Development of Recovery and Removal Techniques of Dilute Reactive Nitrogen to Realize Nitrogen Circulating Society

■ＰＭ　Toru Wakihara

The University of Tokyo, Professor

■PJ participating institutions

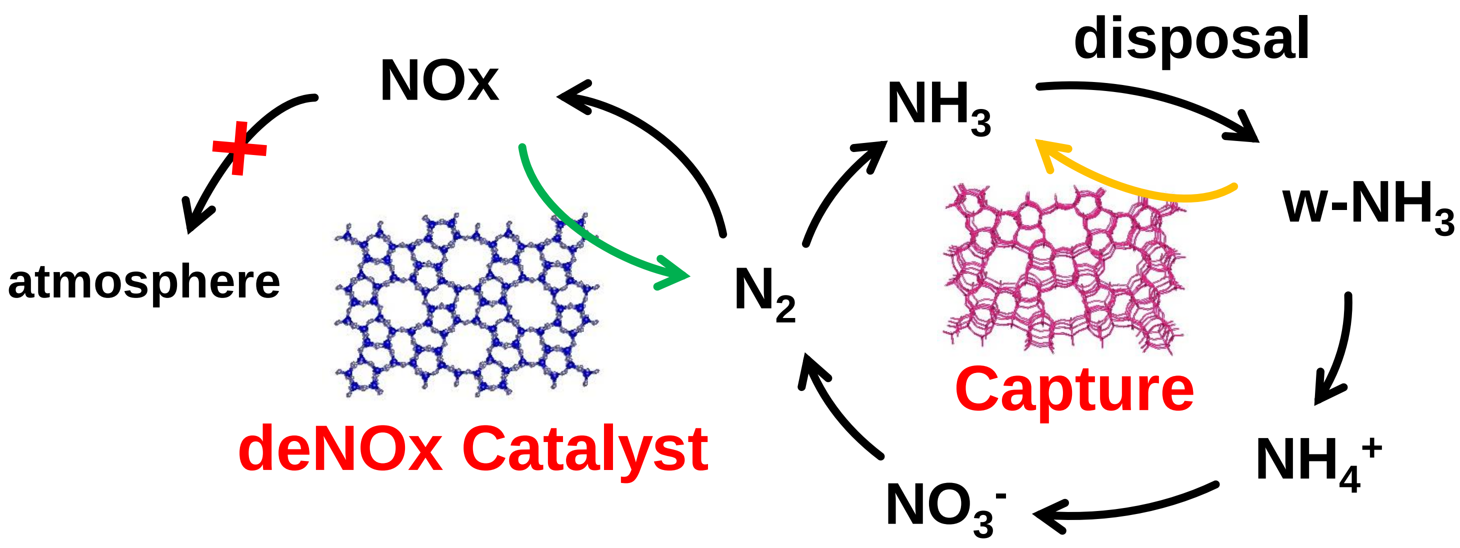
The University of Tokyo

The National Institute of Advanced Industrial Science and Technology

Japan Fine Ceramics Center

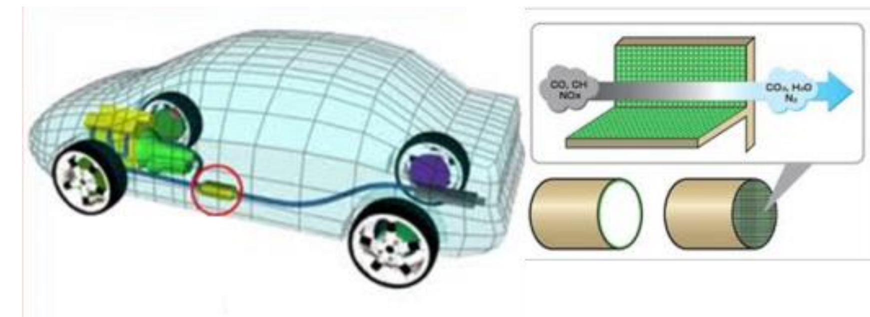
Mitsubishi Chemical Corporation

Project Overview



For building a nitrogen recycling society, development of denitrification and ammonia recovery technology is an urgent issue

Exhaust Gas (NOx)



Industrial Wastewater (w-NH_3)

- Although the transition to electric vehicles has been proposed for the realization of a carbon-neutral society, in Europe, reluctant to fully transition to electric vehicles.
- Considering the introduction of e-fuel, an internal combustion engine (especially for truck transportation) is essential.
- Truck-mounted catalyst does not need to be replaced even after running 1 million km → Cost reductions, wage increases, etc. are expected
- From the viewpoint of the nitrogen cycle, Realization of breaking away from the present treatment system wasting energy (industrial waste liquid, livestock farm, sewage treatment plant)
- Cost reduction by reducing manufacturing cost of urea for fertilizer by reusing recovered NH_3

Final Aim

- **Demonstration of NH_3 recover from wastewater at pilot facilities**
- **Pilot scale test using zeolite for high durability NOx purification**
- **Demonstration of NOx purification without NH_3**

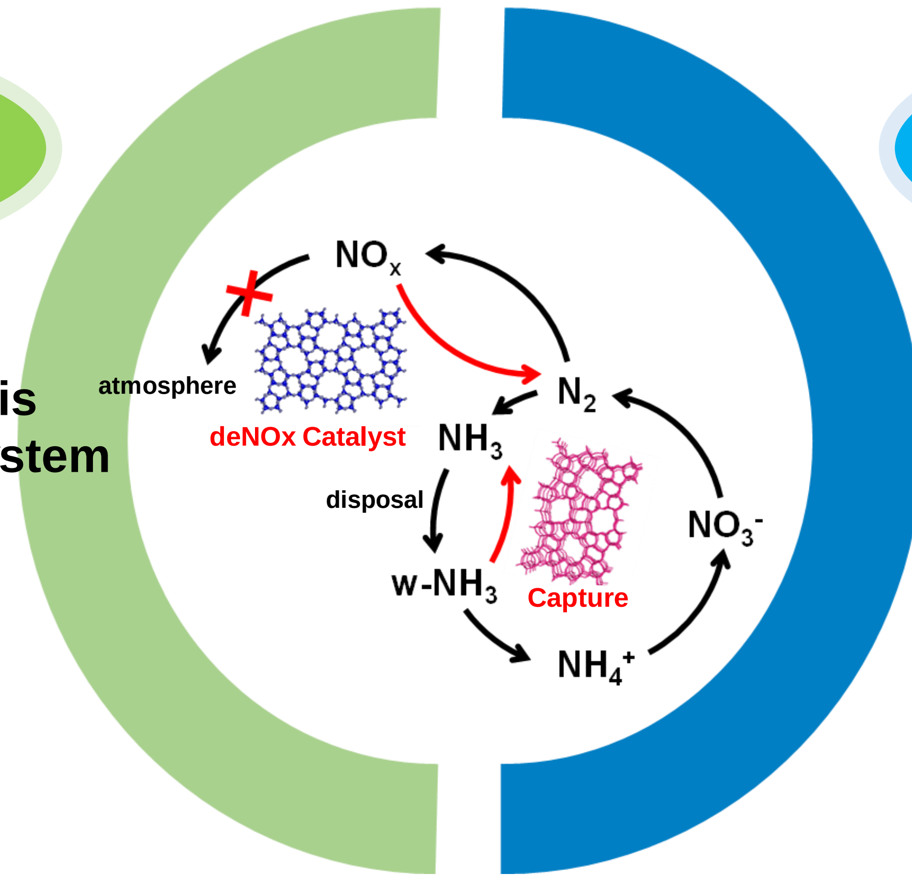
Organization of the Project (at the early stage)

Institutions

- The Univ. of Tokyo
- MCC
- AIST
- JFCC

deNOx

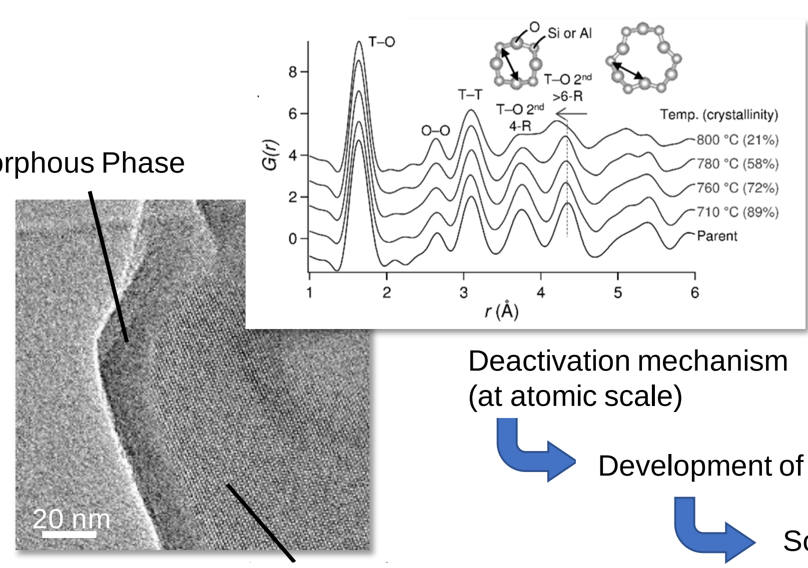
Material Synthesis
Evaluation・Analysis
Development of system



NH_3, NH_4^+

Material Synthesis
Evaluation・Analysis
Development of system

Research Direction

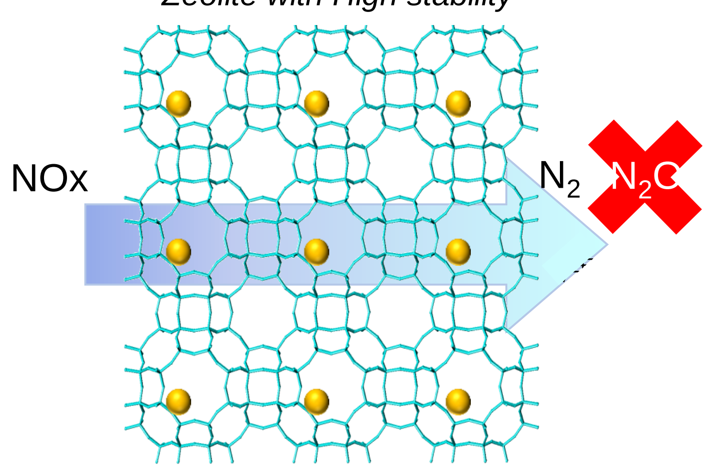


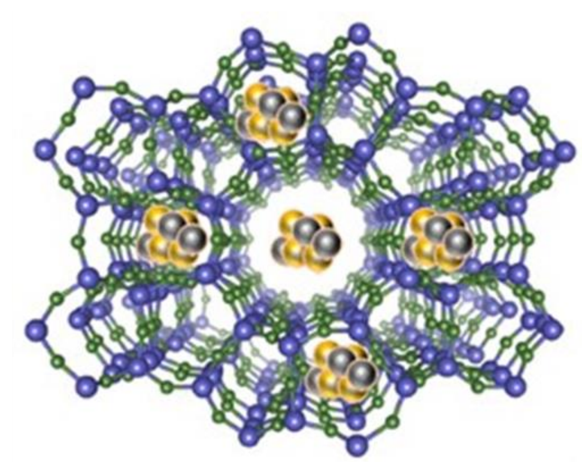
Deactivation mechanism
(at atomic scale)

→ Development of excellent catalyst

→ Social implementation

Zeolite with High stability





Metal Nanocluster Zeolites

New Active Sites

Focus on only zeolites

Organization and core technology (deNOx)

The Univ. of Tokyo

- ✓ Synthesis
- ✓ New System
- ✓ LCA evaluation

JFCC
AIST

- ✓ Analysis
- ✓ Evaluation

MCC
Company A
Company B

- ✓ Scale up
- ✓ Production – Sale

Company C

- ✓ Molding

University of Alicante (Spain)

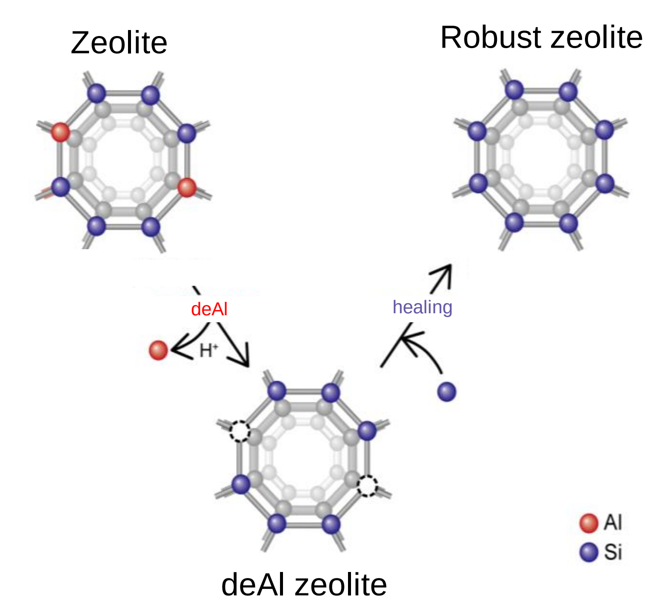
- ✓ Excellent catalyst

Budding

- Photocatalyst
- Plasma reaction
- Defect healing
- Dealumination

Core

- Fast Synthesis
- Flow synthesis
- Defect healing
- Dealumination



✓ Fast synthesis of Excellent zeolite catalyst

→ **High conversion・Low N_2O evolution!**

Organization and core technology (NH_3 capture)

The Univ. of Tokyo
- ✓ Synthesis
- ✓ New System
- ✓ LCA evaluation

JFCC
- ✓ Analysis
- ✓ Evaluation

Nazarbayev University (Kazakhstan)
- ✓ NH_3 removal using natural zeolite and amorphous aluminosilicate

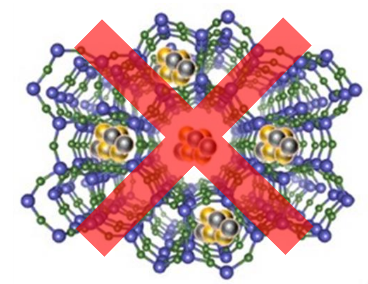
Company A
Company B
Company C
- ✓ Production
- ✓ Sale

Company D
Company E
Company F
- ✓ Recycle
- ✓ Urea Production

Company G
- ✓ Equipment design

Company H
- ✓ Implementation

Company I
- ✓ Molding


Synthetic zeolite

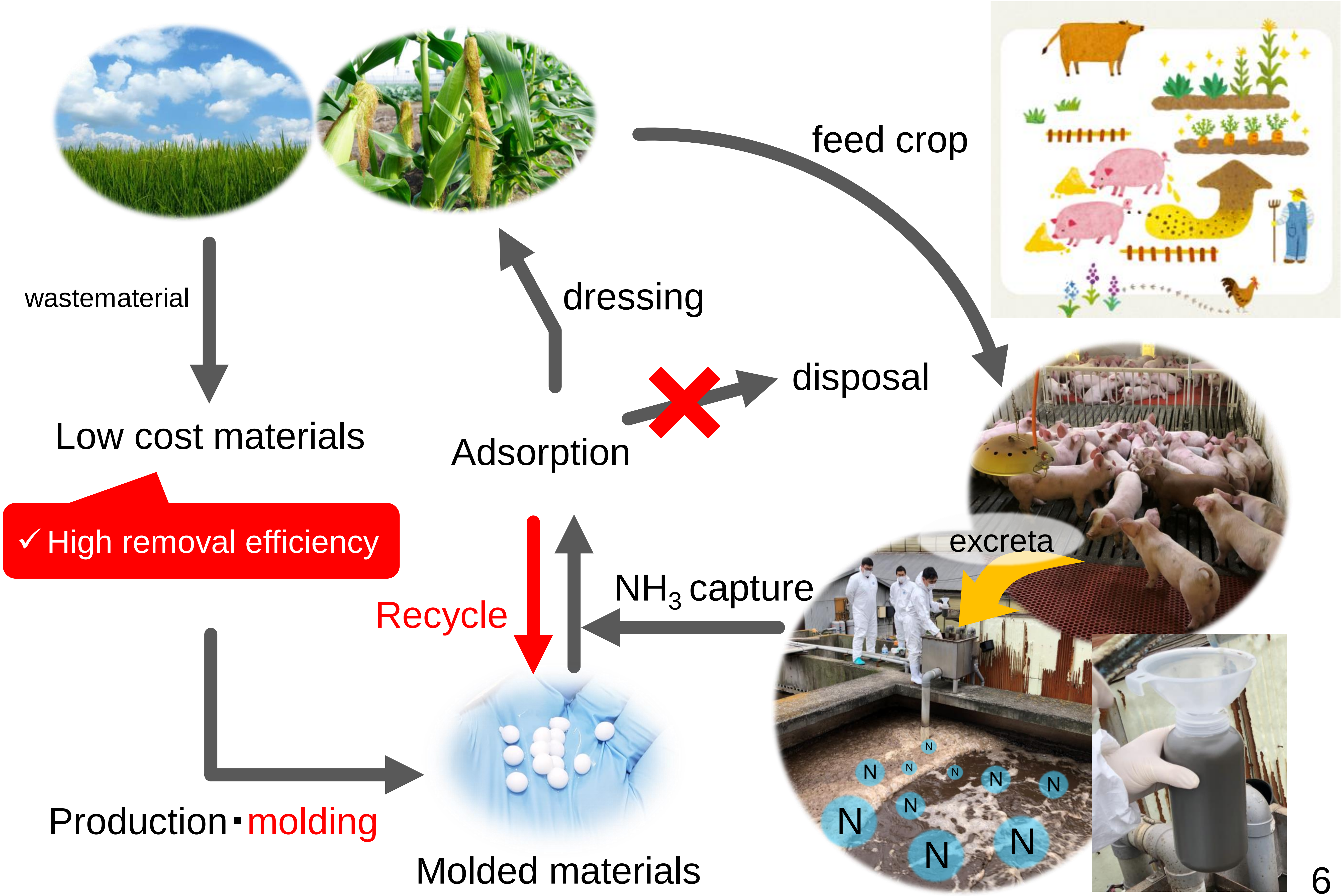
Budding
- Amorphous aluminosilicate
- Waste material

Core
- Amorphous aluminosilicate
- Waste material
- Natural zeolite

- ✓ Low-cost・facile process
- ✓ High removal efficiency

→ **Regional nitrogen circulation system**

Regional nitrogen circulation system

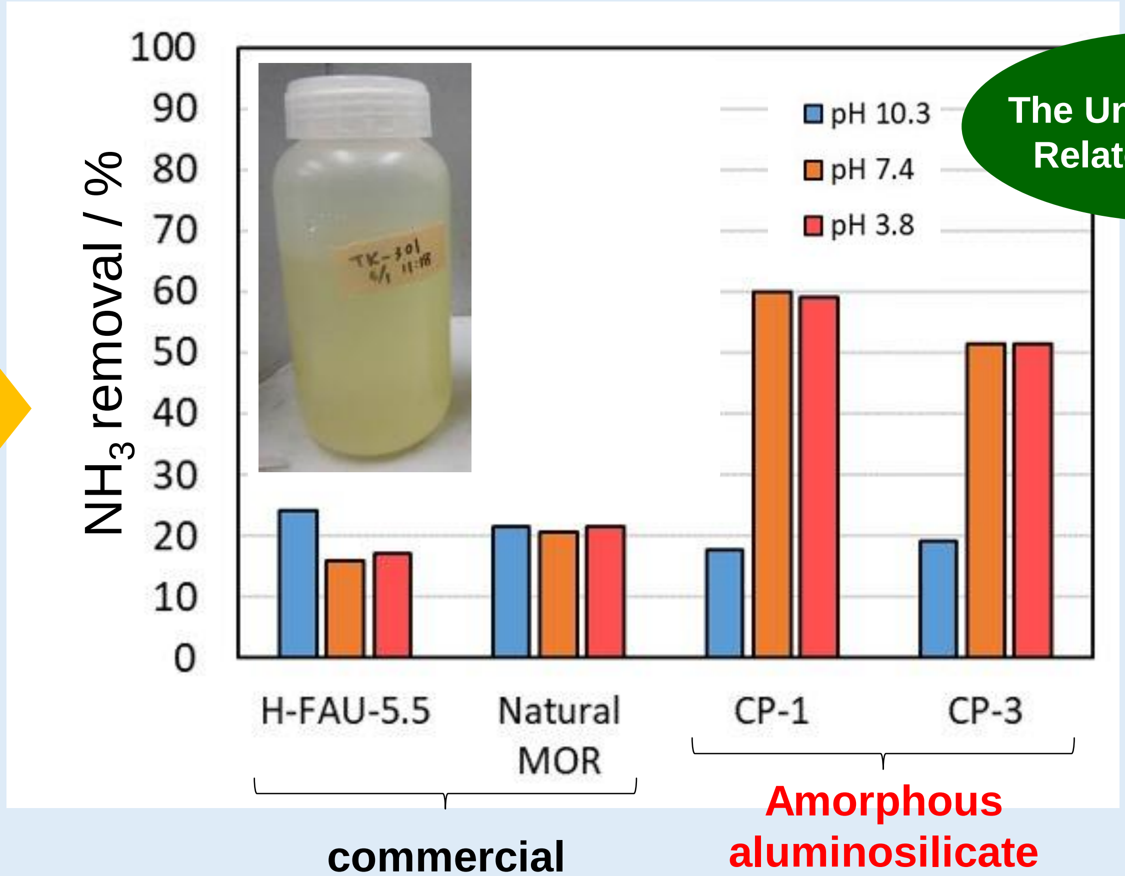


Recovery and recycling from industrial waste liquids

Related Company
Company A–C

exhaust

- ✓ **Highly concentrated (1000-2000 ppm NH_4^+)**
- ✓ **Ammonia odor spreads to the floor in factory**



The Univ. of Tokyo Related Company

As fuel

200 ton / year

Related Company

Compost to the market

Many similar companies

Related Company

Distilled concentrated NH3 water

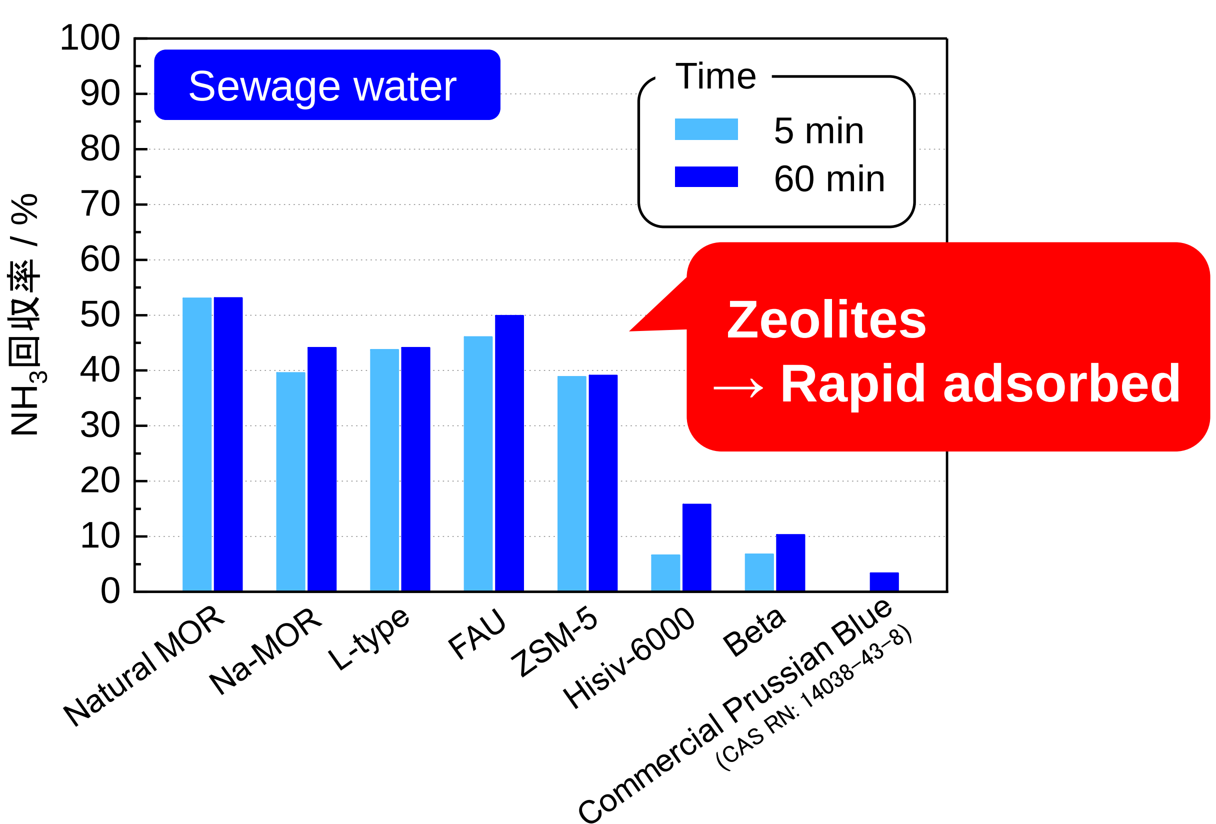
✓ Aim: NH_3 removal over 50% from industrial wastewater

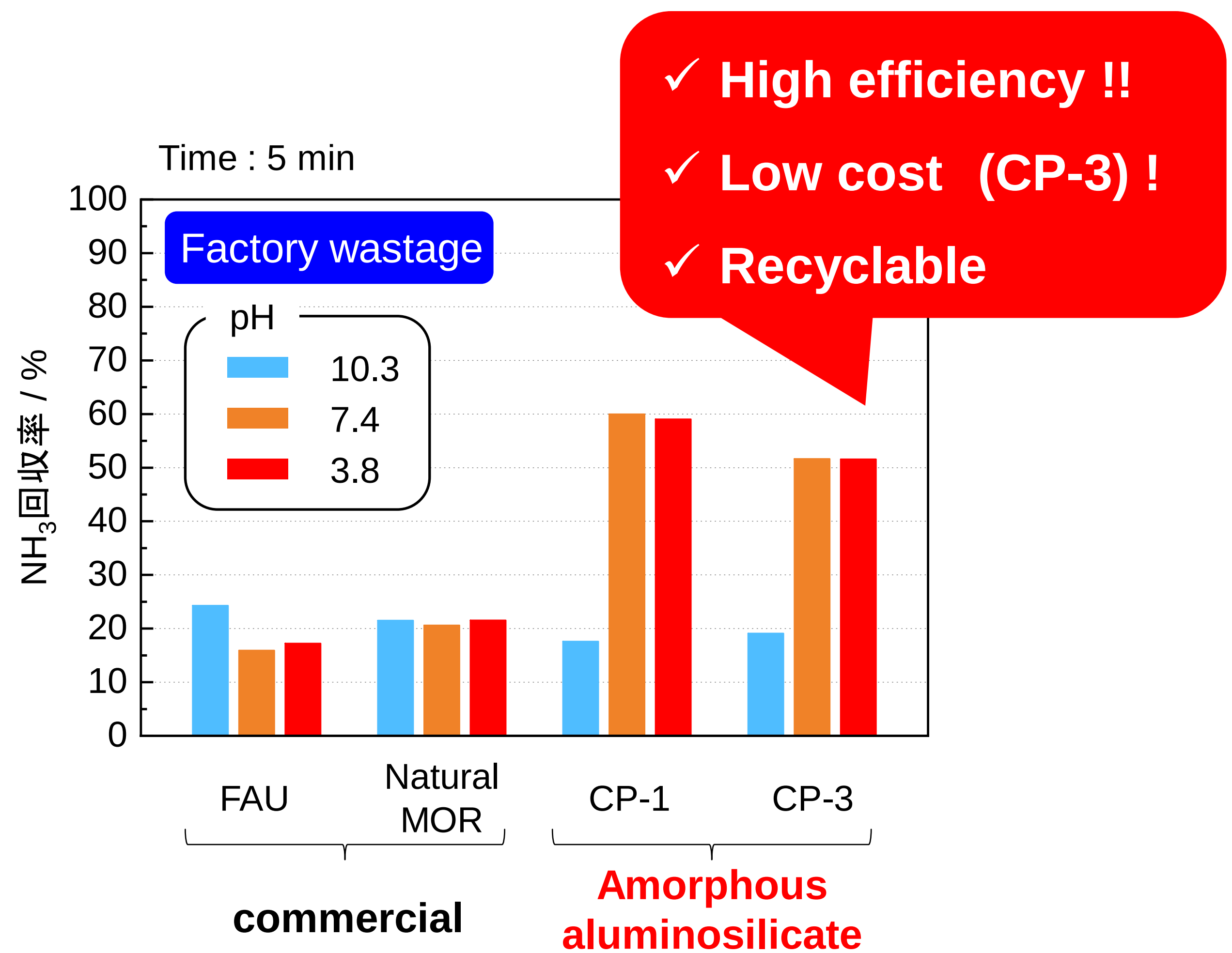
Selection of Materials

List of industrial wastewater

	Sample	NH_4^+ concentration / mM
Sewage water	Position A	1.7~2.3
	Position B	1.6~1.9
	Activated sludge stripper	75
Swine wastewater	-	110
Factory wastage	Company A	70
	Company B	12

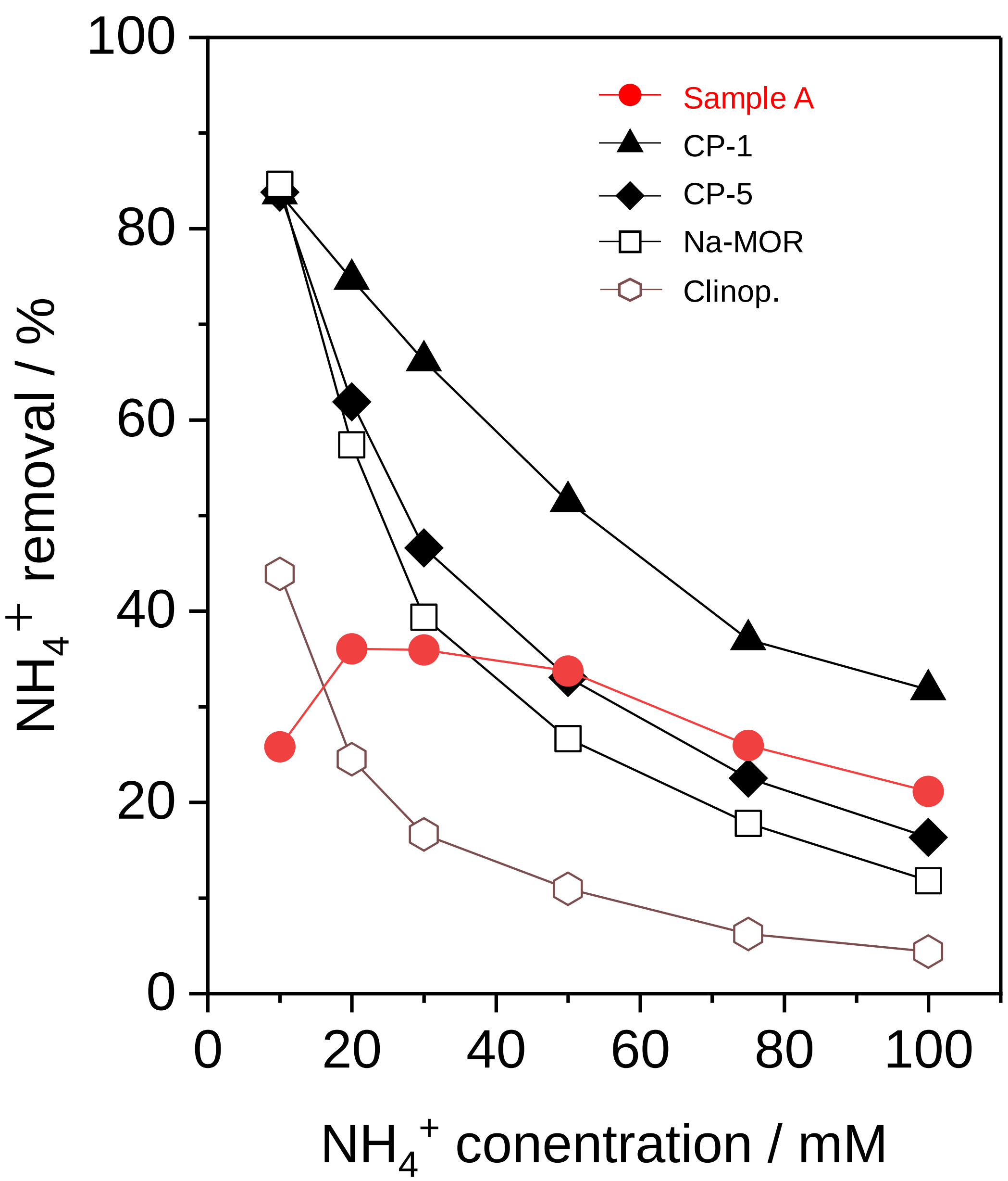
NH_3 removal efficiency



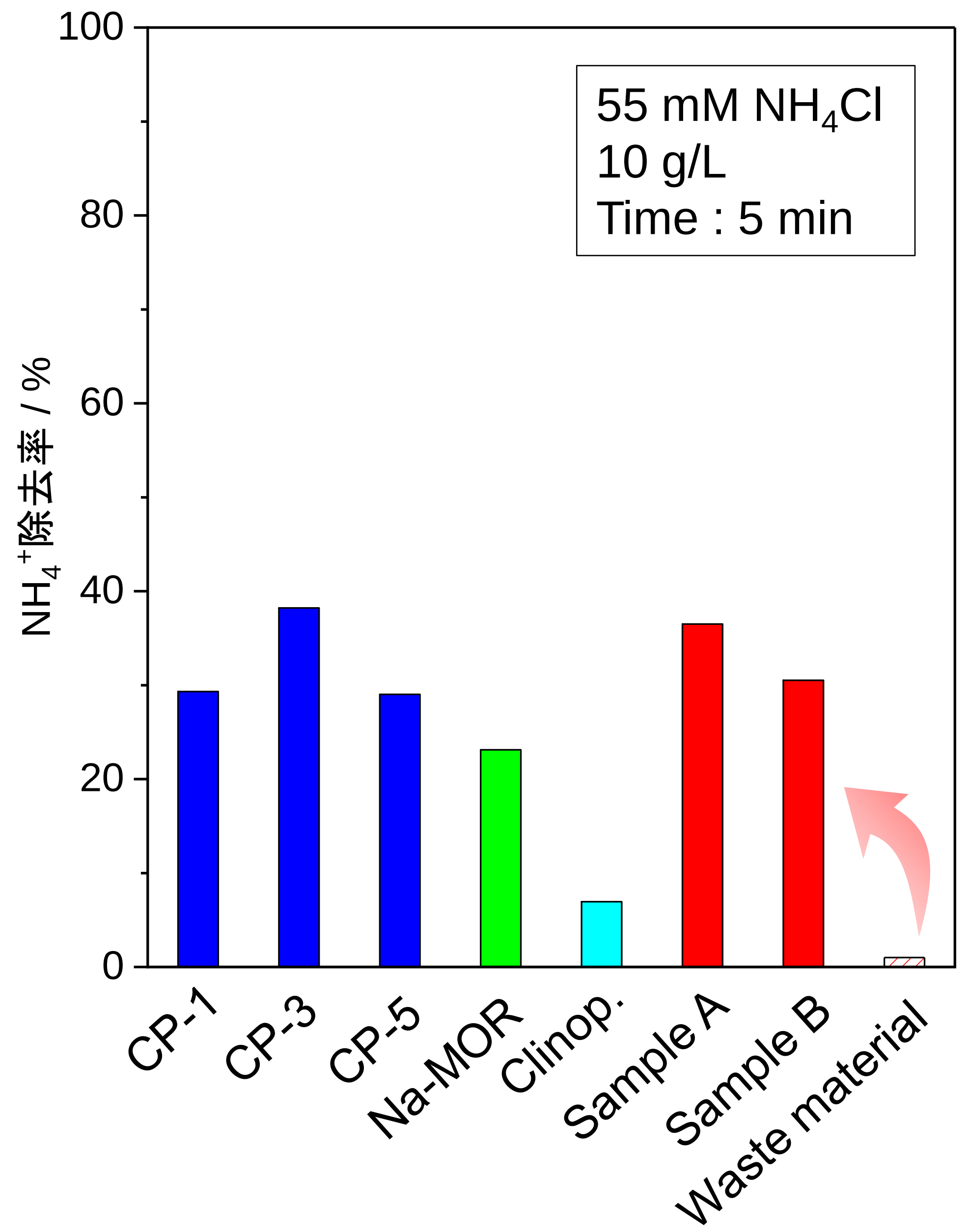


NH_3 removal efficiency

☐ Effect of NH_4^+ concentration

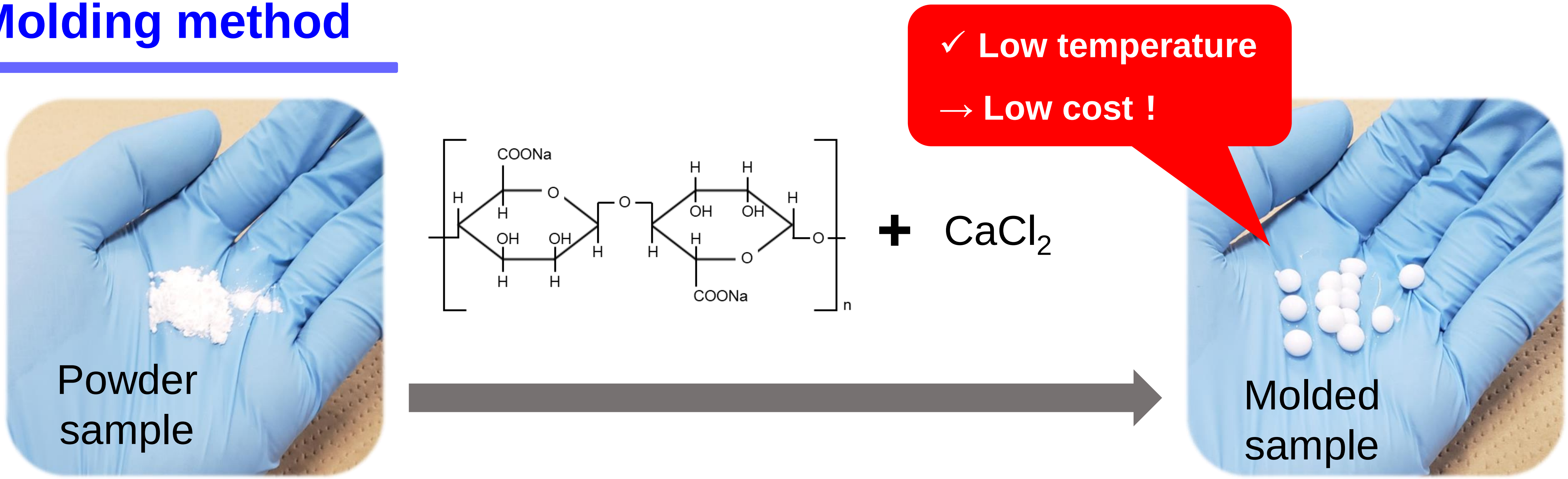


☐ Various adsorbents

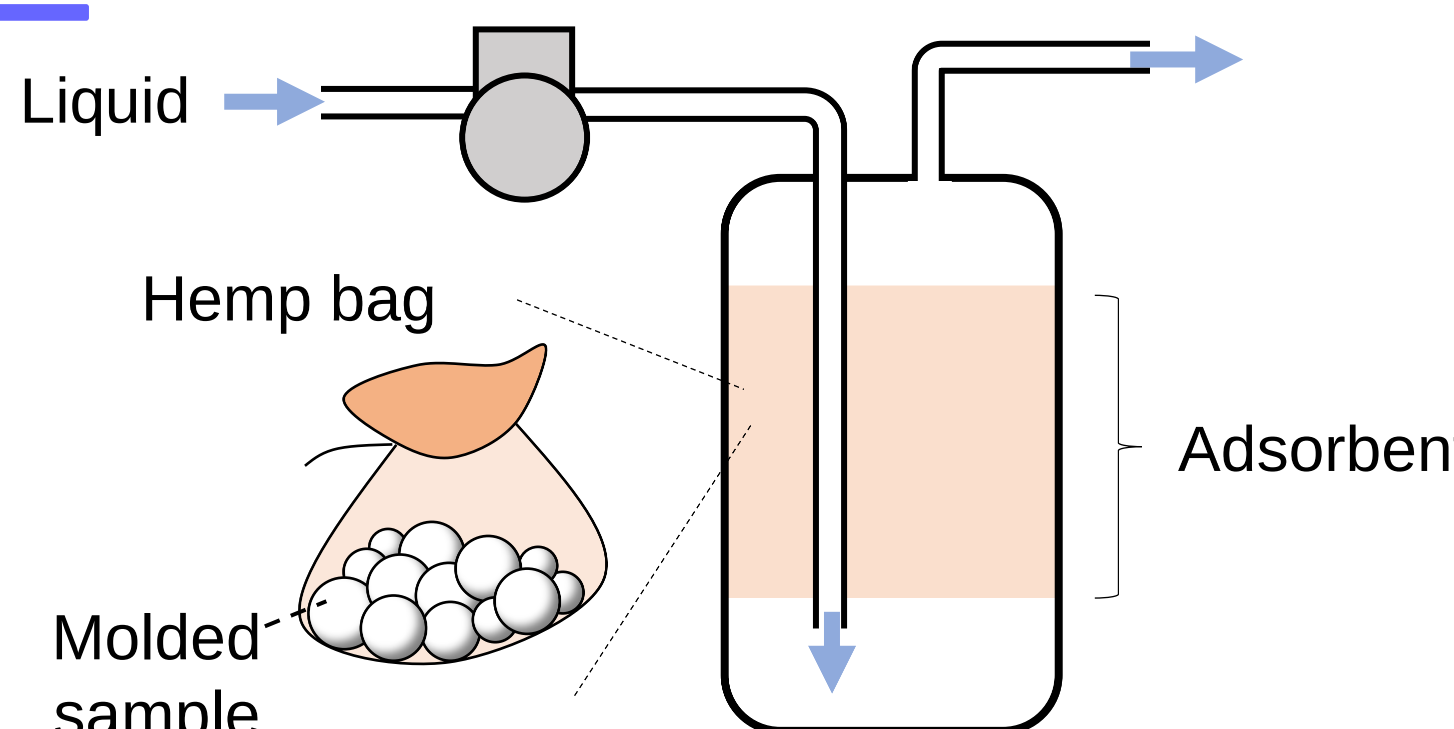


High NH_3 removal (similar to CP samples)

Molding method



Continuous Flow System



LCA （NH_3 capture）

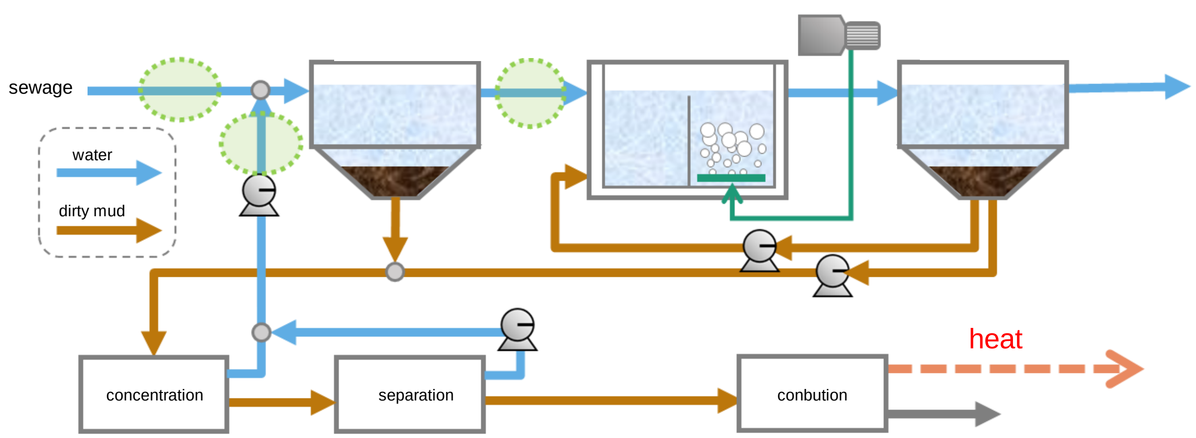
The University of TokyoMaterials

Team: Wakihara, IyogiUrban

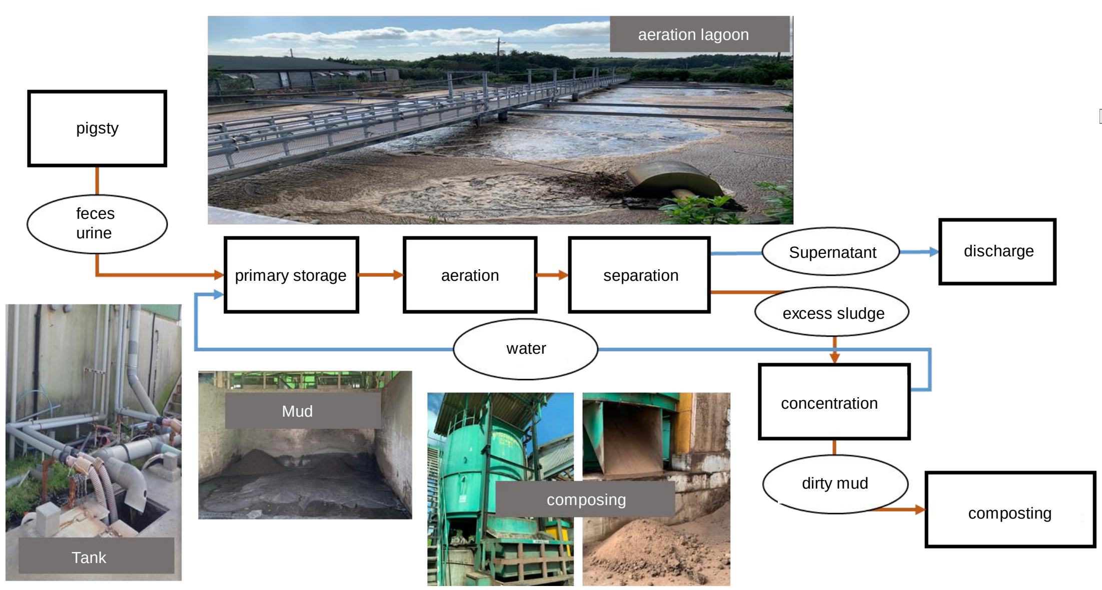
Engineering Team: Katayama, Hashimoto, Tobino

LCA Team: Kanematsu

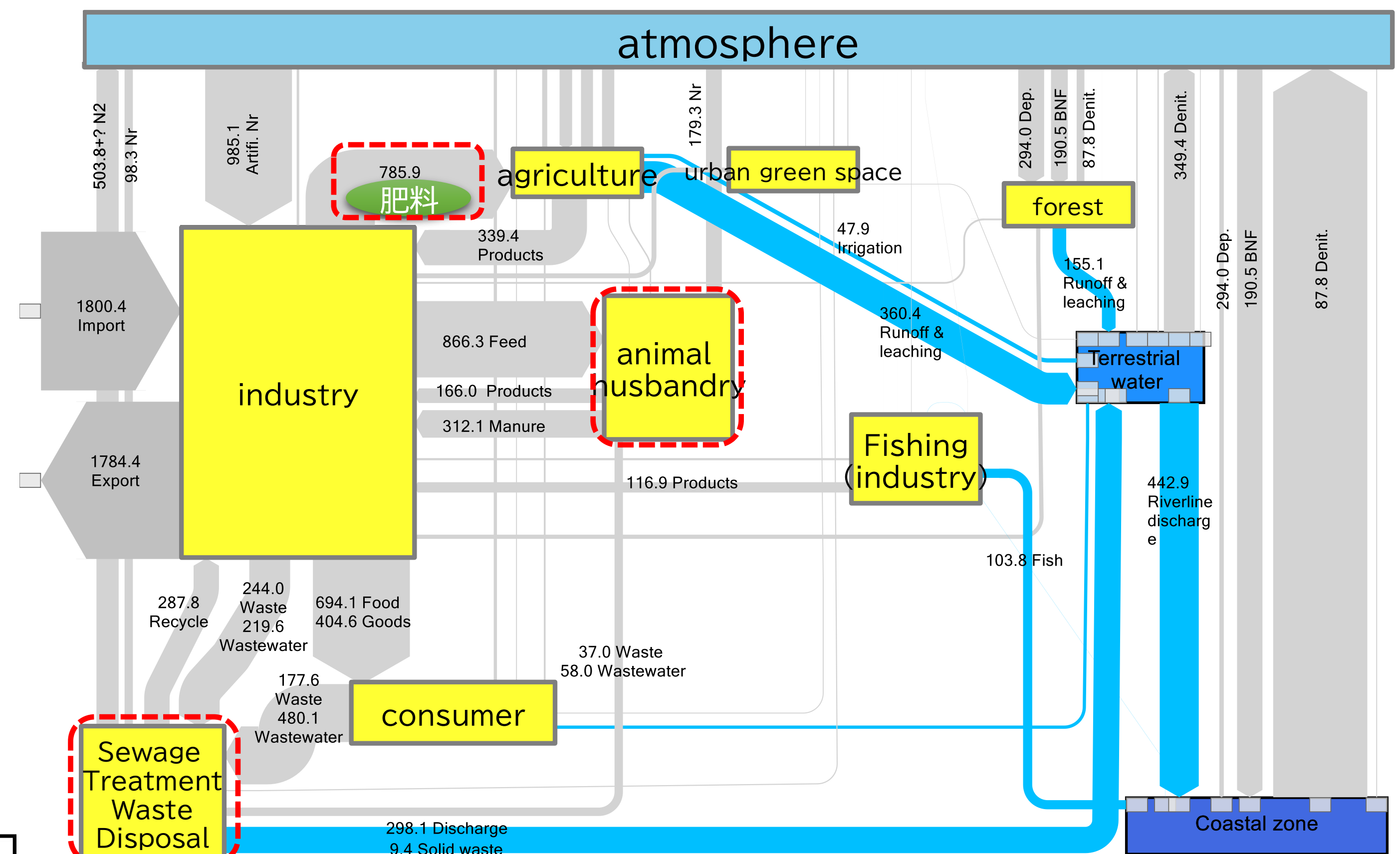
Sewage treatment



Livestock Wastewater Treatment



Nitrogen flow in Japan



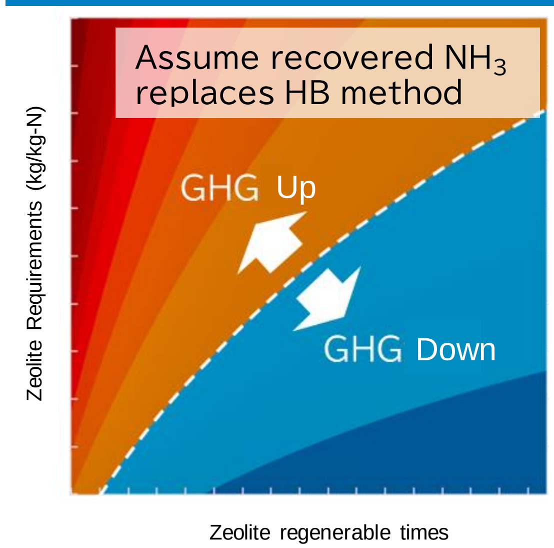
Based on Hayashi *et al.*, (2021)

To transform social systems and processes by moving away from wastewater treatment, which is energy-intensive and dumps resources

LCA and nitrogen flow

Study of LCA framework for exploring material performance conditions

Change in GHG emissions from sewage treatment process



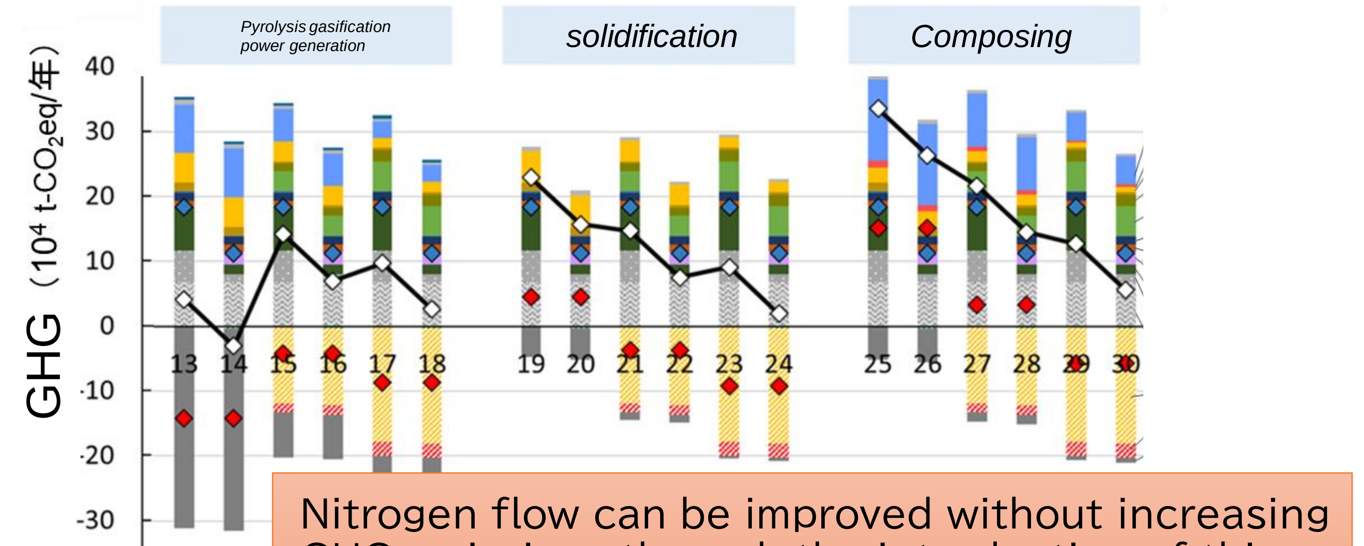
- As an initial LCA, GHG emission intensity during production of Type A zeolite for which inventory data is available is applied.
- Under these conditions, the required amount of zeolite (≒adsorption efficiency) and the number of times the zeolite can be regenerated are identified as having high GHG sensitivity

→ Feedback to the experiment

LCA to guide technology development

LCA for real processes

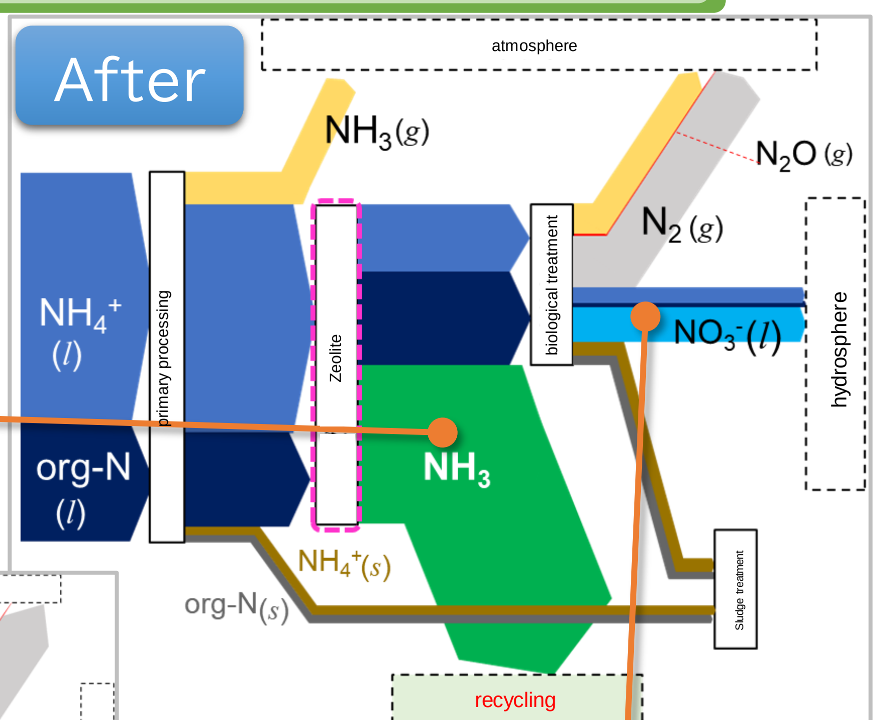
Some excerpts from the evaluation results of 42 cases
(↓even numbers are the results when zeolite was introduced

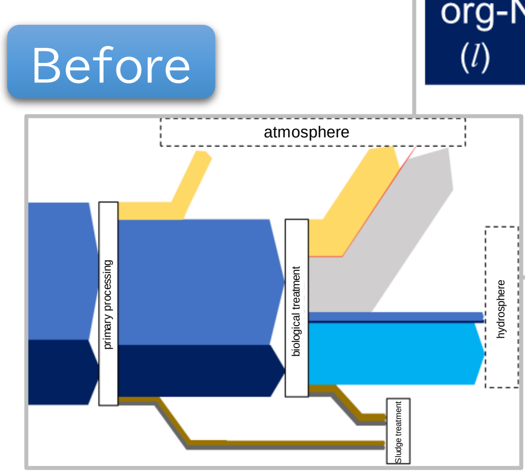


Nitrogen flow can be improved without increasing GHG emissions through the introduction of this technology.

Nitrogen flow changes during sewage treatment process (site units)

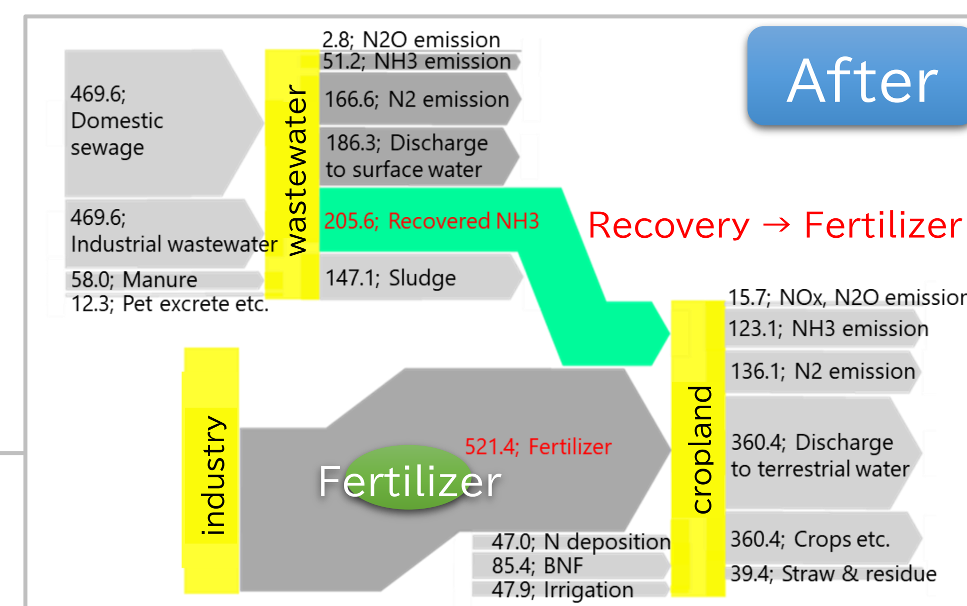
Recycled NH_3 equivalent to 50% of total N from primary treatment

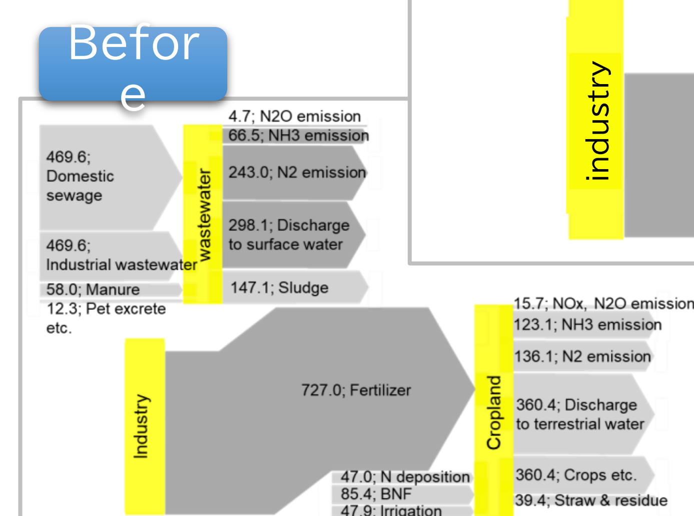




N emissions to the hydrosphere are also reduced by about half.

Flow change in agricultural use of recovered NH_3 (national potential)



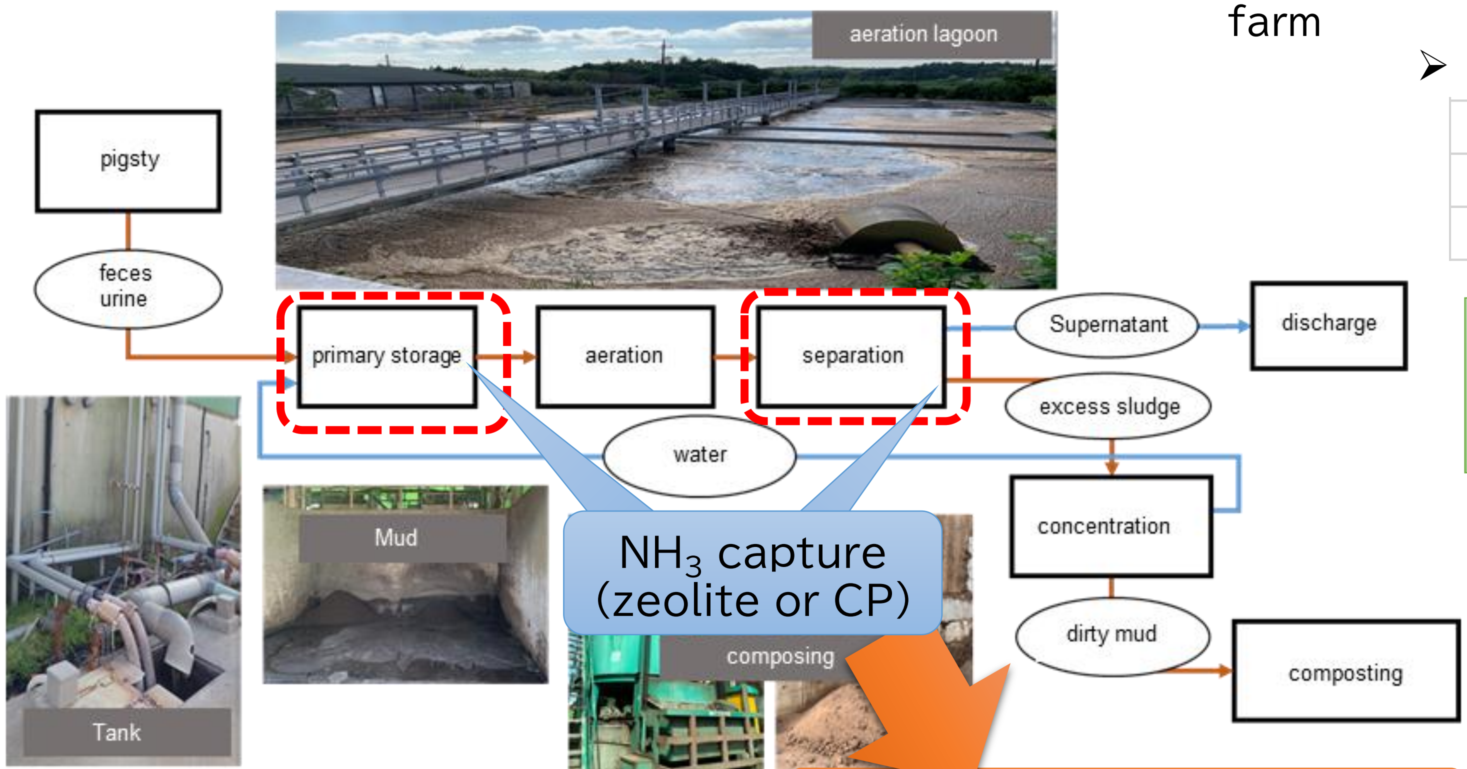


Potential to replace about 30% of industrial fertilizer production

Expand application to livestock wastewater

Modeling of pig farm effluent treatment processes

→ Field survey and interviews were conducted at a pig farm where a lagoon wastewater treatment system is being introduced. Conducted on-site survey and interviews at a pig farm



Significant reduction in aeration power

Regional circulation of NH_3 (agricultural use)

➢ number of pig farms

Mother	count	2000
Child	count	20000
Total	count	22000

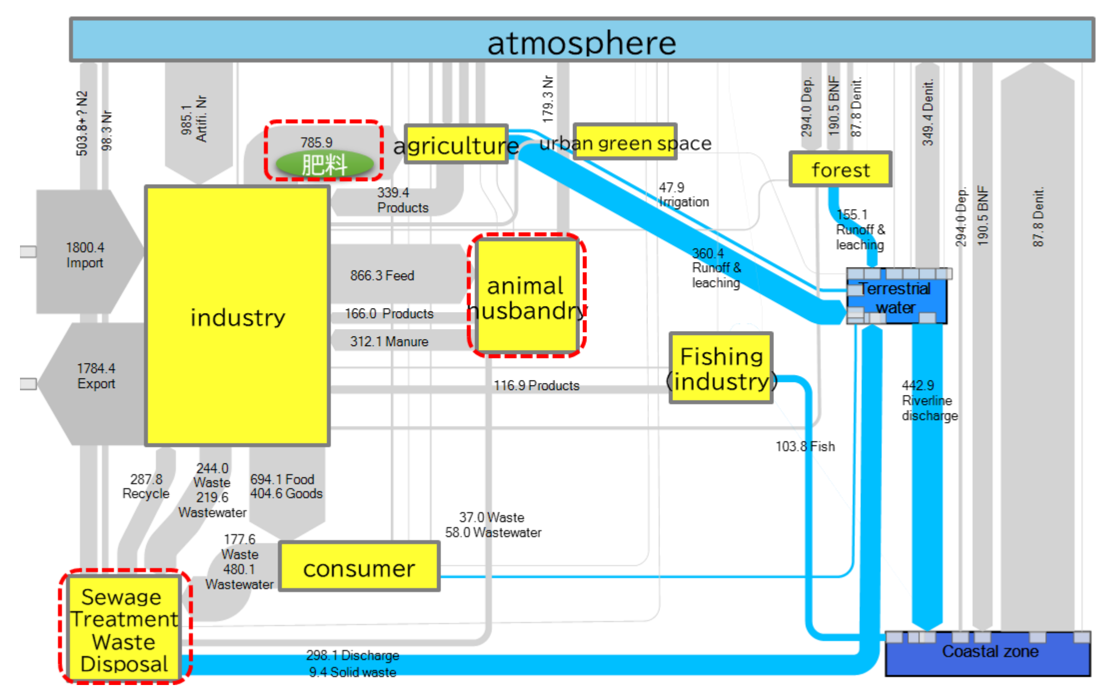
Equivalent to the emissions of a city of tens of thousands of people at one site

➢ Emissions

excrement	kg/day/匹	1.9
urine	kg/day/匹	3.5
Total	kg/day/匹	5.4
BOD	mg/L	24000
SS	mg/L	80000
TN	mg/L	6800
TP	mg/L	2700

More room for further purification compared to sewage treatment
→ large reduction potential per m^3

Modeling is underway to analyze the current situation and evaluate the effectiveness of technology implementation



To quantify the effects of N recovery from sewage + livestock wastewater at the national level

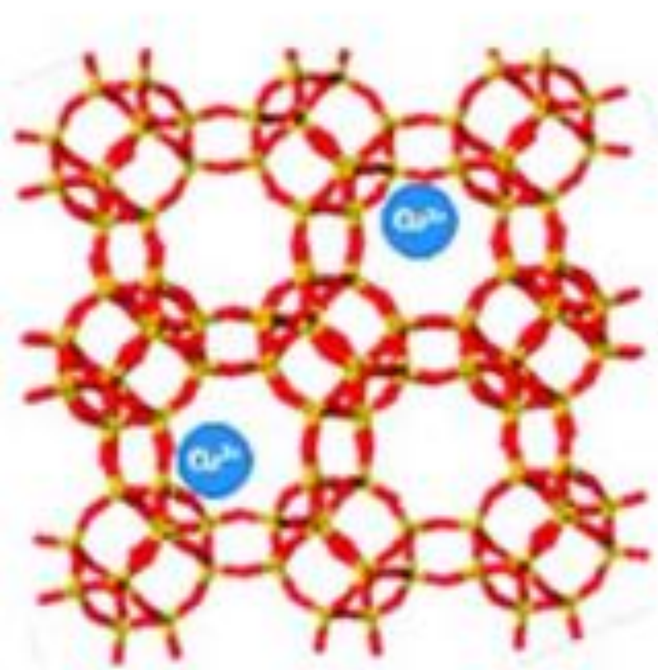
Future development
- ➢ Evaluation of flow when zeolite/CP is applied (per pig farm)
- ➢ Macroscopic flow impact assessment when recycling is implemented

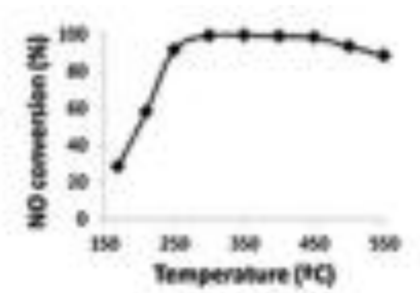
NH_3–SCR (for automobile)

◆ Conventional Cu-excahnged zeolite

Low stability → Decrease of NOx conversion
N_2O prodution

Desired properties for zeolite catalyst





High conversion

High Stability (water vapor)

Low N_2O evolution

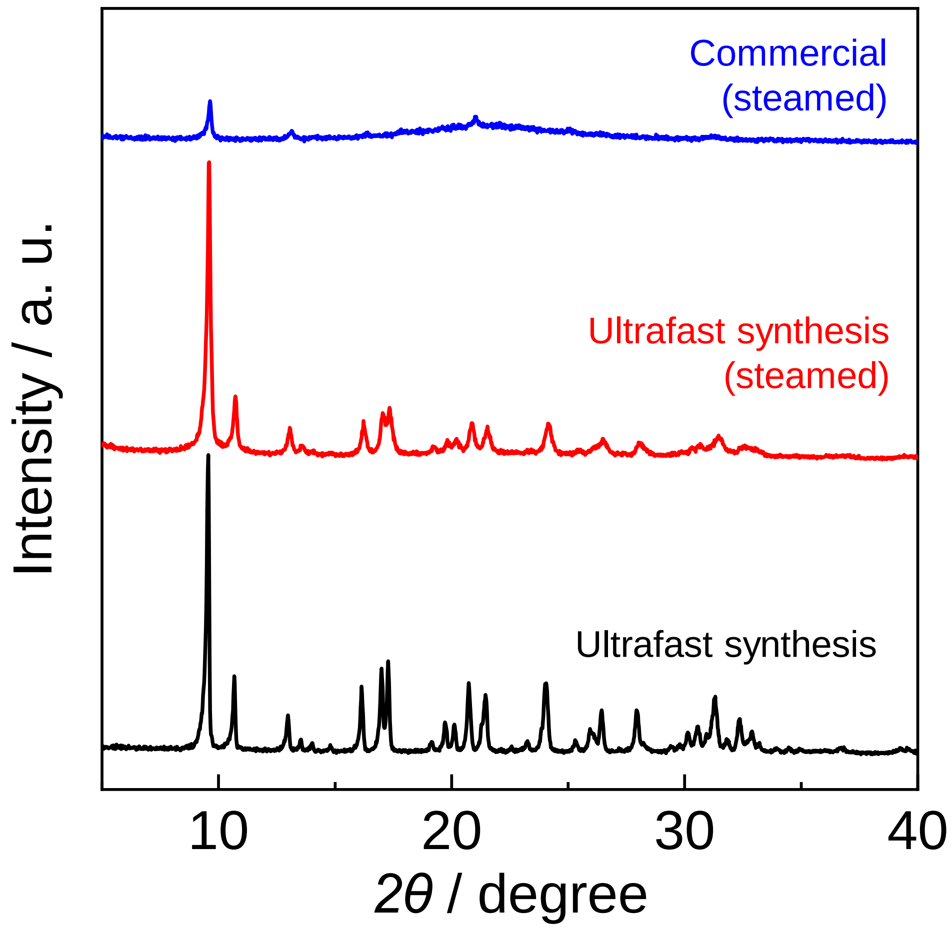
broken catalyst in NH_3-SCR (by urea water)

Hydrothermal stability of zeolites catalyst

Stability against water vapor

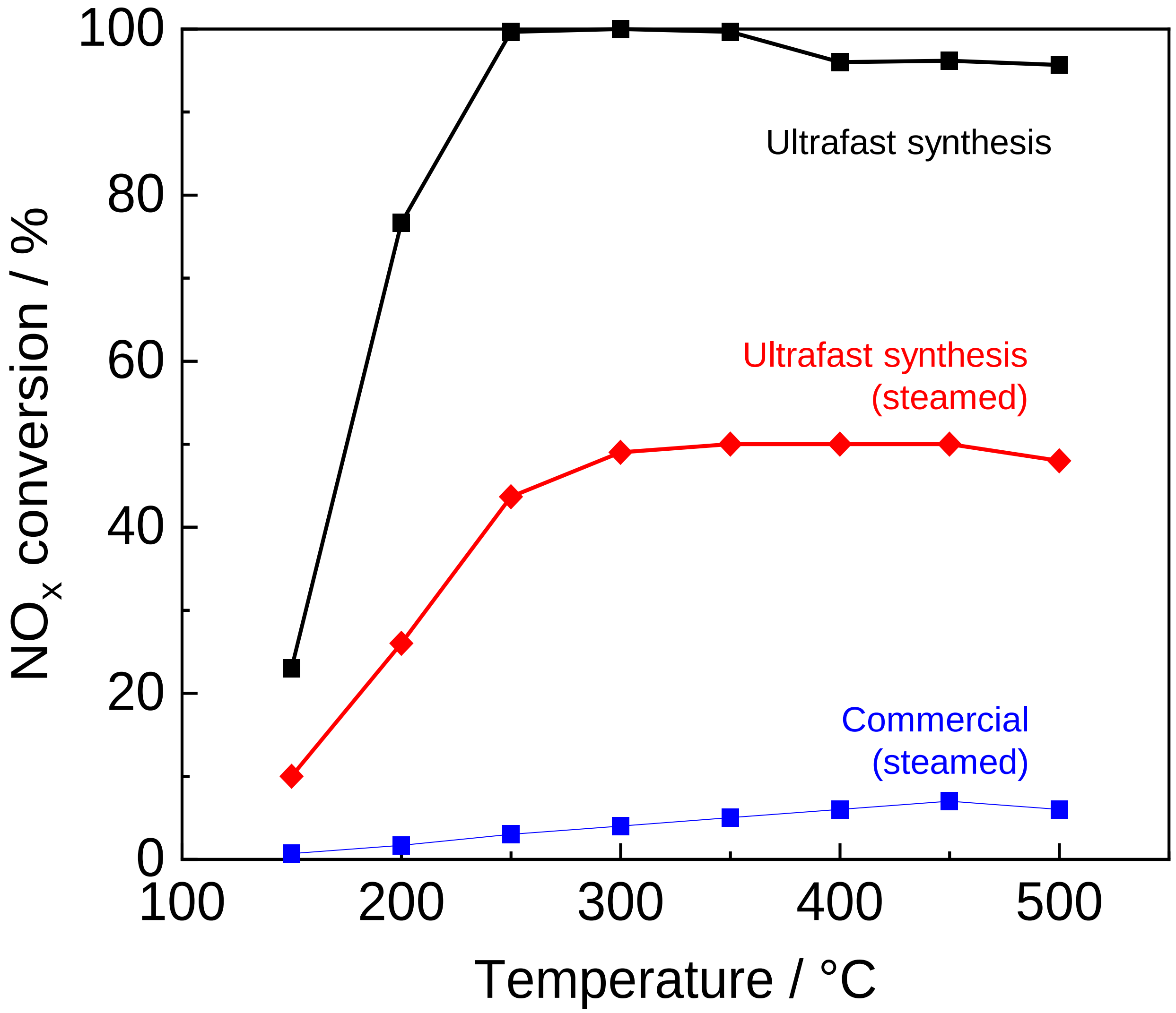
Condition: H_2O-10vol%
900ºC 1 h

X-ray Diffraction



NH_3-SCR

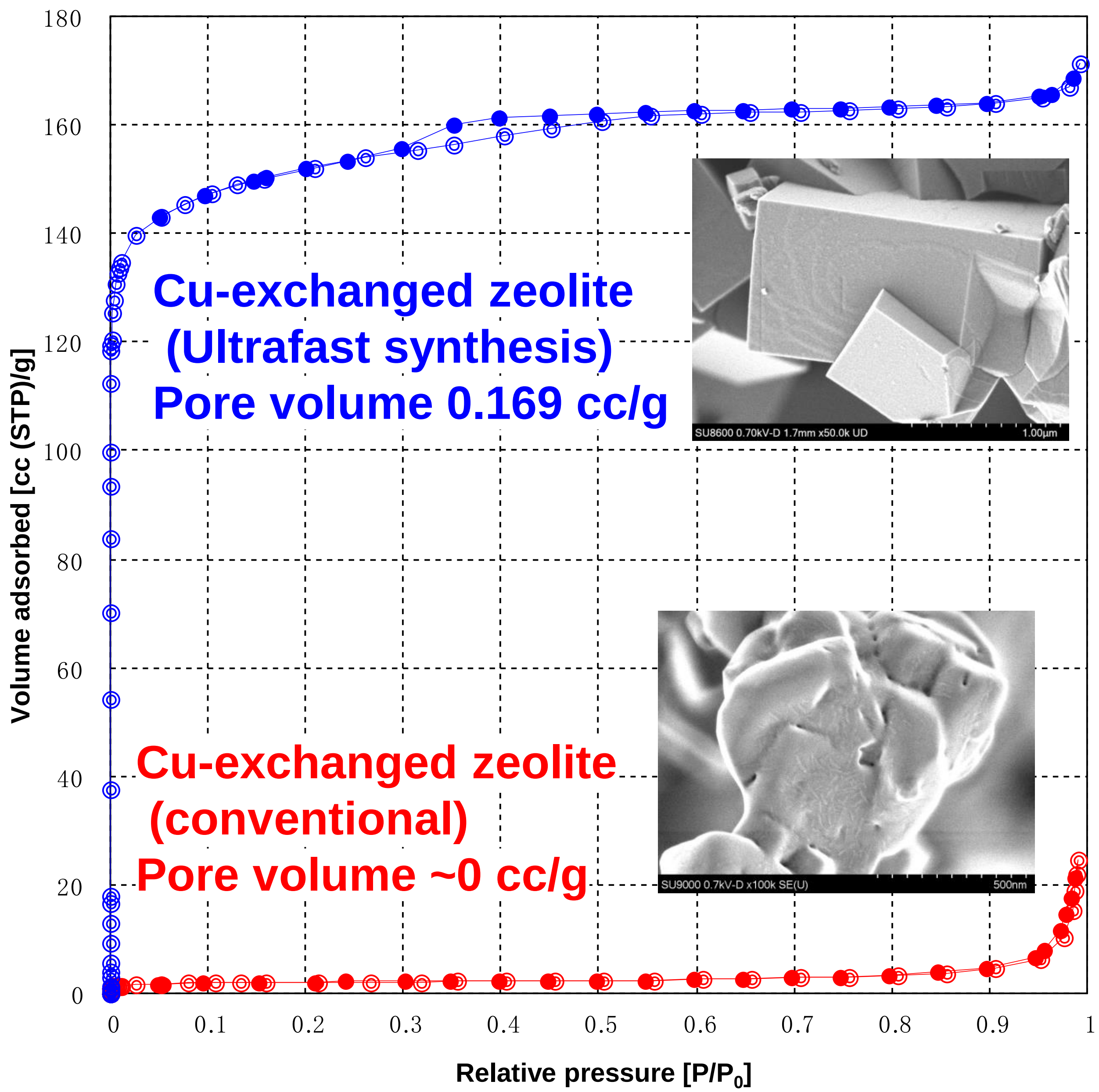
NO 300 ppm, NH_3 300 ppm, 5% O_2
Flow rate 100 cm^3/min



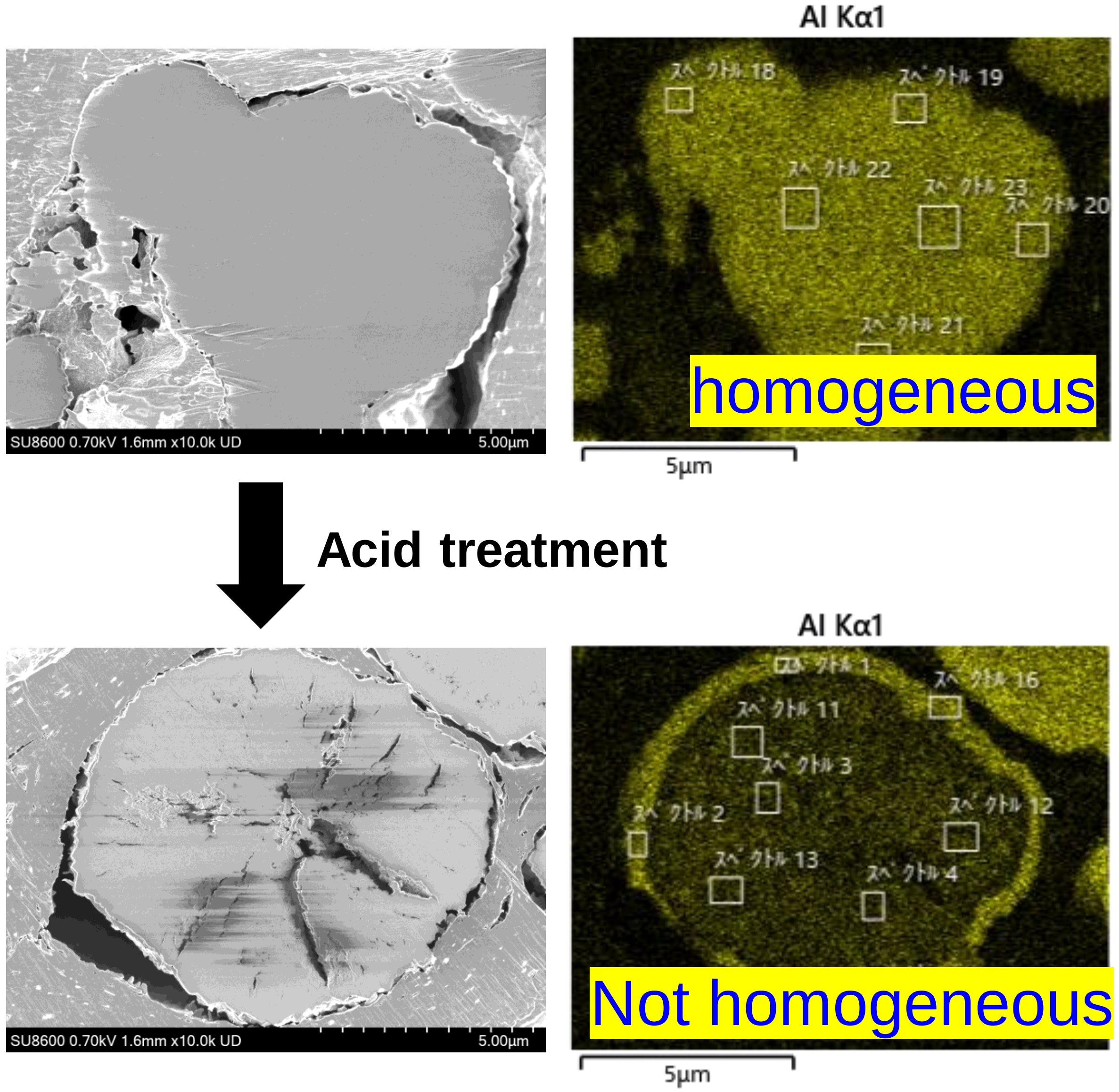
- ✅ Retain the original crystalline structure after steaming (2022 KPI achieved)
- ✅ Better activity than commercial catalyst

Evaluation of degradation of zeolite catalyst

Ar adsorption-desorption



Elemental Mapping

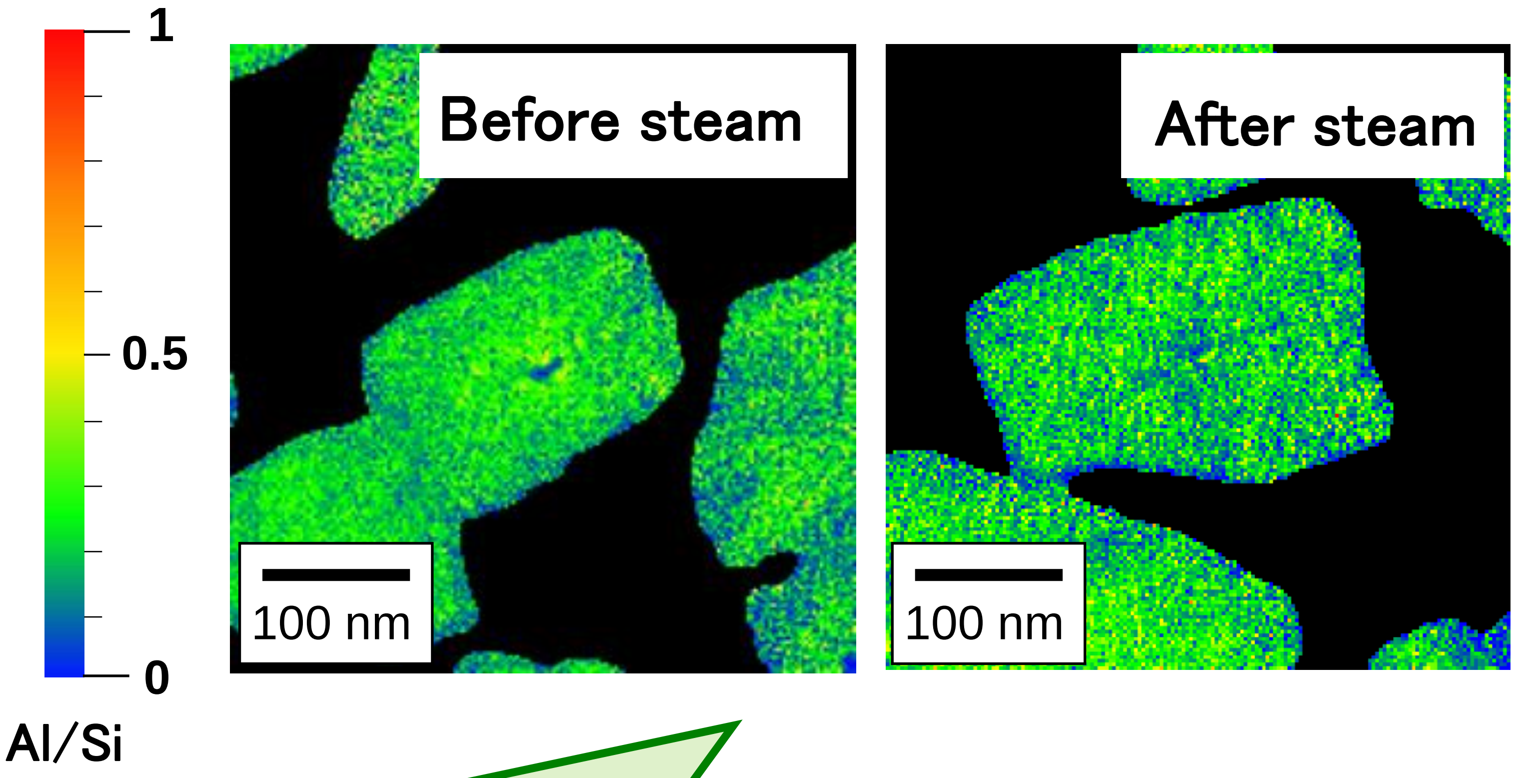


Developed the analysis technique of the degradation and dealumination of zeolite catalyst

STEM-EDS mapping

Establishment of a method for analyzing Si/Al ratio distribution with a spatial resolution of 2.4nm~ for zeolites sensitive to electron beam.

Ex) Cu-exchanged zeolite



Pixel: 2.4nm × 2.4nm

From Qualitative to Quantitative Microdomain Analysis

Quantification of spatial distribution

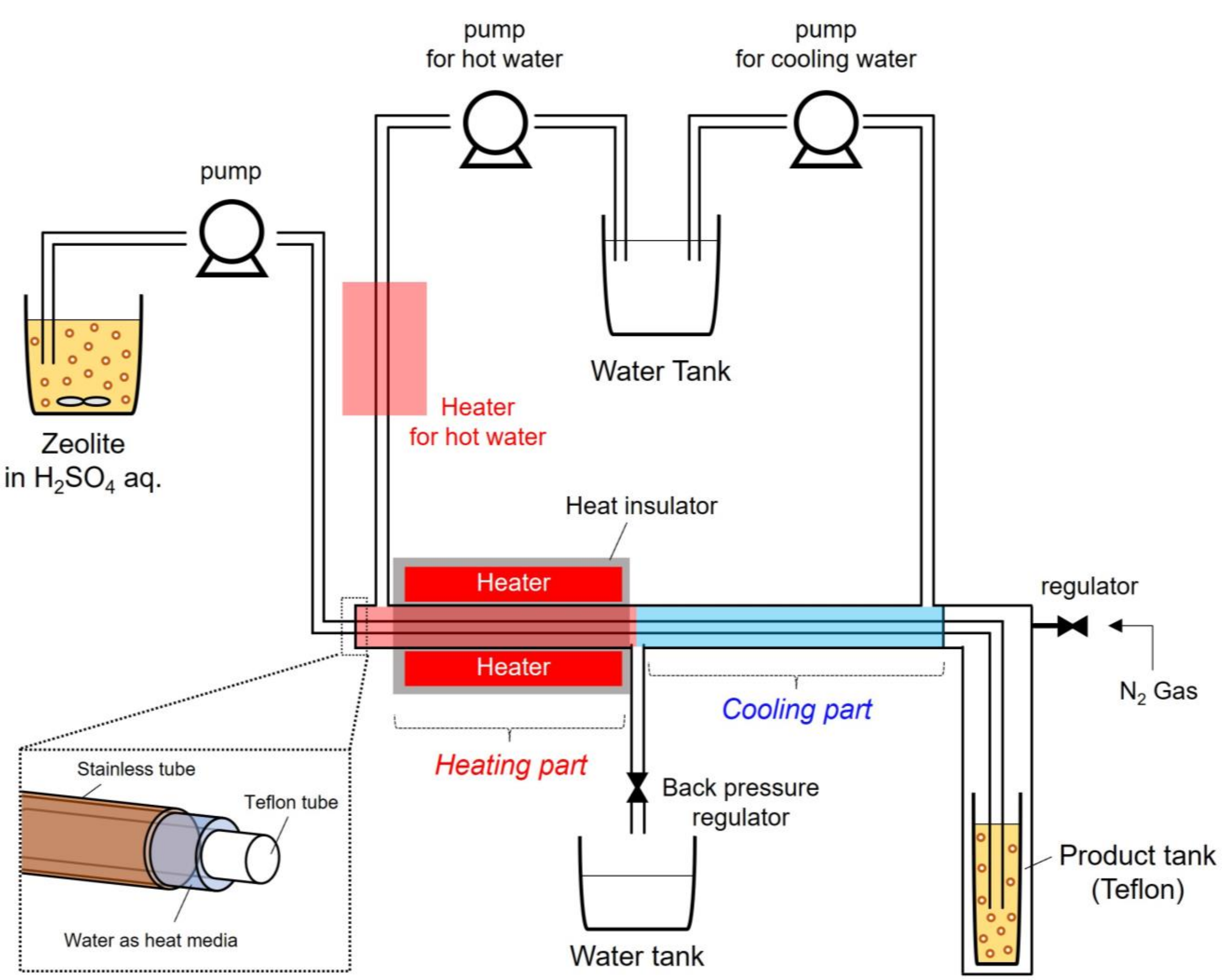
Quantify visual information

→ characterized and analyzed for differences in properties due to their chemical composition.

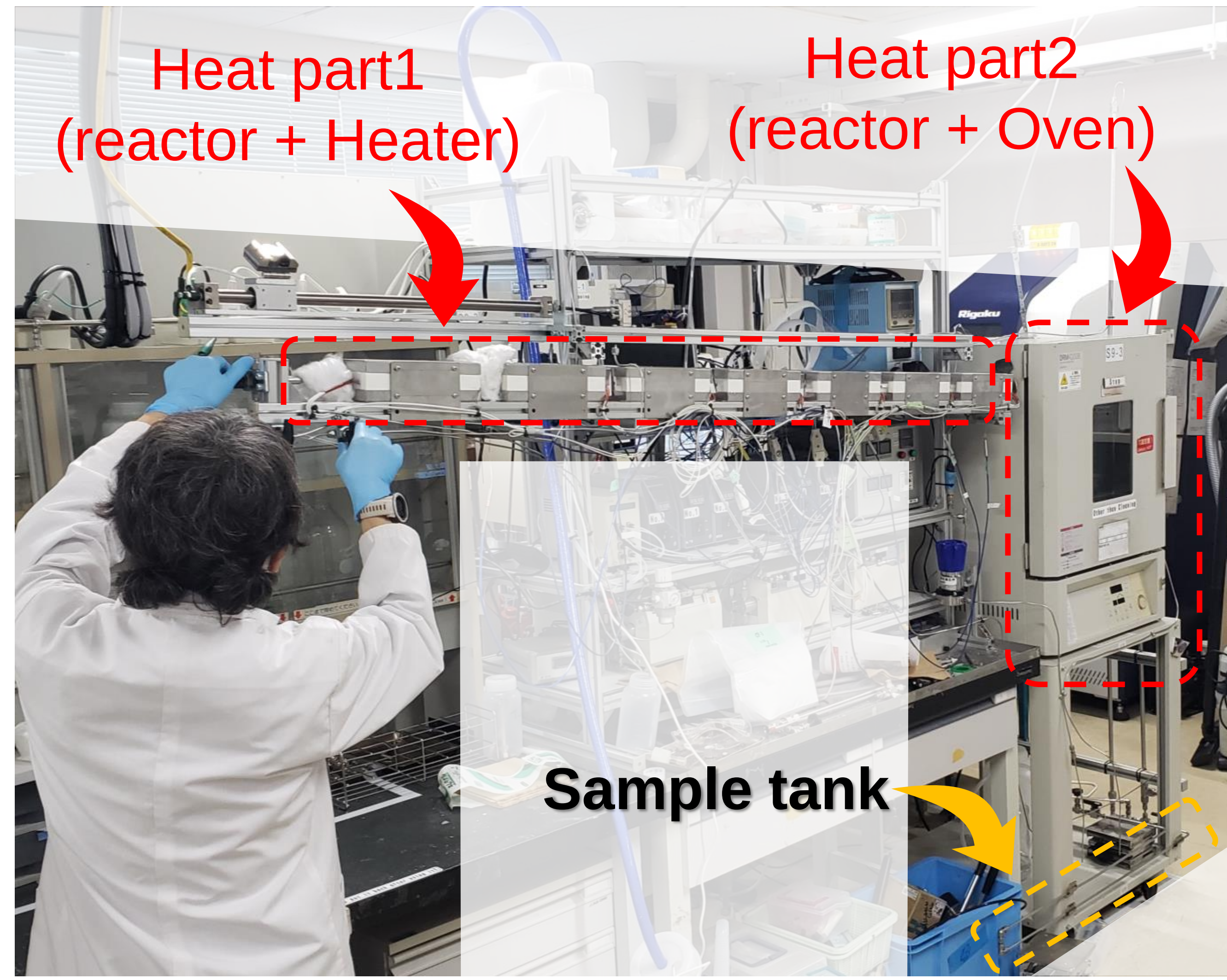
Continuous flow system for synthesis and post–treatment

Flow reactor

◆ deAl of zeolites in flow system



◆ Machine for zeolite synthesis



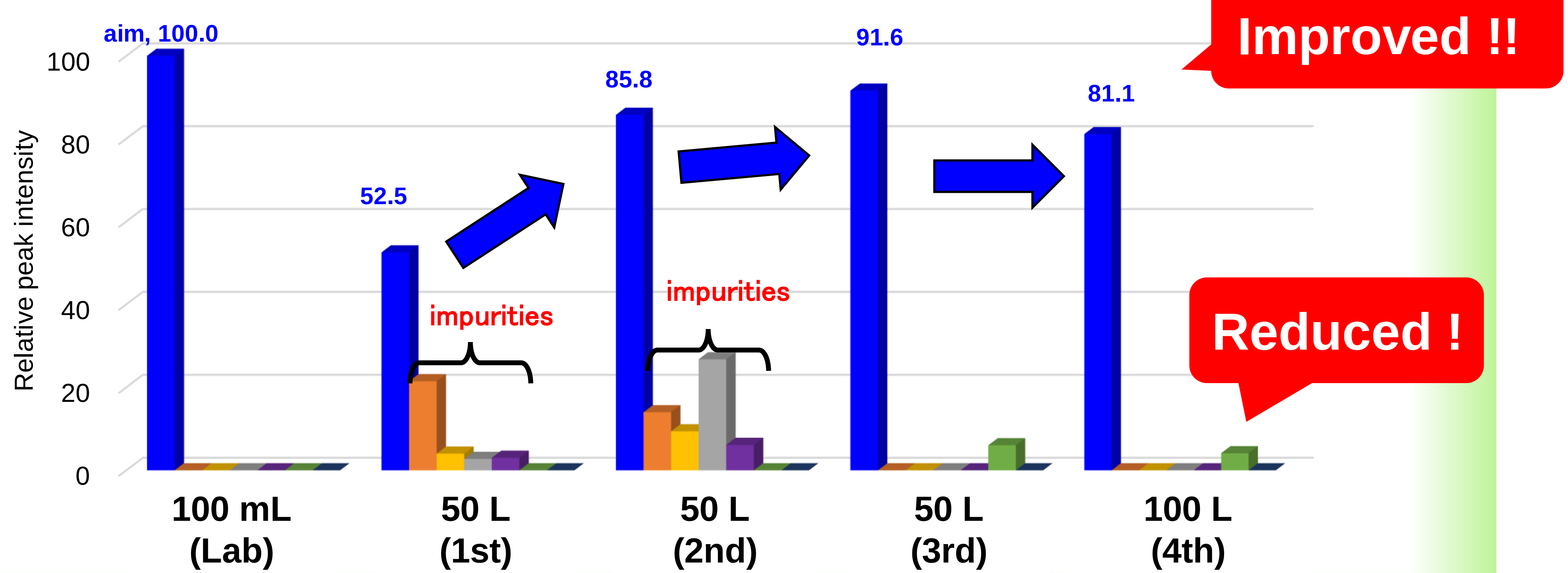
- Publication; ultrafast deAl of Beta in continuous flow reactor

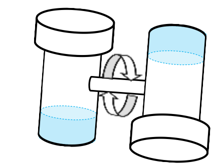
  A. Minami, M. Takemoto, Y. Yonezawa, Z. Liu, Y. Yanaba, A. Chokkalingam, K. Iyoki, T. Sano, T. Okubo, T. Wakihara
  Advanced Powder Technology, 33, 103702 (2022).

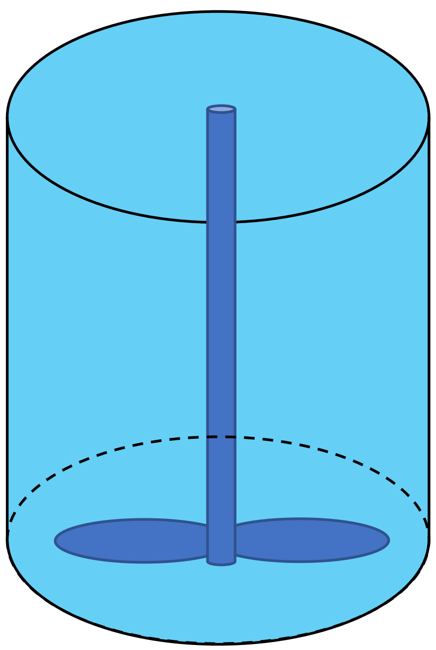
- Started the design of continuous flow reactor for zeolite synthesis

Large Scale Synthesis of zeolites

Optimization

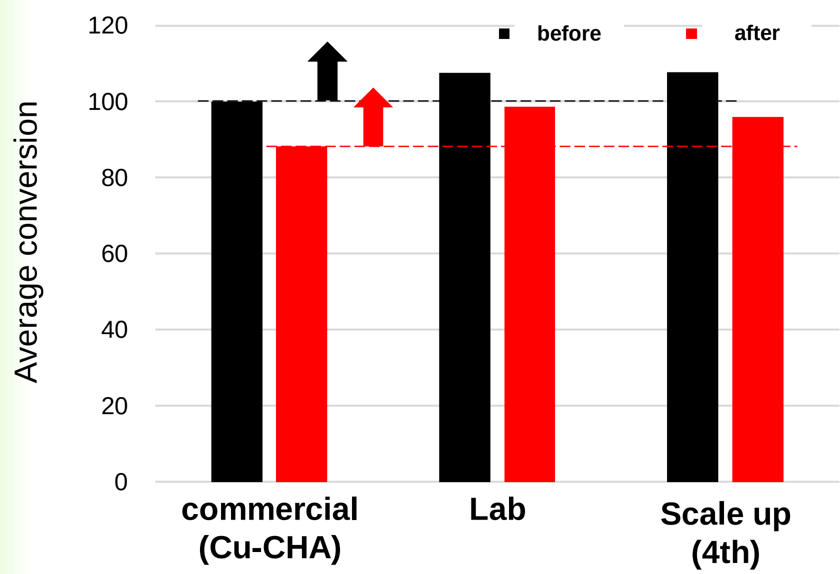




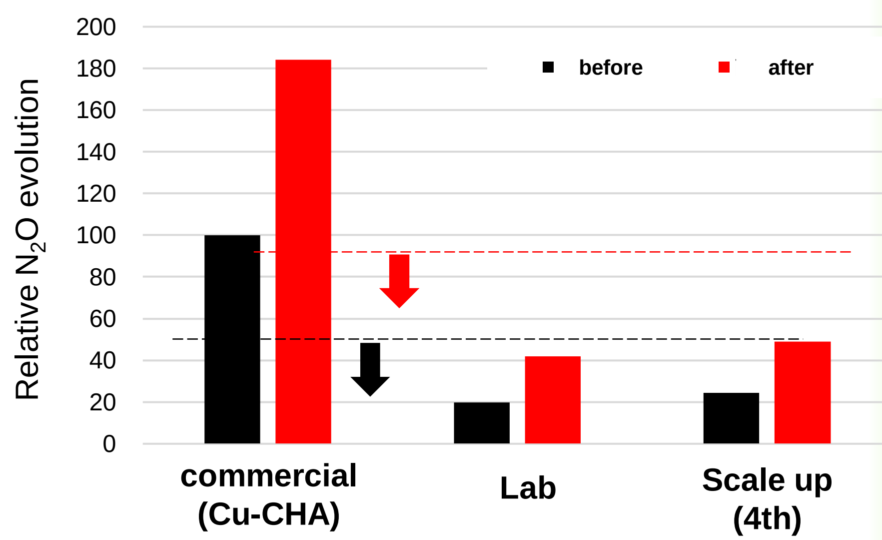


NH_3-SCR(scale up + effect of steaming)

- Average NOx conv. (150-500℃)



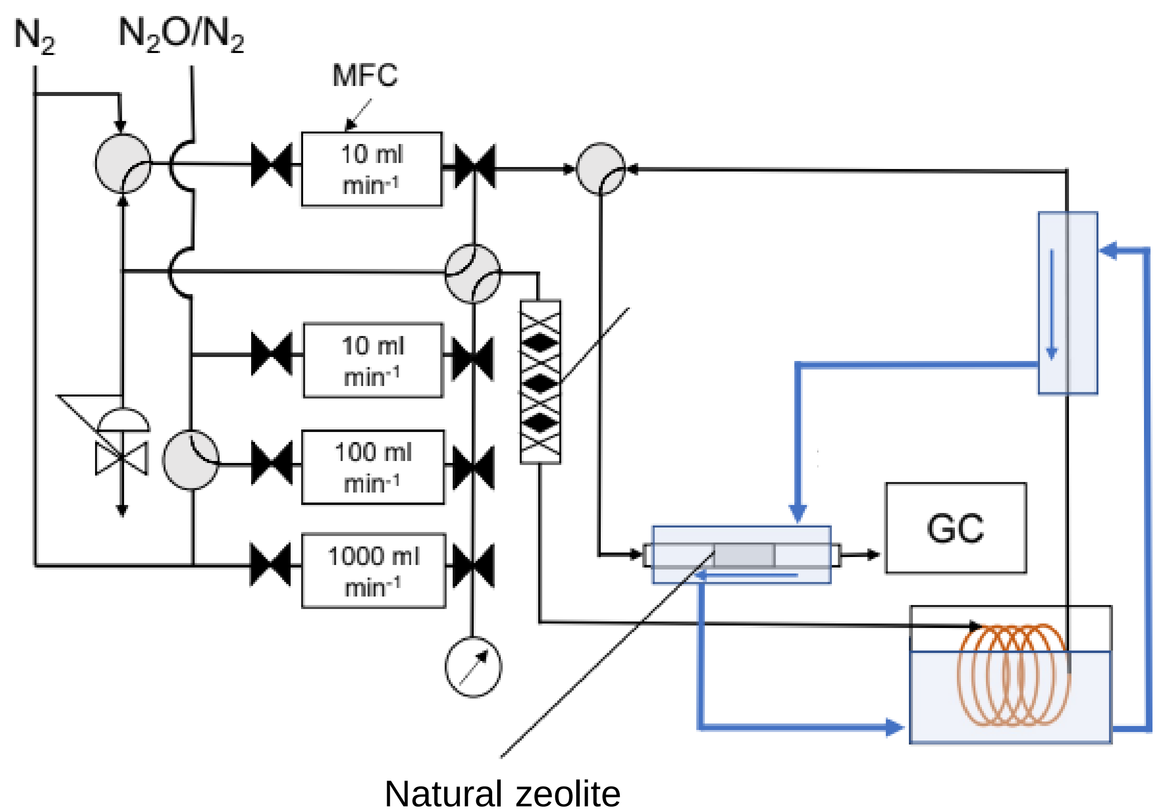
- Average N_2O evolution (150-500℃)



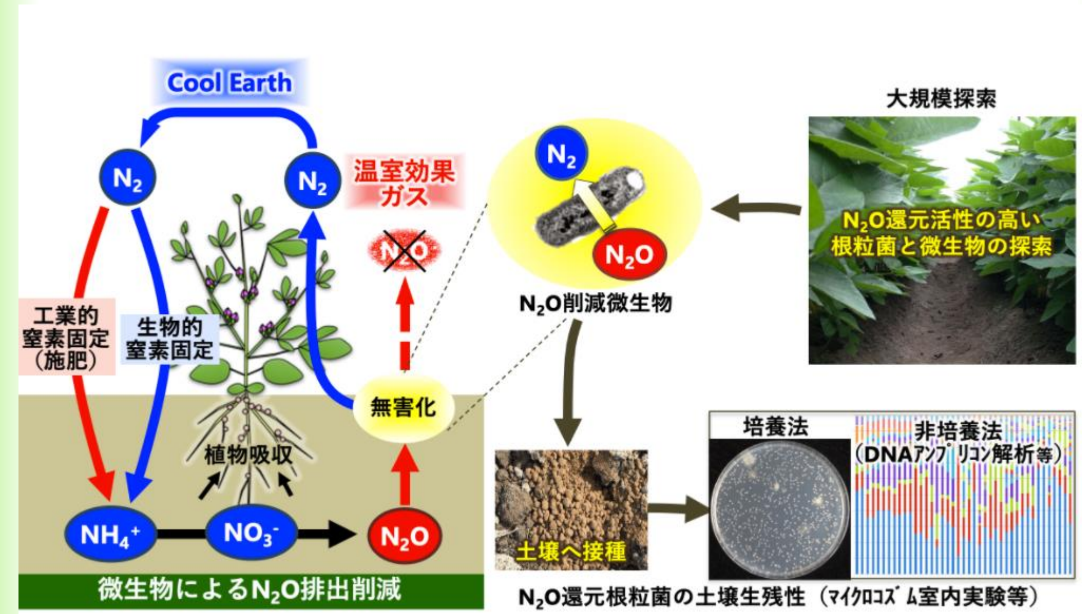
✔ Low N_2O evolution → Future plan: large scale ($2m^3$)

Adsorption and decomposition of dilute N_2O

N_2O capture by natural zeolite



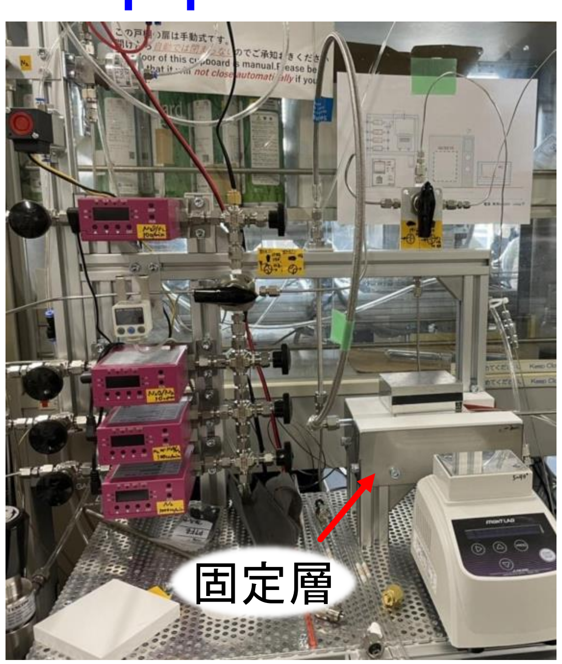
N_2O degradation by rhizobium (Prof. Minamisawa, Tohoku Univ.)



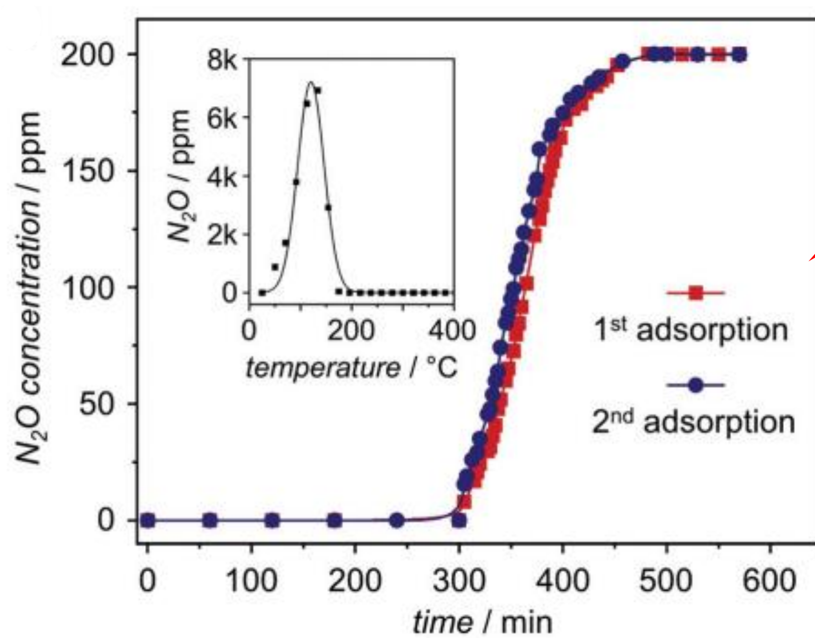
Cited from dSOIL

☐ problem : concentration of N_2O (>100 ppm)

■ **Equipment**



■ **N_2O adsorption-desorption test**



- ✓ **Concentration of N_2O !!**
- ✓ **Increase the amount of adsorbed N_2O by temperature control**

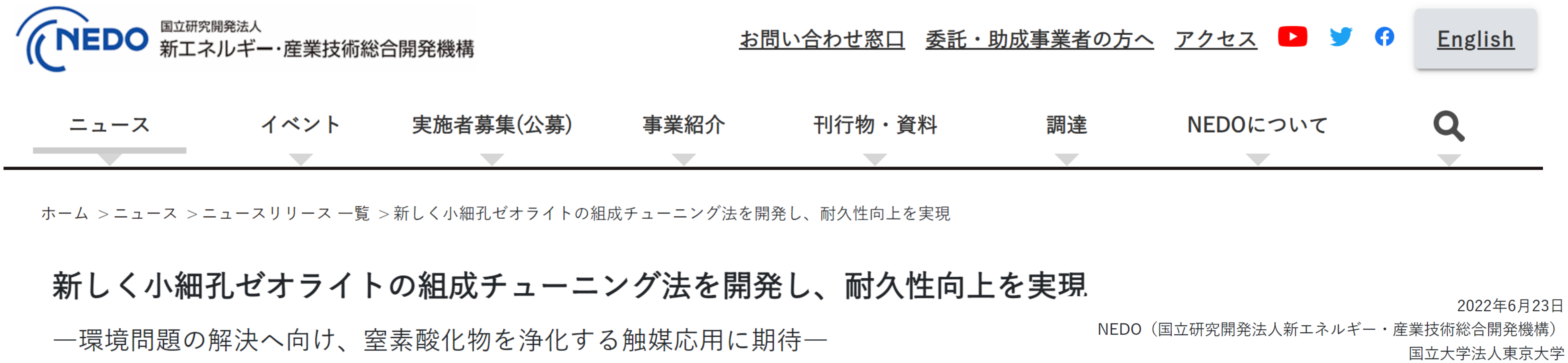
- Hybrid with rhizobium
- Discussion with JACI(> 80 company)
- RFI (submitted)

Publication・Conference・Seminar

Publication (14 papers + 2 submitted papers)

◆ T. Yoshioka, K. Iyoki, Y. Hotta, Y. Kamimura, H. Yamada, Q. Han, T. Kato, C. A. J. Fisher, Z. Liu, R. Ohnishi, Y. Yanaba, K. Ohara, Y. Sasaki, A. Endo, T. Takewaki, T. Sano, T. Okubo, T. Wakihara ***Science Advances***, 8, (2022).

Press Release



Information toward the public

◆ JACI (Japan Association for Chemical Innovation) : discuss about N_2O capture

◆ seminar for middle and high-school students (at the Univ. of Tokyo, 6/5)

◆ Science Agora 2022 ◆ Home page launched

Conference (>25)

Seminar (>8)

Publication List

- R. Simancas, A. Chokkalingam, S. P. Elangovan, Z. Liu, T. Sano, K. Iyoki, T. Wakihara, T. Okubo
  Chemical Science, 12, 7677-7695 (2021)
- C.-T. Chen, K. Iyoki, P. Hu, H. Yamada, K. Ohara, S. Sukenaga, M. Ando, H. Shibata, T. Okubo, T. Wakihara
  Journal of the American Chemical Society, 143, 10986-10997 (2021)
- Y. Sada, A. Chokkalingam, K. Iyoki, M. Yoshioka, T. Ishikawa, Y. Naraki, Y. Yanaba, H. Yamada, K. Ohara, T. Sano, T. Okubo, Z. Liu, T. Wakihara
  RSC Advances, 11, 23082-23089 (2021)
- R. Sato, Z. Liu, C. Peng, C. Tan, P. Hu, J. Zhu, M. Takemura, Y. Yonezawa, H. Yamada, A. Endo, J. García-Martínez, T. Okubo, T. Wakihara
  Chemistry of Materials, 33, 8440-8446 (2021)
- Z. Liu, A. Chokkalingam, S. Miyagi, M. Yoshioka, T. Ishikawa, H. Yamada, K. Ohara, N. Tsunoji, Y. Naraki, T. Sano, T. Okubo, T. Wakihara
  Physical Chemistry Chemical Physics, 24, 4136-4146 (2022)
- K. Iyoki, T. Onishi, M. Ando, S. Sukenaga, H. Shibata T. Okubo, T. Wakihara
  Journal of the Ceramic Society of Japan, 31, 187-194 (2022)
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Main results at this time

NH_3 capture

- Low-cost, quick and simple adsorbent synthesis process
- Recovery of more than 50% NH_3/NH_4^+ ions in actual wastewater
- Collaborating with participating companies, taking into consideration about reuse recovered NH_3.
- Demonstrated recyclability of developed product in NH_3 recovery
- Development of superior adsorbent material using waste raw materials
- Establishment of molding technology for developed products for social implementation
- Started studying the treatment of liquid waste by continuous distribution system

deNOx

- Development of zeolite with both high NOx conversion and low N_2O emissions
- Development of zeolite that maintains crystallinity after exposure to high temperature steam
- Establishment of zeolite production technology on a large scale
- Started synthesis of highly durable zeolite catalyst by continuous flow method

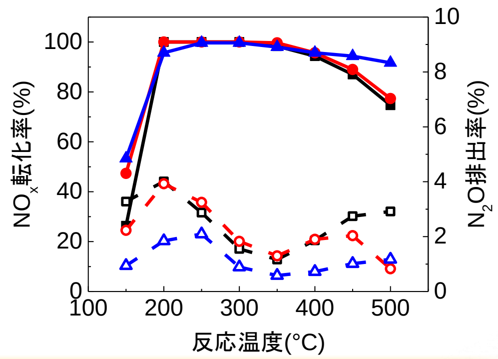
Evaluation of system

- LCA evaluation of adsorption and denitration systems using zeolite production, zeolite, etc.
- Visualization of nitrogen flow/extension of further evaluation targets
- Proof of reduction of emission N and resource saving by introduction of development agents

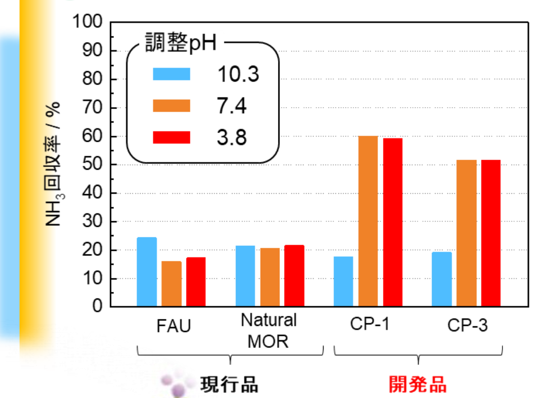
Future Outlook

- ✅ High stability
- ✅ Concentration of N_2O by natural zeolite
- ✅ Scale up synthesis
- ✓ Continuous flow synthesis

✅ High NOx conv. ･Low N_2O

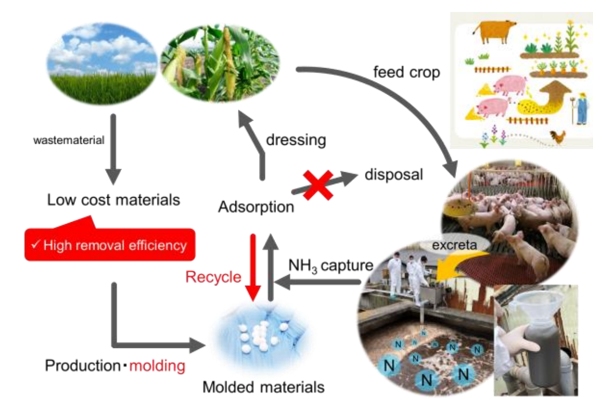


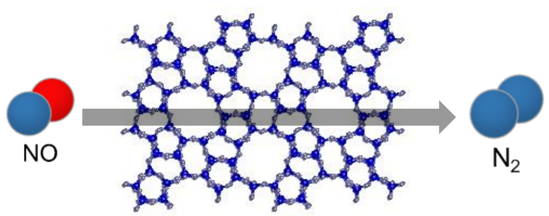
✅ Excellent adsorbent !!



- ✅ Recyclable
- ✅ From waste raw material

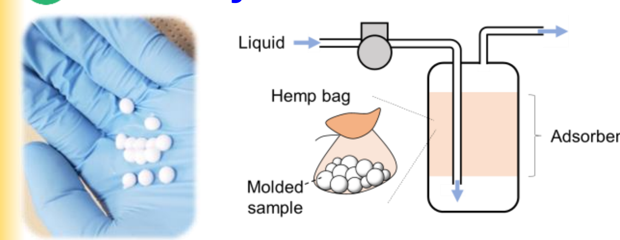
✅ Regional nitrogen cycle !!



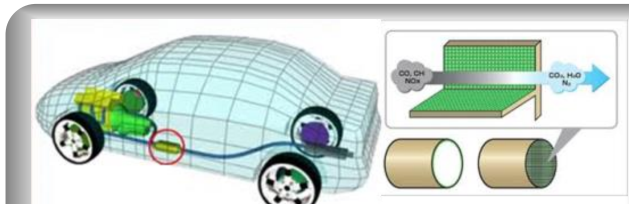


✓ Direct NO decomposition

- ✅ Molding method
- ✅ Flow system



✓ Hybrid with natural zeolite and rhizobium



✓ Pilot scale test

✓ LCA assessment taking into account the increase in greenhouse gases and environmental pollutants

✓ Pilot scale test

Scale-up demonstration test for pilot test ahead of schedule