

# Catalytic properties of Pd–Tl/SiO<sub>2</sub> systems in the reaction of liquid phase oxidation of aldoses

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## Abstract

The influence of thallium addition on the catalytic properties of palladium catalysts supported on SiO<sub>2</sub> in the reaction of aldoses (glucose and lactose) oxidation to aldonic acid was studied. It was found that thallium does not have any activity by itself, but acts as “promoter” for the catalytic activity and selectivity of monometallic Pd/SiO<sub>2</sub> catalysts. The XRD studies proved the presence of intermetallic compounds, which probably increases activity and selectivity of bimetallic catalysts in those reactions. The same interaction was found using ToF-SIMS. The TPO studies show that palladium oxidation occurs at much higher temperatures than in the case of thallium. A reaction involving bimetallic catalysts in oxidizing atmosphere at 333 K should not lead to surface oxidation of palladium and thus their deactivation.

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

## 1. Introduction

Oxidation of organic compounds on metal catalysts has been known for a long time, but there has been a renewed interest in recent years because these reactions are environmentally safer than stoichiometric oxidations.

Catalytic oxidation reactions are conducted either in the gas phase at high temperatures with short contact time, or in the liquid phase usually at temperatures lower than 373 K. Catalysts are supported or unsupported zerovalent metals of groups 8–11, usually platinum, palladium or silver, and the oxidizing agent is molecular oxygen.

Liquid phase oxidations on metal catalysts were employed during the last century for the oxidation of carbohydrates. Carbohydrates are produced in nature by photosynthesis and can be used as a feedstock for the chemical industry. New compounds of very interesting properties can be obtained as a result of catalytic oxidation of carbohydrates.

One of such products is gluconic acid used in food and pharmaceutical industry and also as a biodegradable chelating agent.

Nowadays, this acid is produced in industry with the use of enzyme oxidation of glucose.

Another product of oxidation of carbohydrates is lactobionic acid. This monocarboxylic acid and its salts are non-toxic substances used in food and pharmaceutical industry as acidifying and chelating agents. Moreover, lactobionic acid possesses all properties of PHA acids used in cosmetics. Lactobionic acid binds water and keeps it in the epidermis. An addition of this acid into cosmetic specimens prevents water loss and gives an effect of smoothing out and skin softening. Lactobionic acid has antioxidizing properties too. Nowadays, lactobionic acid is produced in industry with the use of microbiological oxidation of lactose.

Lately there has been an increasing interest in the production of gluconic acid and lactobionic acid by catalytic oxidation of carbohydrates. The reactions of oxidations of aldoses are usually carried out in solution using oxygen or air as an oxidation agent in the presence of supported noble metals (Pt, Pd). However, the selectivity of those monometallic catalysts, for example supported Pd, is not higher than 60%. The same we observed for conversion which is lower than selectivity [1,2].

In order to improve the selectivity and reduce the deactivation of palladium catalysts their modification with heavy metals is suggested [3–8]. We noticed that selectivity of supported

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palladium catalysts could be improved by an addition of bismuth [2,9–13].

In this paper we would like to present an influence of the addition of other heavy metals, i.e. thallium, on the activity and selectivity of palladium catalysts in the reaction of the oxidation of aldoses to aldonic acids. Moreover, the physicochemical properties of bimetallic systems were determined using X-ray diffraction studies, secondary mass ion spectrometry (ToF-SIMS) and temperature-programmed techniques (TPO and TPD). Because of the presence of aldonic salts, which show strong chelating properties in the reaction medium, the amount of Pd and Tl dissolved in the solution during glucose and lactose oxidation was studied.

## 2. Experimental

### 2.1. Catalysts preparation

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

Bimetallic Pd–Tl/SiO<sub>2</sub> catalysts containing 5 wt.% Pd and 0.1, 0.5, 1, 2, 4, 5, 8 wt.% Tl were obtained from 5% Pd/SiO<sub>2</sub> catalyst by repeated impregnation of this system with water solution of Tl<sub>2</sub>CO<sub>3</sub> (a.q., POCh Gliwice S.A.) according to the procedure described above.

### 2.2. Catalytic measurements

The oxidation of aldose solution ( $C_{0\text{glucose}} = 1.00 \text{ mol l}^{-1}$  (a.q., POCh Gliwice S.A.),  $C_{0\text{lactose}} = 0.50 \text{ mol l}^{-1}$  (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<sup>-1</sup>) 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 scheme of the reactor was included elsewhere [2].

The reaction was conducted at 333 K, pH 9. The mixture was stirred at 1300 rpm, and oxygen was bubbled through at 1.01 min<sup>-1</sup>. Samples of the reaction medium were taken every 20 min, filtered and analyzed using a liquid chromatograph LaChrom (Merck 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 mm × 3.3 mm i.d., 45 000 plates m<sup>-1</sup>, using water solution of ACN as a mobile phase.

### 2.3. Characterization of catalysts

Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using Cu K $\alpha$  radiation

( $\lambda = 154.18 \text{ pm}$ ). Crystalline phases were identified by references to the PDF data files.

### 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 <sup>69</sup>Ga<sup>+</sup> primary ion gun and a high mass resolution time of flight mass analyzer. Three different working modes of primary Ga<sup>+</sup> 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 analyzed area was irradiated with the 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  $1 \times 10^{13}$  ions/cm<sup>2</sup>. Secondary ions emitted from the bombarded surface are mass separated and counted in a time of flight (ToF) analyzer. Spectra were recorded with high mass resolution ( $m/\Delta m$ ) at the 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 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 spectra collected for the selected number of points by rastering the primary ion beam over the analyzed area. The catalyst samples were prepared by pressing pellets.

Temperature-programmed oxidation (TPO) measurements were carried out with a series of catalysts: 5% Pd/SiO<sub>2</sub>, 5% Pd–5% Tl/SiO<sub>2</sub> and 5% Tl/SiO<sub>2</sub>. Measurements of temperature-programmed oxidation (TPO) were carried out in a standard flow apparatus using a katharometer as a detector. Before the thermooxidation process, each catalyst was reduced in hydrogen at 573 K for 1 h. A mixture containing 95% of helium and 5% of oxygen, a flow-rate 40 cm<sup>3</sup> min<sup>-1</sup> and a linear rate of temperature increase in 10 K min<sup>-1</sup> were used in this study.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis of reaction mixture. Thallium and palladium losses from the catalysts in reaction mixture during 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-AES analysis.

## 3. Results and discussion

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

$$X (\%) = [1 - (C/C_0)] \times 100,$$

$$S (\%) = [C_A/(C_0 - C)] \times 100$$

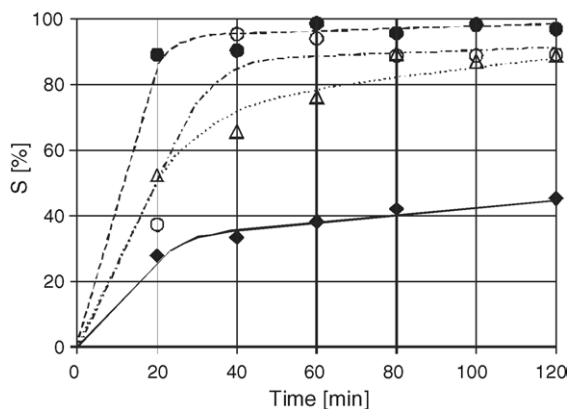


Fig. 1. Conversion of glucose in the presence of the catalysts: 5% Pd/SiO<sub>2</sub> (◆), 5% Pd-0.5% Tl/SiO<sub>2</sub> (▲), 5% Pd-3% Tl/SiO<sub>2</sub> (○), 5% Pd-5% Tl/SiO<sub>2</sub> (●) and 5% Pd-8% Tl/SiO<sub>2</sub> (△), as a function of time.

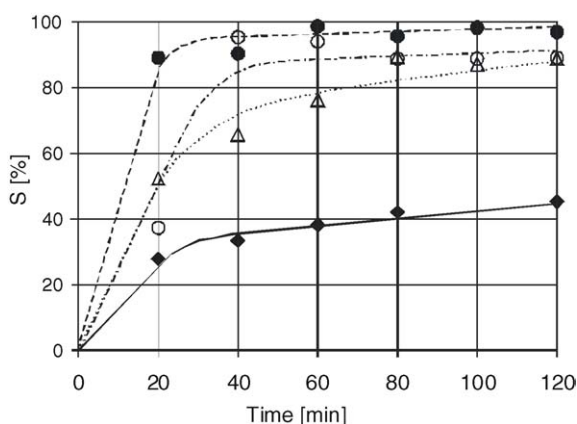


Fig. 2. Selectivity of the catalysts: 5% Pd/SiO<sub>2</sub> (◆), 5% Pd-3% Tl/SiO<sub>2</sub> (○), 5% Pd-5% Tl/SiO<sub>2</sub> (●) and 5% Pd-8% Tl/SiO<sub>2</sub> (△) in the reaction of glucose oxidation to form gluconic acid, as a function of time.

where  $C_0$  was a molar concentration of aldose (glucose, lactose) at the beginning of the oxidation process,  $C$  a molar concentration of aldose after time  $t$ , and  $C_A$  was a molar concentration of aldonic acid (gluconic acid, lactobionic acid) after time  $t$ .

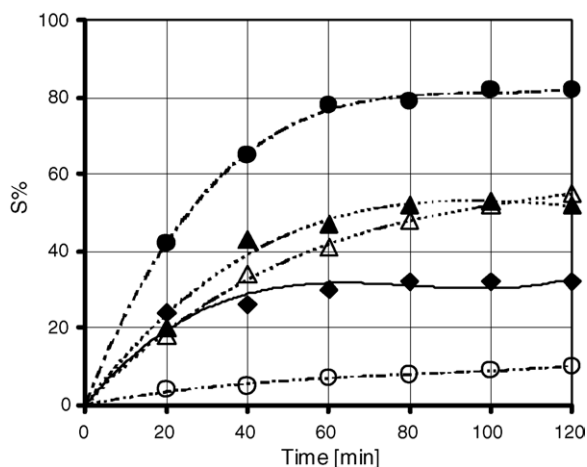


Fig. 3. Selectivity of the catalysts: 5% Pd/SiO<sub>2</sub> (◆), 5% Pd-1% Tl/SiO<sub>2</sub> (▲), 5% Pd-3% Tl/SiO<sub>2</sub> (△), 5% Pd-5% Tl/SiO<sub>2</sub> (●) and 5% Pd-8% Tl/SiO<sub>2</sub> (○) in the reaction of lactose oxidation to form lactobionic acid, as a function of time.

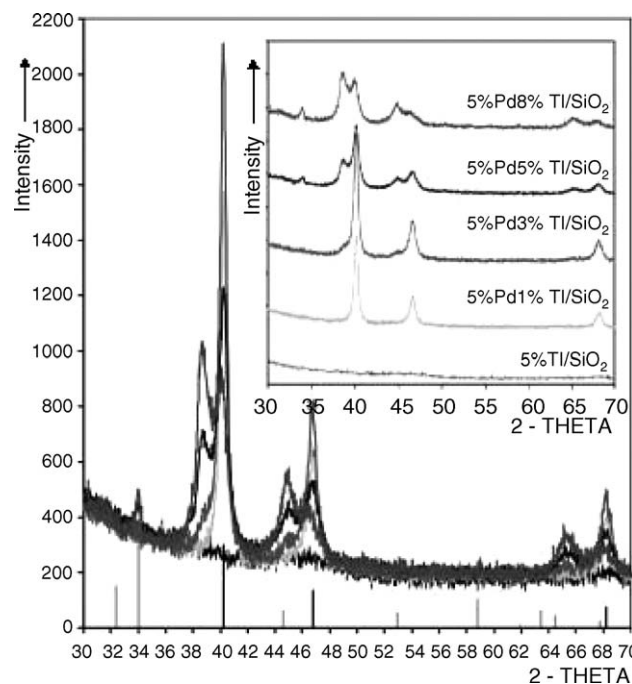


Fig. 4. Diffractograms of Pd-Tl/SiO<sub>2</sub> catalysts. Crystalline phases: Pd (—) and Tl (—) were identified by references to the PDF data file.

Fig. 1 shows the conversion of glucose of palladium catalysts supported on silica and modified with thallium. The addition of less than 3 wt.% of thallium to the 5% Pd/SiO<sub>2</sub> catalyst does not significantly influence the value of conversion, which is not high and approaches 30% like in the case of using monometallic palladium catalyst. Bimetallic system which contains 5% Tl proved the highest activity, over 50%. However, introduction of more than 5 wt.% of thallium into the system leads to a decrease in the conversion.

Similar results we obtained for bimetallic Pd-Tl/SiO<sub>2</sub> catalysts in the reaction of oxidation of lactose to lactobionic acid. The addition of 0.1–1 wt.% Tl to the monometallic catalyst does not significantly influence the value of conversion, which

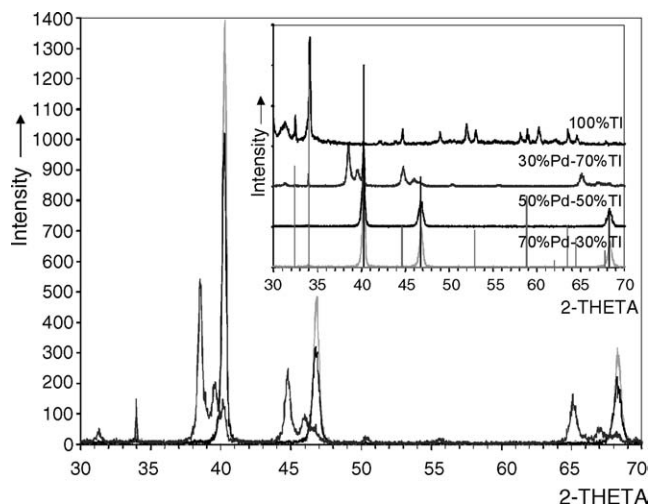


Fig. 5. Diffractograms of unsupported Pd-Tl systems. Crystalline phases: Pd (—) and Tl (—) were identified by references to the PDF data file.

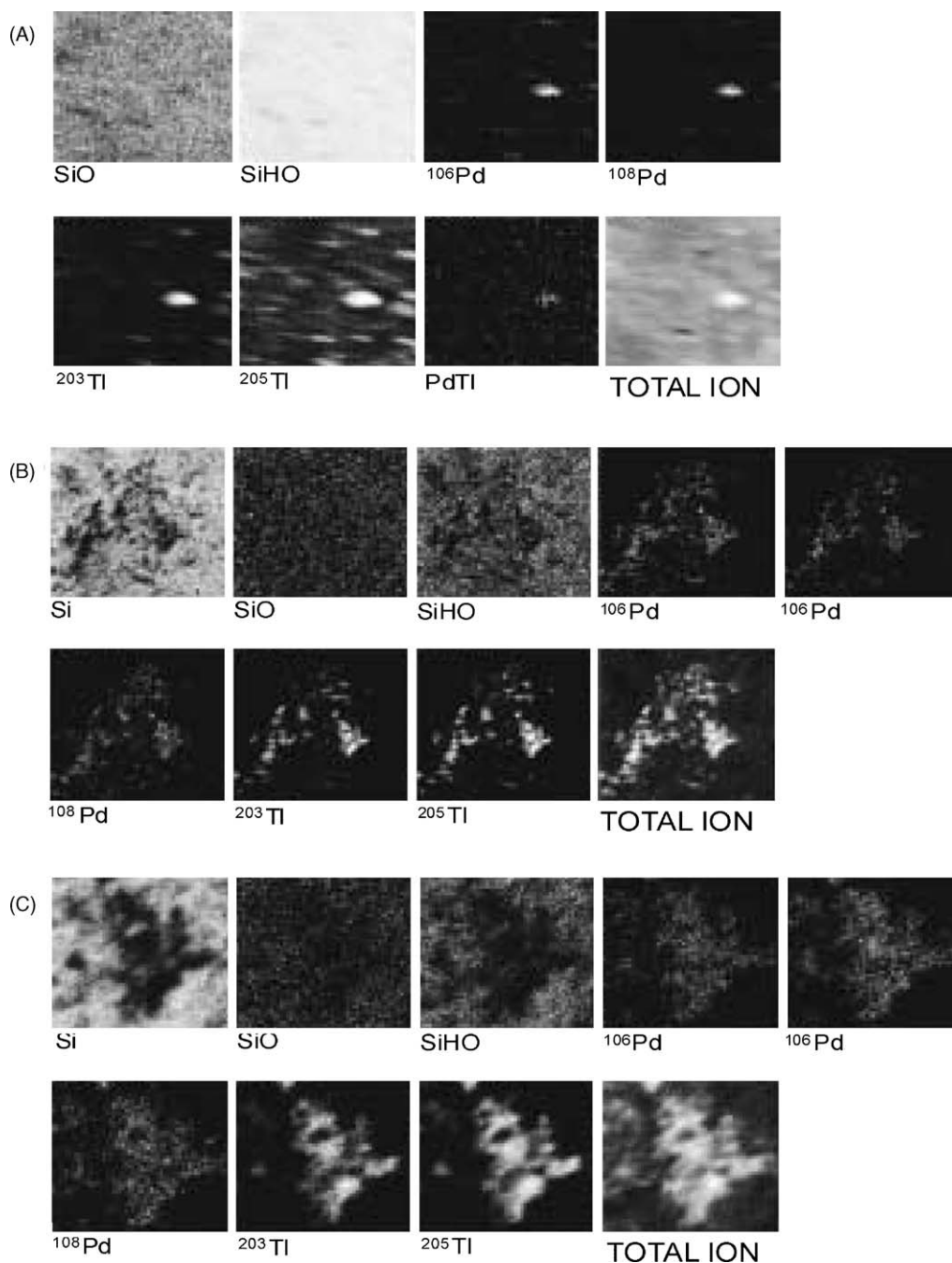


Fig. 6. Ionic view of microarea of 5% Pd–5% Tl/SiO<sub>2</sub> catalysts after reduction in H<sub>2</sub>. Images were recorded from area: (a) 500 μm × 500 μm, (b) 68.3 μm × 68.3 μm and (c) 20.5 μm × 20.5 μm. The pattern was obtained with ToF-SIMS IV spectrometer (ION-TOF, Münster, Germany) using gallium gun (<sup>69</sup>Ga, 25 keV) as a source of primary ions in the static mode.

approaches 25%. The catalysts containing 3–5 wt.% of thallium proved the higher activity in this process, over 30%. Introducing 8 wt.% of thallium into the system leads to a decrease in the conversion.

Fig. 2 shows the selectivity of palladium catalysts promoted with thallium in the reaction of glucose oxidation to gluconic acid. The addition of small amounts of thallium to palladium catalysts (5% Pd–0.1% Tl/SiO<sub>2</sub>, 5% Pd–0.5% Tl/SiO<sub>2</sub>, 5% Pd–1% Tl/SiO<sub>2</sub>) does not influence the selectivity and those results are not presented in the picture. However, palladium catalysts con-

taining 3–8 wt.% of thallium show a particularly high selectivity, above 90%.

Fig. 3 shows the selectivity of palladium catalysts supported on silica and modified with thallium in the reaction of oxidation of lactose to form lactobionic acid. In the case of using monometallic palladium catalyst value of selectivity is not high and approaches 30%. Catalysts containing 5% Pd–5% Tl/SiO<sub>2</sub> show a particularly high selectivity exceeding 80%. The probable reason for such significant changes is the interaction between palladium and thallium.

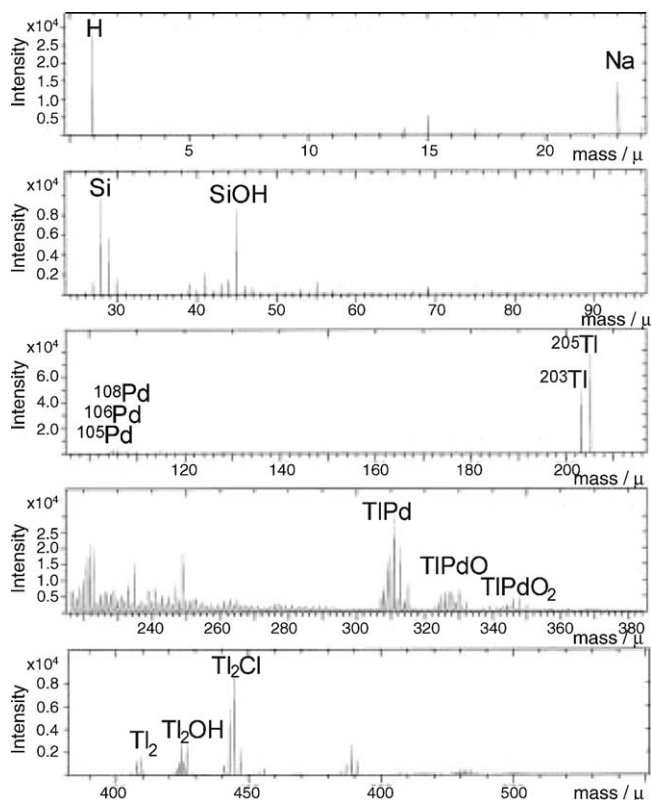


Fig. 7. Secondary ions mass spectra of 5% Pd–5% Tl/SiO<sub>2</sub> catalyst after reduction at 533 K and oxidation at 533 K in air atmosphere.

Palladium catalysts promoted with thallium after an identical treatment to the one in the case of catalytic studies were characterized by XRD.

The XRD studies of sample bimetallic catalysts after their reduction are presented in Fig. 4.

Metallic palladium was observed in all supported bimetallic systems. On the other hand, the presence of metallic thallium was observed only in the case of catalysts containing 5 and 8% of thallium. New maxima which appeared in diffractograms of bimetallic systems suggested the formation of intermetallic compounds on the surface.

To get to know better the nature of the interaction between palladium and thallium, unsupported systems containing: 70% Pd–30% Tl, 50% Pd–50% Tl, 30% Pd–70% Tl and 100% Tl were prepared. After calcination (air, 4 h, 773 K) and reduction (H<sub>2</sub>, 2 h, 533 K), the samples were characterized by XRD. In Fig. 5 the X-ray diffractograms are reported.

In the case of bimetallic unsupported systems the same diffraction maxima as in the case of Pd–Tl/SiO<sub>2</sub> catalysts are also observed. The diffractograms obtained from bimetallic systems show additional maxima, which could prove the formation of Pd–Tl intermetallic compounds whose stoichiometry was not identified by references to the PDF data file.

It proves that for Pd–Tl systems the ligands effect, which is caused by a strong interaction between Pd and Tl, probably plays a dominant role. As a result, intermetallic compounds are formed. They may be responsible for the high selectivity of the catalysts studied in the reactions of glucose and lactose oxidation.

We have used ToF-SIMS spectrometry to study the distribution of Tl and Pd atoms at the surface of bimetallic catalysts. This technique made it possible to observe the changes of catalyst surface which are invisible for XRD.

Fig. 6 shows an ionic view of microarea of palladium catalyst supported on silica and modified with thallium after the reduction in hydrogen atmosphere for 2 h at 260 °C. The brightness of the particular regions in the images corresponds to the intensity of secondary ions emission.

These results demonstrate that thallium is deposited on Pd particles, thereby generating bimetallic particles of various compositions. The presence of signal which came from PdTl<sup>+</sup> ions in the ToF-SIMS spectra indicates the formation of intermetallic compounds of PdTl type on the surface of Pd–Tl/SiO<sub>2</sub> catalysts.

Taking into consideration the formation of intermetallic ions of TIPd type, one can assume that the modification of catalytic properties of Pd–Tl/SiO<sub>2</sub> bimetallic systems results from the interaction between atoms of active Pd and Tl. Due to that interaction, the character and binding energy between the adsorbed particle and metal being the active centre can undergo changes, which consequently leads to the changes of selectivity of the whole system, which was observed in the study.

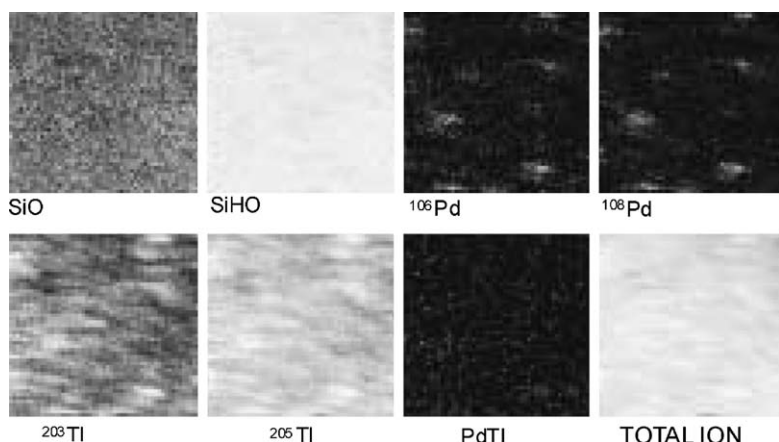


Fig. 8. Ionic view of microarea (500 μm × 500 μm) of 5% Pd–5% Tl/SiO<sub>2</sub> catalyst after activation in oxidizing atmosphere (4 h, 533 K, air). The pattern was obtained with ToF-SIMS IV spectrometer (ION-TOF, Münster, Germany) using gallium gun (<sup>69</sup>Ga, 25 keV) as a source of primary ions in the static mode.

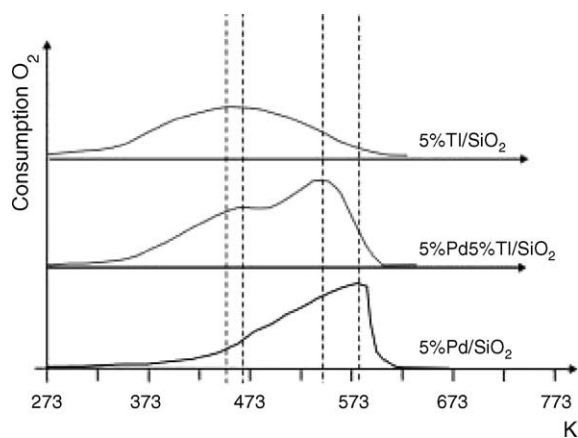


Fig. 9. Results of TPO measurements of monometallic and bimetallic catalysts. TPO spectra were measured for low rate of oxidation mixture (95% He + 5% O<sub>2</sub>) 40 cm<sup>3</sup> min<sup>-1</sup> and a linear increase in temperature 10 K min<sup>-1</sup>.

It is worth noticing that PdTi type compounds are stable in oxidizing atmosphere (Figs. 7 and 8). The reactions of aldoses oxidation occur in the oxidizing atmosphere and it cannot be excluded that in these conditions oxygenated systems of PdTiO and PdTiO<sub>2</sub> type were formed on the surface of the carrier. They may also be responsible for the high selectivity of the catalysts studied in the reactions of aldoses oxidation.

Mono- and bimetallic catalysts samples after reduction at 573 K underwent temperature-programmed oxidation (TPO) measurements (Fig. 9).

The results in Fig. 9 show that the oxidation of palladium, thallium and bimetallic catalyst occurs in the same temperature range (323–623 K). The temperature at which the maximum oxidation rate of Pd takes place is higher than observed for thallium. Due to such differences in the temperatures at which maxima of oxidation rate of Ti and Pd are observed, the oxidation of palladium at a temperature at which liquid phase oxidation of glucose to gluconic acid occurred does not seem very probable. Thus, the presence of thallium can prevent the surface oxidation of palladium.

Because gluconic acid and lactobionic acid are good chelating agents, the post-reaction mixture was studied with the aim of determining the presence of palladium and thallium. The results of ICP-AES analysis of the reaction mixture after the catalytic test are presented in Table 1.

The results presented in Table 1 show that the amounts of thallium transferred into the mixture depend on the percentage content of this metal in the catalyst. The reason why thallium and palladium are passed into the mixture is the presence of gluconian or lactobionian. When the catalysts were put in water and submitted to analogous oxidation conditions as in the case of sugar solution, only trace quantities of those metals were found.

The recognition of thallium transfer to reactive solution is very important due to the high toxicity of thallium compounds. Because of that, commercial application of Pd–Ti/SiO<sub>2</sub> systems

Table 1  
ICP analysis of reaction mixture after catalytic tests

Catalysis	Reaction medium	Pd 363.47 [71] (ppm)	Tl 190.864 [136] (ppm)
5% Pd–0.1% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.30	b.d.l.
5% Pd–0.5% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.58	b.d.l.
5% Pd–1% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.36	b.d.l.
	Lactose (0.5 mol dm <sup>-3</sup> )	0.42	b.d.l.
5% Pd–3% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.48	0.85
5% Pd–5% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.33	5.34
	Lactose (0.5 mol dm <sup>-3</sup> )	0.47	7.65
	H <sub>2</sub> O	b.d.l.	b.d.l.
5% Pd–8% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.63	12.05
5% Ti/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	–	59
	Lactose (0.5 mol dm <sup>-3</sup> )	–	65
	H <sub>2</sub> O	–	b.d.l.
5% Pd/SiO <sub>2</sub>	Glucose (1 mol dm <sup>-3</sup> )	0.29	–
	Lactose (0.5 mol dm <sup>-3</sup> )	0.45	–
	H <sub>2</sub> O	b.d.l.	–

The reaction conditions were: time of tests = 2 h, [catalyst] = 3.2 g dm<sup>-3</sup>, 333 K, pH 9, stirring at 1300 rpm and oxygen bubbled at 1 l min<sup>-1</sup>. b.d.l. means below direction limit).

to carbohydrates oxidation seems unlikely at this stage. However, the study of such systems is essential as far as nature of the interactions of metallic components is concerned.

#### 4. Conclusions

Palladium catalysts supported on SiO<sub>2</sub> modified with thallium show much higher selectivity than palladium catalysts in the reactions of glucose and lactose oxidation. During the process of catalyst activation in hydrogen atmosphere at 533 K, intermetallic compounds of PdTi type are formed as a result of Pd and Ti interaction. A rise in the selectivity observed for bimetallic catalysts in the described reactions is probably connected with the formation of those compounds.

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