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Journal of Membrane Science 308 (2008) 250–257
journal of MEMBRANE SCIENCE
www.elsevier.com/locate/memsci

Low temperature ethanol steam reforming in a Pd-Ag membrane reactor Part 1: Ru-based catalyst

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Received 6 April 2007; received in revised form 28 September 2007; accepted 1 October 2007
Available online 6 October 2007

Abstract

The ethanol steam reforming has been carried out in a membrane reactor consisting of a Ru-based catalyst bed packed into a thin wall Pd-Ag permeator tube produced via cold-rolling and diffusion welding of metal foils. The experimental tests have been performed in the temperature range 400–450 °C with the aim of studying the performances of the membrane reactor in terms of hydrogen yields.

The main investigated operating parameters have concerned the water/ethanol feed molar ratio (8.4–13.0), the pressure inside the membrane (150–200 kPa), the sweep gas mode (co-current and counter-current) and the spatial velocity.

In all the tests, ultra pure hydrogen has been separated through the Pd-Ag membrane: especially, operating at 450 °C and 200 kPa, a hydrogen yield higher than 80% has been produced thus demonstrating the membrane ability of promoting the reaction conversion (shift effect).

Keywords: Ethanol steam reforming; Ru catalyst; Membrane reactor; Pd-based membranes; Hydrogen production

1. Introduction

Hydrogen is being considered as a clean energy vector: the value of this statement could be strongly emphasized when the hydrogen is produced by an environmental friendly process. The hydrogen production from hydrocarbons and alcohols has been widely studied and applied: especially, at the present in large size plants (>10,000 $Nm^3\,h^{-1}$) hydrogen is produced by the hydrocarbons conversion into syngas and the following water gas shift reaction where the CO is converted into CO_2 and hydrogen. Mainly, the methane reforming and then the gasification of coal are the processes used for producing hydrogen: however, the use of fossil fuels increases the global warming as a consequence of the large releases of carbon dioxide. Therefore, the hydrogen production starting from biofuels such as the ethanol obtained from biomasses could contribute to stabilize the carbon dioxide concentration and reduce the greenhouse effect.

Many authors [1–11] studied the ethanol steam reforming in traditional reactors being an endothermic catalysed reaction whose conversion increases with the temperature:

$$C_2H_5OH + H_2O \Leftrightarrow 2CO + 4H_2 \qquad \Delta H_{298K} = 239.47\,kJ\,mol^{-1} \tag{1}$$

If the water gas shift reaction is used for converting the CO the complete reaction is:

$$C_2H_5OH + 3H_2O \Leftrightarrow 2CO_2 + 6H_2 \qquad \Delta H_{298K} = 157.09\,kJ\,mol^{-1} \tag{2}$$

Usually, catalysts based on Rh, Ru, Pd, Pt, Ni, Co and Cu are used on supports of Al_2O_3, SiO_2, MgO and La_2O_3. The reaction conversion and selectivity of the products (mainly H_2, CO, CO_2 and in minor part, CH_4, CH_3CHO and C_2H_4) depend

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doi:10.1016/j.memsci.2007.10.001

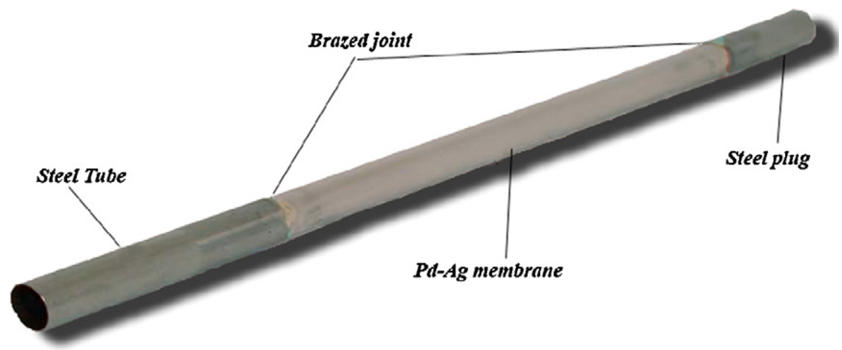

Fig. 1. View of a Pd-Ag permeator tube.

on the catalyst used as well as on the operating temperature. A large excess of water in the feed stream increases the hydrogen selectivity and reduces the coke formation that may poison the catalyst particularly when the reaction is operated at low temperature.

An interesting alternative approach to the traditional reactors consists on the use of membrane reactors for carrying out the steam reforming in order to increase the ethanol conversion at lower temperature [12]. In fact, a membrane reactor is a device in which a reaction and a selective separation take simultaneously place: in this way, the continuous removal of one of the product permits obtaining reaction conversion beyond the thermodynamic equilibrium which is an upper limit to be considered in a traditional reactor (shift effect) [13–16]. In practice, when a dehydrogenation reaction is performed, the use of a membrane selectively permeable to the hydrogen permits to build a reactor producing and separating pure hydrogen with high reaction conversions. Dense palladium (and its alloys) membranes are only permeable to the hydrogen and are used for manufacturing permeators and membrane reactors aimed at separating and producing hydrogen: several studies report the use of these membranes [16–21]. Especially, the use of dense Pd-Ag membranes permits to maximize the shift effect and produce directly ultra pure hydrogen without the need of any other purification unit.

In this paper, low temperature tests of a membrane reactor consisting of a dense thin wall Pd-Ag tube packed with a Ru-based catalyst are reported. The effect of some operating parameters (water/ethanol feed molar ratio, temperature, pressure, sweep gas mode and spatial velocity) has been investigated. The tests have been carried out at relatively low temperatures (400–450 °C): under similar experimental conditions, in traditional reactors the hydrogen yields expected are very low [1]. As a matter of fact, the ability of the membrane of promoting the reaction conversion (i.e. the shift effect) has been demonstrated.

2. Experimental

The membrane reformer consists of a dense Pd-Ag tube hosting in the lumen side the catalyst bed: the hydrogen permeated through the membrane is recovered in the shell side of the reactor where a nitrogen stream is used as sweep gas.

2.1. Pd-Ag permeators

The Pd-Ag thin wall tubes have been produced by diffusion welding of rolled metal foils according to a previously described technique [22,23]. The Pd-Ag tubular membrane is joined, by brazing, at its ends to a stainless steel tube and to a steel plug, as shown in Fig. 1. Especially, the obtained permeator tube is assembled inside the membrane module in a finger-like (or tube-in-tube) configuration: in order to permit its elongation and contraction due to the hydrogenation cycles, the membrane tube is fixed to the module at one end. In this way, any detrimental mechanical stress on the thin wall tube is avoided: long-term tests already demonstrated the complete hydrogen selectivity and durability of these permeators which separated ultra pure hydrogen from gas mixtures showing no formation of defects (holes, cracks) under thermal and hydrogenation cycling [24]. The geometrical details of the Pd-Ag permeator tubes are reported in Table 1.

2.1.1. Permeation tests

The permeation tests on the Pd-Ag tubes were carried out under controlled temperature and transmembrane differential pressure conditions: pure hydrogen produced by electrolysis of deionised water was fed in the lumen side in the pressure range of 120–200 kPa, while the hydrogen permeated through the membrane was collected in the shell side at atmospheric pressure by a nitrogen stream of 7.44×10^{-4} mol s^{-1}. Isothermal conditions were assured by a heating system consisting of a plat-

Table 1
Geometrical characteristics of the Pd-Ag permeators used in this work

Tubular membrane	Material supplier	Inner diameter mm	Wall thickness (μm)	Length (mm)
PX1	Platecxis	10	50	147
GF	Goodfellow	10	60	144