

Hydrogen Production Using Membrane Reactors

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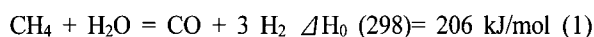
Abstract: Methane steam reforming (MSR) reaction for hydrogen production was studied in a membrane reactor (MR) using two tubular membranes, one Pd-based and one of porous alumina. A higher methane conversion than the thermodynamic equilibrium for a traditional reactor (TR) was achieved using MRs. The experimental temperature range was 350-500°C; no sweep-gas was employed during reaction tests to avoid its back-permeation through the membrane and the steam/methane molar feed ratio (m) varied in the range 3.5-5.9. The best results (the difference between the MR conversion and the thermodynamic equilibrium was of about 7%) were achieved with the alumina membrane, working with the highest steam/methane ratio and at 450°C. Silica membranes prepared at KRICT laboratories were characterized with permeation tests on single gases (N₂, H₂ and CH₄). These membranes are suited for H₂ separation at high temperature.

Keywords: hydrogen purification, membrane reactor, Pd reactor, CO₂ hydrogenation, silica membrane

1. Introduction

Hydrogen is a valuable gas and its demand in refineries is continuously increasing due to the growing need for environment friendly fuels[1]. Also new technologies such as the fuel cells, requiring CO-free hydrogen as feed, are promoting improvements in the hydrogen production cycle.

One of the main technologies for hydrogen and syngas (H₂ and CO mixture) production is the catalytic methane steam reforming (MSR)[2]. This process starts from natural gas that is abundant and mainly constituted by methane



the carbon monoxide content is reduced, producing at the same time more hydrogen, by water gas shift reaction (lightly exothermic):



MSR reaction is equilibrium limited and globally endothermic, thus a high temperature is applied for a satisfactory methane conversion. Typically, conventional processes, using a temperature of about 850°C, a pressure of 100-400 kPa, steam/methane molar ratio between 2.5 and 4.1 (a steam excess prevents carbon deposition) reach methane conversion of about 80%[3].

The request to reduce energy consumption, to recover and reuse waste streams, minimising also the environmental impact, suggests implementing innovative approaches in process design and development. A promising answer to this challenge is offered by the Process Intensification strategy[4] consisting in innovative design and process development methods. Substantial improvements in chemical and any other manufacturing and processing, significantly decreasing production costs but also equipment size, energy consumption, waste generation, and improving remote control, information fluxes and process flexibility are expected.

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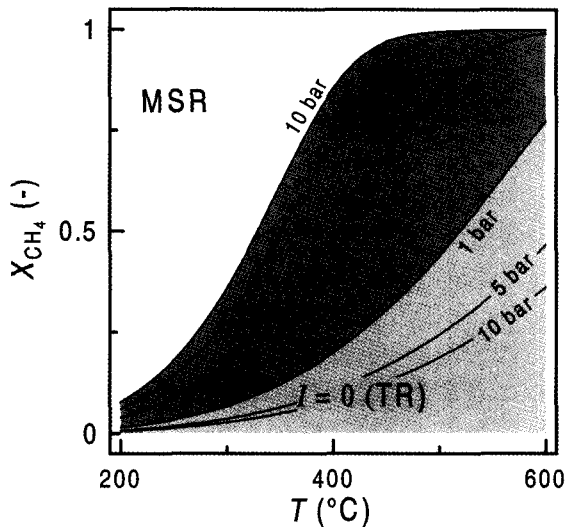


Fig. 1. Equilibrium CH_4 conversion vs T for TR and MR. Steam/methane ratio=3⁷.

MSR is an energy onerous process[5], therefore, the use of a membrane reactor (MR) with hydrogen selective membranes, increasing methane conversion and reducing the H_2 purification section, follows the Process Intensification strategy. The membrane role consists in removing hydrogen from reaction side, thus shifting the chemical equilibrium towards a higher methane conversion. Inorganic membranes, like dense metallic (Pd-based) or porous ceramic membranes (SiO_2 , Al_2O_3 , ZrO_2 , TiO_2 , zeolite) are the most suited for this high temperature reaction.

Figure 1 shows the advantage of using a MR in terms of CH_4 conversion with respect to a traditional reactor (TR), as can be predicted by simulating a MR equipped with an ideal Pd-based membrane (infinitely

selective to hydrogen)[6]. Two aspects can be put in evidence: the first is related to the possibility of reaching a high conversion in MRs at a temperature lower than TR. The second is connected to the positive pressure effect even for reactions characterized by an increase in the number of moles (e.g. MSR); in fact, MR equilibrium conversion increases with pressure while that of a TR decreases. This positive effect in MR is due to the increase in permeation at higher pressure. A high operating pressure is positive since it reduces the reactor volume and is useful for subsequent applications (e.g. ammonia production).

Other experimental works on MRs showed that using an alumina membrane containing dispersed Pd particles[7] and different alumina membranes[8] for MSR, a conversion higher than equilibrium of 200% and 20%, respectively, can be achieved.

This work analysed the use of a MR with inorganic (alumina and Pd-based) membranes for MSR. Furthermore, silica membranes prepared at KRICT laboratories were characterized by means of permeation tests, since they can be used at high temperature for H_2 separation, or H_2O selective separation in MRs for reactions such as CO_2 hydrogenation for methanol production[9].

2. Experimental

2.1. Methane Steam Reforming Reaction Tests

A MR prototype using tubular membranes is depicted in Figure 2. The membrane was sealed in the SS shell by using SS and graphite gaskets.

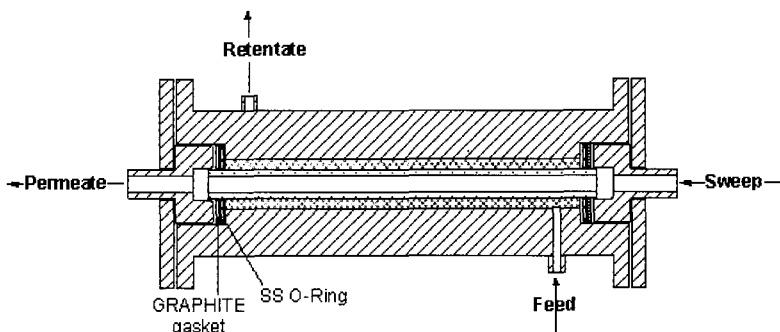


Fig. 2. Tubular MR.

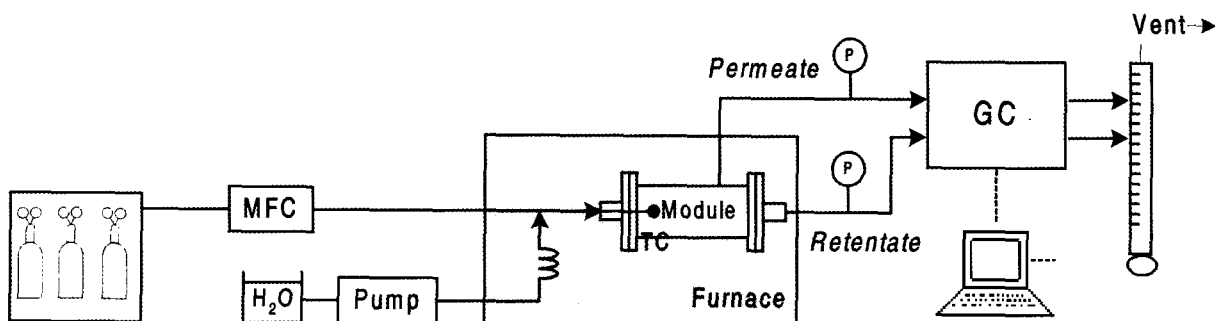


Fig. 3. Scheme of the experimental apparatus. MFC: mass flow controller; MR: membrane reactor; TC: thermocouple; GC: gas chromatograph.

The experimental apparatus used in permeation and reaction tests is illustrated in Figure 3. The SS module containing the membrane was placed in a temperature controlled electric furnace (with PID control). A micro-pump was utilized to feed the liquid water, while a coil in the furnace allowed the water vaporization before its mixing with CH_4 . Mass flow controllers (Brooks Instrument 5850S) were used for controlling the feed flow rate of all inlet gaseous streams. The flow rate of the outlet streams was measured using bubble soap flowmeters; mass flow meter can not be used: a different calibration would be required for any stream composition. The MR outlet streams passed through two condensers and through two adsorbent beds (Drierite® - W.A. Hammond - Aldrich) where water was separated and then the dried streams were analysed by means of a gas chromatograph equipped with a TCD detector and a Carboxen 1000 column.

2.2. Materials

Two tubular membranes were used for MSR reaction tests at ITM laboratories:

- (1) a porous alumina membrane (SCT, France), with pore diameter of 5 nm;
- (2) a Pd-based membrane realised by means of "Electroless-plating" technique on an alumina porous support.

Reaction tests were performed packing a commercial Ni-based catalyst (Ni-5256 E 3/64", Engelhard).

2.3. Preparation of Silica Membranes

The disk of 316 L porous stainless steel support (Mott Metallurgical) was modified by silica xerogels with particle size of 100 nm obtained by drying colloidal silica sols with a rotary evaporator. The silica xerogel was pressed into the macropores of one side of the stainless steel disk by a press under 10 MPa, followed by calcination at 650°C. Additional modification of the support was conducted by dip-coating into a boehmite sol, therefore creating a γ -alumina layer. A polymeric silica sol was used to synthesize the silica top layer on the modified supports by a dip-coating procedure. The calcination of γ -alumina layer and silica top layer was carried out at 650°C and 500°C, respectively.

2.4. Permeation Tests on Silica Membranes Supplied by KRICT

Single gas permeation experiments were carried out on three silica membranes prepared at KRICT on flat stainless steel supports.

A stainless steel module for both reaction and permeation experiments was designed and realised at ITM (Figure 4) using silicon o-rings as sealing.

Pressure drop method, with a trans-membrane total pressure difference (ΔP^{TM}) acting as permeation driving force, was adopted during permeation measurements. A pressure controller was used for setting feed pressure, whereas permeate pressure was atmospheric. No sweep-

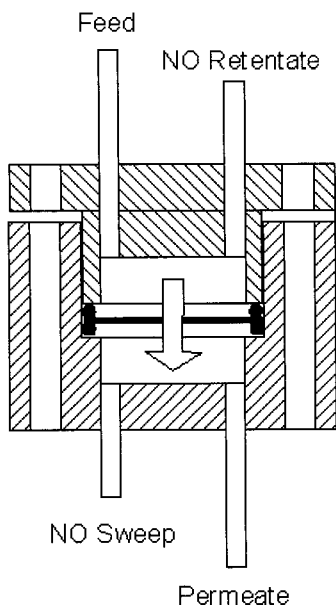


Fig. 4. Scheme of the SS cell used in permeation tests with flat membranes.

gas was used. This experimental technique avoid a possible permeance underestimation that can occur as a consequence of the sweep gas back-diffusion[10].

Before permeation tests the membranes were heated at a rate of 1°C/min in a hydrogen flux. The permeance [mol/ m² s Pa] for each gas is calculated as:

$$\text{Permeance}_i = \frac{\text{Permeating Flux}_i}{\Delta P^{\text{TM}}}$$

where the permeating flux is in [mol/m²s].

The ideal separation factor between *i* and *j*, is defined as the ratio of pure gas permeances measured at the same temperature:

$$\text{ideal } SF(i/j) = \frac{\text{Permeance}_i}{\text{Permeance}_j}$$

3. Results and Discussion

3.1. MSR Reaction Tests

The membranes used for reaction tests were initially characterized by means of permeation tests with single gases. The Pd-based membrane permeance was one

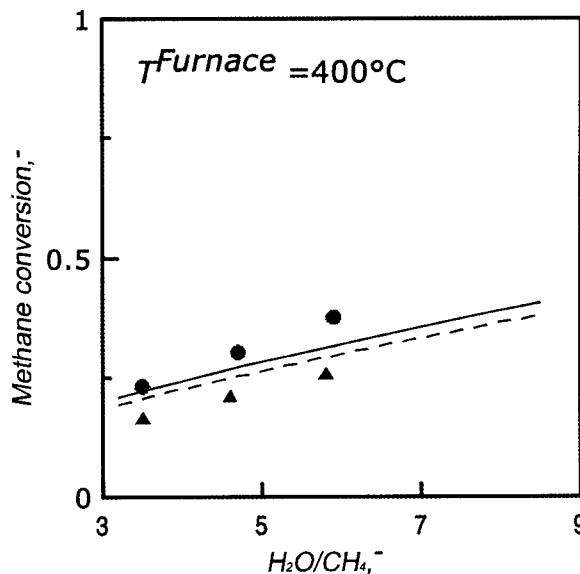


Fig. 5. Methane conversion experimental data as a function of the steam/methane molar feed ratio, $T=400^\circ\text{C}$. (●) MR-P ($P^{\text{Reaction}}=105\text{ kPa}$), (▲) MR-Pd ($P^{\text{Reaction}}=121\text{ kPa}$). $Q_{\text{H}_2\text{O}}^{\text{Feed}}=235\text{ SCCM}$. Equilibrium conversion at 105 kPa (continuous line) and 121 kPa (dashed line).

order of magnitude lower than that of the alumina membrane. This is due to a not uniform Pd layer, as also confirmed by SEM analysis.

Reaction tests were performed in the temperature range 350-500°C and the steam/methane molar feed ratio (*m*) was varied in the range 3.5-5.9, maintaining the water flow rate equal to 235 cm³(STP)/min. No sweep-gas was employed to avoid its back-permeation through the membrane.

Two different operative pressures were considered for the two tubular membranes:

- MR-P: porous alumina membrane, $\Delta P^{\text{TM}} = 4\text{ kPa}$;
- MR-Pd: Pd-based membrane, $\Delta P^{\text{TM}} = 20\text{ kPa}$.

The MR conversion overcame the equilibrium one of a TR for a temperature higher than 350°C, therefore no data obtained at 350°C are reported here.

Figure 5 shows MR methane conversion at 400°C. In particular, MR-P conversion was higher than the TR thermodynamic equilibrium and the conversion improvement increased with *m* up to 19%. However, the methane conversion in the MR-Pd was always lower than TR thermodynamic equilibrium.

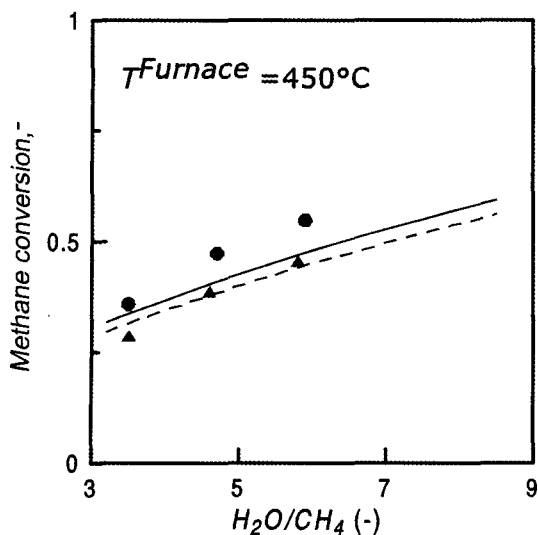


Fig. 6. Methane conversion experimental data as a function of the steam/methane molar feed ratio, $T=450^{\circ}\text{C}$. (●) MR-P ($P^{\text{Reaction}}=105\text{ kPa}$), (▲) MR-Pd ($P^{\text{Reaction}}=121\text{ kPa}$). $Q_{\text{H}_2\text{O}}^{\text{Feed}}=235\text{ SCCM}$. Equilibrium conversion at 105 kPa (continuous line) and 121 kPa (dashed line).

At 450°C only MR-P exhibited an improved methane conversion, again higher than TR thermodynamic equilibrium (Figure 6). MR-Pd conversion was very close to the equilibrium.

MR-P methane conversion was significantly higher than TR thermodynamic equilibrium also at 500°C (Figure 7); however, MR-Pd did not show any advantage even at this high temperature.

The dominant transport mechanism through the membranes used in this work is Knudsen diffusion. Therefore, the permeation increases with ΔP^{TM} and decreases with temperature. On the contrary, methane conversion increases with temperature and decreases with pressure; therefore temperature and pressure have contrasting effects on permeation and reaction.

At 350°C the low conversion value and, consequently, the low product concentration on the reaction side did not allow their selective permeation. However, at 400°C (Figure 5) the conversion value was enough for the product selective permeation, even if the high temperature has a negative effect on permeation. The reaction experiments were carried out at different values of T^{Furnace} , maintaining constant the total $\Delta P^{\text{TM}}_{\text{TOT}}$ value.

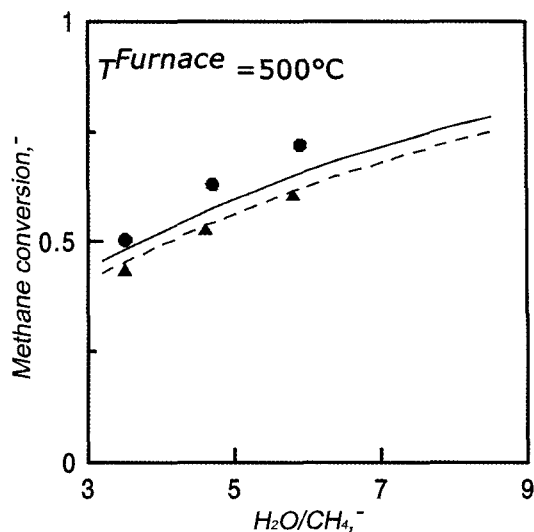


Fig. 7. Methane conversion experimental data as a function of the steam/methane molar feed ratio, $T=500^{\circ}\text{C}$. (●) MR-P ($P^{\text{Reaction}}=105\text{ kPa}$), (▲) MR-Pd ($P^{\text{Reaction}}=121\text{ kPa}$). $Q_{\text{H}_2\text{O}}^{\text{Feed}}=235\text{ SCCM}$. Equilibrium conversion at 105 kPa (continuous line) and 121 kPa (dashed line).

even if for each species the ΔP_i^{TM} value, that is the permeation driving force, varied. Therefore, increasing T^{Furnace} the conversion increased together with the partial pressures of the products and also their selective permeation.

In this work, MR experimental data were better than those relative to the equilibrium conditions of a TR when the conversion was higher than 20-25%; therefore such conversion value can be considered as a limit to overcome in order to realize a selective permeation of the products through the membrane.

At 450°C (Figure 6) better performances for the MRs with respect to a TR were accomplished. A high temperature allowed to obtain increased conversion values and also higher partial pressures for the products, favouring the product selective permeation.

At 500°C (Figure 7) the MR-P showed better methane conversion than a TR, however the increase in conversion was less pronounced than that observed at 450°C . The MR-Pd reactor, instead, showed worse performance with respect to 450°C .

In fact, at 500°C the reaction rate is very high, therefore only a small fraction of the catalytic bed is

Table 1. KRICT Silica membranes Permeation Experimental Data

Membrane	T [°C]	ΔP [kPa]	Permeance [nmol/m ² s Pa]			$^{ideal}SF$	
			H ₂	N ₂	CH ₄	H ₂ /N ₂	H ₂ /CH ₄
KRICT1	175	150	2.32	-	-	-	-
KRICT2	195	200	1.46	0.54	0.67	2.7	2.2
		250	1.52	-	-	-	-
KRICT3	195	200	1.56	0.58	0.80	2.7	2.0

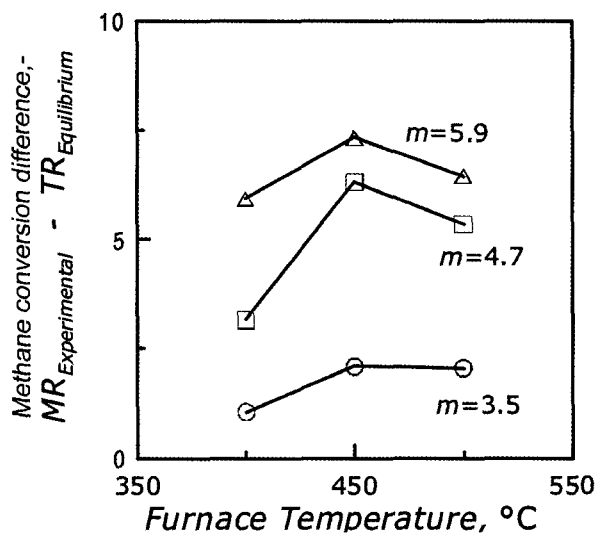


Fig. 8. Methane conversion difference between MR-P and TR thermodynamic equilibrium as a function of $T^{Furnace}$ for m equal to (○) 3.5, (□) 4.7 and (△) 5.9. $P^{Reaction} = 105$ kPa; $P^{Permeate} = 101$ kPa.

involved; the remaining reactor fraction is available for the permeation of water and the product back-diffusion.

Figure 8 reports the conversion difference between MR-P reactor and TR equilibrium as a function of $T^{Furnace}$ for various m values. This difference presents a maximum at about 450°C for every m , confirming the previous considerations on the influence of $T^{Furnace}$ on product selective permeation. Working with $m=5.9$ the conversion difference between MR-P and TR thermodynamic equilibrium increases from 6 to 7%, passing from 400 to 450°C and decreases at 500°C.

The experimental data showed a conversion higher than the thermodynamic equilibrium for MR-P starting from $T=400$ °C; at 350°C the conversion was lower than TR equilibrium. The reactor MR-Pd did not overcome the TR thermodynamic equilibrium at 400°C,

Table 2 Kinetic Diameters of the Gases Used in Permeation Experiments

Molecule	H ₂	N ₂	CH ₄
Kinetic diameter, Å	2.89	3.64	3.80

however at 450°C and $m>4$ the conversion was higher than thermodynamic equilibrium of a TR. This performance is related to the non ideal behaviour of the Pd-based membrane: in fact, all species, not only the reaction products but also reactants, permeated through the membrane lowering the methane conversion.

3.2. Permeation Tests on Silica Membranes Supplied by KRICT

Single gas (N₂, H₂, CH₄) permeation tests were performed for studying the possible application of KRICT membranes for H₂ separation.

Table 1 is a summary of experimental permeances and ideal separation factors. Considering KRICT2 membrane, H₂ permeance depends on the applied ΔP^{TM} and therefore some contribution of viscous flow through defects was present. Furthermore, for KRICT2 and KRICT3 membranes CH₄ permeance was higher than that of N₂ even though it presents a larger kinetic diameter (Table 2). This indicates that the main contribute was related to the molecular mass, demonstrating that transport mainly occurred by Knudsen diffusion. Therefore, it is expected to have positive results also by testing these membranes in MSR reaction tests.

4. Conclusions

Two tubular membranes, a Pd-based one (MR-Pd) and a porous alumina membrane (MR-P), were used in

MSR reaction experiments with a commercial Ni-based catalyst (Engelhard).

The experimental data showed methane conversion higher than that of a TR thermodynamic equilibrium at temperature higher than 350°C. Furthermore, it was shown that a conversion higher than 20-25% can be considered as a limit to overcome in order to realize a selective permeation of the products through the membrane, thus overcoming the TR equilibrium conversion.

Better results were obtained with the MR-P reactor instead of MR-Pd, due to the non ideal behaviour of the Pd-based membrane. In fact, the highest methane conversion (73%) measured in these experiments was achieved with the MR-P reactor at 500°C and with the highest m value used (5.9). The best results in terms of difference between MR and TR thermodynamic equilibrium conversion were achieved with the MR-P reactor at 450°C and with $m=5.9$. These results are due to the contrasting effect of temperature on reaction and permeation (governed by Knudsen diffusion mechanism).

In addition, three flat silica membranes supplied by KRICT were characterised by means of permeation tests with pure H₂, N₂ and CH₄, showing a Knudsen diffusion mechanism. These membranes are of potential interests for MR application in dehydrogenation reactions such as MSR.

This study showed the possibility of lowering the operative temperature in the MSR process with respect to traditional systems (~850°C) by means of MRs. Better MR results are expected by the use of more selective membranes, thus simplifying the hydrogen purification section.

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