Preparation of bi- and multimetallic supported catalysts by Controlled Surface Reactions

Ph.D. Dissertation

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Budapest, 2010
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. State of art</td>
<td>1</td>
</tr>
<tr>
<td>2.1. Bimetallic supported catalysts: influence of the promoter on the catalytic performance</td>
<td>1</td>
</tr>
<tr>
<td>2.1.1. Electronic effect in catalysis by alloys</td>
<td>2</td>
</tr>
<tr>
<td>2.1.2. Geometric effect</td>
<td>2</td>
</tr>
<tr>
<td>2.1.3. The occurrence of mixed-sites</td>
<td>2</td>
</tr>
<tr>
<td>2.1.4. Some comments</td>
<td>3</td>
</tr>
<tr>
<td>2.2. Classification of methods used for the preparation of supported bimetallic catalysts with exclusive “active metal – modifier” interaction</td>
<td>3</td>
</tr>
<tr>
<td>2.3. Conventional preparation techniques</td>
<td>5</td>
</tr>
<tr>
<td>2.3.1. Impregnation methods</td>
<td>5</td>
</tr>
<tr>
<td>2.3.2. Ion exchange</td>
<td>5</td>
</tr>
<tr>
<td>2.3.3. Precipitation methods</td>
<td>5</td>
</tr>
<tr>
<td>2.4. Non-conventional preparation techniques</td>
<td>6</td>
</tr>
<tr>
<td>2.4.1. Sol-gel synthesis</td>
<td>6</td>
</tr>
<tr>
<td>2.4.2. Solvated Metal Atom Dispersion (SMAD) method</td>
<td>6</td>
</tr>
<tr>
<td>2.4.3. The use of heterobinuclear complexes or clusters</td>
<td>7</td>
</tr>
<tr>
<td>2.4.4. Anchoring type surface reactions</td>
<td>7</td>
</tr>
<tr>
<td>2.4.4.1. General aspects of anchoring</td>
<td>7</td>
</tr>
<tr>
<td>2.4.4.2. Anchoring reactions based on the reactivity of surface hydroxyl groups</td>
<td>8</td>
</tr>
<tr>
<td>2.4.4.3. Preparation via ions anchored onto the support</td>
<td>9</td>
</tr>
<tr>
<td>2.4.5. Redox methods</td>
<td>9</td>
</tr>
<tr>
<td>2.4.6. Application of Surface Organometallic Chemistry on metal (SOMC/M) approach</td>
<td>10</td>
</tr>
<tr>
<td>2.4.6.1. Chemical-vapour-deposition technique (CVD)</td>
<td>10</td>
</tr>
<tr>
<td>2.4.6.2. Use of Controlled Surface Reactions (CSRs)</td>
<td>11</td>
</tr>
<tr>
<td>2.4.6.3. Formation of monolayer coverage of surface organometallic species (SOMS)</td>
<td>12</td>
</tr>
<tr>
<td>2.5. Literature study on the characterization of supported bimetallic catalysts</td>
<td>14</td>
</tr>
<tr>
<td>2.5.1. Chemisorption of H\textsubscript{2}, O\textsubscript{2} and CO</td>
<td>14</td>
</tr>
<tr>
<td>2.5.2. Electron Microscopy and Diffraction</td>
<td>15</td>
</tr>
<tr>
<td>2.5.3. Temperature programmed reduction (TPR)</td>
<td>15</td>
</tr>
<tr>
<td>2.5.4. Infrared spectroscopy</td>
<td>16</td>
</tr>
<tr>
<td>2.5.5. Mössbauer spectroscopy</td>
<td>16</td>
</tr>
<tr>
<td>2.5.6. Solid-state nuclear magnetic resonance (NMR) spectroscopy</td>
<td>17</td>
</tr>
<tr>
<td>2.5.7. X-Ray photoelectron spectroscopy (XPS)</td>
<td>17</td>
</tr>
<tr>
<td>2.5.8. Extended X-ray absorption fine structure (EXAFS) spectroscopy</td>
<td>18</td>
</tr>
<tr>
<td>2.6. Literature study on the use of supported bimetallic catalysts in various reactions</td>
<td>18</td>
</tr>
<tr>
<td>2.6.1. Use of supported bimetallic catalysts prepared by CVD in various reactions</td>
<td>18</td>
</tr>
<tr>
<td>2.6.2. Use of supported bimetallic catalysts prepared by CSRs in various reactions</td>
<td>19</td>
</tr>
<tr>
<td>2.6.3. Use of supported bimetallic catalysts prepared by SOMC/M in various reactions</td>
<td>19</td>
</tr>
<tr>
<td>3. Objectives of the study</td>
<td>22</td>
</tr>
<tr>
<td>4. Experimental methods</td>
<td>23</td>
</tr>
<tr>
<td>4.1. Materials used</td>
<td>23</td>
</tr>
<tr>
<td>4.2. Preparation of monometallic catalysts</td>
<td>23</td>
</tr>
<tr>
<td>4.3. The Controlled Surface Reactions with SnR\textsubscript{4}</td>
<td>25</td>
</tr>
<tr>
<td>4.3.1. Tin anchoring step I</td>
<td>25</td>
</tr>
<tr>
<td>4.3.1.1. Tin anchoring in the stirred tank reactor</td>
<td>25</td>
</tr>
<tr>
<td>4.3.1.2. Tin anchoring in the circulation reactor</td>
<td>26</td>
</tr>
<tr>
<td>4.3.2. Decomposition of SOMS (step II)</td>
<td>28</td>
</tr>
<tr>
<td>4.3.2.1. Decomposition of SOMS in reductive atmosphere</td>
<td>28</td>
</tr>
<tr>
<td>4.3.2.2. Decomposition of SOMS in oxidative atmosphere</td>
<td>28</td>
</tr>
<tr>
<td>4.3.3. Calculation of the overall material balance of tin anchoring</td>
<td>29</td>
</tr>
</tbody>
</table>
4.3.4. Computer modelling ................................................................. 29
4.4. Catalysts characterization .......................................................... 29
  4.4.1. CO and H₂ chemisorption .................................................. 29
  4.4.2. TPR measurements .......................................................... 29
  4.4.3. FTIR measurements ......................................................... 29
  4.4.4. XPS measurements .......................................................... 30
  4.4.5. Mössbauer spectroscopic measurements ............................... 30
  4.4.6. EXAFS measurements ...................................................... 30
5. Results and discussion ............................................................... 31
  5.1. Computer modeling of -Sn(C₂H₅)₃ and -Sn(C₃H₇)₂ moieties anchored onto the platinum cluster ......................................................... 31
  5.2. Molecular design of new type of catalysts prepared via tin anchoring technique. Formation of multilayer coverage of tin organometallic species ........................................ 31
  5.3. Use of CSRs for modification of 3 wt% Pt/SiO₂ catalyst with Sn(C₂H₅)₄ .................................................. 38
    5.3.1. Tin anchoring in the presence of adsorbed hydrogen ................ 38
      5.3.1.1. Influence of the initial tetraethyltin concentration (Sn₄/Pt₄) on the step I ........................................ 38
      5.3.1.2. Influence of the type of anchored SOMS on the TPD profile. Tin anchoring in the presence of adsorbed hydrogen ........................................ 39
      5.3.1.3. Material balance of tin anchoring in the presence of adsorbed hydrogen ........................................ 42
      5.3.1.4. Influence of the reaction temperature on tin anchoring step I .................................................. 44
      5.3.1.5. Influence of the duration on tin anchoring step I .......................................................... 45
    5.3.2. Tin anchoring in excess of hydrogen ................................... 46
      5.3.2.1. Tin anchoring in excess of hydrogen using Sn(C₂H₅)₄ as tin precursor compound ........................................ 46
      5.3.2.2. Tin anchoring in excess of hydrogen using Sn(CH₃)₄ as tin precursor compound ........................................ 49
    5.3.3. Tin anchoring in the presence of trace amount of oxygen .......... 52
    5.3.4. Reactions with the involvement of the silica support .............. 57
    5.3.5. Characterization by chemisorption techniques ....................... 58
    5.3.6. Characterization by FTIR spectroscopy ................................ 58
    5.3.7. Characterization by Mössbauer spectroscopy ......................... 59
      5.3.7.1. Characterization of catalysts prepared in excess of hydrogen .................................................. 59
      5.3.7.2. Characterization of catalysts prepared in the presence of trace amount of oxygen ........................................ 60
      5.3.7.3. The influence of atmosphere and the type tin precursor compounds used in tin anchoring on the Mössbauer spectroscopy results ........................................ 61
    5.3.8. Transformation of (O)- and (H)-type Sn-Pt catalysts followed by EXAFS ........................................ 62
    5.3.9. Low temperature CO oxidation over Sn-Pt/SiO₂ catalysts .......... 63
    5.3.10. Use of supported Sn-Pt/SiO₂ catalysts in various catalytic reactions .................................................. 66
  5.4. Peculiarities of the modification of Pt/Al₂O₃ catalysts with Sn(C₂H₅)₄ by CSRs ........................................ 66
    5.4.1. Study of Sn(C₂H₅)₄ anchoring onto alumina support ................ 67
    5.4.2. Study of the tin anchoring over Pt/Al₂O₃ catalysts .................. 68
    5.4.3. Elementary steps involved in the anchoring of Sn(C₂H₅)₄ onto supported platinum ........................................ 70
  5.5. Tin anchoring over Pt/Al₂O₃ catalysts using circulation reactor system ........................................ 75
    5.5.1. Study of tin anchoring in the circulation reactor .................... 76
    5.5.2. Characterization of Sn-Pt/Al₂O₃ catalysts prepared in the circulation reactor ........................................ 79
      5.5.2.1. Characterization by H₂ and CO chemisorption .................. 79
      5.5.2.2. Characterization by Temperature Programmed Reduction ........ 79
      5.5.2.3. Characterization by XPS measurements ........................................ 80
      5.5.2.4. Characterization by FTIR spectroscopy of adsorbed CO ........ 82
  5.6. Modification of commercial Re-Pt/Al₂O₃ catalysts with Sn(C₂H₅)₄ ........................................ 82
    5.6.1. Modification of Re-Pt/Al₂O₃ catalysts with Sn(C₂H₅)₄ in the stirred tank reactor ........................................ 83
    5.6.2. Study of tin anchoring over Re-Pt/Al₂O₃ catalyst in the circulation reactor ........................................ 85
  5.7. Application of CSRs for qualitative determination of the efficiency of re-reduction
of 5 wt% Pt/Al₂O₃ catalyst ................................................................. 87
5.8. Use of supported Sn-Pt/Al₂O₃ and Sn-Re-Pt/Al₂O₃ catalysts in various catalytic
tions ....................................................................................................... 88
5.9. Comparison of supported Ge-Pt/C catalysts prepared by conventional impregnation
and CSRs ............................................................................................... 89
  5.9.1. Modification of 5 wt% Pt/C catalyst with Ge(C₂H₅)₄ by CSRs ......................... 89
  5.9.2. Chemisorption properties of Ge-Pt/C catalysts prepared by CSRs and conventional
impregnation .......................................................................................... 91
5.10. Preparation of various types of supported Snₓ-Mₓ (M= Pd, Rh and Ru) catalysts by
CSRs ........................................................................................................ 92
  5.10.1. Modification of 1.7 wt% Pd/SiO₂ catalyst with Sn(C₂H₅)₄ .................................. 92
  5.10.2. Modification of 5 wt% Pd/C catalyst with Sn(C₂H₅)₄ ....................................... 94
  5.10.3. Modification of 1 wt% Rh/SiO₂ catalyst with Sn(C₂H₅)₄ ................................. 96
  5.10.4. Modification of 1 wt% Rh/Al₂O₃ catalyst with Sn(C₂H₅)₄ ............................... 97
  5.10.5. Modification of 4 wt% Rh/Al₂O₃ catalyst with Sn(C₂H₅)₄ ............................... 98
  5.10.6. Modification of 5 wt% Rh/Al₂O₃ catalyst with Sn(C₂H₅)₄ ............................... 98
  5.10.7. Modification of 5 wt% Rh/MgO catalyst with Sn(C₂H₅)₄ ................................. 99
  5.10.8. Modification of 1.77 wt% Ru/Al₂O₃ catalyst with SnR₄ (R= CH₃ and C₂H₅) .... 100
  5.10.9. Modification of 5 wt% Ru/Al₂O₃ catalyst with Sn(C₂H₅)₄ ............................... 101
  5.10.10. Comparison of anchoring to different metals .............................................. 102
6. Summary ............................................................................................... 104
  6.1. Conclusions ...................................................................................... 104
  6.2. New scientific findings ....................................................................... 107
7. Abbreviations used ................................................................................ 108
8. References ............................................................................................. 109

Appendix
Acknowledgement
Affirmation
1. Introduction

The great importance of bimetallic catalysts was first evidenced in catalytic naphtha reforming. Since the introduction of the alumina supported Re-Pt reforming catalyst in 1968 the preparation and use of supported bimetallic catalysts which could remain on-stream for a period of a year or even longer have obtained great scientific and industrial interest. In addition to Chevron’s Re-Pt/Al₂O₃ catalysts other bimetallic systems such as Ir-Pt/Al₂O₃ and Sn-Pt/Al₂O₃ became important in reforming and aromatization technologies. Some of the promoter metals have catalytic properties of their own (Re, Ir), while others are catalytically inactive (Sn, Ge or Pb). In the refining industry the most frequently applied modifier is Sn and the mechanism of its influence has been extensively studied. It has been proposed that tin atoms have several positive effects: (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 diminish the rate of coke formation and thus increase the lifetime of the catalyst. As a consequence, for a given catalytic formulation, i.e. Pt-Sn, the influence of the Sn on the properties of Pt depends directly on the reaction considered.

Understanding the surface chemistry that controls the formation of bimetallic surface species has been a goal of researches for many years. Despite the tremendous efforts done in this field the focal issue is still the same, that is (i) how to control surface reactions involved in the formation of bimetallic surface entities and (ii) how to create an intimate contact between the two metals?

Below an overview about the effect of promoter on the performance of platinum-group metals heterogeneous catalysts is presented. This literature review will be restricted mostly to the preparation of Sn-modified Pt-based supported catalysts and only some examples about the preparation of tin-modified Pt-group metals catalysts by Surface Organometallic Chemistry techniques will be provided.

In the first part, the promotion of monometallic Pt catalysts by addition of a second metal is described from a general point of view in terms of: (i) electronic effects; (ii) geometric effects; (iii) the occurrence of mixed sites. The second part presents the main methods to prepare bimetallic catalysts through the unselective and selective depositions of the precursor of modifier and the use of heterobinuclear complexes. The influence of preparation methods on the chemical state and the spatial distribution of both components are highlighted. In the last part, a short overview is given about the influence of the addition of modifier on some important reactions in which both Pt-based and Pt-group metals are as active phase are involved.

2. State of art

2.1. Bimetallic supported catalysts: influence of the promoter on the catalytic performance

The key factor in designing supported metal catalysts is the knowledge of the reaction mechanisms and information about the role of different types of active sites in a given step of the catalytic reaction. The performance of supported “mono-functional” monometallic catalysts is governed by the metal particle size, metal dispersion, overall morphology of the metal nanocluster, the character of metal-support interaction, and the electronic properties of the metal. In bifunctional supported metal catalysts in addition to the above listed factors the metal/acid balance, and the type and strength of the acid function play a key role in the overall performance.

In bimetallic supported metal catalysts the most crucial issues determining the performance of the catalyst are (i) surface composition, (ii) possible electronic interaction between the two metals, (iii) the presence of both metals in metallic form or the stabilization of one of the metal components in ionic form and (iv) the spatial surface distribution of the modifier in bimetallic particles (random or preferential occupation of sites of a given topology by the modifier).

Several methods have been developed to modify the surface composition and structure of supported bimetallic catalysts. These methods can be used during the main step of catalyst preparation or in a separate step aimed at modifying of the parent catalyst. In case of supported catalysts, the main goal most frequently is to modify selectively either the active phase or the support. Because the surface composition of supported clusters depends strongly on numerous experimental factors (the surface tension, the method of preparation and atmosphere used for treatment, etc.), the exclusive formation of alloys requires much more carefully controlled approaches.
Depending on whether the turnover frequency (TOF), or the rate per unit surface area or per accessible metal atom, is affected or not by the metallic structure the reactions are called as either structure-sensitive or structure-insensitive. Taylor was the first who recognized this concept in 1925. The structure-activity relationships are often explained on the basis of electronic and/or geometric effects. However, geometric and electronic effects cannot often be separated as independent factors.

2.1.1. Electronic effect in catalysis by alloys

To be short, the key point in this model is the interaction between the $d$-band orbitals of the surface sites with the molecular orbitals of reactants and products. Historically, the premises of this concept were suggested by Sabatier.

At the beginning, the behavior of alloy catalysts was interpreted by both the electronic theory of catalysis and the Rigid Band Theory (RBT) of alloys. The former stated that molecules are activated during the adsorption process by either releasing or accepting one electron, whilst the latter postulated that number of $d$-band holes could be decreased by alloying a metal containing more valence electrons, from an electron transfer.

XPS studies and quantum chemical calculations on different alloys provide evidences for redistribution of charges occurred in metals. IR spectroscopy coupled with CO chemisorption also allows to study the electronic modification induced by the second metal. The modification results in a frequency shift in the stretching vibration of linearly adsorbed CO on the surface Pt atoms. For example, based on XPS study and IR spectroscopy of adsorbed CO it was suggested that in Ge-Pt/Al$_2$O$_3$ catalysts Pt atoms when alloyed with Ge are in an electron-deficient state. An increased $d$-vacancy on Pt leads to a smaller contribution of back-donation of Pt $5d$ electrons to the CO $2\pi^*$ orbital and suppresses CO coverage.

2.1.2. Geometric effect

The first elements of this model were developed in the pioneering works by Kobozev, Poltorak and Boronin. It was shown that some reactions need more than one surface atom to proceed. Moreover, a specific arrangement between these atoms is even required to generate the active site. This geometric model was revised by several authors (for example, Dalmon et al.), naming it as “ensemble-size” model. The basic idea is that the rate is the function of the probability to find an ensemble of free and neighbor atoms on which the adsorption of the reactant(s), and its further transformations, can occur.

The IR-monitored chemisorption of CO is a very efficient approach to probe the dilution of an active component $A$. The dilution of $A$ by an inactive component $B$ can be evidenced by (i) a shift of $\nu_{CO}$ to lower values; and (ii) a decrease of the relative intensity of bands corresponding to bridged species. The dilution of active metal surface (Pt) into smaller ensembles by addition of inactive species, such as Sn or Ge, selectively poisons demanding reactions (e.g. hydrogenolysis and coke formation) that requires relatively large clusters or ensembles of adjacent metal atoms. While structure insensitive reactions (double bond hydrogenation, aromatization or isomerization) can occur on single isolated atoms.

2.1.3. The occurrence of mixed-sites

It is difficult to give an unequivocal definition of the mixed-sites. When the promoter is not fully reduced under the reaction conditions, mixed-sites can be described as “metal ion-metal nanocluster ensemble sites” (MIMNES). In these catalysts the metal ions have to be located in the atomic closeness to the metal nanocluster. The MIMNES can contain either one or two metal components.

If a metal can exist on the surface in both forms, i.e., as metal ion and the metal nanocluster, the system will be considered as a mono-element MIMNES. However, systems containing two elements are more common. In most of these systems the metal ions are formed from elements of well known red-ox metals, such as Sn, Ge, Re, Fe, W, Mo, etc. while the metal nanoparticles are noble metals, such as Pt, Ru, etc. It has been demonstrated that mono- and multimetallic MIMNES have significantly higher catalytic activity and selectivity in a given reaction than supported metal nanoclusters.
2.1.4. Some comments

As shown before, the influence of promoter on the performance of the active metal can be interpreted in terms of geometric or electronic effects, and the occurrence of mixed-sites. However, it is well known that some classes of reactions are more sensitive or less sensitive to some of these factors. For instance, the electronic factors play a definite role in the selective hydrogenation of unsaturated hydrocarbons, whilst geometric considerations are prevailing in the hydrogenolysis of alkanes; besides, the occurrence of mixed-sites is a dominating factor in the selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes to unsaturated alcohols.

It has been demonstrated that in Pt-based naphtha reforming catalysts, the electronic modification of Pt particles may be induced by an interaction with an oxide layer of the promoter or by alloy formation. The electronic modification results in a change in the Pt-C bond strength of adsorbed hydrocarbons and hence alters the activity and selectivity of the reforming-type catalysts. The isomerization activity of reforming catalysts can be increased by addition of chlorine and/or strong Lewis acids (metal ions). In this way the bifunctional character of the catalyst is increased.

In the following section, an outlook will be given on the different methods used to synthesize the Sn-Pt catalysts and the influence of the preparation methods on the above mentioned factors.

2.2. Classification of methods used for the preparation of supported bimetallic catalysts with exclusive “active metal - modifier” interaction

There are two main steps in the preparation of bimetallic catalysts. The first one consists of the deposition of the precursors of the active component and modifier separately onto the support, whereas the second step is the transformation of these precursors into the required active phase. The activation of the deposited precursors will obviously have a clear impact on the chemical nature and the mutual interaction between the two components. It can be expected, that treatments in a mild reducing medium at low temperature will maintain the ionic states to some extent, whilst reduction at high temperature in pure $\text{H}_2$ will promote the formation of alloy and/or intermetallic compounds, when it is allowed by thermodynamics. In the following, this aspect will not consider and the attention will be focused on the influence of the deposition method.

The deposition of both active metal and promoter precursors have been well classified by Coq and Figueras within three general methods as shown in Scheme 1:

(i) The non-selective deposition (NSD) in which there is no interaction between the active metal and promoter precursors during the deposition process.

(ii) The selective deposition (SD) in which one precursor, usually modifier, is selectively deposited onto the metallic particles of the other component (usually active metals).

(iii) The deposition of bimetallic complexes or clusters with preformed bonds between two metals.

The choice of both the deposition method and the support will affect the vicinity of active metal and modifier, as well as their chemical state. When NSD is used, close vicinity between the two components of bimetallic catalyst is not always achieved in the final reduced catalyst, and a wide family of mono- and bimetallic particles of different composition exists at the support surface. This drawback is the main reason for the development of SD methods and the deposition of heterobinuclear complexes to achieve a close interaction between the two components.

In the last decade much attention has been paid to metal nano-clusters including supported nanoparticles. The morphology and electronic properties of nano size (1-2 nm) metal and oxide particles are fundamentally different from those of large particles in terms of short range ordering, valence band properties, etc. The two main classes of methods for preparing supported catalysts are: conventional and non-conventional modifications. The conventional modification methods include co-impregnation, consecutive impregnation, co-adsorption, sequential adsorption, ion exchange, precipitation, etc. The conventional preparation methods are not always the most efficient to create small particles.

It is, therefore, desirable to apply non-conventional methods like anchoring-type Controlled Surface Reactions (CSRs), electrochemical methods, "ion-assisted" preparation (sol-gel techniques, use of metal sol precursors, etc.), pulse laser deposition, ship-in-a-bottle synthesis in zeolites to confine them in nano size range.
Scheme 1. Classification of different methods for the preparation of bimetallic catalysts based on the mode of the deposition of the precursors of the active component and modifier.
In NSD of the precursors similar conventional deposition methods are used as in the preparation of monometallic catalysts (see Scheme 1). In this respect non-conventional modification method, such as co-anchoring or successive anchoring based on the interaction of both precursors with surface hydroxyl groups of the support also can be mentioned. As shown in Scheme 1, two types of approaches can be distinguished in the SD: “redox” reactions and the method Surface Organometallic Chemistry on Metals (SOMC/M) or CSRs. The knowledge of the structure of the active site for a given reaction helps to select the kind of deposition method to achieve the rational design of a selective bimetallic catalyst.

2.3. Conventional preparation techniques
2.3.1. Impregnation methods

According to the amount of solution used, two types of impregnation can be distinguished: one is called “incipient wetness” or “dry” impregnation because the volume of the solution containing the precursor does not exceed the pore volume of the support. The second type of impregnation, called “wet” or “soaking”, involves the use of an excess of solution with respect to the pore volume of the support. The weakness of the ion-support interaction in this deposition procedure usually leads to metal particles larger than 4-5 nm after subsequent thermal activation.

As an example, platinum is generally introduced into the Al₂O₃ as chloroplatinic acid, and tin may be introduced as tin chloride, bromide or nitrate. For instance, alumina supported Sn-Pt catalyst were prepared by (i) impregnation of commercial reforming Pt catalyst (0.3 wt% Pt and about 0.6 wt% Cl) with an acetone solution of SnCl₄ 5H₂O; (ii) co-impregnation with appropriate amount of SnCl₂ x 2H₂O and H₂PtCl₆ in dilute HCl; (iii) co-impregnation using an acetone solution containing H₂PtCl₆ and SnCl₂; (iv) co-impregnation with nonacidic precursors Pt(NH₃)₄(OH)₂ x nH₂O and tin (II) tartrate (SnC₄H₄O₆). The latter method resulted in a catalyst containing no chlorine.

Sn-Pt/SiO₂ catalysts were prepared, for example, by successive impregnation with (i) an acetone solution containing H₂PtCl₆ and SnCl₂; (ii) by co-impregnation with appropriate amounts of H₂PtCl₆ x 5H₂O and SnCl₂ x 5H₂O in acetone or with (iii) methylene chloride solution of cis-[PtCl₂(PPh₃)₂] followed by impregnation with an acetone solution of SnCl₂. The main drawback of these approaches is that during high temperature treatment, the formation of bimetallic surface species takes place only by chance. Microscopic homogeneity is not totally fulfilled when preparing bimetallic catalysts with the classical successive or co-impregnation methods. This has been shown for Sn-Pt/Al₂O₃ reforming catalysts.

2.3.2. Ion exchange

One way of creating interaction between the precursor compound and the surface is ionic exchange. Ion exchange consists of replacing an ion in an electrostatic interaction with the surface of a support by another species. This method is based on the amphoteric properties of surface hydroxyl groups, which depend on the pH as follows:

\[ \text{Surf-OH}^+ + \text{OH}^- = \text{Surf-OH} + \text{H}_2\text{O} = \text{SurfO}^- + \text{H}_3\text{O}^+ \quad (2.1) \]

where \( \text{pH}_i \) is characteristic of the oxides and is the isoelectric point or zero point of charge (ZPC) (pH at which the surface will not be changed).

The resulting ion-support interaction is generally strong and leads to nano-sized (1-2 nm) particles after activation. The homogeneous distribution of both active metal and modifier precursors through the grain of the support will be a key factor for their further interaction in the same aggregates. A similar strength of interaction between both transition metal precursors and support will promote this homogeneous distribution. Providing the ion exchange capacity of the surface has not been exceeded, the sequence of deposition of both precursors is of no importance; however, co-exchange is generally preferred.

2.3.3. Precipitation methods

**Co-precipitation**

In this procedure the solution containing both the metal salt and the salt of a compound that will be converted into the support are contacted under stirring with a base in order to precipitate it as...
hydroxides and/or carbonate. After washing, the formed solid can be transformed to oxides by heating. By co-precipitation a uniform distribution on a molecular scale of the different active species in the final catalyst can be attained, at least in principle. In spite of different problems related to this method, several industrially important catalysts are still prepared by co-precipitation.

Deposition-precipitation

This procedure is in principle similar to the co-precipitation method, i.e. a metal hydroxide or carbonate is co-precipitated onto a powdered support through the reaction between the base and the precursor of the metal.

The acidity of the catalyst has been found to be an important parameter in the design of catalysts for the hydrotreating of petroleum and heavy liquids. It is well known that increased acidity leads to increased coke formation resulting in catalyst deactivation and a shorter catalyst life.\textsuperscript{51} Acid sites are also thought to be responsible for cracking, isomerization and dealkylation reactions.\textsuperscript{52} Acidity especially of OH groups present on the support surface can be markedly enhanced by the proximity of other ions. In the industrial preparation of Sn-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts, the tin precursor, often SnCl\textsubscript{4}, is added during the synthesis of the alumina support, i.e. the tin precursor compound is mixed with aluminum nitrate in basic medium.

Srinivasan \textit{et al.}\textsuperscript{53} have prepared alumina supported Sn-Pt catalysts by two methods: (i) co-precipitation of SnCl\textsubscript{4} and aluminum nitrate in basic medium and, then, impregnation with H\textsubscript{2}PtCl\textsubscript{6} and (ii) co-impregnation of an alumina support with hexachloroplatinic acid and SnCl\textsubscript{4} solution. They observed the formation of Pt-Sn alloys by X-ray diffraction, if the co-impregnation method was used. Contrary to that, using co-precipitation method only Pt\textsuperscript{0} was found, the formation of alloys did not occur.

2.4. Non-conventional preparation techniques

In this Chapter some alternative methods which were reported for the preparation of Sn-Pt bimetallic catalysts will be described briefly.

2.4.1. Sol-gel synthesis

It is necessary to stress out that the surface composition of bimetallic catalysts is strongly affected by the preparation method. If the formation of Sn-Pt alloys is to be avoided, tin must be anchored first onto the support by (i) ion exchange, (ii) co-precipitation of Sn and Al\textsubscript{2}O\textsubscript{3} or (iii) by sol-gel synthesis of the Sn/Al\textsubscript{2}O\textsubscript{3} system.

The sol-gel method, i.e., the addition of metal precursor to an alkoxide solution of the support precursor, seems to be a good alternative to the industrial procedure. The sol-gel process involves first the formation of a sol followed by that of a gel.\textsuperscript{54,55} Sol-gel preparation offers excellent control of mixing because of the ability of the sol-gel to alter the relative reactivity of the precursor. The possibility to introduce several components into the solution during the sol-gel step makes this approach especially attractive for the preparation of multicomponent oxides and bimetallic catalysts. For example, Sn-Pt catalysts with high platinum dispersion (up to 90\%) were prepared by the sol-gel method by adding tetrabutyltin to a homogeneous solution containing aluminium tri-sec-butoxide (TBA), followed by impregnation of dried and calcined solids with an aqueous solution of H\textsubscript{2}PtCl\textsubscript{6}.\textsuperscript{56-58} The study of bimetallic particles by XRD and EDX analysis shows only Pt, thus tin must be incorporated into the alumina network. It was proposed\textsuperscript{57} that the effect of tin in catalysts prepared by sol-gel is the modification of the support properties (such as acidity or texture) rather than the Pt activity. For the preparation of silica supported catalysts by sol-gel method the ethyleneglycol solution of Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}, as a support precursor, can be used.

2.4.2. Solvated Metal Atom Dispersion (SMAD) method

Deposition of metal atoms into cold frozen solvents, followed by warming, leads to cluster formation through solvated metal atom intermediates. Bimetallic Sn-Pt catalysts can be prepared in two general ways: (i) the “half-SMAD” process refers to treating parent Pt/Al\textsubscript{2}O\textsubscript{3} catalyst with solvated Sn atoms, thereby ensuring the deposition of Sn\textsuperscript{0} on the Pt clusters; and (ii) the “full-SMAD” process refers to the simultaneous evaporation/trapping/solvation of Pt and Sn atoms simultaneously followed by warming, bimetallic cluster formation and trapping on high surface area alumina.\textsuperscript{59} This method allows the production of ultrafine, zero-valent bimetallic particles. Authors proposed the formation of atomically mixed Sn-Pt metallic clusters, which mostly consist of tin monometallic phase.
(Sn⁰) surrounded by Sn-Pt alloy phase (only 5-8 % of the Sn⁰ is in the form of alloy). The presence of ionic form of tin (Sn²⁺ and Sn⁴⁺) indicates that initial nucleation of tin and Sn-Pt particles may occur when a solvated Sn atom (Sn(Solv)ₖ) is attached to a surface hydroxyl groups. These sites (Al-O,Sn) then serve as an anchoring site for further Sn and Pt atoms. Consequently, this mode of catalyst preparation allows the formation of low-valent surface Sn ions on the support, followed by an interaction of these Sn-containing anchoring sites with Sn-Pt metallic clusters.

2.4.3. The use of heterobinuclear complexes or clusters

Creation of surface sites from heterobinuclear organometallic compounds or inorganic complexes appears to be an interesting trend in the field of catalyst preparation. In this approach individual bimetallic complexes or clusters can merely adsorb or react with dehydroxylated silica or alumina, which is followed by their thermal decomposition in reductive or inert atmospheres.

To obtain tin-platinum supported catalysts, the composition of Sn-Pt bimetallic particles can be controlled effectively by selection of the starting inorganic complexes (e.g. [PtCl₅SnCl₃]²⁻, [PtCl₃(SnCl₂)]²⁻; [PtCl₄(PPh₃)₂], [Pt(SnCl₄)]³⁻, H₂[Pt₂Sn₃Cl₁₅] and [Pt₂Sn₃Cl₆(NBD)]₄⁻ (NDB: 2,5-norbornadiene) or bimetallic ionic compound with Pt/Sn ratio 1 such as [Pt(NH₃)₄][SnCl₆]⁷³,⁷⁴ or [Pt(NH₃)₄][SnCl₄]⁷⁵.

During the preparation of highly dispersed bimetallic catalysts from the above complexes it is necessary to ensure their chemical reaction with the support surface. The concentration of surface OH groups measured by the IR (adsorption at 3000-3750 cm⁻¹) decreases, as a result of the irreversible adsorption of the bimetallic complexes on the support. For example, the attachment of H₂[Pt₂Sn₃Cl₁₅] clusters to the alumina support can be described by the following equation:

\[
\text{Al-OH} + \text{H}_2[\text{Pt}_2\text{Sn}_3\text{Cl}_{15}] \rightarrow \text{Al-[Pt}_5\text{Sn}_3\text{Cl}_{15}]\text{H}_2 + \text{H}_2\text{O}
\]  

(2.2)

The decomposition of anchored complexes at high temperature in a hydrogen atmosphere resulted in the formation of Sn-Pt alloy and monometallic surface species in most cases. It had been demonstrated that the formation of Sn-Pt alloy phases was more pronounced in catalyst prepared from the [Pt(NH₃)₄][SnCl₆] compared to the samples made by conventional co-impregnation of H₂PtCl₆ and SnCl₂. Some studies reported that during the impregnation of support with Sn-Pt complexes only small part of the complex was bound to the surface of the support and the main part of the complex was precipitated just under the drying step.²⁷,²⁸

A series of supported reforming catalysts were synthesized by wet impregnation of alumina with a solution of the complex [(CH₃)₃N]₂[Pt(SnCl₄)] in acetone. The thermal transformations of Sn-Pt/Al₂O₃ catalysts are also studied. It has been shown that the choice of the atmosphere of thermal treatment (inert or oxidizing) can helps to preserve the intimate Sn-Pt interaction (formation of the Sn-Pt alloy), or can results in demixtion (formation of two distinct phases, Pt⁰ and SnO₂).

The principal method for the regulation of catalytic properties of bimetallic catalysts is to change the composition of the active centers. In this respect the methods described above have the following drawbacks:

(i) the use of this method is mainly limited by the availability of high nuclearity clusters and by the narrow choice of metallic couples;
(ii) uncertain stability of the complexes during anchoring procedure and high temperature decomposition in hydrogen;
(iii) “non-removable impurities” (Cl, SnCl₄, etc.); these “impurities”, which cannot be removed without destruction of the complex, are also able to react with the support and to influence the properties of the catalysts.

2.4.4. Anchoring type surface reactions
2.4.4.1. General aspects of anchoring

The above disadvantage can be avoided by using different anchoring techniques. Many heterogeneous catalysts have already been reported to be prepared by anchoring or grafting. These are processes where stable, covalent bonds are formed between homogeneous transition metal complexes (TMC) and an inert polymer or inorganic support. According to the recommendations of the IUPAC, “deposition involving the formation of a strong (e.g. a covalent) bond between the support and the active element is usually described as grafting or anchoring. This is achieved through a chemical
reaction between functional groups (e.g. hydroxyl groups) on the surface of the support and an appropriately selected inorganic or organometallic compound of the active element”. Campbell attempted to distinguish anchoring from grafting as follows: “An anchored catalyst is created by the binding of a species, without substantial change in its structure, to a solid surface. A grafted catalyst is produced when an initial structure bound to the surface is altered considerably by subsequent treatments”.

In addition, because of the strong chemical interaction established during anchoring between transition metal ions and the support, it is possible to prevent migration, sintering and formation of agglomerates during subsequent thermal treatments, in contrast to species deposited by impregnation which are mainly physically adsorbed. The anchoring results in the formation of either nanosized metal particles or atomically dispersed surface entities. Theoretically, the amount of metal chemically bonded to the support cannot exceed the monolayer; however, multilayers can be obtained by several cycles of anchoring-hydrolysis or anchoring-deposition. The application of the anchoring-type surface reactions is more suitable for selective introduction of the modifier onto either the active phase or the support.

Equations (2.3) and (2.4) describe in a generalized manner the reactions involved in surface anchoring processes:

$$\text{AS} + \text{RPC} \rightarrow \text{PSC}$$  (2.3)

$$\text{PSC} + \text{RE} \rightarrow \text{SSS}$$  (2.4)

In the reaction (2.3), Anchoring Site (AS) reacts with Reactive Precursor Compounds (RPC) with the formation of an anchored Primary Surface Complex (PSC). The AS can exist on the active phase or on the support. The PSC is decomposed under properly chosen reaction conditions (Reactive Environment (RE)) to obtain Stabilized Surface Species (SSS) (see reaction (2.4)).

When the support is modified with an ionic surface species, surface hydroxyl groups are the AS, and CSRs, with involvement of the protons of the OH groups, are used. The co-anchoring, or successive anchoring of organic complexes of an active metal (Pt) and modifier (Sn) can be used for the preparation of bimetallic catalysts (NSD) (see details in Chapter 2.4.4.3.).

Reaction between the organometallic compounds and the surface of the supported metals (Surface organometallic chemistry on metals (SOMC/M)) leads to the formation of the bimetallic surface species (SD) (see details in Chapter 2.4.6.).

Some of the surface modification anchoring process requires only creation of a PSC without its further transformation. These processes are known as "one-step" anchoring methods. Examples of one-step anchoring methods are the introduction of -Sn(C₅H₇)₂ surface species on supported rhodium or modification of Pt/Al₂O₃ with trialkyltin species (-Sn(C₂H₅)₃). Application of the two-step anchoring process (equations (2.3) and (2.4)) is more general. The influence of the conditions of reaction (2.4) and RE (H₂, O₂ or H₂S) on the type of SSS formed have been well demonstrated by Yermakov et al.

The chemical nature of a given system controls the formation of the required surface species, which can be used as a precursor of active center. For example, hydrogen treatment of anchored benzyl or allyl complexes of M= Ti or Zr resulted in the formation of surface hydrides (Surf-M-H) which are direct precursors of active centers for ethylene polymerization. Upon using anchoring technique it is possible to predict the nature or the character of the surface species formed, to control the composition of active centers and therefore their reactivity.

2.4.4.2. Anchoring reactions based on the reactivity of surface hydroxyl groups

Surface reactions based on the reactivity of OH groups are widely used to modify metal oxides and hydroxylated supports such as alumina, silica or zeolites. One of the proposed strategies employed to obtain these catalysts was developed by Yermakov. The reaction typically leads to the formation of site-isolated metal complexes with covalent bonds between the metal ion and oxygen atoms of the support.

Different types of hydroxyl groups with different reactivity can be distinguished. It is possible to anchor the fragment of the precursor compounds via one, two or even three surface oxygen, depending on the degree of dehydroxylation of the surface. These studies were mainly devoted to measuring concentration of surface OH groups (or surface “active” hydrogen). The formation of the surface metal
complex is often accompanied by the release of ligands originated from the precursor compounds. Depending on the reactivity of the metal complex, the reaction with surface OH groups can result in a monolayer coverage of the metal complex.

When surface organometallic compounds of group VIII elements (Ni, Pd, Pt) and groups IV and VI elements (Sn, Ge, Pb, Cr, Mo, W) are decomposed in H₂ atmosphere, zero-valent highly dispersed supported surface clusters and low-valent coordinatively unsaturated cations stabilized on the support (Surf-Oₓ-M) are obtained, respectively.

The interaction of tetrabutyltin with the surface OH groups of support was extensively studied by C. Nedez et al. At 25°C some hydrogen-type bondings were proposed to occur between H atoms of the alkyl ligands and surface O atoms. It has been demonstrated that chemical reaction takes place only above 100°C, leading to grafting of a SnBu₃ moiety via a =SiO-SnBu₃ covalent bond. The loss of all butyl ligands and formation of low-valent (=Si-O)₄-Sn cations was observed at T > 250°C.

### 2.4.4.3. Preparation via ions anchored onto the support

For the preparation of bimetallic catalysts co-anchoring, or successive anchoring of organic complexes of an active metal (Pt) and modifier (Sn) can be used. Highly dispersed bimetales can be prepared by anchoring of a complex of a noble metal onto the low-valent cations of an oxophilic metal grafted to a support. Both complexes can interact separately with the OH groups of support surface.

It was shown, that the activation energy of the surface migration of supported metal atoms is small as the character of interaction energy between zero-valent metal atoms and oxide support surface is of Van-der-Waals by origin and does not exceed a few kcal mol⁻¹. The low-valent ions of modifier bound to the support may serve as an energetic trap for migration of atoms or some metal particles. Direct metal-to-metal bonds between the low-valent cations and the precursor of the second metal may be also formed, similar to those observed in bimetallic complexes. It is well known, that the strength of the heteroatomic metal-metal bonds may comprise some tens of kcal mol⁻¹. Very dispersed bimetallic particles can be obtained in the 1-2 nm size range, even after reduction at 550°C.

Anchoring tin ions onto the oxide surface was performed, for example, by the interaction of the vapours of Sn(OOCCH₃)₂ or an alcoholic solution of SnCl₄ with the surface OH groups of SiO₂ or Al₂O₃. Sn-Pt catalysts have been prepared by anchoring platinum complexes (e.g. PtCl₄, Pt(C₅H₇)₂) onto tin ions bonded to the support. An increase of the rate of adsorption of platinum complexes on different tin-containing supports was observed. When a Sn-Pt catalyst prepared in this way was treated in H₂ at 200-600°C, the restoration of the initial concentration of OH groups (before supporting tin) was not observed. This fact probably indicates that the chemical bonds between tin ions and the support surface are maintained during treatment of the catalyst in H₂ atmosphere.

In this preparation it is crucial that the second metal complex introduced onto the surface should react selectively with the low-valent cations anchored onto the support rather than with the support OH groups. It is difficult to prepare the firstly anchored surface species so selectively that all of the metal atoms are bonded firmly to the support and thus all of the reactive hydroxyl groups of the support are removed. Remaining free OH groups are potential targets for the second metal complex. Consequently, supported bimetallics obtained by this method are not generally expected to be uniform in structure. It is noteworthy, that in this approach

(i) one of the metals in these bimetallic catalysts, that is considered as an anchoring site, is in ionic form;
(ii) the modified monometallic support was not always very well defined;
(iii) anchoring reaction used could not be easily monitored.

### 2.4.5. Redox methods

The preparation of bimetallic catalysts by redox methods have been recently reviewed by Barbier. Three different approaches exist for selective deposition of modifier on monometallic catalyst:

(i) the direct redox reactions (DRR) between metallic species of both component - the reductant of the modifier is the parent metal;
(ii) redox reaction of adsorbed reductant (RRA) - the reductant is preadsorbed on the metallic surface of the parent catalyst (hydrogen is most commonly used);
(iii) underpotential deposition (UPD) - in some cases deposition of adatoms or submonolayers of modifier can occur at a higher potential than the thermodynamic potential required for bulk deposition.

Practically the preparation of bimetallic catalysts using DRR can be extensively used for depositing a noble metal with a high standard electrochemical potential onto a non-noble metal with a lower standard electrochemical potential, e.g. the modification of Cu catalysts by the addition of Ru, Pt, Au or Pd:

\[ n\text{Cu}_n + 2M^{n+} \rightarrow n\text{Cu}^{2+} + 2M_n \]  \hspace{1cm} (2.5)

According to the standard electrochemical potentials (Cu/Cu\textsuperscript{2+} = 0.34, Pt/Pt\textsuperscript{4+} = 0.74 and Au/Au\textsuperscript{3+} = 1.00) the redox reaction carried out in the presence of Pt and Au salts will occur to a large extent. The applicability of the technique can be extended significantly by using different ligands which alter the standard redox potentials and consequently the equilibrium potentials via chelating metallic ions.

Bimetallic catalysts can also be prepared by using a reductant that preadsorbs selectively on the metallic surface of the parent catalyst in static or dynamic conditions (RRA). The ions of the modifier are reduced by this reagent and the two metals interact. This technique was extensively studied by Szabo, Nagy, Margitfalvi and co-workers. Using hydrogen, preadsorbed on noble metals as reductant the above method was described as the “adsorption of metallic ions via ionization of adsorbed hydrogen”\textsuperscript{97-101}. In the techniques mentioned above,\textsuperscript{7} electrochemical adsorption of modifier on parent metal occurs at a Nernst potential more negative than that for bulk deposition of the first metal. For hydrogen-adsorbing metals such as Pt, Pd, Rh, Ru, etc., the adsorbed hydrogen is the source of electrons, as shown in equation (2.6):

\[ H_{\text{ads}} \rightarrow H^+ + e^- \] \hspace{1cm} (2.6)

By assuming the complete discharge of the metal ion, the spontaneous metal adsorption via ionization of preadsorbed hydrogen can be written as in equation (2.7):

\[ M^{n+} + zH_{\text{ads}} \rightarrow M_{\text{ads}} + zH^+ \] \hspace{1cm} (2.7)

Consequently, the preparation of bimetallic catalysts by redox reaction requires a parent metal that chemisorbs hydrogen and a modifier that is reducible by hydrogen (Cu, Re, Ir, Rh, Pd, Pt, Au, etc.). All combinations of these metals have been prepared and characterized. At high modifier loading the active metal surface is totally covered and the deposition reaction is terminated. Under such conditions the modifier appears as a three-dimensional deposit. Furthermore preparation of Pt-Au bimetallic catalysts using combination of RRA and DRR approaches has been demonstrated.\textsuperscript{102,103} The technique of catalytic reduction can be extended to reducing agents other than hydrogen (for example, hydrazine, hydroxylamine, ascorbic acid, glucose).

By contrast, the UPD mainly forms submonolayer adatoms structures. The H\textsubscript{2}/H\textsuperscript{+} couple was used to prepare supported catalysts with Pt, Pd, Ru and Rh modified with deposits of Sn, Pb, Fe, Ge and Bi.\textsuperscript{96,98,99,104-107} According to the principle of “underpotential deposition”, a metal can be deposited on another noble metal, at potential higher than the Nernst potential, when there is a difference between the work functions or the electronegativities of these two metals. The electrochemical modification of platinum by tin deposition at a controlled potential has been studied.\textsuperscript{108} In this case the values of electronegativity are: X\textsubscript{Pt} = 2.28 and X\textsubscript{Sn} = 1.72, so tin can be deposited underpotentially on Pt.

All tree variants of the preparation of bimetallic catalysts by redox methods are complementary to one another and by using different experimental conditions, ligands, reductants, and mode of preparation. This approach can apparently be used to prepare any type of bimetallic couple.

2.4.6. Application of Surface Organometallic Chemistry on metal (SOMC/M) approach

The use of different organometallic compounds in the preparation of different mono- and bimetallic catalysts has great scientific importance and practical potential. In this group of processes, SOMC/M or CSRs\textsuperscript{9,14,55,109-122} and chemical-vapour-deposition\textsuperscript{123,124} appear to be very promising.

2.4.6.1. Chemical-vapour-deposition technique (CVD)

A reactive chemical-vapour-deposition technique (CVD) was adapted to prepare Sn-modified silica supported Sn-M/SiO\textsubscript{2} catalysts (M= Rh, Pt).\textsuperscript{125-130} It was shown that under the reaction conditions used most of Sn(\textsubscript{CH\textsubscript{3}})\textsubscript{4} preferably reacted with metal particles than with OH groups of...
SiO$_2$. It was demonstrated by Rh K-edge and Sn K-edge EXAFS, FTIR, TEM and CO adsorption that the modification of parent Rh/SiO$_2$ catalysts by CVD method was highly selective and the exclusive formation of the Rh-Sn alloy phases was observed. Similar results were obtained on CVD-Sn-Pt/SiO$_2$ catalysts. It was suggested by EXAFS measurements at both Sn K-edge and Pt L$_{III}$-edge that Sn atoms located at the first layer of the bimetallic particles until Sn/Pt$=0.26$ ratio. The composition of the bimetallic surface layer with Sn coverage at saturation was Sn/Pt$=3/2$. Further Sn addition did not change the surface composition, where excess of Sn atoms were incorporated into the bulk.

2.4.6.2. Use of Controlled Surface Reactions (CSRs)

Organometallic compounds react with metallic surfaces much faster than with oxides surfaces. This observation resulted in the development of SOMC/M. The strategy of SOMC/M is to utilize controlled surface reactions of organometallic compounds with the metallic surface or metallic oxides, in which the transformation of monometallic materials into homogeneous bimetallic ones is explained in terms of molecular processes. Only non-conventional anchoring-type surface reactions can be used to modify selectively either the active phase (metal) or the support.

In 1984, Margitfalvi$^{132}$ Travers$^{133}$ and Nuzzo$^{134}$ simultaneously and independently described new routes for the preparation of bimetallic catalysts by the reaction of a group IVa organometallic compound with a supported metallic surface of Pt, Rh or Ni, respectively.

The monometallic catalyst is first prepared, giving a well-defined metallic surface, which is then allowed to react with an organometallic molecule, the precursor of the second metal, resulting in a bimetallic catalyst. During the anchoring step the organometallic precursors decompose only partly on the metal particles and Surface Organometallic Species (SOMS) stabilized on the surface of the metal are formed. In SOMS organometallic precursors can maintain a fraction of their alkyl groups.

Anchoring-type surface reaction can yield a metallic surface covered with surface organometallic fragments or adatoms, or a supported alloy depending on the condition of anchoring and the modes and ways used to decompose SOMS in a second step of preparation.$^{86,135-137}$ For catalyst modification, the major advantage of anchoring is that the “chemistry” of the given system (parent catalyst and modifier) controls the formation of desired surface species. This advantage is not often available using conventional modification methods.

Characteristic feature of organometallic approaches used (CSRs$^{32,109,132}$ and Surface Organometallic Chemistry (SOMC)$^{79,138-140}$) so far is that both approaches result in supported bimetallic entities with modifier- active metal interaction almost exclusively. Both methods were successfully applied with the aim to obtain surface species with exclusive Sn-Pt,$^{109,141-143}$ Sn-Rh,$^{14,113,138,144,145}$ Sn-Ni,$^{146,147}$ Sn-Ru,$^{115,116}$ and Sn-Pd interactions.$^{79,114,145}$

For a long time SOMC/M technique was considered as method for the preparation supported bimetallic catalysts with monolayer coverage of modifier over parent metal. It has been emphasized in Ref.$^{138}$: “SOMC differs from organometallic CVD in that the reactions of SOMC result in less than monolayer coverage of the surface, whereas CVD is used to prepare multilayered materials” or “Due to its “monolayer” character, SOMC has been used to prepared relatively well-defined supported metallic catalysts”.

The method of controlled addition of small amounts of the second metal used by Paál and Pirault-Roy et al.$^{148}$ shows some specificity by comparison to the other SOMC methods have already been proposed in the literature. In heterogeneous catalysis on supported metals, some of the reactions occur on specific sites as edges and corners whereas others take place on low-Miller-index facets.$^{149}$ It appears very informative to poison selectively some of these special surface sites. CSRs are mainly used to perform such a selective deposition. Authors drew their inspiration from studies concerning catalyst preparation by redox techniques used originally by Barbier et al.$^{150,151}$ The method was based on SOMC reactions under inert atmosphere between a noble metal supported catalyst in a reduced form and an organometallic precursor. However the grafting took place under operating conditions close to those used in redox preparation. A series of Ge-M/Al$_2$O$_3$ (M= Pt$^{152-154}$ and Rh$^{148,155,156}$) catalysts was prepared by anchoring Ge($n$-C$_4$H$_9$)$_4$ on metal surface, containing preadsorbed hydrogen, implying thus that the amount of Ge grafted would be limited to a monolayer.

It was shown that the amount of the Ge compound introduced had a pronounced effect on the final landing position of Ge. Excess Ge($n$-C$_4$H$_9$)$_4$ resulted in a statistical deposition on the surface of Rh or a
slight diffusion in Rh lattice, while low-Miller-index microfacets were preferentially occupied when the amount of Ge(n-C₃H₇)₄ was markedly lower than that for monolayer coverage. Using the same procedure Sn-Rh/Al₂O₃ catalysts with different Sn/Rh ratios were also prepared. It has been demonstrated, that these tailored catalysts exhibit best performance in various organic reactions, such as transformation of hexane, 2,2,3-trimethylbutane, methyl-cyclopentane or ethylcyclopentane.

In spite of the huge amount of work done in this field, the main question is still the same, i.e. how to control surface reactions involved in the formation of bimetallic surface species. Dumesic et al. have also used tin organometallic precursor compound (Sn(C₅H₄)₅OAc) for the preparation of Sn-Pt/SiO₂ catalysts. Although a tin organometallic precursor compound was used, the preparation method was an evaporative impregnation technique and not a surface reaction between the Sn and Pt. Despite the novelty and importance of this work, these studies were not designed to achieve a specific Sn/Pt ratio in supported bimetallic nanoclusters. No attempt was made to control either the Sn-Pt interaction or the Sn/Pt alloy ratio. Mössbauer spectroscopy results show that in these catalysts the Sn-Pt alloy formation was exclusive only up to Sn/Pt= 1:1 ratio. At higher Sn/Pt ratios (Sn/Pt=3:1) the majority of tin is associated with the support.

In other studies by this group, the tin organometallic presursor compound has been used in a conventional two-step impregnation procedure (Sn was introduced first onto K-L-zeolite, followed by a calcination step). In these Pt/Sn/K-L catalysts, ionic forms of Sn are dominant (more than 80 %) and also no attempt was made to control the Sn/Pt ratio.

In the next Chapter approach used in our department from 1984 will be described, a two-step anchoring process, in which the exclusive formation of supported bimetallic surface entities is controlled by the chemical nature of a given supported monometallic surface species. This approach allowed us to design various bimetallic catalysts for different types of reactions performed both in reductive and oxidative atmosphere.

As it has been described in the first publication of Margitfalvi et al., the hydrogen adsorbed on noble and transition metals is used as a driving force to control the selectivity of surface reactions involved in this anchoring process. Studies on the reactivity of tin organometallic compounds towards hydrogen adsorbed on noble and different transition metals have revealed new aspects for the preparation of supported bimetallic catalysts. This aspect will be discussed in details in next Chapter. The focus will be laid on the preparation of supported Pt catalysts modified by tin.

### 2.4.6.3. Formation of monolayer coverage of surface organometallic species (SOMS)

The surface chemistry involved in tin anchoring process for the modification of supported platinum catalysts was first described by Margitfalvi et al. in 1984. 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 surface chemistry involved in the two-step anchoring of tetraethyltin can be written as follows:

\[
P t H_{ads} + Sn(C_2H_5)_4 \rightarrow Pt-Sn(C_2H_5)_{(4-x)} + x C_2H_6
\]  \hspace{1cm} (2.8)

PSC

\[
Pt-Sn(C_2H_5)_{(4-x)} + (4-x)/2H_2 \rightarrow Pt-Sn + (4-x) C_2H_6
\]  \hspace{1cm} (2.9)

Surface reaction (2.8) between tetraethyltin and hydrogen adsorbed on supported platinum (PtH_{ads}) is often called as “tin anchoring step I”. The Primary Surface Complex (PSC), described as Pt-Sn(C₅H₄)_{(4-x)}, can be decomposed in a hydrogen atmosphere to obtain supported bimetallic species (step II) (see reaction (2.9)).

Characteristic features of this reaction were first investigated upon using platinum black as well as alumina supported Pt catalysts. Reactivity of alkyl homologues in accordance with the space needed for alkyl groups was found in the following order: CH₃ > C₂H₅ > C₃H₇. Method of CSRs furthermore has been extended to tin dialkyl dichloride as tin precursor compound.

This approach led to the monolayer coverage of platinum clusters by tin organometallic species. Catalyst modification based on this surface chemistry is known as “anchoring metals-to-metals”. CSRs between Sn(C₅H₄)₂ and hydrogen adsorbed on supported platinum provided direct Sn-Pt interaction that was maintained upon decomposition of the formed PSC in a hydrogen atmosphere.
(see reactions (2.8) and (2.9)). The net result is the formation of Sn-Pt alloy-type surface species has been evidenced by Mössbauer spectroscopy. 

Surface -Sn(C₂H₅)(4-x) complexes have also been fully decomposed in low temperature hydrogen plasma. In this case unique Sn-Pt/Al₂O₃ system was prepared in which metallic tin was located at the top of platinum particles as adatoms. It has been demonstrated that the decomposition mode has strong influence on the H/Pt values. The decomposition of surface complexes in plasma and in Temperature Programmed Reduction using H₂ resulted in 0.004 and 0.40 H/Pt ratios, respectively. The H/Pt values increased significantly when plasma decomposed samples were further treated in a H₂ atmosphere at 300°C or 500°C. The increase in H/Pt values was explained by the migration of tin from the surface of platinum particles in to deep layers.

The material balance of tin anchoring can be calculated based on the determination of the amount of hydrocarbons formed in steps I and II. The material balance allows us to calculate the value of x (where x shows the amount of alkyl groups lost in tin anchoring step I). In this way, the stoichiometry of tin anchoring step I can be determined.

It has been demonstrated that upon fine tuning of reaction conditions the number of alkyl groups in the -SnR₄(4-x) surface complexes can be controlled. Upon using 0.5 wt% Pt/Al₂O₃ parent catalysts and initial concentration of SnR₄ around [Sn]₀ = 10⁻⁴–10⁻³ M the value of x was found about 1. Introduction of gas-phase hydrogen under the tin anchoring step I resulted in the increase of the value of x. With increasing Pt content and decreasing dispersion the value of x increased up to 1.2-1.3. Over supported Ni catalysts the value of x was found to be between 1 and 3 while over skeletal Raney Ni catalyst the anchored -SnR₄(4-x) surface complexes had lost all its alkyl groups during tin anchoring step I.

In the absence of preadsorbed hydrogen, tetraalkyl tin compounds can catalytically decompose and form equimolar amounts of alkane and alkene. Equation (2.10) is the predominant side reaction for Sn(C₂H₅)₄. If reaction conditions are suitable, this reaction can occur even in the presence of adsorbed hydrogen. Thus experimental conditions of anchoring must be chosen to avoid the formation of alkene by-products. Formation of unsaturated hydrocarbon by-products during anchoring indicates the loss of control over the formation of bimetallic surface species.

\[ \text{Sn(C}_2\text{H}_5)_4 \rightarrow \text{Sn} + 2 \text{C}_2\text{H}_6 + 2 \text{C}_2\text{H}_4 \]  

(2.10)

The rate of tin anchoring step I (see surface reaction (2.8)) strongly depends on: (i) the type, content and dispersion of parent metal (M), (ii) the type of support, (iii) the amount and reactivity of adsorbed hydrogen, (iv) the initial concentration of the tetraalkyl tin in the reaction solution ([Sn]₀), (v) the Sn₂/M ratio in the reaction mixture, (vi) the solvent used, (vii) the reaction temperature (T_r), (viii) the nature of alkyl groups in tin precursor compound.

The earlier results showed that the clear separation of the anchoring and decomposition steps cannot always be done. The main difference between our approach and methods developed by other research groups is that an attempt was done to separate the anchoring and decomposition steps I and II (see surface reactions (2.8) and (2.9)).

It has to be emphasized that the exclusive formation of tin-metal interaction in tin anchoring step I requires special control to avoid (i) reactions with the involvement of surface OH groups and (ii) adsorption of tetraalkyl tin onto the support.

In order to minimize the tin-support and to maximize the tin-metal interaction in tin anchoring step I the following measures were taken: (i) use of relatively low concentration of tetraalkyl tin; (ii) avoiding high reaction temperature; (iii) use of short reaction time; and (iv) strong separation of reaction (2.8) from reaction (2.9).

The above measures provided a definite guaranty both for the exclusive introduction of tin onto platinum (or other metals) and the suppression of tin-support interaction. However, the disadvantage of the above strict approach was the strong limitation of the amount of tin introduced. The amount of tin introduced onto the metal exclusively is controlled by the chemical nature of PSC formed on the top of the metal particles. It is due to (i) limited number of surface platinum atoms available for anchoring, and (ii) steric hindrance caused by the volume of the alkyl groups in PSC formed (see Scheme 2).
As emerges from earlier results of our department, the amount of tin anchored is strongly controlled by the size of the alkyl groups of tetra alkyl tin used.\textsuperscript{162} Beyond a definite coverage level, the alkyl groups of PSC formed created a specific “shiel ding” as shown in Scheme 3. The longer the alkyls chain the higher the shielding effect. It has been demonstrated that depending on the particle size of platinum and upon using Sn(CH\textsubscript{3})\textsubscript{4}, Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}, and Sn(C\textsubscript{4}H\textsubscript{9})\textsubscript{4} at monolayer coverage the following Sn/Pt, ratios were obtained: 0.6, 0.4, and 0.3, respectively.\textsuperscript{167}

Scheme 3. Anchoring of -Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} moieties onto supported platinum catalyst.

2.5. Literature study on the characterization of supported bimetallic catalysts

It is important to know the chemical state of the metal atoms in bimetallic catalysts is described by their oxidation state, ligand environments, structure and stoichiometry. Many physical and chemical methods are used in catalysis research to characterize solid catalysts and to search for correlations between structure and performance of catalysts.

2.5.1. Chemisorption of \(\text{H}_2\), \(\text{O}_2\) and \(\text{CO}\)

Chemisorption of \(\text{H}_2\), \(\text{O}_2\) and \(\text{CO}\) can be used to quantify the number of metal atoms accessible to the probe molecule.\textsuperscript{127,142,168,169} The addition of tin decreases the accessibility of platinum.\textsuperscript{166} On unsupported Sn-Pt system (Pt, Pt\textsubscript{3}Sn, PtSn, and PtSn\textsubscript{2}) Verbeek and Sachtler\textsuperscript{170} found a drastic decrease in \(\text{D}_2\) and \(\text{CO}\) adsorption when the Sn/Pt ratio increased. They concluded that there was both a significant enrichment of the surface alloy in tin and strong electronic effect, resulting in drastic lowering of the heat of adsorption of \(\text{H}_2\) on the Pt atom of the alloy surface.

It is necessary to mention that the amount of chemisorbed \(\text{H}_2\) is never zero. The presence of tin on platinum caused a decrease in \(\text{H}_2\) or \(\text{CO}\) chemisorption,\textsuperscript{9,157,168,171} but an increase of the oxygen consumption.\textsuperscript{168} The decrease of \(\text{H}_2\) and \(\text{CO}\) chemisorption is explained by the decrease of the number of accessible Pt atoms due to the increased number of surface Sn atoms. The increase in the \(\text{O}_2\) chemisorption was explained by the following reaction which represents phase segregation:\textsuperscript{168}

\[
\text{Pt}_\text{Sn}_z/\text{SiO}_2 + \frac{1}{2} (y+zx)\text{O}_2 \rightarrow (\text{PtO}_\text{y})(\text{SnO}_\text{z})_x/\text{SiO}_2
\]  

(2.11)

The values of \(z\) were about 1 and 2, respectively at 25\(^\circ\)C and 300\(^\circ\)C. Apparently, at 25\(^\circ\)C and 300\(^\circ\)C, the tin atoms react with oxygen to give SnO and SnO\(_2\), respectively. It was proposed\textsuperscript{172} that the oxygen reacts on both surface Pt atoms and Sn atoms located on the bimetallic particles, but does not react with the (=SiO\(_2\))-Sn\(_{2+}\) surface species.

Upon investigation of the Ru-Sn system, Coq \textit{et al.}\textsuperscript{115} observed that the addition of tin generates some differences in the amount of irreversibly adsorbed hydrogen (H\(_\text{irr}\)) as a function of Ru particle size. The ratio H\(_\text{irr}\)/Ru decreases linearly with the amount of tin on large particle of Ru, in the range expected, if one tin atom covers one surface Ru atom. However, on small Ru particles, the “toxicity”
of tin for H₂ adsorption is initially much higher. This change might suggest a particular localization of the tin atoms introduced first.

Nevertheless, on quite large platinum particles of Pt/SiO₂ catalyst (D= 0.38) a great “toxicity” of the tin atoms introduced first was observed in Ref. 168 These results indicate that upon using low tin contents (0< Sn/Pt <0.3), the tin atoms are located on particular sites of the surface of the metallic particle. For higher tin content, a part of the tin atoms could migrate inside the particle or could even migrate on the support, in the close vicinity of the metallic particle.

2.5.2. Electron Microscopy and Diffraction

Electron microscopy of various mono- and bimetallic supported Group VIII catalysts shows that the average metallic particle size in the bimetallic catalysts is slightly higher than the particle size in the corresponding monometallic catalysts. Typical particle size histograms obtained for silica supported Rh₅Snₓ, RuSnₓ and NiSnₓ indicate that there is an increase in size of each metallic particle when Sn is introduced. 136 For example, Conventional Transmission Electron Microscopy (CTEM) of the bimetallic material Rh₅[Sn(n-Bu)₂]/SiO₂ gives a narrow particle size distribution centered at ca. 2.2 nm. The increase of average diameter (0.7 nm) compared to that of the monometallic catalyst is consistent with the formation of no more than one or two monolayers of Sn on the Rh particles. 175

Using Scanning Transmission Electron Microscopy (STEM-EDAX), it was demonstrated that the bimetallic particles have a homogeneous composition and that Sn is never observed alone on the carrier. 122 The signal of Sn is always associated with the signal of Rh. Examination of Rh₅[Sn(n-Bu)₂]/SiO₂ by EDAX was not possible because the electronic beam decomposes the organic fragments and causes a “contamination effect”. Nevertheless, this is an indirect confirmation that the alkyl ligands are on the metal particles. A sample that was treated at 300°C in order to remove the alkyl groups showed a composition of Sn and Rh atoms in an atomic ratio close to 0.8 with a narrow particle size distribution. 173

Selective hydrogenolysis of Sn(n-Bu)₄ on a Pt/SiO₂ catalyst was studied by Humblot et al. 142 Even if the organotin fragments are grafted resulting one to one coverage, after their complete hydrogenolysis at 300°C, about 40% of the platinum is still accessible to H₂ chemisorption. This finding can be explained by the increase of the particle diameter (+ 0.5 Å) which prevents a close packing of the tin atoms around the particle and leaves some Pt atoms still accessible to the hydrogen. 142 In other study the average metallic particle diameters were 1.6 and 2.2 nm for Pt/SiO₂ and PtSn₀.₃/SiO₂, respectively. 172

2.5.3. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) data can be used to determine the quantity of hydrogen required to reduce the sample and the temperature of maximum consumption of H₂. It is worth noting that two types of Pt oxides are considered in the literature, one in weak interaction with the support and the other in strong interaction. 174,175 The former one may be reduced at low temperatures (<100°C), and the latter requires high temperatures (ca. 240°C). Literature data indicate that the temperature region in the interval between 250 and 350°C can be attributed to the reduction of SnOₓ species in close proximity to metallic Pt or PtOₓ and upon reduction resulting in alloy formation. Armendáriz et al. 174 have pointed out that the position of the reduction peaks of the Sn-Pt alloy phases strongly depends on the tin concentration, and with increasing the Sn content in the Sn-Pt alloy, the shift to higher temperature (from 350 to 420°C) can be expected. It is accepted in the literature that high temperature peaks up to 700°C corresponds to the reduction of separate SnOₓ species with strong interaction with the support. It is worth for mentioning that the TPR peak of monometallic Sn/Al₂O₃ sample appeared also at high temperatures (about 500°C) as it was previously reported. 176,177

It has been demonstrated that in the reduction of bimetallic Sn-Pt/Al₂O₃ systems, 166 hydrogen consumption is lower than that needed for the reduction of Pt⁴⁺ to Pt⁰ and Sn⁴⁺ to Sn²⁺ seen in the corresponding monometallic systems. Either one phase (alloy type?) is not re-oxidized and thus remains in a metallic form, or an oxide phase is not reduced during the TPR. XANES data have shown that platinum is fully reduced after hydrogen treatment. Thus the first hypothesis was retained. The reduction peak of tin oxides is not visible, indicating that no independent tin is presented on the support. It has been proposed that the bimetallic catalyst may be described as Pt/SnOₓ/Al₂O₃ with Pt probably in interaction with tin oxide.
2.5.4. Infrared spectroscopy

Infrared spectroscopy is one of the techniques that can be used for detailed investigation of the geometric and electronic structure of metal surfaces via the adsorption of probe molecules (usually CO, NO, etc.).

It has been suggested by FTIR results over Sn-Pt/SiO\textsubscript{2} prepared by CVD method\textsuperscript{124} that during modification with tin the morphology of the Pt particles was not essentially changed, but the surface of Pt atoms was diluted by incorporated Sn atoms. Thermodesorption of adsorbed CO on reduced Sn-Pt/SiO\textsubscript{2} catalysts showed no shift of the ν\textsubscript{co} frequency (2084 and 2080 cm\textsuperscript{-1} for parent and tin-modified catalysts, respectively), suggesting negligible electronic effect of Sn atoms on the Pt atoms when both are reduced.\textsuperscript{168} These results seem to contradict Burch's\textsuperscript{39} statement that there is no geometric effect without an electronic one. This statement came from studies carried out on Sn-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts in which the major part of the tin atoms were in the ionic form (Sn\textsuperscript{4+}) on the support.

The addition of tin by SOMC method resulted in a shift of +6 cm\textsuperscript{-1} (from 2033 to 2039 cm\textsuperscript{-1}) referred to Pt/Al\textsubscript{2}O\textsubscript{3} catalyst, which was interpreted as a decrease in electronic density of the Pt atoms.\textsuperscript{166}

The presence of both linear and bridged bonded CO on Rh\textsubscript{4}Sn\textsubscript{4}(n-C\textsubscript{3}H\textsubscript{7})\textsubscript{2}/SiO\textsubscript{2} suggested that the metal surface atoms in the bimetallic material are not isolated from one another. In contrast to that, on Sn/Rh alloy-type surface species the disappearance of the ν\textsubscript{co} bridged band was observed, in agreement with the concept of "site isolation."\textsuperscript{138}

Upon increasing Sn content in Sn-Rh/SiO\textsubscript{2} catalysts prepared by CVD method, the ν\textsubscript{co} shifted from 2076 to 2068, 2064 and 2050 cm\textsuperscript{-1} for Sn/Rh= 0.18, 0.31 and 0.45, respectively. The observed red shift of the linear CO peak induced by the increasing amount of Sn may be caused by the electronic modification of Rh sites and/or the decrease of dipole-dipole coupling of CO on the surface.\textsuperscript{127}

2.5.5. Mössbauer spectroscopy

Mössbauer spectroscopy\textsuperscript{179} was performed on the bimetallic surface organometallic complexes described as Rh\textsubscript{4}SnBu\textsubscript{4}/SiO\textsubscript{2} and Pt\textsubscript{4}SnEt\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{36} The spectra obtained at liquid N\textsubscript{2} temperature gave isomer shifts of IS= 1.4 mm s\textsuperscript{-1} and 1.29 mm s\textsuperscript{-1}, respectively, and QS= 2.7 mm s\textsuperscript{-1} and 3.16 mm s\textsuperscript{-1}, respectively. These values are compared with those of some molecular and surface analogues. The isomer shift for the surface organometallic complexes is characteristic of covalently bonded Sn\textsuperscript{4+}. The quadrupole splitting (QS) represents the degree of asymmetry of the electron sphere around of tin.\textsuperscript{180} For Pt\textsubscript{4}SnEt\textsubscript{4}/Al\textsubscript{2}O\textsubscript{3}, the value of the quadrupole splitting is close to that obtained with the well characterized =Si-O-SnBu\textsubscript{3}\textsuperscript{39} or tin triethyl halides.\textsuperscript{181} The relatively high value of QS is in agreement with the fact that three equivalents and one different ligand are placed around the tin atom. For Rh\textsubscript{4}SnBu\textsubscript{4}/SiO\textsubscript{2}, the QS is intermediate between X-SnBu\textsubscript{3} (X is O or M) and Sn-Rh alloy or physisorbed SnBu\textsubscript{4}.\textsuperscript{89,137}

Direct evidence for Sn-Pt alloy formation has been obtained from Mössbauer studies.\textsuperscript{4,68,86,182} Bacaud \textit{et al.}\textsuperscript{185} have studied the state of Sn-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts with Sn and Pt contents (wt%) of 0.47-0.47, 0.5-0.95 and 0.2-0.5 by Mössbauer spectroscopy, pointing out the special features in the spectra of some highly dispersed species. The reduction of these catalysts in hydrogen resulted in ionic species (Sn\textsuperscript{4+} and Sn\textsuperscript{2+}) and different amounts and compositions of Sn-Pt alloys (Pt\textsubscript{4}Sn, PtSn, PtSn\textsubscript{3}, PtSn\textsubscript{4}). It was mentioned that in these catalysts relatively high amount of platinum unalloyed with tin was also present.

Kuznetsov \textit{et al.} reported\textsuperscript{68} that Pt-Sn/p-Al\textsubscript{2}O\textsubscript{3} catalysts prepared by impregnation of support with isopropanol solution containing a mixture of [PtCl\textsubscript{4}(SnCl\textsubscript{3})]\textsuperscript{2-} and [PtCl\textsubscript{3}(SnCl\textsubscript{2})]\textsuperscript{3-} complexes are multicomponent. The presence of highly dispersed species in Sn\textsuperscript{4+}, Sn\textsuperscript{2+} and Sn\textsuperscript{0} valent states interacting with both support surface and Pt has been evidenced. Platinum, according to these authors,\textsuperscript{68} forms nearly all possible alloys with Sn. After a rather large number of redox cycles, Sn\textsuperscript{4+} compounds and Sn-Pt alloys are reproducibly formed on the catalyst surface. The amount and composition of Sn\textsuperscript{4+} compounds tend to change most dynamically. The change is associated with strong interaction of some of the Cl\textsuperscript{-} ions and the Sn with the support lattice.

Li \textit{et al.} reported that tin was observed in forms whose isomer shifts were similar or the same as SnO\textsubscript{2}, SnO, SnCl\textsubscript{4}, SnCl\textsubscript{2}, Sn\textsuperscript{0} and Sn-Pt alloy in Sn-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts.\textsuperscript{4,183} In case of Pt supported on a
co-precipitated tin oxide-alumina catalyst, alloy formation occurs to a much smaller extent than it does on a material prepared by co-impregnation with the chloride complex of both metals.\textsuperscript{3}

It has been evidenced in our department earlier that the decomposition of PSC, described as Pt-, Sn(C\textsubscript{2}H\textsubscript{4})\textsubscript{4}, in hydrogen at 500°C resulted in the formation of Pt\textsubscript{2}Sn (3 < x < 4) alloy-type surface species.\textsuperscript{86} It has been shown that this alloy-type surface species is highly sensitive to air, contamination of the reduced catalyst with a minor amount of oxygen even at 25°C results in partial oxidation to SnO\textsubscript{2} (25%). Both SnO\textsubscript{2} and Pt\textsubscript{2}Sn alloy phases were detected in the re-reduced catalyst. However, anchoring SnCl\textsubscript{2} onto lithiated Pt/Al\textsubscript{2}O\textsubscript{3} catalyst and subsequent reduction of the catalyst in H\textsubscript{2} did not result in the formation of Sn-Pt alloy, indicating an exclusive tin-alumina interaction.\textsuperscript{86}

The behavior of Sn-Pt supported on silica catalysts significantly differs from that of supported on alumina. Ref.\textsuperscript{4} shows that the reduction of tin to Sn\textsuperscript{0} is much easier when silica is used as a support.

\subsection{2.5.6. Solid-state nuclear magnetic resonance (NMR) spectroscopy}

Solid-state nuclear magnetic resonance (NMR) spectroscopy in heterogeneous catalysis principally allows the characterization of the chemical and structural environment of atoms in the catalysts. Interaction between tetraalkyl tin SnR\textsubscript{4} (R= Me, Et, i-Pr, Bu) and surface of partially dehydroxylated silica,\textsuperscript{89,91,184} \(\gamma\)-, \(\eta\)-, and \(\eta\)-aluminas,\textsuperscript{185} silica-alumina\textsuperscript{186} was followed by IR and \(^{13}\text{C}\) and \(^{119}\text{Sn}\) NMR spectroscopies. At room temperature, all of the complexes studied are physisorbed. A chemical reaction takes place above 100°C leading to the surface species grafted via a covalent bond. At low surface coverage, and for R\(\neq\) Me, the alkyl ligands of surface complex \(=\text{Si-O-SnR}\) are folded toward the surface, and the terminal methyl group interacting with surface of hydroxyl groups via hydrogen-type bonding (i.e., \(=\text{C-H}•••\text{OH}\)). This interaction is not observed when R= Me; the distances between the concerned atoms are certainly not favorable.\textsuperscript{91}

The \(^{119}\text{Sn}\) MAS NMR spectral data suggest that on silica support Sn remains essentially tetracoordinated. The free rotation of tin in \((=\text{SiO})_2\)-SnR\textsubscript{2} \((=\text{SiO})_3\)-SnR would be completely suppressed, resulting probably in a higher relaxation time and lower intensity of the NMR signal.\textsuperscript{91}

The various NMR data coupled with published data for molecular analogs indicate that the tin atoms can be tetra- (\(\delta= 80\) ppm) or pentacoordinated (around -230 and -170 ppm) on alumina surface.\textsuperscript{185} The fifth ligand coordinated to tin may be either a OH group or a surface O\textsuperscript{-2} ion. These results demonstrate the extreme sensitivity of tin chemical shifts to molecular environment.

A bimetallic Rh\textsubscript{4}Sn(C\textsubscript{2}H\textsubscript{4})\textsubscript{4}/SiO\textsubscript{2} catalyst was prepared by stepwise hydrogenolysis of Sn(n-C\textsubscript{2}H\textsubscript{4})\textsubscript{4} on silica supported rhodium catalyst at 150°C.\textsuperscript{173,185} In solid state MAS \(^{13}\text{C}\) NMR spectroscopy no signal could be detected, in agreement with the well-known phenomenon of “knight shift” due to the rhodium particle. In this study the exclusive modification of the Rh by tin was achieved only when the amount of Sn(n-C\textsubscript{2}H\textsubscript{4})\textsubscript{4} introduced was less than monolayer (Sn/Rh\textsubscript{4} < 1). For a Sn/Rh\textsubscript{4} ratio higher than ca. unity, a weak \(^{13}\text{C}\) CP-MAS solid-state NMR signal corresponding to \(=\text{SiOSn}(n-C\textsubscript{2}H\textsubscript{4})_3\) was always observed on the silica surface.

Mössbauer and solid state NMR data, obtained on Re\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}/SnR\textsubscript{4} metathesis catalysts (R= Me, Et or n-Bu), suggest two kinds of tin sites, with the tin atom linked to the surface by one or two Sn-O-Re bonds.\textsuperscript{188}

The complex \([(\text{CH}_3)_2\text{N})_3\text{[Pt(SnCl}_3\text{)_3]}\] was selected as a molecular precursor to prepare PtSn/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3} reforming catalysts.\textsuperscript{71} The \(^{195}\text{Pt}\) and the \(^{119}\text{Sn}\) NMR spectra of the precursor complex show signals centered at \(\delta= -5902\) ppm and \(\delta= -128\) ppm, respectively. In contrast, the \(^{119}\text{Sn}\) NMR spectrum of the catalysts after the deposition onto the support is completely different. One broad signal at \(\delta= -615\) ppm and second narrower signal at \(\delta= -730\) ppm were observed corresponding to partially hydrolyzed mono- and bimetallic species, respectively.

A series of SnO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts prepared by the co-precipitation method with the SnO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} mole ratio 1 were characterized by \(^{119}\text{Sn}\) MAS NMR spectroscopy.\textsuperscript{189} \(^{119}\text{Sn}\) CP/MAS NMR spectrum shows one narrow line at -603 ppm (chemical shift of SnO\textsubscript{2}) superimposed on a very broad line, indicating a strong interaction between Al\textsubscript{2}O\textsubscript{3} and SnO\textsubscript{2}.

\subsection{2.5.7. X-Ray photoelectron spectroscopy (XPS)}

As the depth analyzed by X-Ray photoelectron spectroscopy (XPS) is 4 nm, Pt/Sn ratios obtained by XPS are always lower than bulk values established by X-ray fluorescence. Determination of the
XANES spectra show that the Pt is completely reduced after treatment in H₂. The Sn 3d₅/₂ peak usually contains two contributions. The first is Sn⁰ with binding energy of 484.6 eV and the second is Sn²⁺ and/or Sn⁴⁺, which cannot be separated as their binding energies are too close (486.6 and 486.4 eV, respectively).

XPS was used to determine the oxidation state of both metals in bimetallic Rh,Sn-Pt/Al₂O₃ catalyst. The XPS signal was deconvoluted into ca. 75% of Sn²⁺ and/or Sn⁴⁺ and ca. 25% of Sn⁰. The Rh 3d₅/₂ and 3d₃/₂ binding energies correspond to metallic rhodium. After complete hydrogenolysis at 350°C, only Sn⁰ and Rh⁰ were found. For the catalyst Pt(Sn-n-Bu)₀.₄/SiO₂, tin was found as Sn⁰ and Sn²⁺,⁴⁺ in similar proportions according to XPS measurements. Increase of the reaction temperature up to 150°C resulted in catalyst, in which tin is found as Sn⁰. After activation of the catalyst in H₂ atmosphere at 500°C a part of the tin was found as Sn⁰ (ca. 70%) and the remaining one was found as ionic tin (Sn²⁺ and/or Sn⁴⁺).

In the case of Pd-Sn catalyst it has been demonstrated that the addition of Sn shifts the XPS d-lines of Pd by several electron volts to lower values. Tin either donates electrons to Pd or induces a redistribution of the d-electrons. A higher electron density at the Pd atom would stabilize the adsorption of an electrophilic element like chlorine.

### 2.5.8. Extended X-ray absorption fine structure (EXAFS) spectroscopy

*In situ* extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopy were used to study the state of platinum in Sn-Pt/Al₂O₃ catalyst prepared by SOMC/M techniques. The presence of Pt and Sn in the first coordination shell of platinum and an increase in the number of filled valence state of Pt indicate the formation of a Sn-Pt bimetallic phase. While the XANES spectra show that the Pt is completely reduced after treatment in H₂ at 500°C. The results obtained by EXAFS indicate that, besides Pt and Sn, O atoms are present in the first coordination shell of platinum, but with a Pt-O distance longer than for platinum oxide or calcined Pt catalysts (2.24 vs 2.02 Å). These findings can be rationalized assuming the formation of a highly dispersed bimetallic Sn-Pt alloy phase, which is stabilized on the Al₂O₃ surface through Pt-O-Sn bonds leading to a high degree of dispersion. Tin oxide phase acts as an anchoring site for the PtSn clusters. Similarly, Li and Klabunde, using a Sn-Pt/Al₂O₃ catalyst prepared by so-called SMAD method, have proposed a model where a tin oxide underlayer serves as nucleation sites for further Pt and Sn clusters. This model is similar to the suggestion of Meitzner et al. that the platinum clusters are anchored to the alumina through the bonding of a few Pt atoms to Sn²⁺ ions at the Al₂O₃ surface. The principal difference is the presence of a Sn-Pt alloy phase in samples prepared by SOMC method.

### 2.6. Literature study on the use of supported bimetallic catalysts in various reactions

#### 2.6.1. Use of supported bimetallic catalysts prepared by CVD in various reactions

The use of supported bimetallic Rh- and Pt-based catalysts prepared by CVD in various reactions is demonstrated in Table 1.

#### Table 1. Use of supported bimetallic catalysts prepared by CVD in various catalytic reactions

<table>
<thead>
<tr>
<th>Parent catalyst</th>
<th>Anchoring step</th>
<th>Decomposition</th>
<th>Sn/M</th>
<th>Catalytic reaction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 wt% Rh/SiO₂</td>
<td>SnMe₃ vapour (&lt;0.6 kPa) at 150°C in a close circulating system</td>
<td>Reduced at 300°C for 1 h, followed by evacuation <em>in situ</em> before catalytic run</td>
<td>Sn/Rh= 0-1</td>
<td>1- NO dissociation and NO-H₂ reaction; 2- Hydrogenation of acetophenone, 2-butane, styrene, 1-hexene</td>
<td>123, 125-128, 129</td>
</tr>
<tr>
<td>1.7 wt% Pt/SiO₂</td>
<td>SnMe₃ vapour at 150°C in a close circulating system</td>
<td>Reduced at 300°C for 1 h.</td>
<td>Sn/Pt= 0-0.5</td>
<td>1- Catalytic synthesis of unsaturated nitriles from NO-isobutane, NO-isobutene, NO-propene; 2- Catalytic synthesis of unsaturated nitriles from NO-C₃H₅, NO-CH₄</td>
<td>130, 124</td>
</tr>
</tbody>
</table>
2.6.2. Use of supported bimetallic catalysts prepared by CSRs in various reactions

Bimetallic catalysts prepared by CSRs earlier in our department were used in various reactions. Catalytic behavior of these new types of catalysts and those prepared by conventional impregnation method was compared.\textsuperscript{109,110,132}

In first attempts this type of Sn-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts were tested in hydrocarbon reactions.\textsuperscript{109,110,132,191-193} The main goal of these studies was the modeling of reactions taking place in naphtha reforming. Upon using n-hexane and methyl cyclopentane mostly kinetic (stationary and transient\textsuperscript{194}) and deactivation tests were performed on these catalysts. It was shown that the formation of benzene could be strongly hindered by simultaneous introduction of metallic tin onto the platinum and ionic tin onto the support.\textsuperscript{110,132}

This method of catalyst modification was successfully applied in the area of fine chemistry. Ni/Al\textsubscript{2}O\textsubscript{3} hydrogenation catalysts modified with Pb(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} via CSRs were successfully used for the selective hydrogenation of acrylonitrile to propionitrile.\textsuperscript{195} The addition of Pb strongly suppressed the hydrogenation of the nitrile group.

The modification of the skeletal nickel catalysts with tin was aimed to suppress the formation of isopropanol in the reductive amination of acetone.\textsuperscript{146,147} Upon modification the skeletal Ni catalyst with different SnR\textsubscript{4} compounds (R= C\textsubscript{2}H\textsubscript{5}, C\textsubscript{4}H\textsubscript{9}) surface anchoring reaction was highly selective. The introduction of tetraalkyl tin onto the catalyst resulted in an increase of the formation of diisopropylamine and slight decrease of the formation of alcohol. Upon using dibenzyl (or diethyl) dichloride tin for the modification of the Ni catalysts strong suppression of the selectivity towards isopropanol could be achieved. On these modified catalysts the ratio of primary to secondary amines was controlled by the amount of tin introduced and the formation of isopropyl alcohol was strongly suppressed.\textsuperscript{146,147}

The enantioselective hydrogenation of ethyl pyruvate has been studied on tin-promoted Pt/Al\textsubscript{2}O\textsubscript{3} catalysts using Sn(CH\textsubscript{3})\textsubscript{4} and Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} as tin precursor compounds.\textsuperscript{196} It was shown that upon anchoring of -SnR\textsubscript{4-x} moieties onto Pt the enantioselectivity of the Pt/Al\textsubscript{2}O\textsubscript{3}-dihydrocinchonidine catalyst system was not influenced, while the rate of hydrogenation showed a volcano type dependence. The hydrogenation activity was completely suppressed at relatively low tin coverage (Sn/Pt < 0.10). The highest hydrogenation rate was measured over catalysts containing surface complex -SnR\textsubscript{4-x} (Sn/Pt = 0.025) on the platinum surface.\textsuperscript{196}

2.6.3. Use of supported bimetallic catalysts prepared by SOMC/M in various reactions

Selected results on using of supported bimetallic Pt-based catalysts prepared by SOMC/M in various reactions are demonstrated in Table 2. A short overview is given with including of the precursor of organometallic compounds used, preparation details on both tin anchoring step I and decomposition step II (if it exist) and modifier/active metal (E/M) ratio. Data presented in Table 2 and 3 were restricted to results obtained in Basset‘s, Figueras‘s, Ferretti’s and Stytsenko‘s groups.

In Table 3 selected results of various reactions over supported bimetallic Pd-, Rh-, Ru- and Ni-based catalysts prepared by SOMC/M are listed.
<table>
<thead>
<tr>
<th>Parent catalyst</th>
<th>Anchoring step</th>
<th>Decomposition</th>
<th>E/M ratio (or E wt%)</th>
<th>Catalytic reaction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4 wt% Pt/Al₂O₃</td>
<td>E(n-Bu)₄ (E= Sn, Ge, Pb), AlEt₃, ZnEt₂, solvent: n-heptane, under H₂, at T= 90°C for τ: 72 h</td>
<td>Dried under vacuum at t&lt;sub&gt;r&lt;/sub&gt;: 350°C in H₂ for 4 h</td>
<td>Sn/Pt= 0.11-0.36; Ge/Pt= 0.22; Al/Pt= 0.21; Zn/Pt= 0.15-0.54;</td>
<td>Hydrogenation of para-chloronitrobenzene to para-chloroaniline</td>
<td>197</td>
</tr>
<tr>
<td>1.4 wt% Pt/Al₂O₃</td>
<td>E(n-Bu)₄ (E= Sn, Ge, Pb), AlEt₃, ZnEt₂, solvent: n-heptane, under bubbling H₂, at T= 90°C</td>
<td>Dried under vacuum at t&lt;sub&gt;r&lt;/sub&gt;: 350°C in H₂ for 4 h</td>
<td>Sn/Pt= 0.11-0.36; Ge/Pt= 0.22; Al/Pt= 0.21; Zn/Pt= 0.15</td>
<td>Conversion of n-hexane, methycyclopentane, 2,2,3,3-tetramethylbutane</td>
<td>15</td>
</tr>
<tr>
<td>0.6 wt% Pt/Al₂O₃</td>
<td>Sn(n-Bu)₄, Sn/Pt=0.5-2, solvent: n-heptane, 1 atm of H₂, T&lt;sub&gt;r&lt;/sub&gt;: 25°C for τ: 7 h</td>
<td>Washed with n-heptane, t&lt;sub&gt;r&lt;/sub&gt;: 550°C in H₂</td>
<td>Sn/Pt= 1.1-1.4 addition of H₂O-Sn/Pt= 0.8</td>
<td>Dehydrogenation of isobutane to isobutene</td>
<td>169</td>
</tr>
<tr>
<td>1.57 wt% Pt/SiO₂</td>
<td>Sn(n-Bu)₄, Sn/Pt=0.2-0.85, without solvent, 30 mbar of H₂, T&lt;sub&gt;r&lt;/sub&gt;: 50°C for τ: 24 h</td>
<td>t&lt;sub&gt;r&lt;/sub&gt;: 550°C in H₂ for 10 h</td>
<td>Sn/Pt= 0.07; 0.21; 0.31</td>
<td>Dehydrogenation of isobutane to isobutene</td>
<td>168</td>
</tr>
<tr>
<td>1.3 wt% Pt/SiO₂</td>
<td>SnMe₂, solvent: n-heptane, under H₂, T&lt;sub&gt;r&lt;/sub&gt;: 50°C for τ: 24 h</td>
<td>Washed with n-heptane, Dried under vacuum (10&lt;sup&gt;4&lt;/sup&gt; Torr) at 50°C for 1 h</td>
<td>Sn/Pt= 0.35-0.63</td>
<td>Hydrogenation of unsaturated triketone: oxopromegestone to trimegestone</td>
<td>201</td>
</tr>
<tr>
<td>1 wt% Pt/SiO₂</td>
<td>Sn(n-Bu)₄, solvent: n-heptane or n-decane H₂ flow, T&lt;sub&gt;r&lt;/sub&gt;: 90 or 150°C for τ: 4 h</td>
<td>Washed with n-heptane; dried in Ar at 90°C; t&lt;sub&gt;r&lt;/sub&gt;: 500°C for 2 h.</td>
<td>Sn/Pt= 0.06-1.41</td>
<td>Hydrogenation of crotonaldehyde, cinnamaldehyde, butyraldehyde, 2-butanol, benzaldehyde, cyclohexene, (-)-menthone, (+)-isomenthone, and (+)-pulegone; Stereoselective hydrogenation of terpenes</td>
<td>117, 202, 205</td>
</tr>
<tr>
<td>1 wt% Pt/SiO₂</td>
<td>Sn(n-Bu)₄, Men₃Sn-Men₃ (Men= menthyl), solvent: n-heptane or n-decane H₂ flow, T&lt;sub&gt;r&lt;/sub&gt;: 120°C for τ: 4 h</td>
<td>Washed with n-heptane; dried in Ar</td>
<td>Sn/Pt= 0.8</td>
<td>Racemic and enantioselective hydrogenation of acetophenone and 3,4-dimethoxyacetophenone</td>
<td>206</td>
</tr>
</tbody>
</table>
Table 3. Use of different supported bimetallic catalysts prepared by SOMC/M in various reactions. Selected results.

<table>
<thead>
<tr>
<th>Parent catalyst</th>
<th>Anchoring step</th>
<th>Decomposition</th>
<th>E/M ratio (or E wt %)</th>
<th>Catalytic reaction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09 wt% Pd/Al₂O₃ (D= 0.05-0.56)</td>
<td>E(n-Bu)₄ (E= Sn, Ge, Pb), Sb(n-Bu)₃</td>
<td>Dried at 110°C, t_red: 300 and 500°C in H₂</td>
<td>Sn wt%= 0.02-0.11; Ge wt%= 0.02-0.05; Pb wt%= 0.02-0.07; Sb wt%= 0.02-0.12;</td>
<td>Hydrogenation of isoprene and valylene</td>
<td>79, 207</td>
</tr>
<tr>
<td></td>
<td>solvent: n-heptane, Tᵢ= 90°C for τᵢ: 0.25-72 h.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09 wt% Pd/Al₂O₃ (D= 0.54)</td>
<td>Sn(n-Bu)₄, solvent: n-heptane, Tᵢ= 90°C for τᵢ: 0.25-48 h.</td>
<td>Dried at 120°C, t_red: 300 and 500°C in H₂</td>
<td>Sn wt%= 0.02; 0.06; 0.11</td>
<td>Conversion of chlorobenzene</td>
<td>114</td>
</tr>
<tr>
<td>1.03 wt% Rh/Al₂O₃ (D= 0.8)</td>
<td>E(n-Bu)₄ (E= Sn, Ge, Pb), solvent: n-heptane, H₂= 30 mbar, Tᵢ= 100°C for 0.3-19 h.</td>
<td>Without additional decomposition</td>
<td>Sn/Rh= 0.1-0.92; Ge/Rh= 0.1-0.92; Pb/Rh= 0.1-0.96;</td>
<td>Hydrogenation of citral</td>
<td>208, 209</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6-1.32 wt% Rh/Al₂O₃ (D= 0.74-1.4)</td>
<td>E(n-Bu)₄ (E= Sn, Ge, Pb), Sb(n-Bu)₃, solvent: n-heptane, Tᵢ= 90°C in H₂ atm.</td>
<td>Dried under vacuum at 25°C, t_red: 400°C in H₂ for 4 h</td>
<td>Sn/Rh= 0.21-1.6; Ge/Rh= 0.20-0.70; Pb/Rh= 0.37-0.73; Sb/Rh= 0.19</td>
<td>Conversion of n-hexane, methylcyclo- pentane, 2,2,3,3-tetra-methylbutane</td>
<td>14</td>
</tr>
<tr>
<td>1.2 wt% Rh/SiO₂ (D= 0.9)</td>
<td>Sn(n-Bu)₄, solvent: n-heptane, H₂= 30 mbar, Tᵢ= 50-150°C for τᵢ: 0.5 and 2 h.</td>
<td>Without additional decomposition</td>
<td>Sn/Rh= 0.5</td>
<td>Hydrogenation of butan-2-ol, trans-hex-2-ene-1-ol and hex-5-ene-1-ol</td>
<td>144</td>
</tr>
<tr>
<td>0.3-0.9 wt% Ru/Al₂O₃ (D= 0.75)</td>
<td>E(n-Bu)₄, (E= Sn, Ge, Pb), solvent: n-heptane, Tᵢ= 25°C</td>
<td>Dried under vacuum, t_red: 400°C in H₂</td>
<td>Sn/Ru= 0.26-0.84; Ge/Ru= 0.18; Pb/Ru= 0.33</td>
<td>Hydrogenolysis of 2,2,3,3-tetramethylbutane</td>
<td>210</td>
</tr>
<tr>
<td>0.93-1.0 wt% Ru/Al₂O₃ (D= 0.35-0.75)</td>
<td>E(n-Bu)₄, (E= Sn, Ge, Pb, Si), Sb(n-Bu)₃, solvent: n-heptane, Tᵢ= 25°C in H₂ atm.</td>
<td>Dried under vacuum, t_red: 400°C in H₂</td>
<td>Sn/Ru= 0.26-0.84; Ge/Ru= 0.18; Si/Ru= 0.20; Pb/Ru= 015-0.23; Sb/Ru= 0.13</td>
<td>1- Conversion of benzene, n-hexane, 2-methylpentane, 2,2,3,3-tetramethylbutane 2- Hydrogenation of para-chloronitrobenzene to para-chloroaniline</td>
<td>115, 211</td>
</tr>
<tr>
<td>1.01 wt% Ru/ZrO₂ (D= 0.80)</td>
<td>Sn(n-Bu)₄, solvent: n-heptane, Tᵢ= 80°C in H₂ atm.</td>
<td>Dried under vacuum at 25°C, t_red: 300°C in H₂</td>
<td>Sn wt%= 0.27-0.53</td>
<td>Hydrogenation of cinnamaldehyde</td>
<td>212</td>
</tr>
<tr>
<td>56 wt% Ni/SiO₂</td>
<td>Sn(n-Bu)₄, Sn(Pb), solvent: n-hexane or benzene, Tᵢ= 25°C in H₂ atm for τᵢ: 20 h</td>
<td>Solvent was evaporated, dried at 70-80°C in He, calcined at 400°C for 3h t_red: 400°C for 2 h</td>
<td>Sn wt%= 2, 5</td>
<td>1- Hydrogenolysis of ethane, n-hexane, cyclohexane; 2- Hydrogenation of 1,3-butadiene and isoprene</td>
<td>119, 120, 137, 213</td>
</tr>
</tbody>
</table>
3. Objectives of the study

Earlier catalytic results obtained in the hydrogenation of crotonaldehyde (CA) into crotylalcohol, shows that the introduction of tin onto Pt/SiO$_2$ catalyst resulted in significant increase of the selectivity for the hydrogenation of the aldehyde group. It is noteworthy that the addition of tin led to the increase of the overall rate of hydrogenation. This was attributed to the formation of new type of active sites. One more important issue should also be mentioned, i.e. the selectivity of carbonyl group (S$_{C=O}$) hydrogenation strongly depended on the amount of tin anchored (Sn/Pt ratio) and high S$_{C=O}$ selectivities can be obtained at relatively high Sn/Pt ratios. In order to achieve high Sn/Pt ratios the general procedure used earlier for tin anchoring had to be changed.

Based on the above results obtained in crotonaldehyde hydrogenation it was concluded that further selectivity improvement could be achieved when more tin could be introduced onto platinum. However, in this case the following questions should have to be answered:

(i) How to increase the amount of tin introduced onto platinum without its incorporation to the support?

(ii) Is it possible to create a second or multiple layers of tin organic moieties at the top of the PSC?

(iii) How to use PSC as a landing site for additional amount of SnR$_4$?

The goal of this study

In the original method used in our department hydrogen adsorbed on supported metals was the driving force for tin anchoring resulting in a monolayer of tin organic moieties at the metal surface. In the present study new aspects of anchoring of tin and germanium organometallic compounds (SnR$_4$, R$_5$SnSnR$_3$ (R= CH$_3$, C$_2$H$_5$) and Ge(C$_2$H$_5$)$_4$) onto different SiO$_2$, Al$_2$O$_3$ and active carbon supported metals will be described.

The goal of this work is to demonstrate the advantages of catalyst preparation based on CSRs:

- Finding the ways to increase the amount of Sn (or Ge) anchored onto supported metals without its introduction into the support.

- Study of CSRs in the presence of large excess of SnR$_4$ and H$_2$.

- Showing that the anchoring is a stepwise process leading to the formation of multilayered surface complexes. This study provides proofs for this build-up process.

- Study of peculiarities of CSRs in the absence and presence of excess hydrogen.

- Investigation of the influence of the reaction temperature and the duration of re-reduction in hydrogen on the activity of different metals in tin anchoring reaction.

- Study of CSRs using partially or fully oxidized catalysts.

- Investigation of the influence of the duration of tin anchoring on the type of SOMS formed. Kinetic results obtained on supported Pt catalysts will provide new information about the elementary steps involved in anchoring of SnR$_4$ onto platinum.

- Preparation of new types of selective catalysts.

In this study the focus will be laid on the investigation of interactions involved both in the tin anchoring step and the build-up of different tin organometallic moieties layer by layer on small supported metal clusters.

It will be described that the “fingerprint” character of the Temperature Programmed Decomposition curves can be used for the characterization of tin-modified catalysts. It will be demonstrated that decomposition of surface organometallic complexes in hydrogen or oxygen results in the exclusive formation of supported alloy-type Sn-Pt surface species or Lewis-acid type sites consisting of SnO$_x$ species anchored onto the active metal, respectively.

The modification of alumina supported platinum catalysts with tetraethyltin by CSRs using a “one pot” circulation type reactor set-up will be demonstrated. The use of this approach for the modification of commercial reforming-type Pt-Re/Al$_2$O$_3$ catalysts with tin will be also presented.

CSRs will also be used to prepare various types of Sn$_x$-M$_y$ (M= Pt, Pd, Rh, Ru) supported catalysts, with exclusive formation of metal-metal interaction. The activity of different supported metals in tin anchoring reaction will be compared.
Characterization of the bimetallic catalysts by chemisorption of CO and H₂, TPR, FTIR, Mössbauer and EXAFS spectroscopy will also be presented and discussed.

4. Experimental methods

4.1 Materials used

Organometallic compounds:
In this study the following tin and germanium organometallic compounds were used:

**Tetramethyltin:** Sn(CH₃)₄ (95%) (Aldrich).

**Tetrethyltin:** Sn(C₂H₅)₄ (97%) (Aldrich).

**Hexamethylditin:** (CH₃)₃SnSn(CH₃)₃ (99%) (Strem Chemicals, Inc.).
FW= 327.59, mp= 23°C, bp= 85-88°C/45 mm, nD²₀ = 1.54, d= 1.58 (20°C) (air sensitive).

**Tetraethylgermanium:** Ge(C₂H₅)₄ (98%) (Aldrich).
FW= 188.84, bp= 163-164°C, nD²₀ = 1.4420, d= 0.998 (25°C).

Solvents:
In this study the following hydrocarbon solvents were used:

**Benzene** (99.5 wt %) (Reanal). Prior to its use benzene was purified from thiophene. The method of purification of benzene from thiophene is known as Fieser method.\(^{214}\) One liter of benzene was mixed with 80 cm³ H₂SO₄ (conc.) at 25°C for 1.5 h. Immediately after the mixing the colour of the acidic phase was changed to dark yellow. After 1.5 h of mixing the solutions were carefully separated, and fresh portion of sulphuric acid was added to benzene. This operation was repeated three or four times. In the last step after separation from almost colourless sulphuric acid, benzene was treated three times with 200 cm³ of 1.0 M NaOH in water, followed by washing with demineralised water until pH of 7 (operation was repeated three times) and then dried over CaCl₂ overnight. After the above purification procedure benzene was refluxed and then distilled over sodium and kept under zeolite prior to its use.

**n-Hexane** (>95.0 %) (Reanal). The solvent was refluxed on sodium and then distilled and kept under zeolite (or sodium) prior to its use.

**Decane** purum (≥98.0 %) (GC) (Fluka)

**C₆ fraction** (the composition in wt %: n-C₆: 90, iso-C₆: 6, C₅: 2, MCP: 1, benzene: 1) (Hungarian Oil Company)

**Low octane number desulfurated naphtha (naphtha)** (the composition in wt%: n-paraffins - 25.34, iso-paraffins - 32.47, naphtenes - 31.44, aromatics - 10.75; boiling range: 55 - 180°C, density 0.7466 g/ml, mean molecular weight= 120) (Hungarian Oil Company)

4.2. Preparation of monometallic catalysts

Characteristic features of the supported monometallic catalysts used in this study are shown in Table 4.

3 wt% Pt/SiO₂ catalyst (PtSi-3.0-A,B)
The silicalag prepared in the Boreskov Institute of Catalysis (Novosibirsk, Russian Federation) containing 0.02 wt% impurities was used as a support. Surface area (S= 302 m² g⁻¹), pore volume (Vₚ= 0.95 cm³ g⁻¹) and mean pore diameter (dₚ= 12 nm) were determined by N₂ adsorption. The silica supported monometallic catalyst containing 3 wt% Pt (InCat Pt-1) provided by Boreskov Institute of Catalysis (Novosibirsk, Russian Federation) was obtained by ion-exchange technique using [Pt(NH₃)₄]Cl₂ as precursor compound. The ion-exchange was carried out at 30-35°C for 1 h and pH= 10 adjusted by ammonia solution. After filtration, the catalyst was washed free of chloride ion with demineralised water until pH= 7, and then dried in two steps at 60°C and 120°C for 3 and 2 h, respectively, (heating rate= 0.3°C min⁻¹). The catalyst was reduced under hydrogen at 300°C for 4 h (heating rate= 1.5°C min⁻¹). The H/Pt ratio of the PtSi-3.0-A catalyst used was 0.52 measured by hydrogen chemisorption.

The same method of preparation was applied for the synthesis of the PtSi-3.0-B catalyst. As emerges from Table 4, slightly lower values 0.37 and 0.42 corresponding to hydrogen and CO chemisorption respectively were obtained for this catalyst.
Table 4. Characteristic features of the supported monometallic catalysts used

<table>
<thead>
<tr>
<th>Designation</th>
<th>Metal</th>
<th>Support</th>
<th>Metal precursor</th>
<th>M, wt%</th>
<th>H/M</th>
<th>CO/M</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSi-3.0-A</td>
<td>Pt</td>
<td>SiO₂</td>
<td>[Pt(NH₃)₂]Cl₂</td>
<td>3.0</td>
<td>0.52</td>
<td>-</td>
<td>InCat Pt-T</td>
</tr>
<tr>
<td>PtSi-3.0-B</td>
<td>Pt</td>
<td>SiO₂</td>
<td>[Pt(NH₃)₂]Cl₂</td>
<td>3.0</td>
<td>0.37</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>PtAl-0.3-A</td>
<td>Pt</td>
<td>Al₂O₃</td>
<td>H₂PtCl₆</td>
<td>0.3</td>
<td>0.76</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>PtAl-0.3-B</td>
<td>Pt</td>
<td>Al₂O₃</td>
<td>H₂PtCl₆</td>
<td>0.3</td>
<td>-</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td>PtAl-0.35</td>
<td>Pt</td>
<td>Al₂O₃</td>
<td>H₂PtCl₆</td>
<td>0.35</td>
<td>-</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>PtAl-5.0</td>
<td>Pt</td>
<td>Al₂O₃</td>
<td>H₂PtCl₆</td>
<td>5.0</td>
<td>0.25</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>RePtAl-0.17</td>
<td>Pt</td>
<td>Al₂O₃</td>
<td>Unknown</td>
<td>0.17</td>
<td>0.05</td>
<td>0.29</td>
<td>Petroleum Research Center, Libya</td>
</tr>
<tr>
<td>RePtAl-0.21</td>
<td>Pt</td>
<td>Al₂O₃</td>
<td>Unknown</td>
<td>0.36</td>
<td>0.07</td>
<td>0.44</td>
<td>Petroleum Research Center, Libya</td>
</tr>
<tr>
<td>PtCl-5.0</td>
<td>Pt</td>
<td>C</td>
<td>H₂PtCl₆</td>
<td>5.0</td>
<td>0.29</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>PdSi-1.7</td>
<td>Pd</td>
<td>SiO₂</td>
<td>[Pd(NH₃)₂]Cl₂</td>
<td>1.7</td>
<td>-</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>PdC-5.0</td>
<td>Pd</td>
<td>C</td>
<td>Unknown</td>
<td>5.0</td>
<td>0.50</td>
<td>-</td>
<td>Selcat SQ3</td>
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<tr>
<td>RhSi-1.0</td>
<td>Rh</td>
<td>SiO₂</td>
<td>RhCl₃ x 3 H₂O</td>
<td>1.0</td>
<td>0.11</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>RhAl-1.0</td>
<td>Rh</td>
<td>Al₂O₃</td>
<td>RhCl₃ x 3 H₂O</td>
<td>1.0</td>
<td>0.30</td>
<td>-</td>
<td>Air Products &amp; Chemicals Co.</td>
</tr>
<tr>
<td>RhAl-4.0</td>
<td>Rh</td>
<td>Al₂O₃</td>
<td>RhCl₃ x 3 H₂O</td>
<td>4.0</td>
<td>0.60</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>RhAl-5.0</td>
<td>Rh</td>
<td>Al₂O₃</td>
<td>RhCl₃ x 3 H₂O</td>
<td>5.0</td>
<td>0.30</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>RuAl-1.77</td>
<td>Ru</td>
<td>Al₂O₃</td>
<td>Ru(acac)₃</td>
<td>1.77</td>
<td>0.44</td>
<td>0.47</td>
<td>Air Products &amp; Chemicals Co.</td>
</tr>
<tr>
<td>RuAl-5.0</td>
<td>Ru</td>
<td>Al₂O₃</td>
<td>Ru(acac)₃</td>
<td>5.0</td>
<td>0.08</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

*Dispersion was measured by oxygen chemisorption (O/Ru).

Three different alumina supported platinum catalysts with low platinum content were used in this study.

0.3 wt% Pt/Al₂O₃ catalyst (PtAl-0.3-A) was prepared by impregnation of γ-Al₂O₃ spheres using H₂PtCl₆ in 1 M HCl as described in our recent study. The value of specific surface area (S) was measured by N₂ adsorption, while mercury porosimetry was used for the determination of total pore volume (Vₜ) and average pore radius (R) of the support. Their average values are as follows: S = 135 m² g⁻¹; Vₜ = 0.66 cm³ g⁻¹ and R = 8.4 nm. The impregnation of alumina was carried out at 75°C for 1.5-2.0 h. After impregnation the catalyst was washed and dried in air in two steps at 60°C and 120°C for 3 and 2 h, respectively. The catalyst was reduced under hydrogen at 500°C for 4 h. The chlorine content of the catalyst was 1.0 wt%.

0.3 wt% Pt/Al₂O₃ catalyst (PtAl-0.3-B) was provided by Boreskov Institute of Catalysis. Platinum and chlorine content of catalysts was 0.3 and 1.0 wt%, respectively. Surface area (S = 204 m² g⁻¹), pore volume (Vₜ = 0.64 cm³ g⁻¹) and mean pore diameter (dₚ = 15.2 nm) of catalyst were determined by N₂ adsorption. Further characteristics of the catalyst were given in Table 4.

0.35 wt% Pt/Al₂O₃ catalyst (PtAl-0.35) was a reforming-type monometallic catalyst from Engelhard (E-301).

5.0 wt% Pt/Al₂O₃ catalyst (PtAl-5.0) was received from Engelhard (E-4759).

0.17 wt% Pt-0.36 wt% Re/Al₂O₃ catalyst (RePtAl-0.17) was received from Petroleum Research Center, Tripoli, Libya.

0.21 wt% Pt-0.34 wt% Re/Al₂O₃ catalyst (RePtAl-0.21) was received from Petroleum Research Center, Tripoli, Libya.

5.0 wt% Pt/C catalyst (PtC-5.0) was prepared by conventional impregnation of the functionalized activated carbon with an aqueous solution of H₂PtCl₆ and then was dried at 120°C overnight. A commercial granular activated carbon derived from a pit of peach (GA-160 from Carbonac) with a final particle size between 100 and 140 mesh was used. This support was purified, functionalized with HNO₃, and then dried according to the technique described elsewhere. The textural properties of the activated carbon were only slightly modified by the functionalization treatment with HNO₃ (S_HET = 876 m² g⁻¹ and V_micropore = 0.29 cm³ g⁻¹). Prior to the anchoring step I, the parent Pt/C catalyst was re-reduced in flowing H₂ at 350°C for 3 h. It should be mentioned, that catalysts supported on
functionalyzed carbon can not tolerate higher reduction temperatures, due to the instability of surface groups of the support above 400°C.\textsuperscript{230,231}

PtGe1-4-Cl\textsubscript{1} series of catalysts were prepared by conventional impregnation of the Pt/C catalyst with a solution of GeCl\textsubscript{4}. The impregnation was carried out at 25°C for 6 h, using a volume of impregnation solution/mass of support ratio of 30 ml g\textsuperscript{-1}, and stirring rate of 600 rpm.

1.7 wt\% Pd/SiO\textsubscript{2} catalyst (PdSi-1.7) was prepared by ion exchange using [Pd(NH\textsubscript{3})\textsubscript{4}]Cl\textsubscript{2} as a precursor compound and a commercial silica support (Ventron, unit surface area \(S_{BET} = 285\) m\textsuperscript{2} g\textsuperscript{-1}, pore volume \(V_p = 1.06\) cm\textsuperscript{3} g\textsuperscript{-1}, pore diameter \(d_p > 10\) nm).\textsuperscript{223} The silica support dried in air at 150°C for 24 h was ion exchanged with a solution of the palladium compound (2.5 g l\textsuperscript{-1} Pd solution, 30 ml g\textsuperscript{-1} catalyst). After 24 h of ion exchange, the catalyst was washed with diluted NH\textsubscript{3}OH, filtered and dried at 105°C for 24 h. The dried catalyst was reduced in flowing H\textsubscript{2} at 100 and 200°C for 1 and 2 h, respectively. The dispersion of palladium on the silica support measured by CO chemisorption was 23 %. The above Pd content and dispersion value accounts for 5.2 x 10\textsuperscript{13} metal particle m\textsuperscript{-2} silica support.

5 wt\% Pd/C catalyst (PdC-5.0) (Selcat SQ3 powdered and pre-reduced) were obtained from Chinoin. The unit surface area of the carbon support of Selcat catalysts was \(S_{BET} = 1000\) m\textsuperscript{2} g\textsuperscript{-1}, and the dispersion of palladium measured by CO chemisorption was around CO/Pd= 50 %.\textsuperscript{223} Prior to the activity test, catalyst was pretreated in nitrogen at 150°C for 1 h followed by treatment in a hydrogen atmosphere at 200°C for 2 h. The catalyst was then cooled to room temperature under H\textsubscript{2} flow.

1 wt\% Rh/SiO\textsubscript{2} catalyst (RhSi-1.0) was prepared by impregnation of SiO\textsubscript{2} (BASF D11-11, 20–40 mesh, surface area \(S_{BET} = 136\) m\textsuperscript{2} g\textsuperscript{-1}, pore volume \(V_p = 1.34\) cm\textsuperscript{3} g\textsuperscript{-1}) with aqueous solutions of RhCl\textsubscript{3} x 3H\textsubscript{2}O (Fluka).\textsuperscript{224} The silica was impregnated with an aqueous solution containing Rh, dried at 110°C for 12 h, and calcinated at 400°C during 2 h. Before characterization or catalytic testing, the samples were reduced in \textit{in situ} in H\textsubscript{2} flow (50 cm\textsuperscript{3} min\textsuperscript{-1}) at 500°C for 2 h.

1 and 5 wt\% Rh/Al\textsubscript{2}O\textsubscript{3} catalysts (RhAl-1.0 and RhAl-5.0, respectively) were prepared by impregnating γ-Al\textsubscript{2}O\textsubscript{3} support (Degussa P110 C 1, surface area 100 m\textsuperscript{2} g\textsuperscript{-1}) with the solutions of RhCl\textsubscript{3} x 3H\textsubscript{2}O (Fluka) to yield a nominal 1 and 5 wt% metal.\textsuperscript{225} The impregnated powders were dried at 100°C. Before any measurements, the catalysts were oxidized for 30 min and reduced for 1 h at 400°C \textit{in situ}. After oxidation and reduction the samples were cooled to the room temperature in flowing H\textsubscript{2}.

4 wt\% Rh/Al\textsubscript{2}O\textsubscript{3} catalyst (RhAl-4.0) was received from Air Products & Chemicals Co.

5.0 wt\% Rh/MgO catalyst (RhMg-5.0) was prepared by vigorous stirring of high surface area magnesia support (\(S_{BET}= 252\) m\textsuperscript{2} g\textsuperscript{-1}) with the solutions of RhCl\textsubscript{3} x 3H\textsubscript{2}O (Fluka) in distilled water.\textsuperscript{226} After 1 h the colorless aqueous phase was removed on a rotary evaporator at 40°C. After drying in vacuum oven at 100°C for 15 h the resulting beige solid were first dried under N\textsubscript{2} at 150°C for 0.5 h and then reduced in flowing H\textsubscript{2} at 300°C for 3 h.

1.77 wt\% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst (RuAl-1.77) was prepared by contacting ruthenium acetyl-acetonate (Ru(acac))\textsubscript{3}, Heraeus) in toluene solution with γ-Al\textsubscript{2}O\textsubscript{3}, (Rhone Poulenc, particle size 62–125 μm, surface area 220 m\textsuperscript{2} g\textsuperscript{-1}) for several hours.\textsuperscript{227} After drying under vacuum at 60°C the resulting solids were first dried under N\textsubscript{2} at 200°C and then reduced in flowing H\textsubscript{2} at 400°C for 2 h.

5 wt\% Ru/Al\textsubscript{2}O\textsubscript{3} catalyst (RuAl-5.0) was received from Air Products & Chemicals Co.

4.3. The Controlled Surface Reactions with SnR\textsubscript{4}

We have developed a two steps method to introduce modifier onto supported metal catalysts using CSRs.\textsuperscript{109,215} The two main steps are as follows: (i) anchoring reaction (step I, which takes place only in the presence of a solvent), and (ii) decomposition of SOMS formed in H\textsubscript{2} or O\textsubscript{2} atmosphere (step II).

4.3.1. Tin anchoring step I

4.3.1.1. Tin anchoring in the stirred tank reactor

In this preparation method flow reactors are used both for the catalyst pretreatment and decomposition of formed SOMS. Prior to the anchoring step I, a known amount of parent monometallic catalyst (generally W\textsubscript{cat}= 1 g) is re-reduced in a hydrogen atmosphere. The temperature of catalysts pretreatment is in the range of t\textsubscript{pret}= 200-500°C, depending on the type of the metal and the support. After that, the catalyst is cooled down to room temperature in pure hydrogen, followed by purging with oxygen free pure argon for 0.5 h to remove physisorbed hydrogen. In the next step, the sample is introduced into the reactor without any contact with air.
The tin anchoring step I is usually carried out in a three-neck stirred glass reactor equipped with gas and liquid sampling.\textsuperscript{215,216} Three reactors with total volume 52, 74 and 123 cm\textsuperscript{3} have been used.

The tin anchoring step I, i.e. the reaction between tin organometallic compound and hydrogen adsorbed on the active metal was investigated under argon atmosphere in deoxygenated solvent (generally 10 cm\textsuperscript{3}) introduced into the reactor via a syringe. The temperature of the reactor is maintained at desired temperature (usually T\textsubscript{r} = 50\textdegree C) by thermostat. In selected experiments, the influence of the reaction temperature on tin anchoring step I was investigated in the range T\textsubscript{r} = 25-65\textdegree C. Upon achieving the required reaction temperature (after ca. 10 min of stirring), reaction was started by injection of the desired amount of tin organometallic compound. The Sn\textsubscript{A}/Pt\textsubscript{a} ratio was varied in the range of 0.05-35. It should also be mentioned that, in present study, the duration of tin anchoring step I was sufficiently enhanced comparing to that used in earlier studies.\textsuperscript{109}

These experimental conditions were used for the preparation of catalysts in the presence of adsorbed hydrogen (in other words, in the absence of gas-phase H\textsubscript{2}). In case of the catalyst preparation in the presence of excess H\textsubscript{2}, the inert atmosphere (Ar) was replaced by H\textsubscript{2}.\textsuperscript{215,216} For the preparation of the catalysts with addition of oxygen during tin anchoring step I, the Sn anchoring was started in argon atmosphere; after 40-50 min of the reaction a small amount of O\textsubscript{2} (usually 20 cm\textsuperscript{3} g\textsuperscript{-1} cat) was added into the reactor and the tin anchoring was continued.\textsuperscript{215,216}

In this approach the tin anchoring process was monitored by GC analysis by measuring the amount of hydrocarbons formed as well as by determining the decrease of the concentration of tetraalkyl tin in the solution.\textsuperscript{215,218}

However, the decrease of the concentration of SnR\textsubscript{4} in the solution is due to both the tin anchoring reactions and the adsorption of tetraalkyl tin onto the support. Although the latter process is much slower then tin anchoring, therefore it cannot be neglected, especially when high initial tin concentration is used. The amount of adsorbed SnR\textsubscript{4} was determined from the washing solutions collected after the first and second washing cycles with an aromatic solvent.

The amount of anchored tin calculated from the concentration change of SnR\textsubscript{4} in the liquid phase was defined as Sn\textsubscript{anch} = (Sn\textsubscript{0}) - (Sn\textsubscript{final} - Sn\textsubscript{ads}), where Sn\textsubscript{0} is the amount of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} introduced, Sn\textsubscript{final} is the amount of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} measured in the liquid phase at the end of tin anchoring, and Sn\textsubscript{ads} is the amount of adsorbed SnR\textsubscript{4} determined from the washing solutions.

After tin anchoring step I, prior to the decomposition of SOMS formed, the catalyst was washed at 50\textdegree C four times with deoxygenated solvent used in anchoring reaction to remove adsorbed tetraalkyl tin compound. The adsorbed solvent was removed by washing three times with n-hexane at the same temperature. In the subsequent washing with n-hexane the amount of tetraalkyl tin in the solution was below the detection limit. The washing procedure is partly accomplished in the above glass reactor and partly in a Schlenk-type filter connected to the vacuum line. The former has also been used to dry the catalysts under vacuum (at 5 Torr) at 50\textdegree C for 1 h to remove the trace of solvents used in the previous washing steps.

The washing procedure allowed us to remove the adsorbed tin organic compound from the support even upon using extremely high initial Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} concentrations ([Sn\textsubscript{0}] = 28 M x 10\textsuperscript{-2}). The above procedure prior to the decomposition experiment required 2 h. During the above procedure special care was taken to avoid the contact of surface organometallic species with air.

Tin anchoring step I was monitored by determining the amount of hydrocarbons by GC and a 3 m long Al\textsubscript{2}O\textsubscript{3} column (inner diameter: 3 mm) operated at 100\textdegree C. A correction was done for the amount of hydrocarbons dissolved in the solvent used. The analysis of the liquid phase for tetraethyltin during anchoring step I was accomplished by GC at 160\textdegree C using a 4 m long Chromosorb WAW-DMCS column (inner diameter: 3 mm) coated with 10 wt\% Silicone DC 410.

It is necessary to mention that upon using different types of tin and germanium organometallic compounds the above procedure was only slightly altered. These changes mainly concerned the atmosphere, temperature (T\textsubscript{r}) and the duration (\texttau\textsubscript{r}) of the anchoring step I.

### 4.3.1.2. Tin anchoring in the circulation reactor

For the “one-pot” catalyst modification a column type reactor has been chosen.\textsuperscript{212} During pretreatment procedures and decomposition of SOMS formed this reactor was used as a continuous-flow gas reactor, while during tin anchoring and washing as a circulation type fix-bed liquid phase reactor. In the latter mode the solution of tetraethyltin was circulated using of a pump.
The reactor-setup is shown in Scheme 4. The reactor set-up had two parts: a circulation reactor (I) and a liquid handling vessel (II). The reactor had an inner diameter of 50 mm. The length of the reactor was chosen to modify maximum 250 g of supported catalyst. In this study results of the modification of 120 g catalyst in one experiment will be demonstrated. The total volume of solvent used in tin anchoring process was 540 ml in each experiment. The bottom of the reactor was filled with quartz spheres. The free gas volume above the liquid phase was 100 cm$^3$. The circulation reactor (I) was equipped with inlet and outlet ports both for gases and the liquid. An electric oven was used to heat the circulation reactor up to 500°C. The glass tube located in the center of the reactor was used for the removal of the solution from the reactor and its forwarding to the circulation pump. The attached gas manifold allowed to introduce argon, hydrogen, oxygen or air into (I), and connect (I) to the vacuum line. The liquid handling vessel (II) was used to prepare the solution applied for the washing procedure. Vessel (II) was connected to a circulation type bath heater and was also equipped with an argon gas purge to remove trace of dissolved oxygen from the solvents used.

Scheme 4. The scheme of the circulation reactor setup used for the modification of parent catalyst with tetraalkyl tin compounds. I - Circulation reactor, II - solvent handling vessel. 1- Electric oven, 2-catalyst bed, 3- quartz spheres, 4- gas volume, 5- septum, 6- thermocouple, 7- effluent tube, 8- quartz filter, 9- septum, 10- argon gas-diffuser, 11- washing solution, 12- heating mantle, 13- septum, 14- circulation pump, 15- inlet, 16- gas outlet, 17- liquid drain.

Prior to the tin anchoring step I, the parent 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$^{-1}$ for 2 h. After conditioning the catalyst bed was wetted with the solvent and hydrogen bubbled through the reactor for additional 0.5 h.

The modification started by injection of appropriate amount of Sn(C$_2$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. Reactor (I) was also equipped with a drain valve to replace the solutions used both for the modification and the washing procedure. Both the upper part of the reactor and its bottom, as well as all of the glass tubes connecting the reactor and the circulating pump were insulated to prevent substantial cooling of the circulating solution.

It is necessary to mention that the result of blank experiment with parent catalyst using standard preparation procedure and highest reaction temperature ($T_r$= 65°C) but without injecting the tin precursor compound unambiguously confirmed the lack of any sintering of the Pt particles during the modification.

The preparation of catalysts with high tin content requires high excess of Sn(C$_2$H$_5$)$_4$ in the solution. However, the use of high concentration of Sn(C$_2$H$_5$)$_4$ should be avoided as it can result in a concentration gradient of anchored tin along the catalyst bed. For this reason the calculated amount of Sn(C$_2$H$_5$)$_4$ used for anchoring was divided into equal portions and injected into the reactor during equal periods of time in the 0$^{th}$, 60$^{th}$ and 120$^{th}$ minute.
The amount of anchored tin calculated from the concentration change of Sn(C\(\text{2}\)H\(\text{5}\)H\(\text{5}\))\(\text{4}\) in the liquid phase was defined as Sn\(_{\text{anch}}\) = (N x Sn\(_{0}\)) - (Sn\(_{\text{final}}\)) - (Sn\(_{\text{ads}}\)), where Sn\(_{0}\) is the amount of Sn(C\(\text{2}\)H\(\text{5}\)H\(\text{5}\))\(\text{4}\) introduced per one injection, N is number of injections, Sn\(_{\text{final}}\) is the amount of Sn(C\(\text{2}\)H\(\text{5}\)H\(\text{5}\))\(\text{4}\) measured in the liquid phase at t= 250 min after anchoring reaction, and Sn\(_{\text{ads}}\) is the amount of adsorbed Sn(C\(\text{2}\)H\(\text{5}\)H\(\text{5}\))\(\text{4}\) determined from the washing solutions.

The type of solvents used, the temperature (T,) and the duration (τ,) of tin anchoring, the amount of tetraethyltin introduced per one injection and N is number of injections, were the variable experimental parameters in this study.218,232

4.3.2. Decomposition of Soms (step II)

The decomposition of surface organometallic species (SOMS) (step II) is accomplished by using Temperature Programmed Decomposition (TPD) technique using both reductive (hydrogen) and oxidative (air or oxygen) atmospheres.233

4.3.2.1. Decomposition of SOMS in reductive atmosphere

When a catalyst is heated under temperature programming in a stream of hydrogen, the decomposition of surface complexes will proceed as a function of the temperature/reactivity relationship of the catalyst. The behavior of the catalyst can be assessed by continuously monitoring the change in the concentration of hydrocarbons evolved during decomposition.

The interpretation of TPD spectra is generally used to analyze the types of SOMS anchored. It is necessary to mention that the maximum of TPD peaks position are sensitive to experimental conditions. The important parameters that have to be optimized in TPD experiments are: (i) flow rate of carrier gas (\(\vartheta_{\text{flow}}= 30 \text{ cm}^3 \text{ min}^{-1}\)); (ii) heating rate \(\beta = d\text{T}/d\text{t} = 5^\circ\text{C min}^{-1}\) (\(\beta\)); (iii) signal intensity. An in-house standardization technique was applied for the calculation of the amount of the hydrocarbons formed.109

The temperature range used in TPD experiments was 25 – 350°C. The products of decomposition (C\(\text{2}\)H\(\text{6}\) and C\(\text{2}\)H\(\text{4}\) or CH\(\text{4}\)) were analyzed by GC (see details above) by periodical analysis of gas phase.

The TPD peaks were numerically integrated. The integrated values were used to calculate the material balance of tin anchoring. No loss of tin was observed during the TPD experiments. However, if the washing procedure was omitted (or insufficient), desorption of SnR\(_4\) from the support was observed during the TPD experiment. After the decomposition the tin content of the modified catalysts was determined by Atomic Absorption Spectroscopy (AAS) and was compared with the amount of tin calculated from the overall material balance of tin anchoring. The experimental error of the AAS measurements was 3 %.

The series of TPD curves obtained in step II were deconvoluted.215,216 The presence of different forms of anchored SOMS, with different extent of dealkylation and different environment anchored both onto metal particles and support reveals at least nine peak maxima around 20°C, 50°C, 80°C, 110°C, 140°C, 170°C, 200°C, 230°C and 260°C. The reproducibility of the position of peak maxima and the half width of each deconvoluted TPD peaks were in the range of ±6° and 12°C, respectively. The stepwise appearance of new decomposition peaks was used in the consecutive deconvolution procedure. The position of TPD peaks was fixed for the subsequent deconvolution. Suggesting a Gaussian form for all individual TPD peaks, the heights of the peaks were calculated.215,216

In order to obtain reproducible results in TPD experiments after the formation of SOMS in anchoring step I the following new measures were done: (i) removal of unreacted SnR\(_4\) adsorbed onto the support by careful washing procedure; (ii) using the same amount of sample in each series of experiments compared (W\(_{\text{cat}}\approx 0.4\) g), (iii) introduction of the sample containing SOMS into a continuous-flow gas reactor under an inert atmosphere; (iv) decomposition of the above surface complex immediately after the preparation. It should be mentioned that in our earlier studies the TPD experiments were carried out next day after the preparation of SOMS.109 Due to this fact the minor contamination of samples containing SOMS by air could not be avoided.

4.3.2.2. Decomposition of SOMS in oxidative atmosphere

The decomposition of SOMS formed was accomplished by TPD technique using air or oxygen. The use of oxidative atmosphere in the decomposition of SOMS formed has been described in our
recent studies. The analysis of CO\(_2\) during the TPD in oxidative atmosphere was carried out by GC using a column filled with activated carbon (length: 1 m; inner diameter: 3 mm).

The flow rate of dry air (or oxygen) during the TPD run was 30 ml min\(^{-1}\) and the heating rate was \(\beta = \frac{dT}{dt} = 5^\circ\text{C min}^{-1}\). After raising the temperature up to 100°C the catalyst was kept at this temperature for 1 h. In the next step the catalyst was heated up to 200°C (heating rate 5°C min\(^{-1}\)) and kept at this temperature for additional 1 h. In the final step the catalyst was heated up to 350°C and maintained at this temperature for one more hour. The catalysts prepared in this way were cooled to room temperature in dry air.

### 4.3.3. Calculation of the overall material balance of tin anchoring

The amount of hydrocarbons formed in step I and II, \(n^I\), mol g\(_{\text{cat}}^{-1}\) and \(n^II\), mol g\(_{\text{cat}}^{-1}\), respectively) allowed to obtain full material balance of tin (or germanium) anchoring. In step I a correction was done for the amount of hydrocarbons dissolved in the solvent used. The amount of tin calculated in this way had a good agreement with the amount of tin determined by AAS.

The material balance allowed us to calculate the value of \(x\) (\(x = 4n^I/(n^I + n^II)\)) (see reaction (2.8)). In this way the stoichiometry of tin anchoring reaction could be determined, i.e. the amount of alkyl groups reacted per one tin atom in the anchoring step I. Further details on the preparation and analysis can be found elsewhere.

### 4.3.4. Computer modelling

The computer modelling was performed using the MSI: InsightII program package. The optimized geometries of the SnR\(_n\) and the SnR\(_m\)(O) molecules were determined by the Discover module, using the \textit{esff} forcefield. The relative orientations of the first layer SnR\(_n\) and the second layer SnR\(_m\) molecules and also the positions of the adsorbed molecules (complexes) were set manually. Further details can be found elsewhere.

### 4.4. Catalysts characterization
#### 4.4.1. CO and H\(_2\) chemisorption

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 H\(_2\) for 2 h, evacuated at 7 x 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 H\(_2\) and CO chemisorption measurements are similar and equal to 7-8%.

#### 4.4.2. TPR measurements

TPR experiments were performed in a quartz flow reactor. A thermal conductivity detector was adapted to monitor the H\(_2\) 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 H\(_2\) 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 % H\(_2\)-N\(_2\)) was fed to the reactor with a flow rate of 10 cm\(^3\) min\(^{-1}\). Catalysts were previously calcined “in situ” at 350°C for 2 h.

#### 4.4.3. FTIR measurements

\textit{In situ} infrared spectra were recorded at room temperature using Nicolet Impact 400 FTIR instrument. In the spectral region 2200-1800 cm\(^{-1}\) the resolution was 1 cm\(^{-1}\), however due to the low intensity and the strong broadening the resolution of the bridged CO was in the range of 4 cm\(^{-1}\). The description of the cell and the high vacuum apparatus used can be found elsewhere. Catalyst samples were ground-sieved, pressed onto self-supporting discs and were mounted in the sample holder. The weight of the self-supporting discs was about 2.5–4.0 mg cm\(^{-2}\). The calculated band intensities were corrected for the weight of the sample. The thermal treatment of the sample was accomplished in a heated attachment chamber located above the IR cell. Further details on the experimental set-up and the methods used can be found elsewhere.
FTIR measurements of pyridine adsorption were carried out as described in Ref.\textsuperscript{235} Spectra were recorded on a Nicolet 5PC spectrophotometer. The IR spectrum in the 1400-1700 cm\textsuperscript{-1} region has been determined for pyridine adsorbed on acidic solids. The spectrum of pyridine coordinatively bonded to the surface is markedly different from that of the pyridinium ion. This permits the differentiation of the acid type on the surface of acidic solids. From the frequency shift of one of the bands of coordinately bonded pyridine over that found in the liquid phase, and from the relative retention of the band upon evacuation and heating, a very rough estimation of the strength of surface Lewis sites can be inferred. After dehydrating a disc of sample at 400°C for 3 h, a background spectrum was usually recorded, and then pyridine was admitted. Generally, approximately 0.05 moles (excess) of pyridine was initially admitted, and then the spectrum was recorded after evacuation at various elevated temperatures. All spectra were recorded after cooling the sample to room temperature. The situation when pyridine was pumped out at 150°C indicated that the pyridine was relatively weakly held to the surface sites.

4.4.4. XPS measurements

XPS spectra were acquired with a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer and a Mg Kα 300 W (hv = 1253.6 eV, 1 eV = 1.602 × 10\textsuperscript{-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 H\textsubscript{2} for 2 h at 530°C before being transferred to the analysis chamber. Before recording the spectra, the sample were maintained in the analysis chamber until a residual pressure of 5 × 10\textsuperscript{-8} Pa was reached. The spectra were collected at pass energy of 50 eV. Binding energies (BE) were referred to the C1s 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 %.

4.4.5. Mössbauer spectroscopic measurement

Mössbauer spectra were recorded at 300 and 77 K with a constant acceleration spectrometer using a Ba\textsuperscript{119}SnO\textsubscript{3} source. Details on the experimental set-up and the methods used can be found elsewhere.\textsuperscript{236} All isomer shifts were referred to SnO\textsubscript{2}. A standard least squares minimization routine was used to fit the spectra as a superposition of Lorentzian lines. The catalyst samples were kept in a specially designed glass sample holder sealed under inert gas or vacuum and hold at 77 K.

Samples with different Sn/Pt ratios (ca. 0.5 g) were transferred into a specially designed glass sample holder without any contact with air. The catalyst samples were in situ treated with hydrogen at 200°C and 300°C for 1.5 h in the Mössbauer cell.

4.4.6. EXAFS measurements

The extended X-ray absorption fine structure (EXAFS) measurements were made at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline at the APS. Measurements were made in transmission mode. A cryogenic double-crystal Si(111) monochromator was used in conjunction with an Rh- or Pt-coated mirror to minimize the presence of harmonics for the Pt and Sn edges, respectively.

The sample thickness was chosen to give an absorbance of about 1.0 in the Sn and Pt edge regions: approximately 0.1 g of catalyst. The sample was centered in a 45 × 2-cm, continuous-flow, in situ EXAFS cell fitted with Kapton\textsuperscript{TM} windows. Prior to the EXAFS measurements, the catalysts were heated to various temperatures in a gas mixture conducive to either oxidation (5 v/v % O\textsubscript{2}- He) or reduction (4 v/v % H\textsubscript{2}- He). The EXAFS data were collected at room temperature in the presence of the pretreatment gas.
5. Results and discussion

5.1. Computer modeling of Sn(C$_2$H$_5$)$_3$ and Sn(C$_2$H$_5$)$_2$ moieties anchored onto the platinum cluster

Three-dimensional platinum clusters with Pt (111) plain surface were used for modeling. The size of the cluster is as follows: nine platinum atoms in the diagonal of the lowest hexagonal surface and either two or three layers of platinum at the top. The overall size of this hypothetical metal cluster was 2.2 nm. The calculated ratio of Pt$_{\text{surf}}$/Pt$_{\text{total}}$ for the cluster having three layers of Pt is 0.56, i.e. very close to the H/Pt ratio found by hydrogen chemisorption for 3 wt% Pt/SiO$_2$ catalyst (H/Pt = 0.52, see PtSi-3.0-A catalyst in Table 4).

We have calculated the amount of tin organic moieties with general formula of Sn(C$_2$H$_5$)$_3$ or Sn(C$_2$H$_5$)$_2$ at the top of the above Pt cluster by building up a monolayer of either Sn(C$_2$H$_5$)$_3$ or Sn(C$_2$H$_5$)$_2$. The results of modeling by use of a Pt cluster made from three layers of Pt atoms are shown in Figure 1A and 1B. Figure 1A shows the top view of anchored Sn(C$_2$H$_5$)$_3$, while Figure 1B the side view of anchored Sn(C$_2$H$_5$)$_2$. Further details of the modeling can be found elsewhere.

![Figure 1](image_url)

**Figure 1.** Computer modeling of organometallic moieties anchored onto the platinum cluster. A- Anchoring of SnR$_3$ (top view); B- anchoring of SnR$_2$ (side view).

Table 5. Computer modeling of anchoring Sn(C$_2$H$_5$)$_3$ and Sn(C$_2$H$_5$)$_2$ moieties onto small Pt cluster

<table>
<thead>
<tr>
<th>Number of Pt layers</th>
<th>Pt$<em>{\text{surf}}$/Pt$</em>{\text{total}}$</th>
<th>number of Sn(C$_2$H$_5$)$_3$</th>
<th>number of Sn(C$_2$H$_5$)$_2$</th>
<th>Sn/Pt$_s$ for -Sn(C$_2$H$_5$)$_3$</th>
<th>Sn/Pt$_s$ for -Sn(C$_2$H$_5$)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two</td>
<td>0.68</td>
<td>22</td>
<td>27</td>
<td>0.38</td>
<td>0.47</td>
</tr>
<tr>
<td>Three</td>
<td>0.56</td>
<td>25</td>
<td>30</td>
<td>0.31</td>
<td>0.37</td>
</tr>
</tbody>
</table>

*The size of the Pt cluster is 2.2 nm.

Results of computer modeling indicate that the monolayer of tin organometallic species with general formula of Sn(C$_2$H$_5$)$_3$ or Sn(C$_2$H$_5$)$_2$ over PtSi-3.0-A catalyst can result in Sn/Pt$_s$ ratios between 0.31-0.38 and 0.37 - 0.47, respectively (Sn- amount of tin anchored, Pt$_s$- number of surface Pt atoms) (see Table 5).

5.2. Molecular design of new type of catalysts prepared via tin anchoring technique.

**Formation of multilayer coverage of tin organometallic species**

Our aim was to find the modes and ways to increase the amount of tin introduced directly to the parent metal. Consequently, the increase of the Sn/Pt$_s$ ratios in the bimetallic catalysts required the creation of new anchoring sites for tetraalkyl tin. We came to the conclusion that for exclusive introduction of tin onto the parent metal only the PSC can be used as a new anchoring site. However, the new approach required the creation of coordinative unsaturation in PSC. The key issue was to find proper reaction condition to alter the stoichiometry $x$ of PSC formed, and force tetraalkyl tin to anchor onto the second layer, as shown in Scheme 5. The fate of the PSC formed during step I strongly depends on (i) the active metal content, (ii) the metal dispersion, (iii) the type of the support, (iv) the type and the amount of tin precursor compound introduced (Sn$_0$/M$_i$ ratio), (v) the solvent used,
(vi) the presence or absence of excess of hydrogen (vii) the reaction temperature and (viii) duration of tin anchoring reaction.

The high extent of dealkylation of PSC also means high extent of unsaturation, that is the ability of -Sn(C₂H₅)₂ moieties to donate or accept electrons. The Coordinatively Unsaturated Primary Surface Complexes (CUPSC) with general formula -SnR₄₋ₓ (where x > 1) are considered to be one of these new sites, which can be used to anchor additional amount of Sn(C₂H₅)₄, provided that the concentration of tetraalkyl tin in the reaction mixture is high enough. We proposed that these CUPSC can be considered as donors, while Sn(C₂H₅)₄ as an acceptor of electrons. The surface chemistry involved in the formation of multilayered surface organometallic species anchored exclusively onto the silica supported platinum was first described by us in 1998.

Scheme 5. Formation of new anchoring sites over supported Pt catalysts.

The material balance of tin anchoring in an Ar atmosphere indicates that in the presence of adsorbed hydrogen under monolayer coverage of platinum by PSC the average value of x is around 1.5 (see the value of x in Table 6 (experiment I-1)). This fact pointed out that Pt nanoclusters are covered by -SnR₃ and -SnR₂ moieties formed almost in 1:1 ratio.

In the presence of excess of H₂ both the rate of tin anchoring and the values of x are much higher than in its absence (compare w₀ and x values in Table 6 for experiments II-1-4 and I-1-5). These facts indicate that excess of hydrogen strongly influences both the rate of tin anchoring and the amount of alkyl groups reacted. Consequently, in excess of H₂ the extent of coordinative unsaturation of Sn-alkyl entities increases, that is, in this way higher Sn/Ptᵣ ratios can be obtained. As shown in Table 6 (see experiment II-4), Sn-Pt/SiO₂ catalysts with exclusive formation of tin-platinum interaction and high Sn/Ptᵣ ratio up to 2:1 were prepared. This finding was further supported by Mössbauer spectroscopy measurement (see Section 5.3.7).

The possible formation of “naked” tin (x=4) in step I should also be mentioned. This form of tin can migrate into the bulk of platinum and form alloy-type species even during the tin anchoring step I.

Results obtained in the presence of added oxygen also indicate that high Sn/Ptᵣ ratios can be reached even at relatively low initial Sn₀/Ptᵣ ratios. In argon atmosphere and in the absence of oxygen in order to reach Sn/Ptᵣ= 1.6 the Sn₀/Ptᵣ ratio should be 33.5, while in the presence of oxygen the Sn/Ptᵣ ratio 2.0 was reached already at Sn₀/Ptᵣ= 6.7 (compare experiments I-4 and III-2 in Table 6).
Further details of surface reactions leading to the formation of either mono- or multilayered SOMS over Pt/SiO$_2$ catalyst will be given below (see Section 5.3.).

These data indicate that the Sn/Pt$_s$ ratio can be increased substantially under following conditions applied in tin anchoring: (i) increased initial concentration of Sn(C$_2$H$_5$)$_4$ (Sn$_0$/Pt$_s$); (ii) increased reaction time; (iii) increased reaction temperature ($T_r$); (iv) carrying out anchoring reaction in the presence of excess of hydrogen; (v) addition of trace of O$_2$ during tin anchoring step I.

Table 6. Formation of Sn-Pt/SiO$_2$ catalysts with high Sn/Pt$_s$ ratio in the presence of adsorbed hydrogen (I), in the presence of excess of H$_2$ (II) and in the presence of trace amount of O$_2$ (III). Selected results.

<table>
<thead>
<tr>
<th>Exp. N°</th>
<th>Sn$_0$/Pt$_s$</th>
<th>$\tau$, min</th>
<th>$T_r$, °C</th>
<th>$w_0$</th>
<th>$x$</th>
<th>Sn/Pt$_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>1.6</td>
<td>150</td>
<td>50</td>
<td>0.4</td>
<td>1.4</td>
<td>0.39</td>
</tr>
<tr>
<td>I-2</td>
<td>1.6</td>
<td>150</td>
<td>60</td>
<td>2.1</td>
<td>1.7</td>
<td>0.80</td>
</tr>
<tr>
<td>I-3</td>
<td>5.3</td>
<td>150</td>
<td>50</td>
<td>1.4</td>
<td>1.3</td>
<td>0.80</td>
</tr>
<tr>
<td>I-4</td>
<td>33.5</td>
<td>150</td>
<td>50</td>
<td>3.5</td>
<td>1.0</td>
<td>1.64</td>
</tr>
<tr>
<td>I-5</td>
<td>9.2</td>
<td>420</td>
<td>50</td>
<td>2.1</td>
<td>1.0</td>
<td>2.35</td>
</tr>
<tr>
<td>II-1</td>
<td>0.6</td>
<td>120</td>
<td>50</td>
<td>0.6</td>
<td>3.3</td>
<td>0.58</td>
</tr>
<tr>
<td>II-2</td>
<td>1.3</td>
<td>120</td>
<td>50</td>
<td>3.2</td>
<td>3.0</td>
<td>0.82</td>
</tr>
<tr>
<td>II-3</td>
<td>4.1</td>
<td>120</td>
<td>50</td>
<td>8.6</td>
<td>2.3</td>
<td>1.68</td>
</tr>
<tr>
<td>II-4</td>
<td>8.8</td>
<td>210</td>
<td>50</td>
<td>8.9</td>
<td>2.2</td>
<td>2.05</td>
</tr>
<tr>
<td>III-1$^a$</td>
<td>1.0</td>
<td>280</td>
<td>50</td>
<td>0.3$^b$</td>
<td>0.7</td>
<td>1.01</td>
</tr>
<tr>
<td>III-2$^a$</td>
<td>6.7</td>
<td>280</td>
<td>50</td>
<td>1.7$^b$</td>
<td>0.9</td>
<td>2.01</td>
</tr>
<tr>
<td>III-3$^a$</td>
<td>8.8</td>
<td>280</td>
<td>50</td>
<td>2.1$^b$</td>
<td>1.1</td>
<td>2.35</td>
</tr>
<tr>
<td>III-4$^a$</td>
<td>8.5</td>
<td>420</td>
<td>50</td>
<td>2.0$^b$</td>
<td>0.7</td>
<td>2.93</td>
</tr>
</tbody>
</table>

$^a$ Addition of 20 cm$^3$ g$^{-1}$ O$_2$ in the 40th minute of tin anchoring; $^b$ initial rates measured before addition of O$_2$.

Catalyst: PtSi-3.0-A. Further abbreviations used have been given in Section 7.

According to our earlier studies, surface reactions involved in the multilayer tin coverage, which take place in the presence of high excess of tetraalkyl tin can be written as follows:

\[
P tH_{ads} + SnR_4 \rightarrow Pt-SnR_3 + RH \quad (5.1)
\]

\[
P t-SnR_3 + x H_{ads} \rightarrow Pt-SnR_{(3-x)} + x RH \quad (5.2)
\]

\[
P t-SnR_{(3-x)} + n SnR_d \rightarrow Pt-\{SnR_{(3-x)}-(SnR_d)_n\} \quad (5.3)
\]

\[
P t-\{SnR_{(3-x)}-(SnR_d)_n\} + n y H_{ads} \rightarrow Pt-\{SnR_{(3-x)}-(SnR_{(4-y)})_n\} + n y RH \quad (5.4)
\]

\[
P t-\{SnR_{(3-x)}-(SnR_{(4-y)})_n\} + m SnR_d \rightarrow Pt-\{SnR_{(3-x)}-(SnR_{(4-y)})_n-(SnR_d)_m\} \quad (5.5)
\]

MLSC

Reactions (5.1) and (5.2) describe the formation of PSC and CUPSC, respectively. The CUPSC interacts with Sn$_d$ used in large excess (reaction (5.3)) resulting in Surface Species in the Second Layer (SSSL). 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 (5.4)), which can also interact with tetraalkyl tin (reaction (5.5)). The net result is the formation of slab-like Multilayered Surface Complex (MLSC) on the Pt surface. Upon systematic variation of reaction conditions it is possible to prepare various catalysts containing partially dealkylated Pt-$\{SnR_{(3-x)}-(SnR_{(4-y)})_n\}$ units with desired values of $x$, $y$ and $n$. It is necessary to mention that reactions (5.1)-(5.5) take place only in the presence of a solvent.

This anchoring process is presented in Scheme 6, which shows two routes for tin anchoring. Route 1 takes place in excess of hydrogen, while route 2 in excess of tetraalkyl tin. According to our
experience Route 1 is more preferable than route 2, as it provides high tin coverage and strongly
decreases the amount of tin introduced onto the support either by adsorption or side reaction with the
involvement of the surface OH groups of the support. \cite{215,216}

![Scheme 6. Scheme of tin anchoring in the presence of excess of hydrogen (route 1) or excess of tin
tetraalkyl (route 2).](image)

**Figure 2.** Computer modeling of the formation of the second layer of tin organic complex. **A**-
Anchoring of SnR₄ onto -SnR₃ (top view); **B**- anchoring SnR₄ onto -SnR₂ (side view). Pt - blue; Sn -
green; R in -SnR₃ in the first layer - dark blue; R in -SnR₂ in the first layer - yellow; R in SnR₄ in the
second layer - pink.

The formation of the second layer in the form of -Sn(C₂H₅)₄ at the top of PSC containing surface
species with general formula of -Sn(C₂H₅)₃ and -Sn(C₂H₅)₂ is shown in Figure 2A and 2B,
respectively. The above figures show that the second layer of tin organic moieties can be formed both
at the *top* and *side* sites of platinum. However, there is a strong difference between the above two
forms. The second layer at the *top site* can interact with hydrogen formed on the platinum sites, while
the second layer on the *side site* can also interact with spilled-over hydrogen available on the support.

Similar surface species have been suggested by Didillon *et al.* \cite{173} When Rh/SiO₂ catalyst was
selectively modified with Sn\((n\)-C₄H₉\)_₄, the presence of similar surface structures \((\text{Rh})₂\text{Sn}[\text{Sn}(n-
C₄H₉)_₃]₂\) have also been suggested for the tin coverages between 0.7< Sn/Rh< 1. \cite{173} The presence of
the majority of the Sn atoms (75 %) in an oxidized form (Sn°° and/or Sn°) and the rest in the
zerovalent state (ca. 25% of Sn°) evidenced by Mössbauer and XPS experiments was in agreement
with proposed surface structure. \cite{238} However it is necessary to emphasize that in this study the
exclusive modification of the Rh by Sn was achieved only when the amount of Sn\((n\)-C₄H₉\)_₄ introduced
was less than one monolayer (Sn/Rh< 1). For a Sn/Rh ratio higher than 1.5, a weak \(^{13}\)C CP-MAS
solid-state NMR signal corresponding to \( \equiv \text{SiOSn}(n\text{-C}_4\text{H}_9)_3 \) was always observed on the silica surface. From above results the following conclusion has been done: “above a certain value, which is probably close to the saturation of the metallic surface, the organotin complex then reacts or migrates onto the silica support”.\(^{117}\)

In two years after our first publication concerning the formation of multilayered SOMS, the existence of similar two-layered structures have also been demonstrated for \( \text{SiO}_2 \) supported Sn-Pt catalysts by Ferretti et al.\(^{202}\) Based on the observed global stoichiometry and the shape of the kinetic curves for Sn/Pt < 0.70 at \( T_r = 90^\circ \text{C} \) the formation of an organobimetallic supported phase of the type \( \text{Pt}_3\text{Sn-Sn}(n\text{-C}_4\text{H}_9)_3 \) was proposed (see Scheme 7A), in which tin retained its tetrahedral configuration. It has been assumed that at the beginning, all the \( \text{Sn}(n\text{-C}_4\text{H}_9)_4 \) molecules that react onto supported platinum lose their four \( n \)-butyl groups, giving PtSn sites where \( \text{Sn}^0 \), existing probably in a form of an adatoms. The rest of the tin is fixed on this Pt\( _3\text{Sn} \) phase, forming Sn-Sn bonds, with detachment of one butyl group. When the preparation temperature was 90°C, according to XPS measurements tin was found as \( \text{Sn}^0 \) and ionic tin (\( \text{Sn}^{\text{II,IV}} \)) in similar proportions.\(^{205}\) When the preparation temperature was increased up to \( T_r = 150^\circ \text{C} \) all butyl groups were removed, tin was present as \( \text{Sn}^0 \) adatoms “decorating” and isolating Pt surface atoms (see Scheme 7B). It is necessary to mention that the existence of a Sn-Pt alloy diluting unalloyed Pt atoms was evidenced by EXAFS only after activation of the samples in \( \text{H}_2 \) at 500°C.\(^{203}\) However, even at low Sn/Pt ratios (Sn/Pt= 0.40) the presence of oxidized tin, probably located at the metal-support interface, was always observed after activation of the bimetallic samples in \( \text{H}_2 \) (\( \text{Sn}^0/(\text{Sn}^0+\text{Sn}^{\text{II,IV}}) = 0.67 \)).\(^{117}\)

\[ \text{Scheme 7. Proposed organobimetallic (A) and bimetallic (B) supported phases formed by reaction between Pt/\text{SiO}_2 and Sn(n\text{-C}_4\text{H}_9)_4 at T_r = 90^\circ \text{C} and 150^\circ \text{C}, respectively.}\]

Based on results obtained it was concluded that upon modifying with \( \text{Sn}(n\text{-C}_4\text{H}_9)_4 \) it is impossible to prepare bimetallic catalysts with exclusive Sn-Pt interaction at Sn/Pt ratio higher than unity. It has been proposed that Sn/Pt= 1.4 ratio obtained at \( T_r = 150^\circ \text{C} \) might be attributed to the loss of the control in tin anchoring reaction and appearance of the tin-anchored species on the support, along with the previously mentioned organobimetallic supported phase.\(^{202,239}\)

It is necessary to emphasize that \( \text{Sn}(n\text{-C}_4\text{H}_9)_4 \) has low reactivity, that is why high temperature during tin anchoring is required. However, the use of high temperature (\( T_r > 90^\circ \text{C} \)) give possibility for selective modification only at very low initial tin concentration because of the increased competition between the metallic active sites and the OH groups of the support. In spite of that strong evidences of the existence of the above mentioned two layered structures upon modifying with \( \text{Sn}(n\text{-C}_4\text{H}_9)_4 \) were presented, the tetrabutyltin, as precursor compound, is not a proper choice for the preparation of the catalysts with high Sn/Pt ratios.

Any new approach aimed to increase the tin coverage requires creation of new sites for tin anchoring. According to results of our studies the addition of trace of \( \text{O}_2 \) led to the immediate formation of ethylene that is the surface chemistry of tin anchoring was altered.\(^{145,221,240,241}\) New types of tin anchoring sites were created when both PSC and CUPSC were mildly oxidized to Oxidized Surface Organometallic Complex (OSOC), with a general formula of -Sn\( _a\text{R}_b\text{O}_c \).\(^{215,216}\) In this case as shown in Scheme 8 the lone pair of electrons of the oxygen atom in -Sn\( _a\text{R}_b\text{O}_c \) moieties are involved in the tin anchoring. As far as the number of anchoring sites increased further, the amount of tin anchored also significantly increased.\(^{215,216}\)
Scheme 8. Tin anchoring in the presence of trace amount of oxygen (route 3).

It has been proposed that in the presence of oxygen the build-up of the second and subsequent layers can be written as follows:\textsuperscript{216}

\[
\text{Pt-Sn}_a(C_2H_5)_bO_c + y \text{Sn(C}_2H_5)\text{a}_4 \rightarrow \text{Pt-Sn}_a(C_2H_5)_bO_c\{\text{Sn(C}_2H_5)\text{a}_4\}_y \quad (5.6)
\]

In reaction (5.6) Oxygen-Containing Multilayer Species (MLSOC) are formed, which instantaneously react with the formation of ethylene, water and MLSC (II) according to reaction (5.7). The approach using trace amount of oxygen during tin anchoring (see Scheme 8) will be denoted as route 3.\textsuperscript{216}

The analysis of Figures 2 and 3 indicates that the decomposition of tin organic moieties in the second and, probably, in the third layer can result in at least two different bimetallic Sn-Pt species. In the first species, the tin-platinum interaction is not disturbed by any other interaction. These species

---

**Figure 3.** Computer modeling of the formation of the MLSOC. Anchoring site: -SnR\textsubscript{2}(O). Pt - blue; Sn - green; Oxygen - red; R in the first layer of -SnR\textsubscript{2}(O) - yellow; R in SnR\textsubscript{4} in the second layer - pink.
were formed from organometallic moieties located at the top site of Pt. The organometallic moieties formed at the side site of platinum upon increasing either the size or the number of layers can also interact with the platinum-support interface. In this case, the formed bimetallic surface species still have direct Sn-Pt interaction, but this interaction is slightly disturbed either by the support or the support-metal interface. It is not excluded that the above interaction is reflected by one of the high-temperature TPD peaks.

Consequently, the main requirements for the formation of multilayered SOMS are the creation of coordinative unsaturation in PSC and the use of high excess of SnR₄. However, the use of high initial SnR₄ concentration may lead to the increase of the probability of tin introduction onto the support. As it has already been mentioned earlier in our and other studies, in this side reaction surface OH groups and/or spilled over hydrogen are involved. This reaction can be written as follow:

\[ x \text{Surf-OH} + \text{SnR}_4 \rightarrow \text{Surf-O}_x\{-\text{SnR}_{4-x}\} + x \text{RH} \]  
\[ \text{OMSAS} \]  

Surface reaction (5.8) 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 as shown in Scheme 9.

![Scheme 9](image)

In case of zeolites, due to their strong acidic character, the contribution of surface reaction (5.8) can be very pronounced. As emerges from our results the reactivity of the H-MOR (H-Mordenite) support towards SnR₄ (R= CH₃, C₂H₅) is higher in the presence of Pt than in its absence. This phenomenon has been attributed to the involvement of spillover hydrogen in the tin anchoring process. However, it has been demonstrated that at coverage under the monolayer (Sn/Pt < 0.5) the modification of Pt/H-MOR with tin was selective (exclusive formation of Sn-Pt interaction).

It is noteworthy that under identical experimental conditions the surface OH groups of alumina support showed higher reactivity towards tin precursor compound than those of the silica. However, it was shown that under properly chosen reaction conditions ([Sn]₀ = 0.05 M, T= 40°C) even in the case of Pt/Al₂O₃ catalysts the formation of tin species anchored onto platinum is exclusive up to Sn/Ptₙ = 1.4-1.6. In this respect one important issue has to be mentioned. The increase of the concentration of tetraalkyl tin in the solution leads also to an increased rate of adsorption of tetraethyltin onto the support. Although the adsorbed Sn(C₂H₅)₄ can be washed out from the support by a solvent there is certain rational concentration limit for Sn(C₂H₅)₄ (Sn/Ptₙ = 20). Above this concentration limit the wash out procedure is incomplete, that is certain amount of tetraethyltin remains on the support.

The decomposition of SOMS formed (step II) has been carried out by Temperature Programmed Decomposition (TPD) technique as a gas-solid reaction in the temperature range between 25-350°C. The decomposition of SOMS in a hydrogen atmosphere at high temperature led to the formation of different individual Sn-Pt alloy phases, depending on the Sn/Pt ratio. These Sn-Pt catalysts will be referred to (H) type catalysts. More details on the decomposition of various types of SOMS will be given below.
When the decomposition has been performed in an oxygen atmosphere the surface of platinum is covered by SnO\(_x\) species ((O) type catalysts). Upon subsequent reduction this tin-oxide type species can be partially or fully reduced resulting in alloy type bimetallic nanoparticles. In case of silica support the reduction in a hydrogen atmosphere above 350°C was complete, while on alumina supported platinum part of tin-oxide migrated onto the support.\(^{237,242}\)

5.3. Use of CSRs for modification of 3 wt% Pt/SiO\(_2\) catalyst with Sn(C\(_2\)H\(_5\))\(_4\).

5.3.1. Tin anchoring in the presence of adsorbed hydrogen

5.3.1.1. Influence of the initial tetraethyltin concentration (Sn\(_0\)/Pt\(_s\)) on the of step I

Figure 4 shows the kinetic curves of the formation of ethane in a series of experiments when the initial concentration of tetraethyltin was systematically changed. As emerges from Figure 4 upon increasing the initial concentration of Sn(C\(_2\)H\(_5\))\(_4\) (Sn\(_0\)/Pt\(_s\)) both the initial rate of step I and the amount of hydrocarbons formed increased. High initial concentration of tetraethyltin provides high rates of tin anchoring; however the increase of the concentration of [Sn]\(_0\) has a limit. At high initial concentration of tetraalkyl tin the latter can interact with the OH groups of support, especially in the case of Al\(_2\)O\(_3\) or zeolite. This way the formation of alloy type Sn-Pt nanoparticles is not exclusive.

As seen from Figure 4, the kinetic curves of ethane formation show two distinct parts. In the first 15-20 min, the formation of ethane is fast, which is followed by a relatively slow part, the rate of the reaction decreases almost by a factor of 10, especially at higher Sn\(_0\)/Pt\(_s\) ratios. The fast rate part is however maintained up to 35 - 45 % of conversion. At low Sn(C\(_2\)H\(_5\))\(_4\) concentration (Sn\(_0\)/Pt\(_s\) = 0.09), the second part cannot be seen as the reaction has been terminated, due to the total consumption of tetraethyltin. The total consumption means the amount of Sn(C\(_2\)H\(_5\))\(_4\) reacted in step I plus the amount of tetraethyltin weakly adsorbed onto the support. The latter was completely removed by the washing procedure used. Further data related to the rate and material balance of step I obtained at different initial Sn(C\(_2\)H\(_5\))\(_4\) concentrations are summarized in Table 7. Detailed analysis of data in Table 7 will be given in Chapter 5.3.1.3.

### Table 7. General data related to modification of PtSi-3.0-A catalyst with Sn(C\(_2\)H\(_5\))\(_4\) in the presence of adsorbed hydrogen.

<table>
<thead>
<tr>
<th>No</th>
<th>[Sn](_0), M x 10(^{-2})</th>
<th>Sn(_0)/Pt(_s), x 10(^{-6})</th>
<th>(w_{0,s}), x 10(^{-6})</th>
<th>(n_{9,s}), x 10(^{-6})</th>
<th>(n_{C2H4,I}), x 10(^{-6})</th>
<th>(n_{C2H4,II}), x 10(^{-6})</th>
<th>(x)</th>
<th>TOF, (s^{-1} x 10^{-4})</th>
<th>Sn, wt%(^a)</th>
<th>Sn/Pt(_s),(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.09</td>
<td>0.07</td>
<td>6.9</td>
<td>-</td>
<td>11.7</td>
<td>1.48</td>
<td>0.15</td>
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<td>1.01</td>
<td>4.44</td>
<td>2.23</td>
<td>2.35</td>
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\(^a\) Sn content calculated from the overall material balance of tin anchoring;  
\(^b\) Amount of Sn anchored per surface Pt atom calculated using H/Pt= 0.52;  
\(^c\) Duration of tin anchoring step I (\(\tau_r\)): 2 h.

Catalyst re-reduced in H\(_2\) atmosphere at \(T_{red}= 300^\circ\)C for 1 h; catalyst amount: \(W_{cat}= 1\) g; atmosphere of step I: Ar; solvent: benzene; reaction temperature \(T_r= 50^\circ\)C; duration of tin anchoring step I (\(\tau_r\)): 2.5 h.
5.3.1.2. Influence of the type of anchored SOMS on the TPD profile. Tin anchoring in the presence of adsorbed hydrogen

In one of our earlier studies, it has been shown that the TPD profile strongly depends on the Sn/Pt ratios, that is, on the type of anchored surface organometallic entities formed. The “fingerprint” character of the TPD curves has been used for the preliminary characterization of supported Sn-Pt catalysts prepared by CSRs (see Figure 5A-D).

The TPD technique provides an opportunity to differentiate between different forms of SOMS. The higher the temperature of the TPD peak of ethane the stronger the interaction between Sn-C, namely higher is the activation energy for the hydrogenolysis of the Sn-C bond.

The series of TPD curves obtained in step II (see reaction (2.9)) were deconvoluted and numerically integrated. The deconvolution of TPD curves for a various series of Sn-Pt supported catalysts with different tin content resulted in almost similar peak positions for all catalysts with Sn/Pt ratios up to 2.5.

The analysis of the deconvoluted TPD pattern provided further evidences for the formation of different types of anchored SOMS and allowed us to distinguish between PSC, SSSL, MLSC and OMSAS. Depending on the reactivity of anchored SOMS with hydrogen TPD peaks detected at different temperatures correspond to various SOMS having both different extent of dealkylation (stoichiometry) and environment. The starting point in this respect is the suggestion that differences in the TPD profiles are attributed to the decomposition of different types of SOMS anchored onto different sites of active metal or support.

As follows from the general observation in surface organometallic chemistry: the higher the temperature of these TPD peaks the lower the reactivity of the given SOMS. It has to be emphasized that SOMS resulting in a higher temperature peak should have stronger bonds than the Sn-C bonds in PSC. Consequently, the appearance of high-temperature peaks can be attributed to the high thermal stability of Sn-C bonds.

As shown in Figure 5A-D, the decomposition pattern of different SOMS in a hydrogen atmosphere (see reaction (2.9)) showed significant differences depending on the Sn/Pt ratio used for tin anchoring. Experimental evidences indicated that OMSAS has the highest temperature TPD peak (above > 190 - 200°C on silica or alumina) consequently the loss of control of anchoring reaction can easily be monitored by analysis of the TPD pattern of the decomposition of SOMS formed.

As emerges from Figure 5A, the species involved in the formation of monolayer coverage decomposed below 100°C. The increase of the amount of tin anchored up to monolayer coverage
(Sn/Pt = 0.39) leads only to a slight increase of the peak intensities in this temperature range, as shown in Figure 5A.

Figure 5. The influence of the Sn/Pt ratio on the TPD pattern. A- (•), Sn/Pt = 0.25, (Sn/Pt = 0.07); (☐), Sn/Pt = 0.42, (Sn/Pt = 0.12); (■), Sn/Pt = 1.58, (Sn/Pt = 0.39). B- (■), Sn/Pt = 1.58, (Sn/Pt = 0.39); (△), Sn/Pt = 3.01, (Sn/Pt = 0.56); (●), Sn/Pt = 3.2, (Sn/Pt = 0.67); C- (◇), Sn/Pt = 5.28, (Sn/Pt = 0.79); (◇), Sn/Pt = 9.83, (Sn/Pt = 1.15); D- (◇), Sn/Pt = 10.78, (Sn/Pt = 1.33); (□), Sn/Pt = 21.11, (Sn/Pt = 1.58); (◇), Sn/Pt = 33.50, (Sn/Pt = 1.64). Catalyst: PtSi-3.0-A. Conditions of the tin anchoring: atmosphere of step I: Ar; solvent: benzene; reaction temperature T_r = 50°C.

The deconvolution of three TPD curves at coverage under monolayer presented in Figure 5A is shown in Figure 6A-C. The deconvolution of the TPD pattern shows that under monolayer coverage there are only three low temperature peaks (at 20, 50 and 80°C). These peaks are attributed to the decomposition of surface complexes -Sn(C_2H_5)_{4-x} with x = 1-3 (-SnR_3, -SnR_2 and -SnR) anchored onto various Pt sites (kink, corner and plain sites). It is necessary to mention that in sample with exact monolayer coverage (see sample with Sn/Pt = 0.39 in Figure 6C) the appearance of a shoulder around 110°C with very low intensity was observed. This small peak had been assigned to the formation of a new type of surface species, what can be specified as SSSL.

The increase of the Sn/Pt ratio up to 3.2 resulted in broadening of the TPD curve up to 150°C, without showing any further higher-temperature peaks (see Figures 5B and 7A). The TPD peaks around 110 and 140°C, which were not observed at coverage under monolayer, have relatively high intensities; consequently these peaks were related to the formation of the SSSL. In these experiments the increased Sn/Pt ratio from 1.6 to 3.2 can be considered as a driving force to obtain the SSSL.
Figure 6. Deconvolution of the TPD pattern of samples with under monolayer coverage of SOMS presented in Figure 5A. A - Sn/Pt\textsubscript{s} = 0.07; B - Sn/Pt\textsubscript{s} = 0.12; C - Sn/Pt\textsubscript{s} = 0.39. Catalyst: PtSi-3.0-A. (■), Measured and (■), fitted.

Upon increasing the concentration of tetraethyltin from \(\text{Sn/Pt}_s = 5.3\) up to \(\text{Sn/Pt}_s = 9.8\) (see Figure 5C) further TPD peak at 170\(^\circ\)C was detected. The lack of TPD peaks above 200\(^\circ\)C indicates also that no tin has been introduced onto the support (see Figure 5C). Upon further increase of the \(\text{Sn/Pt}_s\) ratio up to 33.5 an additional new peak at 200\(^\circ\)C and shoulders around 230 and 260\(^\circ\)C were detected, as shown in Figures 5D, 7B and 7C. However, it is necessary to mention that the contribution of small peaks above 200\(^\circ\)C, even at the highest initial concentration of \(\text{Sn(C}_2\text{H}_5)_4}\) used for tin anchoring, are relatively low, representing less than 10\% of the total amount of ethane formed (see Figures 5D, 7B and 7C).

Figure 7. Deconvolution of the TPD pattern of samples with \(\text{Sn/Pt}_s\) ratios higher than monolayer coverage. A - Sn/Pt\textsubscript{s} = 0.67; B - Sn/Pt\textsubscript{s} = 1.33; C - Sn/Pt\textsubscript{s} = 1.64. Catalyst: PtSi-3.0-A. (■), Measured and (■), fitted.

The nine TPD peaks discussed above were divided into the following four different regions: low-temperature region up to 80\(^\circ\)C (peaks \#1-3), intermediate region between 110 and 140\(^\circ\)C (peaks \#4 and 5), high-temperature region between 170 and 200\(^\circ\)C (peaks \#6 and 7) and region above 200\(^\circ\)C (peaks \#8 and 9). The stepwise appearance of new TPD peaks indicates that the increase of the \(\text{Sn/Pt}_s\) ratio leads to the formation of different types of SOMS. We suggest that the above temperature regions of TPD curves can represent at least four different types of SOMS (PSC, SSSL, MLSC and OMSAS, respectively).

In our earlier study it was shown that the shoulders around 230 and 260\(^\circ\)C were tentatively attributed to \(\text{Sn(C}_2\text{H}_5)_4\) adsorbed onto the support (OMSAS). It should be mentioned that during decomposition of OMSAS on alumina support parallel to the formation of ethane high temperature...
ethylene TPD peak was also observed even in the presence of hydrogen using TPD technique. The formation of ethylene provides indirect evidence for the formation of OMSAS. \cite{110,132,242}

Consequently, only the first three TPD peak regions can be attributed to the decomposition of different type of SOMS anchored onto supported platinum, such as PSC, SSSL, MLSC.

**Figure 8.** The dependence of the amounts of ethane related to the area of each TPD peaks on the Sn/Pt$_s$ ratios. The position of temperature maxima of TPD peaks: A - (▲), 20°C; (●), 50°C; (♦), 80°C and (♦), sum of the amount of ethane formed in the first three peaks up to 80°C; B - (▲), 110°C; (●), 140°C; (♦), 170°C and (♦), 200°C.

Catalyst: PtSi-3.0-A. The tin anchoring was carried out in benzene at $T_r= 50^\circ\text{C}$ in the presence of adsorbed hydrogen. Results obtained from deconvoluted TPD spectra.

After deconvolution of TPD curves the amount of ethane related to each TPD peaks were calculated. The dependence of the amounts of ethane related to the area of each TPD peaks on the Sn/Pt$_s$ ratios exhibits a very interesting relationship, as shown in Figures 8A and 8B. The amount of ethane corresponding to the first peak at 20°C increases in the whole range of Sn/Pt$_s$ ratios (see Figure 8A). It means that the surface concentration of the corresponding SOMS increases with increasing of Sn/Pt$_s$ ratio. This is the only moiety, which shows this type of behaviour. Figures 8A and 8B show that the amount of ethane formed (with the exception of peak at 20°C) after reaching a certain level remains almost constant. This finding indicates that the surface concentration of corresponding surface species reaches a certain stationary value corresponding to the full coverage of the given type of SOMS (see Figures 8A and 8B).

Based on the calculation of the amount of ethane formed in the first three TPD peaks up to 80°C it is concluded that for all Sn/Pt$_s$ ratios the monolayer coverage (Sn/Pt$_{s}$= 0.42) is not exceeded. These data prove that the coverage of PSC in the first layer found experimentally is very close to the value calculated by molecular modeling.\cite{215}

The analysis of the decomposition pattern of PSC (see Figure 8A), SSSL and MLSC (see Figure 8B) in a hydrogen atmosphere clearly reflects the stepwise character of the anchoring process,\cite{215,216,241} namely, the tin containing slabs build-up step by step.

**5.3.1.3. Material balance of tin anchoring in the presence of adsorbed hydrogen**

Increase of the initial tin concentration appeared to be the key experimental variable to increase the amount of tin anchored. As emerges from Figure 9A-B the initial Sn$_0$/Pt$_s$ ratio has strong influence on the initial rate of tin anchoring (see Figure 9A) and amount of ethane and ethylene evolved during step I and II (Figure 9B). Corresponding data are presented in Table 7. As shown in Figure 9A the increase of the initial Sn$_0$/Pt$_s$ ratio up to 10.8 results in strong linear increase of the initial rate of tin anchoring step I. Upon further increase of the Sn$_0$/Pt$_s$ ratio up to 33.5 only slight increase of the initial rate of step I ($w_0$) is observed.

As seen from Figure 9B upon increasing the initial concentration of Sn(C$_2$H$_5$)$_4$ the amount of hydrocarbons formed in steps I and II ($n^1$, $n_{CH4}^1$ and $n^{11}$) has increased. It is necessary to mention that at low concentration of Sn(C$_2$H$_5$)$_4$, i.e. up to [Sn]$_0$ = 2.5 x 10$^{-2}$ M, only trace amount of ethylene was observed (see Table 7). At higher concentrations small amount of ethylene was detected.
Figure 9. The influence of the initial Sn/Pt ratio on the (A)- initial rate of tin anchoring in the presence of adsorbed hydrogen (▲); (B)- amount of hydrocarbons evolved during step I and II: (●), n\(^5\), (▲), n\(_{C2H4}\) and (■), n\(^4\); (C)- the stoichiometry of tin anchoring step I: (◊); and (D)- amount of Sn anchored per surface Pt atom: (◆). Catalyst: PtSi-3.0-A.

Figure 10. Summary of the results related to modification of PtSi-3.0-A catalyst with tetraethyltin in the presence of adsorbed hydrogen. (A)- The reaction order with respect to the Sn(C\(_2\)H\(_5\))\(_4\): (◊), the lowest ([Sn\(_0\]) = 0.1 x 10\(^{-5}\) M); (●), medium (0.2 x 10\(^{-5}\) M ≤ [Sn\(_0\]) ≤ 8.1 x 10\(^{-5}\) M) and (◆), the highest initial tin concentration ([Sn\(_0\]) ≥ 8.6 x 10\(^{-5}\) M); (B)- the influence of the Sn/Pt ratio on the stoichiometry of tin anchoring step I: (◆).

Furthermore, monitoring the gas-phase concentrations of hydrocarbons formed in the first and second step of tin anchoring allowed us to calculate the overall material balance of the process. These data are also included in Table 7. The calculated material balance for tin (see Sn/Pt ratios) was compared to the amount of tin determined in the catalysts by AAS. This comparison shows a very good agreement between calculated data and chemical analysis.\(^{215}\) This is a very important point indicating that in the two steps of CSRs monitored by GC the amount of undetected alkyl groups is negligible.
Two important experimental parameters were calculated from the material balance: (i) the value of $x$, and (ii) the Sn/Pt$_s$ ratio. The value of $x$ shows the amount of alkyl groups reacted in the first step of anchoring (step I). In other words $x$ reveals to the stoichiometry of surface reaction (2.8). As shown from data given in Table 7 and Figure 9C this value is in the range of 1.5 - 1.0. The decrease of $x$ observed at high initial Sn/Pt$_s$ ratio (see Figure 9C and Table 7) suggests that, in addition to the formation of the above forms of tin organic moieties, anchoring of -SnR$_4$ species onto the first layer, i.e. the formation of a second layer, can also take place. The obtained Sn/Pt$_s$ ratio shows a strong dependence on the initial Sn$_0$/Pt$_s$ ratio (see Figure 9D). Data given in Table 7 and Figure 9D show that in the presence of adsorbed hydrogen the highest Sn/Pt$_s$ ratio obtained experimentally reaches a value of ca. 1.6.

Figure 10A shows that in the presence of adsorbed hydrogen the reaction order of tin anchoring reaction strongly depends on the initial tin concentration. In the medium concentration interval ($0.2 \times 10^{-2} \leq [\text{Sn}]_0 \leq 8.1 \times 10^{-3} \text{ M})$ the reaction order with respect to the tetraethyltin is about 0.86. As shown in Figure 10A the increase of the initial tin concentration ($[\text{Sn}]_0 \geq 8.6 \times 10^{-2} \text{ M}$) resulted in a decrease of the reaction order to 0.31. Only one experimental point corresponding to the lowest tin concentration ($[\text{Sn}]_0 = 0.1 \times 10^{-2} \text{ M}$) does not fit to the general trend. It is possible that at the lowest tin concentration the rate of tin anchoring is comparable with the rate of the formation of coordinatively saturated -SnR$_4$ surface species strongly adsorbed onto the Pt (the formation of Pt-SnR$_4$ type surface species will be discussed in Chapter 5.4.3).

Table 7 and Figure 10B also shows that the overall value of $x$ is a function of Sn/Pt$_s$. In this respect three distinct areas of Sn/Pt$_s$ can be distinguished:

(i) $x$ has almost constant value around 1.45 up to Sn/Pt$_s$ = 0.47;
(ii) $x$ is decreasing from 1.45 to 1.0 in the range of Sn/Pt$_s$ = 0.47 - 1.15;
(iii) the value of $x$ is constant and close to one if Sn/Pt$_s$ > 1.15.

As seen in Figure 10B and Table 7, depending on the amount of tin anchored, the stoichiometry of the formed surface species is changing. At high Sn/Pt$_s$ ratios the formation and the amount of surface species containing -SnR$_4$ moieties increases.

### 5.3.1.4. Influence of the reaction temperature on tin anchoring step I

The influence of the reaction temperature on the step I was investigated in the range between $T_r$= 27°C and 60°C. The corresponding experimental data are given in Table 8 and Figure 11. The initial rate showed temperature dependence in the range of 27-55°C. The calculated energy of activation was $42.6 \pm 1.9 \text{ kJ mol}^{-1}$. The experiment carried out at $T_r$= 60°C did not fit into the overall trend observed. In this experiment, both the initial rate of step I ($w_0$) and the Sn/Pt$_s$ ratio were much higher than in other experiments. This may indicate that new type of surface reaction was involved in the tin anchoring at $T_r$= 60°C.

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$^a$ Amount of Sn anchored per surface Pt atom calculated using H/Pt = 0.52;
$^b$ As far as the washing of the adsorbed and unreacted Sn(C$_2$H$_5$)$_4$ was done at $T_r$= 50°C, $x$ values could not be calculated accurately. Catalyst: PtSi-3.0-A, [Sn]$_0$= 1.3 $\times 10^{-5}$ M, Sn$_0$/Pt$_s$= 1.58, catalyst amount: $W_{cat}$= 1 g.
Sn/Pt₅⁰ ratios given in Table 8 shows that the increase of the reaction temperature up to Tₑ = 50°C results in coverages under monolayer, while at 60°C, the build-up of the SSSL is already noticeable. This observation is further supported by TPD results presented in Figure 11. The TPD pattern clearly shows the differences between the SOMS formed at Tₑ = 27, 50 and 60°C. The appearance of the new peak at 110°C is an indication of the formation of the second layer. Indeed, in the experiment at Tₑ = 60°C, the Sn/Pt₅⁰ was ca. 0.8, i. e. it was almost twice as much as the corresponding monolayer coverage.

These results imply that the overall amount of anchored tin can be increased by changing the temperature of tin anchoring. The variation of the reaction temperature in the above range did not result in any additional side reactions as no other products were detected in step I and no TPD peaks at 200°C and above were detected.

5.3.1.5. Influence of the duration on tin anchoring step I

![Figure 12](image.png)

**Figure 12.** Influence of the duration of tin anchoring (τₑ) on the form of the TPD pattern. A- τₑ = 2.5 h, (sample A, Sn₀/Pt₅⁰ = 9.83, Sn/Pt₅⁰ = 1.15; see experiment 11 in Table 7); B- τₑ = 7 h, (sample B, Sn₀/Pt₅⁰ = 9.20, Sn/Pt₅⁰ = 2.35; see experiment 16 in Table 7). Catalyst: PtSi-3.0-A. Conditions of tin anchoring step I: atmosphere: in the presence of adsorbed hydrogen; Tₑ = 50°C. (■), Measured and (■), fitted.
The increase of the duration of tin anchoring can also be used to increase the Sn/Pt ratio. As emerges from Table 7 (compare experiment 11 and 16) under the same experimental conditions and upon increasing the duration of tin anchoring from 2.5 h up to 7 h (samples A and B, respectively) the amount of tin anchored can be increased almost twice. The deconvoluted TPD curves of two different Sn-modified catalysts are given in Figures 12A and 12B.

Upon increasing the time of tin anchoring the TPD pattern of SOMS decomposing above 100°C is significantly altered. However, it is important to note that in sample B the intensity of TPD peaks around and above 200°C is quite pronounced (see Figure 12B). This fact indicates that the prolonged time of tin anchoring leads also to the introduction of small portion of tin onto the support.

5.3.2. Tin anchoring in excess of hydrogen

5.3.2.1. Tin anchoring in excess of hydrogen using Sn(C$_2$H$_5$)$_4$ as tin precursor compound

Figures 13A and 13B show the kinetic curves of tin anchoring obtained in an argon atmosphere and in excess of hydrogen, respectively. These figures show that in the presence of excess of hydrogen the rate of tin anchoring is much higher than in its absence (compare Figures 13A and 13B). The above comparison indicates also that in excess of hydrogen the amount of ethane formed after 120 minutes exceeds strongly that of formed in the presence of adsorbed hydrogen. These facts indicate that excess of hydrogen strongly influences both the rate of tin anchoring and the amount of alkyl groups reacted (see Figure 13 and Table 9). In this way both the amount of tin anchored and the extent of coordinative unsaturation is strongly controlled.

Table 9. General data related to modification of PtSi-3.0-A catalyst with Sn(C$_2$H$_5$)$_4$ in excess of hydrogen.

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$^a$ Sn content calculated from the overall material balance of tin anchoring;
$^b$ Amount of Sn anchored per surface Pt atom calculated using H/Pt= 0.52;
$^c$ Catalyst amount: W$_{cat}$ = 3 g;
$^d$ Duration of tin anchoring step I (τ$_r$): 3.5 h.
Catalyst re-reduced in H$_2$ atmosphere at $t_{red}$ = 300°C for 1 h; catalyst amount: W$_{cat}$ = 1 g; atmosphere of step I: H$_2$; solvent: benzene; reaction temperature T$_r$ = 50°C; duration of tin anchoring step I (τ$_r$): 2 h.

As shown in the previous Chapter 5.3.1.2, upon decomposing different types of SOMS in hydrogen atmosphere (step II) various TPD peaks appear at different temperatures depending on the Sn/Pt ratio used in tin anchoring step (see Figures 5A-D).

The decomposition pattern of SOMS obtained both in the presence of adsorbed hydrogen (sample I-3 in Table 6) and in excess of hydrogen (sample II-3 in Table 6) is compared in Figures 14A and 14B.

As it has already been discussed in an argon atmosphere MLSC can also be obtained. However, under almost identical experimental condition of tin anchoring (T$_r$ and Sn/Pt ratio) in excess of hydrogen the Sn/Pt values are about two times higher than in the presence of adsorbed hydrogen\(^{215}\) (compare data I-3 and II-3 given in Table 6 and captions to Figure 14A-B).
Figure 13. Kinetic curves of tin anchoring under different experimental conditions. A- Kinetic curves of ethane and ethylene formation in the presence of adsorbed hydrogen. Conditions of tin anchoring: $T_r = 50^\circ$C, atmosphere of step I: Ar, Sn$_0$/Pt$_s$ = 5.28, (Sn/Pt$_s$ = 0.79); (■), ethane, (■), ethylene. B- Kinetic curve of ethane formation in excess of hydrogen. Conditions of tin anchoring: $T_r = 50^\circ$C, atmosphere of step I: H$_2$, Sn$_0$/Pt$_s$ = 4.12, (Sn/Pt$_s$ = 1.68); (■), ethane. Catalyst: PtSi-3.0-A.

In sample II-3 (see Figure 14B) the intensities of the low-temperature TPD peaks, corresponding to the monolayer coverage (see TPD peaks at 20, 50 and 80$^\circ$C), are relatively low, however TPD peaks around 110 and 140$^\circ$C, corresponding to SSSL, have high intensities. Contrary to that in sample I-3 (see Figure 14A) the TPD peak around 110$^\circ$C has relatively high intensity but the TPD peak around 140$^\circ$C has a very low intensity. This fact indicates that in sample I-3 the formation of the SSSL is less pronounced than in sample II-3. The observed alterations in the TPD pattern indicate that excess of hydrogen strongly enhances the formation of SSSL, resulting in high Sn/Pt$_s$ ratios. The lack of TPD peaks above 200$^\circ$C (see Figures 14A and 14B) indicates also that no tin has been introduced onto the support.$^{215,216}$

Based on results presented in Table 9 the following main conclusions can be drawn:

- As shown in Figure 15A the initial rate of tin anchoring ($w_0$) strongly depends on the initial Sn$_0$/Pt$_s$ ratios. As emerges from Figure 15A the increase of the initial Sn$_0$/Pt$_s$ ratio up to 4.1 (that corresponds to Sn/Pt$_s$ ratio 1.68) results in strong linear increase of the initial rate. At higher Sn$_0$/Pt$_s$ ratios (Sn$_0$/Pt$_s$ > 4.1) the further increase of Sn$_0$/Pt$_s$ ratio has much less influence on the initial rate of step I.

- As emerges from Figure 16A at low [Sn$_0$] concentrations ([Sn$_0$]$< 3.3 \times 10^{-2}$ M) the reaction order with respect to the tetraethyltin is about 0.88. The only point corresponding to the lowest tin concentration ([Sn$_0$]$_0$ = 0.5 $\times$ 10$^{-2}$ M) is out from the general trend. At [Sn$_0$] concentrations

---

Figure 14. Decomposition of SOMS formed in an argon atmosphere (A) and in excess of hydrogen (B). A- Sample I-3 (Sn$_0$/Pt$_s$ = 5.3, Sn/Pt$_s$ = 0.79); B- sample II-3 (Sn$_0$/Pt$_s$ = 4.1, Sn/Pt$_s$ = 1.68). Catalyst: PtSi-3.0-A. (■), Measured and (■), fitted.
higher than $3.3 \times 10^{-2}$ M the value the reaction order with respect to the Sn($C_2H_5)_4$ decreases to 0.25.

![Figure 15](image1.png)

**Figure 15.** The influence of the initial Sn$_0$/Pt$_s$ ratio on the (A) initial rate of tin anchoring in excess of hydrogen ($\Delta$); (B) amount of hydrocarbons evolved during step I and II: ($\Diamond$, $n^I$ and ($\Box$, $n^II$); (C) the stoichiometry of tin anchoring reaction I: ($\Diamond$); and (D) amount of Sn anchored per surface Pt atom: ($\Diamond$). Catalyst: PtSi-3.0-A.

![Figure 16](image2.png)

**Figure 16.** Summary of the results related to modification of 3 wt% Pt/SiO$_2$ catalyst with tetraethyltin in excess of hydrogen. (A)- The reaction order with respect to the Sn($C_2H_5)_4$: ($\bullet$), low ($0.5 \times 10^{-2}$ M $\leq$ [Sn]$_0$ $\leq$ $3.3 \times 10^{-2}$ M) and ($\bullet$), high initial tin concentration ($3.3 \times 10^{-2}$ M $\leq$ [Sn]$_0$ $\leq$ $25.3 \times 10^{-2}$ M); (B)- the influence of the Sn/Pt$_s$ ratio on the stoichiometry of tin anchoring: ($\Diamond$).

- Upon increasing the of the initial Sn$_0$/Pt$_s$ ratio the amount of ethane formed during step I and II ($n^I$ and $n^II$) increases (see Figure 15B and Table 9). During tin anchoring in the excess of hydrogen ethane was the only product formed, the formation of ethylene was not observed.
- As emerges from Figure 15C very high extent of coordinative unsaturation has been obtained when tin anchoring has been carried out in the presence of excess of hydrogen. The increase of Sn$_0$/Pt$_s$ ratio (as well as Sn/Pt$_s$ ratio, see Figure 16B) results in decrease of the value of $x$. Data given in Table 9 and Figure 15C show that upon increasing the Sn$_0$/Pt$_s$ ratio up to 4.1, fast decrease of the value of $x$ from 3.3 to 2.3 was observed. The decrease of the value of $x$ is less pronounced (from 2.3 to 1.6) in the concentration interval between 4.1 $\leq$ Sn$_0$/Pt$_s$ $\leq$ 32.6. As
shown in Figure 16B the value of \( x \) linearly depends on the amount of tin anchored, and the highest \( x \) values were obtained at low Sn/Pt\(_s\) ratio. It is suggested that these samples should contain “naked” tin with \( x = 4 \).

- The obtained Sn/Pt\(_s\) ratio shows a strong dependence on the initial Sn\(_0\)/Pt\(_s\) ratio (see Figure 15D). Data given in Table 9 and Figure 15D indicate that in excess of hydrogen the highest Sn/Pt\(_s\) ratio obtained experimentally reaches a value of 2.92.

### 5.3.2.2. Tin anchoring in excess of hydrogen using Sn(CH\(_3\))\(_4\) as tin precursor compound

Further increase of the initial rate of tin anchoring can be achieved by replacing tetraethyltin with tetramethyltin. The kinetic curves of tin anchoring using Sn(\( \text{C}_2\text{H}_5\))\(_4\) and Sn(CH\(_3\))\(_4\) are shown in Figure 17. Upon using relatively low Sn\(_0\)/Pt\(_s\) ratio (Sn\(_0\)/Pt\(_s\) around 1.3, see caption to Figure 17), in case of tetramethyltin the initial rate of tin anchoring is about twice as high as for tetraethyltin (6.2 vs. 3.2 \( \times 10^6 \) mol g\(_{\text{cat}}\)\(^{-1} \times \text{min}^{-1}\)). These results are in agreement with the reactivity trend known for the cleavage of the Sn-C \( \sigma \)-bond in tin organometallic species: Bu (the most stable) < Pr < Et < Me (the most reactive). However it is necessary to mention that this pronounced difference in the initial rate can be observed only up to monolayer tin coverage (Sn/Pt\(_s\) ≤ 1). Further increase of initial tin concentration (Sn\(_0\)/Pt\(_s\) ≥ 1.3) resulted in comparable values of the \( w_0 \) for Sn(\( \text{C}_2\text{H}_5\))\(_4\) and Sn(CH\(_3\))\(_4\).

**Figure 17.** Kinetic curves of tin anchoring in excess of hydrogen using Sn(CH\(_3\))\(_4\) and Sn(\( \text{C}_2\text{H}_5\))\(_4\) as tin precursor compound. (■), Methane (\( T_r = 50^\circ\text{C}, \text{Sn}_0/\text{Pt}_s = 1.3, \text{(Sn/Pt}_s = 1.24)\)); (■), ethane (\( T_r = 50^\circ\text{C}, \text{Sn}_0/\text{Pt}_s = 1.3, \text{(Sn/Pt}_s = 0.82)\)). Catalyst: PtSi-3.0-A.

As emerges from Figure 17 the shape of the kinetic curves of tin anchoring using these two modifiers is different. Both kinetic curves have fast and slow rate parts. As shown in Figure 17 in the first 20 minutes of the reaction about 60 % conversion can be reached using Sn(CH\(_3\))\(_4\) as tin precursor compound. Upon modification with Sn(\( \text{C}_2\text{H}_5\))\(_4\), to achieve the similar value of conversion, more prolonged reaction time is needed (\( \tau_r = 45 \text{ min} \)).

Under the same experimental condition of tin anchoring the replacement of Sn(\( \text{C}_2\text{H}_5\))\(_4\) for Sn(CH\(_3\))\(_4\) resulted in evident increase of the Sn/Pt\(_s\) ratio (0.82 vs. 1.24, compare experiment 2 in Table 9 with experiment 5 in Table 10). The results also show that in the case of tetramethyltin anchoring reaction is almost complete up to Sn/Pt\(_s\) = 1.3, i.e., all amount of tin introduced have been anchored. Further results of Sn(CH\(_3\))\(_4\) anchoring in the presence of excess of hydrogen over PtSi-3.0-A catalyst are summarized in Table 10. It is necessary to mention that taking into account high reactivity of Sn(CH\(_3\))\(_4\) high initial concentrations was not applied. As far as these catalysts were mainly prepared for Mössbauer studies, in some experiment enriched \(^{119}\text{Sn(CH}_3\text{)}\(_4\) was also used for the modification (see Table 10).

The influence of the amount of tin anchored on the decomposition pattern was demonstrated in Figure 18. The increase of the Sn/Pt\(_s\) ratio resulted in a slight broadening of the TPD pattern up to 200°C (see Figure 18). As emerges from Figure 19A-C, the intensities of the TPD peaks around 110, 140 and 170°C, corresponding to SSSL and MLSC, increases substantially upon increasing the Sn/Pt\(_s\) ratio. The TPD peak around 200°C has relatively low and almost constant contributions, around 2-6 % of the total amount of methane formed. It is necessary to mention that the contribution of small peaks
above 200°C are very low representing about 5% of the total amount of methane formed, indicating that amount of tin introduced onto the support is negligible.\textsuperscript{215,216}

Table 10. General data related to modification of PtSi-3.0\textsuperscript{A} catalyst with Sn(CH\textsubscript{3})\textsubscript{4} in excess of hydrogen.

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\textsuperscript{a} Sn content calculated from the overall material balance of tin anchoring;

\textsuperscript{b} Amount of Sn anchored per surface Pt atom calculated using H/Pt = 0.52;

\textsuperscript{c} Catalyst amount: W\textsubscript{cat} = 1 g;

\textsuperscript{d} Enriched \textsuperscript{119}Sn(CH\textsubscript{3})\textsubscript{4} was used as tin precursor compound.

Catalyst re-reduced in H\textsubscript{2} atmosphere at t\textsubscript{red} = 300°C for 1 h; catalyst amount: W\textsubscript{cat} = 2.5 g; atmosphere of step I: H\textsubscript{2}; solvent: benzene; reaction temperature T\textsubscript{r} = 50°C; duration of tin anchoring step I: 2.5 h.

As emerges from Figure 20A at low [Sn\textsubscript{0}] concentrations ([Sn\textsubscript{0}] ≤ 1.2 x 10\textsuperscript{-2} M) the reaction order with respect to the tetramethyltin is about 0.79. At [Sn\textsubscript{0}] concentrations higher than 1.2 x 10\textsuperscript{-2} M value the reaction order with respect to the Sn(CH\textsubscript{3})\textsubscript{4} decreases to 0.37.

The slightly higher value of \(x\) obtained at similar coverages for the catalysts modified with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} can be explained if we assume that the hydrogenolysis of anchored -Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{(4-x)} surface species is more easily compared to that of -Sn(CH\textsubscript{3})\textsubscript{(4-x)} (see Figure 20B). At this point it is necessary to mention that more precise comparison of the hydrogenolysis activity of Sn-C σ-bonds in Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} and Sn(CH\textsubscript{3})\textsubscript{4} can be done using both (i) tin anchoring in the argon atmosphere and (ii) lower reaction temperature (T\textsubscript{r}). Under these experimental conditions pronounced decrease of the initial rate of tin anchoring and strong separation of the formation and further decomposition of PSC can be achieved. It
has been demonstrated\textsuperscript{215,216} that the nature of the alkyl groups in tin precursor compound has strong influence on the rate of both the formation of PSC and further hydrogenolysis of anchored -SnR\(_{4-x}\) surface species. Extent of dealkylation of PSC (the value of \(x\)) strongly depends on (i) surface coverage, (ii) the alkyl chain lengths in SnR\(_4\) complexes used. The hydrogenolysis of SnR\(_4\) on the metallic surface is governed by steric limitations due to the bulkiness of the alkyl ligands or more precisely the “cone angle” of the anchored -SnR\(_{4-x}\) surface species. The longer the alkyl group the higher the shielding effect of anchored alkyl groups.

\textbf{Figure 19.} The influence of the Sn/Pt\(_s\) ratio on the deconvolution of the TPD peaks. A- Sn/Pt\(_s\) = 0.90; B- Sn/Pt\(_s\) = 1.19; C- Sn/Pt\(_s\) = 1.31. Conditions of tin anchoring step I: \(^{119}\)Sn(CH\(_3\)_3)\(_4\) was used as tin precursor compound; atmosphere: H\(_2\); \(T_r = 50^\circ\text{C}\) (see experiments 2, 4 and 7 in Table 10). ( ), Measured and ( ), fitted.

\textbf{Figure 20.} Summary of the results related to modification of PtSi-3.0-A catalyst with tetramethyltin in excess of hydrogen. (A)- The reaction order with respect to the Sn(CH\(_3\)_3)\(_4\): ( ), low ([Sn]\(_0\) \(\leq\) 1.2 x 10\(^{-2}\) M) and ( ), high initial tin concentration (1.3 x 10\(^{-2}\) M \(\leq\) [Sn]\(_0\) \(\leq\) 13.4 x 10\(^{-2}\) M); (B)- the influence of the Sn/Pt\(_s\) ratio on the stoichiometry of tin anchoring: ( ), Sn(CH\(_3\)_3)\(_4\) and ( ), Sn(C\(_2\)H\(_5\))\(_4\), given for comparison.

Comparing different tetraalkyltin compounds, Nedez \textit{et al.} have demonstrated\textsuperscript{91} that some kind of interactions is suppressed using Sn(CH\(_3\)_3)\(_4\), because the alkyl chain length is insufficient and the distances between the concerned atoms is not favorable for the interaction. It was shown that the temperature of the reaction of SnR\(_4\) complexes with silica support strongly depends on the nature of the alkyl ligands: the shorter the hydrocarbon ligand, the higher the temperature necessary for reaction to occur. At \(T_r = 150^\circ\text{C}\), when Sn(C\(_2\)H\(_5\))\(_4\) and Sn(CH\(_3\))\(_4\) reacted with the surface of partially dehydroxylated at 200°C silica support, \textit{ca.} 1 mol of C\(_2\)H\(_6\) and 0.3 mol of CH\(_4\) per mol of surface Sn, evolved, respectively. Inverse tendency was observed during the interaction between 3 wt% Re\(_2\)O\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) and SnR\(_4\) (R= Me, Et or n-Bu) in metathesis catalysts at Sn/Re= 0.55 ratio.\textsuperscript{188} The amounts of gases released off decrease in the order Sn(CH\(_3\))\(_4\) > Sn(C\(_2\)H\(_5\))\(_4\) > Sn(C\(_4\)H\(_9\))\(_4\), in accordance with the increasing bulkiness of R. However Sn(CH\(_3\))\(_4\) appears to behave in a different way, as the
concentration of \( \text{Re}_2\text{O}_3 \) increases up to 6 wt%; the anchoring activity of \( \text{SnR}_4 \) complexes decreases in the following order: \( \text{Sn(C}_2\text{H}_5)_4 > \text{Sn(C}_4\text{H}_9)_4 \equiv \text{Sn(CH}_3)_4 \).

In Ref.\(^{246} \) the controlled hydrogenolysis of \( \text{Me}_x\text{SnR}_{4-x} \) (0 ≤ x ≤ 4; R= Me, \( n \)-Bu, tert-Bu, neopentyl, cyclohexyl) onto \( \text{Rh/SiO}_2 \) at \( T_r = 25^\circ\text{C} \) for 80 h was followed by quantitative and qualitative analysis of evolved gases (\( \text{Sn}_0/\text{Rh}_s = 0.5 \)). At the “pseudo-equilibrium”, after 80 h, there is still alkyl groups bounded to anchored tin and generally, the remaining alkyl group is the bulkiest one. It has been demonstrated that, non bulky methyl fragments, which can approach the surface quite easily, generally eliminate first and then, in the successive steps of the hydrogenolysis, the bulkiest group, R, would be eliminated.

This short literature survey showed that quite contradictory results were obtained concerning to the hydrogenolysis activity using different \( \text{SnR}_4 \) complexes. The dependence on numerous variables and the complexity of surface reactions taking place during both tin anchoring and further hydrogenolysis can be the reason of such contradiction.

5.3.3 Tin anchoring in the presence of trace amount of oxygen

In the absence of oxygen, when Pt is fully reduced and tetraethyltin is used as tin precursor compound, the formation of ethylene during tin anchoring step I is negligible. However, in the presence of small amount of oxygen or slight oxidation of platinum (or incomplete reduction of Pt) formation of ethylene from \( \text{Sn(C}_2\text{H}_5)_4 \) was observed. The appearance of ethylene had been attributed to the following surface reaction:\(^{215} \)

\[
\text{PtO}_x + x \text{Sn(C}_2\text{H}_5)_4 \rightarrow \text{Pt}[-\text{Sn(C}_2\text{H}_5)_2]_x + 2x \text{C}_2\text{H}_4 + x \text{H}_2\text{O} \quad (5.9)
\]

In this reaction the hydrogen of the ethyl group is used to remove the oxygen from the oxidized forms of Pt. It is suggested that in surface reaction (5.9) coordinative unsaturated SOMS are formed. Reaction (5.9) takes place if the oxidation of Pt precedes the addition of \( \text{Sn(C}_2\text{H}_5)_4 \).

Tin anchoring shown in Figure 21A was studied after a mild oxidation. The re-reduced Pt/SiO\(_2\) catalyst was oxidized by purging the catalyst with oxygen at 50\(^\circ\text{C} \) for 1 h in an absence of solvent. In this experiment (see Figure 21A) the formation of ethane and ethylene was observed and ethylene was the major reaction product. The formation of ethylene indicates that tetraethyltin was involved in an oxidation-reduction type reaction (5.9).

Similar surface reaction, i.e., the formation of ethylene can be expected if the formed PSC or CUPSC are mildly oxidized in the 50th minute (see reaction (5.7)).\(^{215,216} \) The difference in the product formation during the tin anchoring step in the absence and presence of oxygen is shown in Figure 21B.

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**Figure 21.** Anchoring tin onto platinum oxidized at 50\(^\circ\text{C} \). **A** - Oxidation prior to the anchoring step; amount of (\( \square \)), ethylene and (\( \bullet \)), ethane formed. **B** - Oxidation during tin anchoring step I (20 cm\(^3\) \( \text{g}^{-1} \text{cat}^{-1} \) \( \text{O}_2 \) added in the 50th minute): amount of (\( \triangle \)), ethane and (\( \Delta \)), ethylene formed on platinum oxidized during tin anchoring; Amount of (\( \mathbf{\square} \)), ethane and (\( \mathbf{\bigtriangleup} \)), ethylene formed on fully reduced platinum. Catalyst: 3 wt\% Pt/SiO\(_2\), \( \text{Sn}_0/\text{Pt}_s = 8.8 \).

General data related to the modification of PtSi-3.0-A catalyst with \( \text{Sn(C}_2\text{H}_5)_4 \) in the presence of oxygen are summarized in Table 11. Characteristic features of catalysts with different \( \text{Sn/Pt}_s \) ratios prepared in the presence of oxygen added during tin anchoring step are also given in Table 6 (series of samples: III). As emerges from these data the increase of the initial concentration of tetraethyltin
results in a pronounced increase of the amount of tin anchored, consequently upon using this mode of tin anchoring Sn-Pt/SiO\textsubscript{2} catalysts with high Sn/Pt\textsubscript{s} ratios up to 2.9 can be prepared.\textsuperscript{216}

**Table 11.** General data related to modification of PtSi-3.0-A catalyst with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} in the presence of oxygen added during tin anchoring step I.

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<th>( n_{\text{C}_2\text{H}_4} ) x 10\textsuperscript{-6}</th>
<th>( n_{\text{C}_2\text{H}_4}^{\text{i}} ) x 10\textsuperscript{-6}</th>
<th>( x )</th>
<th>TOF ( s^{-1} x 10^{-4} )</th>
<th>Sn, wt% \textsuperscript{a}</th>
<th>Sn/Pt\textsubscript{s} \textsuperscript{b}</th>
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<td>4.81</td>
<td>2.2</td>
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<td>92.2</td>
<td>0.71</td>
<td>4.17</td>
<td>2.78</td>
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\textsuperscript{a} Sn content calculated from the overall material balance of tin anchoring; 
\textsuperscript{b} Amount of Sn anchored per surface Pt atom calculated using H/Pt = 0.52; 
\textsuperscript{c} Catalyst amount: \( W_{\text{cat}} = 1 \) g; 
\textsuperscript{d,e} Duration of tin anchoring step I (\( \tau_r \)): 2 and 7 h, respectively. 
Catalyst re-reduced in H\textsubscript{2} atmosphere at \( T_{\text{red}} = 300 \) °C for 1 h; catalyst amount: \( W_{\text{cat}} = 2 \) g; initial atmosphere of step I: Ar with following oxidation during tin anchoring (20 cm\textsuperscript{3} g\textsubscript{cat}\textsuperscript{-1} O\textsubscript{2} added in the 50th minute); solvent: benzene (10 cm\textsuperscript{3} g\textsubscript{cat}\textsuperscript{-1}); reaction temperature \( T_r = 50 \) °C; duration of tin anchoring step I (\( \tau_r \)): 4.5 h.

**Figure 22.** Oxidation during tin anchoring reaction. A- Time dependence of the formation of ethane (\( \square \)) and ethylene (\( \bullet \)) in the tin anchoring step I. Conditions of tin anchoring: \( T_r = 50 \) °C, Sn\textsubscript{0}/Pt\textsubscript{s} = 1.72, (Sn/Pt\textsubscript{s} = 0.88), solvent: benzene; 20 cm\textsuperscript{3} g\textsubscript{cat}\textsuperscript{-1} O\textsubscript{2} added in the 50th minute. The arrow indicates the moment of addition of oxygen. B- TPD pattern of the decomposition of surface complexes formed on reduced (\( \square \)) (Sn\textsubscript{0}/Pt\textsubscript{s} = 1.58, Sn/Pt\textsubscript{s} = 0.39) and oxidized during tin anchoring samples (\( \bullet \)) (Sn\textsubscript{0}/Pt\textsubscript{s} = 1.72, Sn/Pt\textsubscript{s} = 0.88). Catalyst: PtSi-3.0-A.

As shown in Figures 21B and 22A the addition of oxygen leads to the immediate formation of ethylene. The fast formation of ethylene is an indication that the addition of oxygen has no significant negative influence on the overall rate of tin anchoring. Upon increasing the Sn\textsubscript{0}/Pt\textsubscript{s} ratio (see Table 11) the amount of ethylene strongly increases. The decomposition of SOMS formed on reduced and
oxidized sample during tin anchoring catalysts is shown in Figure 22B. The comparison of these TPD curves clearly demonstrates the build-up of the multilayer. In the absence of oxygen under similar experimental condition monolayer coverage has been obtained (Sn/Pt = 0.39), while the addition of oxygen results in an increase of this ratio up to 0.88. In this way the efficiency of tin anchoring significantly increased.

The influence of the amount of tin anchored on the decomposition pattern is demonstrated in Figure 23. As shown in Figure 23 the increase of the Sn/Pt ratio from 0.20 up to 2.46 results in pronounced broadening of the TPD curves and appearance of new high-temperature peaks.

Figure 24A-C shows the deconvolution of the TPD pattern of the samples 6, 9 and 12 in Table 11. The increase of the Sn/Pt ratio from 1.4 up to 6.7 results in significant increase of the intensity of TPD peaks in the temperature range between 100 and 200°C. Correspondingly, the amount of tin anchored is doubled (see Table 11). Both increases can be considered as an indirect evidence for the formation of SSSL and MLSC. The increase of the Sn/Pt ratio from 6.7 to 9.2 (compare Figures 24B and 24C) resulted in only minor changes in the intensities of peaks around 110, 140, 170 and 200°C, in the same way the amount of tin anchored increased only slightly (see Table 11).

![Figure 23](image_url)

Figure 23. The influence of the Sn/Pt ratio on the decomposition pattern. (○), Sn/Pt = 0.20; (△), Sn/Pt = 0.46; (□), Sn/Pt = 1.14; (●), Sn/Pt = 1.43; (■), Sn/Pt = 2.01; (▲), Sn/Pt = 2.46. Catalyst: PtSi-3.0-A.

![Figure 24](image_url)

Figure 24. Influence of the initial tin concentration on the deconvolution of the TPD peaks. Catalysts with different Sn/Pt ratios prepared in the presence of oxygen added during tin anchoring step I. The Sn/Pt ratio of samples A- 1.14; B- 2.01 and C- 2.46. Catalyst: PtSi-3.0-A. Conditions of tin anchoring: 20 cm³ g⁻¹ O₂ added in the 40th minute; T_r = 50°C. (●), Measured and (■), fitted.

It is interesting to note that upon increasing the Sn/Pt ratio the intensity of two additional small peaks around 230 and 260°C slightly increased. However, the latter two peaks had only minor and
almost constant contribution (about 5-7%) to the total amount of hydrocarbons formed. These TPD peaks were attributed to the formation of OMSAS.

The series of deconvoluted TPD curves obtained in step II were numerically integrated. The stepwise appearance of new TPD peaks (PSC→SSSL→MLSC→OMSAS) indicates that the increase of the Sn/Pt ratio leads to the formation of different types of SOMS in different environments (details see in Chapter 5.3.1.2.). The dependence of the amounts of ethane related to the area of TPD peaks with maxima at different temperatures on the Sn/Pt ratios is shown in Figure 25A-B. Figures 25A and 25B show that the amount of ethane formed, after reaching a certain level, remains almost constant. This finding indicates that the surface concentration of corresponding surface species reaches a certain stationary value corresponding to the full coverage of the given type of SOMS and in further step the built up of next layer of SOMS, which requires higher temperature for decomposition, begins.

![Figure 25](image)

**Figure 25.** The dependence of the amounts of ethane related to the area of each TPD peaks on the Sn/Pt ratios. The position of temperature maxima of TPD peaks: A- (▲), 20°C; (▲), 50°C; (▲), 80°C and (▲), sum of the amount of ethane formed in the first three peaks up to 80°C; B- (▲), 110°C; (▲), 140°C; (▲), 170°C and (▲), 200°C.

Catalyst: PtSi-3.0-A. The tin anchoring was carried out in benzene at T_r= 50°C in the presence of oxygen added during tin anchoring step I. Results obtained from deconvoluted TPD peaks.

According to our earlier results, the amount of ethane formed in the first three TPD peaks up to 80°C corresponds to a monolayer coverage (Sn/Pt\_s= 0.42). As shown in Figure 25B TPD peak at 170°C corresponding to the MLSC appears only in samples with Sn/Pt ratios higher than 0.42 and reaches its stationary level at Sn/Pt ratios about 1.5. The next TPD peak at 200°C is detected only in samples with Sn/Pt≥ 1.5. The amount of ethane formed at 200°C is terminated after reaching Sn/Pt= 2.0, as shown in Figure 25B. The comparison of the dependences obtained on samples prepared in an argon atmosphere (see Figure 9A-B) with those prepared in the presence of oxygen (Figure 25A-B) shows that the calculated values of the amounts of ethane formed in the first four TPD peaks up to 110°C are quite similar. It can be proposed that build-up of corresponding tin-containing SOMS was finished before the addition of oxygen. The calculated stationary Sn/Pt ratios up to 110°C in both cases corresponds to Sn/Pt\_s= 0.68. However the amount of ethane formed in the TPD peaks at 140, 170 and 200°C (compare Figures 25B and 9B) considerably increases in samples prepared in the presence of oxygen. As emerges from Figure 25B, almost double amount of ethane formed was observed in the TPD peak at 200°C compared to the value calculated for peak at 110°C. The equal amounts of ethane were formed at stationary level in the TPD peaks at 140 and 170°C (see Figure 25B) and these values were comparable with that obtained for the sum of the amounts of ethane formed in the TPD peaks up to 80°C (Figure 25A).

The above observations, although they did not allow us an exact assignment, provided information supporting our assumption about stepwise character of the build-up process involved in the tin anchoring.

Based on results presented in Table 11, Figures 26 and 27 the main conclusions can be drawn as follows:

- As far as the duration of tin anchoring reaction has strong influence on all experimental data (see Table 11), only experiments with similar reaction time can be compared.
Figure 26. The influence of the initial Sn$_{0}$/Pt$_{s}$ ratio on the (A) initial rate of tin anchoring in the presence of oxygen added during anchoring step I (▲); (B) amount of hydrocarbons evolved during step I and II: n$^{1}$- (◇), $\tau_{r}$ = 2 h; (◆), $\tau_{r}$ = 4.5 h; (♦), $\tau_{r}$ = 7 h; n$^{2}$- (△), $\tau_{r}$ = 2 h; (▲), $\tau_{r}$ = 4.5 h; (▲), $\tau_{r}$ = 7 h; n$^{3}$- (□), $\tau_{r}$ = 2 h; (■), $\tau_{r}$ = 4.5 h; (■), $\tau_{r}$ = 7 h; (C) stoichiometry of tin anchoring reaction I: (◇), $\tau_{r}$ = 2 h; (◆), $\tau_{r}$ = 4.5 h; (△), $\tau_{r}$ = 7 h; and (D) amount of Sn anchored per surface Pt atom: (◇), $\tau_{r}$ = 2 h; (◆), $\tau_{r}$ = 4.5 h; (▲), $\tau_{r}$ = 7 h. Catalyst: 3 wt% Pt/SiO$_{2}$.

Figure 27. Summary of the results related to modification of 3 wt% Pt/SiO$_{2}$ catalyst with tetraethyltin in the presence of oxygen added during anchoring step I. (A) The reaction order with respect to the Sn(C$_{2}$H$_{5}$)$_{4}$: (◇), initial tin concentration: $0.2 \times 10^{-2}$ M $\leq$ [Sn]$_{0}$ $\leq$ $6.6 \times 10^{-2}$ M; (◆), the highest initial tin concentration ([Sn]$_{0}$ $\geq$ $8.9 \times 10^{-2}$ M); (B) the influence of the Sn/Pt$_{s}$ ratio on the stoichiometry at different reaction time in tin anchoring step I: (◇), $\tau_{r}$ = 2 h; (◆), $\tau_{r}$ = 4.5 h; (▲), $\tau_{r}$ = 7 h.

- It is necessary to mention that in these experiments the initial rate of tin anchoring was measured before addition of oxygen (the reactions were started in an argon atmosphere). As shown in Figure 26A, the initial rate of tin anchoring ($w_{0}$) strongly depends on the initial Sn$_{0}$/Pt$_{s}$ ratios; increase of the initial Sn$_{0}$/Pt$_{s}$ ratio resulted in linear increase of $w_{0}$.
• Upon increasing both the initial Sn\textsubscript{0}/Pt\textsubscript{s} ratio and the duration of tin anchoring step I the amount of hydrocarbons formed during step I and II (\(n_1\), \(n_{C_{2}H_{4}}\) and \(n_{II}\)) increases (see Figure 26B and Table 11). However, as emerges from Table 11 the \(n_{C_{2}H_{4}}/n_1\) ratio remains almost constant in all experiment (\(n_{C_{2}H_{4}}/n_1= 0.30\)). Only strong increase of the duration of tin anchoring (\(\tau_r = 7\) h) results in an increase of \(n_{C_{2}H_{4}}/n_1\) ratio up to 0.55.

• Data given in Table 11 and Figures 26C and 27B indicate that the value of \(x\) is in the range of 0.75 - 1.2. Table 11 and Figure 26C also shows that \(x\) is almost constant in the range of Sn\textsubscript{0}/Pt\textsubscript{s} = 0.75 - 1.4. Slight increase of \(x\) up to 1.2 was observed in the concentration interval 1.4 ≤ Sn\textsubscript{0}/Pt\textsubscript{s} ≤ 9.2. The influence of the Sn/Pt\textsubscript{s} ratio on the stoichiometry presented in Figure 27 B shows similar character and slight increase of the value of \(x\) observed at Sn/Pt\textsubscript{s} > 1.

• The Sn/Pt\textsubscript{s} ratio shows a strong dependence on the initial Sn\textsubscript{0}/Pt\textsubscript{s} ratio (see Figure 26D). It is worth mentioning that in the presence of oxygen added during tin anchoring step I the highest Sn/Pt\textsubscript{s} ratio obtained experimentally reaches a value of 2.93.

• As seen from Figure 27A, the reaction order with respect to the tetraethyltin is about 0.90. The only point corresponding to the highest tin concentration ([Sn\textsubscript{0}]= 8.9 x 10\textsuperscript{-2} M) is slightly different from common trend.

• This approach, i.e. the addition of oxygen, is a very effective way to introduce increased amount of tin onto the platinum selectively.

5.3.4. Reactions with the involvement of the silica support

Silica treated in a hydrogen atmosphere at 300°C appeared to be almost inert. In the presence of 4.3 x 10\textsuperscript{-2} M tetraethyltin the amount of ethane formed after 2 h was 3.4 x 10\textsuperscript{-6} mol g\textsubscript{cat}\textsuperscript{-1}. Under identical initial concentration [Sn\textsubscript{0}] the reaction on Pt/SiO\textsubscript{2} catalyst resulted in 82.5 x 10\textsuperscript{-6} mol g\textsubscript{cat}\textsuperscript{-1} ethane and 2.4 x 10\textsuperscript{-6} mol g\textsubscript{cat}\textsuperscript{-1} ethylene (see experiment 9 in Table 7). Upon increasing the concentration of tetraethyltin up to 27.9 x 10\textsuperscript{-2} M the amount of ethane formed over silica was 20.9 x 10\textsuperscript{-6} mol g\textsubscript{cat}\textsuperscript{-1}. Using this amount of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} in modification of the Pt/SiO\textsubscript{2} catalyst resulted in 104 x 10\textsuperscript{-6} mol g\textsubscript{cat}\textsuperscript{-1} ethane and 25 x 10\textsuperscript{-6} mol g\textsubscript{cat}\textsuperscript{-1} ethylene (see experiment 15 in Table 7).

![Figure 28. Comparison of TPD pattern of surface complexes for med on silica support (■) and on Pt/SiO\textsubscript{2} catalyst (■). Reaction conditions: [Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}]\textsubscript{0} = 4.31 x 10\textsuperscript{-2} M, T\textsubscript{r} = 50°C.](image_url)

Although the amount of C\textsubscript{2} hydrocarbons (ethane and ethylene) formed over SiO\textsubscript{2} at high concentration of tetraethyltin cannot be neglected it should be mentioned that in the above two experiments the initial rate of surface reaction with the involvement of surface OH groups was still 60 and 20 times lower than on Pt/SiO\textsubscript{2} catalyst ([Sn\textsubscript{0}]= 4.3 x 10\textsuperscript{-2} M and 27.9 x 10\textsuperscript{-2} M, respectively). These results also indicate that extremely high initial concentration of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} should be avoided since under these conditions the exclusive anchoring of tin onto platinum cannot be guaranteed.

The corresponding TPD patterns are shown in Figure 28. It is necessary to mention that over silica support parallel to the formation of ethane an ethylene peak at 340°C was also detected (not shown). The low temperature ethane peak around 200°C was attributed to the decomposition of -Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}
species anchored onto the silica, while the high temperature peak around 340°C was ascribed to the adsorbed form of tetraethyltin. It should be mentioned that tin alkyls are very stable organometallic compounds, their decomposition requires high temperature. For instance, in gas phase tetraalkyl tin compounds thermally decompose with measurable rate above 440°C. 247 There is one additional important remark: the TPD peak at 340°C was never observed over Pt/SiO₂ catalyst. This is an additional proof that during tin anchoring and subsequent washing the adsorbed forms of tetraethyltin can be removed.

5.3.5. Characterization by chemisorption techniques

Chemisorption data obtained on various Sn-modified Pt/SiO₂ catalysts are summarized in Table 12. The introduction of tin decreases significantly the number of Pt sites involved in both CO and hydrogen chemisorption. However, the decrease of the H/Pt ratios observed at high Sn/Pt (at./at.) ratios is more pronounced than that of the CO/Pt one.166,217 These results are in good agreement with corresponding literature data248 and our earlier results obtained on different alumina233,242 and silica supported241 bimetallic Sn-Pt catalysts with broad Sn/Pt atomic ratios and different Pt content.

5.3.6. Characterization by FTIR spectroscopy

The characteristic frequencies of the linear and bridged CO bands for parent Pt/SiO₂ and bimetallic Sn-Pt/SiO₂ catalysts with different Sn/Pt ratios are also summarized in Table 12. As it was mentioned in Chapter 2.5.4 in situ FTIR spectroscopy is one of the techniques that can be used for a more detailed investigation of the geometric and electronic structure of metal surfaces via the adsorption of probe molecules.249-252 The chemisorption of CO has often been used to examine the nature of the surface of noble or transition metal atoms through the frequency shift of the stretching vibration of CO adsorbed.178,253

Table 12. Chemisorption data and in situ FTIR results obtained on various Sn-Pt/SiO₂ catalysts

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<th>Exp. N°</th>
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<th>H/Pt</th>
<th>CO/Pt</th>
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<td>1865 (0.86)</td>
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<td>0.099</td>
<td>0.183</td>
<td>2069 (5.898)</td>
<td>n.m. (n.m)</td>
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</table>

a Amount of Sn anchored per Pt atom calculated from AAS analysis and the overall material balance of tin anchoring;
b Frequency and normalized intensity data (the latter are given in parenthesis);
c,d Parent PtSi-3.0-B and Sn-Pt/SiO₂ catalysts, respectively.
Tin anchoring was carried out in benzene at T_r = 50°C in the presence of excess hydrogen. FTIR spectra measured after 40 min of equilibration; n.a. - not analyzed; n.m. – not measurable.

Our results obtained on the parent PtSi-3.0-B catalyst are in a good agreement with literature data.141,254,255 FTIR results presented in Table 12 indicate that the addition of tin onto the Pt/SiO₂ catalyst decreases slightly both the frequency and the intensity of both CO bands. Upon increasing the Sn/Pt ratio a slight stepwise red shift of the carbonyl stretching frequency (from 2083 to 2069 cm⁻¹) occurs. The observed behaviour of our Sn-Pt/SiO₂ catalyst is characteristic for tin-modified supported
platinum catalysts and has been attributed to the dilution of the platinum surface with tin, and thus the decrease of the number of Pt-Pt neighbours by increasing the Sn/Pt ratio.

On the parent Pt/SiO$_2$ and the Sn-Pt/SiO$_2$ catalyst with low Sn/Pt ratio (Sn/Pt= 0.18, see sample 3 in Table 12) the bridged CO band appears around 1865 cm$^{-1}$. Upon increasing the tin content the intensity of bridged CO band strongly diminishes.

### 5.3.7. Characterization by Mössbauer spectroscopy

#### 5.3.7.1. Characterization of catalysts prepared in excess of hydrogen

Mössbauer spectroscopy provides information on oxidation states, phases, lattice symmetry, and lattice vibrations. Results presented in Section 5.3.2 indicate that the use of excess of hydrogen in catalyst modification strongly enhances the formation of MLSC, resulting in high Sn/Pt$_s$ ratios. Upon using this mode of tin anchoring Sn-Pt/SiO$_2$ catalyst with ratio Sn/Pt$_s$= 2.05 was prepared (see experiment 7 in Table 9).

The decomposition of MLSC anchored onto platinum was accomplished both in reductive and oxidative atmospheres. The use of reductive atmosphere provides alloy-type Sn-Pt nanoclusters, while the oxidative one should give finely dispersed SnO$_x$ surface entities over platinum. These two catalysts are distinguished as (H)- and (O)-type samples, respectively.

In order to differentiate between (H)- and (O)-types of Sn-Pt/SiO$_2$ catalysts Mössbauer spectroscopy measurements have been accomplished. The samples were analyzed as received and after reduction in a hydrogen atmosphere at 200 and 300$^\circ$C, respectively. Figure 29 display the Mössbauer spectra of catalysts prepared in the presence of excess of hydrogen (see experiment 7 in Table 9). These results are summarized in Table 13.

The contribution of the Sn-Pt bimetallic component in most of the Mössbauer spectra of Sn-Pt/SiO$_2$ catalysts was composed of two singlets: one with isomer shifts (IS) around 1.20-1.30 mm s$^{-1}$, and another, at 1.98-2.35 mm s$^{-1}$. These two components are denoted as Sn-Pt(a) and Sn-Pt(b), respectively.

According to Charlton et al. the Sn-Pt(a) component is assigned to a Sn substitutional alloy (with a solubility of a few wt% of Sn) in cubic Pt, while the Sn-Pt(b) can be attributed to various intermetallic alloys (NiAs-type PtSn$_3$, hexagonal Pt$_2$Sn$_3$, CaF$_2$-type SnPt$_2$, and orthorombic PtSn$_4$) which exhibit different isomer shifts in a linear dependence of the tin content.

In all reduced samples the tin-rich phase (Sn-Pt(b)) is the main component, however ionic forms of tin exist in all samples except sample (H)$_{300}$. The contribution of tin-rich phase is different in all

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**Figure 29.** Mössbauer spectra obtained at 77 K of Sn-Pt/SiO$_2$ catalyst prepared in excess of hydrogen with Sn/Pt$_s$ ratio= 2.05 (see sample 7 in Table 9).

According to Charlton et al. the Sn-Pt(a) component is assigned to a Sn substitutional alloy (with a solubility of a few wt% of Sn) in cubic Pt, while the Sn-Pt(b) can be attributed to various intermetallic alloys (NiAs-type PtSn$_3$, hexagonal Pt$_2$Sn$_3$, CaF$_2$-type SnPt$_2$, and orthorombic PtSn$_4$) which exhibit different isomer shifts in a linear dependence of the tin content.

In all reduced samples the tin-rich phase (Sn-Pt(b)) is the main component, however ionic forms of tin exist in all samples except sample (H)$_{300}$. The contribution of tin-rich phase is different in all
samples varying in the range of 18-70%. This variation is very pronounced in (O)-type sample, but it is negligible in (H)-type catalyst after hydrogen treatment. The (H)-type sample as received has also a tin oxide phase. The results show that this ionic form of tin can be reduced easily and after reduction at 300°C the Sn-Pt alloy phase is fully restored.

Table 13. Mössbauer parameters obtained from 77 K spectra of Sn-Pt/SiO₂ catalyst prepared in excess of hydrogen (see sample 7 in Table 9).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Species</th>
<th>IS, mm s⁻¹</th>
<th>QS, mm s⁻¹</th>
<th>FWHM, mm s⁻¹</th>
<th>RI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H) form</td>
<td>Sn⁴⁺</td>
<td>0.09</td>
<td>0.64</td>
<td>0.86</td>
<td>55</td>
</tr>
<tr>
<td>as received</td>
<td>Sn-Pt(a)</td>
<td>1.25</td>
<td>-</td>
<td>1.45</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>1.98</td>
<td>-</td>
<td>1.03</td>
<td>18</td>
</tr>
<tr>
<td>(H) form</td>
<td>Sn⁴⁺</td>
<td>0.43</td>
<td>0.19</td>
<td>0.80</td>
<td>8</td>
</tr>
<tr>
<td>T₁H₂≈ 200°C</td>
<td>Sn-Pt(a)</td>
<td>1.30</td>
<td>-</td>
<td>1.17</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.17</td>
<td>-</td>
<td>1.31</td>
<td>54</td>
</tr>
<tr>
<td>(H) form</td>
<td>Sn-Pt(a)</td>
<td>1.32</td>
<td>-</td>
<td>1.44</td>
<td>49</td>
</tr>
<tr>
<td>T₁H₂≈ 300°C</td>
<td>Sn-Pt(b)</td>
<td>2.21</td>
<td>-</td>
<td>1.46</td>
<td>51</td>
</tr>
<tr>
<td>(O) form</td>
<td>Sn⁴⁺</td>
<td>0.08</td>
<td>0.72</td>
<td>0.99</td>
<td>100</td>
</tr>
<tr>
<td>as received</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(O) form</td>
<td>Sn⁴⁺</td>
<td>0.48</td>
<td>-</td>
<td>1.57</td>
<td>16</td>
</tr>
<tr>
<td>T₁H₂≈ 200°C</td>
<td>Sn-Pt(a)</td>
<td>1.24</td>
<td>-</td>
<td>1.30</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.35</td>
<td>-</td>
<td>1.56</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Sn²⁺</td>
<td>2.60</td>
<td>1.42</td>
<td>1.44</td>
<td>7</td>
</tr>
<tr>
<td>(O) form</td>
<td>Sn⁴⁺</td>
<td>0.62</td>
<td>-</td>
<td>0.83</td>
<td>7</td>
</tr>
<tr>
<td>T₁H₂≈ 300°C</td>
<td>Sn-Pt(a)</td>
<td>1.20</td>
<td>-</td>
<td>1.20</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.17</td>
<td>-</td>
<td>2.17</td>
<td>70</td>
</tr>
</tbody>
</table>

IS: isomer shift, mm s⁻¹; QS: quadrupole splitting, mm s⁻¹; FWHM: full-width at half-maximum, mm s⁻¹; RI: relative spectral area (%). Errors on IS, QS and RI values are 0.03 mm s⁻¹ and +/- 10 rel. %, respectively. Catalyst: PtSi-3.0-A. Conditions of tin anchoring: solvent: benzene; T₁= 50°C; Sn₀/Ptₛ= 8.8 (Sn/Ptₛ= 2.05); atmosphere: in the presence of excess hydrogen.

Data given in Table 13 show also that the Mössbauer spectra of (O)- and (H)-type Sn-Pt/SiO₂ catalysts are different. The (O)-type catalyst as received contains only Sn⁴⁺ species. After reduction of this sample at 200°C it still contains Sn⁴⁺ and Sn²⁺ species. Moreover, the reduction of (O)-type sample at 300°C cannot fully restore the alloy phase.

5.3.7.2. Characterization of catalysts prepared in the presence of trace amount of oxygen

Mössbauer spectroscopy was used to characterize Sn-Pt/SiO₂ catalysts with high Sn/Ptₛ ratios prepared by using CSRs. These catalysts were active and highly selective in hydrogenation of crotonaldehyde. Figure 30 display the Mössbauer spectra of catalysts prepared in the presence of trace amount of oxygen. The corresponding data calculated from these spectra are summarized in Table 14.

Data given in Figure 30 and Table 14 indicate that the Sn-Pt/SiO₂ catalysts contain two forms of tin: (i) alloy-type, and (ii) Sn²⁺ species. The majority of tin is alloyed with platinum, while the minority is in Sn²⁺ form (see isomer shifts (IS) in the range of 1.49- 2.31 mm s⁻¹, and 3.33-3.82 mm s⁻¹, respectively⁴,68,261,262). The broad line of the alloyed phases indicates that our Sn-Pt/SiO₂ catalysts contain different types of Sn-Pt alloy phases.

In sample III-1 the Pt-rich phase (Sn-Pt(a)) is the main component (70.4% vs. 13.6%), while in sample III-3 the Sn-rich phase (Sn-Pt(b)) prevails (54.4 % vs. 31.7%). This fact indicates also that upon increasing the Sn/Ptₛ ratio a gradual enrichment of the alloy phase in tin takes place.

The existence of Sn²⁺ species in catalysts shows that certain part of tin anchored onto the platinum cannot be fully reduced. Upon increasing the Sn/Ptₛ ratio the proportion of Sn²⁺ species remains almost constant. The mean value was around 15 %. However the initial concentration of tin [Sn₀] used in tin anchoring for the preparation of III-3 sample (Sn/Ptₛ= 2.46) was in 6 times higher than that of III-1 sample (Sn/Ptₛ= 1.14) ([Sn₀]= 8.9 x 10⁻² M and 1.5 x 10⁻² M, respectively). As far as the ratio of Sn²⁺ species was almost constant in all three samples (see Table 14) its formation was attributed to the use
of oxygen during the anchoring reaction. It is tentatively suggested that this form of tin appears on the platinum-support interface. Hence the ratio of Sn$^{2+}$ species is independent of the amount of tin anchored for this reason the introduction of tin onto the support can be excluded.

### Table 14. Mössbauer parameters of Sn-Pt/SiO$_2$ catalyst prepared in the presence of trace amount of oxygen (samples III-1-3, corresponding to experiments 6, 9 and 12 in Table 11, respectively).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Species</th>
<th>IS, mm s$^{-1}$</th>
<th>QS, mm s$^{-1}$</th>
<th>FWHM, mm s$^{-1}$</th>
<th>RI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-1</td>
<td>Sn-Pt(a)</td>
<td>1.56</td>
<td>-</td>
<td>1.23</td>
<td>70.4</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.31</td>
<td>-</td>
<td>0.75</td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>Sn$^{2+}$</td>
<td>3.33</td>
<td>0.71</td>
<td>0.75</td>
<td>16.0</td>
</tr>
<tr>
<td>III-2</td>
<td>Sn-Pt(a)</td>
<td>1.56</td>
<td>-</td>
<td>0.97</td>
<td>38.0</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.20</td>
<td>-</td>
<td>1.03</td>
<td>46.7</td>
</tr>
<tr>
<td></td>
<td>Sn$^{2+}$</td>
<td>3.69</td>
<td>0.92</td>
<td>0.87</td>
<td>15.3</td>
</tr>
<tr>
<td>III-3</td>
<td>Sn-Pt(a)</td>
<td>1.49</td>
<td>-</td>
<td>1.03</td>
<td>31.7</td>
</tr>
<tr>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.15</td>
<td>-</td>
<td>1.13</td>
<td>54.4</td>
</tr>
<tr>
<td></td>
<td>Sn$^{2+}$</td>
<td>3.82</td>
<td>1.19</td>
<td>0.76</td>
<td>13.9</td>
</tr>
</tbody>
</table>

IS: isomer shift, mm s$^{-1}$; QS: quadrupole splitting, mm s$^{-1}$; FWHM: full-width at half-maximum, mm s$^{-1}$; RI: relative spectral area (%). Errors on IS, QS and RI values are 0.03 mm s$^{-1}$ and ± 10 rel. %, respectively. III-1- Sn/Pt$_{1}$= 1.14; III-2- Sn/Pt$_{1}$= 2.01; III-3- Sn/Pt$_{1}$= 2.46. Catalyst: PtSi-3.0-A.

![Figure 30](image-url)

**Figure 30.** Mössbauer spectra of Sn-Pt/SiO$_2$ catalysts with different Sn/Pt$_{1}$ ratios prepared in the presence of trace amount of oxygen. The Sn/Pt$_{1}$ ratios of samples (III-1), 1.14; (III-2), 2.01; and (III-3), 2.46. Samples III-1-3 correspond to experiments 6, 9 and 12 in Table 11, respectively.

#### 5.3.7.3. The influence of atmosphere and the type tin precursor compounds used in tin anchoring on the Mössbauer spectroscopy results

The influence of the type of tin precursor compounds and reaction atmosphere on the selectivity of tin anchoring over the PtSi-3.0-A catalyst is summarized in Table 15.

The results of Mössbauer spectroscopy indicate that the modification of Pt with Sn using CSRs was highly selective even at high Sn/Pt$_{1}$ ratios, i.e., almost all tin introduced was exclusively anchored onto the platinum. The Sn/Pt$_{1}$ ratio was increased up to 2.5 resulting in at least two types of supported bimetallic nanoclusters: the Pt-rich (Sn-Pt(a)) and Sn-rich (Sn-Pt(b)) alloy phases as shown in Table 15.
Table 15. The influence of reaction atmosphere and tin precursor compound used on the selectivity of tin anchoring. Selected Mössbauer spectroscopy results.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Sn/Pt</th>
<th>Species</th>
<th>IS, mm s^{-1}</th>
<th>QS, mm s^{-1}</th>
<th>FWHM, mm s^{-1}</th>
<th>RI, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>119SnMe₄, Ar</td>
<td>0.36</td>
<td>Sn-Pt(a)</td>
<td>1.39</td>
<td>-</td>
<td>1.19</td>
<td>75.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.42</td>
<td>-</td>
<td>1.35</td>
<td>25.1</td>
</tr>
<tr>
<td>119SnMe₄, H₂</td>
<td>1.31</td>
<td>Sn⁴⁺</td>
<td>0.49</td>
<td>0.42</td>
<td>0.59</td>
<td>6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(a)</td>
<td>1.31</td>
<td>-</td>
<td>1.27</td>
<td>37.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.32</td>
<td>-</td>
<td>2.00</td>
<td>48.8</td>
</tr>
<tr>
<td></td>
<td>Sn⁴⁺</td>
<td>2.88</td>
<td>2.11</td>
<td>-</td>
<td>1.06</td>
<td>9.2</td>
</tr>
<tr>
<td>SnEt₄, H₂</td>
<td>2.05</td>
<td>Sn-Pt(a)</td>
<td>1.32</td>
<td>-</td>
<td>1.44</td>
<td>49.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.21</td>
<td>-</td>
<td>1.46</td>
<td>51.0</td>
</tr>
<tr>
<td>SnEt₄, O₂</td>
<td>2.46</td>
<td>Sn-Pt(a)</td>
<td>1.49</td>
<td>-</td>
<td>1.03</td>
<td>32.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.15</td>
<td>-</td>
<td>1.13</td>
<td>54.0</td>
</tr>
<tr>
<td></td>
<td>Sn⁴⁺</td>
<td>3.82</td>
<td>1.19</td>
<td>-</td>
<td>0.76</td>
<td>14.0</td>
</tr>
<tr>
<td>Sn₂Me₆, H₂</td>
<td>2.29</td>
<td>Sn⁴⁺</td>
<td>0.64</td>
<td>0.40</td>
<td>0.59</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(a)</td>
<td>1.37</td>
<td>-</td>
<td>0.91</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sn-Pt(b)</td>
<td>2.02</td>
<td>-</td>
<td>1.43</td>
<td>71.0</td>
</tr>
</tbody>
</table>

IS: isomer shift, mm s^{-1}; QS: quadrupole splitting, mm s^{-1}; FWHM: full-width at half-maximum, mm s^{-1}; RI: relative spectral area (%). Errors on IS, QS and RI values are 0.03 mm s^{-1} and ± 10 rel. %, respectively. The catalyst samples were re-reduced in situ in hydrogen at 623 K for 2 h in the Mössbauer cell. Mössbauer parameters obtained from 77 K spectra. Catalyst: PtSi-3.0-A.

As emerges from Table 15 using various types of tin precursor compounds (SnMe₄, SnEt₄ and Me₃Sn-SnMe₃) and Ar, H₂ or O₂ atmosphere during tin anchoring different proportions between the Pt-rich and Sn-rich alloy phases can be obtained. The lowest amount (25 %) of tin-rich alloy phase was determined in samples with monolayer tin coverage (Sn/Pt = 0.36), while in sample prepared using hexamethylditin, as tin precursor compound, the Sn-Pt(b) alloy-type phase prevails (71 %). This fact indicates that upon using different experimental conditions series of Sn-Pt catalysts with gradual enrichment in Sn-rich alloy phase can be prepared. It was demonstrated in our earlier studies216,240,244,259 that catalysts with high Sn/Pt, ratios were active and highly selective in hydrogenation of α,β-unsaturated aldehydes.

5.3.8. Transformation of (O)- and (H)-type Sn-Pt catalysts followed by EXAFS

In the reduced sample the presence of platinum and tin in the first coordination shell of Pt and an increase of the number of filled valence state of platinum indicate the formation of a Pt-Sn bimetallic phase.263 The X-ray absorption near edge structure (XANES) Pt spectrum (see Figure 31) shows that in the presence of hydrogen platinum easily reduces to Pt⁰. The results of the extended X-ray absorption fine structure (EXAFS) measurements obtained under oxidizing and reducing conditions are demonstrated in both Table 16 and Scheme 10A.

As emerges from the EXAFS spectrum of Sn-Pt/SiO₂ catalyst reduced at 300°C (see Figure 31 and Table 16), the Sn (as Sn⁰) is clearly coordinated with Pt, showing no sign of oxide. The presence of mainly Pt-Sn and small amount of Sn-Sn bonds indicates that the modification of Pt/SiO₂ catalyst is exclusive without any interaction with the support. The results also demonstrate that after reduction in hydrogen at 300°C the surface contains nearly isolated Sn atoms (< 4 atoms per cluster) interacting strongly with the fairly large Pt cluster (see Scheme 10A and Table 16). As shown in Table 16 the increase of the reduction temperature up to 500°C results in disappearance of Sn-Sn bonds. Under these reduction conditions the presence of Pt-Sn and Pt-Pt interactions were evidenced.

The Pt EXAFS spectra under oxidizing conditions show that the oxidation of Pt remains incomplete at 300°C and that strong interactions of Pt-Sn and Pt-Pt are still present under these conditions. The obtained results indicate that the bulk of the Pt remains Pt⁰.

As shown in Scheme 10B, at low temperature (< 200°C) under oxidizing conditions, a bond between the Sn and Pt still remains. The Sn has been oxidized to Sn⁴⁺ (there is little evidence for Sn⁵⁺), with the Sn-Sn bond being replaced by a Sn-O-Sn link. At higher temperatures (>300°C) the Sn-Pt bond is replaced by a Sn-O-Pt bond, with the oxidized species being primarily SnO₂ (see Scheme 10B).
Figure 31. Fourier Transform of Sn K edge EXAFS spectra for oxidized (A), and reduced (B) Sn-Pt/SiO$_2$ catalyst. Near edge spectra for oxidized (A) and reduced (B) catalyst (inset); Sn-Pt/SiO$_2$ catalyst with Sn/Pt= 0.47 ratio. Conditions of tin anchoring step I: $^{119}$Sn(CH$_3$)$_4$ was used as tin precursor compound; atmosphere: H$_2$; $T_r$= 50°C. Catalyst: PtSi-3.0-Å.

Table 16. Results of EXAFS measurements obtained under oxidizing and reducing conditions.

<table>
<thead>
<tr>
<th>Condition</th>
<th>d (Å)</th>
<th>C.N.</th>
<th>Potential CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidized (300 °C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn-O</td>
<td>2.06</td>
<td>6.0</td>
<td>6</td>
</tr>
<tr>
<td>Sn-Pt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn-Sn</td>
<td>3.29</td>
<td>2.0</td>
<td>2 [linear]</td>
</tr>
<tr>
<td>Pt-O</td>
<td>2.04</td>
<td>1.8</td>
<td>4</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>2.79</td>
<td>3.7</td>
<td>12</td>
</tr>
<tr>
<td>Pt-Sn</td>
<td>2.78</td>
<td>0.6</td>
<td>12</td>
</tr>
<tr>
<td>Reduced</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn-Sn (300 °C)</td>
<td>2.82</td>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td>Sn-Pt (300 °C)</td>
<td>2.82</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>Pt-Sn (500 °C)</td>
<td>2.80</td>
<td>2.0</td>
<td>12</td>
</tr>
<tr>
<td>Pt-Pt (500 °C)</td>
<td>2.78</td>
<td>6.1</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 10. A- Surface transformations observed on Sn-modified Pt catalyst under oxidizing and reducing conditions at 300°C. B- Proposed mechanism of oxidation at temperature below 200°C and higher than 300°C.

It is especially interesting that the transformation of (O)-type catalysts into (H)-type catalysts is reversible. EXAFS measurements have confirmed that the Sn is easily oxidized and reduced. Consequently, it can be concluded that the catalyst consisted of mononuclear SnO$_x$ species that “decorate” the surface without forming larger clusters.

5.3.9. Low temperature CO oxidation over Sn-Pt/SiO$_2$ catalysts

The Sn-Pt/SiO$_2$ catalysts prepared by CSRs showed high activity in low temperature CO oxidation. Selected TPO results obtained at $P_{CO}$= 16 Torr are shown in Figure 32. The temperature, at which 50% CO conversion has been achieved ($T_{50}$), was used to compare the activity of catalysts. This values are shown as a function of the Sn/Pt (at./at.) ratio in Figure 32.

The following main conclusions can be drawn from Figure 32:
- The addition of tin strongly increases the activity of catalysts.
- Catalysts with Sn/Pt (at./at.) ratio around 0.2-0.5 have high activity even at room temperature at $P_{CO}$= 16 Torr.
- Type of tin precursor compound (Sn(CH$_3$)$_4$, Sn(C$_2$H$_5$)$_4$) and temperature of tin anchoring have only minor influence on the activity of catalysts.
- The loss of activity at high Sn/Pt ratios was attributed to the poisoning effect of tin.
Both 300 and 77 K \textit{in situ} Mössbauer spectra of (O)-type Sn-Pt/SiO$_2$ catalyst with Sn/Pt$_s$ = 1.31 at different experimental condition are shown in Figure 33.

**Figure 32.** Activity of Sn-Pt/SiO$_2$ catalysts in CO oxidation at $P_{CO}=16$ torr. Dependence of $T_{50}$ values of the Sn/Pt (at/at) ratio. Tin precursor compound: Sn(C$_2$H$_5$)$_4$, $T_r$: (▲), 30°C; (▲), -40°C; (■), 50°C. (■), Tin precursor compound: Sn(CH$_3$)$_4$, $T_r$= 50°C. Catalyst: PtSi-3.0-A.

**Figure 33.** Mössbauer spectra of (O)-type Sn-Pt/SiO$_2$ catalyst with Sn/Pt$_s$ = 1.31 at different experimental condition (see experiment 7 in Table 10). Catalyst: PtSi-3.0-A.

A - Spectra obtained at 300 K; B - spectra obtained at 77 K. Catalyst samples: a) as received, b) after reduction at 573 K in hydrogen, c) \textit{in situ} measurement in CO oxidation at 300 K, d) \textit{in situ} reduction in hydrogen at 300 K, e) \textit{in situ} measurement in CO oxidation at 300 K, f) \textit{in situ} treatment in CO.

The following main conclusions can be drawn from Mössbauer spectroscopy results shown in Figure 33:

- After the reduction in H$_2$ the majority of tin (85 %) is in the form of alloy phases.
- In the presence of CO + O$_2$ mixture:
  - both Pt-rich and Sn-rich alloy phases are oxidized to Sn$^{4+}$ in a high proportion;
  - a new type of alloy phase PtSn (1:1) is formed (23 %);
  - two forms of Sn$^{4+}$ can be differentiated as (i) stable Sn$^{4+}$(ox) phase and (ii) highly mobile one, well-dispersed Sn$^{4+}$(sf).
- Treatment of the oxidized catalyst at room temperature either with H$_2$ or CO partially restores the initial alloy phases (in H$_2$: 67-86%).
Mössbauer spectroscopy has been recently used to follow compositional and structural changes of Sn-Pt/SiO\(_2\) catalysts during CO oxidation reaction. The results show that the Sn-Pt alloys with different compositions are oxidized and strongly reconstructed. Time dependence of the transformation of different Sn-Pt alloys and SnO\(_x\) phases during the catalytic run is shown in Figure 34A-B. As seen from Figure 34A-B, Sn-Pt/SiO\(_2\) catalysts reduced at 300\(^\circ\)C contain two forms of tin: (i) alloy-type, and (ii) Sn\(^{2+}\) species. The majority of tin is alloyed with platinum (81.5 %), while the minority is in Sn\(^{2+}\) form (18.5 %) (see isomer shifts (IS) in the range of 1.51 – 2.28 mm s\(^{-1}\), and 3.34 mm s\(^{-1}\), respectively). We determined four Sn-Pt alloy-type species in this catalyst (alloy 1: Sn dissolved in Pt (Sn < 6 at %); alloy 2: Pt\(_3\)Sn phase; alloy 3: PtSn (1:1) phase and alloy 4: tin-rich Pt\(_2\)Sn\(_3\) and/or PtSn\(_4\) phases).

**Figure 34.** Results obtained from deconvolution of the \(^{119}\)Sn Mössbauer spectra. A - (■), alloy 1 (IS= 1.21 mm s\(^{-1}\); Sn dissolved in Pt (Sn < 6 at %); ( ), alloy 2 (IS= 1.51 mm s\(^{-1}\); Pt-rich Pt\(_3\)Sn phase); (◇), alloy 3 (IS= 1.91 mm s\(^{-1}\); PtSn (1:1) phase); (◆), alloy 4 (IS= 2.28 mm s\(^{-1}\); Sn-rich Pt\(_2\)Sn\(_3\) and PtSn\(_4\) phases). B - (■), Sn\(^{4+}\) (ox) (IS= -0.35-0.07 mm s\(^{-1}\)); ( ), Sn\(^{4+}\) (sf) (IS= 0.42-0.62 mm s\(^{-1}\)); (◇), Sn\(^{2+}\) (ox) (IS= 3.34 mm s\(^{-1}\)); (◆), Sn\(^{2+}\) (sf) (4.26 mm s\(^{-1}\)). Catalyst: PtSi-3.0-A, \[^{119}\text{Sn(CH}_3)_4\]O = 1.3 x 10\(^{-2}\) M, Sn/Pt = 1.3, Sn/Pt\(_s\) = 1.28 (see experiment 6 in Table 10).

The time dependence of the decomposition of these alloys exhibits a very interesting relationship, as shown in Figure 34A. As emerges from Figure 34A the transformation of four Sn-Pt alloy-type species should have consecutive character (PtSn\(_1\) → PtSn\(_2\) → Pt\(_2\)Sn\(_3\) → PtSn → PtSn). The character of kinetic curves indicates that the decomposition of alloys 2 and 4 starts immediately after the addition of CO + O\(_2\) mixture at room temperature. As shown in Figure 34A-B during first 5 min these alloy phases are transformed in high extent into oxidized Sn\(^{4+}\) (sf) species and alloy phases with lower Sn content 2 → 1 and 4 → 3. After 5 min of the oxidation reaction the degree of the conversion of alloy phases 2 and 4 was 52.8 and 64.2 %, respectively.

**Scheme 11.** The supported nanocluster re-reduced in hydrogen at 300\(^\circ\)C before (A) and after (B) its reconstruction in the presence of CO + O\(_2\) mixture.
After 1 h of CO oxidation Sn$^{+4}$ (sf) and Sn$^{+4}$ (ox) species are the main products (91.3 %) and only small amount (6.6 %) of Pt$_3$Sn alloy phase ( alloy 2) and traces of Sn$^{+2}$ (sf) (2.1 %) can still be observed in the spectrum. These new results are in a good agreement with our earlier studies of low temperature CO oxidation.$^{217,237,258}$

The schematic view of the supported nanocluster re-reduced in hydrogen at 300°C before (A) and after (B) its reconstruction in the presence of CO + O$_2$ mixture is shown in Scheme 11.

It has been demonstrated that alloy phases are transformed to Sn$^{+4}$ oxide species and PtSn alloys with decreased tin content: PtSn$_4$ $\rightarrow$ PtSn$_3$ $\rightarrow$ PtSn $\rightarrow$ Pt$_3$Sn. Platinum-rich alloy (Pt$_3$Sn) is converted finally to Pt metal and SnO$_2$ moieties.$^{258}$

It is suggested that the activity increase is attributed to the in situ formation of “Sn$^{n+}$ - Pt” active site ensembles involved in CO activation. The transformation of Sn$^0$ to Sn$^{n+}$ was evidenced by in situ Mössbauer and FTIR spectroscopy. The corresponding DFT calculations revealed the formation of “Sn$^{n+}$ - Pt” active site ensembles.$^{258}$

### 5.3.10. Use of supported Sn-Pt/SiO$_2$ catalysts in various catalytic reactions

Supported Sn-Pt/SiO$_2$ catalysts prepared by the methods described in Chapter 5.3.3 were used in selective hydrogenation of unsaturated aldehydes to unsaturated alcohols.$^{215,216,240,244,259,265}$ In these studies crotonaldehyde was hydrogenated into crotyl alcohol with high selectivity both in gas and liquid phases. Reaction induced selectivity enhancement was also observed. Upon using in situ Mössbauer spectroscopy it was demonstrated that metallic tin is oxidized by crotonaldehyde to form a very mobile Sn$^{+4}$ layer. This Lewis acid-type surface species in the vicinity of Pt is involved in the carbonyl activation, while the alloyed form of tin strongly suppresses the re-adsorption of primarily formed unsaturated alcohols. The net result is the high selectivity to the unsaturated alcohols.

This approach has been extended to the modification of Pt catalysts used in citral hydrogenation.$^{241}$ The catalytic behaviour of different bimetallic Sn-Pt/SiO$_2$ catalysts with broad Sn/Pt atomic ratios and at three Pt contents (0.45, 0.72 and 1.25 wt%) was studied in liquid-phase citral hydrogenation. Results show that Sn-modified catalysts are highly selective for the hydrogenation of the carbonyl group and selectivity strongly depends on both the Pt loading and the amount of tin anchored. Results of CO chemisorption, Mössbauer spectroscopy and catalytic test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis) clearly show that tin was introduced exclusively onto the platinum.

Various Sn-Pt/SiO$_2$ catalysts with different Sn content prepared by using CSRs were also tested in hydrogen-assisted 1,2-dichloroethane dechlorination.$^{266}$ To understand the role of ionic Sn species in Pt-Sn catalyzed dechlorination reactions, two different procedures were used to modify Pt/SiO$_2$ catalysts with Sn: (i) via conventional impregnation and (ii) by CSRs. Both types of catalysts with a Pt/Sn (at./at.) ratio less than one exhibited high steady-state selectivity towards ethylene formation. Characteristic feature of these catalysts was the increase of selectivity with time on stream. The CSRs catalyst exhibited higher initial selectivity toward ethylene than the co-impregnated one, while the steady state ethylene selectivity was higher for the co-impregnated catalysts.$^{266}$

Sn-Pt/SiO$_2$ catalysts were also tested in liquid phase hydrogenation of benzonitrile.$^{267}$ The addition of tin to Pt in the range of (Sn/Pt)$_{\text{surface}}$=0.5-1.25 led to an increase in the TOF by a factor of 2. It was assumed that tin is involved in the activation of CN triple bond. Catalytic data obtained over supported Sn-Pt/SiO$_2$ catalysts are given in Appendix (see Tables A-1 and A-2).

### 5.4. Peculiarities of the modification of Pt/Al$_2$O$_3$ catalysts with Sn(C$_2$H$_5$)$_2$, by CSRs

In this Chapter the details of the preparation of Sn-Pt/Al$_2$O$_3$ catalysts with high Sn/Pt ratios will be given. This study was aimed to extend the formation of multilayered SOMS to alumina supported platinum catalysts. The decomposition of SOMS has been carried out by TPD technique both in reductive and oxidative atmospheres (see Chapter 5.2).

The decomposition of multilayered SOMS in a hydrogen atmosphere, similarly to the decomposition of PSC (see reaction (2.9)), leads to the formation of alloy-type bimetallic nanoclusters:

$$\text{Pt} - \{ \text{SnR}_3 \} + \alpha/2 \text{H}_2 \rightarrow \text{Pt-Sn}_\alpha + \alpha \text{RH} \quad (5.10)$$
It has been shown that the formation of alloy-type Pt-Sn surface species results in: (i) decrease of H\textsubscript{2} and CO chemisorption; (ii) decreased chemisorption of hydrocarbons; and (iii) high affinity towards oxygen.\textsuperscript{216}

The decomposition of SOMS in O\textsubscript{2} results in the formation of supported platinum covered and surrounded by finely dispersed tin-oxide with Lewis-acid character.\textsuperscript{233,242} The decomposition of multilayered SOMS in the presence of oxygen can be written as follows:

\[
\text{Pt} \cdot \{\text{SnR}_{3-x}(\text{SnR}_{4-y})_{m}(\text{SnR}_{4})_{n}\} + \beta \text{O}_2 \rightarrow \text{Pt} \cdot (\text{SnO}_z)_{n} + \gamma \text{CO}_2 + \eta \text{H}_2\text{O} \quad (5.11)
\]

In this case the formation of “metal ion-metal nanocluster ensemble sites” has been suggested. It is necessary to mention that the modification of Pt/Al\textsubscript{2}O\textsubscript{3} catalyst with tetraethyltin results in more complex surface chemistry. Parallel to tin anchoring onto platinum a surface reaction with the involvement of the support OH groups (see reaction (5.8) in Chapter 5.2) also takes place. Consequently, on Pt/Al\textsubscript{2}O\textsubscript{3} catalyst the formation of the organometallic species anchored to the support (OMSAS) according to equation (5.8) can not be excluded.

**5.4.1. Study of Sn(C_2H_5)_4 anchoring onto alumina support**

Upon comparing silica and alumina supported Pt catalysts it was observed that under identical experimental condition ([Sn(C_2H_5)_4]\textsubscript{0} = 25.3 mM, solvent: benzene, T\textsubscript{r} = 50°C, \tau_r = 2 h) the tin precursor compound reacted with the surface OH group of alumina,\textsuperscript{233,242} while no such side reaction was evidenced on silica.\textsuperscript{215} However, it should be emphasized that the rate of this side reaction is much slower than that of the tin anchoring one.\textsuperscript{215,233,242}

**Figure 35.** Reaction of Sn(C_2H_5)_4 with γ-Al_2O_3. Amount of alumina: 1 g; [Sn]\textsubscript{0} = 25.32 mM, T\textsubscript{r} = 50°C; solvent: benzene. Temperature of hydrogen treatment of alumina (t\textsubscript{red}): ( ), 300°C; ( ), 400°C; ( ), 500°C.

**Figure 36.** Decomposition of surface complexes formed on alumina support. Temperature of hydrogen treatment of alumina support (t\textsubscript{red}): A- 400°C; B- 500°C; ( ), ethane, and ( ), ethylene.
Tetraethyltin reacts with surface OH groups of support resulting in the formation of tin-containing surface species anchored onto alumina via surface oxygen atoms (OMSAS) and elimination of ethane (see reaction (5.8) in Chapter 5.2). As seen from Figure 35, the rate of the reaction of Sn(C₂H₅)₄ with γ-Al₂O₃ support strongly depended on the temperature of hydrogen pretreatment.

The decomposition of tin-containing surface species formed gives two ethane and one ethylene peaks, as shown in Figure 36. The first ethane TPD peak around 180-190°C was attributed to the decomposition of OMSAS (Surf-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 Sn(C₂H₅)₄ adsorbed onto surface oxygen or aluminum ions of Al₂O₃.

5.4.2. Study of the tin anchoring over Pt/Al₂O₃ catalysts

The kinetic curves of the formation of ethane and ethylene in the tin anchoring reaction over Pt/Al₂O₃ catalysts are shown in Figures 37A and 37B. These results were obtained on two different catalysts; however, the character of the kinetic curves was quite similar. As seen from Figure 37A-B, there are two distinct parts in the kinetic curves. In both cases the initial part shows high rate. This behaviour strongly resembles the character of the kinetic curves obtained over Pt/SiO₂ catalyst. In both experiments ethylene is formed in small amount. It is worth for mentioning that in both experiments the Sn/Ptₐ ratio is 2.3 ± 0.05. These data indicate that in both cases multilayered SOMS are formed.

![Figure 37](image1)

**Figure 37.** Kinetic curves of the formation of ethane (■) and ethylene (▲) in the tin anchoring step I. A– Catalyst: PtAl-0.3-B, B– Catalyst: PtAl-0.35. Reaction conditions: W_cat = 1 g; [Sn]₀ = 25.32 mM; atmosphere: in the presence of adsorbed hydrogen; solvent: benzene; T_r = 50°C.

![Figure 38](image2)

**Figure 38.** Decomposition of SOMS in hydrogen atmosphere. A- Sn₀/Ptₐ= 0.45 (Sn/Ptₐ= 0.34); B- Sn₀/Ptₐ= 2.56 (Sn/Ptₐ= 1.39); C- Sn₀/Ptₐ= 10.74 (Sn/Ptₐ= 2.16) (see experiments 2, 4 and 6 in Table 17). Catalyst: PtAl-0.3-B. Reaction conditions: W_cat = 1 g; atmosphere of step I: Ar; solvent: benzene; T_r = 50°C. (■), Measured and (▲), fitted.

The decomposition of surface complexes formed over PtAl-0.3-B catalyst in hydrogen atmosphere is shown in Figure 38A-C. Figure 38A shows the decomposition pattern of SOMS under monolayer
coverage (Sn/Pt = 0.34), while Figures 38B and 38C show pattern at multilayer coverages (Sn/Pt = 1.39 and 2.16, respectively). As shown in Figure 38A-C, upon increasing the Sn/Pt ratio the character of the TPD curves has been altered. The end of the decomposition has been shifted to the high-temperature region as demonstrated in Figure 38A-C. Similar decomposition pattern has been observed upon tin anchoring onto Pt/SiO$_2$.

The TPD pattern is completely different from that of on pure alumina. The high-temperature peak around 250-270°C, which was ascribed to tetraethyltin adsorbed onto alumina, was never observed on Sn-Pt/Al$_2$O$_3$ catalysts. However, the peak around 200°C is detected at high initial concentration of Sn(Pt) catalysts, as shown in Figure 38A-C. These results indicate that the modification of Pt/Al$_2$O$_3$ catalysts with Sn(Pt) results in Sn-Pt bimetallic catalysts in which two forms of tin can be distinguished: (i) tin anchored onto the Pt and (ii) tin anchored onto the Al$_2$O$_3$. The formation of tin anchored onto the platinum is exclusive up to Sn/Pt$_s$ = 1.39.

General data related to the modification of PtAl-0.3-B catalyst with Sn(C$_2$H$_5$)$_4$ in the presence of adsorbed hydrogen are summarized in Table 17. Upon increasing the initial concentration of tetraethyltin both the initial rate of step I and the amount of hydrocarbons formed increased.

Table 17. General data related to the modification of PtAl-0.3-B catalyst with Sn(C$_2$H$_5$)$_4$ in the presence of adsorbed hydrogen

<table>
<thead>
<tr>
<th>No</th>
<th>[Sn]$_0$, mM</th>
<th>Sn$_0$/Pt$_s$</th>
<th>$w_{pt}$ x 10$^{-6}$</th>
<th>$n^1$ x 10$^{-6}$</th>
<th>$n_{244}^1$ x 10$^{-6}$</th>
<th>$n^2$ x 10$^{-6}$</th>
<th>x</th>
<th>TOF, s$^{-1}$ x 10$^{-4}$</th>
<th>Sn, wt%$^a$</th>
<th>Sn/Pt$_s$$^b$</th>
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<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.15</td>
<td>0.05</td>
<td>1.5</td>
<td>0.1</td>
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</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.46</td>
<td>0.19</td>
<td>4.0</td>
<td>0.2</td>
<td>10.7</td>
<td>1.08</td>
<td>2.9</td>
<td>0.04</td>
<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>1.06</td>
<td>0.24</td>
<td>8.3</td>
<td>0.5</td>
<td>25.1</td>
<td>1.00</td>
<td>3.7</td>
<td>0.1</td>
<td>0.76</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>2.56</td>
<td>0.53</td>
<td>13.3</td>
<td>0.6</td>
<td>41.3</td>
<td>1.00</td>
<td>8.1</td>
<td>0.18</td>
<td>1.39</td>
</tr>
<tr>
<td>5</td>
<td>6.1</td>
<td>5.25</td>
<td>0.64</td>
<td>17.0</td>
<td>0.9</td>
<td>52.4</td>
<td>0.98</td>
<td>9.7</td>
<td>0.21</td>
<td>1.62</td>
</tr>
<tr>
<td>6</td>
<td>11.1</td>
<td>10.74</td>
<td>0.80</td>
<td>23.3</td>
<td>1.8</td>
<td>72.0</td>
<td>1.00</td>
<td>12.2</td>
<td>0.28</td>
<td>2.16</td>
</tr>
<tr>
<td>7</td>
<td>25.3</td>
<td>23.64</td>
<td>0.92</td>
<td>26.2</td>
<td>2.0</td>
<td>82.2</td>
<td>0.97</td>
<td>14.0</td>
<td>0.32</td>
<td>2.47</td>
</tr>
</tbody>
</table>

$^a$ Sn content calculated from the overall material balance of tin anchoring; $^b$ Amount of Sn anchored per surface Pt atom calculated using CO/Pt = 0.71; Catalyst re-reduced in H$_2$ atmosphere at $t_{red} = 500^\circ C$ for 2 h; catalyst amount: W$_{cat}$ = 1 g; atmosphere of step I: Ar; solvent: benzene; reaction temperature $T_r = 50^\circ C$; duration of tin anchoring step I ($\tau_r$): 2 h.

Figure 39. The reaction order with respect to the Sn(C$_2$H$_5$)$_4$ over PtAl-0.3-B in the presence of adsorbed hydrogen. (●), Low ([Sn]$_0$ ≤ 2.5 mM) and (◆), high initial tin concentration (2.5 mM ≤ [Sn]$_0$ ≤ 25.3 mM).

As shown in Table 17 the value of x is around 1 and it is almost independent of the Sn$_0$/Pt ratio. As emerges from Figure 39 at low [Sn]$_0$ concentration ([Sn]$_0$ ≤ 2.5 mM) the reaction order with respect to the tetraethyltin is about 0.81. At high initial concentrations ([Sn]$_0$ ≥ 2.5 mM, Sn$/$Pt$ ≥$ 2.56) the value of the reaction order decreases to 0.25.
Table 18. Summary of results of tin anchoring onto Pt/Al₂O₃ catalysts with low Pt content

<table>
<thead>
<tr>
<th>No</th>
<th>[Sn]₀, mM</th>
<th>Sn/Ptᵦ</th>
<th>w₀, x 10⁻⁶</th>
<th>n¹, x 10⁻⁶</th>
<th>n², x 10⁻⁶</th>
<th>x</th>
<th>Sn/Ptᵦ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtAl-0.3-B-1</td>
<td>0.15</td>
<td>0.15</td>
<td>0.05</td>
<td>1.5</td>
<td>4.7</td>
<td>0.98</td>
<td>0.14</td>
</tr>
<tr>
<td>PtAl-0.3-B-2</td>
<td>0.51</td>
<td>0.46</td>
<td>0.19</td>
<td>4.0</td>
<td>10.7</td>
<td>1.08</td>
<td>0.34</td>
</tr>
<tr>
<td>PtAl-0.3-B-3</td>
<td>1.01</td>
<td>1.06</td>
<td>0.24</td>
<td>8.3</td>
<td>25.1</td>
<td>1.00</td>
<td>0.76</td>
</tr>
<tr>
<td>PtAl-0.35-1</td>
<td>0.15</td>
<td>0.11</td>
<td>0.04</td>
<td>1.3</td>
<td>4.4</td>
<td>0.90</td>
<td>0.09</td>
</tr>
<tr>
<td>PtAl-0.35-2</td>
<td>0.51</td>
<td>0.37</td>
<td>0.13</td>
<td>4.2</td>
<td>14.6</td>
<td>0.88</td>
<td>0.31</td>
</tr>
<tr>
<td>PtAl-0.35-3*</td>
<td>0.10</td>
<td>0.73</td>
<td>0.24</td>
<td>7.4</td>
<td>24.3</td>
<td>0.93</td>
<td>0.52</td>
</tr>
<tr>
<td>PtAl-0.35-4</td>
<td>2.53</td>
<td>1.85</td>
<td>0.31</td>
<td>9.4</td>
<td>34.9</td>
<td>0.85</td>
<td>0.72</td>
</tr>
</tbody>
</table>

* Amount of Sn anchored per surface Pt atom calculated using CO/Pt ratio; b Duration of tin anchoring step I (τₗ): 4 h.

Catalysts re-reduced in H₂ atmosphere at t_{red} = 500°C for 2 h; catalyst amount: W_{cat} = 1 g; atmosphere: Ar; solvent: benzene; reaction temperature Tₗ = 50°C; duration of tin anchoring step I (τₗ): 2 h.

It is necessary to mention that the behaviour of these two alumina supported catalysts (PtAl-0.3-B and PtAl-0.35) in tin anchoring reaction is almost identical (see Table 18). It is worth mentioning that, as shown in Table 1, the dispersion values of Pt in both catalysts determined from CO/Pt ratio is also similar. As seen from data given in Table 18, the value of stoichiometry of tin anchoring is around \( x = 0.95 ± 0.06 \) and it is independent of the Sn/Ptᵦ ratio.

5.4.3. Elementary steps involved in the anchoring of Sn(C₂H₅)₄ onto supported platinum

In this Chapter kinetic results obtained in the two steps tin anchoring process will be summarized and the focus will be laid on the influence of the duration of tin anchoring on the type of SOMS formed. This study shall provide new information about the elementary steps involved in the anchoring of tetraethyltin onto platinum.

In the next set of experiments upon using the same initial concentration of Sn(C₂H₅)₄, step I has been terminated after different reaction time. The TPD pattern of these samples obtained in a hydrogen atmosphere is compared and the results are given in Figure 40A-D. As emerges from Figure 40A-D, the TPD pattern of these samples shows marked differences depending on the duration of step I. The sample obtained after 100 minutes of reaction (see Figure 40D) strongly resembles earlier results, i.e., it contains no major TPD peaks in the temperature range above 100°C.

Short reaction times, contrary to our previous studies, result in quite complex TPD profiles (see Figures 40A and 40B). Samples obtained at τₗ = 4 and 10 minutes after injection of tin organic compound contain two broad TPD peaks. After deconvolution, the first broad peak, representing around 45% of the total amount of ethane formed, contains three low-temperature peaks around 20, 40, and 80°C, while the high-temperature peak consists of two major peaks around 170 and 200°C and a small shoulder above 200°C. In these samples the contribution of the peaks around 110 and 140°C is small. The small shoulders above 200°C detected around 230 and 260°C account for less than 1.0% of the total amount of hydrocarbons formed. This fact indicates that under these experimental conditions the amount of tin adsorbed onto the alumina support is negligible (see Chapter 5.3.1.2).

The results of deconvolution of the TPD peaks are summarized in Table 19. These data clearly show the time dependence of the formation of different surface entities. The obtained Sn/Ptᵦ ratios indicate that conditions used for tin anchoring results in monolayer tin coverage (Sn/Ptᵦ < 0.4). After 10 minutes of the reaction the amount of tin anchored is constant within the experimental error. However, upon increasing the reaction time the stoichiometric value of \( x \) shows a characteristic increase (see Table 19). This experimental finding provides further prove with respect to the formation of new species at the very beginning of tin anchoring.

The low value of \( x \) obtained after τₗ = 4 and 10 minutes (\( x = 0.32 \) and 0.37) indicates that surface species formed should contain both -Sn(C₂H₅)₃ and -Sn(C₂H₅)₂ type surface species and the formation of -Sn(C₂H₅)₄ prevails. However, after τₗ = 100 minutes of the reaction the value of \( x \) is close to one (see Table 19), i.e., the sample should contain only -Sn(C₂H₅)₃ type surface species. It should be emphasized that this sample resulted in only low-temperature TPD peaks below 100°C, which are characteristic for the decomposition of PSC with monolayer coverage (see Figure 5A).
Figure 40. The influence of the duration of step I on the shape of the TPD pattern and the deconvolution of TPD peaks. Catalyst: PtAl-0.3-B; [Sn]₀ = 0.51 mM; Sn₀/Pt₀ = 0.46. A- Reaction time (τᵣ): 4 min (Sn/Ptₜ = 0.14); B- 10 min (Sn/Ptₜ = 0.37); C- 60 min (Sn/Ptₜ = 0.33) and D- 100 min (Sn/Ptₜ = 0.33). ( ), Measured and ( ), fitted.

Table 19. Deconvolution of the TPD peaks obtained over PtAl-0.3-B catalyst.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>τᵣ, min.</th>
<th>Sn/Pt₀</th>
<th>x</th>
<th>Amount of C₂H₆ form in different TPD peaks, ( n^{1H} \times 10^{-6} ) mol/gcat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1st peak</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>°C</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0.14</td>
<td>0.32</td>
<td>0.57</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.37</td>
<td>0.37</td>
<td>1.66</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>0.39</td>
<td>0.74</td>
<td>2.07</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>0.34</td>
<td>0.74</td>
<td>2.30</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0.34</td>
<td>1.08</td>
<td>3.91</td>
</tr>
</tbody>
</table>

[Sn(C₂H₅)₃]₀ = 0.51 mM; Sn₀/Pt₀ = 0.46.
The results given in Table 19 indicate that the intensity of all TPD peaks above 100°C (peaks No 4-9) passes through a maximum. However, after $\tau_r = 100$ minutes of reaction the intensity of these peaks decreases to a value close to the detection limit.

Based on the “fingerprint” character of the TPD curves, the nine TPD peaks were divided into the following four different regions: (i) low-temperature region up to 80°C (peaks No 1-3), intermediate region between 110 and 140°C (peaks No 4 and 5), high-temperature region between 170 and 200°C (peaks No 6 and 7) and region above 200°C (peaks No 8 and 9). The latter temperature range is characteristic for tetraethyltin adsorbed onto the support. We suggest that the above temperature regions of TPD peaks can represent at least four different types of surface entities (surface species $A$, $B$, $C$, and $D$, respectively). The time dependence of the formation of these four different types of surface species exhibits a very interesting relationship, as shown in Figure 41.

According to our earlier results and discussions made above surface species $A$ should represent $\text{Sn(C}_2\text{H}_5)_3$ type surface species anchored onto the platinum. Surface species $D$ can be assigned to $\text{Sn(C}_2\text{H}_5)_4$ adsorbed to the support. The question is how to assign surface species $B$ and $C$.

In our previous studies, the high-temperature peaks around 170 and 200°C were attributed to surface species, such as multilayered surface complexes. However, at the very beginning of tin anchoring it is hard to assume that a second layer (or even multilayer) of tin organic moieties at the top of the PSC can be formed immediately after introduction of $\text{Sn(C}_2\text{H}_5)_4$. Consequently, the formation of surface species in the second and multilayer can be excluded. This suggestion is supported by the value of $x$ measured. Formation of surface complexes in the second layer (see Chapter 5.3.1.3) resulted in $x$ value in the range of 1.5-1.0. The low $x$ values of samples obtained at short reaction time (see Table 19) indicates also that $\text{Sn(C}_2\text{H}_5)_4$ surface species strongly adsorbed onto the Pt is a dominating one. As it has already been discussed in Chapter 5.3.1.2, upon decomposition this coordinatively saturated surface species should also give high-temperature TPD peaks.

![Figure 41](image)

**Figure 41.** Time dependence of the formation of different type surface species during tin anchoring. Results obtained from deconvoluted TPD peaks (see results given in Table 19). (■), Sum of the amount of ethane formed in the first three peaks up to 80°C (peaks No 1-3, *surface species* $A$); (●), sum of the amount of ethane formed in the fourth and fifth peaks (temperature region between 110-140°C) (*surface species* $B$); (♦), sum of the amount of ethane formed in the sixth and seventh peaks (temperature region between 170-200°C) (*surface species* $C$); (♣), sum of the amount of ethane formed above 200°C (temperature region between 230-260°C) (peaks No 8-9, *surface species* $D$). Catalyst: PtAl-0.3-1B; [Sn$_0$] = 0.51 mM; Sn$_0$/Pt$_r$ = 0.46.

The time dependence shown in Figure 41 as well as data given in Table 19 show that surface reactions involved in tin anchoring under monolayer coverage should have *consecutive character*. The time dependence clearly shows that at the very beginning of tin anchoring there are only two primary products, i.e., in this period only two classes of major surface entities are formed, namely surface species $A$ and $C$. However, Figure 41 demonstrates that after $\tau_r = 100$ minutes all major and minor species are transformed into surface species $A$. The character of kinetic curves indicates also that after $\tau_r = 10$ minutes of reaction surface species $C$ are transformed into $B$ and $A$. Surface species $B$ appeared to be also unstable as after $\tau_r = 60$ minute reaction it were transformed into $A$. 

72
Phenomena confirming the consecutive character of surface reactions involved in anchoring of tetraethyltin onto supported platinum were also observed on another alumina supported catalyst PtAl-0.35. These results are shown in Figure 42. It is necessary to mention, that the initial tin concentration was about five times higher than that of used in experiments shown in Figure 40 (compare \([\text{Sn}]_0\) values for experiments PtAl-0.3-B-2 and PtAl-0.35-4 in Tables 18). TPD profiles shown in Figure 42 strongly resemble TPD patterns obtained on catalyst PtAl-0.3-B (see Figures 40A and 40B), when the duration of tin anchoring step I was also 4 and 10 minutes. The low value of the stoichiometry of tin anchoring (\(x = 0.34\) and \(x = 0.40\); see values of \(x\) given in comments to Figure 42) indicates that the -Sn(C\(_2\)H\(_5\))\(_4\) type of coordinatively saturated surface species is a dominant at this short reaction time.

![Figure 42](image)

Figure 42. The influence of the duration of tin anchoring step I on the TPD pattern of SOMS formed. Catalyst: PtAl-0.35; \([\text{Sn}]_0\) = 2.53 mM; Sn\(_0\)/Pt\(_s\) = 1.85. Reaction time (\(\tau\)) \(=\) 4 min (\(x = 0.34\), Sn/Pt\(_s\) = 0.20); \(\square\), 10 min (\(x = 0.40\), Sn/Pt\(_s\) = 0.55); \(\bigcirc\), 20 min (\(x = 0.75\), Sn/Pt\(_s\) = 0.56).

Decomposition pattern of the surface complexes formed after 20 minutes showed marked differences. TPD pattern resulted in a slight increase of peaks at 40 and 75°C (surface species A) and pronounced increase of peaks at 110 and 140°C (surface species B), but high temperature peaks at 170 and 200°C (surface species C) became a minor component. The considerable decrease of the contribution of surface species C is reflected in the increase of value \(x\) from \(x = 0.34\) (\(\tau\) = 4 min) up to \(x = 0.75\) (\(\tau\) = 20 min) (see comments to Figure 42). Consequently, the comparison of the TPD patterns, obtained at short and prolonged time of tin anchoring (see Figures 40C and 42), shows that the higher the Sn\(_0\)/Pt\(_s\) ratio used, the faster the transformation of strongly adsorbed -Sn(C\(_2\)H\(_5\))\(_4\) surface entities into surface species A and B. Accordingly, the increase of Sn\(_0\)/Pt\(_s\) ratio resulted in an increase of both the mobility and the reactivity of surface species C. Based on all facts discussed above it has been proposed, that surface species C is located exclusively on supported metal nanoclusters.

The change of tin concentration in liquid phase during tin anchoring can be determined by GC (this analysis provided the sum of reacted and adsorbed tetraethyltin). As shown in Figure 43 these values have been compared with the amount of tin anchored, which was calculated from the kinetic curve of ethane formation. This calculation is based on the assumption that stoichiometry of tin anchoring \(x\) equal to one (see Table 18). In this case the number of ethane molecules evolved at moment \(t\) is equal to the number of tin-containing SOMS anchored onto Pt and, consequently, to the number of Sn atoms anchored.

The results presented in Figure 43 show that the largest difference between curves calculated by both methods appears at the beginning of the tin anchoring, after ca. 15 minutes. As reaction proceeds this difference decreases and after 100 minutes completely disappears. As mentioned above, the liquid phase analysis provided the sum of reacted and adsorbed tetraethyltin, but calculation of tin anchored from ethane formation related only to the amount of tin anchored during step I. Consequently, the observed difference between concentration determined by gas and liquid phase analysis results from the presence of strongly adsorbed -Sn(C\(_2\)H\(_5\))\(_4\) form. The concentration of this form has a maximum at 15 minutes of reaction time.
Figure 43. Kinetics of tin anchoring over catalyst PtAl-0.35. ( ), Time dependence of the concentration change of Sn(C$_2$H$_5$)$_4$ in the liquid phase during anchoring reaction, and ( ), amount of tin calculated from ethane formation. Reaction conditions: catalyst amount: W$_{cat}$ = 1 g; [Sn]$_0$ = 1.01 mM, Sn/Pt$_s$ = 0.73, (Sn/Pt$_s$ = 0.52); atmosphere: in the absence of gas phase hydrogen; solvent: benzene; T$_r$ = 50°C (see sample PtAl-0.35-3 in Table 18).

Similar results were also obtained on silica supported PtSi-3.0-A catalysts. The trend was the same, i.e., the decrease of the reaction time increases the intensity of high-temperature TPD peaks between 170 and 200°C. Upon increasing the reaction time the contribution of low-temperature peaks below 110°C increases with parallel decrease of the high-temperature TPD peaks. Consequently, the observed phenomenon is general, i.e., it is independent of the support and the metal loading.

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

\[
\begin{align*}
\text{PtH}_a + \text{SnR}_4 & \rightarrow \text{Pt-SnR}_3 + \text{RH} \\
\text{Pt} + \text{SnR}_4 & \leftrightarrow \text{Pt-SnR}_4 \\
\text{Pt-SnR}_4 + \text{PtH}_a & \rightarrow \text{Pt-SnR}_3 + \text{Pt} + \text{RH} \\
\text{Pt-SnR}_3 + \text{PtH}_a & \rightarrow \text{Pt-SnR}_2 + \text{Pt} + \text{RH} \\
\text{Pt-SnR}_2 + \text{Pt-SnR}_4 & \rightarrow \text{Pt-[SnR}_2-[\text{SnR}_4]} + \text{Pt} \\
\text{Pt-[SnR}_2-[\text{SnR}_4]} + \text{Pt} & \rightarrow 2\text{Pt-SnR}_3
\end{align*}
\]

Reaction (5.12) corresponds to reaction (5.1) in our earlier scheme (see formation of PSC in Chapter 5.2). This reaction leads to the formation of A type surface species with low-temperature TPD peaks. Reaction (5.13) is an equilibrium reaction leading to the formation of surface species C, what can be considered as tetraethyltin strongly bonded to the platinum. It has to be emphasized again that both surface species A and C have to be primary products (see explanations given to Figure 41). Due to the peculiarities of this system, when the duration of step I is very short, only SOMS, such as Pt-SnR$_3$ and Pt-SnR$_4$, can be considered as primary products of tin anchoring onto platinum.

Due to coordinative saturation surface species C is much less reactive towards adsorbed hydrogen than A, for this reason it should give a high-temperature TPD peak. 220 Figure 41 shows also that this surface species reacts further with the formation of surface species A and B (reactions (5.14) and (5.16), respectively). Surface species B corresponds to TPD peaks between 110 and 140°C. Consequently, surface species B should have an intermediate activity between surface species A and C. As it seen from Figure 41, the formation of surface species B has a slight S-character, for this reason it is considered that it cannot be a primary product. In our earlier studies 215,216 these peaks have been attributed to surface complexes in the second layer.

In the presence of hydrogen adsorbed on Pt (PtH$_a$), surface species A can lose one more alkyl group leading to the formation of coordinatively unsaturated -SnR$_2$ surface species (reaction (5.15)). This reaction has been considered in our earlier scheme as one of the key reactions responsible for the formation of multilayered SOMS. 215,216 This type of surface species is highly reactive and will interact with surface species C in reaction (5.16) leading to the formation of surface complex in the second layer.
The kinetic curve of the formation of surface species $D$ has also an S-character and passes through a maximum. This species is completely consumed after 60 minutes of reaction time. This species decomposes above 200°C, i.e., its decomposition requires the highest energy of activation. For this reason it should be formed on the support. However, its relatively fast consumption strongly indicates that it should be located close to the Pt sites. Consequently, we suggest that this surface species should be located at the metal-support interface and has similar stoichiometry as surface species $C$.

In this Chapter new kinetic results obtained in the two-step tin anchoring process are summarized. Experimental evidences indicated that below monolayer coverage of SOMS, and under condition of short reaction time parallel to the formation of anchored $-\text{SnR}_3$ moieties new surface species are formed, such as anchored $-\text{SnR}_4$ and its derivatives. As the tin anchoring reaction proceeds these new surface entities are transformed into $-\text{SnR}_3$ moieties. This finding has been supported by the following experimental evidences: (i) complete change of the TPD pattern of samples, as reaction proceeds (see Figures 40 and 42); (ii) alteration of the stoichiometry of tin anchoring (see data given in Table 19); (iii) pronounced time dependence of the formation of different surface species (see Figure 41).

The fact that the amount of tin anchored (see Sn/Pt ratio in Table 19) is almost independent after $\tau_r = 10$ minutes, but the contribution of different peaks on the TPD curves is strongly altered, is an indication for the transformation of SOMS primary formed on supported metal nanoclusters. This suggests also that some of the surface species formed at short reaction time have high mobility at the Pt surface. Based on the evidences given above, elementary steps involved in anchoring of $\text{SnR}_4$ onto Pt are presented in Scheme 12.

![Scheme 12](image)

Scheme 12. Elementary steps involved in anchoring of tetraalkyl tin onto platinum$^a$). Experimental evidences have been found supporting both (A) and (B) reaction pathways.$^{220}$

$a)$ Schematic image has been shown without taking in to account the number of Sn-Pt bonds between anchored SOMS and Pt.

### 5.5. Tin anchoring over Pt/Al$_2$O$_3$ catalysts using circulation reactor system

The use of a circulation reactor for the modification of Pt/Al$_2$O$_3$ catalyst with tetraethyltin has been demonstrated in one of our earlier studies.$^{232}$ This technical innovation resulted in a scale-up of the modification procedure. The new approach allowed to increase the amount of modified catalyst from a few grams to 250 g. The use of the "one-pot" circulation reactor system had an advantage with respect to the modification in the stirred tank reactor: (i) all of the elementary steps of the modification were done in the same reactor; (ii) the presence of fixed bed catalyst suppressed the crashing of the catalyst during the anchoring process; (ii) the use of high rate of circulation and low [Sn]$_0$ in the liquid phase provided better condition to eliminate mass and heat transfer related problems; (iii) provided better condition for the removal of unreacted tetraethyltin; and (iv) good reproducibility of anchoring process. Further details can be found elsewhere.$^{218,232}$
5.5.1. Study of tin anchoring in the circulation reactor

Figure 44 displays the typical kinetic pattern of tin anchoring. The preparation of catalysts with high tin content requires high excess of tetraethyltin in the solution. However, the use of high concentration of \( \text{Sn}(\text{C}_2\text{H}_5)_4 \) should be avoided as it can result in a concentration gradient of anchored tin along the catalyst bed.\(^{218,232} \) For this reason the calculated amount of \( \text{Sn}(\text{C}_2\text{H}_5)_4 \) used for anchoring was divided into equal portions and injected into the reactor during equal periods of time in the 0\( ^{\text{th}} \), 60\( ^{\text{th}} \) and 120\( ^{\text{th}} \) minute.

**Figure 44.** Kinetic patterns of tin anchoring. **A**- Kinetic curve of ethane formation (●) during tin anchoring reaction. The arrows indicate the addition of new portions of \( \text{Sn}(\text{C}_2\text{H}_5)_4 \). **B**- Time dependence of the concentration change of tin tetraethyl in the liquid phase (●). **C**- The sum of anchored and adsorbed tin as a function of reaction time. (●), Amount of tin calculated from the concentration change of \( \text{Sn}(\text{C}_2\text{H}_5)_4 \) in the liquid phase, (■), amount of tin calculated from ethane formation. Catalyst: \( \text{PtAl-0.3-A} \); \( [\text{Sn}]_0 = 3.8 \text{ mmol} \); solvent: naphtha; \( T = 50^\circ \text{C} \).
Figure 44A shows the formation of ethane. Figure 44B exhibits the concentration change of tetraethyltin in the liquid phase during anchoring reaction, while Figure 44C reveals to the amount of tin fixed onto the Pt/Al\(_2\)O\(_3\) catalyst, i.e., it shows the sum of anchored and adsorbed tetraethyltin. The amount of tin fixed onto the Pt/Al\(_2\)O\(_3\) catalyst (calculated from the concentration change of Sn(C\(_2\)H\(_5\))\(_4\) in the liquid phase) is compared to the amount of tin calculated from ethane formation in Figure 44C.

These figures confirm that the rate of tin anchoring is relatively fast in the first 10-15 minutes. This period accounts for about 70% of the total amount of ethane formed, but less than 50% of the total amount of tin fixed. These data indicate that in SOMS formed in the first 10-15 minutes the extent of unsaturation is high and the amount of adsorbed Sn(C\(_2\)H\(_5\))\(_4\) is negligible. As seen from Figures 44A and 44C after introduction of the third portion of Sn(C\(_2\)H\(_5\))\(_4\) the increase of the amount of ethane is very low, but the accumulation of tetraethyltin in the catalyst increases further. These data show that in the third period mostly adsorption of Sn(C\(_2\)H\(_5\))\(_4\) takes place. In this experiment the amount of adsorbed Sn(C\(_2\)H\(_5\))\(_4\) was 1.26 x 10\(^{-3}\) mol, while the amount of tin anchored was 3.84 x 10\(^{-3}\) mol. The latter value corresponds to 0.35 wt% tin introduced or ratio Sn/Pt\(_s\) = 2.26 (see experiment 2 in Table 20).

Table 20. Summary of results obtained in the modification of parent PtAl-0.3-A catalyst with Sn(C\(_2\)H\(_5\))\(_4\) in a circulation reactor

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>(T_r), (\degree)C</th>
<th>(Sn_0), mmol(^a)</th>
<th>(n^1) x 10(^6)</th>
<th>(n_{total}^I) x 10(^6)</th>
<th>(n_{C2H4}^I) x 10(^6)</th>
<th>(x)</th>
<th>(Sn_a) wt%(^b)</th>
<th>(Sn_a) wt%(^c)</th>
<th>(Sn/Pt_s)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>3.8</td>
<td>26.0</td>
<td>41.4</td>
<td>1.7</td>
<td>1.54</td>
<td>0.20</td>
<td>0.20</td>
<td>1.28</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>3.8</td>
<td>32.6</td>
<td>87.4</td>
<td>12.2</td>
<td>1.09</td>
<td>0.36</td>
<td>0.35</td>
<td>2.26</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>7.6</td>
<td>42.0</td>
<td>128.6</td>
<td>26.0</td>
<td>0.99</td>
<td>0.51</td>
<td>0.49</td>
<td>3.14</td>
</tr>
<tr>
<td>4</td>
<td>65</td>
<td>3.8</td>
<td>56.7</td>
<td>185.4</td>
<td>39.6</td>
<td>1.01</td>
<td>0.67</td>
<td>0.66</td>
<td>4.23</td>
</tr>
</tbody>
</table>

\(^a\) Amount of Sn(C\(_2\)H\(_5\))\(_4\) introduced per one injection; \(^b, c\) Calculated from the overall material balance of tin anchoring and AAS data, respectively; \(^d\) Amount of Sn anchored per surface Pt atom calculated from AAS data and the CO/Pt = 0.82. Amount of catalysts: \(W_{cat}\) = 120 g; atmosphere of tin anchoring step I: hydrogen; solvent: naphtha; number of Sn(C\(_2\)H\(_5\))\(_4\) injections: 3; overall reaction time: \(\tau\) = 250 minutes.

Table 20 shows the summary of tin anchoring in the series of experiments carried out at three different temperatures. Entries No 2 and 3 in Table 20 illustrates results obtained upon varying the amount of Sn(C\(_2\)H\(_5\))\(_4\) introduced per one injection (\(Sn_0\)). Upon increasing both the reaction temperature and the total amount of Sn(C\(_2\)H\(_5\))\(_4\) introduced during tin anchoring step I (\(n^I\)) increased (see Table 20). As far as tin anchoring step I was carried out in the presence of gas phase hydrogen, therefore no ethylene was detected.

The TPD patterns of SOMS formed at three different temperatures are given in Figure 45A-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. Figure 45A-C shows that upon increasing the temperature of tin anchoring from \(T_r\) = 40 up to 65°С the maximum of TPD ethane peaks
is shifted from 170°C to 200°C. Parallel to the shift in the peak position the intensities of the TPD peaks in the temperature range between 110 and 200°C increased also.

In our earlier studies it has been demonstrated\textsuperscript{215,216} 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 (5.8) can give both ethane and ethylene (see Figure 36 in Chapter 5.4.1). The formation of ethylene provides indirect evidence for the formation of OMSAS upon modifying a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}.

Results given in Figure 45A indicate that at T\textsubscript{r}= 40°C the introduction of tin onto platinum is exclusive. As emerges from results given in Table 20 and Figure 45B and 45C the increase of the temperature of tin anchoring up to T\textsubscript{r}= 65°C resulted in an increase of both the total amount of hydrocarbons (n\textsubscript{total}\textsuperscript{H}) and amount of ethylene (n\textsubscript{C2H4}\textsubscript{H}) formed in step II. These data indicate that the increase of the reaction temperature results in the increase of the contribution of surface reaction (5.8) with the involvement of surface OH groups of alumina.

In our earlier studies it has been unambiguously demonstrated\textsuperscript{213,242} that at T\textsubscript{r}= 50°C upon using pure Al\textsubscript{2}O\textsubscript{3} support the rate of surface reaction (5.8) is comparable with the rate of tin anchoring onto the Pt only at relatively high initial concentration of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} ([Sn]= 25.3 mM). In this study the use of high concentration of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} was avoided as the total amount of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} 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 Al\textsubscript{2}O\textsubscript{3} support towards Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} 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 Al\textsubscript{2}O\textsubscript{3} support.

It has been demonstrated in Chapter 5.4.1 that upon modifying \textgamma-Al\textsubscript{2}O\textsubscript{3} support with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} two ethane (at 180-190°C and 250-270°C) and one ethylene (at 310-330°C) TPD peaks were observed (see Figure 36). However, Figures 45B and 45C 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 ethylene peaks were observed around 170-200°C and 170-185°C, respectively (see Figures 45B and 45C). 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/Al\textsubscript{2}O\textsubscript{3} catalysts with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} results in Sn-Pt bimetallic catalysts in which two forms of tin can be distinguished: (i) tin anchored onto the platinum and (ii) tin anchored onto the support. As emerges from results given in Table 20 and Figure 45A, the formation of tin anchored onto the platinum is exclusive up to Sn/Pt\textsubscript{r}=1.28.

The analysis of x values given in Table 20 can provide information about the stoichiometry of anchored SOMS. In experiment No 1 the x value is 1.54, which indicates that in a hydrogen atmosphere at T\textsubscript{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\textsuperscript{215,216} that the use of excess of hydrogen during tin anchoring resulted in high extent of dealkylation of SOMS in both the first and the second layer. The formation of SOMS with high extent of dealkylation (see equations (5.2) and (5.4)) reflects the increase of the x value.

As can be seen from results given in Table 20, the increase of both the reaction temperature (see experiments No 2 and 4) and the amount of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} introduced per one injection (compare experiments No 2 and 3) resulted in the increase of the Sn/Pt\textsubscript{r} ratios, but the values of x were close to one. It has been mentioned that these experimental conditions are favored the formation of both multilayered SOMC on platinum and OMSAS.

In our earlier studies it has been shown\textsuperscript{215,216} that upon increasing of the reaction temperature and/or the amount of [Sn]\textsubscript{r} introduced the reactivity of unsaturated SOMS to form corresponding second or multilayer complexes also increases. In these multilayered SOMS the R/Sn ratio is higher compared to the coordinatively unsaturated one. The surface chemistry related to the formation of multilayered SOMC (see reactions (5.3) and (5.5)) indicates that the increase of the amount of anchored tin (the increase of the Sn/Pt\textsubscript{r} ratio) should result in a decrease of the value of x.\textsuperscript{216} 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 \( \gamma \)-Al\(_2\)O\(_3\) it has been also demonstrated\(^{233,242}\) that Sn(C\(_2\)H\(_5\))\(_4\) reacts with surface hydroxyl groups resulting in the release of only one ethyl group per grafted tin (\( x = 1.0 \)) (see reaction (5.8)). That is why anchoring of tin both onto the alumina support and onto the platinum in a form of multilayers results in almost the same values of \( x \). Consequently, in this case the information with respect to the stoichiometry of anchored SOMS is not sufficient to define exactly the degree of the selectivity of tin anchoring step I.

The amount of C\(_2\) hydrocarbons formed in steps I and II (\( n^I \) and \( n_{total}^II \), respectively) allowed us to calculate the overall material balance of tin anchoring. These data are also included in Table 20. The calculated material balance for tin was compared with the amount of tin determined by AAS. This comparison shows a very good agreement.

### 5.5.2. Characterization of Sn-Pt/Al\(_2\)O\(_3\) catalysts prepared in the circulation reactor

#### 5.5.2.1. Characterization by \( \text{H}_2 \) and CO chemisorption

Table 21 displays the values corresponding to \( \text{H}_2 \) and CO chemisorption experiments. The addition of tin to parent PtAl-0.3-A catalyst decreases both H/Pt and CO/Pt ratios.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sn, wt% (^a)</th>
<th>Sn/Pt (^b)</th>
<th>H/Pt (^c)</th>
<th>CO/Pt (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>-</td>
<td>-</td>
<td>0.76</td>
<td>0.82</td>
</tr>
<tr>
<td>PtSn(0.20 wt%)/Al(_2)O(_3)</td>
<td>0.20</td>
<td>1.28</td>
<td>0.17</td>
<td>0.44</td>
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<tr>
<td>PtSn(0.35 wt%)/Al(_2)O(_3)</td>
<td>0.35</td>
<td>2.26</td>
<td>0.14</td>
<td>0.39</td>
</tr>
<tr>
<td>PtSn(0.49 wt%)/Al(_2)O(_3)</td>
<td>0.49</td>
<td>3.14</td>
<td>0.12</td>
<td>0.29</td>
</tr>
<tr>
<td>PtSn(0.66 wt%)/Al(_2)O(_3)</td>
<td>0.66</td>
<td>4.23</td>
<td>0.09</td>
<td>0.27</td>
</tr>
</tbody>
</table>

\(^a\) 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 500ºC.

The decrease of hydrogen chemisorption induced by tin is more pronounced than that of the CO. On parent Pt/Al\(_2\)O\(_3\) catalyst the ratio CO\(_\text{chem}\)/H\(_\text{chem}\) ([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 H\(_2\) molecule. Hence, the drastic decrease of the H\(_2\) 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 to a lower extent, due to site blocking or electronic effect. It is worth mentioning that the pronounced decrease of the H/Pt and CO/Pt values takes place at relatively low Sn content, i.e., for PtSn(0.2 wt\%)/Al\(_2\)O\(_3\) catalyst. Further increase of the Sn content resulted in much smaller decrease of both the H/Pt and the CO/Pt values.

#### 5.5.2.2. Characterization by Temperature Programmed Reduction

Figure 46 shows TPR profiles of parent PtAl-0.3-A and PtSn/Al\(_2\)O\(_3\) bimetallic catalysts, previously treated in oxygen at 350ºC for 2 h ((O)-type of catalysts). TPR data can be used to determine the amount of \( \text{H}_2 \) required to reduce the sample and to evaluate the temperature of maximum consumption of hydrogen.

In parent PtAl-0.3-A catalyst the main reduction peak is located at 240ºC, whereas a small shoulder at 110ºC is also detected. Literature data indicate that there are two types of Pt oxides in monometallic catalyst, one with weak and the other with strong interaction with the support.\(^{174}\)

The TPR patterns of both tin-modified catalysts contain peaks that appear at low temperature (in the range between 100 and 250ºC) corresponding to the reduction of unalloyed Pt species. The medium temperature region of the TPR patterns, in the range between 250 and 360ºC with temperature of maximum consumption of hydrogen at about 300-310ºC, can be probably attributed to the reduction of SnO\(_x\) species in close proximity to metallic Pt or PtO\(_x\). This form upon reduction in hydrogen results in Sn-Pt alloy-type species. The twin peaks in the temperature range between 360 and 700ºC probably corresponds to the reduction of separate SnO\(_x\) species with strong interaction with the support. Armendáriz et al.\(^{174}\) have pointed out that the position of the reduction peaks of the Sn-Pt alloy phases strongly depends on the tin concentration, and with increasing the Sn content in the Sn-Pt
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 Sn-Pt alloy nanoclusters. The other peaks centered at 450 and 460°C for Sn-Pt/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.¹⁷⁶,¹⁷⁷

![Figure 46](image)

**Figure 46.** Temperature Programmed Reduction profiles of parent PtAl-0.3-A (1) and Sn-Pt/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.

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 Sn-Pt co-reduction in both bimetallic catalysts is high.

### 5.5.2.3. Characterization by XPS measurements

XPS spectra show that the Pt 4f peaks overlaps with the Al 2p peaks of the alumina support. However, application of a curve synthesis procedure, known in the literature, permits to determine the binding energies of Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> indicating the presence of platinum in metallic form.²¹⁸

The XPS spectra after in situ reduction at 500°C are shown in Figures 47 and 48. Data correspond to the Sn 3d<sub>5/2</sub> level of PtSn(0.49 wt%)/Al₂O₃ and PtSn(0.66 wt%)/Al₂O₃ catalysts, respectively. From the deconvolution of both spectra presented in Figures 47 and 48, 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.¹⁶⁶,²⁶⁹,²⁷⁰ It must be noted that Homs et al.²⁷¹ attributed the peaks at 483.6 eV and 485 eV to Sn⁰ and Sn in a PtSn alloy (Sn<sub>al</sub>⁰), 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<sub>5/2</sub> for SnO has a BE at 486.5 eV, while the Sn 3d<sub>5/2</sub> line for SnO₂ has a BE at 486.5 eV.¹⁶⁶,²⁷⁰,²⁷² Consequently, the second peak in our catalysts will be assigned to supported Sn²⁺ and/or Sn⁴⁺ oxides.

Table 22 shows data obtained by XPS, such as binding energies corresponding to Sn 3d<sub>5/2</sub> and Sn/Pt surface atomic ratios. The 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 indicates that the extent of reducibility of Sn in Sn-Pt/Al₂O₃ catalysts is high, these results agrees well with those obtained by 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 SnOₓ as shown in Scheme 13.

---

80
Figure 47. XPS spectra corresponding to Sn3d$_{5/2}$ signals of PtSn(0.49 wt%)/Al$_2$O$_3$ catalyst reduced at 500°C.

Figure 48. XPS spectra corresponding to Sn3d$_{5/2}$ signals of PtSn(0.66 wt%)/Al$_2$O$_3$ catalyst reduced at 500°C.

Table 22. Characterization of Sn-Pt/Al$_2$O$_3$ catalysts by XPS.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BE Sn 3d$_{5/2}$ (eV) $^a$</th>
<th>Sn/Pt $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSn(0.49 wt%)/Al$_2$O$_3$</td>
<td>485.3 (42 %) 487.6 (58 %)</td>
<td>3.13 (2.68)</td>
</tr>
<tr>
<td>PtSn(0.66 wt%)/Al$_2$O$_3$</td>
<td>485.0 (30 %) 487.1 (70 %)</td>
<td>3.12 (3.61)</td>
</tr>
</tbody>
</table>

$^a$ Percentage of each species in parentheses;
$^b$ Amount of Sn anchored per Pt atom calculated from the XPS measurement and AAS data (in parentheses).

Scheme 13. The presence of different forms of tin in Sn-Pt/Al$_2$O$_3$ catalysts with high Sn/Pt ratios: (i) tin anchored onto the platinum and (ii) tin anchored onto the Pt-support interface and the bulk alumina support.

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.
5.5.2.4. Characterization by FTIR spectroscopy of adsorbed CO

The CO chemisorption on Sn-Pt/Al₂O₃ catalysts was also followed by FTIR as shown in Figure 49. As emerges from results obtained on the (H)-type catalysts the introduction of tin has no influence on the CO vibrational frequencies.

Contrary to that on the (O)-type catalysts the CO vibrational frequencies are significantly changed, probably due to the electronic interaction between platinum and the anchored SnOₓ moieties. In this case the formation of “metal ion-metal nanocluster ensemble sites” has been suggested as shown in Scheme 14:

Scheme 14. The formation of “metal ion-metal nanocluster ensemble sites” over supported platinum catalysts.

The relatively high Sn/Ptᵣ ratio of our Sn-Pt/Al₂O₃ catalysts indicates that a part of tin introduced should be stabilized in its ionic form. Our earlier results confirmed that this ionic form of tin is strongly bound to the surface of the alumina support. The stabilization of ionic forms of tin was significantly enhanced by the decomposition of SOMS in an oxidative atmosphere. The pyridine adsorption on catalyst samples prepared by decomposition of SOMS either in hydrogen atmosphere or in the presence of oxygen showed also distinct difference, i.e., the bands at 1455 and 1625 cm⁻¹ appeared exclusively in samples decomposed in O₂ atmosphere. Literature data indicate that this band was attributed to new type of Lewis-acid sites originated from tin-oxide anchored onto alumina. The new Lewis-acid sites should be formed in the close vicinity of platinum. The formation of the above bands at 1455 and 1625 cm⁻¹ was also evidenced in catalyst prepared in circulation reactor.

5.6. Modification of commercial Re-Pt/Al₂O₃ catalysts with Sn(C₅H₅)₄

As far as Re-Pt/Al₂O₃ catalyst is still the most widely used one in naphtha reforming, this study was aimed to investigate the possible improvement of industrial Re-Pt catalysts by tin modification based on SOMC in order to reduce benzene and aromatic content and maintain high octane rating in the reforming of n-octane and straight run wide boiling range desulfurized naphtha. This work was done in the frame of research contract between Petroleum Research Center (Tripoli, Libya) and Chemical Research Center, HAS (Budapest, Hungary).

Rhenium oxide supported on alumina and silica-alumina is a well known metathesis catalyst for alkenes. It has been demonstrated that further enhancement in activity of Re-based catalyst by a factor 5-10 can be obtained by adding a SnR₄ promoter (R= Me, Et or Bu).
It has already been evidenced earlier by Buffon et al.\textsuperscript{273} that an organorhenium intermediate is formed upon treating the Re\textsubscript{2}O\textsubscript{7}/Al\textsubscript{2}O\textsubscript{3} catalyst with a SnR\textsubscript{4} promoter via a single alkylation of Re site:

\[
\text{Surf-O-Re(=O)}_3 + \text{SnR}_4 \rightarrow \text{Surf-O-Re(=O)}_2(\text{-O-SnR}_3)(\text{-R})
\]  

(5.18)

An alkyl R ligand of this species might undergo an electrophilic attack from a remaining surface OH groups with release of an alkane:

\[
\text{Surf-O-Re(=O)}_2(\text{-O-SnR}_3)(\text{-R}) + \text{Surf-OH} \rightarrow [\text{Surf-O-}]	ext{Re(=O)}_2(\text{-O-SnR}_3) + \text{RH}
\]  

(5.19)

It has been also proposed by Buffon et al.\textsuperscript{188} that a double alkylation which involves two Re sites cannot be ruled out and this reaction leads to the formation of highly active in metathesis Re-alkylidene species and release of an alkane.

5.6.1. Modification of Re-Pt/Al\textsubscript{2}O\textsubscript{3} catalysts with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} in the stirred tank reactor

Introduction of tin onto alumina supported commercial bimetallic Re-Pt catalysts is more complex task than the selective modification of Pt/Al\textsubscript{2}O\textsubscript{3} catalysts with tetraethyltin. In addition to the tin anchoring both onto the platinum and Al\textsubscript{2}O\textsubscript{3} support the reaction ability of Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} towards Re/Al\textsubscript{2}O\textsubscript{3} should also be considered.

Taking into account the possibility of both undesired reactions with involvement of OH groups of support and alumina supported rhenium the use of low reaction temperatures ($T_r$ = 27\textdegree{}C) in tin anchoring can be recommended. The influence of both the reaction temperature and the Sn\textsubscript{0}/Pt\textsubscript{s} ratio on the tin anchoring process over bimetallic RePtAl-0.17 and RePtAl-0.21 catalysts in the stirred tank reactor is summarized in Table 22.

| Catalyst | $T_r$, \textdegree{}C | Sn\textsubscript{0}/Pt\textsubscript{s} | $w_0 \times 10^6$ | $x$ | Sn (wt\%) | Sn/Pt (at./at.)$^a$
|----------|----------------|----------------|----------------|---|------------|----------------|
| RePtAl-0.17 | 27 | 1.19 | 0.2 | 0.77 | 0.06 | 0.61
| RePtAl-0.17 | 27 | 4.89 | 0.4 | 0.84 | 0.17 | 1.68
| RePtAl-0.17 | 40 | 14.68 | 0.9 | 0.89 | 0.36 | 3.50
| RePtAl-0.17$^b$ | 50 | 63.71 | 1.4 | 1.29 | 0.40 | 3.90
| RePtAl-0.17 | 50 | 73.41 | 1.4 | 0.66 | 0.51 | 4.89
| RePtAl-0.17 | 65 | 72.70 | 3.0 | 0.75 | 0.60 | 5.81
| RePtAl-0.21 | 27 | 1.36 | 0.72 | 1.07 | 0.13 | 1.00
| RePtAl-0.21 | 27 | 2.76 | 0.75 | 1.04 | 0.20 | 1.57
| RePtAl-0.21 | 27 | 4.95 | 1.2 | 0.94 | 0.33 | 2.58

$^a$ Amount of tin anchored related to total amount of Pt;

$^b$ Catalyst amount: W\textsubscript{cat} = 3 g; solvent: benzene.

Catalyst RePtAl-0.17 (0.17 wt\% Pt-0.36 wt\% Re/Al\textsubscript{2}O\textsubscript{3}); catalyst RePtAl-0.21 (0.21 wt\% Pt-0.34 wt\% Re/Al\textsubscript{2}O\textsubscript{3}) (see Table 1); catalyst amount: W\textsubscript{cat} = 8 g; duration: 2 h; solvent: naphtha.

In the case of RePtAl-0.17 catalyst (see Table 22) the increase of both the temperature of tin anchoring from $T_r$ = 27\textdegree{}C up to 65\textdegree{}C and the Sn\textsubscript{0}/Pt\textsubscript{s} ratio from 1.19 to ca. 73 results in significant increase of initial reaction rate ($w_0$) and the tin content of the catalysts (from 0.06 to 0.6 wt\%). It is interesting to note that the stoichiometry of the tin anchoring reaction in desulfurized naphtha is below one and changes in the interval of $x$ = 0.66 - 0.89. The value of $x$ < 1 indicates that surface species formed should contain both anchored -Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{1-(4-x)} and strongly adsorbed -Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4 type surface species. However, as shown in Table 22 the reactivity of tetraethyltin with Pt-Re catalyst is higher in benzene than in naphtha. In this case more than one ethyl group ($x$ = 1.29) reacts in tin anchoring step I.

Table 22. Modification of bimetallic RePtAl-0.17 and RePtAl-0.21 catalysts by tetraethyltin

The kinetics of the formation of ethane under condition of tin anchoring at low temperature ($T_r$ = 27\textdegree{}C) is demonstrated in Figure 50A. Figure 50A shows that the rate of tin anchoring step strongly depends on the initial concentration of tetraethyltin. It is interesting to note that at low concentration of tetraethyltin (Sn\textsubscript{0}/Pt\textsubscript{s} = 1.19) the rate of surface reaction decreases very quickly and after 100 minutes
the formation of ethane is terminated. However, at higher Sn/Pt$_s$ ratio (Sn$_0$/Pt$_s$ = 4.89) the rate of surface reaction is relatively high even after 2 h.

**Figure 50.** Influence of the Sn$_0$/Pt$_s$ ratio on the formation and decomposition of surface complexes on RePtAl-0.17 catalyst. A- Kinetic curves of ethane formation in the tin anchoring step I; B- TPD of SOMC in hydrogen atmosphere; ( ), Sn$_0$/Pt$_s$ = 1.19 (Sn/Pt= 0.61); ( ), Sn$_0$/Pt$_s$ = 4.89 (Sn/Pt= 1.68). T$_r$ = 27°C.

The decomposition of SOMS is shown in Figure 50B. The increase of the amount of tin anchored leads to the increase of the intensities of the ethane TPD peaks in the temperature range between 100 and 230°C. The wide TPD curves shown in Figure 50B indicate the existence of different types of surface species with different extent of dealkylation and different environment.

**Figure 51.** Influence of the Sn$_0$/Pt$_s$ ratio on the formation and decomposition of surface complexes on RePtAl-0.21 catalyst. A- Kinetic curves of ethane formation in the tin anchoring step I; B- TPD of SOMS in hydrogen; ( ), Sn$_0$/Pt$_s$ = 1.36 (Sn/Pt= 1.00); ( ), Sn$_0$/Pt$_s$ = 2.76 (Sn/Pt= 1.57); ( ), Sn$_0$/Pt$_s$ = 4.95 (Sn/Pt= 2.58). T$_r$ = 27°C.

The kinetic behaviour of tin anchoring onto RePtAl-0.21 catalyst is shown in Figure 51A. In these experiments, a relatively low Sn$_0$/Pt$_s$ ratios and low reaction temperature (T$_r$ = 27°C) were used. The increase of the Sn$_0$/Pt$_s$ from 1.36 to 4.95 led to the increase of the amount of tin anchored from 0.13 to 0.33 wt%, however, within the experimental error no change in the stoichiometry of tin anchoring reaction ($x \sim 1$) is observed (see the $x$ value in Table 22).

The higher the concentration of tetraethyltin used in the tin anchoring step I the higher are the intensities of ethane peaks in TPD, as shown in Figure 51B. The increase of the Sn$_0$/Pt$_s$ ratio up to 4.95 resulted in the appearance of a small shoulder detected at 250°C. It is necessary to mention that at highest Sn$_0$/Pt$_s$ ratio (Sn$_0$/Pt$_s$= 4.95) parallel to the ethane formation a small peak of ethylene was also observed (not shown). However the overall amount of ethylene does not exceed 5 % of the total amount of C$_2$ hydrocarbons formed in TPD experiment. The formation of ethylene and the appearance of high temperature peak about 250°C in TPD might indicate that part of the tin was introduced onto the support and/or rhenium.
Based on our recent CO chemisorption and TPR results, it has been concluded that tin added to RePtAl-0.17 and RePtAl-0.21 bimetallic catalysts mainly alloyed with platinum, forming Sn-Pt and trimetallic Sn-Re-Pt alloy-type phases. TPR revealed that calcinations at 350°C significantly changed the phase structure of multimetallic catalysts. However, tin content and reduction temperature only slightly altered the CO uptake of Re-Pt/Al₂O₃ catalysts.

5.6.2. Study of tin anchoring over Re-Pt/Al₂O₃ catalyst in the circulation reactor

Table 23 shows the summary of tin anchoring in the circulation reactor in the series of experiments carried out on RePtAl-0.21 catalyst. It is necessary to mention that the behaviour of both catalysts RePtAl-0.17 and RePtAl-0.21 in tin anchoring reactions is quite similar, that is why only the modification of catalyst RePtAl-0.21 will be demonstrated.

Table 23. Modification of bimetallic commercial RePtAl-0.21 catalyst with tin in circulation reactor

<table>
<thead>
<tr>
<th>No</th>
<th>Tᵣ, °C</th>
<th>[Sn]₀, mM</th>
<th>[Sn]/Pt₀</th>
<th>[Sn]/Ptₐ</th>
<th>w₀, x 10⁻⁶</th>
<th>n₁, x 10⁻⁶</th>
<th>n², x 10⁻⁶</th>
<th>x</th>
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<td>31.6</td>
<td>143.5</td>
<td>0.72</td>
<td>0.52</td>
<td>4.05</td>
</tr>
</tbody>
</table>

a Total amount of Sn introduced in step I related to surface atom of Pt;
b Calculated from the overall material balance of tin anchoring;
c Amount of tin anchored related to total amount of Pt.

Amount of catalyst: 120 g; number of injections: 4; solvent: naphtha; reaction time: 4 h.

Tin anchoring reactions were carried out in the presence of hydrogen; therefore ethylene was not detected in these experiments. Figure 52 displays the kinetic pattern of tin anchoring (experiment 1 in Table 2).
Table 23). In this experiment relatively low initial tin concentration per one injection was applied for the modification ([Sn]₀ = 5.1 mM; Sn/Pt₀ = 4.4), because the total amount of Sn(C₂H₅)₄ used was divided in four equal portions and it was introduced in the 0th, 35th, 90th and 150th minute of the reaction. That is why the values of [Sn]/Pt related to total amount of Sn introduced in step I per surface atom of Pt are also included in Table 23. Figure 52A shows the formation of ethane, Figure 52B exhibits the concentration change of Sn(C₂H₅)₄ in liquid phase during tin anchoring, while Figure 52C indicates the amount of tin anchored onto the Pt-Re/Al₂O₃ catalyst. These figures confirm that the rate of tin anchoring is relatively fast in the first 15-20 minutes. This period accounts for about 40% of the total amount of ethane formed. As emerges from Figure 52C, good agreement was observed between the amount of anchored tin calculated from concentration change in liquid phase and that of calculated from ethane formation. Consequently, the amount of adsorbed Sn(C₂H₅)₄ in this experiment was negligible. It is necessary to mention that even in the first portion of washing solution the concentration of tetraethyltin was not measureable.

The use of high excess of tetraethyltin in solution and higher reaction temperature Tᵣ = 42°C results in an increase of the amount of tin anchored (Sn = 0.54 wt%, Sn/Pt = 4.18). As seen from Figure 53C, after introduction of the fourth portion of Sn(C₂H₅)₄ mostly adsorption of tetraethyltin took place. It is necessary to mention that measured concentration of Sn(C₂H₅)₄ in washing solution was 2.2 x 10⁻³ mol.

The TPD patterns of the surface complexes formed at different temperatures are shown in Figure 54. The appearance of ethylene during the decomposition of SOMS formed indicates that the increase of the temperature of tin anchoring leads to partial introduction of tin onto the alumina. The increase of the temperature of tin anchoring results in an increase of the ethylene formation and thus increases the probability of this side reaction.
Figure 54. The influence of the reaction temperature ($T_r$) on the decomposition pattern. $[\text{Sn}]_0 = 14.18$ mM. A- Formation of ethane: ($\bullet$), $T_r = 27^\circ C$ (Sn/Pt= 1.60); ($\square$), $T_r = 32^\circ C$ (Sn/Pt= 2.92); ($\square$), $T_r = 42^\circ C$ (Sn/Pt= 4.05). B- Formation of ethylene: ($\bigotimes$), $T_r = 27^\circ C$; ($\square$), $T_r = 32^\circ C$; ($\square$), $T_r = 42^\circ C$.

It is important to note that high amount of tetraethyltin used during step I ($[\text{Sn}]_t / \text{Pt}$ ratio ca. 50) can be a reason for the enhancement of the activity of Pt-support interface and activity of the alumina support. But it is noteworthy, that the overall amount of the ethylene formed varied from 7 to 11 % of the total amount of $C_2$ hydrocarbons. Consequently, in these catalysts the tin exist in two different forms (i) Sn-Pt alloy type of species and (ii) ionic species stabilized on the Pt-support interface (and/or support).

5.7. Application of CSRs for qualitative determination of the efficiency of re-reduction of 5 wt% PtAl$_2$O$_3$ catalyst

We have demonstrated earlier$^{221}$ that CSRs method can be applied for the qualitative determination of the efficiency of re-reduction of supported platinum catalysts. The influence of both the temperature and duration of re-reduction in H$_2$ atmosphere on the activity of PtAl-5.0 catalyst in tin anchoring step I are demonstrated in Table 24.

As shown in Table 24 the parent catalyst has very low activity in tin anchoring after pretreatment at $t_{\text{red}}= 50^\circ C$ (see experiment 1 in Table 24). As seen from Figures 55A and 55C, upon increasing of the temperature of the re-reduction in H$_2$ atmosphere ($t_{\text{red}}$) up to 200$^\circ C$ only slight increase of both the initial rate of tin anchoring ($w_0$) and the stoichiometry of tin anchoring reaction ($x$) are observed. Re-reduction of parent catalyst up to 200$^\circ C$ has no influence on the amount of Sn anchored per surface Pt atom (see experiments 1-3 in Table 24 and Figure 55D). Further increase of $t_{\text{red}}$ in H$_2$ atmosphere from 200$^\circ C$ up to 400$^\circ C$ (see experiments 3-5 in Table 24) results in strong increase of $w_0$, $x$ and Sn/Pt$_s$ values (see Figures 55A, 55C and 55D).

Table 24. General data related to modification of PtAl-5.0 catalyst with Sn(C$_2$H$_5$)$_4$.

<table>
<thead>
<tr>
<th>No</th>
<th>$t_{\text{red}}$, $^\circ C$</th>
<th>$\tau_{\text{red}}$, h</th>
<th>$w_0$, x $10^{-6}$</th>
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</table>

$^a$ Duration of the re-reduction in H$_2$ atmosphere;

$^b$ Tin content calculated from the overall material balance of tin anchoring;

$^c$ Amount of Sn anchored per surface Pt atom calculated using H/Pt = 0.25;

Catalyst amount: $W_{\text{cat}} = 0.5$ g; initial concentration of SnEt$_4$ $[\text{Sn}]_0 = 1.3 \times 10^{-2}$ M; Sn$_0$/Pt$_s$ = 4.0; solvent: benzene; atmosphere: Ar; reaction temperature: $T_r = 50^\circ C$; duration: 4 h.
Upon increasing of the $t_{\text{red}}$ the amount of ethylene formed in step I decreases (see Figure 55B and $n_{\text{C}_2\text{H}_4}$ values in Table 24).

![Graphs A, B, C, D](https://example.com/graphs.png)

**Figure 55.** The influence of the temperature of re-reduction in H$_2$ atmosphere ($t_{\text{red}}$) on the (A) - initial rate of tin anchoring ($\Diamond$), (B) - $n_{\text{C}_2\text{H}_4}/n^1$ ratio ($\triangle$), (C) - the stoichiometry of tin anchoring reaction I ($\blacklozenge$) and (D) - amount of Sn anchored per surface Pt atom ($\heartsuit$). Catalyst: PtAl-5.0 (see Table 1).

As shown in Figures 55B, the decrease of $n_{\text{C}_2\text{H}_4}/n^1$ ratio is more pronounced up to $t_{\text{red}} = 300^\circ$C. The formation of ethylene indicates that Sn(C$_2$H$_5$)$_4$ is involved in an oxidation-reduction type reaction. These results demonstrate that the efficiency of re-reduction of ionic form of Pt can be increased upon increasing the $t_{\text{red}}$. Almost complete reduction of Pt$^{\text{IV}}$ forms can be achieved at $t_{\text{red}} = 400^\circ$C ($n_{\text{C}_2\text{H}_4}/n^1 = 0.04$). One of the reason of the deviation in $n_{\text{C}_2\text{H}_4}/n^1$ value observed on the catalyst re-reduced at $t_{\text{red}} = 50^\circ$C can be the low activity in tin anchoring reaction (see experiment 1 in Table 24).

The increase of the efficiency of Pt reduction results in an increase of both the $x$ value and Sn/Pt$_s$ ratio. Data show that over completely reduced Pt the hydrogenolysis of the Sn-C bonds is almost complete and mostly “naked” Sn atoms anchored to the Pt are formed ($x = 3.5$).

### 5.8. Use of supported Sn-Pt/Al$_2$O$_3$ and Sn-Re-Pt/Al$_2$O$_3$ catalysts in various catalytic reactions

The modification procedure in circulation type reactor system was aimed at developing naphtha reforming catalyst.$^{232}$ The Sn-Pt/Al$_2$O$_3$ catalysts prepared in this way were tested both in $n$-hexane transformation and naphtha reforming and resulted in reformate with reduced aromatic and increased iso-paraffin content. The activity difference between (O)-type and (H)-type catalysts was demonstrated in our studies,$^{233,242}$ while results related to the extension of the modification to Pt-Re/Al$_2$O$_3$ catalysts with tin was published recently.$^{275}$

Upon using Sn-Pt/Al$_2$O$_3$ catalysts prepared by tin anchoring additional new evidences were obtained with respect to (i) the mode and way to control the selectivity of reforming type catalysts, (ii) the alterations of the reaction routes in hydrocarbon conversions and (iii) the role of tin in reforming catalysts. In these studies it was demonstrated that the use of CSRs could be considered as a powerful tool for studying the mechanism of hydrocarbon reactions catalyzed by bifunctional catalysts.

The bimetallic Sn-Pt/Al$_2$O$_3$ catalysts were characterized by test reactions of the metallic phase (cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH)). The significant
increase of the activation energies in CHD over bimetallic catalysts clearly indicates an electronic modification of the Pt phase, what can be related to the alloy formation. Besides that, a blocking effect of Pt by Sn can be responsible for the decrease in the dehydrogenation activities. Decrease of the activity in CPH over Pt-Sn/Al₂O₃ catalysts was related to dilution of the surface Pt atoms with tin.²¹⁸

The presence of Sn-Pt alloy phase together with oxidized Sn species in Sn-Pt/Al₂O₃ catalysts favors the catalytic behavior in n-butane dehydrogenation, thus increasing the n-butane conversion and decreasing the coke deposition.²¹⁸ Catalytic data obtained over supported Sn-Pt/Al₂O₃ and Sn-Re-Pt/Al₂O₃ catalysts are given in Appendix (see Table A-2).

5.9. Comparison of supported Ge-Pt/C catalysts prepared by conventional impregnation and CSRs

It is known that the addition of germanium onto supported noble metals significantly alters their catalytic properties.¹⁴,¹⁴¹,¹⁴₈,²⁷₆,²⁷₇ The promoting effect of Ge has been evidenced in transformation of hydrocarbons,¹⁴,¹⁴₅,²⁷₉ selective hydrogenation of fine chemicals,²⁷₆,²₈₀ reduction of aromatics.²⁶ It has been demonstrated that the intimate contact between the noble metal and the modifier, i.e., the selective modification of catalytically active sites can only be achieved by either (i) "redox-type" surface reactions²⁷₆,²₈₁ or (ii) using CSRs.¹⁴,¹⁴¹,¹⁴₈,¹⁵₃

In this chapter the details of the preparation of Ge-Pt/C catalysts emphasizing the differences between two methods: (i) conventional impregnation (CI) and (ii) CSRs will be described. The aim of this study is to find modes and ways to increase the amount of Ge anchored onto the Pt and maintain the overall control of germanium anchoring, i.e., suppressing the amount of Ge introduced onto the support.

5.9.1. Modification of 5 wt% Pt/C catalyst with Ge(C₂H₅)₄ by CSRs

In order to achieve high germanium content high initial concentration of Ge(C₂H₅)₄ was used (see Ge/Ptₐ ratio in Table 25) and the temperature of anchoring step I (T₁) was increased up to 155°C.

Table 25. Summary of data of germanium anchoring over PtC-5.0 catalyst by CSRs.

<table>
<thead>
<tr>
<th>No</th>
<th>T₁</th>
<th>Solvent</th>
<th>Ge/Ptₐ</th>
<th>w₀ x 10⁻⁶</th>
<th>n¹ x 10⁻⁶</th>
<th>n² x 10⁶</th>
<th>x</th>
<th>Ge wt% a</th>
<th>Ge/Ptₐ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtGe1-SR</td>
<td>55</td>
<td>hexane</td>
<td>25.0</td>
<td>0.3</td>
<td>7.1</td>
<td>38.8</td>
<td>0.62</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>PtGe2-SR</td>
<td>105</td>
<td>decane</td>
<td>24.7</td>
<td>2.7</td>
<td>98.4</td>
<td>25.4</td>
<td>3.18</td>
<td>0.22</td>
<td>0.29</td>
</tr>
<tr>
<td>PtGe3-SR</td>
<td>155</td>
<td>decane</td>
<td>28.6</td>
<td>20.0</td>
<td>350.8</td>
<td>21.7</td>
<td>3.77</td>
<td>0.68</td>
<td>0.87</td>
</tr>
</tbody>
</table>

²Ge content calculated from the material balance of germanium anchoring;
²²Amount of Ge anchored per surface Pt atom, calculated using CO/Pt=0.42.

Catalyst: PtC-5.0; [Ge(C₂H₅)₄]= 15.5 10⁻² M; atmosphere of anchoring step I: H₂; duration: 4 h.

It is necessary to mention that the results of blank experiment using Pt free carbon support under standard preparation conditions unambiguously confirmed the lack of any reaction between Ge(C₂H₅)₄ and carbon support even at 155°C. For this reason anchoring of Ge(C₂H₅)₄ onto the functionalized carbon support by CSRs can be excluded. Similar results have been reported by Crabb and Ravikumar²²⁵ for the deposition of Ge atoms on Pt/C catalysts using SOMC techniques, indicating that the reaction between Pt and the Ge precursor is highly selective.

The main experimental data of Ge anchoring are summarized in Table 25. These results show that the value of x is in the range of 0.62-3.77 and it strongly depends on the temperature of Ge anchoring.

It has been found by Nedez et al.²⁸³ that Ge(n-C₅H₁₀)₄ reacts irreversibly with surface hydroxyl groups of SiO₂, Al₂O₃ or SiO₂-Al₂O₃ at about 250°C, resulting in the release of one butyl ligand per grafted germanium (x=1.0) and formation of highly thermal stable (up to 400°C) grafted -OGe(n-C₅H₁₀)₃ complex. Consequently, due to the high thermal stability of Ge-C bond, the high extent of loss of the alkyl groups of the PSCs (Pt-Ge(C₅H₁₀)(4-x)) can entirely be attributed to the involvement of Pt.

The formation of ethane during germanium anchoring at three different temperatures is shown in Figure 56A-C. Germanium anchoring was carried out in the presence of gas phase hydrogen, therefore no ethylene was detected. As seen from the kinetic curves presented in Figure 56A-C upon increasing the value of T₁ both the initial rate of anchoring step I and the amount of ethane formed increased.
The $w_0$ values (see Table 25) showed good temperature dependence, resulting in an apparent energy of activation for anchoring step I of $50.8 \pm 4$ kJ mol$^{-1}$. Slightly lower value of the activation energy ($42.6 \pm 1.9$ kJ mol$^{-1}$) was reported in our earlier studies for surface reaction between Sn(C$_2$H$_5$)$_4$ and preadsorbed hydrogen on Pt/SiO$_2$ catalyst.$^{219}$

![Figure 56](image_url)

**Figure 56.** Kinetic curves of (●) ethane formation during germanium anchoring in excess hydrogen. A- $T_r=55^\circ$C; B- $T_r=105^\circ$C; C- $T_r=155^\circ$C. Catalyst: PtC-5.0.

As far as almost constant Ge$_0$/Pt$_s$ ratio (Ge$_0$/Pt$_s=26$), but different reaction temperatures were used in germanium anchoring experiments the change of the shape of TPD patterns given in Figure 57 clearly reflects the differences between the SOMS formed at various temperatures ($T_r=55, 105$ and $155^\circ$C).

The sample PtGe1-SR obtained at $T_r=55^\circ$C has the broadest TPD profile as shown in Figure 57. The contribution of the low-temperature TPD peaks (LTP) below $75^\circ$C is relatively low, whereas the contribution of the high-temperature peaks (HTP) between $140$ and $200^\circ$C is high to the total amount of ethane formed.

Unusually low activity at $T_r=55^\circ$C (see values $w_0$ and Ge/Pt$_s$ in Table 25) and the low value of $x$ ($x=0.62$) indicates that Ge(C$_2$H$_5$)$_4$ is highly stable at this temperature and the extent of anchoring reaction is relatively low. Consequently, in this case mainly chemisorption of Ge(C$_2$H$_5$)$_4$ onto platinum surface takes place.

In our earlier studies it has been demonstrated$^{220}$ that the appearance of HTP can be attributed to the formation of coordinatively saturated -Sn(C$_2$H$_5$)$_4$ surface species strongly adsorbed onto the platinum. Due to coordinative saturation these species are much less reactive towards hydrogen than those having less alkyl groups.

At $T_r=105^\circ$C and $155^\circ$C the presence of hydrogen resulted in high extent of dealkylation of -Ge(C$_2$H$_5$)$_{4-x}$, what is reflected by low $n^H$ and high $x$ values (see data given in Table 25).

The high value of $x$ ($x=3.0$ or $4.0$) indicated that in step I coordinatively unsaturated moieties -Ge(C$_2$H$_5$)$_x$ ($x=3.0$) and “naked” Ge ($x=4.0$) were exclusively anchored onto the platinum. Moreover, this finding indicated also that upon performing surface reaction at $T_r=155^\circ$C the hydrogenolysis of the Ge-C bonds in anchored SOMS was almost complete and mostly “naked” Ge atoms were formed. “Naked” Ge atoms can be present on the platinum surface as adatoms and can migrate into the bulk of...
platinum leading to site isolation effects and forming surface or bulk alloy type species even during the anchoring step I.

![Graph showing TPD patterns](image)

**Figure 57.** Influence of the reaction temperature on the TPD patterns of SOMS formed during germanium anchoring. ( ), Catalyst PtGe1-SR (T_r = 55°C); ( ), catalyst PtGe2-SR (T_r = 105°C); ( ), catalyst PtGe3-SR (T_r = 155°C).

The increase of the temperature of germanium anchoring up to 155°C resulted in pronounced increase of the Ge/Pt ratio (Ge/Pt = 0.87) and the temperature maximum of TPD curve was shifted to 170°C (see Figure 57). As emerges from Figure 57 the appearance of HTP TPD peak at 170°C and shoulder at 250°C can be attributed to the high thermal stability of Ge-C bond in SOMS with general formula of -Ge(C\textsubscript{2}H\textsubscript{5}).

### 5.9.2. Chemisorption properties of Ge-Pt/C catalysts prepared by CSRs and conventional impregnation

As emerges from data presented in Table 26 the H/Pt ratio in parent Pt/C catalyst is lower than the CO/Pt ratio. Similar results were reported by Rodriguez-Reinoso,\textsuperscript{284} whereas in Ref.\textsuperscript{285} the opposite tendency was demonstrated. Several studies have been carried out by Coloma et al.\textsuperscript{285} which relate Pt dispersion to active carbon support characteristics such as surface heterogeneity, surface electronic properties, porous structure and content of oxygen surface groups on the support.

Table 26 shows that the introduction of germanium onto parent Pt/C catalyst results in significant decrease of both H\textsubscript{2} and CO chemisorption values. The trend in the decrease of the H/Pt and CO/Pt ratios as a function of Ge/Pt ratio is different for catalysts prepared by CI and CSRs. As far as H\textsubscript{2} chemisorption is an activated process, the presence of Pt-Pt sites is needed to break the H-H bond prior to the chemisorption, whereas on single Pt atoms CO adsorption can take place in the linear mode. Consequently, the H/Pt ratios decrease faster than the CO/Pt one. In the PtGe1-3-SR series of catalysts even at lowest Ge content (Ge/Pt = 0.04) the amount of chemisorbed hydrogen is strongly diminished and remains very low and almost constant (see Table 26).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ge, wt%</th>
<th>Ge/Pt \textsuperscript{a} (at./at.)</th>
<th>H/Pt</th>
<th>CO/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>-</td>
<td>-</td>
<td>0.29</td>
<td>0.42</td>
</tr>
<tr>
<td>PtGe1-CI</td>
<td>0.08</td>
<td>0.04</td>
<td>0.26</td>
<td>0.39</td>
</tr>
<tr>
<td>PtGe2-CI</td>
<td>0.22</td>
<td>0.12</td>
<td>0.22</td>
<td>0.33</td>
</tr>
<tr>
<td>PtGe3-CI</td>
<td>0.61</td>
<td>0.33</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>PtGe4-CI</td>
<td>1.83</td>
<td>0.98</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>PtGe1-SR</td>
<td>0.08</td>
<td>0.04</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>PtGe2-SR</td>
<td>0.22</td>
<td>0.12</td>
<td>0.04</td>
<td>0.08</td>
</tr>
<tr>
<td>PtGe3-SR</td>
<td>0.68</td>
<td>0.37</td>
<td>0.03</td>
<td>0.07</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ge/Pt values calculated from the actual Pt and Ge content determined by AAS; PtGe1-4-CI and PtGe1-3-SR catalysts prepared by CI and CSRs, respectively.
It is necessary to mention that our results are in a good agreement with chemisorption data presented for Ge-Rh/Al₂O₃ catalysts prepared by SOMC in Ref. It is noteworthy that in catalysts prepared by CSRs the CO/Pt ratios are also low, but that they are still twice as high as the amount of hydrogen chemisorbed.

The decrease of H/Pt and CO/Pt ratios in Ge-Pt catalyst can be attributed to two effects: (i) site blocking and (ii) electronic effect induced by Ge. Literature data indicate that due to the electron acceptor effect of Ge, CO chemisorption sharply decreases even at very low modifier contents. It is suggested that Pt atoms when alloyed with Ge are in an electron-deficient state and thus the CO coverage is suppressed. Contrary to that in PtGe1-4-CI series of catalysts, the decrease of the chemisorption values is less pronounced.

Scheme 15. Influence of the preparation method on the location of Ge Pt-Ge/C in catalysts.

It has been demonstrated that the surface composition of supported bimetallic catalysts strongly depends on the method of their preparation. Scheme 15 shows that in Pt-Ge/C catalysts prepared by CI method the main part of Ge is located on the support. Contrary to that exclusive formation of alloy-type surface entities can only be achieved by using of CSRs method.

Two test reactions (cyclohexane dehydrogenation (CHD) and cyclopentane hydrogenolysis (CPH)) were applied to characterize the catalysts prepared. Only slight decrease of the reaction rates in CHD indicated that the introduction of germanium by CI resulted in only very slight electronic modification of Pt. On the other hand, the similar hydrogenolytic activity in CPH reaction of PtGe-CI catalysts with respect to the monometallic Pt/C strongly indicated that major part of Ge is located either on the support or at a considerable distance from Pt. The decrease in the exposed metallic Pt area observed in PtGe1-3-SR series of catalysts in CHD reaction can be related to the formation of PtGe alloy. These catalysts showed low activity in CPH reaction, indicating the loss of Pt ensemble sites required for this reaction when Ge was added to Pt by using CSRs. In citral hydrogenation reaction these Ge-Pt/C catalysts modified by Ge(C₂H₅)₄ were successfully applied. Catalytic data obtained over supported Pt-Ge/C catalysts are given in Appendix (see Tables A-1 and A-2).

5.10. Preparation of various types of supported Snₓ-Mₓ (M= Pd, Rh and Ru) catalysts by CSRs

In this Chapter the results of first and second steps of surface reactions are summarized upon using different supports, different metals and metal loadings. Influence of reaction conditions and the type of tetraalkyl tin compound used has also been investigated in details. Data given below clearly represent that the method of CSRs in catalyst preparation can be extended to other systems as supported Pt and this process can be generally used.

5.10.1. Modification of 1.7 wt% Pd/SiO₂ catalyst with Sn(C₂H₅)₄

In order to achieve high tin content high initial concentration of Sn(C₂H₅)₄ was used (see [Sn]₀ values and Sn₀/Pd₀ ratios in Table 27).

As shown in Table 27 atmosphere of tin anchoring appeared to be the key experimental variable to increase the amount of tin anchored onto PdSi-1.7 catalyst (see Sn/Pd values). The initial rate of tin anchoring (w₀) strongly depends on the initial Sn₀/Pd₀ ratios, data show that in the presence of excess of hydrogen the tin anchoring reaction is faster than in its absence. Good reproducibility of tin anchoring was demonstrated (compare experiments 3 and 4 in Table 27).

In the presence of adsorbed hydrogen (see experiment 1 in Table 27), ethylene was the major product formed in step I, ethane was formed only in small amount (nC₂H₄/n= 0.72).
The presence of excess of hydrogen resulted in high extent of dealkylation of -Sn(C₂H₅)₄, what is reflected by low \( n^I \) and high \( x \) values (compare experiments 1 and 2 in Table 27). The TPD profile also showed significant changes compared to the experiment carried out in an argon atmosphere (see Figure 58).

**Table 27.** General data related to modification of PdSi-1.7 catalyst with Sn(C₂H₅)₄.

<table>
<thead>
<tr>
<th>No</th>
<th>Atm.</th>
<th>[Sn]₀, M x 10⁻²</th>
<th>Sn₀/Pd₀</th>
<th>( w₀ ), x 10⁻⁶</th>
<th>( n^I ), x 10⁻⁶</th>
<th>( n^II ), x 10⁻⁶</th>
<th>( x )</th>
<th>TOF, s⁻¹ x 10⁻⁴</th>
<th>Sn, wt% (^a)</th>
<th>Sn/Pd, (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar</td>
<td>4.6</td>
<td>14.1</td>
<td>0.05</td>
<td>84.3</td>
<td>60.3</td>
<td>68.6</td>
<td>2.20</td>
<td>0.2</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>4.6</td>
<td>12.8</td>
<td>40</td>
<td>297</td>
<td>-</td>
<td>27.8</td>
<td>3.66</td>
<td>181.4</td>
<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>H₂</td>
<td>4.6 (^c)</td>
<td>5.7</td>
<td>16</td>
<td>250</td>
<td>-</td>
<td>104.8</td>
<td>2.82</td>
<td>72.6</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>H₂</td>
<td>4.6 (^d)</td>
<td>5.9</td>
<td>16</td>
<td>271</td>
<td>-</td>
<td>110.4</td>
<td>2.84</td>
<td>72.6</td>
<td>1.13</td>
</tr>
</tbody>
</table>

\(^a\) Tin content calculated from the overall material balance of tin anchoring;  
\(^b\) Amount of Sn anchored per surface Pd atom calculated using CO/Pd= 0.23;  
\(^c\) Catalyst amount: \( W_{cat} = 4.3 \) g; duration: 3 h;  
\(^d\) Amount of tin introduced per one injection; number of injections: 2.

Catalysts were re-reduced in H₂ atmosphere at \( t_{red} = 300 \)°C for 2 h; catalyst amount: \( W_{cat} = 1 \) g; solvent: benzene; reaction temperature: \( T_r = 50 \)°C; duration: 2 h.

**Figure 58.** Temperature programmed decomposition of anchored SOMS. Tin anchoring in the presence of excess of hydrogen (■) and in an argon atmosphere (▲). Catalyst: PdSi-1.7.

In the presence of excess of hydrogen the \( x \) value is higher than in its absence. The result shows that performing tin anchoring in hydrogen atmosphere at high \( \text{Sn}_0/\text{Pd}_0 \) ratio (\( \text{Sn}_0/\text{Pd}_0 = 12.8 \)) the hydrogenolysis of the Sn-C bonds in anchored SOMS is almost complete and mostly “naked” Sn atoms anchored to the Pd are formed (\( x = 3.66 \)). However, it is important to note that even in the absence of excess of hydrogen (in Ar atmosphere) the \( x \) value is higher then 2, in accordance with elevated hydrogenolysis activity of Pd.

\[ \text{H}_2, 1.7 \text{ wt\% Pd/SiO}_2, \text{ EtOH} + \text{HCl}, \text{ room}, 3-4 \text{ h.} \quad (5.20) \]

\( A \) - (±)-4-Azido-5-oxo-1-pivaloyl-1,3,4,5-tetrahydrobenz[c,d]indole;  
\( B \) - (±)-4-Amino-5-oxo-1-pivaloyl-1,3,4,5-tetrahydrobenz[c,d]indole hydrochloride.
Tin-modified Pd/SiO\textsubscript{2} catalysts were tested in the liquid-phase hydrogenation of azide of the N-pivaloyl derivative of Uhle's ketone (A) into the appropriate amine hydrochloride (B) at room temperature and atmospheric pressure of hydrogen (see reaction (5.20) and Table 28). Catalytic hydrogenation of tricyclic indole derivatives was performed by G. Dörnyei.\textsuperscript{288,289}

Table 28. Liquid-phase hydrogenation of azide of the N-pivaloyl derivative of Uhle's ketone (A) over Sn-Pd/SiO\textsubscript{2} catalyst.

<table>
<thead>
<tr>
<th>(W_{\text{cat}}) g</th>
<th>(A), M (\times 10^{-2})</th>
<th>EtOH, ml</th>
<th>(T_r), °C</th>
<th>(P_{H_2}), atm</th>
<th>Time, h</th>
<th>Conversion, %</th>
<th>Yield, %</th>
<th>Selectivity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 (H)</td>
<td>3</td>
<td>40</td>
<td>25</td>
<td>1</td>
<td>3</td>
<td>100</td>
<td>66</td>
<td>100</td>
</tr>
<tr>
<td>0.2 (O)</td>
<td>3</td>
<td>80</td>
<td>25</td>
<td>1</td>
<td>4</td>
<td>100</td>
<td>91</td>
<td>100</td>
</tr>
</tbody>
</table>

(H)- and (O)-types of Sn-Pd/SiO\textsubscript{2} catalyst (Sn/Pd\textsubscript{s} = 2.21; see experiment 2 in Table 27).

5.10.2. Modification of 5 wt% Pd/C catalyst with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}

The influence of the temperature and duration of re-reduction on the activity of PdC-5.0 catalyst in tin anchoring reaction I was demonstrated in Table 29.

Table 29. General data related to modification of PdC-5.0 catalyst with Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4}.

<table>
<thead>
<tr>
<th>No</th>
<th>(t_{\text{red}}), °C</th>
<th>(\tau_{\text{red}}), h\textsuperscript{a}</th>
<th>(w_0), (\times 10^4)</th>
<th>(n^I), (\times 10^6)</th>
<th>(n_{C_2H_4}), (\times 10^6)</th>
<th>(x)</th>
<th>(\text{TOF}, \text{s}^{-1} \times 10^4)</th>
<th>Sn, wt%\textsuperscript{b}</th>
<th>Sn/Pd,\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
<td>2</td>
<td>0.04</td>
<td>23.9</td>
<td>20.5</td>
<td>142.9</td>
<td>0.57</td>
<td>0.03</td>
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<td>2</td>
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<td>116.5</td>
<td>112.2</td>
<td>2.83</td>
<td>1.7</td>
<td>1.14</td>
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<td>272.0</td>
<td>121.0</td>
<td>146.0</td>
<td>2.60</td>
<td>1.9</td>
<td>1.24</td>
</tr>
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<td>4</td>
<td>200</td>
<td>2</td>
<td>1.8</td>
<td>282.0</td>
<td>162.0</td>
<td>151.2</td>
<td>2.60</td>
<td>1.3</td>
<td>1.29</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>4</td>
<td>2.1</td>
<td>297.0</td>
<td>173.0</td>
<td>177.7</td>
<td>2.50</td>
<td>1.5</td>
<td>1.41</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>0.5</td>
<td>1.6</td>
<td>316.7</td>
<td>209.7</td>
<td>175.2</td>
<td>2.58</td>
<td>1.1</td>
<td>1.46</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>2</td>
<td>1.9</td>
<td>319.3</td>
<td>186.0</td>
<td>189.5</td>
<td>2.51</td>
<td>1.4</td>
<td>1.51</td>
</tr>
</tbody>
</table>

\(t_{\text{red}}\): Duration of the re-reduction in H\textsubscript{2} atmosphere;
\(\tau_{\text{red}}\): Tin content calculated from the overall material balance of tin anchoring;
\(w_0\): Amount of Sn anchored per surface Pd atom calculated using CO/Pd = 0.50;
Catalyst amount: \(W_{\text{cat}} = 1\) g; \([\text{Sn}]_0 = 6.6 \times 10^{-2}\) M; \(\text{Sn/Pd}_s = 3.0\); solvent: benzene; atmosphere: Ar; reaction temperature: \(T_r = 50\) °C; duration: 4.5 h.

CSR\textsubscript{s} between Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} and hydrogen adsorbed on reduced Pd (Pd\textsuperscript{0}) proceeds via stepwise hydrolysis of the Sn-C bond with elimination of ethane and formation of PSC. The formation of PSC and elimination of ethylene indicates that Sn(C\textsubscript{2}H\textsubscript{5})\textsubscript{4} is involved in an oxidation-reduction type reaction over ionic form of Pd (Pd\textsuperscript{δ+}). It can be seen from Figure 59 that the temperature and duration of re-reduction in H\textsubscript{2} atmosphere has strong influence on the form of the kinetic curves of the ethane and ethylene formation. As shown in Figure 59 the contribution of both reactions strongly depends on the ratio between reduced and ionic forms of palladium. As emerges from Figure 59 the higher the extent of reduction of the catalyst the higher amount ethane (\(n_{C_2H_6}\)) and the lower amount ethylene (\(n_{C_2H_4}\)) formed.

Figures 59A, 59B and 59C also represent that the alteration of the correlation between the initial rate of ethane (\(w_0\)) and ethylene formation (\(w_{0_{C_2H_4}}\)) (\(w_0 > w_{0_{C_2H_4}}\), \(w_0 = w_{0_{C_2H_4}}\), \(w_0 < w_{0_{C_2H_4}}\), respectively) strongly depends on the degree of reduction of Pd.

Based on results presented Table 29 and visualized in Figure 60 the following main conclusions can be drawn:

The increase of the temperature of the re-reduction in H\textsubscript{2} atmosphere resulted in a slight increase of the initial rate of ethane formation in tin anchoring (\(w_0\)) as shown in Figure 60A. After pretreatment of Pd/C catalyst at \(t_{\text{red}} = 400\) °C for 2 h (see experiment 1 in Table 29) the loss of the activity in tin anchoring step I was observed.
Figure 59. The influence of the temperature and duration of re-reduction in H₂ atmosphere on the kinetic pattern of tin anchoring. (●), Ethane; (▲), ethylene.
A- t_red = 200°C for 2 h (see experiment 2 in Table 29);
B- t_red = 100°C for 4 h (see experiment 5 in Table 29);
C- t_red = 50°C for 0.5 h (see experiment 6 in Table 29).

Figure 60. The influence of the temperature (t_red) and duration of re-reduction in H₂ atmosphere on the (A)- initial rate of tin anchoring: (●), short time, (▲), prolonged time; (B)- n_C2H4/n^1 ratio: (●), short time, (▲), prolonged time; (C)- the stoichiometry of tin anchoring reaction I: (●), short time, (▲), prolonged time; and (D)- amount of Sn anchored per surface Pd atom: (●), short time, (▲), prolonged time. Catalyst: PdC-5.0.
Upon increasing of the $t_{\text{red}}$ the amount of ethylene formed in step I (or $n_{\text{C}_2\text{H}_4}/n^I$ ratio) decreases (see $n_{\text{C}_2\text{H}_4}/n^I$ values in Table 29 and Figure 60B). These results demonstrate that the efficiency of re-reduction of ionic form of Pd (Pd$^{+\delta}$) can be enhanced by increasing of the $t_{\text{red}}$. However, reduction temperature used ($t_{\text{red}} \leq 200^\circ\text{C}$) was not sufficient for full reduction of highly dispersed palladium (the lowest $n_{\text{C}_2\text{H}_4}/n^I$ value obtained was around 0.4).

The $x$ value higher then 2.5 was observed in all experiments performed after reduction at $t_{\text{red}} \leq 200^\circ\text{C}$ (see Figure 60C). Decrease of the temperature of the re-reduction in H$_2$ atmosphere resulted in 25% increase of the amount of tin anchored onto PdC-5.0 catalyst (see Figure 60D).

5.10.3. Modification of 1 wt% Rh/SiO$_2$ catalyst with Sn(C$_2$H$_5$)$_4$

The results of modification of silica supported Rh catalyst are summarized in Table 30 and Figure 61. Chemisorption data of parent and tin-modified catalysts are given in Table 31.

**Table 30.** General data related to modification of RhSi-1.0 catalyst with Sn(C$_2$H$_5$)$_4$.

<table>
<thead>
<tr>
<th>No</th>
<th>[Sn]$_0$ x 10$^{-2}$ M</th>
<th>Sn$_0$/Rh$_s$</th>
<th>$w_0$ x 10$^{-6}$</th>
<th>$n^I$ x 10$^{-6}$</th>
<th>$n^{II}$ x 10$^{-6}$</th>
<th>x</th>
<th>TOF$_s$, s$^{-1}$ x 10$^{-4}$</th>
<th>Sn, wt%</th>
<th>Sn/Rh$_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>7.3</td>
<td>0.20</td>
<td>23.7</td>
<td>10.7</td>
<td>2.76</td>
<td>1.7</td>
<td>0.10</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>3.8</td>
<td>17.4</td>
<td>0.33</td>
<td>38.0</td>
<td>18.2</td>
<td>2.71</td>
<td>2.8</td>
<td>0.17</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>5.1</td>
<td>24.0</td>
<td>0.56</td>
<td>42.6</td>
<td>36.3</td>
<td>2.16</td>
<td>4.8</td>
<td>0.23</td>
<td>1.02</td>
</tr>
<tr>
<td>4</td>
<td>7.6</td>
<td>34.2</td>
<td>0.80</td>
<td>44.0</td>
<td>59.4</td>
<td>1.70</td>
<td>6.9</td>
<td>0.31</td>
<td>1.34</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>36.4</td>
<td>0.15</td>
<td>30.7</td>
<td>112.5</td>
<td>0.86</td>
<td>1.3</td>
<td>0.43</td>
<td>1.86</td>
</tr>
</tbody>
</table>

$^a$ Tin content calculated from the overall material balance of tin anchoring.

$^b$ Amount of Sn anchored per surface Rh atom calculated from the CO/Rh= 0.20.

$^c$ $W_{\text{cat}}= 0.36$ g; Reaction atmosphere: Ar.

Catalyst re-reduced in H$_2$ atmosphere at $t_{\text{red}}= 500^\circ\text{C}$ for 2h; $W_{\text{cat}}= 1$ g; reaction atmosphere: H$_2$; solvent: benzene; reaction temperature $T_r= 50^\circ\text{C}$; duration: 2 h.

The increase of the initial tin concentration (see values [Sn]$_0$ and Sn$_0$/Rh ratios in Table 30) appeared to be the key experimental variable to increase the amount of tin anchored. The TPD profile showed marked differences depending on the initial Sn$_0$/Rh$_s$ ratios as seen in Figure 61.

![Figure 61](image)

**Figure 61.** The influence of the Sn$_0$/Rh$_s$ ratio on the decomposition pattern. (●), Sn$_0$/Rh$_s$ = 7.3 (Sn/Rh$_s$ = 0.45); (■), Sn$_0$/Rh$_s$ = 17.4 (Sn/Rh$_s$ = 0.73); (◇), Sn$_0$/Rh$_s$ = 24.0 (Sn/Rh$_s$ = 1.02); (□), Sn$_0$/Rh$_s$ = 34.2 (Sn/Rh$_s$ = 1.34). Catalyst: RhSi-1.0.

The initial rate of tin anchoring ($w_0$) strongly depends on the initial Sn$_0$/Rh$_s$ ratios. Data show that in the presence of excess of hydrogen the tin anchoring reaction is faster than in its absence. In the presence of adsorbed hydrogen (see experiment 5 in Table 30), ethylene was the major product formed in step I, ethane was formed only in small amount ($n_{\text{C}_2\text{H}_4}/n^I = 0.88$).

As emerges from Table 30 in the presence of excess of hydrogen the $x$ value is also higher than in its absence. The presence of excess hydrogen resulted in high extent of dealkylation of -Sn(C$_2$H$_5$)$_{4-x}$, what is reflected by high $x$ values. The results show that in the presence of excess of hydrogen upon
increasing the Sn/Rh, ratio the value of $x$ decreases from 2.76 to 1.70. In the presence of adsorbed hydrogen the $x$ value is about 1 ($x = 0.86$).

Data given in Table 31 show that the introduction of tin to parent $RhSi-1.0$ catalyst results in significant decrease in both $H_2$ and CO chemisorption. The decrease of hydrogen chemisorption induced by tin is more pronounced than that of the CO.

**Table 31.** Chemisorption properties of parent $RhSi-1.0$ and bimetallic Sn-Rh/SiO$_2$ catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Sn$_0$/Rh$_s$</th>
<th>Sn, wt%</th>
<th>Sn/Rh$_s$</th>
<th>H/Rh</th>
<th>CO/Rh</th>
<th>Chemisorption of $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Rh/SiO_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.93</td>
<td>19.86</td>
<td>0.119  0.393</td>
</tr>
<tr>
<td>1</td>
<td>7.3</td>
<td>0.10</td>
<td>0.45</td>
<td>4.34</td>
<td>13.41</td>
<td>0.047  0.265</td>
</tr>
<tr>
<td>2</td>
<td>17.4</td>
<td>0.17</td>
<td>0.73</td>
<td>2.00</td>
<td>12.22</td>
<td>0.022  0.242</td>
</tr>
<tr>
<td>3</td>
<td>24.0</td>
<td>0.23</td>
<td>1.02</td>
<td>0</td>
<td>10.35</td>
<td>0  0.205</td>
</tr>
<tr>
<td>4</td>
<td>34.2</td>
<td>0.31</td>
<td>1.34</td>
<td>0</td>
<td>9.32</td>
<td>0  0.185</td>
</tr>
<tr>
<td>5</td>
<td>36.4</td>
<td>0.43</td>
<td>1.86</td>
<td>0</td>
<td>8.39</td>
<td>0  0.166</td>
</tr>
</tbody>
</table>

$^a$ $\text{ml g}^{-1}$

The tin-modified catalysts were tested in the liquid phase hydrogenation of crotonaldehyde at 50°C. The maximum crotylalcohol selectivity (30 %) was obtained at 5 % conversion over Sn-Rh/SiO$_2$ catalyst with Sn/Rh$_s = 1.34$. Catalytic reaction was performed in Universidad de Concepción (Chile) by G. Pecchi.$^{290}$

5.10.4. Modification of 1 wt% $Rh/Al_2O_3$ catalyst with Sn(C$_2$H$_5$)$_4$

Results obtained in the modification of alumina supported Rh catalysts are shown in Figure 62 and Table 32. Increase of the initial tin concentration and duration of tin anchoring step I appeared to be the key experimental parameters to increase the amount of tin anchored (compare experiments 2 and 5 in Table 32).

![Figure 62](image_url)

**Figure 62.** Influence of the temperature and duration of re-reduction on the formation of ethane (■) and ethylene (■) during tin anchoring over RhAl-1.0 catalyst. A- Re-reduction at 400°C for 1 h.; B- re-reduction at 500°C for 2 h.

Data in Table 32 indicate that the initial rate of tin anchoring ($w_0$) strongly depends on both (i) the temperature of catalysts re-reduction prior to tin anchoring ($t_{\text{red}}$) and (ii) the initial Sn$_0$/Rh$_s$ ratio. Results show that in the presence of excess of hydrogen the tin anchoring reaction is faster than in its absence. Quite good reproducibility of tin anchoring can be attained using different amounts of catalyst (compare experiments 3 and 4 in Table 32, $W_{\text{cat}} = 3.64$ g and 1 g, respectively).

As seen from Figure 62, the temperature and duration of re-reduction of parent catalyst has strong influence on the amount of ethane and ethylene formed during anchoring reaction. In the presence of
adsorbed hydrogen (see experiments 1, 2 and 5 in Table 32), ethylene was the major product formed in step I \( \frac{n_{\text{C}_2\text{H}_4}}{n^*} \) ratio was around 0.75).

In the presence of excess of hydrogen the \( x \) value is higher than in its absence. The results show that performing tin anchoring in hydrogen atmosphere the hydrogenolysis of the Sn-C bonds in anchored SOMS is almost complete and mostly “naked” Sn atoms anchored onto the Rh are formed \( (x \geq 3.23) \). However, it is necessary to mention that even in the presence of adsorbed hydrogen the \( x \) value is around or even higher than 2.

### Table 32. General data related to modification of RhAl-1.0 catalyst with Sn(C\(_2\)H\(_5\))\(_4\)

<table>
<thead>
<tr>
<th>No</th>
<th>Atm</th>
<th>[Sn](_0), M</th>
<th>Sn(_0/\text{Rh}_s)</th>
<th>( \text{w}_{\text{cat}} \times 10^{-6} )</th>
<th>( n^I \times 10^{-6} )</th>
<th>( n^\text{II} \times 10^{-6} )</th>
<th>( x )</th>
<th>TOF, ( \text{s}^{-1} \times 10^{-4} )</th>
<th>Sn, wt% (^a)</th>
<th>Sn/Rh (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar</td>
<td>0.10</td>
<td>38.6</td>
<td>0.3</td>
<td>33.0</td>
<td>23.0</td>
<td>35.4</td>
<td>1.93</td>
<td>1.8</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>Ar</td>
<td>0.10</td>
<td>37.8</td>
<td>0.2</td>
<td>65.4</td>
<td>50.0</td>
<td>45.8</td>
<td>2.35</td>
<td>1.1</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>H(_2)</td>
<td>0.20</td>
<td>76.4</td>
<td>2.1</td>
<td>113.0</td>
<td>0.0</td>
<td>26.8</td>
<td>3.23</td>
<td>12.0</td>
<td>0.42</td>
</tr>
<tr>
<td>4</td>
<td>H(_2)</td>
<td>0.20</td>
<td>84.8</td>
<td>2.4</td>
<td>146.0</td>
<td>0.0</td>
<td>15.7</td>
<td>3.61</td>
<td>13.9</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>Ar</td>
<td>0.28</td>
<td>108.6</td>
<td>0.8</td>
<td>141.0</td>
<td>81.0</td>
<td>2.54</td>
<td>4.8</td>
<td>0.66</td>
<td>1.90</td>
</tr>
</tbody>
</table>

\(^a\) Tin content calculated from the overall material balance of tin anchoring;
\(^b\) Amount of Sn anchored per surface Rh atom calculated using H/Rh= 0.30.
\(^c\) Duration of step I (\( \tau_r \)): 2 h, 3 h and 4 h, respectively;
\(^d\) Catalyst was re-reduced in H\(_2\) atmosphere at \( t_{\text{red}} = 500^\circ \text{C} \) for 2 h;
\(^e\) Catalyst amount: \( W_{\text{cat}} = 3.64 \text{ g} \); solvent: benzene; reaction temperature \( T_r = 50^\circ \text{C} \).

### 5.10.5. Modification of 4 wt% Rh/Al\(_2\)O\(_3\) catalyst with Sn(C\(_2\)H\(_5\))\(_4\)

The influence of the re-reduction temperature and atmosphere of tin anchoring on the amount of tin anchored onto RhAl-4.0 catalyst was summarized in Table 33. The increase of the re-reduction temperature and use of excess of hydrogen in the tin anchoring step I appeared to be the key experimental variables to increase the amount of tin anchored (see Table 33).

### Table 33. General data related to modification of RhAl-4.0 catalyst with Sn(C\(_2\)H\(_5\))\(_4\)

<table>
<thead>
<tr>
<th>No</th>
<th>( t_{\text{red}} ), (^\circ\text{C} )</th>
<th>Atm.</th>
<th>Sn(_0/\text{Rh}_s)</th>
<th>( \text{w}_{\text{cat}} \times 10^{-6} )</th>
<th>( n^I \times 10^{-6} )</th>
<th>( n^\text{II} \times 10^{-6} )</th>
<th>( x )</th>
<th>TOF, ( \text{s}^{-1} \times 10^{-4} )</th>
<th>Sn, wt% (^a)</th>
<th>Sn/Rh (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>Ar</td>
<td>7.5</td>
<td>2.4</td>
<td>97.4</td>
<td>31.9</td>
<td>3.01</td>
<td>1.7</td>
<td>0.38</td>
<td>0.14</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>Ar</td>
<td>5.6</td>
<td>2.4</td>
<td>167.0</td>
<td>37.1</td>
<td>3.27</td>
<td>1.7</td>
<td>0.61</td>
<td>0.22</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>H(_2)</td>
<td>6.3</td>
<td>4.6</td>
<td>267.0</td>
<td>36.3</td>
<td>3.52</td>
<td>3.3</td>
<td>0.90</td>
<td>0.33</td>
</tr>
</tbody>
</table>

\(^a\) Sn content calculated from the overall material balance of tin anchoring;
\(^b\) Amount of Sn anchored per surface Rh atom calculated using H/Rh= 0.60.
Catalyst amount: \( W_{\text{cat}} = 1 \text{ g} \); duration of re-reduced in H\(_2\) atmosphere: 2 h; [Sn]\(_0\): 0.13 M; solvent: benzene; duration of tin anchoring step I (\( \tau_r \)): 2.5 h.

The results show that in the presence of excess of hydrogen the tin anchoring reaction is faster than its absence, as indicated by the low ethylene formation. Complete reduction of Rh\(^{5+}\) forms has been achieved even at \( t_{\text{red}} = 200^\circ \text{C} \) \( (n_{\text{C}_2\text{H}_4}/n^* = 0.004) \). Upon increasing the reduction temperature of parent catalyst up to \( t_{\text{red}} = 400^\circ \text{C} \), in CSRs (step I) carried out in the presence of adsorbed hydrogen, ethane was the single reaction product formed. High extent of dealkylation of anchored SOMS was observed in all experiments \( (3 \leq x \leq 3.5) \). As emerges from Table 33 in the presence of excess of hydrogen the \( x \) value is slightly higher than in its absence.

### 5.10.6. Modification of 5 wt% Rh/Al\(_2\)O\(_3\) catalyst with Sn(C\(_2\)H\(_5\))\(_4\)

Modification of alumina supported Rh catalyst with high metal loading is demonstrated in Table 34 and Figure 63. As seen from data given in Table 34 the increase of the duration of tin anchoring (\( \tau_r \)) and number of injections of the tin precursor compound appeared to be the key experimental
variables to increase the amount of tin anchored (see $\text{Sn/Rh}_s$ values). The initial rate of tin anchoring ($w_0$) strongly depends on the initial Sn$_0$/Rh, ratios. As seen from Figure 63, after 2 h of tin anchoring a strong decrease of the rate of the formation of ethane and an instantaneous formation of ethylene was observed. The increase of the number of injections of the tin precursor compound accompanied with filling the reactor with additional portions of hydrogen resulted in both exclusive ethane formation during tin anchoring and strong increase of the $\text{Sn/Rh}_s$ values (see experiment 3 in Table 34). This result shows that the hydrogenolysis of the Sn-C bonds in anchored SOMS is almost complete and mostly “naked” Sn atoms anchored to the Rh are formed in all experiments ($x \geq 3.3$).

**Table 34.** General data related to modification of RhAl-5.0 catalyst with Sn(C$_2$H$_5$)$_4$

<table>
<thead>
<tr>
<th>No</th>
<th>$\tau_r$, h</th>
<th>$[\text{Sn}]_0$, M</th>
<th>Sn$_0$/Rh</th>
<th>$w_0$, x $10^{-6}$</th>
<th>$n^I$, x $10^{-6}$</th>
<th>$n^\text{C}_2\text{H}_4^I$, x $10^{-6}$</th>
<th>$x$, TOF, s$^{-1}$ x $10^{-4}$</th>
<th>Sn, wt%$^a$</th>
<th>Sn/Rh$_s$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>0.28</td>
<td>22.5</td>
<td>6.5</td>
<td>376.0</td>
<td>86.0</td>
<td>39.0</td>
<td>3.62</td>
<td>7.4</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.06</td>
<td>4.7</td>
<td>2.5</td>
<td>385.0</td>
<td>161.0</td>
<td>77.7</td>
<td>3.33</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0.06$^c$</td>
<td>4.7</td>
<td>2.6</td>
<td>848.0</td>
<td>0.0</td>
<td>50.8</td>
<td>3.77</td>
<td>2.9</td>
</tr>
</tbody>
</table>

$^a$ Tin content calculated from the overall material balance of tin anchoring;

$^b$ Amount of Sn anchored per surface Rh atom calculated using H/Rh$=0.30$;

$^c$ Amount of tin introduced per one injection; number of injections: 3.

Catalysts were re-reduced in $\text{H}_2$ atmosphere at $t_{\text{red}}=400^\circ$C for 1 h; catalyst amount: $W_{\text{cat}}=1$ g; solvent: benzene; reaction temperature $T_r=50^\circ$C; reaction atmosphere: $\text{H}_2$.

![Figure 63](image)

**Figure 63.** The influence of added hydrogen on the CSRs over RhAl-5.0 catalyst. A- First step of tin anchoring: amount of ( ), ethane, and ( ), ethylene formed; Sn$_0$/Rh$=4.7$, Sn/Rh$_s=0.79$, $T_r=50^\circ$C; B- Decomposition of anchored SOMC in step II: ( ), amount of ethane formed.

5.10.7. Modification of 5 wt% Rh/MgO catalyst with Sn(C$_2$H$_5$)$_4$

Results obtained in the modification of magnesia supported Rh parent catalyst with Sn(C$_2$H$_5$)$_4$ are given in Table 35 and Figure 64. Chemisorption properties and catalytic activities in low temperature CO oxidation of parent Rh/MgO and Sn-modified Rh/MgO catalysts are presented in Table 36.

The increase of the initial tin concentration (see values $[\text{Sn}]_0$ and Sn$_0$/Rh$_s$ ratios in Table 35) and temperature of tin anchoring reaction ($T_r$) appeared to be important parameters to increase the amount of tin anchored. The initial rate of tin anchoring ($w_0$) strongly depends on the initial Sn$_0$/Rh$_s$ ratios. The results presented in Table 35 show that the hydrogenolysis of the Sn-C bonds in anchored SOMS is almost complete and mostly “naked” Sn atoms anchored onto the Rh are formed in all experiments ($x \geq 3.2$).

The increase of the initial Sn$_0$/Rh$_s$ ratios and temperature of tin anchoring results in broadening of the TPD curve up to 120°C, without showing any further high temperature peaks attributed to the formation of OMSAS (see Figure 64).
Table 35. General data related to modification of RhMg-5.0 catalyst with Sn(C₂H₅)₄

<table>
<thead>
<tr>
<th>No</th>
<th>Tᵣ, °C</th>
<th>[Sn]₀, M</th>
<th>Sn₀/Rhₜ</th>
<th>W₀, x 10⁻⁶</th>
<th>n¹, x 10⁻⁶</th>
<th>n¹, x 10⁻⁶</th>
<th>x</th>
<th>TOF, s⁻¹ x 10⁻⁴</th>
<th>Sn, wt%</th>
<th>Sn/Rh ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.12</td>
<td>5.9</td>
<td>1.4</td>
<td>147</td>
<td>36.2</td>
<td>3.21</td>
<td>1.9</td>
<td>0.54</td>
<td>0.38</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.25</td>
<td>11.8</td>
<td>3.6</td>
<td>294</td>
<td>60.6</td>
<td>3.32</td>
<td>5.0</td>
<td>1.05</td>
<td>0.73</td>
</tr>
<tr>
<td>3</td>
<td>65</td>
<td>0.25</td>
<td>12.1</td>
<td>n.m.</td>
<td>590</td>
<td>124.6</td>
<td>3.30</td>
<td>n.m.</td>
<td>2.12</td>
<td>1.47</td>
</tr>
</tbody>
</table>

¹ Sn content calculated from the overall material balance of tin anchoring; 
² Amount of Sn anchored per surface Rh atom calculated using CO/Rh= 0.25. Catalyst re-reduced in H₂ atmosphere at tᵣₑᵣᵢₜᵢ = 300 °C for 2h; catalyst amount: Wₑᵢᵦᵢ = 3.5 g; atmosphere of step I: H₂; solvent: benzene; duration: 4 h; n.m.: not measured.

Table 36. Chemisorption properties and catalytic activities in CO oxidation of parent Rh/MgO and bimetallic Sn-Rh/MgO catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Sn₀/Rhₜ</th>
<th>Sn, wt%</th>
<th>Sn/Rh</th>
<th>H/Rh ²</th>
<th>CO/Rh ²</th>
<th>T₅₀  °C ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/MgO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24.8</td>
<td>24.75</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>5.9</td>
<td>0.54</td>
<td>0.38</td>
<td>7.54 (9.93)</td>
<td>18.79 (18.99)</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>11.8</td>
<td>1.05</td>
<td>0.73</td>
<td>3.13 (6.01)</td>
<td>16.13 (17.70)</td>
<td>n.m.</td>
</tr>
<tr>
<td>3</td>
<td>12.1</td>
<td>2.12</td>
<td>1.47</td>
<td>2.35 (5.35)</td>
<td>15.34 (13.82)</td>
<td>120</td>
</tr>
</tbody>
</table>

¹ The first number: chemisorption data obtained on (H)-type catalysts; in parentheses: (O)-type catalysts; 
² Activity of (H)-type catalysts in CO oxidation, expressed as the temperature at which 50 % conversion has been obtained (p₃₀= 80 torr, p₃₂= 40.5 torr, heating rate= 5°C min⁻¹, temperature ramp from 25 to 300°C); n.m.: not measured.

Figure 64. The influence of the Sn₀/Rhₜ ratio and the temperature of tin anchoring (Tᵣ) on the decomposition pattern. ( ), Sn₀/Rhₜ=5.89, Tᵣ= 50°C (Sn/Rhₜ= 0.38); ( ), Sn₀/Rhₜ=11.78, Tᵣ= 50°C (Sn/Rhₜ= 0.73); ( ), Sn₀/Rhₜ=12.12, Tᵣ= 65°C (Sn/Rhₜ= 1.47). Catalyst: RhMg-5.0.

Data given in Table 36 show that the introduction of tin onto parent RhMg-5.0 catalyst results in significant decrease in both H₂ and CO chemisorption values. Moreover, (H)-type Sn-Rh catalysts have slightly lower chemisorption values than the catalysts of (O)-type. As emerges from data presented in Table 36, the decrease of hydrogen chemisorption induced by tin is more pronounced than that of the CO. Introduction of small amount of tin has no influence on the activities of (H)-type catalysts in CO oxidation reaction and even slight activity decrease was observed upon using the catalyst with highest Sn/Rh ratio (Sn/Rhₜ= 1.47).

5.10.8. Modification of 1.77 wt% Ru/Al₂O₃ catalyst with SnR₄ (R= CH₃ and C₂H₅) 

The influence of the type of tin precursor compound, Snₐ/Ruₐ ratio and temperature of tin anchoring (Tᵣ) on the amount of tin anchored onto RuAl-1.77 catalyst in hydrogen atmosphere was summarized in Table 37.
Table 37. General data related to modification of RuAl-1.77 catalyst with Sn(CH₃)₄ and Sn(C₂H₅)₄

| No | T_r, °C | SnR₄ | Sn₀/Ruₙ | w₀, x 10⁻⁶ | n_I, x 10⁻⁶ | nᵐ, x 10⁻⁶ | x | TOF, s⁻¹ x 10⁻⁴ | Snₐ, wt% | Sn/Ruₙ  
|----|---------|------|---------|------------|-------------|-------------|---|----------------|--------|--------
| t  | 50      | SnEt₄ | 17.0    | 2.35       | 64.8        | 46.2        | 2.34 | 4.8            | 0.33   | 0.34
| 2  | 50      | SnEt₄ | 34.5    | 2.63       | 115.0       | 76.4        | 2.40 | 5.4            | 0.57   | 0.59
| 3¹ | 50      | SnEt₄ | 36.2    | 2.71       | 117.2       | 78.8        | 2.39 | 5.6            | 0.58   | 0.60
| 4  | 60      | SnEt₄ | 35.2    | 7.56       | 162.0       | 118.3       | 2.31 | 15.5           | 0.83   | 0.86
| 5  | 50      | SnMe₄ | 33.6    | 4.82       | 148.8       | 219.6       | 1.62 | 9.9            | 1.09   | 1.13

|      |        |       |         |            |             |             |     |                |        |        
| a   |        |       |         |            |             |             |     |                |        |        
| b   |        |       |         |            |             |             |     |                |        |        
| c   |        |       |         |            |             |             |     |                |        |        
| d   |        |       |         |            |             |             |     |                |        |        

As shown in Figure 65, both the type of tin precursor compound and Sn₀/Ruₙ ratios have strong influence on the TPD pattern of the SOMS formed. Upon using Sn(CH₃)₄, the intensity of TPD peaks around and above 200°C is relatively high. This fact indicates that the modification of RuAl-1.77 catalyst with Sn(CH₃)₄ leads also to the introduction of small portion of tin onto the support.

As shown in Table 37, the increase of both the initial tin concentration (see Sn₀/Ruₙ ratios in Table 37) and temperature of tin anchoring reaction (T_r) and the use of more reactive tin organic compound (Sn(CH₃)₄) increased the amount of tin anchored. The initial rate of tin anchoring (w₀) strongly depends on the type of tin precursor compound and temperature of tin anchoring (T_r) (see Table 37). The results show also that the value of x strongly depends on the type of tin precursor compound used. Under the same experimental conditions the degree of hydrogenolysis of the Sn-C bonds in anchored -Sn(C₂H₅)₄ₙ₁₋₄ surface species is higher than in the case of -Sn(CH₃)₄ₙ₁₋₄ₙ.

5.10.9. Modification of 5 wt% Ru/Al₂O₃ catalyst with Sn(C₂H₅)₄

Data obtained from the modification of alumina supported Ru catalyst with high metal loading are shown in Table 38.

As emerges from the data in Table 38 the increase of both the re-reduction temperature (t_red) and Sn₀/Ruₙ ratio and even the use of excess of hydrogen in the tin anchoring step I has no significant
influence on the amount of tin anchored at T_red = 50°C. The increase of the temperature of tin anchoring (T_red) and the use of more reactive tin organic compound (Sn(CH₃)₄) can be recommended.

Table 38. General data related to modification of RuAl-5.0 catalyst with Sn(C₂H₅)₃

<table>
<thead>
<tr>
<th>No</th>
<th>t_red, °C</th>
<th>Atm</th>
<th>Sn₀/Ru₀</th>
<th>w₀ x 10⁶</th>
<th>n₁ x 10⁶</th>
<th>n₂ x 10⁴</th>
<th>x</th>
<th>TOF, s⁻¹ x 10⁻⁴</th>
<th>Sn₀ wt%</th>
<th>Sn₀/Ru₀⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>Ar</td>
<td>31.3</td>
<td>0.2</td>
<td>25.0</td>
<td>18.2</td>
<td>58.8</td>
<td>1.19</td>
<td>0.8</td>
<td>0.25</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>Ar</td>
<td>33.7</td>
<td>0.7</td>
<td>17.8</td>
<td>1.6</td>
<td>47.1</td>
<td>1.10</td>
<td>2.9</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>450</td>
<td>Ar</td>
<td>32.3</td>
<td>0.6</td>
<td>18.5</td>
<td>2.5</td>
<td>43.4</td>
<td>1.20</td>
<td>2.6</td>
<td>0.18</td>
</tr>
<tr>
<td>4*</td>
<td>350</td>
<td>H₂</td>
<td>67.3</td>
<td>0.7</td>
<td>38.9</td>
<td>-</td>
<td>31.6</td>
<td>2.21</td>
<td>2.9</td>
<td>0.21</td>
</tr>
</tbody>
</table>

a Sn content calculated from the overall material balance of tin anchoring;
b Amount of Sn anchored per surface Rh atom calculated using H/Ru = 0.08;
c Initial concentration of Sn(C₂H₅)₃ [Sn₀]₀ = 0.25 M.

Catalyst amount: W_cat = 1 g; Duration of re-reduced in H₂ atmosphere: 2 h; [Sn₀]₀: 0.12 M; solvent: benzene; T_red: 50°C; duration of tin anchoring step I (τ_I): 2 h.

After re-reduction of parent catalyst in H₂ atmosphere at t_red = 250°C, ethylene was the major product formed in step I (n₂/C₂H₄ / n₁ = 0.73). The increase of the re-reduction temperature (see experiments 2 and 3 in Table 38) resulted in strong decrease of ethylene formation in step I (n₂/C₂H₄ / n₁ = 0.09 and 0.14, respectively) which was accompanied by simultaneous increase of the initial rate of tin anchoring (w₀). These results demonstrate that the efficiency of re-reduction of ionic form of Ru can be enhanced upon increasing the t_red with a maximum at 350°C (n₂/C₂H₄ / n₁ = 0.09).

Data shows that the presence of excess of hydrogen resulted in an increase of the extent of dealkylation of -Sn(C₂H₅)_₄, this fact is indicated by the increase of both n₁ and x values.

5.10.10. Comparison of anchoring to different metals

The main goal of this study was to find the modes and ways to increase the amount of tin introduced directly onto the parent metal. In this respect the focus was laid on the study of the influence of high initial tin concentration (Sn₀/M₀) on the peculiarities of tin anchoring over different supported catalysts. The key issue was to find proper reaction condition to increase the stoichiometry x of PSC formed.

The summary of the results related to modification of various supported catalysts with Sn(C₂H₅)₃ in the presence of adsorbed hydrogen and excess of hydrogen is given in Figures 66 and 67, respectively. Figure 66A shows that in the presence of adsorbed hydrogen upon increasing of the initial Sn₀/M₀ ratio the rate of tin anchoring decreases in the following order: PtAl > PtSi ≋ PdC ≋ RhAl-4.0 >> RuAl > RhAl-1.0 ≋ RhSi ≋ PdSi. Alumina supported Pt catalysts with the lowest platinum content (PtAl-0.3-B and PtAl-0.35) have the highest rate of anchoring and resulted in high Sn/M₀ ratios (Sn/M₀ around 2.5) as shown in Figure 66A and Figure 66B, respectively.

It is necessary to emphasize that in the presence of adsorbed hydrogen the surface chemistry of tin anchoring over catalysts with the lowest values of TOF (RhAl-1.0, RhSi-1.0, and PdSi-1.7) altered. In this case ethylene was the major reaction product; ethane was formed only in small amount. The formation of high amount of ethylene (or butenes) during tin anchoring over Rh and Pd supported catalysts is known in the literature. It was shown (see Chapter 5.3.1.1) that over reduced Pt catalysts all the tin at the beginning of tin anchoring decreases in the following order: PtAl > PtSi ≋ PdC ≋ RhAl-4.0 >> RuAl > RhAl-1.0 ≋ RhSi ≋ PdSi. Alumina supported Pt catalysts with the lowest platinum content (PtAl-0.3-B and PtAl-0.35) have the highest rate of anchoring and resulted in high Sn/M₀ ratios (Sn/M₀ around 2.5) as shown in Figure 66A and Figure 66B, respectively.

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PtSi > RhAl ≡ RhMg ≡ RhSi ≡ RuAl-1.77 > RuAl-5.0 (PdSi-1.7 catalyst was not shown). As seen from Figure 67B, in the presence of excess of hydrogen silica supported Pt, Pd, Rh and alumina supported RhAl-1.0 catalysts with high amount of tin anchored (Sn/M\textsubscript{s} > 1) were prepared.

**Figure 66.** Summary of the results related to modification of various supported catalysts with tetraethyltin in the presence of adsorbed hydrogen at T\textsubscript{r} = 50\textdegree C. The influence of the initial Sn/M\textsubscript{s} ratio on the (A)- rate of tin anchoring step I (TOF); (B)- amount of Sn anchored per surface metal atom. Catalysts: ( ), PtSi-3.0; ( ), PtAl-0.3-B; ( ), PtAl-0.35; ( ), PtAl-2.7; ( ), PtAl-5.0; ( ), PdSi-1.7; ( ), PdC-5.0; ( ), RhSi-1.0; ( ), RhAl-1.0; ( ), RhAl-4.0; ( ), RuAl-5.0.

**Figure 67.** Summary of the results related to modification of various supported catalysts with tetraethyltin in the presence of excess of hydrogen at T\textsubscript{r} = 50\textdegree C. The influence of the initial Sn/M\textsubscript{s} ratio on the stoichiometry of tin anchoring in the presence and absence of gas-phase hydrogen. As seen from Figure 68B, in the presence of excess of hydrogen the reactivity of anchored SOMS decreased in the following order: PtSi ≡ RhAl ≡ RhMg > PtSi > RhSi > RuAl. In the presence of adsorbed hydrogen (see Figure 68A) the influence of the Sn/M\textsubscript{s} ratio on the stoichiometry of tin anchoring is more complex. The value of x decreases in the following order: PtAl-5.0 ≡ RhAl-4.0 > PdC-5.0 > RhAl-1.0 ≡ PdSi-1.7 > PtAl-2.7 ≡ PtSi-3.0 > RuAl-5.0 ≡ PtAl-0.3-B ≡ PtAl-0.35 ≡ RhSi-1.0. Based on these results it can be concluded that in the presence of adsorbed hydrogen the noble metal content appeared to be the key experimental variables to change the stoichiometry of tin anchoring. As seen from Figure 68A, upon increasing the metal loading the coordinative unsaturation of tin-containing SOMS formed increases.

Consequently, the fate of the PSC formed during step I strongly depends on (i) the type and content of active metal, (ii) the metal dispersion, (iii) the type of the support, (iv) the amount of tin precursor compound anchored, (v) the presence or absence of gas-phase hydrogen.
The results presented in Chapter 5.10 clearly demonstrated that the preparation of bimetallic catalysts with increased tin content by method of CSRs can be extended to other supported Group VIII metals.

The method has been successfully applied for the modification with tin of supported catalysts with extremely high metal loading (40 wt% Pt/C). These bimetallic Sn-Pt/C catalysts display an outstanding performance on the CO and ethanol electrooxidation reactions.

A clear correlation between PtSn phase and the electrocatalytic activity has been established. Catalytic data obtained over supported Sn-Pt/C catalysts are given in Appendix (see Table A-2).

6. Summary

6.1. Conclusions

New aspects of anchoring of tin and germanium organometallic compounds (Sn(CH$_3$)$_4$, Sn(C$_2$H$_5$)$_4$, (CH$_3$)$_3$SnSn(CH$_3$)$_3$, Ge(C$_2$H$_5$)$_4$) onto different SiO$_2$, Al$_2$O$_3$, MgO and active carbon supported metals have been described. Controlled Surface Reactions were used to prepare various types of supported E$_x$-M$_y$ (E= Sn, Ge; M= Pt, Pd, Rh, Ru) catalysts with exclusive formation of metal-metal interaction. In this study the details of anchoring reactions was discussed. The variation of parameters of CSRs allowed the preparation of different supported bi- and multimetallic catalysts with high E/M ratios.

This doctoral thesis was restricted mostly to the preparation of Sn-modified Pt-containing supported catalysts.

- The main goal of this study was to find the modes and ways to increase the amount of tin introduced directly onto the parent metal. It was achieved via formation of multilayered SOMS anchored exclusively onto the supported metal. The key issue is the coordinative unsaturation of Sn-alkyl species in PSC formed.
- Coordinatively unsaturated PSCs were considered as new sites, which can be used to anchor additional amount of tetraalkyl tin, provided that the concentration of tin precursor compound in the reaction mixture is high enough. In excess of hydrogen the extent of coordinative unsaturation can be further increased. Upon using this mode of tin anchoring Sn-Pt/SiO$_2$ catalyst with Sn/Pt ratio 2 was prepared.
- It was shown that other types of new tin anchoring sites were created when both PSC and coordinatively unsaturated PSC were mildly oxidized. The addition of trace amount of oxygen led to the immediate formation of ethylene which indicated that the surface chemistry of tin anchoring was altered. In the presence of added oxygen high Sn/Pt ratios can be reached even at relatively low initial Sn$_0$/Pt$_0$ ratios. Upon using this mode of tin anchoring, Sn-Pt/SiO$_2$ catalysts with highest
Sn/Pt ratio up to 2.9 and exclusive Sn-Pt interaction were prepared. This finding was supported by Mössbauer spectroscopy measurements.

- Reaction conditions favourable for the formation of second- or multilayered tin organic moieties on the active metal were as follows: (i) increased initial concentration of the precursor of modifier; (ii) increased reaction time; (iii) increased reaction temperature \(T_c\); (iv) carrying out anchoring reaction in the presence of excess hydrogen; (v) addition of trace of oxygen during tin anchoring reaction.

- The Temperature Programmed Decomposition profile strongly depended on the Sn/Pt ratios, that is, on the type of anchored SOMS formed. The “fingerprint” character of the TPD curves can also be used for catalyst characterization. The series of deconvoluted TPD curves showed that the concentration of a given surface species reached a certain stationary value, corresponding to the full coverage of the given type of SOMS. In further step the build up of next layer of surface species starts, which requires higher temperature for decomposition. The stepwise appearance of new TPD peaks \((\text{PSC} \rightarrow \text{SSSL} \rightarrow \text{MLSC} \rightarrow \text{OMSAS})\) indicated that the increase of the Sn/Pt ratio led to the build-up of tin containing layers step by step.

- Kinetic results obtained on supported Pt catalysts provided new information about the elementary steps involved in anchoring of tetraethyltin onto platinum. Experimental evidences found on alumina and silica supported catalysts with high and low metal loading indicated that below monolayer coverage of SOMS, and under condition of short reaction time the transformation of SOMS primary formed on supported metal nanoclusters should have consecutive character. This finding was supported by the following experimental evidences: (i) complete change of the TPD pattern of samples, as reaction proceeds; (ii) pronounced time dependence of the formation and decomposition of different surface species; (iii) alteration of the stoichiometry of tin anchoring.

- Decomposition of SOMS in hydrogen resulted in the exclusive formation of supported alloy-type Sn-Pt surface species. As emerges from FTIR data of adsorbed CO and Mössbauer measurements on Sn-Pt/SiO\(_2\) catalyst the platinum nanoclusters were strongly diluted by tin and the most abundant form of tin is Sn-Pt alloy (85-100 %, depending on the Sn/Pt ratio and the mode of preparation).

- The influence of the atmosphere (Ar, H\(_2\) or O\(_2\)) and the type of tin precursor compound used (Sn(CH\(_3\))\(_4\), Sn(C\(_2\)H\(_5\))\(_3\), and (CH\(_3\))\(_2\)Sn-Sn(CH\(_3\))\(_3\)) on the selectivity of tin anchoring over Pt/SiO\(_2\) catalyst was evidenced by Mössbauer spectroscopy. The modification of Pt/SiO\(_2\) catalyst with Sn resulted in at least two types of supported bimetallic nanoclusters, such as the Pt-rich and the Sn-rich alloy phases. Upon using different experimental conditions series of Sn-Pt catalysts with gradual increase of the content of the Sn-rich alloy phase was observed.

- Results of in situ EXAFS spectroscopy indicated that platinum in Sn-Pt/SiO\(_2\) catalyst was exclusively modified with Sn (all tin in Sn\(^\text{II}\) state). The presence of mainly Pt-Sn and small amount of Sn-Sn bonds after reduction at 300°C indicated that the modification of Pt/SiO\(_2\) catalyst was exclusive without any interaction with the support.

- Decomposition of SOMS in oxygen resulted in the formation of Lewis-acid type sites consisting of finely dispersed SnO\(_x\) surface species anchored onto the active metal. In these supported Sn-Pt catalysts the Lewis-acid type active sites, i.e., SnO\(_x\) species, or electron deficient Sn\(^{\delta+}\) entities formed in the atomic closeness of supported platinum nanoclusters, were involved in the creation of "metal ion-metal nano-cluster" ensemble sites. The formation of the above species was evidenced by Mössbauer and FTIR spectroscopy. The atomic closeness of ionic and metallic species provided unusual activity and selectivity to these catalysts in variety of reactions.

- In situ characterization of Sn-Pt/SiO\(_2\) catalyst by EXAFS and Mössbauer spectroscopy showed that tin is easily oxidized and reduced. In reduced catalysts the tin is directly coordinated with Pt, while after oxidation tin is primarily in a form of highly dispersed and reactive SnO\(_2\) over the Sn-Pt nanocluster. Treatment of the oxidized Sn-Pt catalyst at room temperature either with H\(_2\) or CO partially restored the initial alloy phases (in H\(_2\): 67-86%).

- Upon changing conditions of CSRs used for tin anchoring variety of tin containing entities, such as (i) tin enriched platinum, (ii) Sn-Pt alloy phases, (iii) SnO\(_x\) species anchored directly to the Pt surface, (iv) SnO\(_x\) species at the Pt-support interface, (v) SnO\(_x\) species at the support, can be
formed. The formation of the above species was evidenced by chemisorption of CO and H₂, Mössbauer and FTIR spectroscopy.

- Supported Sn-Pt/SiO₂ catalysts prepared by CSRs methods were successfully used in various reactions, such as (i) selective hydrogenation of unsaturated aldehydes to unsaturated alcohols; (ii) citral hydrogenation, (iii) hydrogenation of benzonitrile (iv) hydrogen-assisted 1,2-dichloroethane dechlorination and (v) catalytic test reactions (cyclohexane dehydrogenation and cyclopentane hydrogenolysis).

- Sn-Pt/SiO₂ catalysts prepared by CSRs were highly active in low temperature CO oxidation. The results of Mössbauer spectroscopy showed that the Sn-Pt alloys with different compositions were oxidized and strongly reconstructed. Alloy phases were transformed to Sn⁴⁺ oxide species and Sn-Pt alloys with decreased tin content: PtSn₄ → PtSn₂ → PtSn → Pt₃Sn.

- Peculiarities of the preparation of Sn-Pt/Al₂O₃ catalysts with high Sn/Pt ratios were examined. Modification of Pt/Al₂O₃ catalysts with Sn(C₂H₅)₄ resulted in Sn-Pt bimetallic catalysts in which two forms of tin can be distinguished: (i) tin anchored onto the Pt and (ii) tin anchored onto the Al₂O₃. The formation of tin anchored onto the platinum was exclusive up to Sn/Ptₐ = 1.4.

- The use of a circulation reactor for the modification of alumina supported Pt and Re-Pt catalysts with tetraethyltin was demonstrated. This technical innovation resulted in a scale-up of the modification procedure. The presence of fixed bed catalyst suppressed the crashing of the catalyst during the anchoring process, the use of high rate of circulation eliminated mass and heat transfer related problems and provided better condition for the removal of unreacted tetraethyltin. The perered bi- and multimetallic catalysts were tested both in hydrocarbons transformation and naphtha reforming, resulted in reformate with reduced aromatic and increased iso-paraffin content.

- Sn-Pt/Al₂O₃ catalysts prepared in the circulation reactor were characterized by H₂ and CO chemisorption, Temperature Programmed Reduction and XPS measurements. Results indicated that the extent of reducibility of Sn in Sn-Pt/Al₂O₃ catalysts was high. The formation of Sn-Pt alloy phase and SnO₂ oxides were evidenced. The presence of above active sites favors the catalytic behavior in n-butane dehydrogenation, thus increasing the n-butane conversion and the selectivity to olefins and decreasing the coke deposition. These catalysts were characterized also by test reactions of the metallic phase (cyclohexane dehydrogenation and cyclopentane hydrogenolysis).

- High initial concentration of tetraalkyl tin provided high rates of tin anchoring; however the increase of the concentration of [Sn] had a limit. At high initial concentration of tetraalkyl tin, the latter can interact with the OH groups of support, especially in the case of Al₂O₃. However, it was demonstrated that under properly chosen reaction conditions ([Sn]₀= 0.05 M, T = 40°C) even in the case of Pt/Al₂O₃ catalysts the formation of tin species anchored onto platinum is exclusive up to Sn/Ptₐ = 1.4-1.6.

- Peculiarities of the modification of Pt/C catalyst with Ge(C₂H₅)₄ by CSRs were shown. The goal of this work was to find modes and ways to increase the amount of Ge anchored onto the Pt and maintain the overall control of germanium anchoring, i.e., suppressing the amount of Ge introduced onto the support. It was demonstrated that the surface composition of supported bimetallic catalysts strongly depended on the method of their preparation. By using of CSRs method exclusive formation of alloy-type surface entities up to Ge/Ptₐ = 0.87 at T = 155°C was achieved.

- Upon using CSRs various types of Snₓ-Mₓ (M= Pd, Rh and Ru) catalysts supported on SiO₂, Al₂O₃, MgO and active carbon were prepared with high Sn/M ratios and exclusive formation of metal-metal interaction. Influence of reaction conditions and the type of tin precursor compounds was investigated in details. The obtained results clearly demonstrated that the preparation of bimetallic catalysts by method of CSRs can be extended to other supported Group VIII metals and thus this process can be generally used.

- Application of CSRs for qualitative determination of the efficiency of re-reduction of alumina supported Pt, Rh and Ru catalysts was shown. The influence of both the temperature and duration of re-reduction in H₂ atmosphere on the activity of catalysts in tin anchoring step I was demonstrated. The efficiency of re-reduction of ionic form of Pt, Rh and Ru was increased upon increasing of the f_red. Almost complete reduction of Pt⁶⁺ forms in 5 wt% Pt/Al₂O₃ catalyst was
observed at \( t_{\text{red}} = 400^\circ\text{C} \) (\( n_{\text{C}_2\text{H}_4}/n^\text{I} = 0.04 \)). In the case of 4 wt\% Rh/Al\( _2\)O\( _3 \) catalyst, complete reduction of ionic form of Rh was achieved even at \( t_{\text{red}} = 200^\circ\text{C} \) (\( n_{\text{C}_2\text{H}_4}/n^\text{I} = 0.004 \)). High degree of re-reduction of ionic form of Ru\( ^{5+} \) in a 5 wt\% Ru/Al\( _2\)O\( _3 \) catalyst was obtained at 350\( ^\circ\text{C} \) (\( n_{\text{C}_2\text{H}_4}/n^\text{I} = 0.09 \)).

- The efficiency of re-reduction of ionic form of Pd over 5 wt\% Pd/C catalyst can be increased upon increasing of the \( t_{\text{red}} \). However, reduction temperature used (\( t_{\text{red}} \leq 200^\circ\text{C} \)) was not sufficient for full reduction of highly dispersed palladium (\( n_{\text{C}_2\text{H}_4}/n^\text{I} = 0.4 \)) but after pretreatment at \( t_{\text{red}} = 400^\circ\text{C} \) the catalyst lost its activity.

6.2. New scientific findings

1. In the frame of this study the modes and ways to increase the amount of tin introduced directly onto the parent metal was found. It was achieved via the formation of multilayered SOMS anchored exclusively onto the supported metal. It was proved that the key issue is the coordinative unsaturation of Sn-alkyl species in PSC formed firstly.\(^{215,216,233,241,242}\) Coordinatively unsaturated PSCs were considered as new sites, which are involved in the anchoring of additional amount of tetraalkyl tin, provided that the concentration of tin precursor compound in the reaction mixture is high enough.

2. In the presence of excess hydrogen the extent of coordinative unsaturation can be further increased.\(^{215,215,241,291}\) It was demonstrated that in this case the modification of Pt with Sn was highly selective up to Sn/Pt\(_s\) = 2, namely 100 \% of Sn introduced was anchored to the platinum in the form of Sn-Pt alloy phases.\(^{237}\)

3. It was shown that other types of new tin anchoring sites were created when both PSC and coordinatively unsaturated PSCs were mildly oxidized. Upon using this mode of tin anchoring, Sn-Pt/SiO\(_2\) catalysts with Sn/Pt\(_s\) ratio up to 2.9 and almost exclusive Sn-Pt interaction were prepared.\(^{215,216,241}\) It was evidenced that the platinum nanoclusters were strongly diluted by tin and the most abundant form is Sn-Pt alloy (85-100 \%, depending on the Sn/Pt\(_s\) ratio).\(^{241,259}\)

4. It was concluded that reaction conditions favourable for the formation of second- or multilayered tin organic moieties on the active metal were as follows: (i) increased initial concentration of the precursor of modifier; (ii) increased reaction time; (iii) increased reaction temperature (\( T_r \)); (iv) carrying out anchoring reaction in the presence of excess hydrogen; (v) addition of trace amount of oxygen during anchoring reaction.\(^{215,216,218,222,233,241,259,266,287,291}\)

5. The Temperature Programmed Decomposition profile strongly depended from the Sn/Pt\(_s\) ratios and on the type of anchored SOMS formed. The “fingerprint” character of the TPD curves can also be used for catalyst characterization.\(^{215,216,218,220,222,253,242,243}\)

6. Kinetic results obtained on supported Pt catalysts provided new information about the elementary steps involved in anchoring of tetraethylin onto platinum.\(^{220}\)

7. Decomposition of SOMS in oxygen resulted in the formation of Lewis-acid type active sites in the atomic closeness of supported platinum nanoclusters. It was demonstrated that the formation of “metal ion-metal nano-cluster” ensemble sites provided unusual activity and selectivity to these Sn-Pt catalysts in variety of reactions.\(^{217,218,232,233,237,242,258}\)

8. Upon changing conditions of CSRs a variety of tin-containing entities, such as (i) platinum enriched in tin, (ii) Sn-Pt alloy phases, (iii) SnO\(_x\) species anchored directly to the Pt surface, (iv) SnO\(_x\) species at the Pt-support interface, (v) SnO\(_x\) species at the support, can be formed. The formation of the above species was evidenced by chemisorption of CO and H\(_2\), TPR, XPS, FTIR, Mössbauer and EXAFS spectroscopy.\(^{217,231,237,242,243,258,259,291}\)

9. Based on CSRs a new method was developed for the preparation of different types of supported E\(_x\)-M\(_y\) (E= Sn, Ge; M= Pt, Pd, Rh, Ru) catalysts with exclusive formation of metal-metal interaction and high E/M ratios.\(^{215,222,233,242,259,281}\) The obtained results clearly demonstrated that the preparation of bimetallic catalysts by method of CSRs could be extended to other supported Group VIII metals and thus this process could be generally used. Catalysts prepared in this way showed unique properties in variety of reactions.
10. CSRs can be applied for qualitative determination of the efficiency of re-reduction of alumina supported Pt, Pd, Rh and Ru catalysts.215,221

7. Abbreviations used

\( W_{\text{cat}} \): Amount of catalyst before pretreatment (g); 
\( t_{\text{red}} \): Temperature of the re-reduction of the parent catalyst in \( \text{H}_2 \) atmosphere prior to tin anchoring reaction (°C); 
\( \tau_{\text{red}} \): Duration of the re-reduction of the parent catalyst in \( \text{H}_2 \) atmosphere prior to tin anchoring step I (h); 
\( [\text{Sn}]_0 \): Initial concentration of the tin precursor compound \( \text{SnR}_4 \) (R= CH\(_3\), C\(_2\)H\(_5\)) (M); 
\( \text{Sn}_0/\text{M} \): Initial ratio of Sn introduced per surface atom of active metal; 
\( T_r \): Temperature of tin anchoring step I (°C); 
\( \text{Atm} \): Atmosphere of tin anchoring step I; 
\( \tau_r \): Duration of tin anchoring step I (h); 
\( w_0 \): Initial rate of tin anchoring in step I, calculated from the kinetic curves of ethane formation (mol \( g_{\text{cat}}^{-1} \times \text{min}^{-1} \)); 
\( n^I \): Total amount of hydrocarbons formed in step I (mol \( g_{\text{cat}}^{-1} \)); 
\( n^I_{\text{C}_2\text{H}_4} \): Amount of ethylene formed in step I (mol \( g_{\text{cat}}^{-1} \)); 
\( n^I_{\text{II}} \): Total amount of hydrocarbons formed in step II (mol \( g_{\text{cat}}^{-1} \)); 
\( n^I_{\text{C}_2\text{H}_4} \): Amount of ethylene formed in step II (mol \( g_{\text{cat}}^{-1} \)); 
\( x \): The stoichiometry of tin anchoring reaction I, i.e., the value of \( x = 4n^I/(n^I + n^I_{\text{II}}) \); 
\( \text{TOF} \): Turnover frequency, rates related to the number of active metal surface atoms (s\(^{-1}\)); 
\( \text{Sn/ML} \): Amount of Sn anchored per surface atom of active metal.

Surface species:

CUPSC: Coordinatively Unsaturated Primary Surface Complexes
MIMNES: “Metal ion-metal nanocluster ensemble sites”
MLSC: Multilayered Surface Complex
MLSOC: Oxygen-Containing Multilayer Species
MLSC (II): Multilayered Surface Complex formed after instantaneous decomposition of MLSOC
OMSAS: Organometallic Species Anchored to the Support
OSOC: Oxidized Surface Organometallic Complex
PSC: Primary Surface Complex
SOMS: Surface Organometallic Species
SSS: Stabilized Surface Species
SSSL: Surface Species in the Second Layer

Catalyst types:
(H)-type: SOMS decomposed in a \( \text{H}_2 \) atmosphere
(O)-type: SOMS decomposed in a \( \text{O}_2 \) atmosphere

Techniques:
CSRs: Controlled Surface Reactions
CVD: chemical-vapour-deposition
NSD: Non-Selective Deposition
SD: Selective Deposition
SMAD: Solvated Metal Atom Dispersion
SOMC/M: Surface Organometallic Chemistry on Metals
TPD: Temperature Programmed Decomposition
8. References


### Table A-1: Use of different supported bimetallic E-Pt (E= Sn, Ge) catalysts prepared by CSRs in various reactions. Selected results I.

<table>
<thead>
<tr>
<th>Catalytic reaction</th>
<th>Reaction conditions</th>
<th>Catalysts (E/Pt)</th>
<th>Activity &amp; Selectivity</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>Gas-phase hydrogenation of crotonaldehyde to crotylalcohol (UOL)</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 60°C, 80°C; W&lt;sub&gt;catal&lt;/sub&gt; = 0.04-0.08 g; [C]&lt;sub&gt;r&lt;/sub&gt; = 0.64 mmol dm&lt;sup&gt;3&lt;/sup&gt;; P = 0.1 MPa; Sn/Pt = 0.38-2.9</td>
<td>PtSi-3.0-A (0); Sn-PtSi-3.0-A (1.4); Sn-PtSi-3.0-A (2.5); Sn-PtSi-3.0-A (5)</td>
<td>W&lt;sub&gt;cat&lt;/sub&gt; = 0.5 x 10&lt;sup&gt;3&lt;/sup&gt; (60°C); S&lt;sub&gt;UOL&lt;/sub&gt; = 0 (C= 5 %)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>216, 259, 244, 265</td>
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<td>Liquid-phase hydrogenation of crotonaldehyde to crotylalcohol (UOL)</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 40°C; W&lt;sub&gt;catal&lt;/sub&gt; = 0.05 g; [C]&lt;sub&gt;r&lt;/sub&gt; = 120 mmol g&lt;sub&gt;catal&lt;/sub&gt;&lt;sup&gt;-1&lt;/sup&gt;; P = 0.4 MPa; Sn/Pt = 0.22-1.61</td>
<td>PtSi-3.0-A (0)</td>
<td>W&lt;sub&gt;cat&lt;/sub&gt; = 2.9 x 10&lt;sup&gt;3&lt;/sup&gt;; S&lt;sub&gt;UOL&lt;/sub&gt; = 6 (C= 10 %)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>240</td>
</tr>
<tr>
<td>Liquid-phase hydrogenation of cinnamaldehyde to cinnamyl alcohol (UOL)</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 60°C; W&lt;sub&gt;catal&lt;/sub&gt; = 0.05 g; [C]&lt;sub&gt;r&lt;/sub&gt; = 120 mmol g&lt;sub&gt;catal&lt;/sub&gt;&lt;sup&gt;-1&lt;/sup&gt;; P = 0.35-4 MPa; Sn/Pt = 0.4-2.4</td>
<td>PtSi-3.0-A (0); Sn-PtSi-3.0-A (0.4); Sn-PtSi-3.0-A (1.6)</td>
<td>W&lt;sub&gt;cat&lt;/sub&gt; = 2.2; W&lt;sub&gt;cat&lt;/sub&gt; = 1.1; S&lt;sub&gt;UOL&lt;/sub&gt; = 58 (C= 10 %)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>216</td>
</tr>
<tr>
<td>Liquid-phase hydrogenation of citral to nerol and geraniol (UOL)</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 70°C; W&lt;sub&gt;catal&lt;/sub&gt; = 0.3 g; [C]&lt;sub&gt;r&lt;/sub&gt; = 0.3 ml; P = 0.1 MPa; Sn/Pt = 0.13-1.02 Ge/Pt = 0.15-1.24</td>
<td>PtSi-0.45 (0)</td>
<td>C&lt;sub&gt;cat&lt;/sub&gt; = 88 %; S&lt;sub&gt;cat&lt;/sub&gt; = 0 (at 10 h)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>241</td>
</tr>
<tr>
<td>Liquid-phase hydrogenation of benzonitrile to dibenzylamine (DBA)</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 60°C; W&lt;sub&gt;catal&lt;/sub&gt; = 0.25 g; [C]&lt;sub&gt;r&lt;/sub&gt; = 9.7 mmol; P = 0.4 MPa; Sn/Pt = 0.03-0.35</td>
<td>PtSi-3.0-A (0); Sn-PtSi-3.0-A (0.04)&lt;sup&gt;c&lt;/sup&gt;; Sn-PtSi-3.0-A (0.14)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>TOF = 8.6 x 10&lt;sup&gt;3&lt;/sup&gt;; S&lt;sub&gt;DBA&lt;/sub&gt; = 77&lt;sup&gt;f&lt;/sup&gt;</td>
<td>267</td>
</tr>
<tr>
<td>Hydrogen-assisted 1,2-dichloroethane dechlorination</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 200°C; W&lt;sub&gt;catal&lt;/sub&gt; = 0.15 g; [CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;] = (3700 ppm) + H&lt;sub&gt;2&lt;/sub&gt; (36,800 ppm) + HCl; ϑ&lt;sub&gt;ini&lt;/sub&gt; = 16 cm&lt;sup&gt;3&lt;/sup&gt; min&lt;sup&gt;-1&lt;/sup&gt;; Sn/Pt = 0.36-1.96</td>
<td>PtSi-0.50 (0); Sn-PtSi-0.44 (1.96)&lt;sup&gt;c&lt;/sup&gt;; Sn-PtSi-0.44 (1.96)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>TOF = 4.0 x 10&lt;sup&gt;3&lt;/sup&gt;; S&lt;sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;&lt;sup&gt;ini&lt;/sup&gt; = 0; S&lt;sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;&lt;sup&gt;ss&lt;/sup&gt; = 0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>266</td>
</tr>
</tbody>
</table>

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<sup>a</sup> W<sub>cat</sub>, initial rate, measured from the conversion-contact time dependencies and extrapolated to zero conversion (mol g<sub>catal</sub><sup>-1</sup> s<sup>-1</sup>); S<sub>UOL</sub>, selectivity of unsaturated alcohol measured at C % conversion (%);

<sup>b</sup> W<sub>cat</sub> and W<sub>UOL</sub>, overall initial rate and initial rate of UOL formation, respectively (μmol g<sub>catal</sub><sup>-1</sup> s<sup>-1</sup>); S<sub>UOL</sub>, selectivity of unsaturated alcohol measured at 10 % conversion (%);

<sup>c</sup> Sn/Pt (at/Jat.), amount of Sn anchored related to total amount of platinum;

<sup>d</sup> C<sub>cat</sub>, conversion (%); S<sub>UOL</sub>, selectivity of unsaturated alcohol measured at 10 and 1 h reaction time, respectively (%);

<sup>e</sup> TOF, the turnover frequency values were calculated using initial reaction rate values and the amount of surface Pt atoms determined by H<sub>2</sub> chemisorption (s<sup>-1</sup>); S<sub>DBA</sub>, selectivity of dibenzylamine (%);

<sup>f</sup> Catalyst prepared by co-impregnation;

<sup>g</sup> TOF, the steady-state turnover frequency (s<sup>-1</sup>); S<sub>CH<sub>2</sub>Cl<sub>2</sub></sub><sup>ini</sup> and S<sub>CH<sub>2</sub>Cl<sub>2</sub></sub><sup>ss</sup>, initial selectivity (measured after 0.7 h of time on stream) and steady-state selectivity, respectively (mol %).
<table>
<thead>
<tr>
<th>Catalytic reaction</th>
<th>Reaction conditions</th>
<th>Catalysts (E/Pl.)</th>
<th>Activity &amp; Selectivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reforming of n-hexane</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 510°C; W&lt;sub&gt;ar&lt;/sub&gt; = 0.3 g; P&lt;sub&gt;total&lt;/sub&gt; = 0.1 MPa; P&lt;sub&gt;H&lt;/sub&gt; = 0.7 kPa</td>
<td>Pt-Al-0.3-A (0)</td>
<td>W&lt;sub&gt;ar&lt;/sub&gt; = 0.109; S&lt;sub&gt;Al&lt;/sub&gt; = 50.3; S&lt;sub&gt;Al-C&lt;/sub&gt; = 30.5 (C= 60%)&lt;sup&gt;a&lt;/sup&gt; W&lt;sub&gt;ar&lt;/sub&gt; = 0.075; S&lt;sub&gt;Al&lt;/sub&gt; = 37.5; S&lt;sub&gt;Al-C&lt;/sub&gt; = 42.8 (C= 60%)&lt;sup&gt;a&lt;/sup&gt; W&lt;sub&gt;ar&lt;/sub&gt; = 0.042; S&lt;sub&gt;Al&lt;/sub&gt; = 30.2; S&lt;sub&gt;Al-C&lt;/sub&gt; = 50.7 (C= 60%)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>232</td>
</tr>
<tr>
<td>Reforming of n-octane</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 510°C; W&lt;sub&gt;ar&lt;/sub&gt; = 2.0 g; H&lt;sub&gt;2&lt;/sub&gt;/C&lt;sub&gt;8H&lt;/sub&gt; = 2.2 mol mol&lt;sup&gt;-1&lt;/sup&gt;; P&lt;sub&gt;H&lt;/sub&gt; = 1 MPa; LHSV = 3.3 g g&lt;sup&gt;-1&lt;/sup&gt; h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Pt-Al-0.3-A (0)</td>
<td>C&lt;sub&gt;b&lt;/sub&gt; = 82.7; S&lt;sub&gt;b&lt;/sub&gt; = 49.0; S&lt;sub&gt;Al-C&lt;/sub&gt; = 45.6&lt;sup&gt;a&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 82.6; S&lt;sub&gt;b&lt;/sub&gt; = 31.6; S&lt;sub&gt;Al-C&lt;/sub&gt; = 62.9&lt;sup&gt;a&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 78.2; S&lt;sub&gt;b&lt;/sub&gt; = 25.5; S&lt;sub&gt;Al-C&lt;/sub&gt; = 67.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>242</td>
</tr>
<tr>
<td>Reforming of n-octane</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 480°C; W&lt;sub&gt;ar&lt;/sub&gt; = 2.85 g; H&lt;sub&gt;2&lt;/sub&gt;/C&lt;sub&gt;8H&lt;/sub&gt; = 4.5 mol mol&lt;sup&gt;-1&lt;/sup&gt;; P&lt;sub&gt;H&lt;/sub&gt; = 1 MPa; LHSV = 3.3 g g&lt;sup&gt;-1&lt;/sup&gt; h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>RePt-Al-0.17 (0)</td>
<td>C&lt;sub&gt;b&lt;/sub&gt; = 90.7; S&lt;sub&gt;b&lt;/sub&gt; = 39.3; B&lt;sub&gt;b&lt;/sub&gt; = 0.49; RON = 86.6&lt;sup&gt;a&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 81.4; S&lt;sub&gt;b&lt;/sub&gt; = 17.8; B&lt;sub&gt;b&lt;/sub&gt; = 0.14; RON = 79.8&lt;sup&gt;a&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 92.1; S&lt;sub&gt;b&lt;/sub&gt; = 46.1; B&lt;sub&gt;b&lt;/sub&gt; = 0.50; RON = 89.2&lt;sup&gt;a&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 84.2; S&lt;sub&gt;b&lt;/sub&gt; = 26.7; B&lt;sub&gt;b&lt;/sub&gt; = 0.22; RON = 82.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>275</td>
</tr>
<tr>
<td>Dehydrogenation of n-butane</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 530°C; W&lt;sub&gt;ar&lt;/sub&gt; = 0.2 g; H&lt;sub&gt;2&lt;/sub&gt;/C&lt;sub&gt;4H&lt;/sub&gt; = 1.25 mol mol&lt;sup&gt;-1&lt;/sup&gt;; t&lt;sub&gt;iso&lt;/sub&gt; = 18 cm&lt;sup&gt;3&lt;/sup&gt; min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Pt-Al-0.3-A (0)</td>
<td>C&lt;sub&gt;b&lt;/sub&gt; = 22; S&lt;sub&gt;b&lt;/sub&gt; = 73 (at 10 min)&lt;sup&gt;f&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 31; S&lt;sub&gt;b&lt;/sub&gt; = 84 (at 10 min)&lt;sup&gt;f&lt;/sup&gt; C&lt;sub&gt;b&lt;/sub&gt; = 25; S&lt;sub&gt;b&lt;/sub&gt; = 88 (at 10 min)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>218</td>
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<tr>
<td>Test reactions: dehydrogenation of cyclohexene (CHD) and hydrogenolysis of cyclopentane (CPH)</td>
<td></td>
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<td>Differential flow reactor; C&lt;sub&gt;CHD&lt;/sub&gt; &lt; 5 %; C&lt;sub&gt;CPH&lt;/sub&gt; &lt; 7 %; T&lt;sub&gt;CHD&lt;/sub&gt; = 250-350°C; H&lt;sub&gt;2&lt;/sub&gt;/C&lt;sub&gt;6H&lt;/sub&gt; = 26 mol mol&lt;sup&gt;-1&lt;/sup&gt;; T&lt;sub&gt;CPH&lt;/sub&gt; = 350-500°C; H&lt;sub&gt;2&lt;/sub&gt;/C&lt;sub&gt;5H&lt;/sub&gt; = 29 mol mol&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Pt-Al-0.3-A (0)</td>
<td>W&lt;sup&gt;CHD&lt;/sup&gt; = 123; E&lt;sub&gt;CHD&lt;/sub&gt; = 17; W&lt;sup&gt;CPH&lt;/sup&gt; = 49&lt;sup&gt;f&lt;/sup&gt; W&lt;sup&gt;CHD&lt;/sup&gt; = 22; E&lt;sub&gt;CHD&lt;/sub&gt; = 25; W&lt;sup&gt;CPH&lt;/sup&gt; = 1.8&lt;sup&gt;f&lt;/sup&gt; W&lt;sup&gt;CHD&lt;/sup&gt; = 6; E&lt;sub&gt;CHD&lt;/sub&gt; = 27; W&lt;sup&gt;CPH&lt;/sup&gt; = 0.7&lt;sup&gt;f&lt;/sup&gt;</td>
<td>218</td>
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<td>Low temperature CO oxidation</td>
<td>T&lt;sub&gt;r&lt;/sub&gt;; from -30 to 300°C; dT/dt = 5°C min&lt;sup&gt;-1&lt;/sup&gt;; W&lt;sub&gt;ar&lt;/sub&gt; = 0.15 g; P&lt;sub&gt;CO&lt;/sub&gt; = 5.3 kPa; P&lt;sub&gt;GO&lt;/sub&gt; = 1.2-10.5 kPa; LHSV = 30000 ml g&lt;sup&gt;-1&lt;/sup&gt;h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>PtSi-3.0-A (0)</td>
<td>T&lt;sub&gt;CO&lt;/sub&gt; = 177 (P&lt;sub&gt;CO&lt;/sub&gt; = 10.5 kPa); C&lt;sub&gt;b&lt;/sub&gt; = 0 (at -30°C)&lt;sup&gt;c&lt;/sup&gt; T&lt;sub&gt;CO&lt;/sub&gt; = 69 (P&lt;sub&gt;CO&lt;/sub&gt; = 10.5 kPa); C&lt;sub&gt;b&lt;/sub&gt; = 0 (at -30°C)&lt;sup&gt;c&lt;/sup&gt; T&lt;sub&gt;CO&lt;/sub&gt; = 117 (P&lt;sub&gt;CO&lt;/sub&gt; = 10.5 kPa); C&lt;sub&gt;b&lt;/sub&gt; = 0 (at -30°C)&lt;sup&gt;c&lt;/sup&gt; T&lt;sub&gt;CO&lt;/sub&gt; = 65 (P&lt;sub&gt;CO&lt;/sub&gt; = 1.9 kPa); C&lt;sub&gt;b&lt;/sub&gt; = 0 (at -30°C)&lt;sup&gt;c&lt;/sup&gt; T&lt;sub&gt;CO&lt;/sub&gt; = 27 (P&lt;sub&gt;CO&lt;/sub&gt; = 2.1 kPa); C&lt;sub&gt;b&lt;/sub&gt; = 0 (at -30°C)&lt;sup&gt;c&lt;/sup&gt; T&lt;sub&gt;CO&lt;/sub&gt; = 18 (P&lt;sub&gt;CO&lt;/sub&gt; = 2.1 kPa); C&lt;sub&gt;b&lt;/sub&gt; = 0 (at -30°C)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>216</td>
</tr>
<tr>
<td>CO and ethanol electrooxidation</td>
<td>T&lt;sub&gt;r&lt;/sub&gt; = 25°C; 10 mV/s; 0.5 M EtOH; 0.5 M HClO&lt;sub&gt;4&lt;/sub&gt;; Pt= 194 g cm&lt;sup&gt;-2&lt;/sup&gt;; Sn/Pt= 0.08-0.25</td>
<td>PtC-40 (0)</td>
<td>E&lt;sub&gt;CO,one&lt;/sub&gt; = 620; E&lt;sub&gt;EtOH,one&lt;/sub&gt; = 310&lt;sup&gt;f&lt;/sup&gt; E&lt;sub&gt;CO,one&lt;/sub&gt; = 600; E&lt;sub&gt;EtOH,one&lt;/sub&gt; = 160&lt;sup&gt;f&lt;/sup&gt; E&lt;sub&gt;CO,one&lt;/sub&gt; = 220; E&lt;sub&gt;EtOH,one&lt;/sub&gt; = 120&lt;sup&gt;f&lt;/sup&gt; E&lt;sub&gt;CO,one&lt;/sub&gt; = 210; E&lt;sub&gt;EtOH,one&lt;/sub&gt; = 100&lt;sup&gt;f&lt;/sup&gt;</td>
<td>291</td>
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</table>

* W<sub>B</sub>, initial rate (mol g<sup>-1</sup>cat<sup>-1</sup> s<sup>-1</sup>); S<sub>Al</sub> and S<sub>Al-C</sub>, selectivity of benzene and iso-C<sub>6</sub> hydrocarbons (2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane), respectively (%); C, conversion (%);
* S<sub>EA</sub> and S<sub>EA-C</sub>, selectivity of total aromatics and C<sub>6</sub> iso-paraffins and naphthenes, respectively (%);
* Sn/Pl (at/ct.), amount of Sn anchored related to total amount of platinum;
* C, conversion based on feed (%); Σ<sub>A</sub> and Σ<sub>B</sub>, concentration of aromatic hydrocarbons and benzene in liquid products, respectively (%); RON, Research Octane Number;
* S<sub>CO</sub>, the initial conversion (%); S<sub>Bunetene</sub> selectivity to all butenes at 10 min reaction time (%);
* W<sup>CHD</sup> and E<sub>CHD</sub>, initial reaction rate (mol g<sup>-1</sup>cat<sup>-1</sup> h<sup>-1</sup>) and activation energies (kcal mol<sup>-1</sup>) of the CHD; W<sup>CPH</sup>, initial reaction rate of the CPH (mol g<sup>-1</sup>cat<sup>-1</sup> h<sup>-1</sup>);
* W<sup>CHD</sup>, reaction rate in the CHD (mol g<sup>-1</sup>cat<sup>-1</sup> h<sup>-1</sup>) (W<sup>CHD</sup> = C/W<sub>CHD</sub>), where C, CH conversion, W, Pt weight in the sample, F<sub>CHD</sub>, molar CH<sub>D</sub> flow); C<sub>CPH</sub>, initial conversion in the CPH calculated by extrapolation to t = 0 min (%); ΔC<sub>CPH</sub>, deactivation parameter in the CPH (ΔC<sub>CPH</sub> = (C<sub>CPH</sub> - C<sub>CPH</sub>)/C<sub>CPH</sub>), where C<sub>CPH</sub> and C<sub>CPH</sub> are the conversion at t = 0 and 120 min (%);
* S<sub>EA</sub>, S<sub>Al</sub> and S<sub>Al-C</sub>, selectivity of total aromatics, benzene and isomers (including multi-branched isomers), respectively (%);
* T<sub>CO</sub>, the temperature at which 50% CO conversion has been achieved (°C);
* E<sub>CO,one</sub> and E<sub>EtOH,one</sub>, the onset potential for the CO and ethanol electrooxidation, respectively (mV).
Acknowledgement

The writing of the dissertation has been one of the most significant academic challenges I have ever had to face. Without the support, patience and guidance of the following people this dissertation would not have been completed.

My deepest gratitude is to my advisor, Professor Jozsef Margitfalvi for his valuable instructions, for inspiring me not only to grow as an experimentalist, but also to turn into an independent thinker. I am also very obliged to him for introducing me to the fascinating area of Surface Organometallic Chemistry.

I am grateful to Sándor Gőbölös for his theoretical and practical advices. I am also thankful to him for reading my report; commenting on my views and helping me understand and enrich my ideas.

I take this opportunity to express my deep sense of gratitude to Emília Tálas without her continuous inspiration, support and guidance the thesis could not be completed.

Special thanks are due to my colleagues Ferenc Somodi for his assistance and guidance.

Very special thanks to my colleagues, Mihály Hegedűs, András Tompos, Károly Lázár, Attila Vértes, György Vankó, József Valyon, Ágnes Szegedi, Ferenc Lónyi for the measurements in catalyst characterization and for their help in the evaluation of results.

I am pleased to thank all of the members of the former Department of Organic Catalysis, Millián Lászlóné, Katalin Bojtás, Ildikó Turi, Ernő Tfirst and Sándor Kristyán for their help in my every day work.

I am thankful to all my friends and colleagues from the Boreskov Institute of Catalysis and Institute of Hydrocarbon Processing in Russia.

Finally, and most importantly, none of this would have been possible without the love and patience of my parents and my extended family. I would like to thank my husband Pál Borbáth. His support, encouragement in the past twelve years of my life allowed me to be as ambitious as I wanted.

Whatever I am and whatever I intend to be in future is because of the goodwill and unstinted support that I have received from my family and from my colleagues, their kind cooperation helped me in pursuing the Ph. D. study and no words are enough to acknowledge them.
**Affirmation**

This is to confirm I prepared the doctoral thesis at hand myself and I have cited correctly all publications consulted.

This doctoral thesis has never been submitted in the present form or similar to any board of examiners.

Budapest, September 2010

Irina Borbáth

**NYILATKOZAT**

Alulírott Borbáth Irina kijelentem, hogy ezt a doktori értekezést magam készítettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egyértelműen, a forrás megadásával megjelöltem.

Budapest, 2010 szeptember 3

Borbáth Irina