



Reprint of “Synergetic combination of an enzyme and gold catalysts for glucose oxidation in neutral aqueous solution”[☆]



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ABSTRACT

Glucose oxidation by enzyme takes place in neutral aqueous solution at room temperature, producing gluconic acid in equilibrium with gluconate, while gold catalysts exhibit much higher catalytic activity but in alkali solution to produce sodium gluconate. The combination of glucose oxidase with selected gold catalysts such as Au/ZrO₂ and Au/NanoDiamond led to improved catalytic performance in neutral solution at room temperature. Gold nanoparticles supported on ZrO₂ decomposed hydrogen peroxide (H₂O₂) formed by the oxidation of glucose and depressed the damage of glucose oxidase by H₂O₂. In addition, Au/ZrO₂ utilized H₂O₂ produced by the enzyme to oxidize glucose to gluconic acid. In contrast, gold nanoparticles supported on NanoDiamond were active only for the decomposition of H₂O₂, while the presence of NanoDiamond itself could encourage glucose oxidase for the selective oxidation.

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1. Introduction

Catalytic transformation of biomass derived natural resources to valuable compounds is becoming of immense importance for the sustainable development of chemical industry [1]. Ethanol (C₂ compound) is produced from cones, sugar canes, and cellulose in an amount of 81.40 million tons a year in 2011 in the world [2] and occupies the majority of its commercial production. Glycerol (C₃ compound) which is by-produced in the production of biodiesel oil is produced in an amount of 0.75 million tons/year [3]. Glucose (C₆ compound) is also an important chemical resource which is produced from starch in an amount of 20 million tons/year. In the transformation of these biomass derived resources to valuable compounds, chemical processes have a lot of advantages, for example, higher purity and shorter reaction time, over the biological ones using microorganisms [1].

Gold nanoparticles (hereafter denoted as NPs) supported on base metal oxides, carbon, and polymers exhibit unique and useful catalytic performance leading to green sustainable chemistry [4–6]. For biomass derived resources, supported gold catalysts show interesting catalytic performance. Ethanol can be selectively transformed into acetic acid in aqueous solution on Au/MgAl₂O₄ catalyst [7] and into acetaldehyde by the gas phase oxidation on Au/La₂O₃ and Au/MoO₃ catalysts with molecular oxygen [8,9]. The hydrogenolysis of glycerol on Au/Al₂O₃ at 423 K selectively produces 1,2-propane diol [10]. The aerobic oxidation of glucose in strong aqueous alkali solution can produce sodium gluconate with extremely high rate of reaction on Au/ZrO₂. Turnover frequency per surface exposed gold atoms (TOF) reached 45 s⁻¹ [11].

Glucose oxidation can also be performed using a biocatalyst, namely glucose oxidase (GOx), which gives low initial rate (1.7 × 10⁻⁶ mol L⁻¹ s⁻¹) but a high TOF of 145 s⁻¹. Glucose oxidase can work in neutral solution at room temperature and can produce gluconic acid [12]. Gluconic acid is used as a complexing agent in industrial cleaning of metal surfaces and as a food additive. Since gluconic acid is a mild acid, it is in equilibrium with alkali gluconate under reaction conditions. The amount of strong acid required to obtain gluconic acid can be minimized if the reaction proceeds in neutral or acidic solution. In contrast, supported gold catalysts give much higher initial rate (1.4 × 10⁻⁴ mol L⁻¹ s⁻¹) but in alkali solution at higher temperature [11,13–15].

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Our attempt is to combine glucose oxidase as a biological catalytic system with supported gold NPs as an artificial catalytic system to seek for synergetic improvement in catalytic performance. Vennestrøm et al. have recently reported the combination of glucose oxidase with titanium silicalite-1 to utilize the by-product of one reaction (H_2O_2) for the second one (epoxidation of allyl alcohol) [16]. Our idea, which can be expressed by “a hybrid of an enzyme catalyst with artificial catalysts for the same reaction”, has come out from the instructive and inspiring review article presented by Professor Bernard Delmon [17]. He has proposed a bridged system between man-made functional solids and enzyme. We hope that this paper could present a preliminary example of his concept.

2. Experimental

2.1. Materials

The majority of metal oxide supports used were commercially available metal oxide powders: Al_2O_3 (Sumitomo Chemical, AKP-GO15, $148\text{ m}^2\text{ g}^{-1}$), SiO_2 (Fuji Silysia Chemical, CARICT Q-10, $300\text{ m}^2\text{ g}^{-1}$), TiO_2 (Nippon Aerosil, P-25, $50\text{ m}^2\text{ g}^{-1}$), ZnO (Hakusui Tech, ZINCOX SUPER F-2, $14\text{ m}^2\text{ g}^{-1}$), ZrO_2 (Dai-ichi Kigenso Kagaku Kogyo, RC-100, $80\text{--}120\text{ m}^2\text{ g}^{-1}$), SnO_2 (Sigma–Aldrich, nanopowder, $<100\text{ nm}$), and CeO_2 (Dai-ichi Kigenso Kagaku Kogyo, $166\text{ m}^2\text{ g}^{-1}$). Two types of carbon supports were used, namely, NanoDiamond (ND) (NanoCarbon Research Institute, NanoAmando, $4\text{--}5\text{ nm}$) and KetjenBlack (KB) (Lion, CARBON ECP, $780\text{ m}^2\text{ g}^{-1}$). Reagent grades, NH_4VO_3 , $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$, KMnO_4 , $\text{Fe}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, Na_2CO_3 , NaOH , glucose were used as received. As gold precursors, dimethyl Au^{III} acetylacetonate ($\text{Me}_2\text{Au}(\text{acac})$) was purchased from Tri Chemical Laboratories Inc. Glucose oxidase (from *Aspergillus niger*, $240,000\text{ units g}^{-1}$) was purchased from Wako Pure Chemical Industries.

Table 1
Aerobic oxidation of glucose catalyzed by GOx combined with supported gold NPs.^a

Entry	Catalyst	Initial rate ($\text{mol}_{\text{glucose}}\text{ L}^{-1}\text{ s}^{-1}$) ^b	Conv. after 1 h (%) ^c	
1	GOx	Au/ZrO_2	$(7.4 \pm 1.4) \times 10^{-5}$	98 ± 2
2	GOx	$\text{Au}/\text{NanoDiamond}$	$(5.6 \pm 1.6) \times 10^{-5}$	98 ± 2
3	GOx	$\text{Au}/\text{La}_2\text{O}_3$	5.2×10^{-5}	98
4	GOx	$\text{Au}/\text{Al}_2\text{O}_3$	$(5.4 \pm 1.6) \times 10^{-5}$	96 ± 2
5	GOx	Au/CeO_2	6.2×10^{-5}	95
6	GOx	Au/SnO_2	6.8×10^{-5}	94
7	GOx	Pt/ZrO_2	$(4.9 \pm 0.5) \times 10^{-5}$	93 ± 5
8	GOx	Au/MnO_2	6.5×10^{-5}	91
9	GOx	$\text{Au}/\text{Co}_3\text{O}_4$	5.8×10^{-5}	91
10	GOx	–	$(4.8 \pm 1.5) \times 10^{-5}$	90 ± 3
11	GOx	$\text{Au}/\text{Fe}_2\text{O}_3$	4.2×10^{-5}	88
12	GOx	Au/SiO_2	$(4.5 \pm 0.5) \times 10^{-5}$	87 ± 2
13	GOx	Au/TiO_2	5.8×10^{-5}	86
14	GOx	Au/ZnO	4.5×10^{-5}	84
15	GOx	$\text{Au}/\text{V}_2\text{O}_5$	2.9×10^{-5}	83
16	GOx	Au/NiO	4.5×10^{-5}	73
17	GOx	Au/CuO	3.9×10^{-5}	42
18	GOx	$\text{Au}/\text{KetjenBlack}$	2.5×10^{-5}	76
19	GOx	NanoDiamond	4.2×10^{-5}	93
20	GOx	ZrO_2	3.6×10^{-5}	79
21	GOx	Al_2O_3	3.6×10^{-5}	85
22	GOx	KetjenBlack	2.3×10^{-5}	62
23	–	Au/ZrO_2	6.5×10^{-6}	4
24	–	$\text{Au}/\text{Al}_2\text{O}_3$	9.7×10^{-6}	3

^a Reaction conditions: 2 wt% aqueous glucose solution (31 mL), GOx (0.13 g L^{-1}), 0.5 wt% Au loading catalyst (8.0 mg), glucose/Au = 15,000 (mol/mol), O_2 (60 mL min^{-1}), $30\text{ }^\circ\text{C}$, pH 7.

^b Calculated from a straight line fitted to the conversion–time curve.

^c The pH of the solution was kept at 7 by the titration with 1 M NaOH aqueous solution. Conversion after 1 h was calculated by the amount of NaOH added.

2.2. Preparation of metal oxide supports

V_2O_5 was prepared by calcination of NH_4VO_3 in air at $300\text{ }^\circ\text{C}$ for 4 h. For the preparation of MnO_2 , an aqueous solution (30 mL) of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (50 mmol) was added slowly to an aqueous solution (100 mL) of KMnO_4 (37 mmol) at room temperature, and the mixture was stirred at that temperature for 30 min. The precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 4. The precipitate was collected by filtration, dried at $120\text{ }^\circ\text{C}$ overnight, and then calcined in air at $300\text{ }^\circ\text{C}$ for 4 h.

Fe_2O_3 , Co_3O_4 , NiO , CuO and La_2O_3 were prepared by the neutralization method. An aqueous solution of metal nitrate (0.1 M L^{-1}) was rapidly added into an aqueous solution of Na_2CO_3 (1.2 equiv., 0.1 M L^{-1}) at $70\text{ }^\circ\text{C}$. After stirring for 1 h, the suspension was centrifuged and the precipitate was repeatedly washed with distilled water until the pH reached a steady value of around 6. The precipitate was filtrated, dried at $120\text{ }^\circ\text{C}$ overnight, and then calcined in air at $300\text{ }^\circ\text{C}$ for 4 h.

2.3. Deposition of gold NPs on carbons and metal oxides

All gold catalysts were prepared by the solid grinding (SG) method [18]. Briefly, dimethyl gold acetylacetonate, $\text{Me}_2\text{Au}(\text{acac})$, (8.3 mg) and support (1.0 g) were ground in an agate mortar for 20 min. The mixture was calcined in air at $300\text{ }^\circ\text{C}$ for 4 h or reduced in 20 vol% H_2/N_2 stream at $120\text{ }^\circ\text{C}$ for 2 h. The gold loading was 0.5 wt%.

2.4. Characterization

Transmission electron microscope (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) observations were carried out by using a JEOL JEM-3200FS operating at 300 kV. At least 140 particles of gold were observed to estimate the mean diameters and the standard deviation.

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