Nanosized Gold Catalysis in Low-Temperature CO Oxidation

MATRL 265

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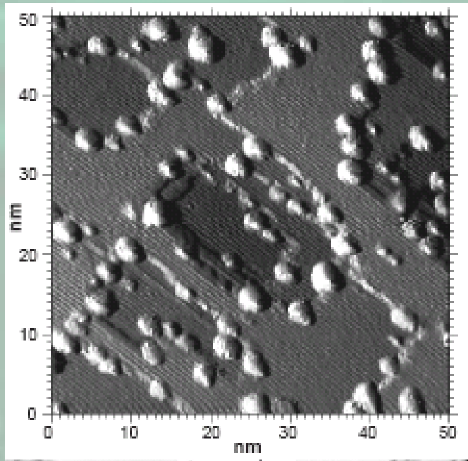
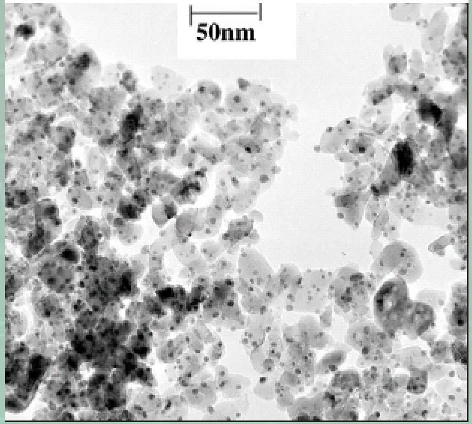
Chem&Biochem Dept.
11/03/08

OUTLINE

- Backgrounds and History
- Preparation Methods
- Origins of Activities
- Active Sites
- Effects of Supporting Materials
- Deactivation Phenomenon



$Au@TiO_2(110)$



$Au@Fe_2O_3$

Valden, M.; Lai, X.; Goodman, D. W. **Science 1998, 281, 1647-1650.**
Haruta,M. **Gold Bulletin 2004 • 37/1–2 27-36**

HISTORY

JOURNAL OF CATALYSIS 115, 301–309 (1989)

Gold Catalysts Prepared by Coprecipitation for Low-Temperature Oxidation of Hydrogen and of Carbon Monoxide

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Received October 7, 1987; revised June 6, 1988

Novel gold catalysts were prepared by coprecipitation from an aqueous solution of $HAuCl_4$ and the nitrates of various transition metals. Calcination of the coprecipitates in air at 400°C produced ultrafine gold particles smaller than 10 nm which were uniformly dispersed on the transition metal oxides. Among them, $Au/\alpha\text{-}Fe_2O_3$, Au/Co_3O_4, and Au/NiO were highly active for H_2 and CO oxidation, showing markedly enhanced catalytic activities due to the combined effect of gold and the transition metal oxides. For the oxidation of CO they were active even at a temperature as low as −70°C.

Graham J. Hutchings **Gold Bulletin 2004 • 37/1–2 3-11**
M. Haruta, N. Yamada, T. Kobayashi and S. Iijima **J. Catal. (1989)115, 301-389**

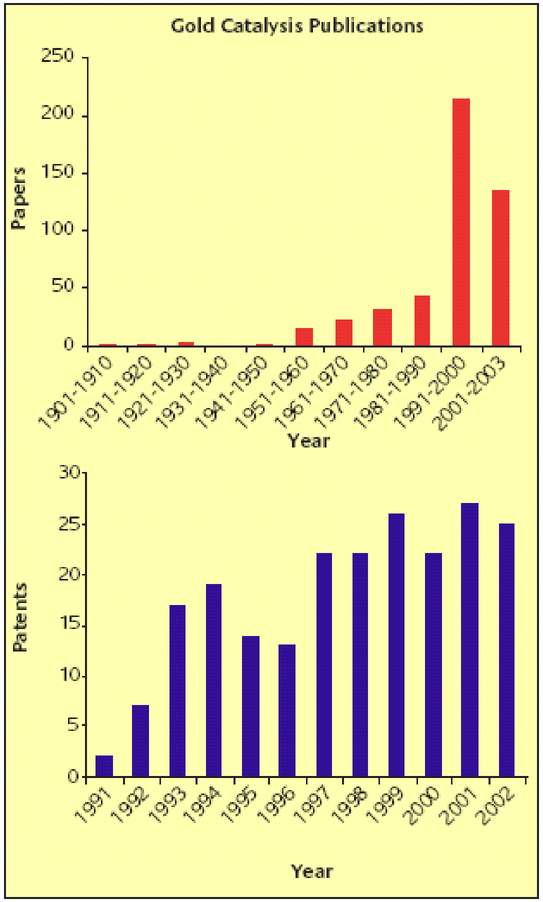
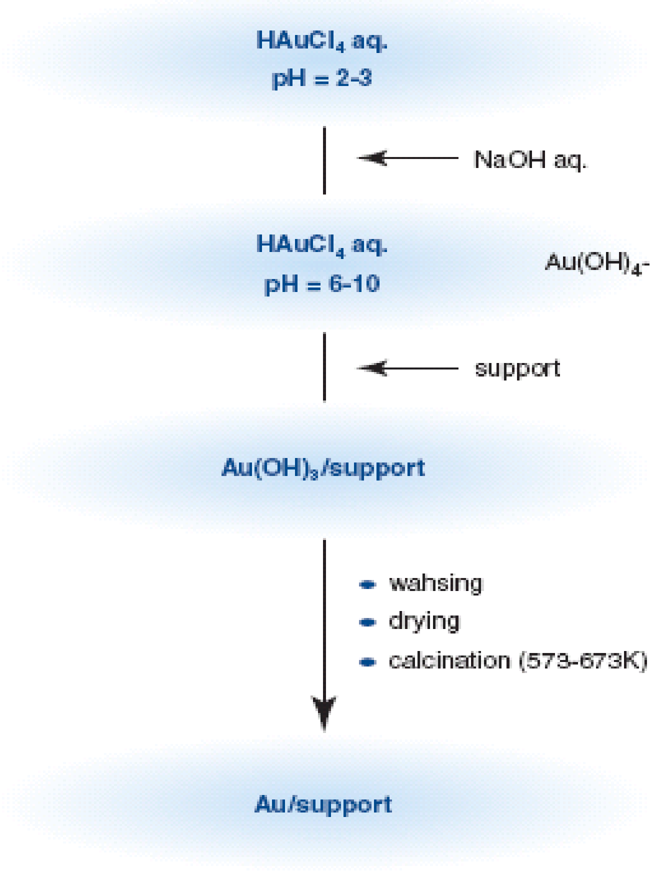
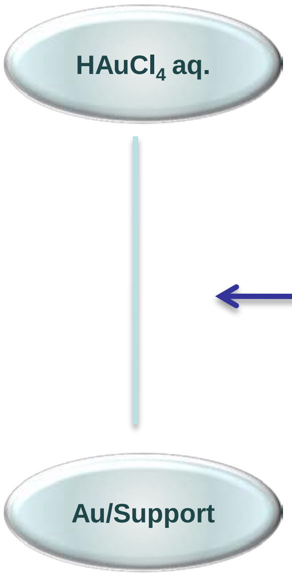


Figure 8
Publications on gold catalysis, red academic publications, blue patents

PREPARATION



Scheme 1 Flow chart of the procedure in the deposition-precipitation method.

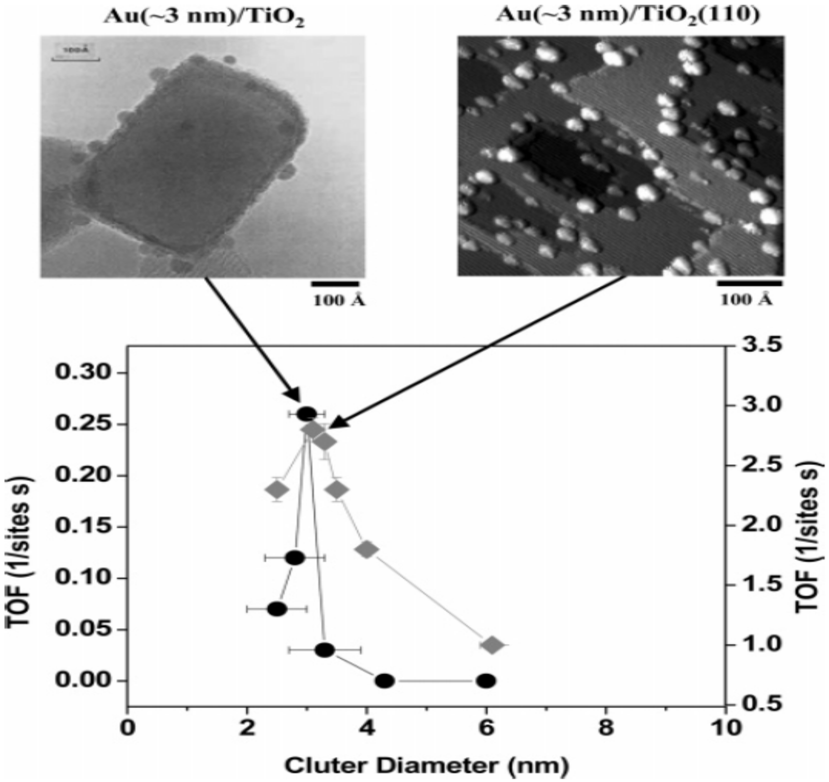


$NaBH_4$ aq.
Support

Haruta, M. **CATTECH (2002), 6(3), 102-115**

ORIGINS-Active Sites

- Particle Size



Santra, A. K.; Kolmakov, A.; Yang, F.; Goodman, D. W. *Jpn. J.* **Appl. Phys 1 2003, 42 (7B), 4795-4798.**
Gottfried, J. M.; Schmidt, K. J.; Schroeder, S. L. M.; Christmann,K. **Surf. Sci. 2003, 536 (1-3), 206-224.**

ORIGINS-Active Sites

- The Thickness

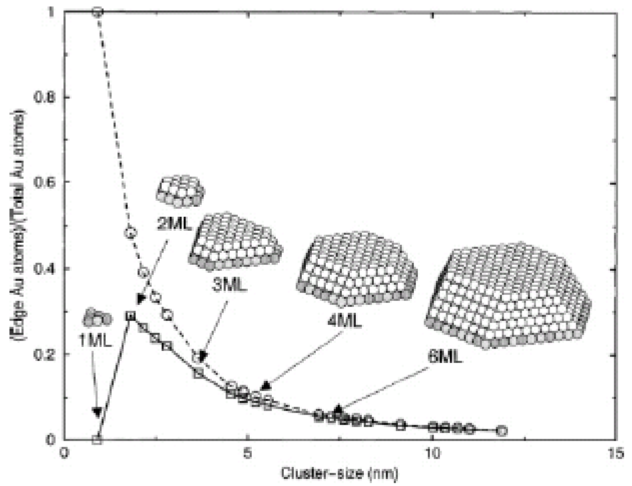


Figure 2. Calculated step density for Au particles on TiO_2 as a function of particle size. (○ and □) Total and "free" step sites on the Au particles. "Free" are the step sites not in direct contact with the support. Lines through the two sets of points are only drawn as a guide to the eye. Insets illustrate the corresponding Wulff constructions for selected particle sizes. Reprinted from ref 31, Copyright 2000, with kind permission of Springer Science and Business Media.

$$CO \longrightarrow CO_{ads}$$

$$O_2 \longrightarrow 2O_{ads}$$

$$O_{ads} + CO_{ads} \longrightarrow CO_2$$

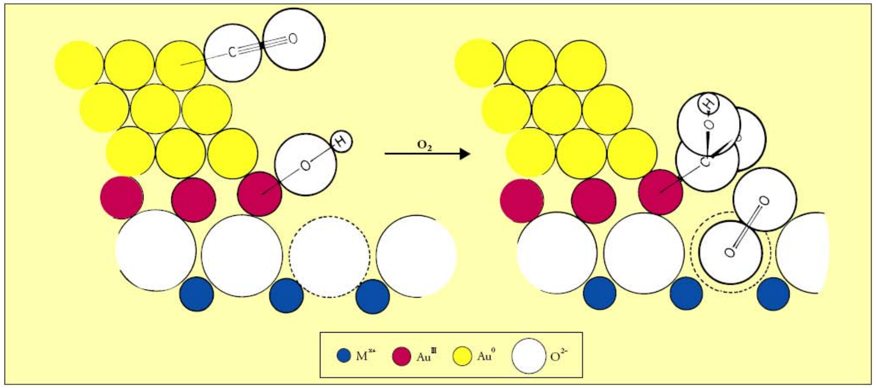


Figure 9
Schematic representation of the mechanism of CO oxidation (10)

Mavrikakis, M.; Stoltze, P.; Norskov, J. K. **Catal. Lett. 2000, 64 (2-4), 101-106.**
G.C. Bond and D.T. Thompson, **Gold Bull. 33 (2000) 41.**

ORIGINS-Supporting Materials

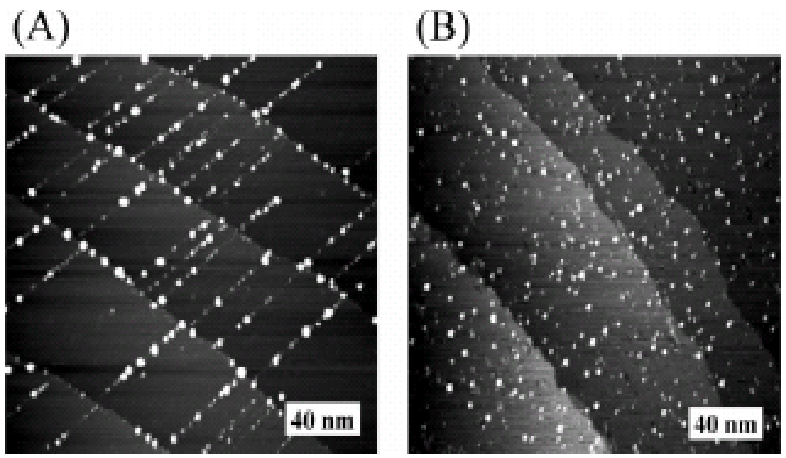


Figure 7. STM images (200 nm × 200 nm) of gold particles supported on a SiO_2 thin film annealed at (A) 1200 (less defective) and (B) 1100 K (more defective). In the film A, gold particles nucleate and grow preferentially at step edges and line defects, while more random distributions of gold particles on terrace regions were observed in the film (B). Reprinted with permission from refs 52 and 53. Copyright 2004 American Chemical Society.

Min, B. K.; Wallace, W. T.; Goodman, D. W.
J. Phys. Chem. B 2004, 108 (38), 14609-14615.
(53) Min, B. K.; Wallace, W. T.; Santra, A. K.; Goodman, D. W.
J. Phys. Chem. B 2004, 108 (42), 16339-16343.

- **Anchoring Sites for Gold Particles**
- Effecting the Dispersion and Shape
- Oxygen Vacancies

ORIGINS-Supporting Materials

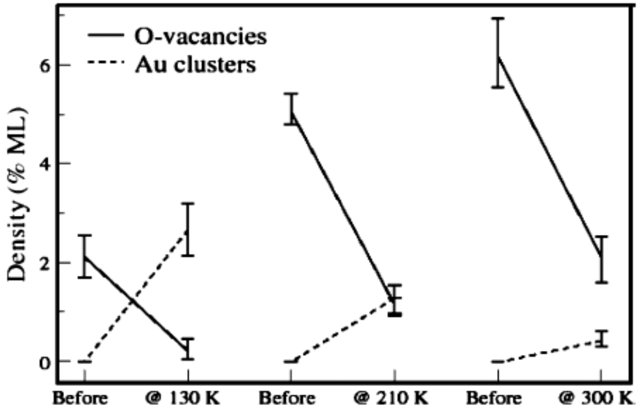


Figure 6. Densities of vacancies and Au clusters before and after deposition of ~0.04 ML Au at different temperatures. 1 ML = 1 vacancy or cluster/TiO_2 (110) unit cell = 5.13×10^{14} cm^{-2}. The data were obtained from corresponding high-resolution STM images. Reprinted with permission from ref 50 (http://link.aps.org/abstract/PRL/v90/p026101). Copyright 2003 by the American Physical Society.

Wahlstrom, E.; Lopez, N.; Schaub, R.; Thostrup, P.; Ronnau, A.; Africh, C.; Laegsgaard, E.; Norskov, J. K.; Besenbacher, F. **Phys.ReV. Lett. 2003 90, 026101-1.**

- Anchoring Sites for Gold Particles
- Effecting the Dispersion and Shape
- **Oxygen Vacancies**

DEACTIVATION

2.6nm(Diameter)/0.7nm(Height)

10 torr $CO:O_2$ for 120 min at 300 K

3.6nm(Diameter)/1.4nm(Height)

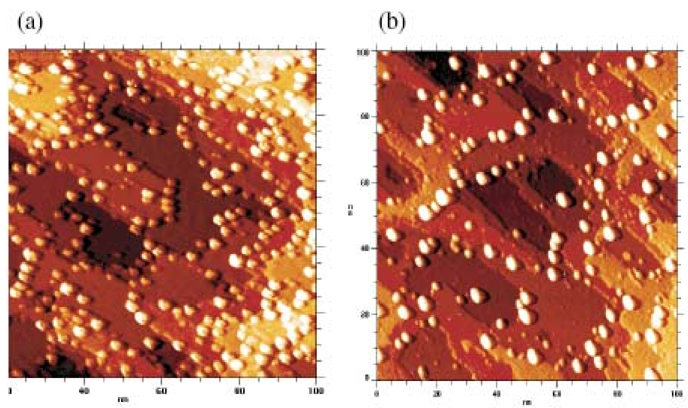


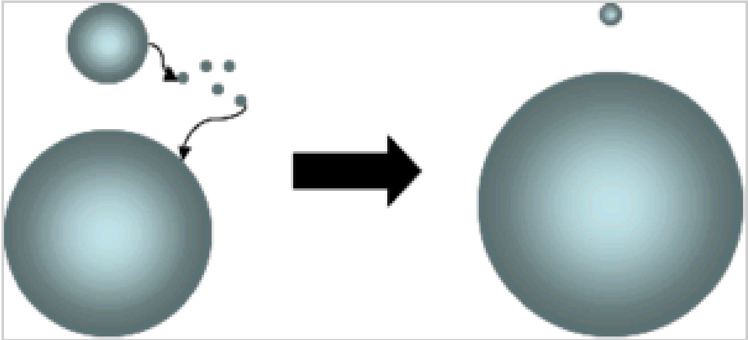
Figure 4. Topographic STM images of 0.25 ML Au clusters on a $TiO_2(110)$ surface (a) before and (b) after 10 torr CO/O_2 exposure for 120 min at room temperature [33].

X.F. Lai and D.W. Goodman,
J. Mol. Catal. A 162 (2000) 33.

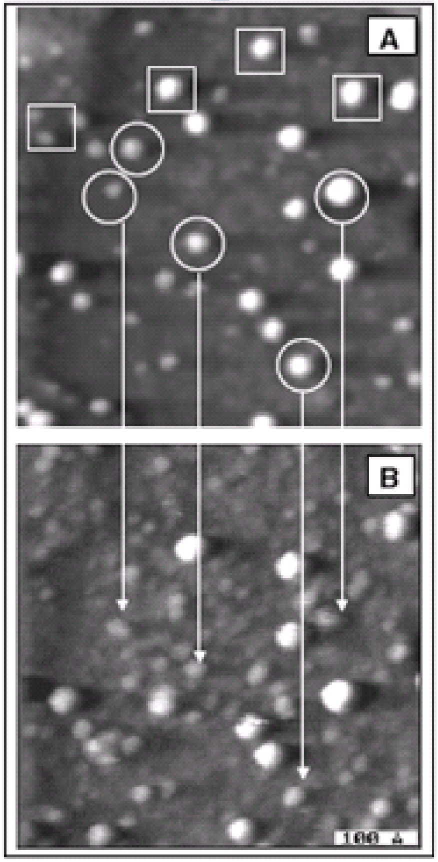
DEACTIVATION

(i) migration of surface clusters and coalescence subsequent to their collision

(ii) Ostwald ripening



Basic schematic of the Ostwald ripening process



A. Kolmakov and D.W. Goodman, B.
Surf. Sci. Lett. 490 (2001) L597.

Thank you for your attention!