Research article

H₂ production via ammonia decomposition in a catalytic membrane reactor

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ABSTRACT

The membrane reactor is proposed in this work as a system with high potential to efficiently recover the hydrogen (H₂) stored in ammonia (NH₃), which has been recently proposed as an alternative for H₂ storage. With this technology, NH₃ decomposition and high-purity H₂ separation are simultaneously performed within the same unit, and high H₂ separation efficiency is achieved at lower temperature compared to conventional systems, leading to energetic and economic benefits. NH₃ decomposition was experimentally performed in a Pd-based membrane reactor over a Ru-based catalyst and the performance of the conventional packed bed reactor were used as benchmark for a comparison. The results demonstrate that the introduction of a membrane in a conventional reactor enhances its performance and allows to achieve conversion higher than the thermodynamic equilibrium conversion for sufficiently high temperatures. For temperatures from and above 425 °C, full NH₃ conversion was achieved and more than 86% of H₂ fed to the system as ammonia was recovered with a purity of 99.998%. The application of vacuum at the membrane permeate side leads to higher H₂ recovery and NH₃ conversions beyond thermodynamic restrictions. On the other hand, the reactor feed flow rate and operating pressure have not shown major impacts on NH₃ conversion.

1. Introduction

World power generation is nowadays largely dependent on the use of fossil fuels. However, with a continuously increasing world population, fossil fuels consumption has achieved an unprecedent scale [1] and their availability is significantly decreasing over time. The depletion of fossil fuels, combined with rising concerns about climate change, is motivating the substitution of conventional technologies and energy sources for power generation with innovative strategies to maintain the continuously increasing worldwide energy demand. Renewable energy is undoubtedly of fundamental importance for a transition towards a less carbon-intensive and more sustainable future [2]. Nevertheless, renewable sources are by nature intermittent and highly fluctuating, therefore renewable energy is not always capable to closely follow the power demand of the grid. Since chemicals offer high energy density and are easily stored, transported and distributed, one option for large scale energy storage could be storing energy in the form of chemical bonds.

Over the last decades, hydrogen (H₂) has gained considerable

attention as an ideal and clean energy carrier [3]. Its reaction with oxygen produces in fact only water as by-product and high efficiencies for energy conversion are achieved when hydrogen is employed as feedstock for power production in fuel cells (FCs). However, its low volumetric energy density (2.9 Wh/L, H₂ gas, 0 °C, 1 atm) and the difficulties associated with gas handling are the main drawbacks associated to hydrogen which have so far prevented H₂-based technologies to achieve popularity for commercial applications in the power production field. A solution to overcome these drawbacks consists in storing hydrogen in the chemical bonds of hydrogen carrier compounds. Liquid fuels generated from hydrogen, such as methanol [4], ammonia [5] and formic acid [6] could in fact be easily transported over long distances, stored for long time and later decomposed to produce hydrogen when required [2].

Among all the possible candidates, ammonia (NH₃) is a particularly promising hydrogen carrier due to its high volumetric energy density, relatively low cost and ease of liquefaction, storage and transportation [5,7–10]. Table 1 shows the boiling point, power density and volume

Table 1
Boiling point, power density and volume density of H_2 and NH_3 [9].

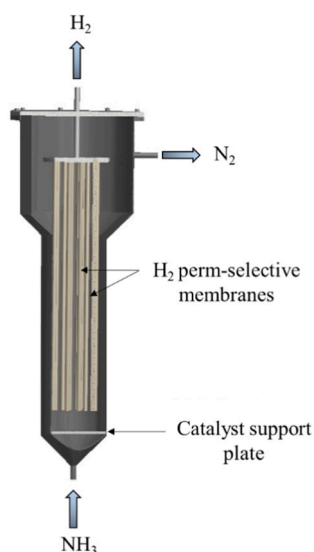| Fuel	Boiling point [°C, @ 1 bar]	Density [g/L]	Energy density [kWh/L]
H_2	−253	71	2.4
NH_3	−33	674	3.5

Fig. 1. Schematic representation of a packed bed membrane reactor for ammonia decomposition.

density of H_2 and NH_3. Since ammonia can be liquefied at higher temperature and lower pressure compared to hydrogen, its liquefaction is less energy intensive and, consequently, storage and transportation can be carried out in smaller and lighter vessels compared to hydrogen. Moreover, the absence of carbon in its molecular structure makes ammonia an attracting and promising route for the production of H_2 to be used in proton exchange membrane fuel cells (PEMFCs) [3,11–17]. In fact, while H_2 traditionally produced from the reforming of fossil fuels in large scale plants inevitably contains CO_x which are responsible for the poisoning of the cell electrodes (even when CO_x concentrations are at ppms level) [18], NH_3 is carbon-free.

In order to use ammonia as feedstock for PEMFCs, the hydrogen stored in its chemical bond has to be recovered through ammonia decomposition into H_2 and N_2. Subsequently, H_2 produced has to be separated from N_2 and purified from possible traces of unconverted ammonia in order to meet the specifications required for a correct functioning of the fuel cell [7,8].

Ammonia decomposition (Eq. 1) usually takes place over a ruthenium-based (Ru-based) catalyst [2,11], which has been identified as the most active metal catalyst for ammonia decomposition [17,19,20].

$$NH_3 \rightleftarrows \frac{1}{2}N_2 + \frac{3}{2}H_2 \quad \Delta H_f^o = 45.92 \; \frac{kJ}{mol} \tag{1}$$
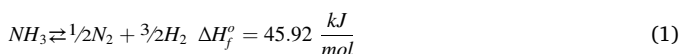
According to the Le Chatelier's principle, the reaction is favoured at low pressures and as it is mildly endothermic it is favoured by high temperature. A conventional system for H_2 recovery from NH_3 would therefore require a reaction unit operating at high temperatures for complete ammonia conversion, followed by a separation system to separate the pure H_2 from N_2 and unconverted NH_3. In order to reduce the footprint of this technology, the membrane reactor technology (see Fig. 1) has been recently considered as a system with a high potential to efficiently recover the H_2 stored in liquid/solid NH_3 [2,21–29]. In this reactor, in fact, the chemical reaction and the selective separation of a product of the reaction occur simultaneously. Moreover, in chemical

reactions limited by the thermodynamic equilibrium, the selective separation of one of the products (H_2 in the specific case of ammonia decomposition) through the membrane wall shifts the thermodynamic equilibrium according to the Le Chatelier's principle allowing the system to go beyond this thermodynamic constraint. The use of a membrane reactor for ammonia decomposition therefore brings several advantages over conventional systems: 1) the high-purity H_2 recovered through the membranes can be fed directly to FCs avoiding the need to introduce any costly separation/purification unit; 2) the thermodynamic equilibrium limitation is circumvented and it is possible to obtain full fuel conversion reducing the downstream cleaning of unconverted species; 3) high H_2 separation efficiencies can be achieved at lower operating temperatures compared to conventional systems, with benefits from an energetic point of view; 4) since the whole process occurs in a single unit, the footprint of this technology is reduced.

The use of a membrane reactor for ammonia decomposition has recently been presented in the literature and for selective H_2 separation Pd-based membranes are typically used, as they show a unique transport mechanism for H_2 permeation [30–34]. Among other, Collins et al. [22] and Itoh et al. [21] demonstrate that with a Pd-based membrane reactor it is possible to achieve significantly higher conversion than with a conventional reactor, while at the same time recovering part of the H_2 produced. The increase in NH_3 conversion can be explained as a consequence of a shifts of the thermodynamic equilibrium due the selective separation H_2 from the reaction products, or, alternatively, according to the Temin-Pyzhev type rate mechanism, it can be also attributed a kinetic enhancement effect due to the removal through the membrane walls of the H_2 produced, which otherwise would have an inhibitory effect on the forward kinetics of the NH_3 decomposition reaction [35]. Some of the above mentioned advantages of membrane reactors over conventional systems have also been experimentally demonstrated at lab scale in the works of Zhang et al. [2] and Jo et al. [29]. However, in these works the reactors used are very small and tantalum tubes are used as membrane support, which show a selective diffusion for H_2 separation, but are extremely expensive for this application. In this work, a membrane reactor up to 40 times larger than those presented in the literature has been constructed and ammonia cracking has been demonstrated under different operating conditions. Objective of this paper is to present the results of an experimental investigation on the catalytic decomposition of ammonia in a composite palladium membrane reactor and compare its performance with those achievable in a conventional packed bed reactor operating under identical conditions. For the experimental investigation, a commercial Ru-based catalyst was selected, and the membranes used are patented double-skin Pd-based membranes, which have shown outstanding performances for H_2 separation as well as good stabilities.

2. Material and methods

2.1. Membrane preparation

The membrane preparation method consists of two steps: 1) coating of the porous supports, 2) application of a protective layer. A detailed description of the method adopted for the preparation of the selective layer of the Pd-based membranes used in this work can be found in the work of Melendez et al. [36]. In this step, a Pd—Ag layer is deposited onto porous tubular alumina (α-Al_2O_3) supports (14/10 mm outer/inner diameter) with a top layer pore size of 100 nm. The deposition of this selective layer is done via electroless plating, a technique which consists of a first activation of the support with Pd seeds and a subsequent immersion of the support in a bath containing a Pd—Ag solution. As the thickness of the selective layer proportionally increases with the plating time, different plating times are set in order to obtain different permeation properties and for the membranes used in this work the thickness of the selective layer has been measured to be 4.61 μm by Scanning Electron Microscope (SEM) analysis. In order to improve the membrane

Table 2
Overview of the experimental conditions investigated in this work.

Experimental conditions	
Permeation temperature [°C]	400, 425, 450
Pressure feed [bar]	2–6
Pressure permeate [bar]	0.01–1
Feed flow rate [L_N/min]	0.5–1.0
Single gas investigated	N_2, H_2
Reaction investigated	$2NH_3 \leftrightharpoons N_2 + 3H_2$

stability, a protective layer is then added onto the selective layer. This protective layer (a porous Al_2O_3-YSZ (yttria-stabilized zirconia) layer of 50 wt% of YSZ with thickness of ~1 μm), which is a patented technology of which more detailed information can be found in the work of Arratibel et al. [31,37], avoids any possible interaction between the selective layer and the catalyst in which the membrane will be immersed during application.

2.2. Experimental methods

In this study, ammonia decomposition has been performed in a tubular membrane reactor over a packed Ru-based catalyst bed, which according to several literature studies is the most active single metal catalyst in presence of high NH_3 concentration [19]. A product available in pelleted form from Alfa Aesar, specifically a 2 wt% Ru-based catalyst supported on alumina pellets of 3 mm, was selected as catalyst. The core of the experimental setup used in this work is the reactor, which is made of SS310, has an inner diameter of 4.5 cm and an active length of 28 cm. A porous stainless steel plate has been welded at its bottom in order to enhance the gas distribution at the reactor inlet, whereas at the free-board of the catalytic bed the reactor has a conical shape which allows to reduce the gas velocity and therefore minimize the risk of catalyst particle escaping from the reactor. The Pd-based membrane was assembled in this reactor where it was fully immersed in a packed bed of 250 g of catalyst. The reactor assembly was placed inside an electrical split-oven with three heating sections (one at the top, one at the middle and one at the bottom of the reactor) each one of which, depending on the temperature measurement provided by a corresponding thermocouple and temperature controller, is able to adjust its power in order to ensure an even distribution of the desired temperature along the reactor. A detailed process flow diagram of the experimental setup is provided as supplementary material to this work (Supplementary material A: set-up).

Pure NH_3 was fed to the reactor where decomposes into N_2 and H_2 and the latter selectively permeates through the Pd-based membrane. The feed flow rate was controlled by mass flow controllers (Bronkhorst) and a back-pressure controller was adopted for system pressure regulation. The retentate, consisting mostly of N_2 and non-recovered H_2, was first sent through a gas filter which aims at protecting the downstream equipment from fine particles, then to a μ-GC (Varian CP- 4900) to measure the retentate composition. The permeate side of the membrane was sent either to a film-flow meter (Horiba Stec VP4) to determine the permeation flux through the membrane or to a Fourier-transform infrared spectrometer (FTIR) form Shimadzu mounting a 10 m gas cell from Specac and an MCT (Mercury-Cadmium-Telluride) detector where the purity of the H_2 stream permeated through the membrane is measured (the MCT detector is able to detect the NH_3 content in the stream down to 0.03 ppm). All the lines connecting the permeate to the analytical section are made of SilcoNert and PEFT in order to prevent any possible NH_3 absorption phenomenon in the gas line which would influence the FTIR reading. The retentate and permeate lines were subsequently mixed and sent to a water absorption unit where possible traces of unconverted NH_3 are absorbed.

In this work, ammonia decomposition has been performed in the temperature range between 400 °C and 450 °C, and experiments have

been carried out at different reaction pressures (2–6 bar) and feed flow rates (0.5–1.0 L_N/min). The permeate side of the membrane was also connected with a vacuum pump (MP301Z-X2 from Acclon technologies) to maximize the difference in partial pressure at both sides of the membrane, and therefore evaluate the influence of the permeate pressure on the performance of the technology. An overview of the experiments carried out in this work is presented in Table 2. As benchmark for the membrane reactor performance, experimental results achieved with the reactor operated without the membrane (conventional packed bed reactor) under similar conditions were used.

Before starting an experiment, the reactor was heated up to the reaction temperature at a heating rate of 2 °C/min in N_2 atmosphere. Once reached the desired operating temperature, pure NH_3 was fed into the reactor and the operating pressure was adjusted. The reaction, and specifically NH_3 conversion, was then monitored for 3 h until steady state operation was observed. NH_3 conversion and H_2 recovery were measured according to Eq. (2) and Eq. (3), where $NH_{3,in}$ and $NH_{3,out}$ are the volumetric flow rates of NH_3 in the reactor feed and in the retentate, respectively. The H_2 recovery refers to the total amount of pure H_2 separated through the membrane compared to the total amount of H_2 fed into the reactor in the form of ammonia.

$$\text{Ammonia conversion} : X_{NH_3} = \frac{NH_{3,in} - NH_{3,out}}{NH_{3,in}} \tag{2}$$

$$\text{H2 recovery factor} : HRF = \frac{H_{2,permeated}}{3/2 \, NH_{3,in}} \tag{3}$$

During the experimental study, two membranes have been tested: one with dead-end configuration and a total active length of 202 mm and one open on both sides and with an active length of 190 mm. After a first reaction stability test carried out with a dead-ended membrane, the effect of a variation of operating conditions (such as pressure, feed flow rate and temperature) on the process performance has been investigated introducing in the membrane reactor a membrane with double sealing. In fact, as in the dead-end configuration the number of sealing points is lower compared to the membranes requiring the sealing at both ends, the use of dead-end supports results in more selective membranes.

2.3. Catalyst characterization

The catalyst characterization has been carried out for both the fresh and used catalyst. Specifically, its crystal structure was analysed by X-ray diffraction (XRD), its surface morphology was observed by scanning electron microscopy (SEM, PhenomProX), the surface area was determined by the Brunauer-Emmett-Teller (BET) method (TriStar II, Micrometrics) and the bulk chemical composition of each present element was analysed with an energy dispersive X-ray detector (EDX) coupled to the SEM. The results of this characterization are reported as supplementary material to this work (Appendix A Supplementary data).

3. Results and discussion

3.1. Single gas permeation studies

Single gas permeation measurements of N_2 and H_2 were carried out in order to determine the ideal perm-selectivity of the Pd-based membranes for the separation of H_2 from N_2. The experiments were carried out at different pressures and temperatures, and with the permeate side of the membrane at atmospheric pressure. Particularly, the gas permeation was measured for temperatures ranging from 390 °C to 490 °C. For a given temperature, the permeance of N_2 and H_2 were then calculated. The N_2 permeance at 450 °C was measured $3 \cdot 10^{-12}$ mol/s/m^2/Pa and $3.7 \cdot 10^{-11}$ mol/s/m^2/Pa for the dead-end membrane and for the membrane with double sealing, respectively. These very low values of N_2 permeance result in extremely high ideal H_2/N_2 perm-selectivities, which were calculated above 500,000 and above 400,000 for the
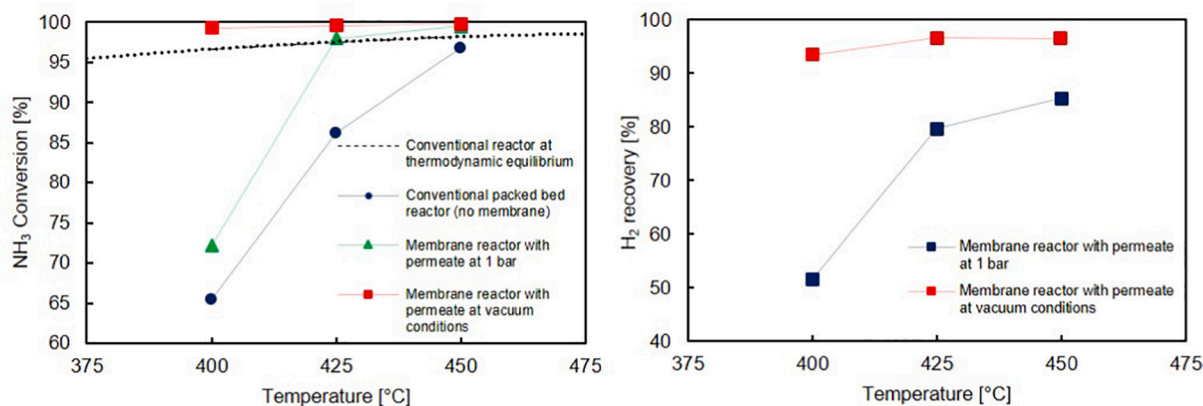
Fig. 2. NH$_3$ conversion (left) and H$_2$ recovery (right) achieved with different reactor configurations at 400–425–450 °C, 4 bar(a) and under a feed flow rate of 0.5 L$_N$/min of pure NH$_3$. All the experimental tests have been carried out with a Pd-based membrane with dead-end configuration.

dead-end membrane and for the double sealed membrane, respectively. These values are among the highest reported in literature [38,39]. The difference observed between these results can be attributed to the sealing process as the H$_2$ permeance in both the configurations is very similar ($> 1.5 \cdot 10^{-6}$ mol/s/m^2/Pa at a maximum temperature of 450 °C).

3.2. Ammonia decomposition

In order to show the benefits of introducing in a packed bed reactor a membrane for hydrogen separation, experiments have been carried out also with the system operated without the membrane and the results achieved have been used as reference. For all these experiments, the reaction has been carried out at 4 bar(a) with a feed flow rate of 0.5 L$_N$/min of pure NH$_3$. Fig. 2 presents the NH$_3$ conversion and H$_2$ recovery as a function of the operating temperature for different reactor configurations. Particularly, the performance of ammonia decomposition are presented for the packed bed membrane reactor with the permeate at atmospheric conditions, for the packed bed membrane reactor with the permeate at vacuum, for a traditional packed bed reactor (with no membrane) and for the reactor operated with no membrane at the thermodynamic equilibrium conditions. It is possible to observe that when the reaction is carried out in a conventional packed bed reactor, the conversion achieved is limited, especially at low temperatures, and cannot reach the thermodynamic equilibrium conversion. On the other hand, when the membrane reactor is adopted the conversion is clearly increased and for temperatures from and above 425 °C NH$_3$ conversions higher than the equilibrium without the membrane are achieved. In agreement with other literature studies, such as [21,22,28,35], these results demonstrate that a membrane reactor exhibits a relatively higher

NH$_3$ conversion then a conventional reactor. However, compared with literature, we demonstrate the use of a much thinner membrane in a membrane reactor with higher conversion and higher recovery. From Fig. 2 it is also possible to observe that the use of vacuum at the permeate side of the membrane enhances the performance of the membrane reactor technology. At 400 °C, where the conversion in the membrane reactor with the permeate at atmospheric pressure is limited, the introduction of vacuum conditions rapidly brings the system to almost full conversion of ammonia. This is related to the fact that when vacuum in the permeate is applied, the driving force for hydrogen separation increases leading to higher hydrogen recoveries, and consequently to faster kinetics and even conversions well beyond the thermodynamic restrictions of the conventional benchmark without the membrane.

In order to show the stability of the membrane reactor, ammonia decomposition has been performed at different temperatures for a continuous operation of 3 h during which the reaction performance have been monitored. Particularly, these experiments have been carried out at 400 °C, 425 °C and 450 °C, at 5 bar(a) feed pressure and keeping the permeate at atmospheric pressure. As it can be observed from Fig. 3, NH$_3$ conversion and H$_2$ recovery have resulted to be overall stable over time. A reaction performance drop has only been detected at the beginning of the test carried out at 400 °C, when the occurring endothermic reaction resulted in a sharp decrease in the reaction temperature with a consequent decrease in the reaction performance. Once the packed bed was brought back to the desired operating condition (set-point temperature of 400 °C) by increasing the power of the electrical oven, NH$_3$ conversion and H$_2$ recovery were restored to their original value.

From these results, it can be observed that temperature has a big
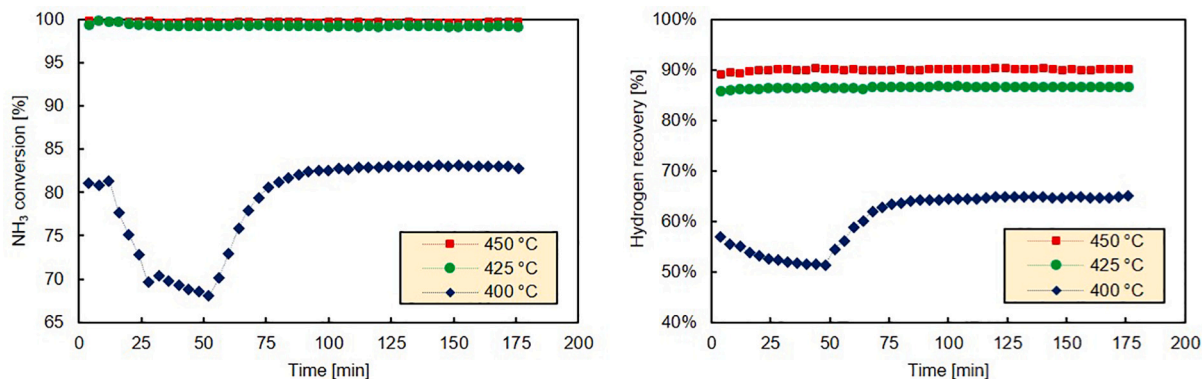

Fig. 3. Results of the stability test for the Pd-based membrane with dead-end configuration. Ammonia conversion (left) and H$_2$ recovery (right) as a function of time at different temperatures for a feed pressure of 5 bar(a) and a permeate pressure of 1 bar.
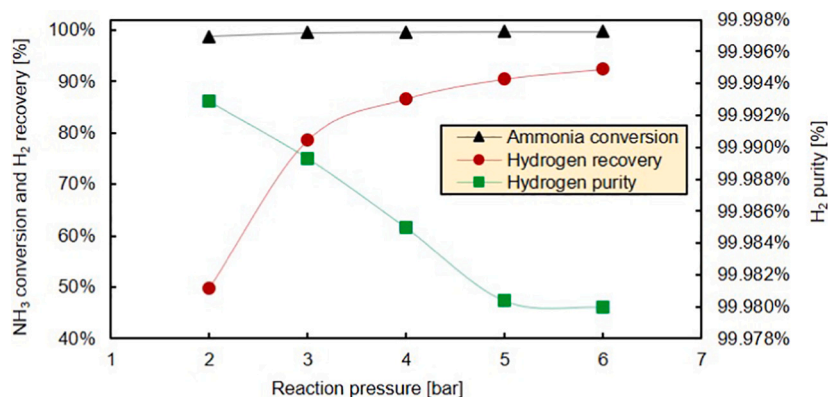
Fig. 4. Influence of the reaction pressure on ammonia conversion, hydrogen recovery and hydrogen purity at 450 °C for a feed flow rate of 0.5 L_N/min of pure NH_3. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

Table 3

NH_3 conversion, H_2 recovery and purity of the permeate at various reaction pressures.

Feed pressure [bar]	NH_3 Conversion (%)	H_2 recovery (%)	H_2 purity (%)
2	98.8%	49.8%	99.993%
3	99.5%	78.6%	99.989%
4	99.6%	86.6%	99.985%
5	99.7%	90.5%	99.980%
6	99.7%	92.4%	99.980%

Temperature 450 °C, feed flow rate 0.5 L_N/min.

impact on the reaction performance. At the lowest temperature investigated (400 °C) the system is limited by kinetics. Relatively low ammonia conversion is therefore achieved and, as a consequence, the H_2 partial pressure inside the reactor is lower. Since the permeate was kept at atmospheric pressure, the driving force for H_2 separation was relatively low and consequently H_2 recovery was only 65%. On the other hand, it can be observed that a slight increase in the operating temperature has a big impact on the reaction performance. A temperature increase is in fact responsible for an improvement in the reaction kinetics, resulting in higher ammonia conversions which in turn lead to higher H_2 partial pressures in the reactor. As a consequence of a higher driving force for H_2 separation, a higher H_2 flux can be separated through the membrane and as a result higher H_2 recovery is achieved. For temperatures from and above 425 °C, virtual full ammonia conversion is achieved and more than 86% of the H_2 fed to the system in the form of ammonia has been recovered from the membrane reactor. During all these experiments, H_2 purity has been determined and a

minimum value of 99.998% has been obtained.

The influence of the reaction operating pressure and of the ammonia feed flow rate on NH_3 conversion, H_2 recovery and H_2 purity were investigated and the results are presented in Fig. 4 (and Table 3) and Fig. 5 (and Table 4), respectively. The experiments have been carried out at 450 °C, which is the highest value in the investigated range of temperatures (400 °C - 450 °C) and can therefore lead to faster membrane deterioration.

From Fig. 4, it is possible to notice that the operating pressure in the retentate does not have a major impact on NH_3 conversion at 450 °C, as in the entire pressure range it is above 98.8%. On the other hand, a trend is observed for H_2 recovery (major effect) and H_2 purity (minor effect). As the driving force for hydrogen separation is higher for increasing operating pressures, H_2 recovery increases with pressure and this increase in more remarked for pressures lower than 4 bar. H_2 recovery values above 90% are achieved for operating pressures higher than 5

Table 4

NH_3 conversion, H_2 recovery and purity of the permeate at various ammonia feed flow rate.

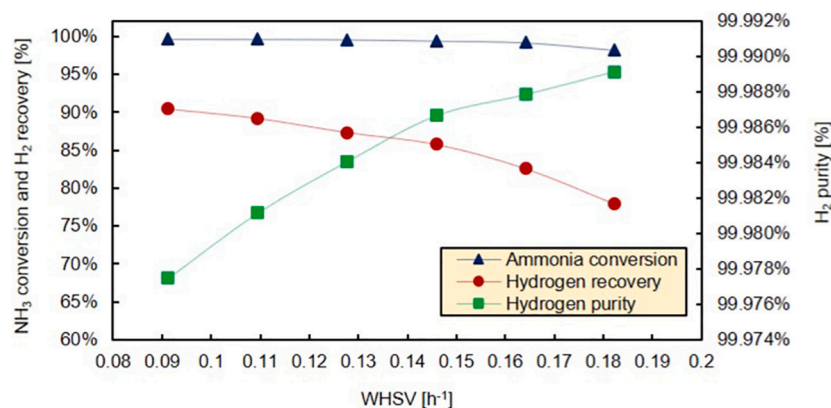| Feed flow rate [L_N/min]	NH_3 Conversion (%)	H_2 recovery (%)	H_2 purity (%)
0.5	99.7%	90.5%	99.978%
0.6	99.7%	89.2%	99.981%
0.7	99.6%	87.4%	99.984%
0.8	99.4%	85.8%	99.987%
0.9	99.2%	82.6%	99.988%
1	98.2%	77.9%	99.989%

Temperature 450 °C, reaction pressure 5 bar.

Fig. 5. Influence of the inlet feed flowrate on ammonia conversion, hydrogen recovery and hydrogen purity at 450 °C and 5 bar(a). The experimental results have been obtained with a Pd-based membrane with double sealing configuration.
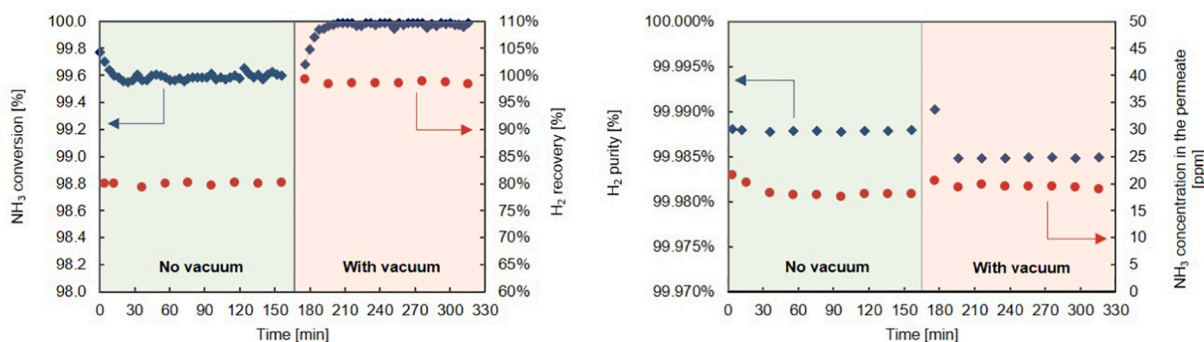
Fig. 6. Influence of the permeate pressure for experiments carried out at 450 °C, 3 bar(a) and a feed flow rate of 0.5 L_N/min of pure NH_3. Left: ammonia conversion and hydrogen recovery; right: hydrogen purity and ammonia concentration (ppm) in the hydrogen recovered. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

bar. Conversely, H_2 purity in the permeate decreases with increasing pressure. This can be related to the fact that as the operating pressure increases, higher N_2 partial pressure is achieved in the reactor and, since the permeation of N_2 linearly increases with the driving force for separation (while for H_2 it increases with the square root of the pressure difference), a pressure increase influences more the nitrogen flux compared to the hydrogen flux. Overall, an increase in the operating pressure leads to a decrease in the purity of hydrogen separated through the membrane although larger amounts of hydrogen are recovered.

Fig. 5 illustrates the influence of the feed flow rate of ammonia on the reaction performance for the reactor operated at 450 °C and 5 bar. Specifically, NH_3 conversion, H_2 recovery and H_2 purity are represented as a function of the weight hourly space velocity (WHSV) which is defined as the weight of the feed flowing per unit weight of the catalyst per hour. The choice to carry out this experiment at an operating pressure of 5 bar is meant to evaluate if an increase in the feed flow rate of ammonia can compensate for the decrease in the H_2 purity detected when the reaction is carried out at relatively high pressure (as observed in Fig. 4). Fig. 5 shows that a slight decrease in NH_3 conversion is detected when the ammonia feed flow rate is increased. Moreover, as the residence time decreases with increasing feed flow rate, a lower amount of H_2 passes through the membrane, resulting in lower H_2 recovery and higher H_2 purity. As expected, the hydrogen purity achieved with the double-sealed membrane was slightly lower compared to the one obtained with the dead-end configuration membrane. However, as for an ammonia feed flow rate of 1 L_N/min the hydrogen purity was 99.9892% in case of double sealed membrane and 99.9975% in case of dead-end configuration, the performance of both the two membranes are still very high and can be considered comparable.

Since both high H_2 recovery and H_2 purity are the targets of a system for ultra-pure hydrogen production, it happens to be clear that a trade-off pressure able to simultaneously ensure high conversion, high H_2 purity and good H_2 recovery is therefore needed. A potential solution to overcome this issue is given by the possibility to maximize the pressure difference across the membrane by applying vacuum conditions at its permeate side. Yet, this technique makes the system more complex, but allows to achieve higher H_2 recovery while keeping the reactor at the low pressure levels at which the highest conversions and H_2 purities are achieved.

As the amount of hydrogen recovered from the membrane increases with the pressure difference between the feed and the permeate, vacuum conditions have therefore been experimentally applied to the permeate side of the membrane. The influence of vacuum conditions in the permeate on NH_3 conversion, H_2 recovery and H_2 purity was investigated in a 5 h and 30 min experiment where the reaction was carried out for 165 min (half the experiment) with the permeate at atmospheric conditions and for the remaining time with the permeate at vacuum. The reaction was carried out at 450 °C, 3 bar and the ammonia feed flow rate was 0.5 L_N/min. The results of this experiment, which are presented in Fig. 6, show that for both the investigated conditions all the process performance parameters are constant over time, resulting in a good process stability. A clear transition is visible between the two conditions investigated. When vacuum is connected from inside the membrane, an increase in the NH_3 conversion and H_2 recovery is in fact detected. While the increase in NH_3 conversion can be considered minor (with no vacuum applied NH_3 conversion is already close to 100%), the increase in the H_2 recovery is very remarkable. When vacuum is applied, H_2 recovery passes in fact from 80.2% to 98.7%. However, a higher driving force across the membrane combined with a retentate composition consisting of basically only N_2 results in an increase in the nitrogen concentration in the permeate side. Consequently, the application of vacuum on the permeate side of the membrane leads not only to an
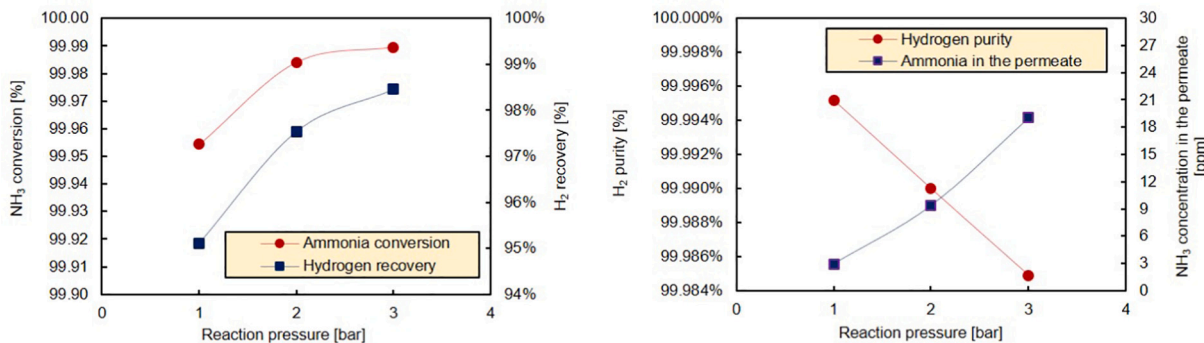

Fig. 7. Influence of the reaction pressure on ammonia conversion, hydrogen recovery, hydrogen purity and NH_3 impurities for the reaction carried out at 450 °C, under a feed flowrate of 0.5 L_N/min of pure NH_3 and with vacuum conditions applied at the permeate side of the membrane. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

Fig. 8. Influence of the feed flowrate on ammonia conversion, hydrogen recovery, hydrogen purity and NH$_3$ impurities for the reaction carried out at 450 °C, 1 bar(a) feed pressure and with vacuum conditions applied at the permeate side of the membrane. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.
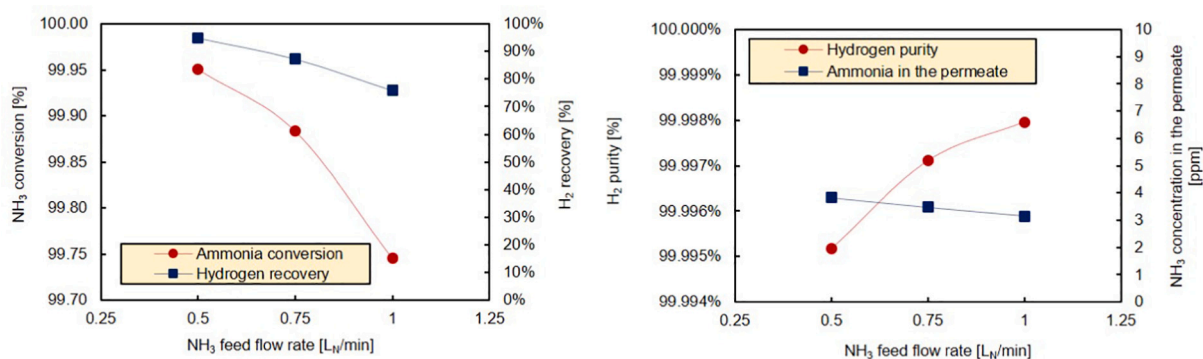
Table 5
Comparison between the experimental results achieved in this work and the results of other studies available in literature [2,21,22].

	This work			Itoh et al. [21]	Collins et al. [22]		Zhang et al. [2]	
Membrane								
• Configuration	Supported tubular Pd-based membranes with a porous Al$_2$O$_3$-YSZ protective layer			Pd-membrane tube	Supported composite Pd-ceramic membrane		Supported tubular Pd-based membranes	
• Selective layer composition	Pd-Ag			Pd	Pd		Pd	
• Selective layer thickness	4.61 μm			200 μm	11.4 μm		6 μm	
• Length	202 mm			65 mm	< 55 mm		–	
Catalyst Type	Ru-based			Ru/SiO$_2$	Ni/Al$_2$O$_3$		CsRu-based	
Temperature [°C]	400	425	450	450	550	600	400	450
Pressure (retentate side of the membrane) [bar]	4			1	16.18		5	
NH$_3$ feed flow rate [mL$_N$/min]	500			10	435		220	
NH$_3$ Conversion								
• Conventional Reactor (no membrane)	65.4%	86.2%	96.8%	73%	17%	–	–	–
• Thermodynamic Equilibrium (no membrane)	96.7%	97.6%	98.2%	–	33%	58%	–	–
• Membrane Reactor with permeate at atmospheric conditions	72.2%	98.0%	99.5%	–	79%	> 94%	98.0%	95.7%
• Membrane Reactor with permeate at vacuum conditions	99.3%	99.6%	99.8%	87%	–	–	–	–
Hydrogen Recovery - Membrane Reactor with permeate at atmospheric conditions	51.6%	79.8%	85.4%	–	–	–	87.5%	78.6%
Hydrogen Recovery - Membrane Reactor with permeate at vacuum conditions	93.5%	96.7%	96.5%	60%	–	–	–	–

increase in the H$_2$ recovery, but also to lower H$_2$ purity in the permeate. A minor increase (1 ppm in average) in the NH$_3$ concentration in the permeate is also detected when vacuum is applied.

The influence on the process performance of a variation in the reaction pressure and feed flow rate was studied also for the scenario in which the permeate is kept at vacuum conditions, and the results are presented in Fig. 7 and Fig. 8.

The experimental results confirm the trend observed in the case of the permeate at ambient conditions. Specifically, as it is possible to see from Fig. 7, an increase in the reaction pressure results in higher H$_2$ recoveries, although at the expenses of a decrease in the purity of H$_2$ recovered. This is related to the fact that the partial pressure of NH$_3$ and N$_2$ are increased in the reactor, and consequently the permeation of these species increases leading to lower H$_2$ purities. The effect of a variation in the ammonia feed flow rate was studied keeping the reaction pressure at atmospheric conditions while applying the vacuum in the permeate side, thus ensuring partial pressure difference for hydrogen separation. From Fig. 8 it is possible to notice that in the entire range of feed flow rate investigated high NH$_3$ conversion and permeate purity are achieved, although H$_2$ recovery significantly decreases when the ammonia feed flow rate is doubled. Specifically, H$_2$ recovery drops from 94.8% to 75.8% when ammonia feed flow rate is increased from 0.5 L$_N$/min to 1 L$_N$/min, but at these specific conditions the H$_2$ recovered has the highest purity (99.998%). Looking at the trend of H$_2$ purity, a decrease in the concentration of NH$_3$ in the permeate could be

expected. However, the experimental results show that the concentration of NH$_3$ in the permeate remains almost constant to a value of about 3 ppm in the entire range of feed flow rate investigated. This might be explained by the positioning of the membrane inside the reactor. The bottom part of the membrane is located just 5 cm above the gas distributor, thus the amount of ammonia expected in this part is the highest along the membrane. As in this position the membrane has a sealing point and given that very tiny defects come from each sealing point, it is possible that the ammonia concentration measured in the permeate is slightly higher than expected when the feed flow rate of ammonia is increased. The ammonia concentration can therefore be reduced by adopting a dead-end membrane configuration or by placing the membrane at a higher position inside the reactor.

A comparison between the experimental results achieved in this work and others available in literature is presented in Table 5. The table lists the main parameters that affect the whole process performance such as pressure (of both retentate and permeate), temperature, membrane active layer thickness and composition, catalyst formulation – where available. The experimental results obtained in this work show that at 450 °C ammonia conversion increases from 96.8% to 99.5% when a membrane is introduced in the reactor, and up to 99.8% when vacuum conditions are applied to the permeate side of the membrane. The benefits of a membrane reactor are even more pronounced as the temperature is reduced [2,22] with an ammonia conversion rising from 65.4% to 99.3% at 400 °C.
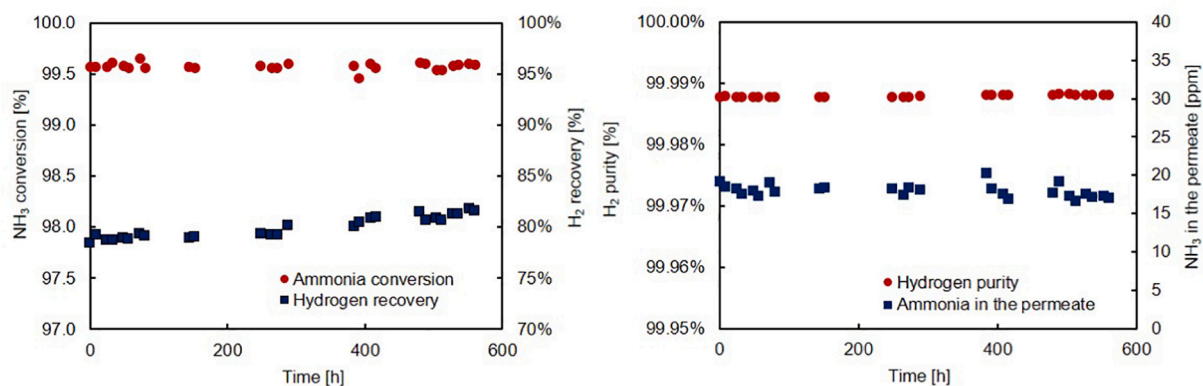
Fig. 9. Stability test of the membrane reactor during ammonia decomposition reaction carried out at 450 °C, 3 bar(a) feed pressure, 0.5 L_N/min ammonia feed flow rate and with the permeate side of the membrane at atmospheric conditions. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

From a comparison with the results obtained by Itoh et al. [21], we obtained an ammonia conversion and H_2 recovery increase of approximatively 15% and 61%, respectively, for the same temperature of operation. The ammonia conversion obtained in this work in the temperature range of 425–450 °C is also significantly higher than those obtained by Collins et al. [22] at 550–600 °C, and comparable or slightly above the values from Zhang et al. [2] at similar T and P conditions.

In order to prove the performance stability of the membranes adopted in this study, the membrane with double sealing has been exposed to reaction for more than 450 h. Specifically, the stability test has been carried out by exposing the membrane to reaction at 3 bar, 450 °C and with the permeate at atmospheric conditions for almost 600 h (discontinuously as over the weekends the system was kept at 450 °C in N_2 atmosphere). From the experimental results presented in Fig. 9 it is possible to conclude that the process performance is stable over time. No decrease in the hydrogen purity is observed, nor in the amount of hydrogen recovered.

4. Conclusions

In this work, the catalytic decomposition of ammonia to recover pure H_2 has been experimentally investigated in a tubular membrane reactor over a Ru-based catalyst and for the selective H_2 separation double-skin Pd-based membranes with either dead-end or double sealing configuration were used. In this reactor, ammonia decomposition into H_2 and N_2 and the selective separation of H_2 occur simultaneously as the pure H_2 produced from ammonia decomposition is extracted in-situ through selective H_2 membranes. The influence of a variation in the operating temperature, operating pressure, feed flow rate and permeate pressure on the reactor performance was studied and as benchmark for the membrane reactor performance experimental results achieved with the conventional reactor without the membrane under similar conditions were used.

The results of this study demonstrate that the introduction of a membrane in a conventional packed bed reactor enhances the performance of the reactor and allows to achieve NH_3 conversion higher than the thermodynamic equilibrium conversion for sufficiently high temperatures. For temperatures from and above 425 °C, virtual full ammonia conversion is in fact achieved and more than 86% of the H_2 fed to the system in the form of ammonia is recovered from the membrane reactor with a minimum purity of 99.998%. When vacuum is applied at the permeate side of the membrane, the driving force for H_2 separation increases leading to higher H_2 recovery, and consequently faster kinetics and conversion well beyond the thermodynamic restrictions. At 400 °C, where the conversion in the membrane reactor with the permeate at atmospheric pressure is limited, the introduction of vacuum conditions

brings the system to almost full NH_3 conversion. The operating pressure and the NH_3 feed flow rate do not have a major impact on NH_3 conversion, whereas trends are visible in regard to H_2 recovery and purity. H_2 purity decreases from 99.993% to 99.980% when the pressure is increased from 2 to 6 bar and H_2 recovery above 90% is achieved for operating pressures higher than 5 bar. As the feed flow rate increases, a lower amount of H_2 passes through the membrane, resulting in lower H_2 recovery and higher H_2 purity. For an NH_3 feed flow rate of 1 L_N/min the H_2 purity was 99.989% for a double sealed membrane and 99.998% in case of dead-end configuration.

The membrane reactor therefore shows several advantages compared to other technologies for ammonia conversion into pure H_2. Among them, the possibility to fully convert the ammonia feedstock into ultra-pure hydrogen within a single device avoiding the introduction in the system of any downstream separation unit for H_2 purification, the consequent break down of the capital cost for the system and the possibility to achieve high H_2 separation efficiencies at lower operating temperatures, with potential benefits from an energetic point of view.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2021.106772.

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