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# Low temperature oxidation of CO over tin-modified $Pt/SiO_2$ catalysts

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**Abstract**

Low temperature oxidation of CO over alloy type $Sn–Pt/SiO_2$ catalysts with different Sn/Pt ratios has been investigated at different CO partial pressure using thermal programmed oxidation (TPO) technique and time on stream (TOS) experiments. The introduction of tin into platinum strongly increased the activity of the catalyst. The activity had a maximum, which depended on both the Sn/Pt (at./at.) ratio and the CO partial pressure. TOS experiments revealed the aging of the $Sn–Pt/SiO_2$ catalysts. FTIR and Mössbauer spectroscopy has been used to follow compositional and structural changes of $Sn–Pt/SiO_2$ catalysts during the catalytic run. The results show that the in situ formed, highly mobile "$Sn^{n+}$–Pt" ensemble sites are responsible for high activity, while formation of relatively stable $SnO_x$ type surface species are involved in the catalyst deactivation. 

*Keywords:* $Sn–Pt/SiO_2$ catalysts; Low temperature CO oxidation; Mössbauer spectroscopy; FTIR spectroscopy; "$Sn^{4+}$–Pt" ensemble sites

## 1. Introduction

In our recent studies it has been shown that $Sn–Pt/SiO_2$ catalysts prepared by an organometallic method using controlled surface reactions (CSR) [1,2] are highly active in the oxidation of CO at room temperature [3,4]. In these catalysts after reduction in hydrogen at 573 K, the supported Sn–Pt nanoclusters contained two alloy phases: (i) a platinum-rich [PtSn(a)], and (ii) a tin-rich one [PtSn(b)], accounting for more than 85% of tin [5]. Preliminary in situ FTIR and Mössbauer spectroscopy results indicated [4] that in CO oxidation both alloy species are oxidized resulting in a pronounced surface reconstruction. The net result of these transformations is the formation of highly active "$Sn^{4+}$–Pt" ensemble sites, where $Sn^{4+}$ sites are in the atomic closeness of Pt.

It is important to note that earlier the formation of "$Sn^{4+}$–Pt" ensemble sites has also been suggested in $Pt/SnO_2$ catalysts used in low temperature CO oxidation [6]. As it has been proposed by Grass and Linz [6] in $Pt/SnO_2$ catalysts the above ensemble sites are located at the perimeter of Pt nanoclusters at the metal–support interface. Contrary to that in our $Sn–Pt/SiO_2$ catalysts the "$Sn^{4+}$–Pt" ensemble sites formed from the Sn–Pt alloy phases in the reversible $PtSn \leftrightarrow Sn^{4+} + Pt$ interconversion taking place at room temperature are located at the surface of the reconstructed supported Sn–Pt nanocluster.

In the present study further experimental evidences will be provided to demonstrate the high activity of alloy type $Sn–Pt/SiO_2$ catalysts in low temperature CO oxidation. In addition, FTIR and Mössbauer

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spectroscopic evidences will be provided to show the surface reconstruction of Sn–Pt/$SiO_2$ catalysts under condition of room temperature CO oxidation.

## 2. Experimental part

A 3% Pt/$SiO_2$ catalyst (CO/Pt = 0.42) was used as a parent catalyst. Tin tetramethyl ($^{119}Sn(CH_3)_4$) and tin tetraethyl ($Sn(C_2H_5)_4$) was applied as tin precursor compounds. The tin anchoring was carried out in benzene at 323 K in a hydrogen atmosphere for 2 h. Details on the preparation of Pt/$SiO_2$ and Sn–Pt/$SiO_2$ catalysts can be found elsewhere [1,3,7].

The decomposition of multilayer organometallic complex (MLOC) was accomplished in both reductive and oxidative atmospheres by temperature programmed reaction (TPRe) technique (heating rate = 5 K/min, temperature ramp from 295 to 613 K), resulting in alloy type Pt–Sn nanoclusters ((H) type catalysts) [5,8] or finely dispersed $SnO_x$ ($x = 2$, or 4) over platinum ((O) type catalysts) [2,5], respectively. In the present study, the preference was given to the use of (H) type catalysts. In both types of Sn–Pt/$SiO_2$ catalysts after reduction at 613 K the tin–platinum alloy phases are the main components and the amount of ionic forms of tin is less than 10–15% [5].

In this study Sn–Pt/$SiO_2$ catalysts with different Sn/Pt (at./at.) ratio were prepared resulting in Sn–Pt/$SiO_2$ catalysts with Sn/Pt (at./at.) ratio up to 1.12. This value strongly exceeds the monolayer coverage of platinum nanoclusters by $SnR_{(4-x)}$ moieties ($Sn_{mono}/Pt$ (at./at.) = 0.2). Chemisorption measurements using CO and hydrogen were done using ASDI RXM-100 equipment. The main characteristics and general properties of catalysts prepared are given in Table 1.

Mössbauer spectra were recorded at 300 and 77 K with a constant acceleration spectrometer using a $Ba^{119}SnO_3$ source. Details on the experimental set-up and the methods used can be found elsewhere [9]. A (H) type Sn–Pt/$SiO_2$ catalyst with Sn/Pt (at./at.) = 0.68 reduced in hydrogen at 573 K for 90 min was investigated after different treatments and in situ in the presence of CO and oxygen. The in situ experiments were carried out at room temperature at a constant flow of $CO + O_2$ (1:1) mixture (2 ml/min for 1.5 h).

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 [10]. Catalyst samples were ground-sieved, pressed onto self-supporting disks and were mounted in the sample holder. The weight of the self-supporting disks 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. The catalysts were re-reduced in hydrogen

Table 1
Characteristic feature of catalysts prepared

| Exp. No. | Conditions of tin anchoring[a], $[Sn]_0/Pt_{surf}$ | Amount of tin anchored, Sn/Pt (at./at.) | Chemisorption data | |
|---|---|---|---|---|
| | | | H/Pt | CO/Pt |
| 1[b] | – | – | 0.366 | 0.421 |
| 2[c] | 0.37 | 0.15 | 0.293 | 0.338 |
| 3[c] | 0.74 | 0.18 | 0.269 | 0.314 |
| 4[c] | 1.61 | 0.27 | 0.218 | 0.288 |
| 5[c] | 2.16 | 0.31 | 0.171 | 0.235 |
| 6[c] | 2.82 | 0.48 | 0.168 | 0.224 |
| 7[c] | 3.36 | 0.56 | 0.164 | 0.223 |
| 8[c] | 4.52 | 0.70 | 0.169 | 0.226 |
| 9[c] | 11.46 | 1.12 | 0.099 | 0.183 |

[a] Ratio of the amount of tin tetraalkyl used to the amount of surface Pt atoms.
[b] Parent Pt/$SiO_2$ catalyst.
[c] Sn–Pt/$SiO_2$ catalysts.

at 613 K for 2 h followed by evacuation at the same temperature for 1 h and cooling to room temperature under vacuum ($10^{-3}$ mbar). FTIR spectra were measured at 10 and 50 Torr pressure of CO, while the oxygen pressure was 5 or 25 Torr, respectively. The spectra were obtained after accumulation of 200 scans. First the background spectra were measured, followed by the introduction of CO. In the presence of CO spectra were taken after 5, 15 and 30 min. Spectra taken after 30 min were used for comparison. In the next step oxygen was added to the IR cell and spectra were taken after 5, 15, 30 and 60 min.

Temperature programmed oxidation (TPO) technique (heating rate = 5 K/min, temperature ramp from 243 to 523 K) was used to study the oxidation of CO with oxygen. In TPO experiments 0.075–0.150 g catalyst was applied using a gas mixture of CO and oxygen in helium. The partial pressure of CO and $O_2$ was in the range 16–79 and 40 Torr, respectively. The space velocity was 30 000 ml $g_{cat}^{-1}$ $h^{-1}$. Similar space velocity was also maintained in TOS experiments. The TPO curves were monitored recording the $m/e = 28$, 32, and 44 signals of CO and oxygen consumed and $CO_2$ formed, respectively. Prior to the reaction the catalysts were re-reduced at 613 K for 1.5 h in a hydrogen atmosphere and cooled down to 243 K in helium. In time on stream (TOS) experiments a gas mixture containing 2.1 vol.% CO and 5.9 vol.% oxygen in helium was applied. Prior to the reaction the catalysts were re-reduced at 613 K for 1.5 h in a hydrogen atmosphere (flow rate 50 ml/min).

## 3. Results

### 3.1. Catalyst preparation and characterization

Table 1 contains the characteristic features of Sn–Pt/$SiO_2$ catalysts prepared. These results indicate that the amount of tin introduced depends on the amount of tin tetraethyl used, i.e., on the $[Sn]_0/Pt_{surf}$ ratio. The introduction of tin decreases significantly with 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. These results are in good agreement to corresponding literature data [11] and our earlier findings [1–5].

### 3.2. Study of CO oxidation using TPO technique

Selected TPO curves obtained at $P_{CO} = 16$ Torr are shown in Fig. 1. The temperature, at which 50% CO conversion has been achieved ($T_{50}$), was used to compare the activity of catalysts. These values are shown as a function of the Sn/Pt (at./at.) ratio in Fig. 2. As

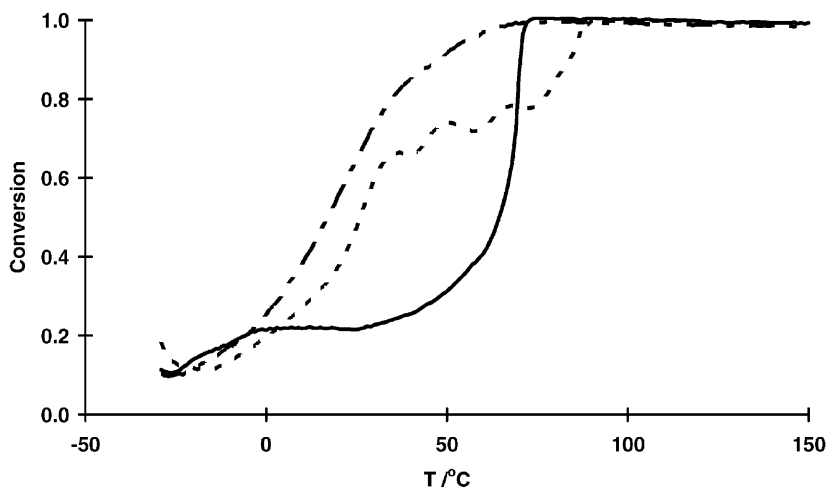


Fig. 1. Temperature programmed oxidation of CO over Pt/$SiO_2$ and Sn–Pt/$SiO_2$ catalysts. $P_{CO} = 16$ Torr, catalysts: (—) Pt/$SiO_2$; (— - —) Sn–Pt/$SiO_2$ (Sn/Pt (at./at.) = 0.27); (- - -) Sn–Pt/$SiO_2$ (Sn/Pt (at./at.) = 0.15). Heating rate: 5 °C/min, $P_{O_2} = 40$ Torr, amount of catalysts: 0.15 g.

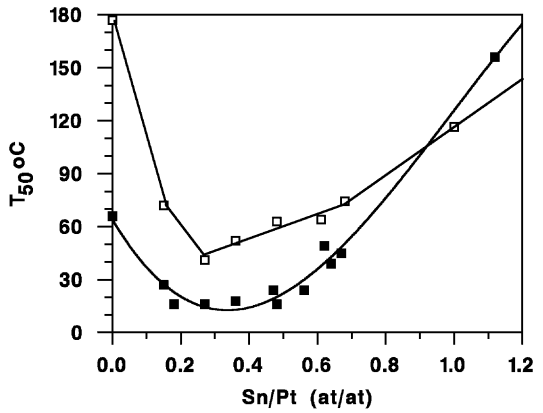


Fig. 2. Activity of Sn–Pt/$SiO_2$ catalysts in CO oxidation. Dependence of $T_{50}$ values of the Sn/Pt (at./at.) ratio. (□) $P_{CO} = 79$ Torr, (■) $P_{CO} = 16$ Torr.

emerges from Fig. 2 the addition of tin has a very pronounced effect on the activity of catalysts. Consequently, these results strongly demonstrate the role of tin in the activation of carbon monoxide. As it can be seen from Fig. 2 the CO partial pressure has also a significant influence on the activity of both Pt/$SiO_2$ and Sn–Pt/$SiO_2$ catalysts. The lower the CO partial pressure the higher the activity of both Pt/$SiO_2$ and Sn–Pt/$SiO_2$ catalysts. This finding is in accordance with the earlier observations [12], and can be related to the negative order in CO, i.e., to the self-poisoning of Pt sites by CO [13]. However, over Sn–Pt/$SiO_2$ catalysts, the poisoning effect of CO is much less than over Pt/$SiO_2$ catalysts. The difference can be attributed to the dissimilarity between the active sites involved in the CO oxidation. We can assume that the reaction occurring on "$Sn^{4+}$–Pt" ensemble sites does not depend very much on CO pressure in the studied range.

At $P_{CO} = 16$ Torr the optimum Sn/Pt (at./at.) ratio was between 0.2 and 0.5, while at higher CO partial pressure (79 Torr) the catalyst with Sn/Pt (at./at.) ratio 0.25 showed the highest activity. The loss of activity at higher Sn/Pt (at./at.) ratios was attributed to the poisoning effect of tin.

Some of the catalysts with low Sn/Pt ratio showed a slight oscillatory behavior in the low temperature region (see Fig. 1), what completely disappeared by increasing the heating rate form 5 to 10 K/min. It is known that supported Pt catalysts show an oscillatory behavior in this reaction [14].

### 3.3. CO oxidation, TOS results

Results of TOS experiments obtained at $P_{CO} = 16$ Torr are shown in Fig. 3. This figure shows moderate deactivation of the Sn–Pt/$SiO_2$ catalyst, however the initial activity of the catalyst could completely be restored after treatment the catalyst with hydrogen

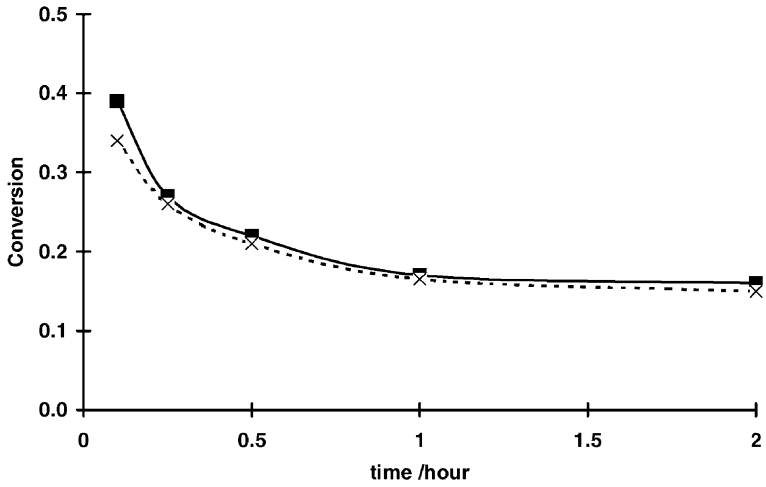


Fig. 3. CO oxidation under TOS conditions. Catalyst Sn–Pt/$SiO_2$ (Sn/Pt (at./at.) = 0.18); Temperature: 25 °C, $P_{CO} = 16$ Torr, $P_{O_2} = 40$ Torr, LHSW = 30 000 ml $g_{cat}^{-1}$ $h^{-1}$. Pretreatment in hydrogen at 613 K for 1.5 h. (■) First run, (×) second run after hydrogen treatment at 298 K.

at room temperature for 30 min. Similar results were obtained on all catalysts with Sn/Pt (at./at.) around 0.2–0.5 both at $P_{CO} = 16$ and 79 Torr.

It should be emphasized that the surface of the Sn–Pt/$SiO_2$ catalyst appeared to be very sensitive towards oxygen. The exposure of the catalyst to pure oxygen at room temperature for 15 min resulted in complete loss of the activity. When a Sn–Pt/$SiO_2$ catalyst (Sn/Pt(at./at.) = 0.48) was tested under TOS condition for 1 h at room temperature followed by a TPO experiment without re-reduction the $T_{50}$ value increased from 24 to 82 °C. However, the re-reduction in hydrogen at 340 °C for 1 h completely restored the original $T_{50}$ value. Similar activity change, i.e., the increase of the $T_{50}$ value from 24 to 75 °C has been observed when a repeated second TPO run was performed without any hydrogen treatment. These experiments indicate that undesired surface reconstruction takes place during the catalytic reaction and oxygen is involved in this process.

### 3.4. Characterization of catalysts by in situ Mössbauer measurements

Both 300 and 77 K in situ spectra were recorded under different experimental conditions on catalyst with Sn/Pt (at./at.) ratio 0.68. The results are shown in Fig. 4(A) and (B), respectively, and the corresponding data are summarized in Table 2.

The 300 K spectra can be considered as the "genuine" in situ spectra since they were obtained under the actual reaction conditions. Actually, the

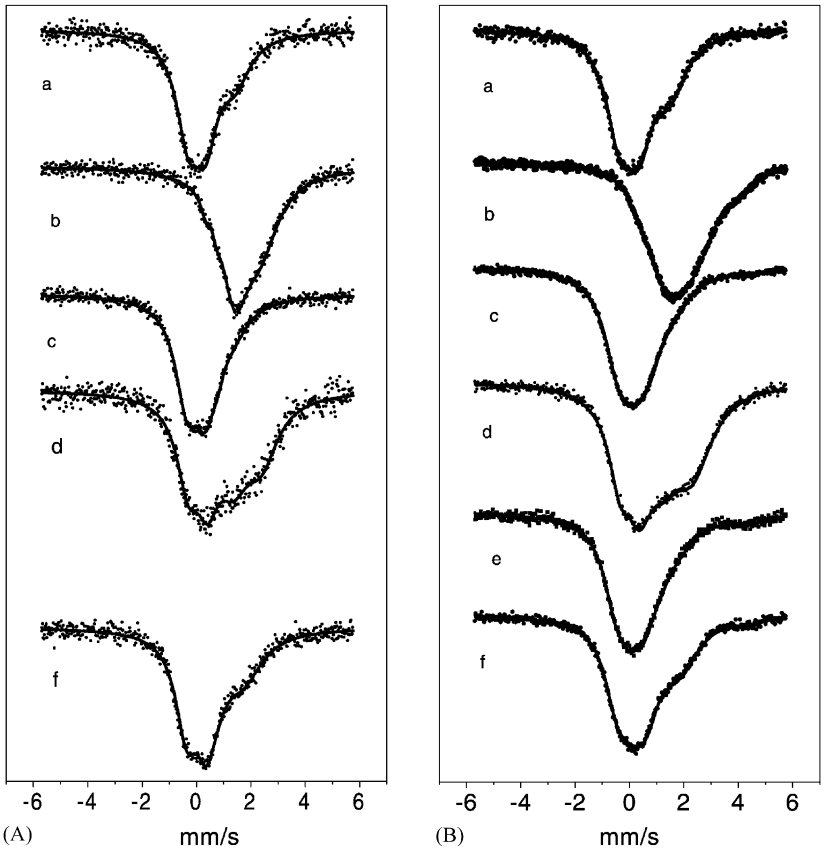


Fig. 4. Mössbauer spectra of (H) type Sn–Pt/$SiO_2$ catalyst with Sn/Pt (at./at.) = 0.68 at different experimental condition. (A) Spectra obtained at 300 K, (B) spectra obtained at 77 K. Catalyst samples: (a) as-received, (b) after reduction at 573 K in hydrogen, (c) in situ measurement in CO oxidation at 300 K, (d) in situ reduction in hydrogen at 300 K, (e) in situ measurement in CO oxidation at 300 K, (f) in situ treatment in CO.

Table 2
Mössbauer parameters obtained from 300 and 77 K spectra of (H) type Pt-Sn/$SiO_2$ used for 300 K oxidation of CO

| Samples[a] | Treatment | Comp. | Temperature (K) | | | | | | | | $\propto f_A$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 300 | | | | 77 | | | | |
| | | | IS | QS | FWHM | RI | IS | QS | FWHM | RI | |
| a | As-received | $Sn^{4+}$(ox) | 0.01 | 0.64 | 1.07 | 77 | 0.00 | 0.72 | 1.17 | 74 | 4.14 |
| | | PtSn(a) | 1.42 | – | 1.16 | 23 | 1.49 | – | 1.43 | 26 | 4.87 |
| b | 573 K in $H_2$ | $Sn^{4+}$(sf) | 0.53 | 0.43 | 0.39 | 4 | 0.49 | 0.42 | 0.59 | 6 | 7.43 |
| | | $Sn^{2+}$ | | | | | 2.88 | 2.11 | 1.06 | 9 | |
| | | PtSn(a) | 1.41 | – | 1.25 | 55 | 1.31 | – | 1.27 | 37 | 3.78 |
| | | PtSn(b) | 2.38 | – | 1.60 | 40 | 2.32 | – | 2.00 | 48 | 6.50 |
| c | 300 K in $CO + O_2$ | $Sn^{4+}$(ox) | 0.01 | 0.72 | 1.06 | 83 | 0.00 | 0.68 | 1.25 | 72 | 2.88 |
| | | $Sn^{4+}$(sf) | 0.93 | – | 0.88 | 8 | 0.86 | – | 1.10 | 16 | 6.28 |
| | | PtSn | 1.60[b] | – | 1.32 | 9 | 1.77 | – | 1.41 | 12 | 4.06 |
| d | 300 K in $H_2$ | $Sn^{4+}$(ox) | 0.05 | 0.71 | 1.03 | 45 | 0.04 | 0.70 | 1.09 | 42 | 5.49 |
| | | PtSn(a) | 1.36 | – | 1.54 | 32 | 1.22 | – | 1.58 | 24 | 4.53 |
| | | PtSn(b) | 2.39 | – | 1.48 | 23 | 2.31 | – | 1.79 | 33 | 7.35 |
| e | 300 K in $CO + O_2$ | $Sn^{4+}$(ox) | | | | | −0.19 | 0.57 | 1.10 | 53 | |
| | | $Sn^{4+}$(sf) | | | | | 0.66 | – | 1.24 | 29 | |
| | | $Sn^{2+}$ | | | | | 3.23 | 2.30 | 1.30 | 7 | |
| | | PtSn(a) | | | | | 1.40 | – | 1.41 | 12 | |
| f | 300 K in CO | $Sn^{4+}$(ox) | 0.00 | 0.73 | 0.99 | 64 | −0.02 | 0.71 | 1.13 | 62 | 3.54 |
| | | $Sn^{4+}$(sf) | 0.80 | – | 1.10 | 8 | 0.88[b] | – | 1.17 | 14 | 5.79 |
| | | PtSn | 1.72 | – | 1.74 | 27 | 1.86 | – | 1.69 | 24 | 3.14 |

[a] As shown in Fig. 3. IS: isomer shift, relative to $SnO_2$ (mm $s^{-1}$); QS: quadrupole splitting (mm $s^{-1}$); FWHM: line width (mm $s^{-1}$); RI: relative intensity (%), $\propto f_A = -d\ln(A_{300}/A_{77})/dT \times 10^{-3}$, where $A_{300}$ and $A_{77}$ are the actual absorption areas of components in the spectra recorded at 300 and 77 K, respectively).

[b] Constrained parameters.

300 K spectra reflect species formed under dynamic reaction conditions, while the 77 K spectra can be attributed to stabilized surface species.

In our recent studies [3,5] the alloy fraction was divided into two alloy type species with isomer shifts between 1.20–1.56 and 2.23–2.35 mm $s^{-1}$, respectively. Based on literature data [15–19] the former alloy species can be assigned either to tin dissolved in Pt (Sn $<$ 6 at.%) or to $Pt_3Sn$ (PtSn(a) phase), while the latter one can be attributed to tin-rich $Pt_2Sn_3$ and $PtSn_4$ phases (PtSn(b) phase). In a recent Mössbauer spectroscopic study preformed at 4.2 K on PtSn/MgO catalysts prepared upon using similar surface chemistry more composition ranges have been distinguished [17]. We confess that intermediate alloy phases with Sn/Pt (at./at.) around one can also be present in our Sn–Pt/$SiO_2$ catalysts. However, because of the substantial overlap of the spectral lines, we had to use the parameters belonging to these two extreme compositions for the fitting procedures. Upon using this approach the alterations in the amount of the Pt- and Sn-rich species could easily be followed. Therefore, in this work we shall differentiate only PtSn(a) and PtSn(b) alloy type species.

In as-received Sn–Pt/$SiO_2$ catalyst the dominating portion of the sample is $Sn^{4+}$ oxide ($Sn^{4+}$(ox)) (see spectrum a in Fig. 4(A) and (B)). It is due to the fact that the sample was kept in air prior the Mössbauer measurements. It is known that supported bimetallic Sn–Pt nanoclusters are very sensitive to oxygen [8]. The reduction of the catalyst at 573 K in hydrogen lead to the formation of bimetallic phases in great excess (see spectrum b in Fig. 4(A) and (B)). Similar to our recent studies [3,5] two Pt–Sn alloy species were distinguished, PtSn(a) with IS between

1.31 and 1.41 mm $s^{-1}$ and PtSn(b) with IS between of 2.32–2.38 mm $s^{-1}$. The $Sn^{2+}$ and $Sn^{4+}$(sf) components amount together to 4 and 15% of area in the spectra recorded at 300 and 77 K, respectively. It is worth mentioning that upon reduction at 573 K the $Sn^{4+}$(ox) species are completely absent. The $Sn^{2+}$ and $Sn^{4+}$(sf) species may have originated from organometallic species formed at the particle peripheries and subsequently become incorporated into the support [18–20]. Another possible explanation for the presence of ionic tin compounds is that their full reduction requires slightly higher temperature and longer time.

As emerges from Fig. 4(A) and (B) the character of in situ Mössbauer spectra taken in the presence of $CO + O_2$ at room temperature has been completely changed compared to the reduced form of the catalyst (compare spectra b and c). The oxidative atmosphere in the presence of CO resulted in: (i) oxidation of both PtSn(a) and PtSn(b) alloy species to $Sn^{4+}$ in a high proportion, and (ii) the appearance of a new alloy species with isomer shift around 1.60–1.77 mm $s^{-1}$. The isomer shift of this species is close to that of the PtSn (1:1) alloy phase [16–18], thus this third component has been denoted as PtSn (1:1) alloy species. In this sample an additional new component comes up with IS between 0.86 and 0.93 mm $s^{-1}$ (and after a repeated $CO + O_2$ treatment at 0.66 mm $s^{-1}$, as well (see spectrum e in Fig. 4(B))). Based on literature analogies this component has been assigned to $Sn^{4+}$ [18,19] and can be attributed to a well-dispersed surface species, $Sn^{4+}$(sf). This type of species has also been observed in our earlier studies [3,5].

After CO oxidation the room temperature treatment in hydrogen resulted also in very substantial changes in the composition of the catalyst. Interestingly, not only the mobile and highly reactive surface species, $Sn^{4+}$(sf), but part of $Sn^{4+}$(ox) is reversibly transformed to the original alloy phases. The reduction of the $Sn^{4+}$(sf) phase is complete and the proportion of $Sn^{4+}$(ox) decreases from 72 to 42% area in the spectrum at 77 K and simultaneously the platinum-rich PtSn(a) and the tin-rich PtSn(b) components reappear in 24 and 33% relative intensity, respectively. This result indicated that in room temperature hydrogen treatment 67% of the original alloy content has been restored. It should be emphasized that after room temperature re-reduction of the Pt–Sn (1:1) alloy phase was completely transformed back to the original alloy phases.

In a subsequent room temperature $CO + O_2$ treatment partial re-oxidation of Sn to $Sn^{4+}$(ox) and $Sn^{4+}$(sf) was evidenced with the simultaneous disappearance of the PtSn(b) component in the catalyst (see spectrum e in Fig. 4(B)). This experiment provided additional prove for the reversibility of nanocluster reconstruction. However, after treatment in pure CO (see spectrum f) the extent of reduction of the oxide phases into the alloy components is very small. This treatment resulted in only slight alteration in the ratio of the $Sn^{4+}$(ox) and $Sn^{4+}$(sf) phases. However, the shift of the IS value from 1.40 to 1.86 mm $s^{-1}$ might indicate on the significant increase of the tin content in this alloy phase. The above shift corresponds to the increase of tin from 6 to 50 at.% in average. In addition, the relative intensity of this PtSn (1:1) component is doubled in comparison to the previous tin-depleted PtSn(a) stage. The latter treatment clearly demonstrates that CO alone interacts with tin, however it is not able to induce any expressed $Sn^{4+} \rightarrow Sn^0$ reduction at room temperature either in the $Sn^{4+}$(ox) or the $Sn^{4+}$(sf) components.

### 3.5. Characterization of catalysts by FTIR

Fig. 5(A)–(D) shows the FTIR spectra of adsorbed CO on different catalysts in both the absence and presence of oxygen. These figures show that in the absence of oxygen upon increasing the Sn/Pt ratio a slight stepwise red shift of the carbonyl stretching frequency (from 2083 to 2069 $cm^{-1}$) occurs. This observation can be attributed to decreased dipole–dipole interaction due to the dilution of the surface of platinum with tin [21–23]. Upon increasing the tin content the intensity of bridged CO band around 1860 $cm^{-1}$ strongly diminishes. This observation is in accordance with earlier findings, i.e., with the decrease of the number of Pt–Pt neighbors upon increasing the Sn/Pt ratio [21–23].

Fig. 5(A)–(D) shows also that over the parent $Pt/SiO_2$ catalyst upon addition of oxygen the intensity of the CO band at 2083 $cm^{-1}$ almost constant, while over Sn–$Pt/SiO_2$ catalysts it decreases and the extent of this decrease strongly depended on the Sn/Pt (at./at.) ratio, and substantial intensity changes were observed over catalysts with Sn/Pt (at./at.) = 0.70

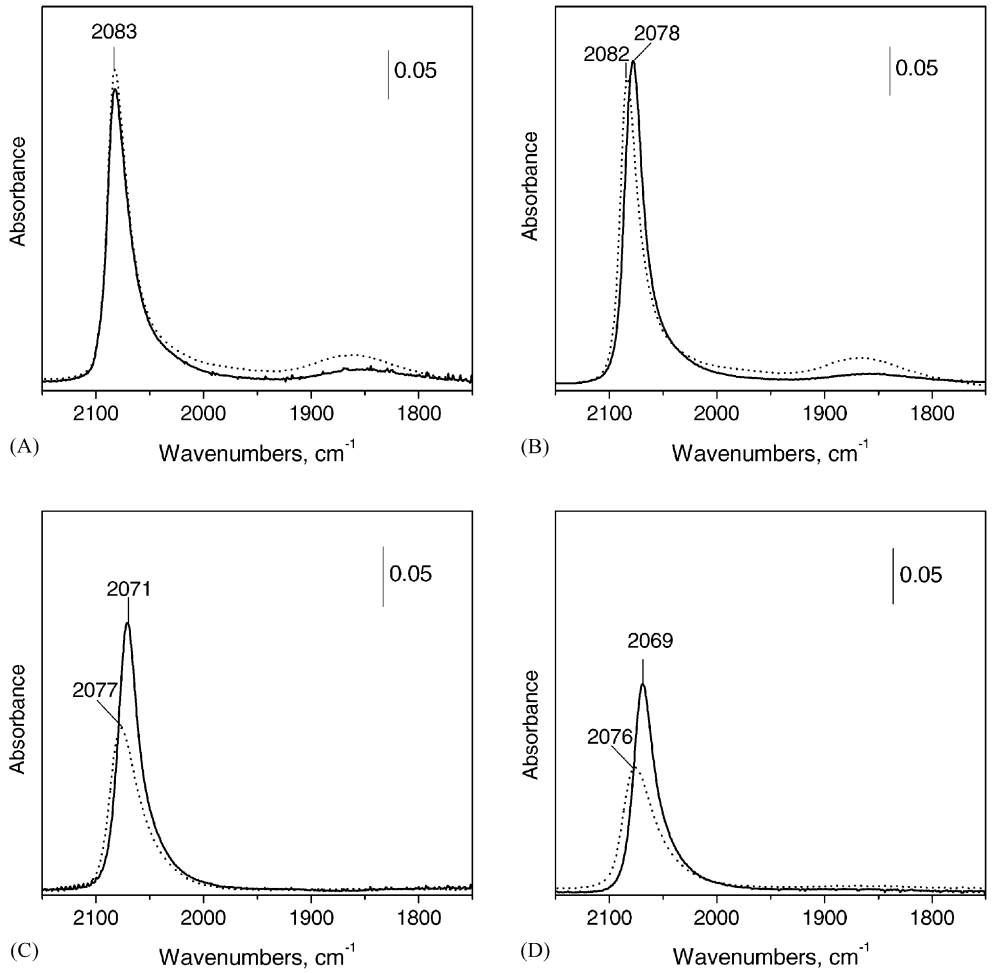


Fig. 5. FTIR spectra of adsorbed CO in the presence (···) and absence of oxygen (—). (A) $Pt/SiO_2$ catalyst, (B) $Sn–Pt/SiO_2$ catalyst (Sn/Pt (at./at.) = 0.18), (C) $Sn–Pt/SiO_2$ catalyst (Sn/Pt (at./at.) = 0.70), (D) $Sn–Pt/SiO_2$ catalyst (Sn/Pt (at./at.) = 1.12). $P_{CO} = 10$ Torr, $P_{O_2} = 5$ Torr. Equilibrated room temperature spectra after 30 min.

and 1.12. On $Sn–Pt/SiO_2$ catalysts in the presence of oxygen a slight blue shift of the linear carbonyl band was also observed. This shift depended also on the Sn/Pt ratio and had a maximum around 7 $cm^{-1}$ over catalyst with Sn/Pt (at./at.) ratio = 1.12.

In all catalysts the introduction of oxygen resulted in a slight increase of the intensity of the bridged CO. Over $Pt/SiO_2$ a slight frequency shift was also observed. On $Pt/SiO_2$ these changes were ascribed to the slight reconstruction of the adsorbed layer of CO, while on $Sn–Pt/SiO_2$ catalysts it was attributed to the formation of free Pt sites. Based on results of Mössbauer spectroscopy we suggest that oxidation induces surface segregation resulting in surface reconstruction. In this process different forms of tin oxide and free Pt sites are formed.

The difference spectra between spectra obtained in the presence of $CO + O_2$ mixture and CO measured at $P_{CO} = 10$ and 50 Torr, respectively, are shown in Fig. 6(A) and (B). These spectra were obtained on $Sn–Pt/SiO_2$ catalyst with Sn/Pt (at./at.) ratio = 0.27. As emerges from Fig. 6(A) at $P_{CO} = 10$ Torr no frequency shift can be seen, however the intensity decrease at 2070 $cm^{-1}$ and the parallel increase at

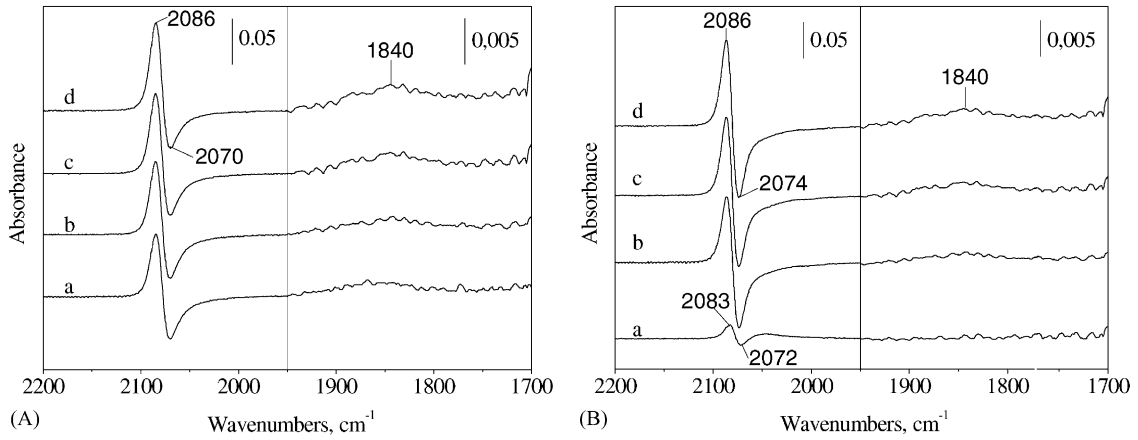


Fig. 6. Difference FTIR spectra of adsorbed CO in the presence and absence of oxygen on Sn–Pt/$SiO_2$ catalyst (Sn/Pt (at./at.) = 0.27). (A) $P_{CO} = 10$ Torr, $P_{O_2} = 5$ Torr; (B) $P_{CO} = 50$ Torr, $P_{O_2} = 25$ Torr. In situ room temperature spectra: (a) 5 min, (b) 15 min, (c) 30 min and (d) 60 min of reaction.

$2086\,cm^{-1}$ is quite substantial already after 5 min. These results indicated on both the fast surface reconstruction and the transformation of the original Sn–Pt alloy phase onto segregated phases of platinum and different forms of tin oxide. Parallel to the above changes notable permanent increase was also observed in the intensities of the $(CO)_{br}$ band around $1840\,cm^{-1}$.

The difference spectra obtained at $P_{CO} = 50$ Torr showed slightly slower stepwise surface reconstruction (see Fig. 6(B)). After 5 min exposure to oxygen the difference spectrum showed only a small decrease of intensity at $2072\,cm^{-1}$ and a corresponding slight increase at $2083\,cm^{-1}$. The increase of the exposure time resulted in both a blue shift of these bands to 2074 and $2086\,cm^{-1}$, respectively, and substantial intensity changes, similar that of measured at 10 Torr.

## 4. Discussion

Upon using controlled surface reactions between hydrogen adsorbed on platinum and tin tetraalkyls a series of Sn–Pt/$SiO_2$ catalysts containing almost exclusively silica supported $Sn_xPt_y$ nanoclusters have been prepared. The Sn/Pt (at./at.) ratio of the nanoparticles was increased up to 1.12. These catalysts with Sn/Pt (at./at.) = 0.2–0.5 showed high activity in low temperature CO oxidation. However, the results of TOS experiments revealed that the Sn–Pt/$SiO_2$ catalysts deactivate, but room temperature treatment in hydrogen completely restores the activity of the catalysts. Based on in situ FTIR and Mössbauer spectroscopic experiments the deactivation can be attributed to oxygen induced surface reconstruction.

As it has been evidenced by Mössbauer spectroscopy the supported $Sn_xPt_y$ nanoclusters contains both a platinum-rich and a tin-rich alloy phases. The ratio of these phases strongly depends on the bulk Sn/Pt (at./at.) ratio. During CO oxidation both alloy phases have been oxidized resulting in at least two different ionic forms of tin and a new alloy phase. However, both spectroscopic and catalytic results (TOS experiments) confirmed that the reconstruction did not led to full separation of tin and platinum as the original activity could be restored by room temperature regeneration in hydrogen. This regeneration clearly confirmed the $Sn^{4+} \leftrightarrow Sn^0$ transformation and partial restoration of both PtSn(a) and PtSn(b) phases. In this respect it is worth comparing the effects of 573 K reduction and room temperature reactivation in hydrogen: the corresponding IS values (i.e., their compositions) of PtSn(a) and PtSn(b) are very close and even their proportion is only slightly altered (compare samples b and d in Table 2).

The calculated $f_A$ values are in good agreement with general considerations, i.e., the low values are characteristic of strong ionic bonds (e.g., for a separate $SnO_2$

phase a value of $1.0 \times 10^{-3}$ is obtained [18]). However, in different tin complexes with looser bonds $f_A$ values close to $10^{-2}$ were obtained [24]. Strong interaction of tin with oxygen is reflected in the $f_A \approx 2.9 \times 10^{-3}$ value estimated for $Sn^{4+}$(ox) after $CO+O_2$ treatments. Contrary to that, after room temperature reactivation in hydrogen (see sample d), $Sn^{4+}$(ox) exhibits a significantly larger $f_A$ value ($5.49 \times 10^{-3}$) than in samples c or a. Further, the surface character of $Sn^{4+}$(sf) is reflected in large $f_A$ values ($6.28 \times 10^{-3}$) after $CO + O_2$ treatments. The comparison of PtSn(a) and PtSn(b) component the $f_A$ values provides further insight, i.e., for the tin-depleted PtSn(a) component, a relatively low $f_A$ value ($\propto f_A = 3.8$–$4.5 \times 10^{-3}$) has been obtained, indicating the incorporation of tin into the core of bimetallic particles. Whereas in PtSn(b) ($f_A \approx 6.5$–$7.4 \times 10^{-3}$) tin is more loosely bound.

The FTIR experiments are in a good accordance with the results of Mössbauer spectroscopy. As emerges from the analysis of difference spectra shown in Fig. 5(A)–(D) the primary interaction of supported Sn–Pt nanoclusters with the CO–oxygen mixture led to a strong reconstruction of supported Sn–Pt nanoclusters. The FTIR results indicated also that the bridged CO band appeared to be very sensitive in reflecting minor surface reconstruction (see Fig. 6(A) and (B)).

The slight frequency shift changes between difference spectra obtained at $P_{CO} = 10$ and 50 Torr can be attributed to the differences in the dipole–dipole interaction between adsorbed CO molecules. The higher coverage of CO, in some extent, slows also down the surface reconstruction induced by oxygen.

During the $CO + O_2$ reaction, the surface of the nanoparticles containing both mono and bimetallic sites is probably covered mostly by $Sn^{4+}$ species, while providing simultaneous access to CO both on free platinum sites and the Pt–Sn (1:1) alloy.

Based on in situ Mössbauer and FTIR spectroscopic results we suggest that in room temperature CO oxidation the supported Sn–Pt nanoclusters are completely reconstructed. The overall result of these transformations is the formation of the following new phases or sites:

(i) Stable tin oxide phase (IS = 0.0 mm s$^{-1}$, QS = 0.6–0.7 mm s$^{-1}$).
(ii) Highly mobile $Sn^{+4}$(sf) phase (IS = 0.86–1.12 mm s$^{-1}$).
(iii) Free platinum sites ($\nu CO^{lin}$ = 2086 cm$^{-1}$, $\nu CO^{br}$ = 1840 cm$^{-1}$).
(iv) An alloy phase, PtSn (1:1) (IS = 1.8 mm s$^{-1}$, QS = 0.6–0.7 mm s$^{-1}$).

Based on our results we suggest that the CO oxidation also takes place on the platinum–$SnO_x$ interface, i.e., on the "$Sn^{4+}$–Pt" ensemble sites similar as it has been suggested by Grass and Linz [6]. However, in our catalysts these sites are located at the surface of the reconstructed bimetallic nanoparticle and not at the metal–support interface. The role of ionic forms of tin in the "$Sn^{4+}$–Pt" ensemble sites is the activation of the chemisorbed CO molecule. Due to this activation the CO molecule is strongly perturbed resulting in high oxidation rates even at room temperature.

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