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Advanced materials and Reactors for Energy storage tHrough Ammonia



H₂ production through Ammonia decomposition in a membrane reactor

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- Ammonia decomposition in conventional systems
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- Lab-scale testing: experimental results
- Outlook on strategies to increase the purity of H₂ produced via NH₃ decomposition
- Conclusions





Introduction



Over the last decades, **hydrogen** has gained attention as an ideal and clean energy carrier.

 \checkmark H₂ is as neutral carbon fuel

 High efficiencies for energy conversion are achieved when it is employed as feedstock for power production

However, its low volumetric energy density and the difficulties associated with gas handling are the main drawbacks associated to H_2 which have so far prevented H_2 - based technologies to achieve popularity for commercial applications in the power production field.



SOLUTION

Hydrogen storage in the chemical bonds of hydrogen carrier compounds.

Liquid fuels generated from hydrogen could in fact be easily transported over long distances, stored for long time and later decomposed to produce H_2 when required.



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Ammonia as a potential H_2 carrier





High volumetric

energy density



Relatively low cost



Easy to liquefy

Easy to store and

transport



Carbon free







H_2 production via NH_3 decomposition



Ammonia decomposition $2 NH_3 \leftrightarrow N_2 + 3 H_2$ $\Delta H_f^o = 45.9 \frac{kJ}{mol}$

- The reaction proceeds with molar expansion \rightarrow Low pressure
 - The reaction is endothermic \rightarrow High temperature





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Ammonia decomposition $2 NH_3 \leftrightarrow N_2 + 3 H_2$

 $\Delta H_f^o = 45.9 \frac{kJ}{mol}$

A conventional system for H_2 recovery from NH_3 would require:



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Process intensification



Process intensification is defined as a set of innovative principles applied in process and equipment design, which can bring benefits in terms of:



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H_2 production via NH_3 decomposition in a catalytic membrane reactor





MEMBRANE REACTOR

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H_2 production via NH_3 decomposition in a catalytic membrane reactor



MEMBRANE REACTOR



 High-purity H₂ is recovered through Pdbased membranes
higher NH₃ conversion can be achieved at lower temperature, hence the system is more efficient while inherently separates a pure H₂ stream

 ✓ since the whole process occurs in a single unit, the footprint of this technology is reduced



Experimental: materials and methods



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Lab-scale experimental set-up for NH₃ decomposition at TUE



<u>Membranes</u>

Double-skin Pd-Ag membranes



 $\frac{\text{Catalyst}}{\succ \text{Ru}/\text{Al}_2\text{O}_3}$





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H_2 production via NH_3 decomposition in a catalytic membrane reactor





- In a conventional packed bed reactor, the conversion achieved is limited, especially by kinetics at low temperatures, and cannot reach the thermodynamic equilibrium conversion.
 - When the membrane reactor is adopted (and permeate is kept at 1 bar), at T > 425 °C NH₃ conversion is higher than the equilibrium without the membrane
 - The use of vacuum at the permeate side of the membrane considerably enhances the NH₃ conversion







H_2 production via NH_3 decomposition in a catalytic membrane reactor



Effect of pressure



Experimental conditions				
Permeate pressure [bar]	I			
Feed flow rate [L _N /min]	0.5			
Temperature [°C]	450			

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 ammonia. The experimental results have been obtained with a Pd-based membrane with double sealing configuration

By increasing pressure in the retentate:

- \succ H₂ recovery increases. Values above 90% are achieved for operating pressures higher than 5 bar.
- \succ H₂ purity in the permeate decreases.







Effect of NH₃ flow rate



Experimental conditions				
ΔP [bar]	4			
Permeate pressure [bar]	I			
Temperature [°C]	450			

Influence of the inlet feed flowrate on ammonia conversion, hydrogen recovery and hydrogen purity at 450 °C and 5 bar(a). The experimental result have been obtained with a Pd-based membrane with double sealing configuration.

By increasing the NH₃ feed flow rate:

- > NH_3 conversion slightly decreases.
- > A lower amount of H_2 passes through the membrane, resulting in lower H_2 recovery and higher H_2 purity.

0%

T





Influence of the permeate pressure for experiments carried out at 450 °C, 3 bar(a) and 0.5 L_N /min of ammonia. Left: ammonia conversion and hydrogen recovery factor (HRF); right: hydrogen purity and ppm of ammonia in the hydrogen recovered. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

By applying vacuum conditions to the permeate side of the membrane:

- The pressure difference across the membrane is maximized
- \rightarrow NH₃ conversion and H₂ recovery increase
- \succ H₂ purity in the permeate decreases
- The process performance parameters are constant over time, resulting in a good process stability.





H₂ production via NH₃ decomposition in a catalytic membrane reactor



Stability test

In order to prove its performance stability, the membrane has been exposed to reaction at 3 bar, 450 °C and with the permeate at atmospheric conditions for almost 600 hours (discontinuously).



Stability test of the membrane reactor using the double sealing membrane for reaction carried out at 450 °C, 3 bar(a), 0.5 L_N /min of ammonia and the permeate at atmospheric conditions. The experimental results have been obtained with a Pd-based membrane with double sealing configuration.

> The process performance resulted to be stable over time.

No decrease in the hydrogen purity, neither in the amount of hydrogen recovered were observed.



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Strategy I: Employment of membranes with thicker selective layer

Membrane code	Thickness selective layer [µm]	H ₂ /N ₂ perm-selectivity (T=450°C and ΔP=1 bar)	H₂ recovery [%]	NH ₃ concentration in the permeate [ppm]
Arenha-2	~ 1	5210	93.2	47 (±2.1)
Arenha-3	~ 6 - 8	68960	84.8	< 0.75

Temperature 500° C, reaction pressure 4 bar(a), ammonia feed flow rate 0.5 L_N/min

- A thicker membrane selective layer results in a lower hydrogen recovery as well as in a lower NH₃ concentration in the permeate
- While with Arenha-3 the NH₃ concentration in the permeate was measured to be below the FTIR detection limit (0.75 ppm), with Arenha-2 the same result can be achieved with the introduction of an NH₃ removal unit downstream the membrane reactor







Strategy 2: Introduction of a H_2 purification unit downstream the membrane reactor

When introducing a H_2 purification unit downstream the membrane reactor:

Thinner membranes can be used with a consequent decrease of investment costs:



- \succ As hydrogen purity depends in this case on the performance of the adsorbent bed and not entirely on the reactor operating conditions, it is possible to operate the reactor at lower temperatures compared to the case in which no hydrogen purification stage is adopted and to accept higher NH_3 concentration at the reactor outlet (permeate side). This brings benefits from an energetic point of view, albeit at the expenses of a slight decrease in the hydrogen recovery.





Strategy 2: Introduction of a H_2 purification unit downstream the membrane reactor



- When the produced H₂ with traces of ammonia is forced to pass through a zeolite 13X bed, it is possible to sharply reduce the ammonia content of the stream.
- In the first part of the experiment (no sorbent) the NH₃ concentration in the permeate is detected to be in the range between 70 and 80 ppm,
- When the H₂ purification unit is connected to the hydrogen permeation stream, the NH₃ concentration decreases to levels below the detection limit of the FTIR

Experimental conditions

Membrane	Arenha-2
Thickness selective layer [µm]	I
Permeate pressure [bar]	I
Temperature [°C]	450
Retentate pressure [bar]	3
$\rm NH_3$ feed flow rate [L _N /min]	0.5
Sorbent	Zeolite I3X



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Hydrogen purification from ammonia









Conclusions



- The membrane reactor is a technology with high potential to efficiently recover H_2 from NH_3 , as NH_3 decomposition into H_2 and N_2 and high-purity H_2 separation are simultaneously performed with several advantages over conventional systems for H_2 production via ammonia decomposition
- To be able to use NH_3 -derived hydrogen for fuel cell applications, the residual ammonia concentration in the H_2 stream must not exceed 0.1 ppm
- Two possible strategies consist in the employment of thicker membranes and in the introduction of a H_2 purification unit downstream the membrane reactor
- Further work will be address in the optimization of the membrane reactor performance and operating conditions, specifically in terms of catalyst loading.







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Thank you for your attention



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