

Effect of external parameters and mass-transfer on the glucose oxidation process catalyzed by Pd-Bi/Al₂O₃

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SUPPORTING INFORMATION

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Figure S1 Local point scanning of Pd3:Bi1 sample

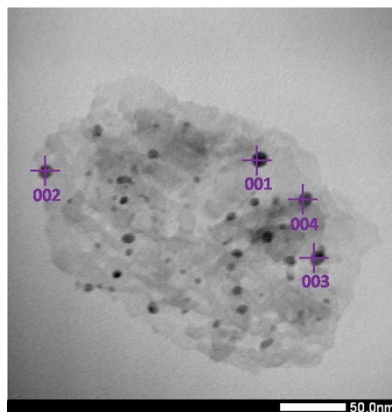


Table S1 Palladium and bismuth atomic percentage on the surface of Pd3:Bi1 sample

Scanning point	Pd content, at. %	Bi content, at. %	Pd:Bi atomic ratio
001	33.5	5.4	6.2
002	22.9	4.6	5.0
003	46.4	4.4	10.5
004	29.7	4.9	6.0

The atomic composition of individual particles for the Pd3:Bi1 sample was studied at points 001-004 with energy dispersive spectrometry (Fig. S1). Table S1 shows the Pd and Bi atomic percentage in the investigated catalyst with respect to the total content of all elements in the sample. Analysis shows a significantly greater presence of palladium compared to bismuth, the atomic ratio between them at the indicated points varies from 6.0 to 10.5. The relatively high content of palladium is likely due to its strong interaction with the support. It is also responsible for the suppression of particle agglomeration during the reduction with hydrogen, and, as a consequence, for their high dispersion.

Values of glucose conversion ($X_{(Glu)}$, %), selectivity for the desired product ($S_{(GluA)}$, %) and yield of gluconic acid ($Y_{(GluA)}$, %) was estimated according to formulas (1–3):

$$X_{(Glu)} = \left(1 - \frac{C_{(Glu)}}{C_{(Glu)0}} \right) \cdot 100\% \quad (1)$$

$$S_{(GluA)} = \left(\frac{C_{(GluA)}}{C_{(Glu)0} - C_{(Glu)}} \right) \cdot 100\% \quad (2)$$

$$Y_{(GluA)} = \left(\frac{S_{(GluA)} \cdot X_{(Glu)}}{100\%} \right) \quad (3)$$

where $C_{(\text{Glu})0}$ is initial glucose concentration (mol/l); $C_{(\text{Glu})}$ is glucose concentration after time interval t (mol/l); $C_{(\text{GluA})}$ is gluconic acid concentration after time interval t (mol/l).

Reaction rate R ($\text{mol}\cdot\text{l}^{-1}\cdot\text{s}^{-1}$) was calculated using the formula (4):

$$\mathbf{R} = \frac{\mathbf{C}(\mathbf{Glu})0 \cdot \mathbf{X}}{150 \text{ min} \cdot 60 \text{ sec}} \quad (4)$$

where $C_{(\text{Glu})0}$ is initial glucose concentration (mol/l); X is glucose conversion (%).

Activity expressed in turnover frequency TOF values (s^{-1}) was calculated using the formula (5):

$$\mathbf{TOF} = \frac{\mathbf{R} \cdot \mathbf{V}}{\mathbf{n}(\mathbf{Pd} + \mathbf{Bi}) \cdot \mathbf{X}(\text{act. surface})} \quad (5)$$

where R is production rate of gluconic acid ($\text{mol}\cdot\text{l}^{-1}\cdot\text{s}^{-1}$); V is volume of reaction mixture (2.76×10^{-2} l); $n_{(\text{Pd+Bi})}$ is amount of palladium and bismuth (mol); $X_{(\text{act. surface})}$ is fraction of active surface without carbon which estimated with using of XPS method and equals to 0.841.

The maximum rate of oxygen dissolution in water (I) and the rate of diffusion of oxygen from the bulk of the liquid towards the external surface of the catalyst (J) were determined as follows:

$$I = k_{\text{GL}} F c_{\text{eq}} \quad (6)$$

$$J = k_{\text{LS}} A_{\text{cat}} c_{\text{eq}} \quad (7)$$

where k_{GL} and k_{LS} are the coefficients of gas-liquid and liquid-solid transfer (m s^{-1}); F is the interfacial area between the gas and liquid phases (m^2); A_{cat} is the external surface area of the catalyst (m^2); c_{eq} is the equilibrium concentration of oxygen in water at 60°C and 1 bar (0.71 mol m^{-3}).

Mass transfer coefficients k_{GL} and k_{LS} were calculated using formulas (8) and (9) deduced from the established correlations of dimensionless Reynolds, Sherwood and Schmidt numbers for slurry reactors:

$$k_{\text{GL}} = \left(\frac{E D_{\text{O}_2-\text{H}_2\text{O}}^4 \rho}{\eta d_{\text{bu}}^2} \right)^{\frac{1}{6}} \quad (8)$$

$$k_{\text{LS}} = \left(\frac{E D_{\text{O}_2-\text{H}_2\text{O}}^4 \rho}{\eta d_{\text{g}}^2} \right)^{\frac{1}{6}} \quad (9)$$

where E is the average dissipation energy of the stirring normalized to the mass of the reaction mixture ($\text{W}\cdot\text{kg}^{-1}$); $D_{\text{O}_2-\text{H}_2\text{O}}$ is the diffusivity of oxygen in water ($\text{m}^2\cdot\text{s}^{-1}$); ρ is the density of 11% aqueous glucose solution equal to $1041.6 \text{ kg}\cdot\text{m}^{-3}$; η is the viscosity ($4.67 \times 10^{-4} \text{ kg m}^{-1}\cdot\text{s}^{-1}$ at 60°C); d_{g} is the mean diameter of the catalyst grains determined by optical microscopy ($d_{\text{g}} = 0.5 \times 10^{-5}$ for the alumina-supported palladium-bismuth catalysts).

The diameter of the oxygen bubble d_{bu} amounts to 3.8×10^{-3} m, as was estimated according to formula:

$$d_{bu} = \left(\frac{4d_0\sigma}{\Delta\rho g} \right)^{1/3} \quad (10)$$

Here d_0 is the diameter of the bubbler aperture (2×10^{-3} m); σ is the water surface tension equal to $0.0662 \text{ N}\cdot\text{m}^{-1}$ at $60 \text{ }^\circ\text{C}$; $\Delta\rho$ is the difference between the densities of water and oxygen at $60 \text{ }^\circ\text{C}$ ($982 \text{ kg}\cdot\text{m}^{-3}$); g is the gravitational acceleration ($9.8 \text{ m}\cdot\text{s}^{-2}$).

The maximum dissipation energy E_{\max} is determined by the power of a stirrer P normalized to the reaction mixture mass:

$$E_{\max} = P/m \approx 20 \cdot 0,83 / 0.02795 = 594 \text{ W}\cdot\text{kg}^{-1} \quad (11)$$

The Wilky-Chang equation was employed for the calculation of the oxygen diffusivity in water $D_{\text{O}_2-\text{H}_2\text{O}}$:

$$D_{\text{O}_2-\text{H}_2\text{O}} = \frac{7.4 \cdot 10^{-8} (\psi_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}})^{0.5} T}{\eta V_{\text{O}_2}^{0.6}} = 4.8 \cdot 10^{-9} \text{ m}^2\text{s}^{-1} \quad (12)$$

Here $\psi_{\text{H}_2\text{O}}$ denotes the dimensionless association factor which equals to 2.26 for water; $M_{\text{H}_2\text{O}}$ is the molar mass of water ($\text{g}\cdot\text{mol}^{-1}$); T is temperature (333 K); η is the viscosity of water expressed in centipoises (0.467 cP at 333 K); V_{O_2} is the molar volume of the dissolved oxygen at its boiling temperature under normal conditions which is $25.6 \text{ cm}^3 \text{ mol}^{-1}$.

The coefficient of the interfacial oxygen gas-liquid mass transfer k_{GL} calculated using expression (8) amounts to $6.0 \times 10^{-4} \text{ m}\cdot\text{s}^{-1}$. The liquid-solid oxygen transport coefficient k_{LS} is $5.5 \times 10^{-3} \text{ m}\cdot\text{s}^{-1}$ for the Pd-Bi/ Al_2O_3 catalyst, according to formula (9).

The interface gas-liquid area was estimated as follows:

$$F = 6\Phi_G V / d_{bu} + A \quad (13)$$

where Φ_G is the volume fraction of gas phase in the aqueous suspension which is always < 0.4 ; V is the volume of the reaction mixture (m^3); A is the area of the swirl formation at the agitation of the reaction mixture ($2.0 \times 10^{-3} \text{ m}^2$); diameter of bubble $d_{bu} = 3.8 \times 10^{-3} \text{ m}$ was estimated according to formula (10). The values of Φ_G equal to 0.01 and V equal to $2.76 \times 10^{-5} \text{ m}^3$ were employed for the calculations. The F value thus obtained is *ca.* $2.46 \times 10^{-3} \text{ m}^2$.

The external surface area of the catalyst sample loaded into the reaction vessel (A_{cat}) was calculated from the optical microscopy data by formula (14) that was derived under the assumption that all the catalyst grains are spherical with equal diameters:

$$A_{\text{cat}} = \frac{6m_{\text{cat}}}{\rho_g d_g} \quad (14)$$

where m_{cat} is the mass of a catalyst sample (kg); ρ_g is the density of the catalyst grains ($\text{kg}\cdot\text{m}^{-3}$); d_g is the mean diameter of the catalyst grains ($d_g = 0.5\times 10^{-5}$ m for the alumina-supported palladium-bismuth catalysts). The ρ_g values were calculated as follows:

$$\rho_g = \rho_m / (1 + V_\Sigma \rho_m) \quad (15)$$

where V_Σ is the specific pore volume evaluated from the data of low-temperature N_2 adsorption ($0.263 \times 10^{-3} \text{ m}^3\cdot\text{kg}^{-1}$); ρ_m is the material density of the support ($\rho_m = 3450 \text{ kg}\cdot\text{m}^{-3}$ for γ -alumina). It was found to be ρ_g is $1809 \text{ kg}\cdot\text{m}^{-3}$ for $\gamma\text{-Al}_2\text{O}_3$.