When gold becomes a catalyst

(Gold als Aktivkomponente in der heterogenen Katalyse)

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- general aspects about metal catalysts
- general aspects about gold
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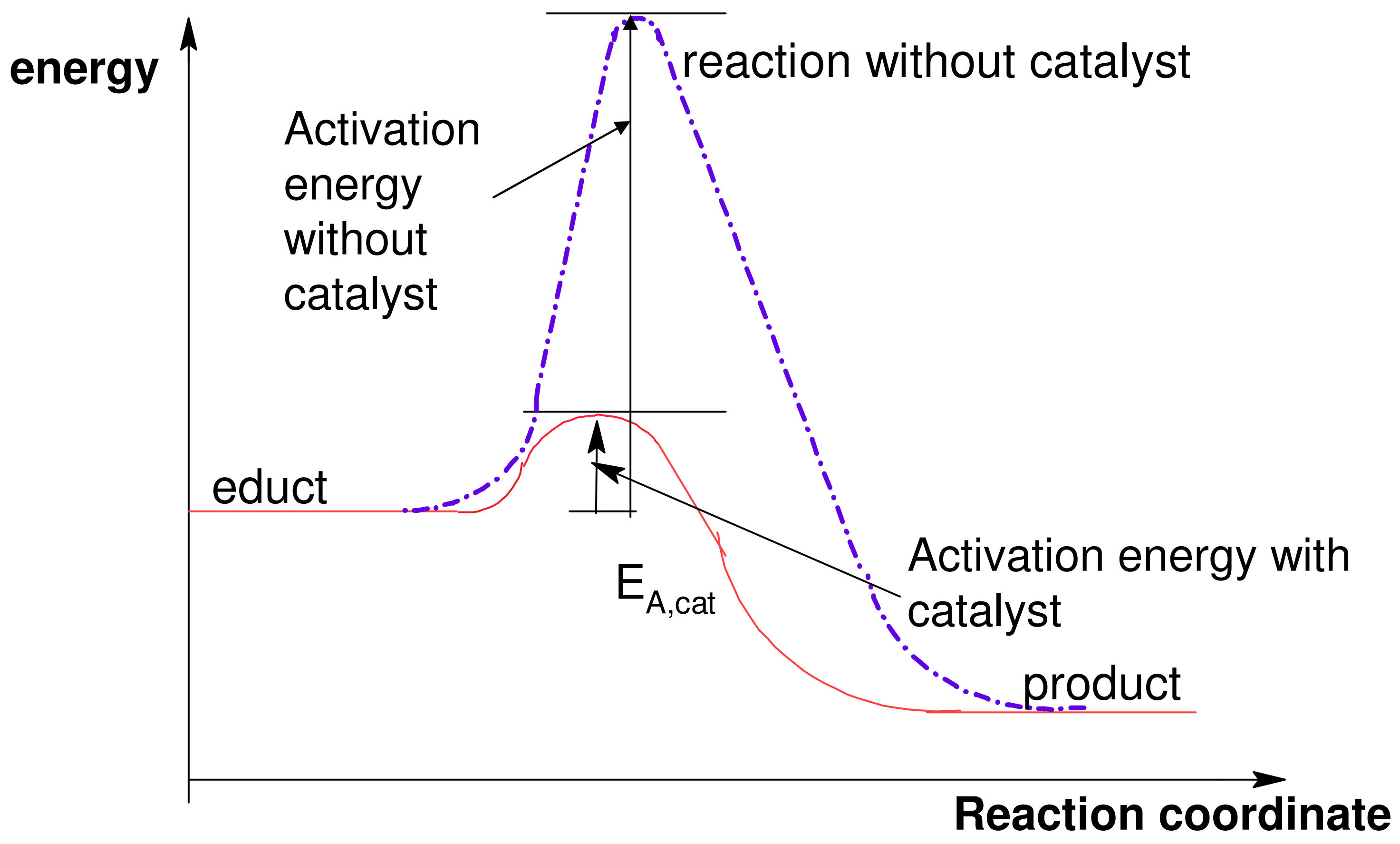
Energetic aspects of catalysis



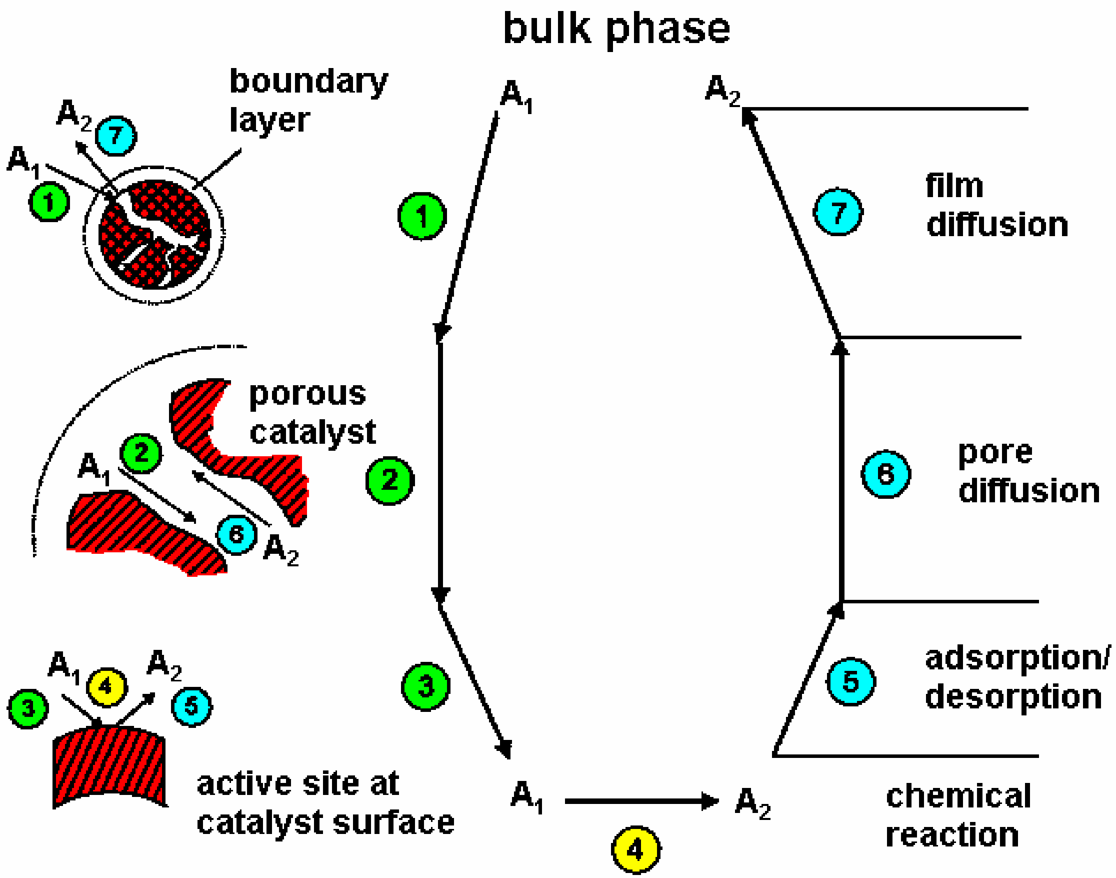
Comparison between homogeous and heterogeous metal catalysts

	homogeneous (molecular)	heterogeneous
catalyst	metal organic complexes	supported metal
dispersion of metal	high	low
activity per mg metal (at same temperatur)	high	low
reaction condition	< 200 ℃	> 200 ℃ < 1000 ℃
catalyst separation	costly	simple

Dispersity

$$D = \frac{\text{number of accesible metal centres}}{\text{total number of metal centres}}$$

Mass transport in het. catalysis



E. Klemm, M. Köstner, G. Emig.
Transport Phenomena and Reaction in Porous Media,
in: F. Schüth, K.S.W. Sing, J. Weitkamp (Hg.), *Handbook of Porous Solids,*
1. Auflage, WILEY-VCH, Weinheim, 2002.

Which main property has gold ?

chemical inert

- No single acid dissolves it
- Unaffected by oxygen
- In nature principally as a free metal

BUT!

Inert is not useless

historical applications

- alloying
- jewelry
- coinage
- in computers: spacecraft, jet aircraft
- elektrode
- gold-198 in cancer treatments and for treating other diseases

Nobel medal

How does gold become a catalyst?

normally: gold‘s power of chemisorption was far too small

Tanaka-tamaru rule:

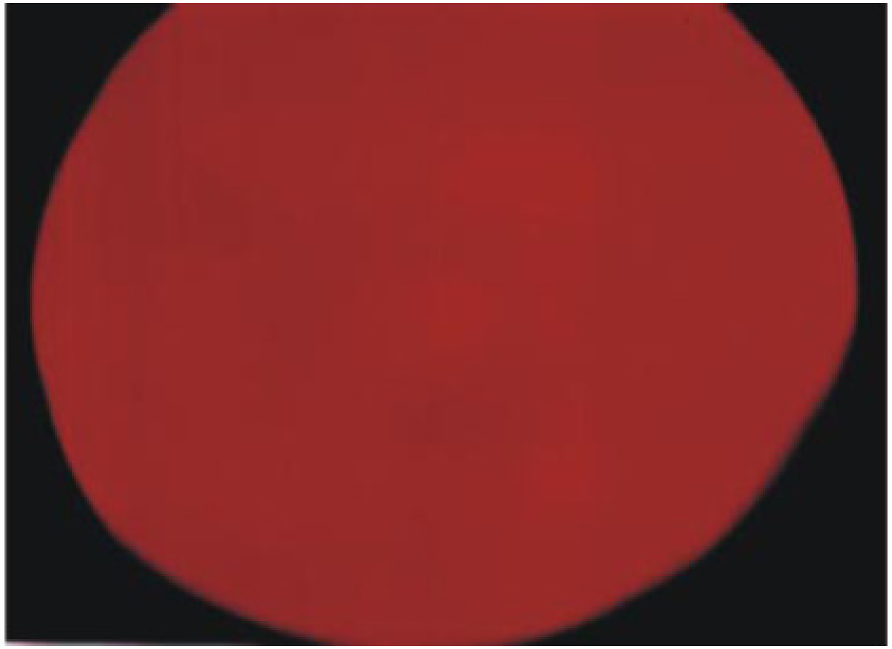
initial enthalpies of chemisorption of oxygen and other molecules	$\propto$	the enthalpies of formation of the most stable oxides

Au_2O_3: H_f = +19.3 kJmol–1

requirement for gold catalyst:

not larger than 10 nm

nanoparticle



Photograph (binocular mikroskopy) of a nanoporous alumina membrane, filled with 10±5 nm gold nanoparticles

G. L. Hornyak, M. Kröll, R. Pugin, Th. Sawitowski, G. Schmid, J.-O. Bovin, G. Karsson, H. Hofmeister, S. Hopfe, *Chem. Eur. J.* 1997, *3*, 1951.

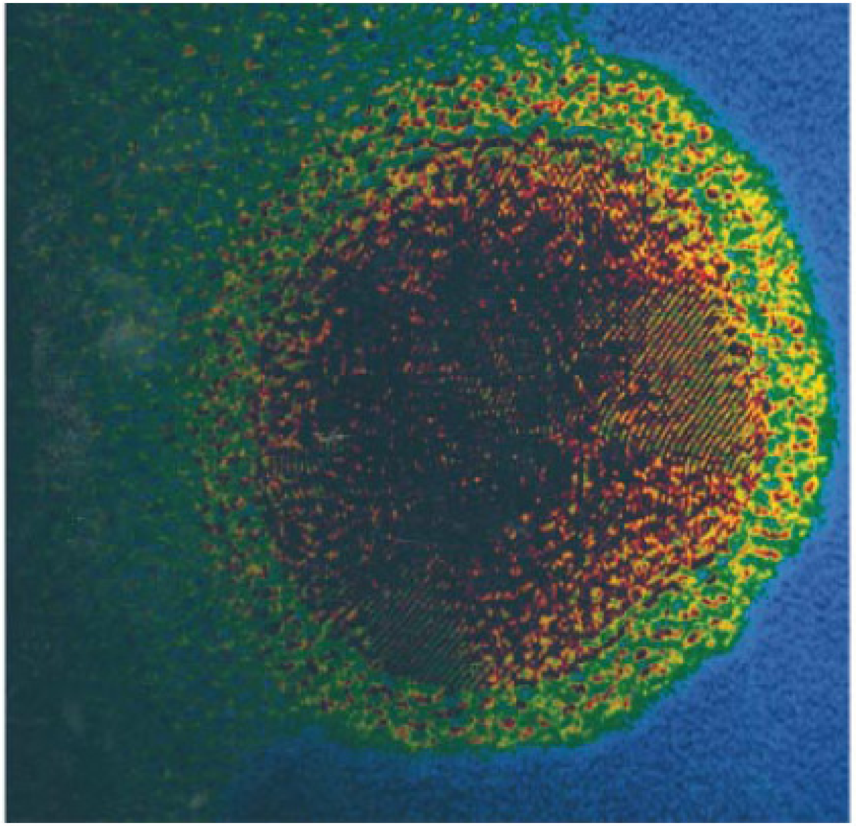
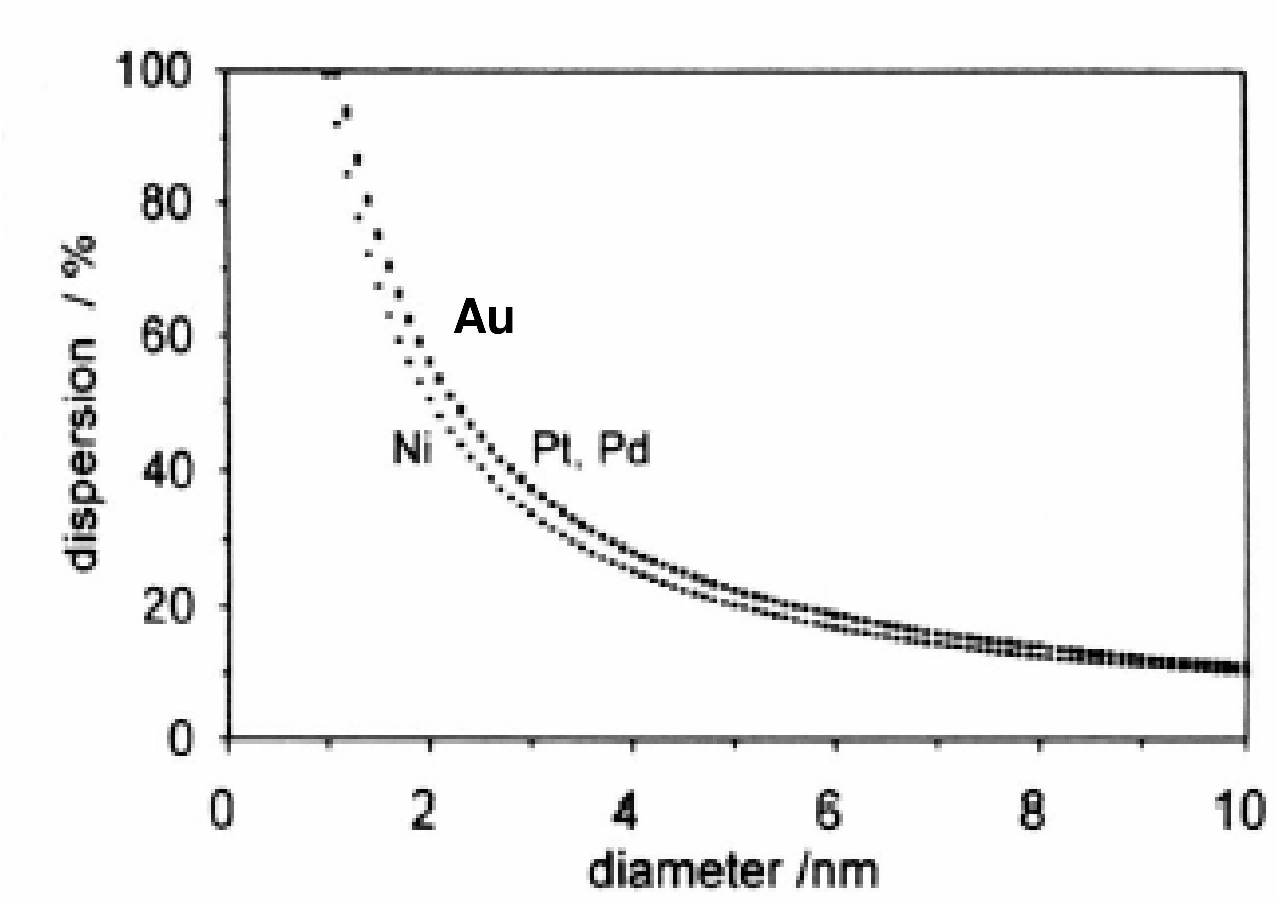


Figure 3. High-resolution transmission electron microscopic (TEM) image of a ligand-protected 11 × 13 nm gold nanoparticle; the polycrystalline gold core and the protecting shell of $P(C_6H_4SO_3Na)_3$ molecules can clearly be distinguished

G. Schmid, B. Corain. Eur. *J. Inorg. Chem.*, 2003, 3081-3098

Dispersity increases, more atoms are available for catalysis

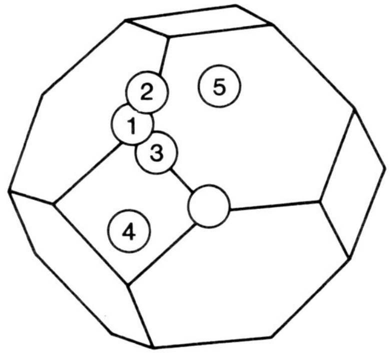


G. Ertl, H. Knözinger, J. Weitkamp (Hg.), *Handbook of Heterogeneous Catalysis*, Volume 2, wiley VCH, Weinheim, 1997, S.441

more part of edges
and corners

→

more activ centres



1 CORNER SITES
2 EDGE SITES, [1 1 1], [1 1 1]
3 EDGE SITES, [1 1 1], [1 0 0]
4 FACE SITES, [1 0 0]
5 FACE SITES, [1 1 1]

Figure 4.10. Surface sites on cubo-octahedra.

J.T. Richardson, *Principles of Catalyst Development*, Plenum Press, London 1989

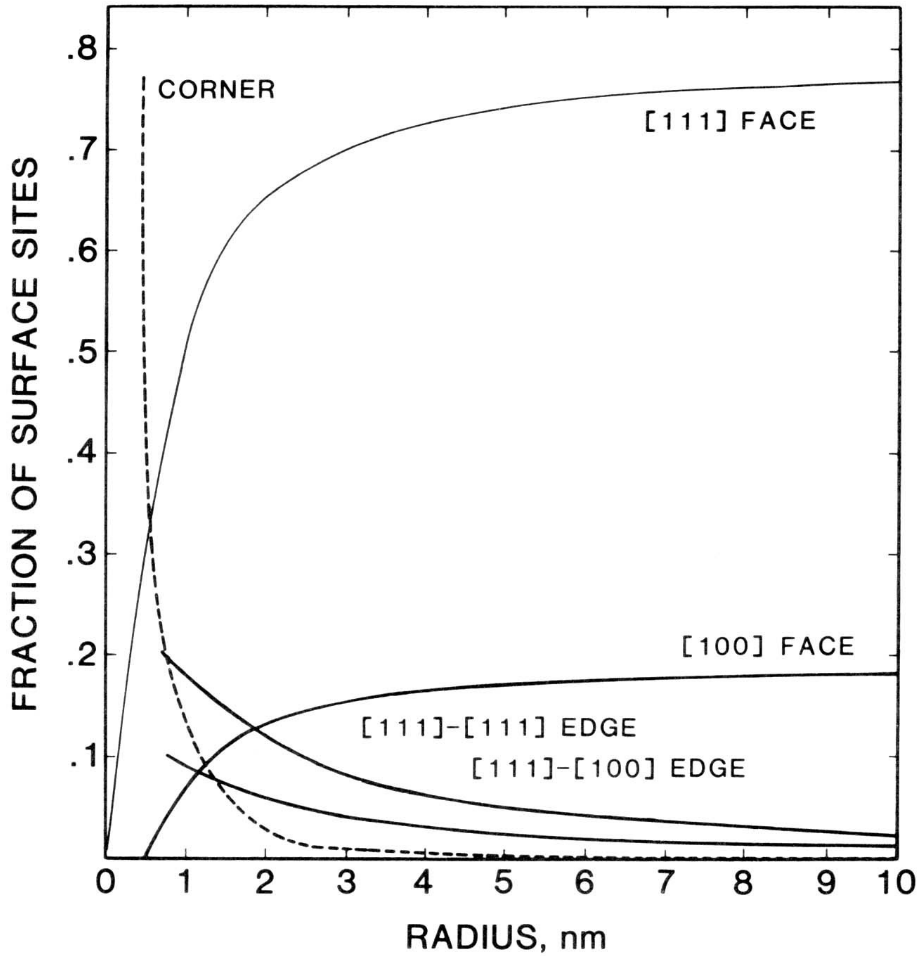


Figure 4.11. Distribution of surface sites with crystallite size.(108)

J.T. Richardson, *Principles of Catalyst Development*, Plenum Press, London 1989

metal crystal: bands continuous, < 1eV

nanoparticle: bands not continuous, 1~5 eV

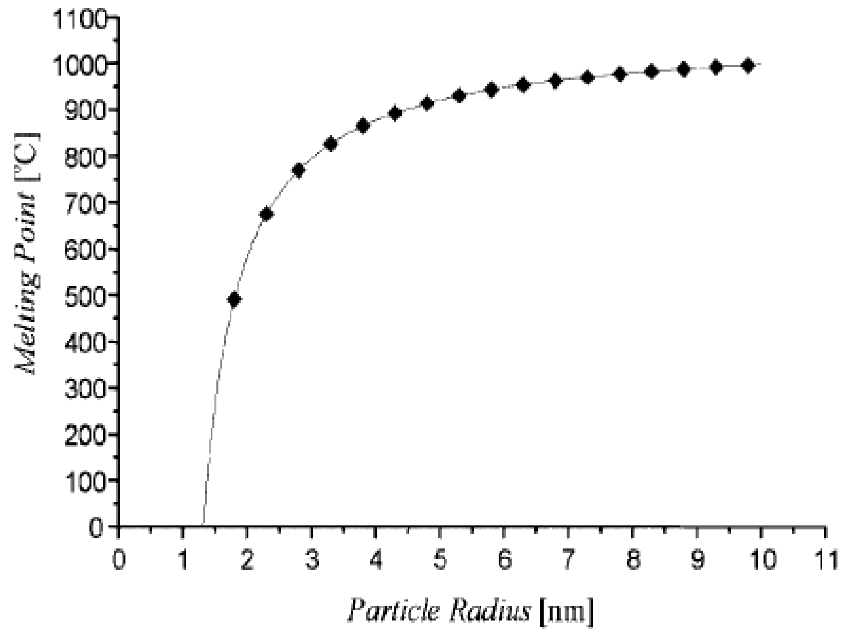
metal ⟶ Semiconductor

problem of deactivation

- the fraction of surface atoms increases, vibrate more freely,

  the melting temperature falls,

  surface atom mobility rises



Aus: G. Schmid, B. Corain. Eur. *J. Inorg. Chem.*, 2003, 3081-3098

Example: Ni

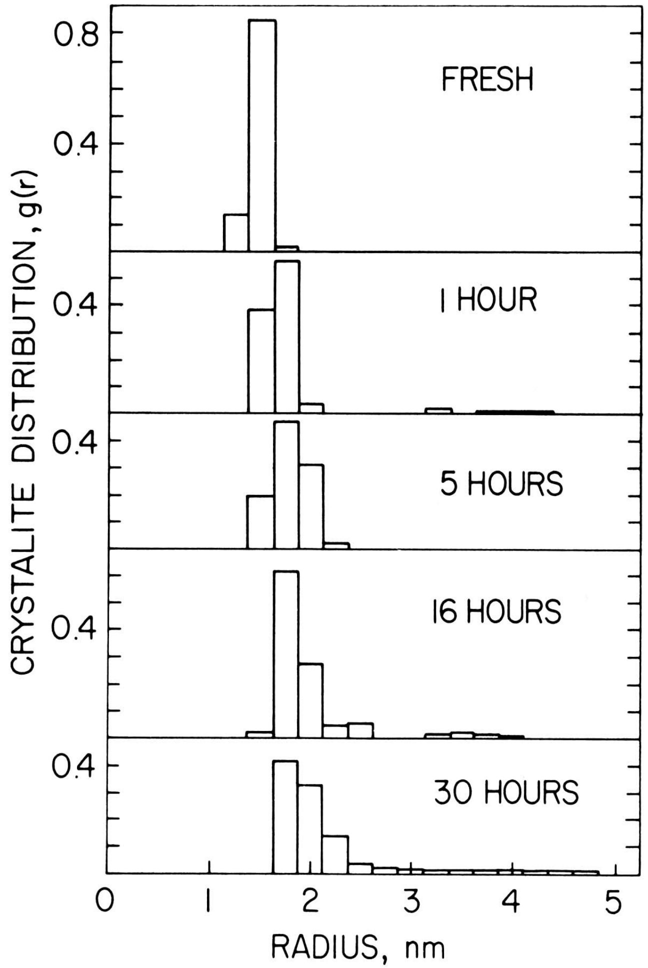


Figure 8.8. Crystallite size distribution changes for crystallite migration of nickel on silica at 500°C.[266]

J.T. Richardson, *Principles of Catalyst Development*, Plenum Press, London 1989

why gold?

- high activity
- good stability
- low temperature

Applicationspossibility

- supported, unsupported

  Al_2O_3, silica gel, MgO, TiO_2, ZrO_2, zeolite, active carbon
- gas phase, liquid phase

examples

CO to CO_2

$$O_2 + Au(0)/TiO_2 \longrightarrow Au(0)/TiO_2 -- O_2$$

$$CO + Au(0)/TiO_2 \longrightarrow Au(0)(CO)/TiO_2$$

$$CO + Au(0)/TiO_2 -- O_2 + Au(0)(CO)/TiO_2 \longrightarrow CO_2 + Au(II)(CO)(O)/TiO_2 + Au(0)/TiO_2$$

$$Au(II)(CO)(O)/TiO_2 \longrightarrow CO_2 + Au(0)/TiO_2$$

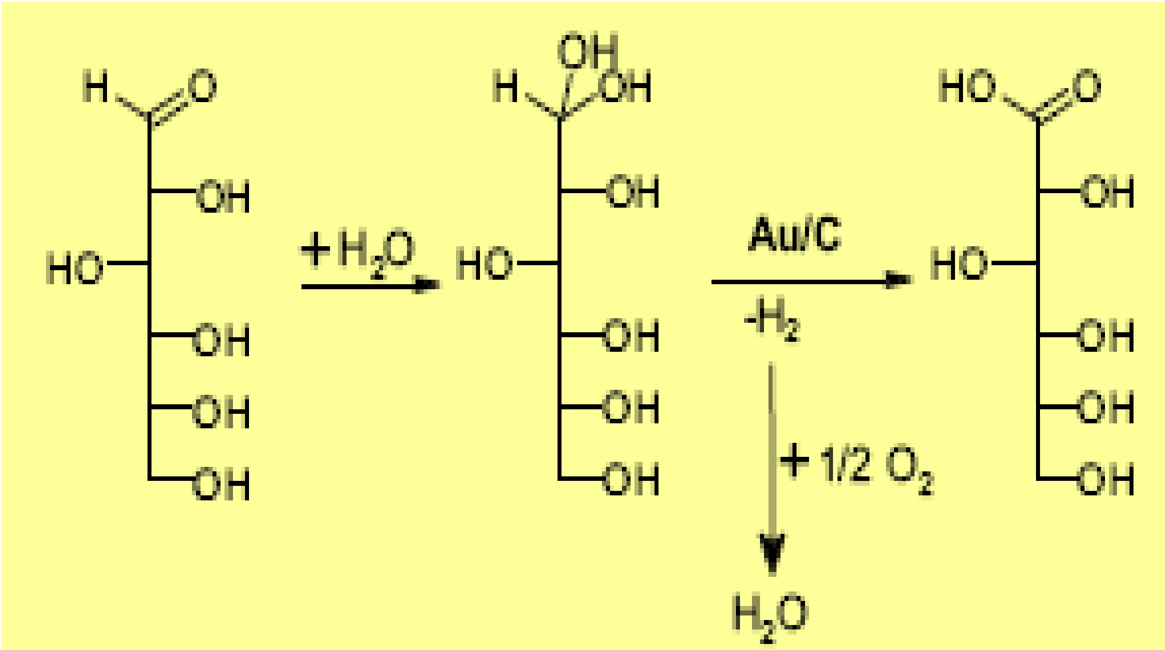
www.chemgeo.uni-hd.de/AC/huttner/heinze/kataja/seminar/au_nano_kat.pdf

- durable masks for fire fighters
- fuel cell system

Water Gas Shift Reaction

$$CO + H_2O \rightarrow H_2 + CO_2$$

glucose to gluconic acid



hydrochlorination of ethyne

$$HCl + HC \equiv CH \xrightarrow{Au/C} CHCl = CH_2$$

- old catalyst: mercuric chloride

  toxicity and rapidly deactivated
- supported catalysts are more active

the best may be yet to come

and a golden future lies ahead

Reference

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Thanks for your attention