

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

What's monodispersed particles

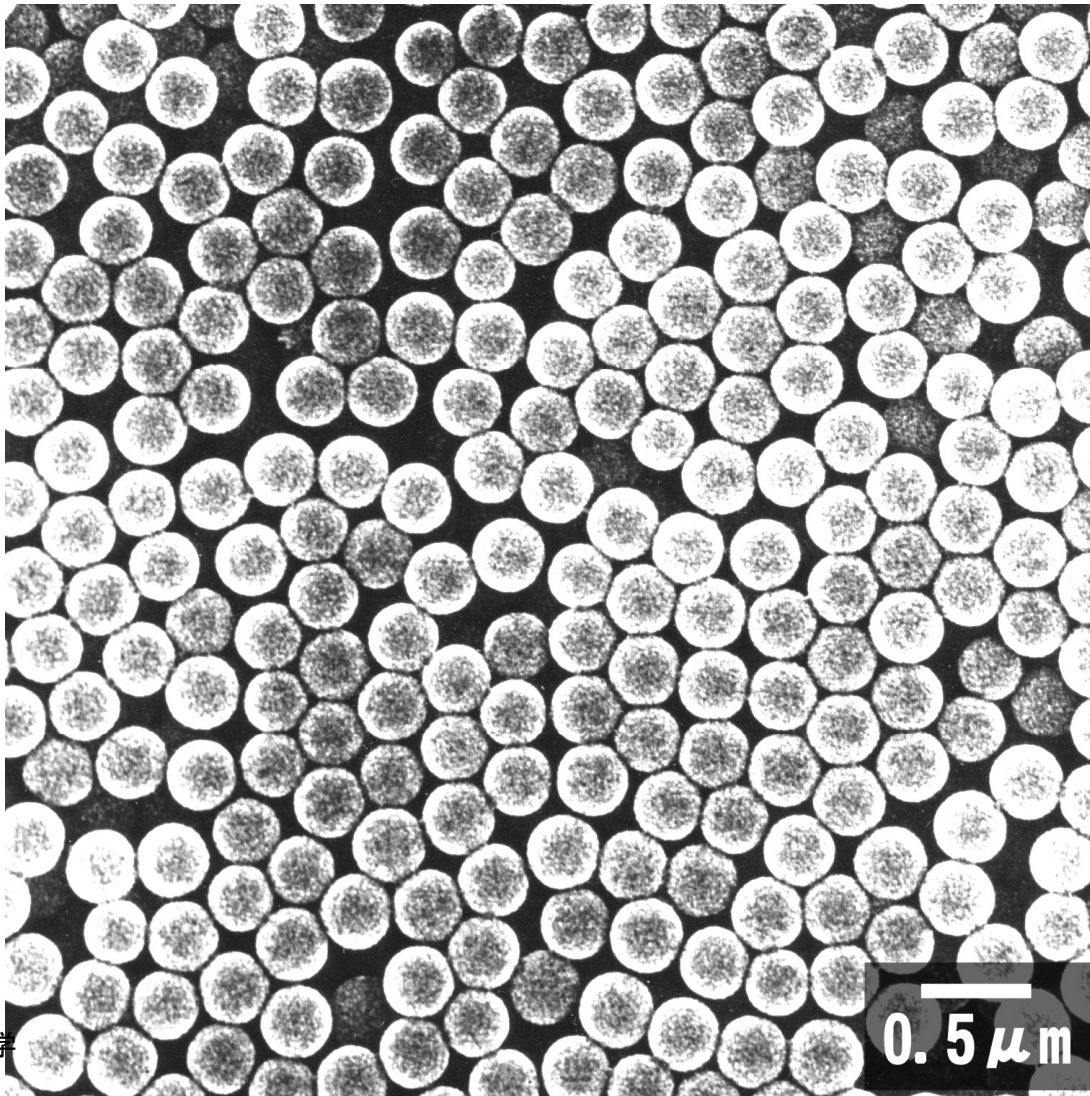
Monodispersed particles refer to a group of particles that are uniform in size, morphology, structure and composition.

In general, the standard deviation of size is within 10%.

Since monodisperse particles have uniform properties as described above, they themselves can be used as functional materials. This is because the characteristics of each individual particle are reflected as they are, rather than being averaged over the whole.

For example, if iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) is not monodisperse particles, it is a bright red paint called red iron oxide. The size is about $1\ \mu\text{m}$, and if the shape is long, it will be yellowish, and if it is flat, it will be bright red.

Stöber Silica fine particles



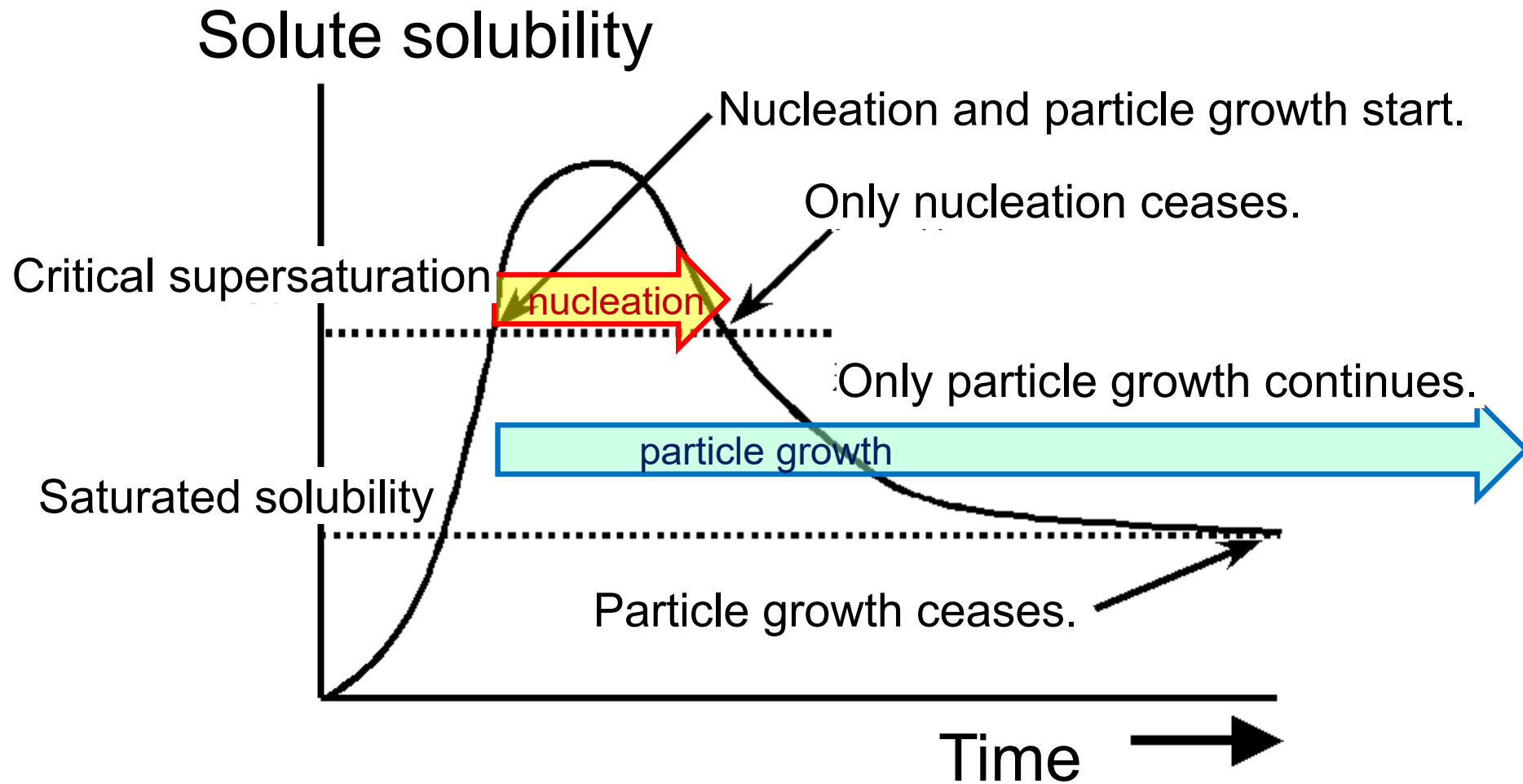
They are beautiful monodisperse particles and are widely used industrially.

General guidelines for monodisperse particle synthesis

- 1. Separation of nucleation and particle growth**
- 2. Prevention of inter-particle coagulation**
- 3. Storing particle precursors**

(T. Sugimoto, *Adv. Colloid Interface Sci.* 28, 65 (1987).)

LaMer model - kinetics



"Separation of Nucleation and Grain Growth"

Nucleation and particle growth can apparently be separated by increasing the time difference between them.

Gibbs-Thomson effect

The Gibbs-Thomson effect on the particle size dependence of solubility is expressed by the following equation.

$$\ln(C_r/C_\infty) = 2\gamma V_M / (rRT)$$

where C_r is the equilibrium solute concentration for a particle of radius r , C_∞ is the equilibrium solute concentration for an infinite plane (solubility), γ is the surface free energy (more precisely, the interfacial free energy at this solid/liquid interface), V_M is the molar volume (volume of 1 mol of substance, ie molar mass/specific gravity), r is the particle radius, R is the gas constant, and T is the temperature.

Roughly speaking, it can be seen that the Gibbs-Thomson effect appears in fine particle systems of about 1 μm or less. At 1 nm, the value is extremely large. At this size, the application of macroscopic thermodynamics is problematic in itself.

Size of stable nuclei

Nucleation

Formation of embryo → Unstable nuclei

Stable nuclei are generated according to the uncertainty principle.

Size of stable nuclei depends on solubility.

A material with high solubility has a large stable nucleus size.

The stable nucleus size of materials with low solubility is small and may not grow.

Separation of nucleation and particle growth

Supersaturation control

- Dilute System or Reservoir
- The supersaturation required for homogeneous nucleation is usually greater than for heterogeneous nucleation

Control of nucleation period

- Remarkably shorten the nucleation period compared to the growth period, etc.

Growth speed control

~ 2 growth modes

Surface reaction controlled growth

- If the growth reaction on the particle surface is rate-determining, it grows in proportion to the $1/2$ power of time
- Growth is slow in principle.

Diffusion controlled growth

- If diffusion is rate-limiting, it grows squarely with time. (parabola)
- In principle, it grows quickly.

Homogeneous nucleation

When n mol of solute precipitates in a solution and a crystalline phase (solid phase) with radius r is formed (homogeneous nucleation), the free energy change $\Delta G(n)$ is as follows.

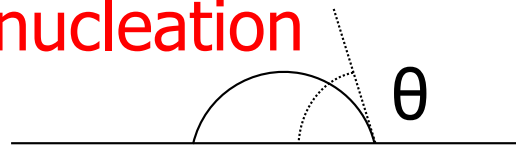
$$\Delta G(n) = 4\pi r^2 \gamma - n\Delta\mu$$

γ is the liquid-solid interfacial energy, $\Delta\mu$ is the free energy per mol, and $\Delta\mu$ is the function of supersaturation. As supersaturation increases, $\Delta\mu$ also increases.

Assuming that the precipitated crystal phase is spherical, the following can be written with v being the molar volume of the crystal phase.

$$\Delta G(n) = 4\pi r^2 \gamma - (4\pi r^3 \Delta\mu)/3v$$

Heterogeneous nucleation



If the wetting angle between the solute and the plane is θ , and the radius of curvature is r , the energy change $\Delta G'(r)$ associated with the precipitation is expressed as follows.

$$\Delta G'(r) = \left\{ 4\pi r^2 \gamma - (4\pi r^3 \Delta\mu)/3v \right\} \times f(\theta)$$

$$f(\theta) = \left\{ (1 - \cos \theta)(2 - \cos \theta - \cos^2 \theta) \right\} / 4$$

$$\therefore 0 \leq f(\theta) \leq 1$$

Differentiate with respect to r and equal to 0. Here, the value of r that maximizes $\Delta G(r)$ is called the critical radius (critical radius of curvature) and is expressed as r^* .

$$r^* = 2\gamma\mathcal{V}/\Delta\mu \quad \text{In other words, it is the size of the stable nucleus.}$$

If the critical radius of curvature is r^* , then the volumes of precipitation nuclei are as follows.

$$\text{Homogeneous} \quad (4\pi/3) \times (r^*)^3$$

$$\text{Heterogeneous} \quad (4\pi/3) \times (r^*)^3 \times f(\theta)$$

The heterogeneous nucleus always has a smaller volume.

The formation rate, J , of homogeneous nucleation and heterogeneous nucleation is as follows.

$$J_{\text{homo}} = N_A \exp(-\Delta G(r^*)/RT)$$

$$J_{\text{hetero}} = N_C \exp(-\Delta G'(r^*)/RT)$$

The rate ratio of homogeneous and heterogeneous nucleation is as follows.

$$N_A \cong N_C$$

$$\therefore J_{\text{homo}}/J_{\text{hetero}} = \exp[-\Delta G(r^*)\{1 - f(\theta)\}]/RT$$

The ratio is always less than one. That is, heterogeneous nucleation is also kinetically advantageous.

Prevention of aggregation

A grey speech bubble with a white border containing the text "DLVO theory".

DLVO theory

Dilute system

- Aggregation is prevented by the electrostatic repulsive force of the electric double layer caused by lowering the salt concentration.

Protective colloids

- By adsorbing them on the particle surface.

Particle fixation

- Brownian motion is suppressed by immobilization on a gel network.

Storing monomers

Reserver

- Oxide particles: Water is the reservoir for O in the oxide. Therefore, the release rate of metal ions should be controlled.
- Metallic particles: Metals have very low solubility, so it is necessary to devise ways to grow them.

Addition from outside

- Like silver halide, the double jet method is used.

Gel-sol method

OUR INSTITUTE

PROF. SUGIMOTO, ETC.

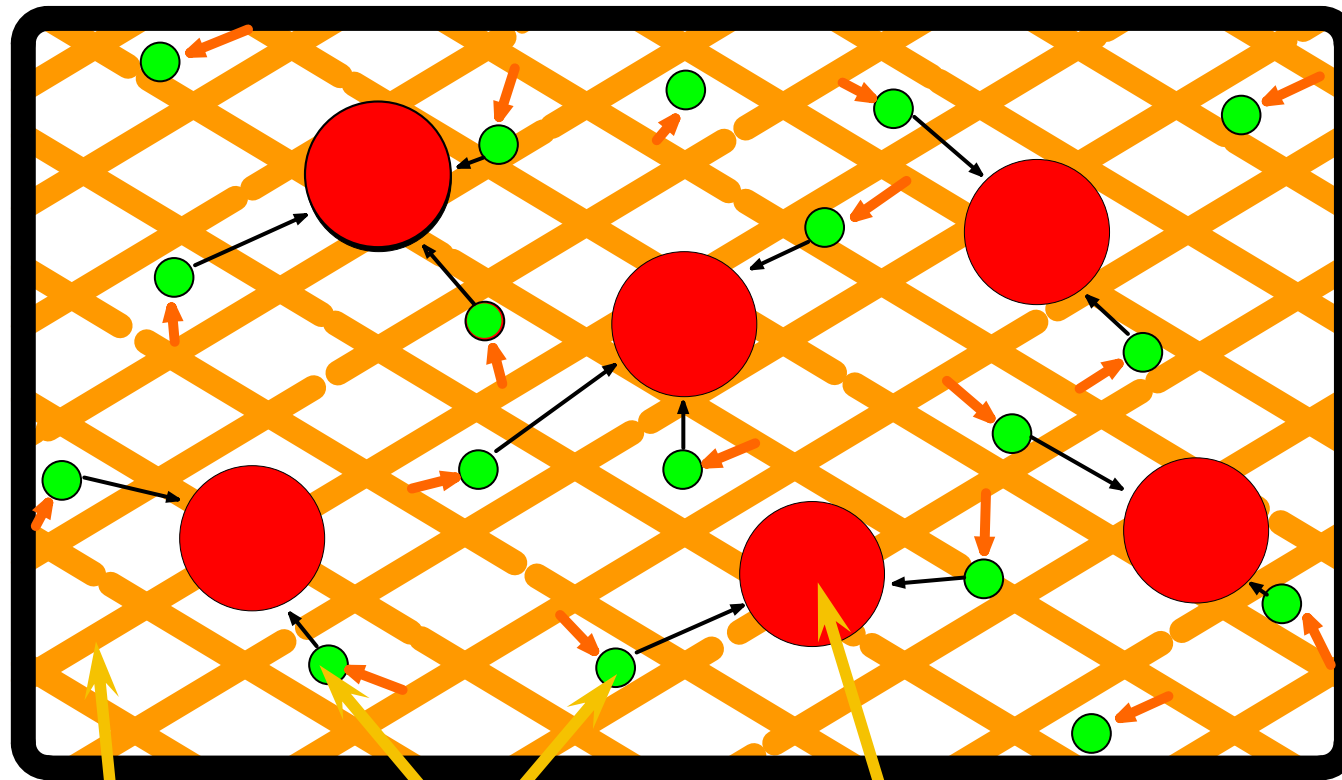
2023/6/27

微粒子合成化学

Aggregation prevention mechanism

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles are immobilized in the gel network.

Gel network of $\beta\text{-FeOOH}$ (intermediate product)



Gel network Monomers

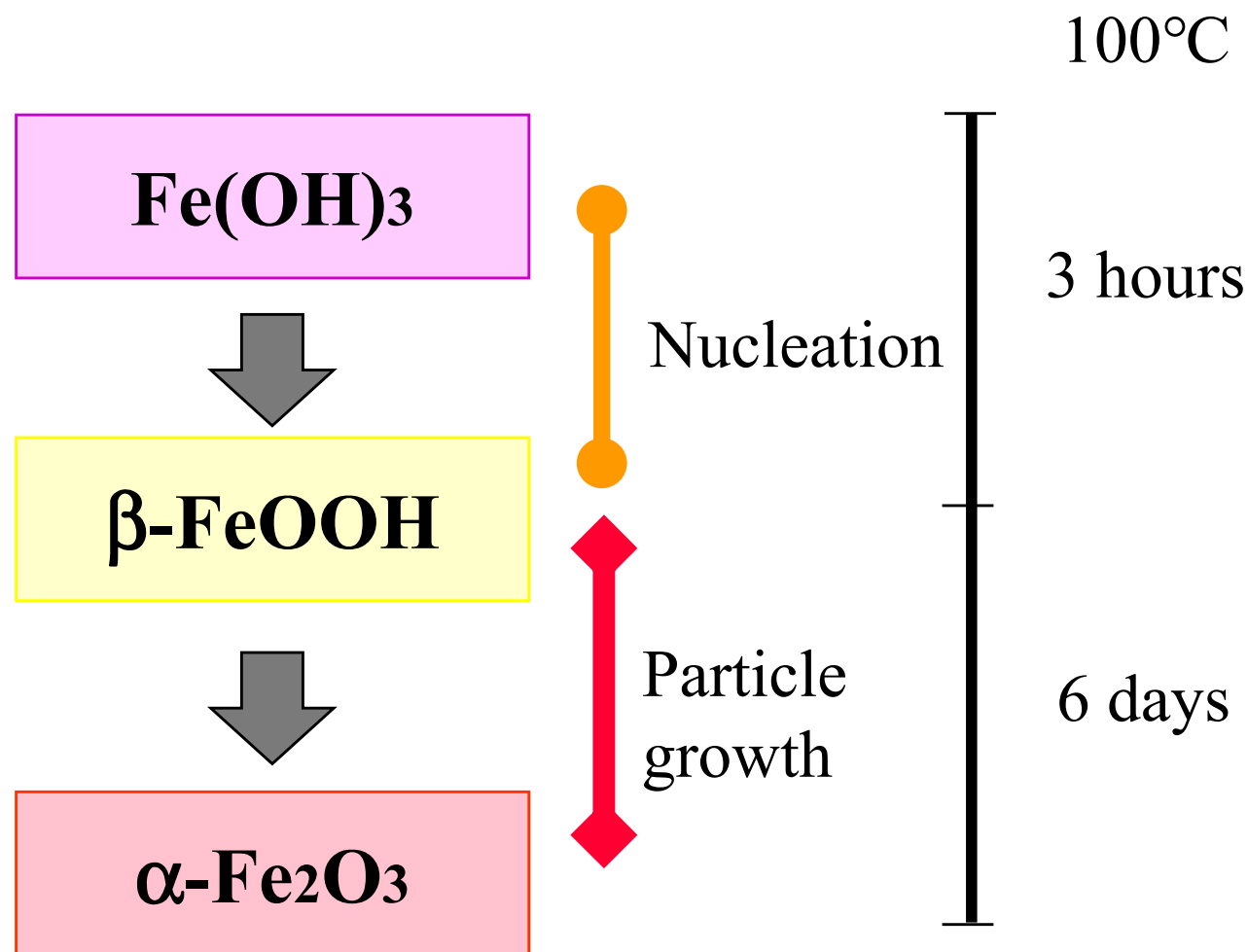
Growing particles

For example, in the synthesis of hematite ($\alpha\text{-Fe}_2\text{O}_3$) particles, a dense amorphous iron hydroxide gel is used as a precursor solid, and the phase transition occurs in two steps: amorphous iron hydroxide \rightarrow hydrated iron oxide (akaganite) \rightarrow hematite. In this case, the intermediate product, iron oxide hydrate, serves as a reservoir for the hematite precursor and has an effect of suppressing aggregation. In addition, the control of the shape of hematite is achieved by the coexistence of adsorptive ions such as sulfate groups and phosphate groups.

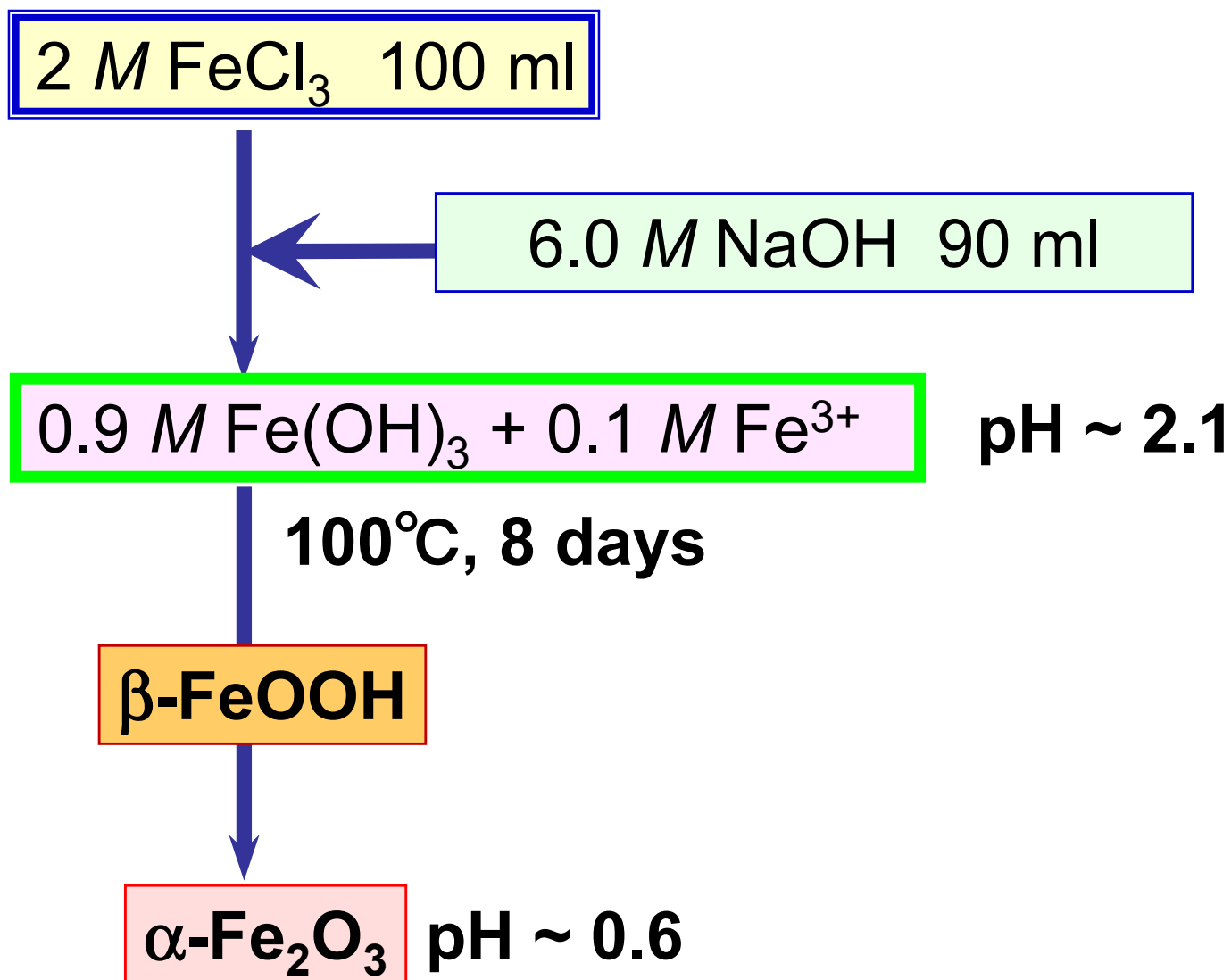
one solution :

Gel-sol method

Preparation of monodisperse hematite particles



Actual experiment

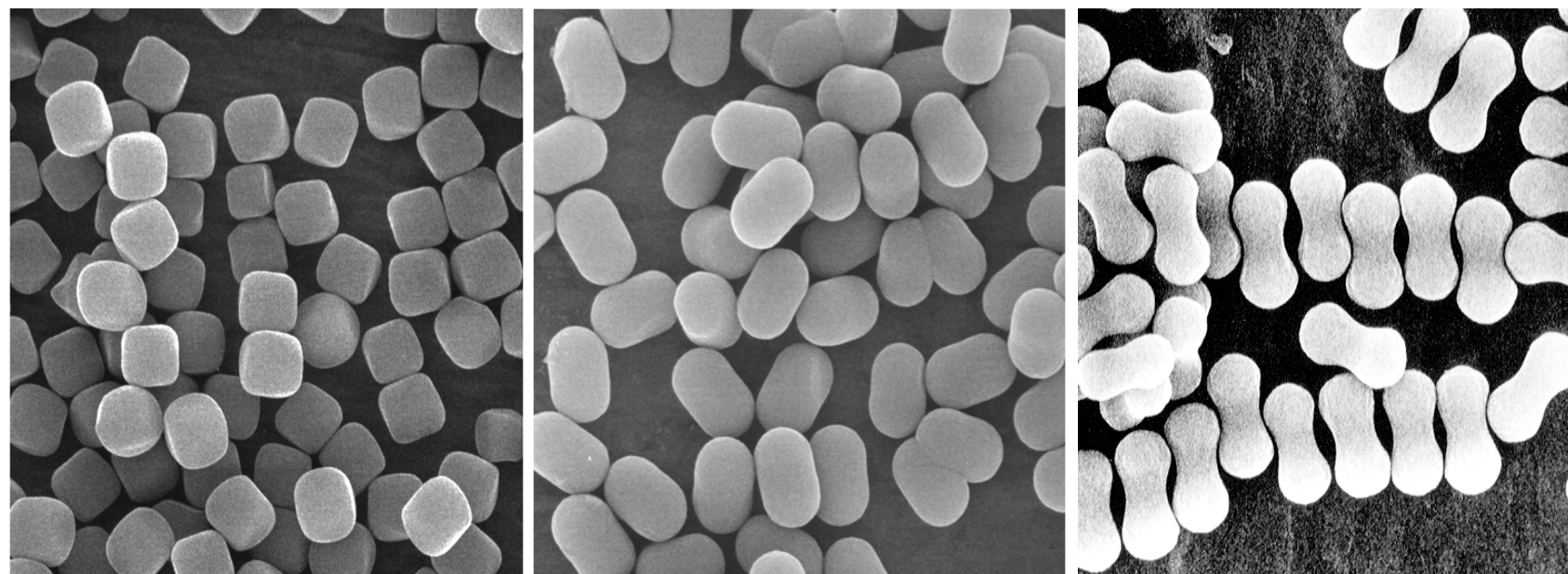


Large-scale synthesis of monodispersed hematite particles

- 1) Set the solution conditions (temperature, pH, etc.) for generating hematite particles
- 2) β -FeOOH is formed as an intermediate compound and finally only hematite is produced without any by-products
- 3) nucleation ends only in the first maximum 8 hours, after which the particles grows for a week
- 4) Particles are trapped in a gel network of ferric hydroxide and β -FeOOH, preventing them from easily moving like Brownian motion, thereby completely suppressing aggregation between particles.

By Gel-sol method

Synthesis of monodisperse hematite particles



Synthesis of Uniform Metallic Nickel Particles from Concentrated Nickel Hydroxide Suspension

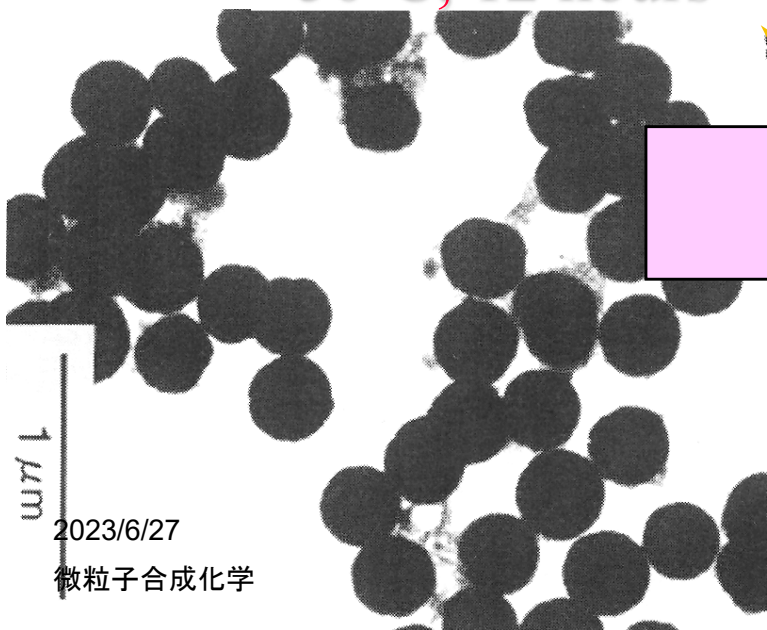
Ni(OH)₂ suspension
With PEG

NaH₂PO₂ addition

50°C, 12 hours

Ni

- 0.1 M Ni(OH)₂ + 4 M NaH₂PO₂
- 0.5 wt% PEG (400,000)



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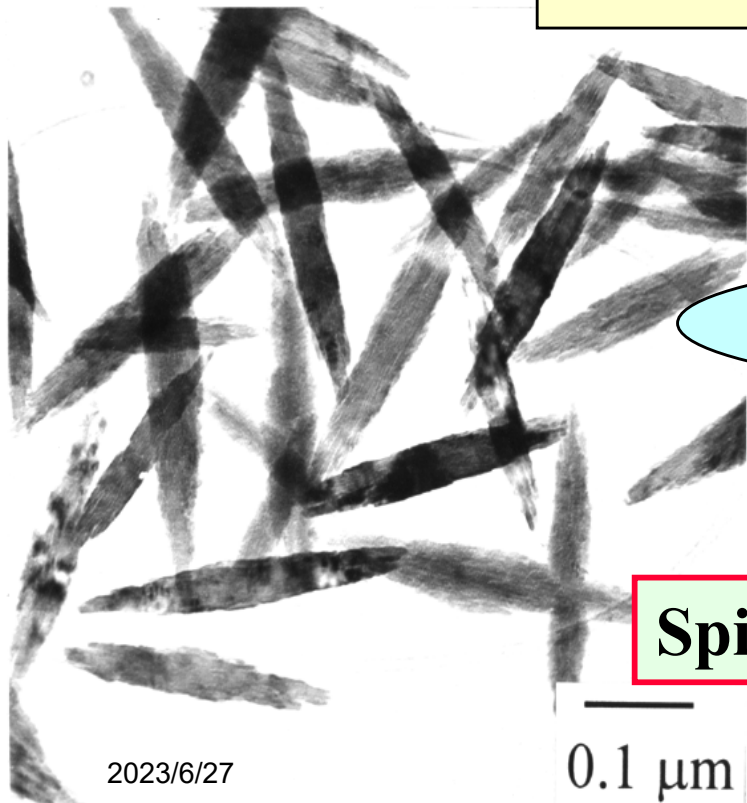
Synthesis of spindle-shaped uniform titania particles by gel-sol method

Titanium isopropoxide: 0.5 M
Triethanolamine: 1.0 M
(inhibitor to rapid hydrolysis)

2M NH₃ aq.

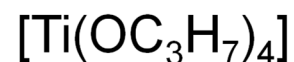
Highly viscous gel-like substance

Spindle type uniform titania particles



0.1 μm

Titanium(IV) isopropoxide (TIPO)



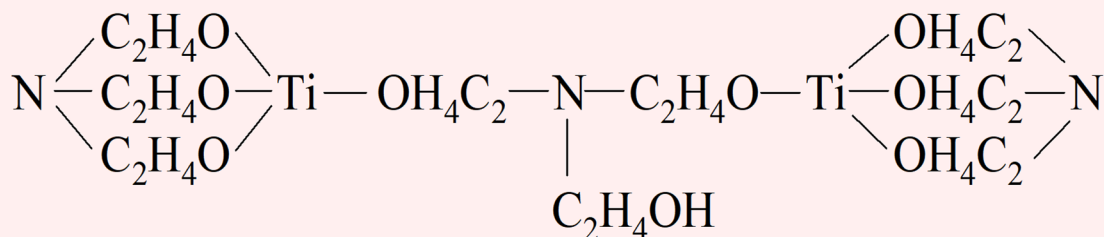
Triethanolamine (TEOA)



TIPO:TEOA = 1:2

$$([\text{TIPO}]_0 = 0.25 \text{ mol dm}^{-3})$$

Stable complex



$$\text{H}_2\text{O} (+\text{HClO}_4 \text{ or } +\text{NaOH})$$

Shape controller

1st aging (100°C, 1 day)

$$\text{Ti}(\text{OH})_4 \text{ gel}$$

2nd aging (140°C, 3 days)

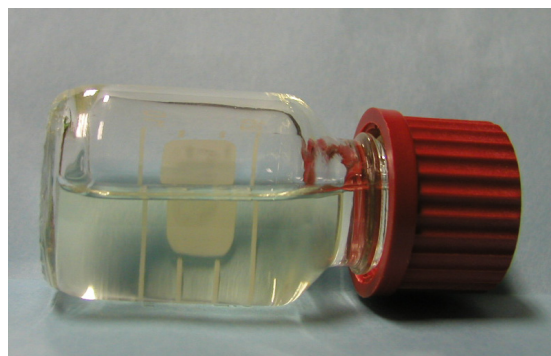
$$\text{TiO}_2 \text{ (anatase)}$$

Synthesis scheme of monodisperse titanium oxide (titania) particles by Gel-Sol method

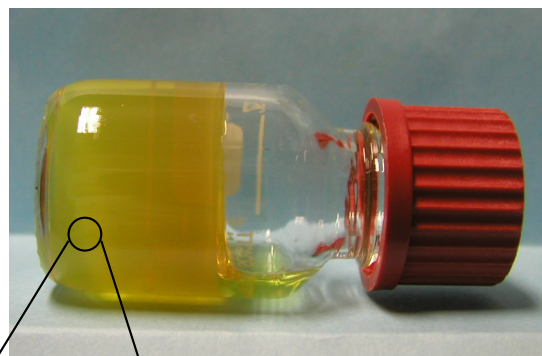
Synthesis of Monodispersed Anisotropic TiO₂ Particles

Gel-Sol Method: Particle Preparation Technique by using Metal Hydroxide Gels

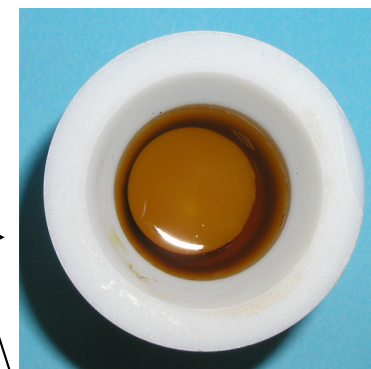
Synthesis of Monodispersed Anisotropic TiO₂ Particles



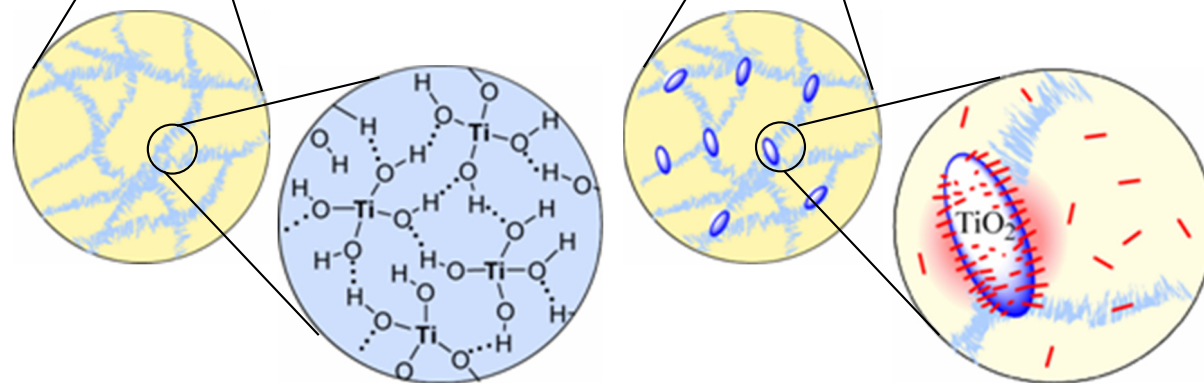
100
°C
24 h



140 °C



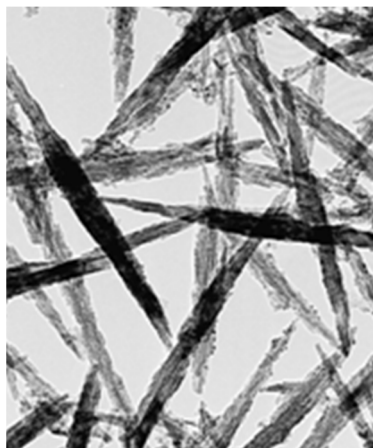
- Ti(OPrⁱ)₄
- Stabilizer (N(CH₂CH₂OH)₃)
- **Shape Controller**
(Amine, Amino Acid)
- pH Controller



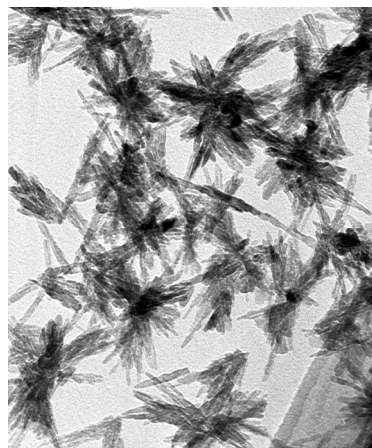
Gel Formation by H-Bonding
Network of Ti(OH)₄

Sol Formation by
Crystal Growth

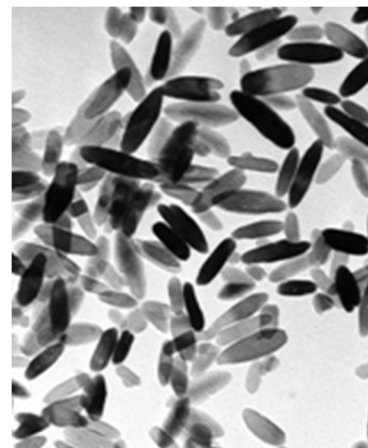
Anisotropic TiO₂ Particles Obtained by the “Gel-Sol” Method



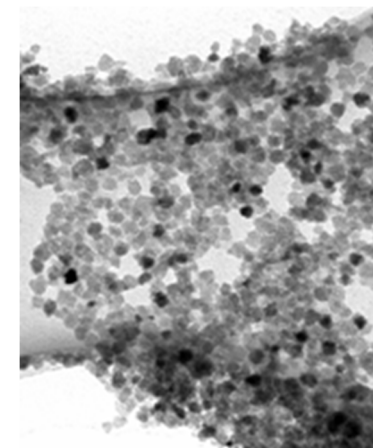
Ethylenediamine
Init pH: 10.5



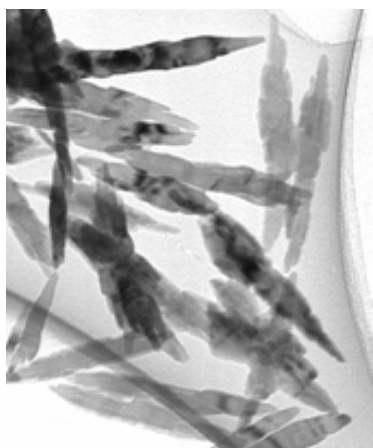
Ethylenediamine
Init pH: 10.5, Seeds



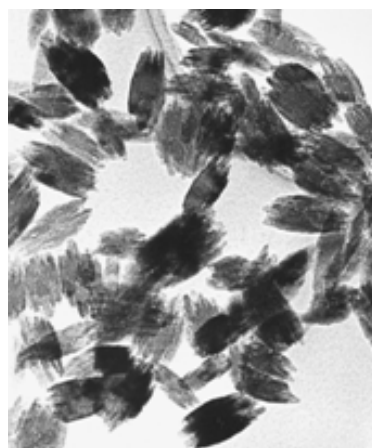
Succinic Acid
Init pH: 10.5



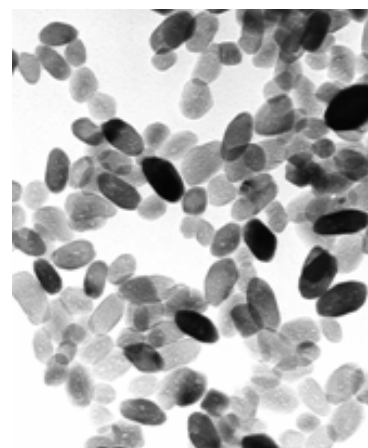
Gluconic Acid
Init pH: 9.5



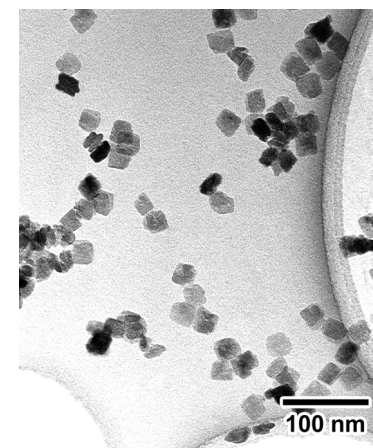
Glutamic Acid
Init pH: 10.5



Oleic Acid
Init pH: 11.5

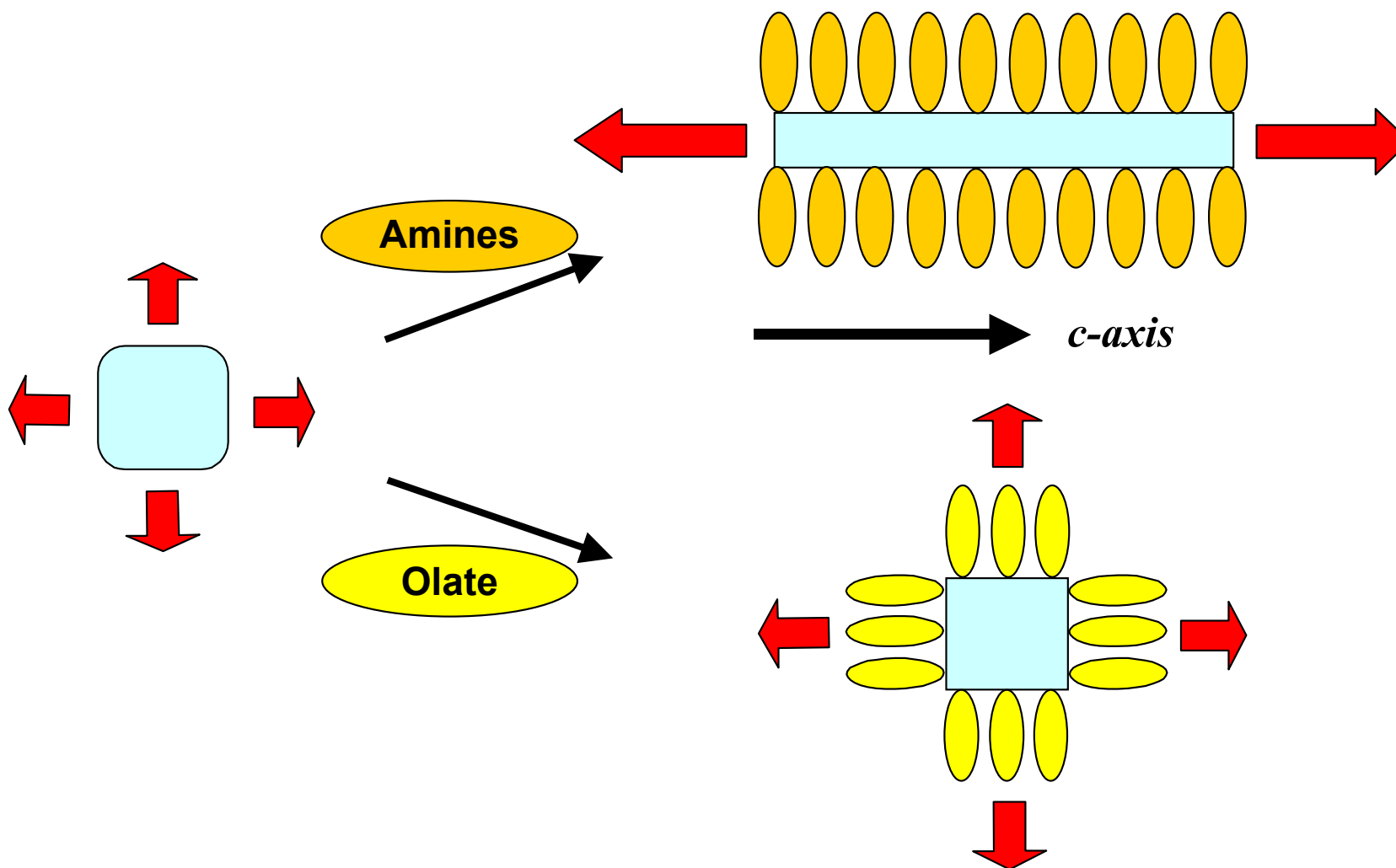


none
Init pH: 10.5



Oleic Acid
Init pH: 9.9

Shape Control by Amines and Oleate

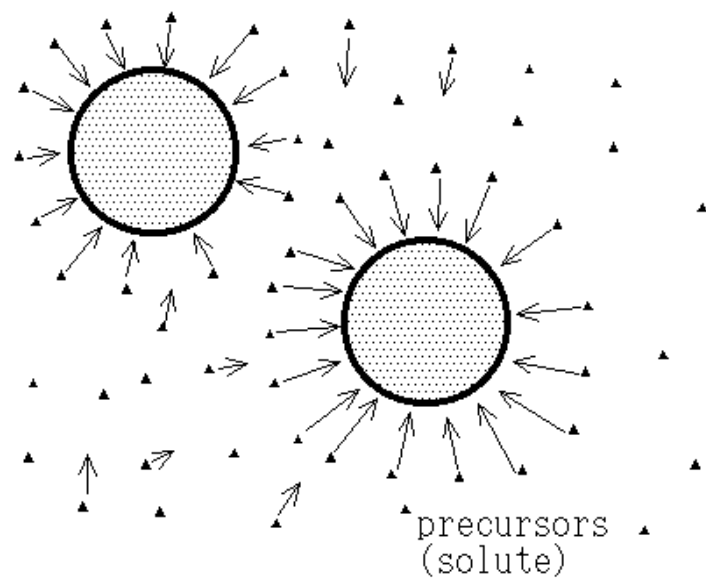


Organic Amines → Adsorb on TiO₂ Surfaces

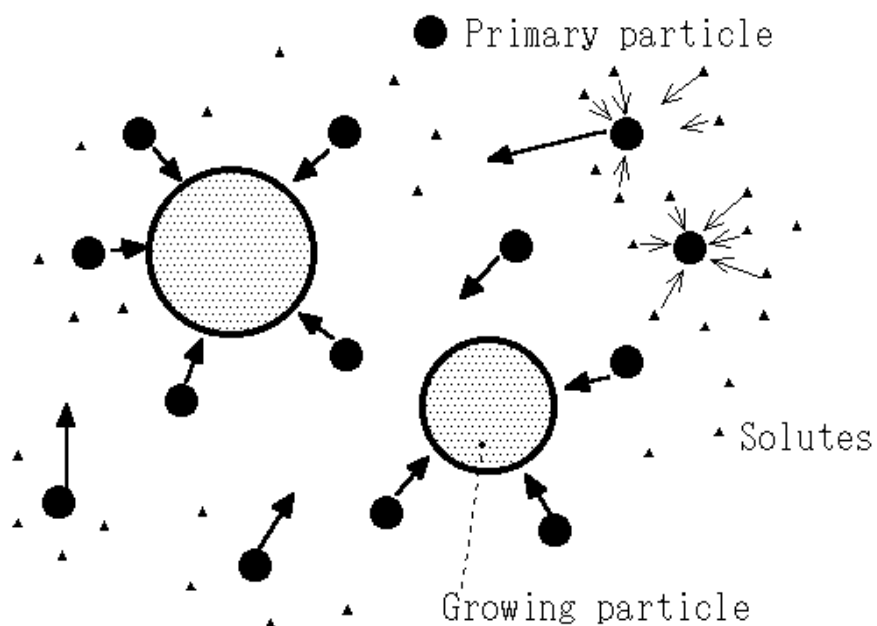
→ Utilization for Organic-Inorganic Hybridization

Comparison of growth mechanism

LaMer mechanism due to direct deposition of solute



Aggregative growth mechanism

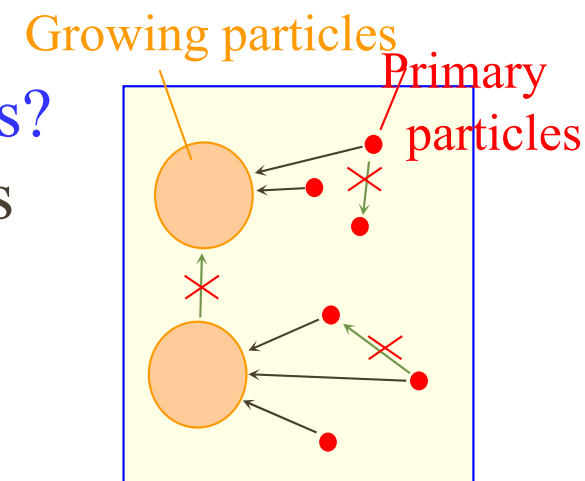


Problems of aggregative growth mode

1. Selective Aggregation into Only Growing Particles?

Why is there no coagulation between primary particles and between growing particles?

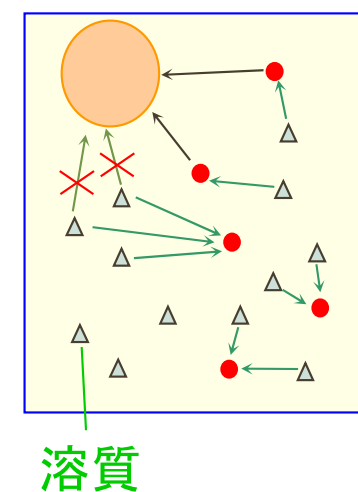
(If these coagulation occur, monodisperse particles cannot be obtained)



2. Isn't the generation of primary particles caused by the direct deposition of solutes?

The mechanism, by which primary particles and nuclei are generated, is the direct deposition of solutes.

Assuming that primary particles are generated during the growth, it means that the formation of the primary particles is due to direct deposition of the solute and the growth of the particles is due to aggregation.



Catalysis

2023/6/27

What is catalyst?

Physical chemistry

- ▶ Physical (adjective)
- ▶ [1] material, material, material world, natural
- ▶ [2] bodily, physical, physical, human
- ▶ [3] Desire for the other's body, lustful
- ▶ [4] physics, physics, physical
- ▶ [5] Natural science according to the laws of nature

What is physical chemistry?

- ▶ Chemistry that captures the movement of materials
- ▶ Let's go to the world of equilibrium and kinetics!

Equilibrium and Kinetics

- ▶ The equilibrium theory is, so called, the story of the paradise utopia world. The energy difference between this world and the present is exactly the Gibbs free energy change. The equilibrium theory is a study that tries to define the most energetically stable situation under given conditions. The equilibrium theory is the numerical analysis of where we are now between the ideal and reality.

Equilibrium and Kinetics

- ▶ Kinetics expresses the degree of effort to reach the paradise. More details will be discussed later in the lecture.
- ▶ In short,
- ▶ Physical chemistry is to formulate and understand the movement of materials.

Equilibrium and Kinetics

- ▶ Equilibrium and Kinetics
 - In equilibrium, the forward and reverse reaction rates are the same.
 - Processes include irreversible and reversible ones.

- ▶ Catalysis as an example of kinetics

What is catalyst?

What is catalyst? ~CatSJ web~

- Consider the reaction $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$ in which water is produced from hydrogen and oxygen. Even if you put a mixed gas of hydrogen and oxygen in a glass container and heat it to 200°C , no reaction will occur. However, when a small amount of copper (Cu) is added to the mixed gas and heated, hydrogen and oxygen react rapidly to produce water. After the reaction, no change occurred in the added copper.

What is catalyst? ~CatSJ web~

- Water is produced for each rotation of the $\text{Cu} \rightarrow \text{CuO} \rightarrow \text{Cu}$ cycle. Cu reacts with oxygen, and the generated CuO reacts with hydrogen to regenerate Cu.
- The two reactions that form the cycle, $\text{Cu} + 1/2 \text{O}_2 \rightarrow \text{CuO}$ and $\text{CuO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{Cu}$, both proceed rapidly. The H_2O formation reaction rate increases in the presence of Cu or CuO. A reaction that proceeds in this manner is called a catalytic reaction. At this time, the substance that is repeatedly consumed and regenerated is called a catalyst.

What is catalyst? ~CatSJ web~

- Catalytic reactions can also be seen in nature. Fluorocarbons reach the stratosphere and are decomposed by ultraviolet rays to produce chlorine atoms (Cl). The following two reactions $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ and $\text{ClO} + \text{O} \rightarrow \text{O}_2 + \text{Cl}$ occur with the oxygen atoms (O) formed by the decomposition of the oxygen molecules produced by the ultraviolet rays. As a whole, the reaction $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ progresses, destroying the ozone layer. Cl reacts with ozone (O_3) and is consumed, and the generated ClO reacts with O to generate O_2 and Cl is regenerated. Cl (and ClO) act as a catalyst.

What is catalyst? ~CatSJ web~

- Enzymes that promote chemical reactions in our body and other living organisms, such as amylase that degrades starch, pepsin that degrades protein, and lipase that degrades fats and oils, also act as catalysts.

What is catalyst? ~CatSJ web~

- Catalysts can be solid, gaseous, or liquid. While they continue to change during their action, they are consumed and regenerated repeatedly, and there is no net increase or decrease before and after the reaction. Reactions that proceed through new pathways created by catalysts have low activation energies and high reaction rates.
- When a certain reaction system is irradiated with light, the reaction rate may increase significantly. Also, in many reactions, the addition of heat increases the reaction rate. However, since light and heat are not substances, they are not called catalysts. However, substances such as titanium dioxide (TiO_2), whose properties change when exposed to light and exhibit catalytic activity, are called photocatalysts.

What is catalyst? ~CatSJ web~

- In addition to increasing the reaction rate, catalysts also have the function of reacting only with specific substances or producing only specific substances. For example, high temperature is required to react ethylene (C_2H_4) with oxygen without using a catalyst, and the products are carbon dioxide and water. When silver is used as a catalyst, ethylene oxide (C_2H_4O) is mainly produced at lower temperatures. Also, when ethanol (C_2H_5OH) is heated with concentrated sulfuric acid, the sulfuric acid acts as a catalyst to produce ethylene and water.

What is catalyst? ~CatSJ web~

- However, when ethanol is brought into contact with heated Cu, acetaldehyde (CH_3CHO) and hydrogen are produced without producing ethylene. Enzymes are catalysts that promote reactions by recognizing specific three-dimensional structures of reactants (substrates). The property of reacting with or producing only a specific substance is called selectivity. Selectivity depends on the type of catalyst. By choosing an appropriate catalyst, the target compound can be selectively produced .

What is catalyst? ~CatSJ web~

- Catalysts are widely used in the chemical industry because they have the property of increasing reaction rates and selectively producing desired compounds. The discovery of an iron catalyst that produces ammonia from nitrogen and hydrogen has led to the industrial production of ammonia and the mass production of nitrogenous fertilizers. As a result, the production of agricultural products has increased dramatically, and it has greatly contributed to solving the food problem associated with the rapid increase in the world's population.

What is catalyst? ~CatSJ web~

- The invention of stereoregular polymerization catalysts for ethylene and propylene by Ziegler and Natta gave birth to the plastics industry and brought about major changes in the material-related industries that followed. Using catalysts, processes have been developed to produce liquid fuels such as naphtha, gasoline, and kerosene, which are raw materials for the organic chemical industry, from crude oil, and to produce various chemicals and intermediate raw materials from naphtha. In addition, catalysts suitable for each reaction are used in almost all chemical processes, including processes for synthesizing pharmaceuticals and agricultural chemicals.

What is catalyst? ~CatSJ web~

- Catalysts are widely used not only for the production of chemical products, but also for the reduction of environmentally hazardous substances. Molybdenum sulfide (MoS) catalysts are used to remove sulfur components in petroleum to produce liquid fuels that do not generate sulfur oxides (SO_x) when burned.

What is catalyst? ~CatSJ web~

- Nitrogen oxides (NO_x), carbon monoxide (CO) and unburned fuel contained in automobile exhaust gas can be removed by using precious metal catalysts such as platinum (Pt)-rhodium (Rh)-palladium (Pd), converting into nitrogen (N₂), carbon dioxide (CO₂) and water (H₂O). Nitrogen oxides (NO_x) in flue gas from factories and power plants are removed using a composite oxide catalyst consisting of vanadium (V), tungsten (W), and titanium (Ti).

What is catalyst? ~CatSJ web~

- In addition, titanium dioxide (TiO_2), which acts as a photocatalyst, is used for antifouling, deodorization, and sterilization in daily necessities such as air purifiers and outer walls of buildings. Catalysts are also used to eliminate odors from fish grills and kerosene stoves. In this way, catalysts have the potential to be used not only in the chemical industry, but in any situation where chemical reactions occur.

What is catalyst? ~CatSJ web~

- Now, why does Cu catalyze the production of water from hydrogen and oxygen, and why does iron (Fe) catalyze ammonia synthesis? In the former case, Cu has the ability to dissociate oxygen molecules (O_2) to generate oxygen atoms (O) and hydrogen molecules (H_2) to generate hydrogen atoms (H). Atomic oxygen and hydrogen are more reactive than molecular oxygen and hydrogen.

What is catalyst? ~CatSJ web~

- The generated O bonds with Cu to form CuO, and CuO reacts with H to produce water. If CuO is too stable, it cannot react with H to form a catalytic cycle. Therefore, metals other than Cu that dissociate hydrogen molecules and oxygen molecules and whose oxides are not too stable can also act as water generation catalysts. Besides Cu, most transition metals act as catalysts for water formation. Most of the main group metals such as magnesium (Mg) can dissociate hydrogen and oxygen.

What is catalyst? ~CatSJ web~

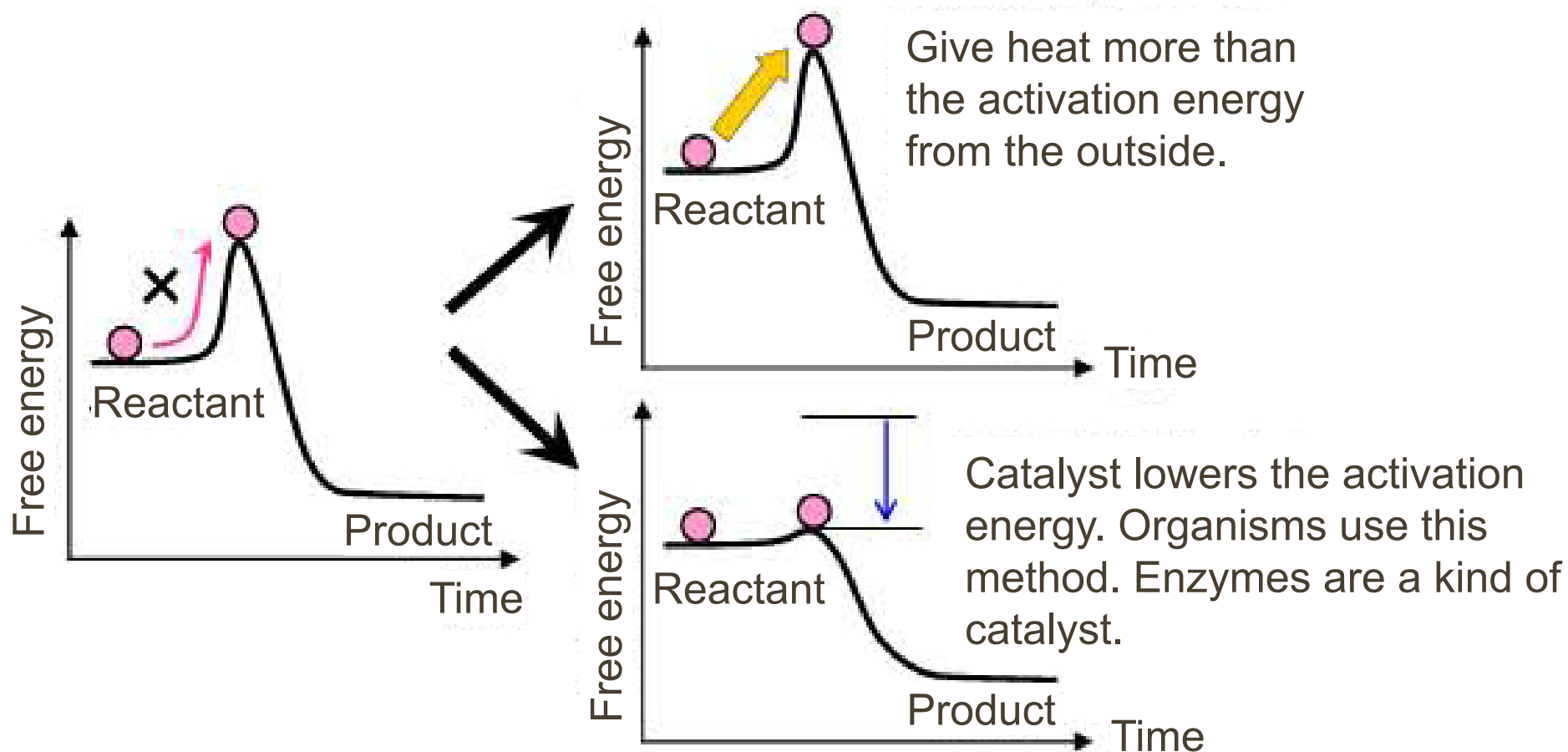
- The catalytic action of iron (Fe) in ammonia synthesis depends on the chemical properties of Fe, which can dissociate not only hydrogen molecules but also nitrogen molecules (N_2) with very strong bonds to generate nitrogen atoms (N). Ziegler-Natta catalysts have a high ability to activate and polymerize olefins, and also have the ability to control the orientation of olefins, making it possible to produce stereoregular polymers. In zeolite catalysts, which are used to convert high-molecular-weight hydrocarbons in crude oil to low-molecular-weight hydrocarbons, protons (H^+) present on the surface act to cleave the C-C bonds of hydrocarbons.

What is catalyst? ~CatSJ web~

- The antifouling, deodorant, and bactericidal effects of titanium oxide (TiO_2) are due to the absorption of light by TiO_2 , which generates excited electrons and holes, which reduce oxygen in the air and oxidize various chemical substances.
- In this way, the properties of suitable catalysts differ depending on the type of reaction, and the mechanisms of action of catalysts also vary.

What is catalyst?

There are two ways to proceed with reactions with high activation energies.

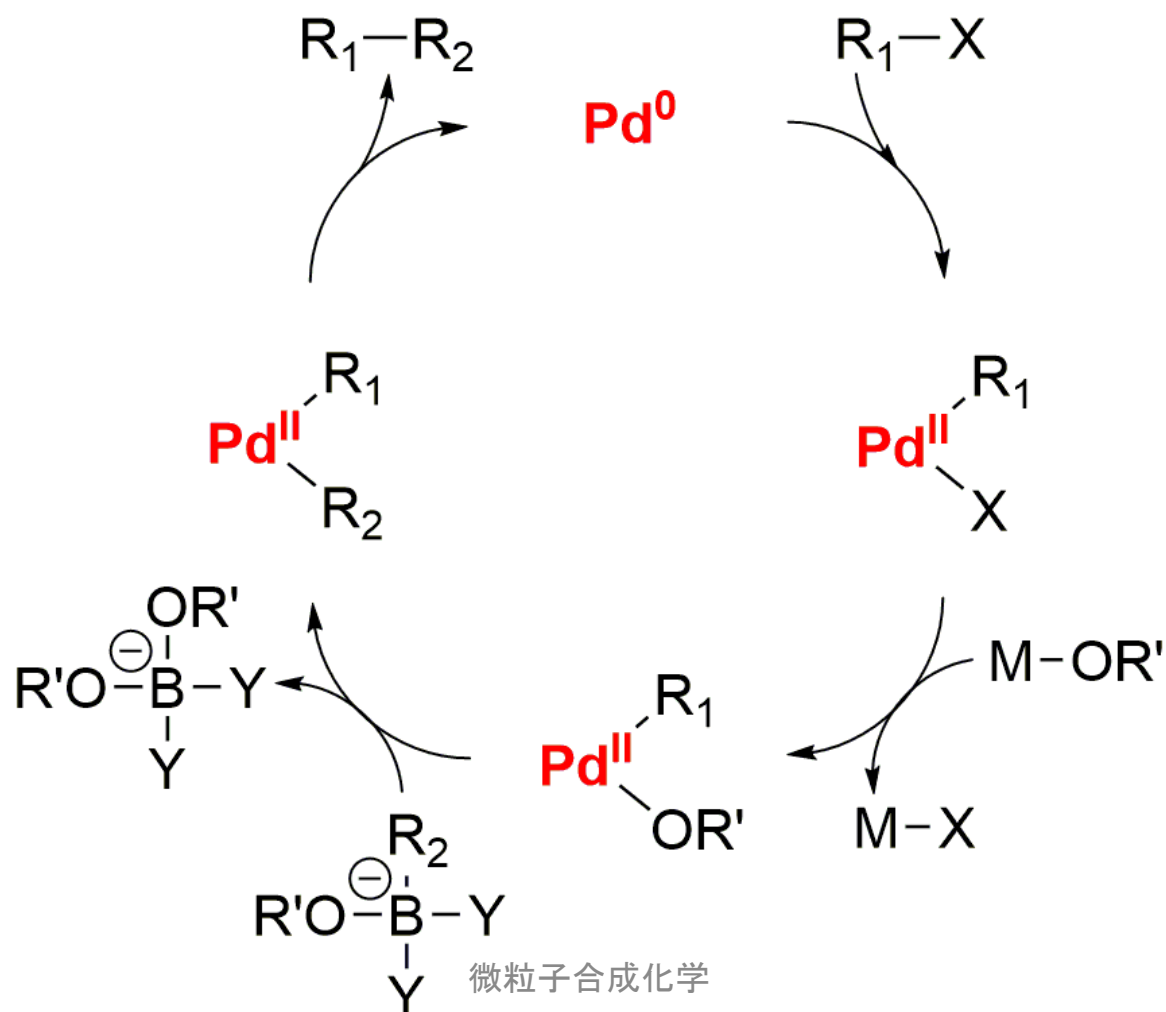


What is catalyst?

Definition of catalyst

A substance that accelerates a chemical reaction even in small amounts, without itself changing before and after the reaction.

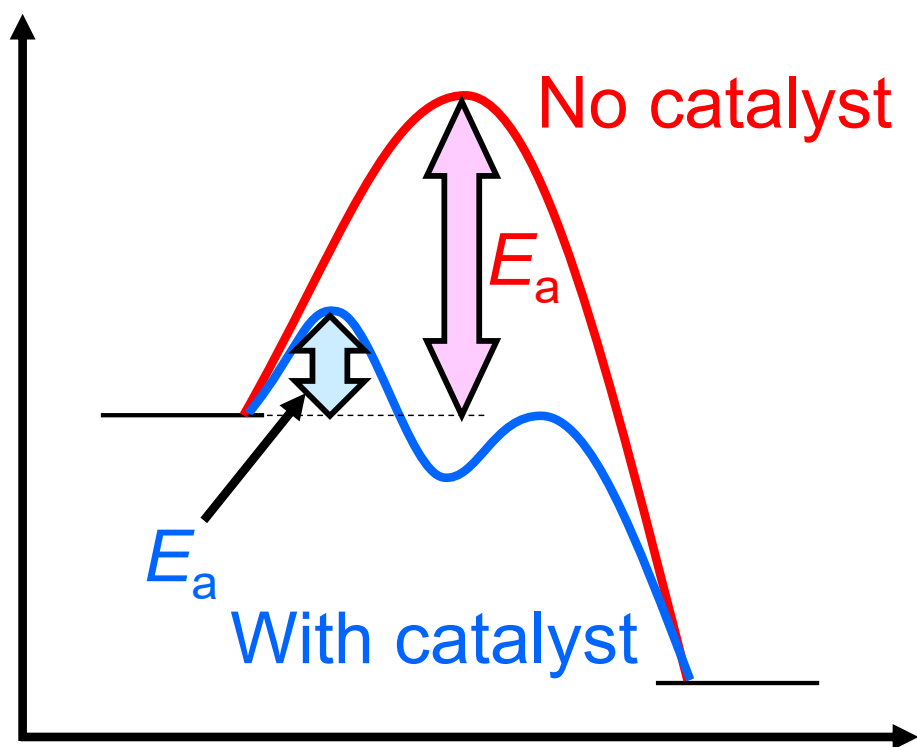
Pd catalyzed Suzuki-Miyaura Coupling (2010 Nobel Prize in Chemistry)



What is catalyst?

Definition of catalyst

A substance that accelerates a chemical reaction even in small amounts, without itself changing before and after the reaction.



If a "catalyst" exists...

→ The reaction path changes.

→ Activation energy decreases.

$E_a < E_a$

→ Reaction rate (constant) increases.

Arrhenius式

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

History of Catalysts

History of Catalysts –No.1

■ Jöns Jacob Berzelius,

20 August 1779 – 7 August 1848

- Swedish chemist and doctor
- Divided chemistry into organic chemistry and inorganic chemistry, and created important chemical terms and concepts such as halogens, allotropes, isomers, organic substances, catalysts, and amorphous (amorphie).

■ Friedrich Wilhelm Ostwald,

2 September 1853 – 4 April 1932

- German (Baltic–German) chemist
- Invented the Ostwald process for producing nitric acid (1902)
- Mention that the catalyst follows kinetics

History of Catalysts –No.2

- **1801**
 - Invention of the fuel cell principle by Humphrey Davy (UK)
- **1817**
 - Public experiment on the combustion of hydrogen, carbon monoxide, ethylene, alcohol, ether, etc. below the ignition point with a heated platinum wire by Humphrey Davy (UK)
- **1836**
 - Discovery of pepsin by Theodor Schwann (Germany)
- **1839**
 - Successful fuel cell power generation experiment by William Robert Grove (UK)

History of Catalysts –No.3

- **1894**
 - Jokichi Takamine's invention of Takadiastase, which is extracted from *Aspergillus oryzae*
- **1897**
 - Discovery of catalytic reduction by adding hydrogen to organic unsaturated compounds by Paul Sabatier (France) (Sabatier–Sendrin reduction)
- **1902**
 - Invention by Fritz Haber and Carl Bosch (Germany) of the production of ammonia from hydrogen and nitrogen over an iron-based catalyst.
- **1902**
 - Nitric Acid Synthesis from Ammonia with a Platinum Catalyst by William Friedrich Ostwald (Germany)

History of Catalysts –No.4

- **1913**
 - William Fründrich Ostwald (Germany) presented the concept of catalysts, which changed the reaction rate but did not change the equilibrium.
- **1913**
 - Mittasch, Schneider et al. of BASF: Synthesis of methanol from water gas using oxide catalysts
- **1925**
 - Franz Fischer and Hans Tropsch (Germany) synthesis of liquid hydrocarbons from carbon monoxide and hydrogen with Fe-based catalysts
- **1949**
 - Catalytic reforming of naphtha with a platinum/alumina catalyst

History of Catalysts –No.5

- **1953**
 - Carl Ziegler (Germany) invented the atmospheric polymerization of ethylene. Later, Giulio Natta (Italy) succeeded in polymerizing propylene. Ziegler–Natta catalyst
- **1972**
 - Honda–Fujishima effect. Generation of hydrogen and oxygen from water
- **1979**
 - Discovery of “Suzuki–Miyaura Coupling”, which binds organohalogen compounds and organoboron compounds using a palladium catalyst
- **1986**
 - Invention of BINAP–ruthenium catalyst by Ryoji Noyori

Catalysts contribute to society

Yokkaichi Asthma

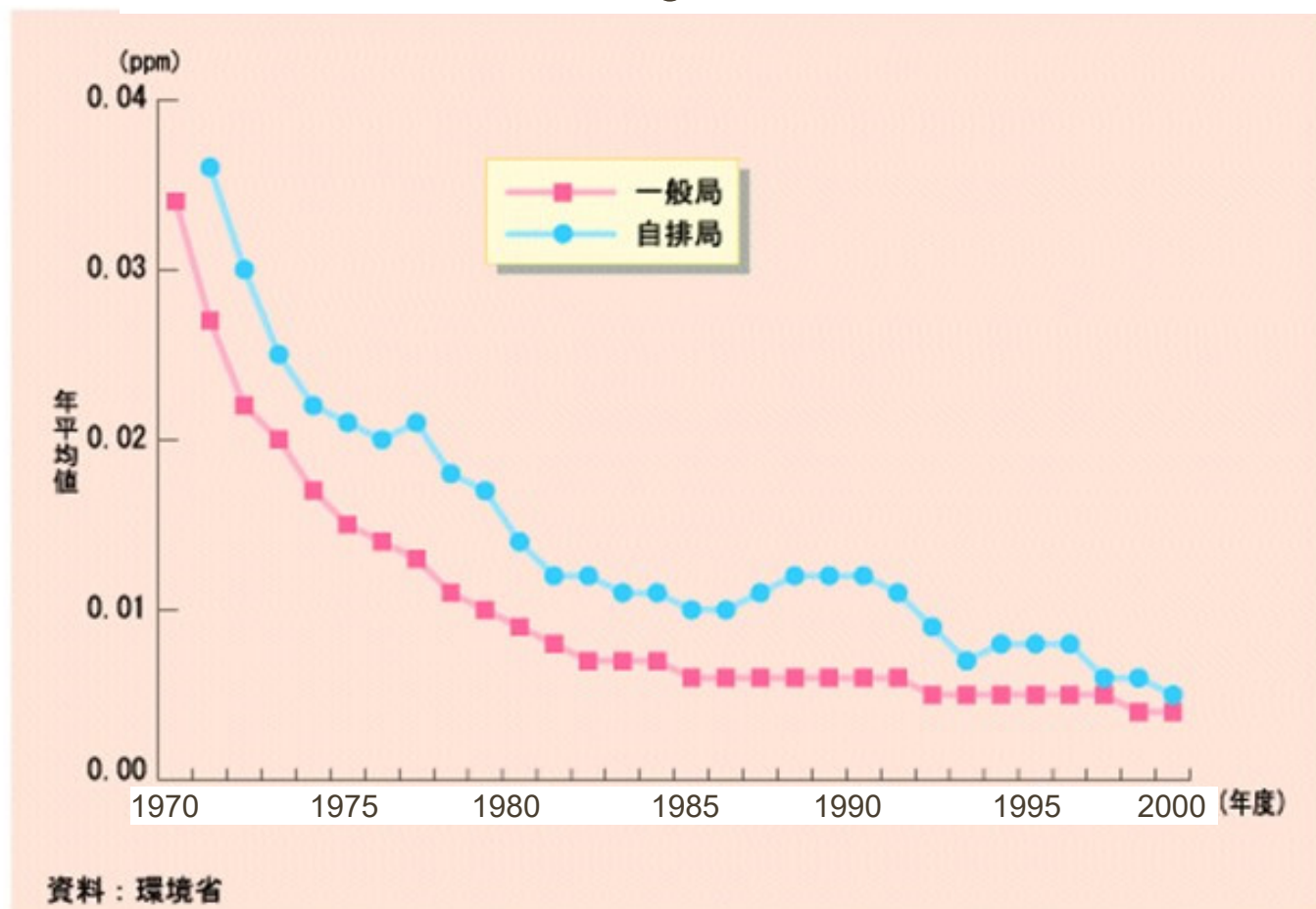


Yokkaichi Asthma

- 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

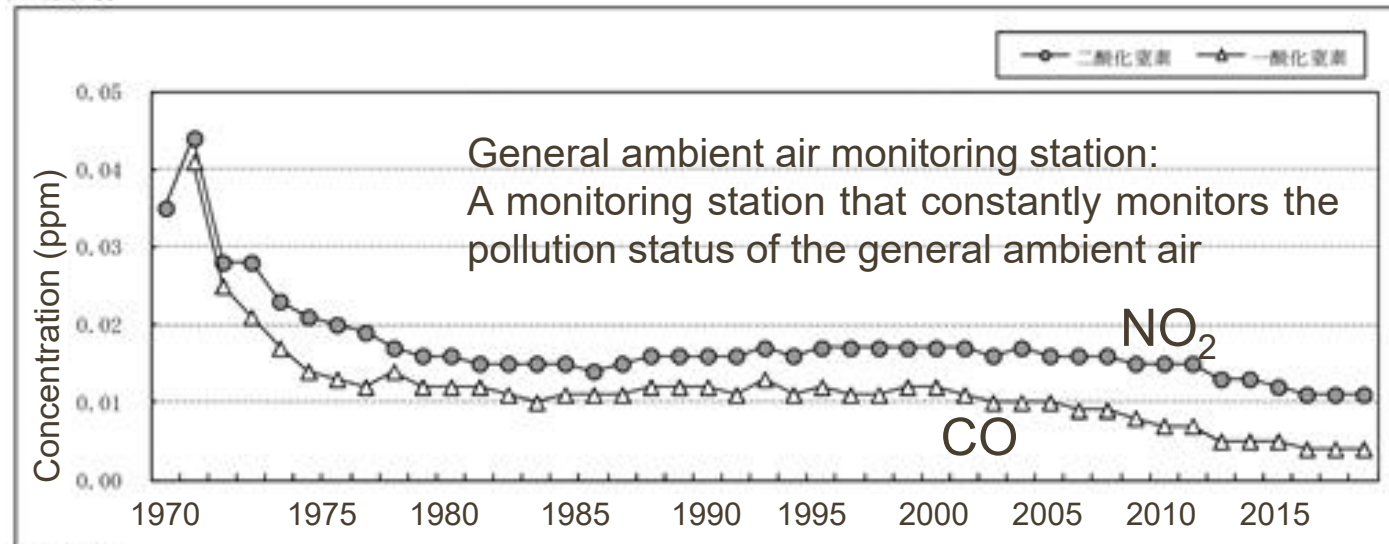


Eliminates sulfur content in fuel oil from the source!
That is the desulfurization catalyst.
Co-Mo-S

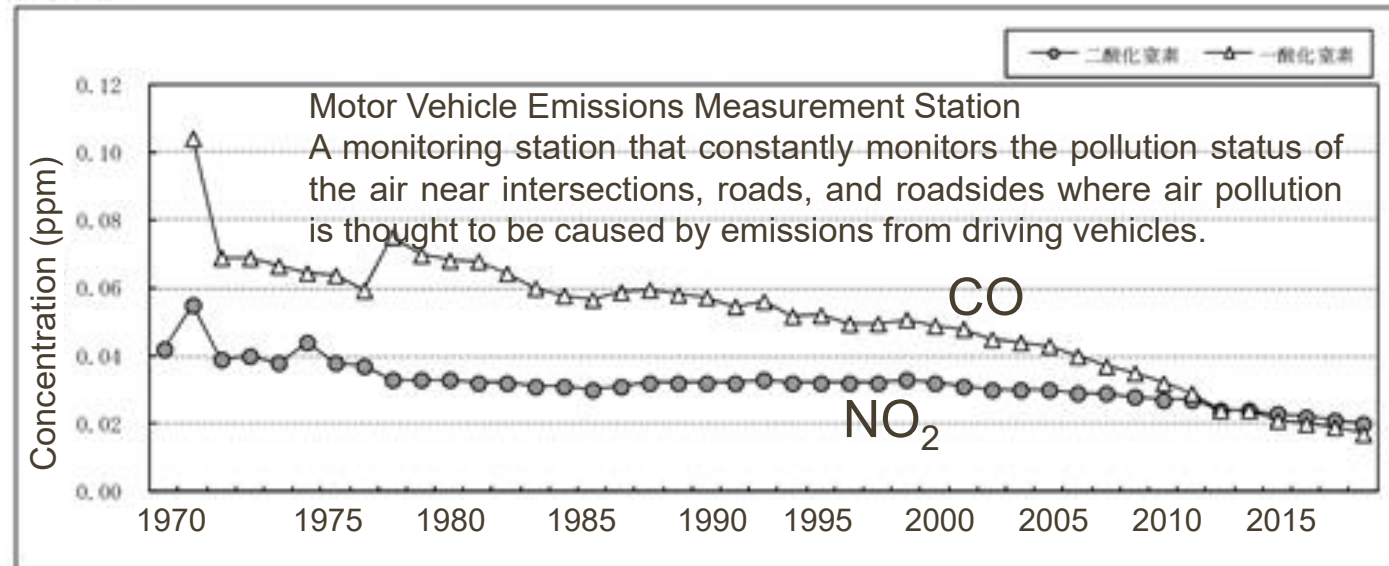
Three-way catalyst, TWC

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

(一般局)



(自排局)



Three-way catalyst, TWC

