Modern Alchemy: Catalysis by Gold Nano-particles: Part 1

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1. Overview on Gold
2. CO Oxidation at Low Temperatures
3. Catalyst Preparation
When man discovered **Gold**?

5 – 7 thousands years ago

A symbol of Eternity (Eternal Youth, Beauty, and Power).

The metal in the **Sun**, The **Sun** in the soil.

The body of God is composed of **gold**.
Gold Masks (Mycenae ruins in Greece)
Gold in Arts & Culture

- **Thread**: *kimono*
  
  $1 \text{ g} \rightarrow 3,000 \text{ m}$

- **Paste, Paint**: lacquered ware, chinaware

- **Foil**: $1 \text{ g} \rightarrow 0.5 \text{ m}^2$ wide, $0.1 \mu \text{ m}$ thick

- **Colloids**: 10-50 nm, Venetian red
  
  Purple gold for pottery
Golden Pavilion (Kyoto)

1397: by Shogun Yoshimitsu ASHIKAGA

1955: Reconstructed

1987: Renewed
Gold Colloids in crystal glass

Au diameter
20 nm

Surface plasmon absorption
530 nm
How much amount of **Gold** do we have on the earth?
150,000 ton = $15 \times 10^{10}$ g

77 years vs 30 years

- Olympic Pools 3

- Per person: 26 g = a simple neck less
Gold in Science & Technology

Alchemy → Chemistry
(high value) (functional materials)

Electronics: switching devices,
micro-electronic circuits

Nano-technology:
Self assembly of organic molecules on Au

Size effects: Nano-particles → Catalysts
Clusters → ?
What is a Catalyst?

- A catalyst is defined as a substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process.

\[ A + B \rightarrow C \rightarrow F \quad k_1 \gg k_2, k_3 \quad \text{selective to C} \]

\[ \quad \rightarrow D \rightarrow F \quad k_3 \gg k_1, k_4 \quad \text{selective to D} \]
Market Sales of Catalysts: $8.9 \times 10^9$

2003

- Environmental: 23%
- Refinery: 26%
- Polymer: 26%
- Chemical: 25%

* only manufacturing fees

# Catalytic Metals: 3d →4d→ 5d

<table>
<thead>
<tr>
<th>Group</th>
<th>VIII</th>
<th>IB</th>
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</thead>
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<tr>
<td>Valence Orbital</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>3d</td>
<td>Fe NH₃</td>
<td>Co Gasoline</td>
</tr>
<tr>
<td>4d</td>
<td>Ru</td>
<td>Rh Fine Chemials</td>
</tr>
<tr>
<td>5d</td>
<td>Os Toxic</td>
<td>Ir</td>
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- **Base**
- **Noble**
- **Exclld.**
- **Minor**
- **Major**
- **Frontier**
Most Reactions are **Structure Sensitive** over Au Catalysts.

**< Conventional >**

![Conventional Catalyst](image)

**Poorly Active**

**< Novel >**

![Novel Catalyst](image)

**Highly Active**
Au/TiO$_2$ Prepared by Impregnation

Au : 3wt%
TiO$_2$ : JRC-TIO4

Calcined at 573K
Au/Fe$_2$O$_3$ Prepared by Coprecipitation

Au/Fe=1/19
Calcined at 673K
Au/Fe$_2$O$_3$ Prepared by Coprecipitation

Au/Fe = 1/19
Calcined at 673K
Oxidation of CO and of H\textsubscript{2}

Number of Papers on Au Catalysts

Number of Papers

Year


Low-Temperature Oxidation of CO

\[ \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{O} = \text{C} = \text{O} \]

- Indoor air quality control
- H\(_2\) purification for fuel cells

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>R. T. Activity</th>
<th>Moisture</th>
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<tr>
<td>Gold</td>
<td>High</td>
<td>Activated</td>
</tr>
<tr>
<td>Other Noble Metals</td>
<td>Low</td>
<td>Activated</td>
</tr>
<tr>
<td>Base Metal Oxides</td>
<td>Medium</td>
<td>Deactivated</td>
</tr>
</tbody>
</table>
Active Sites in Au Catalysts

1) Cations: Fe$_2$O$_3$, La$_2$O$_3$, CeO$_2$

2) Clusters: MgO, Mg(OH)$_2$, TiO$_2$

3) Junction Periphery: Al$_2$O$_3$, SiO$_2$, Fe$_2$O$_3$, ……
Au Cations (Au$^+$ or Au$^{3+}$): CO$+\text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

Spectators: Is Au strongly contacted?


NaCN leaching

Actors: stable under reaction?

TEM image of Au particles supported on CeO$_2$

HRTEM image of a Au particle on CeO$_2$ during observation.

HRTEM images of Au particles during observation

 Beam Off  On  Off  On

 a  b  c  d  e

 Au Atomic layer

CO oxidation at room temp. over model Au/TiO$_2$ catalyst

Two atomic layers are key to the high catalytic activity.

At the perimeter, CO adsorbed on Au surfaces reacts with oxygen activated on the support surfaces.

Water enhances the dissociation of O₂ and carbonate intermediates.
A Model at the Perimeter Interfaces

Bond and Thompson, Gold Bull., 33 (2000) 41
Three Major Factors Controlling the Activity and Selectivity

- Strong Contact with the Supports
- Type of the Supports
- Size of Au Particles
Effect of Contact Structure on CO Oxidation


The graph shows the Turnover Frequency (TOF) for CO oxidation on Gold and Platinum catalysts supported on TiO₂. The TOF values are given in units of (s⁻¹). The graph indicates that Gold supported on TiO₂ has a significantly higher TOF compared to Platinum supported on TiO₂.
Enhancing Effect of Moisture on CO Oxidation

M. Date et al,
Angew. Chem. Int. Ed.
TOF of CO Oxidation vs Particle Diameter

CO Oxidation

- Au/TiO₂ (273 K)
- Pt/SiO₂ (437 K)

FT-IR for CO over Au/TiO$_2$

How to deposit Au as nanoparticles & clusters on a variety of substrates?

Metal oxides

Activated carbons

Organic polymers
Deposition of Au NPs on Metal Oxides

Well-Mixed Precursors

Co-sputtering
Coprecipitation
Amorphous Alloys

Surface Interaction with the Support

Gas-Phase Grafting
Liquid-Phase Grafting
Deposition-Precipitation

Calcination
Co-precipitation

**Au-Fe Hydroxides**

- Washing
- Drying
- Calcination at 400°C

**Au-Fe Oxides**

Chemical reaction:

```
HAuCl₄ + Fe(NO₃)₃
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pH=8.9

`Na₂CO₃`
Deposition-Precipitation Method

HAuCl₄ aq. pH = 2–3

NaOH aq.

HAuCl₄ aq. pH = 6–10

Au(OH)₄⁻

(Conc., Temp., pH)

Support

Au(OH)₃ / Support

Washing

Drying

Calcination at 573–673K

Au / Support
Au/TiO$_2$ Prepared by Deposition Precipitation

Au : 3.3wt%
TiO$_2$ : JRC-TIO4

pH=7, 343 K
Calcined at 673K

Structure of Au/TiO$_2$ Interface

Epitaxial Contact
Gas Phase Grafting of Organo Au Complex
Adsorbed State of Organic Au Complex

dimethyl Au(III) acetyl-acetonate
Au/MCM-41 : Gas Phase Grafting

Adsorption at room temp.

Calcination at 573K

M. Okumura et al.
Summary

- **Perimeter interfaces** are key to the genesis of unique catalytic performance of Au for gas phase reactions. Therefore, preparation methods are of crucial importance.

- Three factors define the catalytic performance of Au: *Strong contact* with the support, *Selection of the support* material, and *Size* of Au particles.

- At the periphery of Au particles, CO adsorbed on the Au surfaces reacts with oxygen molecule or OH groups to form CO$_2$ in the gas phase.