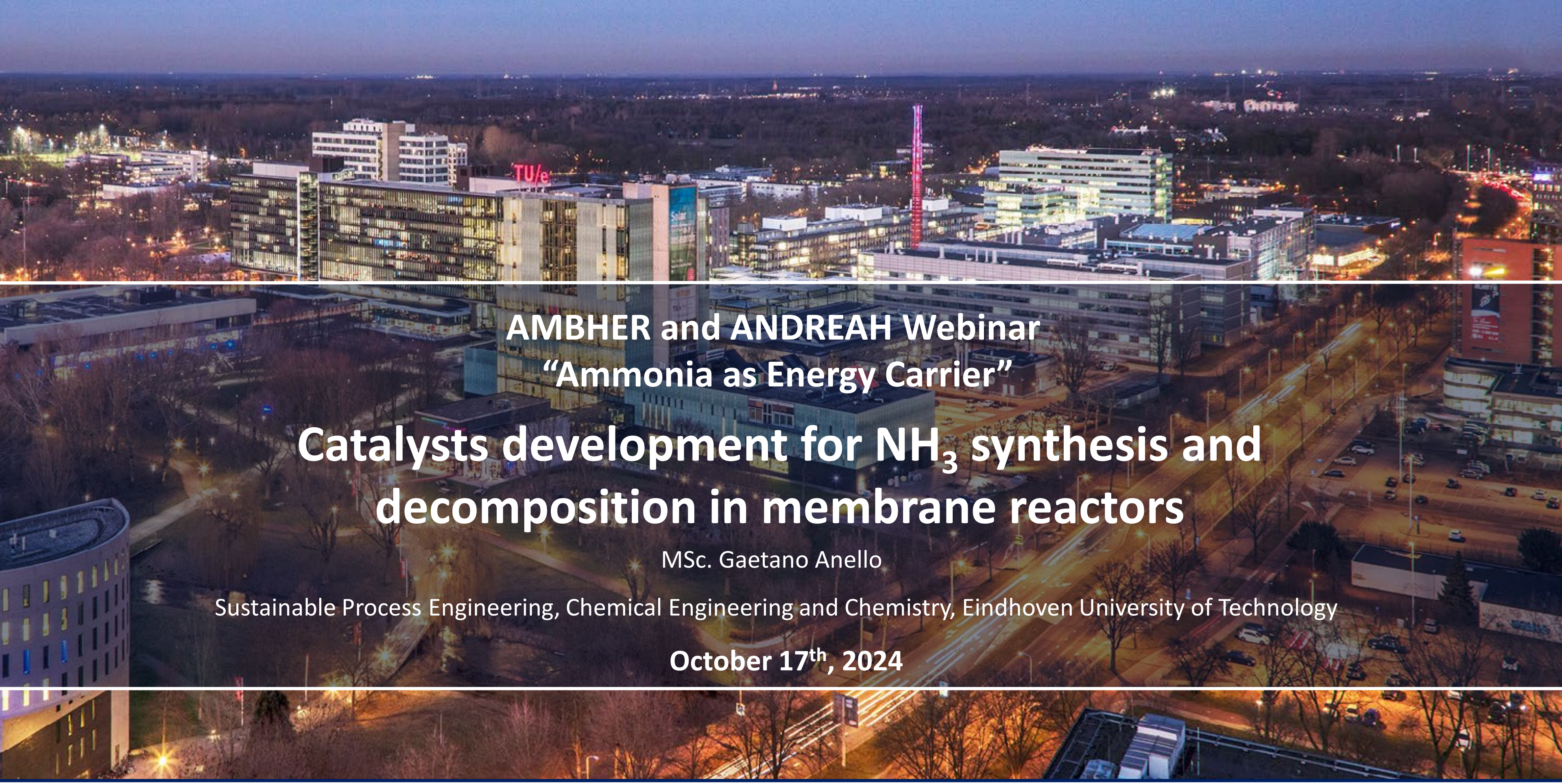


AMBHER and ANDREAH Webinar
"Ammonia as Energy Carrier"

Catalysts development for NH_3 synthesis and decomposition in membrane reactors

MSc. Gaetano Anello

Sustainable Process Engineering, Chemical Engineering and Chemistry, Eindhoven University of Technology

October 17th, 2024

AMBH₂ER AndreaH TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

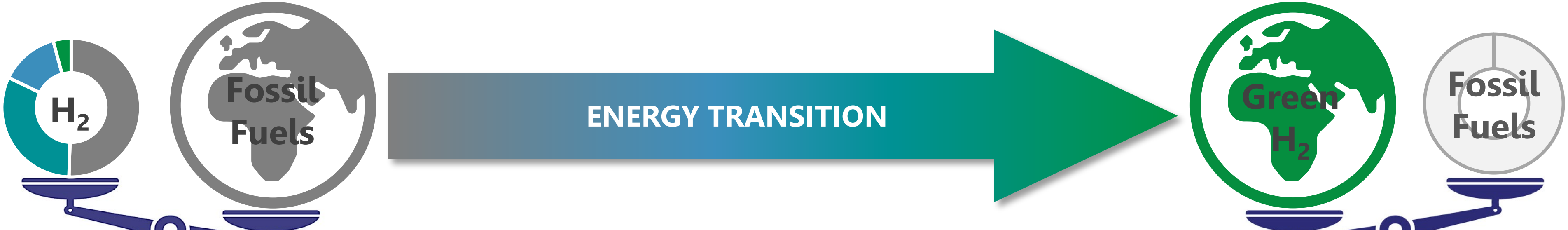
Overview

- *Hydrogen & Ammonia*
- *Process Intensification strategy*
- *Catalysts for NH_3 synthesis and decomposition*
- *Results*
- *Conclusions*

Introduction

Hydrogen as flagship of the Energy Transition

	GREY HYDROGEN	BLUE HYDROGEN	TURQUOISE HYDROGEN	GREEN HYDROGEN
Process	Steam Reforming Gasification	Steam Reforming Gasification (carbon capture ≈90%)	Pyrolysis	Electrolysis
Source	Methane Coal	Methane Coal	Methane	Renewable electricity

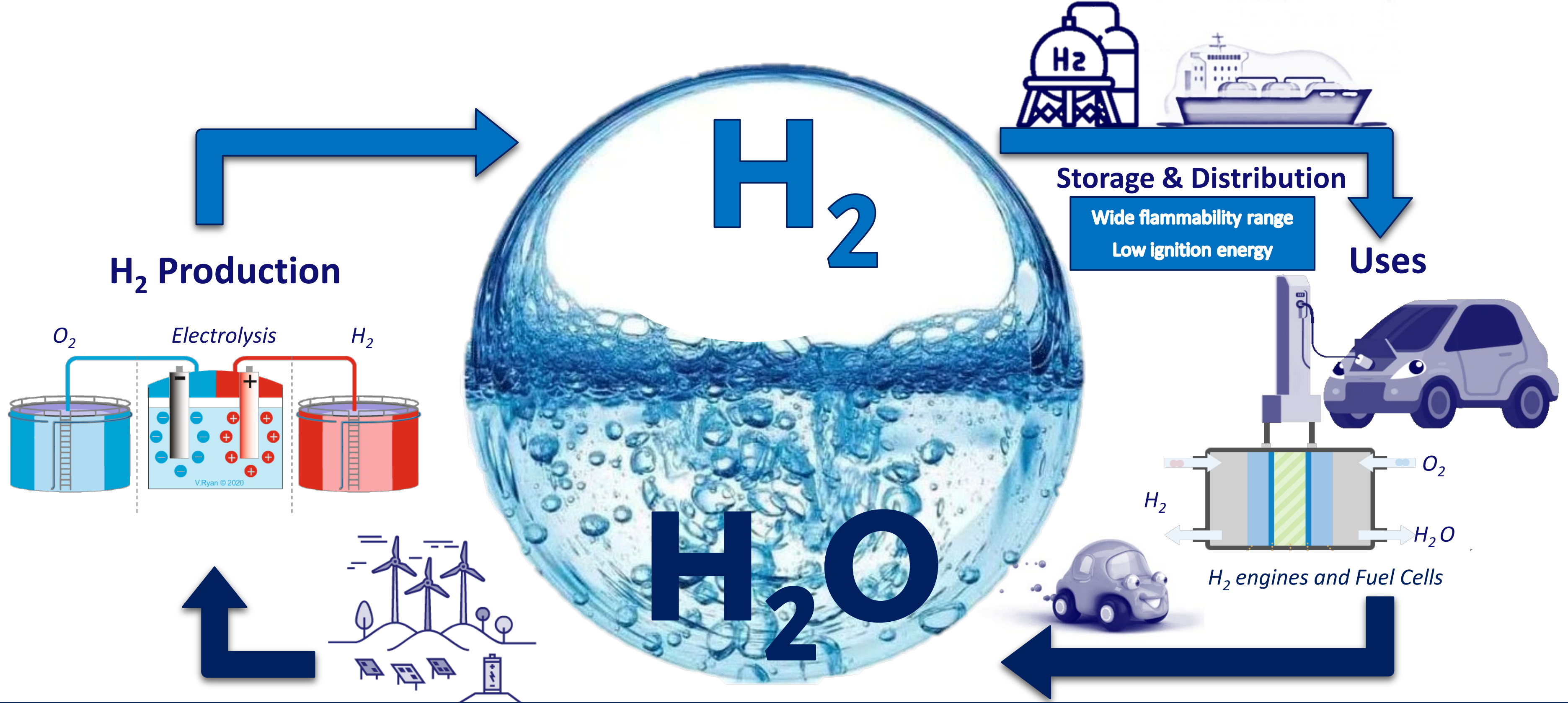


[01] **Kovac A. et al.** – *Hydrogen in energy transition: A review* – International Journal of Hydrogen Energy, v. 46, 10016-10035 (2021)

[02] **Capurso T. et al. –** *Perspective of the role of hydrogen in the 21st century energy transition* – Energy Conversion and Management, v. 251, 114898 (2022)

Hydrogen

Renewable green hydrogen cycle



H$_2$ Production

Storage & Distribution

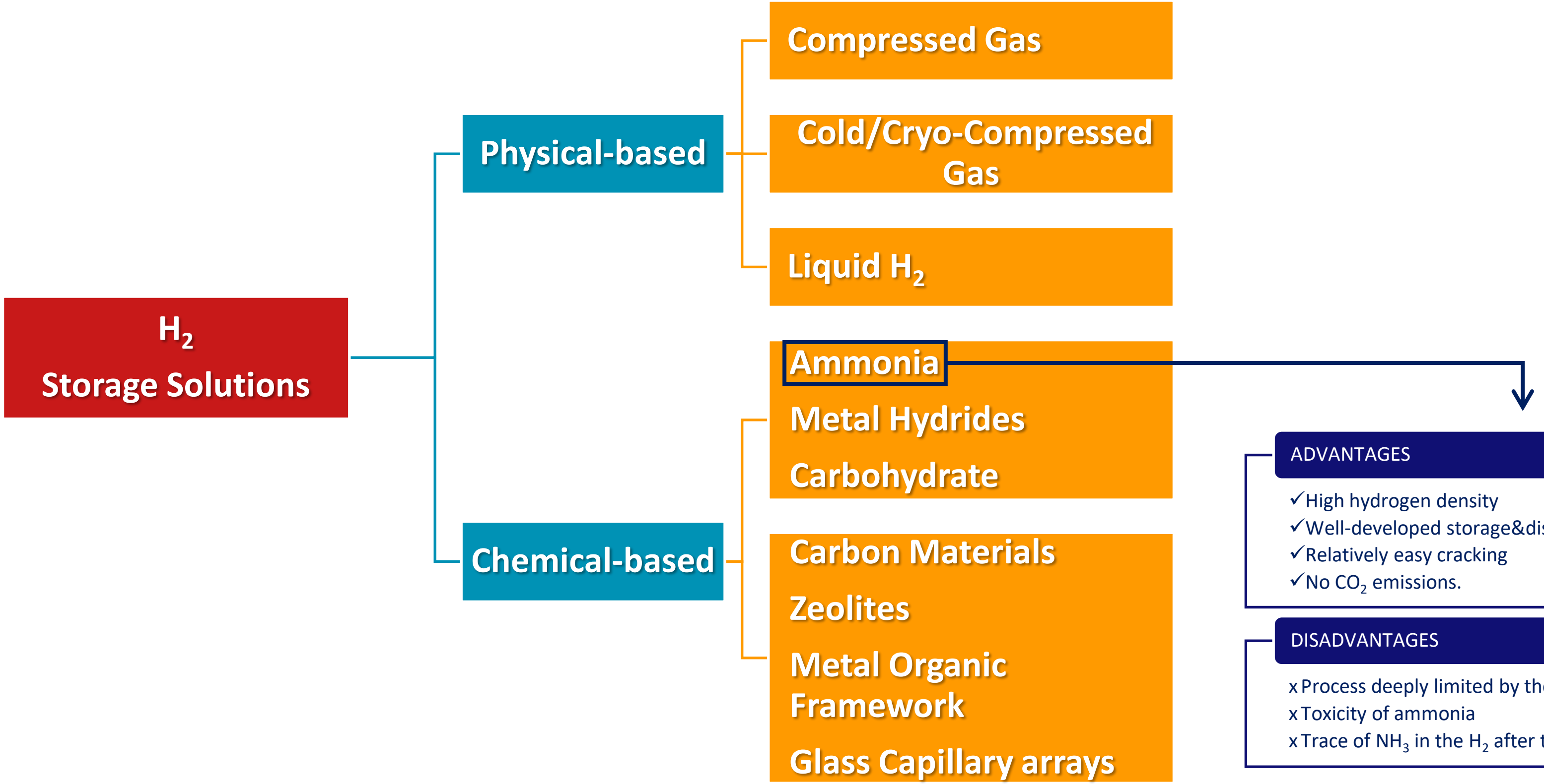
Wide flammability range
Low ignition energy

Uses

H$_2$ engines and Fuel Cells

Hydrogen

Storage solutions



H_2 Storage Solutions

- **Physical-based**
  - Compressed Gas
  - Cold/Cryo-Compressed Gas
  - Liquid H_2
- **Chemical-based**
  - Ammonia
  - Metal Hydrides
  - Carbohydrate
  - Carbon Materials
  - Zeolites
  - Metal Organic Framework
  - Glass Capillary arrays

ADVANTAGES

- ✓High hydrogen density
- ✓Well-developed storage&distribution infrastructure
- ✓Relatively easy cracking
- ✓No CO_2 emissions.

DISADVANTAGES

- x Process deeply limited by thermodynamics
- x Toxicity of ammonia
- x Trace of NH_3 in the H_2 after the decomposition

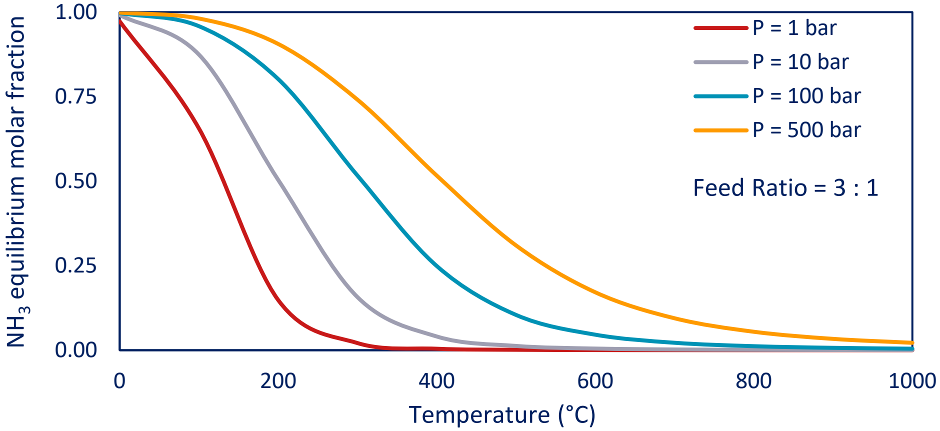
[03] https://www.energy.gov/eere/fuelcells/hydrogen-storage (Accessed on 09.09.2024)
[04] **Morandi R. and Groth K. M.** – *Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis* – International Journal of Hydrogen Energy, v. 44, 12254-12269 (2019)

Ammonia synthesis

Thermodynamic limits

The conversion of nitrogen and hydrogen in ammonia is deeply limited by thermodynamics at high T.

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \qquad \Delta H_r^\circ = -92.4\ kJ \cdot mol^{-1}$$



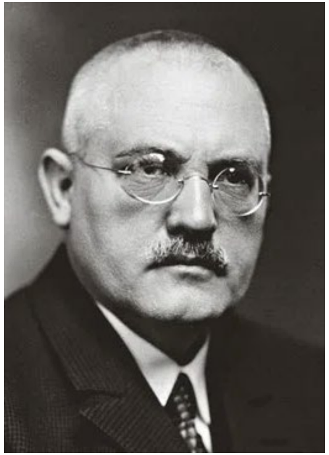
High yields are thermodynamically possible at low temperature, but heterogeneous catalysts are inactive at ambient condition due to their own activation temperature.

Ammonia synthesis

Haber-Bosch Process

Fritz Haber
(1868 – 1934)

The Nobel Prize in Chemistry 1918
was awarded to Fritz Haber
"for the synthesis of ammonia
from its elements".



Carl Bosch
(1874 – 1940)

The Nobel Prize in Chemistry 1931
was awarded to Carl Bosch
"in recognition of the contributions
to the invention and development of
chemical high-pressure methods".

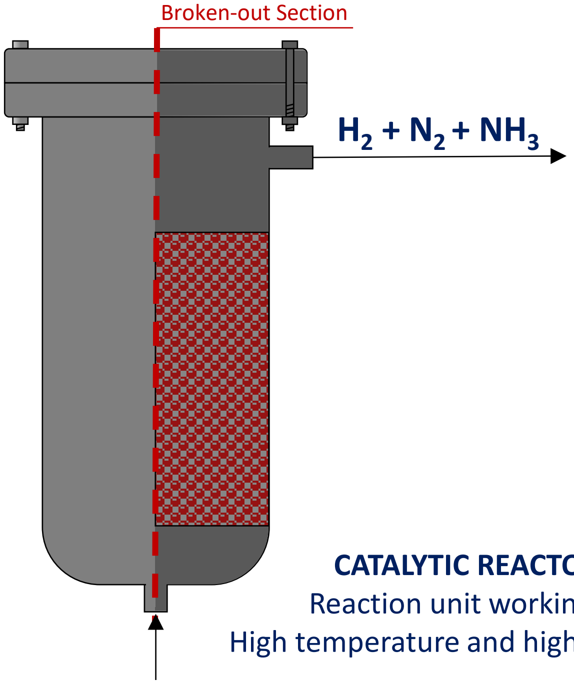
Ammonia is the second largest synthetic chemical product; more than 90 % of world consumption is manufactured from nitrogen and hydrogen in a catalytic process originally developed by *Fritz Haber* and *Carl Bosch* using a promoted iron-catalyst discovered by *Alwin Mittasch*.

An $H_2 - N_2$ mixture reacts over an iron-based catalyst at high temperatures in a range of 400 – 500 °C and pressures above 100 bar with recycle of the unconverted part of the reactants.

[05] https://www.nobelprize.org/ [Accessed on 11.10.2024]
[06] **Appl M.** – *Ullmann's Encyclopedia of Industrial Chemistry, Ammonia 2: Production Processes* – Wiley-VCH (2011)

Ammonia synthesis

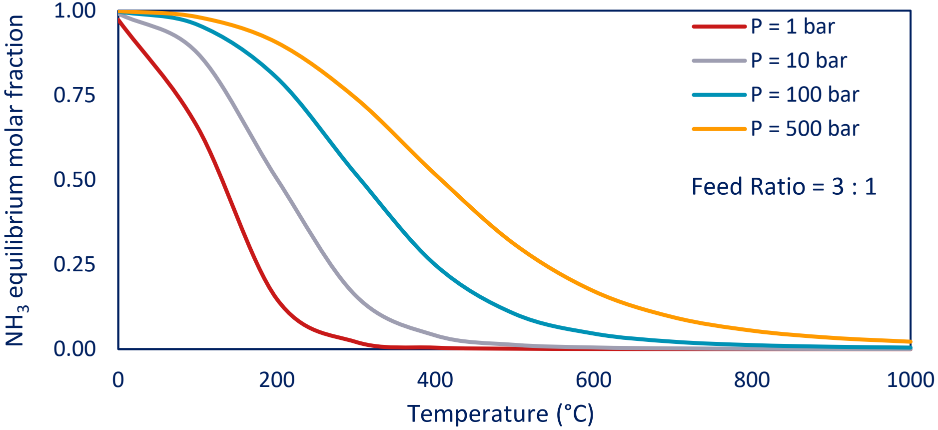
Conventional system



CATALYTIC REACTOR

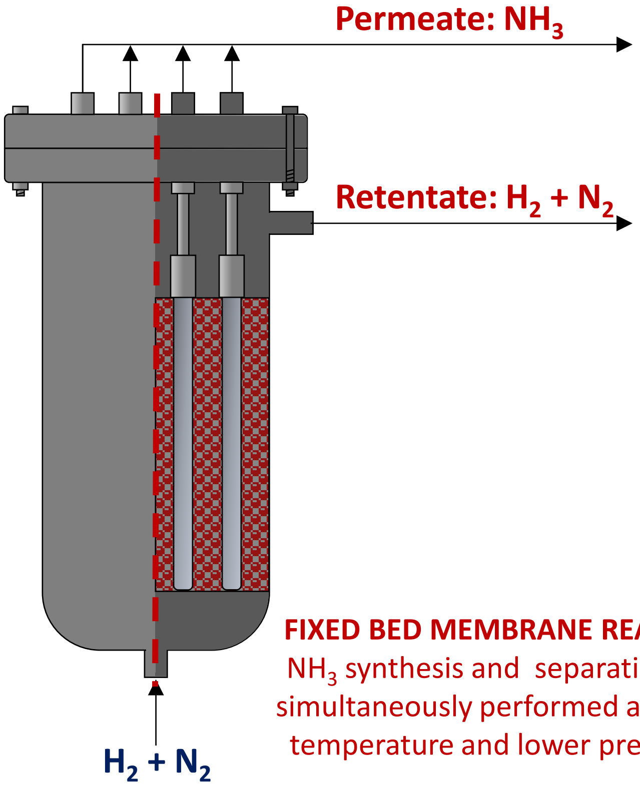
Reaction unit working at
High temperature and high pressure.

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$



Ammonia synthesis

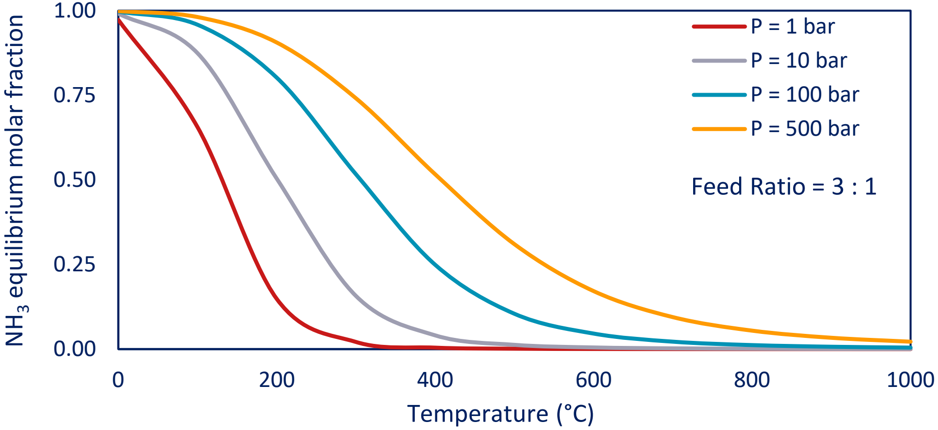
Membrane reactor



FIXED BED MEMBRANE REACTOR

NH_3 synthesis and separation are simultaneously performed at lower temperature and lower pressure.

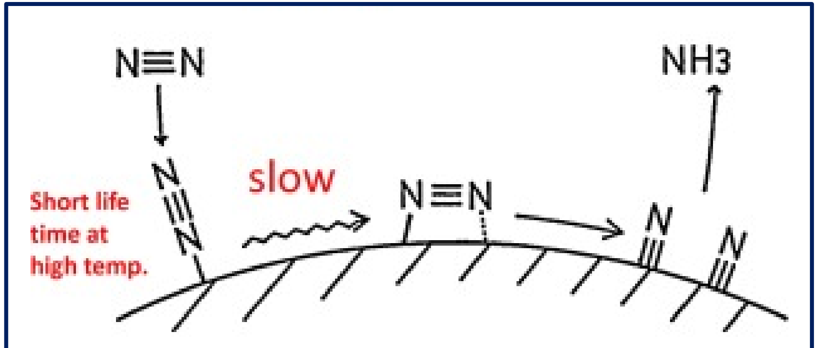
$$N_2 + 3H_2 \rightleftarrows 2NH_3$$



Catalysts for ammonia synthesis

Second-generation catalysts

Ru-based as second-generation catalysts for NH_3 synthesis, due to the higher activity at lower temperatures and pressures than the conventional iron catalyst.



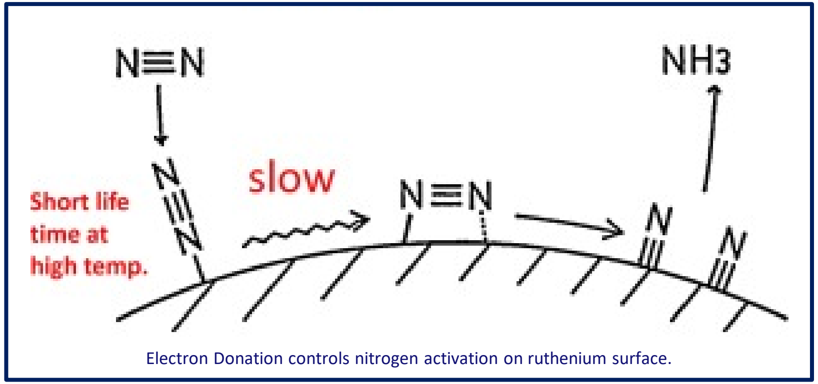
Electron Donation controls nitrogen activation on ruthenium surface.

[07] **Ertl G.** – *Primary steps in catalytic synthesis of ammonia* – Journal of Vacuum Science & Technology A, v. 1, 1247-1253 (1983)
[08] **Song Z. et al.** – *Structure and reactivity of Ru nanoparticles supported on modified graphite surfaces: A study of the model catalysts for ammonia synthesis* – Journal of American Chemical Society, v. 126, 8576–8584 (2004)
[09] **Huang J. et al.** – *Inhibited hydrogen poisoning for enhanced activity of promoters-Ru/$Sr_2Ta_2O_7$ nanowires for ammonia synthesis* – Journal of Catalysis, v. 389, 556-565 (2020)
[10] http://www.statista.com/statistics/1046426/ruthenium-price/ (Accessed on 12.06.2024)

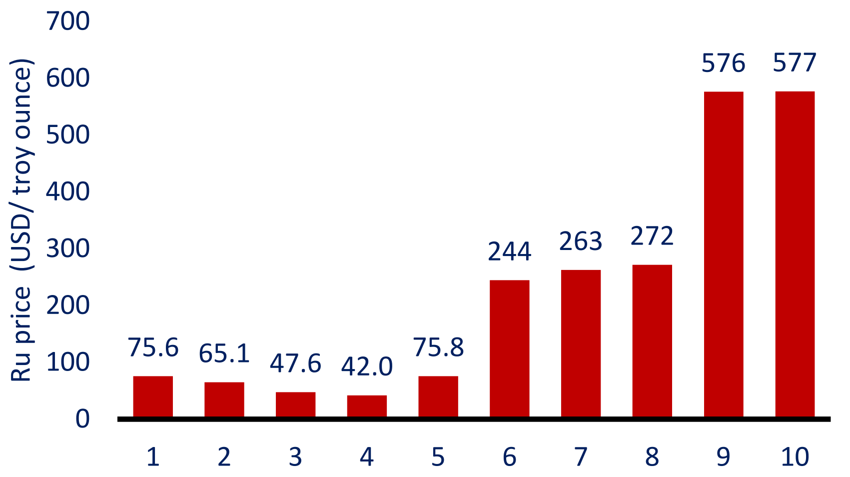
Catalysts for ammonia synthesis

Second-generation catalysts

Ru-based as second-generation catalysts for NH_3 synthesis, due to the higher activity at lower temperatures and pressures than the conventional iron catalyst.



Electron Donation controls nitrogen activation on ruthenium surface.



Main drawbacks:

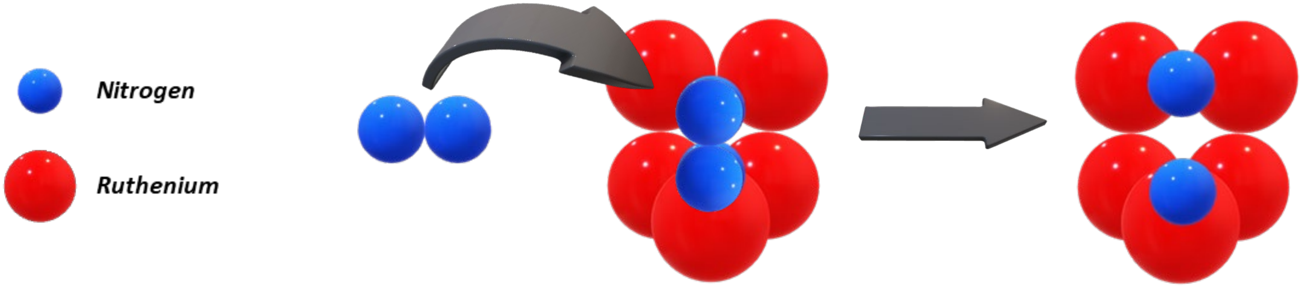
- ➢ High cost;
- ➢ Hydrogen poisoning.

[07] **Ertl G.** – *Primary steps in catalytic synthesis of ammonia* – Journal of Vacuum Science & Technology A, v. 1, 1247-1253 (1983)
[08] **Song Z. et al.** – *Structure and reactivity of Ru nanoparticles supported on modified graphite surfaces: A study of the model catalysts for ammonia synthesis* – Journal of American Chemical Society, v. 126, 8576–8584 (2004)
[09] **Huang J. et al.** – *Inhibited hydrogen poisoning for enhanced activity of promoters-Ru/$Sr_2Ta_2O_7$ nanowires for ammonia synthesis* – Journal of Catalysis, v. 389, 556-565 (2020)
[10] http://www.statista.com/statistics/1046426/ruthenium-price/ (Accessed on 12.06.2024)

Catalysts for ammonia synthesis

Second-generation catalysts: B5 sites

Dahl et al. have studied the sticking probability of dinitrogen on ruthenium. It has been shown that the active site for N_2 dissociation is the so-called B5-site, made of five ruthenium atoms: two at step edges and three at the lower terraces.



Moreover, particle size effect of Ru-based catalysts for NH_3 synthesis has been reported. Ruthenium clusters with 1.8 – 3.5 nm diameter are believed to bear B5-site.

[11] **Dahl S. et al.** – *Role of steps in N_2 activation on Ru(0001)* – Physical Review Letters, v. 83, 1814 (1999)
[12] **Aika K.** – *Role of alkali promoter in ammonia synthesis over ruthenium catalysts - Effect on reaction mechanism* – Catalysis Today, v. 286, 14-20 (2017)

Catalysts for ammonia synthesis

Second-generation catalysts: Ceria and Magnesia as supports

MgO: High Specific Surface Area and high density of basic sites with strong interaction with Ru-clusters.

CeO_2: enables electron donation from partially reduced ceria atoms to metallic ruthenium.

$MgOCeO_2$: Combination of the characteristics of both supports.

[13] **Aika K. et al.** – *Preparation and Characterization of Chlorine-Free Ruthenium Catalysts and the Promoter Effect in Ammonia Synthesis* – Journal of Catalysis, v. 136, 126-140 (1992)
[14] **Wang X. et al.** – *Highly efficient Ru/MgO–CeO_2 catalyst for ammonia synthesis* – Catalysis Communications – v. 12, 251-254 (2010)
[15] **Javaid R. et al.** – *Effect of reaction conditions and surface characteristics of Ru/CeO2 on catalytic performance for NH_3 synthesis as a clean fuel* – International Journal of Hydrogen Energy, v. 46, 18107-18115 (2021)

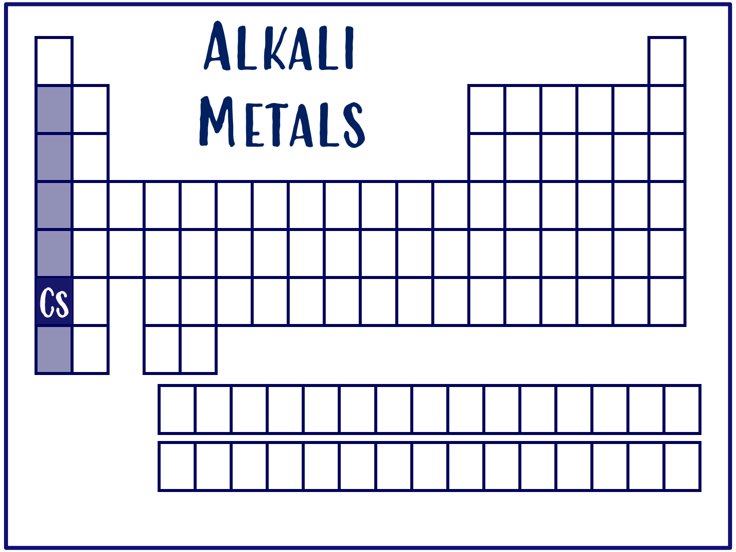
Catalysts for ammonia synthesis

Second-generation catalysts: Alkali metals as promotors

Alkali metals can ensure the Ru-surface reconstruction and influence the surface morphology of the catalyst.

The surfaces exposed could provide new active B5-sites and, at the same time, they are more resistant to poisoning by hydrogen.

Cesium can promote the electron donation from metallic ruthenium to the N_2 triple bond.



[16] **Linag C. et al**. – *Graphitic Nanofilaments as Novel Support of Ru–Ba Catalysts for Ammonia Synthesis* - Journal of Catalysis, v. 211, 278-282 (2002)
[17] **Narasimharao K. et al.** – *Carbon covered Mg–Al hydrotalcite supported nanosized Ru catalysts for ammonia synthesis* – Journal of Molecular Catalysis A: Chemical, v. 411, 157-166 (2016)
[18] **Javaid R. et al.** – *Influence of Reaction Conditions and Promoting Role of Ammonia Produced at Higher Temperature Conditions in Its Synthesis Process over Cs-Ru/MgO Catalyst* – Chemistry Select, v. 4, 22184-2224 (2019)
[19] **Zheng J. et al.** – *Efficient Non-dissociative Activation of Dinitrogen to Ammonia over Lithium-Promoted Ruthenium Nanoparticles at Low Pressure* - Angewandte Chemie International Edition, v. 58, 17335-17341 (2019)

Catalysts for ammonia synthesis

Second-generation catalysts: Cluster size and synthesis methods

Synthesis method	Cluster size (nm)	Reference
Impregnation	2 - 30	[20],[21]
Co-precipitation	2 - 6	[22],[23]
Polyol Reduction	1 - 5	[24],[25]

- ✓ *SIMPLE*
- ✓ *SINGLE-STEP PROCESS*
- ✓ *ALLOWS PREPARATION OF NANOSTRUCTURED POWDERS*

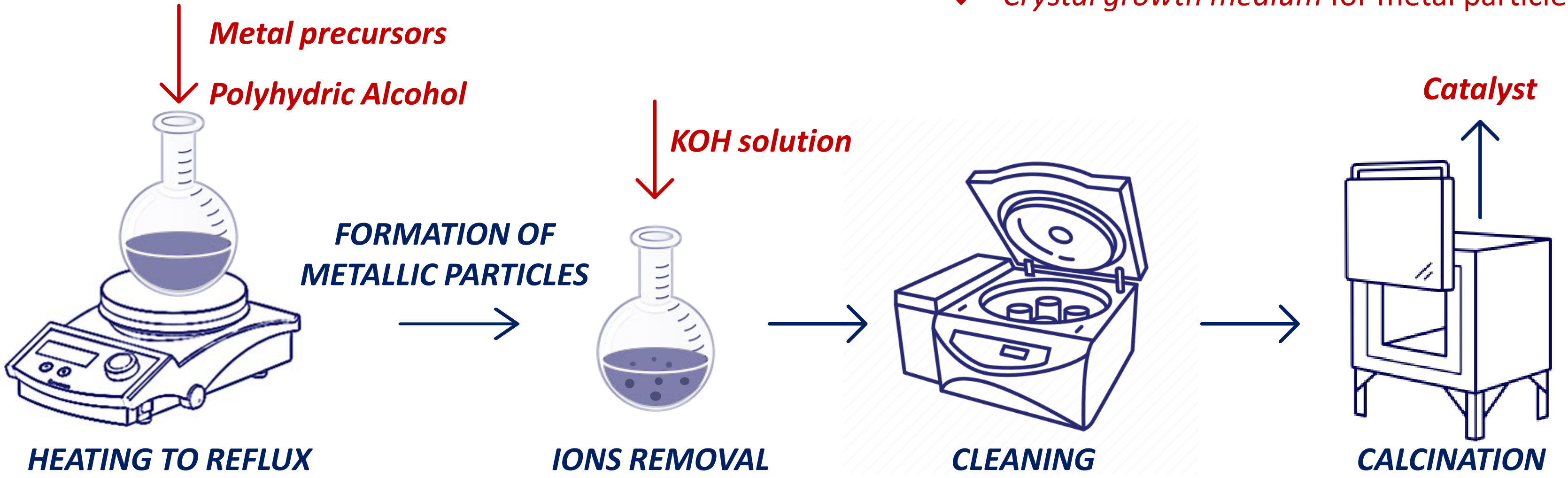
[20] **Hansen T. W. et al.** – *Support effect and active sites on promoted ruthenium catalysts for ammonia synthesis* – Catalysis Letters, v. 84, 7-12 (2002)
[21] **Liu J. et al.** – *Ru-nanoparticles embedded in mesoporous carbon microfibers: preparation, characterization and catalytic properties in the hydrogenation of D-glucose* – Physical Chemistry Chemical Physics, v. 13, 3758-3763 (2010)
[22] **Zhang L. et al.** – *Highly efficient Ru/Sm_2O_3-CeO_2 catalyst for ammonia synthesis* – Catalysis Communications – v. 15, 23-26 (2011)
[23] **Komvokis V. G. et al.** – *Catalytic decomposition of N_2O over highly active supported Ru nanoparticles (≤3nm) prepared by chemical reduction with ethylene glycol* – Applied Catalysis B: Environmental, v. 103, 62-71 (2011)
[24] **Miyazaki A. et al.** – Preparation of Ru nanoparticles supported on γ-Al2O3 and its novel catalytic activity for ammonia synthesis – Journal of Catalysis, v. 204, 364-371 (1998)
[25] **Fievet F. et al.** – *Preparing Monodisperse Metal Powders in Micrometer and Submicrometer Sizes by the Polyol Process*, MRS Bulletin, v. 14, 29-34 (1989)

Catalysts for ammonia synthesis

Polyol Reduction Method

ROLE OF ETHYLENE GLYCOL:

- *Solvent* for the starting compound
- *Reducing agent* for the metal species
- *Crystal growth medium* for metal particles



Metal precursors

Polyhydric Alcohol

FORMATION OF METALLIC PARTICLES

KOH solution

Catalyst

HEATING TO REFLUX

IONS REMOVAL

CLEANING

CALCINATION

[25] **Fievet F. et al. –** *Preparing Monodisperse Metal Powders in Micrometer and Submicrometer Sizes by the Polyol Process*, MRS Bulletin, v. 14, 29-34 (1989)
[26] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)
[27] **Komarneni S. et al. –** *Microwave-Polyol Process for Pt and Ag Nanoparticles*, Langmuir, v. 18, 5959-5962 (2002)
[28] **Saadatjou N. et al.** – *Ruthenium Nanocatalysts for Ammonia Synthesis* – A Review, Chemical Engineering Communications, v. 202, 420-448 (2015)
[29] **Fiévet F. et al.** – *The polyol process: a unique method for easy access to metal nanoparticles with tailored sizes, shapes and compositions* – Royal Society of Chemistry, v. 47, 5187-5233 (2018)

Catalysts for ammonia synthesis

Catalysts list

	Support		Active Phase	Promoter
Catalyst	**CeO_2** mol.%	**MgO** mol.%	**Ru** wt%	**Cs** wt%
Ru/MgO	-	100.0	5.0	-
Ru/CeO_2	100.0	-	5.0	-
Ru/MgOCeO_2	50.0	50.0	5.0	-
Cs-Ru/CeO_2	100.0	-	5.0	1.0
Cs-Ru/MgOCeO_2	50.0	50.0	5.0	1.0

Non-promoted catalysts

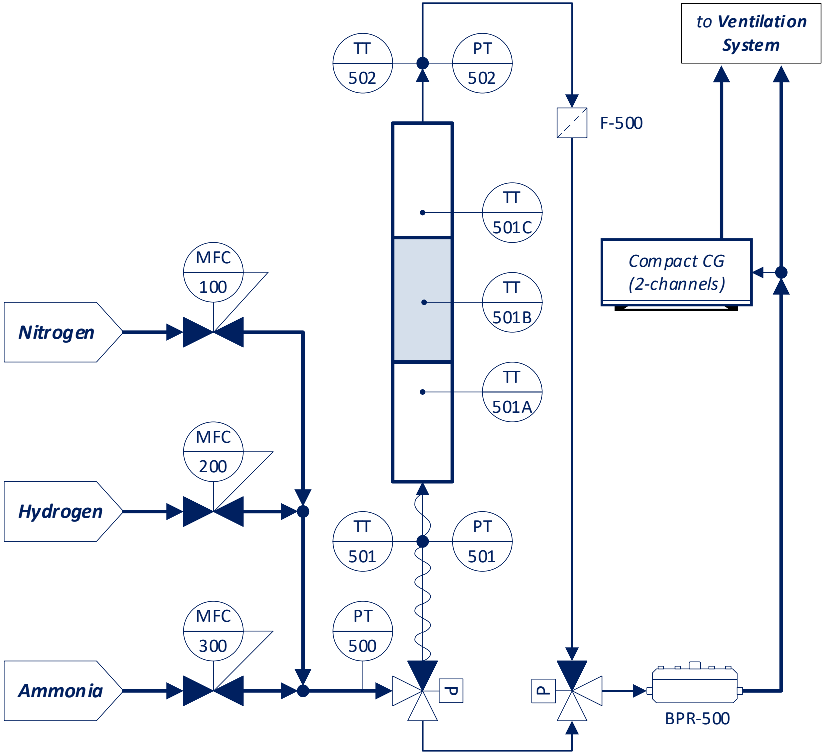
Promoted catalysts

[20] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)

Catalysts for ammonia synthesis

Catalytic activity tests: Experimental conditions

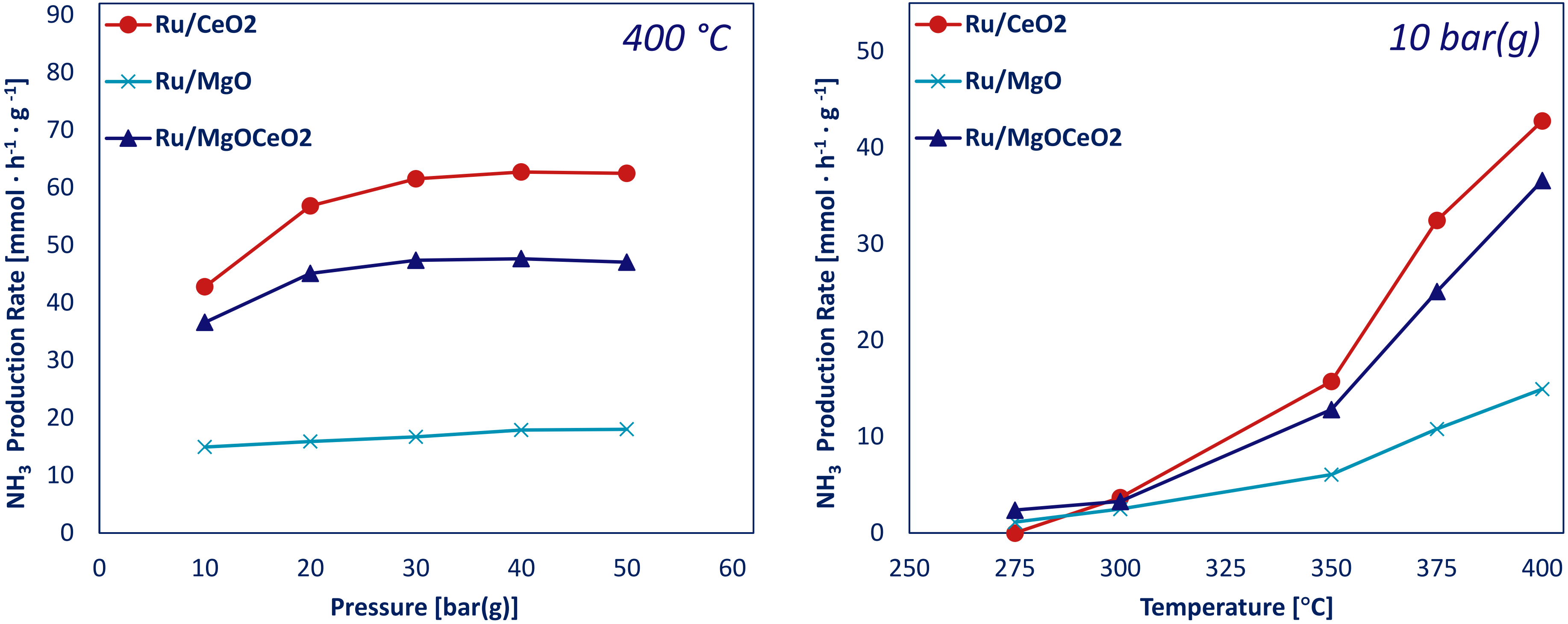
- *Amount of catalyst:* ***1 g***
- *Amount of Silicon Carbide:* ***5 g***
- *Particle Size Distribution:* ***106 – 315 µm***
- *Reactor Inner Diameter:* ***10 mm***
- *Bed Length:* ***~ 50 mm***
- *Total Feed Flow Rate:* ***450 Nml·min^{-1}***
- *Feed Ratio:* ***mol H_2 : mol N_2 = 2 : 1***



[20] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)

Catalysts for ammonia synthesis

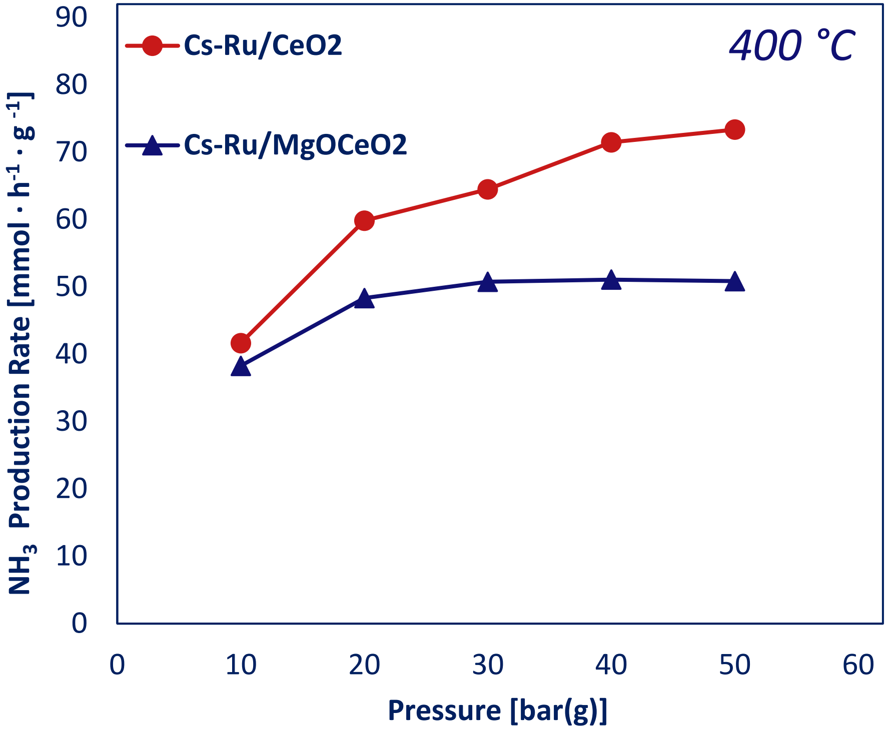
Catalytic activity tests: non-promoted catalysts

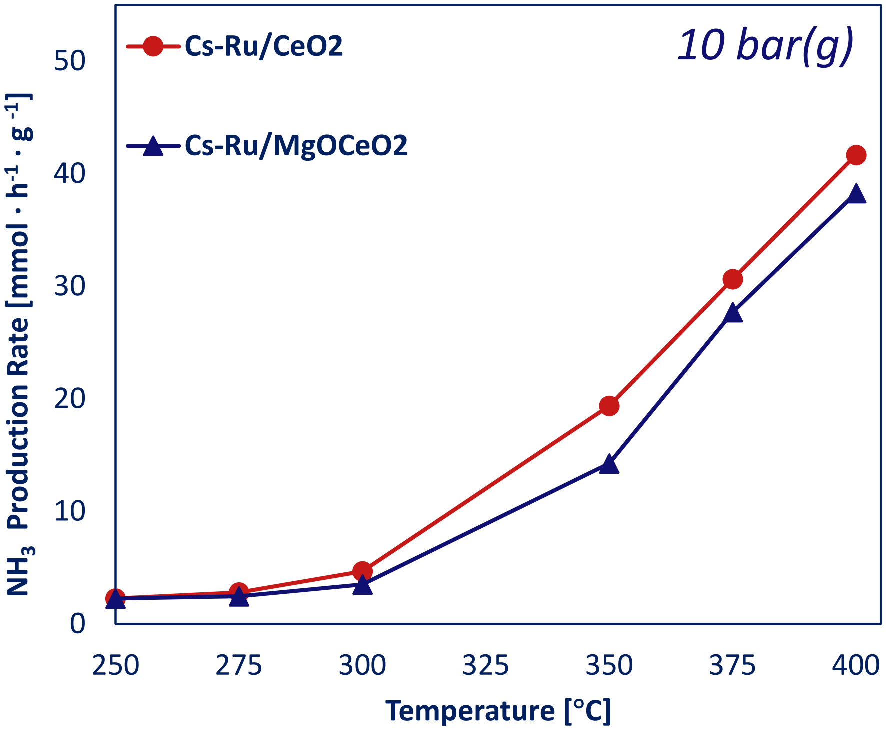


[20] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)

Catalysts for ammonia synthesis

Catalytic activity tests: promoted catalysts





[20] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)

Catalysts for ammonia synthesis

Comparison with literature

Catalyst	Synthesis Method	Ru content	Cs content	Reaction Pressure	Reaction Temperature	Feed Ratio	NH_3 production rate	Reference
		wt%	wt%	bar	°C	$mol_{H2} : mol_{N2}$	$mmol \cdot g_{CAT}^{-1} \cdot h^{-1}$	-
Ru/CeO_2	WI	3.0	0	25	375	1.5	4.7	[16]
$Ru/MgOCeO_2$	CP - WI	5.0	0	1	375	3	4.0	[29]
K-Ru/MgO	WI	4.0	0	30	400	3	8.9	[30]
Ru/CeO2	HTS - HTS	3.0	0	10	400	3	5.0	[31]
$Cs\text{-}Ru/CeO_2$	HTS - WI	2.5	4	30	375	3	19	[32]
$Cs\text{-}Ru/CeO_2$	PRM	4.5	1	10	375	2	31	[20]*

[16] **Javaid R. et al.** – *Effect of reaction conditions and surface characteristics of Ru/CeO2 on catalytic performance for NH_3 synthesis as a clean fuel* – International Journal of Hydrogen Energy, v. 46, 18107-18115 (2021)
[20] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)
[29] **Saito M. et al.** – *Synergistic effect of MgO and CeO_2 as a support for ruthenium catalysts in ammonia synthesis* – Catalysis Letters, v. 106, 107-110 (2006)
[30] **Yang X. et al.** – *Low temperature ruthenium catalyst for ammonia synthesis supported on BaCeO3 nanocrystals* – Catalysis Communications, v. 11, 867-870 (2010)
[31] **Lin B. et al.** – *Morphology Effect of Ceria on the Catalytic Performances of Ru/CeO_2 Catalysts for Ammonia Synthesis* – Industrial & Engineering Chemical Research, v. 57, 9127-9135, (2018)
[32] **Li W. et al.** – *Influence of CeO2 supports prepared with different precipitants over Ru/CeO_2 catalysts for ammonia synthesis* – Solid State Sciences v. 99, 105983 (2020)

Catalysts for ammonia synthesis

Conclusions

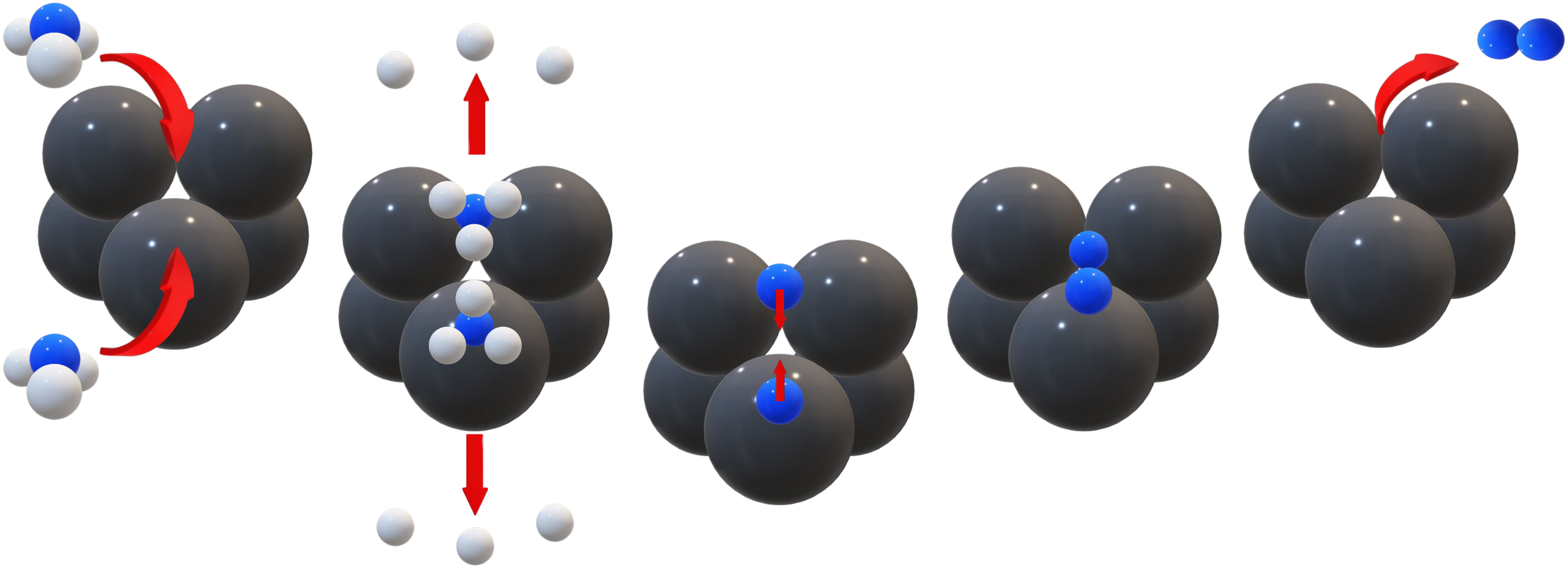
- *Ru-based catalysts with different supports and Cs as promotor have been successfully synthetized via polyol reduction method.*
- *The <u>support</u> and the <u>promotor</u> have a relevant influence on the surface characteristics of the catalysts. More specifically, the electronic properties are fundamental in order to favor the electron donation from metallic Ru to nitrogen triple bond.*
- *The Cs-Ru/CeO_2 has shown better performances at lower temperature and pressure with a production rate about 3 mmol·h^{-1}·g^{-1} at 10 bar and 250°C. This suggests a promising route for ammonia synthesis at milder condition.*

[20] **Anello G. et al.** – *Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method* – International Journal of Hydrogen Energy, v. 86, 922-930 (2024)

Catalysts for ammonia decomposition

Catalytic formulation: Ruthenium and B5-sites

Moreover, ruthenium clusters with 1.8 – 3.5 nm diameter are believed to bear B5-site.



[07] **Kim H. et al.** – Ammonia decomposition over Ru catalysts supported on alumina with different crystalline phases – Catalysis Today, v. 411–412, 2023, 113817
[11] **Dahl S. et al.** – *Role of steps in N_2 activation on Ru(0001)* – Physical Review Letters, v. 83 (1999)

Catalysts for ammonia decomposition

Catalysts list

Catalyst	Cs loading wt%	Ru loading wt%	Cs/Ru ratio w/w
$3RuCeO_2$	-	3	-
$5RuCeO_2$	-	5	-
$7RuCeO_2$	-	7	-
$2Cs\text{-}5RuCeO_2$	2	5	0.4
$10Cs\text{-}5RuCeO_2$	10	5	2

Ru-loading investigation ($3RuCeO_2$, $5RuCeO_2$, $7RuCeO_2$)

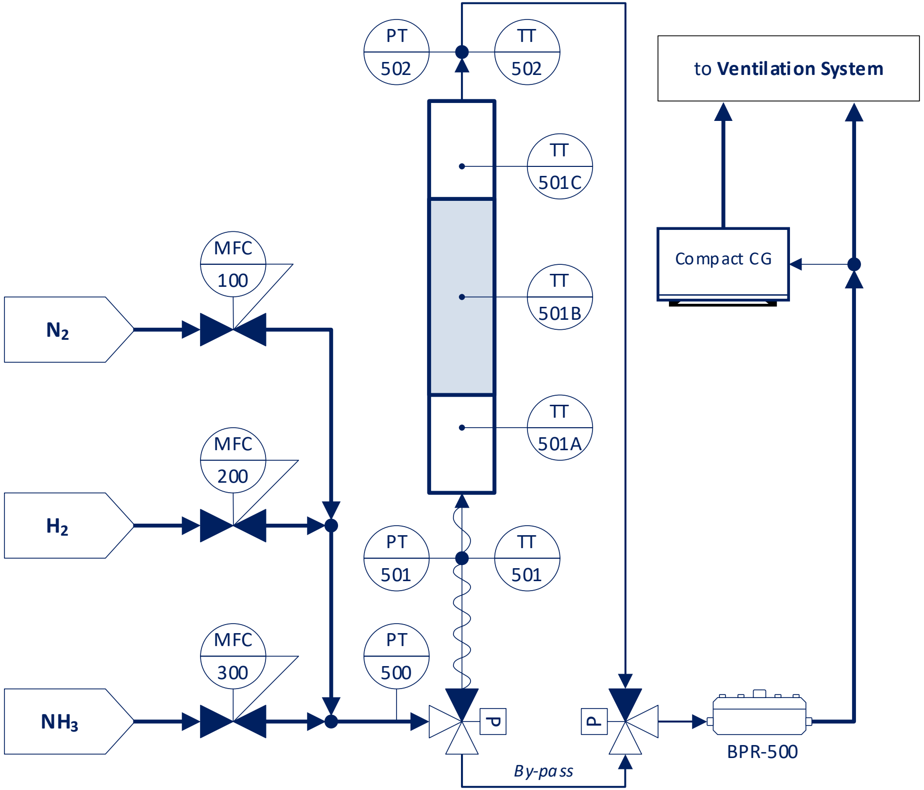
Cs/Ru mass ratio investigation ($7RuCeO_2$, $2Cs\text{-}5RuCeO_2$, $10Cs\text{-}5RuCeO_2$)

[33] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation

Catalysts for ammonia decomposition

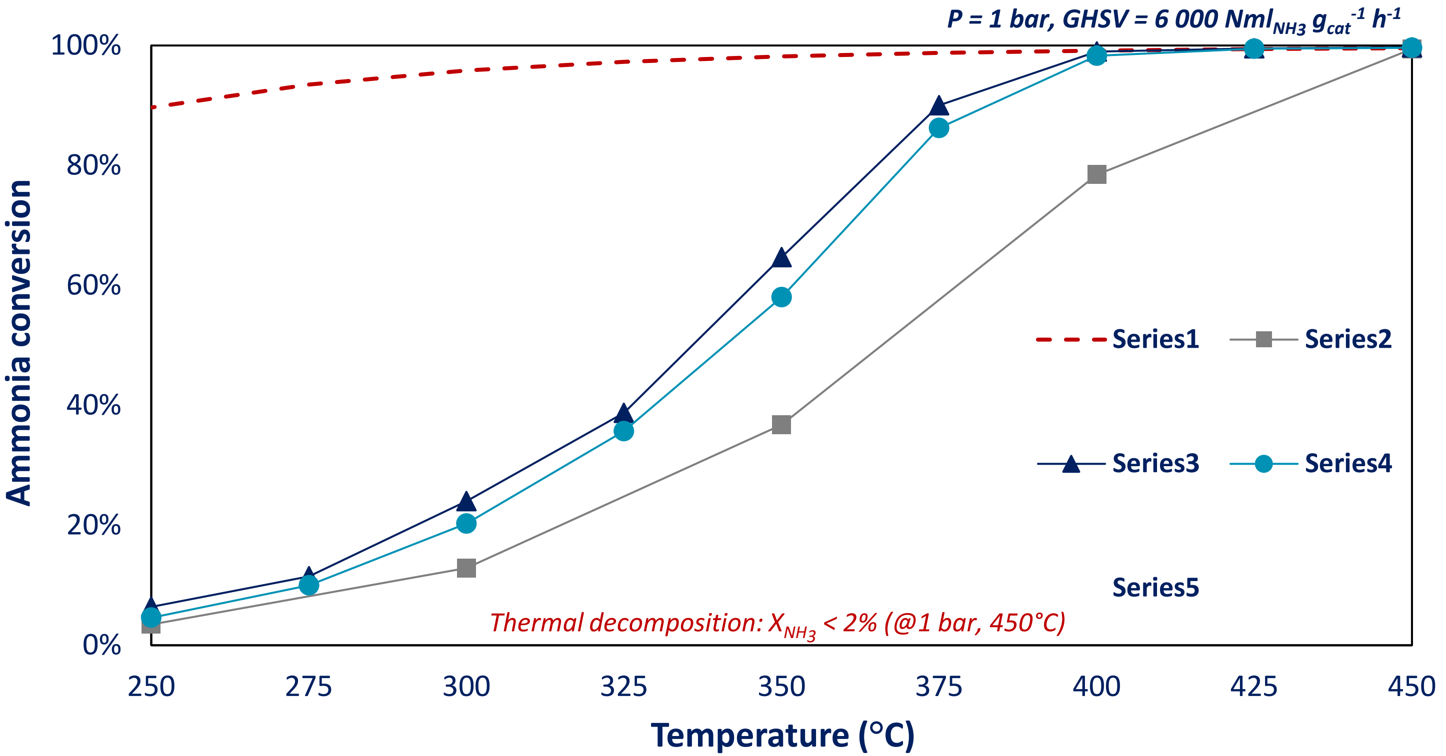
Activity tests

- *Amount of catalyst:* ***1 g***
- *Amount of Silicon Carbide:* ***5 g***
- *Particle Size Distribution:* ***150 – 250 µm***
- *Reactor Inner Diameter:* ***10 mm***
- *Reactor Length:* ***~ 50 mm***
- *GHSV:* ***6 000 – 30 000 Nml*** $\boldsymbol{g_{cat}\ h^{-1}}$



Catalysts for ammonia decomposition

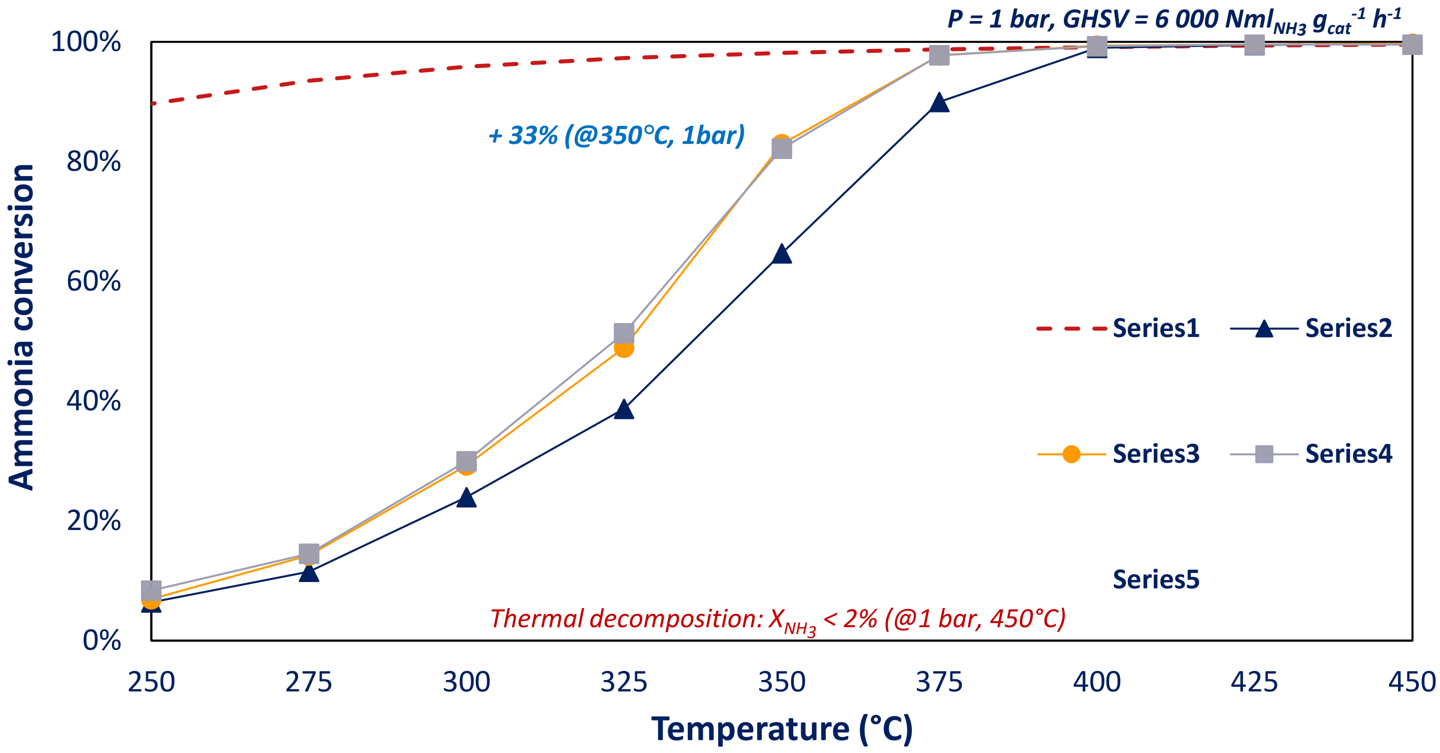
Activity tests: Ruthenium loading investigation



[33] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation

Catalysts for ammonia decomposition

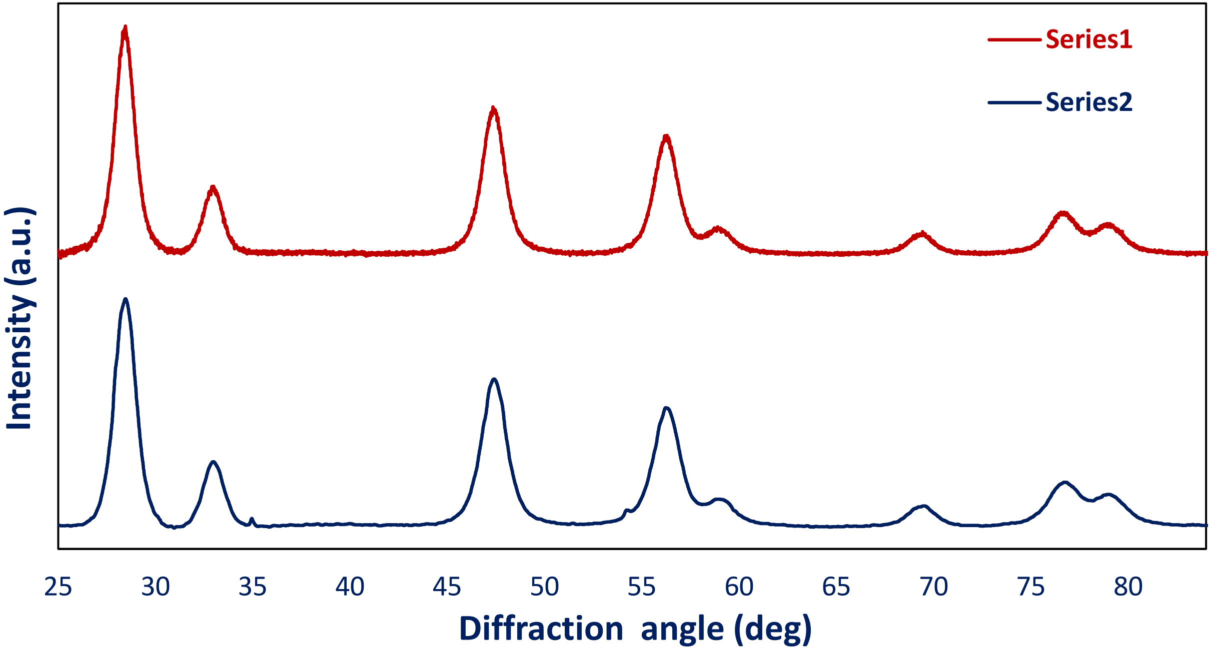
Activity tests: Cs/Ru ratio investigation



[33] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation

Catalysts for ammonia decomposition

X-Ray Diffractometry analysis



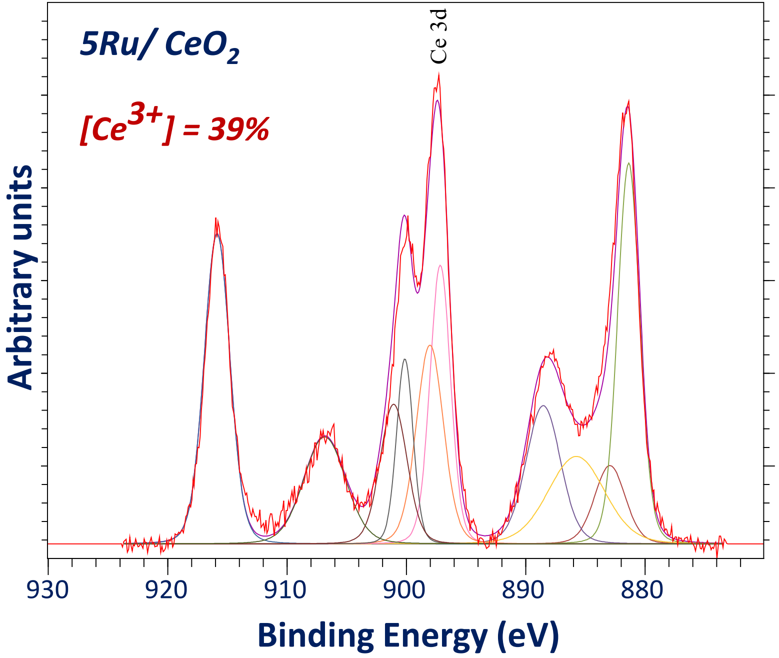
Main peaks' location for cubic lattice of CeO_2 : 28.5° , 33.1° , 47.5° , 56.4° , 58.2° , 69.5° , 76.0° , 77.9°

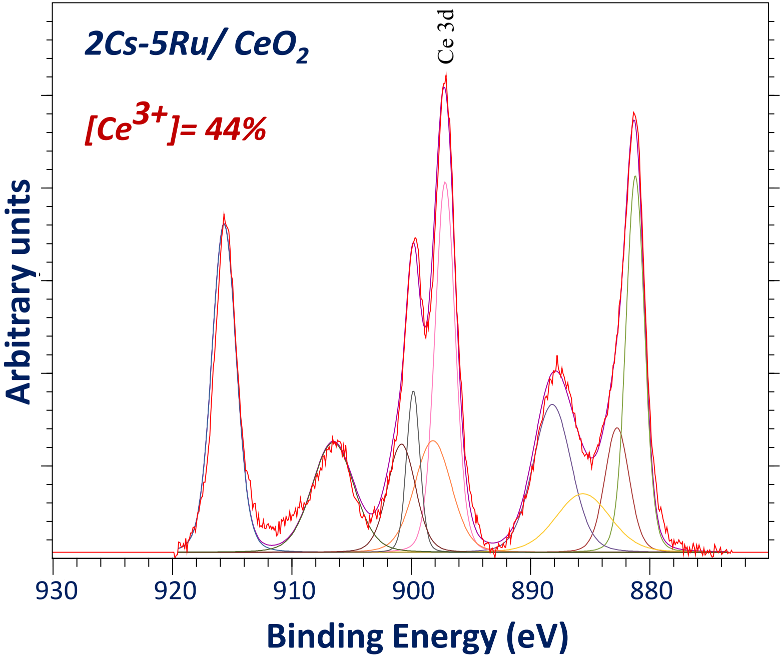
[33] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation

[34] **Peng Z. et al.** – *Uniform dispersion of ultrafine ruthenium nanoparticles on nano-cube ceria as efficient catalysts for hydrogen production from ammonia-borane hydrolysis*, Sustain. Energy Fuels, v. 7, 821-831 (2022)

Catalysts for ammonia decomposition

XPS deconvoluted spectra Cerium 3d

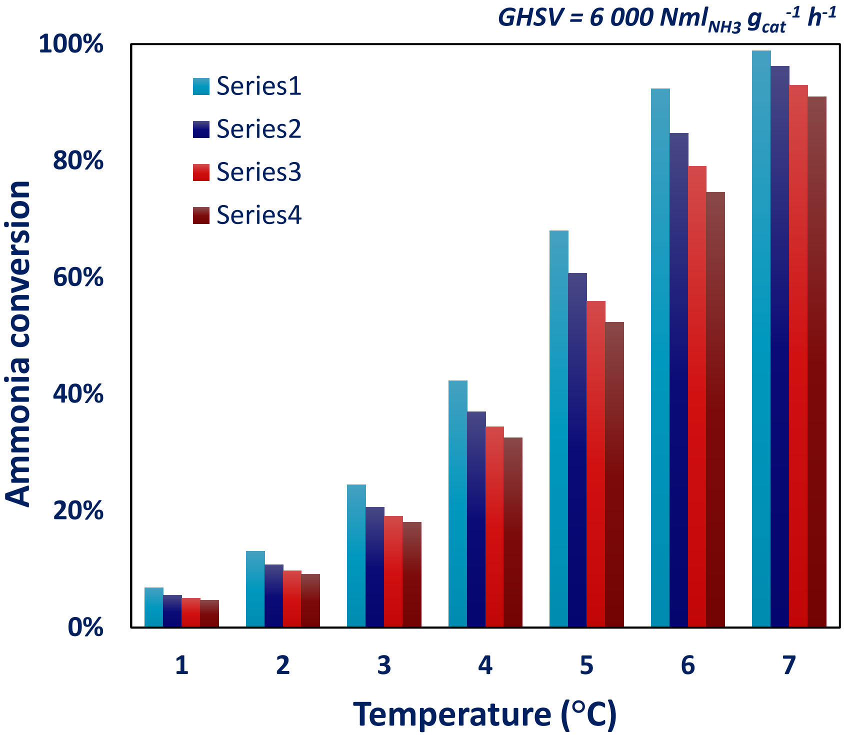




[21] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation
[35] **Lin B. et al.** – *Effect of ceria morphology on the catalytic activity of Co/CeO2 catalyst for ammonia synthesis* – Catalysis Communication v. 101, 15-19 (2017)

Catalysts for ammonia decomposition

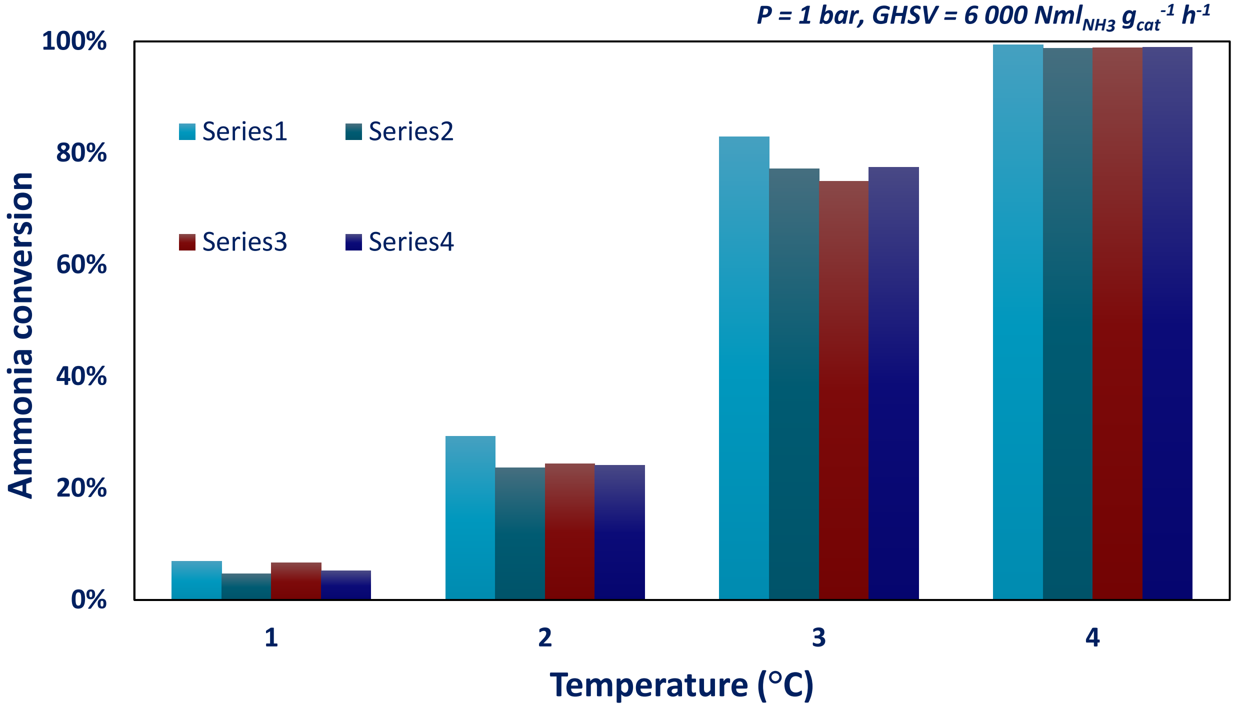
Pressure influence



[33] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation

Catalysts for ammonia decomposition

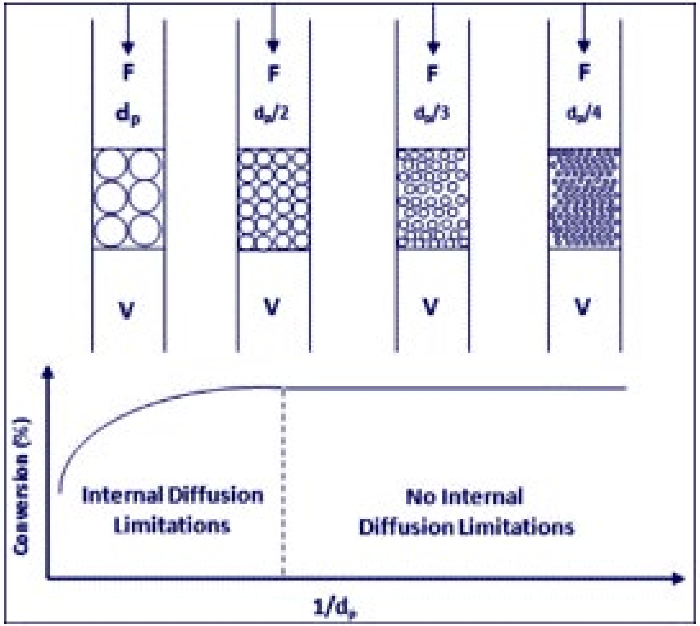
Stability tests

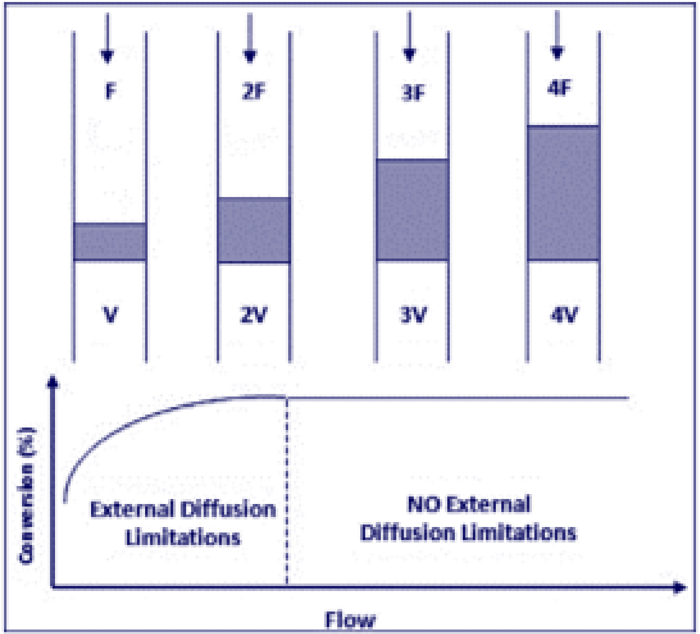


[33] **Anello G. et al.** – *Low-temperature ammonia decomposition over CsRuCeO2 produced via polyol reduction method* – In preparation

Catalysts for ammonia decomposition

Mass transfer limitation evaluation

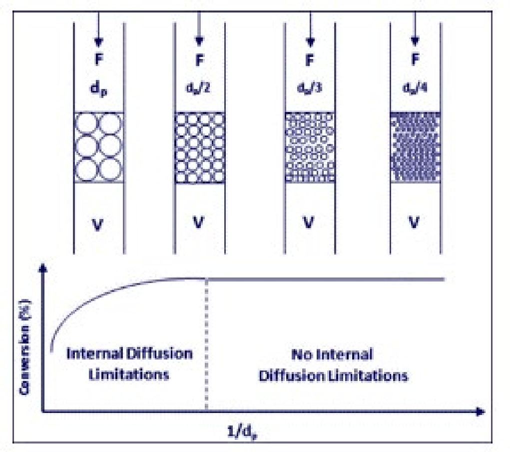


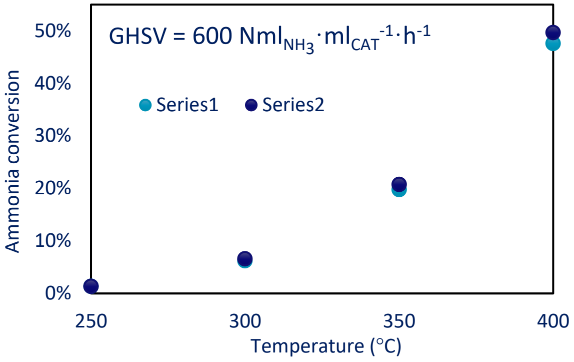


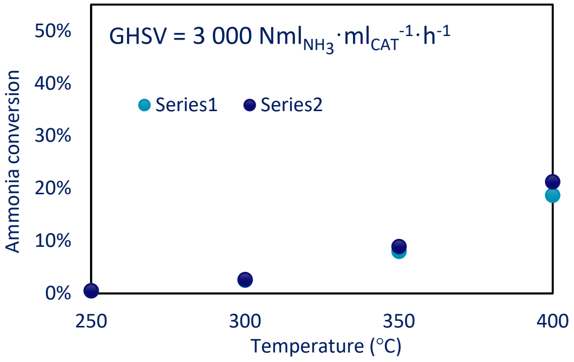
[36] **Talebian-Kiakalaieh A. et al.** – *Theoretical and experimental evaluation of mass transfer limitation in gas phase dehydration of glycerol to acrolein over supported HSiW catalyst*, Journal of the Taiwan Institute of Chemical Engineer, v. 59 (2016)

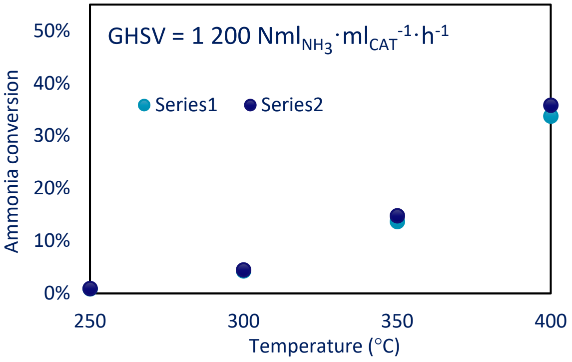
Catalysts for ammonia decomposition

Internal mass transfer limitation



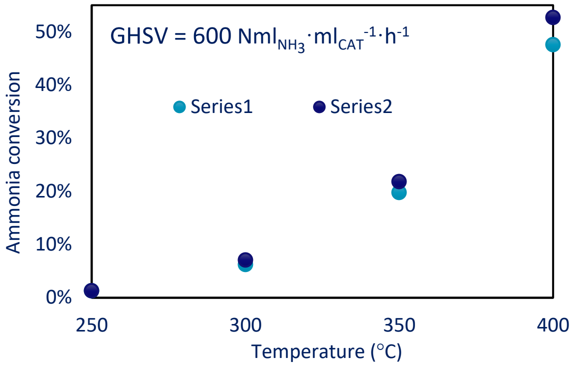


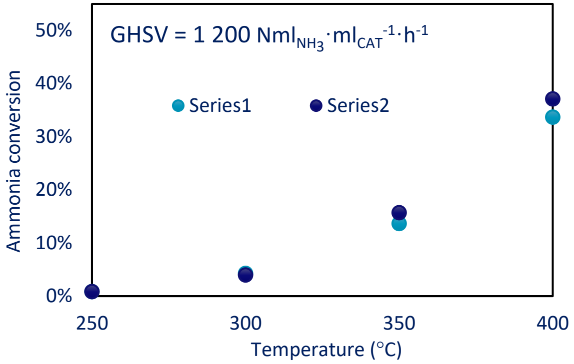


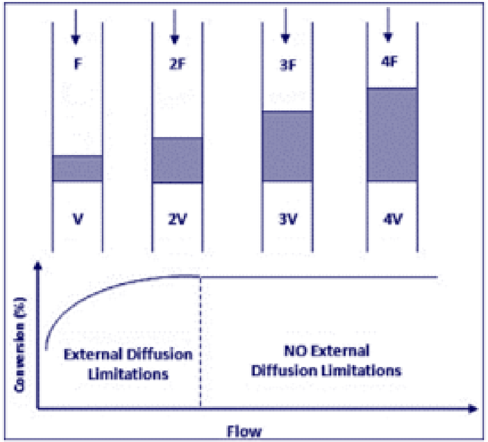


Catalysts for ammonia decomposition

External mass transfer limitation







Catalysts for ammonia decomposition

Conclusions

- *Ru-based-CeO_2-supported catalysts where successfully synthesized via PRM.*
- *The non-promoted catalyst (5Ru/CeO_2) allowed an ammonia conversion reaching the equilibrium already between 375 and 400°C (1 bar, 6 000 $Nml_{NH3}\ g_{cat}^{-1}\ h^{-1}$).*
- *The addition of cesium (2Cs-5Ru/CeO_2) to the catalytic formulation resulted in an increase of ammonia conversion by 33% (350°C, 1 bar, , 6 000 $Nml_{NH3}\ g_{cat}^{-1}\ h^{-1}$).*
- *The overall conversion decreased less then 1% over 500 hours of test at 400°C, proving the high stability of the synthesized catalyst over time.*

APOLO

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

engie

ChemistryNL

THANK YOU

Any questions?

Contact us!