



Advancements in low-temperature ammonia decomposition on Cs-Ru/CeO₂ catalysts: a kinetic study

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APOLO



3rd

**SYMPOSIUM on 氢能
AMMONIA ENERGY**

SEP 23-26, 2024 SHANGHAI CHINA

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Overview

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



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 

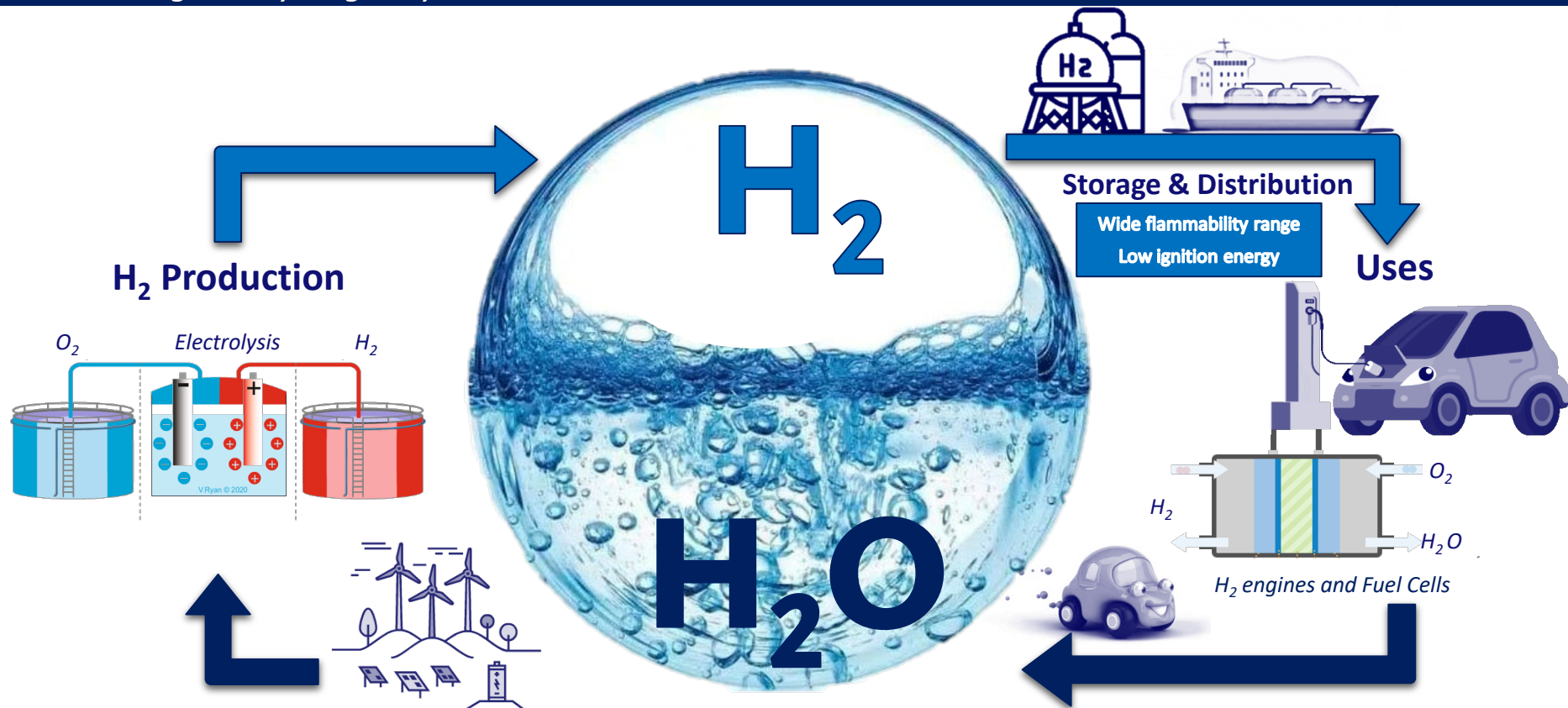


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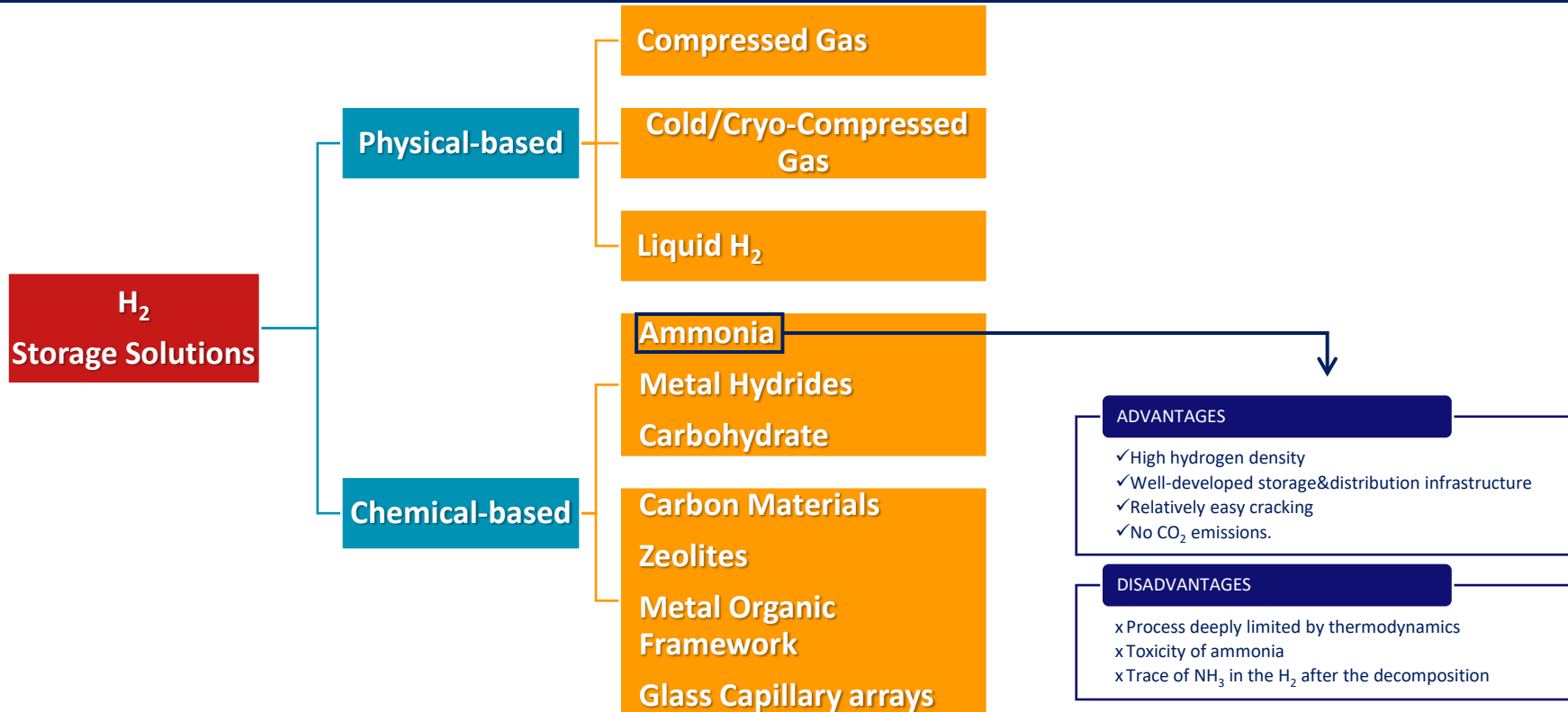
Hydrogen

Renewable green hydrogen cycle



Hydrogen

Storage solutions

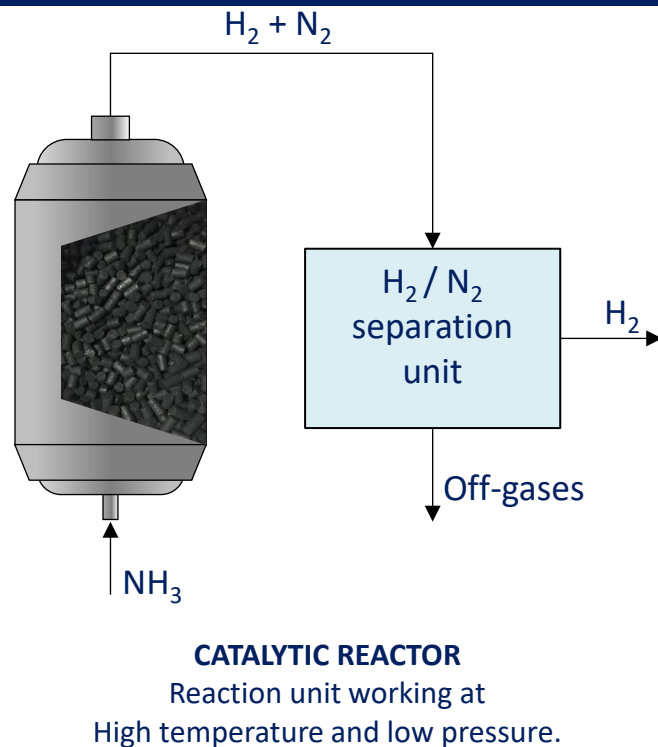
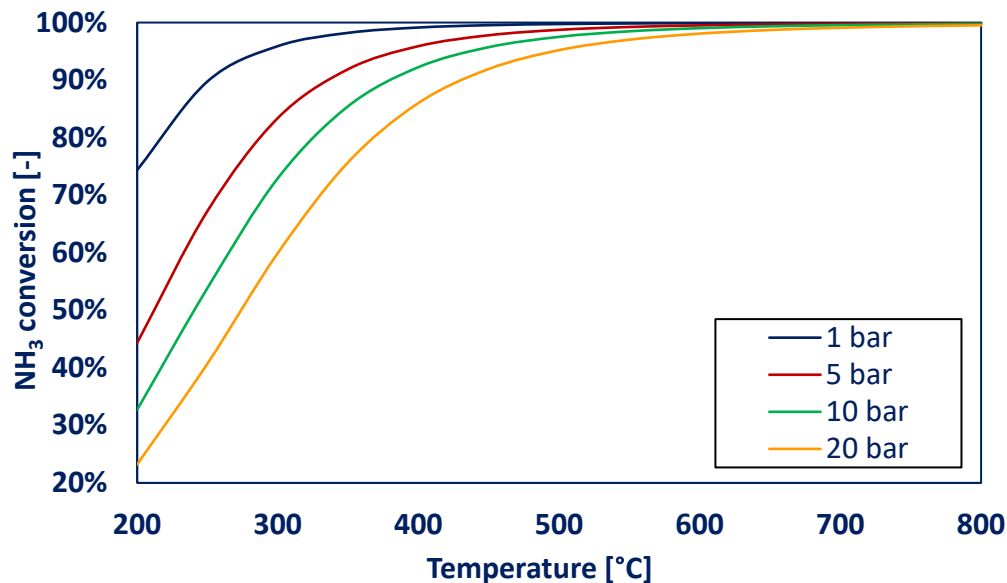


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Ammonia decomposition

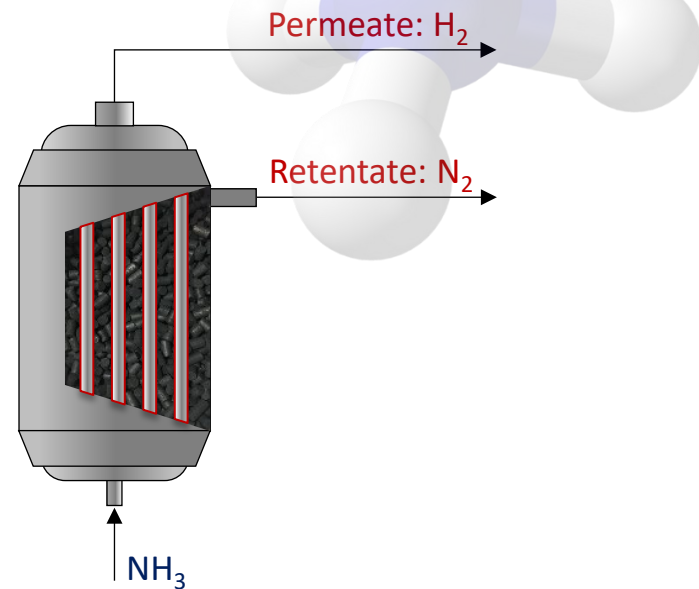
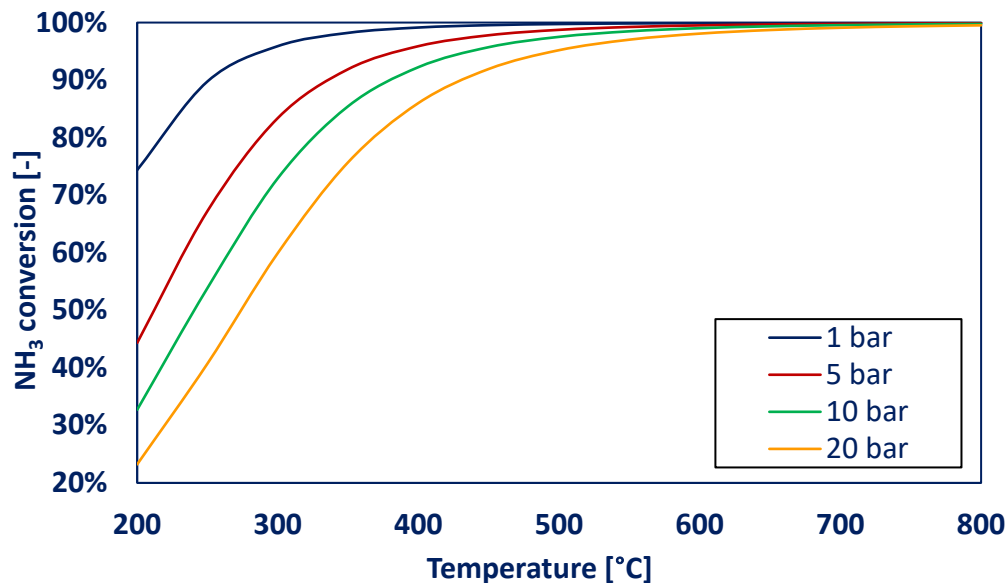
Conventional system



[05] Cechetto V. et al. – Advances and Perspectives of H₂ Production from NH₃ Decomposition in Membrane Reactors – Energy Fuels v. 37, 10775-10798 (2023)

Ammonia decomposition

Process intensification: Catalytic Membrane Reactor



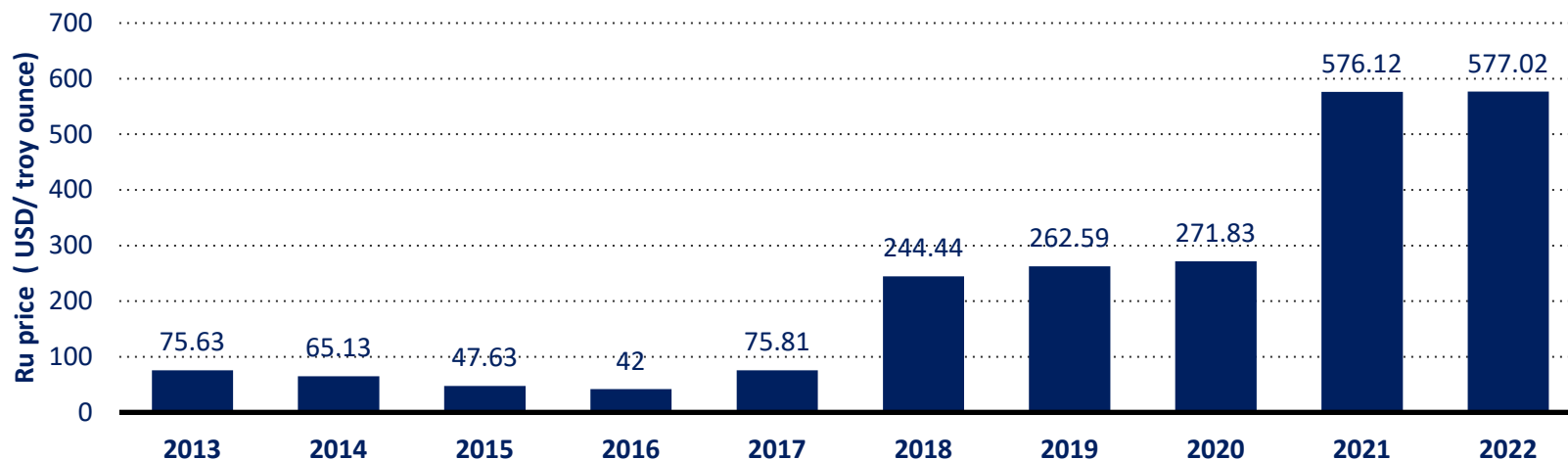
CATALYTIC MEMBRANE REACTOR

NH₃ decomposition and high-purity H₂ separation are simultaneously performed.

Catalysts for ammonia decomposition

Ruthenium as active phase

Ruthenium-based catalysts are employed for ammonia decomposition due to their excellent activity at lower temperatures. Therefore, to efficiently use this precious resource, developing Ru-based catalysts with low loading, high activity and high stability has become a research hotspot.

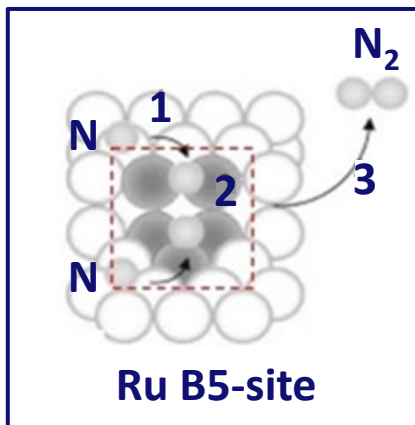


[06] <http://www.statista.com/statistics/1046426/ruthenium-price/> (Accessed on 12.06.2024)

Catalysts for ammonia decomposition

Catalytic formulation: Ruthenium and B5-sites

B5-type surface sites can be responsible for the specific activity of Ru catalysts. B5-type site consists of an arrangement of three Ru atoms in one layer and two further Ru in the layer directly above this at a monoatomic step on an Ru(0001) terrace .



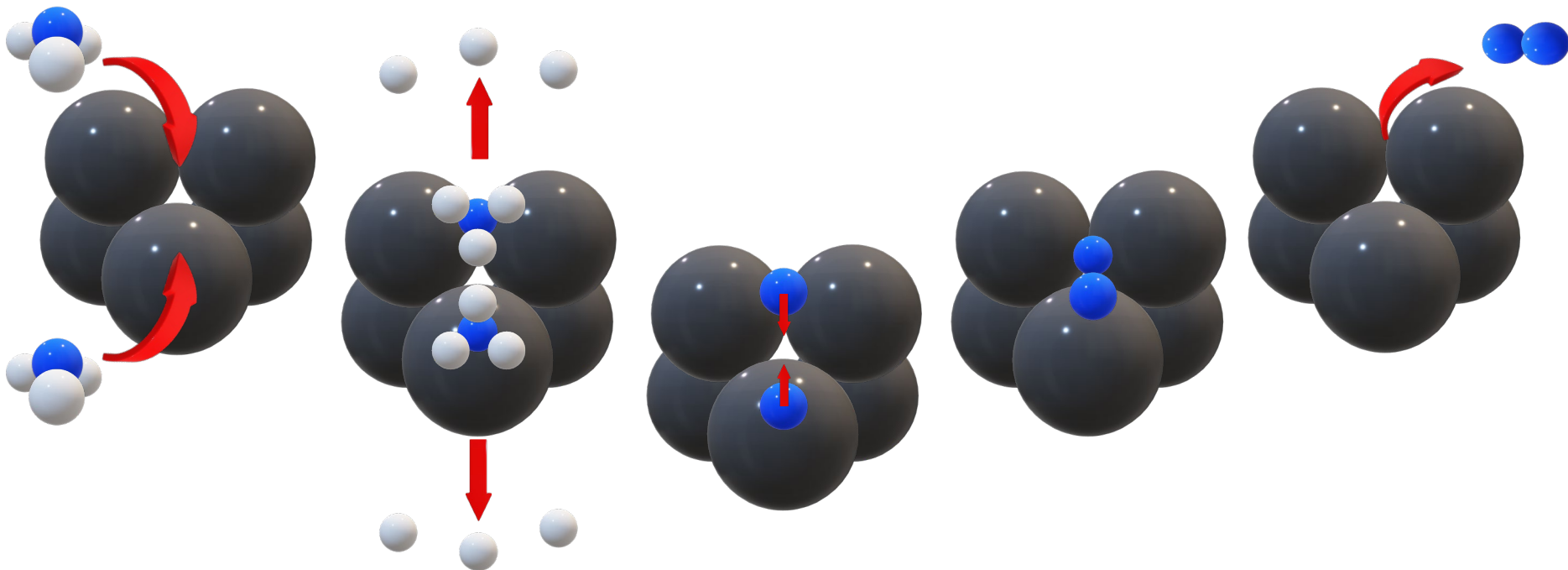
[07] Kim H. et al. – Ammonia decomposition over Ru catalysts supported on alumina with different crystalline phases – Catalysis Today, v. 411–412, 2023, 113817

[08] Dahl S. et al. – Role of steps in N₂ activation on Ru(0001) – Physical Review Letters, v. 83 (1999)

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

[08] Dahl S. et al. – Role of steps in N_2 activation on Ru(0001) – *Physical Review Letters*, v. 83 (1999)

Catalysts for ammonia decomposition

Catalytic formulation: Support and promotor

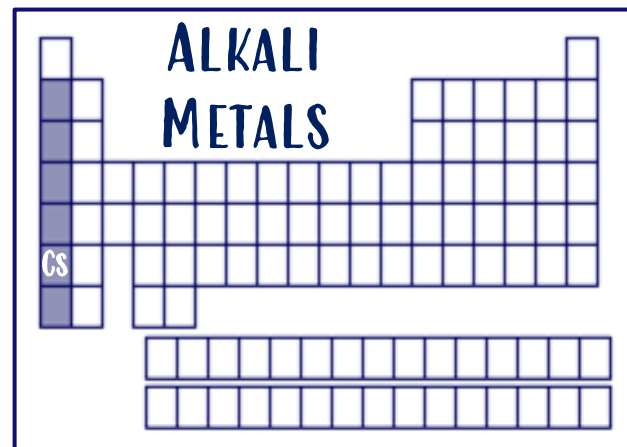


Ceria enables electron donation from partially reduced cerium atoms to metallic ruthenium.

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.



[09] 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)

[10] Javid R. et al. – Effect of reaction conditions and surface characteristics of Ru/CeO₂ on catalytic performance for NH₃ synthesis as a clean fuel – International Journal of Hydrogen Energy, v. 46, 18107-18115 (2021)

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Catalysts for ammonia decomposition

Cluster size and synthesis methods

Synthesis method	Cluster size (nm)	Reference
Impregnation	2 - 30	[14],[15]
Co-precipitation	2 - 6	[16],[17]
Polyol Reduction	1 - 5	[18],[19]

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

[14] Hansen T. W. et al. – Support effect and active sites on promoted ruthenium catalysts for ammonia synthesis – Catalysis Letters, v. 84, 7-12 (2002)

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[16] Zhang L. et al. – Highly efficient Ru/Sm₂O₃-CeO₂ catalyst for ammonia synthesis – Catalysis Communications – v. 15, 23-26 (2011)

[17] Komvokis V. G. et al. – Catalytic decomposition of N₂O over highly active supported Ru nanoparticles (≤3nm) prepared by chemical reduction with ethylene glycol – Applied Catalysis B: Environmental, v. 103, 62-71 (2011)

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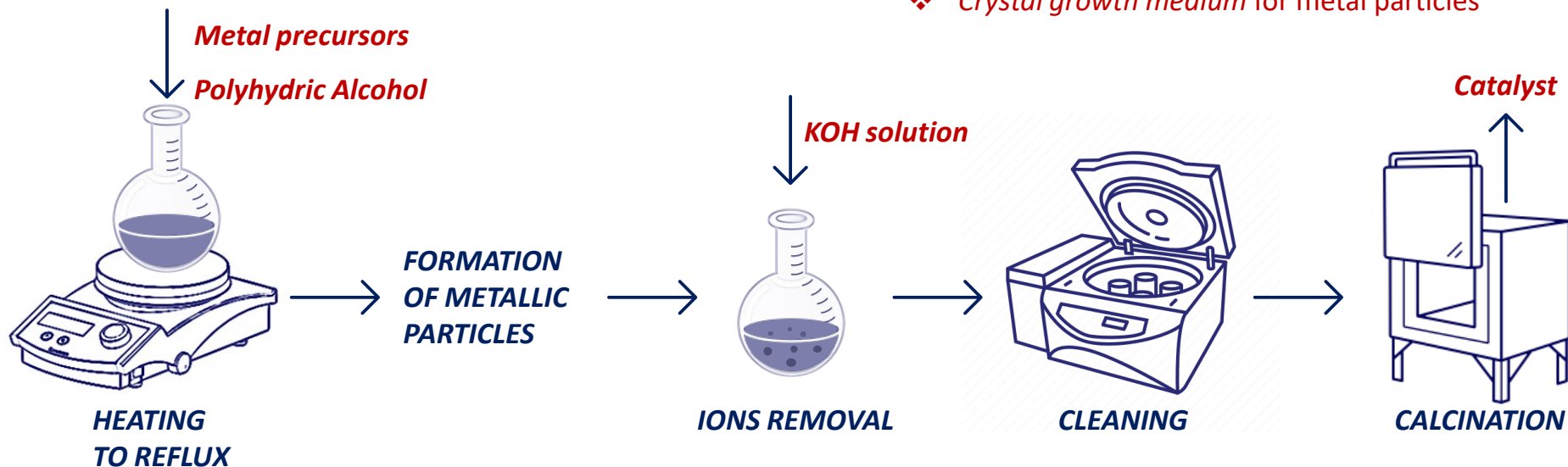
[19] Fievet F. et al. – Preparing Monodisperse Metal Powders in Micrometer and Submicrometer Sizes by the Polyol Process, MRS Bulletin, v. 14, 29-34 (1989)

Catalysts for ammonia decomposition

Polyol Reduction Method

ROLE OF ETHYLENE GLYCOL:

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



[19] Fievet F. et al. – *Preparing Monodisperse Metal Powders in Micrometer and Submicrometer Sizes by the Polyol Process*, MRS Bulletin, v. 14, 29-34 (1989)

[20] Komarneni S. et al. – *Microwave-Polyol Process for Pt and Ag Nanoparticles*, Langmuir, v. 18, 5959-5962 (2002)

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Catalysts for ammonia decomposition

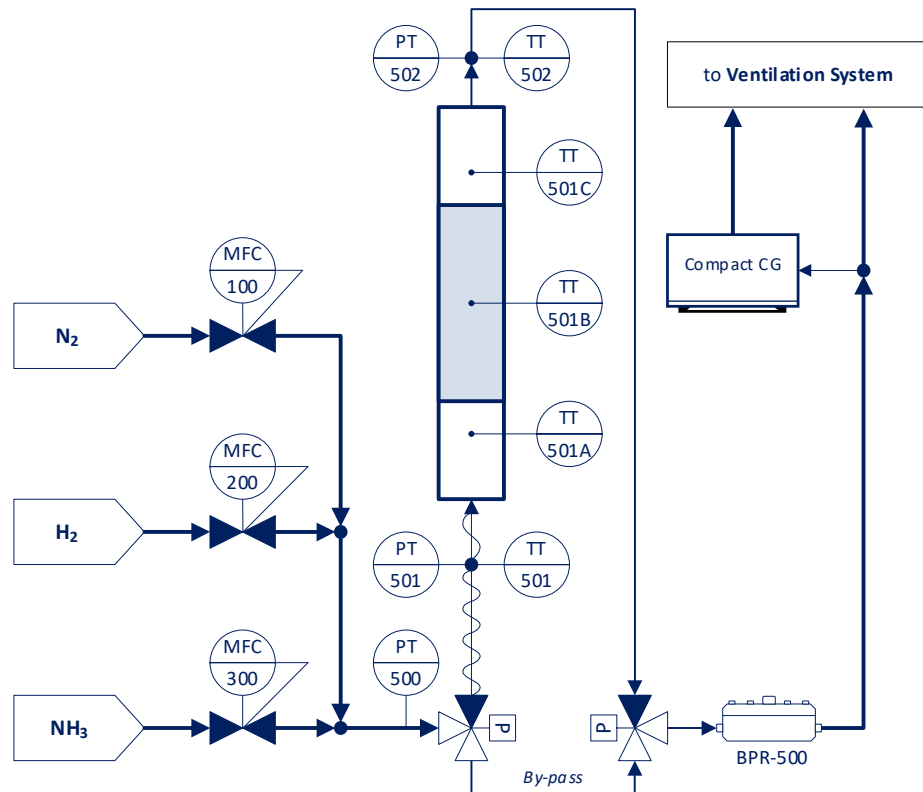
Catalysts list

		Catalyst	Cs loading wt%	Ru loading wt%	Cs/Ru ratio w/w	
<i>Ru-loading investigation</i>		3RuCeO ₂	-	3	-	<i>Cs/Ru mass ratio investigation</i>
		5RuCeO ₂	-	5	-	
		7RuCeO ₂	-	7	-	
		2Cs-5RuCeO ₂	2	5	0.4	
		10Cs-5RuCeO ₂	10	5	2	

Experimental Setup

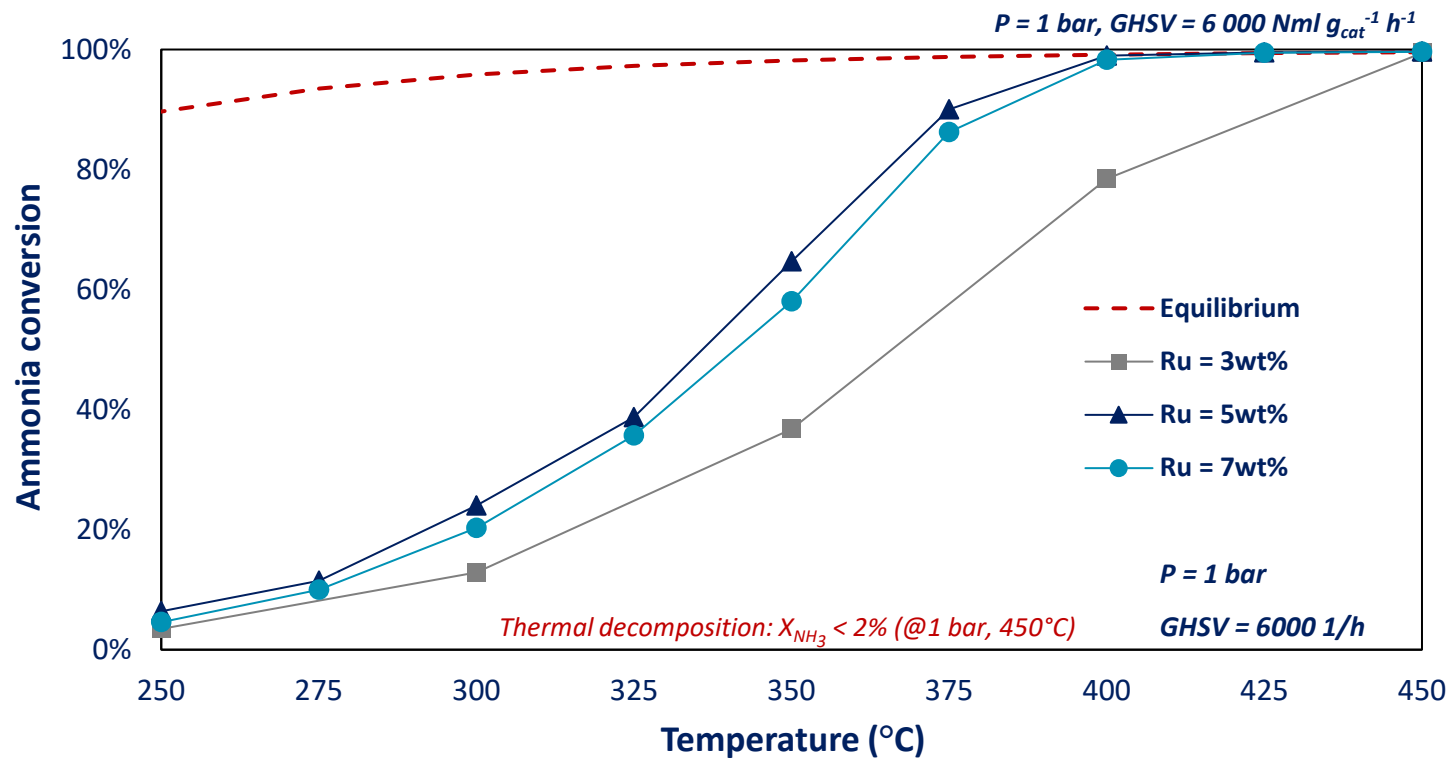
Activity tests

- 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 $\text{Nml g}_{\text{cat}} \text{h}^{-1}$**



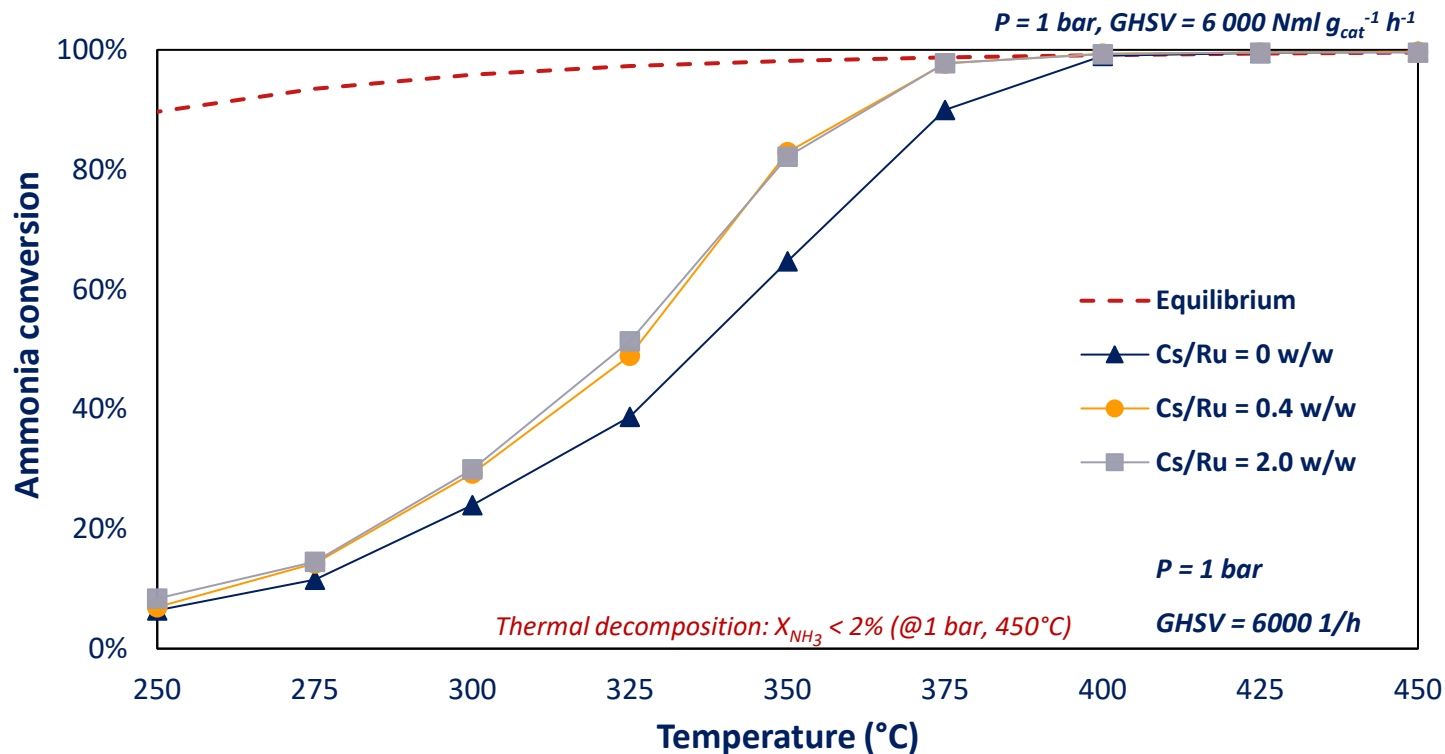
Results

Activity tests: Ruthenium loading investigation



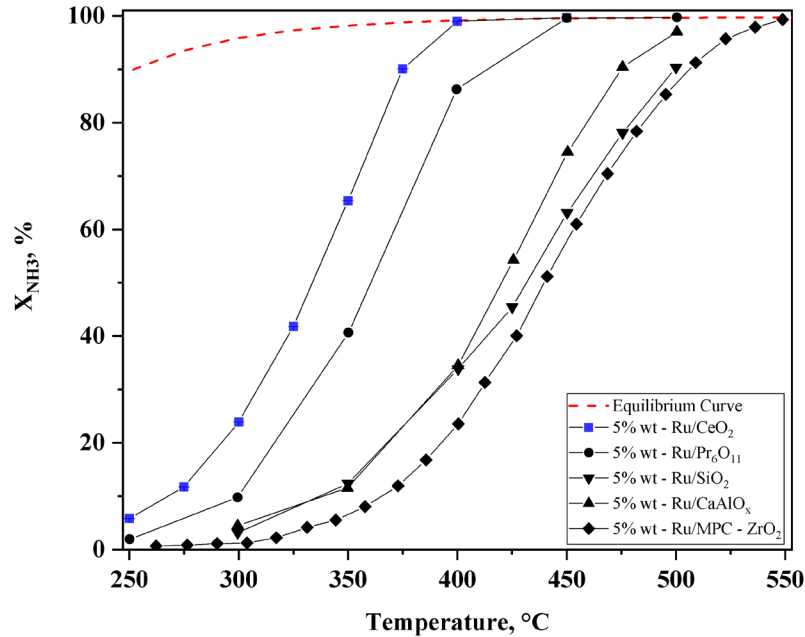
Results

Activity tests: Cs/Ru ratio investigation



Results

Literature comparison

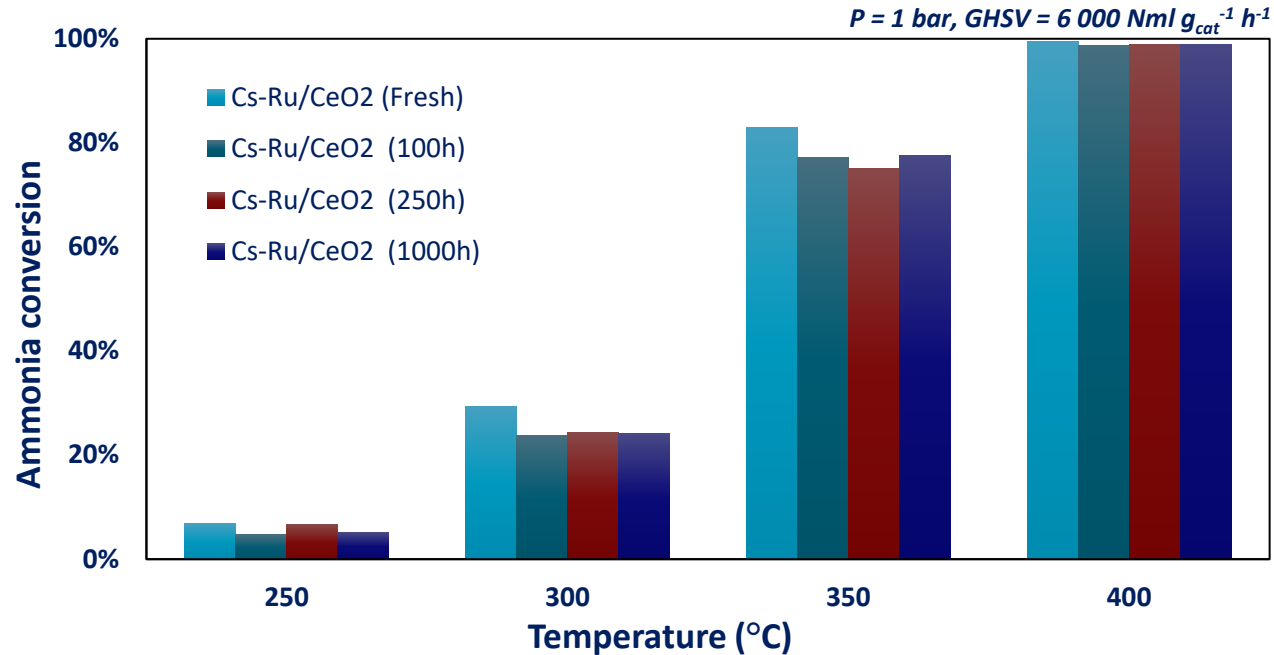


This superior performance can be primarily attributed to several factors:

- *The synthesis technique used*
- *The optimization of ruthenium loading for the specific support*
- *The synergistic effect between the support and the active phase*

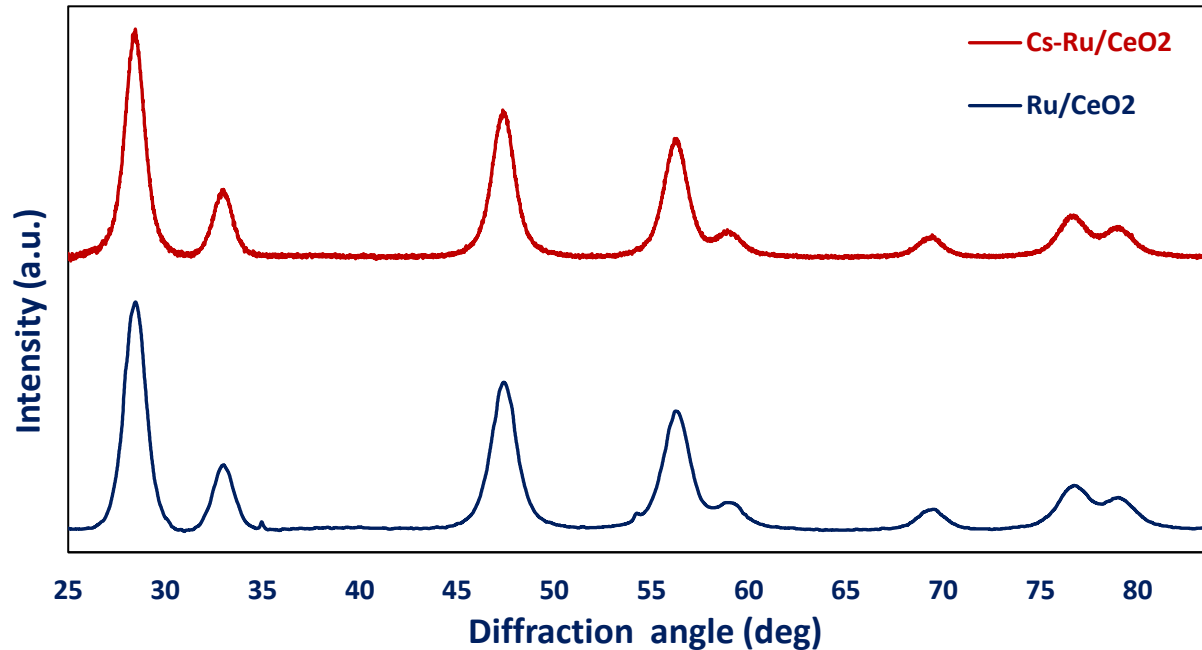
Results

Long term tests employing 2Cs-5Ru/CeO₂



Characterization

X-Ray Diffractometry analysis

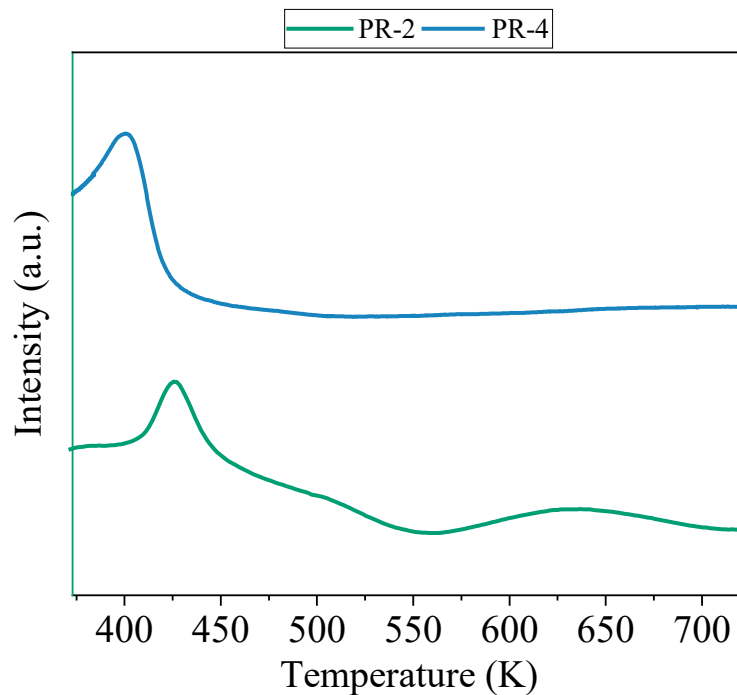


Main peaks' location for cubic lattice of CeO₂: 28.5°, 33.1°, 47.5°, 56.4°, 58.2°, 69.5°, 76.0°, 77.9°

[23] 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)

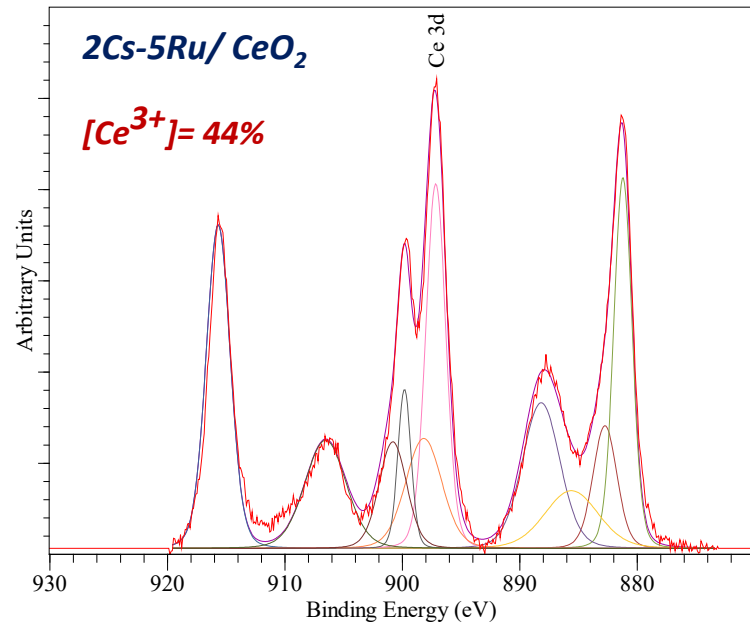
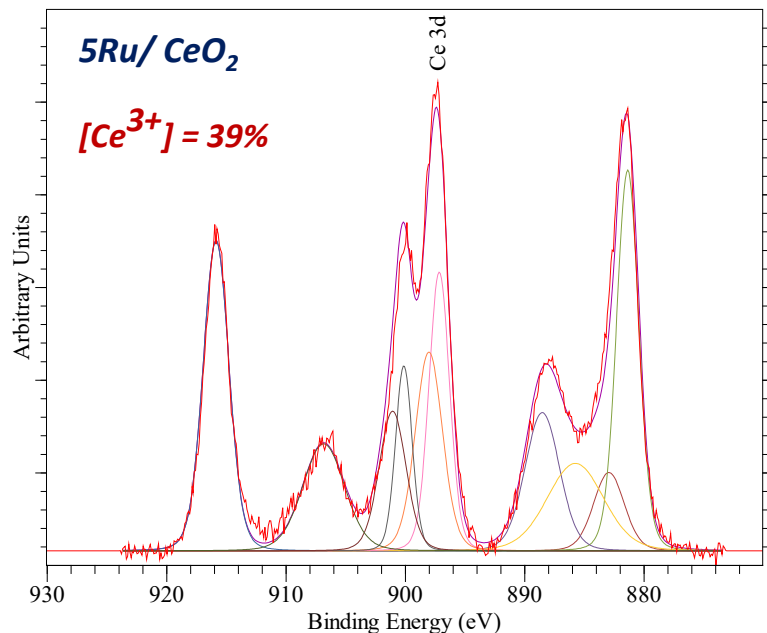
Characterization

H₂ – Temperature Programmed Reduction



Characterization

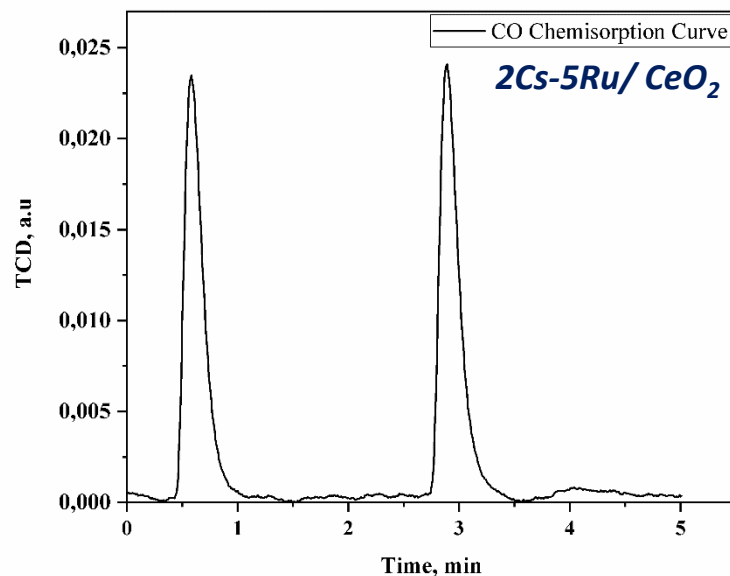
XPS deconvoluted spectra Cerium 3d



[24] 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)

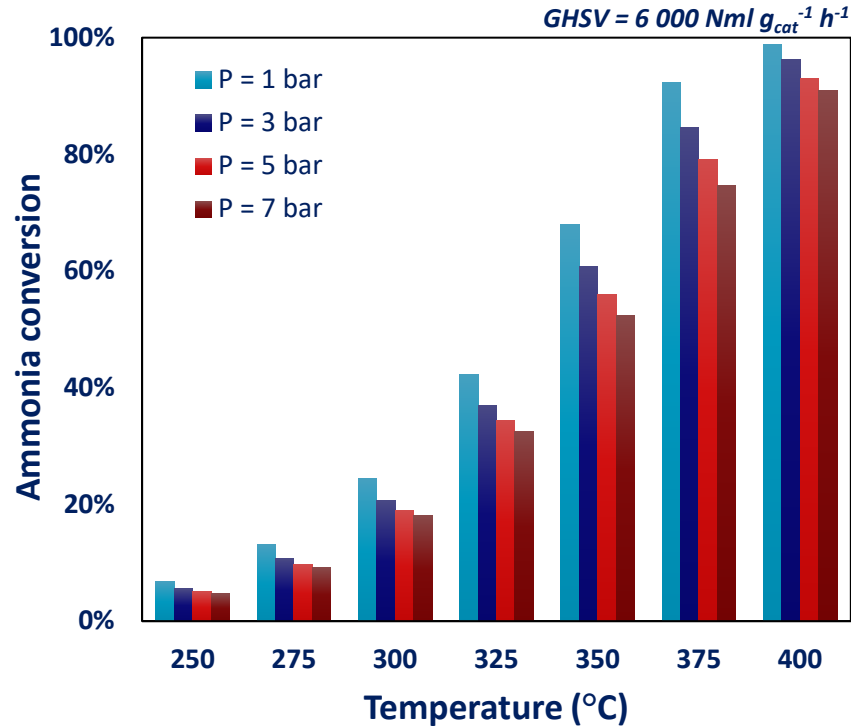
Characterization

CO – Pulse Chemisorption



Results

Pressure influence



Conclusions

- ❖ *Ru-based-CeO₂-supported catalysts were successfully synthesized via PRM.*
- ❖ *The non-promoted catalyst (5Ru/CeO₂) allowed an ammonia conversion reaching the equilibrium already between 375 and 400°C (1 bar, 6000 Nml g_{cat}⁻¹ h⁻¹).*
- ❖ *The addition of cesium (2Cs-5Ru/CeO₂) to the catalytic formulation resulted in an increase of ammonia conversion by 33% (350°C, 1 bar, 6000 Nml g_{cat}⁻¹ h⁻¹).*
- ❖ *The overall conversion decreased less than 1% over 1000 hours of test at 400°C, proving the high stability of the synthesized catalyst over time.*



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Thank you for your attention! Any question?