

Activity and selectivity of Pd–Bi/SiO₂ catalysts in the light of mutual interaction between Pd and Bi

S. Karski*

Institute of General and Ecological Chemistry, Technical University of Lodz, ul. Żeromskiego 116, 90-924 Lodz, Poland

Received 27 January 2006; received in revised form 8 March 2006; accepted 9 March 2006

Available online 24 April 2006

Abstract

This work is devoted to the study of interactions between Pd and Bi in Pd–Bi/SiO₂ catalysts and their connection with activity and selectivity of those systems in the selective oxidation of glucose and lactose.

In the oxidation of glucose, high activity and selectivity of Pd–Bi/SiO₂ systems having higher bismuth content were observed. For those systems the formation of BiPd and Bi₂Pd took place.

In the case of lactose oxidation better catalytic properties were found for Pd–Bi/SiO₂ systems with a small amount of bismuth, where mainly a binary alloy BiPd is formed.

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Keywords: Pd–Bi catalysts; Catalytic oxidation of aldoses; ToF-SIMS study of catalysts

1. Introduction

Supported bimetallic palladium catalysts are attractive due to their high activity and selectivity in a large number of chemical reactions.

The first example of promoting Pd by the addition of a second metal deals with Lindlar catalyst Pd–Pb/CaCO₃, used with success for the selective hydrogenation of alkynes [1].

Since then a lot of papers showing high activity and selectivity of Pd–M systems not only in the reactions of hydrogenation of unsaturated aliphatic hydrocarbons [1–13] but also in the hydrogenation of aromatics [14–17], nitrogen-containing compounds [18–23] and in the hydrodehalogenation [24–27] have been published. In those papers Pb, Bi, Ag, Cr, Fe, Au and Ru were used as a second metal.

Bimetallic palladium systems are also characterized by high selectivity in some oxidation reactions. A great interest has been paid to the promoting role of post-transition metals like bismuth and lead in the Pd-based catalysts for the selective oxidation of alcohols or aldehydes in aqueous solutions. This effect was studied in the oxidation of aldoses [28–37].

The addition of small amounts of Pb to palladium catalysts drastically improved the selectivity of Pd–Pb catalyst for the direct production of methyl methacrylate from methacrolein, methanol and oxygen in the liquid phase process [38].

High selectivity of Pd–Te catalysts has been found for the oxidative acetoxylation of butadiene [38].

The presented examples prove that bimetallic palladium systems form an important group of heterogeneous catalysts.

The performance of bimetallic palladium catalysts can be interpreted in terms of geometric or electronic effects, the occurrence of mixed-sites and the disappearance of β-PdH. Applying a few different ways of explanation of the effect of co-metal on the performance of Pd catalysts is connected with the fact that the same classes of reactions are more or less sensitive to some of those factors. However, in each case understanding of the influence of the addition of the second metal to palladium catalysts on their performance involves good knowledge of the chemical state of both Pd and co-metal and the degree of an intimate interaction between those two components.

This work presents the study of interactions between Pd and Bi in Pd–Bi/SiO₂ systems using XRD and ToF-SIMS techniques. The obtained results prove a strong interaction between Pd and Bi leading to the formation of two binary alloys with the compositions BiPd and Bi₂Pd. In the Pd–Bi/SiO₂ systems with a small amount of bismuth (1–3 wt.%) mainly intermetallic com-

* Tel.: +48 42 631 30 94.

E-mail address: karski@mail.p.lodz.pl.

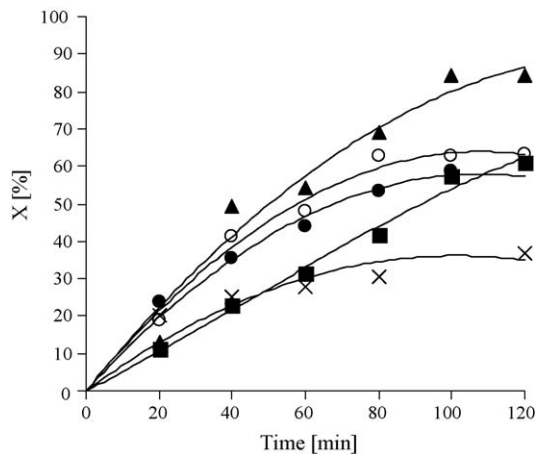


Fig. 1. Conversion of glucose in the presence of catalysts: 5% Pd/SiO₂ (x), 5% Pd-2% Bi/SiO₂ (■), 5% Pd-4% Bi/SiO₂ (●), 5% Pd-5% Bi/SiO₂ (○) and 5% Pd-8% Bi/SiO₂ (▲), as a function of time.

pound BiPd is formed. For the bimetallic Pd-Bi/SiO₂ catalysts with high amount of bismuth (5–8 wt.%) both BiPd and Bi₂Pd are formed. A possible role of those intermetallic compounds in the catalytic properties of Pd-Bi/SiO₂ for the oxidation of glucose and lactose was analysed.

2. Experimental

2.1. Catalysts preparation

A catalyst containing 5 wt.% of palladium supported on silica (Aldrich, 250 m²/g) was prepared from water solutions of PdCl₂ (a.q., POCh Gliwice) by aqueous impregnation. Water evaporated at an increased temperature (353 K) under vacuum. The catalyst was dried in air at 383 K for 6 h, calcined at 773 K for 4 h in air atmosphere and then reduced in hydrogen atmosphere for 2 h at 533 K.

Bimetallic Pd-Bi/SiO₂ catalysts containing 5 wt.% Pd and 0.25, 0.5, 1, 2, 4, 5, 8 wt.% Bi were obtained from 5% Pd/SiO₂

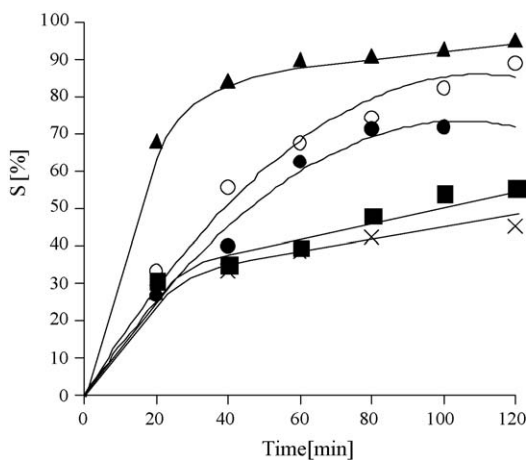


Fig. 2. Selectivity of catalysts: 5% Pd/SiO₂ (x), 5% Pd-2% Bi/SiO₂ (■), 5% Pd-4% Bi/SiO₂ (●), 5% Pd-5% Bi/SiO₂ (○) and 5% Pd-8% Bi/SiO₂ (▲), as a function of time.

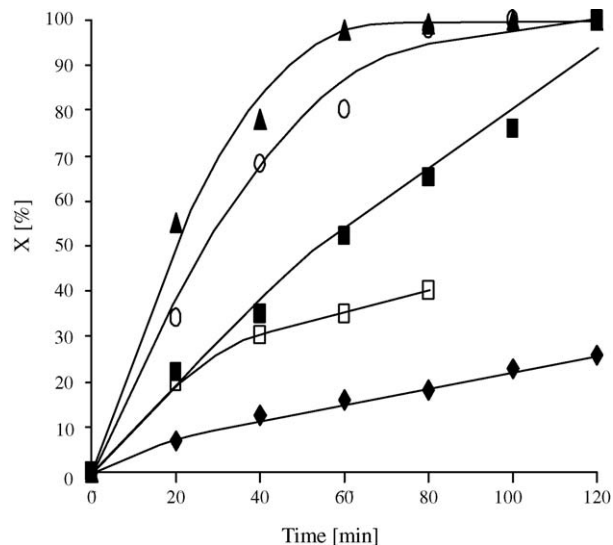


Fig. 3. Conversion of lactose in the presence of the catalysts: 5% Pd/SiO₂ (◆), 5% Pd-1% Bi/SiO₂ (■), 5% Pd-3% Bi/SiO₂ (▲), 5% Pd-5% Bi/SiO₂ (○) and 5% Pd-8% Bi/SiO₂ (□), as a function of time.

catalyst by repeated impregnation of this system with water solution of Bi(NO₃)₃·5H₂O (a.q., POCh Gliwice) according to the procedure described above.

2.2. Catalytic measurements

The oxidation of aldose solution (C_0 Glucose = 1.00 mol l⁻¹ (a.q., POCh Gliwice S.A.), C_0 Lactose = 0.50 mol l⁻¹ (a.q., POCh Gliwice S.A.)) 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.

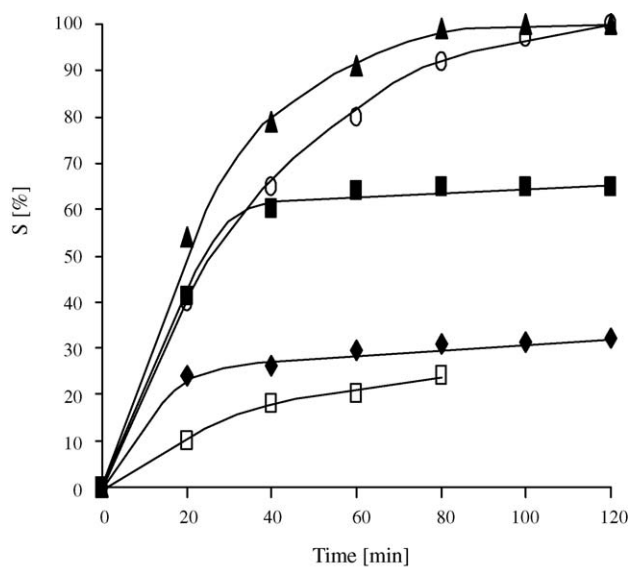


Fig. 4. Selectivity to lactobionic acid in the reaction of lactose oxidation in the presence of catalysts: 5% Pd/SiO₂ (◆), 5% Pd-1% Bi/SiO₂ (■), 5% Pd-3% Bi/SiO₂ (▲), 5% Pd-5% Bi/SiO₂ (○) and 5% Pd-8% Bi/SiO₂ (□), as a function of time.

The acids formed during the oxidation of glucose and lactose were neutralized by the addition of aqueous solution of sodium hydroxide to maintain constant pH=9 in the reaction medium.

The oxidation of glucose was conducted at 333 K and lactose at 343 K, 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 analysed 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 products were separated on an amino-propyl-silicone column $150 \text{ mm} \times 3.3 \text{ mm I.D.}$, $45,000 \text{ plates m}^{-1}$, using water solution of ACN as a mobile phase.

2.3. Characterization of catalysts

2.3.1. Powder X-ray diffraction (XRD)

Patterns were obtained with a Siemens D5000 diffractometer using Cu K α radiation ($\lambda = 154.18 \text{ pm}$). Crystalline phases were identified by references to the PDF data files.

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

The 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 $^{69}\text{Ga}^+$ primary ion gun and high mass resolution time of flight mass analyzer. Three different working modes of primary Ga^+ gun were used during measurements. High current bunched mode characterized by high mass resolution was 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 $500 \mu\text{m} \times 500 \mu\text{m}$ area of the sample surface. During the measurement, the analysed area was irradiated with pulses of 25 keV ions at 10 kHz repetition rate and an average ion current 2.5 pA. The analysis time was 50 s giving an ion dose below static limit of $1 \times 10^{13} \text{ ions/cm}^2$. Secondary ions emitted from the bombarded surface are mass separated and counted in a time of flight (ToF) analyser. Spectra were recorded with high mass resolution ($m/\Delta m$) at 29 m.u. 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

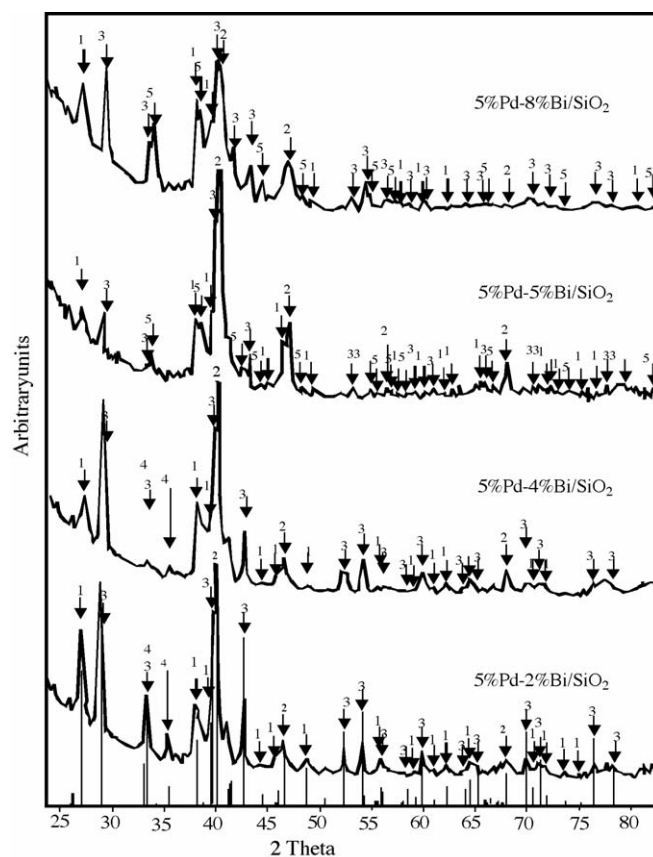


Fig. 5. Diffractograms of 5% Pd–2% Bi/SiO₂, 5% Pd–4% Bi/SiO₂, 5% Pd–5% Bi/SiO₂ and 5% Pd–8% Bi/SiO₂ catalysts. Crystalline phases were identified by references to the ASTM data files. 1: Bi; 2: Pd; 3: BiPd; 4: BiPd; 5: Bi₂Pd.

of the surface show peak intensities of the corresponding secondary ions in the mass spectra collected for the selected number of points by rastering the primary ion beam over the analysed area.

The catalyst samples were prepared by pressing pellets.

2.3.3. ICP AES analysis of reaction mixture

Bismuth and palladium losses from the catalysts in reaction mixture during the catalytic tests were determined by analyzing the filtered solution by ICP using an optical emission spectrometer IRIS AP (Thermo Jarrel Ash) with horizontal observation of the plasma. The MLS—1200 Mega Microwave Digestion System (Milestone) was used for complete digestion of the samples for ICP analysis.

Table 1
Phase composition analysis of catalysts Pd–Bi/SiO₂ samples.

Catalyst	Bi (Bismuth) syn	Pd (Palladium) syn	BiPd (Bismuth Palladium) C	BiPd (Sobolevskite) Q	Bi ₂ Pd (Bismuth Palladium) C
5% Pd2% Bi/SiO ₂	+	+	+	+	–
5% Pd4% Bi/SiO ₂	+	+	+	+	–
5% Pd5% Bi/SiO ₂	+	+	+	+	+
5% Pd8% Bi/SiO ₂	+	+	+	+	+

3. Results and discussion

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

$$X(\%) = \left[1 - \left(\frac{C}{C_0} \right) \right] \times 100$$

$$S(\%) = \left[\frac{C_A}{C_0 - C} \right] \times 100$$

where C_0 was a molar concentration of glucose or lactose at the beginning of the oxidation process, C was a molar concentration of glucose or lactose after time t , C_A was a molar concentration of gluconic acid or lactobionic acid after time t .

Fig. 1. shows the conversion of glucose for a chosen monometallic system containing 5 wt.% Pd/SiO₂ and for palladium catalysts supported on silica and modified with bismuth.

The presented picture shows that the conversion of palladium catalysts modified with bismuth is considerably higher than in the case of monometallic system. Together with a rise in the percentage content of bismuth, there is a rise in the conversion of glucose. Catalysts samples 5% Pd–5% Bi/SiO₂ and 5% Pd–8% Bi/SiO₂ show the highest conversion.

Fig. 2. shows the selectivity of Pd–Bi/SiO₂ catalysts in the oxidation of glucose. Similarly as it was in the case of conversion catalysts containing 5% Pd–5% Bi/SiO₂ and 5% Pd–8% Bi/SiO₂ show a particularly high selectivity in this reaction.

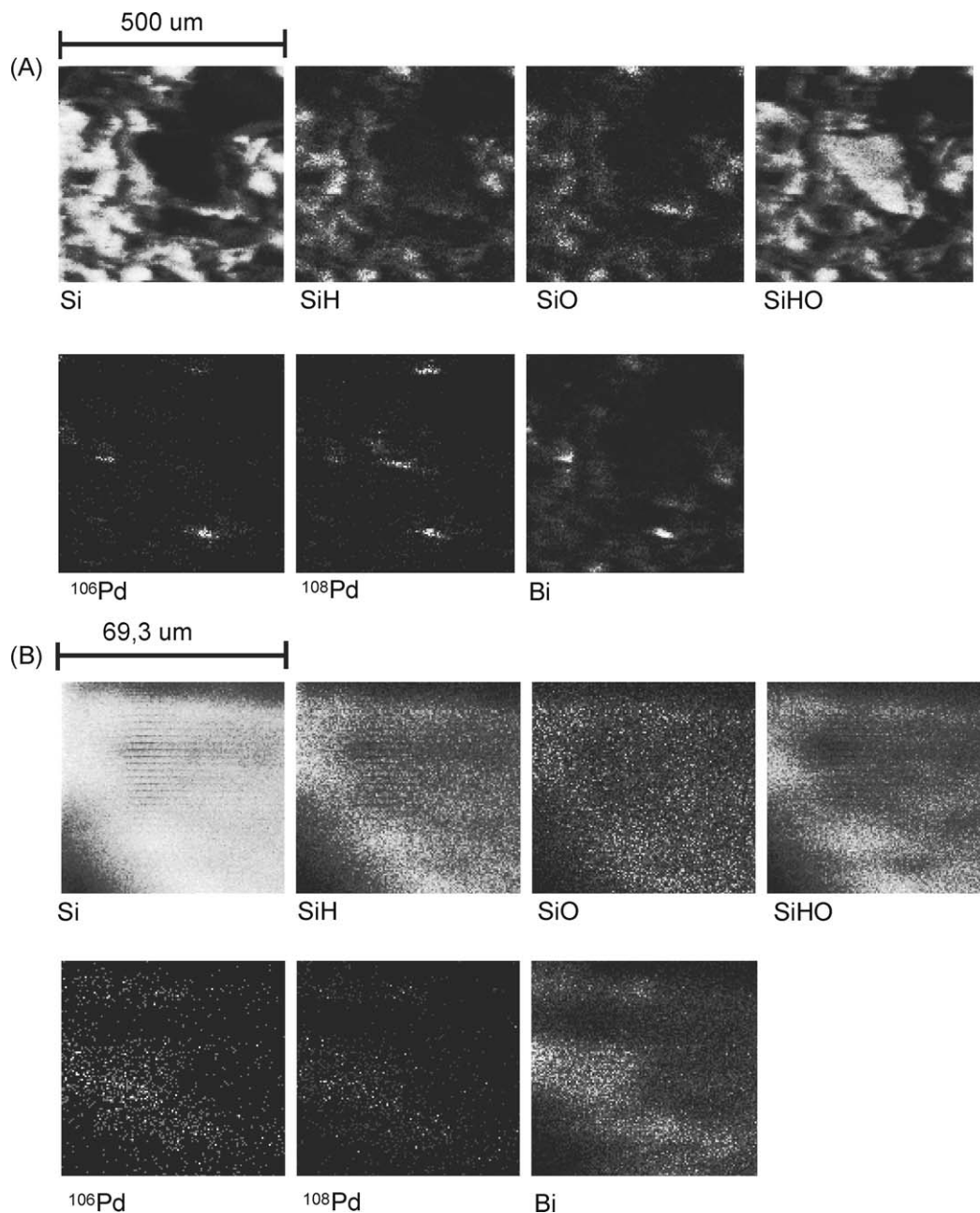


Fig. 6. Positive secondary ions ToF-SIMS images of 5% Pd–5% Bi/SiO₂ catalyst. The analysed area of the surface: (A) 500 μm × 500 μm; (B) 69.3 × 69.3 μm.

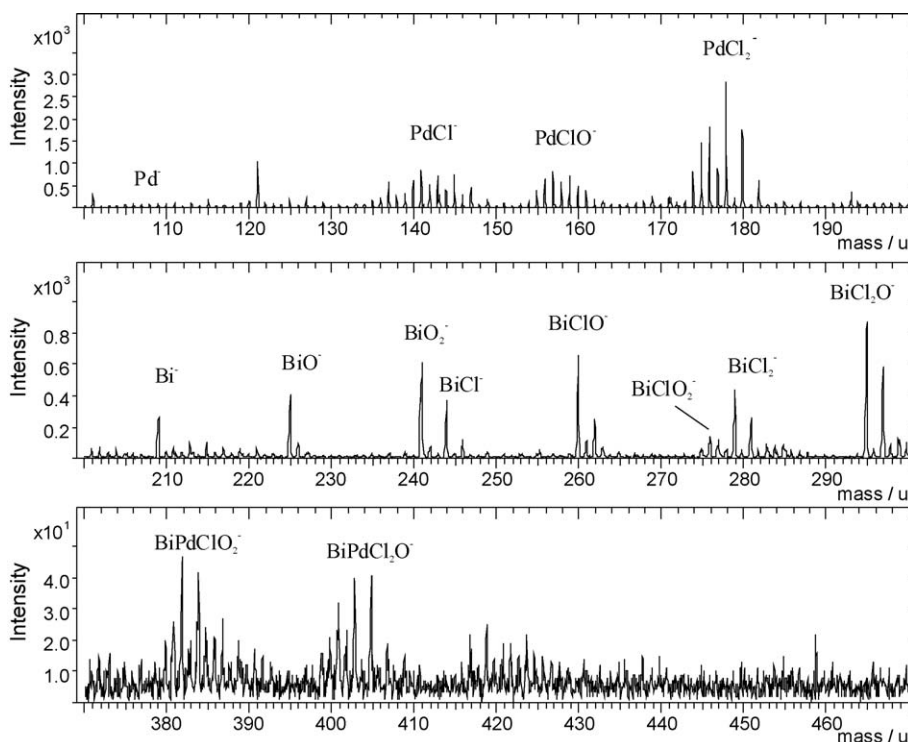


Fig. 7. The ToF-SIMS (-) spectra of the catalyst 5% Pd–5% Bi/SiO₂.

The addition of small amounts of bismuth to palladium catalysts (5% Pd–0.25% Bi/SiO₂, 5% Pd–0.5% Bi/SiO₂ and 5% Pd–1% Bi/SiO₂) does not significantly influence either selectivity or conversion in the oxidation of glucose.

Activity and selectivity in the oxidation of lactose were studied over the same systems, which were used in the oxidation of glucose, in order to improve understanding of the performance of Pd–Bi/SiO₂ catalysts.

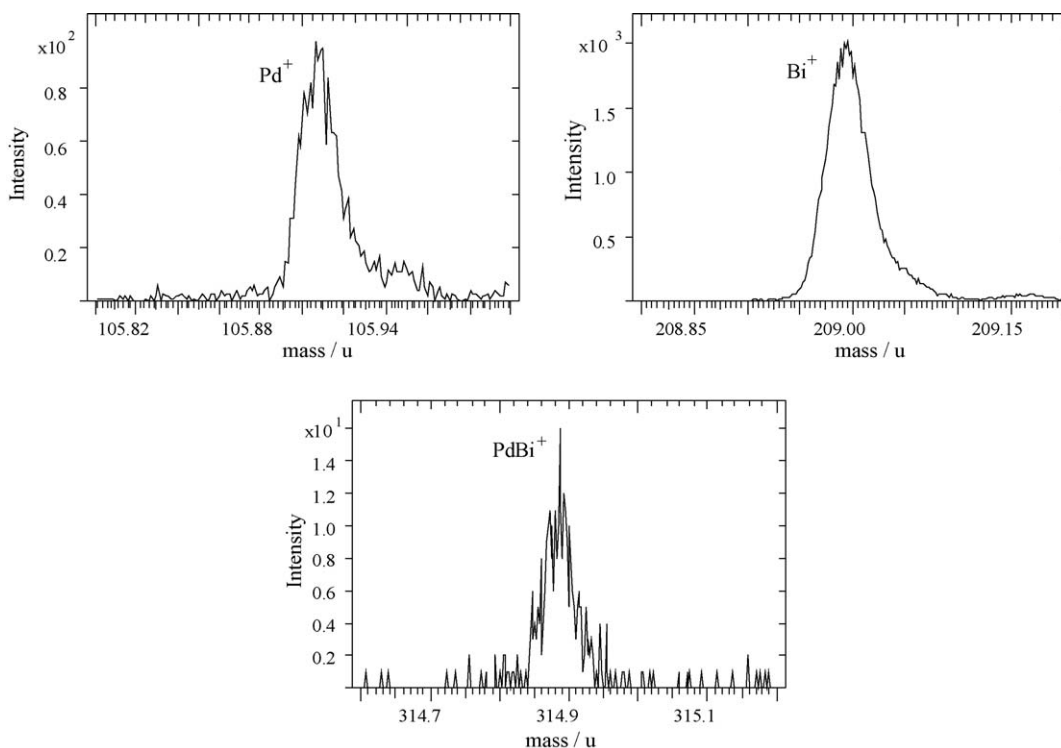


Fig. 8. The ToF-SIMS (+) spectra of the catalyst 5% Pd–5% Bi/SiO₂.

Figs. 3 and 4. show the conversion and selectivity of Pd–Bi/SiO₂ catalysts with a constant palladium content (5 wt.%) and a different amount of bismuth (1–8 wt.%) in the oxidation of lactose. Similarly as it was in the case of oxidation of glucose, bimetallic systems Pd–Bi/SiO₂ display better catalytic properties than monometallic palladium catalysts. However, bimetallic systems containing a small amount of bismuth (1–3 wt.%) are characterized by the highest activity and selectivity in this reaction. Bimetallic catalyst 5% Pd–1% Bi/SiO₂ in the oxidation of glucose showed similar catalytic properties as a monometallic 5% Pd/SiO₂, but in the oxidation of lactose this bimetallic catalyst had both high activity and selectivity.

The reactions of glucose and lactose oxidation were performed in the presence of the same catalysts using identical activation conditions. Significant differences in the behaviour of those bimetallic systems were observed in the studied reaction. Bimetallic catalysts Pd–Bi/SiO₂ with a small amount of bismuth (1–3 wt.%) are more effective in the oxidation of lactose, whereas bimetallic systems containing a large amount of bismuth (5–8 wt.%) seem to be better in the oxidation of glucose.

Bimetallic Pd–Bi/SiO₂ systems before catalytic measurements were activated in pure hydrogen at temperature 533 K. Activation of those catalysts in such conditions and with a different content of components will promote the formation of intermetallic compounds with a various composition. The change of the surface structure of the bimetallic Pd–Bi/SiO₂ catalysts should also change their behaviour in the studied reactions.

In order to explain the differences in the behaviour of Pd–Bi/SiO₂ systems in the reactions of glucose and lactose

oxidation XRD and ToF-SIMS measurements were made for chosen catalysts.

Fig. 5. presents diffractograms of the following catalysts: 5% Pd–2% Bi/SiO₂; 5% Pd–4% Bi/SiO₂, 5% Pd–5% Bi/SiO₂ and 5% Pd–8% Bi/SiO₂. Regardless of the percentage content of bismuth in the studied catalysts Pd–Bi/SiO₂ the presence of phase of metallic palladium and bismuth as well as the formation of intermetallic compounds are always observed. In the Pd–Bi/SiO₂ systems with a small content of bismuth (1–3 wt.%) intermetallic compounds of BiPd type are formed, whereas for the systems containing more than 5 wt.% Bi both BiPd and Bi₂Pd are observed. Table 1. presents all the results of XRD studies.

The presence of intermetallic compounds on the surface of studied catalysts are also confirmed by ToF-SIMS measurements. Fig. 6. shows ion ToF-SIMS images of 5% Pd–5% Bi/SiO₂. The studies reveal lack of homogeneity of the sample. Palladium and bismuth are found in distinct clusters on the studied area 500 μm × 500 μm, and so they are not evenly dispersed on the carrier. The concentration of palladium and bismuth is the highest on the same areas of the studied sample, which proves the fact that both metals appear together on the analysed surface. Moreover, in the spectrum of secondary ions maxima of signal intensity for the following mass: 314, 315 and 317 ascribed to intermetallic compound BiPd were found. ²⁰⁹Bi was connected with three isotopes of palladium: ¹⁰⁵Pd, ¹⁰⁶Pd and ¹⁰⁸Pd, respectively (Figs. 7 and 8).

Bismuth is a well-known promoter of palladium catalysts for the selective oxidation of carbohydrates with molecular oxygen. Wenkin et al [28,39] presented interesting results connected

Table 2

ICP analysis of reaction mixture after catalytic tests. The reaction conditions were: time of tests = 2 h, [catalyst] = 3.2 g dm⁻³, 333 K, pH = 9, stirring at 1300 rpm, and oxygen was bubbled at 1 l min⁻¹

Catalyst	Pretreatment steps	Reaction medium	Pd (ppm) (363.470(71) nm)	Bi m(ppm) (223.061(117) nm)
5% Pd–1% Bi/SiO ₂	Air, 4 h, 773 K H ₂ , 2 h, 533 K	Glucose (1 mol dm ⁻³)	b.d.l.	0.3585
5% Pd–5% Bi/SiO ₂	Air, 4 h, 773 K H ₂ , 2 h, 533 K	Glucose (1 mol dm ⁻³)	b.d.l.	28.27
5% Pd–8% Bi/SiO ₂	Air, 4 h, 773 K H ₂ , 2 h, 533 K	H ₂ O	b.d.l.	0.2163
		Glucose (1 mol dm ⁻³)	b.d.l.	57.90
3% Bi/SiO ₂	Air, 4 h, 773 K H ₂ , 2 h, 533 K	Glucose (1 mol dm ⁻³)	b.d.l.	20.425
		H ₂ O	b.d.l.	1.041
5% Pd–1% Bi/C ^a	H ₂ , 2 h, 533 K Air, 4 h, 773 K H ₂ , 2 h, 533 K	Glucose (1 mol dm ⁻³)	b.d.l.	1.494
		Glucose (1 mol dm ⁻³)	b.d.l.	7.697
5% Pd–5% Bi/C ^a	H ₂ , 2 h, 533 K Air, 4 h, 773 K H ₂ , 2 h, 533 K	Glucose (1 mol dm ⁻³)	b.d.l.	30.16
		Glucose (1 mol dm ⁻³)	b.d.l.	32.42
5% Pd–8% Bi/C ^a	H ₂ , 2 h, 533 K Air, 4 h, 773 K H ₂ , 2 h, 533 K	Glucose (1 mol dm ⁻³)	b.d.l.	44.63
		Glucose (1 mol dm ⁻³)	b.d.l.	58.24

^a C: Polish active carbon obtained from plum stones (specific surface area 741 m²/g).

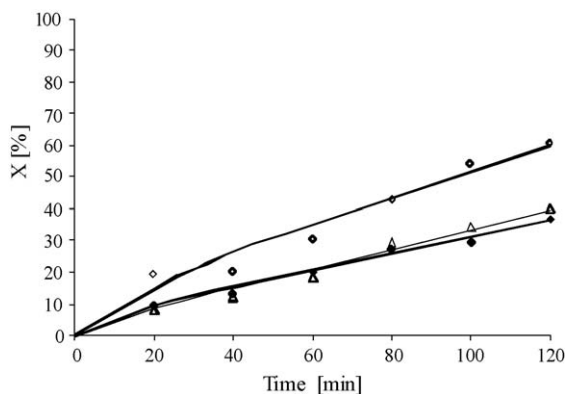


Fig. 9. Conversion of glucose in the presence of catalysts 5% Pd–5% Bi/SiO₂ oxidized in air at 773 K and reduced in H₂ atmosphere at the temperatures: (◇) 533 K, (◆) 773 K, (△) 973 K, as a function of time.

with the role of bismuth as a promoter in the Pd–Bi catalysts for the selective oxidation of glucose. They measured the promoting effect of dissolved bismuth on monometallic catalyst Pd/C for different Bi concentrations in the solution [39]. They stated that soluble bismuth can participate in the promoting effect, but its influence depends on the Bi concentration in the reaction medium. On the basis of those results they suggested that the dissolved bismuth could be responsible for an increasing catalytic activity of bimetallic Pd–Bi catalysts.

In the studies of Pd–Bi/SiO₂ catalysts we also observed leaching of Bi into the reaction medium (Table 2.). The amount of Bi losses increases with the Bi content in bimetallic catalysts but we did not observe any clear correlation with the catalytic activity.

Active sites formed “in situ” can probably appear on the surface of bimetallic systems Pd–Bi which underwent activation under mild conditions, where permanent intermetallic compounds are not observed. In our catalytic studies bimetallic systems Pd–Bi/SiO₂ after activation in air atmosphere at 773 K and reduction in H₂ atmosphere at 533 K were used. Such an activation leads to the formation of thermodynamically stable intermetallic phases. XRD and ToF-SIMS studies of Pd–Bi/SiO₂ systems proved the presence of intermetallic compounds of BiPd and Bi₂Pd type, while Wenkin et al. reported the occurrence of BiPd, Bi₂Pd₅ and BiPd₃ in the active phase of carbon-supported bismuth-palladium catalysts [28]. The differences probably result from surface chemical reactivity of the supports (C, SiO₂) used for the preparation of bimetallic catalysts as well as activation conditions.

The importance of activation conditions of Pd–Bi/SiO₂ systems is reflected in the catalytic oxidation of glucose. Samples which were reduced at a temperature of 773–973 K in hydrogen atmosphere showed a significantly lower conversion in comparison with the systems reduced at 533 K (Fig. 9.). XRD analysis of systems reduced at higher temperatures (Fig. 10) shows disappearance of Bi₂Pd phase, which is the most active in the studied reaction [28].

In the light of presented results, active sites formed during the activation steps of bimetallic catalysts seem to play a

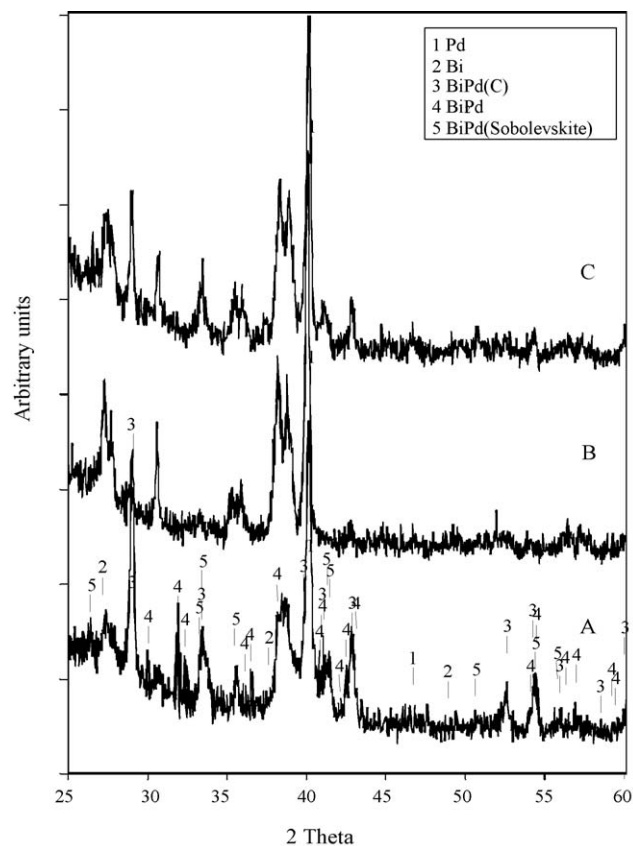


Fig. 10. Diffractograms of 5% Pd–5% Bi/SiO₂ catalysts reduced at H₂ at the temperature: A: 533 K, B: 773 K, C: 973 K. Crystalline phases were identified by references to the ASTM data files.

very important role in oxidation of glucose over Pd–Bi/SiO₂ catalysts.

Bimetallic catalysts Pd–Bi/SiO₂ with a higher content of bismuth (5–8 wt. %), in the case of which the presence of intermetallic compounds BiPd and Bi₂Pd was found, are characterized by high activity and selectivity particularly in the reaction of glucose oxidation. Bimetallic systems with a small amount of bismuth (1–3 wt. %) in which the presence of BiPd was found, show high activity and selectivity in the oxidation of lactose. At the first sight, those experimental results do not seem to be clear. However, we should remember that necessary surface structure and electronic state of catalyst components should vary corresponding to the raw materials (glucose and lactose). This is probably the main reason for different behaviours of lactose and glucose (molecules with different size).

4. Conclusions

The activation of bimetallic Pd–Bi/SiO₂ systems in pure hydrogen at temperature 533 K leads to the formation of two binary alloys with the compositions BiPd and Bi₂Pd. The addition of a small amount of bismuth (1–3 wt. %) to the palladium catalysts has a positive influence on the catalytic properties Pd–Bi/SiO₂ systems in the oxidation of lactose. For those catalysts the formation of BiPd alloy was observed.

Bimetallic catalysts Pd–Bi/SiO₂ containing a high amount of bismuth (5–8 wt.%) were found more effective in the oxidation of glucose. For those systems XRD and ToF-SIMS measurements showed the presence of BiPd and Bi₂Pd.

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