

Enabling ammonia utilization as a hydrogen carrier: Performance assessment of catalytic membrane reactors for NH_3 decomposition

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1. Introduction

Climate change mitigation efforts have triggered the search for renewable energy sources and alternative fuels. Towards this direction hydrogen has received increased attention as a sustainable energy carrier that, if produced from renewable sources, can lead to highly efficient and clean power generation. However, hydrogen does not occur naturally and has a low volumetric energy density; thus there are significant difficulties in storing and transporting hydrogen, hindering its application for on-site power generation. In order to move to a hydrogen based economy, safe and sustainable processes for hydrogen storage and transportation need to be established. Various methods have already been proposed, e.g. liquid hydrogen, compressed hydrogen, metal hydrides, inorganic and organic chemical hydrides, etc. Among them ammonia has been identified as a potential candidate, since it poses exceptionally high hydrogen storage capacity (17.6 wt%, 120 g/L) and is easy to be stored and transported as a liquid under ambient temperature and moderate pressure (~ 8 bar). Moreover, ammonia can be easily produced in large quantities with well-established processes, using conventional or renewable hydrogen. However, the crucial step towards utilization of ammonia as an H_2 carrier is the development of an efficient system for ammonia decomposition and hydrogen purification (from the mixture of H_2 , N_2 and NH_3), on-site of application [1,2].

Several catalysts have been investigated as potential candidates for the ammonia decomposition reaction. Iron, platinum, palladium, rhodium, and ruthenium were the first elements considered because of their known catalytic activity in the ammonia synthesis reaction. Ganley et al. [3] studied several metals for their performance in ammonia decomposition and reported their activity in a decreasing order to be $\text{Ru} > \text{Ni} > \text{Rh} > \text{Co} > \text{Ir} > \text{Fe} > \text{Pt} > \text{Cr} > \text{Pd} > \text{Cu} > \text{Te, Se, Pb}$. Although Ru shows the best activity among these metals, its activity at lower temperatures is not adequate. In attempts to address this shortcoming, the effect of catalyst formulation, catalyst synthesis, supports and promoters on Ru have been investigated. Moreover, large scale use of Ru may not be sustainable due to its high cost and scarcity. Consequently, derivatives of other transition metals, like Ni, Fe and Co on a variety of supports have also been explored extensively for ammonia decomposition. Taking into account cost, activity and stability issues, Ni seems to be the most attractive alternative if large scale application has to be considered [4,5].

When ultra pure H_2 is needed, such as in the case of PEM fuel cells, very high NH_3 conversion must be achieved, followed by a highly efficient purification step. In these cases the application of membrane reactors seems to be a very promising option since hydrogen removal through H_2 -selective membranes shifts the equilibrium, leading to increased NH_3 conversion and H_2 purification simultaneously, in one step. The integration of more than one processes in the same unit is fully in line with process intensification strategies; the main industrial trend in process research and development. Among different membrane materials proposed for this application, Pd-based membranes seem to have the highest potential, since they are 100% H_2 selective, allowing for the production of ultra pure H_2 readily available for application [6,7].

Several researchers have investigated NH_3 decomposition in membrane reactors for dilute NH_3 feeds such as coal gasification streams and purge streams from NH_3 plants [8-11]. Although these cases are similar from a fundamentals perspective, the operating conditions, reaction

kinetics and generally the process formulation are significantly different. The main target of this study is to develop a flexible and reliable model in order to quickly assess the performance of a potential membrane reactor working with different operating conditions, catalysts and membrane materials.

2. Model development

A conceptual sketch of a membrane reactor is depicted in Fig. 1. In order to assess the performance of a catalytic membrane reactor and to compare its behavior with a conventional reactor, a mathematical model was developed. The model is based on the differential equations describing the operation of a conventional PFR, taking into account the gas permeation rate through the membrane. Details on the model formulation and the solution algorithm can be found in [12].

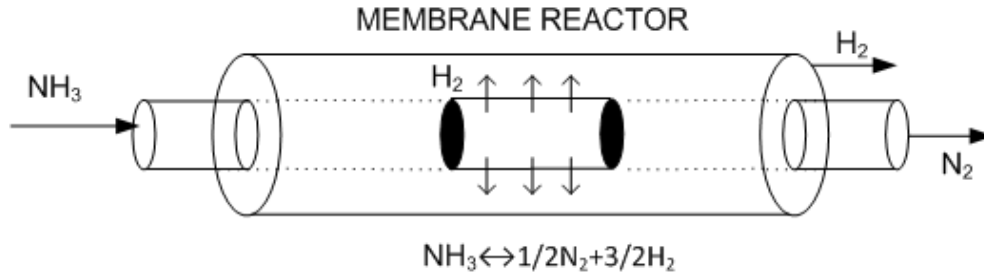


Figure 1: Conceptual sketch of a membrane reactor for NH_3 decomposition

Reaction kinetics

The generally accepted Temkin-Pyzhev equation (1) was used to express the rate of NH_3 decomposition:

$$r_{\text{NH}_3} = k \left[\frac{P_{\text{N}_2}}{K_{\text{eq}}^2} \left(\frac{P_{\text{H}_2}^3}{P_{\text{NH}_3}^2} \right)^{1-a} - \left(\frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3} \right)^a \right] \quad (1)$$

where,

$$k = k_0 e^{-E/RT} \quad (2)$$

$$\log \left(\frac{1}{K_{\text{eq}}} \right) = 2250.3T^{-1} + 4.1523 - 1.5105 \log(T) - 2.5898 \cdot 10^{-4}T + 1.4896 \cdot 10^{-7}T^2 \quad (3)$$

The first term in brackets of Eq. (1) is the rate of ammonia synthesis while the second term is the rate of ammonia decomposition. The kinetic parameters (k_0 , E and α) used in this study were derived by Collins et al. [13] for $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts.

3. Results and Discussion

Figure 2 shows thermodynamic calculations for equilibrium conversion of NH_3 at different pressures and temperatures. The calculations show that equilibrium limitations are essentially insignificant at temperatures above 500 °C. Therefore, the performance of a reactor may be restricted due to kinetic rather than thermodynamic limitations. The NH_3 decomposition rate, Eq. (1), is strongly dependent on hydrogen and ammonia partial pressures and to a less extent on nitrogen partial pressure. This means that the application of a H_2 -selective membrane reactor could also help to also overcome the kinetic limitation by reducing the H_2 partial pressure in the feed side.

This is evident in Fig. 3 which shows NH_3 conversion across the reactor at 15 bar, 500 °C and 100 h^{-1} GHSV for a conventional PFR and two CMRs. CMR-1 and CMR-2 represent membrane reactors with Pd-based membranes having an H_2 permeance of 10^{-9} and $10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, respectively. The performance of the PFR in the employed process conditions is well below the equilibrium conversion, although the GHSV is relatively low. CMR-1 slightly improves

performance compared to the conventional reactor, because of the low H_2 permeance of the membrane, which allow recovering only 23% of the produced H_2 potential. However, by employing a membrane with higher H_2 permeance, results to almost complete NH_3 decomposition (conversion beyond the thermodynamic limit) as well as to 97.3% H_2 recovery. Moreover, the application of a membrane reactor can change the manner in which pressure affects the extent of reaction. Specifically, a gas phase reaction which preferentially occurs at low pressure in a conventional tubular PFR, such as NH_3 decomposition, can also attain maximum conversion at high pressures in a CMR. This is expected to increase process efficiency and consequently reduce the system's capital and operational costs.

4. Conclusions

In this study a mathematical model was developed in order to assess the performance of a membrane reactor compared to a conventional PFR for NH_3 decomposition, in the way towards enabling ammonia utilization as a hydrogen carrier. The results of the study showed the high application potential of a Pd-based membrane reactor in order to attain 100% NH_3 decomposition, and more than 97% recovery of pure H_2 . However, it is often pointed out that the high cost of Pd-based membranes could hinder the large scale application of this technology. Therefore, the performance of other membrane materials (e.g. microporous ceramic membranes) has also to be examined as a potential alternative.

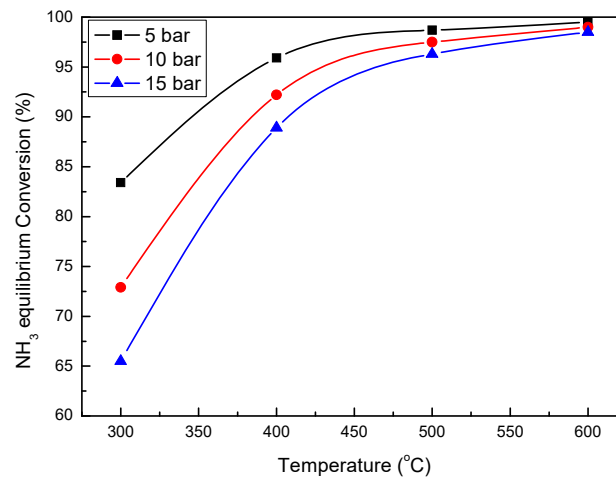


Figure 2: Equilibrium conversion of NH_3 at different pressures and temperatures.

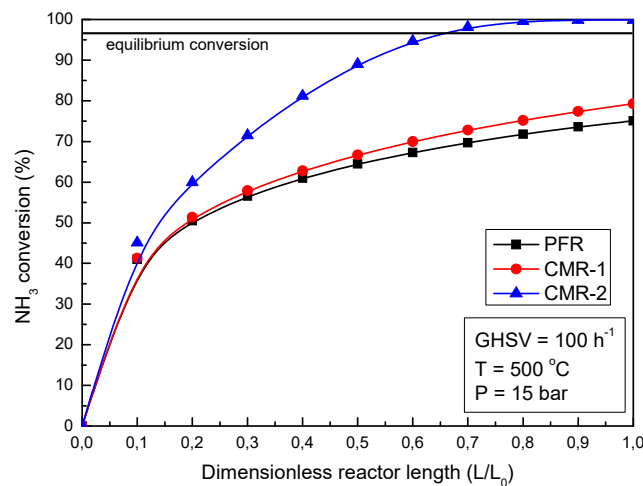


Figure 3: NH_3 conversion with reactor's axial position for a conventional PFR and two CMRs.

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