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NEW APPROACHES TO PREPARE SUPPORTED Sn-Pt BIMETALLIC CATALYSTS

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Abstract

General principles of modification of supported Pt catalysts with tin tetraalkyls are summarized and a new approach to prepare supported Sn-Pt catalysts is described. The new approach leads to the formation of Multilayered Organometallic Complexes (MLOC) anchored onto supported platinum. The formed MLOC can be decomposed either in reductive or oxidative atmosphere with the formation of new type of supported Sn-Pt catalysts with high Sn/Pt_s ratios. The decomposition in a reductive atmosphere leads to the formation of alloy-type bimetallic phases, while the decomposition in the presence of oxygen provides Lewis-acid type surface species anchored to supported platinum.

Keywords: Controlled surface reactions, tin tetraethyl, *n*-hexane, Pt/Al₂O₃, Sn-Pt/Al₂O₃

INTRODUCTION

Supported bimetallic catalysts have obtained great importance both in the transformation of hydrocarbons [1,2] and in the production of fine chemicals [3,4]. These catalysts can be prepared using different methods [5,6], however, exclusive formation of supported bimetallic surface entities can only be achieved by using Controlled Surface Reactions (CSRs) [7-10]. The combination of CSRs with methods of Surface Organometallic Chemistry (SOC) appeared to be a very powerful tool to prepare alloy-type Sn-Pt entities on variety of supports, such as alumina and silica [9].

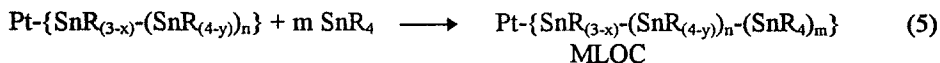
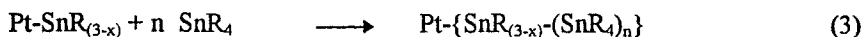
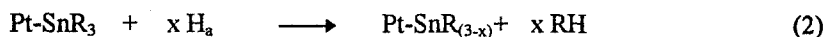
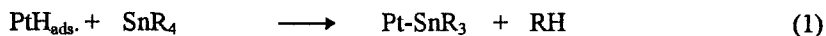
Dedicated to Professor Pál Tétényi on the occasion of his 70th birthday

In this work the general approach used to prepare surface organometallic species on supported platinum is described and details on the preparation of Sn-Pt/Al₂O₃ catalysts with high Sn/Pt_s ratios will be given.

Surface chemistry

The reaction between tin tetraalkyls and adsorbed hydrogen has been first described in 1984 [7]. This reaction provided direct tin-platinum interaction, what was maintained upon decomposition of the formed primary surface complex in hydrogen atmosphere [10, 11]. Upon using our earlier approach monolayer coverage of platinum by tin organometallic species could be achieved. Depending on the particle size of platinum the monolayer coverage resulted in Sn/Pt_s ratios around 0.3-0.6 [10].

Recently we have demonstrated that upon modification of Pt/SiO₂ catalysts with tin tetraethyl high Sn/Pt_s ratio (Sn/Pt_s=3) can be obtained without introduction of tin into the support [12]. The new results indicated that in the presence of large excess of tin tetraethyl in addition to the earlier proposed CSRs further anchoring-type reactions take place, leading to the formation of multilayer organometallic complexes (MLOC). The formation of MLOC was strongly enhanced by excess hydrogen introduced. The surface chemistry involved in the formation of MLOC can be described by the following surface reactions [12]:



Equation (1) is related to the formation of primary surface complex (PSC) with monolayer tin coverage, while equation (2) outlines the formation of coordinatively unsaturated surface species that interacts with tin tetraethyl used in large excess (see reaction (3)). In reaction (3) surface species in the second layer (SSSL) are formed similar to that suggested earlier for supported rhodium modified with tin tetrabutyl [9]. In the formation of SSSL tin-tin dative bonds are involved. In the presence of adsorbed hydrogen on platinum SSSL can also be partially hydrogenolyzed, resulting in coordinatively unsaturated species in the second layer (reaction (4)), which can also interact with tin tetraalkyl (reaction

(5)). The net result is the formation of multilayered organometallic complex (MLOC) anchored to the platinum. It is suggested that MLOC anchored to the platinum have a slab-like form. The length of these slabs can be different, however results obtained on Pt/SiO₂ indicate that they contain at least three tin atoms. In this paper reactions (1)- (5), which take place in the presence of a solvent, will be referred as *tin anchoring reactions*.

The decomposition of MLOC is carried in the absence of solvent in a gas-solid reaction. The decomposition pattern of MLOC in a hydrogen atmosphere clearly reflected the stepwise character of the anchoring process. The decomposition in a hydrogen atmosphere led to the formation of bimetallic surface entities with unique catalytic properties [10,12,13]. Recent Mössbauer results confirmed that even at Sn/Pt_s = 2.5 more than 90 % of tin introduced was in the form of an alloy [14].

This study was aimed to extend the formation of MLOC to alumina supported platinum catalysts. Further goal of this study was to decompose the formed MLOC both in reductive and oxidative atmospheres. The results indicated that the decomposition of MLOC in the presence of oxygen resulted in a new catalytic system in which supported platinum is covered by tin in ionic form. In this new type of Sn-Pt/Al₂O₃ catalyst the metallic and Lewis-acid type active sites are at atomic distance from each other.

EXPERIMENTAL

Three different alumina supported platinum catalysts were used in this work. *Catalyst A* is a reforming-type monometallic catalyst (Engelhard E-301). *Catalyst B* was prepared by impregnation using H₂PtCl₆ in 1 M HCl. The support surface area (S= 135 m²/g), total pore volume (V_p= 0.66 cm³/g) and average pore radius (R= 8.4 nm) was determined by N₂ adsorption and mercury porosimetry, respectively. The impregnation of alumina was carried out at 75°C for 1.5-2.0 hours. After impregnation the catalyst was washed and then dried in air in two steps at 60°C and 120°C for 3 and 2 hours, respectively. The catalyst was reduced under hydrogen for 4 hours at 500°C. *Catalyst C* (Incat Pt-3) was provided by Borekov Institute of Catalysis [15]. Platinum and chlorine content of catalysts was 0.3 and 1.0 wt.%, respectively.

Catalysts characterization. The H/Pt and CO/Pt ratios were determined by chemisorption using ASDI 100 equipment (Advanced Scientific Designs, Inc.). FTIR measurements of pyridine adsorption was carried out as described elsewhere [16].

Catalysts modification. The catalyst was re-reduced in hydrogen prior to the tin anchoring step at 400°C for 4 hours. Anchoring reaction was carried out at 50°C, for 1.5 - 4 hours. The decomposition of surface organometallic complexes was carried out in a hydrogen atmosphere as described elsewhere [12], while the

decomposition in the presence of oxygen was carried out using 10 vol. % oxygen in nitrogen. In both cases the heating rate was 5 °C/min.

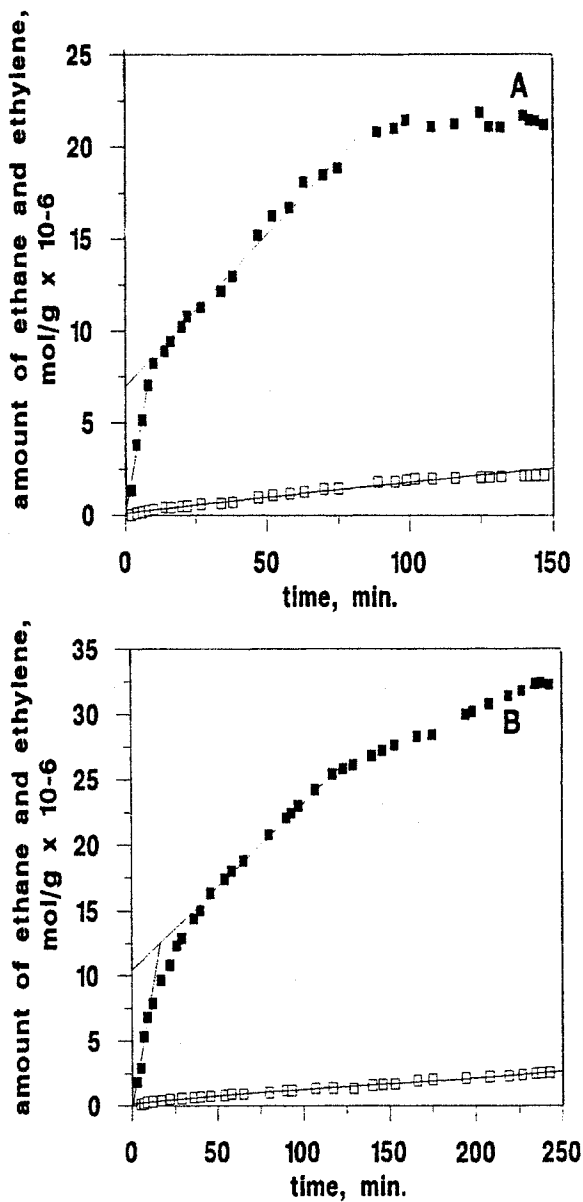


Fig. 1. Kinetic curves of the formation of ethane and ethylene in the tin anchoring step. $T_r = 50^\circ\text{C}$; amount of catalysts: 1 g; solvent: benzene. A - Catalysts type C, $[\text{SnEt}_4]_0 = 25.32 \text{ mM}$; B - Catalyst type A, $[\text{SnEt}_4]_0 = 12.66 \text{ mM}$. (■), ethane; and (□), ethylene

Hydrocarbon reactions. The transformation of *n*-hexane was carried out at atmospheric pressure and 510°C in a continuous-flow reactor operated in a periodic mode. Details on the reactor-setup and product analysis can be found elsewhere [7].

RESULTS AND DISCUSSION

The kinetic curves of the formation of ethane in the tin anchoring reactions are shown in Fig. 1(A and B). These results were obtained on two different catalysts, however, the character of the kinetic curves is the same. There are two distinct parts in the kinetic curves. In both cases the initial part has high rate. This part is followed by a slower one, which is maintained up to *ca.* 100 min. This behavior strongly resembles the behavior of Pt/SiO₂ catalyst [12]. Consequently, the first part of the kinetic curve is attributed to the formation of PSC, while the second part to the formation of MLOC. In both experiments ethylene was formed in small amount.

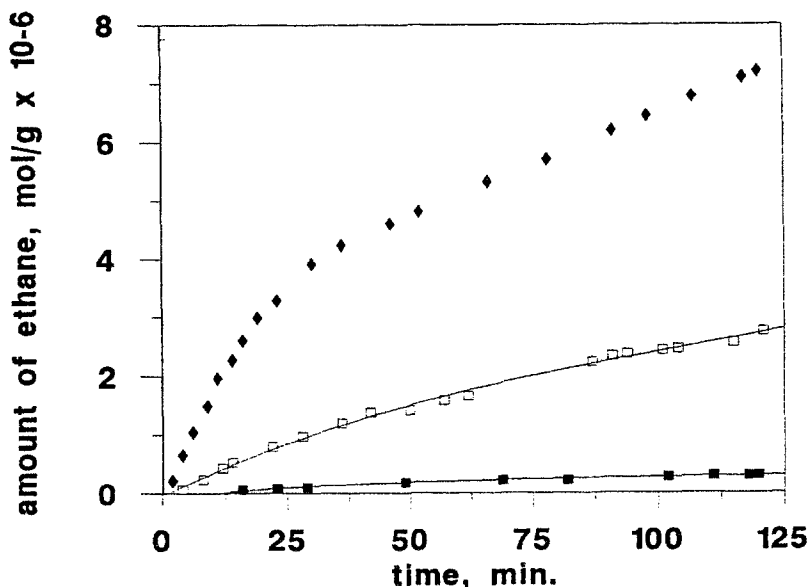


Fig. 2. Reaction of tin tetraethyl with alumina support.
 $T_r = 50^\circ\text{C}$; amount of alumina: 1 g; solvent: benzene; $[\text{SnEt}_4]_0 = 25.32 \text{ mM}$.
Temperature of hydrogen treatment: (■), 300°C; (□), 400°C; (◆), 500°C

It is worth mentioning that in both experiments the ratio between tin anchored and surface platinum atoms (Sn/Pt_s) was 2.3 ± 0.05 . These data indicate that in both cases MLOC was formed.

It is noteworthy that contrary to the silica support, the alumina support showed higher activity when it was allowed to react with tin tetraethyl. As emerges from Fig. 2 the rate of this reaction strongly depended on the temperature of hydrogen pretreatment.

The decomposition pattern of surface complexes, formed during the tin anchoring step, in hydrogen atmosphere is shown in Fig. 3(A-C). Figure 3(A) shows the decomposition pattern around monolayer coverage ($\text{Sn}/\text{Pt}_s=0.34$), while Fig. 3(B and C) show similar pattern at multilayer coverages, at $\text{Sn}/\text{Pt}_s=1.39$ and 2.16 , respectively. As seen in Fig. 3(A-C), upon increasing the Sn/Pt_s ratio the character of the TPR curves has been altered and the end of the decomposition has been shifted to the high temperature region. Similar decomposition pattern has been observed upon anchoring tin onto Pt/SiO_2 [12].

The decomposition pattern of tin tetraethyl introduced onto pure alumina is shown in Fig. 4. The TPR pattern is completely different from that on $\text{Pt}/\text{Al}_2\text{O}_3$. Tentatively the first peak around $185\text{-}190^\circ\text{C}$ was attributed to tin containing surface species anchored to alumina, while the high temperature peak around $250\text{-}270^\circ\text{C}$ was ascribed to tin tetraethyl adsorbed onto alumina. The latter peak was not observed on $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts, however, the former one around 190°C was detected only at high initial concentration of tin tetraethyl, resulting in $\text{Sn}/\text{Pt}_s=2.16$ (see Fig. 3(C)). At lower Sn/Pt_s ratios (see Fig. 3(A and B)) no decomposition products were detected around 200°C .

These results indicate that the modification of $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts with tin tetraethyl results in Sn-Pt bimetallic catalysts in which two forms of tin can be distinguished: (i) tin anchored to the platinum and (ii) tin anchored to the alumina. The formation of tin anchored to the platinum is exclusive up to $\text{Sn}/\text{Pt}_s=1.6$.

The decomposition of MLOC in the presence of oxygen resulted in mostly CO_2 , although ethane and ethylene were also detected in small amounts. The TPO peaks (not shown) for CO_2 appeared at 100 and 200°C . Catalysts prepared by decomposition in oxygen will be denoted as Sn-Pt/ Al_2O_3 (O), while catalysts decomposed in hydrogen as Sn-Pt/ Al_2O_3 (H).

Chemisorption results obtained on tin modified samples are summarized in Table 1. The introduction of tin onto $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts strongly decreased the amount of chemisorbed hydrogen and CO. The introduction of tin resulted in more pronounced decrease of the hydrogen chemisorption than CO chemisorption. On these platinum catalysts the ratio of $\text{CO}_{\text{chem}}/\text{H}_{\text{chem}}$ was around one, while on tin modified catalysts this ratio was in the range of 2 -3. This indicates that tin probably occupies sites responsible for the activation of dihydrogen. It was a substantial difference in the chemisorption properties of catalyst samples decomposed in hydrogen and oxygen. It is interesting to note

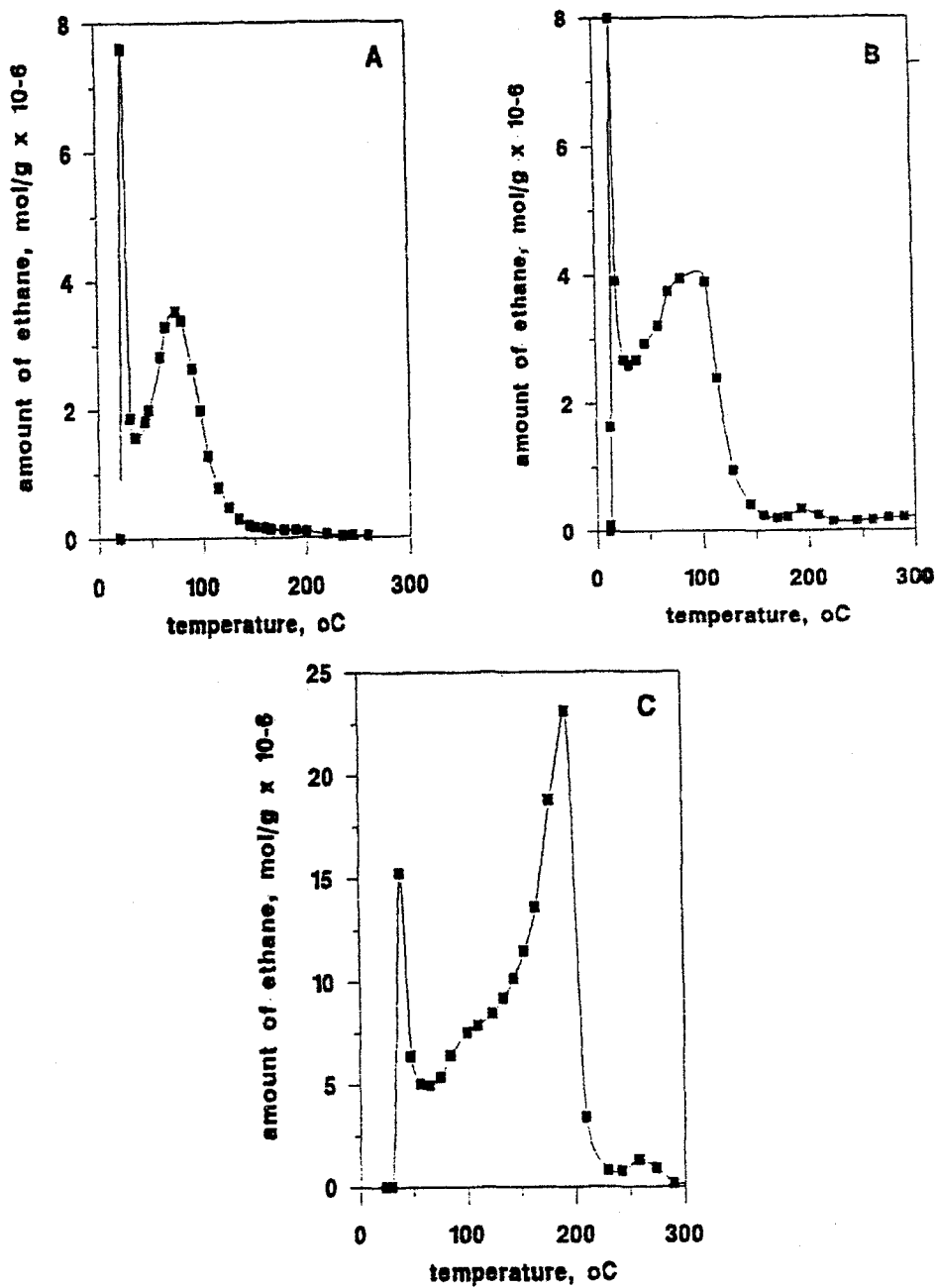


Fig. 3. Decomposition of PSC and MLOC in hydrogen atmosphere.
 A - $\text{Sn}_0/\text{Pt}_s = 0.45$, $\text{Sn}/\text{Pt}_s = 0.34$; B - $\text{Sn}_0/\text{Pt}_s = 2.56$, $\text{Sn}/\text{Pt}_s = 1.39$; C - $\text{Sn}_0/\text{Pt}_s = 10.74$, $\text{Sn}/\text{Pt}_s = 2.16$. Catalyst type C

that decomposition in the presence of oxygen has relatively larger effect on the chemisorption of CO than that of H₂.

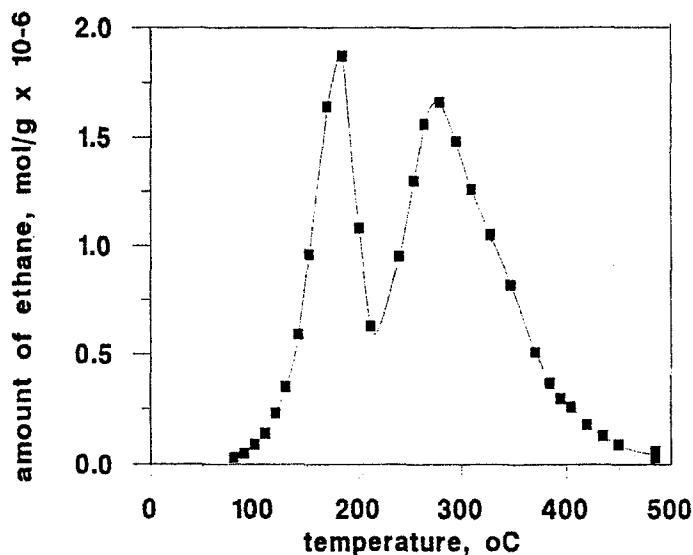


Fig. 4. Decomposition of tin tetraethyl reacted with alumina support. [SnEt₄]₀ = 25.32 mM; Temperature of hydrogen treatment: 400°C

The pyridine adsorption on samples decomposed in hydrogen atmosphere or in the presence of oxygen showed also distinct differences. The band at 1625 cm⁻¹ appeared exclusively in samples decomposed in oxygen atmosphere. This band was attributed to new type of Lewis-acid sites originating from tin. This new Lewis-acid site should be formed in the close vicinity of platinum.

Some of the prepared Sn-Pt/Al₂O₃ catalysts were tested in the dehydrocyclization of *n*-hexane. In the transformation of *n*-hexane catalysts, prepared by decomposition of MLOC both in hydrogen and oxygen atmospheres, were compared. The results are summarized in Fig. 5(A and B).

As emerges from Fig. 5(A) the activity of catalysts modified with tin is in the same range as that of the parent Pt/Al₂O₃ catalyst. However, as shown in Fig. 5(B) the selectivity of the benzene formation was strongly suppressed on both catalysts. The decrease of the aromatization selectivity was more significant on catalysts decomposed in the presence of oxygen (Sn-Pt/Al₂O₃ (O)). Parallel to the suppression of the aromatization activity the isomerization activity of the modified catalysts increased, while no measurable difference in the formation of C₁-C₅ hydrocarbons was observed on tin modified and unmodified Pt/Al₂O₃ catalysts.

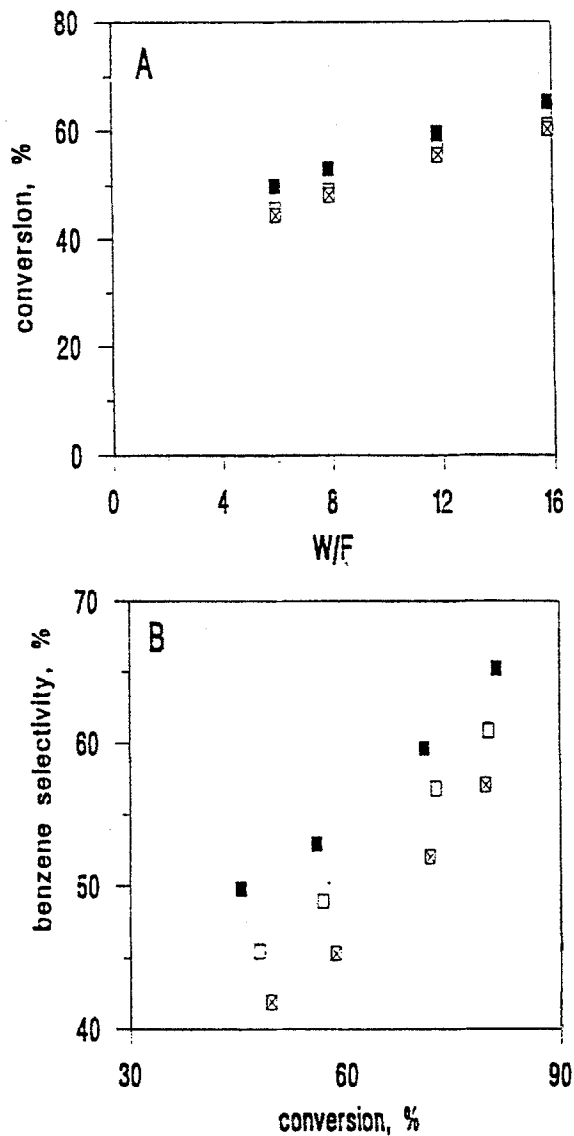


Fig. 5. Comparison of the activity and selectivity of modified and unmodified catalysts. A - the dependence of the conversion of the contact time, $W/F : (\text{g}_{\text{cat}} \times \text{sec}/\text{mol}) \times 10^4$; B - conversion - benzene selectivity dependencies. (■), Pt/Al₂O₃; (□), Sn-Pt/Al₂O₃ (H); (⊠), Sn-Pt/Al₂O₃ (O). Parent catalyst type B. In both tin modified catalysts the Sn/Pt_s = 2.6. Reaction temperature: 510°C; H/CH = 20; amount of catalyst: 0.3 g

Table 1

Comparison of the chemisorption properties of tin modified Pt/Al₂O₃ catalysts prepared by decomposition of MLOC in hydrogen or in the presence of oxygen

Catalyst	Sn/Pt _s *	H/Pt	H/Pt	CO/Pt	CO/Pt
		(H)**	(O)***	(H)**	(O)***
Pt/Al ₂ O ₃ - B	-	0.38	-	n.a.	-
Sn-Pt/Al ₂ O ₃ - B	0.71	0.21	0.17	0.51	0.44
Sn-Pt/Al ₂ O ₃ - B	2.50	0.17	0.13	0.49	0.29
Pt/Al ₂ O ₃ - C	-	0.34	-	0.36	-
Sn-Pt/Al ₂ O ₃ - C	1.85	0.16	-	0.32	-
Sn-Pt/Al ₂ O ₃ - C	2.90	0.05	-	0.15	-

* Calculated from AAS analysis and the overall material balance of tin anchoring,

** Catalysts prepared by decomposition in hydrogen,

*** Catalysts prepared by decomposition in the presence of oxygen.

CONCLUSION

In this study the use of anchoring type Controlled Surface Reactions (CSRs) to prepare different types of supported Sn-Pt catalysts was briefly reviewed. The tin anchoring process was modified resulting in Sn-Pt/Al₂O₃ catalysts with high Sn/Pt_s ratios. It was also demonstrated that these catalysts are active in hydrocarbon reactions even at high Sn/Pt_s ratios. The decomposition of formed MLOC in the presence of oxygen resulted in a new type of Sn-Pt/Al₂O₃ catalyst, which showed lowered aromatization and increased isomerization selectivity even at 510°C. It has been suggested that the decomposition of MLOC in the presence of oxygen leads to the formation of Lewis-acid type active sites in the close vicinity of platinum. However, the results indicated that in the surface reaction due to the higher reactivity of alumina, compared to silica, at high concentration of tin tetraethyl the formation of MLOC is not exclusive, part of tin was introduced into the support. Further studies are in progress to suppress anchoring of tin onto the support.

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REFERENCES

1. Z. Paál: in *Catalytic Naphtha Reforming*, G.J. Antos, A.M. Aitani, J.M. Parera (eds.), p. 19. Marcel Dekker, New York 1995.
2. L. Guzzi, A. Sárkány: *Selectivity of Bimetallic Catalysts. Structure and Reactivity. Catalysis, Special Periodical Report*, J.J. Spivey, S.K. Agreval (eds.), Vol. 11, Chapter 8, p. 318. Royal Society of Chemistry, London 1994.
3. B. Didillon, A.El. Mansour, J.P. Candy, J.P. Bournonville, J.M. Basset: in *Heterogeneous Catalysis, Fine Chemicals II, Stud. Surf Sci. Catal*, M. Guisnet, J. Barrault, C. Bouchoule, D. Duprez, G. Pérot, R. Maurel, C. Montassier (eds.), Vol. 59, p. 137. Elsevier, Amsterdam 1991.
4. V.D. Stytsenko: *Appl. Catal.*, **126**, 1 (1995).
5. Z. Paál, A. Gyóry, I. Uszkurat, S. Olivier, M. Guérin, C. Kappenstein: *J. Catal.*, **168**, 164 (1997).
6. R. Bacaud, P. Bussière, F. Figueras: *J. Catal.*, **69**, 399 (1981).
7. J. Margitfalvi, M. Hegedűs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó, F. Nagy: in *Proc. 8th Int. Congress on Catalysis*, Vol.4, p. 903. Berlin (West) 1984.
8. Ch. Travers, J.P. Bournonville, G. Martino: in *Proc. 8th Int. Congress on Catalysis*, Vol. 4, p. 891. Berlin (West) 1984.
9. J.P. Candy, B. Didillon, E.L. Smith, T.B. Shay, J.M. Basset: *J. Mol. Catal.*, **86**, 179 (1994).
10. J.L. Margitfalvi, E. Tálas, S. Göbölös: *Catal. Today*, **6**, 73 (1989).
11. Cs. Vértés, E. Tálas, I. Czakó-Nagy, J. Ryczkowski, S. Göbölös, A. Vértés, J. Margitfalvi: *Appl. Catal.*, **68**, 149 (1991).
12. J.L. Margitfalvi, I. Borbáth, E. Tfirst, A. Tompos: *Catal. Today*, **43**, 29 (1998).
13. J.L. Margitfalvi, A. Tompos, I. Kolosova, J. Valyon: *J. Catal.*, **174**, 246 (1998).
14. A. Vértés, J. L. Margitfalvi, I. Borbáth, K. Lázár, Gy. Vanko, A. Tompos: unpublished results.
15. V.A. Drozdov, V.B. Fenelonov, L.G. Okkel, T.I. Gulyaeva, N.V. Antonicheva, N.S. Sludkina: *Appl. Catal.*, **172**, 7 (1998).
16. E.P. Parry: *J. Catal.*, **2**, 371 (1963).