CO Selox Reaction Using Y-type Zeolite Catalytic Membranes

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Abstract: The production of CO-free hydrogen streams for feeding PEM-Fuel Cells using catalytic zeolite membrane reactors was analysed by means of selective oxidation. Tubular FAU (Na-Y) zeolite membranes, prepared by a secondary growth method and Pt-loaded, were used in a *flow-through* MR configuration. The catalytic tests were carried out at 200°C and at different pressures with a simulated dry reformate shifted gas mixture (H_2 ca. 60%, CO 1%, plus O_2, N_2, CO_2). The operative O_2/CO stoichiometric equivalent feed ratio was $\lambda = 2$. These catalytic tests, reducing the CO concentration down to $10 \sim 50$ ppm, verified the possibility of MR integration after using a low temperature water-gas shift unit of a fuel processor to convert hydrocarbons into hydrogen-rich gas.

1. Introduction

Fuel cells with proton exchange membrane (PEM-FCs) operating at low temperatures (around 80°C) are being actively developed for portable and transportation power applications. However, small amounts ($10 \sim 100$ ppm) of carbon monoxide in the hydrogen feed dramatically reduce the FC performance[1]. H_2 - rich mixtures obtained from reforming or partial oxidation still contain ca. 1% CO, even after using a low temperature water-gas-shift reactor.

CO selective oxidation (Selox) is widely recognized as the most simple and cost-effective approach for the final purification of H_2 - rich streams without significant hydrogen losses[2]. Typically, Pt-supported catalysts are used[3], in the form of fixed bed or monoliths[2,4,5,6]; the use of catalytic membrane reactors (MRs) has been recently investigated in a few papers [7-9].

Zeolite supported catalysts proved able to promote CO oxidation selectively also owing to the "molecular sieve effect"[10]. CO and O_2, having larger molecular sizes and also higher chemisorbing properties than H_2, are more adsorbed on the catalysts in the zeolite pores than the conventional alumina supported catalysts.

The combination of zeolite membranes with chemical reactors in multifunctional applications owing to their thermal and chemical resistance and easy catalytic activation is an interesting possibility. In the catalytic membrane the zeolite molecular sieve effect works in synergy with the Pt catalytic activity, resulting in an assemblage of nanoreactors. These catalytic MRs have numerous advantages over conventional fixed bed reactors: the catalytic surface directly available, reduced by-pass problems and small pressure drop. Moreover, the unidirectional transport in the zeolite layer substitutes a counterdiffusion transport of catalyst pellets, with the potential of intensified catalysis and increased selectivity[11].

Different methods for the controlled preparation of

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supported zeolite membranes by seeding technique (secondary growth) have been established. The secondary growth method, decoupling zeolite nucleation from crystal growth, allows optimising the conditions of each step independently, suppressing the secondary nucleation[12].

In the present work, tubular supported zeolite membranes (Na-Y), prepared with a secondary growth, were used. The Y-type (FAU) zeolite has large pores of 0.74 nm with 1.3 nm cavities[13]. These membranes were Pt-loaded by ion-exchange and their application in MRs was analysed for CO Selox., considering a *flow-through* MR configuration at 200°C. The feed streams simulated a dry reformate shifted gas stream after its upgrading by means of a high and low temperature water gas shift (H_2 ca. 60% and CO 1%). The CO_2 was added in the feed for a more realistic evaluation.

Different pressures (up to 540 kPa) were considered since Steam reforming is conducted at elevated pressures (about 800~1,100 kPa) and higher pressures are preferred in industry to minimize reactor size and energy use.

2. Materials and Methods

Tubular Na-Y zeolite membranes were prepared by means of the secondary growth method (Fig. 1).

The materials used for the membrane preparation are listed in Table 1. Zeolite crystals were seeded on the support for implanting nucleation sites; the crystal growth was accomplished by means of a hydrothermal treatment. The zeolite layer was created on the inner surface of the supports; therefore, it is protected against mechanical damage during the module assembly.

The seeding was accomplished in two different ways[14], while the hydrothermal treatment was identical:

1. Membrane A1 prepared on support with d_{pore} = 60 nm;
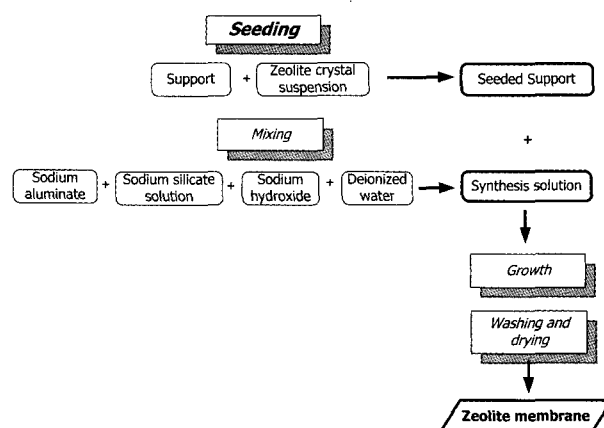2. Membranes B1 and B2 prepared on support with d_{pore} = 100 nm.

Fig. 1. Scheme of the preparation of zeolite (FAU) supported membranes.

Table 1. Materials Used in the Membrane Preparation

Supports:
a-Al_2O_3 tubes (Inocermic GmbH, Germany)
I.D. = 7 mm
O.D. = 10 mm
inner layer d_{pore} = 100 nm and 60 nm

Seeds:
Molecular sieve-Na–X (Aldrich), ca. 2 μm in size

Reagents:
Sodium aluminate (Carlo Erba Reagenti)
Sodium silicate solution (Aldrich)
Sodium hydroxide (NaOH pellets, 97%, Carlo Erba Reagenti)
Deionised water

The catalytic Pt-Y membranes were obtained from Na-Y membranes by means of ion-exchange. Before catalytic tests the Pt-Y membrane were calcined in air at 250°C and reduced in H_2 to obtain the platinum metallic form[14].

Scanning electron microscopy (SEM) using a Cambridge Zeiss LEO 400 microscope was employed for checking the surface morphology and thickness of the zeolite layer over the support surface. Energy dispersive X-ray (EDX) performed with EDAX-Phoenix (SUTW Detector, analyzer: Si/Li crystal) was used to investigate the presence of siliceous species in the po-

rous support. Powder X-ray diffractometry (XRD) with a Philips PW 1730/10 X-ray diffractometer (using Ni-filtered Cu $K_{\alpha 1}$+ $K_{\alpha 2}$, λ = 1.542 Å) was performed on the material scratched from the surface of the samples.

The membrane quality was evaluated by permeation tests with pure gases (H_2 and N_2) at room temperature. The trans-membrane pressure difference (ΔP^{TM}), the permeation driving force, was set by controlling the pressure at the feed side, with atmospheric pressure on the permeate side. No sweep-gas was used. The permeating flux (J) was measured in steady state by means of soap flow meters, and then used for calculating the gas permeance:

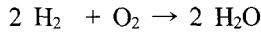$$Permeance = \frac{J}{\Delta P^{TM}} \tag{1}$$

The ratio of the permeances of two pure gases measured in the same conditions is the ideal separation factor (SF).

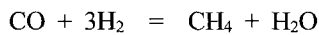The reactions involved in the Selox process are:

1. CO oxidation

   2 CO + O_2 → 2 CO_2 *desired*

2. H_2 oxidation

   2 H_2 + O_2 → 2 H_2O
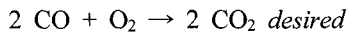
3. Reverse water gas shift

   CO_2 + H_2 = CO + H_2O

4. Methanation

   CO + $3H_2$ = CH_4 + H_2O

While water gas shift is beneficial in its forward direction, methanation reactions are always detrimental and should be avoided. As also observed in this work, methanation does not occur over Pt-based catalysts. As a result, CO is exclusively converted to CO_2.

The process parameter λ, the O_2/CO stoichiometric equivalent feed ratio, is a function of the molar flow rates of oxygen and carbon monoxide:

$$\lambda = 2\frac{F_{O2}^{Feed}}{F_{CO}^{Feed}} \tag{2}$$

The CO and the O_2 conversions were based on the oxygen and the carbon monoxide consumption, respectively, using the inlet and outlet measured flow rates (F_i).

$$X_{CO} = \frac{F_{CO}^{Feed} - F_{CO}^{Permeate}}{F_{CO}^{Feed}} \tag{3}$$

$$X_{O2} = \frac{F_{O2}^{Feed} - F_{O2}^{Permeate}}{F_{O2}^{Feed}} \tag{4}$$

The selectivity to CO_2 (desired reaction) was calculated as the ratio of O_2 consumed for the CO oxidation over the total O_2 consumption:

$$S = \frac{1}{2}\frac{\left(F_{CO}^{Feed} - F_{CO}^{Permeate}\right)}{\left(F_{O_2}^{Feed} - F_{O_2}^{Permeate}\right)} =$$
$$= \frac{1}{\lambda}\frac{X_{CO}}{X_{O_2}} \tag{5}$$

It is known that CO conversion is higher at higher λ; but as λ increases, the selectivity toward CO decreases, consuming more H_2.

The CO_2 formation is linearly related to the CO conversion and hence to the stream upgrade value. Therefore, catalyst efficiency, defined as CO_2 yield, indicative of the CO removal with effective oxygen use, was calculated as the ratio between the CO_2 outlet flow rate to the O_2 feed flow rate:

$$Y_{CO2} = \frac{F_{CO2}^{Formed}}{F_{O2}^{Feed}} \tag{6}$$

By using the O_2 conversion (Eq. 4), selectivity (Eq. 5) and CO conversion (Eq. 3), Eq. 6 can be rewritten as:

$$Y_{CO2} = \frac{F_{CO2}^{Formed}}{F_{O2}^{Feed}} = \frac{F_{CO}^{Reacted}}{F_{O2}^{Feed}} = 2\,X_{O_2}\,S = \frac{F_{CO}^{Feed} - F_{CO}^{Permeate}}{F_{O_2}^{Feed}} = \frac{2}{\lambda}X_{CO} \tag{7}$$

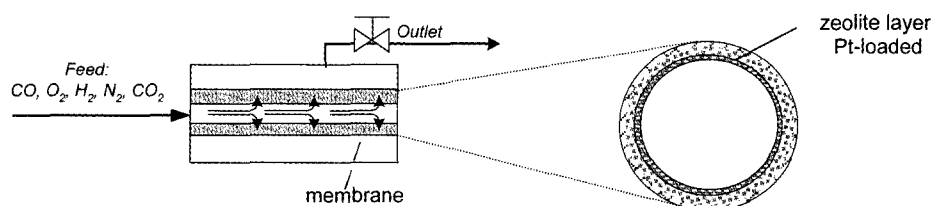The reaction tests were performed in a *flow-through*

Fig. 2. Tubular MR *Flow-through* configuration used in the reaction tests.

Table 2. Feed Gas Molar Compositions and Operating Conditions Used in the Reaction Experiments

	CO %	N_2 %	CO_2 %	H_2 %	O_2 %	λ —	T °C	P kPa
Membrane A1	1	37	-	Bal.	1.1	2.2	200	100~400
		23	15	Bal.				100~400
Membrane B1		37	-	Bal.	1	2		200~300
Membrane B2		37	-	Bal.	1	2		170~540

MR operating in continuous mode: the reactant mixture forced through the membrane (Fig. 2).

The reaction pressure was varied by means of a regulation valve on the outlet stream. The MR module was placed into a furnace with PID control. The feed flow rate of all inlet gases was fixed by using mass flow controllers (MFCs, Brooks Instrument). The MR outlet stream composition was analyzed by a microgaschromatograph (Micro GC 3000A, Agilent) equipped with TCD detectors and Molsieve 5A PLOT and PLOT Q columns. The CO detection limit was 5 ppm.

The CO conversion and selectivity were determined periodically until the reaction reached steady state.

The feed compositions and the operating conditions considered are reported in Table 2.

Desirably, the O_2 required for the Selox reaction is about two times the stoichiometric amount required to react the CO in the reformate. If the amount of O_2 exceeds the stoichiometric amount needed about twice, excessive consumption of H_2 results. On the other hand, insufficient CO oxidation will occur if the amount of O_2 is substantially less than about twice the stoichiometric amount needed. Therefore, the catalytic tests were carried out at $\lambda = 2 \sim 2.2$.

3. Results and Discussion

The XRD analyses confirmed the presence of FAU topology on the support surface. EDX analyses confirmed the absence of the silicon species across the support pores, this data verified the absence of the synthesis solution infiltration in the support pores during the hydrothermal treatment.

Fig. 3-a reports the hydrogen permeance measured at room temperature for the Na-Y membranes prepared with different seeding conditions. The permeation data indicate that a better quality for membranes B1 and B2 (support d_{pore} = 100 nm) which present lower permeance and higher selectivity than the A1 membrane (support d_{pore} = 60 nm).

The H_2/N_2 ideal separation factor is reported in Fig. 3-b; it is less than 4. Higher values are not expected because these molecules have kinetic diameters significantly smaller than NaY membrane pores; however, in the present work, the catalytic activity in the CO Selox reaction is principal role of the FAU membranes.

The better permeation properties of membranes B1 and B2 are also related to a higher permeance reduction with respect to the bare support (Fig. 4). A better
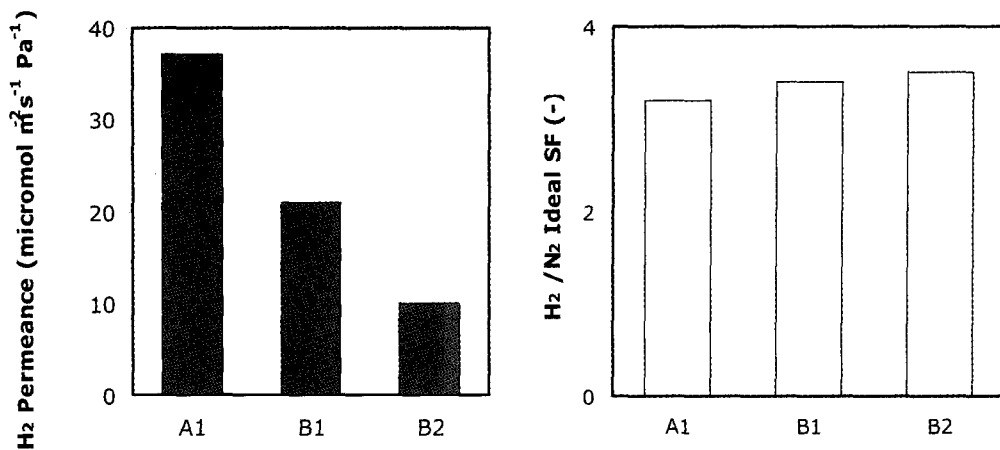
Fig. 3. a) H_2 permeance; b) Ideal SF H_2/N_2 at room temperature for the different Na-Y membranes.
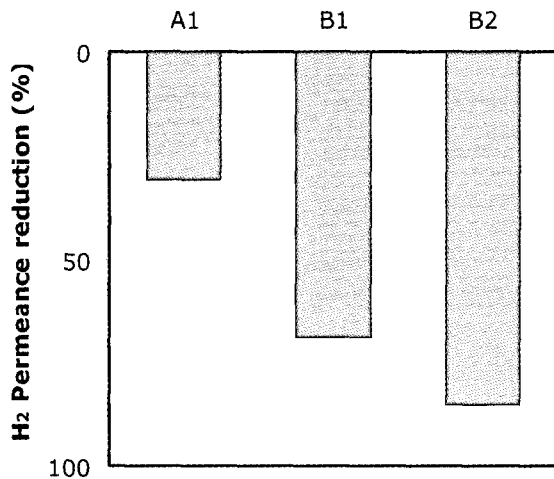

Fig. 4. H_2 permeance reduction for the Na-Y membranes with respect to the bare supports.

support coverage was achieved for membranes B1 and B2 even if they were prepared using 100 nm supports, which are more permeable than the 60 nm ones.

Fig. 5 a~d compare the cross-section and top-view of a zeolitic membrane and the bare support (d_{pore} = 100 nm). A clear modification of the support cross section is shown. The zeolite layer (25 μm) is very compact and uniform with small (1.5~2.5 μm) and well intergrown crystals on the support surface.

The results of the catalytic tests on the three different PtY membranes are presented in the following figures.

Fig. 6 reports the steady-state values of CO conversion *versus* the selectivity measured at 200°C for

the three membranes. High activity of CO oxidation means reduced size of catalytic membrane reactor, while high CO_2 selectivity means better O_2 use. However, working at λ = 2 a complete CO conversion can be achieved with a selectivity around 50%.

Membranes B1 and B2 provided very low CO concentration in the MR outlet with a higher selectivity than membrane A1. The increase in the reaction pressure was advantageous for CO conversion, but resulted in a lower selectivity.

Fig. 7 reports the reaction data as CO_2 yield *versus* CO conversion. The experimental data are lined up on the line with a slope $2/\lambda$. An efficient and selective system should be located, on this line, in the diagram upper part (total CO conversion and high CO_2 yield). Therefore, the increase in the reaction pressure is useful in improving both CO conversion and CO_2 yield owing to the increasing role of adsorption (in- creasing loadings) with increasing pressure. Even if the selectivity was reduced by increasing the reaction pressure (Fig. 6), however, both CO conversion and CO_2 yield were improved (Fig. 7).

The CO concentration measured at the MR exit at steady state conditions, varying the operating pressure is reported in Fig. 8. The increase in the reaction pressure resulted in a better CO removal for all the MRs considered. This effect is more marked for membrane A1.
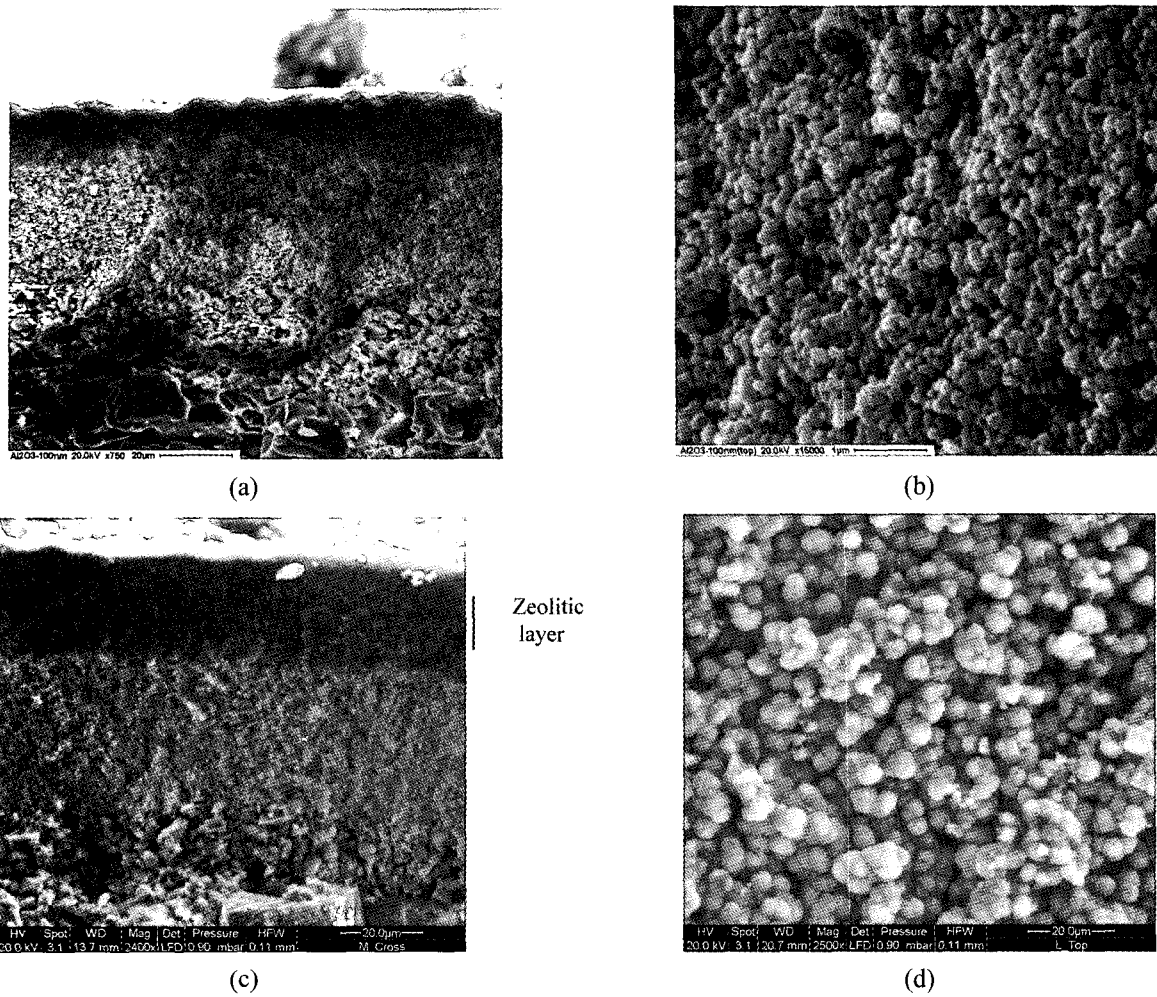
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(a)

(b)

Zeolitic layer

(c)

(d)

Fig. 5. SEM analysis: (a) cross section and (b) top-view of α-Al_2O_3 support (d_{pore} = 100 nm); (c) cross section and (d) top-view of B1 membrane.
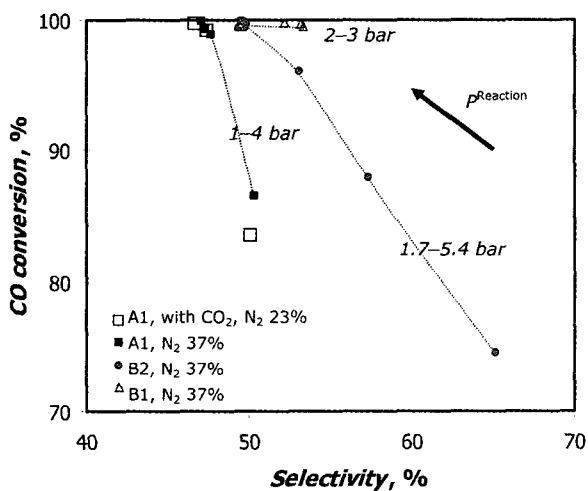

Fig. 6. CO conversion *versus* the selectivity measured at 200°C.

However, good results were obtained in terms of CO reduction with membranes B1 and B2 that effectively lowered the CO amount to less than 30 ppm, also at low pressure values. Therefore, ca. 2 times the stoichiometric amount of oxygen (O_2/CO = 1) was enough to completely oxidize 10,000 ppm (1%) CO.

A deep CO removal (c. 10 ppm) was achieved also for membrane A1 operating at 400 kPa and no CO_2 in the feed. The addition of CO_2 (15%) to the A1 feed stream slightly reduced the MR performance (Fig. 8, open squares). A more pronounced CO_2 effect was observed at 100 kPa, while the difference in the CO content measured in the MR outlet stream was lower at higher reaction pressures.
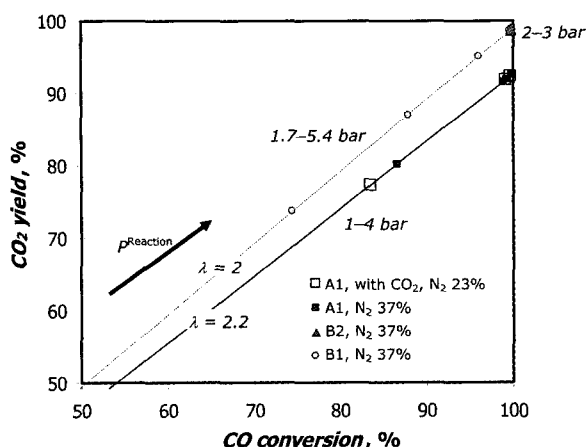
Fig. 7. CO conversion *versus* the selectivity measured at 200°C.
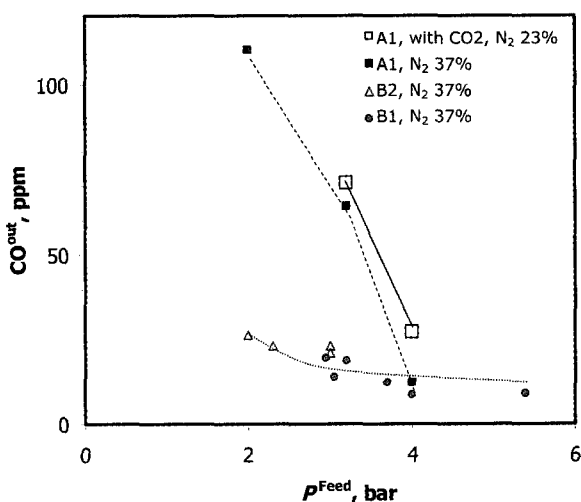

Fig. 8. Measured CO concentration in the MR outlet stream *versus* the reaction pressure at 200°C.

The performance of the membranes considered seem to be related to their permeation properties: the less permeable membrane is the more effective membrane in the catalytic Selox tests.

The promising results suggest the CO Selox MR integration after the high and low temperature water gas shift units in the H_2 production cycle (Fig. 9).

The catalytic MR can effectively operate at the same temperature conditions as the low-temperature shift reactor (200~220°C). No heat exchangers should be required for temperature reduction between the water gas shift and Selox units.
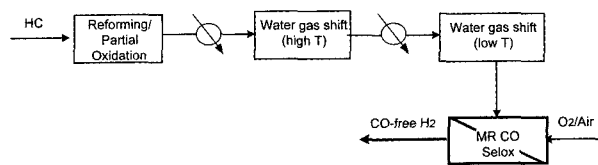

Fig. 9. Schematic description of a hydrogen production process. CO Selox in MRs.

4. Conclusions

Catalytic MRs with Pt-Y membranes, operating in a *flow-through* configuration for CO Selox reaction, succeeded in reducing the outlet CO concentration from 10,000 ppm (1%) down to 10~50 ppm. These good results were achieved at 200°C, using a quite low O_2/CO stoichiometric equivalent feed ratio ($\lambda=2$) and operating at moderate pressure values (less than 600 kPa). The good selectivity measured (> 50%) at a complete CO removal is important for improved fuel consumption efficiency.

The better the membrane quality the higher the CO removal also at low reaction pressure values.

The results here presented confirm the good potentiality of catalytic membranes for the final purification of H_2-rich streams, allowing the hydrogen final use e.g., in fuel cell applications.

References

1. B. Rohland and V. Plzak, The PEMFC-integrated

CO oxidation - a novel method of simplifying the fuel cell plant, *Journal of Power Sources* **84**, 183-186 (1999).

2. A. Manasilp and E. Gulari, Selective CO oxidation over Pt/alumina catalysts for fuel cell applications, *Applied Catalysis B*37 17-25 (2002).

3. Y. Choi and H. G. Stenger, Kinetics, simulation and insights for CO selective oxidation in fuel cell applications, *Journal of Power Sources* **129**, 246-254 (2004).

4. S. H. Oh and R. M. Sinkevitch, Carbon monoxide removal from hydrogen-rich fuel cell feed streams by selective catalytic oxidation, *Journal of Catalysis*, **142**, 254-262 (1993).

5. M. J. Kahlich, H. A. Gasteiger, and R. J. Behm, Kinetics of the selective CO oxidation in H_2-rich gas on Pt/Al_2O_3, *Journal of Catalysis*, **171**, 93-105 (1997).

6. I. Rosso, C. Galletti, G. Saracco, E. Garrone, and V. Specchia, Development of A zeolites-supported noble-metal catalysts for CO preferential oxidation: H_2 gas purification for fuel cell, *Applied Catalysis B*, **48**, 195-203 (2004).

7. Y. Hasegawa, A. Ueda, K. Kusakabe, and S. Morooka, Oxidation of CO in hydrogen-rich gas using a novel membrane combined with a microporous SiO_2 layer and a metal-loaded γ-Al_2O_3 layer,

Applied Catalysis A, **225**, 109-115 (2002).

8. Y. Hasegawa, K. Kusakabe, and S. Morooka, Selective oxidation of carbon monoxide in hydrogen-rich mixtures by permeation through a platinum-loaded Ytype zeolite membrane, *Journal of Membrane Science*, 190, 1-8 (2001).

9. P. Bernardo, C. Algieri, G. Barbieri, and E. Drioli, Catalytic (PtY) membranes for the purification of H_2rich streams, *Catalysis Today*, **118**, 90-97 (2006).

10. M. Kotobuki, A. Watanabe, H. Uchida, H. Yamashita, and M. Watanabe, *Chem. Letters*, **34**, 866 (2005).

11. V. Teplyakov, M. Tsodikov, M. Magsumov, I. Moiseev, and F. Kapteijn, Intensification of gas phase catalytic processes in nanochannels of ceramic catalytic membranes, *Desalination*, **199**, 161-163 (2006).

12. C. Algieri, G. Golemme, S. Kallus, and J. D. F. Ramsay, Preparation of thin supported MFI membranes by in situ nucleation and secondary growth, *Microporous and Mesoporous Materials*, **47**, 12 (2006).

13. D. W. Breck, Zeolite molecular sieves, New York: Wiley-Interscience (1974).

14. C. Algieri, P. Bernardo, G. Barbieri, and E. Drioli, Preparation of Catalytic (PtY) membranes for the purification of H_2rich streams (2006), *in preparation.*