Supporting Information

Continuous catalytic oxidation of glycerol to carboxylic acids by using nanosized gold/alumina catalysts and a liquid-phase flow reactor

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Experimental details

Materials

Tetrachloroauric(III) acid tetrahydrate (HAuCl₄·4H₂O) was obtained from Kishida Chemical Co. Ltd. (Osaka, Japan). Sodium hydroxide, glycerol, and sulfuric acid were obtained from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Activated alumina (Al₂O₃) powder (material: Alumina N, Activity: I; specific surface area: 150 m²/g; particle size: 50–200 µm) was obtained from MP Biomedicals, Inc. (Santa Ana, California, USA).

Preparation of the catalysts

Five catalysts were prepared by means of the deposition–precipitation method established by Haruta et al.¹. First, an acidic Au solution was prepared by dissolving a calculated amount (Au content of completed catalyst=1.0 wt%) of HAuCl₄·4H₂O in distilled water at 343 K. The acidic Au solution was then neutralized by the addition of a thin solution of NaOH in water. The pH of the neutralized acidic Au solution was adjusted to the desired value by the further addition of NaOH. Powdered activated alumina support was then added to the pH-adjusted Au solution. After stirring for 2 h at 343 K, the catalyst precursor was washed several times with distilled water and then
filtered. The obtained catalyst powder was dried overnight at room temperature and then calcined at 673 K for 4 h.

**Catalytic reaction tests**

Catalytic reaction tests were performed by using a stainless-steel liquid-phase flow reactor (inside diameter: 9.4 mm; length: 50 mm; Eyela, Tokyo, Japan) with Teflon filters installed at the inlet and outlet of the reaction chamber. The reaction chamber was filled with catalyst and then heated by means of an electric aluminum-block heater. The reactant, a mixture of glycerol with or without NaOH, was fed into the reactor via a diaphragm pump (SIMDOS 10; KNF, Freiburg, Germany). Oxygen was introduced into the reactor via a mass-flow controller (STEC, Tokyo, Japan). The reactant and oxygen were mixed by using a gas–liquid mixer and then introduced into the reaction chamber. Figure S1 shows an outline of the setup used for the catalytic reaction tests and photograph of reaction chamber and filter. Reaction products were analyzed by means of high-performance liquid chromatography (Shimadzu, Kyoto, Japan). Calibration curves for quantitative analyses were prepared by using commercial reagents of high purity. Reaction products were neutralized by the addition of H$_2$SO$_4$, which replaced the
carboxylic acid counter cation (Na\(^+\)) with H\(^+\). In the long-term catalytic reaction test, we shut down and re-started the reactor several times during the test period.

**Figure S1.** Outline of the setup used for the catalytic reaction tests and photograph of a reaction chamber and a filter.
**Analysis of the catalysts**

A scanning transmission electron microscope (ARM-200F; JEOL, Tokyo, Japan) was used to examine the surface morphology of the catalysts. To determine the Au content of the catalysts, the Au in the catalysts (weight of Au/Al₂O₃ catalyst ≈ about 45 mg) was removed from the support by dissolving the catalysts in aqua regia (about 2 mL). The solution of Au in aqua regia was then diluted, and the amount of Au was determined by using an inductively coupled plasma optical emission spectrometer (SPS-3100; Seiko Instruments Inc., Chiba, Japan).

**Fructose pre-treatment**

The concentration of fructose in water was 0.3 mol/L. The reductant solution was fed by a pump, and the flow rate was 0.25 mL/min. During the reduction period, the connector for the reaction chamber was for only liquid feeding with one inlet. The temperature was kept at 343 K for 5 h. After the pre-treatment, the connector was changed to gas–liquid type, as described above.
Calculation of TOF

The turnover frequency (TOF) of the catalysts was calculated by using the following equation:

\[
\text{TOF (h}^{-1}\text{)} = \frac{\text{[Amount of glycerol converted (mol h}^{-1}\text{)]}}{\text{[Au in the catalyst (mol)]}}
\]

Carbon balance of the long-term catalytic test

Carbon balance was calculated by using following equation:

Carbon balance (%) =
Sum of the yields (%) of all detected products by the HPLC analysis

Figure S2 (a). Time course of the carbon balance of Figure 2
**Figure S2 (b).** Time course of the carbon balance of Figure 3

**Histogram of STEM analysis (Figure 4(a))**

**Figure S3(a).** Histogram of STEM analysis of Figure 4(a). Counted nanoparticles: 118. The STEM images for this histogram are Figure 4(a) in the main manuscript and as follows (We checked 8 STEM images shown in the main manuscript (1 image) and in the next page (7 images)).
Figure S3 (b). Other STEM images for preparation of the histogram (Figure S3 (a))

Reference (Supporting Information)

(1) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B.,
Low-Temperature Oxidation of CO over Gold Supported on TiO2, α-Fe2O3, and Co3O4.
J. Catal. 1993, 144 (1), 175-192.