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CATALYTIC REACTION MECHANISMS

Selective Oxidation of Glucose to Gluconic Acid over Bimetallic Pd–Me Catalysts (Me = Bi, Tl, Sn, Co)[1]

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Abstract—Catalytic properties of bimetallic Pd–Bi, Pd–Tl, Pd–Sn, and Pd–Co catalysts supported on C (from plum stones) and SiO_2 were studied in the reaction of glucose oxidation to gluconic acid. Catalysts modified with Bi show the best selectivity and activity. The results obtained from research on 5% Pd–5% Bi/C and 5% Pd–5% Bi/SiO_2 catalytic systems were compared with the results for a commercial catalyst containing 1% Pt–4% Pd–5% Bi supported on active carbon (Degussa). For both Pd–Bi/support catalysts and 1% Pt–4% Pd–5% Bi/C, similar selectivity in the reaction of glucose oxidation was observed. XRD studies proved the presence of intermetallic compounds BiPd and Bi_2Pd, which probably increase the selectivity of PdBi/SiO_2 catalysts.

INTRODUCTION

Studies of alloy catalysts were of considerable interest in the 1950s in conjunction with the burgeoning electronic theories of catalysis, but then they fell into disfavor. More recently they have been revived, stimulated by the industrial importance of bimetallic catalysts. Bimetallic catalysts form the basis for many important catalytic processes. Understanding of their improved activities or selectivities compared with catalysts involving only one metal is still a challenge.

The Pt–Re, Pt–Ir, and Pt–Sn catalysts are very important in reforming naphtha [1–7]. Nowadays, the largest volume of alloy Pt–Rh catalysts is being used in the catalytic detoxication of car exhaust gases [8–12].

Bimetallic catalysts that contain Pd play a very important role in chemical processes, too. It was found that Pd–Pt alloys show high selectivity in oxidation of hydrogen to hydrogen peroxide [13]. Supported palladium catalysts are characterized by high selectivity in the reaction of oxidation of various organic compounds, which can be increased by the addition of such metals as Bi, Tl, Co, Sn, Pb, and others. One such reaction is selective oxidation of glucose to gluconic acid [14–22].

In this paper we would like to present the influence of the addition of heavy metals to palladium supported catalysts on their selectivity in this reaction. The highest selectivity in the reaction of liquid phase oxidation of glucose is achieved in the case of bismuth, so most of this paper deals with the study of Pd–Bi/C and Pd–Bi/SiO_2 catalysts in this reaction. Because of the presence of gluconic salts, which show strong chelating properties in the reaction medium, the amount of metals in the solution during glucose oxidation was studied.

EXPERIMENTAL

Catalyst Preparation

Aqueous solutions of metal inorganic salt chlorides, carbonates, or nitrates were used for the preparation of all bimetallic catalysts (Table 1). The catalysts were prepared by repeated impregnation of a 5 wt % Pd catalyst supported on active carbon from plum stones (HPSDD, S_{BET} = 750 m^2/g) or silica (Aldrich, 250 m^2/g), the preparation of which was described elsewhere [14, 15, 21, 22]. Water was evaporated in increased temperature under vacuum. The catalysts were dried in air at 110°C for 6 h. Then, the catalysts were oxidized in an air atmosphere and reduced in hydrogen. Descriptions of the treatment steps of the catalyst used in this study are given in Table 1.

Catalytic Measurements

The oxidation of glucose solution (1.00 mol/l) was performed in a thermostatted glass reactor of 400 ml equipped with a stirrer, an oxygen supply system, a burette containing NaOH (1.00 mol/l) and a pH electrode. The acids formed during the oxidation of glucose were neutralized by the addition of an aqueous solution of sodium hydroxide to maintain constant pH = 9 in the reaction medium. The scheme of the reactor was included elsewhere [15].

The reaction was conducted at 60°C and pH = 9. The mixture was stirred at 1300 rpm, and oxygen was bubbled through at 1.0 l/min. 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

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[1] This article was submitted by the authors in English.

Table 1. Descriptions of catalyst preparation

Catalyst, wt %	Metallic precursors		Conditions of treatment steps	
	active metal	promotor	oxidation in air	reduction in H_2
5%Pd–1%Bi/C	$PdCl_2$ (a. q., POCh Gliwice)	$Bi(NO_3)_3 \cdot 5H_2O$ (a. q., POCh Gliwice)	260°C, 2 h	260°C, 2 h
5%Pd–3%Bi/C				
5%Pd–5%Bi/C				
5%Pd–8%Bi/C				
5%Pd–2%Bi/SiO_2			500°C, 4 h	260°C, 2 h
5%Pd–4%Bi/SiO_2				
5%Pd–5%Bi/SiO_2				
5%Pd–8%Bi/SiO_2				
5%Pd–5%Tl/C	$PdCl_2$ (a. q., POCh Gliwice)	$TlNO_3$ (a. q., POCh Gliwice)	260°C, 2 h	260°C, 2 h
5%Pd–5%Tl/SiO_2		Tl_2CO_3* (Johnson Matthey Chemicals Limited)	500°C, 4 h	260°C, 2 h
5%Pd–5%Co/C	$PdCl_2$ (a. q., POCh Gliwice)	$Co(NO_3)_2 \cdot 6H_2O$ (a. q., POCh Gliwice)	260°C, 2 h	260°C, 2 h
5%Pd–5%Sn/C	$PdCl_2$ (a. q., POCh Gliwice)	$SnCl_2$ (a. q., POCh Gliwice)	260°C, 2 h	260°C, 2 h

150 × 3.3 mm ID, 45000 plates m^{-1}, using a water solution of ACN as a mobile phase.

Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using CuK_α radiation (λ = 154.18 pm). Crystalline phases were identified by references to the ASTM data files.

ICP AES (Inductively Coupled Plasma–Atomic Emission Spectrometer) analysis of reaction mixture. Bismuth and palladium losses from the catalysts in the 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.

RESULTS AND DISCUSSION

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

$$X = (1 - C_{GL}/C_{GLU}) \times 100\%,$$

$$S = (C_{GLC}/(C_{GLU} - C_{GL})) \times 100\%,$$

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

Figure 1a shows the conversion of glucose in the presence of palladium catalysts containing 5 wt % palladium and 5 wt % Me (Me = Bi, Tl, Sn, Co). The highest conversion was observed for palladium promoted with bismuth (5% Pd–5% Bi/C).

Figure 1b shows the selectivity of the Pd–Me/C catalysts (Me = Bi, Tl, Co, Sn) in the reaction of oxidation of glucose to gluconic acid. The results obtained prove a considerable influence of used metals on their selectivity. As was observed for conversion, the highest selectivity is achieved in the case of bismuth.

Studies of the influence of the carrier on the selectivity of palladium catalysts proved that palladium supported on silica showed similar selectivity to systems supported on active carbon [15]. Modification of those systems with bismuth leads to much better selectivity.

Figure 2 shows an influence of bismuth content on selectivity. An increase in bismuth content is accompanied by an increase in selectivity. Systems containing 5–8 wt % Bi show high selectivity (about 90%). These systems also show high conversion (about 60%).

Catalytic properties of catalysts obtained in the Institute of General and Ecological Chemistry at the Technical University of Lodz were compared with a commercial catalyst containing 1% Pt–4% Pd–5% Bi/C (Degussa) recommended for the reaction of liquid phase oxidation of organic compounds. The results obtained from studies of conversion and selectivity lead to the conclusion that the selectivity of 5% Pd–5% Bi/C and 5% Pd–5% Bi/SiO_2 is comparable to, and even a little higher than, that of the commercial system. In the case of conversion, lower values (about 60%) are observed only for the (Pd–Bi)/SiO_2 system.

To get to know better the reasons for the rise in selectivity of palladium catalysts promoted with bis-

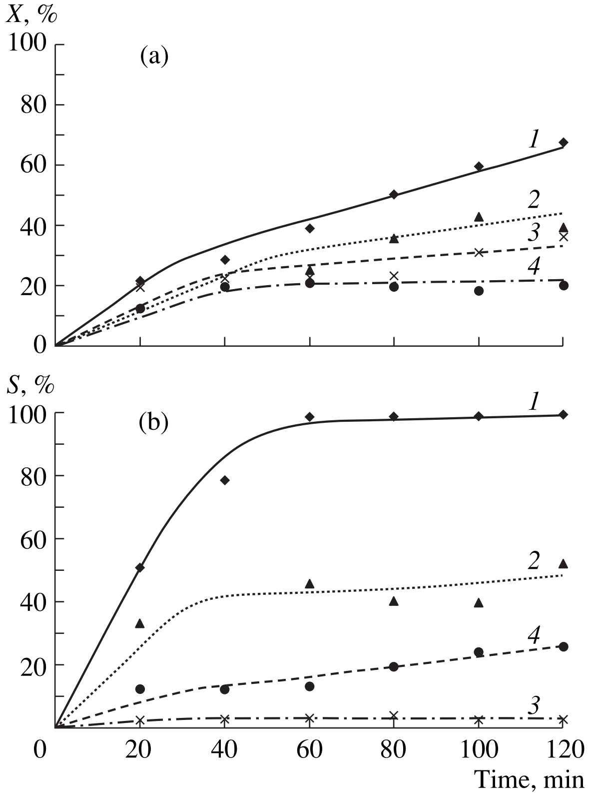

Fig. 1. Conversion (a) and selectivity (b) of glucose in the presence of the catalysts 5% Pd–5% Bi/C (*1*), 5% Pd–5% Tl/C (*2*), 5% Pd–5% Sn/C (*3*), and 5% Pd–5% Co/C (*4*) as a function of time.

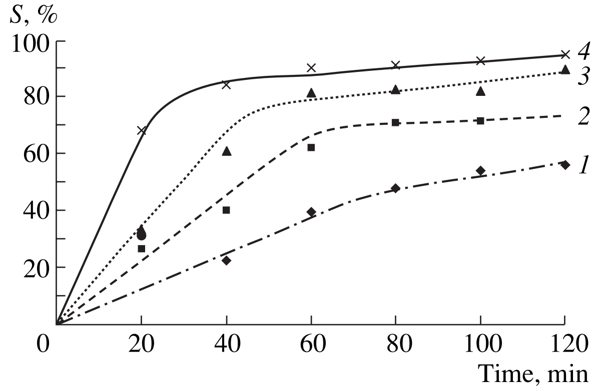

Fig. 2. Selectivity of the catalysts 5% Pd–2% Bi/SiO_2 (*1*), 5% Pd–4% Bi/SiO_2 (*2*), 5% Pd–5% Bi/SiO_2 (*3*), and 5% Pd–8% Bi/SiO_2 (*4*) as a function of time.

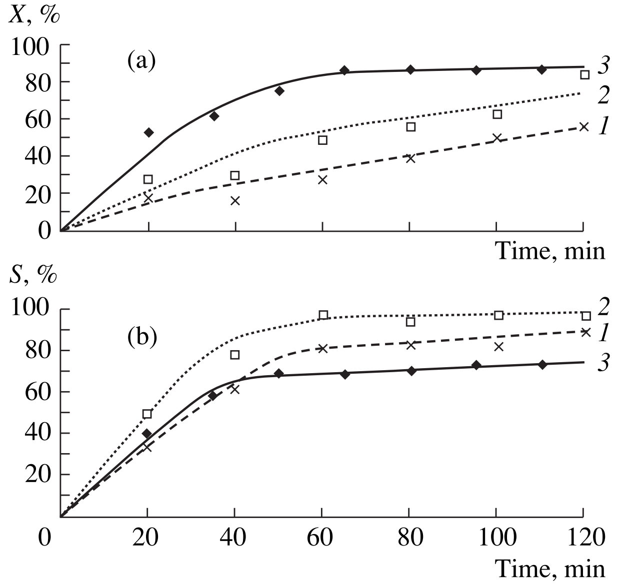

Fig. 3. Conversion and selectivity of the catalysts 5% Pd–5% Bi/C (*1*), 5% Pd–5% Bi/SiO_2 (*2*), and 1% Pt–4% Pd–5% Bi/C Degussa (*3*), as a function of time.

muth, X-ray studies of those systems were carried out after an identical treatment to the one in the case of catalytic studies.

The XRD studies of sample 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 after reduction at 260°C are presented in Fig. 4.

Regardless of the percentage content of Bi, the presence of metallic Pd and Bi is always observed in the systems studied. For small amounts of bismuth in Pd–Bi/SiO_2 systems reduced at 260°C, intermetallic compounds of BiPd type are formed. In the case of a higher content of Bi, that is, 5% Pd–5% Bi/SiO_2 and 5% Pd–8% Bi/SiO_2, intermetallic compounds of Bi_2Pd type of defined stoichiometry richer in Bi are formed with the exception of metallic Pd and Bi.

Taking into consideration the formation of intermetallic compounds of defined stoichiometry of BiPd and Bi_2Pd types, one can assume that the modification of the catalytic properties of Pd–Bi/SiO_2 bimetallic systems results from a ligand effect consisting in electron interaction between atoms of active Pd and surrounding Bi atoms, which play the role of ligands. Due to those interactions, the character and binding energy between the adsorbed particle and the metal that is the active center can undergo changes, which consequently leads to changes in the selectivity of the whole system, which were observed in the studies.

The presence of metallic Bi and Pd on the surface of the systems studied does not, however, exclude the influence of the ensemble effect.

The reaction of glucose oxidation was carried out in aqueous solution (1 mol/l) at 60°C. The gluconic acid thus obtained was neutralized with NaOH solution in order to maintain a constant pH = 9 (±0.1 pH). The production of sodium gluconate is, however, a matter of great importance, because gluconic acid is known to be a good chelating agent for heavy metals [23]. Because of this, partial dissolution of metals during catalytic processes can take place. The ICP analyses of the reaction mixture after catalytic tests are summarized in Table 2. Those results show partial dissolution of added

Table 2. Amounts of metals dissolved in the reaction mixture during the process of glucose oxidation (b.d.l.—below detection limit)

Catalyst, wt %	$Pd_{363.470}$ (71) nm	Dissolved inactive metals			
		$Bi_{223.061}$ (117) nm	$Tl_{377.572}$ (69) nm	$Sn_{235.484}$ (110) nm	$Co_{228.616}$ (113) nm
5%Pd–1%Bi/C	b.d.l.	7.70	–	–	–
5%Pd–3%Bi/C	b.d.l.	25.16	–	–	–
5%Pd–5%Bi/C	b.d.l.	32.42	–	–	–
5%Pd–8%Bi/C	b.d.l.	58.24	–	–	–
5%Pd–2%Bi/SiO_2	b.d.l.	8.52	–	–	–
5%Pd–4%Bi/SiO_2	b.d.l.	18.92	–	–	–
5%Pd–5%Bi/SiO_2	b.d.l.	28.70	–	–	–
5%Pd–8%Bi/SiO_2	b.d.l.	57.90	–	–	–
5%Pd–5%Tl/C	0.24	–	39.27	–	–
5%Pd–5%Tl/SiO_2	0.33	–	b.d.l.	–	–
5%Pd–5%Co/C	0.29	–	–	–	51.41
5%Pd–5%Sn/C	0.26	–	–	11.88	–

inactive metals for all the catalysts used in this reaction. The amount of metal dissolved from the catalyst in the solution depends on the promoting element.

Unlike in the case of inactive metals, the dissolution of palladium was rarely detected under the present experimental conditions.

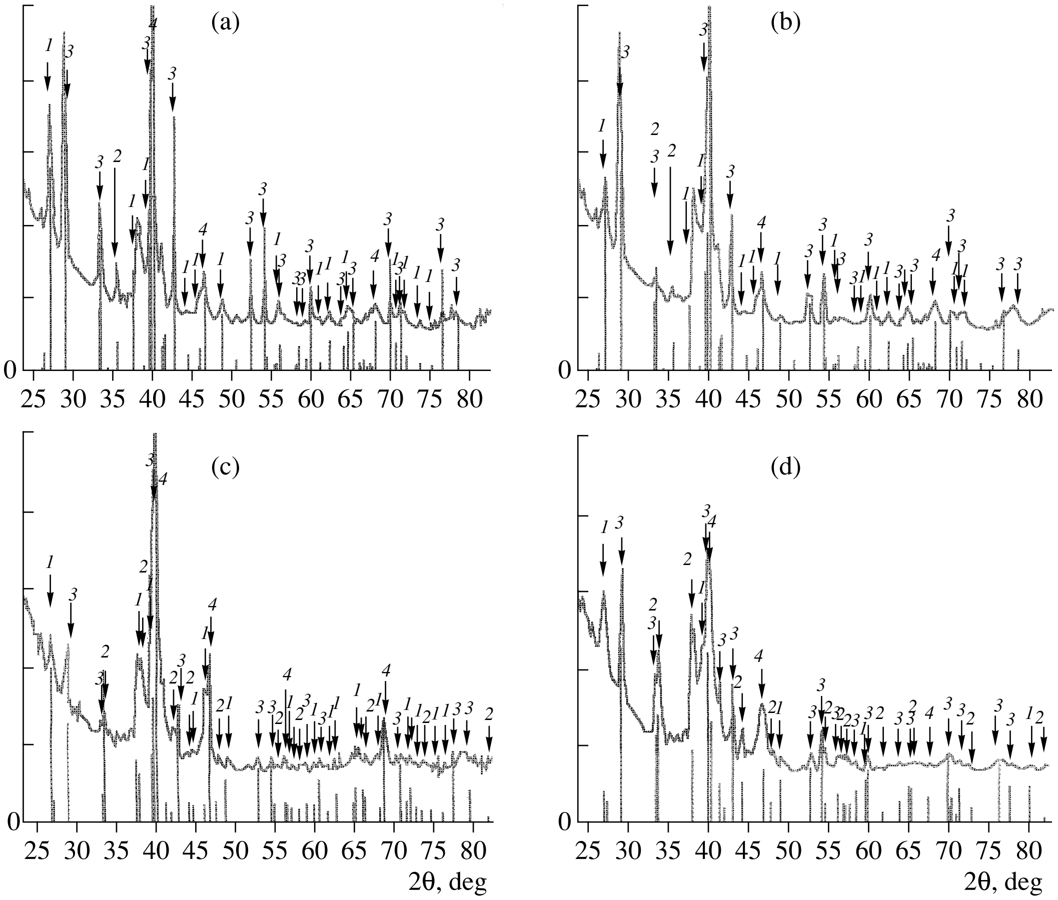

Fig. 4. Diffractograms of (a) 5% Pd–2% Bi/SiO_2, (b) 5% Pd–4% Bi/SiO_2, (c) 5% Pd–5% Bi/SiO_2, and (d) 5% Pd–8% Bi/SiO_2 catalysts. Crystalline phases were identified by references to the ASTM data files.

CONCLUSIONS

The research we carried out proved that the best catalytic properties in the reaction of selective oxidation of glucose are shown by bismuth promoted systems. In the case of other metals (Tl, Co, Sn), it is necessary to do further research connected with the application of other preparation methods and the conditions of thermal treatment.

During the process of catalyst activation in a hydrogen atmosphere at 260°C, compounds of defined stoichiometry of BiPd type for small amounts of bismuth, and also Bi_2Pd for 5 wt % Pd–5 wt % Bi/SiO_2 and 5 wt % Pd–8 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 reaction described is probably connected with the formation of those compounds.

The transfer of Bi, Tl, Sn, and Co into the reaction solution observed during the oxidation process is connected with the chelating properties of gluconic acid.

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