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Influence of the temperature and pH on selective glucose oxidation process with Pd3:Bi1/Al_2O_3 catalyst

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Alumina-supported Pd3:Bi1 catalyst (where 3:1 indicates the atomic ratio between two metals) was obtained by the method of simultaneous diffusion impregnation using acetic acid solutions $Pd(acac)_2$ and $Bi(ac)_3$. After removing the solvent, the catalyst powders were subjected to temperature treatment in the atmosphere of argon (500 °C), oxygen (350 °C), and hydrogen (500 °C). Metal mass content determined by XRF equals 3.5 % for Pd and 2.4 % for Bi. Particle diameter determined by TEM ranges from 1 to 9 nm with maximum at 4 nm.

The Pd3:Bi1 catalyst was tested in the glucose oxidation reaction for 150 min at pH varied from 6 to 12; the temperature was maintained at 60 °C. The reaction was also conducted without pH control. During uncontrolled pH-process, the reaction proceeded for a short time until pH 3.4 was reached and practically stopped after that. Gluconic acid yield was less than 1%. At pH level 6-7, the conversion of glucose slightly increased and reached 3.6% and 17.1%, respectively. At the same time, in the cases considered, the selectivity towards gluconic acid remains equal to > 99.9 %. It is assumed that in the acidic and neutral medium, the low activity of the catalyst is associated with surface poisoning by oxygen, which leads to the formation of the inactive layer of palladium oxide, or by obtained gluconic acid. pH increase to 8-9 caused a significant conversion increase to 51.0% and 56.6%, respectively. With pH increase to 10-11, the conversion of glucose continued to increase, however, in addition to gluconic acid, fructose was found as a by-product associated with glucose isomerization in alkaline media [1]. At pH 11, the selectivity towards gluconic acid decreased to 80.8%. In a strongly alkaline medium (pH 12), both glucose and reaction products were destroyed, and the selectivity towards gluconic acid was 43.2%. The by-product formation was intensive at this point and was presented by formic, oxalic, and glyoxalic acids, as well as by ethyleneglycol.

Catalytic tests of the Pd3:Bi1 sample were conducted in temperature range from 20 to 60 °C, at pH level 9 and [Glu] : [Pd] ratio of 5000:1. At a temperature of 20 °C (room temperature), the reaction barely proceeded, and by the end the conversion of glucose reached 1.7%. A temperature increase to 30 °C led to an increase of reaction rate by a factor of 4 compared to the reaction conducted at room temperature. In this case, conversion reached 6.9%. At 40 °C, the reaction rate increased another 2.5 times. A temperature increase to 60°C led to glucose conversion value of 56.6%. The highest activity is achieved at 60 °C (~0.26 s^{-1}). Within the temperature range of 20-60 °C, the reaction proceeded selectively without any by-product formation or their concentrations were below the detection limit. For 70 °C and 80 °C, formation of fructose as a by-product was observed. At 90 °C the by-product formation became significant and included formic, oxalic, and glyoxalic acids, as well as ethylene glycol. The apparent activation energy was calculated by the graphical method using the Arrhenius equation, which was 67.7 kJ/mol. For activation energy calculation temperature range of 20-60 °C was used since higher temperatures favour intense by-product formation.

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References

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