Nano-material Processing and Surface Physical Chemistry

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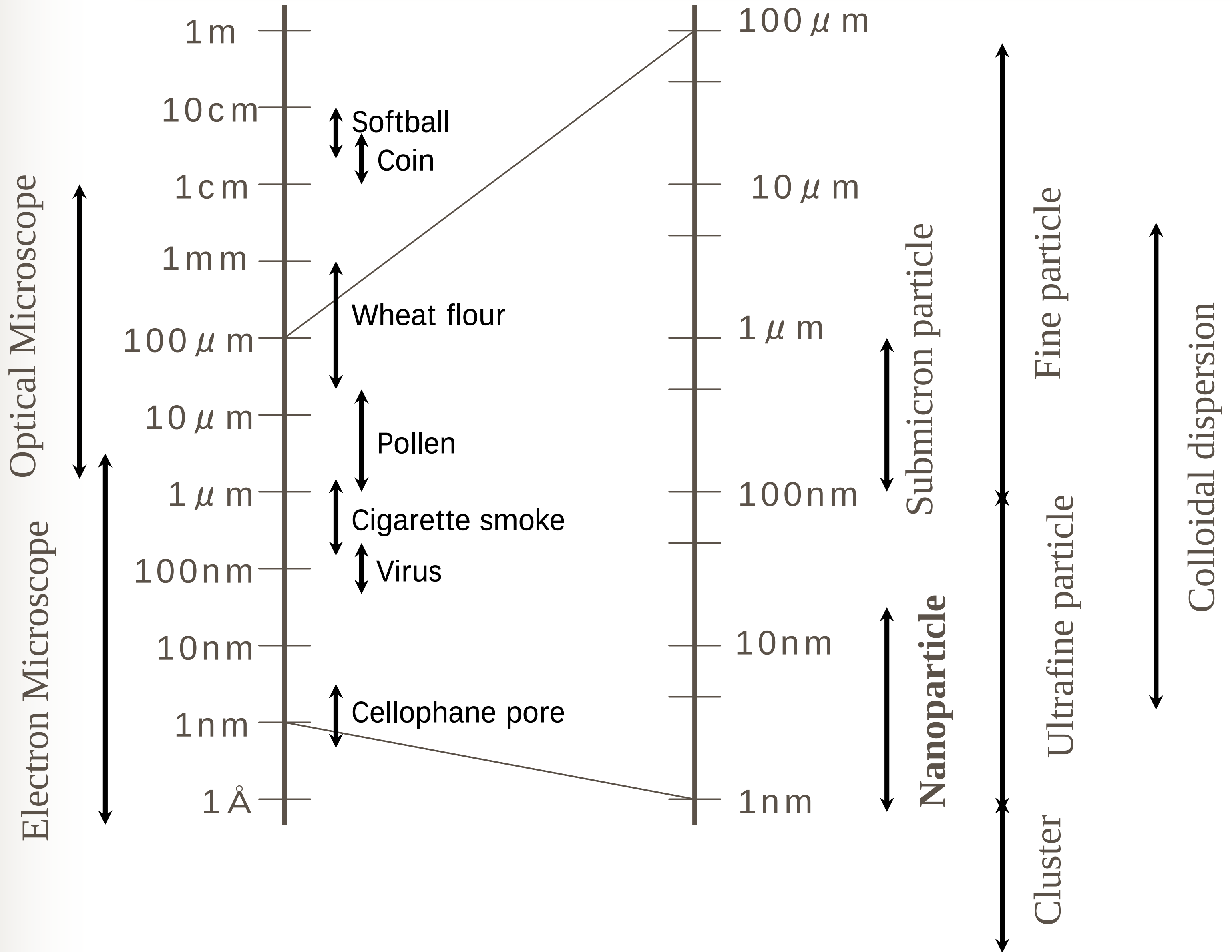
Nanoparticles

Nanoparticles

- 10^{-9} m = 1 nm
- Billionth.
- A particle is composed of several atoms.
- Characters are expected different from bulk.
- Number of surface atom becomes equal to that of bulk atom.

Classification of particles



Catalysis

Catalyst

- Industrial catalyst
  - activity, selectivity, life, treatment
- Design
  - surface control
  - bulk control
- Surface control
  - Metal catalyst →species, valence, composition, size

Activity

- Turnover frequency an active site
  - Surface reaction rate at one active site
- The whole activity of catalyst

Dependent on the total surface

Moreover, it strongly depends on the surface structure

Life

- Catalyst life
  - Maintain the same activity for a long time
  - Life should more than 1 month.
  - Loss of activity
    - as a result of sintering, change in characters, etc.

Selectivity

- Catalyst changes a specific reaction rate.
  - CO hydrogenation
    - Cu: $CO + 2H_2 \rightarrow CH_3OH$
    - Ni: $CO + 3H_2 \rightarrow CH_4 + H_2O$
    - Co, Fe: $6CO + 9H_2 \rightarrow C_6H_6 + 6H_2O$
    - Rh: $2CO + 2H_2 \rightarrow CH_3COOH$
    - Rh: $2CO + 4H_2 \rightarrow C_2H_5OH + H_2O$
  - Of course, the reaction conditions affects the rate.

Size control

- The whole catalytic activity is enhanced by increase in the total surface area.
- TOF (Turnover Frequency) sometimes depends on the size.
  - Quantum effect.

Catalyst design

- Detailed characterization of surface
- Precise control of surface

↓

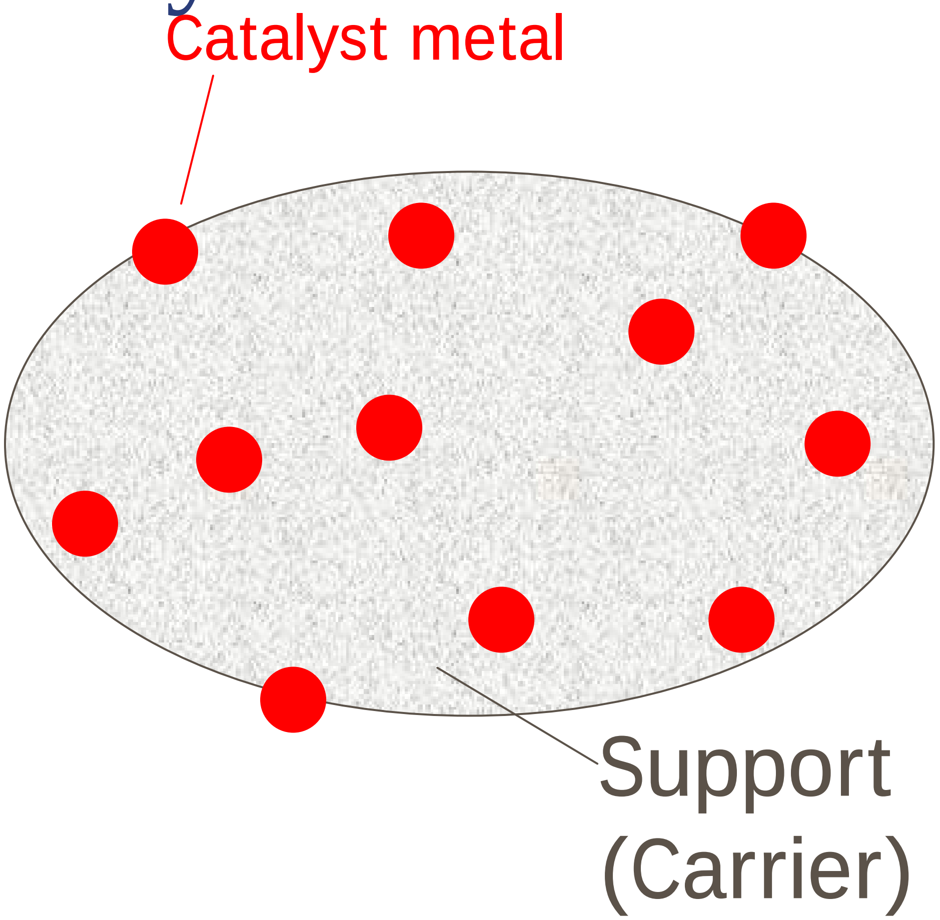
- Control of nanostructure of the surface and its evaluation is important.

Classification of catalysts

- Homogeneous catalysts
  - Same phase ← reactant, catalyst, etc.
  - Ex. Acetic acid synthesis:
    - Rh complexes catalyst = liquid phase
- Heterogeneous catalysts
  - different phase
  - Ex. Solid catalysts
    - supported catalysts、unsupported catalysts

Supported catalysts

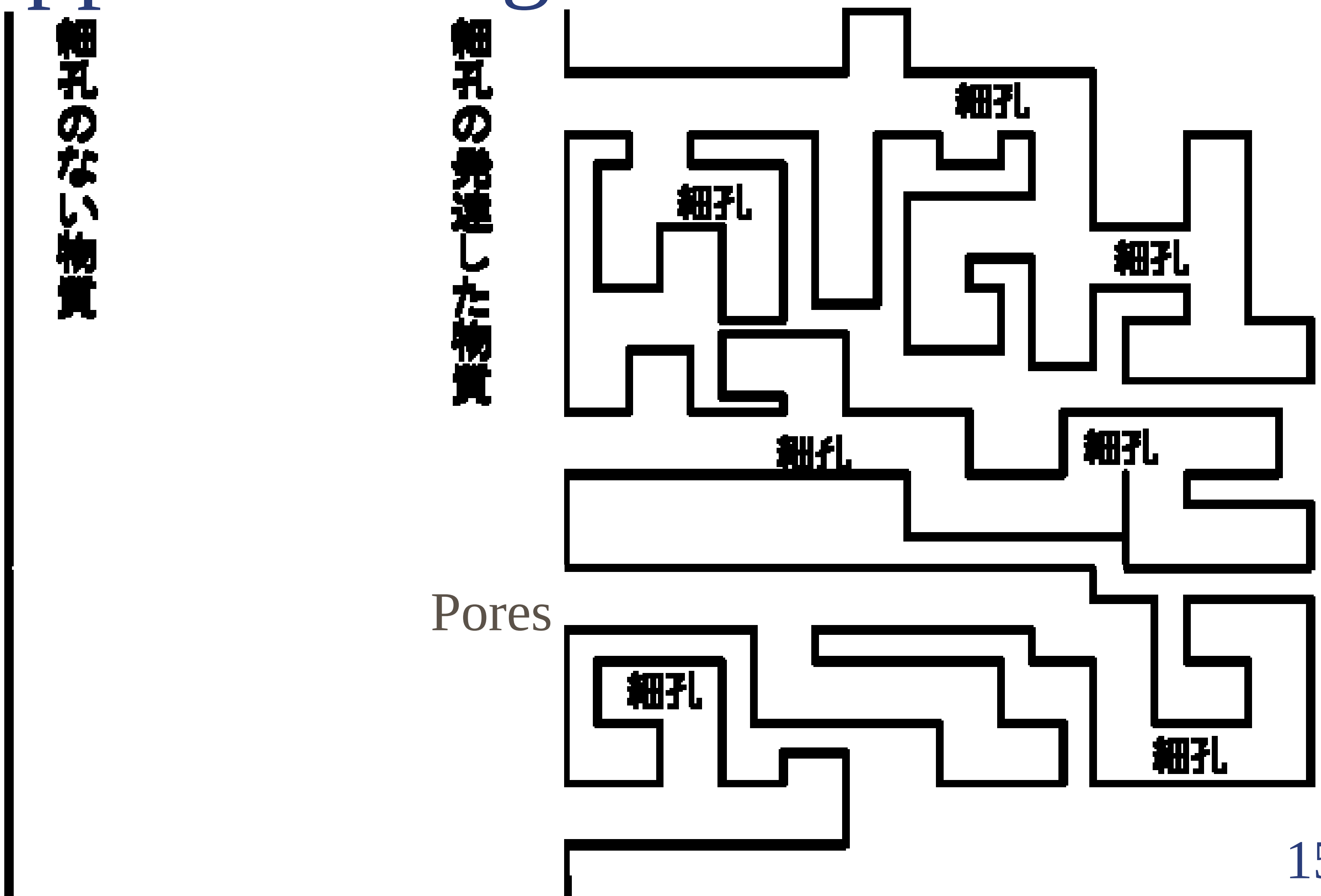
- Metal particles are supported on a carrier.
- The carrier is a porous material.

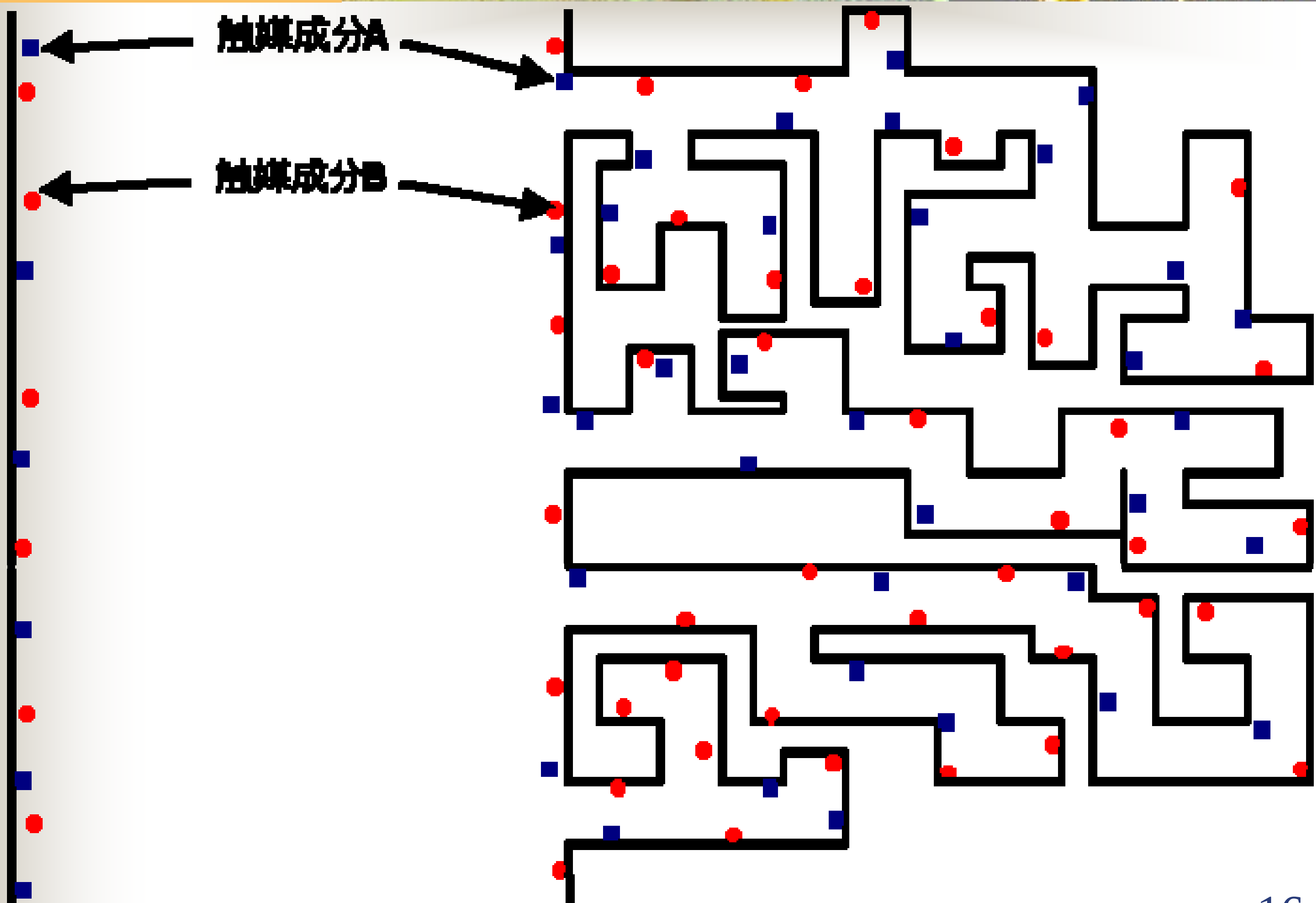


Supported metal catalysts

- Supports
  - Almost all supports are metal oxides.
  - They have many pores.
  - They have excellent tolerance against mechanical intention.
- Catalyst metal
  - They are well dispersed on the support.
  - Their size is expected to be 1~2 nm.
  - But, 5～50nm is general for industrial catalysts.

Supports： large surface area




触媒成分A
触媒成分B

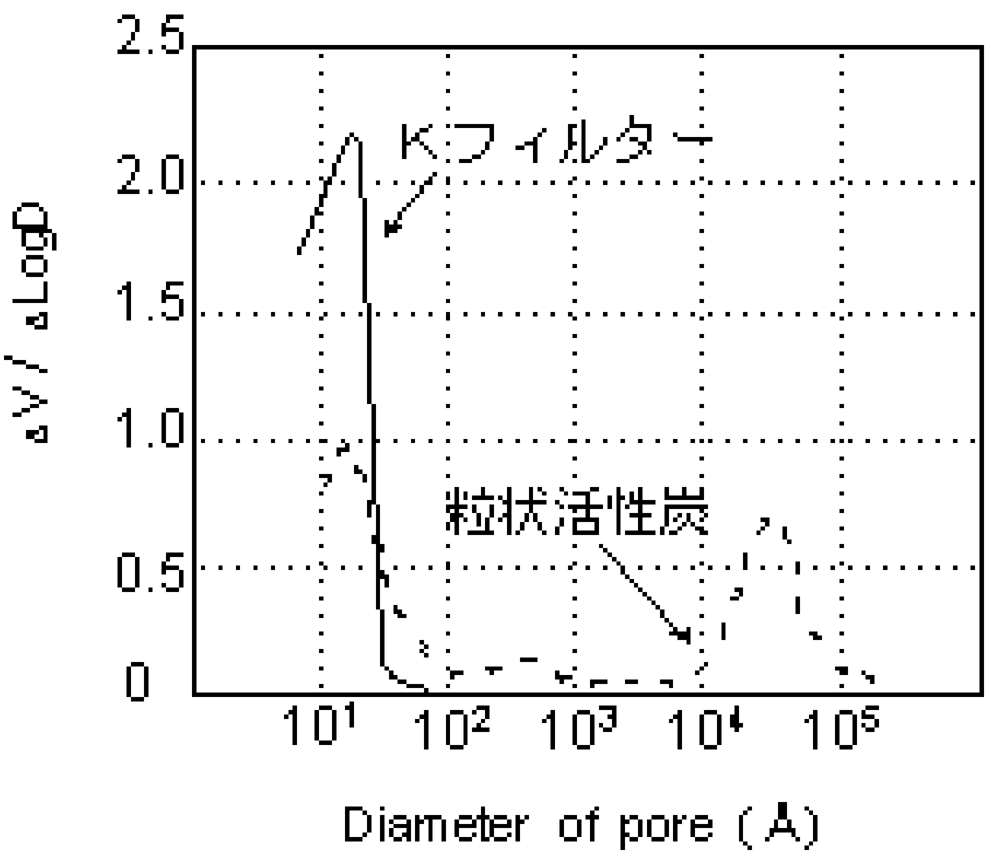
Examples of supports: active carbons

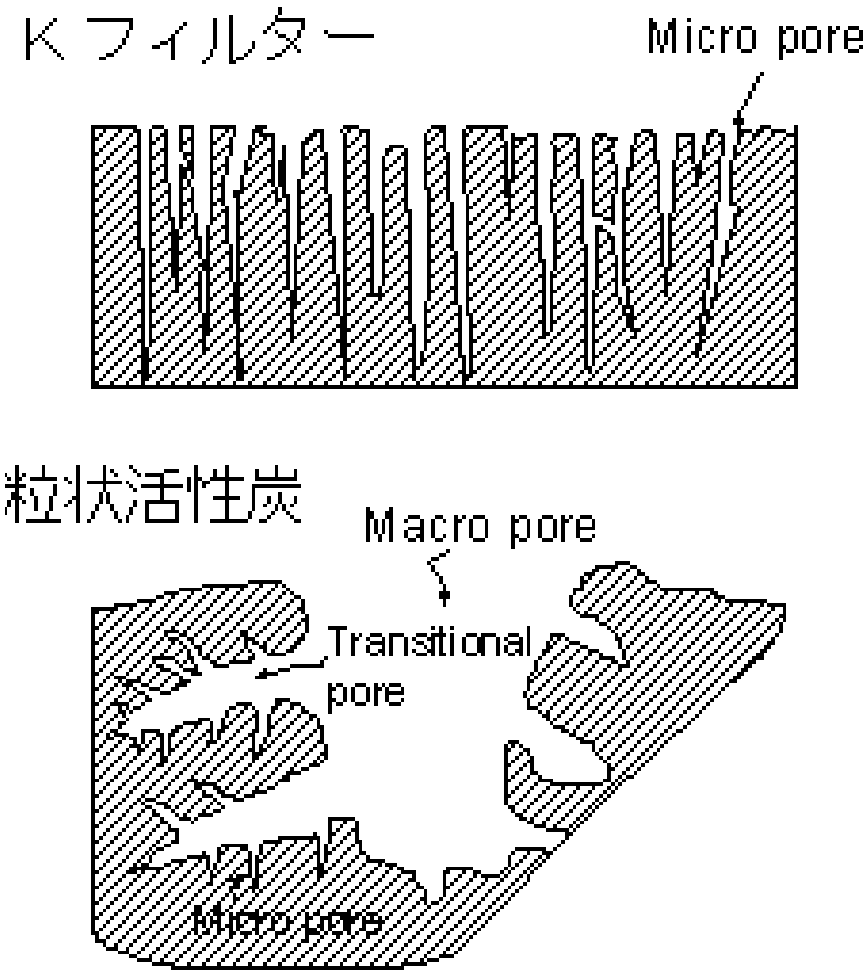
- Yashigara AC

Anthracic AC

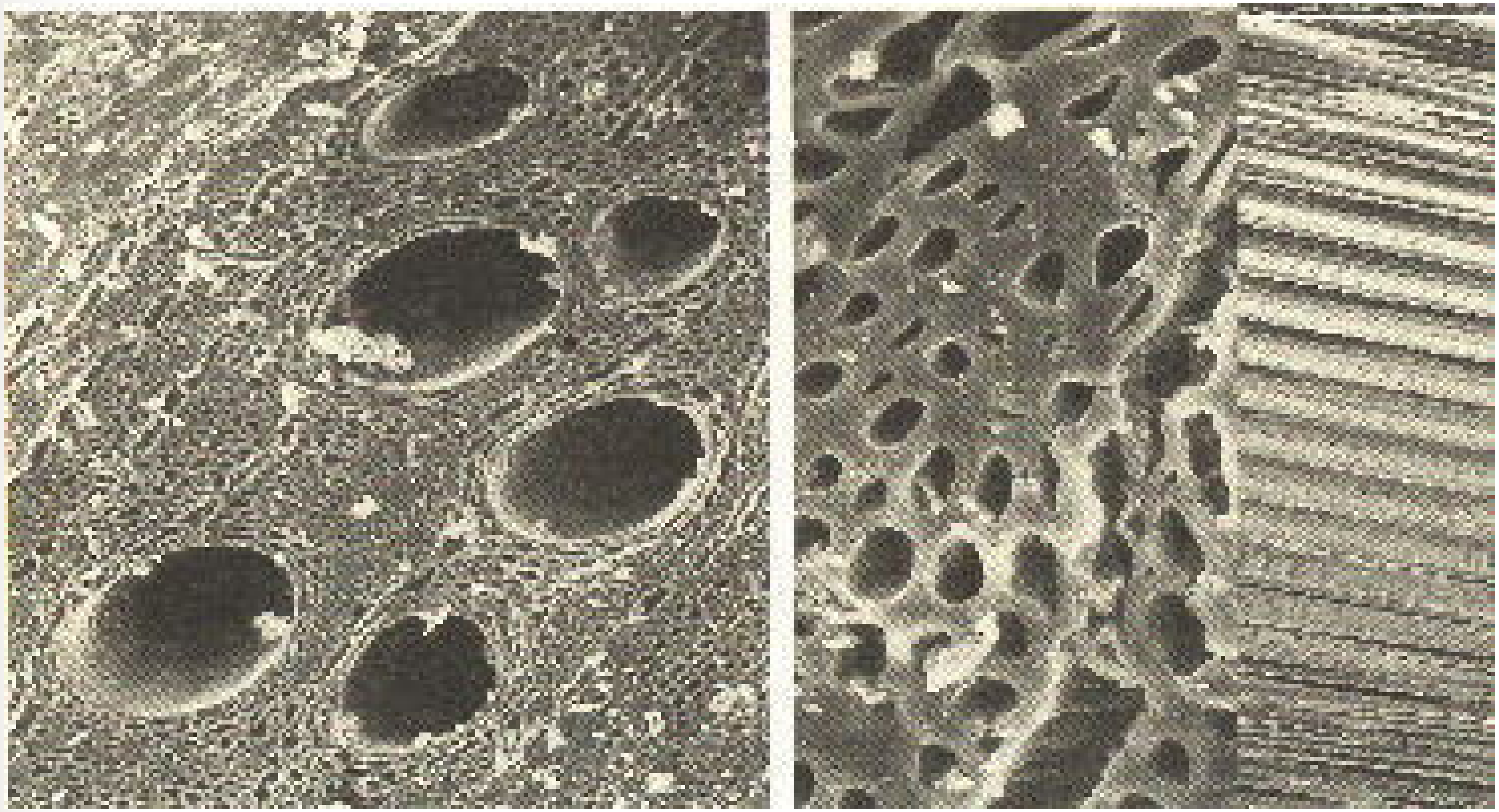
- Charcoal AC

Active carbons





Charcoal surface



Supported metal catalysts

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  - Almost all supports are metal oxides.
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- Catalyst metal
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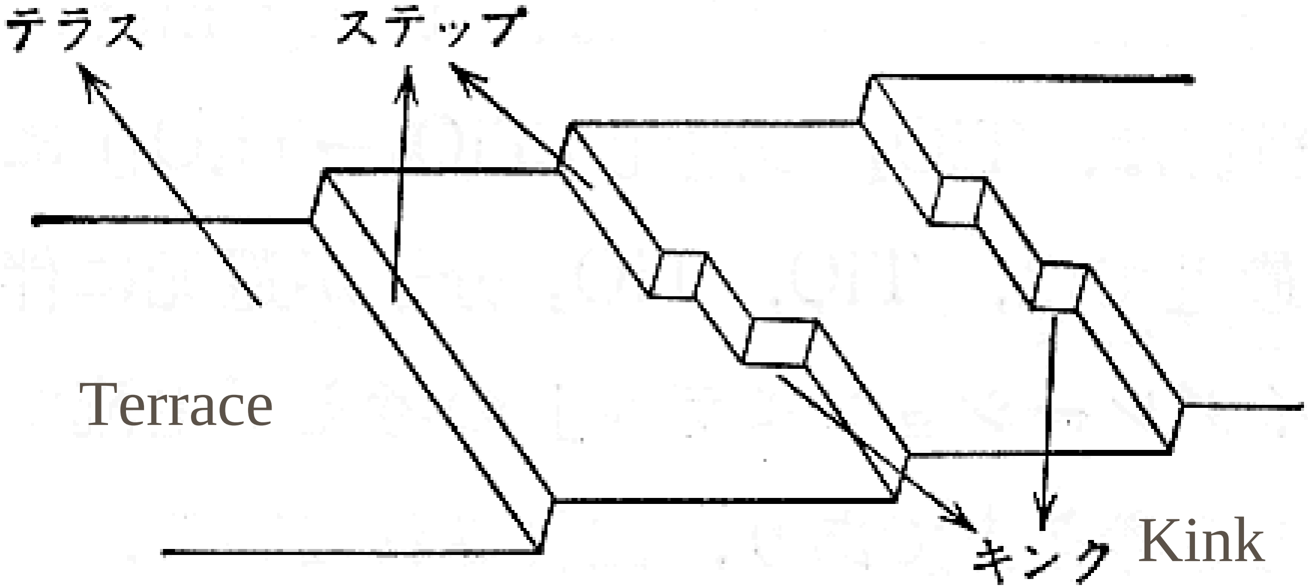
  - Their size is expected to be 1~2 nm.
  - But, 5〜50nm is general for industrial catalysts.

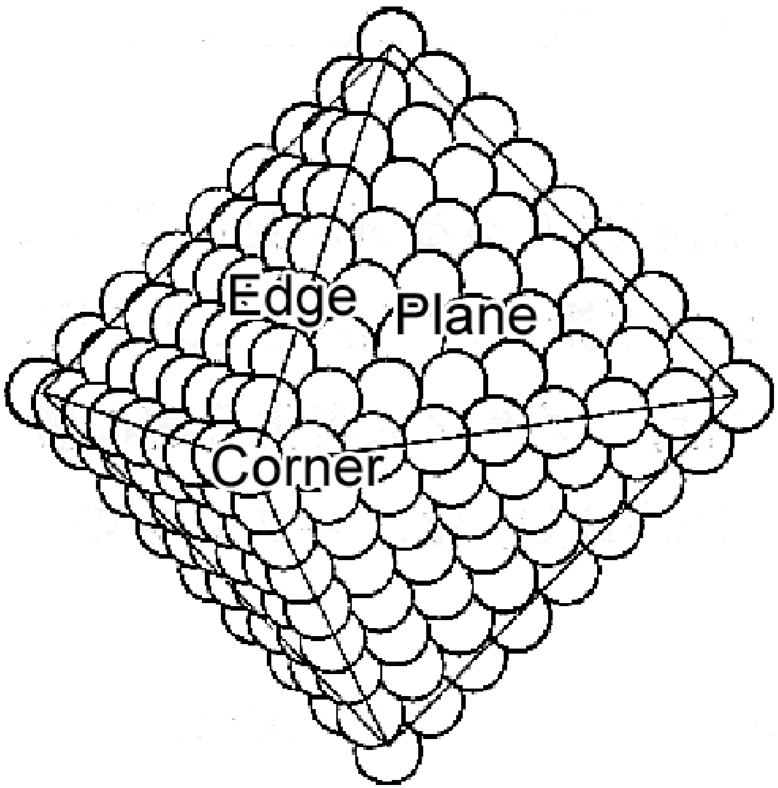
Surface structure

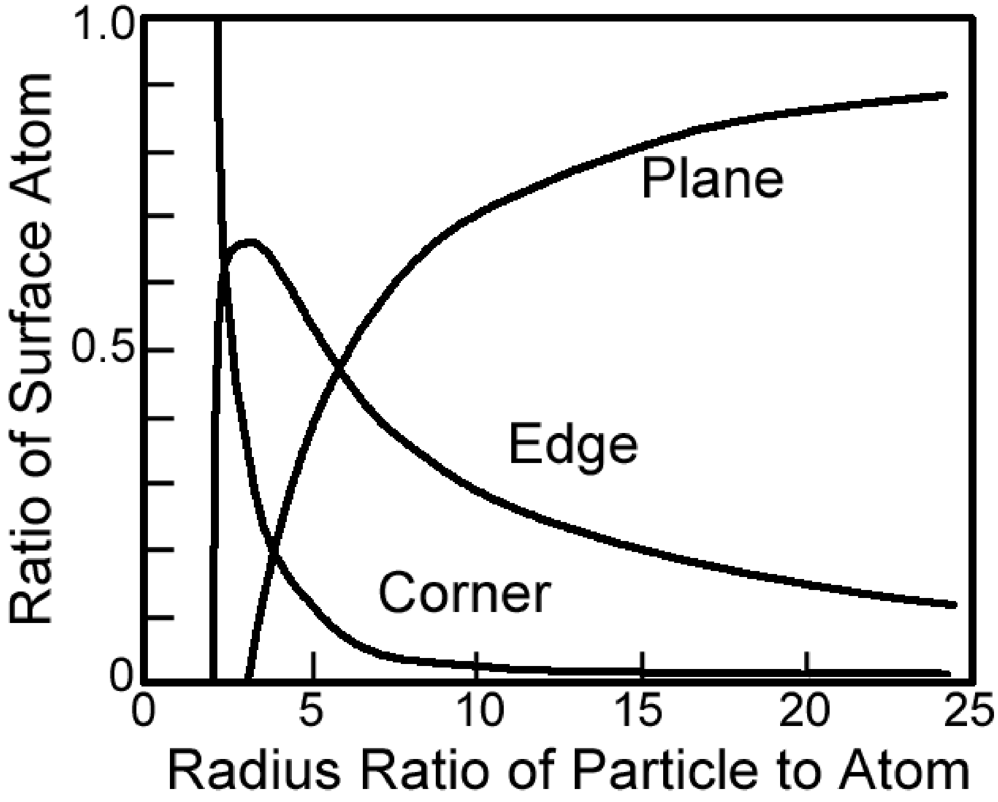


金属単結晶表面上の原子.

Atoms of single crystalline metal surface

Surface structure





Adsorption and catalytic reaction

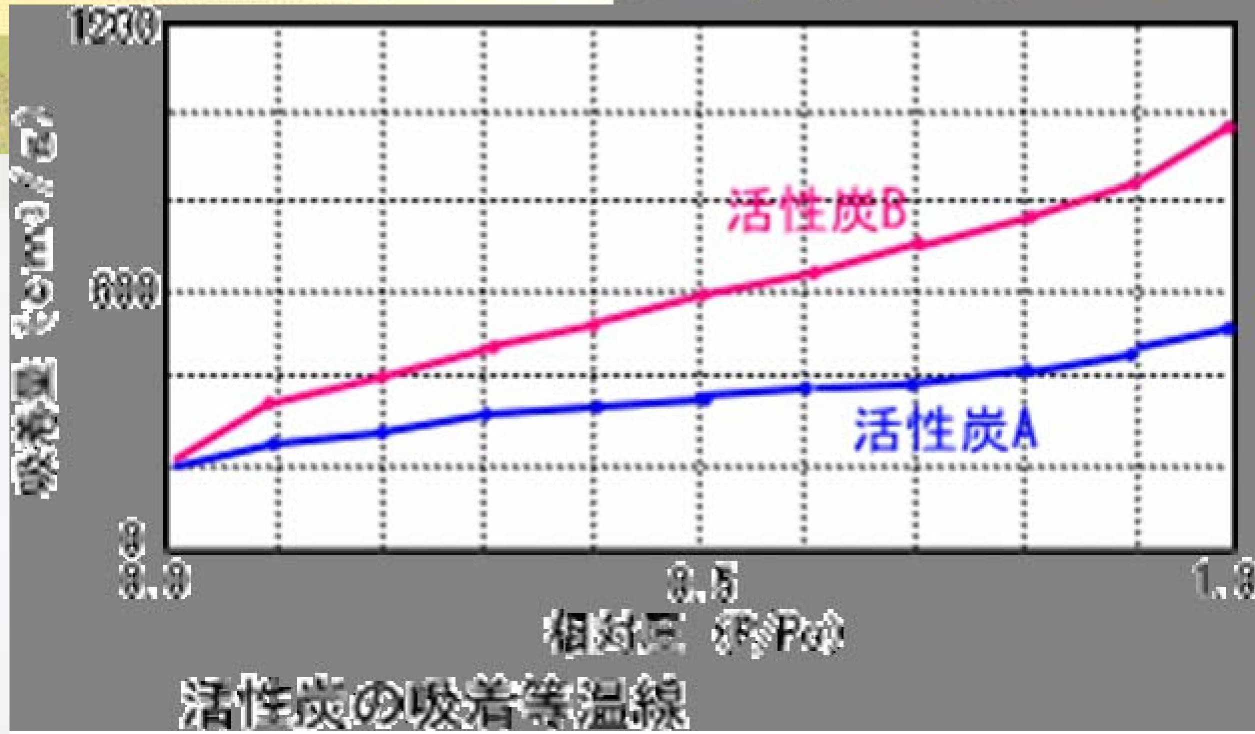
Adsorption

- Physisorption 蠅的吸着 like a fly
  - week： always
- Chemisorption 蚊的吸着 like a mosquito
  - strong： chemical bonding

Table Chemisorption and physisorption

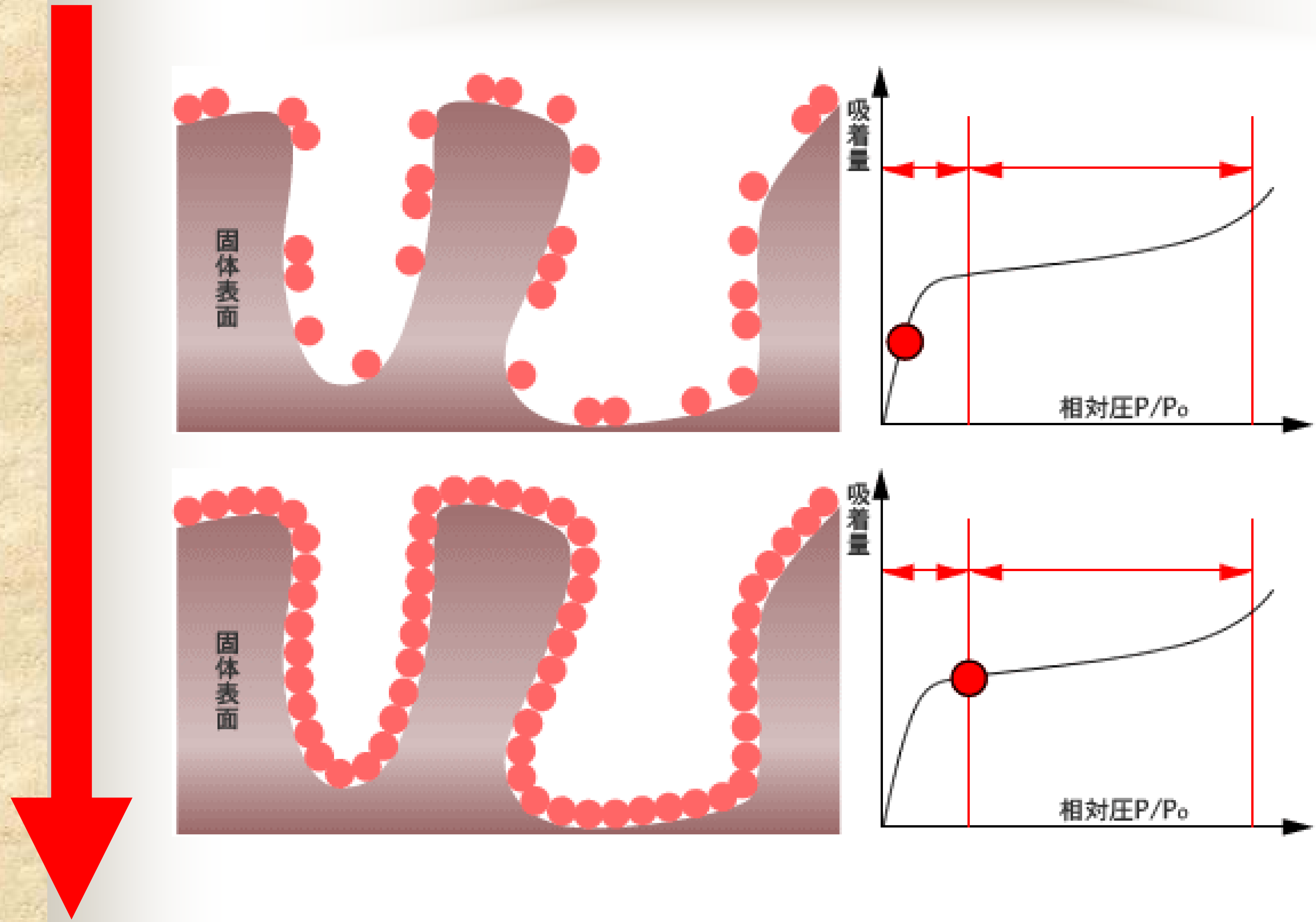
Features	Chemisorption	Physisorption
Force	Chemical bond	van der Waals
Place	Selective	nonselective
Structure	Monolayer	Multilayer
ΔH	10～100 k cal/mol	2~3 kcal/mol
Activation energy	Large	Small
Rate	Slow	Rapid
Adsorption and desorption	sometimes irreversible	reversible
Typical type	Langmuir	BET

Physisorption

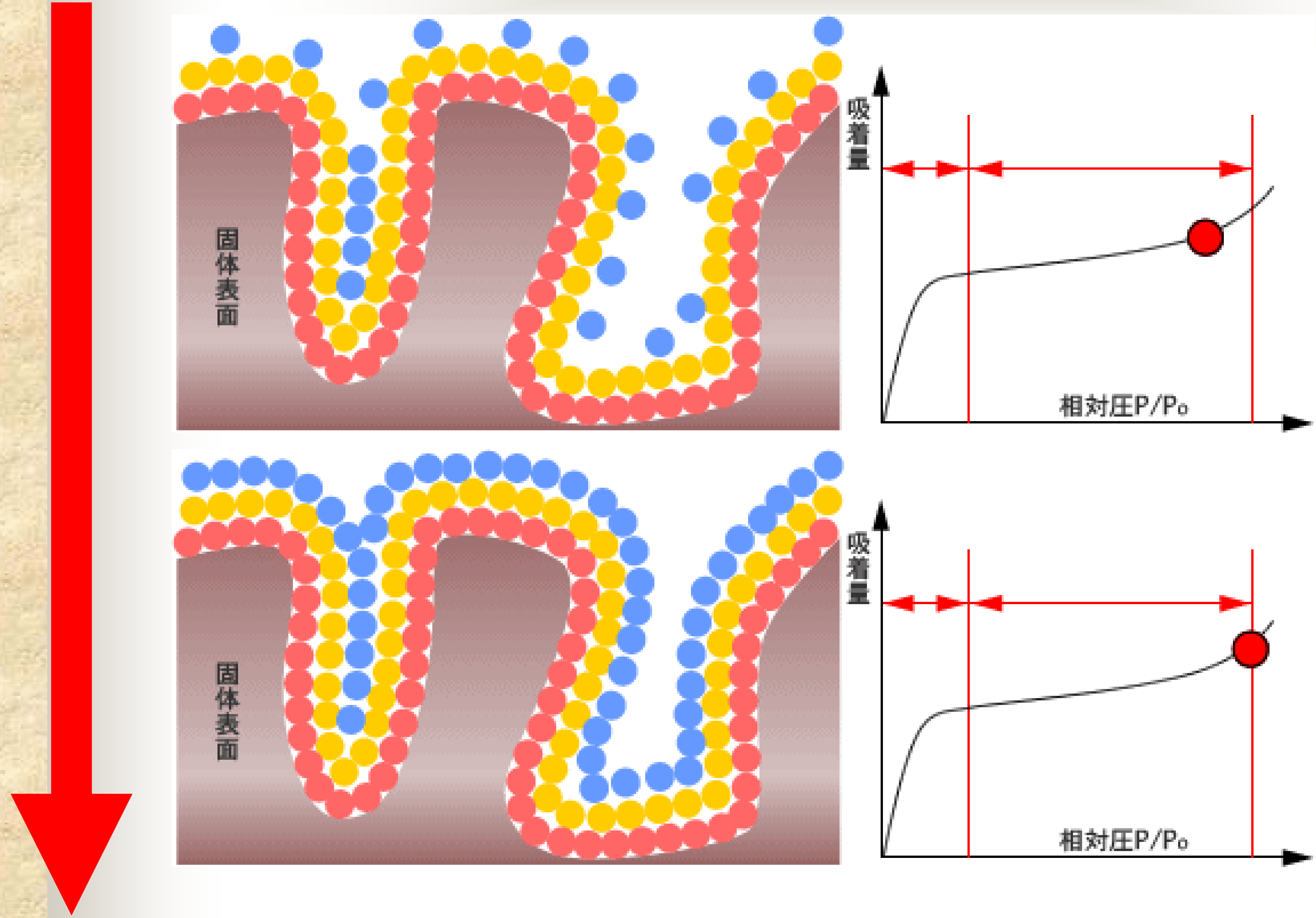


試料		比表面積 (m²/g)	細孔容積 (ml/g)		平均細孔直径	資料質量 (g)
		BET法	メソポア	ミクロポア		
			10_3000Å	＜10Å		
1	活性炭A	1050	0.56	0.36	30	0.200
2	活性炭B	1600	1.48	0.27	35	0.210

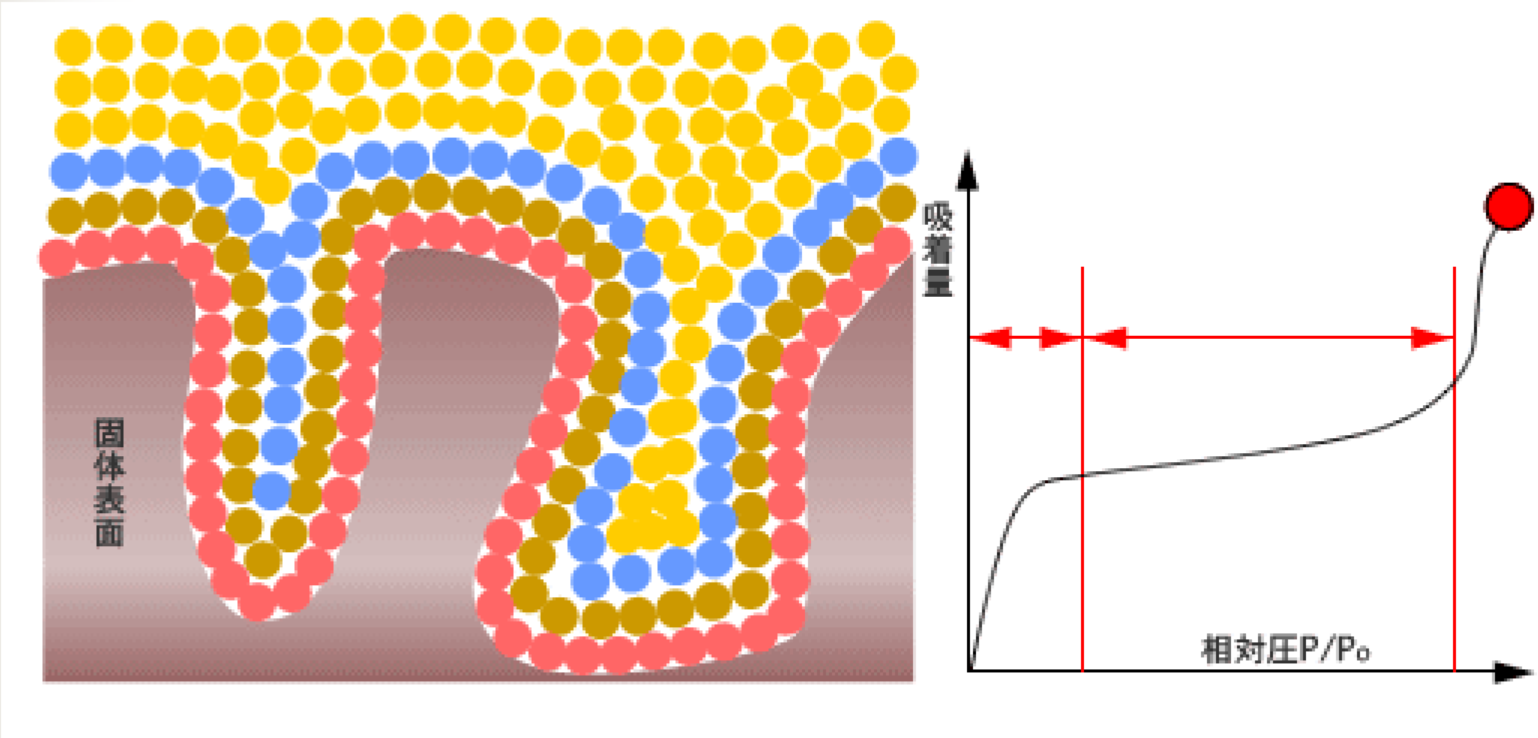
Physisorption



Physisorption



Physisorption



Physisorption

BETの式：一定温度で吸着平衡状態であるとき、
吸着平衡圧Pと、その圧力での吸着量Vの関係

$$\frac{P}{V(P_0-P)} = \frac{1}{V_mC} + \left(\frac{C-1}{V_mC}\right)\left(\frac{P}{P_0}\right)$$

但し、

- P_0：　飽和蒸気圧
- V_m：　単分子層吸着量、気体分子が固定表面で単分子層を形成した時の吸着量
- C：　吸着熱などに関するパロラメータ＞0

この関係式はP/P_0：0.05～0.35の範囲でよく成立する

Adsorption to reaction

Catalysis

- Physisorption
- Chemisorption
- Surface reaction
- Desorption

To this line, it means ADSORPTION

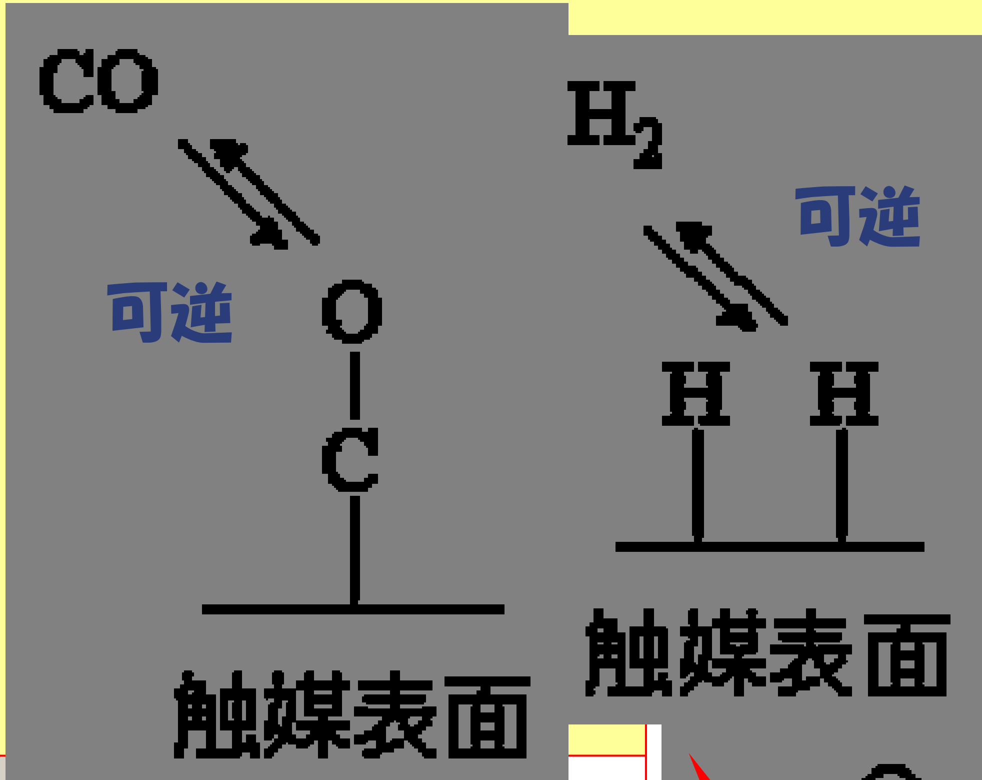
Ex: methanol synthesis

- Synthesis gas into methanol

$$CO + 2H_2 \rightarrow CH_3OH$$

C=O: nondissociative adsorption.

H-H: dissociative adsorption.

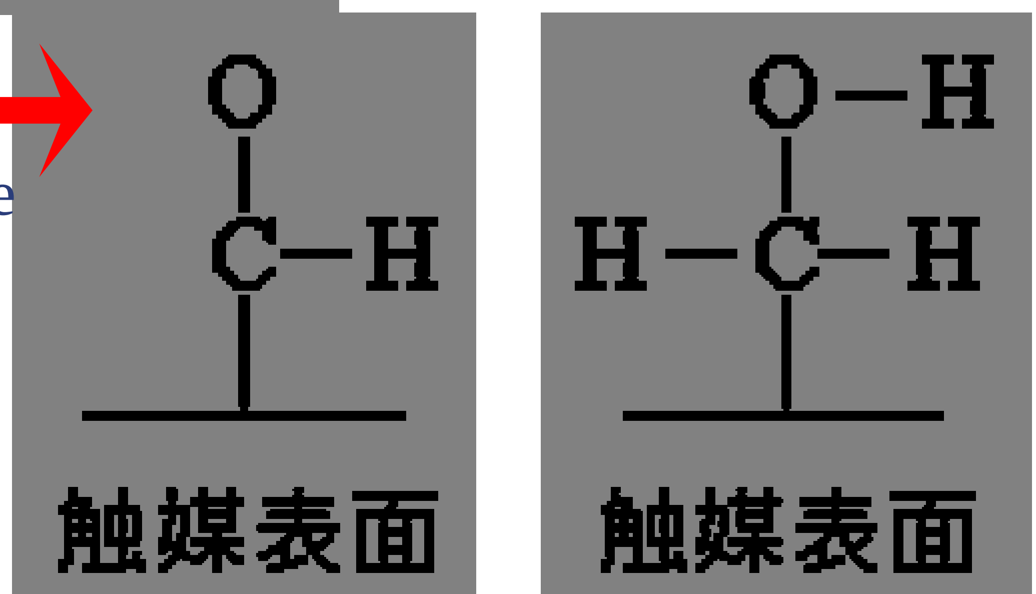


Physisorption
→chemisorption

irreversible

Surface reaction

CH_3OH



Surface reaction

- Irreversible path
  - in extremely low counteraction rate
- Surface reaction often = rate determining
  - Surface reaction includes many steps.
  - Arrenius plot is useful to decide the rate-determining step.

Ex: methanol synthesis

- Synthesis gas into methanol

$CO + 2H_2 \rightarrow CH_3OH$

CO gas→CO（chemisoption）

H_2 gas→ H_2 （chemisoption）→2H（dissociative adsorption）

CO（ad.）+H→CHO（ad.）　＜rate determining＞

CHO（ad.）+H→CH_2O（ad.）

CH_2O（ad.）+H→CH_3O（ad.）

CH_3O（ad.）+H→ CH_3OH（ad.）

CH_3OH（ad.）→（desorption）CH_3OH

Activation energy

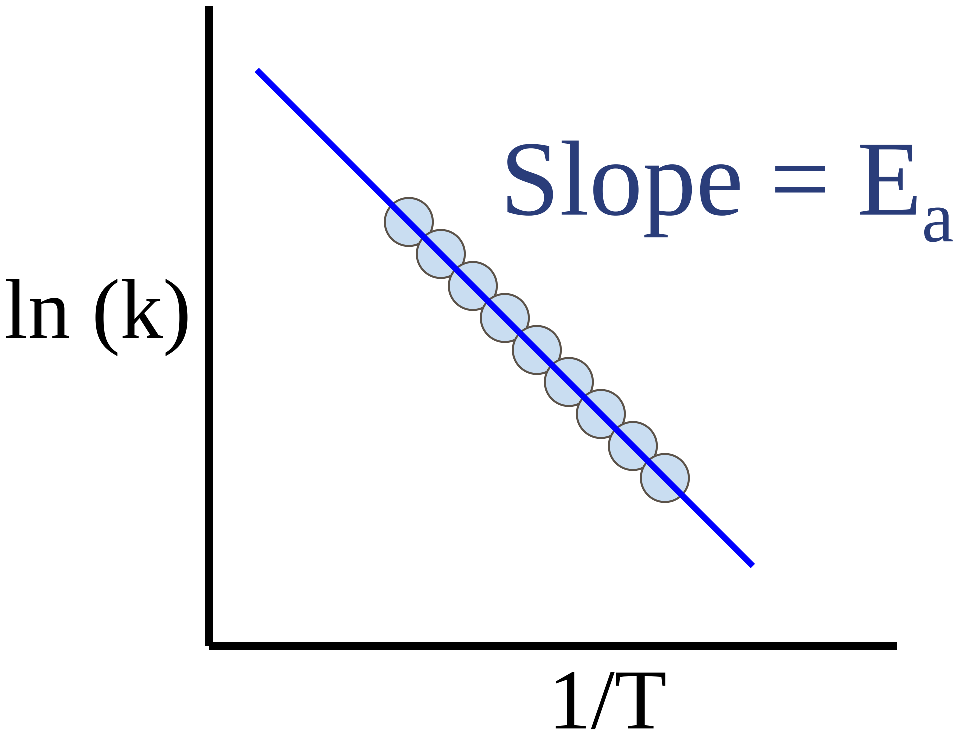
- Arrenius equation

$$k = A\exp\left(-\frac{E_a}{RT}\right)$$

- where A is frequency factor, E is activation energy.

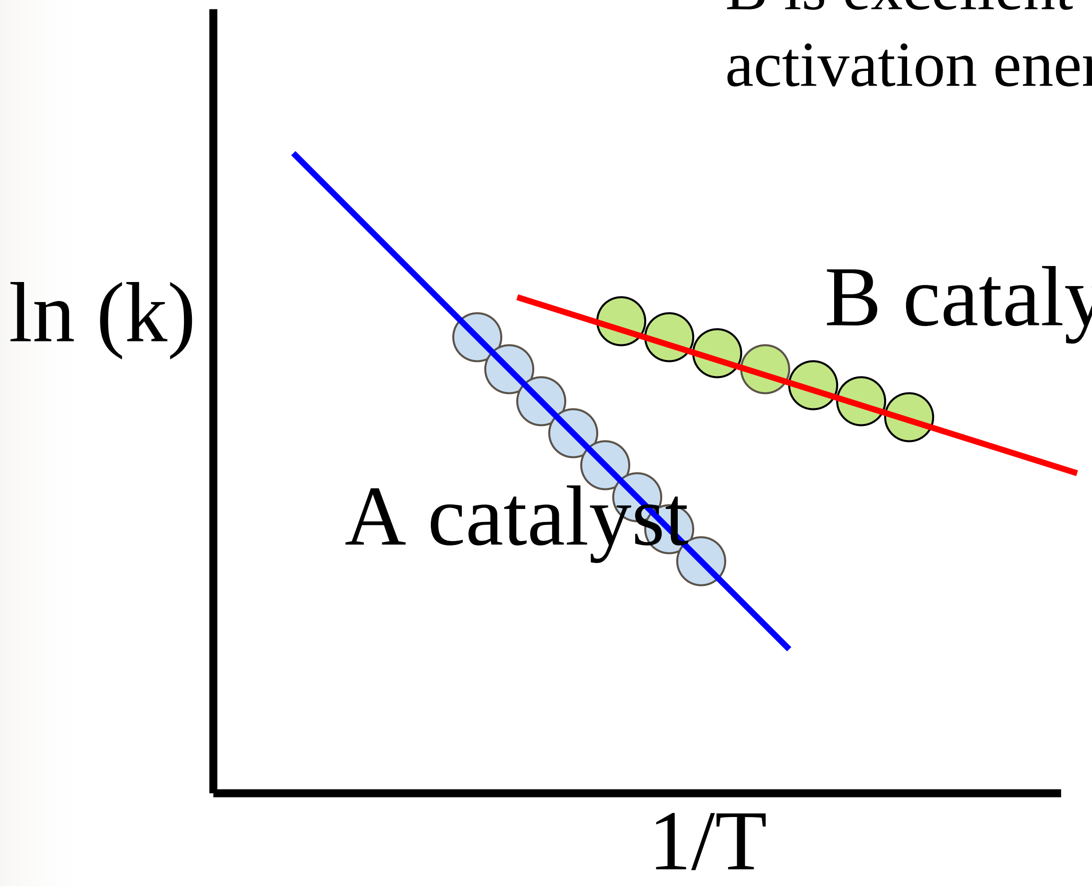
Apparent activation energy

- Plot ln (k)＝y axis, 1/T＝x axis.
- Slope = Ea (apparent activation energy)



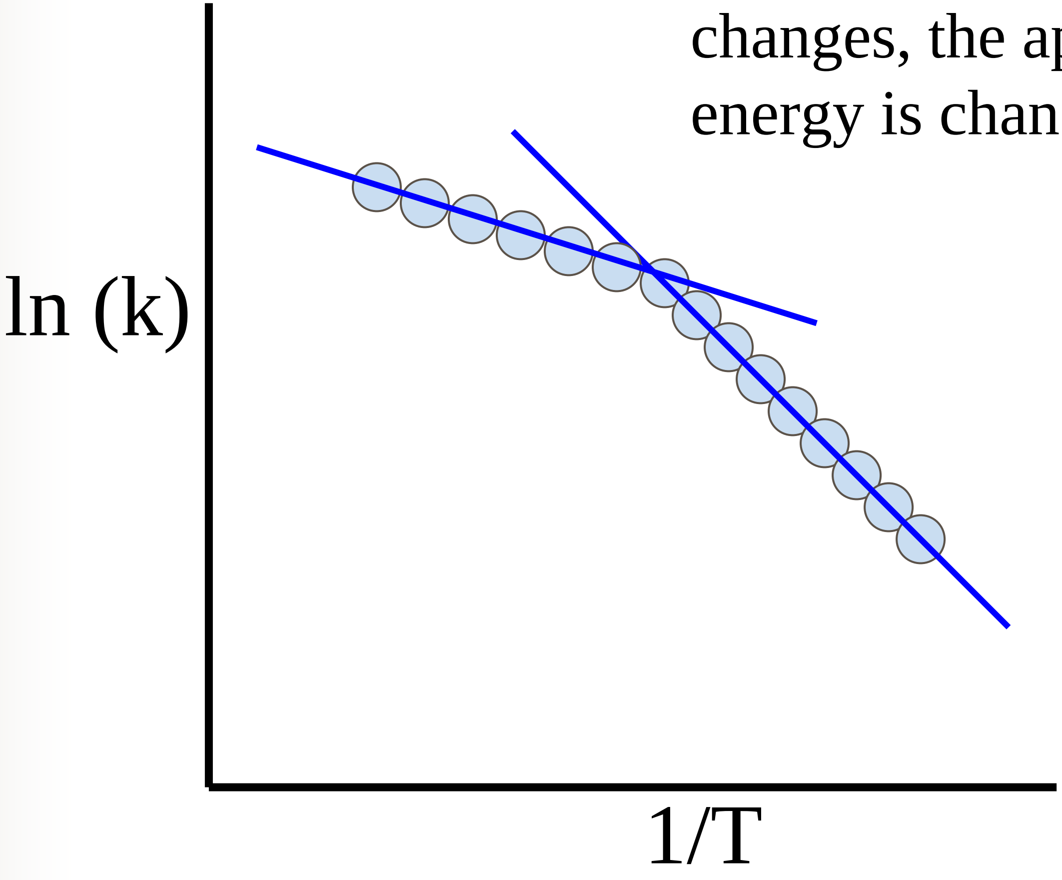
Evaluation of catalyst

B is excellent because of lower activation energy.

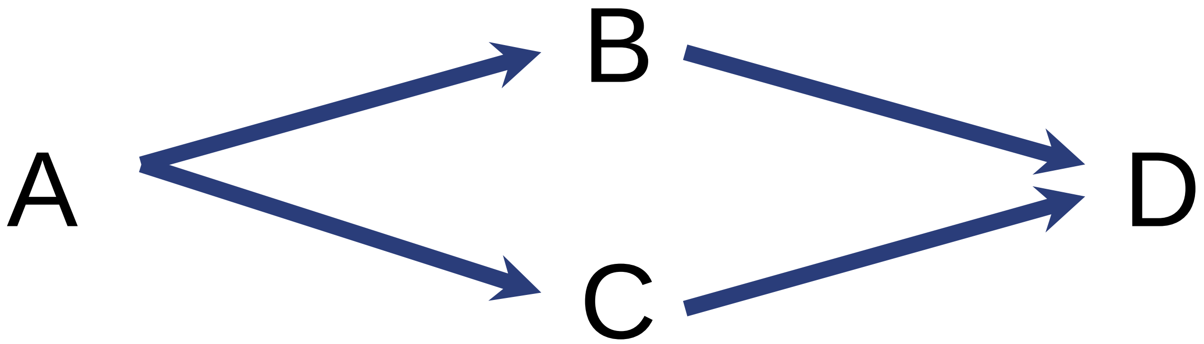


Change in activation energy

When the rate-determining step is changes, the apparent activation energy is changed.



Reaction path



When the rate-determining step is changes, the apparent activation energy is changed.

Catalytic reactions

Structure-sensitive or structure-insensitive

- Insensitive
  - Surface area effect
- Sensitive
  - Activity depends on size.
    - Higher in smaller size
    - Higher in larger size
    - Maximum in a specific size

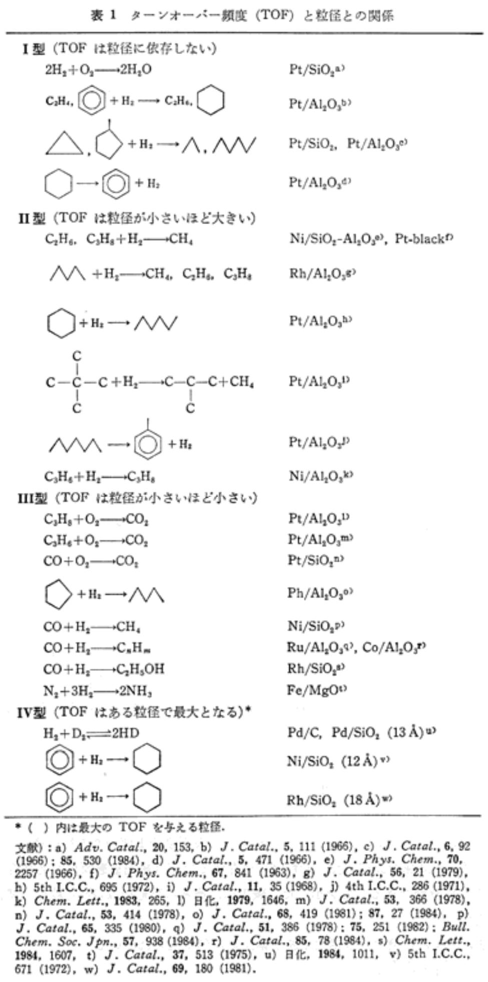


表 1 ターンオーバー頻度 (TOF) と粒径との関係

I 型 (TOF は粒径に依存しない)	
$2H_2+O_2 \longrightarrow 2H_2O$	Pt/SiO_2 a)
C_2H_4, + H_2 ⟶ C_2H_6,	Pt/Al_2O_3 b)
+ H_2 ⟶	Pt/SiO_2, Pt/Al_2O_3 c)
⟶ + H_2	Pt/Al_2O_3 d)
II 型 (TOF は粒径が小さいほど大きい)	
C_2H_6, $C_3H_8+H_2 \longrightarrow CH_4$	Ni/SiO_2-Al_2O_3 e), Pt-black f)
$+H_2 \longrightarrow CH_4$, C_2H_6, C_3H_8	Rh/Al_2O_3 g)
+ H_2 ⟶	Pt/Al_2O_3 h)
C–C(C)(C)–C + H_2 ⟶ C–C(C)–C + CH_4	Pt/Al_2O_3 i)
⟶ + H_2	Pt/Al_2O_3 j)
$C_3H_6+H_2 \longrightarrow C_3H_8$	Ni/Al_2O_3 k)
III型 (TOF は粒径が小さいほど小さい)	
$C_3H_8+O_2 \longrightarrow CO_2$	Pt/Al_2O_3 l)
$C_3H_6+O_2 \longrightarrow CO_2$	Pt/Al_2O_3 m)
$CO+O_2 \longrightarrow CO_2$	Pt/SiO_2 n)
+ H_2 ⟶	Ph/Al_2O_3 o)
$CO+H_2 \longrightarrow CH_4$	Ni/SiO_2 p)
$CO+H_2 \longrightarrow C_nH_m$	Ru/Al_2O_3 q), Co/Al_2O_3 r)
$CO+H_2 \longrightarrow C_2H_5OH$	Rh/SiO_2 s)
$N_2+3H_2 \longrightarrow 2NH_3$	Fe/MgO t)
IV型 (TOF はある粒径で最大となる)*	
$H_2+D_2 \rightleftharpoons 2HD$	Pd/C, Pd/SiO_2 (13 Å) u)
+ H_2 ⟶	Ni/SiO_2 (12 Å) v)
+ H_2 ⟶	Rh/SiO_2 (18 Å) w)

* ( ) 内は最大の TOF を与える粒径.

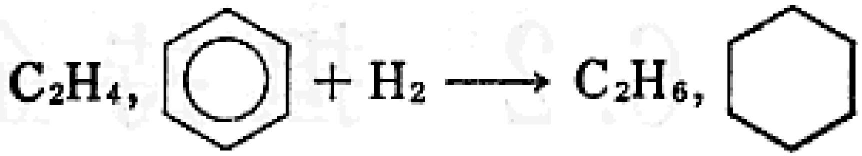
文献) : a) *Adv. Catal.*, **20**, 153, b) *J. Catal.*, **5**, 111 (1966), c) *J. Catal.*, **6**, 92 (1966) ; **85**, 530 (1984), d) *J. Catal.*, **5**, 471 (1966), e) *J. Phys. Chem.*, **70**, 2257 (1966), f) *J. Phys. Chem.*, **67**, 841 (1963), g) *J. Catal.*, **56**, 21 (1979), h) 5th I.C.C., 695 (1972), i) *J. Catal.*, **11**, 35 (1968), j) 4th I.C.C., 286 (1971), k) *Chem. Lett.*, **1983**, 265, l) 日化, **1979**, 1646, m) *J. Catal.*, **53**, 366 (1978), n) *J. Catal.*, **53**, 414 (1978), o) *J. Catal.*, **68**, 419 (1981) ; **87**, 27 (1984), p) *J. Catal.*, **65**, 335 (1980), q) *J. Catal.*, **51**, 386 (1978) ; **75**, 251 (1982) ; *Bull. Chem. Soc. Jpn.*, **57**, 938 (1984), r) *J. Catal.*, **85**, 78 (1984), s) *Chem. Lett.*, **1984**, 1607, t) *J. Catal.*, **37**, 513 (1975), u) 日化, **1984**, 1011, v) 5th I.C.C., 671 (1972), w) *J. Catal.*, **69**, 180 (1981).

Structure-insensitive reaction

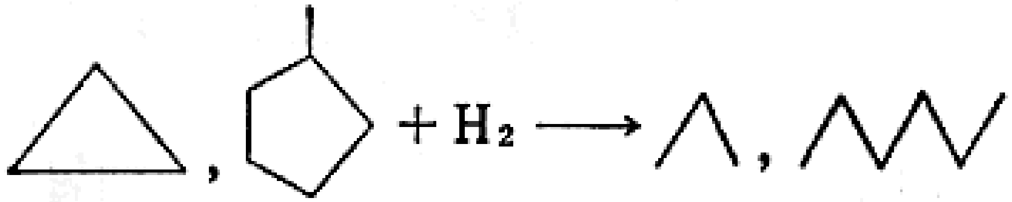
ターンオーバー頻度（TOF）と粒径との関係

I 型（TOF は粒径に依存しない）

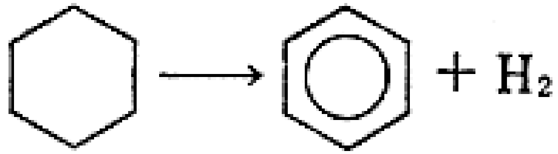
$2H_2 + O_2 \longrightarrow 2H_2O$　　Pt/SiO_2[a]



Pt/Al_2O_3[b]



Pt/SiO_2, Pt/Al_2O_3[c]



Pt/Al_2O_3[d]

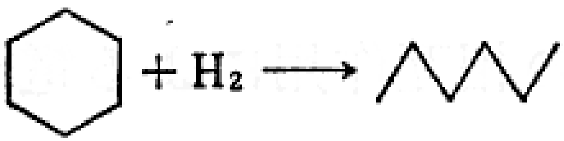
Structure-sensitive reaction

ターンオーバー頻度（TOF）と粒径との関係

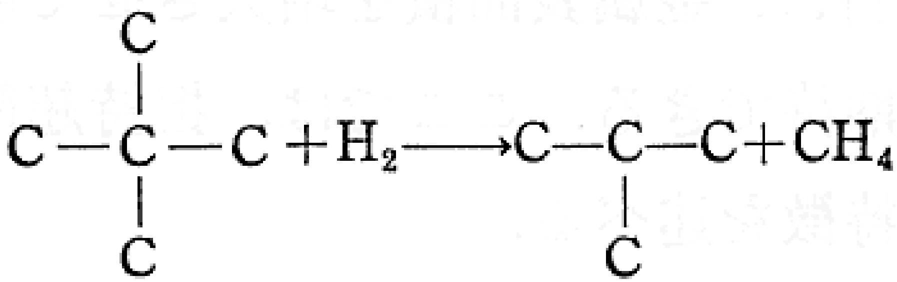
II 型（TOF は粒径が小さいほど大きい）

$C_2H_6,\ C_3H_8 + H_2 \longrightarrow CH_4$ Ni/SiO_2-Al_2O_3 e), Pt-black f)

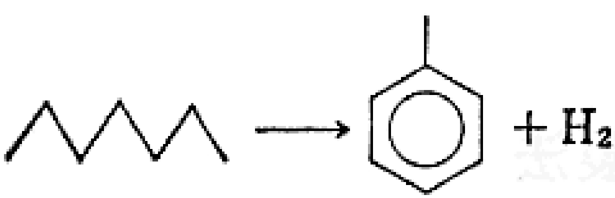
Rh/Al_2O_3 g)



Pt/Al_2O_3 h)



Pt/Al_2O_3 i)



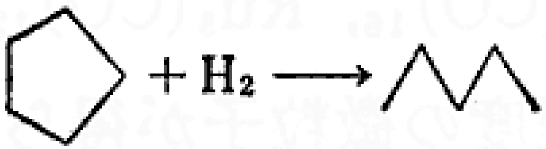
Pt/Al_2O_3 j)

$C_3H_6 + H_2 \longrightarrow C_3H_8$ Ni/Al_2O_3 k)

Structure-sensitive reaction

ターンオーバー頻度（TOF）と粒径との関係

III型（TOF は粒径が小さいほど小さい）

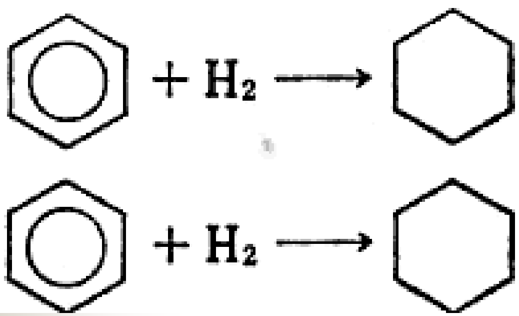
$C_3H_8 + O_2 \longrightarrow CO_2$	Pt/Al_2O_3[l)]
$C_3H_6 + O_2 \longrightarrow CO_2$	Pt/Al_2O_3[m)]
$CO + O_2 \longrightarrow CO_2$	Pt/SiO_2[n)]
	Ph/Al_2O_3[o)]
$CO + H_2 \longrightarrow CH_4$	Ni/SiO_2[p)]
$CO + H_2 \longrightarrow C_nH_m$	Ru/Al_2O_3[q)], Co/Al_2O_3[r)]
$CO + H_2 \longrightarrow C_2H_5OH$	Rh/SiO_2[s)]
$N_2 + 3H_2 \longrightarrow 2NH_3$	Fe/MgO[t)]

Structure-sensitive reaction

ターンオーバー頻度（TOF）と粒径との関係

IV型（TOF はある粒径で最大となる）*

$H_2 + D_2 \rightleftharpoons 2HD$ — Pd/C, Pd/SiO_2 (13 Å)[u]



Ni/SiO_2 (12 Å)[v]

Rh/SiO_2 (18 Å)[w]

Catalyst preparation

Method

- Impregnation
    - Including incipient wetness method, etc.
  - Immerse support materials in metal salt solution.
  - Drying it up and calcining it well.
- Ion exchange
- Coprecipitation

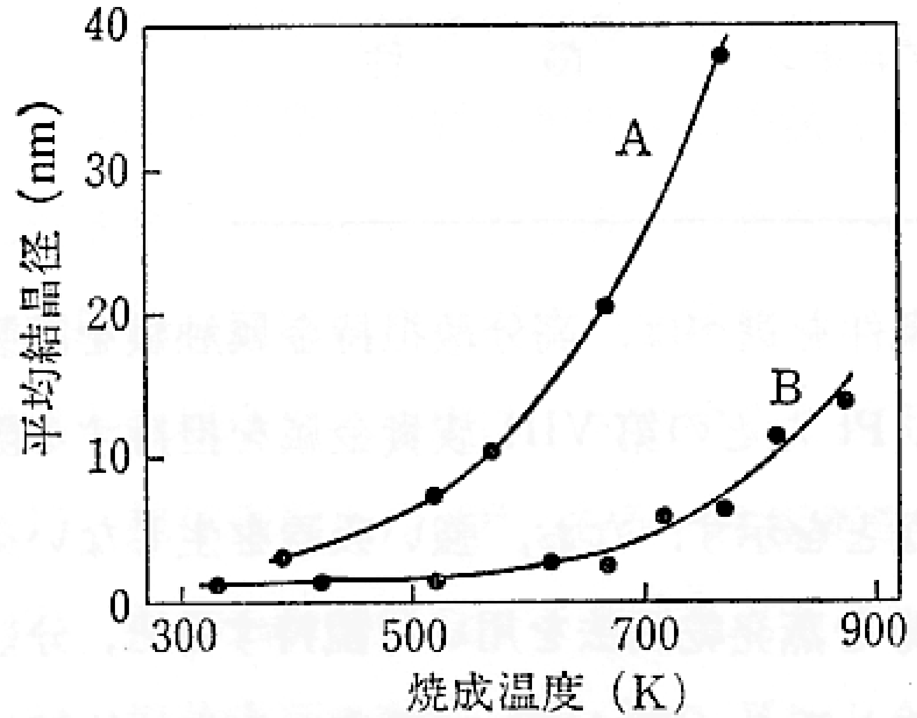
Disadvantages

- Impregnation
  - Easy control for loading.
  - Very difficult to decrease catalyst metal size.
- Ion exchange
  - Easy control for metal size.
  - Very difficult to increase loading.

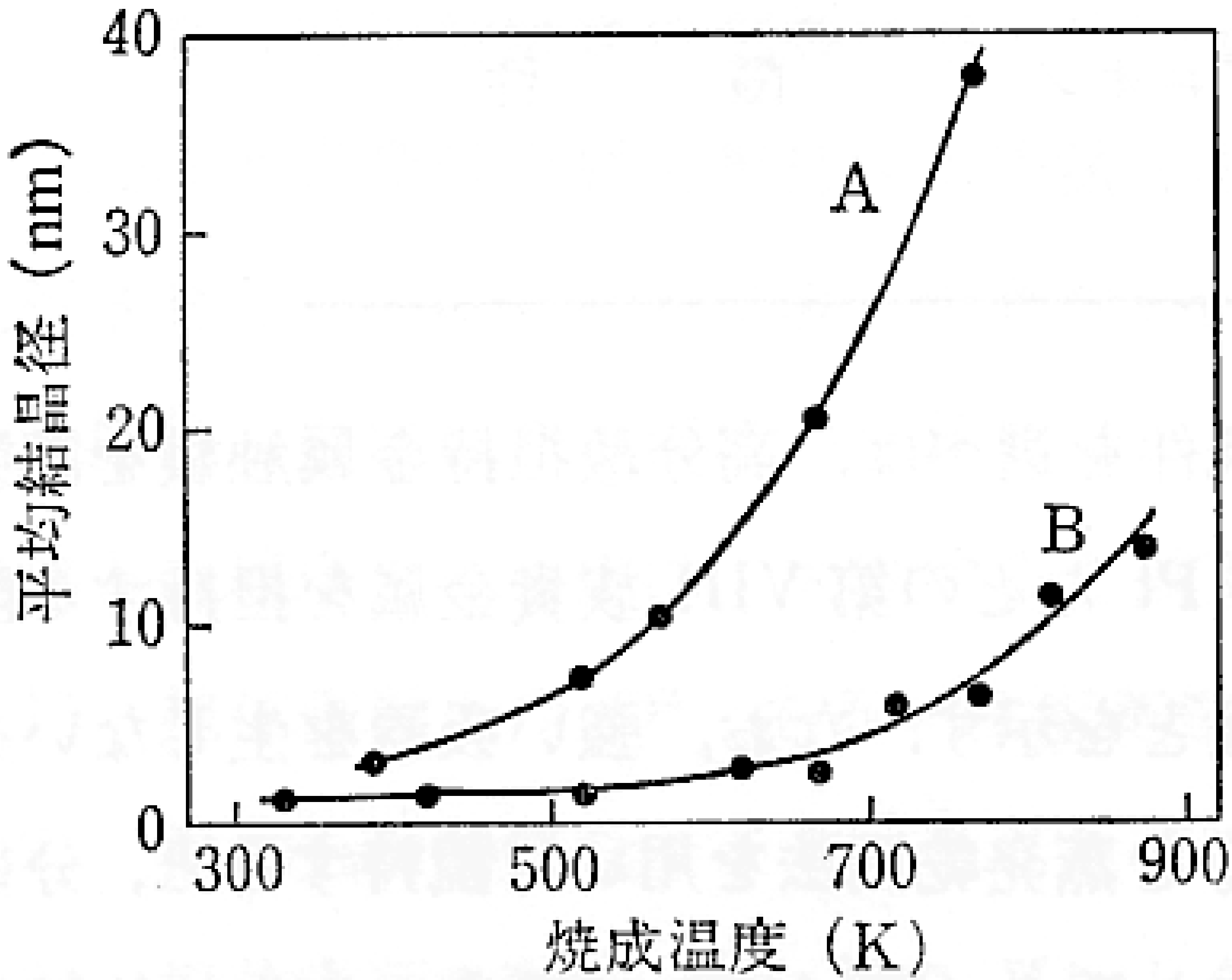
Preparation and dispersity

Dispersity:
ratio of surface metal number to that of bulk.

Dispersity depends on the average size of catalyst metal.



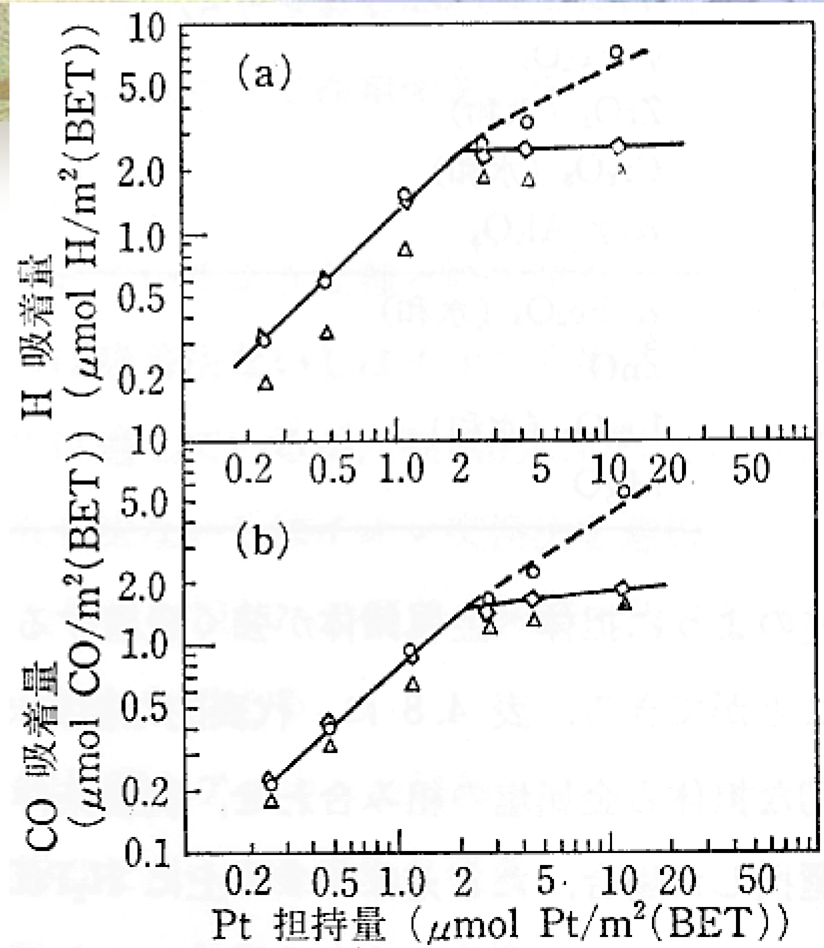
調製法と Pt/SiO_2 触媒の分散度および熱安定性. Pt 2.5 wt%, Davison 70 シリカゲル, A：含浸法, H_2PtCl_6, B：イオン交換法, $[Pt(NH_3)_4]Cl_2$, 焼成温度は還元処理前の温度.
荒井弘通, 表面, 17, 680 (1979)


40
30
20
10
0
平均結晶径（nm）
A
B
300
500
700
900
焼成温度（K）

Preparation and dispersity

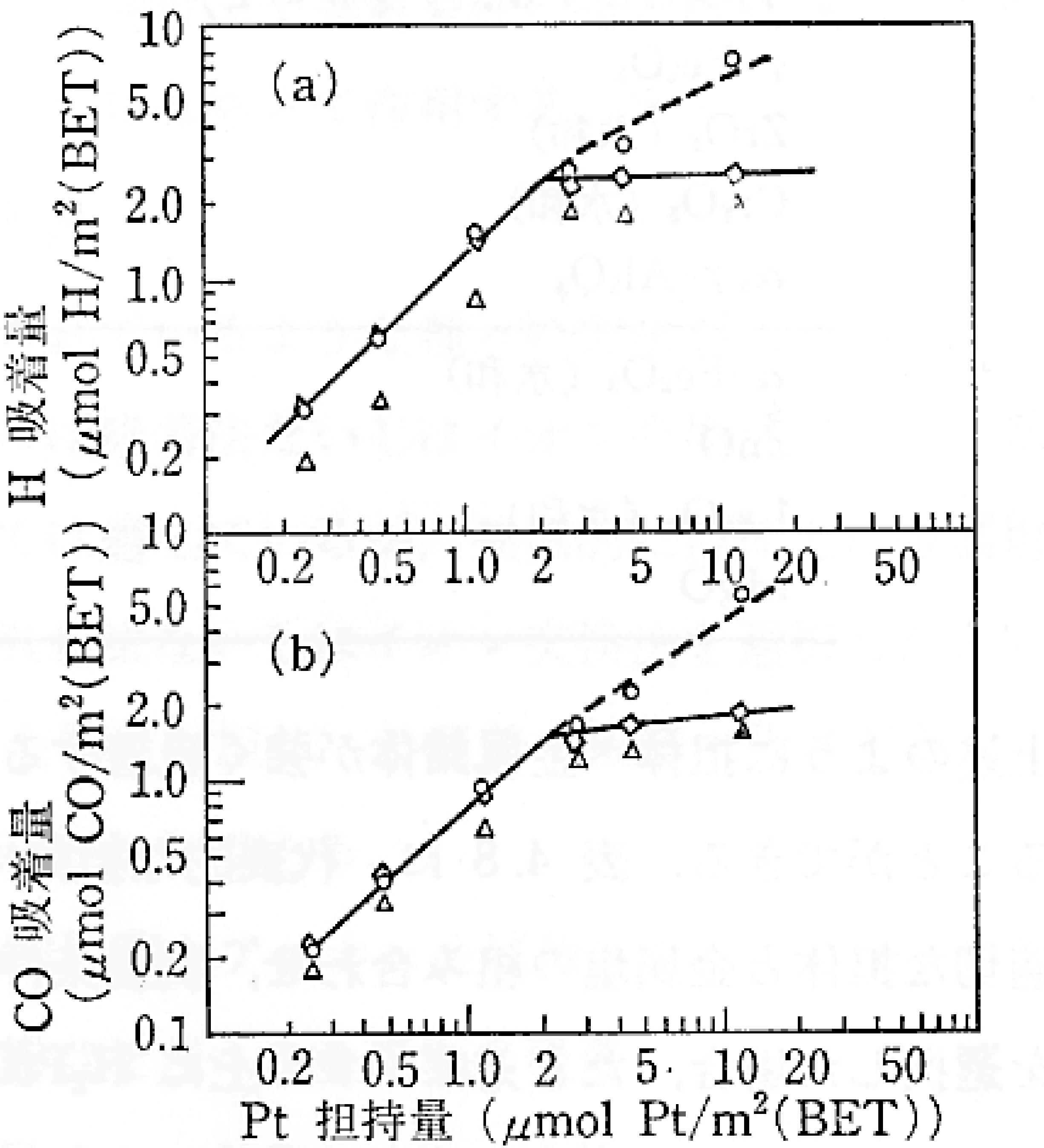
H, CO uptakes are proportional to number of surface atom.

H, CO uptakes are large.
↓
Active surface is large.



$Pt/\gamma\text{-}Al_2O_3$ 上の H(a) および CO (b) の吸着量と Pt の担持率．○：水素中 300℃, 2 h, △：水素中500℃, 2 h, ▲：水素中 750℃, 2 h, ◇：酸素中 500℃, 5 h.

H. C. Yao, M. Sieg, H. K. Plummer, Jr., *J. Catal.*, 59, 367 (1979)

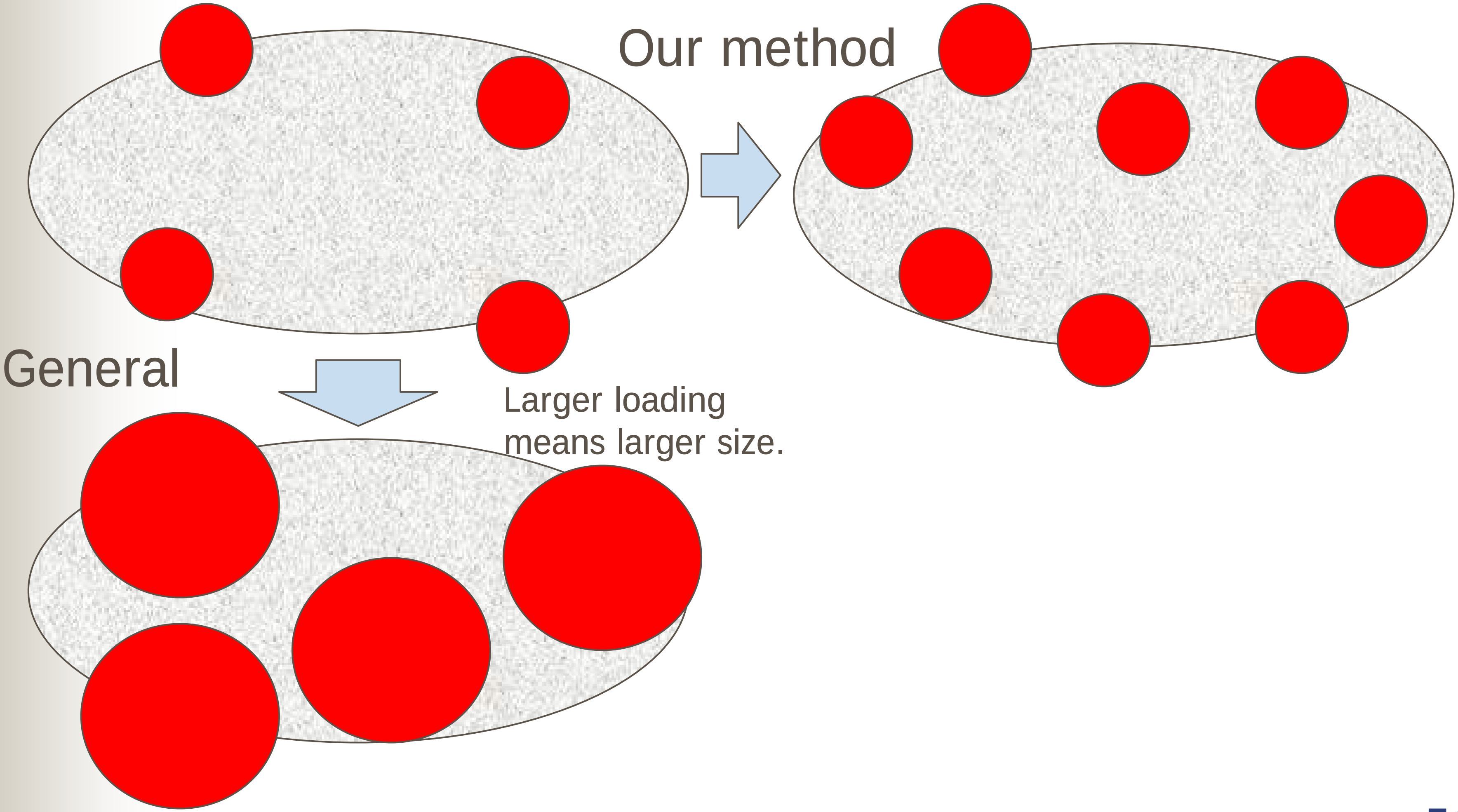


(a)
H 吸着量 (μmol H/m²(BET))
10
5.0
2.0
1.0
0.5
0.2
(b)
CO 吸着量 (μmol CO/m²(BET))
10
5.0
2.0
1.0
0.5
0.2
0.1
0.2 0.5 1.0 2 5 10 20 50
Pt 担持量 (μmol Pt/m²(BET))

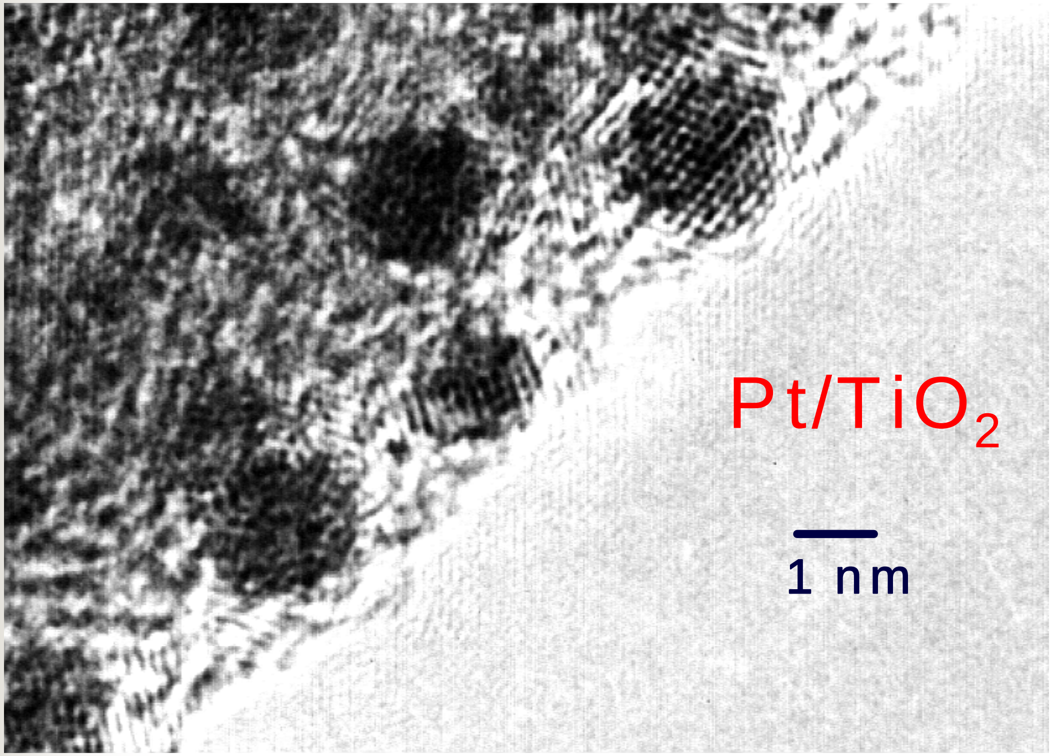
Control of dispersity (metal size)

- Disadvantages of conventional method
  - In order to increase dispersity, metal loading should be decreased.
  - To control 1~2 nm in size, loading is limited to be 3~5 wt% for Pt.
  - The whole catalytic activity depends on the metal loading. If possible, larger loading becomes higher activity for higher productivity.

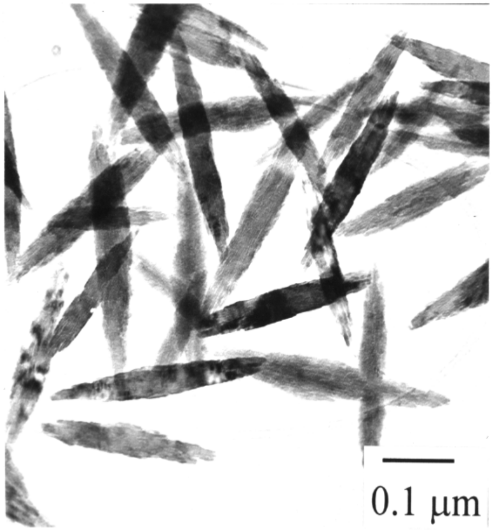
Loading is increased but size should be the same.



Selective Deposition of Noble Metal Nanoparticles on Well-Defined Oxide Particle and their Application to Hydrogenation Catalyst



Support:
- Single-crystalline anatase-type TiO_2
- Monodispersed particles prepared by the Gel-Sol method.



Tadao SUGIMOTO and Atsushi MURAMATSU, IMRAM

Selective Deposition Method

[Noble metal salt] = 2.0×10^{-4} mol dm^{-3}
($HAuCl_4$; $RuCl_3$, $RhCl_3$, $PdCl_2$, H_2IrCl_6, H_2PtCl_6)

↓ ← NaOH

Formation of precursor complex

Storing at room temp. for 24 h — pH ~7

↓ ← Support particles = 1.6 g dm^{-3}

Ultrasonic dispersion (30 min)

↓

Selective deposition

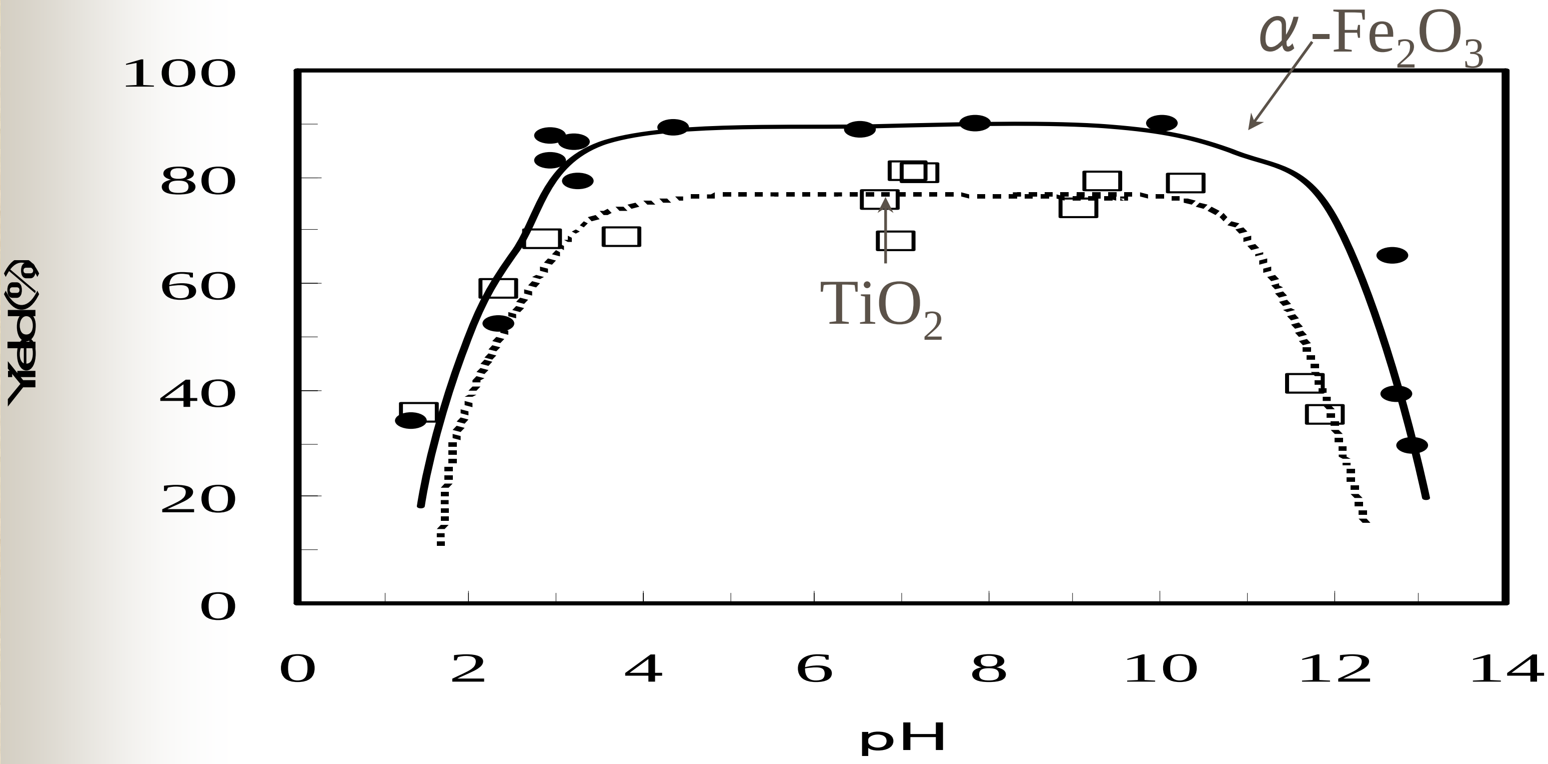
Aging（100℃, 48 h） → Reduction by H_2 if necessary

↓

Metal nanoparticles of Au, Ru, Rh, Pd, Ir, and Pt

Effect of pH on yields of Pt precursor

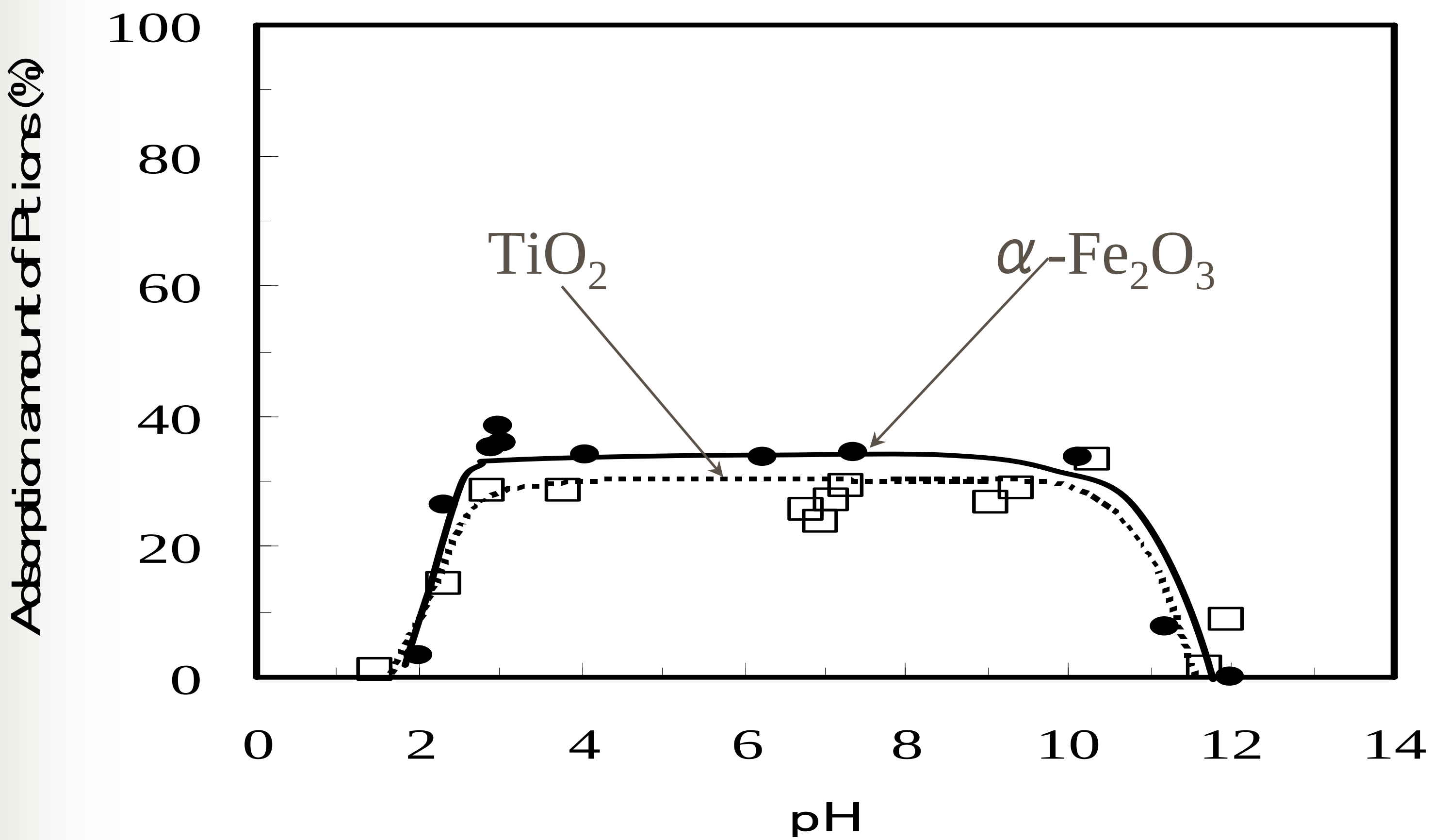
(100℃, 2days)



Selective Deposition Method

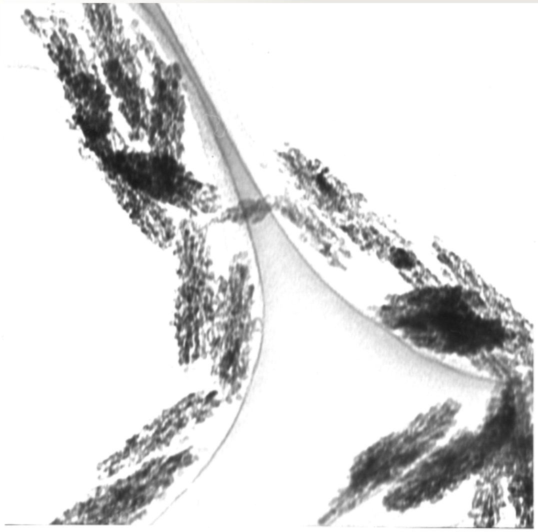
Effect of pH on adsorption of Pt ions

(25℃, 2days)



Selective Deposition Method

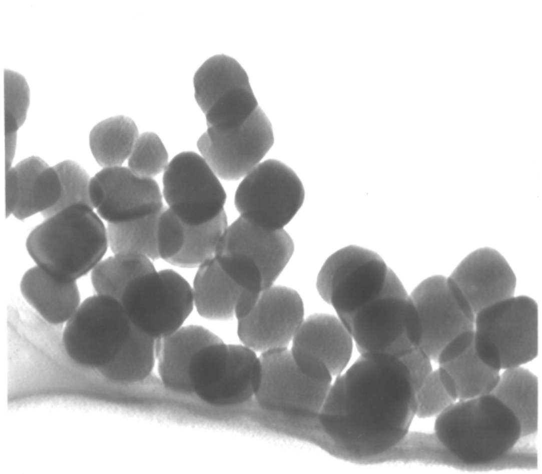
α-Fe_2O_3 多結晶エリプソイド



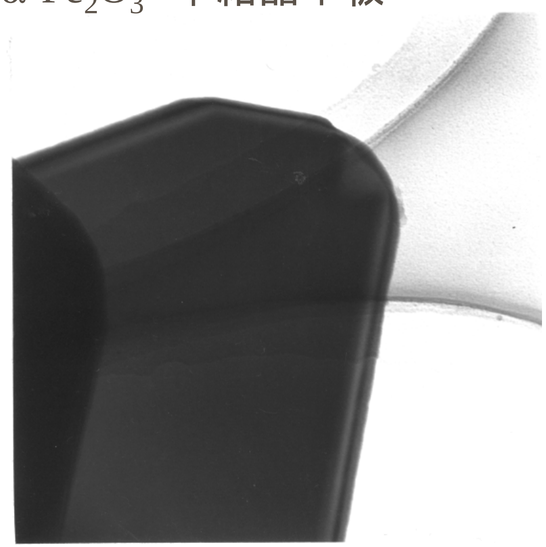
α-Fe_2O_3 単結晶エリプソイド

0.1 µm

α-Fe_2O_3 単結晶擬似立方体

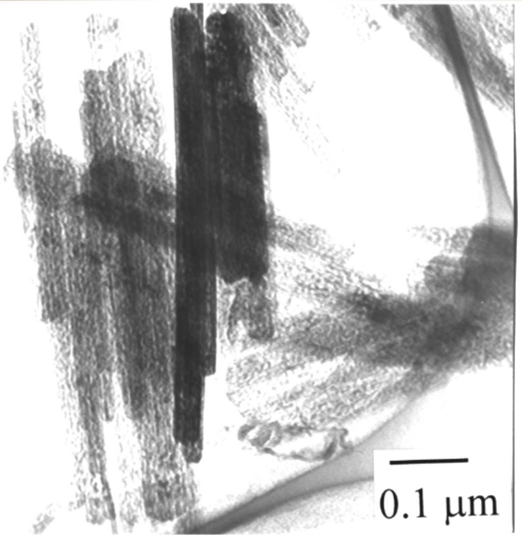


α-Fe_2O_3 単結晶平板

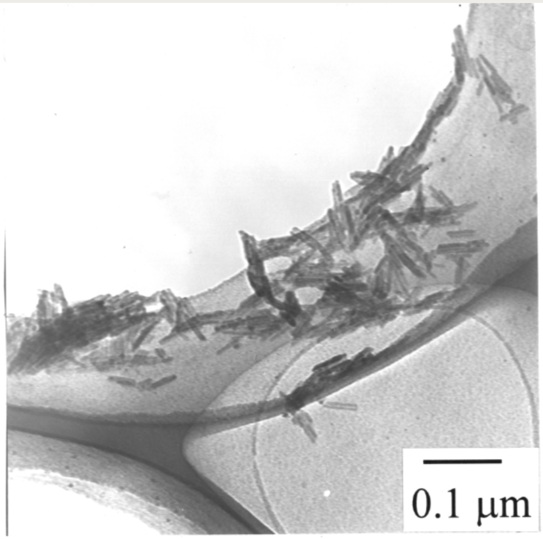


Selective Deposition Method

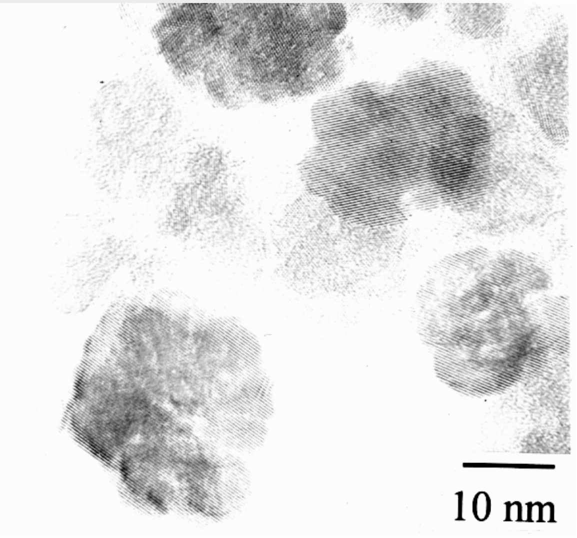
α-FeOOH



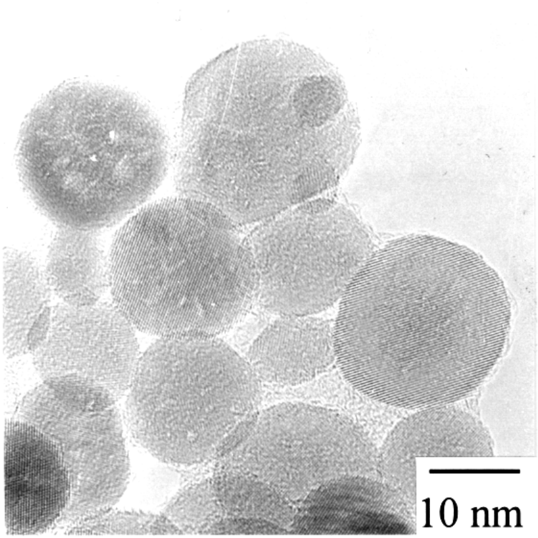
β-FeOOH



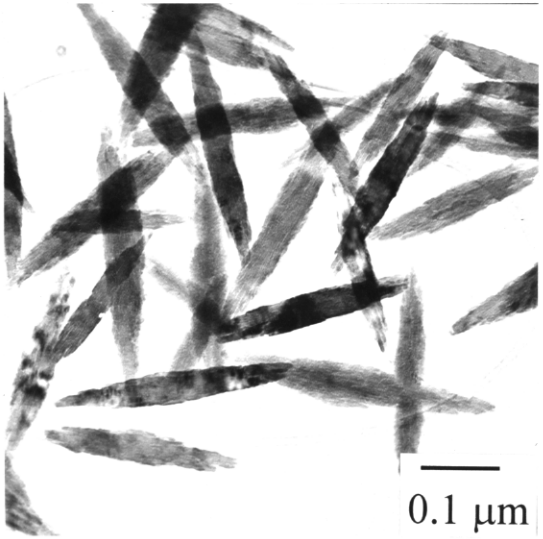
ZrO_2(A)
Rough surfaces



ZrO_2(B)
Smooth surfaces



TiO_2



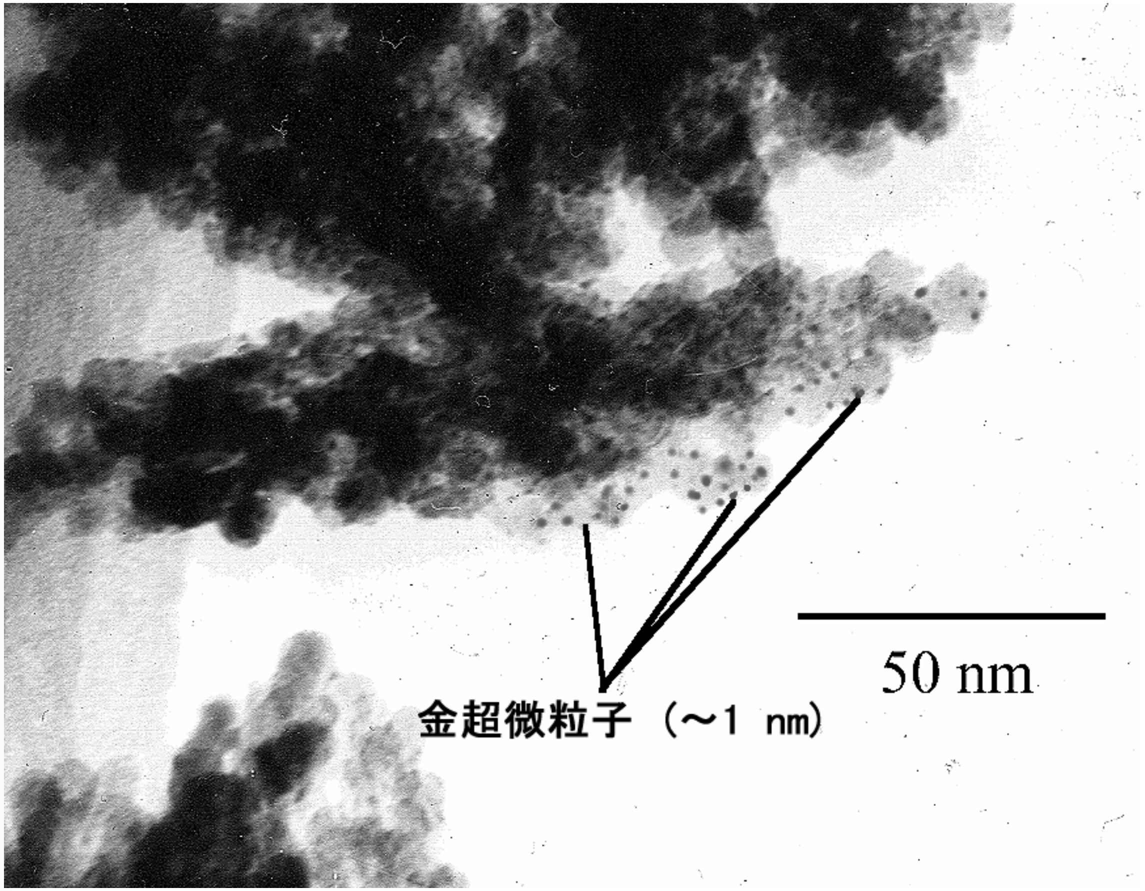
Selective Deposition Method

Table Catalytic properties of supported Pt nanoparticles.

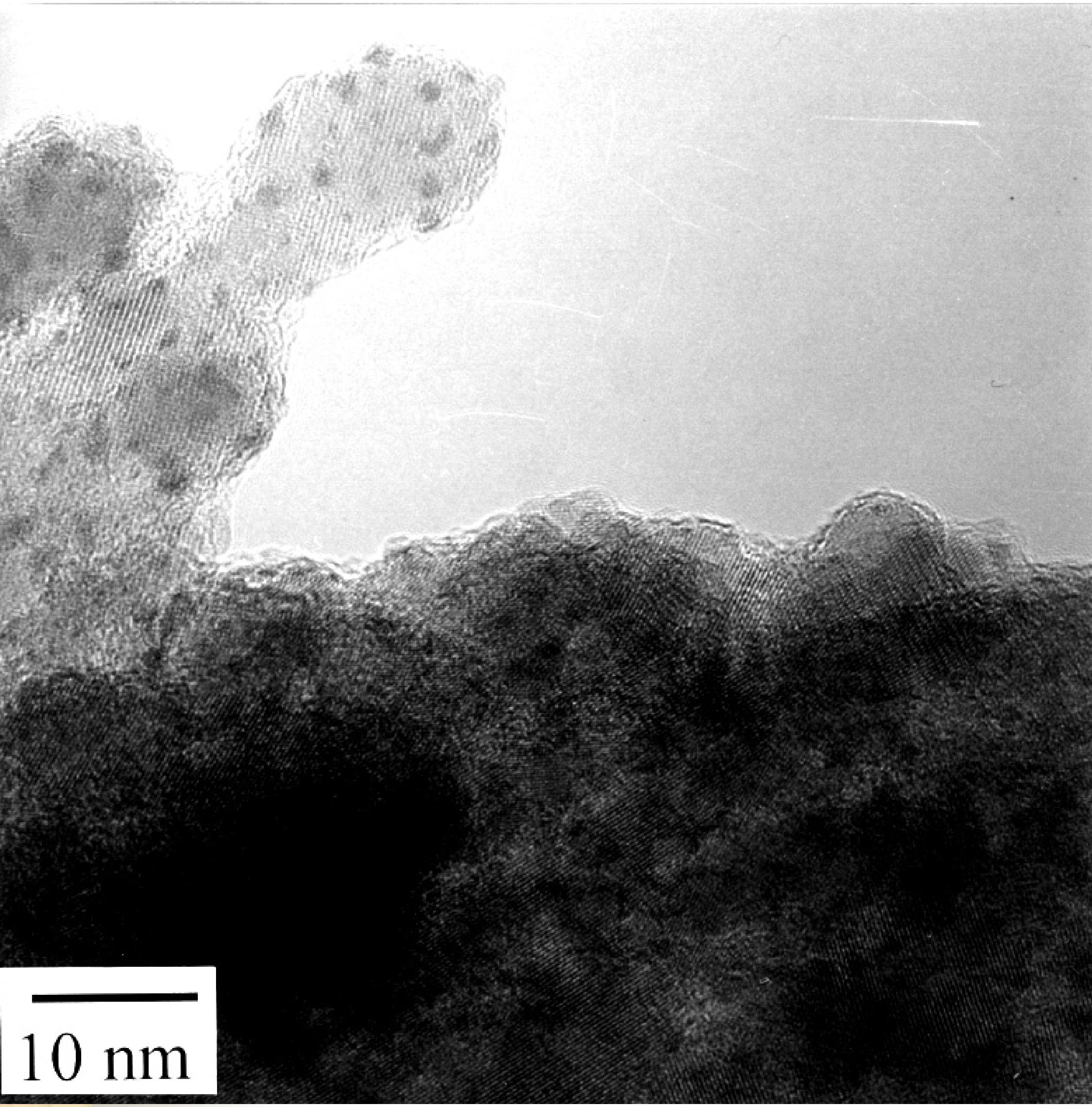
Support	Specific surface area (m^2 g^{-1})	Method	Pt loading (wt%)	Particle size (nm)	Dispersity (H/M)	1-octene conversion (%)
TiO_2, ellipsoid (anatase)	37.5	***This study***	3.0	1.1	0.99	11.9
		This study	18.9	1.3	0.86	35.7
		Ion-exchange method	3.6	1.4	0.98	3.7
		Impregnation method	20.0	6.3	0.40	9.7
α-Fe_2O_3, ellipsoid (A)*	136	***This study***	22.0	2.0	0.09	4.6
SiO_2 (prepare by Stober method)	4.20	***This study***	13.6	10 - 50	0.31	5.0
ZrO_2 (B)**	118	***This study***	18.0	2.4	0.86	19.4
Al_2O_3 CSJ-ref. cat ALO6	156	***This study***	18.0	1.6	0.85	52.1
		Ion-exchange method	3.0	1.2	1.00	10.6
		Impregnation method	18.0	4.8	0.28	21.2

Selective Deposition method → Highly dispersed catalysts with high loading

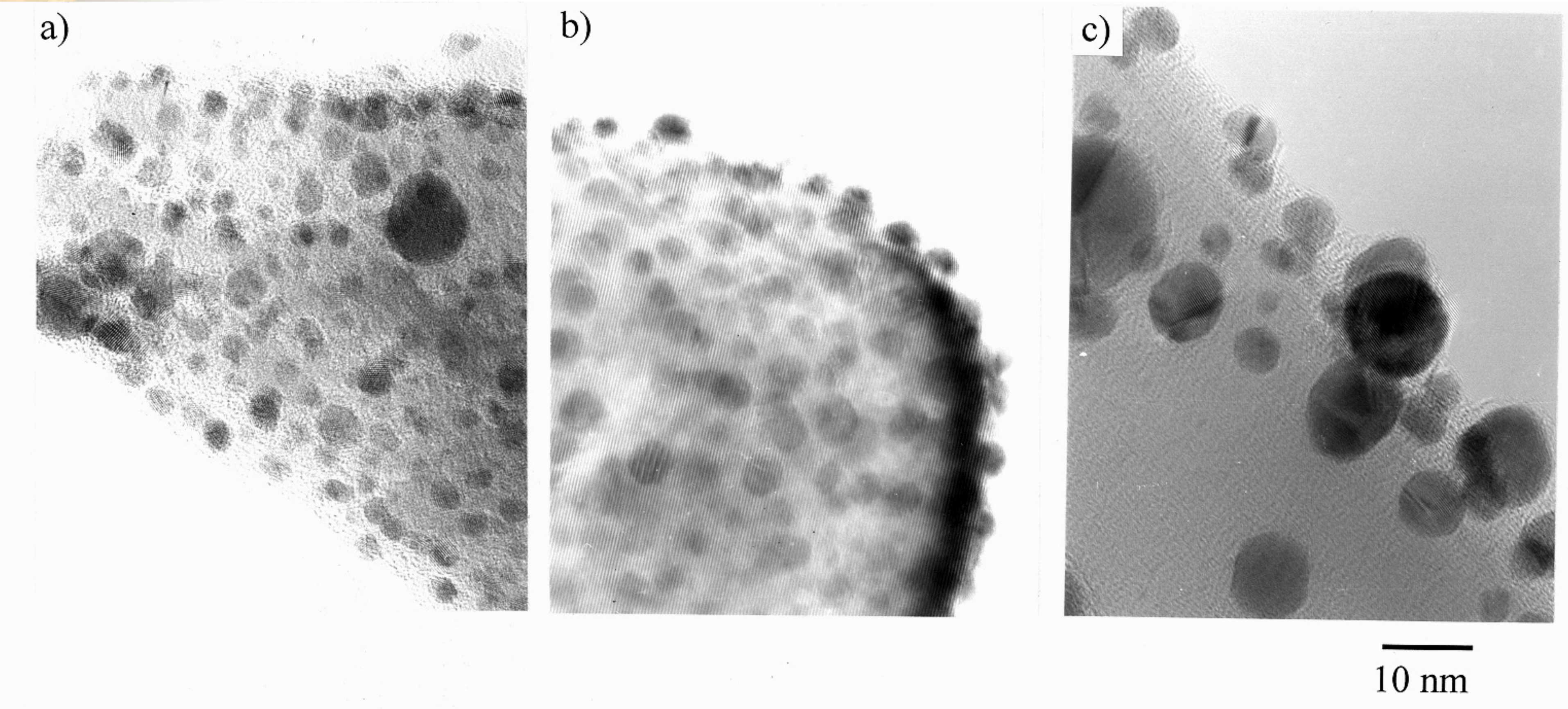
Au / hematite



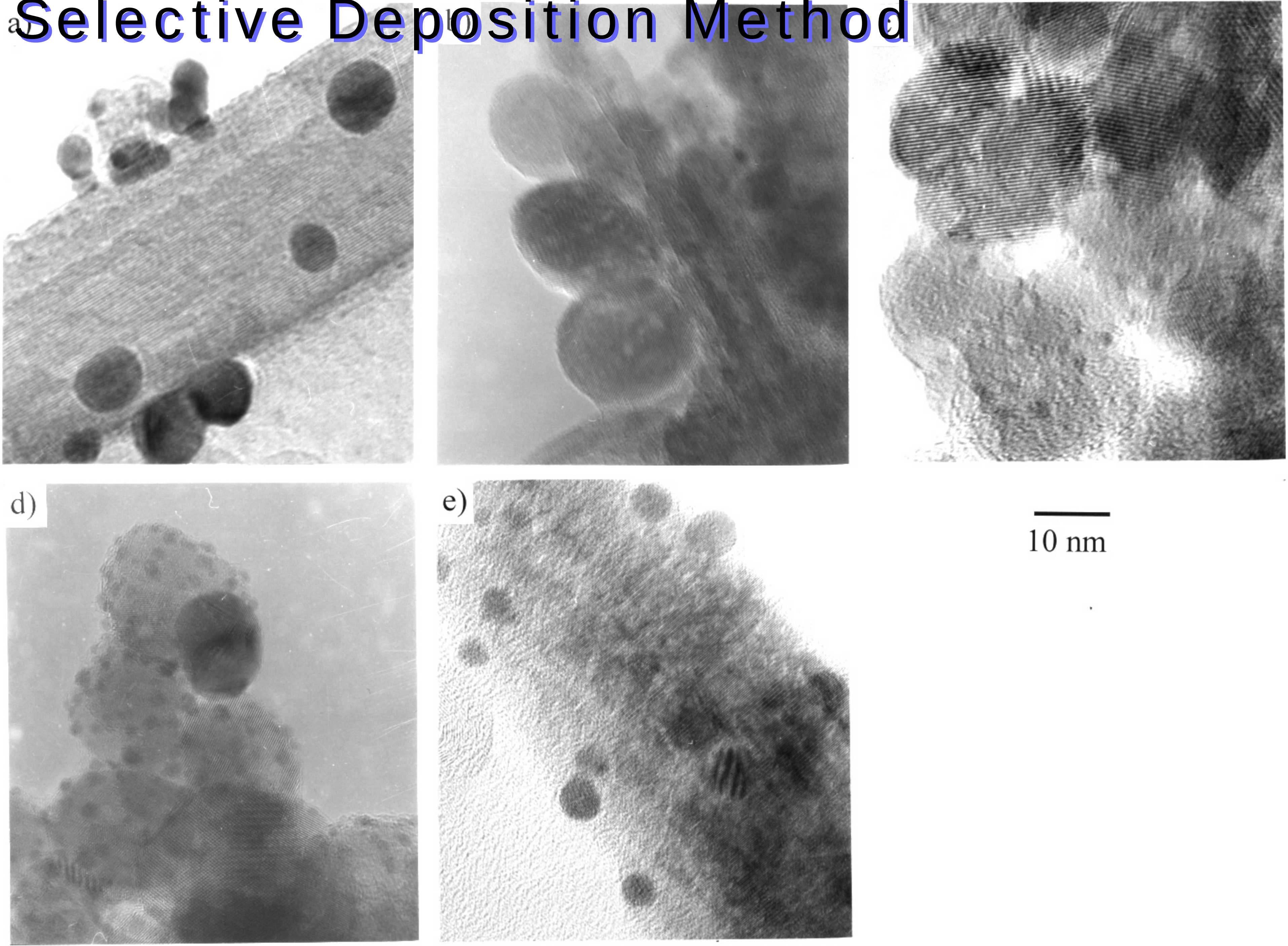
Selective Deposition Method



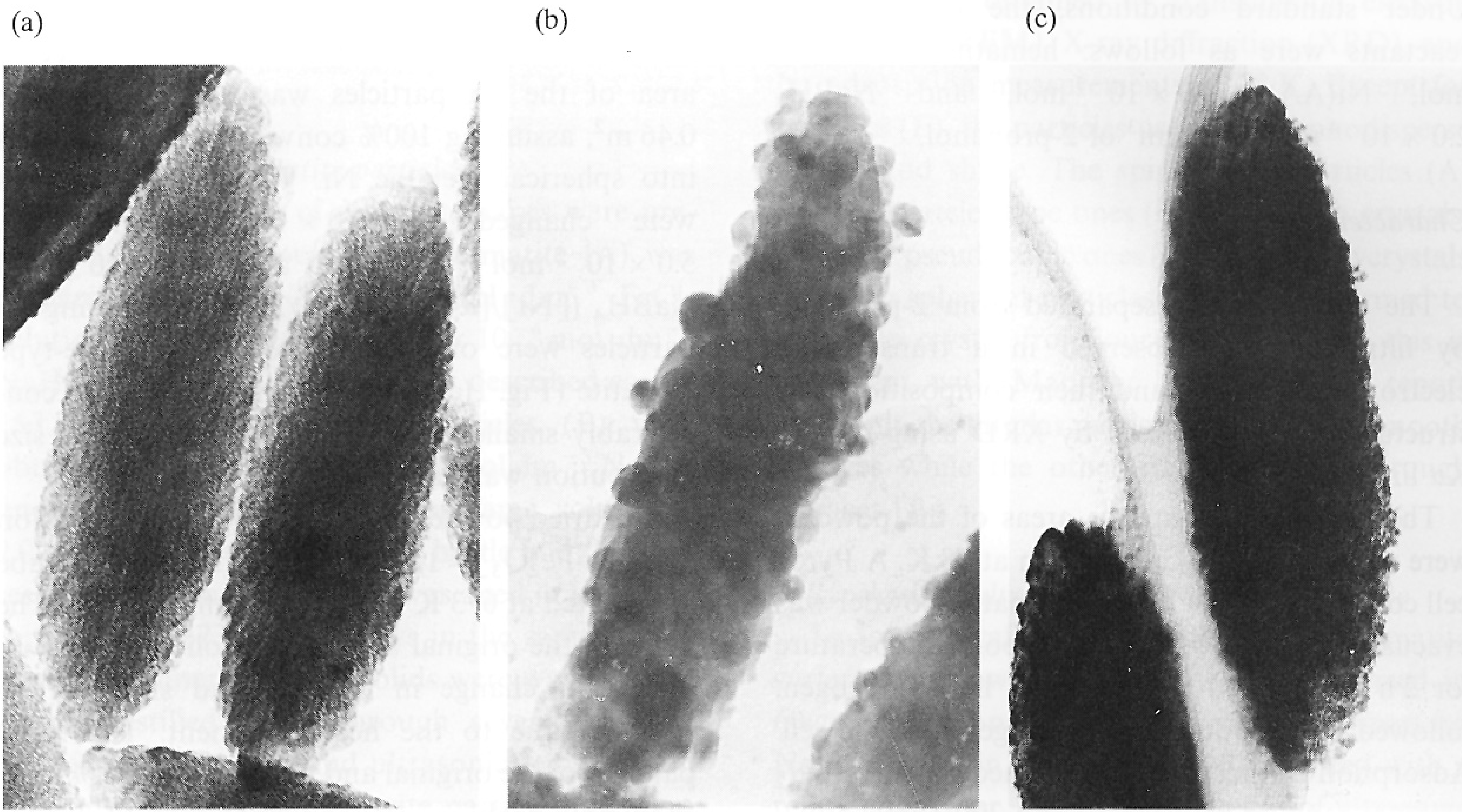
Selective Deposition Method



Selective Deposition Method

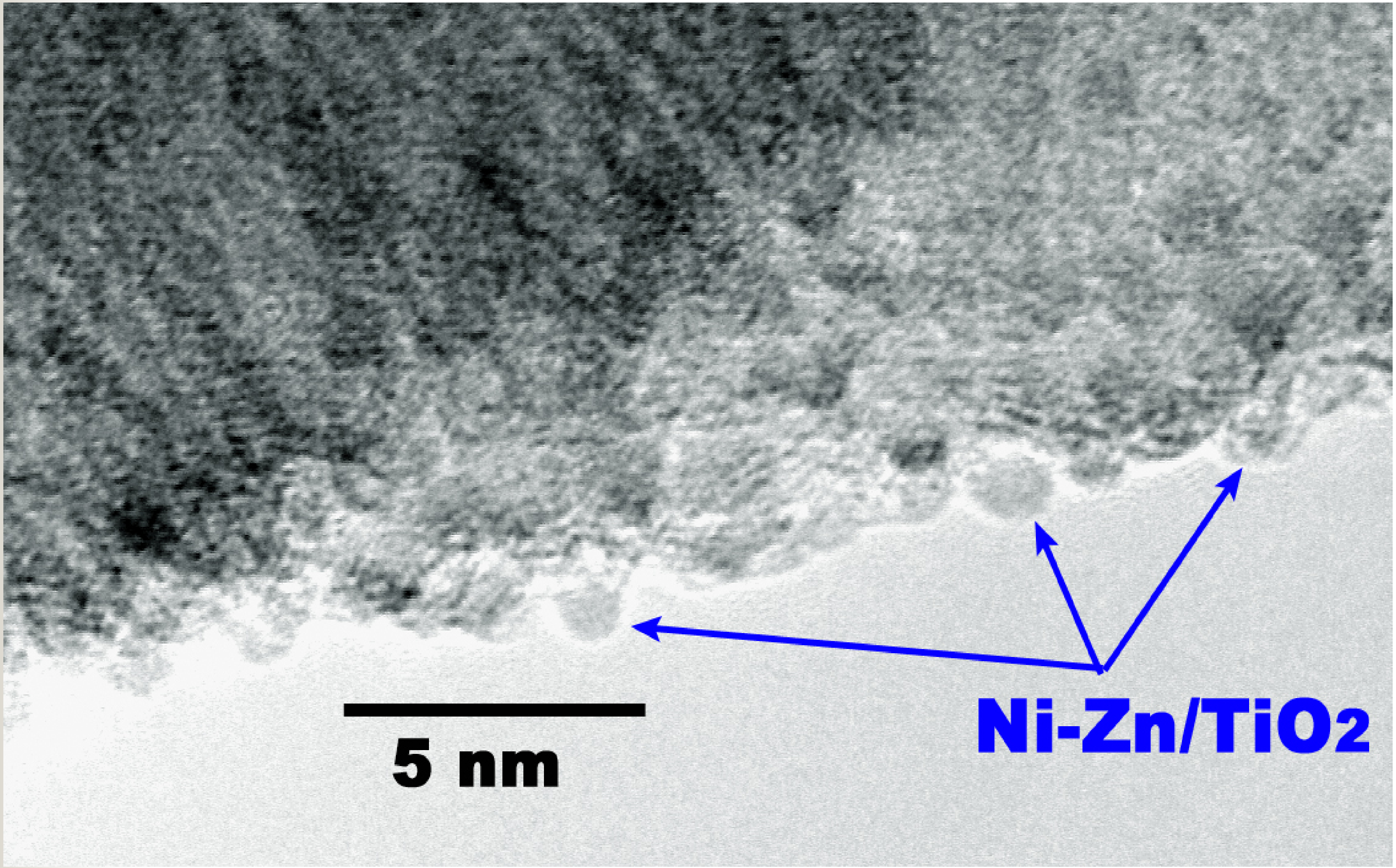


Selective Reductive Deposition Method

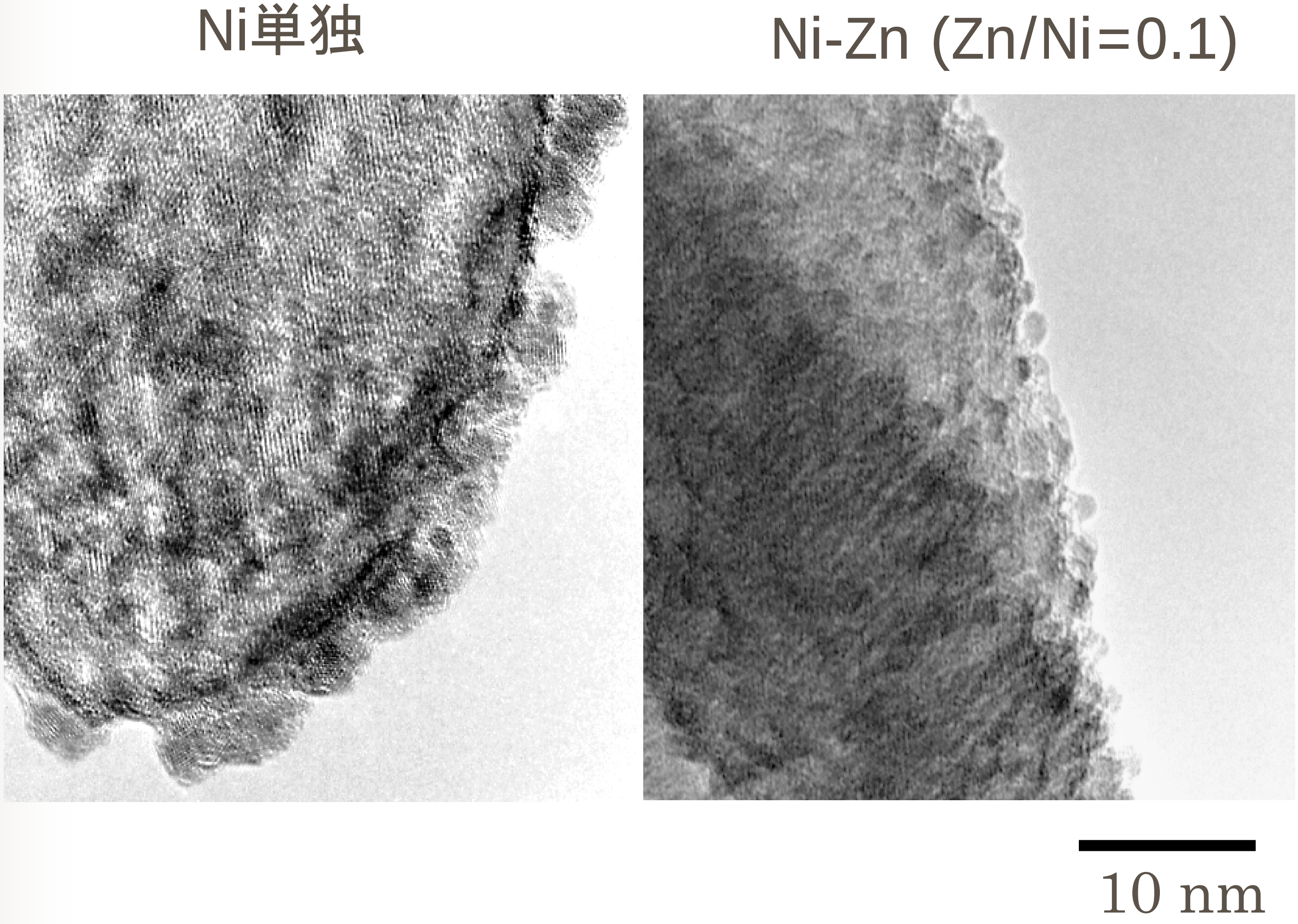


Hematite　　20wt% Ni/hematite　　5wt%Ni/hematite 25nm

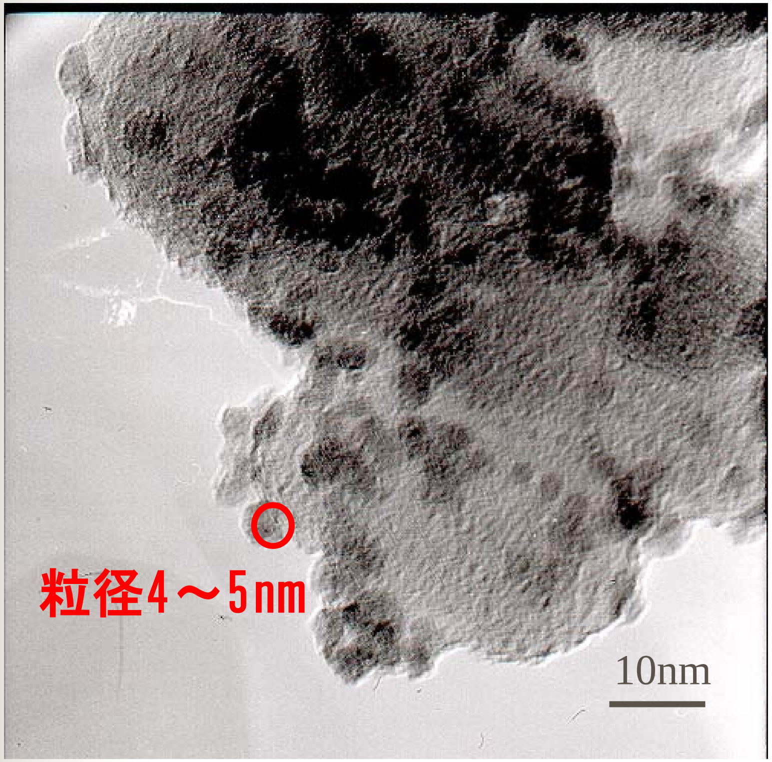
Ni-Zn/TiO_2 (Zn/Ni=0.1)



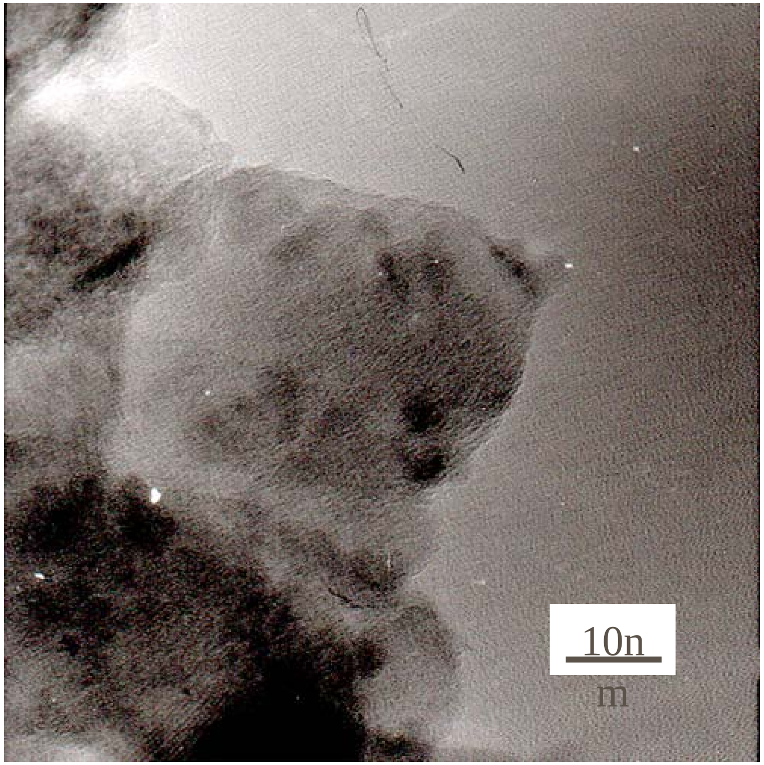
Zn addition decreased the size.



Liquid-Phase Selective Reductive Deposition Method



Zn/Ni=0.2



Zn/Ni=1.0

Very Hot Topic!

Visible light utilization
－Preparation of Ti-O-S photocatalyst －

Muramatsu Lab.
IMRAM, Tohoku Univ.