Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

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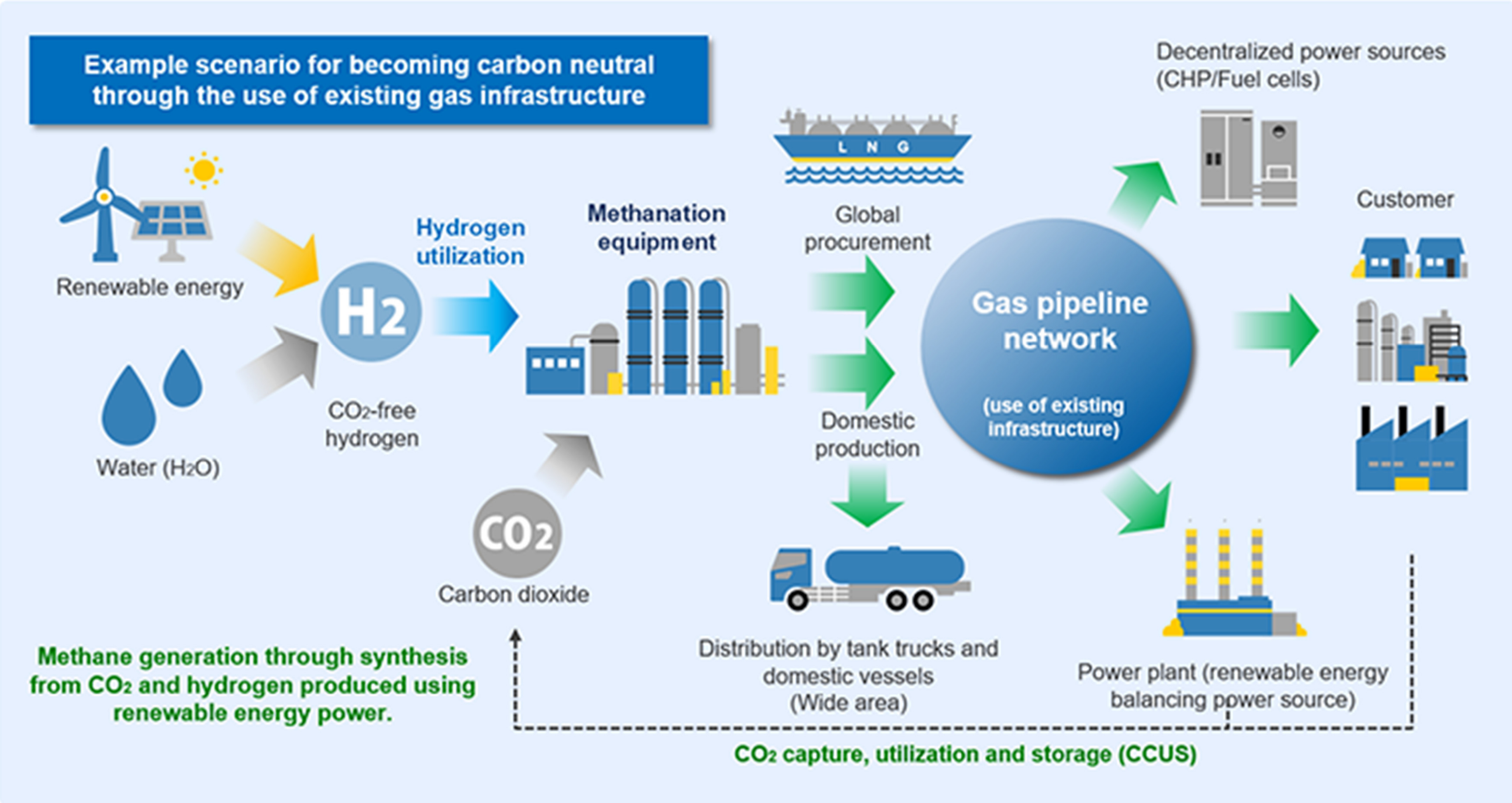
Lecture Plan

April 11, Introduction and Physical chemistry
April 18, Nanoparticles and colloids in our daily experiences
April 25, Nanoparticles and colloids in our daily experiences
May 9, Dispersion and aggregation of particles
May 16, Dispersion and aggregation of particles
May 23, DLVO theory
May 30, DLVO theory
June 6, Theory of monodispersed particles synthesis
June 13, Liquid-phase synthesis of functional nanoparticles
June 20, Liquid-phase synthesis of functional nanoparticles
June 27, Environmental catalysts
July 4, Adsorption phenomena and catalytic reaction
July 11, Catalyst preparation methods
July 18, Catalyst preparation methods
July 25, Summary

Catalysts contribute to society

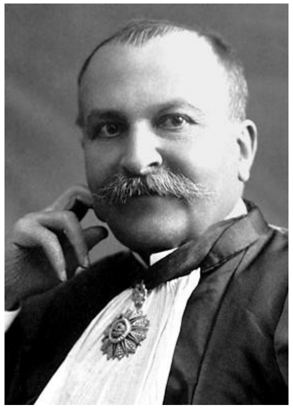
Methanation technology and CO_2 emissions



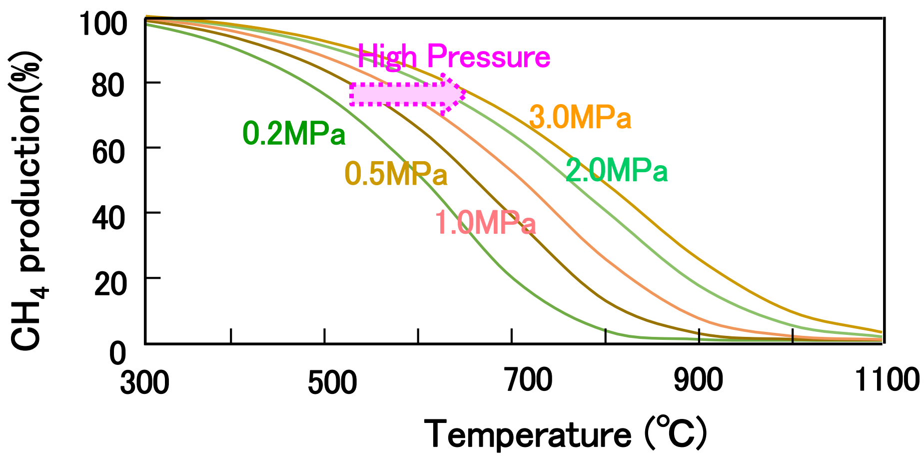
Methane production (methanation) technology

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H = -165\ kJ/mol\ (298K)$$

- At the beginning of the 20th century, Sabatier (France) discovered a technology to thermochemically produce methane from CO_2 (carbon dioxide) and H_2 (hydrogen) using a catalyst.
- Ni-based and Ru-based catalysts are often used as catalysts.
- It is an exothermic reaction, and low temperature and high pressure are advantageous.
- As methane production technology from CO2, in addition to thermochemical methods, electrochemical, photoreduction, biological methods, etc. are being researched and developed.

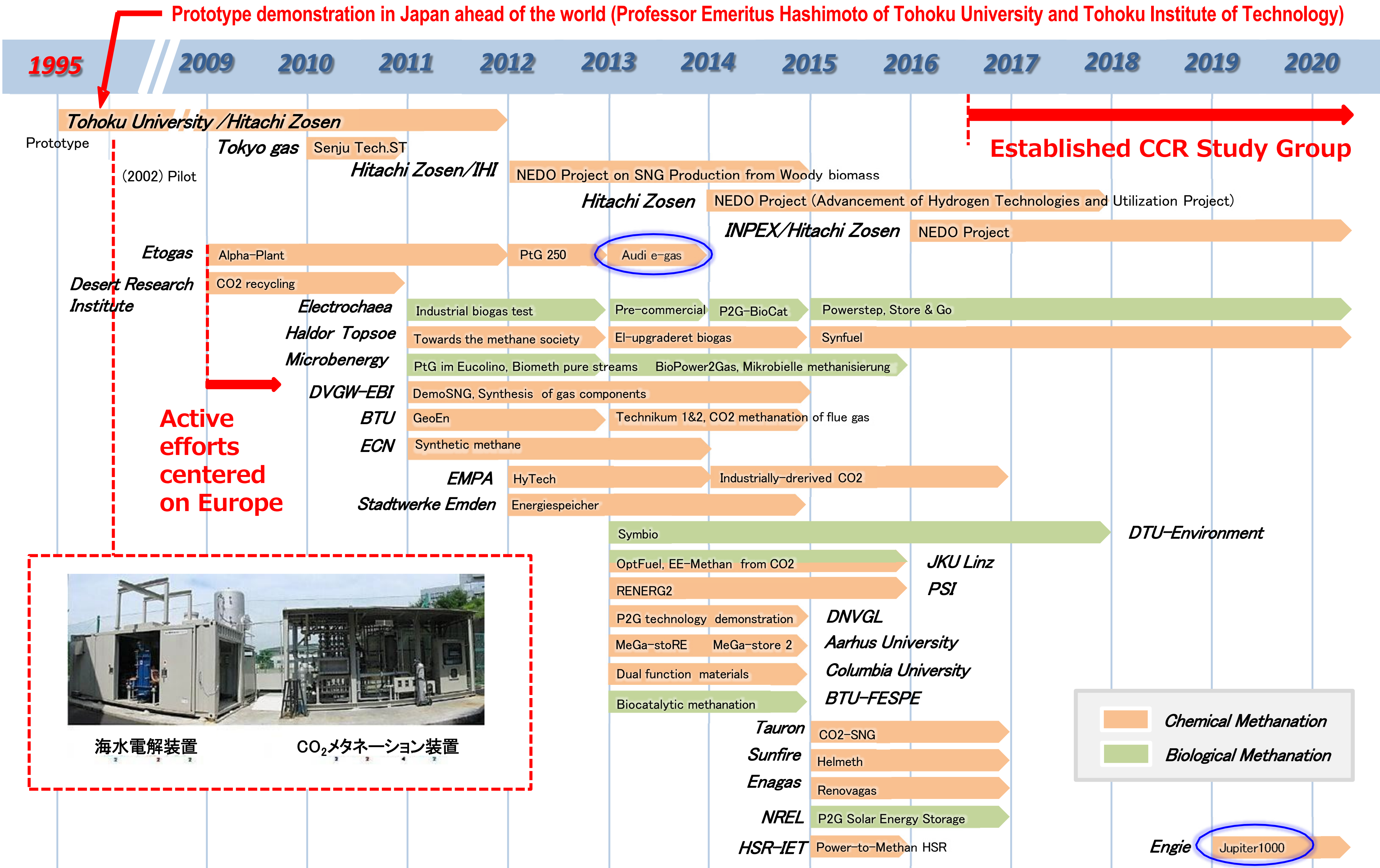


Paul Sabatier
(1912 Nobel Prize in Chemistry)



Temperature and pressure dependence (equilibrium) in the hydrogenation reaction of CO_2

Recent related business example: methanation technology



出典: "Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO_2", M. Bailera et al. Renewable and Sustainable Energy Reviews 69 (2017) 292–312 、CCR研究会による調査

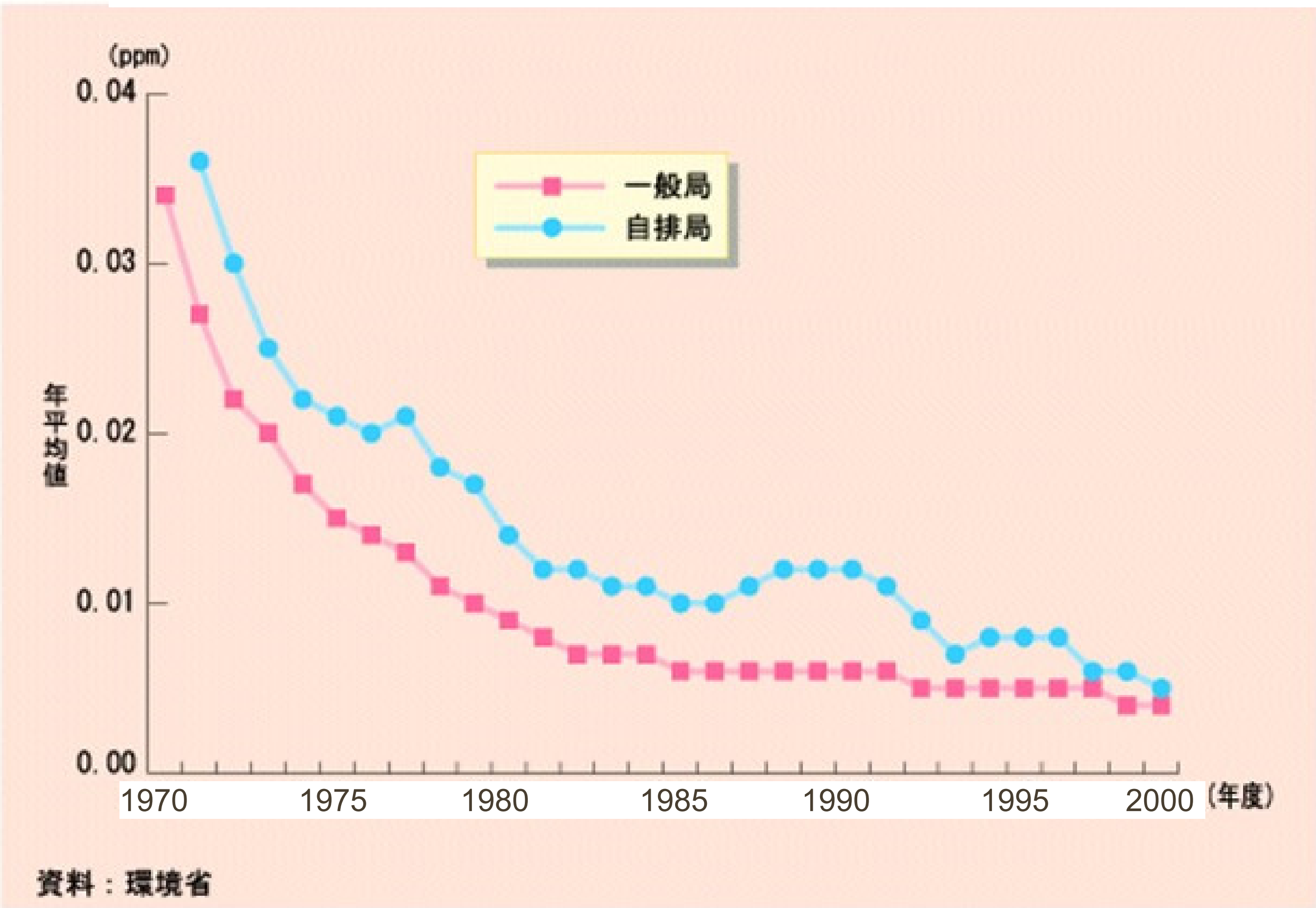
Yokkaichi Asthma

Yokkaichi Asthma

- In 1967, when the first victim of Yokkaichi asthma occurred, a test facility for flue gas desulfurization began operation at the No. 2 industrial complex's thermal power plant.
- Flue gas desulfurization technology was also developed. In 1968, the sulfur content in the fuel, which was about 3% at the time, was succeeded in reducing to 1.7 using a heavy oil indirect desulfurization unit (Ni-Mo-Co desulfurization catalyst) installed at the oil refinery of the No. 2 industrial complex.
- Yokkaichi's air pollution has dramatically improved as a result of various measures to prevent pollution, such as the introduction of desulfurization equipment and switching to high-quality fuel with low sulfur content.

Practical application of desulfurization and denitrification catalysts

Trends in annual average sulfur dioxide concentration



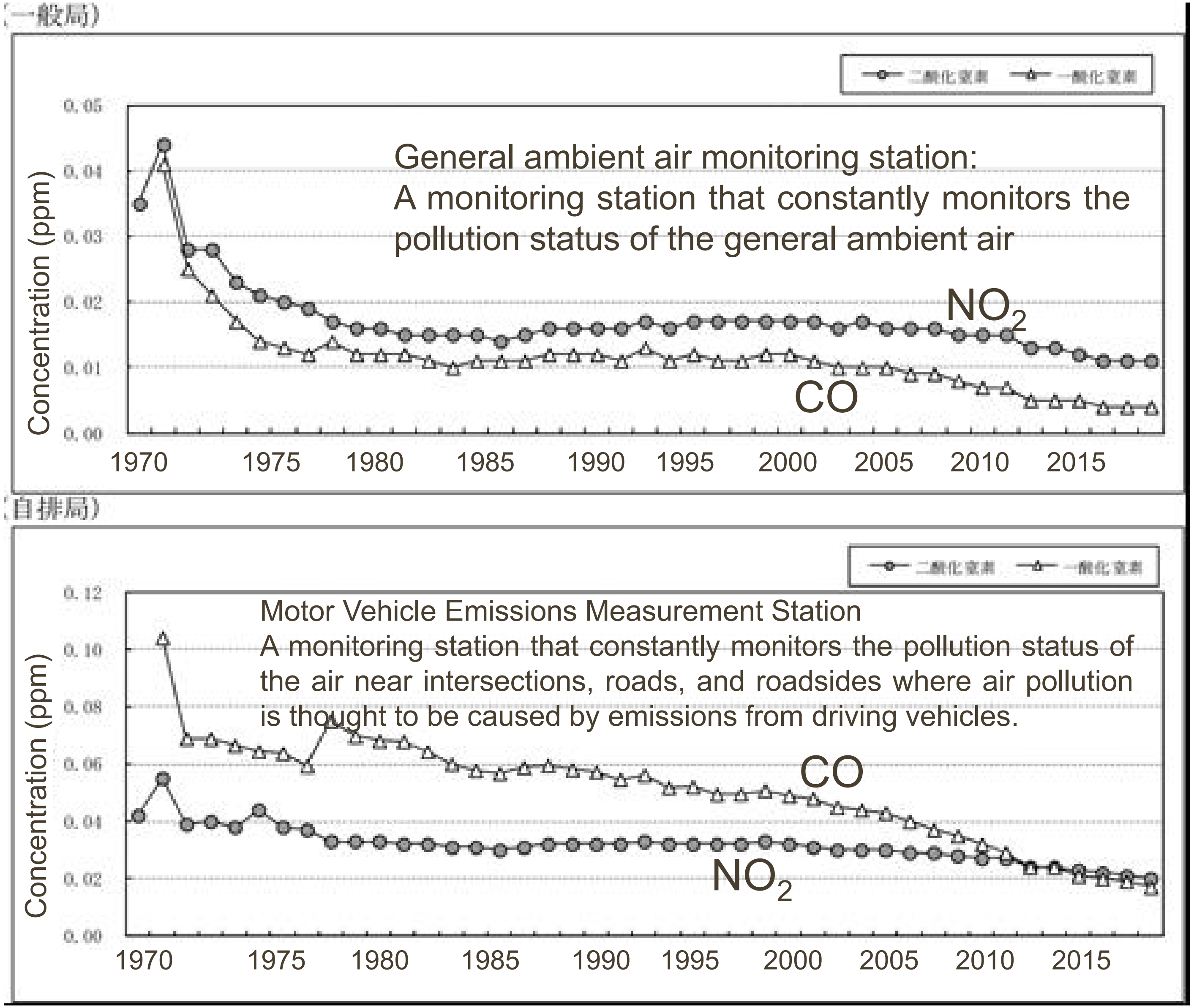
Eliminates sulfur content in fuel oil from the source!

That is the desulfurization catalyst.

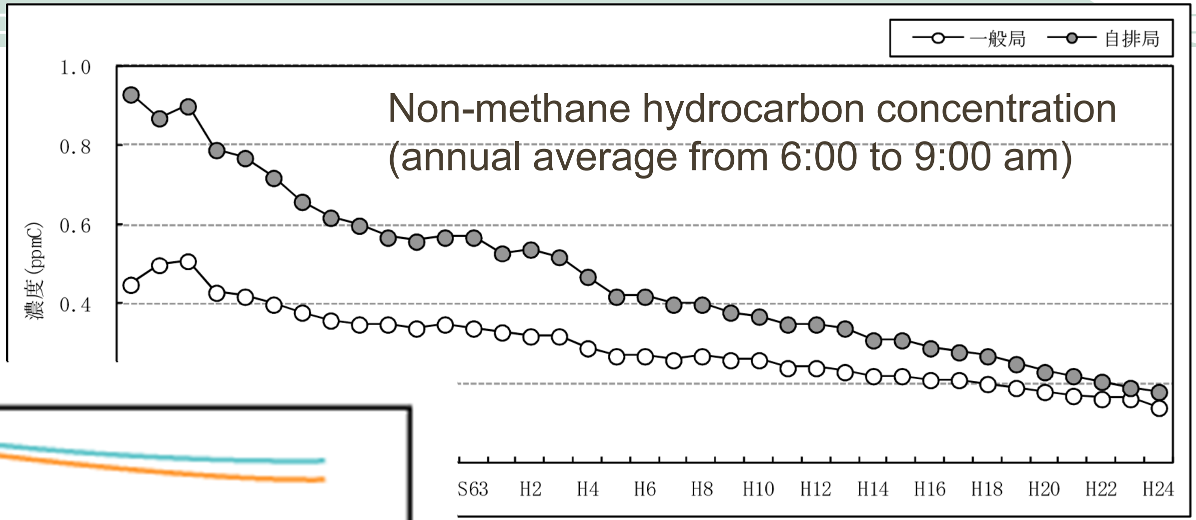
Co-Mo-S

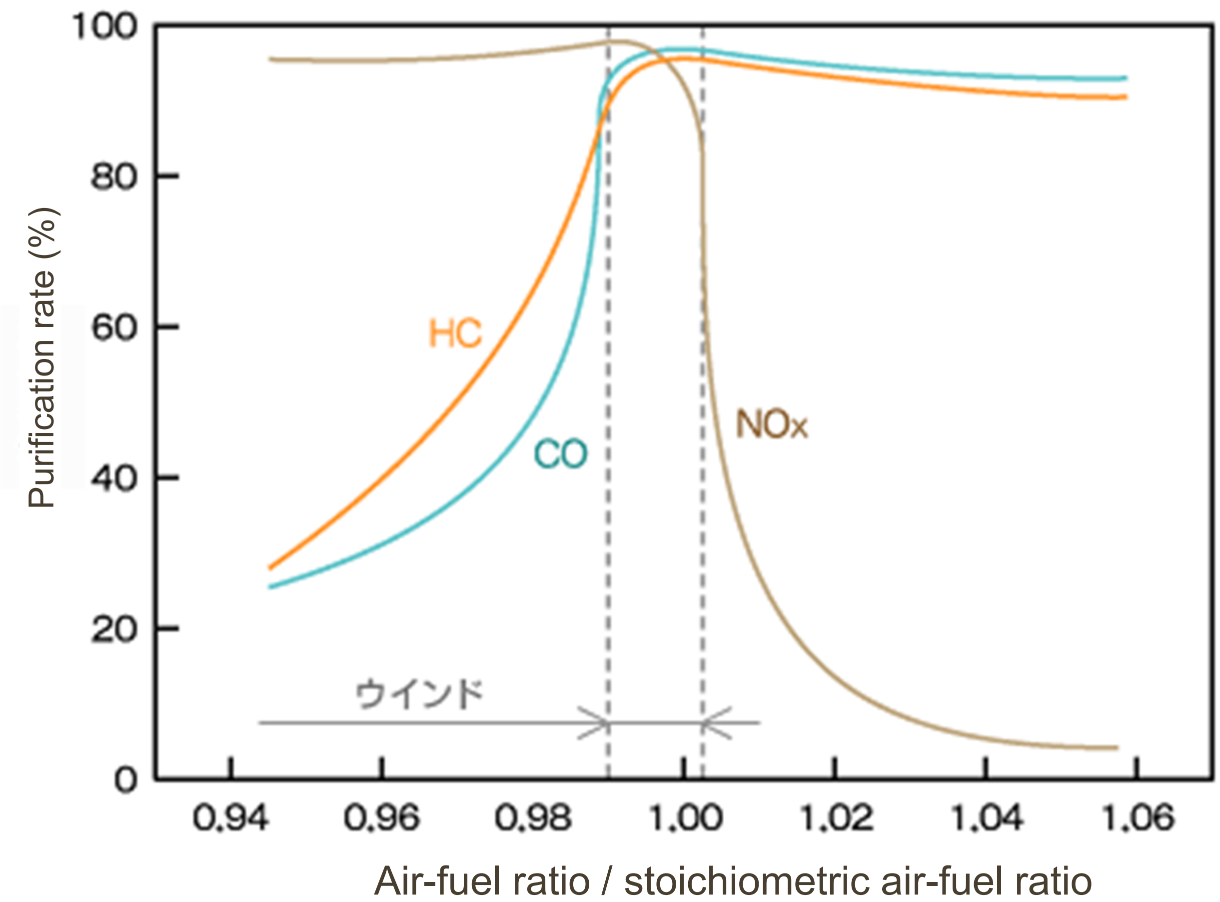
Three-way catalyst, TWC

- CO, NOx, HC removal catalyst from engine exhaust gas



Three-way catalyst, TWC



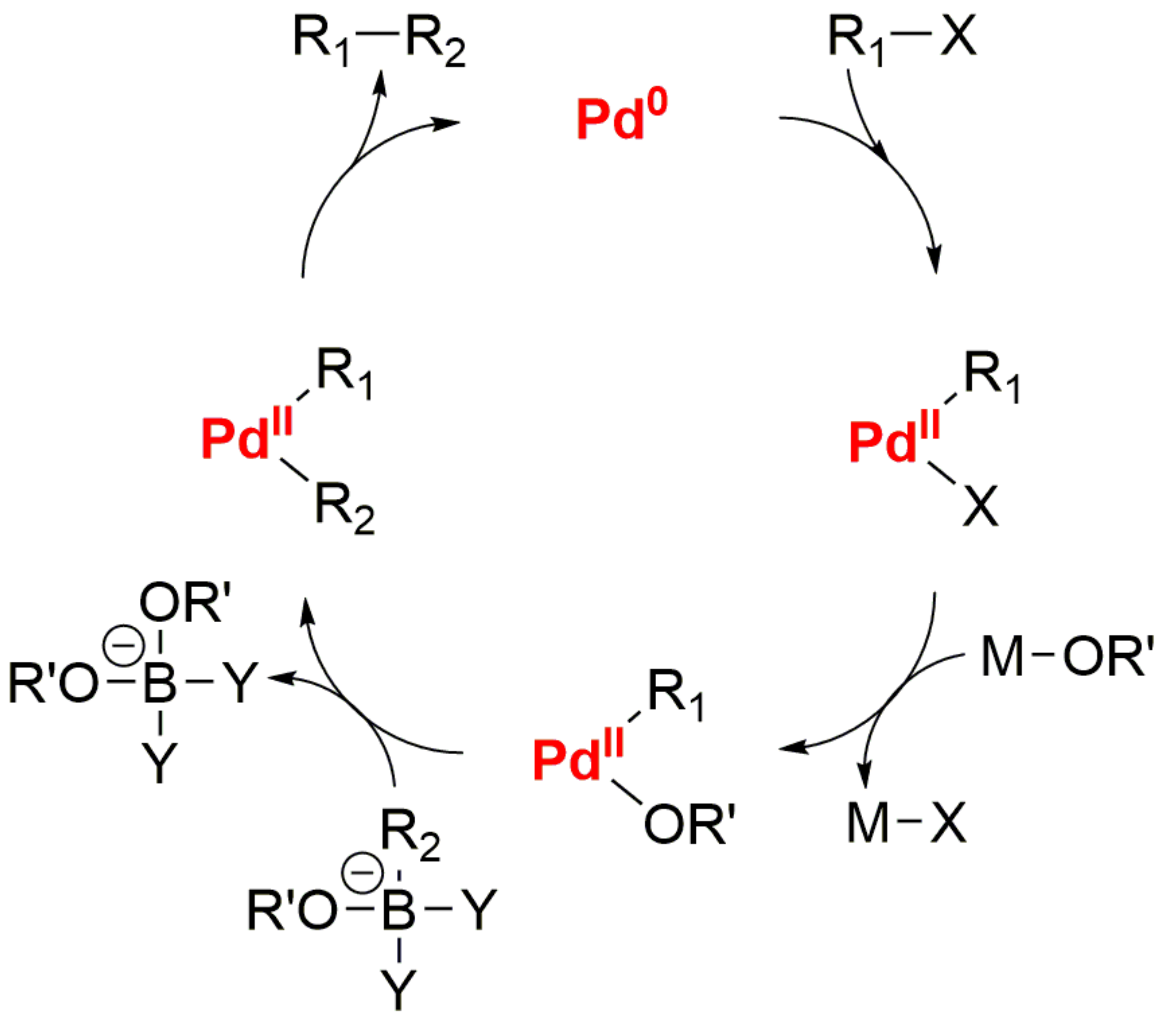


Basics of catalytic chemistry

What is catalyst？

Definition of catalyst **Material itself seems not changed before and after a reaction, but even small amount it accelerates the chemical reaction.**

Suzuki-Miyaura Coupling over Pd catalyst (Novel prize on 2010)



What is catalyst？

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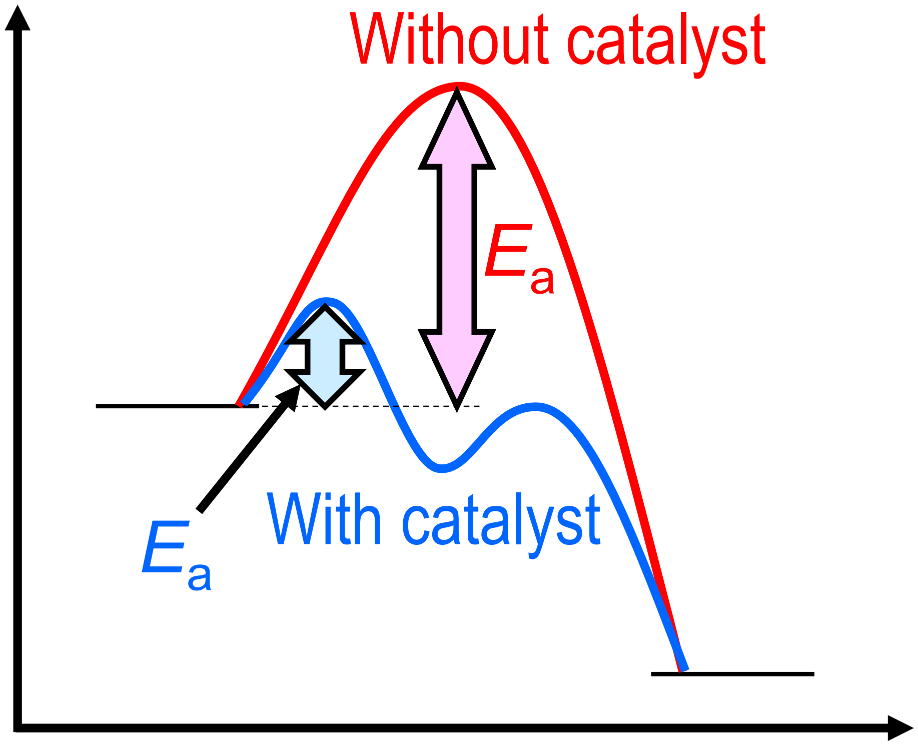


Catalyst affects

→ change reaction path

→ Activation energy is decreased.

$E_a < E_a$

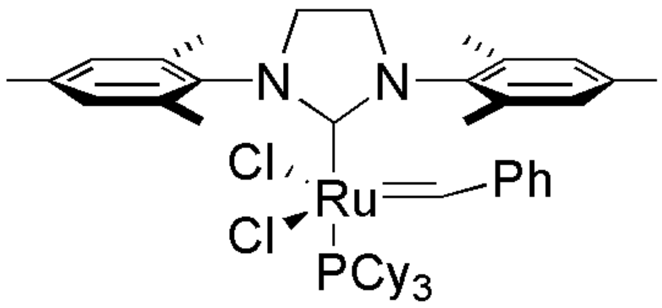
→ Reaction rate constant is increased.

Arrhenius eauation

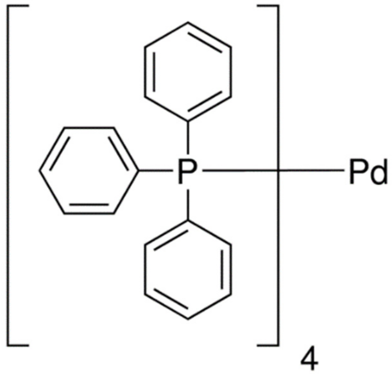
$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Kinds of catalyst an examples

Homogeneous catalyst: the same phase as reactant such as metal complexes and enzyme

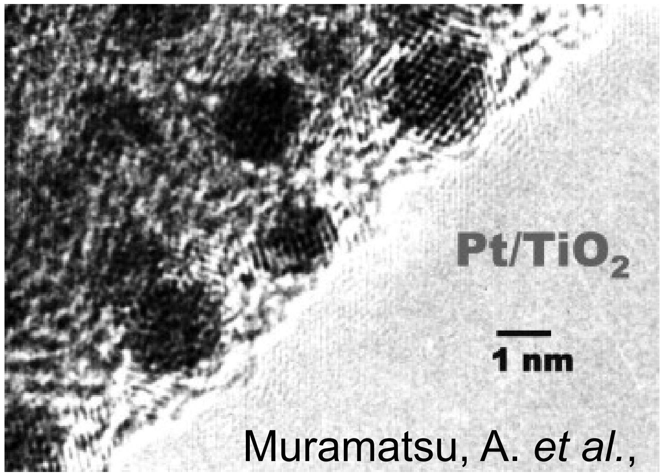


Grubbs catalyst: Olefin metathesis
(Novel prize on 2005)



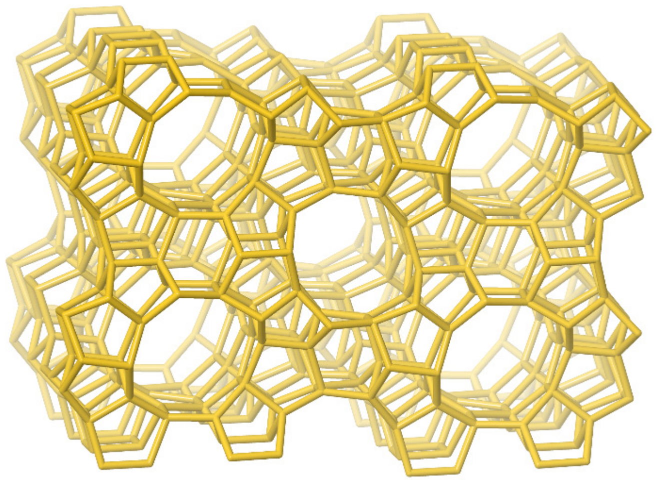
Pd catalyst: Cross-coupling
(Novel prize on 2010)

Heterogeneous catalyst: different phase from reactant such as supported catalyst, oxides, etc.



Muramatsu, A. *et al.*, *Catal. Today* **2008**, *132*, 81–87.

Supported catalyst: oxidation



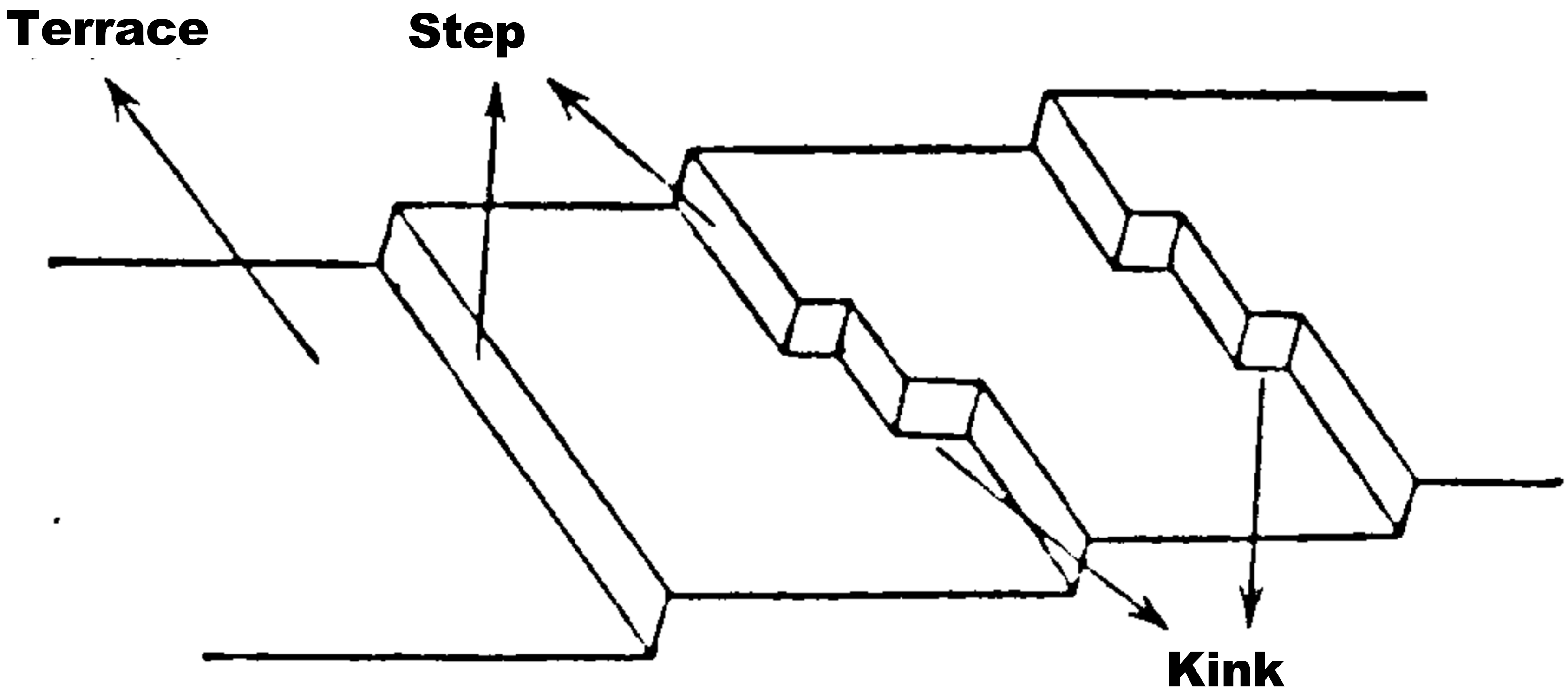
Zeolite: acid-based reaction

Homogeneous vs. Heterogeneous catalysts

	Homogeneous (Including enzyme)	Heterogeneous
Material	Always solved in solvent	Solid metals or oxides
Reaction phase	Homogeneous liquid	Liquid-solid, solid-solid, gas-solid
Stability, Temperature	Low < 200 ^oC	High Even >1000 ^oC
Selectivity	High ※Enzymes also have high "substrate selectivity"	Low
Separation and reuse	Difficult (Extraction operation, etc. required)	Easy (Filtration and centrifugation is enough.)
Analysis of re-action mechanism	Comparatively easy	Difficult

"Where" does the reaction occur in a heterogeneous catalyst? ？

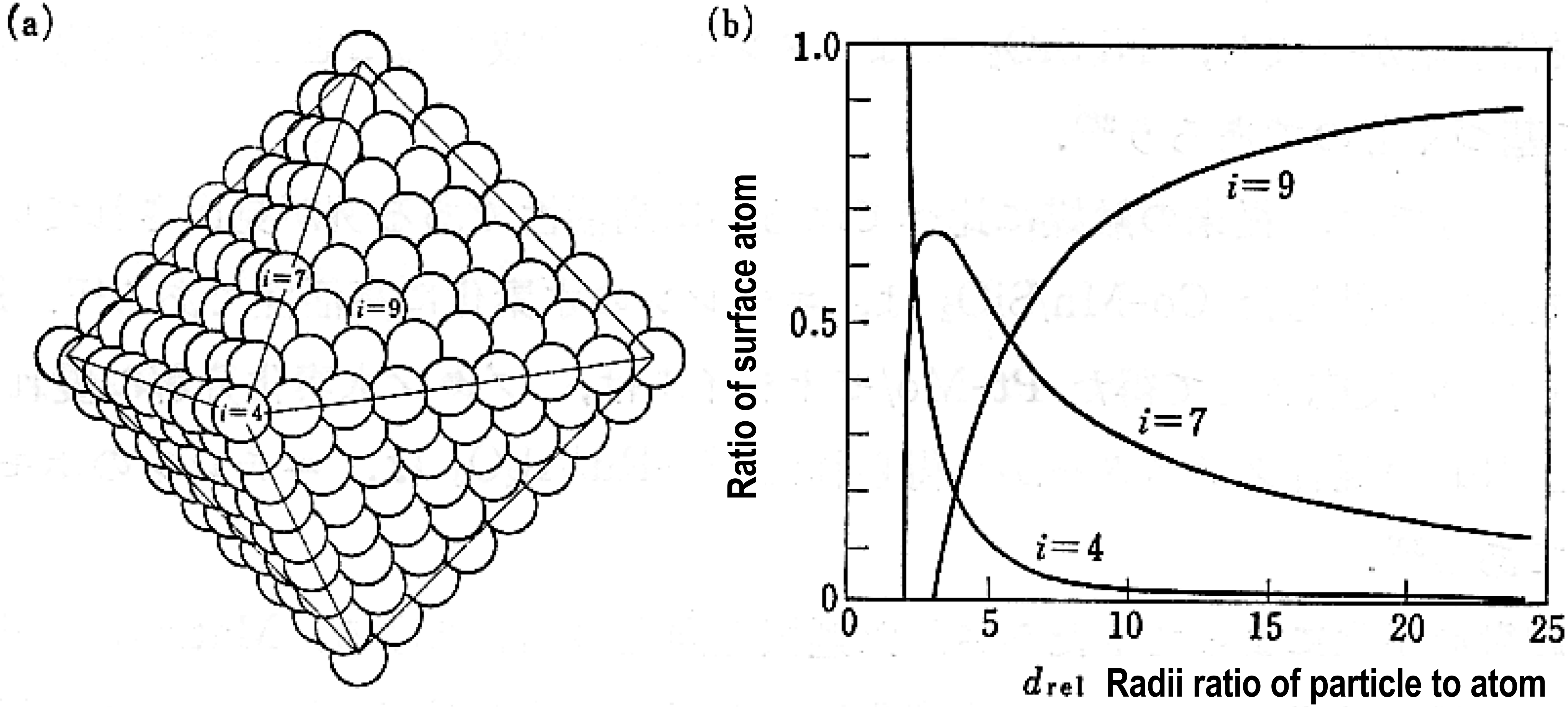
The substrate is activated at the "coordinatively unsaturated" site on the top surface of the solid so that a catalytic reaction occurs.



野副, *表面科学* **1990**, *11*, 131–137.

How to increase coordinatively unsaturated sites on a solid surface? ？

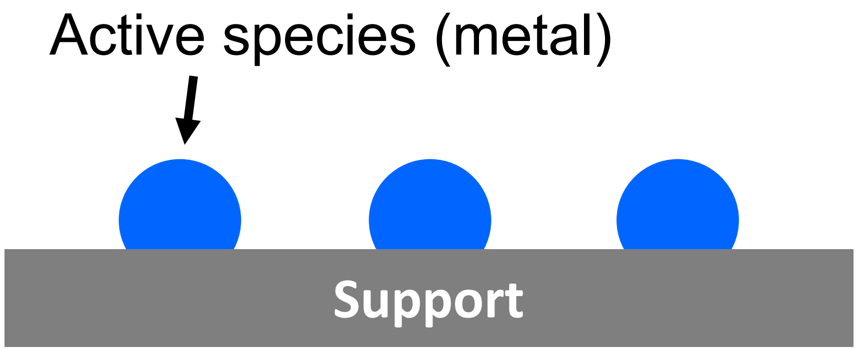
How to enhance catalytic activity？



野副, *表面科学* **1990**, *11*, 131–137.

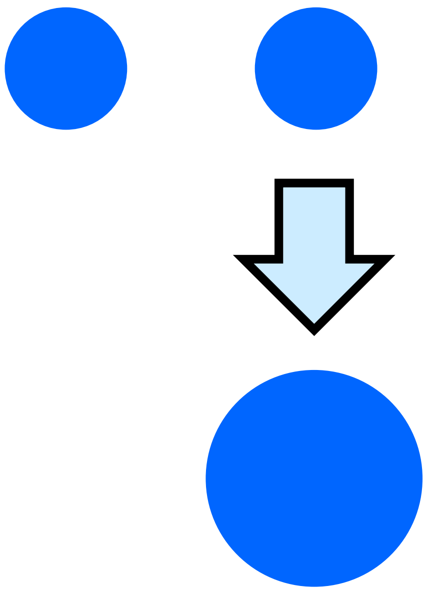
Generally, if the weight is the same, the smaller the particle size, the higher the catalytic activity. → "nanoparticles"

How to make good use of metal microparticles? : supported catalyst



Support: Putting a metal on a support with a high specific surface area.

→ The interaction with the carrier stabilizes the fine metal particles and maintains a highly dispersed state.

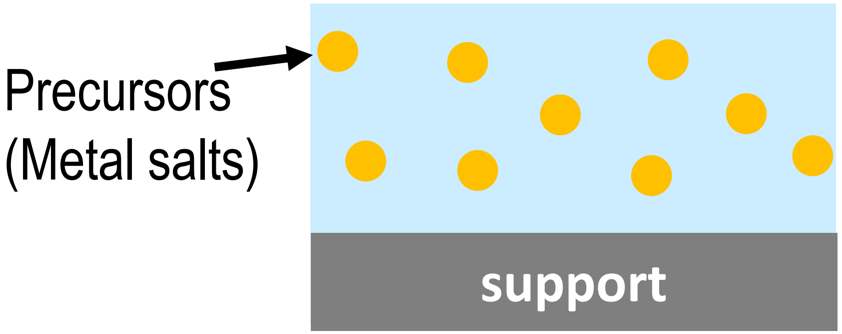


In the absence of a carrier, fine particles agglomerate due to their high surface energy.

※In order to suppress aggregation, protection with organic ligands is necessary.

Supported catalyst preparation method 1: Evaporation to dryness

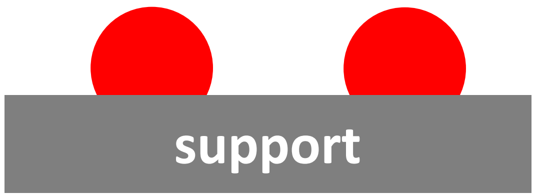
(i) In solvent



※Nitrates, acetylacetonate complexes, etc. are mainly used as metal precursors. Since halogens often remain, halides are generally avoided.

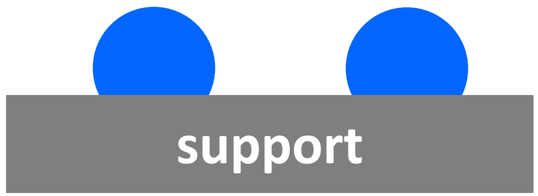
(ii) Evaporation of solvent (Forced loading of precursors)

(iii) Calcination (pyrolysis, sintering)



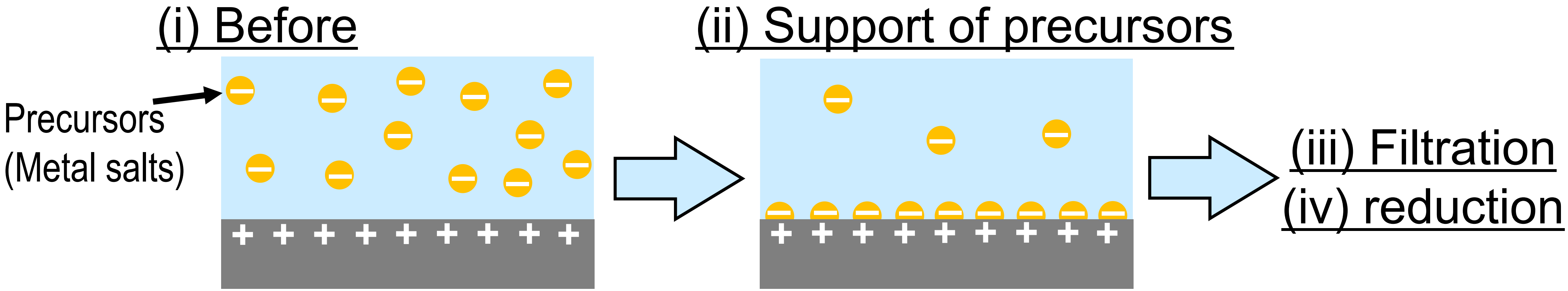
※In the case of a carbon support, do not use an oxygen atmosphere.

(iv) Reduction

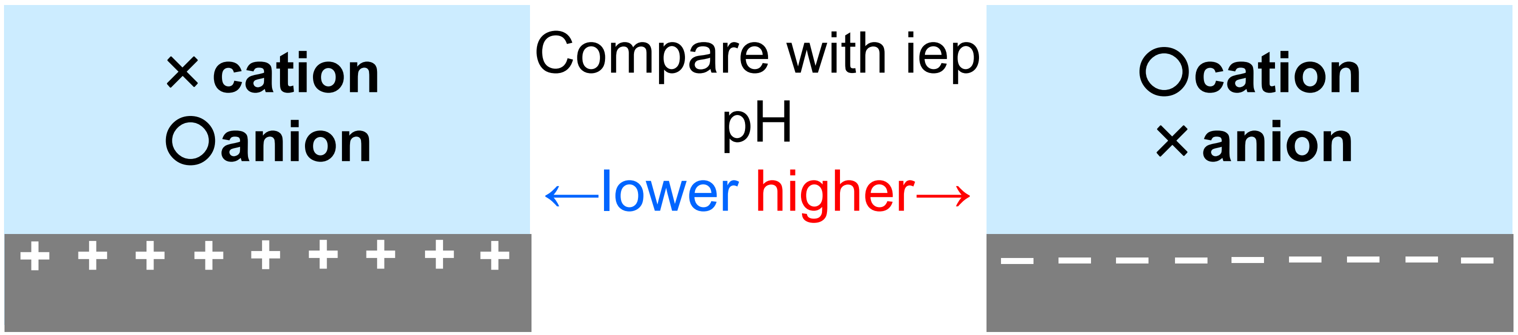


※Unless you want a supported "oxide" catalyst.

Supported catalyst preparation method 1: ion exchange



Point of ion exchange method: Isoelectric point (iep) of carrier

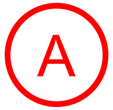


Oxides	iep (pH)
SiO_2	1.0–3.0
TiO_2	4.7–6.2
Al_2O_3	6.5–9.4
MgO	12.1–12.7

It is important to adjust the pH according to the charge on the precursor and carrier surface.

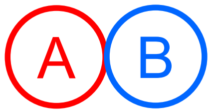
Unique catalysis of alloy catalysts : Ligand and effect ensemble effect

Ligand effect



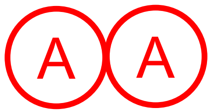
Reactions that can be accelerated by one metal atom A

⇩ **Alloying**



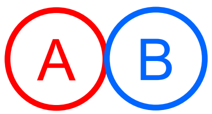
The second metal B changed the electronic state of A and changed the catalytic activity.

Ensemble effect



Reactions that can be accelerated by metal ensembles (active sites composed of multiple metal atoms A)

⇩ **Alloying**



The second metal B disrupted the metal ensemble and lowered the catalytic activity. (It can be used to suppress side reactions that you do not want to proceed)

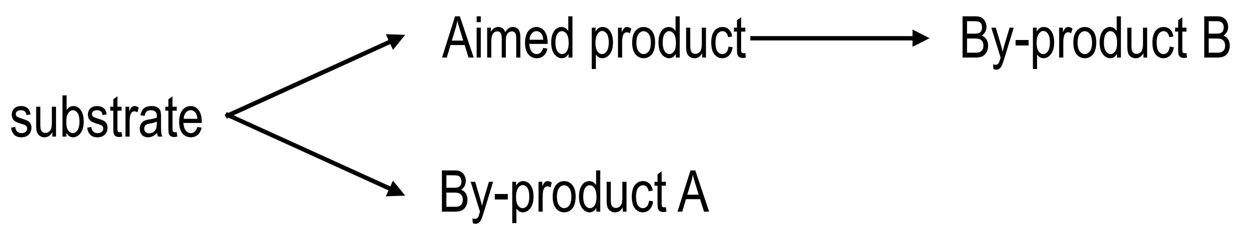
Evaluation of catalytic performance

The following three points are important for catalytic performance..

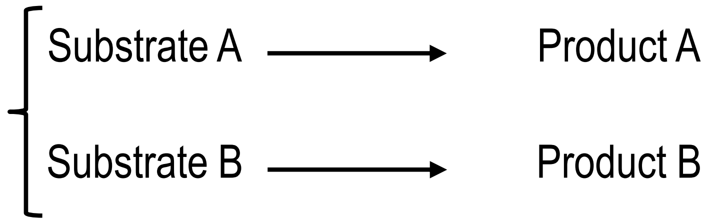
1. Activity (reaction rate): Turnover frequency, TOF

2. Selectivity

(A) Product selectivity



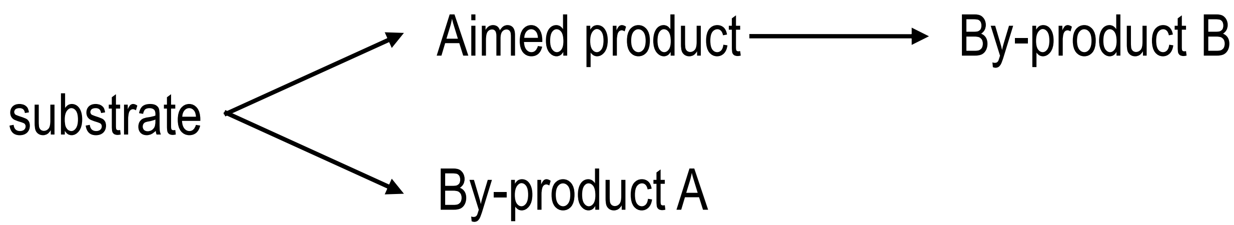
(B) Substrate selectivity (substrate specificity for enzyme)



3. endurance (lifetime): Turnover number, TON

It is difficult to obtain the reaction rate one by one. …

Evaluation of catalytic performance 2: Relationship between conversion, yield and selectivity



1. Conversion
   = (amount of substrate consumed) / (amount of substrate used)

2. Yield)
   = (amount of aimed product) / (amount of substrate used)

3. Selectivity
   = (amount of aimed product) / (amount of substrate consumed)

Thus, 「Yield = Conversion × Selectivity」

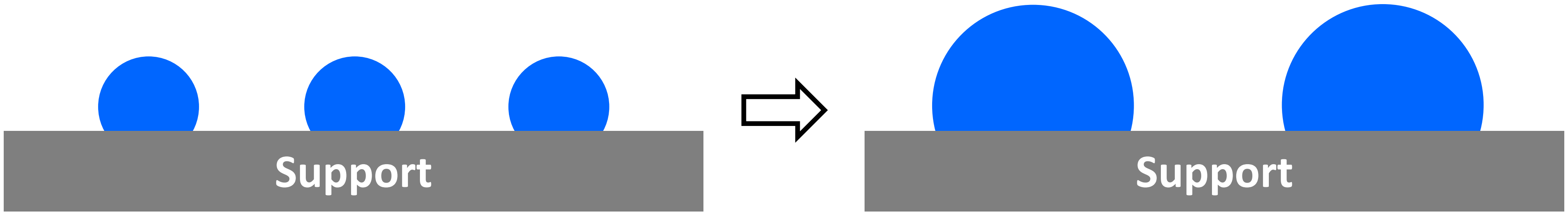
※Product distribution, (amount of aimed product) / (amount of all products)
Note that there are many papers and studies that confuse this with selectivity.

Degradation and regeneration of catalyst

Most catalysts degrade for a variety of reasons, even though ``Definition of catalyst: they themselves remain unchanged before and after the reaction."

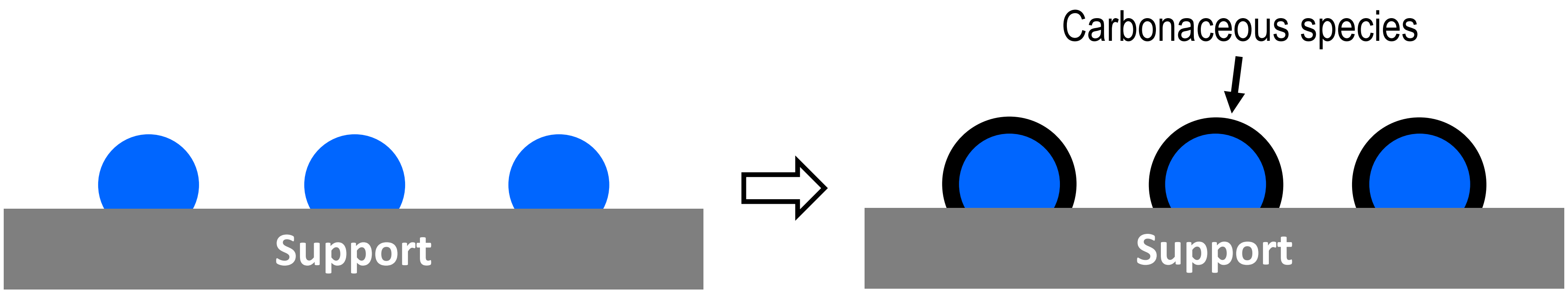
1. Derived from structural change of catalyst: aggregation of supported species, phase transition, elution of active species, etc.

*Since the catalyst itself has changed, it is difficult to regenerate.

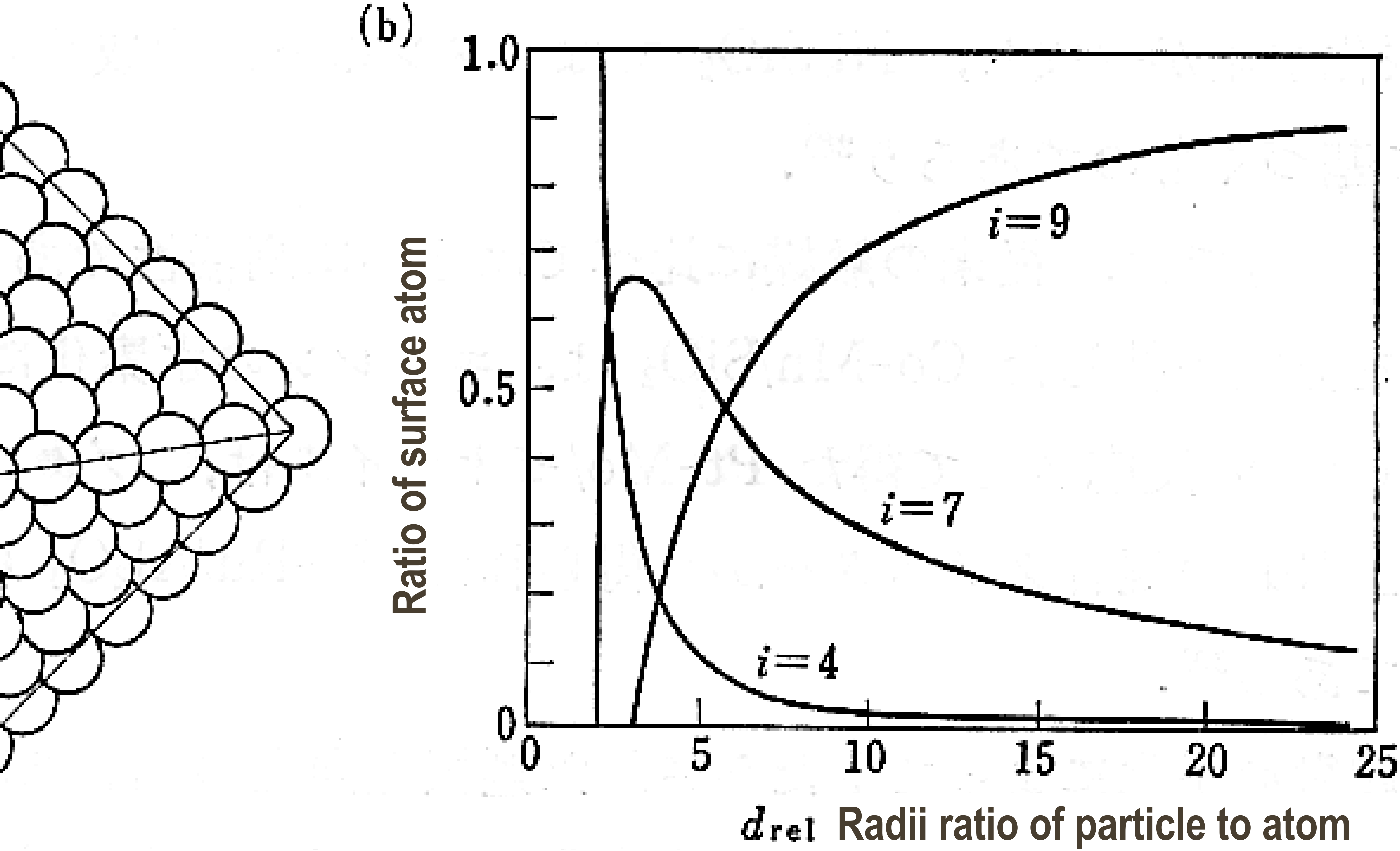


2. Derived from external factors: Poisoning by substrates and products (e.g. coking)

* It can be regenerated by removing the poisoning substance. (e.g. calcination)



Fundamentals of catalytic reactions



Generally, if the weight is the same, the smaller the particle size, the higher the catalytic activity. → “nanoparticles”

Structural Sensitivity / Structural Insensitivity

- **Structure insensitive**
  - Only the effect of increasing the surface area appears
- **Structure sensitive**
  - Catalytic activity depends on particle size.
    - The smaller the particle size, the greater the catalytic activity.
    - The larger the particle size, the greater the catalytic activity.
    - Catalytic activity is maximized at a certain particle size

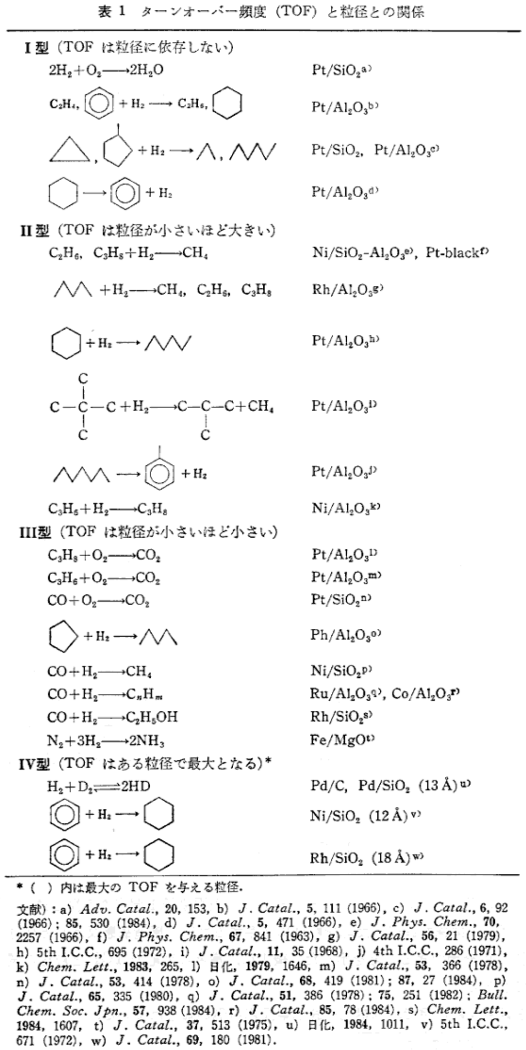


表 1 ターンオーバー頻度（TOF）と粒径との関係

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.

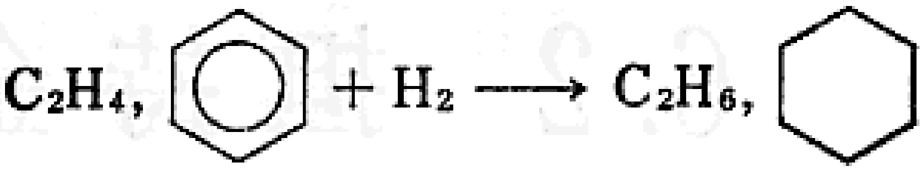
文献）: a) *Adv. Catal.*, **20**, 153, b) *J. Catal.*, **5**, 111 (1966), c) *J. Catal.*, **6**, 92 (1966); **85**, 530 (1984), d) *J. Catal.*, **5**, 471 (1966), e) *J. Phys. Chem.*, **70**, 2257 (1966), f) *J. Phys. Chem.*, **67**, 841 (1963), g) *J. Catal.*, **56**, 21 (1979), h) 5th I.C.C., 695 (1972), 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).

Structural Sensitivity / Structural Insensitivity

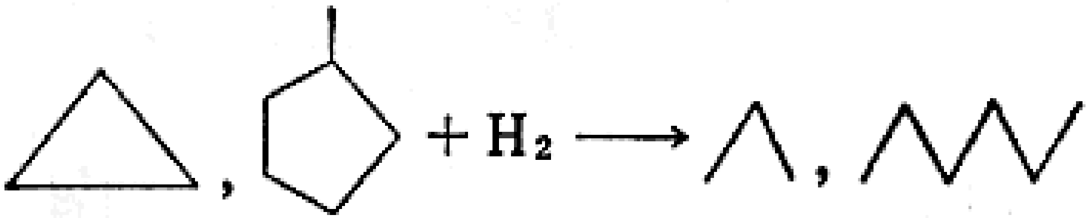
Relationship between Turnover Frequency (TOF) and catalyst particle size

I 型 TOF is independent on the size: Structure insensitive

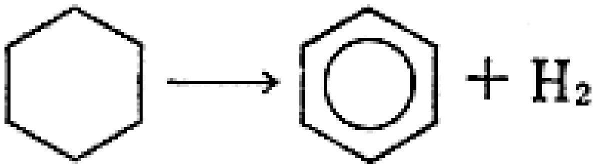
$2H_2 + O_2 \longrightarrow 2H_2O$ Pt/SiO_2[a)]



Pt/Al_2O_3[b)]



Pt/SiO_2, Pt/Al_2O_3[c)]



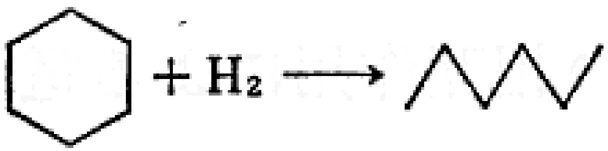
Pt/Al_2O_3[d)]

Structural Sensitivity / Structural Insensitivity

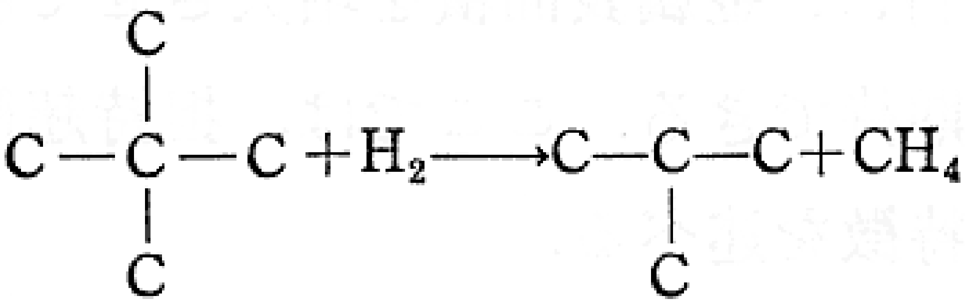
II 型 The larger TOF, the smaller the size: Structure sensitive

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

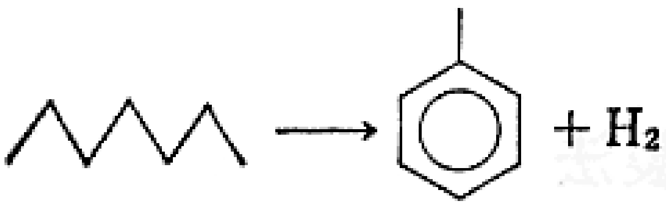
Rh/Al_2O_3[g)



Pt/Al_2O_3[h)



Pt/Al_2O_3[i)

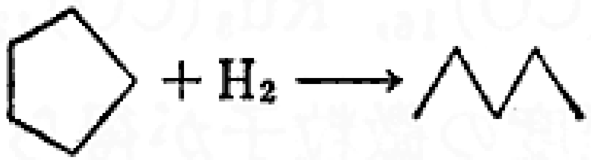


Pt/Al_2O_3[j)

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

Structural Sensitivity / Structural Insensitivity

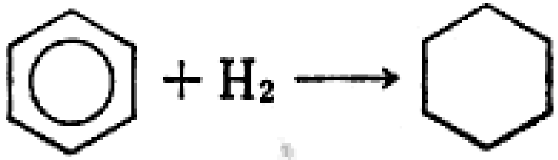
III型 The smaller TOF, the smaller the size: Structure sensitive

$C_3H_8 + O_2 \longrightarrow CO_2$	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)]

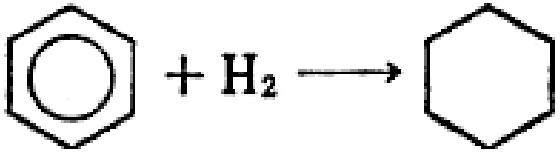
Structural Sensitivity / Structural Insensitivity

IV型 TOF is the largest at a specific size: Structure sensitive

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



Ni/SiO_2 (12 Å) v)



Rh/SiO_2 (18 Å) w)

Adsorption and castalysis

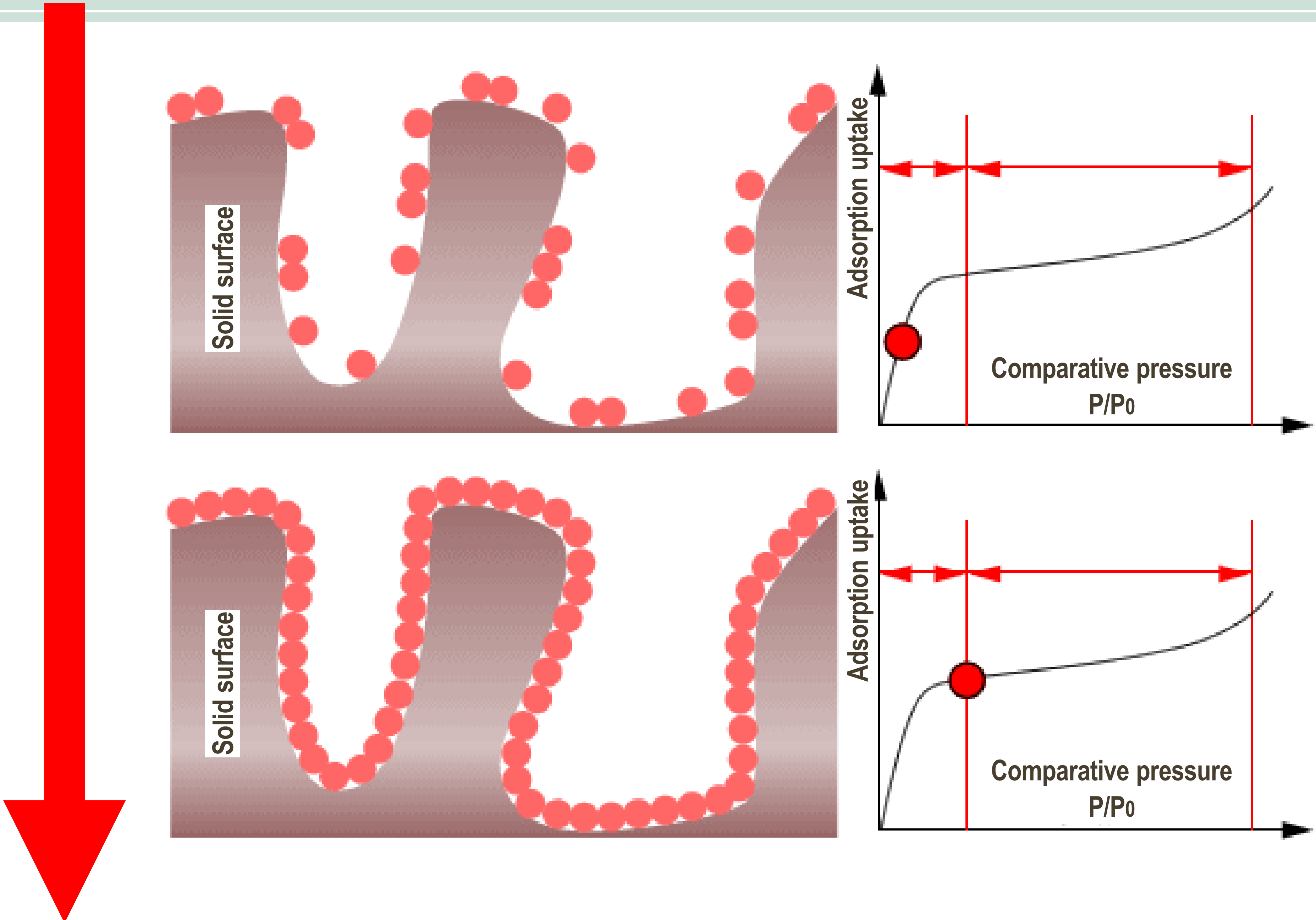
Adsorption is start of catalytic reaction

- **Physisorption**
  - Weak adsorption:　always
- **Chemisorption**
  - Strong adsorption：　chemical bonding

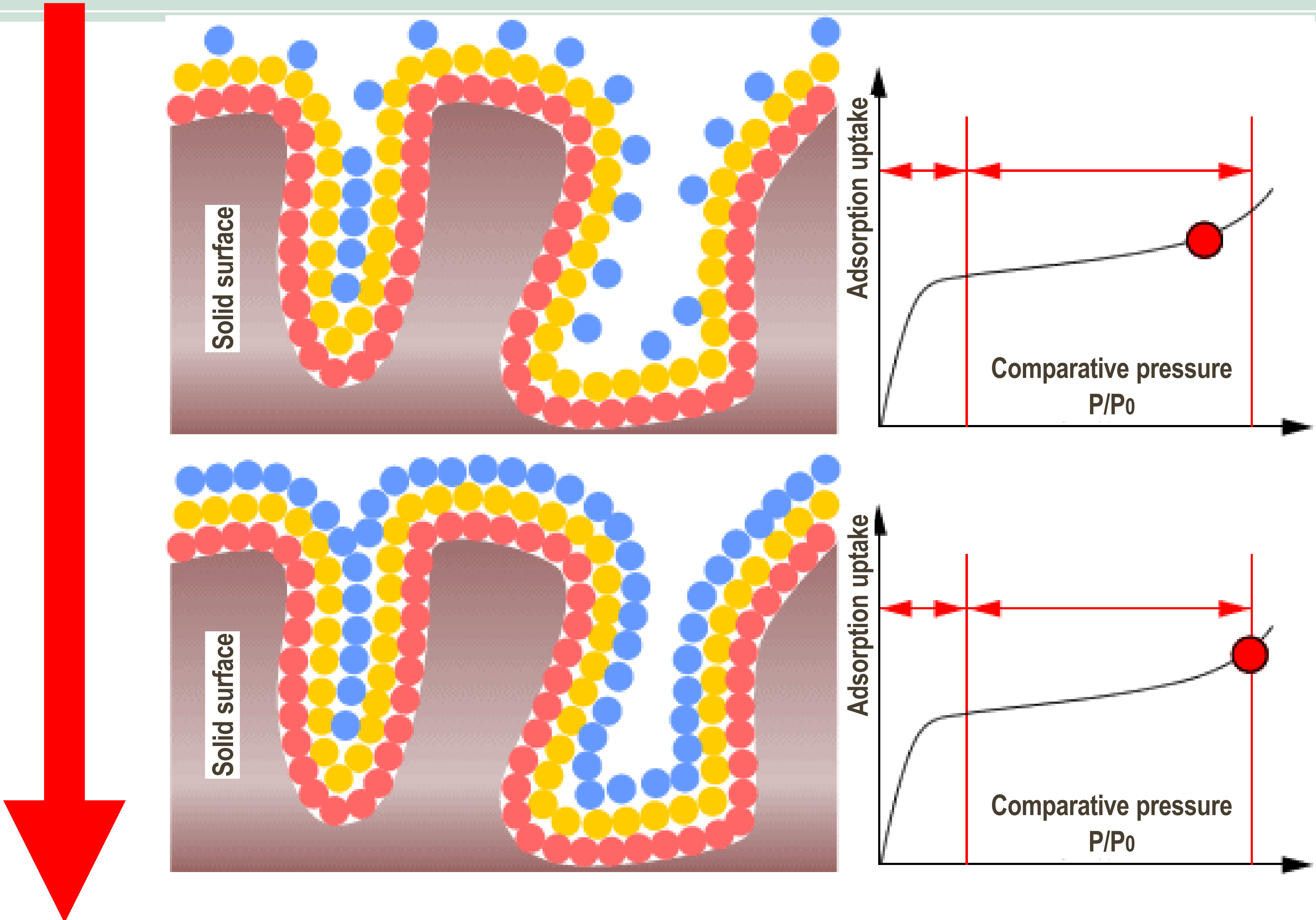
Table　Chemisorption and physisorption

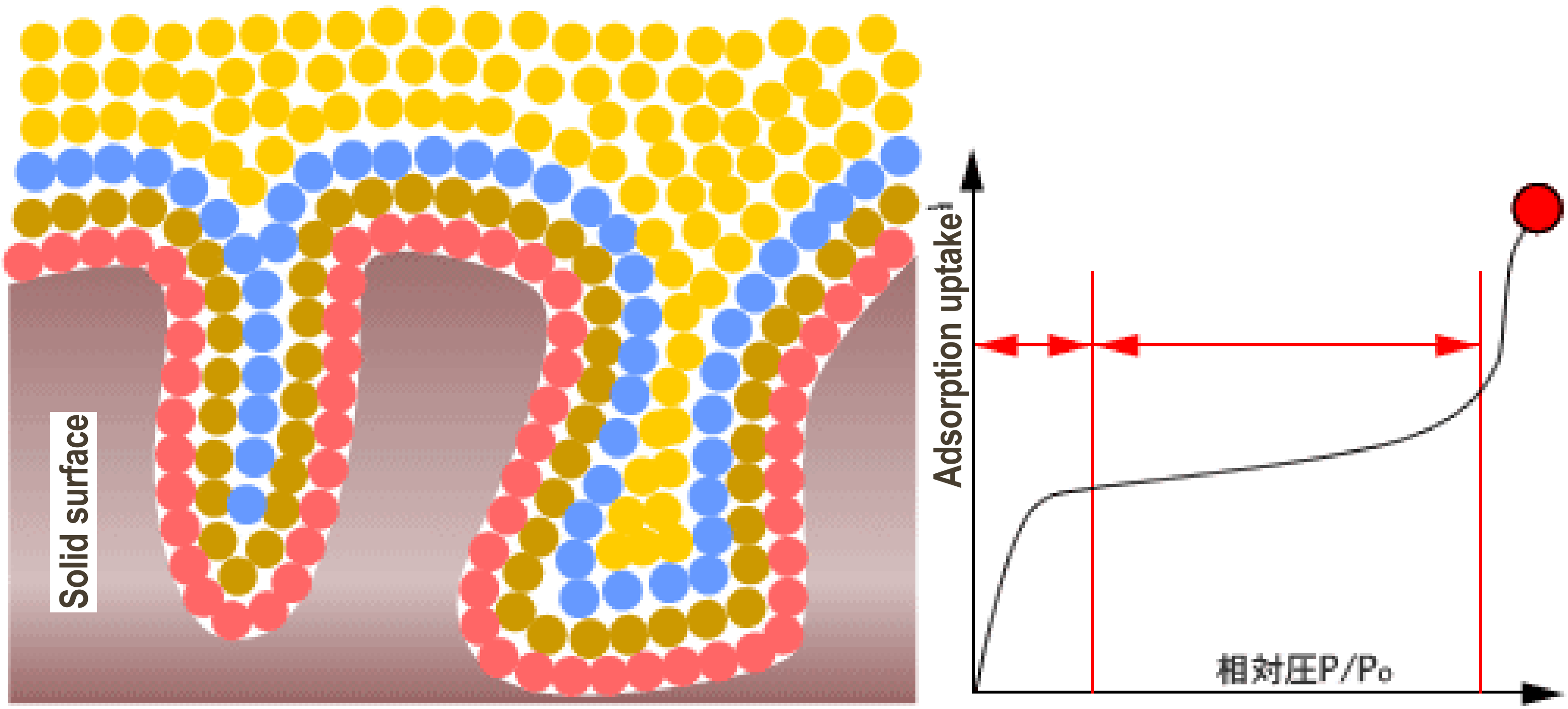
Features	Chemisorption	Physisorption
Origin of adsorption	Chemical bond	van der Waals force
Site	Selective	Non-selective
Structure	Monolayer	Multilayer
Heat of adsorption	10～100 k cal/mol	A few kcal/mol
Activation energy	Large	Small
Rate	Slow	Rapid
Adsorption and Desorption	Reversible or Irreversible	Reversible
Typical adsorption	Langmuir type	BET type

Physisorption



Physisorption

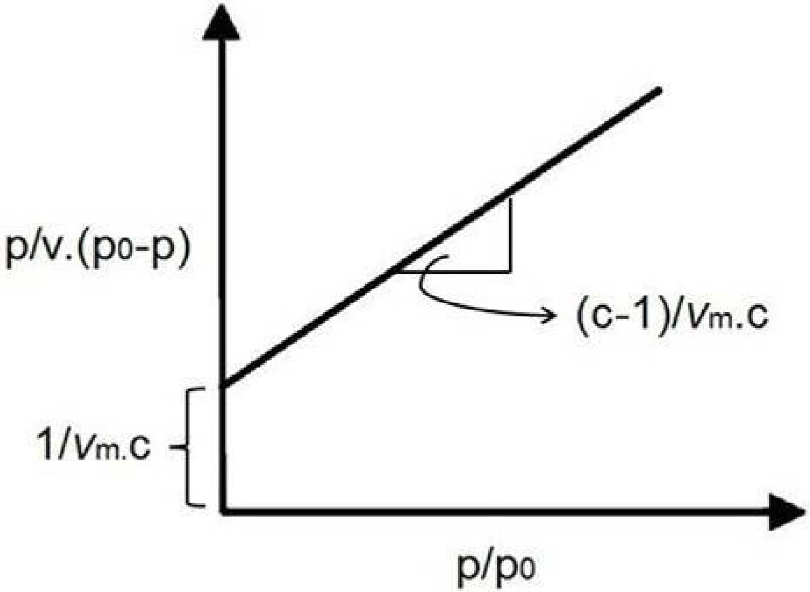



Solid surface
Adsorption uptake
相対圧P/Po

Brunauer–Emmett–Teller Isotherm (BET) Isotherm

$\text{slope} = \left(\frac{C-1}{V_m C}\right), (cm^{-3})$ $c\ (intercept) = \frac{1}{V_m C}, (cm^{-3})$ $V_m = \frac{1}{Slop+Intercept}$

$$\frac{P}{V(P^o - P)} = \frac{1}{V_m C} + \left(\frac{C-1}{V_m C}\right)\frac{P}{P^o}$$



Surface Area/Total Surface Area

$$Surface\ area(S_{total}) = \frac{V_m N s}{V}$$

BET Surface Area/Specific Surface Area

$$BET\ surface\ area = \frac{S_{total}}{a}$$

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Chemisorption

Chemisorption

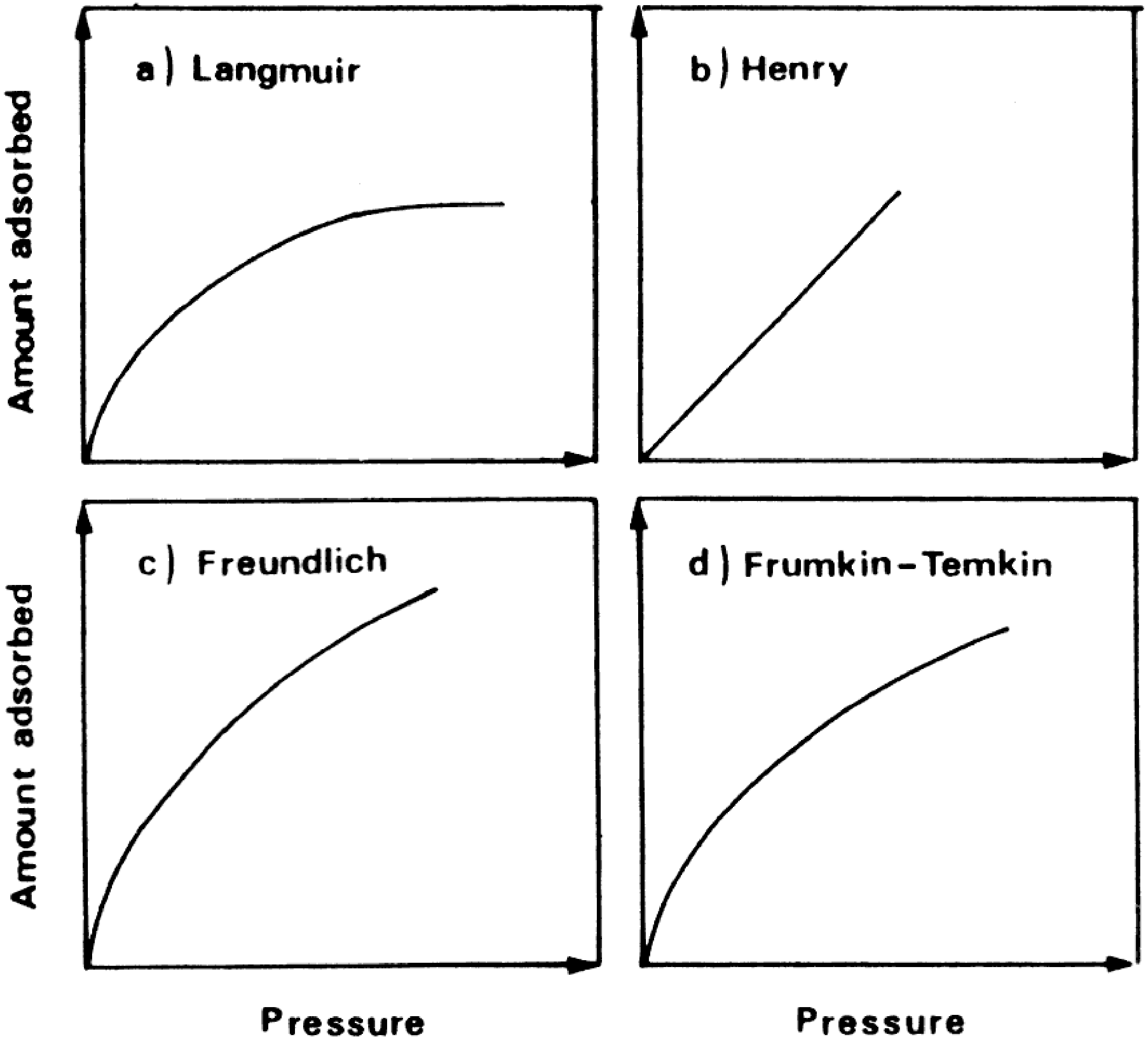
- **Dissociated adsorption**

  Ex. CO + M(adsorption site) → C–M + O–M

- **Non-dissociated adsorption**

  Ex. CO + M(adsorption site) → CO–M

Adsorption isotherm



Adsorption isotherm

- **Langmuir**

$$v = \frac{abp}{1+ap} \qquad v = \frac{ab\sqrt{p}}{1+a\sqrt{p}}$$

$$\theta/(1-\theta) = ap$$

$$\theta/(1-\theta) = a\sqrt{p}$$

- **Henry**

$$\theta = ap \qquad \theta << 1$$

p: adsorption equilibrium pressure
v: adsorption uptake
b: saturated uptake
θ= *v* / *b*

- **Freundlich**

$$v = ap^{1/n} \qquad (1 < n < 10)$$

- **Frumkin-Temkin**

$$v = A \ln Bp$$

Adsorption isotherm

- **Langmuir**
  - Most chemisorptions are applicable.
  - The theory is that the heat of adsorption is irrelevant to the amount of adsorption, but this may not always be the case.
- **Henry**
  - Although it is a formula that linearly increases the amount of adsorption, it is often regarded as a part of the Langmuir type.
- **Freundlich**
  - The heat of adsorption is linearly related to In v (amount of adsorption).
  - The middle part is close to the Langmuir type, so it is difficult to identify.
- **Frumkin–Temkin**
  - A special case has been presented for ammonia and nitrogen adsorption on metallic iron.
  - The heat of adsorption decreases linearly with the amount of adsorption.

Chemisorption

- **Langmuir equation**

$$\frac{d\theta}{dt} = k_f(1-\theta)C_A - k_b\theta \qquad (1)$$

k_f, k_b, Reaction rate constants of adsorption and desorption

$$\theta = q / q_m \qquad (2)$$

q_m, Saturated adsorption amount

***dq/dt* = 0** in equilibrium, then,

$$q = q_m\theta = q_m \frac{K_A C_A}{1 + K_A C_A} \qquad (3)$$

K_A, Adsorption constant

Chemisorption

・**Freundlich equation（from experimental）**

$$q = kC_A^{\ n} \qquad (4)$$

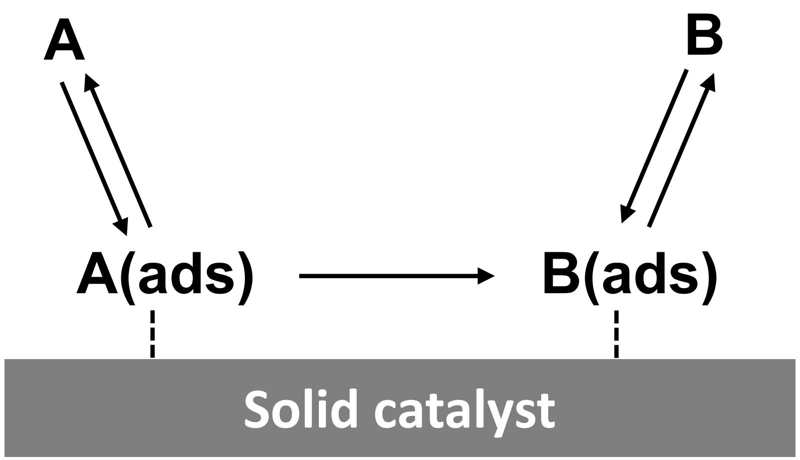
***k*, *n*,** Freundlich constant

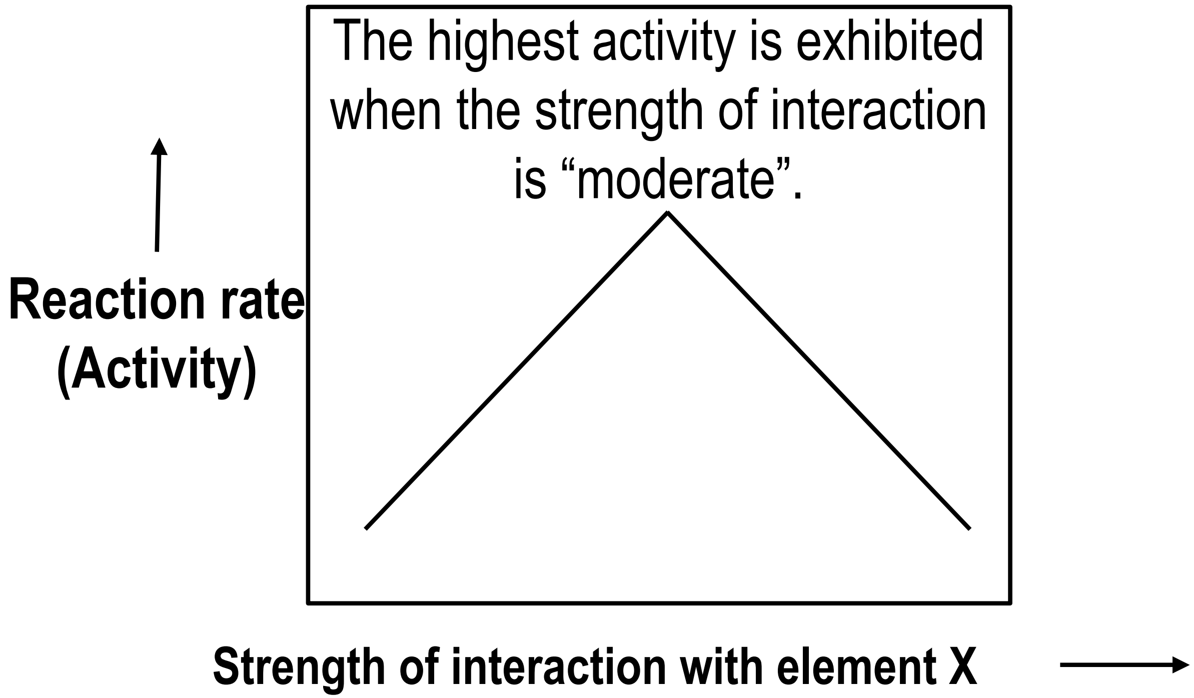
C_A, Equilibrium concentration of adsorbate

Importance of Adsorption to Surfaces: Volcanic Activity Orders

In order for the solid catalytic reaction to proceed, it is a major premise that the substrate is chemisorbed and activated on the catalyst surface.

1. Substrate adsorption: If too weak, no reaction will occur.
2. Desorption of products: If it is too strong, the next reaction will not occur (=poisoning). → It often becomes a volcano plot.

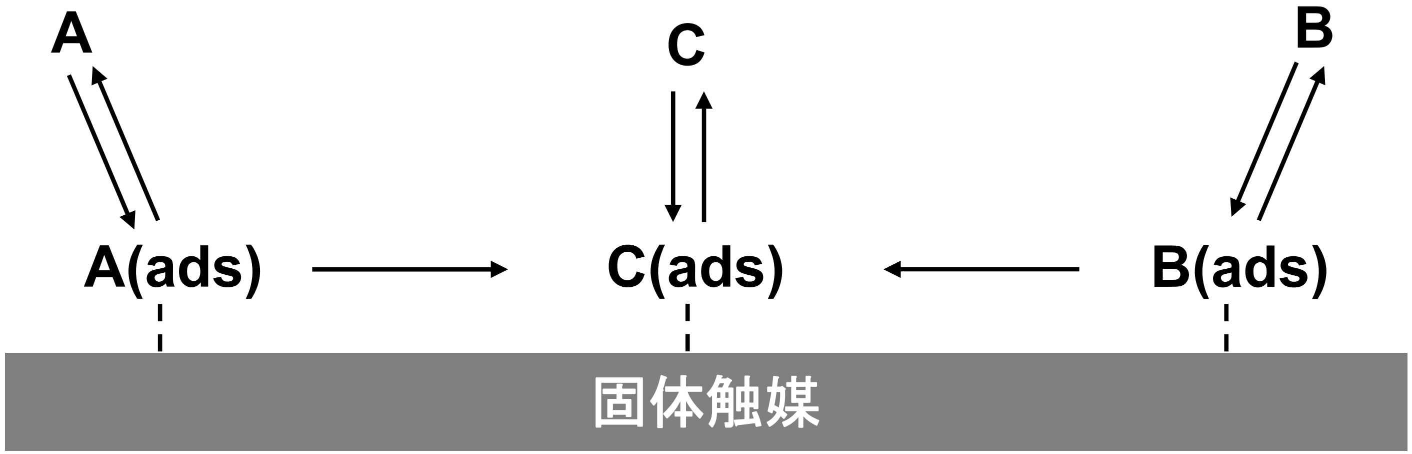




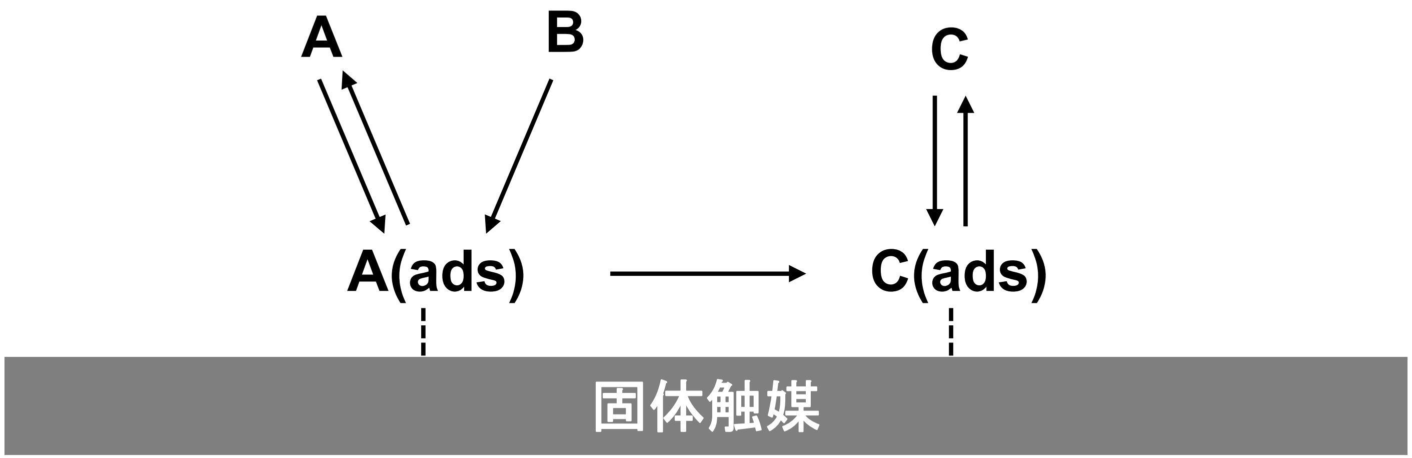
Intermolecular Reaction Mechanism Considering Adsorption: L-H and E-R Mechanism

The reaction between Substrate A and Substrate B (intermolecular reaction) is roughly explained by the following two mechanisms..

1. Langmuir-Hinshelwood mechanism: Both A and B are adsorbed on the catalyst and activated.



2. Eley-Rideal mechanism: B collides with A, adsorbed and activated on the catalyst, and then reacted.



From adsorption to catalytic reaction

Catalytic reaction

- **Physisorption**
- **Chemisorption**
- **Surface reaction**
- **Desorption**

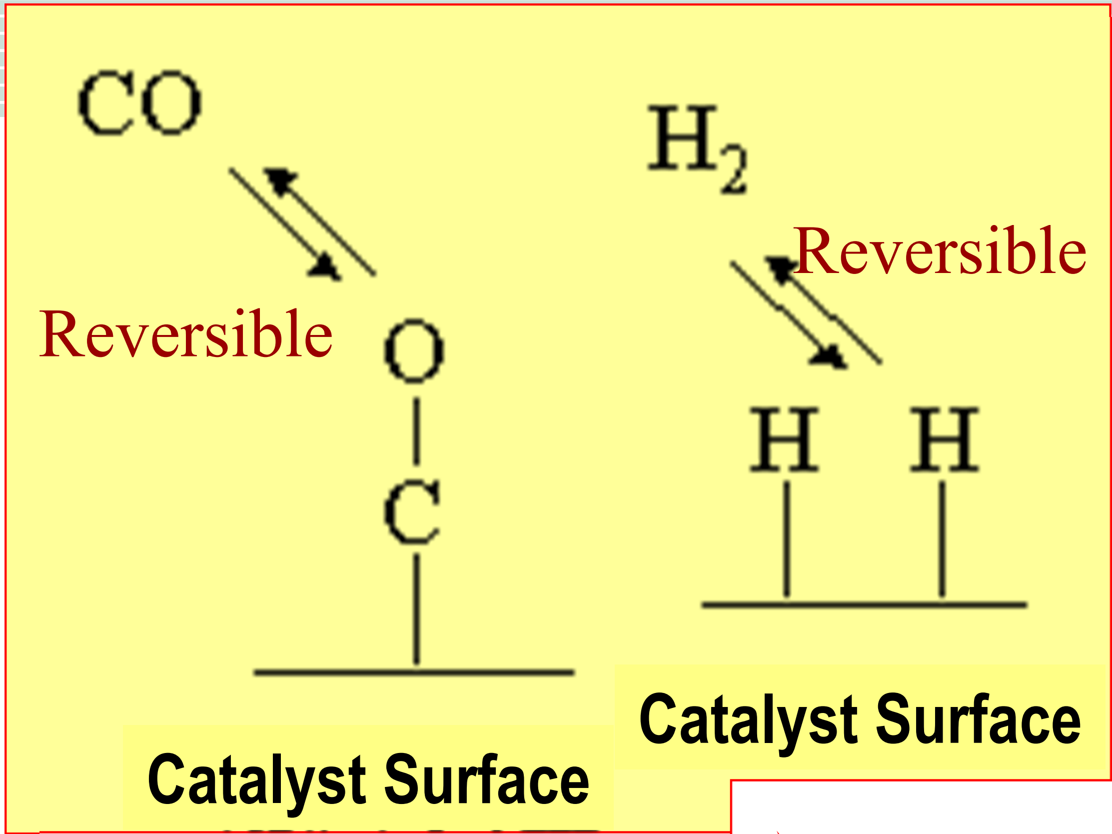
If it ends here, it is simply an adsorption phenomenon.

Example： Methanol synthesis reaction

- Synthesis gas conversion into methanol

$$CO + 2H_2 \rightarrow CH_3OH$$

Keys are non-dissociation of C=O and dissociation of H-H.

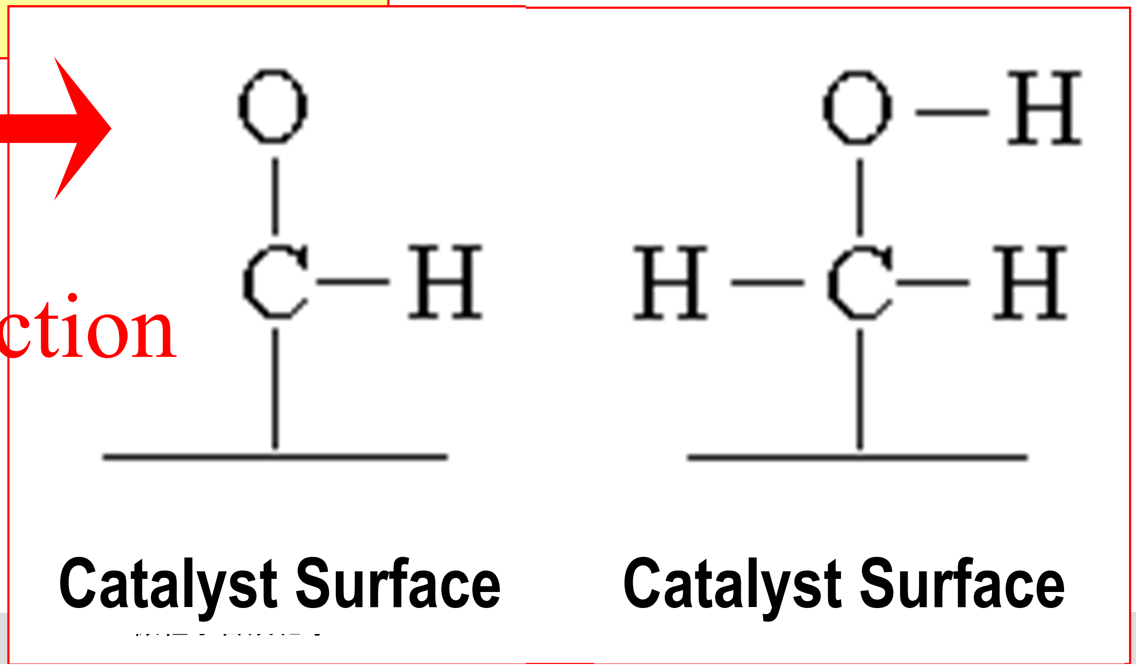


Physisorption
→chemisorption

Irreversible

Surface reaction

CH_3OH



Surface reaction

- **There are many irreversible processes.**
  - When the reverse reaction is overwhelmingly unfavorable
- **Surface reactions are often the rate-limiting step.**
  - Surface reactions also have many stages.
  - You can find out where the rate-limiting step is by an Arrhenius plot.

Example： methanol synthesis

- Synthesis gas conversion into methanol

  $CO + 2H_2 \rightarrow CH_3OH$

CO gas→**CO**（chemisorption）

H_2 gas → **H_2** （chemisorption）→**2H**（Dissociative adsorption ）

CO（Adsorption）**+H**→**CHO**（Adsorption）　＜律速段階＞

CHO （Adsorption） **+H**→**CH_2O** （Adsorption）

CH_2O （Adsorption） **+H**→**CH_3O** （Adsorption）

CH_3O （Adsorption） **+H**→ **CH_3OH** （Adsorption）

CH_3OH （Adsorption） → （Desorption） **CH_3OH**

Activation energy

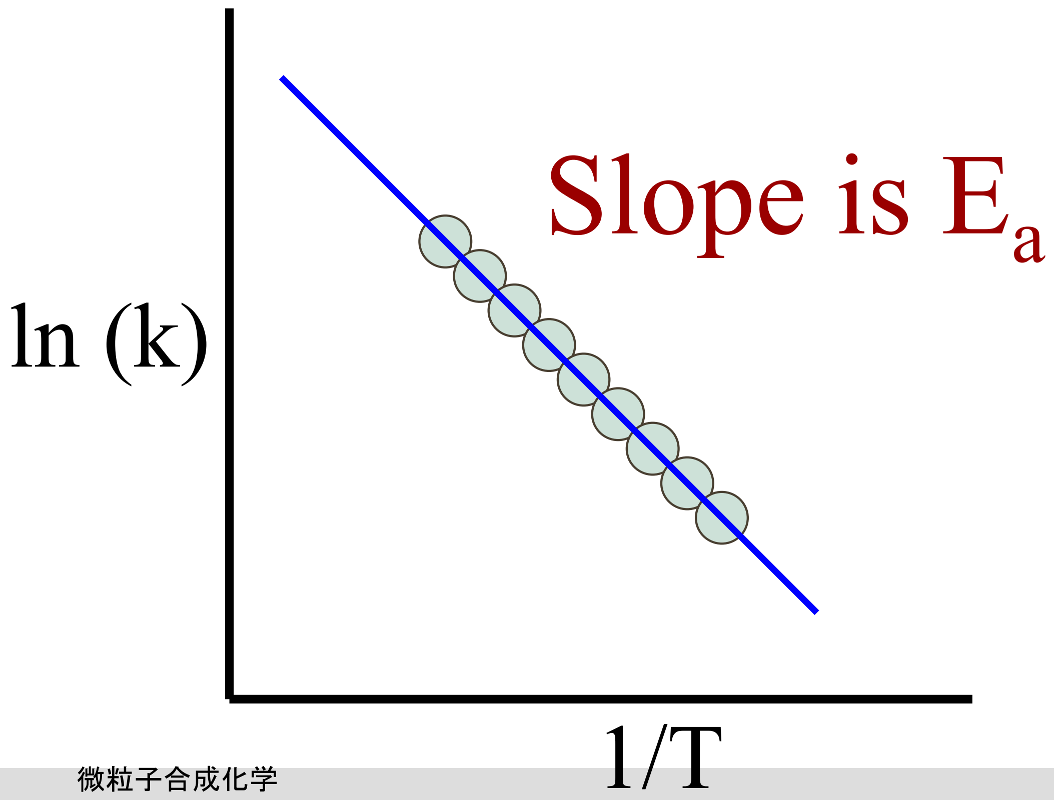
- Arrhenius equation
  Reaction rate constant *k*

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

- where A is the frequency factor and E is the activation energy. This equation indicates that the activation energy can be obtained if the rate constants at different temperatures are known.
- It is important that the Arrhenius equation has the same form as the Boltzmann distribution equation. Activation energy is the energy required to become an intermediate in the middle of a reaction. This indicates that the ratio of the intermediates to be present governs the reaction rate.
- Reaction rate analysis is important in clarifying the reaction mechanism in reactions where various substances coexist.

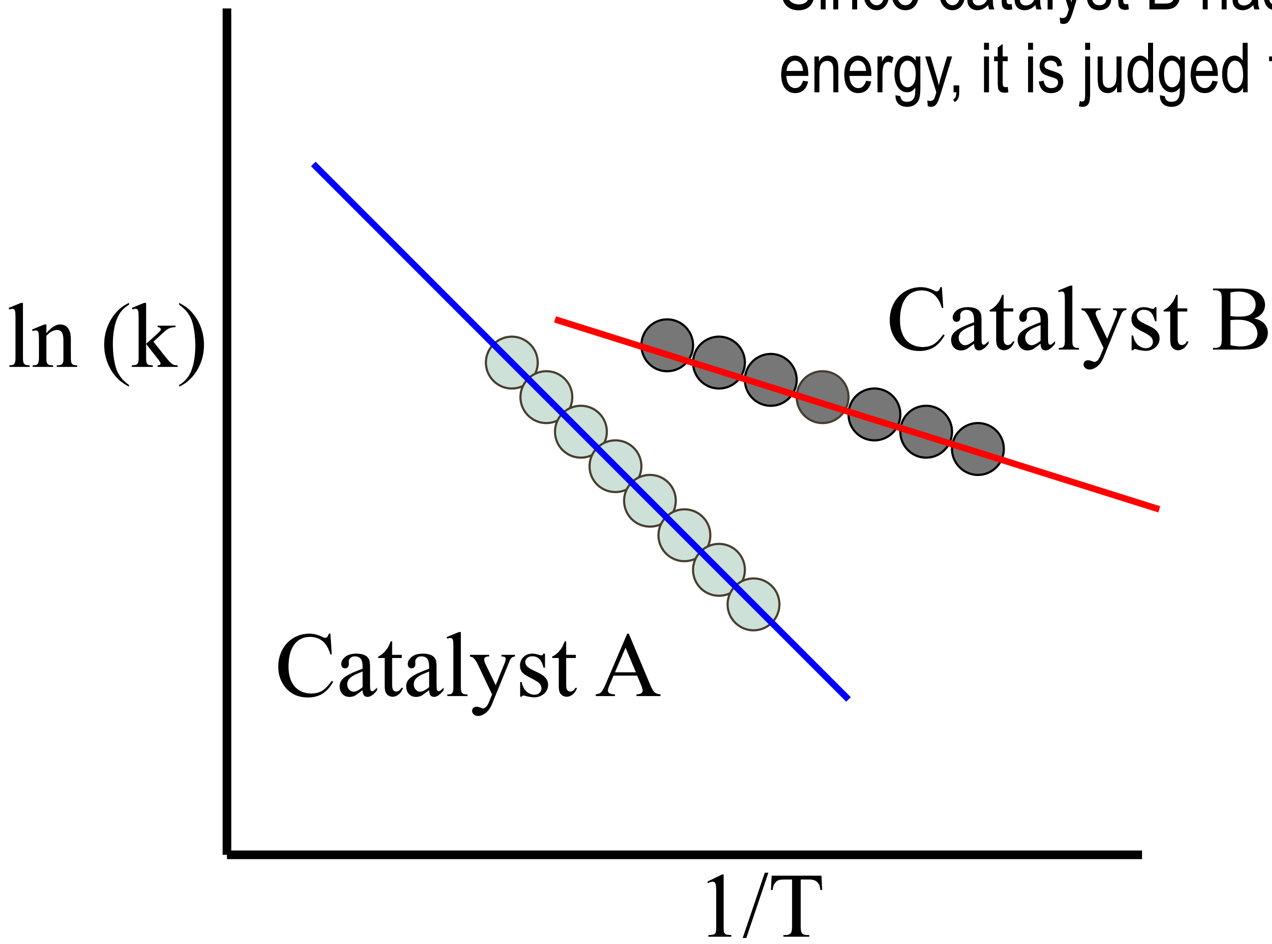
Apparent activation energy

- **From the experimental data, plotting ln (k) = y-axis and 1/T = x-axis, the slope is Ea = activation energy.**

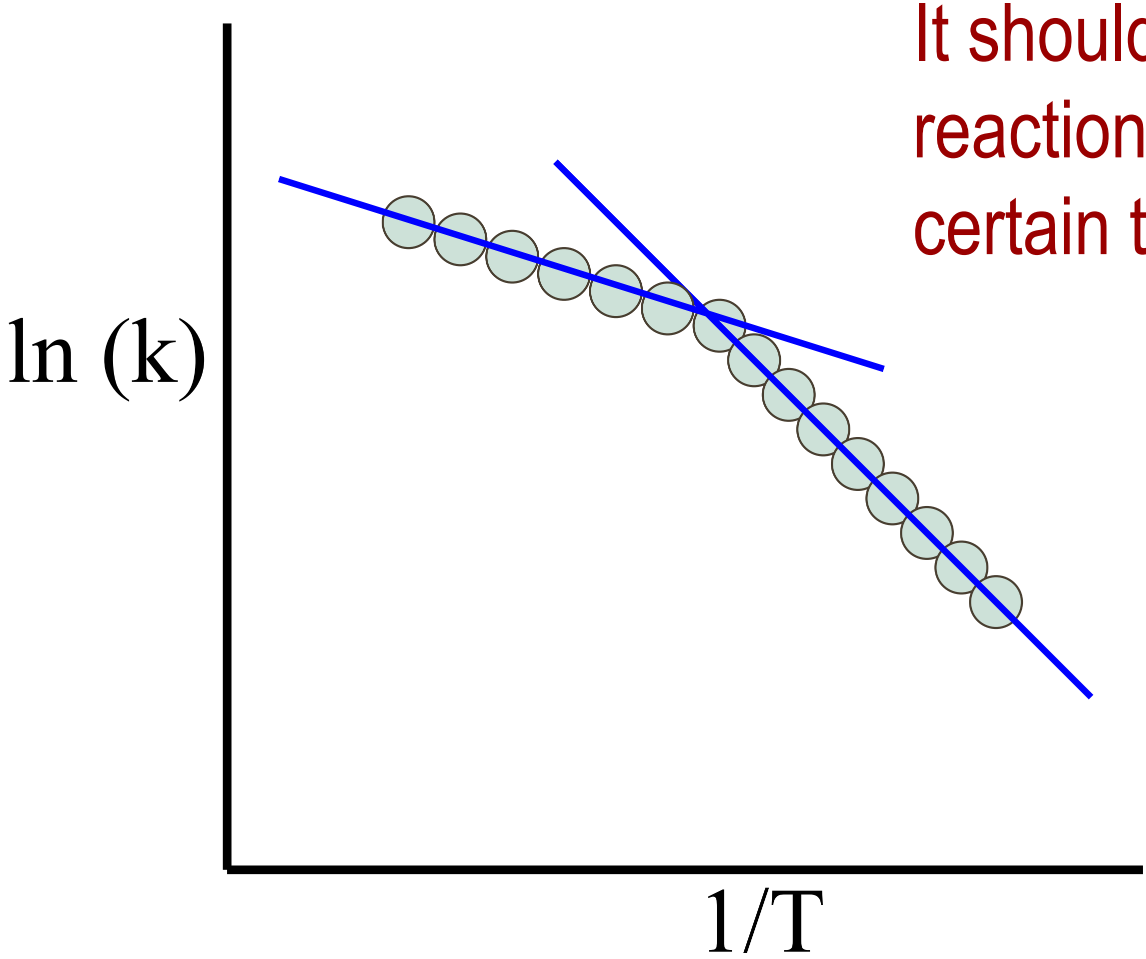


Working of catalyst

Since catalyst B has a smaller activation energy, it is judged to be more effective.

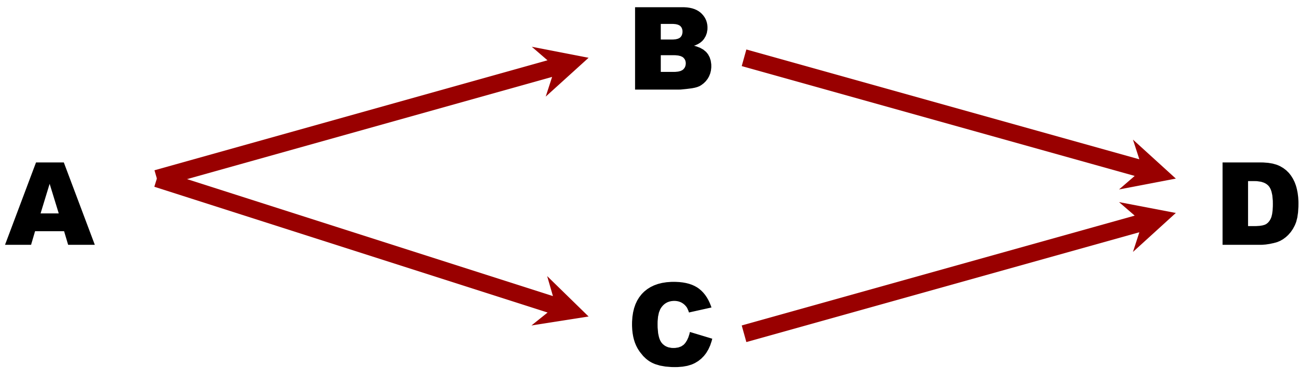


Change the activation energy?



It should be understood that the reaction path changed in a certain temperature range.

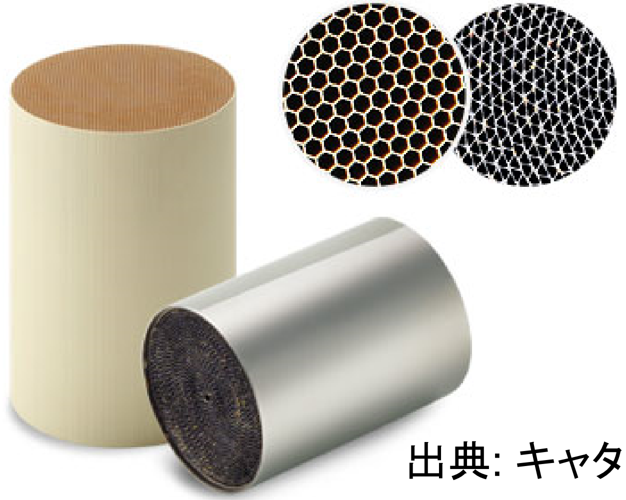
Reaction paths



When the rate-limiting step changes, the activation energy changes.

The state of catalytic science: research and development that meets social and industrial needs

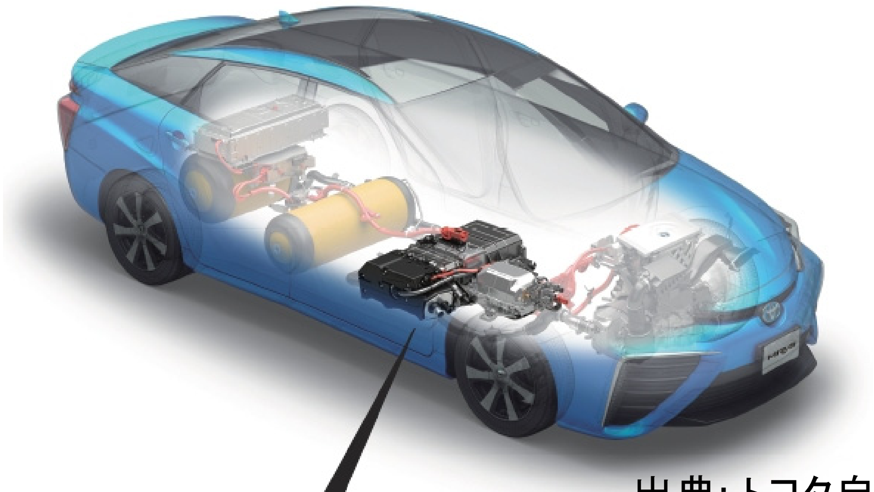
Haber-Bosch method (NH_3 synthesis)
→ To deal with population growth (fertilizer synthesis)



出典: キャタラー

Exhaust gas purification
→ For environmental conservation

Catalytic cracking, desulfurization, etc.
→ For large-scale utilization of petroleum and environmental conservation



出典: トヨタ自動車

Fuel cell
→ For de-fossil fuel