Kinetics of gas adsorption on gold nanoparticles in catalysts, real-time monitored by plasmon resonance investigation

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Overview

1. Introduction
   - Surface vs. bulk in nanoparticles
   - Localized surface plasmon resonance in a metal NP
   - Au NP - based catalysts for CO oxidation

2. Size and shape of active Au NPs: aberration-corrected TEM

3. Oxygen / Au NPs interaction
   - Charge transfer ?
   - Two-step kinetics
   - Active vs. non active catalysts
### Metallic nanocristals

**Au NPs**

<table>
<thead>
<tr>
<th>Diameter</th>
<th>total N</th>
<th>surface N</th>
<th>Surface/total Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 nm</td>
<td>6700</td>
<td>1500</td>
<td>22 %</td>
</tr>
<tr>
<td>4 nm</td>
<td>1990</td>
<td>670</td>
<td>34 %</td>
</tr>
<tr>
<td>2 nm</td>
<td>250</td>
<td>170</td>
<td>67 %</td>
</tr>
</tbody>
</table>

Number of 4 nm diameter NPs in 1 g of Au: $10^{18}$

Specific surface $\sim 100 \text{ m}^2$
Metallic nanocristals

A.S. Barnard,
Metallic nanocrystals

- Cuboctahedra
- Octahedra
- Truncated octahedra
- Truncated cube
- Icosahedra


L. Delannoy, R. Chantry, Z. Li, Y. Borensztein, C. Louis, *to be published*

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Color effects in gold particles: plasmon resonance

Lycurgus cup (4th century, Rome), British Museum


Lightened from outside Lightened from inside

Teapot in ruby glass, Kunckel, v. 1680


Lightened from outside

Im(\(\alpha\))

Absorption

Absorption around 540 nm: green

\(\rightarrow\) red colour
Plasmon resonance in a metal sphere

Plasmon resonance for: \( \varepsilon(\omega) + 2 \varepsilon_m \approx 0 \)

Effect of the embedding medium

Effect of the shape of the particle (ellipsoid)

Effect of the substrate

Effect of adsorbed species

Polarizability: \( \alpha = 4\pi R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2 \varepsilon_m} \)

\( \mathbf{p} = \varepsilon_0 \alpha \mathbf{E} \)

induced dipole

\( \varepsilon(\omega) \)

dielectric function of the metal

dielectric function of the embedding medium

\( \varepsilon_m \)

Plasmon = collective oscillation of the surface conduction electrons induced by an oscillating applied electric field
Plasmon resonance of gold spheres on an oxide powder

B. Van Duppen, L. Delannoy, YB, unpublished

PVA colloid Au NPs on Al₂O₃

PVA colloid Au NPs on TiO₂

Absorption of the powder alone

B. Van Duppen, L. Delannoy, YB, unpublished
Plasmon resonance of gold spheres on an oxide powder

Plasmon resonance:

\[ \varepsilon_{Au}(\omega) + 2 \varepsilon_m = 0 \]

\[ \varepsilon_m \approx \frac{1}{2} \left( 1 + \varepsilon_{subs} \right) \]

Crude approximation to get an idea

- \( \varepsilon_{Al_2O_3} \approx 2.4 \)
- \( \varepsilon_{TiO_2} \approx 7 \)

Absorption of the powder alone

B. Van Duppen, L. Delannoy, YB, unpublished
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   • Two-step kinetics
   • Active vs. non active catalysts
Gold was considered inactive till the 80's. In 1987 Haruta* showed that Au NPs are active for the CO oxidation:

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2
\]


**Keypoints:**
- size < 5 nm
- active at room temperature
- supported on reducible oxide: \( TiO_2 > CeO_2 > Al_2O_3 \)

1. Fundamental interest: what is the mechanism?

2. Applications

- CO oxidation in catalytic exhausts
  
  80% of vehicle pollution comes from the engine cold-start

- Purification of hydrogen for fuel cells

Methanol reforming:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO}_2 + \varepsilon(\text{CO})
\]

Problem of poisoning of the Pt anode by CO

![Diagram of engine with Pt-Rh catalyst, washcoat of alumina-ceria, and cordierite (MgO, Al_2O_3, SiO_2).]
Gold-nanoparticle-based catalyst for CO oxidation

Some issues:

1. What is the size of the more active particles?
   - Is there a minimal size?
   - What shape? 3D ou 2D?
     - Electronic microscopy and reactivity

2. Does oxygen adsorb on Au NPs? Is there any charge transfer?
   - Optical studies (plasmon resonance)

3. What are the active sites (adsorption / dissociation of O₂)?
   - Optical studies and reactivity
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Gold-nanoparticle-based catalyst for oxidation reactions

- Gold was considered inactive till the 80’s.
- In 1987 Haruta* showed that Au NPs are active for the CO oxidation

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


- Keypoints:
  - size < 5 nm
  - active at room temperature
  - supported on reducible oxide:
  \[ \text{TiO}_2 > \text{CeO}_2 > \text{Al}_2\text{O}_3 \]
  - maximum activity around 2-3 nm (?)

Difficulties:

- The actual samples display size and shape distributions
- The very small nanoparticles (< 1 nm) are not easily visualisable
- Some minority NPs can provide the activity of a catalyst

Aberration-corrected High-angle annular darkfield (HAADF) scanning transmission electron microscopy (STEM)
Size and shape of the active Au nanoparticles

Aberration-corrected scanning transmission electron microscopy


"High catalytic activity for carbon monoxide oxidation is correlated with the presence of bilayer clusters that are ~ 0.5 nanometer in diameter and contain only ~ 10 gold atoms."


"These studies have shown that a bilayer Au structure is a critical feature for catalytically active Au nanoparticles, along with low coordinated Au sites, support-to-particle charge transfer effects, and quantum size effects."

...in agreement with previous results on model catalysts
High catalytic activity for carbon monoxide oxidation is correlated with the presence of bilayer clusters that are ~0.5 nanometer in diameter and contain only ~10 gold atoms.

For the current catalyst, gold nanoclusters have diameters larger than 1 nm and bilayer structures and/or diameters of about 0.5 nm are not mandatory to achieve the high activity.

Figure 2. Aberration-corrected HAADF-STEM images and size distribution of the gold particles of Au/FeO$_2$ catalyst prepared by the colloidal deposition method.
Size and shape of the active Au nanoparticles

**Au / TiO₂**: Deposition Precipitation with Urea

HAuCl₄ + TiO₂ (or Al₂O₃) + urea (CO(NH₂)₂)

**Thermal treatment in hydrogen** (300 °C) → very small Au° particles (1-5 nm)
**Thermal treatment in air** (500 °C) → small Au° particles (2-6 nm)

Size and shape of the active Au nanoparticles

Au / TiO2 reduced 300°C

- Extremely active
- Majority: 2-4 nm

Au / TiO2 calcined 500°C

- Very active
- Majority: 2-5 nm

Size and shape of the active Au nanoparticles

Aberration-corrected High-angle annular dark field (HAADF) STEM

Au / TiO2 calcined 500°C

Size and shape of the active Au nanoparticles

**Aberration-corrected High-angle annular dark field (HAADF) STEM**

Main conclusions about the active Au NPs for the oxidation of CO

1. The active Au particles on TiO$_2$ are 3D (truncated octahedron)
2. Their size is 1.5 - 3 nm
3. Bigger particles are not or very few active
4. Active Au/TiO$_2$ catalysts don't have clusters < 1 nm, nor bilayer clusters
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Near Ambient Pressure XPS (Berkeley)

« Adsorbed $O_2$ and $O_2^-$ may play a key role in supplying reactive oxygen »

0.2 Torr $O_2$

UHV

"Model" catalyst
Evaporated
Au NPs / TiO$_2$(110)

« Au NPs supported on TiO$_2$ do not donate or accept additional charge when the sample is exposed to $O_2$ »
Near Ambient Pressure XPS (Berkeley)

« Adsorbed \( \text{O}_2 \) and \( \text{O}_2^- \) may play a key role in supplying reactive oxygen »

1. Model catalyst: Au NPs evaporated on TiO\(_2\)(110)
2. Low pressure of \( \text{O}_2 \) (0.2 Torr)

« Au NPs supported on TiO\(_2\) do not donate or accept additional charge when the sample is exposed to \( \text{O}_2 \) »
"Real" catalysts: chemical Au NPs dispersed on oxide powder

Poorly Active → Au colloids (PVA) / Al₂O₃

→ round "big" Au° particles (4 - 6 nm)

Very Active → Au / TiO₂: Deposition-Precipitation with Urea

HAuCl₄ + TiO₂ (or Al₂O₃) + urea (CO(NH₂)₂)

H₂O/80°C

water washings → drying RT/vacuum

complex with Au³⁺

Thermal treatment

small and flatter particles (1 - 5 nm)
Oxygen adsorption on Au NPs? Charge transfer?

- Operando investigation on Au colloids on Al\textsubscript{2}O\textsubscript{3}: switch from H\textsubscript{2} to O\textsubscript{2}
  - Better controlled Au NPs: 4 - 6 nm spherical colloids
  - Al\textsubscript{2}O\textsubscript{3} not reducible (i.e. no effect expected with O\textsubscript{2})

- If oxygen adsorbs on Au NPs, we expect a modification of the plasmon resonance

![Diagram of Au colloids and PVA colloid on Al\textsubscript{2}O\textsubscript{3}]

- Decrease of the electron density
- Red shift of the plasmon resonance
Oxygen adsorption on Au NPs? Charge transfer?

Monitoring the optical response changes with gases

Devoted cell for in-situ study

Comparison between
- a reducing gas (H₂)
- and an oxidant one (O₂)

Differential Diffuse Reflectance

\[
\text{DDR: } \frac{\Delta R}{R} = \frac{R_{O_2} - R_{H_2}}{R_{H_2}}
\]
Oxygen adsorption on Au NPs? Charge transfer?

Monitoring the optical response changes with gases

**Devoted cell for in-situ study**

Comparison between
- a reducing gas ($\text{H}_2$)
- and an oxidant one ($\text{O}_2$)

**Differential Diffuse Reflectance**

$$\text{DDR: } \Delta R = \frac{R_{\text{O}_2} - R_{\text{H}_2}}{R}$$

under $\text{H}_2$  under $\text{O}_2$
Oxygen adsorption on Au NPs? Charge transfer?

Inactive catalyst: Au colloids / Al₂O₃

Differential Diffuse Reflectance (DDR)

$$\Delta R = \frac{R_{O_2} - R_{H_2}}{R_{H_2}}$$

Surface plasmon absorption of Au / Al₂O₃

The DDR spectrum appears as a derivative of the plasmon resonance (mainly due to a red shift)

Oxygen adsorption on Au NPs? Charge transfer?

Reversibility

H₂ $\rightarrow$ O₂

increasing amount of O₂

increasing amount of H₂

kinetics

O₂ $\rightarrow$ H₂

Au colloid
Oxygen adsorption on Au NPs? Charge transfer?

Charge transfer from Au to oxygen

\[ \varepsilon(\omega) = 1 - \frac{\Omega_p^2}{\omega(\omega + i\tau^{-1})} + \varepsilon^{ib}(\omega) \]

\[ \hbar \Omega_p = \sqrt{\frac{N e^2}{\varepsilon_o m}} \approx 9 \text{ eV} \]

\[ \hbar \Omega_p^{mod} = \left( \frac{(N - \Delta N) e^2}{\varepsilon_o m} \right)^{1/2} = \hbar \Omega_p \left( 1 - \frac{\Delta N}{N} \right)^{1/2} \]

Borensztein, Delannoy, Barrera, Louis,
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Oxygen adsorption on Au NPs? Charge transfer?

Effect of temperature

H₂ → O₂

\[ \Delta R = \frac{R_{O_2} - R_{H_2}}{R_{H_2}} \]

- a larger amount of oxygen is adsorbed on Au at larger temperature
- the adsorption is faster
- two-step process

T = 22 °C

T = 90 °C

Kinetics:
Kinetic effects: 2-step process

T = 90 °C

Au colloidal

O₂ introduction

H₂ introduction
Kinetic effects: 2-step process

$T = 90 \, ^\circ C$

$tentative picture of the O_2 adsorption$

$O_2$ introduction

$H_2$ introduction

$H_2$ purging

very reactive sites
( perimeter, edge or corner sites )
"We propose that under operational conditions, Au particles will have such atomic oxygen at the metal/oxide interface perimeter forming a nano-scale Au-oxide.

It is oxygen from this part of the system that is responsible for the CO oxidation reaction."
Kinetic effects: 2-step process

O\textsubscript{2} introduction

T = 90 °C

H\textsubscript{2} introduction

\textit{tentative picture of the O\textsubscript{2} adsorption}

H\textsubscript{2} purging

very reactive sites (perimeter, edge or corner sites)
Kinetic effects: 2-step process

O₂ introduction

T = 90 °C

H₂ introduction

Tentative picture of the O₂ adsorption

Tentative picture of the O₂ desorption

Au colloid

O₂ introduction

H₂ introduction

O₂ purging

H₂ introduction

Kinetic effects: 2-step process
Conclusions

We combined electron microscopy, reactivity measurements, plasmon resonance studies, for investigating Au-based catalysts

1. In "usual" catalysts, the active Au particles are 3D, 1-3 nm large

2. Oxygen adsorbs on Au NPs and induces a charge transfer, visible by a reversible shift of the surface plasmon resonance

3. A long-wavelength resonance is present for the highly catalytic Au / TiO$_2$:
   • Extremely sensitive to oxygen
   • Is it related to specific sites (perimeter?) on which O$_2$ would adsorb easily, and for a nanoscale oxide ?

   \textit{Is this the key-point for the reactivity ?}

Perspectives

1. Better understand the origin of the long wavelength resonance
2. Role of the support (TiO$_2$, Al$_2$O$_3$...) 
3. Environnmental XPS
4. Vibrational methods : IR , SFG, SERS
5. Local studies of Au NPs under reactive gas by use of Environmental STM