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NH_3 Energy+ (October 31, 2018)

Analysis of influence of operating pressure on dynamic behavior of ammonia production over ruthenium catalyst under high pressure condition

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Agenda

- Introduction: background for development of ruthenium (Ru) catalyst for ammonia production
- Influence of pressure to space-time yield (STY) of Ru-Cs/MgO catalyst for NH_3 production, and its kinetic analysis by Temkin equation model
- Influence of pressure to STY of Ru/CeO_2 catalyst for NH_3 production under high pressure condition, and application of different macroscopic model to kinetic analysis
- Summary

Background

Plant for production of ammonia fuel will be much smaller than those currently used by considering deployment of distributed energy system using green hydrogen.

Direction in process development [1]

■ Lower pressure condition

⇒ reduction of power for feed gas compression

■ Lower temperature operation

⇒ higher ammonia concentration under limitation of equilibrium

■ More efficient start-up operation

Expectation of high activity of Ru catalyst

[1] M. Reese et al., *Ind. Eng. Chem. Res.*, **55**, 3742-3750 (2016)

Demonstration plant in Fukushima renewable energy institute, AIST (FREA)

M. Kai (JGC) et al.; Demonstration of CO_2-Free Ammonia Synthesis Using Renewable Energy-Generated Hydrogen (16:30 – 16:45)

Purpose of this study

<u>Previous studies for ammonia synthesis using Ru catalyst</u>

Ru/ Al_2O_3, Ru/MgO, Ru-Cs / Al_2O_3, Ru-Cs / MgO, Ru-Ba / MgO, Ru-La / MgO, …

[1] K. Aika, *Catal. Today*, 286, 14-20 (2017)
[2] S. E. Siporin and R. J. Davis, *J. Catal.*, **225**, 359-368 (2004)
[3] F. Rosowski et al., *Catal. Lett.*,**36**, 229-235 (1996)

However, there is a small number of studies for influences of operation variables (pressure, temperature, H_2/N_2 flow ratio) for design of ammonia synthesis process using Ru/CeO_2.

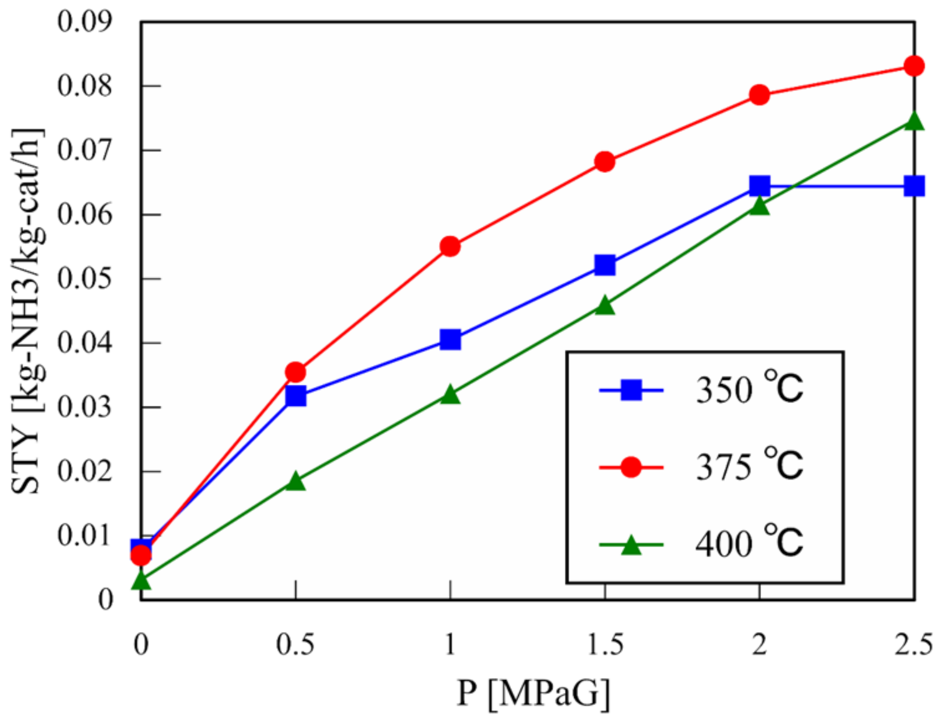
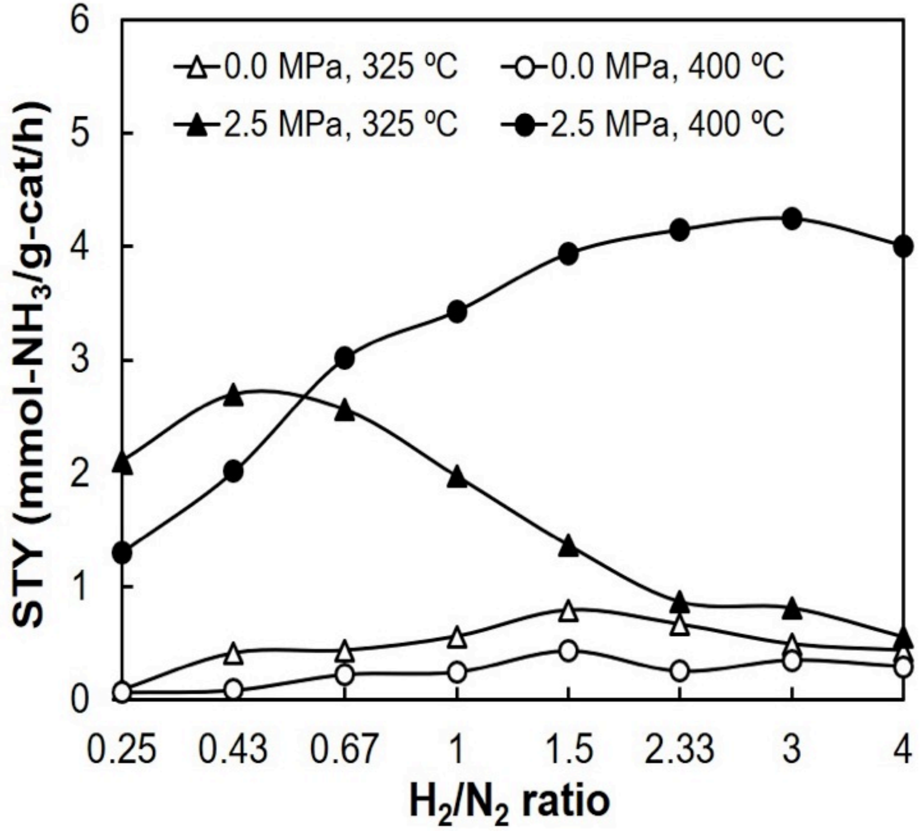


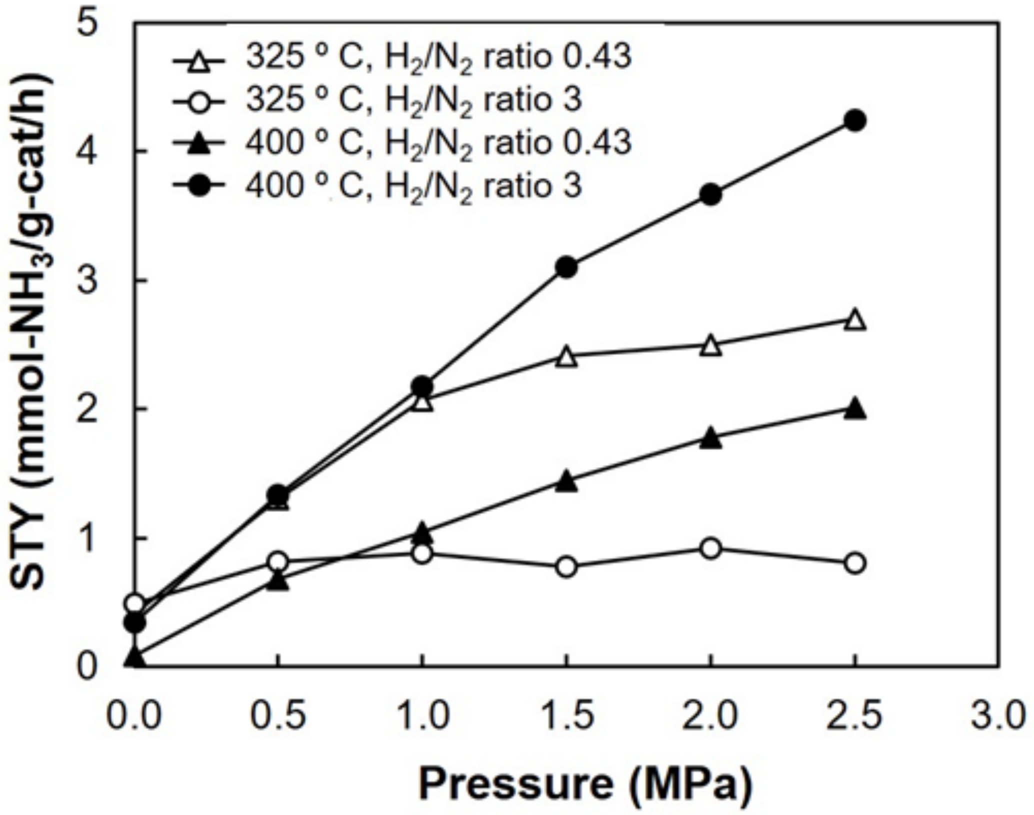
Fig. Influence of pressure to reaction behavior on Ru/CeO_2

A purpose of this study is to clarify influence of operating pressure to dynamic behavior of ammonia production over the Ru catalysts (Ru-Cs/MgO, Ru/CeO_2) . Characteristics of reaction behavior on Ru catalyst will be discussed by using different types of macro kinetic models (LHHW equation models).

Influence of pressure to space-time yield (STY) of Ru-Cs/MgO catalyst for NH_3 production

The loadings of Ru and Cs on MgO support in the as-prepared catalyst were 2.0 and 6.4 wt-%, respectively.





Kinetic analysis of NH_3 production on Ru catalyst using Temkin equation model

$N_2 + 2^* \leftrightarrow 2N(a)$ (i)

$H_2 + 2^* \leftrightarrow 2H(a)$ (ii)

$N(a) + H(a) \leftrightarrow NH(a) + ^*$ (iii)

$NH(a) + H(a) \leftrightarrow NH_2(a) + ^*$ (iv)

$NH_2(a) + H(a) \leftrightarrow NH_3 + 2^*$ (v)

RDS: $r = k_1 p_N \theta_v^2 - k_2 \theta_N^2$

$K_1 = \theta_H^2 / p_H \theta_v^2$ $K_2 = p_A \theta_v^4 / \theta_N \theta_H^3$

$\theta_v + \theta_H + \theta_N = 1$

Langmuir-Hinshelwood (LHHW) equation model

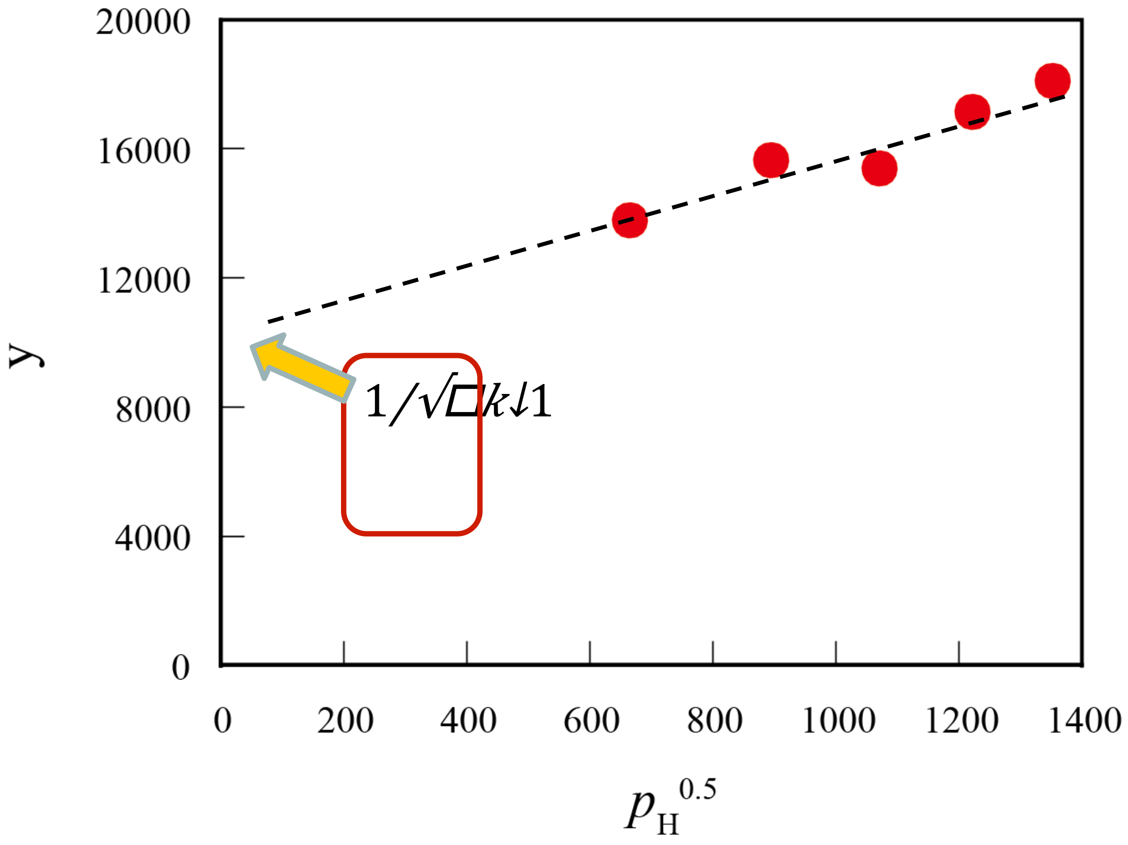
$r = k_1 [p_N - p_A^2 / (K_p^2 p_H^3)] / [1 + (K_H p_H)^{0.5} + (K_1^{-1.5} K$

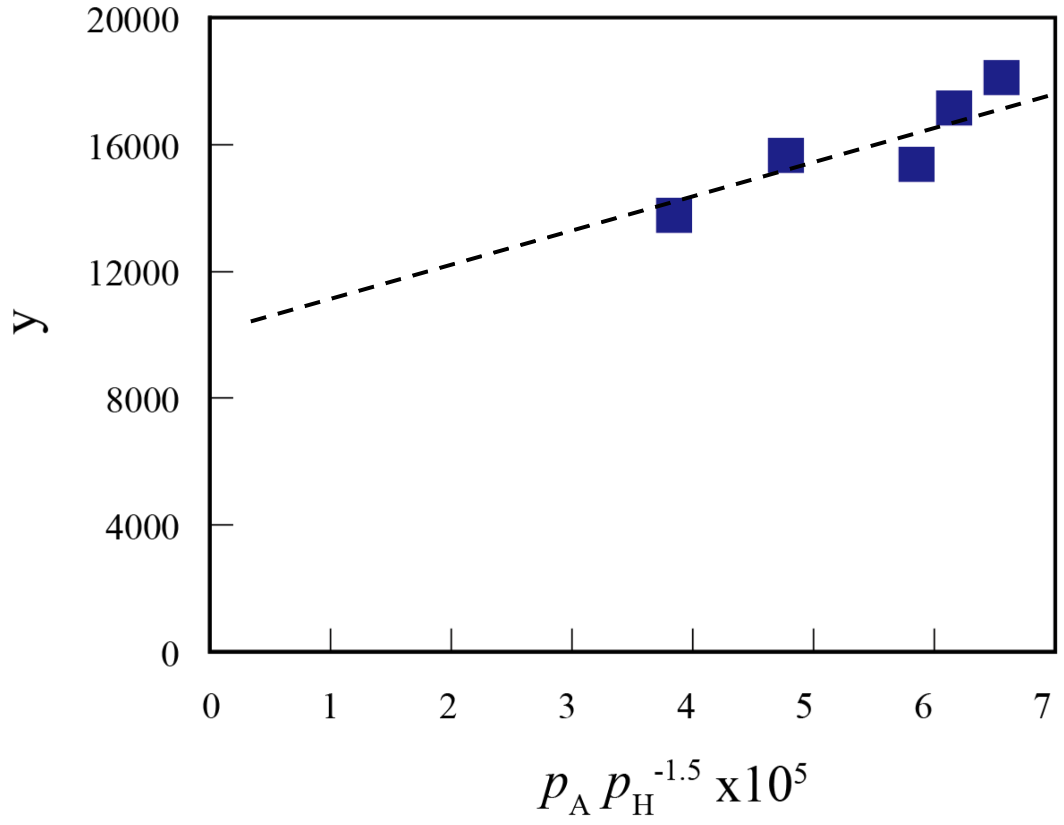
For graphical analysis of experimental data

$[p_N - p_A^2 / (K_p^2 p_H^3) / r]^{1/2} = 1/\sqrt{k_1} + \sqrt{K_H / k_1}\, p_H^{0.5} + (1/\sqrt{k_1})(1/K_1^{1.5} K_2) p_A p_H^{-1.5}$

Kinetic analysis of NH_3 production on Ru-Cs/MgO

- T=400℃, $H_2/N_2=3$, P=0 – 2.5 MPaG

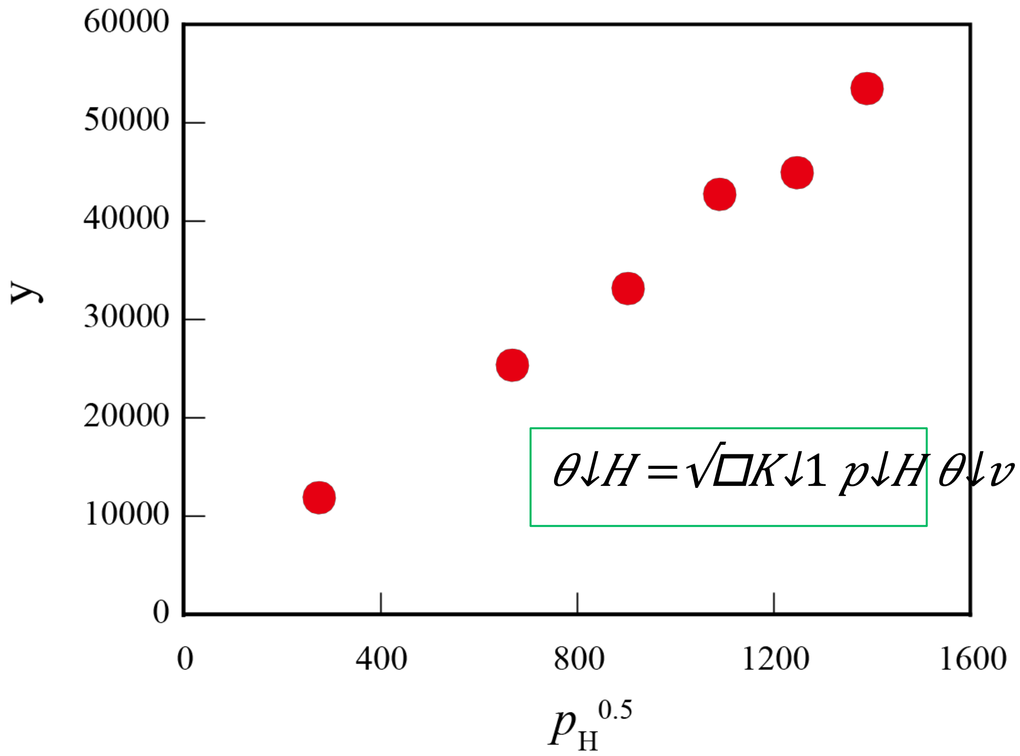


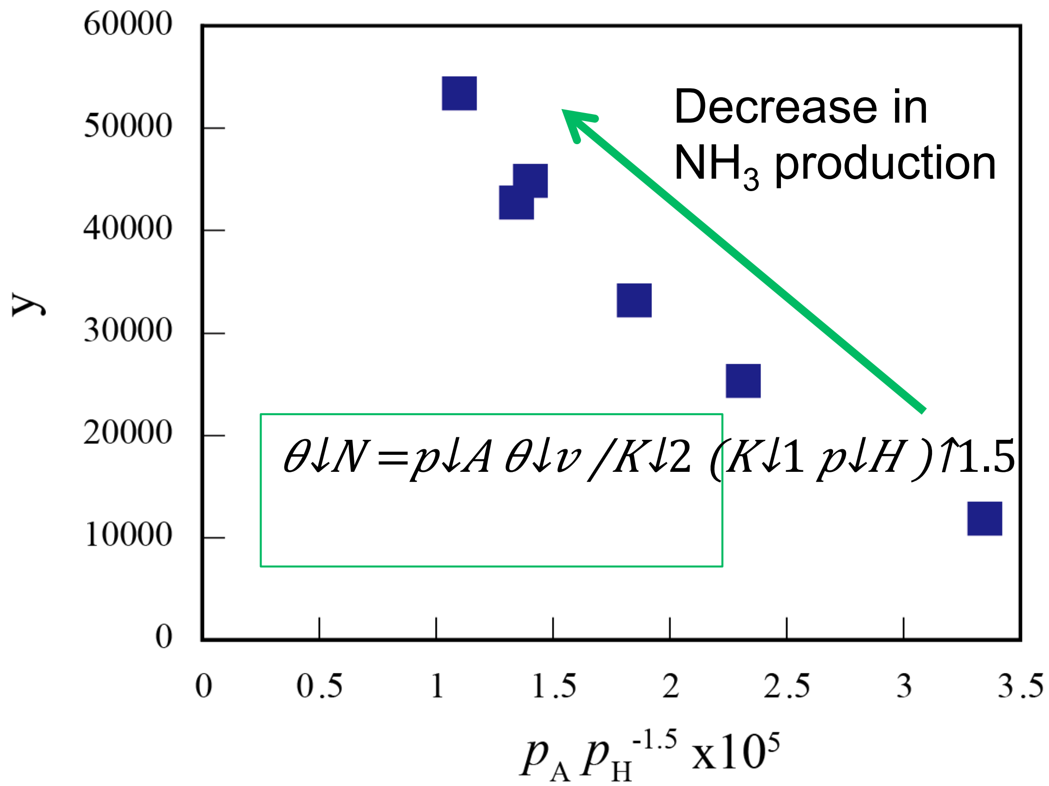


$$y=\left[\frac{p_N-p_A^2/(K_p^2\, p_H^3)}{r}\right]^{1/2}=\frac{1}{\sqrt{k_1}}+\sqrt{\frac{K_H}{k_1}}\,p_H^{0.5}+\left(\frac{1}{\sqrt{k_1}}\right)\left(\frac{1}{K_1^{1.5}\,K_2}\right)p_A\,p_H^{-1.5}$$

Kinetic analysis of NH_3 production on Ru-Cs/MgO

- T=325℃, $H_2/N_2=3$, P=0 – 2.5 MPaG

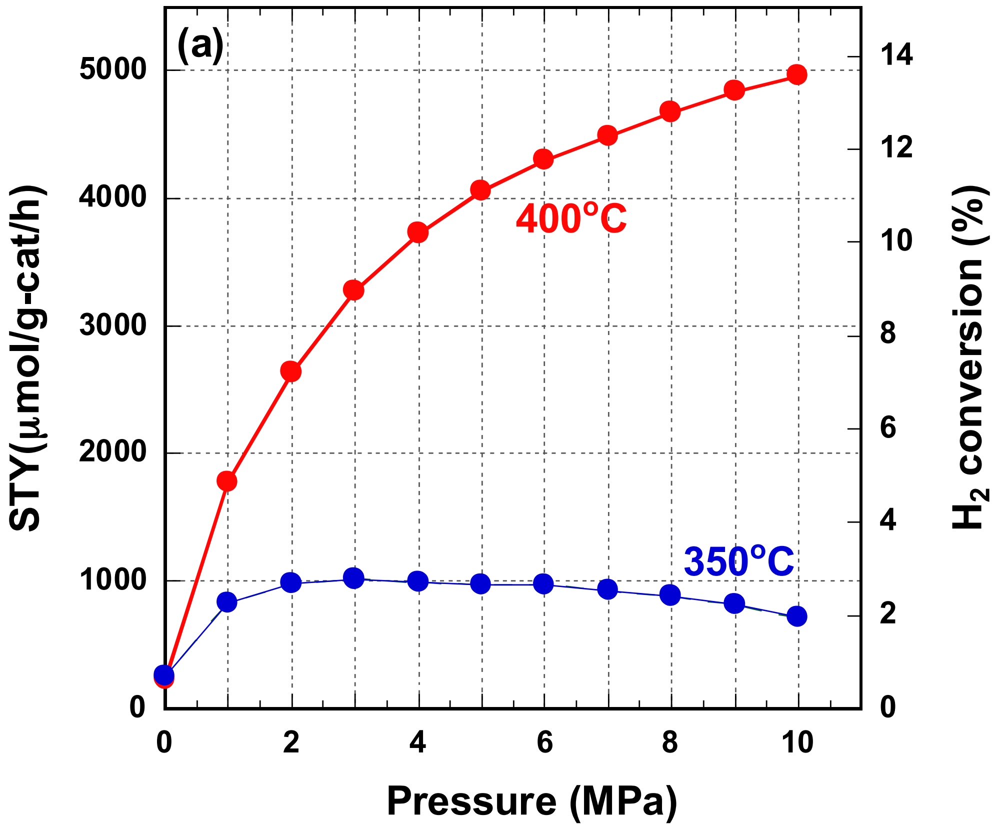




The surface concentration of adsorbed nitrogen is higher than that of hydrogen at higher temperature conditions. It is considered by H_2-TPD experiments that this decrease in hydrogen adsorption is due to the significant increase in the competitive adsorption of ammonia species.

Laboratory kinetic experiments for 3 wt% Ru/CeO_2

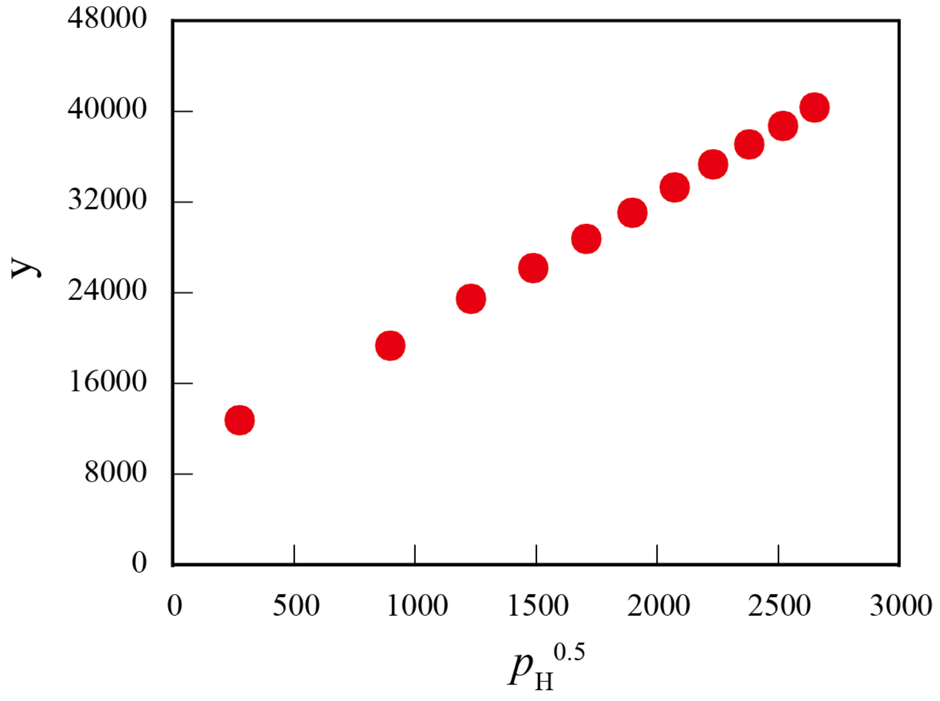
- Experimental set up: SUS tubular reactor (ϕ14 mm x 370 mm) , catalyst volume ≒ 2 mL
- Operating condition for pretreatment of catalyst:
  T = 600 ℃, P = 0 MPaG, H_2 / N_2 flow ratio (γ) = 3.0, t = 30 min
- Operating condition for ammonia synthesis:
  T = 325 – 425 ℃, P = 0 – 10 MPaG, H_2 / N_2 flow ratio (γ) = 0.25 – 4.0, SV = 3000 h^{-1}

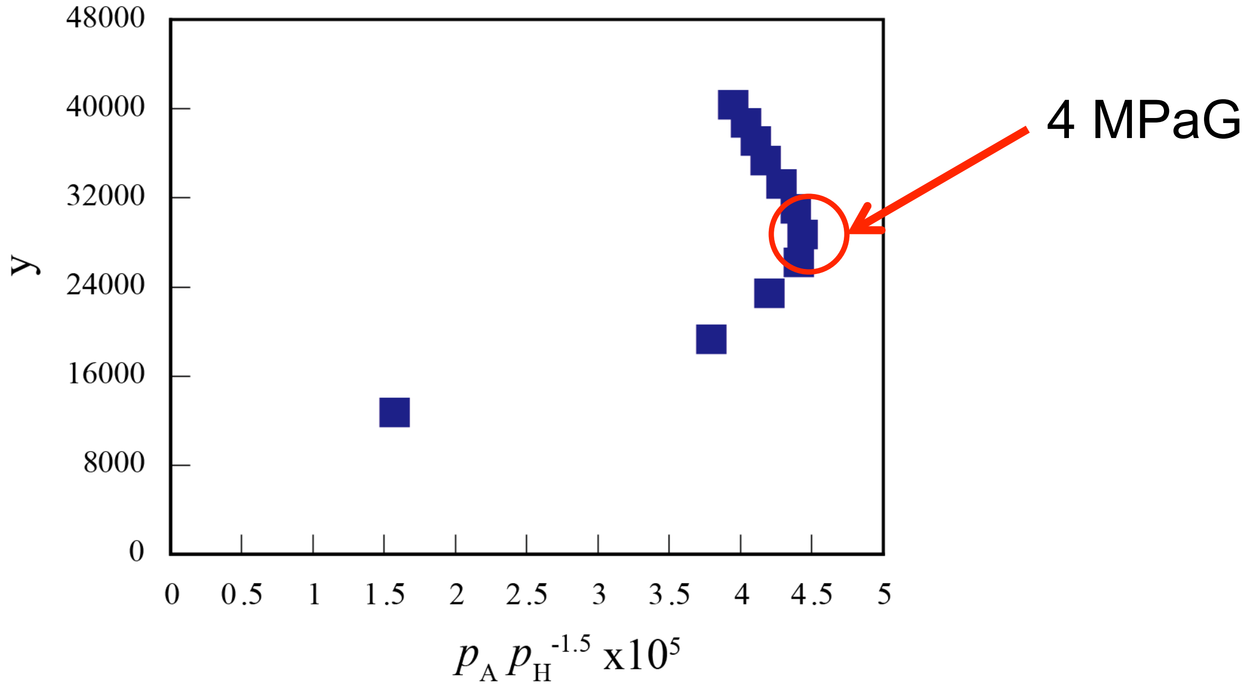


When flow ratio of H_2 to N_2 (γ) was 3 and temperature was 400 ℃, catalytic activity for NH_3 production increased with operating pressure (< 10 MPaG). Moreover, it was seen that STY was increased by setting the value of γ at 1.

Kinetic analysis of NH_3 production on Ru/CeO_2

- T=400℃, H_2/N_2=3: Applicabitity of Temkin equation model is poor.





$$r = k \cdot P_N^l \cdot P_H^m \cdot P_{NH3}^n$$

l [−]	m [−]	n [−]
0.37	0.30	-2.1

In kinetic analysis of NH_3 production on Ru/CeO_2 that was prepared by using other REO support, increase in *m* (negative to positive) was seen by increasing pressure.

Application of macro kinetic model based on different mass balance equation for absorbed species

$N_2 + 2^* \leftrightarrow 2N(a)$ (i)
$H_2 + 2^* \leftrightarrow 2H(a)$ (ii)
$N(a) + H(a) \leftrightarrow NH(a) + {}^*$ (iii)
$NH(a) + H(a) \leftrightarrow NH_2(a) + {}^*$ (iv)
$NH_2(a) + H(a) \leftrightarrow NH_3 + 2^*$ (v)

RDS: $r = k_1 p_N \theta_v^2 - k_2 \theta_N^2$

$K_1 = \theta_H^2 / p_H \theta_v^2$ $K_2 = p_A \theta_v^4 / \theta_N \theta_H^3$

$\theta_v + \theta_H + \theta_{NH2} = 1$

Langmuir-Hinshelwood (LHHW) equation model

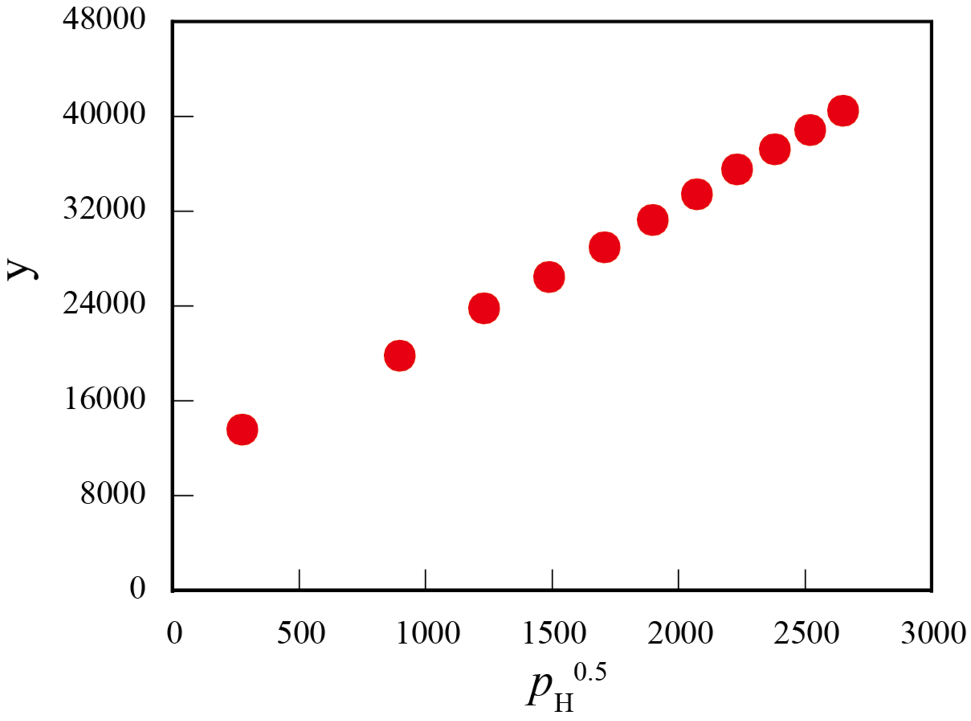
$$r = k\left(p_N - p_A^2 / K^2 p_H^3\right) / \left(1 + (K_1 p_H)^{0.5} + K_a p_A / p_H^{0.5}\right)^2$$

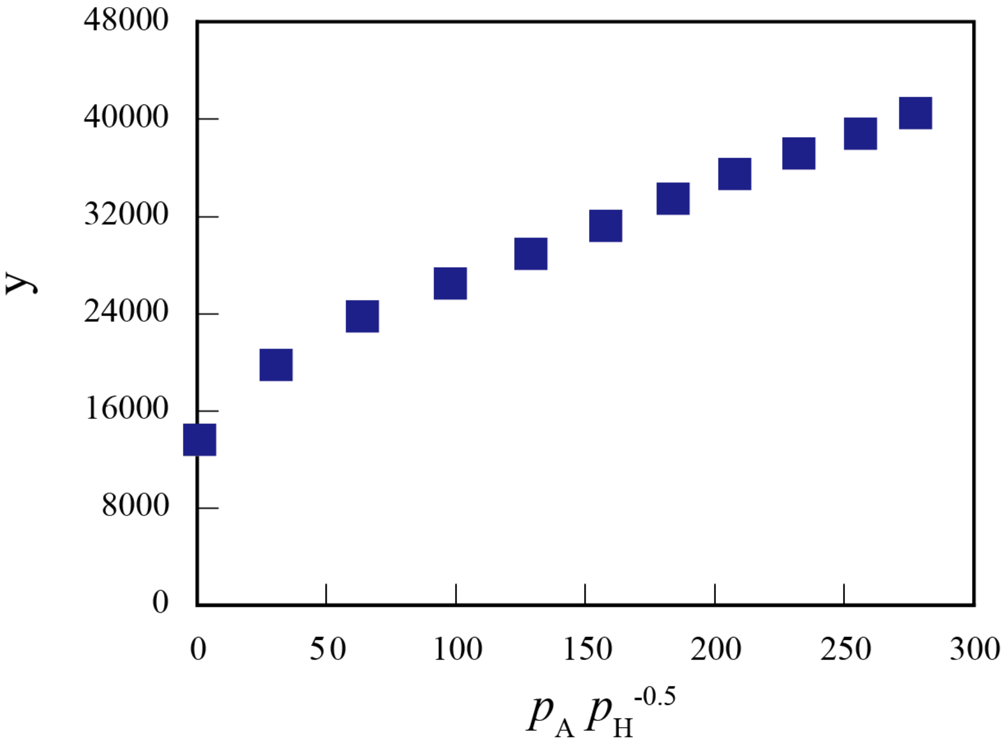
For graphical analysis of experimental data

$$\left[p_N - p_A^2 / K^2 p_H^3 \; / r\right]^{0.5} = 1/k^{0.5} + (K_1/k)^{0.5} p_H^{0.5} + K_a /$$

Kinetic analysis of NH_3 production on Ru/CeO_2

- T=400℃, $H_2/N_2=3$





$$r = k\left(p_N - p_A^2 / K^2 p_H^3\right) / \left(1 + (K_1 p_H)^{0.5} + K_a p_A / p_H^{0.5}\right)^2$$

It was considered that competitive adsorption of hydrogen radical and nitrogen hydride radicals was a key factor for retardation of progress of ammonia production by using Ru/CeO_2.

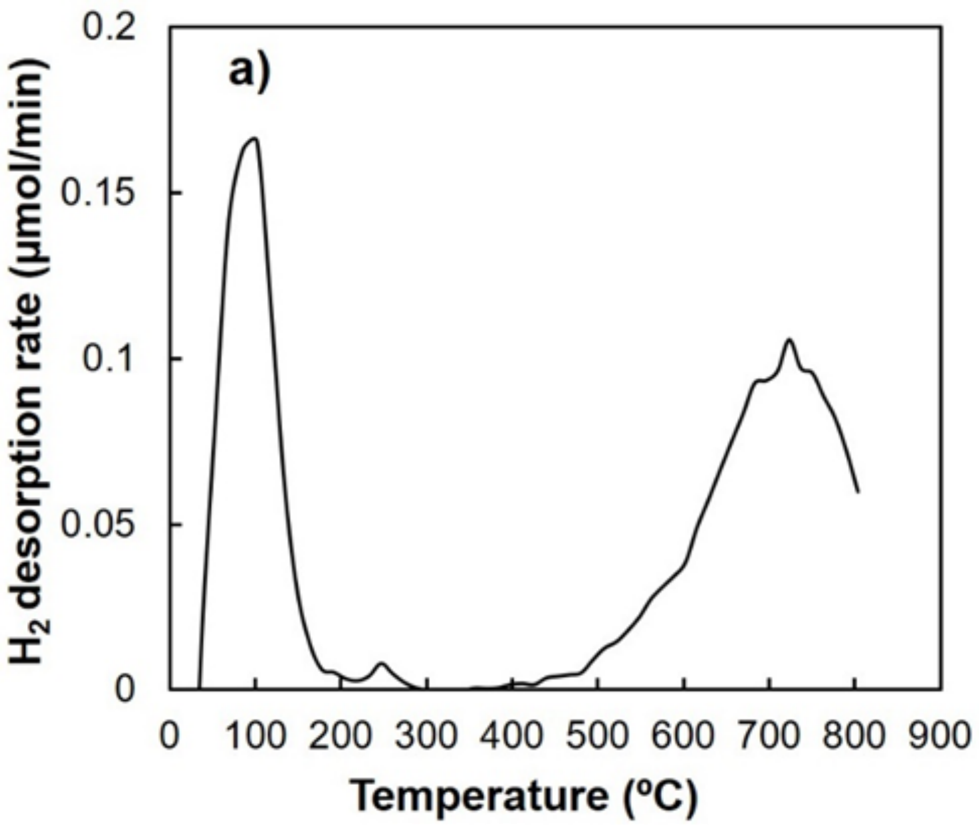
Summary

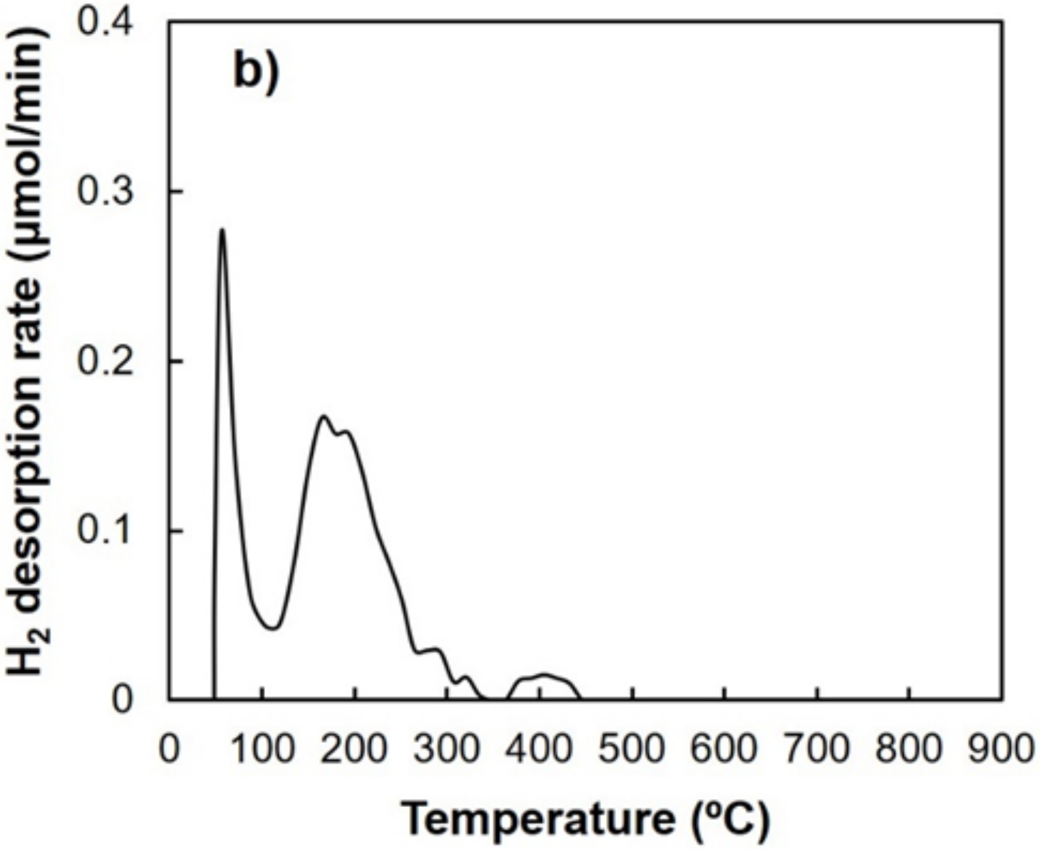
- By graphical analysis of STY data for Ru-Cs/MgO by using Temkin equation model, it was seen that higher temperature condition is preferable due to decrease in hydrogen adsorption, which could lead to increase in high catalytic activity with operating pressure.
- By graphical analysis of STY data for Ru/CeO_2 by using macro kinetic model based on different mass balance equation for absorbed species, it was considered that competitive adsorption of hydrogen radical and nitrogen hydride radicals was a key factor for enhancement of STY under high pressure conditions.

Acknowledgement

This work was supported by Council for Science, Technology and Innovation (CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), "Energy carriers" (funding agency: Japan Science and Technology Agency, JST).

H2-TPD profile of Ru-Cs/MgO catalyst



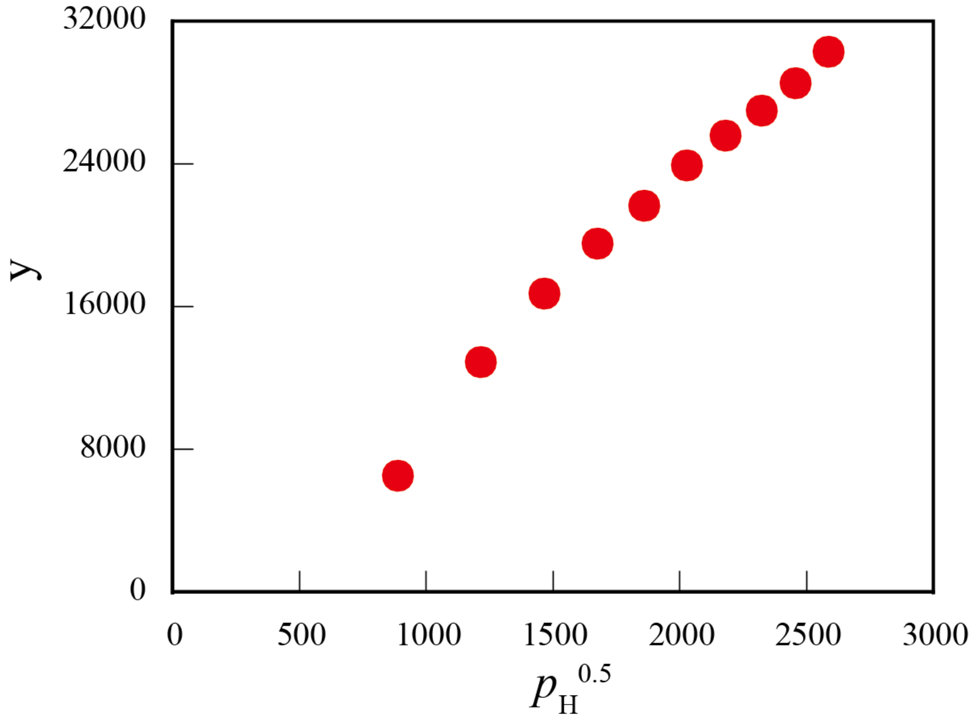


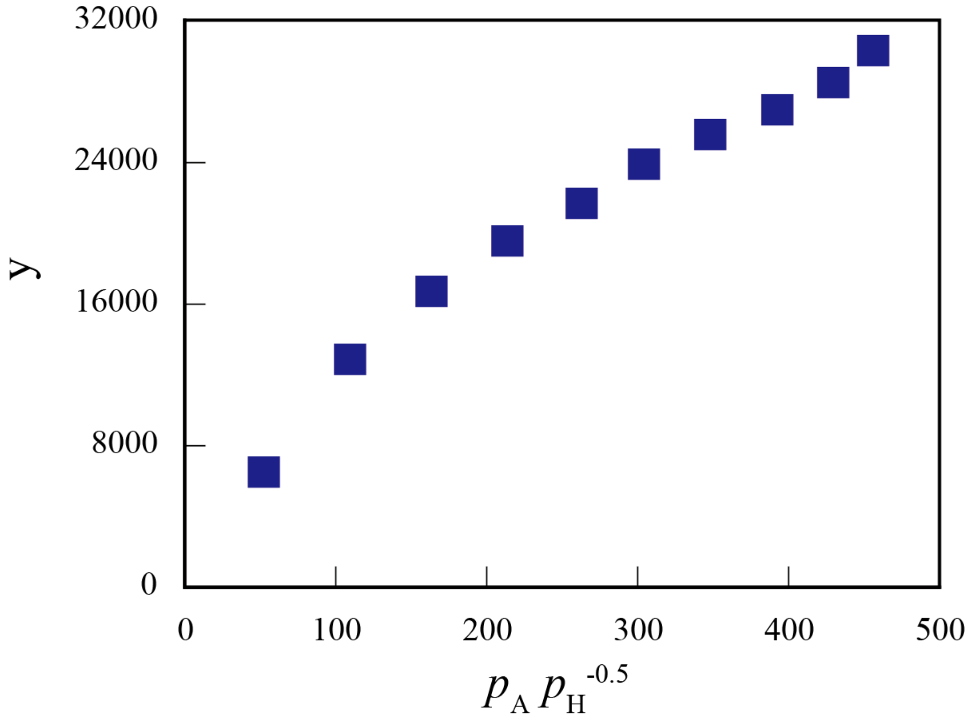
a) TPD under Ar flow

b) TPD under NH_3/Ar flow

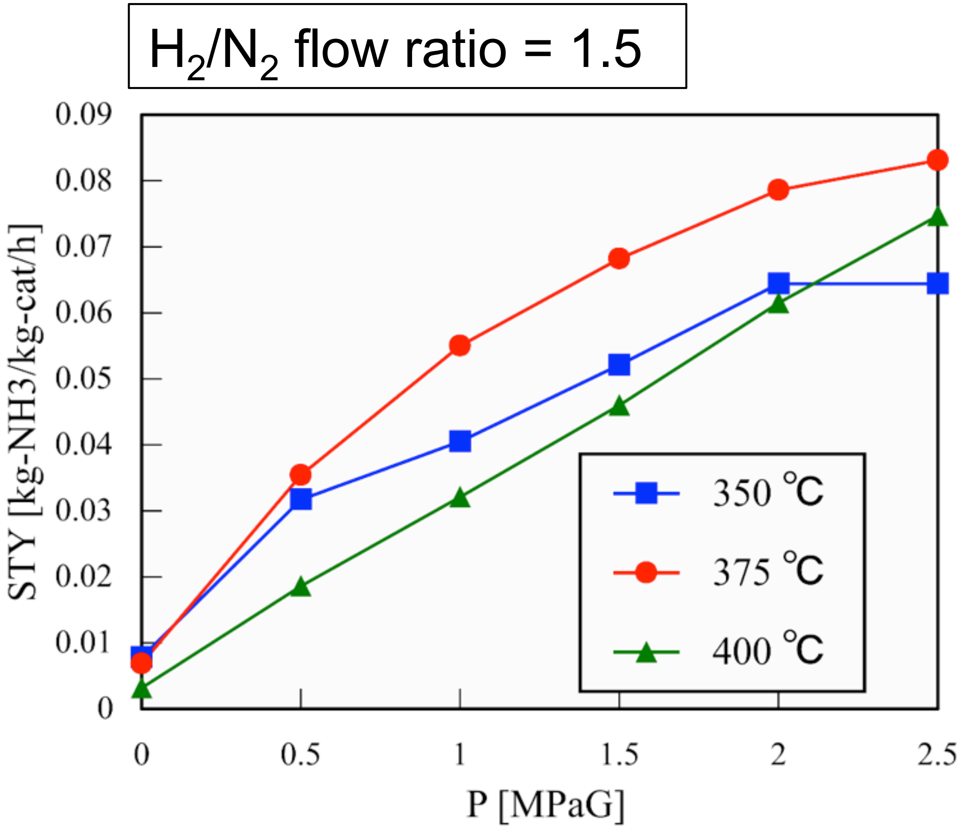
Kinetic analysis of NH_3 production on Ru/CeO_2 that was prepared by using other REO support

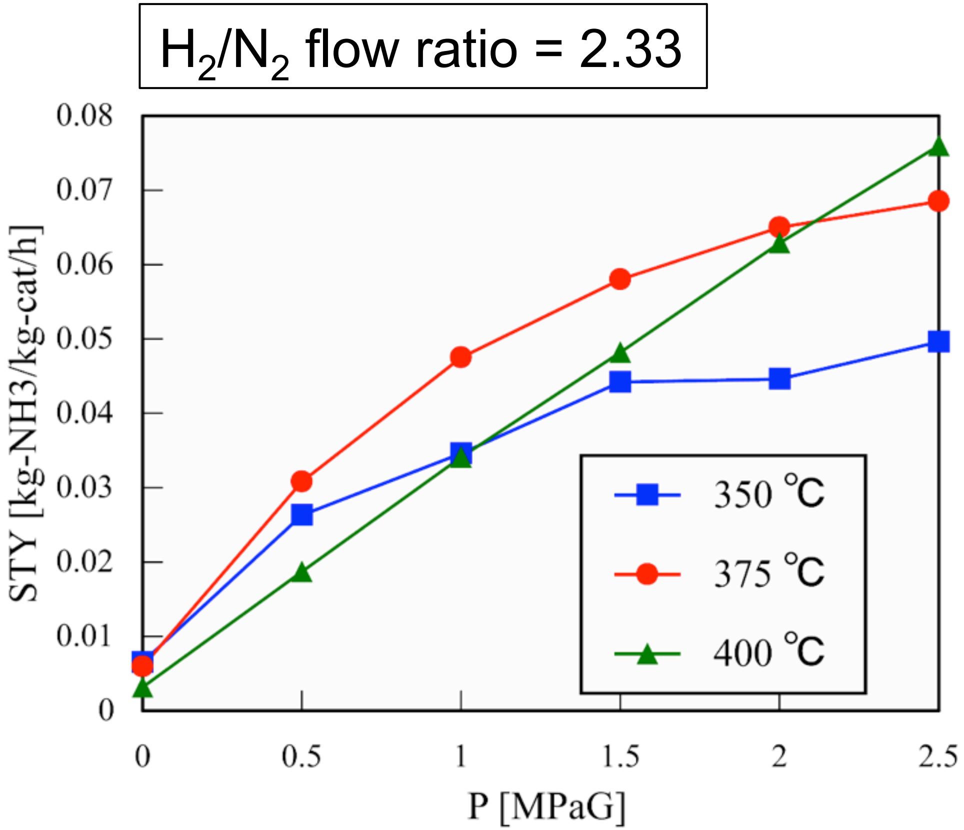
- T=400℃, H_2/N_2=3





Influence of H2/N2 to STY for Ru/CeO_2 under low pressure conditions





It is expected that increase in operating pressure could enhance reactivity of Ru/CO_2 in a case when T = 400 ℃.