

Ammonia as hydrogen storage medium

Citation for published version (APA): Anello, G. (2025). *Ammonia as hydrogen storage medium: Development of materials for ammonia synthesis and* decomposition in membrane reactors. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Eindhoven University of Technology.

Document status and date: Published: 05/02/2025

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.

• The final author version and the galley proof are versions of the publication after peer review.

 The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- · Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
 You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Ammonia as hydrogen storage medium: Development of materials for ammonia synthesis and decomposition in membrane reactors

Gaetano Anello

Ammonia as hydrogen storage medium: Development of materials for ammonia synthesis and decomposition in membrane reactors

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof. dr. S. K. Lenaerts, voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op woensdag 5 februari 2025 om 11:00 uur

door

Gaetano Anello

geboren te Maratea, Italië

Dit proefschrift is goedgekeurd door de promotoren en de samenstelling van de promotiecommissie is als volgt:

Voorzitter:	prof. dr. ir. E. Rebrov
1º Promotor: 2º Promotor:	prof. dr. eng. F. Gallucci prof. dr. ir. J. van der Schaaf
Leden:	prof. dr. ir. D. Borello (Sapienza Università di Roma, Italy) prof. dr. G. Manzolini (Politecnico di Milano, Italy) prof. dr. M. Creatore prof. dr. ir. M. van Sint Annaland
Adviseur:	dr. M. Khamphasith (ENGIE Lab Crigen, France)

Het onderzoek of ontwerp dat in dit proefschrift wordt beschreven is uitgevoerd in overeenstemming met de TU/e Gedragscode Wetenschapsbeoefening.

The research described in this dissertation was conducted in the Inorganic Membranes and Membrane Reactors Group, a division of Sustainable Process Engineering, within the Chemical Engineering and Chemistry Department of Eindhoven University of Technology, The Netherlands. This work was funded through the Top Consortia for Knowledge and Innovation (TKI), ChemistryNL, in collaboration with ENGIE (Project No. CHEMIE.PGT.2021.004). Additionally, parts of this research were conducted as part of the European projects *Ammonia and MOF Based Hydrogen storagE for euRope* (AMBHER, Grant agreement No. 101058565), *AmmoNia baseD membRane rEActor for green Hydrogen production* (ANDREAH, Grant agreement No. 101112118) and Advanced POwer conversion technoLogies based on Onboard ammonia cacking through novel membrane reactors (APOLO, Grant agreement No. 101138466).

© Gaetano Anello, Eindhoven, The Netherlands, 2025.

All rights reserved. No part of this material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording, or by any information storage and retrieval system, without prior permission of the author.

Cover by Gaetano Anello.

Printed by ProefschriftMaken.

A catalogue record is available from the Eindhoven University of Technology Library. ISBN: 978-90-386-6262-6.

Contents

Summary	xi
Nomenclature	xv
Table of acronyms and abbreviations	xv
Table of superscripts	xv
Table of symbols and units	xvi

Chapter 1

Gener	al intr	oduction	1
1.1	Hydrogen as flagship of the energy transition2		2
1.2	Hydro	gen storage via ammonia	4
	1.2.1	Ammonia synthesis	5
	1.2.2	Ammonia decomposition	7
1.3	Memb	rane reactor technology	8
1.4	Frame	work of the dissertation1	2
1.5	Refere	nces1	5

opmer	nt of carbon membranes for ammonia decomposition	.21
ct		.22
Introduction		
Experi	mental	.24
2.2.1	Membrane preparation	24
2.2.2	Membrane characterization	26
2.2.3	Experimental setup	26
2.2.4	Experimental method	27
Result	s and discussion	.29
Conclusions		.38
References		
	opmer Introd Experi 2.2.1 2.2.2 2.2.3 2.2.4 Result Conclu Refere	opment of carbon membranes for ammonia decomposition Introduction Experimental 2.2.1 Membrane preparation

Enhai	nced a	mmonia decomposition in a structured membrane reactor	43
Abstra	ict		44
3.1	Introduction4		
3.2	Experimental		
	3.2.1	Structured catalyst preparation	46
	3.2.2	Structured catalyst characterization	48
	3.2.3	Palladium-based membrane preparation and experimental setup	49
3.3	Result	s and discussion	51
	3.3.1	Structured catalyst characterization	51
	3.3.2	Structured membrane reactor performance evaluation	55
3.4	Conclu	isions	62
3.5	References		

Devel	opmer	nt of Ru-based catalysts for low-temperature NH3 decomposition	67
Abstra	ict		68
4.1	Introduction		69
4.2	Experi	mental	71
	4.1.1	Materials	71
	4.1.2	Catalysts preparation	71
	4.1.3	Catalysts characterization	72
	4.1.4	Activity tests	74
4.3	Result	s and discussion	76
	4.3.1	Optimization of ruthenium loading	80
	4.3.2	Optimization of cesium/ruthenium mass ratio	83
4.4	Conclu	isions	92
4.5	Refere	nces	93

Low-t	temperature NH $_3$ decomposition in a packed bed membrane reactor	99
Abstra	nct	100
5.1	Introduction	101
5.2	Experimental	102
5.3	Results and discussion	106
5.4	Conclusions	111
5.5	References	112

Mode	eling a	nd simulation of NH $_3$ synthesis in a packed bed membrane reactor	115
Abstra	act		116
6.1	Intro	duction	117
6.2	Meth	odology	118
	6.2.1	Membrane reactor configuration	
	6.2.2	Reaction scheme and kinetics	119
6.3	Basis	and assumptions for the reactor model	120
6.4	Math	ematical model validation	123
	6.4.1	Validation of the packed bed reactor	123
	6.4.2	Validation of the permeation module	125
6.5	Study	of the membrane performance	127
	6.5.1	Ideal membrane case study	128
	6.5.2	Real membrane case study	
6.6	Opera	ational condition study: sweep gas-to-feed ratio vs. ΔP	136
6.7	Heat	management study: effect of temperature	140
6.8	On th	e effect of feed ratio	143
6.9	Packed bed reactor vs. packed bed membrane reactor		146
6.10	Conc	usions	149
6.11	Refer	ences	150

Devel	opmer	nt of ruthenium-based catalysts for ammonia synthesis	153
Abstra	ict		154
7.1	Introd	uction	155
7.2	Experi	imental	157
	7.2.1	Materials	157
	7.2.2	Catalysts preparation	157
	7.2.3	Catalysts characterization	158
	7.2.4	Catalytic tests	159
7.3	Result	s and discussion	162
	7.3.1	Characterizations	162
	7.3.2	Catalytic tests	164
7.4	Conclu	isions	174
7.5	Refere	ences	175

Concl	usions	and Outlook	
8.1	Conclu	isions	
	8.1.1	Ammonia decomposition	
	8.1.2	Ammonia synthesis	
8.2	Outloo	ok & recommendations	
8.3	Refere	ences	

Appendices and Supplementary Material	
Appendix A	
Experimental setup	
Appendix B	
Membrane characterization: perm-porometry setup	
Appendix C	
Modeling of a packed bed membrane reactor: Supplementary material	
Appendix D	
Polyol reduction method	
References	
Research Output	
Research Output	
Research Output Journal articles Journal articles out of the scope of this dissertation	
Research Output Journal articles Journal articles out of the scope of this dissertation Conference contributions: Oral presentations	
Research Output Journal articles Journal articles out of the scope of this dissertation Conference contributions: Oral presentations Conference contributions: Poster presentations	
Research Output Journal articles Journal articles out of the scope of this dissertation Conference contributions: Oral presentations Conference contributions: Poster presentations Other contributions.	211 211 211 211 212 213 213 214
Research Output Journal articles Journal articles out of the scope of this dissertation Conference contributions: Oral presentations Conference contributions: Poster presentations Other contributions Acknowledgements	211 211 211 211 212 213 213 214 215

Summary

In the pursuit of more sustainable energy solutions, hydrogen is considered the ultimate clean energy carrier, as it can be produced from water electrolysis using renewable energy, it is a carbon-free energy source and only water is emitted as byproduct from its combustion. However, the transportation and storage of hydrogen pose challenges due to its low volumetric energy density and to the safety risks associated with its handling. Among the various possible hydrogen storage solutions, one of the most interesting is the storage in chemical bonds, as in methanol, methane, and particularly ammonia. This route is attractive because all the processes involved in ammonia production, storage and distribution are already fully operational on a large scale. Furthermore, ammonia can be easily stored in liquid form under milder conditions, thereby providing a higher hydrogen density, and finally ammonia conversion to hydrogen (or ammonia combustion to power) does not produce direct carbon dioxide emissions.

Two key chemical processes are required to implement ammonia as a hydrogen storage medium: ammonia synthesis and ammonia decomposition. These reactions are followed by the critical steps of separating and purifying the resulting product streams to ensure the desired quality and purity. Therefore, this work proposes a process intensification strategy through membrane reactor technology, employing novel Rubased catalysts and inorganic membranes. This approach allows, in one case, to decompose ammonia, while simultaneously removing hydrogen, and, in the other case, to synthesize and separate ammonia into a single unit. The membrane reactor configuration can potentially enable higher conversions at less severe operating conditions, according to Le Châtelier's principle, resulting in higher efficiencies and lower costs.

Firstly, in **Chapter 1**, a brief literature review on hydrogen storage, ammonia synthesis and ammonia decomposition is discussed.

Afterward, in **Chapter 2** the development of carbon membranes for hydrogen separation from ammonia and nitrogen within ammonia decomposition was studied. The effect of the membrane coupling was investigated through an experimental study of the operating parameters. More specifically, operating at 5 bar and temperatures ranging from 450 to 500 °C, ammonia conversion exceeding 90% was achieved, with conversion approaching thermodynamic equilibrium at temperatures above 475 °C.

In **Chapter 3**, the combination of a structured catalyst and a Pd-based membrane for ammonia decomposition was evaluated. The structured catalyst is based on a commercial silicon carbide 40 PPI open-cell foam. The catalyst ($3 \text{ wt}\% \text{ Ru/CeO}_2$) was coated by in situ-solution combustion deposition method with sequential cycles to reach the desired catalyst loading (0.31 g cm^{-3}). Several techniques were employed to characterize the sample, namely TEM, SEM, XRD, TPR analysis and adhesion test. A double-skinned Pd-based membrane was prepared by depositing a selective layer by electroless plating onto porous asymmetric α -Al₂O₃ support. The results demonstrated a successful integration of structured catalyst and membrane, with the conversion surpassing the thermodynamic limits.

In **Chapter 4**, ruthenium-based catalysts were synthesized via polyol reduction method using cerium oxide as support and cesium as promoter. After structural and chemical characterizations, through XRD, N₂-physisorption, H₂-TPR, H₂-TPD, CO₂-TPD and XPS, the catalysts were tested for ammonia decomposition in the range of temperatures 250 - 450 °C, and pressures 1 - 7 bar. Ruthenium content and cesium content in the catalytic formulation were optimized. The catalyst containing 5 wt% ruthenium and 2 wt% cesium demonstrated the highest activity, approaching equilibrium conversion within the temperature range of 375 - 400 °C.

The integration of the newly catalyst developed in Chapter 4 with a palladium-based membrane was investigated in **Chapter 5.** The results showed an ammonia conversion exceeding 99% at 375 °C and 6 bar. Moreover, an ammonia conversion of approximately 99.7% was obtained at 425 °C and 4 bar, with hydrogen recovery of 86.5% and hydrogen purity exceeding 99.99%. This high single-pass efficiency suggests that pure hydrogen production from ammonia can be energy-efficient without requiring extremely high temperatures, reducing operational costs.

In **Chapter 6**, a packed bed membrane reactor model for ammonia synthesis was developed, employing a ruthenium-based catalyst. The in-situ removal of ammonia is modeled by considering mass, momentum, and energy balances in the retentate and permeate side, including sweep gas to enhance separation efficiency and the heat management. The results of this study show that an ammonia permeance greater than $1\cdot10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹ and an ammonia-to-hydrogen selectivity of 50 are required to achieve significant benefits from membrane integration. Finally, investigating the feed ratio in the permeate side revealed that a hydrogen-to-nitrogen feed ratio of 1.5 and sweep gas-to-feed ratio of 6 lead to optimal reactor performance. The results suggest that membrane reactors offer a promising route for improving the efficiency of the

ammonia synthesis process, reducing overall energy consumption and operational costs.

In **Chapter 7**, ruthenium-based catalysts were synthesized using the polyol reduction method, with various metal oxides as supports and cesium as a promoter. The resulting catalysts were characterized by several characterization techniques and evaluated for ammonia synthesis over a temperature range of 275 to 400 °C and pressures between 10 and 50 bar. The catalysts demonstrated an ammonia production rate approximately four times higher than similar catalytic formulations reported in the literature under the same conditions. The Cs-Ru/CeO₂ catalyst, with cesium loading about 1 wt% and a ruthenium loading about 5 wt%, showed the best performance, achieving an ammonia production of nearly 73 mmol h^{-1} g_{cat}⁻¹ at 400 °C and 50 bar.

The dissertation is concluded with **Chapter 8** where the outcomes of the aforementioned chapters are summarized and connected to an outlook on membrane reactor technologies for ammonia as hydrogen carrier.

Nomenclature

Table of acronyms and abbreviations

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joiner-Halenda
EDX	Energy-Dispersive X-ray spectroscopy
FEG	Field Emission Gun
GC	Gas Chromatograph
ICP	Inductively Coupled Plasma
IS-SCD	In Situ – Solution Combustion Deposition
OCF	Open-Cell Foam
OES	Optical Emission Spectrometry
PBMR	Packed Bed Membrane Reactor
PBR	Packed Bed Reactor
PRM	Polyol reduction Method
SEM	Scanning Electron Microscopy
SMR	Structured Membrane Reactor
SR	Structured Reactor
SSA	Specific Surface Area
TCD	Thermal Conductivity Detector
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Table of superscripts

R	Retentate
Р	Permeate
i	Inner/Internal
0	Outer/Outside

Table of symbols and units

WHSV	Weight hourly space velocity	$(Nml h^{-1} g_{cat}^{-1})$
GHSV	Gas hourly space velocity	(h^{-1})
Τ	Temperature	(°C)
Р	Pressure	(bar)
R	Universal gas constant	$(J \text{ mol}^{-1} \text{ K}^{-1})$
L	Reactor length	(m)
D_r^i	Inner reactor diameter	(m)
D_m^i	Inner membrane diameter	(m)
D_m^o	Outer membrane diameter	(m)
Α	Internal reactor cross section	(m ²)
A_m^i	Internal membrane cross section	(m ²)
u	Space velocity based on the empty reactor cross-section	(m s ⁻¹)
ε	Bed porosity	$(m_v^3 m_r^{-3})$
$ ho_c$	Catalyst density	$(kg_{cat} m_{cat}^{-3})$
d_p	Catalyst particle diameter	(m)
ϑ_i	Stoichiometric coefficient of the species <i>i</i>	(-)
ν_i	Stoichiometric number of the species <i>i</i>	(-)
μ_i	Viscosity of the species <i>i</i>	(Pa s)
μ_{mix}	Viscosity of the gas mixture	(Pa s)
ρ_{mix}	Density of the gas mixture	$(mol m^{-3})$
M _i	Molar mass of species <i>i</i>	$(g mol^{-1})$
M _{mix}	Molar mass of the gaseous mixture	$(g \text{ mol}^{-1})$
q	Hydrogen-to-nitrogen molar ratio	$(\operatorname{mol}_{H_2} \operatorname{mol}_{N_2}^{-1})$
$\lambda(q)$	Stoichiometric parameter	(-)
r	Reaction rate	$(mol h^{-1} l_{cat}^{-1})$
ΔH_{298K}	Heat of reaction at 298 K	(kJ mol ⁻¹)
η	Fractional conversion	(-)
τ	Time factor	$(h l_{cat} mol^{-1})$
F _i	Molar flow rate of the species <i>i</i>	$(mol h^{-1})$
F	Molar flow rate	$(mol h^{-1})$
G	Mass flux	$(\text{kg s}^{-1} \text{ m}^{-2})$
<i>a</i> _{<i>i</i>}	Activity coefficient of the species <i>i</i>	(atm)
Υ _i	Fugacity coefficient of the species <i>i</i>	(-)
P _i	Partial pressure of the species <i>i</i>	(atm)

E _a	Activation energy	(J mol ⁻¹ K ⁻¹)
k ₀	Pre-exponential factor	$(\text{mmol } \text{h}^{-1} \text{g}_{\text{cat}}^{-1})$
<i>y</i> _i	Concentration in gas phase of the species <i>i</i>	(-)
K_{H_2}	Adsorption equilibrium constant of hydrogen	$(kcal mol^{-1})$
K_{NH_3}	Adsorption equilibrium constant of ammonia	(kcal mol ⁻¹)
U	Global heat transfer coefficient	$(W m^{-2} K^{-1})$
h	Heat transfer coefficient	$(W m^{-2} K^{-1})$
ΔH_T	Heat of reaction at temperature T	(J mol ⁻¹)
ΔH_{298K}	Heat of reaction at 298 K	(kJ mol ⁻¹)
$c_{p,i}$	Specific heat capacity at constant pressure of the species <i>i</i>	$(J \text{ mol}^{-1} \text{ K}^{-1})$
Δc_p	Change in specific heat capacity at constant pressure	$(J \text{ mol}^{-1} \text{ K}^{-1})$
λ_i	Thermal conductivity of the species <i>i</i>	$(W m^{-1} K^{-1})$
λ_{mix}	Thermal conductivity of the gas mixture	$(W m^{-1} K^{-1})$
Re	Reynolds number	(-)
Pr	Prandtl number	(-)
Nu	Nusselt number	(-)
ΔΡ	Pressure difference across the membrane	(bar)
ΔP_{Ergun}	Pressure difference along the reactor	(bar)
SF	Sweep gas-to-feed ratio	(-)
Ji	Permeation molar flux of the species <i>i</i>	$(mol s^{-1} m^{-2})$
\mathcal{P}_i	Permeance of the species <i>i</i>	(mol s ⁻¹ m ⁻² Pa ⁻¹)
$S_{i/j}$	Selectivity for the species <i>i</i> over the species <i>j</i>	(-)
r_p	Membrane pore radius	(m)
$F_{i,tm}^R$	Retentate molar flow crossing the membrane of the species <i>i</i>	$(mol s^{-1})$
$F_{i,bp}^{P}$	Permeate molar flow going back to retentate of the species <i>i</i>	(mol s ⁻¹)

General introduction

1.1 Hydrogen as flagship of the energy transition

During the last century, fossil fuels have been a key driver of human development, influencing nearly every aspect of modern society. However, the utilization of carbonbased fuels led to a dramatic increase in greenhouse gas emissions, namely carbon dioxide (CO₂) and methane (CH₄), which are major contributors to global warming and air pollution [1]. In 2022, greenhouse gas emissions increased by 1%, hitting a new devastating record of 41.3 Gt of carbon dioxide equivalent (GtCO₂-eq) [2]. As a consequence, to meet the growing energy needs of the global population while reducing the human environmental impact, a shift towards new approaches and energy sources is needed, in accordance with international agreements, to drive the current economy towards more sustainable choices.

In the pursuit of more sustainable energy solutions, hydrogen (H₂) is considered the ultimate clean energy carrier, as only water is emitted from its conversion to power. Hydrogen is commonly categorized by a color code, which reflects the processes and the hydrogen sources employed in its production, as illustrated in Figure 1.1. Particularly relevant to the energy transition is "green hydrogen", which is produced using renewable energy sources. Green hydrogen can be obtained from water through electrolysis process, which can be directly powered by renewable electricity from wind or photovoltaic systems [3,4]. Once produced, hydrogen can be utilized to generate power (e.g., fuel cells, power systems), or it can be directly burnt in internal combustion engines, reducing drastically the greenhouse gas emissions [5]. Furthermore, the gravimetric density of hydrogen is approximately seven times higher than that of conventional fossil fuels [6,7]. Recently, the share of green hydrogen could achieve cost competitiveness with "gray hydrogen", produced from fossil fuels, by 2050 [8].



Figure 1.1. H₂ color-based classification, reflecting production and processes sources [9].

To attain cost parity, improvements are needed in technical efficiency, reduction of equipment production costs and material prices, and scaling up of manufacturing processes. Progress in these areas has been underway for some time [10]. Alkaline water electrolysis for hydrogen production has reached a level of maturity, with commercially available installations operating at megawatt scale. Additionally, technologies utilizing proton exchange membrane (PEM) and solid oxide (SO) electrolyzers have also made significant advancements. A comparative analysis of the operating characteristics of these systems is provided in previous work [11].

Still, the use of hydrogen as an energy carrier is strongly hindered by the problems connected with the transport and storage of this gas, due to its highly flammable nature and its low ignition energy, even at atmospheric conditions [12]. Furthermore, gaseous hydrogen occupies a significant volume and has a low energy density, making its storage in large quantities complex [13–15]. Consequently, expensive infrastructures are needed for hydrogen transportation and storage, particularly considering that hydrogen requires stringent safety measures. Additionally, it tends to diffuse through materials due to its high diffusivity, causing losses over time and necessitating careful attention in the selection of storage materials. All these factors contribute to making hydrogen storage one of the primary challenges in implementing a hydrogen-based energy system for energy transition [16,17].



Figure 1.2. Hydrogen storage solutions classification.

Thus, physical-based storage methods have limitations in terms of cost, efficiency, and safety [18]. Therefore, to establish a feasible hydrogen fuel system, these critical issues must be assessed and solved. During the last decades, alternative storage solutions are being explored and developed. These are material- and chemical-based storage solutions, which include metal hydrides (M_xH_y), methanol (CH₃OH) and ammonia (NH₃) [12,19,20]. More specifically, among all the available options depicted in Figure 1.2, ammonia can be considered as one of the most promising solutions since the infrastructure involved in its production, storage and distribution are already fully operating. Additionally, ammonia can be easily stored as a liquid at relatively low

pressures and moderate temperatures (-33 °C, at atmospheric pressure), which makes it easier to handle compared to hydrogen gas. Furthermore, its liquid form provides a high hydrogen density at higher temperature (liquid ammonia at -33.5 °C, 121 kg_{H2} m⁻³ while liquid hydrogen at -252.9 °C, 70 kg_{H2} m⁻³) [21]. In particular, recent cost estimations evaluate that storing hydrogen in the form of ammonia for 182 days is approximately 25 times cheaper than storing hydrogen [22,23].

In evaluating the safety concerns related to different energy carriers, it is essential to consider both their flammability and toxicity, as well as their potential for explosion. Ammonia, while not flammable in air, has a significant explosion limit range (16 - 25%), furthermore liquid ammonia has much higher apparent toxicity than gasoline or methanol. This means that even at relatively low concentrations, ammonia can pose a severe health risk [24]. Therefore, significant safety issues are associated with the handling of ammonia in the transportation sector. However, a recent EU-funded report concluded that "the use of ammonia as a transport fuel would not pose more risks than those associated with currently used fuels" [25].

1.2 Hydrogen storage via ammonia

Using ammonia as a hydrogen carrier presents several challenges that must be addressed to make it a viable option for hydrogen storage and transport. A commonly adopted approach involves the ammonia value chain illustrated in Figure 1.3.



Figure 1.3. Ammonia as chemical for hydrogen storage (adapted from [26]).

The process involves multiple stages, each characterized by distinct energy requirements. Firstly, hydrogen obtained from renewable sources is combined with atmospheric nitrogen through the Haber-Bosch process [27,28]. The production of ammonia requires high temperatures and pressures to catalyze the chemical reaction, thus the energy demand of this step is extremely high. Transitioning to renewable energy sources for ammonia production remains an ongoing challenge. Secondly, optimizing the hydrogen release step is critical. Extracting hydrogen from ammonia requires significant energy input. Once hydrogen is obtained, it can be used as an energy source in various processes, including electricity production through fuel cells or as fuel [27–29]. However, to effectively use ammonia as a hydrogen storage strategy, it is crucial to address the associated challenges and issues related to both its synthesis and decomposition processes.

1.2.1 Ammonia synthesis

Nowadays, after about a century of operation, the main path to produce ammonia is still via Haber-Bosch process, in which nitrogen (N₂) and hydrogen (H₂) are combined in the presence of an iron-based catalyst. The reaction is exothermic and occurs with a decrease in volume, therefore it is favored at low temperatures and high pressures. However, the process requires temperatures in the range of 400 – 500 °C and pressures in the range of 50 – 300 bar to achieve efficient nitrogen fixation [30]. These conditions favor a relatively high kinetic rate at the expense of low conversions (below 20%) due to the thermodynamic limitations [31]. As a result, the process is energy-intensive and consumes approximately 1 - 2% of the world's total energy production, emitting more than 300 million metric tons of CO₂ yearly [32].

Furthermore, these conditions pose engineering challenges related to heat and pressure management. The choice of operational conditions is a compromise between reaction kinetics, yield, and energy efficiency. Higher temperatures accelerate the reaction but require more energy to maintain operational conditions. High pressures are necessary to shift the equilibrium towards ammonia formation but demand more robust and costly equipment. Thus, industrially, since further increase in temperature is unfeasible due to the reverse reaction occurring (ammonia decomposition) and possible catalyst deactivation, conventional ammonia synthesis is run in multistage adiabatic packed bed reactors with interstage water cooling over an iron-based catalyst [33]. These catalysts have been fully developed and therefore in the last years there were not significant successes towards future advancements. In this overview,

ruthenium (Ru) catalyst emerged as second-generation catalyst for NH_3 synthesis, due to the higher activity at lower temperatures and pressures in ammonia synthesis than the conventional catalyst [34].

The interest in Ru-based materials arises from several potential advantages offered. Firstly, Ru-based catalysts have shown higher catalytic activity for nitrogen fixation reaction at milder operating conditions compared to the commercial Fe-based ones [35]. This can have significant energy-saving implications as it reduces the energy needed to heat up the reaction chamber. On the other hand, Ru-based catalysts show two main drawbacks: high costs and potential hydrogen poisoning. Ruthenium is present at a concentration of approximately 1 μ g kg⁻¹ in Earth's crust, which results in high capital costs and then limits further applications [36]. Furthermore, the mining of ruthenium is sensitive to wars and human conflicts, as geopolitical instability can disrupt supply chains and impact production. Such events can lead to fluctuations in availability, affecting prices and access to this critical resource. Figure 1.4 shows the significant fluctuations in the price of this precious metal. Moreover, at high hydrogen partial pressure, excess of hydrogen atoms covers ruthenium active sites, reducing the efficient dissociative adsorption of N₂ on the catalyst surface [37].



Figure 1.4. Average ruthenium price worldwide from [38].

Thus, to overcome these drawbacks and increase the performance of the catalyst for ammonia synthesis, a possible approach is the maximization of the catalytic activity of ruthenium through the maximal exposure of the active sites. Reducing the size to atomic clusters will greatly increase the surface area, which in turn increases the level of catalytic activity, leading to the efficient exploitation of ruthenium resources. In case of Ru-based catalysts, in particular, the activity is highly dependent on the particle size, which can influence the presence of the desirable B5 active sites. Dahl et al. have studied the sticking probability of H_2 on ruthenium. It has been shown that the active site for N_2 dissociation is the so-called B5 site, consisting of five ruthenium atoms: two at step edges and three at the lower terraces [39]. Moreover, according to several studies ruthenium clusters with a diameter in the range 1.8 - 3.5 nm are believed to bear a significant amount of these active sites [40].

Synthesis method strongly affects the properties of the resulting produced material and influences the active phase cluster diameter, determining the chemical activity of the entire system and the final physical properties of the prepared catalyst. Javaid et al. addressed the effect of the preparation method on ruthenium-based catalyst for ammonia synthesis [41]. The results showed that the catalysts prepared by different methods have different physical properties, that, in turn, affect the ammonia synthesis activity [42]. For instance, wetness impregnation usually yields relatively bigger clusters with a large size distribution. Due to the increase in cluster size, there are fewer B5 sites.

1.2.2 <u>Ammonia decomposition</u>

The effective use of ammonia as a hydrogen storage medium requires its decomposition via an endothermic equilibrium reaction, followed by the separation and purification of the resulting hydrogen. Ammonia decomposition reaction is a reversible process, increasing the overall gas volume. Thus, elevated temperatures and low pressures positively affect the ammonia conversion. Furthermore, a thermodynamic study of the ammonia decomposition reaction revealed that an almost complete NH₃ conversion is achievable at 420 °C and atmospheric pressure [43]. Still, NH₃ decomposition cannot be conducted at low temperatures due to kinetic limitations. Therefore, this reaction is typically conducted in a temperature range of 500 - 600 °C and a pressure range of 1 - 3 bar, in the presence of a suitable catalyst.

So far, several active phases were explored, such as nickel, cobalt and ruthenium [44]. Among all, ruthenium-based catalysts show high activity at relatively low temperatures and, therefore, they are widely investigated. The downside of employing ruthenium as active phase is connected with the extremely high cost of this metal and limited availability [45]. Therefore, it would be beneficial to enhance the catalytic activity by

maximizing the exposure of active sites, ensuring low ruthenium loading, while simultaneously guaranteeing high activity and high stability.

It is widely acknowledged in the open literature that ruthenium nanoparticles smaller than 8 nm exhibit optimal catalytic activity for hydrogen production via ammonia decomposition [46]. This reaction is structure-sensitive, with several studies pointing out the significance of B5-type sites in the activity of Ru-based catalysts for ammonia decomposition, similarly to their role in the ammonia synthesis reaction [47]. By controlling the size of ruthenium clusters, it is possible to maximize the presence of active B5 sites, enhancing the efficiency of ammonia decomposition while ensuring the maximum dispersion of expensive metal [48].

1.3 Membrane reactor technology

Being ammonia and hydrogen the target reaction products of ammonia synthesis and decomposition, respectively, a possible strategy to improve significantly the reaction rate is shifting the equilibrium via in situ removal of the target products from the reaction chamber.

Only few attempts to exceed single-pass equilibrium conversion have been carried so far in the open literature for ammonia synthesis. For instance, Smith et al. proposed an integrated ammonia synthesis and separation employing a ruthenium-based catalyst and manganese chloride on silica as adsorbent [49]. The authors demonstrated the advantages of the proposed synergistic system achieving conversions beyond reaction equilibrium [31]. Parallelly, the use of membrane reactors is considered a promising solution for shifting the equilibrium in thermodynamically limited catalytic reactions, either through the selective removal of a product or a by-product. This approach has been explored, for instance, in dimethyl ether synthesis [50,51] and water-gas shift reaction [52,53]. While the cited studies highlight the advantages offered by the membrane reactor configuration (i.e., enhanced conversion, lower energy requirements for a desired throughput), still few studies discuss the potential of this technology for ammonia synthesis.

On the other hand, membrane reactor technology has recently been proved as a promising solution for hydrogen recovery from ammonia, allowing simultaneous ammonia decomposition into hydrogen and nitrogen along with high purity hydrogen separation, all within a single device [54,55]. Moreover, the membrane reactor

technology was proved to enable a lower temperature conversion in accordance with the Le Châtelier's principle, as the selective separation of one of the products through the membrane wall shifts the equilibrium allowing the system to overcome the thermodynamic constraints.

In membrane reactors, various types of membranes can be utilized to enhance chemical reactions and separation processes simultaneously, offering significant advantages in terms of efficiency and selectivity. Among them, carbon membranes (CMs) and palladium (Pd) membranes show promising features. Carbon membranes show exceptional properties, including high thermal and chemical stability, mechanical strength, and selective permeability [56]. Furthermore, the performance of carbon membranes can be tailored by adjusting their porosity and surface chemistry, making them versatile for different industrial and environmental applications. Additionally, their resilience at high temperatures and harsh chemical environments makes them suitable for demanding processes, offering a promising solution for efficient and sustainable separation technologies [57,58]. The selectivity of carbon membranes can be relatively low compared to other membranes, such as palladium-based membranes, primarily due to their broad pore size distribution and limited control over pore size during synthesis. Improving the selectivity involves several strategies focused on optimizing the membrane's structure, composition, and processing conditions. For instance, the carbonization process plays a crucial role in determining the membrane's properties. By controlling the carbonization temperature, heating rate, and the atmosphere in which the process occurs, it is possible to tailor the pore structure [59]. Turing the features of the polymeric precursor and the presence of additives has a significant impact on the features of the final membrane [56,60].

On the other hand, palladium-based membranes are highly specialized materials for hydrogen separation and purification. The unique properties of Pd-based membranes arise from their ability to absorb hydrogen into their lattice structure and then release it on the other side, a process known as "solution-diffusion." This feature makes them particularly valuable in applications such as hydrogen recovery, fuel cell technology, and hydrogen purification. Additionally, palladium membranes can operate at high temperatures and aggressive chemical environments, further enhancing their utility in industrial processes [61,62].

In Figure 1.5, images of a carbon-based membrane and a palladium-based membrane fabricated and tested within this study are shown.



Figure 1.5. Carbon-based membrane (left) and double-skinned Pd-based membrane (right) fabricated and tested in the framework of this dissertation.

While few works in literature have been devoted to the applications of CMs in ammonia processes, the use of Pd-based membranes for selectively separate H₂ has been recently discussed in literature [63–65]. For instance, Israni et al. successfully carried ammonia decomposition in a packed bed membrane reactor using both conventional top-layer and nanopore Pd-membranes. The proposed results demonstrate that the selective removal of H₂ from the retentate side resulted in an increase in NH₃ conversion [66]. Nailwal et al. studied ammonia decomposition under various operating conditions in both single-tube systems. The authors reported an ammonia conversion of 93% at 500 °C and 1 bar in a packed bed membrane reactor , whereas the reported conversion in a conventional packed bed reactor at similar operating conditions is about 80%, demonstrating the beneficial effect of the Pd-based membrane coupling on ammonia conversion [67].

On the downside, palladium-based membranes, while highly efficient for hydrogen separation due to their selectivity and permeability, are extremely expensive, as palladium is a rare metal. Additionally, palladium is prone to embrittlement, especially when exposed to impurities like sulfur or carbon monoxide, which can degrade its performance over time [66]. The membranes are also sensitive to high temperatures and mechanical stress, which can cause cracks or degradation [68]. Therefore, to address the challenges of membranes for hydrogen separation, several solutions are being explored [69]. These innovations aim to make membranes for hydrogen separation more cost-effective, durable, and efficient for large-scale applications.

While material innovation is fundamental to advancing this technology, a complementary techno-economic evaluation could provide critical insights into the practicality of scaling these materials for industrial use. For instance, understanding the costs associated with raw materials, fabrication techniques, and long-term maintenance could guide the selection of synthesis pathways that balance performance with affordability. Additionally, coupling this material-focused research with a techno-economic assessment would help identify potential cost drivers and highlight areas for economic optimization. Equally important is the life cycle analysis, which provides a comprehensive evaluation of the environmental impact associated with membrane reactors. While membrane reactors often promise reduced greenhouse gas emissions during operation compared to traditional technologies, the production of high-performance membranes can involve energy-intensive processes, rare materials, or hazardous by-products that may partially offset these environmental gains.

1.4 Framework of the dissertation

The central theme of this dissertation is to explore the potential of ammonia as an effective hydrogen carrier, with a particular emphasis on advancing material development to maximize reaction efficiency. The proposed investigation encompasses a comprehensive approach, including the synthesis and characterization of catalysts and membranes, optimization of material properties, and evaluation of membrane reactor performance. To facilitate this research, two types of reactors were designed and constructed, complemented by an experimental setup detailed in Appendix A. The developed setup is versatile, designed to handle both ammonia synthesis and decomposition, with capabilities up to 65 bar and 450 °C. It can function as either a membrane reactor or a packed bed reactor, making it adaptable for different process requirements. This flexibility allows for efficient hydrogen production or ammonia synthesis under various conditions, enhancing its utility in applications involving ammonia as a hydrogen carrier. The reactors enable the study of ammonia synthesis and decomposition within both packed bed and packed bed membrane configurations, providing a robust platform for assessing and enhancing the performance of ammoniabased hydrogen storage systems.

This work begins with the development and optimization of carbon membranes, prepared on a tubular porous alumina support, tested for ammonia decomposition in a membrane reaction setup in **Chapter 2**. Operating at 5 bar and temperatures ranging from 450 to 500 °C, NH₃ conversion exceeding 90% was achieved, with conversion approaching thermodynamic equilibrium at temperatures above 475 °C.

In **Chapter 3**, ammonia decomposition into nitrogen and hydrogen was, for the first time, carried in a structured membrane reactor. The performance of the structured catalyst and the effect of hydrogen permeation through a Pd-based membrane were evaluated. The structured catalyst is based on a commercial silicon carbide 40 PPI open-cell Foam. The catalyst (3 wt% Ru/CeO₂) was coated by in situ-solution combustion deposition method with sequential cycles to reach the desired catalyst loading (0.31 g cm⁻³). TEM, SEM, XRD, TPR analysis and adhesion tests were used to characterize the prepared sample. A double-skinned palladium-based membrane has been prepared depositing a selective layer by electroless plating onto porous asymmetric alumina support. The results demonstrated a successful integration of structured catalyst and membrane. The beneficial effects of the proposed structured membrane reactor configuration enabled an increase in conversion up to 29% compared with the structured catalyst system.

In **Chapter 4**, ruthenium-based catalysts with different ruthenium loading were synthesized via polyol reduction method using cerium oxide as support and cesium as promoter. Ruthenium content was varied between 3 and 7 wt% while cesium content was varied between 0 and 10 wt%. The prepared samples were characterized through XRD, N₂-physisorption, H₂-TPR, H₂-TPD, CO₂-TPD and XPS. Then, the catalysts were tested for ammonia decomposition in the range of temperatures 250 - 450 °C and pressures 1 - 7 bar. The catalyst composed of 5 wt% ruthenium and 2 wt% cesium demonstrated the highest activity, approaching the equilibrium curve in the temperature range of 350 - 400 °C range. A high hydrogen production rate (up to 1.9 mol h⁻¹ g_{cat}⁻¹) was achieved at 30 000 Nml h⁻¹ g_{cat}⁻¹, 450 °C and 1 bar. This result marks the highest production rate reported in the literature so far, underscoring the efficacy of the new catalyst under these conditions. Finally, the catalyst synthesis process was successfully scaled up to produce 25 g of material per batch. Each batch was tested to verify that the desired catalyst properties were maintained. This result is particularly interesting in view of possible industrial-scale applications.

In **Chapter 5**, the integration of the newly developed catalyst of Chapter 4 with a palladium-based membrane allowed an ammonia conversion greater than 99.7% at 425 °C and 4 bar, with hydrogen recovery of 86.5% and purity exceeding 99.99%. This high single-pass efficiency, combined with high hydrogen purity, highlights that hydrogen production from ammonia can be carried at moderate temperatures, reducing operational costs.

In **Chapter 6**, a reactor model was developed based on integrating a ruthenium-based catalyst into a membrane reactor. The in-situ removal of ammonia was modeled by considering mass, momentum, energy balances in the retentate and permeate side, including sweep gas to enhance both the separation and the heat management. The results show that the membrane performance is crucial in order to boost hydrogen conversion in an isothermal packed bed membrane reactor. More specifically, an ammonia permeance greater than $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹ and a selectivity for ammonia over hydrogen equal to 50 are required to ensure significant benefits from the membrane addition, on the other hand selectivity for ammonia over nitrogen deeply influences both ammonia purity and ammonia recovery. This leads to a trade-off value of approximately one hundred. In conclusion, the analysis of the feed ratio on the permeate side demonstrated that a hydrogen-to-nitrogen feed ratio of 1.5, coupled with a sweep gas-to-feed ratio of 6, resulted in optimal hydrogen conversion, along with improved ammonia purity and recovery within the first half of the reactor length. These results underscore the potential of membrane reactors as an effective strategy for

enhancing the ammonia synthesis process. By integrating membrane technology, it is possible to significantly improve reaction efficiency, which can lead to lower energy consumption and reduced operational costs.

In **Chapter 7**, ruthenium-based catalysts were synthesized using the polyol reduction method, with various metal oxides as supports and cesium as a promoter. The resulting catalysts were characterized by XRD, ICP-OES, nitrogen physisorption, and XPS. These catalysts were evaluated for ammonia synthesis over a temperature range of 275 to 400 °C and pressures between 10 and 50 bar. The catalysts demonstrated an ammonia production rate approximately four times higher than similar catalytic formulations reported in the literature under the same conditions. The Cs-Ru/CeO₂ catalyst, with cesium loading about1 wt% and a ruthenium loading about 5 wt%, showed the best performance, achieving an ammonia production of nearly 73 mmol h⁻¹ g_{cat}⁻¹ at 400 °C and 50 bar. XPS analysis revealed an increased Ce³⁺/Ce⁴⁺ ratio, which enhanced the number of oxygen vacancies and facilitated the dissociative adsorption of nitrogen, a key step in the ammonia synthesis reaction.

The dissertation concludes with **Chapter 8**, which summarizes the outcomes of the aforementioned chapters and provides an outlook on the future of membrane reactor technologies for ammonia as a hydrogen carrier.

1.5 References

- 1. Wan, Z.; Tao, Y.; Shao, J.; Zhang, Y.; You, H. Ammonia as an Effective Hydrogen Carrier and a Clean Fuel for Solid Oxide Fuel Cells. *Energy Convers Manag* **2021**, *228*, 113729, doi:10.1016/j.enconman.2020.113729.
- 2. CO2 Emissions in 2022. CO2 Emissions in 2022 2023, doi:10.1787/12ad1e1a-en.
- 3. Tarhan, C.; Çil, M.A. A Study on Hydrogen, the Clean Energy of the Future: Hydrogen Storage Methods. *J Energy Storage* **2021**, *40*, 102676, doi:10.1016/j.est.2021.102676.
- 4. El-Shafie, M.; Kambara, S. Recent Advances in Ammonia Synthesis Technologies: Toward Future Zero Carbon Emissions. *Int J Hydrogen Energy* **2023**, *48*, 11237–11273, doi:10.1016/j.ijhydene.2022.09.061.
- 5. Capurso, T.; Stefanizzi, M.; Torresi, M.; Camporeale, S.M. Perspective of the Role of Hydrogen in the 21st Century Energy Transition. *Energy Convers Manag* **2022**, *251*, 114898, doi:10.1016/j.enconman.2021.114898.
- Yang, J.; Sudik, A.; Wolverton, C.; Siegel, D.J. High Capacity Hydrogen Storage Materials: Attributes for Automotive Applications and Techniques for Materials Discovery. *Chem Soc Rev* 2010, *39*, 656–675, doi:10.1039/b802882f.
- 7. Kovač, A.; Paranos, M.; Marciuš, D. Hydrogen in Energy Transition: A Review. *Int J Hydrogen Energy* **2021**, *46*, 10016–10035, doi:10.1016/j.ijhydene.2020.11.256.
- Nnabuife, S.G.; Hamzat, A.K.; Whidborne, J.; Kuang, B.; Jenkins, K.W. Integration of Renewable Energy Sources in Tandem with Electrolysis: A Technology Review for Green Hydrogen Production. *Int J Hydrogen Energy* 2024, doi:10.1016/j.ijhydene.2024.06.342.
- 9. Incer-Valverde, J.; Korayem, A.; Tsatsaronis, G.; Morosuk, T. "Colors" of Hydrogen: Definitions and Carbon Intensity. *Energy Convers Manag* **2023**, *291*, 117294, doi:10.1016/J.ENCONMAN.2023.117294.
- Wang, M.; Wang, Z.; Gong, X.; Guo, Z. The Intensification Technologies to Water Electrolysis for Hydrogen Production - A Review. *Renewable and Sustainable Energy Reviews* 2014, 29, 573–588.
- 11. Kovač, A.; Paranos, M.; Marciuš, D. Hydrogen in Energy Transition: A Review. *Int J Hydrogen Energy* **2021**, *46*, 10016–10035, doi:10.1016/j.ijhydene.2020.11.256.
- 12. Aziz, M.; TriWijayanta, A.; Nandiyanto, A.B.D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies (Basel)* **2020**, *13*, 1–25, doi:10.3390/en13123062.
- Shipman, M.A.; Symes, M.D. Recent Progress towards the Electrosynthesis of Ammonia from Sustainable Resources. *Catal Today* 2017, 286, 57–68, doi:10.1016/j.cattod.2016.05.008.
- 14. Le, P.A.; Trung, V.D.; Nguyen, P.L.; Bac Phung, T.V.; Natsuki, J.; Natsuki, T. The Current Status of Hydrogen Energy: An Overview. *RSC Adv* 2023, *13*, 28262–28287.
- 15. Aziz, M.; TriWijayanta, A.; Nandiyanto, A.B.D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies (Basel)* **2020**, *13*, doi:10.3390/en13123062.
- 16. Andersson, J.; Grönkvist, S. Large-Scale Storage of Hydrogen. *Int J Hydrogen Energy* 2019, 44, 11901–11919.
- 17. Qureshi, F.; Yusuf, M.; Arham Khan, M.; Ibrahim, H.; Ekeoma, B.C.; Kamyab, H.; Rahman, M.M.; Nadda, A.K.; Chelliapan, S. A State-of-The-Art Review on the Latest Trends in Hydrogen Production, Storage, and Transportation Techniques. *Fuel* **2023**, *340*, doi:10.1016/j.fuel.2023.127574.
- 18. Ball, M.; Wietschel, M. The Future of Hydrogen Opportunities and Challenges. *Int J Hydrogen Energy* **2009**, *34*, 615–627, doi:10.1016/J.IJHYDENE.2008.11.014.
- 19. Kovač, A.; Paranos, M.; Marciuš, D. Hydrogen in Energy Transition: A Review. *Int J Hydrogen Energy* **2021**, *46*, 10016–10035, doi:10.1016/j.ijhydene.2020.11.256.
- Klerke, A.; Christensen, C.H.; Nørskov, J.K.; Vegge, T. Ammonia for Hydrogen Storage: Challenges and Opportunities. *J Mater Chem* 2008, 18, 2304–2310, doi:10.1039/b720020j.
- Makepeace, J.W.; He, T.; Weidenthaler, C.; Jensen, T.R.; Chang, F.; Vegge, T.; Ngene, P.; Kojima, Y.; de Jongh, P.E.; Chen, P.; et al. Reversible Ammonia-Based and Liquid Organic Hydrogen Carriers for High-Density Hydrogen Storage: Recent Progress. *Int J Hydrogen Energy* 2019, 44, 7746–7767, doi:10.1016/j.ijhydene.2019.01.144.
- Nemmour, A.; Inayat, A.; Janajreh, I.; Ghenai, C. Green Hydrogen-Based E-Fuels (E-Methane, E-Methanol, E-Ammonia) to Support Clean Energy Transition: A Literature Review. Int J Hydrogen Energy 2023, 48, 29011–29033, doi:10.1016/j.ijhydene.2023.03.240.
- Ren, J.; Musyoka, N.M.; Langmi, H.W.; Mathe, M.; Liao, S. Current Research Trends and Perspectives on Materials-Based Hydrogen Storage Solutions: A Critical Review. *Int J Hydrogen Energy* 2017, *42*, 289–311, doi:10.1016/J.IJHYDENE.2016.11.195.

- 24. Klerke, A.; Christensen, C.H.; Nørskov, J.K.; Vegge, T. Ammonia for Hydrogen Storage: Challenges and Opportunities. *J Mater Chem* **2008**, *18*, 2304–2310, doi:10.1039/b720020j.
- 25. Lundtang, J. General Rights Safety Assessment of Ammonia as a Transport Fuel;
- 26. Wan, Z.; Tao, Y.; Shao, J.; Zhang, Y.; You, H. Ammonia as an Effective Hydrogen Carrier and a Clean Fuel for Solid Oxide Fuel Cells. *Energy Convers Manag* **2021**, *228*, 113729, doi:10.1016/J.ENCONMAN.2020.113729.
- Qureshi, F.; Yusuf, M.; Arham Khan, M.; Ibrahim, H.; Ekeoma, B.C.; Kamyab, H.; Rahman, M.M.; Nadda, A.K.; Chelliapan, S. A State-of-The-Art Review on the Latest Trends in Hydrogen Production, Storage, and Transportation Techniques. *Fuel* **2023**, *340*, doi:10.1016/j.fuel.2023.127574.
- 28. Le, P.A.; Trung, V.D.; Nguyen, P.L.; Bac Phung, T.V.; Natsuki, J.; Natsuki, T. The Current Status of Hydrogen Energy: An Overview. *RSC Adv* 2023, *13*, 28262–28287.
- Aziz, M.; TriWijayanta, A.; Nandiyanto, A.B.D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies (Basel)* 2020, 13, doi:10.3390/en13123062.
- Vojvodic, A.; Medford, A.J.; Studt, F.; Abild-Pedersen, F.; Khan, T.S.; Bligaard, T.; Nørskov, J.K. Exploring the Limits: A Low-Pressure, Low-Temperature Haber-Bosch Process. *Chem Phys Lett* **2014**, *598*, 108–112, doi:10.1016/j.cplett.2014.03.003.
- 31. Smith, C.; Torrente-Murciano, L. Exceeding Single-Pass Equilibrium with Integrated Absorption Separation for Ammonia Synthesis Using Renewable Energy—Redefining the Haber-Bosch Loop. *Adv Energy Mater* **2021**, *11*, doi:10.1002/aenm.202003845.
- Wang, W.; Patil, B.; Heijkers, S.; Hessel, V.; Bogaerts, A. Nitrogen Fixation by Gliding Arc Plasma: Better Insight by Chemical Kinetics Modelling. *ChemSusChem* 2017, 10, 2145– 2157, doi:10.1002/cssc.201700095.
- Liu, H. Ammonia Synthesis Catalyst 100 Years: Practice, Enlightenment and Challenge. *Cuihua Xuebao/Chinese Journal of Catalysis* 2014, 35, 1619–1640, doi:10.1016/S1872-2067(14)60118-2.
- 34. Song, Z.; Cai, T.; Hanson, J.C.; Rodriguez, J.A.; Hrbek, J. Structure and Reactivity of Ru Nanoparticles Supported on Modified Graphite Surfaces: A Study of the Model Catalysts for Ammonia Synthesis. *J Am Chem Soc* **2004**, *126*, 8576–8584, doi:10.1021/ja031718s.
- 35. Marakatti, V.S.; Gaigneaux, E.M. Recent Advances in Heterogeneous Catalysis for Ammonia Synthesis. *ChemCatChem* **2020**, *12*, 5838–5857, doi:10.1002/cctc.202001141.
- 36. Ertl, G. Primary Steps in Catalytic Synthesis of Ammonia; 1983; Vol. 1;.

- Huang, J.; Yuan, M.; Li, X.; Wang, Y.; Li, M.; Li, J.; You, Z. Inhibited Hydrogen Poisoning for Enhanced Activity of Promoters-Ru/Sr2Ta207 Nanowires for Ammonia Synthesis. J Catal 2020, 389, 556–565, doi:10.1016/j.jcat.2020.06.037.
- 38. Statistic_id1046426_global-Ruthenium-Price-2013-2022.
- Dahl, S.; Logadottir, A.; Egeberg, R.C.; Larsen, J.H.; Chorkendorff, I.; Törnqvist, E.; NØrskov,
 J.K. Role of Steps in N2 Activation on Ru(0001). *Phys Rev Lett* **1999**, *83*, 1814–1817,
 doi:10.1103/PhysRevLett.83.1814.
- Karim, A.M.; Prasad, V.; Mpourmpakis, G.; Lonergan, W.W.; Frenkel, A.I.; Chen, J.G.; Vlachos, D.G. Correlating Particle Size and Shape of Supported Ru/γ-Al 203 Catalysts with NH3 Decomposition Activity. *J Am Chem Soc* 2009, 131, 12230–12239, doi:10.1021/ja902587k.
- 41. Javaid, R.; Nanba, T. Effect of Preparation Method and Reaction Parameters on Catalytic Activity for Ammonia Synthesis. *Int J Hydrogen Energy* **2021**, *46*, 35209–35218, doi:10.1016/j.ijhydene.2021.08.082.
- 42. Javaid, R.; Nanba, T. Effect of Preparation Method and Reaction Parameters on Catalytic Activity for Ammonia Synthesis. *Int J Hydrogen Energy* **2021**, *46*, 35209–35218, doi:10.1016/j.ijhydene.2021.08.082.
- 43. Su, T.; Guan, B.; Zhou, J.; Zheng, C.; Guo, J.; Chen, J.; Zhang, Y.; Yuan, Y.; Xie, W.; Zhou, N.; et al. Review on Ru-Based and Ni-Based Catalysts for Ammonia Decomposition: Research Status, Reaction Mechanism, and Perspectives. *Energy and Fuels* **2023**, *37*, 8099–8127, doi:10.1021/acs.energyfuels.3c00804.
- 44. Su, Z.; Guan, J.; Liu, Y.; Shi, D.; Wu, Q.; Chen, K.; Zhang, Y.; Li, H. Research Progress of Ruthenium-Based Catalysts for Hydrogen Production from Ammonia Decomposition. *Int J Hydrogen Energy* **2024**, *51*, 1019–1043, doi:10.1016/j.ijhydene.2023.09.107.
- 45. Le, T.A.; Cuong Do, Q.; Kim, Y.; Kim, T.-W.; Chae, H.-J. A Review on the Recent Developments of Ruthenium and Nickel Catalysts for CO X-Free H 2 Generation by Ammonia Decomposition. *Korean J. Chem. Eng* **2021**, *38*, 1087–1103, doi:10.1007/s11814-021-0767-7.
- 46. Chen, C.; Wu, K.; Ren, H.; Zhou, C.; Luo, Y.; Lin, L.; Au, C.; Jiang, L. Ru-Based Catalysts for Ammonia Decomposition: A Mini-Review. *Energy and Fuels* **2021**, *35*, 11693–11706, doi:10.1021/acs.energyfuels.1c01261.
- 47. Raróg-Pilecka, W.; Miśkiewicz, E.; Szmigiel, D.; Kowalczyk, Z. Structure Sensitivity of Ammonia Synthesis over Promoted Ruthenium Catalysts Supported on Graphitised Carbon. *J Catal* **2005**, *231*, 11–19, doi:10.1016/J.JCAT.2004.12.005.

- 48. Fang, H.; Liu, D.; Luo, Y.; Zhou, Y.; Liang, S.; Wang, X.; Lin, B.; Jiang, L. Challenges and Opportunities of Ru-Based Catalysts toward the Synthesis and Utilization of Ammonia. *ACS Catal* **2022**, *12*, 3938–3954, doi:10.1021/acscatal.2c00090.
- 49. Smith, C.; Torrente-Murciano, L. Exceeding Single-Pass Equilibrium with Integrated Absorption Separation for Ammonia Synthesis Using Renewable Energy—Redefining the Haber-Bosch Loop. *Adv Energy Mater* **2021**, *11*, doi:10.1002/aenm.202003845.
- 50. Poto, S.; Gallucci, F.; Fernanda Neira d'Angelo, M. Direct Conversion of CO2 to Dimethyl Ether in a Fixed Bed Membrane Reactor: Influence of Membrane Properties and Process Conditions. *Fuel* **2021**, *302*, 121080, doi:10.1016/J.FUEL.2021.121080.
- 51. Beltermann, N.; Weiske, S.; Becka, R.; Samsun, R.C.; Peters, R.; Stolten, D.; Müller, T.E. An Evaluation of Direct Dimethyl Ether (DME) Synthesis from Hydrogen and Carbon Dioxide Based on CFD Reactor Simulations. *Int J Hydrogen Energy* **2023**, *48*, 39373–39388, doi:10.1016/J.IJHYDENE.2023.05.260.
- 52. Živković, L.A.; Pohar, A.; Likozar, B.; Nikačević, N.M. Reactor Conceptual Design by Optimization for Hydrogen Production through Intensified Sorption- and Membrane-Enhanced Water-Gas Shift Reaction. *Chem Eng Sci* **2020**, *211*, 115174, doi:10.1016/J.CES.2019.115174.
- 53. Bang, G.; Moon, D.K.; Kang, J.H.; Han, Y.J.; Kim, K.M.; Lee, C.H. High-Purity Hydrogen Production via a Water-Gas-Shift Reaction in a Palladium-Copper Catalytic Membrane Reactor Integrated with Pressure Swing Adsorption. *Chemical Engineering Journal* **2021**, *411*, 128473, doi:10.1016/J.CEJ.2021.128473.
- 54. Cechetto, V.; Anello, G.; Rahimalimamaghani, A.; Gallucci, F. Carbon Molecular Sieve Membrane Reactors for Ammonia Cracking. *Processes* **2024**, *12*, 1168, doi:10.3390/pr12061168.
- Cechetto, V.; Di, L.; Gutierrez, R. ScienceDirect Ultra-Pure Hydrogen Production via Ammonia Decomposition in a Catalytic Membrane Reactor. *Int J Hydrogen Energy* 2022, 47, 21220–21230, doi:10.1016/j.ijhydene.2022.04.240.
- 56. Rahimalimamaghani, A.; Pacheco Tanaka, D.A.; Llosa Tanco, M.A.; Neira D'Angelo, F.; Gallucci, F. Effect of Aluminium Acetyl Acetonate on the Hydrogen and Nitrogen Permeation of Carbon Molecular Sieves Membranes. *Int J Hydrogen Energy* 2022, 47, 14570–14579, doi:10.1016/j.ijhydene.2022.02.198.
- 57. Sazali, N. A Review of the Application of Carbon-Based Membranes to Hydrogen Separation. *J Mater Sci* **2020**, *55*, 11052–11070, doi:10.1007/s10853-020-04829-7.
- 58. Rahimalimamaghani, A.; Pacheco Tanaka, D.A.; Llosa Tanco, M.A.; Neira D'Angelo, F.; Gallucci, F. New Hydrophilic Carbon Molecular Sieve Membranes for Bioethanol

Dehydration via Pervaporation. *Chemical Engineering Journal* **2022**, *435*, 134891, doi:10.1016/J.CEJ.2022.134891.

- 59. Ismail, N.H.; Salleh, W.N.W.; Sazali, N.; Ismail, A.F.; Yusof, N.; Aziz, F. Disk Supported Carbon Membrane via Spray Coating Method: Effect of Carbonization Temperature and Atmosphere. *Sep Purif Technol* **2018**, *195*, 295–304, doi:10.1016/j.seppur.2017.12.032.
- 60. Rahimalimamaghani, A.; Pacheco Tanaka, D.A.; Llosa Tanco, M.A.; Neira D'Angelo, M.F.; Gallucci, F. Ultra-Selective CMSMs Derived from Resorcinol-Formaldehyde Resin for CO2 Separation. *Membranes (Basel)* **2022**, *12*, 1–21, doi:10.3390/membranes12090847.
- 61. Yun, S.; Ted Oyama, S. Correlations in Palladium Membranes for Hydrogen Separation: A Review. *J Memb Sci* **2011**, *375*, 28–45, doi:10.1016/j.memsci.2011.03.057.
- 62. Basile, A.; Gallucci, F.; Tosti, S. Synthesis, Characterization, and Applications of Palladium Membranes. *Membrane Science and Technology* **2008**, *13*, 255–323, doi:10.1016/S0927-5193(07)13008-4.
- 63. Arratibel Plazaola, A.; Pacheco Tanaka, D.A.; Van Sint Annaland, M.; Gallucci, F. Recent Advances in Pd-Based Membranes for Membrane Reactors. *Molecules* **2017**, *22*, 1–53, doi:10.3390/molecules22010051.
- 64. Basile, A.; Gallucci, F.; Tosti, S. Synthesis, Characterization, and Applications of Palladium Membranes. *Membrane Science and Technology* **2008**, *13*, 255–323, doi:10.1016/S0927-5193(07)13008-4.
- 65. Yun, S.; Ted Oyama, S. Correlations in Palladium Membranes for Hydrogen Separation: A Review. *J Memb Sci* **2011**, *375*, 28–45, doi:10.1016/j.memsci.2011.03.057.
- Israni, S.H.; Nair, B.K.R.; Harold, M.P. Hydrogen Generation and Purification in a Composite Pd Hollow Fiber Membrane Reactor: Experiments and Modeling. *Catal Today* 2009, 139, 299–311, doi:10.1016/j.cattod.2008.02.020.
- 67. Nailwal, B.C.; Chotalia, P.; Salvi, J.; Goswami, N.; Muhmood, L.; Adak, A.K.; Kar, S. Ammonia Decomposition for Hydrogen Production Using Packed Bed Catalytic Membrane Reactor. *Int J Hydrogen Energy* **2024**, *49*, 1272–1287, doi:10.1016/j.ijhydene.2023.09.229.
- Nordio, M.; Melendez, J.; van Sint Annaland, M.; Pacheco Tanaka, D.A.; Llosa Tanco, M.; Gallucci, F. Comparison between Carbon Molecular Sieve and Pd-Ag Membranes in H2-CH4 Separation at High Pressure. *Int J Hydrogen Energy* 2020, 45, 28876–28892, doi:10.1016/j.ijhydene.2020.07.191.
- 69. Rodrigues, S.C.; Whitley, R.; Mendes, A. Preparation and Characterization of Carbon Molecular Sieve Membranes Based on Resorcinol–Formaldehyde Resin. *J Memb Sci* **2014**, *459*, 207–216, doi:10.1016/J.MEMSCI.2014.02.013.

Chapter 2

Development of carbon membranes for ammonia decomposition

This chapter is based on the following paper:

V. Cechetto, G. Anello, A. Rahimalimamaghani, F. Gallucci. "Carbon Molecular Sieve Membrane Reactors for Ammonia Cracking", Processes, 12(6), 1168, 2024

Abstract

Palladium-based membranes, while showing the highest performance for hydrogen separation, have their drawbacks. The excessive cost of palladium, a rare and expensive material, and the reactivity to impurities like sulfur, carbon monoxide, and other contaminants, can potentially limit their application. To overcome these challenges, one promising solution lies in the development of carbon-based membranes. Carbon-based membranes are highly selective for hydrogen due to their fine-tuned pore structure. Additionally, they are more resistant to chemical degradation, compared with palladium membranes. Therefore, a carbon membrane was fabricated on a tubular porous alumina support through the carbonization of a polymer-based solution and subsequently tested for ammonia decomposition in a membrane reactor setup. Operating at 5 bar and temperatures ranging from 450 to 500 °C, NH₃ conversion exceeding 90% were achieved, with conversion approaching thermodynamic equilibrium at temperatures above 475 °C. Simultaneously, the carbon membrane facilitated the recovery of hydrogen from ammonia, yielding recoveries of 8.2 – 9.8%. The residual ammonia concentration (0.59 vol.% at 500 °C and 5 bar), is insufficient for achieving fuel cell-grade hydrogen, which requires ammonia levels below 0.1 ppm. However, the integration of an adsorption unit containing a fixed bed of zeolite 13X successfully reduced ammonia concentration, enabling the production of fuel cell-grade hydrogen. Despite performance far from being comparable with the ones achieved in the literature with palladium membranes, this study underscores the viability of carbon membranes for the production of hydrogen suitable for fuel cell applications, highlighting their competitiveness and promising role in the field.

2.1 Introduction

The challenges and opportunities of hydrogen (H₂) production from ammonia (NH₃) decomposition were discussed in Chapter 1. The literature highlights that a key challenge to the widespread production of hydrogen from ammonia is the development of reliable, efficient, and scalable processes that integrate ammonia decomposition reactors with hydrogen purification systems [1]. In this framework, the membrane reactor has emerged as a promising technology, offering a solution that enables the efficient integration of ammonia decomposition, as per Equation 2.1, while simultaneously effecting hydrogen separation, all within a single integrated device [2].

$$NH_3 \leftrightarrow 0.5N_2 + 1.5H_2 \tag{2.1}$$

Moreover, employing a membrane reactor has demonstrated the ability to reduce the reactor's operating temperature and increase its operating pressure compared to conventional systems, which typically require temperatures exceeding 700 °C attain complete conversion [3]. This results in higher energy efficiency due to the lower temperature conditions and improved reactor compactness thanks to the elevated pressure levels [4–6]. The selective separation of H₂ from the reaction zone, which is favored at high pressure, enhances the reaction rates and shifts the equilibrium towards the formation of reaction products resulting in increased feedstock conversions.

Hydrogen production via ammonia decomposition has been experimentally studied in numerous works available in the literature [7–9] and the best performance in terms of ammonia conversion, hydrogen recovery and purity has been achieved using a Ru-based catalyst to promote ammonia decomposition and palladium (Pd) membranes for hydrogen separation [2]. This can be attributed to the outstanding permeance and selectivity towards hydrogen separation of Pd-based membranes compared to other types of membranes.

In this work, the integration of carbon-based membranes into a membrane reactor for hydrogen recovery from ammonia is proposed. Carbon membranes are in fact less expensive compared to Pd-based membranes, thus the costs associated with the reaction unit are reduced upon their utilization. Carbon membranes have previously been evaluated for ammonia decomposition in the study conducted by Jiang et al. [10]. The authors performed ammonia decomposition over a Ru/Y/K/Al₂O₃ catalyst with different types of membranes and demonstrated that the residual ammonia concentration in the hydrogen produced strongly depends on the separation

performance of the membrane. Specifically, carbon membranes were proven to have significantly lower performance compared to palladium-silver (Pd-Ag) membranes during ammonia decomposition: the decomposition of an ammonia flow 250 ml min⁻¹ over 3 g of catalyst at 450 °C and 7 bar resulted in the production of hydrogen with residual NH₃ concentrations of approximately 50 ppm when implementing a 80 mm long 1.8 µm thick Pd-Ag membrane, whereas under similar operating conditions the residual NH₃ concentrations was measured to be approximately 10 000 ppm when implementing a 220 mm long 0.9 µm thick carbon membrane.

While a comparison between the performance of carbon-based membranes and palladium-based membranes is therefore available in literature, to the best of the authors' knowledge the applicability of carbon membranes to produce fuel cell-grade hydrogen has not been demonstrated yet. In this study, a carbon membrane was prepared, characterized, and tested for ammonia decomposition in a fixed bed membrane reaction configuration, implementing a downstream hydrogen purification unit to remove residual ammonia.

2.2 Experimental

2.2.1 <u>Membrane preparation</u>

The carbon membrane employed in this work was prepared starting from asymmetric tubular porous alumina (Al_2O_3) support with subsequent coating, polymerization and carbonization under controlled conditions. In detail, the preparation procedure (Figure 2.1), for which the chemicals listed in Table 2.1 were used, was carried out according to the following steps:



Figure 2.1. Schematic of the carbon membrane fabrication process.

(i) Support preparation. The support was prepared starting from asymmetric porous α -Al₂O₃ tube with an outer diameter (OD) of 10 mm, an inner diameter (ID) of 7 mm and an external layer average pore size about 100 nm (Rauschert GmbH, Germany). As reported in a previous work [11], the porous alumina tube is connected on one side to a dense alumina cap and on the other side to a dense alumina tube, through appropriate glass sealing. This allows one of the sides to be completely closed, whereas the other one is open to ensure the permeation gas outlet, resulting in a dead-end configuration.

(ii) Polymeric precursor synthesis. Along with the support preparation, another preliminary step to the fabrication of the carbon membrane is the synthesis of the oligomer employed in the dipping solution [11,12]. The resin was synthesized via an acid-catalyzed phenol-formaldehyde condensation, as follows. Phenol (69 g) was gradually melted at 60 °C in a four-necked round-bottom flask equipped with a Graham condenser. Upon liquefying, oxalic acid (1.5 g) was added to the solution and the temperature was increased up to 90 °C, while adding formaldehyde solution (54 g) to the flask with a rate of 2 ml min⁻¹. After 8 hours, the obtained product was washed and separated by centrifugation (three cycles of 15 minutes at 4 400 rpm and 10 °C). Finally, the obtained oligomer was dried under vacuum at 50 °C for 24 hours.

(iii) **Dipping solution preparation.** Then, the dipping solution was prepared dissolving the synthesized Novolac (30 g) in N-Methyl-2-Pyrrolidone (83.2 g), with aluminum acetylacetonate (0.8 g) as additive [11]. A high shear mixer (Thinky ARE-250, Japan) was used to ensure the efficient mixing of the chemicals at 2 000 rpm for two cycles with a duration of 30 minutes each. Next, formaldehyde (1.6 g) was added with a subsequent mixing step, again at 2 000 rpm for 30 minutes. Finally, oxalic acid (0.4 g) was added to the solution and mixed at the same speed for additional

(iv) Dip coating. This step was carried out by an automated system that cyclically lowered and raised the support within a glass cylinder containing the dipping solution.

(v) Polymerization. Once the coating was completed, the coated support is polymerized in a rotary oven at 80 °C for 24 hours. The coated support was connected to a rotating mount while drying to ensure a more homogeneous active layer thickness. Furthermore, nitrogen (N_2) gas was employed to provide an inert atmosphere.

(vi) Carbonization. Finally, the polymeric layer on the porous support underwent carbonization in a tubular three-zone oven (Nabertherm, Germany). A heating rate of approximately 1 °C min⁻¹ was applied until reaching a temperature of about 800 °C where it was held for 4 hours. Throughout the carbonization step, a nitrogen flow of about 3 l min⁻¹ was applied to avoid carbon combustion.

Chemical	CAS n.	Purity	Brand	Supplier
Formaldehyde solution	50-00-0	37.0%	Sigma-Aldrich®	VWR International BV
Phenol	108-95-2	99.9%	Sigma-Aldrich®	VWR International BV
N-Methyl-2-Pyrrolidone	872-50-4	99.5%	Sigma-Aldrich®	Merck Life Science NV
Aluminum acetylacetonate	13963-57-0	99.9%	Sigma-Aldrich®	Merck Life Science NV
Oxalic acid	144-62-7	98.0%	Sigma-Aldrich®	VWR International BV

Table 2.1. List of chemicals used for carbon membrane's synthesis.

2.2.2 <u>Membrane characterization</u>

The pore size distribution measurements of the fabricated carbon membrane were conducted using a laboratory-made capillary condensation perm-porometer, with detailed information provided in Appendix B.

2.2.3 <u>Experimental setup</u>

The carbon membrane, whose preparation procedure has been outlined in the previous section, was tested in an experimental setup specifically designed for ammonia decomposition. The setup comprises four main modules: (1) the feed module, (2) the permeation or reaction module, (3) the hydrogen purification module, and (4) the retentate and permeate analysis module. In the feed module, EL-FLOW® Prestige mass flow controllers (Bronkhorst®, The Netherlands) regulate the desired flow rate of feed gases from gas bottles (Linde Gas Benelux BV, The Netherlands) containing 5.0 purity N_2 , 5.0 purity H_2 and 3.7 purity NH_3 , to the system. The permeation module includes a stainless-steel vessel with an inner diameter of 45 mm and a length of 280 mm, in which the membrane is connected to the flange, positioned in the middle of the reactor and fully immersed in a packed bed of 250 g of commercial 2 wt% Ru/Al₂O₃ catalyst in 3 mm pellet form (Alfa Aesar[®], Massachusetts, USA). The reactor's inlet is equipped with a porous stainless-steel plate to guarantee even gas distribution and the reactor's freeboard is configured in a conical shape to decrease the gas velocity and mitigate the potential for escape of catalyst particles during the experimental campaign. Moreover, the pressure of the system is controlled by means of an EL-PRESS® pressure controller (Bronkhorst[®], The Netherlands) and, given the endothermic nature of the ammonia decomposition reaction, an electrical three-zone split furnace (Elicra Electrowarmte BV, The Netherlands) is used to supply heat to the reactor.

The hydrogen purification module employs a bed of zeolite 13X at ambient conditions for NH_3 removal from the permeate stream, whereas the retentate and permeate analysis module comprises the instrumentation for measuring permeation flux through the membrane and the composition of both retentate and permeate streams. Specifically, a high precision SF-1U/2U film flow meter (Horiba Stec Co. Ltd., Japan) and a mass flow meter (Bronkhorst[®], The Netherlands) are used to quantify the permeation flux through the membrane, a CP-4900 micro gas chromatograph (Varian Inc., California) is used to measure the composition of the retentate and permeate streams leaving the reactor, and a Fourier-Transform infrared Spectrometer (Shimadzu, Japan) equipped with a 5 m gas cell (Specac Ltd, England, UK) and a Mercury-Cadmium-Telluride (MCT) detector is employed to measure the residual ammonia concentration of the permeate stream leaving the hydrogen purification module. This instrument is capable of accurately determining residual concentrations of ammonia as low as 0.75 ppm. A set of high precision SF-1U/2U film flow meters (Horiba Stec Co. Ltd., Japan) was employed to calibrate the mass flow controllers and quantify ammonia-free gas flows. The permeate and retentate streams leaving the analysis module are directed to a water absorption unit to prevent the release of the residual NH₃ traces into the atmosphere and eventually vented.

2.2.4 Experimental method

After completing the preparation procedure, the carbon membrane underwent sealing and testing in helium-ethanol system to ensure the absence of undesired leakages from both the sealings and the membrane surface. Once confirmed leak-free, the membrane was installed in the reactor. The system was gradually heated to 500 °C at a rate of 2 °C min⁻¹ under a nitrogen atmosphere. Subsequently, the system was transitioned to a hydrogen atmosphere until steady permeation was attained. Single gas (H₂, N₂ and NH₃) and binary mixtures (H₂/N₂) permeation tests were subsequently performed.

Gas permeation measurements for pure H₂, N₂ and NH₃ were conducted at temperatures ranging from 400 °C to 500 °C, with pressure difference across the membrane (ΔP) ranging between 1 and 5 bar, while maintaining atmospheric conditions on the permeate side. Pressure changes between the measurements at different temperatures

were conducted in an N₂ atmosphere, with a heating rate of approximately 2 °C min⁻¹. Based on the gas permeation tests, the H₂, N₂ and NH₃ permeances as well as the ideal H_2/N_2 and H_2/NH_3 selectivities of the membrane, were subsequently calculated. H_2 and N_2 permeation tests were performed with the aim to assess if the presence of N_2 next to H₂ in the feed stream has an influence on the gas permeation through the membrane. A H_2/N_2 mixture containing H_2 concentrations ranging between 50 vol.% and 95 vol.% was fed to the reactor at 450 °C for ΔP ranging between 1 and 5 bar. The permeate side was kept at atmospheric conditions. The reactor was then cooled down in N_2 atmosphere using a cooling rate of 2 °C min⁻¹ and, once room temperature was achieved, the catalyst was introduced in the reactor. Subsequently, the reactor was heated up under N_2 atmosphere and permeation tests under reactive conditions were performed. Specifically, ammonia decomposition was performed at 450, 475 and 500 °C keeping the retentate and permeate sides of the membrane at 5 bar and atmospheric conditions, respectively. At each temperature, a flow rate of 500 Nml min⁻¹ of pure NH₃ was fed to the reactor, the operating pressure was varied, and the reaction performance was monitored until steady state operation was achieved. The gas permeation through the membrane, the composition of the streams leaving at the permeate and retentate sides of the membrane, and the NH₃ concentration in the permeate stream downstream of the hydrogen cleanup unit were then measured 5 times. Subsequently, the permeation fluxes (J_i), the permeances (\mathcal{P}_i), the selectivities ($S_{i/j}$), the NH₃ conversion (x_{NH_3}), and the H_2 recovery (*HR*) were calculated according to the definitions provided in Equation 2.2 to Equation 2.6:

$$J_i = \frac{F_i}{A_m} \tag{2.2}$$

$$\mathcal{P}_i = \frac{J_i}{\Delta P} \tag{2.3}$$

$$S_{i/j} = \frac{\mathcal{P}_i}{\mathcal{P}_j} \tag{2.4}$$

$$x_{NH_3} = \frac{F_{NH_3, in} - F_{NH_3, out}}{F_{NH_3, in}} \cdot 100$$
(2.5)

$$H_2 recovery = \frac{2 \cdot F_{H_2, out}^p}{3 \cdot F_{NH_3, in}} \cdot 100$$
(2.6)

where F_i is the molar flow of the species *i*, ΔP is the pressure difference across the membrane, and A_m is the membrane area.

2.4 Results and discussion

In Figure 2.2, the pure hydrogen permeation flux (a) and the hydrogen permeance through the membrane (b) as a function of the transmembrane pressure difference across the membrane for different temperatures are represented.



Figure 2.2. (a) Hydrogen permeation flux (b) and hydrogen permeance through the membrane as a function of the pressure difference across the membrane at different values of temperature.

As illustrated in Figure 2.2a, the hydrogen permeation flux through the membrane increases with increasing pressure. This is due to the higher driving force for separation available when pressure increases. Moreover, the increase of hydrogen permeance with temperature, which is visible in Figure 2.2b, indicates the dominance of activated transport mechanisms such as molecular sieving and surface diffusion. The negative slope of hydrogen permeation as a function of pressure indicates then the negligible contribution of viscous flow through the membrane and therefore the absence of defects on the membrane's surface [13]. In defect-free membranes, the absence of cracks or voids eliminates physical pathways for gas molecular, thereby preventing pressure-driven viscous flow. This ensures that molecular transport mechanisms dominate, making the contribution of viscous flow negligible. Conversely, the presence of structural defects introduces non-selective pathways that enable viscous flow to prevail, compromising the membrane's molecular transport efficiency and selectivity. This result is also confirmed by the fact that nitrogen permeation through the membrane was not observed in any of the tested conditions.

Temperature	$\boldsymbol{\mathcal{P}}_{H_2}$	$\boldsymbol{\mathcal{P}}_{N_2}$	$\boldsymbol{\mathcal{P}}_{NH_3}$	$S_{H_{2/N_{2}}}$	$S_{H_2/_{NH_3}}$
(°C)	(mol s ⁻¹ m ⁻² Pa ⁻¹)	(mol s ⁻¹ m ⁻² Pa ⁻¹)	(mol s ⁻¹ m ⁻² Pa ⁻¹)	(-)	(-)
400	9.8·10 ⁻⁸	< 5.9·10 ⁻¹⁰	6.0·10 ⁻⁹	> 165	16
450	1.0.10-7	< 5.9.10-10	6.2·10 ⁻⁹	> 169	16
500	1.0.10-7	< 5.9.10-10	8.1·10 ⁻⁹	> 170	12

Table 2.2. H_2 , N_2 and NH_3 permeance and ideal H_2/N_2 and H_2/NH_3 selectivity of the membrane used in this work, evaluated at $\Delta P = 1$ bar, for different values of temperature.

The measured permeances of hydrogen, nitrogen, and ammonia at 400, 450, and 500 °C, with a pressure difference across the membrane of 1 bar, are outlined in Table 2.2, along with the corresponding H_2/N_2 and H_2/NH_3 ideal selectivity. Additionally, in Figure 2.3, the permeance of NH₃, H₂ and N₂ at different temperatures is depicted as a function of their kinetic diameter. Since nitrogen permeation through the membrane was not observed, in Table 2.2 and Figure 2.3, N₂ permeance and H_2/N_2 selectivity are reported under the assumption of the worst-case scenario. This entails considering nitrogen permeation flow rate through the membrane to be as low as the low detection limit of the film flow meters used for nitrogen permeation measurement (0.2 ml min⁻¹).

Hydrogen is the species showing the highest permeance and this can be explained analyzing the pore size distribution of the membrane, given in Figure 2.4. This analysis reveals that the majority of the pores exceed the kinetic diameter of hydrogen (0.289 nm), indicating that hydrogen permeation through the membrane is promoted. Nitrogen permeation through the membrane is on the other hand less favored since only about 26% of the pores show a bigger size compared to its kinetic diameter(0.364 nm). This permeance pattern, which is consistent with findings of other works previously reported in the literature [14–16], confirms the contribution of molecular sieving to the permeation mechanism through the membrane observed from Figure 2.2.



Figure 2.3. Permeance of single gases at $\Delta P = 1$ bar and different temperatures as a function of their kinetic diameter.

As far as NH₃ concerns, despite its smaller kinetic diameter (0.260 nm), it shows a lower permeance compared to the one of H₂. The main reason for this phenomenon lies in the contribution of molecular sieving to the permeation mechanism. Ammonia permeation can in fact only take place through those pores which have a larger size compared to its kinetic diameter and is therefore inhibited through about 24% of the pores. Moreover, a similar behavior of permeation compared to hydrogen was observed in literature for helium (He), which has the same kinetic diameter as NH₃. As this behavior has been ascribed to higher adsorption affinity of H₂ in carbon membranes compared to He [17], the same explanation might justify the trend of NH₃ permeation compared to the one of H₂ experienced in this study.



Figure 2.4. Pore size distribution of the supported carbon membrane used in this work measured via perm-porometry.



Figure 2.5. Hydrogen permeation flux at different hydrogen partial pressure difference across the membrane for pure hydrogen and binary H_2/N_2 mixtures with different compositions at 450 °C.

In Figure 2.5 the H_2 permeation flux through the membrane is depicted as a function of the hydrogen partial pressure difference across the membrane for both pure H_2 and for H_2/N_2 feed mixtures with hydrogen concentrations ranging from 50 vol.% to 90 vol.%. As observed, at a given hydrogen partial pressure difference across the membrane, hydrogen recovery remains independent of the hydrogen concentration in the feed mixture. These results, which are in line with other studies available in the literature [18], show that this type of carbon membranes are not subject to mass transfer limitations and that no reduction in the hydrogen permeation flux through the membrane is expected during ammonia decomposition compared to operation in pure hydrogen environment.

Following the binary mixture permeation tests, single gas permeation tests were repeated in order to assess whether high operation temperature has an impact on the separation performance of the membrane. The hydrogen, nitrogen and ammonia permeation fluxes through the membrane were measured to be similar to those measured before the binary mixture permeation tests, indicating that the membrane separation properties were stable during operation at high temperatures. Pure hydrogen and nitrogen permeation tests were then repeated after the catalyst introduction in the reactor and, specifically, following the cooling and re-heating of the reactor prior to performing permeation tests under reacting conditions. The hydrogen permeation displayed a marginal increment, while nitrogen, which had previously remained undetectable during single gas permeation tests, became discernible. Particularly, for a ΔP of 1 bar and 450 °C the H₂ and N₂ permeances were measured to be $1.0 \cdot 10^{-7}$ and $3.8 \cdot 10^{-9}$, respectively, resulting in an ideal H₂/N₂ selectivity of 26; at 500 °C the H₂ and N₂ permeances were measured to be $1.1 \cdot 10^{-7}$ and $3.7 \cdot 10^{-9}$, respectively, resulting in an ideal H_2/N_2 selectivity of 29. A postmortem helium-ethanol leakage test confirmed the absence of defects on the membrane surface. However, the observed increase in N_2 permeation was attributed to the degradation of the membrane's sealing, which occurred during the cooling and reheating phases of the reactor's operation.

The performance of the membrane reactor for ammonia decomposition operated at 5 bar and under a feed flow rate of 500 Nml min⁻¹ of pure ammonia are reported in Table 2.3 and Figure 2.6 for different operating temperatures. In agreement with findings in the existing literature, a temperature increase yields an increase in both NH₃ conversion and H₂ recovery [8,19–25]. In fact, higher temperatures favor both the kinetics and thermodynamics of ammonia decomposition, leading to increased NH₃ conversion. This brings NH₃ conversion closer to the calculated thermodynamic

equilibrium conversion (without hydrogen separation membrane) for temperatures higher than 475 °C. Simultaneously, as NH_3 conversion increases, so does the hydrogen partial pressure in the reactor. This, in turn, results in a higher driving force for hydrogen separation and ultimately into a higher recovery.



Figure 2.6. NH_3 conversion, H_2 recovery, and residual NH_3 concentration in the permeate achieved in the membrane reactor as a function of reaction temperature (5 bar, 500 Nml min⁻¹ of pure NH_3).

From Table 2.3 and Figure 2.6 it is also noteworthy that a temperature increase has also a positive impact on hydrogen purity, as for increasing temperatures the residual NH₃ concentration in the permeate decreases. These results, which align with previous studies [24,26], can be ascribed to the fact that a lower amount of NH₃ is available for separation when temperature increases due to a higher NH₃ conversion. Although these results show that the H₂ obtained at the permeate side of the membrane reactor may not be directly used for systems requiring ultra-pure hydrogen as feedstock, the residual NH₃ concentration of the permeate stream was measured to be below 0.75 ppm downstream of the purification unit. These results, consistent with other studies reported in the literature [27–30], demonstrate that commercially available adsorbent materials are effective in reducing the residual ammonia concentration in the produced hydrogen stream to levels suitable for proton exchange membrane (PEM) fuel cells applications (ammonia concentration below 0.1 ppm).

Temperature	x_{NH_3}	HR	$y^P_{NH_3}$
(°C)	(%)	(%)	(%)
450	91.38 ± 0.29	8.15 ± 0.01	4.01 ± 0.08
475	97.87 ± 0.18	8.98 ± 0.13	1.30 ± 0.05
500	98.49 ± 0.05	9.84 ± 0.02	0.59 ± 0.00

Table 2.3. NH₃ conversion, H₂ recovery and NH₃ concentration in the permeate at different reaction temperatures (Reaction pressure of 5 bar, NH₃ feed flow rate of 500 Nml min⁻¹).

Table 2.4, divided into three sections, presents a comparison between the results achieved in this study, the results obtained in previous investigations using ceramic and metallic supported Pd-Ag membranes [26,31], and the outcomes of the study by Jiang et al. [10] involving a carbon membrane. The H₂ recovery and the NH₃ conversion achieved during ammonia decomposition follow a trend which is dependent on the hydrogen permeation properties of the membranes. Particularly, the lower hydrogen permeance and length of the membrane used in this work results in a lower H₂ recovery and NH₃ conversion compared to the ones achieved with Pd-based membranes in previous studies.

Carbon membranes show in fact lower hydrogen permeance compared to Pd-based membranes due to the different transport mechanism governing permeation. The different permeation mechanisms through the membrane also justifies the significantly lower selectivity towards hydrogen achieved in this study compared to the one achieved with Pd-Ag membranes. While in fact the selective layer of Pd-based membranes is dense and hydrogen permeation takes place because palladium acts as a catalyst for hydrogen splitting, the permeation of gases through a carbon membrane, being its selective layer porous, mainly depends on the pore size distribution, which enables also other gases to permeate in case pores with diameter larger than their kinetic diameter are available.

Accordingly, the residual ammonia concentration in the hydrogen produced in this study is significantly higher compared to the results achieved implementing Pd-based membranes for hydrogen separation. These results are well in agreement with the findings of Jiang et al. [10], who observed an increase in the residual NH_3 concentration in the hydrogen stream from approximately 50 to 10 000 ppm when replacing in their system for ammonia decomposition a 80 mm long 1.8 μ m thick Pd-Ag membrane with

a 220 mm long 0.9 μ m thick carbon membrane. From Table 2.4, it is possible to observe that Jiang et al. obtained much higher NH₃ conversion and H₂ recovery as well as lower residual NH₃ concentrations compared to the results obtained in this work. Although the results were obtained under different operating conditions, making a direct quantitative comparison between the two sets of outcomes challenging, better results in this work could be achieved through the optimization of the installed membrane area in relation to the amount of catalyst used and the residence time of NH₃ in the reactor.

In all the scenarios presented in Table 2.4, fuel cell-grade hydrogen containing residual NH_3 concentration greater than 0.1 ppm could not be achieved at the reactor outlet. This implies that the hydrogen produced in this systems may not directly be used as feedstock for PEM fuel cells. In a previous work [24], as well as in the work authored by Sitar et al. [32] the addition of a hydrogen purification stage downstream of the membrane reactor implementing Pd-based membranes was demonstrated to be an effective solution to produce fuel cell-grade hydrogen. A similar result was achieved in this work implementing downstream the reactor implementing a carbon membrane, an adsorption unit for residual NH_3 removal consisting of a fixed bed of zeolite 13X particles. In light of these results, this study demonstrates that carbon membranes, despite the requirement for scaling-up membrane length and potential enhancement in their H_2 permeation properties, represent a possible alternative to Pd-based membranes for the production of fuel cell-grade hydrogen. Carbon membranes are in fact less expensive compared to Pd-based membranes, thus the costs associated with the reaction unit are reduced upon their utilization.

	Cechetto et al. [31]	Cechetto et al. [33]	Jiang et al. [10]	This work
Catalyst type	Ru/Al ₂ O ₃	Ru/Al ₂ O ₃	Ru/Y/K/Al ₂ O ₃	Ru/Al ₂ O ₃
Ruthenium content (wt%)	2	2	3	2
Catalyst amount (g)	250	250	3	250
Reaction pressure (bar)	5	5	7	5
Permeate pressure (bar)	1	1	1	1
WHSV (Nml $h^{-1} g_{cat^{-1}}$)	120	120	5 000	120

Table 2.4. *(Section 1)* Comparison of experimental results from the present study and literature data: Reactor operating conditions.

	Cechetto et al. [31]	Cechetto et al. [33]	Jiang et al. [10]	This work
Membrane configuration	Tubular	Tubular	Tubular	Tubular
Support material	Al_2O_3	Hastelloy X	N/A	Al_2O_3
Selective layer composition	Pd-Ag	Pd-Ag	Carbon	Carbon
Selective layer thickness (µm)	~ 6 - 8	~ 6 - 8	~ 0.9	< 1
Membrane length (mm)	195	90	220	80
Membrane area (cm ²)	85.8	39.6	34.1	25.1
H2 permeance (mol s ⁻¹ m ⁻² Pa ⁻¹)	1.2.10-6	6.6.10-7	-	1.10-7
H ₂ /N ₂ ideal selectivity (-)	68 960	5 890	-	26

Table 2.4. *(Section 2)* Comparison of experimental results from the present study and literature data: Membrane characteristics and performance at 450 °C and 1 bar(g).

Table 2.4. *(Section 3)* Comparison of experimental results from the present study and literature data: Reactor performance.

	Cechetto et al. [31]	Cechetto et al. [33]	Jiang et al. [10]	This work
Temperature (°C)	NH ₃ conversion (%)			
450	99.7	98.2	98.9	91.4
475	99.8	99.2	-	97.9
500	99.8	99.3	-	98.5
Temperature (°C)	H ₂ recovery (%)			
450	87.8	55.5	93.7	8.2
475	88.9	60.7	-	9.0
500	88.9	62.9	-	9.8
Temperature (°C)	NH ₃ concentration in the permeate (%)			
450	11.8	-	< 10 000	40 000
475	6.1	-	-	13 000
500	1.6	-	-	6 000

2.5 Conclusions

In this work, a carbon membrane was prepared on a tubular porous alumina support and subsequently tested for H₂ separation during ammonia decomposition. Consistent with literature results, the H₂/N₂ mixture permeation tests demonstrated the membrane did not suffer from mass transfer limitation phenomena during permeation. No decrease in H₂ permeation flux through the membrane is thus expected during ammonia composition compared to operation under a pure hydrogen environment. During the experimental tests for ammonia decomposition reaction, NH₃ conversion exceeding 90% was achieved across the entire range of operating conditions investigated, with conversion approaching the thermodynamic equilibrium values at temperatures starting from 475 °C. The hydrogen recovered from NH₃ through the carbon membrane amounts to 8.2 – 9.8% in the temperature range of 450 and 500 °C.

Despite being a relatively low value for H_2 recovery, better results could be achieved in this study by optimizing the installed membrane area related to the catalyst amount used and the residence time of NH_3 within the reactor. This optimization could involve the implementation of additional membranes as well as the use of longer membranes, thereby increasing the effective membrane area, enhancing separation performance.

Although the hydrogen recovered on the permeate side of the reactor could not meet the purity specification required for PEM fuel cell applications, fuel cell-grade H₂ production could be achieved implementing a H₂ purification unit comprising a fixed bed of zeolite 13X downstream the reactor. Thus, while the H₂ separation performance of carbon-based membranes are far from being comparable with the ones achievable with Pd-based membranes, this work demonstrates that carbon membranes can still be regarded as a competitive alternative for the production of fuel cell-grade hydrogen.

Carbon membranes are less expensive compared to Pd-based membranes, thus the costs associated with the reaction unit are reduced upon their utilization. However, it must be mentioned that when designing a membrane reactor-assisted NH₃-to-H₂ system, it should be taken into account that the different separation performance of the implemented membranes affects the ultimate design of the system. On one hand, while the implementation of carbon membranes can lead to a decrease in the costs associated with the reaction unit, on the other hand, their lower selectivity towards H₂ may necessitate larger units for residual ammonia removal and, in the case of PEM fuel cells for on-board applications, a separate unit for residual N₂. The economic optimum of the system is therefore given by the design solution that minimizes the sum of the costs associated with both the reaction and the hydrogen purification units.

2.6 References

- Morlanés, N.; Katikaneni, S.P.; Paglieri, S.N.; Harale, A.; Solami, B.; Sarathy, S.M.; Gascon, J. A Technological Roadmap to the Ammonia Energy Economy: Current State and Missing Technologies. Chemical Engineering Journal 2021, 408, 127310, doi:10.1016/J.CEJ.2020.127310.
- 2. Cechetto, V.; Di Felice, L.; Gallucci, F. Advances and Perspectives of H2 Production from NH3 Decomposition in Membrane Reactors. Energy and Fuels 2023, 37, 10775–10798.
- Sun, S.; Jiang, Q.; Zhao, D.; Cao, T.; Sha, H.; Zhang, C.; Song, H.; Da, Z. Ammonia as Hydrogen Carrier: Advances in Ammonia Decomposition Catalysts for Promising Hydrogen Production. Renewable and Sustainable Energy Reviews 2022, 169.
- Le, T.A.; Kim, Y.; Kim, H.W.; Lee, S.U.; Kim, J.R.; Kim, T.W.; Lee, Y.J.; Chae, H.J. Ru-Supported Lanthania-Ceria Composite as an Efficient Catalyst for COx-Free H2 Production from Ammonia Decomposition. Appl Catal B 2021, 285, 119831, doi:10.1016/J.APCATB.2020.119831.
- Valera-Medina, A.; Amer-Hatem, F.; Azad, A.K.; Dedoussi, I.C.; De Joannon, M.; Fernandes, R.X.; Glarborg, P.; Hashemi, H.; He, X.; Mashruk, S.; et al. Review on Ammonia as a Potential Fuel: From Synthesis to Economics. Energy and Fuels 2021, 35, 6964–7029.
- 6. Valera-Medina, A.; Xiao, H.; Owen-Jones, M.; David, W.I.F.; Bowen, P.J. Ammonia for Power. Prog Energy Combust Sci 2018, 69, 63–102, doi:10.1016/J.PECS.2018.07.001.
- Zhang, Z.; Liguori, S.; Fuerst, T.F.; Way, J.D.; Wolden, C.A. Efficient Ammonia Decomposition in a Catalytic Membrane Reactor to Enable Hydrogen Storage and Utilization. ACS Sustain Chem Eng 2019, 7, 5975–5985, doi:10.1021/acssuschemeng.8b06065.
- Zhang, J.; Xu, H.; Li, W. High-Purity COx-Free H2 Generation from NH3 via the Ultra Permeable and Highly Selective Pd Membranes. J Memb Sci 2006, 277, 85–93, doi:10.1016/J.MEMSCI.2005.10.014.
- Itoh, N.; Oshima, A.; Suga, E.; Sato, T. Kinetic Enhancement of Ammonia Decomposition as a Chemical Hydrogen Carrier in Palladium Membrane Reactor. Catal Today 2014, 236, 70–76, doi:10.1016/j.cattod.2014.02.054.
- Jiang, J.; Dong, Q.; McCullough, K.; Lauterbach, J.; Li, S.; Yu, M. Novel Hollow Fiber Membrane Reactor for High Purity H2 Generation from Thermal Catalytic NH3 Decomposition. J Memb Sci 2021, 629, 119281, doi:10.1016/J.MEMSCI.2021.119281.
- 11. Rahimalimamaghani, A.; Pacheco Tanaka, D.A.; Llosa Tanco, M.A.; Neira D'Angelo, F.; Gallucci, F. Effect of Aluminium Acetyl Acetonate on the Hydrogen and Nitrogen

Permeation of Carbon Molecular Sieves Membranes. Int J Hydrogen Energy 2022, 47, 14570–14579, doi:10.1016/j.ijhydene.2022.02.198.

- 12. Rahimalimamaghani, A.; Pacheco Tanaka, D.A.; Llosa Tanco, M.A.; Neira D'Angelo, M.F.; Gallucci, F. Ultra-Selective CMSMs Derived from Resorcinol-Formaldehyde Resin for CO2 Separation. Membranes (Basel) 2022, 12, 1–21, doi:10.3390/membranes12090847.
- Gilron, J.; Soffer, A. Knudsen Diffusion in Microporous Carbon Membranes with Molecular Sieving Character. J Memb Sci 2002, 209, 339–352, doi:10.1016/S0376-7388(02)00074-1.
- Medrano, J.A.; Llosa-Tanco, M.A.; Cechetto, V.; Pacheco-Tanaka, D.A.; Gallucci, F. Upgrading Biogas with Novel Composite Carbon Molecular Sieve (CCMS) Membranes: Experimental and Techno-Economic Assessment. Chemical Engineering Journal 2020, 394, 124957, doi:10.1016/J.CEJ.2020.124957.
- Llosa Tanco, M.A.; Medrano, J.A.; Cechetto, V.; Gallucci, F.; Pacheco Tanaka, D.A. Hydrogen Permeation Studies of Composite Supported Alumina-Carbon Molecular Sieves Membranes: Separation of Diluted Hydrogen from Mixtures with Methane. Int J Hydrogen Energy 2021, 46, 19758–19767, doi:10.1016/J.IJHYDENE.2020.05.088.
- Llosa Tanco, M.A.; Pacheco Tanaka, D.A.; Rodrigues, S.C.; Texeira, M.; Mendes, A. Composite-Alumina-Carbon Molecular Sieve Membranes Prepared from Novolac Resin and Boehmite. Part I: Preparation, Characterization and Gas Permeation Studies. Int J Hydrogen Energy 2015, 40, 5653–5663, doi:10.1016/J.IJHYDENE.2015.02.112.
- 17. Suda, H.; Haraya, K. Gas Permeation through Micropores of Carbon Molecular Sieve Membranes Derived from Kapton Polyimide; 1997;
- Nordio, M.; Melendez, J.; van Sint Annaland, M.; Pacheco Tanaka, D.A.; Llosa Tanco, M.; Gallucci, F. Comparison between Carbon Molecular Sieve and Pd-Ag Membranes in H2-CH4 Separation at High Pressure. Int J Hydrogen Energy 2020, 45, 28876–28892, doi:10.1016/j.ijhydene.2020.07.191.
- Israni, S.H.; Nair, B.K.R.; Harold, M.P. Hydrogen Generation and Purification in a Composite Pd Hollow Fiber Membrane Reactor: Experiments and Modeling. Catal Today 2009, 139, 299–311, doi:10.1016/J.CATTOD.2008.02.020.
- Kim, T.W.; Lee, E.H.; Byun, S.; Seo, D.W.; Hwang, H.J.; Yoon, H.C.; Kim, H.; Ryi, S.K. Highly Selective Pd Composite Membrane on Porous Metal Support for High-Purity Hydrogen Production through Effective Ammonia Decomposition. Energy 2022, 260, 125209, doi:10.1016/J.ENERGY.2022.125209.
- 21. Cerrillo, J.L.; Morlanés, N.; Kulkarni, S.R.; Realpe, N.; Ramírez, A.; Katikaneni, S.P.; Paglieri, S.N.; Lee, K.; Harale, A.; Solami, B.; et al. High Purity, Self-Sustained, Pressurized Hydrogen

Production from Ammonia in a Catalytic Membrane Reactor. Chemical Engineering Journal 2022, 431, 134310, doi:10.1016/J.CEJ.2021.134310.

- 22. Liu, J.; Ju, X.; Tang, C.; Liu, L.; Li, H.; Chen, P. High Performance Stainless-Steel Supported Pd Membranes with a Finger-like and Gap Structure and Its Application in NH3 Decomposition Membrane Reactor. Chemical Engineering Journal 2020, 388, 124245, doi:10.1016/J.CEJ.2020.124245.
- 23. Rizzuto, E.; Palange, P.; Del Prete, Z. Characterization of an Ammonia Decomposition Process by Means of a Multifunctional Catalytic Membrane Reactor. Int J Hydrogen Energy 2014, 39, 11403–11410, doi:10.1016/J.IJHYDENE.2014.05.161.
- Cechetto, V.; Di Felice, L.; Gutierrez Martinez, R.; Arratibel Plazaola, A.; Gallucci, F. Ultra-Pure Hydrogen Production via Ammonia Decomposition in a Catalytic Membrane Reactor. Int J Hydrogen Energy 2022, 47, 21220–21230, doi:10.1016/J.IJHYDENE.2022.04.240.
- 25. Itoh, N.; Kikuchi, Y.; Furusawa, T.; Sato, T. Tube-Wall Catalytic Membrane Reactor for Hydrogen Production by Low-Temperature Ammonia Decomposition. Int J Hydrogen Energy 2021, 46, 20257–20265, doi:10.1016/J.IJHYDENE.2020.03.162.
- Cechetto, V.; Di Felice, L.; Medrano, J.A.; Makhloufi, C.; Zuniga, J.; Gallucci, F. H2 Production via Ammonia Decomposition in a Catalytic Membrane Reactor. Fuel Processing Technology 2021, 216, 106772, doi:10.1016/J.FUPROC.2021.106772.
- Cha, J.; Jo, Y.S.; Jeong, H.; Han, J.; Nam, S.W.; Song, K.H.; Yoon, C.W. Ammonia as an Efficient COX-Free Hydrogen Carrier: Fundamentals and Feasibility Analyses for Fuel Cell Applications. Appl Energy 2018, 224, 194–204, doi:10.1016/J.APENERGY.2018.04.100.
- Alagharu, V.; Palanki, S.; West, K.N. Analysis of Ammonia Decomposition Reactor to Generate Hydrogen for Fuel Cell Applications. J Power Sources 2010, 195, 829–833, doi:10.1016/J.JPOWSOUR.2009.08.024.
- 29. Chellappa, A.S.; Powell, M.R.; Fountain, M.; Call, C.J.; Godshall, N.A. COMPACT FUEL PROCESSORS FOR PEM FUEL CELLS;
- 30. Choudhary, T. V; Sivadinarayana, C.; Goodman, D.W. Catalytic Ammonia Decomposition: CO x-Free Hydrogen Production for Fuel Cell Applications; 2001; Vol. 72;.
- Cechetto, V.; Agnolin, S.; Di Felice, L.; Pacheco Tanaka, A.; Llosa Tanco, M.; Gallucci, F. Metallic Supported Pd-Ag Membranes for Simultaneous Ammonia Decomposition and H2 Separation in a Membrane Reactor: Experimental Proof of Concept. Catalysts 2023, 13, doi:10.3390/catal13060920.

- Sitar, R.; Shah, J.; Zhang, Z.; Wikoff, H.; Way, J.D.; Wolden, C.A. Compact Ammonia Reforming at Low Temperature Using Catalytic Membrane Reactors. J Memb Sci 2022, 644, 120147, doi:10.1016/J.MEMSCI.2021.120147.
- Cechetto, V.; Di, L.; Gutierrez, R. ScienceDirect Ultra-Pure Hydrogen Production via Ammonia Decomposition in a Catalytic Membrane Reactor. Int J Hydrogen Energy 2022, 47, 21220–21230, doi:10.1016/j.ijhydene.2022.04.240.

Chapter 3

Enhanced ammonia decomposition in a structured membrane reactor

This chapter is based on the following paper:

J. Zuniga, G. Anello, J. J. Aragón, M. del Mar Díaz de Guereñu, A. Arratibel, G. Marino, C. Italiano, A. Vita, F. Gallucci. "Enhanced ammonia decomposition in a Structured Membrane Reactor using a Ru-coated SiC Open-Cell Foam and a Pd-based membrane", Under review at International Journal of Hydrogen Energy.

Abstract

Ammonia decomposition into nitrogen and hydrogen has been, for the first time, carried in a structured membrane reactor in this work. The performance of the structured catalyst and the effect of hydrogen permeation through a Pd-based membrane were evaluated. The structured catalyst is based on a commercial silicon carbide 40 PPI open-cell foam. The catalyst (3 wt% Ru/CeO₂) was coated by in situsolution combustion deposition method with sequential cycles to reach the desired catalyst loading (0.31 g cm⁻³). TEM, SEM, XRD, TPR analysis and adhesion tests were used to characterize the prepared sample. A double-skinned palladium-based membrane was prepared depositing a selective layer by electroless plating onto a porous asymmetric α -Al₂O₃ support. The results demonstrated a successful integration of the structured catalyst with the membrane. The beneficial effects of the proposed structured membrane reactor configuration enabled an increase in conversion up to 29% compared with the structured catalyst system. Furthermore, at fixed flow rate, the structured membrane reactor can achieve comparable conversion at operating temperatures about 55 °C lower than in the case of the structured reactor. Moreover, the proposed configuration enabled a conversion higher than the thermodynamic value at 4 and 5.5 bar at fixed temperature (480 °C) and fixed feed flow rate (62 ml min⁻¹).

3.1 Introduction

In the previous chapters, the primary opportunities associated with membrane reactor technologies were highlighted. Conventional packed bed reactors (PBRs) and packed bed membrane reactors (PBMRs) are limited by heat and mass transfer phenomena, which can significantly impact the performance of the reactor. In membrane reactors, where separation and reaction occur simultaneously, managing heat distribution is crucial for optimal operation. One key challenge is ensuring uniform heat transfer across the membrane, as temperature gradients can cause uneven reaction rates or membrane degradation. For example, in high-temperature applications like hydrogen (H₂) production from ammonia (NH₃) decomposition, poor heat transfer can lead to localized hotspots, which not only affect catalyst performance but also increase the risk of membrane failure due to thermal stress. Furthermore, mass transfer limitations not only influence catalyst utilization efficiency, but also H₂ diffusion from reaction sites to the membrane surface. Parallelly, heat transfer limitations could inhibit fast heat supply and, as a consequence, hinder the endothermic catalytic NH₃ decomposition reaction and the membrane separation performance, as both phenomena are extremely sensitive to temperature. Moreover, in PBRs, the catalyst costs, primarily driven by the use of noble metal to maintain excellent catalytic activity, constitute a significant portion of total materials cost.

All the above mentioned limitations could be overcome by implementing a specialized structured network, which maximizes specific surface areas, improves catalysts utilization, enhances heat and mass transfer rates, and ultimately leads to compact, lightweight reactors with reduced overall manufacturing costs [1–3]. In this regard, structured catalysts such as open-cell foam (OCF) based catalysts, integrated with hydrogen-selective membranes in a structured membrane reactor (SMR) can represent a promising option to enhance the NH_3 decomposition process. Among all the different solutions that can be used as carriers to prepare structured catalysts, OCF with appreciable thermal conductivity can enhance radial and axial heat transport by two to three orders of magnitude due to heat conduction through their chaotic internal structure [4–6]. This property allows easier management of the heat involved in the reaction [7]. Structured systems can effectively enhance heat and mass transfer between reagents flow and channel walls, leading to improved temperature distribution throughout the reaction volume [8–10].

Thus, the focus of this work is to evaluate the performance of a structured OCF-based catalyst, coupled with a Pd-based membrane in a SMR, for the ammonia decomposition

reaction. The Pd-based membrane was fabricated realizing a Pd-Ag-based selective layer, deposited by electroless plating, onto a commercial porous asymmetric α -Al₂O₃ support. Prior to tests with Pd-membrane, the performance of the structured catalyst was evaluated closing the permeate side, simulating a structured reactor (SR) system.

The activity tests were conducted using a Ru-based structured catalyst prepared from a commercial silicon carbide (SiC) OCF. This carrier was loaded with a 3 wt% Ru/CeO₂ catalyst as active phase, prepared via In Situ-Solution Combustion Deposition (IS-SCD) method [11,12]. The catalytic system was characterized by X-Ray Diffraction (XRD), Temperature Programmed Reduction (TPR), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), and adhesion tests. Finally, the enhancement of NH₃ decomposition performance in a SMR was investigated.

3.2 Experimental

3.2.1 Structured catalyst preparation

3 wt% Ru/CeO₂ catalytic layers were deposited on a commercial 40 PPI SiC-based OCF (Lanik s.r.o., Czech Republic) via IS-SCD method. The SiC-based support was supplied with proper geometric features to host a tubular membrane with an outer diameter of 14 mm. The geometrical parameters and the physical properties of the OCF employed in this study are detailed in Table 3.1.

iouni employeu în tins study.		
Pore density	(ppi)	40
Diameter	(mm)	40
Length	(mm)	100
Hole area	(mm ²)	1.05
Pore diameter	(mm)	1.13
Strut thickness	(mm)	0.35
Face diameter	(mm)	1.48
Thermal conductivity	(W m ⁻¹ K ⁻¹)	0.40
Void fraction	(-)	0.85
Bed porosity	(%)	85.5
Geometric surface area	(m ² m ⁻³)	1 243
Exposed surface area	(mm²)	1 463

 Table 3.1. Geometrical and physical properties of the open-cell

 foam employed in this study

The IS-SCD method is based on the Solution Combustion Synthesis (SCS) that is a complex self-sustained chemical process, initiated in a homogeneous solution of precursors. This synthesis method involves an exothermic, rapid and self-sustaining chemical reaction where the combustion reactions supply the required heat. Details on SCS and the deposition procedure are extensively reported in previous works [13–17]. Briefly, before use, the OCF employed as support was cleaned using a water/acetone solution (50:50 vol.%) in ultrasonic bath for 30 minutes at room temperature and dried at 120 °C for 1 hour. Subsequently, 31.23 g of catalyst (0.31g cm⁻³) was deposited on the foam dipping the support in a aqueous solution containing high-purity reagents (Sigma-Aldrich[®], Massachusetts, USA). Specifically, cerium (III) nitrate hexahydrate $(Ce(NO_3)_3 \cdot 6H_2O)$ and ruthenium nitrosyl nitrate $(Ru(NO)(NO_3)_x(OH)_y, x + y = 3)$ were used as precursors of the ruthenium and cerium oxide components, respectively, while urea (CH₄N₂O) was employed as fuel. Multiple cycles were needed to deposit the designed amount of active phase. In each cycle, IS-SCD starts with dehydration and thermal decomposition of the homogeneous solution and involves several thermally coupled exothermic reactions, which result in the formation of a homogeneous distributed catalytic layer on the OCF, associated with a large amount of gases released.



Figure 3.1. Photographs of (left) bare and (right) coated 40 PPI SiC-based OCF.

The resulting structured catalysts were finally calcined at 600 °C in static air for 2 hours. Figure 3.1 shows the photographs of the bare and coated SiC open-cell foam. Details on calculations are reported in a previous work [18]. The large hole in the middle of the structure allows for membrane installation while the three small holes can be used for either installing thermocouples or for installing vertical supports.

3.2.2 Structured catalyst characterization

In this study, a comprehensive analysis of the synthesized catalyst was performed. Various characterization techniques were utilized to determine the structural, morphological, and chemical properties of the catalyst. These techniques include X-ray diffraction (XRD) for phase identification. XRD analysis was performed on D8 Advance diffractometer (Bruker Corporation, Massachusetts, USA) equipped with Cu K α radiation (λ = 1.5418 Å, 50 kW, 40 mA) at a scan rate of 1.5 deg min⁻¹ for a diffraction angle range about 23 – 80 degrees. The peaks were assigned using the PCPFWIN database.

H₂ temperature programmed reduction (H₂-TPR) analysis was performed on a ChemiSorb 2750 (Micromeritics[®], Georgia, USA) equipped with a thermal conductivity detector (TCD). In a typical H₂-TPR test, the as-calcined catalyst was reduced by a 5 vol.% H₂/Ar gas mixture (30 Nml min⁻¹) while the temperature was increased from room temperature to 1 000 °C at a rate of 20 °C min⁻¹. The hydrogen consumption was determined based on the H₂-TPR patterns of known amounts of CuO. The Multivolume Pycnometer 1305 (Micromeritics[®], Georgia, USA) was used to obtain true volume and relative densities/porosities of powders and OCFs. The chamber containing the sample is first pressurized with helium. Next, expansion of this gas into a precisely measured volume results in a pressure drop. The sample volume, density and porosity are then easily calculated from the two pressure readings as displayed on the digital indicator.

Detailed morphological and structural analysis was performed through Transmission Electron Microscopy (TEM) and High Resolution Transmission Electron Microscopy (HR-TEM) analyses were performed using a JEM-F200 microscope (JEOL Ltd., Tokyo) equipped with a Field Emission Gun (FEG) operating at 200 kV with a point resolution of 2.3 Å. The reduced samples were subjected to ultrasonic irradiation in isopropyl alcohol and dispersed over holey carbon copper grids. Scanning Electron Microscope (SEM) analysis was performed employing a XL-30 FEG scanning electron microscope (Philips N.V., The Netherlands) operated at 5 - 20 kV. The fully automated VHX-7000 digital optical microscope (Keyence, Japan) was used to capture high-resolution images of the coated catalytic layer. The mechanical strength of the coated catalytic layer was evaluated by ultrasonic treatment (USC 900D, 45 kHz, 130 W) in 50 vol.% petroleum ether solution. The weight loss percentage refers to the amount of deposited catalyst.

3.2.3 Palladium-based membrane preparation and experimental setup

Parallelly, a double-skinned Pd-based membrane was prepared as previously reported by Arratibel et al. [19] onto a tubular porous asymmetric α -Al₂O₃ support (Rauschert Kloster Veilsdorf, Germany) with an outer and inner diameter of 14 and 10 mm, respectively. The pore size at the outer layer of the support is 100 nm. A Pd-Ag-based selective layer of about 4 – 5 µm-thick was simultaneously deposited by electroless plating, followed by an annealing treatment at 550 °C for 4 hours. The selective layer was then coated with a mesoporous YSZ/ γ -Al₂O₃ (~ 1 µm-thick) layer by dip-coating and calcined at 550 °C. The so-prepared membrane (104 mm long) was integrated with the Ru-based structured catalyst (100 mm long) produced for this work. After that, the membrane was sealed with graphitic ferrules and the assembly (see Figure 3.2) was connected to the reactor flange. The catalytic activity tests were conducted feeding pure ammonia to the reactor where it decomposes to produce nitrogen and hydrogen employing the experimental setup reported in Figure 3.3.



Figure 3.2. Pd-based membrane surrounded by the Ru-based structured catalyst.



Figure 3.3. Schematic representation of the experimental setup used in this work.

The feed flow rate was controlled by EL-FLOW® mass flow controllers (Bronkhorst®, The Netherlands), while the retentate side pressure is regulated by an EL-PRESS® pressure controller (Bronkhorst®, The Netherlands). The permeate side was operated at atmospheric pressure, while the permeated flow was measured with a mass flow meter (Bronkhorst®, The Netherlands). Then, the permeated gases were analyzed with a 990 Micro Gas Chromatograph System (Agilent Technologies Inc., California, USA) equipped with a TCD, while the retentate stream was analyzed with a 7890A Gas Chromatograph System (Agilent Technologies Inc., California, USA), also equipped with a TCD. After determining the composition of both the retentate and permeate streams, the gas flows underwent a cleaning step to remove the residual ammonia.

Once the membrane-catalyst assembly is loaded into the reactor, a heating procedure under N_2 atmosphere takes place, reaching 400 °C with a heating rate of 3 °C min⁻¹. Nitrogen permeation was checked at 5 bar before membrane activation. The palladium membrane was activated feeding a gas mixture with low oxygen content (5 vol.% O_2 , 95 vol% N_2) for 2 minutes. Then, the system is flushed with nitrogen to remove the oxygen present into the reactor. Before starting the experiment with ammonia, hydrogen permeation through the membrane was measured at 400 °C and 1 bar of pressure difference between the retentate and the permeate side.

In this study, the ammonia decomposition reaction experiments were performed in the temperature range 380 - 480 °C, in the reaction pressure range 2.6 - 5.5 bar and for different feed flow rates (62 - 300 Nml min⁻¹). Subsequently, the ammonia conversion (x_{NH_3}) and the H₂ recovery (*HR*) were calculated according to Equations 3.1 and Equation 3.2, respectively.

$$x_{NH_3} = \frac{F_{NH_3,in} - F_{NH_3,out}}{F_{NH_3,in}} \cdot 100$$
(3.1)

$$H_2 recovery = \frac{2 \cdot F_{H_2,out}^p}{3 \cdot F_{NH_3,in}} \cdot 100$$
(3.2)

As benchmark for the structured membrane reactor performance, experimental results for the structured reactor were obtained with the catalyst loaded into the same reactor closing the permeate side under the same reaction conditions.

3.3 Results and discussion

3.3.1 <u>Structured catalyst characterization</u>

XRD analysis (Figure 3.4) was used to identify the crystal phases of 3 wt% Ru/CeO₂ catalyst deposited on the OCF support. The diffraction patterns of this catalyst, collected in the diffraction angle range of 23 – 80 degrees, show the typical peaks characteristic of the fluorite structure of ceria, corresponding to the (111), (200), (220), (311), (222), and (400) planes (JCPDS card No. 34 – 0394) [20]. The peaks are located at diffraction angles of 28.59°, 33.12°, 47.54°, 56.42°, 59.18° and 69.49°. Weak diffraction peaks related to the RuO₂ phase (JCPDS card No. 21 – 1172) are also present at diffraction angles of 35.2°, 40.2° and 54.4°. There is a slight shift towards higher angles of the CeO₂ peaks, suggesting the formation of a solid solution (Ru-O-Ce) through the partial incorporation of Ru (ionic radius = 0.62 Å) into the CeO₂ matrix (ionic radius = 0.97 Å). Crystallite size was calculated using Scherrer equation, from the most intense reflection observed for CeO₂ (111) crystallographic structures, the obtained value was approximately 12.5 nm.



Figure 3.4. XRD patterns of the prepared 3 wt% Ru/CeO₂ catalyst.

The reducibility of the synthesized samples was studied by H₂-TPR, and the results are displayed in Figure 3.5. The signal at the highest temperature (819 °C) corresponds to the reduction of the structural ceria lattice. The H₂ reduction profile in the low temperature zone (20 - 200 °C) shows a double peak, indicating the presence of
different types of ruthenium species interacting with the substrate with a different degree of strength. The reduction peaks centered at 81 °C could be assigned to the adsorbed oxygen or well dispersed ruthenium species interacting strongly with CeO₂ surface [21]. The reduction peak at 137 °C, on the other hand, could be attributed to the reduction of RuO_x particles that weakly interacted with CeO₂ surface [22]. The peaks between 200 and 400 °C are generally attributed to the reduction of the support at low temperature (ceria surface) [23]. The experimental hydrogen consumption and the relative reducibility of the synthesized sample were also calculated. The calculated hydrogen consumption was 15.62 mmol_{H₂} g_{RuO₂}⁻¹, leading to a reduction of 92.52%.



Figure 3.5. H₂-TPR profiles of the prepared 3 wt% Ru/CeO₂ catalyst.

Figure 3.6 shows the TEM micrographs of the catalyst deposited onto the SiC-based OCF. Agglomerated catalyst particles with a prevalent regular circular shape, ranging in size from 30 to 127 nm, were evidenced (Figure 3.6a). Ruthenium could not be distinguished on all catalysts particles even based on the magnified TEM images (Figure 3.6b), which probably attributed to the smaller size of ruthenium highly dispersed over CeO₂ and to the formation of Ru-O-Ce solid solution in agreement with XRD and TPR results. More specifically, the magnified image in Figure 3.6c shows fringes with d-spacing of 0.21 and 0.31 nm, attributed to the (101) and (111) planes of ruthenium and cerium oxide, respectively.



Figure 3.6. TEM micrographs of catalytic layer scraped from fresh coated SiC-OCF.

The SEM images of the bare OCF are presented in Figure 3.7. The micrographs display a sufficiently rough surface, thus confirming that no special treatment is required for applying the catalytic layer. This type of morphology, characterized by the presence of multiple anchorage points, allows the catalytic layer to bind strongly to the substrate.



Figure 3.7. SEM micrographs: (a) bare and (b) detail of the bare OCF surface.



Figure 3.8. Optical microscope images: (a) view of the catalytic layer deposited on the OCF and (b) cross-section view of catalytic layer thickness.

A homogeneous morphology of the catalytic layer was also evidenced in Figure 3.8a. Despite the relatively high catalyst loading (0.31 g cm⁻³), the structured catalyst shows the absence of pore-blocking phenomena. This feature highlights the methodical and controlled deposition of the layer throughout the combustion process, preventing any local accumulation. These finer details are crucial for ensuring precise control over the coating process, especially when dealing with complex 3D structures. As shown in Figure 3.8b, the cross-section views obtained by intentionally breaking off a small part (strut) of the structure show a good interconnection between the support and the coated layer. The catalytic layer thickness appears to be in the range of 23.8 – 26.6 µm.

3.3.2 Structured membrane reactor performance evaluation

The performance of the structured membrane reactor for the ammonia decomposition reaction was evaluated as a function of temperature, pressure and ammonia inlet flowrate. The relevant parameters evaluated include ammonia conversion, H_2 recovery and H_2 purity. In order to show the benefits of introducing a Pd-based membrane for hydrogen separation in a structured reactor, firstly, ammonia conversion was measured over the structured catalyst, closing the permeate and directing all the obtained products through the retentate, thereby simulating the operation of a structured reactor. The achieved results were used as reference. Then, to evaluate the performace of the structured membrane reactor, the permeate line was opened, allowing the gases to flow through the membrane. Figure 3.9 displays the evolution of SMR performance as a function of the reaction temperature at fixed pressure (4 bar) and fixed flow rate (62 ml min⁻¹).

The integration of the Ru-based structured catalyst with the Pd-based membrane increased the ammonia conversion at lower temperatures, as it is depicted in Figure 3.9a. In this figure, it is possible to observe that more than 70% of conversion can be reached already at 380 °C. This suggests that a high conversion per pass is achievable. As expected, given the endothermicity of the reaction and the low decomposition rate, for both structured reactor and structured membrane reactor the ammonia conversion is significanty limited at lower temperatures and it increases sharply as the temperature is increased, as also reported in [24].

Furthermore, at fixed flow rate, the SMR can achieve comparable conversion at operating temperatures approximately 55 °C lower than in the case of SR. It is worth noting that the equilibrium conversion was approached in the SMR already at 425 °C. In agreement with other literature studies [25,26], the results demonstrate the benefits of the membrane reactor technolgy, such as an ammonia conversion up to 29% higher then a conventional reactor. Furthermore, the SMR reached 98.4% conversion at 450 °C, with a corresponding hydrogen purity of 99.2%.



Figure 3.9. (a) Ammonia conversion and (b) hydrogen purity and hydrogen recovery as a function of rection temperature at fixed pressure (4 bar) and feed flow rate (62 Nml min⁻¹).

Figure 3.10a displays the impact of the operating pressure on the performance of both SR and SMR configurations. Ammonia conversion in the SMR increases along with the operating pressure, whereas in the SR increasing the pressure has a detrimental effect. Furthermore, Figure 3.10b shows that operating pressure affects H_2 recovery, as increasing pressure, the driving force for permeation increases parallely, this, in turn, enhances recovery. Moreover, the hydrogen permeation through the membrane decreases the concentration of hydrogen on the retentate side, thus subtracting a product of the reaction and shifting the equilibrium, according with the Le Châtelier's principle. The results presented are in line with previous studies, that report a higher ammonia conversion in membrane reactor sytstems compared to conventional systems [27]. Notably, according to the Temkin-Pyzhev rate mechanism, hydrogen has an inhibitory effect on the ammonia decomposition reaction kinetic. This effect has been reported for Ru-, Pt- and Fe-based ammonia decomposition catalysts. As a result, the enhanced ammonia conversion can also be attributed to a kinetic effect due to hydrogen removal from the reaction evironnement [28,29]. Even though the increased pressure has a negative effect on the equilibrium, yet at 4 and 5.5 bar the SMR overcomes the equilibrium limits.

On the other hand, the increase of pressure has a negative effect on the hydrogen purity in the permeate stream. This can be attributed to the permeation mechanism of nitrogen and hydrogen through the membrane. Increasing the pressure leads to a higher nitrogen partial pressure in the reactor. As nitrogen permeation increases linearly with the nitrogen partial pressure, whereas hydrogen permeation increases with the square root of the pressure difference, a pressure increase has a higher impact on nitrogen flux rather than the hydrogen flux. Thus, increasing the operating pressure reduces the purity of hydrogen separated by the membrane, but results in a higher recovery of hydrogen.



Figure 3.10. (a) Ammonia conversion and (b) hydrogen purity and hydrogen recovery as a function of reaction pressure at fixed temperature ($480 \,^{\circ}$ C) and feed flow rate ($62 \,$ Nml min⁻¹).



Figure 3.11. Ammonia conversion as a function of rection temperature at different pressures, with a fixed feed flow rate $(62 \text{ Nml min}^{-1})$ in the structured membrane reactor.

Figure 3.11 shows the ammonia conversion as a function of the reaction temperature for the SMR in all the range of pressure tested. As previously discussed with respect to Figure 3.9, ammonia conversion in the SMR increases along with the operating temperature, in all the range of pressures tested. However, in a membrane reactor for ammonia decomposition the pressure increase has two main opposite effects. On one hand, ammonia conversion is positively influenced by pressure as an additional driving force for hydrogen permeation, that removes one of the products, shifting the equilibrium according to the Le Châtelier's principle. On the contrary, ammonia conversion is negatively influenced by pressure as the ammonia decomposition reaction, which proceeds with a volume increase, is thermodinamically favoured at low pressures. The presence of this two opposite effects can explain why the higher conversion was achived at 4 bar at 380 °C.

Figure 3.12 shows the effect of the ammonia feed flow rate on reaction performance for both the reaction systems operated at 480 °C and 4 bar. Specifically, for both SR and SMR configurations, ammonia conversion decreases as the ammonia feed flow rate increases. Parallelly, the obtained results show a lower H_2 recovery, due to the lower residence time, which corresponds to a higher hydrogen purity, reaching up to 99.8%.



Figure 3.12. (a) Ammonia conversion and (b) hydrogen purity and hydrogen recovery as a function of the ammonia feed flow rate at fixed temperature (480 °C) and pressure (4 bar).

A successful integration between the properties of the fabricated structured catalyst and the developed membrane was achieved in this study. Moreover, the SiC-based OCF employed as carrier for the catalytic layer in this work exhibits high thermostability, thermal conductivity, mechanical strength, and chemical inertness. The ability of this material to maintain a homogeneous temperature distribution within the structured catalyst during the ammonia decomposition reaction has also been confirmed in previous literature [30]. Furthermore, Pd-based membranes are highly effective for hydrogen separation, however they operate within a specific temperature range of 400 to 550 °C [31]. This necessitates the use of catalysts that are active within this temperature range.

The combination of the catalyst and membrane examined in this work fulfills these requirements, ensuring alignment of the working functions of both components. The beneficial effect of the structured catalyst on ammonia conversion might be linked to the endothermic nature of the reaction. As such, for the ammonia decomposition reaction, the efficient radial heat transport and high radial mixing ensured by the structured catalyst can play a crucial role for enhancing hydrogen production [32,33]. Furthermore, the large ratio between the geometric reaction surface area and the reaction volume, along with the enanched heat transfer rate per unit volume, contributed to the improved performance of the SMR reported in this work. Owing to the enanched heat and mass transfer, the structured catalysts can represent a valid substitute of ceramic pellet catalysts in ammonia decomposition, ensuring an efficient and compact reactor design [34].

3.4 Conclusions

A Ru-based structured catalyst was produced by depositing a 3 wt% Ru/CeO₂ catalytic layer via In Situ-Solution Combustion Deposition method on a commercial 40 PPI SiC-based open-cell foam. The resulting thin and uniform catalytic layer showed an excellent adhesion strength revealed by a weight loss of 1.7%. Parallely, a palladium-based membrane was fabricated, depositing a thin palladium layer on a porous alumina support by electroless plating. Then, the structured catalyst and the membrane were integrated in a structured memerbane reactor and tested for ammonia decomposition reaction. Results showed that the addition of the Pd-based membrane to the system leads to an increase in conversion up to 29% compared with the catalyst alone in the structured reactor configuration.

Furthermore, at a fixed flow rate, the structured membrane reactor can achieve comparable ammonia conversion at operating temperatures approximately 55 °C lower than that in a structured reactor. Moreover, the operating pressure was proved to have a significant impact on the reactor performance. More specifically, the structured membrane reactor was able ot overcome the equilibrium limitations at 4 and 5.5 bar at fixed temperature (480 °C) and feed flow rate (62 Nml min⁻¹). The advantageous effects of the structured catalyst for ammonia conversion may be linked to the efficient radial heat transport and high radial mixing, which are crucial for enhancing hydrogen production. These results open up a new route for ammonia decomposition in more compact and volumetrically efficient reactors.

3.5 References

- Ho, P.H.; Sanghez De Luna, G.; Ospitali, F.; Fornasari, G.; Vaccari, A.; Benito, P. Open-Cell Foams Coated by Ni/X/Al Hydrotalcite-Type Derived Catalysts (X = Ce, La, Y) for CO2methanation. Journal of CO2 Utilization 2020, 42, doi:10.1016/j.jcou.2020.101327.
- Vita, A.; Pino, L.; Cipit, F.; Lagan, M.; Recupero, V. Structured Reactors as Alternative to Pellets Catalyst for Propane Oxidative Steam Reforming. Int J Hydrogen Energy 2010, 35, 9810–9817, doi:10.1016/j.ijhydene.2010.03.140.
- Kiewidt, L.; Thöming, J. Multiscale Modeling of Monolithic Sponges as Catalyst Carrier for the Methanation of Carbon Dioxide. Chemical Engineering Science: X 2019, 2, 100016, doi:10.1016/j.cesx.2019.100016.
- 4. Bracconi, M.; Ambrosetti, M.; Maestri, M.; Groppi, G.; Tronconi, E. A Fundamental Analysis of the Influence of the Geometrical Properties on the Effective Thermal Conductivity of Open-Cell Foams. Chemical Engineering and Processing - Process Intensification 2018, 129, 181–189, doi:10.1016/j.cep.2018.04.018.
- Frey, M.; Romero, T.; Roger, A.C.; Edouard, D. Open Cell Foam Catalysts for CO2 Methanation: Presentation of Coating Procedures and in Situ Exothermicity Reaction Study by Infrared Thermography. Catal Today 2016, 273, 83–90, doi:10.1016/j.cattod.2016.03.016.
- 6. Tronconi, E.; Groppi, G.; Visconti, C.G. Structured Catalysts for Non-Adiabatic Applications. Curr Opin Chem Eng 2014, 5, 55–67, doi:10.1016/j.coche.2014.04.003.
- Frey, M.; Bengaouer, A.; Geffraye, G.; Edouard, D.; Roger, A.C. Aluminum Open Cell Foams as Efficient Supports for Carbon Dioxide Methanation Catalysts: Pilot-Scale Reaction Results. Energy Technology 2017, 5, 2078–2085, doi:10.1002/ente.201700188.
- 8. Bianchi, E.; Heidig, T.; Visconti, C.G.; Groppi, G.; Freund, H.; Tronconi, E. Heat Transfer Properties of Metal Foam Supports for Structured Catalysts: Wall Heat Transfer Coefficient. Catal Today 2013, 216, 121–134, doi:10.1016/j.cattod.2013.06.019.
- 9. Bracconi, M.; Ambrosetti, M.; Maestri, M.; Groppi, G.; Tronconi, E. A Fundamental Investigation of Gas/Solid Mass Transfer in Open-Cell Foams Using a Combined Experimental and CFD Approach. Chemical Engineering Journal 2018, 352, 558–571, doi:10.1016/j.cej.2018.07.023.
- Moncada Quintero, C.W.; Ercolino, G.; Poozhikunnath, A.; Maric, R.; Specchia, S. Analysis of Heat and Mass Transfer Limitations for the Combustion of Methane Emissions on PdO/Co304 Coated on Ceramic Open Cell Foams. Chemical Engineering Journal 2021, 405, 126970, doi:10.1016/j.cej.2020.126970.

- 11. Ricca, A.; Truda, L.; Palma, V. Study of the Role of Chemical Support and Structured Carrier on the CO2 Methanation Reaction. Chemical Engineering Journal 2019, 377, 120461, doi:10.1016/j.cej.2018.11.159.
- 12. Moncada Quintero, C.W.; Ercolino, G.; Poozhikunnath, A.; Maric, R.; Specchia, S. Analysis of Heat and Mass Transfer Limitations for the Combustion of Methane Emissions on PdO/Co304 Coated on Ceramic Open Cell Foams. Chemical Engineering Journal 2021, 405, 126970, doi:10.1016/j.cej.2020.126970.
- Italiano, C.; Drago Ferrante, G.; Pino, L.; Laganà, M.; Ferraro, M.; Antonucci, V.; Vita, A. Silicon Carbide and Alumina Open-Cell Foams Activated by Ni/CeO2-ZrO2 Catalyst for CO2 Methanation in a Heat-Exchanger Reactor. Chemical Engineering Journal 2022, 434, doi:10.1016/j.cej.2022.134685.
- Liu, L.; Yao, Z.; Deng, Y.; Gao, F.; Liu, B.; Dong, L. Morphology and Crystal-Plane Effects of Nanoscale Ceria on the Activity of CuO/CeO2 for NO Reduction by CO. ChemCatChem 2011, 3, 978–989, doi:10.1002/cctc.201000320.
- Gil, S.; Garcia-Vargas, J.M.; Liotta, L.F.; Pantaleo, G.; Ousmane, M.; Retailleau, L.; Giroir-Fendler, A. Catalytic Oxidation of Propene over Pd Catalysts Supported on CeO2, TiO2, Al2O3and M/Al2O3oxides (M = Ce, Ti, Fe, Mn). Catalysts 2015, 5, 671–689, doi:10.3390/catal5020671.
- Italiano, C.; Llorca, J.; Pino, L.; Ferraro, M.; Antonucci, V.; Vita, A. CO and CO2 Methanation over Ni Catalysts Supported on CeO2, Al2O3 and Y2O3 Oxides. Appl Catal B 2020, 264, 118494, doi:10.1016/j.apcatb.2019.118494.
- 17. Chen, L.; Zhou, W.; Huo, C.; Li, L.; Cui, M.; Qiao, X.; Fei, Z. Improved Metal-Support Interaction in Ru/CeO2 Catalyst via Plasma-Treated Strategy for Dichloroethane Oxidation. Appl Catal A Gen 2023, 660, 119215, doi:10.1016/j.apcata.2023.119215.
- Italiano, C.; Drago Ferrante, G.; Pino, L.; Laganà, M.; Ferraro, M.; Antonucci, V.; Vita, A. Silicon Carbide and Alumina Open-Cell Foams Activated by Ni/CeO2-ZrO2 Catalyst for CO2 Methanation in a Heat-Exchanger Reactor. Chemical Engineering Journal 2022, 434, doi:10.1016/j.cej.2022.134685.
- Arratibel, A.; Pacheco Tanaka, A.; Laso, I.; van Sint Annaland, M.; Gallucci, F. Development of Pd-Based Double-Skinned Membranes for Hydrogen Production in Fluidized Bed Membrane Reactors. J Memb Sci 2018, 550, 536–544, doi:10.1016/j.memsci.2017.10.064.
- 20. Liu, P.; Niu, R.; Li, W.; Wang, S.; Li, J. Morphology Effect of Ceria on the Ammonia Synthesis Activity of Ru/CeO 2 Catalysts. Catal Letters 2019, 149, 1007–1016, doi:10.1007/s10562-019-02674-1.

- 21. Lin, B.; Liu, Y.; Heng, L.; Wang, X.; Ni, J.; Lin, J.; Jiang, L. Morphology Effect of Ceria on the Catalytic Performances of Ru/CeO2 Catalysts for Ammonia Synthesis. Industrial & amp; Engineering Chemistry Research 2018, 57, 9127–9135, doi:10.1021/acs.iecr.8b02126.
- Gil, S.; Garcia-Vargas, J.M.; Liotta, L.F.; Pantaleo, G.; Ousmane, M.; Retailleau, L.; Giroir-Fendler, A. Catalytic Oxidation of Propene over Pd Catalysts Supported on CeO2, TiO2, Al2O3and M/Al2O3oxides (M = Ce, Ti, Fe, Mn). Catalysts 2015, 5, 671–689, doi:10.3390/catal5020671.
- 23. Chen, L.; Zhou, W.; Huo, C.; Li, L.; Cui, M.; Qiao, X.; Fei, Z. Improved Metal-Support Interaction in Ru/CeO2 Catalyst via Plasma-Treated Strategy for Dichloroethane Oxidation. Appl Catal A Gen 2023, 660, 119215, doi:10.1016/j.apcata.2023.119215.
- Itoh, N.; Oshima, A.; Suga, E.; Sato, T. Kinetic Enhancement of Ammonia Decomposition as a Chemical Hydrogen Carrier in Palladium Membrane Reactor. Catal Today 2014, 236, 70–76, doi:https://doi.org/10.1016/j.cattod.2014.02.054.
- García-García, F.R.; Ma, Y.H.; Rodríguez-Ramos, I.; Guerrero-Ruiz, A. High Purity Hydrogen Production by Low Temperature Catalytic Ammonia Decomposition in a Multifunctional Membrane Reactor. Catal Commun 2008, 9, 482–486, doi:10.1016/j.catcom.2007.07.036.
- 26. Lee, J.E.; Lee, J.; Jeong, H.; Park, Y.K.; Kim, B.S. Catalytic Ammonia Decomposition to Produce Hydrogen: A Mini-Review. Chemical Engineering Journal 2023, 475, 146108, doi:10.1016/j.cej.2023.146108.
- 27. Liu, J.; Ju, X.; Tang, C.; Liu, L.; Li, H.; Chen, P. High Performance Stainless-Steel Supported Pd Membranes with a Finger-like and Gap Structure and Its Application in NH3 Decomposition Membrane Reactor. Chemical Engineering Journal 2020, 388, 124245, doi:https://doi.org/10.1016/j.cej.2020.124245.
- Lamb, K.; Hla, S.S.; Dolan, M. Ammonia Decomposition Kinetics over LiOH-Promoted, A-Al2O3-Supported Ru Catalyst. Int J Hydrogen Energy 2019, 44, 3726–3736, doi:10.1016/j.ijhydene.2018.12.123.
- Di Carlo, A.; Vecchione, L.; Del Prete, Z. Ammonia Decomposition over Commercial Ru/Al2O3 Catalyst: An Experimental Evaluation at Different Operative Pressures and Temperatures. Int J Hydrogen Energy 2014, 39, 808–814, doi:10.1016/j.ijhydene.2013.10.110.
- Pinzón, M.; Romero, A.; de Lucas Consuegra, A.; de la Osa, A.R.; Sánchez, P. Hydrogen Production by Ammonia Decomposition over Ruthenium Supported on SiC Catalyst. Journal of Industrial and Engineering Chemistry 2021, 94, 326–335, doi:10.1016/j.jiec.2020.11.003.

- Cerrillo, J.L.; Morlanés, N.; Kulkarni, S.R.; Realpe, N.; Ramírez, A.; Katikaneni, S.P.; Paglieri, S.N.; Lee, K.; Harale, A.; Solami, B.; et al. High Purity, Self-Sustained, Pressurized Hydrogen Production from Ammonia in a Catalytic Membrane Reactor. Chemical Engineering Journal 2022, 431, doi:10.1016/j.cej.2021.134310.
- Young, K.; Been, H.; Song, D.; Jung, U. ScienceDirect Ammonia Decomposition over Ru-Coated Metal- Structured Catalysts for COx-Free Hydrogen Production. Int J Hydrogen Energy 2023, 52, 534–545, doi:10.1016/j.ijhydene.2023.08.004.
- 33. Sinn, C.; Wentrup, J.; Pesch, G.R.; Thöming, J.; Kiewidt, L. Chemical Engineering Research and Design Structure-Heat Transport Analysis of Periodic Open-Cell Foams to Be Used as Catalyst Carriers. 2020, 6, 209–219, doi:10.1016/j.cherd.2020.12.007.
- Ho, P.H.; Ambrosetti, M.; Groppi, G.; Tronconi, E.; Palkovits, R.; Fornasari, G.; Vaccari, A.; Benito, P. Metallic Foams for Energy and Environmental Applications; 1st ed.; Elsevier B.V., 2019; Vol. 178; ISBN 9780444641274.

Chapter 4

Development of ruthenium-based catalysts for low-temperature ammonia decomposition

This chapter is based on the following paper:

G. Anello, R. Fiorillo, G. De Felice, M. Khamphasith, C. Italiano, M. van Sint Annaland, F. Gallucci. *"Tailored Cs-Ru/CeO2 catalysts for low-temperature ammonia decomposition: characterization and catalytic performance"*, Submitted.

Abstract

Ammonia decomposition can become a crucial process for hydrogen production, providing a carbon-free hydrogen carrier. The main drawback of this process is its high energy requirement. Therefore, the development of new catalysts that operate under milder reaction conditions would represent a significant advancement in the field. Thus, this study focuses on optimizing the performance of ruthenium-based catalysts synthesized via the polyol reduction method for more efficient low temperature ammonia decomposition, with particular emphasis on the effects of ruthenium as active phase and cesium as promoter. Following structural and chemical characterizations, through XRD, N₂-physisorption, H₂-TPR, H₂-TPD, CO₂-TPD and XPS, the catalysts were tested for ammonia decomposition over a temperature range of 250 – 450 °C, and a pressure range of 1 - 7 bar. The results show that both the active phase and promoter loadings significantly influence catalytic performance, with specific combinations yielding higher ammonia conversion and improved hydrogen production efficiency. Effectively, the addition of cesium to the catalytic formulation resulted in an increase in the ammonia conversion of approximately 28% (at 350 °C, 1 bar, 6 000 Nml h⁻¹ g_{cat}⁻¹). A hydrogen production rate as high as approximately $1.9 \text{ mol } h^{-1} \text{ g}_{cat}^{-1}$ was achieved at $30\ 000\ \text{Nml}\ h^{-1}\ g_{\text{cat}^{-1}}$, $450\ ^{\circ}\text{C}$ and 1 bar, which is the highest rate reported in the literature to the best of the authors' knowledge. The study provides valuable insights into the design of more efficient catalysts for ammonia decomposition, highlighting the potential of ruthenium-promoter systems for clean hydrogen generation.

4.1 Introduction

The effective utilization of ammonia (NH₃) as a hydrogen (H₂) storage medium also involves the step of ammonia decomposition through an endothermic equilibrium reaction and the separation and purification of the produced hydrogen. The ammonia decomposition reaction is a reversible endothermic process that produces hydrogen and nitrogen (N₂) proceeding with an increase of the overall gas volume. Thus, higher temperatures and lower pressures positively affect the ammonia conversion. Furthermore, a thermodynamic study of the ammonia decomposition reaction revealed that an almost complete NH₃ conversion is achievable at approximately 420 °C and atmospheric pressure [1]. Still, effectively, NH₃ decomposition cannot be conducted at lower temperatures due to kinetic limitations.

As a consequence, this reaction is typically conducted in a temperature range of 500 – 600 °C and a pressure range of 1 – 3 bar, in the presence of a catalyst. To date, several active phases have been explored, with nickel (Ni), cobalt (Co), and ruthenium (Ru) emerging as the most effective options [2]. Among the various active phases, ruthenium-based catalysts demonstrate superior activity at relatively low temperatures, and as a result, catalytic formulations employing this transition metal have been extensively investigated. The downside of employing ruthenium as active phase is connected with the extremely high cost of this metal and limited availability in the Earth's crust [3]. Therefore, it would be beneficial to enhance catalytic activity by maximizing the exposure of active sites, ensuring low ruthenium loading, while simultaneously guaranteeing high activity and high stability.

The focus of this Chapter is to investigate the catalytic activity of Ru-based catalysts synthesized via the polyol reduction method for ammonia decomposition. The polyol reduction method is a one-step chemical process that enables the simultaneous production and dispersion of metal nanoparticles. In this synthesis method, a polyol serves both as a solvent for the salt precursors and as a reducing agent [4,5]. The polyol reduction method is simple, fast, relatively inexpensive, easy to scale up and allows the production of nanoclusters ranging from 1 to 5 nm and exhibiting regular volume and outline [6,7]. For ruthenium catalysts, this aspect is extremely important, as the ability to obtain nanoclusters increases the number of active sites, thereby enhancing catalytic activity and allowing for a more efficient use of this expensive metal. Furthermore, there is a general consensus in the open literature that ruthenium cluster smaller than 8 nm have the optimal catalytic activity for hydrogen production from ammonia decomposition [8].

Moreover, ammonia decomposition is a structure-sensitive reaction, and several studies agree on the role of B5-type sites in the activity of Ru-based catalysts for ammonia decomposition, similarly to ammonia synthesis reaction [9]. The B5-type site consists of three ruthenium atoms in one plane and two ruthenium atoms located in the plane directly above this. The concentration of the B5-type sites is strongly connected to the dimensions of the ruthenium clusters; more specifically, literature studies pointed out that ruthenium clusters ranging from 1.8 to 3.5 nm correspond to the highest amount of B5 sites [10,11]. Therefore, control of the ruthenium cluster size via the polyol reduction method could allow for an abundance of active B5 sites, beneficial for ammonia decomposition, while simultaneously guaranteeing, the maximum dispersion of the expensive transition metal [12].

Ruthenium was used as active phase supported on cerium oxide (ceria, CeO₂) with different nominal loadings. Increasing the active phase loading enhances the amount of catalytically active material available to promote the reaction. This can lead to higher conversions, as more active sites are available to facilitate the reaction. However, increasing the active phase loading does not always lead to a proportional improvement in catalytic activity. The distribution of the active phase on the support is crucial: high dispersion ensures that more active sites are accessible. Consequently, activity tests were performed on different catalysts with the same support while varying the active phase loadings to assess the impact of active phase amount on ammonia conversion and overall catalytic activity.

In addition, the effect of cesium (Cs) as promotor was investigated. First, cesium can significantly modify the electronic properties of ruthenium by increasing the electron density at the ruthenium active sites, promoting the interaction of the promoter with the active metal [13,14]. Furthermore, cesium can enhance the dispersion of ruthenium on the ceria support. In turn, ruthenium dispersion can influence the active surface area available for the reaction [15]. Moreover, cesium can prevent sintering and agglomeration of ruthenium by stabilizing the dispersed ruthenium clusters, thus ensuring a longer operational life [16].

The structural and chemical properties of the synthesized catalysts were investigated using advanced characterization techniques. The catalysts performance was evaluated over a temperature range of 250 – 450 °C, a pressure range of 1 – 7 bar, and Weight Hourly Space Velocity varying between 6 000 and 30 000 Nml h⁻¹ g_{cat}⁻¹.

4.2 Experimental

4.1.1 <u>Materials</u>

Ethane-1,2-diol ($C_2H_6O_2$, ReagentPlus[®] grade, Sigma-Aldrich[®]), ruthenium(III) chloride hydrate (RuCl₃·xH₂O, Ru content 45 – 55%, Sigma-Aldrich[®]), cerium(III) nitrate hexahydrate (CeN₃O₉·6H₂O, 99%, Sigma-Aldrich[®]), cesium nitrate (CsNO₃, 99.99%, Sigma-Aldrich[®]), potassium hydroxide (KOH, Reagent grade, VWR Chemicals[®]) were employed in the synthesis for the catalysts tested in this work, without further purification. For all the synthesis steps detailed in the *Catalyst preparation* section (see section 4.2.2), ultrapure water (Type 1, electric resistivity < 18.2 M Ω cm at 20 °C) produced with a Purelab[®] Flex 1 purification system (Elga LabWater Ltd., England, UK), was used.

4.1.2 <u>Catalysts preparation</u>

The detailed procedure for catalyst preparation via the polyol reduction is reported in previous work [17]. Briefly, for all the non-promoted catalysts, the salt precursors of ruthenium and cerium were dissolved in ethane-1,2-diol (concentration of ruthenium chloride fixed at 4.7 g ml⁻¹), with the required amount determined to achieve a nominal ruthenium loading of 3, 5 and 7 wt% in the final catalysts. Similarly, for the promoted catalysts, the solution was prepared by also adding the cesium precursor to obtain a nominal cesium loading of cesium equal to 2 and 10 wt%. Furthermore, to serve as a reference, bare cerium oxide was prepared using the same synthesis method, employing only the salt precursor of cerium.

The so-prepared solution containing the dissolved precursor salts was placed in a three-neck round-bottom flask. The mixture was heated to 110 °C and maintained at this temperature for 2 hours, then allowed to cool naturally.

Subsequently, a potassium hydroxide solution was added to the mixture through a fusion 6000X syringe pump (Chemyx Inc., Texas, USA) at a flow rate of 2 ml min⁻¹. Next, the obtained gel was aged for 10 minutes, washed with ultrapure water, and separated using a 5810R centrifuge (Eppendorf, Germany) to recover the particles and remove liquid residues from the solid phase. Finally, the catalyst was dried at 120 °C for 12 hours and then calcined at 550 °C for 4 hours using a heating ramp of approximately 2 °C min⁻¹. More details regarding the synthesis method are reported in Appendix D.

Table 4.1 summarized the synthesized materials along with their corresponding codes and characteristic compositions.

Table 4.1. Summary of materials prepared in the current study.				
Catalyst	Code	Ru	Cs/Ru	
		(wt%)	$(g_{Cs} g_{Ru}^{-1})$	
CeO ₂	Ceria	-	-	
Ru/CeO ₂	3Ru	3	-	
Ru/CeO ₂	5Ru	5	-	
Ru/CeO ₂	7Ru	7	-	
Cs-Ru/CeO2	2Cs5Ru	5	2	
Cs-Ru/CeO ₂	10Cs5Ru	5	10	

4.1.3 Catalysts characterization

The properties of the as-prepared catalysts were investigated through several techniques. Powder X-ray diffraction (XRD) patterns were recorded via a MiniFlex 600 benchtop X-ray diffractometer (Rigaku[®], Japan) equipped with a Ni β -filtered Cu-K α radiation operating at 40 kV and 15 mA, with a scan step of 0.01 degrees and a scan rate of 1 deg min⁻¹ over the diffraction angle (2 θ) range from 20 to 75 degrees. Data analysis was conducted using the software SmartLab Studio II v. 4.5.421.0 (Rigaku[®], Japan). Nitrogen adsorption isotherms were collected at -196 °C with a 3Flex system (Micromeritics[®], Georgia, USA). Before starting the measurement, the samples were degassed under vacuum conditions at 250 °C. The surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) method. High-resolution transmission electron microscopy (HR-TEM) and energy-dispersive X-ray spectroscopy (EDX) mapping images were obtained using a cold field transmission electron microscope (JEM-F200, Jeol, Japan) at an operating voltage of 200 kV.

Hydrogen temperature-programmed reduction (H_2 -TPR) analysis were conducted using an Autochem HP 2950 (Micromeritics[®], Georgia, USA) equipped with a thermal conductivity detector (TCD). First, each sample was placed in a U-shaped quartz tube and pretreated at 150 °C for 60 minutes under an argon flow, then cooled to 100 °C. Subsequently, the sample was heated to 450 °C at a rate of 10 °C min⁻¹ under a flow of 10 vol.% H₂ in argon. During this process, the TCD monitored the gas concentration changes, providing insights into the progression of the reduction reactions. Ammonia temperature programmed desorption (NH₃-TPD) and carbon dioxide temperature programmed desorption (CO2-TPD) analysis were conducted to assess acidity and basicity of the catalyst using an Autochem HP 2950 (Micromeritics[®], Georgia, USA) equipped with a TCD. For each TPD analysis, the catalyst was placed in a U-shaped quartz tube and exposed to the target gas, either ammonia or carbon dioxide, which was adsorbed onto the sample. For NH₃-TPD analysis, 0.1 g of sample was pretreated increasing the temperature from ambient conditions to 150 °C under argon flow (40 ml min⁻¹) at a rate of 10 °C min⁻¹. Then, the catalyst was reduced under a flow of 10 vol.% H₂ in argon and then cooled down to room temperature. Subsequently, the sample was saturated with ammonia. Finally, the desorption was performed under argon flow by heating the sample from ambient conditions up to 900 °C at a rate of 10 °C min⁻¹. Similarly, for the CO₂-TPD analysis, prior to the measurements, the catalyst was pretreated and reduced under a flow of 10 vol.% H₂ in argon. Afterward, a mixture of 10 vol.% CO_2 in helium was employed to saturate the sample. Then, the sample was gradually heated to 900 °C at a rate of 10 °C min⁻¹. During this process, the temperature is gradually increased to induce the desorption of the adsorbed carbon dioxide from the catalyst surface.

X-ray photoelectron spectroscopy (XPS) analysis was conducted with a K-Alpha X-ray photoelectron spectrometer system (Thermo Scientific[™], Massachusetts, USA). All the obtained spectra were deconvoluted employing the software CasaXPS v.2.3.23rev1.2K (Casa Software Ltd, Devon, UK).

4.1.4 Activity tests

The activity tests on the synthesized catalysts were performed in a lab-scale experimental setup designed and constructed for this purpose, as illustrated in Figure 4.1, with further details provided in Appendix D.



Figure 4.1. Schematic representation of the experimental setup employed to perform activity tests for the ammonia decomposition reaction.

Prior to activity tests, the calcined catalyst powder was compressed into pellets using a 10 mm die, applying a load of $1\,10^4$ kg for 20 minutes using an Atlas 15T manual hydraulic press (Specac Ltd, England, UK). After forming each tablet, this was ejected from the die, then crushed in an agata mortar, and then sieved using woven wire mesh sieves (Retsch Gmbh, Germany) to obtain samples with a particle size ranging from 150 to 250 μ m.

First, 1 g of catalyst was diluted with 5 g of silicon carbide (SiC) (VWR Chemicals[®], Belgium), both having a similar particle size. This solid mixture was loaded into a stainless-steel reactor (SS316L, 10 mm inner diameter, 50 mm length). Top and bottom

of the bed were also filled with SiC (500 μ m). Silicon carbide served to maintain isothermal operation and prevent the formation of hotspots into the catalytic bed. The temperature is measured with three K-type thermocouples, one at the beginning of the catalytic bed, one placed in the middle of the bed and the last one was placed at the outlet of the catalytic bed.

The desired gas flow rates were supplied to the reactor via EL-FLOW® Select mass flow controllers (Bronkhorst®, The Netherlands) from gas bottles (Linde Gas Benelux BV, The Netherlands) containing 5.0 purity N_2 , 5.0 purity H_2 and 3.7 purity NH_3 . The operating pressure was controlled thanks to a combination of an Equilibar® Low Flow series back pressure regulator (Precision Fluid Control, North Carolina, USA) and an EL-PRESS® dual valve pressure controller (Bronkhorst®, Netherland).

The reactor feed stream was preheated using a 1-meter-long electric heat trace cable (Chromalox Isopad GmbH, Germany) applied along the feed line. Prior to the reaction tests, the catalysts underwent in situ reduction at 450 °C, feeding 400 Nml min⁻¹ of a 10 vol.% H₂ : N₂ mixture for approximately 8 hours. The complete reduction of the catalyst was verified by tracking the concentrations of both water and hydrogen in the outlet stream, analyzed with a compact gas chromatograph (GC) (Global Analyzer Solutions[™], The Netherlands) located downstream of the reactor. The GC, which has two TCDs, measures the concentration of gaseous products. Calibration for all relevant compounds was conducted both before and after the tests. Data analysis was performed using the Chromeleon 7.3.2 Chromatography Data System (Thermo Scientific[™], Massachusetts, USA).

Finally, pure NH₃ was fed to the reactor at a weight hour space velocity (*WHSV*) of 6 000, 18 000 and 30 000 Nml h^{-1} g_{cat}⁻¹. Reaction tests were performed over a temperature range of 250 – 450 °C and a pressure range of 1 – 7 bar.

4.3 Results and discussion

All the catalysts produced for this work show a specific surface area (SSA) in the range $80 - 90 \text{ m}^2 \text{ g}^{-1}$. The addition of the promoter did not lead to a significant change in the SSA. This indicates that cesium is effectively dispersed over the catalyst and functions as a structural promoter, as also mentioned in previous works [17,18].

The XRD patterns of the synthesized catalysts are presented in Figure 4.2. These patterns exhibit the characteristic peaks of the cubic fluorite structure (JCPDS card No. 43 – 1002) at 28.4°, 33°, 47.4°, 56.3°, 58.9°, and 69.4° [19,20]. At low ruthenium loadings, no peaks corresponding to ruthenium were detected, which can be attributed to the low concentration and uniform distribution of ruthenium on the catalyst surface, as noted by previous studies [21,22]. This also indicates that the ruthenium clusters in the catalysts produced in this study were small [23,24]. It is worth noting, the ceria peaks for Ru-based materials are broader compared to those of bare ceria, indicating the presence of metal in the catalyst samples.



Figure 4.2. XRD patterns of the synthesized materials.

On the other hand, as the ruthenium loading increases, the diffraction peaks corresponding to this element appear, indicating larger particle sizes due to the aggregation of ruthenium particles. The observed peaks at 28.1° , 35.1° and 54.2° can be assigned to the tetragonal RuO (JCPDS card No. 21 - 1172) [25,26]. This occurs because,

at higher metal loadings, the number of ruthenium atoms exceeds the capacity for effective dispersion over the cerium oxide surface, resulting in clustering rather than fine dispersion. This behavior has been noted in several studies examining the catalytic properties and performance of Ru-based catalysts [27]. Furthermore, no peaks indicative of other impurities were found in the XRD patterns of any of the samples.

Figure 4.3 shows HR-TEM images of Ru-based catalysts at various magnifications. All samples display agglomerates of nearly spherical nanoparticles, creating a mesoporous network. Notably, no significant changes are observed when varying the active phase concentration from 3 to 7 wt%.



Figure 4.3. HR-TEM images at varying magnifications of (a - c) 3Ru, (d - f) 5Ru, and (g - i) 7Ru.

High-magnification TEM images in Figure 4.4 display a variety of lattice fringes with average interplanar spacing of 0.312 nm, 0.271 nm, and 0.191 nm, indexed to the primarily exposed (111), (200), and (220) crystal planes of CeO_2 (JCPDS card No. 040593). Additionally, an average interplanar spacing of 0.206 nm was observed, corresponding to the (101) crystal planes of Ru (JCPDS card No. 060663).



Figure 4.4. High Magnification HR-TEM images of 7Ru catalyst.

Moreover, doping with cesium does not result in substantial changes in the catalysts morphology, as demonstrated by HR-TEM images of Cs-promoted catalysts at various magnifications (Figure 4.5).



Figure 4.5. HR-TEM images at different magnifications of (a, c, e) 2Cs5Ru and (b, d, f) 10Cs5Ru.

4.3.1 Optimization of ruthenium loading

The optimization of ruthenium loading is essential for maximizing the valorization of the noble metal. In some cases, a higher amount of active phase can lead to improved catalytic performance, but only up to a certain limit. Beyond this point, further increases in the active phase loading may not result in significant activity enhancement and could even be detrimental, causing issues such as sintering or aggregation of active particles [28]. This phenomenon is known as the "optimal loading effect", which can vary depending on the type of reaction catalyzed and the materials used. Therefore, in this study, various loadings of ruthenium (3, 5 and 7 wt%) were investigated at ambient pressure and fixed *WHSV* of 6 000 Nml h⁻¹ g_{cat}⁻¹. The results of this investigation are presented in Figure 4.6, along the theoretical equilibrium ammonia conversion calculated using AspenPlus v.11 (Aspen Technology Inc., Massachusetts, USA), which serves as a benchmark for evaluating catalytic performance under the investigated reaction conditions. Prior to catalytic experiments, a blank test was performed using the empty reactor at 450 °C, which resulted in an ammonia conversion of less than 2% at 1 bar and *WHSV* of 6 000 Nml h⁻¹ g_{cat}⁻¹.



Figure 4.6. Influence of the ruthenium loading on ammonia conversion as a function of temperature (1 bar, 6 000 Nml h^{-1} g_{cat}⁻¹).

Within this experimental study, the catalyst 5Ru showed the highest activity, approaching the equilibrium curve in the range 375 – 400 °C. This can be attributed to a balance between two key factors: ruthenium dispersion and the availability of active sites. More specifically, a loading of ruthenium below 5 wt% might show lower catalytic activity due to a lower number of active sites available to catalyze the reaction [29,30]. On the other hand, a ruthenium loading above 5 wt% can lead to several issues that diminish the catalytic activity and reaction rate. When the metal loading is excessively high, ruthenium particles tend to aggregate and form larger clusters. This phenomenon, known as sintering, reduces the specific surface area of ruthenium available for the reaction, thereby decreasing the reaction rate. Additionally, higher loading can negatively impact the atomic dispersion of the ruthenium itself, as discussed by Zheng et al. [28]. When the ruthenium loading exceeds the optimal level, several synergistic dynamics between active phase and support can be compromised.

For instance, the redox properties of CeO₂ can be limited. Notably, CeO₂ is known for its ability to store and release oxygen due to its oxygen defect-rich crystalline structure [31]. The synergistic active phase-support interaction can be further compromised due to the formation of undesirable surface species. From a crystalline perspective, an excess of ruthenium can also induce structural changes in CeO₂. The deposition of substantial amounts of ruthenium can induce stress on the CeO₂ structure, leading to modifications of its crystalline properties. Additionally, the excess ruthenium can affect the thermal stability of the catalyst. Ruthenium has a high propensity to sinter at elevated temperatures, and excessive loading can accelerate this process, leading to a rapid decrease in the available active surface area and a decline in catalytic efficiency over time.

H₂-TPR analysis on the non-promoted catalysts reveals that materials with different ruthenium loadings exhibit distinct reduction peaks at various temperature ranges, indicating differences in reducibility. According to the profiles shown in Figure 4.7, as the active phase loading increases a shift of the reduction interval towards higher temperatures can be detected. The increase in the temperature of the reduction peaks in the TPR profiles with increasing ruthenium loading can be attributed to the presence of larger ruthenium clusters. Larger clusters exhibit a smaller specific surface area and lower contact area with the reducing gas, making their reduction more difficult and requiring higher temperatures [30,32].

Another crucial aspect is the crystalline deformation of ceria, which is inherently characterized by the presence of oxygen vacancies in its crystal lattice. When the ruthenium loading increases, the interaction between the ruthenium clusters and the ceria lattice becomes more significant, inducing further crystalline deformations. These deformations can possibly stabilize the oxidized species of ruthenium, making them more difficult to reduce and therefore shifting the reduction peaks towards higher temperatures.



Figure 4.7. H₂-TPR analysis for catalysts with different Ru-loading.

4.3.2 Optimization of cesium/ruthenium mass ratio

The results of the activity tests for catalysts with varying Cs/Ru mass ratios, conducted at ambient pressure and a fixed *WHSV* of 6 000 Nml h^{-1} g_{cat}⁻¹ are reported in Figure 4.8. The cesium content was varied between 0 and 10 wt%, while keeping the ruthenium loading the same, resulting in Cs/Ru mass ratio ranging from 0 to 2.



Figure 4.8. Influence of the cesium loading on ammonia conversion as a function of temperature (1 bar, 6 000 Nml h^{-1} g_{cat}⁻¹).

The activity tests revealed an improvement in catalytic performance with increasing cesium loading, highlighting the beneficial effect of cesium as a promoter. Specifically, at 350 °C, the conversion increased by approximately 28%, compared to non-promoted catalysts. This enhancement can be attributed to cesium's promoting effect, which occurs through electron donation. Cesium alters the electron density of the active site, and, as a consequence, it facilitates the recombination of N₂, which is considered the rate determining step for the ammonia decomposition reaction, thus allowing an efficient turnover of the active sites [33]. The promotion mechanism described requires maintaining a highly reduced condition of cesium, as oxygen can partially neutralize its promoting effect. Therefore, the promotion occurs at contact points between the Ru crystallites and Cs atoms. This is also known as "hot ring promotion" [34,35]. In addition, the contribution of this mechanism is highly dependent on the ruthenium dispersion and is greater for smaller crystallites [36]. Therefore, small clusters, such as those achievable with the polyol reduction method, are extremely beneficial.

The 5Ru and 2Cs5Ru catalysts were characterized via CO_2 -TPD, along with bare CeO_2 as reference. As reported in Figure 4.9, all curves show low-temperature peaks at about 100 °C. This peak might be related to weak interaction between CeO_2 and CO_2 , as also confirmed by the analysis of the support, in which the peak is present. In the sample 2Cs5Ru, the elevated temperature peak is located at approximately 780 °C and is significantly more pronounced than for the 5Ru catalyst. The high temperature CO_2 desorption peak can be associated with the presence of strong basic sites, as also reported in previous work [37]. Im et al. suggested that the basic strength of the catalyst could be related to the activity for ammonia decomposition [38]. Indeed, the basicity of the catalysts plays a crucial role in the adsorption and desorption of ammonia, correlating with the dissociation of the nitrogen-hydrogen bond.



Figure 4.9. CO₂-TPD results for 2Cs5Ru, 5Ru and bare ceria.

Desorption studies with ammonia are reported in Figure 4.10 for the samples 2Cs5Ru, 5Ru and bare CeO_2 . By comparing the NH₃-TPD curves of different samples, it is possible to underline that the introduction of ruthenium and cesium led to differences in ammonia adsorption among the samples, thus influencing the distribution of acidic sites on the surface [39]. Upon the metals addition, the desorption temperatures shifted towards higher temperature ranges, as compared with the bare support. Furthermore, the increased desorption peak temperatures for the sample 2Cs5Ru, also as compared to the sample 5Ru, coupled with broader and larger peaks, indicate a greater density of acidic sites due to the addition of cesium, especially in the region of the weak acid sites [40]. This implies that the promoter can enhance the adsorption of NH₃, thereby facilitating its dissociation.



Figure 4.10. NH₃-TPD results for 2Cs5Ru, 5Ru and bare ceria.

From the Arrhenius plot (Figure 4.11), which shows the logarithm of the ammonia reaction rate plotted against the inverse of temperature, the activation energy (E_A) and the pre-exponential factor (k_0) for the catalysts 5Ru and 2Cs5Ru were determined.



Figure 4.11. Arrhenius plots for the catalysts 5Ru and 2Cs5Ru.

The calculated values are reported in Table 4.2. The similarity in the activation energies for both catalysts suggests that the presence of the promoter does not alter the energy barrier of the reaction pathway. However, the substantial increase in the preexponential factor indicates that the enhancement of the reaction rate is directly linked to the frequency with which reactant molecules collide. A higher k_0 indicates that collisions occur more frequently, thereby increasing the chances of a reaction [41,42], indicating an increase in the available active surface area or greater ease with which reactant molecules can reach these active sites [43–45]. Therefore, the promoter can improve the dispersion of the active phase on the catalyst surface, thus increasing the accessibility of the active sites, as also suggested by Inokawa et al. [46].

Catalyst	Ea	ko
code	kJ mol ⁻¹	mmol h ⁻¹ g _{cat} ⁻¹
5Ru	70.40	$1.65 \cdot 10^8$
2Cs5Ru	72.72	3.66.108

Table 4.2. Activation energy and pre-exponential factor for
the catalysts 5Ru and 2Cs5Ru.

No beneficial effect emerged when increasing the Cs/Ru mass ratio above 2:5. This may be attributed to the promotional effect of cesium being observable only when it directly interacts with ruthenium, thereby facilitating electron donation. Another important factor to consider is the maximum solubility of cesium in the synthesis solution. Adding more cesium in this case is unlikely to lead to a greater amount of promoter being effectively incorporated into the catalyst structure. Additionally, the limited solubility of cesium could lead to a non-uniform distribution of the promoter on the catalyst. Under saturation conditions, cesium may precipitate locally, leading to suboptimal dispersion and lower effectiveness as a promoter, thereby diminishing the potential for further improvements in catalytic performance with increased loading. The formation of cesium aggregates or crystallites unevenly distributed can negatively affect the catalyst structure, limiting access to active sites and reducing the promoter effectiveness.

To accurately analyze the surface composition and chemical state of the produced catalysts, the samples 5Ru and 2Cs5Ru were characterized via XPS, as shown in Figure 4.12. The Ce 3d orbital signals were deconvoluted in ten peaks, six assigned to $3d^{10}4f^0$ of Ce⁴⁺, while four peaks belong to $3d^{10}4f^1$ of Ce³⁺ [47]. Based on the Ce 3d XPS spectra, the surface concentrations of Ce³⁺ relative to the total surface cerium species on 5Ru and 2Cs5Ru are approximately 39% and 45%, respectively. This suggests an enrichment in Ce³⁺ of the promoted catalyst surface, along with an increased generation of oxygen vacancies. The electron-rich environment around oxygen vacancies causes a strong interaction between Ru and Ce, which significantly affects the migration and desorption of hydrogen species [48,49]. The increased electron density can facilitate electron transfer during chemical reactions. In other words, ruthenium atoms can more efficiently donate electrons to the adsorbed nitrogen atoms produced from the dissociation of ammonia [50]. This is consistent with the XRD results, which show a minor shift to higher diffraction angles. The shift to higher diffraction angles suggests a
reduction in the lattice parameter, which can be linked to lattice distortions or stress. Such shifts are often observed when defects, like oxygen vacancies, are introduced. The formation of oxygen vacancies changes the local environment in the lattice, leading to strain or stress that affects the diffraction pattern [51].



Figure 4.12. High resolution XPS spectra of Ce 3d for the catalysts (a) 5Ru and (b) 2Cs5Ru.



The catalyst 2Cs5Ru was further tested at higher *WHSV* values, ranging from 6 000 to 30 000 Nml h^{-1} g_{cat}⁻¹. The results of these tests are presented in Figure 4.13.

Figure 4.13. (a) Ammonia conversion and (b) hydrogen productivity as function of reaction temperature for different values of *WHSV*.

The experimental results indicate that, as anticipated, *WHSV* has a negative impact on ammonia conversion. This behavior may be associated with the influence of residence time. Higher *WHSV* corresponds to shorter residence time, which may inhibit ammonia

conversion [52]. Specifically, rapid gas flow reduces the interaction time between gas molecules with catalyst particles, thereby limiting the conversion of ammonia to hydrogen and nitrogen [53]. Conversely, lower *WHSV* values increase the contact time between gas molecules and particles, facilitating higher conversion. However, this may come at the expense of overall productivity (Figure 4.13b). The hydrogen production rate reached a value of approximately 1.9 mol h⁻¹ g_{cat}⁻¹ at 30 000 Nml h⁻¹ g_{cat}⁻¹, 450 °C and 1 bar. This represents the highest production rate documented in the literature to date, highlighting the effectiveness of the novel catalyst under these conditions.

For many potential applications of hydrogen derived from ammonia, such as fuel cells, it is necessary to supply hydrogen at relatively high pressures. Additionally, several process intensification strategies, including the integration of tailored membrane in the reaction chamber, require operating at higher pressures than ambient conditions [54,55]. To mitigate additional compression costs and associated emissions, the performance of the catalyst 2Cs5Ru was studied over a pressure range of 1 - 7 bar, despite the evident thermodynamic limitations in absence of membranes. The results are shown in Figure 4.14.



Figure 4.14. Ammonia conversion as a function of the reaction temperature and operating pressure (6 000 Nml $h^{-1} g_{cat}^{-1}$).

The results indicate that ammonia conversion decreases as the pressure increases from 1 to 7 bar, which is consistent with thermodynamic expectations. However, an ammonia conversion of approximately 90% is still achieved at 7 bar and 400 °C.

Finally, the catalyst 2Cs5Ru was tested over an overall time span of about 500 hours. As depicted in Figure 4.15, the catalyst maintained its high activity up to 350 °C, with only a very limited decrease in conversion over time. The high stability of the promoted catalysts in terms of ammonia conversion over a time span of about 500 hours is quite remarkable, as, to the best of the authors' knowledge, stability test of Ru-based catalyst for ammonia decomposition reported in the literature were performed up to only 120 hours [56].



Figure 4.15. Long-term stability tests at different reaction temperatures for the catalyst 2Cs5Ru.

The scalability of the synthesis procedure was thoroughly evaluated to determine its potential for larger-scale applications. The amount of catalyst produced per single batch was progressively increased from approximately 1 to 25 g. Characterization analysis and activity tests indicated that, as the batch size increased, the obtained catalysts consistently exhibited similar properties. This systematic approach allowed us to assess not only the feasibility of scaling up the synthesis method but also the consistency and quality of the produced catalyst.

4.4 Conclusions

Ru-based CeO₂-supported catalysts were successfully synthesized via the polyol reduction method. The non-promoted catalyst with optimized ruthenium loading (5 wt% Ru/CeO₂) allowed an ammonia conversion reaching thermodynamic equilibrium (above 99% at 400 °C and 1 bar) already in a temperature range of approximately 375 and 400 °C (1 bar, 6 000 Nml h^{-1} g_{cat}⁻¹). After determining the optimal amount of ruthenium, the subsequent parameter under investigation was the inclusion of cesium as promoter, with a specific focus on varying the Cs/Ru mass ratio. The addition of cesium to the catalytic formulation resulted in an increase in the ammonia conversion by approximately 28% (350 °C, 1 bar, 6 000 Nml h⁻¹ g_{cat} ⁻¹), improving from 64.7 to 82.9%; however, no beneficial effect emerged increasing the amount of cesium above 2:5 mass ratio. A H₂ production rate up to 1.9 mol h^{-1} g_{cat}⁻¹ was obtained at 30 000 Nml h⁻¹ g_{cat}⁻¹, 450 °C and 1 bar. This result marks the highest production rate reported in the literature so far, underscoring the efficacy of the novel catalyst under these conditions. Furthermore, the promoted catalyst was tested over an overall time span of 500 hours to verify the long-term stability, proving the stability of the synthesized catalyst over time. Finally, the results demonstrate that using this synthesis method makes it possible to produce even larger quantities while maintaining the desired properties and performance of the catalyst, thereby supporting its viability for larger-scale applications.

4.5 References

- Su, T.; Guan, B.; Zhou, J.; Zheng, C.; Guo, J.; Chen, J.; Zhang, Y.; Yuan, Y.; Xie, W.; Zhou, N.; et al. Review on Ru-Based and Ni-Based Catalysts for Ammonia Decomposition: Research Status, Reaction Mechanism, and Perspectives. Energy and Fuels 2023, 37, 8099–8127, doi:10.1021/acs.energyfuels.3c00804.
- Su, Z.; Guan, J.; Liu, Y.; Shi, D.; Wu, Q.; Chen, K.; Zhang, Y.; Li, H. Research Progress of Ruthenium-Based Catalysts for Hydrogen Production from Ammonia Decomposition. Int J Hydrogen Energy 2024, 51, 1019–1043, doi:10.1016/j.ijhydene.2023.09.107.
- Le, T.A.; Cuong Do, Q.; Kim, Y.; Kim, T.-W.; Chae, H.-J. A Review on the Recent Developments of Ruthenium and Nickel Catalysts for CO X-Free H 2 Generation by Ammonia Decomposition. Korean J. Chem. Eng 2021, 38, 1087–1103, doi:10.1007/s11814-021-0767-7.
- Ammar, S.; Fiévet, F. Polyol Synthesis: A Versatile Wet-Chemistry Route for the Design and Production of Functional Inorganic Nanoparticles. Nanomaterials 2020, 10, 1–8, doi:10.3390/nano10061217.
- Shu, R.; Li, R.; Lin, B.; Luo, B.; Tian, Z. High Dispersed Ru/SiO2-ZrO2 Catalyst Prepared by Polyol Reduction Method and Its Catalytic Applications in the Hydrodeoxygenation of Phenolic Compounds and Pyrolysis Lignin-Oil. Fuel 2020, 265, 116962, doi:10.1016/j.fuel.2019.116962.
- Lagarteira, T.; Delgado, S.; Fernandes, C.; Azenha, C.; Mateos-Pedrero, C.; Mendes, A. The Role of Pt Loading on Reduced Graphene Oxide Support in the Polyol Synthesis of Catalysts for Oxygen Reduction Reaction. Int J Hydrogen Energy 2020, 45, 20594–20604, doi:10.1016/j.ijhydene.2020.02.022.
- 7. Komvokis, V.G.; Marti, M.; Delimitis, A.; Vasalos, I.A.; Triantafyllidis, K.S. Catalytic Decomposition of N2O over Highly Active Supported Ru Nanoparticles (≤3nm) Prepared by Chemical Reduction with Ethylene Glycol. Appl Catal B 2011, 103, 62–71, doi:10.1016/j.apcatb.2011.01.009.
- Chen, C.; Wu, K.; Ren, H.; Zhou, C.; Luo, Y.; Lin, L.; Au, C.; Jiang, L. Ru-Based Catalysts for Ammonia Decomposition: A Mini-Review. Energy and Fuels 2021, 35, 11693–11706, doi:10.1021/acs.energyfuels.1c01261.
- 9. Raróg-Pilecka, W.; Miśkiewicz, E.; Szmigiel, D.; Kowalczyk, Z. Structure Sensitivity of Ammonia Synthesis over Promoted Ruthenium Catalysts Supported on Graphitised Carbon. J Catal 2005, 231, 11–19, doi:10.1016/J.JCAT.2004.12.005.

- Wang, Z.Q.; Ma, Y.C.; Lin, J.X. Ruthenium Catalyst Supported on High-Surface-Area Basic ZrO2 for Ammonia Synthesis. J Mol Catal A Chem 2013, 378, 307–313, doi:10.1016/j.molcata.2013.07.003.
- 11. García-García, F.R.; Guerrero-Ruiz, A.; Rodríguez-Ramos, I. Role of B5-Type Sites in Ru Catalysts Used for the NH3 Decomposition Reaction. Top Catal 2009, 52, 758–764, doi:10.1007/s11244-009-9203-7.
- 12. Fang, H.; Liu, D.; Luo, Y.; Zhou, Y.; Liang, S.; Wang, X.; Lin, B.; Jiang, L. Challenges and Opportunities of Ru-Based Catalysts toward the Synthesis and Utilization of Ammonia. ACS Catal 2022, 12, 3938–3954, doi:10.1021/acscatal.2c00090.
- Aika, K. ichi; Takano, T.; Murata, S. Preparation and Characterization of Chlorine-Free Ruthenium Catalysts and the Promoter Effect in Ammonia Synthesis: 3. A Magnesia-Supported Ruthenium Catalyst. J Catal 1992, 136, 126–140, doi:10.1016/0021-9517(92)90112-U.
- Wang, Y.; Wildfire, C.; Khan, T.S.; Shekhawat, D.; Hu, J.; Tavadze, P.; Quiñones-Fernández, R.; Moreno, S. Effects of Support and Promoter on Ru Catalyst Activity in Microwave-Assisted Ammonia Synthesis. Chemical Engineering Journal 2021, 425, 130546, doi:10.1016/J.CEJ.2021.130546.
- 15. Cholach, A.R. Adjustment of Active Sites in Catalytic Ammonia Synthesis over Metal Alloys and Clusters: A Theoretical Study. Appl Catal A Gen 2018, 562, 223–233, doi:10.1016/J.APCATA.2018.06.017.
- Aika, K.; Shimazaki, K.; Hattori, Y.; Ohya, A.; Ohshima, S.; Shirota, K.; Ozaki, A. Support and Promoter Effect of Ruthenium Catalyst: I. Characterization of Alkali-Promoted Ruthenium/Alumina Catalysts for Ammonia Synthesis. J Catal 1985, 92, 296–304, doi:10.1016/0021-9517(85)90264-7.
- Anello, G.; De Luna, G.; De Felice, G.; Saker, A.; Di Felice, L.; Gallucci, F. Development of Ruthenium-Based Catalysts for Ammonia Synthesis via Polyol Reduction Method. Int J Hydrogen Energy 2024, 86, 922–930, doi:10.1016/J.IJHYDENE.2024.08.408.
- Narasimharao, K.; Seetharamulu, P.; Rama Rao, K.S.; Basahel, S.N. Carbon Covered Mg-Al Hydrotalcite Supported Nanosized Ru Catalysts for Ammonia Synthesis. J Mol Catal A Chem 2015, 411, 157–166, doi:10.1016/j.molcata.2015.10.019.
- Shao, R.; Zhang, L.; Wang, L.; Wang, J.; Zhang, X.; Han, S.; Cheng, X.; Wang, Z. Cerium Oxide-Based Catalyst for Low-Temperature and Efficient Ammonia Decomposition for Hydrogen Production Research. Int J Hydrogen Energy 2024, 68, 311–320, doi:10.1016/j.ijhydene.2024.04.197.

- Sorbino, G.; Di Benedetto, A.; Italiano, C.; Thomas, M.; Vita, A.; Ruoppolo, G.; Landi, G. Novel Ni-Ru/CeO2 Catalysts for Low-Temperature Steam Reforming of Methane. Int J Hydrogen Energy 2024, doi:10.1016/J.IJHYDENE.2024.07.385.
- 21. Lin, B.; Fang, B.; Wu, Y.; Li, C.; Ni, J.; Wang, X.; Lin, J.; Au, C.T.; Jiang, L. Enhanced Ammonia Synthesis Activity of Ceria-Supported Ruthenium Catalysts Induced by CO Activation. ACS Catal 2021, 11, 1331–1339, doi:10.1021/acscatal.0c05074.
- 22. Javaid, R.; Nanba, T. Effect of Reaction Conditions and Surface Characteristics of Ru/CeO2 on Catalytic Performance for Ammonia Synthesis as a Clean Fuel. Int J Hydrogen Energy 2021, 46, 18107–18115, doi:10.1016/j.ijhydene.2020.07.222.
- Javaid, R.; Matsumoto, H. Influence of Reaction Conditions and Promoting Role of Ammonia Produced at Higher Temperature Conditions in Its Synthesis Process over Cs-Ru/MgO Catalyst. 2019, doi:10.1002/slct.201803813.
- 24. Iwamoto, J.; Itoh, M.; Kajita, Y.; Saito, M.; Machida, K. ichi Ammonia Synthesis on Magnesia Supported Ruthenium Catalysts with Mesoporous Structure. Catal Commun 2007, 8, 941–944, doi:10.1016/j.catcom.2006.05.052.
- 25. B., N.; Y., V.; Abdul Razack, S. Enhanced Formation of Ruthenium Oxide Nanoparticles through Green Synthesis for Highly Efficient Supercapacitor Applications. Advanced Powder Technology 2020, 31, 1001–1006, doi:10.1016/J.APT.2019.12.026.
- 26. Akshatha, S.; Sreenivasa, S.; Kumar, K.Y.; Archana, S.; Prashanth, M.K.; Prasanna, B.P.; Chakraborty, P.; Krishnaiah, P.; Raghu, M.S.; Alrobei, H. Rutile, Mesoporous Ruthenium Oxide Decorated Graphene Oxide as an Efficient Visible Light Driven Photocatalyst for Hydrogen Evolution Reaction and Organic Pollutant Degradation. Mater Sci Semicond Process 2020, 116, 105156, doi:10.1016/J.MSSP.2020.105156.
- Araia, A.; Wang, Y.; Robinson, B.; Jiang, C.; Brown, S.; Wildfire, C.; Shekhawat, D.; Hu, J. Microwave-Assisted Ammonia Synthesis over Cs-Ru / CeO 2 Catalyst at Ambient Pressure : Effects of Metal Loading and Support Particle Size. Catal Commun 2022, 170, 106491, doi:10.1016/j.catcom.2022.106491.
- Zheng, W.; Zhang, J.; Xu, H.; Li, W. NH3 Decomposition Kinetics on Supported Ru Clusters: Morphology and Particle Size Effect. Catal Letters 2007, 119, 311–318, doi:10.1007/s10562-007-9237-z.
- Pinzón, M.; Romero, A.; de Lucas Consuegra, A.; de la Osa, A.R.; Sánchez, P. Hydrogen Production by Ammonia Decomposition over Ruthenium Supported on SiC Catalyst. Journal of Industrial and Engineering Chemistry 2021, 94, 326–335, doi:10.1016/j.jiec.2020.11.003.

- Li, L.; Wang, Y.; Xu, Z.P.; Zhu, Z. Catalytic Ammonia Decomposition for CO-Free Hydrogen Generation over Ru/Cr2O3 Catalysts. Appl Catal A Gen 2013, 467, 246–252, doi:10.1016/j.apcata.2013.07.003.
- 31. Li, C.; Shi, Y.; Zhang, Z.; Ni, J.; Wang, X.; Lin, J.; Lin, B.; Jiang, L. Improving the Ammonia Synthesis Activity of Ru/CeO2 through Enhancement of the Metal–Support Interaction. Journal of Energy Chemistry 2021, 60, 403–409, doi:10.1016/j.jechem.2021.01.031.
- Lucentini, I.; García Colli, G.; Luzi, C.D.; Serrano, I.; Martínez, O.M.; Llorca, J. Catalytic Ammonia Decomposition over Ni-Ru Supported on CeO2 for Hydrogen Production: Effect of Metal Loading and Kinetic Analysis. Appl Catal B 2021, 286, doi:10.1016/j.apcatb.2021.119896.
- 33. Parker, L.A.; Carter, J.H.; Dummer, N.F.; Richards, N.; Morgan, D.J.; Golunski, S.E.; Hutchings, G.J. Ammonia Decomposition Enhancement by Cs-Promoted Fe/Al2O3 Catalysts. Catal Letters 2020, 150, 3369–3376, doi:10.1007/s10562-020-03247-3.
- 34. Chen, Y.L.; Juang, C.F.; Chen, Y.C. The Effects of Promoter Cs Loading on the Hydrogen Production from Ammonia Decomposition Using Ru/c Catalyst in a Fixed-Bed Reactor. Catalysts 2021, 11, 1–15, doi:10.3390/catal11030321.
- 35. Larichev, Y. V.; Moroz, B.L.; Moroz, E.M.; Zaikovskii, V.I.; Yunusov, S.M.; Kalyuzhnaya, E.S.; Shur, V.B.; Bukhtiyarov, V.I. Effect of the Support on the Nature of Metal-Promoter Interactions in Ru-Cs+/MgO and Ru-Cs+-Al2O3 Catalysts for Ammonia Synthesis. Kinetics and Catalysis 2005, 46, 891–899, doi:10.1007/s10975-005-0153-1.
- Szmigiel, D.; Bielawa, H.; Kurtz, M.; Hinrichsen, O.; Muhler, M.; Raróg, W.; Jodzis, S.; Kowalczyk, Z.; Znak, L.; Zieliński, J. The Kinetics of Ammonia Synthesis over Ruthenium-Based Catalysts: The Role of Barium and Cesium. J Catal 2002, 205, 205–212, doi:10.1006/jcat.2001.3431.
- 37. Furusawa, T.; Kuribara, H.; Kimura, K.; Sato, T.; Itoh, N. Development of a Cs-Ru/CeO2 Spherical Catalyst Prepared by Impregnation and Washing Processes for Low-Temperature Decomposition of NH3: Characterization and Kinetic Analysis Results. Ind Eng Chem Res 2020, 59, 18460–18470, doi:10.1021/acs.iecr.0c03112.
- Im, Y.; Muroyama, H.; Matsui, T.; Eguchi, K. Ammonia Decomposition over Nickel Catalysts Supported on Alkaline Earth Metal Aluminate for H2 Production. Int J Hydrogen Energy 2020, 45, 26979–26988, doi:10.1016/j.ijhydene.2020.07.014.
- Shao, R.; Zhang, L.; Wang, L.; Wang, J.; Zhang, X.; Han, S.; Cheng, X.; Wang, Z. Cerium Oxide-Based Catalyst for Low-Temperature and Efficient Ammonia Decomposition for Hydrogen Production Research. Int J Hydrogen Energy 2024, 68, 311–320, doi:10.1016/j.ijhydene.2024.04.197.

- Lucentini, I.; Casanovas, A.; Llorca, J. Catalytic Ammonia Decomposition for Hydrogen Production on Ni, Ru and Ni[Sbnd]Ru Supported on CeO2. Int J Hydrogen Energy 2019, 44, 12693–12707, doi:10.1016/j.ijhydene.2019.01.154.
- Guraya, M.; Sprenger, S.; Rarog-Pilecka, W.; Szmigiel, D.; Kowalczyk, Z.; Muhler, M. The Effect of Promoters on the Electronic Structure of Ruthenium Catalysts Supported on Carbon. In Proceedings of the Applied Surface Science; Elsevier, November 15 2004; Vol. 238, pp. 77–81.
- 42. Rossetti, I.; Pernicone, N.; Forni, L. Promoters Effect in Ru/C Ammonia Synthesis Catalyst; 2001; Vol. 208;.
- 43. Kotarba, A.; Dmytrzyk, J.; Raróg-Pilecka, W.; Kowalczyk, Z. Surface Heterogeneity and Ionization of Cs Promoter in Carbon-Based Ruthenium Catalyst for Ammonia Synthesis. Appl Surf Sci 2003, 207, 327–333, doi:10.1016/S0169-4332(03)00008-4.
- 44. Osozawa, M.; Hori, A.; Fukai, K.; Honma, T.; Oshima, K.; Satokawa, S. Improvement in Ammonia Synthesis Activity on Ruthenium Catalyst Using Ceria Support Modified a Large Amount of Cesium Promoter. Int J Hydrogen Energy 2022, 47, 2433–2441, doi:10.1016/j.ijhydene.2021.10.204.
- 45. Larichev, Y. V. Effect of Cs+ Promoter in Ru/MgO Catalysts. Journal of Physical Chemistry C 2011, 115, 631–635, doi:10.1021/jp109737p.
- 46. Inokawa, H.; Ichikawa, T.; Miyaoka, H. Catalysis of Nickel Nanoparticles with High Thermal Stability for Ammonia Decomposition. Appl Catal A Gen 2015, 491, 184–188, doi:10.1016/j.apcata.2014.12.004.
- Ye, R.P.; Li, Q.; Gong, W.; Wang, T.; Razink, J.J.; Lin, L.; Qin, Y.Y.; Zhou, Z.; Adidharma, H.; Tang, J.; et al. High-Performance of Nanostructured Ni/CeO2 Catalyst on CO2 Methanation. Appl Catal B 2020, 268, doi:10.1016/j.apcatb.2019.118474.
- Wang, Z.; Luo, H.; Wang, L.; Li, T.; Li, S.; Liu, Y.Q. Promotion of Low-Temperature Catalytic Activity of Ru-Based Catalysts for Ammonia Decomposition via Lanthanum and Cesium Codoping. ACS Sustain Chem Eng 2024, 12, 5620–5631, doi:10.1021/acssuschemeng.4c00176.
- Shin, J.H.; Jung, U.; Kim, J.; Kim, K.D.; Song, D.; Park, Y.; An, B.S.; Koo, K.Y. Elucidating the Effect of Ce with Abundant Surface Oxygen Vacancies on MgAl2O4-Supported Ru-Based Catalysts for Ammonia Decomposition. Appl Catal B 2024, 340, 123234, doi:10.1016/J.APCATB.2023.123234.
- 50. Shao, R.; Zhang, L.; Wang, L.; Wang, J.; Zhang, X.; Han, S.; Cheng, X.; Wang, Z. Cerium Oxide-Based Catalyst for Low-Temperature and Efficient Ammonia Decomposition for

Hydrogen Production Research. Int J Hydrogen Energy 2024, 68, 311–320, doi:10.1016/j.ijhydene.2024.04.197.

- 51. Ansari, S.A.; Khan, M.M.; Kalathil, S.; Nisar, A.; Lee, J.; Cho, M.H. Oxygen Vacancy Induced Band Gap Narrowing of ZnO Nanostructures by an Electrochemically Active Biofilm. Nanoscale 2013, 5, 9238–9246, doi:10.1039/c3nr02678g.
- Chiuta, S.; Everson, R.C.; Neomagus, H.W.J.P.; Van Der Gryp, P.; Bessarabov, D.G. Reactor Technology Options for Distributed Hydrogen Generation via Ammonia Decomposition: A Review. Int J Hydrogen Energy 2013, 38, 14968–14991, doi:10.1016/j.ijhydene.2013.09.067.
- 53. Badescu, V. Optimal Design and Operation of Ammonia Decomposition Reactors. Int J Energy Res 2020, 44, 5360–5384, doi:10.1002/er.5286.
- 54. Sayas, S.; Morlanés, N.; Katikaneni, S.P.; Harale, A.; Solami, B.; Gascon, J. High Pressure Ammonia Decomposition on Ru-K/CaO Catalysts. Catal Sci Technol 2020, 10, 5027–5035, doi:10.1039/d0cy00686f.
- 55. Cechetto, V.; Anello, G.; Rahimalimamaghani, A.; Gallucci, F. Carbon Molecular Sieve Membrane Reactors for Ammonia Cracking. Processes 2024, 12, 1168, doi:10.3390/pr12061168.
- Chung, D.B.; Kim, H.Y.; Jeon, M.; Lee, D.H.; Park, H.S.; Choi, S.H.; Nam, S.W.; Jang, S.C.; Park, J.H.; Lee, K.Y.; et al. Enhanced Ammonia Dehydrogenation over Ru/La(x)-Al2O3 (x = 0–50 Mol%): Structural and Electronic Effects of La Doping. Int J Hydrogen Energy 2017, 42, 1639–1647, doi:10.1016/J.IJHYDENE.2016.08.020.

Chapter 5

Low-temperature ammonia decomposition in a packed bed membrane reactor

Abstract

In this chapter, a process intensification strategy for the ammonia decomposition reaction is proposed, integrating a palladium-based membrane with the rutheniumbased catalyst developed in Chapter 4. This approach aims to enhance the overall efficiency of the reaction, leveraging the selective permeation capabilities of the palladium membrane alongside the catalytic properties of the previously established catalyst. High ammonia conversions were obtained in the range of temperatures 375 – 425 °C, suggesting that high single-pass conversion is attainable. Moreover, an ammonia conversion of greater than 99.7% was obtained at 425 °C and 4 bar, with hydrogen recovery of 86.5% and hydrogen purity exceeding 99.99%. Ammonia conversion in the packed bed membrane reactor increases with higher operating pressure, exceeding thermodynamic limitations at 4 and 6 bar. The results demonstrated that the reaction conditions could be optimized to synthesize and simultaneously separate hydrogen with high purity form the products stream, ultimately contributing to a more cost-effective process.

5.1 Introduction

In the last decade, the need to address climate change and the depletion of fossil fuel reserves has been becoming a pressing issue. Hydrogen has emerged as a clean and versatile energy carrier, with the potential to replace conventional fossil fuels in various applications, including transportation, power generation, and industrial processes [1]. Hydrogen can be produced through the decomposition of ammonia (NH₃), which not only serves as a hydrogen vector but also provides a pathway for efficient hydrogen storage and transport [2]. However, the effective and efficient decomposition of ammonia into nitrogen (N₂) and hydrogen (H₂) requires advanced catalytic systems that can operate under varying conditions, particularly at lower temperatures to enhance economic feasibility.

Catalysts based on ruthenium (Ru) have shown remarkable catalytic activity for ammonia decomposition [3,4]. Despite these advantages, the high cost of ruthenium presents a significant barrier to its widespread application, necessitating the development of more cost-effective and efficient catalyst systems [5]. Therefore, advancements in catalyst preparation techniques are required, in order to enhance the dispersion of ruthenium, exploiting efficiently this resource. While ruthenium exhibits promising activity as a catalyst, the integration of a selective hydrogen-permeable membrane can significantly improve the overall efficiency of ammonia decomposition. Palladium (Pd)-based membranes have garnered attention for their exceptional hydrogen permeability and selectivity [6,7]. These membranes enable the selective removal of hydrogen from the reaction environment, effectively shifting the equilibrium of the decomposition reaction toward increased hydrogen production.

Thus, in this Chapter, the combination of the 2Cs5Ru catalyst, optimized in Chapter 4, with a Pd-based membrane was tested. The results showed that the integration of the membrane not only allows pure hydrogen production but also facilitates the reaction process by preventing hydrogen accumulation, which can hinder further ammonia decomposition and poison the catalyst. This approach offers a pathway to enhance the overall efficiency of hydrogen production from ammonia while minimizing energy input.

5.2 Experimental

Following the initial small-scale testing conducted in Chapter 4, the 2Cs5Ru catalyst was prepared in greater quantities and tested in a larger-scale reactor to assess its performance under expanded operating conditions. Approximately 25 g of catalyst were synthesized in a single batch via polyol reduction method. No significant differences were observed in terms of textural and activity properties when comparing the larger-scale production with the smaller-scale batch production of this catalyst.

Before conducting the reaction tests, the calcined catalyst powder was compressed into pellets using a 10 mm die, applying a load of $1 \cdot 10^4$ kg for 20 minutes using an Atlas 15T manual hydraulic press (Specac Ltd, England, UK). After forming each tablet, this was ejected from the die, then crushed in an agata mortar and pestle, and then sieved using woven wire mesh sieves (Retsch Gmbh, Germany) to obtain samples with a particle size ranging from 500 to 1 000 µm. The reactor was loaded with 10 g of catalyst, diluted with 170 g of silicon carbide (SiC) (VWR Chemicals[®], Belgium) to ensure isothermal operation and avoid local hotspots.

The membrane employed in this work was prepared according to the methodology reported by Arratibel et al. [8]. A Pd-Ag selective layer was deposited through electroless plating on porous asymmetric α -Al₂O₃ support (Rauschert Kloster Veilsdorf, Germany) with an outer and inner diameter of 14 and 10 mm, respectively. The outer layer of the support features a pore size of 100 nm. To enhance the stability of the membrane, a protective layer is subsequently applied on top of the selective layer. This protective layer consists of a porous Al₂O₃-YSZ (yttria-stabilized zirconia) layer applied by dip-coating technique and calcined at 550 °C. The Pd-based membrane was placed in this reactor where it was fully immersed in the catalytic packed bed of 2Cs5Ru and silicon carbide.

Reaction tests with the developed catalyst and membrane were conducted in a dedicated experimental setup, of which a schematic is reported in Figure 5.1.



Figure 5.1. Schematic representation of the experimental setup employed in this study to conduct ammonia decomposition reaction tests.

The tests were performed by feeding about 1 000 Nml min⁻¹ of pure ammonia into the system via an EL-FLOW[®] Prestige mass flow controllers (Bronkhorst[®], The Netherlands). The ammonia feed stream was preheated using a 1-meter-long electric heat trace cable (Chromalox Isopad GmbH, Germany) applied along the feed line. The reaction vessel utilized in this study is a tubular reactor made of SS316Ti, featuring an internal diameter of 30 mm and a length of 300 mm. Its design accommodates both the membrane and catalyst particles, as shown in Figure 5.2.



Figure 5.2. 3D renderings of the reactor used in this study, shown as (a) empty, (b) with membrane only, and (c) as packed bed membrane reactor.

To ensure isothermal operation along its length, the reactor was placed inside a threezone split furnace (Elicra Electrowarmte BV, The Netherlands). The reaction (or retentate) pressure is managed by an EL-PRESS[®] pressure controller (Bronkhorst[®], The Netherlands). Both the permeate and retentate streams were analyzed with a compact gas chromatograph (Global Analyzer Solutions[™], The Netherlands), equipped with two thermal conductivity detectors to accurately quantify the gaseous products composition. High Precision SF-1U/2U Film Flow Meter (Horiba Stec Co. Ltd., Japan) where employed to calibrate the mass flow controllers and quantify NH₃-free gas flows. Prior to and following the tests, the gas chromatograph was calibrated for all relevant compounds. All collected data were then analyzed using the software Chromeleon 7.3.2 Chromatography Data System (Thermo Scientific[™], Massachusetts, USA).

Prior to the experiments, a blank test was conducted feeding $1\,000$ Nml min⁻¹ at atmospheric pressure to the empty reactor. The results indicated an ammonia conversion of approximately 6% at 400 °C and 10% at 450 °C. Subsequently, single gas tests for both nitrogen and hydrogen were performed, feeding these gas up to 10 000 Nml min⁻¹. The single gas permeation through the membrane was measured at

450 °C, with a pressure difference between the retentate and permeate zones ranging from 1 to 5 bar. During the tests involving the Pd-based membranes, the temperature was increased at a rate of 2 - 3 °C min⁻¹ while supplying nitrogen until the system reached at least 350 °C, thereby preventing hydrogen embrittlement phenomenon [9]. No nitrogen was detected (below detection limit, 0.2 Nml min⁻¹) while all the fed hydrogen permeated through the membrane.

After installing the membrane onto the reactor flange and placing the solid particles inside the reaction vessel, a heating procedure was initiated under a nitrogen atmosphere, gradually reaching 450 °C at a heating rate of 2 °C min⁻¹. The activation of both the Pd-membrane and the catalyst occurs by introducing a reducing gas mixture (10 vol.% H₂ in N₂) for 24 hours.

In this study, the ammonia decomposition reaction was investigated over a temperature range of 350 - 425 °C, a reaction pressure range of 2 - 6 bar, and a weight hourly space velocity (*WHSV*) of approximately 6 000 Nml h⁻¹ g_{cat}. Following this, the ammonia conversion (x_{NH_3}) and hydrogen recovery (x_{NH_3}) were calculated according to Equation 5.1 and Equation 5.2, respectively.

$$x_{NH_3} = \frac{F_{NH_3, in} - F_{NH_3, out}}{F_{NH_3, in}} \cdot 100$$
(5.1)

$$H_2 recovery = \frac{2 \cdot F_{H_2, out}^P}{3 \cdot F_{NH_3, in}} \cdot 100$$
(5.2)

To establish a benchmark for the performance of the membrane reactor, experimental results were performed in packed bed reactor configuration maintaining the same reaction conditions.

5.3 Results and discussion

The performance of the packed bed membrane reactor (PBMR) for ammonia decomposition was assessed under varying temperatures and pressures, with key parameters including ammonia conversion, hydrogen recovery, and hydrogen purity. To highlight the advantages of incorporating a palladium-based membrane for hydrogen separation, initial measurements were conducted using a conventional packed bed reactor (PBR) setup. In this configuration, the permeate side was closed, channeling all reaction products through the retentate. The results obtained with this configuration serve as a benchmark. Subsequently, to evaluate the performance of the PBMR, the permeate line was opened, enabling gases to pass through the membrane and separate hydrogen selectively. Figure 5.3 illustrates the PBMR's performance trend with respect to reaction temperature, maintaining a constant pressure of 4 bar and a fixed space velocity of 6 000 Nml h⁻¹ g_{cat}⁻¹. As expected, due to the endothermic nature of the reaction, ammonia conversion is significantly restricted at lower temperatures for both the PBR and PBMR. However, conversion rises sharply as the temperature increases, as also reported by Li et al. [10].

Integrating the Cs-promoted Ru-based catalyst with the Pd-based membrane yielded remarkable ammonia conversion levels, surpassing the thermodynamic equilibrium already at 400 °C, as shown in Figure 5.3a. The data indicate that conversion about 97% are achievable even at 375 °C, suggesting that high single-pass conversion is attainable. The results at 350 °C indicate the advantages connected with the integration of the palladium-based membrane, as an ammonia conversion up to approximately 15% higher then a conventional reactor was obtained. The results are in agreement with other literature studies [11,12]. Furthermore, at 425 °C an hydrogen recovery of more than 86% was reached, with a corresponding hydrogen purity exceeding 99.99%.



Figure 5.3. (a) Ammonia conversion and (b) hydrogen purity and hydrogen recovery as a function of temperature at fixed pressure (4 bar) and *WHSV* (6 000 Nml h^{-1} g_{cat}⁻¹).

Figure 5.4a displays the impact of the operating pressure on the performance of both PBR and PBMR. Notably, ammonia conversion in the PBMR increases with the operating pressure, whereas in the PBR increasing the pressure has a negative effect. According to the Le Châtelier's principle, ammonia decomposition reaction is favoured at low

pressures; however, pressure variations can significantly affect product separation in membrane-based systems. At high pressures, the permeation of hydrogen through the membrane is often enhanced due to a higher partial pressure differential across the membrane, facilitating efficient hydrogen extraction [13].



Figure 5.4. Effect of reaction pressure on (a) ammonia conversion, (b) hydrogen purity and hydrogen recovery at fixed temperature (375 °C) and *WHSV* (6 000 Nml $h^{-1} g_{cat}^{-1}$).

This selective removal of hydrogen can shift the equilibrium towards more ammonia decomposition. In addition, Figure 5.4b demonstrates that increasing the operating pressure positively influences hydrogen recovery, as higher pressure intensifies the driving force for permeation, thereby enhancing recovery.

The permeation of hydrogen through the membrane effectively lowers the hydrogen concentration on the retentate side, removing a reaction product and thereby shifting the equilibrium toward further ammonia decomposition, in accordance with Le Châtelier's principle. These findings are consistent with previous studies, which report that membrane reactor systems achieve higher ammonia conversions compared to conventional reactors due to their ability to selectively remove products and drive the reaction forward [14].

According to the Temkin-Pyzhev rate mechanism, the rate of ammonia decomposition is significantly inhibited by the presence of hydrogen; specifically, an increase in hydrogen partial pressure correlates with a reduction in the ammonia decomposition rate. This inhibitory effect of H_2 has been experimentally validated by several research groups under comparable conditions, confirming that elevated H_2 levels hinder the decomposition reaction [15]. This phenomenon is particularly important in membrane reactor design, as the selective removal of H_2 can alleviate this inhibition, promoting a higher decomposition rate and increasing overall reactor efficiency [16,17]. At 375 °C, the PBMR overcomes the equilibrium limits at 4 and 6 bar. Conversely, increasing pressure negatively impacts hydrogen purity in the permeate stream due to the distinct permeation mechanisms of nitrogen and hydrogen through the membrane, described in Chapter 3.

Finally, a comparison with findings from the literature reveals that the results achieved in this study not only align with but significantly outperform previously reported ammonia decomposition rates. The Cs-promoted Ru-based catalyst, when integrated with the Pd-based membrane, demonstrated notably higher ammonia conversion, particularly at reduced temperatures where traditional systems struggle to reach high efficiency. This high-performance catalyst-membrane system underscores the benefits of combining selective catalytic activity with a permeable membrane, showcasing the potential of advanced catalytic design in boosting reaction efficiency. As presented in Table 5.1, these findings position the developed reactor as a promising alternative for efficient ammonia decomposition, suggesting a practical pathway to achieve high hydrogen recovery and purity under milder operating conditions compared to conventional systems.

Catalyst	Membrane	WHSV	Reaction Temperature	Reaction Pressure	Permeate Pressure	X _{NH3}	HR	Ref.
		(Nml h ⁻¹ g _{cat} ⁻¹)	(°C)	(bar)	(bar)	(%)	(%)	
Ru Al ₂ O ₃	Pd	120	400	4	Vacuum	99.3	93.5	[7]
Ba-CoCe	Pd-Au	1 200	485	5	1	99	91	[18]
Ru/Y/K/Al ₂ O ₃	Pd-Ag	< 5 922	450	7	1	> 99.1	> 90.6	[19]
Ru/Al ₂ O ₃	Pd	5 670	430	6	Vacuum	99.4	97.5	[9]
Ru/Al ₂ O ₃	Pd	1 127	450	6	1	> 99	> 90	[20]
Cs-Ru/CeO ₂	Pd-Ag	6 000	375	6	1	99.3	84.5	This work

Table 5.1. Comparison of the current study with packed bed membrane reactors employingPd-based membranes reported in the literature.

5.4 Conclusions

The process to produce the catalyst 2Cs5Ru (Cs-Ru/CeO₂) developed in Chapter 4 was succesfully scaled up and integrated with a Pd-based membrane in a fixed bed membrane reactor. The results indicate that the proposed process intensification strategy achieved high NH₃ conversion, approaching the thermodynamic equilibrium at temperatures as low as $375 \,^{\circ}$ C. Ammonia conversion exceeding 97% are achievable within the temperature range $375 - 425 \,^{\circ}$ C at 4 bar, suggesting that high single-pass conversion is attainable. Furthermore, ammonia conversion greater than 99.7% was obtained at $425 \,^{\circ}$ C and 4 bar, with hydrogen recovery of 86.5% and hydrogen purity exceeding 99.99%. Additionally, NH₃ conversion in the PBMR increases with higher operating pressure, surpassing thermodynamic limitations at 4 and 6 bar.

The proposed combination of membrane and catalyst demonstrates superior performance compared to other configurations reported in the literature. By optimizing the synergy between catalyst activity and membrane selectivity, this configuration achieves elevated ammonia conversion alongside improved hydrogen recovery. The membrane effectively removes hydrogen, reducing inhibition and shifting the equilibrium to favor ammonia decomposition. Meanwhile, the catalyst maintains high activity under the operating conditions, complementing the membrane's separation efficiency. This integrated approach not only improves reaction rates but also maximizes hydrogen purity and recovery, presenting a clear advantage over conventional systems documented in previous studies.

5.5 References

- 1. Muradov, N.Z.; Veziroğlu, T.N. From Hydrocarbon to Hydrogen–Carbon to Hydrogen Economy. Int J Hydrogen Energy 2005, 30, 225–237, doi:10.1016/J.IJHYDENE.2004.03.033.
- Makepeace, J.W.; He, T.; Weidenthaler, C.; Jensen, T.R.; Chang, F.; Vegge, T.; Ngene, P.; Kojima, Y.; de Jongh, P.E.; Chen, P.; et al. Reversible Ammonia-Based and Liquid Organic Hydrogen Carriers for High-Density Hydrogen Storage: Recent Progress. Int J Hydrogen Energy 2019, 44, 7746–7767, doi:10.1016/j.ijhydene.2019.01.144.
- Su, Z.; Guan, J.; Liu, Y.; Shi, D.; Wu, Q.; Chen, K.; Zhang, Y.; Li, H. Research Progress of Ruthenium-Based Catalysts for Hydrogen Production from Ammonia Decomposition. Int J Hydrogen Energy 2024, 51, 1019–1043, doi:10.1016/j.ijhydene.2023.09.107.
- Chen, C.; Wu, K.; Ren, H.; Zhou, C.; Luo, Y.; Lin, L.; Au, C.; Jiang, L. Ru-Based Catalysts for Ammonia Decomposition: A Mini-Review. Energy and Fuels 2021, 35, 11693–11706, doi:10.1021/acs.energyfuels.1c01261.
- 5. Statistic_id1046426_global-Ruthenium-Price-2013-2022.
- Bang, G.; Moon, D.K.; Kang, J.H.; Han, Y.J.; Kim, K.M.; Lee, C.H. High-Purity Hydrogen Production via a Water-Gas-Shift Reaction in a Palladium-Copper Catalytic Membrane Reactor Integrated with Pressure Swing Adsorption. Chemical Engineering Journal 2021, 411, 128473, doi:10.1016/J.CEJ.2021.128473.
- Cechetto, V.; Di Felice, L.; Medrano, J.A.; Makhloufi, C.; Zuniga, J.; Gallucci, F. H2 Production via Ammonia Decomposition in a Catalytic Membrane Reactor. Fuel Processing Technology 2021, 216, 106772, doi:10.1016/J.FUPROC.2021.106772.
- 8. Arratibel, A.; Pacheco Tanaka, A.; Laso, I.; van Sint Annaland, M.; Gallucci, F. Development of Pd-Based Double-Skinned Membranes for Hydrogen Production in Fluidized Bed Membrane Reactors. J Memb Sci 2018, 550, 536–544, doi:10.1016/j.memsci.2017.10.064.
- Kim, T.W.; Lee, E.H.; Byun, S.; Seo, D.W.; Hwang, H.J.; Yoon, H.C.; Kim, H.; Ryi, S.K. Highly Selective Pd Composite Membrane on Porous Metal Support for High-Purity Hydrogen Production through Effective Ammonia Decomposition. Energy 2022, 260, 125209, doi:10.1016/J.ENERGY.2022.125209.
- 10. Li, N.; Zhang, C.; Li, D.; Jiang, W.; Zhou, F. Review of Reactor Systems for Hydrogen Production via Ammonia Decomposition. Chemical Engineering Journal 2024, 495.
- 11. García-García, F.R.; Ma, Y.H.; Rodríguez-Ramos, I.; Guerrero-Ruiz, A. High Purity Hydrogen Production by Low Temperature Catalytic Ammonia Decomposition in a

Multifunctional Membrane Reactor. Catal Commun 2008, 9, 482–486, doi:10.1016/j.catcom.2007.07.036.

- 12. Lee, J.E.; Lee, J.; Jeong, H.; Park, Y.K.; Kim, B.S. Catalytic Ammonia Decomposition to Produce Hydrogen: A Mini-Review. Chemical Engineering Journal 2023, 475, 146108, doi:10.1016/j.cej.2023.146108.
- Itoh, N.; Oshima, A.; Suga, E.; Sato, T. Kinetic Enhancement of Ammonia Decomposition as a Chemical Hydrogen Carrier in Palladium Membrane Reactor. Catal Today 2014, 236, 70–76, doi:10.1016/j.cattod.2014.02.054.
- 14. Liu, J.; Ju, X.; Tang, C.; Liu, L.; Li, H.; Chen, P. High Performance Stainless-Steel Supported Pd Membranes with a Finger-like and Gap Structure and Its Application in NH3 Decomposition Membrane Reactor. Chemical Engineering Journal 2020, 388, 124245, doi:https://doi.org/10.1016/j.cej.2020.124245.
- 15. Li, G.; Kanezashi, M.; Yoshioka, T.; Tsuru, T. Ammonia Decomposition in Catalytic Membrane Reactors: Simulation and Experimental Studies. AIChE Journal 2013, 59, 168–179, doi:10.1002/aic.13794.
- Lamb, K.; Hla, S.S.; Dolan, M. Ammonia Decomposition Kinetics over LiOH-Promoted, A-Al2O3-Supported Ru Catalyst. Int J Hydrogen Energy 2019, 44, 3726–3736, doi:10.1016/j.ijhydene.2018.12.123.
- 17. Di Carlo, A.; Vecchione, L.; Del Prete, Z. Ammonia Decomposition over Commercial Ru/Al2O3 Catalyst: An Experimental Evaluation at Different Operative Pressures and Temperatures. Int J Hydrogen Energy 2014, 39, 808–814, doi:10.1016/j.ijhydene.2013.10.110.
- Cerrillo, J.L.; Morlanés, N.; Kulkarni, S.R.; Realpe, N.; Ramírez, A.; Katikaneni, S.P.; Paglieri, S.N.; Lee, K.; Harale, A.; Solami, B.; et al. High Purity, Self-Sustained, Pressurized Hydrogen Production from Ammonia in a Catalytic Membrane Reactor. Chemical Engineering Journal 2022, 431, 134310, doi:10.1016/J.CEJ.2021.134310.
- 19. Jiang, J.; Dong, Q.; McCullough, K.; Lauterbach, J.; Li, S.; Yu, M. Novel Hollow Fiber Membrane Reactor for High Purity H2 Generation from Thermal Catalytic NH3 Decomposition. J Memb Sci 2021, 629, 119281, doi:10.1016/J.MEMSCI.2021.119281.
- Sitar, R.; Shah, J.; Zhang, Z.; Wikoff, H.; Way, J.D.; Wolden, C.A. Compact Ammonia Reforming at Low Temperature Using Catalytic Membrane Reactors. J Memb Sci 2022, 644, 120147, doi:10.1016/J.MEMSCI.2021.120147.

Chapter 6

Modeling and simulation of ammonia synthesis in a packed bed membrane reactor

This chapter is based on the following paper:

I. Gargiulo, G. Anello, S. Richard, F. Gallucci. "Modeling and simulation study of a packed bed membrane reactor for ammonia synthesis: assessing the role of membrane performance and operating conditions", Under review at International Journal of Hydrogen Energy.

Abstract

Ammonia has gained attention in recent years as a potential hydrogen energy carrier. However, nowadays, the main route to synthesize ammonia is via the energy intensive Haber-Bosch process. Therefore, ongoing research focuses on exploring new sustainable methods for ammonia production. In this study a reactor model was developed based on integrating a ruthenium-based catalyst into a membrane reactor as process intensification strategy. The mathematical model was initially fitted using experimental data from a packed bed reactor. It was then applied to evaluate the feasibility of a packed bed membrane reactor, focusing on the membrane's performance requirements to improve the process. Specifically, the study examined how the membrane could enhance hydrogen conversion, ammonia purity, and ammonia recovery. The results obtained in the isothermal packed bed membrane reactor suggest that the membrane performance is crucial in order to boost hydrogen conversion. More specifically, an ammonia permeance higher than 1.10-7 mol s-1 m-2 Pa-1 and an ammonia-to-hydrogen selectivity of 50 are required to ensure significant benefits from the membrane integration, on the other hand, the ammonia-to-nitrogen selectivity deeply influences both ammonia purity and ammonia recovery. This leads to a tradeoff value for ammonia-to-nitrogen selectivity of approximately 100. Furthermore, in the adiabatic case study, the heat exchange investigation between feed gas and sweep gas highlights the importance of the latter as cooling fluid. With a sweep gas-to-feed ratio of 6, a pressure difference across the membrane of 20 bar, the packed bed membrane reactor can reach a hydrogen conversion of 90%, ammonia recovery and ammonia purity of 97% and 6% respectively, as a result of temperature control. Finally, the packed bed membrane reactor's optimal operating conditions were achieved by tuning the permeate temperature and optimizing the hydrogen-to-nitrogen feed flow ratio on both sides. The identified optimal state is characterized by a hydrogen-to-nitrogen molar feed ratio of 1.5, coupled with an inlet sweep gas temperature of 200 °C, enabling the packed bed membrane reactor to achieve an H₂ conversion of approximately 93%, along with ammonia recovery and ammonia purity of 99.1 and 5.65%, respectively. Hence, the mathematical model demonstrates that an adiabatic membrane reactor with the integration of heat exchange has the potential to attain greater hydrogen conversion compared to the equilibrium constraint observed in a conventional packed bed reactor.

6.1 Introduction

Despite the harsh operative conditions (50 - 200 bar and 400 - 500 °C), the vast majority of ammonia (NH₃) is still globally produced via the Haber-Bosch process, that accounts for approximately 2% of the entire global energy consumption and 1.2% of global carbon dioxide emissions [1,2]. These energy-intensive conditions are required by the severe thermodynamic limitations connected with the ammonia synthesis reaction from nitrogen (N₂) and hydrogen (H₂). As a result, the production of ammonia per single pass remains relatively low, with the effluent ammonia fraction typically in the range of 20 - 25 % [3,4]. Thus, industrially, since further increase in temperature is unfeasible due to the reverse reaction occurring (ammonia decomposition) and possible catalyst deactivation, conventional ammonia synthesis is conducted in multistage adiabatic packed bed reactors with interstage cooling over an iron-based catalyst [5]

Since ammonia is the sole product of the reaction, a potential strategy to substantially enhance the rate of ammonia synthesis is to shift the equilibrium by continuously removing NH_3 from the reaction zone. However, there have been only relatively few studies in literature that have successfully surpassed single-pass equilibrium conversion for ammonia synthesis. For example, Smith et al. proposed an integrated system for ammonia synthesis and separation that utilized ruthenium (Ru) catalysts and manganese-based absorbent. Their work demonstrated the benefits of this synergistic approach, achieving conversions that exceeded the reaction equilibrium [6].

The use of membrane reactors has emerged as a promising method to shift equilibrium of thermodynamically constrained catalytic reactions through the selective removal of products or by-products. This has been applied in various processes, such as dimethyl ether synthesis [7,8], and water-gas shift reaction [9,10]. While these studies highlight the benefits of membrane reactor configurations, such as improved conversion and lower energy requirements for a given output, there are still only a limited number of studies in the open literature on the potential application of this technology for ammonia synthesis.

Among these, Zhang et al. discussed the feasibility and advantages of a membrane system in the framework of an isothermal packed bed reactor with the conventional iron-based catalysts and considered the impact of membrane properties on the reactor performance. The authors found that achieving minimum selectivity thresholds is essential for successfully enhancing the process. Ideally, an ammonia-to-nitrogen selectivity higher than 10 and an ammonia-to-hydrogen selectivity higher than 4 is required. Nevertheless, it has to be pointed out that the authors in this study did not discuss nor report the influence of the heat of reaction. Ammonia synthesis is an exothermic transformation, thus the heat released by the reaction might as well influence the system from a kinetic and thermodynamic point of view, as well as the stability and selectivity of the membrane [11]. More recently, Kucuk et al. modelled a structured microreactor, whose channels were coated with iron-based catalyst, with heat exchange and membrane (ZnCl₂-based immobilized molten-salt) separation integrated. The proposed system achieved a 47% nitrogen conversion, surpassing the corresponding equilibrium conversion of 40%; thus, the reported results support the feasibility of overcoming the thermodynamic limits in the Haber-Bosch process [12].

The present work focuses on a theoretical study on one-dimensional packed bed membrane reactor (PBMR) for ammonia synthesis, designed to identify the minimum membrane requirements in terms of ammonia permeance and selectivity, relative to the packed bed membrane reactor (PBR) performance. The main aim is to prove the feasibility of this application on the ammonia synthesis process and establish a benchmark for membrane technology development.

6.2 Methodology

6.2.1 <u>Membrane reactor configuration</u>

The membrane reactor design proposed in this work is illustrated in Figure 6.1, featuring a shell-and-tube configuration. The inner tube represents a tubular membrane, while the catalyst particles are located in the shell. This structure creates two distinct zones: the retentate side, where the feed is introduced and the reaction occurs along the reactor's length, and the permeate side, where gases selectively permeate through the membrane. On the permeate side, a sweep gas is injected and mixed with the permeating gases. As illustrated in Figure 6.1, the feed stream and the sweep gas stream are in a co-current configuration.



Figure 6.1. Schematic representation of the packed bed membrane reactor proposed in this study.

6.2.2 <u>Reaction scheme and kinetics</u>

Ammonia synthesis involves the reaction between nitrogen and hydrogen, as represented by Equation 6.1:

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \tag{6.1}$$

A kinetic model of the reaction was obtained from a previous study by Rossetti et al. that utilized a Ru/C catalyst [13]. In their work, the authors derived the overall reaction rate from the classical Temkin equation, incorporating an additional adsorption term, as expressed in Equation 6.2:

$$\frac{d\eta}{d\tau} = k_f \cdot \lambda(q) \cdot \frac{(a_{N_2})^{0.5} \cdot \left[\frac{(a_{H_2})^{0.375}}{(a_{NH_3})^{0.25}}\right] - \frac{1}{K_a} \cdot \left[\frac{(a_{NH_3})^{0.75}}{(a_{H_2})^{1.125}}\right]}{1 + K_{H_2} \cdot (a_{H_2})^{0.3} + K_{NH_3} \cdot (a_{NH_3})^{0.2}}$$
(6.2)

where $d\eta/d\tau$, expressed in mol h⁻¹ l_{cat}⁻¹, represents the reaction rate of defective reactant, k_f is the kinetic constant of the reaction, a_i indicates the partial activities of the involved species, K_a is the reaction equilibrium constant in terms of activities, K_{H_2} and K_{NH_3} are the adsorption equilibrium constants of hydrogen and ammonia respectively, q is the hydrogen-to-nitrogen molar feed ratio, and $\lambda(q)$ is the stochiometric parameter. These parameters are determined according to the equations presented in Appendix C (Table C1).

6.3 Basis and assumptions for the reactor model

The developed model is a 1-D phenomenological membrane reactor model, grounded on the following assumptions:

- 1) Plug flow behavior, with negligible radial gradients of concentrations and temperature, assuring $r/L \ll Re \cdot Sc \ll r/L$.
- 2) Steady-state conditions.
- 3) Negligible pressure drops in the permeate side.
- 4) The membrane material is considered inert.
- 5) Pseudo-homogeneous model.
- 6) Negligible mass and energy transport limitations inside the catalyst pellets and at the surface of the pellets.

The mass balance equations for both the retentate and permeate side are presented in this section. The subsequent equations apply to each component of the gas mixture:

$$\frac{dF_i^R}{dL} = \vartheta_i \cdot (r_i) \cdot \rho_c \cdot (1-\varepsilon) \cdot \frac{\pi}{4} \cdot \left(D_r^{i^2} - D_m^{o^2}\right) - J_i \cdot (\pi \cdot D_m^o)$$
(6.3)

$$\frac{dF_i^p}{dL} = J_i \cdot (\pi \cdot D_m^o) \tag{6.4}$$

$$J_i = \mathcal{P}_i \cdot (P_i^R - P_i^P) \tag{6.5}$$

where J_i and \mathcal{P}_i represent the flux and permeance, respectively, of the component *i* permeating through the membrane. The flux is calculated according to Equation 6.5 with the pressure difference considered positive when the flow proceeds from the retentate to the permeate side.

Likewise, the energy balance equations are computed for retentate and permeate side.

$$\frac{dT^{R}}{dL} = \frac{(r) \cdot (-\Delta H)_{T^{R}} \cdot \rho_{c} \cdot (1-\varepsilon) \cdot \frac{\pi}{4} \cdot \left(D_{r}^{i^{2}} - D_{m}^{o^{2}}\right)}{\sum_{i} F_{i}^{R} \cdot c_{p,i}^{R}} - \frac{U \cdot \pi \cdot D_{m}^{i} \cdot (T^{R} - T^{P})}{\sum_{i} F_{i}^{R} \cdot c_{p,i}^{R}}$$
(6.6)

$$\frac{dT^P}{dL} = \frac{U \cdot \pi \cdot D_m^i \cdot (T^R - T^P)}{\sum_i F_i^P \cdot c_{p,i}^P}$$
(6.7)

$$(U)^{-1} = \frac{1}{h^{p}} + \frac{\frac{D_{m}^{i}}{2} \cdot \ln\left(\frac{D_{m}^{o}}{D_{m}^{i}}\right)}{k} + \frac{D_{m}^{i}}{D_{m}^{o}} \cdot \frac{1}{h^{R}}$$
(6.8)

Here, *U* is the global heat transfer coefficient, which characterizes three successive heat transfer phenomena: (i) convection in the inner tube, (ii) conduction through the membrane, and (iii) convection in the outer tube. The heat transfer coefficient for the reaction zone (h^R), was calculated according to the correlation of Li and Finlayson [14], as shown in Equation 6.14, which takes in account the heat transfer of a packed bed by referring to a Reynolds number depending on particle diameter, as shown in Equation 6.9. The heat transfer coefficient for the permeate zone (h^P) was calculated using the Dittus-Boelter correlation, as reported in Equation 6.13, which considers a smooth concentric annulus [15].

Equation 6.9 to Equation 6.14 describe the dimensionless numbers employed in this work, which play a crucial role in characterizing the heat and mass transfer phenomena within the system. Each equation provides a framework for understanding the relationships between various physical properties and helps in predicting the behavior of the system under different operating conditions.

$$Re^{R} = \frac{d_{p} \cdot G^{R}}{\mu_{mix}^{R}}$$
(6.9)

$$Re^{P} = \frac{D_{m}^{i} \cdot G^{P}}{\mu_{mix}^{P}} \tag{6.10}$$

$$Pr^{R} = \frac{\mu_{mix}^{R} \cdot c_{p,mix}^{R}}{\lambda_{mix}^{R}}$$
(6.11)

$$Pr^{P} = \frac{\mu_{mix}^{P} \cdot c_{p,mix}^{P}}{\lambda_{mix}^{P}}$$
(6.12)

$$Nu^{P} = 0.023 \cdot Re^{P^{0.8}} \cdot Pr^{P^{0.4}} = \frac{h^{P} \cdot D_{m}^{i}}{\lambda_{min}^{P}}$$
(6.13)

$$Nu^{R} = 0.17 \cdot Re^{R^{0.79}} \cdot \left(\frac{Pr^{P}}{0.7}\right)^{1/3} = \frac{h^{R} \cdot d_{p}}{\lambda_{mix}^{R}}$$
(6.14)

All the gas properties, including density, viscosity, specific heat, thermal conductivity, used in this work can be found in the Appendix C. In Equation 6.15 and Equation 6.16, the molar flux of the mixture in the retentate and permeate side are provided.

$$G^{R} = \frac{F_{tot}^{R} \cdot M_{mix}^{R}}{A}$$
(6.15)

$$G^{P} = \frac{F^{P}_{tot} \cdot M^{P}_{mix}}{A^{i}_{m}}$$
(6.16)

Lastly, the conductivity, in this case referred to carbon membranes, was computed by considering the thermal conductivity contribution of the carbon-based selective layer laying on top of alumina tubular support. This calculation is based on the correlations presented in the work of Poto et al. [7].

The Ergun equation (Equation 6.17) for estimating the pressure drops was applied only to the retentate side, while the pressure on the permeate side was kept fixed.

$$\frac{dP}{dL} = -\left[\frac{150 \cdot \mu_{mix} \cdot u \cdot (1-\varepsilon)^2}{\varepsilon^3 \cdot d_p^2} + \frac{1.75 \cdot (1-\varepsilon) \cdot \rho_{mix} \cdot u^2}{\varepsilon^3 \cdot d_p}\right] \cdot 10^{-5}$$
(6.17)

Here, μ_{mix} and ρ_{mix} are the viscosity and the density of the gas mixture respectively, u is the space velocity based on the empty cross-section of the reaction vessel, ε is the porosity of the bed and d_p is the diameter of the catalyst particles.

The boundary conditions applied to solve the model are discussed in this section. At the entrance of the reactor, the inlet temperatures and pressures and the inlet gas compositions, along with the sweep gas are known. Therefore, the following boundary conditions, apply at L = 0:

$$T^{R} = T^{R}(0)$$
$$T^{P} = T^{P}(0)$$
$$P^{R} = P^{R}(0)$$
$$F_{i}^{R} = F_{i}^{R}(0)$$
$$F_{i}^{P} = F_{i}^{P}(0)$$

where *i* takes values from 1 to 3, representing the three species present in the system.

6.4 Mathematical model validation

The mathematical model consisting of nine ordinary differential equations with corresponding boundary conditions was implemented and solved using MATLAB® R2022a (MathWorks Inc., Massachusetts, USA). The *ode15s* integration method was employed, along with a set of algebraic equations concerning reaction rates and gas properties. The performance of the packed bed membrane reactor is assessed based on H₂ conversion, as expressed in Equation 6.18, which takes into account the porous nature of the membrane, thus a direct and reverse permeation can occur [7]:

$$x_{H_2} = \frac{F_{H_2,in}^R - F_{H_2,out}^R - F_{H_2,tm}^R}{F_{H_2,in}^R - F_{H_2,bp}^P} \cdot 100$$
(6.18)

where $F_{H_2,tm}^R$ stands for the hydrogen amount potentially able to pass across the membrane leaving the reaction zone, while $F_{H_2,bp}^P$ refers to the term associated with hydrogen permeating back into the reaction zone from the permeate side. Additionally, other parameters, such as NH₃ recovery and NH₃ purity, as outlined in Equations 6.19 and Equation 6.20 respectively, were evaluated to assess the performance of the PBMR. NH₃ recovery indicates the proportion of ammonia that can be collected on the permeate side, compared to its production in the retentate. Meanwhile, NH₃ purity provides insight into the composition of the stream exiting the membrane, offering essential data for the subsequent separation step.

$$NH_3 \, recovery = \frac{F_{NH_3}^P}{F_{NH_3}^R + F_{NH_3}^P} \cdot 100 \tag{6.19}$$

$$NH_3 purity = \frac{F_{NH_3}^P}{F_{N_2}^P + F_{H_2}^P + F_{NH_3}^P} \cdot 100$$
(6.20)

6.4.1 Validation of the packed bed reactor

Before delving into the reactor's performance, the mathematical model was first validated by comparing its prediction with experimental data retrieved from Rossetti et al. [13]. The validation process involved a comparison with data sets from various kinetic tests performed within a temperature range of 370 - 460 °C and a pressure range of 50 - 100 bar, with the hydrogen-to-nitrogen feed flow ratio (q^R) set at 1.5 and 3, and varying the gas hourly space velocity (*GHSV*) in the range of $0.5 \cdot 10^5 - 4 \cdot 10^5$ h⁻¹, defined as the ratio of the normal feed flow rate and the catalyst volume.
In order to validate the mathematical model, a fitting study was carried out, by varying the bed porosity (ε) and consequently the active bed length(L), which is not reported in the work by Rosetti et al. As illustrated in Figure 6.2, bed porosity values ranging from 0.3 and 0.5 were investigated. A mean relative deviation below 16% was achieved in all cases except for two tests, where the deviations were 20% and 30%, respectively. Details of the validation tests are provided in Appendix C.



Figure 6.2. Model fitting of outlet NH₃ molar fraction based on experimental tests (T = 430 °C, 100 bar) for (a) $q^R = 1.5$ and (b) $q^R = 3$.

6.4.2 Validation of the permeation module

Once the packed bed reactor was validated, the model was extended to integrate a membrane, by using Equation 6.3 and Equation 6.4. In this overview, the choice of an NH₃ permeable membrane for a membrane reactor is critical, and various types of membranes can be considered. This selection is influenced by various factors, including operating conditions, feedstock composition, and the required product purity. Additionally, the chemical resistance and long-term stability of the membrane are crucial considerations. Membrane materials used in NH₃ synthesis and NH₃ separation processes include zeolite membranes [16], molten salt-based membrane [17], polymeric membranes [18], ceramic membranes [19] and silica membranes [20]. This study focuses on ceramic membranes, particularly carbon membranes, due to their chemical resistance, cost-effectiveness, and the feasibility of tuning their characteristics.

Experimental gas permeation tests were performed using carbon membranes, and the results were utilized into the model for validation. Under condition that no reaction was occurring, the model successfully predicted the permeance of each component at different ΔP (Figure 6.3) while keeping the same temperature for the specific case. This validation process confirmed the accuracy of the membrane reactor model.



Figure 6.3. Permeation module validation with experimental singlegas tests at 300 °C for (a) H_2 permeance, (b) N_2 permeance and (c) NH_3 permeance. *(continued on the next page)*



Figure 6.3. *(continued)* Permeation module validation with experimental single-gas tests at 300 °C for (a) H_2 permeance, (b) N_2 permeance and (c) NH_3 permeance.

6.5 Study of the membrane performance

Preliminary studies were conducted on the isothermal membrane reactor to examine how the membrane's performance would impact the reactor's capabilities in terms of H₂ conversion, NH₃ recovery and NH₃ purity. All the operational conditions and design specifications of the reactor selected for this study are detailed in Table 6.1, where:

- Temperature and pressure were established based on the lower boundary limit where the kinetic law was determined.
- Sub-stoichiometric feed ratio was selected due to hydrogen poisoning associated with Ru-based catalysts. In this case the conversion is reported in terms of H₂ conversion, as H₂ is the limiting reagent.
- ✤ Reactor length and reactor diameter were chosen to ensure *L/D* > 30, thereby guaranteeing negligible radial dispersion [21].
- The Peclet number was employed to determine the appropriate axial velocity to neglect axial dispersion.
- Sweep gas-to-feed ratio (*SF*) equal to 1 was selected to have a match between the feed flow rate and the sweep gas flow rate.

Parameter	Units	Value			
Temperature	(°C)	370			
Pressure	(bar)	50			
q^R	$(mol_{H_2}:mol_{N_2})$	1.5			
SF	(-)	1			
ΔP	(bar)	0			
Reactor length	(m)	1			
Reactor diameter	(m)	0.033			
GHSV	(h-1)	35			
Bed porosity	$(m_v^3 m_r^{-3})$	0.4			
Catalyst bed density	(kg m-3)	590			

Table 6.1. PBMR parameters in isothermal conditions.

6.5.1 Ideal membrane case study

In assessing potential membrane performance benchmarks, selectivity (S_{NH_3/H_2} , S_{NH_3/N_2} , S_{H_2/N_2}) and permeance of each gas (\mathcal{P}_{H_2} , \mathcal{P}_{N_2} , \mathcal{P}_{NH_3}) were considered during this study. The literature survey, as previously discussed regarding hypothetical membranes suitable for NH₃ separation, led to the selection of ceramic membranes, specifically silica and zeolite membranes, as suitable for NH₃ separation, therefore were chosen as reference. For instance, Camus et al. studied silica and zeolite membranes, observing an ammonia permeance of $1 \cdot 10^{-8} - 1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹ at 80 °C and 10 bar [19]. Meanwhile, Kanezashi et al. investigated silica membranes over a wide temperature range, reporting an ammonia permeance of $1 \cdot 10^{-9}$ mol s⁻¹ m⁻² Pa⁻¹ [20]. Consequently, the initial range of ammonia permeance investigated in this study was set at $0 - 1 \cdot 10^{-6}$ mol s⁻¹ m⁻² Pa⁻¹.

The membrane was considered to be ideal, implying that the pore size distribution was designed to exclusively allow the passage of ammonia and hydrogen, as they possess the smallest molecules size with very similar kinetic diameters (0.260 and 0.290 nm, respectively). Thus, during the simulation, nitrogen permeation was neglected, resulting in $S_{H_2/N_2} = \infty$ and $S_{NH_3/N_2} = \infty$. Considering the potential transport mechanisms within the membrane, molecular sieving is the preferred phenomenon, as it enables separation based on the kinetic diameter of individual molecules. Conversely, if the pores are larger and not specifically tailored to exclusively permit ammonia passage, the transport mechanism may shift towards Knudsen diffusion [22]. For this mechanism, the well-known Knudsen selectivity is expressed in Equation 6.21.

$$S_{K,i/j} = \sqrt{\frac{M_j}{M_i}} \tag{6.21}$$

From the molecular masses of the two components, the Knudsen selectivity of ammonia over hydrogen was found to be 0.34. This value was taken as reference for establishing the selectivity range under investigation, which is defined as $S_{NH_3/H_2} = 0.5 - 50$.

Hydrogen conversion is significantly influenced by the ammonia permeance of the membrane, as shown in Figure 6.4a. The increasing trend reaches a plateau when the ammonia permeance is about $0.4 \cdot 10^{-6}$ mol s⁻¹ m⁻² Pa⁻¹, indicating that the system has achieved thermodynamic equilibrium between the reaction and permeation zones. The investigation on hydrogen conversion as a function of ammonia permeance, evaluated

at different ammonia-to-hydrogen selectivity values, demonstrates that for \mathcal{P}_{NH_3} values greater than 0.4 \cdot 10⁻⁶ mol s⁻¹ m⁻² Pa⁻¹, no further effect is observed. These results align with previous literature studies [11].

In Figure 6.4b, the ammonia transmembrane molar flow $(F_{NH_3, tm})$ is presented as a function of ammonia permeance for different values of S_{NH_3/H_2} . The results show that $F_{NH_3, tm}$ does not increase significantly with selectivity, indicating that this molar flow depends primarily on NH₃ permeance rather than the ammonia-to-hydrogen selectivity. Although an increase in permeance is observed, it is not substantial enough to significantly impact the passage of ammonia across the membrane and, consequently, the hydrogen conversion.

Then, the study focused on hydrogen back-permeating from the permeate zone to the retentate zone $(F_{H_2, bp})$. Figure 6.4c shows that this molar flow increases with the NH₃ permeance (the negative sign indicates opposite direction with respect to the mass balance), whereas $F_{H_2, bp}$ decreases as the selectivity increases. This behavior can be explained by the fact that an increase in S_{NH_3/H_2} results in reduced hydrogen loss from the retentate side, maintaining a higher partial pressure and reducing the driving force from the permeate to retentate side, thus leading to a decrease in back-permeation.

Avoiding excessive hydrogen accumulation in the retentate zone is crucial due to catalyst-related reasons, and a loss of hydrogen in the permeate zone necessitates additional sweep gas reintegration. Simultaneously, with less H₂ back-permeation, ammonia partial pressure in the permeate is kept low, allowing enhanced ammonia permeation. Thus, as shown in Figure 6.4c, higher ammonia-to-hydrogen selectivity enables a higher NH₃ recovery, which reaches a maximum when the NH₃ permeance is about $0.1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹. This value, together with an ammonia-to-hydrogen selectivity of 50, was selected as final value and considered for the rest of the study.



Figure 6.4. Study of membrane performance with respect to NH₃ permeance showing the impact on (a) H₂ conversion, (b) NH₃ transmembrane flow, (c) H₂ back-permeation flow and (d) NH₃ recovery, for different values of S_{NH_3/H_2} . (continued on the next page)



Figure 6.4. *(continued)* Study of membrane performance with respect to NH₃ permeance showing the impact on (a) H₂ conversion, (b) NH₃ transmembrane flow, (c) H₂ back-permeation flow and (d) NH₃ recovery, for different values of S_{NH_3/H_2} .

6.5.2 <u>Real membrane case study</u>

After this initial optimization, also nitrogen permeation was considered, hence also the influence of ammonia-to-nitrogen selectivity was examined. A broad range of selectivity values was selected based on literature studies.

As shown in Figure 6.5a, there is no significant correlation between hydrogen conversion and S_{NH_3/N_2} , even with a three-order magnitude increase. This observation is consistent with the findings reported by Zhang et al. [11]. Therefore, the amount of nitrogen loss on the retentate side, $F_{N_2, tm}$, was evaluated as a key performance parameter to determine the minimum required ammonia-to-nitrogen selectivity.

The results reported in Figure 6.5b indicate that with lower values of S_{NH_3/N_2} , the nitrogen flow decreases, and beyond a selectivity value of approximately 100, the decrease becomes less pronounced.

Analyzing the trends in ammonia recovery and purity, as shown in Figure 6.5c, they exhibit opposite behaviors. This phenomenon can be attributed to the fact that as S_{NH_3/N_2} increases, a greater amount of ammonia passes through the membrane, thereby shifting the equilibrium towards the product side.



Figure 6.5. Impact of S_{NH_3/N_2} on (a) H₂ conversion, (b) N₂ transmembrane flow, (c) NH₃ purity and recovery. *(continued on the next page)*



Figure 6.5. *(continued)* Impact of S_{NH_3/N_2} on (a) H₂ conversion, (b) N₂ trans-membrane flow, (c) NH₃ purity and recovery.

This results in a higher NH₃ concentration in the retentate zone, with some NH₃ not being fully removed by the membrane, leading to a decrease in its recovery. In contrast, purity follows the opposite trend, increasing as expected, since more NH₃ is separated while less nitrogen crosses the membrane. Based on these findings, a minimum value of $S_{NH_3/N_2} = 100$ is set as a required parameter for the membrane.

Figure 6.6 illustrates H_2 conversion as a function of both ammonia-to-nitrogen and ammonia-to hydrogen selectivity under three different NH₃ permeance scenarios. The result indicates that as the ammonia permeance increases, a corresponding rise in H_2 conversion is observed. For each S_{NH_3/H_2} value, the H₂ conversion consistently plateaus at approximately $S_{NH_3/N_2} = 100$. Similar trends are observed for NH₃ purity and recovery, as shown in Figure C3, in Appendix C. Focusing on the N₂ conversion depicted in Figure C5 in Appendix C, a decreasing trend is observed with increase of S_{NH_3/H_2} . This behavior may be attributed to the S_{H_2/N_2} decrease as S_{NH_3/H_2} increases, resulting in a greater possibility of N_2 permeating the membrane. The N_2 transmembrane flow increases with selectivity, as depicted in Figure C4, leaving less N₂ available to react on the retentate side. In contrast, H_2 conversion increases with selectivity due to the dependence from the H₂ back-permeation which decreases as the selectivity increases. Similar considerations apply to the stream purity which decreases with increasing S_{NH_3/H_2} . This condition eventually hits a plateau when $\mathcal{P}_{NH_3} = 1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹. While the N₂ transmembrane flow remains dependent on selectivity, the amount of NH₃ passing through the membrane becomes less sensitive on selectivity and stabilizes at this permeance value, as previously mentioned. Nevertheless, higher NH₃ recovery can be achieved, as recovery depends solely on the NH₃ molar flow across the membrane, which increases with NH₃ permeance and, simultaneously, with S_{NH_3/H_2} .



Figure 6.6. Impact of S_{NH_3/N_2} on H₂ conversion, with \mathcal{P}_{NH_3} equal to (a) $1 \cdot 10^{-9}$, (b) $1 \cdot 10^{-8}$ and (c) $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹, for different values of S_{NH_3/H_2} . (continued on the next page)



Figure 6.6. *(continued)* Impact of S_{NH_3/N_2} on H₂ conversion with \mathcal{P}_{NH_3} equal to (a) $1 \cdot 10^{-9}$, (b) $1 \cdot 10^{-8}$ and (c) $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹, for different values of S_{NH_3/H_2} .

Consequently, a \mathcal{P}_{NH_3} of $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹ demonstrates that optimal performance is achieved when coupled with an S_{NH_3/H_2} of 50 and an S_{NH_3/N_2} of 100. These properties reflect a trade-off among conversion, purity and recovery. The optimal membrane features determined from this preliminary analysis are detailed in Table 6.2.

Membrane performance indicators	Units	Value
\mathcal{P}_{NH_3}	(mol s ⁻¹ m ⁻² Pa ⁻¹)	$1 \cdot 10^{-7}$
S_{NH_3/H_2}	(-)	50
S_{NH_3/N_2}	(-)	100

Table 6.2. Membrane optimal features identified from the preliminary study.

6.6 Operational condition study: sweep gas-to-feed ratio vs. transmembrane pressure difference

It is crucial to maintain a high partial pressure difference of ammonia across the membrane to enhance the driving force and, consequently, ammonia separation. To achieve this, a strategic approach involves utilizing gases in the permeate side to minimize the partial pressure of ammonia on that side. Simultaneously, the partial pressure of the reactants must be high enough to prevent their passage across the membrane. To address this challenge, a sweep gas composed of the two reactants, H_2 and N_2 , was considered. The investigation initially focused on an adiabatic solution, neglecting heat exchange in the shell-and-tube reactor configuration. Subsequently, heat exchange between the retentate and permeate side was incorporated into the analysis. In this context, Equations 6.6 and 6.7 were applied within the model, accounting for all the gas properties depending on temperature, as detailed in the Appendix C. Finally, a study on the sweep gas-to-feed ratio (*SF*) and transmembrane pressure difference (ΔP) was conducted to assess their potential impact on reactor performance. As mentioned before, the inlet reaction temperature was established based on lower limit of the kinetic rate law.

Thus, for simplicity the operating conditions of the reactor were kept consistent with the previous configuration, and the sweep gas inlet temperature was also set at 370 °C. Pressure in the permeate was varied according to the desired ΔP in the case study, ranging up to a maximum of 50 bar which aligns with the pressure on the retentate side. The outcomes of this study (yet without heat exchange) are presented in Figure 6.7a, where the conversion is assessed across a range of *SF* values between 0 and 50 for each ΔP . As *SF* increases, the conversion rises and eventually reaches a plateau. However, the rate at which this plateau is attained is determined by the pressure. This phenomenon occurs because the increase in *SF* leads to a decrease in the partial pressure of ammonia

in the sweep gas stream, thereby enhancing the driving force for ammonia permeation through the membrane. At the same time, a larger pressure difference between retentate and permeate creates a stronger driving force, facilitating the migration of the species from retentate to permeate. Notably, as the ΔP increases, the plateau is achieved more rapidly, together with a higher conversion. Consequently, it can be inferred that once the sweep gas flow rate attains a sufficiently high value, further increases do not significantly lower the partial pressure of ammonia in the sweep gas, leading to a negligible change in terms of hydrogen conversion.

Likewise, when considering the heat exchange between the retentate and permeate zone, shown in Figure 6.7b, for each ΔP value, the conversion plateau is reached at a lower SF, accompanied by a simultaneous inversion of the trend. This effect arises because, as SF increases, the residence time in the permeate decreases, resulting in faster NH₃ removal. Simultaneously, an increase in ΔP , promotes additional NH₃ separation (see Figure 6.7c) which accelerates the reaction rate, alongside a rise in temperature. However, the speed eventually reaches a speed at which further increases in SF yields no additional improvement. At this breakthrough point, as ΔP continues to rise, the reaction accelerates but the conversion rate subsequently starts to decline due to elevated temperature. Thus, for $SF \le 6$, higher ΔP leads to higher conversion, whereas as SF increases, the conversion trend rises with a decrease in ΔP . Additionally, larger ΔP values result in a quicker attainment of the plateau, and in all the cases, the achieved conversion is consistently higher than in the no-heat exchange case. As a matter of fact considering the heat exchange between the two concentric tubes, the temperature profile is kept much more uniform (Figure 6.8a) than the other cases, leading to reach higher conversion, due to the presence of the sweep gas, acting as cooling fluid, in view of the exothermicity of the reaction. In this case, as ΔP decreases, a reduced driving force is established between the two parts, causing less loss of sweep gas towards the retentate side. This helps in maintaining a high amount of cooling gas in the permeate side. In contrast, when examining the parameters of ammonia recovery and purity, Figure 6.7c and Figure 6.7d, it becomes evident that their upward trends are contingent on the increase in ΔP . This aligns with expectations since a higher pressure difference results in a higher different partial pressure of ammonia, allowing more ammonia to pass through and be separated. As the sweep gas increases, more hydrogen and nitrogen are present in the permeate, leading to a decrease in purity. In terms of the recovery factor, when the driving force decreases, obviously less ammonia can be detached, leading to a lower ammonia recovery. Thus, a $\Delta P = 40$ bar and SF = 6 were picked as best trade-off conditions for the membrane reactor.



Figure 6.7. Effect of the sweep gas-to-feed ratio (*SF*) considering adiabatic conditions, on (a) H₂ conversion without heat exchange between retentate and permeate, (b) H₂ conversion considering heat exchange between retentate and permeate, (c) NH₃ purity and (d) NH₃ recovery considering heat exchange between retentate and permeate, for different values of ΔP . (continued on the next page)



Figure 6.7. (*continued*) Effect of the sweep gas-to-feed ratio (*SF*) considering adiabatic conditions, on (a) H₂ conversion without heat exchange between retentate and permeate, (b) H₂ conversion considering heat exchange between retentate and permeate, (c) NH₃ purity and (d) NH₃ recovery considering heat exchange between retentate and permeate, for different values of ΔP .

6.7 Heat management study: effect of temperature

The mathematical model with the implementation of all the discussed parameters was further analyzed with a focus on heat management, considering the sweep gas as a cooling fluid. Figure 6.8a highlights two different cases: the dashed lines illustrate the temperature profile of an adiabatic membrane reactor without considering heat exchange between retentate and sweep gases, whereas the solid ones depict the temperature profile of an adiabatic membrane reactor when heat transfer between these two zones is considered. This demonstrates that the presence of a sweep gas contributes to a flatter temperature profile, facilitating higher conversion. Furthermore Figure 6.8b displays the temperature profile of both sides for the specific case of SF = 10, where it is clearly shown that the flat profile in the retentate zone is due to the presence of the sweep gas whose temperature profile slowly increases. As the retentate releases heat to the permeate, temperature peaks in the retentate are moderated, resulting in a flatter temperature gradient.



Figure 6.8. (a) Temperature profile along the reactor length for an adiabatic PBMR considering heat exchange (HE) and not (NHE), between the retentate and permeate side for $\Delta P = 30$ bar, for different values of SF; (b) temperature profile in the retentate and permeate sides for of *SF* = 10 and $\Delta P = 30$ bar. (*continued on the next page*)



Figure 6.8. (*continued*) (a) Temperature profile along the reactor length for an adiabatic PBMR considering heat exchange (HE) and not (NHE), between the retentate and permeate side for $\Delta P = 30$ bar, for different values of SF; (b) temperature profile in the retentate and permeate sides for of *SF* = 10 and $\Delta P = 30$ bar.

Interestingly adjusting the inlet flow temperature on the permeate side can enhance the final conversion even further. Figure 6.9a illustrates this investigation by varying the inlet permeate temperature, revealing that at T = 200 °C the highest conversion is achieved. This outcome is ascribed to the observation that at temperature values above the reaction zone temperature, the sweep gas acts as a heating fluid, raising the reaction temperature and consequently limiting achievable conversions. Additionally, as T_{in}^{P} increases, the heat driving force between the two zones decreases. Figure 6.9b presents the final temperature reached on both in retentate and permeate side by varying the inlet sweep gas flow temperature. This clearly indicates that the permeate stream is not able to completely cool down the retentate stream. Therefore, an extra cooling strategy would be needed.



Figure 6.9. Effect of the permeate flow inlet temperature (T_{in}^{p}) on (a) H₂ conversion and (b) outlet temperature of permeate (T_{out}^{p}) and retentate (T_{out}^{R}) .

6.8 On the effect of feed ratio

A key factor influencing ammonia production is the hydrogen-to-nitrogen feed flow ratio. In this specific study a value of 1.5 was selected due to the favorable activity of the ruthenium-based catalyst in an under-stoichiometric environment. Therefore, the sweep gas-to-feed ratio was consistently kept constant to the inlet of the retentate side. However, also the composition of the sweep gas is crucial as it directly affects both the efficiency of ammonia removal and the reaction equilibrium.

Figure 6.10 presents two scenarios using different feed gas ratios and sweep gas-tofeed ratios to highlight how these factors affect reactor performance in terms of hydrogen conversion and ammonia purity, with respect to the ΔP . In Figure 6.10a when using SF = 0, the ratio does not exhibit a significant effect; as expected, whereas ΔP plays a more crucial role. As ΔP increases, H₂ conversion rises due to the larger ammonia partial pressure difference across the membrane. Simultaneously, an increase in ammonia purity is observed due to the lack of gas in the permeate stream. Figure 6.10b shows the case study for SF = 6, where the maximum in terms of H₂ conversion is reached at $\Delta P = 20$ bar. For ΔP lower than this value, the H₂ conversion is slightly lower when $q^P = 3$. The reason is correlated to a different partial pressure, (i.e., higher H₂ concentration in the permeate) leading to potential back-permeation. However, this difference diminishes as the pressure in the permeate decreases, reaching a maximum before experiencing a slight decline with further increases in ΔP (see section 6.6).



Figure 6.10. Effect of ΔP on H₂ conversion and NH₃ purity for sweep gas-to-feed ratio (a) SF = 0 and (b) SF = 6, for different values of sweep gas feed ratio (q^P).



Figure 6.11. Effect of ΔP on H₂ conversion and NH₃ purity for sweep gas feed ratio (a) $q^P = 1.5$ and (b) $q^P = 3$, for different values of sweep gas-to-feed ratio (*SF*).

Figure 6.11a and Figure 6.11b, representing sweep gas feed ratios of 1.5 and 3 respectively, illustrate the reactor's performance with *SF* ranging from 0 to 10. It is evident that in both cases, the highest conversion is achieved with *SF* = 6 – 10 at ΔP = 20 bar, with the behavior reversing as the difference of pressure increases. As anticipated, *SF* = 0 allows for the highest purity, but it results in the lowest conversion.

For the optimal reactor parameters, setting SF = 6 or SF = 10 at high ΔP shows no significant difference in conversion. However, SF = 6 appears to offer an advantage in terms of ammonia purity. Therefore, SF = 6 was selected as the final value, independently of the feed ratio of the sweep gas, along with a $\Delta P = 20$ bar. For a precise determination of the optimal reactor parameters, an economic evaluation would be necessary to identify the most cost-effective choice.

6.9 Packed bed reactor vs. packed bed membrane reactor

By integrating a membrane with the selected optimal characteristics, it was possible to study and compare two different reactor configurations: a conventional packed bed reactor and a packed bed membrane reactor operating at 370 °C and 50 bar.

Figure 6.12a presents the isothermal case scenario, where the H_2 conversion trend along the reactor length clearly demonstrates the benefits of integrating a membrane. The PBMR configuration effectively overcomes the severe limitations imposed by thermodynamic equilibrium. By enabling selective ammonia removal via the membrane, the equilibrium constraint on hydrogen conversion can be shifted, resulting in higher overall conversion and improved NH_3 recovery.

Subsequently, Figure 6.12b, shows a comparison between a conventional PBR and a PBMR operating under adiabatic conditions. In the conventional reactor, where operating conditions and design are chosen to reach equilibrium, the conversion remains nearly constant. The adiabatic membrane reactor achieves a final conversion that exceeds the one of the conventional adiabatic reactor by approximately 63%, revealing the substantial advantages of membrane reactor technology for ammonia synthesis application.



Figure 6.12. Comparison of performance in terms of hydrogen conversion for a PBR and a PBMR operated under (a) isothermal and (b) adiabatic conditions.

The comparison of the reactor performance considering heat exchange between retentate and permeate side is showed in Figure 6.13. The red continuous line indicates a temperature peak at the reactor inlet, a result of the high reaction rate in this region. Therefore, the co-current configuration ensures the highest driving force in this zone.



Figure 6.13. Hydrogen conversion and retentate temperature as a function of the reactor length in PBR and PBMR configurations comparing adiabatic and non-adiabatic operations.

Parameter	Units	Value	
TR	(°C)	370	
T^p	(°C	200	
PR	(bar)	50	
ΔΡ	(bar)	20	
q^R	$(mol_{H_2} mol_{N_2}^{-1})$	1.5	
q^P	$(mol_{H_2} mol_{N_2}^{-1})$	1.5	
SF	(-)	6	
\mathcal{P}_{NH_3}	(mol s ⁻¹ m ⁻² Pa ⁻¹)	$1 \cdot 10^{-7}$	
S_{NH_3/H_2}	(-)	50	
S_{NH_3/N_2}	(-)	100	
L	(m)	1	
D_r^i	(m)	0.033	

Table 6.4. Optimal operating conditions of the PBMR.

6.10 Conclusions

This study investigated the impact of a membrane-enhanced process on ammonia production by developing a 1-D phenomenological non-isothermal reactor model. The model was validated through experimental tests conducted using a Ru/C catalyst. Under base conditions (T = 370 °C, P = 50 bar, q = 1.5, SF = 1, $\Delta P = 0$ bar) the results demonstrated a significant enhancement in H₂ conversion upon integrating a membrane into the packed bed reactor. Notably, an NH₃ selectivity of 50 towards H₂ and 100 towards N₂, along with a minimum NH₃ permeance requirement of $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹, exceeded the thermodynamic equilibrium limits of the conventional packed bed reactor.

The study delved into the influence of various process parameters. Simulations were performed for different co-current sweep gas flow rate values, with the application of ΔP , showing the possibility to further improve the reactor performance in terms of H₂ conversion. However, after the sweep gas flow reached a plateau, further increases in *SF* flow rate did not lead to any additional conversion change. The optimal conditions were identified for *SF* = 6 and ΔP = 20 bar. Considering the sweep gas as a cooling fluid, the study of heat exchange between the two sides revealed improved performance. Analyzing the temperature gradient highlighted the importance of treating the sweep gas as a cooling fluid, allowing a controlled temperature profile and, thereby, improved reactor performance by adjusting the permeate side temperature. Finally, investigating the feed ratio on the permeate side revealed that $q^P = 1.5$ and SF = 6 lead to the maximum hydrogen conversion, as well as higher NH₃ purity and recovery, at 5.65% and 99.1%, respectively.

The results suggest that membrane reactors offer a promising route for improving the efficiency of the ammonia synthesis process by reducing overall energy consumption and operational costs. This can be achieved through lower operating pressures, equilibrium shifting via selective separation, reduced recycling and separation energy, enhanced heat integration, and decreased feedstock and catalyst usage, improving both efficiency and cost-effectiveness.

6.11 References

- 1. Patil, B.S.; Hessel, V.; Lang, J.; Wang, Q. Plasma-Assisted Nitrogen Fixation Reactions. RSC Green Chemistry 2016, 2016-January, 296–338, doi:10.1039/9781782623632-00296.
- 2. Wang, W.; Patil, B.; Heijkers, S.; Volkerh,]; Bogaerts, A. Nitrogen Fixation by Gliding Arc Plasma:Better Insight by Chemical Kinetics Modelling., doi:10.1002/cssc.201700095.
- Rouwenhorst, K.H.R.; Engelmann, Y.; Van 'T Veer, K.; Postma, R.S.; Bogaerts, A.; Lefferts, L. Plasma-Driven Catalysis: Green Ammonia Synthesis with Intermittent Electricity. Green chemistry 2020, 22, 6258–6287, doi:10.1039/D0GC02058C.
- 4. Marakatti, V.S.; Gaigneaux, E.M. Recent Advances in Heterogeneous Catalysis for Ammonia Synthesis. ChemCatChem 2020, 12, 5838–5857, doi:10.1002/CCTC.202001141.
- 5. Liu, H. Ammonia Synthesis Catalyst 100 Years : Practice, Enlightenment and Challenge. Chinese Journal of Catalysis 2014, 35, 1619, doi:10.1016/S1872-2067(14)60118-2.
- Smith, C.; Torrente-Murciano, L.; Smith, C.; Torrente-Murciano, L. Exceeding Single-Pass Equilibrium with Integrated Absorption Separation for Ammonia Synthesis Using Renewable Energy—Redefining the Haber-Bosch Loop. Adv Energy Mater 2021, 11, 2003845, doi:10.1002/AENM.202003845.
- Poto, S.; Gallucci, F.; Fernanda Neira d'Angelo, M. Direct Conversion of CO2 to Dimethyl Ether in a Fixed Bed Membrane Reactor: Influence of Membrane Properties and Process Conditions. Fuel 2021, 302, doi:10.1016/j.fuel.2021.121080.
- Beltermann, N.; Weiske, S.; Becka, R.; Samsun, R.C.; Peters, R.; Stolten, D.; Müller, T.E. An Evaluation of Direct Dimethyl Ether (DME) Synthesis from Hydrogen and Carbon Dioxide Based on CFD Reactor Simulations. Int J Hydrogen Energy 2023, 48, 39373–39388, doi:10.1016/J.IJHYDENE.2023.05.260.
- Živković, L.A.; Pohar, A.; Likozar, B.; Nikačević, N.M. Reactor Conceptual Design by Optimization for Hydrogen Production through Intensified Sorption- and Membrane-Enhanced Water-Gas Shift Reaction. Chem Eng Sci 2020, 211, doi:10.1016/J.CES.2019.115174.
- Bang, G.; Moon, D.K.; Kang, J.H.; Han, Y.J.; Kim, K.M.; Lee, C.H. High-Purity Hydrogen Production via a Water-Gas-Shift Reaction in a Palladium-Copper Catalytic Membrane Reactor Integrated with Pressure Swing Adsorption. Chemical Engineering Journal 2021, 411, 128473, doi:10.1016/J.CEJ.2021.128473.

- 11. Zhang, Z.; Way, J.D.; Wolden, C.A. Design and Operational Considerations of Catalytic Membrane Reactors for Ammonia Synthesis. AIChE Journal 2021, 67, doi:10.1002/aic.17259.
- 12. Kucuk, E.; Hasan Koybasi, H.; Avci, A.K. Beyond Equilibrium Ammonia Synthesis in a Membrane and Heat Exchange Integrated Microreactor: A Modeling Study. Fuel 2024, 357, 129858, doi:10.1016/J.FUEL.2023.129858.
- 13. Rossetti, I.; Pernicone, N.; Ferrero, F.; Forni, L. Kinetic Study of Ammonia Synthesis on a Promoted Ru/C Catalyst. Ind Eng Chem Res 2006, 45, 4150–4155, doi:10.1021/ie051398g.
- Warren M. Rohsenow; James P. Hartnett; Young I. Cho 3. HEAT TRANSFER IN PACKED AND FLUIDIZED BEDS 13.1. INTRODUCTION. In Handbook of Heat Transfer, 1st edition; 1998.
- 15. Dirker, J. HEAT TRANSFER COEFFICIENTS IN CONCENTRIC ANNULI; 2002;
- Wei, Q.; Lucero, J.M.; Crawford, J.M.; Douglas Way, J.; Wolden, C.A.; Carreon, M.A. Ammonia Separation from N 2 and H 2 over LTA Zeolitic Imidazolate Framework Membranes. J Memb Sci 2021, 623, doi:10.1016/j.memsci.2021.119078.
- 17. Laciak, D. V; Pez, G.P.; Burban, P.M. Part 2. Separation of Ammonia Rrom Nitrogen Ana Hydrogen at High Temperatures.
- Brown, L.R.; Leblanc, J.R.; Madhaven, S.; Porter, R.E.; Ammonia ; Laciak, D. V; Pez, G.P.U.S.; Pez, G.P.; Laciak, D.V.U.S.; Rousseau, R.W.; Ed; Noble, R.D.; et al. Kirk-Othmer Encyclopedia of Chemical Technology. J. Am. Chem. Soc 1991, 113, 1059.
- Camus, O.; Perera, S.; Crittenden, B.; Van Delft, Y.C.; Meyer, D.F.; Pex, P.P.A.C.; Kumakiri, I.; Miachon, S.; Dalmon, J.-A.; Tennison, S.; et al. Ceramic Membranes for Ammonia Recovery. 2006, doi:10.1002/aic.10800.
- 20. Kanezashi, M.; Yamamoto, A.; Yoshioka, T.; Tsuru, T. Characteristics of Ammonia Permeation Through Porous Silica Membranes. 2009, doi:10.1002/aic.12059.
- 21. Klinkenberg, A.; Krajenbrink, H.J.; Lauwerier, H.A. Diffusion in a Fluid Moving at Uniform Velocity in a Tube. Ind Eng Chem 1953, 45, 1202–1208, doi:10.1021/IE50522A024.
- 22. Medrano, J.A.; Llosa-Tanco, M.A.; Pacheco-Tanaka, D.A.; Gallucci, F. Transport Mechanism and Modeling of Microporous Carbon Membranes., doi:10.1016/B978-0-12-816350-4.00002-7.

Chapter 7

Development of ruthenium-based catalysts for ammonia synthesis

This chapter is based on the following paper:

G. Anello, G. De Luna, G. De Felice, A. Saker, L. Di Felice, F. Gallucci. "Development of rutheniumbased catalysts for ammonia synthesis via polyol reduction method", International Journal of Hydrogen Energy, 86, 920 – 930, 2024

Abstract

In this Chapter, ruthenium-based catalysts were synthesized via polyol reduction method with different metal oxides as support and cesium as promoter. The samples were characterized through X-Ray diffractometry, inductively coupled plasma combined with optical emission spectrometry, nitrogen-physisorption and X-ray photoelectron spectroscopy. Then, the catalysts were tested for ammonia synthesis in the range of temperatures 275 – 400 °C and pressures 10 – 50 bar in a laboratory scale experimental setup. The synthesized catalysts allowed an ammonia production rate approximately four times higher compared with the performances of similar catalytic formulations in literature (evaluated at same conditions). The best performance was achieved with the Cs-Ru/CeO₂ (1 wt% Cs, 5 wt% Ru), reaching an ammonia production of nearly 73 mmol h^{-1} g_{cat}⁻¹ at 400 °C and 50 bar. As shown by the X-ray photoelectron spectroscopy analysis, the increased Ce^{3+}/Ce^{4+} ratio led to an enhancement of oxygen vacancies, which favored the dissociative adsorption of nitrogen, which is the limiting step in the ammonia synthesis reaction. Such high catalytic activity can be ascribed to the beneficial effect of the polyol reduction method for the maximization of the exposure of active sites.

7.1 Introduction

Nowadays the main path to produce ammonia is still via Haber-Bosch process, in which nitrogen (N₂) and hydrogen (H₂) are combined in the presence of a Fe-based catalyst. The reaction is an exothermic reaction and occurs with a decrease in volume, therefore it is favored at low temperatures and high pressures. However, the process requires temperatures in the range of 400 – 500 °C and pressures in the range of 50 – 300 bar to achieve efficient nitrogen fixation [1]. These conditions favor a high kinetic rate at the expense of low conversions (below 20%) due to the thermodynamic limitations [2]. As a result, the process is energy-intensive and consumes approximately 1 - 2% of the world's total energy production, emitting more than 300 million metric tons of carbon dioxide per year [3].

For these reasons, ongoing research and technological advancements aim to address these limitations and explore alternative methods to be able to produce a more sustainable ammonia at milder conditions. To improve this process, the development of more performant materials, such as catalysts containing ruthenium (Ru), is required. The interest in Ru-based materials arises from several potential advantages offered. Firstly, Ru-based catalysts have shown higher catalytic activity for nitrogen fixation reaction at lower temperatures and pressures compared to the commercial Fe-based ones [4]. This can have significant energy-saving implications as it reduces the energy needed to heat up the reaction vessel. On the other hand, Ru-based catalysts show two main drawbacks: high costs and potential hydrogen poisoning. Ruthenium is present at a concentration of approximately 1 μ g kg⁻¹ in the Earth's crust, which results in high capital costs and then limits further applications [5]. Furthermore, at high hydrogen partial pressure, excess of hydrogen atoms covers ruthenium active sites, reducing the efficient dissociative adsorption of N₂ on the catalyst surface [6].

Thus, to overcome these drawbacks and increase catalytic performance through the maximal exposure of the active sites, Ru-based catalysts were prepared via polyol reduction method and tested for ammonia (NH₃) synthesis in a dedicated experimental setup. Javaid et al. addressed the effect of the preparation method on ruthenium-based catalyst for ammonia synthesis. The results showed that the catalysts prepared by different methods had different physical properties, that, in turn, affect the ammonia synthesis activity. In particular, high surface area and high dispersion of the active phase contributed to the higher catalytic activity [7].

As described in Chapter 4, the polyol reduction method is a chemical process developed for the synthesis of nanoparticles, particularly metal nanoparticles. This method involves the reduction of metal salts precursors in the presence of a polyol, which serves as reducing agent, as solvent and as surfactant [8]. It is widely used due to its simplicity, versatility, and ability to produce monodisperse nanoparticles in the range of 1 - 5 nm with well-defined sizes and shapes [9,10]. This is a crucial aspect for ruthenium catalysts since reducing the size to nanoclusters will greatly increase the amount of exposed sites, which in turn increases the level of catalytic activity, leading to the efficient exploitation of ruthenium resources. However, this method was not yet applied in literature for the synthesis of catalysts for ammonia production.

Moreover, previous works demonstrated that Ru-clusters in the range of 1.8 - 3.5 nm are able to bear a significant number of B5-sites. This type of site consists of clusters of five ruthenium atoms arranged in two levels that are able to favor nitrogen dissociation by the enhanced back-donation mechanism from ruthenium into the π^* anti-bonding orbital of N₂ [11–14]. This mechanism is described by Reyes et al. and involves the stabilization of the bond between metal particle and nitrogen molecule, ensuring a high electron density in proximity of the electronegative atoms of N₂, and, at the same time, the donation of electron to the π^* anti-bonding orbital of N₂. Therefore, the control of ruthenium cluster size via a tailored synthesis method enables the abundance of active B5 sites beneficial for ammonia synthesis [16].

In this Chapter, ruthenium was employed as active phase with a nominal loading of 5 wt% while different supports were explored: cerium oxide (ceria, CeO₂), magnesium oxide (magnesia, MgO), and a blend of these two oxides (MgOCeO₂). The function of a support in a catalyst is of primary importance as it can influence catalytic activity by modifying the electronic properties of the active phase metal clusters [17]. Furthermore, the support can influence the structure and morphology of the clusters that are responsible for changing the distribution of the active sites. For this reason, metal oxides are often employed as support due to their redox property, surface oxygen vacancies and surface protonation. Moreover cesium (Cs) was added to the catalytic formulation as promotor to lower the energy barrier for N₂ adsorption via electronic interaction of the promoter with the active metal [18,19]. In particular, cesium was found to influence the redistribution and agglomeration of ruthenium atoms [20]. The above mentioned catalysts were tested in a temperatures range of 275 - 400 °C and in a pressures range of 10-50 bar. The results indicate that the chosen catalytic formulation, combined with the tailored synthesis method, enhanced process performance under milder conditions compared to similar Ru-based catalytic formulation reported in literature.

7.2 Experimental

7.2.1 <u>Materials</u>

Ru-based catalysts were prepared via polyol reduction method starting from the following chemicals: ethane-1,2-diol ($C_2H_6O_2$, ReagentPlus® grade, Sigma-Aldrich®), cerium(III) nitrate hexahydrate (CeN₃O₉·6H₂O, 99%, Sigma-Aldrich®), magnesium nitrate hexahydrate (MgN₂O₆·6H₂O, ACS reagent, Sigma-Aldrich®), cesium nitrate (CsNO₃, 99.99%, Sigma-Aldrich®), potassium hydroxide (KOH, Reagent grade, VWR Chemicals®) and ruthenium(III) chloride hydrate (RuCl₃·*x*H₂O, Ru content 45 – 55%, Sigma-Aldrich®). All chemicals were used as received, without any additional pretreatment. Ultrapure water (Type 1, electric resistivity < 18.2 MΩ cm at 20 °C) produced using a Purelab® Flex 1 purification system (Elga LabWater Ltd., England, UK), was used for all the synthesis steps and characterizations.

7.2.2 <u>Catalysts preparation</u>

According to the polyol method [8,21,22] metallic precursors for support, active phase, and promoter were dissolved in ethane-1,2-diol, with the concentration of ruthenium chloride fixed at 4.7 g ml⁻¹. Consequently, the required amount of all precursors was determined to achieve a nominal loading of ruthenium equal to 5 wt% of the final catalyst. Regarding the bimetallic-supported catalysts, the amounts of cerium nitrate and magnesium nitrate were determined to obtain catalysts with a Ce/Mg molar ratio of approximately 1:1. For Cs-promoted catalysts, the solution was prepared to obtain catalysts with a nominal loading of cesium equal to 1 wt%.

The so-prepared solution containing the dissolved precursor salts was placed in a three-neck round-bottom flask. The mixture was heated to 110 °C and maintained at this temperature for 2 hours, then allowed to cool naturally.

Afterward, a KOH solution was added to the mixture through a syringe pump using a flowrate of 2 ml min⁻¹. After this step, the resulting gel was aged for 10 minutes, washed five times with ultrapure water, and separated using a 5810R centrifuge (Eppendorf, Germany) to recover the particles and remove liquid residues from the solid phase.

Finally, the catalyst was dried at 120 °C for 12 hours and then calcined at 550 °C for 4 hours using a heating ramp of 2 °C min⁻¹. More details on the synthesis method are reported in Appendix D. The prepared catalysts are listed in Table 7.1.

		Support		Active Phase	Promoter
Catalyst	Code	CeO ₂	Mg0	Ru	Cs
		(mol.%)	(mol.%)	(wt%)	(wt%)
Ru/MgO	PR-1	-	100.0	5.0	-
Ru/CeO2	PR-2	100.0	-	5.0	-
Ru/MgOCeO ₂	PR-3	50.0	50.0	5.0	-
Cs-Ru/CeO2	PR-4	100.0	-	5.0	1
Cs-Ru/MgOCeO2	PR-5	50.0	50.0	5.0	1

Table 7.1. List of catalysts prepared and tested in this study.

7.2.3 <u>Catalysts characterization</u>

The as-prepared catalysts were characterized through several techniques. X-Ray Diffractometry (XRD) analysis were performed using a MiniFlex600 (Rigaku[®], Japan) operating with a Ni β -filtered Cu-K α radiant at 40 kV and 15 mA. A scan step of 0.01 degrees and a scan rate of 1 deg min⁻¹ were employed over the diffraction angle (2 θ) range of 20 – 75 deg. Data analysis was conducted using the software SmartLab Studio II v. 4.5.421.0 (Rigaku[®], Japan).

The nitrogen adsorption was measured by a 3Flex (Micromeritics[®], Georgia, USA) system as a function of relative pressure at -196 °C. Data analysis was conducted using the software 3Flex v5.03 (Micromeritics[®], Georgia, USA) according to ASTM Test Method D4222-03 (2008) and Practice D4641-12. Prior to the measurements, the samples were pretreated for 6 hours under vacuum conditions at 250 °C. The surface area was calculate based on the Brunauer-Emmett-Teller (BET) model and both the pore size and pore volume were calculated based on the Barrett-Joiner-Halenda (BJH) model. The system was verified to ensure that the error in data collection remained below 5%.

Inductively Coupled Plasma (ICP) combined with Optical Emission Spectrometry (OES) was used to measure metal loadings of catalysts via an iCAP[™] PRO ICP-OES system (Thermo Scientific[™], Massachusetts, USA) and the data were analyzed through the Qtegra Intelligent Data Solution software (Thermo Scientific[™], Massachusetts, USA).

The calibration of the instrument was performed using ICP standard solutions. More specifically, ruthenium ICP standard 1 000 mg l-1 Ru in 7% HCl aqueous solution (*Certipur*[®] grade, Supelco[®]) and cesium ICP standard 1 000 mg l⁻¹ Cs in 5 vol.% HNO₃ aqueous solution (TraceCERT® grade, Supelco®) were employed to prepare 20 ml of stock solution with a concentration of 50 mg l⁻¹ of both metals. Then, from the prepared stock solution, 5-points calibration lines were built in the range 1 – 5 mg l⁻¹ for both ruthenium and cesium. Before the measurements, the catalysts were dried overnight, then they were digested in acidic media. Firstly, 10 mg of dried catalyst were dissolved in a 1:1 volumetric ratio solution of hydrogen peroxide (30 vol.% H_2O_2 , in aqueous solution, ACS reagent grade, Acros Organics[™]) and nitric acid (69 vol.% HNO₃, in aqueous solution, EMSURE® ACS reagent grade, Supelco®) at ambient condition. After digestion, the acid mixture was diluted with ultrapure water to ensure a metal concentration of approximately 2.5 mg l⁻¹. Different emission lines spectra were measured for both ruthenium (wavelengths 240.272 nm, 245.657 nm, 266.161 nm, 267.876 nm, 269.206 nm) and cesium (wavelengths 393.109 nm, 404.076 nm, 535.353 nm), averaged to obtain the final actual concentration. The iCAP[™] PRO ICP-OES system allowed an error in data collection below 2%.

Furthermore, ultrahigh vacuum X-ray photoelectron spectroscopy (XPS) analyses were performed using a K-Alpha XPS spectrometer (Thermo Scientific[™]). All the spectra were deconvoluted with CasaXPS (Casa Software Ltd, Devon, UK). Hydrogen temperature-programmed reduction (H₂-TPR) was carried out in Autochem HP 2950 (Micromeritics[®], Georgia, USA). Firstly, the samples were pretreated at 150 °C for 1 hour under argon flow followed by cooling down to 100 °C. Then, the sample was heated up to 450 °C at a heating rate of 10 °C min⁻¹ under a flow of 10 vol.% H₂ in argon.

7.2.4 <u>Catalytic tests</u>

Activity tests over promoted and unpromoted catalysts were conducted using a dedicated experimental setup, of which a schematic is reported in Figure 7.1. Further details are provided in Appendix A. Briefly, the experimental setup consists of three main sections: gas feeding section, reaction section and analysis section. The gas feeding section is composed by EL-FLOW[®] Select mass flow controllers (Bronkhorst[®], The Netherlands), used to supply the desired flowrates from gas bottles (Linde Gas Benelux BV, The Netherlands) containing 5.0 purity N₂, 5.0 purity H₂ and 3.7 purity NH₃. The reactor feed stream was preheated using a 1-meter-long electric heat trace cable (Chromalox Isopad GmbH, Germany) applied along the feed line.


Figure 7.1. Schematic representation of the experimental setup employed to perform activity tests for the ammonia synthesis reaction.

The reaction section is represented by a fixed bed stainless steel reactor with 10 mm inner diameter and 100 mm length. The reactor was placed in an electric box oven to avoid ammonia condensation and heated up by an electric heating block. The temperature was measured with three K-type thermocouples, one at the beginning of the catalytic bed, one placed in the middle of the bed and the last one was placed at the outlet of the catalytic bed.

The operating pressure was controlled thanks to a combination of an Equilibar[®] Low Flow series back pressure regulator (Precision Fluid Control, North Carolina, USA) and an EL-PRESS[®] dual valve pressure controller (Bronkhorst[®], Netherland).

Finally, the analysis of the outlet stream was performed by a compact gas chromatograph (GC) (Global Analyzer Solutions[™], The Netherlands) connected to the downstream of the reactor, equipped with two thermal conductivity detectors (TCDs) to quantify the gaseous products. The GC was calibrated for all the relevant compounds both before and after the tests. All the collected data were analyzed through the

software Chromeleon 7.3.2 Chromatography Data System (Thermo Scientific^M, Massachusetts, USA). The system was checked to ensure that the error in data collection is below 1%.

Prior to the activity measurements, the calcined catalyst powder was packed into a 10 mm die and subjected to a load of $1 \cdot 10^4$ kg for 20 minutes to produce a tablet. The obtained tablet was ejected from the die, crushed, and sieved to produce samples with a particle size of $106 - 315 \mu$ m. The reactor was loaded with 1 g of catalyst, diluted with 5 g of silicon carbide (SiC, Alfa Aesar®) to ensure isothermal operation and avoid local hotspots. The mixed powders were introduced in the reactor with the same particle size. Before the reaction tests, the catalyst was reduced in-situ at 550 °C, feeding 450 Nml min⁻¹ of a 10 vol.% H₂:N₂ mixture for 4 hours. The complete reduction of the catalyst was confirmed by monitoring both water and hydrogen concentration in the outlet stream. Afterward, a gas mixture H₂:N₂ with a 2:1 volumetric ratio was fed to the reactor with a total volumetric flow rate of 450 Nml min⁻¹ and a Weight Hour Space Velocity (*WHSV*) of 27 000 Nml h⁻¹ g_{cat}⁻¹. The reaction tests were performed in the temperature range 250 - 400 °C and in the pressure range of 10 - 50 bar.

7.3 Results and discussion

In this section, the main findings from both material characterization and experimental tests are presented and analyzed. The results are discussed in relation to the research objectives, highlighting key trends. Comparisons with relevant literature are made to contextualize the findings and explore their implications.

7.3.1 Characterizations

The results of the nitrogen physisorption analysis in terms of specific surface area and pore dimensions are reported in Table 7.2.

	Surface Area	Pore size	Pore volume
Catalyst code	(BET)	(BJH)	(BJH)
	$(m^2 g^{-1})$	(nm)	(cm ³ g ⁻¹)
PR-1	133	14.2	0.574
PR-2	84	4.90	0.131
PR-3	142	12.7	0.618
PR-4	82	5.30	0.140
PR-5	132	11.4	0.524
PR-4 PR-5	82 132	5.30 11.4	0.140 0.524

Table 7.2. Surface area, pore size and pore volume for the synthesized catalysts.

As can be seen from Table 7.2, the catalysts PR-1, PR-3 and PR-5 show a higher surface area and pore volume compared with the samples PR-2 and PR-4. In addition, the Cs-promoted catalysts exhibit nearly the same surface area as the catalyst without promoter. This suggests that cesium is well dispersed over the catalyst surface, and it acts as a structural promoter, as also discussed in Narasimharao et al. [17]. It is worth noting that the pore size distribution is a crucial parameter for the dispersion of the active metal Ru. The average pore size of the catalysts PR-2 and PR-4 is about 5 nm, while for the catalysts PR-1, PR-3 and PR-5 is in the range 10 – 15 nm. According to Liu et al. the pore diameter of the support around 3 – 5 nm improve the dispersion of the active metal ruthenium, preventing sintering and agglomeration phenomena [23].

Afterward, the ICP-OES measurements were conducted to evaluate the actual ruthenium and cesium loadings on the different catalytic systems. The values obtained are reported in Table 7.3.

Table 7.5. Ruthemum and cestum content for the catalysis prepared in this study.					
	Rutheniu	m content	Cesium content		
Catalyst Code	Nominal	Measured	Nominal	Measured	
	(wt%)	(wt%)	(wt%)	(wt%)	
PR-1	5.0	4.5	0	-	
PR-2	5.0	3.8	0	-	
PR-3	5.0	4.2	0	-	
PR-4	5.0	4.5	1	0.83	
PR-5	5.0	4.3	1	0.81	

Table 7.3. Ruthenium and cesium content for the catalysts prepared in this study.



Figure 7.2. XRD patterns of the synthesized catalysts.

Figure 7.2 presents the X-ray diffraction patterns of the synthesized Ru-based catalysts. The XRD patterns of the fresh catalysts PR-2 and PR-4 revealed the characteristic peaks of cubic fluorite structure (JCPDS card No. 34 – 0394), with the main peaks located at

28.5°, 33.1°, 47.5°, 56.4°, 59.2°, 69.3° [24,25]. No additional peaks assignable to ruthenium or cesium were detected. This might be related to both the low amount of ruthenium and the small size of ruthenium clusters, as also described by Javaid et al. [26]. The diffraction patterns of the catalyst PR-1 were identified only as a cubic MgO phase (JCPDS card No. 77 – 2364) [27]. Also in this case, no peaks assigned to ruthenium were observed. It suggests that the ruthenium metal particles obtained in this study were significantly small [28,29]. Furthermore, the XRD patterns of the PR-3 and PR-5 show predominantly the characteristic peaks of ceria. This is in line with the results reported in literature, as the MgO peaks in the XRD patterns start to appear at a ceria content higher than 50 mol.%. [30]. No characteristic peak of other impurities was detected in the XRD patterns of all the samples.

7.3.2 <u>Catalytic tests</u>

The catalytic activity of the unpromoted catalysts on various supports, at a fixed temperature of 400 °C and a pressure of 10 bar, is reported in Figure 7.3. The mentioned tests were performed both increasing and decreasing the temperature and pressure. No significant difference in the obtained results was observed.



Figure 7.3. Ammonia production rate (a) as a function of the reaction pressure at 400 °C, and (b) as a function of the reaction temperature at 10 bar. *(continued on the next page)*



Figure 7.3. *(continued)* Ammonia production rate (a) as a function of the reaction pressure at 400 °C, and (b) as a function of the reaction temperature at 10 bar.

The catalyst PR-2 showed the best performance among the unpromoted catalysts, with an ammonia production up to 62 mmol h^{-1} g_{cat}⁻¹ at 50 bar and 400 °C. Compared with the Ru-based benchmark catalyst Ba-Ru/AC (8.3 mmol h^{-1} g_{cat}⁻¹ at 400 °C and 10 bar), the ammonia synthesis rate at 400 °C of the PR-2 synthesized in this work is approximately four times higher [31–33]. The higher performance of PR-2 can be related to ceria unique oxygen storage capacity and its electronic properties, which allow the electron migration to metallic Ru and then from metallic Ru to the antibonding orbitals of nitrogen, weakening the nitrogen triple bond and promoting its cleavage. Indeed, several authors reported that the electronic environment of ceria might contribute to catalytic activity due to electron donation to Ru species [34,35].

Partially reduced ceria is an n-type semiconductor, thus it has a large number of free electrons. The electron delocalization can favor the electronic transfer to the nitrogen triple bond [36,37]. Furthermore, Tian et al. suggest that rare earth oxide supports promote the formation of low-valence species as consequence of elevated temperature reduction, thereby enhancing the metal–support interaction with ruthenium. This interaction favors the formation of a high electron density in correspondence with ruthenium particles. As a result, the dissociation of N_2 molecules is faster [38]. Liu et al.

also demonstrated that the presence of oxygen vacancies enhanced the adsorption of nitrogen, leading to better performance on ammonia synthesis activity [23].

To verify this hypothesis, XPS was employed to investigate the surface chemical state of Ce, O, and Ru in the catalyst PR-2. The Ce 3d XPS spectrum was deconvoluted in ten peaks, as reported in Figure 7.4 a, of which six peaks can be attributed to Ce⁴⁺ and four peaks can be assigned to Ce³⁺. The Ce³⁺ concentration is related to the formation of oxygen vacancies, and it can be estimated by the ratio of the sum of peak areas of Ce³⁺ to the area of all peaks [39]. It resulted that the Ce³⁺ concentration for the sample PR-2 is approximately 39%. Moreover, the abundance of Ce³⁺ species can cause charge imbalance and hence the promotion of unsaturated chemical bonds on the catalyst surface.



Figure 7.4. High resolution XPS spectra of the catalyst PR-2 (a) Ce 3d, (b) O 1s, (c) Ru 3d. *(continued on the next page)*



Figure 7.4. *(continued)* High resolution XPS spectra of the catalyst PR-2 (a) Ce 3d, (b) O 1s, (c) Ru 3d.

In addition, O 1s could be deconvoluted into three peaks at 529.4 eV, 530.6 eV, and 531.9 eV, which can be assigned to the lattice oxygen bound to the metal cations (O_L), oxygen vacancies (O_V) and surface-chemisorbed oxygen species or hydroxyl species (O_c) [40,41], respectively. It is possible to evaluate the concentration of oxygen

vacancies by the ratio O_V/O_L that for the catalyst PR-2 is about 59%. Lin et al. suggested that besides the transformation of Ce⁴⁺ to Ce³⁺ also other factors can contribute to the generation of oxygen vacancies, for instance the increase in concentration of surface oxygen defects on the surface of ceria due to ruthenium incorporation [42]. This phenomenon might be related to ruthenium species preferentially locating in correspondence of oxygen vacancies or other defect sites of CeO₂, resulting in the formation of M – O – Ce bonds, which in turn favors the electron transfer between the metallic species and the oxide supports [43]. Finally, the Ru 3d XPS of the catalyst corresponds to a doublet of Ru 3d_{5/2} and Ru 3d_{3/2}. The peaks at 281.4 eV and 282.7 eV can be assigned to ruthenium oxides, respectively Ru⁴⁺ and Ru⁶⁺, while the peak at 280.2 eV can be assigned to metallic Ru [44].

Furthermore, as illustrated in Figure 7.3, it is noteworthy that the NH_3 production rate reaches a plateau with increasing pressure. This might be due to a poisoning effect as H_2 inhibition on Ru active sites suppresses the catalyst performance at higher pressures (i.e., higher H_2 partial pressure resulting in increased catalyst poisoning) [45].

Varying the temperature while keeping the total pressure at 10 Bar, the catalyst PR-3 showed a higher catalytic activity in the lower temperature range. Thus, additional cesium-promoted catalysts employing ceria and the ceria-magnesia blend as supports (PR-4 and PR-5) were synthesized and tested. The results are reported in Figure 7.5.



Figure 7.5. Ammonia production rate as a function of (a) the reaction pressure at 400 °C, and as a function of (b) the reaction temperature at 10 bar.

The catalyst PR-4 showed the best performance, reaching an ammonia production of nearly 73 mmol h^{-1} g_{cat}⁻¹ at 400 °C and 50 bar. Moreover, the presence of the cesium enabled ammonia synthesis at temperature as low as 250 °C and 10 bar with a

productivity of about 3 mmol $h^{-1} g_{cat}^{-1}$. Furthermore, also on the PR-5 the effect of Cs promotion can be detected. The ammonia production reached 51 mmol $h^{-1} g_{cat}^{-1}$ at 400 °C and 50 bar, with an increase of approximately 8%, compared with the unpromoted catalyst.



Figure 7.6. (*continued on the next page*) High resolution XPS spectra of the catalyst PR-4 (a) Ce 3d, (b) O 1s, (c) Ru 3d.



Figure 7.6. *(continued)* High resolution XPS spectra of the catalyst PR-4 (a) Ce 3d, (b) O 1s, (c) Ru 3d.

The obtained results can be ascribed to the promoting effect of cesium through electron donation from metallic ruthenium to the nitrogen triple bond. This effect leads to the lowering of the nitrogen dissociating barrier that is the limiting step of ammonia synthesis reaction [46]. Thus, more active sites can be released and be accessible for further nitrogen adsorption. It is also important to mention that the above-described promotion mechanism implies a highly reduced condition of the cesium, as oxygen can partially neutralize the promoting effect. Therefore, a close contact with the ruthenium particles, also known as "hot ring promotion", is crucial [47]. The contribution of this "hot ring", is highly dependent on the ruthenium dispersion and is higher for smaller crystallites [48]. For this reason, small clusters, as the ones achievable with the polyol reduction method, are extremely beneficial for ammonia synthesis.

Furthermore, the XPS deconvoluted spectra of the sample PR-4 are depicted in Figure 7.6. The XPS profiles showed a further enrichment in Ce³⁺of the catalyst surface, thus the catalyst exhibits a higher Ce³⁺ concentration (44%) than the catalyst PR-2. This suggests that is the cesium inside the structure inducing an increased generation of oxygen vacancies. This is in line with XRD results, where a minor shift to higher

diffraction angle values was observed. Peak shift can be connected with residual stress (induced defect) in the material, caused by oxygen vacancies in the lattice [49].

Moreover, H₂-TPR profiles of PR-2 and PR-4 are shown in Figure 7.7. In accordance with data reported in the literature, RuO_x species are reduced below 180 °C. The decrease of the temperature of the reduction peaks in the TPR profiles of the PR-4 compared to PR-2 can be attributed to several interconnected phenomena. Firstly, larger particles exhibit a smaller specific surface area and a reduced contact area with the reducing gas, thus making the reduction process more challenging and requiring higher temperatures [50]. Therefore, the shift towards higher temperatures in the reduction peaks can be considered as an indication of the presence of larger Ru particles. Furthermore, the low temperature reduction generally is also connected to the removal of surface oxygen. The presence of more reducible surface Ce⁴⁺ ions can be attributed to the oxygen vacancies formed, because oxygen vacancies can boost the transition from Ce⁴⁺ to Ce³⁺ [51,52]. Furthermore, Manaka et al. suggested that the catalysts with lower temperature reduction peaks had higher ammonia synthesis efficiencies due to the presence of stronger interactions between the active phase and support [53].



Figure 7.7. H₂-TPR profiles of the catalysts PR-2 and PR-4.

Typically, Ru-based catalysts exhibit an order of reaction with respect to hydrogen approaching and overcoming -1, this indicates a strong inhibition by hydrogen [54,55]. Thus, a catalytic formulation that is less inhibited by H_2 is highly desirable. In the present study, the catalyst PR-4 showed an increase of the ammonia production rate along with the pressure. This might indicate a less relevant poisoning effect at high hydrogen partial pressures. This is in line with previous literature studies that discuss the role of cesium as inhibitor of the hydrogen poisoning [56]. Finally, in Table 7.4 the obtained results were compared with the performance of similar catalysts already present in literature produced via different synthesis methods and tested under similar experimental conditions.

Under similar reaction conditions, the $Cs-Ru/CeO_2$ catalyst (PR-4) synthesized via polyol reduction method shows better performance. This indicates the beneficial effect of the polyol method in the building of the ruthenium clusters, allowing lower cluster size and then a higher number of B5-sites.

Catalyst	Synthesis Method	Ru content (wt%)	Cs content (wt%)	P (bar)	T (°C)	Feed Ratio	NH ₃ production rate (mmol h ⁻¹ g _{cat} ⁻¹)	Ref.
		(((bui)	(9)	(1101112 1 11101112)	(Internet Bear)	
Ru/CeO ₂	WI	3.0	0.0	30	375	2	4.7	[57]
Ru/MgOCeO ₂	CP - WI	5.0	0.0	1	375	3	4.0	[58]
K-Ru/MgO	WI	4.0	0.0	30	400	3	8.9	[59]
Ru/CeO2	HTS - WI	1	0.0	10	400	3	5.1	[42]
Ru/CeO2	HTS - WI	10	0.0	10	400	3	18.0	[42]
Cs-Ru/CeO ₂	HTS - WI	2.5	4.0	30	375	3	19.0	[60]
Cs-Ru/CeO2	PRM	4.5	0.83	10	375	2	31.1	This Work
WI = Wetness impregnation, CP = Co-precipitation, HTS = Hydro-thermal synthesis, PRM = Polyol reduction								

Table 7.4. Comparison of the performance of polyol catalysts with similar catalytic formulations from the literature.

7.4 Conclusions

Ruthenium-based catalysts employing different supports and cesium as promotor have been successfully synthetized via polyol reduction method. Both support and promotor have a relevant influence on the surface characteristics of the catalysts. The most performant synthesized catalyst (PR-4) allowed an ammonia production up to 73 mmol h^{-1} g_{cat}⁻¹ at 50 bar and 400 °C. More specifically, electronic properties such as the abundance of Ce³⁺ and oxygen vacancies of the support were found to be crucial in order to favor the electron donation from metallic Ru to nitrogen triple bond. Furthermore, through the polyol reduction method it was possible to synthesize directly in one step the catalyst. This is particularly favorable as it ensured a close contact between cesium and ruthenium atoms, allowing the so-called "hot ring promotion". Moreover, the ammonia production rate of the catalysts PR-2 and PR-4 presented in this work outperforms the performance of similar catalytic formulation shown in the open literature. Finally, the synthetized Cs-Ru/CeO₂ catalyst (PR-4) showed activity at lower temperature and pressure with an ammonia production rate of about 3 mmol h^{-1} g_{cat}⁻¹ at 10 bar and 250 °C. To the best of the authors' knowledge, most of the thermochemical catalysts investigated in literature are not active in these conditions. Comparable results have been reported in the literature at similar pressures, though at a higher reaction temperature of 300 °C. This suggests a promising route for ammonia synthesis at milder condition. The ruthenium-based catalysts proposed in this work offer high activity per volume, enabling smaller catalyst volumes, lower operating pressures, and higher conversion per pass. However, while these catalysts provide energy savings, the benefits may be offset by increased ammonia refrigeration energy demands at lower pressures.

7.5 References

- Vojvodic, A.; Medford, A.J.; Studt, F.; Abild-Pedersen, F.; Khan, T.S.; Bligaard, T.; Nørskov, J.K. Exploring the Limits: A Low-Pressure, Low-Temperature Haber-Bosch Process. Chem Phys Lett 2014, 598, 108–112, doi:10.1016/j.cplett.2014.03.003.
- 2. Smith, C.; Torrente-Murciano, L. Exceeding Single-Pass Equilibrium with Integrated Absorption Separation for Ammonia Synthesis Using Renewable Energy—Redefining the Haber-Bosch Loop. Adv Energy Mater 2021, 11, doi:10.1002/aenm.202003845.
- Wang, W.; Patil, B.; Heijkers, S.; Hessel, V.; Bogaerts, A. Nitrogen Fixation by Gliding Arc Plasma: Better Insight by Chemical Kinetics Modelling. ChemSusChem 2017, 10, 2145– 2157, doi:10.1002/cssc.201700095.
- 4. Marakatti, V.S.; Gaigneaux, E.M. Recent Advances in Heterogeneous Catalysis for Ammonia Synthesis. ChemCatChem 2020, 12, 5838–5857, doi:10.1002/cctc.202001141.
- 5. Ertl, G. Primary Steps in Catalytic Synthesis of Ammonia; 1983; Vol. 1;.
- Huang, J.; Yuan, M.; Li, X.; Wang, Y.; Li, M.; Li, J.; You, Z. Inhibited Hydrogen Poisoning for Enhanced Activity of Promoters-Ru/Sr2Ta207 Nanowires for Ammonia Synthesis. J Catal 2020, 389, 556–565, doi:10.1016/j.jcat.2020.06.037.
- Javaid, R.; Nanba, T. Effect of Preparation Method and Reaction Parameters on Catalytic Activity for Ammonia Synthesis. Int J Hydrogen Energy 2021, 46, 35209–35218, doi:10.1016/j.ijhydene.2021.08.082.
- Fievet, F.; Ammar-Merah, S.; Brayner, R.; Chau, F.; Giraud, M.; Mammeri, F.; Peron, J.; Piquemal, J.Y.; Sicard, L.; Viau, G. The Polyol Process: A Unique Method for Easy Access to Metal Nanoparticles with Tailored Sizes, Shapes and Compositions. Chem Soc Rev 2018, 47, 5187–5233, doi:10.1039/c7cs00777a.
- Komvokis, V.G.; Marti, M.; Delimitis, A.; Vasalos, I.A.; Triantafyllidis, K.S. Catalytic Decomposition of N2O over Highly Active Supported Ru Nanoparticles (≤3nm) Prepared by Chemical Reduction with Ethylene Glycol. Appl Catal B 2011, 103, 62–71, doi:10.1016/j.apcatb.2011.01.009.
- Miyazaki, A.; Balint, I.; Aika, K.I.; Nakano, Y. Preparation of Ru Nanoparticles Supported on γ-Al2O3 and Its Novel Catalytic Activity for Ammonia Synthesis. J Catal 2001, 204, 364–371, doi:10.1006/jcat.2001.3418.
- Casey-Stevens, C.A.; Lambie, S.G.; Ruffman, C.; Skúlason, E.; Garden, A.L. Geometric and Electronic Effects Contributing to N2 Dissociation Barriers on a Range of Active Sites on Ru Nanoparticles. Journal of Physical Chemistry C 2019, 123, 30458–30466, doi:10.1021/acs.jpcc.9b09563.

- 12. Dahl, S.; Logadottir, A.; Egeberg, R.C.; Larsen, J.H.; Chorkendorff, I.; Törnqvist, E.; NØrskov, J.K. Role of Steps in N2 Activation on Ru(0001). Phys Rev Lett 1999, 83, 1814–1817, doi:10.1103/PhysRevLett.83.1814.
- 13. Gavnholt, J.; Schiøtz, J. Structure and Reactivity of Ruthenium Nanoparticles. Phys Rev B Condens Matter Mater Phys 2008, 77, 1–10, doi:10.1103/PhysRevB.77.035404.
- Karim, A.M.; Prasad, V.; Mpourmpakis, G.; Lonergan, W.W.; Frenkel, A.I.; Chen, J.G.; Vlachos, D.G. Correlating Particle Size and Shape of Supported Ru/γ-Al 203 Catalysts with NH3 Decomposition Activity. J Am Chem Soc 2009, 131, 12230–12239, doi:10.1021/ja902587k.
- 15. Reyes, Y.I.A.; Yang, K.S.; Thang, H.V.; Coluccini, C.; Chen, S.Y.; Chen, H.Y.T. Mechanistic Understanding of N2 Activation: A Comparison of Unsupported and Supported Ru Catalysts. Faraday Discuss 2023, 243, 148–163, doi:10.1039/d2fd00172a.
- Fang, H.; Liu, D.; Luo, Y.; Zhou, Y.; Liang, S.; Wang, X.; Lin, B.; Jiang, L. Challenges and Opportunities of Ru-Based Catalysts toward the Synthesis and Utilization of Ammonia. ACS Catal 2022, 12, 3938–3954, doi:10.1021/acscatal.2c00090.
- 17. Narasimharao, K.; Seetharamulu, P.; Rama Rao, K.S.; Basahel, S.N. Carbon Covered Mg-Al Hydrotalcite Supported Nanosized Ru Catalysts for Ammonia Synthesis. J Mol Catal A Chem 2015, 411, 157–166, doi:10.1016/j.molcata.2015.10.019.
- Aika, K. ichi; Takano, T.; Murata, S. Preparation and Characterization of Chlorine-Free Ruthenium Catalysts and the Promoter Effect in Ammonia Synthesis: 3. A Magnesia-Supported Ruthenium Catalyst. J Catal 1992, 136, 126–140, doi:10.1016/0021-9517(92)90112-U.
- Hammer, B.; Nørskov, J.K. Theoretical Surface Science and Catalysis—Calculations and Concepts. Advances in Catalysis 2000, 45, 71–129, doi:10.1016/S0360-0564(02)45013-4.
- 20. Javaid, R.; Nanba, T. Stability of Cs/Ru/MgO Catalyst for Ammonia Synthesis as a Hydrogen and Energy Carrier. 2022, doi:10.3390/en15103506.
- 21. Fiévet, S.F.; Piquemal, J.-Y. A Review from the Pioneer Group in Polyol-Mediated Synthesis The Polyol Process: A Unique Method for Easy Access to Metal Nanoparticles with Tailored Sizes, Shapes and Compositions. Chem. Soc. Rev 2018, 47, 5187, doi:10.1039/c7cs00777a.
- 22. Zhang, J.; Xu, H.; Ge, Q.; Li, W. Highly Efficient Ru/MgO Catalysts for NH3 Decomposition: Synthesis, Characterization and Promoter Effect. Catal Commun 2006, 7, 148–152, doi:10.1016/J.CATCOM.2005.10.002.

- 23. Liu, P.; Niu, R.; Li, W.; Wang, S.; Li, J. Morphology Effect of Ceria on the Ammonia Synthesis Activity of Ru/CeO 2 Catalysts. Catal Letters 2019, 149, 1007–1016, doi:10.1007/s10562-019-02674-1.
- 24. Yu, D.; Peng, C.; Yu, X.; Wang, L.; Li, K.; Zhao, Z.; Li, Z. Facile Preparation of Amorphous CenMnOx Catalysts and Their Good Catalytic Performance for Soot Combustion. Fuel 2022, 307, doi:10.1016/j.fuel.2021.121803.
- Peng, Z.; Wang, Y.; Yin, C.; Qiu, S.; Xia, Y.; Zou, Y.; Xu, F.; Sun, L.; Chu, H. Uniform Dispersion of Ultrafine Ruthenium Nanoparticles on Nano-Cube Ceria as Efficient Catalysts for Hydrogen Production from Ammonia-Borane Hydrolysis. Sustain Energy Fuels 2022, 7, 821–831, doi:10.1039/d2se01542k.
- Javaid, R.; Nanba, T. Effect of Reaction Conditions and Surface Characteristics of Ru/CeO2 on Catalytic Performance for Ammonia Synthesis as a Clean Fuel. Int J Hydrogen Energy 2021, 46, 18107–18115, doi:10.1016/j.ijhydene.2020.07.222.
- Niu, H.; Yang, Q.; Tang, K.; Xie, Y. A Simple Solution Calcination Route to Porous MgO Nanoplates. Microporous and Mesoporous Materials 2006, 96, 428–433, doi:10.1016/j.micromeso.2006.07.013.
- Javaid, R.; Matsumoto, H. Influence of Reaction Conditions and Promoting Role of Ammonia Produced at Higher Temperature Conditions in Its Synthesis Process over Cs-Ru/MgO Catalyst. 2019, doi:10.1002/slct.201803813.
- Iwamoto, J.; Itoh, M.; Kajita, Y.; Saito, M.; Machida, K. ichi Ammonia Synthesis on Magnesia Supported Ruthenium Catalysts with Mesoporous Structure. Catal Commun 2007, 8, 941–944, doi:10.1016/j.catcom.2006.05.052.
- Saito, M.; Itoh, M.; Iwamoto, J.; Li, C.Y.; Machida, K.I. Synergistic Effect of MgO and CeO2 as a Support for Ruthenium Catalysts in Ammonia Synthesis. Catal Letters 2006, 106, 107–110, doi:10.1007/s10562-005-9615-3.
- Osozawa, M.; Hori, A.; Fukai, K.; Honma, T. ScienceDirect Improvement in Ammonia Synthesis Activity on Ruthenium Catalyst Using Ceria Support Modified a Large Amount of Cesium Promoter. Int J Hydrogen Energy 2021, 47, 2433–2441, doi:10.1016/j.ijhydene.2021.10.204.
- 32. Feng, J.; Liu, L.; Ju, X.; Wang, M.; Zhang, X.; Wang, J.; Chen, P. For Ammonia Synthesis under Mild Conditions. 2022, doi:10.1021/acssuschemeng.2c01635.
- 33. Kitano, M.; Inoue, Y.; Yamazaki, Y.; Hayashi, F.; Kanbara, S.; Matsuishi, S.; Yokoyama, T.; Kim, S.-W.; Hara, M.; Hosono, H. Ammonia Synthesis Using a Stable Electride as an Electron Donor and Reversible Hydrogen Store. Nature Chemistry 2012 4:11 2012, 4, 934–940, doi:10.1038/nchem.1476.

- 34. Niwa, Y.; Aika, K.I. The Effect of Lanthanide Oxides as a Support for Ruthenium Catalysts in Ammonia Synthesis. J Catal 1996, 162, 138–142, doi:10.1006/jcat.1996.0268.
- 35. Li, C.; Shi, Y.; Zhang, Z.; Ni, J.; Wang, X.; Lin, J.; Lin, B.; Jiang, L. Improving the Ammonia Synthesis Activity of Ru/CeO2 through Enhancement of the Metal–Support Interaction. Journal of Energy Chemistry 2021, 60, 403–409, doi:10.1016/j.jechem.2021.01.031.
- Popescu, I.; Trotuş, I.T.; Marcu, I.C. Study by Electrical Conductivity Measurements of Semiconductive and Redox Properties of Ceria and Phosphated Ceria Catalysts. Appl Catal B 2012, 128, 55–63, doi:10.1016/j.apcatb.2012.01.037.
- 37. Wang, X.; Peng, X.; Zhang, Y.; Ni, J.; Au, C.T.; Jiang, L. Efficient Ammonia Synthesis over a Core-Shell Ru/CeO 2 Catalyst with a Tunable CeO 2 Size: DFT Calculations and XAS Spectroscopy Studies. Inorg Chem Front 2019, 6, 396–406, doi:10.1039/c8qi01244j.
- Tian, F.; Li, J.; Chen, W.; Tang, L.; Wu, M. Innovative Progress of Thermal Ammonia Synthesis under Mild Conditions. Int J Hydrogen Energy 2024, 78, 92–122, doi:10.1016/j.ijhydene.2024.06.206.
- Lin, B.; Liu, Y.; Heng, L.; Ni, J.; Lin, J.; Jiang, L. Effect of Ceria Morphology on the Catalytic Activity of Co/CeO2 Catalyst for Ammonia Synthesis. Catal Commun 2017, 101, 15–19, doi:10.1016/j.catcom.2017.07.015.
- 40. Lin, B.; Fang, B.; Wu, Y.; Li, C.; Ni, J.; Wang, X.; Lin, J.; Au, C.T.; Jiang, L. Enhanced Ammonia Synthesis Activity of Ceria-Supported Ruthenium Catalysts Induced by CO Activation. ACS Catal 2021, 11, 1331–1339, doi:10.1021/acscatal.0c05074.
- Wang, Y.; Wang, R. Effects of Chemical Etching and Reduction Activation of CeO2 Nanorods Supported Ruthenium Catalysts on CO Oxidation. J Colloid Interface Sci 2022, 613, 836–846, doi:10.1016/j.jcis.2022.01.062.
- 42. Lin, B.; Liu, Y.; Heng, L.; Wang, X.; Ni, J.; Lin, J.; Jiang, L. Morphology Effect of Ceria on the Catalytic Performances of Ru/CeO2 Catalysts for Ammonia Synthesis. Ind Eng Chem Res 2018, 57, 9127–9135, doi:10.1021/acs.iecr.8b02126.
- Lin, B.; Wu, Y.; Fang, B.; Li, C.; Ni, J.; Wang, X.; Lin, J.; Jiang, L. Ru Surface Density Effect on Ammonia Synthesis Activity and Hydrogen Poisoning of Ceria-Supported Ru Catalysts. Chinese Journal of Catalysis 2021, 42, 1712–1723, doi:10.1016/S1872-2067(20)63787-1.
- 44. Huang, H.; Dai, Q.; Wang, X. Morphology Effect of Ru/CeO2 Catalysts for the Catalytic Combustion of Chlorobenzene. Appl Catal B 2014, 158–159, 96–105, doi:10.1016/j.apcatb.2014.01.062.

- Shadravan, V.; Cao, A.; Bukas, V.J.; Grønborg, M.K.; Damsgaard, C.D.; Wang, Z.; Kibsgaard, J.; Nørskov, J.K.; Chorkendorff, I. Enhanced Promotion of Ru-Based Ammonia Catalysts by in Situ Dosing of Cs. Energy Environ Sci 2022, 15, 3310–3320, doi:10.1039/d2ee00591c.
- Kowalczyk, Z.; Krukowski, M.; Raróg-Pilecka, W.; Szmigiel, D.; Zielinski, J. Carbon-Based Ruthenium Catalyst for Ammonia Synthesis: Role of the Barium and Caesium Promoters and Carbon Support. Appl Catal A Gen 2003, 248, 67–73, doi:10.1016/S0926-860X(03)00150-9.
- Larichev, Y. V.; Moroz, B.L.; Moroz, E.M.; Zaikovskii, V.I.; Yunusov, S.M.; Kalyuzhnaya, E.S.; Shur, V.B.; Bukhtiyarov, V.I. Effect of the Support on the Nature of Metal-Promoter Interactions in Ru-Cs+/MgO and Ru-Cs+-Al2O3 Catalysts for Ammonia Synthesis. Kinetics and Catalysis 2005, 46, 891–899, doi:10.1007/s10975-005-0153-1.
- Szmigiel, D.; Bielawa, H.; Kurtz, M.; Hinrichsen, O.; Muhler, M.; Raróg, W.; Jodzis, S.; Kowalczyk, Z.; Znak, L.; Zieliński, J. The Kinetics of Ammonia Synthesis over Ruthenium-Based Catalysts: The Role of Barium and Cesium. J Catal 2002, 205, 205–212, doi:10.1006/jcat.2001.3431.
- 49. Ansari, S.A.; Khan, M.M.; Kalathil, S.; Nisar, A.; Lee, J.; Cho, M.H. Oxygen Vacancy Induced Band Gap Narrowing of ZnO Nanostructures by an Electrochemically Active Biofilm. Nanoscale 2013, 5, 9238–9246, doi:10.1039/c3nr02678g.
- 50. Javaid, R.; Nanba, T. Ru/CeO2/MgO Catalysts for Enhanced Ammonia Synthesis Efficiency. Top Catal 2023, 66, 452–460, doi:10.1007/s11244-023-01789-5.
- 51. Ma, C.; Wen, Y.; Yue, Q.; Li, A.; Fu, J.; Zhang, N.; Gai, H.; Zheng, J.; Chen, B.H. Oxygen-Vacancy-Promoted Catalytic Wet Air Oxidation of Phenol from MnO: X-CeO2. RSC Adv 2017, 7, 27079–27088, doi:10.1039/c7ra04037g.
- 52. Araia, A.; Wang, Y.; Robinson, B.; Jiang, C.; Brown, S.; Wildfire, C.; Shekhawat, D.; Hu, J. Microwave-Assisted Ammonia Synthesis over Cs-Ru/CeO2 Catalyst at Ambient Pressure: Effects of Metal Loading and Support Particle Size. Catal Commun 2022, 170, 106491, doi:10.1016/j.catcom.2022.106491.
- 53. Manaka, Y.; Nagata, Y.; Kobayashi, K.; Kobayashi, D.; Nanba, T. The Effect of a Ruthenium Precursor on the Low-Temperature Ammonia Synthesis Activity over Ru/CeO2. Dalton Transactions 2020, 49, 17143–17146, doi:10.1039/d0dt01974g.
- 54. Siporin, S.E.; Davis, R.J. Isotopic Transient Analysis of Ammonia Synthesis over Ru/MgO Catalysts Promoted by Cesium, Barium, or Lanthanum. J Catal 2004, 222, 315–322, doi:10.1016/j.jcat.2003.10.018.

- 55. Bécue, T.; Davis, R.J.; Garces, J.M. Effect of Cationic Promoters on the Kinetics of Ammonia Synthesis Catalyzed by Ruthenium Supported on Zeolite X. J Catal 1998, 179, 129–137, doi:10.1006/jcat.1998.2212.
- Osozawa, M.; Hori, A.; Fukai, K.; Honma, T. ScienceDirect Improvement in Ammonia Synthesis Activity on Ruthenium Catalyst Using Ceria Support Modified a Large Amount of Cesium Promoter. Int J Hydrogen Energy 2021, 47, 2433–2441, doi:10.1016/j.ijhydene.2021.10.204.
- 57. Javaid, R.; Nanba, T. Effect of Reaction Conditions and Surface Characteristics of Ru/CeO2 on Catalytic Performance for Ammonia Synthesis as a Clean Fuel. Int J Hydrogen Energy 2021, 46, 18107–18115, doi:10.1016/j.ijhydene.2020.07.222.
- Saito, M.; Itoh, M.; Iwamoto, J.; Li, C.-Y.; Machida, K. Synergistic Effect of MgO and CeO2 as a Support for Ruthenium Catalysts in Ammonia Synthesis. Catal Letters 2006, 106, 107– 110, doi:10.1007/s10562-005-9615-3.
- 59. Yang, X.L.; Zhang, W.Q.; Xia, C.G.; Xiong, X.M.; Mu, X.Y.; Hu, B. Low Temperature Ruthenium Catalyst for Ammonia Synthesis Supported on BaCeO3 Nanocrystals. Catal Commun 2010, 11, 867–870, doi:10.1016/J.CATCOM.2010.03.008.
- 60. Li, W.; Liu, P.; Niu, R.; Li, J.; Wang, S. Influence of CeO2 Supports Prepared with Different Precipitants over Ru/CeO2 Catalysts for Ammonia Synthesis. Solid State Sci 2020, 99, 105983, doi:10.1016/J.SOLIDSTATESCIENCES.2019.105983.

Chapter 8

Conclusions and Outlook

8.1 Conclusions

Through this thesis, the importance of transitioning away from fossil fuels to renewable energy sources, with ammonia (NH_3) serving as hydrogen (H_2) energy carrier, has been highlighted. This approach can be seen as essential for tackling climate change and reducing emissions. On one hand, this strategy involves replacing fossil fuels as coal, oil, and gas with renewable energy produced from hydropower, wind, and solar to drastically reduce emissions. On the other, it includes hydrogen production via renewable electricity through electrolysis, followed by storage or transportation in the form of ammonia.

However, to implement this innovative approach, several issues need to be addressed. Therefore, an extensive investigation on both ammonia synthesis and ammonia decomposition was performed in this dissertation. It was demonstrated that selectively removing the product, either hydrogen or ammonia, using membrane reactor technologies positively impact conversion, surpassing the limits imposed by thermodynamic equilibrium. Furthermore, driven by the strong motivation to develop functional materials, shared by all the described routes, it was demonstrated that tailored ruthenium-based catalysts and engineered selective membranes can significantly enhance the reaction rates of ammonia synthesis and decomposition, opening up routes for new investigation and further development. The main conclusions drawn from this study, based on the findings presented in the previous chapters, are summarized in the following sections.

8.1.1 Ammonia decomposition

The implementation of an NH₃-based energy system requires research efforts to address challenges across the entire value chain of green ammonia, encompassing its production, distribution, and utilization [1]. Given the inherently energy-intensive nature of ammonia decomposition reaction, achieving high energy efficiency presents a significant challenge; however, this remains a crucial factor for its practical application in hydrogen storage and transport. The process requires elevated temperatures, typically between 500 - 600 °C, which leads to substantial energy consumption. However, improving efficiency is essential to make ammonia a viable hydrogen carrier on a large scale. In this thesis, several pathways were explored to address this challenge.

Firstly, in Chapter 2, a process intensification strategy was proposed, which integrates a carbon membrane within a fixed bed reactor. In the experimental tests conducted under ammonia decomposition conditions, NH_3 conversion greater than 90% were achieved across the entire range of operating parameters tested. Ammonia conversion approaching the thermodynamic equilibrium was reached at temperatures from 475 °C onward. Regarding hydrogen recovery, the carbon membrane used in the system demonstrated a hydrogen recovery rate of 8.2 – 9.8% within the temperature range of 450 – 500 °C. This highlights the membrane's ability to selectively recover hydrogen at high temperatures; though improvements in hydrogen recovery efficiency would be necessary for scaling up the process or optimizing it for industrial use.

Then, in Chapter 3, an advanced catalyst design was proposed, fabricating a structured catalyst, to facilitate heat transfer, minimizing energy losses and improving thermal efficiency. Unlike conventional catalysts, which are typically used in powder or pellet form, structured catalysts are designed with a geometry that enhances catalytic activity, heat transfer, and gas flow dynamics, all of which are critical for the energy-intensive ammonia decomposition process. Furthermore, the results indicate that incorporating a Pd-based membrane into the system significantly enhances ammonia decomposition performance, leading to an increase in conversion in the structured reactor configuration by up to 29% compared to the use of the catalyst alone. This improvement highlights the synergistic effect between the structured catalyst and the membrane in optimizing the ammonia decomposition process.

In Chapter 4, the development of more efficient catalysts was tackled. Developing more performant catalysts, tailoring the electronic and structural properties, can increase reaction rates, allowing for more hydrogen to be generated at lower temperatures. After determining the optimal amount of ruthenium, the addition of cesium to the catalytic formulation resulted in further improvement. More specifically, at 350 °C the ammonia conversion increased approximately 28%. A H₂ production rate up to 1.9 mol g_{cat⁻¹} h⁻¹ was obtained at 30 000 Nml h⁻¹ g_{cat⁻¹}, 450 °C and 1 bar. This result marks the highest production rate reported in the literature so far, underscoring the efficacy of the new catalyst under these conditions. Finally, the promoted catalyst was tested over an overall time span of 500 hours to verify the long-term stability, proving the stability of the synthesized catalyst over time. Also the scalability of the synthesis procedure was assessed. The amount of catalyst synthesized per single batch was progressively increased from 1 to 25 g. Scaling up the synthesis procedure to produce up to 1 000 g of catalyst is considered feasible at the laboratory scale, provided that a suitably sized vessel is obtained. The high hydrogen production rates and easy

scalability combined with catalyst stability make this synthesis method particularly suitable for larger-scale applications.

Furthermore, in Chapter 5, a preliminary study on the integration of the catalyst developed in Chapter 4 and a palladium-based membrane was conducted. The results demonstrated that it was possible to achieve conversion over 97% in the temperature range of 375 – 425 °C at 4 bar. Thus, it suggests that high single-pass conversion is feasible even at moderate temperatures. This is particularly beneficial for ammonia decomposition, as it means the process can be efficient without needing extremely high temperatures, reducing energy costs.

8.1.2 <u>Ammonia synthesis</u>

Ammonia production, traditionally conducted via the Haber-Bosch process, requires high temperatures (400 - 500 °C) and pressures (50 - 300 bar) to convert nitrogen (N_2) and hydrogen into ammonia [2]. The energy demands of this process present significant challenges for sustainable and efficient production, particularly as the global push for green ammonia (produced using renewable energy) intensifies [3]. Therefore, in this thesis, several key challenges and approaches to improve energy efficiency in ammonia synthesis were proposed.

In Chapter 6, a packed bed membrane reactor was modeled, to combine the reaction and separation processes in a single unit. The results demonstrated a substantial enhancement in hydrogen conversion upon introducing the membrane into the packed bed reactor. Notably, a selectivity for NH₃ over H₂ of 50 and a selectivity for NH₃ over N₂ of 100, along with a minimum NH₃ permeance of $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹, are required. The results demonstrated that it is possible to exceed the equilibrium limits of the packed bed reactor, resulting in a significant increase in conversion.

Finally, in Chapter 7, the development of tailored catalysts for ammonia synthesis was studied to improve the process efficiency. Traditional iron-based catalysts require high temperatures and pressures to achieve acceptable reaction rates [4]. Thus, this research focused on developing more performant catalysts, operating at lower temperatures and pressures, reducing energy consumption. The most performant synthesized catalyst allowed an ammonia production up to 73 mmol h⁻¹ g_{cat}⁻¹ at 50 bar and 400 °C, surpassing similar catalytic formulation found in literature (0.39 – 28.2 mmol h⁻¹ g_{cat}⁻¹ at 50 bar and 400 °C).

8.2 Outlook & recommendations

In light of the present results, ammonia could be a realistic solution for the storage and transportation of hydrogen, in spite of the fact that more research should be carried out to reach the optimal conditions for both ammonia synthesis and decomposition. However, the implementation of the green ammonia cycle implies the successful implementation of a green supply chain. As of now, 96% of hydrogen is produced from fossil resources through steam reforming of methane, partial oxidation, and coal gasification processes. The remaining 4% is obtained from electrolysis [5]. Compared to the electrolysis process, the fossil-based route has clear advantages in production cost and capacity, but with an obvious drawback in producing massive greenhouse gases contributing to environmental pollution. Thus, in this thesis, process intensification strategies were proposed aiming to significantly enhance efficiency and reduce energy consumption, in order to increase the competitiveness of the green hydrogen and, therefore, improve sustainability.

Moreover, although significant experimental and modeling efforts have been made in ammonia synthesis and ammonia decomposition at the proof-of-concept and lab-scale stages, more comprehensive studies are expected in the coming years [6,7]. To achieve a deeper and more accurate understanding of reaction kinetics, integrating a microkinetic model with computational fluid dynamics (CFD) simulations will be essential. CFD excels at capturing gas residence time, pressure, and other fluid dynamics, and this combination will provide a complete description of reactive flow, spanning from the nanoscale (microkinetic model) to the full reactor scale.

However, to prove the economic feasibility of using ammonia as a hydrogen carrier with the process intensification strategies proposed in this work, a techno-economic assessment (TEA) combined with a life cycle assessment (LCA) should be carried. More specifically, TEA should be directed to quantify the cost of the ammonia-based hydrogen supply chain, including the production, storage, transportation, and conversion of ammonia back to hydrogen. For instance, when comparing carbon-based membranes and palladium-membranes for applications as hydrogen separation, various factors should be considered for economic evaluation.

Generally, carbon membranes represent a cheaper solution than palladium-based ones [8]. Carbon membranes can be produced from polymer precursors, which reduces raw material costs. Moreover, palladium is a precious metal, and its cost is much higher. The price of palladium can be volatile, leading to uncertainties in long-term cost estimation.

Additionally, Pd-based membranes often require alloying with silver or other precious metals to improve performance, adding to the total cost. Both carbon- and palladiumbased membranes may suffer from degradation over time, especially in extreme temperatures or harsh chemical environments [9]. Due to their high hydrogen flux, Pd-based membranes can achieve faster separation with less membrane area, however they operate efficiently only at high temperatures [10], whereas carbon membranes usually require lower energy inputs due to their lower operating temperatures. However, their lower permeability can sometimes necessitate larger membrane areas or longer operational times, increasing energy costs indirectly. Therefore, the answer is not straightforward because each membrane type offers different trade-offs in terms of cost, performance, durability, and operational requirements. In light of these factors, a comprehensive techno-economic evaluation is essential to determine which technology is the most cost-effective for a specific application.

Furthermore, an LCA should be conducted to evaluate the environmental impacts associated with the ammonia-to-hydrogen supply chain. This includes greenhouse gas emissions, water usage, and energy consumption across the life cycle stages. It will be crucial to conduct sensitivity analyses to test how changes in key assumptions (e.g., energy prices, technology efficiency, transport distances) affect the overall feasibility. This will help identify critical cost drivers and environmental impact factors.

Looking at the comparison proposed earlier, it is important to underline that the production of carbon membranes may have a lower environmental impact than mining and refining palladium. Additionally, carbon-based materials are generally easier to recycle or dispose of. Notably, the environmental footprint of palladium production is high, due to energy-intensive mining and refining processes. However, the higher efficiency in hydrogen separation and purity could offset some of these impacts in long-term use.

Finally, in order to open up the route for ammonia as efficient hydrogen carrier, it is necessary to compare the costs and environmental impacts of ammonia with other carriers (e.g., liquid hydrogen, methanol) to validate its competitive edge. By combining TEA and LCA, it will be possible to provide a comprehensive model of the economic feasibility and environmental impact of ammonia as a hydrogen carrier. However, for a full techno-economic analysis, application-specific factors such as transport distance, safety and handling considerations, infrastructure availability, energy efficiency and purity requirements will determine the most suitable carrier.

8.3 References

- 1. Yin, S.F.; Xu, B.Q.; Zhou, X.P.; Au, C.T. A Mini-Review on Ammonia Decomposition Catalysts for on-Site Generation of Hydrogen for Fuel Cell Applications. Appl Catal A Gen 2004, 277, 1–9, doi:10.1016/j.apcata.2004.09.020.
- Valera-Medina, A.; Amer-Hatem, F.; Azad, A.K.; Dedoussi, I.C.; De Joannon, M.; Fernandes, R.X.; Glarborg, P.; Hashemi, H.; He, X.; Mashruk, S.; et al. Review on Ammonia as a Potential Fuel: From Synthesis to Economics. Energy and Fuels 2021, 35, 6964–7029.
- Rouwenhorst, K.H.R.; Engelmann, Y.; Van 'T Veer, K.; Postma, R.S.; Bogaerts, A.; Lefferts, L. Plasma-Driven Catalysis: Green Ammonia Synthesis with Intermittent Electricity. Green Chemistry 2020, 22, 6258–6287, doi:10.1039/d0gc02058c.
- 4. Vandervell, H.D.; Waugh, K.C. On the Role of Promoters in Promoted Iron Catalysts Used in the Industrial Synthesis of Ammonia. Chem Phys Lett 1990, 171, 462–468, doi:10.1016/0009-2614(90)85247-A.
- Vidas, L.; Castro, R. Recent Developments on Hydrogen Production Technologies: Stateof-the-Art Review with a Focus on Green-Electrolysis. Applied Sciences (Switzerland) 2021, 11, doi:10.3390/app112311363.
- Kucuk, E.; Hasan Koybasi, H.; Avci, A.K. Beyond Equilibrium Ammonia Synthesis in a Membrane and Heat Exchange Integrated Microreactor: A Modeling Study. Fuel 2024, 357, 129858, doi:10.1016/j.fuel.2023.129858.
- Morlanés, N.; Katikaneni, S.P.; Paglieri, S.N.; Harale, A.; Solami, B.; Sarathy, S.M.; Gascon, J. A Technological Roadmap to the Ammonia Energy Economy: Current State and Missing Technologies. Chemical Engineering Journal 2021, 408, 127310, doi:10.1016/J.CEJ.2020.127310.
- Nordio, M.; Melendez, J.; van Sint Annaland, M.; Pacheco Tanaka, D.A.; Llosa Tanco, M.; Gallucci, F. Comparison between Carbon Molecular Sieve and Pd-Ag Membranes in H2-CH4 Separation at High Pressure. Int J Hydrogen Energy 2020, 45, 28876–28892, doi:10.1016/j.ijhydene.2020.07.191.
- 9. Arratibel, A.; Pacheco Tanaka, A.; Laso, I.; van Sint Annaland, M.; Gallucci, F. Development of Pd-Based Double-Skinned Membranes for Hydrogen Production in Fluidized Bed Membrane Reactors. J Memb Sci 2018, 550, 536–544, doi:10.1016/j.memsci.2017.10.064.
- 10. Basile, A.; Gallucci, F.; Tosti, S. Synthesis, Characterization, and Applications of Palladium Membranes. Membrane Science and Technology 2008, 13, 255–323, doi:10.1016/S0927-5193(07)13008-4.

Appendices and Supplementary Material

Appendix A

Experimental setup

The experimental setup is designed as a flexible experimental platform that allows for the operation of three different types of experiments by simply changing the reactor configuration. Using a differential plug flow reactor, this setup facilitates kinetic tests to determine the kinetic laws of catalysts or sorbent materials employed in the research projects. Additionally, by incorporating a separation module, permeation tests involving N₂, H₂, and NH₃ can be conducted with various types of membranes, such as carbon- or palladium-based membranes. Furthermore, using a membrane reactor, this experimental setup enables the performance of both ammonia synthesis and ammonia decomposition reactions. This last configuration is illustrated in the P&ID presented in Figure A1. This setup allows for a wide operational range, as it can function at temperatures up to 450 °C and pressures up to 65 bar.



Figure A1. P&ID of the experimental setup designed and constructed for this dissertation.

Appendix B

Membrane characterization: perm-porometry setup

The perm-porometry analysis method is based on the capillary condensation of liquids in porous media. From Kelvin equation (Equation B1), it is known that, in a capillary, the vapor condensation takes place at lower pressures than the saturated vapor pressure. Moreover, the smaller the characteristic dimensions of the capillary, the lower the pressure at which the above mentioned phenomenon will occur. Thus, it is possible to send to the porous membrane a mixture of a non-condensable gas and a condensable vapor, then the permeation rate of the non-condensable gas can be measured as a function of the vapor pressure of condensable vapor. This procedure allows to estimate the pore size distribution as the permeation of the non-condensable gas in larger pores is hindered by larger vapor pressures [1–3].

$$R \cdot T \cdot ln\left(\frac{p_V}{p_s}\right) = 2 \cdot v \cdot \frac{\sigma \cdot \cos\theta}{r_p}$$
(Eq. B1)

First, the membrane underwent a 24 hours drying procedure under nitrogen atmosphere at 300 °C and at a pressure difference of 5 bar between retentate and permeate to eliminate any condensed water from the pores. Subsequently, the system was cooled to room temperature and helium was employed as non-condensable gas to measure the permeance in the dry membrane. Later, condensable vapor was gradually introduced by injecting demi water into the helium stream to occlude the pores of the fabricated membranes at 70 °C and at a pressure difference of 2 bar. The pore size was calculated according to Kelvin's equation, where *R* is the universal gas constant, *T* is the temperature of the system, p_v is the vapor pressure, p_s is the saturated vapor pressure, *v* is the molar volume of the liquid, σ is the vapor-liquid surface tension, θ is the contact angle and r_p is the pore radius. Of note, the application of Kelvin equation for pores lower that 2 nm can lead to inaccuracies [2]. However, the vapor pressure reduction described by the Kelvin equation still occurs for pores considerably smaller, therefore it is still possible to assign a quantitative measure [4]. In Figure B2, a schematic representation of the perm-porometer setup utilized in this study is presented.



Deionized water tank

Figure B1. Schematic representation of the perm-porometer setup designed to measure the pore size distribution of tubular carbon-based membranes using water as adsorbate and helium or nitrogen as inert gas.

Appendix C

Modeling of a packed bed membrane reactor: Supplementary material

Equations to determine kinetic expression parameters (Rossetti et al.)

The kinetic expression parameters are determined according to the equations provided in Table C1, where the hydrogen-to-nitrogen feed ratio (q) is specified as either 1.5 or 3. The stoichiometric parameter($\lambda(q)$) takes a value of 1 when q = 3 and a value of 3 when q = 1.5. The fractional conversion (η) is defined as a function of the ammonia outlet mole fraction($y_{NH_3,out}$), while the parameter a(q) takes a value of 2 when q = 3, and a value of 2.5 when q = 1.5. The time factor (τ) is defined as the ratio of the catalyst volume to the molar feed flow rate of either nitrogen (if q = 3) or hydrogen (if q = 1.5). The activity coefficients (a_i) are function of the parameter $\beta(q)$, which is set to 1 when q = 3 and is set to 0.5 when q = 1.5.

Parameter	Units	Equation	
k _r	$\left(\text{mol } \mathbf{h}^{-1} {l_{\text{cat}}}^{-1} \right)$	$9.02 \cdot 10^8 \cdot exp\left(\frac{-23.0}{R \cdot T}\right)$	(Eq. C1)
K _a	(-)	$exp \begin{pmatrix} -2.691122 \cdot log_{10}(T) & -5.519265 \cdot 10^{-5} \cdot T + 1.848863 \cdot 10^{-7} \cdot T^2 + \\ &+ 2001.6 \cdot T^{-1} + 2.6899 \end{pmatrix}$	(Eq. C2)
a_{N_2}	(atm)	$\frac{1 - \eta \cdot \beta(q)}{1 + q - 2 \cdot \eta \cdot \beta(q)} \cdot P \cdot \gamma_{N_2}$	(Eq. C3)
a_{H_2}	(atm)	$\frac{q-3\cdot\eta\cdot\beta(q)}{1+q-2\cdot\eta\cdot\beta(q)}\cdot P\cdot\gamma_{_{H_2}}$	(Eq. C4)
a_{NH_3}	(atm)	$\frac{2 \cdot \eta \cdot \beta(q)}{1 + q - 2 \cdot \eta \cdot \beta(q)} \cdot P \cdot \gamma_{_{NH_3}}$	(Eq. C5)
η	(-)	$a \cdot \left(\frac{y_{NH_3,out}}{1 + y_{NH_3,out}}\right)$	(Eq. C6)
γ_{N_2}	(-)	$\begin{array}{l} 0.93431737 + 0.3101804 \cdot 10^{-3} \cdot T + 0.295896 \cdot 10^{-3} \cdot P - 0.2707279 \cdot 10^{-6} \cdot T^2 + \\ + 0.4775207 \cdot 10^{-6} \cdot P^2 \end{array}$	(Eq. C7)
γ_{H_2}	(-)	$exp\left\{exp(-3.8402 \cdot T^{0.125} + 0.541) \cdot P - exp(-0.1263 \cdot T^{0.5} - 15.98) \cdot P^{2} + 300 \cdot exp(-0.011901 \cdot T - 5.941) \cdot \left[exp\left(-\frac{P}{300}\right) - 1\right]\right\}$	(Eq. C8)
γ_{NH_3}	(-)	$\begin{array}{l} 0.1438996 + 0.2028538 \cdot 10^{-2}T - 0.4487672 \cdot 10^{-3} \cdot P - 0.1142945 \cdot 10^{-5} \cdot T^2 + \\ + 0.2761216 \cdot 10^{-6} \cdot P^2 \end{array}$	(Eq. C9)
K_{H_2}	(kcal mol ⁻¹)	$exp\left(\frac{-56.9024}{R} + \frac{37656}{R \cdot T}\right)$	(Eq. C10)
K _{NH3}	(kcal mol ⁻¹)	$exp\left(\frac{-34.7272}{R} + \frac{29228}{R \cdot T}\right)$	(Eq. C11)

Validation of the model by using literature kinetic test (Rossetti et al.)

Table C2 Experimental data from Rossetti et al

The validation of the model was performed using experimental results retrieved from the study by Rossetti et al. [5], with the tests reported in Table C2. This table presents a list of the experiments along with their respective operative conditions. All comparisons between model predictions and experimental results are presented in Figure C1, except for Test 15 and Test 16, which are shown in Figure 6.2.

Tuble G2. Experimental data nom nossetti et al.						
Test	Pressure	Temperature	Feed ratio			
name	(bar)	(°C)	(vol. H ₂ : vol. N ₂)			
Test 2	100	370	1.5			
Test 3	85	370	1.5			
Test 4	85	430	1.5			
Test 7	70	370	3			
Test 8	70	430	3			
Test 10	85	370	3			
Test 11	85	430	3			
Test 13	100	370	3			
Test 15	100	430	1.5			
Test 16	100	430	3			
Test 17	70	430	1.5			
Test 18	50	430	1.5			
Test 19	100	400	1.5			
Test 20	70	400	1.5			
Test 21	50	400	1.5			
Test 22	100	460	1.5			
Test 23	70	460	1.5			
Test 24	50	460	1.5			



Figure C1. Model validation by using tests from Rossetti et al. (continued on the next page)


Figure C1. (continued) Model validation by using tests from Rossetti et al.

Pressure drops along the reactor length

In the reaction side (or retentate), where the spherical catalyst particles with a diameter of $1.65 \cdot 10^{-3}$ m are placed, the pressure distribution along the reactor is determined using Equation 6.17. Figure C2 shows a negligible pressure drop along the reactor length, which resulted in approximately 0.001 bar overall.



Figure C2. Pressure drop profile across the packed bed on the retentate side as a function of the reactor length.

<u>Knudsen selectivity</u>

For a porous membrane, the Knudsen selectivity of species *i* to species *j* ($S_{K,i/j}$), as provided in Equation C12, is defined as the ratio of their Knudsen diffusion coefficients ($D_{K,i}$). As described in Equation C13, the Knudsen diffusion coefficient of a species depends on its molar mass (M_i) and the membrane characteristics. In this equation, r_p represents the pore radius of the membrane, R is the universal gas constant. Consequently, $S_{K,i/j}$ is equal to the square root of the inverse ratio of their molar masses.

$$S_{K,i/j} = \frac{D_{K,i}}{D_{K,i}} = \sqrt{\frac{M_j}{M_i}}$$
 (Eq. C12)

$$D_{K,i} = \frac{2}{3} \cdot \frac{r_p}{\sqrt{\pi}} \cdot \sqrt{\frac{8 \cdot R \cdot T}{M_i}}$$
(Eq. C13)





* Membrane performance evaluation

Figure C3. Impact of S_{NH_3/N_2} on (a, c, e) NH₃ purity and (b, d, f) NH₃ recovery for different values of S_{NH_3/H_2} with \mathcal{P}_{NH_3} equal to (a, b) $1 \cdot 10^{-9}$, (c, d) $1 \cdot 10^{-8}$ and (e, f) $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹.



• N₂ permeation across the membrane and H₂ back permeating

Figure C4. Impact of S_{NH_3/N_2} on (a, c, e) N₂ trans-membrane permeation flow and (b, d, f) H₂ back-permeation flow for different values of S_{NH_3/H_2} with \mathcal{P}_{NH_3} equal to (a, b) $1 \cdot 10^{-9}$, (c, d) $1 \cdot 10^{-8}$ and (e, f) $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹.



Figure C5. Impact of S_{NH_3/N_2} on nitrogen conversion for different values of S_{NH_3/H_2} with \mathcal{P}_{NH_3} equal to (a) $1 \cdot 10^{-9}$, (b) $1 \cdot 10^{-8}$ and (c) $1 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹.

Case study: real membrane in a non-isothermal PBMR



Figure C6. Effect of *GHSV* on H₂ conversion (a) for different value of pressure difference across the membrane and sweep gas-to-feed ratio and (b) effect of *GHSV* on H₂ conversion and NH₃ recovery for ΔP = 20 bar and *SF* = 6 for non-isothermal operating conditions.

Thermodynamic gas properties

✤ Density

The gas mixture density was calculated via Peng & Robinson cubic Equation of State (EoS), whose implicit form is expressed through the compressibility factor Z [6]:

$$Z^{3} - (1 - B) \cdot Z^{2} + (A - 2 \cdot B^{2} - 2 \cdot B) \cdot Z - (A \cdot B - B^{3} - B^{2}) = 0$$
 (Eq. C14)

where the coefficients A and B are defined by Equation C15 and Equation C16, depending on the temperature and pressure of the system.

$$A = \frac{a \cdot P}{R^2 \cdot T^2}$$
(Eq. C15)

$$B = \frac{b \cdot P}{R \cdot T}$$
(Eq. C16)

The van der Waals one-fluid mixing rules was used to calculate the energy *a* and the volume *b*: according to Equation C17 and Equation C18:

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_{i} \cdot y_{j} \cdot a_{ij}$$
 (Eq. C17)

$$b = \sum_{i=1}^{N} \sum_{j=1}^{N} y_{i} \cdot y_{j} \cdot b_{ij}$$
 (Eq. C18)

where y_i and y_j is the molar fraction of each component in the gas phase, while the parameters a_{ij} and b_{ij} are defined by the critical properties of each gas, as expressed in Equation C19 to Equation C22:

$$a_{ij} = \sqrt{a_i \cdot a_j} \cdot (1 - k_{ij}) \cdot a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i \cdot y_j \cdot a_{ij}$$
(Eq. C19)

$$b_{ij} = \frac{1}{2} \cdot \left(b_i + b_j \right) \cdot \left(1 - \delta_{ij} \right)$$
(Eq. C20)

$$a_{i} = \Omega_{a} \cdot \frac{R \cdot P_{ri}}{T_{ri}^{2}} \cdot \left[1 + m_{i} \cdot \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^{2} = 0.457235529 \cdot \frac{R^{2} \cdot T_{ci}^{2}}{P_{ci}} \cdot \left[1 + m_{i} \cdot \left(1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^{2}$$
(Eq. C21)

$$b_i = \Omega_b \cdot \frac{R \cdot P_{ri}}{T_{ri}} = 0.0777960739 \cdot \frac{R \cdot T_{ci}}{P_{ci}}$$
 (Eq. C22)

where Ω_a and Ω_b are independent with respect to the EoS, and P_{ri} and T_{ri} are the reduced pressure and temperature of component *i*, respectively [6]. The factor m_i depends on the acentric factor (ω_i), as reported in Equation C23 and Equation C24 [7].

if
$$\omega_i \le 0.491$$
 $m_i = 0.37464 + 1.54226 \cdot \omega_i - 0.26992 \cdot \omega_i^2$ (Eq. C23)

if $\omega_i > 0.491$ $m_i = 0.379642 + 1.48503 \cdot \omega_i - 0.164423 \cdot \omega_i^2 + +0.016666 \cdot \omega_i^3$ (Eq. C24)

The critical properties, T_{ci} , P_{ci} and ω_i , are the critical temperature, critical pressure and acentric factor respectively, which are shown in Table C3 [8].

Table C3. Critical properties for each species.				
Species	Т _{с, і}	Р _{с, і}	<i>V</i> _{c, i}	ω_i
	(K)	(MPa)		(-)
H ₂	33.19	1.313	0.064147	-0.215993
N 2	126.2	3.4	0.08921	0.0377215
NH ₃	405.7	11.28	0.07247	0.252608

The factor δ_{ij} and k_{ij} represent the binary interaction parameters between the different gas species. The first one is usually zero, while the second one can be calculated using Equation C25, whose results are shown in Table C4

$$k_{ij} = \frac{1 - 8 \cdot \sqrt{V_{ci} \cdot V_{cj}}}{(V_{ci}^{1/3} + V_{ci}^{1/3})^3}$$
(Eq. C25)

k _{ij}	H ₂	N 2	NH ₃
H ₂	0	0.6495	0.8328
N_2	0.6495	0	0.5536
NH ₃	0.8328	0.5536	0

Table C4. Binary interaction parameters of each species.

* Viscosity

The viscosity of the gas mixture was calculated using the Wilke method [9], shown in Equation C26 to Equation C28:

$$\mu_{mix} = \sum_{i=1}^{N} \frac{\mu_i \cdot y_i}{\sum_{j=1}^{N} (y_i \cdot \phi_{ij})}$$
(Eq. C26)

$$\mu_i = \frac{C_1 \cdot T^{C_2}}{1 + \frac{C_3}{T} + \frac{C_4}{T^2}}$$
(Eq. C27)

$$\phi_{ij} = \frac{\left[1 + \left(\mu_i / \mu_j\right)^{1/2} + \left(M_i / M_j\right)^{1/4}\right]^2}{\left[8 \cdot \left(1 + M_i / M_j\right)\right]^{1/2}}$$
(Eq. C28)

where μ_i is the viscosity of the single gas calculated with the following equation, retrieved from Perry's Chemical Engineers' Handbook [8], together with the specific coefficients shown in Table C5. Additionally, y_i and M_i are the molar fraction and molar mass of the single gas, respectively.

Table C5. Specific coefficients in the viscosity equation for each species. Species *C*₁ *C*₂ *C*₃ *C*₄ 1.797.10-7 0.6850 H_2 -0.59 140 N₂ 0.6081 54.714 0 6.5592·10⁻⁷ NH₃ 4.1855.10-8 0.9806 30.8 0

✤ Specific heat

The specific heat of the gas mixture is calculated according to Equation C29 from Perry's Chemical Engineers' Handbook [8]:

$$c_{p,mix} = \sum_{i=1}^{N} y_i \cdot c_{p,i}$$
 (Eq. C29)

where $c_{p,i}$ is the specific heat capacity of the single species computed according to the correlation (Equation C30) found in the same source [8]. Specific coefficients of each species are reported in Table C6.

$$c_{p,i} = C_1 + C_2 \cdot \left[\frac{C_3/T}{sinh(C_3/T)}\right]^2 + C_4 \left[\frac{C_5/T}{cosh(C_5/T)}\right]^2$$
(Eq. C30)

Table C6. Specific coefficient of each species in the specific heat equation.

Species	<i>C</i> ₁ ·10 ⁻⁵	<i>C</i> ₂ ·10 ⁻⁵	<i>C</i> ₃ ·10 ⁻³	<i>C</i> ₄ ·10 ⁻⁵	<i>C</i> ₅
H ₂	567.6	0.2761	0.0956	2.466	0.0376
N_2	909.79	0.29105	0.0816	1.7016	0.00103
NH ₃	882	0.33427	0.4898	2.036	0.2256

Heat of reaction

The heat of reaction was calculated according to Equation C31 from Perry's Chemical Engineers' Handbook [8]:

$$\Delta H_r(T) = \Delta H_r(T_{ref}) + \int_{T_{ref}}^T \Delta c_P \, dT$$
(Eq. C31)

where reference the temperature used was 298 K, and the standard heat of reaction and the change in specific heat capacity are defined in Equation C32 and Equation C33, respectively. Here, v_i represent the stoichiometric number, $H_{f,T_{ref}}$ is the standard enthalpy of formation, and $c_{p,i}$ is the specific heat capacity, all related to species *i*.

$$\Delta H_{r,T_{ref}} = \sum_{i} \nu_i \cdot H_{f,T_{ref}}$$
(Eq. C32)

$$\Delta c_P = \sum_i \nu_i \cdot c_{p,i} \tag{Eq. C33}$$

* Thermal conductivity

The thermal conductivity of the gas mixture was calculated according to the general equation of Wassiljewa [9], which is expressed as reported in Equation C34:

$$\lambda_{mix} = \sum_{i=1}^{N} \frac{y_i \cdot \lambda_i}{\sum_{j=1}^{N} A_{ij} \cdot y_j}$$
(Eq. C34)

where λ_i is the thermal conductivity of each species, calculated using Equation C35 from Perry's Chemical Engineers' Handbook [8], where the single coefficients are reported in Table C7:

$$\lambda_i = \frac{C_1 \cdot T^{C_2}}{1 + \frac{C_3}{T} + \frac{C_4}{T^2}}$$
(Eq. C35)

Species	<i>C</i> ₁	<i>C</i> ₂	с. С ₃	<i>C</i> ₄
- 	2 653-10-3	0 7452	12	0
N2	3.3143.10-4	0.7722	16.323	373.72
NH ₃	9.66·10 ⁻⁶	1.3799	0	0

Table C7. Specific coefficient of each species in the thermal conductivity equation.

while A_{ij} according to Mason and Saxena study [9] turns to be exactly the same as ϕ_{ij} .

Appendix D

Polyol reduction method

The polyol reduction method is a chemical process developed for the synthesis of nanoparticles, particularly metal nanoparticles. This method involves the reduction of metal salts precursors in the presence of a polyol, which serves as reducing agent, as solvent and as surfactant. This synthesis method begins with the preparation of a solution containing all metal precursor salts required for the desired material to be synthesized. These salts were dissolved in ethane-1,2-diol, while the concentration of ruthenium chloride is fixed at 4.7 g ml⁻¹.

For each material, the prepared solution was placed in a three-neck round-bottom flash. A K-type thermocouple was introduced through one side neck to measure the temperature of the system, while the second side neck served as the inlet of a nitrogen flow of approximately 10 ml min⁻¹, maintaining an inert atmosphere and removing volatile impurities. The middle neck was connected to a 400 mm Graham condenser, equipped with a gas bubbler, used to cool down and condense the vapors, recycling them as liquids back into the synthesis vessel.



Figure D1. Schematic representation of the polyol synthesis method steps.

The reaction vessel was heated to 110 °C using a Pilz[®] 80 W electric mantel (Winkler AG, Germany) connected to a HM-RX1003SO temperature control box (Mohr & co[®]. GmbH, Germany) equipped with a JUMO 702031/8-2000-23 PID controller (ISOHEAT[®] GmbH, Germany). The system was maintained at this temperature for 2 hours to obtain a homogeneous dark colloidal solution. As the temperature rises, the polyol undergoes decomposition, generating reactive species (such as acetaldehyde for ethane-1,2-diol) which act as reducing agents. These reducing agents facilitate the reduction of the metal precursor ions, leading to the nucleation and growth of the desired particles [10–12]. The obtained mixture was then allowed to cool down naturally.

Afterward, a potassium hydroxide solution was added to the mixture through a syringe pump using a flowrate of 2 ml min⁻¹. After this step, the resulting gel was aged for 10 minutes, washed five times with ultrapure water, and separated using a 5810R centrifuge (Eppendorf, Germany) to recover the particles and remove liquid residues from the solid phase.

Finally, the catalyst was dried at 120 °C for 12 hours and then calcined at 550 °C for 4 hours using a heating ramp of approximately 2 °C min⁻¹.

TEM micrograph of Ru-based catalysts described in Chapter 7.

TEM micrographs of the samples PR-2 and PR-4 were collected. However, the images do not show relevant distinguishable features.



Figure D2. TEM micrograph of the catalysts (left) Ru/CeO₂ and (right) Cs-Ru/CeO₂ synthesized via the polyol reduction method.

References

- Huang, P.; Xu, N.; Shi, J.; Lin, Y.S. Characterization of Asymmetric Ceramic Membranes by Modified Permporometry. J Memb Sci 1996, 116, 301–305, doi:10.1016/0376-7388(96)00097-X.
- Tsuru, T.; Hino, T.; Yoshioka, T.; Asaeda, M. Permporometry Characterization of Microporous Ceramic Membranes. J Memb Sci 2001, 186, 257–265, doi:10.1016/S0376-7388(00)00692-X.
- 3. Nakao, S. ichi Determination of Pore Size and Pore Size Distribution: 3. Filtration Membranes. J Memb Sci 1994, 96, 131–165, doi:10.1016/0376-7388(94)00128-6.
- Krantz, W.B.; Greenberg, A.R.; Kujundzic, E.; Yeo, A.; Hosseini, S.S. Evapoporometry: A Novel Technique for Determining the Pore-Size Distribution of Membranes. J Memb Sci 2013, 438, 153–166, doi:10.1016/j.memsci.2013.03.045.
- Rossetti, I.; Pernicone, N.; Ferrero, F.; Forni, L. Kinetic Study of Ammonia Synthesis on a Promoted Ru/C Catalyst. Ind Eng Chem Res 2006, 45, 4150–4155, doi:10.1021/ie051398g.
- Lopez-Echeverry, J.S.; Reif-Acherman, S.; Araujo-Lopez, E. Peng-Robinson Equation of State: 40 Years through Cubics. Fluid Phase Equilib 2017, 447, 39–71, doi:10.1016/j.fluid.2017.05.007.
- 7. Jaubert, J.N.; Mutelet, F. VLE Predictions with the Peng-Robinson Equation of State and Temperature Dependent Kij Calculated through a Group Contribution Method. Fluid Phase Equilib 2004, 224, 285–304, doi:10.1016/j.fluid.2004.06.059.
- 8. Green; Don W; Southard; Marylee Z Perry's Chemical Engineers' Handbook;
- 9. The_Properties_of_Gases_and_Liquids_4th.
- Fiévet, S.F.; Piquemal, J.-Y. A Review from the Pioneer Group in Polyol-Mediated Synthesis The Polyol Process: A Unique Method for Easy Access to Metal Nanoparticles with Tailored Sizes, Shapes and Compositions. Chem. Soc. Rev 2018, 47, 5187, doi:10.1039/c7cs00777a.
- 11. Zhang, J.; Xu, H.; Ge, Q.; Li, W. Highly Efficient Ru/MgO Catalysts for NH3 Decomposition: Synthesis, Characterization and Promoter Effect. Catal Commun 2006, 7, 148–152, doi:10.1016/J.CATCOM.2005.10.002.

12. Fievet, F.; Ammar-Merah, S.; Brayner, R.; Chau, F.; Giraud, M.; Mammeri, F.; Peron, J.; Piquemal, J.Y.; Sicard, L.; Viau, G. The Polyol Process: A Unique Method for Easy Access to Metal Nanoparticles with Tailored Sizes, Shapes and Compositions. Chem Soc Rev 2018, 47, 5187–5233, doi:10.1039/c7cs00777a.

Research Output

<u>Journal articles</u>

- 1. **G. Anello**, R. Fiorillo, G. De Felice, M. Khamphasith, C. Italiano, M. van Sint Annaland, F. Gallucci. *"Tailored Cs-Ru/CeO2 catalysts for low-temperature ammonia decomposition: characterization and catalytic performance"*, Submitted.
- 2. I. Gargiulo, **G. Anello**, S. Richard, F. Gallucci. "Modeling and simulation study of a packed bed membrane reactor for ammonia synthesis: assessing the role of membrane performance and operating conditions", Under review at International Journal of Hydrogen Energy.
- 3. J. Zuniga, **G. Anello**, J. J. Aragón, A. Arratibel, G. Marino. C. Italiano, A. Vita, F. Gallucci. *"Enhanced ammonia decomposition in a structured membrane reactor using a Ru-coated SiC open-cell foam and a Pd-based membrane"*, Under review at *International Journal of Hydrogen Energy.*
- 4. **G. Anello**, G. De Luna, G. De Felice, A. Saker, L. Di Felice, F. Gallucci. "Development of ruthenium-based catalysts for ammonia synthesis via polyol reduction method", International Journal of Hydrogen Energy 86, 922–930 (2024).
- 5. V. Cechetto, **G. Anello**, A. Rahimalimamaghani, F. Gallucci. *"Carbon molecular sieve membrane reactors for ammonia cracking"*, *Processes 12(6)*, 1168 (2024).

Journal articles out of the scope of this dissertation

- 1. G. De Felice, S. Li, **G. Anello**, C. Petit, F. Gallucci, E. Rebrov. "*Plasma assisted non-oxidative methane coupling over Ni-Fe mixed metal oxides*", *Catalysis Today 440*, 114832 (2024).
- 2. V. Vaiano, V. Palma, M. Matarangolo, **G. Anello**. "Comparison of Pt/C electrocatalyst deposition methods for PEM fuel cells", Chemical Engineering Transactions 70, 1525–1530 (2018).

<u>Conference contributions: Oral presentations</u>

- 1. **G. Anello**, R. Fiorillo, G. De Felice, F. Gallucci. "*Advancements in low-temperature ammonia decomposition on Cs-Ru/CeO₂ catalysts: a kinetic study*". 3rd Symposium on Ammonia Energy (SoEA2024), Shanghai, China (September 2024).
- G. Anello, L. Di Felice, F. Gallucci. "Low-temperature ammonia decomposition using a CsRuCeO₂ catalyst". 28th International symposium on chemical reaction engineering (ISCRE28), Turku/Åbo, Finland (June 2024).
- G. Anello, V. Cechetto, A. Rahimalimamaghani, F. Gallucci. "Development of carbon molecular sieve membranes for ammonia decomposition in membrane reactors". 16th International Conference on Catalysis in Membrane Reactors (ICCMR16), Donostia/San Sebastian, Basque Country (October 2023).
- G. Anello, A. Rahimalimamaghani, L. Di Felice, F. Gallucci. "Ammonia synthesis in catalytic membrane reactors: Influence of the support in Ru-based nanocatalysts prepared via polyol reduction method". 2nd Symposium on Ammonia Energy (SoEA2023), Orléans, France (July 2023).
- G. Anello, A. Rahimalimamaghani, L. Di Felice, F. Gallucci. "Polyol reduction synthesis method of Ru-based alkali-promoted nanocatalysts for ammonia production in membrane reactors". 18th Netherlands Process technology Symposium (NPS2023), Enschede, The Netherlands (July 2023).
- G. Anello, A. Rahimalimamaghani, L. Di Felice, F. Gallucci. "Novel Ammonia selective carbon molecular sieve membranes for ammonia synthesis in a catalytic membrane reactor". 15th International Conference on Catalysis in Membrane Reactors (ICCMR15), Tokyo, Japan (August 2022).

Conference contributions: Poster presentations

- 1. **G. Anello**, S. Sonar, M. Creatore, F. Gallucci. "*Decoration of carbon membranes by atomic layer deposited transition metals for NH*₃ *decomposition*". EIRES Energizing Day 2024, Eindhoven, The Netherlands (November 2024).
- G. Anello, V. Cechetto, A. Rahimalimamaghani, F. Gallucci. "Carbon membranes for ammonia decomposition in membrane reactors". 19th NMG-BGM-DGTM Symposium and Poster Day, Veldhoven, The Netherlands (October 2024).
- G. Anello, R. Fiorillo, G. De Felice, F. Gallucci. "Cs-enhanced Ru-based catalysts for low-temperature ammonia decomposition". 19th Netherlands Process technology Symposium (NPS2024), Groningen, The Netherlands (October 2024).
- 4. G. Anello, G. De Felice, C. Petit, S. Li, F. Gallucci, E. Rebrov. "Plasma assisted nonoxidative methane coupling over Ni-Fe mixed metal oxides". 6th International Symposium on Plasmas for Catalysis and Energy Materials (ISPCEM24), Eindhoven, The Netherlands (July 2024).
- G. Anello, A. Rahimalimamaghani, L. Di Felice, F. Gallucci. "Novel selective carbon molecular sieve membranes for ammonia separation". 18th NMG-BGM-DGTM Symposium and Poster Day, Gent, Belgium (October 2022).

<u>Other contributions</u>

- 1. V. Cechetto, **G. Anello**, A. Rahimalimamaghani, F. Gallucci. "*H*₂ production from *NH*₃ in carbon molecular sieve membrane reactors". 9th Symposium on Hydrogen Fuel Cells and Advanced Batteries (HYCELTEC24), Milazzo, Italy (July 2024).
- I. Gargiulo, G. Anello, A. Rahimalimamaghani, L. Di Felice, F. Gallucci. "Simulation and optimization of an ammonia synthesis catalytic membrane reactor". 16th International Conference on Catalysis in Membrane Reactors (ICCMR16), Donostia-San Sebastian, Basque Country (October 2023).
- V. Cechetto, A. Arratibel, S. Agnolin, G. Anello, L. Di Felice, F. Gallucci. "Technoeconomic assessment of a decentralized plant for hydrogen production from ammonia decomposition". 16th International Conference on Catalysis in Membrane Reactors (ICCMR16), San Sebastian, Basque Country (October 2023).
- I. Gargiulo, G. Anello, L. Di Felice, F. Gallucci. "A modeling study on the effect of membrane properties in a packed bed membrane reactor for ammonia synthesis". 2nd Symposium on Ammonia Energy (SoEA2023), Orléans, France (July 2023).
- V. Cechetto, L. Di Felice, A. Arratibel, S. Agnolin, G. Anello, F. Gallucci. "A comparison between Pd-Ag and carbon molecular sieve membranes for hydrogen separation during ammonia decomposition in a membrane reactor". 2nd Symposium on Ammonia Energy (SoEA2023), Orléans, France (July 2023).
- V. Palma, V. Vaiano, M. Matarangolo, G. Anello. "Comparison of Pt/C electrocatalyst deposition methods for PEM fuel cells". 23rd International Congress of Chemical and Process Engineering, (CHISA2018) & 21st Conference on Process Integration, Modelling and Optimization for energy Saving and Pollution Reduction (PRES2018), Prague, Czech Republic (August 2018).

Acknowledgements

Completing this dissertation marks the culmination of a challenging yet fulfilling endeavour, one that would not have been possible without the support, encouragement and friendship of many. I would like to take the opportunity to express my gratitude to those who have played an integral role in shaping both my academic and personal growth, easing my burden and making this journey truly memorable.

First and foremost, I would like to express my deepest gratitude to my promoters, *prof. dr. eng. F. Gallucci* and *prof. dr. ir. J. van der Schaaf*, for their guidance, constant encouragement, and unwavering support throughout my PhD. I extend my appreciation to my advisors from ENGIE Lab Crigen, including *dr. C. Makhloufi, dr. A. Ramirez Santos*, *dr. A. Saker, dr. M. Khamphasith, dr. P. Olivier*, for their invaluable expertise. Thank you all for providing me with the opportunity to pursue my PhD under your expert guidance and supervision.

I am also truly thankful to the Chairman of the Doctorate Committee, *prof. dr. ir. E. Rebrov*, and to all the Committee Members, *prof. dr. ir. D. Borello, prof. dr. G. Manzolini*, *prof. dr. M. Creatore, prof. dr. ir. M. van Sint Annaland* and *dr. M. Khamphasith*. Thank you for dedicating the time and efforts to thoroughly reading and evaluating my dissertation. Your insightful comments and constructive feedback have been invaluable in enhancing the quality of this work.

I would like to sincerely thank everyone who collaborated with me on the research projects that form the foundation of this dissertation. I am especially grateful to *Valentina, Iolanda, Giulia, Roberto, Luca,* and *Arash*. Your invaluable contributions have significantly enriched the quality of this work. Furthermore, I am deeply grateful to all those who supported me in developing my research skills during my time at TU/e. A special thank you to *Clara, Adarsh, Wout, Thijs* and *Anouk*. I greatly appreciate your support and the knowledge you have so generously shared with me along the way.

Dear *Fausto*, thank you for giving me the incredible opportunity to undertake my PhD, for your trust, and for guiding me through numerous projects, teaching duties, and conferences. Your belief in my potential, even when I doubted myself, helped me during this challenging experience. I will always be grateful for your support. Thank you, Prof.

Now is the moment to acknowledge all the people that are hiding behind this dissertation, our heroes, the SPE supporting staff members. Your support has been invaluable in making my PhD experience smoother, and I am profoundly grateful for it. Dear Saskia, thank you for all the kind and encouraging words you have always had for me during these years. I am especially grateful for your understanding when it comes to the administrative side of things. Even when I seem to miss something, you are always there to help me. Dear Carlo, as our safety officer, you hold an important and challenging position, and I deeply appreciate all the effort you put into ensuring we work under the safest possible conditions. Your dedication to safety and care for our well-being has not gone unnoticed. I also enjoyed our conversations about running and appreciate all your advice. Although I am not even close to being a runner yet (and maybe never will be), this year, I promise that I will try harder. Dear Marlies, thank you for all the help you have given me with the analyzers during both my master's and PhD projects, from the DBD setup to my own setup. I truly enjoyed the time we spent together, and I promise to follow your advice to take some days off and visit my parents more often. Dear Peter, I have lost count of the things I have learned from you and the amount of help you have given me on this journey. I do not even know where to begin thanking you. Whenever there is a problem, you are always there to help, and your support has been invaluable. I have also really enjoyed our conversation in the labs, at the coffee machine, and at the FORT. Dear *Erik*, thank you for your support over the years. Together, we built my first setup, and during that process, I cannot even remember how many concepts I learned from you. I truly appreciate the passion you have for explaining and teaching PhD students and others how to use tools and understand how things work. It was always a pleasure to talk with you about motorbikes, dreaming of an MV Augusta or a Ducati. Dear *Joris*, thank you for your continuous help with all the daily tasks, for the breaks, and for making me, after Wout of course, the assistant to the best technicians (or was it the best assistant to the technicians? I cannot remember anymore since Fausto removed the label from my chair). Thank you for all the good moments we shared together. Dear Roberto, when I think about everything you do around here, I honestly cannot imagine how the group managed to function before you joined us. Your dedication and hard work have been remarkable, and I am incredibly grateful for the support you have provided me. Thank you for the laughs and the wonderful moments we shared, they have truly brightened my days.

I would like to thank all my colleagues in the SPE group. To truly express my gratitude, I feel like I need to write another book. Reflecting on our time together, I recall countless memorable experiences and the wonderful moments we shared. Dear *Valentina*, you have been here from the very first day, and all I can say is thank you for always being there. Thank you for all the nice moments we shared, especially during the various conferences around the world. You and Luca (yes, I know one day you will read these words) have been such an important part of this journey. I am just waiting for the right age to tell him all the stories.

Dear *Thijs*, I first met you during my Erasmus days, as soon you were back from your time in Rome. I still remember your encouraging words about my master's thesis about plasma reactors. Thank you for all the amazing moments together. Thank you for introducing me to the real Dutch music culture. I will miss your playlist in the Matrix, but I will try to keep it going and properly annoy Joris.

Dear *Wout*, you started your PhD during my Erasmus, and at that time, we did not have much chance to connect. However, I feel so privileged to have gotten to know you later. I truly admire your proactive attitude and your constant willingness to help, especially when it comes to work in the lab.

Dear *Iolanda*, I still remember the first time I met you at our former university. I was a student representative, and you came to me with your friends to ask about some exam issues, but you were too shy to speak with me. I could have never guessed that, ten years later, we would be here. I feel so lucky to have met you and to have you in my life. You are a kind, funny person and a true friend. I will always cherish the conferences and trips we shared, and I hope we can create even more memories together in the future.

Dear *Clara*, I want to thank you for all the help you have given me since your Erasmus. You have always been there for me and for everyone around you, never expecting anything in return, just to make our research easier. I have so many memories of us in the lab, and I will never forget all the swearing we shared over the daily failures. Thank you for making my research brighter and funnier. Thank you for your friendship; it is amazing to have someone I can truly rely on.

I want to take a moment to express my deep gratitude to *Arash* and *Rouzbeh*. Through your unwavering dedication, I've learned what it truly means to commit oneself to a cause. I have witnessed both of you putting your soul, tears, and sweat into your work, and it has been inspiring to see how much effort and passion you bring to everything you do. Your resilience and drive have not only shaped the success of our projects but have also left a lasting impact on me personally. I will always carry with me the lessons learned from you both, and I am incredibly grateful for the opportunity to have worked with you. Last but not least, thank you for introducing me to the amazing Iranian food.

Dear Zancat, Daniël, and Huub: the Dutch resistance in the SIR group! Dear Zancat, since we were master's students together, I have always admired you as a person and as a scientist (especially after I discovered about the accordion). Dear Daniël, I genuinely appreciate your ability to go straight to the point and your honesty. Dear Hubertus, I truly value your positive attitude and politeness. I will always cherish the memories of the conference we attended together in Finland, completed with the best coffee breaks ever. Thank you all for proudly keeping the Dutch flag flying high and for sharing your culture with us, upholding traditions as carnival parties and enjoying drinks at the FORT, or just for a dinner together. You have made these moments truly special. Dear Dr. Li, it feels like a hundred years ago that, that day of September, I walked into your office to start my master's project. Thank you for your scientific insights and valuable advice on PhD life. But more importantly, thank you for helping us destroy Brandon's team during our football matches! Dear Adarsh, you are one of the most knowledgeable people I have ever met. I truly appreciate your wisdom and kindness. Thank you for the insightful discussions about science and all the other topics we have explored. Dear Giovanni, thank you for the constant updates about the Italian fantasy football, but I will never change my mind or go back to playing that evil game. Dear Shilpa, I would like to thank you for your bright sense of humour and your jokes. Do not worry, I will buy her the best ring ever one day, just not today. Dear Sher, thank you for your patience and kindness, despite all the time that I spent (uninvited) in your office. Dear *Wong*, I deeply admire your politeness and respectful manner. Your kindness and professionalism make working with you a true pleasure and an inspiration. Dear Pablo, although you were here for only a few months, I truly enjoyed our conversations, not only about science but also about our countries and our cultures.

I would like to thank the new generation of PhDs for the freshness you brought to the group. When the old guard (see next section) started leaving, I felt a bit sad. All the people I used to see every day were leaving, and changes can always feel a bit unsettling. But then you started joining the group, and every day became better. Dear *Negar*, *Pranav* and *Alessia*, I appreciated your kindness and open attitude towards everyone. I love our jokes, the funny moments we share, but also the interesting scientific discussions. Querida *Claudia*, the first thing I noticed in you was your calm and peaceful attitude, and at the same time, your strong and determined nature. Guys, your path will be bright and full of success.

I cannot forget to mention the old guard. Dear *Amin* and *Arnab*, it was amazing to be enrolled as PhD just to have you talking to me. Thank you for the amazing time together, every day was better after a funny coffee break together. Dear *Vince*, I will remember forever the carnival parties together (especially the first one) and the crazy88 game. I always enjoyed the time with you and our chats about motorbikes. Dear *Brandon*, I really admire your energy and consistency, commuting a lot every day, working hard and never missing a gym session. Thank you for the amazing moments together, especially the football matches. Dear *Serena* and *Camilla*, your support and help has been invaluable. You have been an example of efficiency and perseverance to me.

During these years, many people joined our group as guests, and I have wonderful memory with all of you. Dear *Rocco, Luana, Matteo, Leonardo P., Leonardo V.*, I always remember you with great pleasure. Every now and then, I look at the pictures from our trips, and I cannot help but smile as I think of the good times we shared together. Dear *Orlando*, I want to thank you for the nice moments together during your time here with us: the student, the supervisor, the professor. Dear *Yasin*, it has been a pleasure to have you here. You are a kind and gentle person, and it was amazing to play beach volleyball with a true champion like you. Dear *Benedetta*, it is always funny to spend a coffee break with you, and your contagious, hilarious laugh is something I will never forget.

I had the pleasure to supervise several students during my PhD journey. Dear *Param*, *Zinovia*, *Davide*, *Alberto*, *Giulia*, *Roberto*, a significant part of this work would not exist without the support of all of you. I also want to extend my thanks to the new generation of master's students *Pepijn*, *Balayogesh*, *Anita*, *Anthony* and *Tijs*, who joined our group as this work was nearing its conclusion, but every one of you is playing an important role, not only on our research projects, but also in my personal growth.

Dear *Param*, my very first student. I still vividly remember the day you walked into my office for our first meeting, before starting your Capita Selecta program. Together, we laid the basis for part of this dissertation, and if it has come this far, it is also thanks to you. As I write these words, you are packing your stuff to embark on your own endeavour. I wish you all the best. You are going to crush it! Always il primo.

Dear *Roberto* and *Alberto*, after you Erasmus, I had the pleasure to have you as colleagues and officemates. In our office, you brought an incredible mix of laughter and seriousness, for which I am grateful. Dear Roberto, it feels like just yesterday that you arrived in our lab, and yet it has already been a year. Little did I know that on that day, I gained a new friend. This year was incredibly challenging and full of responsibilities, but thanks to you, it felt much lighter. Dear Alberto, the day you came back to Eindhoven to bring me your master's thesis was such a pleasure. It was even better when I heard you were going to be our colleague and then my officemate. Now, you are in charge of all the office internal affairs with such ease that, without you, we simply would not survive. Thank you both for the amazing moments we spend together every day. I wish you all the best for your PhD journey, it is just the beginning of something great for you.

Dear Annamaria, Annapaola, Ciro, Cristina, Gianmaria, Raffaele, Serena. Since our Erasmus days, life may have scattered us across Europe, but you will always hold a special place in my heart. Although we do not meet often, staying connected after all this time means so much to me. I truly hope that one day we can reunite and create new memories as joyful and unforgettable as those we have already shared.

Dear *friends from the Fisciano Wind Orchestra*, for every milestone I achieve in my life, I will always thank you. Together, we spent the most beautiful years of our lives traveling and playing across Italy. Those moments remain some of the most cherished in my memory. I hope to see you more often in the future and to relive moments like those that will forever hold a special place in my heart. Thank you for being such an unforgettable part of my life.

To my family. *Mamma, Papà, Biagio,* and *Karen,* thank you for your endless love and unwavering support throughout my life. Your belief in me has always been a constant source of strength, guiding me through every step and decision. Thank you for your patience, for always waiting for me, and for celebrating every milestone, no matter how long it took or how delayed the celebration may have been. I will forever be grateful for all that you have done for me. I love you.

Finally, I dedicate this last paragraph and this entire dissertation, to my dear *Giulia*. As you hold this book, I hope you feel as proud as I did when I held yours. This day would never have come without you by my side. Your boundless patience, unwavering dedication, and limitless love you poured into this journey are beyond measure. The sacrifices you made, giving up weekends, holidays, and moments of celebration, so that I could pursue this dream, will forever be etched in my heart. Thank you for believing in me, even more than I believed in myself. Living with you and your joy, and witnessing your incredible attitude, taught me that happiness can be found even in the darkest of times, if one only remembers to turn on the light. You were my light, guiding me through every challenge, cheering me up after failure, and celebrating me after every success. From this day forward, my time and dedication are yours, for our dreams, and our adventures. I love you. And now, I am glad you are here with me. Not at the end of all things, but at the beginning of everything that truly matters.

Sincerely, Gaetano

Eindhoven, January 2025

About the author



Gaetano Anello was born on October 20th, 1991, in Maratea, Italy. He has cultivated a passion for music since 2005, performing as a musician in various wind orchestras and symphonic orchestras. Alongside his musical pursuits, Gaetano has also focused on his academic endeavors in Chemical Engineering at the University of Salerno, Italy. During his Bachelor's studies, he was elected twice as a student representative to the Teaching Council of the Chemical

Engineering Department. On September 29th, 2017, he earned his Bachelor's degree with a thesis titled "Study and optimization of Pt/C catalyst deposition method on polymeric membranes used in PEM fuel cells.", completed under the supervision of Prof. Dr. Vincenzo Vaiano and Prof. Dr. Vincenzo Palma.

Afterward, Gaetano pursued a Master's degree in Chemical Engineering at the same University. During these years, he continued playing as musician and served as music teacher at the municipal school in Fisciano, Italy. In 2018, he was appointed as artistic director and member of the Board for the municipal wind orchestra of the same city. Thanks to the Erasmus+ program, he completed his graduation project at Eindhoven University of Technology (TU/e), The Netherlands, under the guidance of Dr. Sirui Li and Prof. Dr. Fausto Gallucci. He graduated with full marks on April 26th, 2021, with a thesis titled "Non-thermal plasma technologies for non-oxidative coupling of methane."

Following his Master's degree, since July 15th 2021 Gaetano undertook his doctoral studies in the Sustainable Process Engineering group at TU/e, under the supervision of Prof. Dr. Fausto Gallucci. His PhD project focused on the development of catalysts, inorganic membranes, and membrane reactor technologies. During this period, Gaetano also contributed as a teaching assistant for the Separation Technology and Advanced Process Design courses. Since April 2024, Gaetano has been serving as a reviewer for international peer-reviewed journals in chemical engineering and related fields. With his work on ammonia decomposition and ammonia synthesis, he has contributed to several European projects, and the main results of his research are detailed in this dissertation.

Since November 2024, Gaetano has been working on his postdoctoral research projects at the Sustainable Process Engineering group in the Department of Chemical Engineering and Chemistry at TU/e.

ISBN: 978-90-386-6262-6