No. A-6-1E

PJ: "Development of Global CO_2 Recycling Technology towards "Beyond-Zero" Emission"

Organization: Kyushu University

Contact: Shigenori FUJIKAWA (fujikawa.shigenori.137@m.kyushu-u.ac.jp)

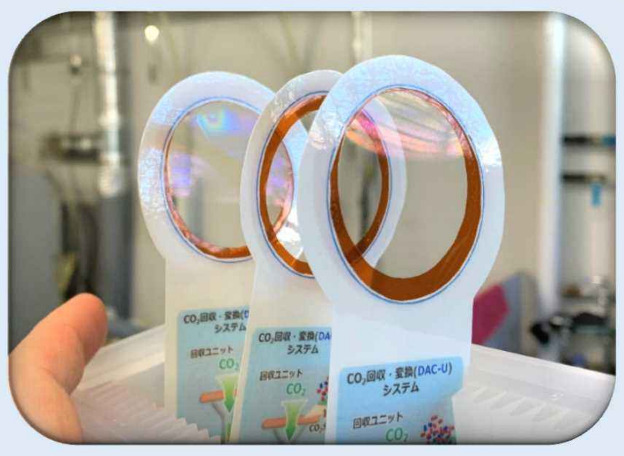
NEDO

MOONSHOT

Toward a Beyond Zero Society through Ubiquitous Carbon Capture and Utilization (CCU)

■ CO2 separation nanomembranes with overwhelming high CO_2 permeability

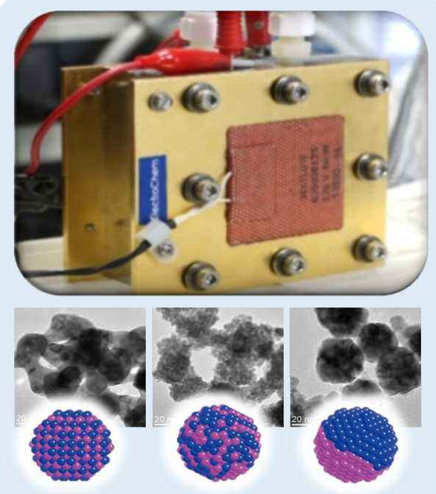
- ●Kyushu University has developed a nanomembrane that is only 1/2500 as thin as the diameter of a hair.
- ●Developed nanomembranes show highest CO_2 permeance , which is 20 times higher than conventional membranes



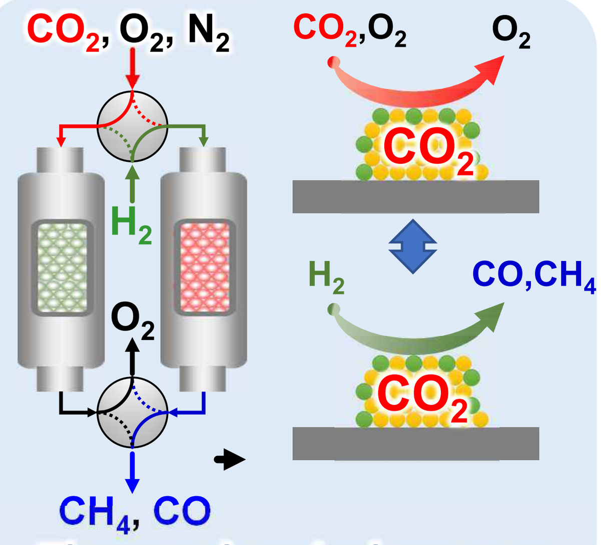
CO_2 separation nanomembrane

■ Catalyst technology for CO_2 conversion and small conversion system

- ●Nanocatalysts and electrochemical process system for highly efficient conversion of CO_2 to useful substances
- ●Novel thermochemical catalysts and processes for simultaneous O_2 removal and CO_2 conversion



Electrochemical process

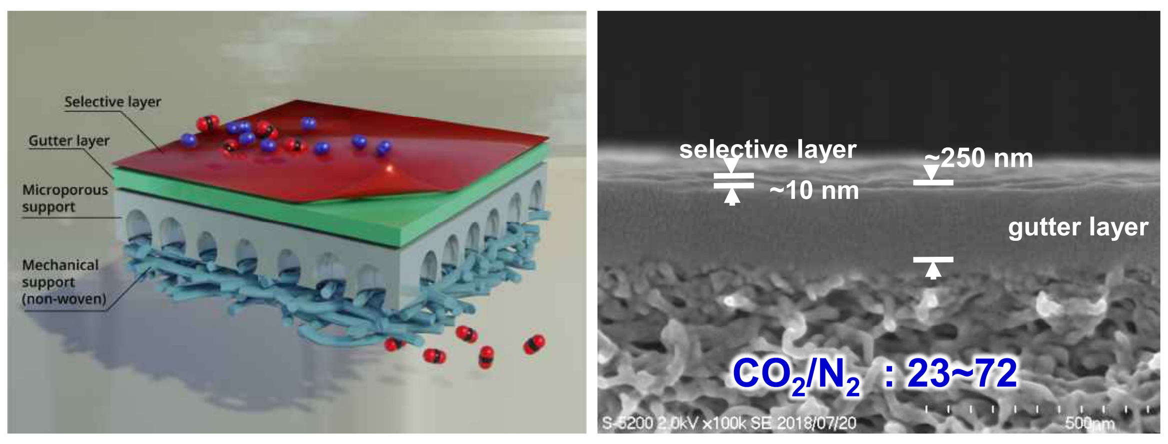


Thermochemical process

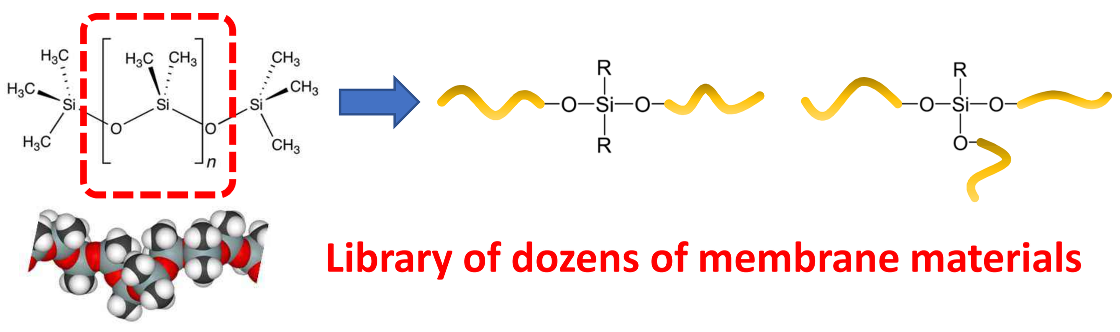
Goals of the Project

Compact, Scalable, Distributed Deployable Direct Air Capture-Utilization (DAC-U) System

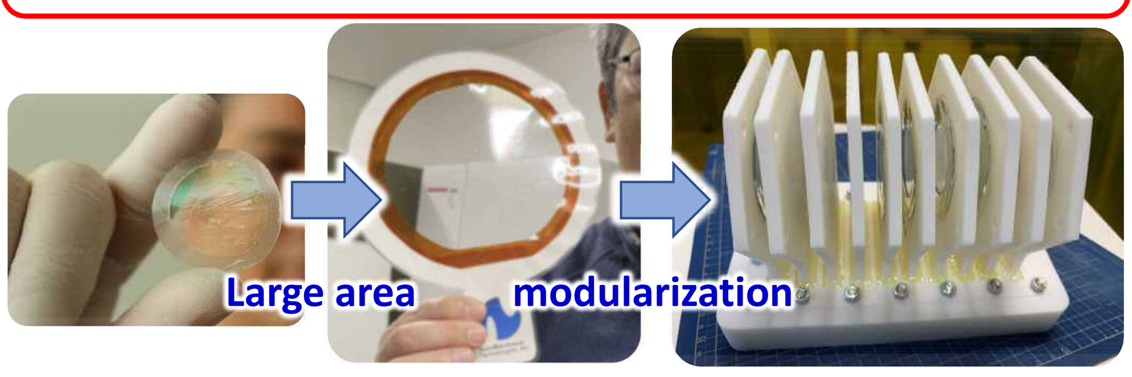
Enhancement of CO_2 selectivity



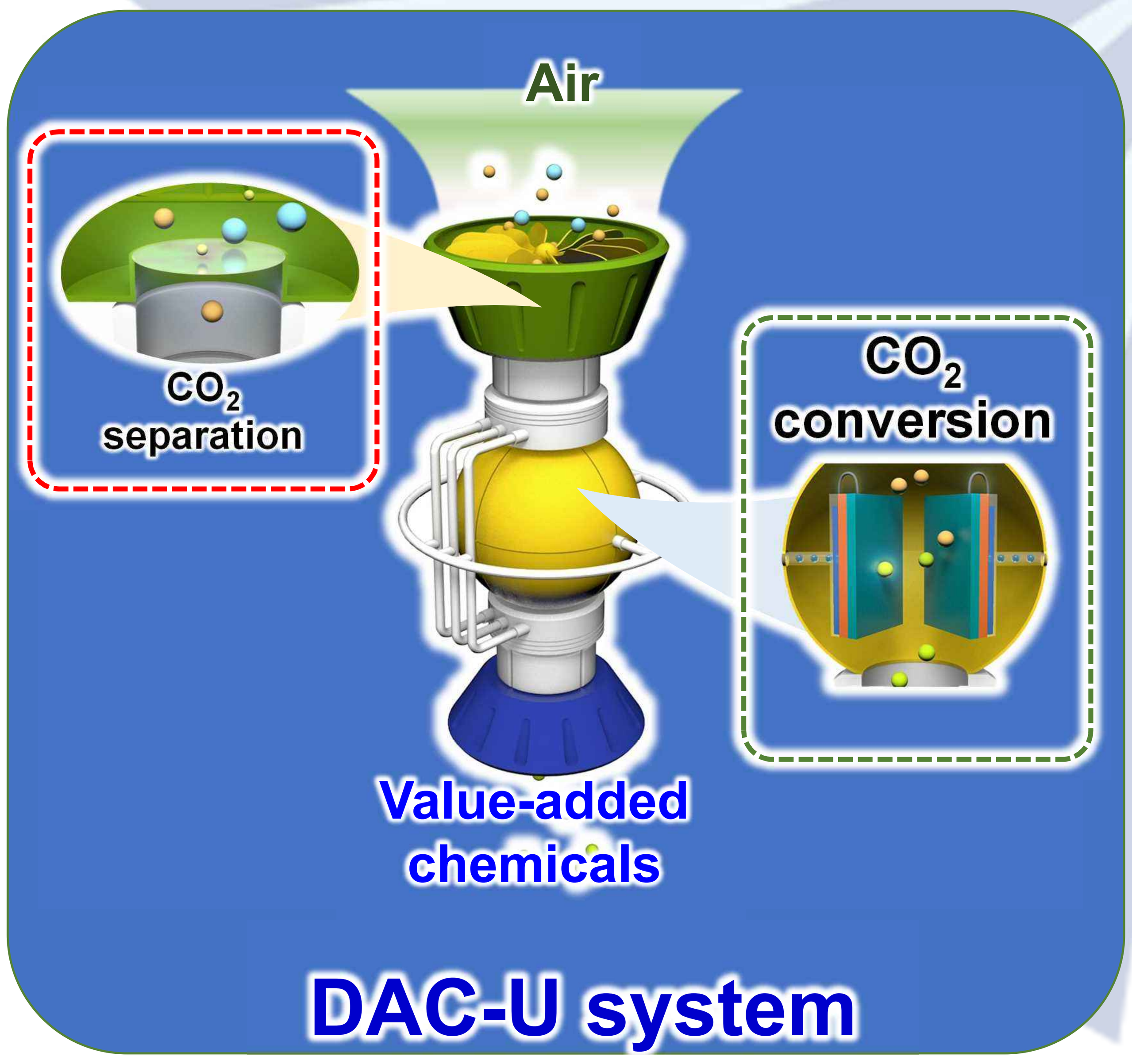
Development of membrane materials



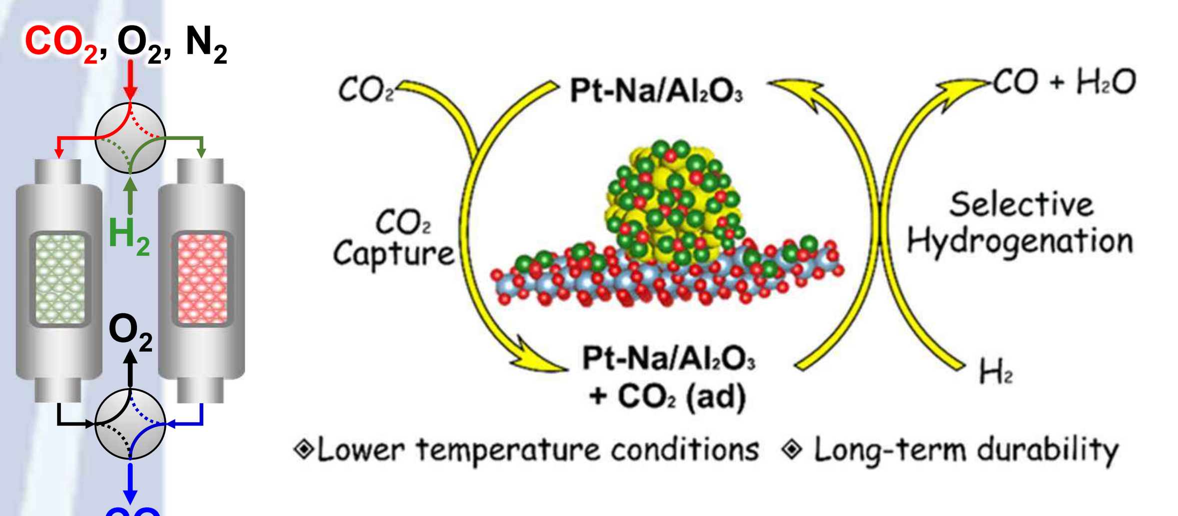
Large area and modularization of nanomembranes



systematization



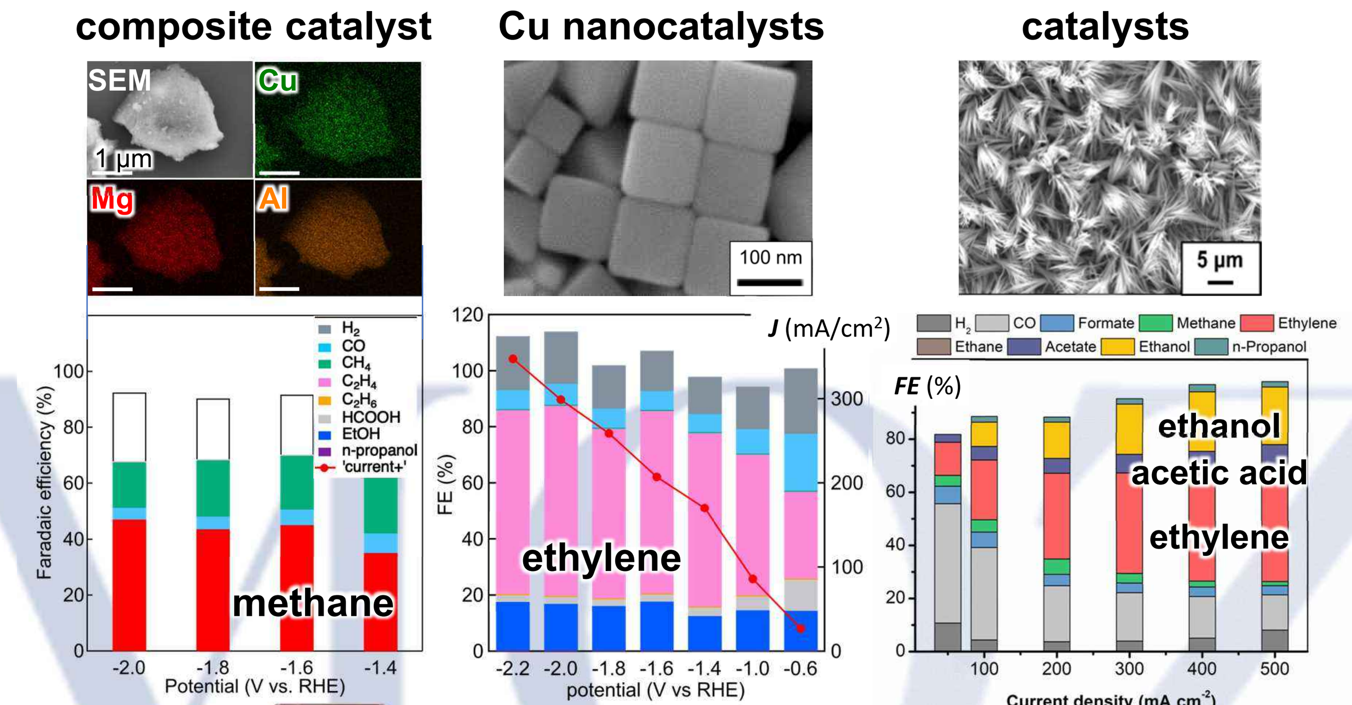
CO_2 absorption and thermochemical CO_2 conversion



ACS Catal. 2022, 12, 4, 2639−2650

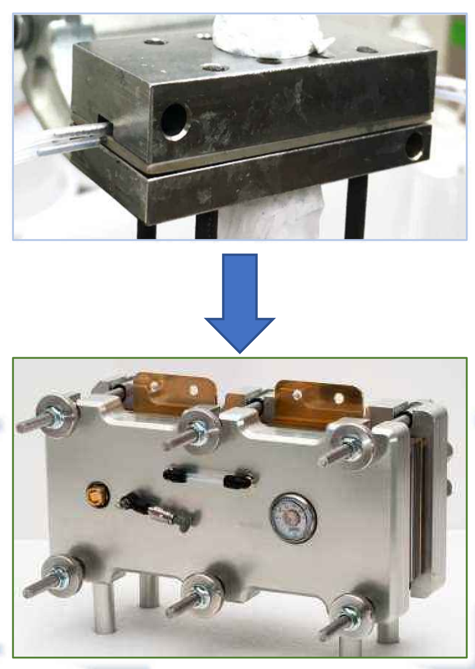
Prof. Ken-ichi SHIMIZU (Hokkaido Univ.)

Nanocatalysts for electrochemical CO_2 conversion



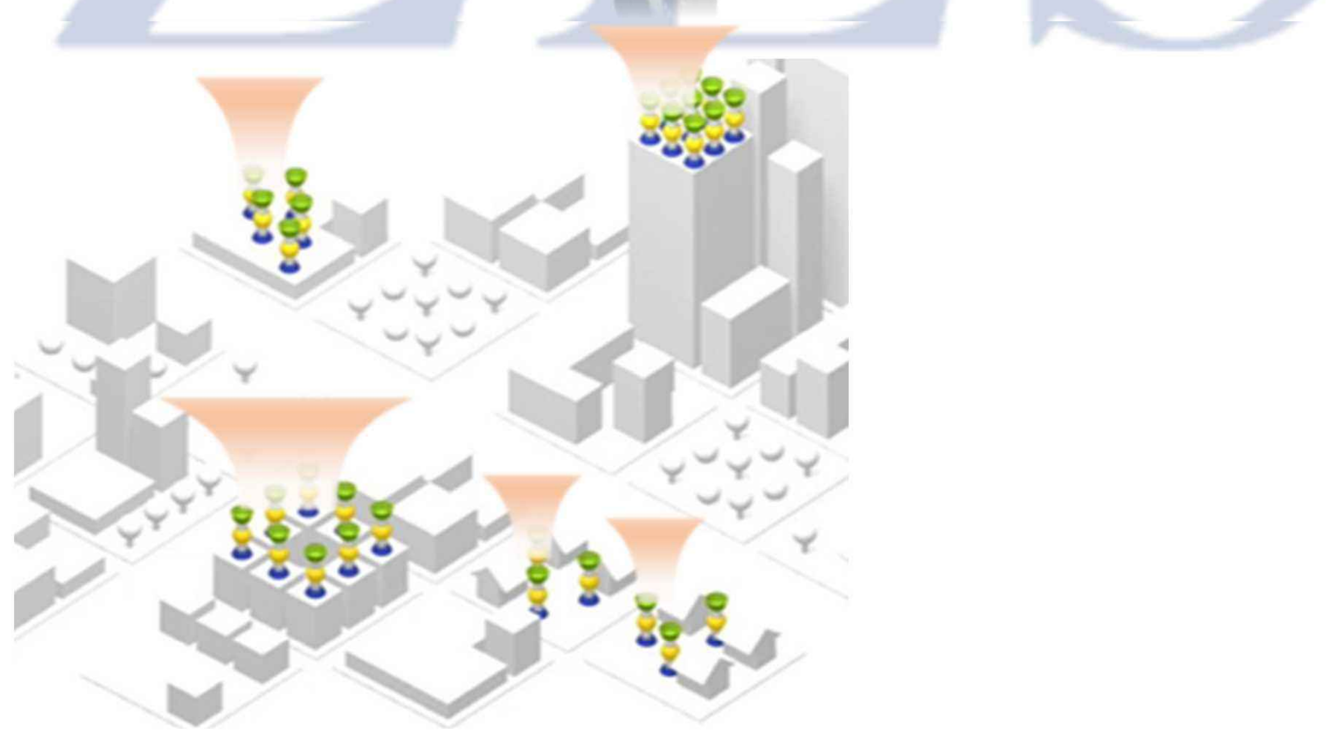
Prof. Miho YAMAUCHI (Kyushu Univ.)

Development of high-performance electrochemical cells



Univ. Illinois at Urbana Champaign

Prof. Paul KENIS



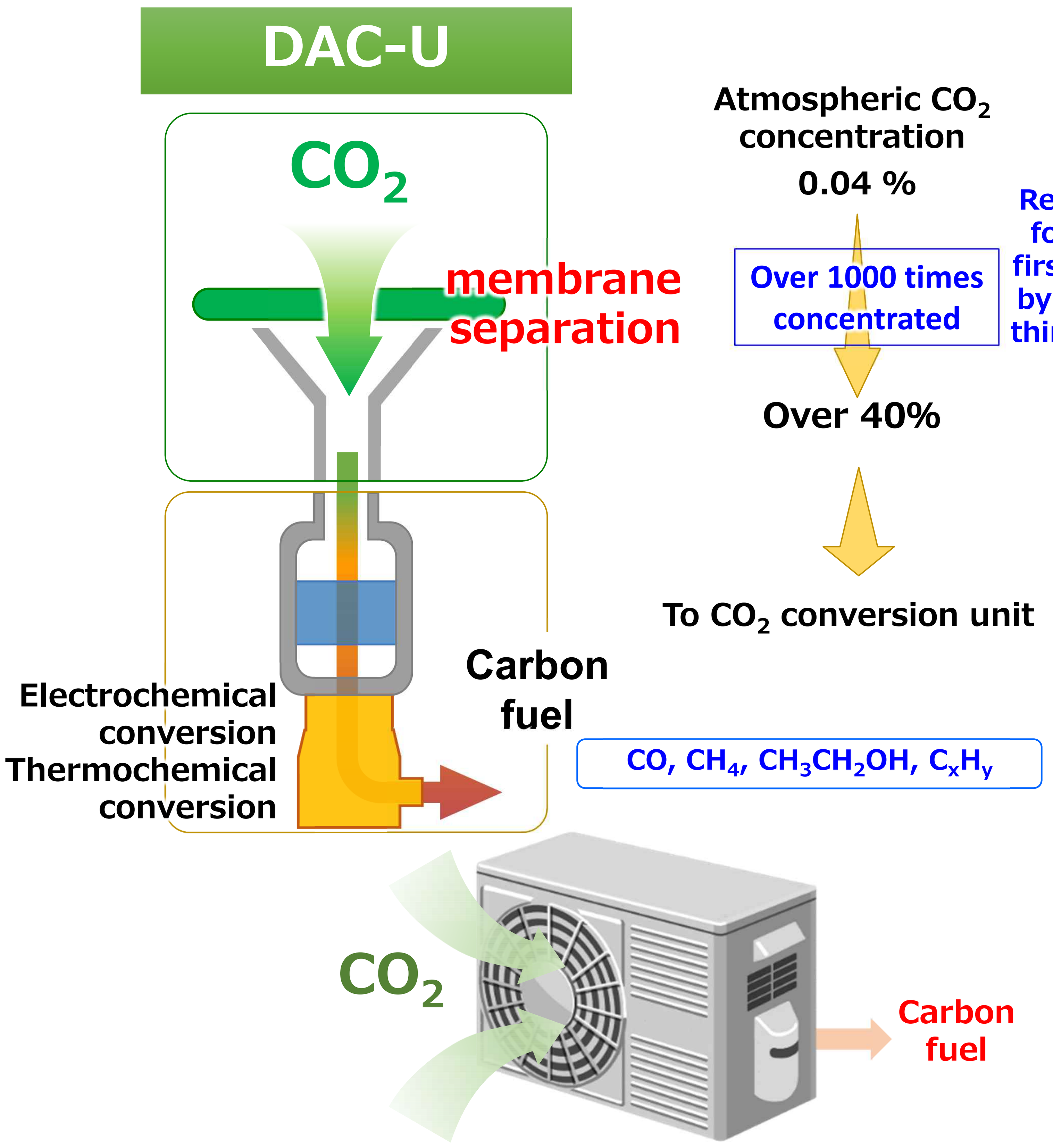
Carbon resource recycling society with decentralized deployment of DAC-U systems

No. A-6-3E
PJ : Moonshot for beyond Zero-Emission Society
Theme: CO_2 capture unit

Organization: Kyushu Univ., Kumamoto Univ., Kagoshima Univ., Osaka Institute of Tech., Hokkaido Univ., NanoMembrane Tech. Inc.

Contact: Prof. Masashi KUNITAKE (Institute of Industrial Nanomaterials, Kumamoto Univ.) kunitake@kumamoto-u.ac.jp

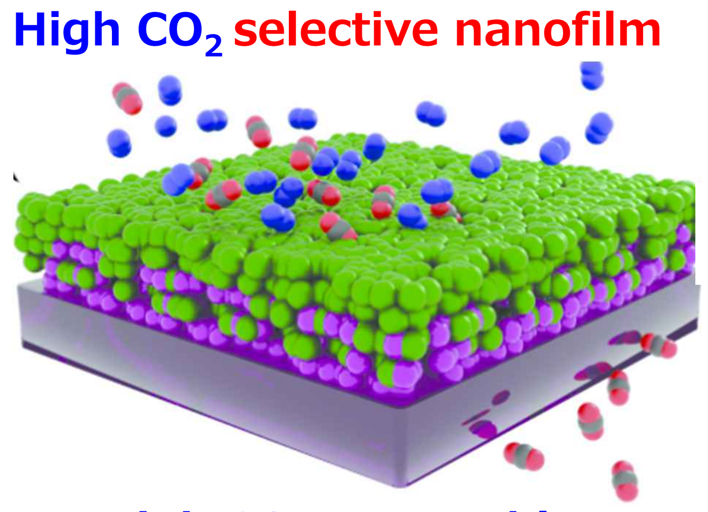
Membrane Separation Technology for CO_2 Recovery with High Scalability and Distributed Arrangements

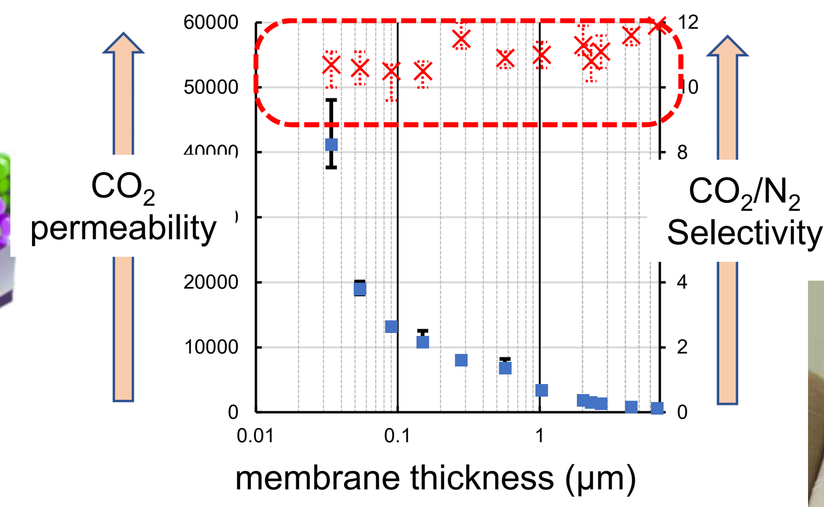


With innovative separation nano-membranes developed in-team that have overwhelmingly high CO_2 permeation capacities, the direct recovery of CO_2 from the atmosphere will be achieved by membrane separation, which was thought to be impossible.

The CO_2 recovery team is in charge of the development of the membrane separation unit in the "Direct Air Capture and Utilization (DAC-U) system" that continuously and consistently performs everything from atmospheric CO_2 capture to carbon fuel production.

High CO_2 selective nanofilm

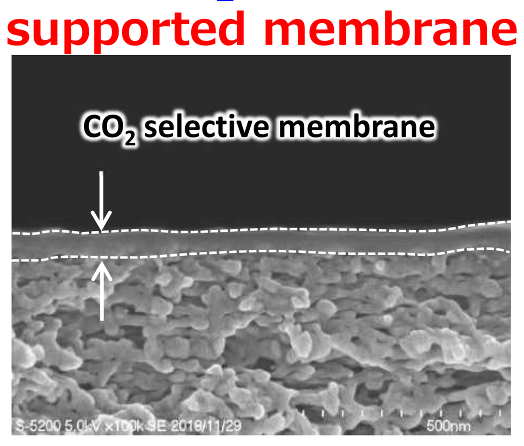


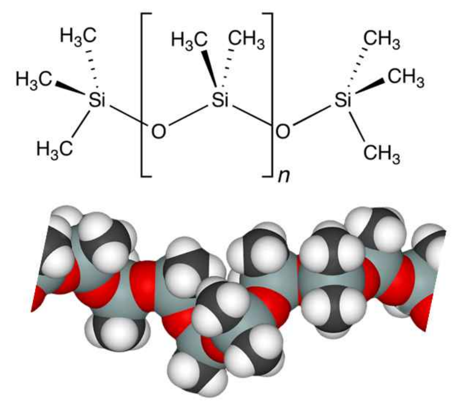


Ultrathin

Fujikawa, et.al., Chem. Lett. **2019**, *48, 11, 1351-1354*

High CO_2 permeable supported membrane



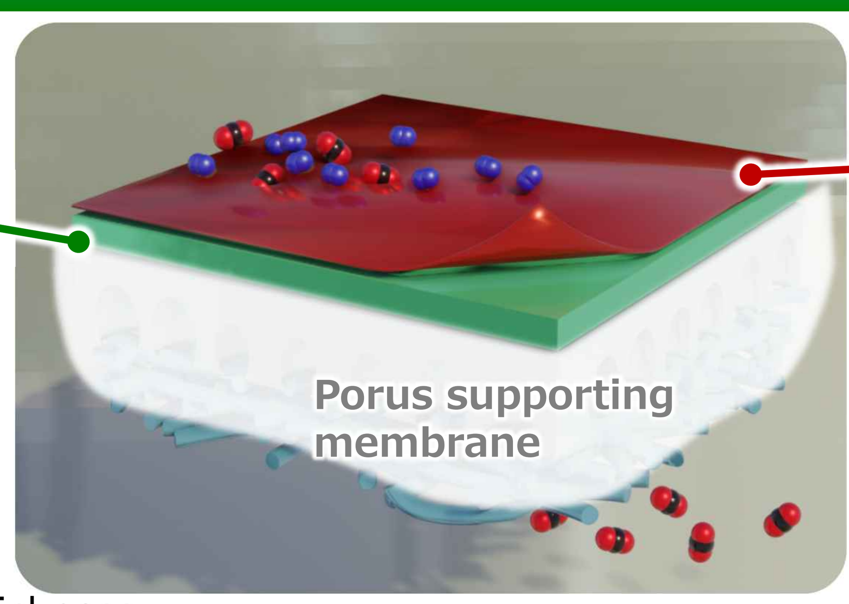


Development of novel permeable membranes based on polydimethylsiloxane(PDMS)

Supported Nanomembrane with high permeability
X
Selective ultra-thin nanofilms with high CO_2 selectivity

Development of Separation Nano-Membranes with High CO_2 Permeability

Support nanomembrane
- Thickness: below 100 nm
- Self-supporting
- Low density
- Surface modification ability



CO_2 selective molecular layer
Thickness:monomolecular layer level

Target performance values 2024
- CO_2/N_2: around 30
- CO_2/O_2: around 10
- CO_2 permeability: 5,000 GPU

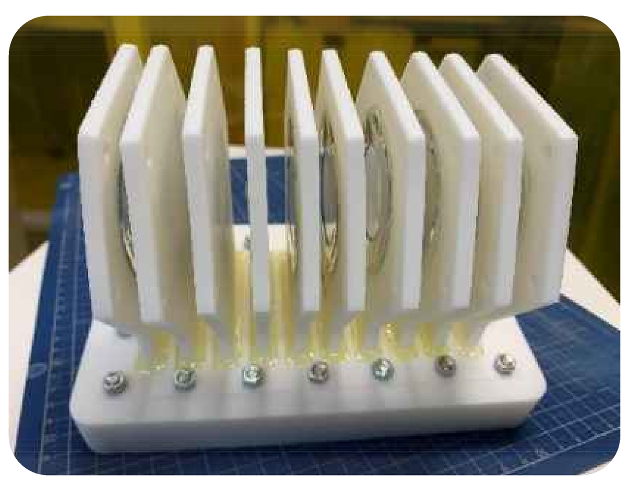
①Design of Selective Layers: "Improve selectivity"
Fabrication of CO_2 selective layers with molecular-thickness
→Screening for CO_2 affinity molecular materials

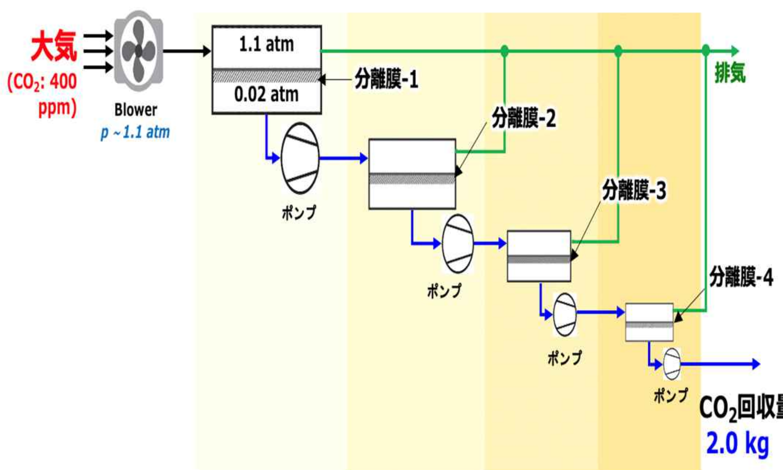
②Design of Selective Layers: "Improve permeability"
Low-density CO_2 permeable PDMS by polymer cross-linking structure.

③ "Integration of selective layer and support membrane "
→ Modification of support membrane surfaces

④Interactions between gas molecules and the surface
→Feedback to design separation membrane materials

⑤"System Construction" with Large-area membranes

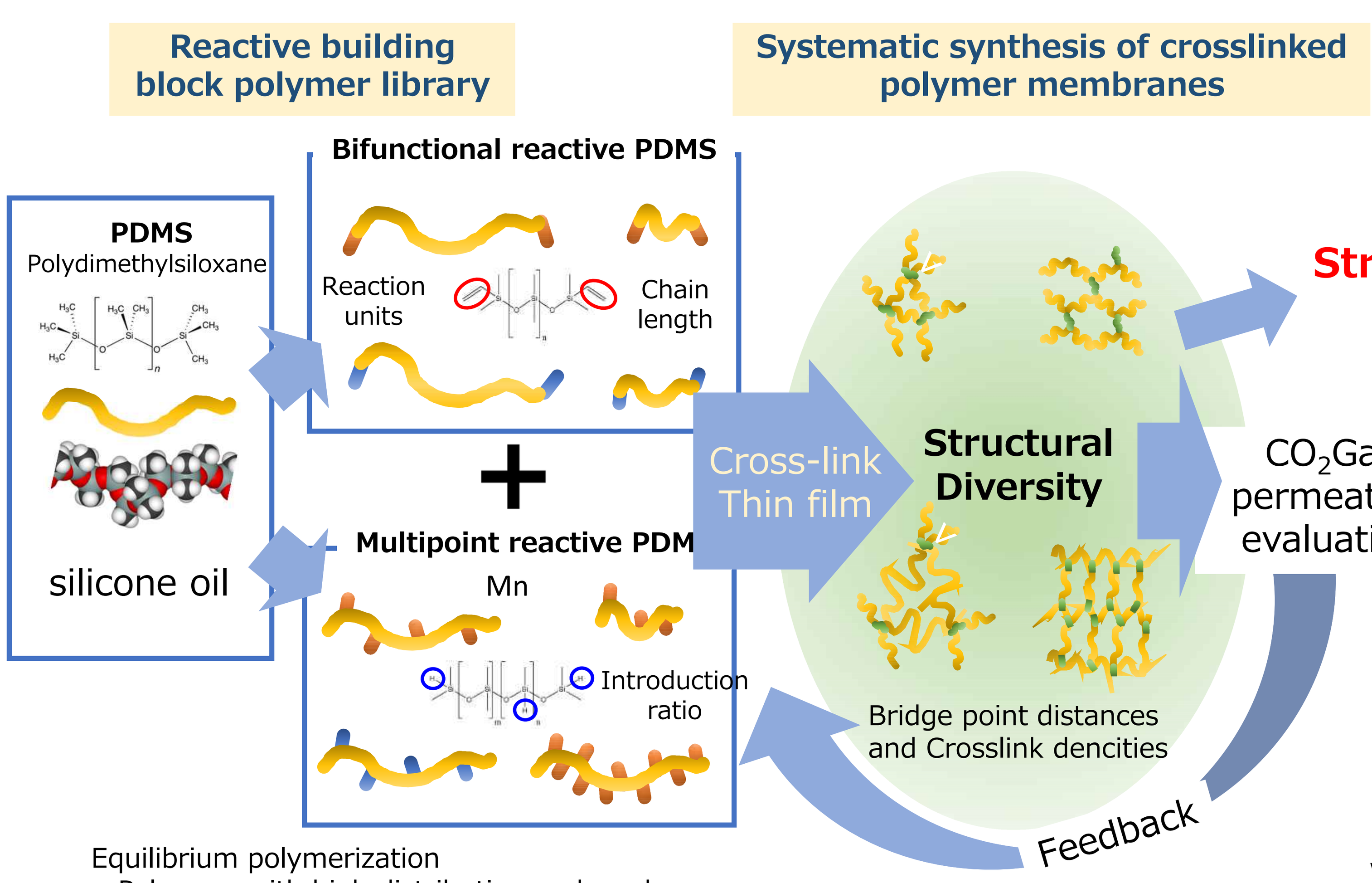




Scale-up large area Modularization

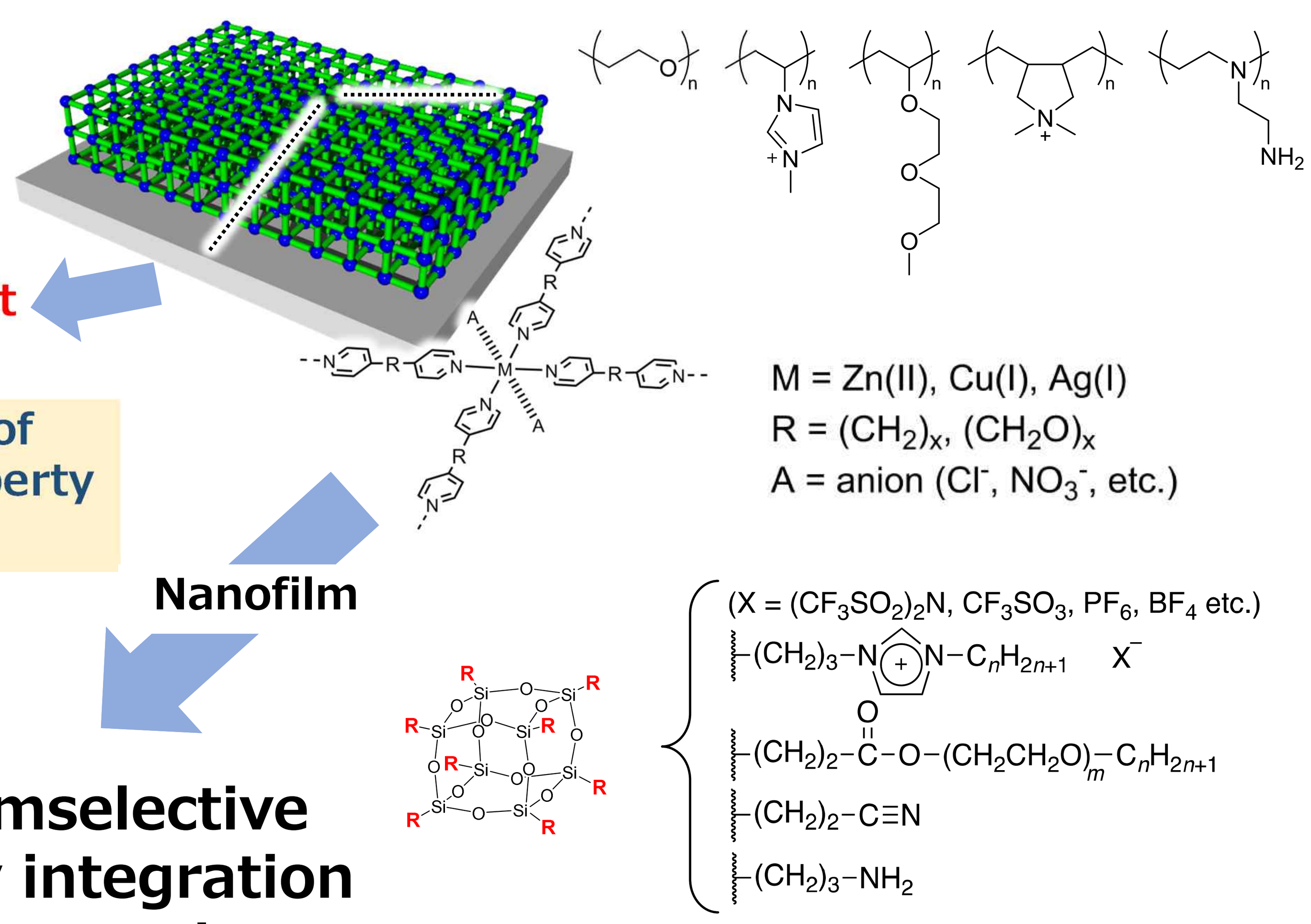
Multi-step concentration Integration as a system

Development of Silicone polymer materials for high CO_2 permeable support membranes



Equilibrium polymerization
・Polymers with high distribution and randomness
・ Easy mass synthesis
Precision anion polymerization
・Structural fine-controlled polymers

Development of polar materials for highly CO_2-selective nanofilms



In cooperation with **Structural Analysis Unit**

Elucidation of Structure-Property correlation

Nanofilm

M = Zn(II), Cu(I), Ag(I)
R = $(CH_2)_x$, $(CH_2O)_x$
A = anion (Cl^-, NO_3^-, etc.)

(X = $(CF_3SO_2)_2N$, CF_3SO_3, PF_6, BF_4 etc.)

High CO_2 permselective membranes by integration with supporting membrane

No.A-6-4E

PJ : Development of Global CO_2 Recycling Technology towards "Beyond-Zero" Emission

Theme: Catalytic hydrogenation of CO_2 under O_2 and its use in DAC-U

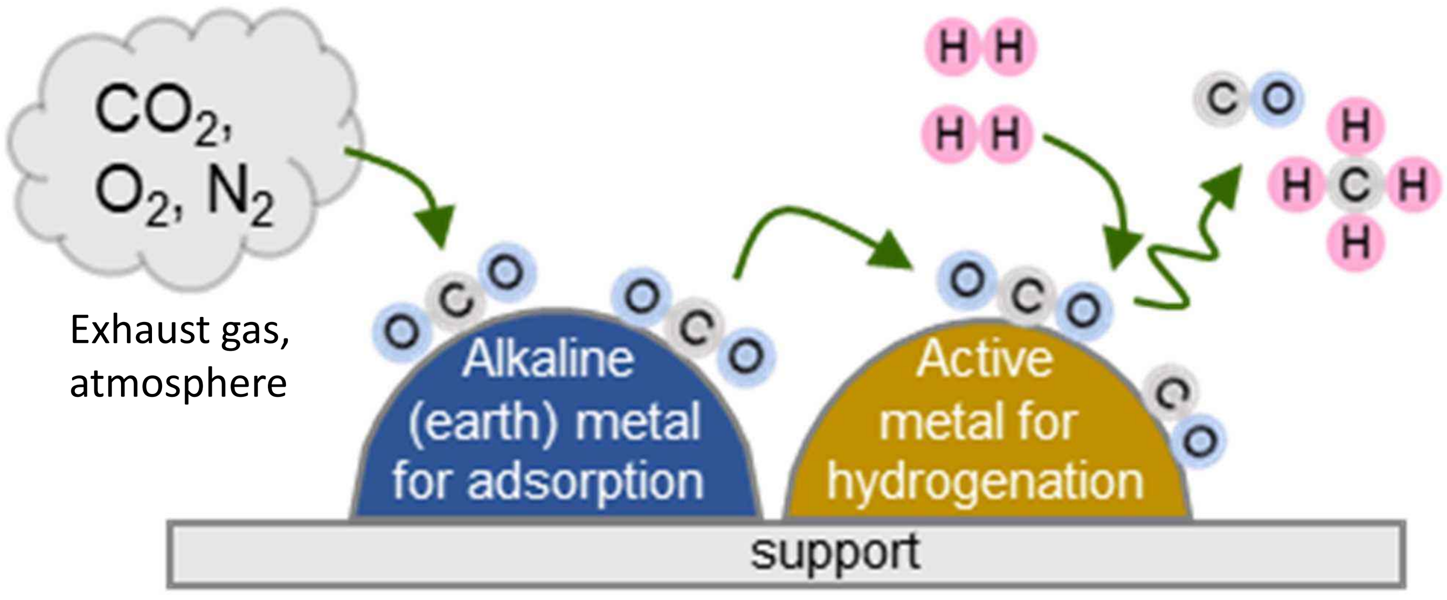
Organization: Hokkaido University

Contact: kshimizu@cat.hokudai.ac.jp

Introduction

CO_2 capture and reduction (CCR) using dual functional material

✓ No need for CO_2 separation and purification
✓ Reaction proceeds even in containing O_2



CH_4 production

(Ru-Ca, Ru-Na, Ni-Na, etc.)

R. J. Farrauto et al. *Chem. Eng. J.*, 2019, 375, 121953.
J. R. González-Velasco et al. *Appl. Catal. B*, 2019 256, 117845
K. Kuramoto et al. *ACS Sustainable Chem. Eng.*, 2021, 9, 3452.

CO production

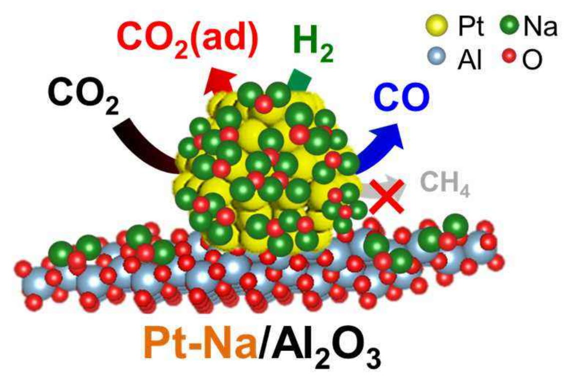
(FeCrCu-K, Ni-Ca.)

Few catalysts are effective for CO formation.

A. Urakawa et al. *J. CO₂ Util.*, 2016, 14, 106.
J. C. Kim et al. *Sustain. Energy Fuels*, 2020, 4, 5543.

This work

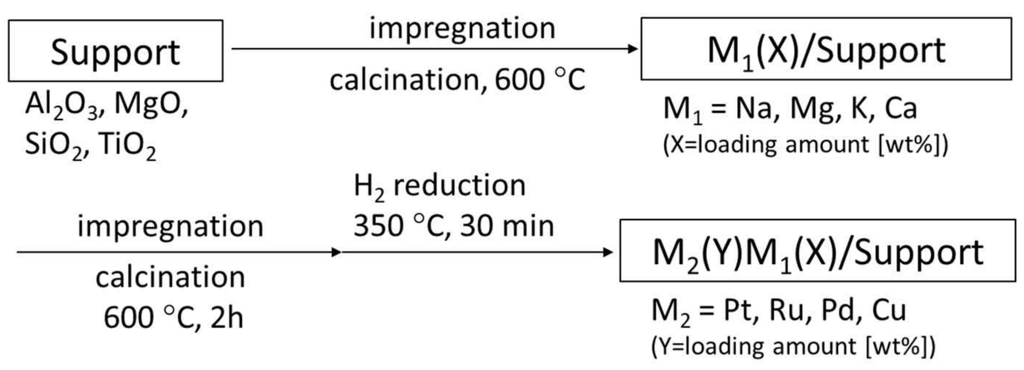
- We developed novel catalyst for selective CO production through CCR.
- This catalyst performed at lower temperature than conventional systems. (350 °C)
- The effect of basic components on selectivity was examined.
- A continuous CO_2 capture and reduction system was developed.



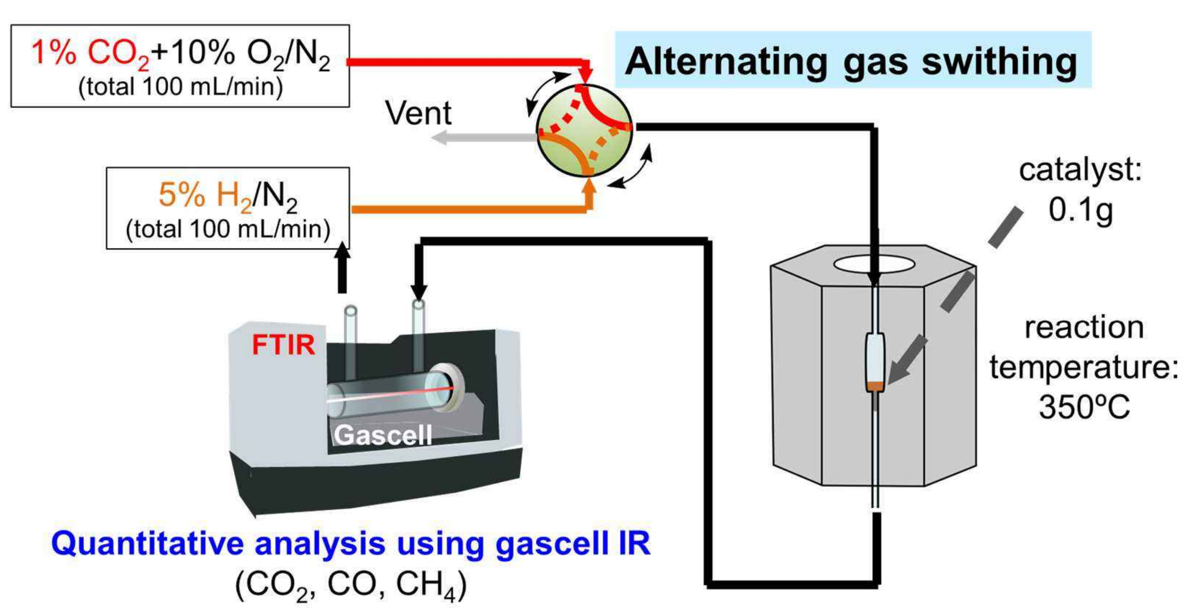
L. Li, S. Miyazaki (co-first author), Z. Maeno, K. Shimizu et al., *ACS Catal.*, 2022, 12, 2639

Experimental

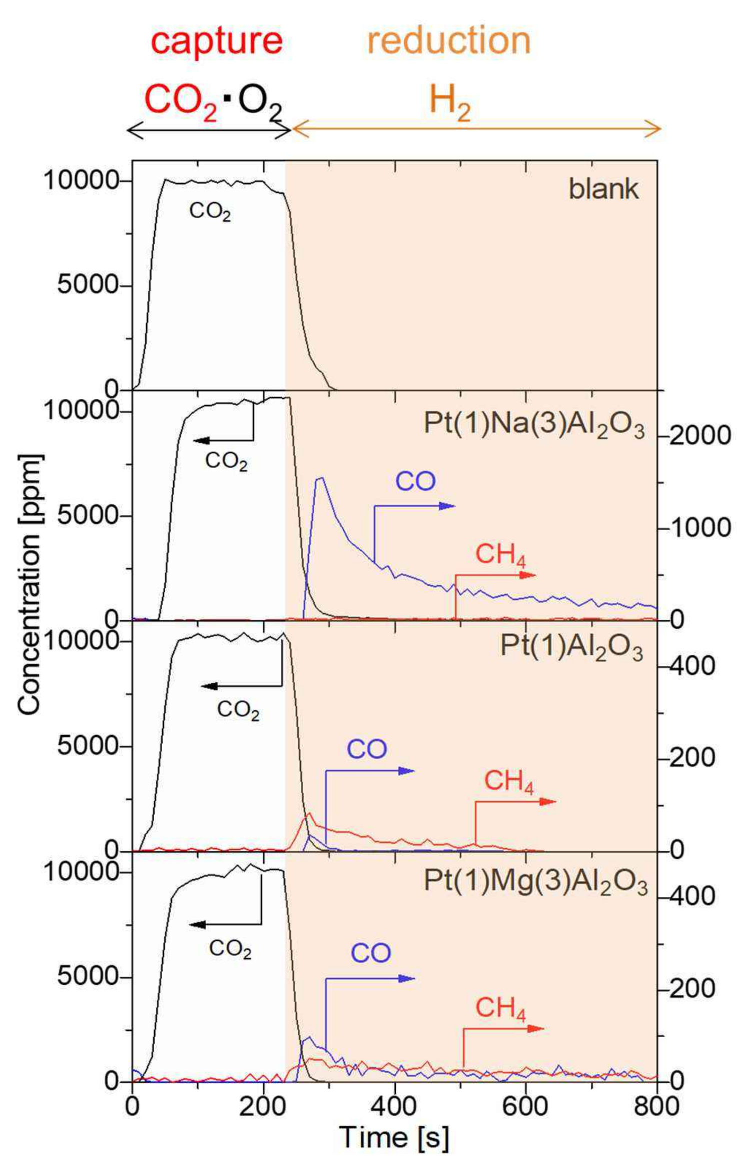
Catalyst preparation: wetness impregnation



CO_2 Capture and reduction (after H_2 pretreatment, 350℃)



Catalyst screening



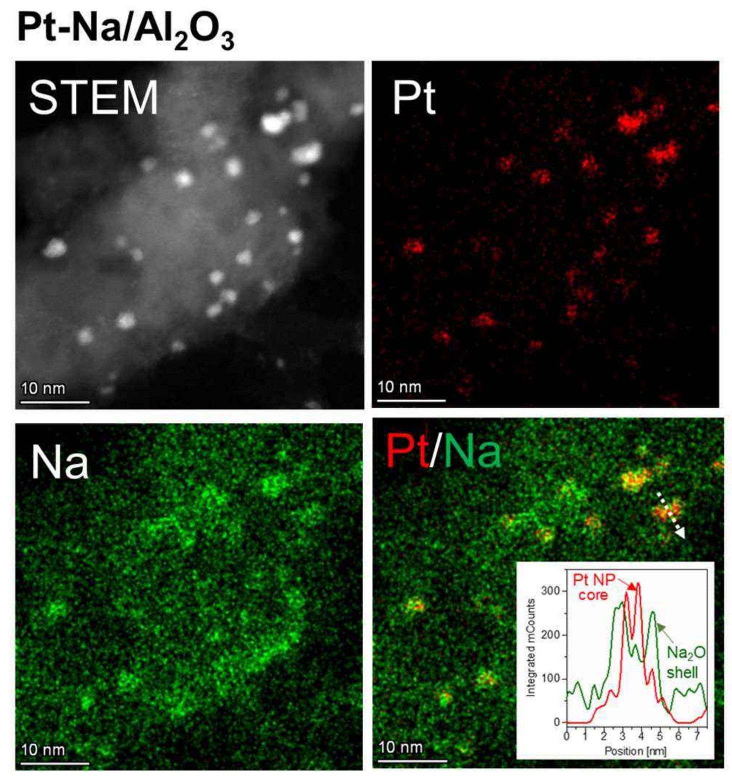
Catalyst	Max CO [ppm]	CO [mmol/g]	CO Sel. [%]	Abs. CO_2 [mmol/g]	Conv $_{abs.\ CO2}$ [%]
Pt(1)/Al_2O_3	37	0.001	11.1	0.08	9
Pt(1)Na(3)/Al_2O_3	1559	0.158	93.2	0.19	89
Pt(1)K(6)/Al_2O_3	57	0.007	31.1	0.12	19
Pt(1)Mg(3)/Al_2O_3	98	0.013	50.8	0.12	22
Pt(1)Ca(6)/Al_2O_3	310	0.041	84.1	1.07	5
Pd(1)Na(3)/Al_2O_3	100	0.006	31.3	0.16	11
Ru(1)Na(3)/Al_2O_3	39	0.006	17.4	0.61	6
Cu(1)Na(3)/Al_2O_3	20	0.003	50.2	0.13	8
Pt(1)Na(3)/MgO	351	0.061	82.4	0.13	57
Pt(1)Na(3)/SiO_2	64	0.006	47.5	0.32	4
Pt(1)Na(3)/TiO_2	303	0.029	61.2	0.39	12

- CH_4 is the main product of Pt/Al_2O_3.
- **Pt-Na/Al_2O_3 has the best CO selectivity, CO production, and conversion rate of absorbed CO_2.**

Characterization

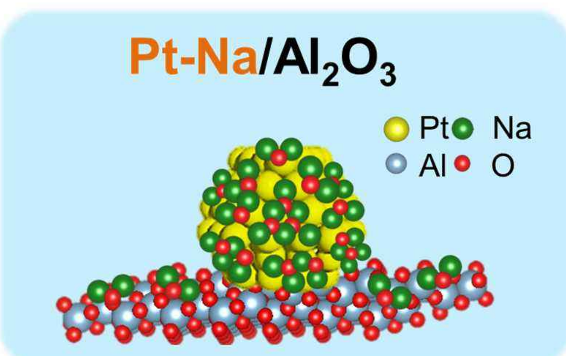
STEM&EDX

Pt-Na/Al_2O_3



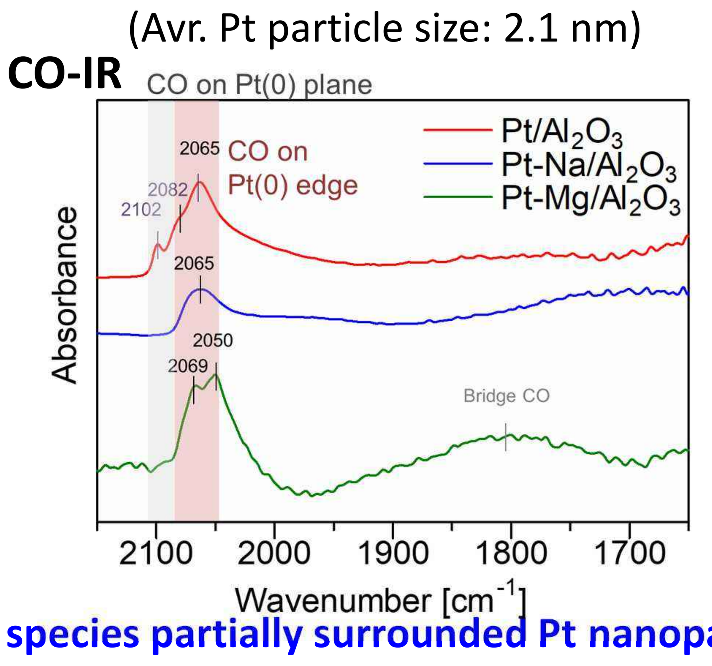
Na species surround Pt nanoparticles

(Avr. Pt particle size: 2.1 nm)



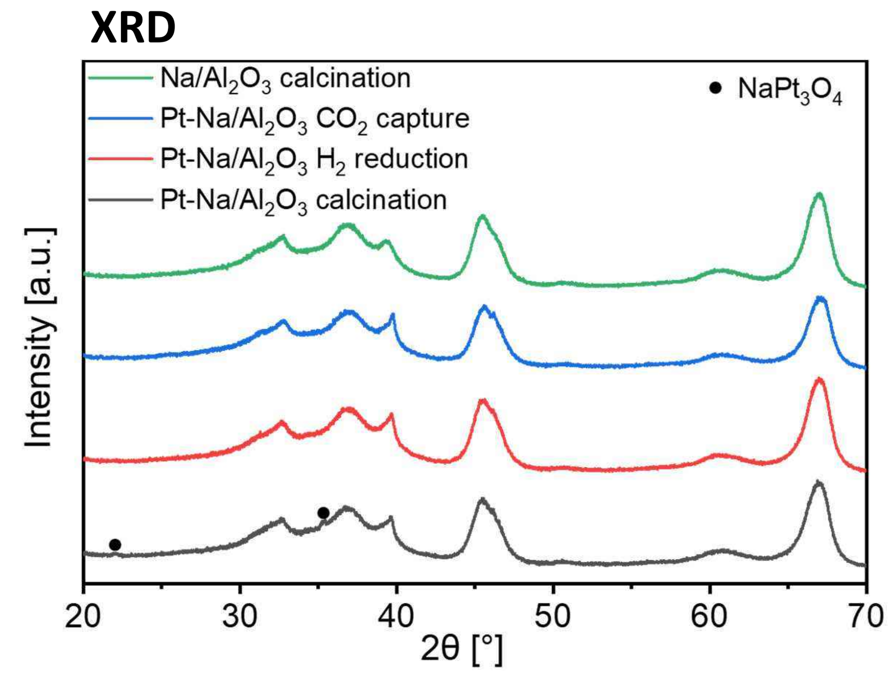
Na modified the surface of Pt nanoparticles (core shell like catalyst)

CO-IR



Na species partially surrounded Pt nanoparticle surface

XRD

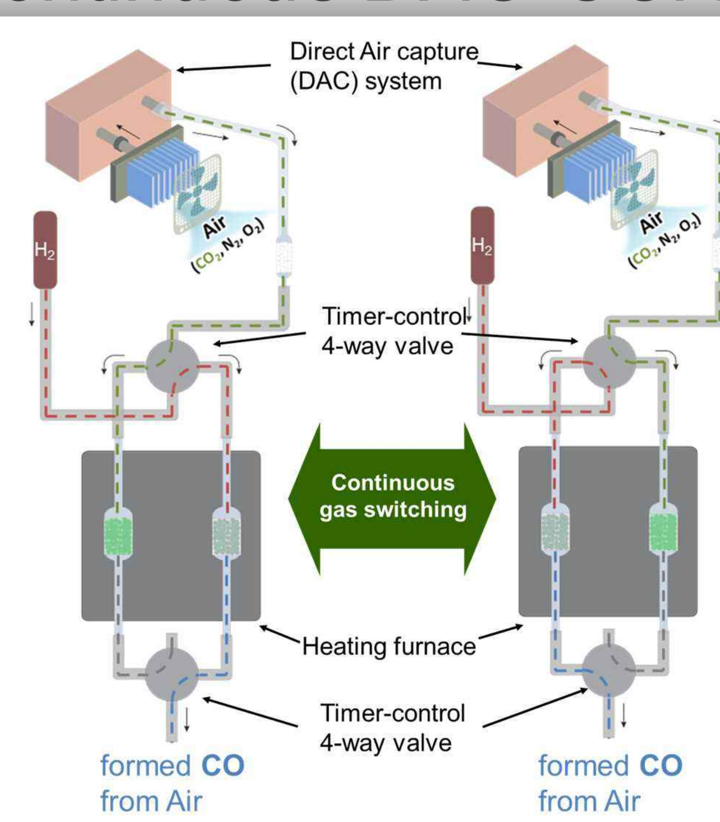


$NaPt_3O_4$ formed on calcined Pt-Na/Al_2O_3

Possible mechanism

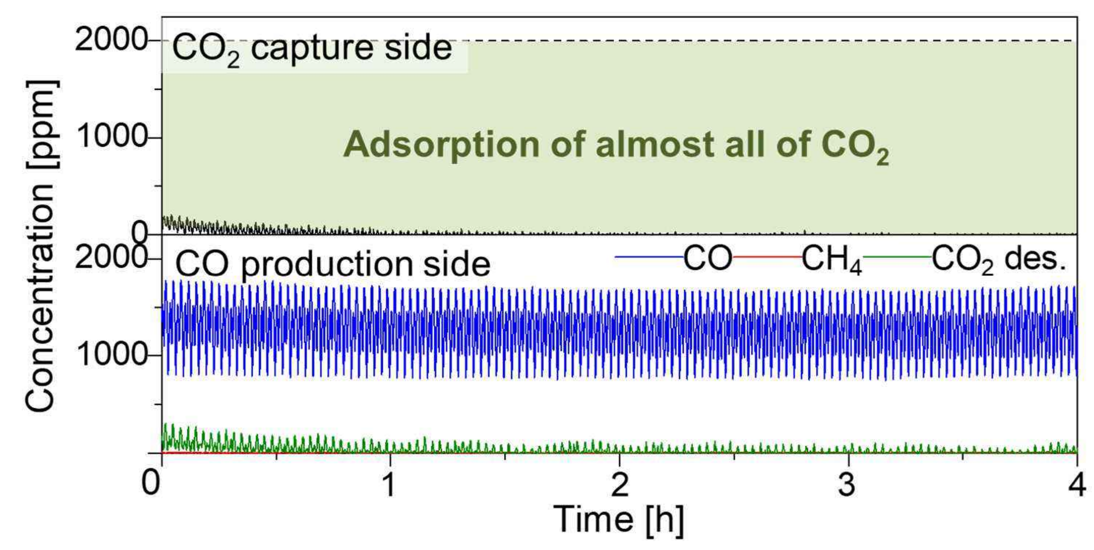
1. Carbonate adsorbed on Na species near Pt nanoparticles
2. Adsorbed CO_2 is rapidly reduced by H_2
3. CO adsorption is suppressed on Pt nanoparticles surrounded by Na species
→ Successive reduction of CO to CH_4 is inhibited and CO is selectively formed

Continuous DAC-CCR operation



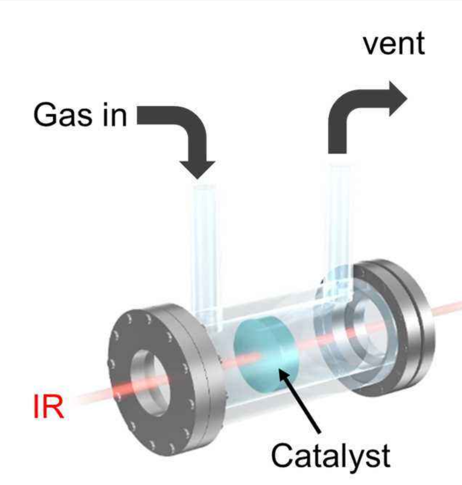
Continuous capture of dilute CO_2 from the air and selective CO generation was demonstrated.

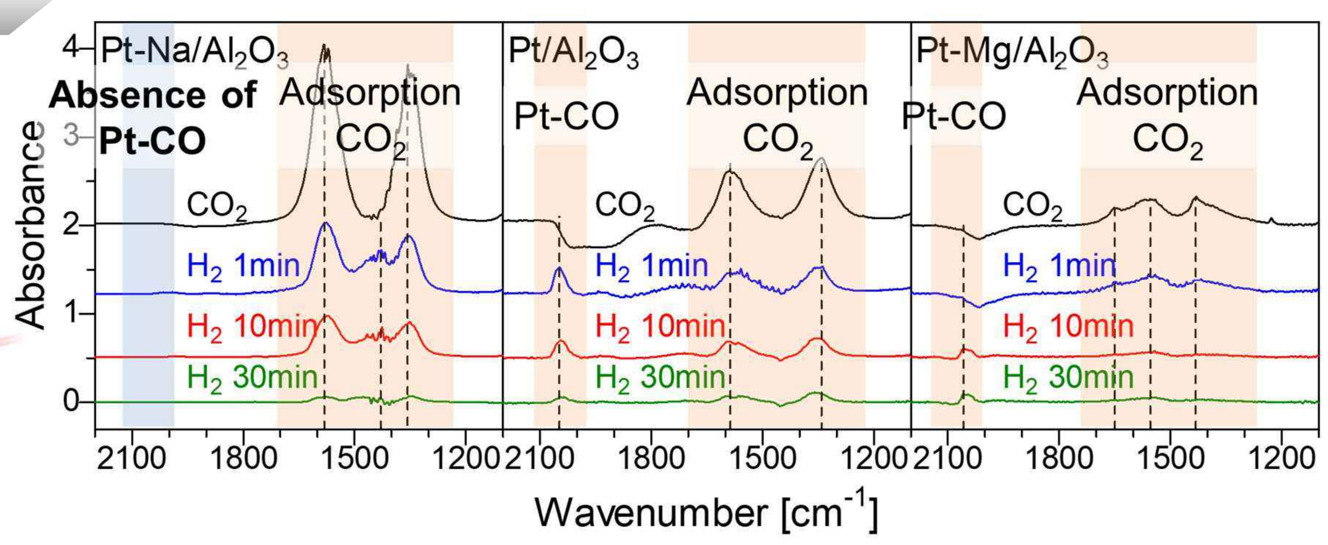
Reaction condition
Catalyst amount ：2 g
Reaction temperature：300°C
Adsorption gas from DAC
：CO_2/1500 ~ 2500 ppm O_2/20%
(80~120 mL/min)
Reduction gas：H_2/100% (100 mL/min)
Valve switching：every 1 min



✓**Continuous generation of CO from dilute atmospheric CO_2.**
✓**High selectivity was maintained in continuous operation. (100h)**

In situ FTIR





The adsorption of the formed CO was suppressed over Na-modified Pt NPs