2017 AIChE Annual Meeting
NH_3 Energy⁺ - Enabling Optimized, Sustainable Energy and Agriculture
NH_3 Energy Fuel Synthesis I (November 2, 2017)

Influence of H_2/N_2 ratio on dynamic behavior of ammonia production on Ru catalyst under low pressure condition

Hideyuki Matsumoto, Javaid Rahat, Tetsuya Nanba
Renewable Energy Research Center (RENRC)
National Institute of Advanced Industrial Science and Technology (AIST)

Agenda

- Introduction: background for development of ruthenium (Ru) catalyst for ammonia production
- Analysis of kinetic data for the developed catalyst supported by a certain rare-earth metal oxide (REO) (Ru-catalyst A) which are acquired by changing H_2/N_2 flow ratio
- Effects of addition of the REO to Ru/MgO (Ru-catalyst B)
  – comparison of preparation methods
- Introduction of construction of demonstration plant in FREA
- 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

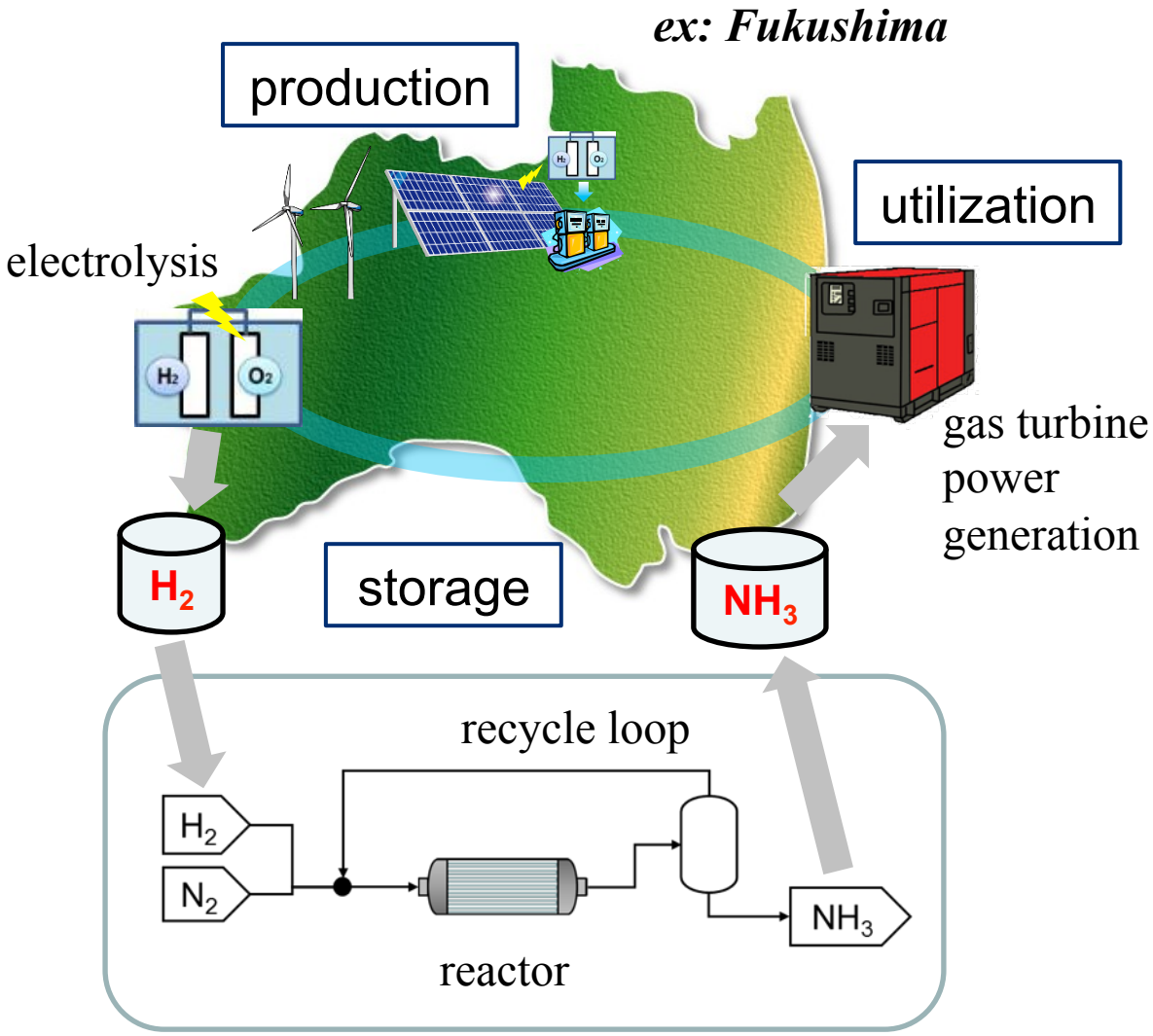
⇒ reduction of power for feed gas compression

- 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)

Purpose of this study

Previous studies for ammonia synthesis using Ru catalyst

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)

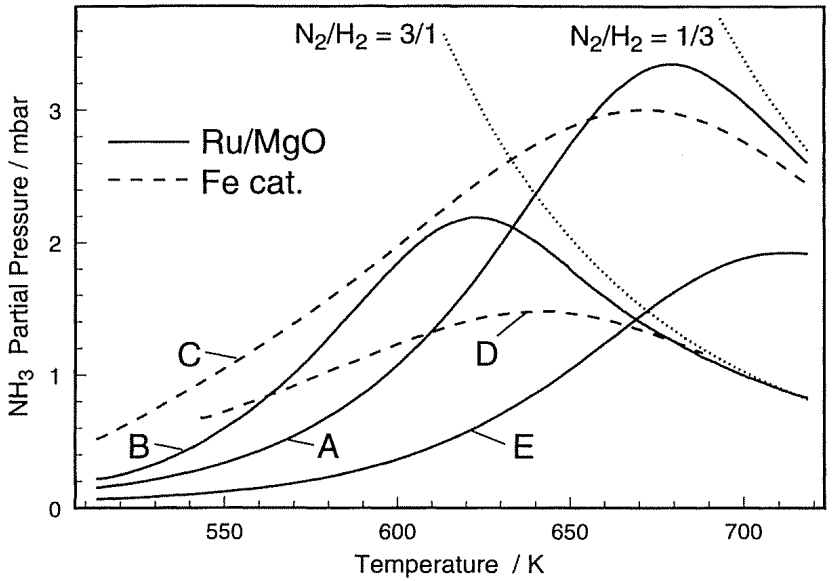


Fig. Influence of N_2/H_2 flow ratio [3]

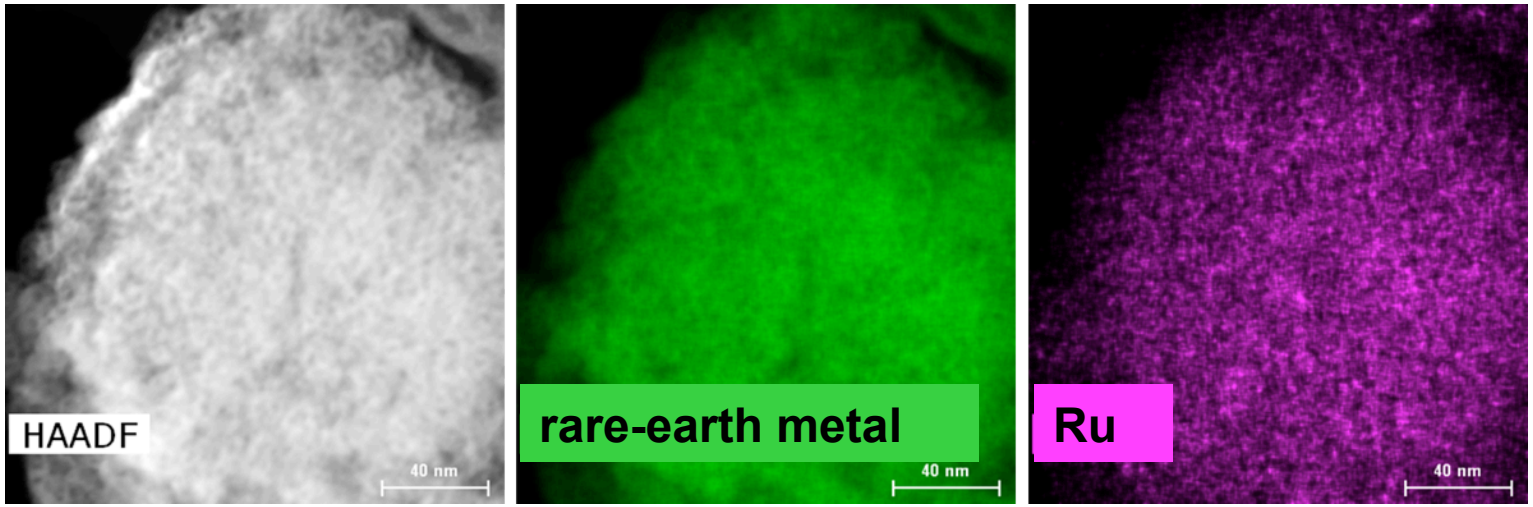
However, there is a small number of studies for influences of operation variables (pressure, temperature, H_2/N_2 flow ratio) for design of ammonia synthesis process using the developed Ru catalyst supported by a certain rare-earth metal oxide (REO) (Ru-catalyst A).

The 1st step

A purpose of this study is to clarify influence of H_2/N_2 flow ratio to dynamic behavior of ammonia production by Ru-catalyst A under low pressure conditions (< 2.5 MPa) . Then effects of addition of REO to Ru/MgO will be discussed.

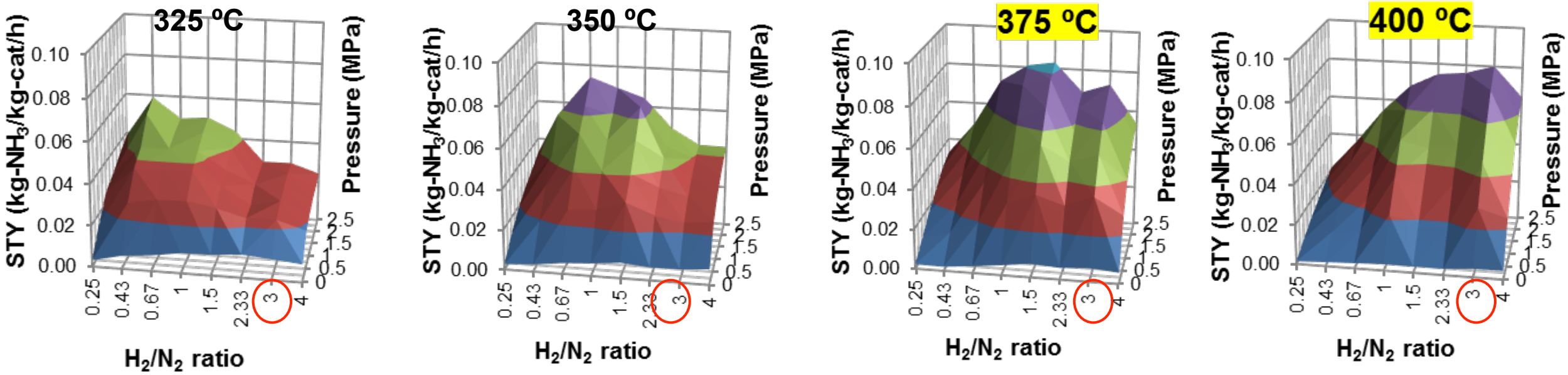
Laboratory kinetic experiments for 3 wt% Ru-catalyst A

- 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:
  $T = 325 – 425$ ℃, $P = 0 – 2.5$ MPaG, H_2 / N_2 flow ratio (γ) = 0.25 – 4.0



STEM images of Ru-catalyst A

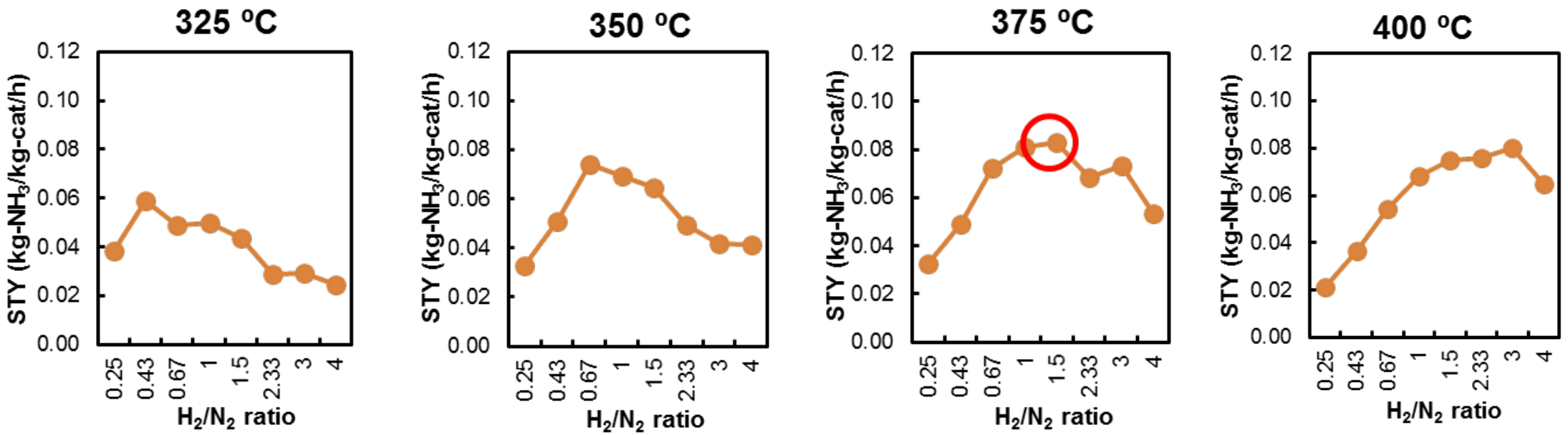
Data maps for space time yield (STY) for NH_3 production by using 3 wt% Ru-catalyst A



Stoichiometric H_2 / N_2 flow ratio (=3) is not suitable for all temperature & pressure conditions.

Influence of H_2/N_2 flow ratio to STY

P =2.5 MPaG

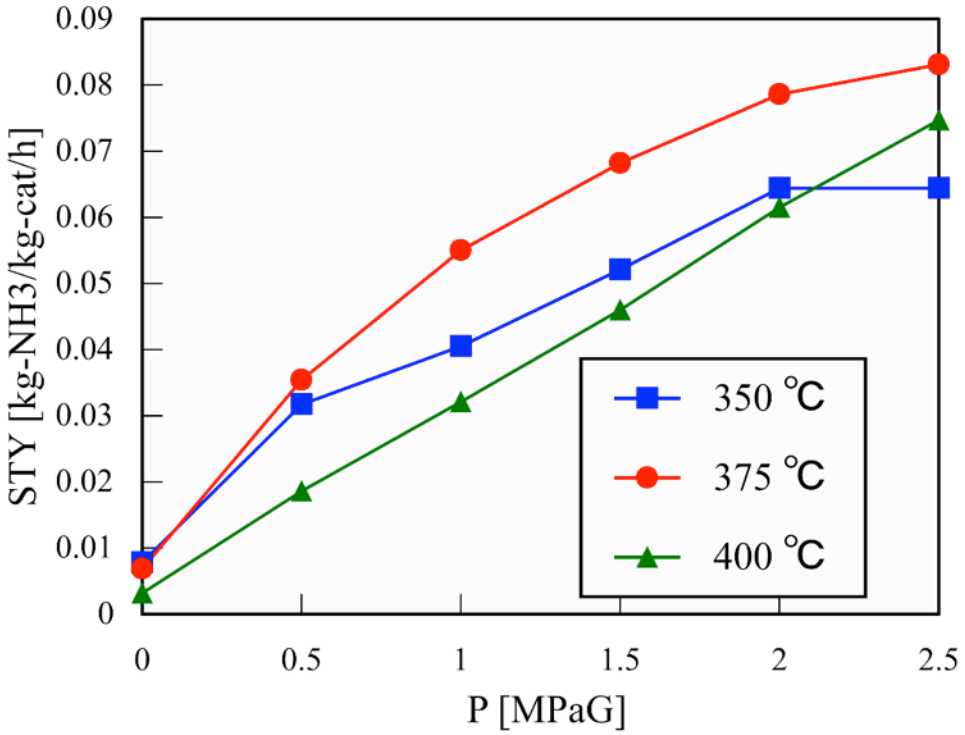


$$r = k \cdot P_{\mathrm{N}}^{l} \cdot P_{\mathrm{H}}^{m} \cdot P_{\mathrm{NH3}}^{n}$$

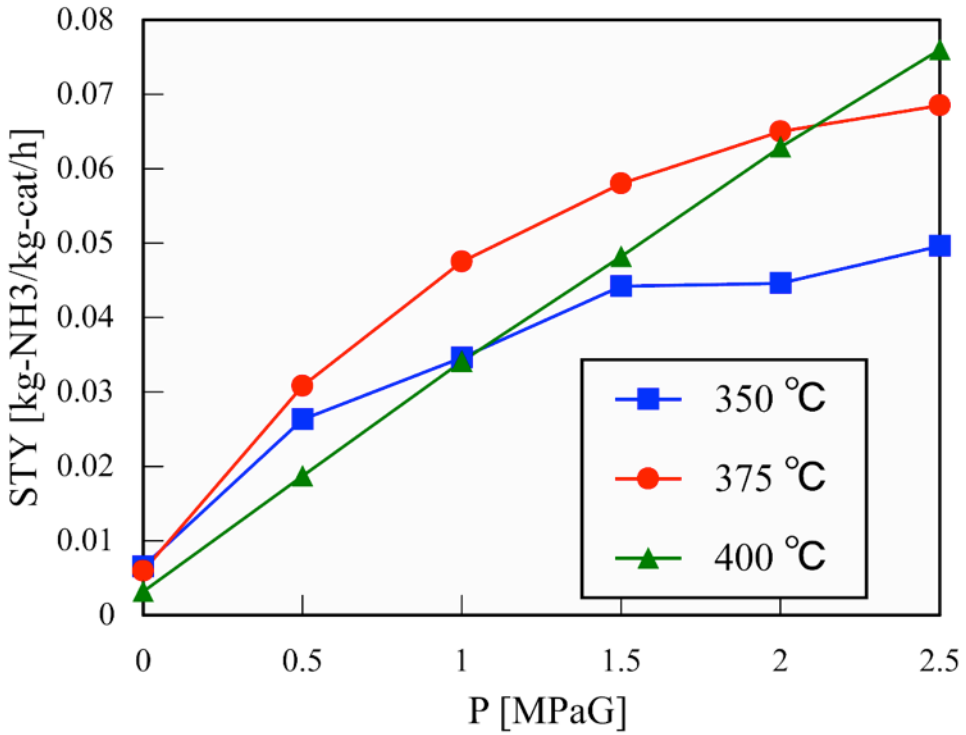
	325 ℃		400 ℃	
	$H_2 / N_2 < 3$	$H_2 / N_2 > 3$	$H_2 / N_2 < 3$	$H_2 / N_2 > 3$
H_2	0.55	0.04	0.83	0.3
N_2	0.46		0.37	
NH_3	-1.3		-2.1	

Influence of operating pressure to STY

H_2/N_2 flow ratio = 1.5



H_2/N_2 flow ratio = 2.33

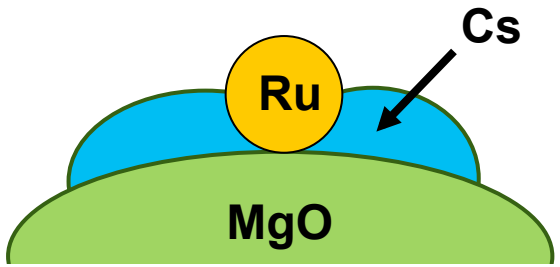


It is expected that increase in operating pressure could enhance reactivity of Ru-catalyst A in a case when T = 400 ℃.

Effect of addition of REO to Ru/MgO

- Introduction: background for development of ruthenium (Ru) catalyst for ammonia production
- Analysis of kinetic data for the developed catalyst supported by a certain rare-earth metal oxide (REO) (Ru-catalyst A)
- Effects of preparation methods on enhancement of activity of the developed catalyst (Ru-catalyst B)

ex: Ru/Cs-MgO

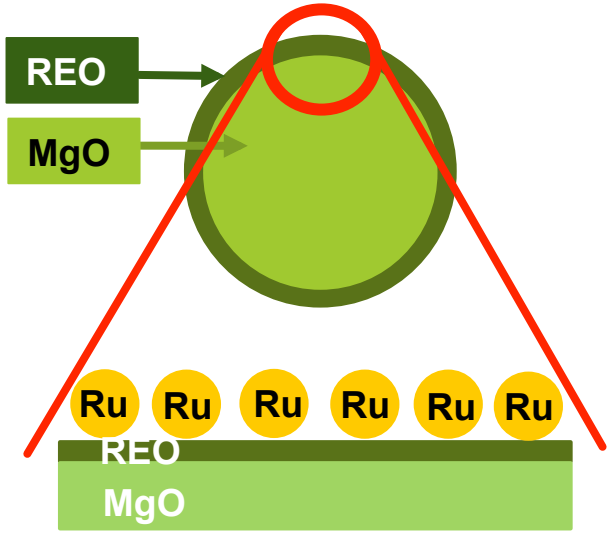


Cesium on MgO support exhibits electron donation properties to ruthenium.

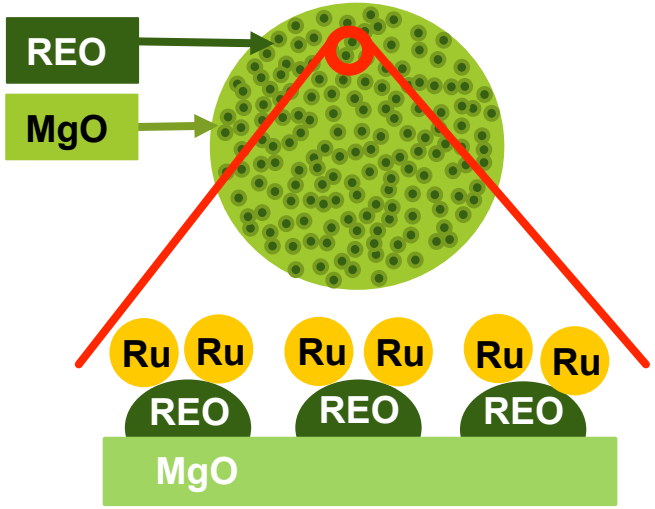
Comparison of different preparation methods

Synthesis of 1 wt-% Ru/MgO-REO (Mg: rare-earth metal = 5 : 1) catalyst

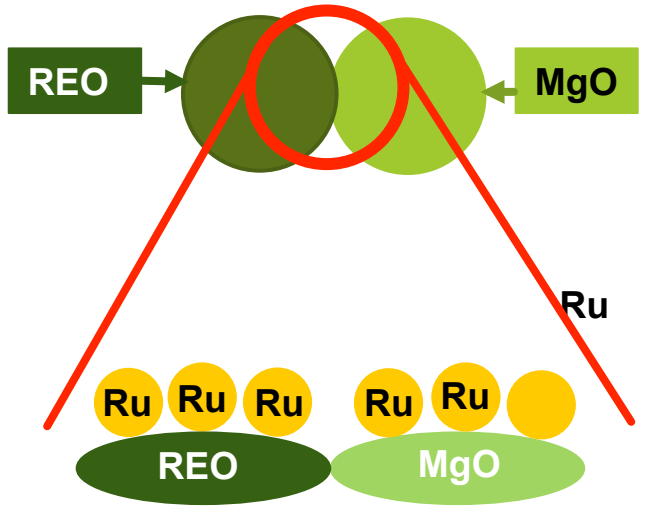
(1) Impregnation



(2) Co-deposition



(3) Physical mixing

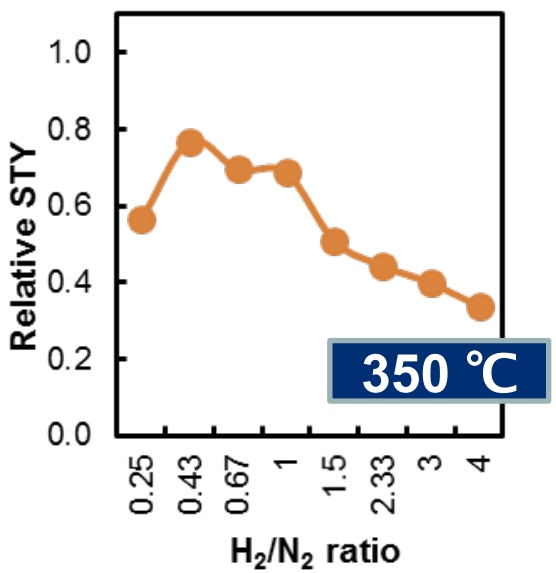


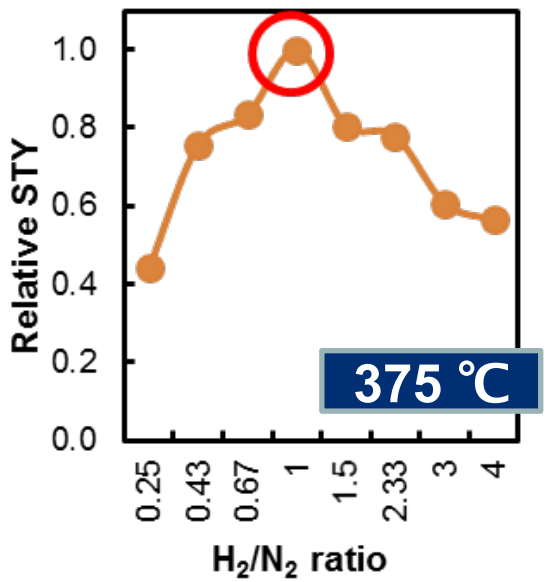
Change in synthesis procedure gives different dispersion of REO.

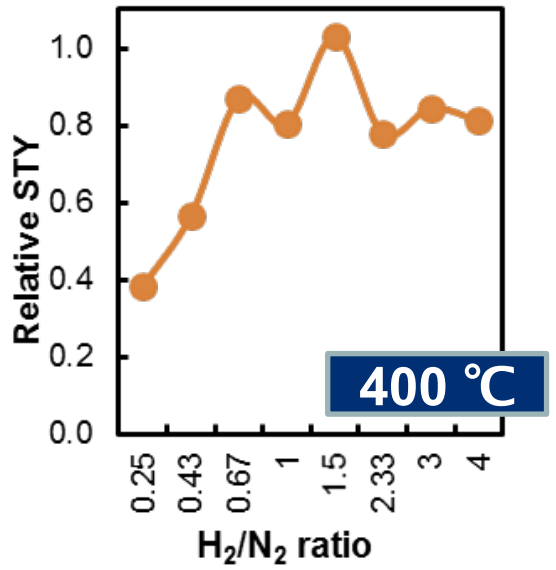
Influence of H_2/N_2 flow ratio to relative STY

(2) Co-deposition

$P = 2.5$ MPaG

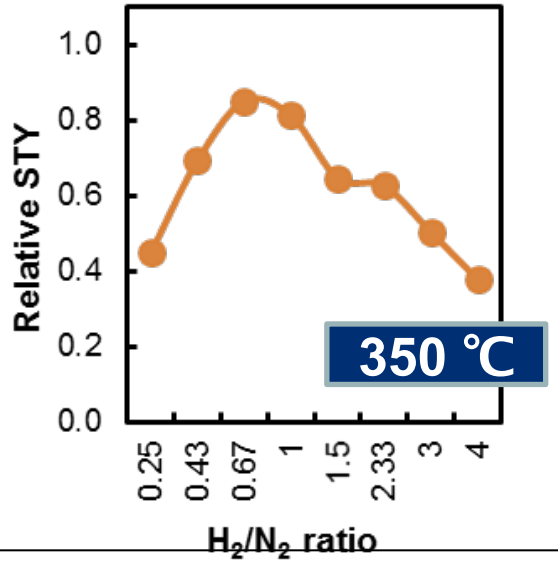


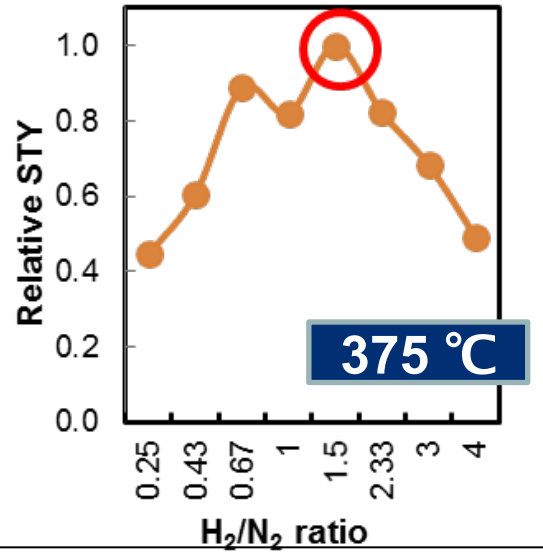


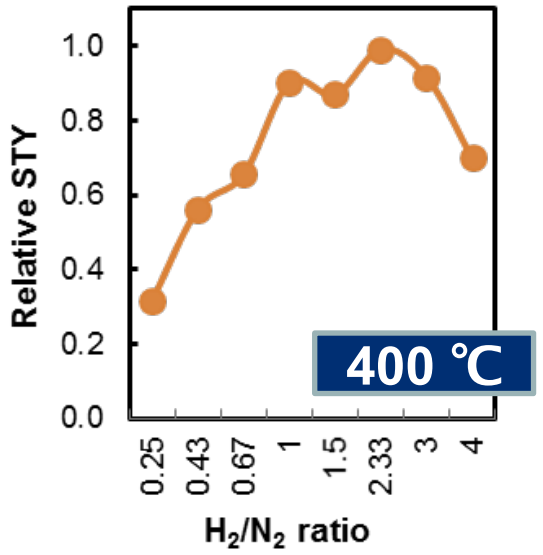


(3) Physical mixing

$P = 2.5$ MPaG

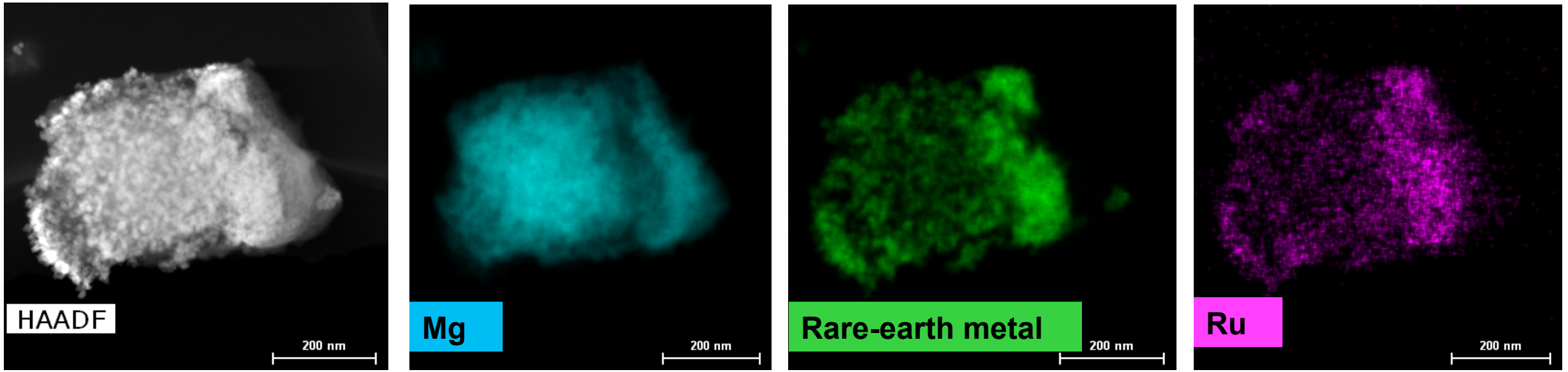






High activity of Ru-catalyst B prepared by physical mixing method

Maximum of STY for 1 wt% Ru-catalyst B that was prepared by that physical mixing method was very close to maximum of STY for 3 wt% Ru-catalyst A in a case of T = 375 °C.

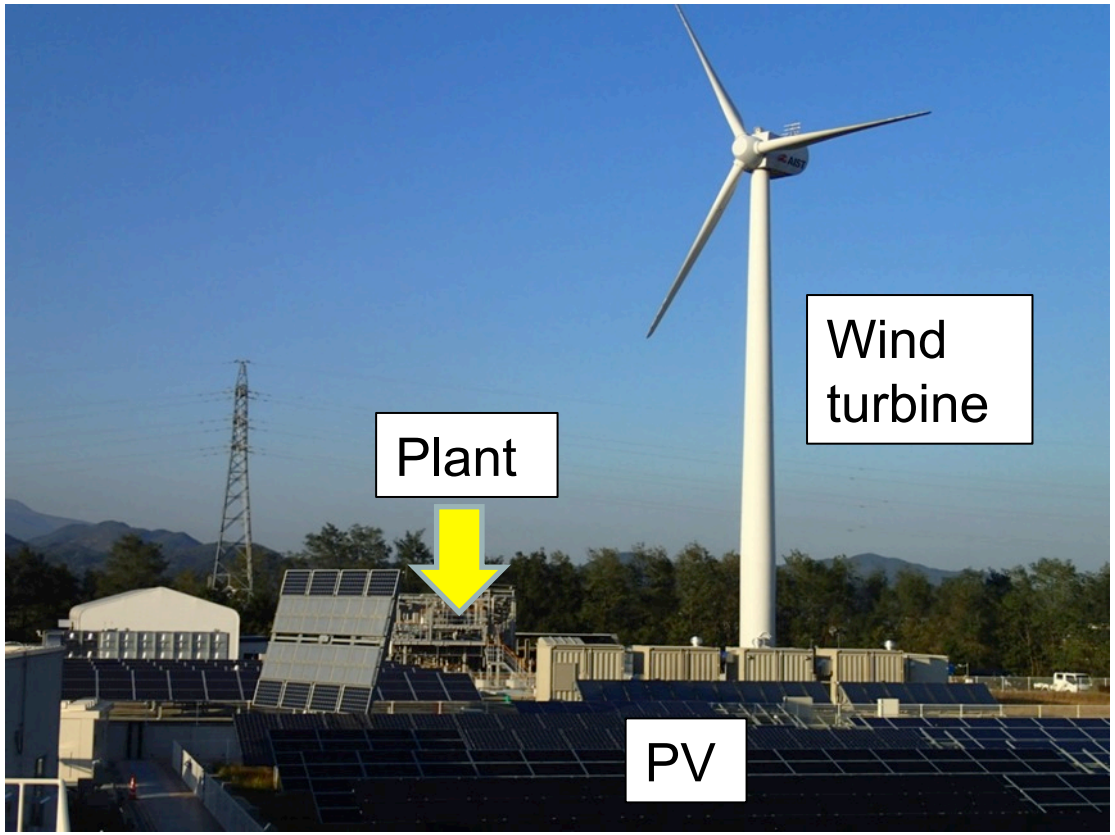


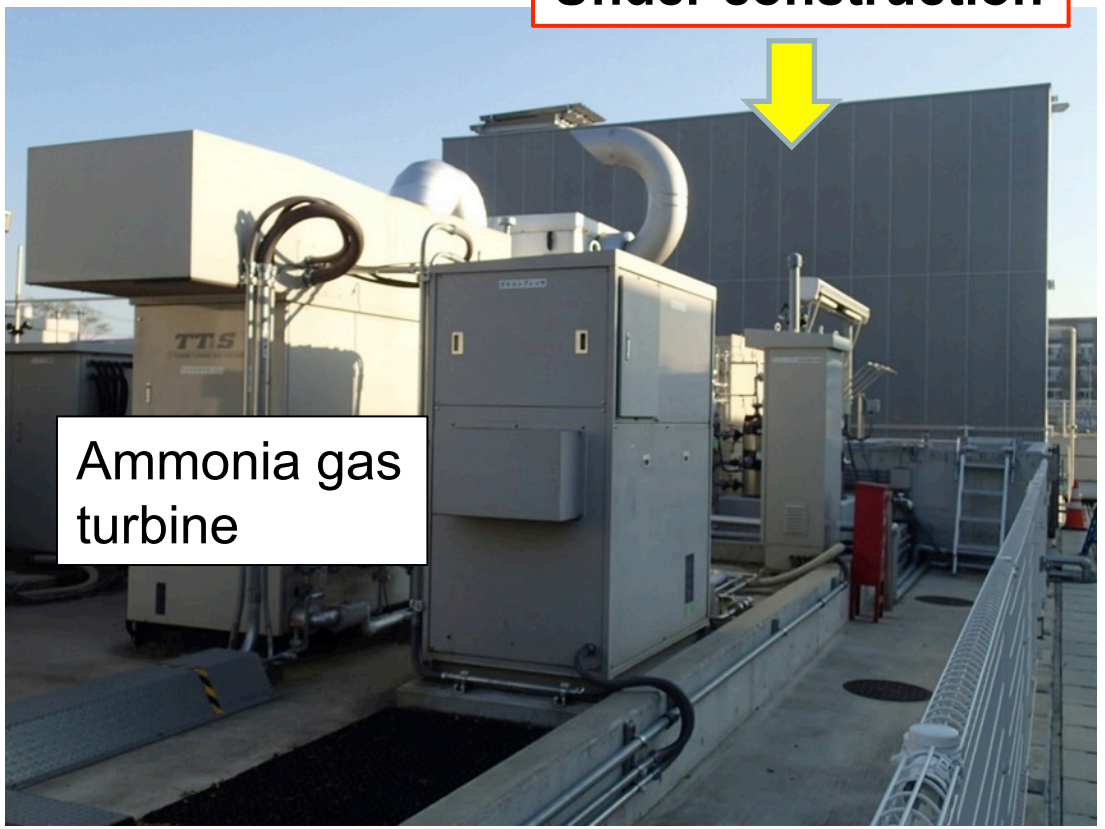
STEM images of Ru-catalyst B after the all experiments

Much ruthenium is present on the rare-earth metal oxide.

Construction of demonstration plant in FREA

Fukushima Renewable Energy Institute, AIST (FREA)





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).

Summary

- The developed Ru-catalyst A performed stable production of ammonia with high STY in an operation range of γ (H_2/N_2 flow ratio)< 3 by increasing reaction temperature.
- It is expected that increase in operating pressure could enhance reactivity of Ru-catalyst A in a case when T = 400 ℃.
- In addition of REO to Ru/MgO, physical mixing method has a potential to enhance of activity of Ru catalyst.