

Physicochemical Characterization of MFI–Ceramic Hollow Fibres Membranes for CO₂ Separation with Alkali Metal Cation

A. Alshebani, Y. Swesi, S. Mrayed, F. Altaher

Abstract—This paper presents some preliminary work on the preparation and physicochemical characterization of nanocomposite MFI-alumina structures based on alumina hollow fibres. The fibers are manufactured by a wet spinning process. α -alumina particles were dispersed in a solution of polysulfone in NMP. The resulting slurry is pressed through the annular gap of a spinneret into a precipitation bath. The resulting green fibres are sintered. The mechanical strength of the alumina hollow fibres is determined by a three-point-bending test while the pore size is characterized by bubble-point testing. The bending strength is in the range of 110 MPa while the average pore size is 450 nm for an internal diameter of 1 mm and external diameter of 1.7 mm. To characterize the MFI membranes various techniques were used for physicochemical characterization of MFI–ceramic hollow fibres membranes: The nitrogen adsorption, X-ray diffractometry, scanning electron microscopy combined with X emission microanalysis. Scanning Electron Microscopy (SEM) and Energy Dispersive Microanalysis by the X-ray were used to observe the morphology of the hollow fibre membranes (thickness, infiltration into the carrier, defects, homogeneity). No surface film, has been obtained, as observed by SEM and EDX analysis and confirmed by high temperature variation of N₂ and CO₂ gas permeances before cation exchange. Local analysis and characterise (SEM and EDX) and overall (by ICP elemental analysis) were conducted on two samples exchanged to determine the quantity and distribution of the cation of cesium on the cross section fibre of the zeolite between the cavities.

Keywords—Physicochemical characterization of MFI, Ceramic hollow fibre, CO₂, Ion-exchange.

I. INTRODUCTION

HOLLOW fibre geometries allow for much higher surface/volume ratios of membranes. Several types of supports are available geometries for the synthesis of zeolite membranes. Flat disks or tubes are frequently used and even the use of monolith type has been reported [1]. To reduce the thickness of the zeolite film, and to ensure its continuity, the pore size of the support for the zeolite/support interface must be sufficiently small. Tubular and multichannel are more resistant than the disks and have larger permeable surfaces. Moreover, they offer membrane surface/area significantly higher ratios seals, thereby reducing costs and the sealing effect of gas leakage. The large majority of zeolite membranes

reported in the literature are synthesized on a porous support which gives them the strength necessary for its application. The zeolite layer on the support should ideally be as thin as possible to allow high permeabilities. Various types of supports were used for the synthesis of supported zeolite membranes, the shape, the chemical composition; the pore structure (size, pore porosity), micro-and macrostructure and pre-treatment can greatly influence the structure and thus the performance final. Some typical examples of materials and their suppliers are listed in Table I. The alumina– α tubes with an asymmetric structure are the supports most widely used. Other ceramic materials have also been used as the alumina– γ [2] of titanium oxide [3], the SiC [4], and zirconia [5] Metal supports, mainly stainless steel, are also used because of their lower price and easier sealing implement by welding [6]. They can be made from different materials such as glass [7], [8], stainless porous ceramics [9] or porous steel [10], [11]. Among porous ceramics, the α -alumina has been studied extensively and there is a wide knowledge on the synthesis of zeolite membranes on these supports. The main disadvantage of these supports is sealing related problems on metallic parts of modules [12], especially at high temperature.

TABLE I
SUPPLIERS OF POROUS INORGANIC MATERIALS LISTED IN THE LIOGRAPHY OF ZEOLITE [13]

Provider supports	materials	support form	Typical pore size (nm)
Pall-Exchia (USA)	α -Al ₂ O ₃	Tube	200, 800
	γ -Al ₂ O ₃	Tube	5
Inocermin GmbH (Germany)	α -Al ₂ O ₃	Tube	60, 100
	α -Al ₂ O ₃	Disk	60, 1800
Poco Graphite (USA)	γ -Al ₂ O ₃	Tube	5, 60
	α -Al ₂ O ₃	Tube	700
Sulzer Chem Tech LTD (Switzerland)	α -Al ₂ O ₃	Tube	200
	γ -Al ₂ O ₃	Tube	5
GKN Sinter Matels Filters GmbH (Germany)	α -Al ₂ O ₃	Disk	100, 200
	SS	Disk	270
GKN Sinter Metals Filters GmbH (Germany)	α -Al ₂ O ₃	Tube	100, 200
NGK Insulators Co. (Japan)	AI	Tube	200, 500
NOK Corp. (Japan)	α -Al ₂ O ₃	Tube	120-150, 150-170
Nikkato Corp. (Japan)	α -Al ₂ O ₃	Tube	1300
Technologies d'or (USA)	α -Al ₂ O ₃	Tube	200
US Filters (USA)	α -Al ₂ O ₃	Tube	100
Trumem international (USA)	AI	Plan	2000-500

In this paper we mainly report on membrane synthesis and ion-exchanged with 1M in solution of CsCl. The ion-exchange was carried out within the pores of a ceramic alumina

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substrate. Among the gaseous separations studied using the membrane ion-exchanged was CO₂ separation. Indeed, the uptake of this gas in anthropogenic emissions is currently considered as an important opportunity to reduce greenhouse gases and global warming which is attached. CO₂/N₂ separation tests on MFI fibres showed selectivities in favor of CO₂. The separation factor was about 4 for ion-exchange membrane at room temperature with mixture CO₂ permeance 1.1 μmol/(m².s.Pa). Although these values are quite promising, performance is still insufficient in view of application. We realized experiments of cation exchange to make more selective transport of CO₂. Our zeolitic materials have a high Al content, therefore a high exchange capacity. In order to compare performance before and after exchange, we have developed an exchange protocol on the module, sealed and the fiber remaining inside of it. The separation factor for ion-exchange membrane with Cs using the protocol of injection inside tubular stainless steel module, was about 18 at room temperature with mixture of permeance 2.23 μmol/(m².s.Pa). The pieces worked on here are about 20-cm long. About 10 fibres were introduced into a matured precursor solution containing Aerosil 380 and TPAOH. Hydrothermal treatment was carried out, as described previously on larger porous alumina tubes [16]-[18].

II. PHYSICAL CHARACTERIZATIONS

The material obtained was submitted to physical characterizations (Scanning Electron Microscopy with EDX analysis, X-Ray Diffraction, N₂ adsorption isotherm). No surface film was observed, but, as in previous larger tubes, crystal was embedded into the porous alumina framework. Fig. 2 (b)) shows a typical micrograph of a fibre cross section before and after zeolite synthesis. We see very well on pictures microscopy, large pores of the support Fig. 2 (a)). Because of these large pores, the effective thickness of the support is 20 microns or less than 10 times its apparent thickness (~ 200 microns).

Scanning Electron Microscopy (SEM) and Energy Dispersive Microanalysis by the X-ray were used to observe the morphology of the hollow fibre membranes (thickness, infiltration into the carrier, defects, homogeneity), but also to determine the size and shape of grains supported zeolite. The observation of the zeolite crystals in the zeolite or fibres prepared by cutting the surface was performed on a Hitachi S-800 microscope operating at 10 kV. The samples were obtained by breaking the samples into small pieces. The cutting has not been performed with a classic saw to avoid structural changes in the cutting, a special saw was used.

On the same device, the local and average concentrations of Al and Si through the fibres before and after the hydrothermal synthesis were measured by energy dispersive analysis by X-ray (EDX) using a microtip -1 μm (Phoenix Edax) with a window parallel to the surface of the membrane were analyzed. EDX analysis confirms that the silica penetrates into the pores of the support as shown in Figs. 1 (a), (b)).

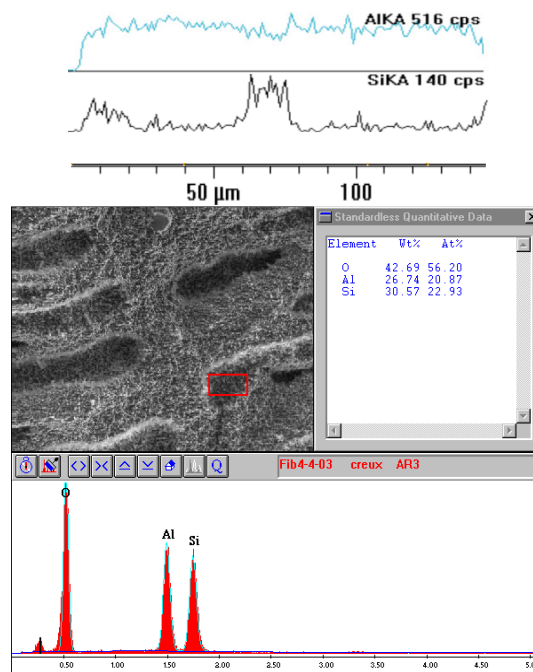
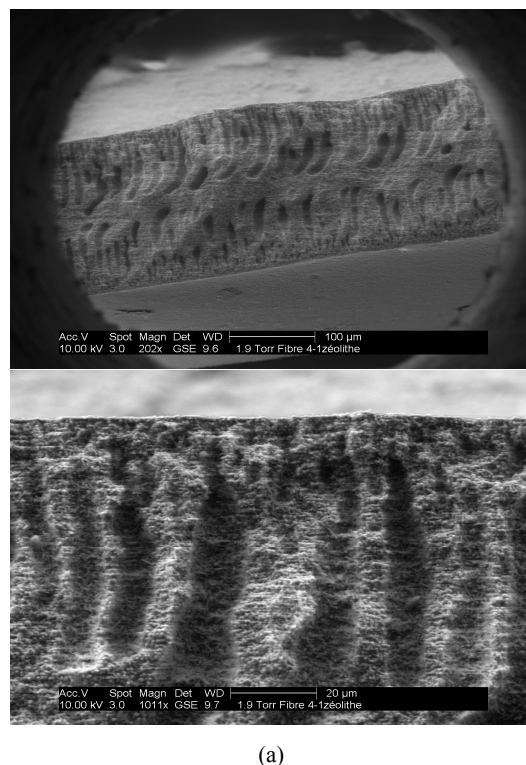
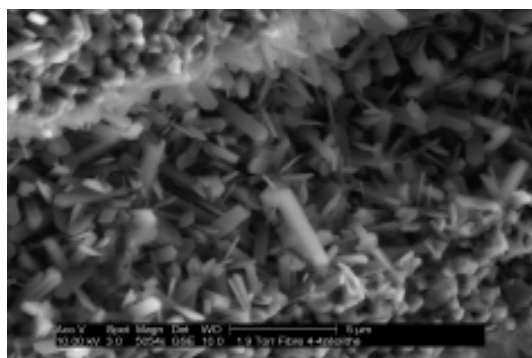


Fig. 1 EDX profiles of a fibre cross section after zeolite synthesis



(a)



(b)

Fig. 2 Scanning electron micrograph (SEM) of α -alumina support (a) Before-MFI synthesis, (b) After-MFI synthesis

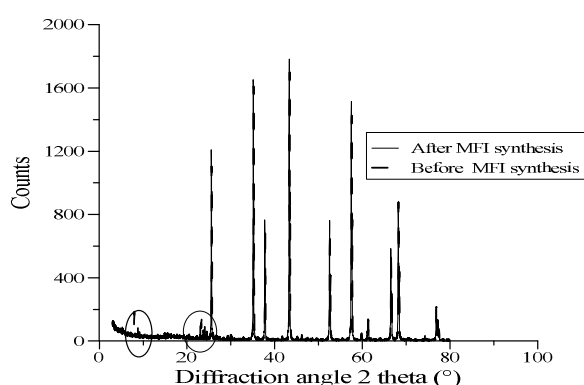


Fig. 3 XRD Patterns of before and after MFI synthesis

The chemical composition of Si, Al and Cs for the tested fibres before and after the synthesis and before and after ion-exchange was determined by atomic emission using an elemental analysis apparatus to inductively coupled plasma (ICP) with prior dissolution in hydrochloric acid solution of 20% wt, see Section V. This technique relies on the production, in a plasma, atomic vapor and measuring the emission intensity of a radiation characteristic of the element to be assayed.

A. Weight Uptake & Elemental Analysis

The measurement of the mass of each fibre reveals an increase of about 10% of the initial weight has a mass of 50 mg zeolite per fibre for supports. A mass of 100 mg per fibre was calculated for membranes synthesized on supports.

B. X-Ray Diffraction

This technique enables the determination of the nature of the crystalline phases by the angles of X-ray diffraction by the crystal planes of the solid. The diffraction angles are connected to the characteristics of the crystal lattice. The structure of the synthesized zeolite material was analyzed using a Philips diffractometer PW 1050/81 (Cu $K\alpha_{1+2}$ radiation). The analysis was performed on the crushed powders before and after hydrothermal synthesis. The diffractogram obtained for virgin fibre and the synthesized membranes is presented above. One can observe the difference

between the signal of the virgin fibre and that of zeolite membranes, especially around 9° and 25° , overlapping diffractograms (Membranes and virgin fibres). Comparing to the JCPDS database, we can recognize that the peaks that appear after the hydrothermal synthesis correspond to a zeolite ZSM-5 as shown in Fig. 3. XRD results show that the material only contains α -alumina and MFI structured crystals.

C. Macro Porosity

Considering the porosity of the support (about 20%), the amount of silica observed is compatible with a full pore-plugging of the alumina support with MFI zeolite. Mercury Intrusive porosimetry allows in fact the determination of the diameter of the entrance of the pores and pore volume in a range of pore sizes larger than the adsorption of nitrogen (between a few nm and more than 100 microns). The principle is to enter a non-wetting liquid (mercury) in the pores of the sample under the effect of pressure P applied to the liquid. The required pressure is inversely proportional to the radius (r) of the pores (Laplace). A Micromeritics Autopore IV 9500 penetrometer was used with two samples mass of 162 mg and 117 mg, were used respectively, for the fibres before and after zeolite synthesis.

As well as the protocol of zeolite synthesis, the quality of the α -alumina support is preponderant for obtaining a high quality membrane. The pore size distributions of our different supports are according to references of receipts supports. The diameters of minimum, medium and maximum pores are reported in Table II. Complete graphs of results of macro porosimetry for the supports (A-004-1 and A-004-2) before MFI-synthesis and membranes are presented in Fig. 4. As reported in Table II the membrane has different separation qualities some of them have been tested and show good separation efficiencies (A, B, D), while others show inefficient to separate gas (C). It is therefore necessary to properly characterize these materials to define the origin of the good (or bad) quality of membranes. Previous work has shown that for a too large pore size it was not possible to completely block the pores of the support with the zeolite [14].

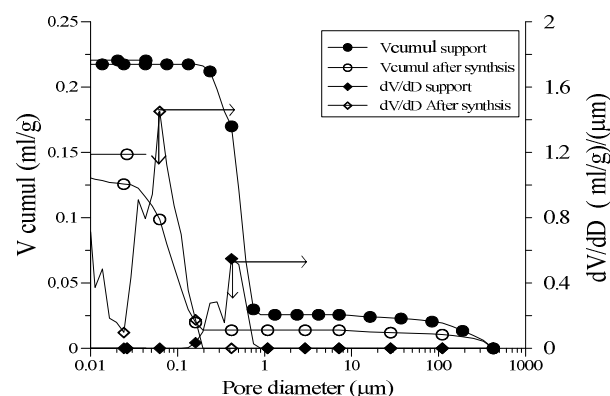


Fig. 4 Cumulated and derivative volumes with pore diameter obtained from mercury porosimetry

TABLE II

SUMMARY OF TESTS MACRO POROSITY MERCURY FOR DIFFERENT SUPPORT

Reference Support	Min. dia	Average dia	Max. dia	Remarks
M51123A2	0.06	0.25	0.35	A
M51129A1	0.06	0.3	0.4	B
M60112A2	0.12	0.53	4	C
KF50803A	0.12	0.44	10	D

A: 3 interruptions of zeolite growth (test).
B: 1 and 3 interruptions of zeolite growth (test)
C: Bad quality
D: Good quality

D. Specific Surfaces-Micro Porosity

Complete adsorption-desorption isotherms of N₂ used to characterize the texture of a porous material: surface area, size distribution and pore size and pore volume. The textural properties of the crushed before and after the synthesis of the zeolite hollow fibres were obtained from the complete adsorption-desorption isotherms of N₂ at 77 K on a fully automatic apparatus ASAP-2020 Micromeritics. The measurement of the specific surface (SBET) reduces to the determination of the amount of molecules adsorbed per gram of solid gas to form a monolayer. This determination is derived from the interpretation of the adsorption isotherm according to the BET theory for relative pressure P/P₀ included between 0.30 and 0.50.

Nitrogen adsorption shows a large increase of specific surface area (from 2.2 m²/g to 33 m²/g), with a bimodal distribution of large macropores and micropores. A considerable increase of the specific surface area is observed between the primary fibre and the synthesized membranes as shown in Fig 5. 2.2 m²/g for α-alumina supports we pass 33 m²/g for the membrane surface is 15 times higher. The nitrogen adsorption isotherm at 77K for membranes present a rapid increase at low relative pressure p/p^o then a plateau characteristic of a Type I isotherm

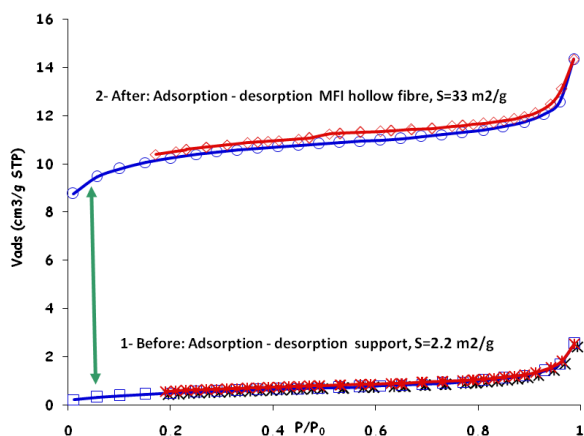


Fig. 5 N₂ adsorption/desorption isotherms at 77 K of a fibre before (bottom) and after (top) zeolite synthesis

III. EXPERIMENTAL METHOD FOR THE INSTALLATION OF HOLLOW FIBRE

After hydrothermal synthesis the fibre is mounted. The fibres used are very fragile with an external diameter of 1.7

mm. and too sensitive to be tested also, they need to be mounted on a support more resistant to carry out separation tests. We have found a method to install or fixe the fibers tightly in a dense alumina tube of internal diameter of 7 mm as shown in Fig. 6 (a). This dense tube can be used in the same type of membrane module as in tubular membranes. The fibre is sealed using adhesives and enamels that are compatible with dense alumina tubes in terms of thermal expansion properties and can handle the operating temperature and pressure. (673 K, sealing under 4 bar pressure differential). Fig. 6 mounted therefore the fibres within dense alumina tubes perforated of 7 mm in inside diameter and 15 cm in length. Many experiments were needed to seal this assembly, sealing which is mounted for achieving the separation tests and gas permeation. We used an enamel, which has the same method of preparation of industrial methods. The assembly itself is made as follows: two rings are first fixed by the enamel at the two ends of the fiber and the permeable distance between it was 12 cm. In first the assembly is heated then the two ring was fixed on fibre membrane within the dense alumina tube with a new layer of enamel. Much of necessary enamel are added to obtain a good seal layers. The dense alumina tube is perforated so that the sweep gas can flow easily around the membrane. Figs. 6 (b) and 7 show the schematic mounting of the membranes used in this work.

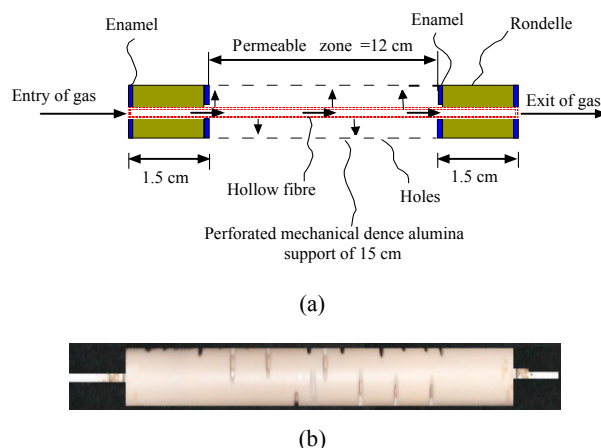
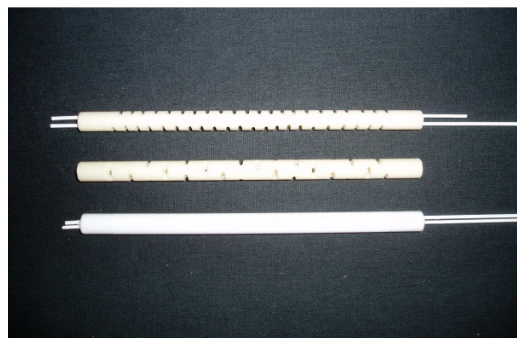


Fig. 6 (a), (b) Schematic mounting of the fibre before sealing enamel at 600 °C C in a dense alumina tube with holes



(a)



(b)

Fig. 7 (a), (b). Photographs of fibres mounted into their mechanical dense alumina support with a new layer of enamel tube. Step before sealing and enamelling

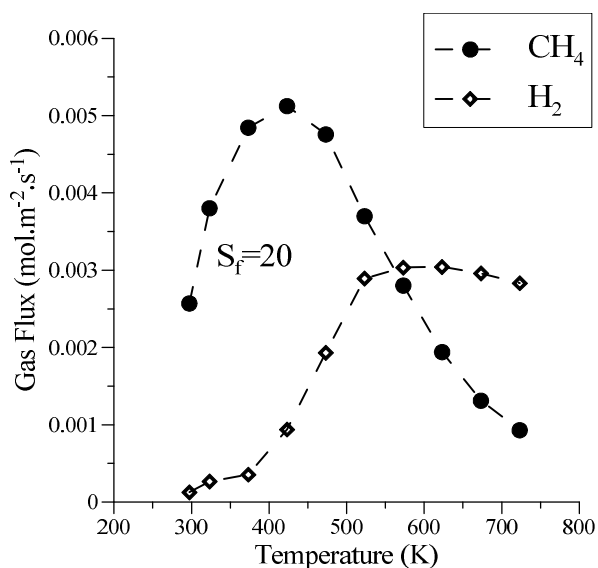


Fig. 8 Mixture separation nC_4H_{10}/H_2 as a function of temperature for H-MFI/ α - Al_2O_3 hollow fibre membrane prepared by the « pore plugging method » at 170 °C for 3 days and fired at 500 °C in air. Temperature range from 300 to 750 K. Conditions: retentate pressure 125 kPa and trans fibre pressure 0.4 kPa. ($S_f = 20$). membrane ref: A-004-3

IV. DYNAMIC CHARACTERIZATION METHODS

A. Separation of Butane/H₂ Mixtures on H-ZSM-5

The objective of n-butane/hydrogen separation is to provide information on the presence of defects in the membrane. After

pre-treatment at 673 K for 4 h, the quality of the prepared membrane was evaluated by gas separation n-butane/ H_2 . One gas separation test of nC_4H_{10}/H_2 was done to characteristics hollow fibre membranes. For mixture gas separation, zeolite pores will be blocked first by n-butane adsorption and when the proportion of n-butane increases, larger and larger pores are blocked by condensation of nC_4H_{10} gas and become unavailable for H_2 transport. Fig. 8 shows the separation performance for a mixture nC_4H_{10}/H_2 as a function of temperature for the H-MFI/ Al_2O_3 membrane ref: A-004-3. It is clear that at low temperature the diffusion of H_2 was blocked by the adsorption of nC_4H_{10} but at the highest temperature the quantity of nC_4H_{10} decreases and the selectivity will be reverse. The separation factor at low temperature was 20 therefore the hollow fibre membrane is classified as a good membrane for next ion exchange experiences.

B. Pure Gas Permeance

Fig. 9 shows the evolution of single gas permeance of several gases with temperature for the MFI-alumina fibre sample 1. As can be seen, the N_2 and H_2 permeance values are higher than $1 \mu mol.m^{-2}.s^{-1}.Pa^{-1}$ at room temperature, in good keeping with the values found in our previous study [16].

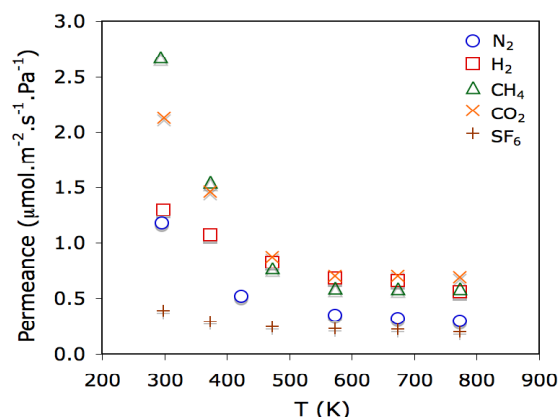


Fig. 9 Evolution of N_2 , H_2 , CH_4 , and CO_2 single gas permeance through sample 1. Conditions: retentate pressure: 104 kPa; trans fibre pressure: 3.2 kPa

This sample shows particularly high CO_2 permeance, with values higher than $2 \mu mol.m^{-2}.s^{-1}.Pa^{-1}$ at room temperature. These permeance values translate into a CO_2/N_2 ideal perm selectivity of about 1.9, higher than the corresponding Knudsen selectivity, ≈ 0.8 . The amount of large intercrystalline defects of the synthesized MFI material is low, as inferred from the low viscous contribution to N_2 permeance after calcination (lower than 2%), obtained from the slope of N_2 permeance with the average pressure.

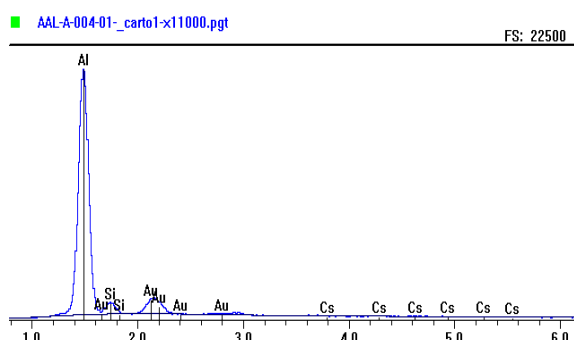
It is interesting to note that this sample shows gas permeance values that are comparable to the highest values obtained on conventional film-like membranes [19], probably due to a comparable MFI equivalent thickness (lower than 1 μm). Moreover, the permeance shows a continuous decrease with temperature, with no indication of permeance increase at higher temperature up to 723 K, as expected for a

nanocomposite architecture [17], [18].

V. ION EXCHANGE

The extent of ion exchange was measured for each sample by ICP. The results are shown in Table III. Local analyzes (EDX) and Global analyzes (elemental analyzes by ICP) were performed on two samples ion-exchanged. These exchanges were performed using two different methods of exchange as mentioned in the experimental section. These analyzes were focused to determine the amount and distribution of cesium cation on the zeolite fibre between the cavities.

The results obtained by EDX as shown in Fig. 10 and the average results of mass percentages of the elements in the fibre, before and after synthesis and calcination obtained by ICP as shown in Table III, shows that the first sample (exchanged by injection inside tubular module) showed that the average value of cesium is 0.5 to 0.6%, which corresponds to an exchange of less than 50% of the sample sites.



Element	keV	Wt%	At%	At Prop	Gross (cps)	Net (cps)
Al	1.487	61.64	76.58	0.0	1553.8	1513.5
Si	1.740	5.83	6.96	0.0	118.8	71.2
Au	2.121	26.27	4.46	0.0	167.2	114.4
O	0.523	5.65	11.84	0.0	24.4	17.7
Cs	4.286	0.60	0.15	0.0	40.2	2.3
Total		100	100	0.0		

Fig. 10 Concentrations of elements in mass and atomic percentages along the thickness of the sample A-004-1 (exchanged by injection inside tubular module)

TABLE III

AVERAGE PERCENTAGE MASS (ICP) FOR BOTH SAMPLES EXCHANGED;
MEMBRANE REF: A-004-1 AND A-004-2

Samples	Cs	Si	Al	Remarks
References	%m	%m	%m	
A-004-01	0.46	4.14	47.38	Limpid white insoluble
A-004-02	0.22	3.90	48.35	Limpid white insoluble

For the sample A-004-2 (ion-exchanged by impregnation), the results obtained by EDX as shown in Fig. 11 and ICP as shown in Table IV showed that the average value of cesium is 0.2 to 0.3% by cesium, less than first ion-exchange method.

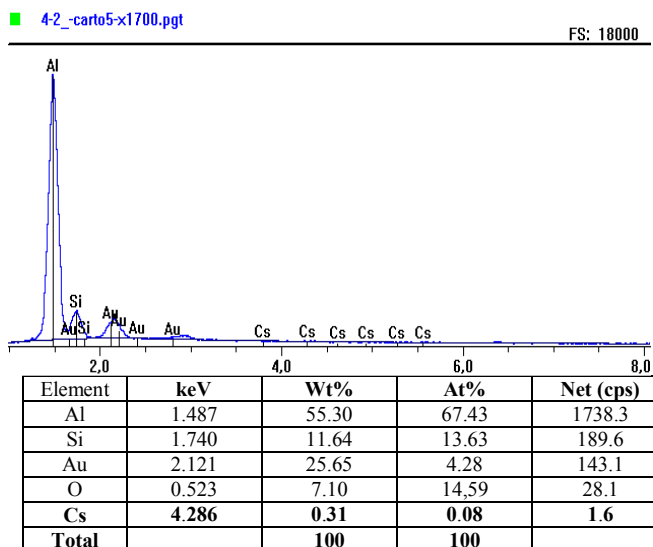


Fig. 11 Concentrations of elements in mass and atomic percentages along the thickness of the sample, membrane ref: A-004-2 (exchanged by impregnation)

According to the results obtained by EDX and ICP on the previous two samples A-004-3 exhibit the same chemical and physical characterization of A-004-1 and A-004-2 samples. Thus, ion exchange was focused on A-004-3 with the help of an injection pump installed in set-up for gas permeance and gas mixture separation to inject the ion-exchanged solution inside membrane module.

Table IV presents the operating conditions and the technique used to perform the ion-exchanged by Cs⁺ for A-004-3 membrane using the mentioned above method.

TABLE IV

OPERATING CONDITIONS FOR THE CATION EXCHANGE MEMBRANE A-004-3

Cation	C (M)	T (K)	Exchange technique used	Time (h)
Cs ⁺	1	353	Circulation in the membrane module with the help of a pump	24

C: Concentration of cesium chloride solution in (M), T: Temperature in (K)

Fig. 12 shows the evolution of percentage of mole fraction of CO₂ with temperature for H-ZSM-5 and exchanged membrane. Cs-ZSM-5 membrane showed an increasing in the percentage of mole fraction and was in the range of 0.74 for an equimolar concentration. The evolution of percentage of mole fraction of CO₂ with temperature which means or explain the fact that He sweeping increases the surface diffusion rate of CO₂ and decrease the permeate pressure. Fig. 13 shows the evolution of mole fraction percentage of CO₂ as a function of the temperature

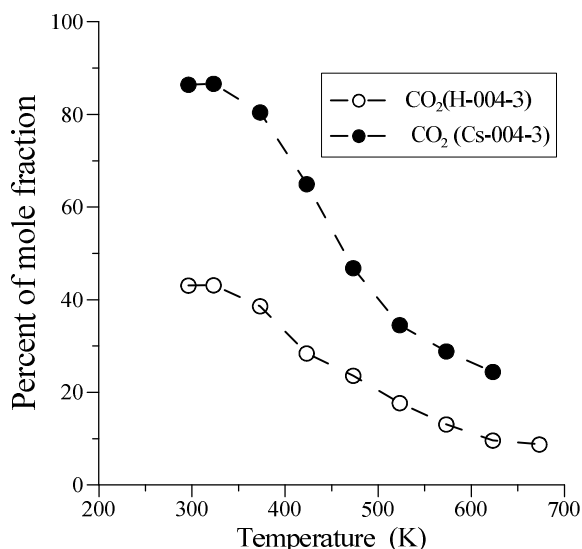


Fig. 12 Evolution of mole fraction percentage of CO₂ as a function of the temperature for samples H-004-3 and Cs-004-3 in the separation of an equimolar CO₂/N₂ mixture

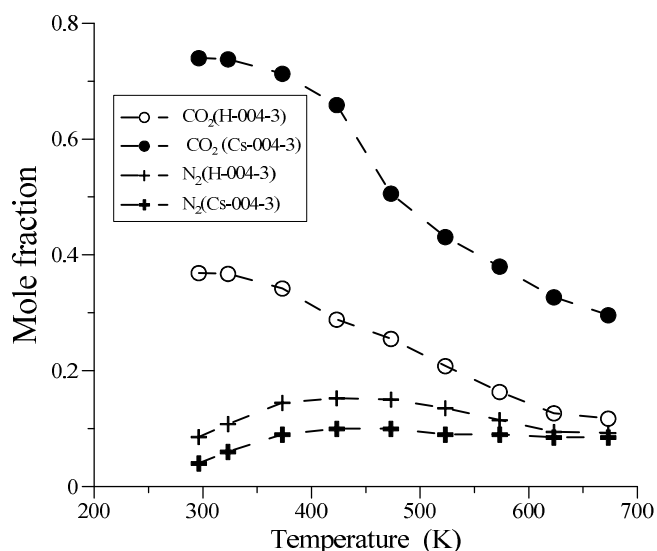


Fig. 13 Evolution of mole fraction percentage of CO₂ as a function of the temperature for samples H-004-3 and Cs-004-3 in the separation of an equimolar CO₂/N₂ mixture

VI. DISCUSSION

This work shows for the first time the synthesis of ceramic hollow fibers alumina/zeolite nanocomposite structure, resistant to high temperature and having high compactness. These materials showed selectivity for CO₂/N₂ with large flows. The supports used are alumina- α hollow fibers. Their properties are summarized in Table V.

TABLE V
 PROPERTIES OF HOLLOW FIBERS USED AS SUPPORT FOR THE SYNTHESIS OF ZEOLIT MEMBRANE

Outside diameter	1.7 mm
Thickness (Walls)	230 μ m
porosity	43%
Test Bubble	2.5 bar

The surface/volume ratio of the membrane is one of the main criteria for design of the separation units. This parameter may be increased by an order of magnitude when the diameter of the membrane tube passes cm wide than the mm. The hollow fibers of alumina used in this work were provided by the Engineering Institute of Interfaces and Biotechnology (Fraunhofer Institute) in Stuttgart. These fibers are prepared by a method of "wet-spinning" of a suspension of alumina particles in a dispersed- α polysulfone/N-methylpyrrolidone solution. The portion in the water causes the precipitation of the polymer with ceramic particles incorporation. The fibers are then calcined to remove polymer and cut to 30 cm length. These hollow alumina fibers were used as supports and subjected to the synthesis of MFI zeolite by the method of pore clogging. The MFI zeolite has been crystallized in the pores of the fibers by hydrothermal synthesis at 443 K for 4 days with a precursor solution of TPAOH + Aerosil 380. After synthesis, the fibers were characterized by SEM (+EDX), XRD and nitrogen adsorption at 77 K. A nanocomposite structure of MFI-alumina was obtained and characterized by scanning electron microscopy (SEM) and dispersion energy X-ray (EDX). In all cases, after the synthesis, the zeolite material was crystallized in the pores of the support without formation of a thin surface layer. The XRD diffractograms indicate the presence of a pure MFI phase. In addition, nitrogen adsorption isotherms at 77K reveals a remarkable increase in the specific surface area after the synthesis of the MFI (from 2.2 to 33 m².g⁻¹), due to the microporosity of the zeolite material. The synthesis was confirmed by the evolution of permeabilities of pure gas permeances at high temperatures on the first sample prepared. To perform the tests of gas permeation and separation, the fibers were mounted in dense alumina perforated tubes 7 mm in inside diameter and 15 cm in length. Many trials were needed to seal this assembly made difficult because of the fragility of fibers and dense alumina tubes (orientation of the drill holes). From the adsorption data available in the literature or calculated, the Stefan-Maxwell modeling provides an equivalent thickness of approximately 1 micron hollow fiber for zeolite studied. The qualities of the membrane prepared were evaluated by gas n-butane/H₂ separation (separation factors of about 20 at room temperature). A preliminary study of the CO₂/N₂ separation was performed according to the supply pressure at room temperature.

VII. CONCLUSION

The results obtained by EDX as shown the average results of mass percentages of the elements in the fibre, before and after synthesis and calcination obtained by ICP shows that the first sample (exchanged by injection inside tubular module) showed that the average value of cesium is 0.5 to 0.6%, which corresponds to a exchange of less than 50% of the sample sites. No surface film, has been obtained, as observed by SEM and EDX analysis and confirmed by high temperature variation of N₂ and CO₂ gas permeances before cation exchange. The MS fittings reflect an equivalent MFI thickness

close to 1 μm . Introduction of exchanged ion of Cs^+ cations into ZSM5-type zeolites was presented by two ion-exchange methods (Impregnation and injection) used. The exchanging H^+ by Cs^+ ions using injection method gave concentrations of exchange less than 50% of the sample sites. This explained that the gas permeance and gas mixture separation depend strongly on the method used which describe the permanent circulation of ion-exchange inside tubular module and also the substituted cations.

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