CO oxidation over Pt/SnO₂ catalysts

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Received: 19 December 2017 / Accepted: 27 February 2018 / Published online: 7 March 2018
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Abstract The influence of treatment conditions on Pt/SnO₂ properties and its catalytic activity in CO oxidation was investigated. It was found that the temperature and atmosphere of catalyst heating had a great impact on the active phase dispersion, the chemical composition of the surface layer and the O₂ adsorption capacity of the Pt/SnO₂ catalysts. TOF–SIMS analysis and XRD measurements showed that the heat treatment in an atmosphere of H₂ promotes the formation of bimetallic compounds of Pt–Sn and different species such as PtOH, PtO₂, PtO₂H, PtOCl, PtSnO, PtSnOH. It was stated that their presence significantly affects the activity of the catalyst in the CO oxidation. The catalyst capacity of O₂ adsorption varied depending on the treatment conditions. The catalyst treated at 600 °C in oxygen showed the greatest ability of oxygen adsorption. A significant difference in the activities between the catalyst samples heated in O₂ or H₂ atmosphere was found. The highest activity was obtained for 1%Pt/SnO₂ sample treated in oxygen at 700 °C. The treatment in hydrogen above 100 °C caused a decrease in the catalyst activity.

Keywords CO oxidation · Pt/SnO₂ catalysts · Oxygen adsorption · Bimetallic Pt–Sn compounds

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Introduction

Carbon monoxide, which poses a danger to our health and has a negative impact on the environment, is usually generated as a result of the incomplete combustion of carbon-containing substances. Catalytic oxidation of CO has found applications in air purification, recombination of CO and O₂ produced in closed cycle CO₂ lasers and CO sensors. Also, this reaction has been studied due to its application in the fuel cell systems to purify the feed hydrogen [1–3].

Effective catalysts for carbon monoxide oxidation are the noble metals deposited on chemically stable oxides such as Al₂O₃ or SiO₂ or on reducible oxides such as Fe₂O₃, NiO, ZnO, SnO₂ [4–10]. In the first case, CO oxidation occurs usually at temperatures above 100 °C, in the second, at lower ones. In the case of gold supported catalysts, CO oxidation occurs even at temperatures below 0 °C [11, 12]. Platinum catalysts supported on reducible oxides also show very high activity for carbon monoxide oxidation.

Researchers have devoted a lot of attention to platinum deposited on SnO₂ surface. Tin dioxide is an n-type semiconductor with a wide band gap (3.6 eV) and rutile bulk structure [13]. In the past decades, SnO₂ has attracted much attention for its various applications in catalysis, gas sensing, rechargeable Li battery and optical electronic devices [13–16]. It should be marked that SnO₂ is one of the most widely used semiconductor oxides for the manufacturing of sensors applied in the environment monitoring [17]. The gas sensors fabricated by using SnO₂ are devoted to the detection of many different gases such as: H₂, H₂S, CH₄ and CO [14, 15]. Chemisorption of oxygen by SnO₂ is crucial for the mechanism of gas detection occurring on resistive semiconductor gas sensors. A detailed mechanism of detection of different gases by resistive semiconductor gas sensors is described in papers [18–20].

In our previous work [21], we described the results of experiments which showed that there was a relationship between adsorption of oxygen on SnO₂ and its activity in CO oxidation. The most surprising feature of CO oxidation over SnO₂ was its high (although short-lived) activity after pretreatment in oxygen at temperatures higher than 500 °C. This phenomenon was explained as a result of the formation of highly reactive O[−] species, which were a kind of oxygen adatoms on the SnO₂ surface. It was also stated that the limiting step of the low temperature CO oxidation over the bare SnO₂ catalyst was the rate of oxygen re-adsorption. The relatively high activity of SnO₂ in the low temperature range was strictly limited by the concentration of adsorbed O[−] species. During CO oxidation, their concentration quickly and irreversibly decreases. Thus, all modifications of tin dioxide which enable oxygen adsorption at low temperatures will promote CO oxidation over SnO₂.

Pt/SnO₂ catalyst and its modifications were confirmed to be very active in oxidation of CO or CH₄ [15, 22–27]. The high catalytic activity of Pt/SnO₂ catalyst is usually explained by the spillover phenomenon [23] or synergism between the oxide and the platinum phases [25, 27]. In earlier works [15, 22], the formation of SnPt alloy phase was suggested. In an additional study [27], the authors assumed

that the reaction takes place at the Pt–SnO₂ interface. The last mechanism assumed adsorption of oxygen on the SnO₂ surface followed by its migration to the reaction sites situated at the border between oxide and platinum metal particles. The results discussed above firmly suggest that the mechanism of CO oxidation over Pt/SnO₂ catalyst is not clear and still controversial. However, in our opinion, it is mainly connected to the mechanism of oxygen adsorption and its transformations to reactive oxygen forms (species).

In the previous work [21], the properties of SnO₂ as a catalyst of CO oxidation were discussed. In the present paper, we have investigated the effect of Pt addition on SnO₂ oxygen adsorption capacity and its catalytic properties.

Materials and methods

Catalyst preparation

Platinum catalysts supported on tin oxide Pt/SnO₂ were prepared by the wet impregnation method. Commercial tin oxide (SnO₂, Aldrich Chemical Company, Inc.) with the specific surface area $a_s = 5.2 \text{ m}^2 \text{ g}^{-1}$ was used as a support for impregnation of Pt. The solution of hexachloroplatinic acid was used as a Pt source. The SnO₂ powder was impregnated with a desired amount of an aqueous H₂PtCl₆ solution. The Pt concentration in the catalyst was 1 wt%. After 24 h, water was evaporated and the samples were dried at 100 °C for 2 h and calcined in air at 400 °C for 2 h. In order to obtain samples with different catalytic activity but with identical Pt loading, the samples after calcination were reduced in hydrogen for 1 h in the temperature range 50–400 °C or heated in oxygen at 400–800 °C for 1 h.

Structural and morphological characterization of samples

X-ray diffraction (XRD) measurements

XRD measurements were performed in order to investigate changes in the phase composition of Pt/SnO₂ catalyst during reduction. These measurements were carried out in a PANalytical X'Pert Pro diffractometer equipped with an Anton Paar XRK900 reactor chamber. The X-ray source was a long fine focus X-ray diffraction copper tube operating at 40 kV and 30 mA. In situ transformations of a selected sample during reduction were analyzed using a mixture of 5% H₂—95% Ar. The sample was heated at a nominal rate of 1 °C per min. At chosen temperatures, X-ray diffraction data were collected. JCPDS-ICDD files were used for phase identification.

TOF–SIMS measurements

Time-of-flight secondary ion mass spectrometry (TOF–SIMS) was applied to characterize the composition of the catalyst surface as well as its changes depending on the treatment conditions. Secondary ion spectra were recorded with a TOF–SIMS

IV mass spectrometer (ION-TOF GmbH, Muenster, Germany). The analyzed area of the sample surface was $100\ \mu\text{m} \times 100\ \mu\text{m}$, and Bi_3^+ was used as a primary ion source. Secondary ions emitted from the catalyst surface were separated and counted in a high mass resolution TOF analyzer. The neutralization of the surface charge was obtained using a pulsed low-energy electron flood gun.

Chemisorption properties

CO chemisorption

CO chemisorption studies were carried out with the use of PEAK-4 apparatus [28]. We assumed that stoichiometry of chemisorption (CO/Pt) is equal to 1. The catalyst of 0.2 g was placed in a glass tube reactor with an internal diameter of 5 mm and was in situ reduced in the temperature range 50–400 °C for 1 h in H_2 stream with a flow rate $40\ \text{cm}^3\ \text{min}^{-1}$. Then the reactor was cooled to room temperature and a flow of H_2 was replaced by argon. Next, the pulses of $0.05\ \text{cm}^3$ CO were introduced to the reactor using a six-way valve. An infrared gas analyzer (Fuji type ZRJ-4) detected changes in the CO concentration behind the reactor.

The CO adsorption measurements were used to determine the dispersion of platinum (fraction exposed).

Oxygen adsorption

Oxygen adsorption was measured using the temperature programmed desorption method (TPD- O_2) with the application of a zirconium oxygen analyzer (Z110, Hitech Instruments Ltd., Luton, England). This device shows very high sensitivity (oxygen detection limit 0.1 ppm) and is highly selective to oxygen. The sample of 0.2 g was placed in a quartz reactor. Next, the samples were heated in O_2 atmosphere in the temperature range 400–800 °C for 1 h. After cooling to room temperature, the oxygen flow was replaced by argon and the temperature programmed desorption of oxygen was recorded in the temperature range 50–800 °C at a heating rate of $20\ ^\circ\text{C}\ \text{min}^{-1}$.

Temperature programmed reduction (TPR)

To check the structural stability of Pt/SnO_2 under reducing atmospheres, temperature programmed reduction (TPR- H_2) was carried out. TPR- H_2 experiments were performed in the PEAK-4 apparatus [28], using H_2/Ar (5 V% H_2 , 95 V% Ar) gas mixture with a flow rate of $40\ \text{cm}^3\ \text{min}^{-1}$ in the temperature range 25–800 °C with a linear ramp rate of $15\ ^\circ\text{C}\ \text{min}^{-1}$. Prior to the TPR- H_2 run, the sample of 0.2 g was in situ pretreated by heating in the gas mixture containing 80 V% O_2 in Ar for 1 h at the temperature of 500 °C, followed by cooling to room temperature. The changes of hydrogen concentration were detected by a thermal conductivity detector (TCD). The same measurement was also performed for the sample of bare SnO_2 .

Catalytic test

The temperature programmed surface reaction (TPSR) method was used to measure catalytic activity. The mass of the sample was 0.2 g and a linear increase in the temperature ($5\text{ }^{\circ}\text{C min}^{-1}$) was used. The reaction gas mixtures in CO oxidation contained 0.5 V% CO (99.5% synthetic air). The adjustment and monitoring of the total gas flow and temperature were computer controlled. For all tests, the total gas flow was kept constant and equal to 40 ml min^{-1} (space velocity 19100 h^{-1}).

The CO conversion was calculated based on the amount of produced CO_2 according to the following equation:

$$C_{\text{CO}} = \frac{c_{\text{CO}_2}}{c_{\text{CO}}} \times 100\% \quad (1)$$

Here c_{CO} and c_{CO_2} are the concentrations of CO and CO_2 in the reactor input and output. The concentration of CO_2 was continuously measured by the infrared gas analyzer (Fuji Electric System Co., type ZRJ-4). The catalytic activity was expressed as inverse temperature of 50% CO conversion ($1/T_{50}$).

Results

Characterization of samples

TPR- H_2 and XRD analysis

Fig. 1 shows the TPR- H_2 profile of SnO_2 and Pt/SnO_2 samples. The reduction of bare SnO_2 occurs in two temperature ranges: $280\text{--}400\text{ }^{\circ}\text{C}$ and above $450\text{ }^{\circ}\text{C}$. One can assume that in the first TPR temperature range, only the surface reduction of SnO_2 occurs according to the reaction:

In the second with the maximum at ca. $700\text{ }^{\circ}\text{C}$, the bulk reduction of SnO_2 to the metallic tin (Sn^0) takes place.

The presence of 1% platinum on the SnO_2 surface promotes reduction. It starts at ca. $50\text{ }^{\circ}\text{C}$ and the peak maxima are shifted towards a lower temperature. One can assume that at the lowest temperatures, hydrogen consumption is associated with the reduction of PtO_x oxides. These oxides can be easily reduced even at room temperature [29]. The presence of metallic platinum facilitates the reduction of tin dioxide. The reduction of SnO_2 is probably facilitated by spillover of hydrogen [30] followed by dissociative adsorption of hydrogen.

By comparison of the area under the TPR profiles (148 a.u. for SnO_2 and 172 for 1% Pt/SnO_2), it can be concluded that the presence of platinum on the surface of tin dioxide caused about a 16% increase in hydrogen consumption. This value is clearly too high. The integrated area of TPR peaks should be rather comparable for both

Fig. 1 TPR-H₂ profiles of the and support SnO₂ and 1%Pt/SnO₂ catalyst pretreated by heating in the gas mixture containing 80 vol.% O₂ in Ar for 1 h at the temperature of 500 °C. The experiments were using H₂/Ar (5 V% H₂, 95 vol.% Ar) gas mixture with a flow rate of 40 cm³ min⁻¹ in the temperature range 25–800 °C with a linear ramp rate of 15 °C min⁻¹

SnO₂ and 1%Pt/SnO₂ catalysts. To explain this discrepancy, it was assumed that the process of SnO₂ reduction without Pt was not total. The reduction of tin oxide by hydrogen under the experimental conditions is connected with the formation of metallic tin (Eq. 3). The melting point of tin is rather low and equals 232 °C. Thus, molten tin might form the shell around the SnO₂ particles. The effect of this phenomenon is that part of the tin dioxide remains still unreduced. In the case of the Pt/SnO₂ catalyst, molten tin creates PtSn alloys with platinum, which inhibits SnO₂ encapsulation. Nevertheless, the results show that SnO₂ is an oxide which is relatively easily reduced. This conclusion means that during Pt/SnO₂ reduction between platinum and tin dioxide, different chemical compounds can easily arise, among them PtSn alloy. Bimetallic PtSn catalysts are very efficient in different catalytic processes such as dehydrogenation or reforming [31, 32]. PtSn catalysts are also used in oxidation processes, including ethanol oxidation, catalytic oxidative dehydrogenation [33], and also in CO oxidation [34, 35] as well as preferential oxidation of CO in the presence of H₂ [36]. Tin in the bimetallic PtSn catalyst is believed to promote oxygen adsorption on the platinum surface [3].

The XRD study was used to determine the minimal temperature at which the interaction between Pt and SnO₂ leads to the formation of PtSn alloy. The sample was heated at a nominal rate of 1 °C/min in an atmosphere of 5% H₂ in argon. To make the XRD results more unequivocal, the catalyst with higher concentration of platinum (20%) was used, since for the 1%Pt/SnO₂ catalyst, the peaks attributed to Pt were not clearly visible.

Fig. 2 presents the XRD phase transformation with the increase in the temperature during the reduction of 20%Pt/SnO₂ catalyst. For the measurements performed at temperatures lower than 300 °C, the X-ray diffraction pattern of the Pt/SnO₂ catalyst shows only the diffraction peaks assigned to the SnO₂ support and metallic platinum. At the reduction temperature equal to 350 °C, the diffraction peaks of metallic platinum disappeared, while the peaks of PtSn₃ were observed. After reduction at 450 °C, the peaks which can be attributed to PtSn₂ are also observed. It must be noted that these alloys can be formed at lower temperatures. The absence of diffraction peaks indicates that their crystals can be very small. The lowest detection limit of the X-ray technique is around 4 nm.

The results presented above show that the relatively high reducibility of SnO₂ leads to the formation of PtSn alloys and different chemical compounds as a result of the interaction between Pt and SnO₂. These compounds, which were identified on the TOF–SIMS spectra and will be discussed in detail in the next Section, can also strongly determine both the adsorption capacity and catalytic properties of Pt/SnO₂ samples.

TOF–SIMS surface analysis

The TOF–SIMS method was used to analyze the chemical composition (elemental and molecular) of the surface of 1%Pt/SnO₂ samples. The measurements were performed for samples treated under different conditions. The results obtained for the calcined catalyst are treated as a reference. For each sample, two spectra (positive and negative secondary ions spectra) were collected. Normalization of each spectrum was performed. In this procedure, the emission intensity of the analyzed secondary ions was divided by the total ion emission achieved for the sample. Normalized intensities of selected ions calculated on the basis of the mass

Fig. 2 Diffractograms for 20%Pt/SnO₂ catalyst sample obtained during the catalyst reduction in a gas mixture containing 5% vol. H₂ and 95% vol. Ar. The sample was heated at a nominal rate of 1 °C/min. At chosen temperatures, X-ray diffraction data were collected. JCPDS-ICDD files were used for phase identification

spectra collected from the surface of the catalyst after their treatment under different conditions are presented in Tables 1 and 2.

Negative secondary ion spectra for all tested samples showed the presence of ions which mainly arise during the calcination of the catalyst precursor: PtO^- , PtOH^- , PtO_2^- , PtO_2H^- , PtOCl^- . The emission intensity of these ions varied depending on the atmosphere in which the catalyst was heated. For obvious reasons, treatment in the reduction atmosphere causes a decrease in the emission intensity of ions derived from Pt–O connections and an increase after heating in oxygen. Nevertheless, the surface of the catalyst after the reduction still contains different platinum-oxygen species. It is worth noticing that PtOCl species are also present on the catalyst surface. It means that the catalyst surface is contaminated with chlorine as a result of the incomplete decomposition of H_2PtCl_6 used in the preparation procedure.

Positive ion spectra for all tested samples showed the presence of ions characteristic of SnO_2 such as Sn^+ , SnO^+ , and also revealed the presence of bimetallic compounds containing Pt and Sn atoms. The last observations are in line with the XRD results (Sect. [TPR- \$\text{H}_2\$ and XRD analysis](#)). Table 2 shows the values of intensity ion emissions for ions derived from bimetallic compounds (PtSn^+ , PtSnO^+ , PtSnOH^+) and from SnO_2 (Sn^+ , SnO^+).

Thus, it can be accepted that platinum with SnO_2 relatively easily creates different Pt–Sn compounds or alloys. They arise actually during the calcination process and their final concentrations depend on the atmosphere and temperature of heating. In the light of these results and their interpretation, one can assume that the surface of the Pt/ SnO_2 catalysts is not clean, but is covered by different species.

The question remains whether these species play a significant or negligently small role in the process of CO oxidation over Pt/ SnO_2 catalysts. This question will be discussed in [Catalytic test](#) section.

Platinum dispersion

Metal dispersion is one of the most fundamental properties of supported metal catalysts and its determination is particularly important for the better understanding of the role of metal in the catalytic process. The dispersion of platinum in the studied catalysts, estimated on the basis of carbon monoxide adsorption is presented in Table 3.

Table 1 Normalized negative spectra for ions derived from platinum–oxygen compounds

Sample name	Normalized intensity					
	Pt	PtO	PtOH	PtO ₂	PtO ₂ H	PtOCl
Calcined	0.18	0.52	0.39	13.48	10.66	3.95
Ar 800 °C	0.52	0.11	0.11	1.08	0.83	0.81
O ₂ 800 °C	0.24	0.77	0.66	21.10	16.58	4.11
H ₂ 200 °C	0.24	0.56	0.38	10.75	8.73	5.41
H ₂ 300 °C	0.75	0.41	0.28	7.57	6.19	3.28

Table 2 Normalized positive spectra for ions derived from SnO_2 and from bimetallic compounds platinum–tin

Sample name	Normalized intensity						
	Sn	SnO	PtSn	PtSnO	PtSnOH	SnCl	SnCl ₂
Calcined	7.11	8.66	0.06	0.14	0.12	2.89	1.75
Ar 800 °C	11.30	9.47	0.08	0.16	0.16	3.45	2.40
O ₂ 800 °C	4.84	5.63	0.02	0.04	0.07	4.18	0.93
H ₂ 200 °C	10.37	0.00	0.08	0.16	0.22	3.09	1.59
H ₂ 300 °C	9.42	0.00	0.14	0.05	0.23	3.21	1.70

The Pt dispersion values for the studied catalyst are not very high. On the one hand, it can be connected with the low surface area of SnO_2 as a carrier, on the other it is related to the platinum surface contamination by various Pt–O–Sn species. Moreover, the presented results clearly show that dispersion of platinum strongly depends on the temperature of 1%Pt/ SnO_2 catalyst reduction. The increase in the reduction temperature at first leads to the increase in the amount of adsorbed CO, and next to its decrease. The maximum was observed at 100 °C. Above 300 °C, the adsorption of CO was negligibly small. The catalyst surface after reduction at a higher temperature becomes totally inactive to CO adsorption. These results mean that only insignificant part of the Pt atoms is exposed at the surface. Based on the relation between the crystallite size and dispersion on supported metal catalysts given by authors of work [37], platinum crystallite size was calculated. The results of these calculations show that the size of the platinum crystallite for the samples reduced at 50 and 100 °C is similar ≈ 8.5 nm, while for the samples reduced at 150 and 200 °C, it is very large (70 nm). On the other hand, it should be noted that in spite of the large size of platinum crystallites, they were not observed in the XRD pattern. To explain this discrepancy, we assumed that it is caused by the formation

Table 3 The volume of CO adsorbed on catalyst surface and dispersion of Pt in the 1%Pt/ SnO_2 catalyst treated under H_2 flow in the temperature range 50–400 °C

Temperature of heating in H_2 flow [°C]	V_{CO} [cm ³ /g]	Dispersion of Pt [%]
50	0.195	22.7
100	0.223	26.0
150	0.031	3.6
200	0.078	9.1
250	0.035	4.0
300	–	–
350	–	–
400	–	–

of PtSn or PtSnO bimetallic compounds which arise at higher temperatures (Tables 1, 2; Fig. 2). These compounds strongly reduce both the number of platinum surface atoms and the total one. However, in calculations, the total number of platinum atoms present in the sample was still the same. In our opinion, this fact causes that in the case of platinum supported on oxides with which different compounds are easily formed, dispersion cannot be a parameter used to calculate the size of Pt crystallites.

Moreover, it must be marked that carbon monoxide shows very high affinity only to the pure platinum [38] surface, therefore when it is not clean enough, adsorption of CO can be very low.

Oxygen adsorption

Oxygen adsorption on Pt/SnO₂ catalysts was studied using temperature programmed desorption (TPD-O₂). The TPD-O₂ profiles of the investigated samples are presented in Fig. 3. For comparison purposes, the TPD-O₂ profile for bare SnO₂ heated at 600 °C in oxygen preceding the TPD-O₂ process is also presented. The results shown in Fig. 3 indicate that all profiles for 1%Pt/SnO₂ catalyst are quite different from the TPD-O₂ profile of bare SnO₂. As it can be seen, the oxygen desorption from SnO₂ takes place in two stages. The maximum of desorption for the first stage occurs at ca. 600 °C and for the second at over 800 °C. TPD-O₂ studies over SnO₂ have been reported in a few works [17, 21, 39–41]. The general conclusion is that the course of TPD-O₂ strongly depends on the pretreatment of the catalyst surface preceding the process of desorption. Nevertheless, the peaks which arise at the highest temperatures are attributed to the removal of lattice oxygen O²⁻. However, the peaks which arise at lower temperatures are attributed to the

Fig. 3 The TPD-O₂ profiles of SnO₂ pretreated under O₂ flow at 600 °C and 1%Pt/SnO₂ catalyst pretreated under O₂ flow in the temperature range 400–800 °C (only selected temperatures are presented). The temperature programmed desorption of oxygen was recorded in the temperature range 50–800 °C at a heating rate of 20 °C min⁻¹

desorption of different oxygen species such as: O_2^- or O^- [21]. The authors of [40, 41] studied interactions between SnO_2 and O_2 . They reported desorption of four kinds of different oxygen species: O_2 at 80 °C, O_2^- at 150 °C, O^- (or O^{2-}) at 450–600 °C and lattice oxygen above 600 °C [40].

The presence of platinum on the surface of SnO_2 completely changes the TPD- O_2 profiles. The most surprising result is that the volume of O_2 released in the TPD- O_2 process for 1%Pt/ SnO_2 samples heated at 500 °C in oxygen was clearly lower than that recorded for bare SnO_2 . It is also worth noting that oxygen starts to desorb at a lower temperature and the high temperature stage of desorption is different than that recorded for SnO_2 . It was earlier mentioned that this stage is connected with desorption of lattice oxygen O^{2-} . As it can be seen, the Pt/ SnO_2 samples after calcination and heating at 400 or 500 °C in oxygen atmosphere are characterized by very low or no lattice oxygen released during the TPD- O_2 process. It can be postulated that the surface of SnO_2 despite heating in oxygen at 400 or 500 °C is either reduced or strongly contaminated.

Taking into account the way of preparation of the Pt/ SnO_2 catalyst, it can be concluded that probably the wet impregnation of the SnO_2 with the strongly acidic H_2PtCl_6 solution may lead to the modification of SnO_2 surface. According to TOF-SIMS results (TOF-SIMS surface analysis section), it can be assumed that the surface of tin dioxide in Pt/ SnO_2 catalysts calcined at temperatures lower than 600 °C is strongly modified by SnCl and SnCl_2 species, which arise during the wet impregnation of SnO_2 with H_2PtCl_6 solution.

For the samples heated in oxygen at the temperature above 600 °C, the shape of TPD- O_2 profiles shows that oxygen was also revealed in two forms. The first desorbs with a maximum at 650 °C and the second above 720 °C. Based on the analysis of these profiles, it can be concluded that oxygen desorbed in the second form was dominate.

Fig. 4 shows the amount of desorbed oxygen calculated on the basis of the TPD- O_2 profiles) depending on the heating in O_2 flow in the temperature range 400–800 °C.

Fig. 4 The amount of oxygen (calculated on the basis of the TPD- O_2 profiles) desorbed from the 1%Pt/ SnO_2 catalyst surface depending on the heating in O_2 flow in the temperature range 400–800 °C

Catalytic test

Fig. 5 shows the conversion of CO as a function of temperature for 1%Pt/SnO₂ sample heated in oxygen at different temperatures. Additionally, the catalyst was also tested in CO oxidation directly after calcination.

The catalytic activity of the sample heated in oxygen at the temperature up to 400 °C is practically identical to that after calcination. However, heating in oxygen at the temperature ≥ 500 °C leads to a very significant increase in catalytic activity. The most active catalyst was obtained by heating in oxygen at the temperature ≥ 700 °C.

Fig. 6 shows the conversion of CO as a function of temperature for 1%Pt/SnO₂ sample reduced in hydrogen at different temperatures in the range of 50–400 °C. As shown in this figure, the catalytic activity strongly depends on the reduction temperature.

The most striking feature of these results is that the activity of samples strongly decreases with the increase in the reduction temperature. The catalyst reduced at 100 °C exhibited the highest activity. The conversion starts at about 130 °C and 100% conversion is recorded at 180 °C. However, for the sample reduced at 300 °C, oxidation of CO starts at 180 °C and 100% conversion is recorded at 220 °C. It is quite obvious that the increase in the reduction temperature will lead to the increase in the reduction of catalysts. Thus, these results unequivocally testify that an increase in the reduction degree of Pt/SnO₂ catalyst causes its gradual deactivation. This deactivation may be caused by the formation different chemical compounds as a result of the interaction between Pt and SnO₂. (Tables 1, 2) or by the strong metal–support interaction (SMSI) effect. In the work [42], a strong interaction of Pt with the support BaSnO₃ and its impact on the catalyst activity in CO oxidation were studied. It was found that reduction promotes interaction between the metal and the support and also leads to the formation of various bimetallic compounds on the

Fig. 5 Conversion of CO as a function of temperature for 1%Pt/SnO₂ sample pretreated in the gas mixture containing 80 V% O₂ and 20 V% Ar. Pretreatment was carried out in the temperature range 400–800 °C with linear increase in the temperature equal to 20 °C min^{−1}. The CO oxidation was carried out to 300 °C with a linear increase in the temperature (5° min^{−1}), reaction gas mixtures contained 0.5 V% CO. For all tests, the total gas flow was kept constant and equal to 40 ml min^{−1}

Fig. 6 Conversion of CO as a function of temperature for 1%Pt/SnO₂ sample pretreated in hydrogen (100% vol. H₂) flow. Pretreatment was carried out in the temperature range 100–400 °C with linear increase in the temperature equal to 15 °C min⁻¹. The CO oxidation was carried out to 300 °C with a linear increase in the temperature (5° min⁻¹), reaction gas mixtures contained 0.5 V% CO. For all tests, the total gas flow was kept constant and equal to 40 ml min⁻¹

catalyst surface, e.g. Pt–Sn, Pt–O–Sn. Modification of catalyst surface composition affects its capacity of O₂ and CO adsorption which can result in the decreased catalytic activity.

According to the results from XRD and TOF–SIMS measurements, also in the case of Pt/SnO₂, the reduction treatment promotes the formation of intermetallic compounds such as PtSn. As was mentioned before, bimetallic PtSn catalysts are very efficient in different catalytic processes [31–36]. PtSn catalysts exhibit superior performance for CO oxidation compared to Pt catalysts. The generally accepted opinion is that the strong adsorption of CO which inhibits O₂ adsorption is the barrier to CO oxidation on Pt catalysts. Tin in the bimetallic PtSn catalyst is believed to promote oxygen adsorption on the platinum surface [3]. In the light of these literature conclusions, it could be expected that the presence of PtSn species would prefer catalytic activity of Pt/SnO₂ catalysts. The results presented above show the opposite trend.

Fig. 7 presents the catalytic activity of 1%Pt/SnO₂ catalyst samples subjected to heat treatment under various conditions. The 1%Pt/SnO₂ catalyst after reduction at 400 °C exhibited the lowest catalytic activity. Simultaneously, both XRD and TOF–SIMS measurements indicate that concentration of PtSn species after reduction at this temperature is the highest. Thus, why does the reduction process cause deactivation of Pt/SnO₂ catalysts despite the fact that concentrations of PtSn species increase?

The above problem is connected with a more general question about the mechanism of CO oxidation over the Pt/SnO₂ catalysts. The literature data [21, 38–41] show that the affinity of CO and O₂ to the platinum surface for these gases is quite different and the sticking coefficient of carbon monoxide is significantly higher than for oxygen. It means that carbon monoxide can be

Fig. 7 The catalytic activity (expressed as inverse of 50% conversion temperature) of 1%Pt/SnO₂ catalyst samples obtained by heating in **a** oxygen (gas mixture: 80 V% O₂ and 20 V% Ar, gas flow 40 ml min⁻¹, temperature range 400–800 °C, linear increase in the temperature equal to 20 °C min⁻¹, **b** hydrogen (100% H₂, gas flow 40 ml min⁻¹, temperature range 100–400 °C, linear increase in the temperature equal to 15 °C min⁻¹) atmosphere

adsorbed on platinum in the presence of oxygen with simultaneous inhibition of O₂ adsorption. That is why the supported platinum catalysts in which the support is able to adsorb oxygen are usually very active in the reaction of CO oxidation. Tin dioxide is a semiconductor which adsorbs oxygen. However, the results shown in work [21] testify that oxygen adsorption practically does not occur at temperatures lower than 300 °C. Moreover, the results shown in Figs. 3 and 4 revealed that the 1%Pt/SnO₂ catalysts practically do not adsorb oxygen at low temperatures. That is why the Pt/SnO₂ samples after heating in oxygen and at temperatures higher than 400 °C show a clear increase in catalytic activity.

Taking into account these considerations, it can be assumed that Pt/SnO₂ catalysts after reduction at a temperature higher than 200 °C lose not only affinity to CO adsorption but also to oxygen. The increase in the reduction temperature causes the increase in Pt–SnO₂ interaction and finally leads not only to the formation of

PtSn alloys but also to different types of PtSnO or PtOCl or SnCl species. Thus, when the catalyst was reduced at temperatures higher than 200 °C, the activity decreased significantly, indicating that during the reduction the surface of Pt is totally poisoned for both CO and oxygen adsorption. In contrast, when the same catalyst was heated in oxygen at 700 °C, its activity significantly increased. In the last case, the process of CO oxidation was observed at room temperature (Fig. 5). This indicated that the poisoning effect observed after reduction did not occur after heating in oxygen atmosphere. It is worth noting that concentration of the species which contain oxygen atoms increased after heating in oxygen atmosphere (Tables 1, 2). This conclusion is rather obvious, but the increase of catalytic activity indicates that mechanism of CO oxidation is other than for reduced samples. For these last samples, the mechanism of CO oxidation can be described by the equations:

If there is a deficiency of CO adsorption sites on Pt surface due to their poisoning by the presence of e.g. PtOCl species (Tables 1, 2), the activity of catalyst is low. During CO oxidation, the catalyst reduced at 300 °C requires about a 50 °C higher temperature to obtain the same conversion in comparison with the catalyst reduced at 100 °C (Fig. 6). Simultaneously, it should be noted that only catalysts reduced at temperatures lower than 250 °C adsorbed CO (Table 3). These results confirm that in the case of reduced Pt/SnO₂ catalyst, active sites are the surface Pt atoms which are very prone to deactivation.

However, the results presented in Figs. 5 and 7a clearly depict that treatment in oxygen causes an increase in the activity of Pt/SnO₂ catalysts. It can be assumed that the whole surface of the catalyst is saturated by oxygen. In this case, the mechanism of CO oxidation could be described by general equations:

These equations show that not only platinum is involved in the process of CO oxidation after catalyst treatment in oxygen atmosphere. Carbon monoxide from the gas phase reacts with oxygen which covers the catalyst surface. Thus, it is intelligible that heating at high temperatures in oxygen atmosphere has a strong and positive influence on the catalytic activity of Pt/SnO₂ catalyst.

Nevertheless, higher activity is limited only to the first TPSR run. The samples pretreated in oxygen at temperature 400 °C show that the second TPSR run is identical to the first one. However, when the sample is pretreated in oxygen at the

temperature ≥ 500 °C, the second TPSR run strongly changes in comparison with the first one. The catalytic activity significantly decreases. This fact indicates that during the first run adsorbed oxygen is completely removed from the surface of catalyst and that during CO oxidation the rate of oxygen re-adsorption is very low.

Conclusions

The conditions of heat treatment significantly affect the properties of the 1%Pt/SnO₂ catalyst and its activity in the CO oxidation. TPD-O₂ profiles indicate that from the catalyst surface desorption of various adsorbed oxygen forms takes place. The amount of adsorbed O₂ depends on the temperature of the catalyst heating. Heat treatment can lead to the formation of bimetallic compounds due to ease of carrier reduction. Reduction conditions greatly promote the formation of Pt–Sn connections. X-ray diffraction (XRD) measurements showed that reduction in H₂ flow leads to the formation of Pt–Sn alloy at about 350 °C but at lower temperatures Pt–Sn connections in TOF–SIMS spectra were observed. In the case of low Pt loading ($\leq 1\%$), the presence of Pt–Sn compounds significantly affects the activity of the catalyst in the CO oxidation and leads to the decrease in the catalyst activity. Therefore, there can exist an optimal ratio between Pt loading and Pt–Sn concentration on the catalyst surface at which the catalyst exhibits high activity in CO oxidation. The analysis of this relationship, however, will require further research. The highest activity achieved for the 1%Pt/SnO₂ catalyst treated in O₂ atmosphere is most probably related to the fact that the reaction can occur in accordance with more than one mechanism.

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