

Low Temperature CO Oxidation over New Type of Sn-Pt/SiO₂ Catalysts

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1. INTRODUCTION

Pt/SnO₂, and Pd/SnO₂ catalysts are widely used as low temperature CO oxidation catalysts [1-4]. With respect to the action of the catalysts a synergism between the oxide and the metal phases has been suggested and bifunctional mechanisms based either on the spillover of both CO and oxygen [3] or only CO [4] from the noble metal to tin oxide has been proposed. In another interpretation the formation SnPt alloy phase has been suggested [5]. Recently an alternative reaction mechanism [6] has been proposed suggesting that the reaction takes place at the Pt-SnO₂ interface, i.e., at the '*Sn^{IV}-Pt*' *ensemble sites*.

Recently we have shown that alloy type Sn-Pt/SiO₂ catalysts prepared by using anchoring type Controlled Surface Reactions (CSRs) between tin tetraalkyls and hydrogen adsorbed on platinum [7] are highly active and selective in gas phase hydrogenation of crotonaldehyde into crotyl alcohol and S_{CO} selectivities as high as 90 % has been reported [8]. Catalytic and Mössbauer spectroscopic results indicate [8,9] that the high S_{CO} selectivity of Sn-Pt/SiO₂ catalysts can be attributed to the in situ formed Sn^{IV} species, which activates the carbonyl group [10]. Consequently, this reaction requires atomic closeness of Pt and Sn^{IV} sites, i.e., the presence of '*Sn^{IV} - Pt*' *ensemble sites*.

Results discussed above firmly suggest that our Sn-Pt/SiO₂ catalysts can be effectively used in low temperature CO oxidation, too. It has been proposed that in an oxidative atmosphere '*Sn^{IV} - Pt*' *ensemble sites* can easily be formed from supported Sn-Pt nanoclusters containing different Sn-Pt alloy phases.

In order to prove the above hypothesis Sn-Pt/SiO₂ catalysts with different Sn/Pt (at/at) ratios were prepared from a parent Pt/SiO₂ catalyst [7,8,9b] using CSRs between tin tetraalkyls and hydrogen adsorbed on platinum. Details of surface chemistry leading to the formation of Multilayered Organometallic Complexes (MLOC) can be found elsewhere [7,11,12]. The decomposition of MLOC anchored onto platinum was accomplished both in oxidative and reductive atmospheres. The use of reductive atmosphere provides alloy type Sn-Pt nanoclusters, while the oxidative one leads to the formation of finely dispersed SnO_x (x= 2,

or 4) over platinum [12]. These two catalysts will be distinguished as (O) and (H) type samples, respectively.

2. EXPERIMENTAL PART

A 3% Pt/SiO₂ catalyst (CO/Pt=0.5) was used as a parent catalyst [7]. Sn(C₂H₅)₄ and Sn(CH₃)₄ were used as tin precursor compounds (catalyst type I and II, respectively). Further experimental details can be found elsewhere [7,11,12]. Chemisorption measurements were done using ASDI RXM-100 equipment. Temperature Programmed Reaction (TPRe) technique [13] was used to study the oxidation of CO with oxygen. The space velocity (SV) was 30.000 ml/(g_{cat})⁻¹ h⁻¹. The TPRe curves were obtained recording the m/e = 28, 32 and 44 signals of CO, oxygen and CO₂, respectively. Prior to the reaction the catalysts were re-reduced at 340 °C for one hour in a hydrogen atmosphere. Mössbauer spectra were recorded at 80 and 300 K using a Ba¹¹⁹SnO₃ source. The catalysts were in situ treated and measured in the Mössbauer cell [14].

Cerius2 program package (MSI Inc.) was used to calculate the interaction of CO with the Sn-Pt metal cluster. The density functional approximation level with the nonlocal BP functional and the DND basis set was used for the system studied. The core electrons of the metal atoms were represented by relativistic effective core potentials (ECPs). The locations of these atoms were fixed during the calculations, their distances were taken from literature [15]. The geometry of the CO and its position relative to the metal cluster was fully optimized.

3. RESULTS AND DISCUSSION

Characteristic features of Sn-Pt/SiO₂ catalyst are given in Table 1. These data indicate that the introduction of tin strongly reduces the chemisorption of CO. Catalysts type (O) have slightly lower CO/Pt values than catalyst type (H). The activity of catalysts investigated by TPRe technique is also included into Table 1. The temperature, at which 50 % conversion has been achieved (T₅₀), was used to compare the activity of Sn-Pt/SiO₂ catalysts in the oxidation of CO.

Results presented below show that the Pt/SiO₂ catalyst is active only at high temperature. However, the introduction of tin significantly increases the activity of catalysts, resulting in a pronounced decrease of the T₅₀ values. The results given in Table 1 indicated that the decrease of the T₅₀ values strongly depended on the tin content and slight difference between (O) and (H) type catalysts was also be found.

Based on the above results the following conclusions can be drawn: (i) the introduction of tin into platinum by using CSRs leads to the formation of new type of active sites; (ii) (H) type catalysts are more active then (O) type, (iii) the activity of catalysts passes through a maximum with the Sn/Pt (at/at ratio). These experimental results indicate that '*Sn*^{IV} – *Pt*' *ensemble site* formed during the reaction is highly active in the oxidation of CO. The

slight difference between (O) and (H) type catalysts can be attributed to the presence of traces of inactive ionic forms of tin in (O) type catalysts after re-reduction at 340 °C.

Table 1. Composition, CO chemisorption and activity of Sn-Pt/SiO₂ catalysts.

Catalysts	Sn/Pt (at/at) [a]	CO/Pt ^[b]		T ₅₀ , °C ^[c]	
		(H) type	(O) type	(H) type	(O) type
Pt/SiO ₂	-	0.550		177	
Sn-Pt/SiO ₂ (I-1)	0.22	n.a.	0.278	100	103
Sn-Pt/SiO ₂ (I-2)	0.41	0.245	0.210	63	69
Sn-Pt/SiO ₂ (I-3)	0.55	n.a.	0.199	n.a.	64
Sn-Pt/SiO ₂ (II-1)	0.60	0.210	0.204	50	73
Sn-Pt/SiO ₂ (I-4)	0.81	0.168	0.177	60	n.a.
Sn-Pt/SiO ₂ (I-5)	0.97	n.a.	0.157	117	130

[a] Sn/Pt (at/at) values calculated from the actual Pt and Sn content determined by AAS; [b] chemisorption data; [c] activity of catalysts in CO oxidation, expressed as the temperature at which 50 % conversion has been obtained; p_{CO} = 80 torr; p_{O₂} = 40.5 torr (heating rate = 5 °C/min, temperature ramp from 25 to 300 °C).

In preliminary time on stream experiments under adiabatic conditions (starting the reaction at 22 °C) using catalyst N° I-4 (O) at SV = 30.000 ml/(g_{cat})⁻¹ h⁻¹ 12 % conversion has been obtained after 3 hours time on stream, that corresponds to TOF as high as 0.13 s⁻¹.

Additional experiments were carried out to investigate the stability of Sn-Pt/SiO₂ catalysts. These results can be summarized as follows: (i) only reduced form of the catalyst show high activity; (ii) the high activity of the catalysts can always be restored after re-reduction; (iii) the re-reduction temperature has an optimum value at 340 °C; (iv) when oxygen is introduced first the activity of catalysts decreases; (v) the decrease of the CO partial pressure from 80 torr to 8 torr resulted in lower T₅₀ values (catalyst II-1 (H): T₅₀ = 39 °C).

Mössbauer spectroscopy has been applied to characterize the Sn-Pt/SiO₂ catalysts prior to the reaction and in situ in the catalytic run. In these experiments catalysts with Sn/Pt (at/at) > 0.6 were investigated. From these studies the following conclusions can be drawn: (i) Sn-Pt/SiO₂ catalysts as received contains two Pt-Sn alloy phases (Pt rich (a) and Sn rich (b)) and one Sn⁴⁺ species (with isomer shifts around 1.30, 2.20; and 0.40 mm/s, respectively) (ii) after reduction at 340 °C only the alloy phases were detected on both (H) type and (O) type catalysts, however in (O) type catalyst the presence of Sn⁴⁺ species in trace amount

cannot be excluded; (iii) the CO + O₂ reaction at room temperature resulted in the appearance of Sn⁴⁺ component on the *surface* of bimetallic particles as can be suggested from the large $\text{dln}(A_{77}/A_{300})/\text{dT}$ respective values.

The high activity Sn-Pt/SiO₂ catalysts prepared by using CSRs was related to the ability of tin to perturbate the CO molecule chemisorbed on Pt. The corresponding density functional calculations of CO chemisorbed on the (11.0) surface of the SnPt alloy clearly supported the possibility of the perturbation of CO both by Sn⁰ and Sn^{IV} species leading to the bent form of CO chemisorbed on Pt. The extent of perturbation was more pronounced in case of CO - Sn^{IV} interaction leading to the decrease of the bond order and increase of the bond length of the CO molecule. The calculations show also that the energy difference between the bent and liner forms of CO interacting with the Snⁿ⁺-Pt ensemble sites has a pronounced minimum for Sn^{IV}. Consequently, the perturbed CO molecule is strongly bent towards Sn^{IV}.

We suggest that our Sn-Pt/SiO₂ catalysts should have various forms of '*Sn^{IV}-Pt ensemble sites*' with different Sn^{IV}:Sn_s:Pt_s ratio. Subsequent increase of the activity of these catalysts in CO oxidation requires the optimization of the Sn^{IV}:Sn_s:Pt_s ratio.

REFERENCES

1. J. Sárkány, M. Bartók and R. Gonzales, J. Catal., 81 (1983) 347.
2. Y. F. Yu Yao, J. Catal., 87 (1984) 152.
3. G. C. Bond, L. R. Molloy, M. J. Fuller, J.C.S. Chem. Comm., (1975) 796.
4. M. Sheintuch, J. Schmidt, Y. Lechtman and G. Yahav, Appl. Catal., 49 (1989) 55.
5. S. Gardner, G. B. Hoflund, M. R. Davidson and D. R. Schryer, J. Catal., 115 (1989) 132.
6. K. Grass and H.-G. Linz, J. Catal., 172 (1997) 446.
7. J. L. Margitfalvi, I. Borbáth, E. Tfirst and A. Tompos, Catal. Today, 43 (1998) 29.
8. J. L. Margitfalvi, Gy. Vankó, I. Borbáth, A. Tompos and A. Vértes, J.Catal., 190 (2000) 474.
9. a) V. Ponec, Appl. Catal. A:General, 149 (1997) 27. b) J. L. Margitfalvi, A. Tompos, I. Kolosova and J. Valyon, J. Catal., 174 (1998) 246.
10. W. Yu, H. Liu, M. Liu and Q. Tao, J. Mol. Catal. A:Chemical, 138 (1999) 273.
11. a) J. Margitfalvi, M. Hegedûs, S. Göbölös, E. Kern-Tálas, P. Szedlacsek, S. Szabó and F. Nagy, Proc. 8th Int. Congress on Catalysis, Vol. 4, VCH Weinheim, 1984, pp. 903-913; b) J. L. Margitfalvi, E. Tálas and S. Göbölös, Catal. Today, 6 (1989) 73.
12. J. L. Margitfalvi, I. Borbáth, M. Hegedûs S. Göbölös and F. Lónyi, React. Kinet. Catal. Lett., 68 (1999) 133.
13. S. Bhatia, J. Beltramini and D. D. Do, Catalysis Today, 7 (1990) 309.
14. K. Lázár, K. Matusek, J. Mink, S. Dobos, L. Guczi, A. Vizi-Orosz, L. Markó and W.M. Reiff, J. Catal., 87 (1984) 163.
15. C. Kappenstein, M., Guérin, K. Lázár, K. Matusek and Z. Paál, J. Chem. Soc., Faraday Trans., 94 (1998) 2463.