Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

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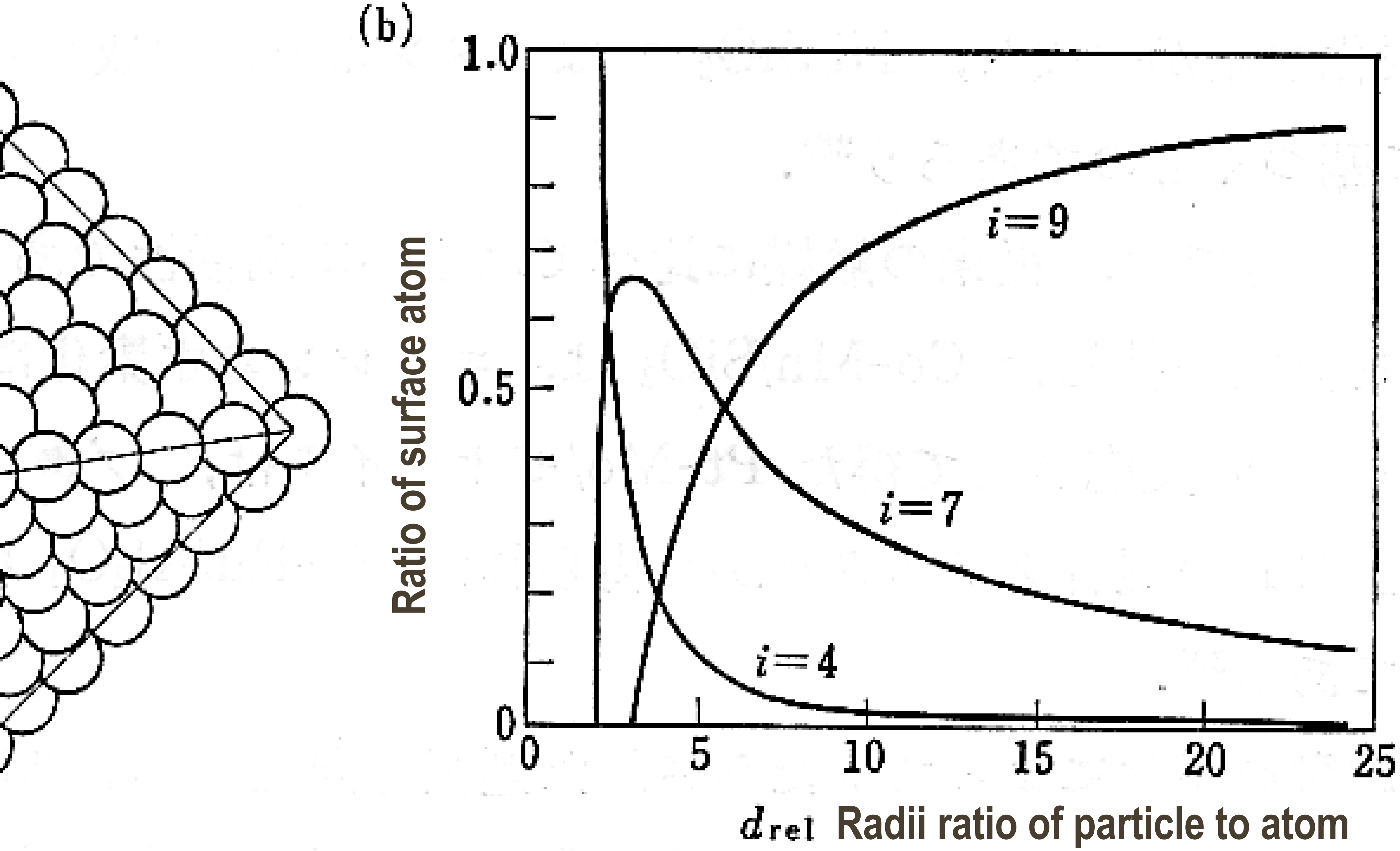
Lecture Plan

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~~ Cancelled

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

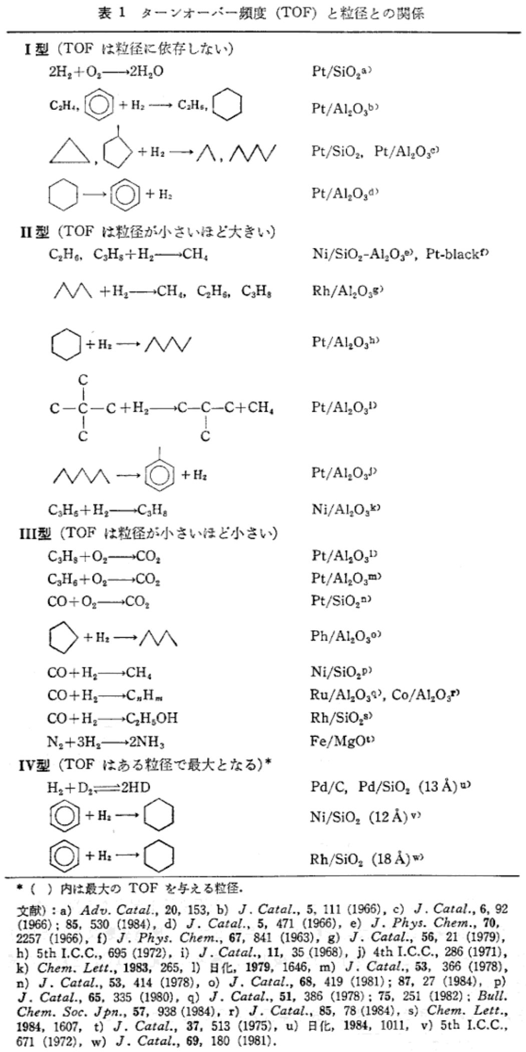


表 1　ターンオーバー頻度（TOF）と粒径との関係

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, + $H_2 \longrightarrow$ C_2H_6,	Pt/Al_2O_3 b)
, + $H_2 \longrightarrow$,	Pt/SiO_2, Pt/Al_2O_3 c)
$\longrightarrow$ + 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, $C_3H_8+H_2 \longrightarrow CH_4$	$Ni/SiO_2\text{-}Al_2O_3$ e), Pt-black f)
+ $H_2 \longrightarrow CH_4$, C_2H_6, C_3H_8	Rh/Al_2O_3 g)
+ $H_2 \longrightarrow$	Pt/Al_2O_3 h)
$C-\overset{C}{\underset{C}{C}}-C+H_2 \longrightarrow C-\underset{C}{C}-C+CH_4$	Pt/Al_2O_3 i)
$\longrightarrow$ + 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)
+ $H_2 \longrightarrow$	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)
+ $H_2 \longrightarrow$	Ni/SiO_2（12 Å）v)
+ $H_2 \longrightarrow$	Rh/SiO_2（18 Å）w)

*（　）内は最大の TOF を与える粒径.

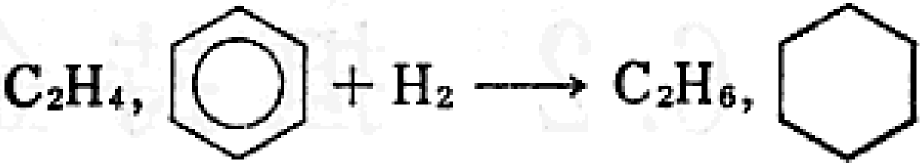
文献）: a) *Adv. Catal.*, 20, 153, b) *J. Catal.*, **5**, 111 (1966), c) *J. Catal.*, **6**, 92 (1966); **85**, 530 (1984), d) *J. Catal.*, **5**, 471 (1966), e) *J. Phys. Chem.*, **70**, 2257 (1966), f) *J. Phys. Chem.*, **67**, 841 (1963), g) *J. Catal.*, **56**, 21 (1979), h) 5th I.C.C., 695 (1972),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

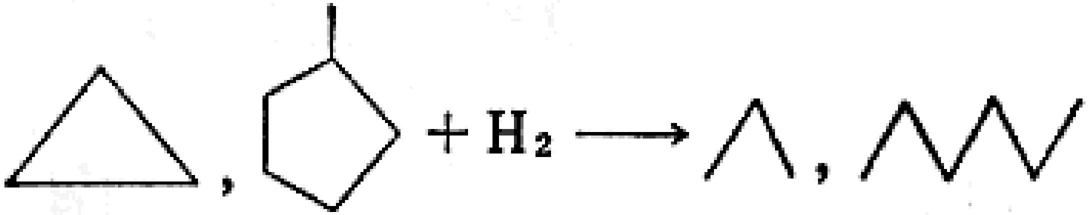
Relationship between Turnover Frequency (TOF) and catalyst particle size

I 型 TOF is independent on the size: Structure insensitive

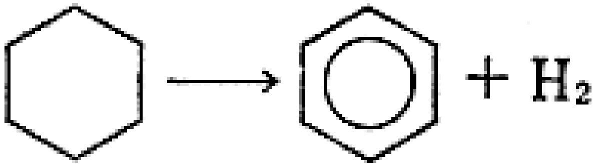
$2H_2+O_2 \longrightarrow 2H_2O$ Pt/SiO_2 a)



Pt/Al_2O_3 b)



Pt/SiO_2, Pt/Al_2O_3 c)



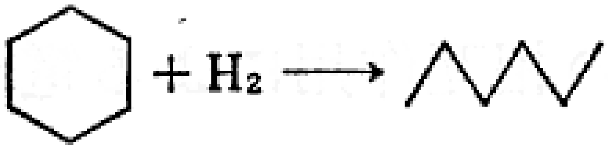
Pt/Al_2O_3 d)

Structural Sensitivity / Structural Insensitivity

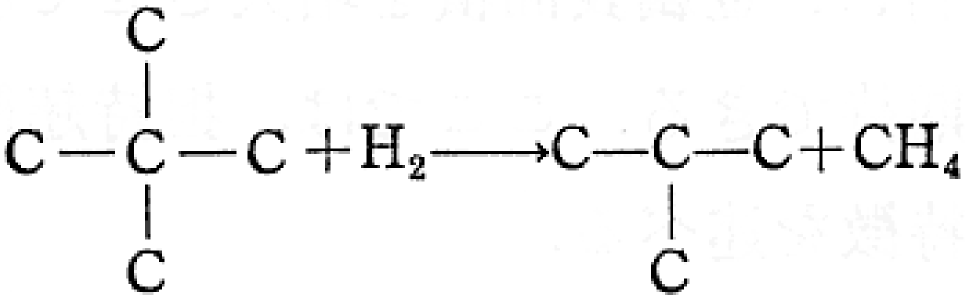
II 型 The larger TOF, the smaller the size: Structure sensitive

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

Rh/Al_2O_3 g)

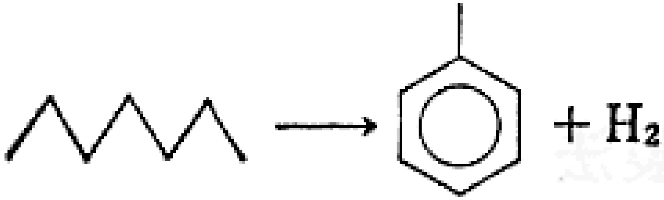


Pt/Al_2O_3 h)



$$\mathrm{C-\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}-C + H_2 \longrightarrow C-\underset{\underset{C}{|}}{C}-C + CH_4}$$

Pt/Al_2O_3 i)

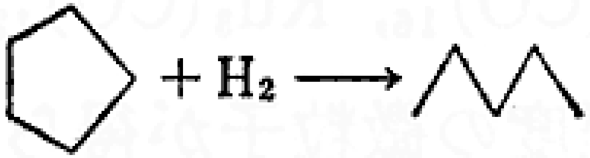


Pt/Al_2O_3 j)

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

Structural Sensitivity / Structural Insensitivity

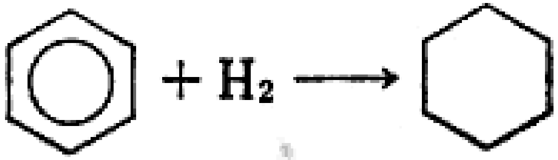
III型 The smaller TOF, the smaller the size: Structure sensitive

$C_3H_8+O_2 \longrightarrow CO_2$	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)

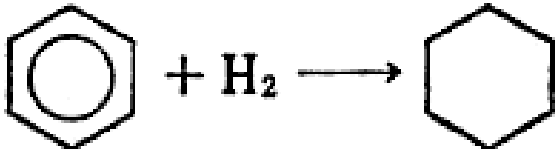
Structural Sensitivity / Structural Insensitivity

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

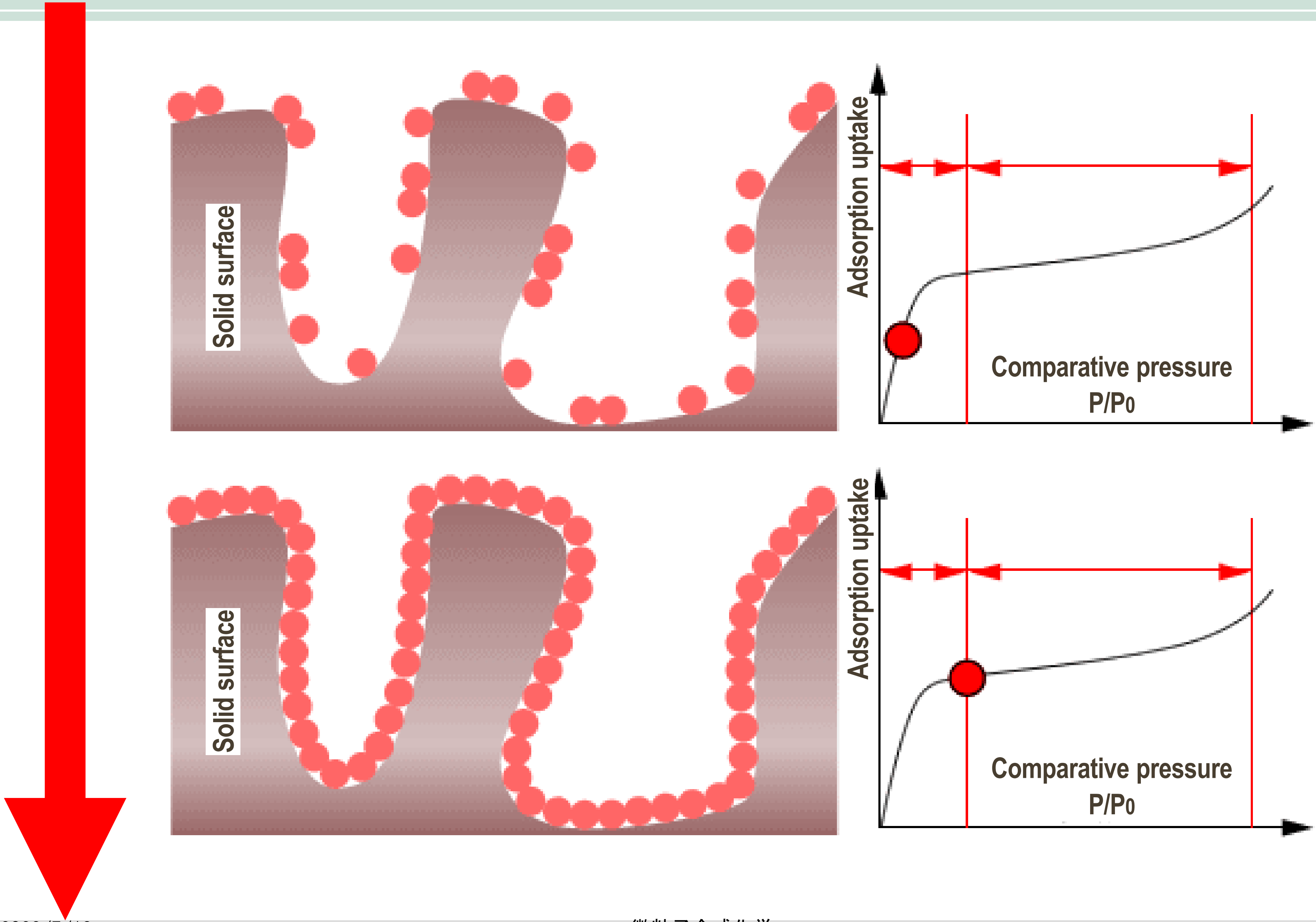
Adsorption is start of catalytic reaction

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

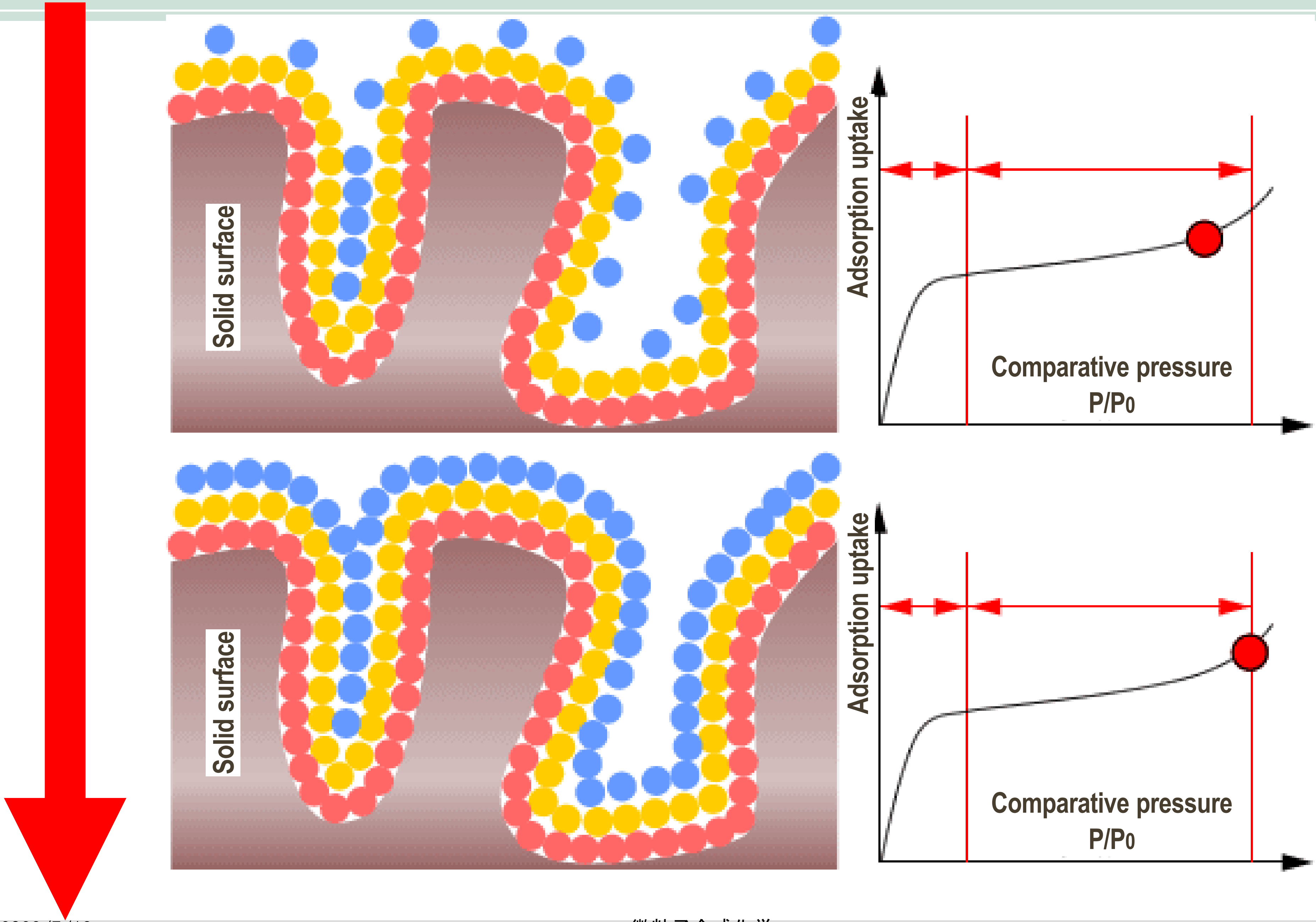
Table　Chemisorption and physisorption

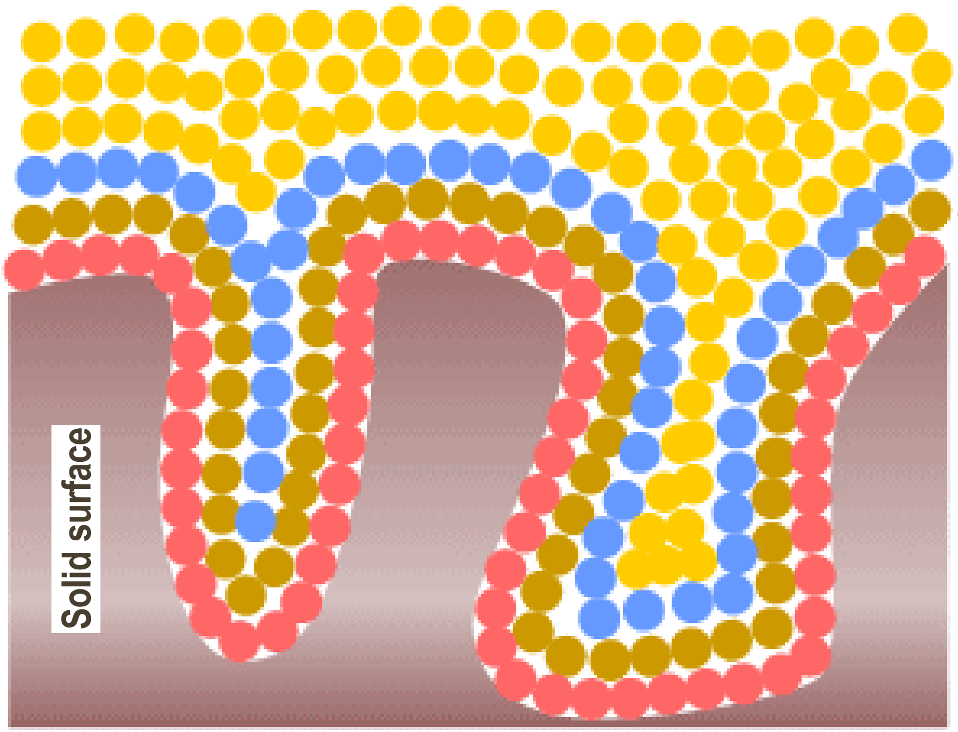
Features	Chemisorption	Physisorption
Origin of adsorption	Chemical bond	van der Waals force
Site	Selective	Non-selective
Structure	Monolayer	Multilayer
Heat of adsorption	10～100 k cal/mol	A few kcal/mol
Activation energy	Large	Small
Rate	Slow	Rapid
Adsorption and Desorption	Reversible or Irreversible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

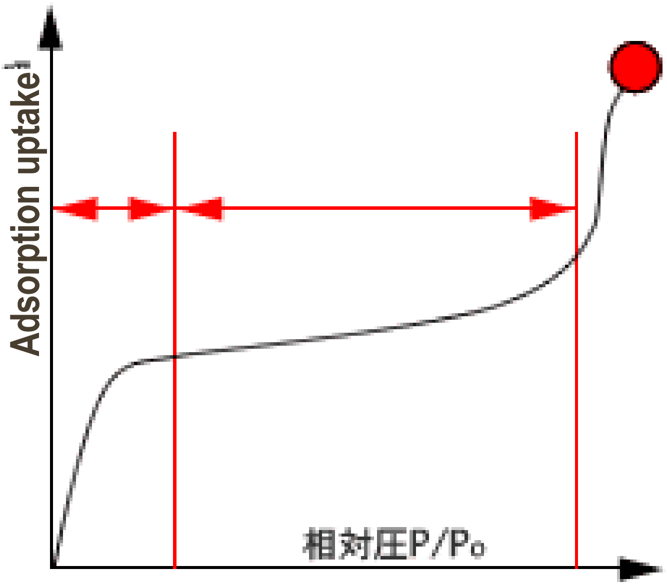
Physisorption



Physisorption



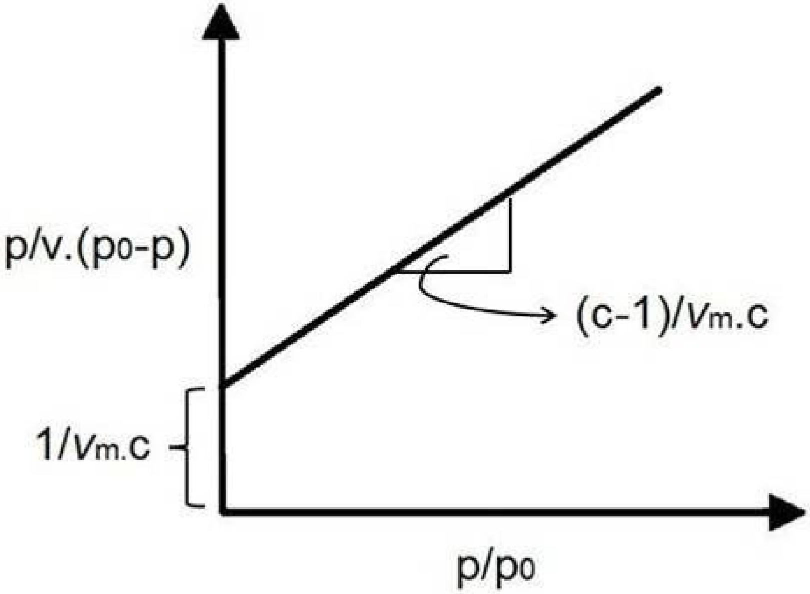

Solid surface


Adsorption uptake
相対圧P/P_0

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

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

Chemisorption

Chemisorption

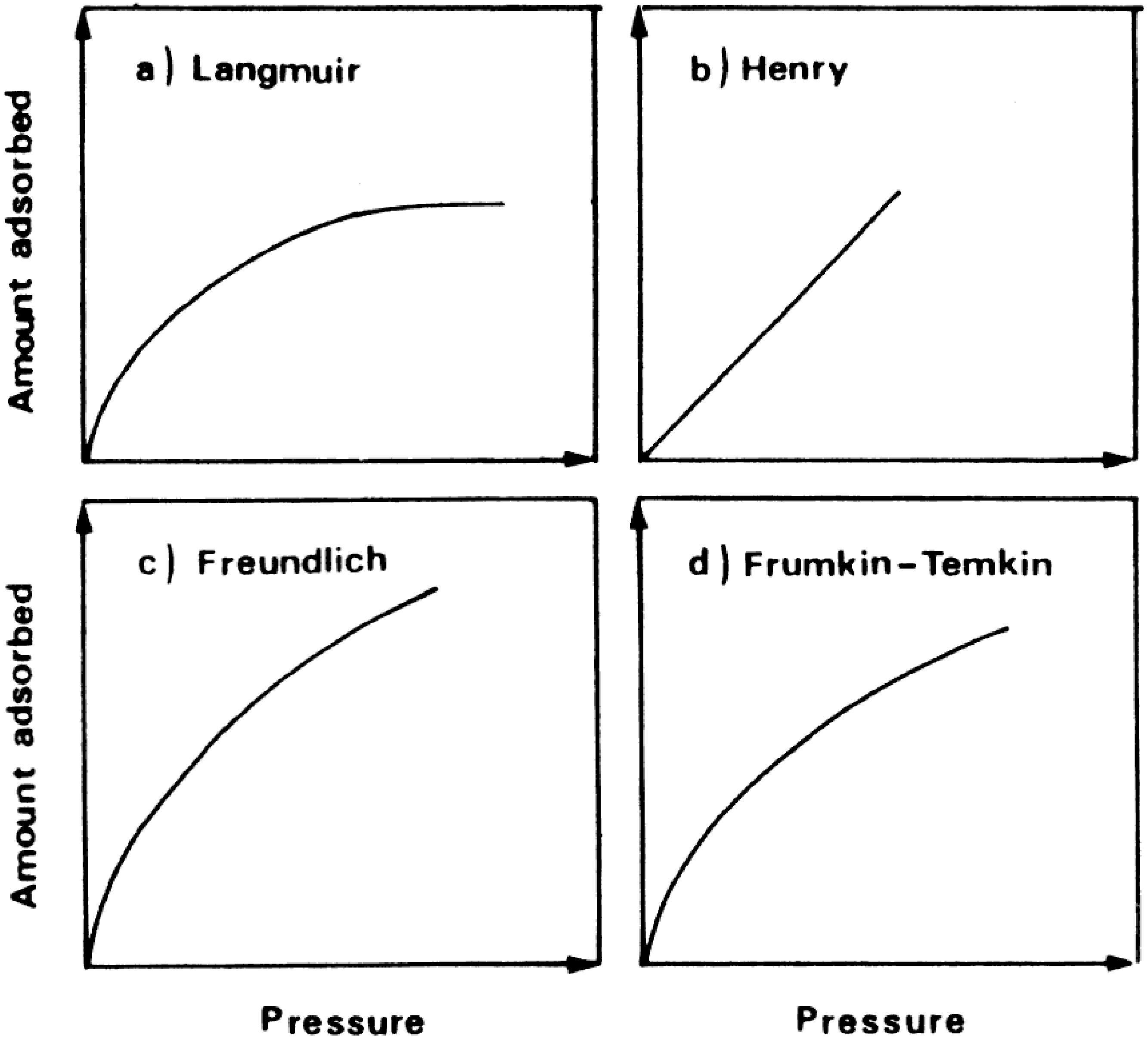
- **Dissociated adsorption**

  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**

$$\theta = ap \qquad \theta \ll 1$$

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

- **Freundlich**

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

- **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 ln 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）**

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

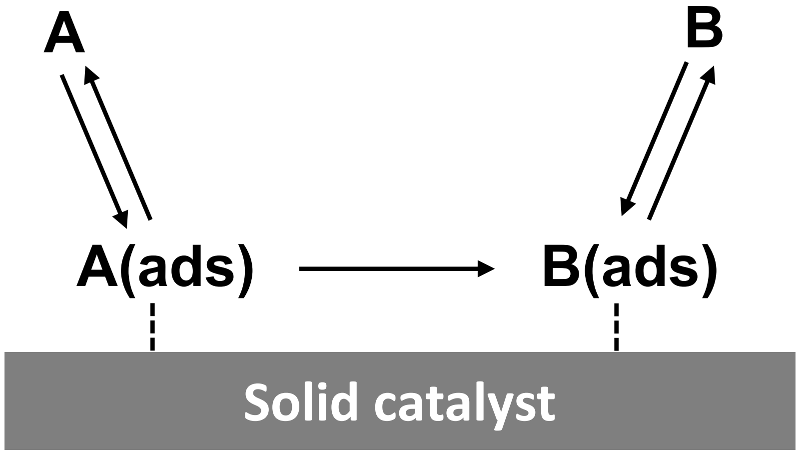
k, ***n***, Freundlich constant

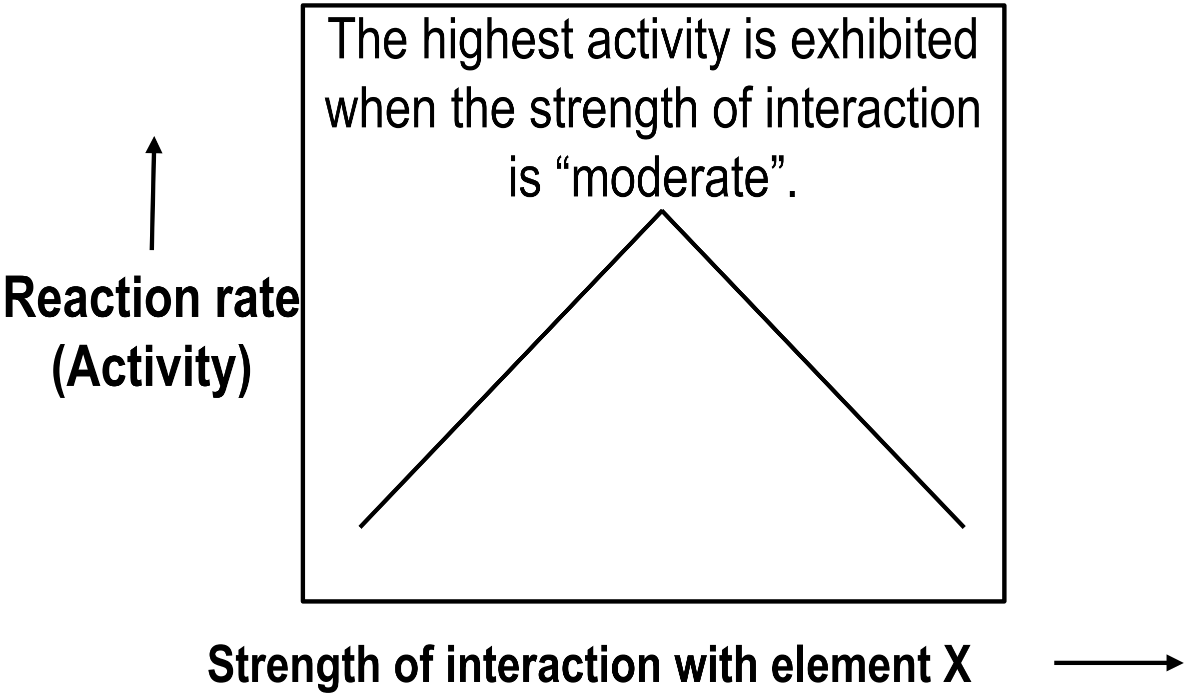
***C*$_A$**, Equilibrium concentration of adsorbate

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.



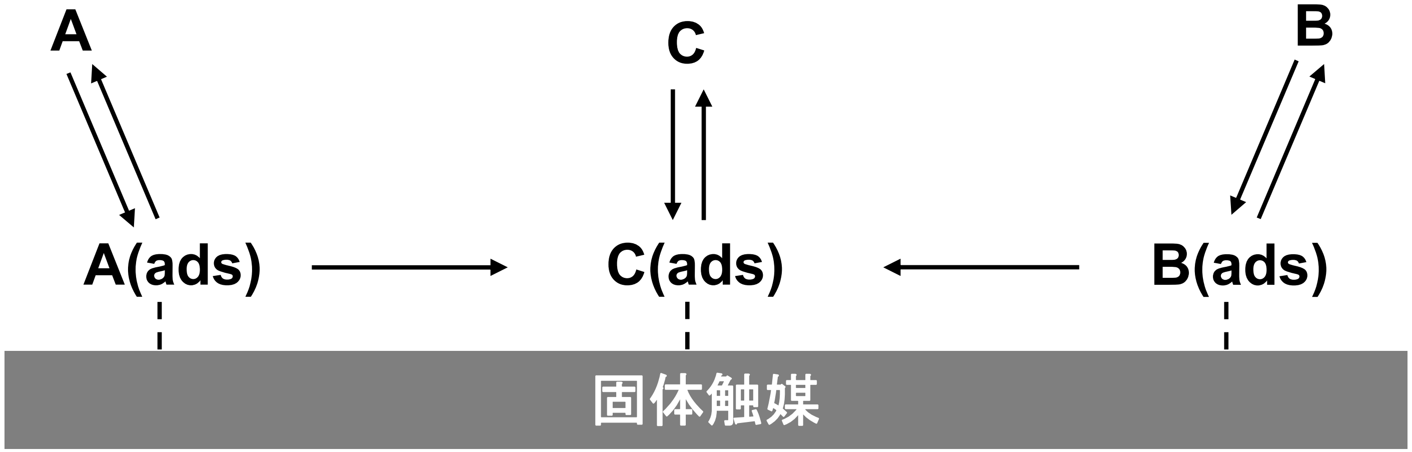


The highest activity is exhibited when the strength of interaction is “moderate”.

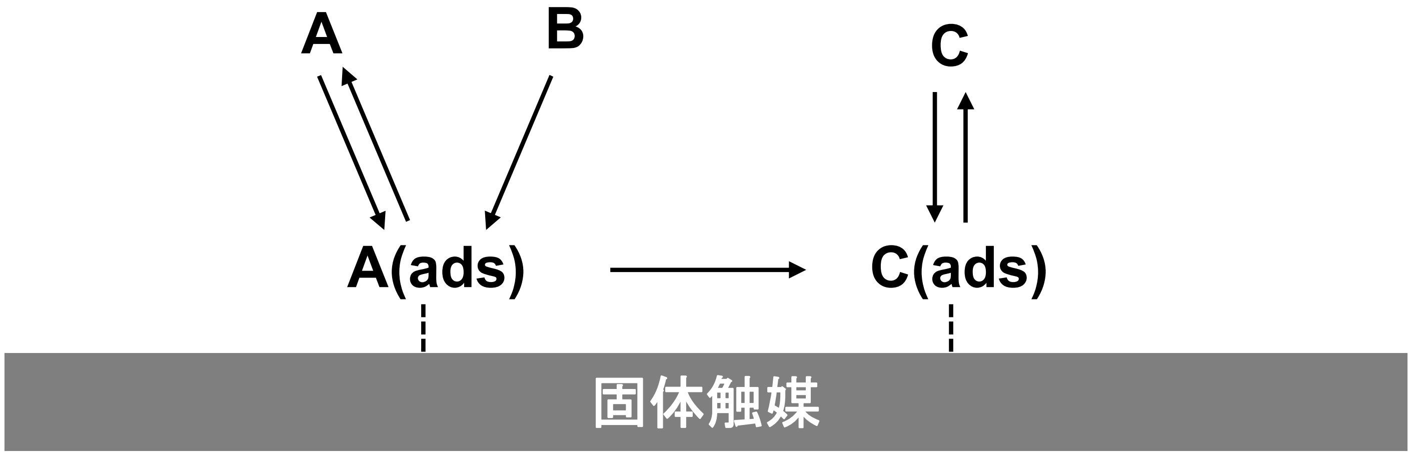
Intermolecular Reaction Mechanism Considering Adsorption: L-H and E-R Mechanism

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.

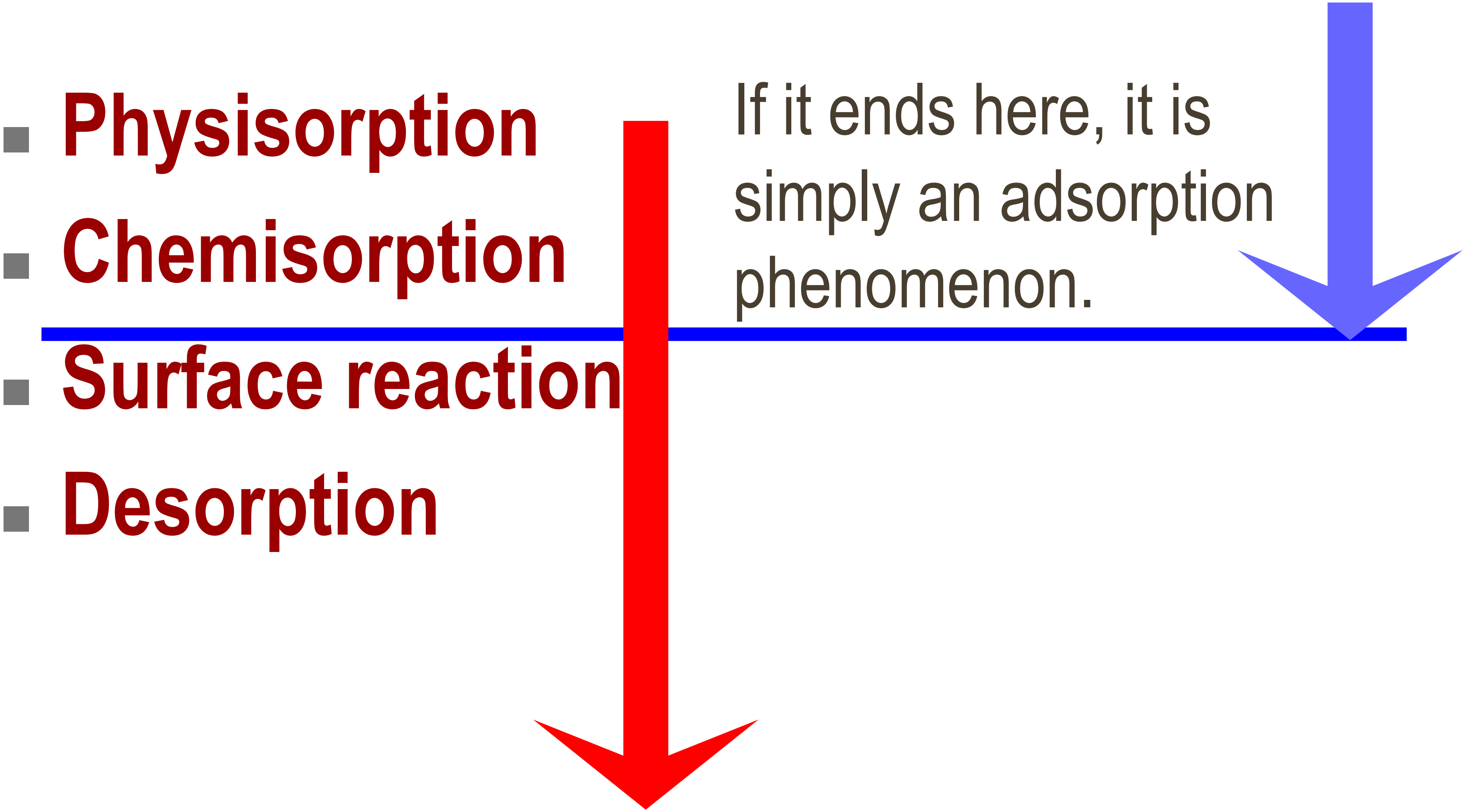


2. Eley-Rideal mechanism: B collides with A, adsorbed and activated on the catalyst, and then reacted.



From adsorption to catalytic reaction

Catalytic reaction



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

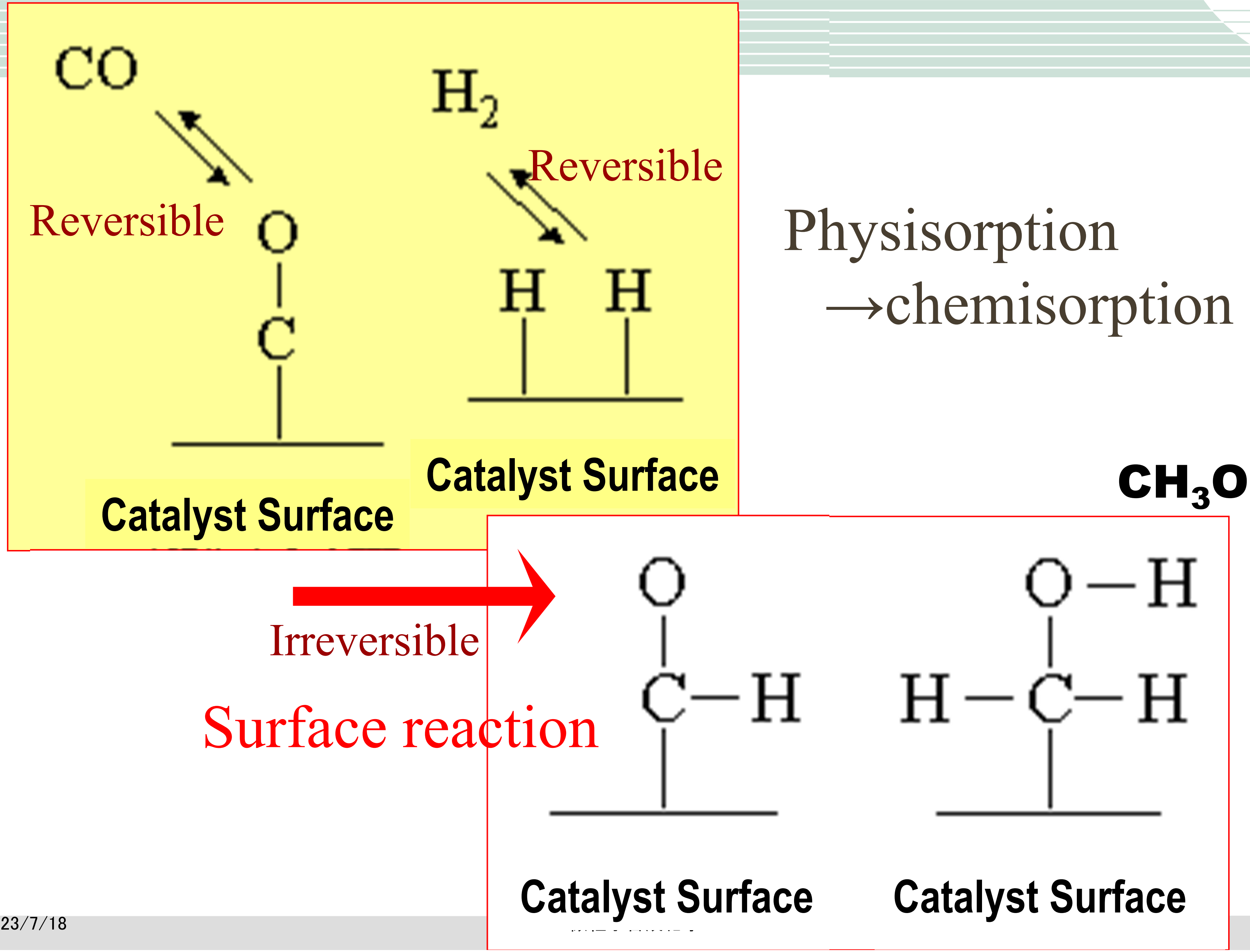
If it ends here, it is simply an adsorption phenomenon.

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.



Reversible

Reversible

Catalyst Surface

Catalyst Surface

Physisorption
→chemisorption

CH_3OH

Irreversible

Surface reaction

Catalyst Surface

Catalyst Surface

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

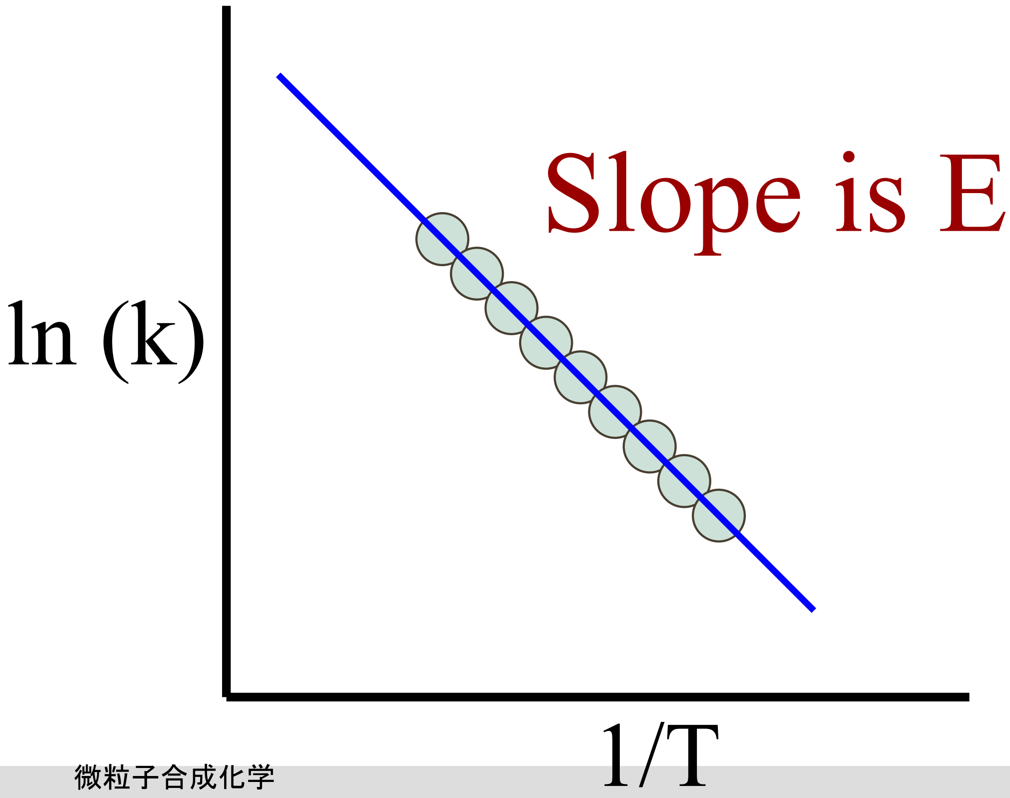
  Reaction rate constant *k*

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

- 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.

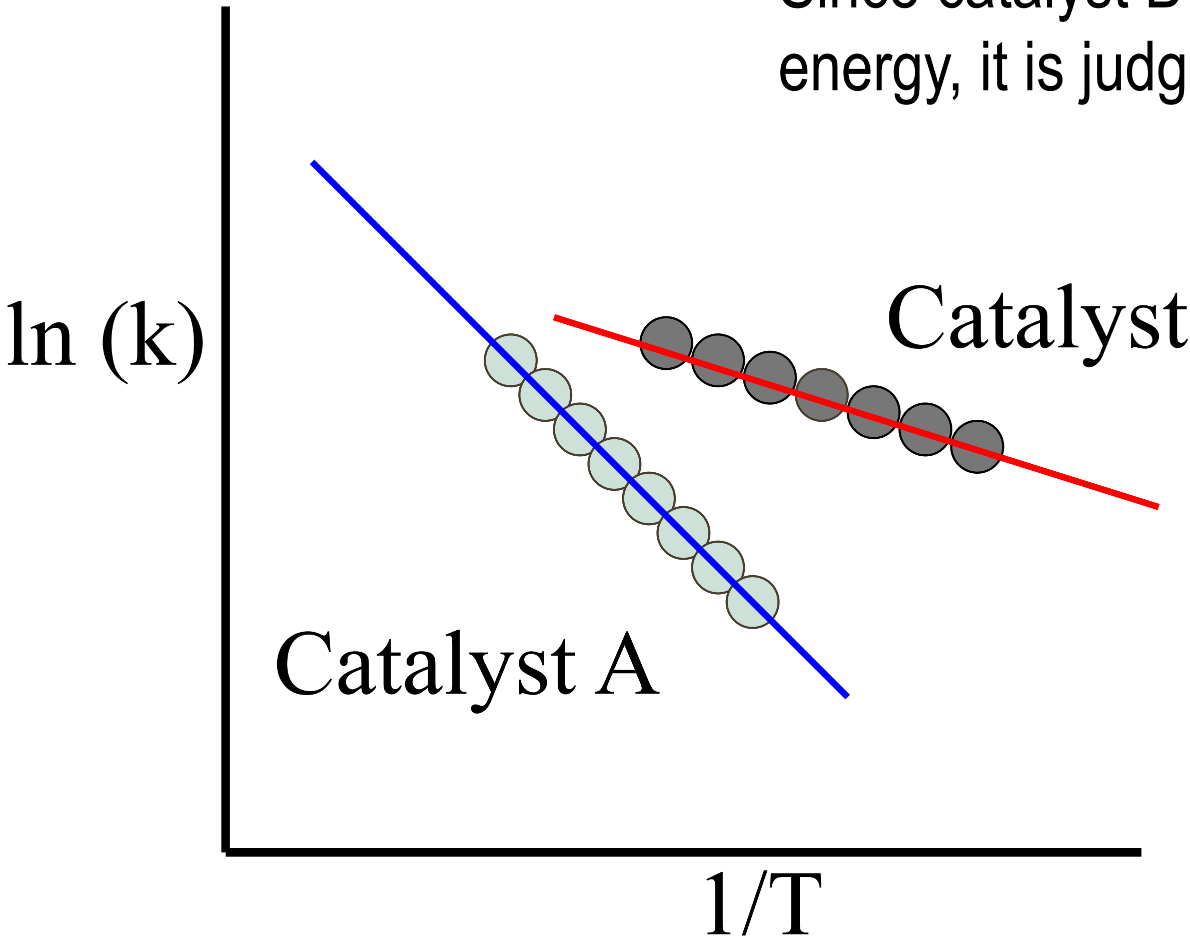
Apparent activation energy

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

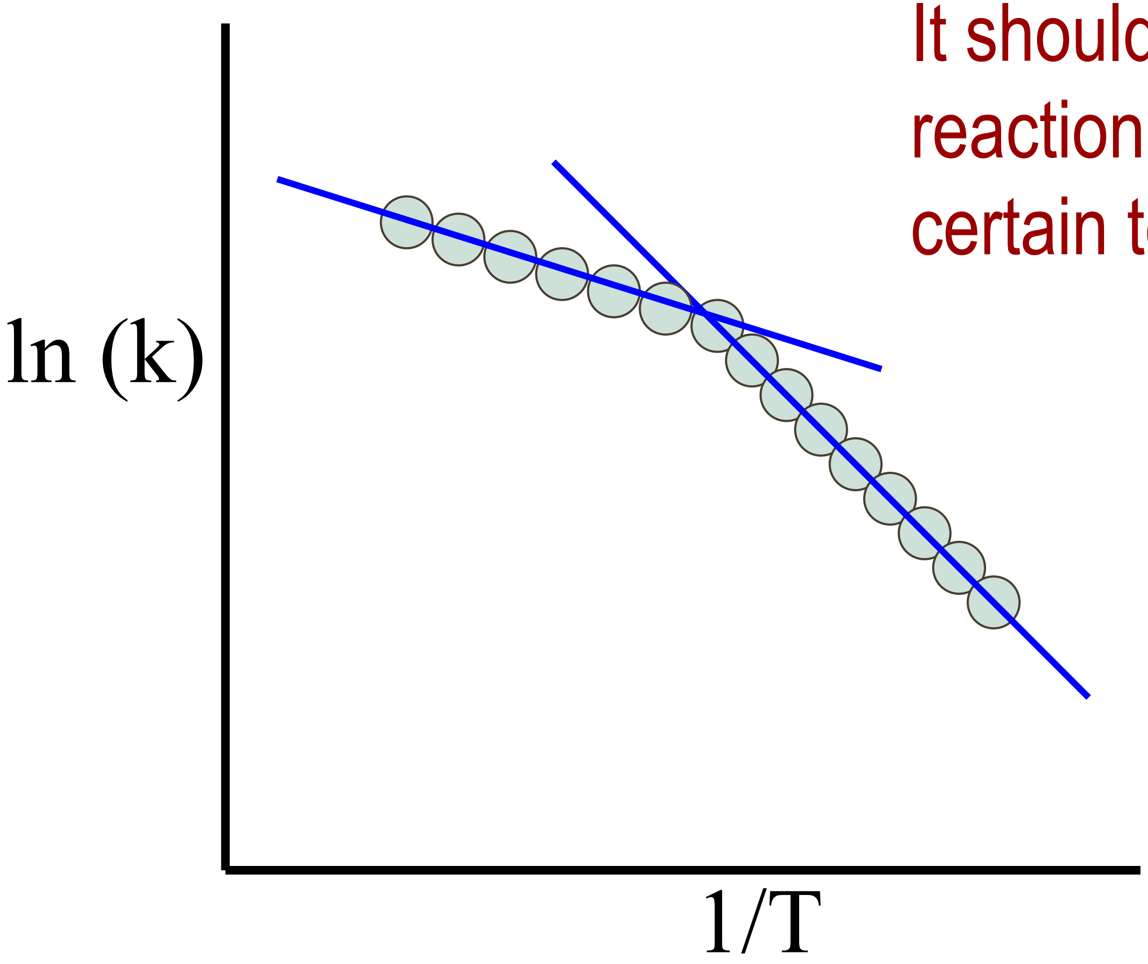


Working of catalyst

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

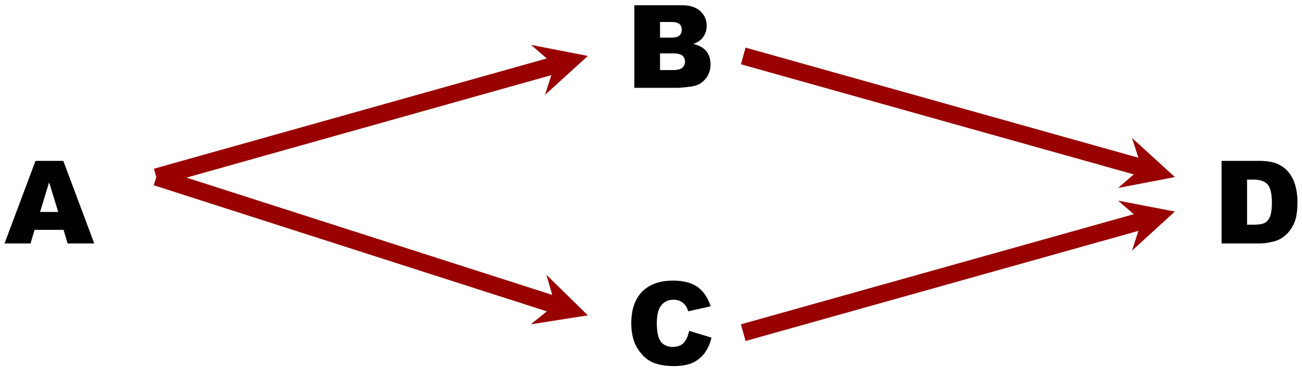


Change the activation energy?



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

Reaction paths



B

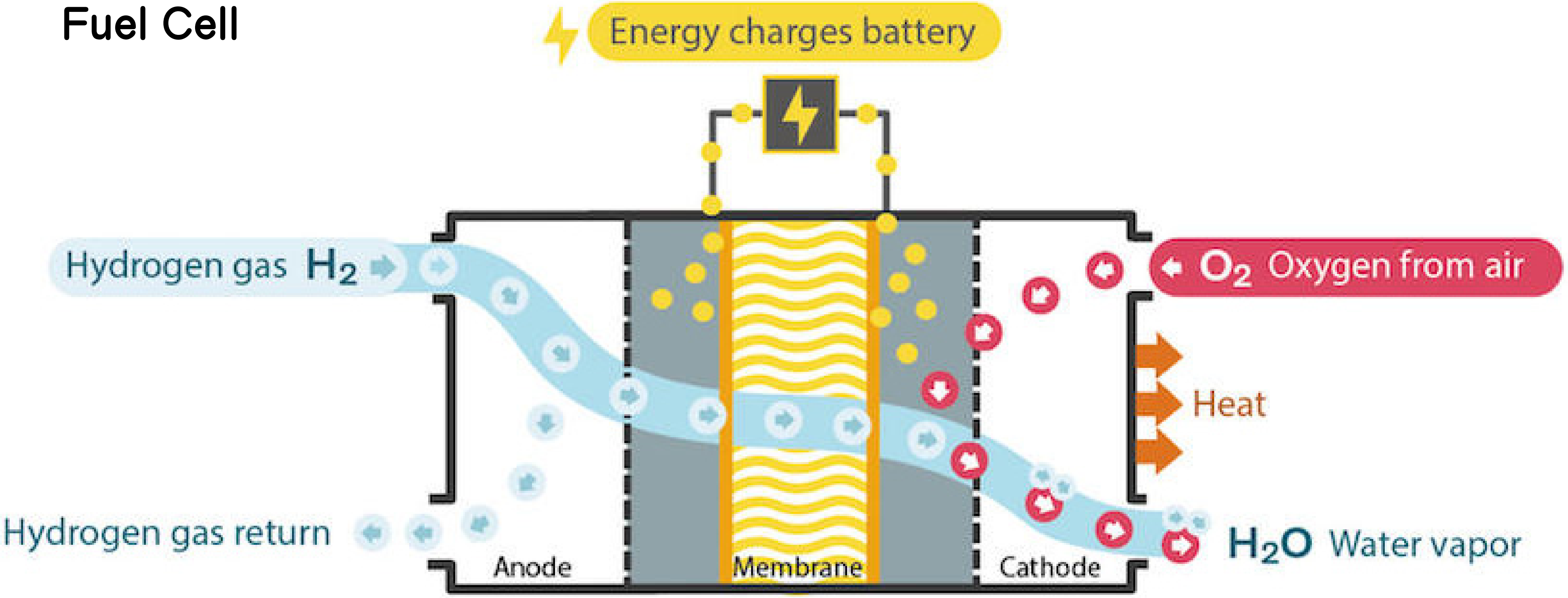
A D

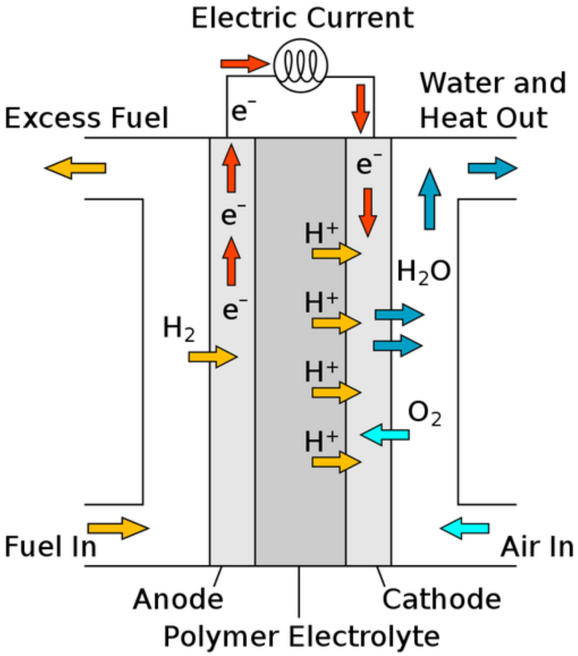
C

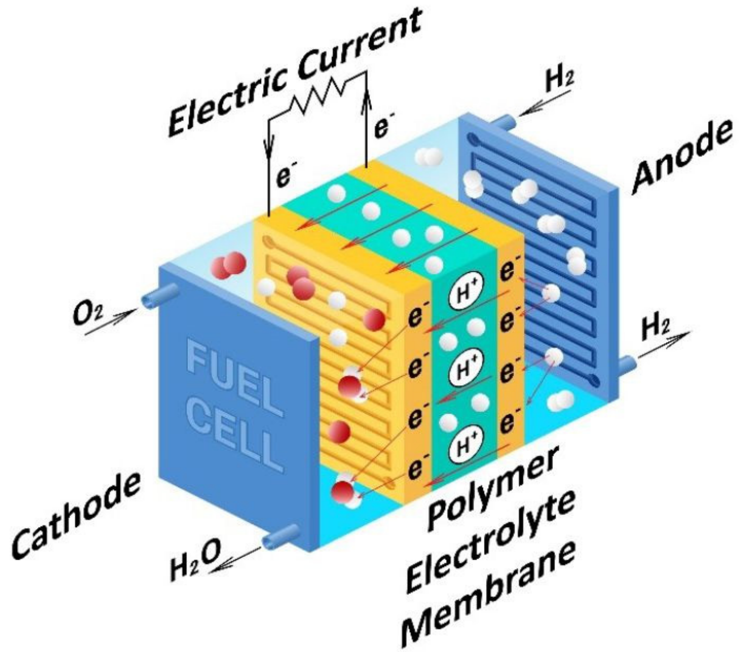
When the rate-limiting step changes, the activation energy changes.

Catalysts contribute to society

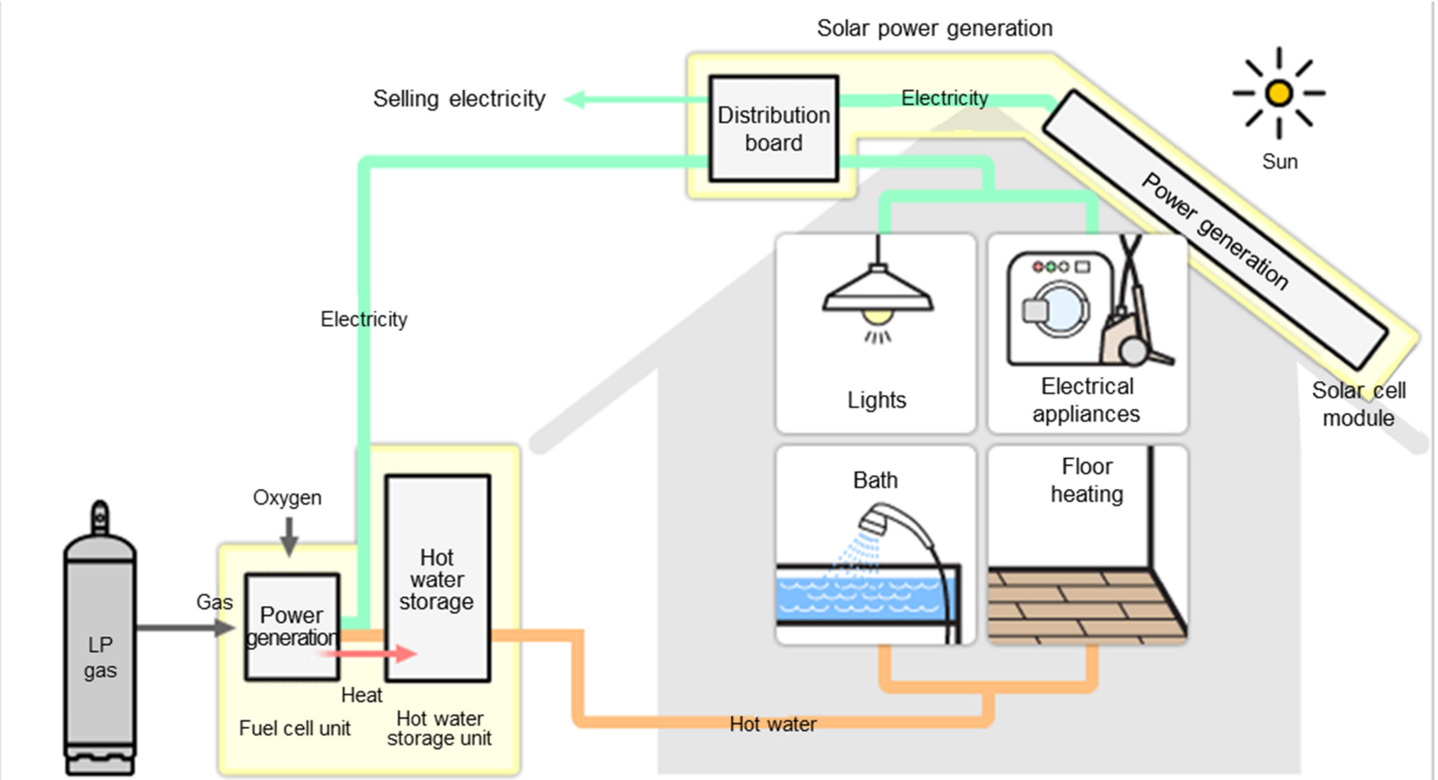
Fuel Cell


Energy charges battery
Hydrogen gas H2
O2 Oxygen from air
Heat
Hydrogen gas return
H2O Water vapor
Anode
Membrane
Cathode

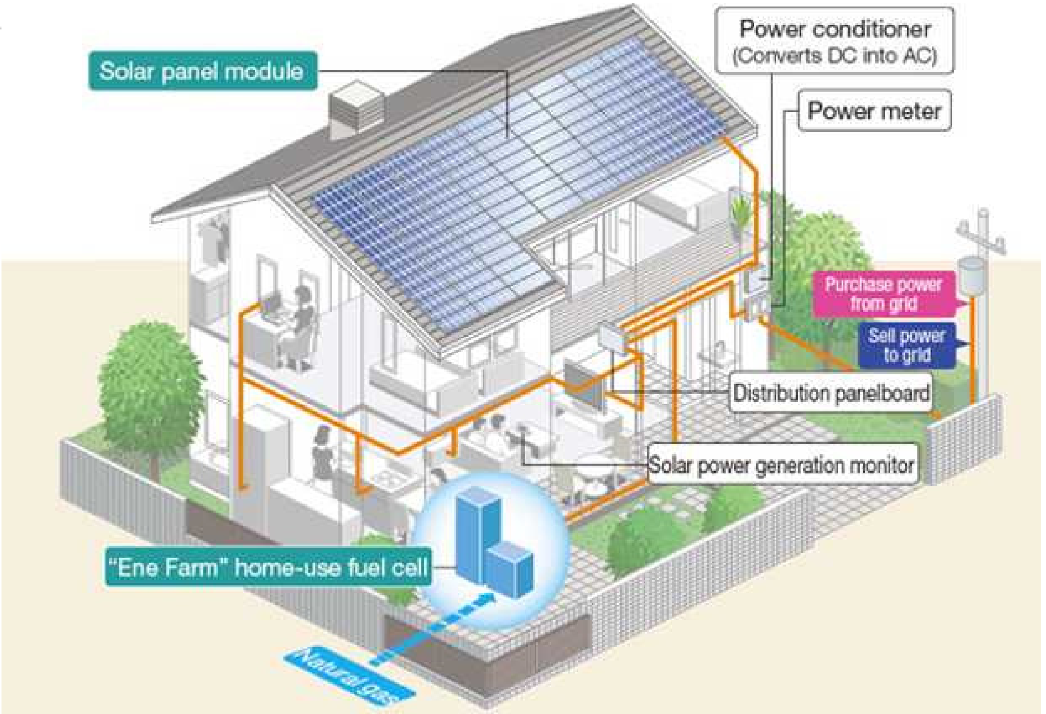

Electric Current
e-
Excess Fuel
Water and Heat Out
e-
e-
e-
H+
H+
H+
H+
H2O
H2
O2
Fuel In
Air In
Anode
Cathode
Polymer Electrolyte

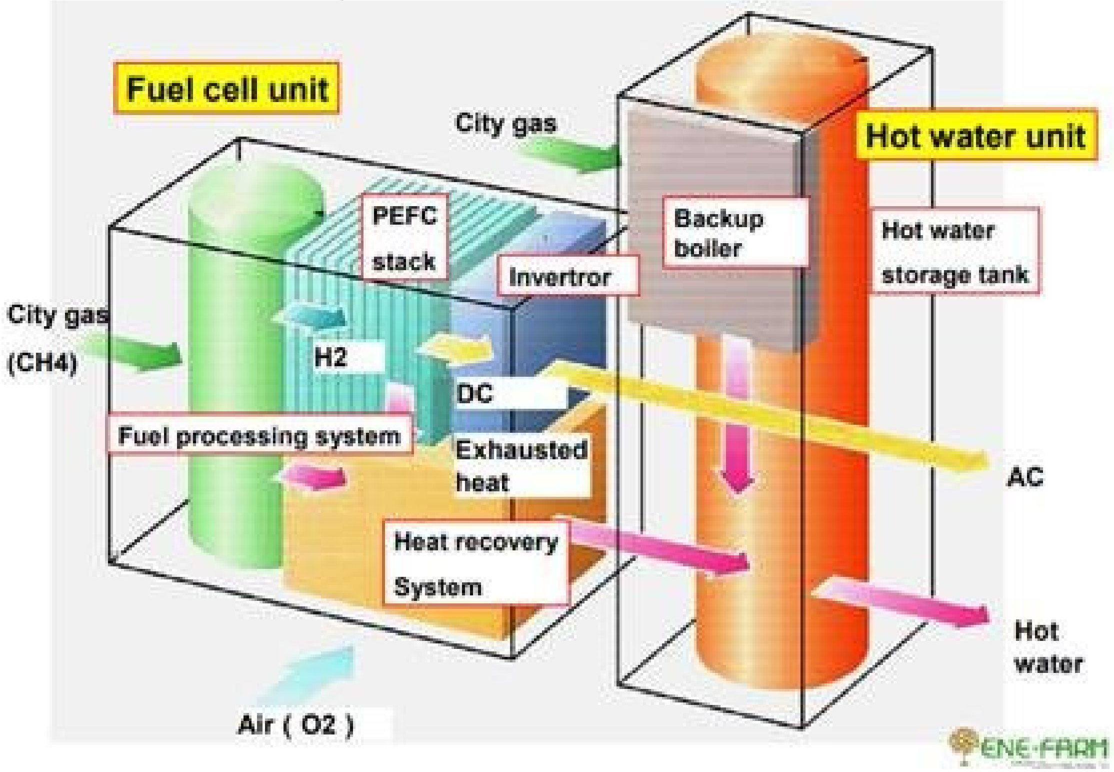

Electric Current
e-
e-
H2
Anode
O2
H2
FUEL CELL
e-
H+
Cathode
H2O
Polymer Electrolyte Membrane

ENE-FARM

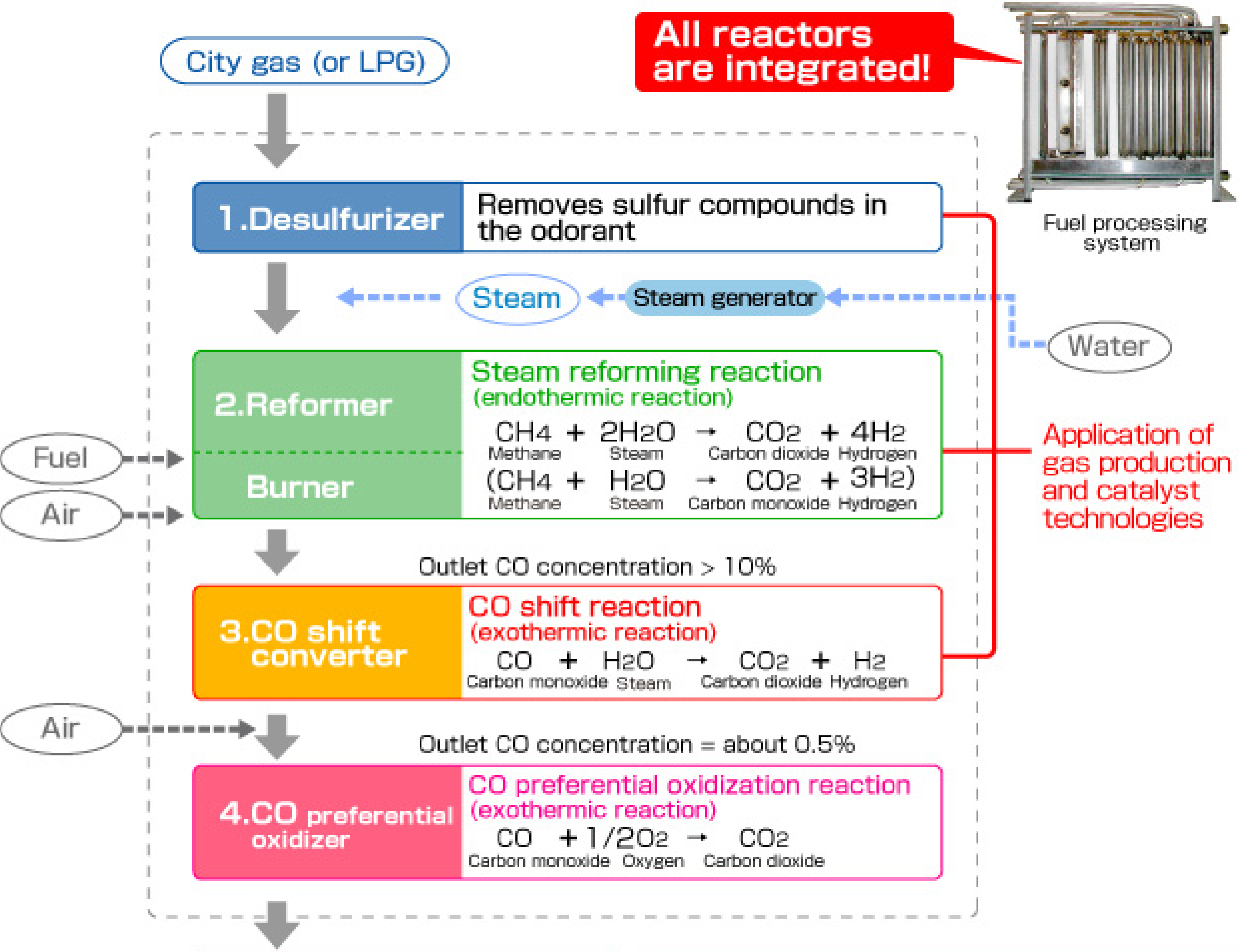


ENEFARM





Catalytic reactions in ENE-FARM



City gas (or LPG)

All reactors are integrated!

Fuel processing system

1.Desulfurizer Removes sulfur compounds in the odorant

Steam ← Steam generator ← Water

2.Reformer / **Burner**

Fuel

Air

Steam reforming reaction (endothermic reaction)

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

Methane Steam Carbon dioxide Hydrogen

$(CH_4 + H_2O \rightarrow CO_2 + 3H_2)$

Methane Steam Carbon monoxide Hydrogen

Outlet CO concentration > 10%

3.CO shift converter

CO shift reaction (exothermic reaction)

$CO + H_2O \rightarrow CO_2 + H_2$

Carbon monoxide Steam Carbon dioxide Hydrogen

Air

Outlet CO concentration = about 0.5%

4.CO preferential oxidizer

CO preferential oxidization reaction (exothermic reaction)

$CO + 1/2O_2 \rightarrow CO_2$

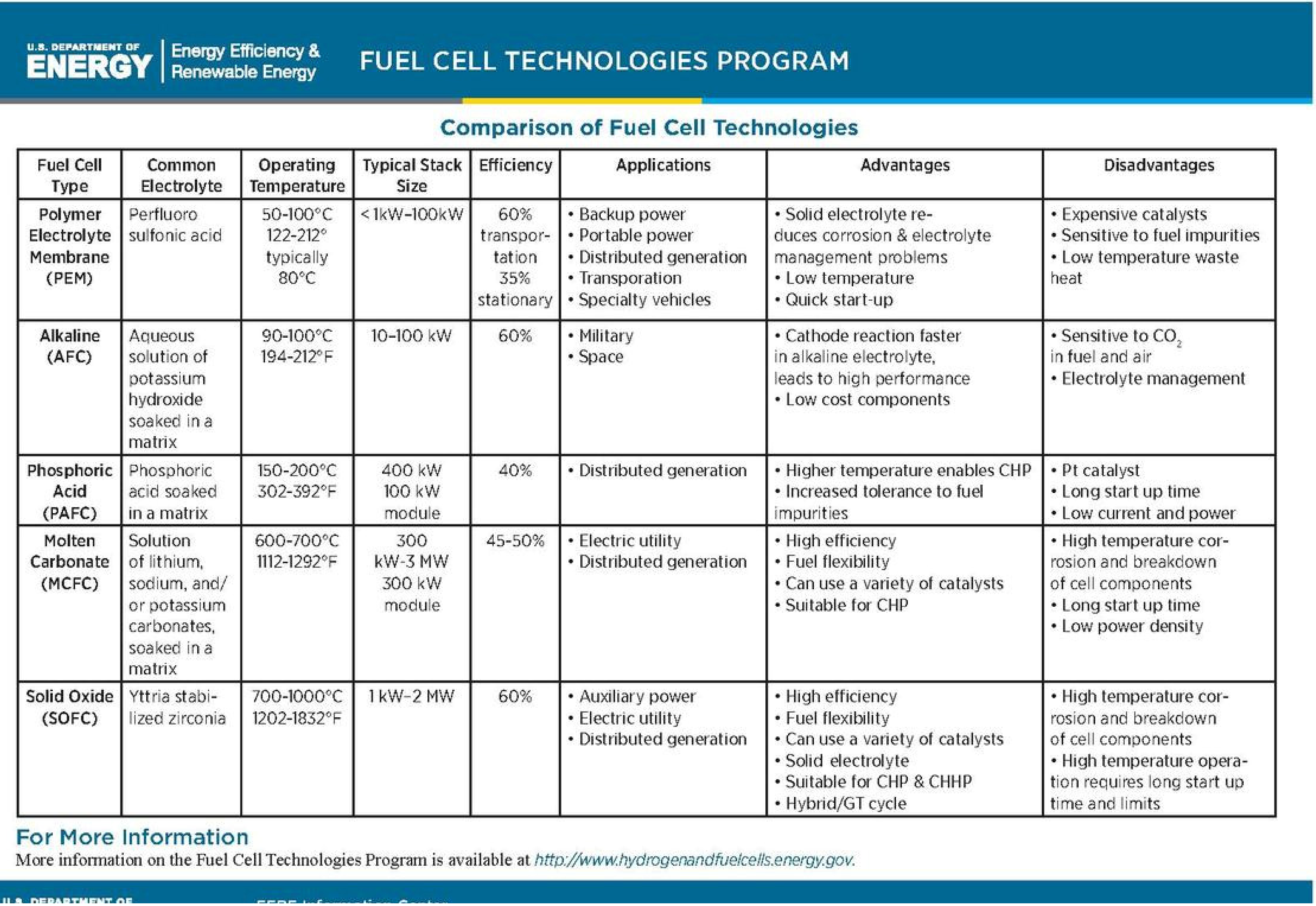
Carbon monoxide Oxygen Carbon dioxide

Application of gas production and catalyst technologies

Fuel hydrogen for ENE・FARM

Typical gas composition	H_2=75%	CO_2=20%
	N_2=3%	CH_4=2%

Osaka Gas developed 10 year maintenance free fuel processing system, making use ofcatalyst technology, one of Osaka Gas'core technologies.



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

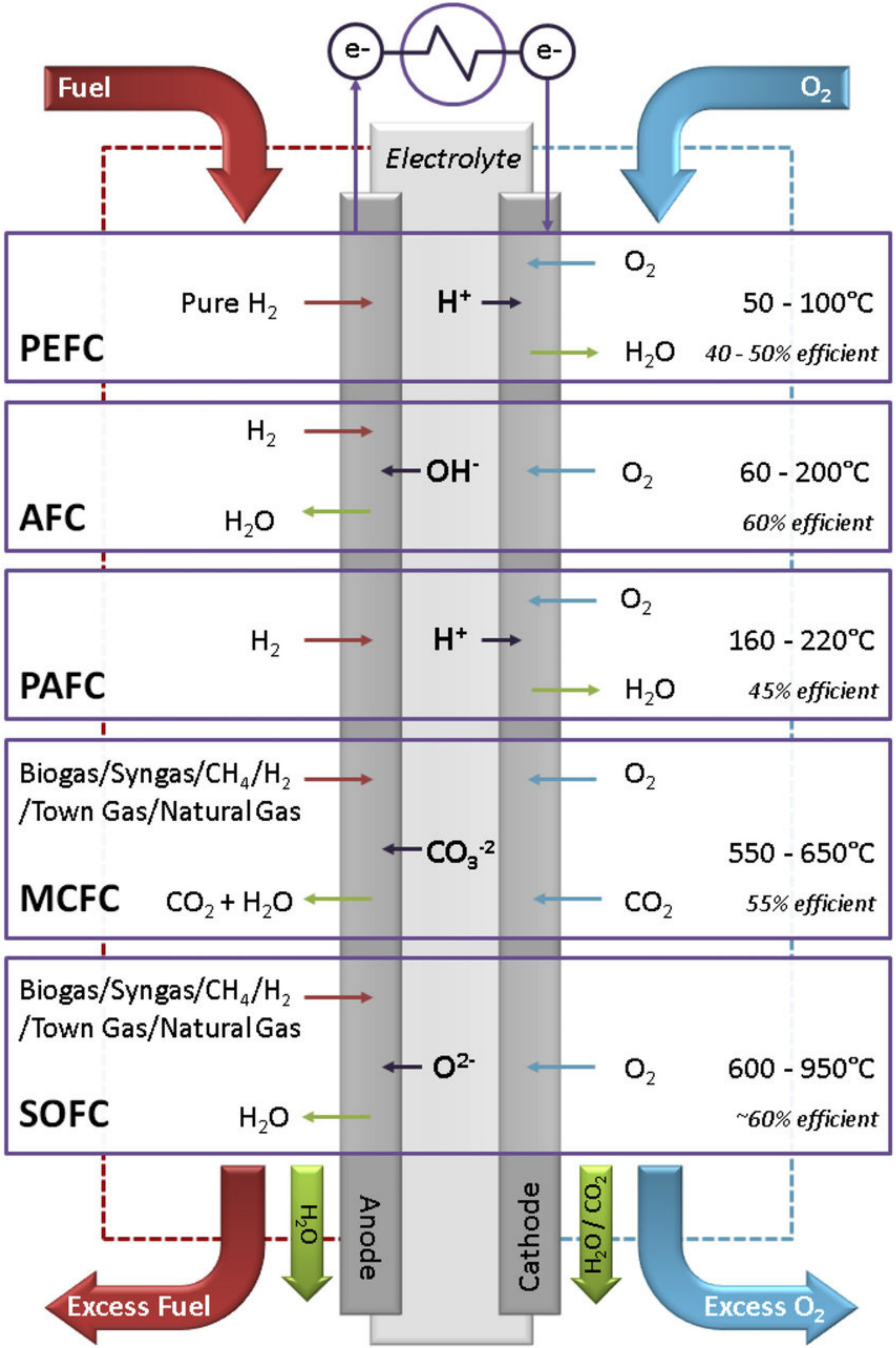
FUEL CELL TECHNOLOGIES PROGRAM

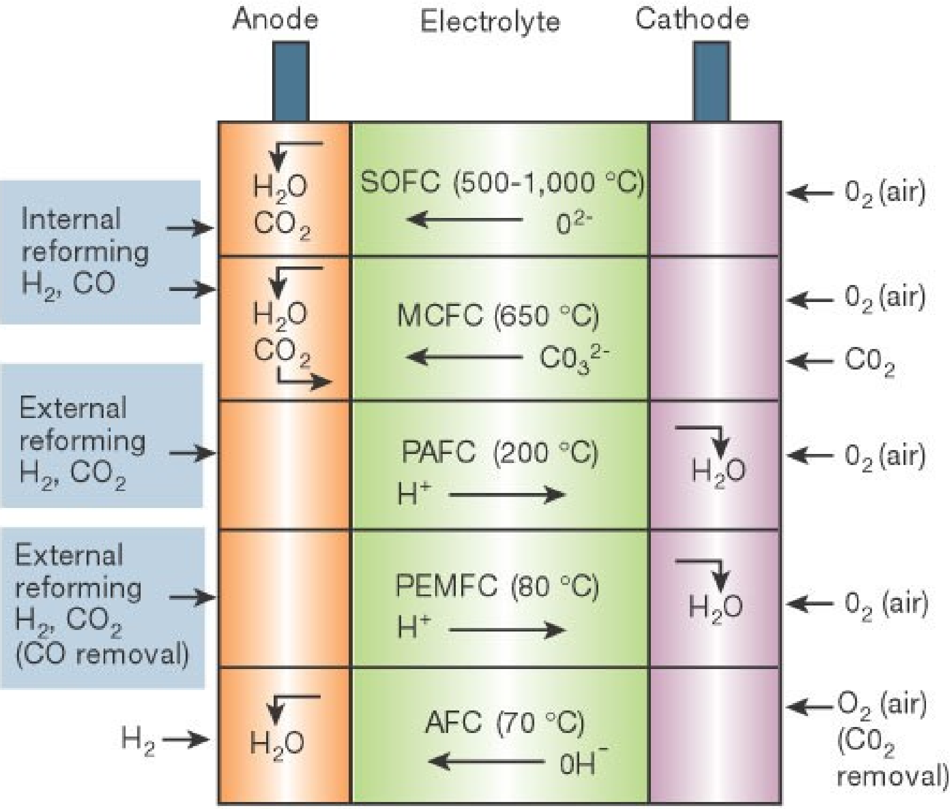
Comparison of Fuel Cell Technologies

Fuel Cell Type	Common Electrolyte	Operating Temperature	Typical Stack Size	Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)	Perfluoro sulfonic acid	50-100°C 122-212° typically 80°C	< 1kW–100kW	60% transportation 35% stationary	• Backup power • Portable power • Distributed generation • Transporation • Specialty vehicles	• Solid electrolyte reduces corrosion & electrolyte management problems • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90-100°C 194-212°F	10–100 kW	60%	• Military • Space	• Cathode reaction faster in alkaline electrolyte, leads to high performance • Low cost components	• Sensitive to CO_2 in fuel and air • Electrolyte management
Phosphoric Acid (PAFC)	Phosphoric acid soaked in a matrix	150-200°C 302-392°F	400 kW 100 kW module	40%	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start up time • Low current and power
Molten Carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600-700°C 1112-1292°F	300 kW-3 MW 300 kW module	45-50%	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Suitable for CHP	• High temperature corrosion and breakdown of cell components • Long start up time • Low power density
Solid Oxide (SOFC)	Yttria stabilized zirconia	700-1000°C 1202-1832°F	1 kW–2 MW	60%	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalysts • Solid electrolyte • Suitable for CHP & CHHP • Hybrid/GT cycle	• High temperature corrosion and breakdown of cell components • High temperature operation requires long start up time and limits

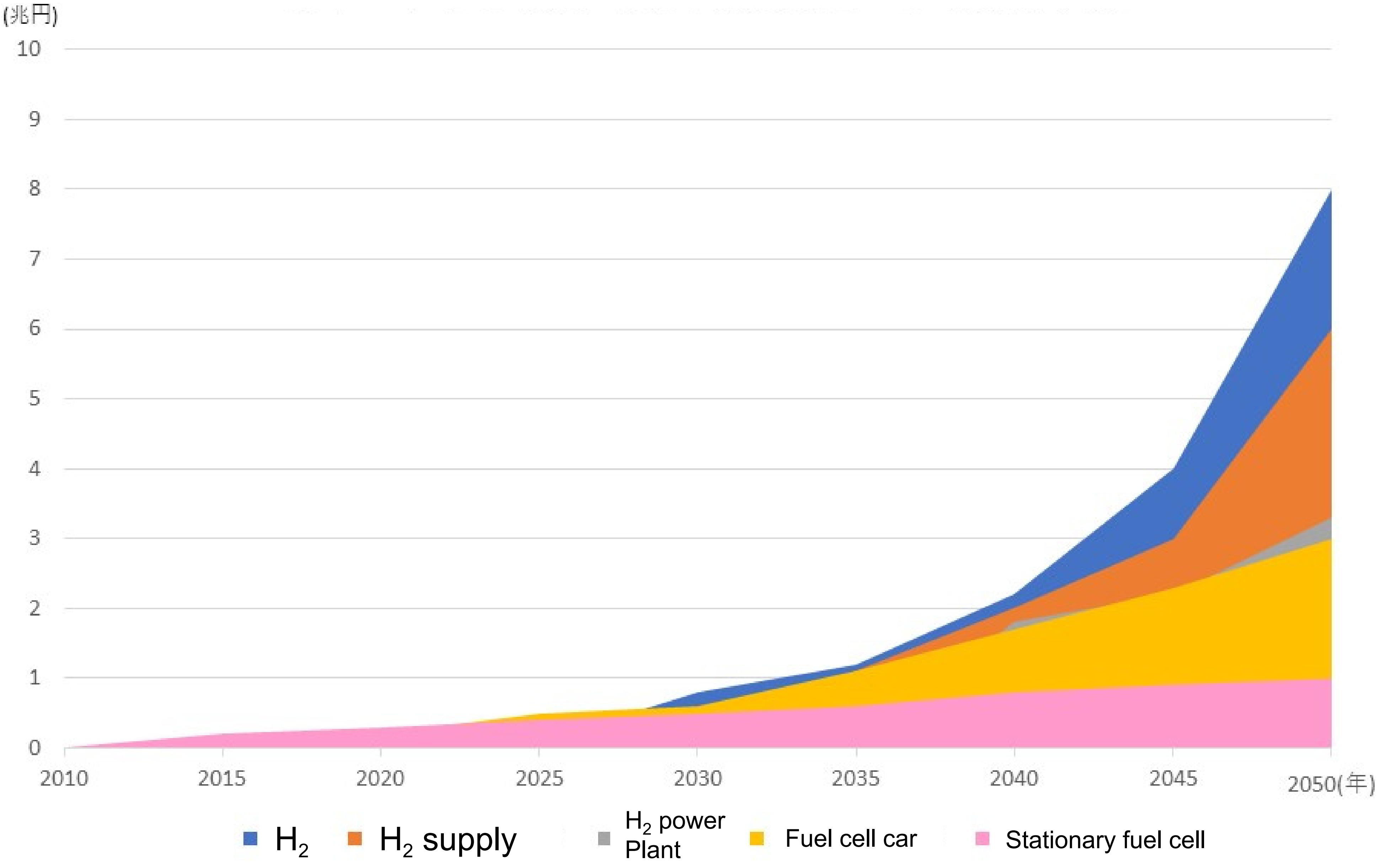
For More Information

More information on the Fuel Cell Technologies Program is available at *http://www.hydrogenandfuelcells.energy.gov.*

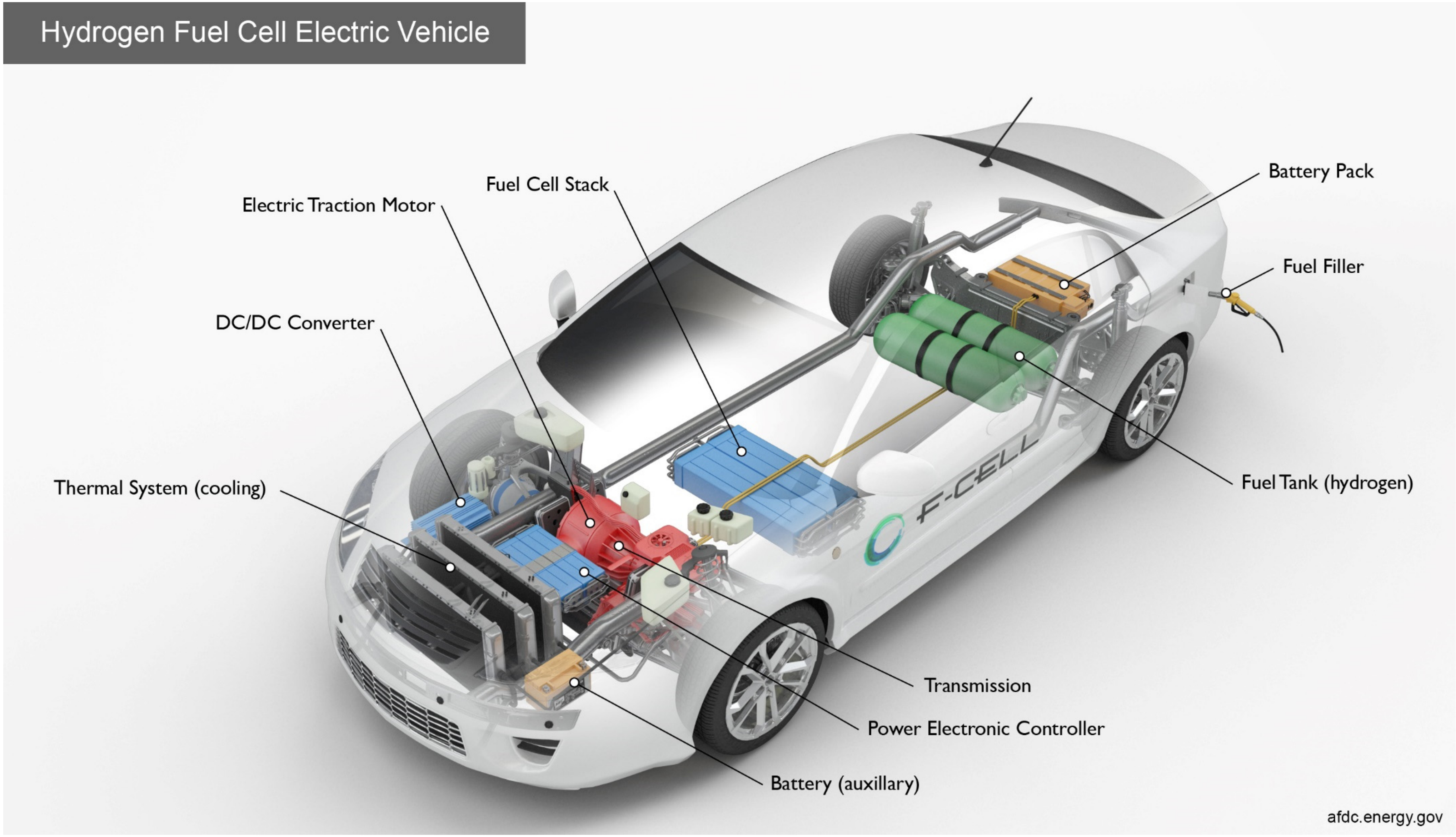

e-
e-
Fuel
O$_2$
Electrolyte
PEFC
Pure H$_2$
H$^+$
O$_2$
50 - 100°C
H$_2$O
40 - 50% efficient
AFC
H$_2$
OH$^-$
O$_2$
60 - 200°C
H$_2$O
60% efficient
PAFC
H$_2$
H$^+$
O$_2$
160 - 220°C
H$_2$O
45% efficient
MCFC
Biogas/Syngas/CH$_4$/H$_2$ /Town Gas/Natural Gas
CO$_3^{-2}$
O$_2$
550 - 650°C
CO$_2$ + H$_2$O
CO$_2$
55% efficient
SOFC
Biogas/Syngas/CH$_4$/H$_2$ /Town Gas/Natural Gas
O^{2-}
O$_2$
600 - 950°C
H$_2$O
~60% efficient
H$_2$O
Anode
Cathode
H$_2$O / CO$_2$
Excess Fuel
Excess O$_2$


Anode
Electrolyte
Cathode
Internal reforming H$_2$, CO
H$_2$O CO$_2$
SOFC (500-1,000 °C)
O^{2-}
O$_2$ (air)
H$_2$O CO$_2$
MCFC (650 °C)
CO$_3^{2-}$
O$_2$ (air)
CO$_2$
External reforming H$_2$, CO$_2$
PAFC (200 °C)
H$^+$
H$_2$O
O$_2$ (air)
External reforming H$_2$, CO$_2$ (CO removal)
PEMFC (80 °C)
H$^+$
H$_2$O
O$_2$ (air)
H$_2$
H$_2$O
AFC (70 °C)
OH$^-$
O$_2$ (air) (CO$_2$ removal)

Market size forecast for hydrogen and fuel cells in Japan

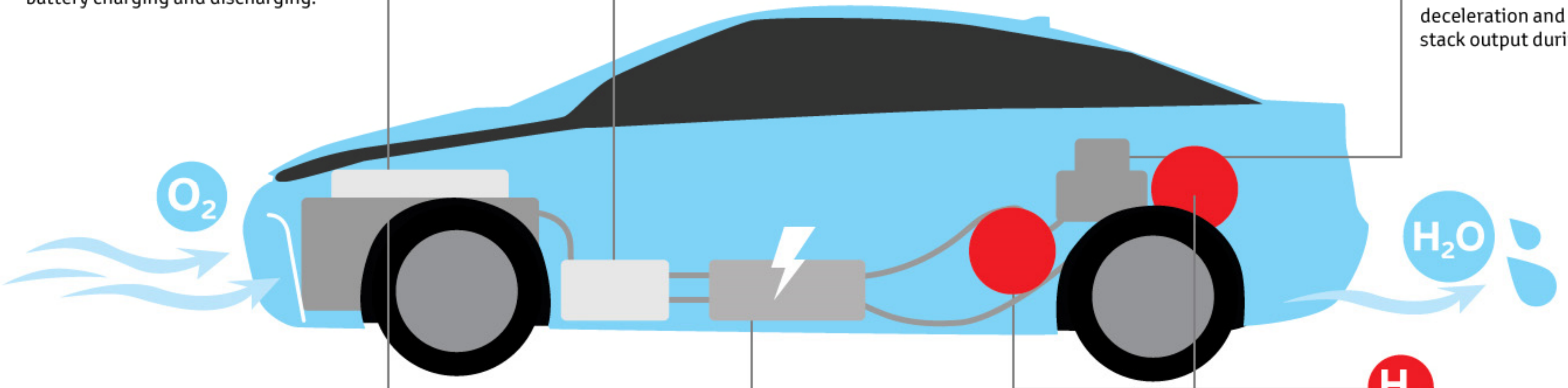


Fuel cell vehicle



afdc.energy.gov

Fuel cell electric technology explained



POWER CONTROL UNIT
A mechanism to optimally control both fuel cell stack output under various operational conditions and drive battery charging and discharging.

FUEL CELL BOOST CONVERTER
A compact, high-efficiency, high-capacity converter newly developped to boost fuel cell stack voltage to 650 V.
A boost converter is used to obtain an output with higher voltage than the input.

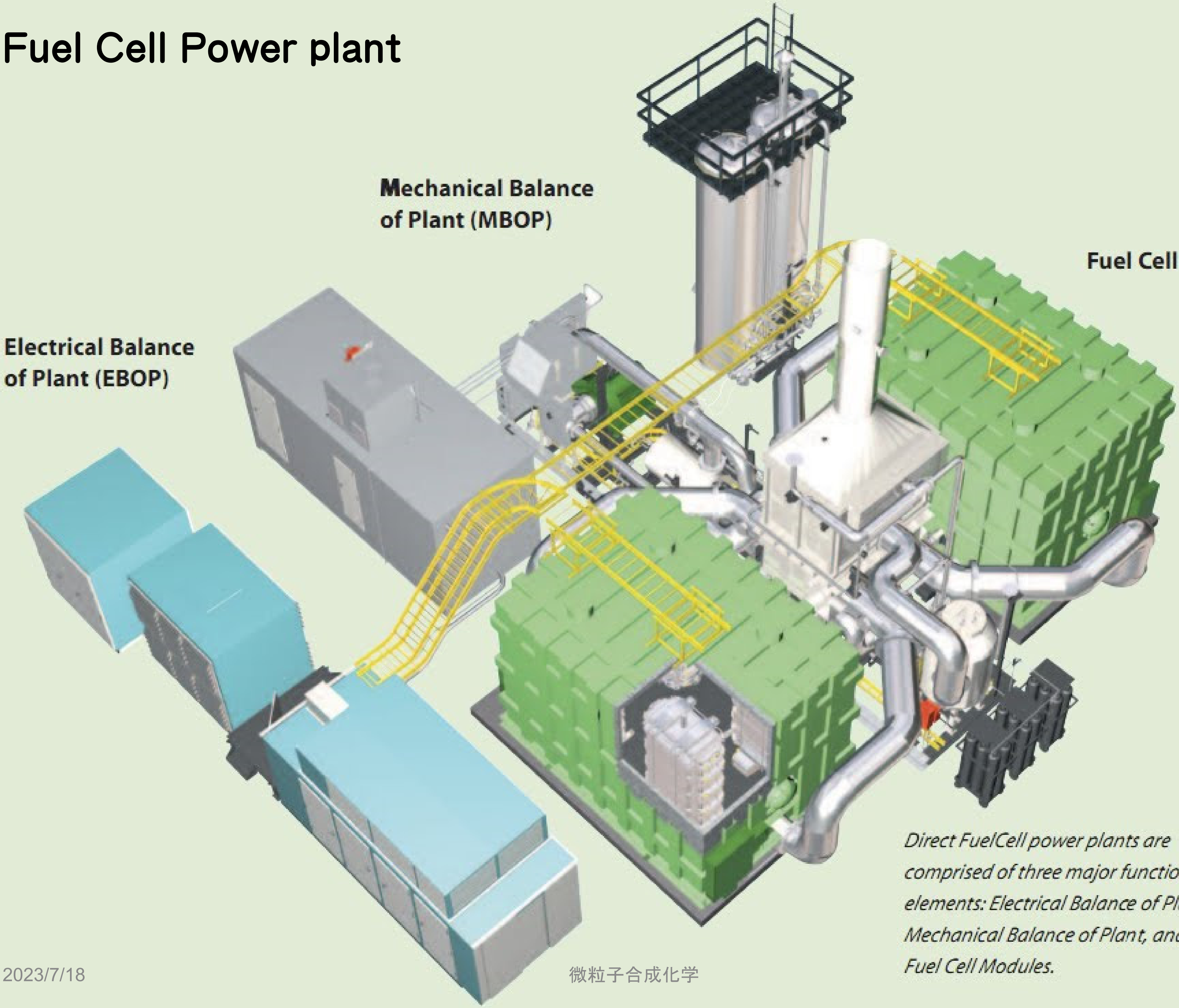
BATTERY
A nickel-metal hydride battery which stores energy recovered from deceleration and assists fuel cell stack output during acceleration.

MOTOR
Motor driven by electricity generated by fuel cell stack and supplied by battery.
Maximum output: 113 kW (154 DIN hp)
Maximum torque: 335 N•m

FUEL CELL STACK
Toyota's first mass-production fuel cell, featuring a compact size and world top level output density.
Volume power density: 3.1 kW/L
Maximum output: 114 kW (155 DIN hp)

HIGH-PRESSURE HYDROGEN TANKS
Tank storing hydrogen as fuel. The nominal working pressure is a high pressure level of 70 MPa (700 bar).
The compact, lightweight tanks feature world's top level tank storage density.
Tank storage density: 5.7 wt%

Fuel Cell Power plant

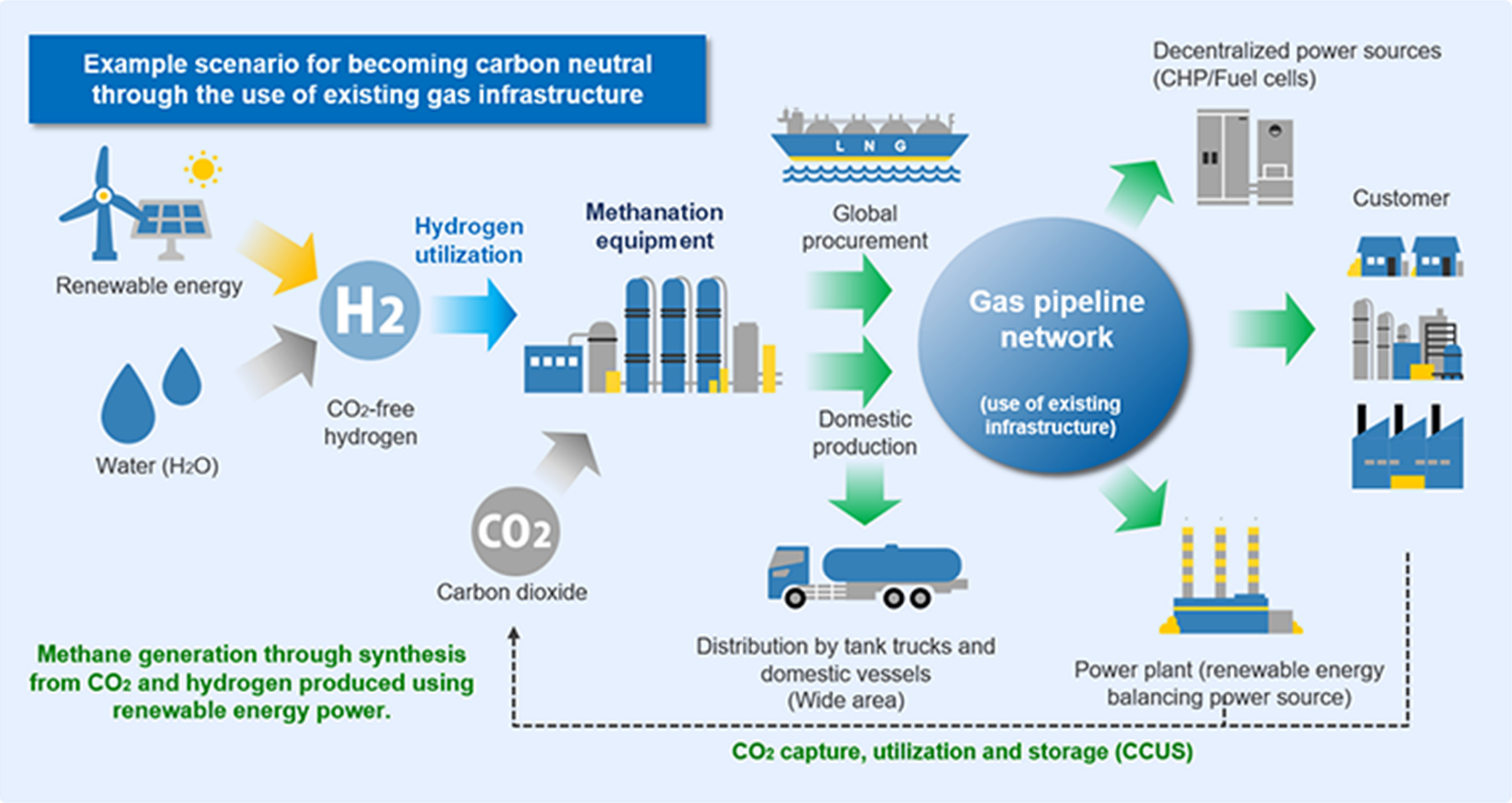


Direct FuelCell power plants are comprised of three major functional elements: Electrical Balance of Plant, Mechanical Balance of Plant, and Fuel Cell Modules.

Fuel Cell Power plant in South Korea

e-methane

Methanation technology and CO_2 emissions



e-methane

Methane production (methanation) technology

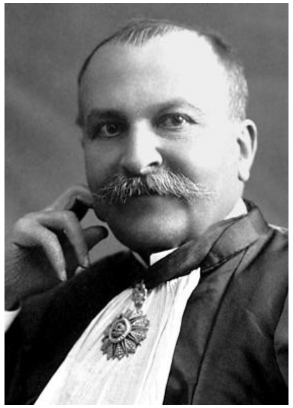
$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H = -165\ \mathrm{kJ/mol}\ (298\mathrm{K})$$

● 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.

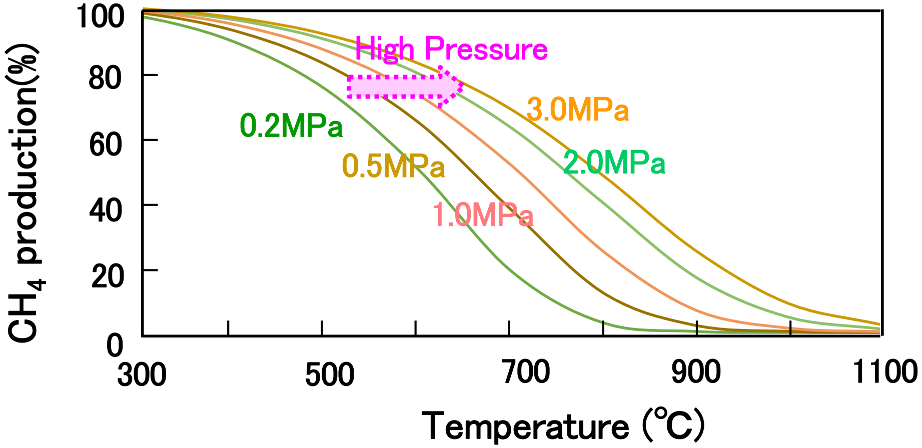
● Ni-based and Ru-based catalysts are often used as catalysts.

● 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.



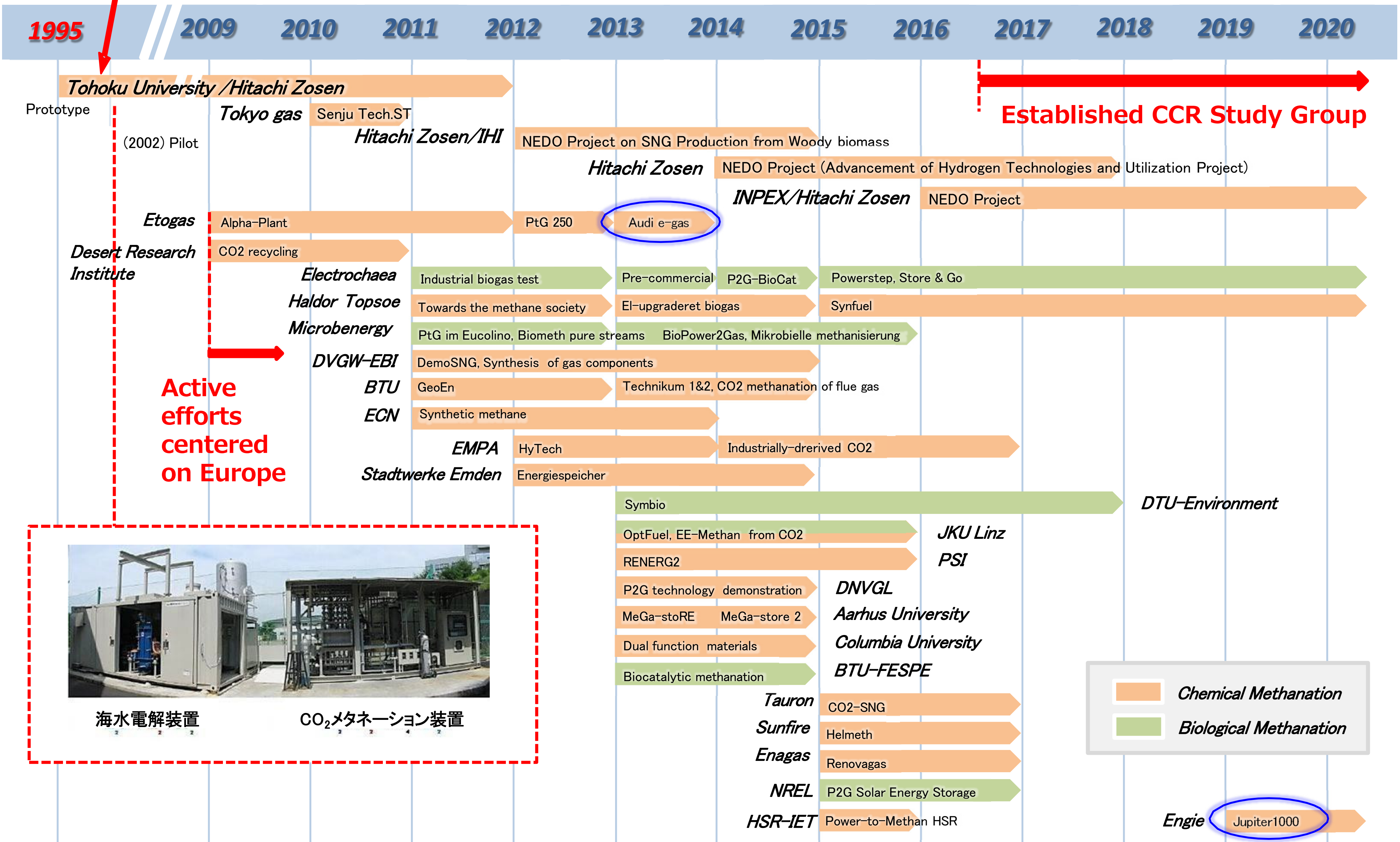
Paul Sabatier
(1912 Nobel Prize in Chemistry)



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)



Tohoku University /Hitachi Zosen

Prototype

(2002) Pilot

Tokyo gas Senju Tech.ST

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

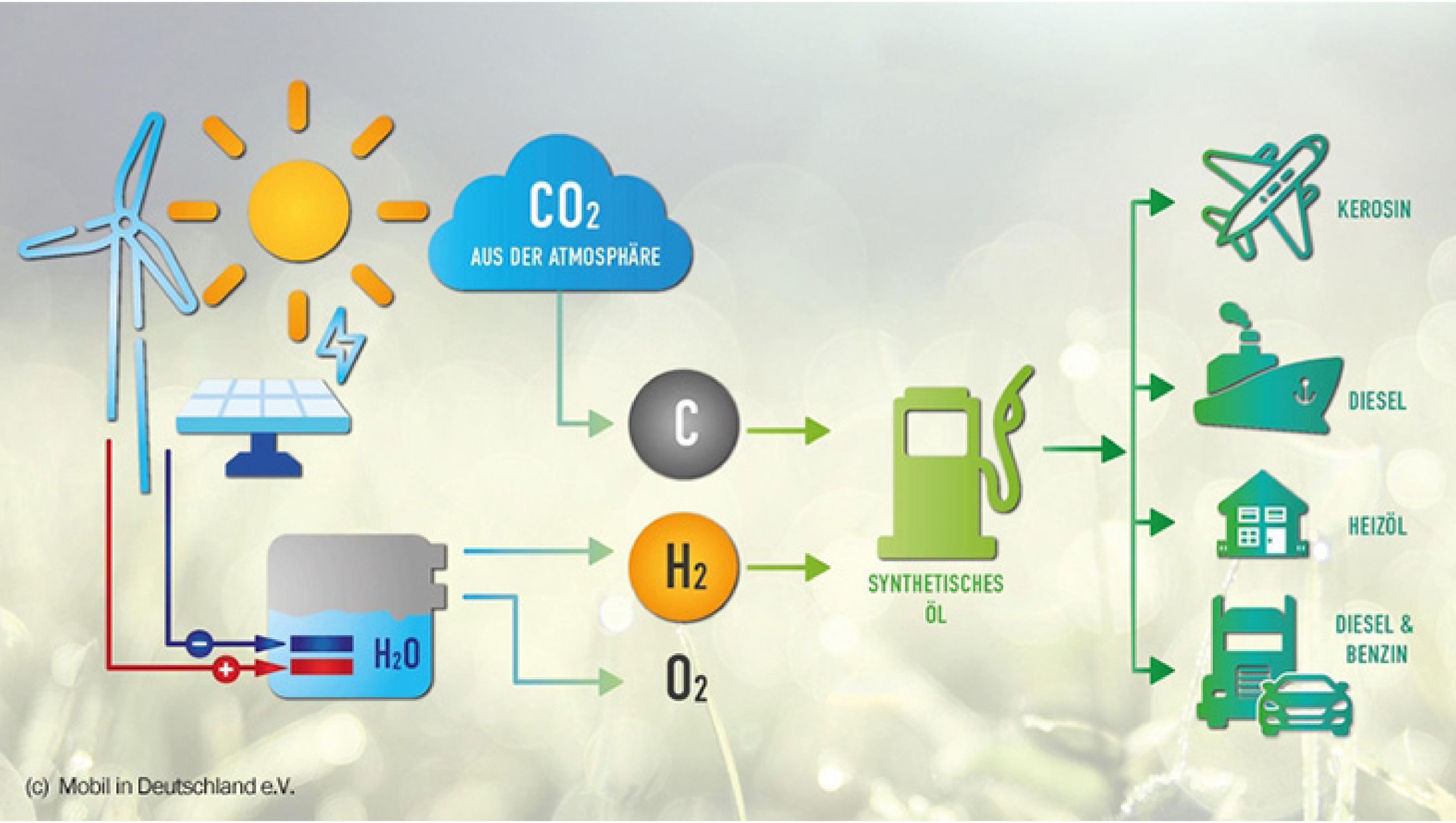
海水電解装置　　CO$_2$メタネーション装置

🟧 *Chemical Methanation*

🟩 *Biological Methanation*

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

e-fuel



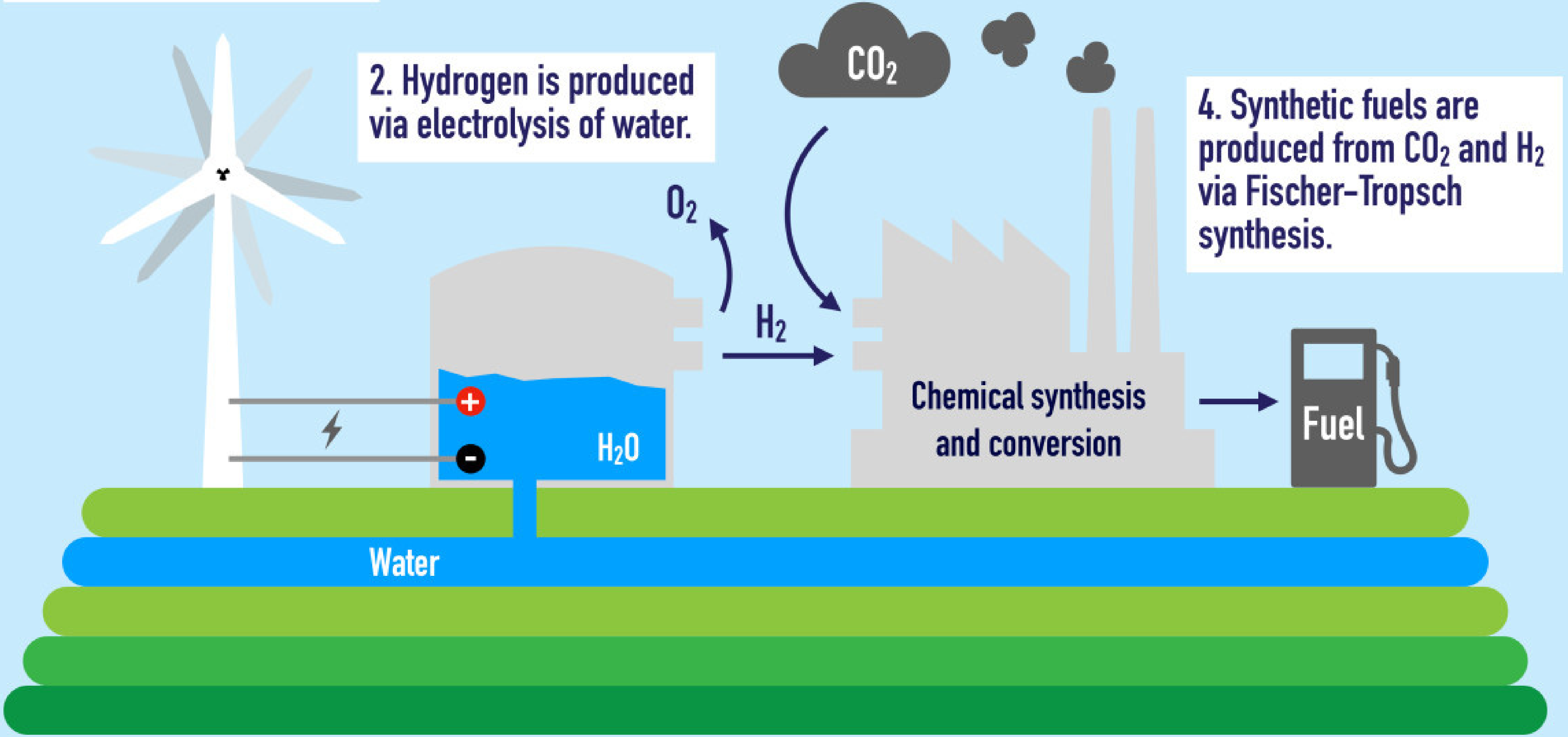
(c) Mobil in Deutschland e.V.

e-fuel

How synthetic fuels are produced

1. Electricity is obtained from renewable sources.

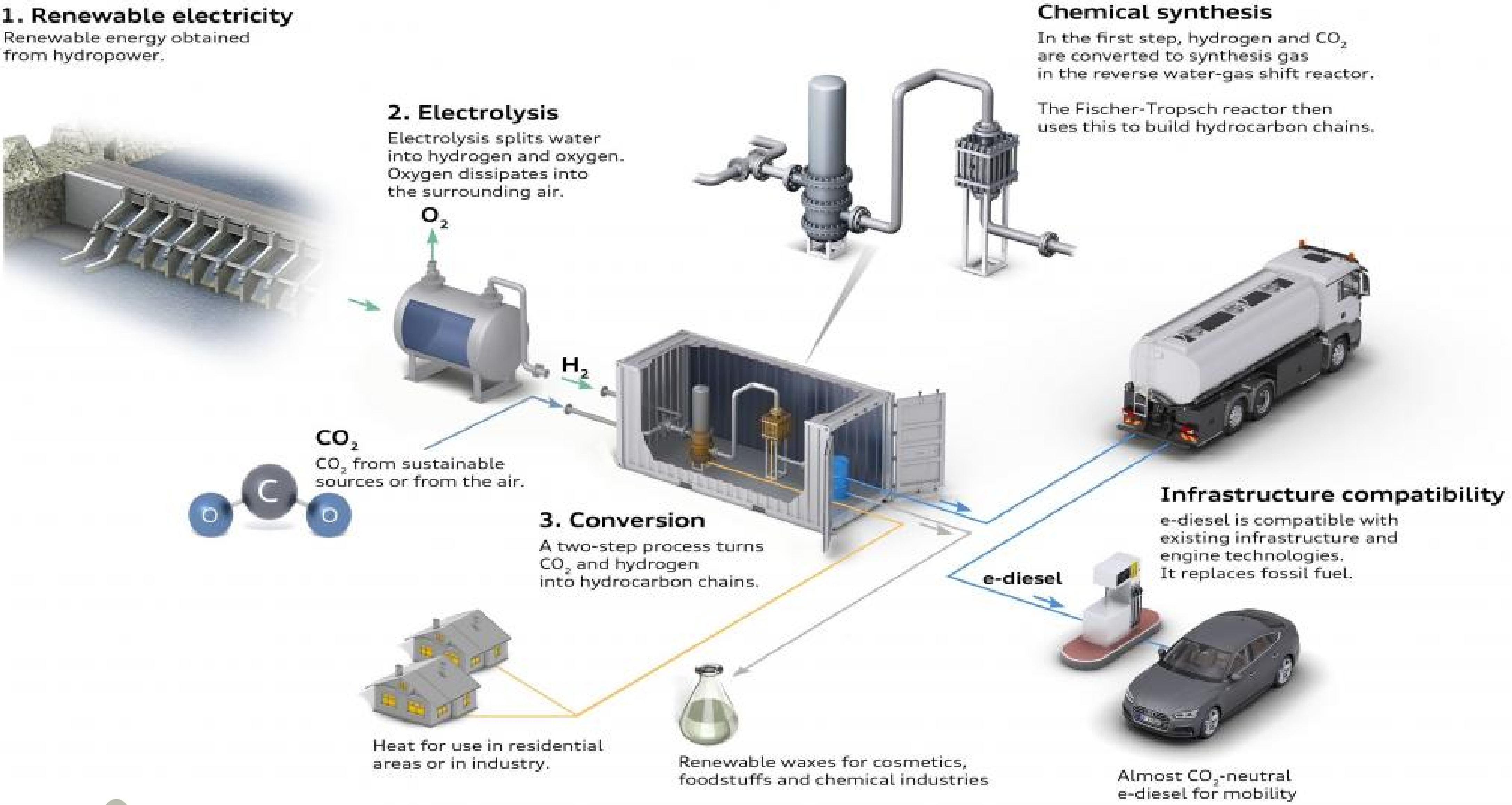
3. CO_2 from sustainable sources or directly from the air.



2. Hydrogen is produced via electrolysis of water.

4. Synthetic fuels are produced from CO_2 and H_2 via Fischer-Tropsch synthesis.

e-fuel



1. Renewable electricity
Renewable energy obtained
from hydropower.

2. Electrolysis
Electrolysis splits water
into hydrogen and oxygen.
Oxygen dissipates into
the surrounding air.

CO_2
CO_2 from sustainable
sources or from the air.

3. Conversion
A two-step process turns
CO_2 and hydrogen
into hydrocarbon chains.

Chemical synthesis
In the first step, hydrogen and CO_2
are converted to synthesis gas
in the reverse water-gas shift reactor.

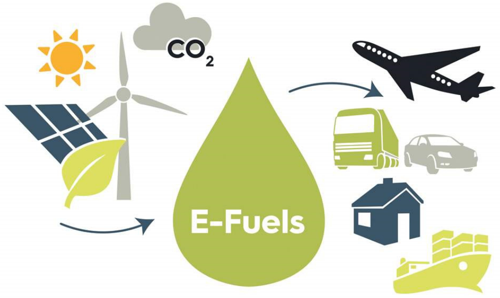
The Fischer-Tropsch reactor then
uses this to build hydrocarbon chains.

Infrastructure compatibility
e-diesel is compatible with
existing infrastructure and
engine technologies.
It replaces fossil fuel.

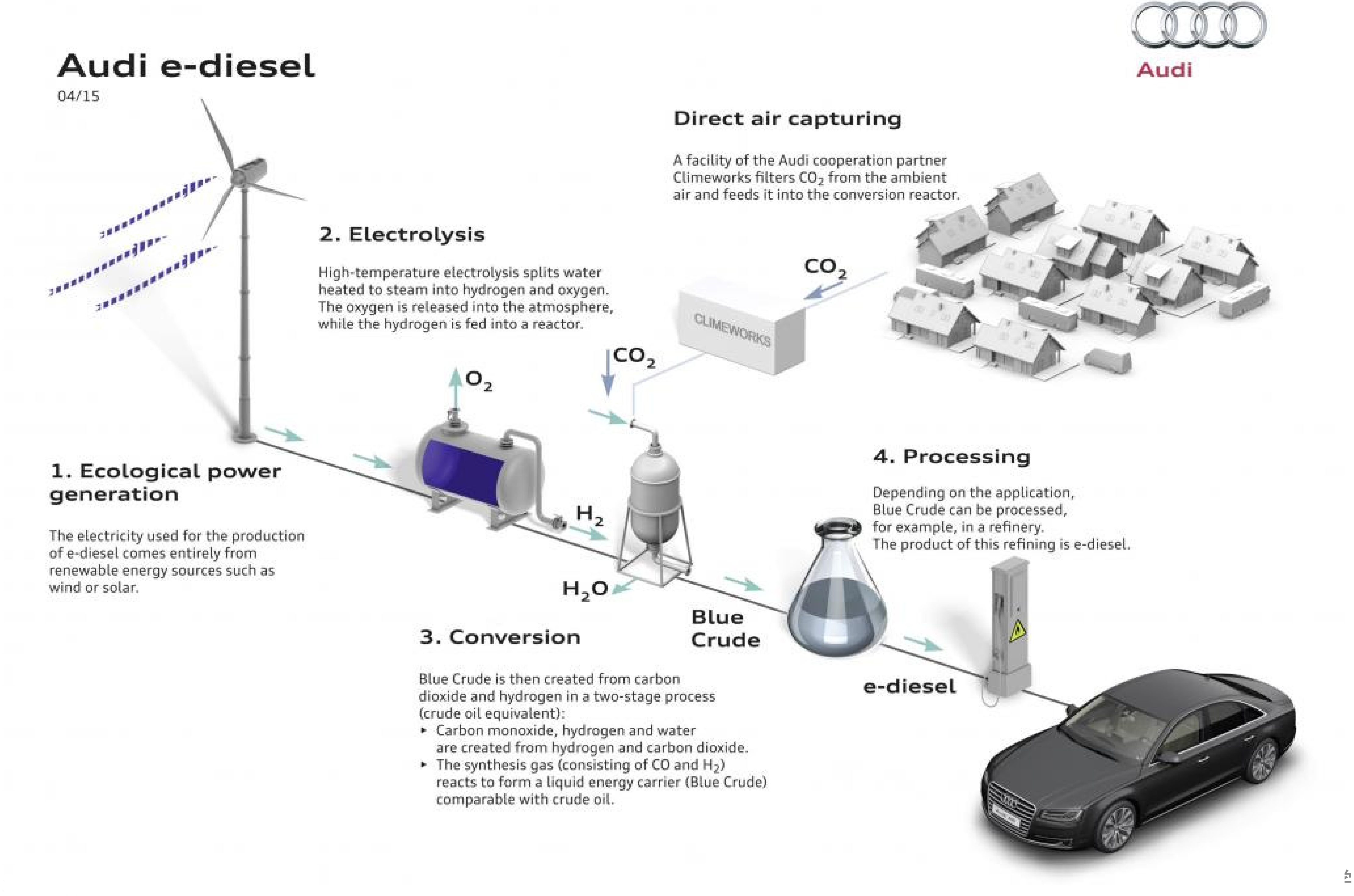
Heat for use in residential
areas or in industry.

Renewable waxes for cosmetics,
foodstuffs and chemical industries

Almost CO_2-neutral
e-diesel for mobility



e-fuel



Audi e-diesel

04/15

Direct air capturing

A facility of the Audi cooperation partner Climeworks filters CO$_2$ from the ambient air and feeds it into the conversion reactor.

1. Ecological power generation

The electricity used for the production of e-diesel comes entirely from renewable energy sources such as wind or solar.

2. Electrolysis

High-temperature electrolysis splits water heated to steam into hydrogen and oxygen. The oxygen is released into the atmosphere, while the hydrogen is fed into a reactor.

3. Conversion

Blue Crude is then created from carbon dioxide and hydrogen in a two-stage process (crude oil equivalent):

- Carbon monoxide, hydrogen and water are created from hydrogen and carbon dioxide.
- The synthesis gas (consisting of CO and H$_2$) reacts to form a liquid energy carrier (Blue Crude) comparable with crude oil.

4. Processing

Depending on the application, Blue Crude can be processed, for example, in a refinery. The product of this refining is e-diesel.

e-fuel

Possibilities of synthetic fuels (e-fuel) that are gaining interest due to EU acceptance

At the Energy Ministers' Meeting on March 28, 2023, the European Union (EU) changed its policy of banning the sale of new engine vehicles from 2035, and allowed the continuation of sales on the condition that "synthetic fuels" were used. Synthetic fuel is a liquid fuel made from carbon dioxide emitted from factories, power plants, etc., and hydrogen. In particular, synthetic fuel made from hydrogen derived from renewable energy is called e-fuel.
Synthetic fuels face challenges in terms of manufacturing technology and cost. However, decarbonization of automobiles in the world, including developing countries, is difficult only by expanding the spread of EVs and fuel cell vehicles. Synthetic fuel can be used not only for existing engine vehicles, but also for transportation machines such as aircraft that are not suitable for EV conversion. In addition, many of the rare metals and rare earths that are used as the core parts of EVs are unevenly distributed in specific countries such as China, Russia, and South Africa. .

2023.3.26 in press

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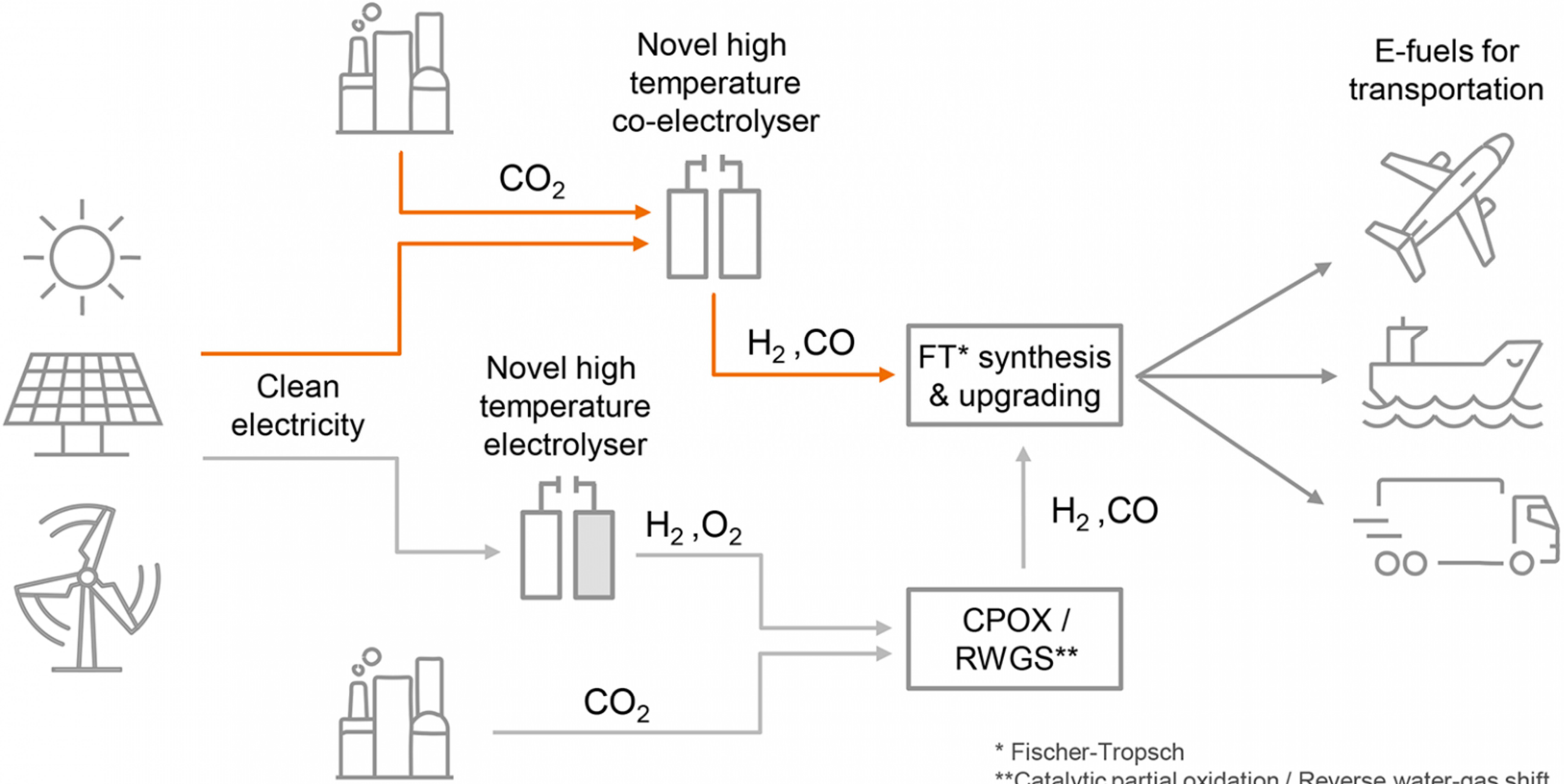
e-fuel



Novel high temperature co-electrolyser

CO_2

H_2 ,CO

Clean electricity

Novel high temperature electrolyser

H_2 ,O_2

FT* synthesis & upgrading

H_2 ,CO

CPOX / RWGS**

CO_2

E-fuels for transportation

* Fischer-Tropsch

**Catalytic partial oxidation / Reverse water-gas shift

e-fuel History of FT synthesis

1902 Sabatier and Sendersen report that methane is formed from CO and hydrogen over Ni and Co catalysts.

1908 Orlov finds ethene from synthesis gas over NiPd catalysts.

1913 BASF patent for “Preparation of a liquid oil from synthesis gas", Co and Os catalysts.

1924 Fischer and Tropsch report about the preparation of

hydrocarbons over an Fe catalyst, the catalyst deactivates rapidly.
The first 4 plants are commissioned (200,000 t/year capacity),

1936

Pichler finds that by increasing the pressure to 15 bar, the lifetime of the catalyst increases

1944 9 plants and a total of 700,000 t/year; Co catalyst (Co, ThO2,

MgO, Kieselguhr)

1955 Sasol I starts (combination of fixed and fluid bed reactors)

1994 Shell starts operating plant in Malaysia (SMDS process)

2005- Several large GTL processes under construction

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- Developed during World War II in order to satisfy the demand for fuel with the abundant coal supply.
- High pressure hydrogenation of CO over metal or transition metal carbide catalysts.
- The process leads to oligomer like large saturated and mostly unbranched alkanes, as well as some oxygenates.
- Fe, Co and Ru are the most widely use catalysts.
- Alkali metal oxide promoters seem essential for good catalytic performance.
- The two main catalytic functions are
    - CO bond activation and dissociation
    - Formation of C-C and C-H bonds

Prof. Franz Fischer

Dr. Hans Tropsch

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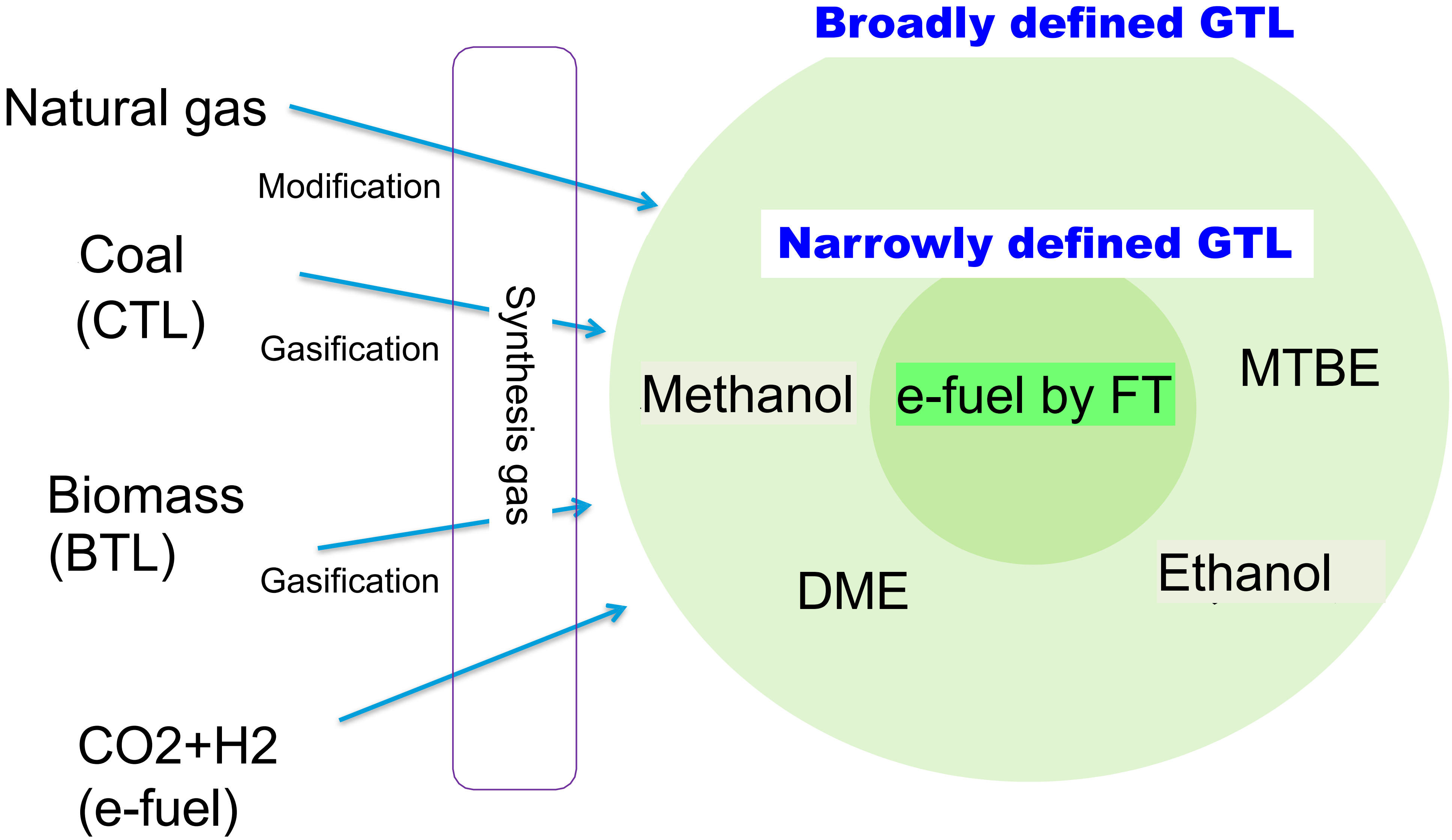
GTL(Gas To Liquid)



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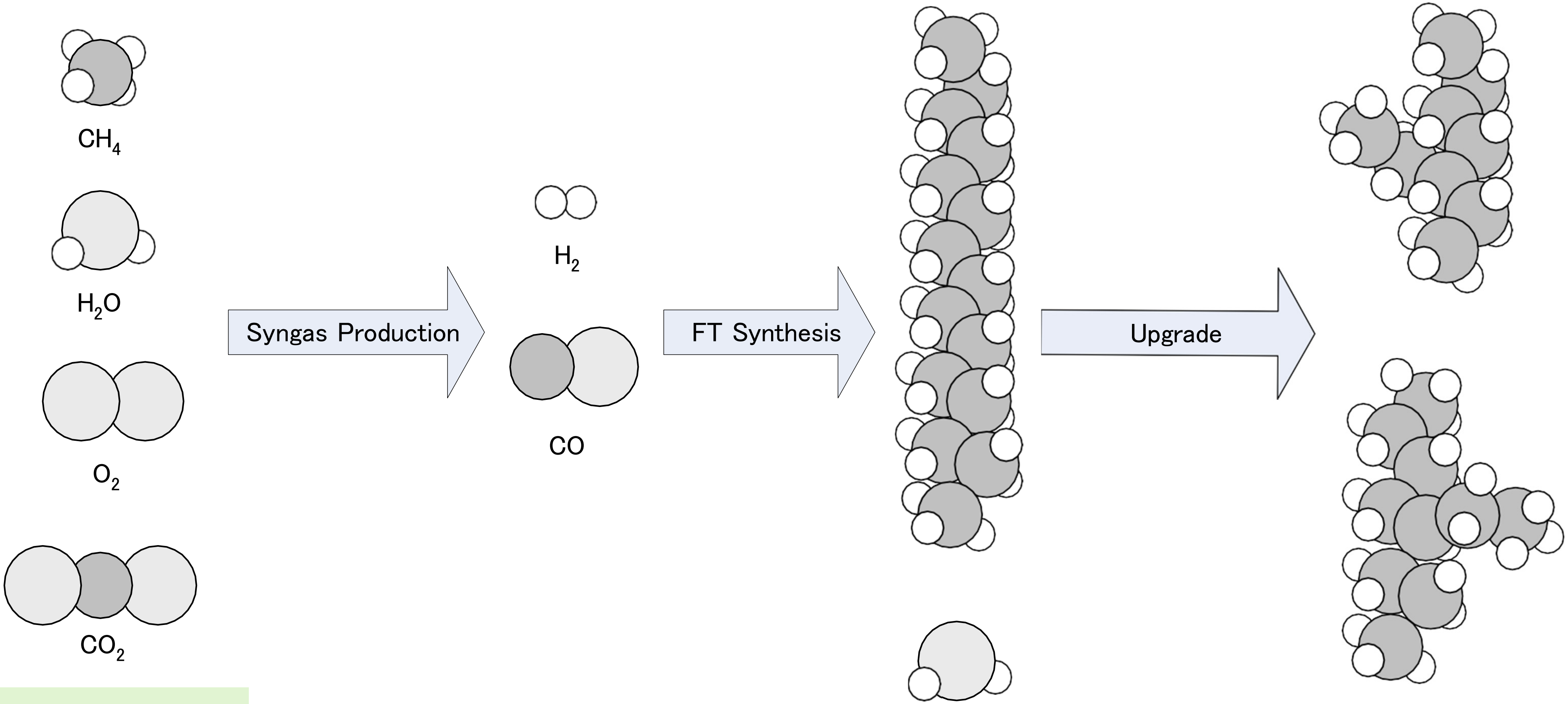
GTL(Gas To Liquid)



CmHn …..

GTL is a technology that produces synthetic gas (CO + H2) from natural gas (mainly CH4) and then produces liquid hydrocarbons through FT synthesis reaction. Synthetic gas can be produced from biomass and other sources, so a wide variety of raw materials can be used.

FT synthesis reaction

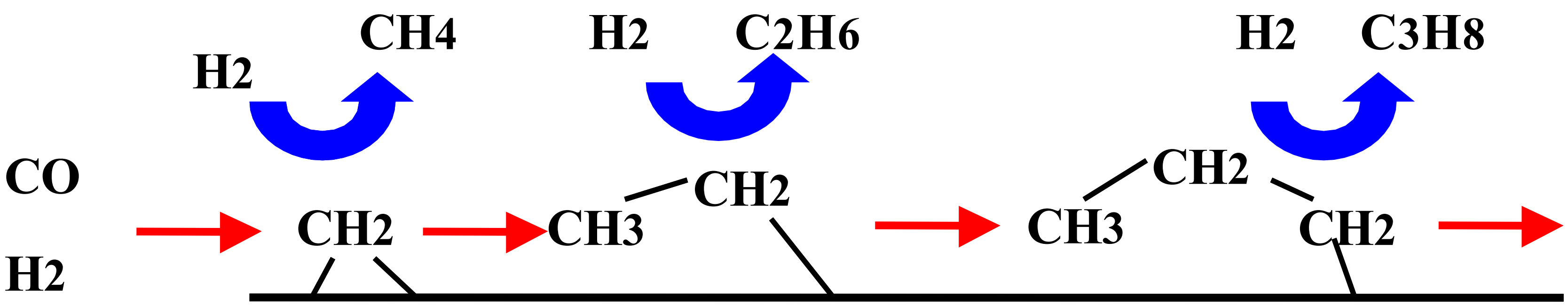
- **FT反応**

$CO+2H_2 \rightarrow -(1/n)(CH_2)_n- + H_2O,\ \Delta H_{298} = -167 kJ/mol-CO$

$H_2/CO=2/1$

exothermic reaction

It is important to remove heat.



→ Chain growth **(Kp)**

Rate at which carbon chains increase

↷ Hydrogenolysis **(Kd)**

Rate of hydrogenation and desorption

Summary

- physical chemistry
  - equilibrium theory
    - DLVO theory
    - rapid aggregation theory
  - Kinetics
    - catalytic chemistry
- Synthesis of monodisperse particles
  - 3 conditions
- A catalyst that contributes to society
  - carbon neutral, e-fuel