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Methanol steam reforming for hydrogen generation via conventional and membrane reactors: A review

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ABSTRACT

In the recent years, hydrogen has gained a considerable interest as an energy carrier useful for various applications and, particularly, for polymer electrolyte membrane fuel cells (PEMFCs) supply. Nevertheless, PEMFCs require high purity hydrogen as a feeding fuel, which shows some limitations regarding storage and transportation. Therefore, to overcome these problems, the in situ hydrogen generation has made attractive both alcohols and hydrocarbons steam reforming reaction. Among other fuels, methanol is an interesting hydrogen source because it is liquid at ambient conditions, possesses relatively high H/C ratio, low reforming temperature (200–300 °C) and it is also producible from biomass. Meanwhile, there is a comprehensive literature about inorganic membrane reactors utilization for hydrogen generation via methanol steam reforming reaction. This review illustrates the earlier state of the art from an experimental point of view about hydrogen production from methanol reforming performed in both conventional and membrane reactors. Furthermore, a short overview about methanol reforming catalysts as well as a discussion on the impact of methanol steam reforming process via inorganic membrane reactors to produce hydrogen for PEMFCs supply is given.

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1. Introduction

During the last decades, there has been a growing interest on developing technologies taking advantage of clean energy sources. The reduction of atmospheric pollution and, namely, the emission of greenhouse gases have become imperative and, among the new

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technologies for mitigating these emissions, fuel cells have the ability to efficiently convert chemical into electrical energy. In particular, PEMFCs are zero-pollutants emission systems because they transform the chemical energy of the electrochemical reaction within hydrogen and oxygen into clean electrical power [1,2]. Generally, they work at $T < 100$ °C, making possible a rapid start-up. Unfortunately, as a principal drawback, PEMFCs need to be supplied by high purity hydrogen since the anodic Pt-based catalyst tolerates less than 10 ppm of CO. The hydrogen is industrially produced as a hydrogen-rich stream mainly via steam reforming of natural gas in conventional reformers (CRs) [3]. Successively, hydrogen is purified to reach the desired purity for the PEMFC supply. Indeed, the reformed stream coming out from the CRs commonly contains hydrogen, CO₂, CO, CH₄ and other byproducts. As a consequence, PEMFCs supply imposes the purification of hydrogen, which commonly takes place in second stage processes, namely water gas shift (WGS) reaction (performed in two reactors operating in series at high and low temperatures), partial oxidation (PROX) and pressure swing adsorption (PSA) [4–6]. Nevertheless, the aforementioned stages of hydrogen purification affect negatively the overall process in terms of costs and efficiency [7]. Hence, at scientific level much attention has gained the development of alternative technologies to generate high purity hydrogen (or, at least, CO_x-free) for PEMFCs supply. Among them, membrane reactors (MRs) technology plays an important role as an alternative solution to the conventional systems (CRs+ further stage of hydrogen purification systems) in terms of combination in a single stage of the reforming reaction for generating hydrogen and its purification without needing any further process/treatment [8]. As shown in Fig. 1, the interest towards this technology is testified by the growing number of scientific publications in the specialized literature.

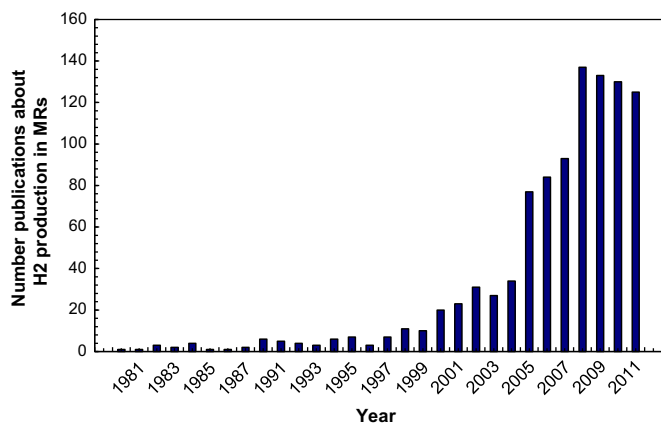


Fig. 1. Number of scientific papers on H₂ production by MR technology vs year. Scopus database: www.scopus.com.

Table 1

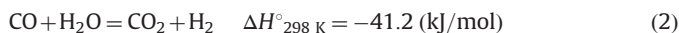
Some of the most significant benefits and drawbacks of MRs utilization.

MRs benefits	MRs drawbacks
Compact unit in combining both reaction and hydrogen purification with a consequent capital costs reduction	High costs and low mechanical resistance in case of dense palladium-MRs
Conversion enhancement of equilibrium limited reactions. Higher conversions than CRs (exercised at the same MRs conditions) or at the same conversion of CRs reached at milder operating conditions	Not high purity hydrogen production in the case of composite Pd-based MRs. Not high hydrogen perm-selectivity in the case of non Pd-based MRs utilization
Direct production of high purity hydrogen in a single unit (in the case of a dense Pd-based MR)	Hydrogen embrittlement at $T < 300$ °C in the case of dense Pd-MRs
Retentate stream of MRs rich in CO ₂ (i.e. the stream not permeated through the membrane) when performing reforming reactions	Contamination of H ₂ S, coke CO, etc. in the case of Pd-MRs

As a particular aspect regarding membrane technology, the inorganic MRs utilization makes possible several benefits over the CRs [10–12], although they also present some drawbacks as summarized in Table 1.

In particular, in the last decades, an extensive literature has been addressed to hydrogen production using inorganic MRs based on both dense and supported Pd-based membranes [13–25], because of their high perm-selectivity to hydrogen with respect to all other gases.

Meanwhile, compared to other feedstocks, methanol exploitation shows various advantages as a hydrogen carrier for fuel cell applications and, namely, it can be produced from renewable sources [9] and the reforming reaction occurs at relatively low temperatures, ca. 240–260 °C [4], compared to the methane reforming, normally performed at 800–1000 °C [10]. Methanol steam reforming (MSR) reaction has been seen as a very attractive and promising process for hydrogen production and, according to the scientific literature on the argument, it can be described by the following chemical reactions:



Reaction (1), represents MSR reaction, reaction (2) represents water gas shift reaction and reaction (3) represents the methanol decomposition reaction. Only the WGS reaction is exothermic and takes place without variation of moles number. The steam reforming reaction besides being endothermic takes place with an increase of moles number. Unfortunately, the main drawback of this process is represented by the CO formation as a byproduct, which – as stated previously – can poison the anodic catalyst of the PEMFCs as well as affect negatively the permeation of Pd-based MRs [26]. Indeed, in the field of MSR reaction performed in CRs, several scientists paid special attention to catalyst optimisation in order to reduce the CO content [27–38].

The aim of this review is then oriented in describing the earlier state-of-the-art about the use of inorganic MRs technology for conducting the MSR reaction targeting the production of PEMFC grade hydrogen.

2. Methanol steam reforming catalyst

MSR has been widely studied and the most common catalysts are based on copper, such as Cu/ZnO/Al₂O₃, working at ca. 240–260 °C [27,39,40]. Copper-based catalysts are very active and low cost, even though they originate a significant concentration of carbon monoxide, show low stability and pyrophoric nature. As an example, Conant et al. [41] studied CuO/ZnO/Al₂O₃ catalyst stability at 250 °C and concluded that, after 60 h of operation, methanol

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