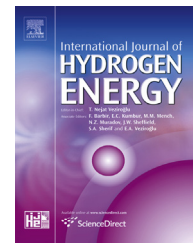


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Characterization of an ammonia decomposition process by means of a multifunctional catalytic membrane reactor

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ABSTRACT

Ammonia decomposition was studied in a multifunctional catalytic membrane reactor filled with Ruthenium catalyst and equipped with palladium-coated membranes. To characterize the system we measured NH_3 conversion, H_2 yield and its partial pressure, the internal and external temperatures of the reactor shell and the electric consumption under several NH_3 flow and pressure conditions. Experimental results showed that the combined effect of Ruthenium catalyst and palladium membranes allowed the reaction to reach the equilibrium in all the conditions we tested. At 450 °C the ammonia conversion resulted the most stationary, while at 7 bar the hydrogen yield was almost independent of both the ammonia flow and temperature. In addition, the experimental system used in this work showed high values of NH_3 conversion and H_2 permeation also without heating the ammonia tank and therefore renouncing to control the feeding gas pressure. When ultra-pure hydrogen is needed at a distal site, a reactor like this can be considered for in situ hydrogen production.

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Introduction

In the last two decades many studies have focused on the hydrogen production and utilization, but the realization of a sustainable hydrogen economy still remains a challenging issue. The increase of H_2 storage safety and a new approach aimed at supplying fuel cell systems directly on-site, require remarkable improvements in hydrogen production, either by thermal cracking or by chemical decomposition [1]. To overcome the limits imposed by the chemical equilibrium, membrane reactors have been proposed to shift this equilibrium and different membrane materials have been tested at this

aim [2]. Hydrogen removal through specific membranes, in fact, shifts the reaction towards the products, leading to an increase in H_2 production by dissociation [3–6]. Among the materials tested for membranes, palladium has been shown to highly improve the hydrogen transport into and out of refractory metals [7,8]. In addition, H_2 selective palladium membranes allow obtaining ultra-pure hydrogen immediately available for the usage. Therefore, membrane reactors became of particular interest in those cases where ultra-pure hydrogen is essential, as when feeding PEM fuel cells [9–12].

Because of the high hydrogen volumetric density, ammonia has been recently considered a promising hydrogen

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carrier [13] and its decomposition extensively studied [14–20]. Ammonia has a worldwide distribution, with a consolidated supply technology at atmospheric pressure and low temperatures. Moreover, it does not contain carbon atoms, the chemical elements responsible of the pollutant carbon-oxides among the decomposition products. At high concentration ammonia is toxic, and even lethal at 2000 ppm, nonetheless it can be simply detected by smell when its concentration is extremely lower than dangerous [21].

In a previous work we showed, by numerical simulation, that the use of a catalytic membrane reactor highly improved ammonia conversion (+18% in the conversion rate at 550 °C) [22]. In another study, we experimentally investigated the effects of Ruthenium catalyst on ammonia dissociation by using a tubular reactor: the results revealed that Ru catalyst allowed the reaction to reach the equilibrium for GHSV (Gas Hourly Space Velocity) values between 300 h⁻¹ and 2400 h⁻¹, when the temperature ranged from 400 °C to 500 °C at 1 bar of pressure. However, for higher values of operative pressure and feeding flow, the reaction reached the chemical equilibrium only when an increase in the temperature was simultaneously imposed [23].

Within this contest, the aim of this work was to investigate the ammonia conversion at different values of temperature, pressure and feeding flow using a commercial membrane reactor [20]. In particular, we studied the ammonia catalytic decomposition in a multifunctional catalytic membrane reactor (CMR) which integrates hydrogen selective palladium-coated membranes and a Ruthenium catalyst in the same unit. Other studies approached the use of CMRs for ammonia dissociation [2,15,21] but all of them made use of a sweep gas to enhance hydrogen removal and, in most of the cases, investigated the reaction in different operative conditions. In this work, we looked for the lowest value of temperature that allowed the reaction to reach the equilibrium without the use of any sweep gas. The hydrogen permeation through the membranes was hence driven by the difference of hydrogen partial pressures between the permeate and the retentate outputs.

Therefore, our working hypothesis was that the use of hydrogen selective membranes, combined with Ruthenium catalyst, could allow the conversion to reach the equilibrium for a wider range of temperatures and feeding flows. In particular, we expected to obtain high values of ammonia conversion also for high GHSV at low temperatures.

Finally, to investigate the usefulness of such a system for *in situ* hydrogen production, we studied the ammonia dissociation at room temperature, when the ammonia in the tank is still liquid [20]. The aim of these further tests was to find out the optimal values of all the parameters that could be controlled by the operator, such as the highest feeding flow and the lowest inner reaction temperature, to make the ammonia dissociation as less dependent as possible on the environmental parameters.

Material and methods

Experimental set-up

A High Temperature Tubular Membrane Reactor (REB Research & Consulting) was filled with 37 ml of Hypermec

10010 Ru catalyst (ACTA), one of the catalysts with the highest activity for ammonia decomposition [19], on Al₂O₃ binder, to completely cover the membranes. The palladium-coated metal membrane reactor ensured a H₂ purity higher than 99.9999%, independent of any hydrogen back-pressure changes [24]. The anhydrous ammonia necessary for the experiments was stored in a tank and was heated, if necessary, to achieve the desired pressure in the reactor circuit (up to 10 bar). A Mass Flow Controller (Bronchorst F-201CV) was used to set the NH₃ flow feeding the reactor. Pipe lines were temperature controlled.

In the tubular CMRs the inner temperature substantially varies along the longitudinal axis, because of the hydrogen removal and the resulting equilibrium shifting. To maintain the reaction temperature at the desired value, three rope heaters (OMEGALUX FGR-030) have been employed to control, independently, the temperature of the catalyst bed in its upper, middle and lower part. To do this, each rope heater was governed by a dedicated temperature controller (West Instruments N6100) connected to a different K-thermocouple [19]. The 3 thermocouples were embedded in the reactor and, in detail, we put the first thermocouple in the upper part of the reactor, where only the catalyst contributes to the ammonia conversion, the second at the midpoint of the reactor, where both the catalyst and the membranes contribute to the reaction and the third below the end of the membranes, where the ultrapure hydrogen is collected. Moreover, to have a complete overview of the thermodynamic process, we placed three other thermocouples at the rope heater contact surfaces on the shell reactor, at the same heights of the inner thermocouples, as shown in Fig. 1.

At the residual output a micrometric valve was used to keep the circuit pressure at the desired value. The outgoing gas, now at atmospheric pressure and room temperature, fed an impingement bottle filled with a solution of H₂SO₄ and water for un-reacted NH₃ measurement ($\phi_{\text{NH}_3}^0$), as described in Di Carlo et al. [23]. Briefly, being the NH₃ a weak base, it highly reacts with the strong acid in the trap, neutralizing the solution. By measuring the time the solution needs to reach the neutralization it is possible to compute the mass flow rate of the un-reacted ammonia.

The permeate output, where the ultra-pure hydrogen is at room temperature and at a pressure value of about 1 atm, was connected to a Mass Flow Meter (Bronchorst F-201CV) for H₂ measurement. Flowing at these operative conditions, the hydrogen temperature quickly decreases, thus allowing, for example, a direct connection to PEM fuel cells ($T < 100$ °C).

In order to have a complete evaluation of the system efficiency, a power analyzer (PCE PA-6000) has been used to measure the electric consumption, namely the Wh, of both the rope heaters and the temperature controllers. Notably, the consumption measured here only comprises the energy used to keep the temperature inside the reactor at the desired value and does not take into account the power needed to heat the tank. This extra power consumption is usually very high and not always commensurate to the increase in the collected hydrogen. To this point, we subsequently looked for the best operative conditions of the system when working in mild environmental pressure and temperature, namely shutting off the ammonia tank heating.

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