Synthesis of Sinter-Resistant Au@Silica Catalysts Derived from Au$_{25}$ Clusters

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**Scheme S1**: General scheme for the synthesis of Au$_{25}$(11-MUA)$_{18}$/SiO$_2$ clusters

**Figure S1**: TEM images of as-synthesized Au$_{25}$(11-MUA)$_{18}$ clusters.
Figure S2: Histogram of Au$_{25}$/SiO$_2$ catalysts calcined at 250°C and 650°C
Figure S3: (a) N$_2$ Adsorption/Desorption isotherms and (b) BJH Pore Size Distributions of Au$_{25}$@SiO$_2$ catalysts as-synthesized (blue) and after calcination at 250°C (red).
Figure S4: Au L₃ edge EXAFS fitting data in k space of Au@SiO₂ calcined at a) 250°C, b) 350°C c) 450°C d) 550°C and e) 650°C.
Figure S5: Au L₃ edge EXAFS fitting data in R space of Au@SiO₂ calcined at a) 250°C, b) 350°C c) 450°C d) 550°C and e) 650°C.
Figure S6: Catalytic activity for 4-nitrophenol reduction reaction over Au@SiO$_2$ calcined at a) 250°C, b) 350°C c) 450°C d) 550°C and e) 650°C
Figure S7: Plot of $\ln[C_t]/[C_0]$ as a function of reaction time in min for 4-nitrophenol reduction reaction over Au@SiO$_2$ catalysts calcined at different temperatures.
Figure S8: Conversion of 4-nitrophenol to 4-aminophenol over Au$_{25}$/SiO$_2$ catalysts calcined at 250°C and 650°C

Rate constant calculation: - 4-nitrophenol reduction follows pseudo-first-order kinetics

\[
Ln\left(\frac{[C_t]}{[C_0]}\right) = -kt
\]

$C_t$ – Concentration of 4-nitrophenolate at time $t$

$C_0$ – Initial concentration of 4-nitrophenolate

k- First order rate constant

t- Time in minutes
Table S1: X-ray crystallographic information of [N(C₈H₁₇)₄][Au₂₅(SCH₂CH₃Ph)₁₈]¹

<table>
<thead>
<tr>
<th>Type</th>
<th>Coordination Number</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-S</td>
<td></td>
<td>2.32 ± 0.01</td>
</tr>
<tr>
<td>Au-Au (core)</td>
<td>1.44</td>
<td>2.79 ± 0.01</td>
</tr>
<tr>
<td>Au-Au(surf)</td>
<td>1.92</td>
<td>2.93 ± 0.06</td>
</tr>
<tr>
<td>Au-Au(staple)</td>
<td>2.88</td>
<td>3.16 ± 0.08</td>
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</table>
### Table S2: Recyclability for styrene epoxidation reaction over Au$_{25}$@SiO$_2$/250°C catalyst

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>Selectivity</th>
<th>TON</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>SO (%)</td>
<td>BA (%)</td>
</tr>
<tr>
<td>First</td>
<td>70.0</td>
<td>92.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Second</td>
<td>62.1</td>
<td>94.2</td>
<td>5.8</td>
</tr>
<tr>
<td>Third</td>
<td>65.2</td>
<td>95.4</td>
<td>4.6</td>
</tr>
<tr>
<td>Fourth</td>
<td>67.5</td>
<td>95.6</td>
<td>4.4</td>
</tr>
<tr>
<td>Fifth</td>
<td>67.1</td>
<td>90.2</td>
<td>9.8</td>
</tr>
</tbody>
</table>

TON: (Conversion* moles of styrene)/(moles of Au)
Calculation of number of surface atoms

1) Average particle size of Au@SiO₂ calcined at 250°C is 2.2nm

Volume of a sphere

\[ V = \left(\frac{4}{3}\right)\pi r^3 \]

Au is F.C.C with lattice constant 0.4080nm

Volume of unit cell \( V = a^3 \)

\[ V = (0.4080nm)^3 = 0.0679nm^3 \]

Each unit cell contains 4 Au atoms

Total Au atoms in a particle = \( \left(\frac{5.5nm^3}{0.0679nm^3}\right) * 4 = 324 \text{ atoms} \)

Surface area of sphere \( A = 4\pi r^2 \)

\[ A = 4\pi(1.1nm)^2 = 15.2nm^2 \]

Surface area of a unit cell \( A = a^2 \)

\[ A = (0.4080nm)^2 = 0.1664nm^2 \]

Each unit cell on surface contains 2 Au atoms

Total Au surface atoms in a particle = \( \left(\frac{15.2nm^2}{0.1664nm^2}\right) * 2 = 182 \text{ atoms} \)

Total no of Au atoms in 20mg catalyst = no of moles of Au \( * 6.02*10^{23} \text{ atoms} \)

\[ = 2.0 * 10^{-6} * 6.02 * 10^{23} \text{ atoms} = 12 * 10^{17} \text{ atoms} \]

Total no of particles in 20mg catalyst

\[ \frac{12 * 10^{17} \text{ atoms}}{328\text{atoms}} = 3.7 * 10^{15} \]

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle

\[ 3.7 * 10^{15} * 182 \text{ atoms} = 6.7 * 10^{17} \text{ surface atoms} \]

No of moles of surface atoms

\[ \frac{6.7 * 10^{17}}{6.02 * 10^{23}} = 11 * 10^{-7} \text{ moles} \]
2) Average particle size of Au@SiO$_2$ calcined at 650°C is 3.2nm

Volume of a sphere

\[ V = \left(\frac{4}{3}\right)\pi r^3 \]

\[ V = \left(\frac{4}{3}\right) \pi \times (1.6nm)^3 = 17.14nm^3 \]

Total Au atoms in a particle = \( \frac{17.14nm^3}{0.0679nm^3} \times 4 = 1009 \text{ atoms} \)

Surface area of sphere \( A = 4\pi r^2 \)

\[ A = 4\pi (1.6nm)^2 = 32.15nm^2 \]

Total Au surface atoms in a particle = \( \frac{32.15nm^2}{0.1664nm^2} \times 2 = 386 \text{ atoms} \)

Total no of particles in 20mg catalyst = \( \frac{12 \times 10^{17} \text{ atoms}}{1009 \text{ atoms}} = 1.2 \times 10^{15} \)

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle

\[ 1.2 \times 10^{15} \times 386 \text{ atoms} = 4.6 \times 10^{17} \text{ surface atoms} \]

No of moles of surface atoms

\[ = \frac{4.6 \times 10^{17}}{6.02 \times 10^{23}} = 7.6 \times 10^{-7} \text{ moles} \]

3) Average particle size of Au/SiO$_2$ calcined at 250°C is 3.2nm

Volume of a sphere

\[ V = \left(\frac{4}{3}\right)\pi r^3 \]

\[ V = \left(\frac{4}{3}\right) \pi \times (1.6nm)^3 = 17.14nm^3 \]

Total Au atoms in a particle = \( \frac{17.14nm^3}{0.0679nm^3} \times 4 = 1009 \text{ atoms} \)

Surface area of sphere \( A = 4\pi r^2 \)

\[ A = 4\pi (1.6nm)^2 = 32.15nm^2 \]

Total Au surface atoms in a particle = \( \frac{32.15nm^2}{0.1664nm^2} \times 2 = 386 \text{ atoms} \)
Total no of particles in 20mg catalyst
\[= \frac{12 \times 10^{17} \text{ atoms}}{1009 \text{ atoms}} = 1.2 \times 10^{15} \]

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle
\[= 1.2 \times 10^{15} \times 386 \text{ atoms} = 4.6 \times 10^{17} \text{ surface atoms} \]

No of moles of surface atoms
\[= \frac{4.6 \times 10^{17}}{6.02 \times 10^{23}} = 7.6 \times 10^{-7} \text{ moles} \]

4) Average particle size of Au/SiO₂ calcined at 650°C is 15.5nm

Volume of a sphere
\[V = \left(\frac{4}{3}\right)\pi r^3 \]

\[V = \left(\frac{4}{3}\right) \pi (7.7nm)^3 = 1911nm^3 \]

Total Au atoms in a particle
\[= \left(\frac{1911nm^3}{0.0679nm^3}\right) \times 4 = 112577 \text{ atoms} \]

Surface area of sphere \[A = 4\pi r^2 \]
\[A = 4\pi (7.7nm)^2 = 744.68nm^2 \]

Total Au surface atoms in a particle
\[= \frac{744.68nm^2}{0.1664nm^2} \times 2 = 8950 \text{ atoms} \]

Total no of particles in 20mg catalyst
\[= \frac{12 \times 10^{17} \text{ atoms}}{28149 \text{ atoms}} = 1.1 \times 10^{13} \]

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle
\[= 1.1 \times 10^{13} \times 8950 \text{ atoms} = 0.98 \times 10^{17} \text{ surface atoms} \]

No of moles of surface atoms
\[= \frac{0.98 \times 10^{17}}{6.02 \times 10^{23}} = 1.6 \times 10^{-7} \text{ moles} \]

References