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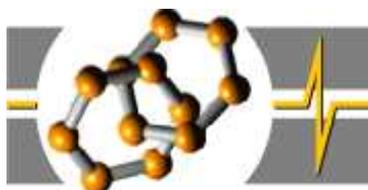
Budapest University of Technology and Economics

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

PhD thesis

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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 maintained its time-on-stream activity for a period of a year or even longer have obtained great scientific and industrial interest.^{1,2}

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. 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 the surface reactions involved in the formation of bimetallic surface entities and (ii) how to create an intimate contact between the two metals?

In supported bimetallic 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).^{2,3,4,5}

2. State of art

Several methods have been developed to modify the surface composition and structure of supported bimetallic catalysts. In case of supported metal catalysts, most frequently the main goal is to modify selectively either the active phase or the support.

There are two general methods to obtain supported bimetallic catalysts: *conventional* and *non-conventional modification*. The conventional modification methods include co-impregnation, consecutive impregnation, co-adsorption, sequential adsorption, ion exchange, deposition-precipitation, co-precipitation. In conventional preparation techniques the formation of bimetallic surface species takes place during the high temperature decomposition of the preadsorbed precursors of both metals in reductive or oxidative atmospheres. These preparation methods are not always the most efficient to create small particles with intimate metal-metal contact. Despite the widespread use, in conventional preparation techniques our knowledge about surface reactions involved in the formation of supported bimetallic entities is limited.

It is, therefore, desirable to apply non-conventional methods like anchoring-type Controlled Surface Reactions (CSRs), sol-gel techniques, pulse laser deposition, solvated metal atom dispersion method, deposition of heterobinuclear complexes or clusters for the preparation of supported bimetallic catalysts. Two types of non-conventional methods using anchoring-type CSRs, i.e. electrochemical and organometallic approaches, are known for the preparation of supported bimetallic catalysts with direct metal-metal interaction.

According to the recommendations of IUPAC, “deposition involving the formation of a strong bond (for example, a covalent) between the support and the active element is usually described as grafting or anchoring. This is achieved through a chemical reaction between

¹ J.H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts, and Applications*, Wiley, New York, 1983.

² B.H. Davis, in: M. E. Davis, S. L. Suib (Eds.), *Selectivity in Catalysis*, ACS Symposium Series 517, American Chemical Society, Washington, DC, 1993, pp. 109-126.

³ J. Margitfalvi, S. Szabó, F. Nagy, in: L. Cerveny (Ed.), *Catalytic Hydrogenation*, Stud. Surf. Sci. Catal., Vol. 27, Elsevier, Amsterdam, 1986, pp. 373.

⁴ B. Coq, A. Goursot, T. Tazi, F. Figueras, D.R. Salahub, *J. Am. Chem. Soc.* 113 (1991) 1485-1492.

⁵ O.S. Alexeev, B.C. Gates, *Ind. Eng. Chem. Res.* 42 (2003) 1571-1587.

functional groups (for example, hydroxyl groups) on the surface of the support and an appropriately selected inorganic or organometallic compound of the active element".⁶

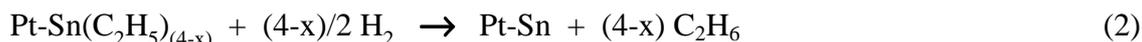
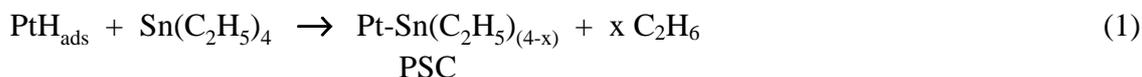
Theoretically, *the amount of anchored surface entities chemically bonded to the support cannot exceed the monolayer coverage; however, multilayers can be obtained by several cycles of anchoring-hydrolysis or anchoring-deposition reaction.*⁶

In addition, because of the strong chemical interaction established via 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 either nanosized metal particles or atomically dispersed ionic surface entities.

In 1984, Margitfalvi,⁷ Travers⁸ and Nuzzo⁹ 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 cluster of Pt, Rh or Ni, respectively.

The monometallic catalyst is first prepared, giving a well-defined metallic nanoparticle, which is then allowed to react with an organometallic molecule, namely the precursor of the second metal, resulting in a bimetallic catalyst. During the anchoring step the organometallic precursors decompose only partly on the metal particle and Surface Organometallic Species (SOMS) stabilized on the surface of the metal are formed. Characteristic feature of different organometallic approaches used (CSRs,^{3,7,10,11} Surface Organometallic Chemistry on Metals (SOMC/M)^{4,12,13,14,15} and chemical vapour deposition¹⁶) result in supported bimetallic entities with modifier- active metal interaction almost exclusively.

As described in first publication of Margitfalvi *et al.*,⁷ the hydrogen adsorbed on noble and transition metals is used as a driving force to control the selectivity of surface anchoring reactions involved in the two steps method. The two main steps are as follows: (i) tin anchoring (step I), and (ii) decomposition of tin- containing SOMS formed in hydrogen or oxygen atmosphere (step II). The basic surface chemistry involved in the modification of monometallic supported Pt catalysts with Sn(C₂H₅)₄ can be written as follows:



CSRs between Sn(C₂H₅)₄ and hydrogen adsorbed on supported platinum resulted in direct Sn-Pt interaction that was maintained upon decomposition of the Primary Surface Complex (PSC) in a hydrogen atmosphere (see reactions (1) and (2)).¹⁷ The net result is the formation

⁶ C. Louis, M. Che, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 1, Wiley-VCH, Weinheim, 1997, pp. 207-216.

⁷ J. Margitfalvi, M. Hegedüs, S. Göbölös, E. Kern-Tálas, P. Szedlacssek, S. Szabó, F. Nagy, in: Proc. 8th Int. Congress on Catalysis, Vol. 4, Berlin (West), 2-6 July 1984, pp. 903-912.

⁸ Ch. Travers, J.P. Bournonville, and G. Martino, in: Proc. 8th Int. Congress on Catalysis, Vol. 4, Berlin (West), 2-6 July 1984, pp. 891-902.

⁹ R.G. Nuzzo, L.H. Dubois, N.E. Bowles, M.A. Trecocke, J. Catal. 85 (1984) 267-271.

¹⁰ J.L. Margitfalvi, E. Tálas, S. Göbölös, Catal. Today 6 (1989) 73-80.

¹¹ J.L. Margitfalvi, H.P. Jalett, E. Tálas, A. Baiker, H.U. Blaser, Catal. Lett. 10 (1991) 325-334.

¹² J.P. Candy, B. Didillon, E.L. Smith, T.B. Shay, J.M. Basset, J. Mol. Catal. 86 (1994) 179-204.

¹³ V. Vetere, M.B. Faraoni, G.F. Santori, J. Podestá, M.L. Casella, O.A. Ferretti, J. Catal., 226 (2004) 457-461.

¹⁴ L. Pirault-Roy, D. Teschner, Z. Paál, M. Guérin, Appl. Catal. A: General 245 (2003) 15-31.

¹⁵ V.D. Stytsenko, Appl. Catal. 126 (1995) 1-26.

¹⁶ T. Inoue, K. Tomishige, Y. Iwasawa, J. Chem. Soc., Faraday Trans. 92(3) (1996) 461.

¹⁷ Cs. Vértés, E. Tálas, I. Czakó-Nagy, J. Ryczkovski, S. Göbölös, A. Vértés, J. Margitfalvi, Appl. Catal. 68 (1991) 149.

of Sn-Pt alloy-type surface species as evidenced by Mössbauer spectroscopy.¹⁷ This approach led to the monolayer coverage of platinum clusters by tin organometallic species.^{7,10}

Surface reaction (1) between tetraethyltin and hydrogen adsorbed on supported platinum (PtH_{ads}) is often called as “tin anchoring step I”. The material balance of tin anchoring can be calculated from the measured amount of hydrocarbons formed in steps I and II. This allows us to calculate the value of x , i.e. the amount of alkyl groups reacted in tin anchoring step I. In this way, the stoichiometry of tin anchoring step I can be determined.¹⁰

SOMC/M technique was considered as a method for the preparation supported bimetallic catalysts with *monolayer* coverage of modifier on the parent metal. It has been emphasized in Ref.¹²: “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 prepared multilayered materials”.

Earlier results showed that the clear separation of the anchoring and decomposition steps cannot always be done.¹⁰ 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 (1) and (2)).

It has to be emphasized that the exclusive formation of tin-metal interaction in tin anchoring step I requires special control to avoid the reactions with the involvement of surface OH groups and the adsorption of tetraalkyl tin onto the support.^{7,10}

In order to minimize the tin-support and to maximize the tin-metal interaction in the anchoring step I the following precautions were taken: (i) the use of relatively low concentration of tetraalkyl tin; (ii) avoiding high reaction temperature; (iii) the use of short reaction time; and (iv) strong separation of reaction (1) from reaction (2).^{7,10}

The above conditions 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 anchored. 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.

As emerges from earlier results of our department, the amount of tin anchored is strongly controlled by the size of the alkyl groups of tetraalkyl tin used.¹⁸ Beyond a definite coverage level, the alkyl groups of PSC formed created a specific “shielding”. 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 $\text{Sn}(\text{CH}_3)_4$, $\text{Sn}(\text{C}_2\text{H}_5)_4$, and $\text{Sn}(\text{C}_4\text{H}_9)_4$ at monolayer coverage the following Sn/Pt_s ratios were obtained: 0.6, 0.4, and 0.3, respectively.¹⁸

In this study Controlled Surface Reactions were used to prepare various types of supported $\text{E}_x\text{-M}_y$ (E= Sn, Ge; M= Pt, Pd, Rh, Ru) catalysts with exclusive formation of metal-metal interaction and high E/M ratios.

The main goal was 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 to the support.
- Study of CSRs in the presence of (i) large excess of the precursor of modifier; (ii) excess of hydrogen (iii) trace amount of oxygen.

¹⁸ J. Margitfalvi, in: Yu.I. Yermakov, V. Likholobov (Eds.), Homogeneous and Heterogeneous Catalysts. *Proc. 5th Internat. Symposium on Relations between Homogeneous and Heterogeneous Catalysis*, VNU Science Press, Utrecht, 1986, pp. 945-964 (and references therein).

- Study of the influence of reaction conditions and type of the precursor of modifier on the selectivity of anchoring reaction.
- Investigation of the dependence of the Temperature Programmed Decomposition profile from the Sn/Pt_s ratios and the type of anchored SOMS. Use of the “fingerprint” character of the TPD curves for the characterization of tin- modified catalysts.
- To demonstrate that decomposition of SOMS in hydrogen or oxygen resulted 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.
- Characterization of the bi- and multimetallic catalysts prepared by chemisorption of CO and H₂, TPR, XPS, FTIR, Mössbauer and EXAFS spectroscopy.
- To demonstrate that kinetic results obtained on supported Pt catalysts provided new information about the elementary steps involved in anchoring of SnR₄ onto platinum.
- Study the peculiarities of the preparation of Sn-Pt/Al₂O₃ catalysts with high Sn/Pt_s ratios.
- Use of a “one pot” circulation reactor set-up for the modification of alumina supported Pt and Pt-Re catalysts with tetraethyltin.
- Application of the CSRs for qualitative determination of the efficiency of re-reduction of different supported catalysts (M= Pt, Pd, Rh and Ru).
- Preparation of new types of selective catalysts for different organic reactions and CO oxidation.

3. Experimental method

Two types of reactors were used in anchoring step I: (i) stirred tank reactor and (ii) circulation reactor. Re-reduced parent catalyst was introduced into the stirred tank reactor without any contact with air and was slurred with solvent in Ar or H₂ atmosphere. The anchoring step I was started by injection of the precursor of modifier and this reaction was monitored by determining the amount of hydrocarbons formed. In anchoring step I three different approaches were used to prepare bi- and multimetallic catalysts: (i) preparation in the presence of adsorbed hydrogen, (ii) preparation in excess of hydrogen, and (iii) preparation in the presence of trace amount of oxygen.

After washing and drying in vacuum, the decomposition of SOMS (step II) was accomplished by using Temperature Programmed Decomposition (TPD) technique using both reductive (hydrogen) and oxidative (air or oxygen) atmospheres.

The amount of hydrocarbons formed in steps I and II, (n^I , mol g_{cat}⁻¹ and n^{II} , mol g_{cat}⁻¹, respectively) were measured using GC. This allowed to obtain full material balance of tin (or germanium) anchoring. These values were in a good agreement with the amount of modifier determined by AAS.

The value of x ($x = 4n^I/(n^I + n^{II})$) (see reaction (1)) was also calculated from the material balance. In this way the stoichiometry of tin anchoring reaction could be determined.

The number of accessible metal atoms in bi- and multimetallic catalysts prepared was measured by chemisorption of CO and H₂. EXAFS and Mössbauer spectroscopy were applied to study the pretreatment induced changes in the oxidation state of platinum and tin in Sn-Pt catalysts. The extent of reducibility of tin in supported Sn-Pt catalysts was investigated by TPR and XPS measurements. The formation of “Sn⁴⁺-Pt” ensemble sites was monitored by Mössbauer and FTIR spectroscopy. Reversibility of oxidation and reduction of tin in Sn-Pt/SiO₂ catalysts was studied by *in situ* EXAFS and Mössbauer spectroscopy. The catalysts prepared by CSRs were tested in low temperature CO oxidation, hydrogenation of different organic compounds, hydrocarbons transformation and naphtha reforming.

4. New scientific results

New aspects of anchoring of tin and germanium organometallic compounds ($\text{Sn}(\text{CH}_3)_4$, $\text{Sn}(\text{C}_2\text{H}_5)_4$, $(\text{CH}_3)_3\text{SnSn}(\text{CH}_3)_3$ and $\text{Ge}(\text{C}_2\text{H}_5)_4$) onto different SiO_2 , Al_2O_3 , MgO and active carbon supported metals were described. In this study the details of anchoring reaction was discussed. The variation of parameters of CSRs allowed the preparation of different supported bi- and multimetallic catalysts with high amount of modifier anchored.

In this doctoral thesis the focus was laid mostly to the preparation of Sn-modified Pt-containing supported catalysts.

- Results of computer modeling indicated (see Figure 1A-B) that the monolayer of tin-containing $-\text{Sn}(\text{C}_2\text{H}_5)_3$ or $-\text{Sn}(\text{C}_2\text{H}_5)_2$ surface species resulted 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).

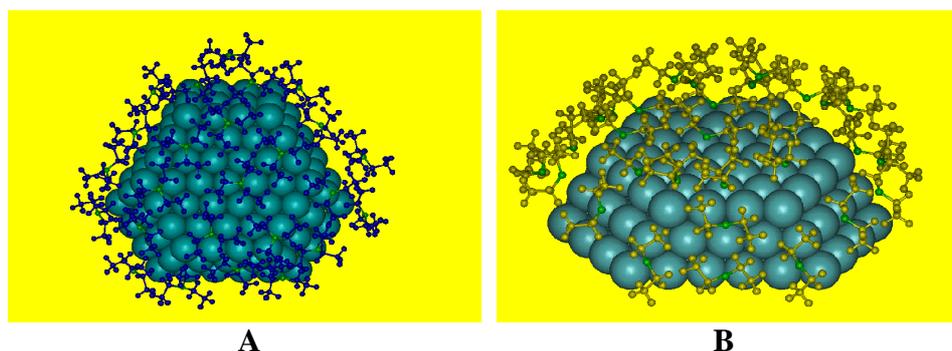


Figure 1. Computer modeling of SOMS anchored onto the platinum cluster made from three layers of Pt atoms. **A-** Anchoring of $-\text{SnR}_3$ (top view); **B-** anchoring of $-\text{SnR}_2$ (side view).

- It was demonstrated that the use of excess hydrogen during tin anchoring resulted in high extent of coordinative unsaturation. In samples with lowest Sn/Pt_s ratio ($\text{Sn}/\text{Pt}_s = 0.6$) the highest x value ($x = 3.3$) was attained.
- It was shown that the addition of trace amount of oxygen led to immediate formation of ethylene (see Figure 2). This indicated that the surface chemistry of tin anchoring was altered.

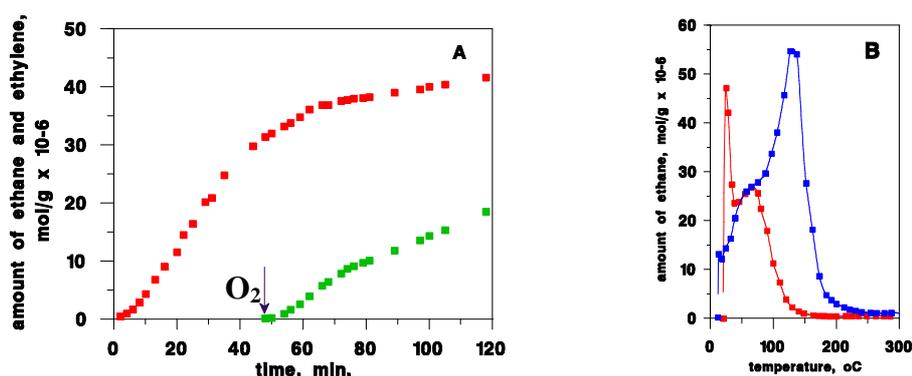
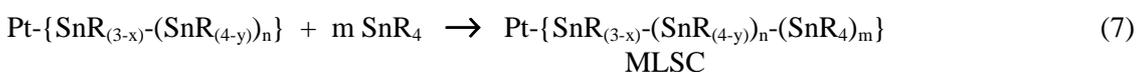
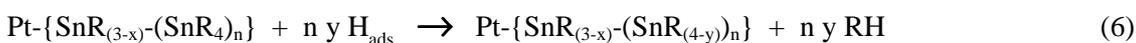
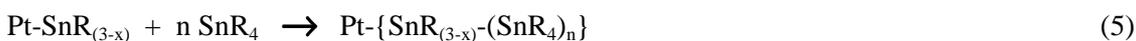


Figure 2. Oxidation during tin anchoring reaction. **A-** Time dependence of the formation of ethane (■) and ethylene (■) in the tin anchoring step I. Conditions of tin anchoring: $T_r = 50^\circ\text{C}$, $\text{Sn}_0/\text{Pt}_s = 1.72$, ($\text{Sn}/\text{Pt}_s = 0.88$), solvent: benzene; $20 \text{ cm}^3_{\text{gcat}}^{-1} \text{ O}_2$ added in the 50th minute. The arrow indicates the moment of addition of oxygen. **B-** TPD pattern of the decomposition of SOMS formed on reduced (■) ($\text{Sn}/\text{Pt}_s = 0.39$) and oxidized during tin anchoring samples (■) ($\text{Sn}/\text{Pt}_s = 0.88$). Catalyst: 3 wt% Pt/ SiO_2 .

In this case the lone pair of electrons of the oxygen atom in oxidized SOMS is involved in the tin anchoring. As far as the number of anchoring surface sites increased further, the amount of tin anchored also significantly increased.

- The increase of the Sn/Pt_s ratios in the bimetallic catalysts required the creation of new anchoring sites for tetraalkyl tin. 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.
- Based on results obtained upon modifying 3 wt% Pt/SiO₂ catalyst with Sn(C₂H₅)₄ the surface reactions involved in building-up multilayer tin coverage, which take place in the presence of high excess of tetraalkyl tin, were written as follows:



Reactions (3) and (4) describe the formation of PSC and coordinatively unsaturated PSCs (CUPSC), respectively. The CUPSC interacts with SnR₄ used in large excess (reaction (5)) 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 (6)), which can also interact with tetraalkyl tin (reaction (7)). The net result is the formation of slab-like Multilayered Surface Complex (MLSC) on the Pt surface. Upon systematic variation of reaction conditions it was possible to prepare various catalysts containing partially dealkylated Pt-{\text{SnR}_{(3-x)}\text{-}\{\text{SnR}_{(4-y)}\}_n} units with desired values of *x*, *y* and *n*. It is noteworthy, that reactions (3)-(7) take place only in the presence of a solvent.

- The formation of the second layer in the form of -Sn(C₂H₅)₄ at the top of PSC containing -Sn(C₂H₅)₃ and -Sn(C₂H₅)₂ surface species was demonstrated by computer modeling (see Figure 3A-B). The figures show that the second layer of tin organic moieties can be formed both at the *top* and *side* sites of platinum.

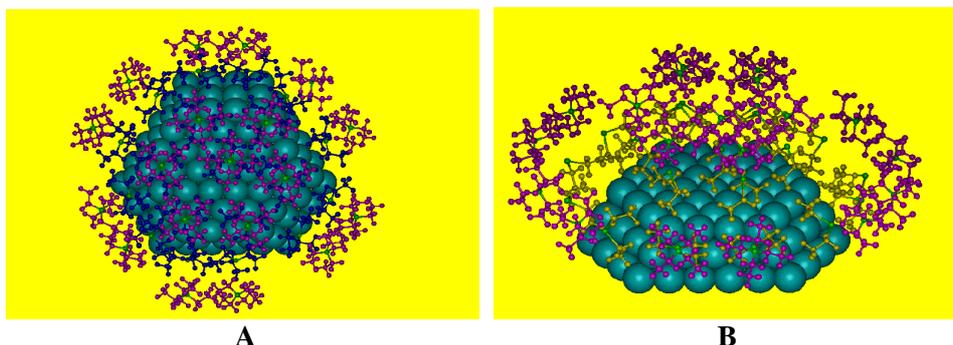
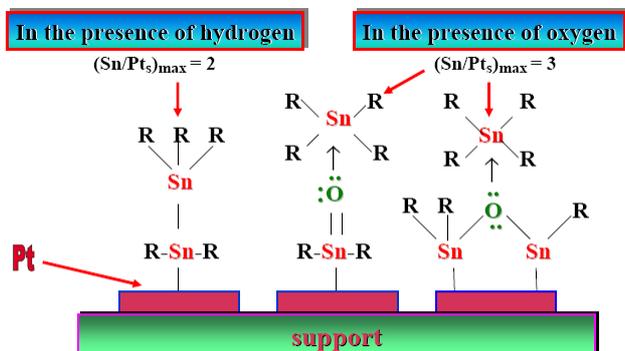


Figure 3. Computer modeling of the formation of the second layer of tin organic complex. **A-** Anchoring of SnR₄ onto -SnR₃ (top view); **B-** anchoring SnR₄ onto -SnR₂ (side view). Pt - blue; Sn - green; R in -SnR₃ in the first layer - dark blue; R in -SnR₂ in the first layer - yellow; R in SnR₄ in the second layer - pink.

- Upon using excess of hydrogen in tin anchoring step I 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. In the presence of added oxygen high Sn/Pt_s

ratios can also be reached even at relatively low initial Sn_0/Pt_s ratios. Upon using this mode of tin anchoring, Sn-Pt/SiO₂ catalysts with the highest Sn/Pt_s ratio up to 2.9 were prepared. The formation of SSSL in the presence of excess hydrogen and trace amount of oxygen with different extent of dealkylation and environment are shown in Scheme 1.



Scheme 1. SOMS formed in the presence of excess hydrogen and trace amount of oxygen.

- The TPD profile strongly depended on the Sn/Pt_s ratios and on the type of anchored SOMS. 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 the further step, the built up of next layer of surface species started, which requires higher temperature for decomposition (**PSC** → **SSSL** → **MLSC** → **OMSAS**). The stepwise appearance of new TPD peaks indicated that the increase of the Sn₀/Pt_s ratio led to the build-up of tin containing layers step by step as shown in Figure 4.

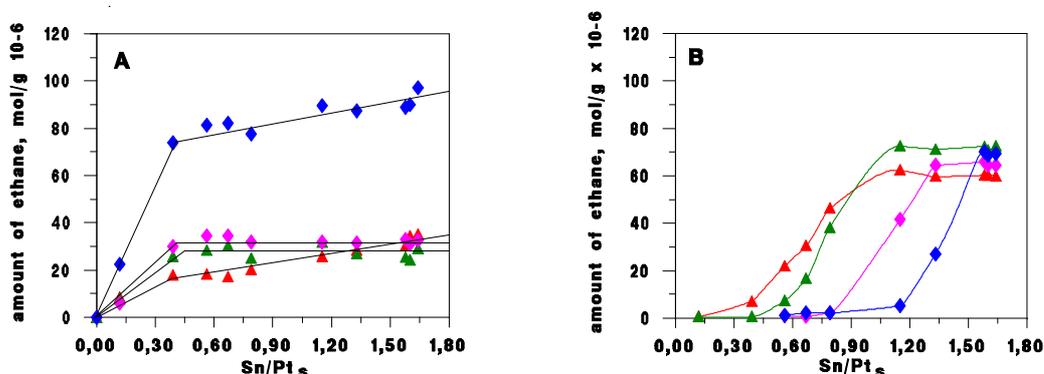


Figure 4. The dependence of the amounts of ethane related to the area of TPD peaks on the Sn/Pt_s ratios. The position of temperature maxima of TPD peaks: **A**- (▲), 20°C; (▲), 50°C; (◆), 80°C and (◆), sum of the amount of ethane formed in the first three peaks up to 80°C; **B**- (▲), 110°C; (▲), 140°C; (◆), 170°C and (◆), 200°C. Results obtained from deconvoluted TPD spectra. Catalyst: 3 wt% Pt/SiO₂. The tin anchoring was carried out in benzene at T_r= 50°C in the presence of adsorbed hydrogen.

- 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/SiO₂ catalyst 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 and the mode of preparation).
- The influence of the atmosphere (Ar, H₂ or O₂) and the type of tin precursor compound used (Sn(CH₃)₄, Sn(C₂H₅)₄ and (CH₃)₃Sn-Sn(CH₃)₃) on the selectivity of tin anchoring over Pt/SiO₂ catalyst was evidenced by Mössbauer spectroscopy. The modification of Pt/SiO₂ catalyst with Sn resulted in at least two types of supported bimetallic nanoclusters,

namely 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/SiO₂ catalyst was exclusively modified with Sn (all tin was in Sn⁰ 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/SiO₂ catalyst with tin was selective 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^{δ+} 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/SiO₂ catalyst by EXAFS and Mössbauer spectroscopy showed that tin could be easily oxidized and reduced. In reduced catalysts the tin was directly coordinated with Pt, while after oxidation tin was primarily in a form of highly dispersed and reactive SnO₂ over the Sn-Pt nanocluster. Treatment of the oxidized Sn-Pt catalyst at room temperature either with H₂ or CO partially restored the initial alloy phases (in H₂- 67-86%).
- It was demonstrated that 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 during the reaction. Alloy phases were transformed to Sn⁴⁺ oxide species and Sn-Pt alloys with decreasing tin content in the order: PtSn₄ → PtSn₂ → Pt₂Sn₃ → PtSn → Pt₃Sn.
- Experimental evidences found on alumina and silica supported catalysts both 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 a *consecutive character*.

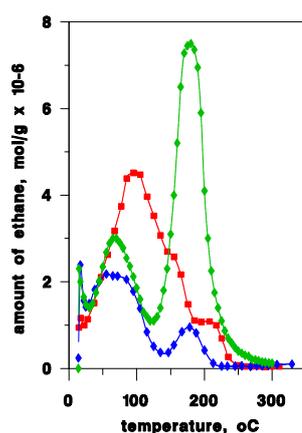


Figure 5. The influence of the duration of tin anchoring step I on the TPD pattern of SOMS formed. Catalyst: 0.35 wt% Pt/Al₂O₃; [Sn]₀ = 2.53 mM; Sn₀/Pt_s = 1.85. Reaction time (τ_r): (◆), 4 min ($x = 0.34$, Sn/Pt_s = 0.20); (◆), 10 min ($x = 0.40$, Sn/Pt_s = 0.55); (■), 20 min ($x = 0.75$, Sn/Pt_s = 0.56).

This finding was supported by the following experimental evidences: (i) complete change of the TPD pattern of samples, as reaction proceeds (see Figure 5); (ii) pronounced time dependence of the formation and decomposition of different surface species; (iii) alteration of the stoichiometry of tin anchoring.

- Peculiarities of the preparation of Sn-Pt/Al₂O₃ catalysts with high Sn/Pt_s ratios were examined. The 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/Pt_s = 1.4.
- The use of a circulation reactor for the modification of alumina supported Pt and Re-Pt catalysts with tetraethyltin was also demonstrated. This technical innovation meant 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.
- Sn-Pt/Al₂O₃ catalysts prepared in the circulation reactor were characterized by H₂ and CO chemisorption, Temperature Programmed Reduction and XPS measurements. Results indicated high reducibility of tin in Sn-Pt/Al₂O₃ catalysts. The formation of Sn-Pt alloy phase and SnO_x oxides was evidenced.
- High initial concentration of tetraalkyl tin provided high rates of tin anchoring; however the increase of the concentration of [Sn]₀ had an upper limit. At high initial concentration of tetraalkyl tin it can interact with the OH groups of support, especially in the case of Al₂O₃. It is worth to note, that under properly chosen reaction conditions ([Sn]₀ = 0.05 M, T_r = 40°C) even in the case of Pt/Al₂O₃ catalysts the formation of tin species anchored onto platinum is exclusive up to Sn/Pt_s = 1.4-1.6.
- Peculiarities of the modification of Pt/C catalyst with Ge(C₂H₅)₄ by CSRs were also shown. The goal 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 (conventional impregnation or CSRs). By using of CSRs method exclusive formation of alloy-type surface entities up to Ge/Pt_s = 0.87 at T_r = 155°C was achieved.
- Application of CSRs for qualitative determination of the efficiency of re-reduction of alumina supported Pt, Rh and Ru catalysts was proved. 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 also demonstrated. The efficiency of re-reduction of ionic forms of Pt, Rh and Ru was increased upon increasing of the temperature (t_{red}). Complete reduction of Pt^{δ+} forms in 5 wt% Pt/Al₂O₃ catalyst was attained at t_{red} = 400°C (n_{C₂H₄}^I/n^I = 0.04; where n_{C₂H₄}^I - the amount of ethylene formed in step I). In a case of 4 wt% Rh/Al₂O₃ catalyst almost complete reduction of ionic form of Rh was achieved at t_{red} = 200°C (n_{C₂H₄}^I/n^I = 0.02). High degree of re-reduction of ionic form of Ru^{δ+} in a 5 wt% Ru/Al₂O₃ catalyst was achieved at 350°C (n_{C₂H₄}^I/n^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_{red}. However, reduction temperature used (t_{red} ≤ 200°C) was not sufficient for full reduction of highly dispersed palladium (n_{C₂H₄}^I/n^I = 0.4) but after pretreatment at t_{red} = 400°C the catalyst lost its activity.

5. Theses

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 [2-4,10,15]. 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 [2,10,15,19]. It was demonstrated that in this case the modification of Pt with Sn was highly selective up to $\text{Sn/Pt}_s = 2$, namely 100 % of Sn introduced was anchored to the platinum in the form of Sn-Pt alloy phases [7].
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/SiO₂ catalysts with Sn/Pt_s ratio up to 2.9 and almost exclusive Sn-Pt interaction were prepared [2,10,15]. 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) [5,15].
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 [2-5,10,14-19].
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 [2-4,6,10,13,17-18].
6. Kinetic results obtained on supported Pt catalysts provided new information about the elementary steps involved in anchoring of tetraethyltin onto platinum [13].
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 [3-4,7-9,11,18].
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 H₂, TPR, XPS, FTIR, Mössbauer and EXAFS spectroscopy [3-7,9,11,19].
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 [2-5,16-17]. 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 [1,2].

6. Application possibilities

Supported bifunctional catalysts containing Sn and Pt have obtained great industrial importance especially in the field of refinery technologies and fine chemistry.

The unique properties of bimetallic catalysts prepared from organometallic precursors are attributed mainly to the bimetallic interactions and the small size of the supported clusters. However, the preparation of catalysts from organometallic precursors can be expensive for large-scale applications. Applications in short term can be possible for processes in pharmaceutical industry, especially when a high selectivity can be obtained with a well-formulated catalyst.

In this respect one of the attractive applications of the catalysts prepared from organometallic precursors is the enantioselective hydrogenation of activated ketones. Highly active and selective catalysts can be obtained when alkyl groups of organotin compounds are partially maintained during CSRs furthermore chiral environment can be generated upon using chiral organotin compounds.

Large number of catalytic reactions, such as catalytic naphtha reforming, hydrogenation of unsaturated carbonyl compounds, oxidation of CO or methanol, requires both metallic sites and Lewis acid sites for activating hydrogen or oxygen and substrate molecules, respectively. It was found that the presence of highly active “ Sn^{4+} -Pt” ensemble sites in Sn-Pt/SiO₂ catalysts prepared by CSRs methods, where Sn⁴⁺ sites are in the atomic closeness of Pt, could fulfil this requirement [3-4,7-9,11,18]. Moreover these types of catalysts are stable enough to withstand repeated treatments in oxygen and hydrogen.

As was shown by us earlier, supported Sn-Pt/SiO₂ catalysts prepared by CSRs method can be successfully used in different reactions, such as (i) selective hydrogenation of unsaturated aldehydes to unsaturated alcohols [5,10]; (ii) citral hydrogenation [15,16], (iii) hydrogenation of benzonitrile [28], (iv) hydrogen-assisted 1,2-dichloroethane dechlorination [12,14] and (v) low temperature CO oxidation [7,9-12].

Alumina supported tin- modified bi- and multimetallic catalysts can be successfully applied in hydrocarbons transformation and naphtha reforming. It is worth for mentioning that over Sn-Pt/Al₂O₃ and Sn-Re-Pt/Al₂O₃ catalysts reformat with reduced aromatic and increased iso-paraffin content can be obtained [3,4,8, HU Pat. 98 02151].

As was demonstrated recently the presence of Sn-Pt alloy phase and SnO_x oxides in Sn-Pt/Al₂O₃ catalysts favors the catalytic behavior in *n*-butane dehydrogenation, thus increasing the *n*-butane conversion and the selectivity to olefins and decreasing the coke deposition [18].

It is important to note that CSRs can be also applied for qualitative determination of the efficiency of re-reduction of supported parent monometallic catalysts [1].

Direct Alcohol Fuel Cells are devices that can extract the chemical energy accumulated in molecules such as hydrogen, methanol or ethanol producing electrical work. Our new results clearly demonstrate that upon using CSRs highly active alloy- type Sn-Pt/C electrocatalysts for electrochemical oxidation of CO and ethanol can be also prepared [19].

The thesis is based on following own publications

1. J.L. Margitfalvi, I. Kolosova, E. Tálás, S. Gőbölös:

Qualitative determination of the efficiency of re-reduction in supported platinum catalysts.

Development of a new method.

Applied Catalysis A: Genaral 154 (1997) 1-6.

IF: 2.020, I: 3

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Catalysis Today 43 (1998) 29-49.

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3. **J.L. Margitfalvi, I. Borbáth, M. Hegedús, S. Gőbölös, F. Lónyi:**
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Patents

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<i>Number of the own publications attached to the thesis:</i>	19
<i>Accumulated impact factors attached to the thesis:</i>	45.306
<i>Accumulated number of independent citations attached to the thesis:</i>	131
<i>Patents:</i>	1
<i>Oral or poster presentations attached to the thesis:</i>	36
<i>Total number of the own publications:</i>	38
<i>Accumulated impact factors:</i>	59,735
<i>Accumulated number of independent citations:</i>	228
<i>Patents:</i>	1
<i>Oral or poster presentations:</i>	71