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Modeling Pdx:Biy nanoclusters and predicting their catalytic activity in the glucose oxidation reaction into gluconic acid

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Samples with a given atomic ratio Pd3:Bi1, Pd5:Bi2, Pd2:Bi1, Pd1:Bi1, and Pd1:Bi2 supported on γ-Al_2O_3 were obtained by the method of simultaneous diffusion impregnation from acetic acid solutions of the precursors $Pd(acac)_2$ и $Bi(ac)_3$ [1]. Palladium supported on γ-Al_2O_3 was prepared as a reference sample. After removing the solvent, the catalyst powders were subjected to temperature treatments in an atmosphere of argon (500 °C), oxygen (350 °C), and hydrogen (500 °C). The total amount of supported metals on the support surface was ~ 4-6.6 wt. %. It was found by TEM that an increase in the amount of introduced bismuth relative to palladium leads to the formation of large aggregates with an average particle diameter of > 50 nm. This phenomenon is probably associated with the sintering of bismuth and palladium particles during heat treatment due to the low melting point of bismuth (271 °C) [2], while in the Pd/Al_2O_3 and $Pd3:Bi1/Al_2O_3$ samples, the particles have an average size of 4 nm.

The evolutionary «USPEX» algorithm [3] and the «VESTA» software package were used to theoretically predict the structural characteristics of nanoclusters with given ratios. The introduction of bismuth to palladium leads to its localization on the bimetallic particle surface. First, the inverted crown-jewel morphological structure is formed, when the basic metal atoms appear on the atoms surface of the precious metal. The tendency of bismuth to diffuse onto the formed particle surface may be due to its lower surface energy compared to palladium [4]. This feature is important for the catalytic process, since the affinity of bismuth for oxygen is higher [5] than that of palladium, and, therefore, bismuth will protect the catalyst active surface from oxidative poisoning.

The obtained catalysts were investigated in the glucose oxidation reaction into gluconic acid at a molar ratio of [Glu]:[Pd] = 5000, a temperature of 60 °C, and a pH of 9. In a catalytic test of the Pd/Al_2O_3 reference sample, 29.1% of glucose was converted to gluconic acid at a selectivity of 93.1%. The highest glucose conversion values (56.6%) with a selectivity for the desired product > 99.9% were observed in the presence of a catalyst with a lower bismuth content corresponding to the stoichiometric $Pd3:Bi1/Al_2O_3$. Testing the sample with the highest bismuth content $Pd1:Bi2/Al_2O_3$ showed that the glucose conversion was comparable to that achieved in the presence of Pd/Al_2O_3 (27.8%). An increase in the proportion of introduced bismuth to 66.6 at. % with respect to the total atomic metals loading in the case of $Pd1:Bi2/Al_2O_3$ led to blocking of active centers and, as a consequence, low catalytic activity of the sample.

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