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

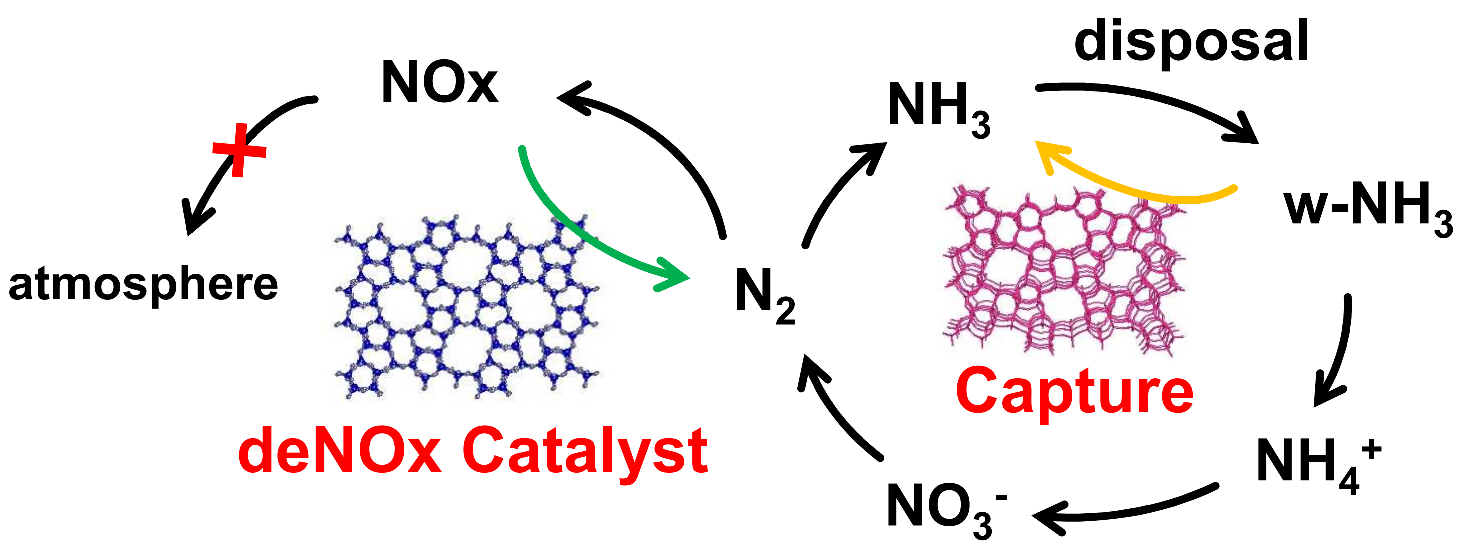
The University of Tokyo

The National Institute of Advanced Industrial Science and Technology

Japan Fine Ceramics Center

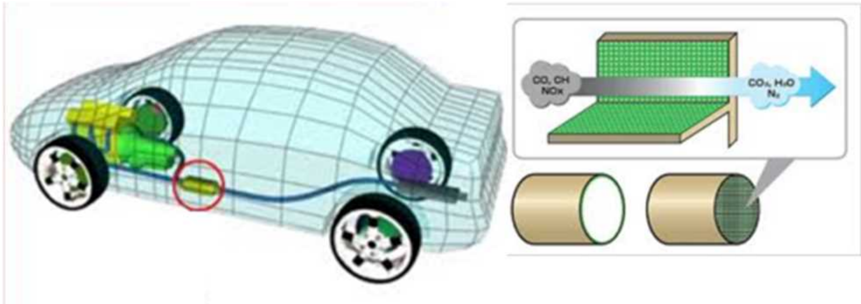
Mitsubishi Chemical Corporation

Project Overview



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

Exhaust Gas (NOx)



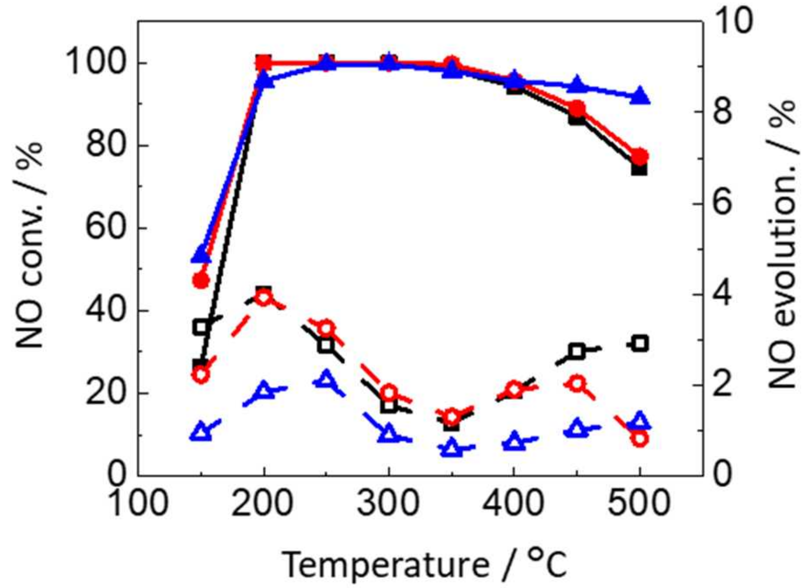
Industrial Wastewater (w-NH_3)

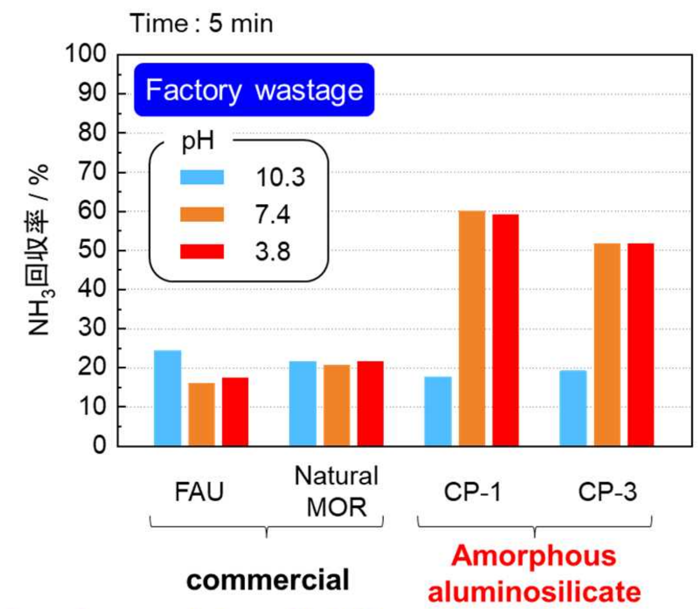
- Although the transition to electric vehicles has been proposed for the realization of a carbon-neutral society, in Europe, reluctant to fully transition to electric vehicles.
- Considering the introduction of e-fuel, an internal combustion engine (especially for truck transportation) is essential.
- 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

Schedule

2020 → **2023** → **2024** → **2029 (Goal)**

Results in 4 years (selected major research results)





- ✅ **High NOx conversion and low N_2O emissions (denitrification))**
- ✅ **Development of high-performance adsorbent (ammonia recovery)**

2024

- ☐ **Development of zeolite that maintains crystallinity even after exposure to 900ºC and 10% water vapor for 5 hours**
- ☐ **NH_3-free NOx purification (more than 50 %)**
- ☐ **Low-cost synthesis of target zeolites**

2029 (Goal)

- ☐ NOx purification (more than 80% with NH_3 free)
- ☐ Demonstration using pilot facilities
- ☐ Development of catalyst with N_2O emission (less than 1/10 of current catalyst)

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)

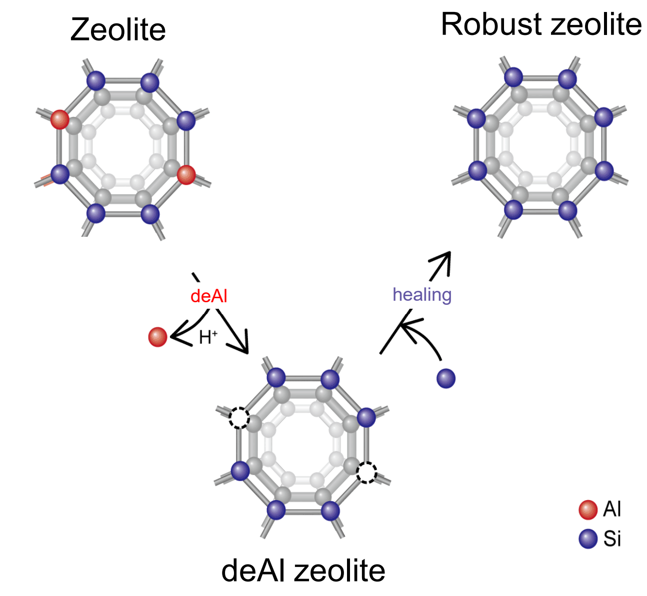
- ✓ Excellent catalyst

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

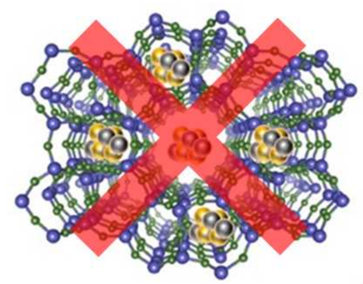
Company A
Company B
Company C
- ✓ Production
- ✓ Sale

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

Company G
- ✓ Equipment design

Company H
- ✓ Implementation

Company I
- ✓ Molding



Synthetic zeolite

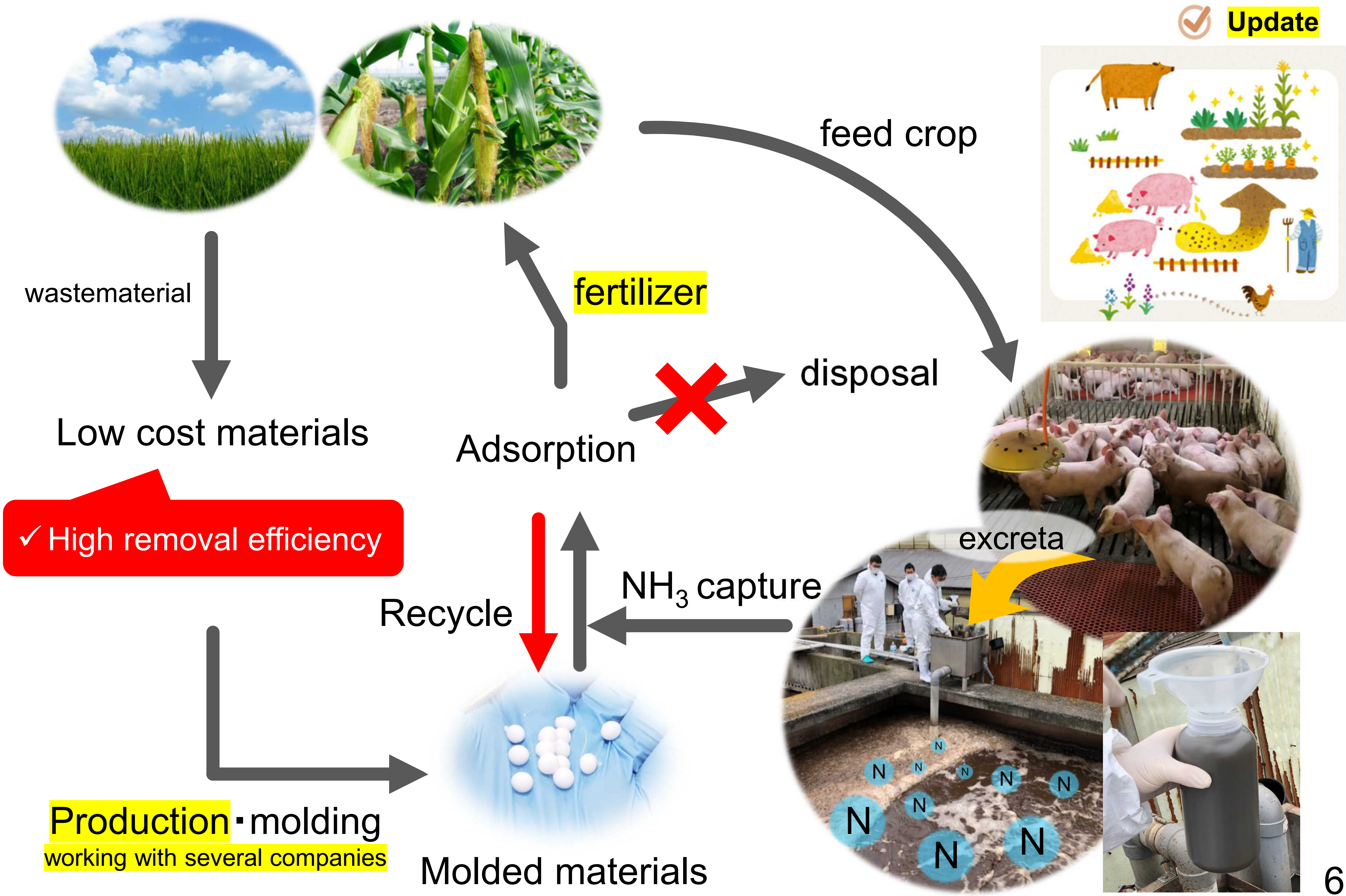
Budding
- Amorphous aluminosilicate
- Waste material

Core
- Amorphous aluminosilicate
- Waste material
- Natural zeolite

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

→ **Regional nitrogen circulation system**

Regional nitrogen circulation system



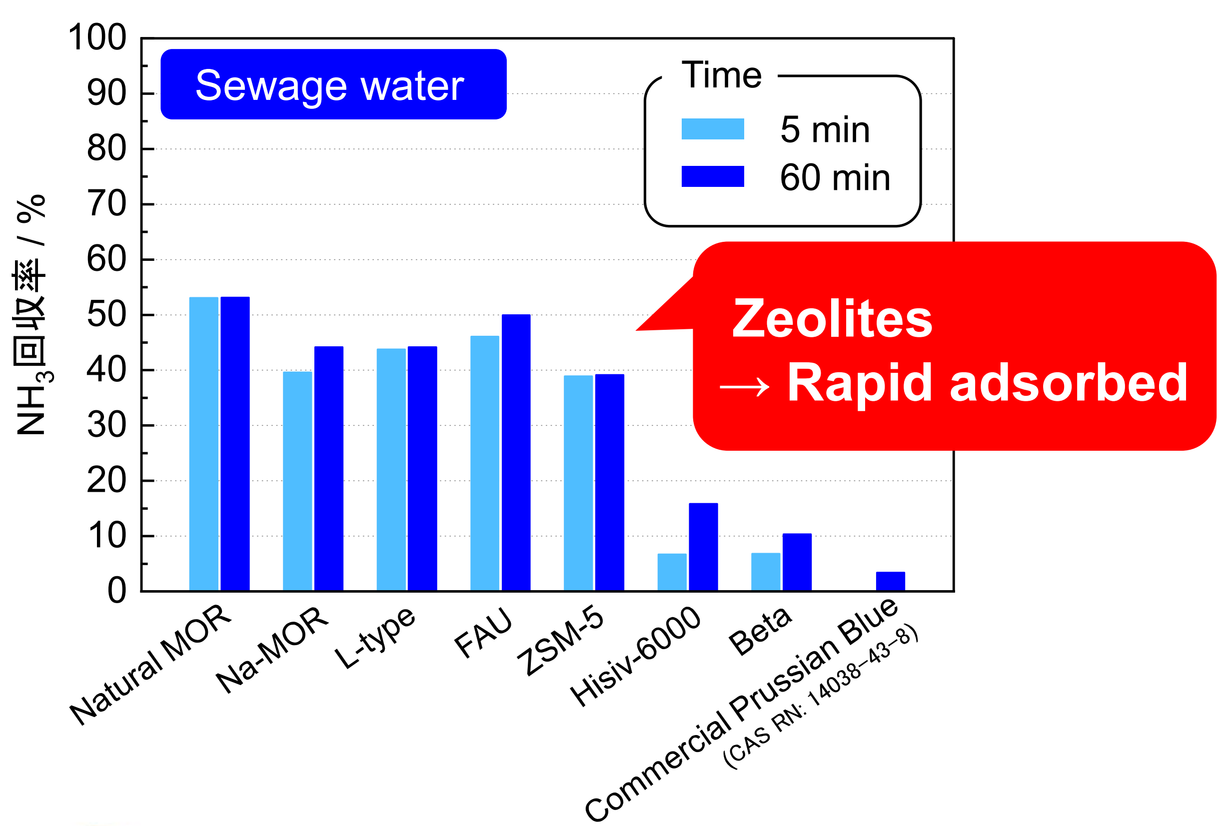
Selection of Materials

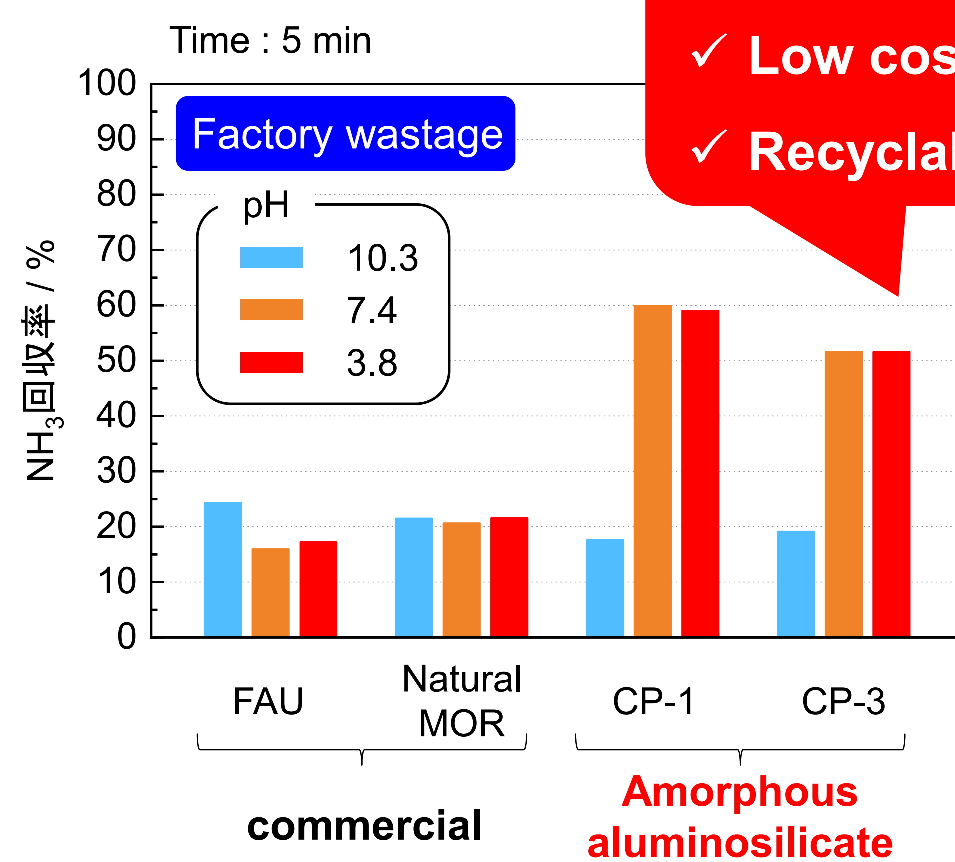
Update

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





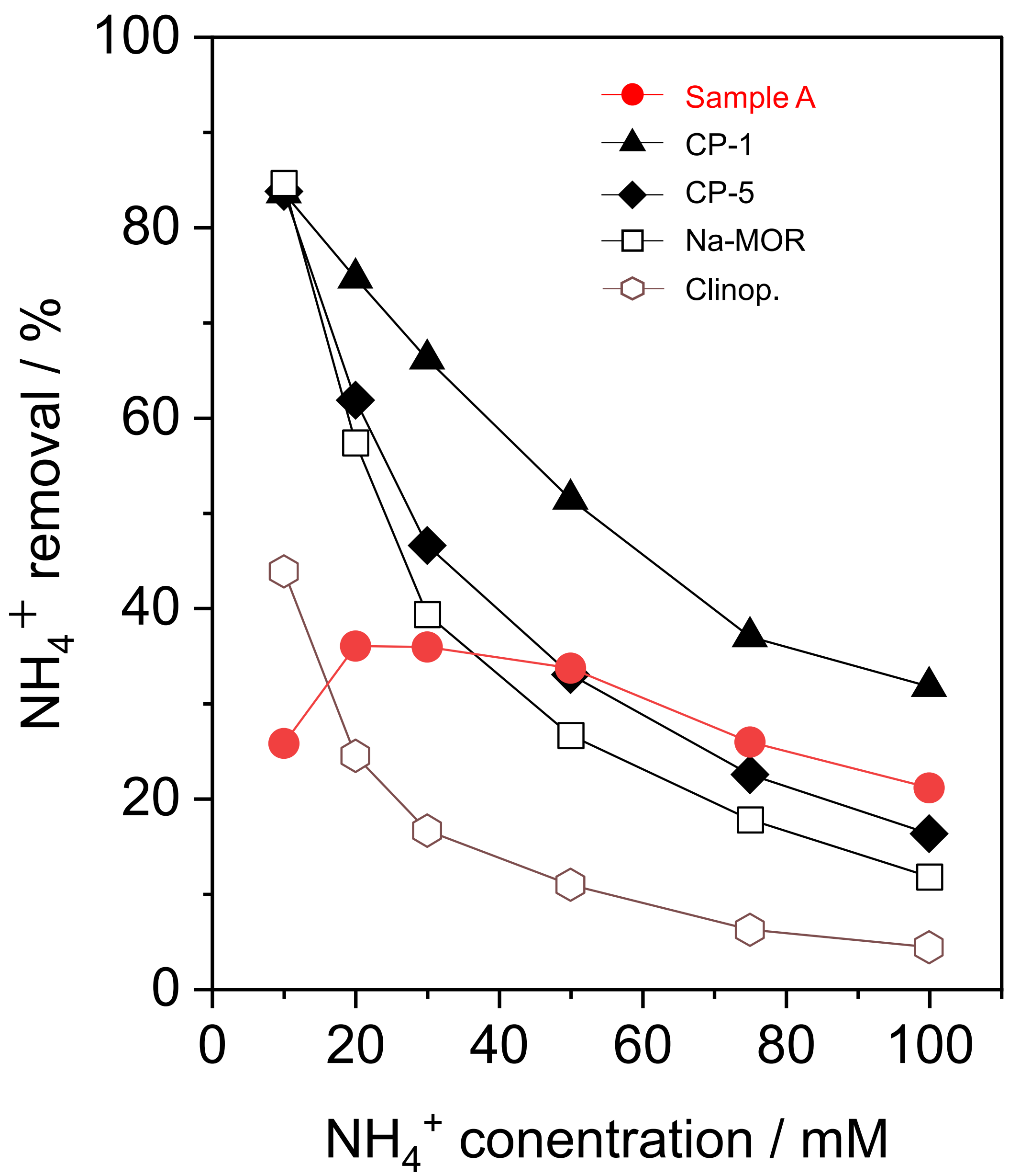
- ✓ High efficiency !!
- ✓ Low cost (CP-3) !
- ✓ Recyclable

Publication about NH_3 removal by CP sample

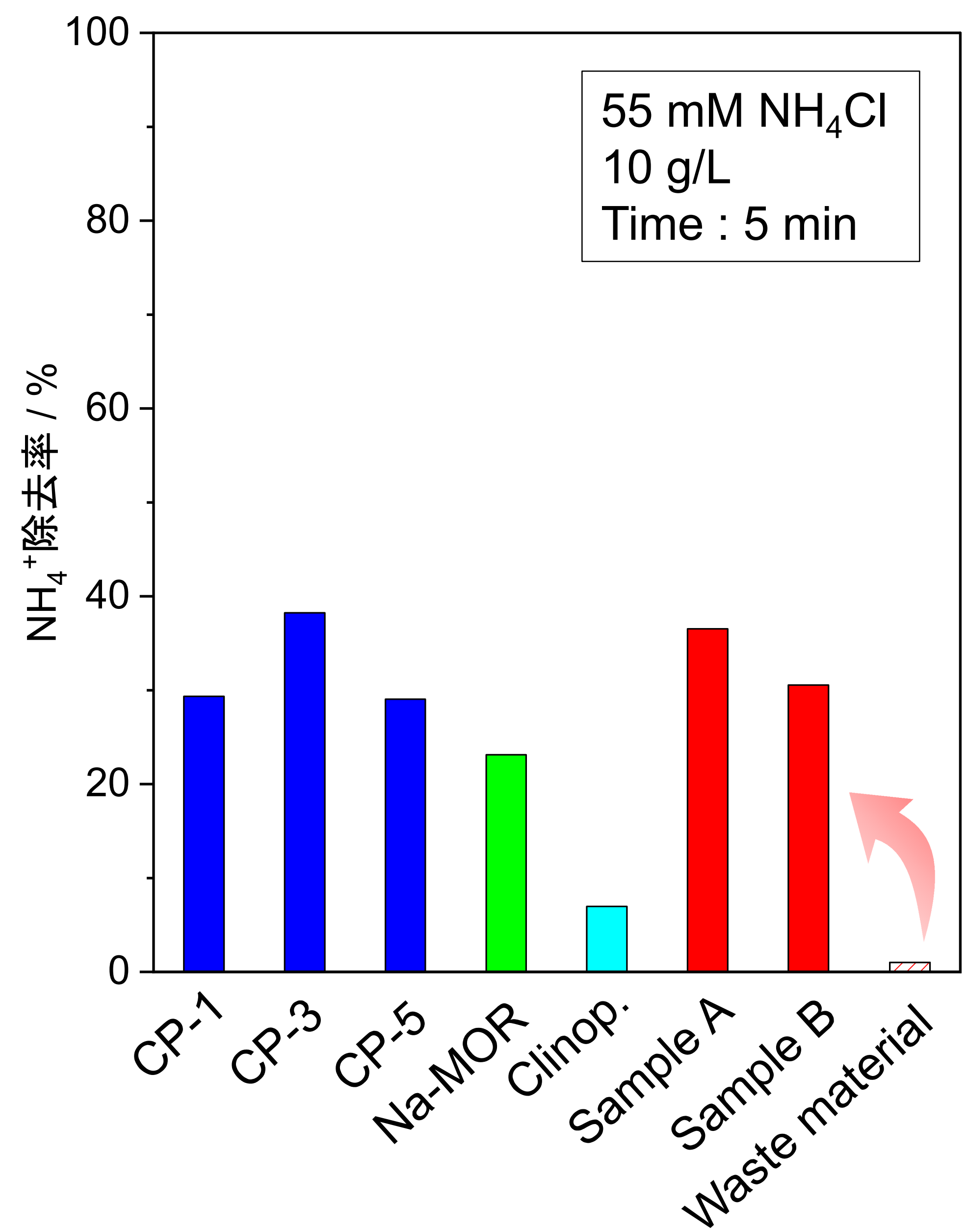
R. Simancas, M. Takemura, C.-T. Chen, K. Iyoki, T. Okubo, T. Wakihara, ***Journal of Non-Crystalline Solids*** 605, 122172 (2023).

NH_3 removal efficiency

□ Effect of NH_4^+ concentration



□ Various adsorbents



✔ High NH_3 removal (similar to CP samples)

LCA （NH_3 capture）

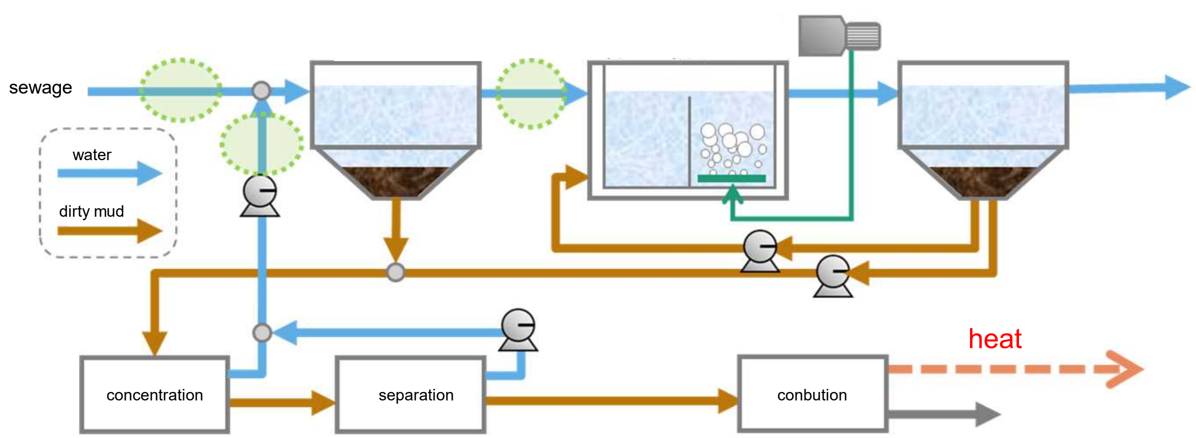
The University of Tokyo

Materials Team: Wakihara, Iyoki

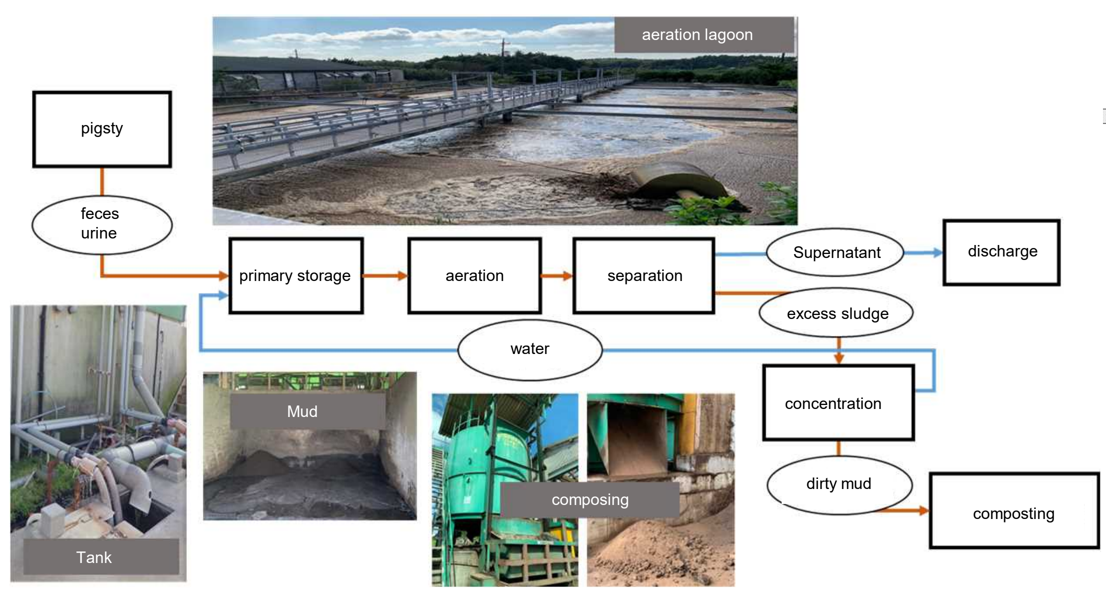
Urban Engineering Team: Katayama, Hashimoto, Tobino

LCA Team: Kanematsu

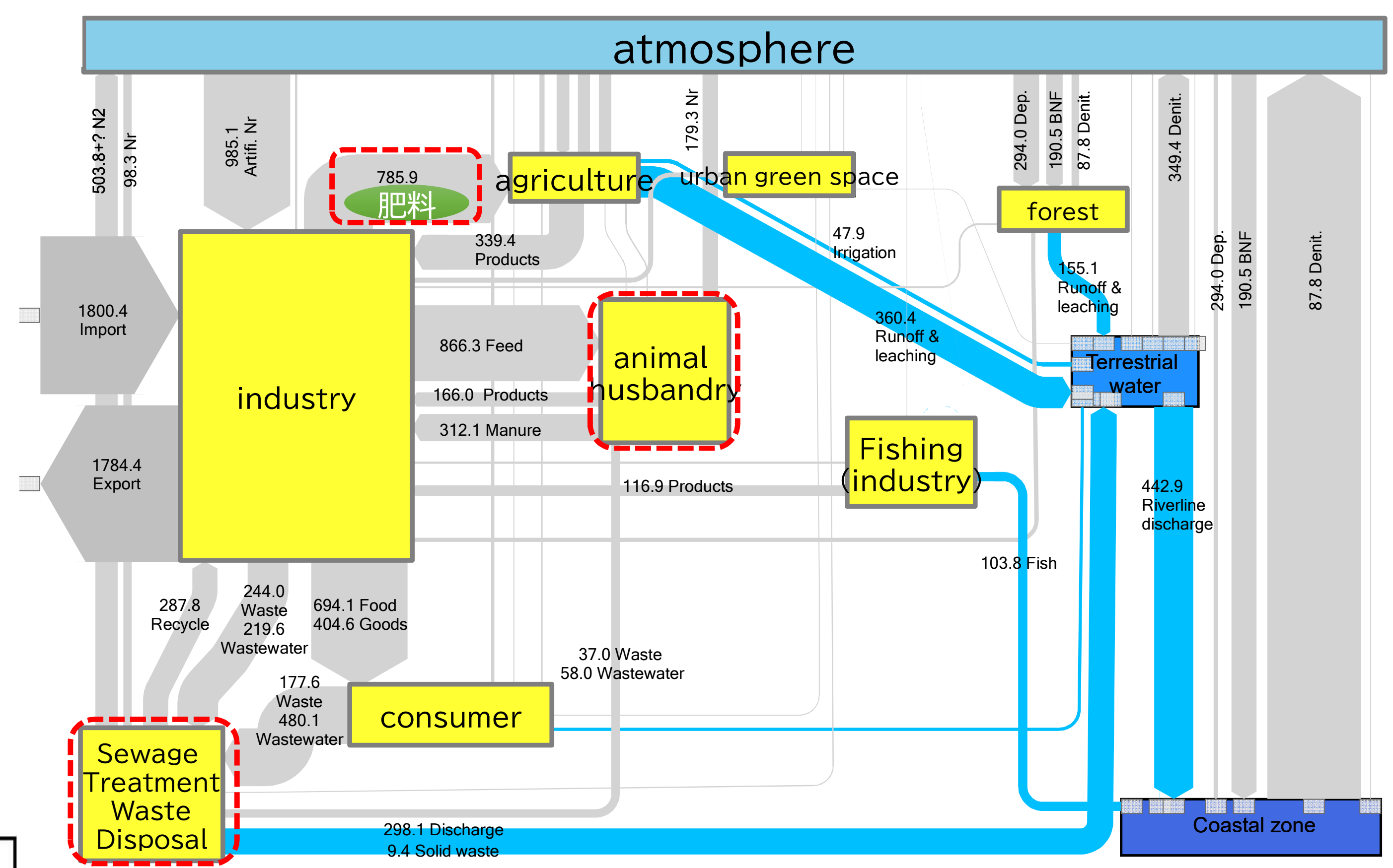
Sewage treatment



Livestock Wastewater Treatment



Nitrogen flow in Japan



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

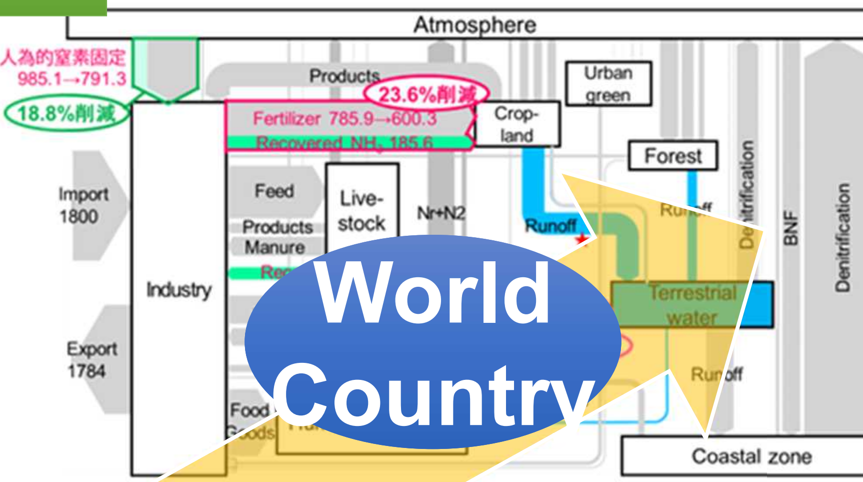
To transform social systems and processes by moving away from wastewater treatment, which is energy-intensive and dumps resources

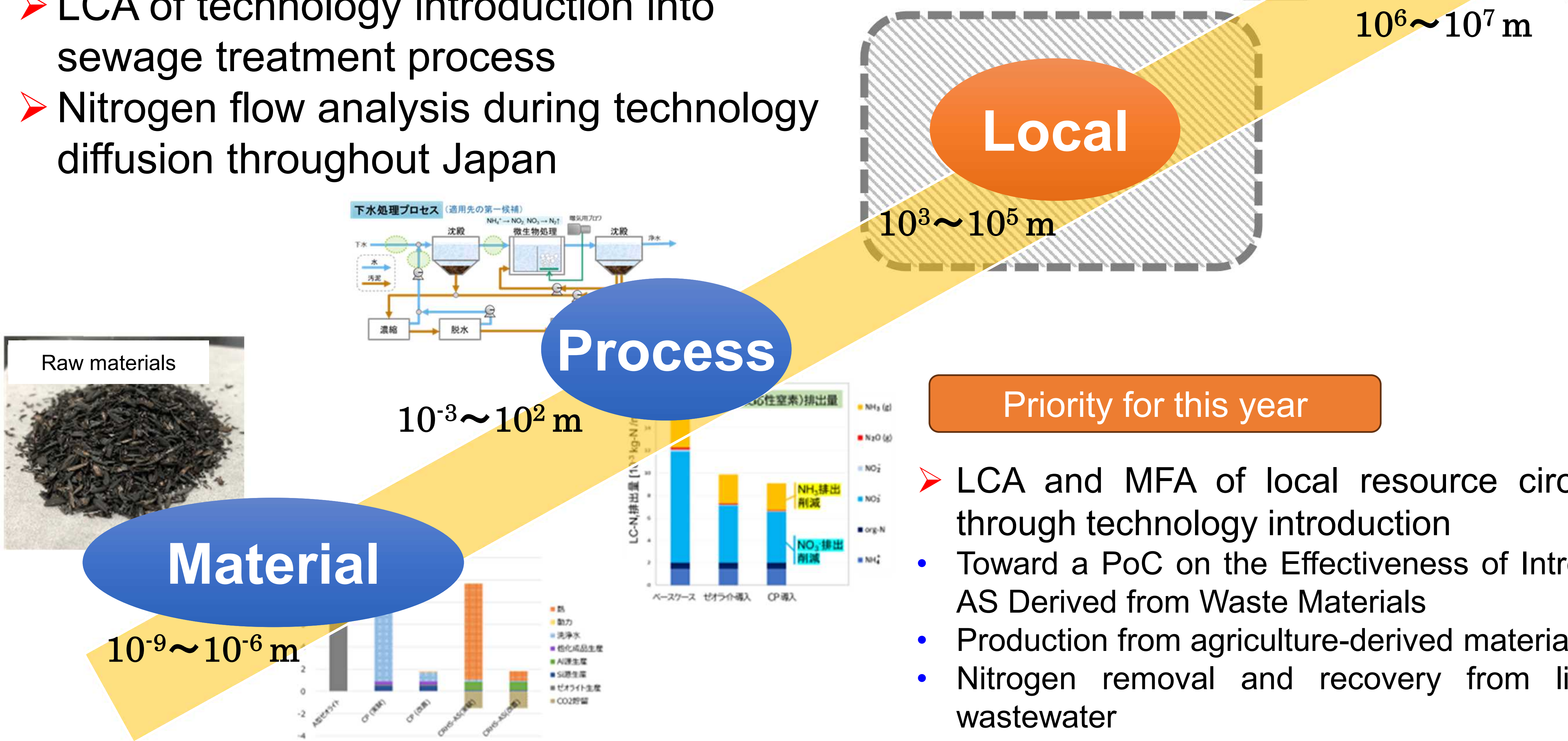
LCA of ammonia recovery from hydrosphere

Priority: Evaluation of Local Resource Circulation

Results

- LCA for production of various materials
  - Zeolite
  - Amorphous Aluminosilicates (AS)
  - Cheap raw materials（waste）
- LCA of technology introduction into sewage treatment process
- Nitrogen flow analysis during technology diffusion throughout Japan





Priority for this year

- LCA and MFA of local resource circulation through technology introduction
  - Toward a PoC on the Effectiveness of Introducing AS Derived from Waste Materials
  - Production from agriculture-derived materials
  - Nitrogen removal and recovery from livestock wastewater
  - Return of nitrogen components to agriculture

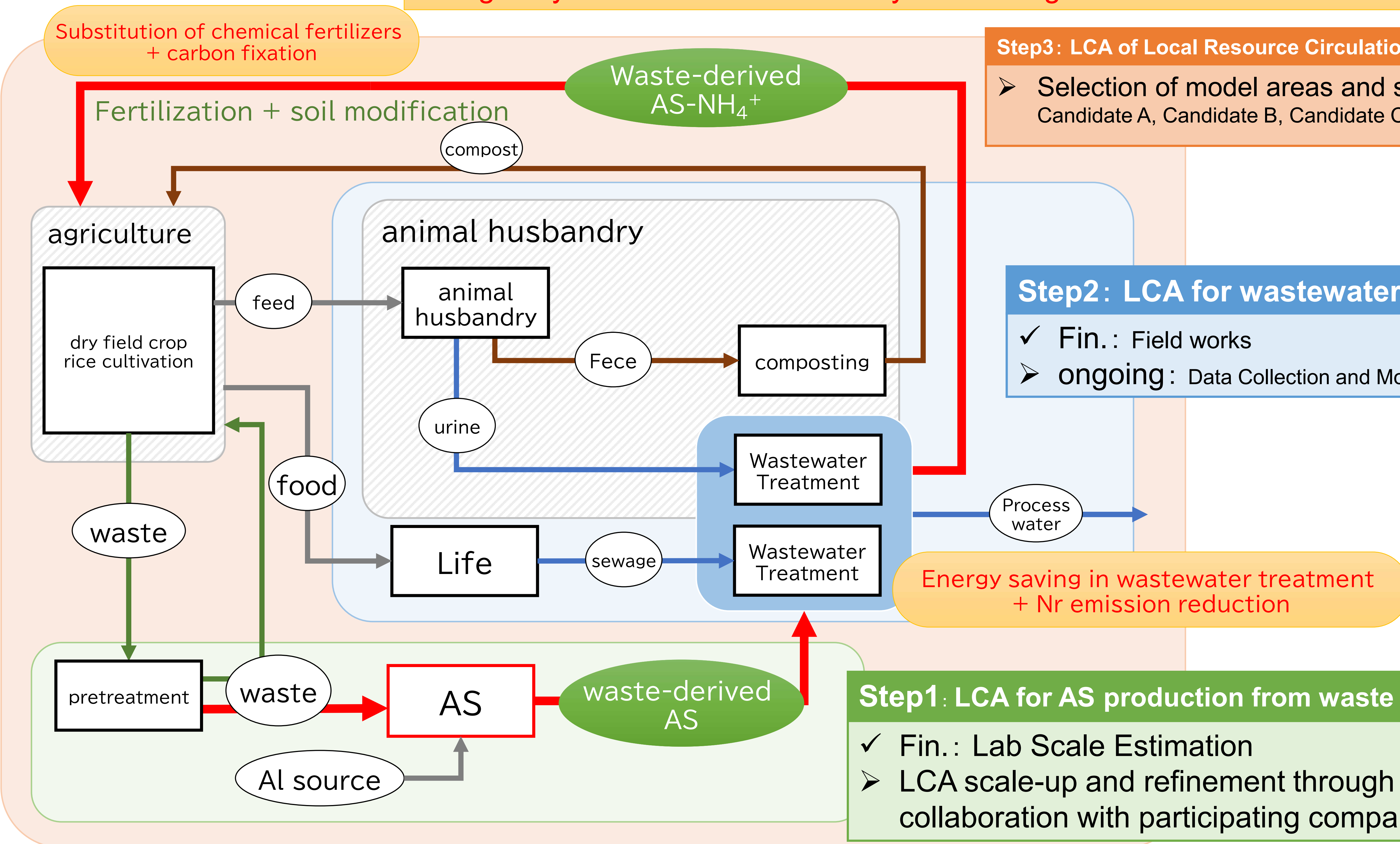
Toward an Evaluation of Local Resource Circulation

- Establishment of a model for farm-livestock partnerships

Nitrogen cycle could be enhanced by introducing AS derived from waste wood

Step3: LCA of Local Resource Circulation

- Selection of model areas and study
  Candidate A, Candidate B, Candidate C



Step2: LCA for wastewater

- ✓ Fin.: Field works
- ongoing: Data Collection and Modeling

Step1: LCA for AS production from waste wood

- ✓ Fin.: Lab Scale Estimation
- LCA scale-up and refinement through collaboration with participating companies

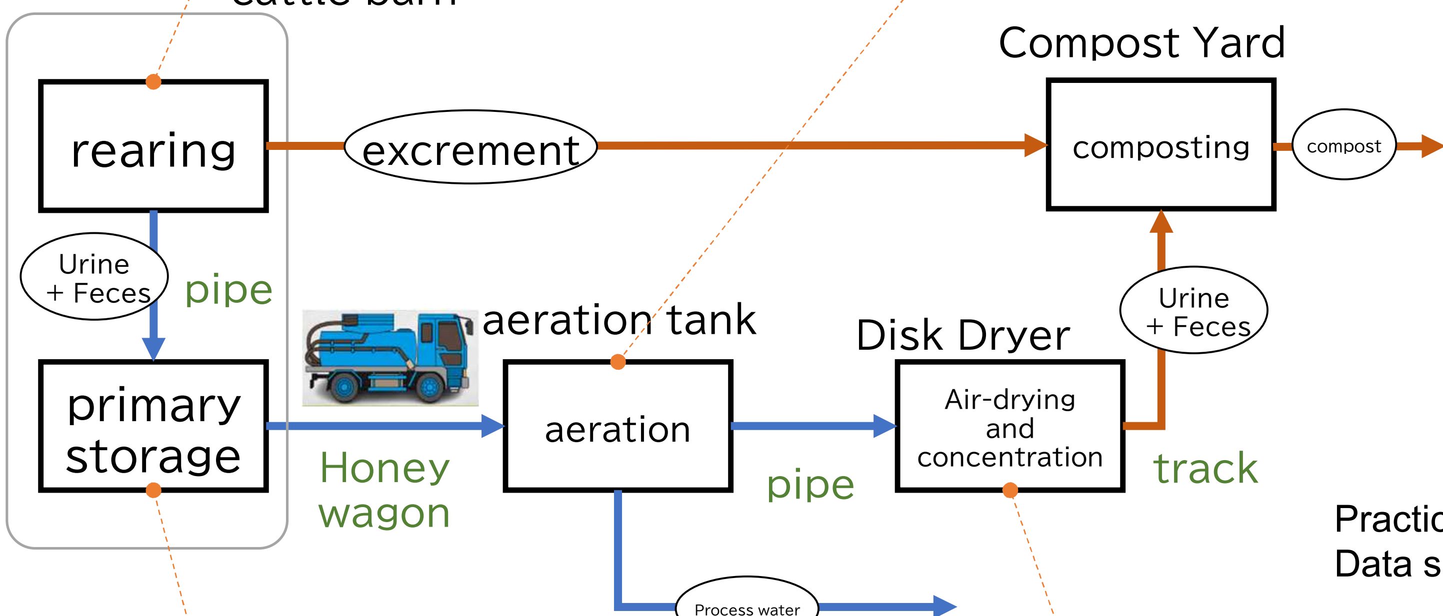
Modeling of livestock wastewater treatment

Survey at dairy complex

➢ Legend: Modeling difficulties

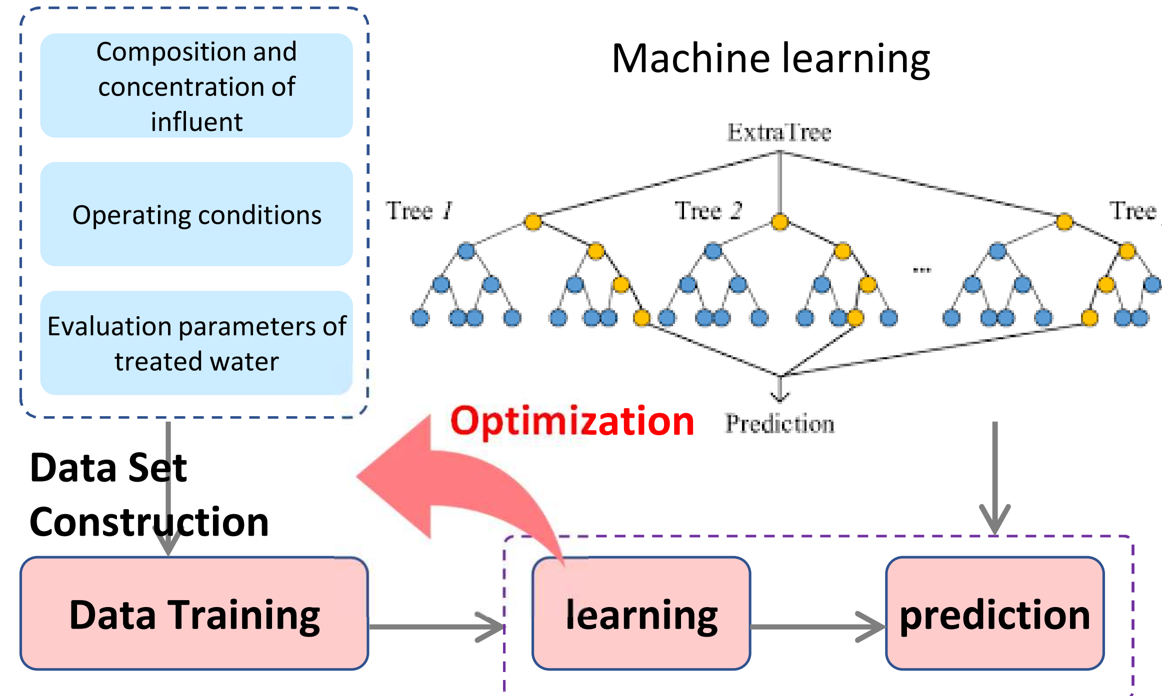
→ Possibly difficult to handle with conventional modeling methods

➢ Timing and quantity of deliveries and deliveries are not consistent.



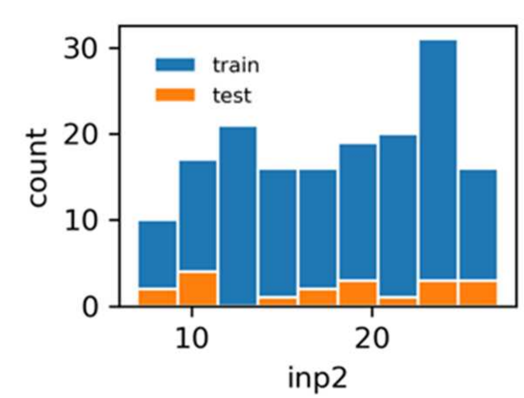
➢ Semi-open, so volume varies with rainwater, etc.

Consideration of modeling with application of machine learning

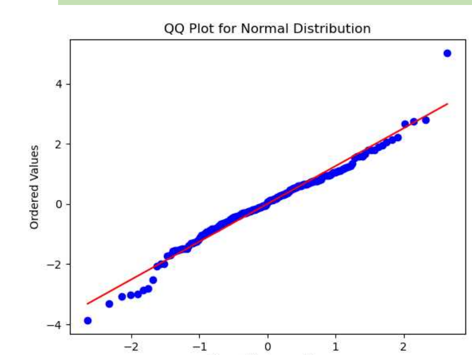


Practicality is being verified for sewage treatment for which a data set is available.
Data sampling of livestock wastewater is an issue that needs to be examined.

Data Set Construction



Evaluation of Forecast Accuracy

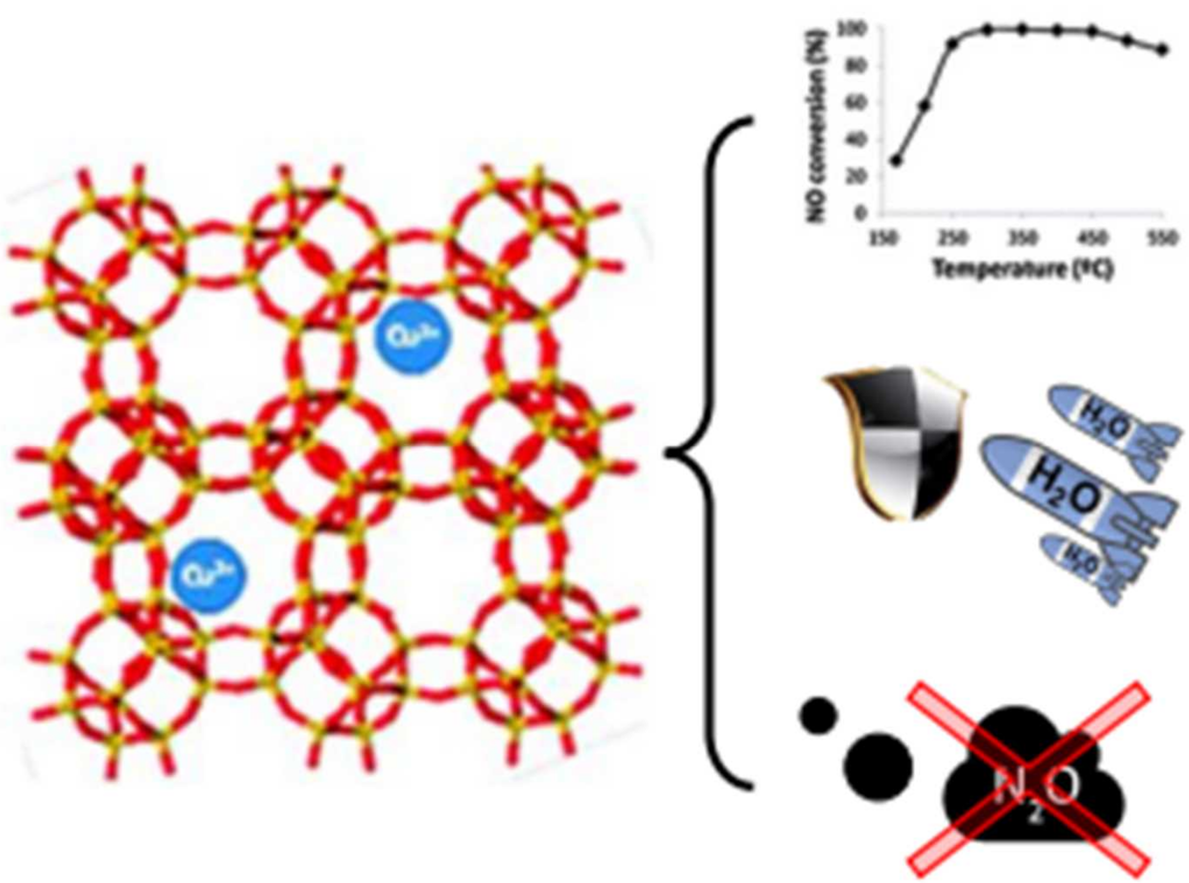


NH_3–SCR (for automobile)

◆ Conventional Cu-excahnged zeolite

Low stability → Decrease of NOx conversion
N_2O prodution

Desired properties for zeolite catalyst



High conversion

High Stability
(water vapor)

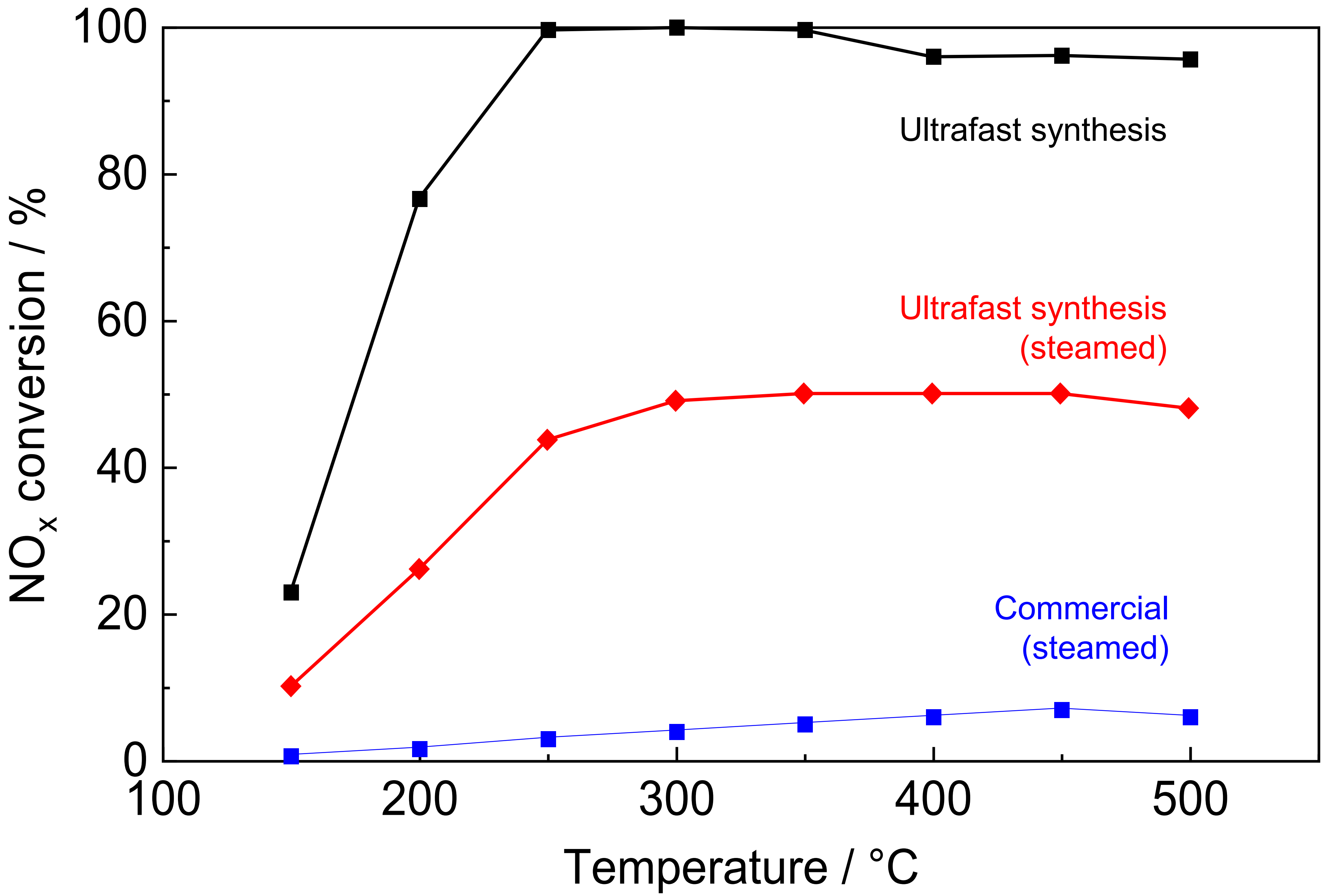
Low N_2O evolution

broken catalyst in NH_3-SCR
(by urea water)

Catalytic activity in NH_3–SCR

NH_3-SCR

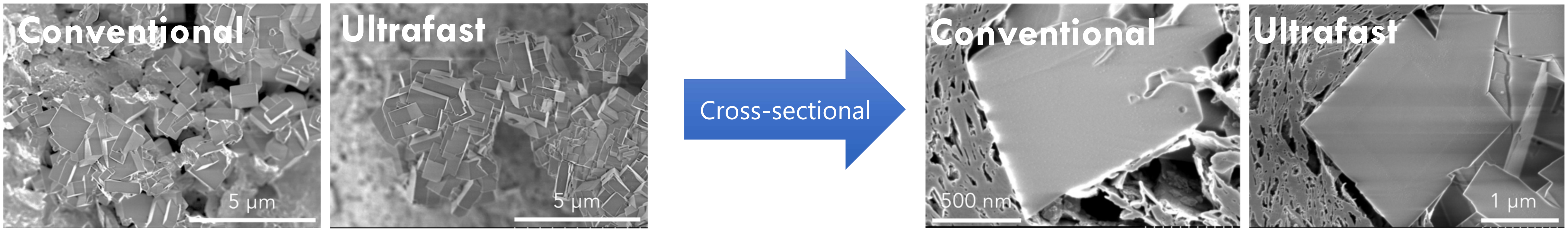
NO 300 ppm, NH_3 300 ppm, 5% O_2
Flow rate 100 cm^3/min

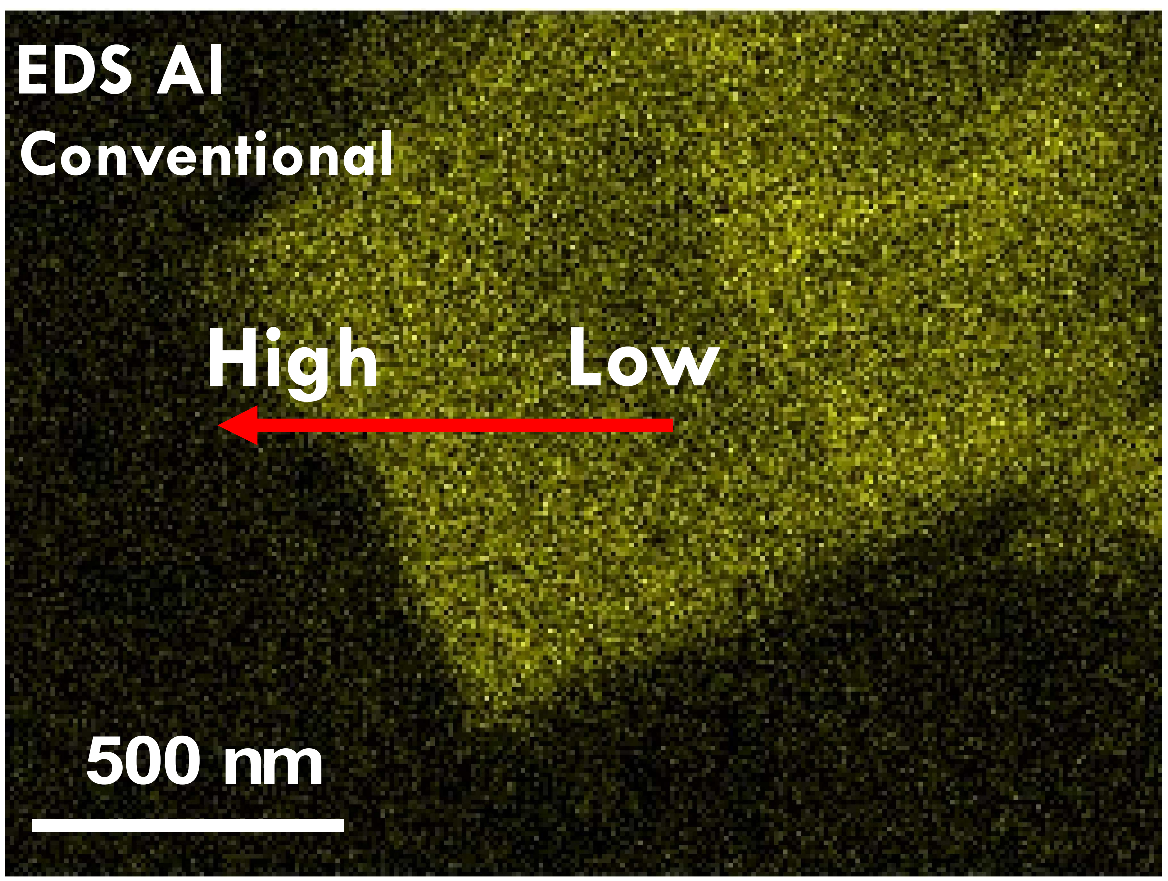


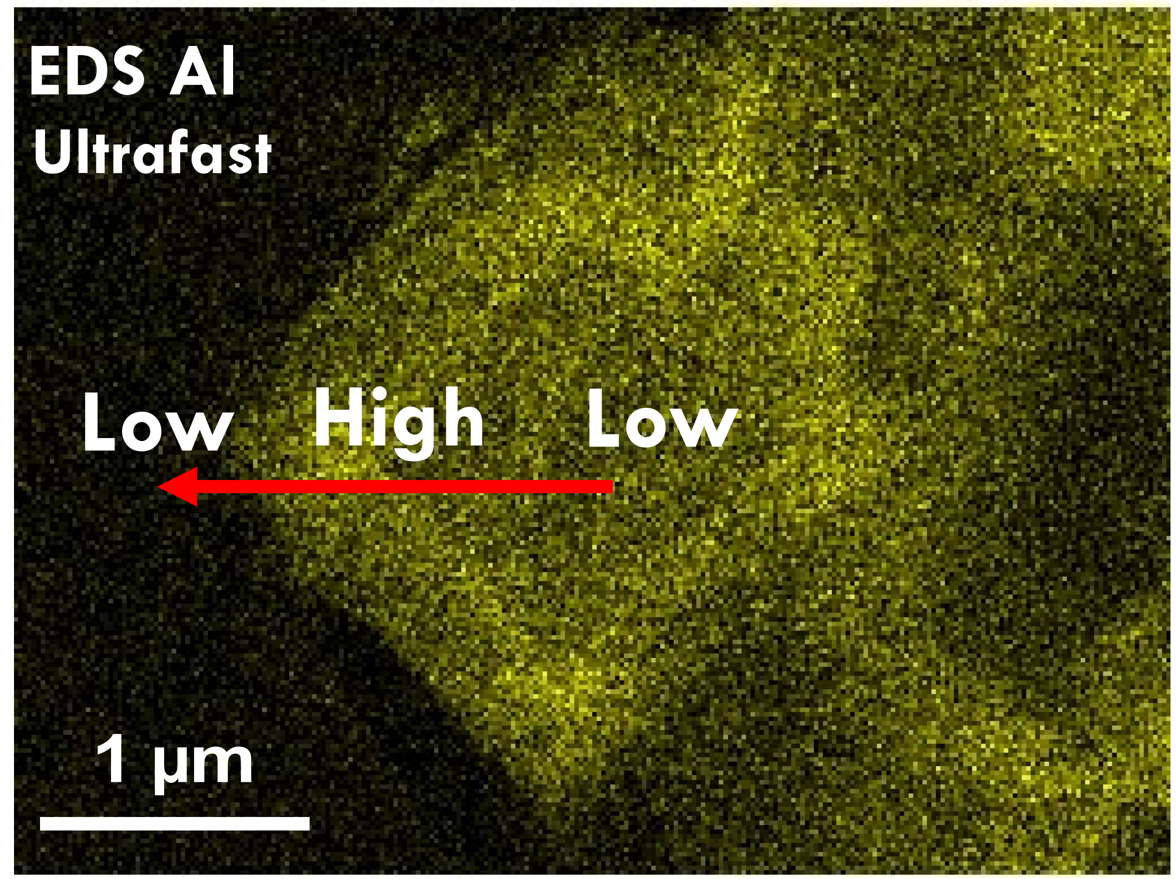
Better activity than commercial catalyst
Even after steaming (H_2O-10vol%、900℃、1 h)

Visualization of zeolite cross-sectional structure and composition distribution using FE-SEM

Update





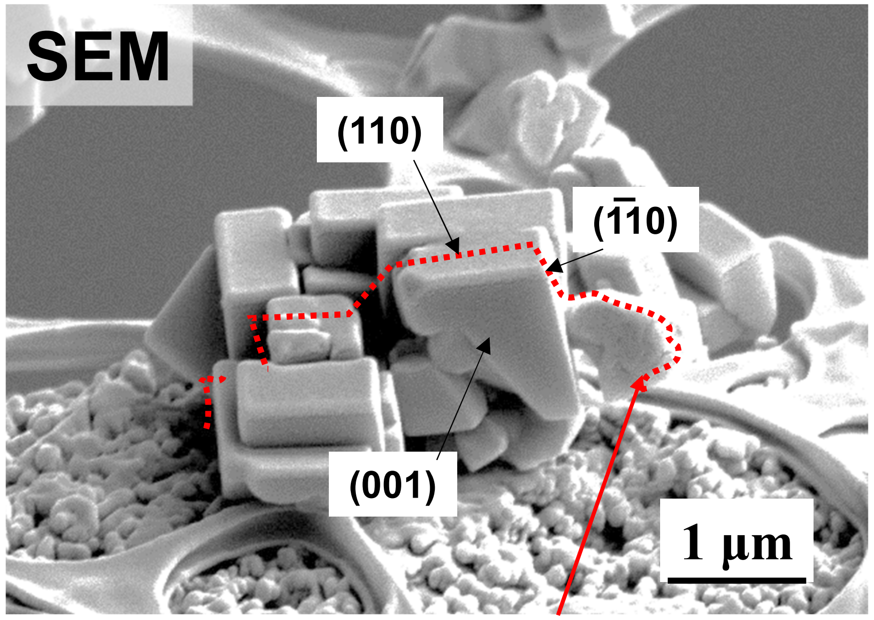


Al concentration differs from the interior to the surface of zeolite in conventional and fast synthesized zeolites.

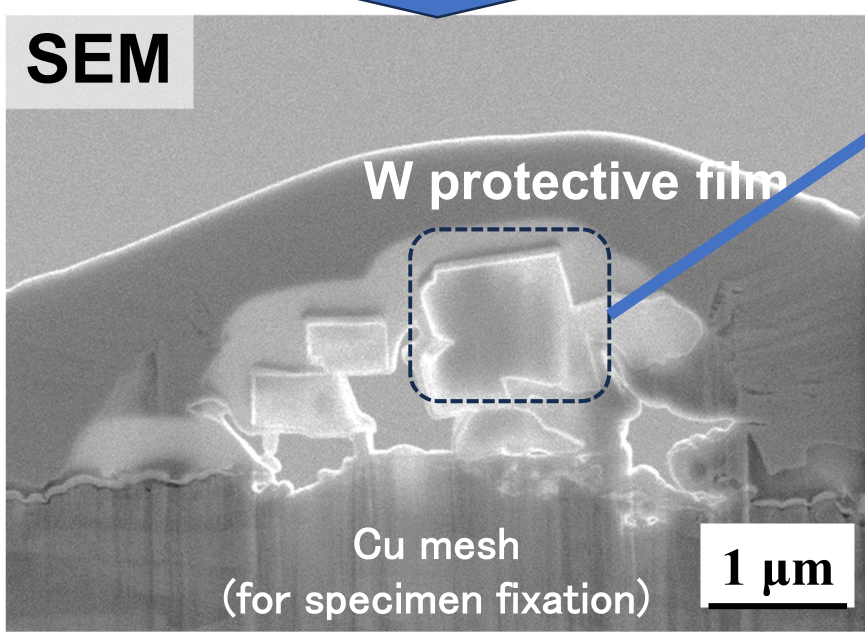
Advancement of evaluation method for compositional distribution of zeolite

Compositional distribution analysis within zeolite crystal particles

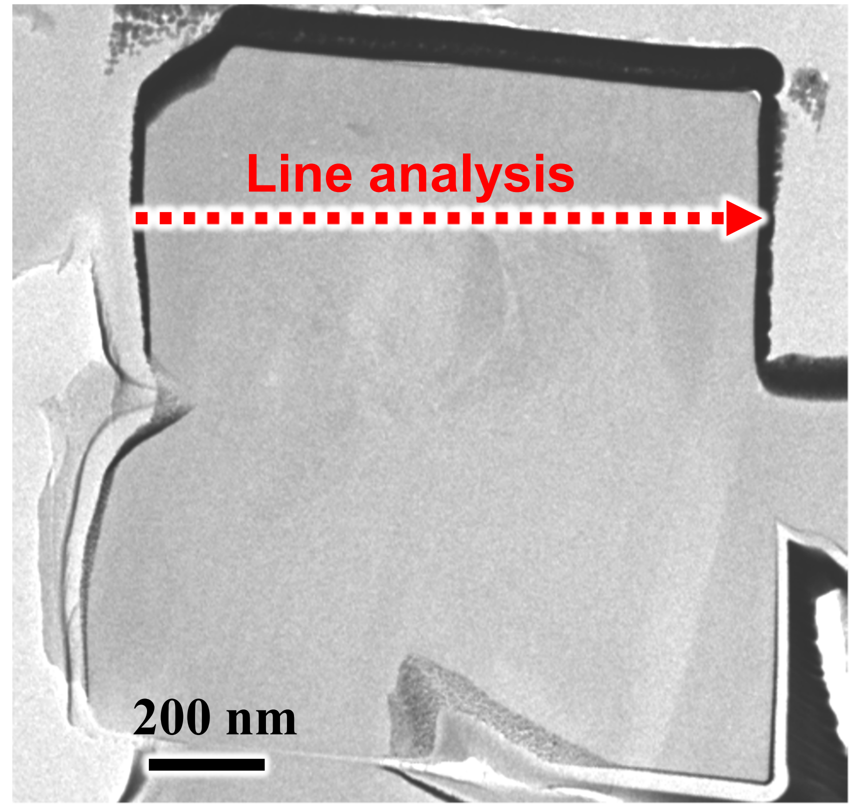
Update

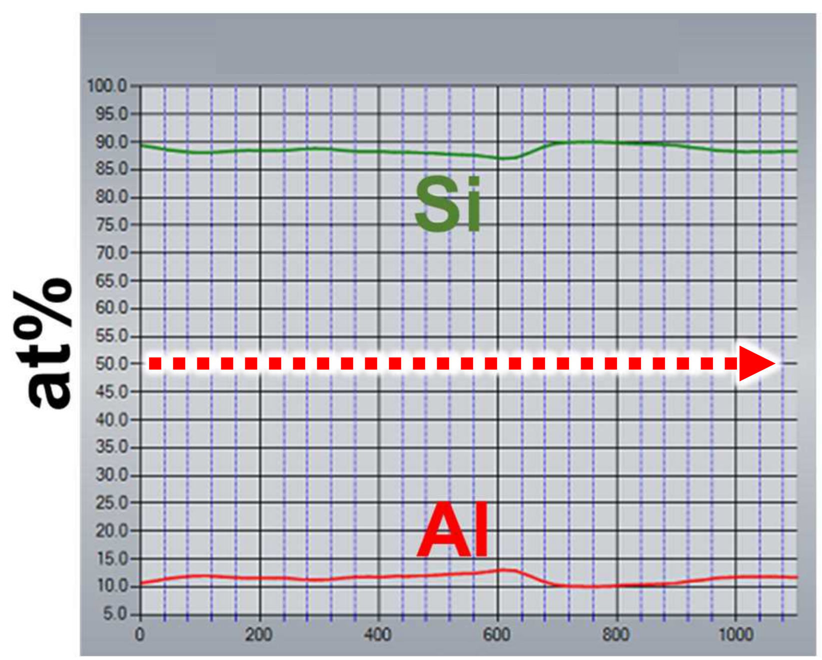


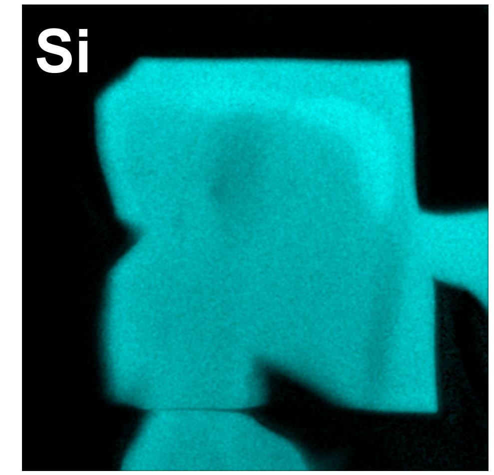
Cut

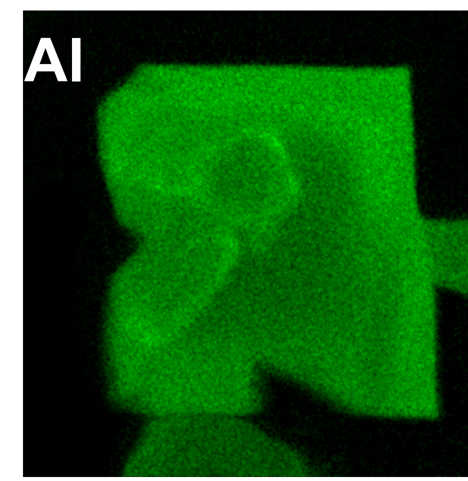


Preparation of TEM specimens thinned by FIB method









Elemental Mapping

Compositional distribution of Si and Al in the particles is almost uniform

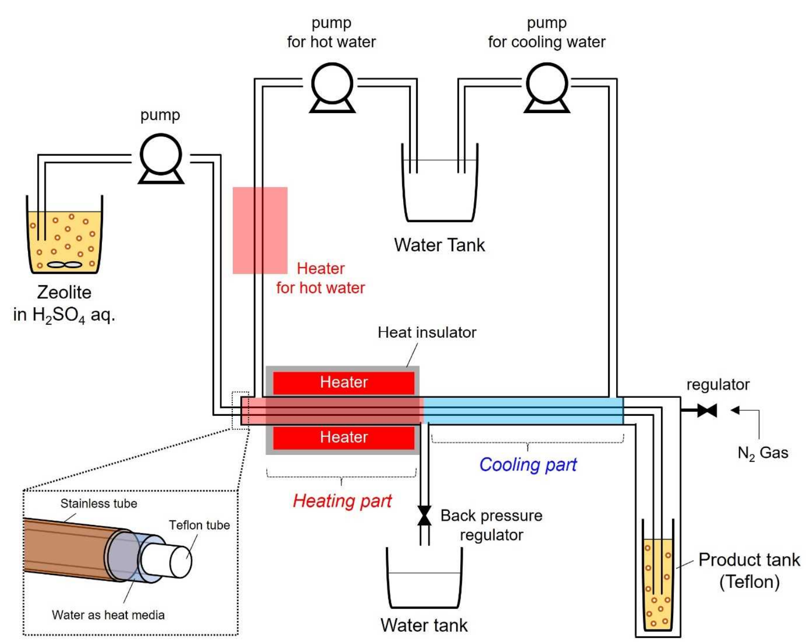
Advancement of evaluation method for compositional distribution of zeolite

Continuous–flow synthesis of zeolites

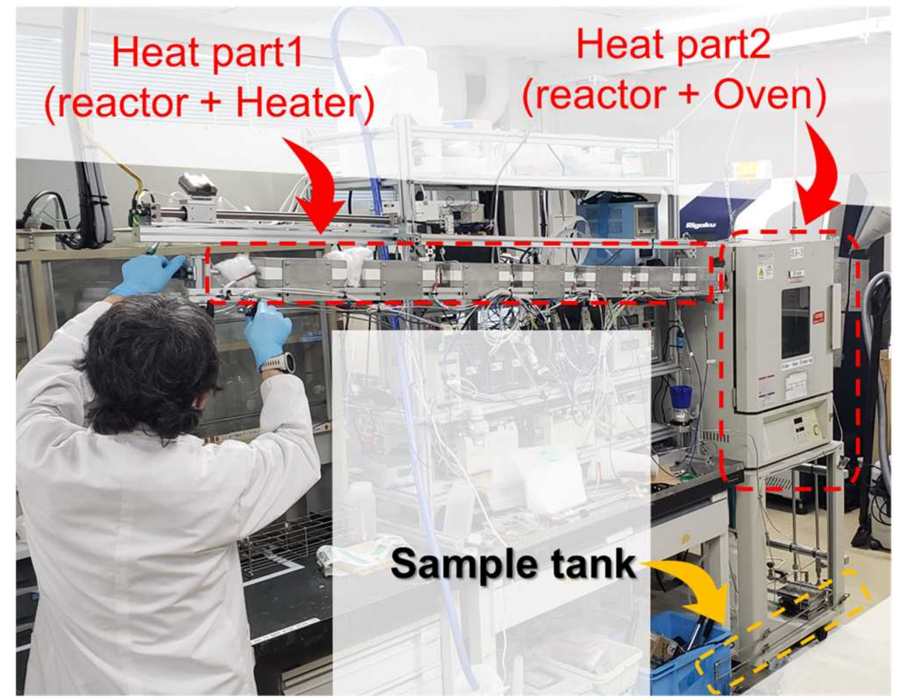
Flow reactor

Update

◆ deAl of zeolites in flow system



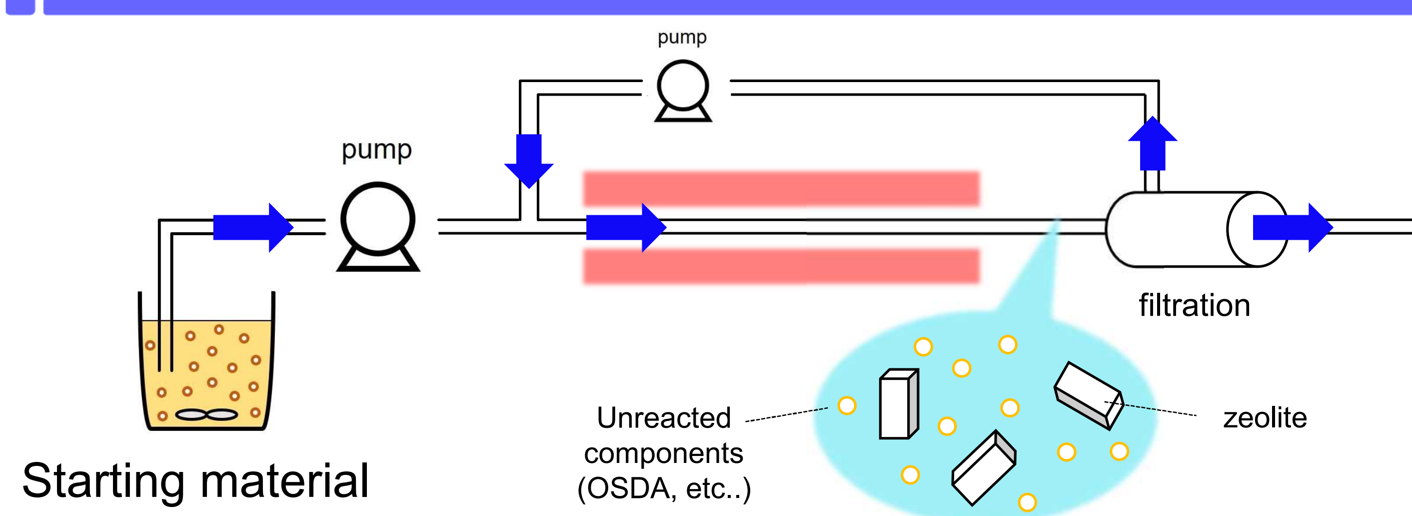
◆ Machine for zeolite synthesis



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).

Recycling of synthetic solutions in distribution systems

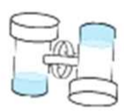


- Recovery and reuse of unreacted organic structure-defining agents
 (successfully achieved by batch synthesis)
- Establishment of distribution system
(Ongoing)

Scale-up synthesis of zeolite catalysts

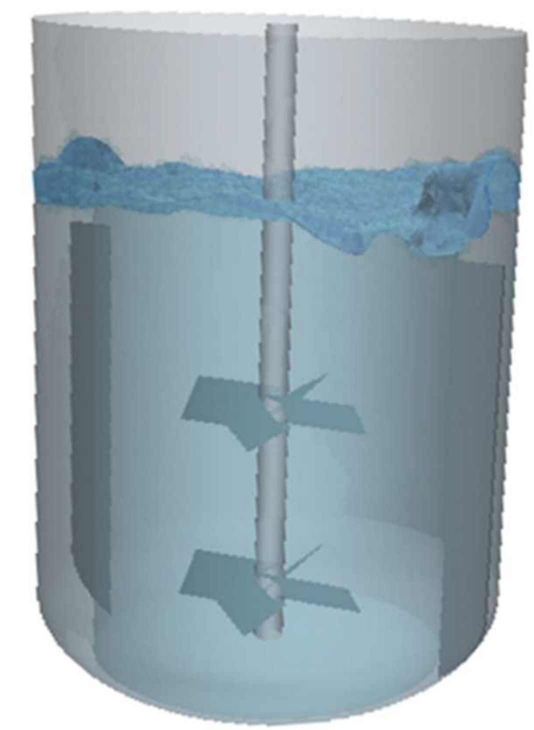
Update

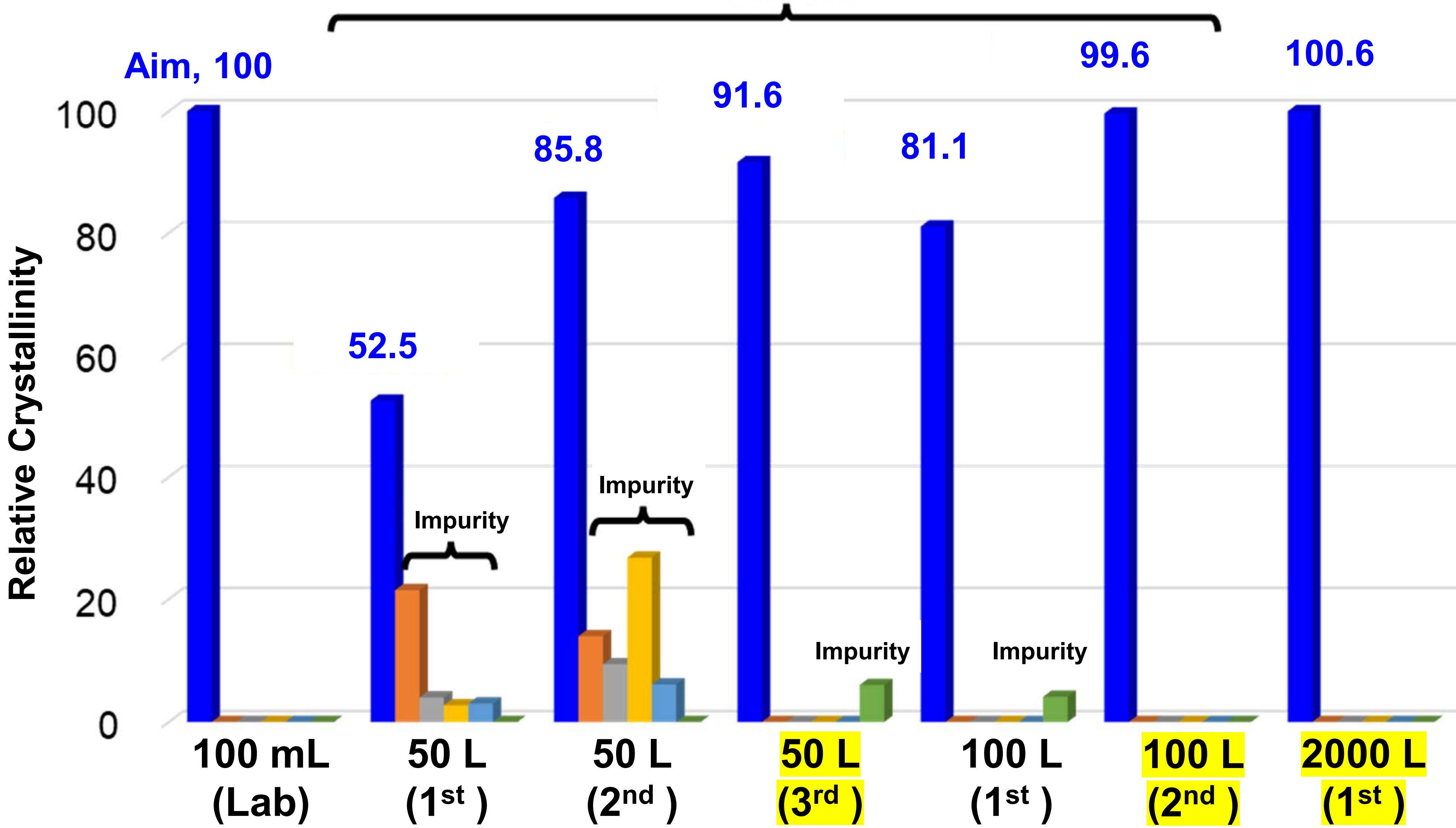
Lab Scale
(~200mL)



Pilot Scale
(50~100L)

mass production Scale
(2000L~)

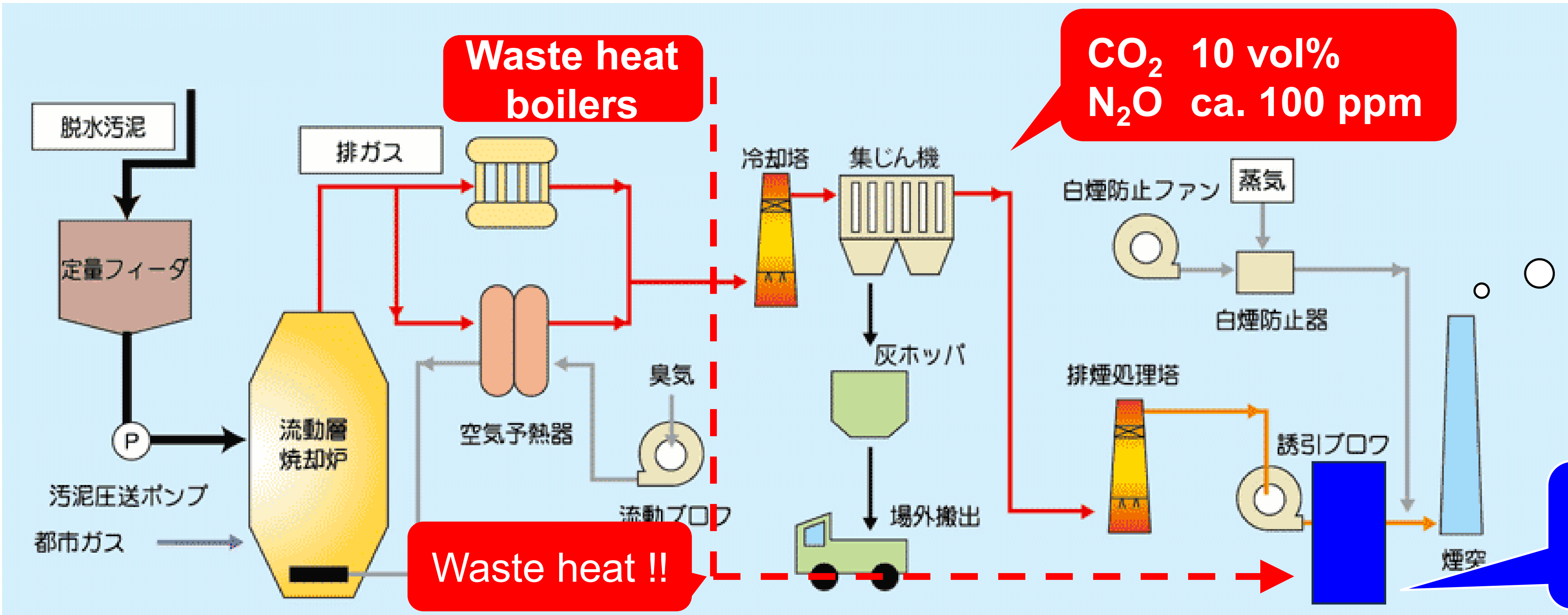




- Impurity reduction in 50L and 100L scale
- Successful synthesis of new zeolite on a mass production scale (2000L)

N_2O enrichment and recovery

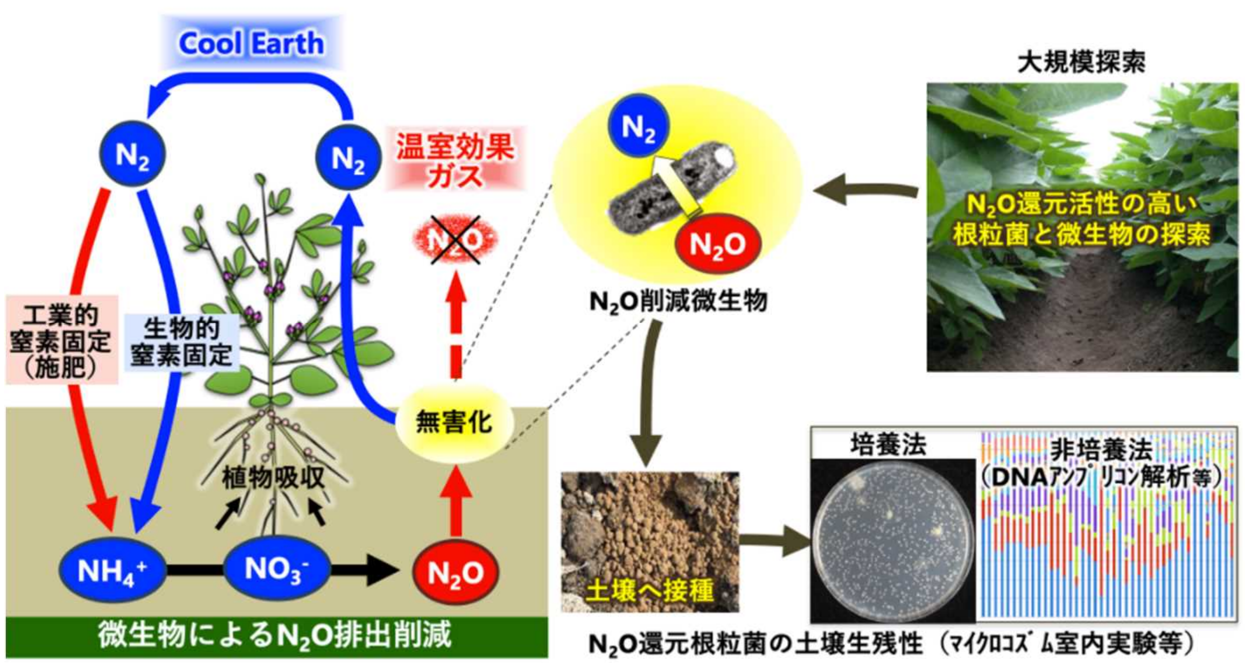
Sewage treatment plant sludge incineration gas



Object
CO_2 ≒0 vol%
N_2O ≒0ppm

- N_2O decomposition
- CO_2 recycle

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



画像出典： dSOILプロジェクトホームページ

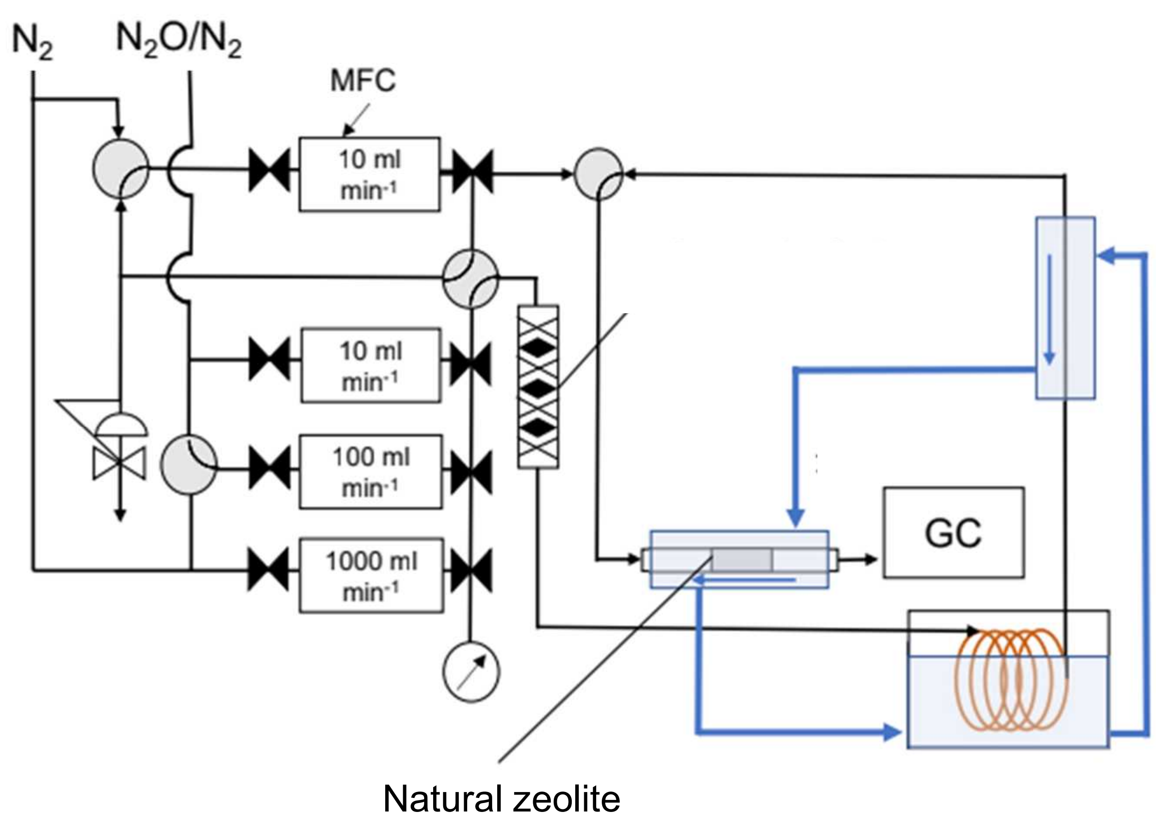
Need to separate and concentrate dilute N_2O in a variety of processing targets

Problem

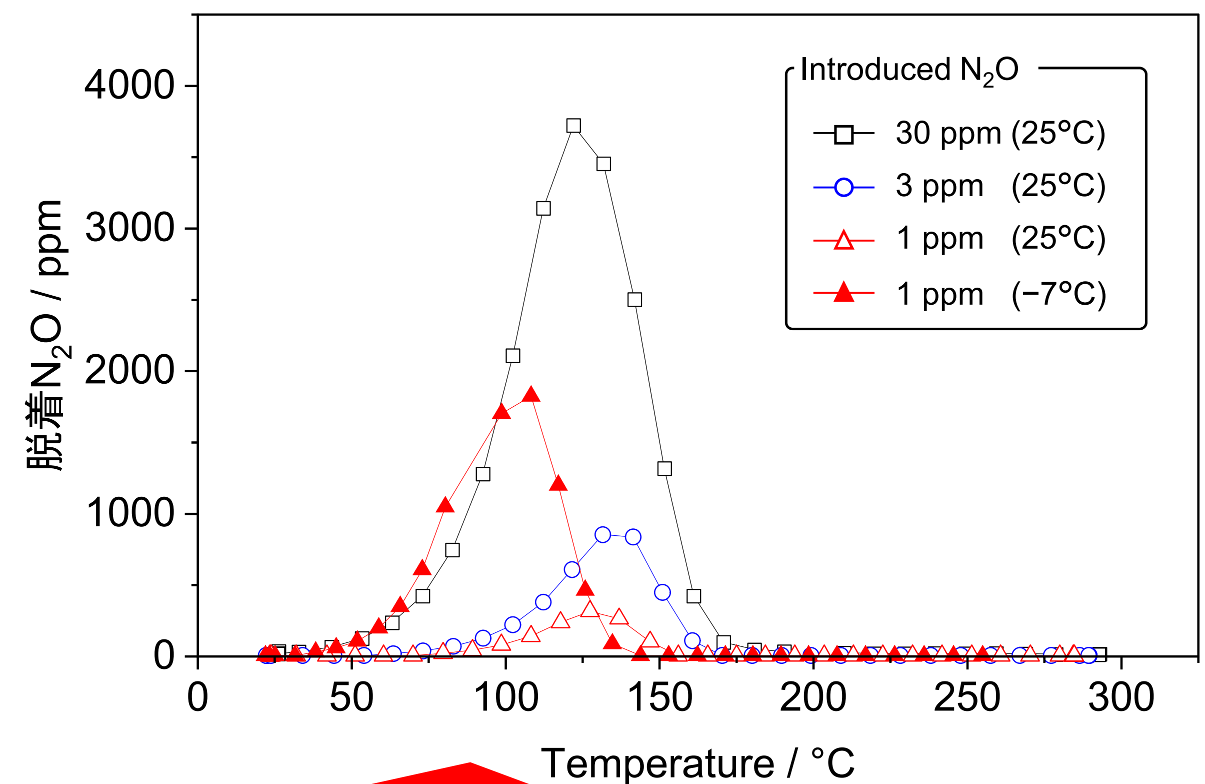
- ☐ Competitive adsorption with CO_2 and H_2O
- ☐ concentration of N_2O (>100 ppm)

System construction using zeolite

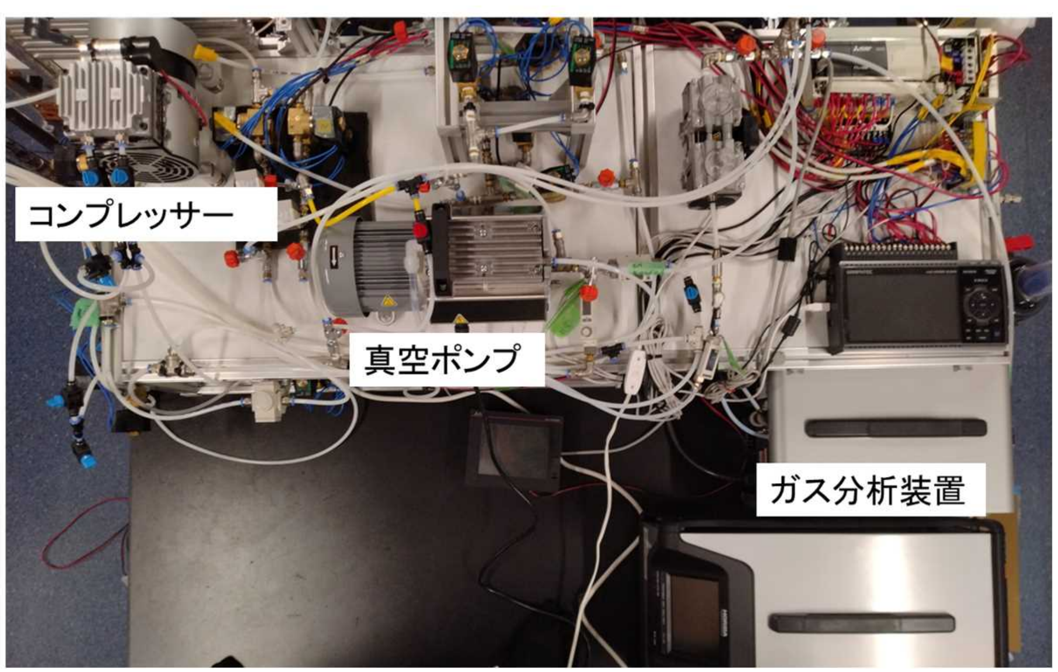
N_2O capture by natural zeolite



■ N_2O adsorption test



■ Equipment for N_2O separation



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

- Concentration of dilute N_2O from mixed gas
- By hybridization with rhizobium bacteria Aiming to concentrate and degrade dilute N_2O

Information dissemination, conference presentations, and seminars

Update

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）
- Semination for middle and high school students in 2023
- Home page launched
- Science Agora 2022

School	Grade	style	date	Participant
School A	1~3rd year (JHS)	onsite	6/23	200
School A	1~3rd year (JHS)	onsite	6/28	200
School B	2nd year (HS)	onsite	6/30	320
School C	2nd year (HS)	onsite	8/2	40
School D		onsite	9/16	500
School E	1st year (HS)	onsite	10/13	41
School F	2nd year (HS)	onsite	10/17	120
School G		onsite	10/26	150
School H		onsite	11/3	200
School I		onsite	11/14	50
School J	1~2nd year (HS)	onsite	11/16	40
Seminar	ES~HS	online	7/16	50
	ES~HS	online	7/23	50

Conference (>30)

Publication List (Excerpts from a total of 22 reports)

Update

- 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)
- P. Hu, K. Iyoki, H. Fujinuma, J. Yu, S. Yu, C. Anand, Y. Yanaba, T. Okubo, T. Wakihara
  Microporous and Mesoporous Materials, 330, 111583, (2022).
- 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).
- A. Minami, P. Hu, Y. Sada, H. Yamada, K. Ohara, Y. Yonezawa, Y. Sasaki, Y. Yanaba, M. Takemoto, Y. Yoshida, T. Okubo, T. Wakihara
  Journal of the American Chemical Society 144, 23313-23320 (2022).
- M. Takemoto, Y. Fujikawa, K. Iyoki, N. Tsunoji, T. Sano, T. Okubo, T. Wakihara
  Journal of the Ceramic Society of Japan, 131, 1-6 (2023).
- T. Yoshioka, K. Iyoki, Y Yanaba, T. Okubo, T. Wakihara
  Journal of the Ceramic Society of Japan, (in Press).
- Y. Yoshida, Y. Sada, T. Sano, T. Okubo, T. Wakihara
  Crystal Growth & Design 23, 2231-2238 (2023).
- R. Simancas, M. Takemura, C.-T. Chen, K. Iyoki, T. Okubo, T. Wakihara
  Journal of Non-Crystalline Solids 605, 122172 (2023).
- T. Shibuya, K. Iyoki, H. Onozuka, M. Takemoto, S. Tsutsuminai, T. Takewaki, T. Wakihara, T. Okubo
  Crystal Growth & Design 23, 3509-3517 (2023).
- B. Li, K. Iyoki, P. Techasarintr, S. P. Elangovan, R. Simancas, T. Okubo, T. Yokoi, T. Wakihara
  ACS Catalysis 13, 15155-15163 (2023).
- J. Yu, K. Iyoki, S. P. Elangovan, H. Fujinuma, T. Okubo, T. Wakihara,
  Chemistry – A European Journal e202303177, (2023).
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Main results at this time

Update

NH_3 capture

- Low-cost, quick and simple adsorbent synthesis process
- Recovery of more than 50% NH_3/NH_4^+ ions in actual wastewater
- Demonstrated recyclability of developed product in NH_3 recovery
- Development of superior adsorbent material using waste raw materials
- Starting Scale-up synthesis
- Collaborating with participating companies, taking into consideration about reuse recovered NH_3

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
- Development of zeolite structural analysis methods
- Establishment of zeolite production technology on a large scale
- Recycle of OSDA

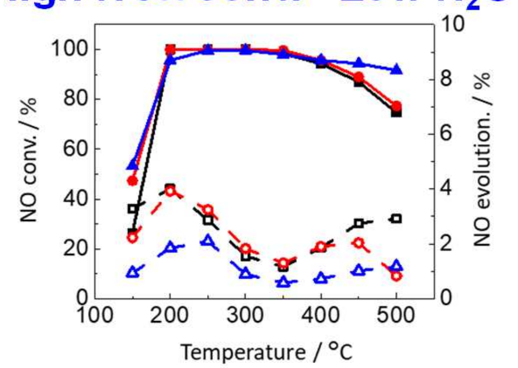
Evaluation of system

- LCA evaluation of adsorption and denitration systems using zeolite production, zeolite, etc.
- Proof of reduction of emission N and resource saving by introduction of development agents
- LCA evaluation of nitrogen cycle in the region

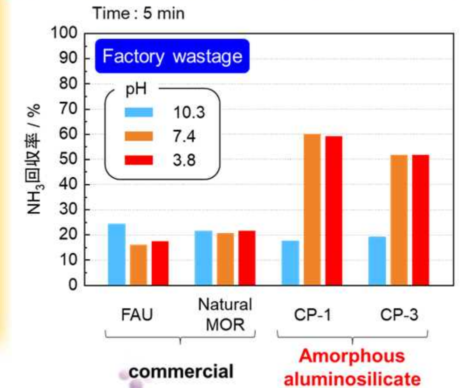
Future Outlook

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

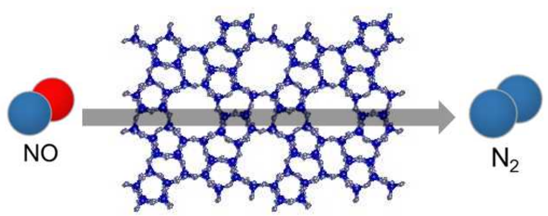
High NOx conv. ·Low N_2O



Excellent adsorbent !!

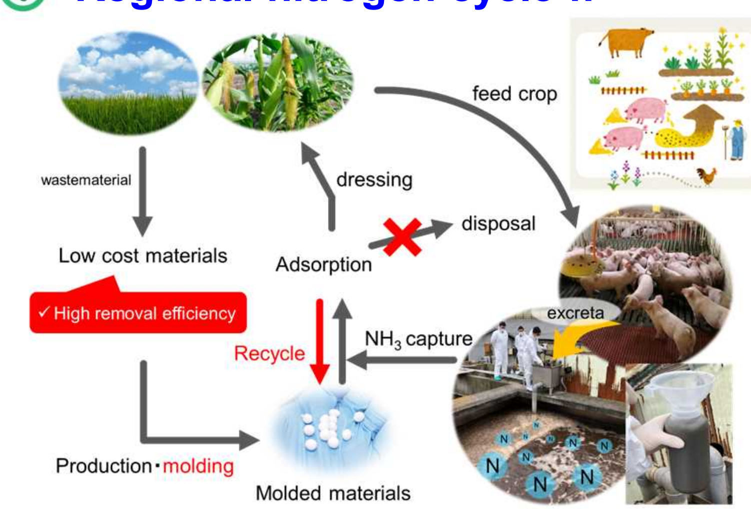


- Recyclable
- From waste raw material

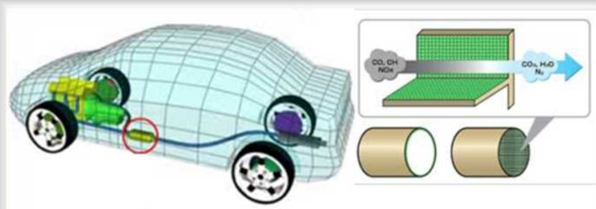


✓ Direct NO decomposition

Regional nitrogen cycle !!

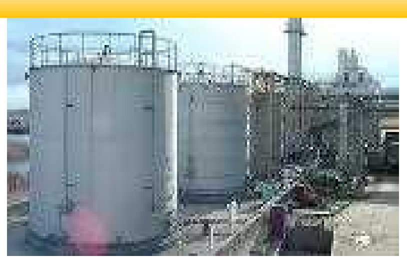


✓ Hybrid with natural zeolite and rhizobium



✓ 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