

Interaction between Pd and Ag on the surface of silica

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Abstract

Palladium, silver and palladium–silver catalysts supported on silica were prepared by coimpregnation of support with solution of AgNO_3 and $\text{Pd}(\text{NO}_3)_2$. The catalysts were characterized by X-ray powder diffraction (XRD), temperature programmed reduction (TPR), time of flight ion mass spectrometry (ToF-SIMS), chemisorption of carbon monoxide and were tested in the reaction of selective oxidation of glucose to gluconic acid.

XRD and TPR studies have shown that an interaction between Pd and Ag on the surface of silica after oxidation at 500°C and reduction at 260°C leads to the formation of solid solutions.

ToF-SIMS images of the surface of 5% Ag/SiO_2 catalyst after oxidation at 500°C and reduction at 260°C show that Ag atoms supported on silica are not distributed homogeneously but tend to form regions of enhanced Ag concentration. Positive ions images of the surface of 5% Pd/SiO_2 catalyst also display regions of enhanced concentration of Pd atoms, but they are more homogeneously distributed on silica.

ToF-SIMS peak intensity ratio $^{108}\text{Pd}^+/^{107}\text{Ag}^+$ for bimetallic 5% Pd –5% Ag/SiO_2 catalysts has a lower value than that obtained for physical mixture 5% Pd/SiO_2 –5% Ag/SiO_2 which indicates that the surface of bimetallic catalyst is enriched with silver atoms.

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1. Introduction

Supported bimetallic systems represent a large part of heterogeneous catalysts which have been used in various reactions important in the chemical, petrochemical and oil industry.

Catalysis of hydrocarbon conversion over supported Pt–Re, Pt–Ir, Pt–Sn and Pt–Ge catalysts has been the subject of numerous patents and papers [1–10]. Those bimetallic systems offered improved activity and stability compared to their monometallic $\text{Pt}/\text{Al}_2\text{O}_3$ predecessor.

Highly selective semihydrogenation of an acetylenic bond is important in a great variety of reactions carried out in industry. Palladium is known as the most selective metal catalyst for those reactions. This selectivity can be improved by certain metals introduced directly into the catalyst (e.g. Pb, Cu, Ru, etc.) [11–13].

A great interest has been recently paid to the promoting role of elements like bismuth, lead or thallium in Pd-based catalysts for the selective oxidation of alcohols into aldehydes and carboxylic acids with molecular oxygen. This effect has been investigated in the oxidation of glucose [14–19].

The main theories put forward to account for the improved properties of bimetallic catalysts tend to involve either geometric and/or electronic effects. An electronic modification of active metals like Pt or Pd may be induced by an interaction with a promotor or by an alloy formation [20–22].

A way of controlling the stability of intermediates consists in adding an element donating electrons to the metal. Such elements can be found among the Group Ib metals [23].

In the past few years various reactions have been studied over supported bimetallic Pd–Ag catalysts [13,24,27,29,30].

The Pd–Ag alloys are formed exothermically [28] with low heat of formation, which means that both components influence each other weakly. This influence can lead to the reorganization in the population of Pd–orbitals. However, bimetallic supported catalysts tend to be rather non ideal.

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The formation of bimetallic particles on a support is very often controlled kinetically rather than thermodynamically. Because of this, the catalyst preparation might not lead to a full thermodynamic equilibrium.

Moreover, the kind of precursor compounds and their chemical interaction with a support can exercise a strong influence over the sequence of metal nucleation and reduction. Therefore, chemical and physical properties of bimetallic surfaces are not simply related to bulk composition, but to the preferential segregation of one component from the bulk to the surface of the catalyst.

In the present paper we report the results of the study of Pd–Ag/SiO₂ catalysts after different treatment in oxidizing and reducing atmosphere. The choice of SiO₂ as a carrier was deliberate due to the fact that recent literature data have concentrated mainly on unsupported and supported systems on such carriers as γ -Al₂O₃ or pumice[25,32,33]. The catalysts were characterized with X-ray diffraction (XRD), time-of-flight secondary ions mass spectrometry (TOF-SIMS), sorption of carbon monoxide, temperature-programmed techniques (TPO, TPR) and were tested in the reaction of selective oxidation of glucose to gluconic acid.

2. Experimental

2.1. Catalyst preparation

Bimetallic Pd–Ag/SiO₂ catalysts containing 5 wt.% Pd and 1, 3, 5 and 8 wt.% Ag were obtained by coimpregnation of support with water solution of AgNO₃ (a.q., POCh Gliwice) and Pd(NO₃)₂ (the MLS-1200 Mega Microwave Digestion System (Milestone) was used for complete digestion of metallic Pd in HNO₃ (a.q., POCh Gliwice)). The water was evaporated at an increased temperature under vacuum. The catalysts were dried in air at 110 °C for 6 h, calcined at 500 °C for 4 h in air atmosphere and then reduced in hydrogen atmosphere for 2 h at 260 °C.

2.2. Catalytic measurements

2.2.1. The oxidation of glucose

The oxidation of glucose solution (1.00 mol l⁻¹) was performed in a thermostated glass reactor of 400 ml equipped with a stirrer, an oxygen supply system, a burette containing NaOH (1.00 mol l⁻¹) and a pH electrode. The acids formed during the oxidation of glucose were neutralized by an addition of aqueous solution of sodium hydroxide to maintain constant pH 9 in the reaction medium.

The reaction was conducted at 60 °C, pH 9. The mixture was stirred at 1300 rpm, and oxygen was bubbled through at 1.01 min⁻¹. Samples of the reaction medium were taken every 20 min, filtered and analyzed using a liquid chromatograph LaChrom (Marck Hitachi) coupled with a variable wavelength UV detector LaChrom L-7400 (Merck Hitachi). The analytical wavelength was 200 nm. The reaction prod-

ucts were separated on an amino-propyl-silicone column 150 × 3.3 mm i.d., 45,000 plates m⁻¹, using water solution of ACN as a mobile phase.

2.2.2. Powder X-ray diffraction (XRD)

Powder X-ray diffraction patterns were obtained with a Simens D5000 diffractometer using Cu K α radiation ($\lambda = 154.18$ pm). Crystalline phases were identified by references to the ASTM data files.

2.2.3. Temperature-programmed reduction (TPR) and sorption CO

The measurements were carried out in AMI-1 (Altamira) apparatus. The catalyst samples (0.15 g), prior to the TPR measurements were calcined at 500 °C for 2 h in mixture of oxygen–argon (10 vol.% of O₂) at a flow rate of 30 cm³ min⁻¹. TPR runs were performed in the temperature range: TPR(1): 20–500 °C; TPR(2): 20–900 °C, using a mixture of hydrogen–argon (10 vol.% of H₂) at a flow rate of 30 cm³/min and a linear temperature growth of 10 °C min⁻¹.

The measurements of CO sorption were carried out with the use of an impulse method at room temperature applying argon as carrier gas. The catalyst samples prior the sorption step were reduced at 260 °C for 2 h using H₂. After this operation the samples of catalysts were argon cooled to room temperature. The volume of dosed carbon monoxide equals 0.57 cm³.

2.2.4. Time of fly secondary mass spectrometry (ToF-SIMS)

Secondary ions mass spectra and images were recorded with a ToF-SIMS IV mass spectrometer manufactured by Ion-Tof GmbH, Muenster, Germany. The instrument is equipped with liquid metal ⁶⁹Ga⁺ primary ion gun and a high mass resolution time of flight mass analyzer. Three different working modes of primary Ga⁺ gun were used during the measurements. High current bunched modes characterized by high mass resolution were applied for spectra acquisition. Images were recorded in a burst alignment mode or extreme crossover mode which provide high lateral resolution. Secondary ion mass spectra were recorded from an approximately 100 μ m × 100 μ m area of the sample surface. During the measurement the analysed area was irradiated with the pulses of 25 keV ions at 10 kHz repetition rate and average ion current 2.5 pA. The analysis time was 50 s giving an ion dose below static limit of 1×10^{13} ions/cm². Secondary ions emitted from the bombarded surface are mass separated and counted in the time of flight (ToF) analyzer. Spectra were recorded with high mass resolution (m/ Δ m) at the 29 m.u. was typically greater than 8000 with the primary ion pulse width 650 ns. For each catalyst mass spectra were recorded from at least three places at the sample surfaces. Prior to the image acquisition secondary ion mass spectra of the sample surface were recorded and then appropriate ion peaks were chosen for the imaging. Images of the surface show peak intensities of the corresponding secondary ions in the mass

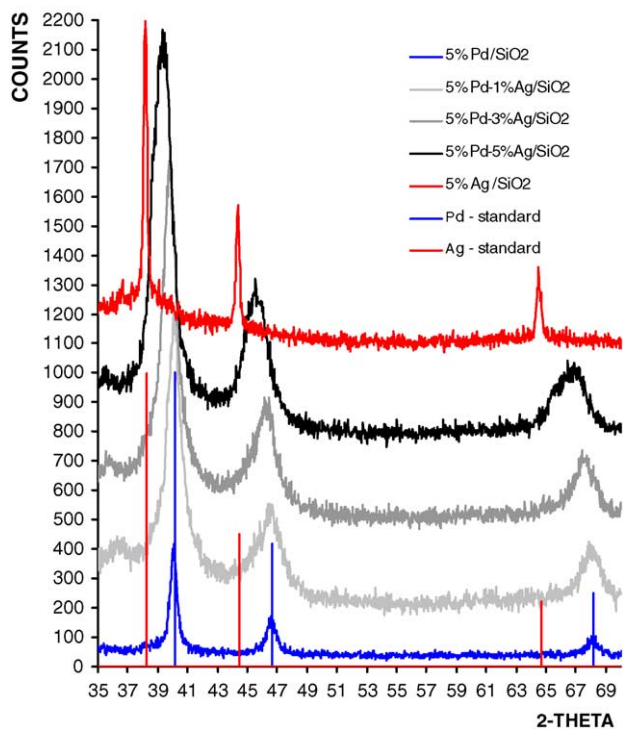


Fig. 1. Diffractograms of Pd/SiO₂, Ag/SiO₂ and Pd–Ag/SiO₂ catalysts. Crystalline phases were identified by references to the ASTM data file.

spectra collected for a selected number of points by rastering the primary ion beam over the analyzed area.

The catalyst samples were prepared by pressing pellets.

3. Result

3.1. XRD

In Fig. 1 the X-ray diffractograms related to the monometallic systems (5% Pd/SiO₂, 5% Ag/SiO₂) and to the bimetallic systems (5% Pd–1% Ag/SiO₂, 5% Pd–3% Ag/SiO₂, 5% Pd–5% Ag/SiO₂) are reported.

According to the Scherrer equation we calculated the metal particle size of monometallic and bimetallic catalysts (as shown in Table 1). The dispersion of the metallic phase is rather poor. However, the addition of silver to palladium catalyst leads to a highly dispersed metallic phase. In the case of 5% Pd–1% Ag/SiO₂ catalyst the particle diameter was smaller than for the catalysts with a higher amount of silver.

Table 1
Metal particle size of the Pd–Ag/SiO₂ catalysts calculated according to the Scherrer equation

Catalyst	Particle diameter (Å)
5% Pd/SiO ₂	472.9112
5% Pd–1% Ag/SiO ₂	159.9625
5% Pd–3% Ag/SiO ₂	209.5465
5% Pd–5% Ag/SiO ₂	209.8798

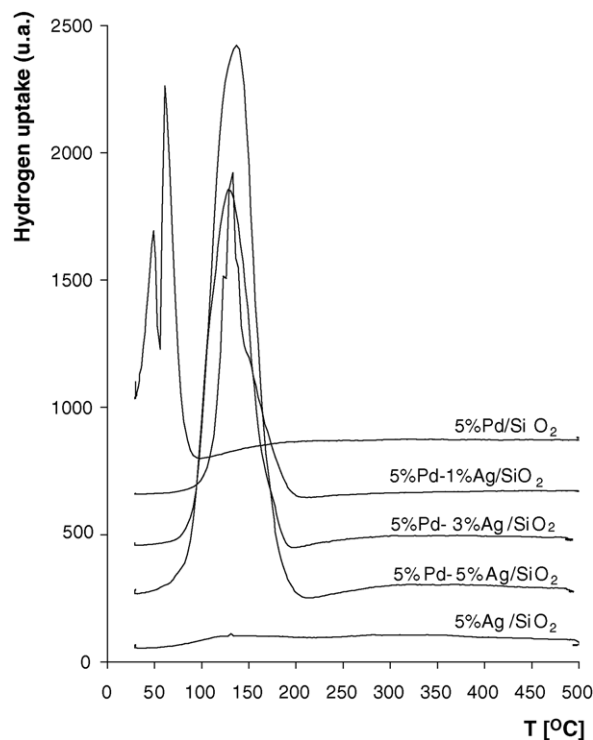


Fig. 2. Temperature programmed reduction (TPR₁) of Pd/SiO₂, Pd–Ag/SiO₂ and Ag/SiO₂ catalysts after their oxidation in oxygen atmosphere at 500 °C for 2 h.

3.2. TPR

Fig. 2 presents TPR₁ spectra obtained for 5% Pd/SiO₂, 5% Ag/SiO₂ and Pd–Ag/SiO₂ bimetallic systems after calcination in O₂ at 500 °C for 2 h.

The calcined samples of the system containing 5% Pd/SiO₂ show two low temperature peaks located in the temperature range of 25–100 °C. This seems to be a complex picture of two overlapping peaks; one connected with hydrogen desorption from β-hydride of palladium formed during the reduction of weakly bonded palladium oxide, and the second peak connected with the reduction of palladium oxide more strongly bonded with the carrier. An alternative, though a less likely explanation, could be the formation of two different forms of palladium oxide in the first stage of contact between the samples and oxygen.

In the TPR₁ profiles of calcined bimetallic systems (5% Pd–1% Ag/SiO₂, 5% Pd–3% Ag/SiO₂ and 5% Pd–5% Ag/SiO₂) one main peak appears with a maximum of reduction rate at around 130 °C. This peak could be attributed to the reduction of a mixed oxide Pd_xAg_yO being formed during the first contact of the samples of bimetallic catalyst with oxygen, when the catalysts surface is not totally stabilized.

Bimetallic catalysts Pd–Ag/SiO₂ contain the same amount of palladium, but a different one of silver, which explains why the area of reduction peaks diminishes with the decrease in Pd/Ag ratio.

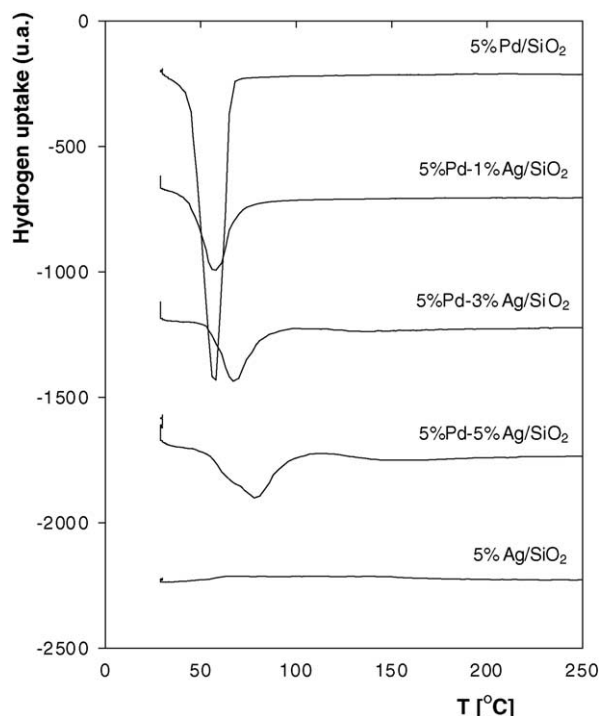


Fig. 3. Temperature programmed reduction (TPR₂) of Pd/SiO₂, Pd–Ag/SiO₂ and Ag/SiO₂ catalysts. Samples which underwent preliminary calcination in O₂ at 500 °C and were treated with hydrogen in the TPR₁ process, were then reoxidized at 500 °C for 2 h.

The peak of hydrogen adsorption was not observed for 5% Ag/SiO₂ system. This is quite a natural situation considering the fact that silver oxide loses oxygen easily at the temperature higher than 250 °C and the samples were calcined at 500 °C.

The catalyst samples which underwent preliminary calcination in O₂ at 500 °C and were treated with hydrogen in the TPR₁ process, were reoxidized at 500 °C for 2 h. Finally TPR₂ measurements were taken and their results are presented in Fig. 3.

3.3. ToF-SIMS

We have used ToF-SIMS spectrometry to study the distribution of Ag and Pd atoms at the surface of both monometallic and bimetallic catalysts after the oxidation reduction treatment.

Fig. 4 shows ToF-SIMS images of the surface of the two 5% Ag/SiO₂ catalyst samples after a different

oxidation–reduction treatment. The brightness of the particular regions in the images corresponds to the intensity of the secondary ions emission. It is clearly visible that Ag atoms are not distributed homogeneously but tend to form regions of enhanced Ag concentration, which grow after an additional oxidation–reduction cycle. The diameter of the biggest visible regions of enhanced Ag concentration before and after the additional oxidation reduction cycle can be characterised as ~1.6 and ~2.5 μm, respectively.

Positive ions images of the 5% Pd/SiO₂ catalyst are presented in Fig. 5. Although the images of 5% Pd/SiO₂ catalyst surface also display regions of enhanced Pd atoms surface concentration contrary to Ag atoms they are more homogeneously distributed across SiO₂ surface.

We have been particularly interested to get information about possible surface enrichment with one of the metals at the surface of the PdAg/SiO₂ catalysts. To investigate this Ag and Pd concentrations at the bimetallic catalyst surface were compared to those of 1:1 physical mixture of 5% Pd/SiO₂ and 5% Ag/SiO₂ catalysts. We have chosen ¹⁰⁸Pd⁺ and ¹⁰⁷Ag⁺ peak intensity ratio in the corresponding ToF-SIMS spectra as a measure of relative surface concentration of palladium and silver atoms. Before the ToF-SIMS measurements physical mixture and bimetallic catalyst were subjected to the same oxidation–reduction treatment. Additionally, the same ratios were calculated from the separately recorded ToF-SIMS spectra of monometallic 5% Pd/SiO₂ and 5% Ag/SiO₂ catalysts. In this case corresponding peak intensities were normalised to the total ion intensity to account for fluctuations in secondary ion yield between different spectra. Calculated ¹⁰⁸Pd⁺ and ¹⁰⁷Ag⁺ peak intensity ratios are summarised in Table 2.

3.4. Chemisorption of CO

The dependence of the amount of CO sorbed at room temperature on the composition of palladium–silver catalysts supported on silica is presented in Fig. 6.

As it can be seen in the figure, CO sorption changes considerably with the change of the composition of the catalysts. The course of the curve presented in Fig. 6 indicates a decrease in the sorption of CO, after a small amount of silver has been added to palladium catalysts.

3.5. Selective oxidation of glucose

The catalytic results are expressed as conversion (*X*, %) and selectivity (*S*, %). Those parameters were defined as:

Table 2
ToF-SIMS peak intensity ratios ¹⁰⁸Pd⁺/¹⁰⁷Ag⁺ for analysed samples

Catalyst	Pretreatments: oxidation at 500 °C and reduction at 260 °C (Pd ⁺ /Ag ⁺ ratio)	Pretreatments: oxidation at 500 °C, reduction at 260 °C, oxidation at 500 °C and reduction at 260 °C (Pd ⁺ /Ag ⁺ ratio)
Bimetallic catalyst 5% Pd 5% Ag/SiO ₂	0.0333	0.0348
Physical mixture (1:1) 5% Pd/SiO ₂ :5% Ag/SiO ₂	0.0471	0.0638
Monometallic catalysts: (1) 5% Pd/SiO ₂ ; (2) 5% Ag/SiO ₂	0.0453	0.0562

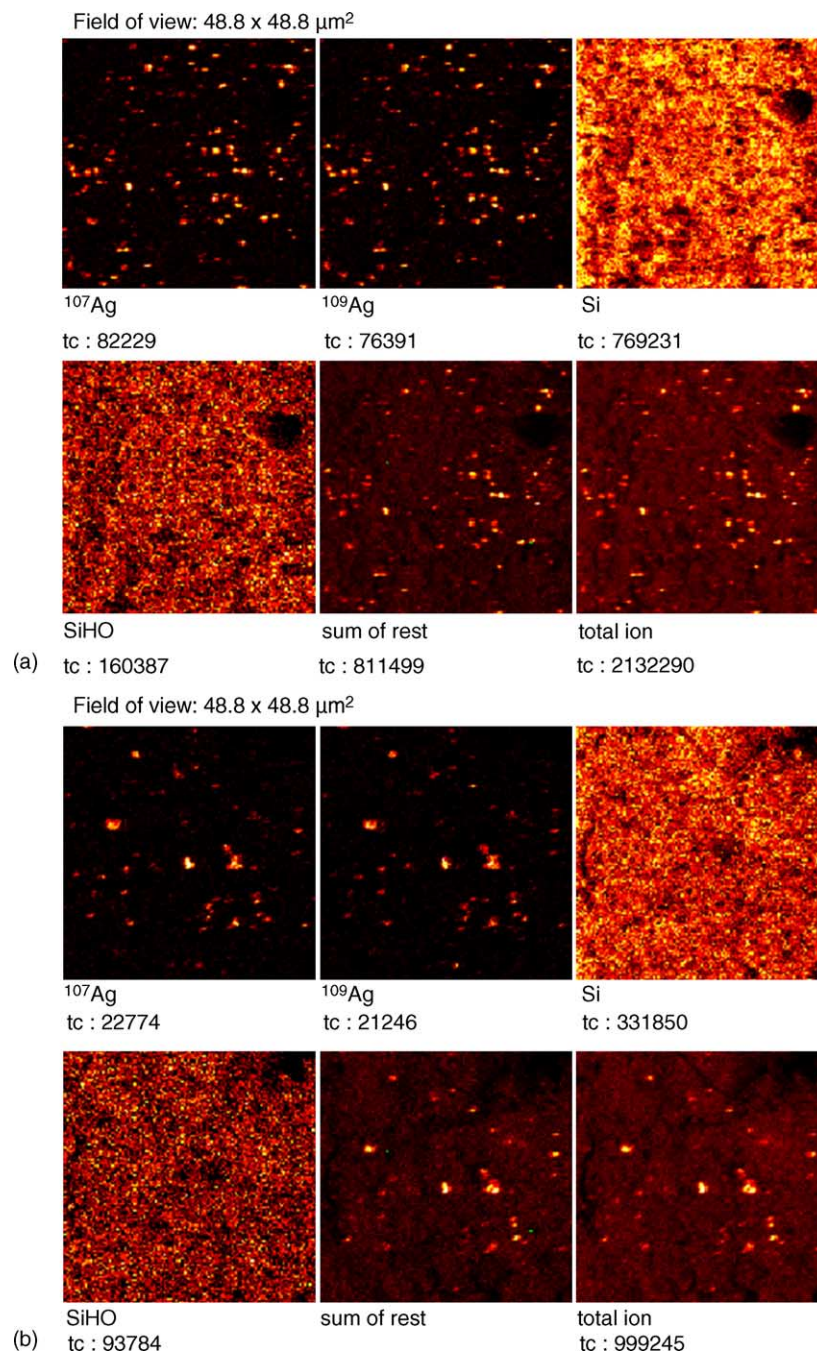


Fig. 4. Positive secondary ions ToF-SIMS images of the 5% Ag/SiO₂ catalyst surface after a single oxidation–reduction cycle (a) and after two subsequent oxidation–reduction cycles (b). The oxidation was carried at 500 °C and reduction at 260 °C. Images were recorded from 48 $\mu\text{m} \times 48 \mu\text{m}$ area with a extreme crossover working mode of primary Ga⁺ gun. Spatial resolution of images was set to 128 \times 128 pixels (tc means total counts).

$$X = \left[1 - \frac{C_{\text{GLU}}}{C_{0\text{GLU}}} \right] \times 100$$

$$S = \left[\frac{C_{\text{GLC}}}{C_{0\text{GLU}} - C_{\text{GLU}}} \right] \times 100$$

where $C_{0\text{GLU}}$ was a molar concentration of glucose at the beginning of the oxidation process, C_{GLU} was a molar con-

centration of glucose after time t , C_{GLC} was a molar concentration of gluconic acid after time t .

Table 3 shows activity and selectivity of 5% Pd/SiO₂, 5% Pd–5% Ag/SiO₂ and 5% Ag/SiO₂ catalysts in the reaction of oxidation of glucose after 2 h running. An addition of silver to palladium catalysts significantly influences both selectivity and conversion. Silver supported catalysts are inactive in this reaction. Those results also confirmed that the surface

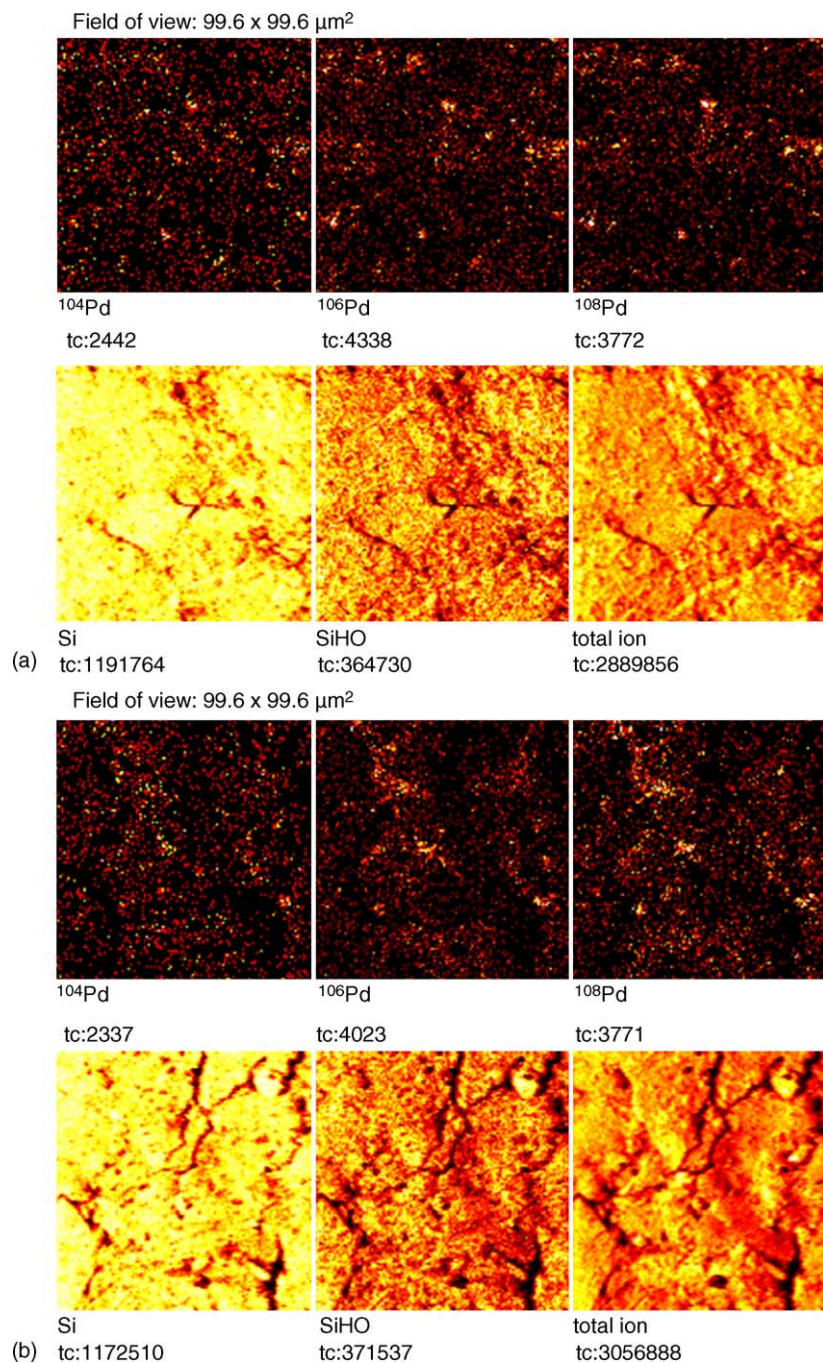


Fig. 5. Positive secondary ions ToF-SIMS images of the 5% Pd/SiO₂ catalyst surface after a single oxidation–reduction cycle (a) and after two subsequent oxidation–reduction cycles (b); the analysed area of the surface 99.6 $\mu\text{m} \times 99.6 \mu\text{m}$; burst alignment working mode of primary Ga⁺ gun; spatial resolution of images was set to 128 \times 128 pixels.

Table 3

Activity and selectivity of 5% Pd/SiO₂, 5% Pd–5% Ag/SiO₂ and 5% Ag/SiO₂ catalysts in the reaction of oxidation of glucose

Catalyst	Activity (X, %)	Selectivity (S, %)
5% Pd/SiO ₂	25	32
5% Pd–5% Ag/SiO ₂	8	2
5% Ag/SiO ₂	0	0

of bimetallic 5% Pd–5% Ag/SiO₂ catalysts is enriched with silver.

4. Discussion

Interactions between Pd and Ag on the surface of silica can lead to the formation of intermetallic compounds on the carrier of the surface [32] as well as solid solutions [33]

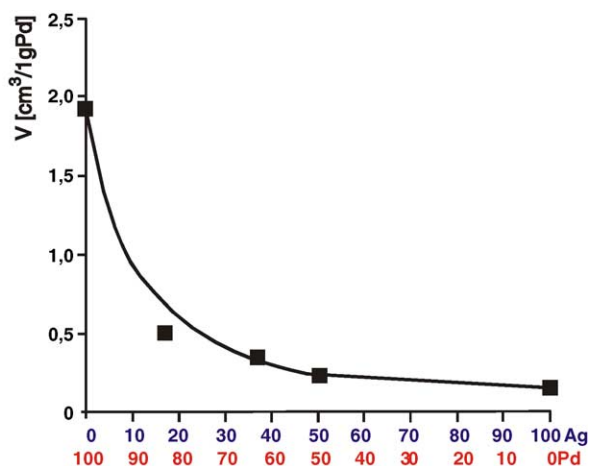


Fig. 6. Sorption of CO at room temperature on the monometallic and Pd–Ag/SiO₂ catalysts after oxidation at 500 °C and reduction at 260 °C.

according to the experimental data found in literature. Thus, the problem is more complicated than it seems from theoretical discussions.

To get to know better the nature of interaction between palladium and silver, X-ray powder diffraction (XRD) studies were performed for mono- and bimetallic catalysts supported on silica (Fig. 1). For monometallic systems 5% Pd/SiO₂ and 5% Ag/SiO₂ the diffractograms exhibit three maxima at an angle 2θ equalling 40,150 (1 1 1), 46,702 (2 0 0) and 68,145 (2 2 0), which correspond to the phase of metallic palladium, and diffraction maxima with an angle 2θ equalling 38,262 (1 1 1), 44,473 (2 0 0) and 64,713 (2 2 0), attributed to the phase of metallic silver. In the case of bimetallic systems three diffraction maxima are also observed. They are found among the diffraction maxima originating from pure Pd and Ag metals.

Similar patterns are obtained for unsupported Pd–Ag samples [33]. Authors of the paper connected those behaviours with the formation of the solid solution in this system. On the basis of the above mentioned results we can state that the studied bimetallic systems: 5% Pd–1% Ag/SiO₂, 5% Pd–3% Ag/SiO₂ and 5% Pd–5% Ag/SiO₂ after oxidation at 500 °C and reduction at 260 °C form palladium–silver solid solutions, whatever the Pd/Ag ratio.

The fact that the position of the peaks is consistent with the metal loadings is worth noticing. For the catalyst consisting of 5% Pd–1% Ag/SiO₂ diffraction maxima are situated very close to the Pd Bragg lines, whereas for the systems with high content of Ag (5% Pd–5% Ag/SiO₂) diffraction maxima are found closer to the Ag Bragg lines. Moreover, the diffractograms obtained for bimetallic systems do not show any other additional maxima, which could prove the formation of Pd–Ag alloy. This is in agreement with thermodynamic data found in the literature [34].

Similarly, temperature-programmed reduction studies prove an existence of weak interactions between Pd and Ag in Pd–Ag/SiO₂ systems. In the TPR₁ profiles (Fig. 2) of cal-

cined bimetallic systems (5% Pd–1% Ag/SiO₂, 5% Pd–3% Ag/SiO₂ and 5% Pd–5% Ag/SiO₂) one main peak appears which could be attributed to the reduction of a mixed oxide Pd_xAg_yO being formed during the first contact of the samples of bimetallic catalyst with oxygen, when the catalysts surface is not totally stabilized.

The catalyst samples which underwent preliminary calcination in O₂ at 500 °C and were treated with hydrogen in the TPR₁ process (Fig. 2.), were reoxidized at 500 °C for 2 h. Finally TPR₂ measurements were taken and their results are presented in Fig. 3. In this case for catalyst 5% Pd/SiO₂ and bimetallic systems Pd–Ag/SiO₂ instead of hydrogen adsorption peaks, we observed desorption peaks only. It leads to a conclusion that total reduction of oxide forms of both palladium and mixed palladium–silver systems took place at room temperature. A peculiar behaviour of Pd is connected with its ability to form hydride phases under normal conditions. The desorption peak observed for 5% Pd/SiO₂ system in the TPR₂ process at a temperature around 50 °C corresponds to β -PdH decomposition.

An addition of small amounts of silver (5% Pd–1% Ag/SiO₂ system) modified the intensity of the hydrogen evolution peak and the negative peak became less intensive suggesting that the β -PdH formation was inhibited. Upon the incorporation of a second metal such as Cu, Sn or Pb the suppression of β -PdH phase was postulated for the supported bimetallic catalyst [31,32]. For the systems containing greater amounts of silver (3–5 wt.% Ag), a shift of the minimum of β -hydride decomposition peak towards higher temperatures was observed together with the increase in concentration of silver. The ratio H/Pd was smaller for catalysts Pd–Ag/SiO₂ than for the monometallic palladium catalyst, which suggests a presence of a mixed bimetallic system. Another thing is the asymmetry or even partial splitting of the desorption peak. Such TPR₂ spectra suggest a presence of metallic phase of different metal content and thus the formation of solid solutions of different composition, which is in good agreement with X-ray studies.

A different behaviour of Pd–Ag/SiO₂ systems in TPR₁ and TPR₂ processes is probably connected with irreversible changes which the catalyst undergoes under the influence of O₂ and H₂ reaching a state which is different from the initial one (TPR₁), but stable in time (TPR₂). After the catalyst reached the stationary state, its surface content, structure and texture did not undergo further changes, and that is why the obtained profiles in TPR₂ are repeatable in the successive cycles.

There is little experimental evidence of enrichment of bimetallic systems Pd–Ag with one of the components. Bouwman et al. [37] studied the surface content of Pd–Ag alloys using measurements of work function of Pd–Ag alloy caused by CO-chemisorption. They found the enrichment of alloy surface with Pd. On the other hand Moss and Thomas [38,39] claimed that Pd–Ag alloys were enriched with Ag after exposing the sample to oxygen. On the basis of microcalorimetric study of O₂ Li and Shen [40] presented the results

of enrichment of Pd–Ag systems with one of the components depending on the atomic ratio of palladium and silver. Comparing the Ag/Pd ratio (from XPS) with the bulk ratio (from AAS) Naganson et al. [41] suggested surface enrichment with Ag for Pd–Ag/Al₂O₃ catalyst after reduction. Relevant results have already been reported for unsupported [42], silica supported [43], pumice supported [26] and alumina supported Pd–Ag catalysts [25].

The results obtained from ToF-SIMS display the enrichment of surface with Ag atoms, which is in good accordance with the results of chemisorption of CO (chapter 3.4.) and kinetic (chapter 3.5.) studies and with the results presented in some previously mentioned papers.

Table 2 presents the results we obtained for Pd–Ag/SiO₂ systems using ToF-SIMS measurements. From the results it can be seen that ¹⁰⁸Pd⁺/¹⁰⁷Ag⁺ peak intensity ratio for bimetallic catalysts has a lower value than that obtained for the physical mixture and that calculated separately for monometallic catalysts. This observation clearly indicates that the surface of bimetallic 5% Pd 5% Ag/SiO₂ catalyst is enriched with silver atoms relative to the surface of reference samples after the oxidation–reduction treatment. Such surface atom enrichment is thermodynamically feasible and has been reported earlier [35].

An interpretation of the chemisorption results for bimetallic catalysts is quite a complex question. It was early suggested that an electron was transferred in a chemisorption process from the reactant to the surface atom, or the reverse. According to the RBT theory the d-band holes of one metal are filled by valance electrons of a second metal. The valance electrons shell electronic configuration of Pd atom is 4d¹⁰5s⁰. In metallic Pd approximately 0.36 electrons of the d-shell are in the s-bond. This leaves an equivalent number of holes in the d-band. The filling of the 4d shell on alloying can therefore arise either by a flow of charge from s-band of Pd or a charge transfer from a second component.

Now, it is recognized that the chemisorption bond on metal is covalent and the extent of electron transfer from one component to the other upon alloying is very small, if any. However, literature data show strong modifications of Pd d-band, which is filled in with the alloys [36]. In Pd alloys intra-atomic charge transfer from 5s to 4d orbitals can take place and can have an influence on the chemisorption process. In our case, we observed a considerable decrease in CO sorption for bimetallic systems after an addition of a small amount of Ag compared to monometallic Pd/SiO₂. This could be caused by the enrichment of the surface of Pd with Ag, which supports the explanation given for the ToF-SIMS measurements.

Then we conclude that the considerable decrease in CO sorption for bimetallic systems after the addition of a small amount of Ag compared to monometallic Pd/SiO₂ is caused by the enrichment of the surface with Ag, which supports the explanation given for the ToF SIMS measurements.

5. Conclusions

The catalytic properties of bimetallic systems depend on the surface composition, which is not the same as that of the bulk. In fact, it is well known that when two metals are present as an alloy the surface will be enriched with the metal that has the lower heat of sublimation. Because of this, in the Pd–Ag system we can expect the enrichment of the surface with the Ag atoms.

XRD and TPR studies have shown that the interaction between Pd and Ag on the surface of silica after oxidation at 500 °C and reduction at 260 °C leads to the formation of palladium–silver solid solutions, whatever the Pd/Ag ratio.

ToF-SIMS studies show that Pd atoms are more homogeneously distributed on the surface of silica than in the case of Ag atoms. ToF-SIMS peak intensity ratio ¹⁰⁸Pd⁺/¹⁰⁷Ag⁺ and results from the CO chemisorption measurements and kinetic study clearly indicate that the surface of bimetallic 5% Pd–5% Ag/SiO₂ catalyst is enriched with silver atoms. In our opinion, ToF-SIMS spectrometry is a very useful method for characterization of the surface of mono- and bimetallic systems. This technique made it possible to observe the changes of catalyst surface which are invisible for XRD. Grant no. 3 TO9 D 067 27.

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