt%)/Al ₂ O ₃	485.0 (30%)	3.12 (3.61)
	487.1 (70%)	

^a Percentage of each species in parentheses.

^b Amount of Sn anchored per Pt atom calculated from the XPS measurement and AAS data (in parentheses).

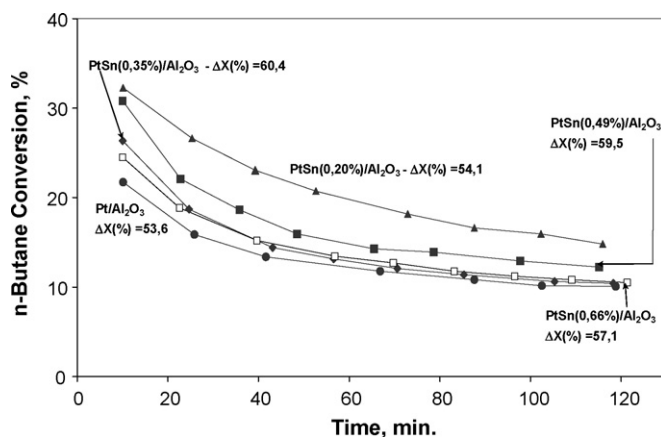


Fig. 6. n-Butane conversion vs. reaction time for different catalysts in n-butane dehydrogenation at 530 °C.

presence of Sn⁰ in bimetallic catalysts (in relatively high concentrations, between 30% and 42%) and the absence of this species in the Sn/Al₂O₃ sample (see our earlier results [30]) indicates that the extent of reducibility of Sn in PtSn catalysts is high, these results agrees well with the ones obtained TPR experiments. Taking into account these results for reduced bimetallic catalysts, it can be concluded that in these catalysts, a certain fraction of tin is Sn⁰, probably alloyed with Pt, and the remaining fraction is Sn²⁺/Sn⁴⁺ oxides. Besides, XPS results showed that the Sn/Pt surface atomic ratios were similar to those of bulk Sn/Pt atomic ratio calculated from the AAS data. Hence, it can be suggested that there is not any surface enrichment in Sn in both catalysts.

Mono- and bimetallic catalysts were tested in the n-butane dehydrogenation at high temperature (530 °C) and the results of n-butane conversion, selectivity to butenes and yield to butenes vs. reaction time are displayed in Figs. 6–8, respectively.

As shown in Fig. 6, the addition of small amount of Sn to Pt resulted in a pronounced increase of the n-butane conversion (see PtSn (0.2wt%)/Al₂O₃ catalyst). For higher tin contents, this effect is not so pronounced. In order to determine the catalyst deactivation, the ΔX parameter ($\Delta X = 100 \cdot (X_0 - X_f)/X_0$, where X_0 is the initial conversion at 10 min reaction time and X_f is the final conversion at 120 min reaction time) was defined. With respect to the activity decrease (ΔX), there are no significant differences between mono and bimetallic catalysts. However, there are important differences in the carbon content of various catalysts determined after the catalytic runs.

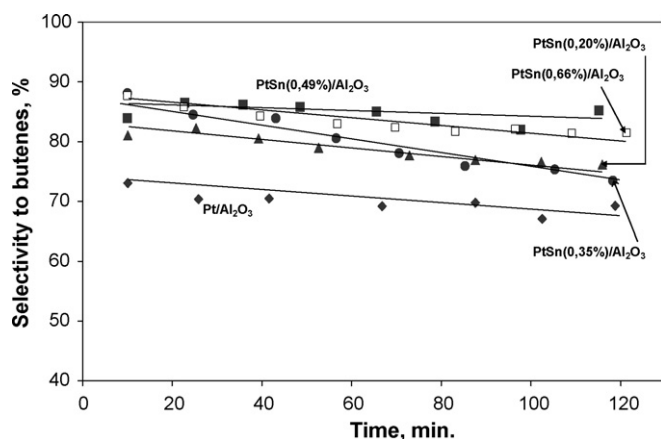


Fig. 7. Selectivity to butenes vs. reaction time for different catalysts in n-butane dehydrogenation at 530 °C.

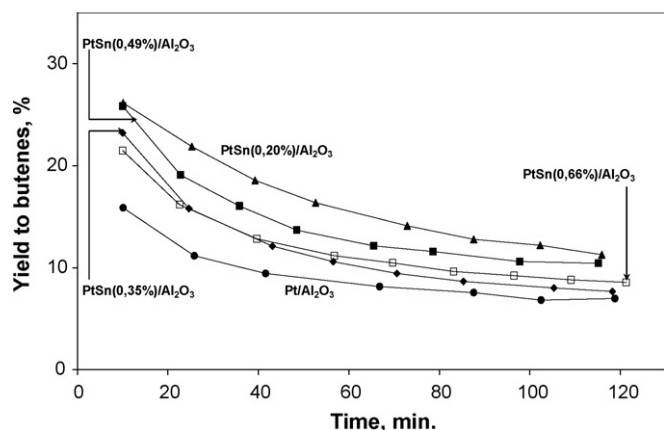


Fig. 8. Yield to olefins vs. reaction time for different catalysts in n-butane dehydrogenation at 530 °C.

Besides, bimetallic catalysts display higher selectivities to all butenes (80–90%) compared to the monometallic sample (70%), this effect is more pronounced for catalysts with higher tin contents, as shown in Fig. 7.

With respect to the yield to all butenes produced by the different catalysts (Fig. 8), all bimetallic catalysts show much higher yields than that of the corresponding monometallic one. In this sense the modification of the metallic phase taking place during the preparation of PtSn/Al₂O₃ catalysts by CSRs is responsible for the significant improvement of the catalytic performance in n-butane dehydrogenation.

In order to determine the quality and quantity of deposited coke, catalysts tested in n-butane dehydrogenation during 2 h at 530 °C, were characterized by Temperature Programmed Oxidation (TPO) experiments, and their profiles are shown in Fig. 9. The TPO profile of Pt/Al₂O₃ shows two oxidation zones. The first one appears at lower temperatures, between 300 and 420 °C. This one was attributed to coke close to the metallic surface, and the latter with a peak at higher temperatures (around 480 °C) was assigned to the carbon deposited on the support [36]. The first oxidation zone practically disappears, as the Sn concentration in the catalysts increases, while the second peak, corresponding to the coke deposited on alumina, is clearly decreases. The low coke deposition observed for the bimetallic catalysts (1.8 and 1.1 wt% C for PtSn(0.20%)/Al₂O₃ and PtSn(0.35%)/Al₂O₃, respectively) with respect to the monometallic one

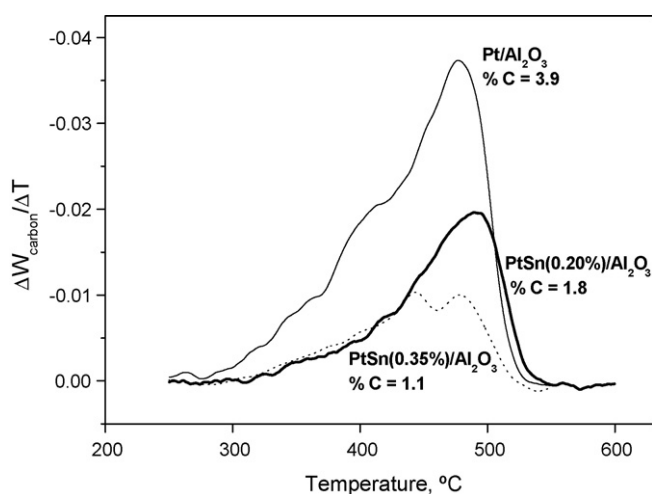


Fig. 9. Temperature Programmed Oxidation (TPO) profiles of mono- and bimetallic catalysts.

(3.9 wt% C) is in accordance with the form of time on stream curves shown in Fig. 8. The higher activity of PtSn/Al₂O₃ catalysts with respect to the monometallic one can be related to the lower extent of coke formation. Taking into account these facts and considering that there are no significant differences in the activity decrease (ΔX) between mono and bimetallic catalysts, it is probable that the main carbon deposition in the monometallic catalyst occurs during the first 10 min of the reaction time that is before the first collected sample.

In the bimetallic catalysts prepared by CSRs, the preparation technique leads to a metallic phase with an intimate PtSn interaction, as observed by TPR, test reactions, XPS and chemisorption measurements. The presence of Pt and Sn in an intimate contact, with probable alloy formation, together with oxidized Sn species in the vicinities of the metallic phase, favours the n-butane conversion, increases the selectivity to olefins and decreases the coke deposition.

4. Conclusion

The modification of alumina supported platinum catalysts with tetraethyltin by CSRs using a “one pot” circulation type reactor set-up was demonstrated. The increase of both the reaction temperature and the amount of Sn(C₂H₅)₄ introduced per one injection resulted in the increase of the Sn/Pt_s ratios. It has been shown that the introduction of tin to platinum is exclusive when the tin anchoring reaction has been carried out at $T_r = 40$ °C (Sn/Pt_s = 1.3). However, the increase of the temperature of tin anchoring and/or use of high initial tin concentration result in the increase of the contribution of surface reaction with involvement of surface OH groups of alumina. Results obtained in tin anchoring show that the modification of Pt/Al₂O₃ catalysts with Sn(C₂H₅)₄ leads to Pt–Sn bimetallic catalysts in which two forms of tin can be distinguished: (i) tin anchored onto the platinum and (ii) tin anchored both onto the Pt-support interface and the alumina support.

Chemisorption, TPR, XPS and both test reactions results obtained after reduction of (O) type of PtSn/Al₂O₃ catalysts in hydrogen clearly indicate that in these catalysts, some part of Sn strongly interacts with Pt resulting in Sn⁰, probably in the form of Sn–Pt alloys and creating dilution and site blocking effects. The other part of tin is stabilized in the form of Sn²⁺/Sn⁴⁺ oxides either at the Pt-support interface or the alumina support. The presence of Pt and Sn in an intimate contact, with probable alloy formation, together with oxidized Sn species in the vicinities of the metallic phase, favours the n-butane conversion, increases the selectivity to olefins and decreases the coke deposition.

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