

CATALYTIC REACTION MECHANISMS

Thallium as an Additive Modifying the Selectivity of Pd/SiO₂ Catalysts¹

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Abstract—Catalytic properties of palladium and bimetallic palladium–thallium catalysts supported on SiO₂ in the reaction of glucose oxidation to gluconic acid were studied. Catalysts modified with thallium showed better selectivity and activity than palladium catalysts. XRD studies proved the presence of intermetallic interactions, which probably increase the selectivity of Pd–Tl/SiO₂ catalysts. Particular attention was paid to the losses of thallium and palladium from the catalysts during the catalytic reaction.

INTRODUCTION

The processes of selective oxidation of carbohydrate play an important role in chemical technology. New compounds with very interesting properties can be obtained as a result of those reactions. One such product is gluconic acid, used in the food and pharmaceutical industries. Recently, there has been an increasing interest in the production of gluconic acid by the catalytic oxidation of glucose. This reaction is 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 was observed for conversion, which is lower than the selectivity [1, 2].

In order to improve the selectivity and reduce of the deactivation of palladium catalysts, their modification with heavy metals is suggested [3–8]. We noticed that selectivity of supported palladium catalysts could be improved by the addition of bismuth [2, 9–12].

In this paper, we present the influence of the addition of another heavy metal, i.e., thallium, on the activity and selectivity of palladium catalysts in the reaction of the oxidation of glucose to gluconic acid.

CATALYSTS PREPARATION

A catalyst containing 5 wt % of palladium supported on silica (Aldrich, 250 m²/g) was prepared from water solutions of Pd/SiO₂ (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 an air atmosphere, and then reduced in a hydrogen atmosphere for 2 h at 533 K.

Bimetallic Pd–Tl/SiO₂ catalysts containing 5 wt % Pd and 0.1, 0.5, 1, 2, 4, 5, or 8 wt % Tl were obtained from 5% Pd/SiO₂ catalyst by repeated impregnation of this system with water solution of Tl₂CO₃ (a.q., POCh Gliwice S.A.) according to the procedure described above.

CATALYTIC MEASUREMENTS

The oxidation of glucose solution (1.00 mol/l) 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), 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 has been 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 1.0 l/min. 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 × 3.3 mm I.D., 45000 plates/m, using a water solution of ACN as the mobile phase.

Powder X-ray diffraction (XRD) patterns were obtained with a Siemens D5000 diffractometer using CuK_α radiation (α = 1.5418 pm). Crystalline phases were identified by references to the ASTM data files.

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-AES (inductively coupled plasma–atomic emission spectrometry) using

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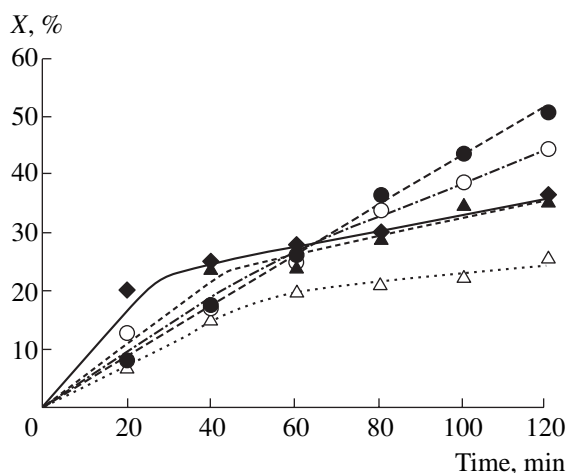


Fig. 1. Conversion of glucose in the presence of the catalysts 5%Pd/SiO₂ (◆), 5%Pd0.5%Tl/SiO₂ (▲), 5%Pd3%Tl/SiO₂ (○), 5%Pd5%Tl/SiO₂ (●), and 5%Pd8%Tl/SiO₂ (△) as a function of time.

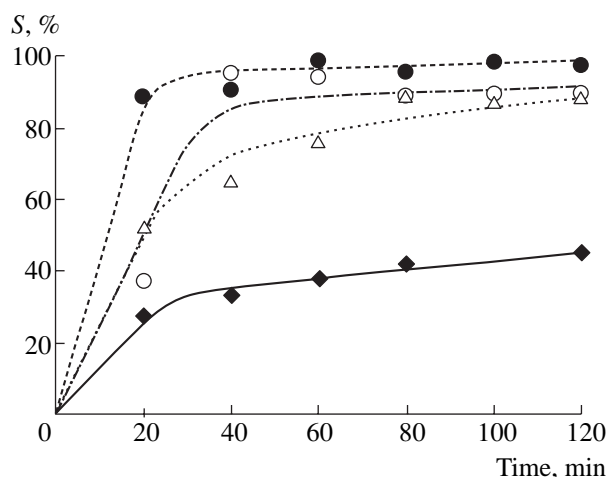


Fig. 2. Selectivity of the catalysts 5%Pd/SiO₂ (◆), 5%Pd3%Tl/SiO₂ (○), 5%Pd5%Tl/SiO₂ (●), and 5%Pd8%Tl/SiO₂ (△) as a function of time.

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.

RESULTS AND DISCUSSION

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

$$X = (1 - (C_{\text{GLU}}/C_{\text{GLU},0})) \times 100\%,$$

$$S = (C_{\text{GLK}}/(C_{\text{GLU},0} - C_{\text{GLU}})) \times 100\%,$$

where $C_{\text{GLU},0}$ was the molar concentration of glucose at the beginning of the oxidation process, C_{GLU} was the molar concentration of glucose after time t , and C_{GLK} was the molar concentration of gluconic acid after time t .

Figure 1 shows the conversion of glucose of palladium catalysts supported on silica and modified with thallium. The addition of thallium to the 5%Pd/SiO₂ catalyst does not significantly influence the value of conversion, which is not high and approaches 35%, as in the case of using monometallic palladium catalyst, and about 50% in the case of bimetallic system containing 5% Tl.

Figure 2 shows the selectivity of palladium catalysts promoted with thallium in the oxidation of glucose to

ICP analysis of reaction mixture after catalytic tests. The reaction conditions were: time of tests = 2 h, [catalyst] = 3.2 g/dm³, 333 K, pH 9, stirring at 1300 rpm, and oxygen was bubbled at 1 l/min

Catalysts	Reaction medium	Pd 363.47 [71] [ppm]	Tl 190.864 [136] [ppm]	Si 251.612 [104] [ppm]
5%Pd0.1%Tl/SiO ₂	Glucose (1 mol/dm ³)	0.300	b.d.l.	12.65
5%Pd0.5%Tl/SiO ₂	Glucose (1 mol/dm ³)	0.578	b.d.l.	8.27
5%Pd1%Tl/SiO ₂	Glucose (1 mol/dm ³)	0.360	b.d.l.	12.56
5%Pd3%Tl/SiO ₂	Glucose (1 mol/dm ³)	0.480	0.85	9.55
5%Pd5%Tl/SiO ₂	Glucose (1 mol/dm ³)	0.327	5.34	10.59
	H ₂ O	b.d.l.	b.d.l.	11.62
5%Pd8%Tl/SiO ₂	Glucose (1 mol/dm ³)	0.630	12.05	12.06
5%Tl/SiO ₂	Glucose (1 mol/dm ³)	—	59	8.60
	H ₂ O	—	b.d.l.	14.50
5%Pd/SiO ₂	Glucose (1 mol/dm ³)	0.290	—	9.05
	H ₂ O	b.d.l.	—	10.80

Note: b.d.l. means below detection limit.



Fig. 3. Diffractograms of the catalysts 5%Pd/SiO₂, 5%Pd1%Tl/SiO₂, 5%Pd3%Tl/SiO₂, 5%Pd5%Tl/SiO₂, 5%Pd8%Tl/SiO₂, and 5%Tl/SiO₂. Crystalline phases were identified by references to the ASTM data files.

gluconic acid. The addition of small amounts of thallium to palladium catalysts (5%Pd0.1%Tl/SiO₂, 5%Pd0.5%Tl/SiO₂, 5%Pd1%Tl/SiO₂) does not influence the selectivity. Palladium catalysts containing 3–8 wt % of thallium show a particularly high selectivity, above 90%. The probable reason for such significant changes is the interaction between palladium and thallium.

Figure 3 shows the XRD studies of sample Pd–Tl/SiO₂ catalysts after reduction at 533 K.

Figure 3 shows diffractograms of catalysts containing different amounts of thallium. They prove the fact that a rise in the percentage content of thallium in catalytic systems causes broadening of the palladium peaks and their division. It probably means that there is an

interaction between Pd and Tl, the nature of which is difficult to describe on the basis of these studies only. This interaction is possibly responsible for the high selectivity of Pd–Tl/SiO₂ catalysts in the reaction of glucose oxidation. Currently, further studies using XRD and XPS techniques are being carried out in order to explain this problem.

Because gluconic acid is a good chelating agent, the postreaction 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 the table.

The results presented in the table 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. When the catalysts were put in water and submitted to analogous oxidation conditions as in the case of a sugar solution, only trace quantities of those metals were found. For all the systems studied, transfer of Si into the mixture was observed.

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–Tl/SiO₂ systems to carbohydrates oxidation seems unlikely at this stage. However, the study of such systems is essential as far as the nature of the interactions of metallic components is concerned.

CONCLUSIONS

The catalysts modified with thallium (which contain >1 wt % Tl) show much better selectivity and activity in the reaction of glucose oxidation to gluconic acid than palladium catalysts. Together with a rise in the percentage content of thallium, there is a rise in the amount of gluconian being a result of the reaction. Catalysts containing 5%Pd5%Tl/SiO₂ show particularly high selectivity, exceeding 90%.

The XRD studies of the sample of Pd–Tl/SiO₂ catalysts after reduction at 533 K prove the presence of interaction between Pd and Tl, which probably leads to the high selectivity of those catalysts.

The results of ICP-AES analysis of the reaction mixture after the catalytic test show that the amounts of thallium transferred into the mixture depend on the percentage content of this metal in the catalyst. For all the

studied systems, transfer of Si into the mixture was observed.

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