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Characterization of porous ceramic membranes for their use in catalytic reactors for methane oxidative coupling

J. Herguido [a,*], D. Lafarga [a], M. Menéndez [a], J. Santamaría [a], C. Guimon [b]
[a] *Department of Chemical Engineering, University of Zaragoza, 50009 Zaragoza, Spain*
[b] *Laboratoire de Physico-Chimie Moléculaire, URA CNRS 474, 6400 Pau, France*

Abstract

Catalytic inorganic membranes were prepared by depositing active materials over porous alumina tubes, using sol–gel and impregnation techniques. The concentration profiles of the different species in the membrane were obtained using XPS. Also, the stability of the membranes was tested by subjecting the samples to different thermal treatments. Different preparation methods are compared with the aim of attaining controlled distributions of the active phases in the membrane. Finally, some reaction results are also presented.

1. Introduction

In previous works, [1–3], a tubular, noncatalytic porous ceramic membrane was used to distribute the oxygen feed to a catalytic bed packed inside the ceramic tube. In this configuration, the beneficial effect of the membrane found for methane coupling stems primarily from the lower oxygen partial pressures attained through the distribution of oxygen. However, in spite of the good yields obtained in our laboratory [2,3], it was found that one of the main problems in using a porous silica or alumina membrane as an oxygen distributor in methane oxidative coupling was to minimize the negative contribution of the membrane itself, which does not have good catalytic properties for this reaction.

One way to overcome this problem is to reduce both the membrane acidity and the surface area in contact with the reactants by means of impregnation with alkaline salts. Another possibility involves modification of the catalytic properties of the membrane, in order to obtain a positive contribution to the reaction. It seems clear that the use of a catalytically active membrane would open up new possibilities to attain higher product yields. Thus, it has been shown [4], that the segregation of reactants on opposite sides of a membrane with a thin active layer can enhance the yield to the intermediate product in a series-parallel network.

The aim of this work is to develop a porous ceramic membrane which can be used as an oxygen distributor to a fixed-bed catalytic reactor while at the same time improving the selectivity of the part of the reaction that takes place on the membrane itself. To this end, different preparation procedures have been tested, in order to obtain thermally stable membranes with a controlled distribution of catalytic material.

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[*] Corresponding author.

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2. Experimental

Different membrane samples were prepared in order to study the distribution along the membrane radius of the various compounds added. A commercial α-alumina membrane (Membralox®, SCT) was used in all cases as the starting material. This membrane has three layers, with pores of 10 μm, 1.4 μm and 200 nm, respectively. The initial membrane was subjected to some of the following treatments:

(a) Several (usually 3 or 4), cycles of deposition of silica inside the membrane, in order to reduce the initial porosity, and to obtain an appropriate permeation flux [1,2]. Each cycle consisted of impregnation with a commercial silica sol for an appropriate length of time, followed by drying at low temperature and calcination at 800°C for 3 hours.

(b) Several cycles of impregnation with a saturated solution of lithium carbonate, to reduce the surface acidity.

(c) Several cycles of impregnation with a solution of magnesium nitrate to obtain a deposition of active material on the membrane. The impregnation cycles of treatments (b) and (c) consisted of immersion for 15 minutes in the corresponding saturated solution, followed by drying at 200°C for 15 minutes. Usually, between 10 and 12 impregnation cycles were used. After the last cycle, a final calcination for 3 h at 800°C was performed.

(d) Calcination using different lengths of time and temperatures, in order to assess the thermal stability of the membrane and of the deposited materials.

The membranes prepared in this part of the work can be classified in two different series, namely, *series A*, where treatments (a), (b) and (d) were carried out, and *series B*, in which treatments (a), (c) and (d) were performed. In this last series, two different methods of deposition of the active phase were used, either in one stage, after treatment (a), or in multiple stages, following each of the cycles of deposition of silica. The features of the different samples studied in this work are summarized in Table 1. Each series is made up by samples coming from the same original tube.

Recent results in our laboratory indicate that, as could be expected from their melting points, more stable membranes can be obtained by employing alumina instead of silica to reduce the initial membrane porosity. However, silica was chosen in this case, in order to measure the distribution of the new material in the membrane using XPS. This technique gave the distribution of Si, Al, Mg, Na and Li across the membrane radius. In addition, mercury intrusion porosimetry and BET measurements were used to assess changes in the pore structure, and SEM to investigate the morphology of the surface.

XPS analyses were performed with a SSI 301 spectrometer using focused monochromatic Al Kα radiation. The Cls line at 284.6 eV was used

Table 1
Characteristics of the membranes studied

Series A	Series B
A1 As-received membrane	B1 As-received membrane
A2 A1 + 4 cycles of silica deposition	B2 B1 + 3 cycles of silica deposition + 12 cycles of impregnation with $Mg(NO_3)_2$
A3 A2 + 12 cycles of impregnation with lithium carbonate	B3 B2 + 3 h of calcination at 900°C
A4 A3 + 12 hours of calcination at 850°C	B4 B2 + 12 h of calcination at 900°C
	B5 B1 + 3 treatments consisting of: one cycle of silica deposition + 3 cycles of impregnation with $Mg(NO_3)_2$
	B6 B5 + 3 h of calcination at 900°C
	B7 B5 + 12 h of calcination at 900°C

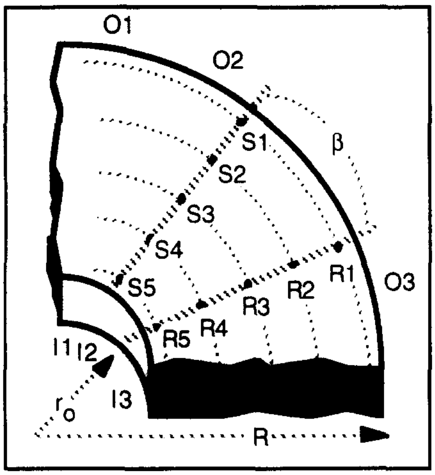

Fig. 1. Location of the XPS measurements.

as an internal standard. The analysis was carried out across several points of thin rings cut from the membrane samples after the different treatments. It was chosen to fracture the membrane rather than to cut it, which gave more irregular rings but avoided the problems of contamination by Fe and C when using steel cutting tools.

The analyses were carried out according to the scheme in Fig. 1. Each of the analysis spots indicated corresponds to a window with a diameter of irradiated area of 300 μm. On each sample, 3 spots were randomly selected on the inner surface (I1 to I3), and on the outer surface (O1 to O3). The radial concentration profiles were obtained at five radial positions and two angular positions (R1 to R5, and S1 to S5, respectively), with a separation angle β between 30 and 90°, depending on the size of the membrane piece used for the analysis.

3. Results

The concentration profiles of the different species are represented as a function of the dimensionless radius, defined as $r^* = (r - r_o)/(R - r_o)$. The comparison between points R1 to R5 and S1 to S5 in all the samples indicated that the surface composition was the same at any value of β. This was to be expected given the method of deposition used, by vertical immersion of the membrane in an aqueous solution containing the desired component. The homogeneity of the samples with respect to the angle of measurement is illustrated in Fig. 2. The axial homogeneity (not shown), was also confirmed using different cuts of the same ceramic tube

3.1. Starting material

XPS analysis carried out on membranes A1 and B1 showed that the original material was homogeneous, with an O/Al atomic ratio of 1.5, as expected from its chemical composition.

3.2. Series A

The oxygen concentration profile (not shown) was not affected by the different treatments, and stayed at a constant value around 60%. Fig. 3 shows that the surface concentration levels of Li achieved with the above described procedure are around 2% in the inner positions of samples A3 and A4. The main difference observed in both

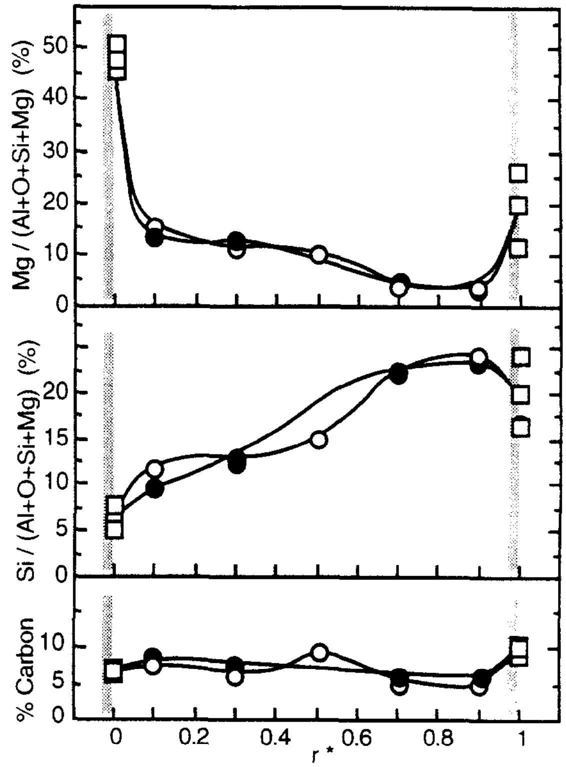

Fig. 2. Testing of angular homogeneity. Concentration profiles of Mg, Si and C. Sample B2, $\beta = 45°$.

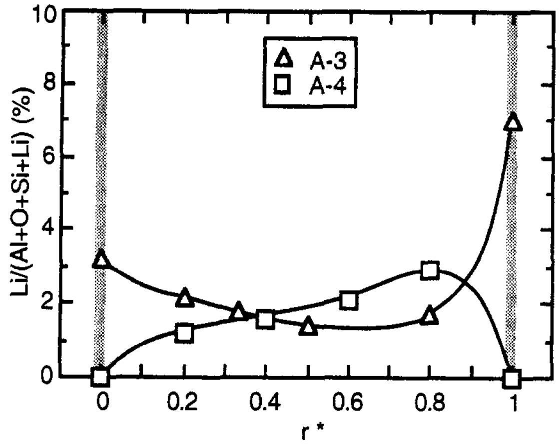

Fig. 3. Li concentration profiles. Series A.

cases is related to the Li concentration at both ends of the membrane. Thus, in sample A3 there is some Li deposited at $r^* = 0$ and $r^* = 1$. Unlike the Li deposited inside, which seems to be more stable, the Li deposits at both ends of the membrane disappear in the subsequent calcination for 12 hours at 850°C (A4). This is probably due to the creation of volatile compounds such as LiOH, which can be formed during calcination by reaction with the water vapour contained in the air atmosphere.

Some complementary information can be obtained from the variation of the Si and Al surface concentration profiles with the different treatments, which is shown in Fig. 4. The concentration of Al atoms shows a minimum at the membrane walls after the treatment with silica sol, to the point that both the internal and the external surfaces appear to be almost completely covered by silica. This can be related to the formation of silica plates on the membrane wall, reported in a previous work [1]. The deposition of silica (A2), and the impregnation with lithium carbonate (A3), gave rise to successive decreases in the percentage of exposed Al atoms inside the membrane. The resulting profile, however, did not seem to be affected by the increase in the calcination time from 3 to 12 hours.

In general, the concentration of Si atoms follows a reverse trend with respect to Al. Thus, a maximum appears at both walls, due to the above mentioned silica coverage, and the silica profiles also do not seem to be affected by calcination. Nevertheless, it is interesting to note that, while decreasing the concentration of Al atoms, the impregnation with lithium carbonate increased the concentration of Si atoms in the inner membrane positions. A possible explanation may be found in the fact that the addition of Li and the subsequent calcination produces some deterioration on the silica deposits giving rise to the disgregation of part of the deposits and to the formation of fissures [1]. SEM observations (not shown), verified that, upon deposition of Li and calcination, the original smooth surface of the silica deposits is transformed into a rough structure with abundant cracks, thus giving rise to a higher value of Si on the exposed surface. Table 2 also shows that the addition of Li causes the practical disappearance of the smallest pores, due to the increase of sintering that takes place in the presence of alkaline compounds.

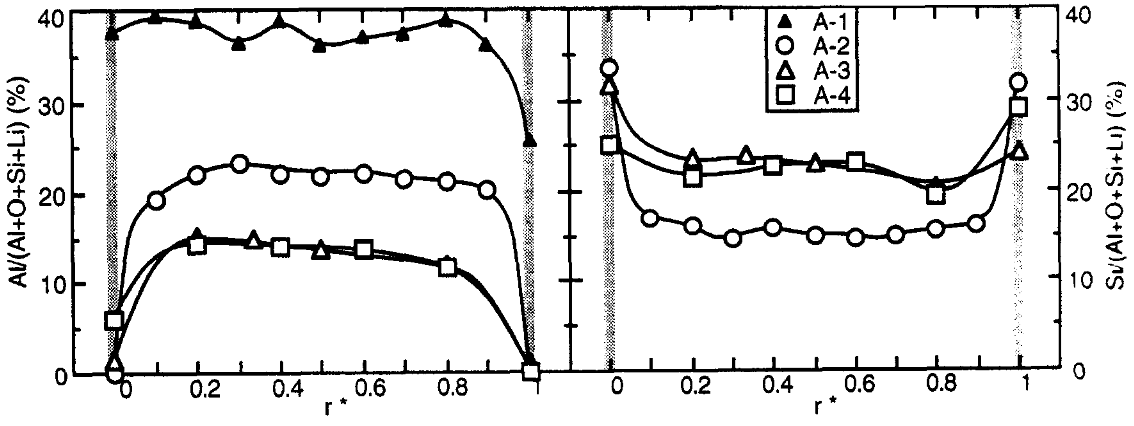

Fig. 4. Al and Si concentration profiles. Series A membranes.

Table 2
Variation of the structural parameters for series A membranes

Sample	Intrusion volume (ml/g)				BET area (m^2/g)	Pore volume (%)
	9 $\mu m < d_p$	1 $\mu m < d_p < 9$ μm	20 nm $< d_p < 1$ μm	$d_p < 20$ nm		
A2	0.0459	0.0022	0.0065	0.0090	2.42	18.53
A4	0.0495	0.0033	0.0092	0.0013	0.76	18.90

3.3. Series B

The comparison of the curves B2 and B5 in Fig. 5 shows the differences introduced when carrying out the overall treatment in one stage (B2), or in three different stages (B5). In the first case, the Si concentration increases from the inside to the outside, with lower concentrations on the tube wall compared to the neighbouring positions, since the Mg deposits cover part of the silica on the walls. On the other hand, considering the multiple-stage process, after the first impregnation with Mg, the surface acidity changes, and as a consequence a significant gelification of silica takes place upon contact with the tube walls, giving rise to the higher concentrations at $r^* = 0$ and $r^* = 1$ (see curve B5). In addition, the division of the process in several stages gives rise to a smoother concentration profile inside the tube. The calcination (B3, B4, B6 and B7), does not seem to have a clear effect on the Si concentration profiles.

Due to the higher concentration of the saturated solution, the Mg content of the membranes was in general considerably higher than the percentages of Li achieved in Series A membranes, with atomic percentages in the inner positions between 3 and 15% (Fig. 6). Also, the Mg concentration was higher at the walls (the concentration in the inner wall reached values in excess of 50%), and in general was higher in the samples treated in one stage (B2 to B4), as could be expected, since there was no further coverage with silica.

An interesting feature of Fig. 6 is that the Mg concentration profiles are decreasing along the radius when the treatment is carried out in one stage, while they are constant or slightly increasing for the multiple-stage treatment. When all the silica is deposited prior to the impregnation, the larger pores in the outer region of the membrane are almost filled with silica [1]. As a consequence, there is more volume available in the inner and middle regions of the membrane to receive the saturated magnesium nitrate solution, and higher Mg surface concentrations are achieved when the solution water is evaporated. On the other hand, when the membranes are treated in multiple stages, there is a gradual modification of the pore

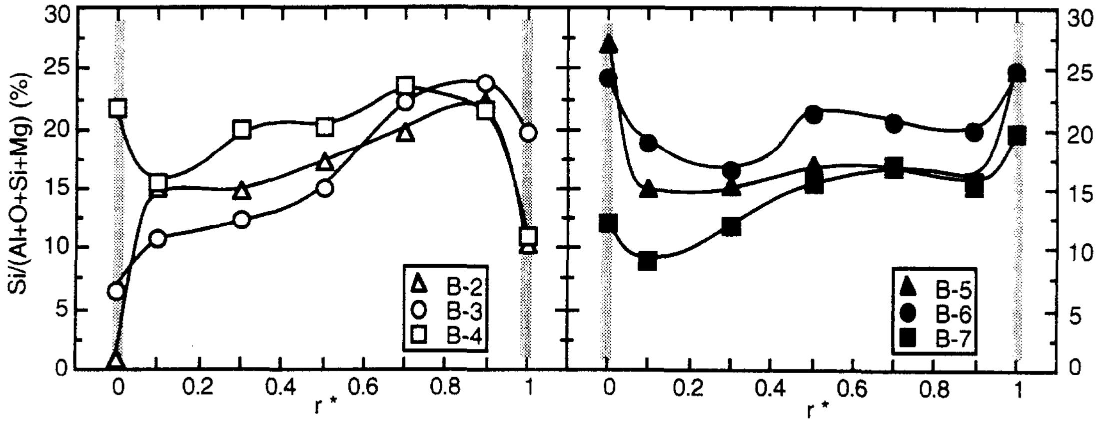

Fig. 5. Comparison of Si concentration profiles in membranes prepared using two different methods.

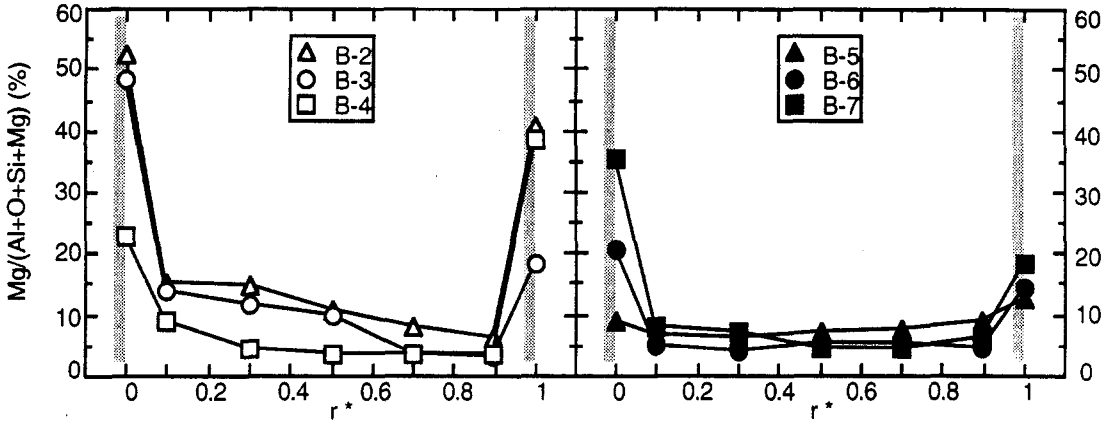

Fig. 6. Comparison of Mg concentration profiles in membranes prepared using two different methods.

structure, and a much smoother concentration profile is obtained.

In the samples prepared in one stage, the calcination at 900°C decreased the amount of Mg on the surface. This effect could be due to partial sintering of the dispersed MgO phase, which would result in a decrease in its surface area, or to reactions with the support to form magnesium silicates or aluminates. For extended periods of calcination time, the differences in the Mg profile obtained in one-stage or in multiple-stage treatments tend to disappear (see curves B4 and B7 in Fig. 6).

The comparison of the pore structure of membranes B2 and B5 (Table 3) shows that the addition of Mg gives rise to different pore size distributions depending on the method of preparation used. Regarding the effect of Mg addition on the thermal stability, the effects are similar to those obtained with the addition of Li, i.e., the calcination of samples B2 and B5 leads to a decrease in the BET surface area and in the volume corresponding to the smallest pores. However, when the membrane is prepared using the multiple-stage procedure the sintering is highest, leading to the practical disappearance of the pores smaller than 20 nm. The observed behaviour can be attributed to the much higher dispersion of Mg throughout the silica deposits that is achieved with the multiple-stage procedure.

3.4. Reaction experiments

As stated in the introduction, the purpose of this investigation is to prepare ceramic membranes with better catalytic properties than the silica–alumina membranes used in previous works. These membranes would then be used as oxygen distributors to carry out methane oxidative coupling in a packed-bed catalytic membrane reactor (PBCMR), instead of the packed-bed noncatalytic membrane reactor (PBNMR) previously employed [1–3]. Given the above results, it seems clear that a one-stage preparation would give a more favorable situation, with a higher stability of the pore structure and a higher concentration of

Table 3
Variation of the structural parameters for series B membranes

Sample	Intrusion volume (ml/g)				BET area (m^2/g)	Pore volume (%)
	9 μm < d_p	1 μm < d_p < 9 μm	20 nm < d_p < 1 μm	d_p < 20 nm		
B2	0.0375	0.0021	0.0054	0.0109	7.22	16.23
B4	0.0559	0.0026	0.0065	0.0020	1.58	19.03
B5	0.0465	0.0115	0.0065	0.0069	3.85	20.56
B7	0.0612	0.0104	0.0057	Negligible	0.17	21.26

Table 4
Methane conversions and hydrocarbon selectivities with different membranes. $CH_4/O_2 = 3:1$. Undiluted, 765°C. Membrane 1: original membrane + γ-Al_2O_3. Membrane 2: original membrane + γ-Al_2O_3 + MgO + Li_2CO_3. Membrane 3: original membrane + γ-Al_2O_3 + MgO + LiCl

Total flow rates: cm^3(STP)/min	CH_4 conversion			C_2+ selectivity		
	100	200	500	100	200	500
Membrane 1	21.38	21.35	19.80	4.45	4.32	3.79
Membrane 2	19.94	17.37	13.98	9.47	8.20	5.04
Membrane 3	21.26	20.87	19.54	22.20	16.22	10.39

Mg at the inner surface. Although the study of the PBCMR for methane oxidative coupling is still proceeding in our laboratory, some of the results obtained concerning the reactivity of the membranes are presented in Table 4.

The activity and selectivity values in Table 4 refer to the intrinsic performance of the membranes, i.e., without a packed catalyst bed on the tube side. The membranes were prepared by deposition of γ-alumina instead of silica (since there was no XPS characterization in this case), followed by successive impregnation with Mg and with Li-containing salts. It can be seen that membrane 1, i.e. the original membrane plus deposited γ-alumina, gives the lowest selectivities at any of the flow rates employed. When Mg and Li were deposited (membrane 2), the selectivities roughly doubled. However, low selectivities were still obtained due to the low Li loadings on the membrane. Higher loadings were obtained by impregnation with a saturated solution of (LiCl) which has a much higher Li concentration than the saturated Li_2CO_3 solution. It can be seen that the corresponding selectivities (membrane 3), were about 4 times higher than those obtained when only alumina was present on the membrane.

4. Conclusions

The addition of alkaline (Li) or alkaline-earth (Mg) compounds in order to modify the catalytic properties of silica/alumina membranes leads to important changes in the pore structure and in the surface composition. Catalytically active membranes for methane oxidative coupling have been prepared using one-stage and multiple-stage methods. XPS measurements showed that both procedures gave axial and angular homogeneity in the distribution of the added components. In the radial direction, however, there is an important variation of the distribution of the active component, which is also a function of the preparation procedure. It is important to note that a one-stage preparation procedure gives rise to a more stable pore structure, and to a high value of concentration of Mg at the inner wall (over 50 atom%). This situation is the most appropriate if the membrane is to be used in methane oxidative coupling, since the initial methane–oxygen contact will take place in a region with a high concentration of active component.

The experiments carried out to test the reactivity of the membranes show that it is possible to obtain a much higher selectivity by doping the membrane with the appropriate active components. This can be applied to improve the performance of previously used packed-bed membrane reactors, in which nonselective reactions occurred on the membrane surface.

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References

[1] D. Lafarga, J. Santamaría and M. Menèndez, Chem. Eng. Sci., 49 (1994) 2005.
[2] J. Coronas, M. Menèndez and J. Santamaría, Chem. Eng. Sci., 49 (1994) 2015.
[3] J. Coronas, M. Menèndez and J. Santamaría, Chem. Eng. Sci., in press.
[4] M.P. Harold, V. Zaspalis, K. Keizer and A.J. Burggraaf, Chem. Eng. Sci., 48 (1993) 2705.