

# Hydrogen production from ammonia through an innovative Pd-Ag membrane reactor

Erasmus S. Napolitano, Adele Brunetti\*, Giuseppe Barbieri

*Institute on Membrane Technology (ITM-CNR), National Research Council, Via Pietro Bucci, cubo 17C, 87036 Rende CS, Italy*

*\*Corresponding author: adele.brunetti@cnr.it*

## **Highlights**

- Advanced membrane reactors for hydrogen production from NH<sub>3</sub>.
- NH<sub>3</sub> dehydrogenation in a Pd membrane reactor with Ru-based catalyst.
- Enhanced efficiency in the presence of hydrogen in the feed

## **1. Introduction**

Ammonia is a promising carrier for hydrogen owing to its high volumetric energy density, low cost, and ease of liquefaction, storage, and transportation. Its effective use as H<sub>2</sub> carrier is strictly related to the effectiveness of the dehydrogenation technology. Membrane reactors (MRs) are considered a suitable technology for this application as they allow to be obtained in a single unit a very highly concentrated H<sub>2</sub> stream with significant improvements in terms of reaction conversion. In this work, we proposed a strategy to further improve the performance of an MR for ammonia decomposition by considering the effect of a traditional reactor (TR) before the MR, to favor the better exploitation of the whole membrane area available for permeation, ensuring a partial pressure of H<sub>2</sub> on the reaction side always higher than that on permeate side [1]. The MR performances was compared with the respective TR operated in the same conditions, showing improvements in performances adopting the mixture feed.

## **2. Methods**

The separation properties of a Pd-Ag (85%-15%<sub>wt</sub>) (supplier TecNALIA, Spain) were analyzed for single gas (H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, CO<sub>2</sub>) and related mixtures at a feed pressure range of 2-4 bar.

Commercial (7 g) Ru-based catalyst (ThermoFisher) was packed in the annulus of the membrane module where the inner tube was the membrane. NH<sub>3</sub> conversion, H<sub>2</sub> recovery and purity were assessed at 400°C as a function of feed pressure (3-4 bar) feeding only NH<sub>3</sub> or a mixture of NH<sub>3</sub>:H<sub>2</sub>:N<sub>2</sub>= 0.34:0.54:0.12, simulating the outlet stream of a TR placed before the MR, having a conversion of 50%.

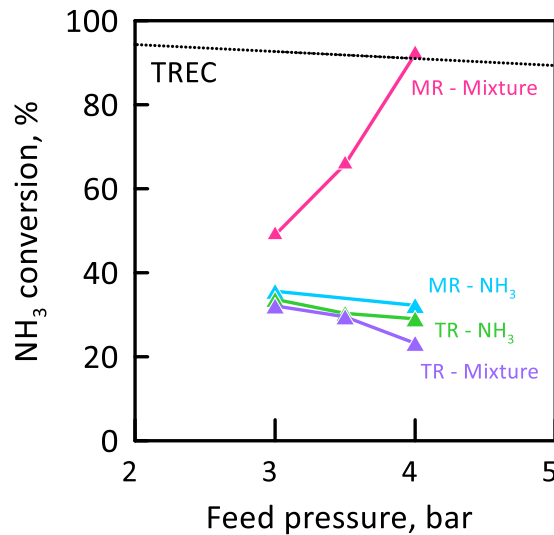
## **3. Results and discussion**

Before reaction experiments, the Pd-based membranes separation properties were measured obtaining a hydrogen permeance of 3276 nmol s<sup>-1</sup> m<sup>-2</sup> Pa<sup>-0.7</sup> and an H<sub>2</sub>/N<sub>2</sub> selectivity of 2350.

Figure 1 shows NH<sub>3</sub> conversion of MR and TR as a function of feed pressure for the different feed analysed. When only NH<sub>3</sub> was fed to MR (Figure 1), the conversion tended to decrease with pressure increase and the results obtained were close to that obtained with TR (29% for TR vs 32% for MR at 4 bar). This can be ascribed to the absence of H<sub>2</sub> in the first part of the reactor, which induced a bad use of the membrane area available for permeation and reflected in H<sub>2</sub> back permeation.

A TR placed before the MR would imply the presence of an already converted stream at the entrance of the MR. As a consequence, the presence of H<sub>2</sub> at the inlet of the MR, simulated by feeding the aforementioned mixture, reflected in a significant improvement of the MR performance (Figure 1) with NH<sub>3</sub> conversion increasing with the feed pressure and slightly exceeding the TREC at 4 bar. Furthermore, as the pressure increased the advantage over TR also increased, with a 1.5 to 3.5 times greater MR conversion at 3 and 4 bar, respectively.

The advantage of feeding MR with mixture was remarkable also in comparison with the results obtained feeding MR with NH<sub>3</sub> only, since the H<sub>2</sub> present in the feed marginalizes the back permeation effect, leading to an increase in conversion with pressure. The conversion improvement corresponded to a higher H<sub>2</sub> recovery (97% at 4 bar) and a H<sub>2</sub> purity up to 98%.



**Figure 1.** NH<sub>3</sub> conversion in MR and TR as a function of the feed pressure at 400°C, Feds: ammonia only and NH<sub>3</sub>:H<sub>2</sub>:N<sub>2</sub>= 0.34:0.54:0.12.

#### 4. Conclusions

In this work we proposed an innovative configuration for enhancing the performance of the Pd-based MR for catalytic ammonia dehydrogenation. The presence of a TR prior to the MR guaranteed a better exploitation of the whole membrane area, owing to an adequate hydrogen partial pressure to avoid back permeation effects in the first part of the reactor. The conversion of the MR fed with the mixture simulating the outlet of TR exceeded the equilibrium value of TR and was greater than that achieved feeding only NH<sub>3</sub>. Both H<sub>2</sub> recovery and purity improved, being always higher than 80% and 98%, respectively.

#### References

- [1] G. Barbieri, A. Brunetti, G. Tricoli, E. Drioli, An innovative configuration of a Pd-based membrane reactor for the production of pure hydrogen. Experimental analysis of water gas shift, J. Power Sources. 182 (2008) 160–167. <https://doi.org/10.1016/j.jpowsour.2008.03.086>.

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#### Keywords

Hydrogen production, Pd-based membrane reactor, membrane