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

PIRE-ECCI/ICMR

Summer Conference

SantaBarbara

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1. Overview on Gold

2. CO Oxidation at Low Temperatures

3. Catalyst Preparation

When man discovered Gold?

5 – 7 thousands year 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 g → 3,000 m

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

- **Foil**: **1 g → 0.5 m^2 wide, 0.1 μ 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 x 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.**

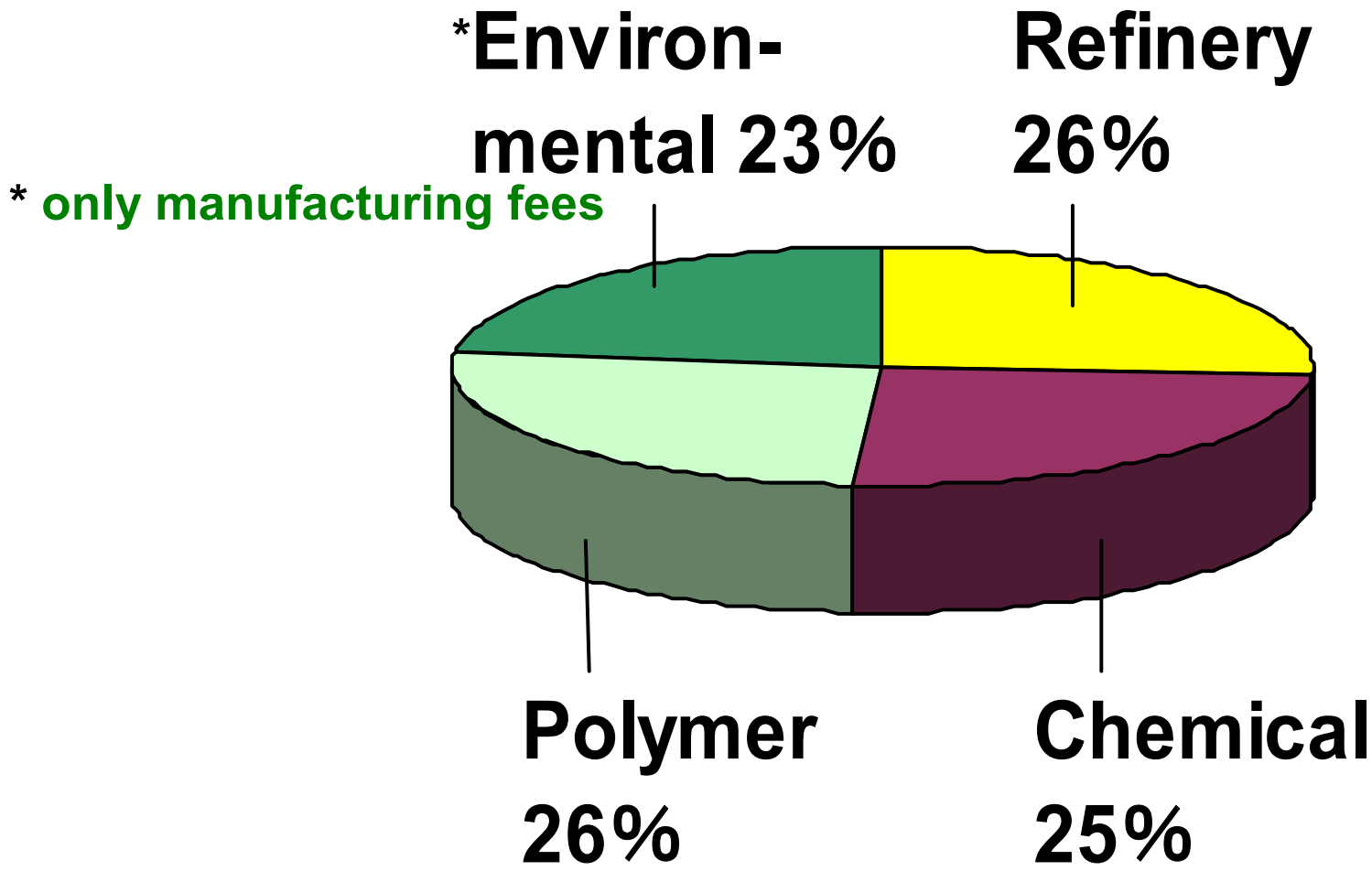
< G. C. Bond: Heterogeneous Catalysis, Oxford Sci. Publ., 1987>

$$A + B \xrightarrow[k1]{} C \xrightarrow[k2]{} F \qquad k1 >> k2, k3 \qquad \text{selective to } C$$

$$\xrightarrow[k3]{} D \xrightarrow[k4]{} F \qquad k3 >> k1, k4 \qquad \text{selective to } D$$

Market Sales of Catalysts : $8.9 x 10^9

2003



Chem. Eng. News, Sept. 20, 1999, pp. 17-25.

Catalytic Metals : 3d →4d→ 5d

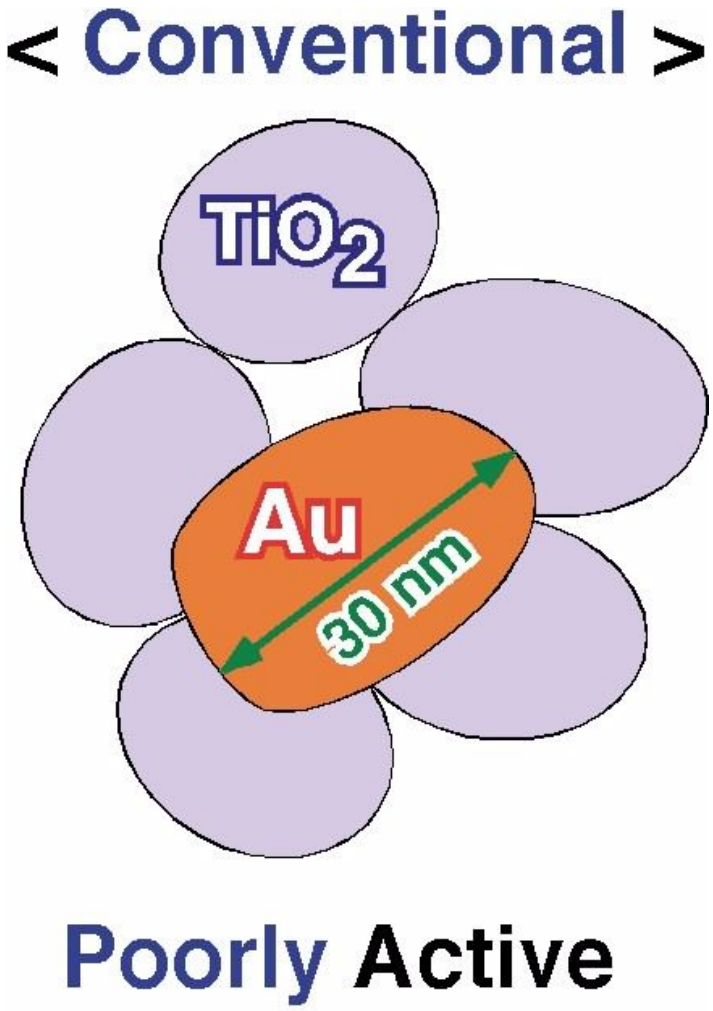
Group / Valence Orbital	VIII			IB
	8	9	10	11
3d	Fe NH_3	Co Gasoline	Ni Fats	Cu CH_3OH
4d	Ru	Rh Fine Chemials	Pd Automobile Exhausts	Ag Ethylene Epoxidation
5d	~~Os~~ ~~Toxic~~	Ir	Pt Cracking	Au

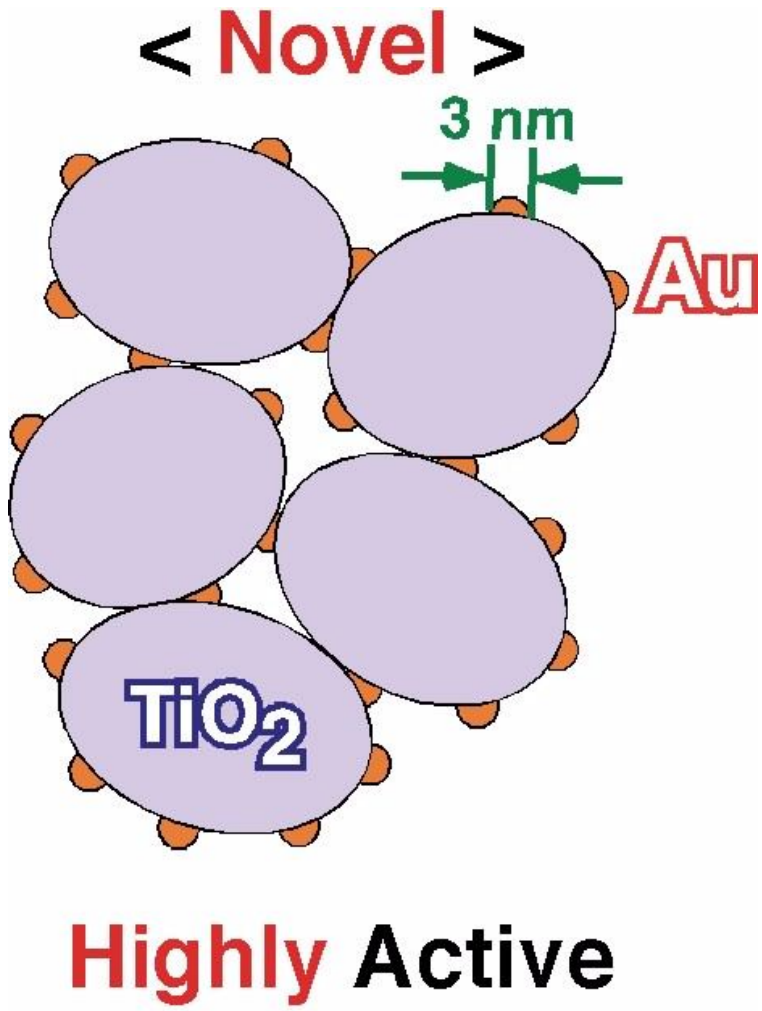
Base

Noble

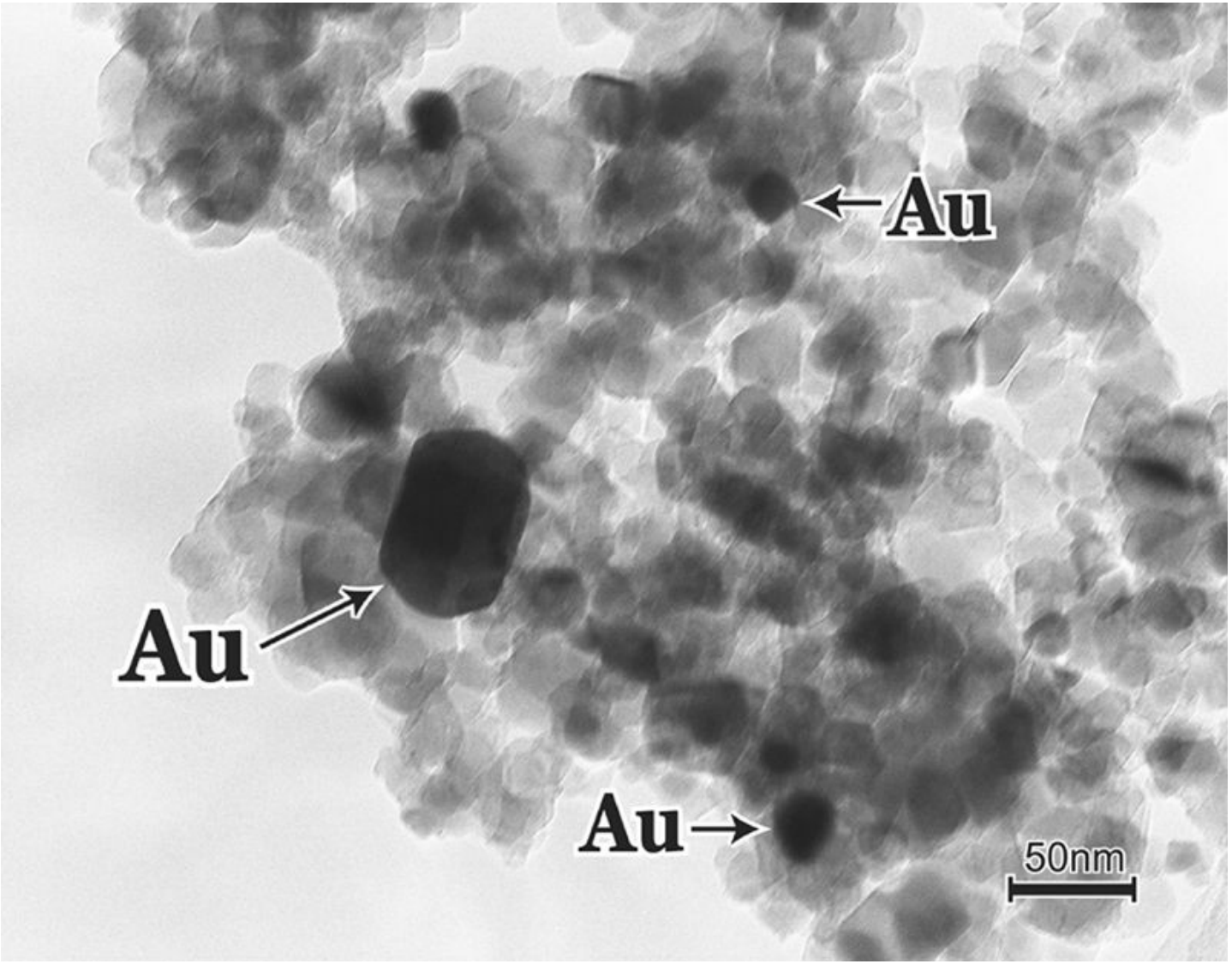
Excld. Minor Major Frontier

Most Reactions are *Structure Sensitive* over Au Catalysts.





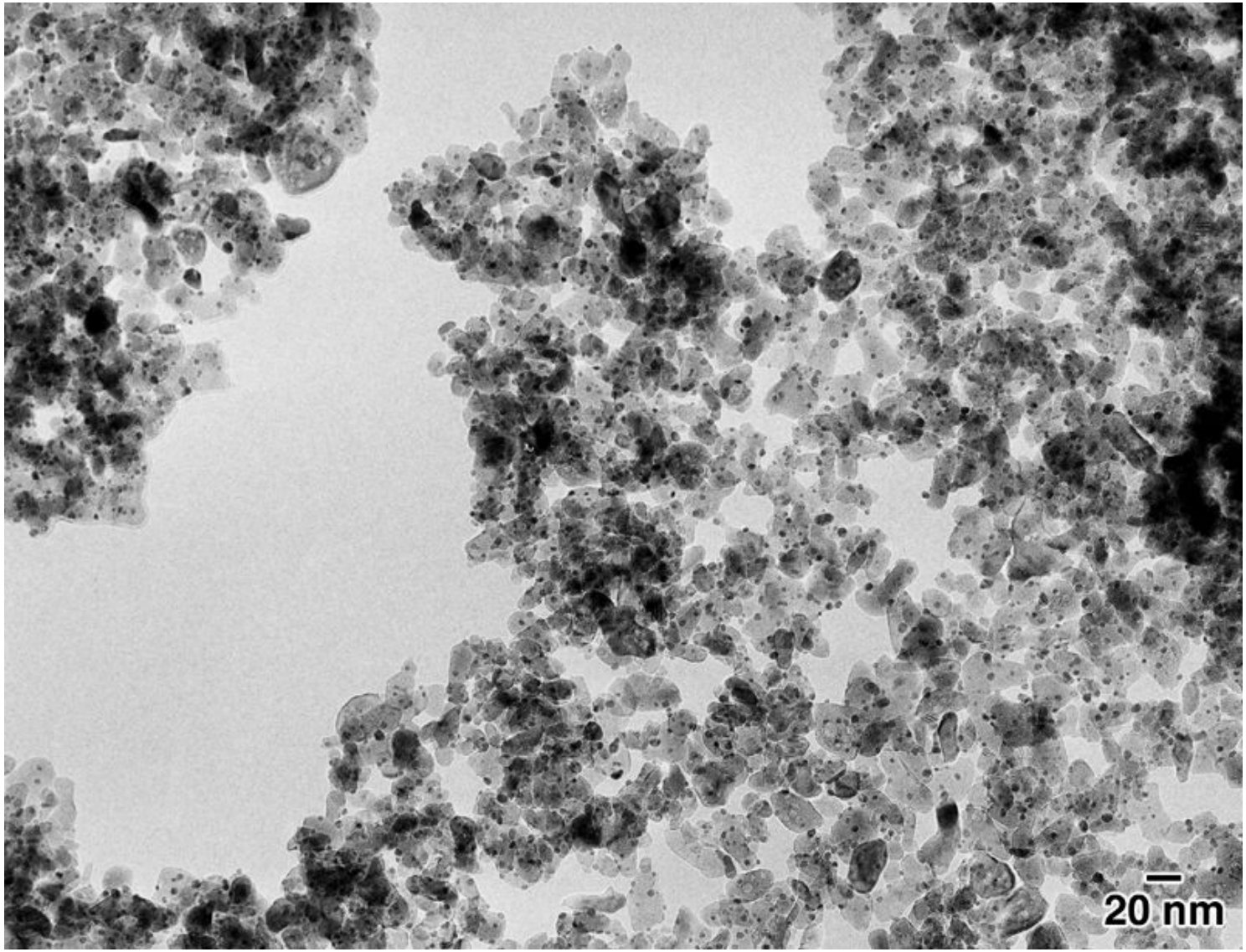
Au/TiO_2 Prepared by Impregnation



Au : 3wt%
TiO_2 : JRC-TIO4

Calcined at 573K

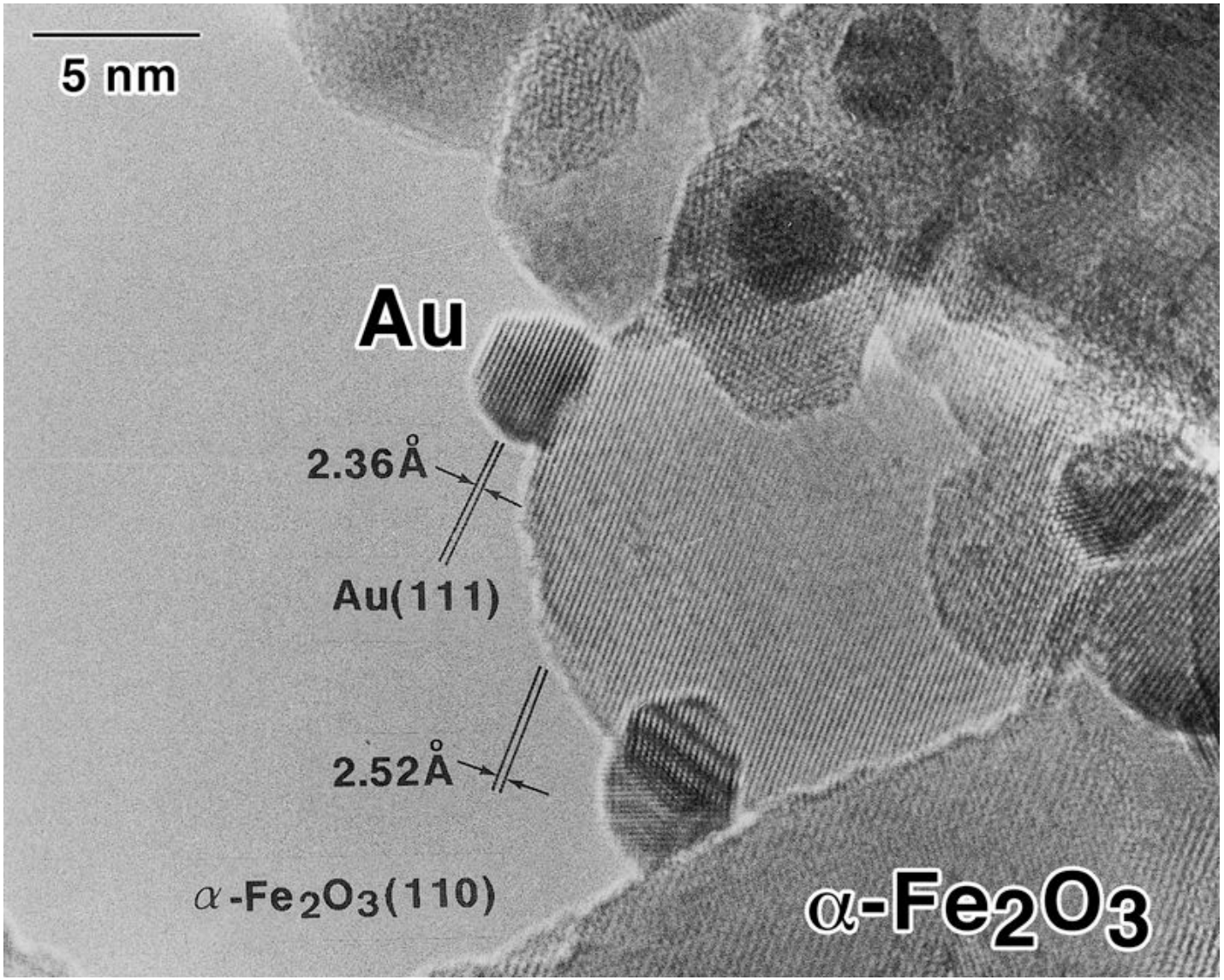
Au/Fe_2O_3 Prepared by Coprecipitation



Au/Fe=1/19

Calcined at 673K

Au/Fe_2O_3 Prepared by Coprecipitation

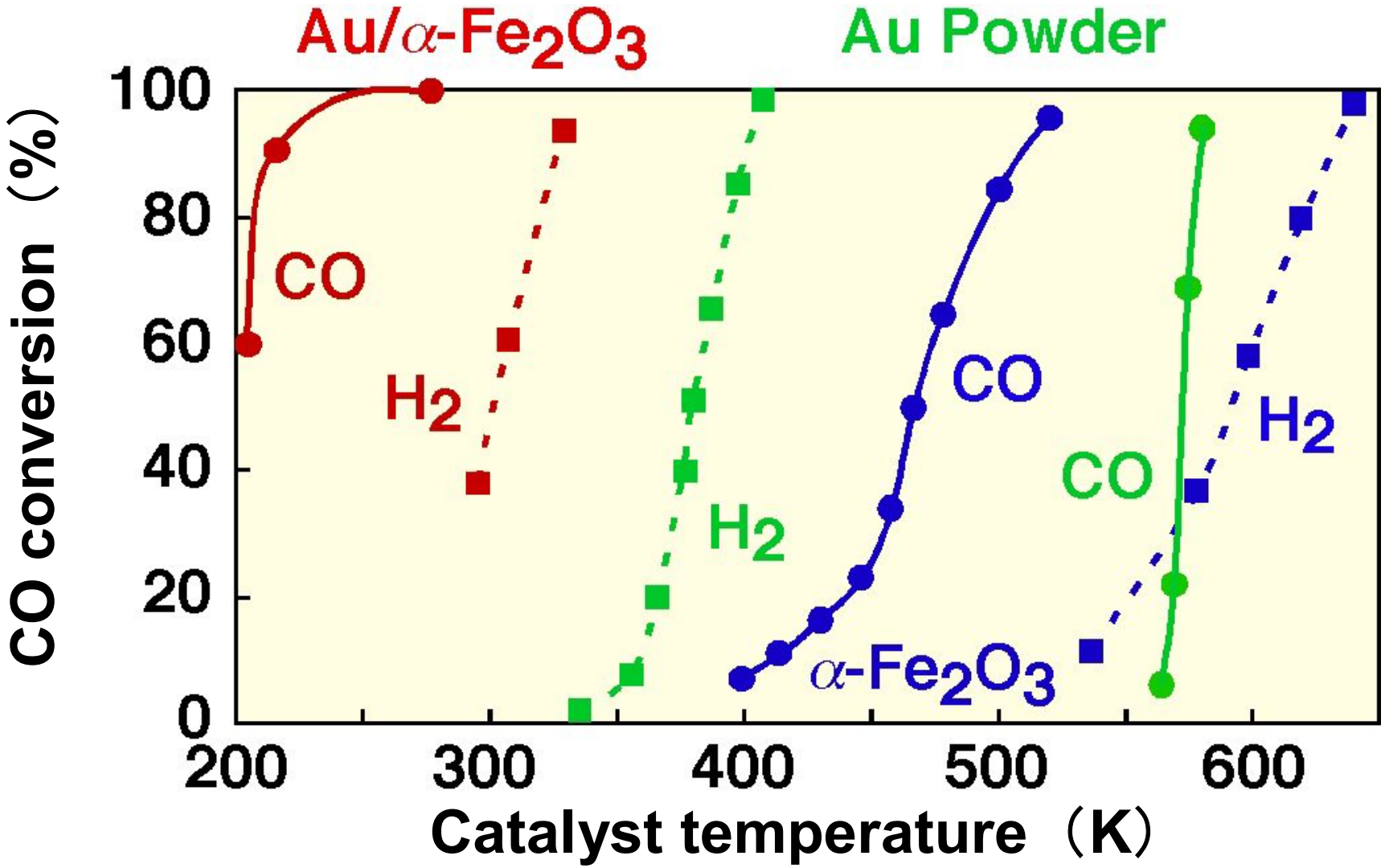


Au/Fe=1/19

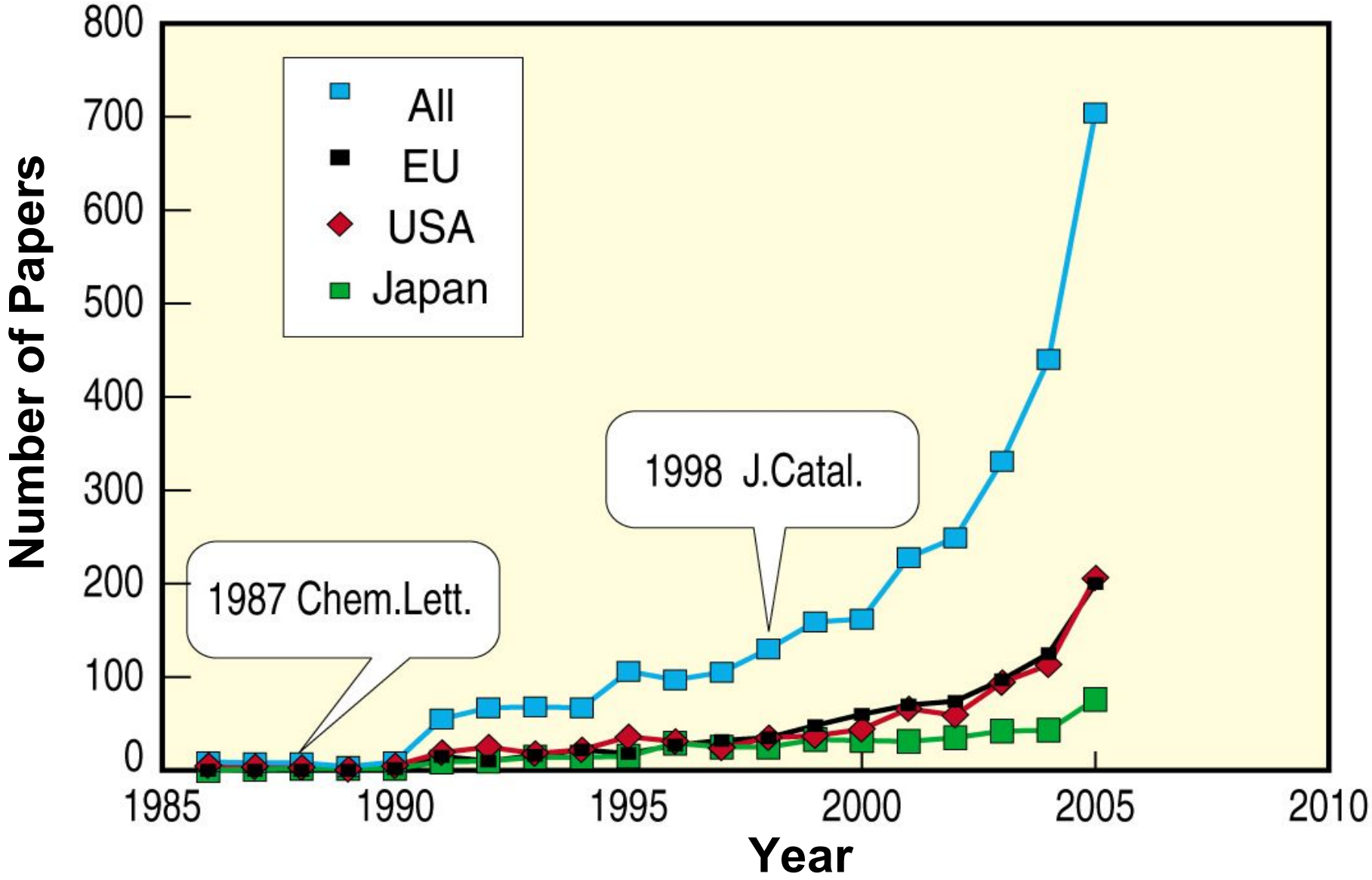
Calcined at 673K

Oxidation of CO and of H_2

M. Haruta et al.,J. Catal. 115,301(1989)



Number of Papers on Au Catalysts




ソタル
改造

Low-Temperature Oxidation of CO

$$CO + \frac{1}{2}O_2 \longrightarrow O{=}C{=}O$$

- Indoor air quality control
- H_2 purification for fuel cells

Catalysts	R. T. Activity	Moisture
Gold	High	Activated
Other Noble Metals	Low	Activated
Base Metal Oxides	Medium	Deactivated

Active Sites in Au Catalysts

< Support >

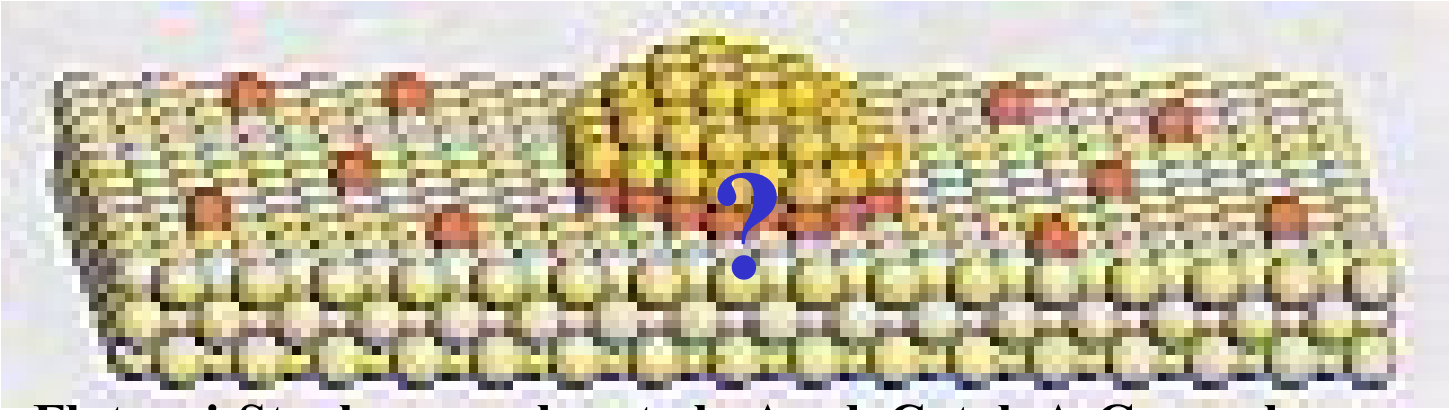
1) **Cations** : Fe_2O_3, La_2O_3 , CeO_2

2) **Clusters** : MgO, $Mg(OH)_2$, TiO_2

3) **Junction Periphery** : Al_2O_3 , SiO_2, Fe_2O_3, ……

Au Cations (Au^{+} or Au^{3+}) : $CO+H_2O \rightarrow CO_2+H_2$

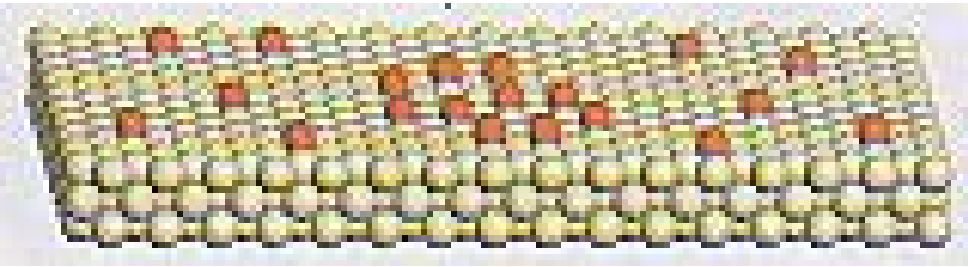
Spectators: Is Au strongly contacted?



NaCN leaching →

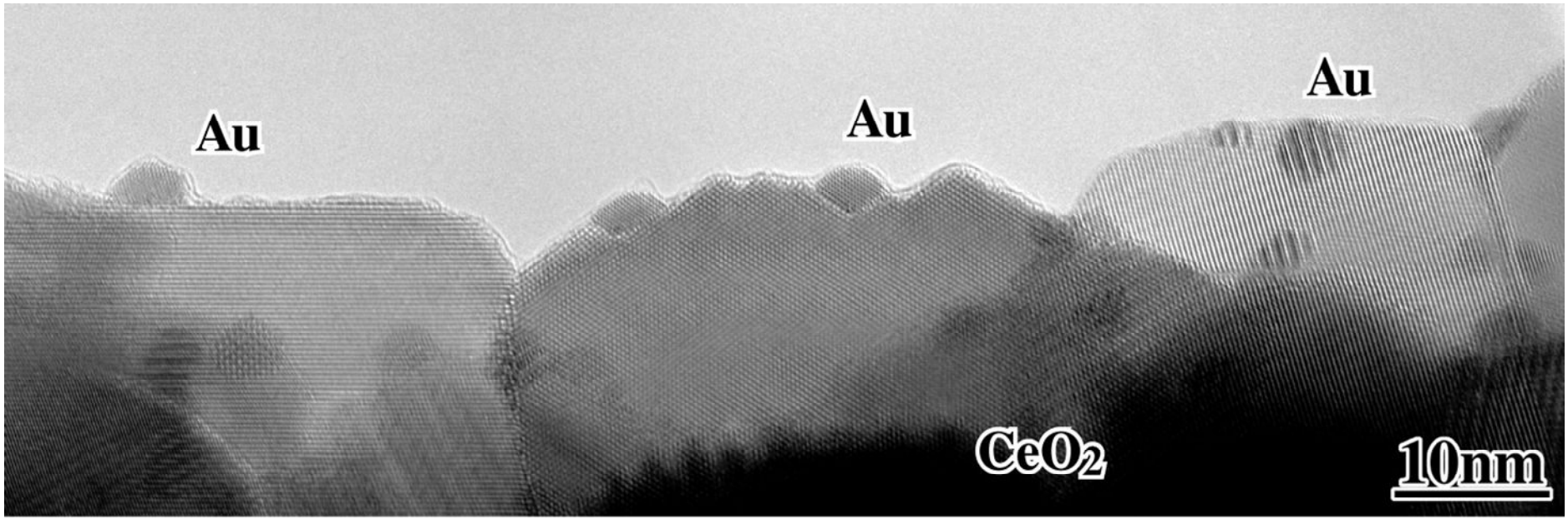
Flytzani-Stephanopoulos et al., Appl. Catal. A:General, (2005).

Actors: stable under reaction?



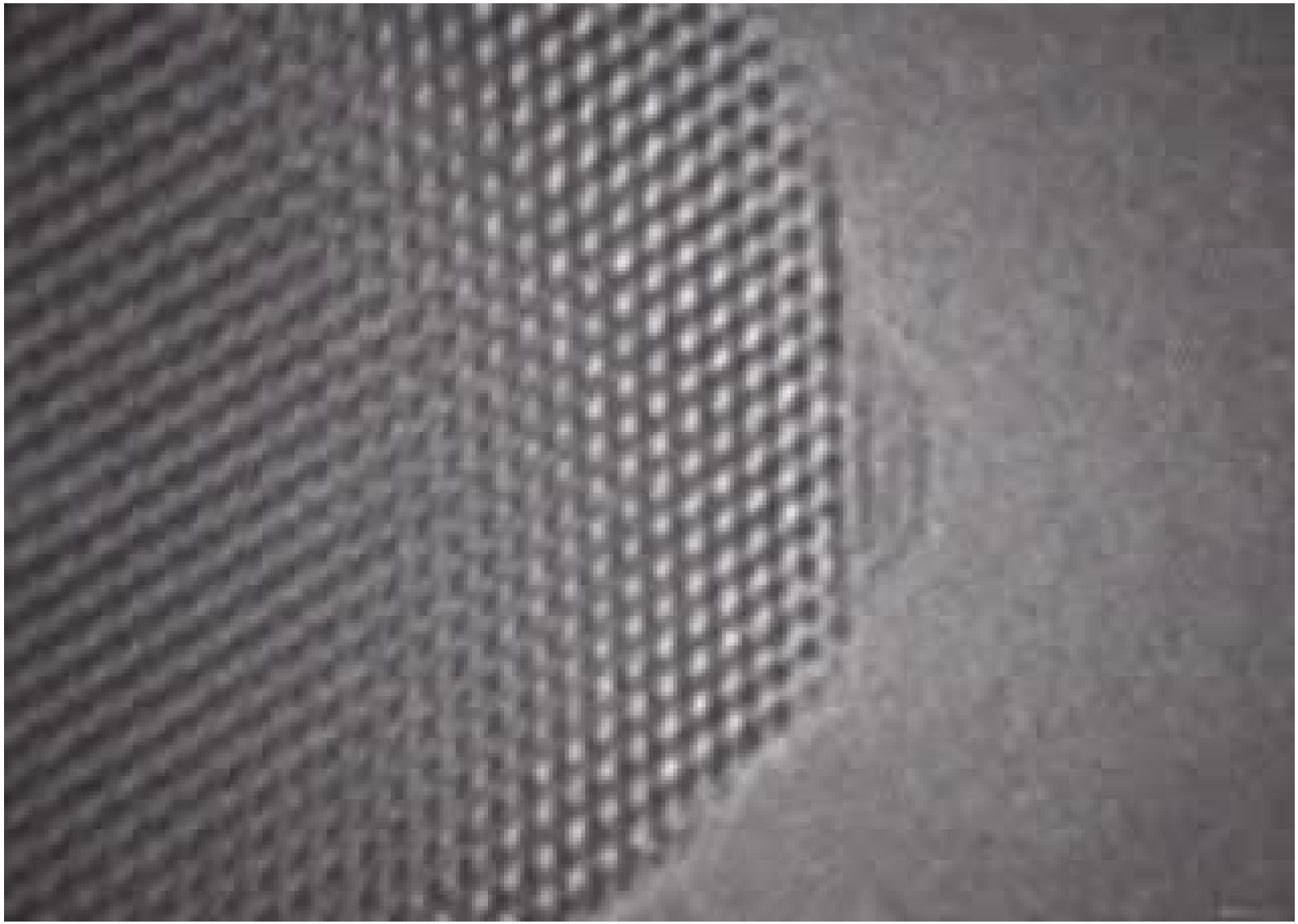
R.J.Davis, Science 301,926(2003)

TEM image of Au particles supported on CeO_2



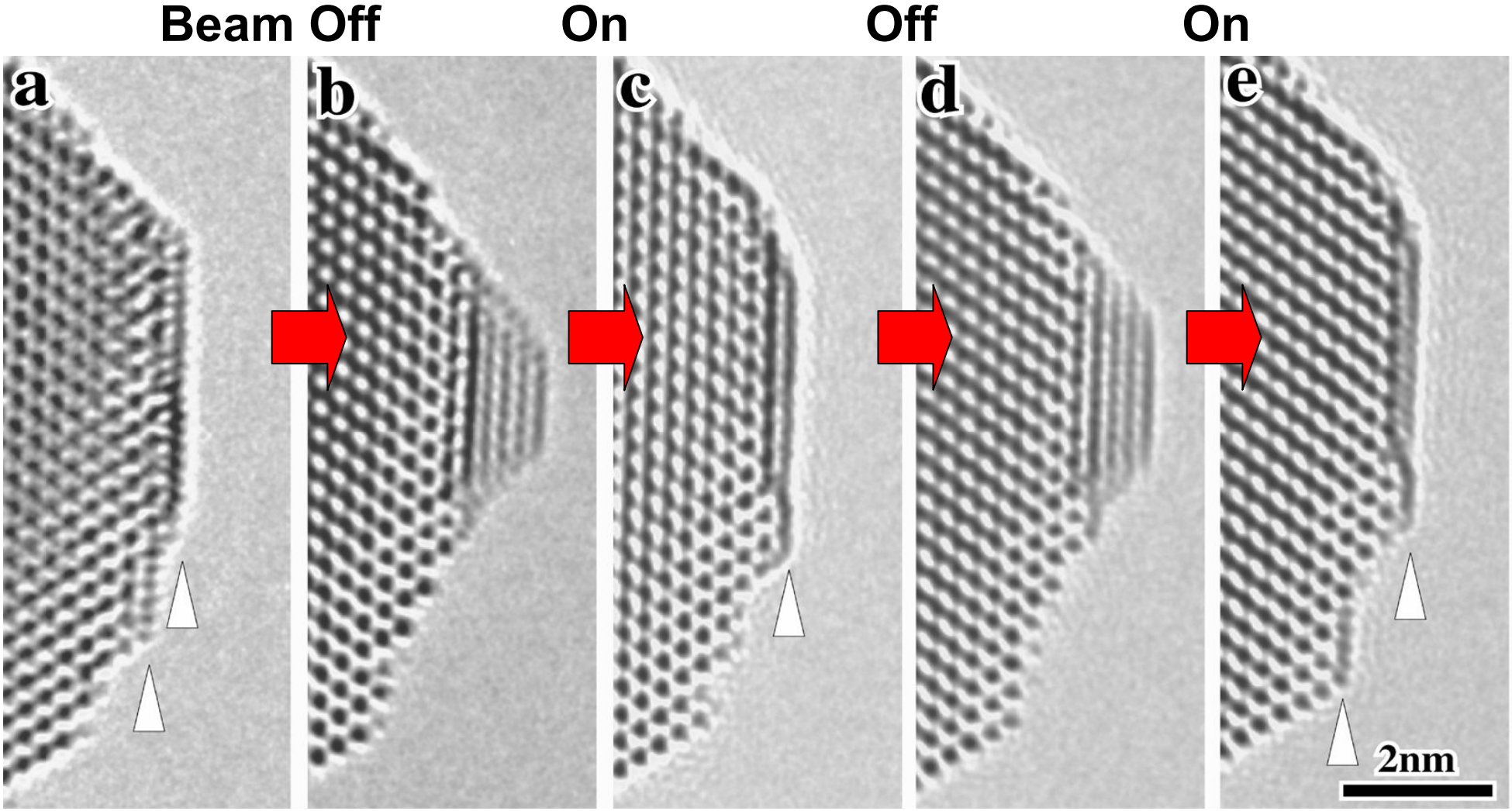
T.Akita, M.Okumura, K.Tanaka, M.Kohyama, M.Haruta, J.Mater.Sci. **40** (2005) 3101.

HRTEM image of a Au particle on CeO_2 during observation



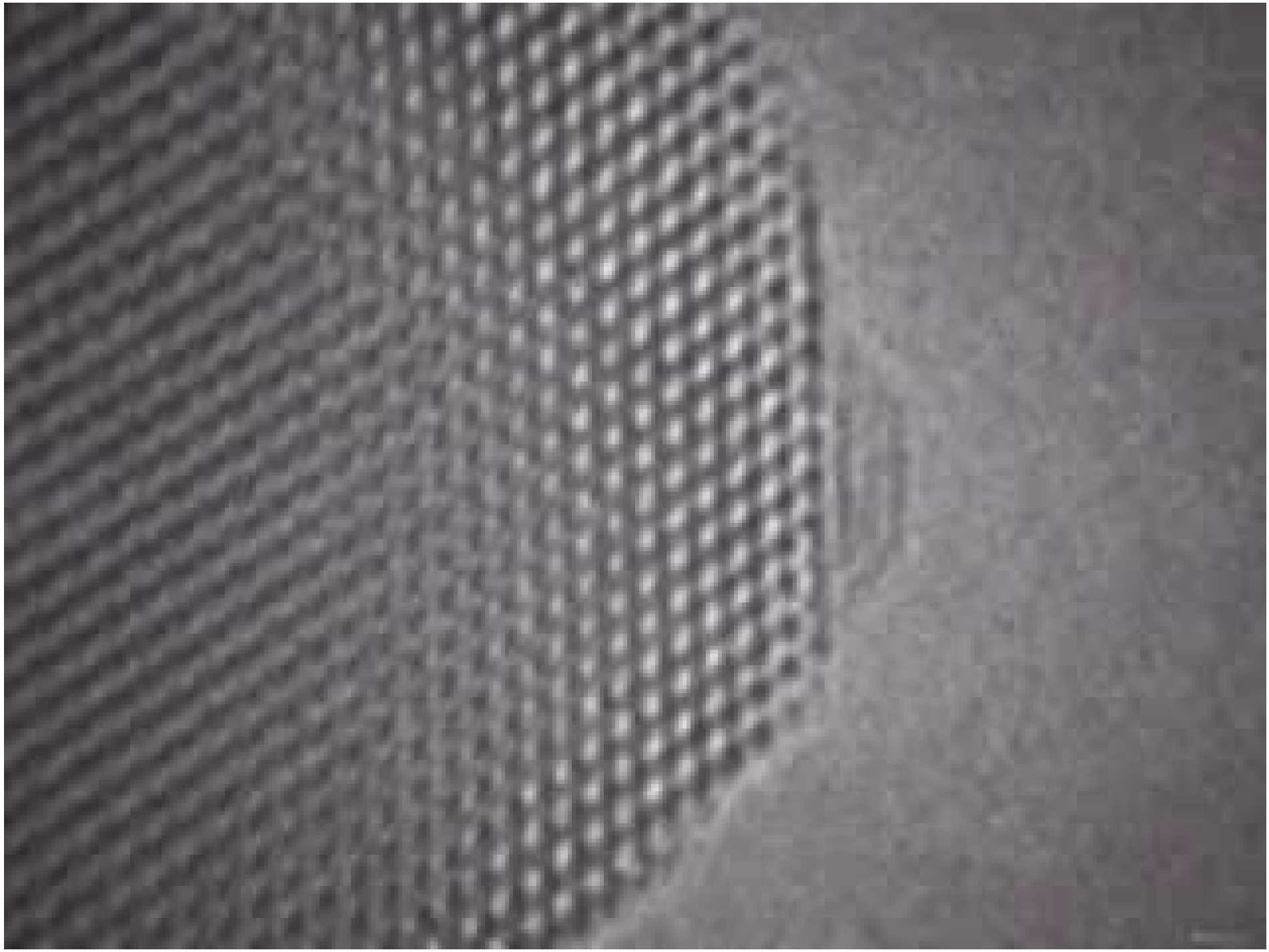
T.Akita et al., J.Mater.Sci. 40 (2005) 3101.

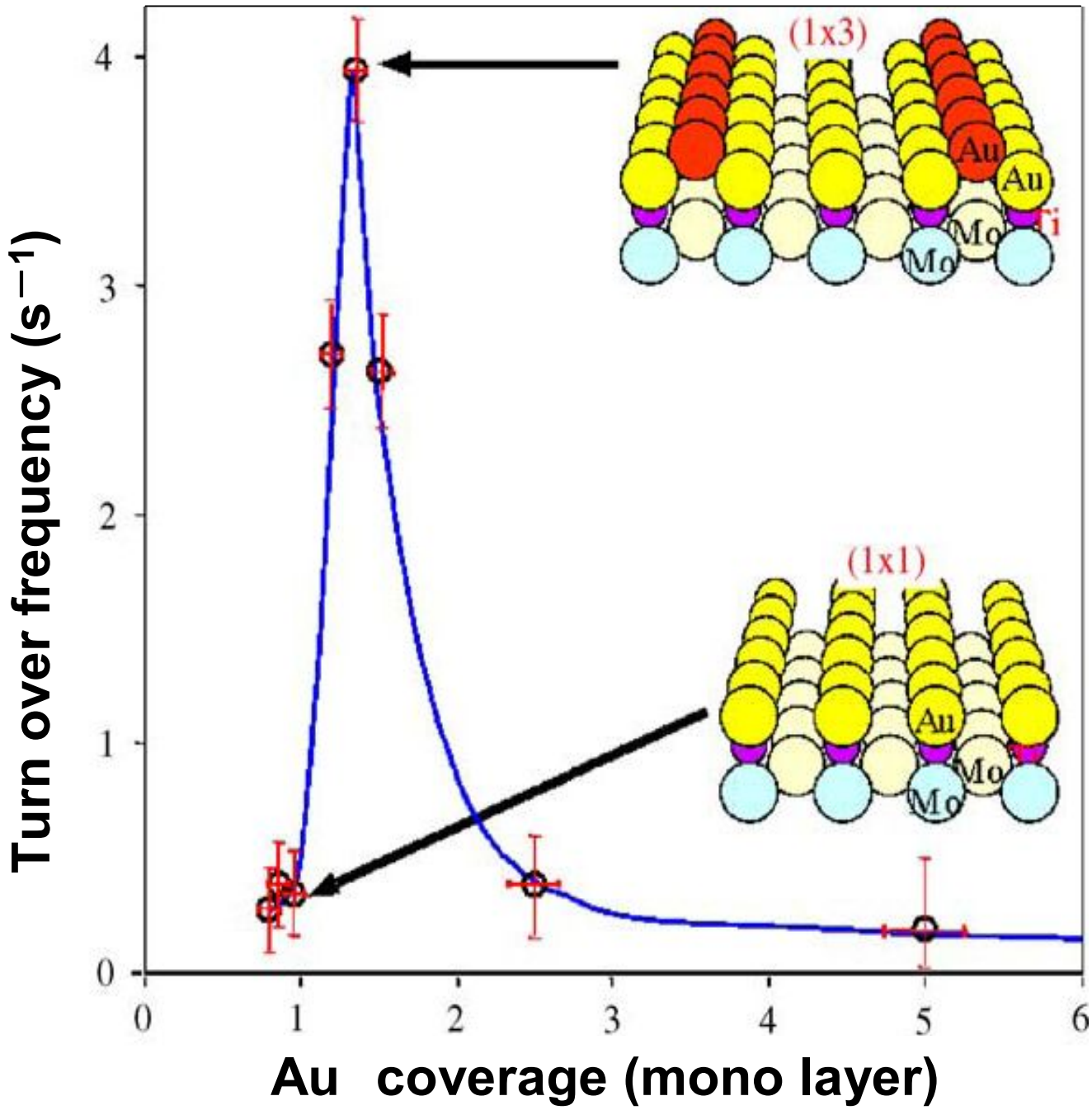
HRTEM images of Au particles during observation



Au Atomic layer

T.Akita et al., J.Mater.Sci. 40 (2005) 3101.



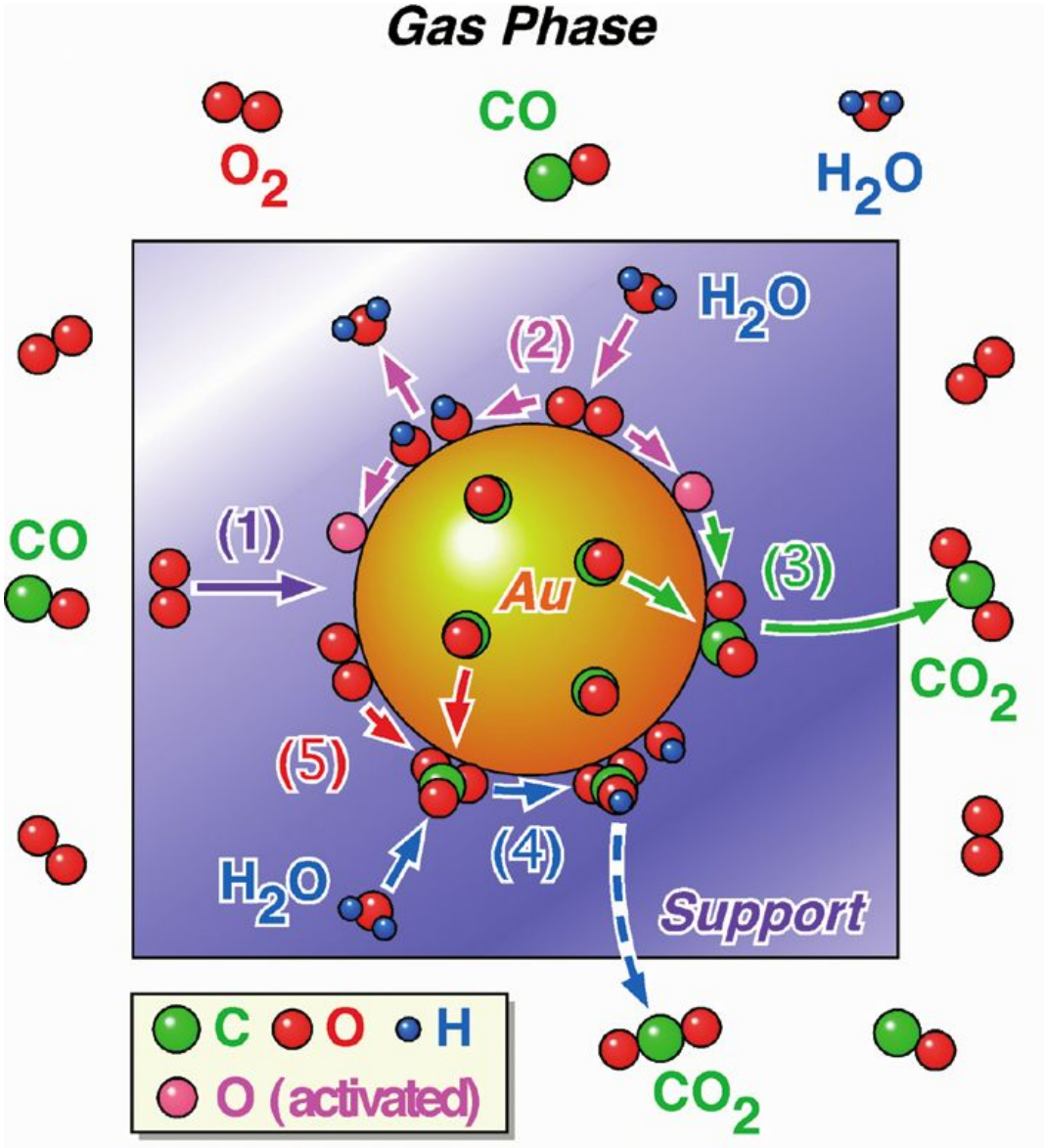


CO oxidation at room temp. over model Au/TiO2 catalyst

Two atomic layers are key to the high catalytic activity.

M. S. Chen, D. W. Goodman, Science 306,252(2004)

Reaction Pathways for CO Oxidation

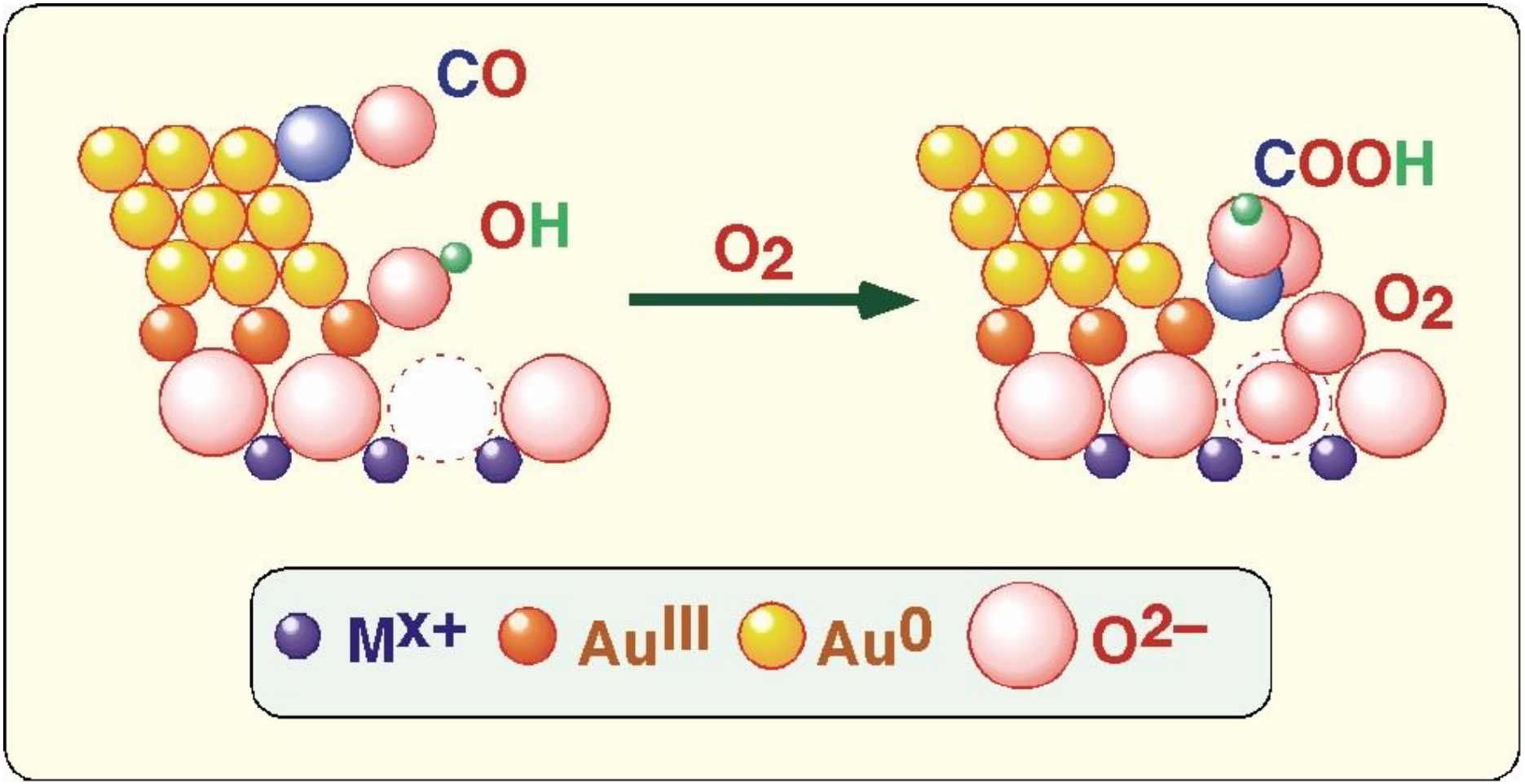


At the perimeter,

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

Water enhances the dissociation of O_2 and carbonate intermediates.

A Model at the Perimeter Interfaces



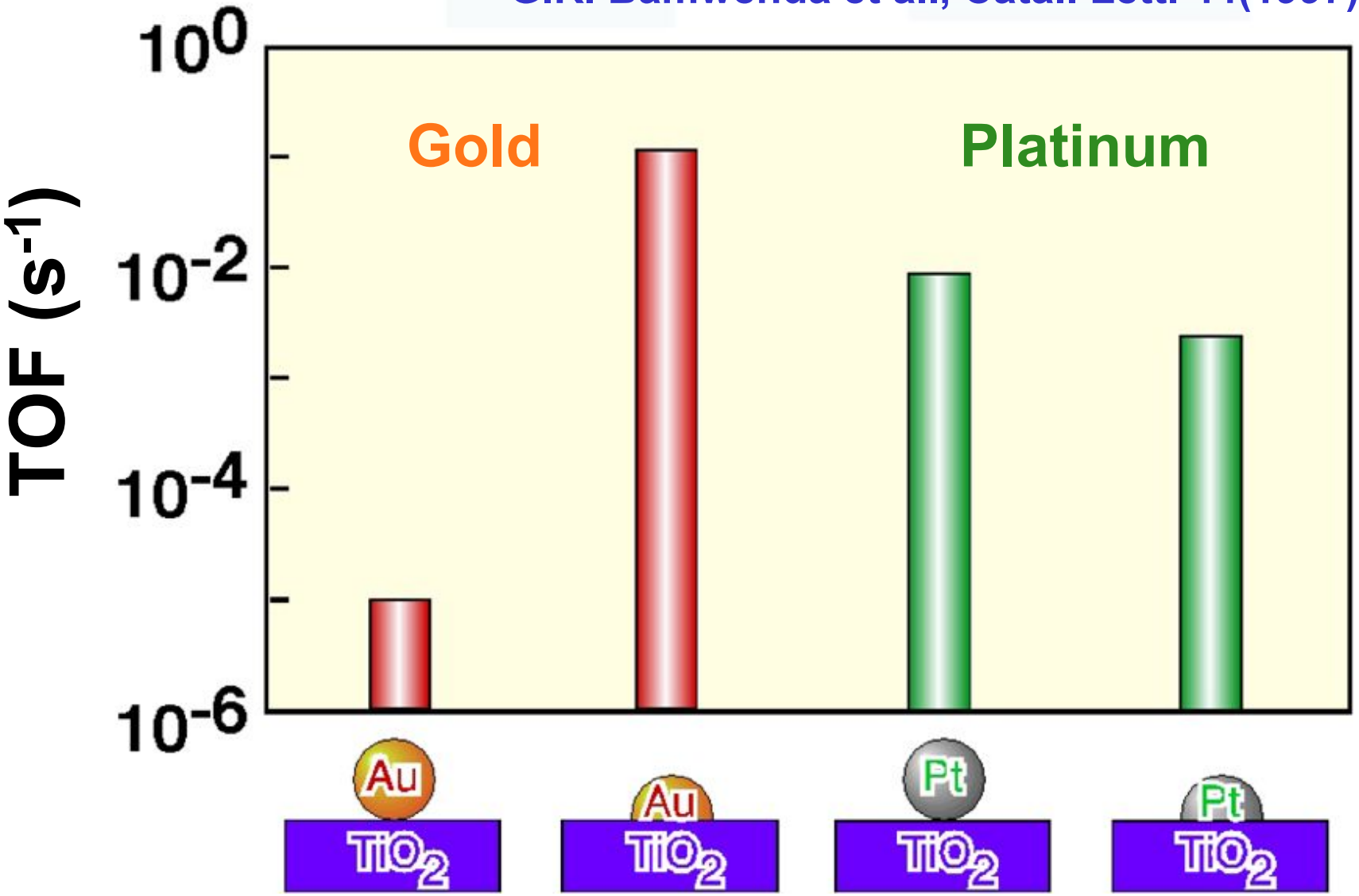
Bond and Thompson, Gold Bull., 33 (2000) 41

Three Major Factors Controlling the Activity and Selectivity

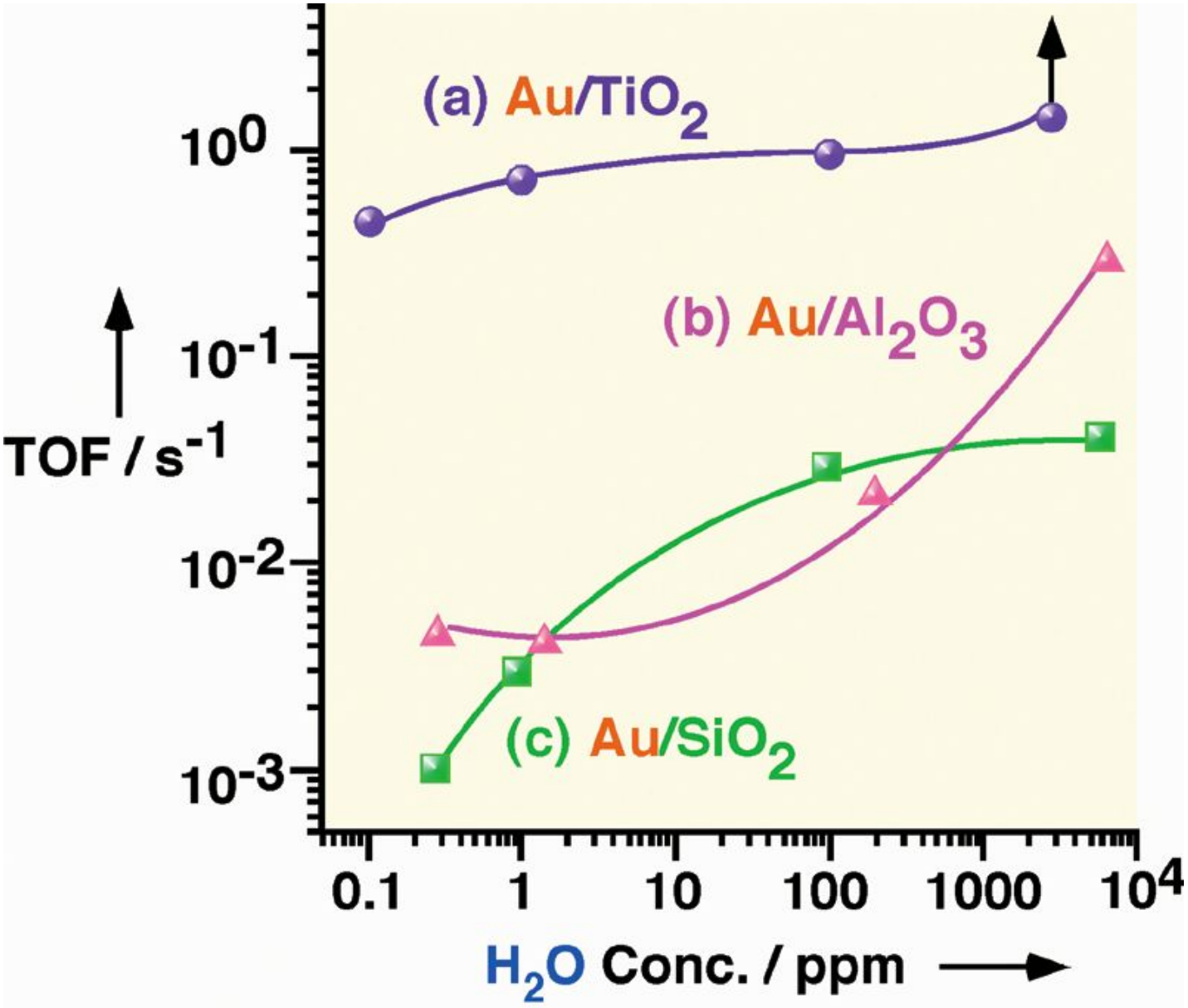
- Strong Contact with the Supports
- Type of the Supports
- Size of Au Particles

Effect of Contact Structure on CO Oxidation

G.R. Bamwenda et al., Catal. Lett. 44(1997)83.

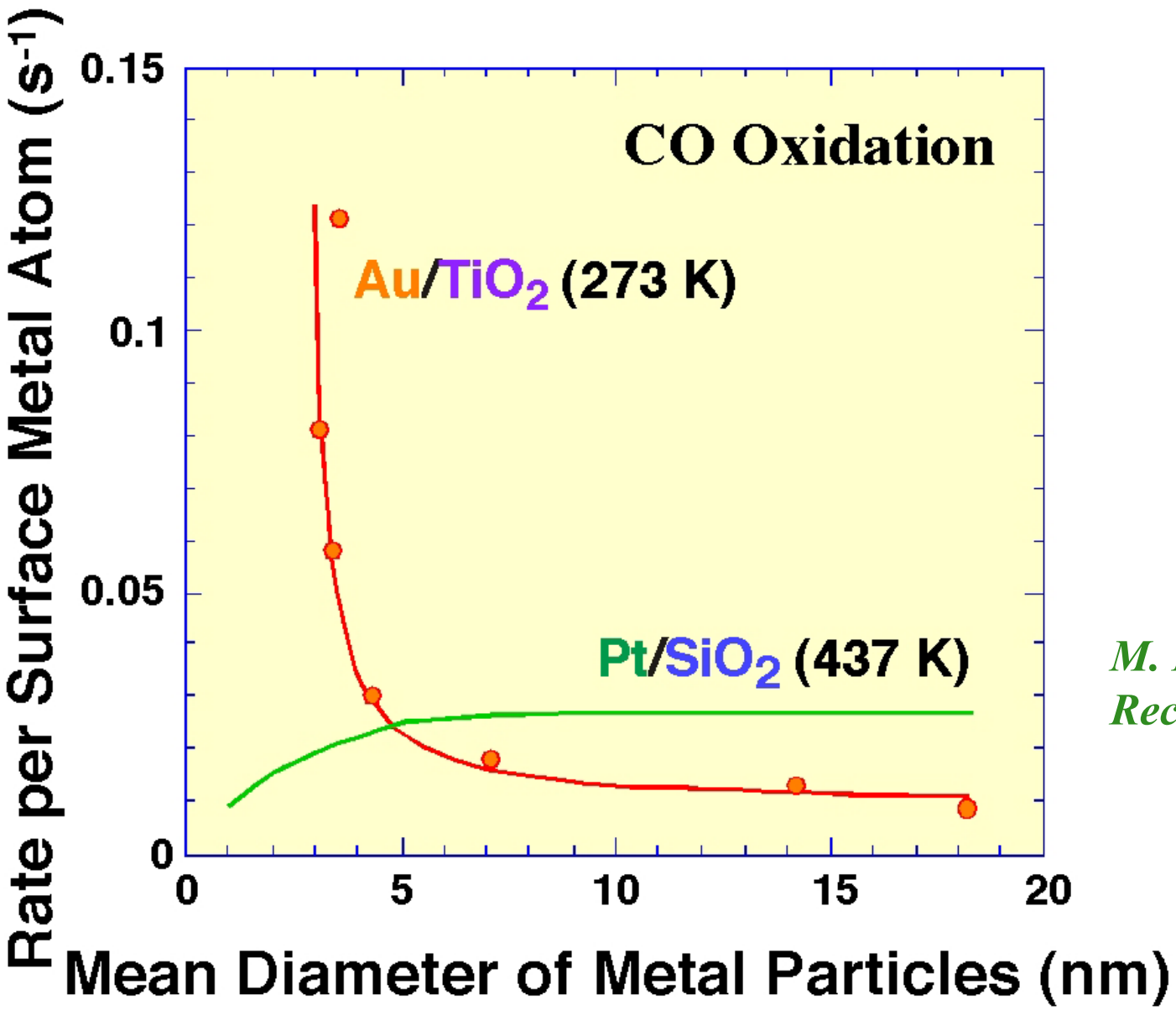


Enhancing Effect of Moisture on CO Oxidation



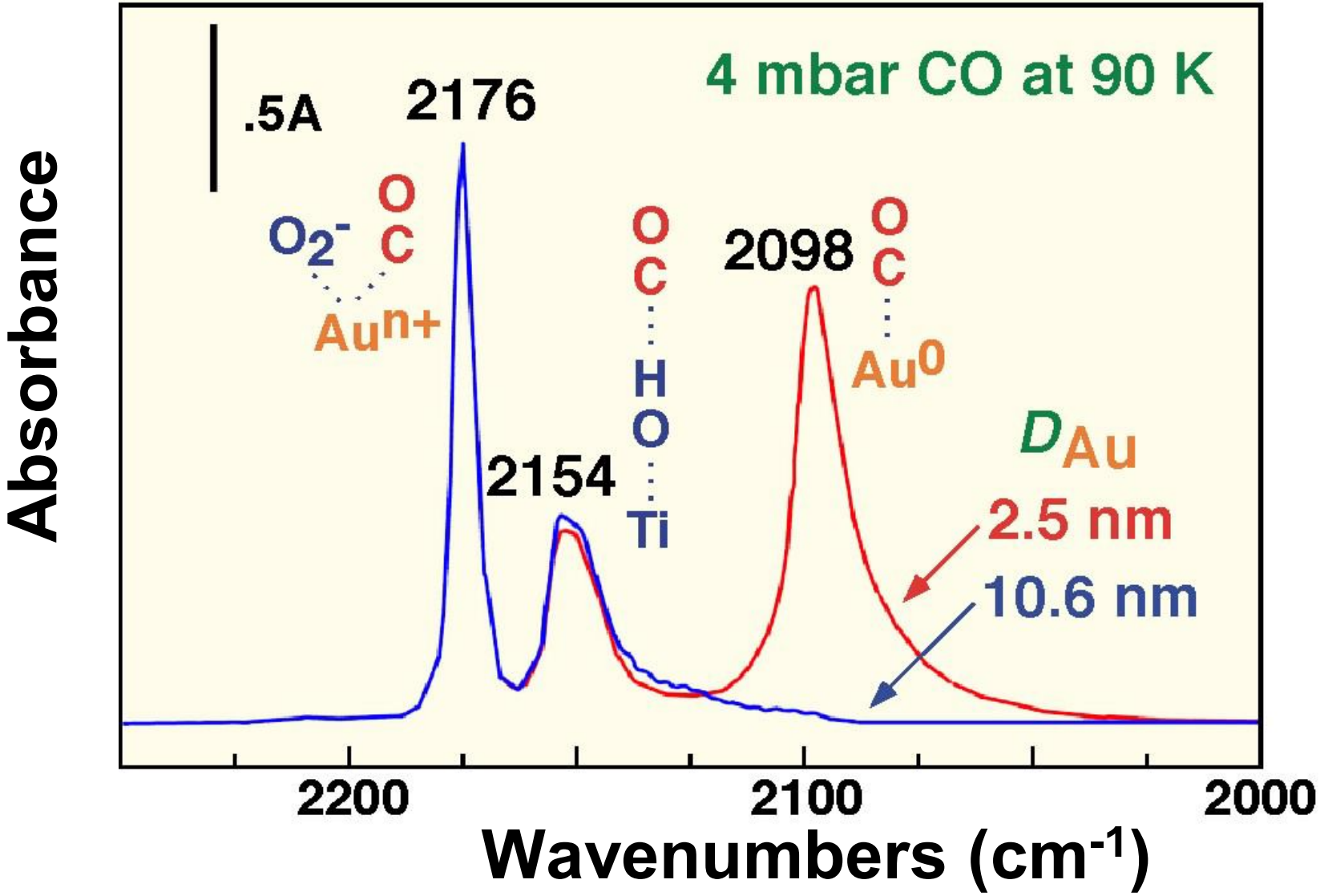
M. Date et al,
Angew. Chem. Int. Ed.
43(2004)2129.

TOF of CO Oxidation vs Particle Diameter



M. Haruta, Chem. Record 3(2003) 75.

FT-IR for CO over Au/TiO_2



F. Boccuzzi et al., J.Catal. 202(2001)256.

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

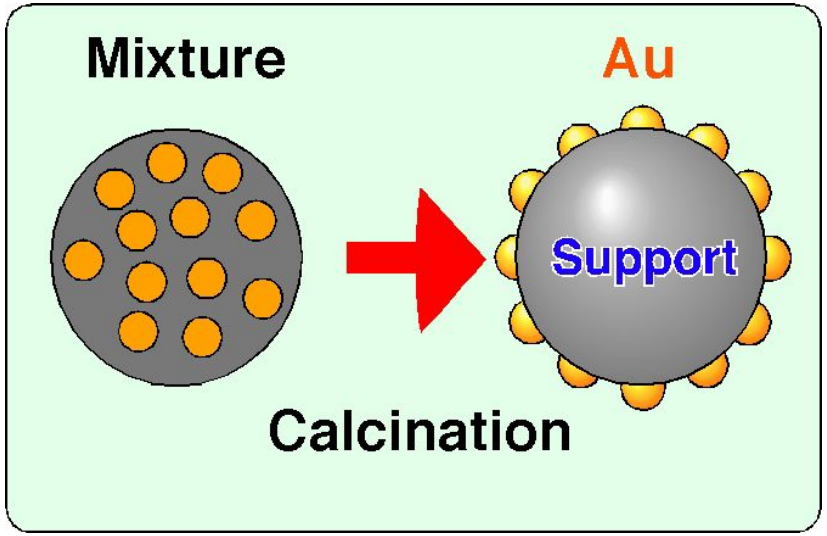
Metal oxides

Activated carbons ?

Organic polymers ?

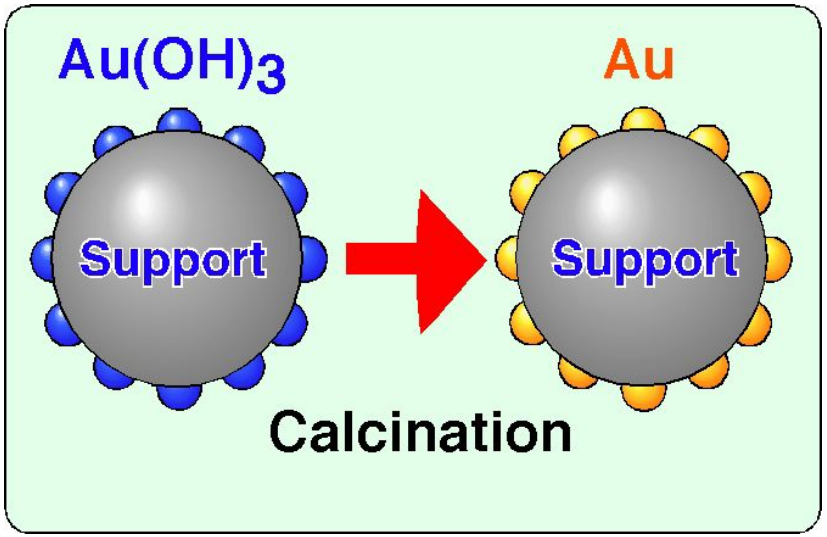
Deposition of Au NPs on Metal Oxides

Well-Mixed Precursors



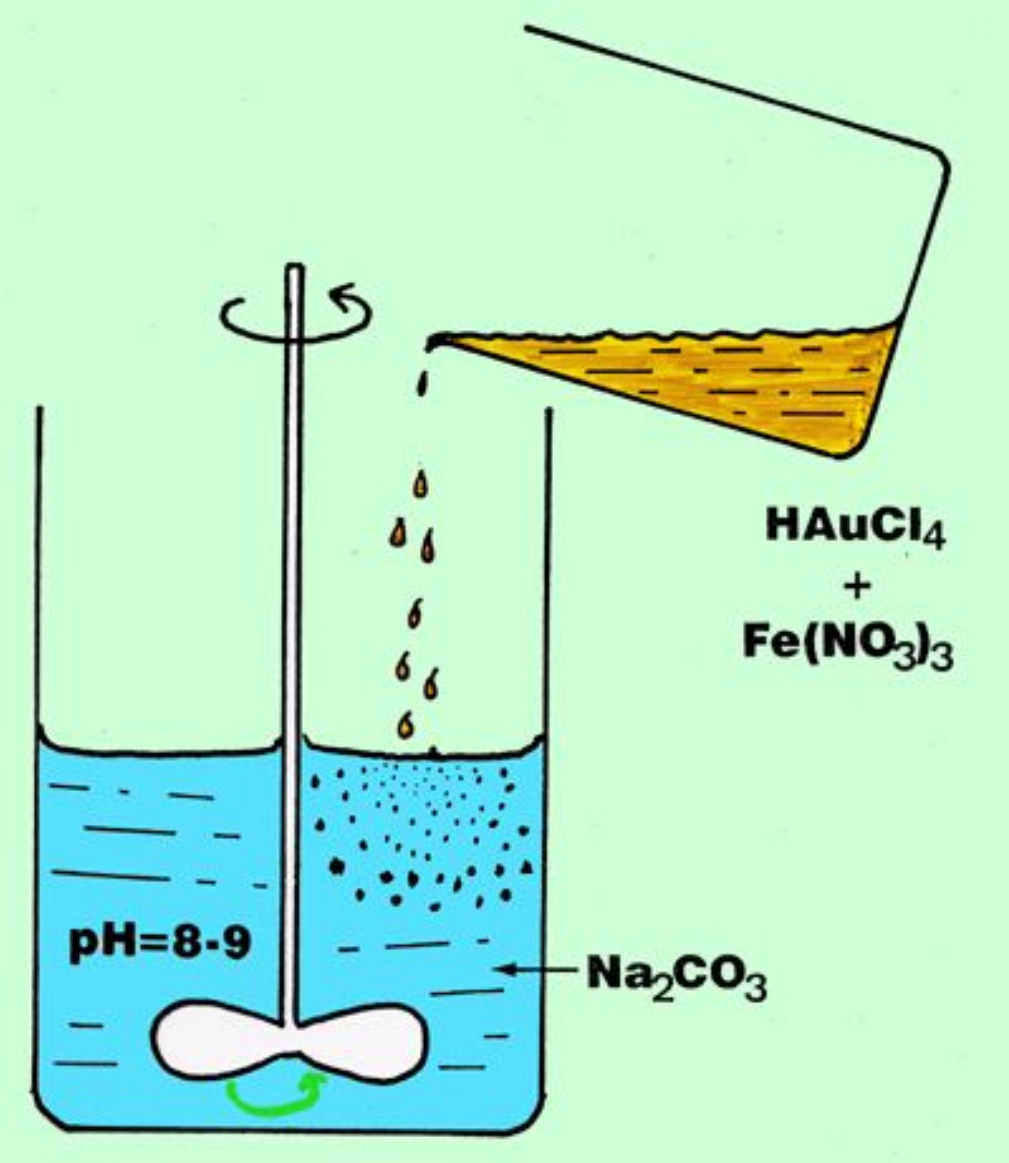
Co-sputtering
Coprecipitation
Amorphous Alloys

Surface Interaction with the Support



Gas-Phase Grafting
Liquid-Phase Grafting
Deposition-Precipitation

Co-precipitation



Au-Fe Hydroxides

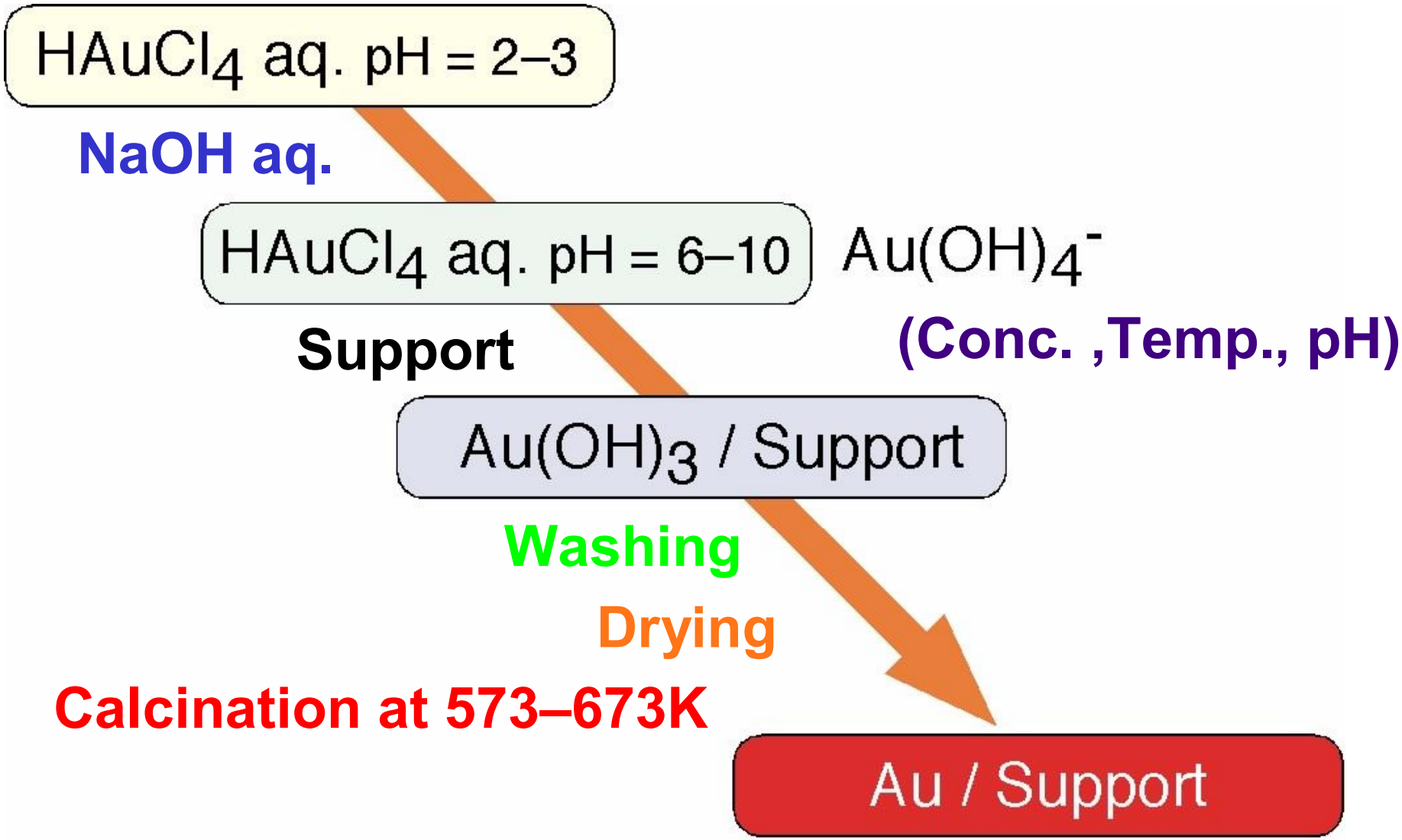
Washing

Drying

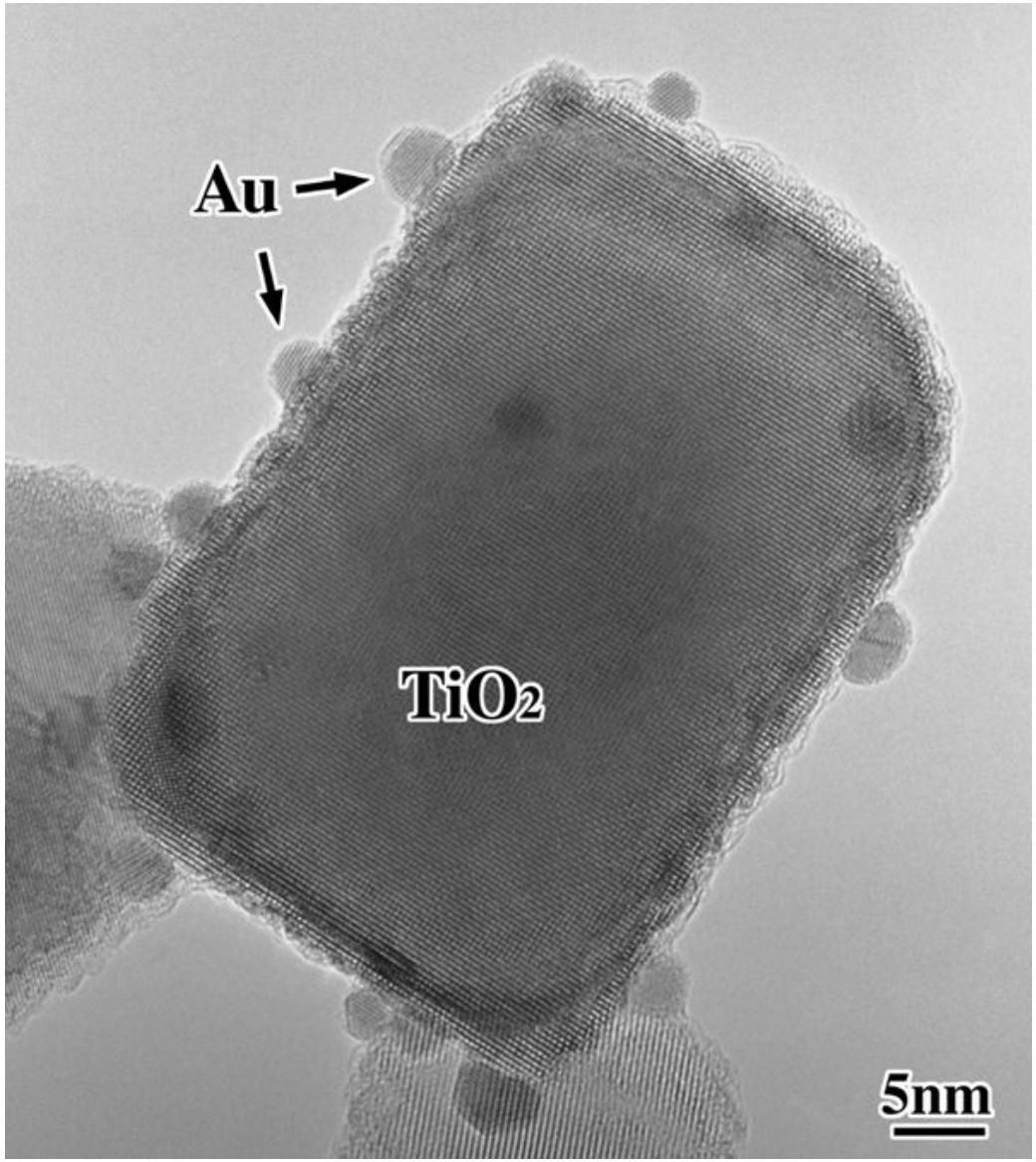
Calcination at 400℃

Au-Fe Oxides

Deposition-Precipitation Method



Au/TiO_2 Prepared by Deposition Precipitation

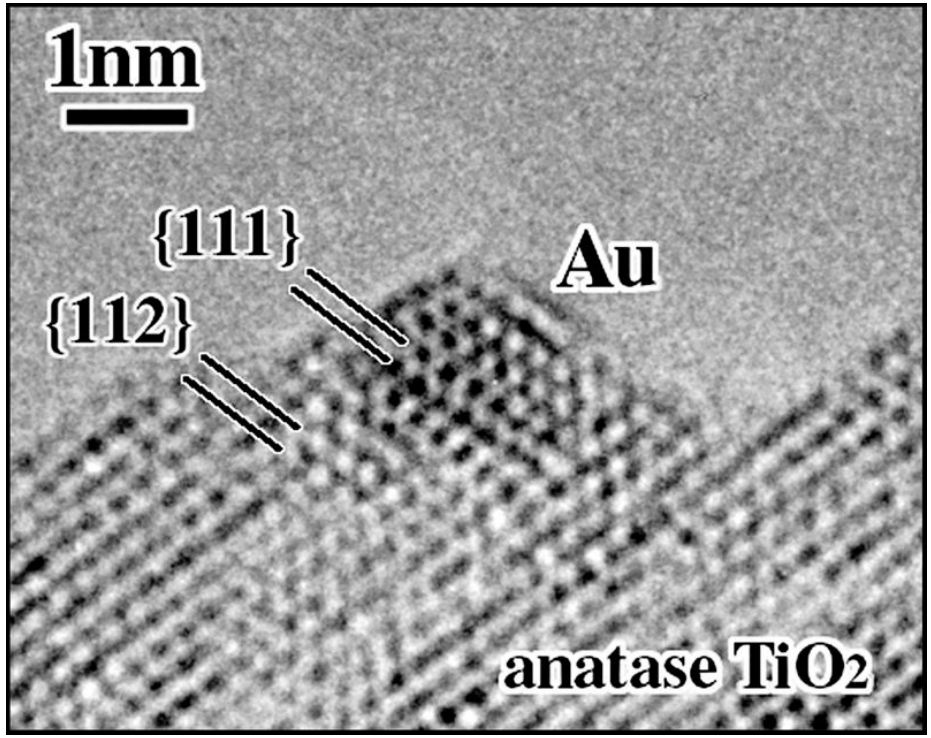


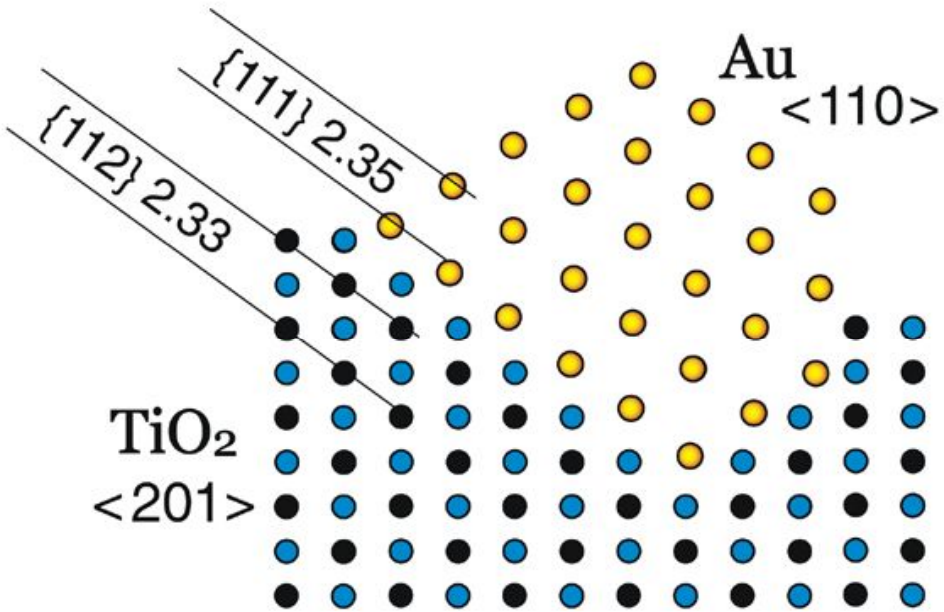
Au : 3.3wt%
TiO_2 : JRC-TIO4

pH=7, 343 K
Calcined at 673K

M. Haruta et al., J. Catal. 144(1993)175.

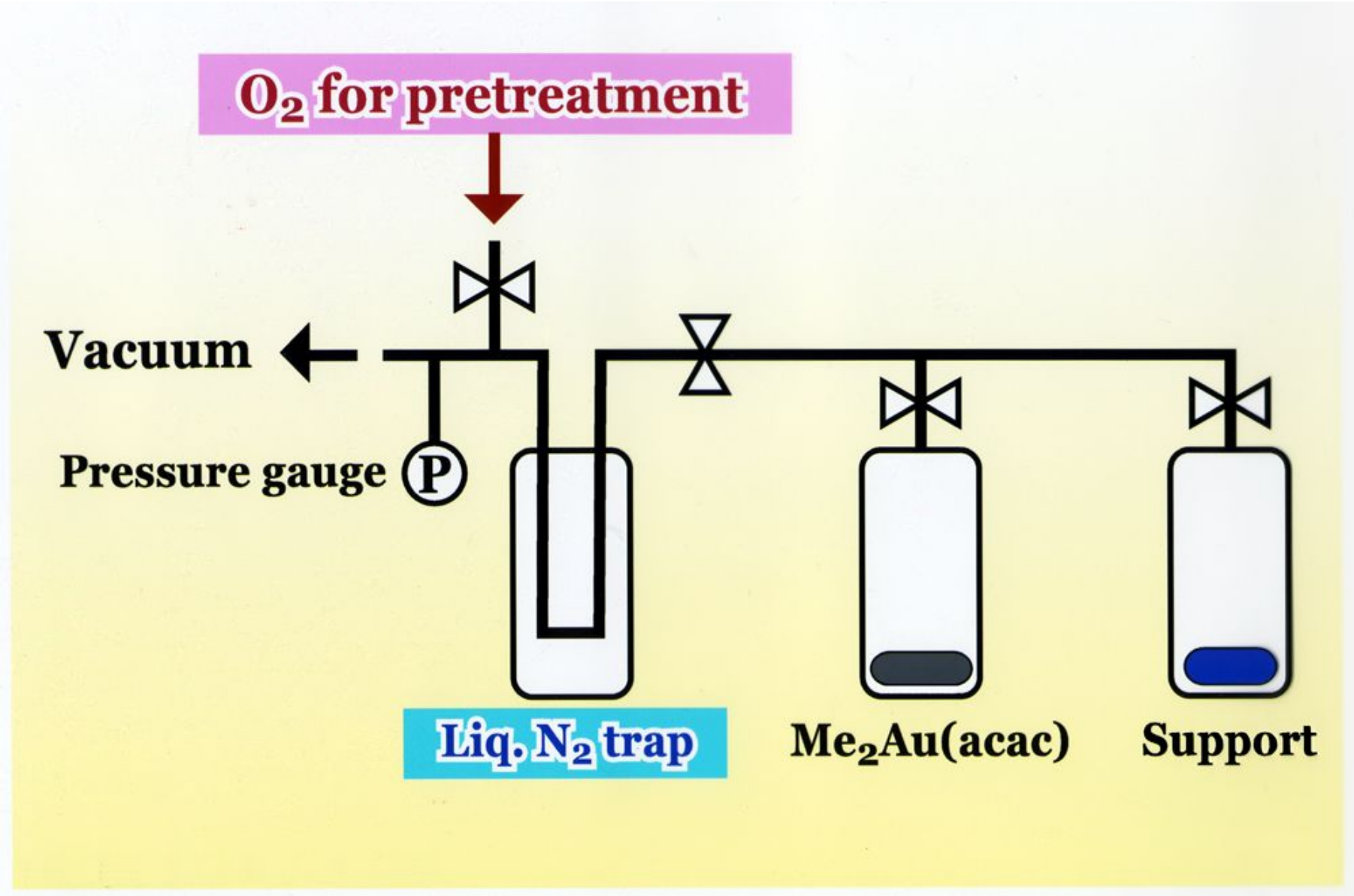
Structure of Au/TiO_2 Interface





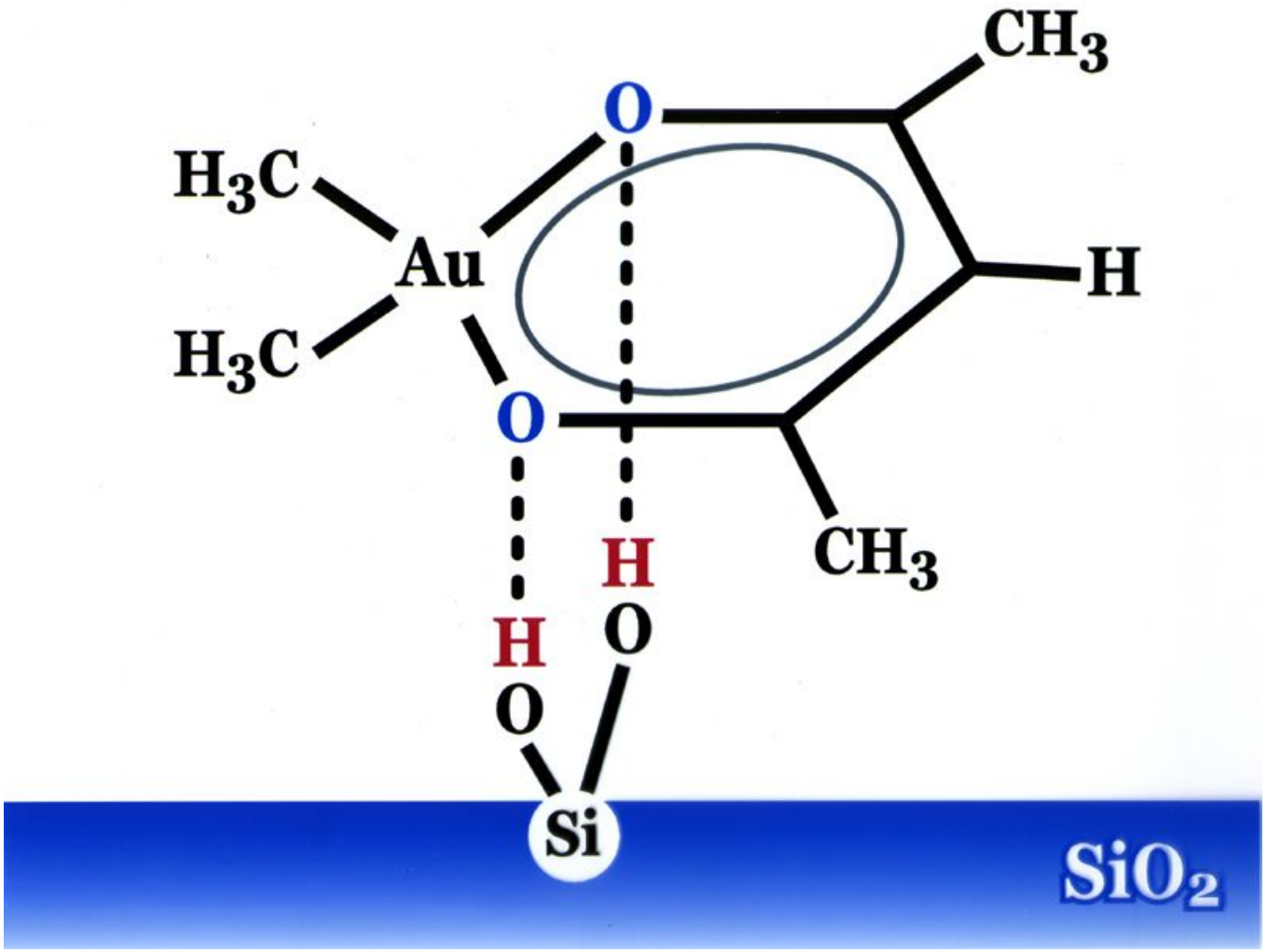
Epitaxial Contact

Gas Phase Grafting of Organo Au Complex

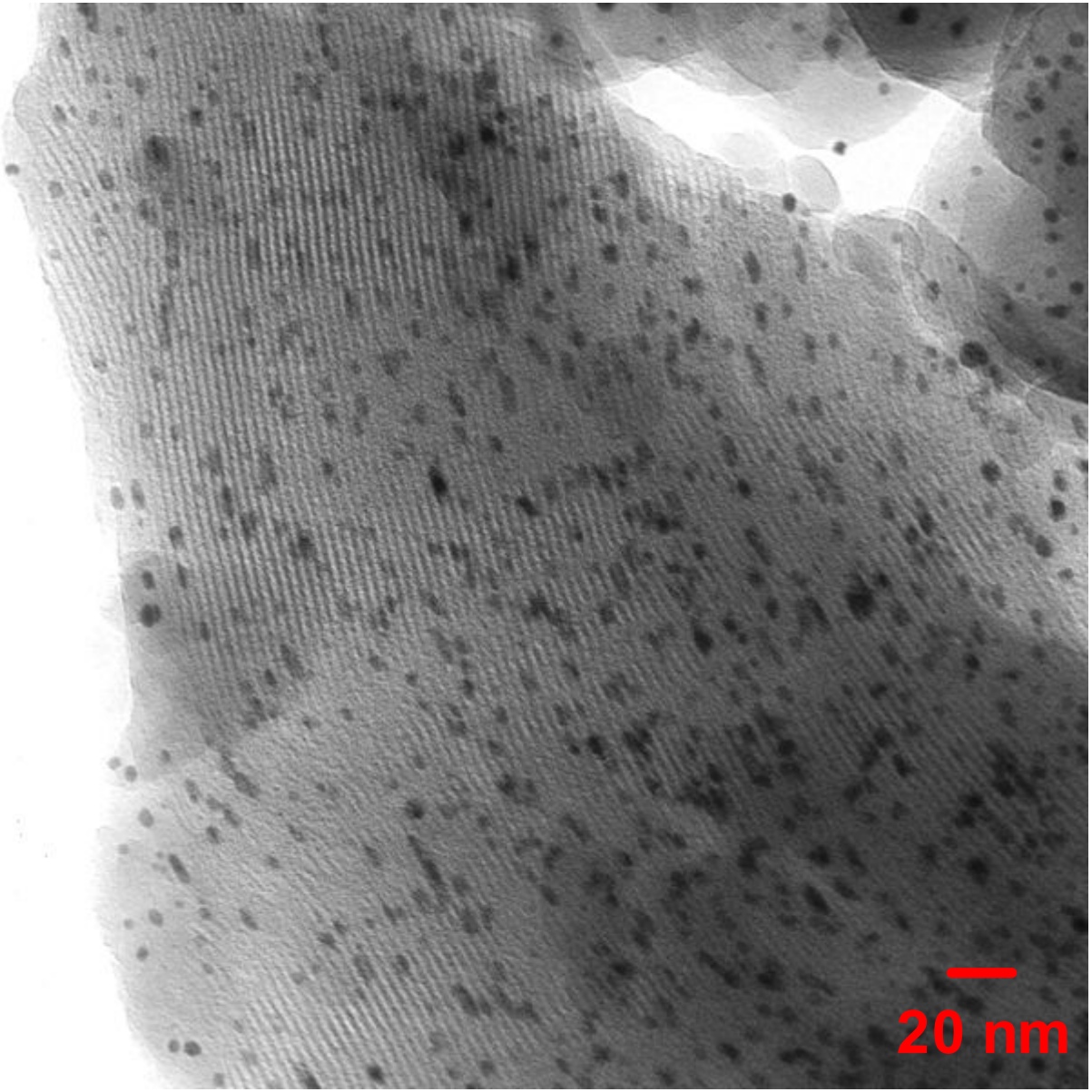


Adsorbed State of Organic Au Complex

dimethyl Au(III) acetyl-acetonate



Au/MCM-41 : Gas Phase Grafting



Adsorption at room temp.

Calcination at 573K

M. Okumura et al.

Chem.Lett.315(1998)

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.