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NH_3 Energy+ (November 14, 2019)

Synthesis and Assessment of Process Systems for Production of Ammonia using Nitric Oxide in Combustion Exhaust Gas

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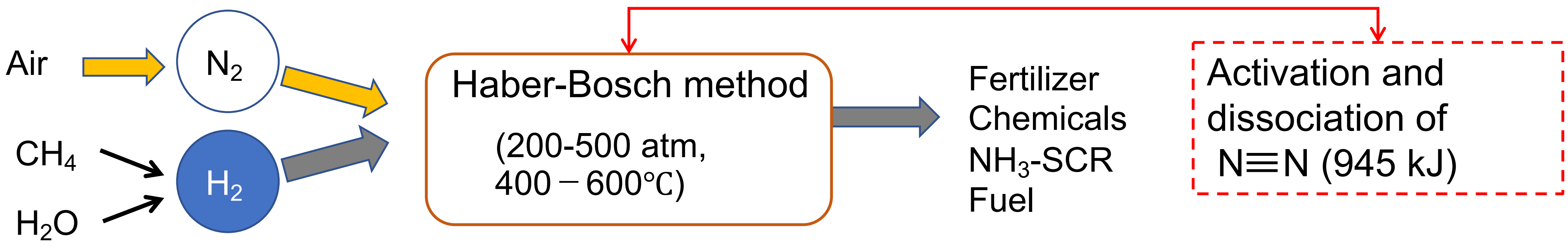
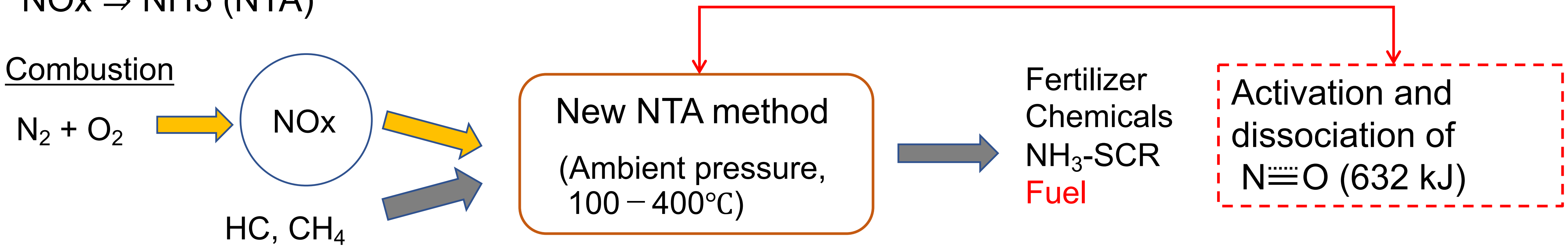
Production of Ammonia using nitric oxide in combustion exhaust gas

■ Industrial Ammonia Production



■ NOx ⇒ NH3 (NTA)

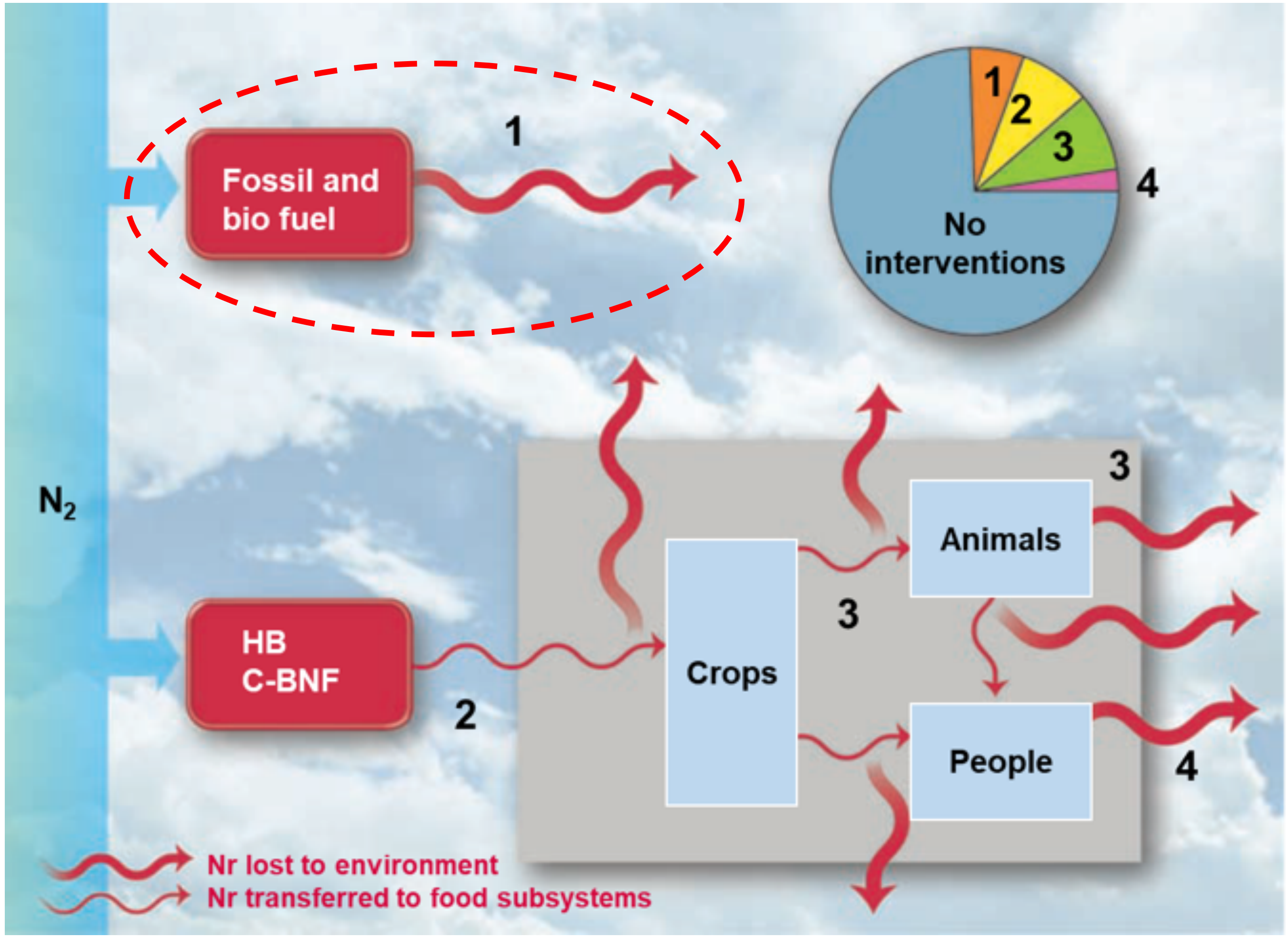


Approx. 250 million ton of NH_3 could be produced by using a half of NOx (4%) in exhaust gas from all the thermal power plants located in Japan.

⇒ Reutilization of produced NH_3 as fuel will bring about decrease in CO_2 emissions.

From the perspective of "Nitrogen Cycle"

Conceptual model of where interventions in the nitrogen cycle can be used to decrease the amount of reactive nitrogen (Nr) created or the amount of Nr lost to the environment.



J. N. Galloway *et al.*: *Science*, **320**, 889-892 (2008)

Agenda

- Background for development of process systems for NH_3 production using NO in combustion exhaust gas (NTA system)
- Development of new catalytic process for conversion of NO to NH_3 (NTA) : NO-CO-H_2O reaction process
- Simulation analysis for effects of application of the proposed NTA system combined with lean-rich cycling operation for combustor (e.g. reciprocating engine generator)
- Conclusions

Reaction route for conversion of reactive nitrogen to ammonia

■ Ammonia formation during catalytic NOx reduction[1]

$$\begin{cases} 2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \\ 4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \end{cases}$$

[1] J.R. Theis *et al.*; *SAE Tech. Pap.* (2011)

It has been reported that complete selectivity for NH_3 is difficult to achieve by means of the NO–H_2 reaction under stoichiometric conditions.

■ Development of catalytic process for conversion of NO to NH_3 (NTA) [2, 3]

$$NO + 2.5CO + 1.5H_2O \xrightarrow{Pt/TiO_2} NH_3 + 2.5CO_2$$

High NO conversion and NH_3 selectivity at ambient pressure and temperatures below 300 ° C

[2] T. Nanba *et al.*; *Chem. Lett.*, **37**, 710-711 (2008)
[3] K. Kobayashi *et al.*; *Catal. Sci. Technol.*, **9**, 2898-2905 (2019)

Effect of the crystal type of TiO_2 on catalytic activity

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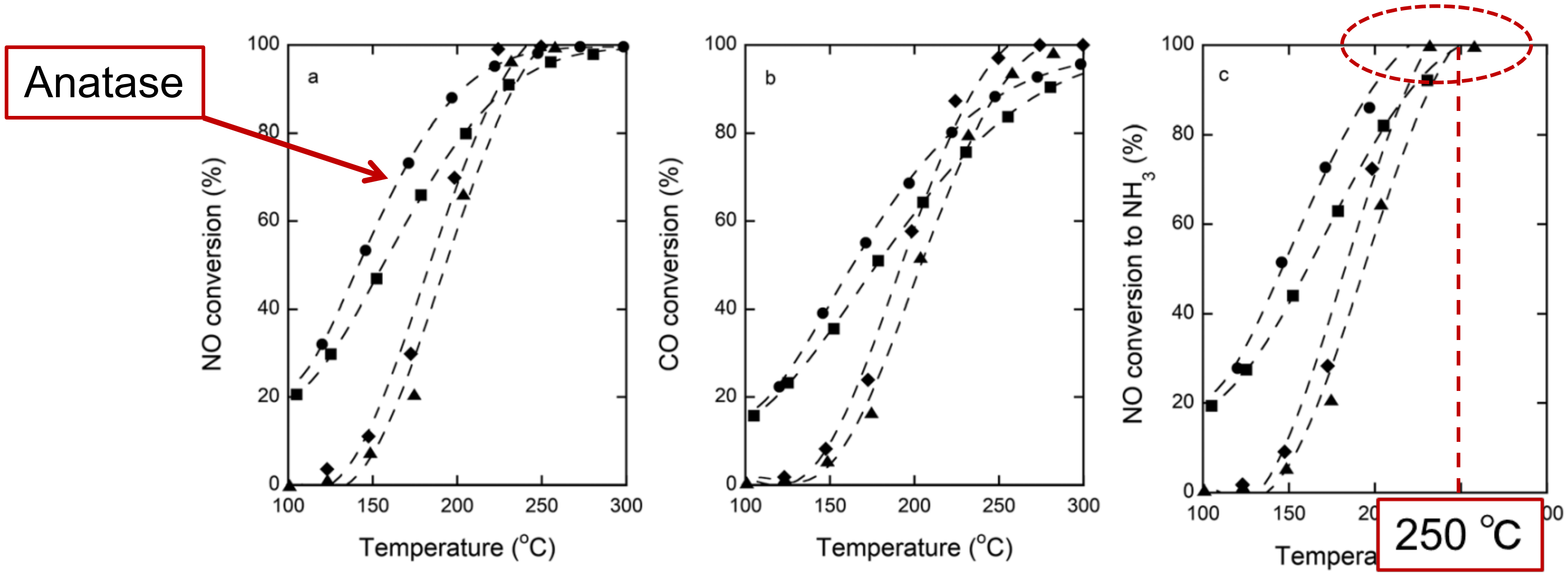
It was shown that Pt/TiO_2 was higher activity than M/TiO_2 (M: Rh, Ir, Ru, Pd).



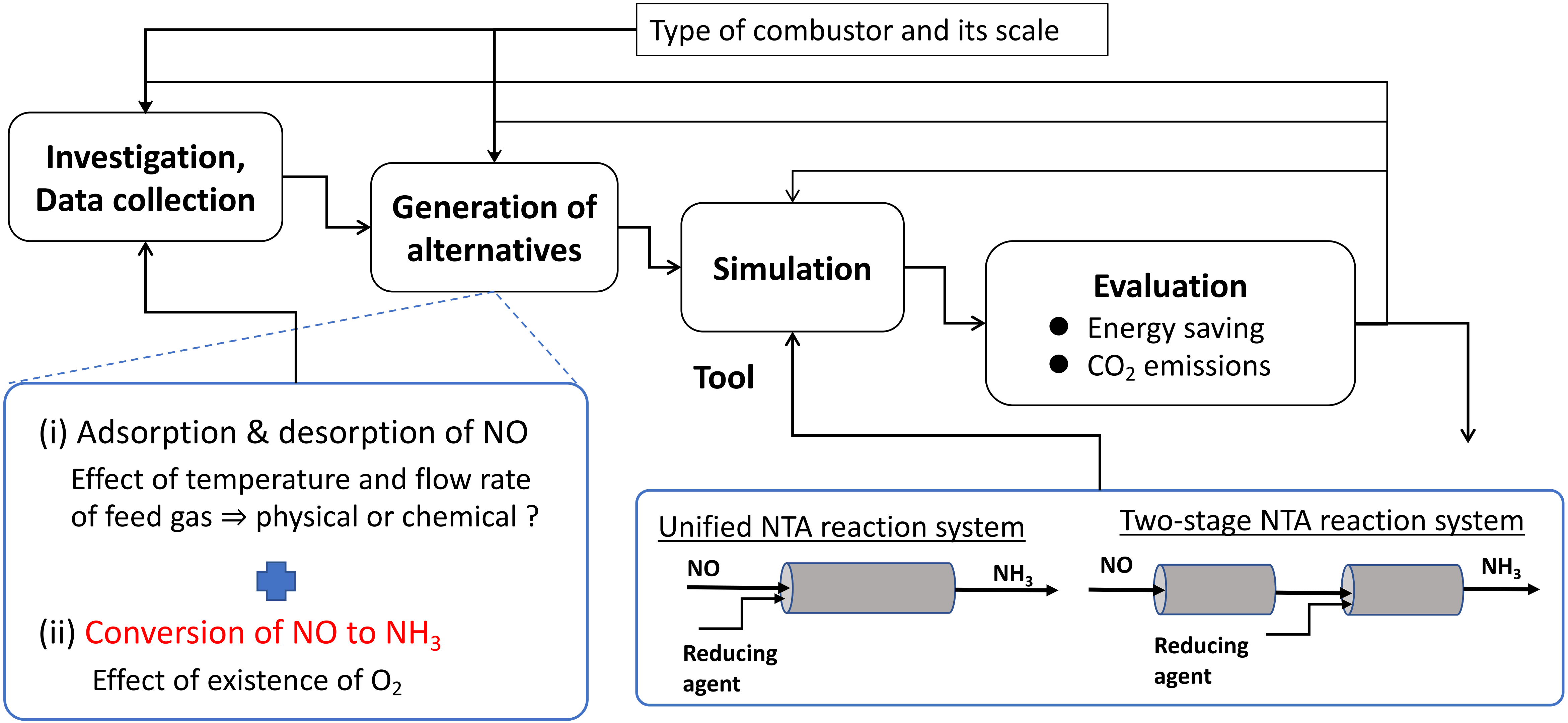
Feed gas
1000 ppm NO, 3000 ppm CO, and 1% H_2O

●: Pt/TiO_2(A)1
■ : Pt/TiO_2 (A)2
◆: Pt/TiO_2(R)
▲ : Pt/TiO_2 (AR)80

※A: anatase, R: rutile

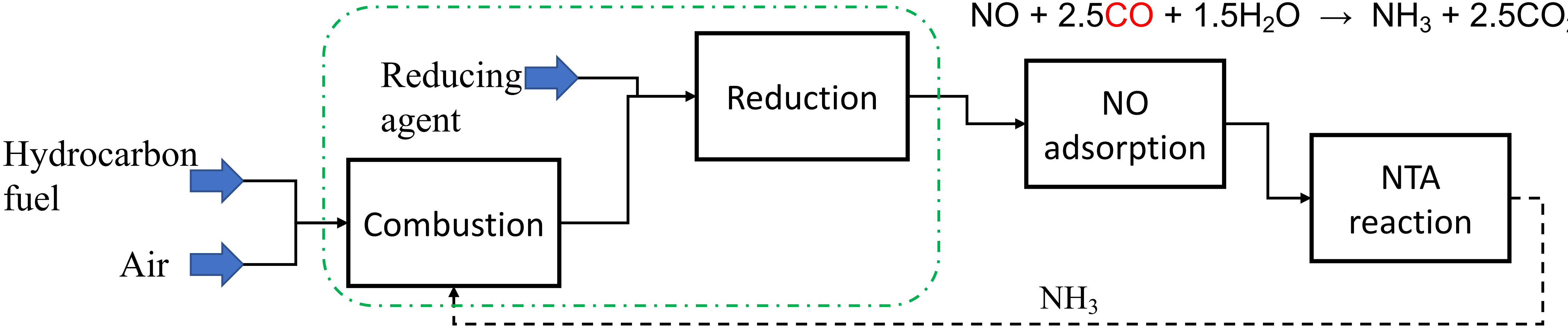
- It was observed by DRIFT (the diffuse reflectance infrared spectroscopy) that CO exhibited strong interaction with platinum on the rutile TiO_2.
- it was estimated that the strong interaction of CO with Pt reduced the reaction activity by comparing with Pt/anatase-TiO_2 catalyst.

Conceptual design of process systems for production of NH_3 using NO in combustion exhaust gas

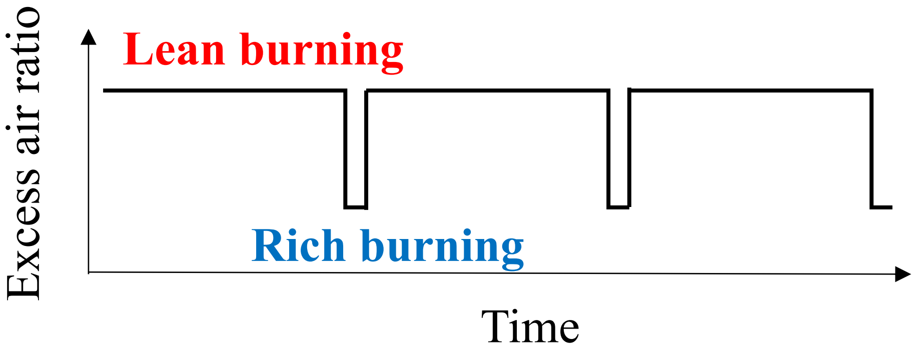


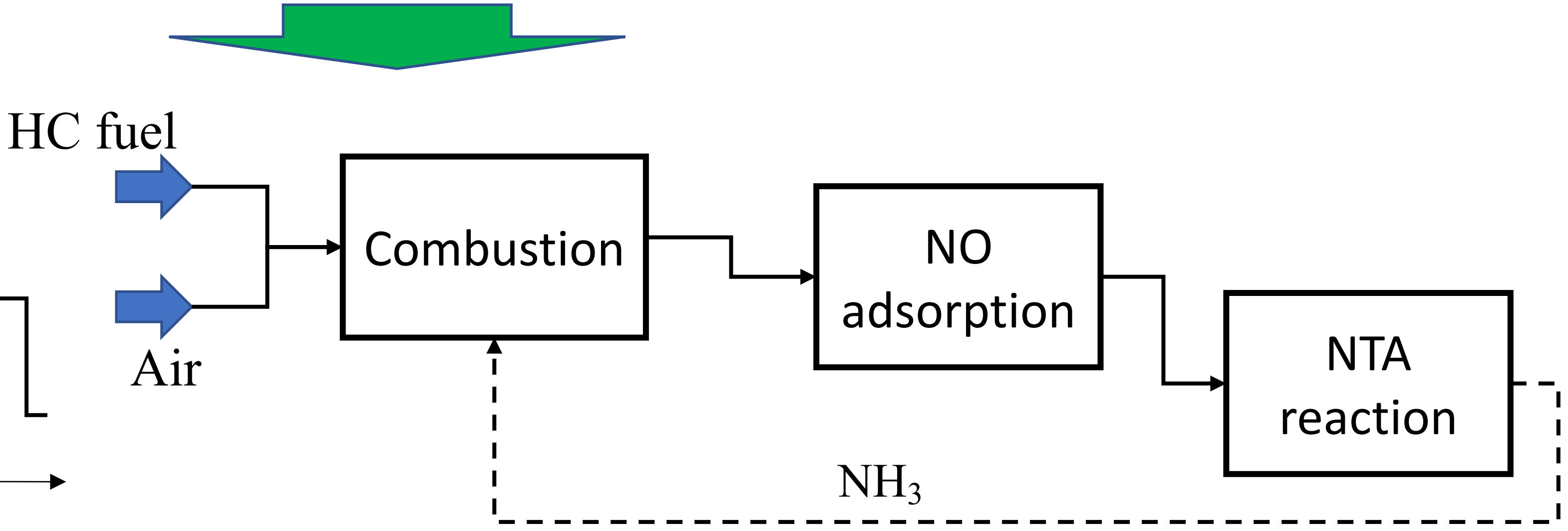
Adaptation of lean-rich cycling operation for combustor

$NO + 2.5CO + 1.5H_2O \rightarrow NH_3 + 2.5CO_2$



For case of reciprocating engine generator





Simulation analysis for effects of application of NTA system

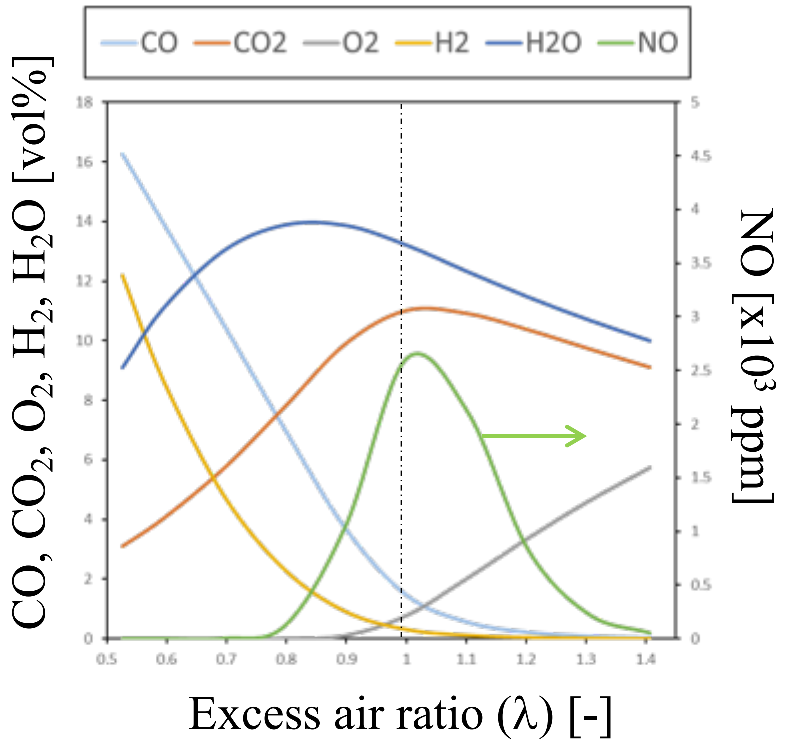
■ Simulation for composition of exhaust gas of combustion engine

Zero-dimensional simulation model

- The extended Zel'dovich mechanism for NO formation
- Six equilibrium reactions for combustion

$$\begin{cases} N_2 + O \rightleftarrows NO + N \\ N + O_2 \rightleftarrows NO + O \\ N + OH \rightleftarrows NO + H \end{cases}$$

Fuel (Model): Decane (T = 300 K, P = 1.5 atm)



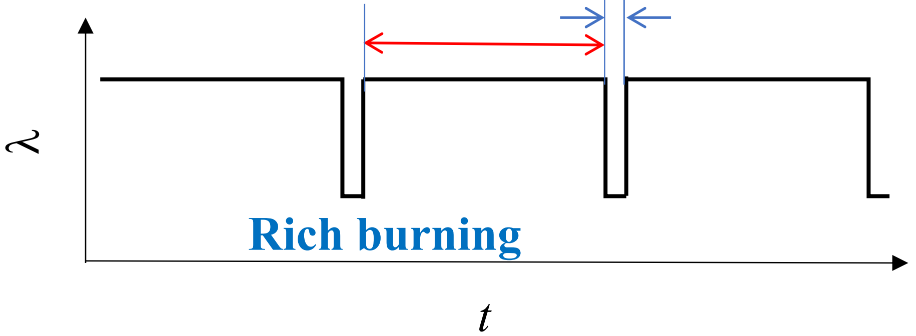
■ Search of optimum ratio of cycle time (rich-burn/lean-burn)

Component ratio in feed to the NTA reactor was the stoichiometric ratio for NO and (CO + H2), i.e. 2 : 5.

Operating conditions

Excess air ratio (λ) in rich-burn = 0.797,0.661,0.526

NO concentration in lean-burn = 500 – 2000 ppm



■ Simulation of NTA process

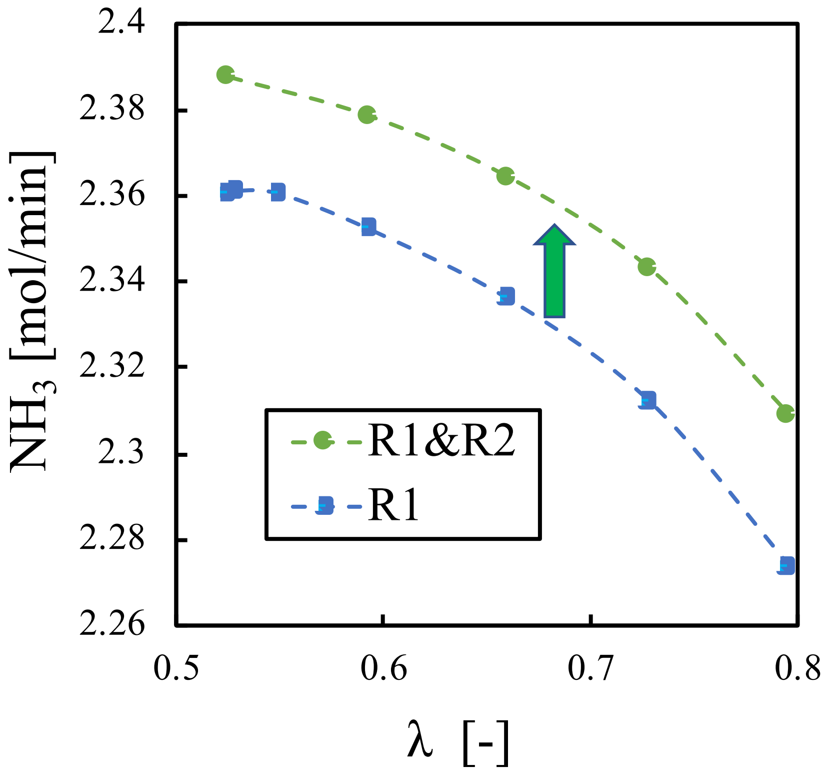
Equilibrium reaction model

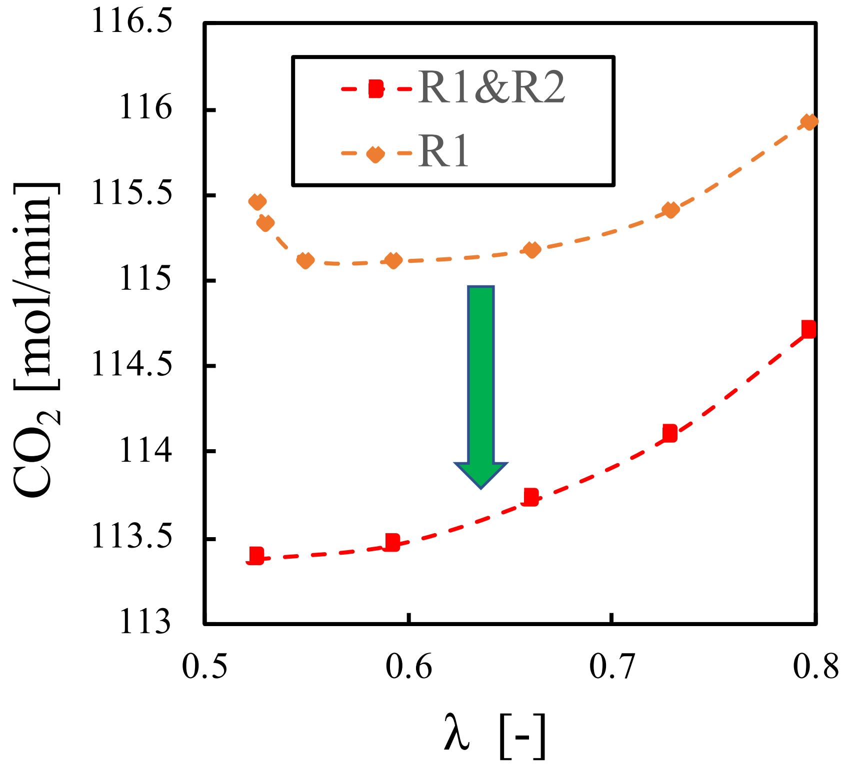
Gibbs reactor model (Aspen HYSYS V9)

Influence of lean-rich cycling operation to reduction in CO_2 emissions in NTA system

R1: $2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2$ **R2**: $2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O$

T = 250 °C
C_{NO} =2000 ppm





Reduction in CO_2 emmisions on the basis of the NH_3 SCR system ⇒ approx. 1%

※**Evaluation index**: Ratio of CO_2 emissions [mol] to the total heat of combustion for the consumed decane and the produced ammonia [kJ]

Influence of lean-rich cycling operation to reduction in CO_2 emissions in NTA system

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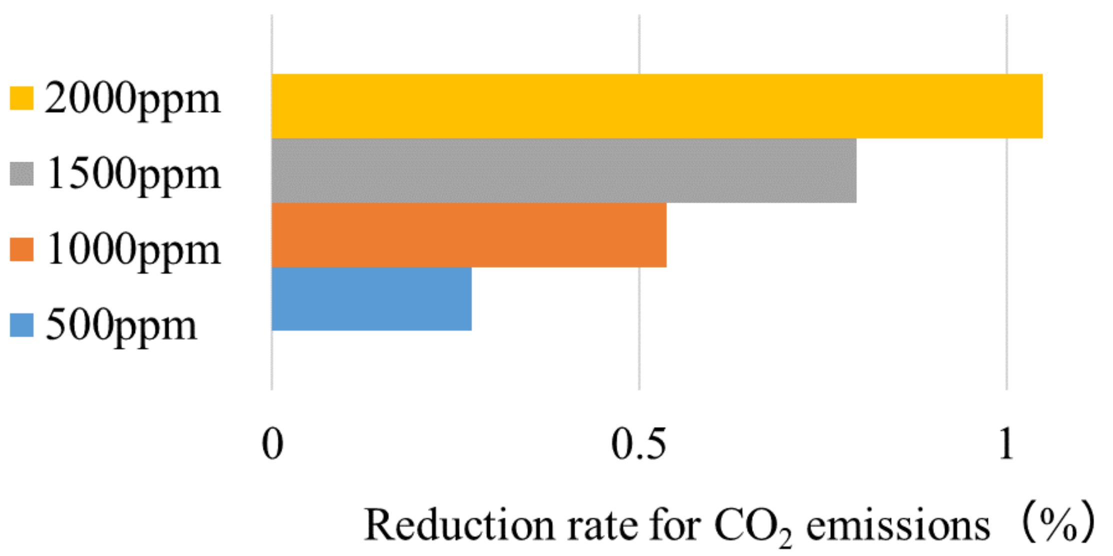
$$\text{Reduction rate for } CO_2 \text{ emissions } (\%) = \frac{(A_0 - A) * 100}{A_0}$$

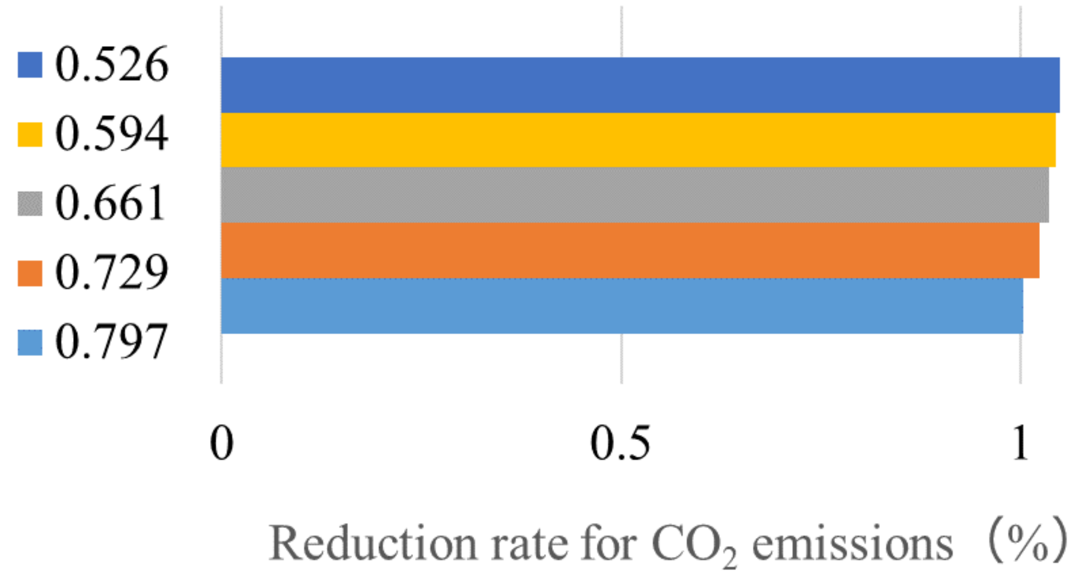
※A_0: NH3 SCR system

$$A = \frac{\text{Amount of } CO_2 \text{ emissions [mol]}}{\text{Heat of combustion for the consumed decane [kJ]} + \text{Heat of the produced NH3 [kJ]}}$$

Influence of NO conc. under lean-bun operation

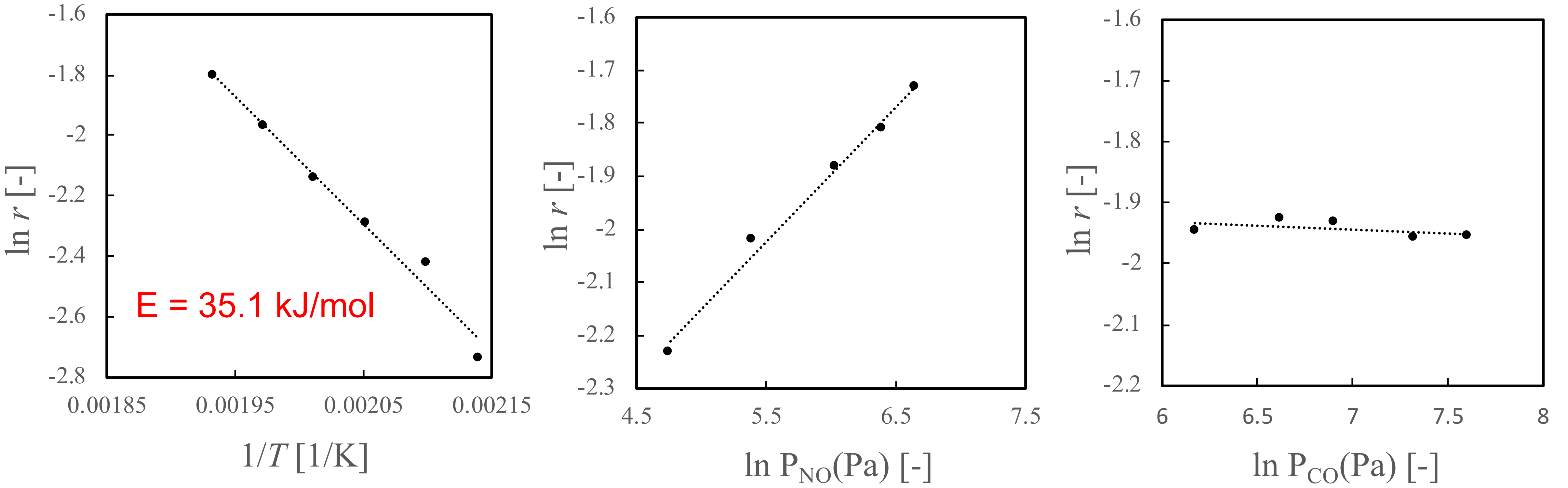


Influence of excess air ratio under lean-bun operation



Simulation of reactor performance of the developed catalyst (Pt/TiO_2 (A))

■ Kinetic analysis of NO-CO-H_2O reaction using Pt/TiO2 (A)



[**Experimental conditions**] T:200～250 ° C , C_{NO}:1000-8000 ppm, C_{CO}:5000-20000 ppm, C_{H2O}:6000-18000 ppm, Total flow rate: 250ml/min, Catalyst : 0.25g

Influence of reaction temperature to behavior of NTA system

R1: $2NO + 5CO + 3H_2O \Rightarrow 2NH_3 + 5CO_2$
R2: $NO + (5/2)H_2 \Rightarrow NH_3 + H_2O$
R3: $3NO + 2NH_3 \Rightarrow (5/2)N_2 + 3H_2O$
R4: $2NO + H_2 \Rightarrow N_2O + H_2O$
R5: $2H_2 + 2NO \Rightarrow 2H_2O + N_2$
R6: $2CO + 2NO \Rightarrow 2CO_2 + N_2$
R7: $CO + H_2O \Rightarrow CO_2 + H_2$

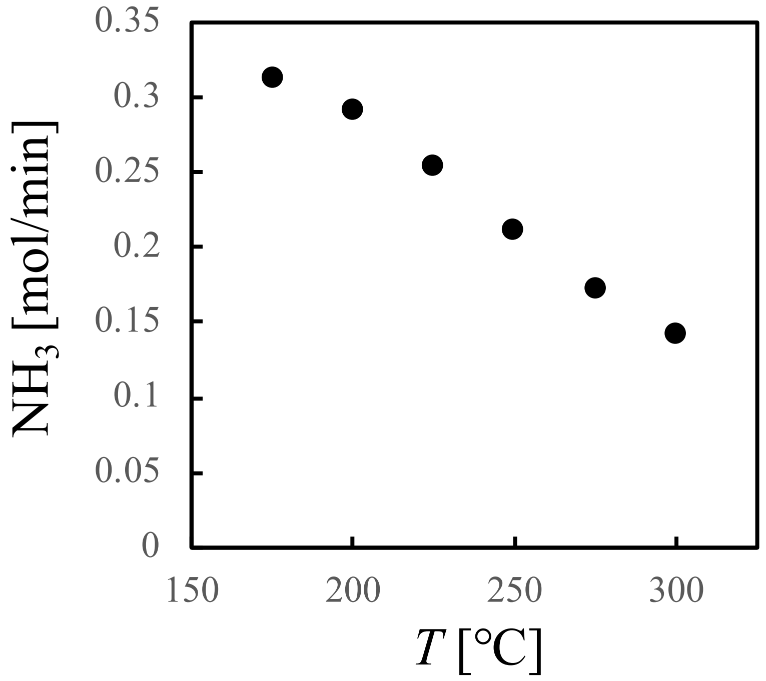
Reaction	A(1/s)	Ea(KJ/mol)
R1	1.76×10^{7}	35.1
R2	2.61×10^{16}	128
R3	1.25×10^{12}	91.1
R4	2.28×10^{10}	85.0
R5	5.29×10^{7}	69.2
R6	1.92×10^{6}	52.3
R7	1.21×10^{2}	56.7

R1 $$r_1 = A_1 exp\left(-\frac{E_{a,1}}{RT}\right) X_{NO} X_{CO} X_{H2O} C_{PGM}$$

R2 $$r_2 = A_2 exp\left(-\frac{E_{a,2}}{RT}\right) X_{NO} X_{H2} C_{PGM}$$

PFR Model
(SimCentral 3.3)

C_{NO} =2000 ppm
<rich-burning>
$\lambda = 0.5935$
$t_R = 1.08$ s



M. Li et al.; *Applied Catalysis B: Environmental*, **242**, 469-484 (2019)

Conclusions

- The developed NTA process using Pt/TiO_2 has demonstrated to be effective under low temperature condition (< 250 °C) by controlling feed of CO, by experiments and simulations.
- It was expected that positive emission of nitric oxide in combustor could enhance reduction of CO_2 emissions by combing with NTA reaction (NO-CO-H_2O reaction).
- Future work is to synthesize the NTA reaction process with a process for adsorption and concertation of nitric oxide, and to asses effects of reduction in CO_2 emissions for the unified system.

Type of combustor

- Flow rate
- Composition
- Temperature
- Pressure

(i) Adsorption & desorption of NO

physical or chemical ?

(ii) Conversion of NO to NH_3

Effect of existence of O_2