Selective oxidation of glucose over supported Au and PdAu catalysts

Oxana P. Taran[1,*], Irina V. Delidovich[1], Nikolay V. Gromov[1, 2], Lyudmila G. Matvienko[1], Pavel A. Pyrjaev[1], Boris L. Moroz[1,2], Valerii I. Bukhtiyarov[1,2] and Valentin N. Parmon[1,2]
[1]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, 630090, Russia*
[2]*Novosibirsk State University, Novosibirsk, 630090, Russia*
*oxanap@catalysis.ru

Introduction

Gluconic acid is the important compound used in pharmaceutical, food and chemical industry. Biotechnology processes for its production being the dominant commercial procedures have a lot of disadvantages. There is an urgent need to establish new catalytic methods of gluconic acid synthesis [1]. Nanodispersed gold catalysts are active in a variety of reactions [2] including carbohydrate oxidation [3].
The aim of this work is the development of active and stable supported gold and palladium-gold catalysts for selective oxidation of glucose into gluconic acid. The dependences of catalytic performance on the preparation method, dispersion of active component and support, as well as on the molar ratio of Pd:Au in the bimetallic catalysts were studied for the first time.

Experimental

The Au/C and Au/Al_2O_3 catalysts were prepared as described earlier [4,5]. The PdAu/C catalysts were synthesized by deposition of $Pd(NO_3)_2$ onto the Au/C precursor followed by reduction in a H_2 flow at 300°C [6], whereas the $AuPd/Al_2O_3$ catalysts were obtained by "a direct redox method", which involves reductive deposition of gold onto pre-reduced Pd particles [7]. They were characterized by TEM, XRD, XPS and tested for oxidation of glucose by molecular oxygen in agitated (900 rpm) aqueous solution using a three-necked glass reactor with a peristaltic pump for alkali (3M NaOH) supply. The reaction conditions were as follows: 60°C, atmospheric pressure, pH = 8.8-9.2, time = 7 h. Analysis of reaction mixture was performed by HPLC technique.

Results/Discussion

Table 1 shows the selected results of catalytic tests of the prepared samples in glucose oxidation. The Au/Al_2O_3 catalysts exhibit higher activities as compared to the Au/C ones (Table 1, Nos. 1-4). The turnover frequencies (TOF) for the oxidation of glucose over the Au/Al_2O_3 catalysts do not depend on the mean surface-volume Au particle diameter (d_{vs}) ranging from 2 to 5 nm. However, the TOF values decrease with an increase in the d_{vs} value from 5 to 25 nm (Fig. 1). The Au/Al_2O_3 catalysts show high stability during a test run, whereas the Au/C catalysts were deactivated possibly due to enlargement of gold nanoparticles under reaction conditions.

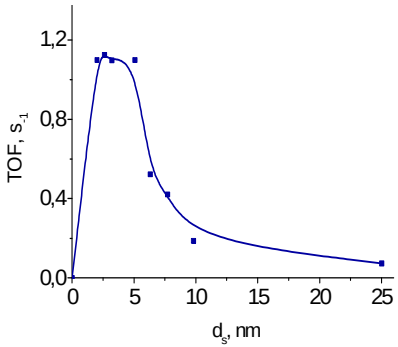

Figure 1. Dependence of TOF on the mean Au particle size in glucose oxidation over the Au/Al_2O_3.

Promotion of Au catalysts with moderate amounts of Pd (Pd:Au ≤ 0.2 mol/mol) leads to about double increase in the catalytic activity (*cf.* Nos 2 and 6, 3 and 7 in Table 1). An increase in the Pd:Au molar ratio results in a decrease in the catalytic activity and selectivity (*cf.* Nos 5 and 6, 7 and 8 in Table 1). Also, stability of the PdAu catalysts under the reaction conditions will be discussed in the report.

Table 1. Catalytic performance of Au and PdAu catalysts in selective glucose oxidation

No.	Catalyst	d_p, nm (TEM)	Glucose conversion, %	Gluconic acid selectivity, %	Catalytic activity, $mol_{Gluconic\ acid}*g_M^{-1}*h^{-1}$
1	Au/C	1.6±0.4	94	96	3.3
2	Au/C	3.2±1.8	100	97	1.5
3	Au/Al_2O_3	2.4±0.5	100	97	9.6
4	Au/Al_2O_3	3.0±0.6	97	96	8.2
5	$Pd_{0.7}Au_{0.3}/C$	3.1±1.0	35	40	0.4
6	$Pd_{0.2}Au_{0.8}/C$	3.0±0.8	81	87	3.4
7	$Au_{0.9}Pd_{0.1}/Al_2O_3$	1.9±0.6	100	95	22.1
8	$Au_{0.5}Pd_{0.5}/Al_2O_3$	2.7±0.7	100	93	8.3

Acknowledgements. This work was supported by RFBR (Grant No. 11-03-01022), Russian Federal Innovation and Science Agency (program "Scientific and Educational Cadres").

References.

1. O.V. Singh, R. Kumar, *Appl. Microbiol. Biotechnol.*, **75,** 713 (2007).
2. L. Prati, G. Martra, *Gold Bull.*, **32**, 96 (1999).
3. Y. Onal, S. Schimpf and P. Claus, *J. Catal.*, **223**, 122 (2004).
4. B. Moroz, P. Pyrjaev, V. Zaikovskii and V. Bukhtiyarov, *Catal. Today*, **144**, 292 (2009).
5. P.A. Pyrjaev, B.L. Moroz et. al., *Kinet Catal*, **51**, 885 (2010).
6. P.A. Pyrjaev, B.L. Moroz, A.N. Simonov, V.I. Bukhtiyarov and V.N. Parmon, Russian Patent Application No.2010113899, assigned to BIC (2010).
7. M. Bonarowska, J. Pielaszek, W. Juszczyk and Z. Karpinski, *J. Catal.*, **195**, 304 (2000).