

Hydrogen purification using membrane reactors

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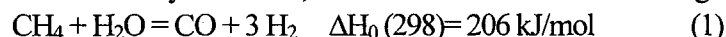
ABSTRACT

Methane steam reforming (MSR) was studied in a membrane reactor (MR) with a Pd-based and a porous alumina membranes. MRs showed methane conversion higher than that foresaw by the thermodynamic equilibrium for a traditional reactor (TR).

Silica membranes prepared at KRICT were characterized with permeation tests on single gases (N₂, H₂ and CH₄). These silica membranes can be also used for high temperature applications such as H₂ separation. CO₂ hydrogenation for methanol production is another reaction where H₂O selective removal can be performed with these silica membranes.

INTRODUCTION

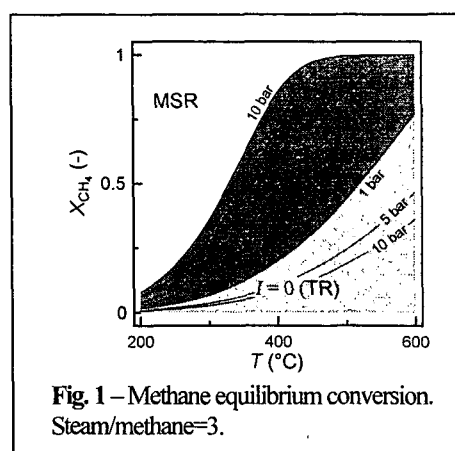
Hydrogen is a clean fuel and its demand is growing up. A typical technology for hydrogen and syngas (H₂ and CO mixture) production is catalytic MSR^{1,2}, since methane is the main natural gas constituent



Carbon monoxide is furthermore oxidate by water gas shift reaction, which is light exothermic:



The reaction is equilibrium limited and endothermic, thus a high temperature is necessary for a satisfactory methane conversion. Typically, traditional processes using a temperature of about 850°C, a pressure of 10-40 bar and steam/methane ratio between 2.5 and 4.1 (a steam excess prevents carbon deposition) and a pressure of 10-40 bar reaches 80% of methane conversion⁴. A high pressure reduces the reaction volume and is useful for the subsequent applications. The use of a MR using hydrogen selective membranes and hence reducing the H₂ purification section follows the Process Intensification strategy for an energy onerous process⁵ such as MSR. Pd-based membranes are interesting for this reaction, but also porous ceramic membranes (Al₂O₃, SiO₂, ZrO₂, TiO₂, zeolite). Figure 1 shows a large advantage of MR use⁶, in fact, the conversion increases



with pressure also for MSR reaction characterised by an increases in the number of moles, when on the contrary in a TR a higher pressure affects strongly methane conversion.

An advantage of using an alumina membrane containing dispersed Pd particles⁷ and alumina⁸ membranes in MSR is a conversion higher than equilibrium of 200% and 20%, respectively. Also simulation studies show higher conversions than that of a TR (at the same operating conditions). In addition, the conversion increases with sweep factor, reaction pressure, etc. The project “*Produzione e Separazione di H₂ con membrane (coreane) altamente selettive*” co-founded by the Italian Ministry of Foreign Affairs analysed the use of a MR for MSR.

EXPERIMENTAL

Methane steam reforming reaction tests

A stainless steel shell prototype was designed and realised for tubular membranes (Fig. 2). The membrane was sealed by using stainless steel and graphite gaskets. Permeation and reaction tests were carried out in an apparatus available at ITM. During reaction MR outlet streams pass through two condensers and through two adsorbent beds (Drierite

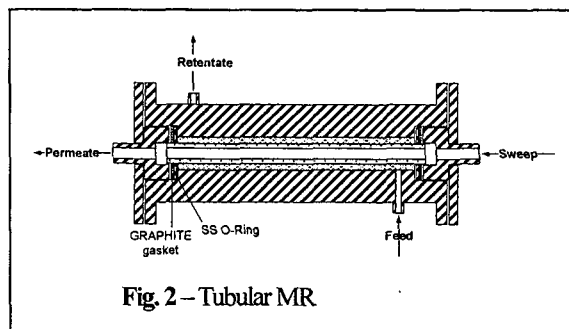


Fig. 2 – Tubular MR

® - 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.

Permeation tests on silica membranes supplied by KRICT

Single gas permeation experiments were carried out on the three silica membranes prepared at KRICT on flat SUS supports. A stainless steel module for both reaction and permeation experiments was designed and realised at ITM (Fig. 3) using silicon o-rings as sealing. Pressure drop method where a trans-membrane total pressure difference (ΔP^{TM} , in Pa) acting as permeation driving force was adopted during the experimental measurements. A pressure controller was used for setting feed pressure, whereas permeate pressure was atmospheric. No sweep-gas was used.

Before permeation tests the membranes were heated at a velocity of 1°C/min in a hydrogen flux. The volumetric permeate flow rate was measured by means of a soap film flow meter. The permeance [$\text{mol}/\text{m}^2 \text{ s Pa}$] for each gas is:

$$\text{Permeance}_i = \frac{\text{PermeatingFlux}_i}{\Delta P}$$

where the permeating flux is in [$\text{mol}/\text{m}^2 \text{ s}$].

The ideal separation factor, the ratio of gas permeance measured at the same temperature, is:

$${}_{\text{ideal}} \text{SeparationFactor}_{i,j} = \frac{\text{Permeance}_i}{\text{Permeance}_j}$$

RESULTS AND DISCUSSION

Methane steam reforming

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

1. a porous alumina membrane (SCT, France), with a pore diameter of 2.5 nm;
2. a Pd-based membrane realised by means of “Electroless-plating” on alumina porous support.

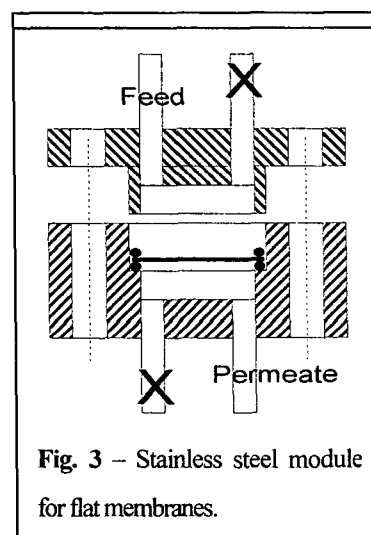


Fig. 3 – Stainless steel module for flat membranes.

The Pd-based membrane permeance was one order of magnitude lower with than the other of alumina. However, also SEM analyses confirmed a no good quality of the Pd layer.

Reaction tests were performed packing a commercial Ni-based catalyst (Ni-5256 E 3/64", Engelhard). No *sweep-gas* was employed to avoid its back-permeation through the membrane. The temperature range was 350-500°C and also the steam/methane molar feed ratio (m) was varied maintaining the water flow rate equal to 235 cm³(STP)/min.

Two different operative modes were considered for the MR:

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

MR conversion overcame the equilibrium one of a TR for a temperature higher than 350°C.

The conversion obtained in the MR-P was significantly higher than that of the thermodynamic equilibrium one even at 500°C (Figure 4). However the MR-Pd did not show advantages with respect to the thermodynamic equilibrium even at a high temperature. At 500°C (Figure 5) the MR-P showed conversions higher than that of TR equilibrium, however conversion increase was less than that measured at 450°C. MR-Pd showed worst performance; in fact, all species, not only the reaction products but also reactants, permeate through the membrane lowering the conversion. Figure 4 reports the difference between the conversion achieved in the reactor MR-P and the TR as a function of furnace temperature and for various m values. This difference presenting a maximum at 450°C for all m values confirms the temperature influence on selective product permeation. The experimental data showed a conversion higher than that of the thermodynamic equilibrium for reactor MR-P starting from $T=400^\circ\text{C}$; at 350°C the conversion was lower than the TR equilibrium. The reactor MR-Pd did not overcome the TR thermodynamic equilibrium, however at $T=450^\circ\text{C}$ and $m>4$ the conversion was higher than thermodynamic equilibrium. This performance is related to the non ideal behaviour of the Pd-based membrane.

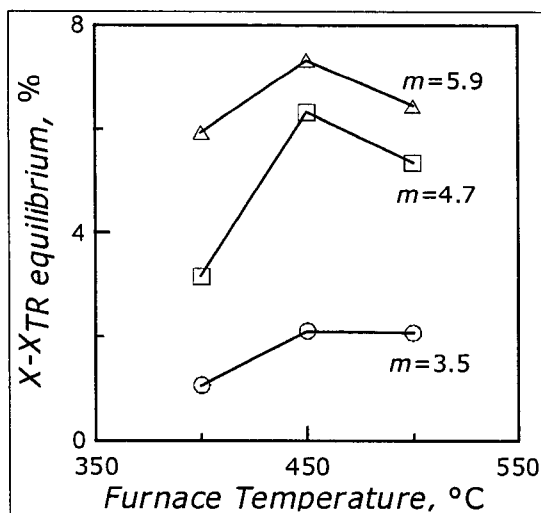


Fig. 4 – Difference between the methane conversion in a MR and in a TR as a function of $T^{Furnace}$ in the reactor MR-P and for m equal to a (O) 3.5, (□) 4.7, (Δ) 5.9.

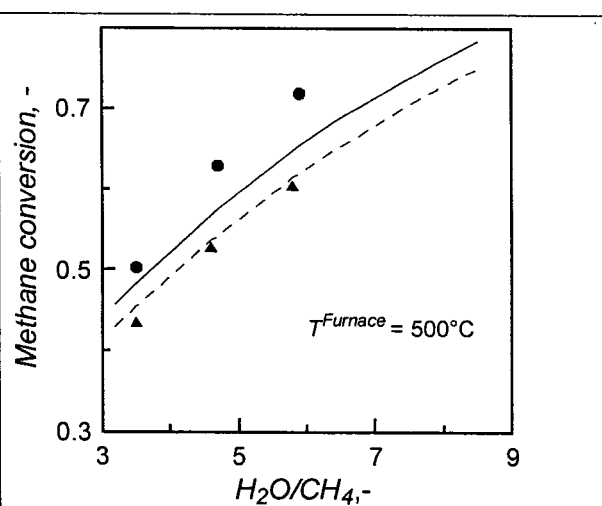


Fig. 5 – Methane conversion experimental data as a function of the molar feed ratio, $T=500^\circ\text{C}$. (Δ) MR-P, (○) MR-Pd.

Equilibrium conversion at 101 kPa (continuous line) and 121 kPa (dashed line).

Permeation tests on silica membranes supplied by KRICT

Single gas, N₂, H₂, CH₄, permeation runs were performed for studying the possible use of KRICT membranes for H₂ separation. Table 1 is a summary of experimental permeance and ideal separation factor. Considering the membrane KRICT2, H₂ permeance depends on the applied ΔP^{TM} and so some contribution of viscous flow through defects was present. Furthermore, for KRICT2 and KRICT3 membranes CH₄ permeance was higher than that of N₂ even if it presents a larger kinetic diameter. This indicates that the main contribute was related to the molecular mass indicating that transport mainly occurred by Knudsen diffusion.

Table 1 - Experimental data obtained on the silica membranes at 195°C.

Membrane	T, °C	ΔP , bar	Permeance, nmol/m ² s Pa			ideal Separation Factor	
			H ₂	N ₂	CH ₄	H ₂ /N ₂	H ₂ /CH ₄
KRICT1	175	1.5	2.32	-	-	-	-
KRICT2	195	2	1.46	0.54	0.67	2.7	2.2
		2.5	1.52	-	-	-	-
KRICT3	195	2	1.56	0.58	0.80	2.7	2.0

Conclusions

A reactor prototype was realised for tubular membranes for hydrogen production and purification by means of MSR. This prototype was before used for membrane characterisation and then in reaction runs. Two tubular membranes were used in permeation and reaction experiments showing methane conversion higher than that of a TR thermodynamic equilibrium.

In addition, three flat silica membranes supplied by KRICT were characterised by means of permeation tests.

Acknowledgement

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