^{197}Au Mössbauer Spectroscopy in the study of gold catalysts

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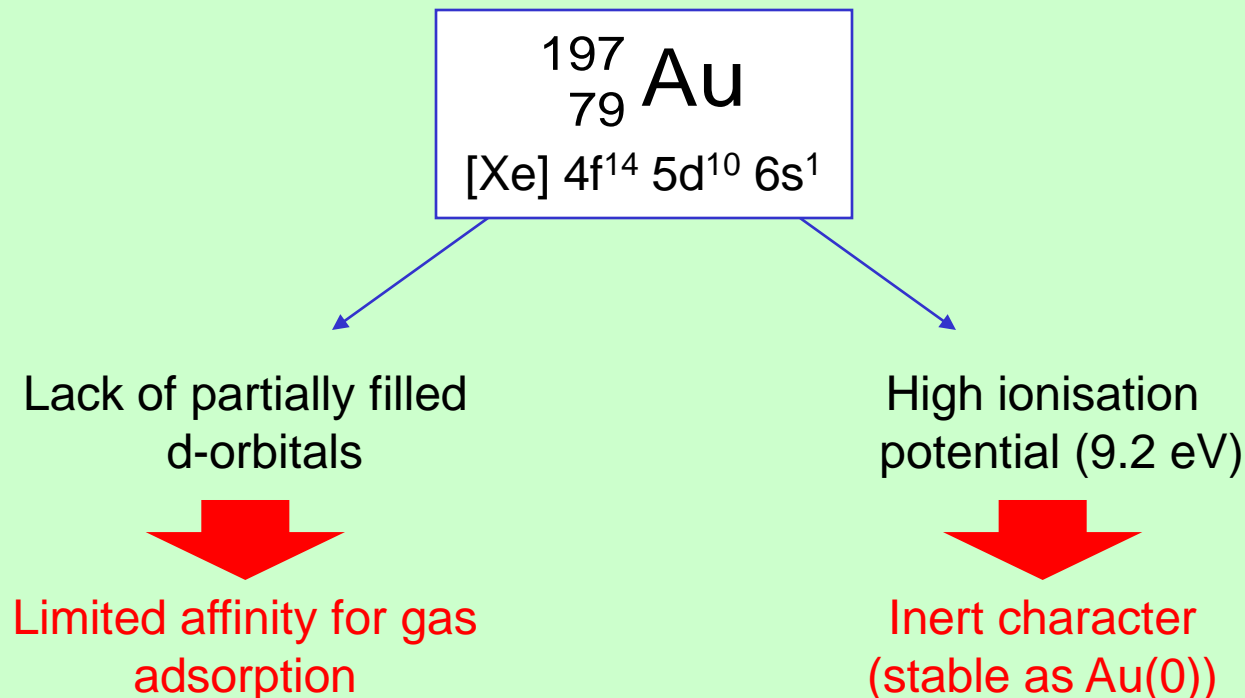UMR 7609 - CNRS
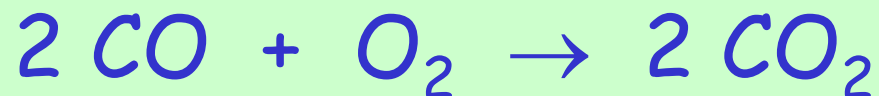Université Pierre et Marie Curie – Paris 6
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Bulk gold is catalytically inactive!

$$^{197}_{79}\text{Au}$$

[Xe] $4f^{14}$ $5d^{10}$ $6s^1$

Lack of partially filled d-orbitals

Limited affinity for gas adsorption

High ionisation potential (9.2 eV)

Inert character (stable as Au(0))

When gold is dispersed on supports with a high surface area, its catalytic properties change substantially

Catalysis by Gold

- Supported gold nanoparticles are highly active in the oxidation of CO at low temperatures [Haruta et al., Chem. Lett. (1987)].
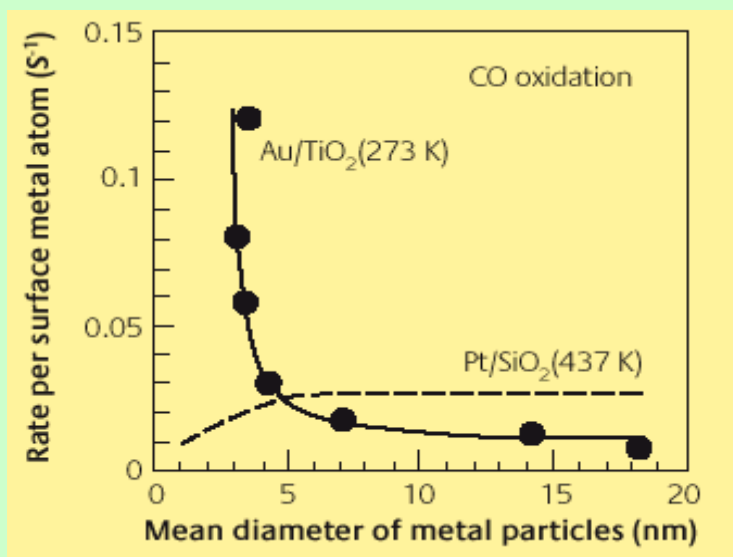
$$2\,CO\ +\ O_2\ \rightarrow\ 2\,CO_2$$
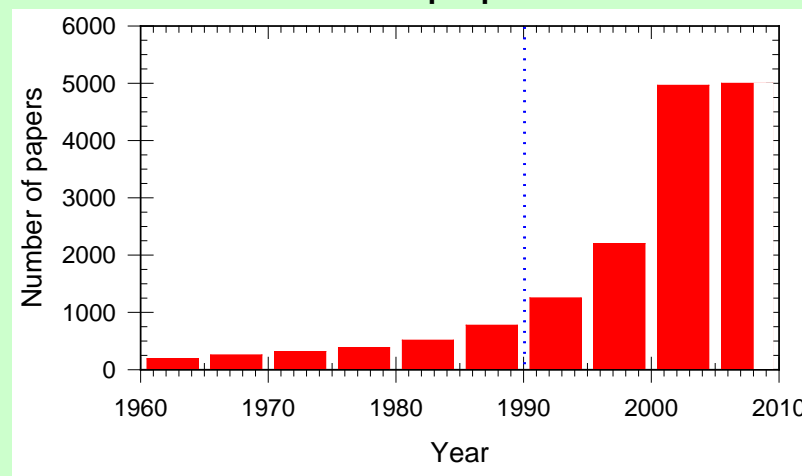

[from Haruta et al., Gold Bull. (2004)].

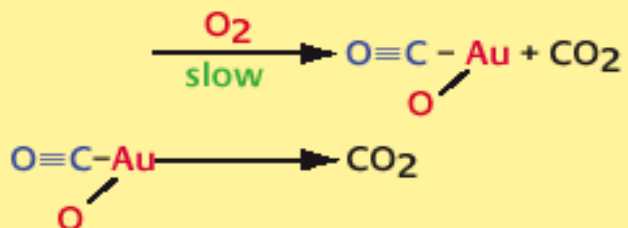Source: Chemical Abstract, 10/2008
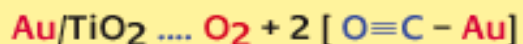
"gold" + "catalysis"

~16300 papers

About 1400 papers on CO oxidation!

The "Bond & Thompson" model

$$CO + Au \rightleftarrows O\equiv C\text{-}Au$$

$$O_2 + Au/TiO_2 \longrightarrow Au/TiO_2 \ .... \ O_2$$

$$Au/TiO_2 \ .... \ O_2 + 2\ [\ O\equiv C - Au\ ]$$

$$\xrightarrow[\text{slow}]{O_2} O\equiv C - Au + CO_2$$

$$O\equiv C\text{-}Au \longrightarrow CO_2$$
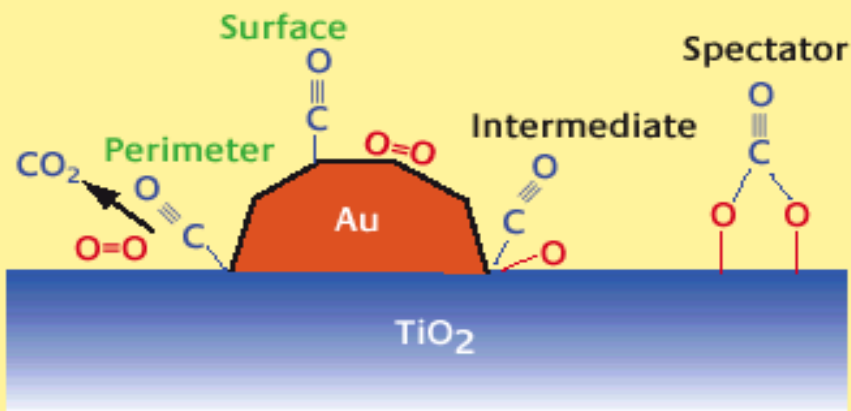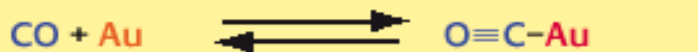
The active site for catalysis is the interface between particle and support.

The interface is formed by gold atoms in a more or less oxidised state.

Recent reviews on gold catalysts
- Bond & Thompson, Catal. Rev.-Sci. Eng. (1999).
- Bond & Thompson, Gold Bulletin (2000).
- Haruta, CATTECH (2002).
- Hutchings, Gold Bulletin (2004).
- C. Louis, Nanoparticles & Catalysis (2008)
- Fierro-Gonzales & Gates, Chem. Soc. Rev. (2008)

[197]Au Mössbauer spectroscopy looks like a technique of choice for the study of these systems.
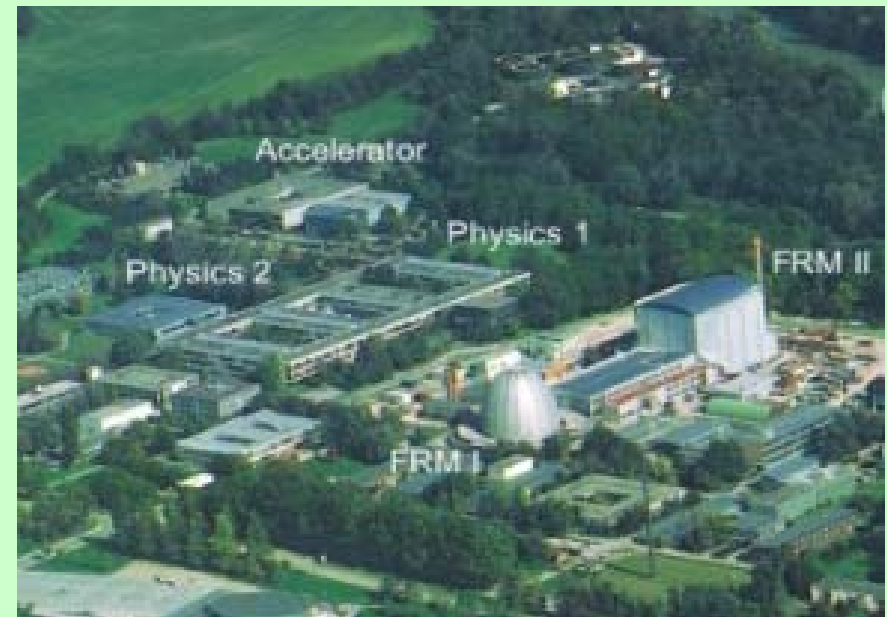
^{197}Au Mössbauer spectroscopy

^{197}Au Mössbauer Transition

- Natural abundance: 100 %.
- E_γ: 77.3 keV
- Natural linewidth: 0.94 mm/s.
- Experimental linewidth: >1.88 mm/s.
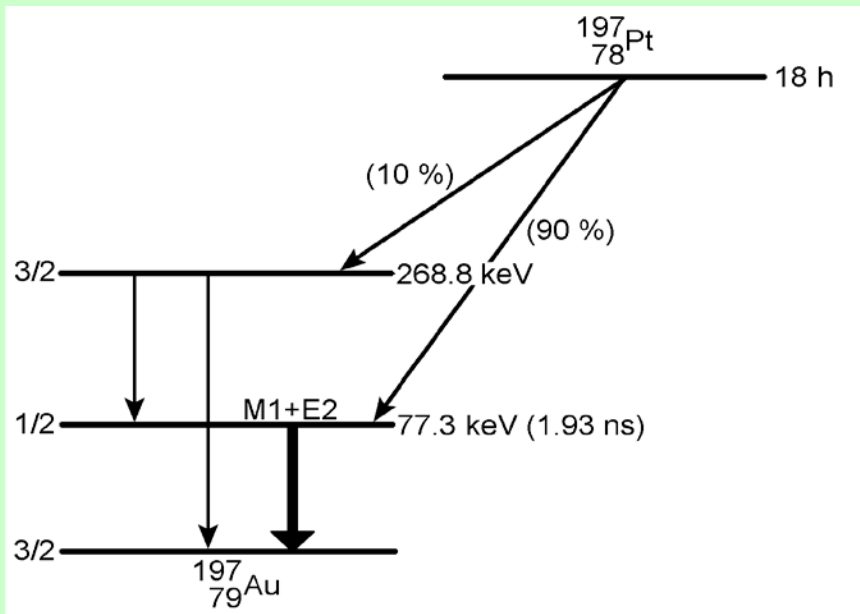
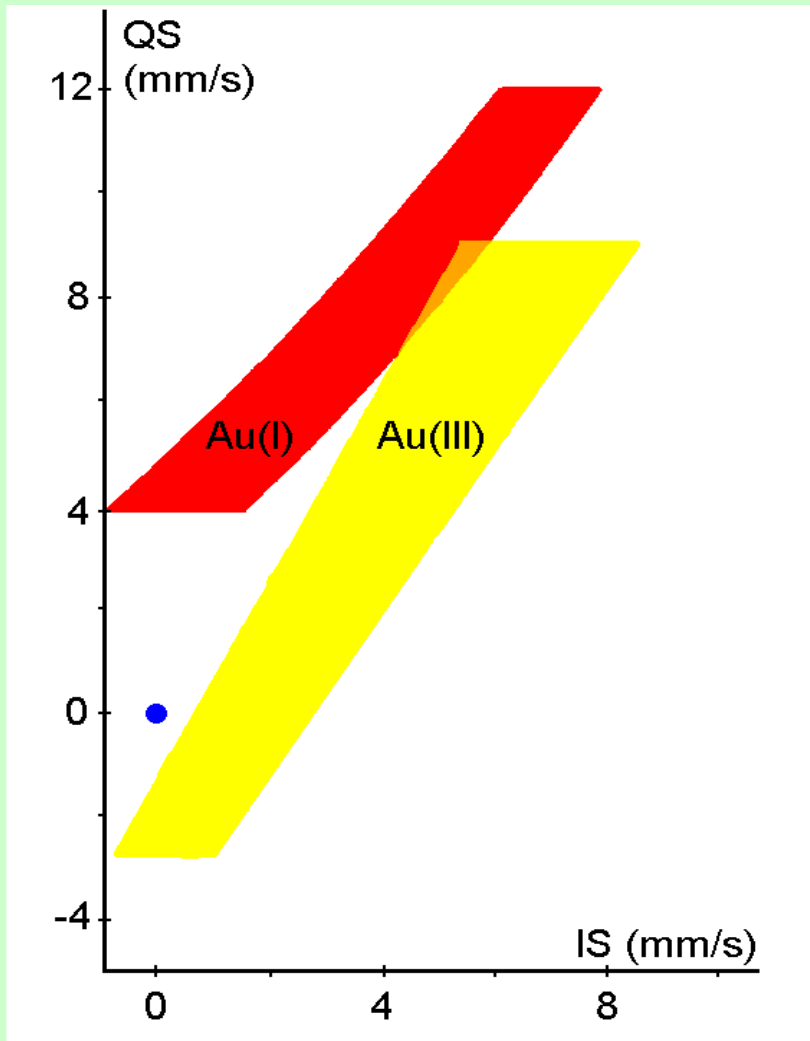## ^{197}Au Mössbauer Source

- Parent isotope: ^{197}Pt.
- Source host: Pt metal.
- $t_{1/2}$: 18 h.
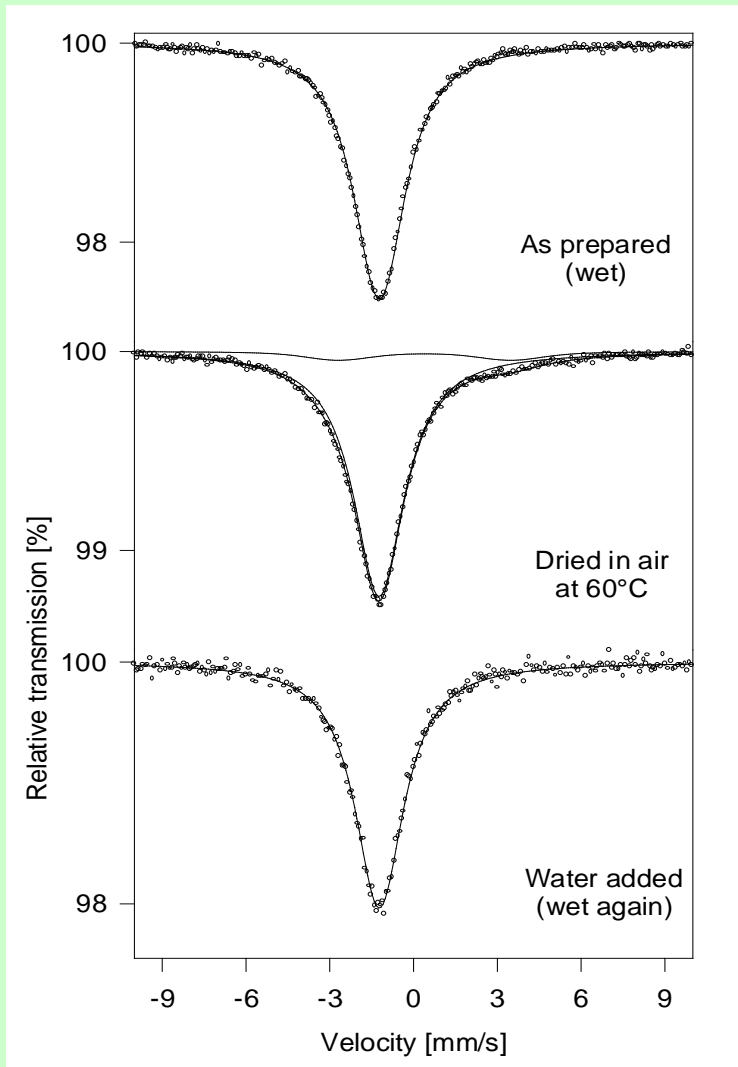- Principal means of production: ^{196}Pt(n,γ)

^{197}Au hyperfine interactions

- Both QS and IS are necessary to determine the chemical state of gold.
- Au(I), $5d^{10}$, linearly coordinated (*sp*):
  - IS correlated to QS, both increasing with the softness of the ligands (from halides to organogold compounds.)
- Au(III), $5d^8$, square planar (*dsp*^{2}):
  - Low-spin, diamagnetic.
  - Positive correlation between IS and QS, both increase as the ligands become softer.
- The IS in Au(III) is usually slightly larger than in Au(I):
  - Incomplete *d*-shell.
  - Greater covalence expected for the higher oxidation state.

The importance of f-factors in ^{197}Au MS

$$E\gamma = 77.3 \text{ keV}$$

As prepared (wet)

Dried in air at 60°C

Water added (wet again)

Relative transmission [%]

Velocity [mm/s]

Example: Au/A-C catalysts

- Used in liquid-phase oxidation of diols. [Prati and Rossi, J. Catal. (1998)]
- Gold particles size ~ 5 nm
- Sample provided in the wet state.
- Drying and wetting cycles and result in:
  - A new Au(I) component in the dried state
  - $f(Au_{WET})/f(Au_{DRY}) = 1.9$ at 4.2K

A precise evaluation of the f-factors is necessary for a correct interpretation of the ^{197}Au Mössbauer spectra.

The first ^{197}Au Mössbauer study of gold catalysts
- Delgass et al., J. Phys. Chem. (1968) -

Mössbauer Spectroscopy of Supported Gold Catalysts[1]

by W. N. Delgass,[2] M. Boudart, and G. Parravano

Department of Chemical Engineering, Stanford University, Stanford, California 94305 (*Received May 7, 1968*)

Supported gold catalysts have been studied by Mössbauer spectroscopy, electron microscopy, and X-ray diffraction to determine the effect of the impregnation compound, the support, and heat treatment on the nature of the catalyst formed. MgO was found to be a more inert support than η-Al_2O_3 toward $HAuCl_4$, and $HAuCl_4$ was found to be more easily decomposed than $KAu(CN)_2$ to give gold particles on η-Al_2O_3. Chemical changes in the gold complexes on alumina after different heat treatments were observed in the Mössbauer spectra of ^{197}Au, thus illustrating the utility of the Mössbauer effect for the study of the genesis of a supported catalyst.

- First demonstration of the ability of ^{197}Au MS to study the chemical interactions of finely divided Au species with a support.
- Comparison of groups of Au/Al_2O_3 and Au/MgO catalysts prepared from different precursors.

"Recent" investigations of gold catalysts.

- The research group of F. E. Wagner (including J. Friedl and A. Kyek) in Munich has been involved in the study of several systems:
  - For acetylene hydrochlorination:
    - Au/Activated-carbon (1991).
  - For methane oxidation:
    - Au/Mg-oxide (1998);
  - For CO oxidation at low temperatures:
    - Au/Fe-oxide (1997-2002);
    - Au/Mn-oxide (2001).
- These works were performed in the framework of different scientific collaborations:
  - G. Hutchings, Cardiff University.
  - Q. Pankhurst, University College London.
  - S. Galvagno, Università di Messina.
- Other research groups were also involved in the study of supported gold catalysts:
  - S. Nasu and Y. Kobayashi (Au/MgO and Au/TiO_2, 1999).
  - A. van der Kraan (Au/TiO_2 and Au/Al_2O_3, 2002).
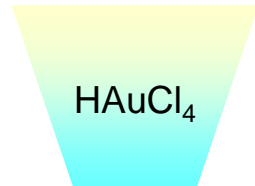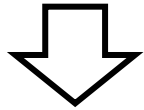 - G. Hutchings, J. A. Moulijn et al. (Au/Fe-oxide, 2006)

Au/Iron-Oxide
- Wagner et al., J. Chem Soc. Faraday Trans. (1997) -

- Au/Fe_2O_3 is one of the most active systems in CO oxidation
- Slightly different preparation methods lead to materials with very different activity.
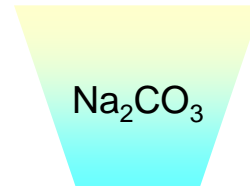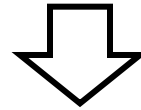
WETNESS IMPREGNATION

α-Fe_2O_3 (solid)

$HAuCl_4$

Acidic

pH 3.4

Acidic

COPRECIPITATION

$HAuCl_4$ + $Fe(NO_3)_3$

Na_2CO_3

Basic

~12

~8

Mild Basic

INVERSE COPRECIPITATION

Na_2CO_3

$Fe(NO_3)_3$ + $HAuCl_4$
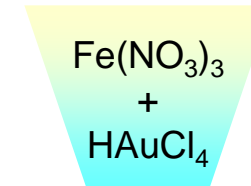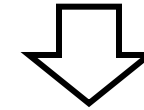
Acidic

~3-4

~8

Mild Basic

The system is "bimetallic" for MS (^{57}Fe and ^{197}Au).

Au/Iron-Oxide
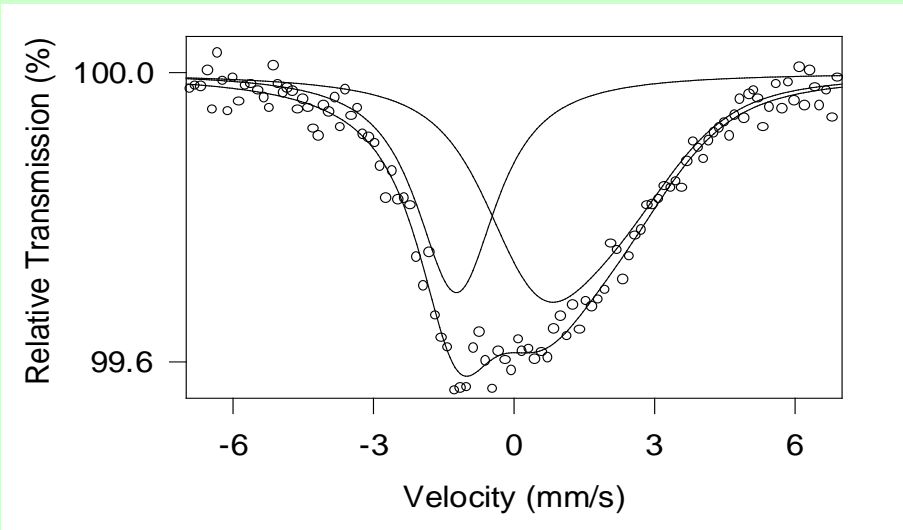## - Coprecipitation -

^{57}Fe Mössbauer spectroscopy (RT)

^{197}Au Mössbauer spectroscopy (LHT)
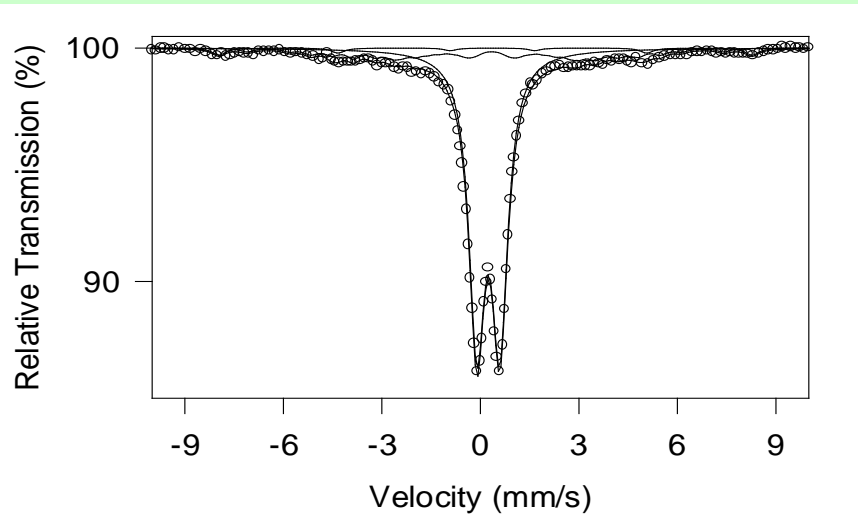
- Ferrihydrite is the dominant species, and increases with the gold loading.

- Few per cent of hematite and goethite are present.

- Both oxidic and metallic gold are species with similar relative intensities.

- The gold metal content is slightly overestimated due to the higher f-factor of metallic gold.

- The ratio between gold metal and oxidic gold is independent of the gold loading
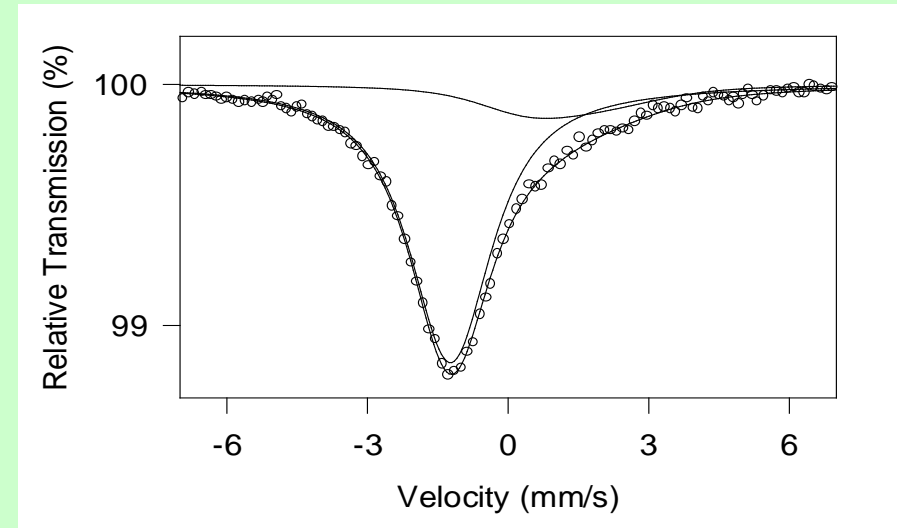
Au/Iron-Oxide
- Inverse Coprecipitation -

^{57}Fe Mössbauer spectroscopy (RT)

^{197}Au Mössbauer spectroscopy (RT)
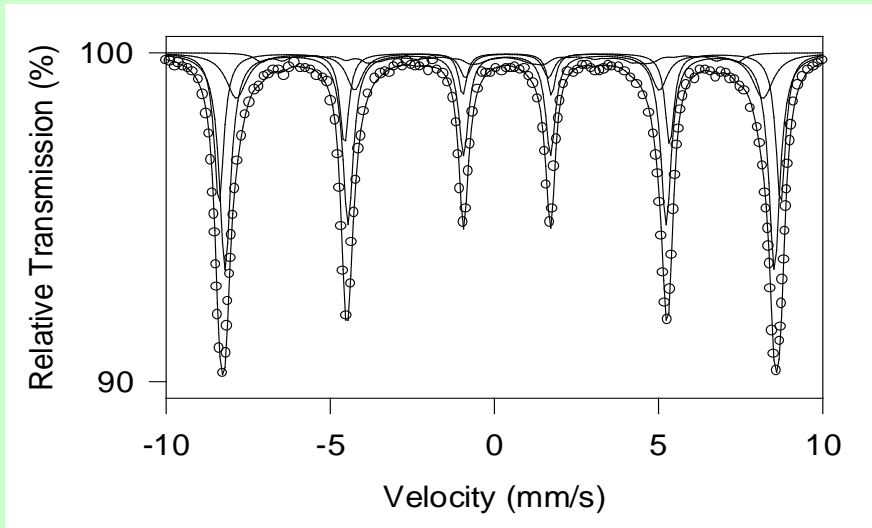
● Inverse coprecipitation leads to the formation of well crystallised hematite.

● Metallic gold is mainly formed.

● Oxidic gold is still present in small amounts.

Direct and inverse coprecipitation produce completely different materials.
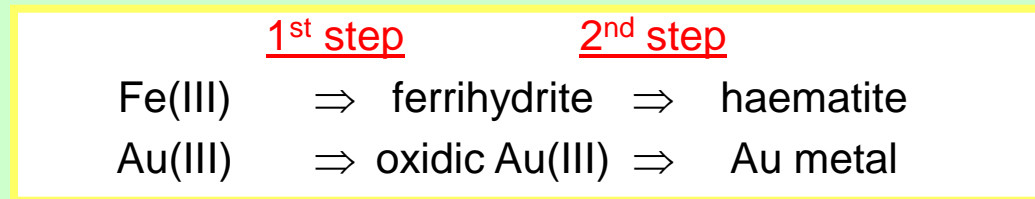
Au/Iron-Oxide
- Effect of the pH on the final structure of the materials -

The main difference between the two coprecipitation methods is the pH of the solutions:

DIRECT COPRECIPITATION

Basic
~12

~8
Mild Basic

INVERSE COPRECIPITATION

Acidic
~3-4

~8
Mild Basic

Mechanism of formation of the solids in two steps.

|	1st step	2nd step
Fe(III)	$\Rightarrow$ ferrihydrite $\Rightarrow$	haematite
Au(III)	$\Rightarrow$ oxidic Au(III) $\Rightarrow$	Au metal

- In direct coprecipitation, both Au(III) and Fe(III) precipitate simultaneously
- In inverse coprecipitation, Fe(III) and Au(III) species precipitate at different times

Coprecipitation of Fe and Au hinders the 2nd step

**The preparation methods largely influences the surface areas of the materials**
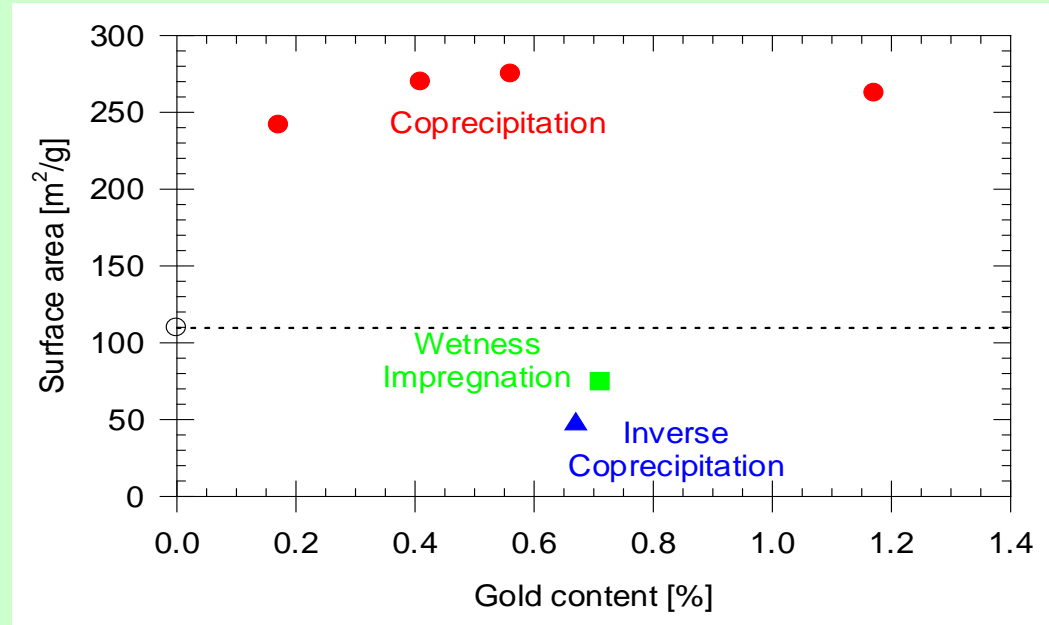
The highest surface areas are obtained for the samples prepared by coprecipitation:
- The surface area increases only slightly with the gold loading.

Au/Iron-Oxide
- Influence of the preparation method on the catalytic activity -

The preparation methods largely influences the catalytic properties of the materials
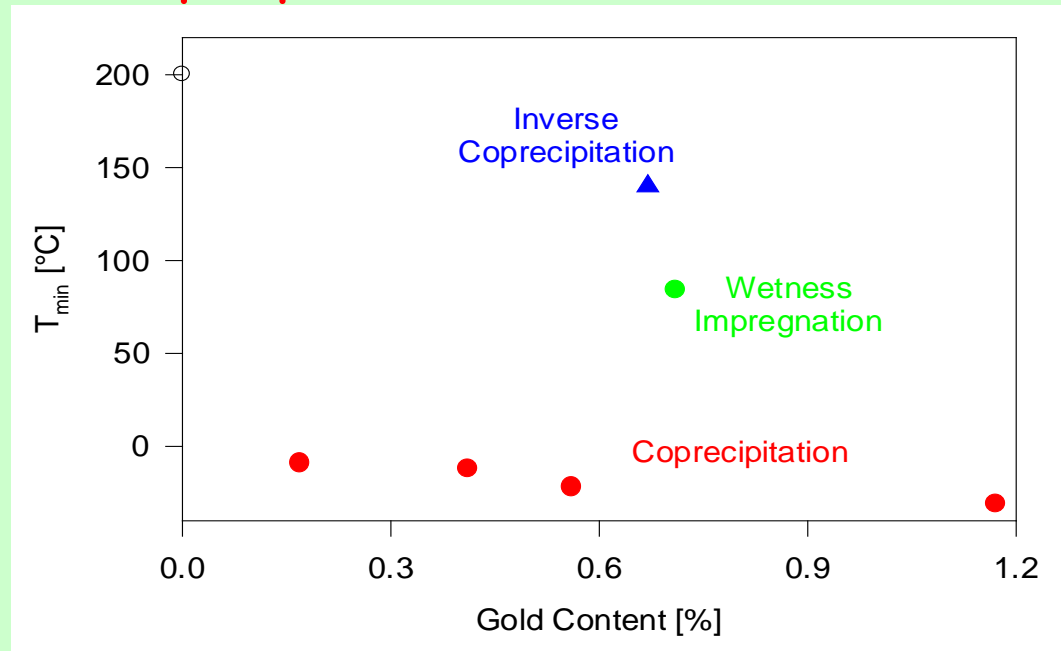
- **The catalytic activity is measured as the minimum temperature to obtain a 4% CO conversion.**

- **The samples obtained by coprecipitation are the best catalysts:**
  - The activity increases with the gold loading and the surface area.

To elucidate the role of the different gold species in the activity, this work was continued by studying materials treated at different temperatures:

- Gold oxyhydroxide is necessary to have active Au/Iron-Oxide catalysts for CO oxidation in. [Finch et al., PCCP (1999)]
- The presence of ferrihydrite seems also necessary to obtain a good catalyst. [Hodge et al., Catal. Today (2002)]

Does the Bond-Thompson model apply?
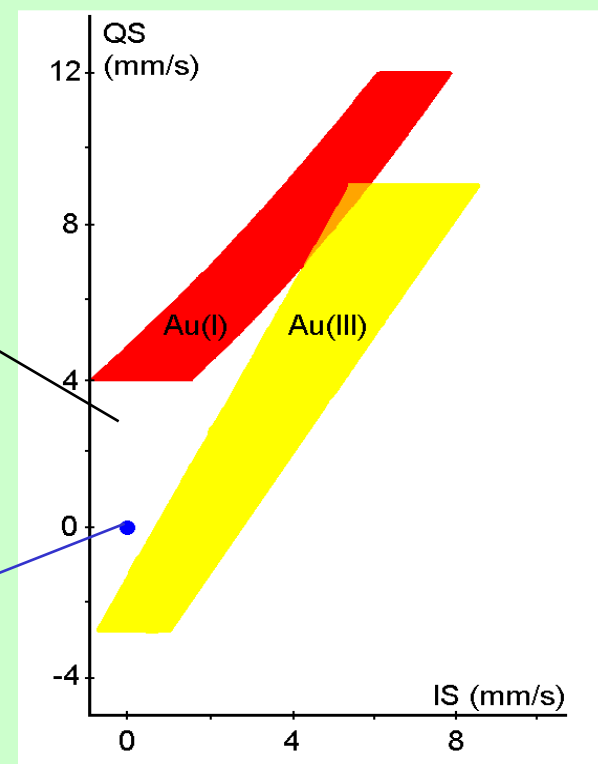
Au/TiO$_2$
- van der Kraan and co-workers (2002) -

- Au/TiO$_2$ is the most studied systems in CO oxidation.
- Good catalysts are usually prepared by Deposition/Precipitation.
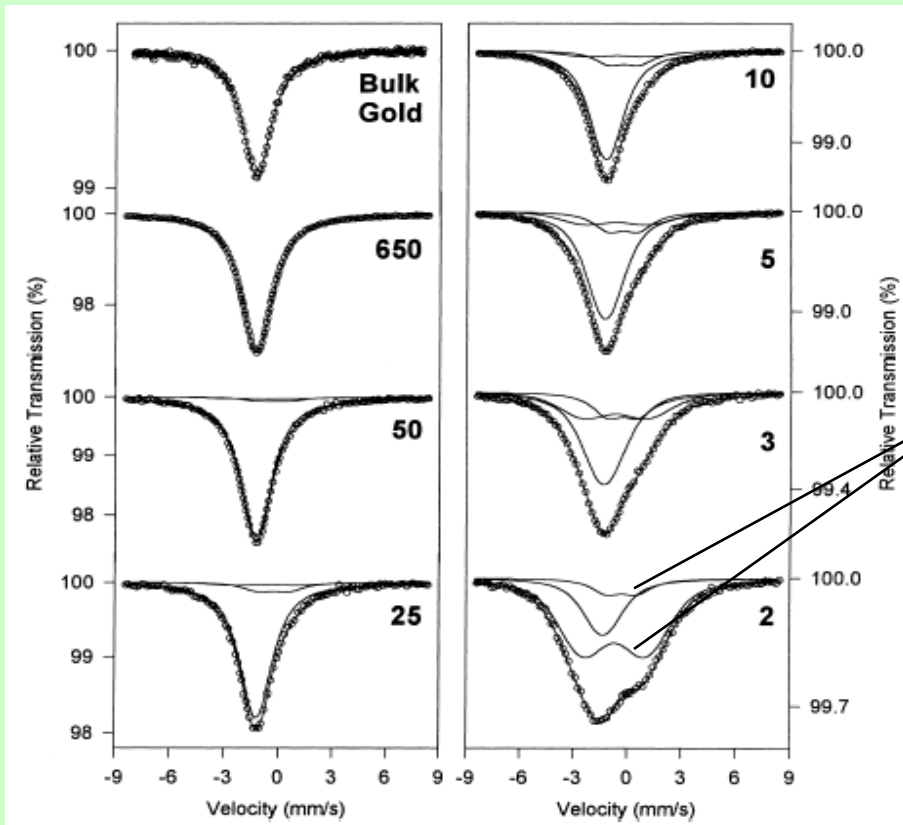 - Homogeneous gold metal nanoparticles (~3 nm) are obtained.

????
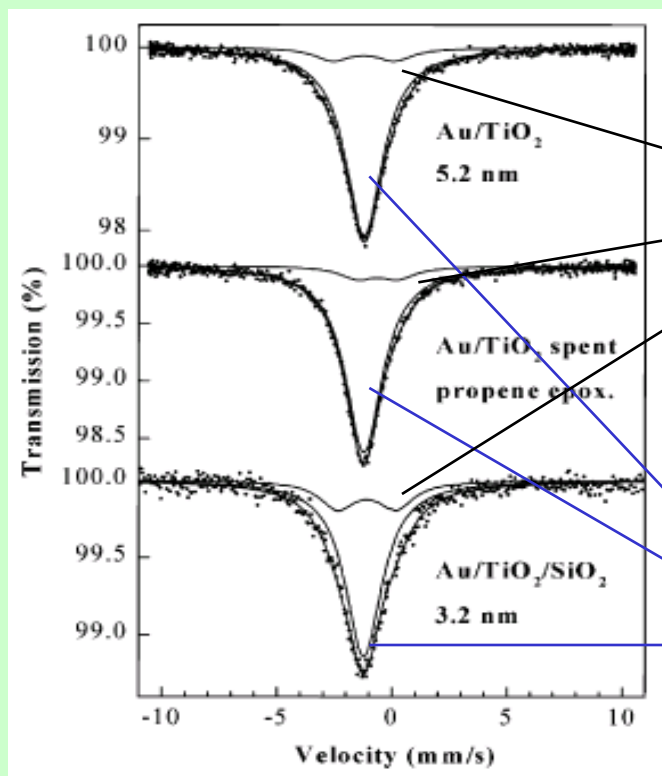
Au metal

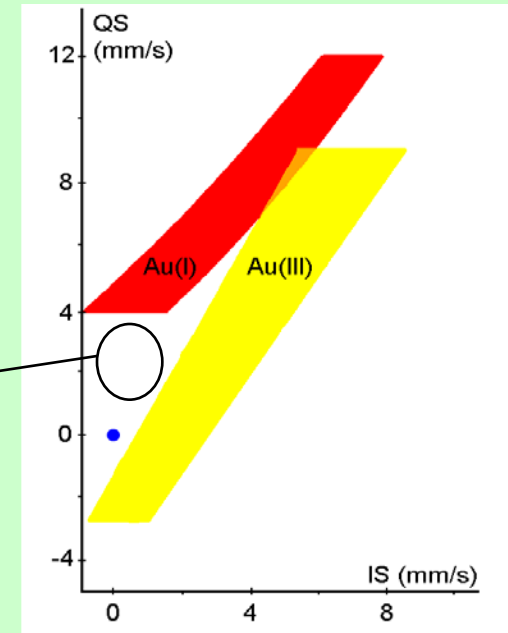[**Zwijnenburg,** et al., J. Phys. Chem. B (2002)]

- The unknown component is probably due to the presence of "surface gold metal":
  - Hyperfine parameters similar to those of gold nanoparticles in mylar.

"Surface" Au Metal

[Stievano et al., J. Non-Crystalline Solids (1999)]
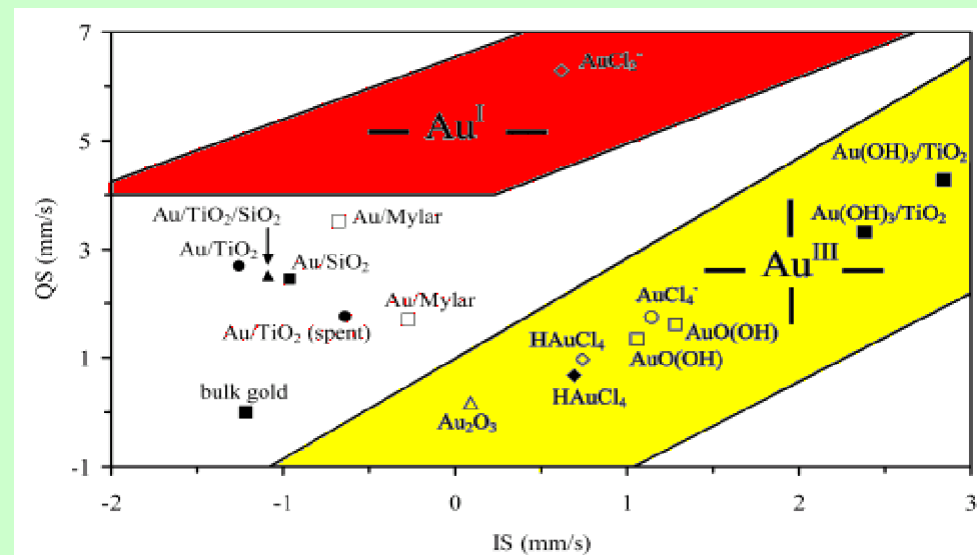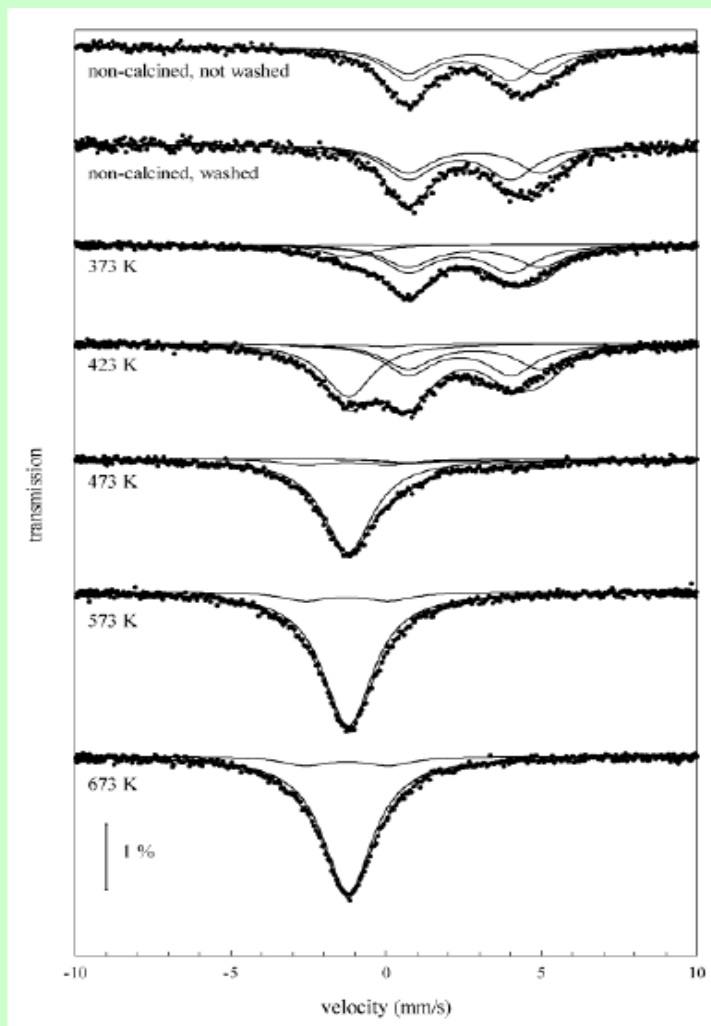
- Surface and core Au atoms are distinguished if the particle size < 6 nm.
- Non-bonding surface atoms exhibit substantial QS.

Au/TiO₂

- Formation of the gold metal particles -

- In the final catalyst, no contribution from oxidic gold is observed

Does the Bond and Thompson model apply?

- The authors suggest that oxidic gold spectral components might hide behind the other more intense contributions…

[**Zwijnenburg,** et al., J. Phys. Chem. B (2002)]

- ^{197}Au Mössbauer spectroscopy is a promising technique for the study of supported gold catalysts.

- It is able to distinguish:

  - Different oxidation states of gold;

  - Presence of surface atoms.

  - "Interactions" of the gold species with the support.

- The precise determination of f-factors is a critical point for a correct interpretation of the spectra.

- Until now, the use of gold catalysts by ^{197}Au MS has been very discontinuous.

- More effort must be made to obtain a precise determination of structure and active species in Au/TiO$_2$ and Au/Fe-oxide catalysts.