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RESEARCH NOTE

Characterization of Sn–Pt/SiO_2 Catalysts Used in Selective Hydrogenation of Crotonaldehyde by Mössbauer Spectroscopy

J. L. Margitfalvi,*[,1] Gy. Vankó,† I. Borbáth,* A. Tompos,* and A. Vértes†

**Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Pusztaszeri út 59-67, 1025 Budapest, Hungary; and †Research Group for Nuclear Methods in Structural Chemistry, Hungarian Academy of Sciences at Eötvös Loránd University, P.O. Box 32, H-1518 Budapest, Hungary*

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Upon treatment of Sn–Pt/SiO_2 catalysts with crotonaldehyde (CA) at 80°C formation of Sn^{4+} species was evidenced by Mössbauer spectroscopy. These results have confirmed the earlier suggestion that the "reaction induced selectivity improvement" observed in the hydrogenation of CA to crotylalcohol over Sn–Pt/SiO_2 catalysts is related to the formation and stabilization of ionic forms of tin in the atomic closeness to the platinum. It is suggested that in our Sn–Pt/SiO_2 catalysts the formed Sn^{4+} species are responsible for the activation of the carbonyl group, while further hydrogenation of crotylalcohol to *n*-butanol is prevented by the presence of a tin enriched Sn–Pt alloy phase on which the readsorption of crotylalcohol is strongly hindered. © 2000 Academic Press

Key Words: **Mössbauer spectroscopy; Sn–Pt/SiO_2 catalysts; controlled surface reactions; selective hydrogenation of crotonaldehyde; reaction induced selectivity improvement.**

INTRODUCTION

Recently it has been reported that supported noble metals promoted by Fe, Sn, and Ge are very promising catalysts to hydrogenate α,β-unsaturated aldehydes into α,β-unsaturated alcohols (1, 2). It has also been demonstrated that high selectivities to unsaturated alcohols ($S_{C=O}$ selectivity) can be achieved over tin modified Pt catalysts (1–3). The $S_{C=O}$ selectivity was further improved upon using Sn–Pt/SiO_2 catalysts prepared by using controlled surface reactions (CSRs) between adsorbed hydrogen and $Sn(C_2H_5)_4$ (4, 5). The selectivity of the Sn–Pt/SiO_2 catalysts prepared by using CSRs showed strong dependence of the Sn_{anch}/Pt_s ratio (Sn_{anch}/Pt_s = number of Sn atoms anchored per surface Pt atom (5)) and $S_{C=O}$ selectivity value as high as 78% (measured at 5% conversion) was obtained in gas phase hydrogenation of CA at 80°C (6).

With respect to the active form of tin involved in selective hydrogenation of the carbonyl group "the modification of the catalyst surface by oxygen retained from the reaction mixture" has been suggested (3). The role of ionic forms of tin in the activation of CA has been suggested by other authors (4–9); *however, the formation of these ionic forms of tin has not been experimentally proved yet.* For this reason, the aim of this research note is to provide direct evidence that (i) in gas phase hydrogenation of CA over Sn–Pt/SiO_2 catalysts prepared by CSRs the high $S_{C=O}$ selectivities are attributed to the formation of ionic forms of tin, (ii) CA is involved in the formation of ionic entities of tin, and (iii) there is an oxygen transfer from CA to tin. Methods of Mössbauer spectroscopy were used to (i) characterize the Sn–Pt/SiO_2 catalysts prepared by using CSRs, and (ii) follow the formation of Sn^{n+} species during the treatment with CA–hydrogen mixture.

EXPERIMENTAL PART

The Sn–Pt/SiO_2 catalysts were prepared from a 3 wt% Pt/SiO_2 catalyst by using CSRs between adsorbed hydrogen and $Sn(C_2H_5)_4$ (5). The tin anchoring procedure was slightly modified as small amount of oxygen (20 cm^3/g_{cat}) has been added to the reactor in the 40th min. It had been reported (5) that the addition of oxygen during the tin anchoring process strongly increases the amount of tin anchored. More details on the surface chemistry involved in the tin anchoring process can be found elsewhere (5, 6). The hydrogenation of CA has been carried out as depicted in our recent papers (4–6).

Mössbauer spectra of samples were recorded at 80 K with a constant acceleration spectrometer using a $Ba^{119}SnO_3$ source. All isomer shifts were referred to SnO_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

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[1] To whom correspondence should be addressed. Fax: 36-1-325-7554. E-mail: joemarg@cric.chemres.hu.

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holder sealed under inert gas or vacuum and hold at 80 K.

Samples type (I) with different Sn$_{anch}$/Pt$_s$ ratios were obtained by decomposition of surface organometallic complexes in a hydrogen atmosphere using temperature-programmed technique ($T_{final} = 350°C$). The Sn$_{anch}$/Pt$_s$ values have been calculated from the material balance of tin anchoring and the CO/Pt ratio (0.52) measured for the parent Pt/SiO$_2$ catalyst. These values were compared with results obtained by analysis of the tin content using AAS (5). Samples type (II) were prepared from the corresponding samples of type (I) by contacting with a CA-hydrogen mixture (11 Torr/750 Torr, 60 cm^3/min) at 80°C for 1 h. The transformation of CA during the treatment procedure was also monitored by GC-MS technique.

RESULTS AND DISCUSSION

Characteristic features of samples type (I) with different Sn$_{anch}$/Pt$_s$ (or Sn/Pt at/at) ratios are given in Table 1. As emerges from these data the increase of the initial concentration of tin tetraethyl results in a pronounced increase in the amount of tin anchored; consequently, upon using this mode of tin anchoring Sn–Pt/SiO$_2$ catalysts with high Sn$_{anch}$/Pt$_s$ ratios can be prepared.

The catalytic results obviously show that the Sn–Pt/SiO$_2$ catalysts are active in the hydrogenation of CA and have very high selectivity toward the formation of crotylalcohol ($S_{C=O}$ selectivity). The $S_{C=O}$ selectivity strongly increases with the Sn$_{anch}$/Pt$_s$ ratio. The $S_{C=O}$ selectivity value equal to 90% is the highest one which has ever been obtained on Pt-containing catalysts in the hydrogenation of crotonaldehyde.

TABLE 1

Characteristic Features of Samples Prepared

Catalysts	[SnR$_4$] (M)	Sn$_{anch}$/Pt$_s$	Sn/Pt at/at	R_o (μmol/g$_{cat}$)		$S_{C=O}$ (%)	
				60°C	80°C	60°C	80°C
Pt/SiO$_2$	—	—	—	0.6	1.6	0	0
Sn–Pt/SiO$_2$ (I-1)	0.010	1.2	0.6	3.3	7.5	65	58
Sn–Pt/SiO$_2$ (I-2)	0.066	2.0	1.0	na	na	71	65
Sn–Pt/SiO$_2$ (I-3)	0.090	2.5	1.3	0.9	2.4	90	77

Note. The Sn$_{anch}$/Pt$_s$ values have been calculated from the material balance of tin anchoring and the CO/Pt ratio (0.52) measured for the parent Pt/SiO$_2$ catalyst. The Sn/Pt (at/at) values were calculated from the actual Pt and Sn content determined by AAS. Conditions of catalytic experiments: $P_{CA} = 11$ Torr, $P_{H_2} = 750$ Torr; amount of catalyst = 0.08 g; flow rate = 30–220 cm^3/min. R_o was determined from the kinetic curves obtained at different space velocities; the selectivity values were measured at 5% conversion. Results were obtained in the "constant activity period" (4).

It is noteworthy that in this reaction a definite time on stream period was needed to obtain the high selectivity values, hence the observed phenomenon was ascribed as "reaction induced selectivity improvement" (3, 4). The formation of the active form of the catalyst takes place in this initial period.

Data given in Table 1 show also that the parent Pt/SiO$_2$ catalyst has no sites to hydrogenate CA into crotylalcohol.

Figure 1 displays the Mössbauer spectra of samples type (I) and (II) with different Sn$_{anch}$/Pt$_s$ ratios. The

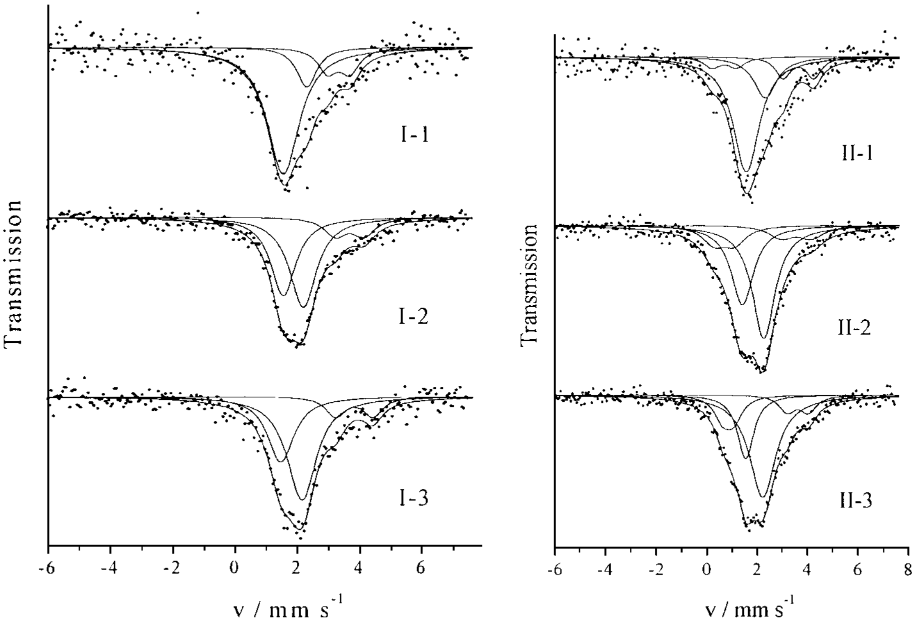

FIG. 1. Mössbauer spectra of Sn–Pt/SiO$_2$ catalyst samples with different Sn$_{anch}$/Pt$_s$ ratios. I, Original samples; II, samples obtained after treatment with crotonaldehyde. The Sn$_{anch}$/Pt$_s$ ratios of samples I-1, I-2, and I-3 are given in Table 1.

TABLE 2

Results of the Computer Evaluation of Mössbauer Spectra

Samples No.	Species	IS (mm s^{-1})	QS (mm s^{-1})	FWHM (mm s^{-1})	RI (%)
I-1	Sn–Pt(a)	1.56	—	1.23	70
	Sn–Pt(b)	2.31	—	0.75	14
	Sn^{2+}	3.33	0.71	0.75	16
I-2	Sn–Pt(a)	1.56	—	0.97	38
	Sn–Pt(b)	2.20	—	1.03	47
	Sn^{2+}	3.69	0.92	0.87	15
I-3	Sn–Pt(a)	1.49	—	1.03	32
	Sn–Pt(b)	2.15	—	1.13	54
	Sn^{2+}	3.82	1.19	0.76	14
II-1	Sn^{4+}	0.69	0.96	0.77	7
	Sn–Pt(a)	1.56	—	1.26	62
	Sn–Pt(b)	2.31	—	1.01	19
	Sn^{2+}	3.64	1.20	0.78	12
II-2	Sn^{4+}	0.71	0.80	1.09	13
	Sn–Pt(a)	1.42	—	1.07	31
	Sn–Pt(b)	2.28	—	1.12	46
	Sn^{2+}	3.57	1.18	1.19	10
II-3	Sn^{4+}	0.85	0.44	0.78	15
	Sn–Pt(a)	1.54	—	0.79	21
	Sn–Pt(b)	2.23	—	1.31	54
	Sn^{2+}	3.63	0.83	0.78	10

Note. 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.

corresponding data calculated from the spectra are summarized in Table 2. Data given in Fig. 1 and Table 2 indicate that the Sn–Pt/SiO_2 catalysts (see samples type (I)) contains two forms of tin: (i) alloy type, and (ii) Sn^{2+} species. The majority of tin is alloyed with platinum, while the minority is in Sn^{2+} form (see isomer shifts (IS) in the range of 1.49–2.31 and 3.33–3.82 mm s^{-1}, respectively (10–13)). The broad line of the alloyed phase indicates that our Sn–Pt/SiO_2 catalysts contain different types of tin–platinum alloy phases.

When fitting the Mössbauer spectra, the alloy fraction was divided into two alloy type species with isomer shifts around 1.39–1.56 and 2.23–2.31 mm s^{-1}, respectively. According to literature data (12, 13) the former species can be related to Pt_3Sn (Sn–Pt(a) phase), while the latter one can be related to $PtSn_4$ (Sn–Pt(b) phase). Note that alloy phases with intermediate compositions were also present, however, because of the substantial overlap of the spectral lines, we used the parameters belonging to these two extreme compositions for the fitting procedures. With this approach variations in the amount of the Pt-rich and Sn-rich phases could be easily followed.

In sample I-1 the platinum-rich phase (Sn–Pt(a)) is the main component (70.4% vs 13.5%), while in sample I-3 the tin-rich phase (Sn–Pt(b)) prevails (54.4% vs 31.7%). This fact points out also that upon increasing the Sn/Pt (at/at) ratio a gradual enrichment in tin of the alloy phase takes place.

It is worth noting that in our earlier study on Sn–Pt/Al_2O_3 catalysts with monolayer tin coverage ($Sn_{anch}/Pt_s = 0.4$) the IS of the alloy phase was in the range of 1.43–1.54 mm s^{-1}, indicating the exclusive formation of the Pt_3Sn alloy phase (14). In the present study the lowest Sn_{anch}/Pt_s ratio was 1.2, which resulted in Sn/Pt (at/at) ratio equal to 0.6, i.e., a value, that is higher than the Sn/Pt (at/at) ratio in the formed Pt_3Sn alloy obtained in case of monolayer tin coverage. In sample I-3 the Sn/Pt (at/at) ratio was 1.3; consequently, in this sample the formation of a tin-enriched alloy phase can be expected. The presence of this alloy phase has been evidenced by Mössbauer spectroscopy.

The existence of Sn^{2+} species in samples type (I) shows that certain part of tin anchored to the platinum cannot be fully reduced. Upon increasing the Sn/Pt (at/at) ratio the special contribution of Sn^{2+} species is almost constant. The mean value is around 15%. As far as the contribution of Sn^{2+} species was almost constant in samples type (I) (see Table 2), its formation was attributed to the use of oxygen during the anchoring reaction. It is tentatively suggested that this form of tin has been appeared on the platinum–support interface. As the ratio of Sn^{2+} species being independent of the amount of tin anchored, the introduction of tin into the support can be ruled out. The latter conclusion is in accordance with earlier experimental findings (5), namely the lack of decomposition peaks related to the formation of surface organometallic species, $–Sn(C_2H_5)_{(4-x)}$, formed on the silica support.

In samples type (II) both the Sn–Pt alloy phases and the Sn^{2+} form is maintained; however, due to the treatment with CA, a new form of tin appeared with IS 0.69–0.85 mm s^{-1}. Based on literature data (10–13) this form of tin was assigned as Sn^{4+}.

The formation of Sn^{4+} species in samples type (II) is considered as an indirect evidence for the “reaction induced activation” of supported Sn–Pt nanoclusters by the substrate. This activation has been suggested in earlier studies (1–4).

In samples type (II), i.e., upon treatment with CA, the contribution of the tin-rich Sn–Pt alloy phase (Sn–Pt(b)) compared to parent Sn–Pt/SiO_2 catalyst (samples type (I)) remained constant (see Table 2). The only exception is catalyst No. 1, which is very poor in this alloy phase (14%). Consequently, in samples I-1 and II-1 the relative error in the determination of the contribution of this phase is high.

Contrary to that the contribution of the platinum rich Sn–Pt phase (Sn–Pt(a)) decreased significantly, i.e., in samples Nos. 1, 2, and 3 upon treatment with CA the decrease in the RI values is 9, 7, and 11%, respectively. This fact suggests that in highly selective Sn–Pt/SiO_2 catalysts the Sn^{4+} species are formed mostly from the platinum rich Sn–Pt alloy phase.

TABLE 3

The Distribution of C_3–C_4 Hydrocarbons Formed during the Pretreatment of Pt/SiO$_2$ and Sn–Pt/SiO$_2$ Catalysts with Crotonaldehyde–Hydrogen Mixture

Catalysts	Propane	Propene	1,3-Butadiene	2-Butene	Butane
Pt/SiO$_2$	17	2	0	13	68
Sn–Pt/SiO$_2$[a]	0	0	91	9	0

[a] $Sn_{anch}/Pt_s = 1.4$; pretreatment at 80°C with crotonaldedyde–hydrogen mixture (11 Torr/750 Torr); samples accumulated in the first hour of pretreatment. The overall yield of hydrocarbons is around 4%.

It is worth mentioning that the IS of the Sn^{4+} species is relatively high. Similar high IS values were measured in oxygen and nitrogen containing tin organometallic compounds (14) and in the presence of delocalized diene type ligands (15), i.e., when strong electron donating ligands are in the coordination sphere of Sn^{4+}. This points to the formation and stabilization of Sn^{4+} species formed in the atomic closeness to the Sn–Pt nanoclusters by electron donor ligands such as CA or C_4 hydrocarbons. The latter were formed from CA during the treatment, i.e., in the period of catalyst activation.

In Table 3 the distribution of C_3 and C_4 hydrocarbons formed from CA on Pt/SiO$_2$ and Sn–Pt/SiO$_2$ catalysts during the treatment are compared. Over Pt/SiO$_2$ butane, while over Sn–Pt/SiO$_2$ butadiene is the main reaction product formed from CA. It is noteworthy that over Pt/SiO$_2$ catalyst C_3 hydrocarbons were also formed. The C_3 hydrocarbons can be formed by catalytic decarbonylation of CA. This observation is in a good agreement with our earlier FTIR data, where chemisorbed CO was detected on Pt after its contact with CA (4). The introduction of tin strongly decreased the decarbonylation reaction and at $Sn_{anch}/Pt_s = 2.3$ the decarbonylation reaction was completely ceased (4).

The formation of butadiene from CA observed only on tin-containing catalysts indicates the alteration of surface chemistry involved in catalyst activation. We consider the formation of butadiene as an indirect evidence for the oxygen transfer from an α,β-unsaturated aldehyde to supported Sn-Pt nanoclusters. This oxygen transfer is involved in the formation of Sn^{4+} species.

With respect to the formation of Sn^{4+}, i.e., species with high IS values, stabilization of SnO_xL_y type surface organometallic species, containing butadiene or CA as a stabilizing ligand, is suggested. These species should be formed in the atomic closeness of the active Sn–Pt phase. The activation of the carbonyl group of CA on these ionic forms of tin should have a crucial role in the selective hydrogenation of CA onto crotylalcohol. Another important issue is the dilution of the platinum surface with metallic tin (presence of tin-rich Sn–Pt(b) alloy phase), which strongly reduces the readsorption of crotylalcohol and its further hydrogenation to butanol.

CONCLUSIONS

In this study experimental evidence was obtained by Mössbauer spectroscopy on the formation of Sn^{4+} species when Sn–Pt/SiO$_2$ catalysts with different Sn/Pt (at/at) ratios were treated with CA at 80°C. The remarkably high selectivity of Sn–Pt/SiO$_2$ catalysts prepared by using CSRs can be attributed to the (i) the presence of ionic forms of tin, which activates the carbonyl group, and (ii) dilution of Pt sites with metallic tin, which suppresses the readsorption of the formed unsaturated alcohol. The strong cooperative effect of the above two phenomena is observed only at high Sn/Pt (at/at) ratios.

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REFERENCES

1. Marinelli, T. B. L. W., Nabuurs, S., and Ponec, V., *J. Catal.* **151**, 431 (1995).
2. Marinelli, T. B. W. L., and Ponec, V., *J. Catal.* **156**, 51 (1995).
3. Ponec, V., *Appl. Catal.* **149**, 27 (1997).
4. Margitfalvi, J. L., Tompos, A., Kolosova, I., and Valyon, J., *J. Catal.* **174**, 246 (1998).
5. Margitfalvi, J. L., Borbáth, I., Tfirst, R., and Tompos, A., *Catal. Today* **43**, 29 (1998).
6. Margitfalvi, J. L., Borbáth, I., and Tompos, A., *in* "Preparation of Catalysts VII" (B. Delmon, *et al.*, Eds.), p. 195. Elsevier, Amsterdam, 1998.
7. Didilon, B., El Mansour, A., Candy, J. P., Bournonville, J. P. and Basset, J. M., *in* "Heterogeneous Catalysts and Fine Chemicals II" (M. Guisnet *et al.*, Eds.), p. 137. Elsevier, Amsterdam, 1991.
8. Poltarzewski, A., Galvagno, S., Pietropaolo, R., and Staiti, P., *J. Catal.* **102**, 190 (1986).
9. Giroir-Frendler, A., Richard, D., and Gallezott, P., *in* "Heterogeneous Catalysis and Fine Chemicals," p. 171. Elsevier, Amsterdam, 1988.
10. Bacaud, R., Bussiere, P., and Figueres, F., *J. Catal.* **69**, 399 (1981).
11. Li, Y. X., Klabunde, K. J., and Davis, B. H., *J. Catal.* **128**, 1 (1991).
12. Kappenstein, Ch., Guerin, M., Lázár, K., Matusek, K., and Paál, Z., *J. Chem. Soc. Faraday Trans.* **94**, 2463 (1998).
13. Hobson, M. C., Jr., Goresh, S. L., and Khare, G. P., *J. Catal.* **142**, 641 (1993).
14. Vértes, Cs., Tálas, E., Czakó-Nagy, I., Ryczkowski, J., Göbölös, S., Vértes, A., and Margitfalvi, J., *Appl. Catal.* **68**, 149 (1991).
15. Harrison, P. G., and Zuckkerman, J. J., *J. Am. Chem. Soc.* **91**, 6885 (1969).
16. Kumar Das, V. G., Mun, L. K., Wei, Ch., Blunden, S. J., and Mak, T. C. W., *J. Organomet. Chem.* **322**, 163 (1987).