No. A-10-1E

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

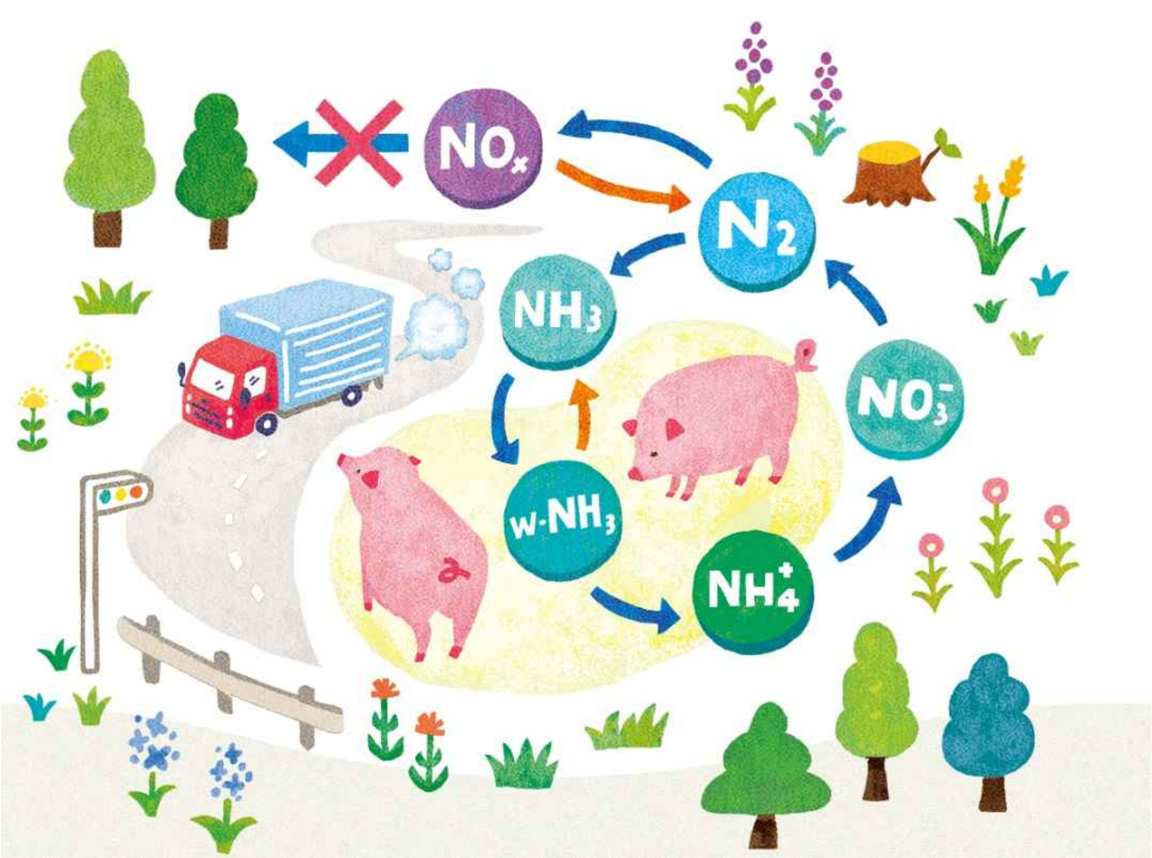
Theme: Future Vision of Nitrogen Circulating Society

Organization: The University of Tokyo Contact: wakihara@chemsys.t.u-tokyo.ac.jp

Efficient circulation for a clean earth

Problems of Human Activity for Nitrogen Circulating Society

Towards a healthy and prosperous society without wasting nitrogen resources



Nitrogen, essential in our lives, is contained as nitrogen molecules (N_2) and ammonia (NH_3). For example, nearly 80% of air is N_2. Also, a lot of food is produced thanks to fertilizers using NH_3. However, nitrogen is currently out of balance due to human activity, and is said to be approaching the limit (planetary boundary) that the earth can accept.

The substances containing nitrogen in question here include not only discarded NH_3, but also nitrogen oxides (NO, N_2O, NO_2, etc., collectively referred to as NOx). Currently, it is required to reduce the environmental load and normalize the balance of nitrogen (nitrogen cycle).

No. A-10-2E

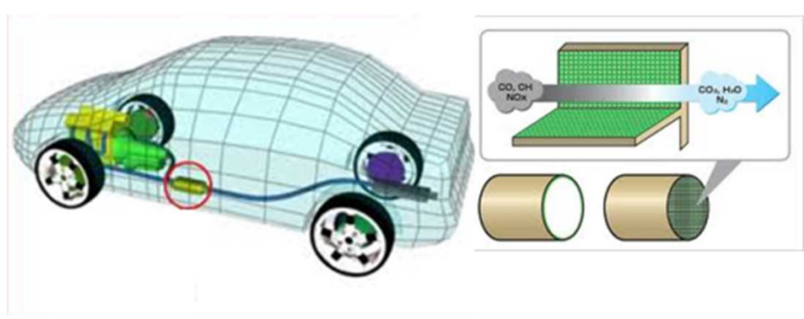
PJ : Development of Recovery and Removal Techniques of Dilute Reactive Nitrogen to Realize Nitrogen Circulating Society

Theme: Synthesis of excellent NH_3 capture and deNOx materials

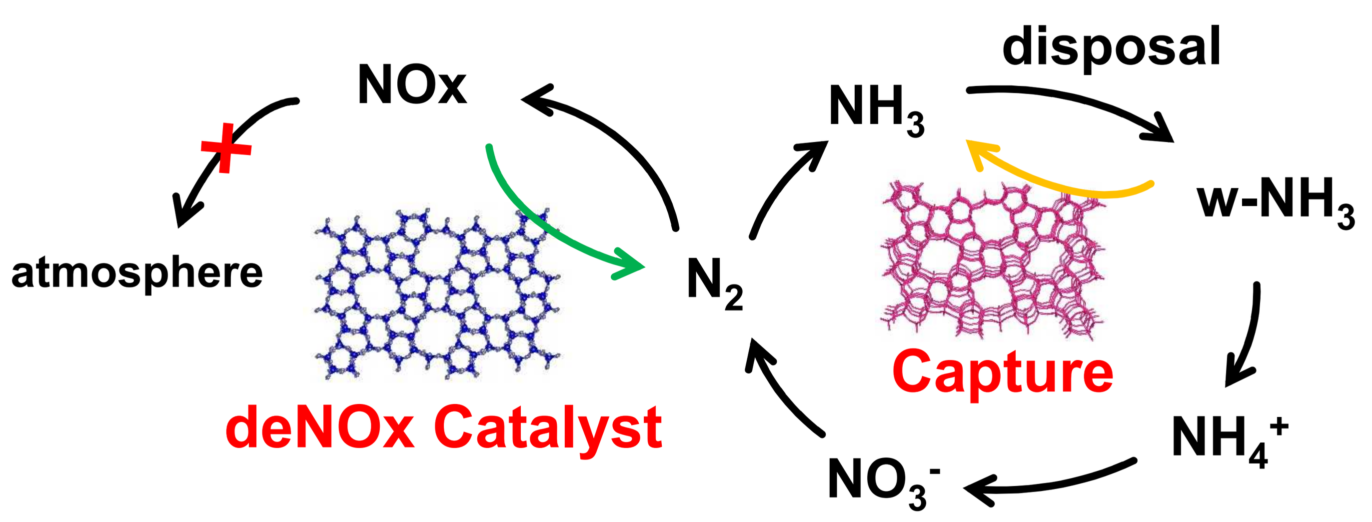
Organization: The University of Tokyo Contact: wakihara@chemsys.t.u-tokyo.ac.jp

Project Overview

Exhaust Gas (NOx)



Industrial Wastewater (w-NH_3)



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

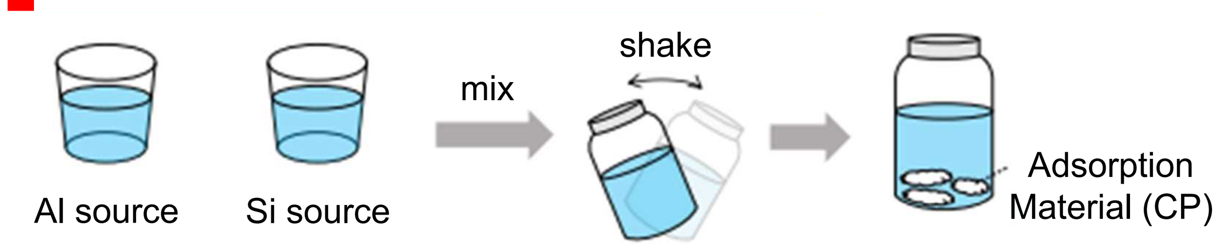
- Although the transition to electric vehicles has been proposed for the realization of a carbon-neutral society, in Europe, reluctant to fully transition to electric vehicles.
- Considering the introduction of e-fuel, an internal combustion engine (especially for truck transportation) is essential.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

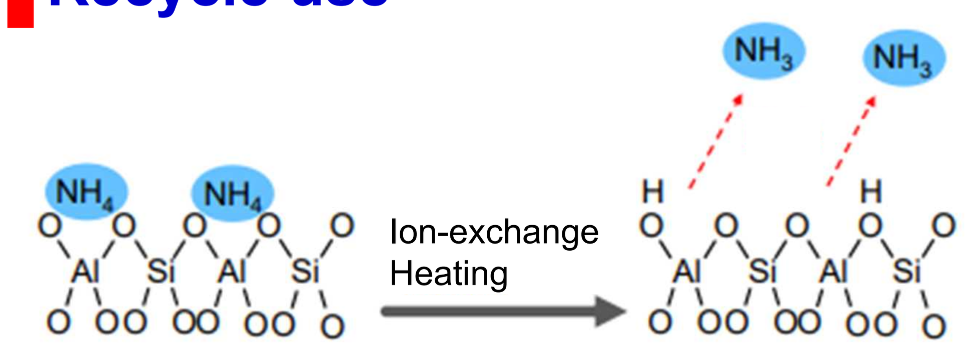
NH_3 Capture

Preparation of amorphous aluminosilicate



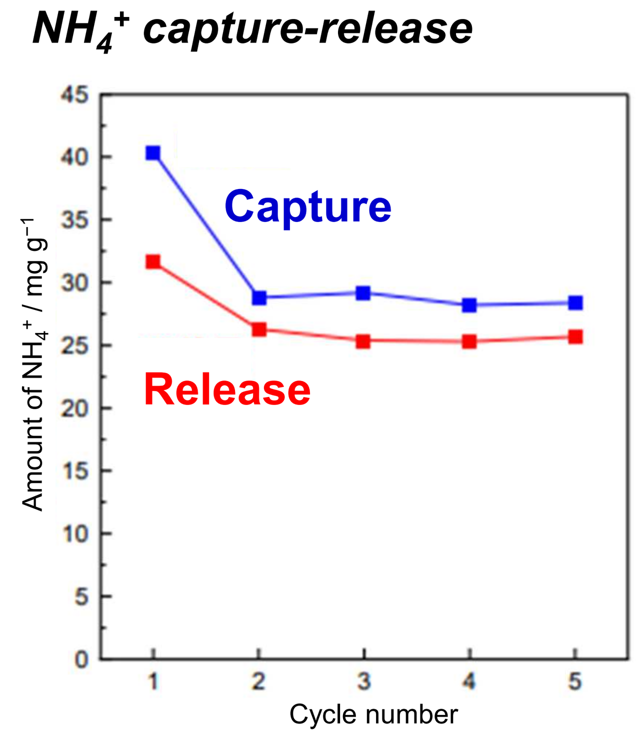
- Facile
- Low Cost
- Fast Synthesis

Recycle use



- High NH_4^+ capture (> 25%)
- Recyclable (keep potential)

NH_4^+ capture-release

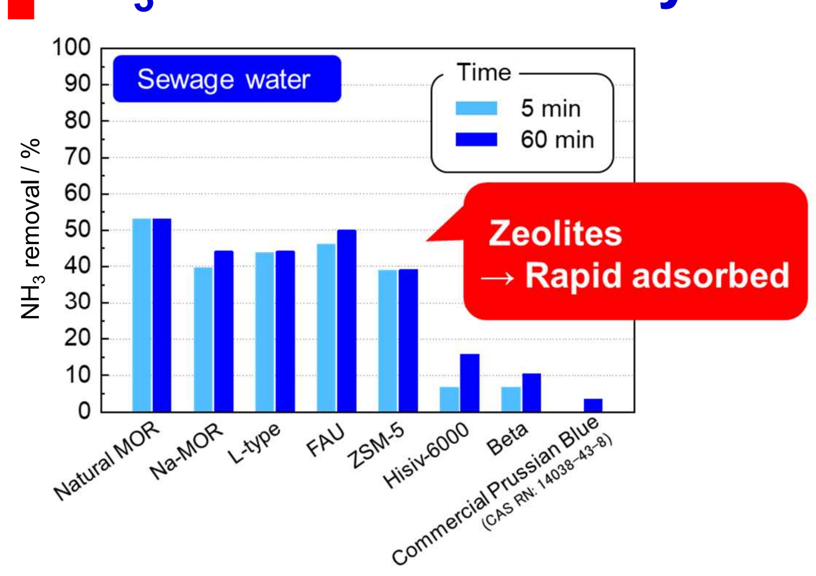


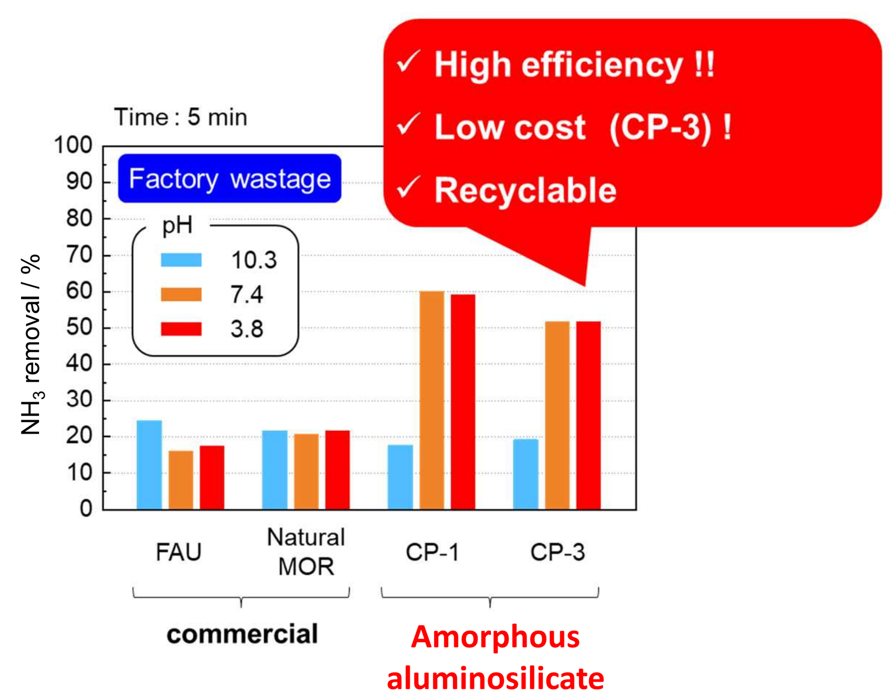
Comparison of Performance

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

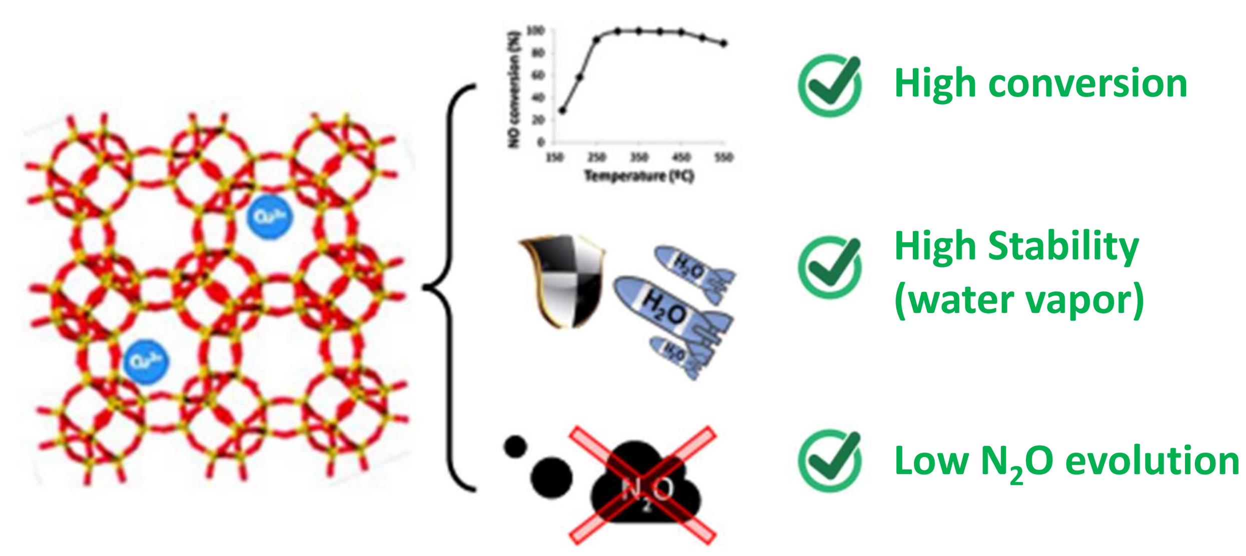




- Achieved high NH_3 removal (> 50%) from industrial wastewater

deNOx Catalyst

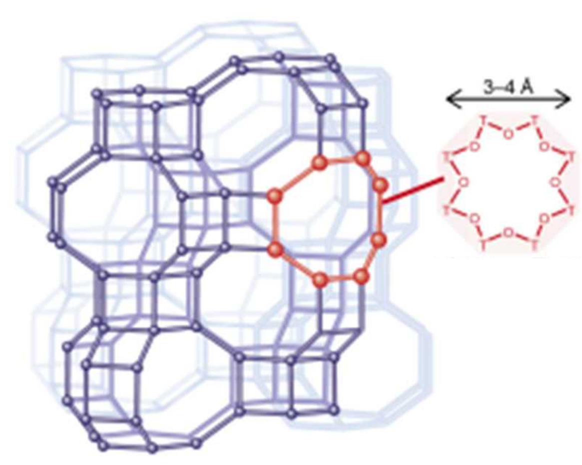
Desired properties for zeolite catalyst



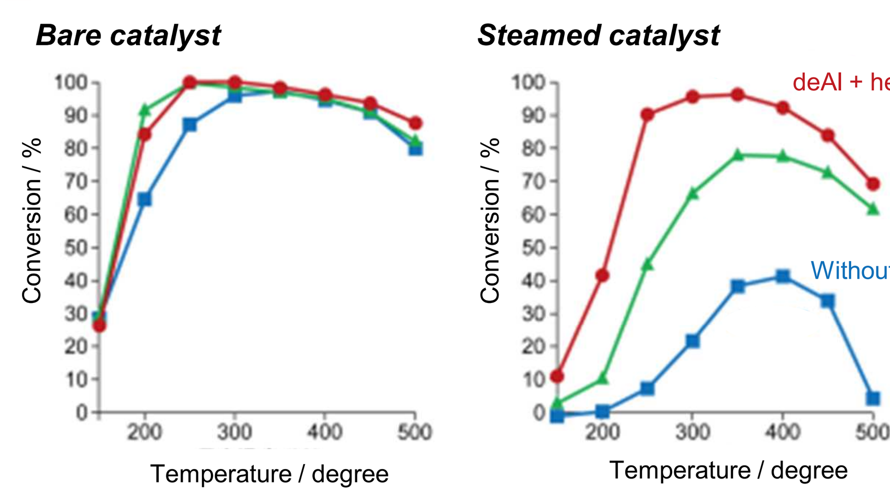
broken catalyst in NH_3-SCR (by urea water)

Novel method for dealumination (de-Al) of zeolite

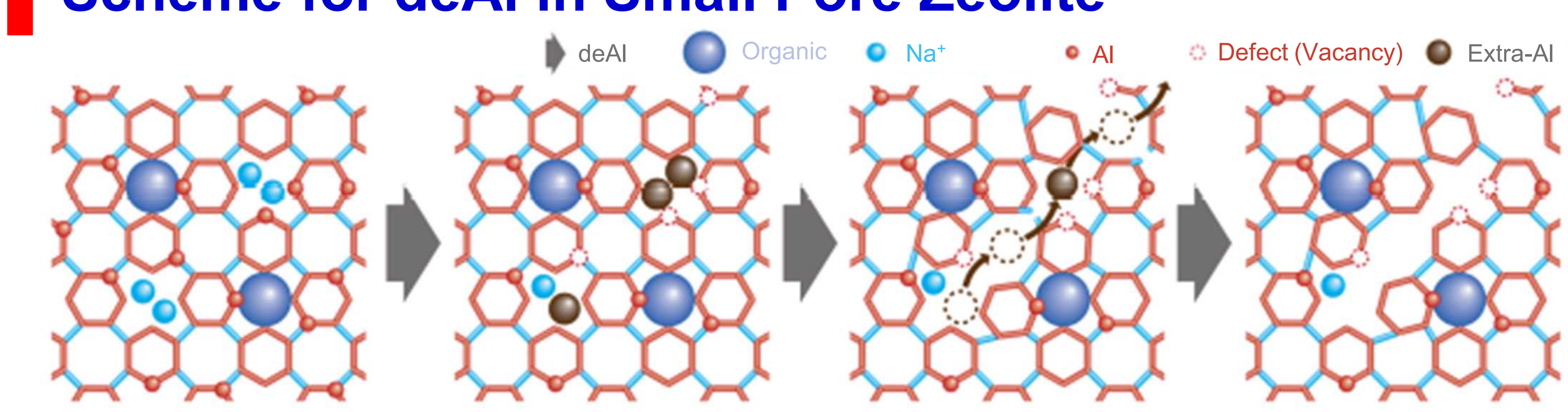
Small Pore Zeolite



NH_3-SCR



Scheme for deAl in Small Pore Zeolite

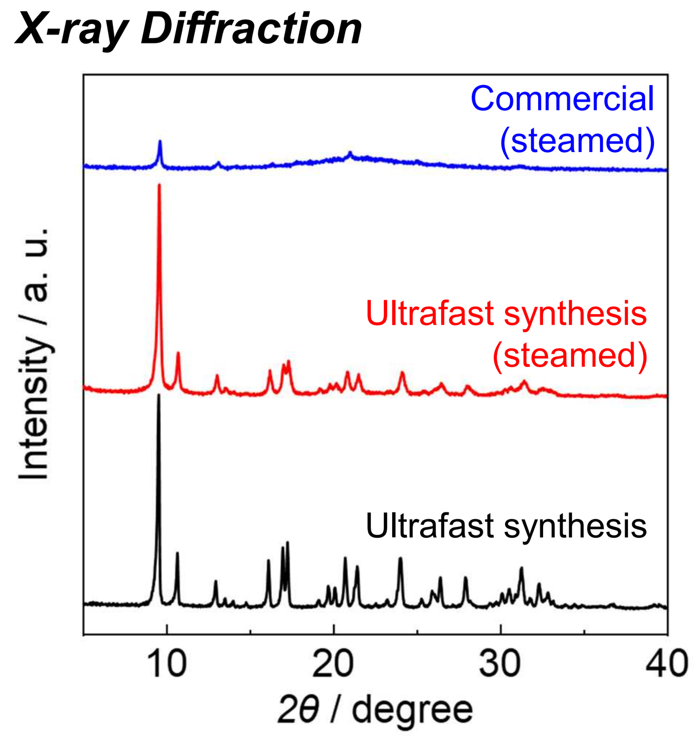


Ultrafast Synthesis of Zeolite with High Stability

Stability against water vapor

Condition: H_2O-10vol%, 900ºC 1 h

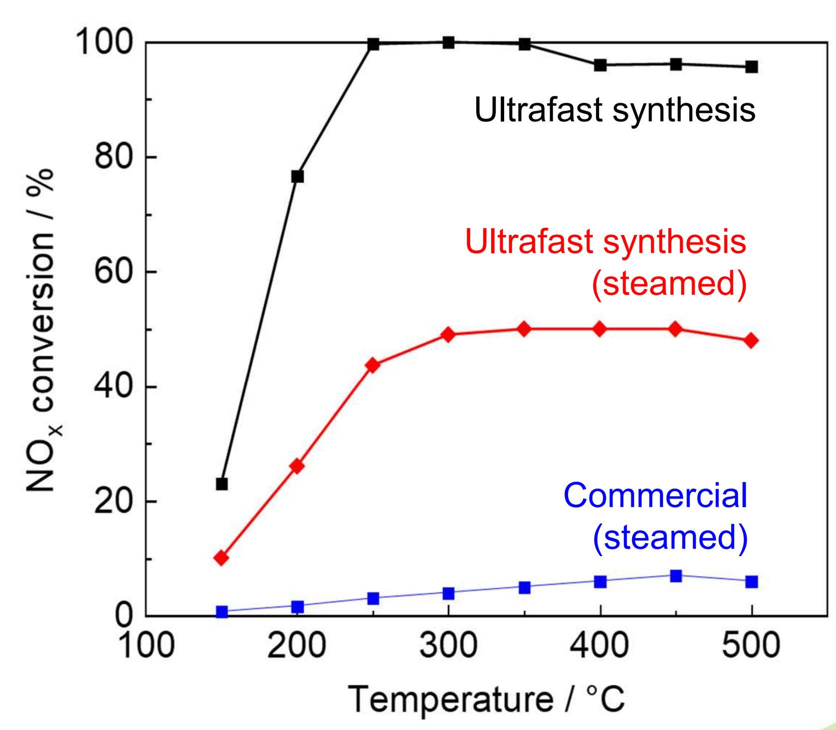
X-ray Diffraction



NH_3-SCR

NO 300 ppm, NH_3 300 ppm, 5% O_2

Flow rate 100 cm^3/min



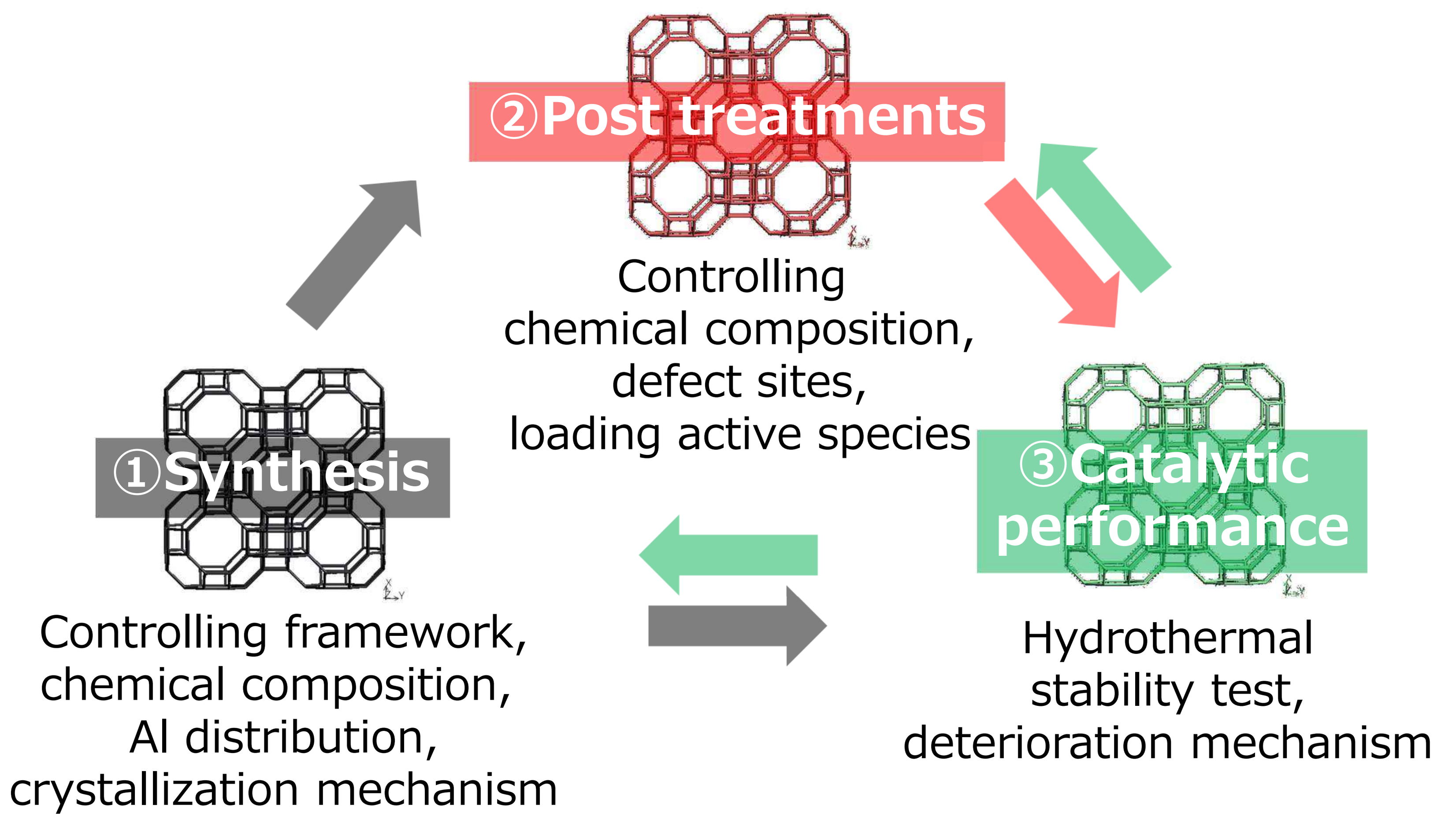
No. A-10-3E

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

Theme: Structural Characterization of Zeolites by SEM and Gas Physisorption

Organization: National Institute of Advanced Industrial Science and Technology (AIST) Research Institution in Sustainable Chemistry
Contact: Dr. KAMIMURA Yoshihiro (yoshihiro-kamimura@aist.go.jp)

●Designing of High-Performance Zeolites: from Synthesis to Evaluation



1.Observation of surface and cross-sectional zeolites
2.Textural pore characterization of zeolites

●AIST Experimental Apparatuses

<Structural analysis>
(Particle size and shape, cross-sectional observation, visualization of Al or other catalytically active species)

Broad ion-milling (Hitachi IM4000plus) Implemented in FY2020

In-lens FE-SEM (Hitachi SU9000)

Semi-in-lens FE-SEM (Hitachi SU8600) +EDS (Oxford Extreme) Implemented in FY2021

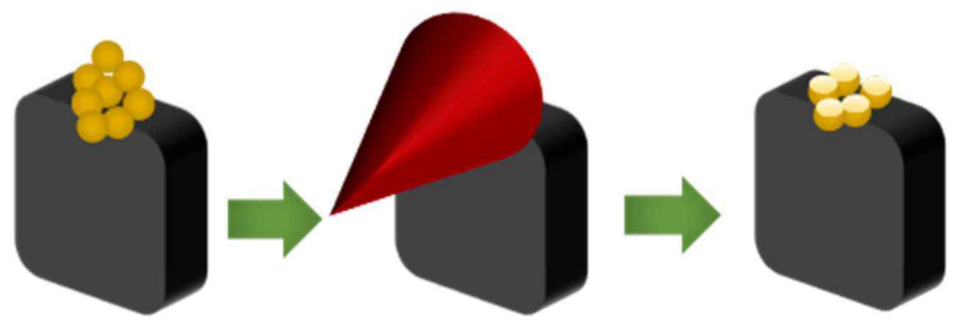
<Porous characterization>
(surface area, pore volume, pore size and shape)

Gas physisorption apparatus (Microtrac-Bel Belsorp MAX)

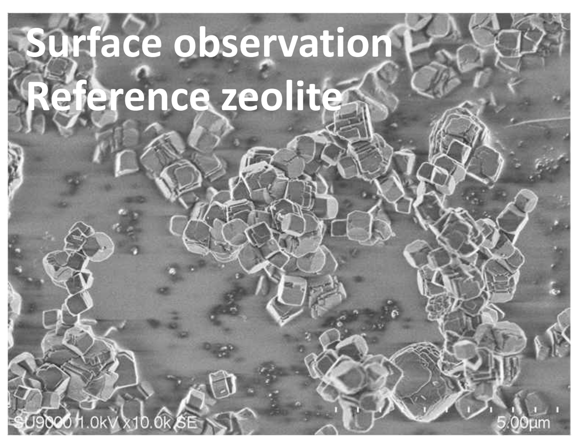
●Preparation of Cross-sectional Surface by Broad Ion Beam (BIB) Method

Step 1: Ion-milling

Operated under less damaging, mild conditions

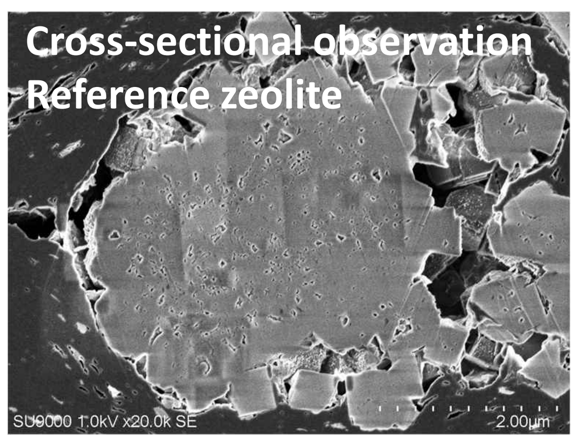


Sample set to Si wafer → Cutting by Ar ion beam → Cross-sectional surface

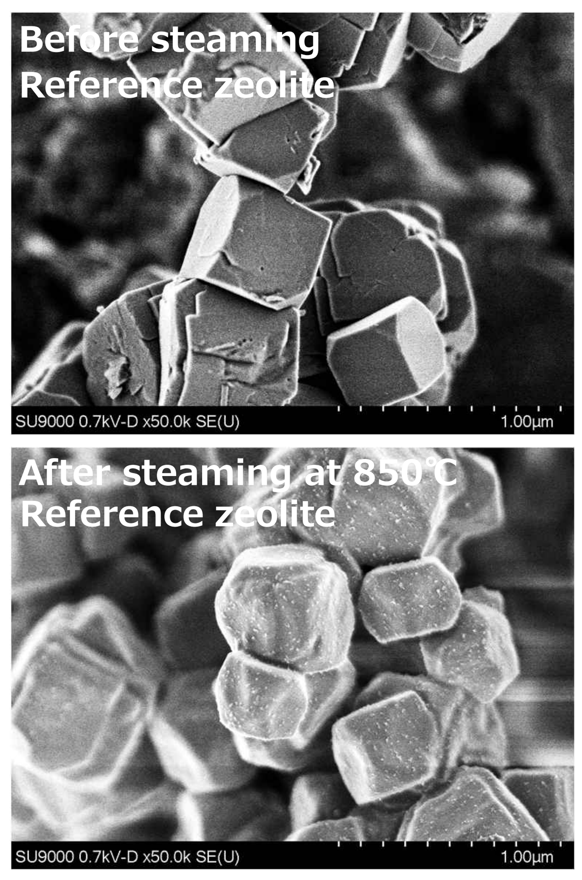


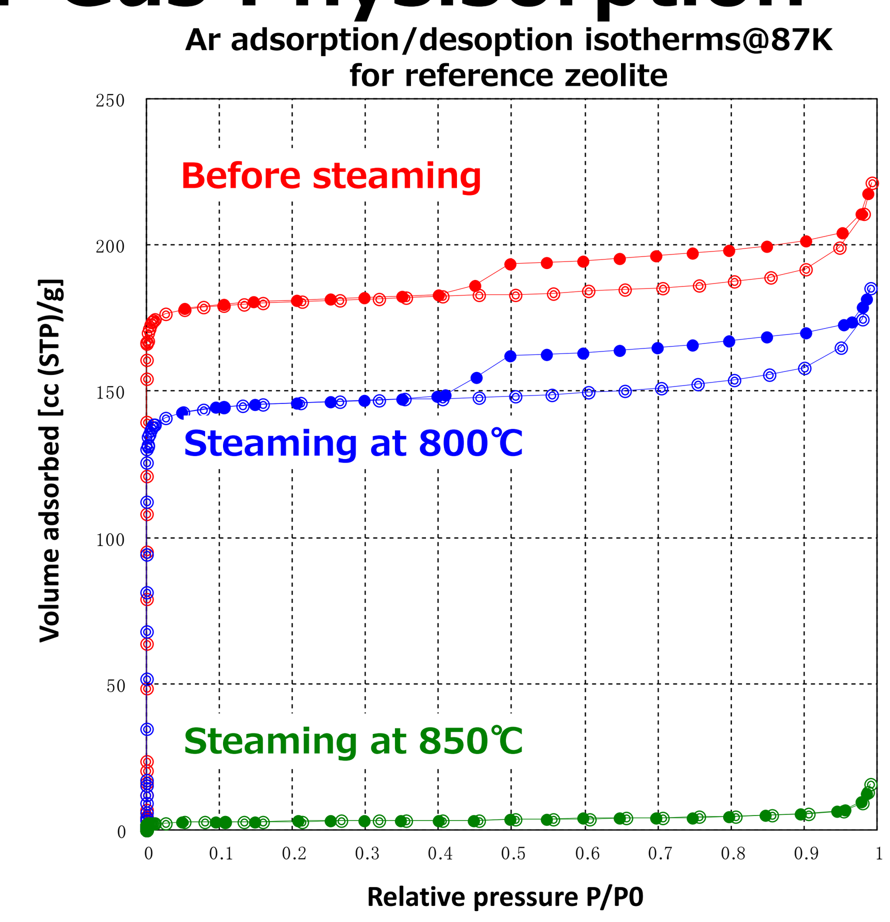
Step 2: Cross-sectional observation by FE-SEM

Use a low electron accelerating voltage to reduce charging and electron beam damage with retaining high-resolution observations.



●Evaluation of Zeolite after Steaming by FE-SEM and Ar Gas Physisorption



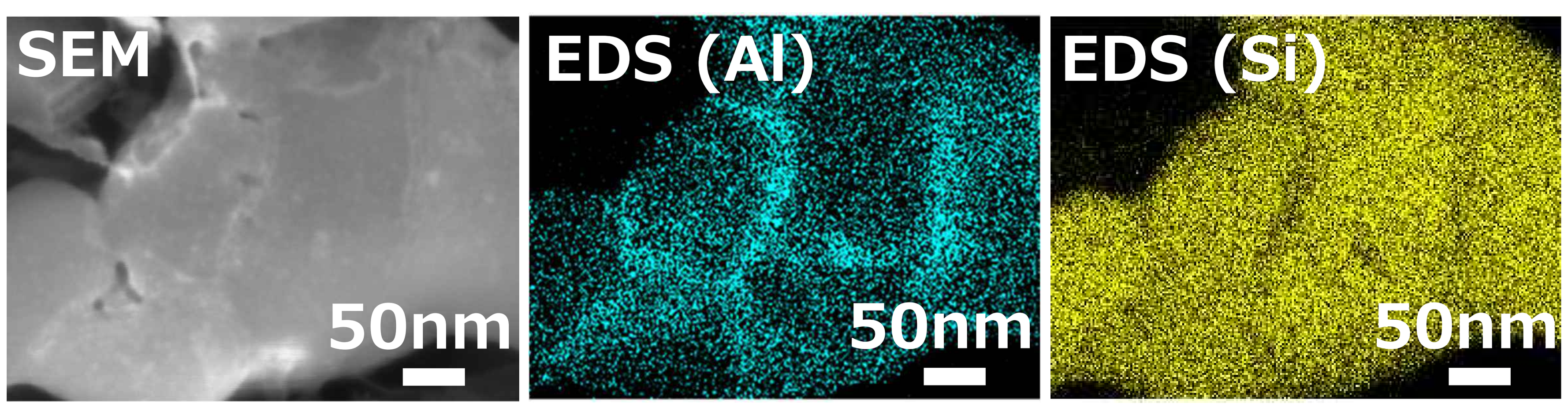


Able to detect the prominent structural change (surface and porous architecture) in zeolites after steaming treatments over 850℃.

●Visualization of Aluminum Zoning

Important points to achieve cross-sectional observation and Al visualization

FE-SEM: Low V_{acc} · High-resoultion EDS: Low energy EDS

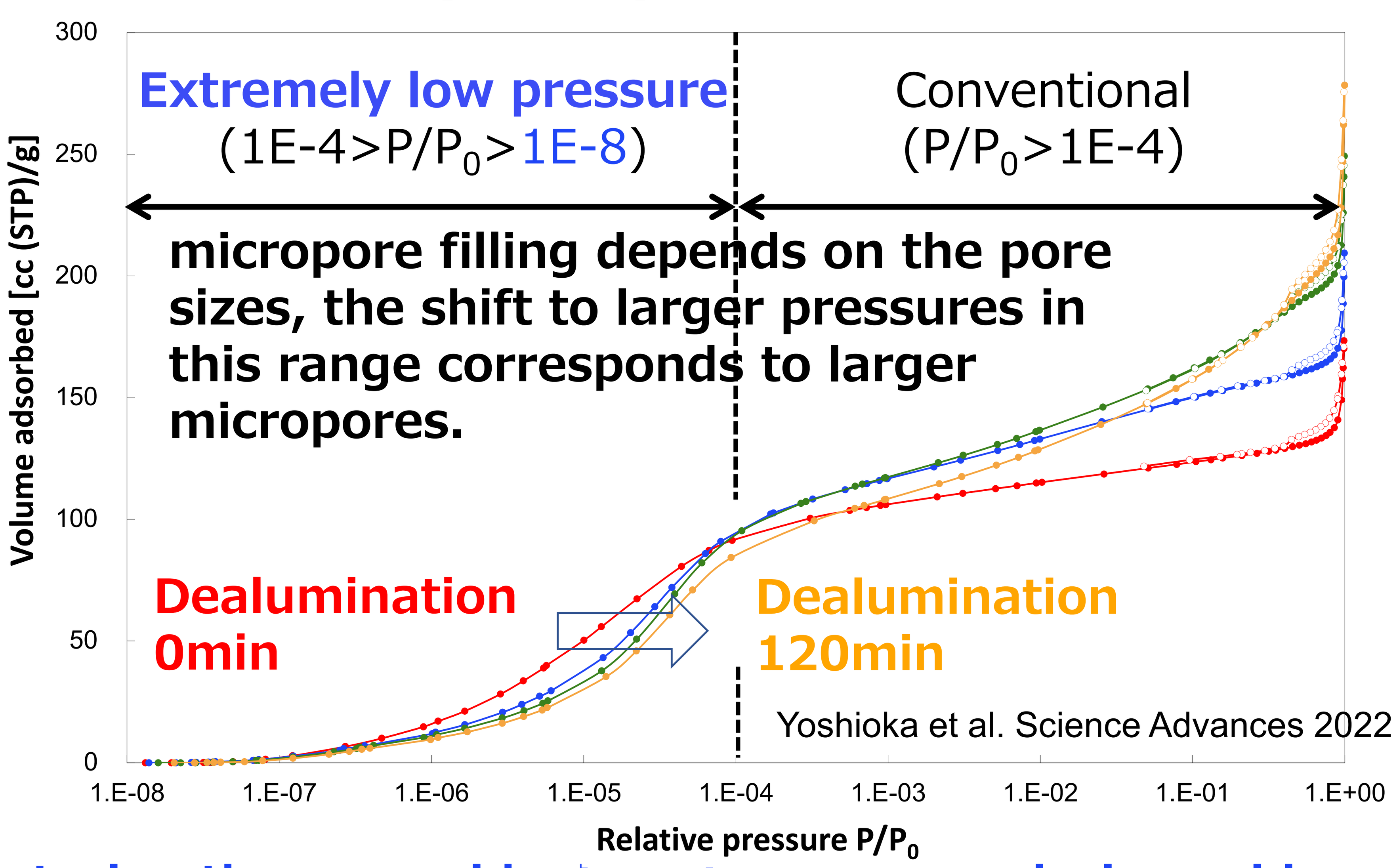


Commercially available zeolite (V_{acc} 3kV, Magnification x300k, EDS time 590s)

Able to visualize Al zoning inside zeolite structure within a resolution of ca. 10nm.

Expected to apply in a deterioration mechanism for zeolites loaded with active species.

●Ar Gas Physisorption for de-Al Zeolite



Capturing the pore widening phenomenon during acid treatment→Key factor to tune zeolites with higher stability.

<Research outline (AIST)>

Zeolite catalysts prepared in this project were evaluated by argon physisorption measurement for extremely low relative pressure region (10^{-8}) and high-resolution scanning electron microscopy. Effect of zeolitic framework structure and composition on hydrothermal stability, state of active species, and dealumination behavior for post-treated zeolites were investigated by surface and cross-sectional (prepared by ion-milling method) observations and pore structure evaluation. Moreover, elemental analysis on cross-sectional surface of zeolite was performed by energy dispersive X-ray spectroscopy, and the correlation between pore structure and aluminum distribution observed inside zeolite particles was investigated.

No. A-10-4E

Project: Development of Recovery and Removal Techniques of Dilute Reactive Nitrogen to Realize Nitrogen Circulating Society
Theme: Development of a method for analyzing the chemical composition distribution in zeolites and their precursor gels

Organization: Japan Fine Ceramics Center
Contact: Yukichi Sasaki (e-mail: sasaki@jfcc.or.jp)

- **We developed a method for analyzing chemical composition distributions (mapping) in zeolites and precursor gels with a spatial resolution of less than 10 nm using STEM-EDS.**

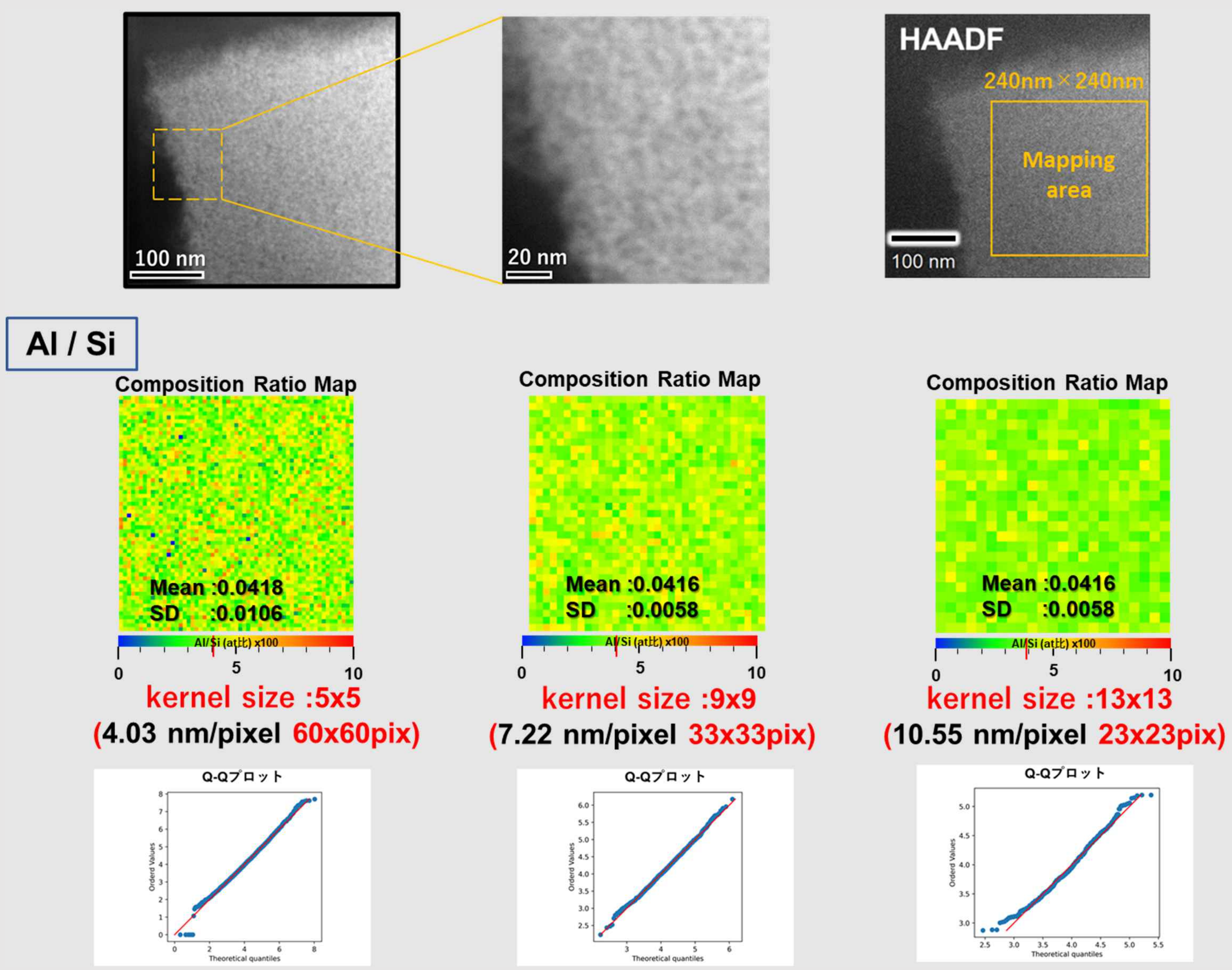
Composition distribution (uniformity) in gels

- ⇨ Affects homogeneity of zeolite nucleation
- ⇨ Influences zeolite crystal size

Composition distribution in zeolite crystals

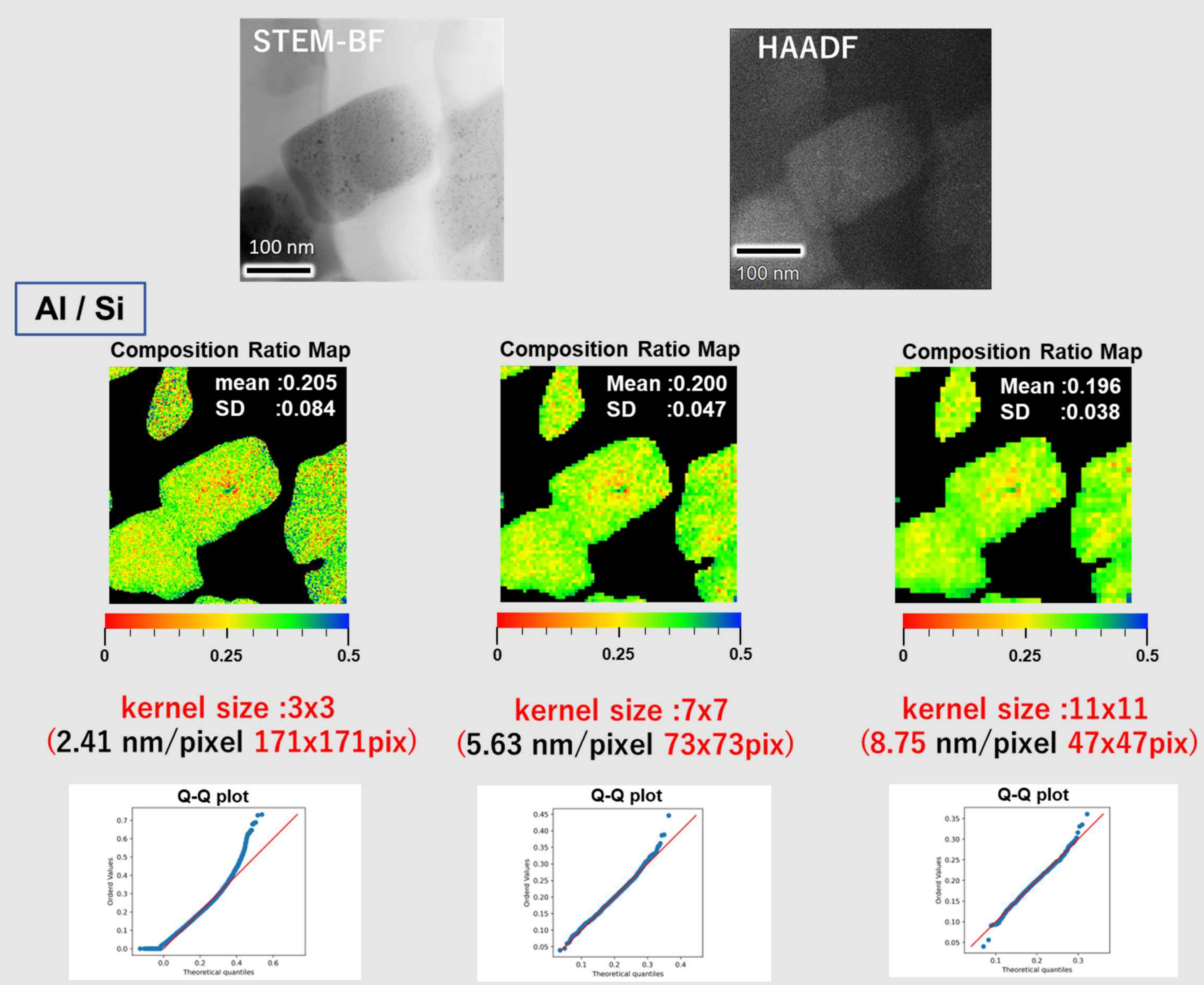
- ⇨ Important for controlling catalytic activity
- ⇨ Also affects catalyst durability

Analysis of a zeolite precursor gel



Steps:
① Confine measurement results to each 0.8×0.8 nm² region to minimize the influence of measurement errors
② Evaluate normality (Q-Q plots) to determine reliability

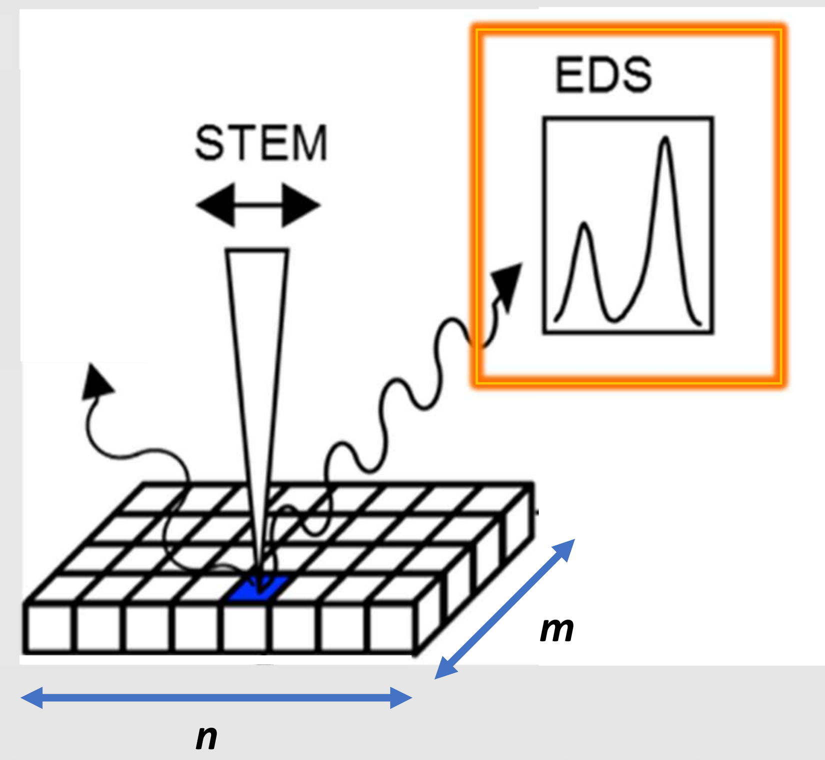
Copper Ion-exchanged Zeolites



- Al concentration gradient from the crystal center (high Al concentration) to the edges (low Al concentration)

STEM-EDS (Hypermapping Method)

JEM-F200

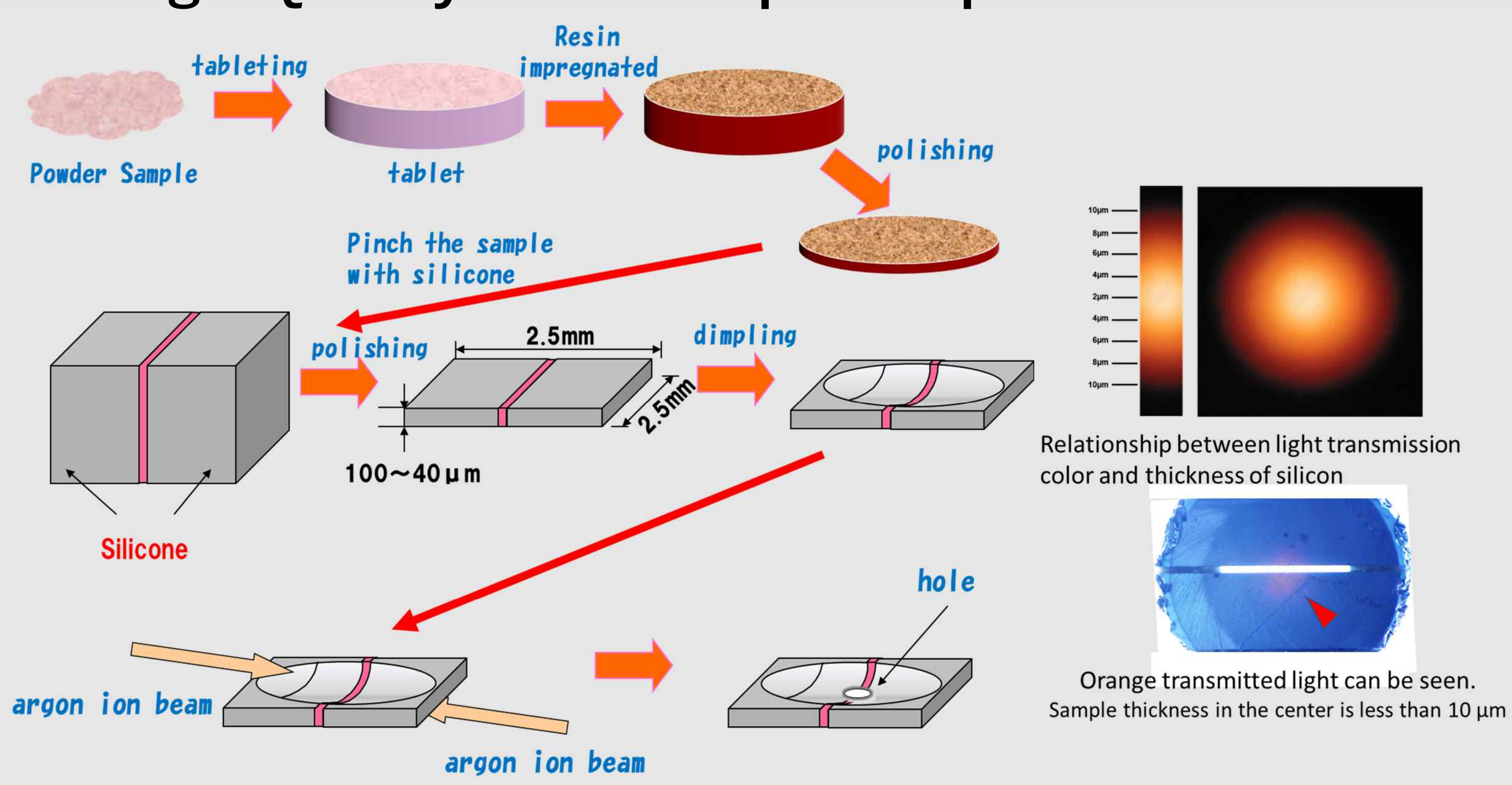


The measurement area is divided into *n* x *m* pixels and quantitative composition analysis performed on each pixel

We determined optimum conditions for quantitative analysis of zeolites and their analogs sensitive to electron irradiation (where pixel size = 0.8 nm)

We developed a calibration method for taking quantitative measurements in combination with SEM-EDS analysis

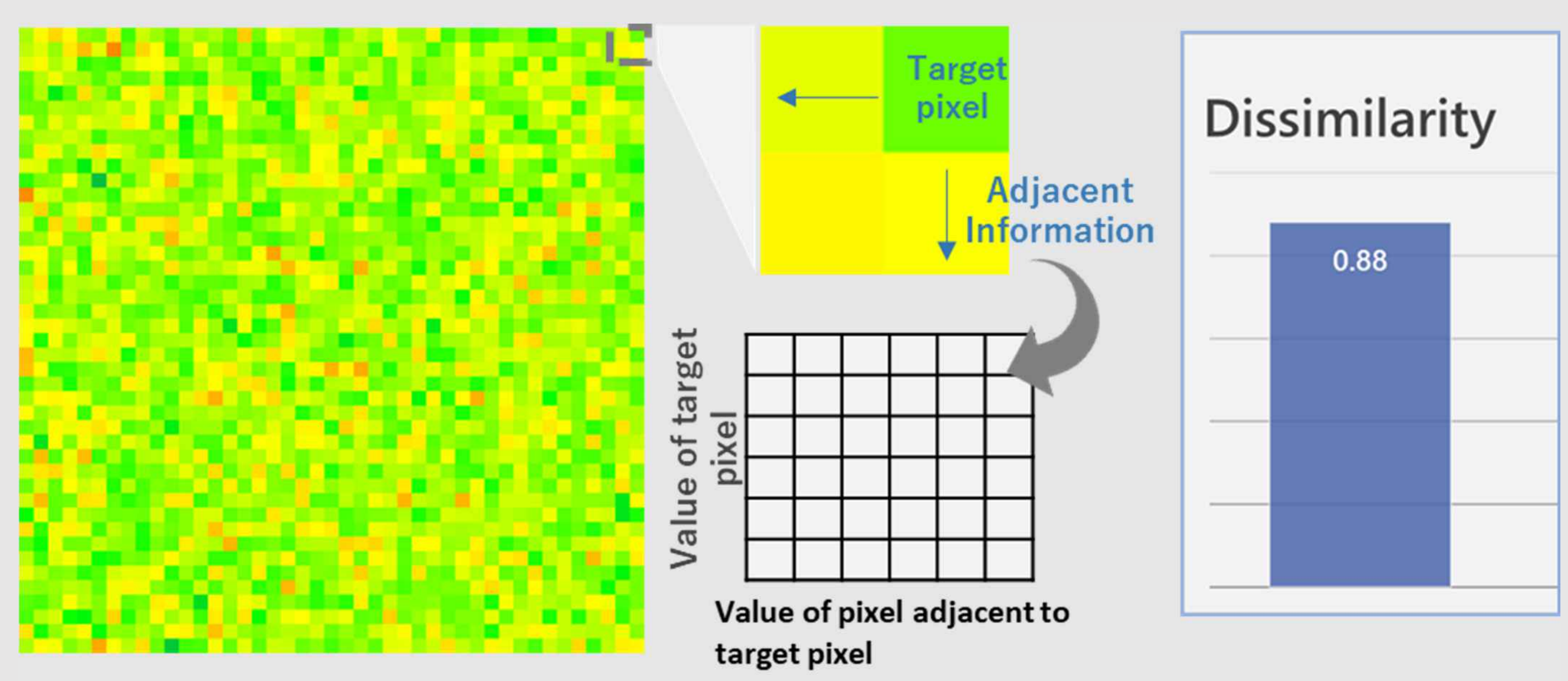
High-Quality TEM Sample Preparation Method



By determining the endpoint from the color of silicon transmission, dimple polishing down to a thickness of 10 μm or less can be achieved. This allows high-quality TEM specimens to be prepared with good reproducibility

Summary

- We determined conditions for quantitative evaluation of Ai/Si ratios of zeolite precursors (aluminosilicate gels) and Cu ion-exchanged zeolites with a spatial resolution of 5-8 nm
- The sample uniformity was evaluated in terms of normality (Q-Q plot), and the results presented as a probability density function.
- (=> We found that there is a compositional gradient within zeolite crystals of sub-μm size.)
- Furthermore, it is possible to quantify the spatial variation in the uniformity (standard deviation) of the sample by texture analysis (see figure below).



Texture Analysis Using the Gray-Level Co-Occurrence Matrix (GLCM)

Converts the value of a target pixel and its surrounding information into a matrix to quantify the "texture" of the image.

No. A-10-5E

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

Theme: Development and mass production of new zeolite catalysts for reduced N_2O emissions.

Organization: Mitsubishi Chemical Corporation

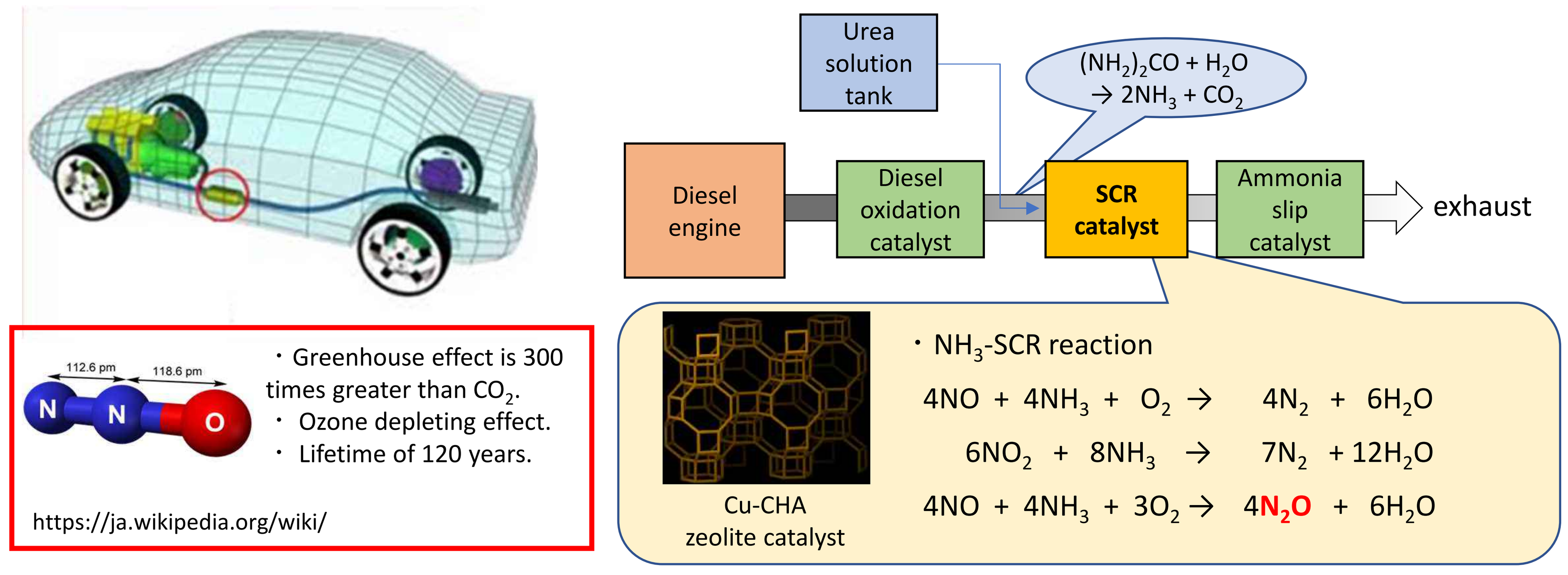
Contact: takewaki.takahiko.mb@m-chemical.co.jp

Outline

2021–2022	2023–2024	2025–2026	2027–2029
①Low-N_2O NH_3-SCR catalyst development・mass production	②Feasibility study of NH_3-free (direct denitration) catalyst	③NH_3-free + low N_2O compatibility Feasibility check, mass production	④ NH_3-free + low N_2O compatibility Feasibility check, mass production

Development Items & Contents	・Further advancement of NOx removal process from internal combustion engines. ・Search and refinement of candidate zeolites for new exhaust gas catalysts. ・Mass production of new zeolite catalysts. ・Pilot demonstration of NOx purification catalyst.
Final Target (FY2029)	To develop innovative new materials for exhaust gas purification catalysts that do not use NH_3 and precious metals, which enable operation under combustion conditions (lean burn engines, etc.) that significantly improve the fuel efficiency of internal combustion engines and drastically reduce CO_2 emissions.
Fiscal Year 2022 Target	・To develop a new exhaust gas catalyst with high durability and low N_2O emission in NH_3-SCR at laboratory level. (New NH_3-SCR catalyst with durability at 800ºC and N_2O emissions half that of the current exhaust gas catalyst (Cu-CHA))
Current Main Results	・The new zeolite catalyst showed better NOx decomposition performance than the current catalyst (Cu-CHA) in the NH_3-SCR reaction before and after the endurance test at 800ºC. ・The N_2O emissions were also successfully reduced by 70-75% compared to the current catalyst both before and after the endurance test. ・The 100 L scale sample was confirmed to have the same catalytic performance as the lab product.

Problems with current SCR catalyst (Cu-CHA).

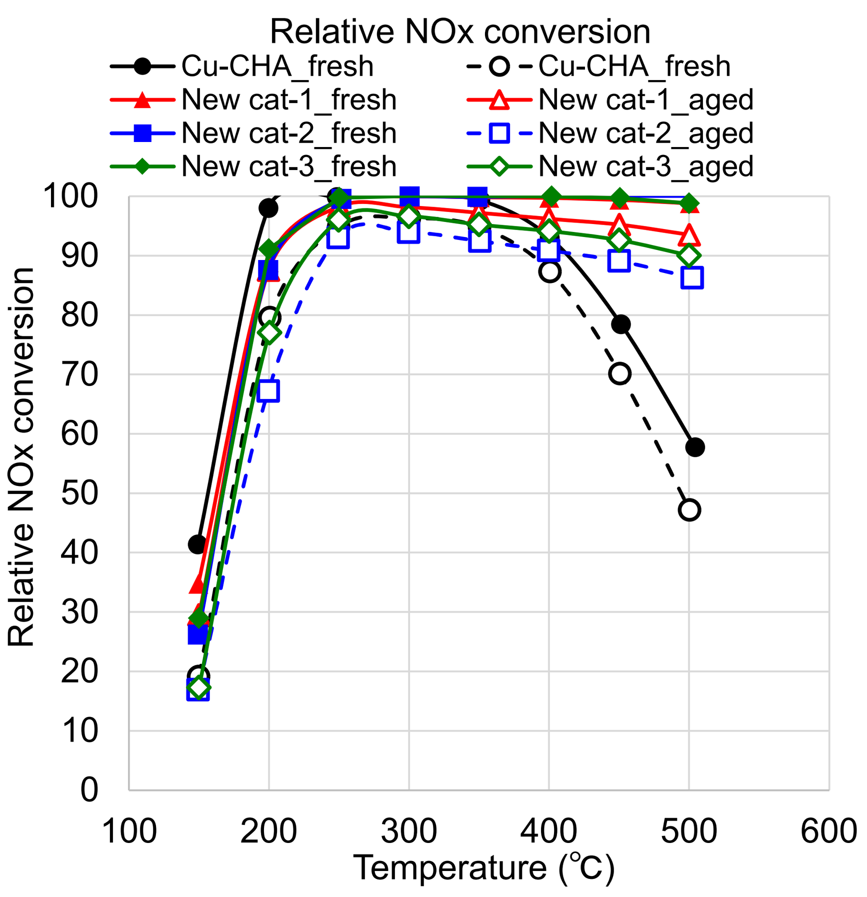


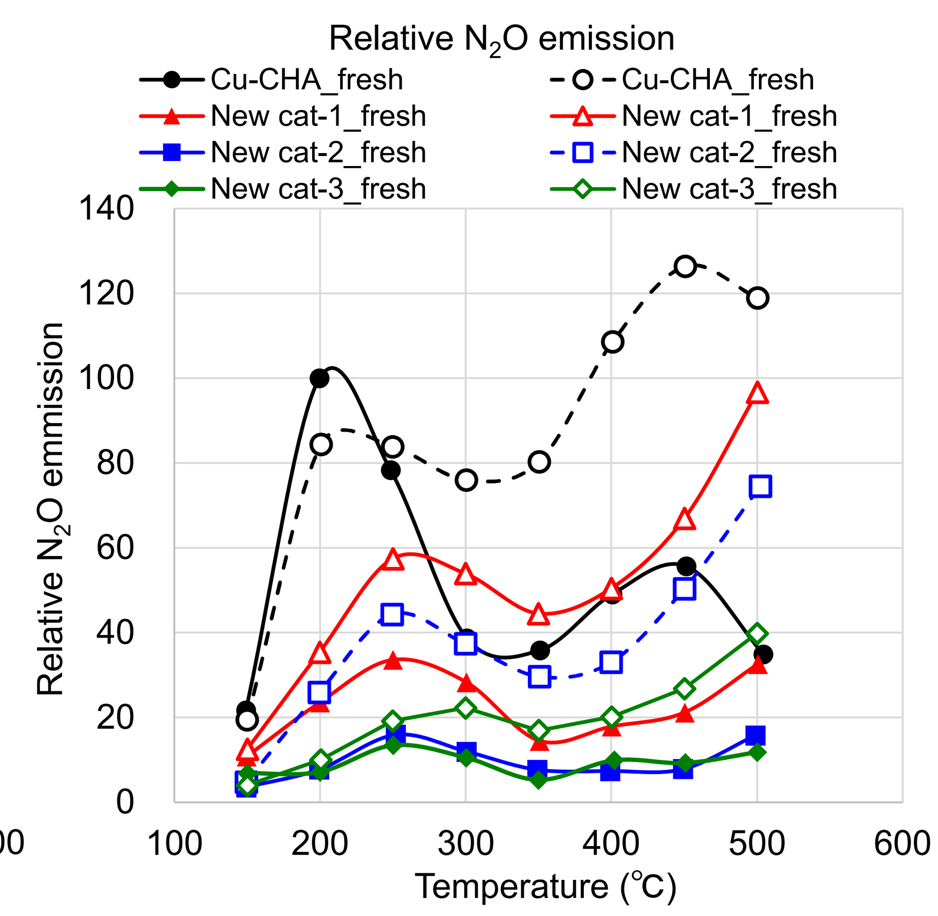
・The NH_3-SCR reaction using Cu-CHA catalyst is mainly used in NOx purification systems for diesel engines.
・Conventional Cu-CHA is known to have high NOx purification and durability performance, but 2-5% is emitted as N_2O.

・This project aims to develop and mass produce a new zeolite catalyst with NOx purification performance and water vapor durability equivalent or superior to Cu-CHA, and with less than half the N_2O emissions.

Comparison of NOx purification performance and N_2O emissions between conventional (Cu-CHA) and new catalyst.

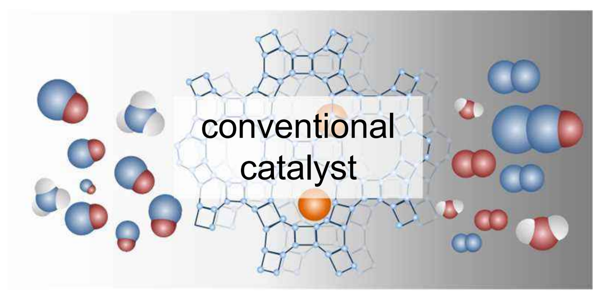
Aging condition：H_2O-10vol%、800ºC 、5h、SV = 3000 h^{-1}
Reaction condition :SV = 200000 h^{-1}, input NOx = 350 ppm, NH_3 = 385 ppm, O_2 = 14 vol%, H_2O = 5 vol%、Catalyst pellet size : 600~1000 μm

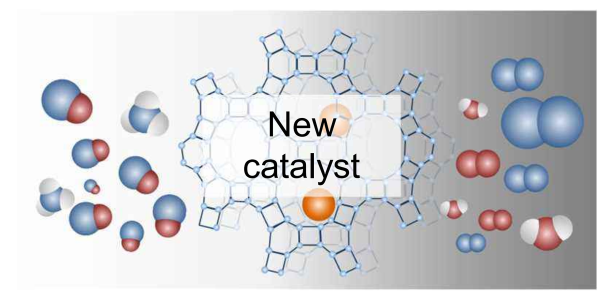


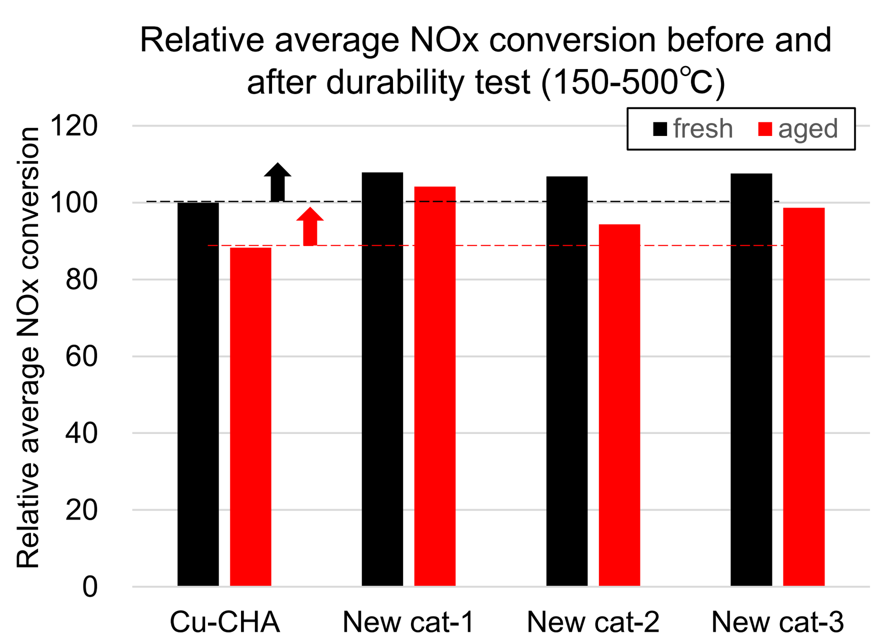


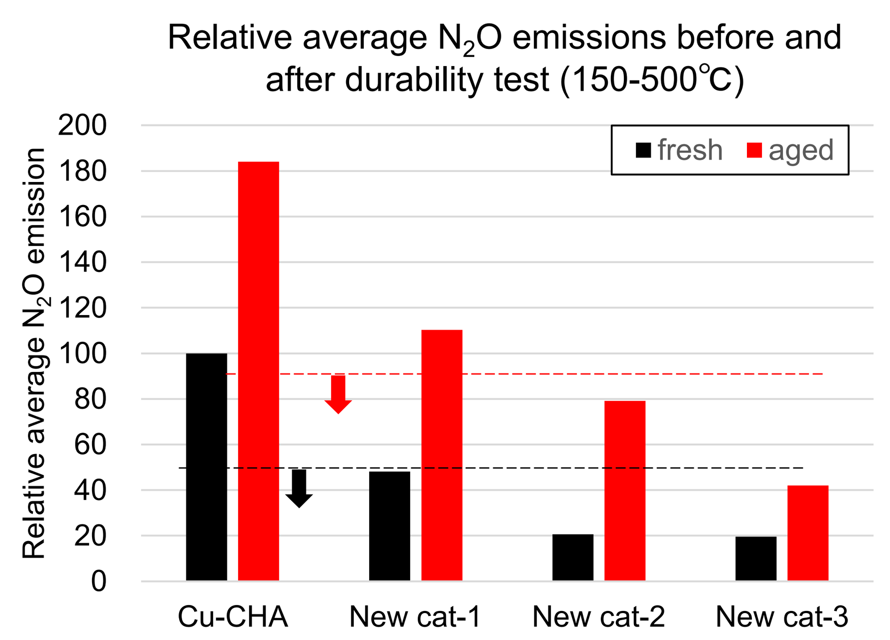
・The new zeolite catalyst had higher NOx purification performance and lower N_2O emissions in all samples before and after steam treatment.

Comparison of average NOx purification performance and N_2O emissions between conventional (Cu-CHA) and new catalyst.



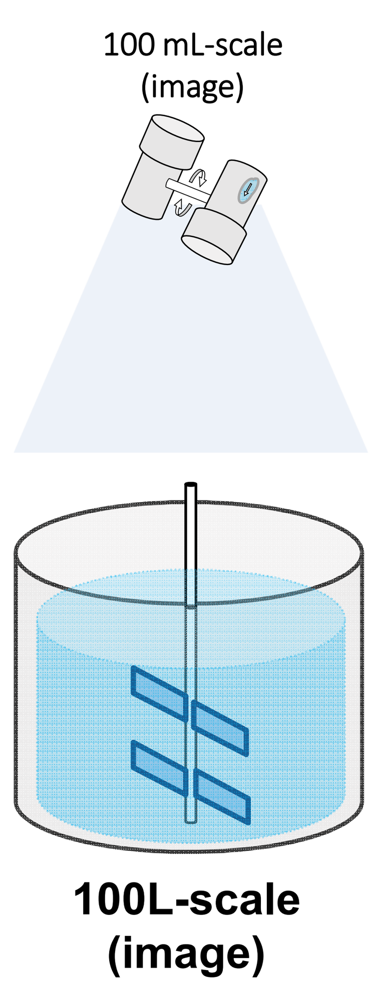


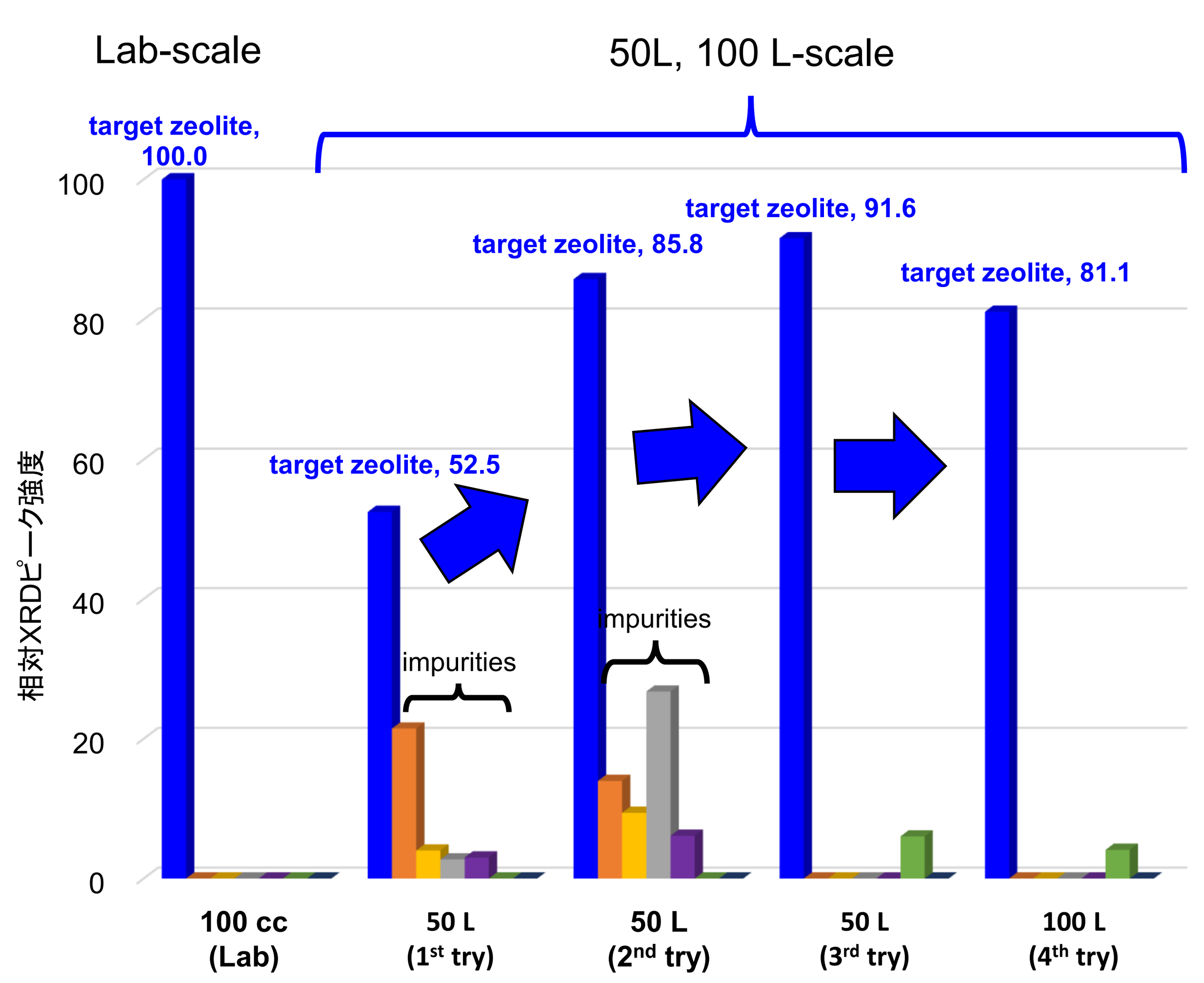




・The new zeolite catalyst showed better NOx decomposition performance in the NH_3-SCR reaction than the conventional catalyst (Cu-CHA) before and after the endurance test at 800ºC. The N_2O emissions were also successfully reduced by 70-75% (compared to the target of 50%) from Cu-CHA both before and after the endurance test.

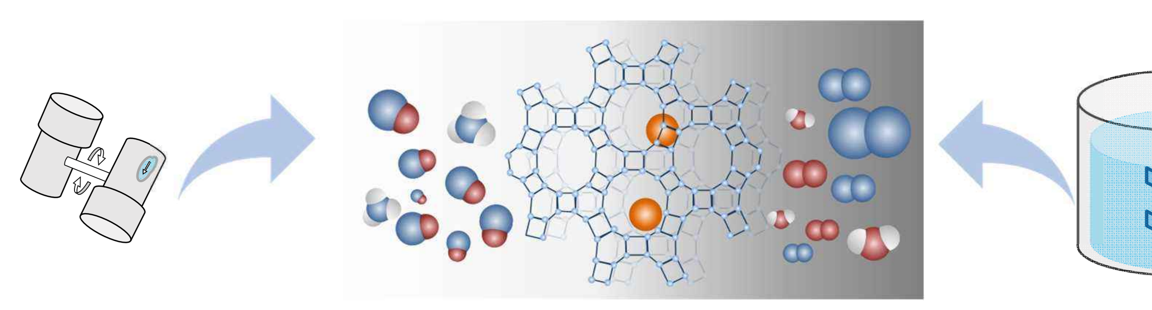
Scale-up synthesis of new zeolite catalysts.

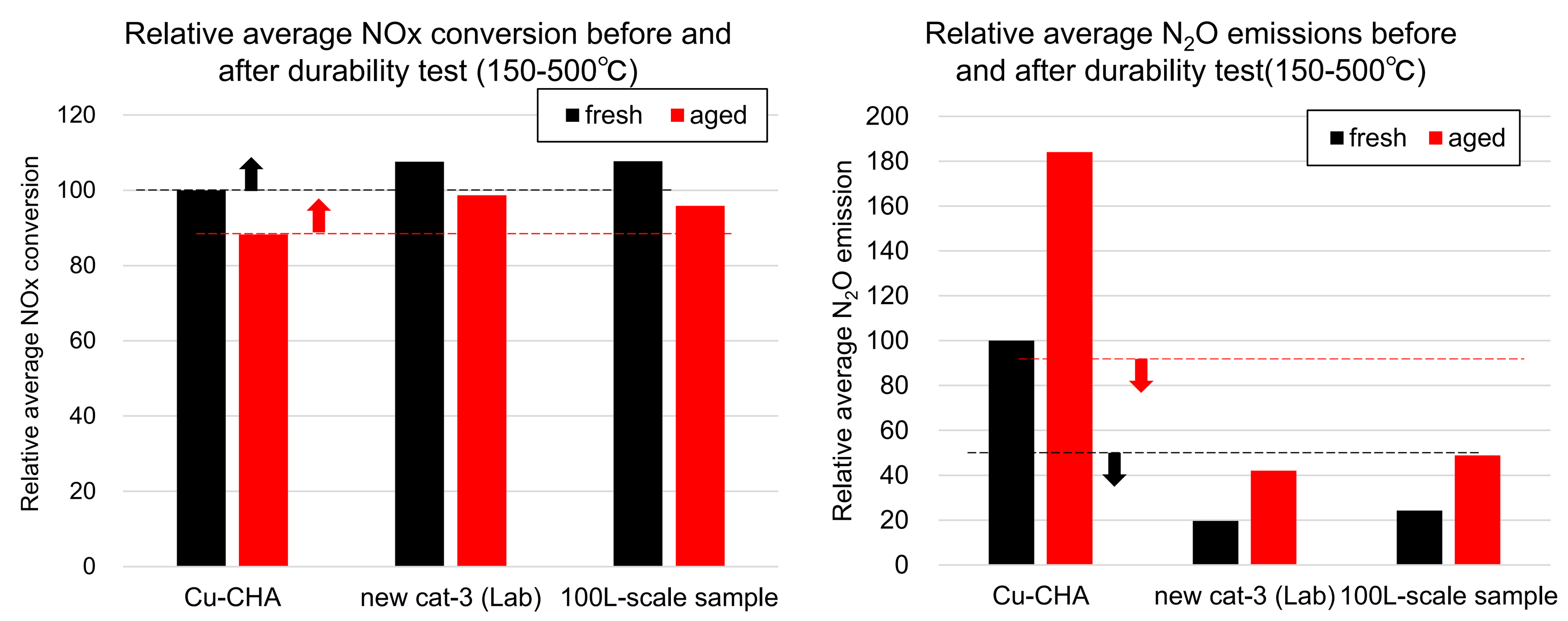




・Succeeded in reducing impurities in 50L and 100L scale prototypes.
・Trial production of mass production scale ($2m^3$) is planned in the future.

Performance evaluation results of scale-up synthetic products.





・The 100 L scale sample was also confirmed to exceed the target performance.

Summary

・The goal is to develop and mass produce a new zeolite catalyst with less than half the N_2O emissions of the conventional catalyst (Cu-CHA) in the NH_3-SCR reaction.
・The new zeolite catalyst showed better NOx decomposition performance than the Cu-CHA before and after the endurance test at 800℃. The N_2O emissions were also successfully reduced by 70-75% from the current catalyst both before and after the endurance test.
・The catalyst was also able to reduce N_2O emissions by 70-75% compared to the current catalyst both before and after the endurance test.

Future plans

・ Mass production scale ($2m^3$) trial production of a new zeolite catalyst.
・ Development and mass production of catalysts that do not use NH_3 (direct denitration).