Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

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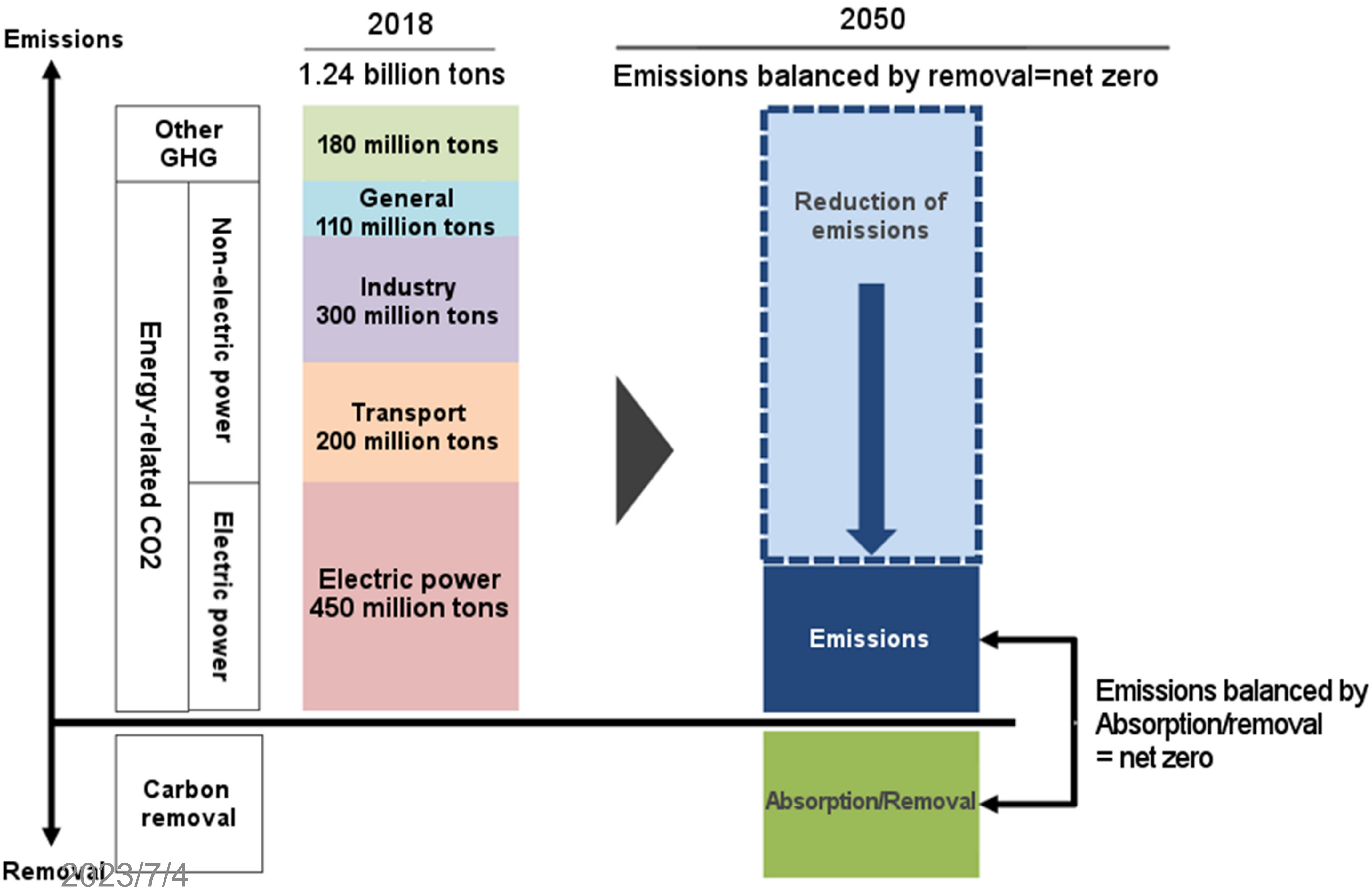
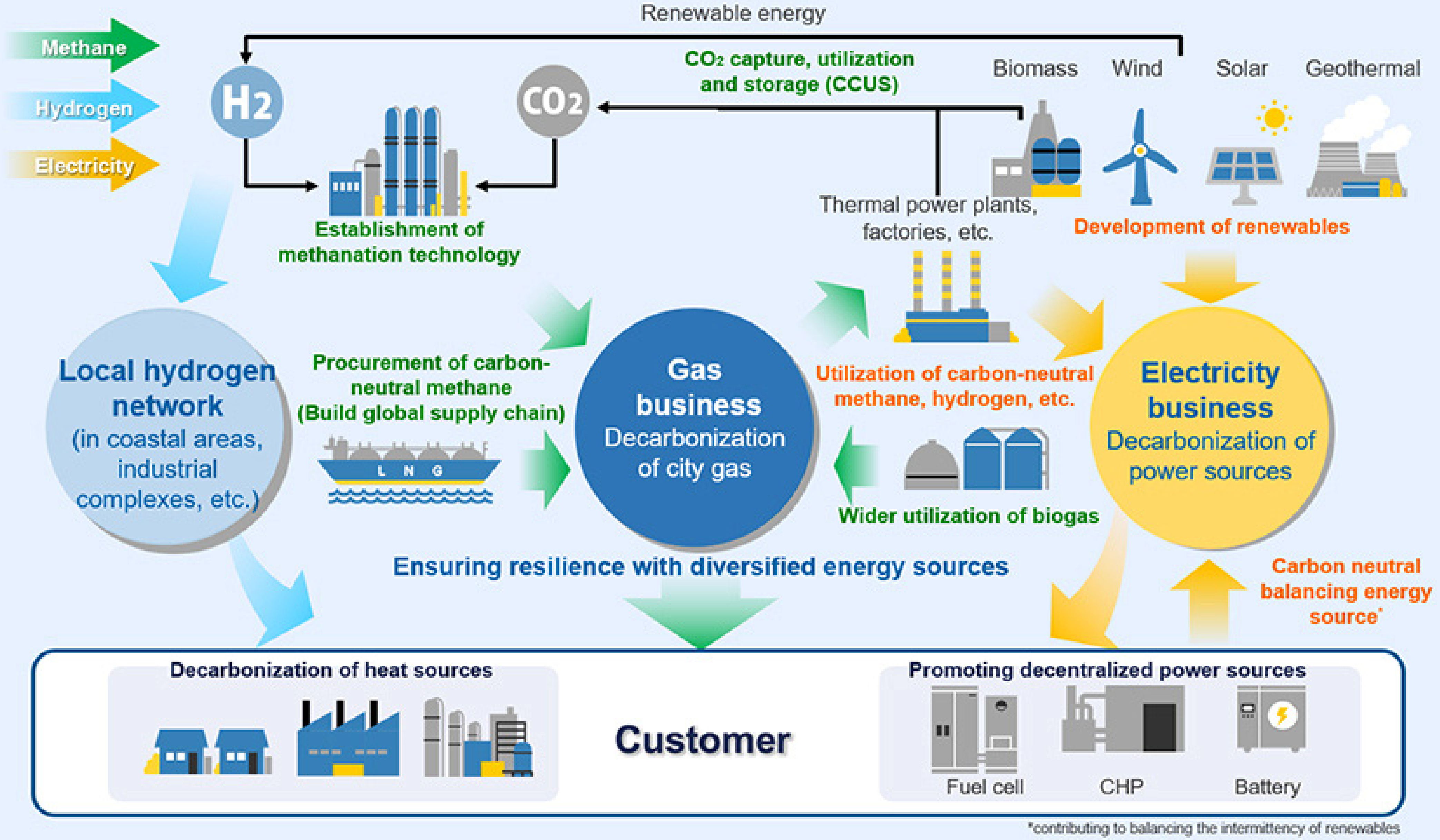
Lecture Plan

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

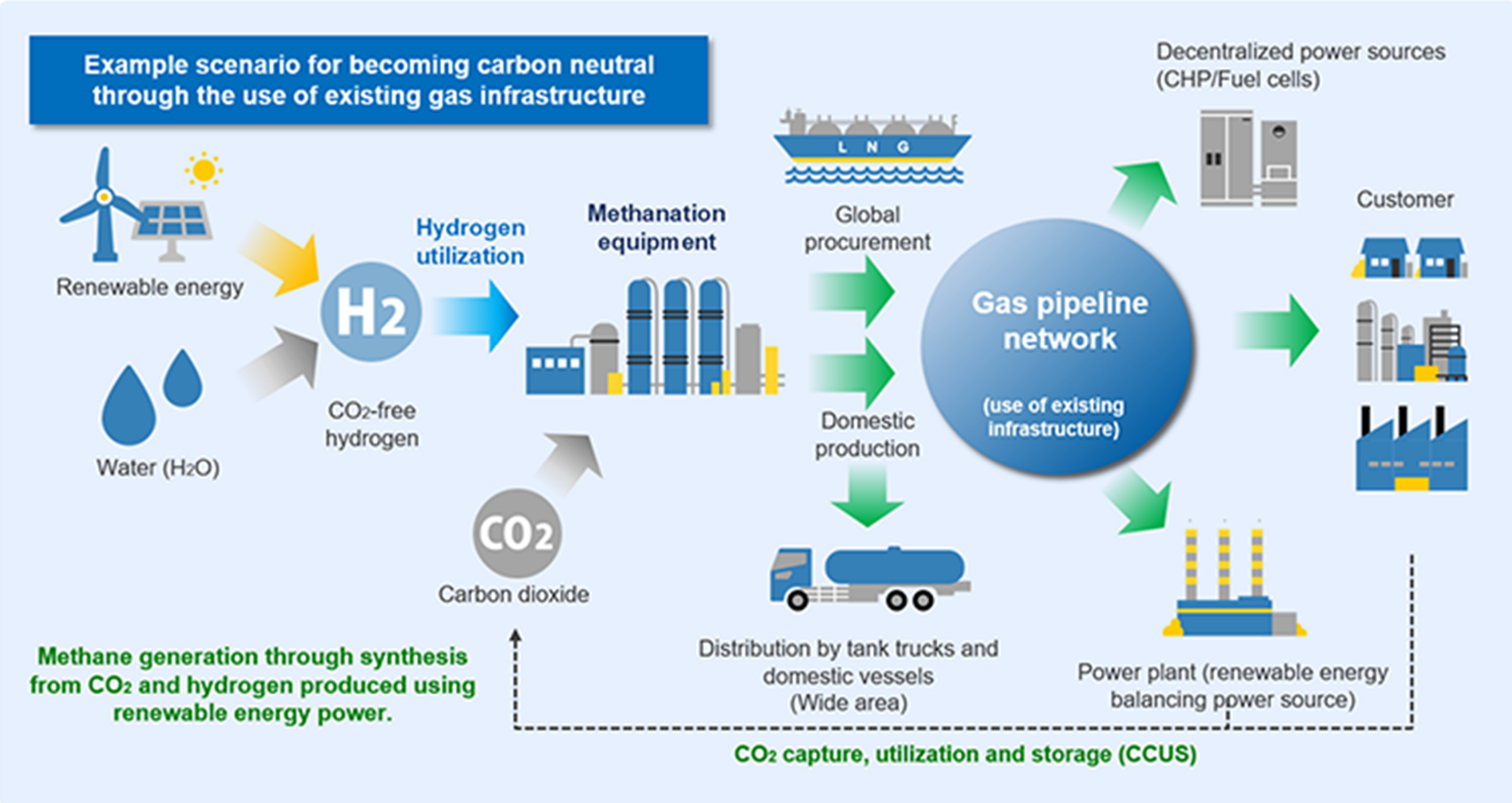
Carbon Neutrality



A world expanding from hydrogen and CO2 obtained by electrolysis from renewable energy power



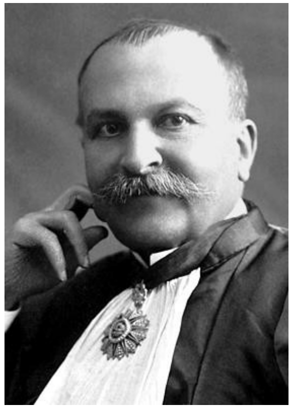
Methanation technology and CO_2 emissions



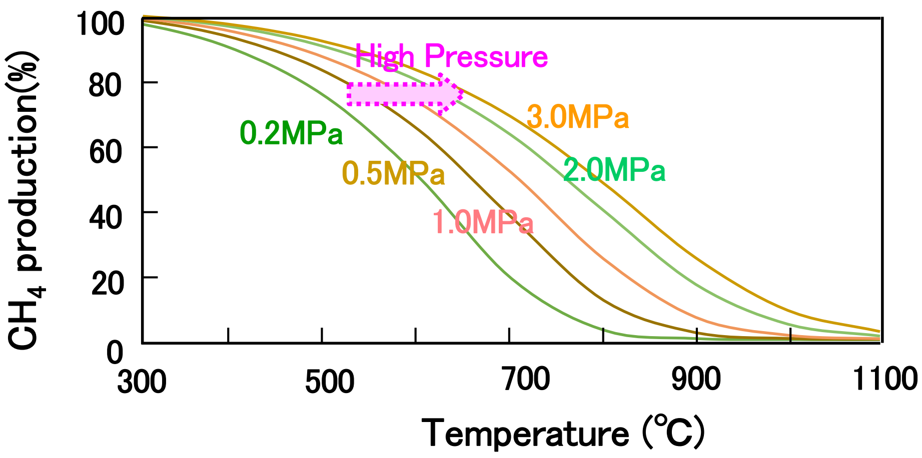
Methane production (methanation) technology

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

- 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

Prototype demonstration in Japan ahead of the world (Professor Emeritus Hashimoto of Tohoku University and Tohoku Institute of Technology)

1995 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020

Tohoku University /Hitachi Zosen

Prototype

Tokyo gas Senju Tech.ST

(2002) Pilot

Hitachi Zosen/IHI NEDO Project on SNG Production from Woody biomass

Hitachi Zosen NEDO Project (Advancement of Hydrogen Technologies and Utilization Project)

INPEX/Hitachi Zosen NEDO Project

Established CCR Study Group

Etogas Alpha-Plant, PtG 250, Audi e-gas

Desert Research Institute CO2 recycling

Electrochaea Industrial biogas test, Pre-commercial, P2G-BioCat, Powerstep, Store & Go

Haldor Topsoe Towards the methane society, El-upgraderet biogas, Synfuel

Microbenergy PtG im Eucolino, Biometh pure streams, BioPower2Gas, Mikrobielle methanisierung

DVGW-EBI DemoSNG, Synthesis of gas components

BTU GeoEn, Technikum 1&2, CO2 methanation of flue gas

ECN Synthetic methane

EMPA HyTech, Industrially-drerived CO2

Stadtwerke Emden Energiespeicher

Active efforts centered on Europe

Symbio *DTU-Environment*

OptFuel, EE-Methan from CO2 *JKU Linz*

RENERG2 *PSI*

P2G technology demonstration *DNVGL*

MeGa-stoRE, MeGa-store 2 *Aarhus University*

Dual function materials *Columbia University*

Biocatalytic methanation *BTU-FESPE*

Tauron CO2-SNG

Sunfire Helmeth

Enagas Renovagas

NREL P2G Solar Energy Storage

HSR-IET Power-to-Methan HSR

Engie Jupiter1000

Chemical Methanation

Biological Methanation

海水電解装置　　CO_2メタネーション装置

2023/7/4

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

Catalysis

2023/7/4

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 $H_2 + 1/2\ O_2 \rightarrow H_2O$ 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 Cu → CuO → Cu cycle. Cu reacts with oxygen, and the generated CuO reacts with hydrogen to regenerate Cu.
- The two reactions that form the cycle, Cu + 1/2 O_2 → CuO and CuO + H_2 → H_2O + 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 $Cl + O_3 \rightarrow ClO + O_2$ and $ClO + O \rightarrow O_2 + Cl$ occur with the oxygen atoms (O) formed by the decomposition of the oxygen molecules produced by the ultraviolet rays. As a whole, the reaction $O_3 + O \rightarrow 2O_2$ 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 (SOx) when burned.

What is catalyst? ～CatSJ web～

- Nitrogen oxides (NOx), 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 (N_2), carbon dioxide (CO_2) and water (H_2O). Nitrogen oxides (NOx) 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.

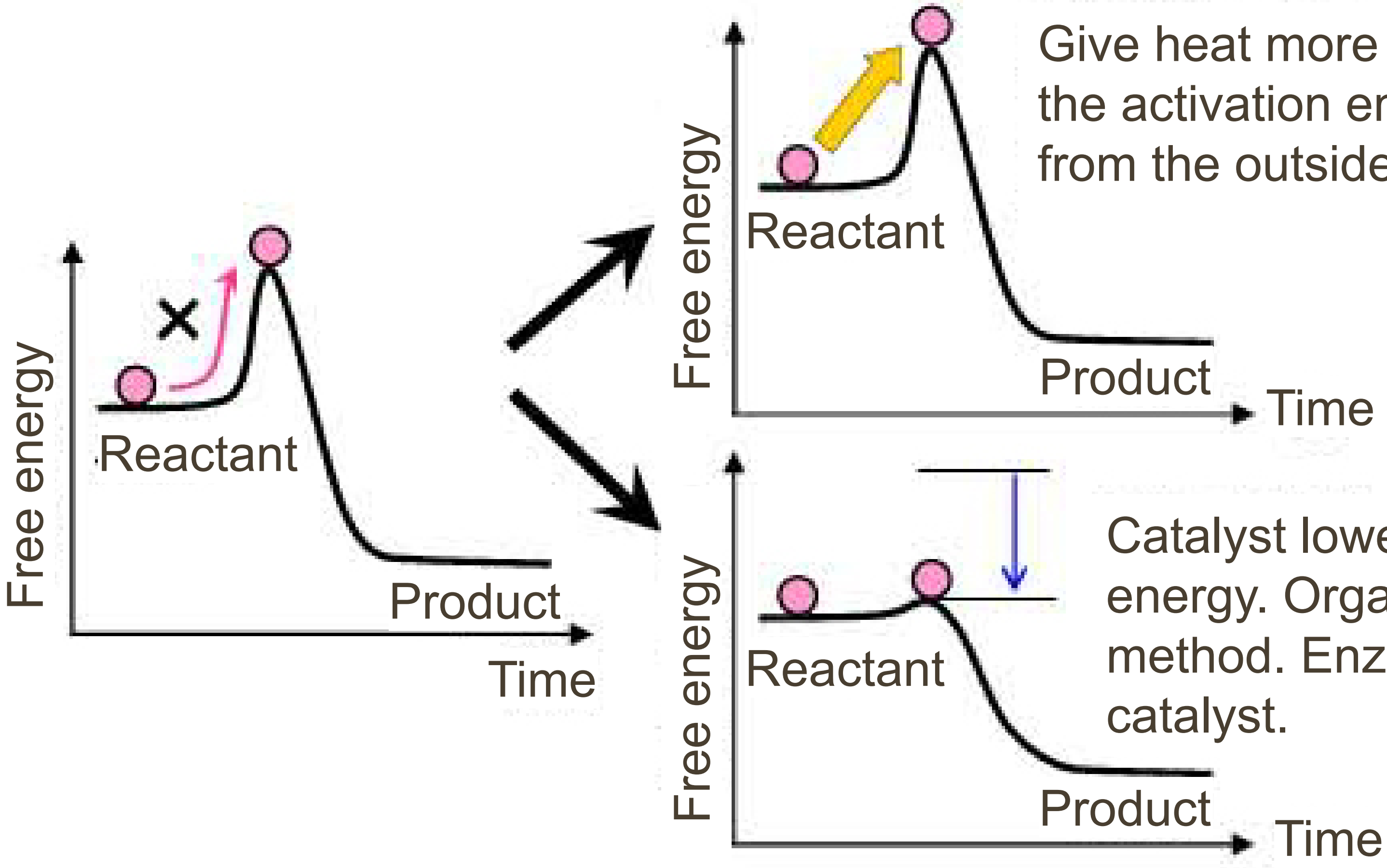
What is catalyst? ～CatSJ web～

- The antifouling, deodorant, and bactericidal effects of titanium oxide (TiO_2) are due to the absorption of light by TiO2, 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.



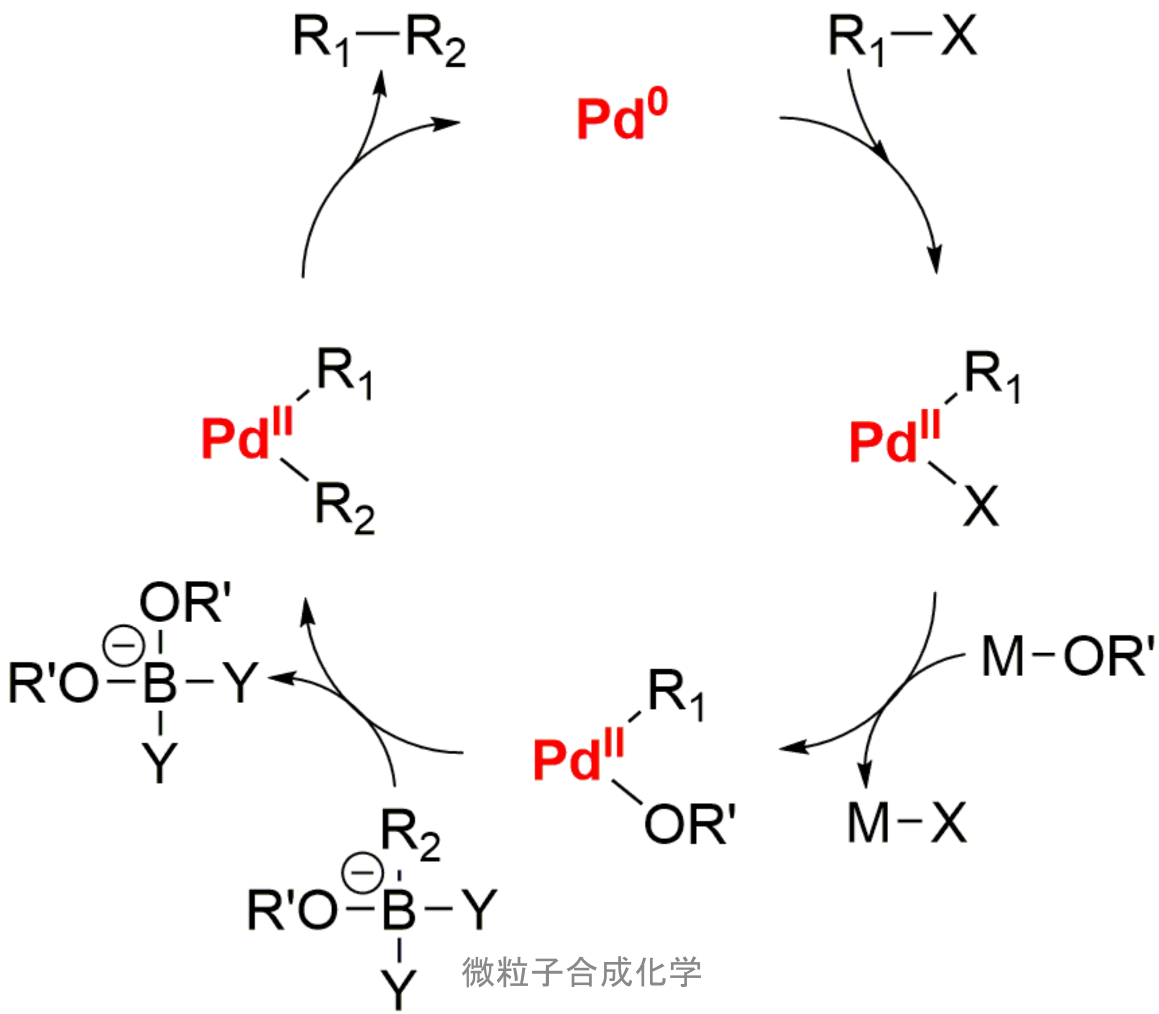
Give heat more than the activation energy from the outside.

Catalyst lowers the activation energy. Organisms use this method. Enzymes are a kind of catalyst.

What is catalyst?

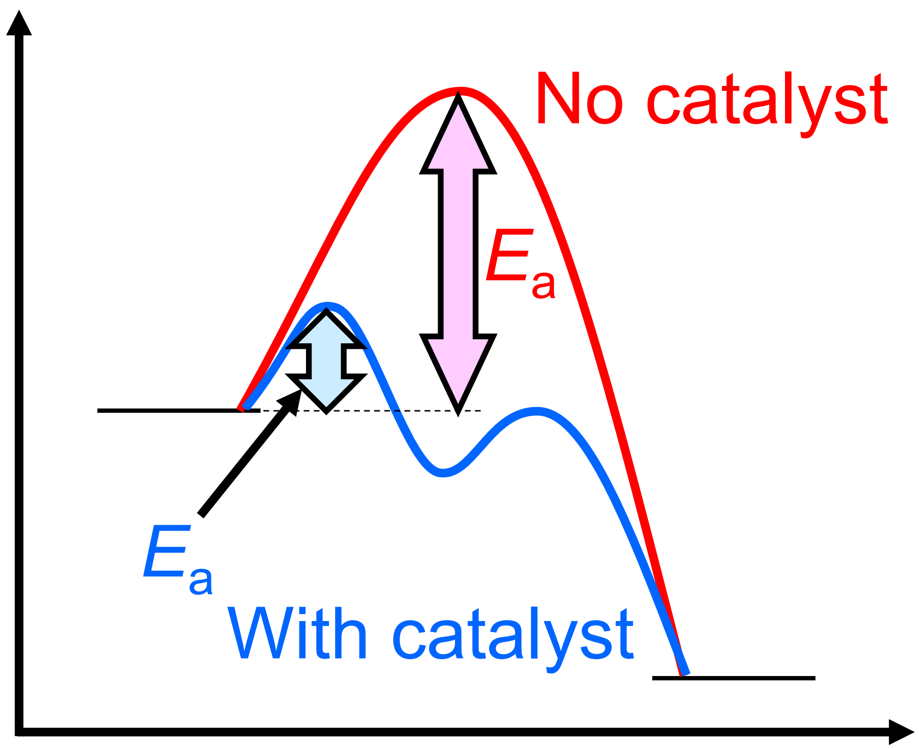
Definition of catalyst **A substance that accelerates a chemical reaction even in small amounts, without itself changing before and after the reaction.**

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.
Ea < Ea
→ 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 Friendrich 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

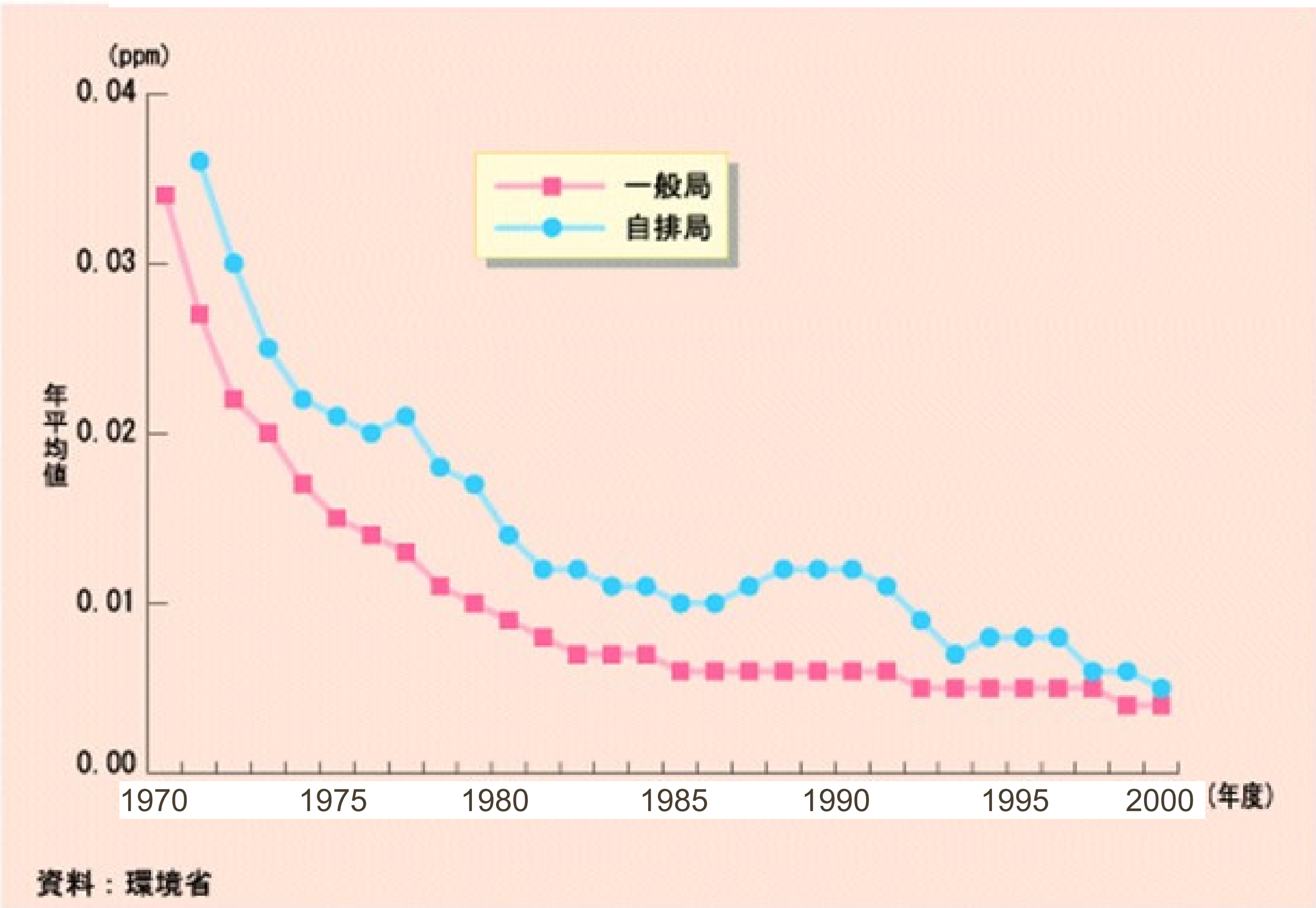
Yokkaichi Asthma

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



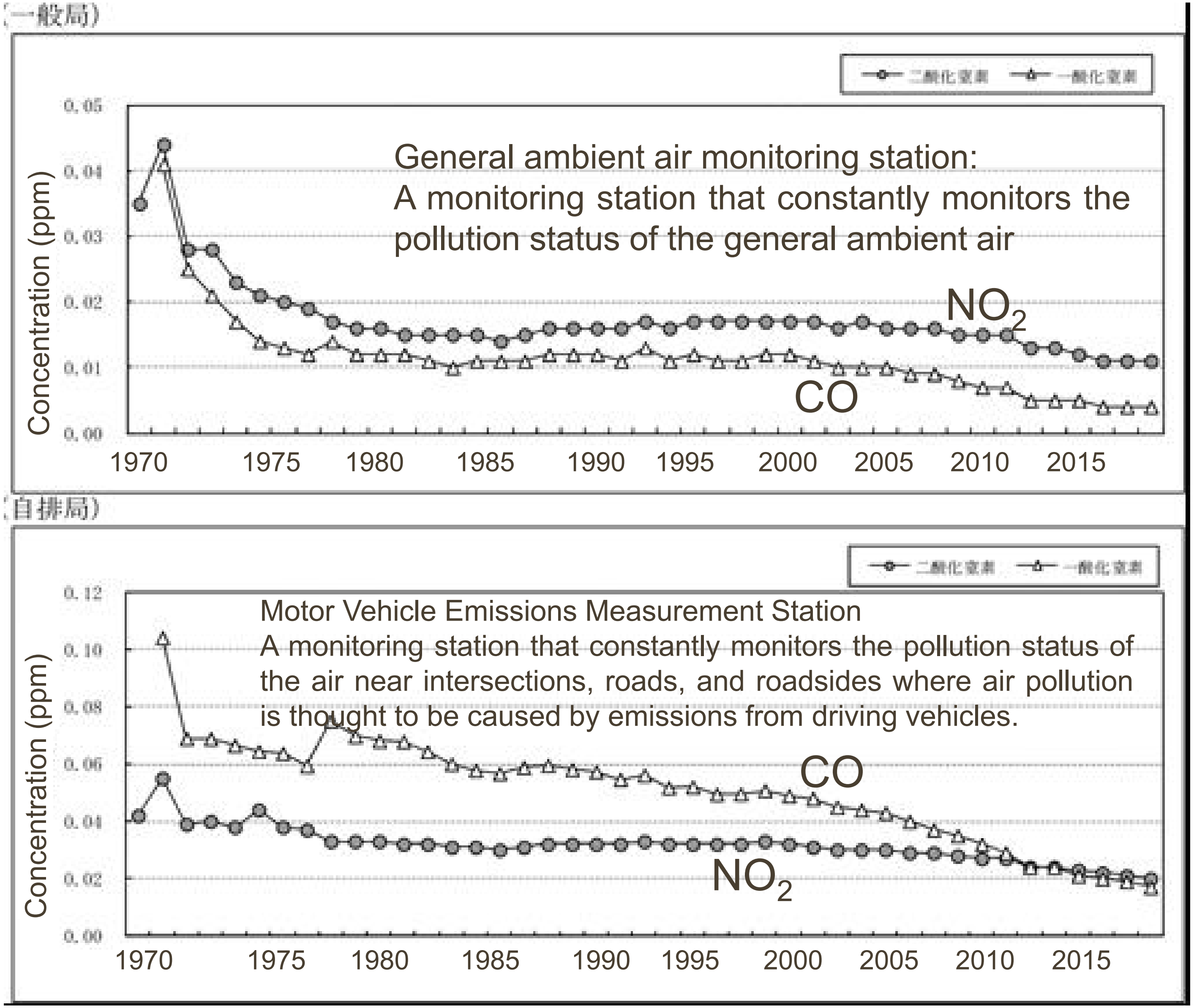
Eliminates sulfur content in fuel oil from the source!

That is the desulfurization catalyst.

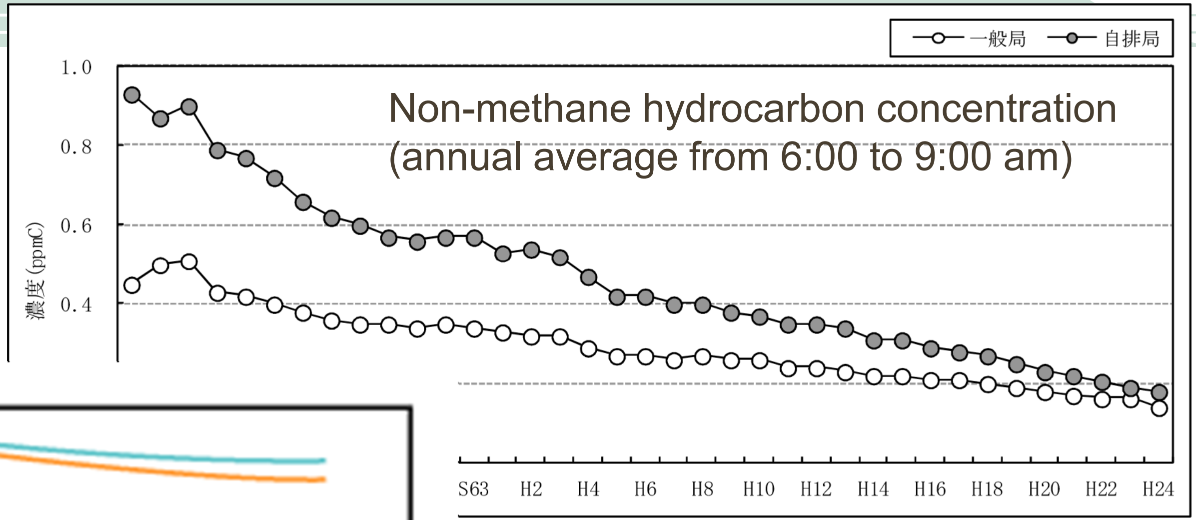
Co-Mo-S

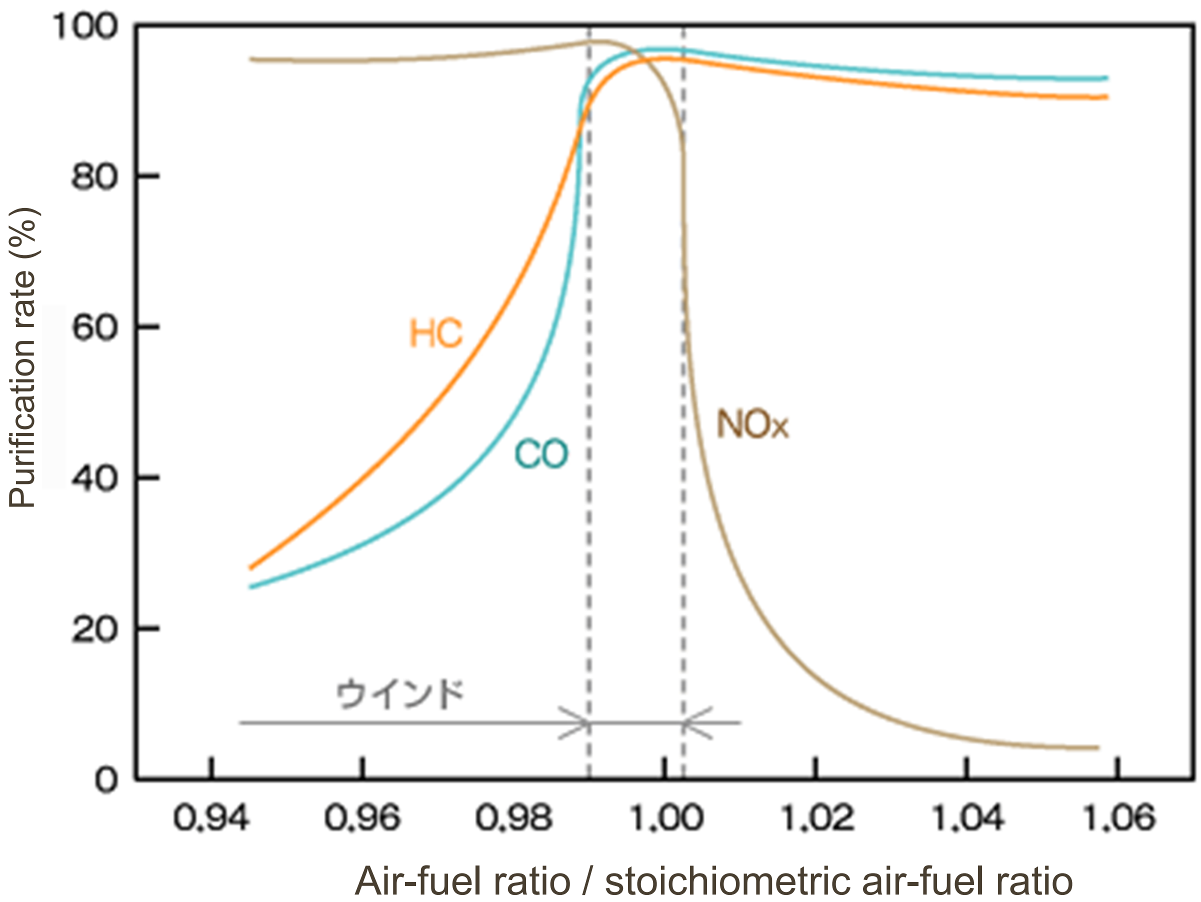
Three-way catalyst, TWC

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

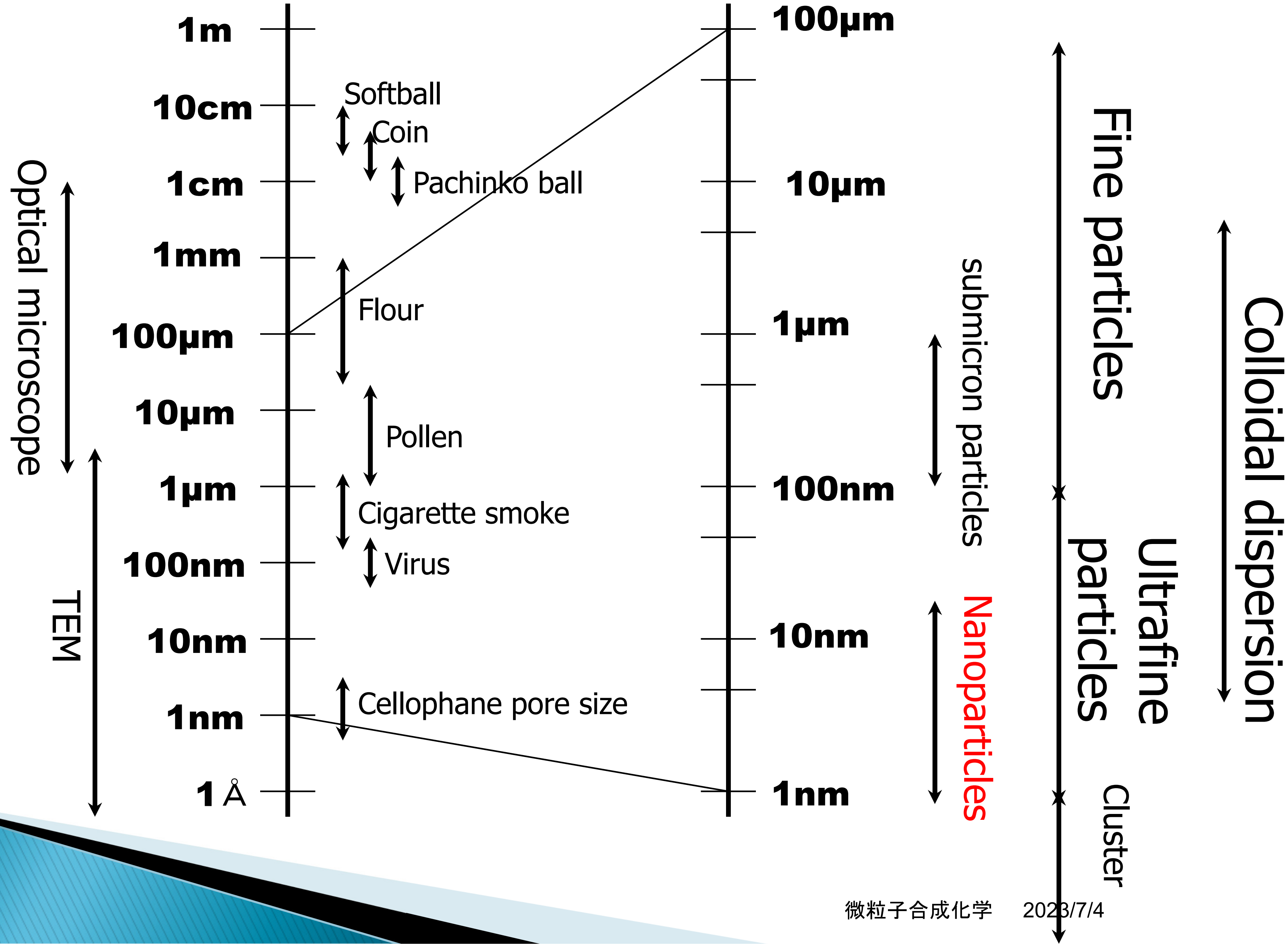


Three-way catalyst, TWC





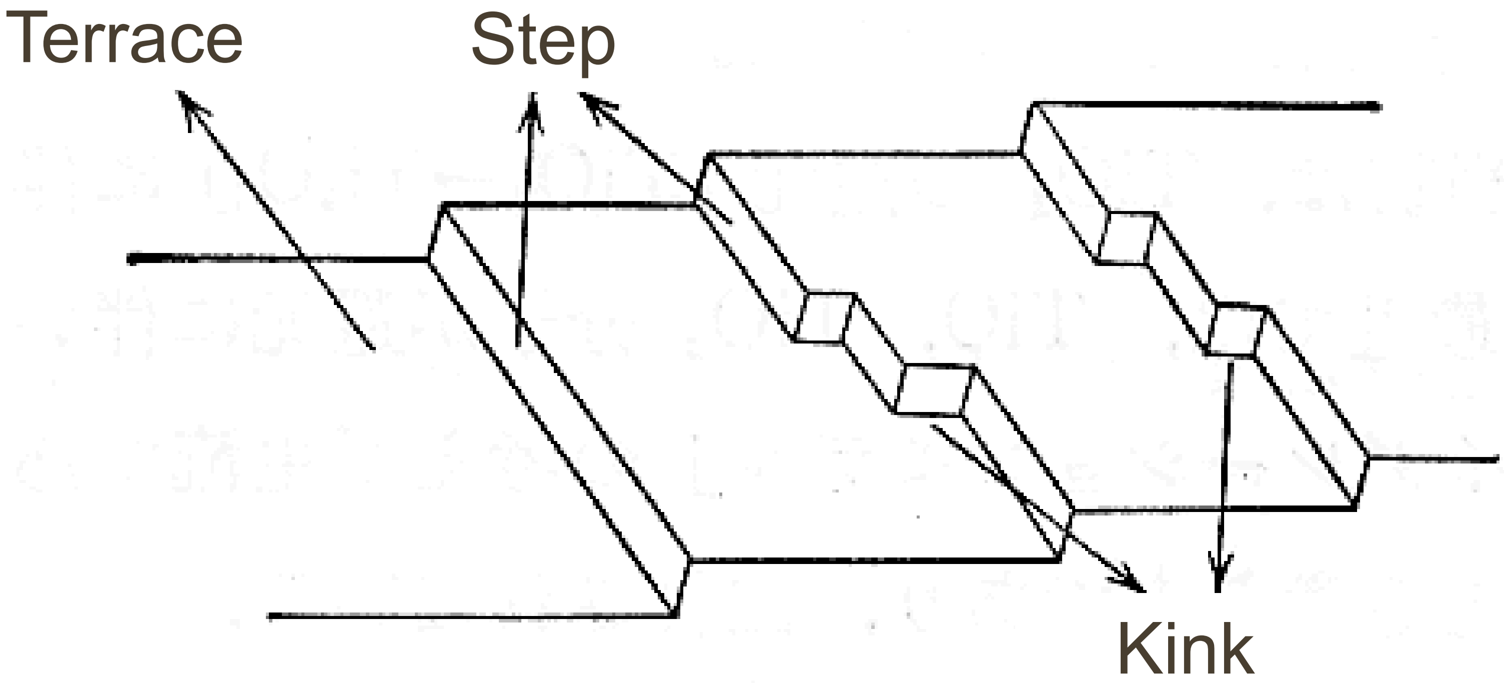
Particle classification by particle size



Nanoparticles

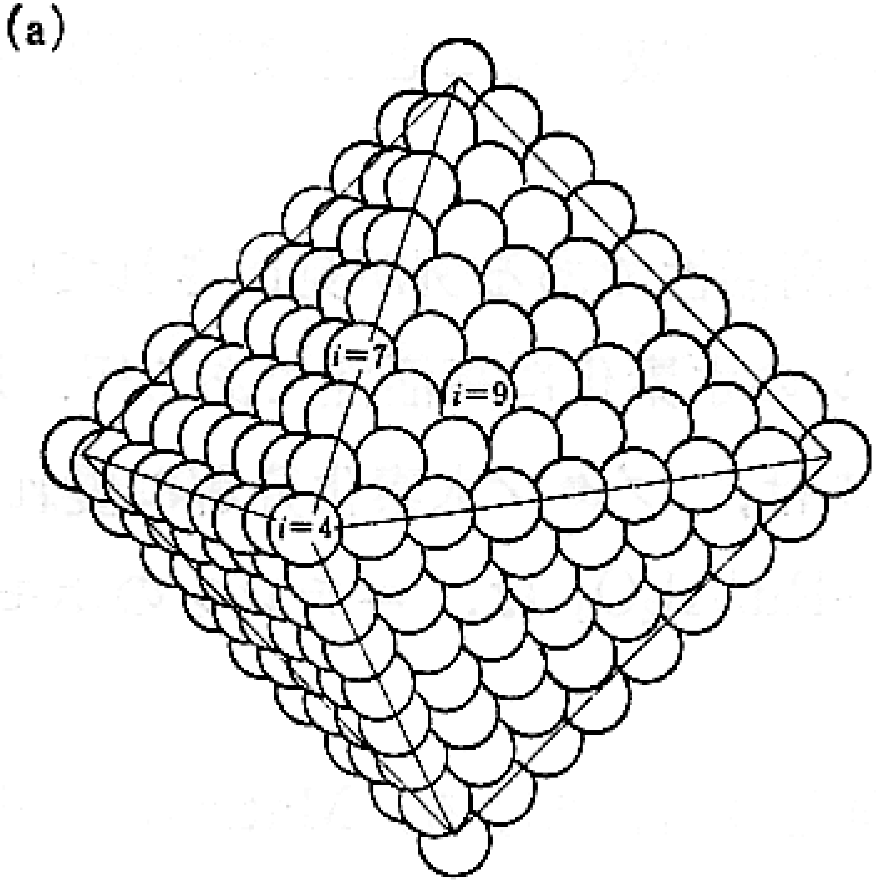
- 10^{-9} m = 1 nm
- The world of 1/1,000,000,000 m
- A material in which several to a dozen atoms are gathered.
- Physical properties different from bulk are expected.
- There is no difference between the number of bulk and surface atoms. There are many atoms with bond unsaturation.

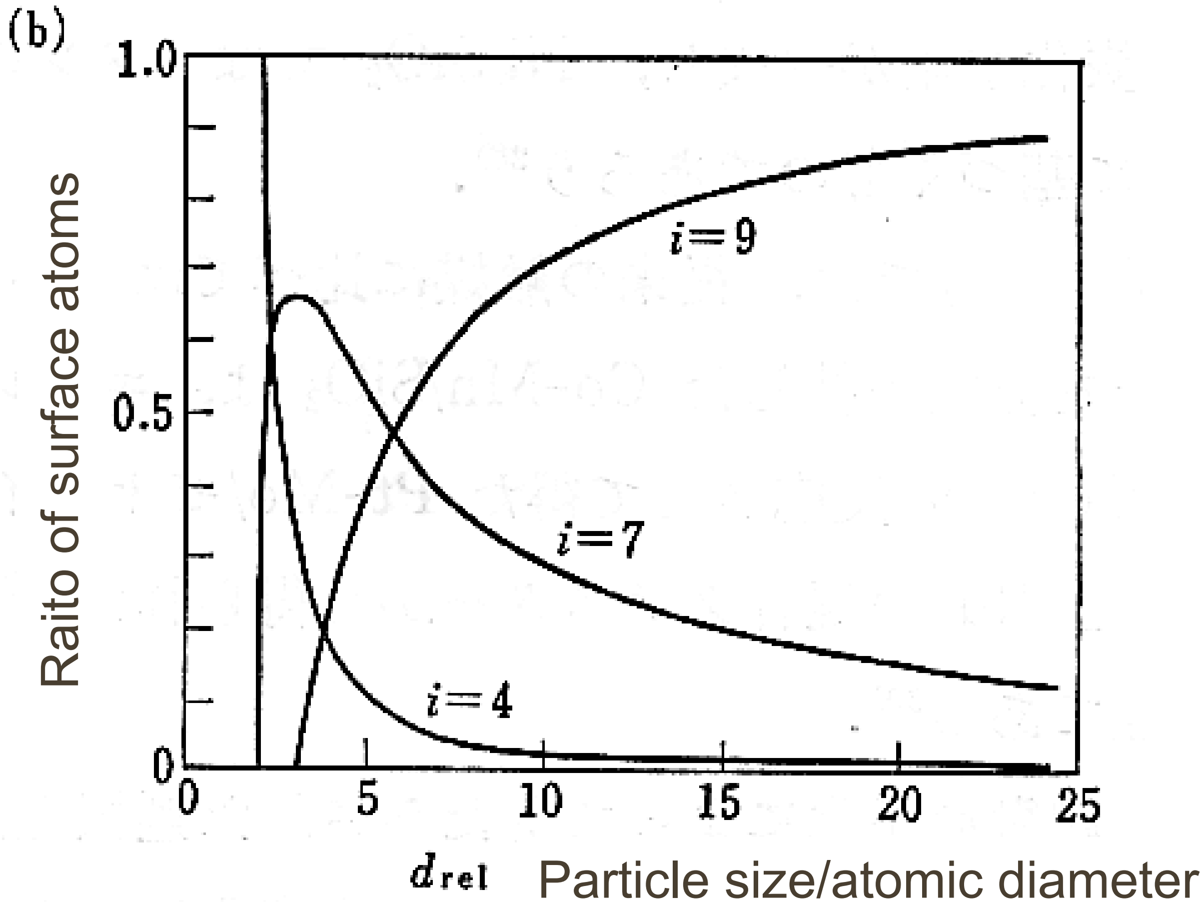
Surface structure and catalytic function



Atoms on the surface of metallic single crystal

Surface structure and catalytic function





Structure and number of metal surface atoms

Calculation of specific surface area

$$A_S = 4\pi r^2, \qquad V = \frac{4}{3}\pi r^3$$

$$\text{Specific surface area} = \frac{A_S}{Vd} = \frac{3}{rd}$$

(*d*: specific gravity)

Catalysts

- **Industrial catalyst**
  - Activity, selectivity, lifetime, workability
- **Catalyst design**
  - Surface control
  - Bulk control
- **Surface control**
  - Metal catalyst → Metal type, valence, composition, particle size, etc.
    - Support effect, ensemble effect, ligand effect

Activity

- **Turnover frequency on an active site**
  - Surface reaction rate on 1 active site
- **Overall catalytic activity**

The activity of the whole catalyst depends on the total surface area.

However, in some cases it is strongly dependent on the structure (see below)

Life time

- **Catalyst life**
  - maintain the same active selectivity
  - For industrial purposes, a service life of several months to one year is required.
  - Deactivation
    - Mainly sintering and changes in the catalyst material itself

Selectivity

- **Change only 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, it also depends on the reaction conditions.

Example of control of oxidation state

- **Mo/SiO_2 catalyst**
  - CO hydrogenation → formation of hydrocarbons and alcohols
    - Mo (Metallic state) → gives lower hydrocarbons
      - CO is dissociated on Mo metal and not converted into alcohols.
    - Mo (4+) → gives very little methanol with low activity
      - CO is non-dissociatively adsorbed on Mo(4+)
    - Mo (Metallic) and Mo (4+) → gives mixed alcohols
      - Dissociated CO is converted into $-CH_2$ to give C-C bond.
      - -CO is added to the end of the product and hydrogenated to convert to alcohol.

Size control

- Increases overall catalytic activity by increasing specific surface area
- TOF (Turnover Frequency) depends on the size.
  - Quantum effect

Calculation of specific surface area

$$A_S = 4\pi r^2, \qquad V = \frac{4}{3}\pi r^3$$

$$\text{Specific surface area} = \frac{A_S}{Vd} = \frac{3}{rd}$$

(d: specific gravity)

The smaller the radius, the larger the specific surface area!

Catalyst design

- Accurate grasp of surface information
- Precise surface feature control

↓

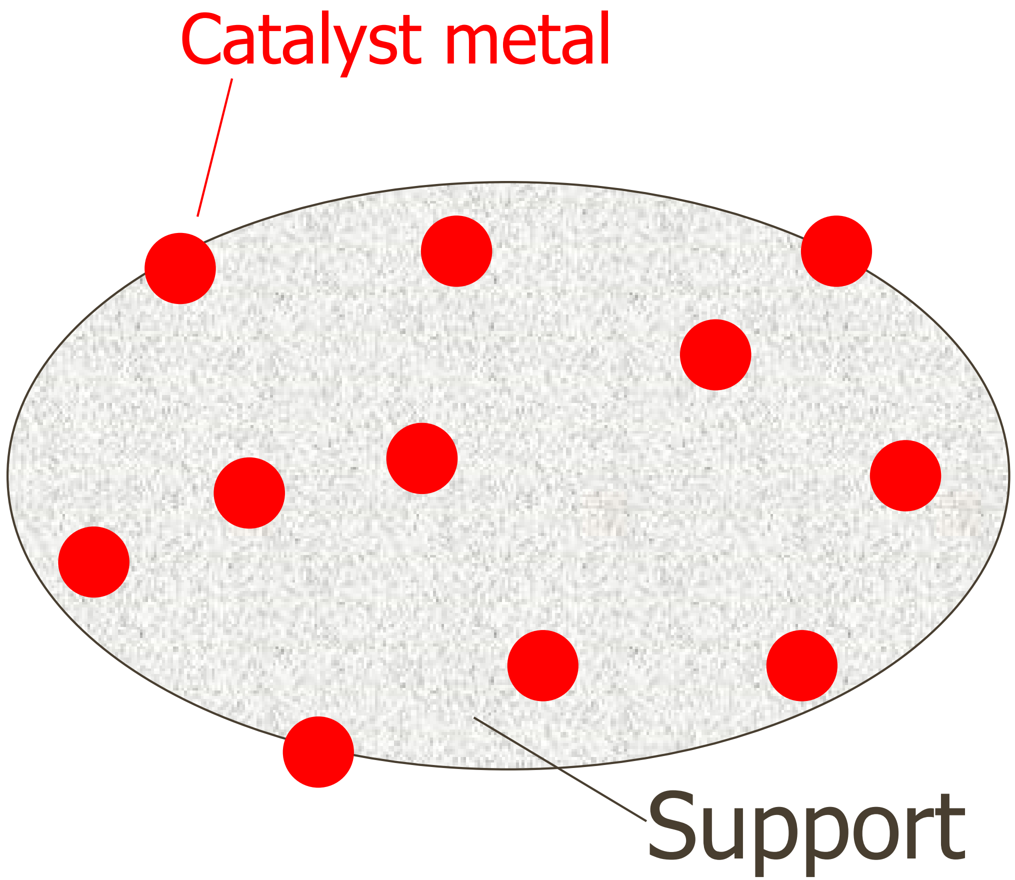
- Local structure control and evaluation are important.

Classification of catalysts

- **Homogenous catalysts**
  - The reactants are in the same phase as the products.
  - Example: Rh catalyst for acetic acid synthesis
    - Homogeneous catalyst is liquid phase.
- **Heterogeneous catalysts**
  - Different phase
  - Example: solid catalyst
    - supported catalysts, unsupported catalysts

Supported metallic catalysts

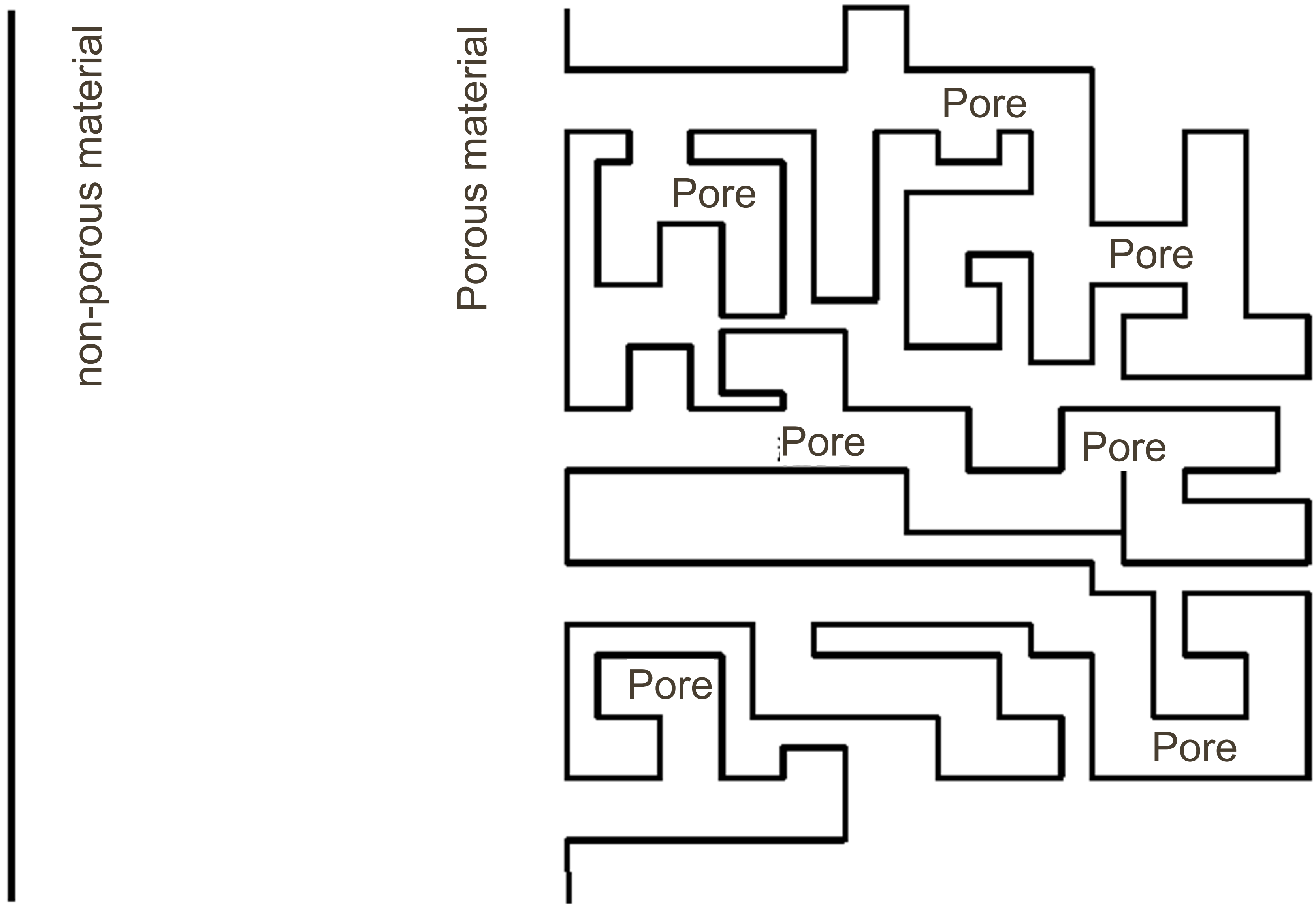
- A catalyst metal is supported on the carrier material.
- The support is in the form of powder or lumps.

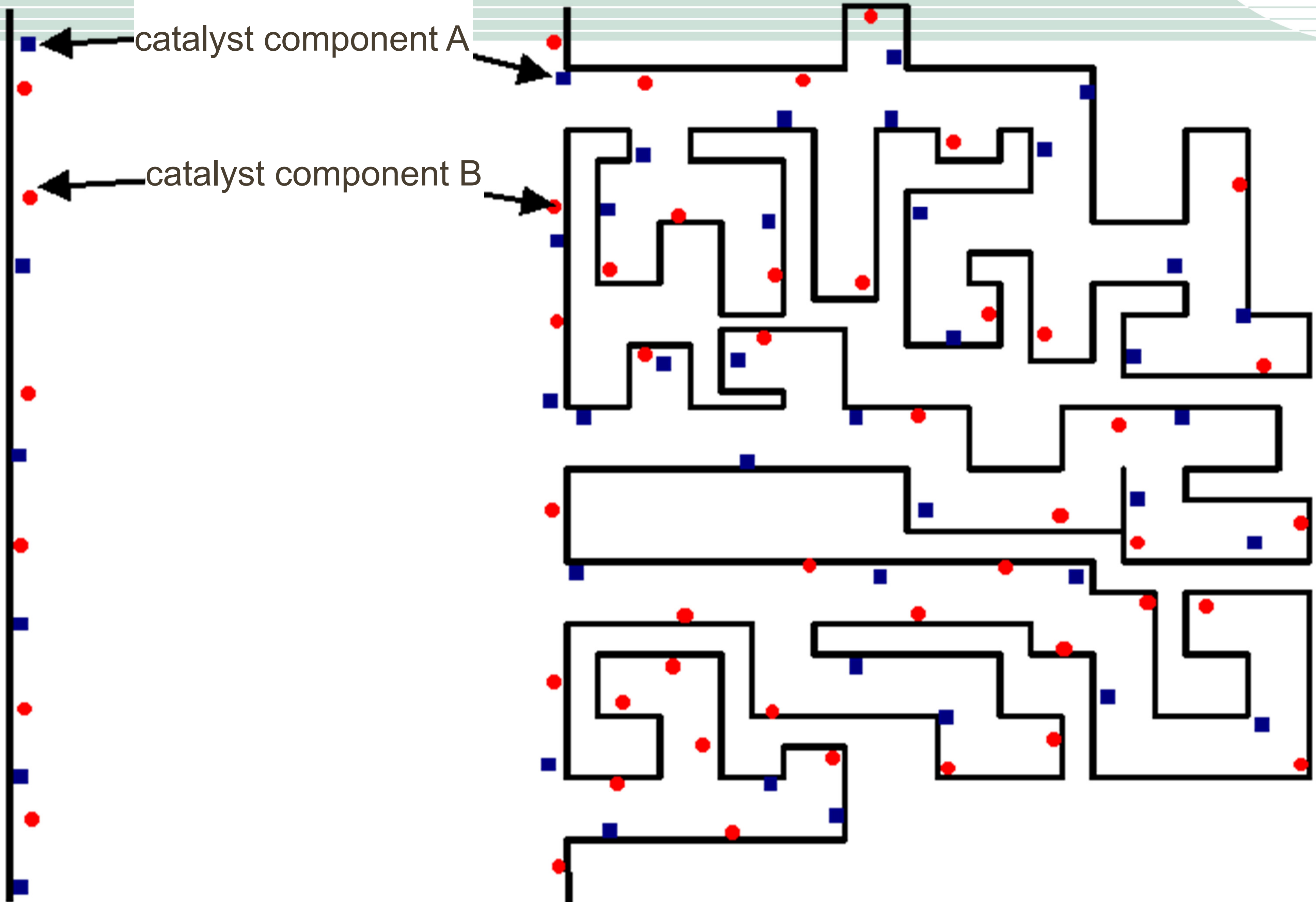


Supported metallic catalysts

- **Support**
  - Mainly metal oxides
  - Many have well-developed pores
  - Excellent mechanical strength
- **Catalyst metals**
  - Carrying and dispersing on a support.
  - The ideal size is several nanometers.
  - Actually, it is often about 5 to 50 nm.

Support: Large specific surface area




catalyst component A
catalyst component B

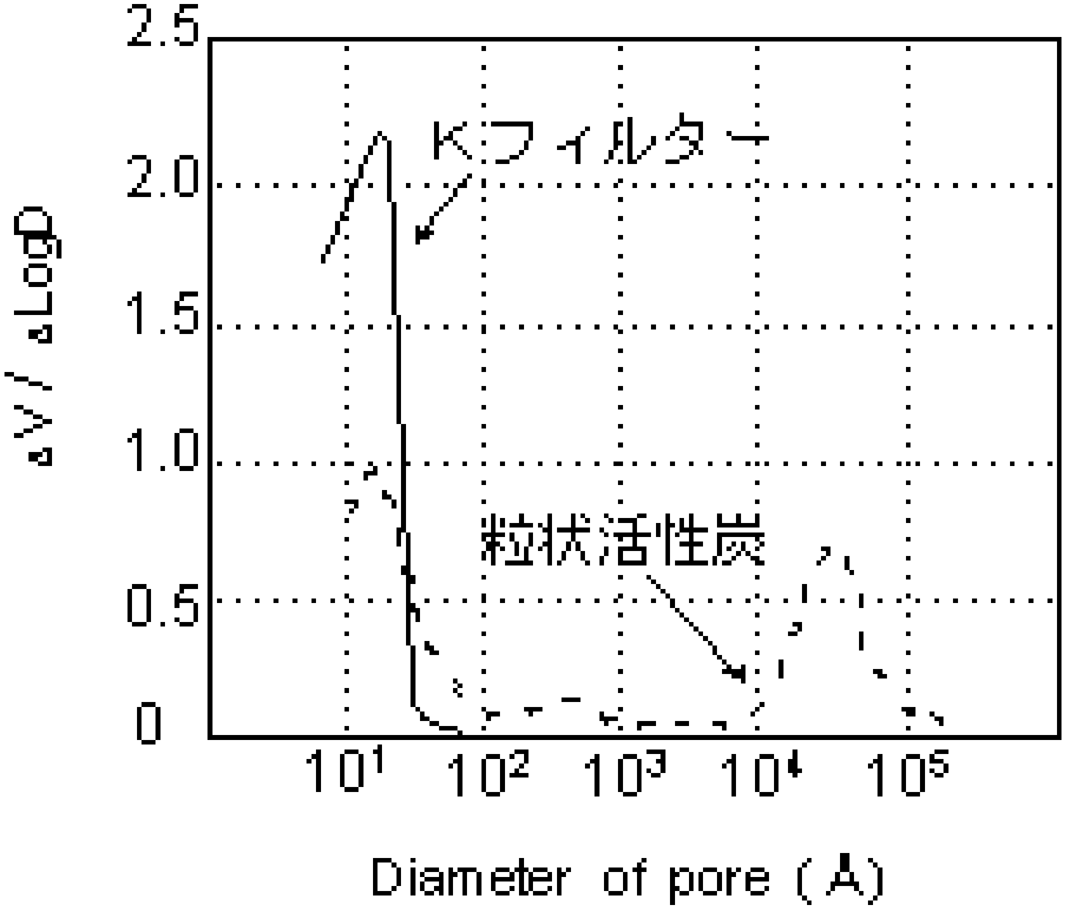
Supports: Activated carbon

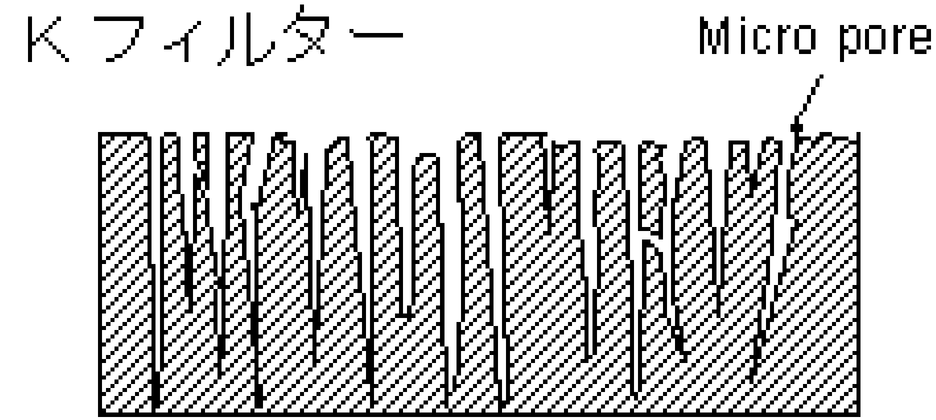
- coconut shell activated carbon

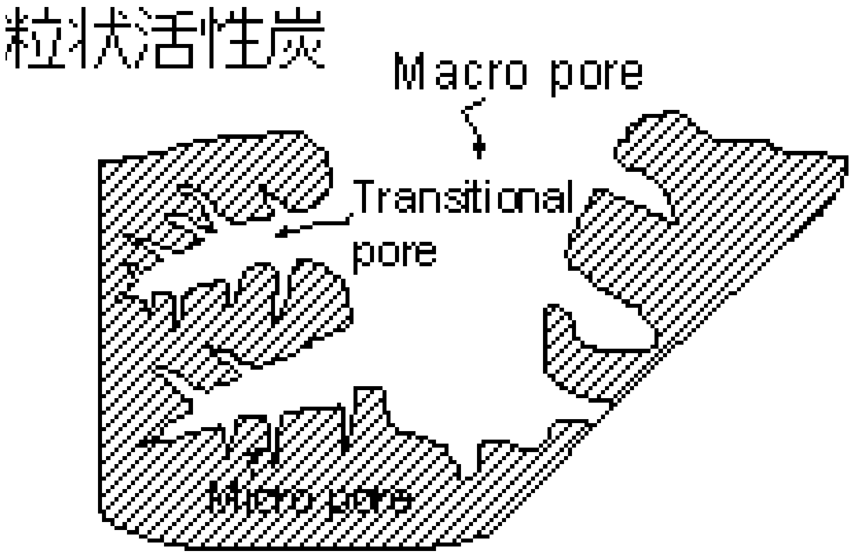
Coal-based activated carbon

- charcoal activated carbon

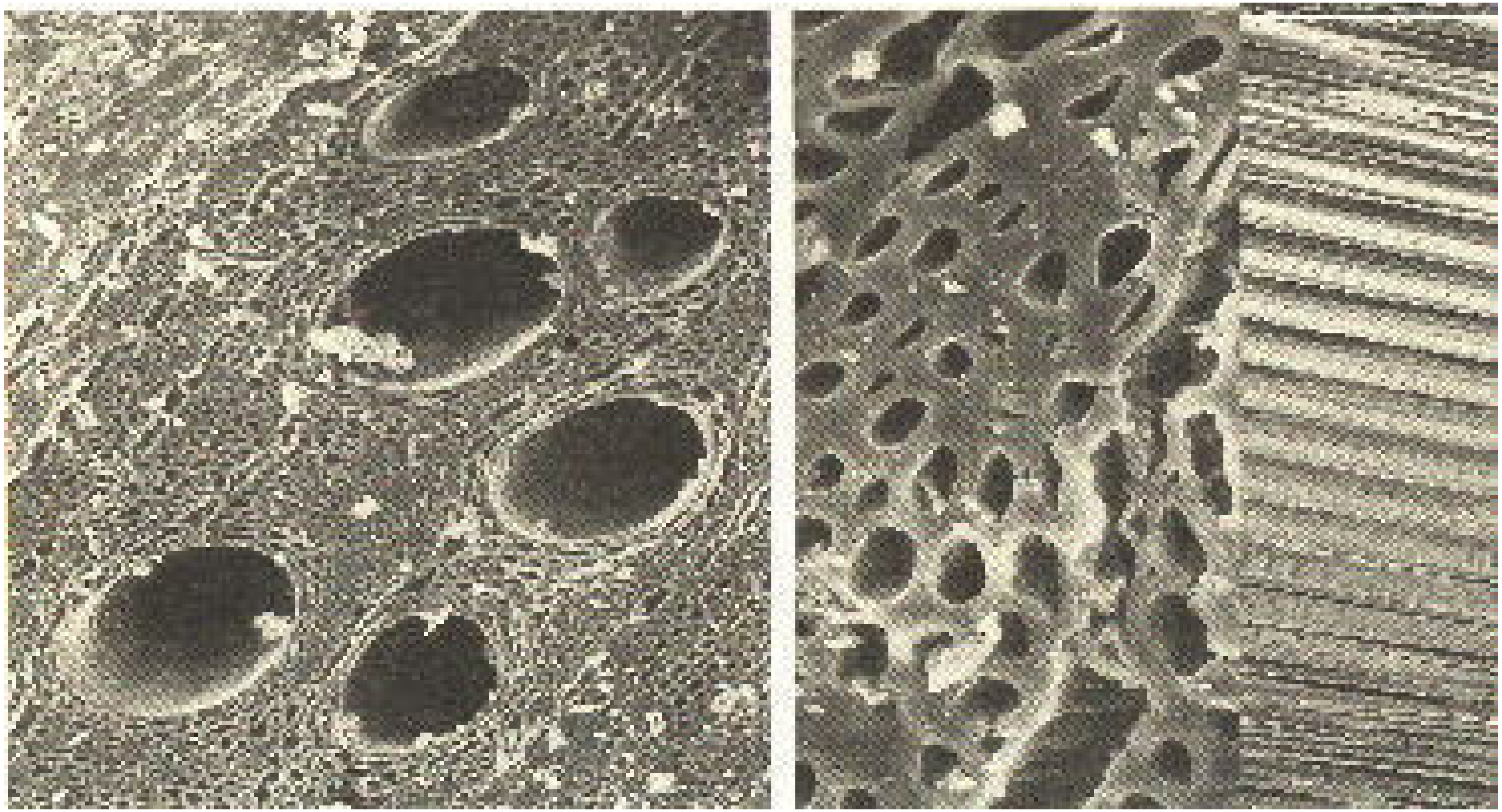
activated carbon







charcoal surface



Fundamentals of catalytic reactions