Supplementary Information

Controlling the selectivity of catalytic oxidation of styrene over nanocluster catalysts

Jinsong Chai, a Hanbao Chong, c Shuxin Wang, b Sha Yang, b Mingzai Wu, *a and Manzhou Zhu* b

a School of Physics and Materials Science, Anhui University, Hefei, Anhui, 230601 (P. R. China)
b Department of Chemistry and Centre for Atomic Engineering of Advanced Materials, Anhui University, Hefei, Anhui, 230601 (P. R. China)
c Modern experiment and Technology center, Anhui University, Hefei, Anhui, 230601 (P. R. China)

1. Synthesis of nanoclusters and nanoparticles.

i) Au25 (SR)18. HAuCl4•3H2O (0.1576 g, 0.4 mmol) was dissolved in 5 mL pure water, and TOAB (0.2558 g, 0.47 mmol) was dissolved in 10 mL toluene. The two solutions were combined in a 25 mL tri-neck round bottom flask. After stirring for 30 min, the organic phase was separated by removing the aqueous layer. The toluene solution of Au (III) was purged with N2 and cooled down to 0 °C in an ice bath over a period of 30 min under magnetic stirring. PhCH2CH2SH (0.17 mL) was added afterwards. The resulting mixture was stirred at a very low speed and then stirred for ~1 hr. After the solution turns clear (~1 hr), the stirring speed was changed to vigorous stirring, and immediately, an aqueous solution of NaBH4 (0.1550 g, 4 mmol, freshly made in 7 mL ice-cold nanopure water) was added all at once. The reaction was allowed to proceed overnight under N2 atmosphere. With the addition of methanol for precipitation of clusters, the product was centrifuged thrice at 7500 rpm to remove excess PhCH2CH2SH, TOAB, and other by-products. The Au25(SR)18 clusters were extracted from the dry samples using pure acetonitrile.

ii) AgxAu25-x (SR)18. An aqueous solution (30 mL) containing HAuCl4 and AgNO3 (the total metal concentration was set to 30 mM) was mixed with atoluene solution (30 mL) of tetraoctylammonium bromide, TOAB (1.1 mmol). The initial mole ratios of Au/Ag precursors were varied up to 1:0.66. After stirring for 30 min, the turbid organic phase was separated, and phenylethane thiol (10 mmol) was added and further stirred for 30 min at room temperature. This solution was cooled in an ice bath for 30 min. An aqueous solution of NaBH4 (0.1550 g, 4 mmol, freshly made in 7 mL ice-cold nanopure water) was added all at once. The reaction was allowed to proceed overnight under N2 atmosphere. With the addition of methanol for precipitation of clusters, the product was centrifuged thrice at 7500 rpm to remove excess PhCH2CH2SH, TOAB, and other by-products. The residual mixture was extracted with CH3CN.

iii) Ag44 (SR)19. 20 mg of AgNO3 were dissolved in the mixture solution of dichloromethane and methanol. The solution was cooled to 0 °C in an ice bath, after that, 10 ml 3,4 - difluorobenzethiol, and then 12 mg tetra-phenylphosphonium bromide were added. After 20-min stirring, 1 mL NaBH4 aqueous solution (45 mg ml-1) and 50 mL triethylamine were added quickly under vigorous stirring. The reaction was aging for 12 h at 0 °C. The aqueous phase was
then removed and the mixture in organic phase was washed several times with water.

iv) \( \text{Au}_{12}\text{Ag}_{32}(SR)_{30} \) chloro (diphenyl-2-pyridylphosphine) gold (I) (AuPPh$_2$PyCl, 10 mg) and 10 mg AgNO$_3$ were used instead of 20 mg AgNO$_3$ in the synthesis of Ag$_{44}$(SR)$_{30}$. All the other conditions were kept unchanged.

v) \text{Au} \text{ nanoparticle.} \ 10 \text{ ml oleylamine was added to a 25 ml flask, and then 400 } \mu\text{l HAuCl}_4 (0.2 g/ml) was added under stirring at 60°C. After 10 min, 200 mg borane-tert-butylamine was dissolve in 1 ml oleylamine and then the solution was added to the Au precursor solution. The above mixture was heated to 90°C and kept for 30 min. Finally, the mixture was cooled to room temperature and washed by methanol for three times, then dried for centrifugation.

vi) \text{Ag and AuAg alloy nanoparticles.} A similar method has been used to synthesize the Ag and AuAg alloy nanoparticle with different amounts of Au or Ag. (a) 34 mg AgNO$_3$ for Ag nanoparticle; (b) 200 \mu\text{l HAuCl}_4 (0.2 g/ml) and 17 mg AgNO$_3$ for AuAg alloy nanoparticle.

2. The optical absorption spectra of nanoclusters.

![Optical absorption spectra](image)

Figure S1. The optical absorption spectra of (a) \( \text{Au}_{25}(SR)_{18} \); (b) \( \text{Au}_x\text{Ag}_{25-x}(SR)_{18} \); (c) \( \text{Ag}_{44}(SR)_{30} \); (d) \( \text{Au}_{12}\text{Ag}_{32}(SR)_{30} \).

3. The catalytic selective oxidation of styrene on nanoparticles.

Table S1. The catalytic performance of Au nanoparticle, AuAg nanoparticle and Ag nanoparticle for the selective oxidation of styrene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalytic</th>
<th>Solvent</th>
<th>Conversion (%)$^*$</th>
<th>Epoxide</th>
<th>Benzaldehyde</th>
<th>Other products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au NPs</td>
<td>Toluene</td>
<td>67.2</td>
<td>25.7</td>
<td>68.0</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>Ag NPs</td>
<td>Toluene</td>
<td>38.3</td>
<td>19.1</td>
<td>76.9</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>AuAg NPs</td>
<td>Toluene</td>
<td>65.6</td>
<td>20.4</td>
<td>76.3</td>
<td>3</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>Au NPs</td>
<td>Toluene and H₂O</td>
<td>66.1</td>
<td>24.5</td>
<td>66.2</td>
<td>9.3</td>
</tr>
<tr>
<td>5</td>
<td>Ag NPs</td>
<td>Toluene and H₂O</td>
<td>38.8</td>
<td>19.9</td>
<td>75.1</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>AuAg NPs</td>
<td>Toluene and H₂O</td>
<td>66.1</td>
<td>21.9</td>
<td>72.8</td>
<td>5.3</td>
</tr>
</tbody>
</table>

*Reaction conditions: 5 mg catalyst, 57 μL (0.5 mmol) styrene, 144 μL (1.5 mmol) TBHP, 2 mL solvent, 10 mg K₂CO₃, 65°C, 24 hours. †Conversion = (converted styrene)/(initial amount of styrene) × 100. †Determined by gas chromatography with internal standard.

### 4. The gas-chromatograph measurement with internal standard

In this study, n-dodecane (≥99.9%, Aldrich) was used as internal standard to improve the quantitative analysis of styrene, epoxide and benzaldehyde. Standard solutions of each substance (styrene, epoxide and benzaldehyde) and n-dodecane (both in 1% v/v) were mixed as following combinations: 1:4, 1:2, 1:1, 1.5:1, 2:1, 2.5:1, 3:1, then subjected to GC vials (1:1 as example shown in Figure S2, Figure S4 and Figure S6). In order to calculate RRF value, peak area ratio of the standard substance to the internal standard was regressed on their concentration ratio. According to the Eq. (1), the slope of the regression equation was used as RRF value.

\[
\frac{A_1}{A_2} = \text{RRF}_{\text{standard substance/ internal standard}} \times \frac{n_1}{n_2}
\]

\[n = \frac{ρv}{M}\]

\[A_1 = \text{peak area of standard substance obtained from GC analysis; } A_2 = \text{peak area of internal standard obtained from GC analysis; } n_1 = \text{amount of substance for standard substance used in analysis; } n_2 = \text{amount of substance for internal standard used in analysis.}\]

The R² values of three regression equations for determination of RRF were found to be higher than 0.999 (as shown in Figure S3, Figure S5 and Figure S7).

![Figure S2. The GC of mixed liquid of standard substance (100 μL styrene) and internal standard (100 μL n-dodecane).](image-url)
Figure S3. Calibration curves for styrene using direct GC method coupling with internal standard

Figure S4. The GC of mixed liquid of standard substance (100 μL epoxide) and internal standard (100 μL n-dodecane).
Figure S5. Calibration curves for epoxide using direct GC method coupling with internal standard.

Figure S6. The GC of mixed liquid of standard substance (100 μL benzaldehyde) and internal standard (100 μL n-dodecane).
Figure S7. Calibration curves for benzaldehyde using direct GC method coupling with internal standard

The conversion and selectivity was determined by direct injection GC method coupling with internal standard. Practically, 2 mL sample was mixed with 20 μL internal standard. The GC test of Au$_{25-x}$Ag$_x$/CNT catalyzed selective oxidation of styrene reaction liquid with internal standard was shown in Figure S8 and Figure S9. The contents of styrene, epoxide and benzaldehyde were calculated according to following equations.

Styrene (n/mL) = (A$_{Styrene}$/A$_{n$-dodecane}$) * (n$_{n$-dodecane}$/RRF$_{Styrene/n$-dodecane}$) * 1/V

Epoxide (n/mL) = (A$_{Epoxide}$/A$_{n$-dodecane}$) * (n$_{n$-dodecane}$/RRF$_{Epoxide/n$-dodecane}$) * 1/V

Benzaldehyde (n/mL) = (A$_{Benzaldehyde}$/A$_{n$-dodecane}$) * (n$_{n$-dodecane}$/RRF$_{Benzaldehyde/n$-dodecane}$) * 1/V

Figure S8. The GC of reaction liquid for Au$_{25-x}$Ag$_x$/CNT catalyzed selective oxidation of styrene
in the toluene solution.

Figure S9. The GC of reaction liquid for Au\textsubscript{25-x}Ag\textsubscript{x}/CNT catalyzed selective oxidation of styrene in the mixed solution containing H\textsubscript{2}O and toluene.

5. The gas-chromatograph-mass-spectrometry measurement.

We performed the selective oxidation of styrene using Au\textsubscript{25}/CNT as catalyst and a mixed solution containing \textsuperscript{18}OH\textsubscript{2} and toluene as solvent. After centrifugation, the reaction liquid was analyzed by gas chromatograph/mass spectrometry (GC-MS). As shown in Figure S5, the reaction liquid contains styrene (4.87 min), benzaldehyde (6.21 min), epoxide (7.92 min) and other by-products. The isotope patterns for benzaldehyde is shown in Figure S6 and epoxide in Figure S7.

Figure S10. The GC of reaction liquid for selective oxidation of styrene.
Figure S11. Mass spectrum of benzaldehyde (6.21).

Figure S12. Mass spectrum of epoxide (7.92).

Figure S13. Typical TEM Images of (a) Au nanoparticle; (b) AuAg nanoparticle; (c) Ag nanoparticle.