Supporting Information

Efficient and selective epoxidation of styrene with TBHP catalyzed by Au$_{25}$ clusters on hydroxyapatite†

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1. Preparation methods

A. HAP-supported AuNPs prepared by impregnation

HAP (1 g) was added to an aqueous solution of HAuCl$_4$ (1.27 mM, 20 mL) and the mixture was stirred for 4 h at room temperature. After evaporating the water, the sample was dried for more than 24 h using a lyophilizer, followed by calcination at 300 °C for 2 h in vacuo. This sample is denoted 0.5Au-HAP(IP).

B. HAP-supported AuNPs prepared by deposition precipitation

The pH value of an aqueous solution of HAuCl$_4$ (1.27 mM, 20 mL) was adjusted to 10 by adding ammonia solution. Then, HAP (1 g) was added and the mixture was stirred for 4 h at room temperature, followed by filtration of the solids. The sample was dried for more than 24 h using a lyophilizer, followed by calcination at 300 °C for 2 h in vacuo. This sample is denoted 0.5Au-HAP(DP).

C. HAP-supported AuNPs prepared by adsorption

HAP (1 g) was added to an aqueous solution of HAuCl$_4$ (1.27 mM, 20 mL) and the mixture was stirred for 12 h at room temperature, followed by filtration of the solids. The sample was dried for more than 24 h using a lyophilizer, followed by calcination at 300 °C for 2 h in vacuo. This sample is denoted 0.5Au-HAP(Ad).

2. Characterization methods

A. Optical spectroscopy

UV-vis absorption spectrum of Au$_{25}$(SG)$_{18}$ in H$_2$O was recorded with a spectrophotometer (Jasco, V-670). Diffuse reflectance UV-vis spectra of the supported Au clusters were recorded by the spectrophotometer using a solid sample cell attachment. All measurements were performed under ambient conditions.

B. Transmission electron microscopy (TEM)

TEM images were recorded digitally with a Gatan slow-scan CCD camera on a JEOL 2011 electron microscope operating at 200 kV. The samples were prepared by dispersing the powder products as slurry in acetone, which was then deposited and dried on a holey carbon film on a Cu grid.
C. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)

The HAADF-STEM observations were carried out using a JEOL JEM-3000F transmission electron microscope (coefficient of spherical aberration Cs=0.6 mm) equipped with a digitally processed STEM imaging system, operating at 300 kV. The samples were directly dispersed on a holey carbon film supported by a copper grid without the use of any solvent. The collection angle of the annular dark field detector was set to 60–200 mrad. The electron probe size was approximately 0.2 nm with a beam convergence semi-angle of 11 mrad. The HAADF-STEM images were recorded for 8.2 s with a digital resolution of 512 × 512 pixels. The noise in the images was reduced by a low-pass filter in the image processing software Gatan Digital Micrograph. The image magnification was calibrated by the lattice spacing of a Si or rutile TiO2 crystal.

D. N2 adsorption/desorption isotherm

Nitrogen adsorption/desorption isotherms at 77 K were measured using a Yuasa Ionics Autosorb-6 after the samples were degassed (1.33 × 10^{-2} Pa) at 150 °C overnight. The specific surface area was calculated following the method of Brunauer, Emmet, and Teller (BET). The method of Barret, Joyner, and Halenda (BJH) was used to determine the pore-size distribution (PSD).

E. Thermogravimetric (TG) analysis

TG analysis of Au_{25}(SG)_{18} was performed on a TG/DTA analyzer (Brucker, TG-DTA2000SA) under N2 flow. The temperature was increased from room temperature to 300 °C at the rate of 10 °C /min and maintained at 300 °C for 2 h. Typically, 5–7 mg of Au_{25}(SG)_{18} was used for the measurement.

F. Inductively-coupled plasma (ICP) measurements

ICP analysis of the supported Au catalyst was performed on an ICP spectrometer (Shimadzu, ICPS-8000). Samples for the analysis of Au and S were prepared by dissolving the Au-HAP catalysts (300 mg) in aqua regalis (5 mL) and subsequently diluting the solution hundredfold and tenfold, respectively. The concentrations of Au and S were determined from the calibration curves plotted for each element in the concentration ranges of 0–20 and 0–15 ppm, respectively.
3. Results

A. Adsorption of Au$_{25}$(SG)$_{18}$ onto HAP

![UV-vis absorption spectrum of original solution of Au$_{25}$(SG)$_{18}$ and filtrate of 0.5Au$_{25}$:SG-HAP composite.]

**Fig. S1** UV-vis absorption spectrum of original solution of Au$_{25}$(SG)$_{18}$ and filtrate of 0.5Au$_{25}$:SG-HAP composite.

B. UV-vis spectra of Au$_{25}$(SG)$_{18}$ and 0.5Au$_{25}$:SG-HAP

![UV-vis spectrum of Au$_{25}$(SG)$_{18}$ dispersed in H$_2$O and diffuse reflectance UV-vis spectrum of 0.5Au$_{25}$:SG-HAP composite.]

**Fig. S2** UV-vis spectrum of Au$_{25}$(SG)$_{18}$ dispersed in H$_2$O and diffuse reflectance UV-vis spectrum of 0.5Au$_{25}$:SG-HAP composite.

C. HAADF-STEM image and size distribution of 0.2Au$_{25}$:SG-HAP sample

![HAADF-STEM image and size distribution of 0.2Au$_{25}$:SG-HAP sample.]

**Fig. S3** (A) Representative HAADF-STEM image of 0.2Au$_{25}$:SG-HAP and (B) size distribution of the Au clusters.
D. TGA analysis of Au$_{25}$(SG)$_{18}$

![TGA result for Au$_{25}$(SG)$_{18}$](image)

**Fig. S4**  TGA result for Au$_{25}$(SG)$_{18}$.

E. Textural properties of HAP-supported Au catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>0.5Au$_{25}$-HAP</th>
<th>0.5Au-HAP(Ad)</th>
<th>0.5Au-HAP(DP)</th>
<th>0.5Au-HAP(IP)</th>
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<tbody>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>27</td>
<td>35</td>
<td>32</td>
<td>24</td>
</tr>
<tr>
<td>Au loading (wt %)$^a$</td>
<td>0.50</td>
<td>0.42</td>
<td>0.49</td>
<td>0.47</td>
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</table>

$^a$Determined by ICP measurement.

F. TEM images and size distribution of 0.5Au-HAP catalysts

![TEM images](image)

**Fig. S5**  TEM image and size distribution of Au particles of (A) 0.5Au-HAP(Ad), (B) 0.5Au-HAP(IP), (C) 0.5Au-HAP(DP).
G. Styrene oxidation over pure HAP

![Graph showing catalytic performance of pure HAP in styrene oxidation. The reaction was performed at 80 °C, in toluene (10 mL) containing TBHP (0.2 g), the catalyst (50 mg) and styrene oxide (40 mg).](image)

**Fig. S6** Catalytic performance of pure HAP in styrene oxidation. The reaction was performed at 80 °C, in toluene (10 mL) containing TBHP (0.2 g), the catalyst (50 mg) and styrene oxide (40 mg).

H. Product distribution of styrene oxidation over 0.5Au25-HAP catalyst

![Graph showing product distribution.](image)

**Fig. S7** Catalytic performance of 0.5Au25-HAP in oxidation of styrene (1). The yields of the products are plotted as a function of time; styrene oxide (2); acetophenon (3); benzaldehyde (4); benzyl alcohol (5); benzoic acid (6). The reaction was performed at 80 °C, in toluene (10 mL) containing TBHP (0.2 g), the catalyst (50 mg) and styrene (40 mg).

I. Kinetic analysis

In order to evaluate the catalytic activities of 0.5Au-HAP, time-evolution of conversion, \( C \), was monitored from the measured yield of 1. The term \(-\ln(1-C)\) is plotted as a function of the reaction time in Fig S8. The rate constant, \( k \), was determined from the slope of the plot in Fig S8 and is summarized in Table S2.
**Fig. S8**  Time course of conversion of styrene at [styrene] = 38.4 mM, [Au] = 0.127 mM. a) 0.5Au_{25}-HAP; b) 0.5Au-HAP(Ad); c) 0.5Au-HAP(IP).

**Table S2**  Rate constants for oxidation of styrene by HAP-supported Au catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>0.5Au_{25}-HAP</th>
<th>0.5Au-HAP(Ad)</th>
<th>0.5Au-HAP(IP)</th>
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<tr>
<td>$k$</td>
<td>0.38</td>
<td>0.37</td>
<td>0.24</td>
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Initial reaction rate, $V_{ini}$ (mol/[h·Au mol]), was determined by the following equation:

$$V_{ini} = \frac{K \cdot C_{styrene}}{C_{Au}}$$

where $C_{styrene}$ and $C_{Au}$ are the initial concentrations of styrene and Au atom in Au-HAP, respectively. The TOF of formation of 2 by 0.5Au_{25}-HAP is calculated to be 114 mol/[h·Au mol].

**References**


**J. Decomposition of styrene oxide over Au-HAP catalysts**

**Fig. S9**  (A) Conversion of styrene oxide (2) over 0.5Au-HAP catalysts; a) 0.5Au-HAP(IP); b) 0.5Au-HAP(Ad); c) 0.5Au_{25}-HAP. (B) Branching fractions of the products obtained at 12 h. The reaction was performed at 80 °C in methylcyclohexane (10 mL) containing TBHP (0.2 g), the catalyst (50 mg) and styrene oxide (45 mg).
K. Recyclability of 0.5Au$_{25}$-HAP

![Graph showing recyclability of 0.5Au$_{25}$-HAP over multiple reaction cycles.]

Fig. S10  Reuse test for 0.5Au$_{25}$-HAP.

L. Oxidation of styrene under O$_2$ over 0.5Au$_{25}$-HAP

<table>
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<tr>
<td><strong>Conversion (%)</strong></td>
<td>21.8</td>
<td>36.4</td>
<td>32.9</td>
<td>14.4</td>
<td>16.2</td>
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</table>

Table S3  Result of styrene oxidation under O$_2$ over 0.5Au$_{25}$-HAP

Reaction conditions: 0.5Au$_{25}$-HAP (100 mg); styrene (0.25 mmol); toluene (10 mL) was heated at 100±5 °C by microwave irradiation at 300 W; reaction time (2 h); O$_2$ (1 atm).