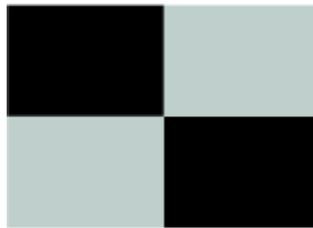




Modern Alchemy: Catalysis by **Gold** Nano-particles: Part 2

*PIRE-ECCI/ICMR
Summer Conference
Santa Barbara
17 August, 2006*



*Masatake Haruta
Tokyo Metropolitan
University*

1. Carbon and **Gold** in Nanotechnology
2. Applications of Gold Catalysts
 - Air Quality Control
 - Propylene Epoxidation**
 - Liquid Phase Aerobic Oxidation
3. Clusters

Nano-Science & Technology

$$\begin{aligned} 1 \text{ nm} &= 1 \times 10^{-3} \mu\text{m} \\ &= 1 \times 10^{-6} \text{ mm} \\ &= 1 \times 10^{-9} \text{ m} \end{aligned}$$

$$1 \text{ mm} = 1 \times 10^{-9} \times 1000 \text{ km}$$

ping pong ball the Earth

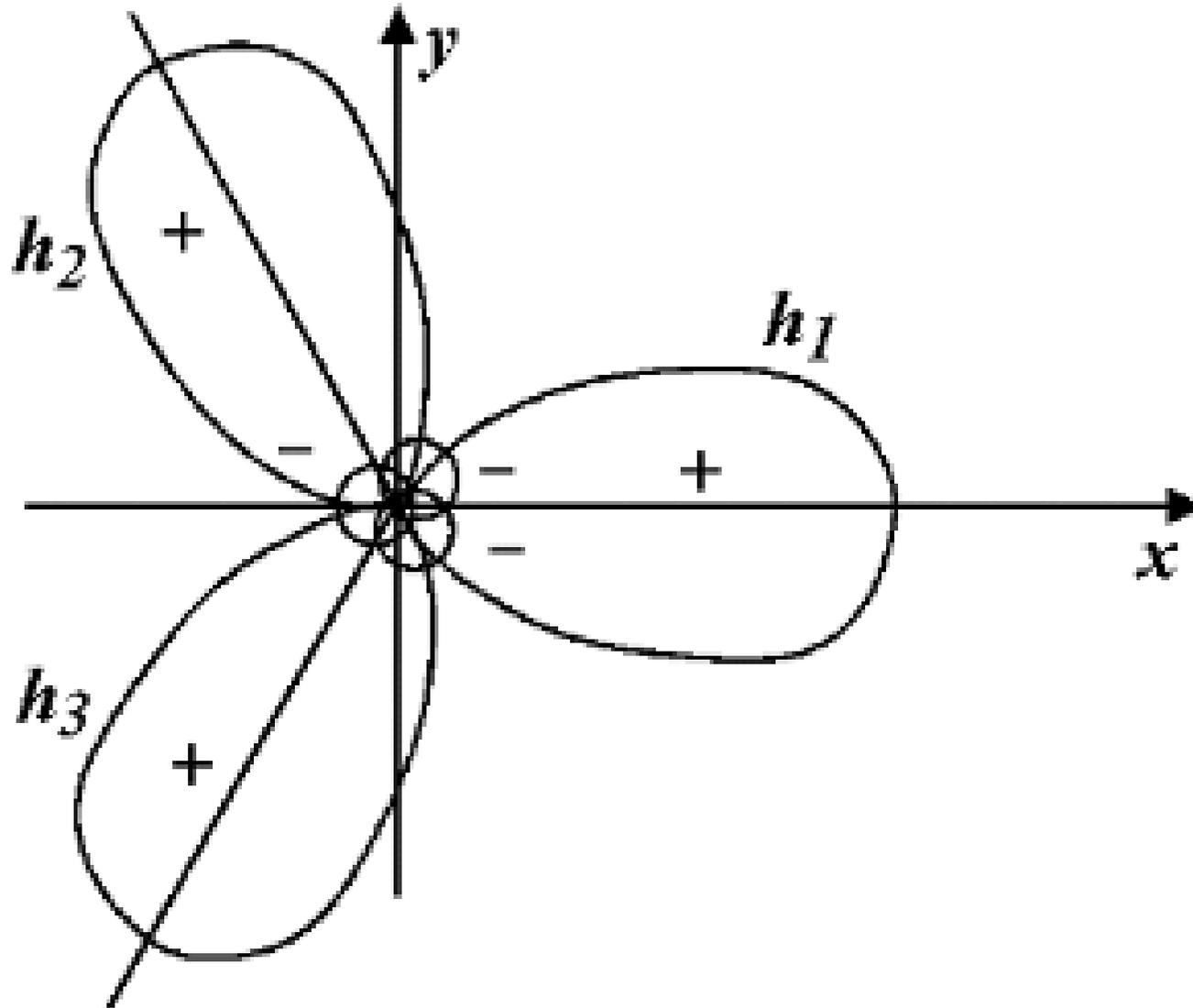
What elements are the major players in Nanotechnology?

- It is a **must** for commercial applications that a material should be stable under ambient atmosphere.

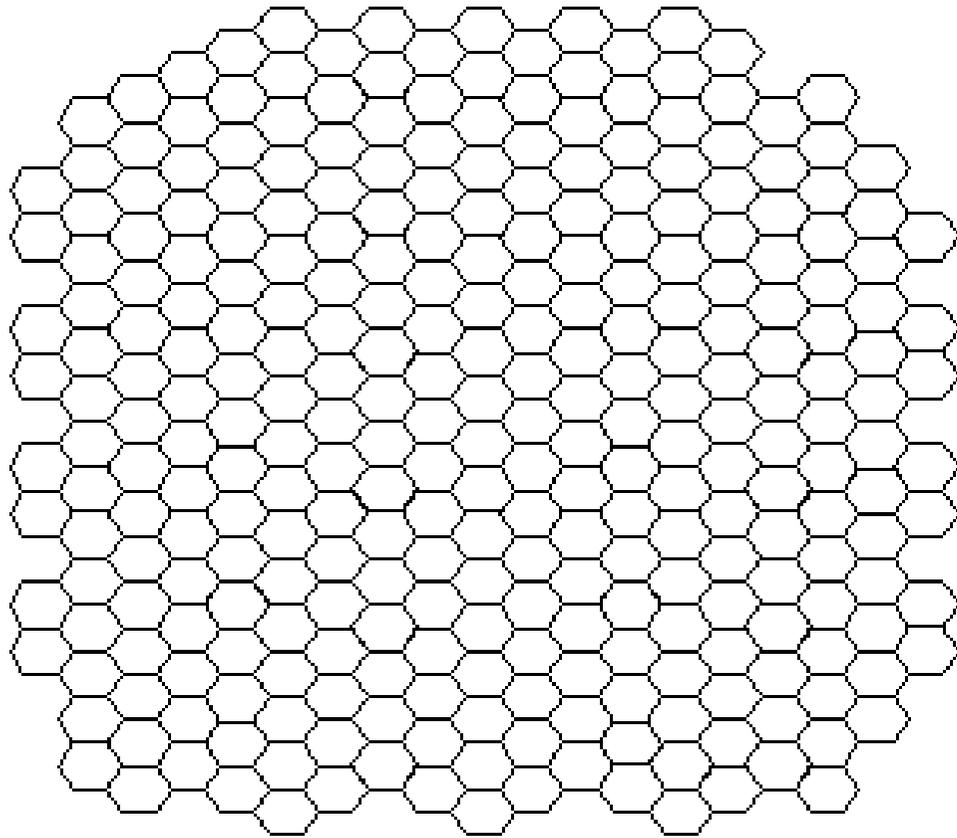
Carbon : 2- and 3- dimensional structure
sp² → graphite, C 60, nanotube, activated C
sp³ → diamond

Gold : Thermodynamically the most stable,
Dramatic size effect, Recyclable.

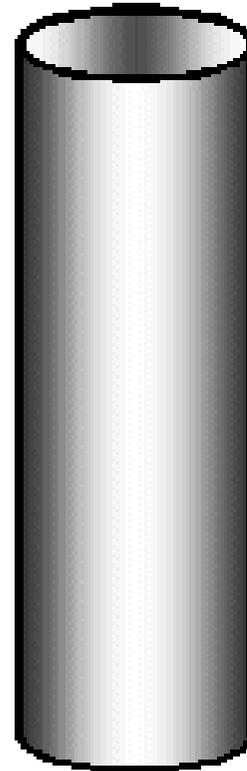
S p 2* hybrid orbital :** ***graphite, fullerene, nanotube



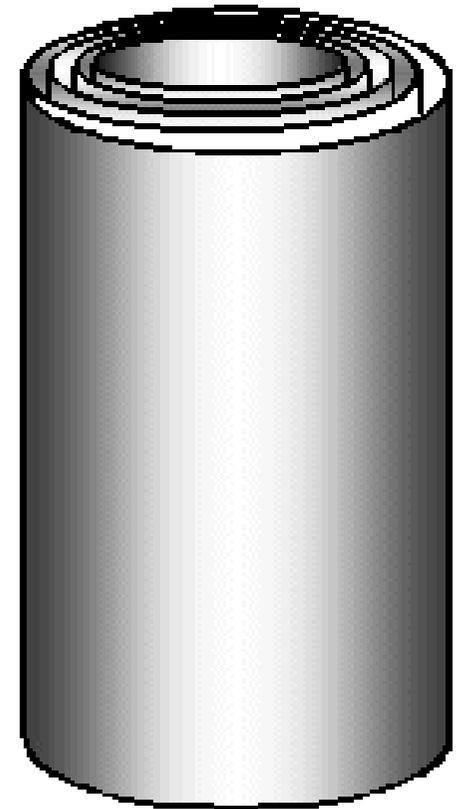
Single and Multi Wall Carbon Nanotube



グラフェンシート

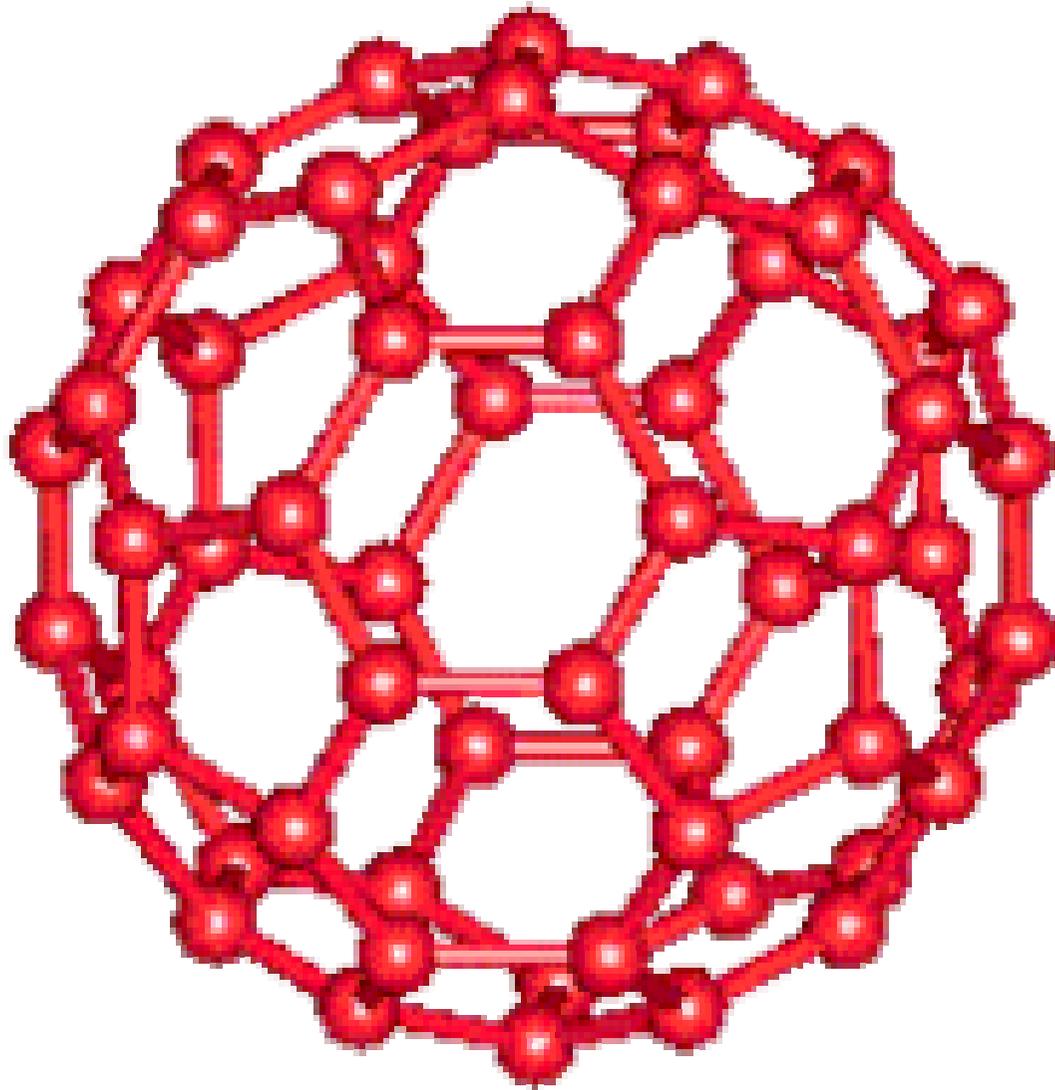


SWCNT



MWCNT

Buckminster fullerene : C60



Presumed by Prof.
Osawa(Kyoto Univ.)

Discovered in 1985

F. Curl Jr.,

H. W. Kroto

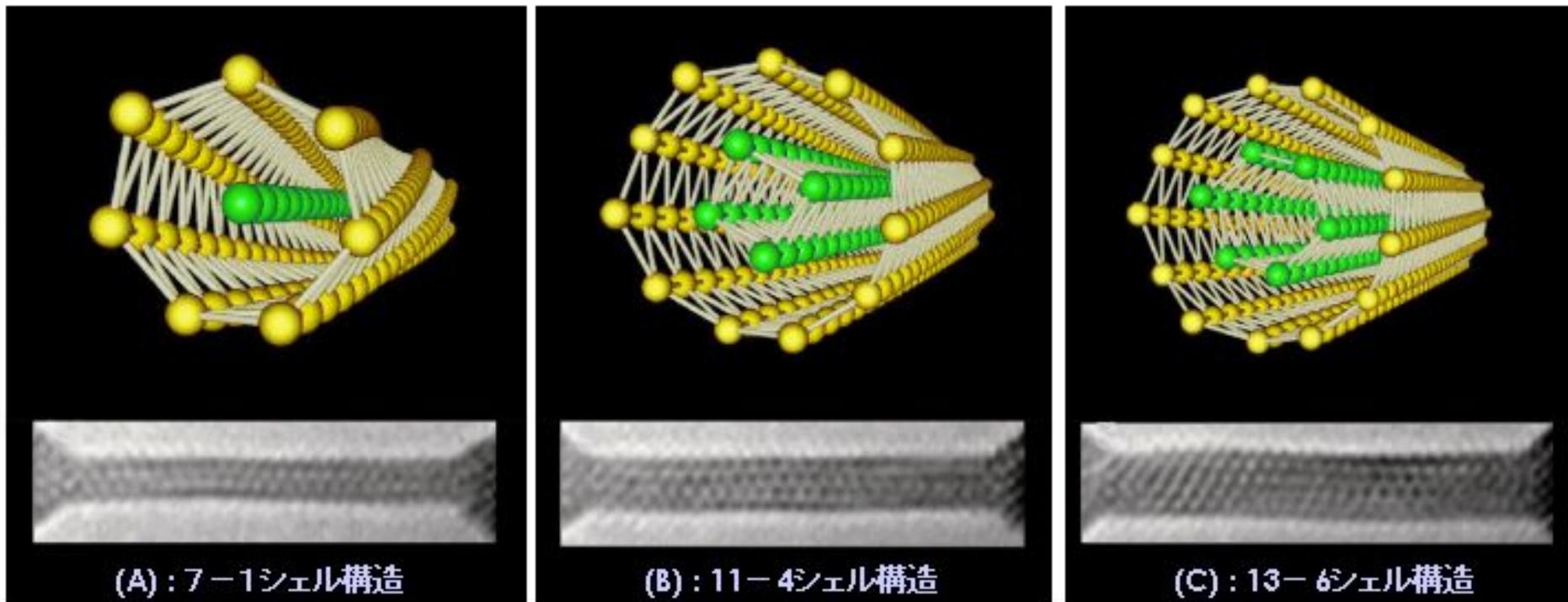
R. E. Smalley

Diameter 1nm

1×10^8 rotation/sec.

Gold Nano-wire : “7” is the magic number.

High Resolution Transmission Electron Microscopy
by Prof. Kunio Takayanagi, Tokyo Inst. Tech.



金のナノワイヤの二重シェル構造モデルの鳥瞰図と電子顕微鏡写真



Gibbs Energy of Reaction

$$\Delta_r G = \Delta_r H - T \Delta_r S$$

Gibbs Energy

Enthalpy

Absolute
Temp. Entropy

0 : equilibrium

heat of reaction under
constant pressure

regularity in
molecular array

+ : not naturally
occurring

+ : endothermic

+ : disordered

— : naturally
occurring

— : exothermic

— : ordered

Gibbs Energies for metal oxide formation : **Yes** or **No** ?

$\Delta_f G^\circ(298\text{K}), \text{kJ/mol O}_2$

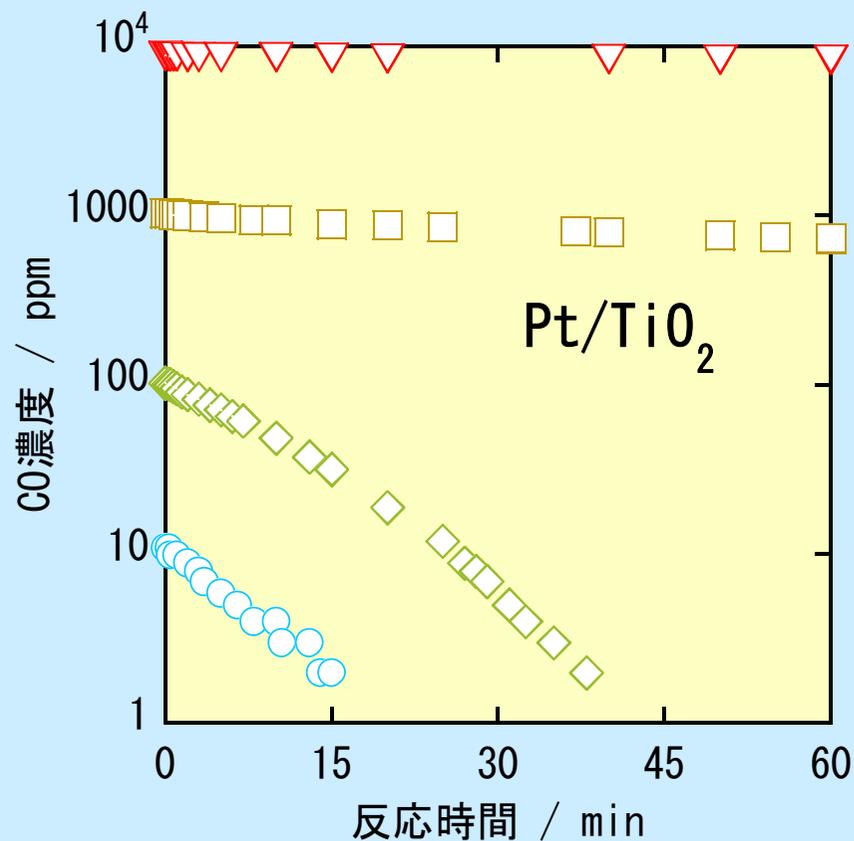
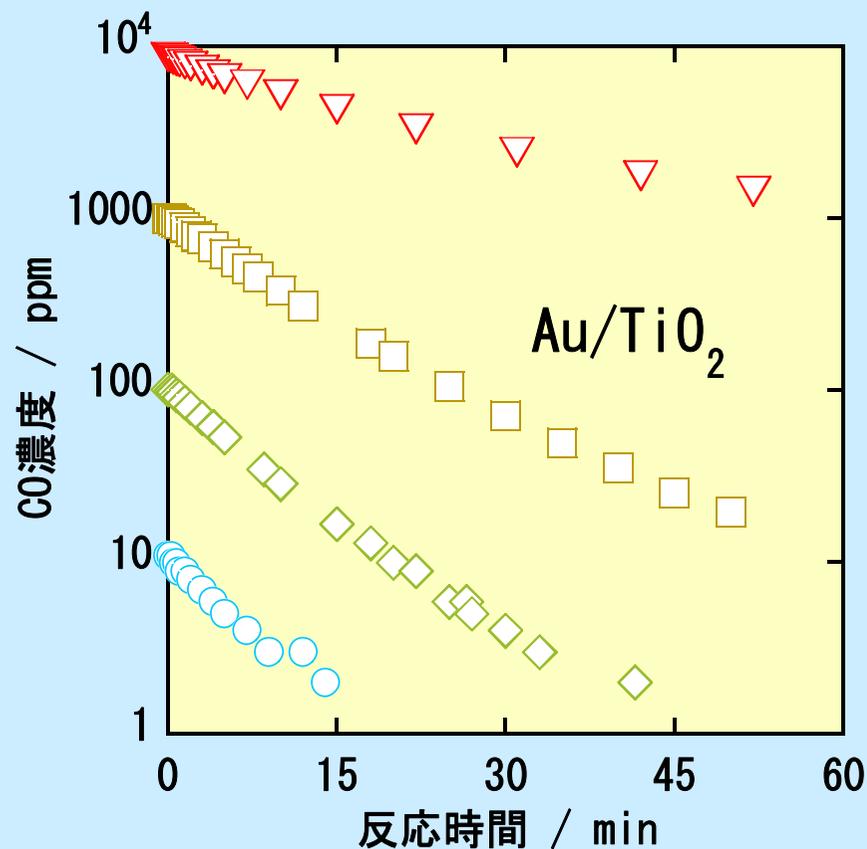


Where are **Gold** Catalysts used?

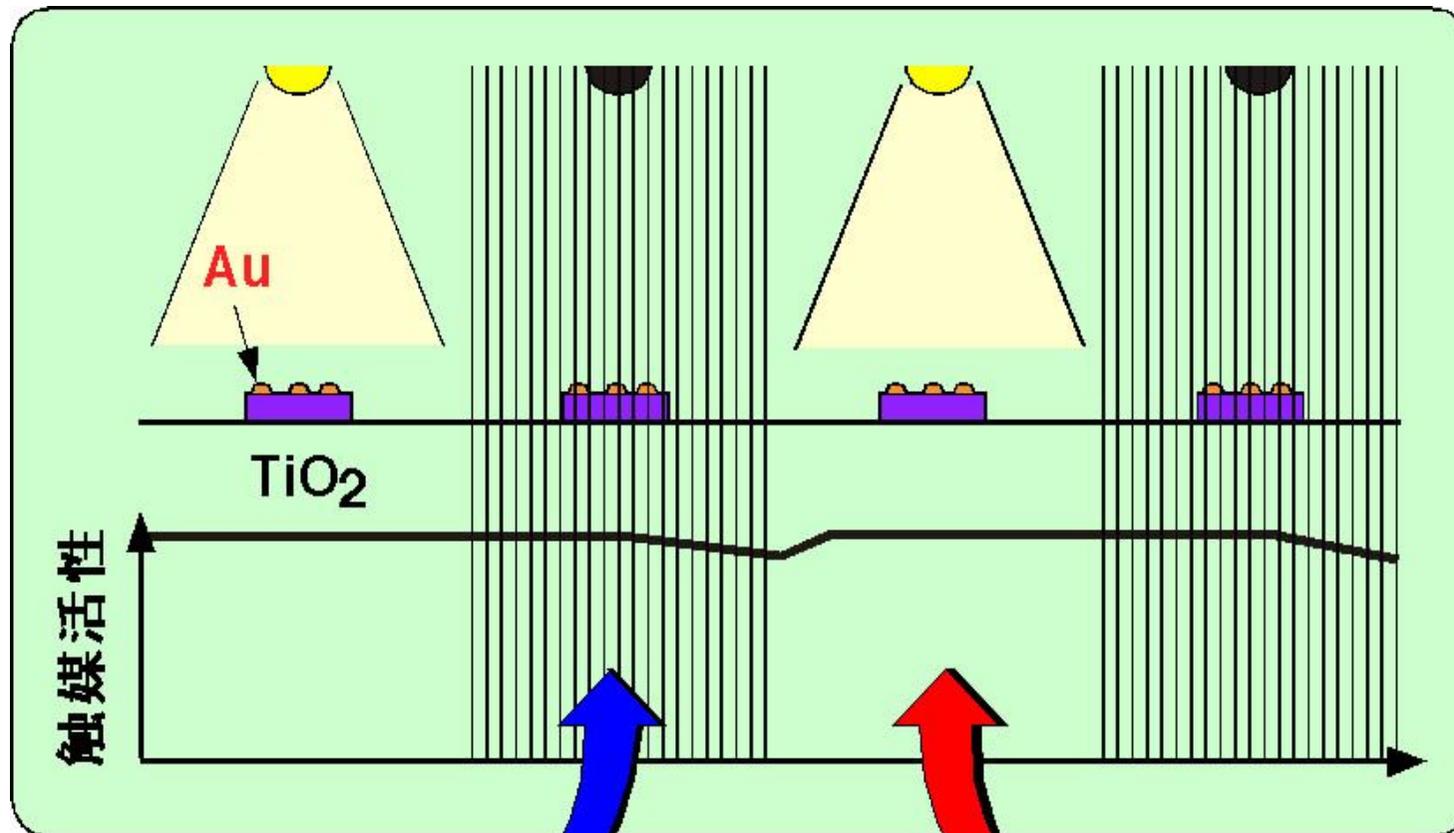
- **Air Purification: CO, HCHO, Odor**
- **H₂ Production: H₂O shift, CO oxid.**
- **Propylene Epoxidation**
- **Aerobic Oxidation: alcohols,
alkenes**
- **Direct H₂O₂ Synthesis**

CO removal from Ambient Air

- 0.1 g catalyst is used for 12L room air at room temp..
- **Gold** catalyst covers a wide range of CO concentration.



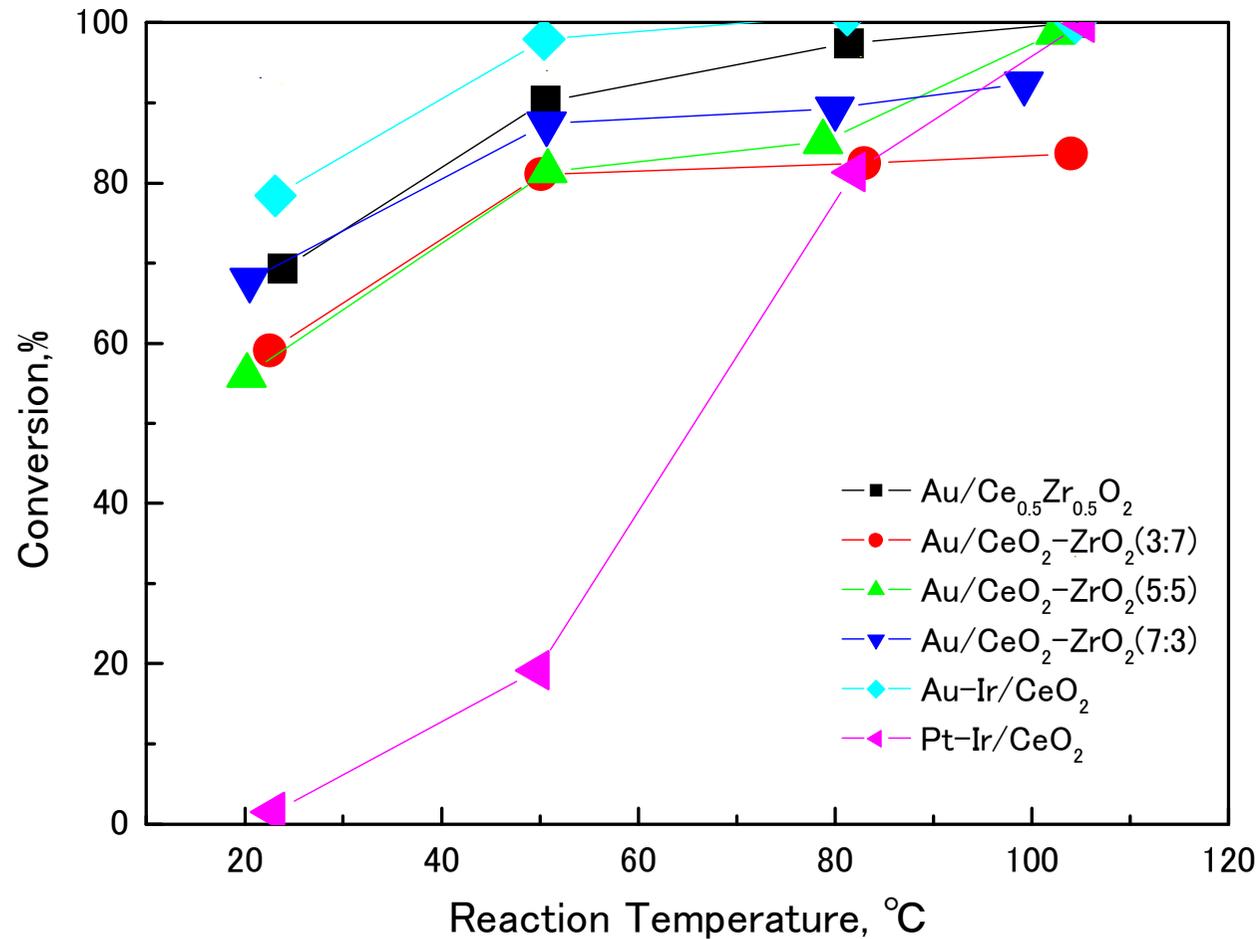
Regeneration of Au/TiO_2 Catalyst by Photo Irradiation



Activity decreases due to the accumulation of contaminants.

Regeneration by photo irradiation?

Oxidative Decomposition of HCHO



New Catalysts:

Au-Ir/CeO₂

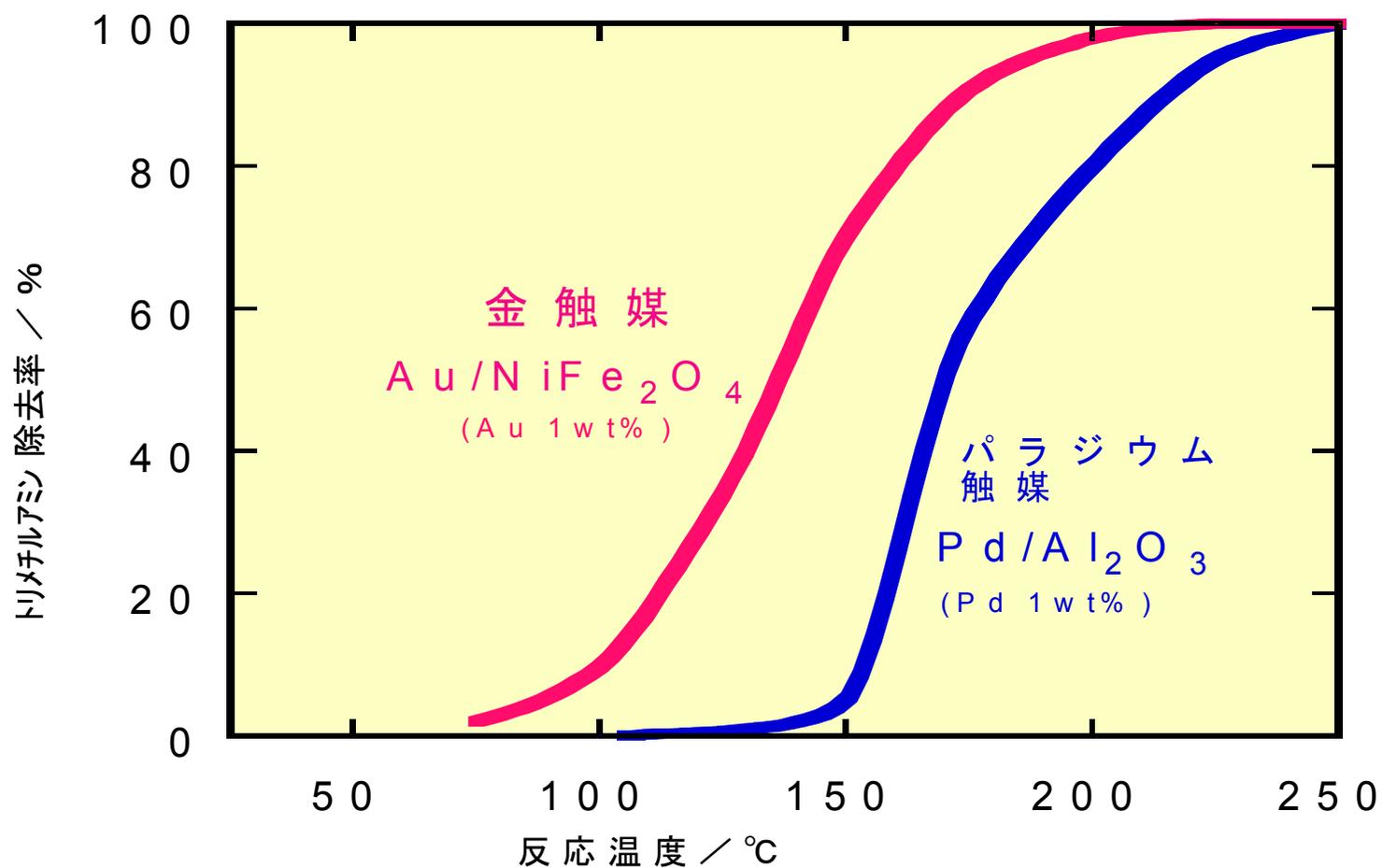
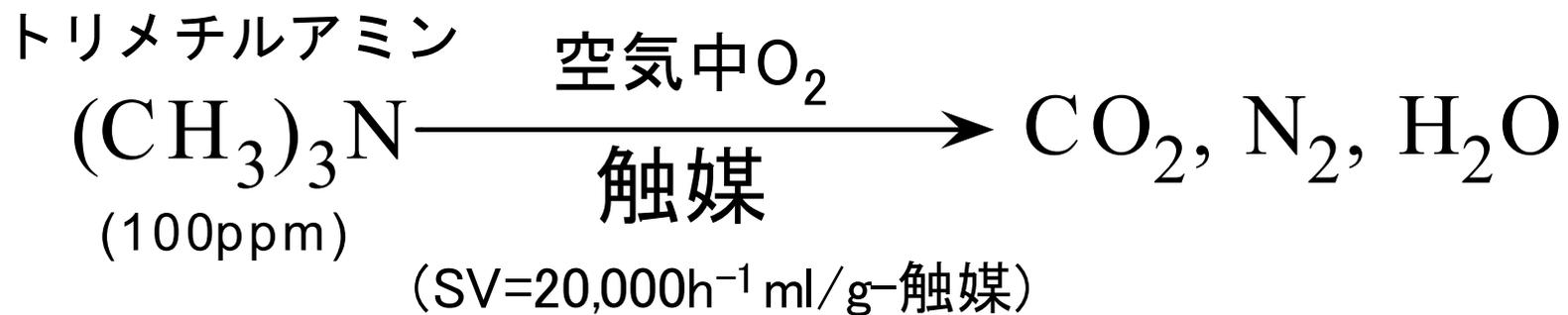
Au/CeO₂-ZrO₂

Conventional Cat.:

Au/Fe₂O₃ (AIST)

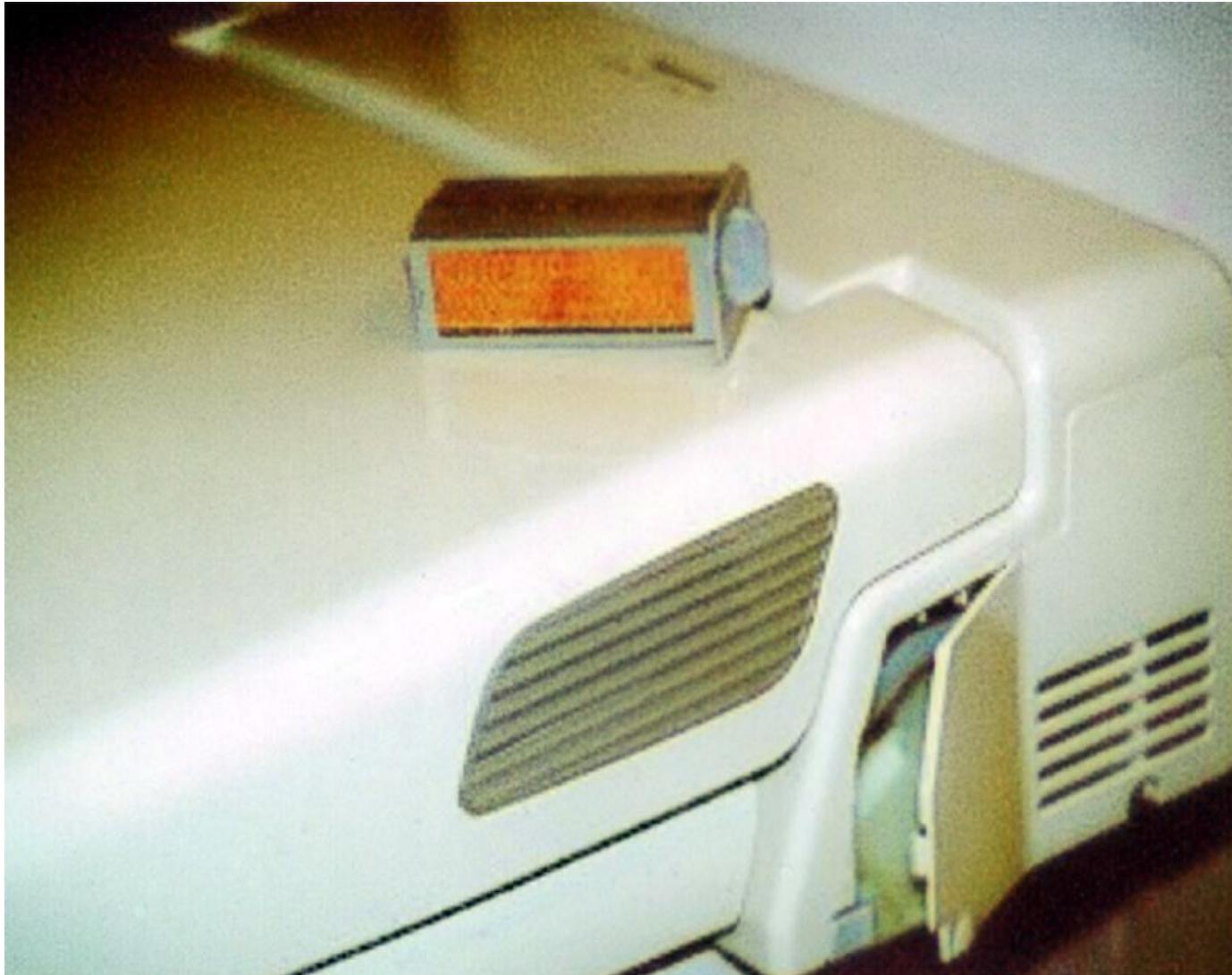
**Pt/CeO₂ (Toyota
Central Lab.)**

Fixed bed Flow reactor, SV=40,000ml/h · g- cat., 50ppm HCHO in air, Cat. :100m



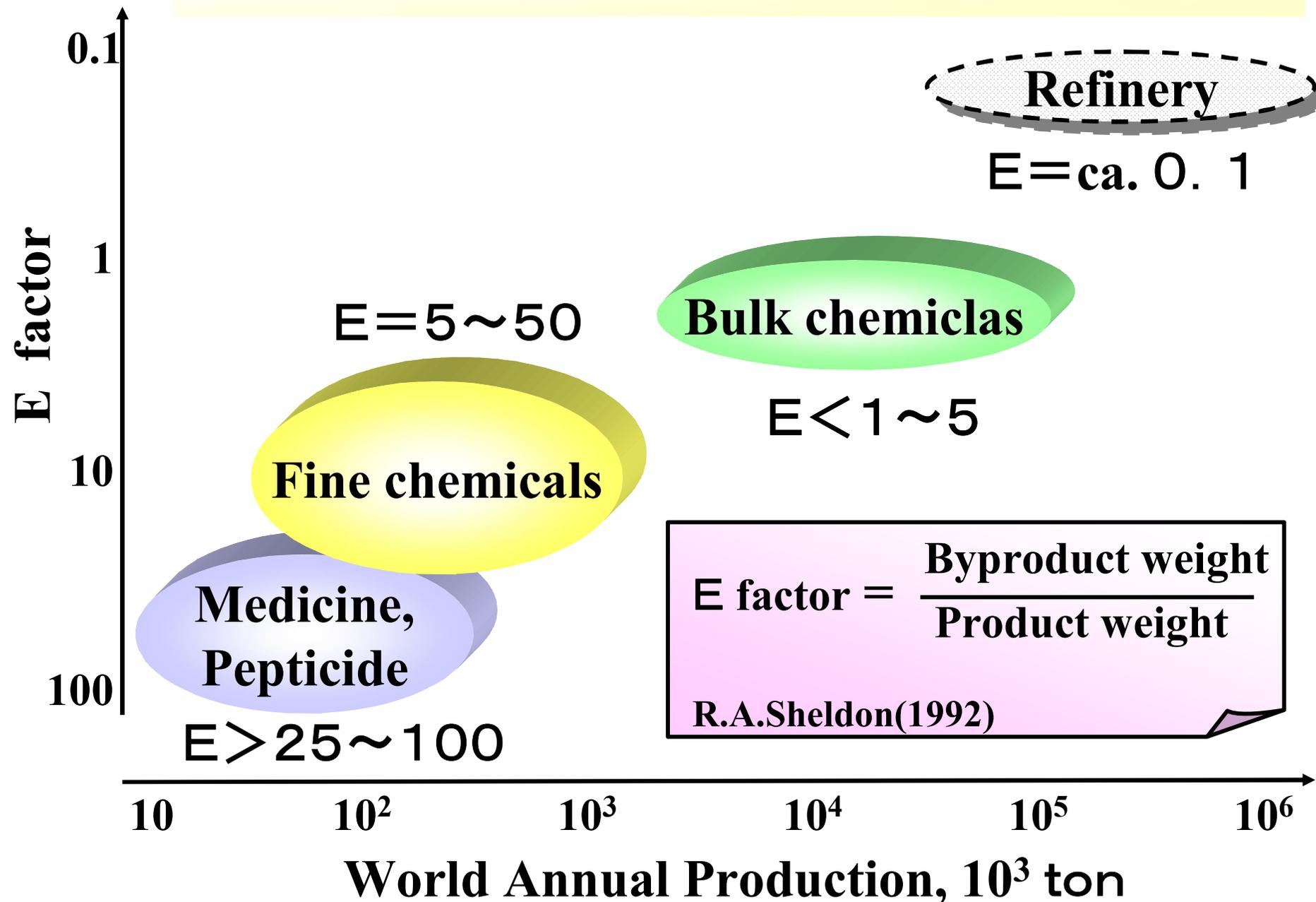
Gold Catalyst as an Odor Eater

1992, "Beauty Toilet", Matsushita Housing Products Co., Ltd.





E factors for Chemical Products



**Gold catalysts may become
a major player in**

Green Sustainable Chemistry!

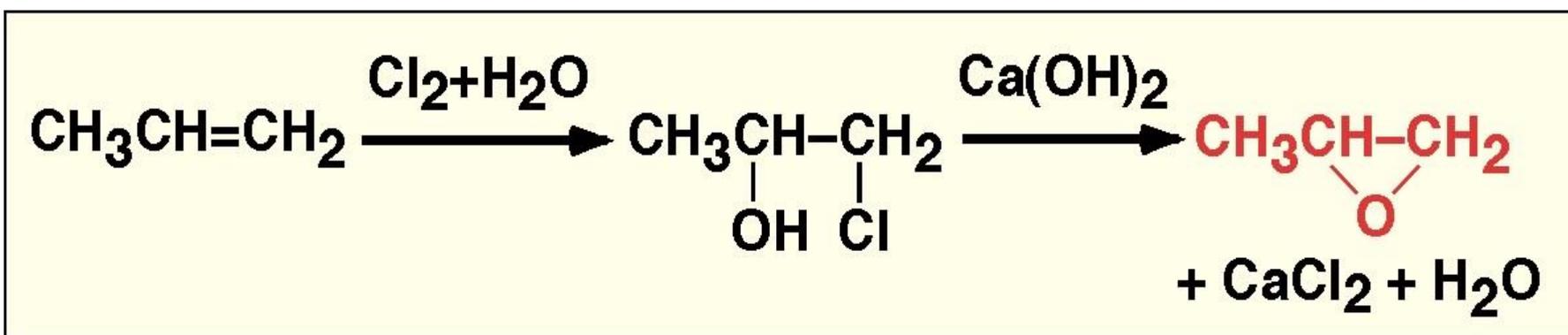
- **Simple reactions consuming minimum process energies (gas phase)**
- **Reactions without using solvents or using water as a solvent**
- **New reactions with high atom efficiency**

Propylene Oxide

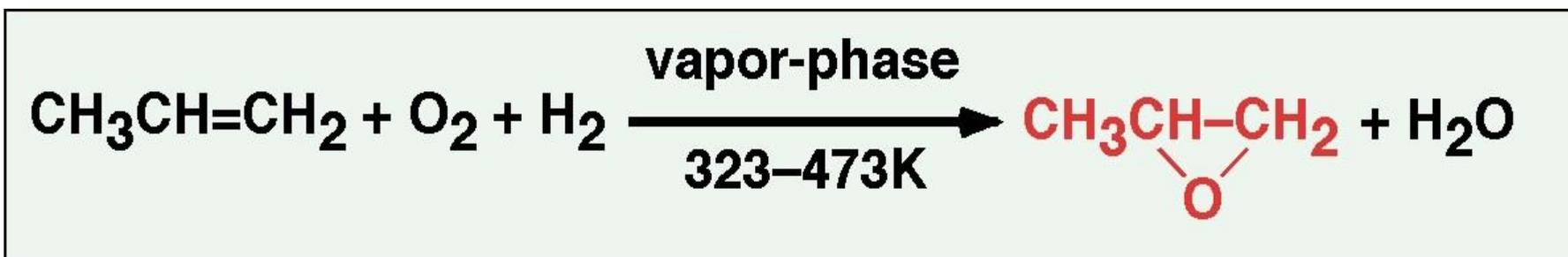
- **World Annual Production = 6 million tons**
 - **Polyurethane (60-60%)**
Propylene glycol (20-25%)
- **Annual Market Growth = above 5%**
- **Market Share = Dow Chem. 30%,
Lyondell 18%**

Synthesis of Propylene Oxide

- Current Industrial Process **Dow Chemical Co.**



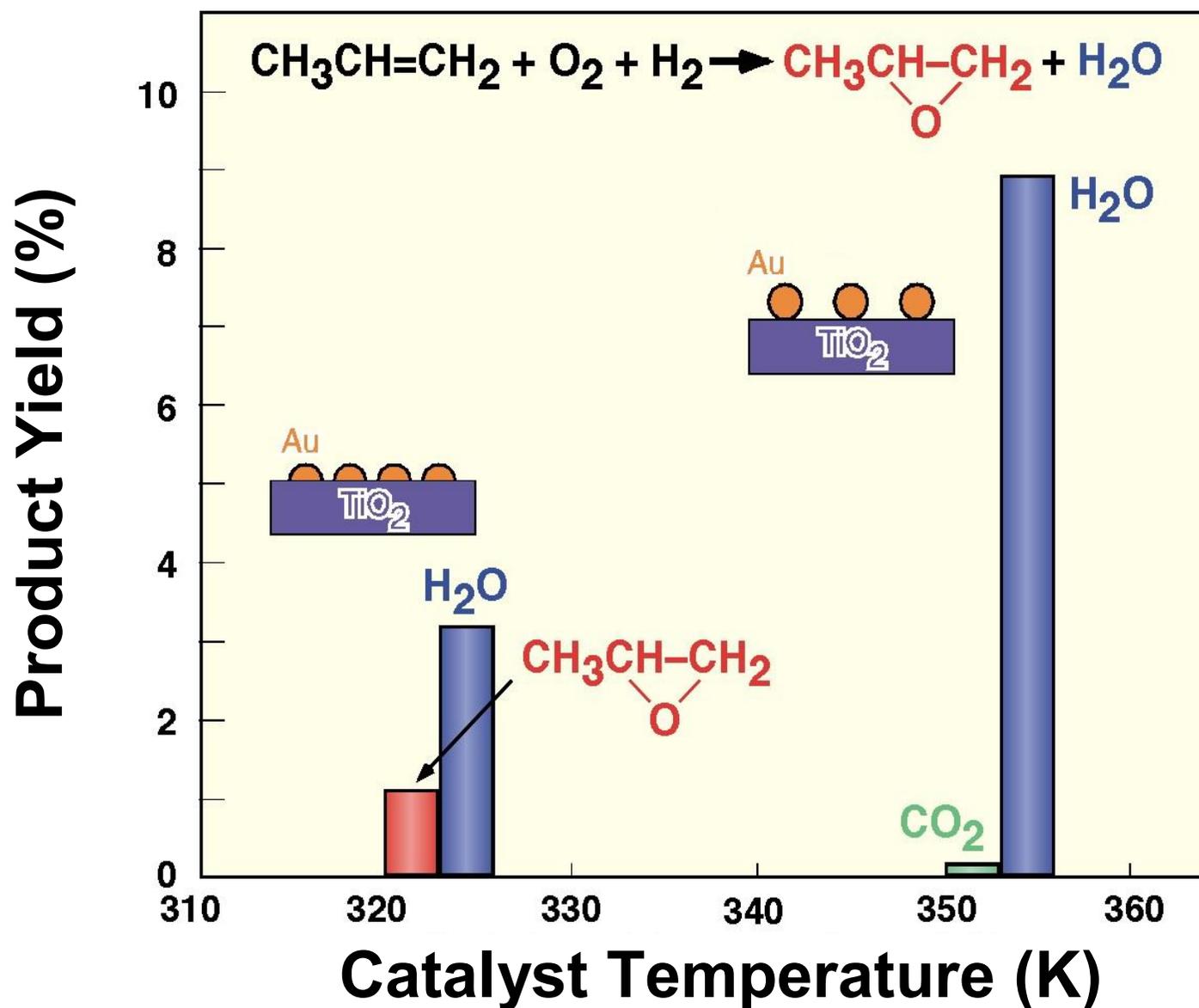
- A New Route **Au/Ti-SiO₂** Hayashi & Haruta, 1994



Three Major Factors Controlling the Activity and Selectivity

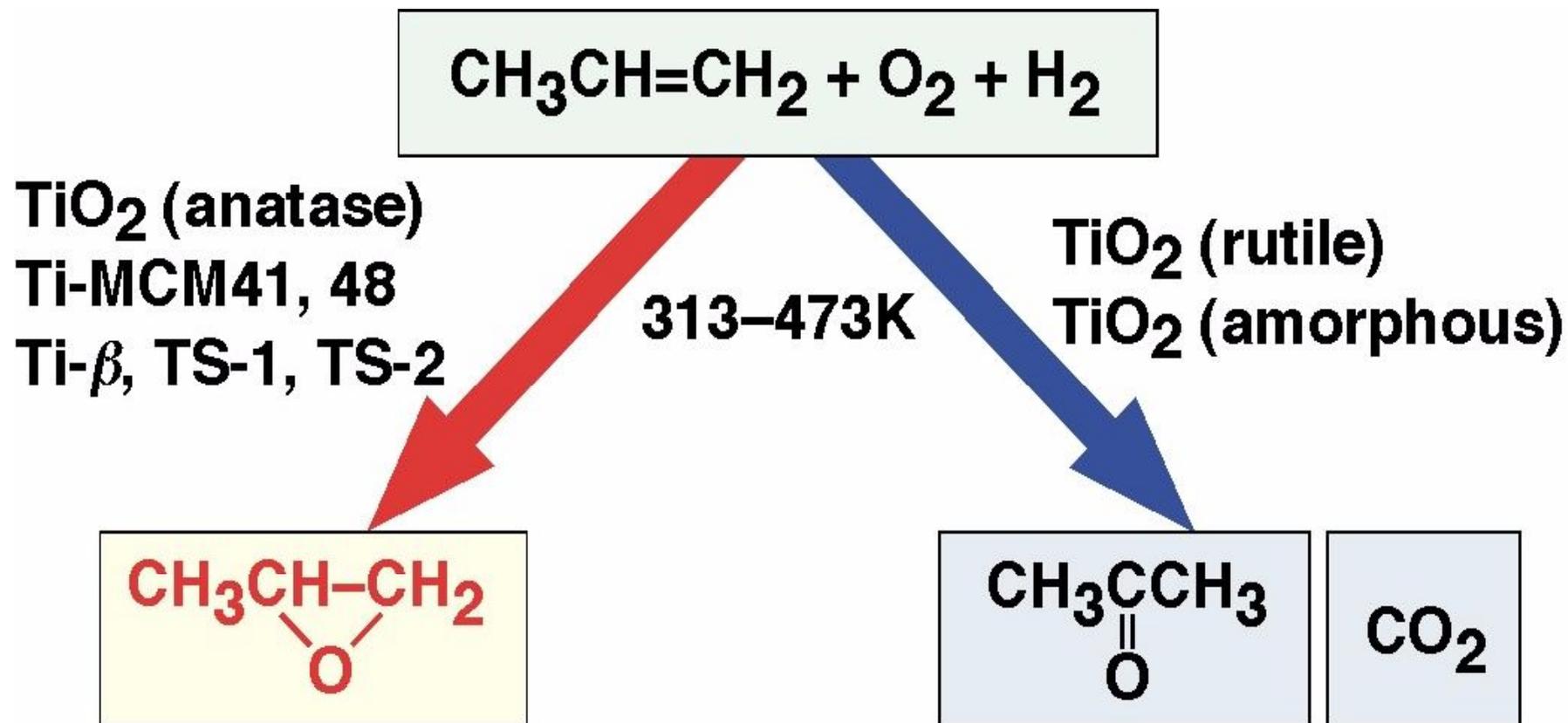
- **Strong **Contact** with the Supports**
- **Type of the **Supports****
- **Size of **Gold** Particles**

Effect of Contact Structure in PO Synthesis



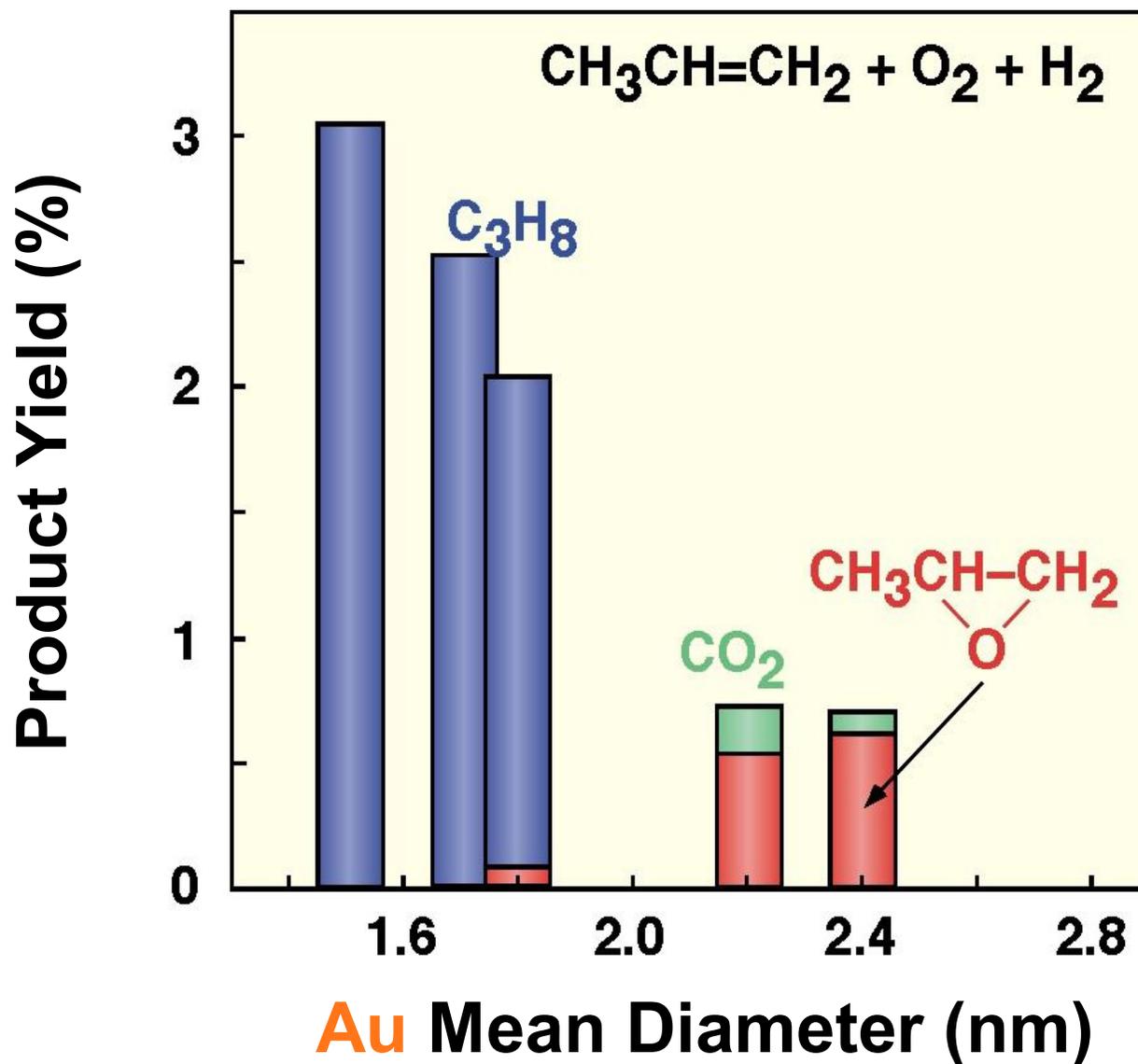
*T. Hayashi et al.,
J. Catal. 178
(1998) 566.*

Support Effect in PO Synthesis



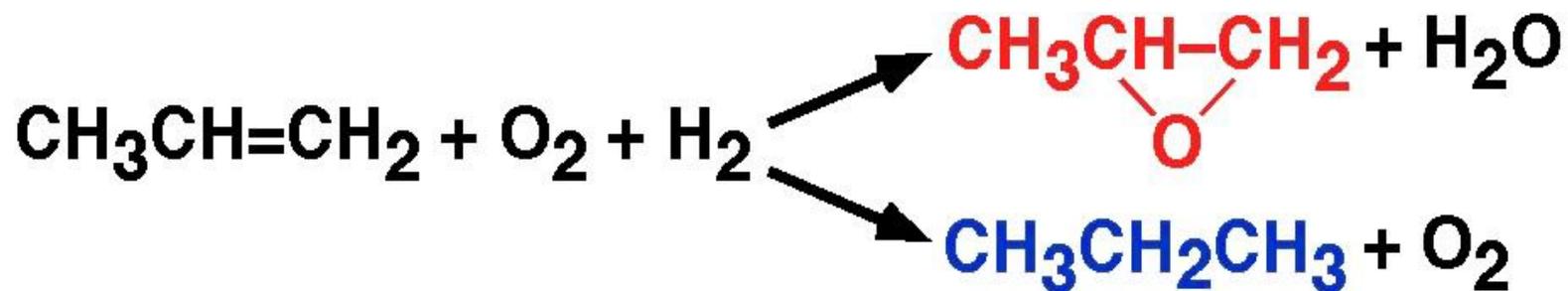
M. Haruta et al., Res. Chem. Intermed. 24(1998)329.

Au Size Effect in PO Synthesis



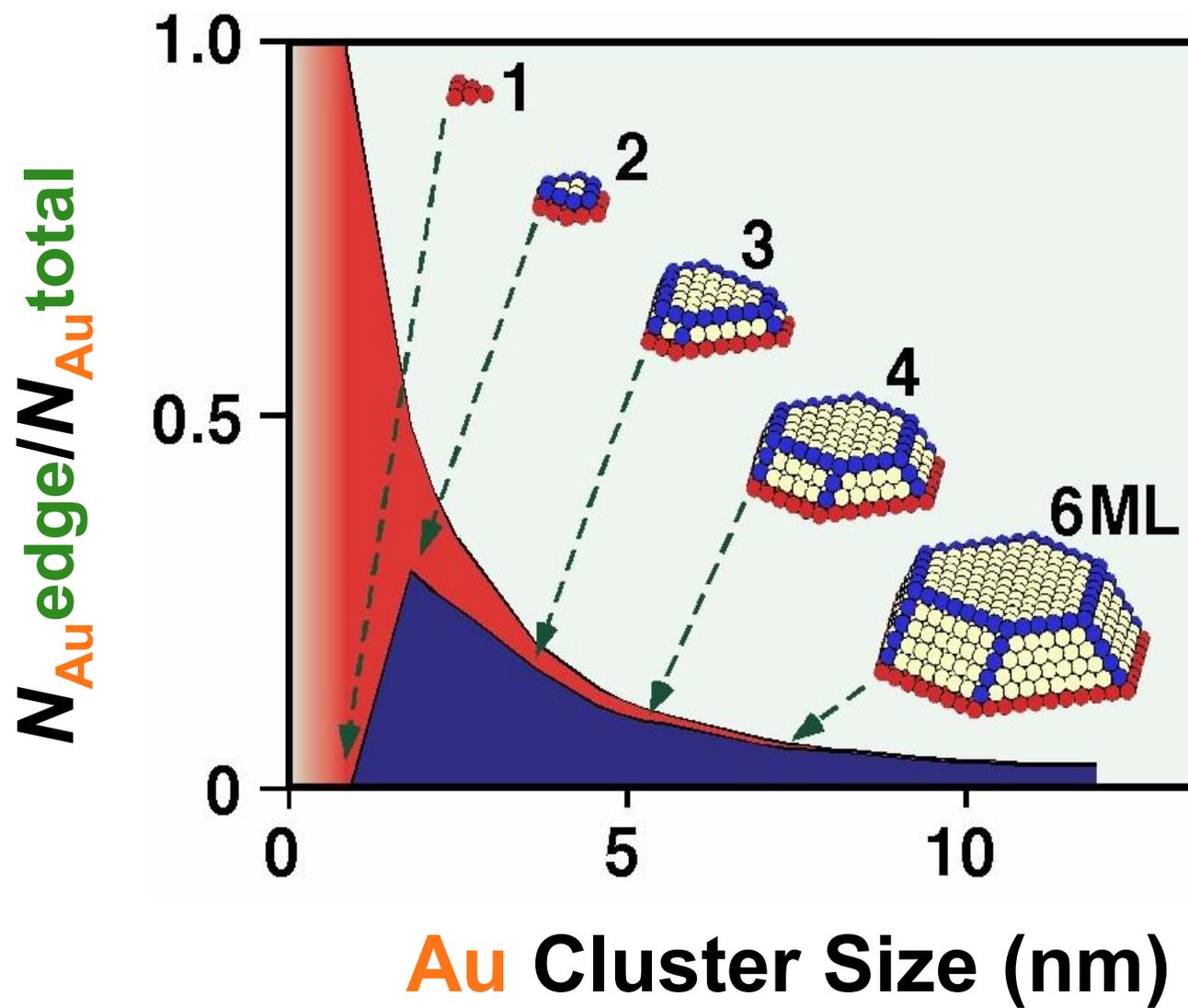
*T. Hayashi et al.,
J. Catal. 178
(1998)566.*

Product Selectivity Changes with Metals



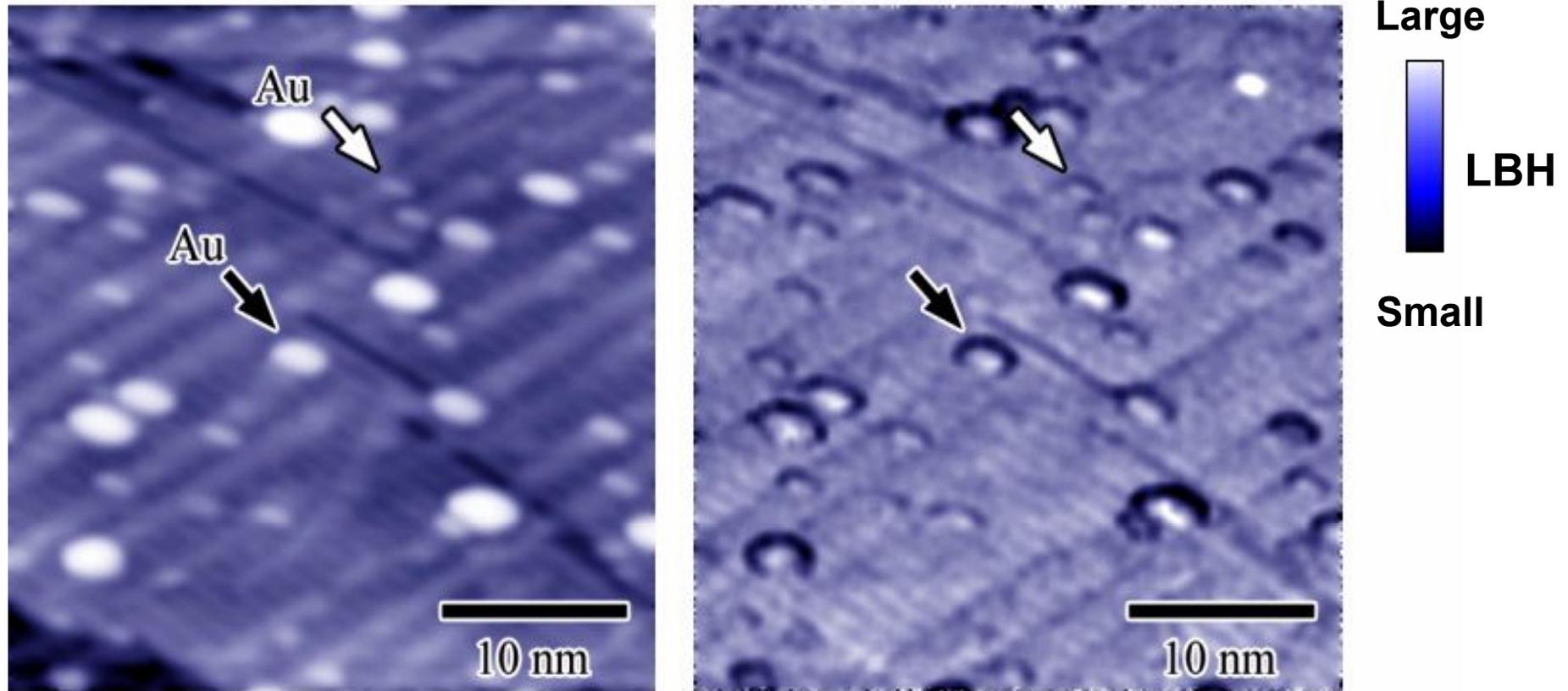
Metal on TiO_2	Load. (wt%)	D_{Au} (nm)	Temp. (K)	Conv. (%)		Selec. (%)	
				C_3H_6	H_2	PO	C_3H_8
Au	1	2.4	353	0.63	—	>99	0
	0.05	1.7	353	3.1	—	0	>99
Pd	1	—	298	57	98	0	98
Pt	1	—	298	12	87	0	92

Step Density of Hemispherical Au



Mavrikakis, Stoltze and Nørskov, Catal. Lett., 64 (2000) 101.

STM & LBH Images of Model **Au**/TiO₂

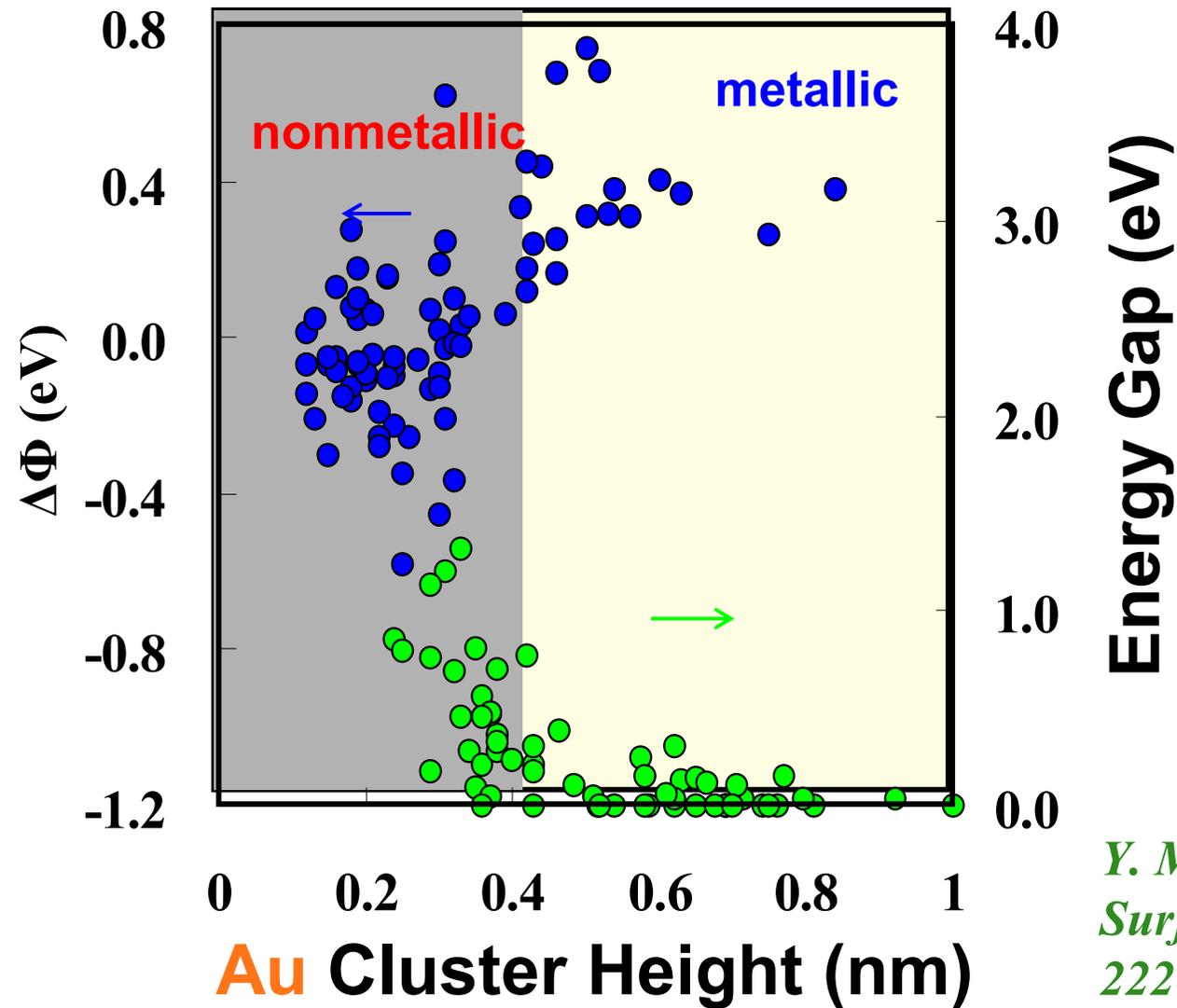


STM

Local Barrier Height

Y. Maeda et al., Appl. Surf. Sci. 222(2003)409.

Work Function and Energy Gap vs Thickness



Y. Maeda et al., Appl. Surf. Sci. 222(2003)409.

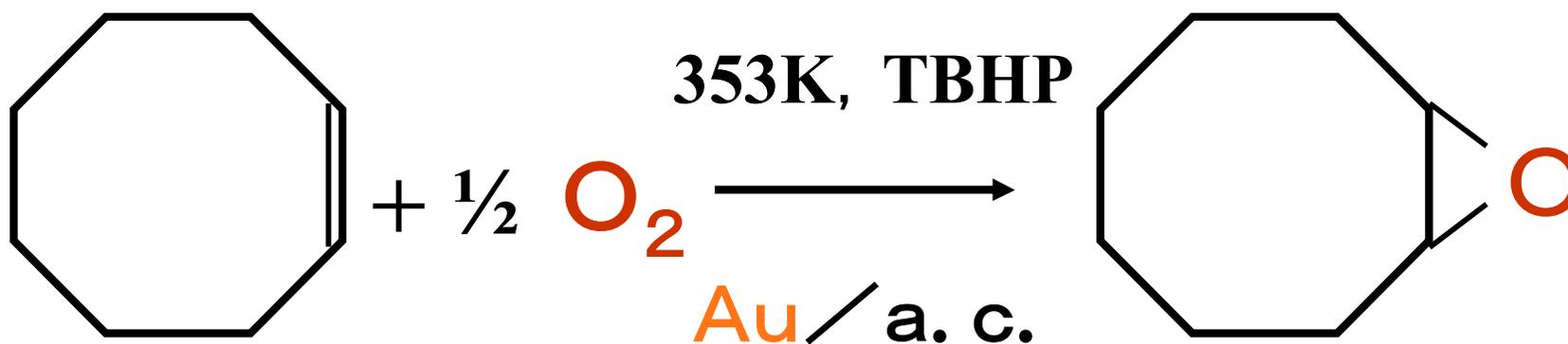


Liquid Phase Aerobic Oxidation

Supports
for Au

- Activated carbons
- Fine polymer particles
- Nanocrystalline CeO_2
- MgAl_2O_3
- $\text{Al}_2\text{O}_3\text{-SiO}_2$

Liquid alkene epoxidation with O_2 in the absence of a solvent



cis-cyclooctene

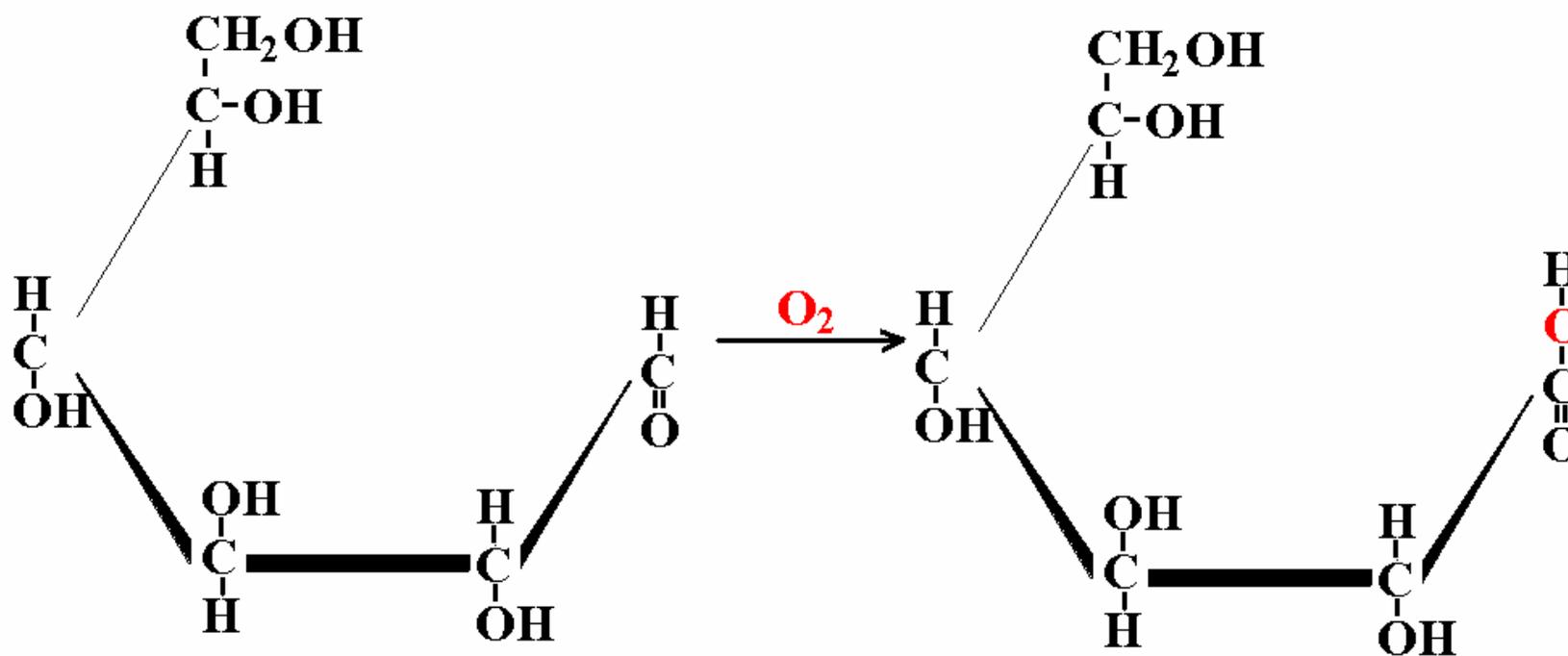
Conv. 7.9%(24h)

Sel. 81%

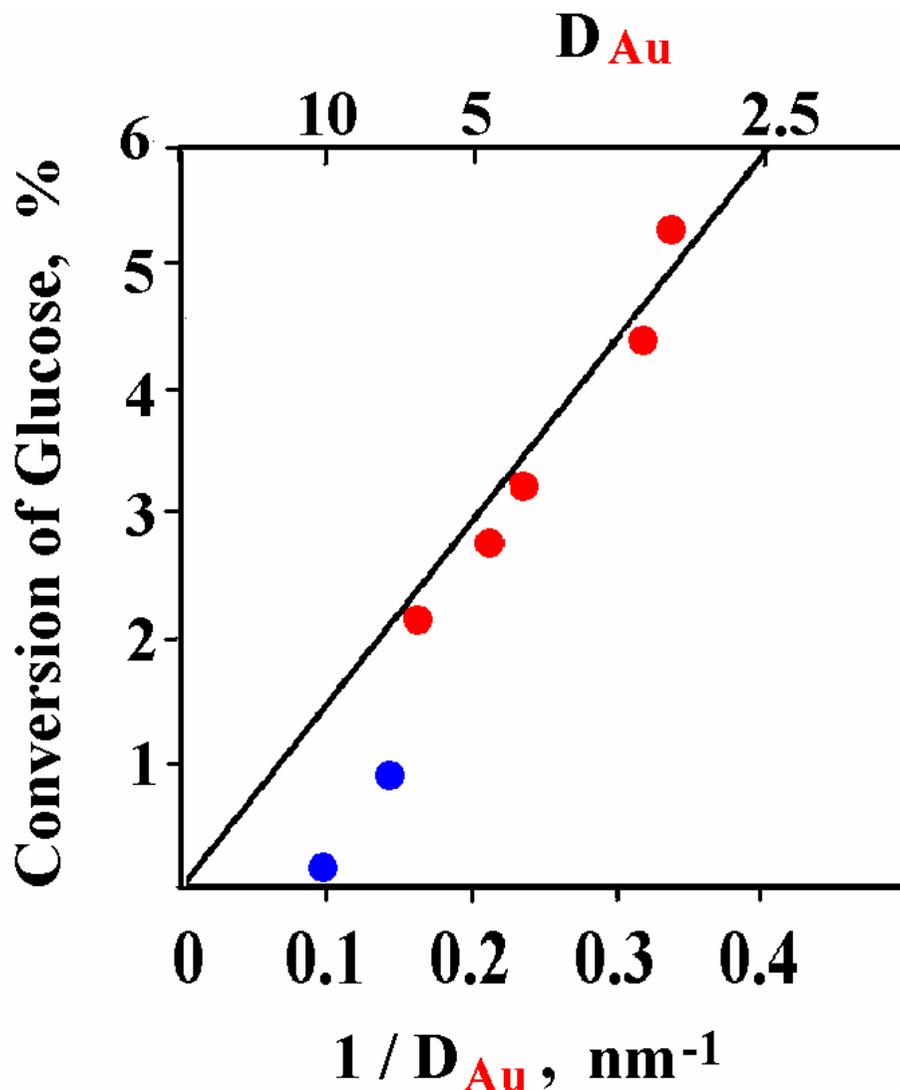
G.T. Hutchings et al., *Nature* 437,
1132(2005)

Liquid Phase Selective Oxidation

Glucose to Gluconic Acid in Water



Conversion vs $1/D_{Au}$ in Glucose Oxidation



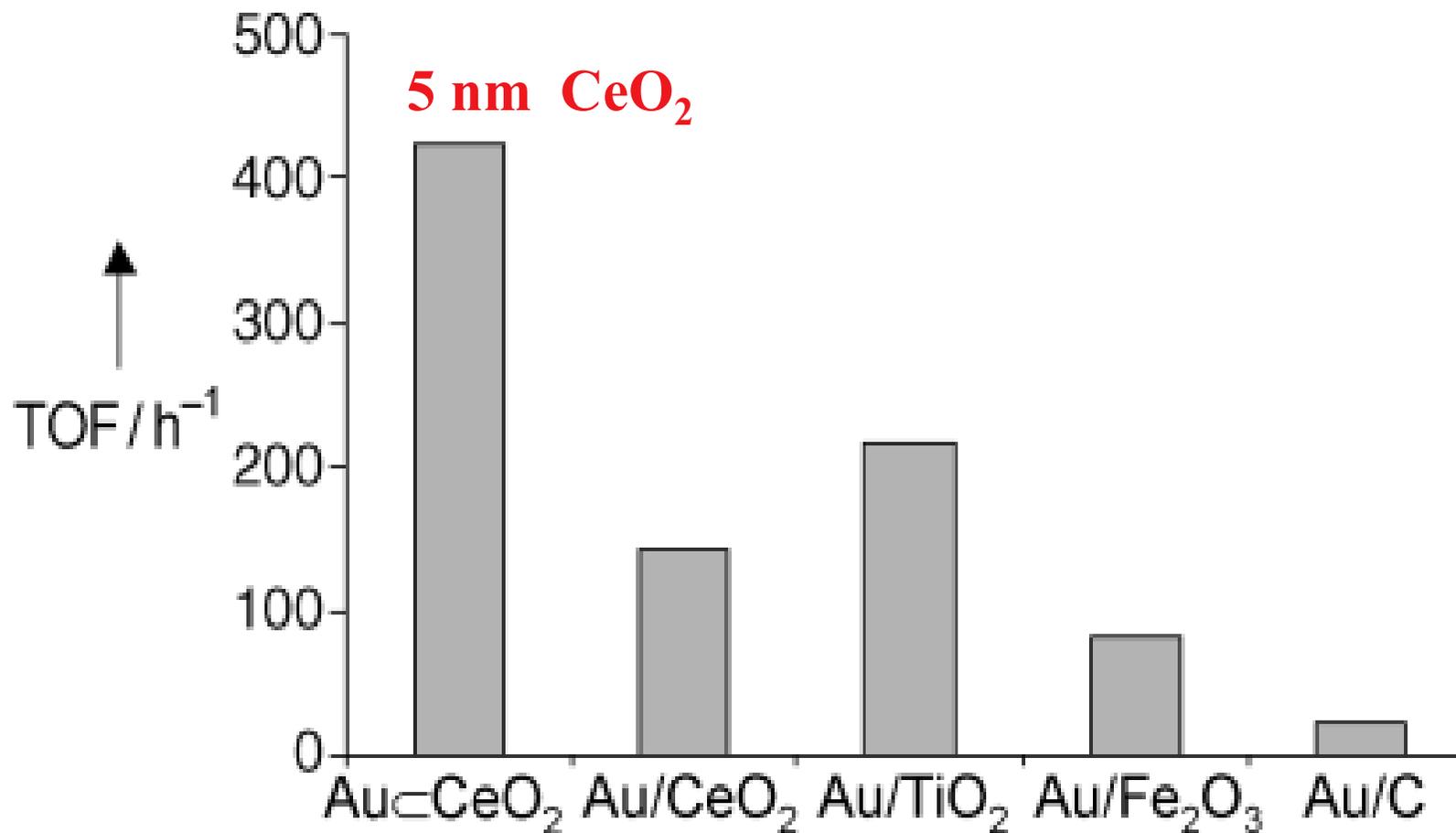
Au / Activated Carbon

**303K,
React. period: 100 s,**

**glucose 0.38M /
H₂O glucose : Au
=12 000**

*M. Rossi et al., Angew. Chem. Int. Ed.
43(2004)5812.*

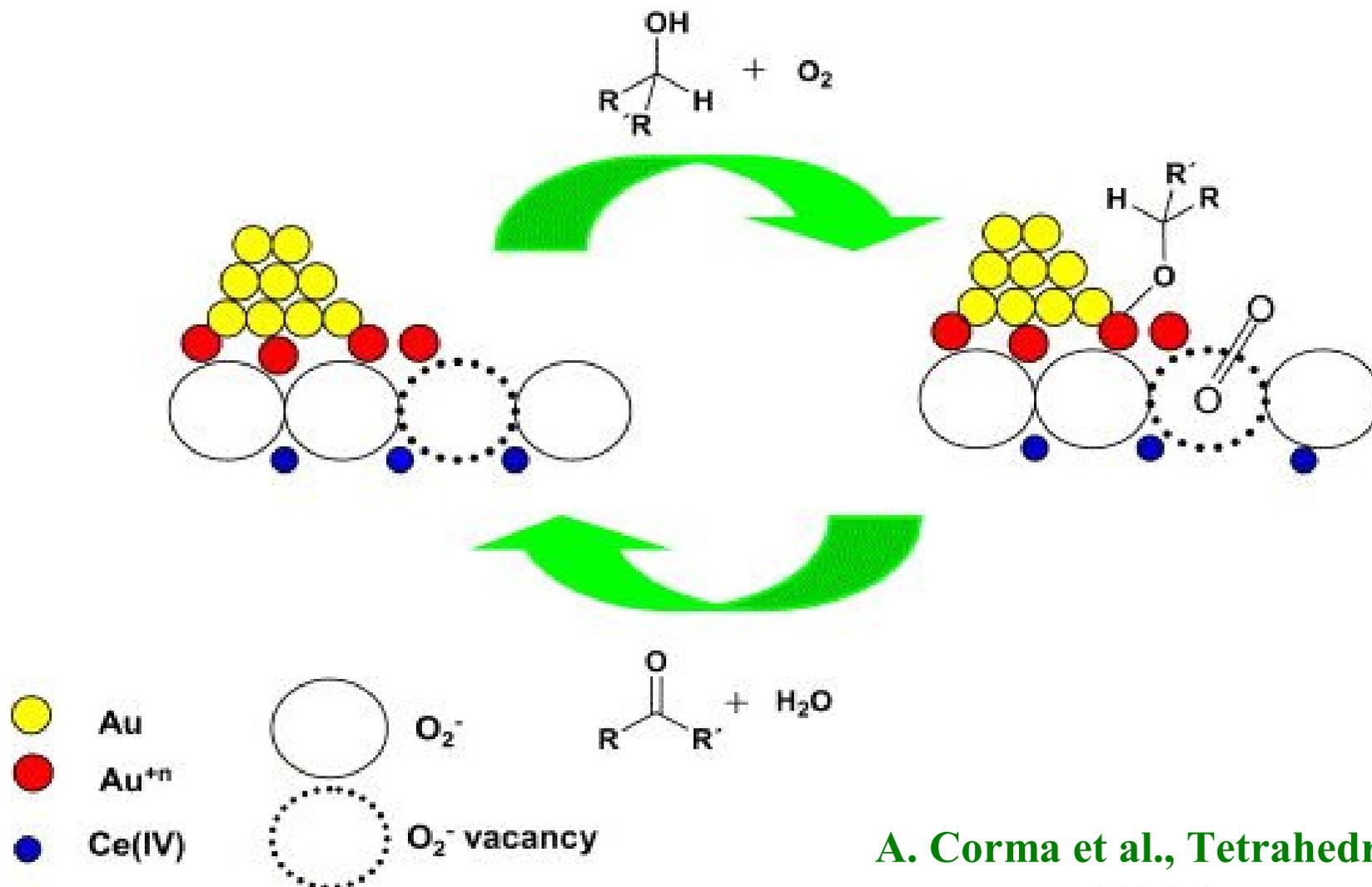
Aerobic oxidation of 3-octanol: Support effect



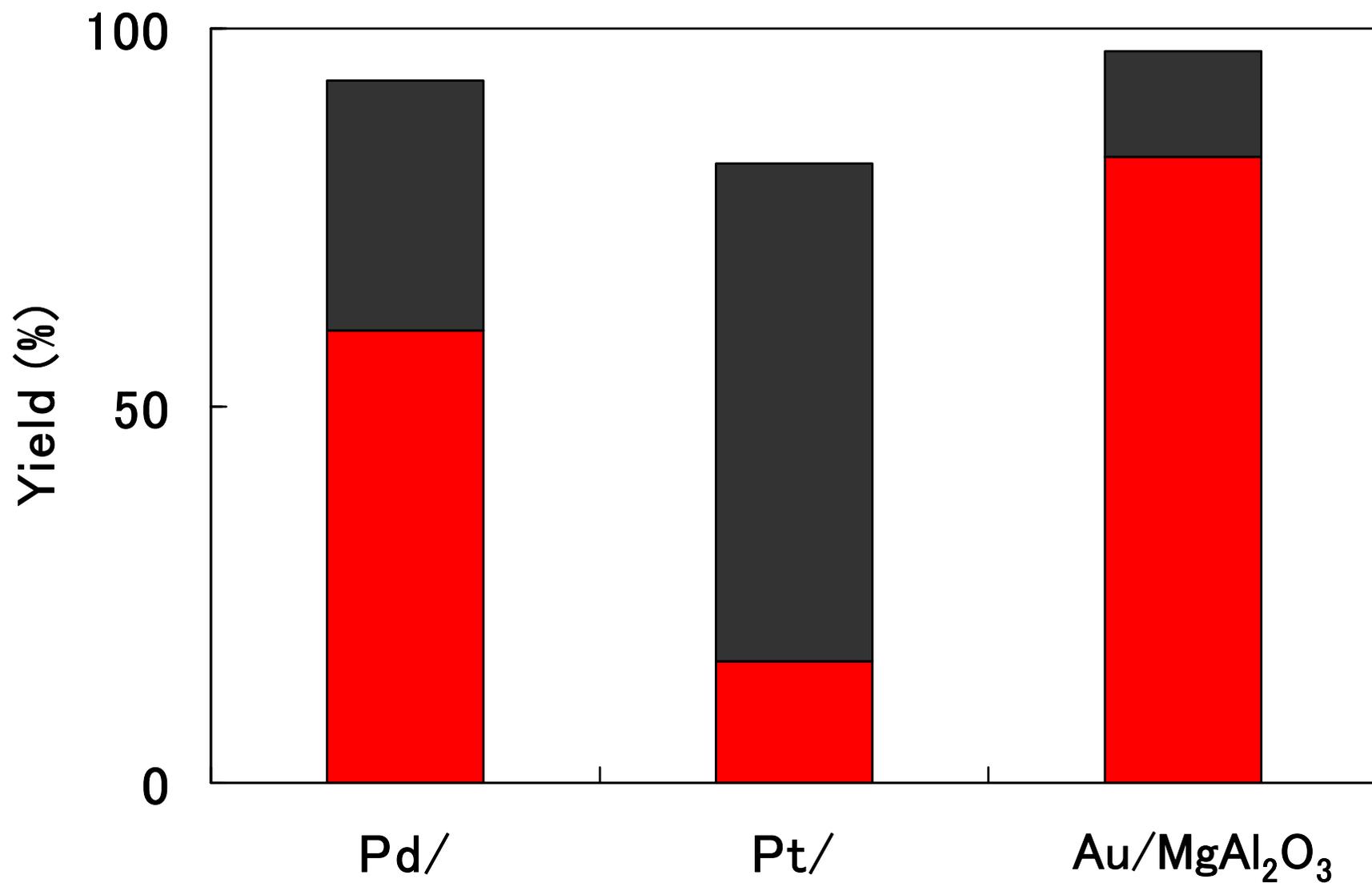
A. Corma et al., *Angew. Chem. Int. Ed.*, 44, 4066(2005)

catalyst

Aerobic alcohol oxidation over Au/CeO₂

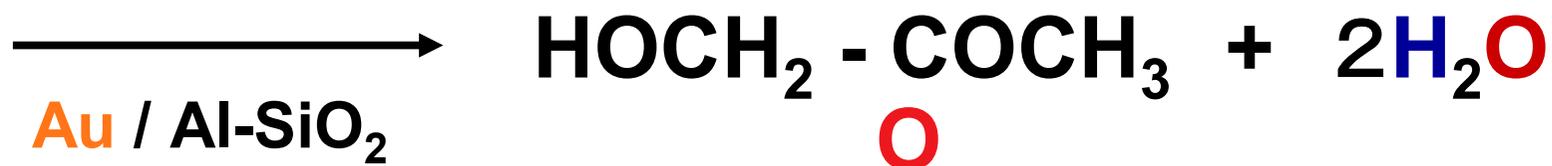


A. Corma et al., *Tetrahedron*,
2006, in press.



C. H. Christensen et al., *Angew. Chem. Int. Ed.* 45, 4648(2006)

Pilot plant for the synthesis of methyl ester glycolate



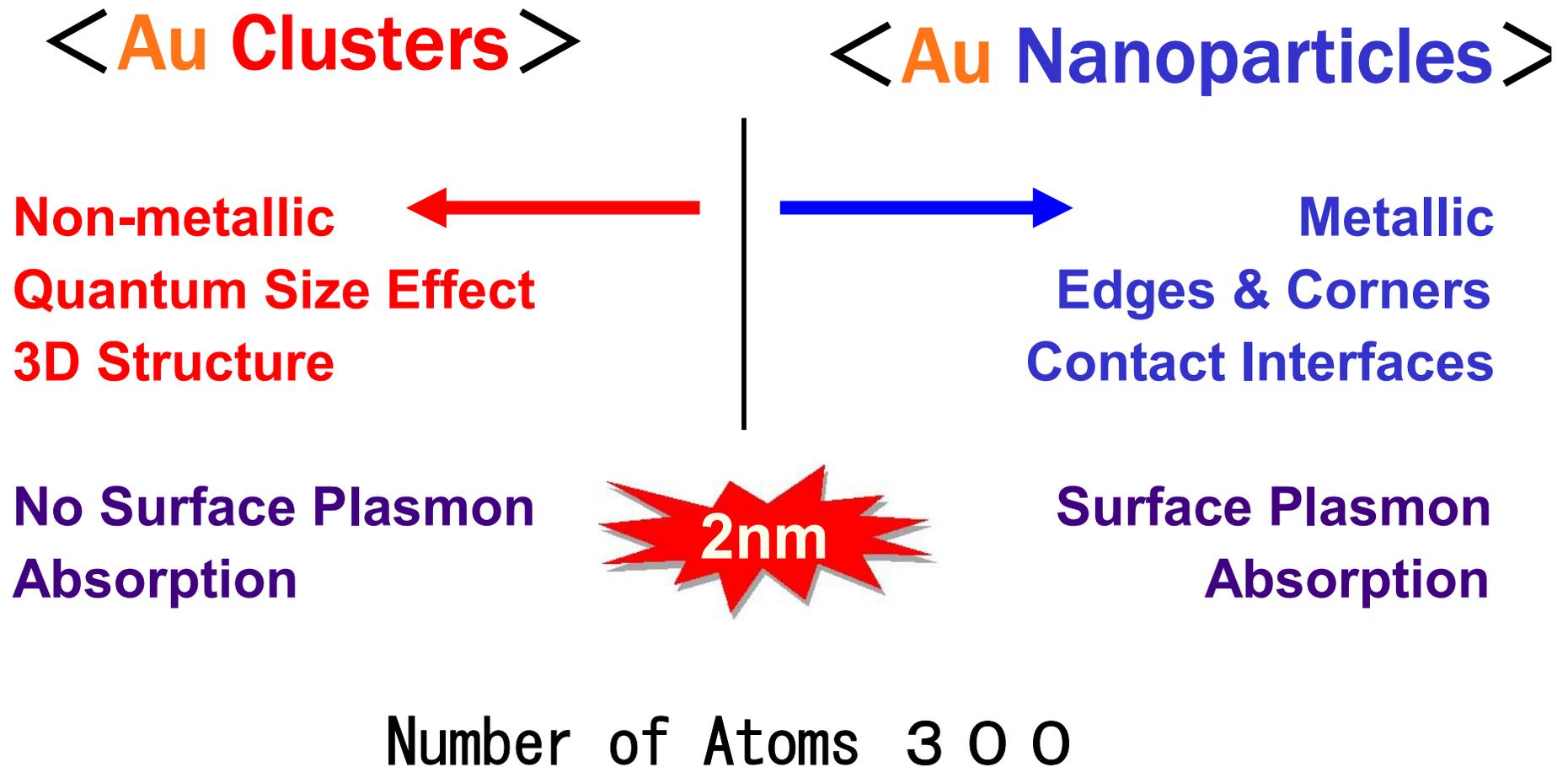
1~2x10⁴ t/year(3 years later)

cleaner for semiconductors and liquid crystals, raw materials for cosmetics and biodegradable polymers

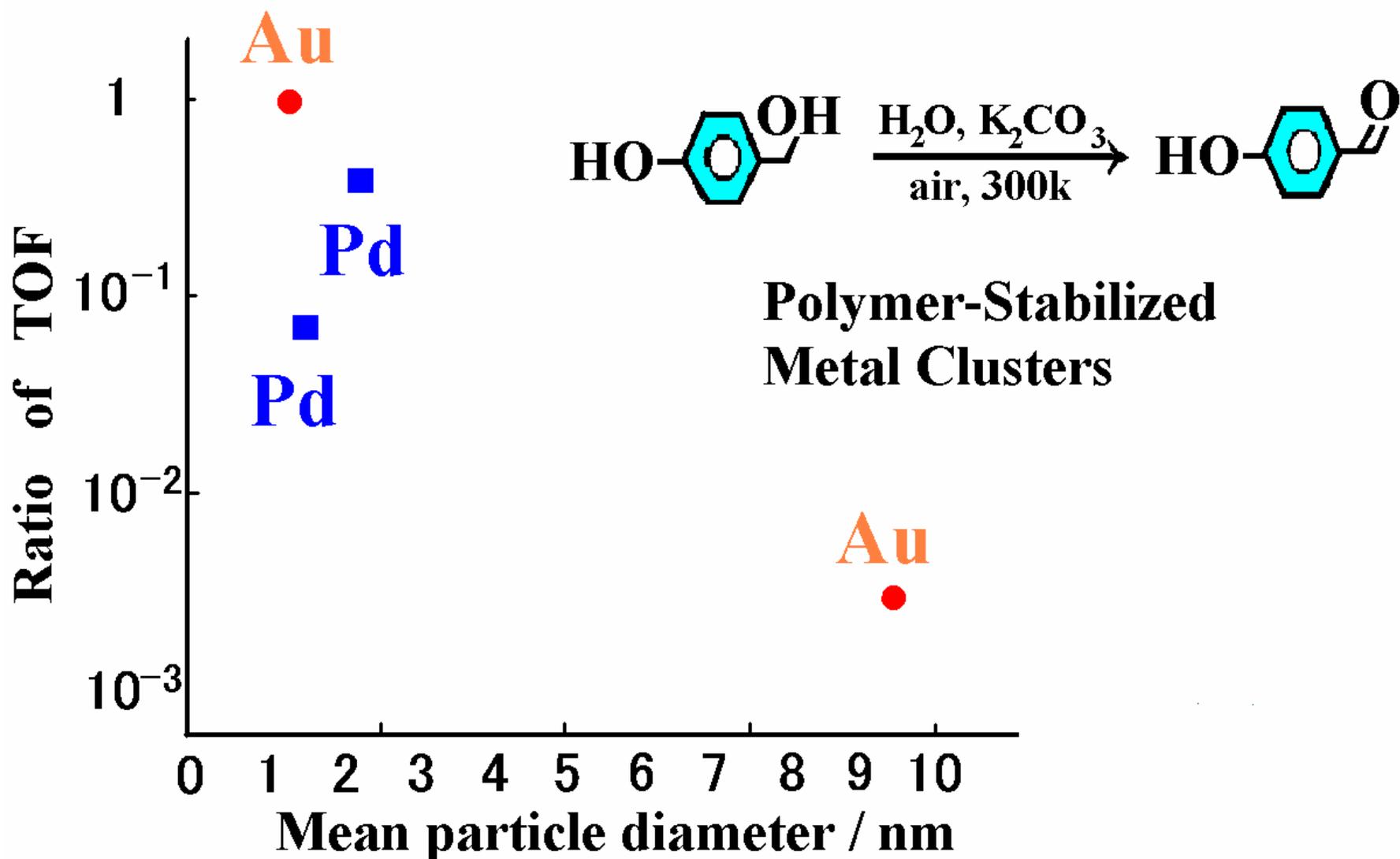
T. Hayashi,
Nippon Shokubai Co.



Reactivities of Au clusters dramatically change with size and structure.

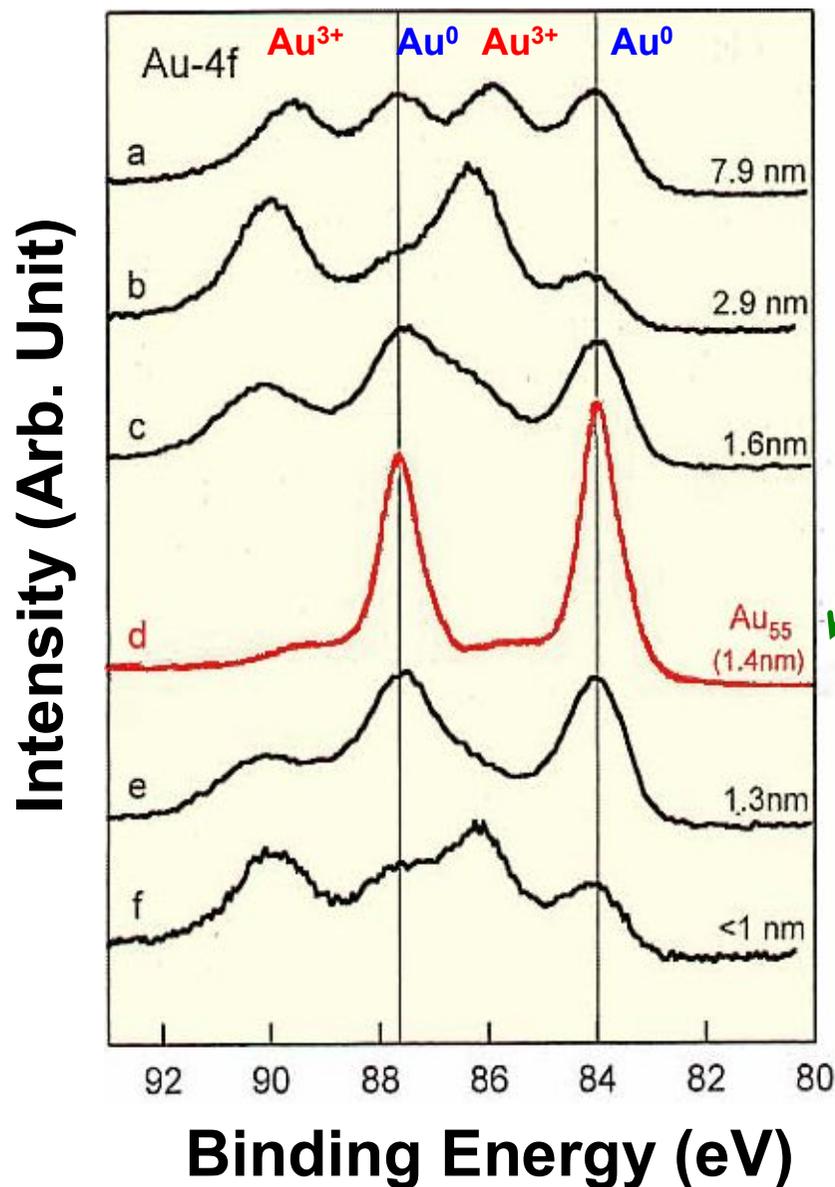


Gold clusters are more active!



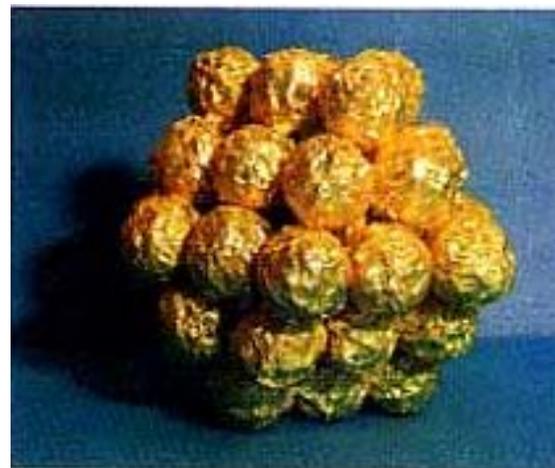
T. Tsukuda et al., *J. Amer. Chem. Soc.* 127, 9374(2005).

XPS of Au after Exposure to Oxygen Atom



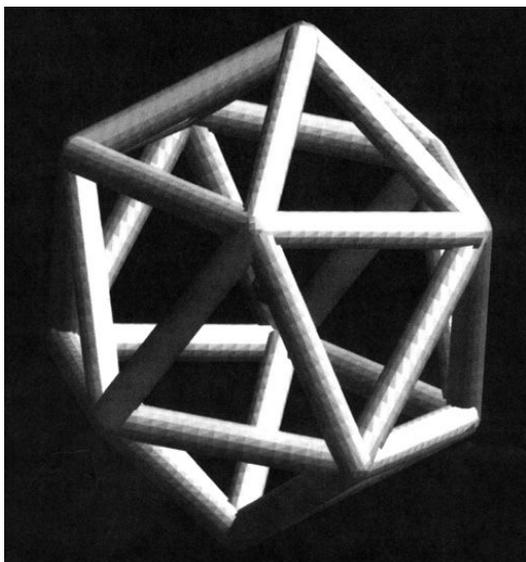
Taken after radio frequency oxygen plasma

Au₅₅ is nobler than bulk gold!

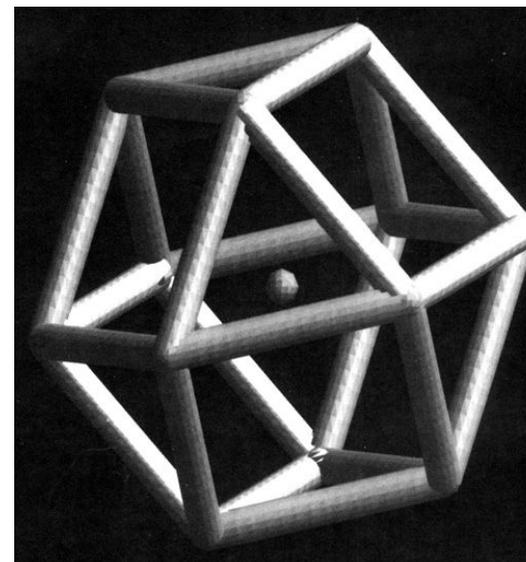


Boyen et al., Science, 297 (2002) 1533

Au₁₃ Clusters Supported on Mg(OH)₂ by DP



*D.H.A. Cunningham
et al.,
J.Catal.177(1998)1.*



Icosahedron

Cubo-Octahedron

$N_{\text{Icosa.}}$: $N_{\text{Cubo-Octa.}}$

58 : 42

7:93

**CO Oxidation
Efficiency (200K)**

100%

4–6%

Summary

- **Gold** catalysts are useful for air purification owing to high oxidation activity at room temperature and to the activity enhancement by moisture.
- **Gold** catalysts have great potentials and capabilities in developing **Green Sustainable Chemistry**.
- Thermodynamic stability and dramatic size effect of **gold clusters** smaller than 2nm is opening an exciting field of science.

Thank you!