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Effect of preparation condition on ammonia synthesis over Ru/CeO_2

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NH_3 synthesis: Nitrogen fixation

NH_3 = CO_2-free Fuel

Conventional Process

$$3H_2 + N_2 \rightarrow 2NH_3 \ (500^{o}C,\ 20MPa)$$

- H_2 production from Fossil Fuels

  → H_2 supplied from Renewable energy

To reduce the amount of CO_2 release

Comparison of the process

General Chemical Process

- Feed: Constant with the optimal flow rate
- Operation: Constant at the optimal condition according to the catalyst activity

Required Process for usage of Renewable H_2

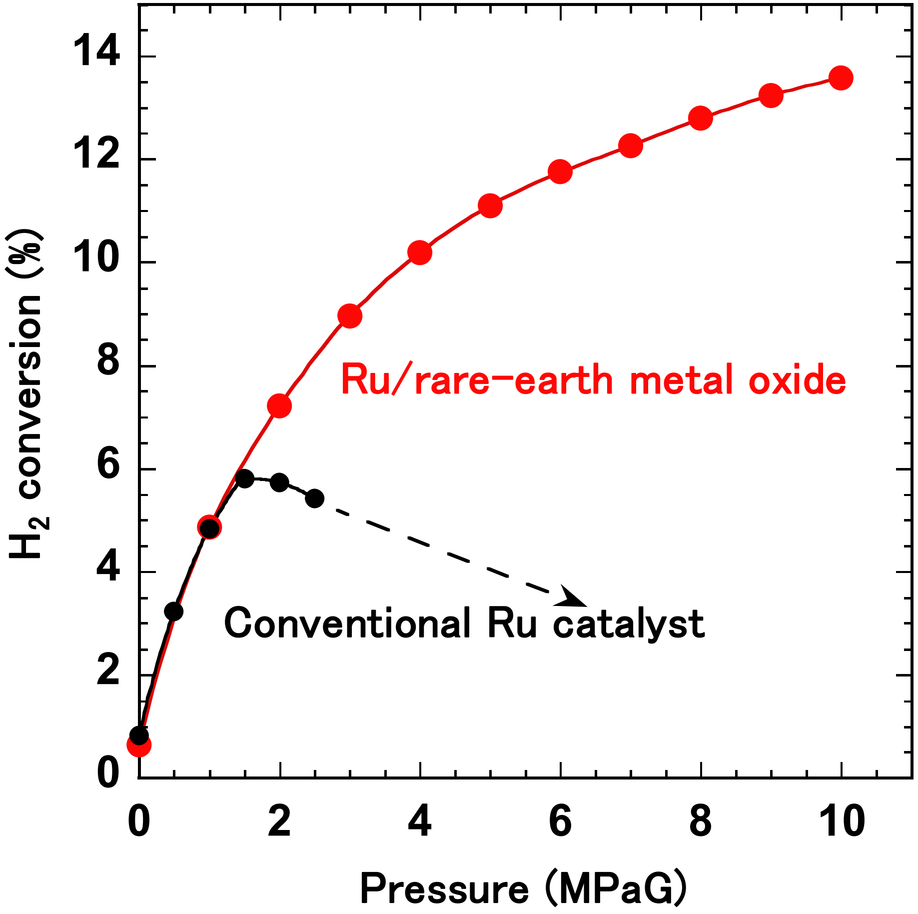
- Feed: Variable
- Operation: Change parameters according to H_2 production from RE

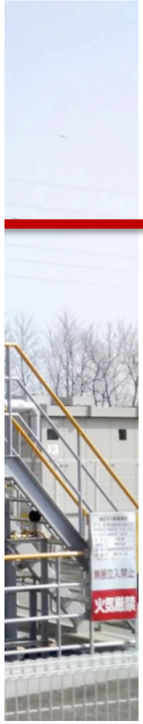
Variable operation process

- Various reaction parameters ⇒ Temp., Press., SV, H_2/N_2

Demonstration plant for NH_3 synthesis

(Tue, Nov 12. Fujimura et al.)





Ru/CeO_2

- Achieved H_2 conversion 24% (400 °C, 5 MPaG)
- Good response against changing condition
- Rapid recovery of activity after shut down and re-start

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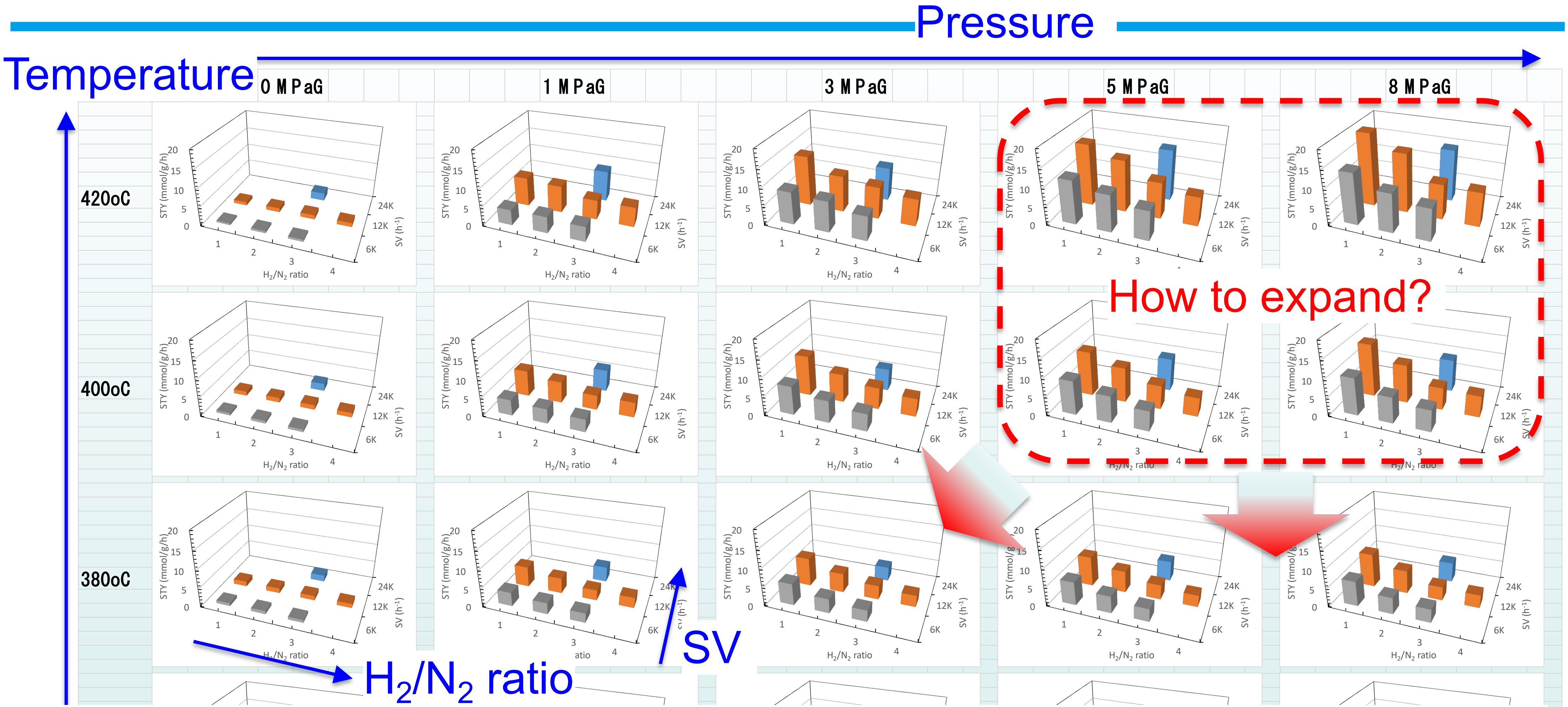
Optimized preparation condition was not obtained, yet

Activity check for plant operation



Objective:

To find the optimum preparation condition of Ru/CeO_2 for obtaining high NH_3 production at lower temperature.

Experiments

【Catalyst preparation】 Ru/CeO_2

CeO_2 (A: 167, B: 133 m^2/g) Daiichi-Kigenso

Ru precursor: $Ru_3(CO)_{12}$, $Ru(NO_3)_3$, $Ru(NO)(NO_3)_3$, $RuCl_3$, $Ru(NH_3)_6Cl_3$, $Ru(acac)_3$, $Ru(dpm)_3$, $[Ru(OH)(NO)(NH_3)_4](NO_3)_2$, Na_2RuO_4

Ru loading: Incipient wetness, 300 ^oC, 10% H_2, 1h calcination

【Activity measurement】 Fixed-bed reactor systems

Pretreatment: 600 °C, 30 min, H_2/N_2 =3, 0 MPaG

> Ambient press condition: Temp 300-600 ^oC, H_2/N_2＝3, SV 40,000 h^{-1}

> High-press condition: Temp 300-450 ^oC, Press 0-10 MPaG, H_2/N_2＝3, SV 12,000 h^{-1}

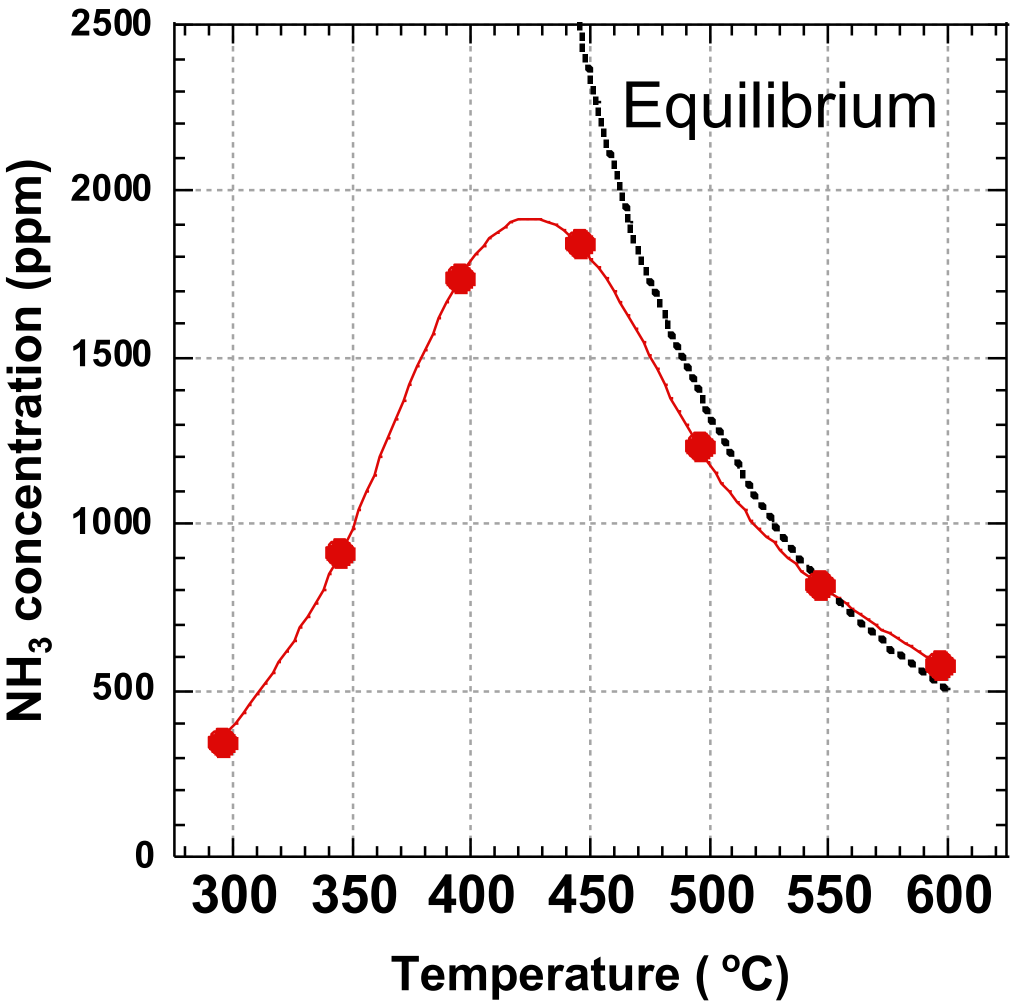
【Characterization】

[N_2 adsorption] Belsorp mini II: Microtrac BEL

[H_2-TPR] Pretreatment: 10% O_2/He, 200 °C,1h

Measurement: 1% H_2/He, -70～900 °C, 10 ^oC/min

NH_3 synthesis activity of Ru/CeO_2 ~ambient~



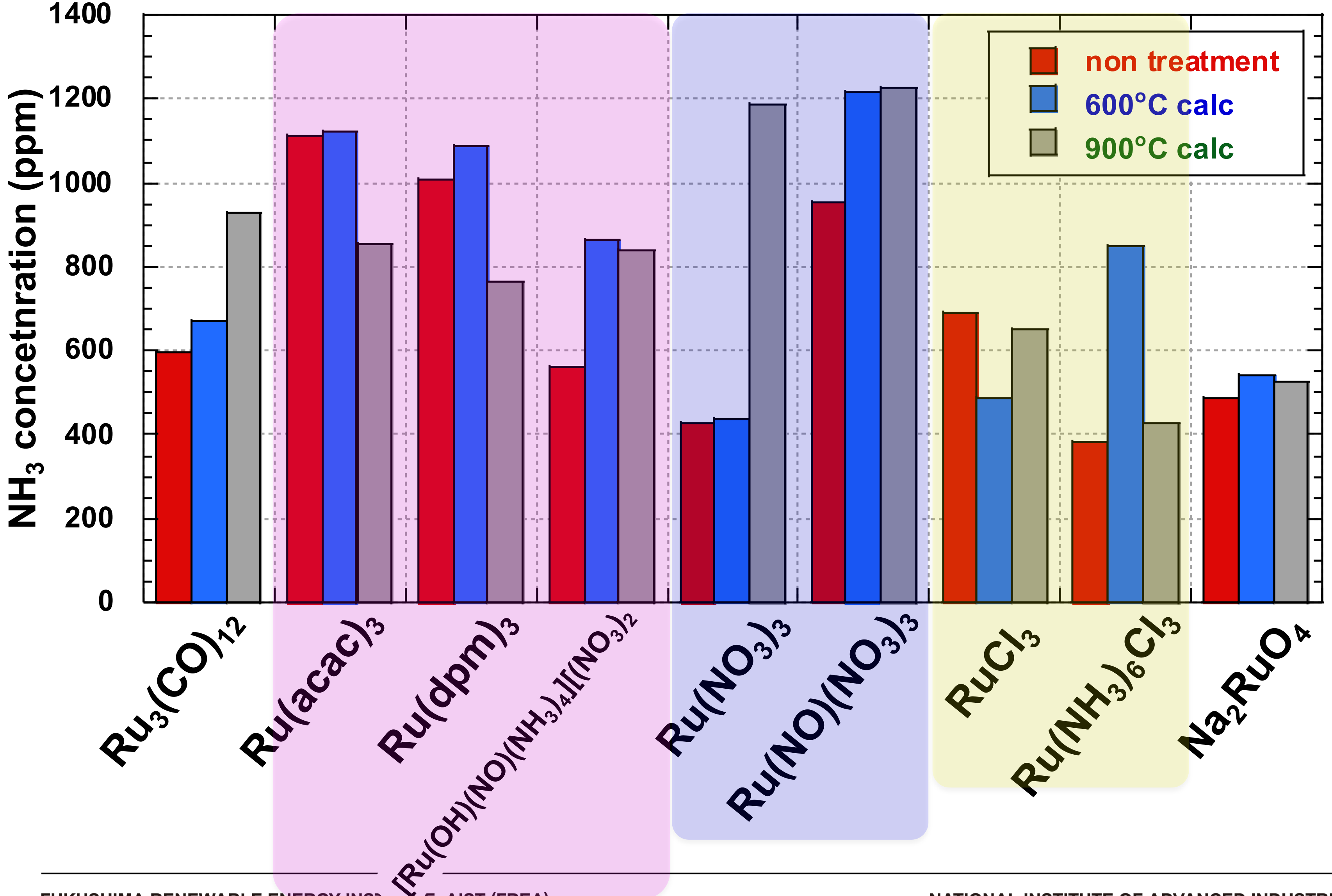
1wt% Ru/CeO_2

Precursor: $Ru(NO)(NO_3)_3$,
CeO_2(A)

- ➢ NH_3 was formed above 300°C.
- ➢ Peak temperature was about 400-450°C

- ➢ To increase Ru loading is effective for low temp activity.
- ➢ Focus on Ru precursor and preparation condition.

Effect of Ru precursor and CeO_2 calcination temperature on NH_3 synthesis



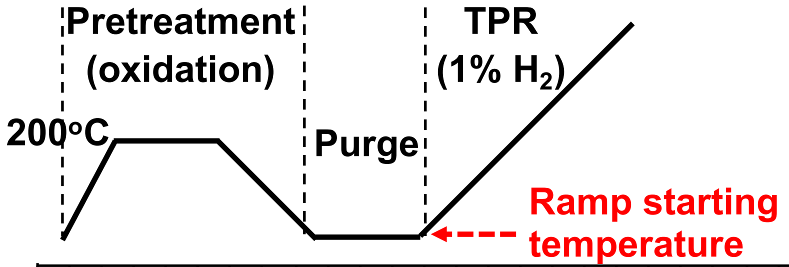
Activity
at 350°C
ambient P

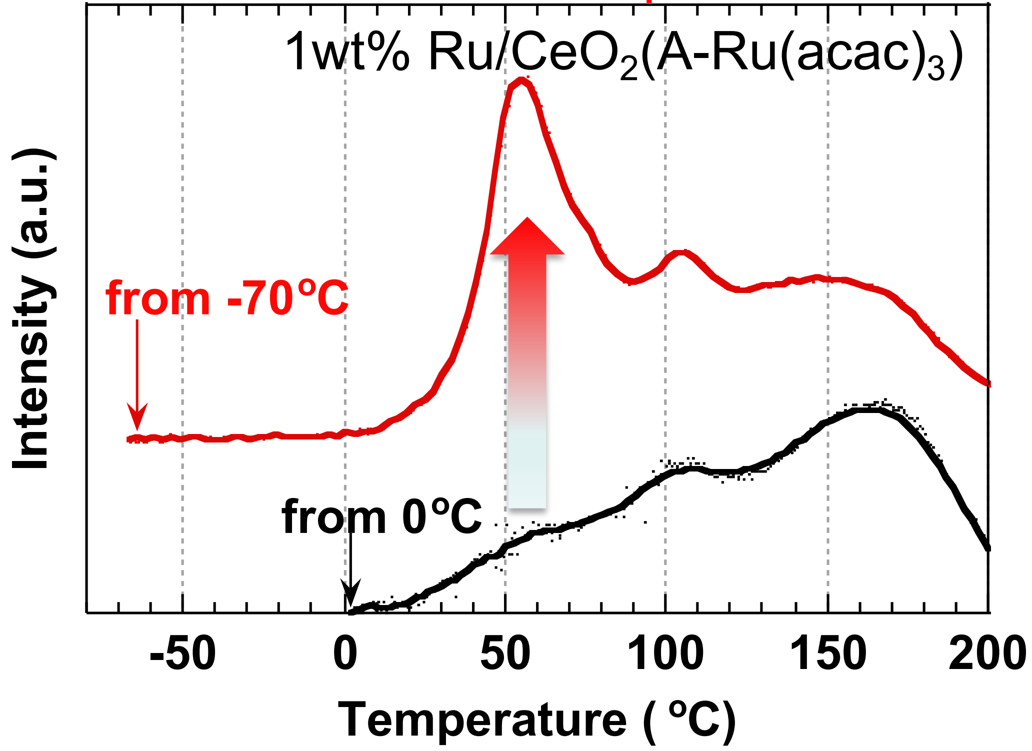
CeO_2 (A) calc.
⇩
Ru loading

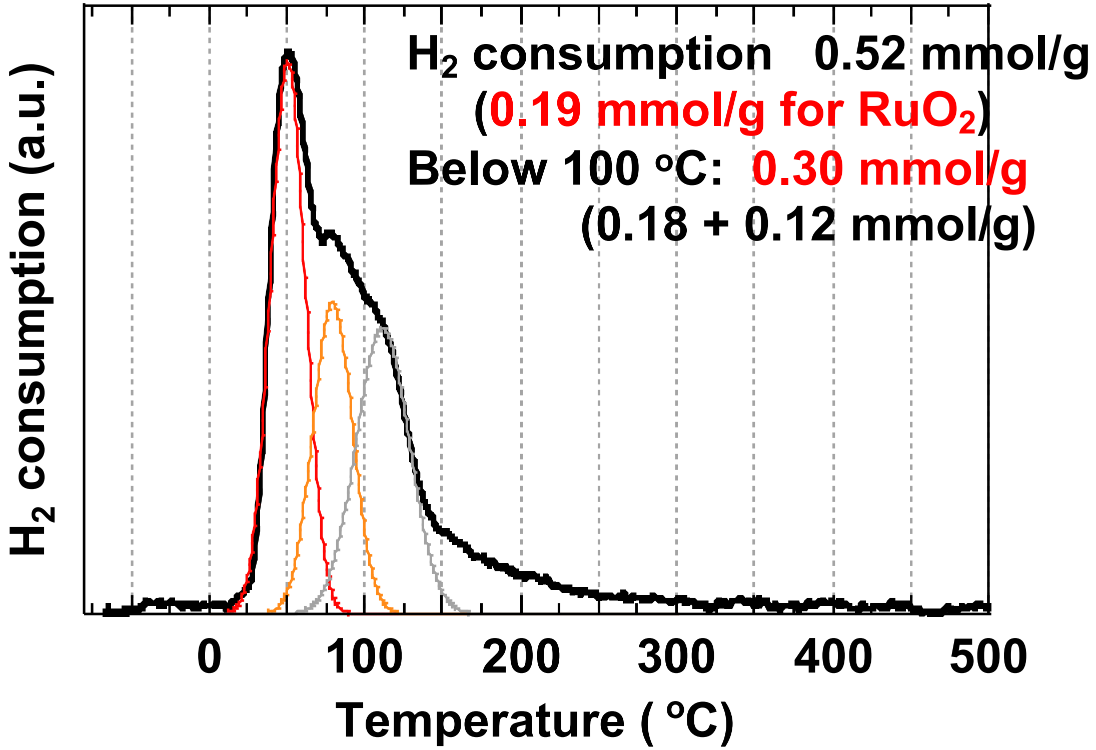
SSA (m^2/g)
Non treat: 167
600°C: 108
900°C: 31

Interaction between Ru and CeO_2 ~H_2-TPR~

H_2-TPR: temperature-programmed reduction by H_2



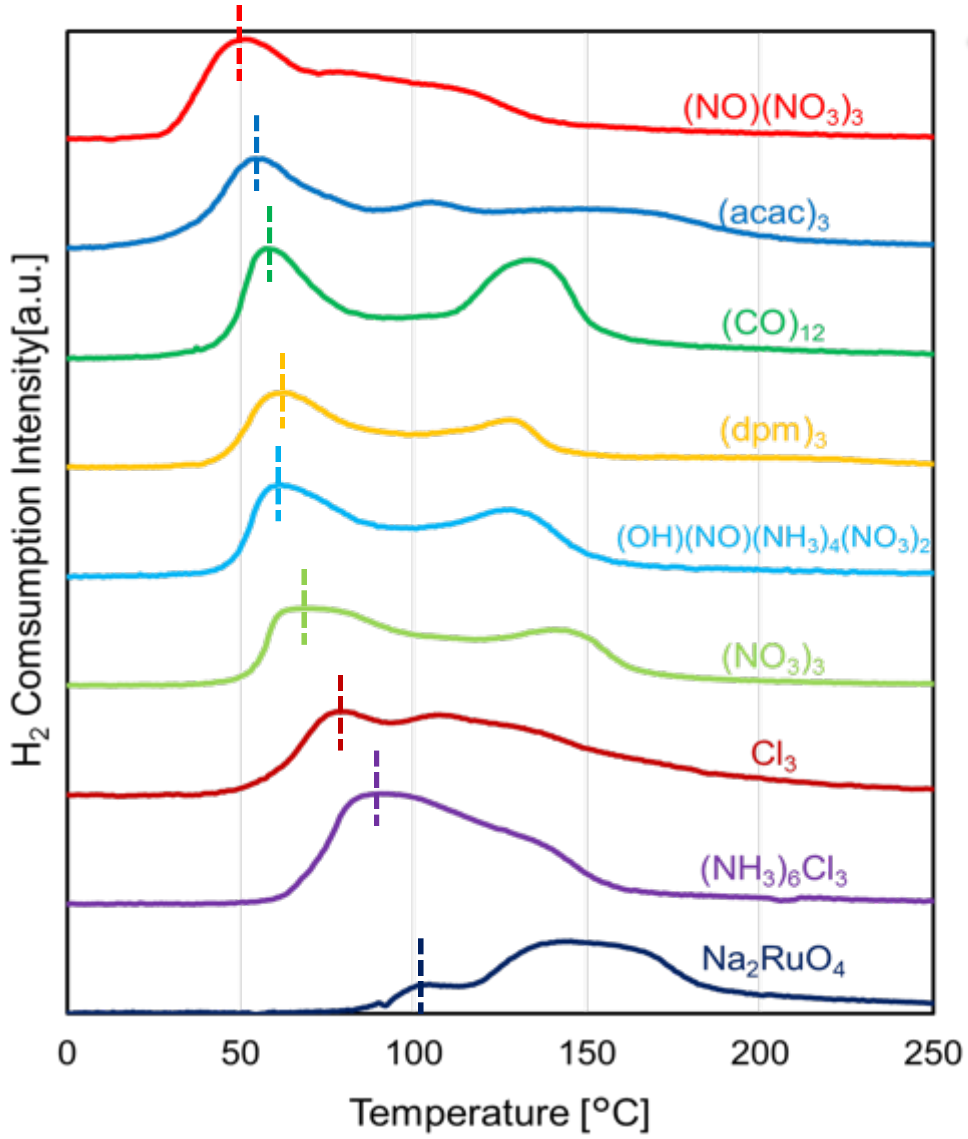




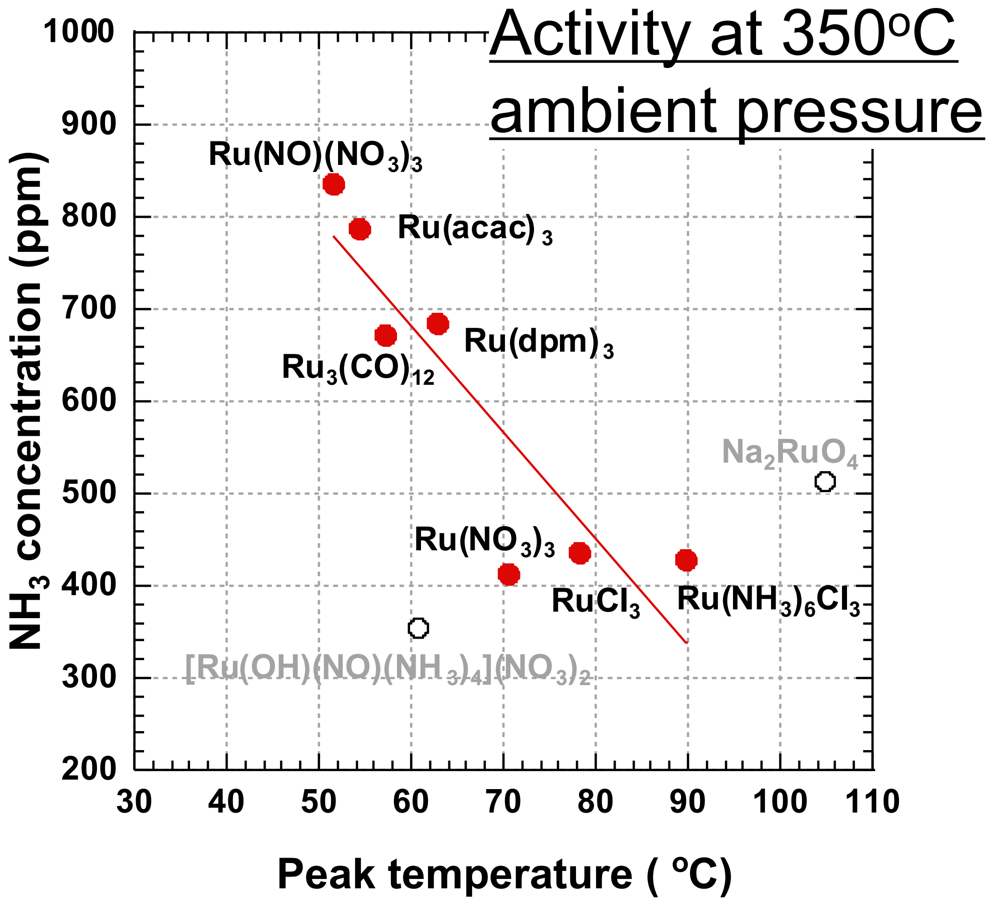
H_2 consumption 0.52 mmol/g
(0.19 mmol/g for RuO_2)
Below 100 °C: 0.30 mmol/g
(0.18 + 0.12 mmol/g)

- H_2 consumption below 100°C included both RuO_x and CeO_2 reductions

Relationship between H_2-TPR profile and catalytic activity ~Precursor effect~



⇦ 1wt% Ru/CeO_2(A) non-treated

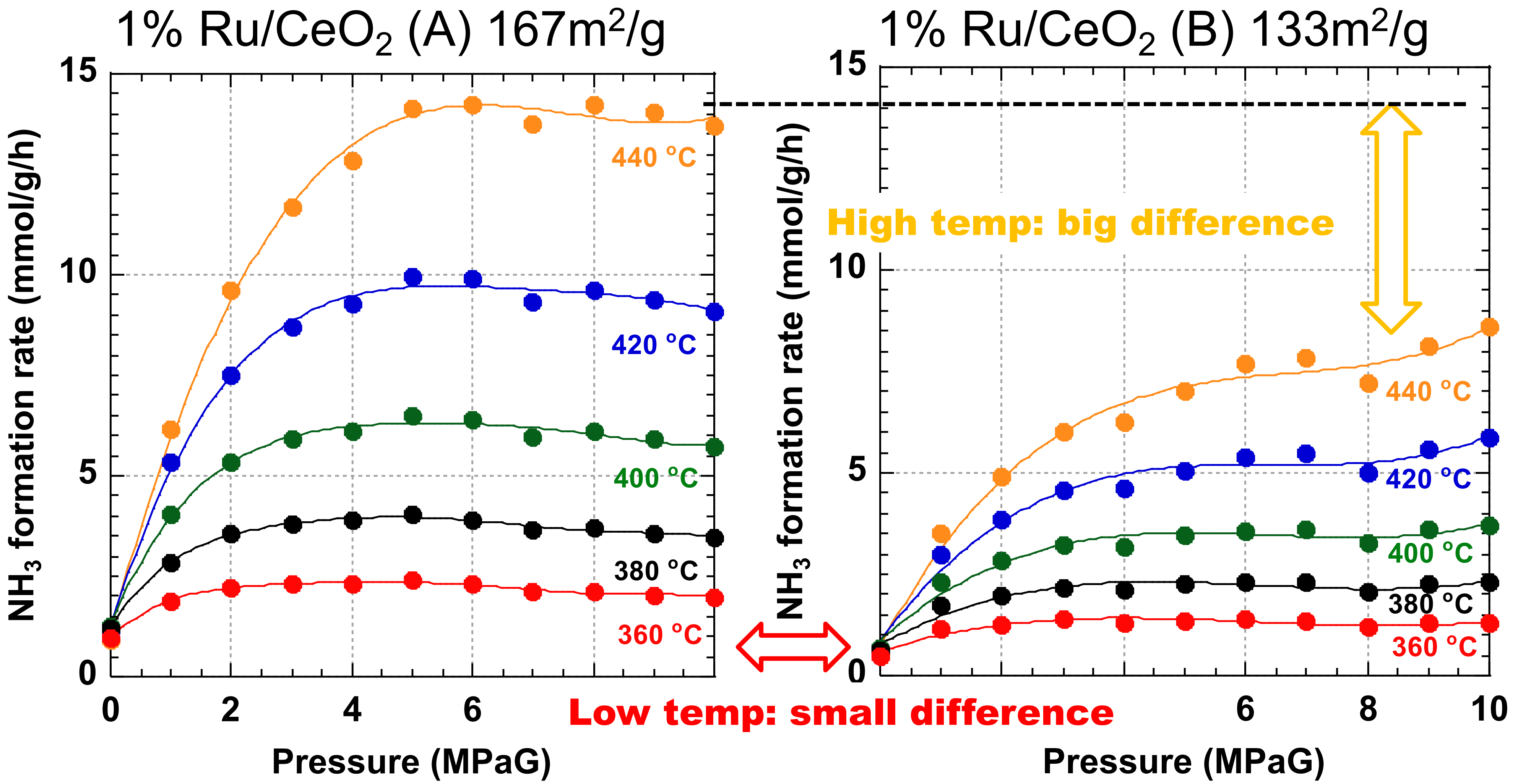


Activity at 350°C ambient pressure

- Peak temperature almost related to low temperature activity.

Effect of CeO_2 on NH_3 synthesis ~High pressure~

Precursor: $Ru(NO)(NO_3)_3$, CeO_2 calcined at 500°C



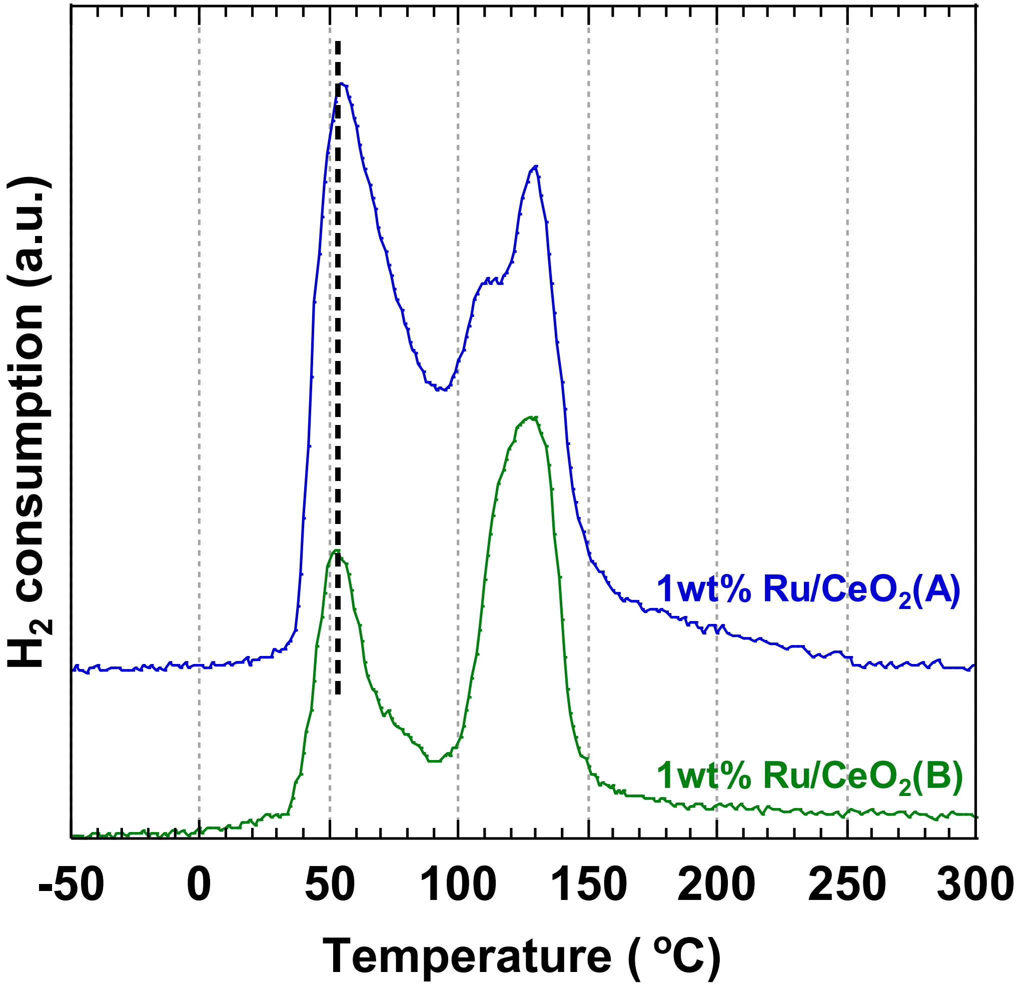
1% Ru/CeO_2 (A) 167m^2/g

1% Ru/CeO_2 (B) 133m^2/g

High temp: big difference

Low temp: small difference

Relationship between H_2-TPR profile and catalytic activity ~CeO_2 effect~



- ➢ Peak temperatures were almost same for both Ru/CeO_2(A) and (B).
- ➢ Pear area for Ru/CeO_2(A) was larger than that for Ru/CeO_2(B).

→ High reducibility of CeO_2 is related to low temperature activity.

Kinetic parameter for 1wt% Ru/CeO_2(A)

$$r = k\,[H_2]^{\alpha}[N_2]^{\beta}[NH_3]^{\gamma}$$

Pressure (MPaG)	Ea (kJ/mol)	α		β		γ	
		325 °C	400 °C	325 °C	400 °C	325 °C	400 °C
0	58.2	0.16	0.96	0.78	0.72	-	-0.28
1	82.6	-0.39	0.15	0.84	0.70	-0.90	-0.30
3	91.4	-0.59	-0.10	0.89	0.83	-0.71	-0.21
5	96.5	-0.71	-0.12	0.92	0.88	-0.61	-0.16
8	98.3	-0.78	-0.40	0.96	0.95	-1.36	-0.18

Summary

- To use renewable hydrogen for NH_3 synthesis, development of Ru/CeO_2 having low temperature activity was studied.
- Catalytic activity was dramatically influenced on chemical state of CeO_2 and Ru precursor.
- Low temperature activity was suspected to relate to CeO_2 reducibility.

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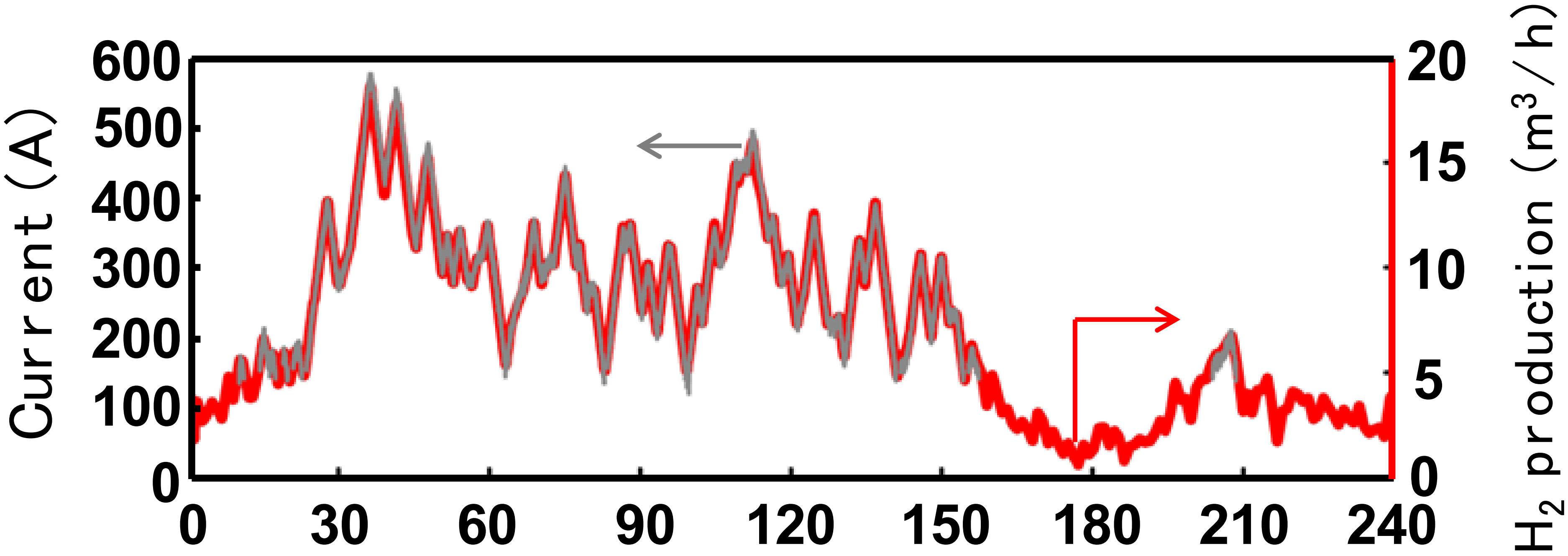
Thank you for kind attention

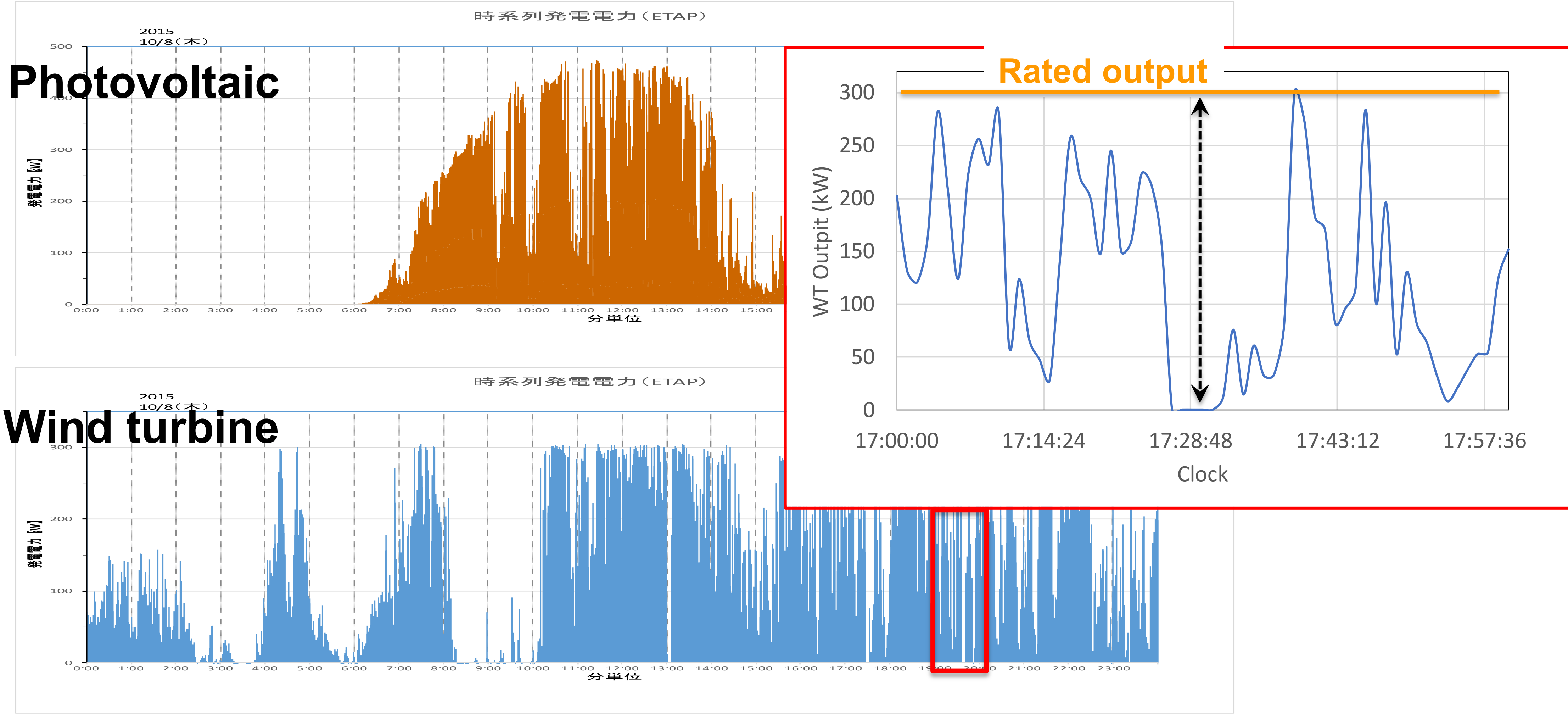
Fluctuation of H_2 feed

Electrolysis by using the fluctuating RE electricity



Fluctuation of Hydrogen production

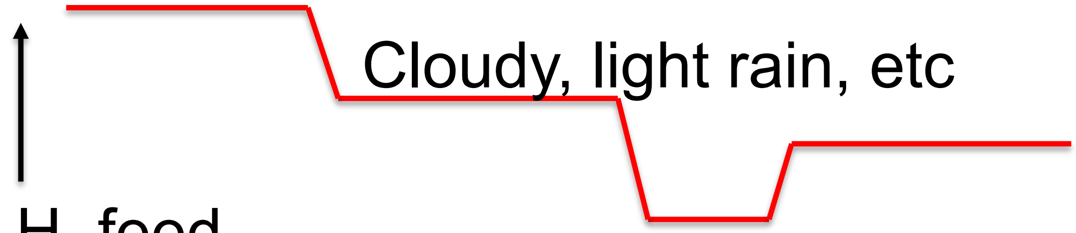
Electric power generation profile: Photovoltaic and Wind



Electricity from PV and WT ⇒ Fluctuation

Catalytic activity under fluctuated H_2 feed for NH_3 synthesis

Operation diagram



Rated operation(Sunny, good wind)

Cloudy, light rain, etc

H_2 feed

Expecting a few days future

- Various reaction parameters
  ⇒ Temp., Press., SV, H_2/N_2

H_2 production from electrolysis

H_2 obtained at ambient temperature and pressure

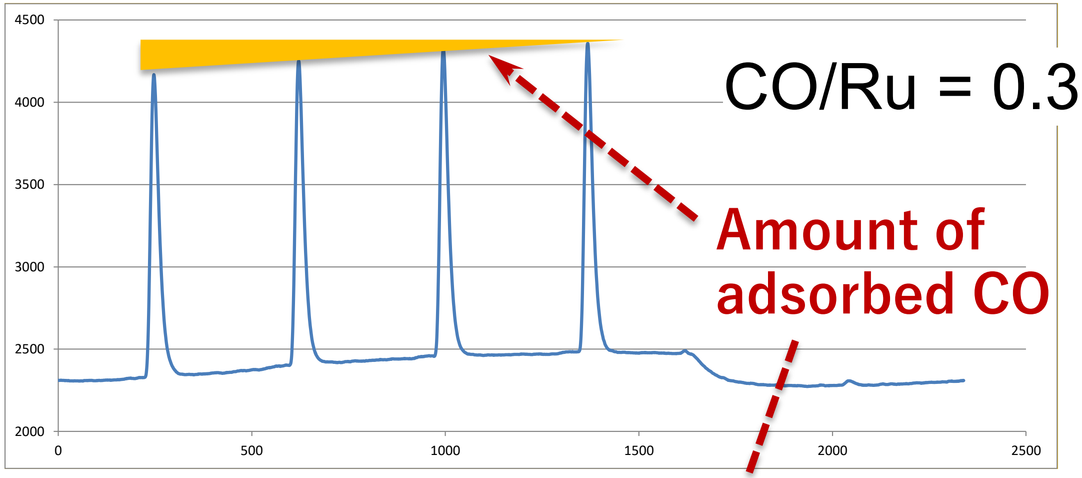
NH_3 synthesis is effective under high temp. and press.

- To reduce energy consumption, lower temperature and pressure than HB process is necessary.

Ru catalysts are candidates

CO pulse adsorption

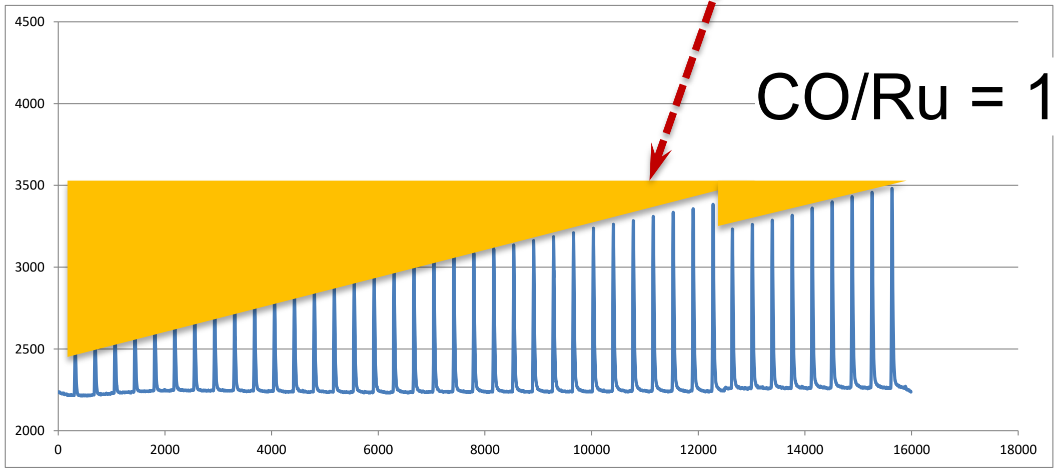
Pretreatment: 200°C, H_2, 5min



CO/Ru = 0.3

Amount of adsorbed CO

Pretreatment: 600°C, H_2, 30min



CO/Ru = 1.3

Precursor: $Ru(NO)(NO_3)_3$,
CeO_2(A)

- High temperature reduction increase CO adsorption

→ High temp reduction induced severe reduction of CeO_2

Reducibility of CeO_2

Kinetic parameter for 1 wt% Ru/CeO2

1wt% Ru/CeO2(A) の速度論パラメータ紹介（やめた方がいいかも）

ピーク位置は同じでも、低温ピークの面積がBは小さい
→　低温・低圧で活性が高いのに寄与