Innovative Circular Technologies for Harmful Nitrogen Compounds/
To Solve Planetary Boundary Issues

Theme 1. Recycling nitrogen compounds in gas phase
to ammonia resource
Development of catalyst technologies for one-step NTA
using hydrocarbons or hydrogen under oxidizing conditions

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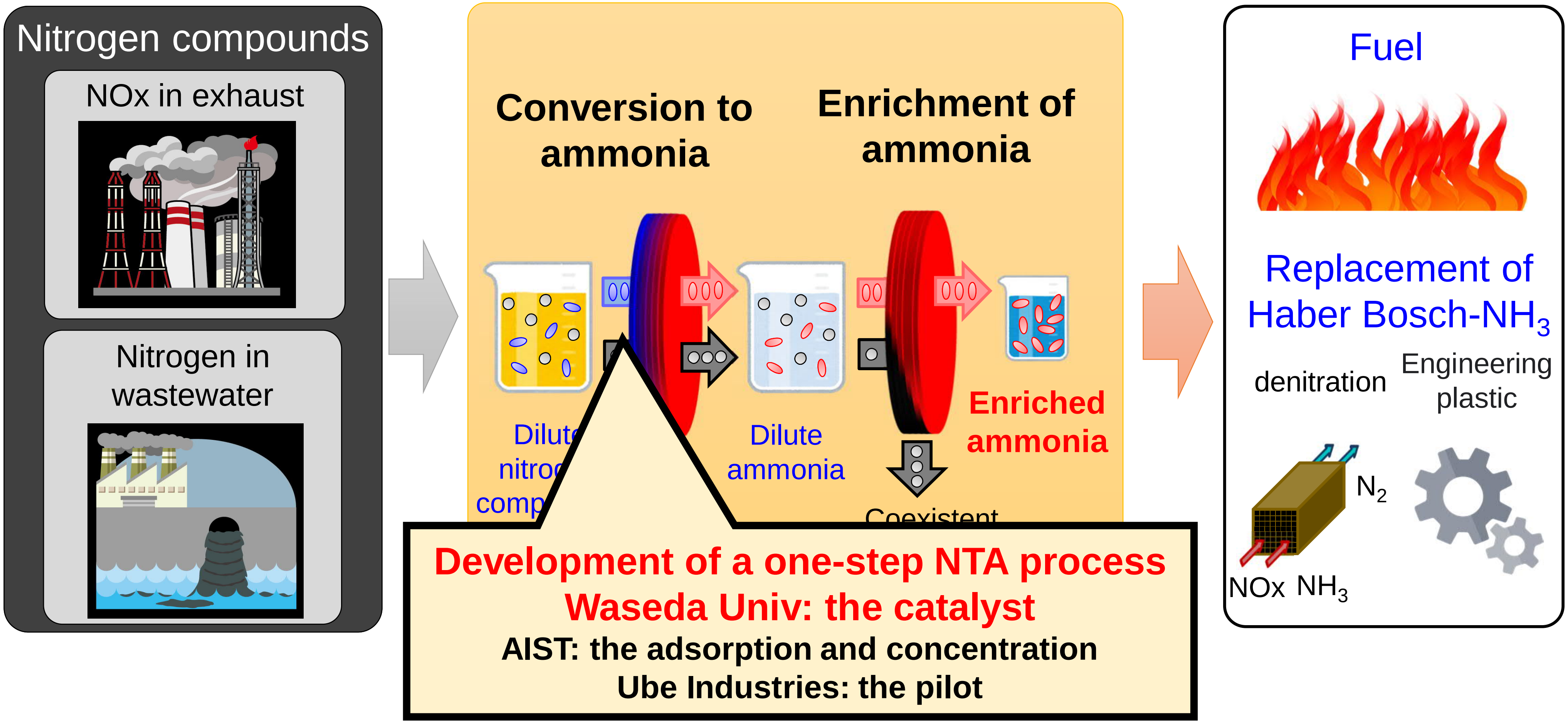
Implementing organizations : National Institute of Advanced Industrial Science and Technology (AIST),
The University of Tokyo, Waseda University,
Tokyo University of Agriculture and Technology, Kobe University,
Osaka University, Yamaguchi University, Kyowa,Hakko Bio Co., Ltd.,
ASTOM Corporation, Toyobo Co., Ltd., FUSO Corporation, Ube Industries, Ltd,

Position in the Project



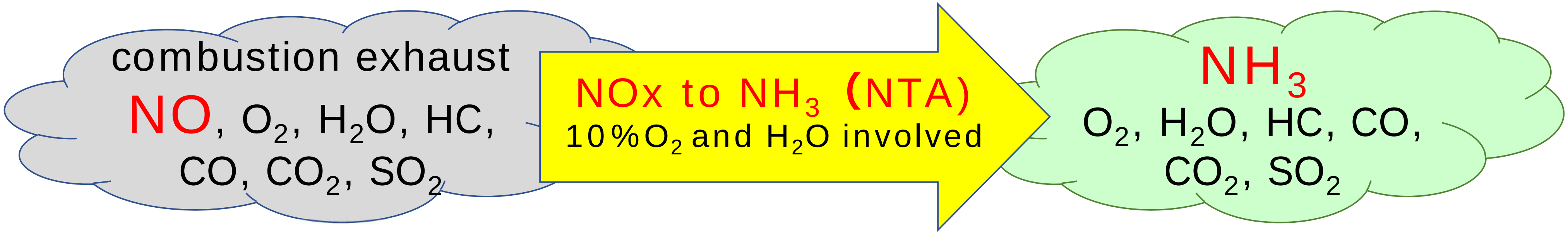
Target of Theme 1 for FY2029：NOx to Ammonia (NTA) reaction at 50% yield, and complete detoxification of exhaust gas

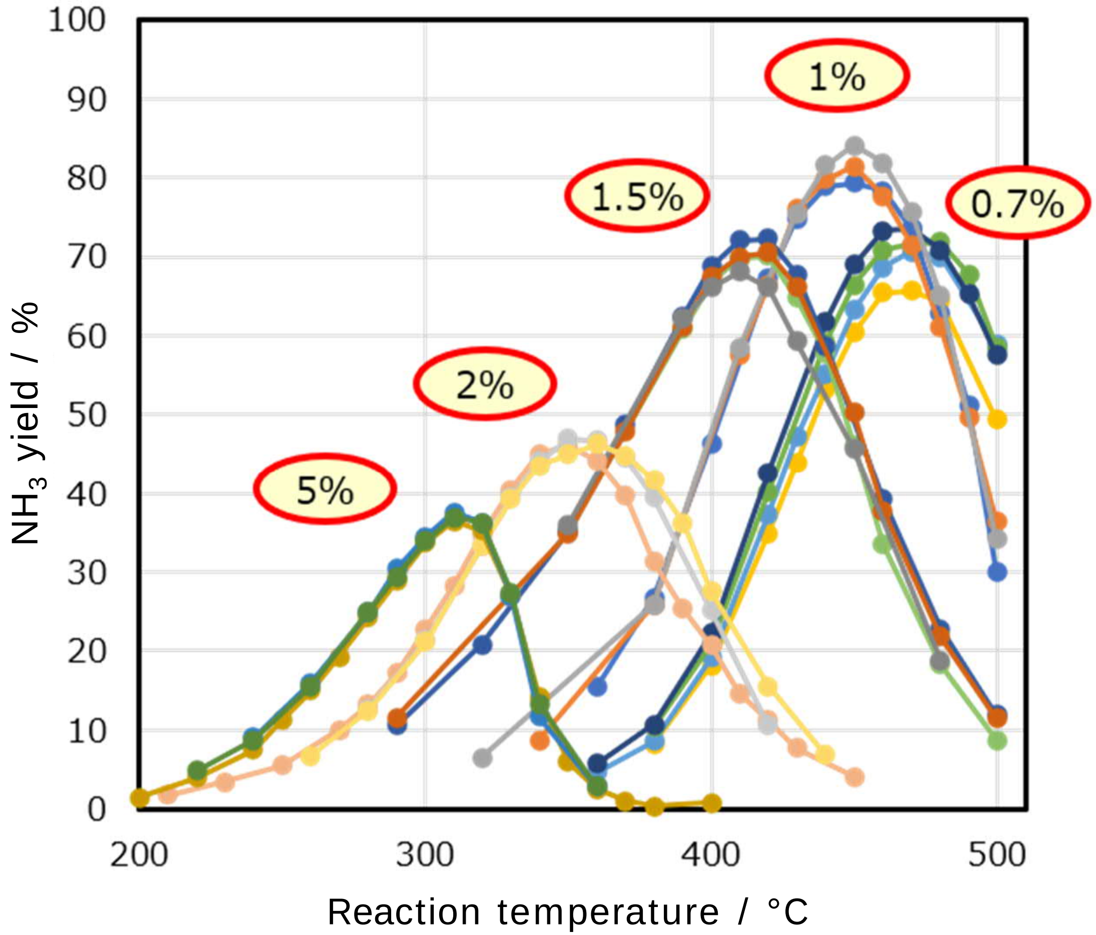
Position of Waseda University:

(1) Development of the NTA process using C_3H_6 as a reductant (C_3H_6 -NTA)
(2) Development of NTA process using H_2 as a reductant (H_2-NTA, new research theme)
(3) Collaboration with AIST: Connected to AIST pilot system for adsorption to recover 95% of generated ammonia

The target for FY2029: Achieve 90% ammonia yield in semi-pilot scale experiments

Achievement 1: C_3H_6-NTA catalyst under oxidizing conditions





1. High performance TiO_2-supported Ag catalysts was discovered from the combination of 23 metals and 10 supports.

2. 80% yield of ammonia was achieved by optimizing the supported amount of Ag and the support.

3. 50% NH_3 yield could be attained at C_3H_6/NO=2, where 0.6% CO_2 is formed at 1000ppm NO concentration.

The numbers in the figure show the Ag loading (wt%). The multiple activity curves show the repetition of the experiment, meaning the stability of the catalyst.

Reaction conditions: NO 1000 ppm, C_3H_6 0.50 %, O_2 10 %, H_2O 10.0 %, N_2 balance, total flow rate 100 mL/min, catalyst 0.6 mL (SV 10,000 h^{-1}).

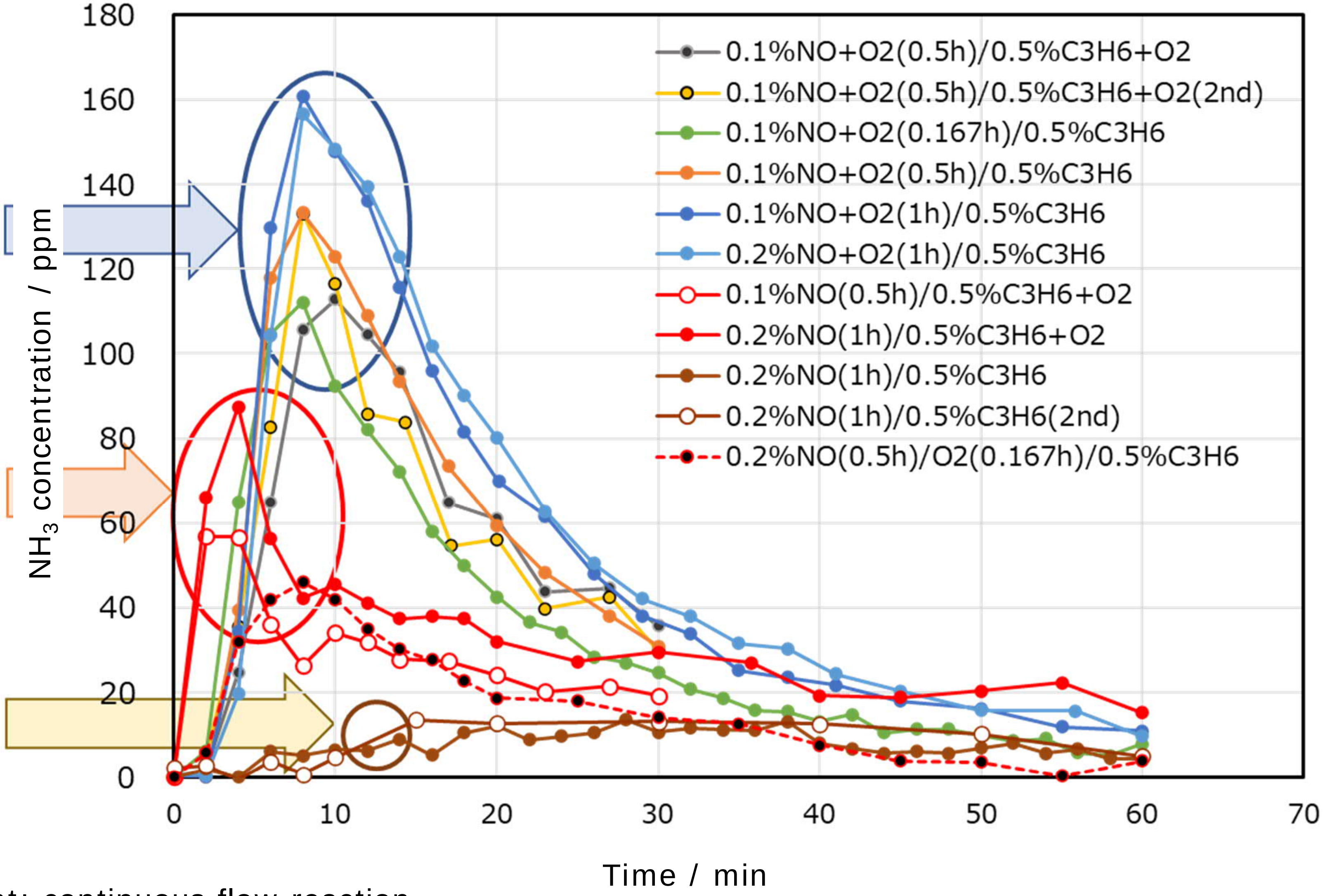
Achievement 2: Active species for NH_3

- NO_2 adsorbed on Ag shows higher NH_3 production activity than adsorbed NO

Ammonia formed in the reaction of adsorbed NO_2 with gaseous C_3H_6

Ammonia formed when adsorbed NO was exposed to gaseous O_2 and then to C_3H_6

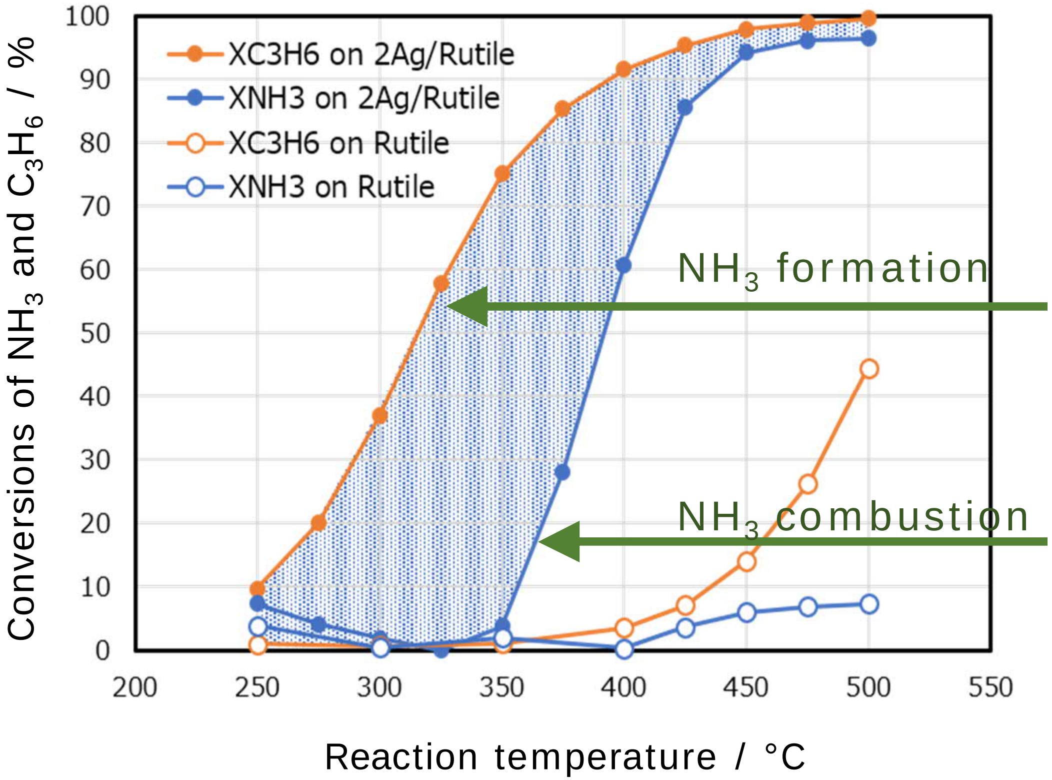
Ammonia formed in the reaction of adsorbed NO with gaseous C_3H_6



The experiment: continuous flow reaction
→ purged by nitrogen for 10 min
→ the switching reaction mentioned above.
Catalyst: 5wt%Ag/ZrO_2 (HY)

Achievement 3: Formation of NH_3 in excess O_2

- Elucidating the reason for high NH_3 production in 10% O_2



NTA reaction route (proposed)

$NO + ½ O_2 \rightarrow NO_2$ (1)

$NO_2 + OH \rightarrow HNO_3$ (2)

$Ag + HNO_3 \rightarrow AgNO_3 + ½ H_2$ (3)

$AgNO_3 + C_3H_6 + O_2$
$\rightarrow Ag + NH_3 + CO_2 + H_2O$ (4)

$C_3H_6 + O_2 \rightarrow CO_2 + H_2O$ (5)

$(HNCO + H_2O \rightarrow NH_3 + CO_2$ (6))

$NH_3 + O_2 \rightarrow N_2, NO, N_2O + H_2O$ (7)

Stoichiometry ignored in (4), (5), and (7).

- NH_3 combustion activity on TiO_2 was very low, while C_3H_6 combustion activity and NH_3 combustion activity were greatly improved by Ag loading in a lower activity temperature range.
- The hatched area indicates the range where NH_3 was produced by eq. 4 but was not yet oxidized by eq. 7.

- Selective reduction of NO to NH_3 in the presence of large excess oxygen is realized.

Summary, Waseda Univ.

Position in the project

Development of NTA catalysts under oxidizing conditions

Target for FY2029

Establishment of materials and basic processes for pilot demonstration of the NTA catalyst system

R&D items

Development of catalyst activation technology for NTA using unburned hydrocarbons under oxygen conditions

Achievements by Waseda University

(1) Development of a NTA process using C_3H_6 as the reductant (C_3H_6-NTA)

・Catalysts showing high NH_3 production activity in the presence of 10% oxygen and 10% water vapor were developed.

・The amount of C_3H_6 required for the reaction of 1000 ppm NO was minimized, and the amount of CO_2 produced was reduced to 0.6%.

(2) Development of NTA process using H_2 as the reductant (H_2-NTA, a new research theme)

・The NTA process using H_2 as a reductant was investigated, and a promising catalyst was discovered.

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