



THE INFLUENCE OF TELLURIUM ADDITION TO SUPPORTED PALLADIUM CATALYSTS ON THEIR CATALYTIC PROPERTIES IN GLUCOSE OXIDATION

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The influence of tellurium addition on the catalytic properties of palladium catalysts supported on silica was investigated. The catalysts modified with Te show better activity, selectivity and stability than monometallic supported palladium catalyst. The studied catalysts were characterized by X-ray powder diffraction (XRD) and time of flight secondary ion mass spectrometry (ToF-SIMS). XRD and ToF-SIMS studies proved the presence of intermetallic compound PdTe, which probably increases activity and selectivity of Pd-Te/SiO₂ catalysts.

INTRODUCTION

Economic factors and the growing social pressure make chemical industry use new, renewable raw materials, whose technological processing leads to the formation of a great amount of valuable products. Carbohydrates such as lactose, glucose or cellulose constitute the main part of biomass and their chemical transformations lead to the formation of a lot of products with interesting properties. For example, in the oxidation of glucose, one of the main products is gluconic acid which has found application in cosmetic, pharmaceutical and food industry.¹⁻⁴

Gluconic acid can be easily obtained by catalytic oxidation of glucose on monometallic systems Pd/support and Pt/support. However, this process is not selective (is not higher than 60% to gluconic acid). Furthermore, these systems easily undergo deactivation because of the fact that oxygen dissolves on the surface layers of metals.⁵⁻⁷ Better results are obtained by using bimetallic and polimetallic catalysts.

The papers presented in literature suggest that the addition of metals such as Pb, Bi, Tl or Sn to

Pd and Pt supported catalysts may modify their activity and selectivity in the reactions of oxidation of carbohydrates in liquid phase.⁸⁻¹⁸ There is no experimental data concerning the influence of the addition of tellurium to palladium catalysts on their selectivity in the reaction of glucose oxidation. However, there are some premises that this element may modify the properties of metallic catalysts, especially selectivity, in the reaction of oxidation.¹⁹⁻³⁰

In this work, the influence of tellurium addition on catalytic properties of palladium catalysts, supported on silica in the glucose oxidation to gluconic acid was studied. On the basis of XRD and ToF-SIMS, the composition of metallic phase on the surface of studied catalysts was determined.

RESULTS AND DISCUSSION

The conversion of glucose and the selectivity towards the gluconic acid after 2 hours run in the presence of monometallic 5%Pd/SiO₂ and 1%Te/SiO₂ and bimetallic Pd-Te/SiO₂ catalysts is presented in Table 1.

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Table 1

Conversion degree of glucose and selectivity to gluconic acid at 120 minute of glucose oxidation over Pd-Te/SiO₂ catalysts. Reaction conditions: T = 60°C, m_{cat} = 1 g, C₀ = 1 mol/dm³, pH = 9, V_{O₂} = 1 dm³/min

Catalyst	X [%]	S _{gluconic acid} [%]
	120 min	120 min
5%Pd/SiO ₂	59.35	73.52
5%Pd-0.1%Te/SiO ₂	59.83	76.69
5%Pd-0.3%Te/SiO ₂	83.23	91.51
5%Pd-0.5%Te/SiO ₂	86.62	90.97
5%Pd-1%Te/SiO ₂	100	99.98
5%Pd-2%Te/SiO ₂	96.23	99.67
5%Pd-5%Te/SiO ₂	76.12	97.37
5%Pd-8%Te/SiO ₂	48.79	98.71
1%Te/SiO ₂	13.73	14.44

The introduction of tellurium to supported palladium catalysts leads to the improvement of catalytic properties in comparison with monometallic palladium system. In the case of 5%Pd/SiO₂, 5%Pd-0.1%Te/SiO₂, 5%Pd-0.3%Te/SiO₂, 5%Pd-0.5%Te/SiO₂ and 5%Pd-1%Te/SiO₂ catalysts in the reaction mixture we detected by HPLC only gluconic acid as a final product of the glucose oxidation. The lower selectivity towards this product observed for those bimetallic systems (Table 1) is probably connected with the adsorption of gluconic acid on the surface of Pd. When the 5%Pd-2%Te/SiO₂, 5%Pd-5%Te/SiO₂ and 5%Pd-8%Te/SiO₂ catalysts were used in the glucose oxidation, besides gluconic acid we detected also fructose and glucaric acid in the reaction mixture. Among studied catalysts, the system characterized by high activity and selectivity (5%Pd-1%Te/SiO₂) has been chosen to further research.

The stability of 5%Pd/SiO₂ and 5%Pd-1%Te/SiO₂ catalysts was determined on the basis of changes of glucose conversion during 10 measurement cycles. The oxidation of glucose was conducted with constant amount of catalyst (m_{cat} = 1 g) without removing it from the reaction mixture. After each measurement cycle, the new portion of glucose was introduced to the reaction. In the reaction mixture only the concentration of glucose

was analysed and on the basis of these values the stability of catalysts was estimated. The problem of the selectivity studies versus long time of the reaction run is being investigated now.

The obtained results (Fig. 1) show that bimetallic 5%Pd-1%Te/SiO₂ catalyst is characterized by high stability. Therefore, the addition of tellurium to monometallic palladium catalyst improves the stability of this system in the studied reaction.

The composition of 5%Pd-1%Te/SiO₂ catalyst was determined using ToF-SIMS and XRD techniques.

In Fig. 2 diffractograms of 5%Pd/SiO₂, 5%Pd-1%Te/SiO₂ and 5%Pd-8%Te/SiO₂ catalysts are shown. For the bimetallic 5%Pd-1%Te/SiO₂ (the atomic ratio Pd/Te = 6) system the additional maxima are observed, what do not occur for the monometallic palladium catalyst. These maxima are connected with the presence of intermetallic compound PdTe in the studied catalyst. The presence of intermetallic compound PdTe in studied catalyst 5%Pd-1%Te/SiO₂ is also confirmed by ToF-SIMS measurements (Fig. 3). Therefore, the presence of intermetallic compound PdTe on the surface of the studied bimetallic catalyst is probably the reason of their high activity and selectivity in the oxidation of glucose.

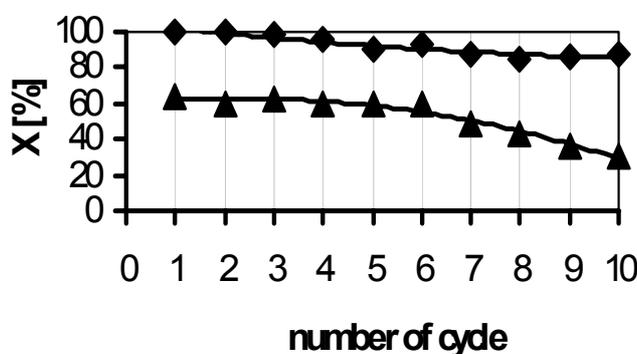


Fig. 1 – Stability of Pd/SiO₂ (▲) and 5%Pd-1%Te/SiO₂ (◆) catalysts in the reaction of glucose oxidation. Reaction conditions: T = 60°C, m_{cat} = 1 g, C₀ = 1 mol/dm³, pH = 9, V_{O₂} = 1 dm³/min.

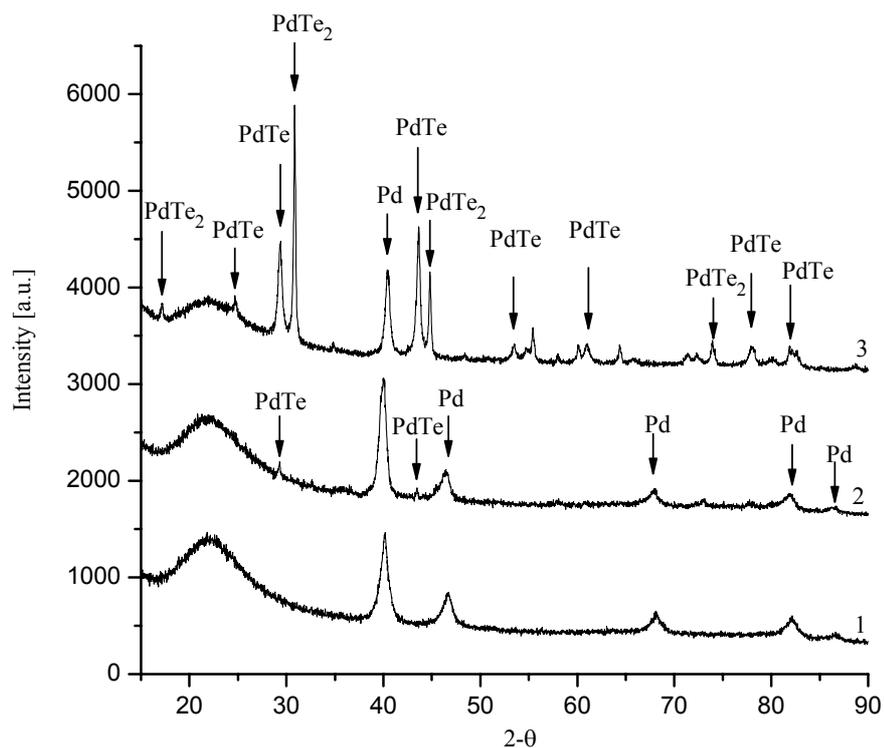


Fig. 2 – X-ray diffraction patterns of: 1-5%Pd/SiO₂; 2-5%Pd-1%Te/SiO₂; 3-5%Pd-8%Te/SiO₂. Catalysts were activated in hydrogen atmosphere for 2 h at 300°C.

Table 2

XRD patterns for 5%Pd/SiO₂, 1%Te/SiO₂, 5%Pd-X%Te/SiO₂ (X = 0.1-8 wt. %) catalysts. Crystalline phase were identified by references to ICDD PDF-2 (ver. 2004) data base

Catalyst	Pd	PdTe	PdTe ₂	Te
5%Pd/SiO ₂	+	-	-	-
5%Pd-0.1%Te/SiO ₂	+	+	-	-
5%Pd-0.3%Te/SiO ₂	+	+	-	-
5%Pd-0.5%Te/SiO ₂	+	+	-	-
5%Pd-1%Te/SiO ₂	+	+	-	-
5%Pd-2%Te/SiO ₂	+	+	-	-
5%Pd-5%Te/SiO ₂	+	+	+	-
5%Pd-8%Te/SiO ₂	+	+	+	-
1%Te/SiO ₂	-	-	-	+

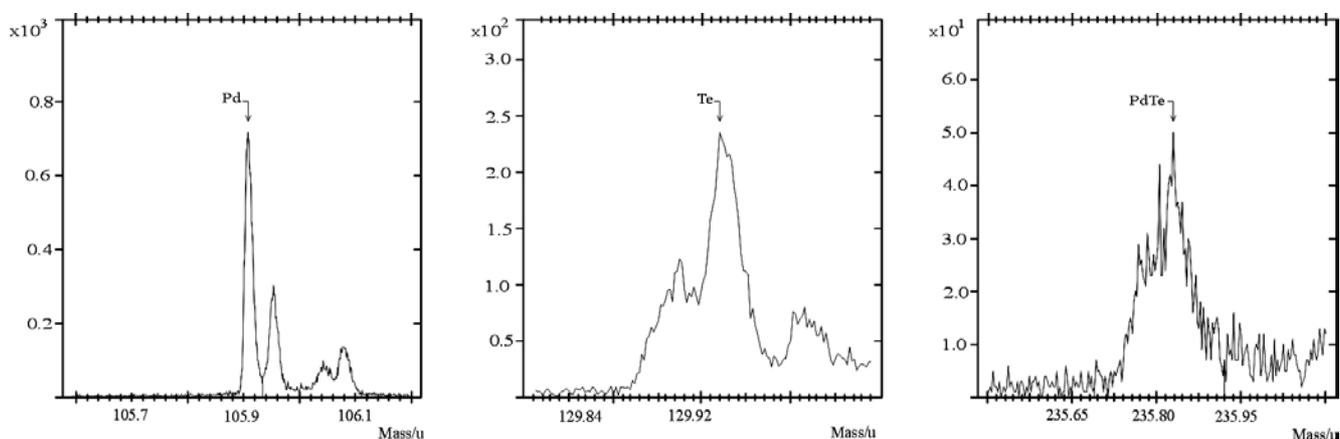


Fig. 3 – The ToF-SIMS (+) spectra of 5%Pd-1%Te/SiO₂ catalyst after reduction at 300°C.

In the case of the bimetallic systems with higher amounts of tellurium (5%Pd-5%Te/SiO₂, 5%Pd-8%Te/SiO₂) two intermetallic phases PdTe and PdTe₂ were detected by XRD (Table 2). The lower activity of those Pd-Te/SiO₂ systems in comparison with the activity of 5%Pd-1%Te/SiO₂ may be caused by the additional presence of intermetallic PdTe₂ phase in the catalysts.

EXPERIMENTAL

1. Catalyst preparation

A wide range of bimetallic catalysts containing 5 wt.% of palladium and 0.1-8 wt.% of tellurium supported on silica (Aldrich, 291 m²/g) was prepared from water solution of PdCl₂ (PdCl₂, POCh Gliwice) and water solution of telluric acid (H₆TeO₆, Sigma-Aldrich) by repeated impregnation. The water was evaporated at an increased temperature under vacuum. The catalysts were dried in air at 110°C for 6 h and then reduced in hydrogen atmosphere for 2 h at 300°C before catalytic measurements.

2. Catalytic measurements

2.1. The oxidation of glucose

The oxidation of glucose solution (1.00 mol·dm⁻³) was performed in a thermostated glass reactor (temperature 60°C) equipped with a stirrer, an oxygen supply system, a pH electrode and a burette containing NaOH (1.00 mol·dm⁻³) to maintain constant pH = 9 in the reaction medium. Samples of the reaction medium were taken periodically, filtered and analyzed using a liquid chromatograph LaChrom (Marck Hitachi) coupled with a variable wavelength UV detector. The analytical wavelength was 200 nm. The reaction products were separated on an amino-propyl-silicone column 150×3,3 mm I.D., 45 000 plates·m⁻¹, using water solution of acetonitrile (ACN) as a mobile phase.

Catalytic results are expressed as conversion (X,%) and selectivity (S,%). Those parameters were defined as: $X = [1 - (C_{GLU}/C_{0GLU})] \cdot 100\%$; $S = [C_{GLC} / (C_{0GLU} - C_{GLU})] \cdot 100\%$, where: C_{0GLU} was a molar concentration of glucose at the beginning of the oxidation process, C_{GLU} was a molar concentration of glucose after time t , C_{GLC} was a molar concentration of gluconic acid after time t .

2.2. Powder X-ray diffraction (XRD)

Powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer. The X-ray source was a copper long fine focus X-ray diffraction tube operating at 40KV and 30 mA. Data was collected in the range 20 - 90° 2θ with step 0.0167° and exposition per one step of 20 s. A PANalytical X'Celerator detector based on Real Time Multiple Strip technology was used. Crystalline phases were identified by references to ICDD PDF-2 (ver. 2004) data base.

2.3. Time of flight secondary ion mass spectrometry (ToF-SIMS)

Secondary ions mass spectra and images were recorded with a ToF-SIMS IV mass spectrometer (Ion-Tof GmbH, Germany). The instrument was equipped with liquid metal ⁶⁹Ga⁺ primary ion gun and a high mass resolution time of

flight mass analyzer. Images were recorded in a burst alignment mode or extreme crossover mode, which provided high lateral resolution. Secondary ion mass spectra were recorded from an approximately 100×100 μm² area of the sample surface. During the measurement, the analysed area was irradiated with the pulses of 25 keV ions at 10 kHz repetition rate and average ion current 2.5 pA. The analysis time was 50 s giving an ion dose below static limit of 1×10¹³ ions/cm². Secondary ions emitted from the bombarded surface were mass separated and counted in the time of flight (ToF) analyzer. Spectra were recorded with high mass resolution (m/Δm) at the 29 m.u. typically greater than 8000 with the primary ion pulse width 650 ns. The catalyst samples were prepared by pressing pellets.

CONCLUSIONS

From the conducted research, it can be concluded that the addition of tellurium to Pd supported catalysts modifies their catalytic properties in the glucose oxidation in liquid phase. Bimetallic systems, for which the formation of intermetallic compound PdTe on the surface is observed, are characterized with the best activity and selectivity to gluconic acid. Moreover, these catalysts show high stability in the studied process.

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