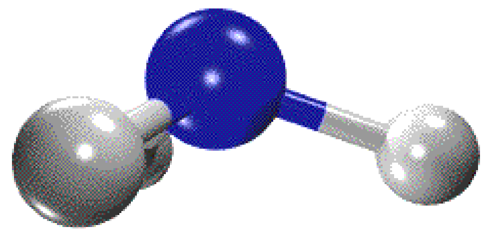
Cross-ministerial Strategic Innovation Promotion Program (SIP)

HIROSHIMA UNIVERSITY

IAMR

Hydrogen Generation from Ammonia for PEM Fuel Cells



20-23 of September 2015

12th Annual NH_3 Fuel Association Conference

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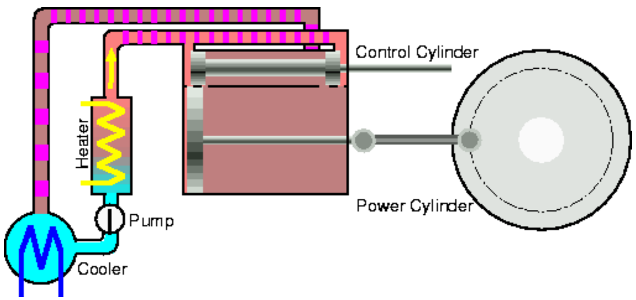
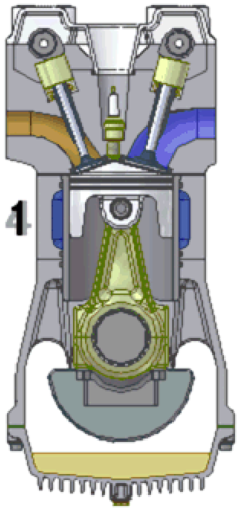
1. Energy and Environmental Issues

History of Industrial Revolution

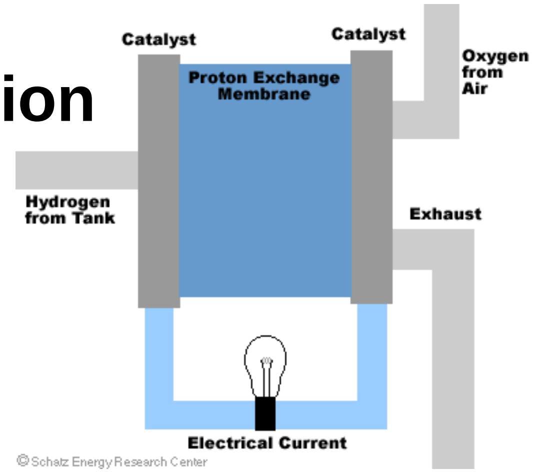
Steam Engine





Internal Combustion Engine

Fuel Cell



Coal

First Industrial Revolution (18th～19th century)

Oil（Natural gas）

Second Industrial Revolution （End of the 19th century ～Early 20th century)

Renewable energy

Third Industrial Revolution （21st century？）

Fossil energy economy

12 billion ton of oil equivalent

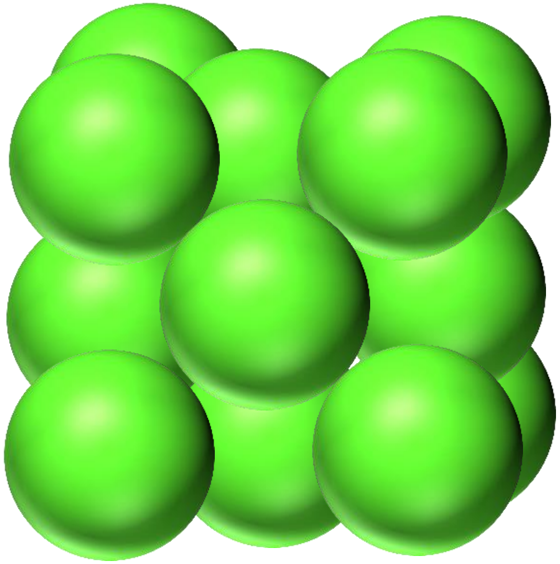
Sustainable economy

Hydrogen carrier

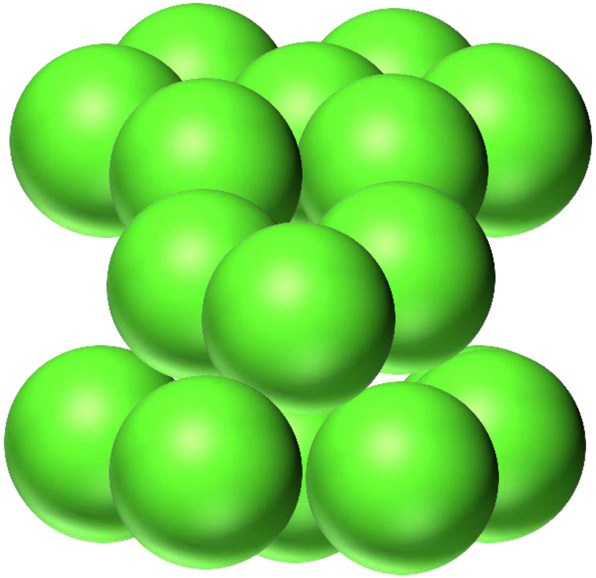
Hydrogen Carriers (solid and liquid carriers)

Volumetric density

Packing ratio



Face-centered cubic structure



Hexagonal closed packed structure

Bulk density of Mg: 0.7g/cm^3

Packing ratio: 74% (theoretical value)

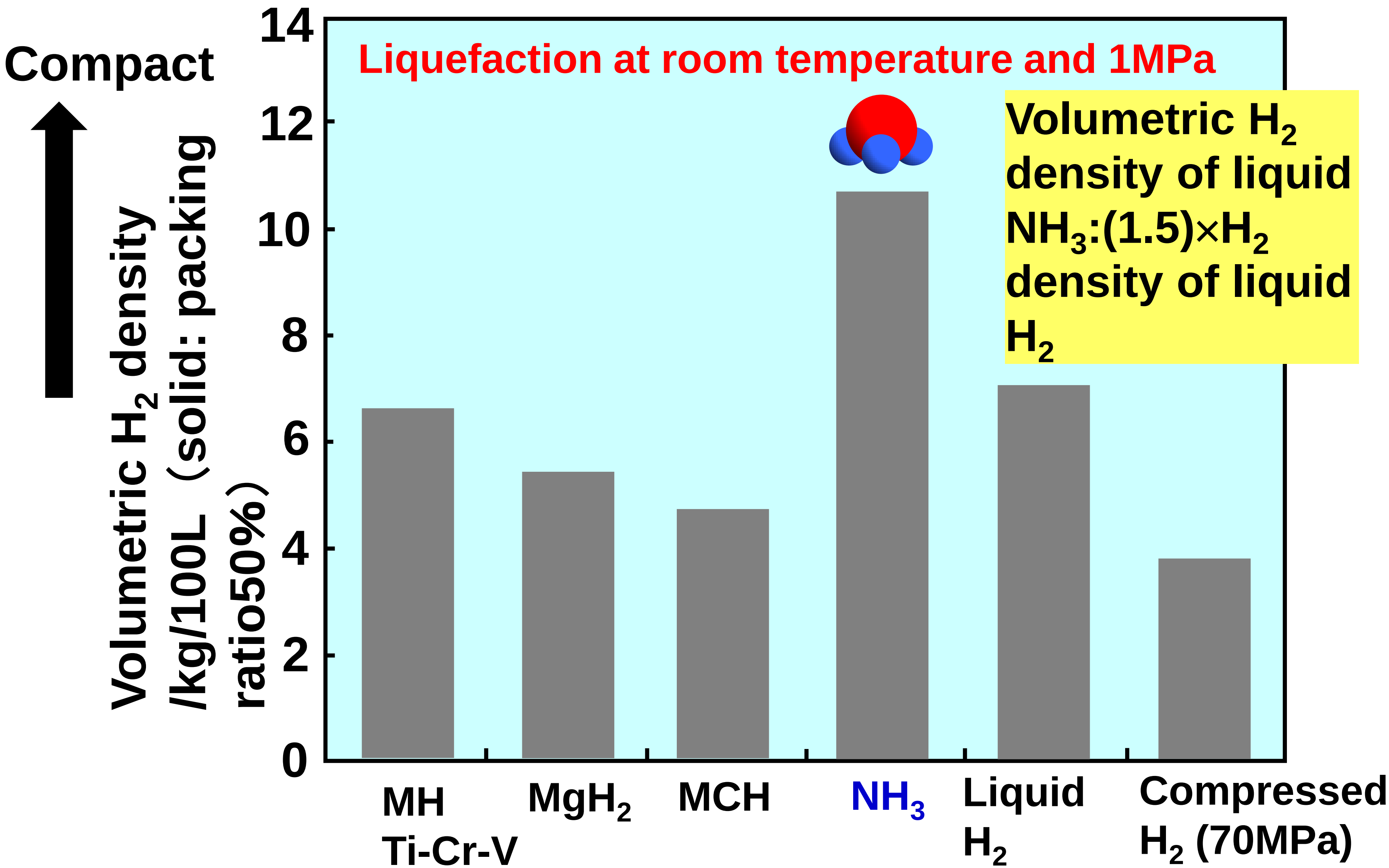
Packing ratio: 40%

Packing ratio(relative density): 40-50% (practical value)

J. Japan Inst. Metals, 62, 893-898 (1998)

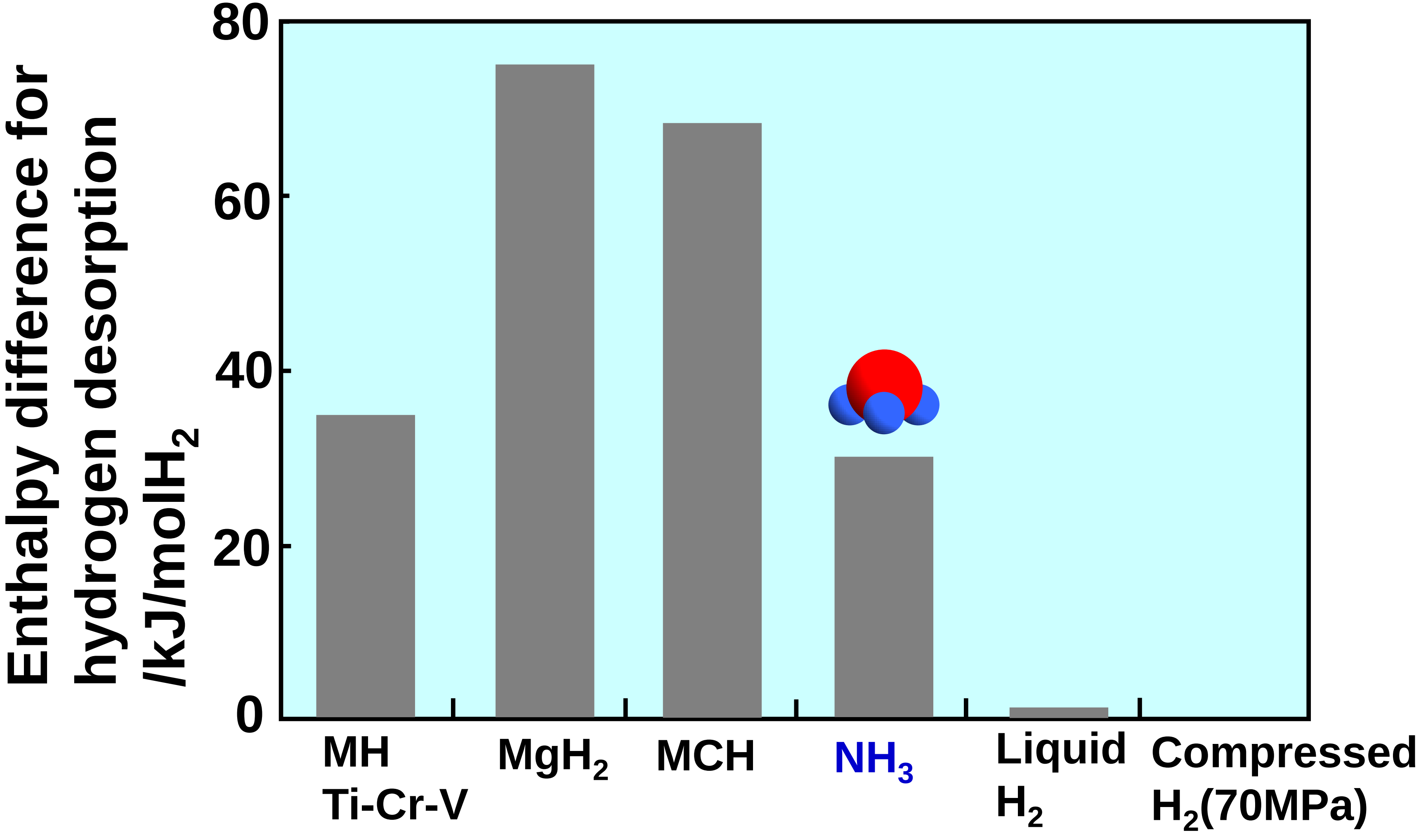
2. Properties of Ammonia

Volumetric H_2 densities of hydrogen carriers



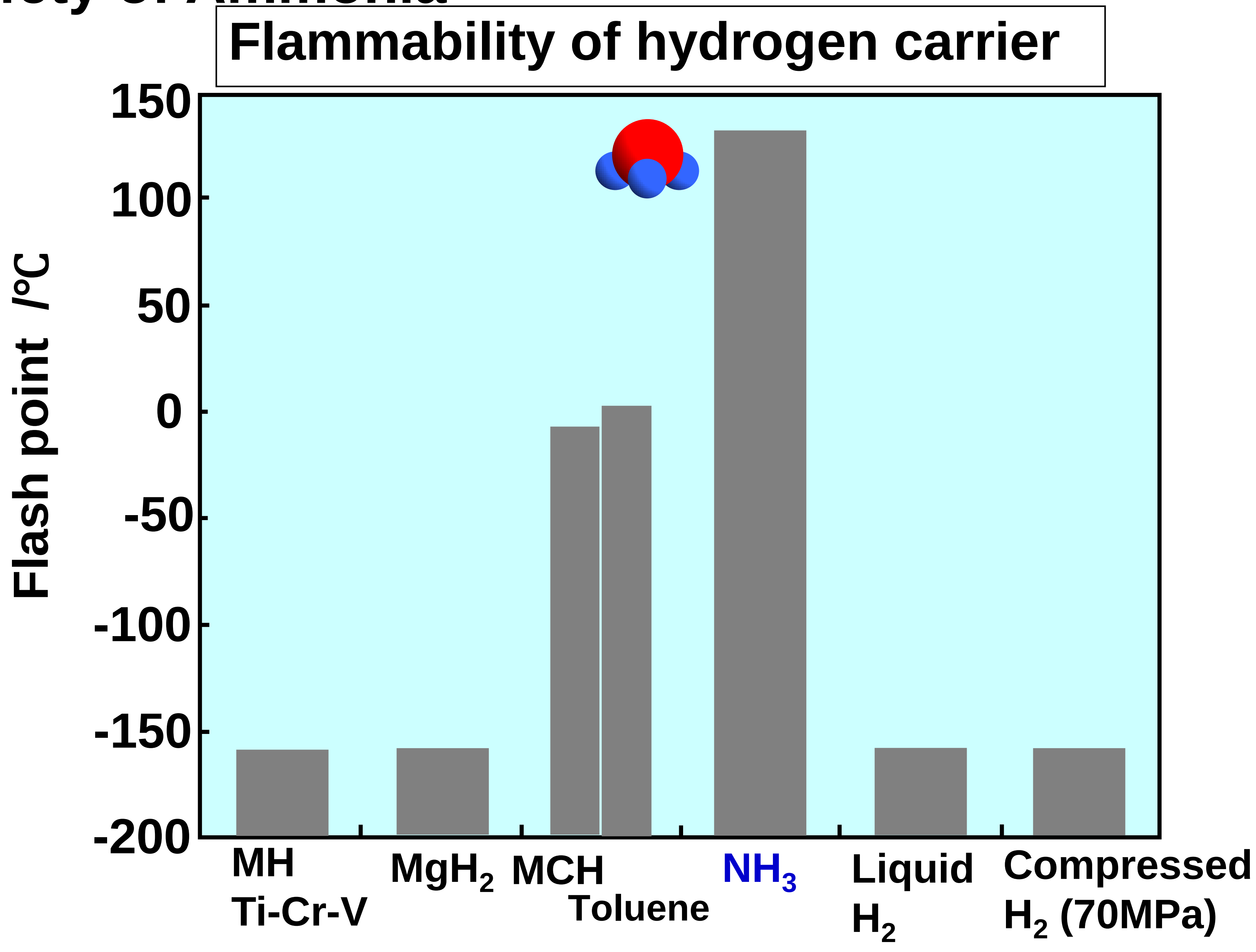
Volumetric H_2 density of ammonia: maximum value

Enthalpy difference (heat of formation) for hydrogen desorption



Heat of formation for NH_3 : about 10% of heat of combustion for H_2

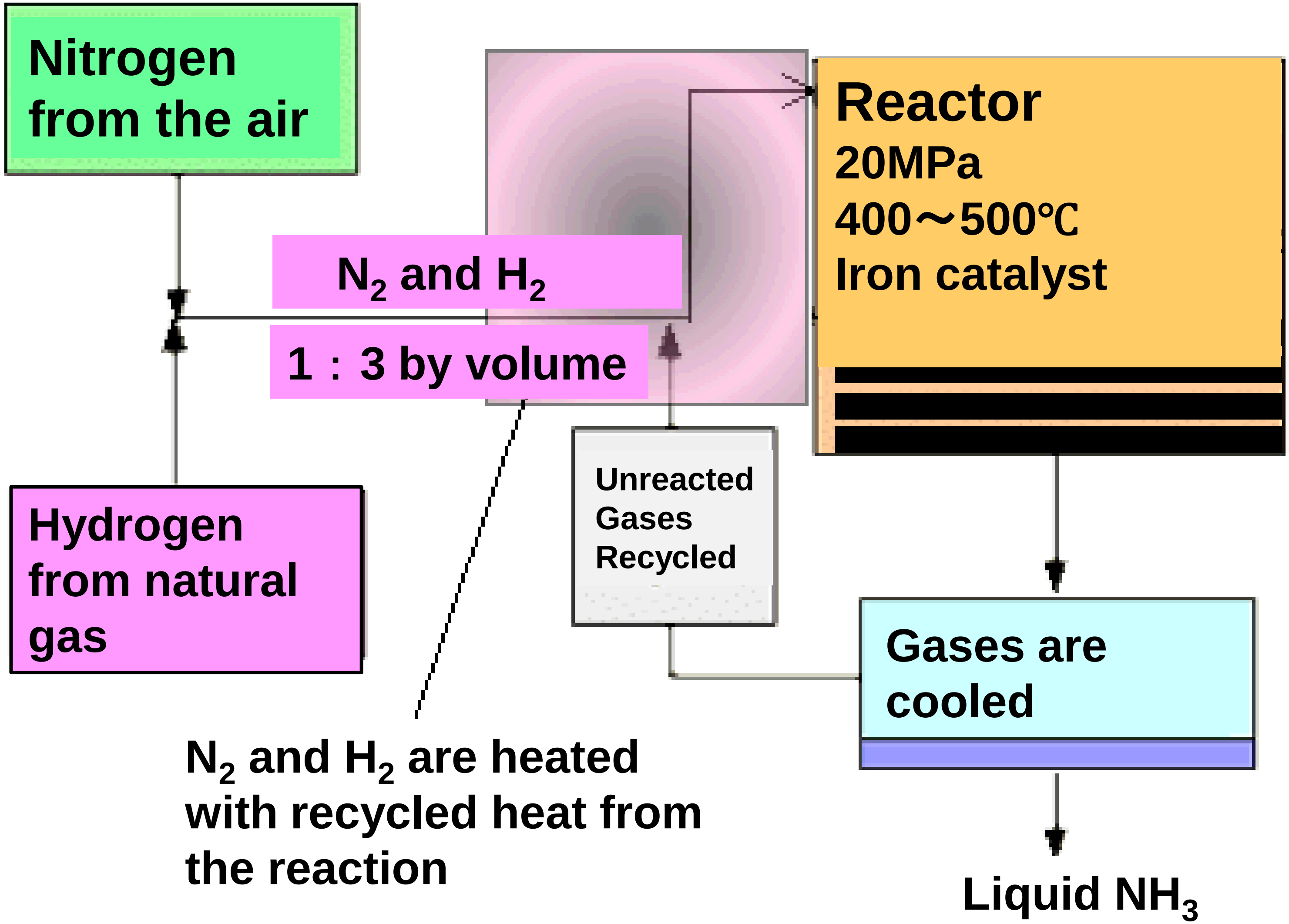
3. Safety of Ammonia



Ammonia concentration 100%(deleterious substance)→Hydrogen carrier

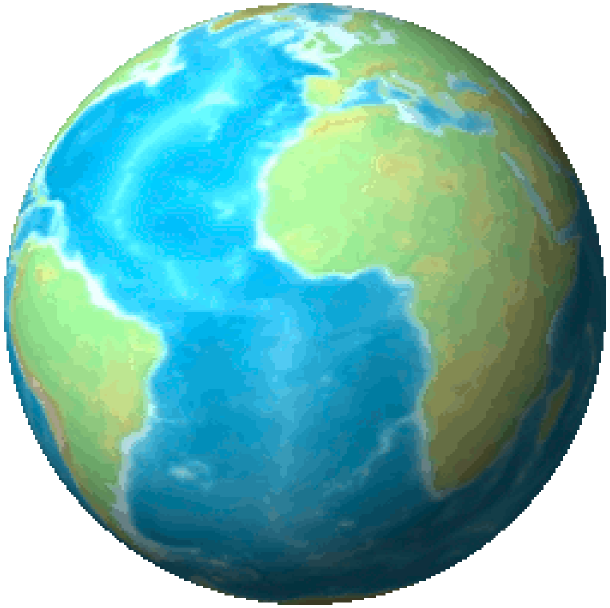
4. Production, Storage and Transportation of Ammonia

Ammonia production process(Haber-Bosch process)



CIF price of NH_3 in Japan : 300-400 yen/kgH_2(\$3/kgH_2)
Compressed H_2 price in Japan: 1000-1100 yen/kgH_2(\$9/kgH_2)

Storage and Transportion of NH_3



World production: 1.8 hundred million ton /year(2013)

Storage 15,000 tons level

http://www.fao.org/3/a-i4324e.pdf

World production capacity: 2.1 hundred million ton /year (2013)

Transport 30,000 tons level by tanker ship

MC331
11500gal, 300psi

900 fuel cell vehicles

Transportation 26tonns by trailer (H_2: 4.6tonns)

5. Ammonia Utilization as a Hydrogen Carrier

Fuel cell vehicle vs. hybrid vehicle

MIRAI
Price: around $60,000

Lexus GS 450h
Price: around $60,000

H_2 price:1000-1100yen/kg ($9/kg)
Fuel consumption rate: 135km/kg
Fuel price:7.4-8.1yen/km(¢6/km)

Gasoline price:130-150yen/L ($1.1/L)
Fuel consumption rate:18.2km/L
Fuel price:7.1-8.2yen/km(¢6/km)

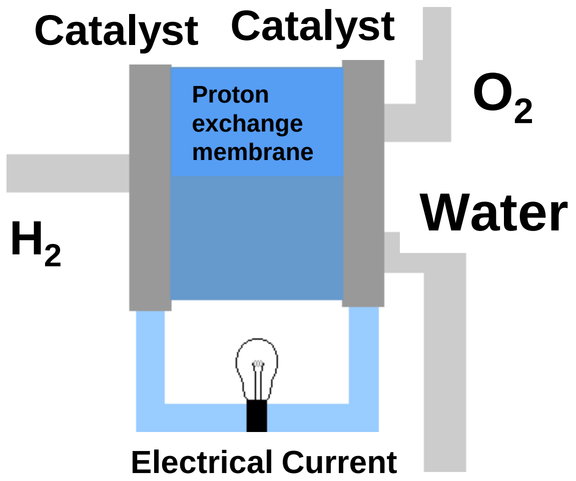
Scenario of Fuel Cell Commercialization Conference of Japan(FCCJ)
2 millions of FCV and construction of around 1,000 hydrogen stations in 2025

Volumetric H_2 density of ammonia: maximum, Enthalpy difference for H_2 desorption: small →Hydrogen station using NH_3: key issue

Specification of hydrogen fuel for FCV （ISO 14687-2:2012）

Species	Concentration
Purity of H_2	99.97%
Total hydrocarbons（C1）	2ppm
Water（H_2O）	5ppm
Oxygen（O_2）	5ppm
N_2, Ar	100ppm
He	300ppm
Carbon Dioxide（CO_2）	2ppm
Carbon Monoxide（CO）	0.2ppm
Total sulphur compounds	0.004ppm
Formaldehyde	0.01ppm
Formic acid	0.2ppm
Ammonia	0.1ppm
Total halogenated compounds	0.05ppm

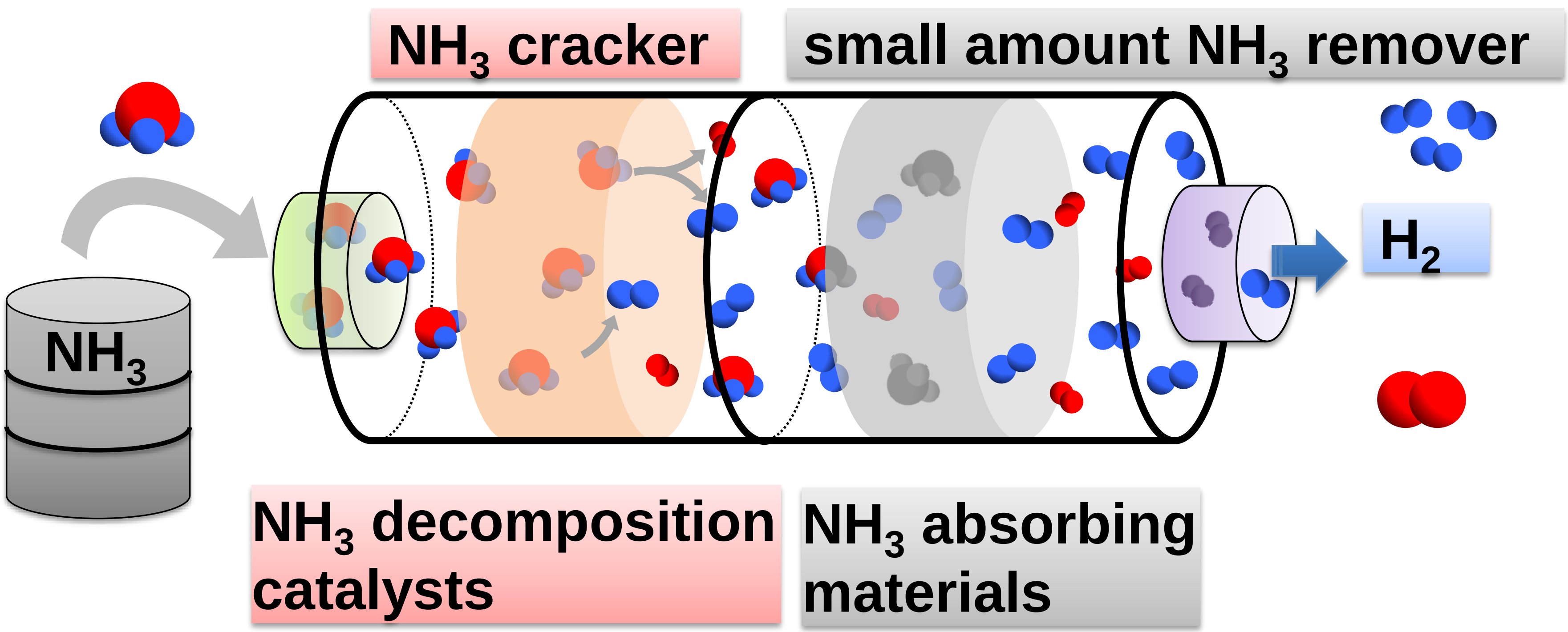
Fuel cell



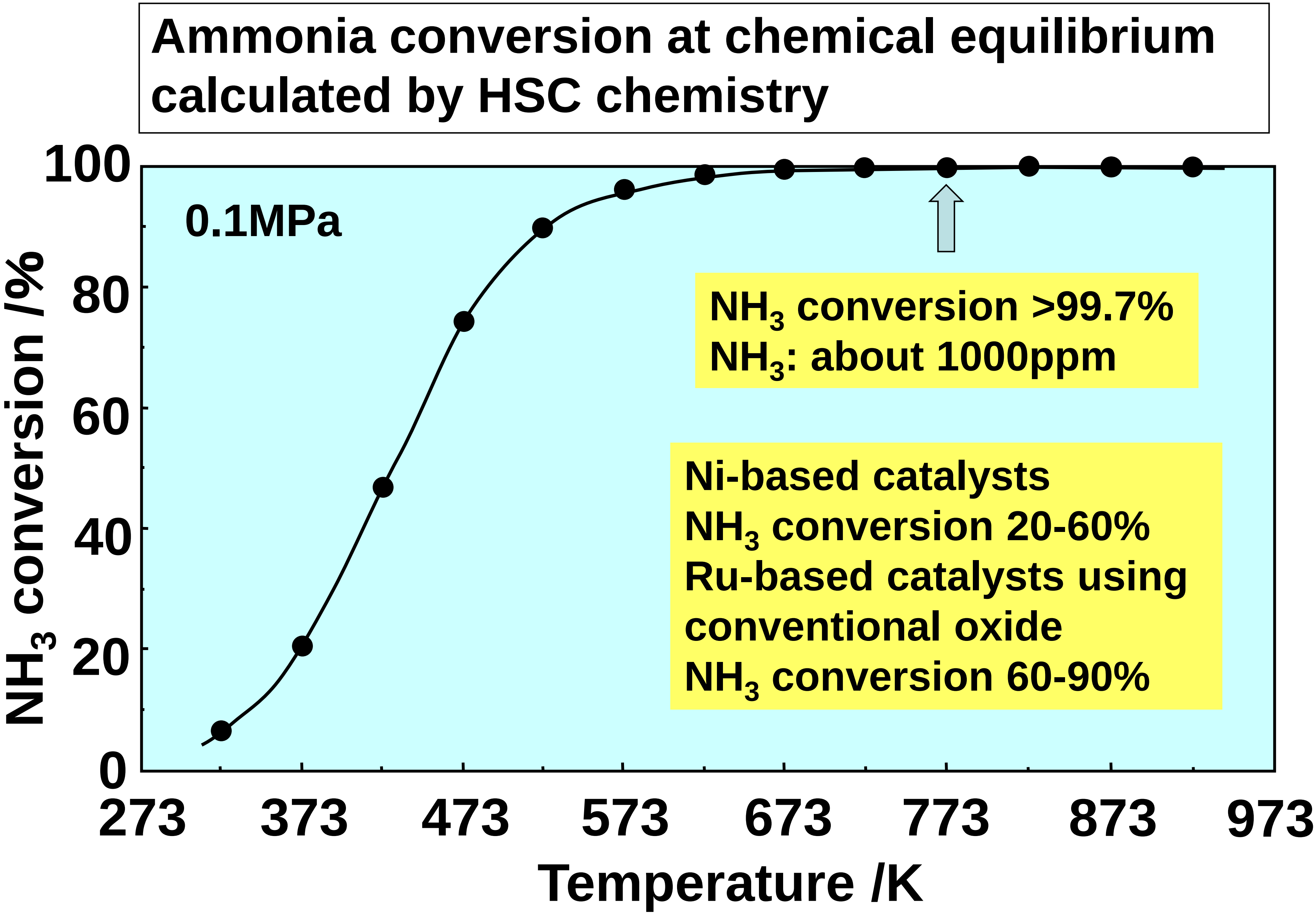
Ammonia concentration below 0.1ppm

Purpose of research and development

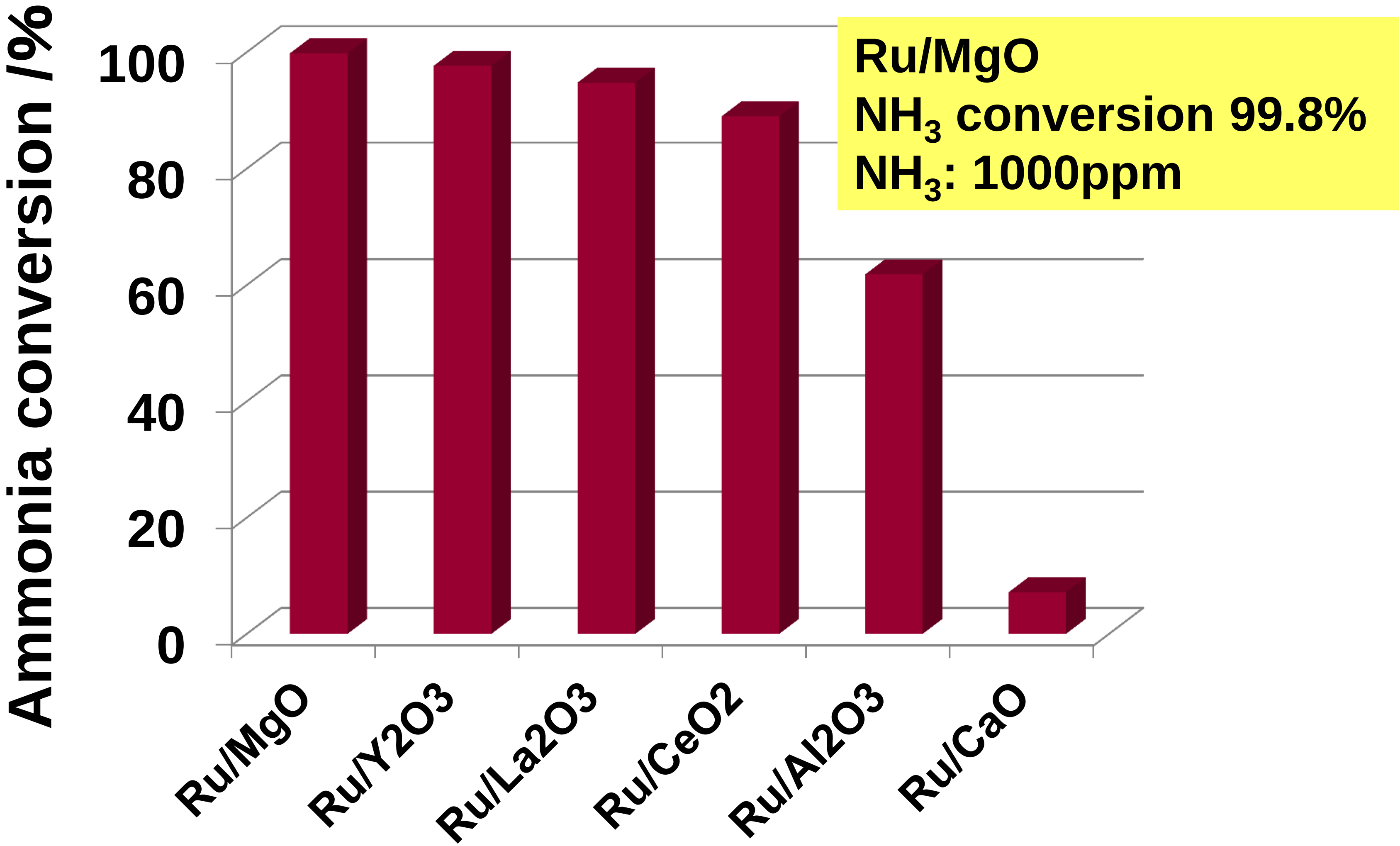
Ammonia decomposition and high purity H_2 supply system ($NH_3 \rightarrow (1/2)N_2 + (3/2)H_2$)



NH_3 decomposition catalysts



Catalytic activity of Ru-based catalysts at 500℃

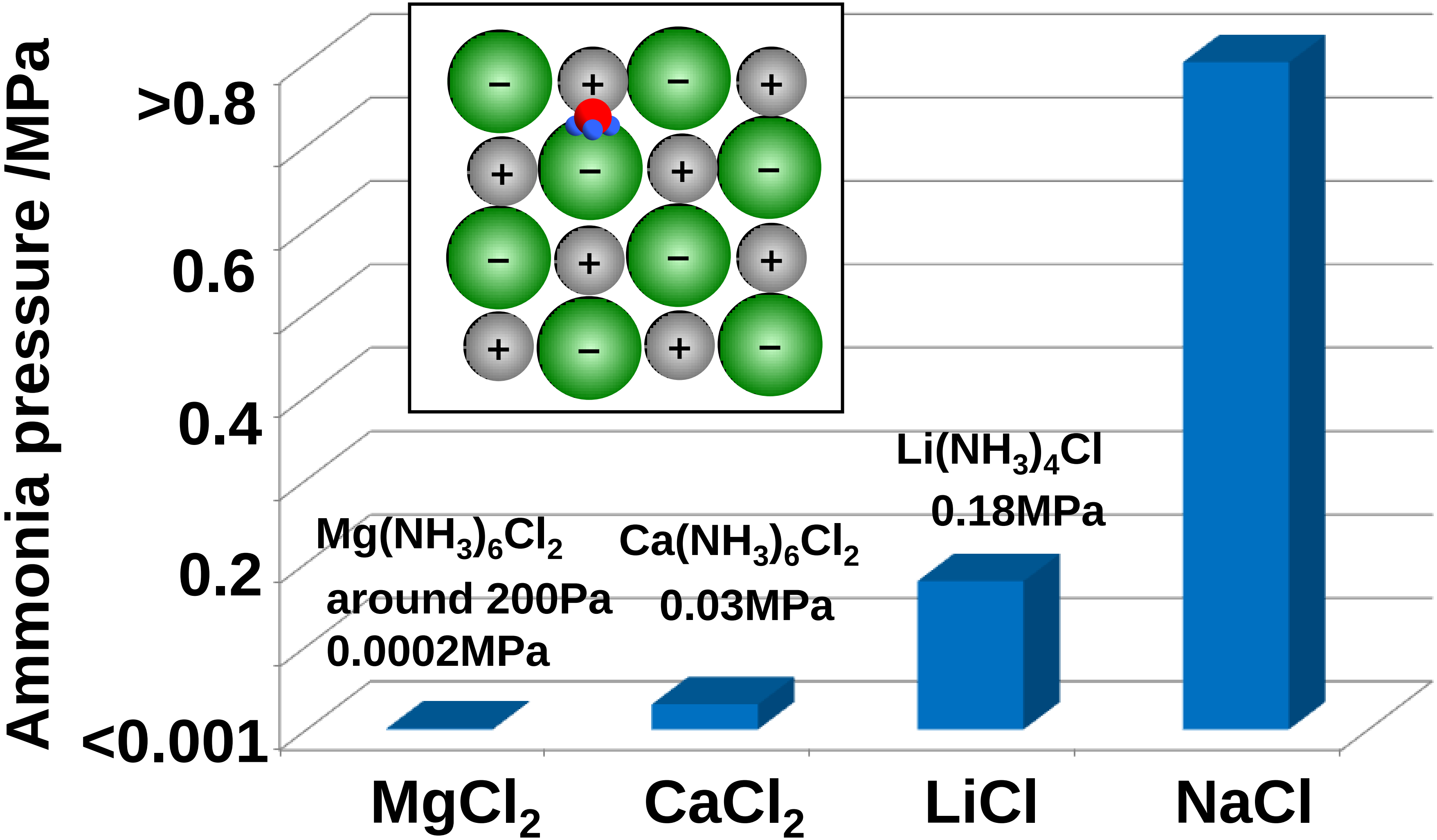


500℃、SV15000h^{-1}

T. Fujitani, A. Takahashi, Effect of Supports on the Ammonia Decomposition Reaction by the Ru Catalyst, The Japan Institute of Energy 24th National Meeting, August 3-4, Sapporo, Japan, 2015

NH_3 absorbing materials

Plateau pressure of metal ammine chloride



2000ppm (0.1MPa)

$MgCl_2$ absorbs ammonia to form 3 kinds of ammine complexes	Standard enthalpy change ΔH^0	Standard entropy change ΔS^0
$MgCl_2 + NH_3 \rightarrow Mg(NH_3)Cl_2$	-87 kJ/mol、	-135 J/molK
$Mg(NH_3)Cl_2 + NH_3 \rightarrow Mg(NH_3)_2Cl_2$	-75 kJ/mol、	-134 J/molK
$Mg(NH_3)_2Cl_2 + 4NH_3 \rightarrow Mg(NH_3)_6Cl_2$	-56 kJ/mol、	-135 J/molK

S. Lysgaard et al., Int. J. Hydrogen Energy, 37, 18927-18936 (2012)

$Mg(NH_3)_6Cl_2$ is formed at room temperature（PCI, XRD, TG-MS)

After activation of $MgCl_2$, $Mg(NH_3)Cl_2$is formed at high temperature of 230-300℃ (PCI, XRD, TG-MS)

van’t Hoff plot: accurate evaluation of ΔH^0 and ΔS^0 for mono-ammine complex

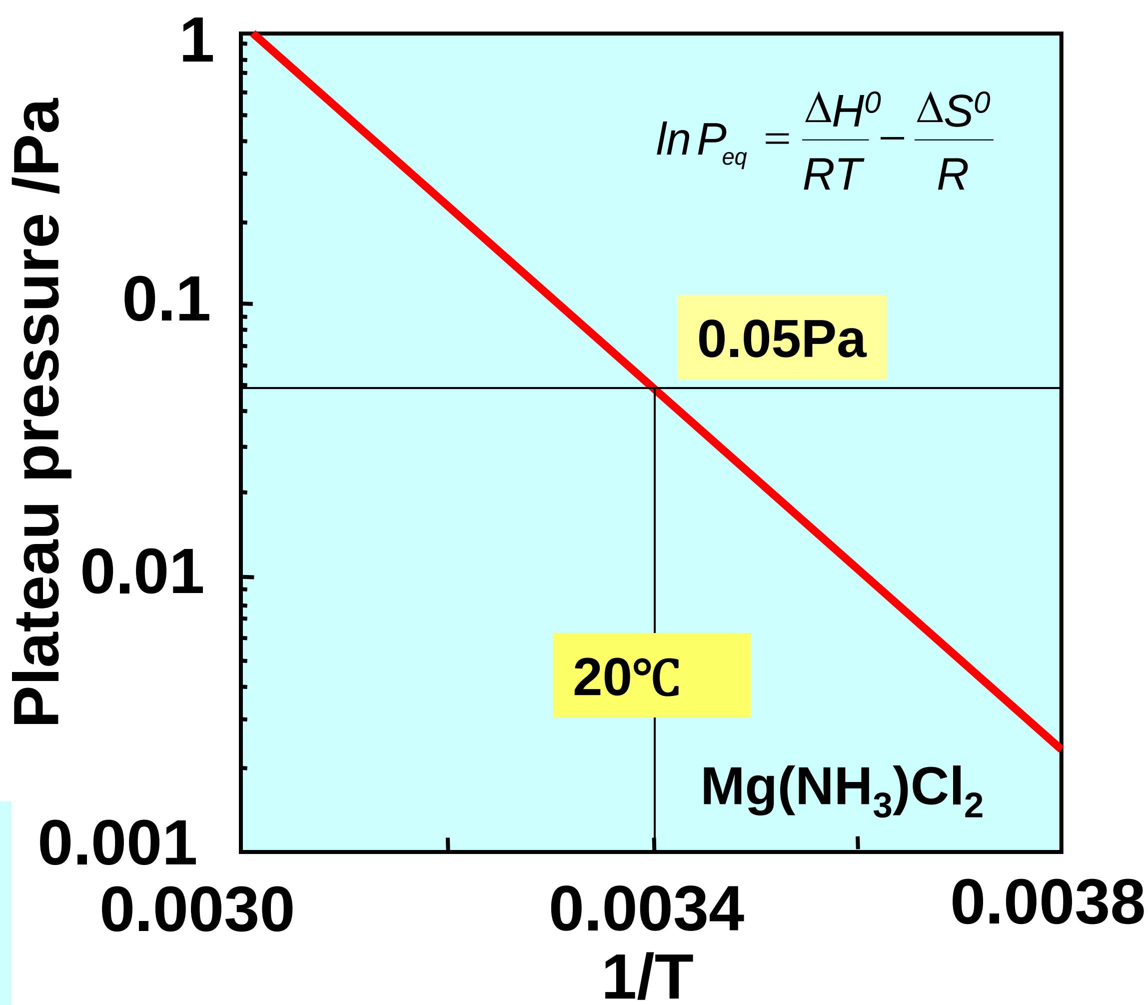
T. Aoki et al., The Iron and Steel Institute of Japan and The Japan Institute of Metals and Materials, Chugoku Shikoku Branch National Meeting, August 19-20, Hiroshima, Japan 2015.

$MgCl_2 + NH_3 \rightarrow Mg(NH_3)Cl_2$

van't Hoff plot for mono-ammine complex of $MgCl_2$

Mono-ammine complex of $MgCl_2$
Revised standard enthalpy change -64 ± 1J/molNH_3
Revised standard entropy change -97 ± 2J/molK

Standard enthalpy change -87kJ/molNH_3
Standard entropy change -135J/molK



NH_3:1000ppm→NH_3:0.5ppm(0.1MPa)

Ammonium Hydrogen Sulfate

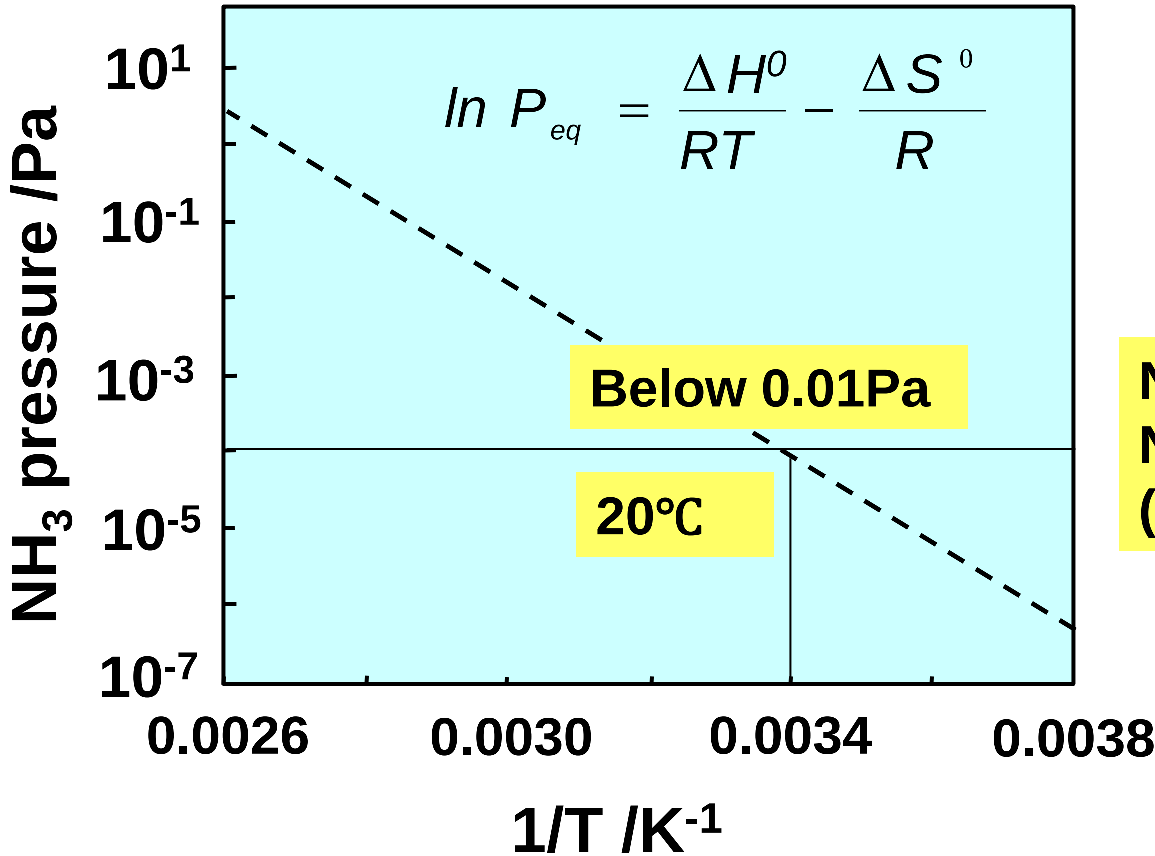
$$NH_4HSO_4 + NH_3 \leftrightarrow (NH_4)_2SO_4$$

Standard enthalpy change -108kJ/molNH$_3$

Standard entropy change -193J/molK (entropy of NH$_3$: 193J/molK)

CRC Handbook of Chemistry and Physics, 92nd Edition

van't Hoff plot for ammonium hydrogen sulfate-ammonia system



NH$_3$:1000ppm →
NH$_3$: below 0.1 ppm
(0.1MPa)

A small amount of NH_3 determination method

Break through testing apparatus

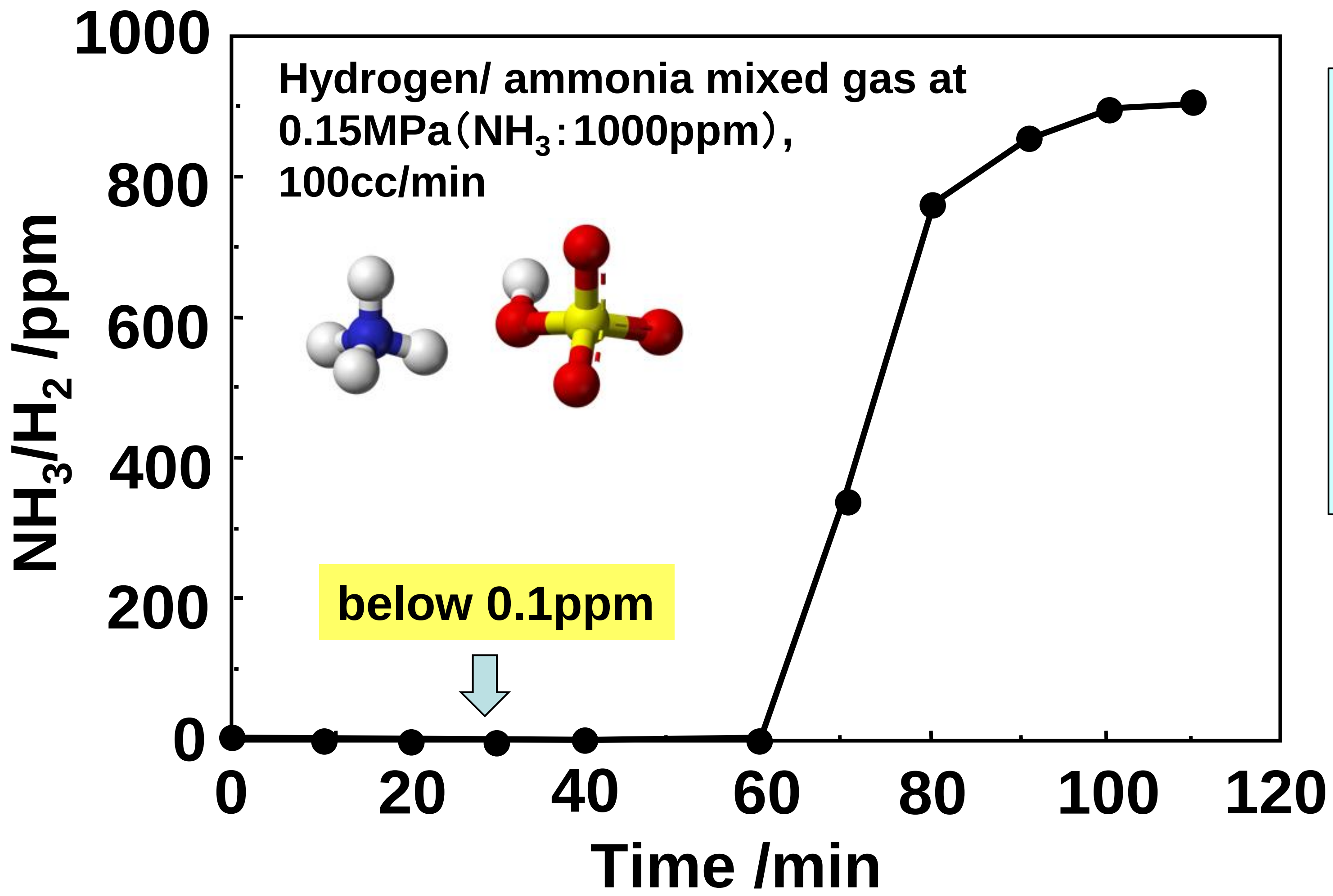
（FTIR - Gas Cell） **Optical path length: 1.5m**

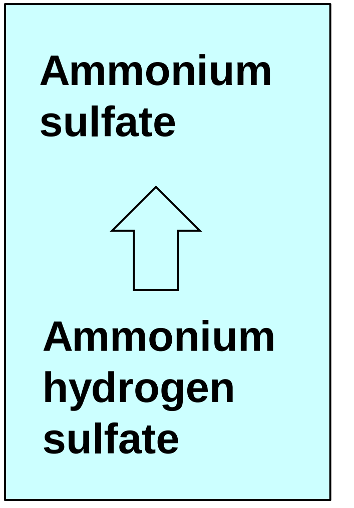
0.1-1000ppm(0.1MPa)

Hydrogen/ ammonia mixed gas around 0.1MPa（NH_3：1000ppm）

T. Kimura et al., The Iron and Steel Institute of Japan and The Japan Institute of Metals and Materials, Chugoku Shikoku Branch National Meeting, August 19-20, Hiroshima, Japan 2015.

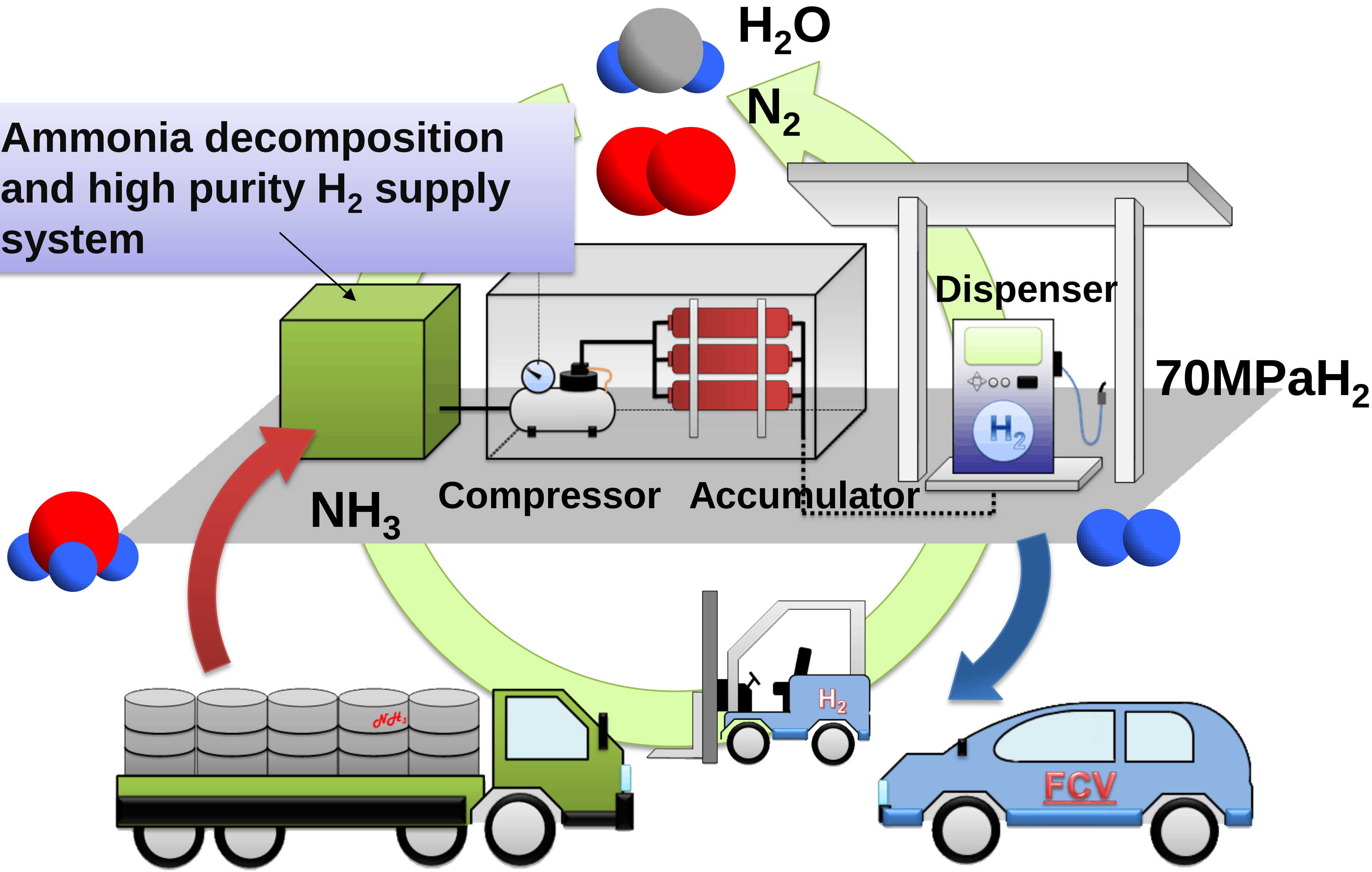
Breakthrough curve for ammonia absorption from H_2/NH_3 in ammonium hydrogen sulfate by FTIR - Gas Cell





NH_3:below 0.1ppm(0.1MPa), 9.2wt%[$(NH_4)_2SO_4$]

Conceptive picture of H_2 station using NH_3



Air contains 80% nitrogen.

6. Summary

1. Ammonia is a hydrogen carrier having maximum volumetric H_2 density of about 11kgH_2/100L.
2. Heat of formation for NH_3 is about 10% of heat of combustion for H_2.
3. Ammonia can transport 4.6 tons of hydrogen by trailer, which corresponds to 900 fuel cell vehicles.
4. High purity hydrogen gas will be produced by Ru-based catalyst, ammonia absorption materials.

Acknowledgement

This work was partially supported by Council for Science, Technology and Innovation(CSTI), Cross-ministerial Strategic Innovation Promotion Program (SIP), “energy carrier”(funding agency : JST)

WHTC 2019

Tokyo, Japan

8th World Hydrogen Technologies Convention
June 2(Sunday)-7(Friday), Tokyo International Forum

All Japan governmental, industrial and academic sectors will provide exhibition and forum for the latest hydrogen technology.

Chair Y. Kojima, Co-Chair H. Takagi




Hosted by WHTC 2019 Organizing Committee
Co-organized with the Hydrogen Energy Systems Society of Japan (HESS)

Promoted by IAHE-International Association of Hydrogen Energy

Thank you for your attention.