2019 AIChE Annual Meeting
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# Carbon-Free $H_2$ Production from $NH_3$ Triggered at Ambient Temperature with Oxide Supported Ru Catalysts

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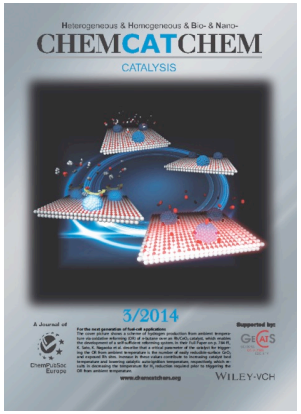
Graduate School of Engineering,
Nagoya University

# Nagaoka Group in Nagoya University

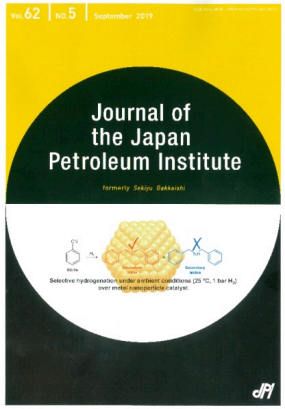
## Development of heterogeneous catalytic process for solving energy and environmental issues

### Cold-start process for hydrogen production


*ChemCatChem,* 6 (2014) 784.
*ChemSusChem*, 2 (2009) 1032.

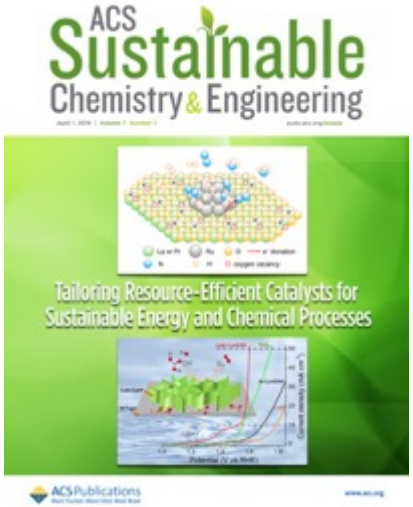
### Nitrile selective hydrogenation



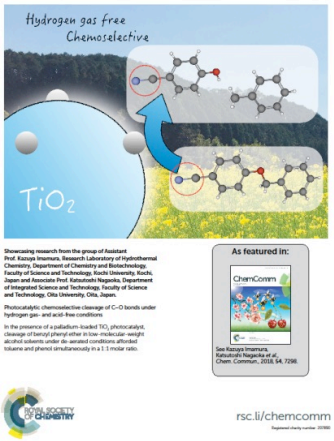

*JPI*, 62 (2019) 220.

*ACS Sustainable Chem. Eng.*, 6 (2018) 17258.

### $NH_3$ synthesis

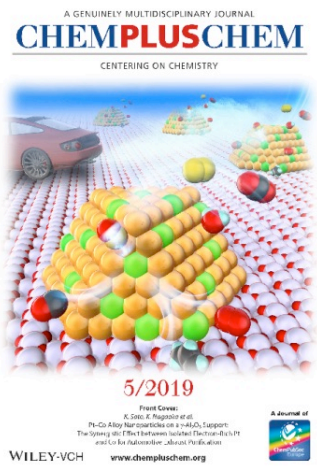



### Photocatalytic C-O bond cleavage




*ChemComm*, 54(2018)7298.

### NOx reduction




*ChemPlusChem*, 84 (2019) 447.

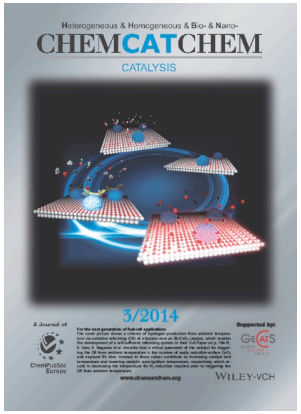
etc.

# Supported multicomponent catalysts

Accurate control of interaction and synergistic effect between metal-metal, -support, and -dopant enables each reactant to optimize reaction kinetics

- High activity
- Excellent selectivity
- Long lifetime
- Unique functions

## Cold-start process for hydrogen production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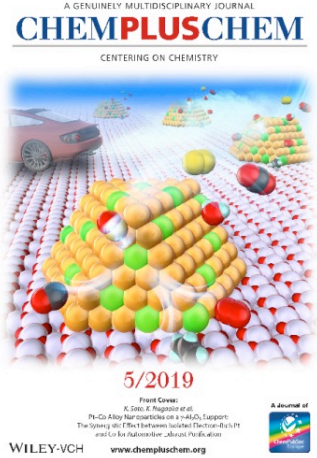


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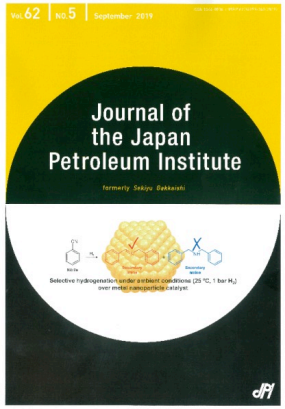


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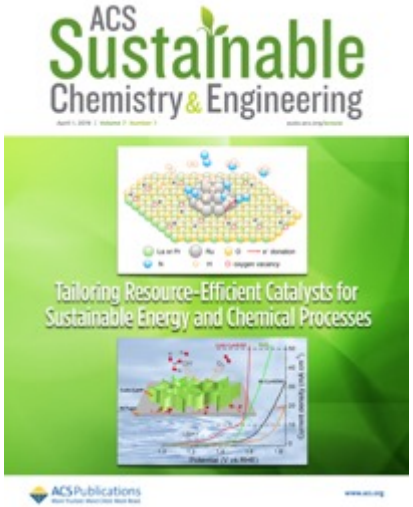
## $NH_3$ synthesis

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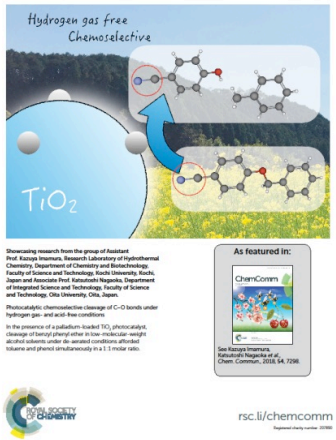
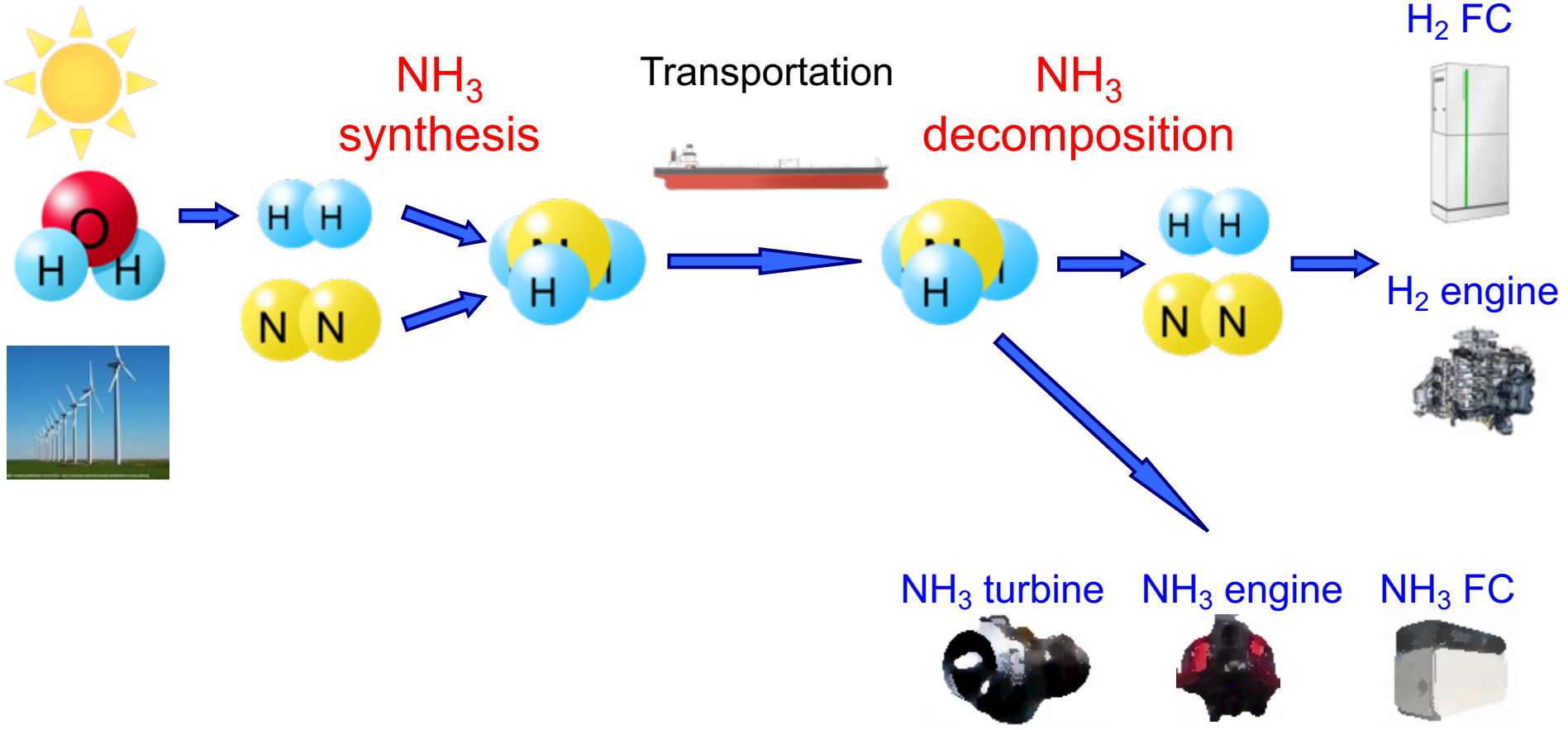



*ChemComm*, 54(2018)7298.

etc.

# $NH_3$ as $H_2$ carrier



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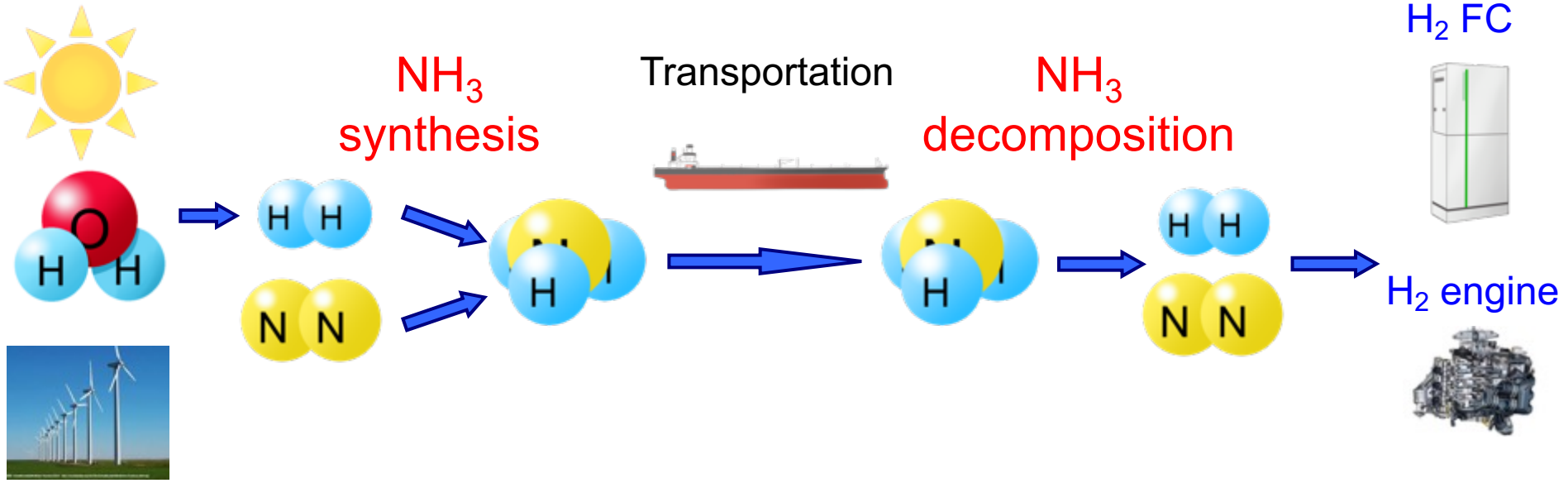
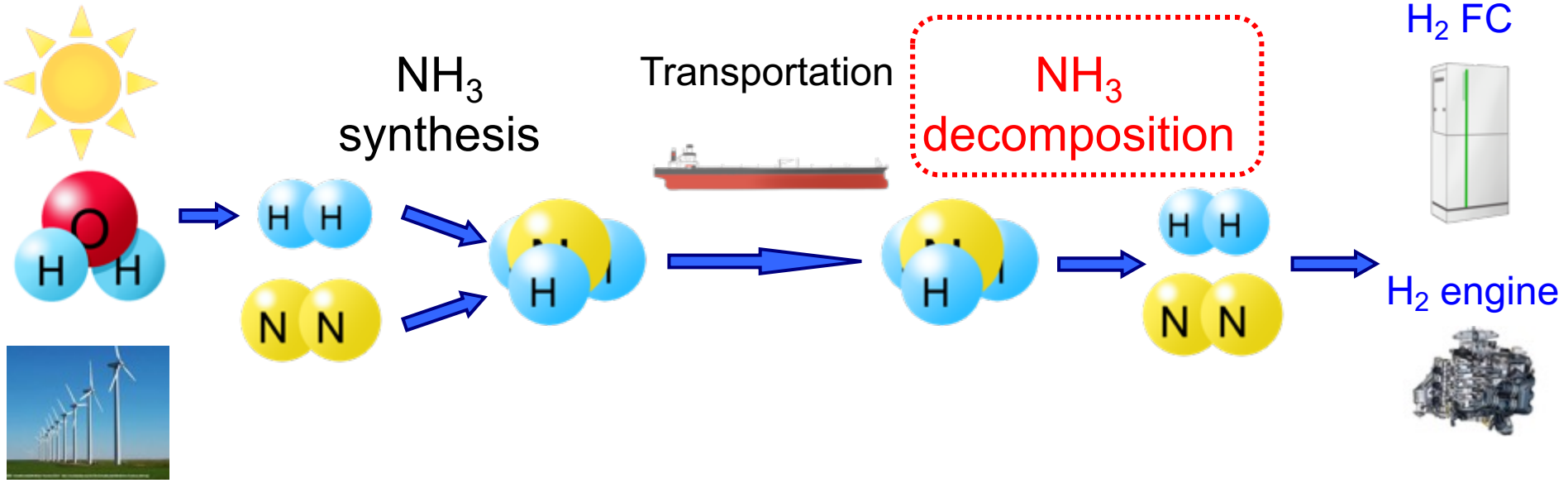



## Key issues

**Development of effective catalysts for synthesis/decomposition of $NH_3$**

# $NH_3$ as $H_2$ carrier

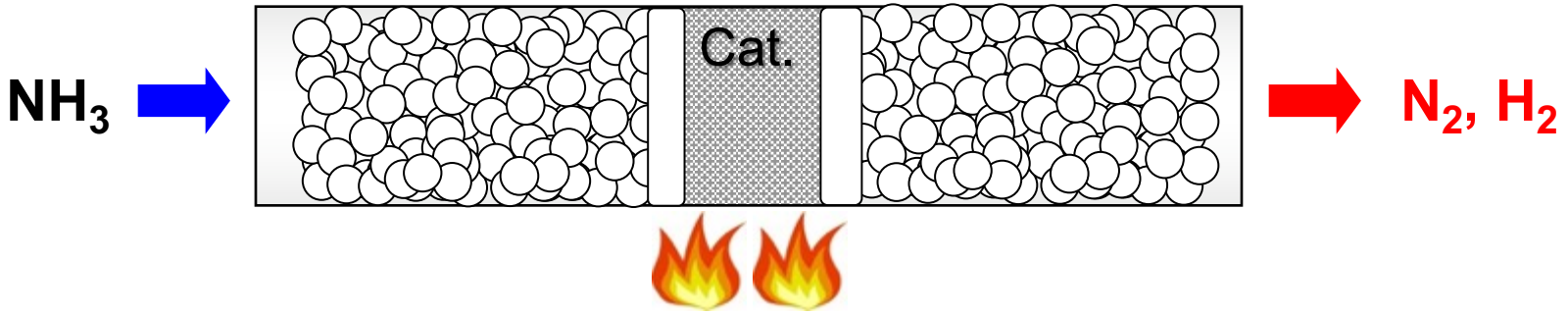



## Contents of talk

## Construction of a facile process for $H_2$ production from $NH_3$

# $NH_3$ decomposition

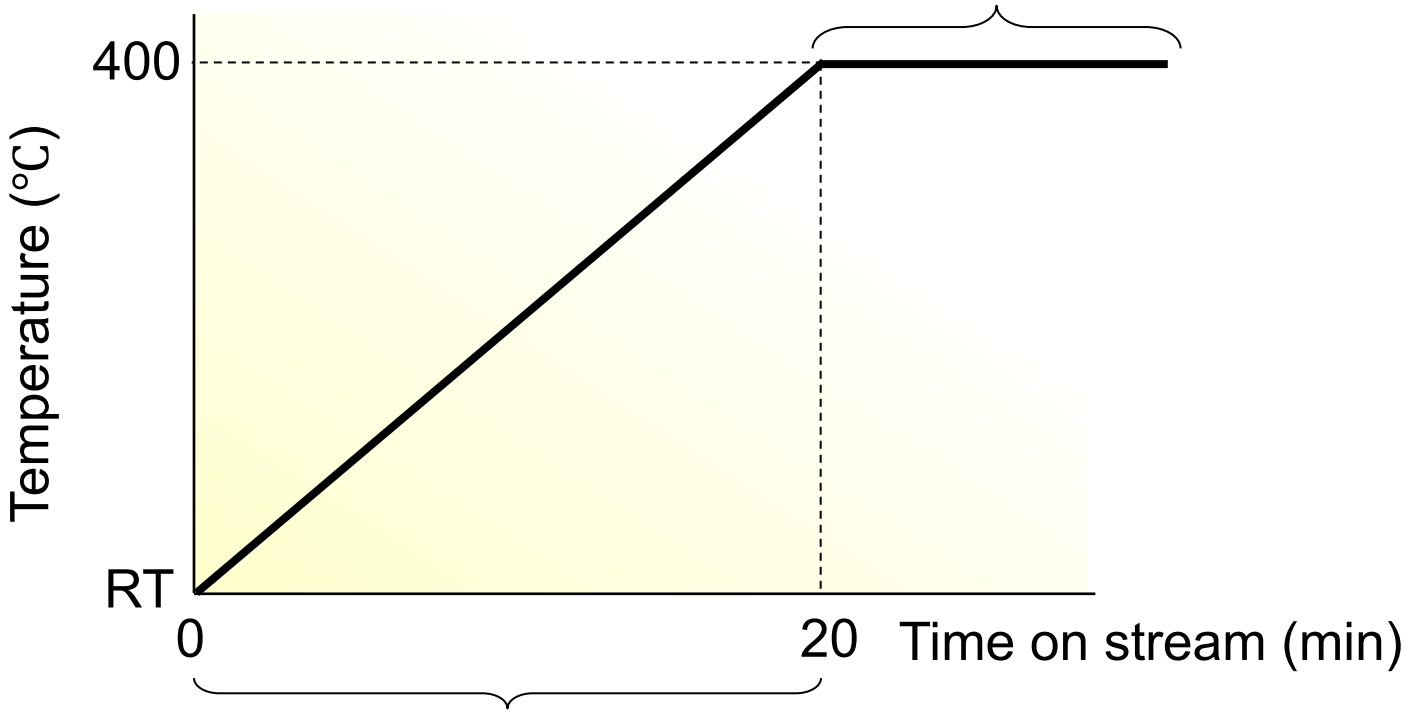
**Convention:** Endothermic reaction and requires external heat




$NH_3 \rightarrow 1.5H_2 + 0.5N_2$ $\Delta H$= +45.4 kJ

# Start-up procedure
# - $NH_3$ decomposition -

$\Delta H > 0$ and requires external heat

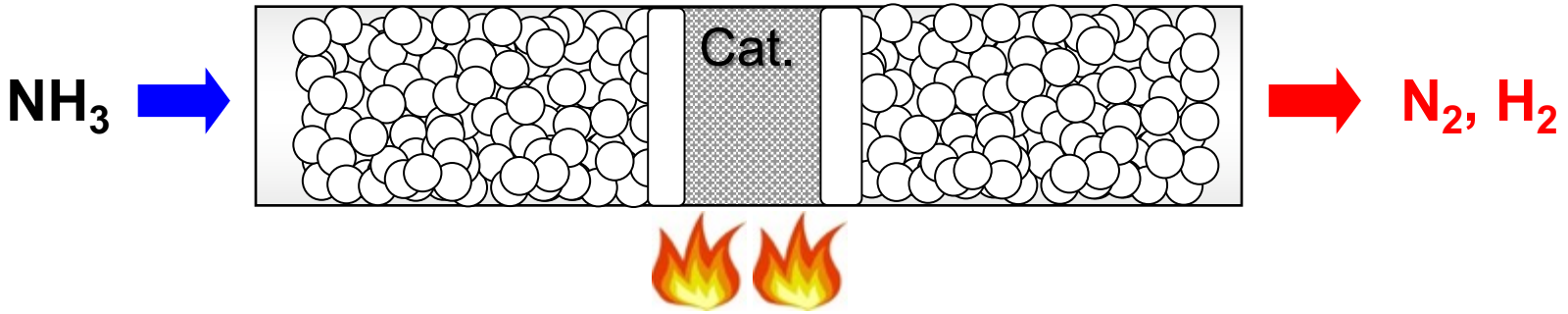



- Catalyst should be heated to 400℃ by external energy and adequate time is required.

- Time lapse delays onset of $H_2$ production and lowers energy efficiency.

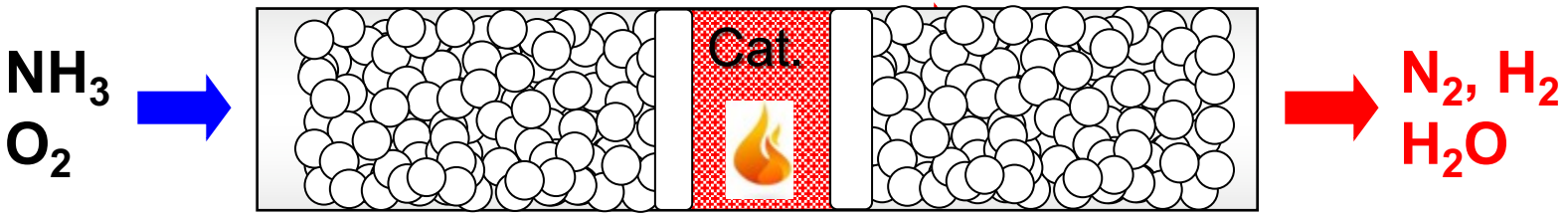
# $NH_3$ oxidative decomposition (AOD)

**Convention:** Endothermic reaction and requires external heat




**This research**: Exothermic reaction and needs no external heat

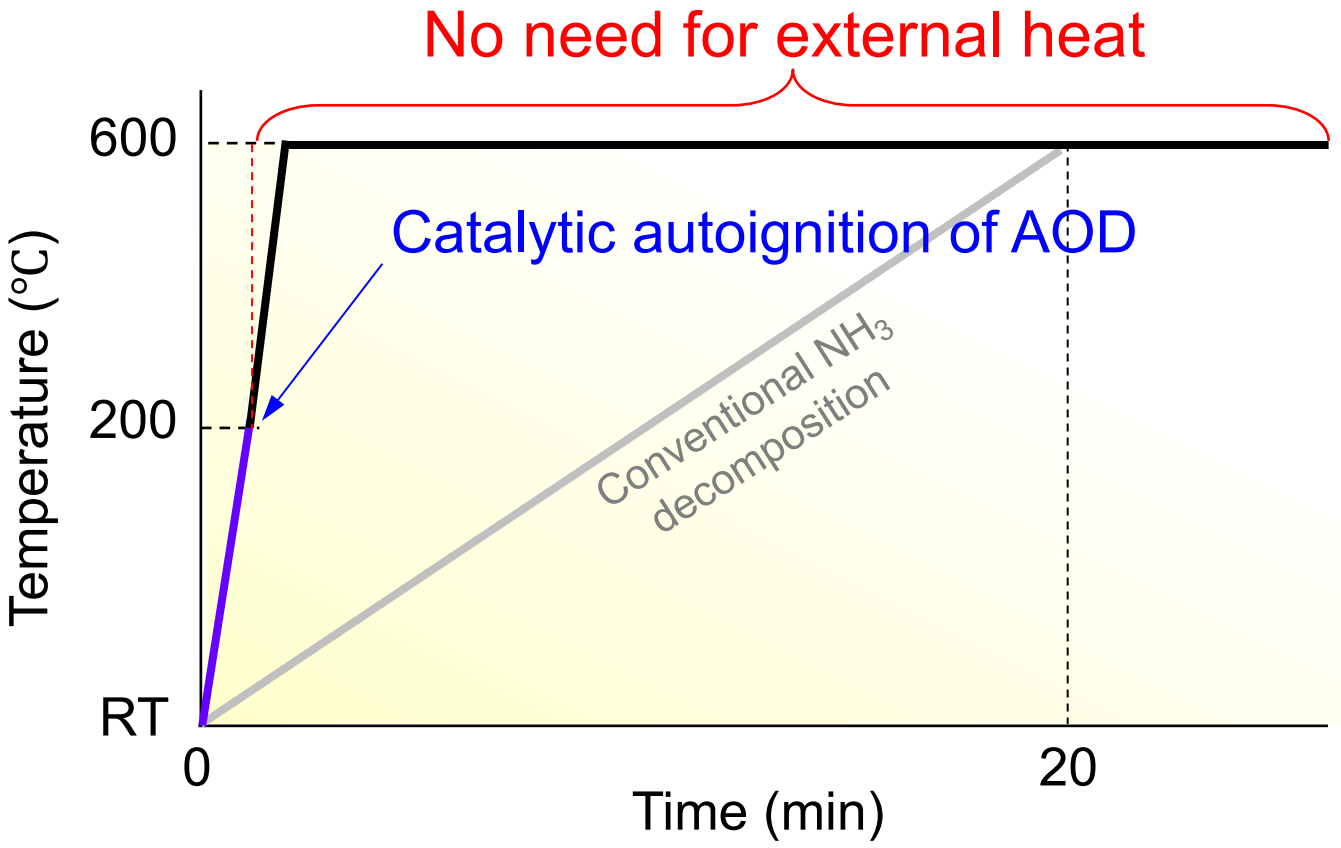
→ $H_2$ formation rate is fast




$$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O \qquad \Delta H<0$$

# Rapid cold-start process for $NH_3$ oxidative decomposition (AOD)

$$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O \quad \Delta H = -75\ kJ/mol$$



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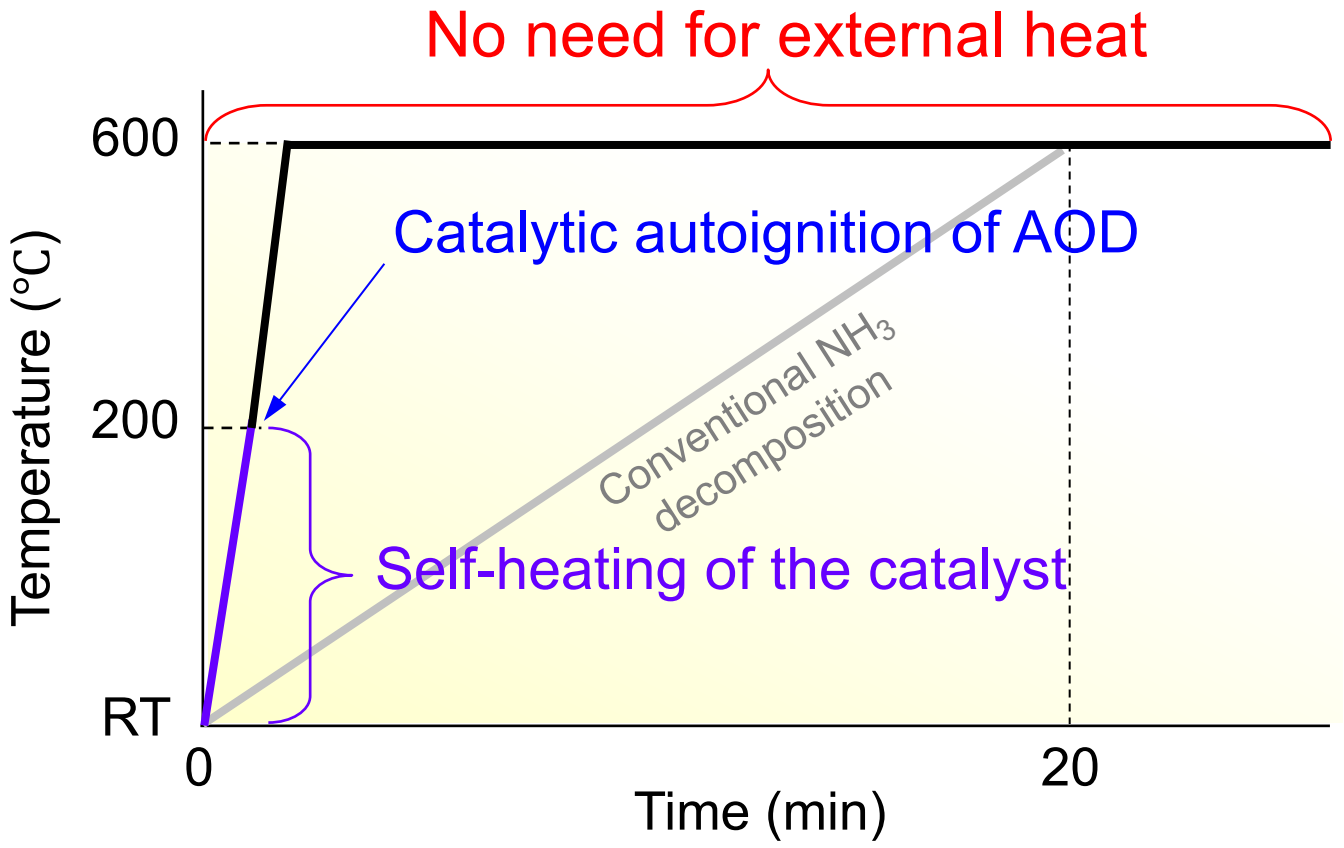
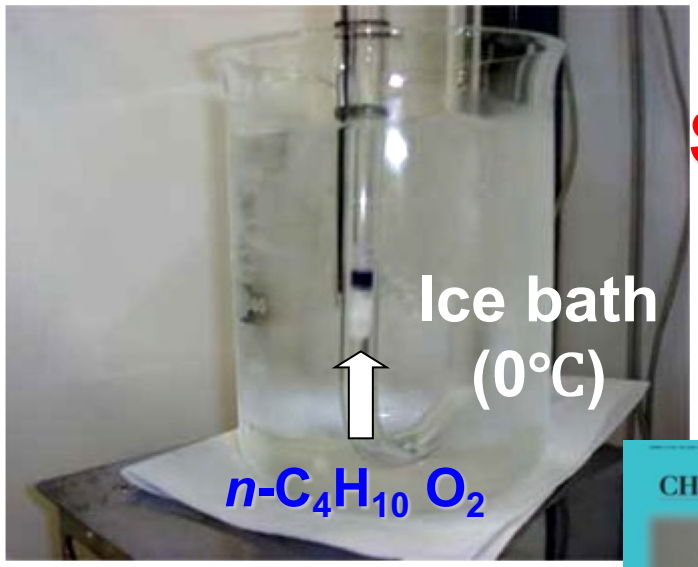


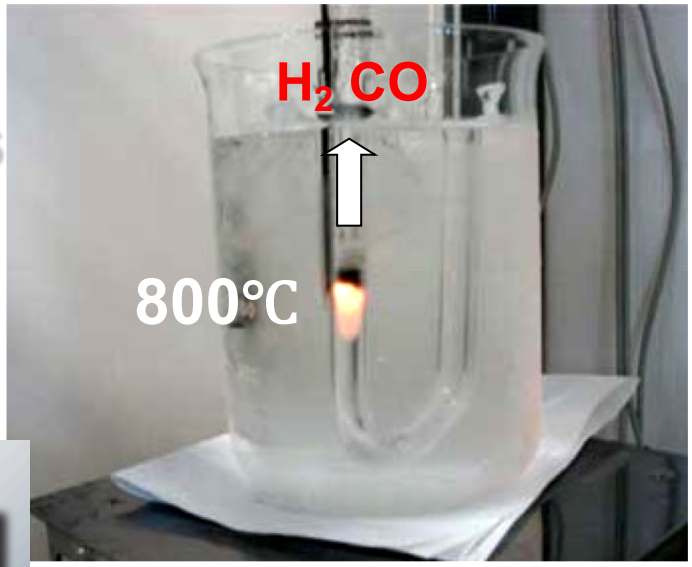

- Heat for self-heating
  1. Heat evolved by $NH_3$ adsorption
  2. Heat generated by oxidation of the reduced catalyst

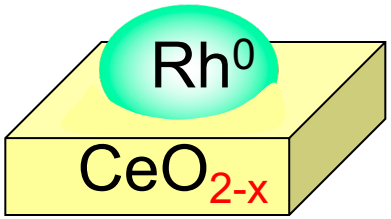
# Rapid cold-start process for oxidative reforming of hydrocarbon

$n$-$C_4H_{10}$+$2O_2$ → $4CO$+$5H_2$ $\Delta H$ = -316 kJ

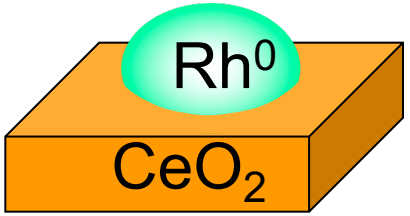



Spontaneous oxidation



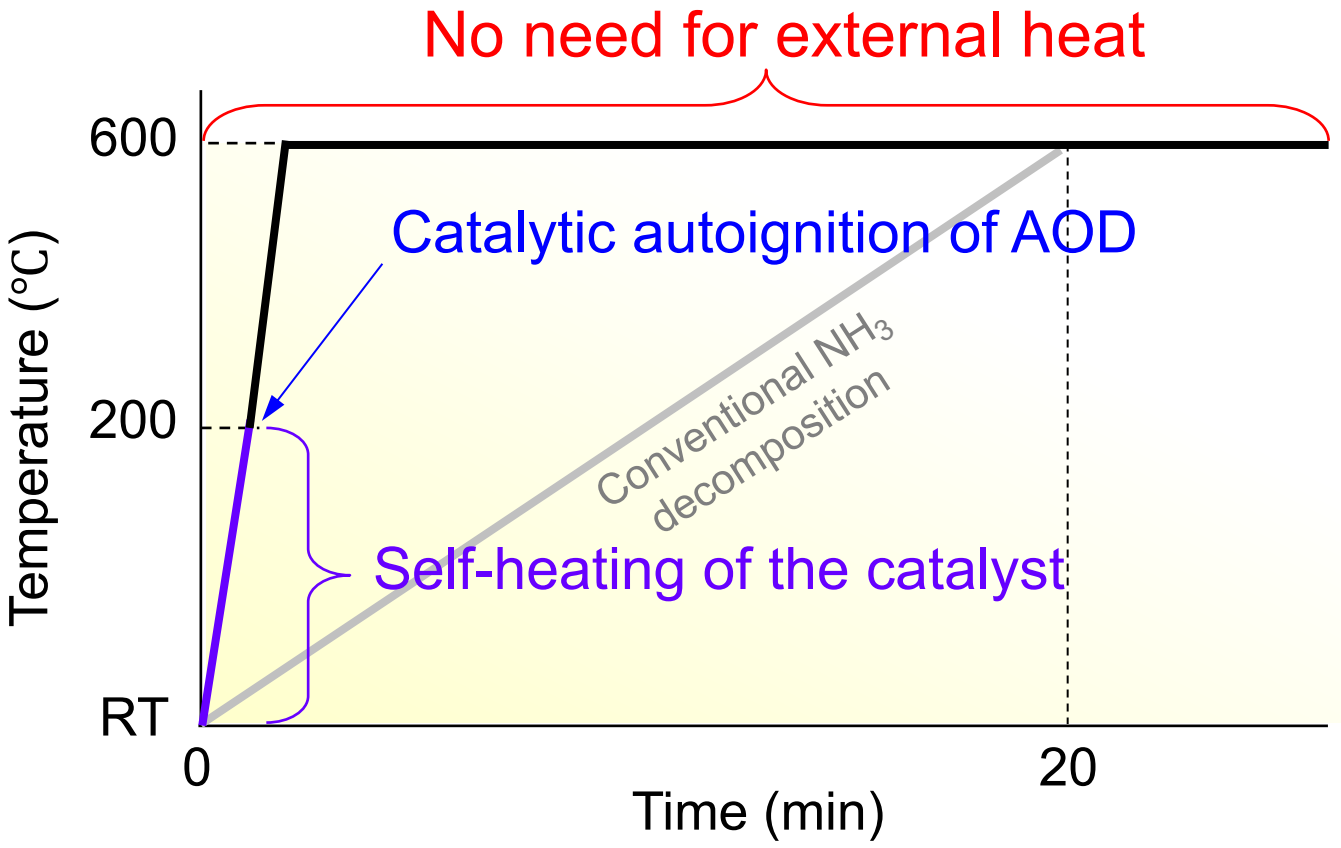





*Chem. Mater.*, 20 (2008) 4177. *ChemSusChem*, 2 (2009) 1032. *Catal. Commun.*, 10(2009)1478. *J. Jpn. Petrol. Inst.*, 52 (2009) 295. *ChemSusChem*, 3 (2010) 1364. *J. Catal.*, 287 (2012) 86. *ChemCatChem*, 6 (2014) 784. *J. Jpn. Petrol. Inst.* 58 (2015) 274.

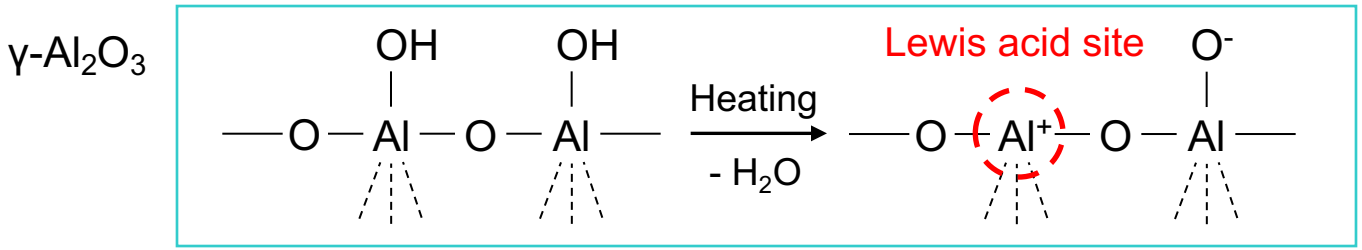
# Rapid cold-start process for $NH_3$ oxidative decomposition (AOD)

$$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O \quad \Delta H = -75\ kJ/mol$$

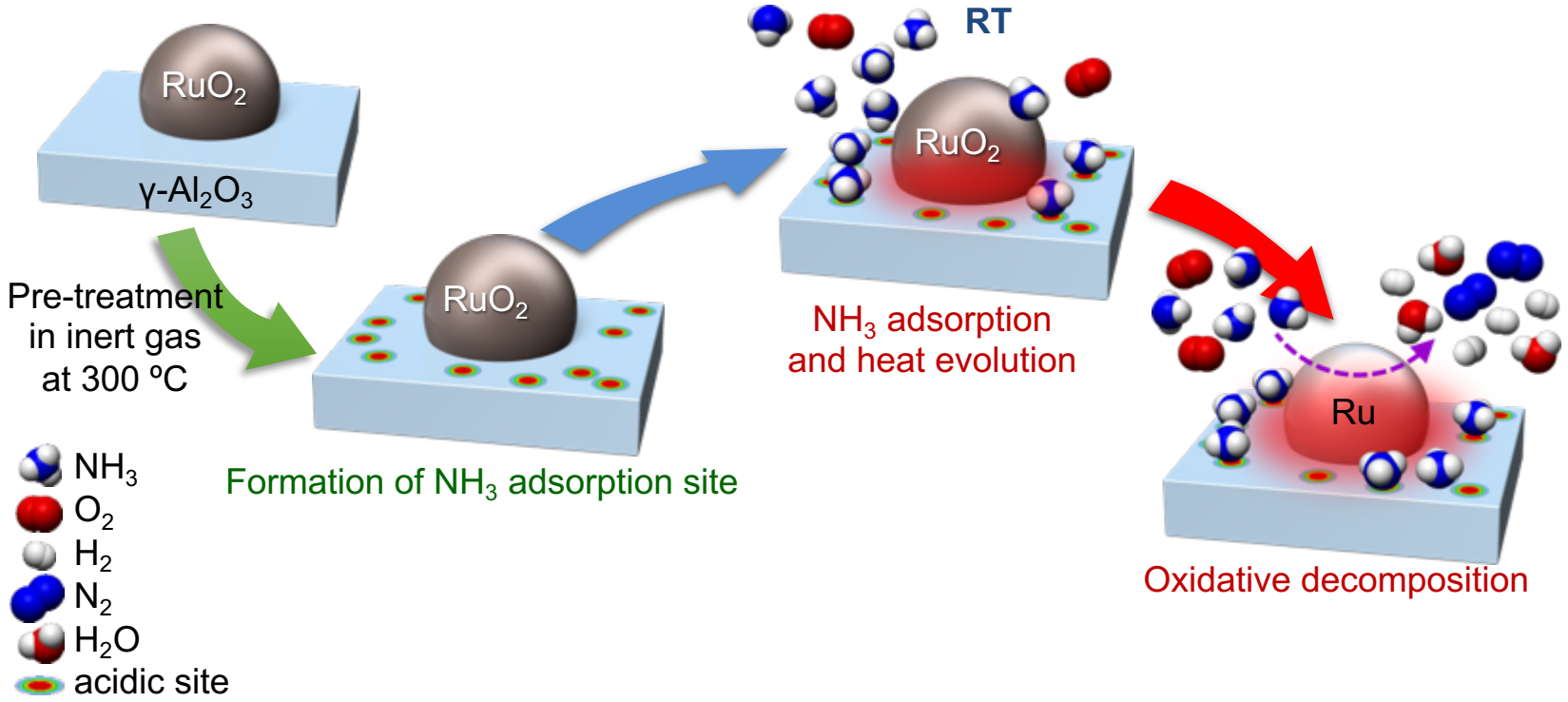



- Heat for self-heating
  1. Heat evolved by $NH_3$ adsorption
  2. Heat generated by oxidation of the reduced catalyst

# Mechanism for triggering AOD at RT




$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O$

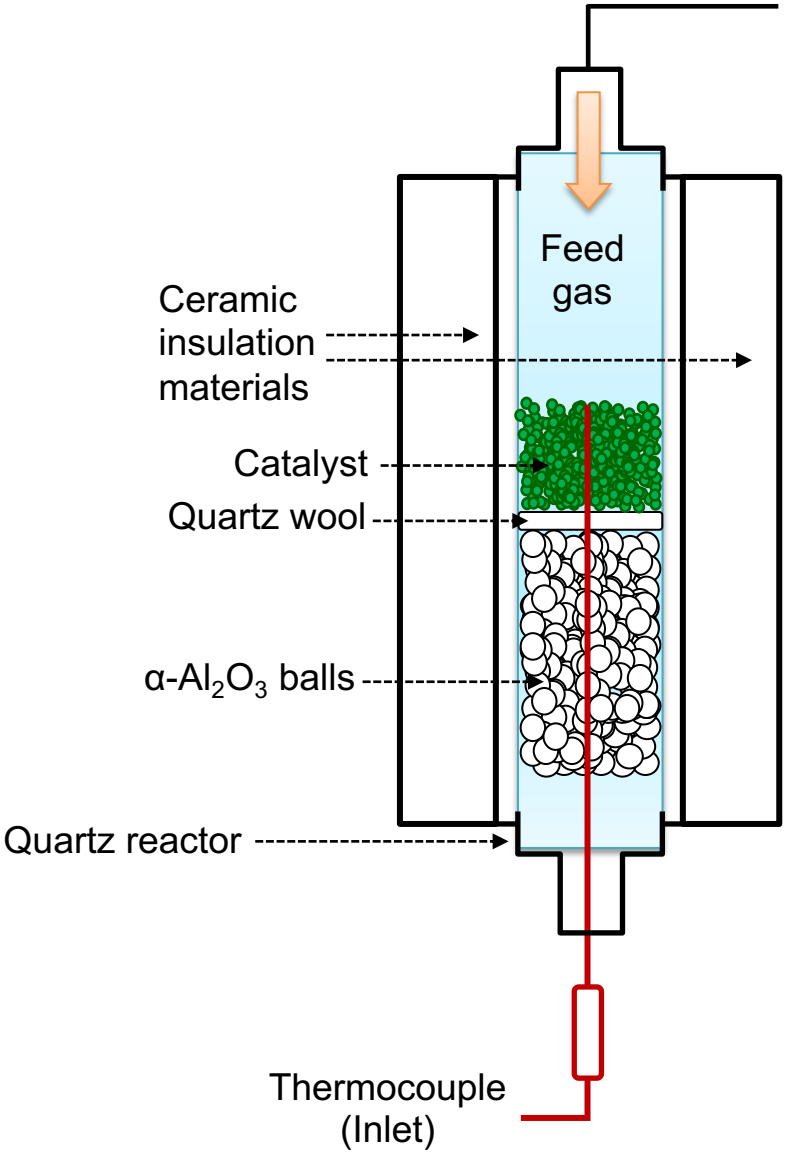



- Heat evolved by $NH_3$ adsorption increases the catalyst temperature to the catalytic auto-ignition temperature.

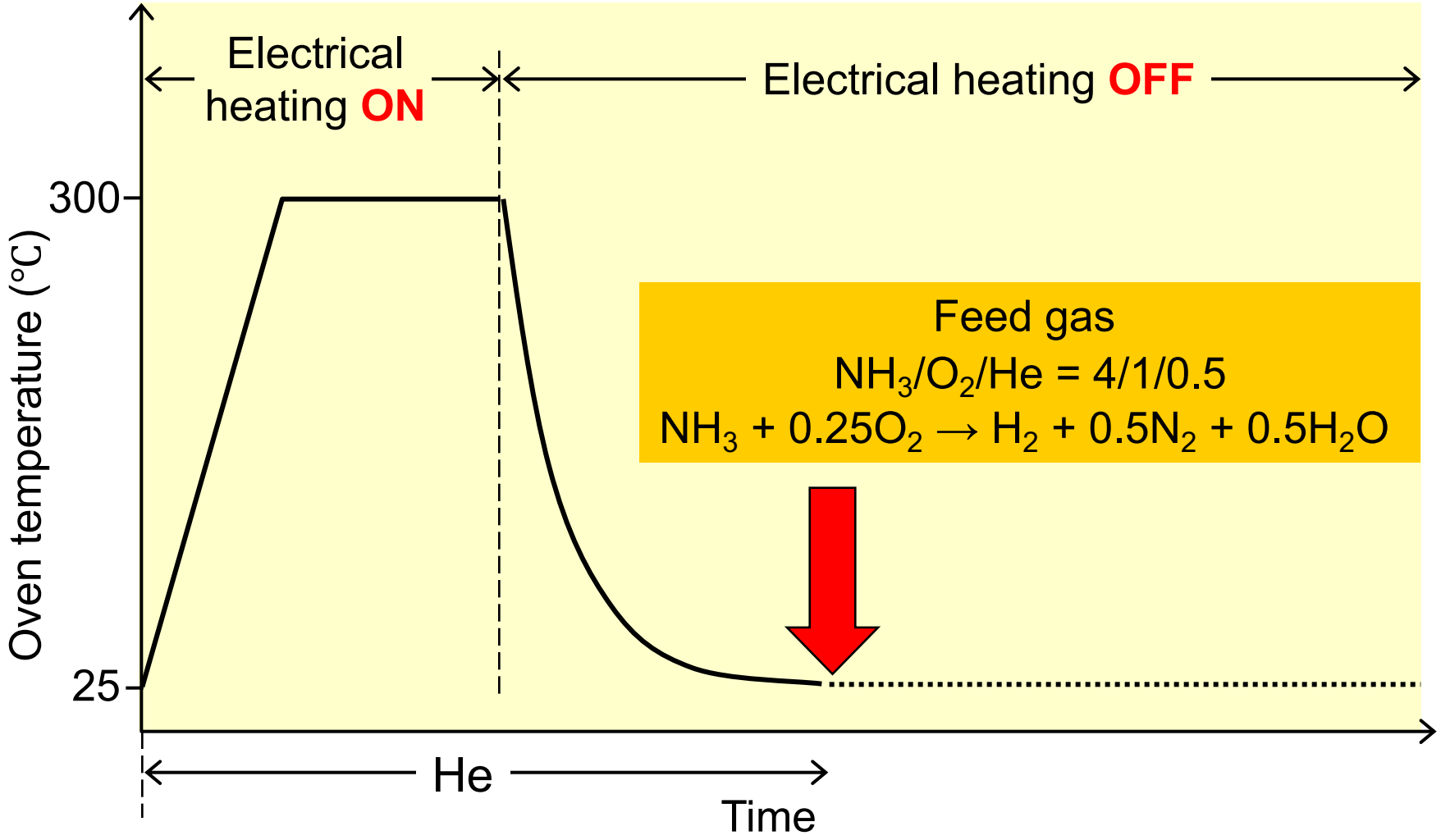
*Sci. Adv.* 3 (2017) e1602747.

# Experimental

- Catalyst: 5 wt% $RuO_2/\gamma\text{-}Al_2O_3$,
  5 wt% $RuO_2/La_2O_3$
- Activity test
  - Flow system
  - Adiabatic condition
  - Pretreatment: He, 300℃, 1 h
  - Initial temperature: RT (～25 ℃)
  - $NH_3/O_2/He$ = 4/1/0.6
  - SV: 62.5 L/(h·g)
  - Catalyst weight: 0.2 g
- Analysis
  - GC-TCD, Q-MS



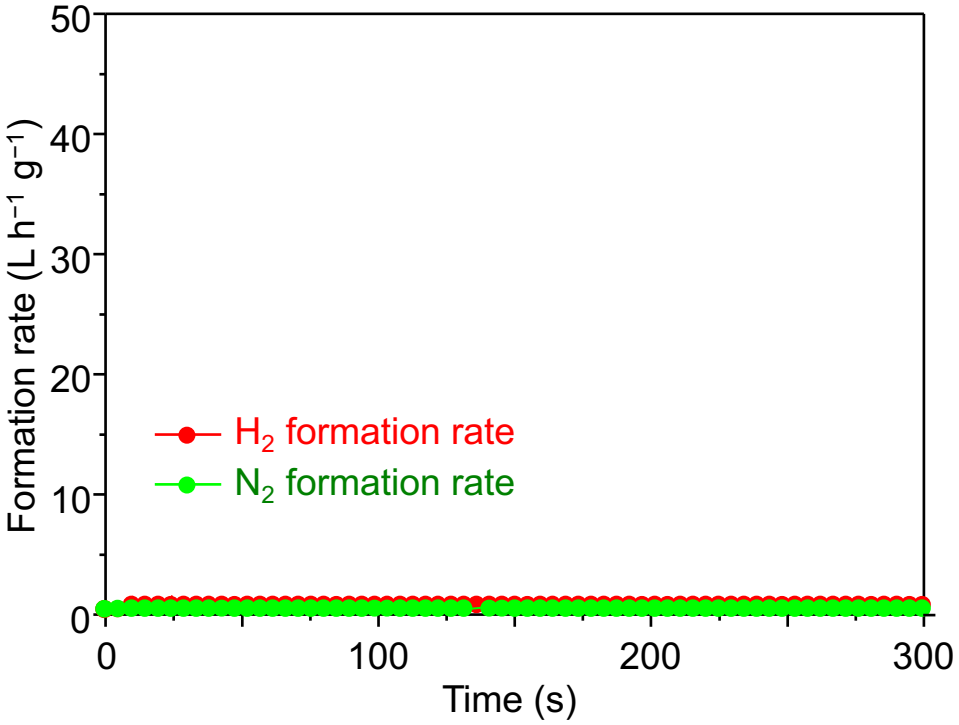
# Procedure of activity tests




- He pretreatment: 300 ℃
- Feed gas was supplied at RT.
- Power of the furnace was switched off during the reaction.

# Activity test for $RuO_2/La_2O_3$

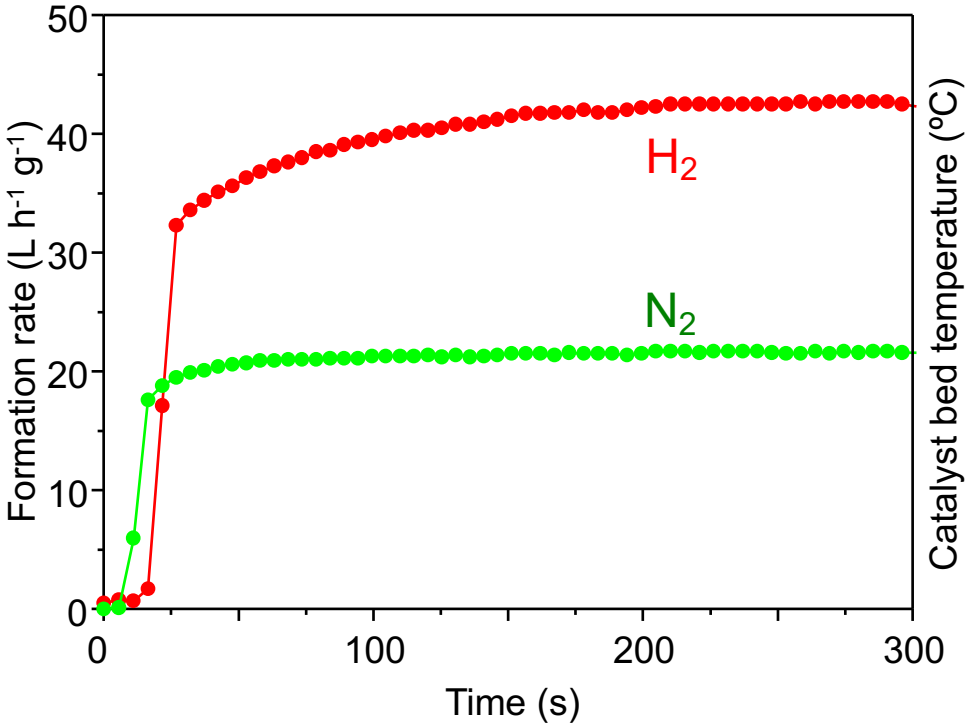
He, 300℃ → $NH_3/O_2$/He, RT

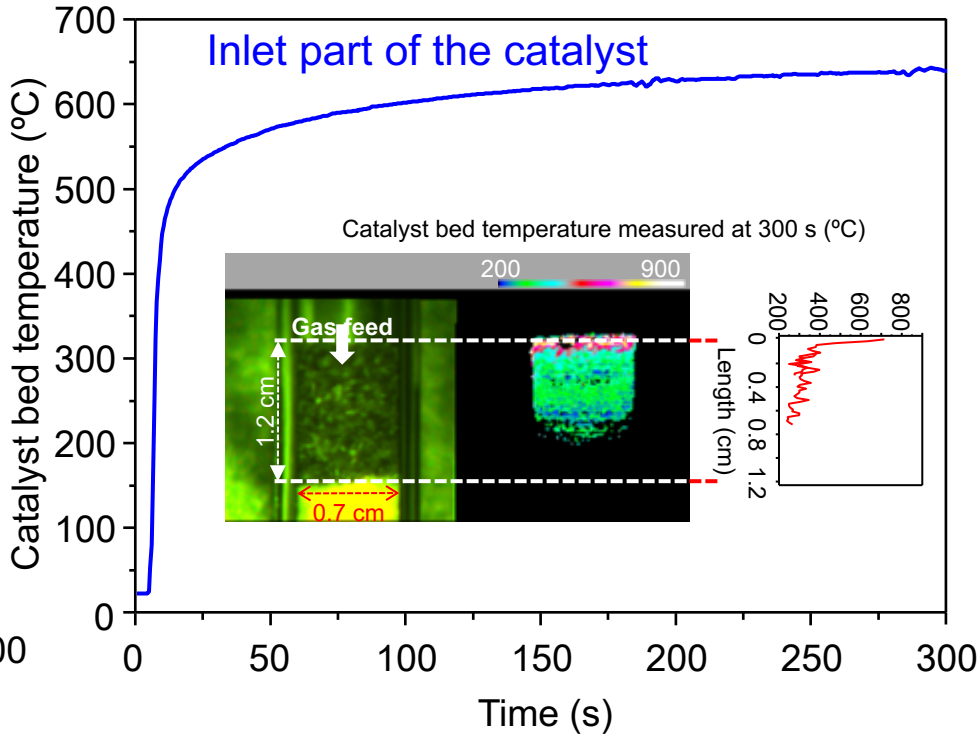



- No products were observed.

# Activity test for $RuO_2/\gamma\text{-}Al_2O_3$

He, 300℃ → $NH_3/O_2$/He, RT



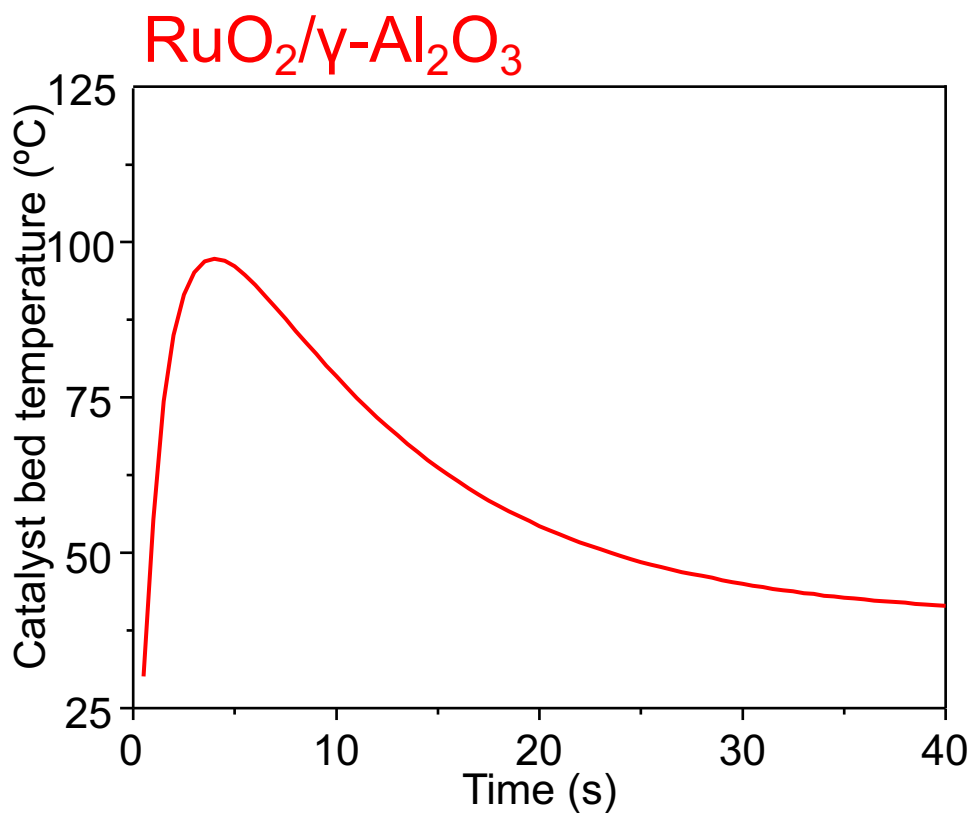



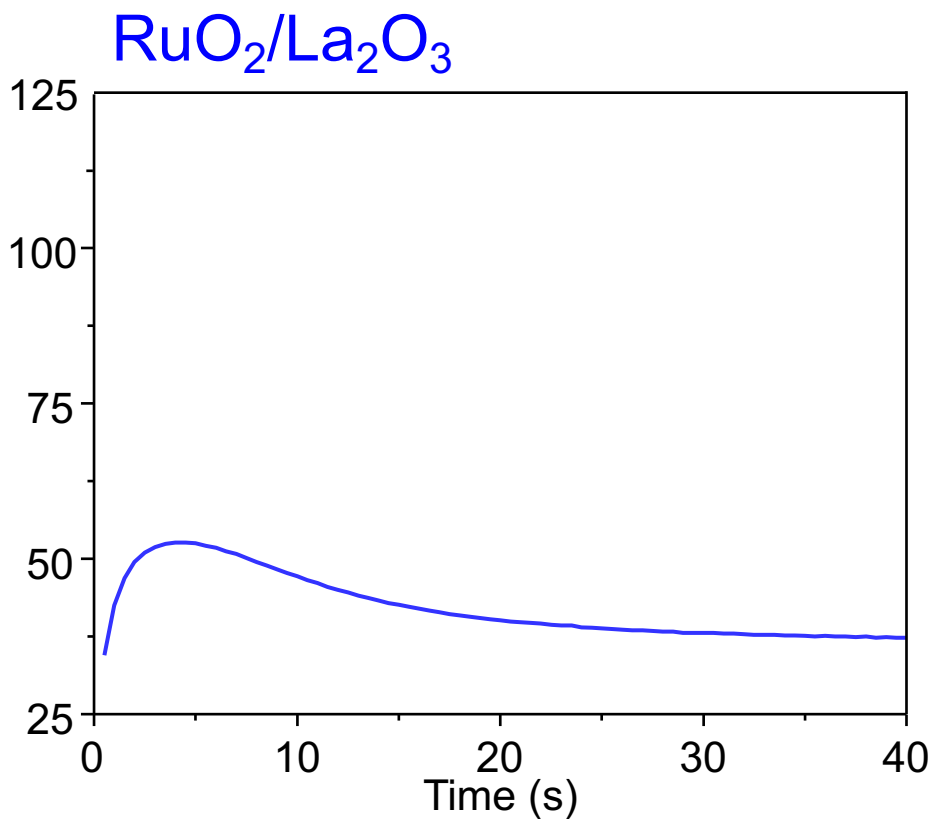

- Within 30 s, { $H_2$ production rate increased to 33 L $h^{-1}$ $g^{-1}$. catalyst bed temperature rose to 522 ℃.
  → AOD is triggered in a very short time without any external heat input.
- NO*x* were not observed during the test.

*Sci. Adv.* 3 (2017) e1602747.

# Rising in catalyst bed temperature through $NH_3$ adsorption

He, 300℃ → $NH_3$/He, RT

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# Rising in catalyst bed temperature through $NH_3$ adsorption

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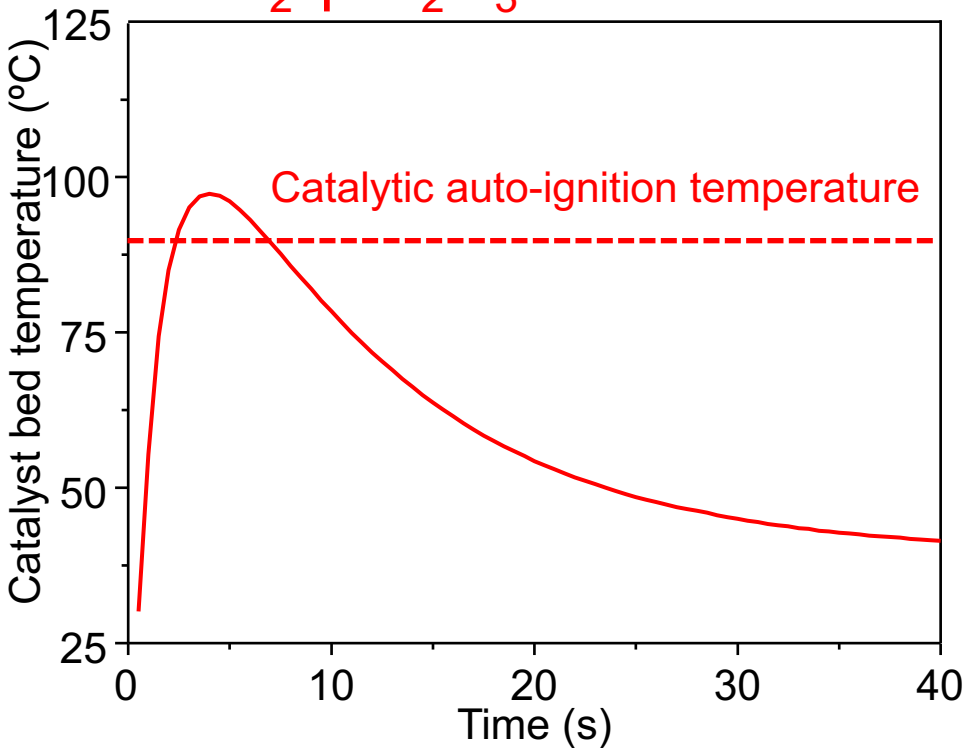
$RuO_2/\gamma\text{-}Al_2O_3$

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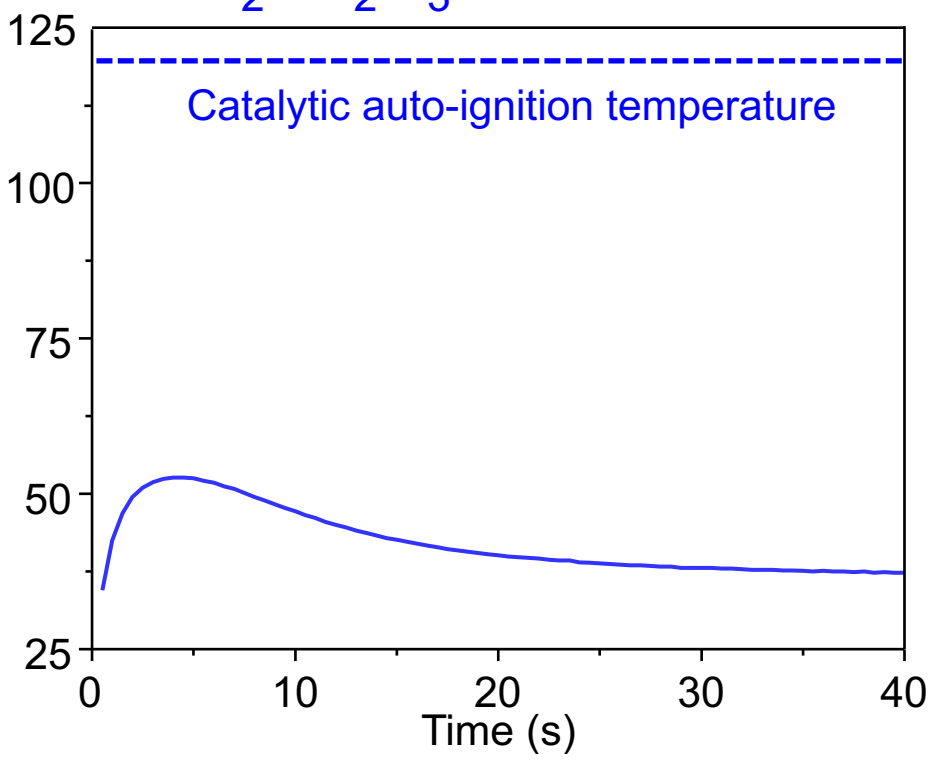



- $RuO_2/\gamma\text{-}Al_2O_3$
  - Heat produced through $NH_3$ adsorption increases the catalyst-bed temperature to catalytic auto-ignition temperature (90℃).

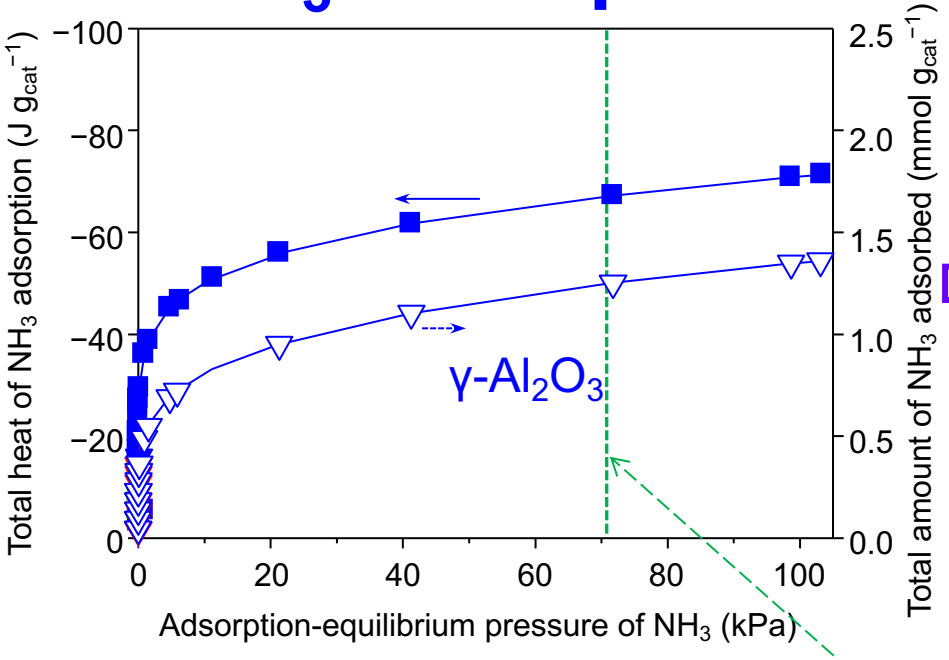
*Sci. Adv.* 3 (2017) e1602747.

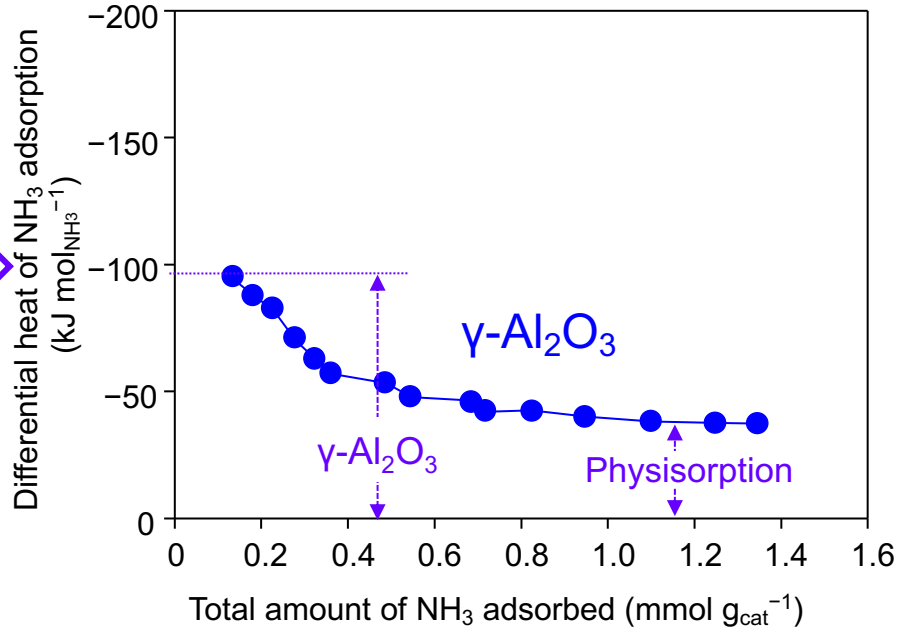
# Differential calorimeter combined with a volumetric gas-adsorption analyzer


Calvet-type heat-flux calorimeter

Volumetric gas-adsorption analyzer

# Role of $RuO_2$ and γ-$Al_2O_3$ for $NH_3$ adsorption and heat evolution (50 ℃)




- γ-$Al_2O_3$
  - Chemisorption on Lewis acid sites heats the catalyst.
  - Physisorption of $NH_3$ contributes to the heat evolution of the catalyst.

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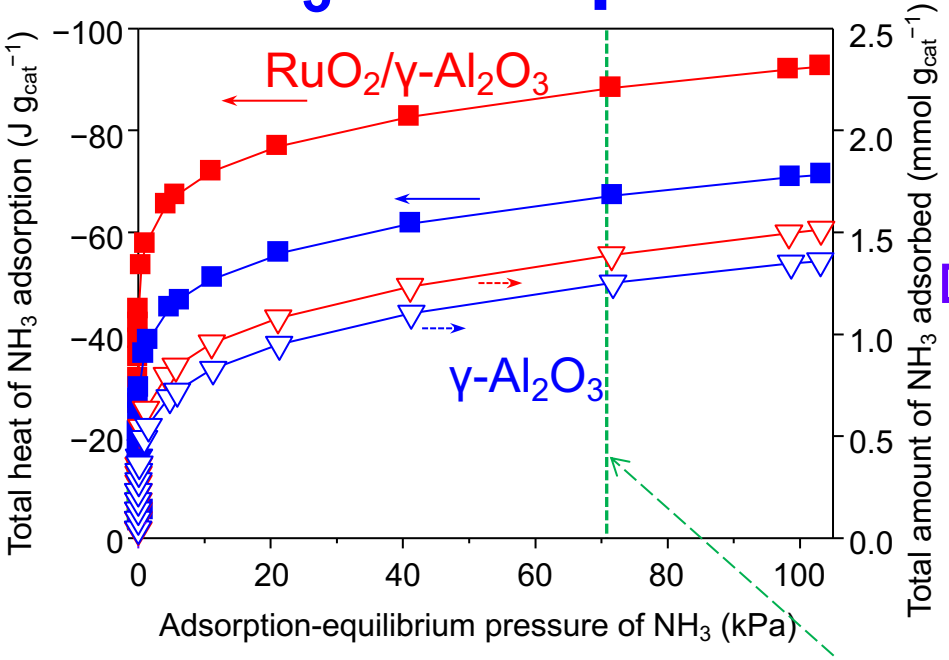
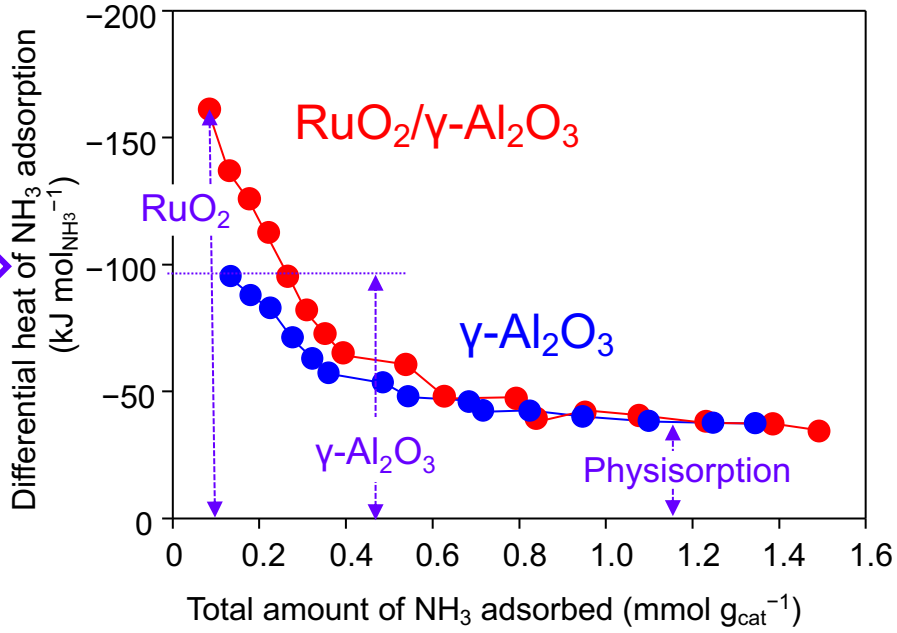
# Role of $RuO_2$ and $\gamma$-$Al_2O_3$ for $NH_3$ adsorption and heat evolution (50 ℃)

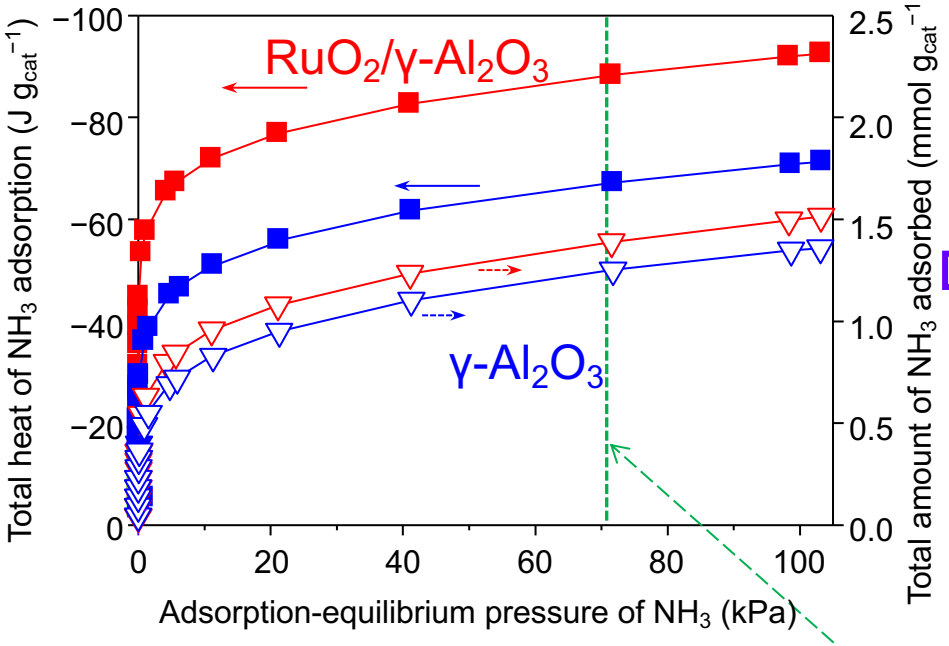


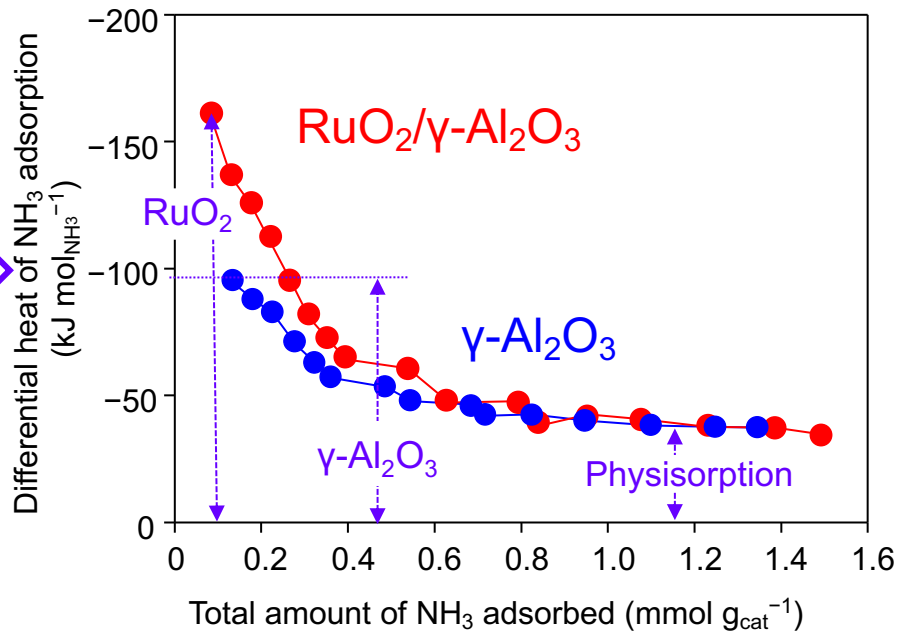




- $\gamma$-$Al_2O_3$
  - Chemisorption on Lewis acid sites heats the catalyst.
  - Physisorption of $NH_3$ contributes to the heat evolution of the catalyst.
- $RuO_2$/$\gamma$-$Al_2O_3$
  - Surface of $RuO_2$ particles serves as strong $NH_3$-adsorption sites.

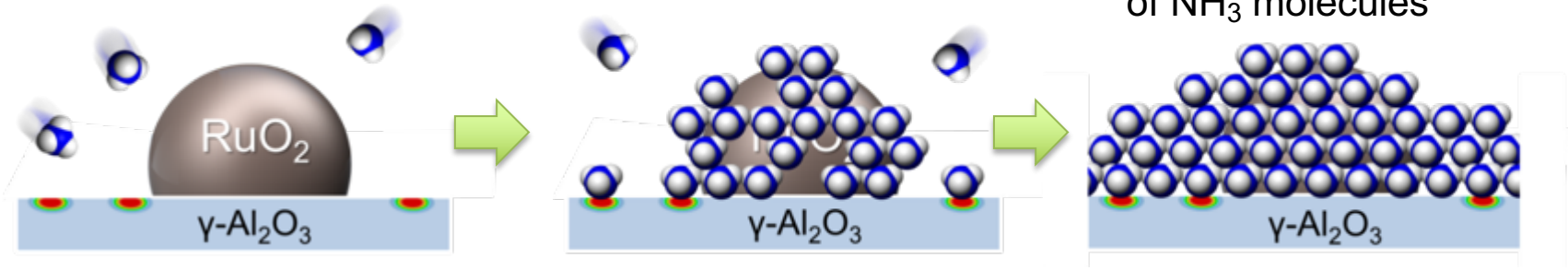
*Sci. Adv.* 3 (2017) e1602747.

# Role of $RuO_2$ and γ-$Al_2O_3$ for $NH_3$ adsorption and heat evolution (50 ℃)




Multilayer physisorption of $NH_3$ molecules



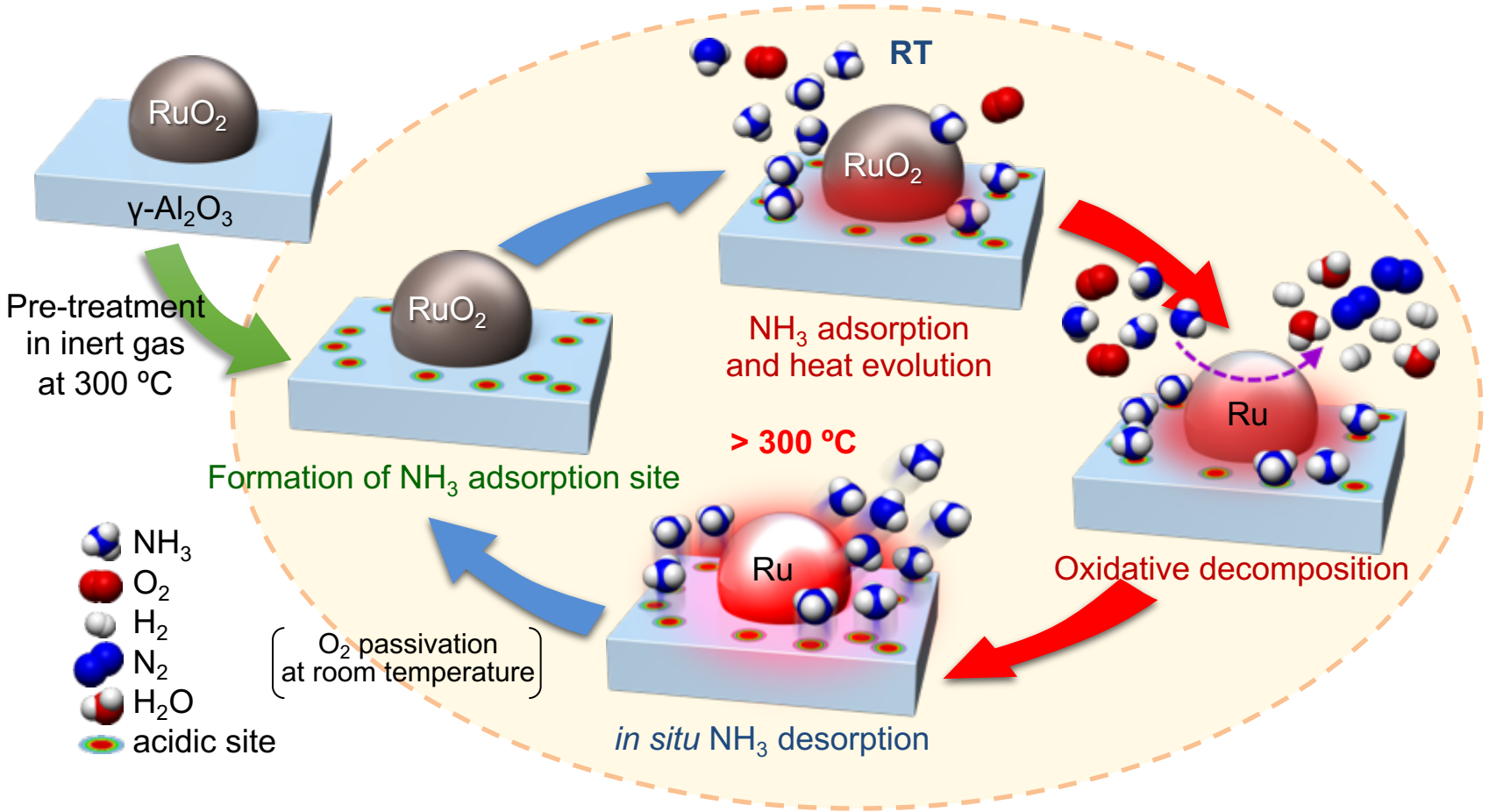

- $NH_3$ is chemisorbed on $RuO_2$ particles and Lewis acid sites on γ-$Al_2O_3$ and subsequently physisorbed as multilayer.

*Sci. Adv.* 3 (2017) e1602747.

# Cyclic process of AOD

$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O$

**Catalytic Cycle Requiring No External Energy**

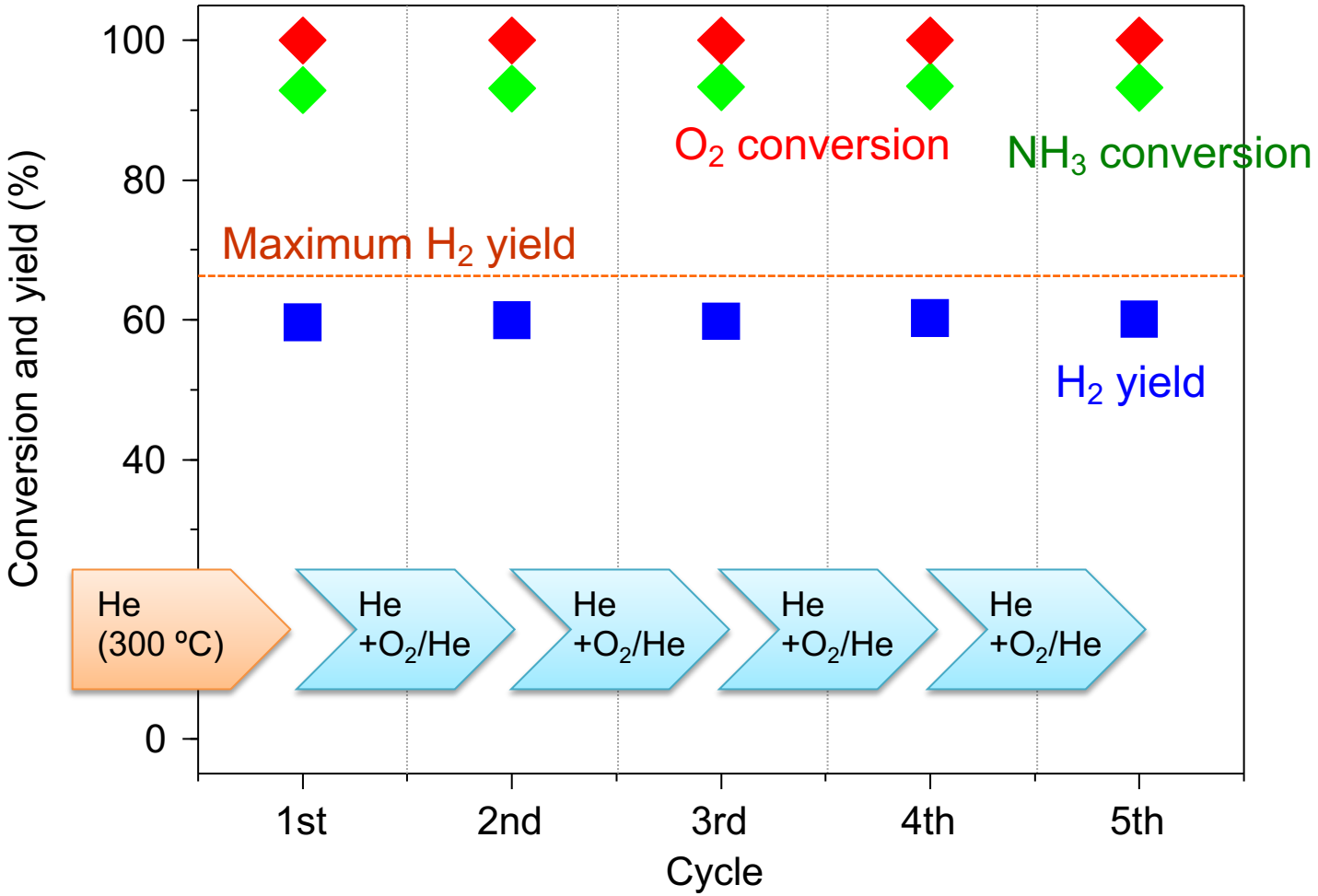



*Sci. Adv.* 3 (2017) e1602747.

# Cycle tests of AOD ($RuO_2/\gamma$-$Al_2O_3$)

He, 300℃ → $NH_3/O_2$/He, RT

$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O$




- $NH_3$ oxidative decomposition was triggered from RT at all cycles.

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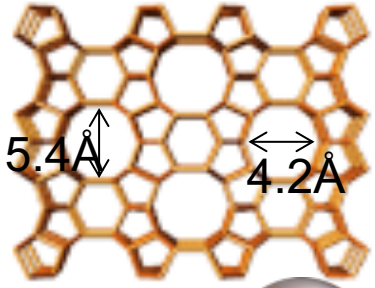
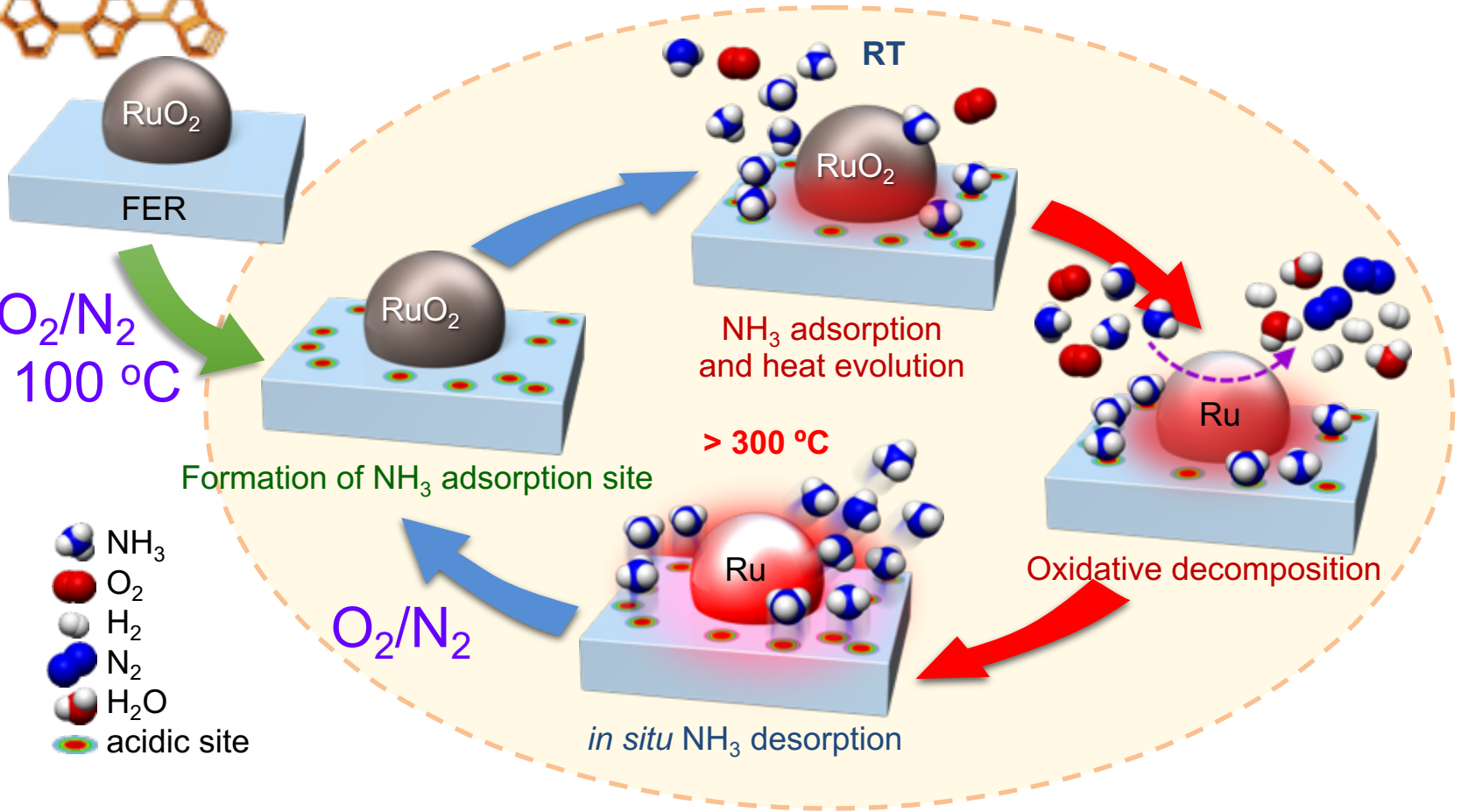
# Cyclic process of AOD

$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O$



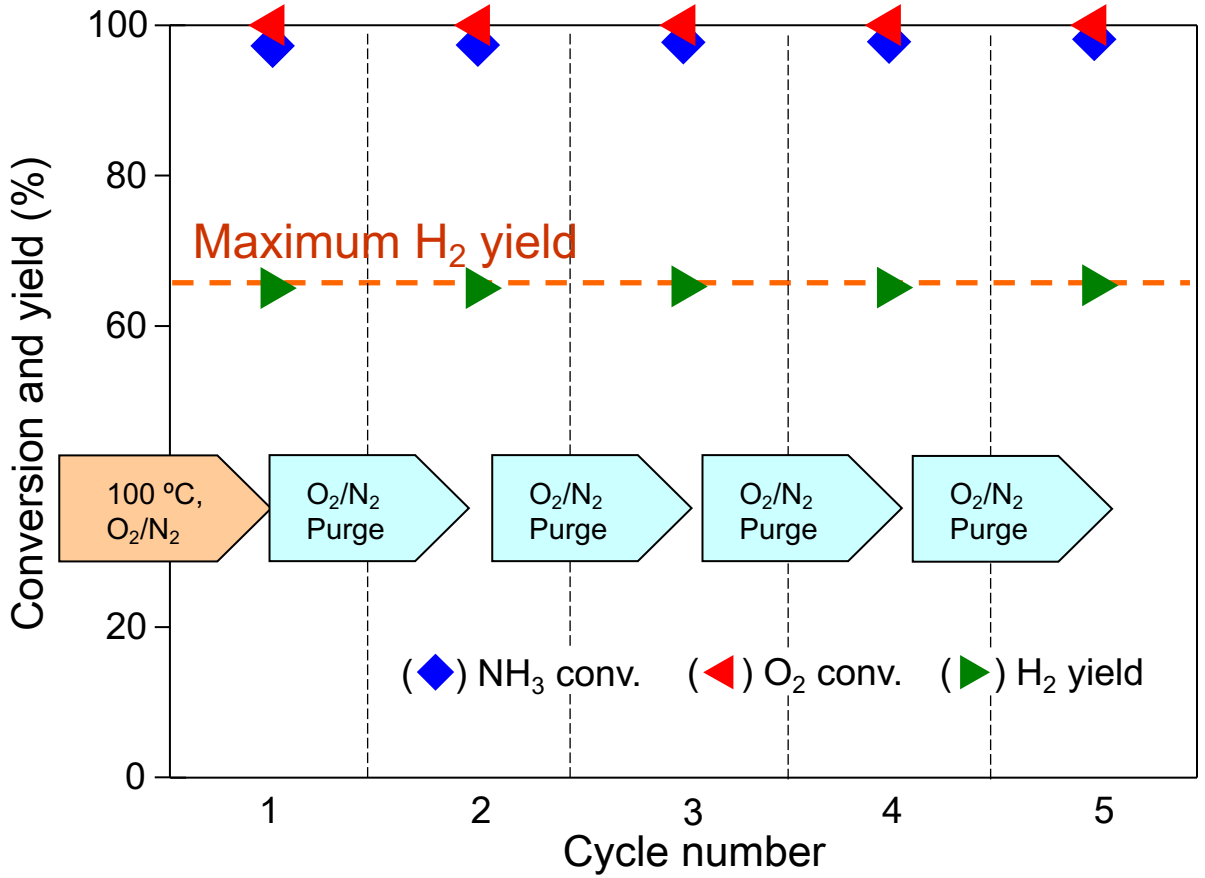

**Catalytic Cycle Requiring No External Energy**




*In preparation*

# Cycle tests of AOD ($RuO_2$/FER)

100 ℃, $O_2/N_2$ → $NH_3/O_2/N_2$=4/1/4, RT



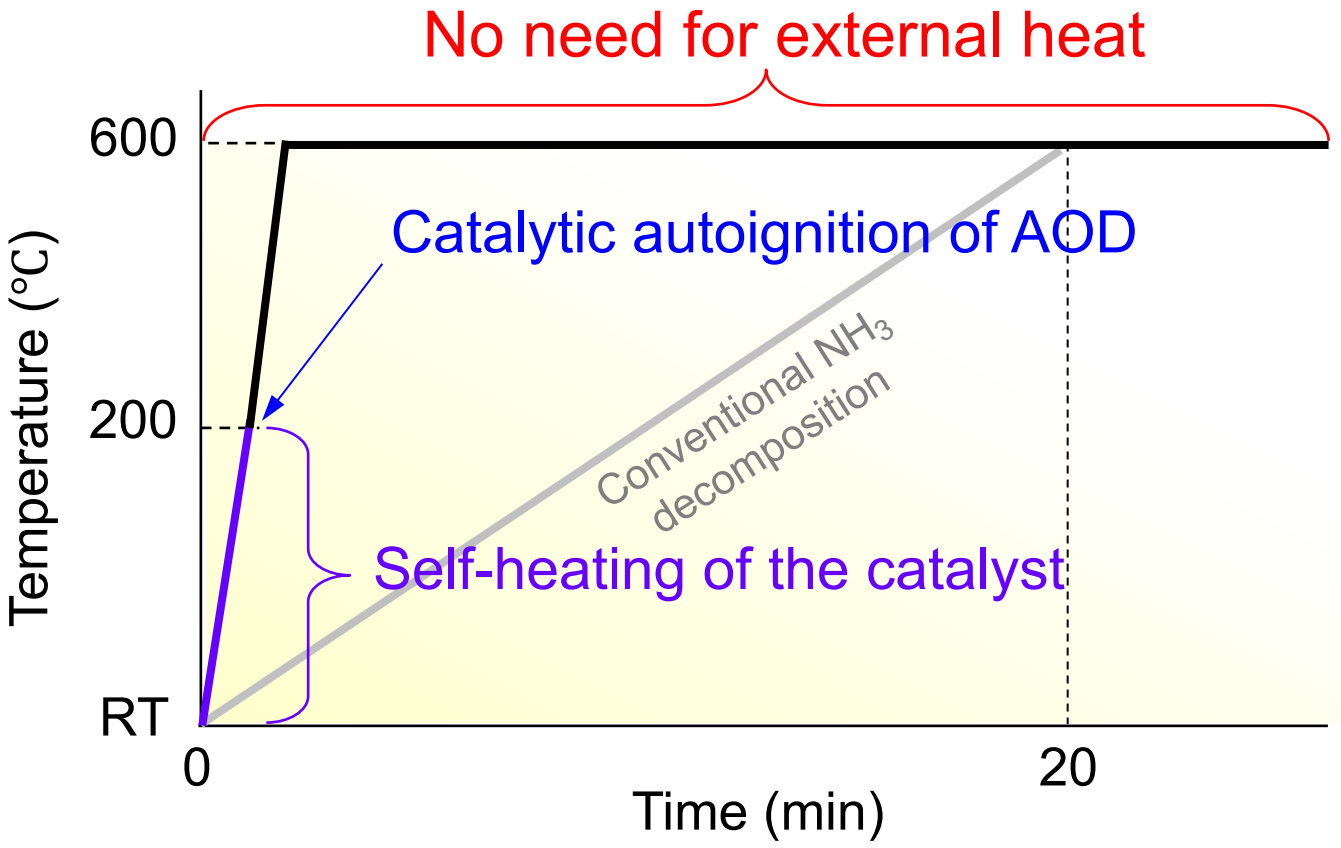

- $O_2/N_2$ was used instead of He.

  →A practical system using $NH_3$ and air would be developed.

*In preparation*

# Rapid cold-start process for $NH_3$ oxidative decomposition (AOD)

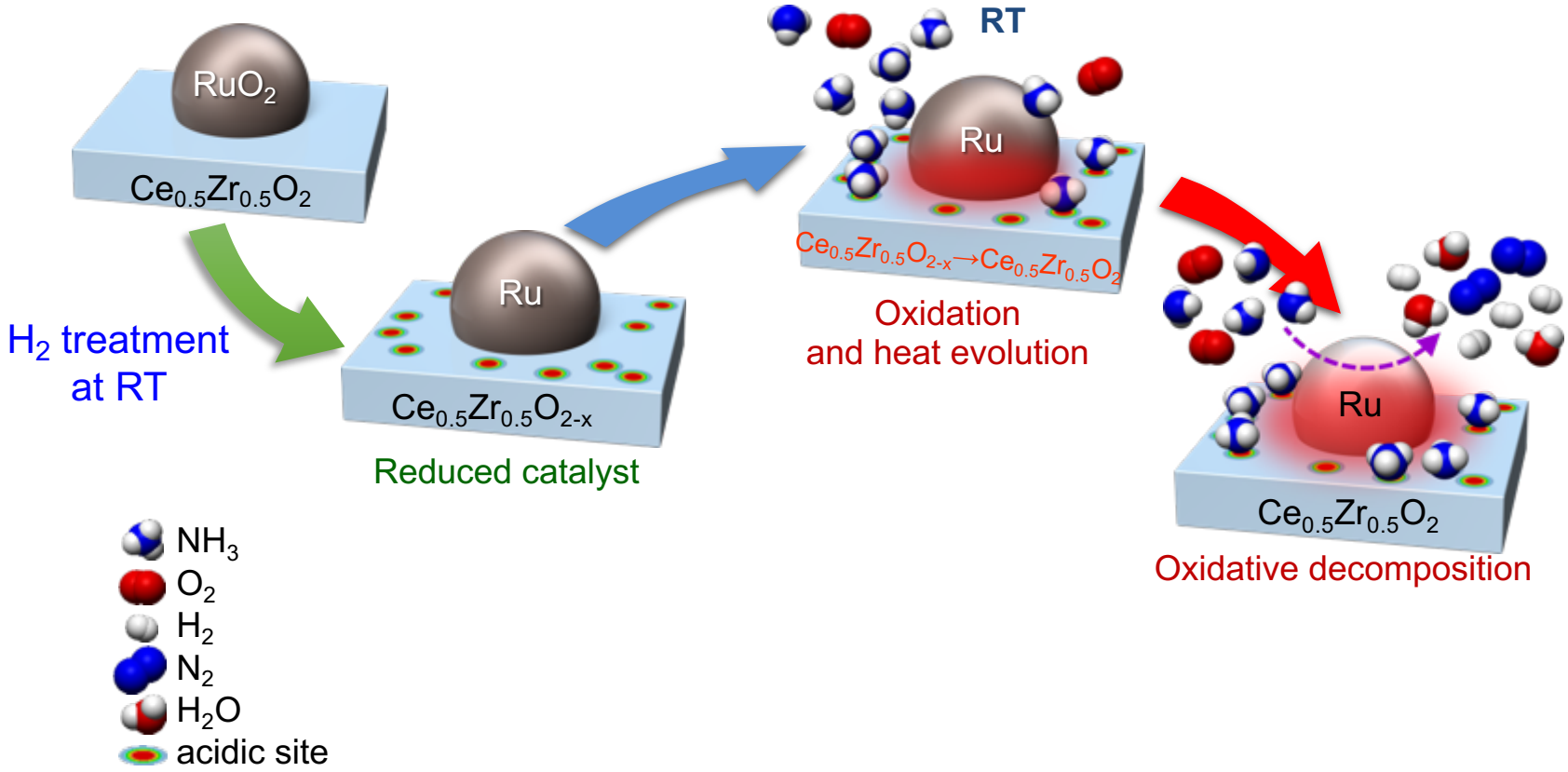
$$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O \quad \Delta H = -75\ kJ/mol$$




- Heat for self-heating
  1. Heat evolved by $NH_3$ adsorption
  2. Heat generated by oxidation of the reduced catalyst

# Mechanism for triggering AOD at RT (1wt%Ru/$Ce_{0.5}Zr_{0.5}O_2$)

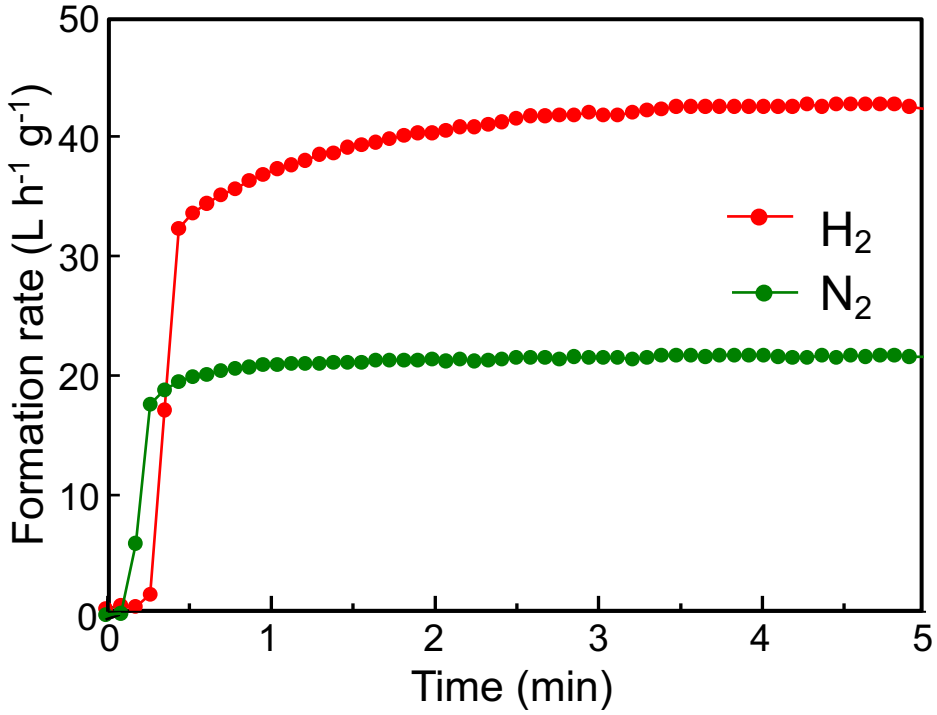
$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O$

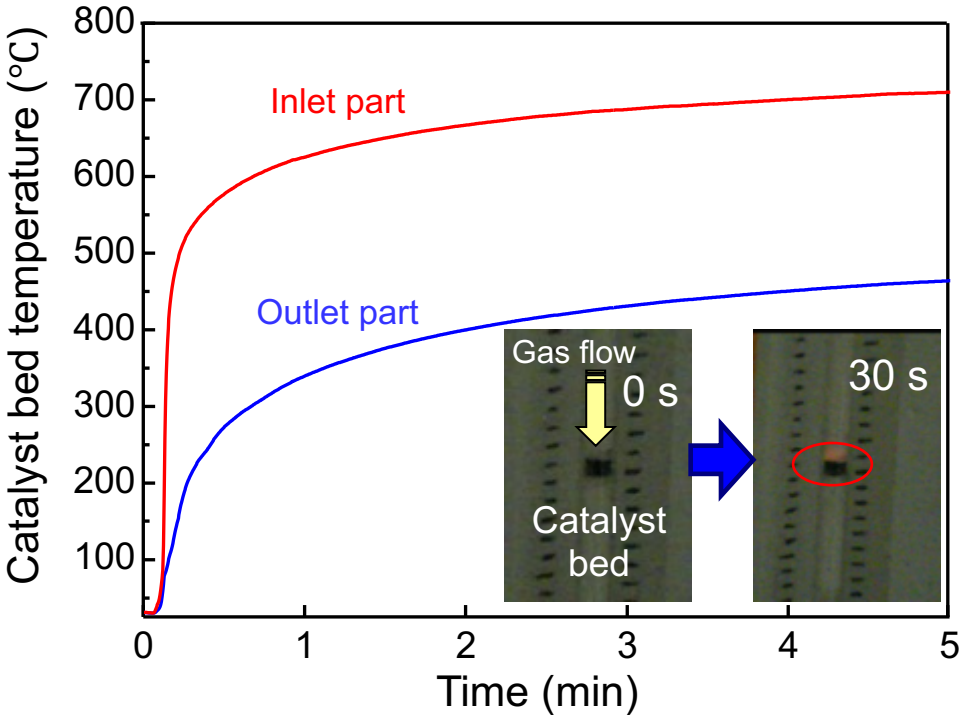



- Heat evolved by catalyst oxidation increases the catalyst temperature to the catalytic auto-ignition temperature.

# Triggering AOD at RT ($Ru/Ce_2Zr_{0.5}O_2$)

$H_2$ reduction, RT → He, 300 ℃ → $NH_3/O_2/He$=4/1/0.5, SV= 62.5 L/(hg), RT



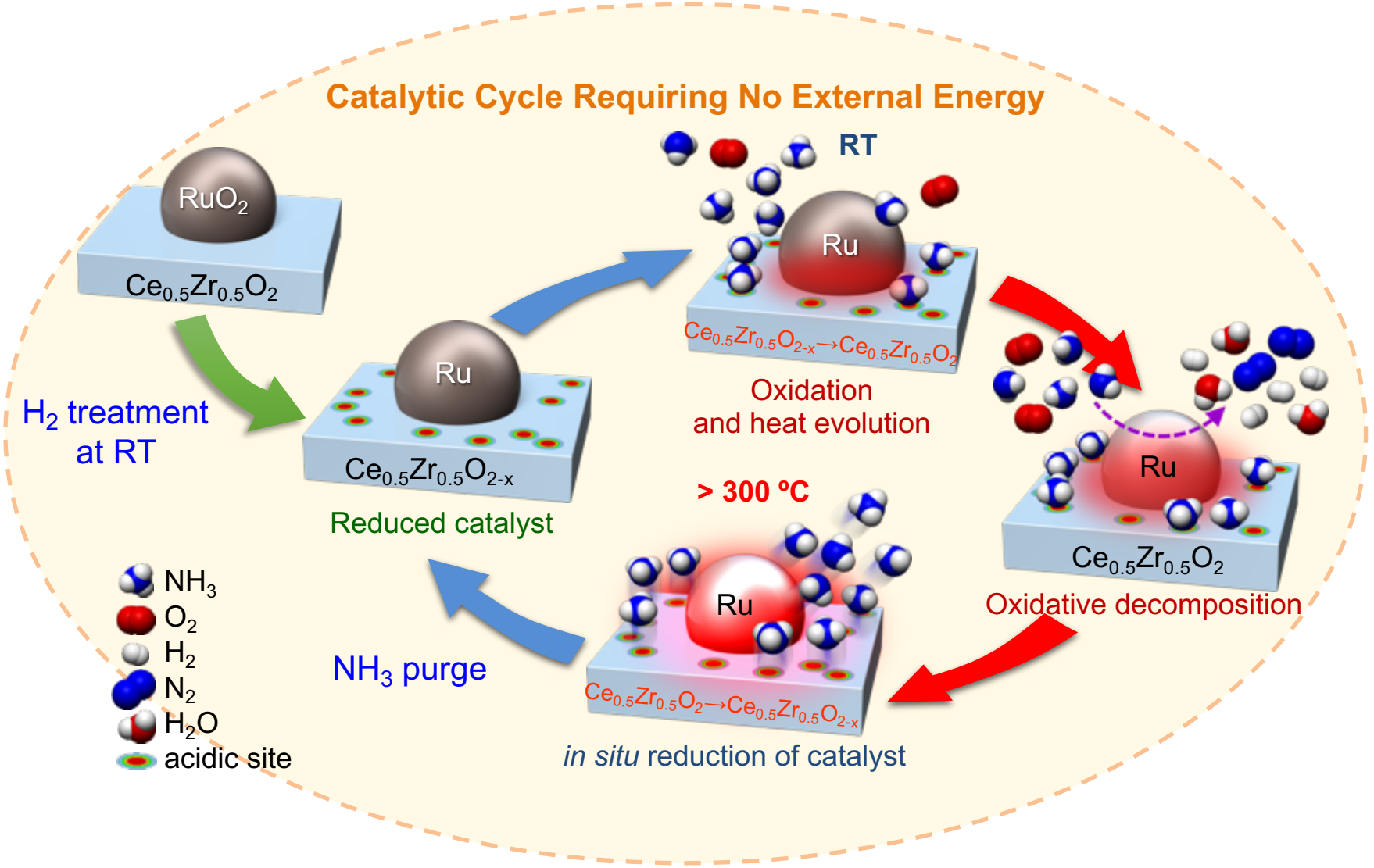




- Within 30 s,
  - $H_2$ production rate increased drastically to 34 L/(hg).
  - catalyst bed temperature rose to 600 ℃.

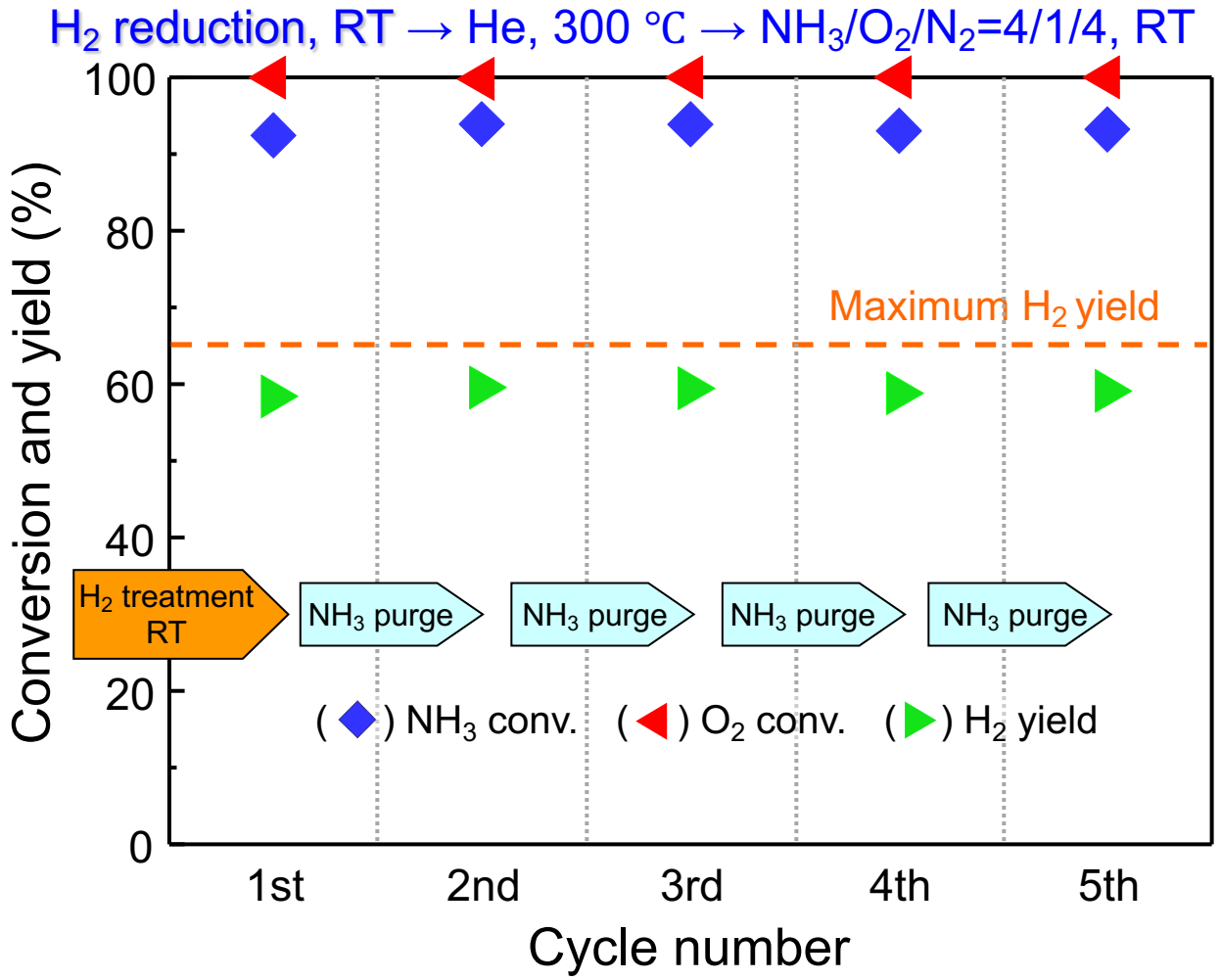
→ AOD is triggered in a very short time without any external heat input.

# Cyclic process of AOD

$NH_3 + 0.25O_2 \rightarrow H_2 + 0.5N_2 + 0.5H_2O$



# Cycle tests of AOD ($Ru/Ce_{0.5}Zr_{0.5}O_2$)

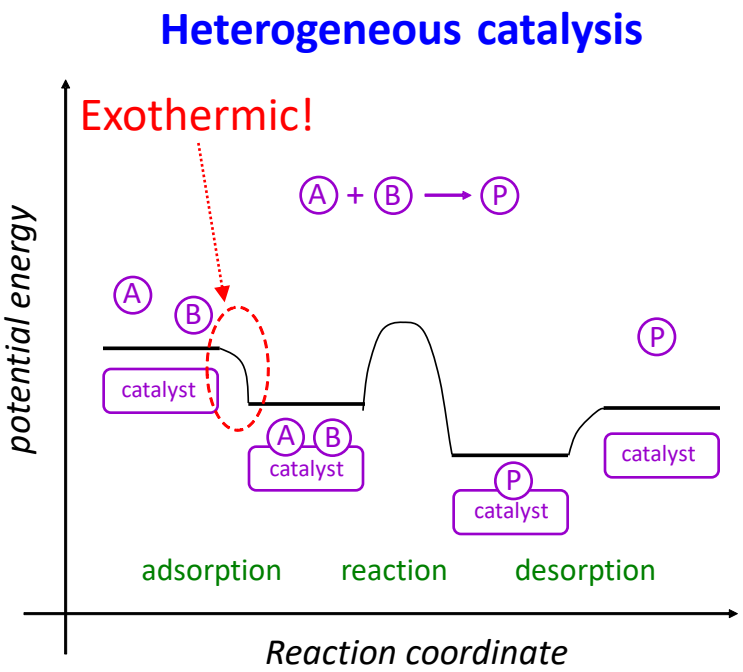



- $NH_3$ oxidative decomposition was triggered from RT at all cycles by the heat produced by oxidation of $Ru/Ce_{0.5}Zr_{0.5}O_{2-x}$ at RT.

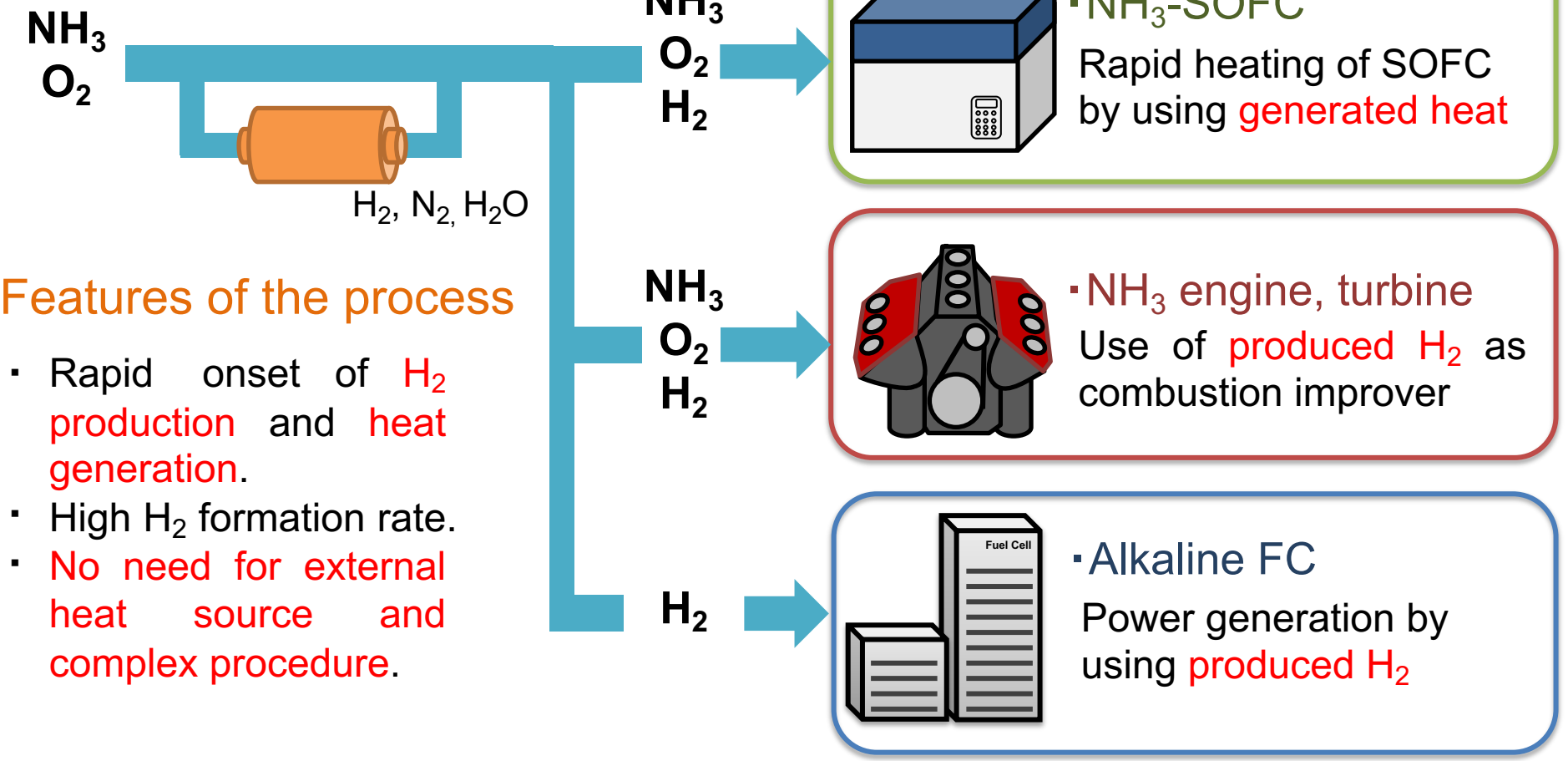
# Summary

- We present innovative process for $H_2$ production without need for heating the catalyst externally for start-up as well as during $NH_3$ oxidative decomposition.

- Strong heat generated by a simple fundamental physicochemical process, namely $NH_3$ adsorption or oxidation of the catalyst, heats the catalyst to catalytic auto-ignition temperature and resultantly permits rapid cold-start process for $H_2$-production.



# Potential applications

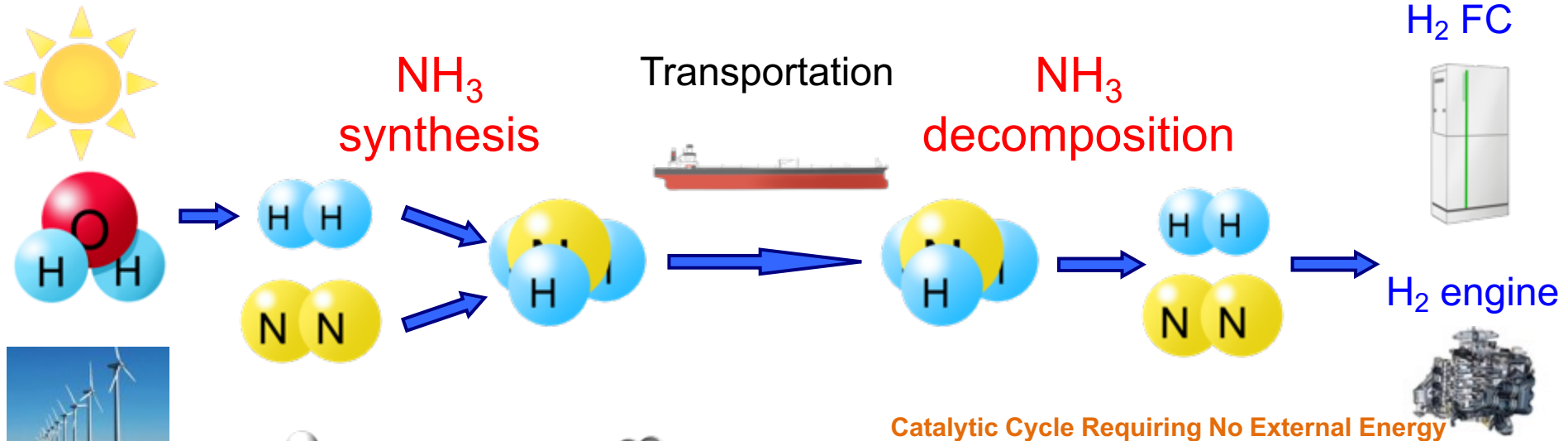


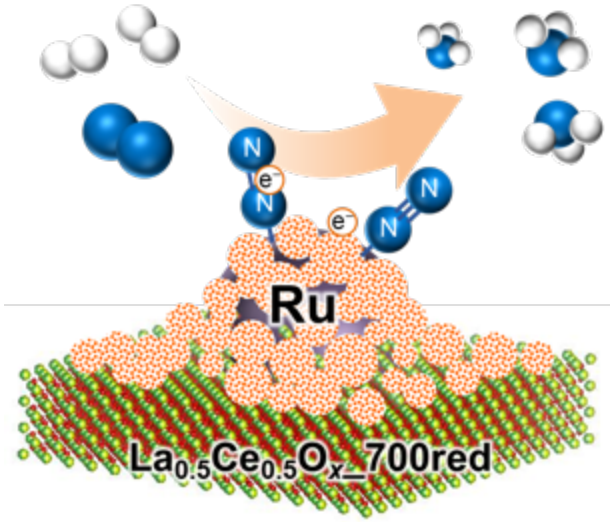

- $NH_3$-SOFC
  Rapid heating of SOFC by using generated heat
- $NH_3$ engine, turbine
  Use of produced $H_2$ as combustion improver
- Alkaline FC
  Power generation by using produced $H_2$

## Features of the process

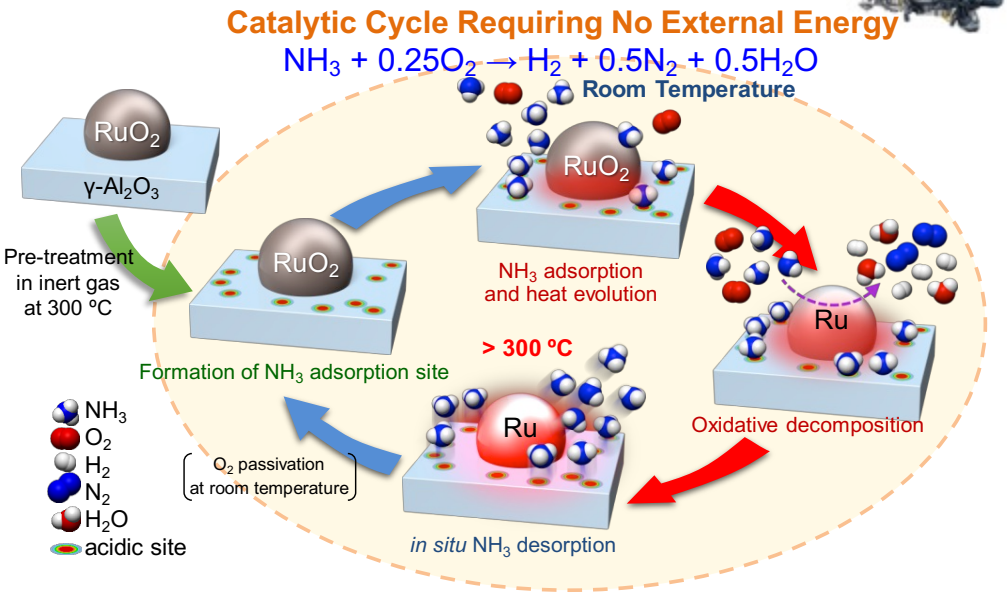
- Rapid onset of $H_2$ production and heat generation.
- High $H_2$ formation rate.
- No need for external heat source and complex procedure.

# We envisage a low-carbon society using $H_2$, in which $NH_3$ plays a role as an energy and $H_2$ carrier!




Oxygen Deficient Composite Oxide (including $Ba^{2+}$, $Ce^{3+}$, and $La^{3+}$)




ChemRxiv, doi.org/10.26434/chemrxiv.7763657.v1

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A. Prof. Saburo Hosokawa
Prof. Ken-ichi Aika
Mr. Masaaiki Uemura

Kotoko Tsujimaru, Takahiro Matsunaga, Ken Matsumoto, Yukiko Kawano, Ryo Tasaki, Yuma Takeishi, Takaaki Eboshi, Kyoko Honda, Manami Kawano, Takeo Terasawa, Kyoko Honnda,

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JST CREST

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Kotoko Tsujimaru, Takahiro Matsunaga, Ken Matsumoto, Yukiko Kawano, Ryo Tasaki, Yuma Takeishi, Takaaki Eboshi, Kyoko Honda, Manami Kawano, Takeo Terasawa, Kyoko Honnda,

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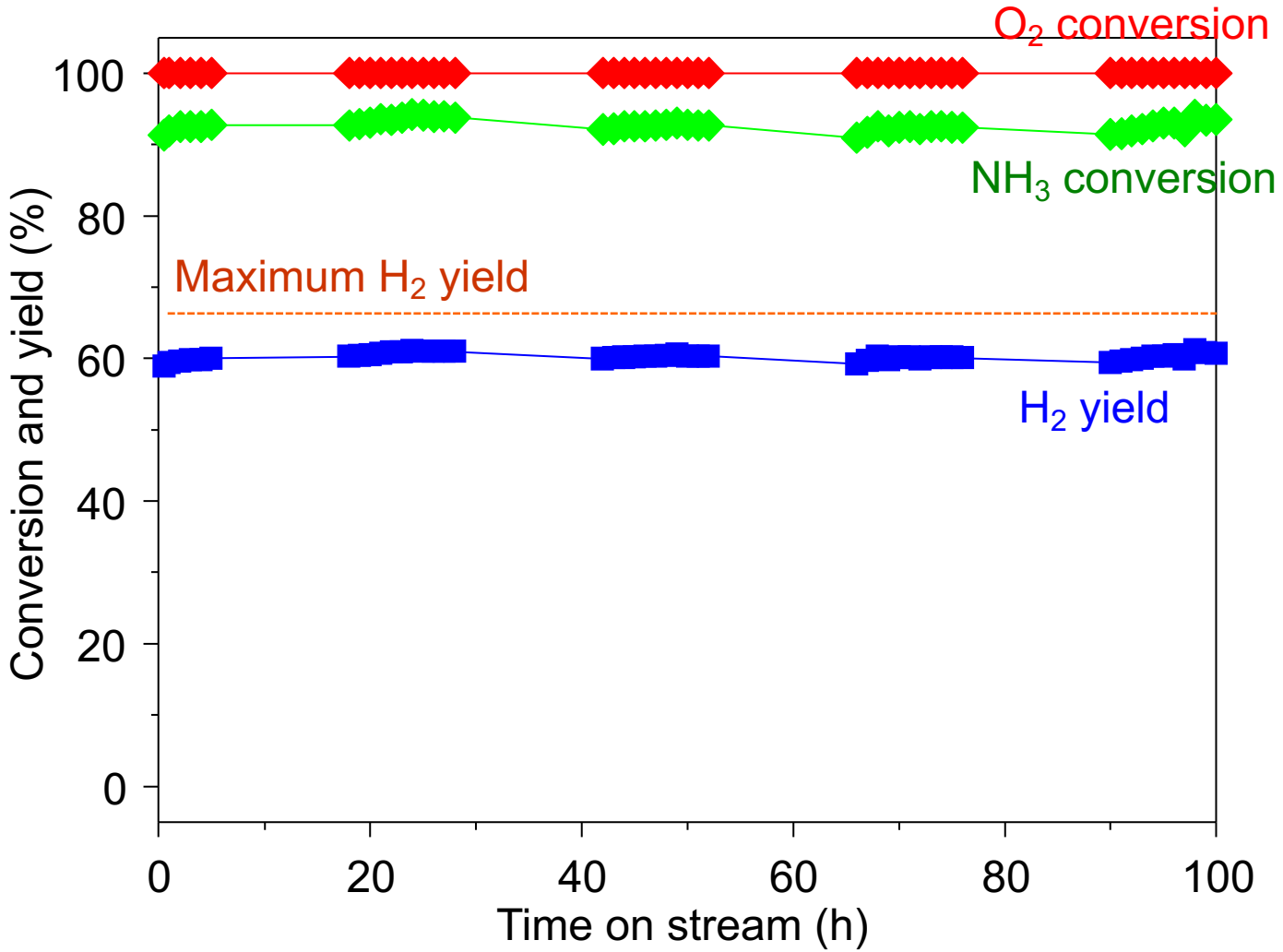
# Long-term activity test ($RuO_2/\gamma\text{-}Al_2O_3$)

He, 300℃ → $NH_3/O_2$/He, RT




- $RuO_2/\gamma\text{-}Al_2O_3$ exhibits high and stable activity at least for 100 h without external heat.
- Ru amount was unchanged before or after long-term reactions or after the cycle tests (XRF).

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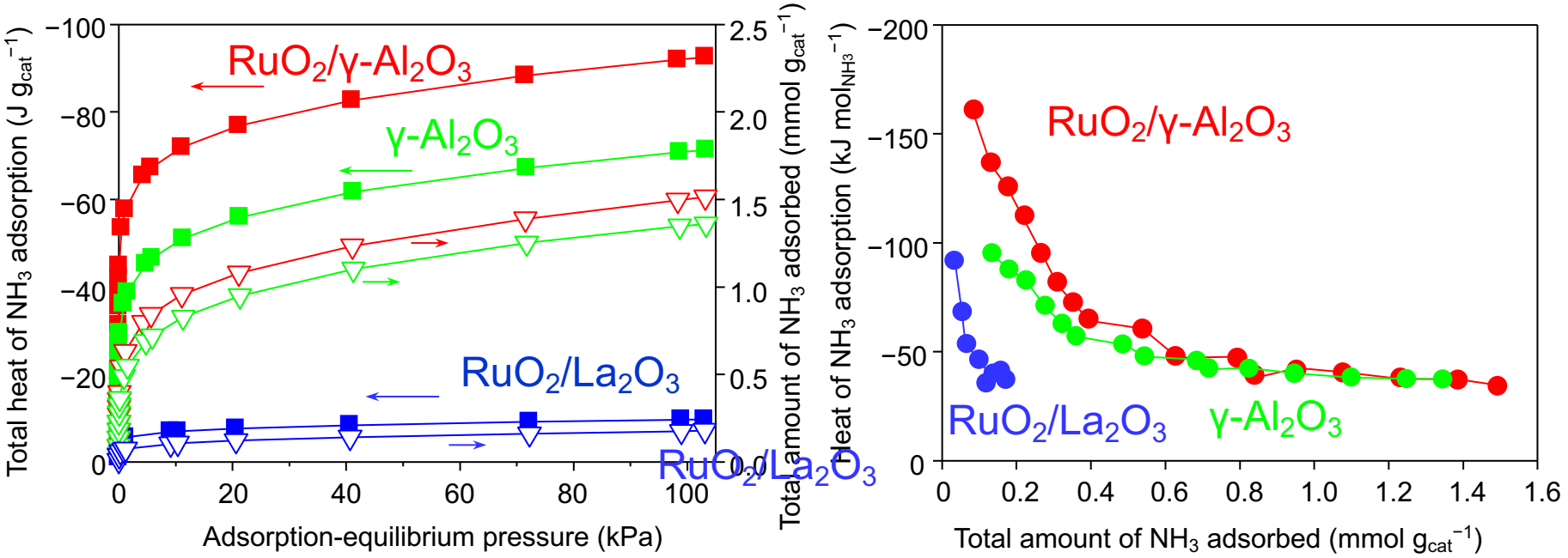
# Influence of Ru loading on γ-$Al_2O_3$




- $RuO_2$/γ-$Al_2O_3$: Heat evolution and adsorption amounts were much higher than those on bare γ-$Al_2O_3$.
  → Surface of $RuO_2$ nanoparticles serves as strong $NH_3$-adsorption sites.

- Physisorption of $NH_3$ also contributes to the heat evolution of the catalyst.

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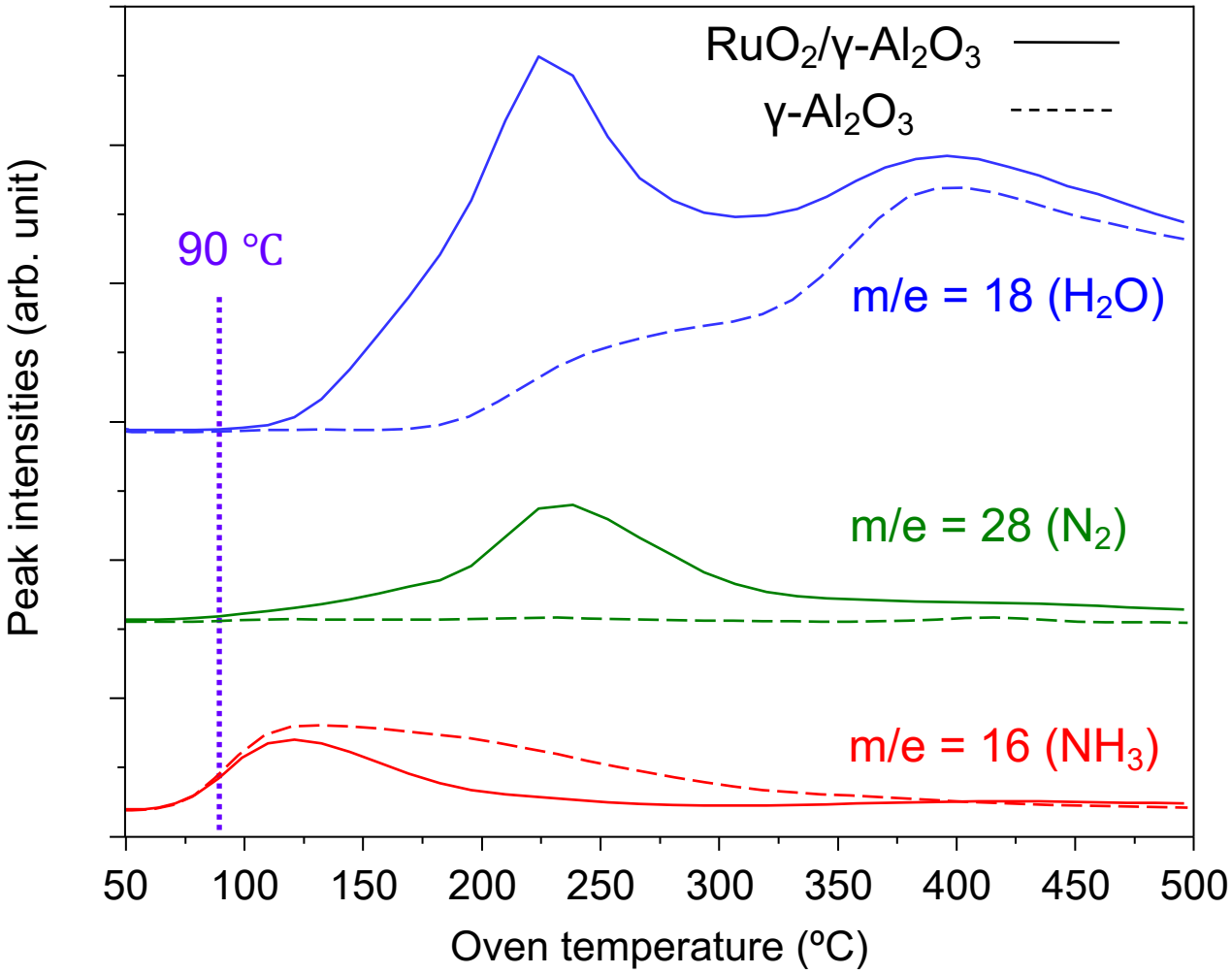
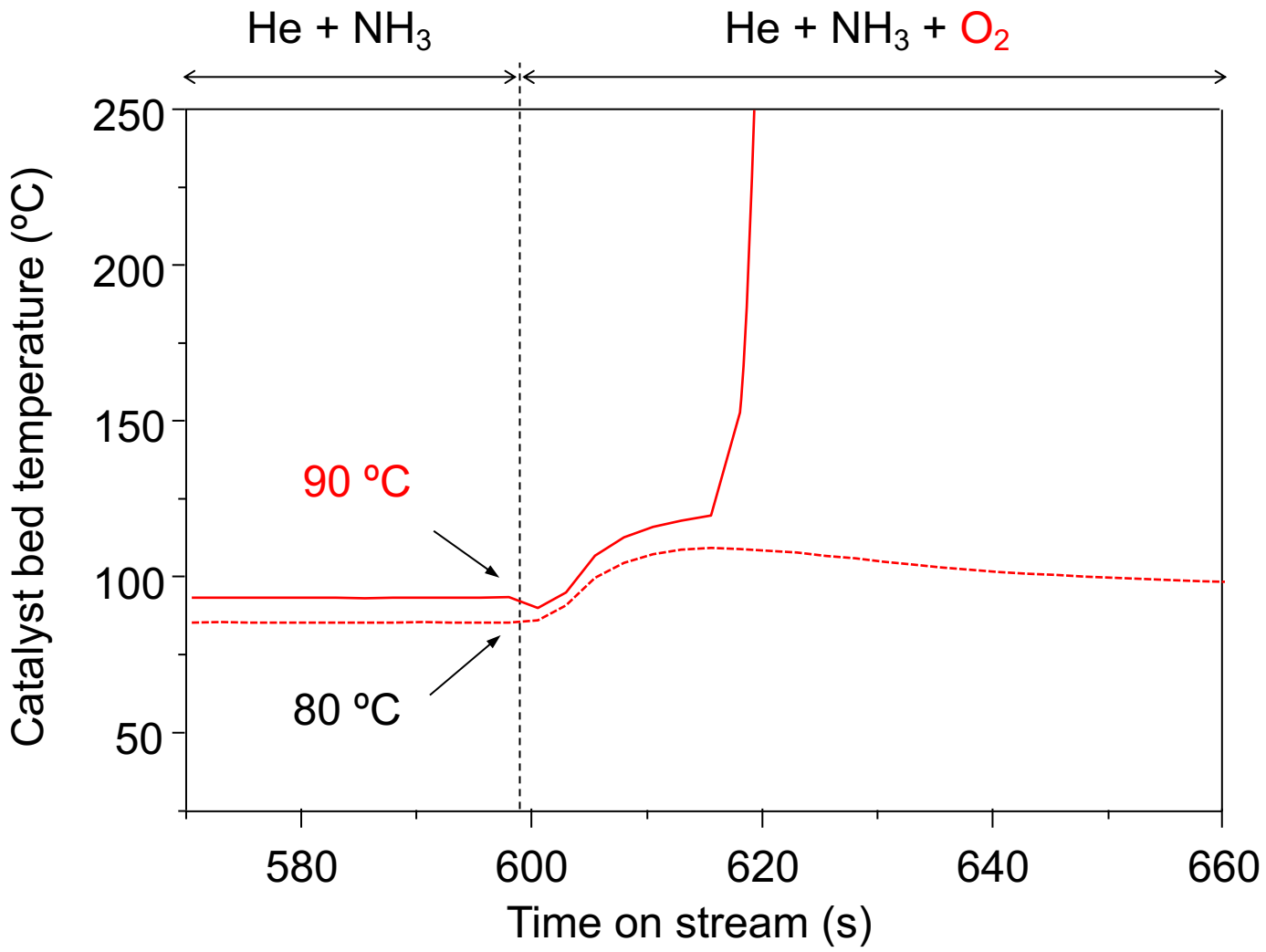
# $NH_3$ TPD

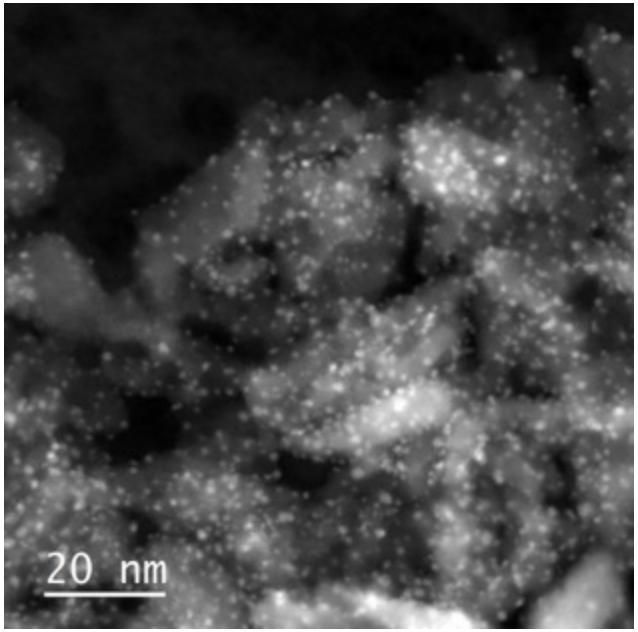

RuO2/γ-Al2O3
γ-Al2O3
90 ℃
m/e = 18 (H2O)
m/e = 28 (N2)
m/e = 16 (NH3)
Peak intensities (arb. unit)
50
100
150
200
250
300
350
400
450
500
Oven temperature (ºC)

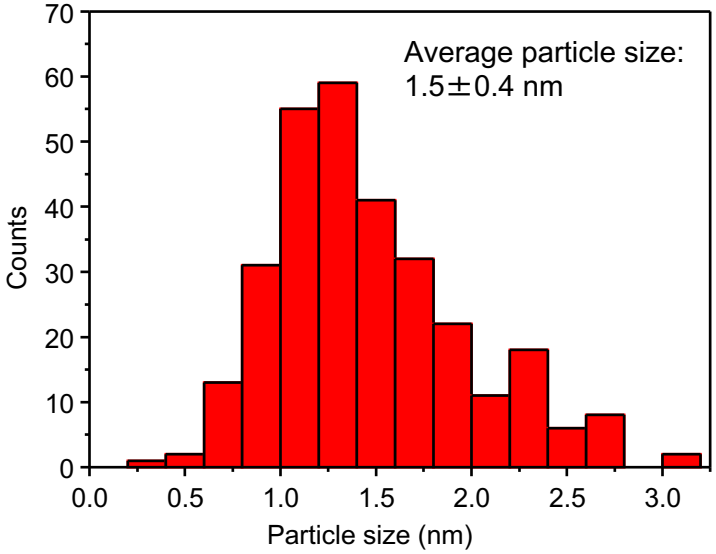
# Determination of catalytic autoignition temperature ($RuO_2/\gamma\text{-}Al_2O_3$)



# Physicochemical property of the catalysts

| Catalyst | Specific surface area ($m^2\ g_{cat}^{-1}$) | CO adsorbed ($\mu mol\ g_{cat}^{-1}$) |
|---|---|---|
| $RuO_2/\gamma\text{-}Al_2O_3$ | 156 | 477 |
| $RuO_2/La_2O_3$ | 23 | 23 |



# Influence of SV (same catalyst weight)

| Gas Hourly Space velocity ($L\ h^{-1}\ g_{cat}^{-1}$) | Feed gas composition ($mL\ min^{-1}$) | Conversion (%) | | $H_2$ yield (%) |
|---|---|---|---|---|
| | $NH_3$:$O_2$:He ratio | $NH_3$ | $O_2$ | |
| 31.25 | 75:18.8:10.4 | 73.89 | 100 | 45.46 |
| 62.5 | 150:37.5:20.8 | 97 | 100 | 63 |
| 125 | 300:75:41.6 | 100 | 100 | 67 |

# Influence of $NH_3/O_2$

$NH_{3\,(g)} + 0.37O_{2\,(g)} \rightarrow 0.76H_{2\,(g)} + 0.5N_{2\,(g)} + 0.74H_2O_{\,(g)}$ $\Delta H = -135$ kJ mol$^{-1}$

$NH_{3\,(g)} + 0.25O_{2\,(g)} \rightarrow H_{2\,(g)} + 0.5N_{2\,(g)} + 0.5H_2O_{\,(g)}$ $\Delta H = -75$ kJ mol$^{-1}$

$NH_{3\,(g)} + 0.09O_{2\,(g)} \rightarrow 1.32H_{2\,(g)} + 0.5N_{2\,(g)} + 0.18H_2O_{\,(g)}$ $\Delta H = 0$ kJ mol$^{-1}$

| $NH_3$:$O_2$ (molar ratio) | Feed gas composition (mL min$^{-1}$) | Maximum $H_2$ yield (%)* | Conversion (%) | | $H_2$ yield (%) |
|---|---|---|---|---|---|
| | $NH_3$:$O_2$:He ratio | | $NH_3$ | $O_2$ | |
| 4:1.5 | 150:563:2.0 | 51 | 100 | 100 | 49 |
| 4:1 | 150:37.5:20.8 | 67 | 96 | 100 | 64 |
| 4:0.38 | 150:143:44.0 | 88 | 27 | 100 | 14 |

# Safety assessment of transport fuels

| Material | Health | Flammability | Flash point (℃) | Hazardous score |
|---|---|---|---|---|
| $NH_3$ | 3 (Deleterious substance 25ppm*) | 1 | 132 | 3 + 1 = 4 |
| $H_2$ | 0 (Explosive range 4-75%) | 4 | -187 | 0 + 4 = 4 |
| Gasoline | 1 (Boiling point 30-220 ℃) | 3 | -43 | 1 + 3 = 4 |

*Association Advancing Occupational and Environmental Health (ACGIH )

- Safety measure is a very important issue for using ammonia as $H_2$ carrier.

N. J. Duijim, F. Farkert, J. L. Paulsen, Safety assessment of ammonia as a transport fuel. https://claverton-energy.com/

# Properties of $H_2$ carriers

| | $NH_3$ | Methyl-cyclohexane ($C_7H_{14}$) | $CH_3OH$/ $H_2O$ | $(CH_3)_2O$/ $3H_2O$ | Liquid hydrogen ($H_2$) |
|---|---|---|---|---|---|
| Molecular mass | 17.03 | 98.19 | 32.04/ (18.02) | 46.07/ (54.05) | 2.016 |
| Boiling point（K） | 240 | 374 | 338 | 249 | 20.3 |
| Density（g/cm$^3$) | 0.682*1 | 0.769 | 0.792/ 1.00 | 0.67(0.5MPa, 293K)/1.00 | 0.0706 |
| $H_2$ content （mass%） | 17.8 | 6.16 | 12.1 | 12.1 | 100 |
| $H_2$ volume density （kg/100L） | 12.1 | 4.73 | 10.3 | 9.86 | 7.06 |
| ΔH for releasing $H_2$（KJ/mol$H_2$） | 30.6 | 67.5 | 43.8 | 45.6 | 0.899 |

（*1,0.1MPa,240K）

- Advantages of $NH_3$
  - It is liquefied at 20 ℃ with a pressure of 0.8 MPa and $H_2$ storage capacity is high.
  - Infrastructure for storage and transportation is well established.
  - A carbon-free $H_2$ storage and transportation system can be constructed.

K. Aika (http://www.jst.go.jp/pdf/pc201311_aika.pdf)