Electronic supplementary information for

**Selective oxidation of glycerol to dihydroxyacetone over Pd-Ag catalyst**

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**Details of procedures in catalyst preparation and reaction tests**

The carbon black (Vulcan-XC72, BET surface area 254 m\(^2\)/g) supplied by Cabot Corporation Ltd. was used as a support of the catalysts. Pd/C and Ag/C catalysts were prepared by impregnating the carbon with an aqueous solution of Pd(NO\(_3\))\(_2\) (N.E. Chemcat Co., Ltd.) and AgNO\(_3\) (Wako Pure Chemical Industries, Ltd.), respectively. The Pd-Ag/C was prepared by co-impregnation method using mixed aqueous solutions of Pd(NO\(_3\))\(_2\) and AgNO\(_3\). The loading amount of Pd and Ag were 2 wt% except noted. After evaporating the solvent and drying at 383 K for 12 h, these catalysts were reduced under H\(_2\) flowing at 473 K for 4 h, followed by passivation with O\(_2\)/He (2%) at room temperature. All catalysts were in powdery form, with less than 0.1 mm.

The pretreatment of catalyst was performed in a glass test tube (70 ml) equipped with magnetic stirrer and balloon filled with oxygen. A 20 ml aqueous solution of glycerol (5 wt%) and 0.050 g bimetallic catalyst were added into the reactor. The reactor was exposed to a vacuum and filled with oxygen. The reactor was then heated to 353 K. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After 4 h, the reactor was cooled down. The catalyst was collected by centrifugation. The wet catalyst was used immediately after the pretreatment.

Activity test was performed in a 190-ml stainless steel autoclave with an inserted glass vessel. The catalyst with or without pretreatment was put into an autoclave together with a spinner and a 20 ml aqueous solution of glycerol. After sealing, the reactor was filled with 0.3 MPa oxygen. The autoclave was then heated to 353 K, and the temperature was monitored using a thermocouple inserted in the autoclave. During the experiment, the stirring rate was fixed at 500 rpm (magnetic stirring). After an appropriate reaction time, the reactor was cooled down. The autoclave contents were transferred to a vial, and the catalyst was separated by filtration. The standard conditions for the reaction were as follows: 353 K reaction temperature, 0.3 MPa initial oxygen pressure, 4 h reaction time, 1 g glycerol, 19 g water and 50 mg supported metal catalyst. The pH of reaction mixture was about 6. The parameters were changed appropriately in order to investigate the effect of reaction conditions. Details of the reaction conditions are described in each result.
The products were analyzed using high performance liquid chromatography (Shimadzu Prominence) equipped with UV-VIS detectors and refractive index detector. An Aminex HPX-87H column (Bio-Rad) was used for separation. We quantified dihydroxyacetone (DHA), glyceraldehyde (GLYALD), glyceric acid (GLYAC), hydroxypyruvic acid (HYPAC), tartronic acid, mesoxallic acid and the degradation products such as glycolic acid and oxalic acid. The conversion and the selectivity were defined on the carbon basis and defined as Eqs. (S1) and (S2).

\[
\text{Conversion} \times 100 = \frac{\sum (\text{mol of product})(\text{number of carbon atoms in a product molecule})}{\sum (\text{mol of product or glycerol})(\text{number of carbon atoms in a product or glycerol molecule})} (S1)
\]

\[
\text{Selectivity} \times 100 = \frac{(\text{mol of the product})(\text{number of carbon atoms in the product molecule})}{\sum (\text{mol of product})(\text{number of carbon atoms in a product molecule})} (S2)
\]

The mass balance was also confirmed in each result and the difference in mass balance was always in the range of the experimental error. The agreement in terms of the mass balance indicated that polymeric by-products were not formed (±10%). The data of reaction time dependence was based on the different runs using a fresh catalyst. The used catalyst was collected by centrifugation under air atmosphere. A slight loss (Ca. 10% in weight) was observed during the recovery process and the reuse experiments were performed in the reduced scale. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500).

**Details of the temperature-programmed reduction**

Temperature-programmed reduction (TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector using 5% H\(_2\) diluted with Ar (30 ml/min). The amount of catalyst was 0.05 g, and temperature was increased from room temperature to 1123 K at a heating rate of 10 K/min.

**Details of the TEM observation**

Transmission electron microscope (TEM) images were taken for determination of the particle size using equipment (HF-2000; HITACHI) operated at 200 kV. The catalysts after the reduction, after the pretreatment with glycerol + O\(_2\) and after use were used as samples for the TEM observation. Supersonic waves dispersed the sample in ethanol. The samples were placed on Cu grids under air atmosphere. The average particle size \((d_i)\) was calculated by \(\frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}\) \((d_i\), particle size; \(n_i\), number of particles with \(d_i\)). Figure S1 shows TEM images of the Pd-Ag/C (Ag/Pd=1), and dark spots are assigned to metal particles. The average particle size of the catalysts after the reduction, after the pretreatment with glycerol + O\(_2\) and after use was estimated to be 4.9 nm, 5.6 nm and 5.8 nm, respectively.
**Figure S1.** TEM images of Pd-Ag/C (Ag/Pd=1). (a) After the reduction at 473 K, (b) after the reduction at 473 K and the pretreatment with glycerol + O$_2$, (c) after the reduction at 473 K, the pretreatment with glycerol + O$_2$ and the catalytic use for 24 h.

**Details of the X-ray diffraction patterns**

X-ray diffraction (XRD) patterns were recorded by a diffractometer (Rigaku Ultima IV). Cu Kα ($\lambda = 0.154$ nm, 45 kV, 40 mA) radiation was used as an X-ray source. The particle size on Pd-Ag/C was calculated by the Scherrer's equation.$^{(S2)}$

**Details of the CO and O$_2$ adsorption measurement**

The amount of CO and O$_2$ chemisorption was measured in a high-vacuum system using a volumetric method. Before adsorption measurements, the catalysts were treated in H$_2$ at 473 K for 1 h. Subsequently, the adsorption was performed at room temperature. Gas pressure at adsorption equilibrium was about 1.1 kPa. The sample weight was about 0.15 g. The dead volume of the apparatus was about 60 cm$^3$. 
**Table S1.** Oxidation of glycerol in the presence or absence of glycolic acid.

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Catalyst amount / mg</th>
<th>Glycolic acid / mmol</th>
<th>Reaction time / h</th>
<th>Conversion / %</th>
<th>DHA</th>
<th>GLYALD</th>
<th>GLYAC</th>
<th>HYPAC</th>
<th>Glycolic acid</th>
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<td>1</td>
<td>Pretreated Pd-Ag/C</td>
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<tr>
<td>4</td>
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<td>24</td>
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</table>

Reduction conditions: 473 K, H$_2$ flow 30 cc/min, 4 h. Pretreatment conditions: 5 wt% glycerol aqueous solution 20 g, O$_2$ pressure 0.1 MPa, 353 K, 4 h. Reaction conditions: 5 wt% glycerol aqueous solution 20 g, initial O$_2$ pressure 0.3 MPa, 353 K.

*Not determined since significant amount of glycolic acid is present in the reaction solution. DHA, dihydroxyacetone; GLYALD, glyceraldehyde; GLYAC, glyceric acid; HYPAC, hydroxypyruvic acid.

**References**
