CO and H₂ oxidation over Pt/BaSnO₃ catalysts

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Abstract This work reports the results of the studies on oxidation of carbon monoxide and H₂ over Pt supported on barium stannate (BaSnO₃—perovskite type oxide). The composition and properties of Pt/BaSnO₃ catalysts were characterized by X-ray diffraction (XRD), time-of-flight secondary ion mass spectrometry (TOF–SIMS), H₂ and CO chemisorption, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS) and tested in the reactions of carbon monoxide and hydrogen oxidation. It was stated that platinum strongly interacts with BaSnO₃. The catalytic activity and adsorption properties of Pt/BaSnO₃ catalysts are determined by these interactions. The presence of different species (which generally can be labelled as [(Pt)BaSnO₃]) resulting from platinum and BaSnO₃ chemical interaction was found by the TOF–SIMS on surface of Pt/BaSnO₃ catalysts. The mechanism of CO and H₂ oxidation over Pt/BaSnO₃ catalysts was discussed in the light of strong interactions between Pt and BaSnO₃.

Keywords Pt/BaSnO₃ catalyst · Oxidation of CO · Oxidation of H₂

Introduction

Perovskite type oxides with a general formula ABO₃ or A₂BO₄ [1] show interesting catalytic properties. They attract great attention as catalysts for many oxidation processes, for example, total oxidation of hydrocarbons (methane, propane) [2, 3],

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chlorinated hydrocarbons [4, 5] and ammonia [6], being therefore proposed as an economical substitute for noble metal-based catalysts. They are also efficient catalysts for the oxidation of carbon monoxide [7–9]. Using perovskite-type oxides as supports for noble metals, one can expect even higher activity of such systems in CO oxidation. The oxidation reaction on perovskite type oxides usually occurs through two different mechanisms introduced by Voorhoeve et al. [10]. The first one, known as a suprafacial mechanism, is connected with chemisorbed oxygen, while the second (the intrafacial mechanism) corresponds to oxidation via lattice oxygen.

The mobility of oxygen is one of the most important factors governing the activity of catalysts according to the intrafacial mechanism. On the other hand, the possibility of oxygen adsorption determines the catalytic activity of perovskite oxides according to the superficial mechanism.

Barium stannate (BaSnO_3) is a typical perovskite oxide with a cubic lattice structure. Under ambient conditions of temperature and partial oxygen pressure it behaves as a pure n-type semiconductor [11]. The electrical properties of barium stannate such as electrical resistance, capacitance or impedance are dependent on temperature, partial oxygen pressure, the nature of the surrounding gases and their concentrations. Hence, in recent years, BaSnO_3 has been considered a very promising gas sensor material for the detection of many different gases like: H_2 or CO [12, 13].

The temperature at which sensitivity to CO reaches its maximum is usually higher than 600 °C [13, 14]. In the case of BaSnO_3 with supported Pt, the sensor operating temperature is markedly lower [15]. It can be assumed that for Pt/ BaSnO_3 sensors the mechanism of CO detection is connected with superficial oxidation of CO, while for BaSnO_3 with the intrafacial one. These processes can be described by the following reactions [12]:

The first reaction concerns the superficial oxidation, whereas the second refers to the intrafacial oxidation leading to the formation of the surface vacancy (V_o^*) connected with the reduction of oxide. Such mechanisms can also be considered as the Eley–Rideal (ER) (reaction 1) and the Mars–van Krevelen (reaction 2) [16, 17].

Thus, it is easy to notice that the sensitivity of sensors to CO is strongly determined by the catalytic property of the sensor material. A similar discussion can be applied to H_2 detection and its oxidation.

Thus, taking the above into consideration, it seems to be interesting to check the catalytic properties of barium stannate, also with supported platinum in CO and H_2 oxidation. To our knowledge, no papers describing the catalytic activity of BaSnO_3 or Pt/ BaSnO_3 catalyst in CO and H_2 oxidation have been published so far. We believe that our studies will lead to a better understanding of the catalytic process associated with CO oxidation over the perovskite type oxides catalyst as well as the

sensing mechanism which occurs during CO or H₂ detection over BaSnO₃ or Pt/BaSnO₃ gas sensors.

Experimental

Catalysts preparation

The synthesis of BaSnO₃ is widely described in works [14, 20–22]. In accordance with [20], the BaSnO₃ precursor was coprecipitated, using appropriate solutions in the reaction of SnCl₄·5H₂O with Ba(NO₃)₂ and NaOH due to the reaction:

The mixture of Ba(NO₃)₂ and SnCl₄ aqueous solution was precipitated by a solution of NaOH (2 mol/L). NaOH was slowly added with constant stirring at room temperature. The obtained white precipitate was washed with distilled water several times, dried at 120 °C for 16 h. It was identified as barium tin hydroxide (section “Characterization of BaSnO₃ sample”), which was calcined at different temperatures for X-ray diffraction tests. The results of this test show that barium tin hydroxide converts totally to BaSnO₃ at temperatures higher than 700 °C (Fig. 1). Thus, the precipitate was finally calcined at 800 °C in air for 4 h. Platinum (1–10 wt%) was deposited on BaSnO₃ by wet impregnation with an aqueous solution of H₂PtCl₆. The samples were dried at 110 °C and calcined in air for 4 h at 400 °C.

SnCl₄·5H₂O, Ba(NO₃)₂, H₂PtCl₆ were of analytical grade, while NaOH was pure grade. All compounds were produced by POCH (Poland).

Fig. 1 XRD phase transformation of precipitate formed in the reaction SnCl₄·5H₂O with Ba(NO₃)₂ during its calcination in air (heating rate 1 °C min^{−1}) in the temperature range of 20–850 °C

Structural and morphological characterization of samples

The specific surface area of BaSnO₃ samples was determined by the BET method using a Carlo Erba Sorptomatic 1900 apparatus.

XRD 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 selected samples during their calcinations or reduction were analyzed using air or a mixture of 5% H₂–95% Ar. The sample was heated at a nominal rate of 1 °C min^{−1}. At chosen temperatures, X-ray diffraction data were collected. JCPDS-ICDD files were used for phase identification.

The particle morphology of samples was investigated by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS) using a S-4700 Hitachi apparatus.

The surface species were examined by TOF–SIMS (time-of-flight secondary ion mass spectrometry). The TOF–SIMS measurements were taken in the static mode using an ION–TOF instrument (TOF–SIMS IV) equipped with a 25-kV pulsed ⁶⁹Ga⁺ primary ion gun.

Chemisorption measurements

The dispersion of platinum

H₂–O₂ titration The catalyst of 0.2 g was placed in a glass tube reactor with an internal diameter of 5 mm. The catalyst was reduced at 200 °C for 4 h in a stream of gas mixture H₂/Ar (5 V% H₂, 95 V% Ar) with a flow rate of 40 cm³ min^{−1}. Then the reactor was cooled to room temperature and a flow of H₂/Ar was replaced by argon. The sorbed hydrogen was titrated by the pulses of 0.05 cm³ oxygen. The changes of oxygen concentration were detected by a thermal conductivity detector (TCD). We assumed that the stoichiometry of chemisorption (H/Pt) is equal to 1, and the equation describing this process is as follows:

CO adsorption The catalyst of 0.2 g was reduced in a stream of gas mixture H₂/Ar (5 V% H₂, 95 V% Ar) with a flow rate of 40 cm³ min^{−1} at 200 °C for 4 h. Then the sample was cooled to room temperature with a flow of argon and pulses of 0.05 cm³ carbon monoxide were introduced on the catalyst. An infrared gas analyzer (Fuji type ZRJ-4) detected the changes in the CO concentration behind the reactor. Molecular, linear adsorption of CO was assumed for dispersion calculation.

Oxygen adsorption

Oxygen adsorption was measured using the temperature-programmed desorption method (TPD–O₂) and temperature-programmed oxidation (TPO). The zirconium

oxygen analyser (Z110, Hitech Instruments Ltd Luton England) was used in these measurements. This device shows very high sensitivity (oxygen detection limit 0.1 ppm) and is highly selective to oxygen. Prior to oxygen desorption, the sample of 0.2 g was in situ pre-treated by heating in ultrapure (99.9999%) O₂ flow for 1 h at the temperature of 600 °C followed by cooling to room temperature. After that, the oxygen flow was replaced by argon and the temperature-programmed desorption of oxygen was recorded in the temperature range 25–800 °C at a heating rate of 20 °C min^{−1}.

Temperature-programmed oxidation (TPO) was carried out using a gas mixture 0.21 V% O₂ balanced by argon. Prior to the TPO test, the sample was heated in O₂ stream at 600 °C for 15 min. After cooling, the sample was subjected to the reduction in H₂ stream (40 mL min^{−1}) at 300 °C for 4 h and cooled in the stream of hydrogen. Next, hydrogen was replaced by argon containing 0.21 V% O₂ (60 mL min^{−1}) and the TPO process was recorded. The temperature was raised from 25 to 400 °C at a heating rate 10 °C min^{−1}.

Temperature programmed reduction (TPR)

To check the structural stability of BaSnO₃ under reducing atmospheres, temperature programmed reduction (TPR-H₂) was carried out. TPR-H₂ experiments were performed in the PEAK-4 apparatus [23] using H₂/Ar (5 V% H₂, 95 V% 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}. Prior to the TPR run, the sample of 0.2 g was in situ pre-treated by heating in O₂ flow for 1 h at the temperature of 600 °C, followed by cooling to room temperature. The changes of hydrogen concentration were detected by a thermal conductivity detector (TCD). The reduction of high purity CuO was used to quantify the H₂ consumption. To check the correlation between the reducibility of BaSnO₃ and its catalytic activity in CO oxidation, temperature programmed reduction by carbon monoxide (TPR-CO) was carried out. This process was performed in the same manner as TPR-H₂, but as the reductive gas the mixture of 3 V% CO and 97 V% Ar was used. The concentration of CO₂ as the product of reduction was continuously measured by the infrared gas analyzer (Fuji Electric System Co., type ZRJ-4).

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 °C min^{−1}) was used. The reaction gas mixtures in CO and H₂ oxidation were 1.5 V% CO + 98.5 V% air and 1 V% H₂ + 99 V% air, respectively. For all tests, the total gas flow was kept constant = 40 mL min^{−1} (space velocity 19,100 h^{−1}).

The CO conversion was calculated based on the amount of produced CO₂ according to the following equation:

$$C_{CO} = \frac{c_{CO_2}}{c_{CO}} \times 100\% \quad (5)$$

Here c_{CO_2} and c_{CO} are the concentration of CO and CO₂ in the reactor inlet and outlet.

The quantitative determination of water vapor in the exhaust gases enables the determination of hydrogen conversion. This value was calculated according to the following equation:

$$C_{H_2} = \frac{c_T}{c_{\max}} \times 100\% \quad (6)$$

Here c_T is the concentration of H₂O vapor behind the reactor in a given temperature, and $c_{\max}$ is the concentration of H₂O vapor behind the reactor when hydrogen conversion was total.

The concentration of CO₂ and CO was continuously measured by the infrared gas analyzer (Fuji Electric System Co., type ZRJ-4) and the concentration of H₂O by humidity sensors H1H-4000-002 (Honeywell).

Results and discussions

Characterization of BaSnO₃ sample

Fig. 1 shows the XRD patterns obtained during calcination “in situ” of the dried BaSnO₃ precursor. It follows that the BaSnO₃ precursor can be identified as Ba₂SnO₂(OH)₈(H₂O)₁₀. In addition, small diffraction peaks corresponding to BaCO₃ are observed. Barium stannate begins to form at the temperature of 400 °C, while at 550 °C Ba₂SnO₄ is also formed. It is worth mentioning that in the whole range of applied calcination temperatures, BaCO₃ occurs next to barium stannate. However, with the increase in the temperature its amount clearly decreases. After cooling the sample, an X-ray measurement was taken at 50 °C. An analysis of the results can be conclude that the preparation method used allows obtaining relatively pure and well-defined BaSnO₃. The observed peaks correspond to the JCPDS data of BaSnO₃ (15-780). The mean crystallite size of BaSnO₃ calculated from the Scherrer equation was about 80 nm and the specific surface area determined by the BET method was 4 m²/g.

In order to get a better insight into the morphology of BaSnO₃, SEM photographs were taken (Fig. 2). The comparison of two magnifications (×1000 and ×2000) reveals large BaSnO₃ agglomerates with the size of 150 μm (Fig. 2a) that consist of smaller (≈ 10 μm) spherical particles (Fig. 2b).

The discrepancy between BaSnO₃ particle sizes observed by XRD and SEM methods may be caused by a strong tendency of separate crystallites toward aggregation.

Fig. 2 SEM pictures of the surface of BaSnO₃, magnification **a** 1000×, **b** 2000×

Characterization of Pt/BaSnO₃ samples

TPR and XRD analysis

Fig. 3 shows the TPR-H₂ profile of the BaSnO₃ and Pt/BaSnO₃ samples. The reduction of BaSnO₃ starts at about 300 °C and occurs in three temperature ranges: 300–450, 450–720 and above 720 °C. One can assume that in the first TPR temperature range the surface reduction of Sn⁴⁺ ions occurs, whereas in the second (with the maximum at ca. 600 °C), the reduction of Sn⁴⁺ to Sn²⁺ takes place in the sub surface layer. The hydrogen consumption above 720 °C could be attributed to the reduction to metallic tin (Sn⁰). Indeed, the XRD diffractogram (not shown here) after finishing the TPR run at 800 °C shows the presence of SnO, Sn and Ba₂SnO₄ in the reduced BaSnO₃ sample. The reduction is not complete and the perovskite

Fig. 3 TPR-H₂ profile for BaSnO₃ 1% Pt/BaSnO₃ and 10% Pt/BaSnO₃ catalysts (5% vol H₂-Ar ramping rate 15 °C min⁻¹)

structure (BaSnO_3) still remains. Besides the reduction, hydrogen assisted decomposition of BaSnO_3 to Ba_2SnO_4 proceed according to the reaction:

Total hydrogen consumption during the BaSnO_3 reduction is equal to $18.2 \text{ cm}^3/\text{g}_{\text{kat}}$, which corresponds to the reduction degree 12% assuming that the complete process of BaSnO_3 reduction is described by the reaction

The presence of 1% platinum on the BaSnO_3 surface promotes the reduction. It starts at ca. 200°C and the peaks' maxima are shifted towards a lower temperature. The total hydrogen consumption reduction is equal to $29.1 \text{ cm}^3/\text{g}_{\text{kat}}$ corresponding to the reduction degree of 19.2%.

The promoting effect of platinum on the BaSnO_3 reduction is even more pronounced for 10% Pt/ BaSnO_3 catalyst. In this case, total hydrogen consumption is $89.1 \text{ cm}^3/\text{g}_{\text{kat}}$, which is equivalent to 58.7% reduction degree. The striking feature for the reduction of 10% Pt/ BaSnO_3 catalyst, not observed for 1% Pt/ BaSnO_3 sample, is the formation of PtSn alloy. Fig. 4 presents the phase transformation with the increase in the temperature during the reduction of 10% Pt/ BaSnO_3 catalyst. At the reduction temperature equal to 600°C , the lines characteristic of PtSn are clearly observed. At the same time, the lines characteristic of metallic platinum disappear. No evidence was obtained for other PtSn alloy phases such as Pt_3Sn , Pt_2Sn_3 , PtSn_2 or PtSn_4 .

The results presented above show that both the presence of metallic platinum and its concentration strongly influence BaSnO_3 reducibility. The relatively high reducibility of BaSnO_3 may cause strong metal support interaction (SMSI) and also lead to the formation of different chemical species such as PtSn (Fig. 4). The phenomenon of strong metal-support interactions is well known in catalysis and has

Fig. 4 XRD phase transformation with the increase in the temperature during the reduction of the 10% Pt/ BaSnO_3 catalyst in 5 V% H_2 –95 V% Ar gas mixture (heating rate 1°C min^{-1})

been repeatedly reported [24–26]. SMSI occurs in the catalysts supported on easily or moderately easily reducible oxides. Thus, it can be assumed that this phenomenon can determine both adsorption and catalytic properties of Pt/BaSnO₃ samples.

Adsorption properties of Pt/BaSnO₃ samples and platinum dispersion

The adsorption properties of Pt/BaSnO₃ samples were studied by the pulse techniques. These techniques are the most universal since they facilitate the estimation of the metal dispersion over the whole range of crystallite magnitudes [27]. The dispersion of platinum in the studied catalysts, estimated on the basis of hydrogen–oxygen titration and CO adsorption, is presented in Table 1. The dispersion calculated from the chemisorption of CO is lower than that calculated from the hydrogen adsorption. As long as the stoichiometry 1:1 (one hydrogen atom on one platinum metal) is beyond discussion, carbon monoxide can be adsorbed either in a linear or bridged form covering respectively one or two platinum atoms. Which structure is formed depends on the sorption conditions and the nature of the support. Nevertheless, regardless of the method of determination, the dispersion calculated by both methods should be similar. On the other hand, in the case of platinum catalysts supported on reducible oxides like BaSnO₃, the hydrogen–oxygen titration method can give inaccurate results because of the possible occurrence of the adsorption sites for O₂ on the support's surface. This fact can explain differences in the values of dispersion.

From Table 1, it is seen that regardless of the method of determination, the dispersion of the studied catalysts is low. It increases with the content of platinum, but for the highest Pt loading (10% Pt/BaSnO₃) it still gains only 11.2%. The low dispersion of platinum in Pt/BaSnO₃ catalysts can result from the very low surface area of BaSnO₃. Barium stannate prepared in our work as a support after treatment at the temperature 800 °C in air for 4 h is well-crystallized, nonporous and exhibits the specific surface area of only 4 m²/g.

It is also worth noticing that the increase in the dispersion with the increase in the platinum loading is not typical. Usually, the reverse trend is observed. The abnormal behavior of our samples is probably connected with non-homogenous distribution of platinum and with the strong interaction of platinum with BaSnO₃. In the case of the

Table 1 Adsorption properties and dispersion of Pt/BaSnO₃ catalysts

Catalyst	Hydrogen–oxygen titration		CO adsorption	
	Adsorption (Ncm ³ /g _{cat})	Dispersion (%)	Adsorption (Ncm ³ /g _{cat})	Dispersion (%)
BaSnO ₃	–	–	–	–
1% Pt/BaSnO ₃	0.019	2.2	< 0.01	< 1
3% Pt/BaSnO ₃	0.116	4.5	0.16	4.6
5% Pt/BaSnO ₃	0.350	8.1	0.36	6.4
10% Pt/BaSnO ₃	0.960	11.2	0.95	8.3

smallest platinum particles, SMSI interactions can involve whole crystallites of platinum. As a consequence, these Pt particles may be not accessible to the adsorption of both H_2 and CO opposite to the biggest one.

The results of the measurements of H_2 and CO sorption discussed so far refer to the Pt/BaSnO₃ catalysts reduced at 200 °C. The reduction at higher temperatures makes the surface of Pt/BaSnO₃ completely unsusceptible to both H_2 and CO chemisorption. Taking this statement into account and the results shown in Fig. 4, it can be concluded that at temperatures higher than 200 °C the formation of different surface chemical compounds occurs as a product interaction between Pt and BaSnO₃. These compounds, which were identified in the TOF–SIMS spectra and will be discussed in detail in the section “TOF–SIMS results” can also strongly determine both adsorption and catalytic properties of Pt/BaSnO₃ samples.

TOF–SIMS results

The TOF–SIMS method was used to analyze the chemical composition (elemental and molecular) of the surface of all Pt/BaSnO₃ samples before and after their reduction with H_2 at 300 °C for 2 h. The analyzed areas of catalysts correspond to a square of $500 \times 500 \mu m$.

The spectra of the samples after their calcination show different ionic species containing tin (SnO₃), barium (BaO, BaO₂, BaOH₂), platinum (PtO, PtO₂, PtOCl) and intermetallic compounds or species, like BaPtO₃, Pt–Sn, Pt–O–Sn or Pt–Sn–O, Pt–Ba–O. The presence of BaO₂ and BaPtO₃ is worth noticing. Barium peroxide (BaO₂) is one of the most common inorganic peroxides. Its crystal structure contains peroxide ions (O_2^{2-}) [28]. Peroxides are very reactive in oxidation reactions, whereas BaPtO₃ can be formed by the reaction of BaO₂ with PtO₂ [29] or PtO₂ with BaCO₃ [30].

The presence of PtSn species on the surface of the Pt/BaSnO₃ catalyst must also be emphasised. Similar bimetallic phases were recorded on the XRD patterns of 10% Pt/BaSnO₃ catalysts (Fig. 4). Bimetallic PtSn catalysts are very efficient in different catalytic processes such as dehydrogenation or reforming [31, 32]. PtSn or Pt₃Sn catalysts are also used in oxidation or electrooxidation processes [33, 35] and also in preferential oxidation of CO in the presence of H_2 [36, 37]. Tin in the bimetallic PtSn catalyst is believed to promote oxygen adsorption on the platinum surface [38].

After the reduction of Pt/BaSnO₃ catalysts, the species containing barium and platinum or platinum and tin are still present on surface of catalysts.

Oxygen adsorption studies

The oxygen adsorption on BaSnO₃ and Pt/BaSnO₃ catalysts was studied using temperature-programmed desorption (TPD-O₂) and temperature-programmed oxidation (TPO) methods, respectively. The TPD-O₂ profile for BaSnO₃ is shown in Fig. 5. The desorption of oxygen starts at 350 °C and occurs in two stages with the desorption maxima at ca. 550 and 660 °C. Such a TPD course suggests that two oxygen species co-exist in BaSnO₃. It is well known that perovskite-type oxides

Fig. 5 TPD-O₂ profile of bare BaSnO₃ (heating in argon with rate of 20° min^{−1}). Prior, the sample was in situ pre-treated by heating in O₂ flow for 1 h at a temperature of 600 °C

show oxygen mobility and storage capacity. Oxygen uptake and release are associated with the existence of structural defects and the change of the oxidation state of the B-site cation. Moreover, the catalytic activity of perovskite-type oxides is also mainly controlled by the nature of the B-site cation. One can assume that in the case of BaSnO₃ oxygen adsorption/desorption behaviors are determined by oxidation–reduction reactions ($\text{Sn}^{+4} \rightleftharpoons \text{Sn}^{+2}$) or, in other words, by thermal decomposition of BaSnO₃ according to reactions:

Ba₃Sn₂O₇, Ba₂SnO₄ are referred to as barium oxostannate(IV) compounds and are described, e.g., in [39, 40].

It is worth noticing that the course of TPD-O₂ and TPR-H₂ profile for the BaSnO₃ sample is similar (compare Figs. 3 and 6). The only significant difference is the

Fig. 6 TPO profiles for Pt/BaSnO₃ samples in gas mixture 0.21 V% O₂ balanced by argon. Prior, the samples were reduced in H₂ stream at 300 °C for 4 h

temperature of peaks maxima shifted towards higher temperatures for the TPD- O_2 profile. The similarity of these profiles is understandable as the thermal decomposition of $BaSnO_3$ according to reactions 9 and 10 in neutral atmosphere may be considered as the process of $BaSnO_3$ ($Sn^{+4} \rightarrow Sn^{+2}$) reduction.

Temperature-programmed oxidation (TPO) was carried out to assess the oxygen adsorption on $Pt/BaSnO_3$ catalysts, depending on platinum concentration. Fig. 6 shows that O_2 adsorption starts already at about 30 °C and the maximum of this process is observed at 230 °C. Basically, the amount of oxygen adsorbed on the samples with lower platinum loading (1 and 3%) is higher than on the catalysts containing more platinum (5 and 10%). Such a finding is in line with the discussion of the SIMS results presented in the previous section.

At this point, it should be emphasized that the process of oxygen adsorption occurs practically at room temperature. This fact explains why the dispersion of platinum obtained in the hydrogen–oxygen titration is relatively high (Table 1).

Catalytic tests

Catalytic activity of $BaSnO_3$ and $Pt/BaSnO_3$ catalysts in oxidation of hydrogen

The reaction between hydrogen and oxygen proceeds according to the equation:

The equation shows that the oxygen–oxygen bond must be broken during the reaction. The dissociation energy of the oxygen molecule is 498.6 kJ mol^{−1} [41]. This value indicates that excluding explosive conditions, reaction 11 does not occur easily. However, the application of a proper catalyst makes the course of this reaction possible even at room temperature.

Fig. 7 TPSR profile of hydrogen conversion with the gas mixture of 1% H_2 + 99% air and with heating rate 5 °C min^{−1} for $BaSnO_3$ (curve 1) and 1% $Pt/BaSnO_3$ catalysts after reduction at 200, 350, and 400 °C (curves 2, 3 and 4)

Fig. 7 (curve 1) shows the conversion of hydrogen as a function of temperature over the BaSnO₃ sample. The gas mixture contained 1 V% H₂, 99 V% air. The catalytic activity of BaSnO₃ is poor, the process of H₂ oxidation starts at a relatively high temperature (ca. 115 °C) and the complete conversion is observed only at the temperature of 450 °C.

For the Pt/BaSnO₃ catalysts, regardless of the Pt concentration, oxidation of H₂ occurs with 100% conversion at room temperature. Such a result could be expected taking into consideration the fact that platinum is the most active metal in hydrogen oxidation [42, 43].

Nevertheless, in the case of 1% Pt/BaSnO₃ catalyst the total H₂ oxidation occurs at room temperature only when it was reduced at 200 °C. The catalyst reduced at higher temperatures shows remarkably lower activity (Fig. 7). The results shown in this figure are representative for all investigated catalysts. However, for the catalysts with higher platinum concentration, the influence of reduction temperature on hydrogen conversion is not so significant.

In the light of these results, it is clear that in the reduction atmosphere BaSnO₃ strongly interacts with platinum leading to the deactivation of the surface platinum atoms, which are the active sites in the reaction of H₂ oxidation. This reaction seems to be one of the best known and extensively studied. So far many different hypotheses have been suggested to explain the mechanism of H₂ oxidation over platinum catalyst [42–44]. It is not well established whether the formation of water molecules over platinum catalyst corresponds to Langmuir–Hinshelwood (LH) or Eley–Rideal (ER) mechanism. The Langmuir–Hinshelwood (LH) mechanism assumes that the adsorption of both substrates (H₂ and O₂) is followed by the reaction on the catalyst's surface and the desorption of reaction products from the surface [45]. The Eley–Rideal (ER) mechanism assumes that at least one of the reacting species H₂ or O₂ should be adsorbed first before undergoing the reaction [46]. Nevertheless, there is a widespread opinion that low temperatures of catalytic H₂ oxidation correspond more likely to the Langmuir–Hinshelwood (LH) mechanism than to the Eley–Rideal (ER) one. The main idea of the (LH) mechanism can be expressed by reactions 12–15:

The hydrogen dissociative adsorption is the first reaction step. In the second, oxygen adsorbs on the platinum surface and its dissociation process generates two oxygen atoms on the surface, which then can react with adsorbed H atoms creating OH groups and H₂O, respectively.

The above considerations show that the activity of platinum catalysts in the reaction of H₂ oxidation is very sensitive to impurities or contaminations which can

cover the platinum surface. These contaminations reduce the number of sites for both H_2 and O_2 adsorption. In the case of the $Pt/BaSnO_3$ catalysts, they undergo deactivation very fast after reduction at temperatures above $350^\circ C$. This deactivation occurs as a result of interactions between $BaSnO_3$ and platinum leading to the formation of different chemical species eminently limiting the catalytic activity of $Pt/BaSnO_3$ catalysts. Therefore, these catalysts are highly active in H_2 oxidation only after reduction at low temperatures ($200^\circ C$). With the increase in reduction temperature, the amount of pure metallic platinum decreases, whereas the concentration of different chemical species contaminating platinum increases. It was earlier stated (section “[Adsorption properties of \$Pt/BaSnO_3\$ samples and platinum dispersion](#)”) that the reduction at temperatures higher than $200^\circ C$ makes the surface of $Pt/BaSnO_3$ completely unsusceptible to both H_2 and CO chemisorption. In the light of this conclusion, the results presented in this section seem profoundly intelligible.

Catalytic activity of $BaSnO_3$ and $Pt/BaSnO_3$ in the reaction of CO oxidation

Fig. 8 shows the conversion of CO as a function of temperature for $BaSnO_3$ catalysts. Barium stannate exhibits very low catalytic activity in this reaction. CO oxidation starts at the temperature of $300^\circ C$ and the total conversion is observed at $500^\circ C$. One can conclude that on the $BaSnO_3$ surface, there were active adsorption sites neither for CO nor O_2 . The fact that $BaSnO_3$ does not contain sites which are able to adsorb oxygen or carbon monoxide excludes the course of CO oxidation according to the suprafacial mechanism.

Hence, we can assume that the reaction of CO oxidation over the $BaSnO_3$ catalyst occurs according to Mars–van Krevelen mechanism (intrafacial oxidation). The process can be described by the following reactions:

Fig. 8 TPSR profile of the CO conversion with gas mixture $1.5\text{ V\% } CO + 98.5\text{ V\% air}$ and with heating rate $5^\circ C\text{ min}^{-1}$ versus temperature for $BaSnO_3$ and $Pt/BaSnO_3$ catalysts after their reduction at 200 , 350 , and $400^\circ C$ (curves 1, 2 and 3 respectively)

Reaction 16 describes the first step of oxidation according to Mars–van Krevelen (MvK) mechanism, which is de facto the reduction of Sn^{4+} into Sn^{2+} . Next, $[\text{Ba}_2\text{SnO}_4 + \text{SnO}]$ species could be re-oxidized into BaSnO_3 by oxygen from the gas phase:

Taking into account reaction 16, one can expect that temperatures at the beginning of both CO conversion and catalyst reduction by CO are close. Curve 4 in Fig. 8 shows the TPR-CO profile of the BaSnO_3 sample. This profile demonstrates that the reduction of BaSnO_3 starts at about 300 °C. Thus, the TPR-CO profile of BaSnO_3 catalyst confirms that the process of reduction begins practically at the same temperature at which CO conversion starts. Therefore, the assumption that CO oxidation over BaSnO_3 samples may be described by Mars–van Krevelen mechanism is rational. On the other hand, the high temperature of the total CO or H_2 oxidation explains why the gas sensors based on BaSnO_3 work usually at temperatures higher than 600 °C [13, 14]. Only under such conditions CO or H_2 oxidation occurs with high rates and yields, which leads to the reduction of oxide and the formation of the surface vacancy (V_o^*) connected with the change of electric conductivity of BaSnO_3 (reaction 2).

The presence of platinum on the BaSnO_3 surface changes its catalytic activity. Carbon monoxide is oxidized at a significantly lower temperature. Nevertheless, these temperatures are still relatively high. For all the studied catalysts, regardless of the platinum content, the total CO oxidation is achieved at the temperature above 100 °C. The factor which strongly influences the conversion of CO over Pt/BaSnO_3 catalysts is the temperature of their reduction. Fig. 8 (curves 1, 2 and 3) depicts the changes in CO conversion versus temperature for 1% Pt/BaSnO_3 catalyst reduced at 200, 350 and 400 °C. After the reduction at 200 °C, the reaction starts practically at the temperature of ca. 60 °C. The increase in the reduction temperature to 350 and 400 °C shifts the temperature of the reaction beginning to about 110 and 150 °C. The decline in the activity results from the strong interactions between Pt and BaSnO_3 discussed above. Although the results shown in Fig. 8 are typical for all Pt/BaSnO_3 catalysts, the influence of the reduction temperature on the activity of the catalyst with higher concentration of platinum is not so spectacular, especially for the samples 5% Pt/BaSnO_3 and 10% Pt/BaSnO_3 . Fig. 9 shows the changes of catalytic activity, expressed as the reciprocal temperature of 10% conversion as a function of reduction temperature for all catalysts under study.

The strong interactions between Pt and BaSnO_3 reduce the concentration of surface platinum atoms which are the active sites for CO adsorption. According to the literature data [47, 48], the sticking coefficient of carbon monoxide is significantly higher than for oxygen or hydrogen. The adsorption of CO on the surface of the platinum catalyst blocks oxygen and hydrogen adsorption. It means that carbon monoxide can be adsorbed on platinum in the presence of oxygen with a simultaneous inhibition of adsorption of O_2 . On the other hand, it is well known that a good catalyst for CO oxidation should provide the surface sites for simultaneous adsorption of both CO and O_2 . For that reason, platinum deposited on unreduced

Fig. 9 Catalytic activity of Pt/BaSnO₃ catalysts in the reaction of CO oxidation, expressed as the reciprocal temperature of 10% conversion versus the temperature of catalysts reduction

oxides such as Al₂O₃ or SiO₂ is usually not very active in the reaction of CO oxidation, contrary to that in which the supports are able to adsorb oxygen, for example: TiO₂ [49], SnO₂ [50] or Fe₂O₃ [51].

As it was shown in Fig. 6, the Pt/BaSnO₃ catalysts after reduction at 300 °C can easily adsorb oxygen even at room temperature. On the other hand, according to the results presented in section “TOF-SIMS results”, the surface of Pt/BaSnO₃ catalysts after their reduction is covered by different chemical species. The presence of these species results from the strong interactions between platinum and BaSnO₃ reducing the number of sites for CO adsorption. It means that Pt/BaSnO₃ catalysts could be more effective in CO oxidation only in the situation when besides the presence of these species, also free Pt atoms (clusters) will be available for CO adsorption. In this way, CO adsorbed on the platinum could react with oxygen held by these species. We believe that it is the case for catalysts with the concentration of platinum higher than 1%. As a result, both the adsorption of CO and the activity of catalysts increase with the content of platinum.

On the other hand, the fact that the catalysts under study are able to adsorb oxygen at room temperature suggests that the process of CO oxidation should be effective also at low temperatures. However, the catalytic activity of investigated catalysts is rather low in spite of the fact the catalysts contain adsorption sites both for CO and O₂ adsorption. In our opinion, it is probably a consequence of the non-dissociative adsorption of oxygen. According to the stoichiometry of CO oxidation, this reaction demands the dissociation of oxygen molecules. The dissociative adsorption of molecular oxygen followed by the reaction between the adsorbed oxygen atom and CO to CO₂ is one of the accepted mechanisms of CO oxidation. In such a case, the reaction rate is limited by the dissociation of O₂. In the case of molecular adsorption, the oxidation of CO occurs at higher temperatures, which ensures appearance of reactive oxygen forms according to the following, well known sequence [52]:

In the temperature range $100\text{ }^\circ\text{C} < T < 180\text{ }^\circ\text{C}$, oxygen adsorption occurs mainly in the form of O_2^- , while above the temperature of $180\text{ }^\circ\text{C}$ to ca. $350\text{ }^\circ\text{C}$ the O^- species predominate [52–55]. The O^- ions are highly reactive. The reactivity of superoxide is also high, though much lower compared to O^- [52–56]. By means of discussed oxygen species, the CO molecules from gas phase can be directly oxidized. The concentration of adsorbed oxygen forms does not have to be strictly related to the concentration of platinum, but its presence facilitates the creation of these forms.

Taking the above into account, the process of CO oxidation does not occur as long as the adsorbed molecules of O_2 transform to the reactive form of oxygen. This conclusion explains also why gas sensors based on Pt/BaSnO₃ work usually at the temperatures higher than $300\text{ }^\circ\text{C}$.

Conclusions

Perovskite oxide BaSnO₃ was prepared to obtain Pt/BaSnO₃ catalysts. The composition and properties of Pt/BaSnO₃ catalysts were characterized. It was stated that platinum strongly interacts with BaSnO₃. The catalytic activity and adsorption properties of Pt/BaSnO₃ catalysts are determined by these interactions. It was also stated that in the process of CO and H₂ oxidation over Pt/BaSnO₃ catalysts different chemical species, like BaPtO₃, Pt–Sn, Pt–O–Sn or Pt–Sn–O, Pt–Ba–O, BaO₂ or BaPtO₃ are involved. These species arise as a result of an interaction between platinum and BaSnO₃ occurring during the calcination and reduction of Pt/BaSnO₃ catalysts. The presence of such species was confirmed by TOF–SIMS and XRD measurements. The mechanism of CO and H₂ oxidation over Pt/BaSnO₃ catalysts depends on interactions between Pt and BaSnO₃. It can be assumed that at a low platinum concentration, Pt–BaSnO₃ interaction involves a whole platinum grain, therefore preventing the adsorption of CO or H₂, and the total oxidation of these gases needs higher temperatures. For higher concentrations of platinum, these interactions become weaker so that the catalyst can adsorb these gases and the process occurs with much higher efficiency.

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