Investigation of Pd-Bi/Al_2O_3 catalysts in the reaction of liquid-phase glucose oxidation.

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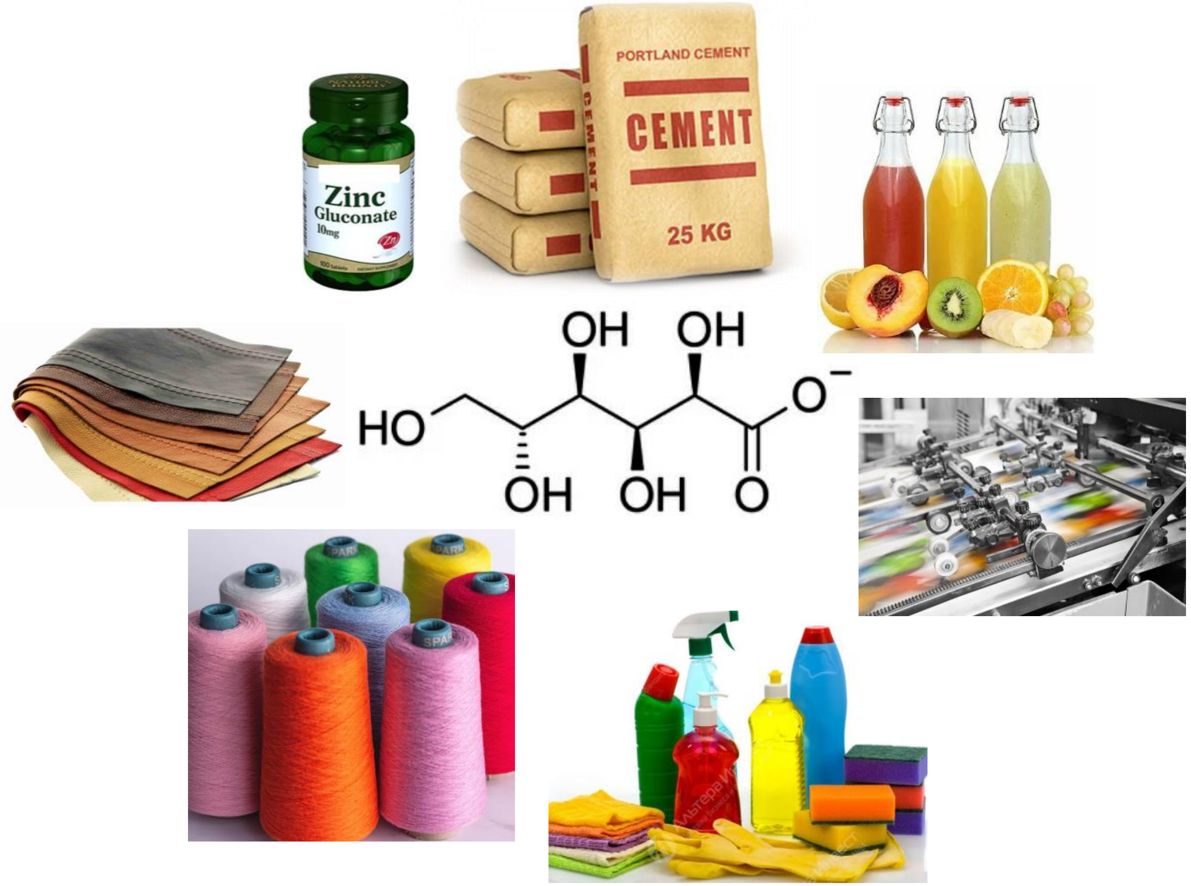
The production of gluconic acid and its derivatives is an important process of fine organic synthesis, since these products are widely used in various fields of industry:



The aim of scientific research: To synthesize supported palladium-bismuth catalysts in various ways and investigate them in the glucose oxidation reaction into gluconic acid

Catalyst preparation

4 catalyst samples were prepared: a monometallic Pd/Al_2O_3, Bi/Al_2O_3 and two bimetallic catalysts obtained by the methods of simultaneous ($PdBi/Al_2O_3$) and sequential ($Pd \rightarrow Bi/Al_2O_3$) impregnation of a support from acetic acid solutions with an atomic ratio of Pd:Bi = 2. The total content of metals on the surface was ~ 2,6%.

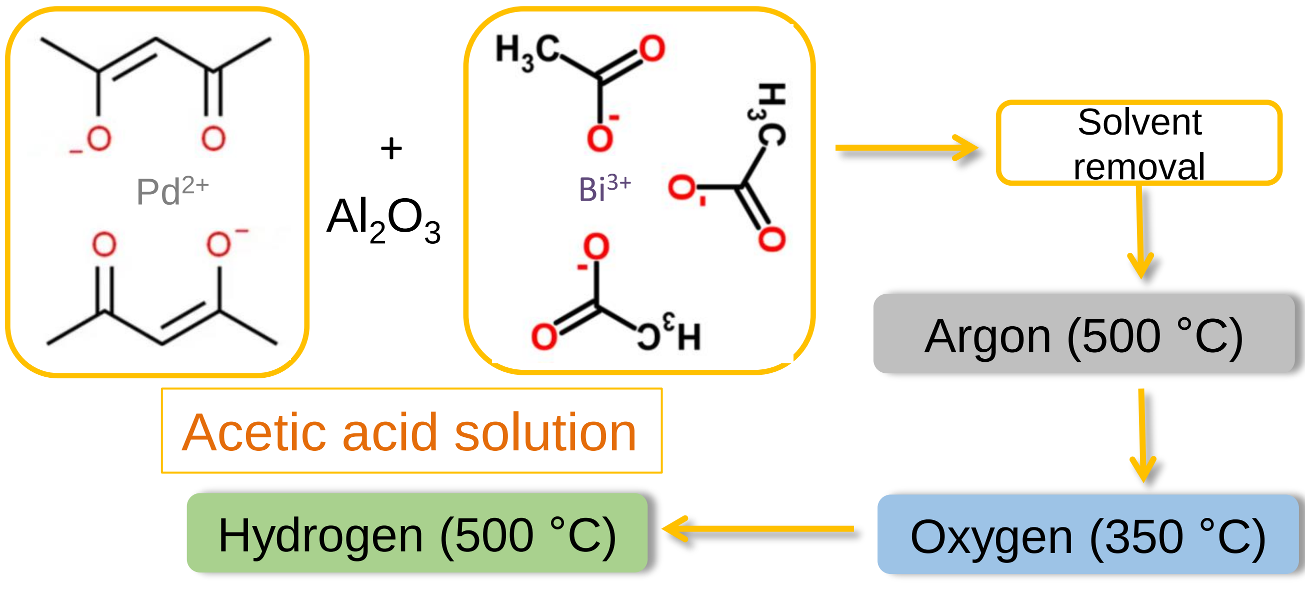


Figure 1 - Catalyst synthesis scheme

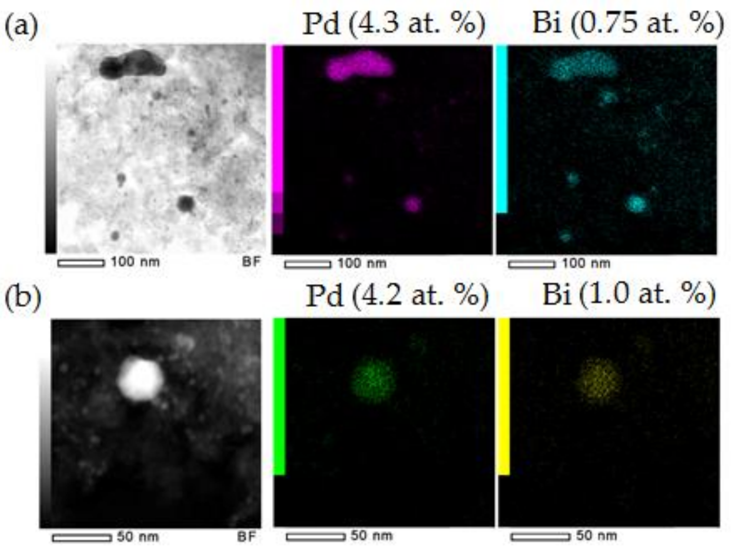


Figure 2 - Elemental mapping of the surface of the $PdBi/Al_2O_3$ catalyst, obtained by EDS at **(a)** 400,000× magnification and **(b)** 1,000,000× magnification.

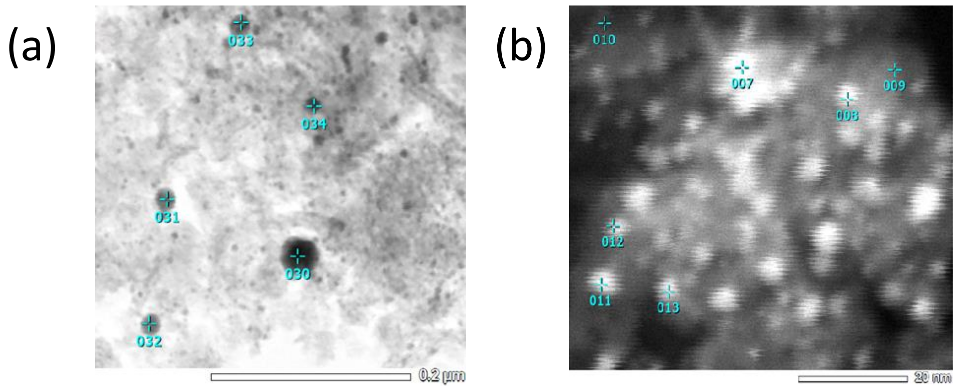


Figure 4 - Pointlike scanning of the sample surface of the catalyst **(a)** $PdBi/Al_2O_3$ and **(b)** Pd $\rightarrow Bi/Al_2O_3$ by EDS

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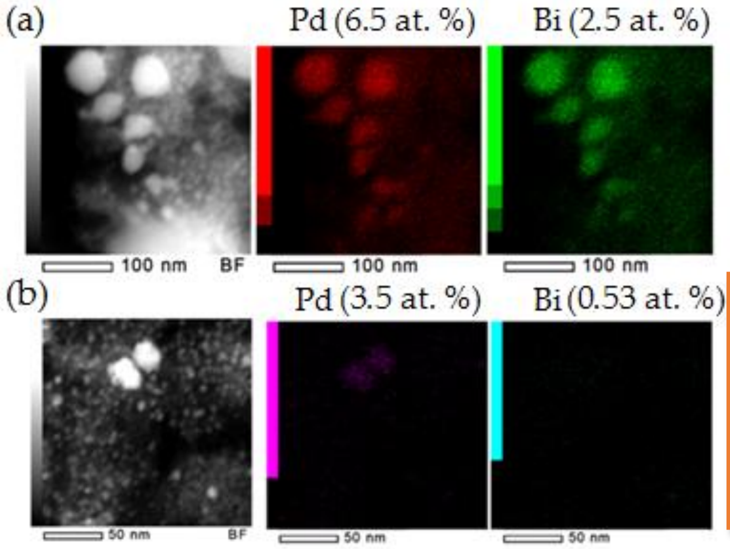

Figure 3 - Elemental mapping of the surface of the $Pd\rightarrow Bi/Al_2O_3$ catalyst by EDS at **(a)** 600,000× magnification and **(b)** 1,000,000× magnification.

The catalyst particles of $PdBi/Al_2O_3$ contain both Pd and Bi. Not all particles are bimetallic in the $Pd\rightarrow Bi/Al_2O_3$ catalyst

Table 1 - Atomic ratio of Pd/Bi at the scan points of the sample surface of the catalysts $PdBi/Al_2O_3$ and $Pd\rightarrow Bi/Al_2O_3$

Point	At(Pd)/At(Bi)	Point	At(Pd)/At(Bi)
7	11.9	13	Pd with impurity Bi
8	Pd with impurity Bi	30	2.4
9	Pd with impurity Bi	31	2.0
10	Absence of Pd and Bi	32	1.6
11	Monometallic Pd	33	1.1
12	Absence of Pd and Bi	34	3.4

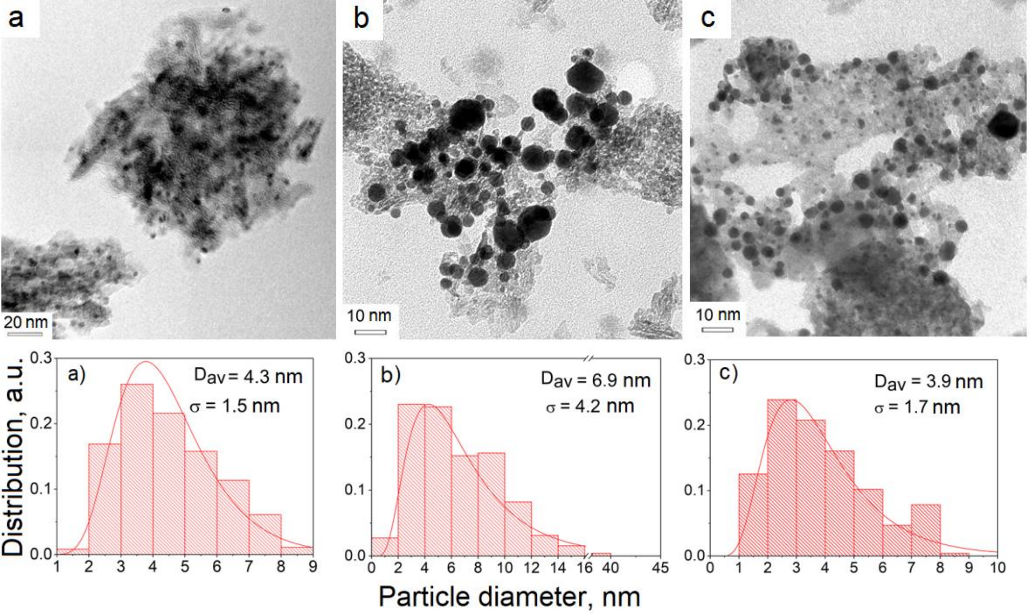

Figure 4 – TEM-micrographs of catalyst particles (a) Pd/Al_2O_3, (b) $PdBi/Al_2O_3$ (c) $Pd \rightarrow Bi/Al_2O_3$ and their size distribution

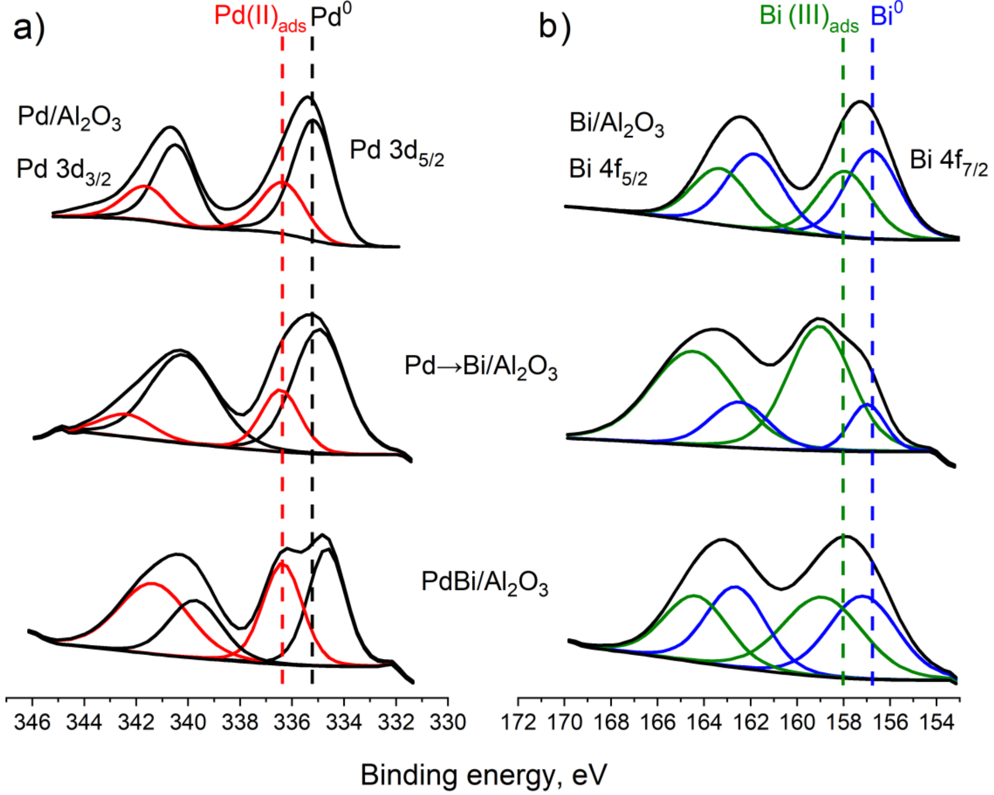

Figure 5 – XPS-patterns of the catalyst surface (a) Pd 3d, (b) Bi 4f.

Table 1 - Binding energy, the proportion of metallic and oxide phases in the samples of catalysts for the of Pd $3d_{5/2}$ and Bi $4f_{7/2}$ levels

Sample	E (Pd $3d_{5/2}$), eV	Pd-phase percentage	E (Bi $4f_{7/2}$), eV	Bi-phase percentage
Pd/Al_2O_3	Pd^0 335.2	68.8	-	-
	$Pd(II)_{ads}$ 336.4	31.2		
Bi/Al_2O_3	-	-	Bi^0 156.8	57.0
			$Bi(III)_{ads}$ 158.0	43.0
$PdBi/Al_2O_3$	Pd^0 334.7	53,8	Bi^0 157.3	47.1
	Pd(II) 336.4	46,2	Bi(III) 159.0	52.9
$Pd \rightarrow Bi/Al_2O_3$	Pd^0 335.0	73,1	Bi^0 157.0	17.1
	Pd(II) 336.4	26,9	Bi(III) 159.0	82.9

Particles of $PdBi/Al_2O_3$ catalyst have large diameters in comparison with the Pd/Al_2O_3 and $Pd \rightarrow Bi/Al_2O_3$. The shift of the peak binding energies of Pd^0, Pd $(II)_{ads}$, Bi^0, $Bi(III)_{ads}$ in bimetallic samples relative to the Pd/Al_2O_3 standard indicate the presence of electronic interaction between Pd and Bi.

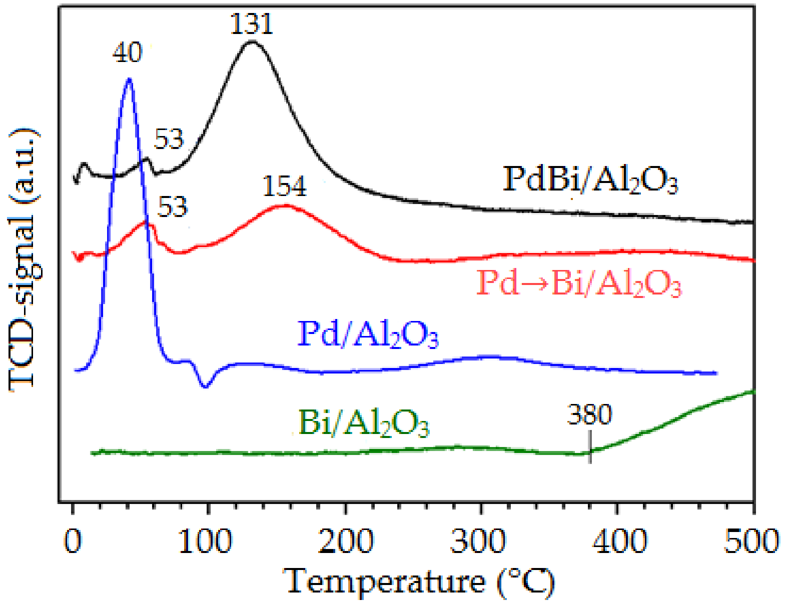

Figure 6 – TPR-profile of catalyst samples surface

A shift in the peak of the reduction of monometallic palladium (53 °C) is observed in the TPR profiles, there are no peaks of desorption of β-hydride Pd (98 °C) and the reduction peak reduction of monometallic bismuth. The appearance of a positive peak at 131-154 °C confirms the presence of an electronic interaction between Pd and Bi. Despite the high selectivity of the process in the presence of both bimetallic catalysts, the highest conversion and activity values were observed for $PdBi/Al_2O_3$.

Catalyst samples were investigated in the oxidation of glucose to gluconic acid at a molar ratio of [Glu]:[Pd] = 5000:1, pH 9, T = 60 °C.

Table 2 - Quantitative reaction parameters: glucose conversion X(Glu), gluconic acid yield Y(GluA), desired product selectivity S(GluA) and activity (TONs, TOFs)

Sample	X (Glu), %	S(GluA), %	Y(GluA), %	TONs	TOFs, min^{-1}
$PdBi/Al_2O_3$	83.7	99.9	83.6	7700	70
$Pd\rightarrow Bi/Al_2O_3$	63.7	97.0	61.8	6357	57.8

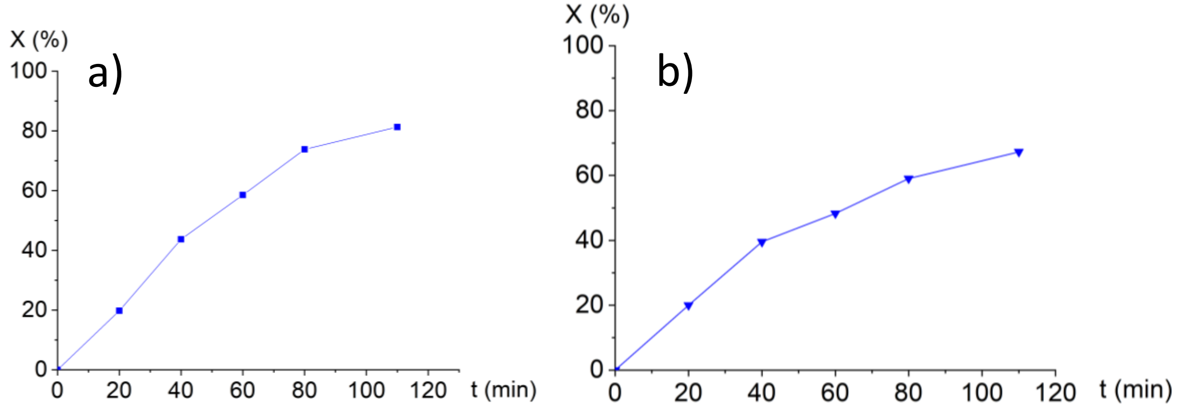

Figure 7 - Dependence of glucose conversion on time in the presence of a) $PdBi/Al_2O_3$; b) $Pd\rightarrow Bi/Al_2O_3$

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The valence-phase state of the samples was studied after catalytic tests and it was found that during the oxidation process, the Pd→Bi/Al_2O_3 catalyst is oxidized, while PdBi/Al_2O_3 retains its state.

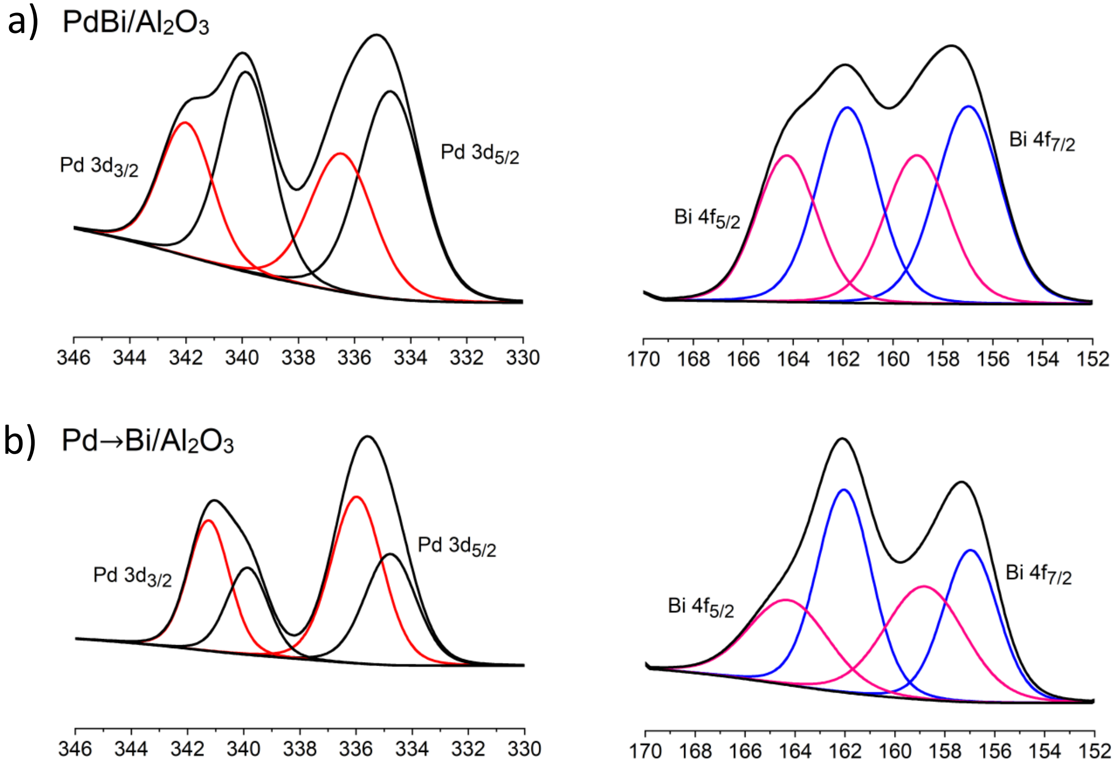

Figure 8 - X-ray photoelectron spectra of the surfaces of catalyst samples after catalytic tests

Table 3 - Binding energy (eV), atomic percent of Pd, Bi and fraction of metal/oxide phases in catalyst samples for Pd $3d_{5/2}$ and Bi $4f_{7/2}$ binding energies after catalytic tests.

Sample	E (Pd $3d_{5/2}$), eV	Pd-phase percentage	E (Bi $4f_{7/2}$), eV	Bi-phase percentage
PdBi/Al_2O_3	Pd^0 334.7	60	Bi^0 156.9	57.1
	$Pd(II)_{ads}$ 336.5	40	Bi_2O_3 159.0	42.9
Pd→Bi/Al_2O_3	Pd^0 334.6	40	Bi^0 156.9	47.8
	Pd_2O_3 335.8	60	Bi_2O_3 158.8	52.2

Conclusion. Co-impregnation of support from acetic acid solutions Pd(acac)2 and Bi(ac)3 makes it possible to obtain bimetallic palladium-bismuth nanoparticles (d_{av} = 7 nm), uniformly distributed over the support surface, stable and active in the glucose oxidation reaction.