

# Catalysis in membrane reformers: a high-performance catalytic system for hydrogen production from methane

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Received 11 November 2003; revised 8 August 2004; accepted 2 December 2004

Available online 17 March 2005

## Abstract

A palladium membrane reactor has been designed and sized to be applied to the dry reforming of methane for pure hydrogen production at a small scale. Three different parameters affecting the reactor operation have been adjusted to tune the reformer and optimise its performance: the extraction conditions, the CO<sub>2</sub>/CH<sub>4</sub> ratio in the reactant mixture composition, and the reactants feed flow rate. By forcing H<sub>2</sub> extraction and adjusting the rates of hydrogen production in the reactor and hydrogen permeation through the Pd membrane, it has been possible to obtain very high CH<sub>4</sub> conversion for mixtures with CO<sub>2</sub>/CH<sub>4</sub> ratios above unity. Reactant mixtures with CO<sub>2</sub>/CH<sub>4</sub> ratios close to 2 offered the best results: high H<sub>2</sub> recovery yields (above 95%) and lower carbon deposition in the catalysts under the severe conditions imposed by the membrane reactor operation. Hydrogen extraction from the reaction side has been shown to enhance the carbon deposition rate on nickel-based reforming catalysts, in which the formation of low-reactivity carbon in the form of fibres has been observed. The dispersion of nickel on high oxygen mobility supports, such as Ce–Zr mixed oxides (Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>), which are chemically stable under reaction conditions, results in highly efficient catalysts capable of keeping their surface free of inactive carbon deposits. This kind of oxide provides an extra source of oxygen that equilibrates the net rates of carbon deposition and removal on the nickel surface, thus avoiding the accumulation of carbon in the catalyst.

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**Keywords:** Palladium membrane reformer; Hydrogen production; Dry methane reforming; Carbon nanofibres; Ni/Al<sub>2</sub>O<sub>3</sub>; Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>; Ni/ZrO<sub>2</sub>; Ni/ZrO<sub>2</sub>–CeO<sub>2</sub>

## 1. Introduction

Although hydrogen production has been a matter of great importance in recent decades, a renewed interest in its production processes has emerged recently, driven by the spectacular advances in fuel cell technology. Up to now only a small fraction of the hydrogen produced is currently used for energy purposes, but the implementation of fuel cell systems and the growing demand for zero-emission fuels in the near future will increase the hydrogen share of the energy market. Its production from abundant sources in an economical way

and with reduced purification costs would make possible the commercialisation of fuel cell-powered systems.

Large-scale hydrogen production from natural gas by steam reforming or autothermal reforming is a well-known process that uses purification methods such as pressure swing adsorption or cryogenics. However, H<sub>2</sub> production at a smaller scale from fossil fuels requires further investigation to meet the requirements of purity, economics, and versatility for its use in fuel processor systems to be coupled to fuel cells [1]. The utilisation of membrane reactors for this purpose is one of the most interesting options to consider, given its advantages related to heat and energy management, and the integration of two different processes (reaction and separation) in a single step.

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Several types of membranes have been tested in methane-reforming reactions for hydrogen separation: ceramic membranes [2,3], porous Vycor glass membranes [4–6], and palladium-based films [7–10]. However, the application of these modules to methane-reforming processes poses additional difficulties compared with other dehydrogenation reactions.

The small differences in the kinetic diameters of reactants and products usually reduce the permselectivity in porous membranes to the values corresponding to a Knudsen-type diffusion mechanism of the different species [3]. Because of this, dense membranes, whose operation is based on a  $H_2$  solution-diffusion mechanism on a permselective film, are usually the preferred choice. Although metals such as Nb, Ta, V, and Zr and their alloys, particularly V–Ni, have greater hydrogen permeability than Pd, they have greater surface resistance to hydrogen transport due to their easier oxidation. On the other hand, the high operation temperature required for these reforming reactions limits the structural stability of  $H_2$  permselective films and the utilisation of materials for membrane synthesis, fitting, sealing, enamelling, etc. As a result, the reactor performance becomes limited and controlled by numerous parameters, such as the thermal stability of its components, their mechanical resistance, their geometry, the membrane permeability and selectivity, not to mention the catalyst stability under the more severe reaction conditions imposed by the removal of hydrogen from the reaction medium, which finally remains one of the most important issues in the design of an efficient fuel processor. Up to now, most of the efforts in this field have been focused on the membrane itself and/or the reactor characteristics, but little attention has been devoted to the catalyst behaviour under the membrane reactor operation conditions. This latter question remains one of the most important challenges to be broached for these systems. Usually, noble metals have been used in membrane reactors to overcome problems related to carbon deposition [11,12]. However, their high price drives the development of alternative catalysts for this process. Some simulation studies concerning the catalytic performance of membrane reactors in the steam reforming of methane have been published in recent years [13–15]. In particular, Hou et al. noted in their study the increased tendency towards catalyst poisoning by carbon deposition and the stronger effect of contaminants such as  $H_2S$  when hydrogen is removed from the reaction zone [15], especially at temperatures below 873 K and pressures below 6 bar. In the case of the dry reforming of methane, the tendency towards carbon formation on the catalyst is even higher.

This communication reports a detailed study of different parameters influencing the operation of a membrane reformer for methane, with carbon dioxide as oxidant; the extraction conditions, the feed flow rate, and the reactant mixture composition have been adjusted to optimise the system performance. Several nickel-based catalysts dispersed on different supports have been prepared and tested in the membrane reactor. This study analyses the catalytic stability

and resistance to carbon deposition of the different samples, revealing that the catalytic behaviour of the nickel-based systems strongly depends on the support characteristics. The design of high oxygen mobility supports that are chemically stable under the severe reaction conditions imposed by the reactor is the key for obtaining an active and stable catalytic system capable of long-term operation in a membrane reformer.

## 2. Experimental

### 2.1. Pd membrane preparation and characterisation

Palladium membranes were prepared by electroless plating deposition on the external surface of a porous 316L stainless-steel (PSS) support from Mott Corp. According to the manufacturer's specifications, the grade of the PSS was 0.5  $\mu\text{m}$ , with an average pore diameter of 3  $\mu\text{m}$  and a porosity of 17%. The permeable zone of the membrane module was designed to have a volume of approximately 2  $\text{cm}^3$  (o.d. 9.5 mm, wall thickness 1.6 mm, length 60 mm). The porous part was welded at both extremes to two 15-cm-long pieces of nonporous 316L stainless steel.

The membrane synthesis involved cleaning of the support, followed by successive sensitising, activation, and plating cycles according to the procedure described by Mardilovich et al. [16]. The activation procedure consisted of successive immersions in an acidic  $\text{SnCl}_2$  bath (sensitising) and in deionised water, followed by an acidic  $\text{PdCl}_2$  bath at room temperature. Then the membranes were rinsed with 0.01 M HCl and with deionised water to prevent hydrolysis of the  $\text{Pd}^{2+}$  ions. After several sensitizing/activation cycles, palladium was deposited at 333 K by an autocatalytic reduction reaction with the use of a plating bath consisting of a basic solution of  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ , NaEDTA, and  $\text{N}_2\text{H}_4$ . Plating was followed by drying at 393 K. After each plating cycle, the membranes were tested for He permeation at room temperature to check for the absence of pores in the palladium film. Membranes that were not dense were submitted to another activation and plating cycle. Dense membranes were used for reaction experiments. This procedure made it possible to synthesise dense palladium membranes with a minimum thickness and maximise the  $H_2$  permeation rate. The thickness of each Pd layer obtained in this way was estimated from the weight increase of the module.

The membrane tube was fixed to a stainless-steel shell with an inlet and an outlet to feed a sweep gas stream. The use of independent Swagelok fittings with graphite ferrules to integrate the membrane in the reactor and to connect it to the experimental setup provided an easily handled gas-tight seal, which avoided leakage problems between the retentate and the permeate sides.

The permeation properties of the synthesised membranes were evaluated for He and  $H_2$  at several temperatures be-

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