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A model procedure for catalytic conversion of waste cotton into useful chemicals

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Abstract

Cotton is grown in about 90 countries in the world. In 2018/2019, world this natural fibers production amounted to 25.8 Mt. Cotton, however, accounts for 24% of the fibers used in the production of textiles in the world. This natural material consists mainly of cellulose and can be used as a raw material for the so-called "sugar economy". In this paper a model procedure for thermally-assisted acidic hydrolysis of model cotton material into glucose and subsequent oxidation of glucose into calcium gluconate over Pd-Au/SiO_2 will be presented. For the first step H_2SO_4 was used as catalyst for hydrolysis of biomass. Cotton hydrolysates were neutralized by $CaCO_3$ and used as a substrate in a second step of the process which was oxidation of glucose over Pd-Au/SiO_2 catalyst. The bimetallic catalysts were prepared by ultrasound assisted coimpregnation method. The structure of Pd-Au/SiO_2 catalysts indicated that small crystallites of palladium and gold are active and selective into gluconate ions formation. These bimetallic systems were used in the catalytic oxidation of glucose in model solution as well as glucose found in cotton hydrolysates. It was stated that this catalytic method of transformation of glucose is good alternative for biological processes using fungal and bacterial species which are sensitive to inhibitors such as furfurals and levulinic acid presented in hydrolysates.

1. Introduction

The global demand for textiles is growing steadily, and this trend looks likely to continue [1-3]. Global production of textile materials was around 85.5 Mt in 2013, and by 2025 it is estimated to grow to 130 Mt [4]. Textiles are used for a vast range of products, including clothing, bed linen, towels and utility fabrics, which quickly become worn-out or fall out of fashion, ending up in landfills. As much as 63% of the textile fibers currently sold are derived from petrochemicals [5] and only 37% from fibers, mainly cotton (24%) [6], wool or linen. Moreover, a large number of chemical substances are used to impart functional features. Among the most frequently used chemicals are reagents for water repellency, fire resistance and protection from UV radiation. Many of these chemicals also prevent their natural biodegradation, in part because they inhibit the growth of microorganisms (fungi, bacteria, etc.). Textiles thus constitute a significant group of wastes, which are difficult to biodegrade in the natural environment.

A possible solution is to convert them by chemical-biological methods into useful energy products, such as biogas or into simple sugars, like glucose and chemical or biological transformation of these products into valuable chemicals like gluconic acid [7-10] or another product, like: hydrogen, vanillin and monolayer-patched graphene [11-14]. Especially, catalytical transformation of glucose into gluconic acid over heterogeneous catalysts is in demand in industry [15-20]. Despite the considerable economic and environmental interest of developing methods for processing waste textiles for use as a fermentation medium or chemical substrate, there is little in the prior literature on this topic [21-24]. Preliminary studies showed that even fabrics based only on natural fibers (cotton, wool) but subjected to chemical treatment are not susceptible to rapid biodegradation in the natural environment, due to the presence of fermentation inhibitors like furfurals and levulinic acid [25]. This is the reason why catalytical transformation is better than biological in the case of such waste utilization.

In this publication a model procedure for thermally-assisted acidic hydrolysis of cotton materials will be developed. The hydrolysates obtained from raw cotton yarn will be used as a substrate in the reaction of catalytic transformation of glucose into gluconic acid over Pd-Au/SiO_2 catalysts. Bimetallic palladium - gold systems were prepared at Lodz University of Technology and used first in the reaction of furfurals hydrogenations [26]. It was stated that those bimetallic systems are useful in the reactions of hydrogen transfer and that is why they were used in the reaction of oxidation of glucose which occurs as a result of the oxidative dehydrogenation mechanism.

2. Results

Figs 1 presents the dependence of conversion and selectivity towards gluconic ions on the time of glucose oxidation over palladium-gold catalysts on silica. For the investigations, the 1 $mol \cdot dm^{-3}$ solution of pure commercial glucose in water was used as a substrate. Monometallic catalysts (5%Pd/SiO_2 and 5%Au/SiO_2) showed rather poor activity in this reaction. The addition of gold to 5%Pd/SiO_2 systems caused an increase in the conversion degree of glucose. Especially, the addition of a small amount of gold to palladium catalysts (0.2-1wt-%) significantly influenced the activity in the oxidation of glucose. However, in the case of 5%Pd-2%Au/SiO_2 and 5%Pd-5%Au/SiO_2 catalysts, in comparison with the bimetallic systems with lower amount of gold, a decrease in activity was observed. Thus, the introduction of gold higher than 1wt-% into Pd-Au/SiO_2 catalysts is groundless from a practical point of view.

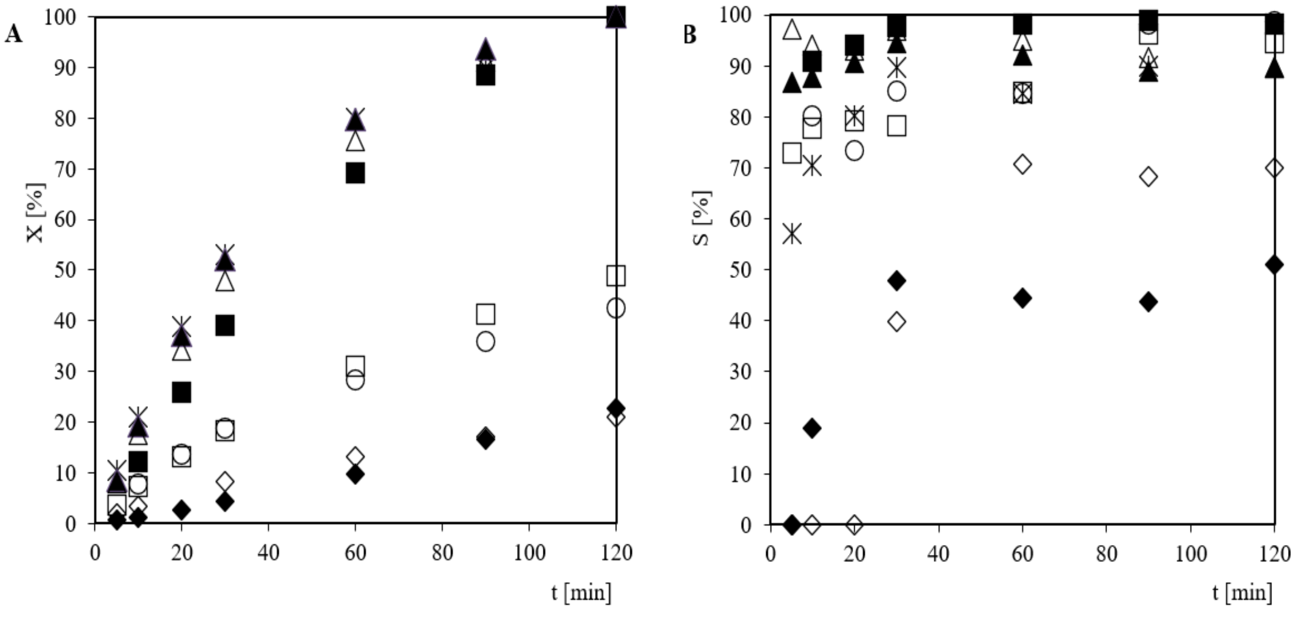


Fig 1. A - Conversion degree of glucose X, B - selectivity to gluconate ions S in the reaction of glucose in presence of the catalysts: 5%Pd/SiO_2 (◆); 5%Au/SiO_2 (◇); 5%Pd-0.2%Au/SiO_2 (▲); 5%Pd-0.5%Au/SiO_2 (△); 5%Pd-1%Au/SiO_2 (■); 5%Pd-2%Au/SiO_2 (□); 5%Pd-5%Au/SiO_2 (○) and 1%Pt-4%Pd-5%Bi/C (Degussa) (×) as a function of time. Reaction conditions: T = 60°C, m_{cat} = 1g, C_0 = 1 $mol \cdot dm^{-3}$, pH = 9, V_{O2} = 1 $dm^3 \cdot min^{-1}$.

All studied bimetallic catalysts are characterized by high selectivity towards gluconic ions. In all cases, the selectivity of Pd-Au/SiO_2 systems was comparable or even higher than in the case of commercial catalyst of Degussa (1%Pt-4%Pd-5%Bi/C).

In order to understand the behavior of Pd-Au/SiO_2 systems in the oxidation of glucose into gluconic acid in aqueous phase, the following studies x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (SEM-EDS), time-of-flight secondary ion mass spectroscopy (ToF-SIMS), x-ray photoelectron spectroscopy (XPS), and temperature programmed reduction (TPR) were conducted. All results of the physicochemical tests of bimetallic catalysts have been presented and thoroughly discussed in our earlier publication in Catalysts [26].

In the obtained diffractograms of all Pd-Au/SiO_2 bimetallic systems, the maxima assigned to the metallic Pd phase are visible. The introduction of gold into the monometallic system causes the appearance of additional maxima on the diffraction patterns, the position of which shifts towards the smaller values of the angle 2θ. The position of this maximum in the diffractogram of 5%Pd-5%Au/SiO_2 catalyst is very close to the maximum corresponding to the gold phase. The above fact indicates the possibility of the formation of solid solutions. The confirmation of the formation of solid solutions for the Pd-Au/SiO_2 systems activated in the hydrogen atmosphere at 300°C is the linear relationship between the interplanar distances as a function of the alloy composition, the so-called Vegard's rule. No additional diffraction maxima were found on the diffraction patterns of bimetallic systems, but only the maxima from the metallic Pd and Au phases, which indicates the lack of strong interactions between these metals, which would be manifested in the formation of intermetallic compounds. The results of the XRD tests are confirmed by the XPS and TRR tests [26].

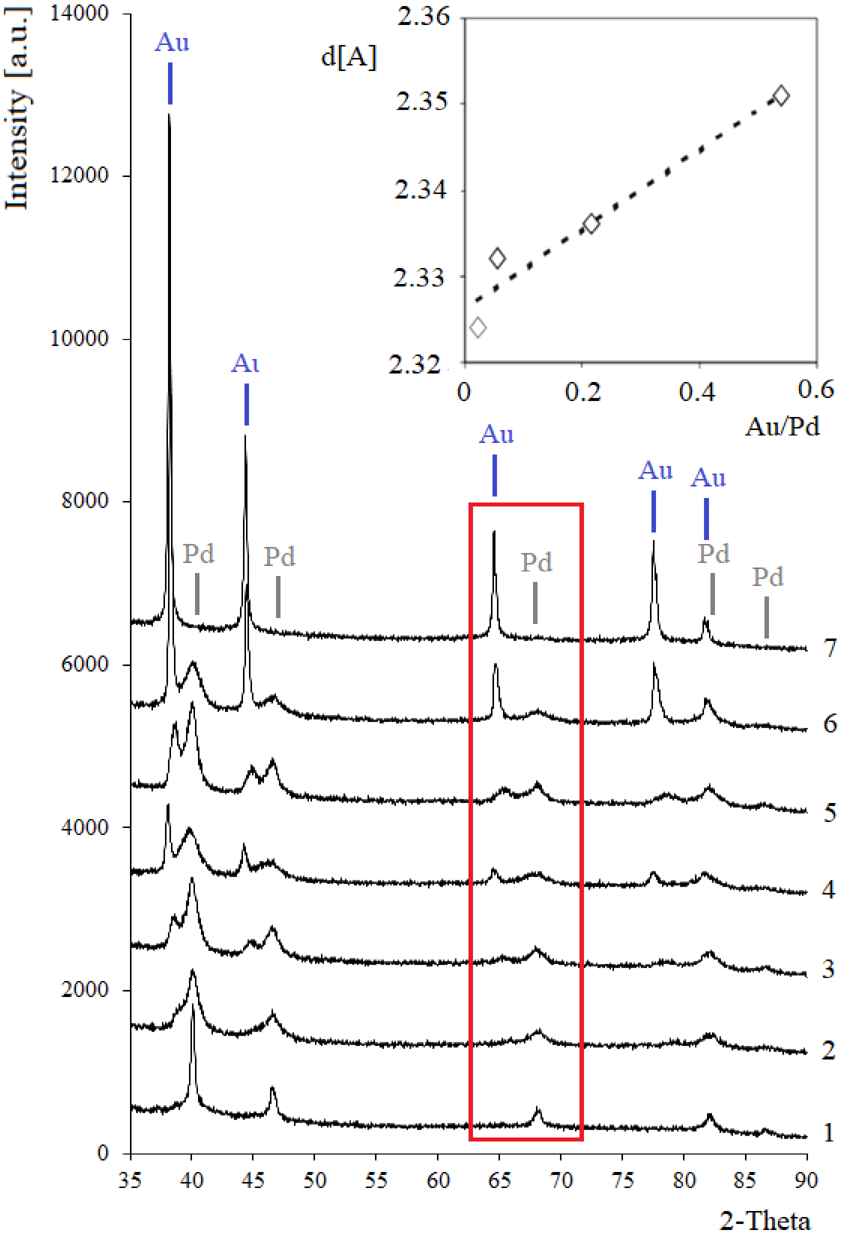


Fig. 2. X-ray diffraction patterns of Pd-Au/SiO_2: (1) 5%Pd/SiO_2; (2) 5%Pd-0.2%Au/SiO_2; (3) 5%Pd-0.5%Au/SiO_2; (4) 5%Pd-1%Au/SiO_2; (5) 5%Pd-2%Au/SiO_2; (6) 5%Pd-5%Au/SiO_2; (7) 5%Au/SiO_2

and the linear relationship of interplanar distances in composition function of these systems (Vegard's rule). Bimetallic catalysts were activated in hydrogen atmosphere for 2 h at 300°C.

The addition of a larger amount of gold (> 2%-wt.) leads to an increase in the intensity of the diffraction peaks attributed to gold metal, which is evidence of the existence of larger Au crystallites on the surface of bimetallic catalysts. Using the Scherrer equation, the average size of the palladium crystallites was estimated and gold in the tested systems Table 1. The results show that the palladium dispersion is greater in the case of bimetallic systems than for the monometallic catalyst of 5%Pd/SiO_2. Better Pd dispersion in bimetallic systems may be the reason for their higher activity and selectivity to gluconic acid. Moreover, for the 5%Pd-1%Au/SiO_2 catalyst the formation of the smallest Au crystallites was also observed. It is well known that the catalytic properties of gold strongly depend on the size of its particles [27]. Literature data show that monometallic gold carrier systems are catalytically active in the process of glucose oxidation when the Au particle size is less than 10 nm [28]. In the case of the tested system 5%Pd-1%Au/SiO_2, estimated Au particle size is 8 nm. This catalyst also showed good catalytic properties in the reaction of glucose oxidation to gluconic acid. Therefore, it cannot be ruled out that gold contributes to the creation of catalytic activity.

Tab. 1. The size of palladium and gold crystallites calculated on the base of XRD measurements in Pd-Au/SiO_2 bimetallic catalysts in relation to activity, selectivity and productivity. Reaction conditions: T = 60°C, m_{cat} = 1g, C_0 = 1 mol·dm^{-3}, pH = 9, V_{O2} = 1 dm^3·min^{-1}.

Catalysts	X* [%]	S* [%]	Productivity of gluconic ions [mol·h^{-1}·g$_{Pd}^{-1}$]	Au/Pd [at/at]	Crystallite size [nm]***	
					Au	Pd
5%Pd/SiO_2	21	51	1.17	0	-	21.3
5%Pd-0.2%Au/SiO_2	100	90	4.94	0.02	b.d.l.	5.7
5%Pd-0.5%Au/SiO_2	100	90	11.72	0.05	15.1	7.7
5%Pd-1%Au/SiO_2	100	99**	13.57	0.11	8.4	8.2
5%Pd-2%Au/SiO_2	49	95**	5.39	0.22	24.4	5.6
5%Pd-5%Au/SiO_2	42	99**	4.79	0.54	41.3	5.8
5%Au/SiO_2	22	70	-	-	43.4	-

*After 2 hours of the glucose oxidation process

*** Gluconic acid was the only product detected by HPLC with Gilson's prepELS II

***Crystallite size calculated on the base of XRD measurements

b.d.l. – below detection limit

Images obtained by ToF-SIMS technique for Pd-Au/SiO_2 catalysts showed non-homogeneous distribution of Au on the silica surface [26]. Bimetallic catalysts tend to form Au-enriched regions, the size of which increases as more gold is introduced into the system. On the basis of the obtained results, it should be stated that the distribution of Pd atoms is better in the case of bimetallic systems than in the case of the monometallic catalyst 5%Pd/SiO_2. Moreover, the calculated relative intensities of the Au_3/Pd peaks show that in the case of the system 5%Pd-1%Au/SiO_2, for which the highest activity in the glucose oxidation reaction was found, the number of surface gold atoms is the highest, which indicates a good dispersion of this metal. On the other hand, the comparable intensities of the Pd peaks obtained for the bimetallic Pd-Au catalysts suggest that the number of surface palladium atoms in these systems is similar (Table 2). Based on the obtained results, it can be assumed that Pd is characterized by a similar distribution of atoms on the support surface in all tested Pd-Au/SiO_2 catalysts. ToF-SIMS tests are in good agreement with the results obtained with the XRD technique.

Tab. 2. The intensity of the positive ion peaks ^{106}Pd and negative ions Au_3 obtained with the ToF-SIMS technique for bimetallic catalysts Pd-Au/SiO_2 reduced in H_2 at 300°C.

Catalyst	Peak intensity $Pd^{*}\cdot 10^6$	Peak intensity $Au_3^{**}\cdot 10^6$	Relative intensity Au_3^{**}/Pd^{*}
5%Pd-0.2%Au/SiO_2	1648	42	0.025

5%Pd-0.5%Au/SiO_2	1727	38	0.022
5%Pd-1%Au/SiO_2	1961	128	0.065
5%Pd-2%Au/SiO_2	1984	71	0.035
5%Pd-5%Au/SiO_2	2062	44	0.021

* $^{106}Pd^{+}$ ion counts /total number of positive ion counts

** Au_3^{-} ion counts / total number of negative ion counts

Figure 3 shows the dependence of the relative intensities of Au_3/Pd as a function of the Au/Pd atomic ratio in bimetallic catalysts. It can be concluded from the presented results that in the case of the 5%Pd-1%Au/SiO_2 system, the largest number of Au atoms is on the catalyst surface. For this catalyst, the highest rate of gluconic acid formation also was found. Thus, it can be assumed that both metals on the support can be responsible for the activity of the bimetallic system. Confirmation of good gold dispersion in 5%Pd-1%Au/SiO_2 bimetallic system are the results obtained from microscopic examinations (SEM-EDX) and CO chemisorption measurements [26].

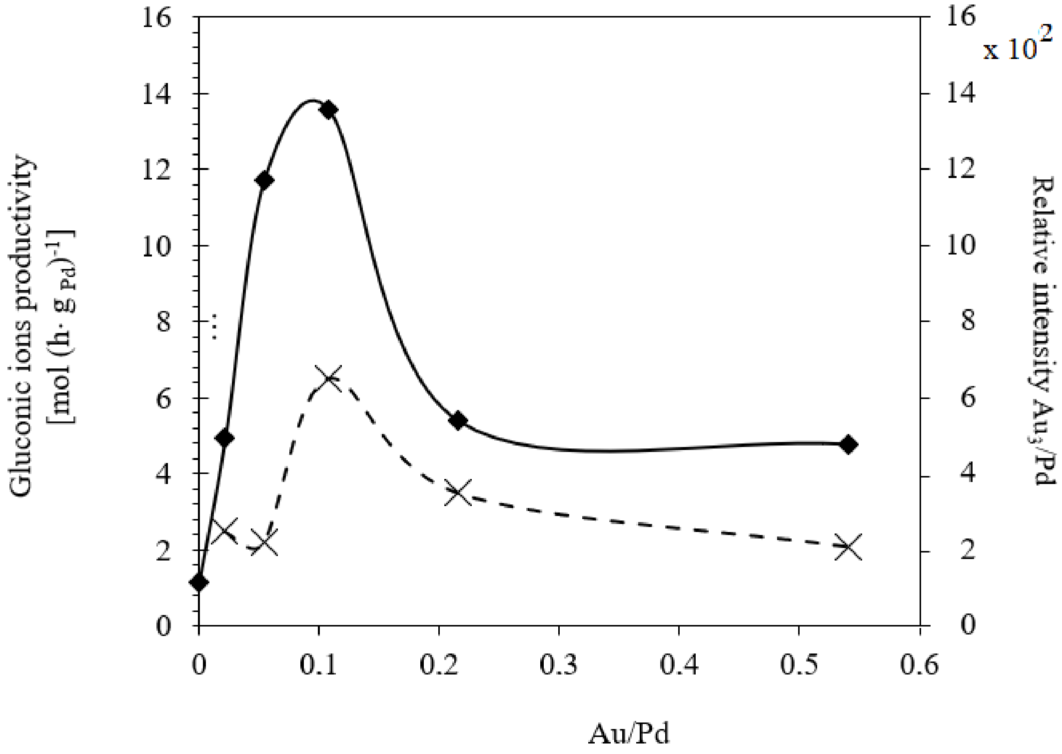


Fig. 3. Gluconic ions productivity (♦) and relative intensity of ions Au_3/Pd (×) as a function of atomic ratio Au/Pd in bimetallic Pd-Au/SiO_2 catalysts. Productivities of gluconic acid was estimated after two hours run over bimetallic catalysts with various composition of active phase. Reaction conditions: T = 60°C, m_{cat} = 1g, C_0 = 1 mol·dm^{-3}, pH = 9, V_{O2} = 1 dm^3·min^{-1}.

Gluconate ions are good chelates for metal ions, and therefore studies of the degree of leaching of Pd and Au ions from the catalysts during the glucose oxidation process were performed. The results of the ICP-AES tests performed for real solutions after glucose oxidation processes are presented in Table 3. In the studies of Pd-Au/SiO_2 catalysts the leaching only of Pd into the reaction medium was observed. The amount of Pd losses is comparable for all bimetallic catalysts. Nevertheless, gold was not detected in the reaction mixture when the process was conducted over bimetallic Pd-Au/SiO_2 catalysts. On the other hand, in the case of monometallic 5%Au/SiO_2 catalysts the presence of trace amount of gold was confirmed by ICP-AES measurement.

Tab. 3. ICP-AES analysis of reaction mixture after catalytic tests. Reaction conditions: T = 60°C, m_{cat} = 1g, C_0 = 1 mol·dm^{-3}, pH = 9, V_{O2} = 1 dm^3·min^{-1}.

Catalyst	Pretreatment steps	Reaction medium	**Pd** [ppm] (247.6 nm)	**Au** [ppm] (242.8 nm)
5%Pd/SiO_2	H_2, 2h, 300 °C	Glucose	0.1148	---
	H2, 2h, 300 °C	H_2O	b.d.l.	---
5%Pd-0.5%Au/SiO_2	H_2, 2h, 300 °C	Glucose	0.1056	b.d.l.
	H_2, 2h, 300 °C	H_2O	b.d.l.	b.d.l.
5%Pd-1%Au/SiO_2	H_2, 2h, 300 °C	Glucose	0.0816	b.d.l.
5%Pd-5%Au/SiO_2	H_2, 2h, 300 °C	Glucose	0.0798	b.d.l.
5%Au/SiO_2	H_2, 2h, 300 °C	Glucose	---	0.0257

b.d.l . – below detection limit

The application of catalyst in technological processes is economical well-founded only it is stable for long-term use. For this reason, the stability of 5%Pd-1%Au/SiO_2 catalyst, which was characterized with the best gluconic acid productivity in the reaction of glucose oxidation in liquid phase, was investigated (Table 4). The stability of catalyst was estimated on the basis of activity changes during ten 2-hour-long measurement cycles. The process of oxidation was conducted for the steady amount of catalyst (m_{cat} = 1 g) without its removal from the reaction mixture in the subsequent cycles. After each 2-hour-long measurement cycle, reaction mixture was decanted and examined by HPLC and ICP-AES, and a fresh charge of glucose solution (V = 0.25 dm^3, C_0 = 1 mol/dm^3) was introduced into the reactor. Bimetallic 5%Pd-1%Au/SiO_2 system was characterized by high stability in the reaction of glucose oxidation. After 10 reaction cycles the activity and selectivity of this catalyst was practically the same as initial values of these parameters. What is more, the ICP-AES measurements of reaction mixture executed after each cycle proved the good stability of the bimetallic systems in the reaction conditions. Only a trace amount of palladium was observed in the reaction mixture after each cycle (Tab. 3). This high stability of 5%Pd-1%Au/SiO_2 system in the oxidation of glucose is a feature for industrial applications.

Tab. 4. ICP-AES analysis of reaction mixture after stability tests of 5%Pd-1%Au/SiO_2 catalyst. Reaction conditions: T = 60°C, m_{cat} = 1g, C_0 = 1 mol·dm^{-3}, pH = 9, V_{O2} = 1 dm^3·min^{-1}.

Number of cycle	1	2	3	4	5	6	7	8	9	10
X [%]	100	96	97	90	92	99	96	94	99	94
S [%]	99*	99*	99*	99*	97*	96*	98*	97*	96*	98*
Pd[ppm] 247.6 nm	0.082	0.145	0.050	0.134	0.049	0.052	0.071	0.102	0.052	0.069
Au [ppm] 242.8 nm	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.

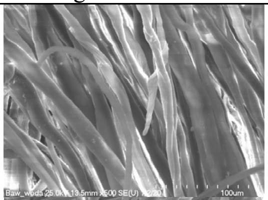
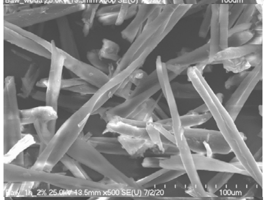
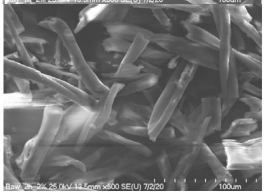
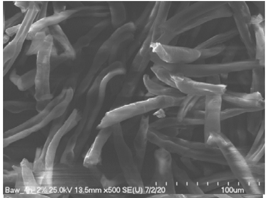
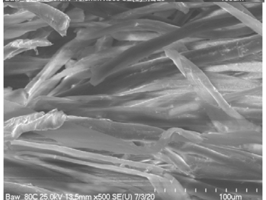
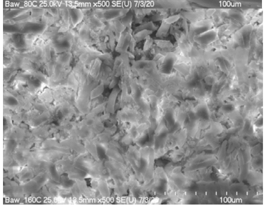
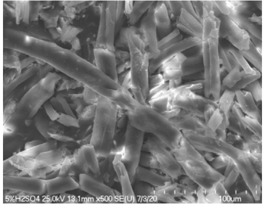
b.d.l . – below detection limit

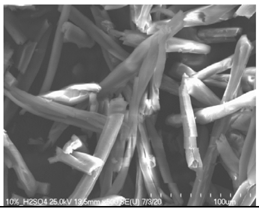
* Gluconic acid was the only product detected by HPLC with Gilson's prepELS II detector

Oxidation of glucose in hydrolysates obtained from cotton waste

Acidic hydrolysis of the cotton yarn was performed in a pressure reactor and the results was summarized in Tab. 5. Cotton fibers consist almost entirely of cellulose (94-100%) and this ist he reason why its hydrolysis leads to glucose as a main product. Prior to HPLC analysis, the samples of the hydrolysates were neutralized with milk of lime to pH 7.5 and filtered through a bed of activated carbon (ERCARBON GE, 100 g), deposited on a vacuum filter. Based on the data collected in the table, it can be seen that an increase in the hydrolysis temperature from 80 to 160°C, as well as the extension of the process time from 1 to 4 hours, favor the depolymerization of cellulose and the formation of larger amounts of glucose. On the other hand, increasing the concentration of sulfuric acid (VI), which catalyses the polysacchar hydrolysis process, above 5% does not cause a further increase in the sugar concentration in the hydrolysates. The SEM images of the solid residue of cotton fibers after hydrolysis presented in the table clearly show that the most significant change in the morphology of the fibers occurred when the process was carried out at high temperature (160°C). In this case, the highest concentration of glucose in the sample was also noted (0.02 mol/dm^3). For this reason, the hydrolyzate obtained in the reaction of 100 g of cotton fiber with 2 dm^3 of 2%H_2SO_4 at the temperature of 160°C for 2 hours was used for further catalytic tests.

Tab. 5. Acidic hydrolysis of cotton fiber. 100 g of comminuted cotton yarn (>0.5 cm long) and 2 dm^3 of the solution of H_2SO_4 (concentration 2 ÷ 10%) were taken each time into the process. The process was carried out from 1 to 4 hours at the temperature of 80-160 °C.

No	Time [h]	C H_2SO_4 [%]	Temp. [°C]	Dry mass of solid residue [g]	$C_{Glucose}$ [mol/dm^3]	Degree of cellulose crystallinity [%]	SEM images of the fiber after hydrolysis -magnification x500
1	2	0	120	92.2	0	91	
2	1	2	120	86.9	0.008	89	
3	2	2	120	81.4	0.010	95	
4	4	2	120	82.8	0.015	99	
5	2	2	80	91.5	0	90	
6	2	2	160	42.9	0.020	99	
7	2	5	120	81.9	0.018	99	

8	2	10	120	84.7	0.018	99	

The degree of crystallinity of cellulose was analyzed for cotton fibers and for solid cotton residues after hydrolysis by X-ray diffraction measurements. A simplified method (Segal peak height method) was used to estimate the crystallinity of cellulose. The results obtained with this method show a tendency to overestimate the value of the degree of crystallinity, while the trends of changes in the value of the crystallinity between the samples are maintained, which enables a comparative analysis of the results. The obtained results are summarized in Table 4. An increase in the degree of crystallinity of cellulose in the samples of solid residue indicates easier depolymerization of amorphous cellulose in the samples.

Hydrolyzate obtained in the reaction of 100 g of cotton fiber with 2 dm^3 of 2% H_2SO_4 at the temperature of 160°C for 2 hours was used for catalytic tests as a substrate. The results of glucose oxidation are presented in Table 6. The catalytic reactions were made over 5%Pd-1%Au/SiO_2 catalyst for three concentrations of glucose (the hydrolyzate was concentrated two and four times by evaporating the solvent at 60°C). Catalyst was used in the amounts corresponding to the catalyst loading in glucose solutions of 1 mol·dm^3 (Table 1, m_{cat} = 1 g, $C_{0\ GLU}$ = 1 mol· dm^{-3}, V_{GLU} = 0.25 dm^3).

Tab. 6. Conversion degree of glucose and selectivity to gluconate ions in the reaction of glucose from hydrolysates of cotton in presence of 5%Pd-1%Au/SiO_2 catalyst. Reaction conditions: T = 60°C, pH = 9, t = 2 h, V_{O2} = 1 dm^3·min^{-1}, V_{GLU} = 0.25 dm^3.

Sample	$C_{0\ GLU}$ [mol· dm^{-3}]	m_{cat} [g]	X [%]	S_{GLC} [%]
1	0.02	0.02	100	100
2	0.04	0.04	100	100
3	0.08	0.08	100	100

The obtained results confirmed the possibility of chemical processing of cotton waste into sodium gluconate.

4. Discussion

Addition of a second metal (Bi, Tl, Sn, Pb, Ag) to supported palladium systems is the known way for modification of catalytic properties, especially selectivity, in the aldoses (glucose, lactose) oxidation to aldonic acids (gluconic acid, lactobionic acid) [16-20]. However, the reason of such modification is still discussed in literature [29-32]. The authors try to explain the promoting addition of gold with different effects. Enache et. al. [29] suggested that Au acts as an electronic promoter for Pd in the reaction of oxidation of primary alcohols to aldehydes and the electronic effect was dominant. On the other hand, Roudgar et. al. [30] who used Pd-Au film in synthesis of vinyl acetate, argued that geometric effects are more important than electronic effects in modification of Pd-Au reactivity. Works of Baddeley et. al. [31] and Gleich et. al. [32], who suggest that the formation of surface ensembles of Pd_xAu_y type plays an essential role in the improvement of reactivity, are in agreement with those theories.

Our earlier studies indicate that glucose oxidation is a structure sensitive reaction [15-20]. For this reason, the dilution of Pd atoms by Au atoms can play an important role in the creation of catalytic properties. In our work we studied the catalytic properties of bimetallic palladium-gold catalysts in which the atomic ratio Au/Pd was in the range of 0-0.55. Among the studied catalysts, the system containing 5%Pd-1%Au/SiO_2 with an atomic ratio Au/Pd about 0.1 showed the best activity and the highest selectivity to gluconic acid. On the basis of XRD and SEM-EDS studies, we stated that in this system both metals Pd and Au have the highest dispersion on the support and are also in a direct contact, which could be the reason for its high selectivity. However, catalytic performance of using Pd-Au/SiO_2

bimetallic catalysts depend strongly on the atomic ratio Au/Pd. The effect of gold addition on the catalytic performance of Pd could be described in different ways:

- *Stabilization of small Pd particles*: Au addition to palladium catalyst facilitates the formation of small particles of Pd and their stabilization under reaction conditions. Our XRD, ToF-SIMS and SEM-EDS studies of bimetallic Pd–Au/ SiO_2 catalysts reveal the presence of good dispersed palladium metallic phase on the surface of catalysts. High dispersed palladium can be responsible for catalytic properties of palladium-gold systems.
- *Alloy Pd-Au formation:* From the results obtained by XRD we determined the presence of solid solutions in the Pd–Au/SiO_2 systems, which composition strongly depends on Au/Pd ratio in bimetallic systems. We conclude that Pd atoms substituted Au atoms in crystalline lattice of gold.
- *Prevention of Pd poisoning:* Bimetallic alloy particles are formed during reduction precursors in H_2. It is well known fact, that gluconic acid can strong adsorbed on the surface of palladium, what is the reason of catalyst deactivation. Our study showed that bimetallic 5%Pd–1%Au/ SiO_2 catalyst are stable in the reaction condition. Even after 10 reaction cycles, this catalyst characterized by high activity and selectivity to gluconic acid. Thus, the addition of gold into supported palladium systems can lead to the prevention of Pd poisoning.

Reviewing listed above considerations, we can conclude that the total influence of Au addition is caused by superposition of various effects.

4. Materials and Methods

4.1. Catalyst preparation

A monometallic catalyst containing 5 wt.% palladium was prepared by wet impregnation of SiO_2 (Sigma Aldrich, 291 m^2/g) with an aqueous solution of $PdCl_2$ (POCH, pure for analysis) acidified to a pH of about 5 using HCl_{aq} (CHEMPUR, 35 -38%, pure for analysis). The preparation was left for 24 hours in an ultrasonic bath with a frequency of 45 kHz. Water was evaporated at 60 °C under vacuum. The 5% Pd/SiO_2 monometallic catalyst was air dried at 110°C for 6 h and reduced under hydrogen atmosphere (H_2, Air Products, Premium Plus, 99.999%, 20 $mL \cdot min^{-1}$) for 2 h at 300°C. A linear temperature rise of 20 $°C \cdot min^{-1}$ was set for all stages of thermal processing of this system. In addition, a 5% Au/SiO_2 (wt.%) monometallic catalyst was prepared from the $AuCl_3$ solution (POCH, wt. 0.21% Au) according to the procedure described above. In order to determine the catalytic and physicochemical properties of bimetallic systems, Pd-Au/SiO_2 catalysts containing 5 wt.% Pd and 0.2, respectively; 0.5, 1, 2, 5, and 10 wt.% Au by the method of co-impregnation of the SiO_2 carrier with aqueous solutions of $AuCl_3$ (POCH, pure, 0.21% Au) and $PdCl_2$ (POCH, anhydrous, pure for analysis) were prepared according to the procedure described above. The catalysts have been subjected to AAS, XRD, ToF-SIMS, SEM-EDS, and XPS tests in order to determine their composition and metal interactions, which may affect the activity and selectivity for individual products in glucose oxidation.

4.2. Catalyst measurements

The oxidation of glucose solution (GLU, POCh Gliwice, pure p. a.; $C_{0\,GLU} = 1.00$ mol/dm^3; $V_{GLU} = 0.25$ dm^3) was performed in a thermostated glass reactor of 0.4 dm^3 equipped with a stirrer, an oxygen supply system, a burette containing NaOH (0.50 mol/dm^3) and a pH electrode. The acids formed during the oxidation of glucose were neutralized by the addition of aqueous solution of sodium hydroxide. The reaction was conducted at 60 °C, pH = 9. In our studies we always added 1 g of the catalyst into reaction mixture. The mixture was stirred at 1300 rpm, and oxygen was bubbled through at 0.9 dm^3 min^{-1}. Samples of the reaction medium were taken periodically, filtered and analyzed using a liquid chromatograph LaChrom (Marck Hitachi) coupled with UV–Vis. The analytical wavelength was 200 nm. The reaction products were separated on an amino-propylo-silicone column 150 mm × 3.3 mm I.D., using water solution of acetonitrile (70% ACN, 0.1% TFA) as a mobile phase.

Gilson's prepELS II detector was used as an additional detector in HPLC system described above. The temperature of spray chamber was 15 °C. The temperature of drift tube was 85 °C. For those parameters the separation of reaction mixture was satisfactory (retention times: fructose – 0.988 min;

glucose – 1.425 min; gluconic acid – 8.230 min; 2-keto-gluconic acid – 13.743 min; guluronic acid – 15.260 min; glucaric acid – 17.250 min) and given the possibility to determine the kind and the amounts of all considered compounds.

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

$$X\,[\%] = [1 - (C_{GLU}/C_{0\,GLU})] \cdot 100\%$$

$$S\,[\%] = [C_{PROD} / (C_{0\,GLU} - C_{GLU})] \cdot 100\%$$

where $C_{0\,GLU}$ 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_{PROD} was a molar concentration of product (fructose, gluconic acid, 2-keto-gluconic acid, guluronic acid, glucaric acid) after time t.

4.3. Synthesis of glucose from cotton yarn

Water solution of glucose was obtained by acidic hydrolysis (H_2SO_4, analytical grade, 95%, P.P.H. "Stanlab" sp. j., Lublin, Poland) of cotton yarn (Ne 2/20 CW (combed, weaving) cotton twists yarn: 30 tex Z 689 x 2 S 542; R 60 tex). The cotton yarn hydrolysis processes were performed in a pressure reactor (Parr Instrument Company Series Mini 4552) with a volume of 7.5 dm^3, at the temperature 120 ÷ 160 °C for. The start of the hydrolysis process was considered to be the moment when the reaction mixture reached the desired temperature. Each time, 100 g of comminuted cotton yarn (>0.5 cm long) and 2 dm^3 of the solution of H_2SO_4 (concentration 0.5 ÷ 10%) were taken into the process. After the 1 ÷ 4 hours of reaction run, the reaction mixture was cooled in the reactor to room temperature and made alkaline with $CaCO_3$ ($CaCO_3$, analytical grade, POCh, Gliwice, Poland) to pH 7.5. The mixture was then filtered on a bed of activated carbon and the glucose concentration was measured by HPLC technique (SYKAM HPLC system completed with: S1125 HPLC Pump System, S 5300 autosampler, S 4115 column thermostat, S 3585 RI detector). The sugars were separated on SETREX IEX-H^+ column (300 mm × 8.0 mm I.D.), at 80 °C, using 0.008 mol/dm^3 H_2SO_4 + 2%(v/v%) ACN (flow 0.8 cm^3/min) as a mobile phase. The quantitative analysis of glucose was performed on the basis of the calibration curve for the range of glucose concentrations 0-10 g/dm^3 (the curve in the analyzed range was linear $y = 0.19733x$; $R^2 = 0.9998803$).

4.4. Physicochemical techniques used for measurements of bimetallic Pd-Au/SiO_2 catalysts

XRD experiments were conducted using a PANalytical X'Pert Pro MPD diffractometer equipped with a PANalytical X'Celerator detector (based on Real Time Multiple Strip technology) to obtain room temperature powder X-ray diffraction patterns. The operating parameters for the X-ray source (copper long fine focus XRD tube) were set to 40 kV voltage and 30 mA current. The range for data collection was 20 - 90° 2θ using a step value of 0.0167° and a dwell time of 20 s. Using the ICDD PDF-2 (ver. 2004) database as a reference, the crystalline phases were identified.

To conduct the TPR measurements, flow apparatus was used in this study [33]. Prior to the TPR measurements, the catalyst samples (0.1g) were flushed with argon for 0.5 h at room temperature. Then, the TPR measurements were conducted with the following set parameters: temperature range of 25–500 °C, hydrogen-argon (5 vol. % of H_2) gas mixture, gas flow rate of 30 cm^3/min, and a linear temperature growth of 20 °C/min.

ToF-SIMS IV mass spectrometer (Ion-Tof GmbH, Germany, liquid metal $^{69}Ga^+$ primary ion gun, high mass resolution time of flight mass analyzer) was used to record secondary ions mass spectra from an estimated 100×100 μm^2 area of the catalyst samples prepared by pressing pellets. Extreme crossover mode or burst alignment mode was used to record the images, giving high lateral resolution. The selected area was irradiated with the following parameters during the measurement: pulses of 25 keV ions, 10 kHz repetition rate, and average ion current 2.5 pA. An ion dose below static limit of 1×1013 ions/cm^2 resulted from the analysis time of 50 s. The time of flight (ToF) analyzer counted and separated by mass the secondary ions that were emitted from the bombarded surface. Spectra of the catalyst samples were recorded with high mass resolution (m/Δm) at the 29 m.u. normally greater than 8000 with the primary ion pulse width of 650 ns.

The catalyst powder samples were analyzed using scanning electron microscopy (SEM) (S-4700 scanning electron microscope by HITACHI, Japan) equipped with energy dispersive spectrometer (EDS) (Thermo Noran, USA). SEM images, at varying magnifications, were recorded using back-scattered electron (BSE) mode with a YAG detector and accelerating voltage of 25 kV. The samples were sputter coated with carbon (Cressington 208 HR system) to reduce electric charging. A series of tests with the same samples was performed using an FEI Quanta 650 SEM equipped with Bruker Energy Dispersive Spectroscopy (EDS) system for chemical microanalysis and to verify the data. The powder catalyst samples were fixed onto sticky, conductive carbon pads with the loose excess powder removed. The data were acquired using the following parameters: 15 kV accelerating voltage, 3.5 A electron beam current, and 10 mm working distance. The composition of each sample was measured from an area of approximately 0.25 mm^2 and repeated three times utilizing different locations on each sample.

The chemical bonding nature at the surface of selected Pd-Au/SiO_2 catalysts was determined by X-ray photoelectron spectroscopy (XPS). Samples were prepared by pressing the catalytic powders onto high purity carbon filled acrylic adhesive tabs (PELCO Tabs™ Carbon Conductive Tabs) with very small impurities of Al and Si, and they were utilized in spectra calibration. The samples were placed into a VersaProbe 5000 (PHI, USA) spectrometer. Survey and high-resolution spectra were taken with a focused, monochromatic Al K-α source (E = 1486.6 eV; 100 µm spot diameter). A cold cathode electron flood gun and low-energy Ar^+ ion-beam source provided induced charge compensation. The operating pressure was $2\cdot10^{-6}$ Pa for Ar gas and the system base pressure was $5\cdot10^{-8}$ Pa. To avoid ion-induced surface damage, surface sputtering was not used. The XPS results for the catalyst samples were fitted with proprietary software (Multipak) and compared to both the NIST database (NIST Standard Reference Database 20, Version 3.5) and prior published data.

4.5. Studies of catalyst stability in the reaction mixture

Gold 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.

5. Conclusions

Pd-Au/SiO_2 catalysts with different metal loadings were tested in the selective oxidation of glucose. Introduction of gold into 5%Pd/SiO_2 system caused to the increase in the catalytic properties, especially selectivity to gluconic acid. Activity of bimetallic catalysts in studied reaction strongly depends on metal ratio. The highest activity and selectivity to gluconic acid was obtained for the systems in which the ratio of Au/Pd was near 0.05÷0.15. In addition, the long-term stability of 5%Pd-1%Au/SiO_2 catalyst was investigated. The examined catalyst was successfully used in 10 runs for the oxidation of glucose; no decrease in activity was observed. A very high selectivity of 5%Pd-1%Au/SiO_2 catalyst during 10 runs was always found.

The obtained Pd-Au/SiO_2 bimetallic catalysts also turned out to be active in the oxidation of glucose produced from cotton waste in the pressure and temperature-assisted acidic hydrolysis process. In the process of glucose oxidation in the hydrolysates, gluconic acid was the only reaction product noted. Such gluconate-containing products made of cotton waste could be used technically in surface cleaning fluids or, after cleaning, as intermediates for the cosmetics industry.

XRD, ToF-SIMS, SEM-EDS and TPR data allowed us to theorize about the possible ways of Au influence on catalytic performance. We determined that the addition of gold causes a significant increase of Pd dispersion in comparison with monometallic 5%Pd/SiO_2 system. What is more, it simultaneously leads probably to the stabilization of small gold crystallites. Bimetallic Pd-Au/SiO_2 systems in which the dispersion of both metallic components was the highest were characterized by high activity and selectivity to gluconic acid.

Secondly, our XRD study revealed changes in crystalline structure of gold in bimetallic catalysts caused by palladium atoms incorporation into crystalline structure of gold. The composition of formed solid solution depend on the Au/Pd ratio in bimetallic systems. The surface composition, examined by

ToF-SIMS and SEM-EDS techniques, reveals the presence of regions on surface bimetallic Pd-Au/SiO_2 catalysts on which both palladium and gold atoms are occurred. The modification of the electronic and geometric properties of Pd upon alloying with gold can be an alternative reason of better activity and selectivity to gluconic acid of Pd-Au/SiO_2 catalysts in oxidation of glucose.

On the basis of our study, we can conclude that the total influence of Au addition to Pd/SiO_2 catalysts is caused by superposition of various effects.

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