Electronic Supplementary Information

Aerobic oxidation of alcohols in the liquid phase with nanoporous gold catalysts

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General Information

For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck, 230-400 mesh). ICP analysis was performed on Shimadzu ICPS-7510 equipment. GC-MS analysis was performed on an Agilent 6890N GC interfaced to an Agilent 5973 mass-selective detector (30 m x 0.25 mm capillary column, HP-5MS). Scanning electron microscope (SEM) observations were carried out using JEOL JSM-6500F and HITACHI FE-SEM S4300 instruments operated at accelerating voltages of 30 and 10 kV, respectively. EDX analysis was carried out using EDAX Genesis with HITACHI FE-SEM S4300 operated at an accelerating voltage of 20 kV. The CV measurements were carried out in a conventional three-electrode cell at ambient temperature by using an Iviumstat electrochemical analyzer (Ivium Technology). Nanoporous gold fixed with gold wire was employed as the working electrodes, and a saturated calomel electrode and a Pt plate were used as the reference and counter electrodes, respectively. TDS measurements were carried out using a WA-1000S system (ESCO Ltd.) with a quadrupole mass spectrometer (QMD422; Balzers). The heating rate was approximately 1 K/s. The AuNPore was washed by water to remove contaminations and exposed to air for 2h (blue line in

Figure 1a) or dipped in 1-phenylethanol (**1b**) for 30 min (blue line in Figure 1b) before the TDS measurements. For the comparison, the TDS spectrum of **1b** was normalized by the peak height. Au(111) substrates were prepared by vacuum-deposition on mica plates as previously reported.[1]

Fabrication of Nanoporous Gold Catalyst

For batch reaction system: Au (99.99%) and Ag (99.99%) were melted with electric arc-melting furnace under Ar atmosphere to form Au/Ag alloy (30:70, in at. %), which was rolled down to thickness of 100 μm. The foil was cut into small pieces (3 x 3 mm square). Treatment of the resulting several chips (total weight: 41.7 mg) with 70 wt. % nitric acid (2.34 mL) for 24 hours at room temperature resulted in the formation of the nanoporous structure by selective leaching of silver. The material was washed with pure water, and acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold (18.6 mg) and its composition was found to be $Au_{97}Ag_3$ by calculation from the weight loss of the silver.

For flow reaction system: Au/Ag alloy (35:65, in at. %) thin film (thickness: 100 nm) was purchased from Imai Kinpaku Co., Ltd. Treatment of the thin film with 70 wt. % nitric acid for 2 hours at 0 °C resulted in the formation of the AuNPore in powder form. The material was washed with pure water, and acetone, successively. Drying of the material under reduced pressure gave the nanoporous gold and its composition was found to be $Au_{87}Ag_{13}$ by EDX analysis.

SEM micrographs of nanoporous gold

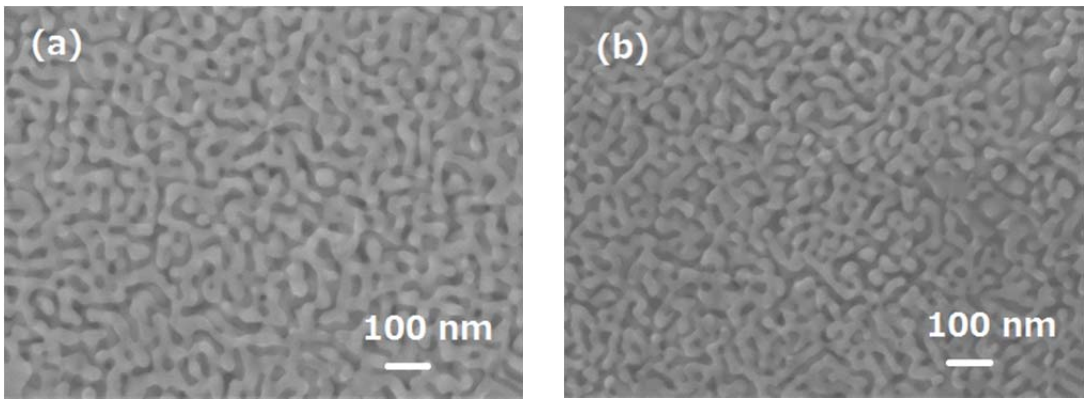


Figure S1. (a) Freshly prepared AuNPore; (b) AuNPore after being used five times for oxidation of 1-phenylbutanol **1a**.

Cyclic voltammogram for nanoporous gold thin film

The amount of reduction charge corresponding to the shaded region in Figure S2 was obtained by integrating the charge passed in the surface oxide stripping reaction recorded for nanoporous gold thin film (12.2 mg), which was marked in the figure. The electrochemically active surface area of the

nanoporous gold is:

$399820 / 2.22 \cdot 10^{6} / 2 = 9.0 \cdot 10^{-2}$ (m^2)

where $2.22 \cdot 10^{6}$ μC m^{-2} is the gold's conversion factor.[2]

Hence, the specific surface area was calculated to be $9.0 \cdot 10^{-2}/0.0122 = 7.38$ m^2/g.

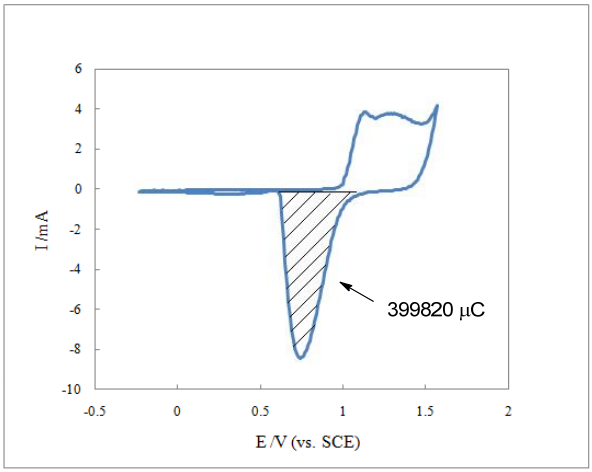


Figure S2. Original cyclic voltammogram for nanoporous gold thin film (12.2 mg) in 0.1 M $HClO_4$ solutions. Scan rate: 5 mV s^{-1}.

XPS analysis

XPS measurements were performed in a Theta Probe system (Thermo Fischer Scientific) with a monochromatized Al Ka Xray source. The detection angle was 23°~83° to the sample surface. The spectra were calibrated with the Au 4f 7/2 peak at 84.0 eV and normalized by the peak area of Au 4f 7/2. From Figure S3, no difference was observed between AuNPore (Figure S3a) and Au(111) (Figure S3b).

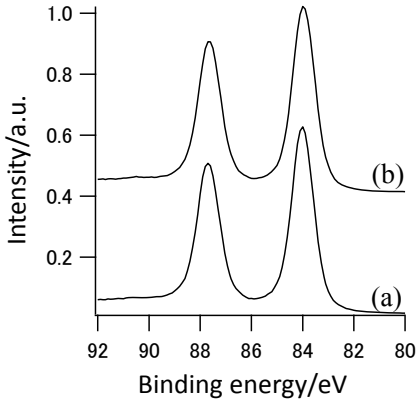


Figure S3. Au 4f XPS spectra of (a) AuNPore and (b) Au(111).

Aerobic oxidation of alcohols with AuNPore catalyst

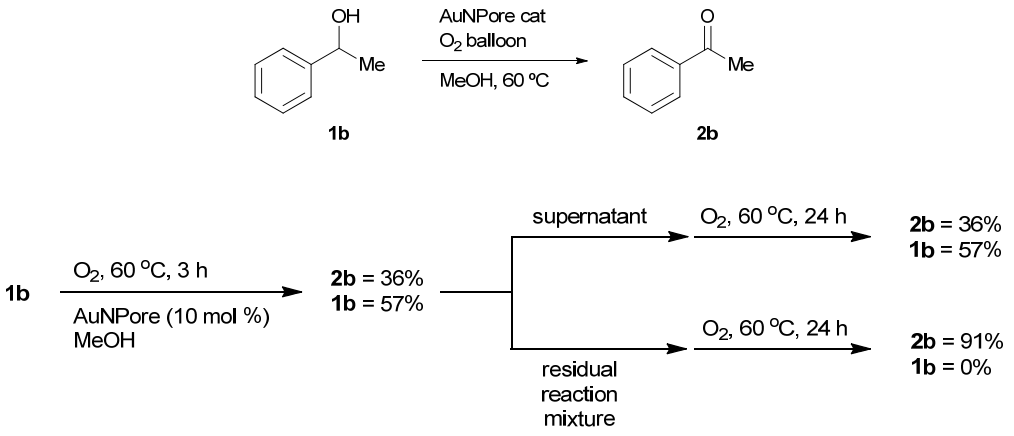
The preparation of **2b** is representative. MeOH (3 mL) and **1b** (36.6 mg, 0.3 mmol) were added successively to the nanoporous gold (6.0 mg, 10 mol %) in a micro reaction vial at room temperature. A balloon filled with O_2 was connected to the vial and the mixture was stirred at 60 °C for 10 h. The catalyst was removed and the reaction mixture was then concentrated under reduced pressure to give a crude material. The chemical yield of product was determined by ^{1}H NMR analysis with *p*-xylene as an internal standard. The recovered catalyst was washed with acetone, aq $NaHCO_3$ solution, 1M HNO_3 solution, distilled water, and acetone, successively, dried in vacuo, and reused.

Calculation of TOF and TON[3]

The AuNPore (6.0 mg) catalyzed reaction of **1a** (0.3 mmol) gave **2a** in 9% yield with 0.5 h. The surface area was electrochemically measured to be 7.38 m^2/g (Figure S2) and the density of surface atoms for the energetically most stable Au(111) surface is $1.4 \cdot 10^{19}$ atoms/m^2. The catalyst was used five times as shown in Table 1. Using these values the TOF and TON were calculated to be 52.4 h^{-1} and 1400, respectively.

Leaching test

The catalytic oxidation of **1b** was carried out for 3 h under the standard conditions, and **2b** was produced in 36% yield at this time, which was determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. Then, a half amount of supernatant of the reaction mixture was transferred to another vessel. After further stirring for 24 h, **2b** was obtained in 91% yield from the original vessel having AuNPore catalyst. In contrast, no progress was observed in the new vessel having no catalyst and **2b** was obtained in 36% yield. Furthermore, leaching of the gold in the reaction of **1b** was not detected by inductively coupled plasma (ICP) analysis (<0.0005%). These results clearly indicated that the current transformation was catalyzed by the AuNPore catalyst.



Flow reaction system

Stainless steel (SUS316) Y-shaped micromixer with inner diameter of 0.5 mm was manufactured by YMC CO., LTD. Stainless steel (SUS316) tube with inner diameter of 2.0 mm and length of 150 mm was purchased from YMC CO., LTD. and it was filled with powdered AuNPore (43 mg, 0.2 mmol). The temperature of the stainless tube was controlled by column thermostat (JASCO CO-2060). Solutions and oxygen gas were introduced to the microflow system using syringe pumps, KDS-100, equipped with gastight syringes purchased from SGE. The syringes, micromixer, and the stainless tube column were connected with PTFE tube with inner diameter of 0.5 mm as shown in Figure S4.

Procedure for oxidation of 1-phenylbutanol **1a** with flow system: A solution of **1a** (0.1 - 0.5 M) in MeOH (flow rate: 3 mL h^{-1}) and oxygen (flow rate: 30 mL h^{-1}) were introduced to helix-shaped micromixer by using syringe pumps. The resulting gas-liquid mixture was then introduced to the column, having AuNPore catalyst, which was kept at 60 °C by the column thermostat. The chemical yield of phenylbutanone **2a** was determined by ^{1}H NMR analysis with *p*-xylene as an internal standard.

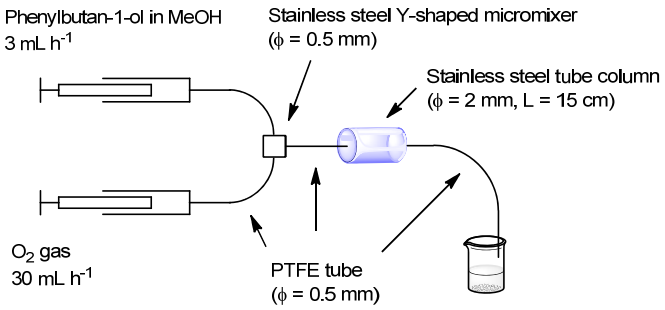


Figure S4. Flow reaction system for aerobic oxidation of 1-phenylbutanol.

Product Identification

All of starting alcohols and products were commercially available. They are identified by ^{1}H NMR and GC-MS.

References

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