Bismuth as an additive modifying the selectivity of palladium catalysts

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Abstract

The influence of bismuth addition on the activity and selectivity of palladium catalysts supported on SiO_2 in the reaction of glucose oxidation to gluconic acid was studied. The catalysts modified with Bi show much better selectivity and activity than palladium catalysts. The XRD studies proved the presence of intermetallic compounds BiPd and Bi_2Pd, which probably increase activity and selectivity of $PdBi/SiO_2$ catalysts in the oxidation of glucose. The TPO studies of catalysts containing 5 wt.% Pd/SiO_2, 3 wt.% Bi/SiO_2 and 5 wt.% Pd–5 wt.% Bi/SiO_2 show that palladium oxidation occurs at much higher temperatures than in the case of bismuth. The maximum rate of Pd oxidation occurs at around 580 K while the maximum rate of Bi oxidation takes place at around 430 K. Considering the above facts, 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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1. Introduction

The catalytic oxidation of glucose to gluconic acid is carried out with air or oxygen in aqueous medium in the presence of supported platinium or palladium catalysts [1–6]. In spite of high selectivity of these systems, they have not been found useful in industry because of their fast deactivation.

In order to decrease the deactivation as well as to improve the selectivity of platinium and palladium catalysts on supports, they are modified by metals like: Bi, Pb, Cd, Tl, etc., the role of which has not been fully defined yet [7–13].

It seems that applying the most adequate preparation and choosing a proper carrier can improve selectivity and prolong the catalyst life. Silica is one of the most often used metal catalyst carriers in industry. It is a relatively cheap, thermally stable carrier whose texture and structure can be modified considerably, which influences the catalytic properties of supported active phase.

In this paper, the activity and selectivity of palladium catalysts supported on SiO_2 and modified with bismuth in the reaction of liquid phase oxidation of glucose to gluconic acid were studied. Moreover, the phase composition of bimetallic systems was determined using X-ray diffraction studies. Because of the presence of gluconic salts, which show strong chelating properties in the reaction medium, the amount of Pd and Bi dissolved in the solution during glucose oxidation was studied.

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2. Experimental

2.1. Catalyst preparation

Catalysts containing 1, 3, 5 and 10 wt.% of palladium supported on silica (Aldrich, $250 \, \text{m}^2 \, \text{g}^{-1}$) were prepared from water solutions of $PdCl_2$ (aq., POCh Gliwice) by aqueous impregnation. The water was evaporated at an increased temperature (353 K) under vacuum. The catalysts were 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/SiO$_2$ catalysts containing 5 wt.% Pd and 0.25, 0.5, 1, 2, 4, 5, 8 wt.% Bi were obtained from 5% Pd/SiO$_2$ catalyst by repeated impregnation of this system with water solution of $Bi(NO_3)_3 \cdot 5H_2O$ (aq., POCh Gliwice) according to the procedure described above.

The preparation of palladium and bismuth-promoted palladium catalyst supported on carbon obtained from plum stones was described elsewhere [12,13].

2.2. Catalytic measurements

2.2.1. The oxidation of glucose

The oxidation of glucose solution ($1.00 \, \text{mol} \, \text{l}^{-1}$) was performed in a thermostated glass reactor of 400 ml equipped with a stirrer, an oxygen supply system, a burette containing NaOH ($1.00 \, \text{mol} \, \text{l}^{-1}$) and a pH electrode. The acids formed during the oxidation of glucose were neutralized by the addition of aqueous solution of sodium hydroxide to maintain constant pH = 9 in the reaction medium. The scheme of the reactor was included elsewhere [12].

The reaction was conducted at 333 K, pH = 9. The mixture was stirred at 1300 rpm, and oxygen was bubbled through at $1.01 \, \text{min}^{-1}$. 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 products were separated on an amino-propylo-silicone column 150 mm × 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)

The powder X-ray diffraction patterns were obtained with a Simens D5000 diffractometer using Cu Kα radiation (λ = 154.18 pm). Crystalline phases were identified by references to the ASTM data files.

2.2.3. 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.

2.2.4. TPO measurements

These were carried out with a series of catalysts: 5% Pd/SiO$_2$, 5% Pd–5% Bi/SiO$_2$ and 3% Bi/SiO$_2$. 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 $40 \, \text{cm}^3 \, \text{min}^{-1}$ and a linear rate of temperature increase of $10 \, \text{K} \, \text{min}^{-1}$ were used in this study.

3. Results and discussion

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

$$X = \left[1 - \left(\frac{C_{GLU}}{C_{0\,GLU}} \right) \right] \times 100\%$$

$$S = \left[\frac{C_{GLC}}{(C_{0\,GLU} - C_{GLU})} \right] \times 100\%$$

where C_{0GLU} is a molar concentration of glucose at the beginning of the oxidation process, C_{GLU} a molar concentration of glucose after time t, and C_{GLC} a molar concentration of gluconic acid after time t.

Figs. 1 and 2 show the dependence of selectivity and conversion on the time of glucose oxidation for palladium catalysts on silica. Together with a rise in the percentage content of palladium, there is a rise
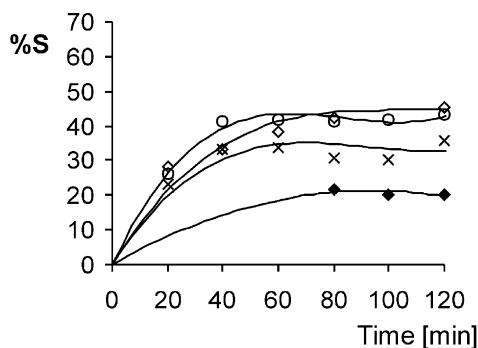
Fig. 1. Selectivity of the catalysts 1 wt.% Pd/SiO$_2$ (◆); 3 wt.% Pd/SiO$_2$ (×); 5 wt.% Pd/SiO$_2$ (◇) and 10 wt.% Pd/SiO$_2$ (○), as a function of time.

Fig. 3. Selectivity of catalysts: 5% Pd–2% Bi/SiO$_2$ (■); 5% Pd–4% Bi/SiO$_2$ (●); 5% Pd–5% Bi/SiO$_2$ (○) and 5% Pd–8% Bi/SiO$_2$ (×), as a function of time.

in the amount of gluconian being a result of the reaction (Fig. 1). Catalyst samples 10 wt.% Pd/SiO$_2$ show the highest selectivity while the catalyst 5 wt.% Pd/SiO$_2$ shows similar selectivity. Thus, introducing amounts of palladium higher than 5 wt.% into catalytic systems is groundless from a practical point of view.

The percentage content of palladium supported on SiO$_2$ does not significantly influence the value of conversion (Fig. 2). For all the catalysts studied, it is not high and approaches 30%.

Figs. 3 and 4 show the conversion and selectivity of palladium catalysts supported on silica and modified with bismuth. The presented tables prove that both selectivity and conversion are considerably higher than in the case of monometallic systems. Catalysts containing 5 wt.% Pd–5 wt.% Bi/SiO$_2$ show a particularly
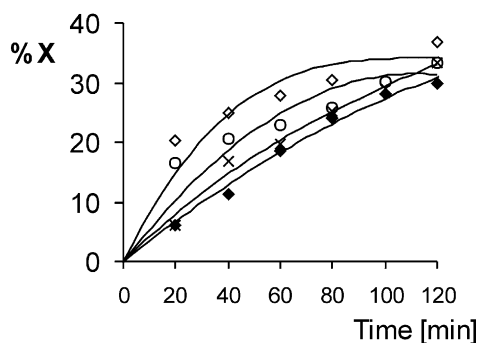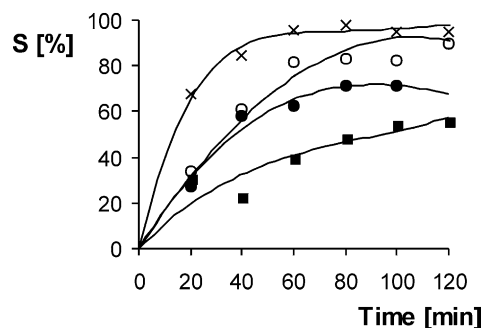
high selectivity exceeding 90% (Fig. 4). After the introduction of bismuth, a double rise in glucose conversion is observed compared with palladium catalysts not modified with this metal. The probable reason for such significant changes is the interaction between palladium and bismuth.

The addition of small amounts of bismuth to palladium catalysts (5 wt.% Pd–0.25 wt.% Bi/SiO$_2$, 5 wt.% Pd–0.5 wt.% Bi/SiO$_2$ and 5 wt.% Pd–1 wt.% Bi/SiO$_2$) does not significantly influence either selectivity or conversion.

The XRD studies of sample catalysts Pd–Bi/SiO$_2$ after reduction at 533 K (Table 1) prove the presence of intermetallic compounds. For low content of bismuth, compounds of BiPd type appear while for higher content of bismuth compounds containing Bi$_2$Pd are formed.
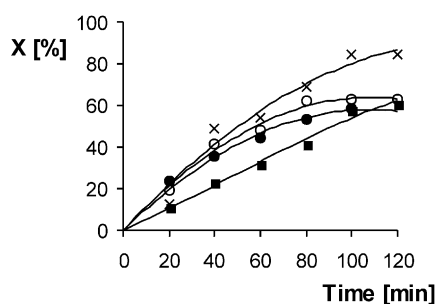

Fig. 2. Conversion of glucose in presence of the catalysts: 1 wt.% Pd/SiO$_2$ (◆); 3 wt.% Pd/SiO$_2$ (×); 5 wt.% Pd/SiO$_2$ (◇) and 10 wt.% Pd/SiO$_2$ (○), as a function of time.

Fig. 4. Conversion of glucose in presence of catalysts: 5% Pd–2% Bi/SiO$_2$ (■); 5% Pd–4% Bi/SiO$_2$ (●); 5% Pd–5% Bi/SiO$_2$ (○) and 5% Pd–8% Bi/SiO$_2$ (×), as a function of time.

Table 1
X-ray diffraction analysis of BiPd/SiO$_2$ catalysts

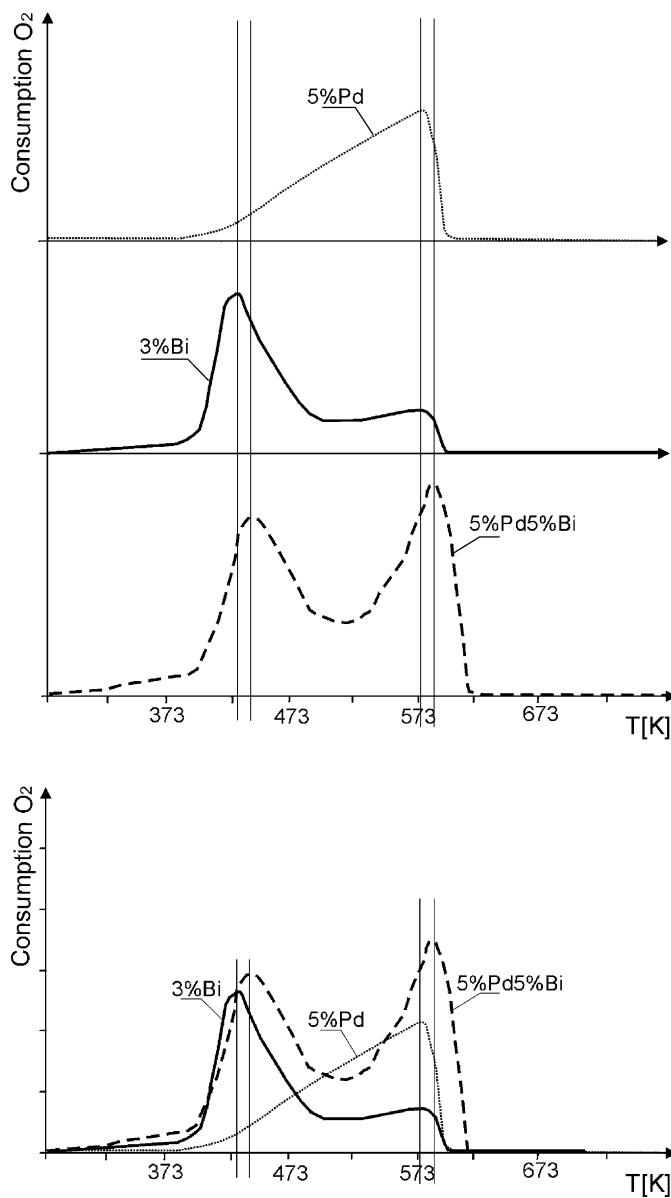| Catalyst	Bi (bismuth) syn	Pd (palladium) syn	BiPd (bismuth palladium) C	BiPd (sobolevskite) Q	Bi$_2$Pd (bismuth palladium) C
2% Bi 5% Pd/SiO$_2$	+	+	+	+	−
4% Bi 5% Pd/SiO$_2$	+	+	+	+	−
5% Bi 5% Pd/SiO$_2$	+	+	−	+	+

Fig. 5. Results of TPO measurements on 5 wt.% Pd/SiO$_2$ (—), 3 wt.% Bi/SiO$_2$ (▬), 5 wt.% Pd–5 wt.% Bi/SiO$_2$ (- - -). TPO spectra were measured for flow rate of oxidation mixture (95% He + 5% O$_2$) 40 cm^3 min^{-1} and linear increase of temperature 10 K min^{-1}.

Table 2
ICP analysis of reaction mixture after catalytic tests

Catalyst	Reaction medium	Pd (ppm) (363.470(71) nm)	Bi (ppm) (223.061(117) nm)
1% Bi 5% Pd/SiO$_2$	Glucose (1 mol dm^{-3})	–	0.3585
5% Bi 5% Pd/SiO$_2$	Glucose (1 mol dm^{-3})	–	28.27
	H$_2$O	–	0.2163
8% Bi 5% Pd/SiO$_2$	Glucose (1 mol dm^{-3})	–	57.90
3% Bi/SiO$_2$	Glucose (1 mol dm^{-3})	–	20.425
	H$_2$O	–	1.041

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}.

It proves that for Pd–Bi the ligands effect, which is caused by a strong interaction between Pd and Bi, plays a dominant role. As a result, intermetallic compounds of defined stoichiometry BiPd and Bi$_2$Pd are formed. They may be responsible for the high selectivity of the catalysts studied in the reaction of glucose oxidation.

The TPO studies prove that the presence of bismuth can, to some extent, prevent the surface oxidation of palladium and prolong the catalysts' life at the same time.

The results in Fig. 5 show that the oxidation of palladium takes place at much higher temperatures than the oxidation of bismuth. Such a phenomenon is observed for both monometallic and bimetallic Pd–Bi systems. The maximum rate of palladium oxidation takes place at around 580 K and in the case of bismuth at around 430 K.

Due to such big differences in the temperatures at which maxima of oxidation rate of Bi 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 bismuth prevents, to some extent, the surface oxidation of palladium.

Because gluconic acid is a good chelating agent, the post-reaction mixture was studied with the aim of determining the presence of palladium and bismuth. The results of ICP-AES analysis of the reaction mixture after the catalytic test are presented in Table 2.

The results presented in the Table 2 show that the amounts of bismuth transferred into the mixture depend on the percentage content of this metal in the

catalyst. The reason why bismuth is passed into the mixture is the presence of gluconian. When the catalysts were put in water and submitted to analogous oxidation conditions as in the case of sugar solution, only trace quantities of this metal were found. For all the systems studied, transfer of palladium into the mixture was not observed.

4. Conclusions

Palladium catalysts supported on SiO$_2$ modified with bismuth show much higher selectivity and activity than palladium catalysts in the reaction of glucose oxidation. During the process of catalyst activation in hydrogen atmosphere at 533 K, compounds of defined stoichiometry of BiPd type for small amounts of bismuth and Bi$_2$Pd for 5 wt.% Pd–5 wt.% Bi/SiO$_2$ catalysts are formed as a result of Pd and Bi interaction. A rise in selectivity observed for bimetallic catalysts in the described reaction is probably connected with the formation of those compounds.

Moreover, the TPO studies prove that the presence of bismuth can prevent the surface oxidation of palladium in the conditions of glucose oxidation.

The transfer of bismuth into the reaction solution observed during the oxidation process is connected with the chelating properties of gluconian.

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