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Catalytic (Pt-Y) membranes for the purification of H_2-rich streams

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Abstract

CO selective oxidation (Selox) for the purification of hydrogen-rich streams was studied in membrane reactors (MRs) using Pt-loaded catalytic membranes. The catalytic membranes were prepared by the ion-exchange of FAU (Na-Y) zeolitic membranes that were synthesized on tubular α-Al_2O_3 supports by a secondary growth method.

The catalytic MR tests were performed analysing the CO conversion, O_2 selectivity and yield of the desired reaction. Different feed compositions (CO, O_2, H_2 and N_2 content and O_2/CO ratio), temperatures and pressures were considered with *space-time* values in the range 0.27–1.2 mg_{Pt} min/cm^3(STP). The CO content in preliminary tests was 10%, 1% in the other experiments. A simulated reformate shifted gas mixture (H_2 = 60%) was also used.

A comparison with other literature data for MRs utilizing different membrane types and packed bed traditional reactors with Pt-based catalysts is also provided.

The identified ranges of operating conditions (temperature, pressure, feed molar O_2/CO ratio and feed concentration) suggest a profitable use of the catalytic MR (Pt-Y zeolite membranes) for CO Selox after the low-temperature water gas shift unit of a fuel processor converting hydrocarbons into hydrogen-rich gas, operating at similar temperature conditions.

Keywords: CO Selox; Membrane reactors; Catalytic Pt-loaded zeolite membranes

1. Introduction

The unique pore structure of zeolites has attracted wide interest in preparing highly dispersed metal catalysts. Metal loaded zeolitic membranes are promising candidates as catalytic membranes for high temperature reactions that are of interest to the petrochemical industry.

Selective CO oxidation (Selox) is known as an interesting and economic approach for CO removal from H_2-rich gas streams produced by reforming processes or available in petrochemical plants (e.g., in ethylene plants), opening their use to some other operations, such as, ammonia synthesis, hydrogenations and fuel cell applications (proton-exchange membrane fuel cells).

A selective catalyst is necessary in order to avoid H_2 consumption, since two competitive reactions take place, CO and H_2 oxidation:

$$2CO + O_2 \rightarrow 2CO_2 \quad (1)$$

$$2H_2 + O_2 \rightarrow 2H_2O \quad (2)$$

Pt-supported catalysts are typically used [1], since CO is more strongly adsorbed than H_2 on the Pt metal surface [2].

Oh and Sinkevitch [3], using a feed mixture $CO:O_2:H_2:N_2$ = 900 ppm:800 ppm:0.85%:balance, found Ru and Rh to be more selective (selectivity of about 80% with a quite total CO conversion) compared to Pt/alumina. However, Ru is known to be active also for CO and CO_2 hydrogenation (methanation, undesired side reaction that causes substantial loss of H_2) above 200 °C, while the rate of this reaction is negligible on Pt/alumina catalysts in the temperature range 150–250 °C (relevant for the CO Selox) [4].

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Kahlich et al. [4], studying the kinetics of CO Selox on a 0.5% Pt/Al_2O_3 catalyst with a more realistic feed mixture ($CO:O_2:H_2:N_2$ = 1:1:75:balance), measured conversion below 80%, even at 250 °C. The selectivity was around 40%. They also estimated the best temperature (200 °C) for CO Selox over a Pt/alumina catalyst and that 2.5 times the stoichiometric amount of oxygen (O_2/CO = 1.25) would be necessary to completely oxidize 1% CO.

Igarashi and co-workers [5] used Pt/zeolite (A-type, mordenite and X-type) catalysts, showing a rather higher selectivity for the Pt/A and Pt/mordenite catalysts and lower conversions than the Pt/Al_2O_3. Using a feed mixture of $CO:O_2:H_2$ = 1:1:98 with a catalyst weight to flow rate ratio of 0.06 g/(cm^3/s), the maximum conversion was 60–80% above 200 °C and the maximum selectivity 30–60%. Moreover, CO selectivity approached 100% reducing the O_2/CO feed ratio to zero. The authors [5] also found that 1% CO in the gas feed was never completely oxidized on a Pt/Al_2O_3 catalyst even with a high O_2 molar fraction (ca. 3%) in the feed gas.

Korotkikh and Farrauto [6] investigated CO Selox by a proprietary Pt/γ-alumina catalyst (monolith) promoted by a base metal oxide in a stream mixture containing 0.1% CO, 20% H_2, 10% H_2O and varying the O_2/CO ratio with the balance N_2. They observed a high selectivity and activity at temperatures below 150 °C.

Manasilp and Gulari [7] studied CO Selox using feed mixtures of $CO:O_2:CO_2:H_2O:H_2:He$ = 1:1:0–25:0–10:60:balance over aluminium oxide supported Pt (1 and 2%) catalysts. Their 2% Pt/alumina sol–gel catalyst selectively oxidized CO down to a few ppm with constant selectivity (ca. 50%) at a high space velocity. Water vapour in the feed considerably increased the catalyst activity, whereas in the absence of water vapour, the fed CO_2 decreased the catalyst activity significantly.

Rosso et al. [8] used Pt, Pd and Ru-based zeolite catalysts, prepared by wet impregnation, in a fixed bed reactor. The Pt-catalysts showed complete CO conversion and a comparatively high selectivity with respect to supported Pd and Ru catalysts. The 1% Pt-3A catalyst showed the best performance: complete CO conversion in a wide temperature range, the highest selectivity for CO oxidation with minimal involvement in side reactions, such as reverse water gas shift.

Most of these Selox catalysts have been studied over fixed bed or monolithic catalysts; the use of catalytic membrane reactors (MRs), promising reactors based on unique short contact time substrates (the membrane), was investigated only in a few papers with metal loaded γ-Al_2O_3 and zeolite Y membranes [9–12]. Working with a feed mixture $CO:O_2:H_2$ = 1.85:1.23:balance, a Pt/γ-Al_2O_3 membrane presented a maximum CO conversion of ca. 50% at 230 °C with a 20% selectivity [9]. The other papers [10–12] report experimental data in terms of CO outlet concentration and measured flux, not in terms of CO conversion and selectivity. The CO concentration was reduced below 10 ppm at 200–250 °C using a Pt-Y membrane [10]. A Pt-Y membrane showed the highest CO oxidation rate with respect to Ru, Rh, Co, Ni, Cu and Ag-loaded membranes [12]; however, the CO was reduced to several hundred ppm.

In the present work, CO Selox in H_2-rich mixtures was studied using catalytic Pt-Y zeolite membranes prepared by ion-exchange. These membranes combine selective permeation with Pt catalytic activity. In particular, Y (FAU) crystals present 0.74 nm pores and 1.38 nm cavities where CO (kinetic diameter = 0.376 nm) and O_2 (kinetic diameter = 0.346 nm) can easily enter and react. The catalytic membrane can be seen as a ''nanoengineered'' catalyst, since catalytically active nanoparticles are entrapped in a thin zeolite layer (a few microns thick). Thus, improved catalyst performance by effectively using the catalytic species, avoiding the problems related to the use of small particles in fixed bed reactors and also to by-pass, are expected from the catalytic membrane.

2. Experimental

2.1. Preparation of catalytic membranes

High flux FAU (Na-Y) zeolite membranes were prepared by a secondary growth method using a new continuous seeding phase [13]. The membranes present the zeolite layer on the inner surface of α-Al_2O_3 tubular supports. Two Pt-Y membranes, denoted as Membranes A and B, were used for the catalytic reaction. The membranes were prepared at the same time, and their characteristics are reported in Table 1.

The Na-Y membranes were Pt-loaded by means of ion-exchange using a Pt-salt ($[Pt(NH_3)_4]Cl_2$) solution (Fig. 1), according to Hasegawa et al. [10]. An aqueous solution of $[Pt(NH_3)_4]Cl_2$ is typically used in the preparation of Pt-based catalysts supported on zeolites, since amminated salts have the advantage of a rapid formation of readily reducible hydrogenates species, while Pt^{2+} ions in aqueous solution are strongly acid and can attach to the zeolite with possible dealumination and membrane destruction [14].

The Pt amount in the membranes was evaluated as the difference between the initial and final solutions used for the ion-exchange by means of atomic absorption spectrometry (GBC 932 PLUS instrument). The Pt load (5 mg) on the membranes was ca. 0.1 wt%.

Before catalytic tests the two Pt-Y membranes were calcined in air (20 cm^3(STP)/min) at 250 °C for 3 h and reduced in a H_2

Table 1
Characteristics of the zeolite Na-Y membranes (Membranes A and B)

Support d_{pore} (nm)	60
ID (mm)	7
OD (mm)	10
Effective membrane length (cm)	8 (glazed ends 1 cm each)
Seeds	Commercial crystals (Na-X, ca. 2 μm in size)
Seeding time (h)	6
Hydrothermal synthesis	24 h, 90 °C
Membrane area (cm^2)	17.6
Membrane thickness (μm)	ca. 10
H_2 permeance at 200 °C	14 μmol/m^2 s Pa (Membrane A) 18 μmol/m^2 s Pa (Membrane B)
H_2/N_2 ideal separation factor	2.45 (Membrane A) 2.87 (Membrane B)

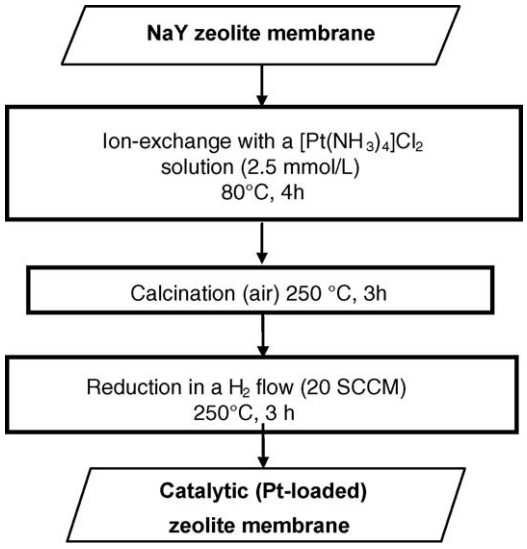

Fig. 1. Preparation method of the Pt-Y zeolite membranes.

flow (20 cm^3(STP)/min) for 3 h in order to obtain the metallic phase.

2.2. Catalytic membrane reaction tests

The MR was used in a *flow-through* configuration (Fig. 2), forcing the permeation of all the feed species through the membrane from the tube towards the annular volume. The reaction pressure, the average of the feed and permeate ones, was varied by means of a regulation valve on the permeate stream.

The operation of the system (flow-through) imposes that all species of the gas mixture permeate completely through the membrane with no accumulation in steady state, as experimentally observed: no pressure increase was measured with time. The slower permeating species such as N_2 occupying the membrane pores obstacle the permeation of faster permeating species (e.g., H_2).

The MR was put into a furnace with PID control. Mass flow controllers (MFCs, Brooks Instrument) were used for controlling the feed flow rate of all inlet gases. Bubble soap flowmeters were used to measure the flow rate of the inlet (during the check phase) and the outlet streams.

In the reaction tests carried out with ca. 10% CO in the feed the chemical analyses on the product stream were performed by means of a gas chromatograph (6890 N, Agilent). The gas chromatograph is equipped with a TCD detector and two columns: an HP-Plot-5A (for separating permanent gases such as H_2, N_2 and CO) and an HP-Poraplot-Q (for other species).

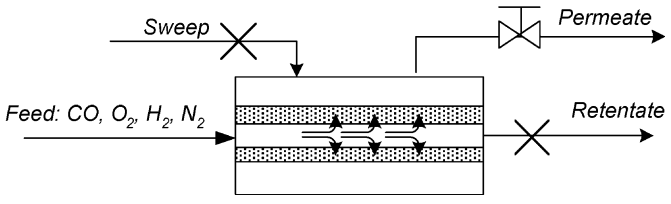

Fig. 2. *Flow-through* MR configuration used in the reaction tests.

In the reaction tests carried out feeding low CO concentrations (ca. 1%), the reaction products were analyzed by a microgas chromatograph (Micro GC 3000 A, Agilent) with TCD detectors and Molsieve 5A PLOT and PLOT Q columns. The CO detection limit of the microgas chromatograph was 5 ppm.

An important parameter is the O_2/CO stoichiometric equivalent feed molar ratio λ, considering the stoichiometry of the reaction (1) (λ = 1 for stoichiometric feed):

$$\lambda = 2\frac{F_{O_2}^{Feed}}{F_{CO}^{Feed}} \tag{3}$$

The CO conversion (X_{CO}) was calculated directly over the CO balance assuming that CO reacts to give only CO_2, also since no methane was detected at the reactor exit.

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

The O_2 conversion (X_{O_2}) was calculated as

$$X_{O_2} = \frac{F_{O_2}^{Feed} - F_{O_2}^{Permeate}}{F_{O_2}^{Feed}} \tag{5}$$

The oxygen selectivity (S) is defined as the ratio of O_2 consumed for the CO oxidation reaction (1) over the total O_2 consumption:

$$S = \frac{1}{2}\frac{(F_{CO}^{Feed} - F_{CO}^{Permeate})}{(F_{O_2}^{Feed} - F_{O_2}^{Permeate})} = \frac{1}{\lambda}\frac{X_{CO}}{X_{O_2}} \tag{6}$$
$$X_{CO} = \lambda S X_{O_2}$$

The higher the λ (higher O_2 concentration), the lower the selectivity (Eq. (6)).

The CO_2 yield is the ratio of the CO_2 produced by reaction (1) to the O_2 in the feed, O_2 being involved in the two parallel reactions ((1) and (2)).

$$Y_{CO_2} = \frac{F_{CO_2}^{Formed}}{F_{O_2}^{Feed}} \tag{7}$$

It can be rewritten using the O_2 conversion (Eq. (5)) and selectivity (Eq. (6)) and also CO conversion (Eq. (4)):

$$Y_{CO_2} = \frac{F_{CO_2}^{Formed}}{F_{O_2}^{Feed}} = \frac{F_{CO}^{Reacted}}{F_{O_2}^{Feed}} = 2SX_{O_2} \tag{7}$$

$$Y_{CO_2} = \frac{F_{CO}^{Feed} - F_{CO}^{Permeate}}{F_{O_2}^{Feed}} = \frac{2}{\lambda}X_{CO} \tag{8}$$

The CO_2 yield is two times the O_2 conversion multiplied for selectivity (Eq. (7)); this means, e.g., that when one O_2 mole is totally converted at unitary selectivity two moles of CO_2 are produced. The same factor of 2 is showed in the relationship between the CO_2 yield and CO conversion (Eq. (8)) due to the CO_2 yield definition; therefore, in the next Fig. 8 the y-scale is 0–2.

CO_2 is a non-valuable product and it is dangerous for the environment; however, in this case the CO_2 formation is

linearly related to the CO conversion and hence to the stream upgrade value. Therefore, the CO_2 yield will be a useful variable in the data discussion and comparison.

In order to compare the results obtained in this work with other data reported in the open literature, the following expression of the *space-time* was considered:

$$\text{space}-\text{time} = \frac{\text{weight}_{\text{active metal}}}{F_{\text{CO}}^{\text{Feed}}}; \left[\frac{\text{mg}}{\text{cm}^3(\text{STP})/\text{min}}\right] \quad (9)$$

Only the weight of the active metal phase contained in the catalyst and the inlet CO flow rate were taken into account.

The reaction tests were carried out at different temperatures (160–240 °C), varying the reaction pressure (1–2.6 bar) and using the feed mixtures described in Table 2. In the following, the feed mixture composition will be in mol% and the volumetric flow rates will be reported at standard temperature and pressure (STP; 25 °C and 101.3 kPa).

Steady-state conversions collected after ca. 3–5 h are reported. No coke formation was analysed also for the very low CO concentration in the feed (ca. 1%). The carbon balance was generally within 1–2%, in a few cases within 5–7%.

No catalytic zeolite pellet was prepared and thus no reaction test was performed in a fixed bed. Experimental data were compared with TR literature data.

3. Results and discussion

Membrane A was tested in catalytic experiments both in the absence and in the presence of H_2. The H_2/CO separation factor measured for the membrane at 200 °C was 2.45 (ideal) or 1.45 using an equimolecular H_2–CO mixture (actual). It is lower than the Knudsen value of 3.74. However, the Y-type zeolite membrane is used as a catalytic membrane and not in a gas separation application also for its large pore size. Therefore, also CO, the slower permeating species, has to pass quantitatively through the membrane for its conversion.

Mixtures 1 and 2 (CO = 10.5%; λ = 1.66) were used as feed. In both cases, the total flow rate was 190 cm^3(STP)/min and the *space-time* was 0.27 mg_{Pt} min/cm^3(STP).

The operating temperature was 200 °C, indicated as the best value for CO Selox in a kinetics study on Pt/Al_2O_3 catalysts [4] and in a study on the selectivity and activity of Pt supported on different zeolites (A-type, mordenite and X-type) and on alumina [5].

Table 2
Feed gas molar compositions (%), stoichiometric equivalent feed molar ratio (λ) and *space-time* values used in the reaction experiments

Mixture	CO	O_2	H_2	N_2	λ	*Space-time* mg_{Pt} min/cm^3(STP)
1	10.5	8.7	–	80.8	1.66	0.27
2	10.5	8.7	80.8	–	1.66	0.27
3	1.3	2.3	96.4	–	3.6	1.2
4	1	1	98	–	2	0.86
5	1	1	87	11	2	0.94
6	1	1	61	37	2	0.86
7	1	1.4	97.6	–	2.8	0.88

1 vol.% = 10,000 ppm

Table 3
Reaction tests in MR using a catalytic Pt-Y membrane (Membrane A) at 200 °C

	Feed molar composition (vol.%)				X_{CO} (%)	*S* (%)
	H_2	CO	O_2	N_2		
Mixture 1	–	10.5	8.7	80.8	~100	100
Mixture 2	80.8	10.5	8.7	–	98	62

λ = 1.66.

Under hydrogen-free conditions (Mixture 1), Membrane A reached 100% CO conversion at 200 °C. A very high CO conversion (98%) and a CO selectivity of 62% were measured when the same membrane was tested in the presence of H_2 (Mixture 2) (Table 3).

The MR data measured with Mixture 2 were compared with those measured by Goerke et al. [15] in microreactors; Fig. 3 reports a general comparison. They used different catalysts (Au/α-Fe_2O_3, CuO/CeO_2 and Au/CeO_2) applied to micro-structured metal foils (channel width = 200 μm, channel height = 70 μm), which were stacked in a clamping device. Their CO maximum conversion was measured at 195 °C, with a feed mixture containing ca. 8% CO (λ = 1.5).

In similar reaction conditions (temperature, pressure, *space-time* and λ) the MR was more efficient than the microreactor (Au/α-Fe_2O_3), a possible explanation is the permeation and Pt catalytic activity combination. The MR conversion (total) is higher than the other two microreactors (55 and 80%); the selectivity is slightly higher even if the MR H_2 feed concentration is twice that of the microreactors using a higher *space-time*.

The catalytic membrane behaviour for CO Selox with H_2-rich streams containing ca. 1% CO, changing the feed composition (H_2 content and O_2/CO ratio), the reaction temperature and pressure was investigated. These tests were carried out using the other Pt-Y membrane (Membrane B) and increasing the *space-time* to ca. 1 mg_{Pt} min/cm^3(STP).

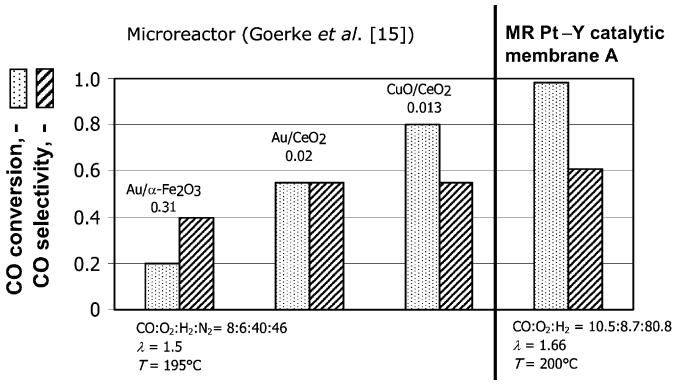

Fig. 3. CO conversion and selectivity in microreactors [15] and in MR. This work, Pt-Y catalytic membrane (Membrane A): *space-time* = 0.27 mg_{Pt} min/cm^3(STP); Goerke et al. [15], microreactors:

Au/α-Fe_2O_3: *space-time* = 0.31 mg_{Au} min/cm^3(STP);
Au/CeO_2: *space-time* = 0.020 mg_{Au} min/cm^3(STP);
CuO/CeO_2: *space-time* = 0.013 mg_{Cu} min/cm^3(STP).

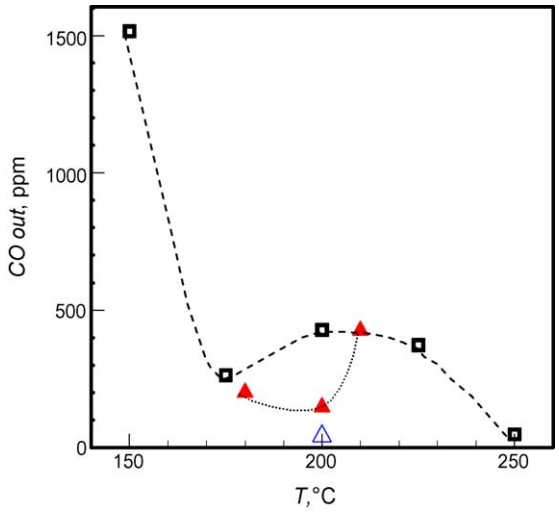

Fig. 4. CO concentration in the MR outlet stream as a function of temperature. Triangles: this work, catalytic membrane (Membrane B), ▲: $P^{Reaction}$ = 1 bar; △: $P^{Reaction}$ = 2 bar; Feed CO:O_2:H_2 = 1.3:2.3:96.4; λ = 3.6; *space-time* = 1.2 mg_{Pt} min/cm^3 (STP). □: data from Hasegawa et al. [9], Feed CO:O_2:H_2 = 4.7:7.5:88.4; λ = 3.2.

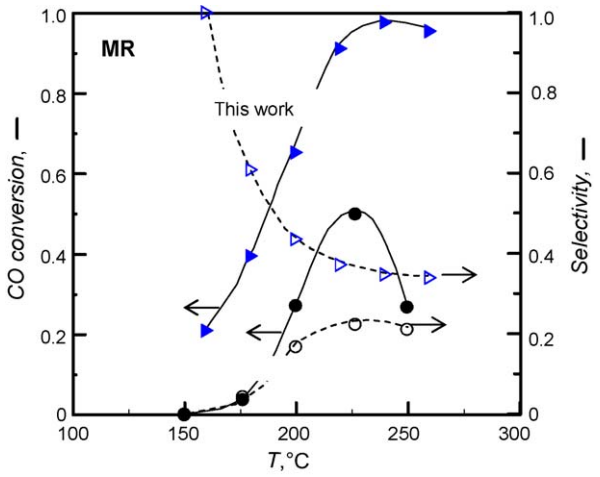

Fig. 5. CO conversion (filled symbols) and selectivity (open symbols) measured as a function of temperature in MRs with Pt-based catalytic membranes. ▶, ▷: this work, (Membrane B), feed O_2:CO:H_2 = 1.4:1:balance; λ = 2.8; 0.88 mg_{Pt} min/cm^3(STP); ●, ○: data from Hasegawa et al. [9], feed O_2:CO:H_2 = 1.85:1.23:balance.; λ = 3.0.

Some reaction experiments were performed feeding Mixture 3 (ca. 350 cm^3(STP)/min; *space-time* = 1.2 mg_{Pt} min/cm^3(STP); λ = 3.6) to the catalytic MR. The furnace temperature was fixed at 180, 200 and 210 °C. The MR output CO concentration is reported in Fig. 4.

Operating at 1 bar Membrane B achieved the better conversion at 200 °C (CO in the permeate side = 146 ppm, Fig. 4). An almost complete CO conversion (X_{CO} = 99.7%, S = 28%, CO_{out} = 42 ppm) was measured at 2 bar and the same temperature of 200 °C. A similar result (CO in the permeate side = 48 ppm) was reported by Hasegawa et al. [9] using a Rh-catalytic membrane (SiO_2/Rh/γ-Al_2O_3), at 250 °C and starting from ca. 5% CO in the feed and λ = 3.2. The present data show a minimum in the CO outlet concentration (maximum CO conversion) at a temperature 20 °C higher than the Hasegawa's results that show also a minimum of CO conversion at a higher temperature. A possible explanation is that the reacting system consists of two competitive reactions; increasing the temperature, the side reaction (2) goes faster consuming more oxygen, which is no longer available for CO oxidation and therefore also CO conversion is lower (Fig. 4). The same behavior was measured by Kahlich et al. [4], Rosso et al. [8] and Han et al. [16].

Other reaction tests were carried out with the Membrane B feeding Mixture 7 (λ = 2.8), at 1 bar and different temperatures in the range 160–240 °C (Fig. 5).

Fig. 5 reports the CO conversion as a function of temperature. CO conversion increases with the temperature as literature data reaching a total value at 230–240 °C; after that a slight decrease was observed. A higher temperature was not investigated being of no interest for CO conversion that can only decrease having achieved the maximum level.

Fig. 5 also reports some data measured in an MR with a Pt/γ-Al_2O_3 membrane (prepared by impregnation) by Hasegawa et al. [9].

The selectivity and its temperature dependence (Fig. 5) differ significantly for the two catalytic membranes. On the Pt-Y Membrane B selectivity steadily decreases with temperature, starting from a very high value (ca. 100%) at 160 °C to about 35% at 260 °C, while in the work of Hasegawa et al. [9] a maximum was reported at 230 °C.

The reaction selectivity is expected to decrease with temperature in Pt-supported catalysts, as shown also by Watanabe et al. [17] with Pt catalysts supported on zeolite. As temperature increases CO is desorbed; this opens up sites for oxygen adsorption and successive reaction. Above a certain temperature the surface fraction covered by CO decreases even further owing also to its improved conversion and hydrogen chemisorbs and reacts in competition with CO; as a consequence, the selectivity towards CO oxidation is reduced [18].

Over the whole temperature range investigated, the Pt-Y Membrane B showed a significantly higher activity and also a better selectivity than that of the Pt/γ-Al_2O_3 membrane [9], using a λ (2.8) similar to the one adopted by Hasegawa et al. [9]. A higher O_2/CO feed ratio usually increases the CO conversion [5,7] but decreases the selectivity, since more hydrogen can react. This comparison evidences the role of the zeolitic layer in the improving of catalytic CO conversion.

Fig. 6 shows a comparison between the data obtained using Membrane B with Mixture 7 and those reported by Rosso et al. [8] for a Pt/zeolite (A-type) catalyst in a packed bed TR. A similar O_2/CO ratio is considered; however, the data reported by Rosso were measured with a feed mixture containing 0.5% CO and also CO_2 and H_2O.

Similar results were obtained in terms of both CO conversion and O_2 selectivity in the temperature range 220–260 °C. At a low-temperature a lower conversion but a higher selectivity were measured in the MR. The lower selectivity reported by Rosso et al. [8] could be the result of a lower feed CO content, as

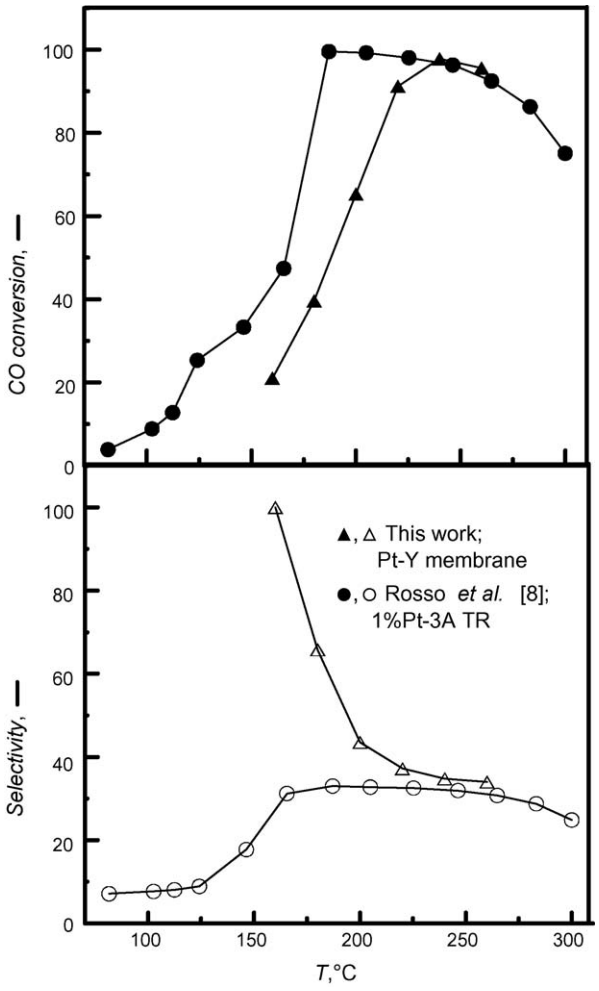

Fig. 6. CO conversion and selectivity as a function of temperature. ▲, △: This work, Pt-Y membrane (Membrane B); Feed O_2:CO:H_2 = 1:1.4:97.6; λ = 2.8; *space-time* = 0.88 mg_{Pt} min/cm^3(STP). ●,○: Rosso et al. [8], 1%Pt-3A catalyst (fixed bed reactor); Feed CO:O_2:H_2:CO_2:H_2O:He = 0.5:0.75:37:18:5:balance; λ = 3; *space-time* = 3 mg_{Pt} min/cm^3(STP).

observed by Kahlich et al. [4]; however, the present catalytic MR operates with a three times lower *space-time* (the catalytic membrane requires a threefold lower Pt amount).

A more appropriate comparison would require the same feed composition, since CO_2 and H_2O can affect the catalyst performance. Manasilp and Gulari [7], using a 2% Pt/Al_2O_3 catalyst observed an increase in the CO maximum conversion from 80 to 97% when 10% water and 25% CO_2 were added in the feed mixture (CO:O_2:H_2:CO_2:H_2O:He = 1:1:60:25:10:3). The selectivity, instead, had a slight increase when water and CO_2 are in the feed. Avgouropulos et al. [19] observed the same effect with a Pt/γ-Al_2O_3 catalyst adding 15% CO_2 and 10% water in the feed. Moreover, Manasilp and Gulari [7] showed with their 2% Pt/Al_2O_3 catalyst a somewhat higher selectivity decreasing the CO inlet concentration from 1 to 0.5% (feed mixture CO:O_2:H_2:CO_2:H_2O:He = 1 or 0.5:1:60:20:10:balance), while the CO conversion increased in the temperature range 110–160 °C.

A comparison between the data of this work (Membrane B) and some data reported in the open literature on CO Selox in traditional reactors (TRs) with Pt-based catalysts is proposed in Fig. 8. These data were all measured at 200 °C, but different feed conditions and *space-times* (ranging from 0.6 to 5) were used. For instance, the number of present species varies from 3 to 6 including sometimes also N_2, He, CO_2 and H_2O, the latter having effect on catalysis. More details about the experimental measurements and literature data are reported in Table 4. In particular, the data related to the Pt-Y catalytic membrane (Membrane B) were obtained with low *space-time* values (ca. 1 mg_{Pt} min/cm^3(STP)). The MR data identify a sort of ''upper bound'' in the CO conversion versus selectivity diagram (dashed lines in Fig. 7). The Pt-Y catalytic membrane Membrane B expands the CO conversion-O_2 selectivity region of TRs, even with low *space-time* values. Therefore, performances similar to those of TRs but using lower Pt amounts can be achieved by the catalytic MR.

Fig. 8 reports the CO_2 yield as a function of the CO conversion measured with the Membrane B. Some lines are drawn for specific λ values (reported in the figure), each of them has slope 2/λ (see Eq. (8)). The CO_2 yield increases linearly with CO conversion (Eq. (7)), varying in the range 0–2 due to the reaction (1) stoichiometry:

$$Y_{CO_2} = 2SX_{O_2} = \frac{2}{\lambda}X_{CO} \quad (10)$$

The CO_2 yield can reach a value of 2 for λ = 1 (O_2 equal or lower than stoichiometric) but the CO conversion is lower than 100%; X_{CO} can be 1 for λ ≥ 1.

An efficient and selective system should be located in the diagram upper part (total CO conversion and high reaction yield). A higher activity of CO oxidation results in the reduced size of catalytic reactor and a higher selectivity reduces the hydrogen consumption (the valuable product).

All experimental data are lined up along the lines at the corresponding λ value, independently of the temperature, pressure and H_2 feed molar fraction and present a yield higher than 50%.

The experimental data distribution along the proper line is a function of temperature, pressure and H_2 feed content.

The O_2/CO feed molar ratio increases the CO conversion; however the CO_2 yield decreases and this means a higher O_2 consumption and hence a higher H_2 oxidation takes place.

A small temperature rise (from 200 to 220 °C) was effective in increasing both CO_2 yield and CO conversion (see line at λ = 2.8). Also the pressure has a positive effect on both CO_2 yield and CO conversion as can be observed for the three different groups of experimental data distributed on the line λ = 2. The different symbols represent the data measured feeding different mixtures, all containing the same molar fraction of O_2 (1%) and CO (1%) but different H_2 (61; 87.5 and 98%) and N_2 (balance) concentrations.

A similar yield was obtained with λ = 2 at 200 °C and 2.6 bar, but the CO conversion was lower than that measured with λ of 2.8 at 220 °C and 1 bar.

A lower hydrogen concentration in the feed (a higher N_2 molar fraction) moves the CO conversion and CO_2 yield

Table 4
Details of the data reported in Fig. 7

	Catalyst	Feed (mol%)							*Space-time* (mg_{Pt} min/cm^3(STP))	$P^{Reaction}$ (bar)	Reference
		CO	O_2	H_2	N_2	He	CO_2	H_2O			
△	Pt-Y membrane B	1.3	2.3	96.4					1.2	2	This work
◀		1	1	98					0.86	1	
▷		1	1	98						2	
◁		1	1	98						2.6	
⊘	Pt/Al_2O_3	1	1	98					5.0	1	Igarashi et al. [5]
●	Pt-A	1	1	98						1	
⊕	Pt-MOR	1	1	98						1	
○	Pt-X	1	1	98						1	
▽	Pt-Y Membrane B	1	1	61	37				0.86	2	This work
▼		1	1	61	37					1	
◘	2% Pt/Al_2O_3	1	1	60		38			3.5	1	Manasilp and Gulari [7]
■		1	1	60		38			1.8	1	
◇	0.5% Pt/γ-Al_2O_3	1	1	75	bal.				0.6	1	Han et al. [16]
◆	0.5% Pt/γ-Al_2O_3	1	1	75	bal.				0.6	1	Kahlich et al. [4]
∗	1% Pt-3A	0.5	0.5	37		bal.	18	5	3.0	1	Rosso et al. [8]
+		0.5	0.75	37		bal.	18	5		1	
×		0.5	1	37		bal.	18	5		1	

towards the diagram upper right end (total conversion and yield).

The N_2 presence has two opposite effects: it increases CO conversion reducing the O_2 selectivity in the meantime. However, better results (a higher CO_2 yield means a better O_2 use) are obtained in the presence of N_2 with Mixture 6 at 200 °C and 2 bar, as shown in Fig. 8. Therefore, a higher pressure and the N_2 addition to the feed stream are useful in order to enhance MR performance.

The promising results shown using Mixture 6 suggest a proper collocation of the CO MR Selox stage after the high and low-temperature water gas shift reactors and before the separation/concentration stage. The catalytic MR for CO Selox operates at the same temperature conditions as the low-temperature shift reactor (200–220 °C) [20]. Therefore, no heat exchangers are required between the water gas shift and Selox reactors.

H_2 (61%) and CO (1%) concentrations in Mixture 6 are in the range of the typical reformate gas stream after its upgrading by means of high and low-temperature water gas shift stages. These streams typically contain 45–70% H_2, the rest being CO_2, H_2O, N_2 (from the fuel or the air) and small concentrations of CO (1–2%) and CH_4. The O_2 (1%) addition required for the Selox reaction can be also added as air without affecting the downstream treatments.

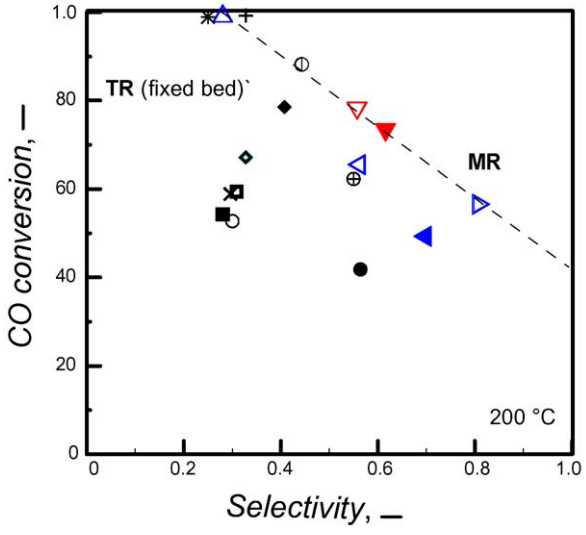

Fig. 7. CO conversion versus selectivity at 200 °C. Triangles: this work, catalytic (Pt-Y) MR; other symbols: data from literature, Pt-based catalysts in TRs. See Table 4 for all details.

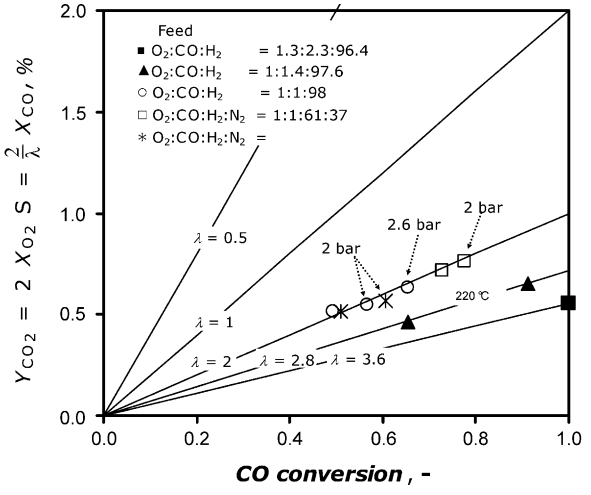

Fig. 8. Measured CO_2 yield versus the CO conversion for the Pt-Y membrane (Membrane B). T = 200 °C and $P^{Reaction}$ = 1 bar when not specified.

The presence of other species such as CO_2 and H_2O in the feed mixture has to be considered for a more complete and realistic evaluation.

4. Conclusions

Pt-loaded catalytic membranes, prepared from FAU (Na-Y) zeolite membranes by ion-exchange, were used for the purification of H_2-rich streams by means of CO Selox.

A CO conversion of 98% and a selectivity of 62% were measured feeding a H_2-rich mixture containing ca. 10% CO at 200 °C (with $\lambda = 1.66$).

An almost complete CO removal (<50 ppm) was achieved operating at 200 °C and 2 bar starting from 1% CO in the feed (with $\lambda = 3.6$).

A slight increase in temperature (from 200 to 220 °C) and operating pressure (up to 2.6 bar) was effective in improving the MR CO conversion and CO_2 yield. The N_2 presence in the feed (more realistic feed stream; $H_2 = 61\%$) increased the MR performance even more.

The present Pt-Y catalytic membrane seems to expand the CO conversion-selectivity region, even with low *space-time* values (ca. 1 mg_{Pt} min/cm^3(STP)) with respect to some TRs data reported in the open literature and obtained with Pt-based catalysts at 200 °C. Therefore, the results obtained confirm the interest in catalytic membranes since the accomplishment of results similar to those achievable in TRs is possible using lower Pt amounts.

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