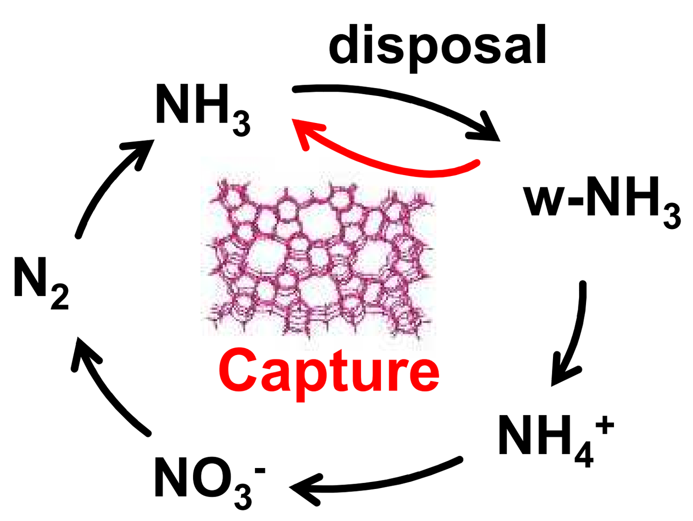
No. A-14-1E
PJ : Development of Recovery and Removal Techniques of Dilute Reactive Nitrogen to Realize Nitrogen Circulating Society
Theme: Synthesis of excellent NH_3 capture materials

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

Project Overview

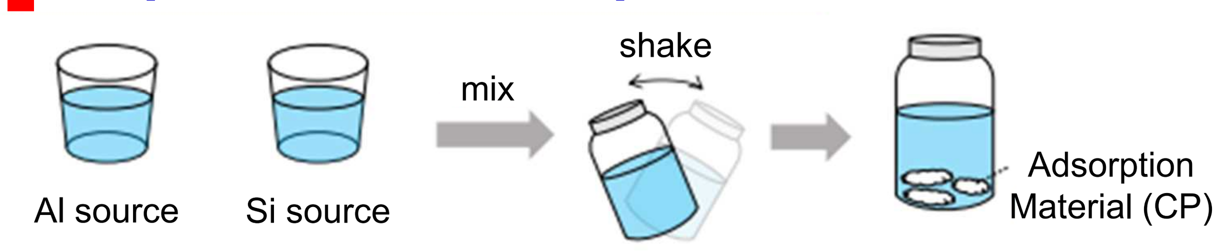


Industrial Wastewater (w-NH_3)

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

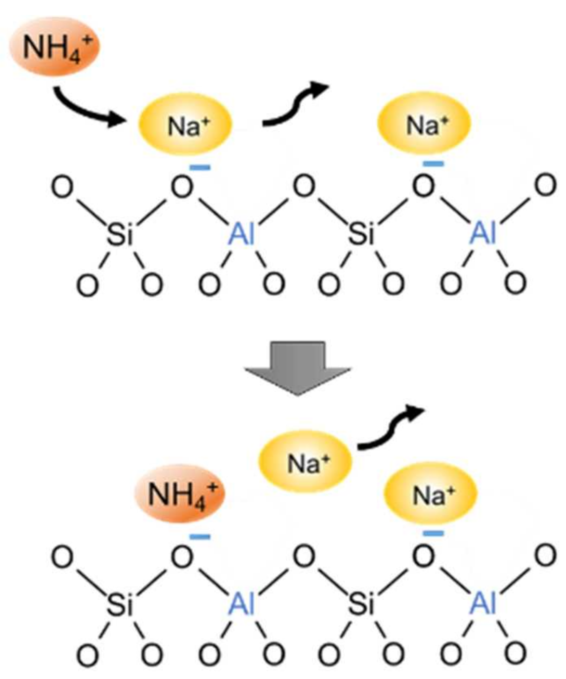
- Although the transition to electric vehicles has been proposed for the realization of a carbon-neutral society, in Europe, reluctant to fully transition to electric vehicles.
- Considering the introduction of e-fuel, an internal combustion engine (especially for truck transportation) is essential.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

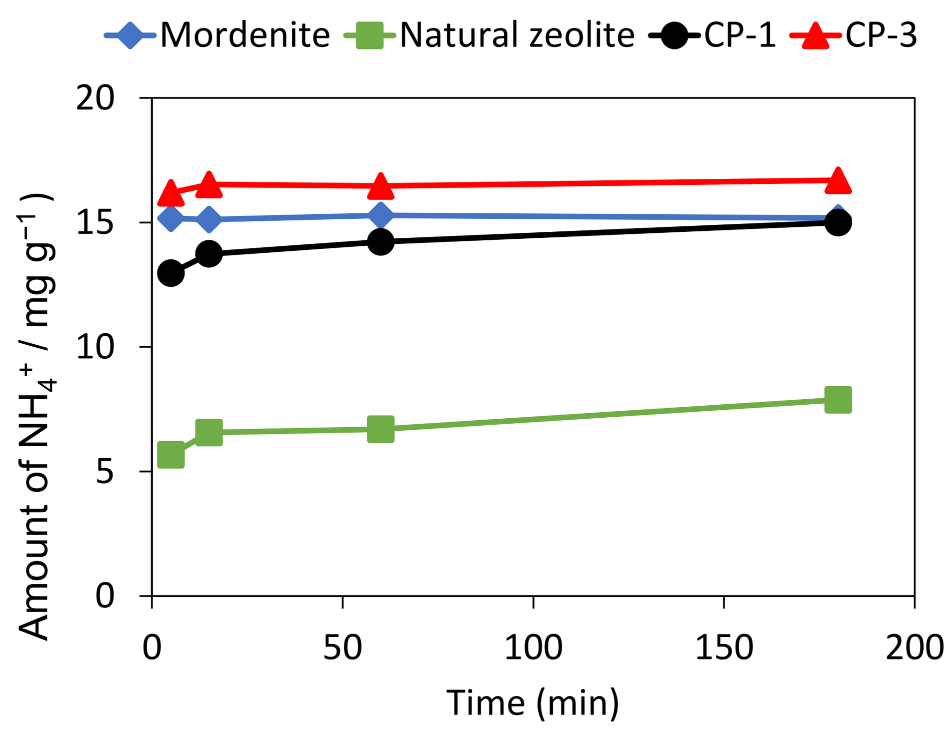
Preparation of amorphous aluminosilicate



- Facile
- Low Cost
- Fast Synthesis

NH_3 capture by ion exchange





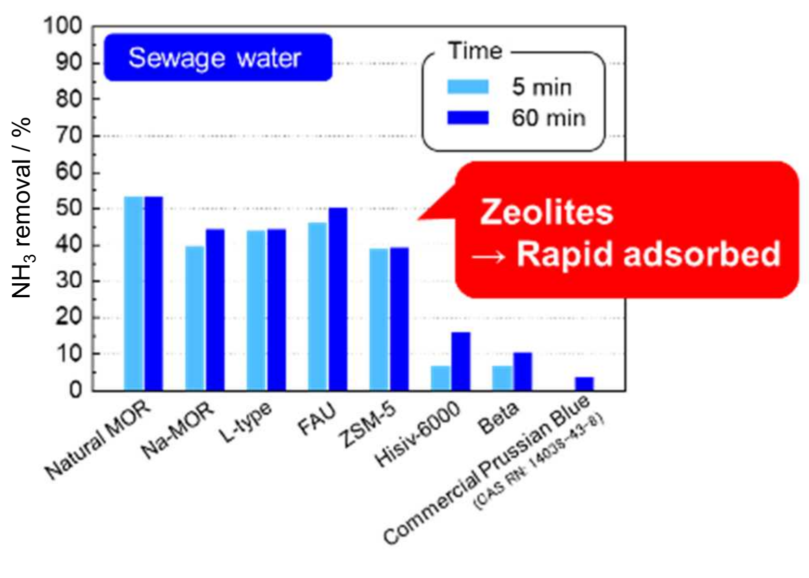
- Fast ammonium uptake

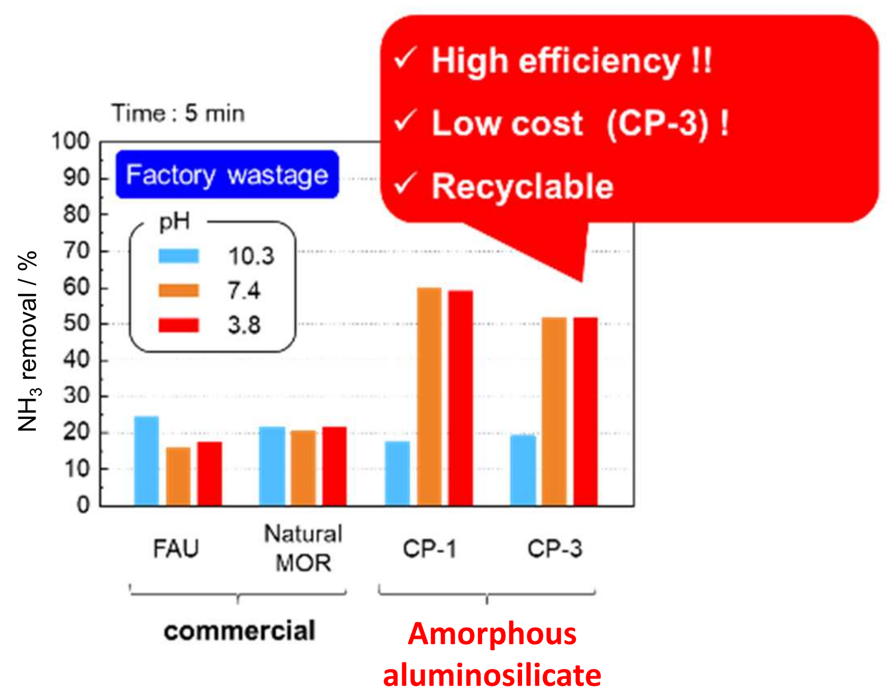
Comparison of Performance

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

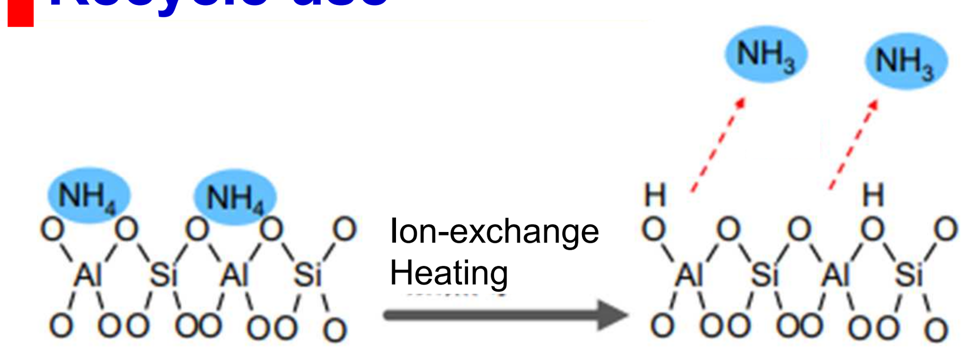
NH_3 removal efficiency

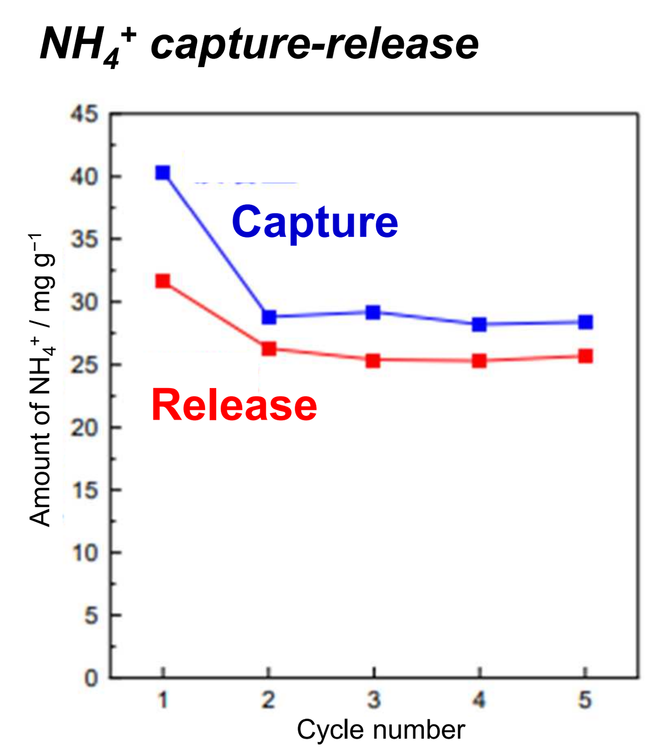




- Achieved high NH_3 removal (> 50%) from industrial wastewater

Recycle use

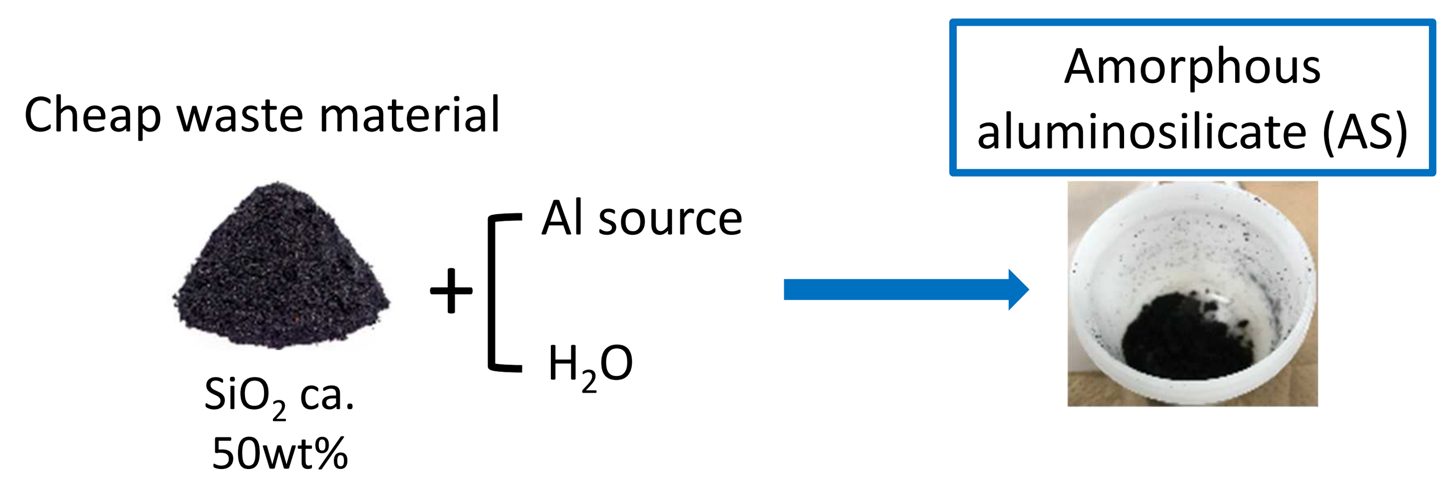




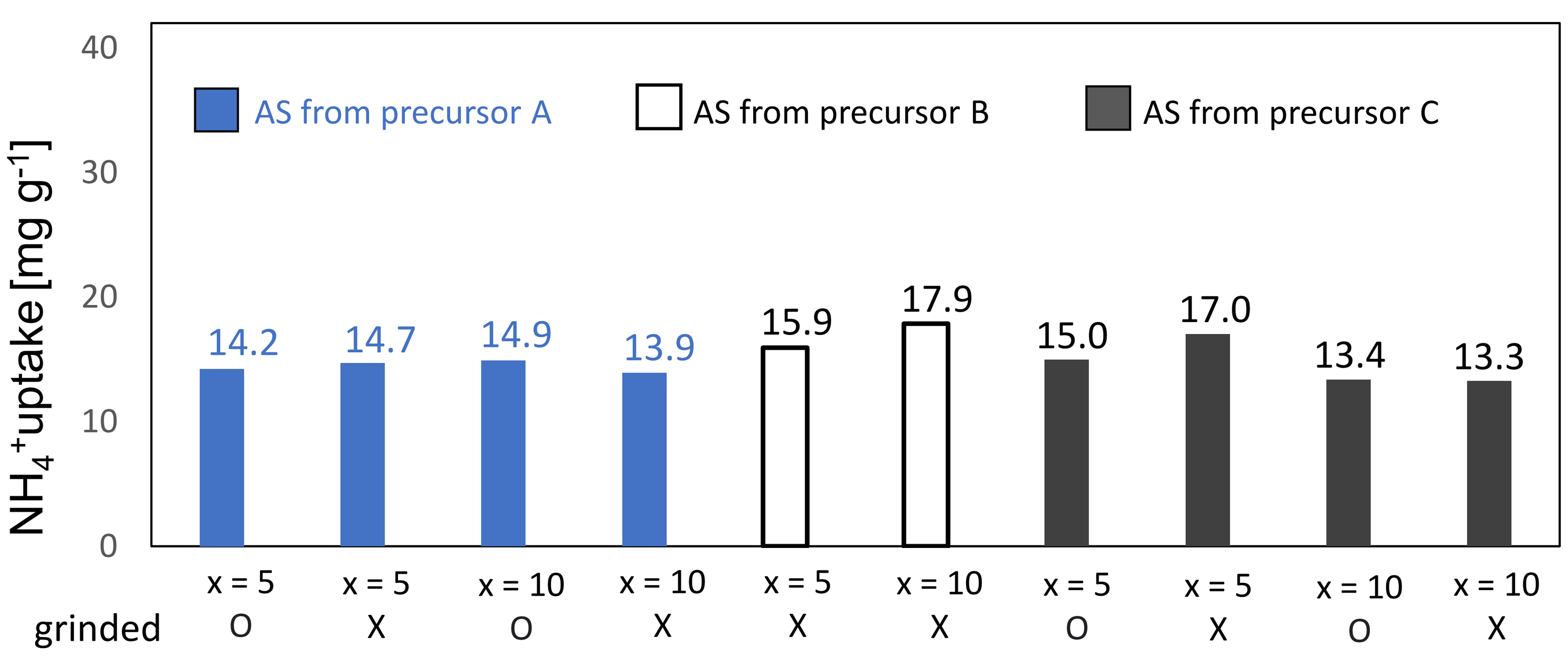
- High NH_4^+ capture (> 25%)
- Recyclable (keep potential)

Amorphous aluminosilicates from alternative sources

SiO_2 obtained from cheap waste materials



Si/Al = 3 , H_2O/SiO_2 = x



- Amorphous aluminosilicate can be prepared from cheap waste materials
- All the products show similar ammonium uptake

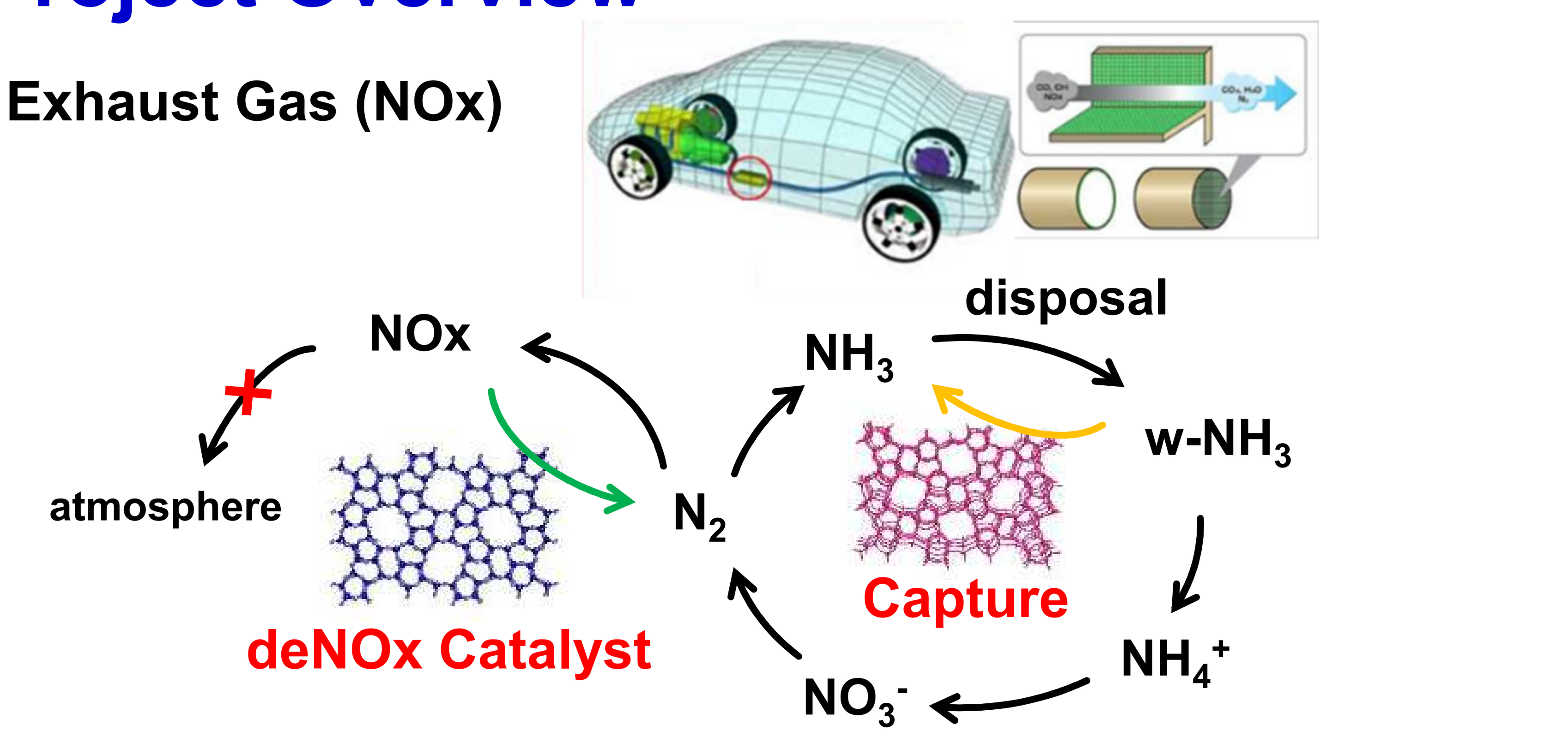
No. A-14-2E

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

Theme: Excellent deNOx materials and processes

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

Project Overview



To create a nitrogen recycling society, development of high-performance denitrification technology is an urgent issue.

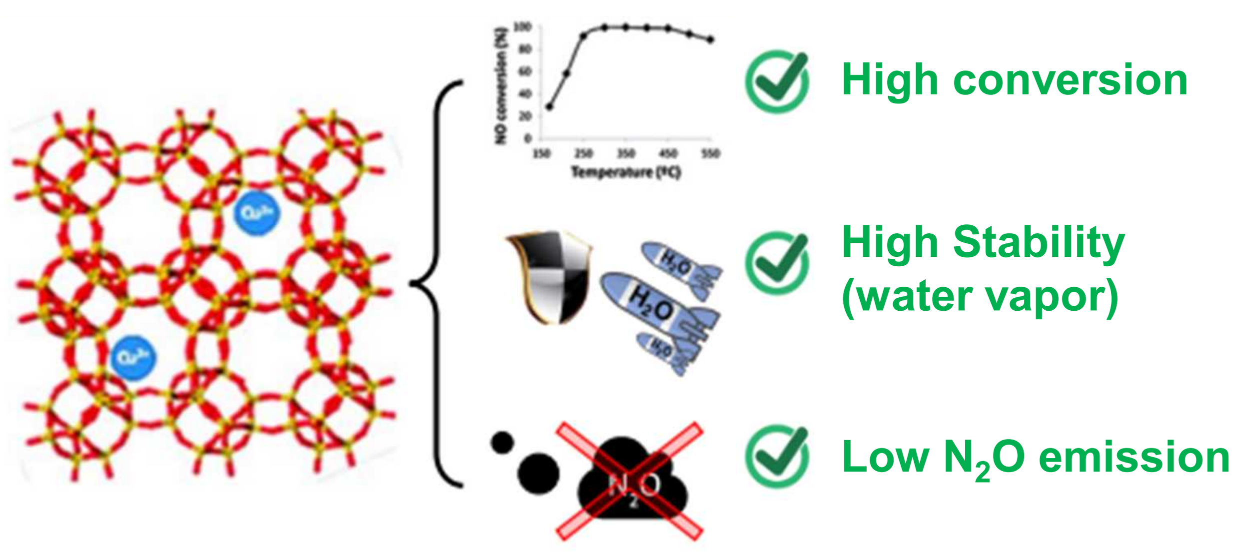
- Although the transition to electric vehicles (EVs) has been proposed to realize a carbon-neutral society, European countries are reluctant to fully adopt EVs.
- Considering the introduction of e-fuel, an internal combustion engine (especially for truck transportation) is still essential.
- Truck-mounted catalyst does not need to be replaced even after running 1 million km. → Cost reduction, wage increase, etc. are expected.
- Cost can be reduced without the usage of reductant NH_3.

Final Aim

- Pilot scale test using zeolite for high-durability NOx purification
- Demonstration of NOx purification without NH_3

deNOx Catalyst for NH_3-SCR

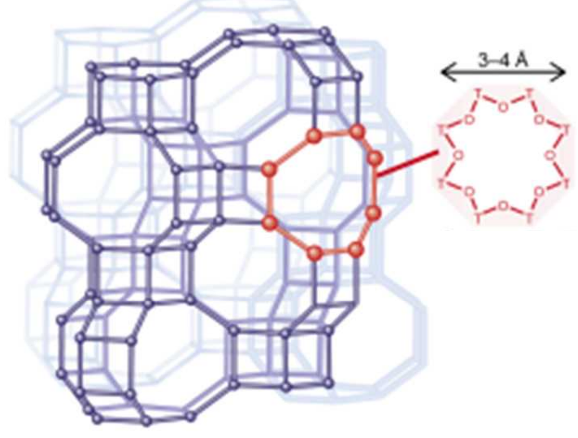
Desired properties for zeolite catalyst



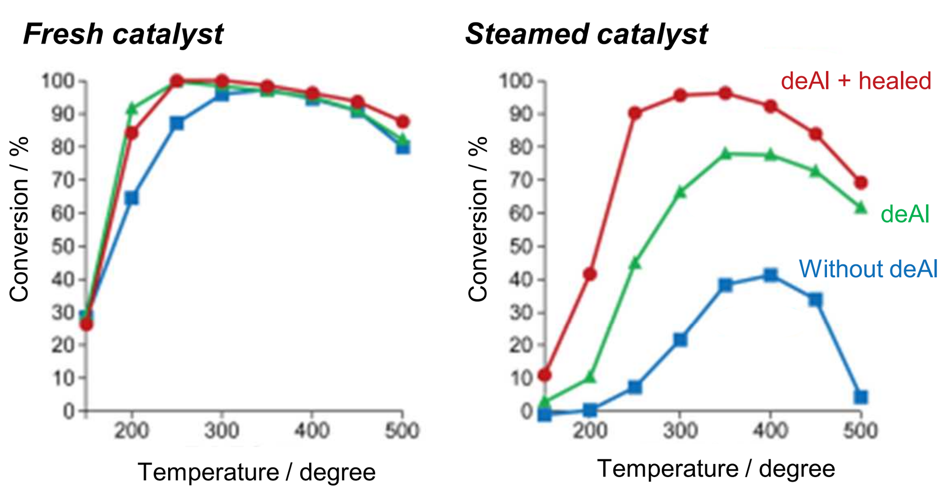
Broken catalyst in NH_3-SCR (by urea water)

Novel method for dealumination (de-Al) of zeolite

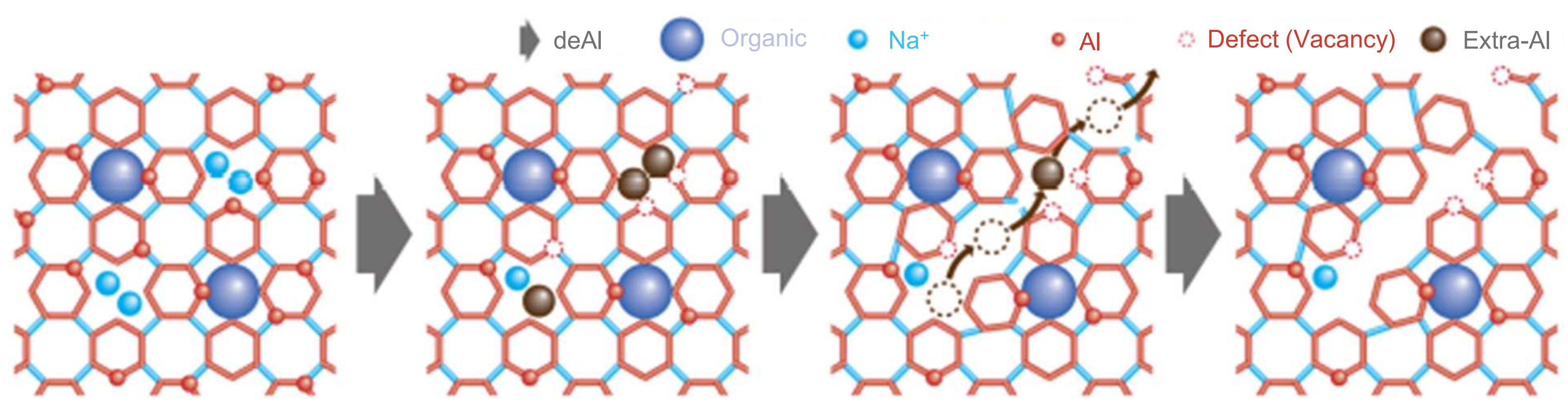
Small Pore Zeolite



NH_3-SCR

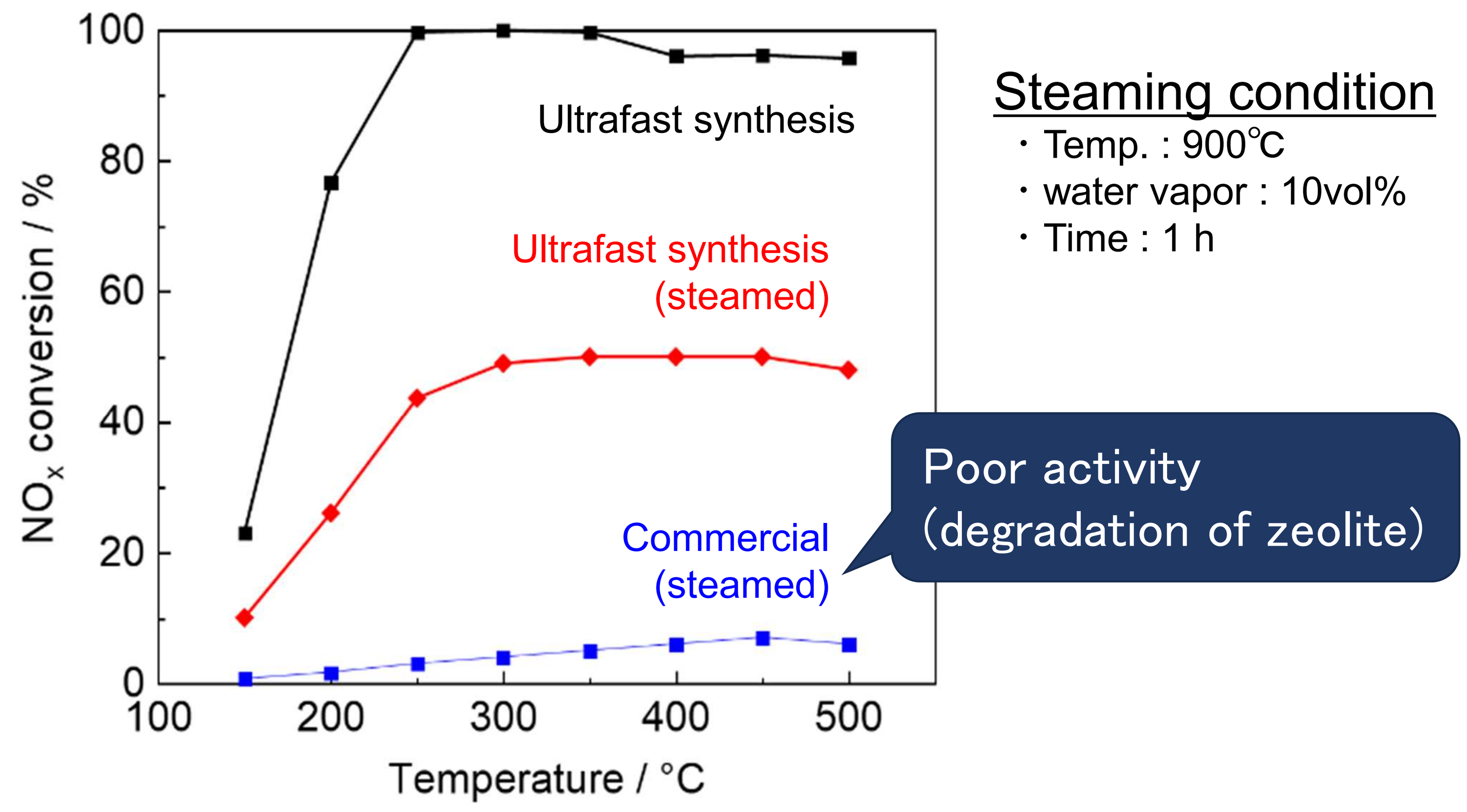


Scheme for deAl in Small Pore Zeolite



NH_3-SCR

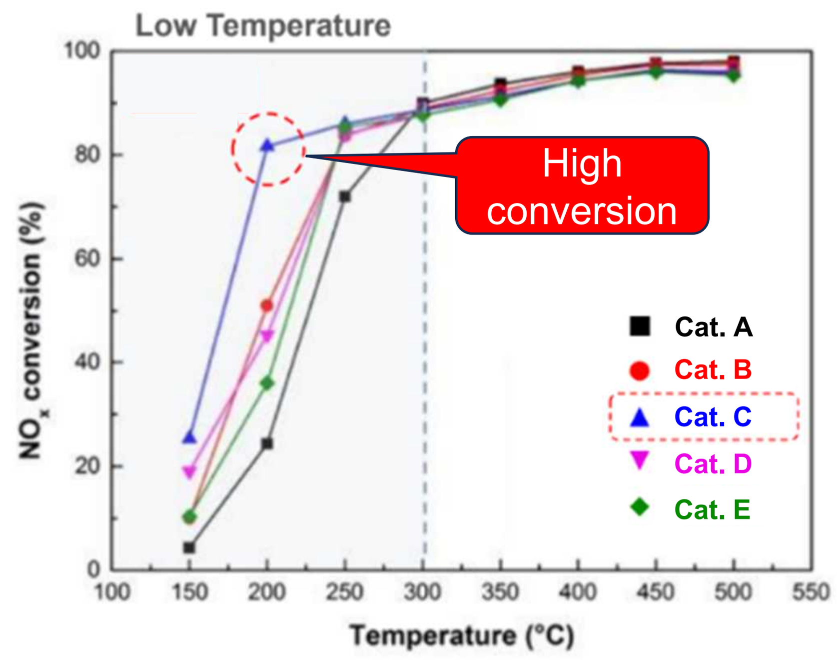
NO 300 ppm, NH_3 300 ppm, 5% O_2 Flow rate 100 cm^3/min



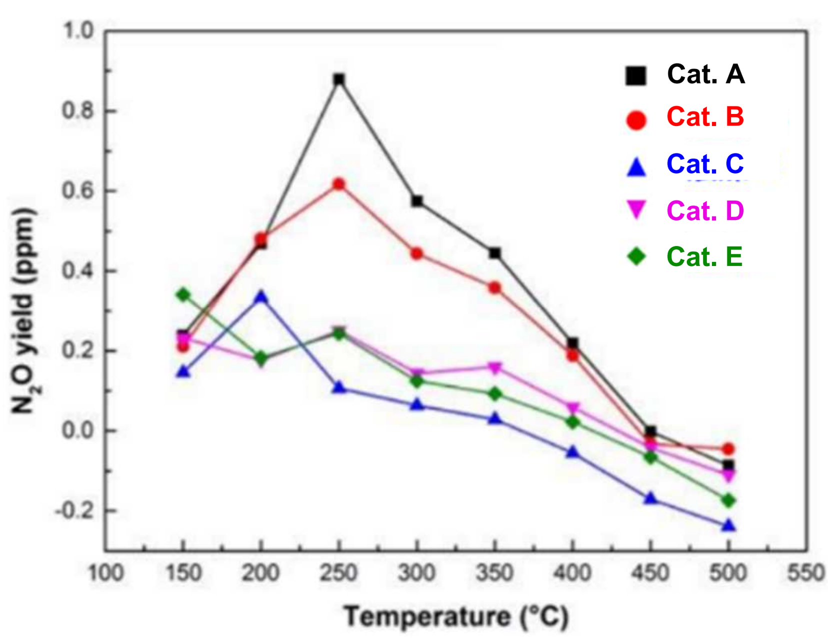
Steaming condition
- Temp. : 900°C
- water vapor : 10vol%
- Time : 1 h

Catalyst for NH_3-SCR with low N_2O emission

NOx conversion

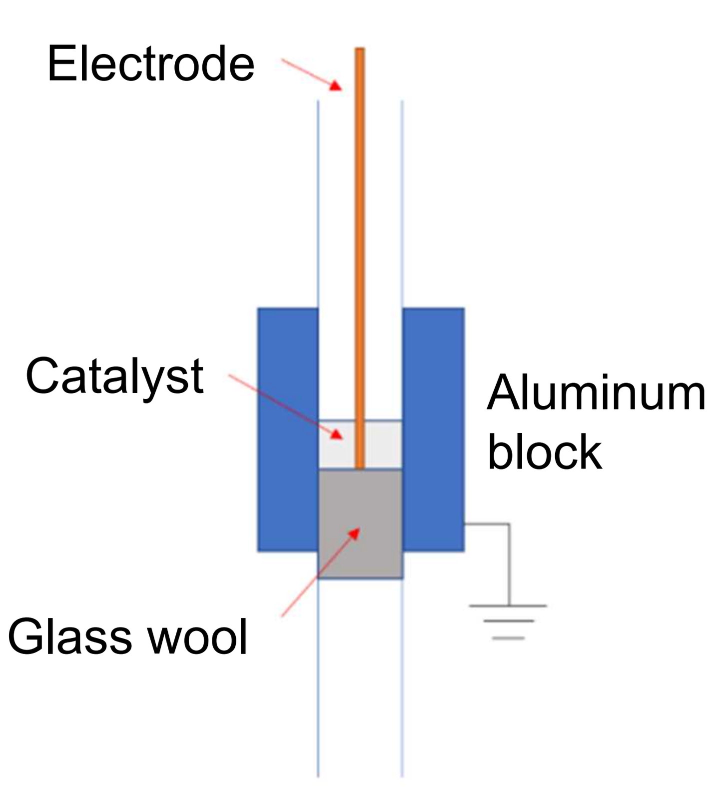


N_2O yield

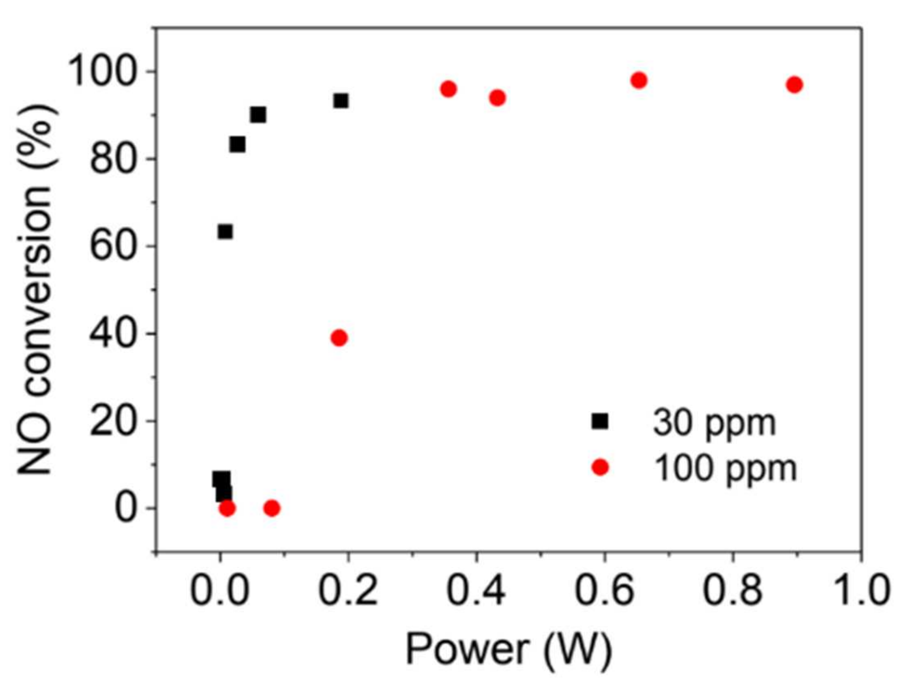


Direct deNOx without using NH_3

deNOx using non-thermal plasma

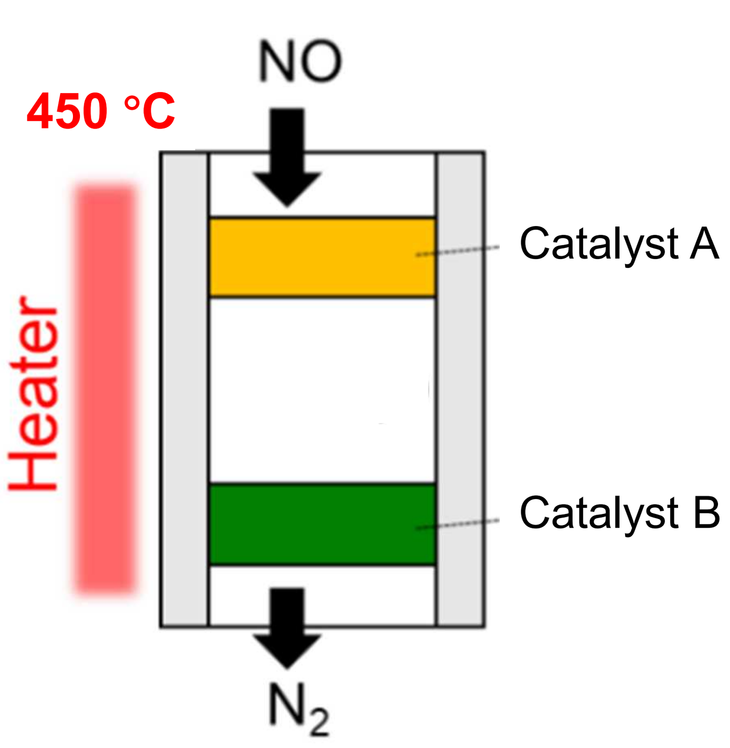


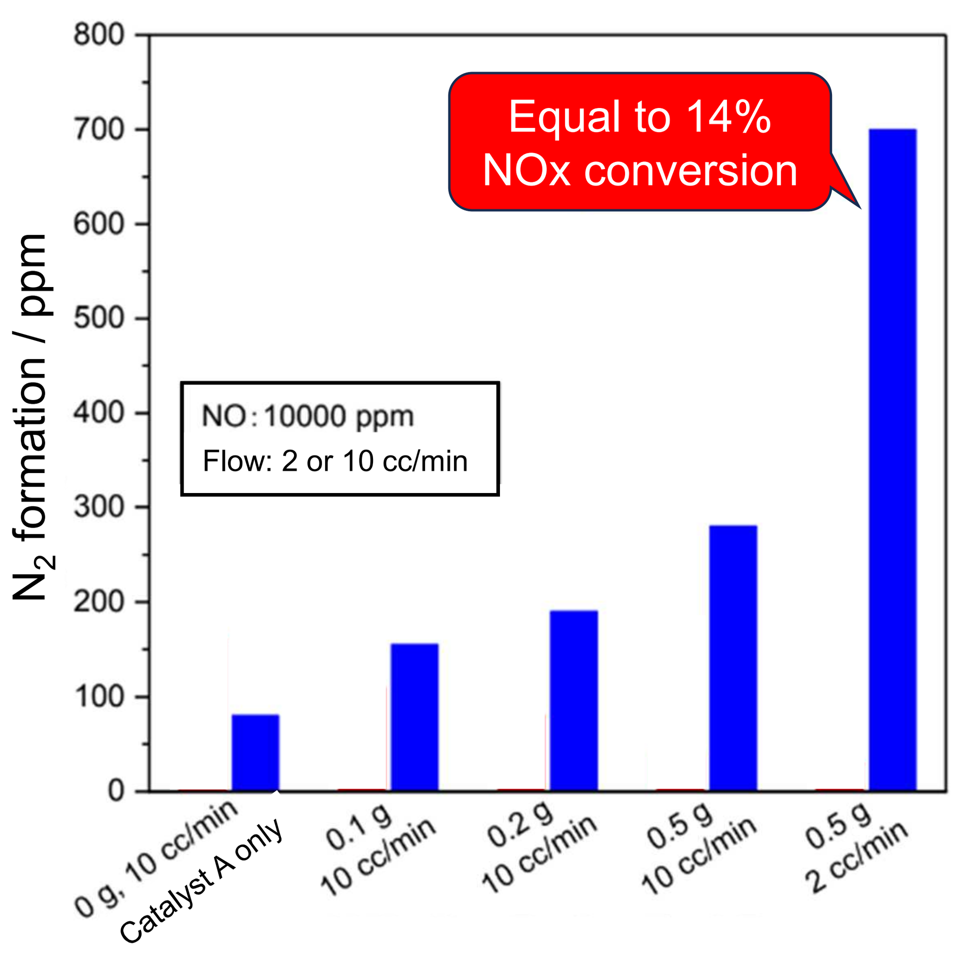
NOx conversion



deNOx using tandem catalysts

deNOx performance





No. A-14-3E

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

Reference zeolite
- Low hydrothermal stability
- Low NOx conversion rate
- Produces N_2O

②Post treatments

Controlling chemical composition, defect sites, loading active species

Expected performance : High NOx conversion rate, High hydrothermal stability, Less production of N_2O

Realize high performance zeolite which can realize both NOx reduction and suppression of N_2O

①Synthesis

Controlling framework, chemical composition, Al distribution, crystallization mechanism

③Catalytic performance

Hydrothermal stability test, deterioration mechanism

● Research objectives ~2024FY

1) Pore structural analysis of nanoporous materials

Developing fundamental gas physisorption analysis protocol toward upgrading the performance of nanoporous material-based catalysts. Feedback the obtained analysis results to the synthesis process for producing high performance NOx reduction catalysis.

2) Structural observation of nanoporous materials

Developing fundamental observation protocol for nanoporous material-based catalysts in micrometer scale by using high-resolution semi-in-lens FE-SEM system. With combining the EDS mapping technique to acquire both high resolution images as well as compositional information.

● AIST experimental apparatuses

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

<Porous characterization>
surface area, pore volume, pore size distribution

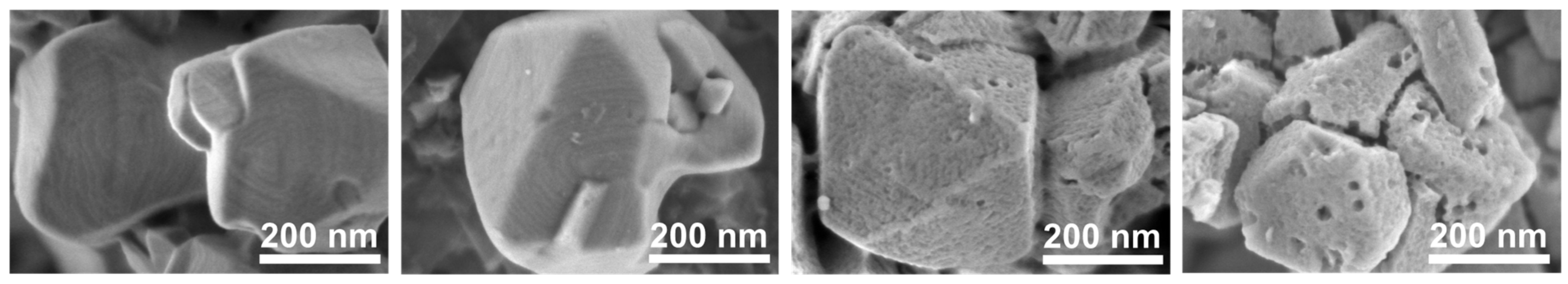
Broad ion-milling (Hitachi IM4000plus)
In operation FY2020

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

Gas physisorption apparatus (Microtrac-Bel Belsorp MAX X)
In operation FY2022

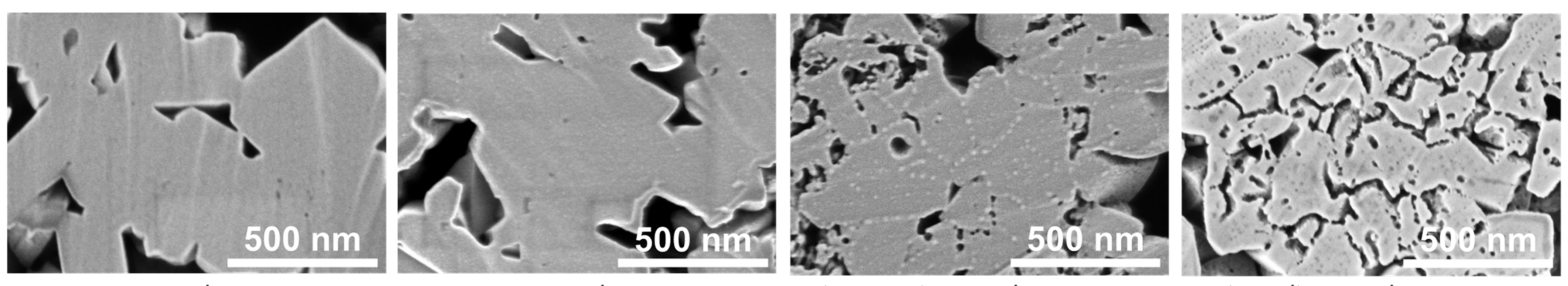
Defect structure evaluation apparatus
→Will be in operation from Jan. 2024

● Top-surface and cross-sectional FE-SEM



Zeolite (parent) (Na-form, Si/Al_{Total} = 2.8) | Zeolite (ion-exchange) (NH_4-form, Si/Al_{Total} = 2.8) | Zeolite (steam) (H-form, Si/Al_{Total} = 2.8) | Zeolite (acid) (H-form, Si/Al_{Total} = 250)

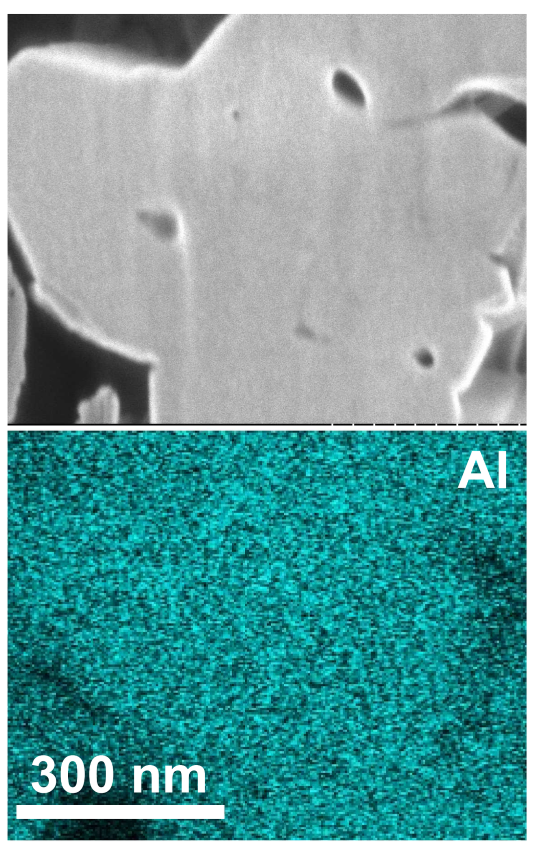
Smooth to rough surface



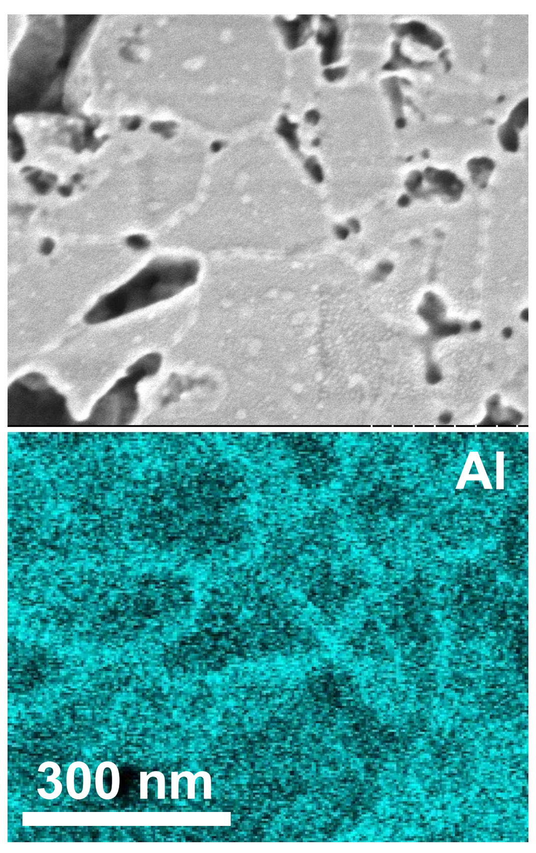
Zeolite (parent) (Na-form, Si/Al_{Total} = 2.8) | Zeolite (ion-exchange) (NH_4-form, Si/Al_{Total} = 2.8) | Zeolite (steam) (H-form, Si/Al_{Total} = 2.8) | Zeolite (acid) (H-form, Si/Al_{Total} = 250)

After steaming : bright contrast appeared
After acid leaching : formation of mesopore

● Al distribution by FE-SEM/EDS



Zeolite (parent) (Na-form, Si/Al_{Total} = 2.8)

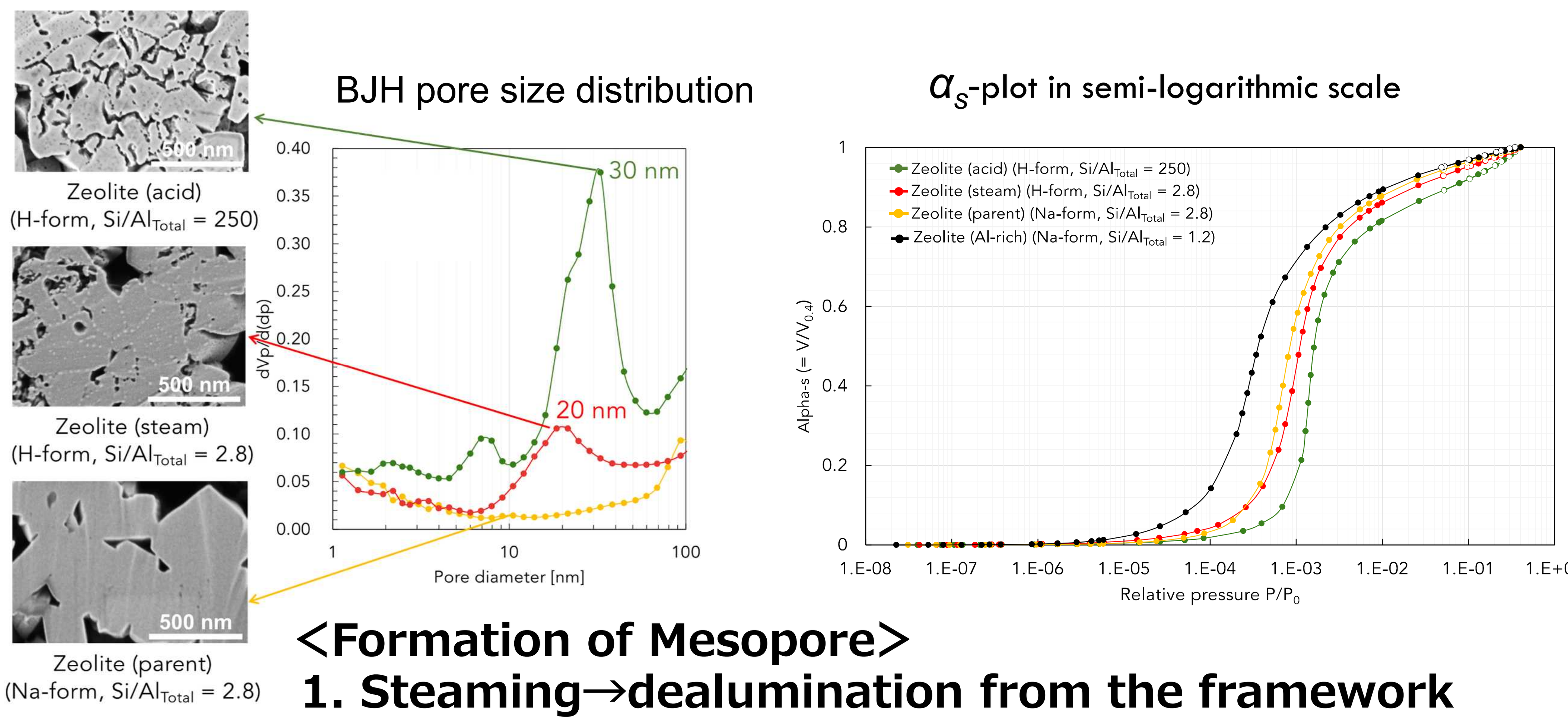


Zeolite (steam) (H-form, Si/Al_{Total} = 2.8)

After dealumination
→high concentration of Al at bright contrast
→Presence of amorphous aluminosilicate

● Pore structure assessment by Ar physisorption

Change in mesopore | **Change in micropore**



<Formation of Mesopore>
1. Steaming→dealumination from the framework
2. Acid leaching→removal of amorphous aluminosilicate
<Micropore>
Same framework, but change in effective pore size

<Research outline (AIST)>

Local structure and porosity of zeolite catalysts prepared in this project were evaluated using Ar physisorption measurement from extremely low relative pressure region (10^{-8}), high-resolution scanning electron microscopy, and energy dispersive X-ray spectroscopy. Particularly, the detailed quantitative textural pore analyses and direct visualization of aluminum distribution as well as dealumination behavior for both steamed and post-treated zeolites were investigated to understand the characteristic features of the existing and developing potential zeolite catalysts. Based on the results obtained in this study, we have developed the fundamental analysis protocol for nanoporous materials to clarify the essential factors governing the hydrothermal stability of zeolites, which will provide an important guide to fabricate optimal zeolite catalysts that would suit the target application aimed in this project.

No. A-14-4E

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

Thema： Chemical composition distribution analysis of zeolite precursor gels

Organization ：Japan Fine Ceramics Center

Contact ：Sasaki. Yukichi （e-mail: sasaki@jfcc.or.jp）

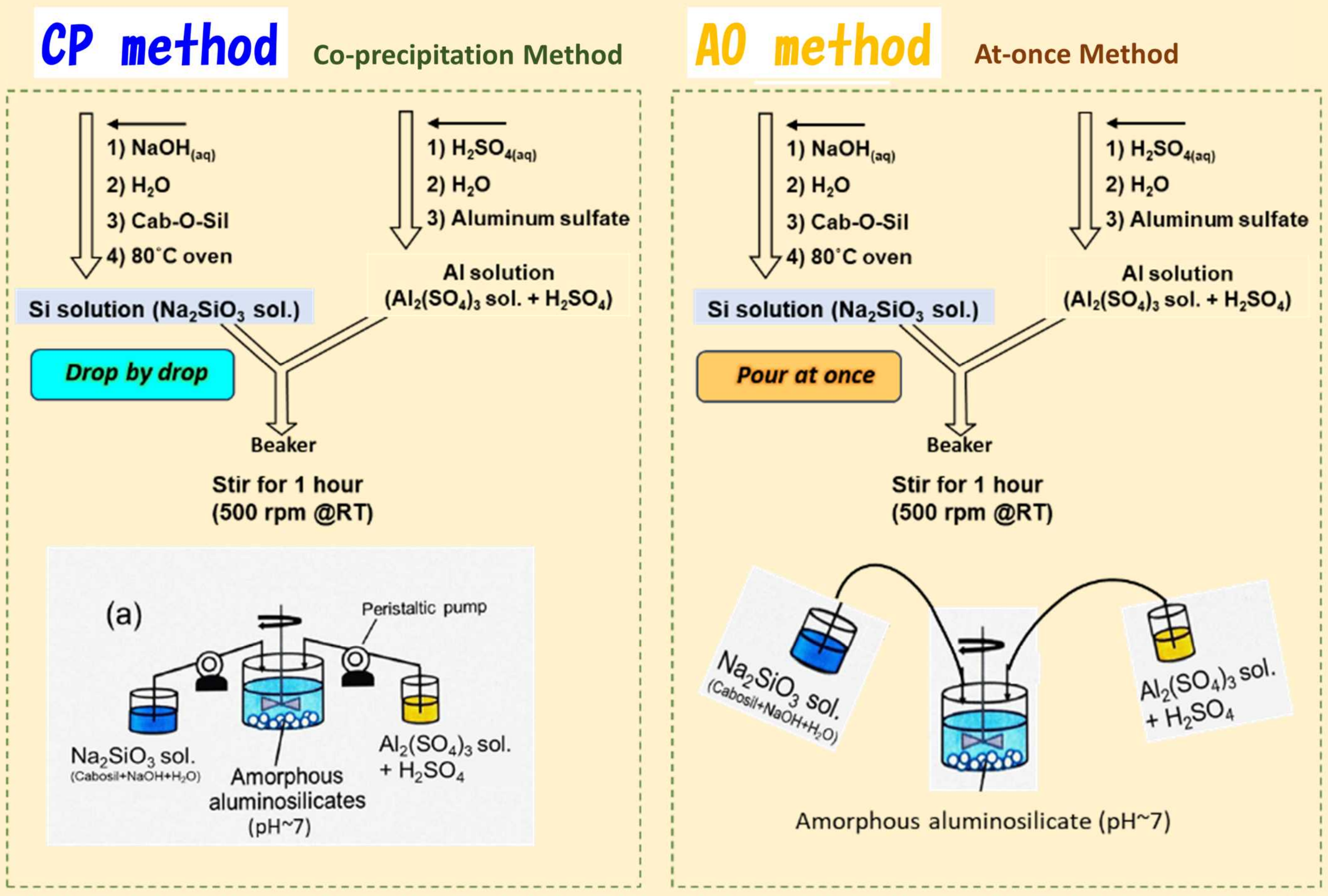
- Chemical composition distribution of zeolite precursor gels with a spatial resolution of less than 10 nm realized by STEM-EDS method was analyzed and its effect on crystallization was discussed.

Composition distribution (uniformity) of the gel is

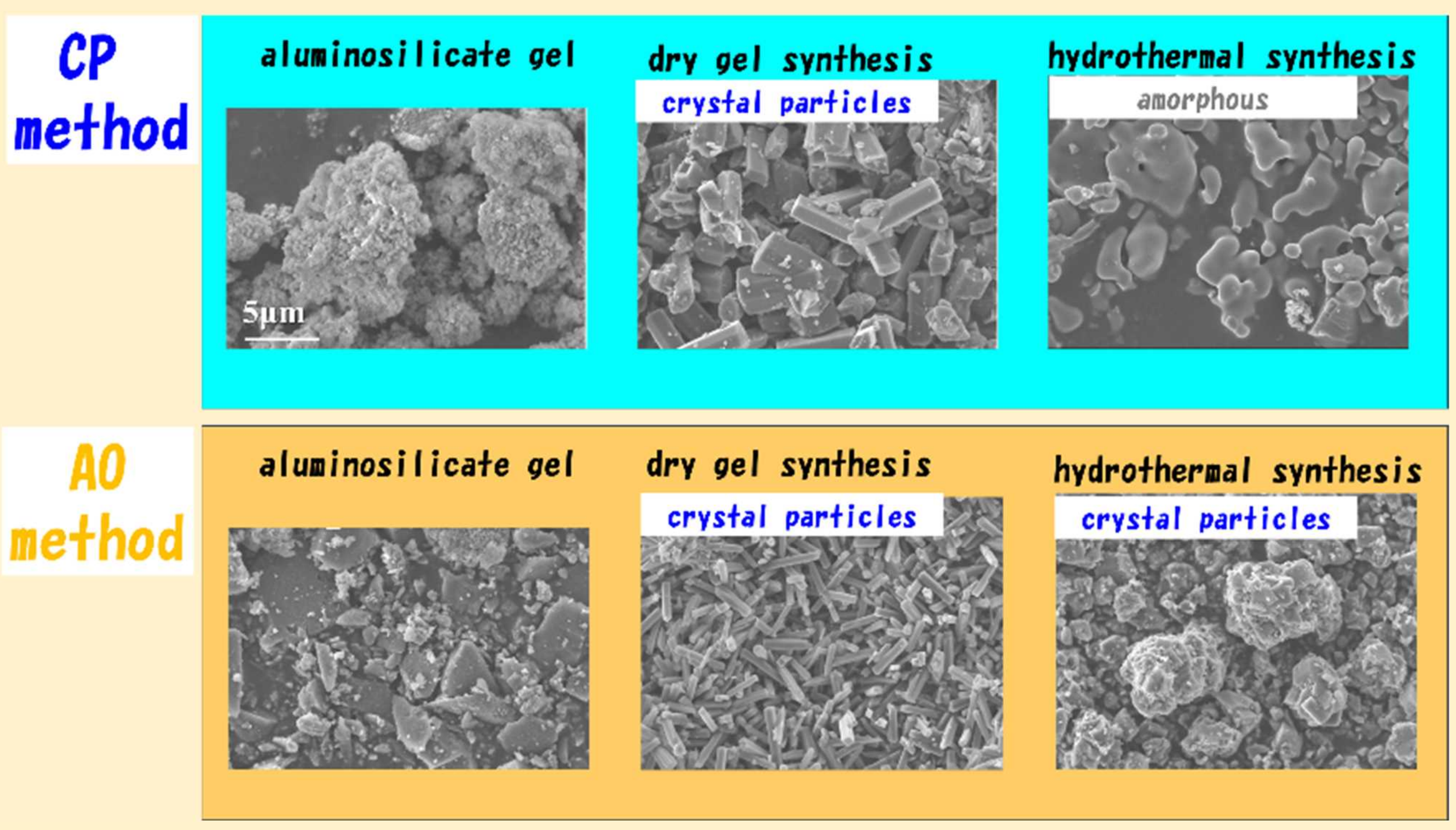
➡ Affects nucleation in zeolite crystallization

➡ Affects zeolite crystal particle size

Precursor gel synthesis conditions and SEM photo of zeolite crystals formed from the gel

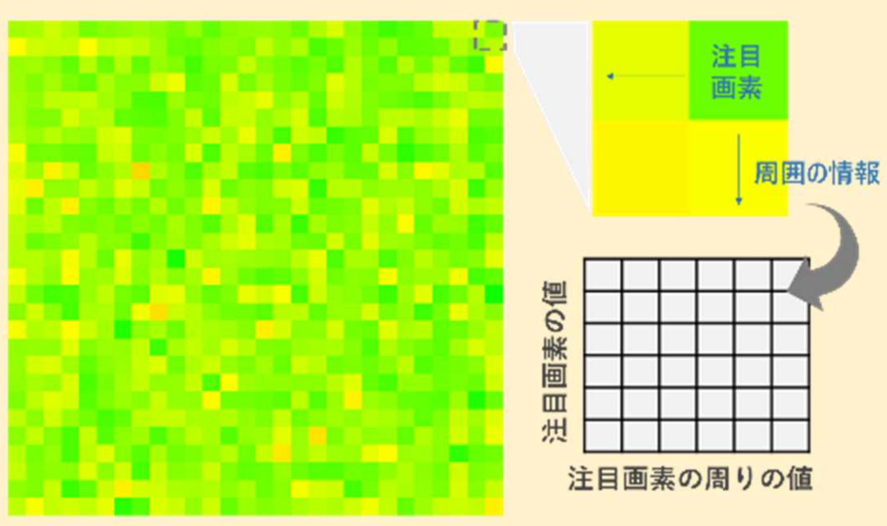


Hikichi, Chem Asian J. 2020, 15, 2029–2034



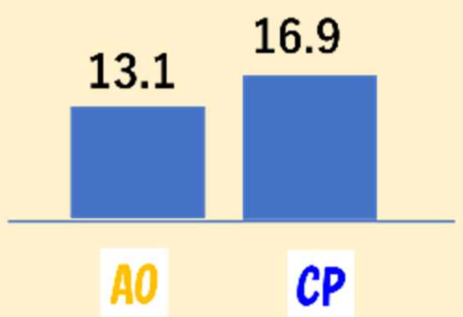
Analysis results of composition distribution (spatial distribution of composition)

Texture analysis (Gray-Level Co-occurrence Matrix, GLCM)

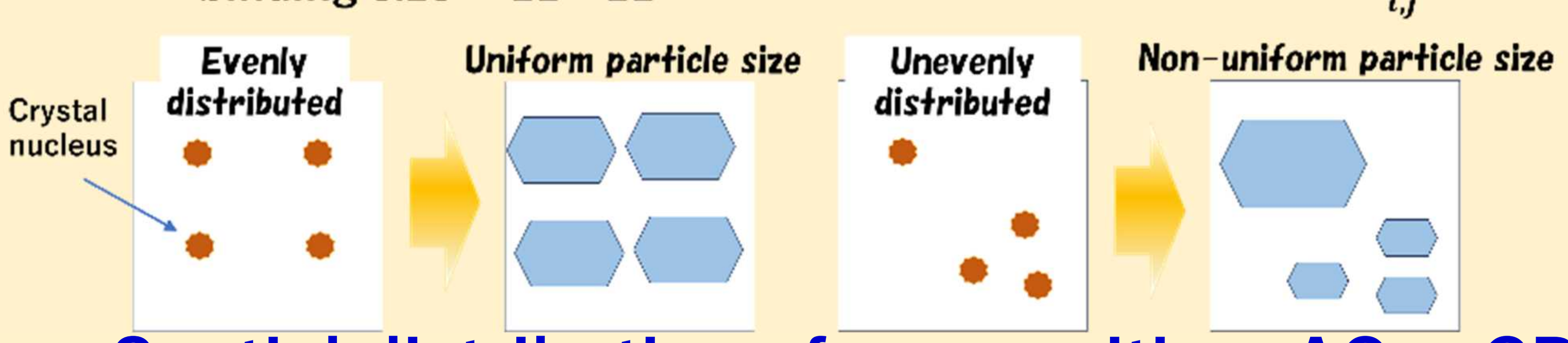


binding size 11×11

Dissimilarity (heterogeneity)



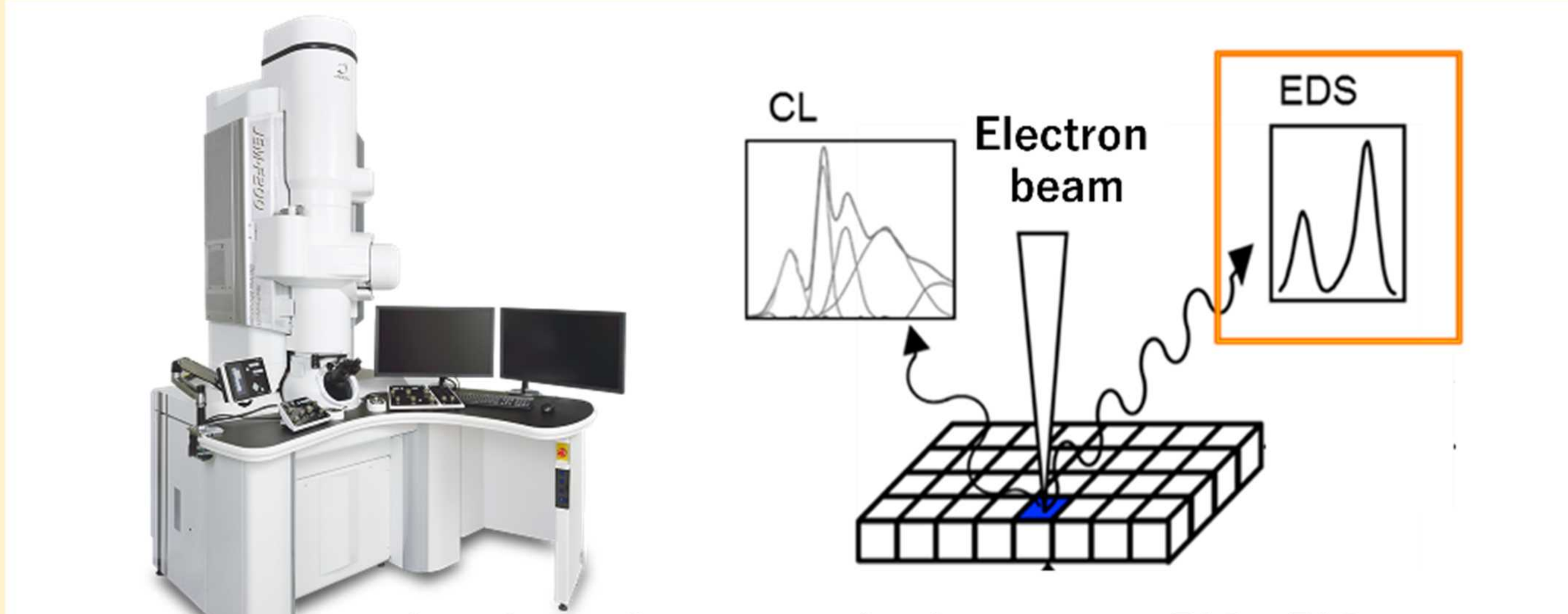
$$Dissimilarity = \sum_{i,j} P(i,j)|i-j|$$



Spatial distribution of composition: AO > CP

Non-uniform spatial distribution results in non-uniform particle size distribution

STEM-EDS (hypermapping method)



acceleration voltage 200kV

Analyzes up to 512×512 areas

EDS spectrum is stored in each pixel

1 pixel ：0.8nm

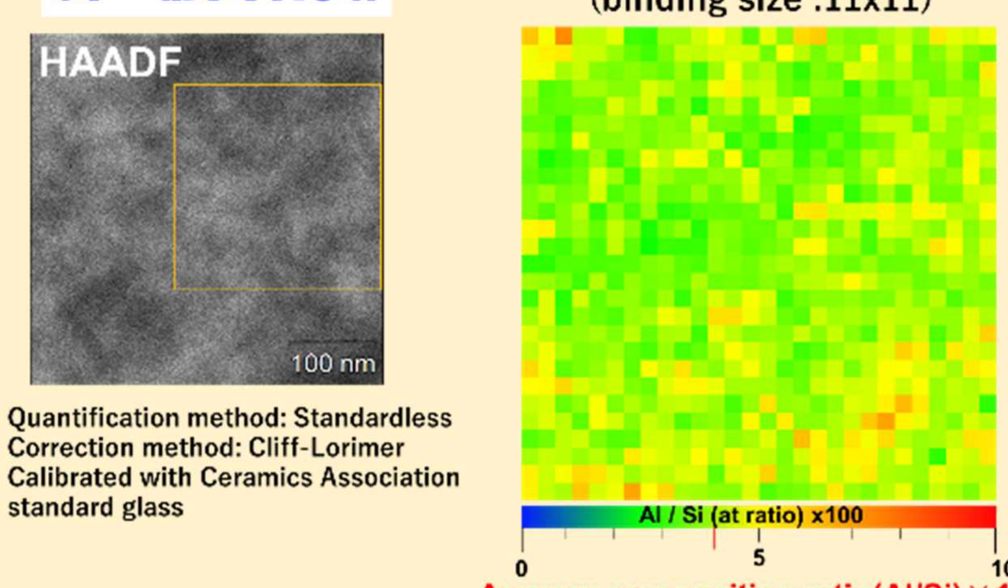
Measurement time: 1 hour

(1 pixel measurement time: 0.0137 seconds)

Analysis results of composition distribution (concentration distribution)

CP method

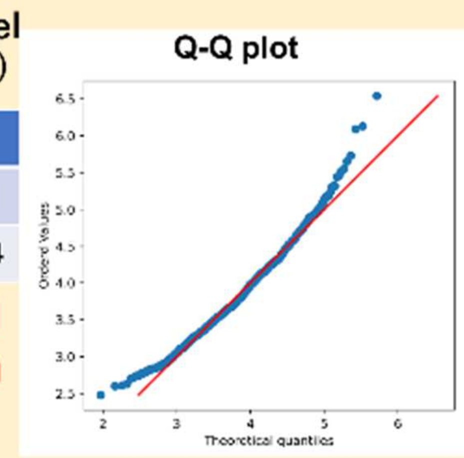
Ai/Si composition ratio distribution (binding size :11x11)



8.75 nm/pixel (27 x 27 pix)

Element	at%
Al K	3.84
Si K	96.14

standard deviation :0.66

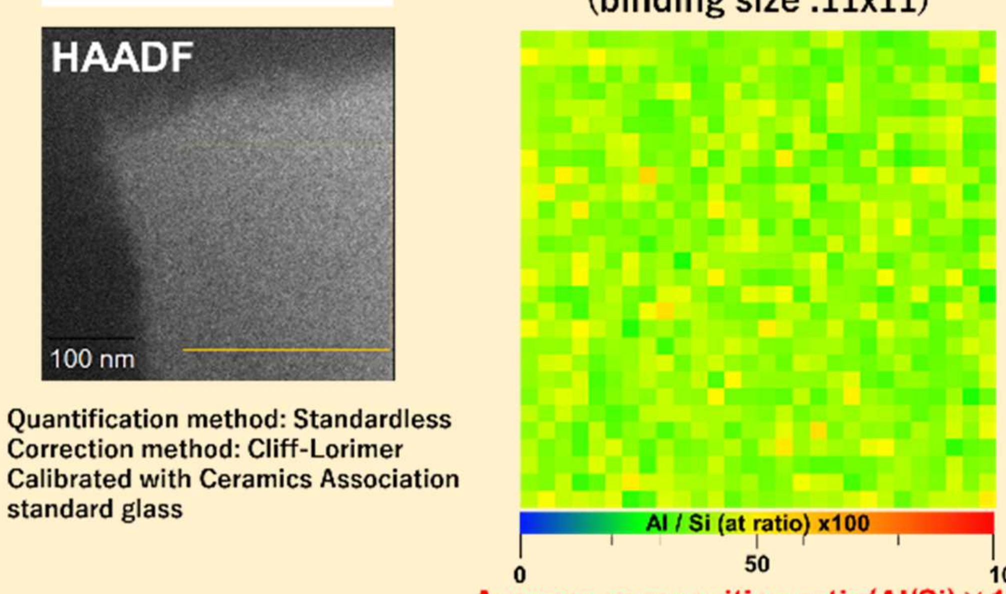


- Quantification method: Standardless
- Correction method: Cliff-Lorimer
- Calibrated with Ceramics Association standard glass

Average composition ratio(Al/Si)×100 ：4.14

AO method

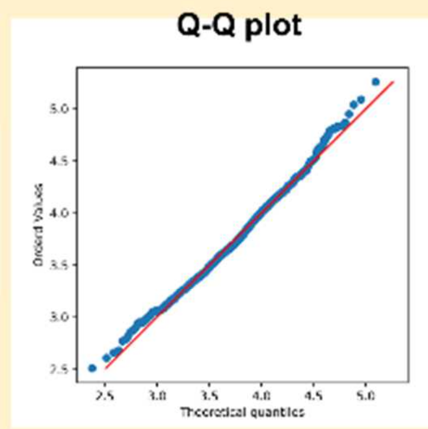
Ai/Si composition ratio distribution (binding size :11x11)



8.75 nm/pixel (27 x 27 pix)

Element	at%
Al K	3.73
Si K	96.25

standard deviation :0.47



- Quantification method: Standardless
- Correction method: Cliff-Lorimer
- Calibrated with Ceramics Association standard glass

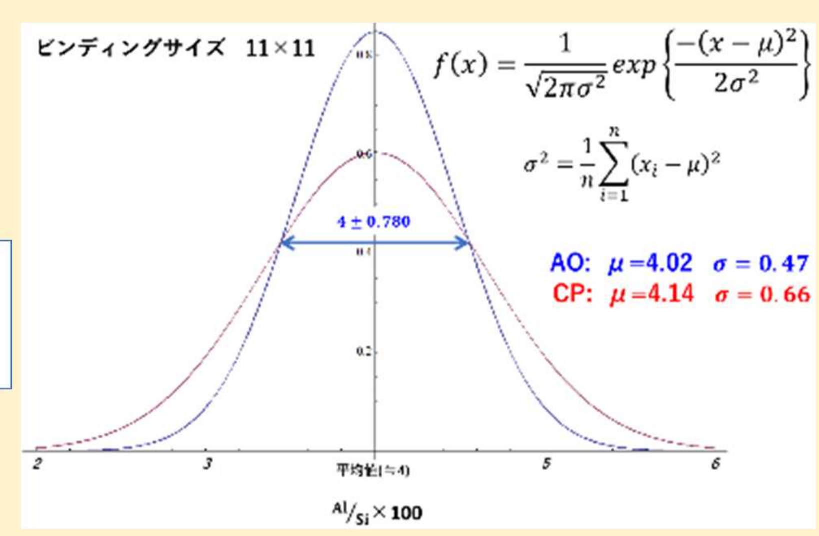
Average composition ratio(Al/Si)×100 ：4.02

Composition uniformity: AO > CP

Relationship between the amount of change in chemical potential of the reaction solution environment and uniform nucleation density (rate)

$$q_r^* = q_1 \times exp\left\{\frac{-\left(\frac{3\pi r^{*3}}{4v}\times\Delta\mu + 2\pi r^{*2}\gamma\right)}{kT}\right\}$$

q_r^*: Critical nuclear density, Δμ: Chemical potential, v: Volume per 1 mol
r^*: Radius of critical nucleus (spherical approximation)
κ: Boltzmann constant, T: Temperature
q_1: Density of crystal growth unit, γ: Surface energy per unit area



High compositional uniformity

⇒ The density of crystal nuclei increases

➡ The number of crystals is large and the crystal size is small

Summary

- We applied the composition distribution measurement method in the micro region (single nano size) established in last year's research to zeolite precursor gel.
- Differences in the uniformity of the gel composition (Ai/Si ratio) and its spatial distribution were observed depending on the method used to prepare the precursor gel (AO method and CP method).
- The differences between zeolite crystals synthesized using gels produced by the AO method and the CP method as raw materials were explained by evaluating the uniformity of composition distribution.

➡ Useful knowledge for process development such as manufacturing scale-up

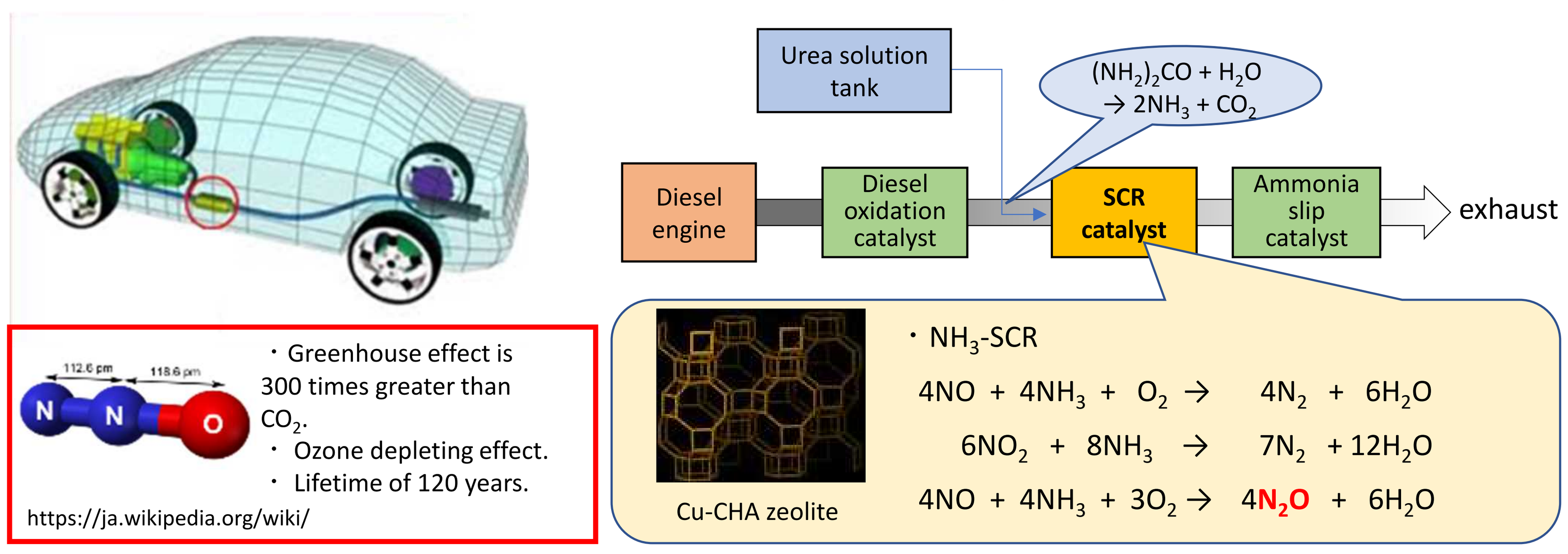
No. A-14-5E
PJ: Development of Recovery and Removal Techniques of Dilute Reactive Nitrogen to Realize Nitrogen Circulating Society
Theme: Development and mass production of new zeolite catalysts to reduce N_2O emissions.
Organization: Mitsubishi Chemical Corporation
Contact: takahiko.takewaki.mb@mcgc.com

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 materials for new exhaust gas catalysts ・Mass production of new zeolite catalysts ・Pilot demonstration of NOx purification catalyst Final target (FY2029)
Final Target (FY2029)	・Develop innovative new materials for exhaust gas purifying catalysts that do not use NH_3 and precious metals, which enable operation under combustion conditions (lean-burn engines, etc.) that significantly improve fuel efficiency of internal combustion engines and drastically reduce CO_2 emissions.
Fiscal Year 2024 Target	・Mass production of zeolite catalysts with low N_2O emissions ・Confirmation of the feasibility of NOx purification catalysts that do not use NH_3 (e.g., performance target: purification rate of 50% or higher at 300℃)
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 800℃. ・N_2O emissions were also successfully reduced by 70-75% compared to the current catalyst both before and after the endurance test. ・Successfully synthesized new zeolite catalysts in 50 L, 100 L, and mass production (2000 L) scale. ・Applied for 3 patents for new zeolite catalyst synthesis method, catalyst preparation method, etc.

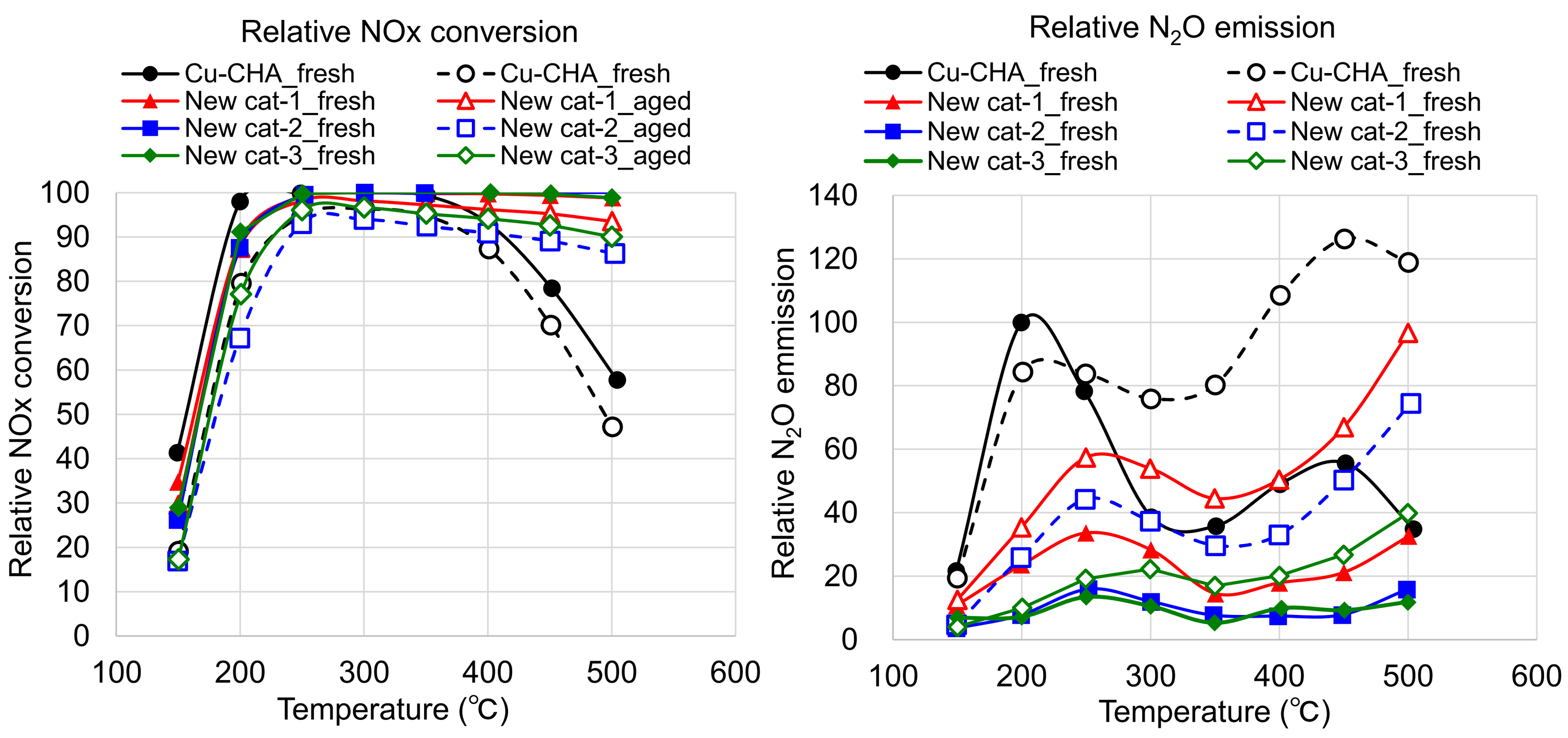
Problems with current SCR catalyst (Cu-CHA).



・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.

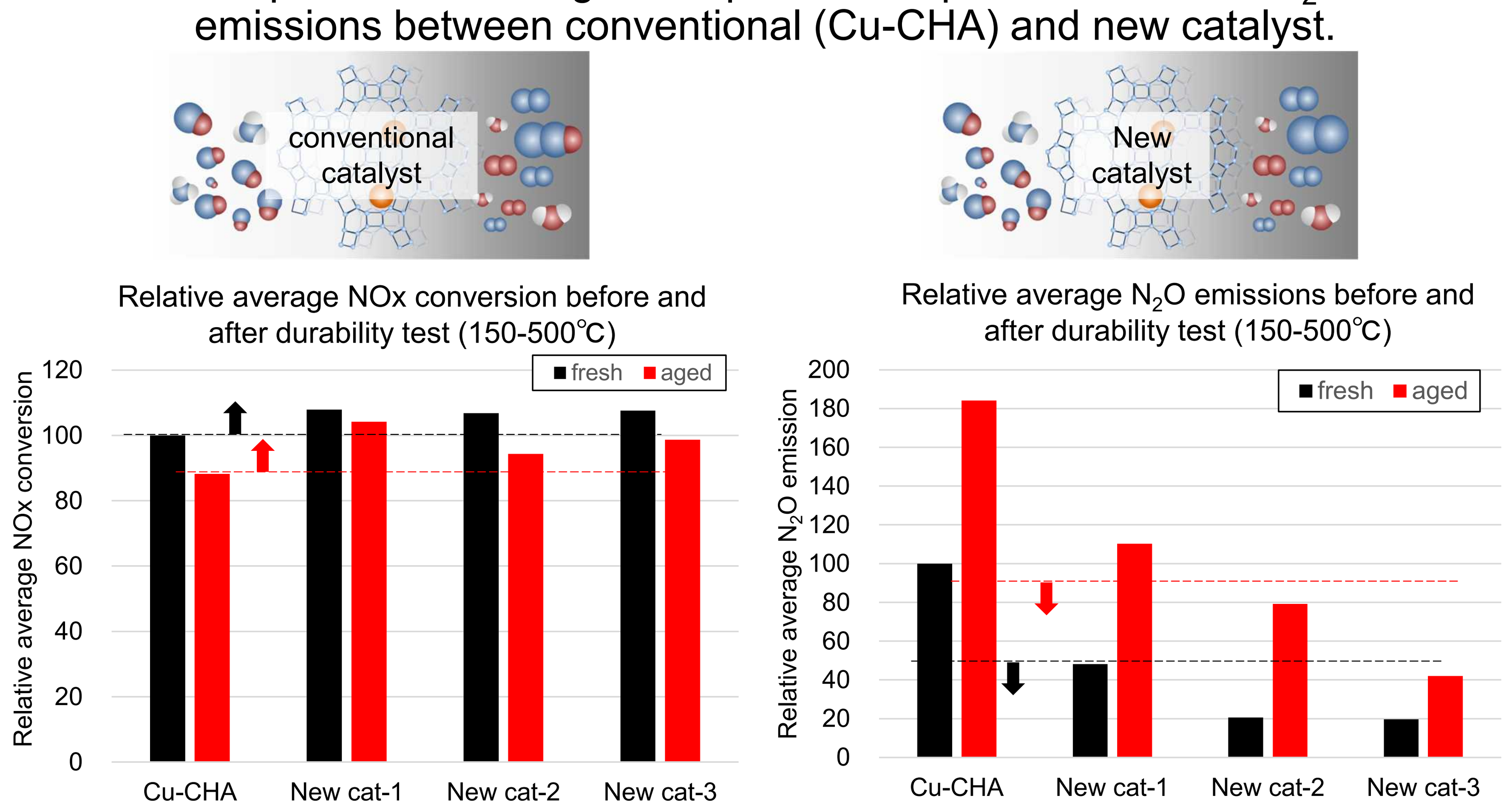
Comparison of NOx purification performance and N_2O emissions between conventional (Cu-CHA) and new catalyst.

Aging condition: H_2O-10vol%, 800℃, 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



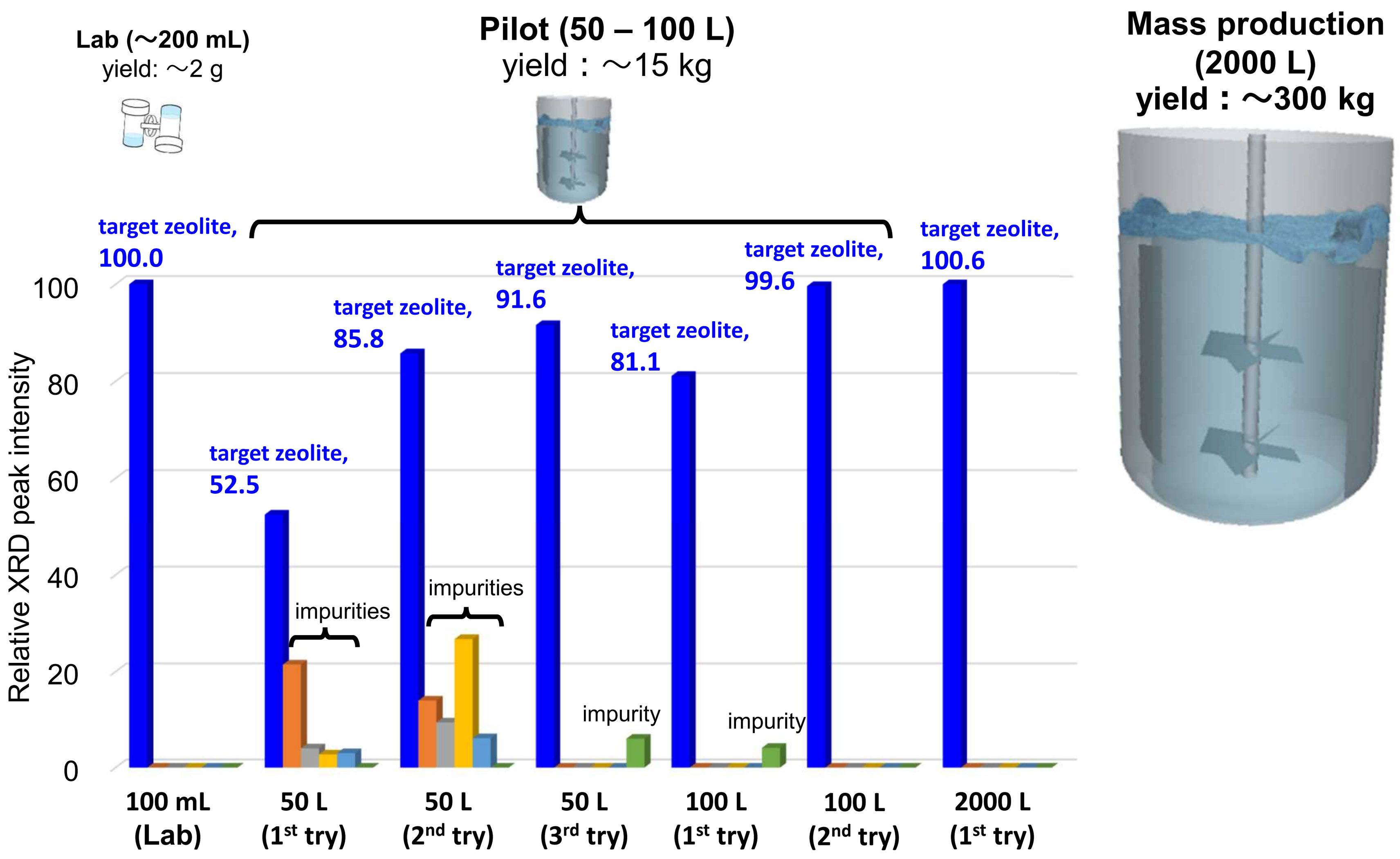
・The new zeolite catalyst had higher NOx purification performance and lower N_2O emissions in all samples before and after steam treatment.

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



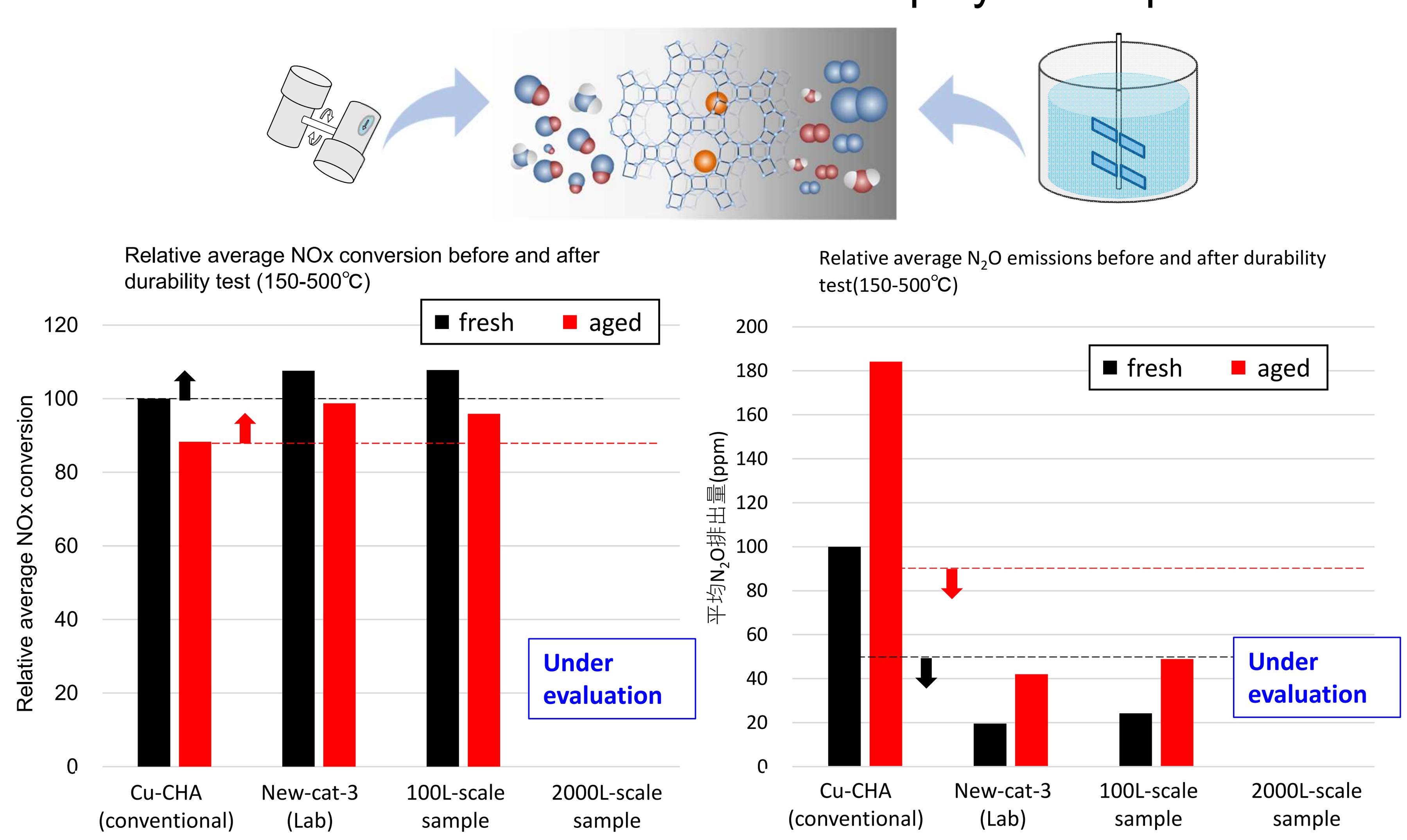
・The new zeolite catalyst showed better NOx decomposition performance in the NH_3-SCR reaction than the conventional catalyst (Cu-CHA) before and after the endurance test at 800℃. The N_2O emissions were also successfully reduced by 70-75% (compared to the target of 50%) from Cu-CHA both before and after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

Scale-up synthesis of new zeolite catalysts.



・Succeeded in reducing impurities in 50L and 100L scale prototypes.
・Success in synthesis of new zeolite in mass production scale (2000L).

Performance evaluation results of scale-up synthetic products.



・The catalyst performance exceeded the target for the 100 L scale sample.
・2 m^3 sample is currently under evaluation.

Direct denitration: screening of various complex oxides

Implementation: Screening

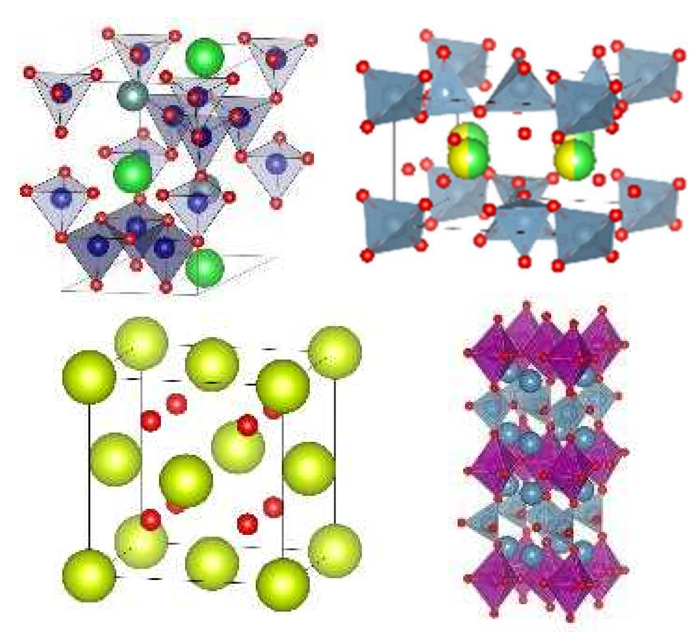
Screening of composite oxide catalysts of various structures with the cooperation of Prof. Motohashi of Kanagawa University.

Outcome: Determined direction of development

We found the possibility of activity in certain types of composite oxides.

Future plans

Aiming to improve activity by further screening of composite oxide materials, increasing specific surface area, and examining supported metals.



Summary

・The goal is to develop and mass produce a new zeolite catalyst with less than half the N_2O emissions of the current catalyst (Cu-CHA) in the NH_3-SCR reaction.
・The new zeolite catalyst showed better NOx decomposition performance than the current catalyst before and after the endurance test at 800℃.
・The N_2O emissions were also successfully reduced by 70-75% compared to the current catalyst both before and after the endurance test.
・Three patents were filed for the synthesis method of the new zeolite catalyst and the catalyst preparation method.Succeeded in synthesizing new zeolite catalysts on a mass production scale (2000 L).

Future Plans

・Development and mass production of catalysts that do not use NH_3 (direct denitration).
・Cost reduction of new zeolite catalyst production method