International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:9, 2014

Separation of CO_2 Using MFI-Alumina Nanocomposite Hollow Fiber Ion-Exchanged with Alkali Metal Cation

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***Abstract*—**Cs-type nanocomposite zeolite membrane was successfully synthesized on an alumina ceramic hollow fibre with a mean outer diameter of 1.7 mm; cesium cationic exchange test was carried out inside test module with mean wall thickness of 230 μm and an average crossing pore size smaller than 0.2 μm. Separation factor of n-butane/H_2 obtained indicate that a relatively high quality closed to 20. Maxwell-Stefan modeling provides an equivalent thickness lower than 1 μm. To compare the difference an application to CO_2/N_2 separation has been achieved, reaching separation factors close to (4,18) before and after cation exchange on H-zeolite membrane formed within the pores of a ceramic alumina substrate.

***Keywords*—**MFI membrane, nanocomposite, Ceramic hollow fibre, CO_2, Ion-exchange.

I. Introduction

THE hollow fibres are a special case of symmetric support in the form of tubes of tens to hundreds of microns in outside diameter. These tubes can be extremely thin and not exceed in some cases the thickness of a human hair (diameter about 100 μm). Their inner diameter is variable, being of the order of half of the outer diameter for the finer fibres. The use of hollow fibre geometry has long been a solution to improve the performance in the membrane separation processes. In the liquid phase (water treatment), the hollow polymeric fibres are commonly used on an industrial scale. Similarly, in the gas separation, they are widely used in industry (for example refineries or production of ammonia). Their low cost, large ratios associated with surface/volume (>1000 m^2/m^3) and compared with the monolithic multi-channel tubes (30-250 m^2/m^3 and 130-400 m^2/m^3), respectively [1] are in the configuration of choice for many membrane. Ceramic hollow fibres are one of the inorganic hollow fibres that have an asymmetric structure, which provides an improved permeability for a given thickness. In addition to their common use in many separation processes, they can also be used as support for the synthesis of composite membranes [2].

There are various methods to prepare hollow fibre ceramic materials, such as spinning coagulation [3], and spinning a solution containing ceramic powders [4]. Recently, the phase inversion method used to prepare polymeric hollow fibre was successfully modified to prepare ceramic hollow fibres [5]. Due to its asserted role in the global climate change, the separation of carbon dioxide from gas emissions is one of the main challenges of membrane researchers and manufacturers at present. Carbon dioxide, caused mainly by emissions of fossil-fuel-related, rose at a rate of 80%, noting that the increase of carbon dioxide from 2011 to 2012 was greater than the average rate of increase over the past ten years [6]. The concentration of carbon dioxide, methane and nitrous oxide in the atmosphere has reached unprecedented levels in the 800,000 the previous year. If the conditions continue like this, the global average temperature may rise by 4.6 degrees by the end of the century than it was the levels of pre-industrial era, and perhaps even more so in some parts of the world. The World Meteorological Organization-the United Nations - has indicated in a report released late last year, that the amount of greenhouse gases in the atmosphere has reached a new record in 2012, continuing the upward trend accelerated, which leads to climate change. There are other results show that the climate change has increased by 32% between 1990 and 2012 due to increased carbon dioxide and other gases retain heat and the long-term, such as methane and nitrous oxide [7]. Global warming continues to accelerate as it occupied in 2013 ranking sixth in the list of more years, increased in temperature. Most zeolite membranes have been implemented in carbon dioxide separation in single tubes, multichannel tubes and monoliths or planar geometries. Kusakabe et al. [8]-[10] have probably the best results reported using the faujasite type zeolite membranes (X and Y) for the separation of CO_2 from CO_2/N_2 equimolar mixtures. These authors obtained CO_2/N_2 separation factor of the order of 100 with pure CO2 permeance of about 0.2 $\mu mol.m^{-2}.s^{-1}.Pa^{-1}$ at 303K. The reference method for CO_2 capture is chemical absorption using amines [11]. The main disadvantage of this method is its high energy consumption due to the regeneration of the solvent [12]. Although the cellulose-based polymers, polyamides, polysulfones, polycarbonates and polyetherimides membranes have been widely used for the separation of carbon dioxide [13], their practical use is limited due to their low selectivity, between 20-50, and very low permeance of about 0.1-10 $nmol.m^{-2}.Pa^{-1}.s^{-1}$ [14]. On the contrary polymeric membranes, inorganic membranes such as zeolite membranes were considered candidates alternative, because of their thermal stability, chemical and mechanical [15], [16] and mainly because of their much higher permeance. CO_2 separation of methane is also important. Methane can be obtained from various sources such as natural gas and biogas. Most of these sources produce a CH_4 rich mixture containing

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significant amounts of other gases such as CO_2 and H_2S. Using zeolite membranes NaY, Hasegawa et al kind. [17] obtained CO_2/CH^4 separation factors of about 20 and pure CO_2 permeance of about 0.1μmol.m^{-2}.s^{-1}.Pa^{-1} in separation equimolar mixture CO_2/CH_4 at 303K. Smith et al. [18] have shown the preparation of zeolite membranes based on carbon hollow fibres, but with neither permeation nor separation tests. Richter et al. [19] published a work based on 'capillaries' (i.e. tubes of about 4 mm diameter), with single gas permeances around 0.5 μmol.m^{-2}.s^{-1}.Pa^{-1}, but no quality testing was provided further, making it very difficult to assess for membrane quality. Xu et al. [20] presented the synthesis of zeolite NaA membranes on 0.4 mm diameter ceramic hollow fibres, showing a continuous 5-μm film offering typical single permeances of ~0.03 μmol.m^{-2}.s^{-1}.Pa^{-1}. Their membrane quality was estimated by pure gas permeance only, which is difficult to use for reliable defect searching [21]. The property of the inorganic cation exchange of the zeolite was observed for the first time 105 years ago. The ease of cation exchange in zeolites and other inorganic lead to a start of interest ion exchange materials for use as agents for softening water. Synthetically Aluminosilicates non-cristallins aluminosilicate materials were mainly used. Recent years, the ion exchange of organic resins was used. Crystalline zeolites have been used commercially as water softeners. Crystalline silicate has three-dimensional space creates a micro porous structure wherein the molecules are adsorbed, most of the exchange with zeolites ion exchange; mineral clays due to their two-dimensional structures may undergo swelling or shrinkage with cation exchange. Zeolite minerals are commonly used for the removal of radioactive ions from the waste. Al or Si atoms may be substituted with other elements (Cs, Li, Na, Cu, P, Ti) in order to modify the reactivity of the materials [22]. The zeolites cation exchange behavior depends on: (1) the nature of the cation species, sizes cation two anhydrous and hydrated, and the charge of cation; (2) the temperature; (3) The concentration of the cation species in solution; (4) The species of anions associated with the cations in solution; (5) The solvent (most exchanges were conducted in aqueous solutions, although some work has been done in organic solvents); and (6) the characteristics of the zeolite structure. Few studies have been focused on the ion-exchanged zeolite membranes and its per selectivity's. Jafer and Budd [23] studied the ion-exchanged on NaA zeolite membranes with K+ but no signifcant change in pervaporation performance was observed. Kusakabe et al. [24] investigated the ion exchanged on NaY zeolite membranes. These kinds of zeolite membranes were ion-exchanged with alkali and alkali earth metal cations (Li^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}). KY-and MgY-zeolite membranes offered higher CO_2:N_2 permeation selectivities than did a NaY-zeolite membrane. The permeation selectivity was found 19.6 at 313 K. The ability of these membranes to absorb binary mixtures was estimated on the basis of single components. When Na. was exchanged with K., the CO_2 permeance increased and the N_2 permeance decreased. The effect of the cation species on sorptivities was examined, the CO_2/N_2 selectivity increased to 30.3. When Na was exchanged with Li, however, N_2 permeance increased almost an order of magnitude, and the CO_2/N_2 separation selectivity decreased to 3.5.

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 substrate. Nanocomposite structure of MFI-type zeolite hollow fibre membranes were then prepared in the porous matrix of α-alumina hollow fibre support via pore-plugging hydrothermal synthesis for MFI/ceramic membranes described in [25]-[27] and ion-exchanged using Cs+ ions. Among the gaseous separations studied using the membrane ion-exchangedwas CO_2 separation. Indeed, the uptake of this gas in anthropogenic emissions is currently considered as an important opportunity to reduce greenhouse gases and global warming CO_2/N_2 separation tests on MFI fibres showed selectivities in favor of CO_2. The separation factor was about 4 for ion-exchange membrane at room temperature with mixture CO_2 permeance 1.1 μmol/(m^2.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 CO_2. 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/(m^2.s.Pa).

II. Experimental Methods

A. Ceramic Hollow Fibre Supports

The hollow ceramic fibres used in this work were provided by the Engineering Institute of Interfaces and Biotechnology (Fraunhofer Institute) Stuttgart (Th Schiestel). To produce these fibres, α-alumina particles having an average-size of 0.33 microns were incorporated into a polymer solution in N-methyl-2-pyrrolidone (NMP) and then mixed for 16 h. It is from this mixture as the phase inversion was completed. The hollow fibres obtained were then calcined to remove all traces of polysulfone. The polymer solution containing the alumina particles (collodion) is then extruded through a spinneret to form hollow fibres by a wet spinning process [28]. Furthermore, an internal fluid is coextruded to avoid closure of the liquid tube by collodion effect of the interfacial tension. The internal fluid may be either a solvent or non-solvent, and the resultant structure differs depending on the case.

The structure properties of the resultant fibres are summarized in Table I.

TABLE I
Properties of the Ceramic Hollow Fibres Used as Supports for Zeolite Membrane Synthesis in This Work

Mean outer diameter, mm	Mean wall thickness, μm	Mechanical stability, (MPa)	Porosity %	First bubble point *(bara)*
1.70	230	112	43	2.5

In order to access the fibre defects and choose comparable supports for the same synthesis batch, all the fibres used are tested using a method based on gas-liquid displacement before synthesis.

First of all, the fibres were carefully mounted on a metal connector using epoxy resin see Fig. 1, immersed in an ethanol at least 24h to ensure that all the pores are occupied by ethanol. Then the test starts with introducing N_2 into the support side of the fibre. It is then possible to determine the presence of the first bubble representing the largest tube defect. During testing, the support kept immersed in ethanol with increasing N_2 pressure, more and more pores will be opened, and the flux through the support under different pressure difference can be measured. With these data, the support pore size can be calculated and the support quality compared according to the pore size distribution.

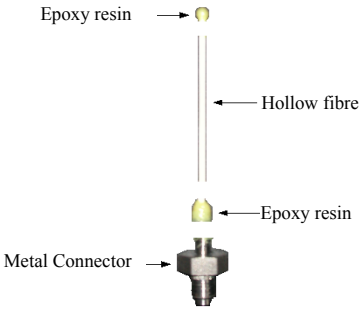

Fig. 1 Mounting of the fibre on a metal connector using epoxy resin to carry out the bubble test of support

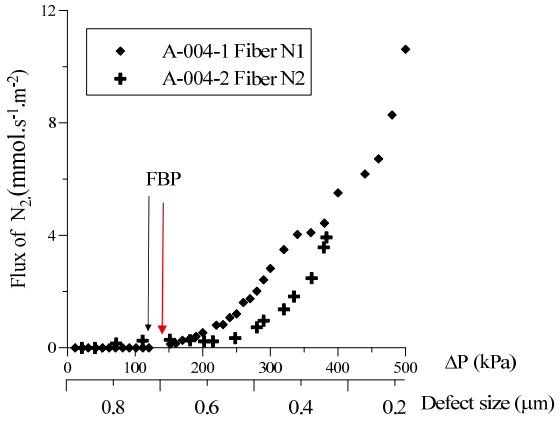

Fig. 2 Evaluation of N_2 flow with differential pressure for a porous support immersed in an ethanol for 24 h. (FBP, First Bubble Point)

According to Laplace Law, the pressure of the first bubble allows the determination of the largest pore size of the fibres. The further increase of the permeating gas flux with the gas overpressure (up to 4 bar by 15 min with 0.1 to 0.2-bar steps) allowed a relative comparison of fibres of similar structure, with regards to the importance of subsequent smaller defects in the fibres. Fig. 2 shows a bubble flow graph obtained for two hollow fibre supports tested in this study (Sample references: A-004-1 and A-004-2). As can be seen in Fig. 2, after a first bubble point (FBP) at 125 (ΔP) a sharp increase is observed in the N_2 flux. This indicates that the average crossing pore size is 0.2 μm. For two these samples, comparable to values on supports used in previous studies [21]-[29].

B. Synthesis of Mfi-Type Zeolite Hollow Fibre Membrane

Clear synthesis solution of molar composition 1.0 SiO2: 0.45 TPAOH : 27.8 H_2O (pH close to 14) was prepared by mixing 6g–fumed SiO_2 (Degussa Aerosil 380) with 50 ml of 0.9M tetrapropyl ammonium hydroxide (TPAOH) after diluted it in deionised water. After 72 maturation under stirring at room temperature, clear solution was obtained. To make sure that no small particles were left in the precursor before being into the Teflon insert of the autoclave, the solution was centrifuged for 40 min. nine 23-cm long ceramic hollow fibres were inserted into a Teflon-lined autoclave containing about 25 ml of precursor solution before the synthesis solution was poured carefully in it [21]. Then the autoclave was sealed and placed in an oven preheated at 170°C. The hydrothermal treatment was performed at 443 K for 89 h. The amount of precursor was calculated on the bases of single tubes considering the ratios precursor volume/porous volume/membrane surface. These calculations are summarized in Table II.

TABLE II
RATIOS OF VOLUME OF PRECURSOR / POROUS VOLUME / SURFACE OF TUBES AND FIBERS

	porous volume (cm^3)	Surface (cm^2)	Volume of precursor (ml)	Ratios (precursor volume / porous volume)	Ratios surface/vol. of precursor (cm^{-1})
Tube	1.302	28.6	18	13.8	1.59
9 Fibres	1.366	84.7	≈ 23.2	15.8	3.9

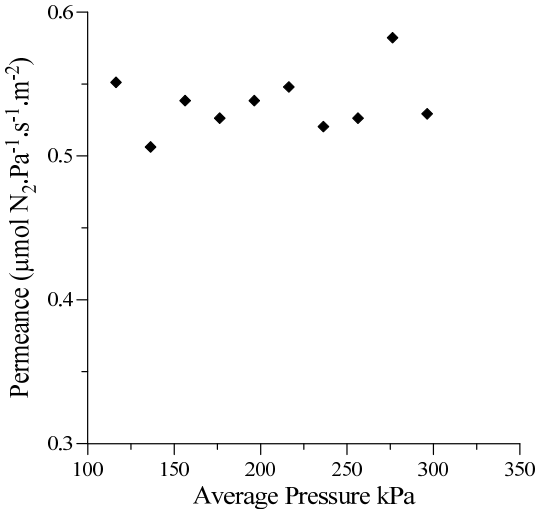

Fig. 3 Check for the presence of any open defect using N2 permeation test of zeolite hollow fibre as a function of the medium pressure before calcination at 773 K. (T = 296.65 K, ΔP = 32 mbar)

After the hydrothermal synthesis, the fibres were washed and then dried at 373 K for 12 h. To ensure that the precursor

of synthesis has penetrated all pores and a stoppered, nitrogen permeance of the membrane is measured. Fig. 3 shows a single N_2 permeation test before calcination step. The gas separation characterisation is also the next step in this study. The membrane was then calcined at 773 K in air for 8h to remove the template molecules.

More details dealing with this one cycle zeolite hydrothermal synthesis and the calcination protocol can be found in [21].

C. Preparation of Ion-Exchanged Cs-Type Zeolite Hollow Fibre Membrane

The gas separation can be improved by considering the exchange of cation by another. The method used to synthesize the fibres gives a MFI zeolite where the valence of cation is a proton (H-ZSM5).

Tests were carried out on small samples of zeolite hollow fibers, firstly by soaking (impregnating) and secondly by injection into the fibre. This allowed physical characterization of these exchanges. Preliminary, cesium cationic exchange tests were carried out on hollow fibre. Zeolite hollow fibre has a 22.8 cm of length; fibre has been chosen and cut into two samples of 7 cm (see Table III). Two different methods of cation exchange were initially proposed to realise ion-exchange of membrane before the fibre is mounted in the module. Table III shows the properties of two samples used as supports for ion-exchanged using Cs solution.

TABLE III
CHARACTERIZATION OF ION- EXCHANGED SAMPLES WITH CESIUM

A	B	C	D	E	F
A-004-1	7	17	4.13×10^{-3}	1.92	impregnation
A-004-2	7	6	1.40×10^{-3}	0.70	syringe

A: Denomination *E: H^+ (mmol)*
B: Length (cm) *F: %m expected in the case of Cs^+ exchange 100%*
D: ZSM-5 mass (mg) G: conditions of exchange Operation

The first method was focused on impregnating the first fiber (A-004-1) completely in a crystallizer containing a solution of 1M cesium chloride. The solution was stirred at 200 rpm/min for 24 h at temperature of 353 K.

The second method was realised by injecting an amount of the same solution using a syringe, inside the sample (A-004-2). One of two ends of the fiber was blocked by Teflon before and after filling of the solution. We then covered the entire length of the outer surface of the fiber with Teflon tape to prevent evaporation of the solution. The solution is then allowed to slowly diffuse into the fiber for 24 h at room temperature. The membranes were then rinsed with DI water and dried at 373 K for 30 min and calcined at 773 K for 3 hr.

A-004-3 membrane already tested was ion-exchanged to compare between an ion-exchanged membrane and protonated membrane. But due to the sealing problems of joints of the module, "in-situ" method of cation exchange was selected. This method does not involve the release of the module and the seals are not stressed (sought). The previously rinsed module and the fibre with water were then circulated with a solution of cation chloride of concentration of 1 M for 24 hrs. Module then rinsed with water to prevent the salt solution from being attached onto the fibre. During the ion-exchange process, a current of nitrogen gas is circulated at the permeate side. This therefore, allows observation of the behavior of the fibre before (zeolite H-ZSM-5) and after ion-exchange (zeolite M -ZSM-5 where M = Cs^+).

Experiments of cation exchange were performed to make membrane more selective to transport of CO_2. 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 the second method (i.e. protocol on the tubular stainless steel module); the fibre remains sealed inside the model before and after cation exchange. A second exchange protocol (syringe), allowed abstracting any problems concerning the sealing of the tubular module during removal or set up the fibre. The solution was already prepared and stirred at 200 rpm/min for 24 h at temperature of 353 K. The fibre inside module then rinsed with demineralised water to prevent the salt solution attaches itself onto the fiber.

However, this method does not facilitate the analysis of the operation and the first data need to be validated [30].

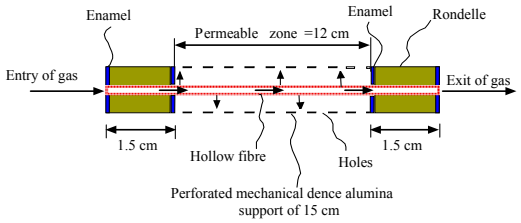

Fig. 4 (a) Schematic mounting of the fibre before sealing enamel at 600°C in a dense alumina tube with holes

Fig. 4 (b) Schematic mounting of the fibre before sealing enamel at 600°C in a dense alumina tube with holes

Fig. 5 Photographs of fibres mounted into their mechanical dense alumina support with a new layer of enamel tube. Step before sealing and enamelling

D. Single Gas Permeance

Before each use of a new hollow fibre membrane or each gas change, the membrane is pre-treated in order to desorb the retained species in the zeolite phase which might distort the measurements of gas transfer [21]-[30].

A pre-treatment protocol was realized before making the

measurements of permeation and gas separation. N_2 (15 ml/mn) was introduced from both retentate and permeate sides and the module heated at a rate of 1°C/min up to 400°C for 6 hour. The pre-treatment is carried out directly in the module used for measurement of the gas permeation and separation, so as to avoid pollution by the ambient atmosphere.

Permeance of pure N_2 and H_2 was measured at different temperatures (293-723K) before ion-exchanged. Permeance of gas mixture of CO_2/N_2 was performed before and after the ion exchange of the membrane at inside pressure (P_r=168 kPa) and pressure drop of (ΔP=0.4 kPa) with equimolar feed $1.12*10^{-4}$ $mol.s^{-1}$ and helium sweep gas flow rate of $4.5*10^{-5}$ $mol.s^{-1}$.

E. Mixture Separation

Before any transport measurement, the hollow fibres were subjected to an in situ high temperature desorption pretreatment at 673 K under 20 $NmL.min^{-1}$ N^2 flow at both sides with a heating ramp of 1 $K.min^{-1}$ for at least 4 h to remove adsorbed species. For all gas mixture separation tests, the separations were carried out by sending the gas mixture into an internal compartment, the outer compartment being swept by a counter-current of pure gas. The mode used was Wicke-Kallenbach mode: the gases to be separated were diluted in dry gas of N_2 (15 v/v.%). The feeding system was kept at about 125 kPa, with a flow rate of 75 Ncm^3/min, N_2 counter-current sweep gas of also 56 Ncm^3/min. The transfibre differential pressure was kept at 0.4 kPa.

Pneumatic valve regulates a differential pressure of zero between the two compartments to limit any convective flow. At the output of the two compartments of the test module, the flow rates are measured and the compositions are analyzed by chromatography (HP 5890), using both TCD and FID detectors. To determine the quality of our membranes before tested for any gas separation, the gas mixture of n-butane/H_2 is separated at room temperature. n-butane/H_2 separation gives the first indication about the quality of the membrane because the strong adsorption of n-butane on zeolite pores will object adsorption of H_2. Then its permeation will be reduced [30]. Thus, the existence of any defects of mesoporous type will be reflected on the quality of the membrane and inverse the selectivity. In addition, the fibre was also tested for separation of CO_2/N_2 before and after ion-exchange. This separation was carried out further with increasing temperature. Undiluted equimolar mixtures (204 Ncm^3/min feed and 12 Ncm^3/min N_2 sweep, 700 Pa trans fibre total pressure) in order to survey a potential application of these materials for CO_2 separation. Keeping equimolar feed, the total feed pressure was varied from 100 to 340 kPa. In both separations, gas flows and feed compositions were controlled by mass-flow controllers (Brooks, type 5850TR). The separation factor (S_f) between two components was calculated based on the formula defined as the permeate-to-feed composition ratio of the first gas, divided by the same ratio of the second one (i.e. mixture of n-butane/hydrogen or case of mixture carbon dioxide/ nitrogen).

III. Result and Discussion

A. Support Pores Volume and Quality Test

Fig. 2 shows two typical bubble flow graph obtained at (ΔP) of 125 and 128 kPa. It is well known that permeance is a measure of the volumetric gas flow rate per unit of fibre surface area per unit of transmembrane pressure. It can be seen also in Fig. 2 a sharp increase in the N_2 flux for two samples (A-004-1 and A-004-2) before MFI Synthesis. Fig. 3 shows the results generated for the permeance of nitrogen before calcination. The results indicate that the zeolite deposited in the porous matrix of samples of medium pores sized of 0.2 µm were not permeable and shown that the zeolite plugged the pores of samples. A separation factor of about 20 for n-butane/H_2 with a permeance of nitrogen of 1.1 $\mu mol/m^2/s/Pa$. Before calcination the nitrogen flow should be zero or very low (i.e. below the detection limit of about 10^{-10} $mol.m^{-2}.s^{-1}.Pa^{-1}$), which explains that the precursor has penetrated into all the pores of the fibre and has blocked it. From these results we conclude that one synthesis cycle should be enough to build a defect-free membrane.

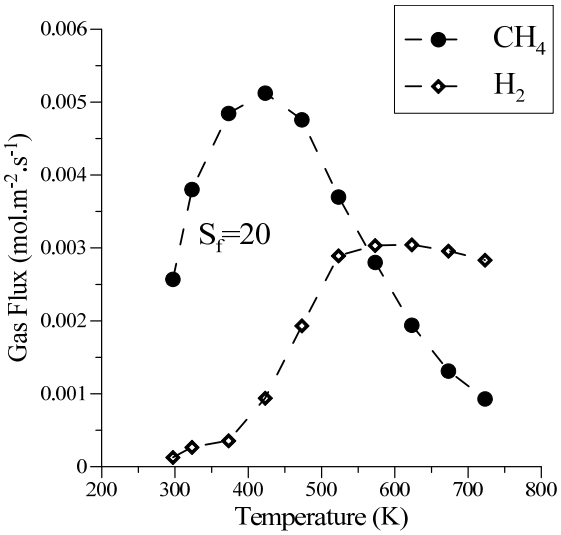

Fig. 6 Mixture separation nC_4H_{10}/H_2 as a function of temperature for H-MFI/α-Al_2O_3 hollow fibre membrane prepared by the « pore plugging method » at 170 °C for 3 days and fired at 500 °C in air. Temperature range from 300 to 750K. Conditions: Retentate pressure 125 kPa and transfibre pressure 0.4 kPa. (Sf = 20). Membrane ref: A-004-3

B. Separation of N-Butane/H_2 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 well be blocked first by n-butane adsorption and when the proportion of n-butane increases, larger and larger pores are blocked by condensation of nC4H10 gas and become unavailable for H_2 transport. Fig. 6

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 nC4H10 but at the highest temperature the quantity of nC_4H_{10} decreases and the selectivity well 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.

C. H_2 and N_2 Permeance

After reaching steady stat conditions, the out flow Q in permeate compartment is measured. The synthesis was confirmed by the evolution of permeabilities of H_2 and N_2 at high temperatures on the sample prepared of reference of A-004-3 (No surface film, has been obtained). Then two measurements of permeance with temperature is performed with a constant pressure ΔP of 3.2 KPa. The gas permeances of N_2 and H_2 were studied in order to evaluate the quality of hollow fibre membrane and their molecular sieving or shape selective transport properties. Gas permeation measurements with mixtures components were also performed for a real evaluation of zeolite membranes quality after ion-exchange. The permeance obtained is generally of the order of 1.11 to 2.3 $\mu.mol.m^{-2}.S^{-1}.Pa^{-1}$ for CO_2 and of the order of 0.12 to 0.06 $\mu.mol.m^{-2}.S^{-1}.Pa^{-1}$ for N_2 gas before and after ion-exchange. From the adsorption data available in the literature or calculated, the Stefan-Maxwell modeling provides an equivalent thickness of approximately 1μm for hollow fiber zeolite studied, membrane ref: A-004-3.

$$N = \frac{c_{sat}\rho\varepsilon D_o^{\infty}}{\tau\ell}\ln\left[\frac{1+\frac{P_R}{P^o}\exp\left(\frac{\Delta S^o_{ads}-R}{R}-\frac{\Delta H^o_{ads}}{RT}\right)}{1+\frac{P_P}{P^o}\exp\left(\frac{\Delta S^o_{ads}-R}{R}-\frac{\Delta H^o_{ads}}{RT}\right)}\right]\exp\left[-\frac{E_D}{RT}\right] \quad (1)$$

The Stefan-Maxwell equation (1) was used to determine the actual thickness of the zeolite layer of the membrane of reference of A-004-3 from pure transmembrane flux of hydrogen gas, as shown in Fig. 7.

This equation expresses the flux of a species based on three types of parameter:

- Parameter interaction molecule / membrane:
- Adsorption parameter: csat, ΔHoads and ΔSoads
- Diffusion parameter: D_0^{∞}: and E_D
- Geometric parameters of the membrane : ε, τ, ρ and L
- Operating parameter: T, P_R, and P_p

The geometric parameters of the membrane of reference of A-004-3, with the exception of the effective thickness L, and operating parameters are known, the parameters of diffusion and adsorption of H_2 in the MFI are taken from the bibliography.

TABLE IV
GEOMETRIC PARAMETERS OF THE COMPOSITE MEMBRANE, MEMBRANE REF: A-004-3

porosity, ε (-)	tortuosity,τ (-)	density MFI, ρ ($Kg.m^{-3}$)	Equivalent thickness of the MFI (m)
0.13	1.2	1.7×10^{-3}	2×10^{-6}

To consider the characteristics of composite material alumina/zeolite used in this study, the porosity and tortuosity of the zeolite have been corrected by the α-alumina, zeolite occupying the porosity of the alumina support. The total porosity of 0.13 has been obtained by multiplying the porosity of the alumina-α (0.43) by this of the MFI zeolite (0.30). Channels of the MFI zeolite being straight and parallel, a tortuosity of 1 was assumed for the MFI [30]. Therefore, the tortuosity of the macroporous support (1.2) is used as the tortuosity of the composite material.

The characteristics of adsorption and diffusion of values of the hydrogen in the H-ZSM-5 were taken from [21].

TABLE V
CHARACTERISTICS OF ADSORPTION AND DIFFUSION OF VALUES OF THE HYDROGEN IN THE H-ZSM-5. FIBRE MEMBRANE REF: A-004-3

adsorbate	$-\Delta\Sigma^o_{ads}$ ($J.mol^{-1}.K^{-1}$)	$-\Delta H^o$ ($mol^{-1}.K^{-1}$)	c_{sat} (mol m^{-3})
H_2	5.9	43	5.4

R: 8.314 $J.mol^{-1}.K^{-1}$ (ideal gas constant)
$D0\infty$: $1.8x10^{-8}$ $m^2.s^{-1}$ (Maxwell-Stefan diffusivity at zero coverage for H_2)
P_R: 104000 Pa (retentate pressure)
P_P: 100800 Pa (permeate pressure)
P_0: 101325 Pa (reference pressure)
E_D: 2000 $J.mol^{-1}$ (diffusion activation energy for H_2)

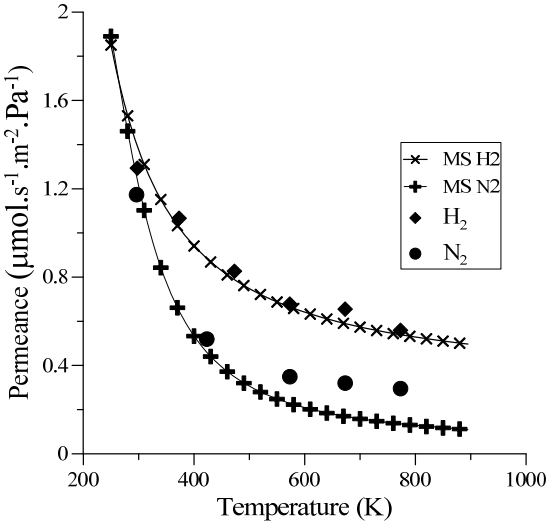

Fig. 7 Evolution of single gas permeance of hydrogen and nitrogen for the membrane H-ZSM-5 and fitting of the Stefan-Maxwell equation (H_2: Pr = 104 kPa, ΔP_{H2} = 3.2 kPa, N_2: Pr = 103.7 kPa; ΔP_{N2}= 3.2 kPa;, T = 298 K). Membrane ref: A-004-3

The Stefan-Maxwell fittings reflect an equivalent thickness of MFI close to 1μm

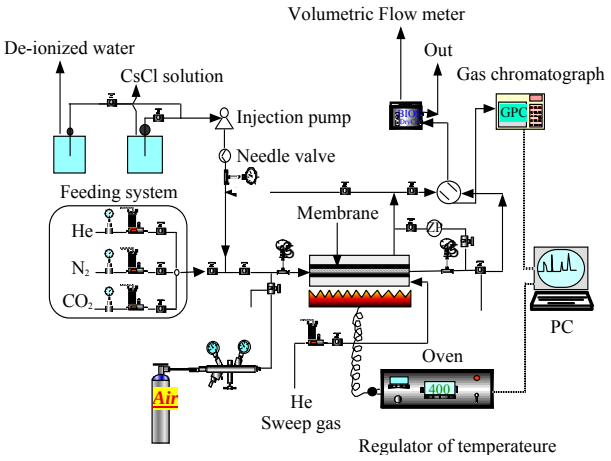

Fig. 8 Set-up for gas permeance and gas mixture separation

D. High Temperature Variation of N_2 and CO_2 Gas Permeance Before and After Cation Exchange-Dynamic Characterization

1. Effect of Temperature

The ion-exchanged fibre membrane (Cs-004-3) was subjected to a number of measures of separating mixture of carbon dioxide/nitrogen. It has been observed that there was a significant difference in the results between the H-ZSM-5 and the Cs-ZSM-5 (H- 004-3 and Cs+-004-3, respectively).

The mixture of CO_2 permeance at ambient temperature decreases for H+ and Cs+ hollow fibre membrane as shown in Fig. 9 This means that the real value of the permeance of nitrogen and CO_2 is not law, if at high temperature a counter-diffusion of helium is obvious, it is not impossible that there is a counter-diffusion of helium at room temperature

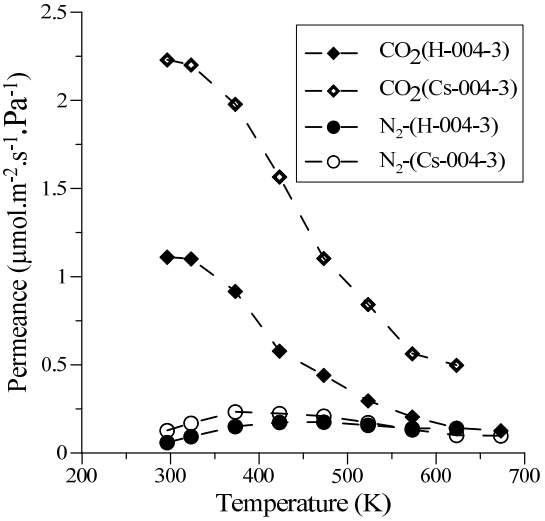

Fig. 9 Evolution of mixture CO_2 and N_2 permeances with temperature for samples H-004-3 and Cs-004-3 in the separation of an equimolar CO_2/N_2 mixture. Operating condition equimolar feed. (Pr = 168 kPa; ΔP = 0.4 kPa, helium sweep flow 4.5* 10^{-5} mol.s^{-1})

2. High Temperature Variation of N_2 and Co_2 Gas Molar Flux Before and After Cation Exchange

The evolution of molar flux of nitrogen and carbon dioxide with temperature before and after cation exchange are measured and shown in Fig. 10. The flow of carbon dioxide increased at room temperature 296 K for ion-exchanged hollow fibre membrane A-004-3. At low temperatures (T <400 K) the flow of nitrogen is very low and lower than that of carbon dioxide. Between 373 and 673 K, the nitrogen flow decreases rapidly as the flow of carbon dioxide begins to decrease strongly.

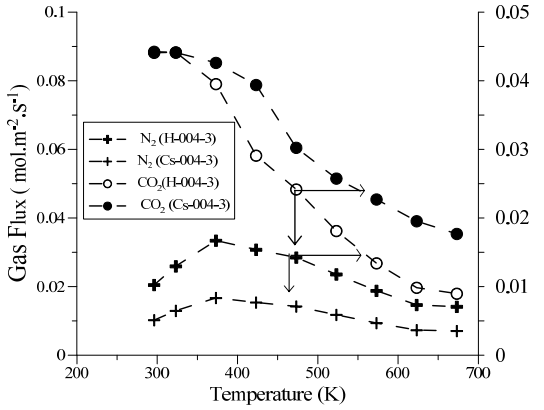

Fig. 10 Evolution of CO_2 and N_2 molar flux with temperature for samples H-004-3 and Cs-004-3 in the separation of an equale molar CO2/N_2 mixture. (Pr = 168 kPa; ΔP = 0.4 kPa. Feed equimolar 1.12*10^{-4} mol.s^{-1}; He sweep flow, 4.13*10^{-5} mol.s^{-1})

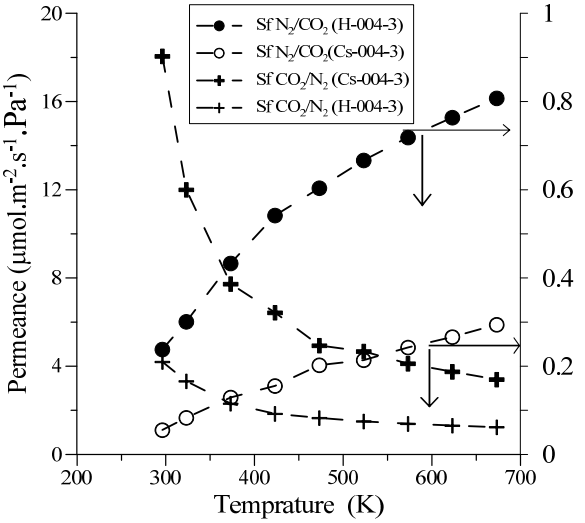

Fig. 11 Evolution CO_2/N_2 and N_2/CO_2 separation factor with temperature, membrane for samples H-004-3 and Cs-004-3 operating condition: equimolar feed 150 Nml / min; Pr = 168 kPa; ΔP = 0.4 kPa

Separation factors were increased for the exchanged membrane than the protonated membrane (H+) as shown in Fig. 11. This means that the permeance of CO_2 and N_2 have varied, depending on ratio. However, about the quality of the exchange, it seems to be confirmed by EDX analysis reveals

the presence of cation exchanged but no trace of chlorine. Cations observed are solely those exchanged with protons of the zeolite and does not appear to be salt residue. If that were the case we would have observed the presence of chlorine in the same places where cations were detected.

Fig. 12 shows the evolution of percentage of mole fraction of CO_2 with temperature for H-ZSM-5 and exchanged membrane. Cs-ZSM-5 membrane showed a 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 CO_2 with temperature which means or explain the fact that He sweeping increases the surface diffusion rate of CO_2 and decrease the permeate pressure

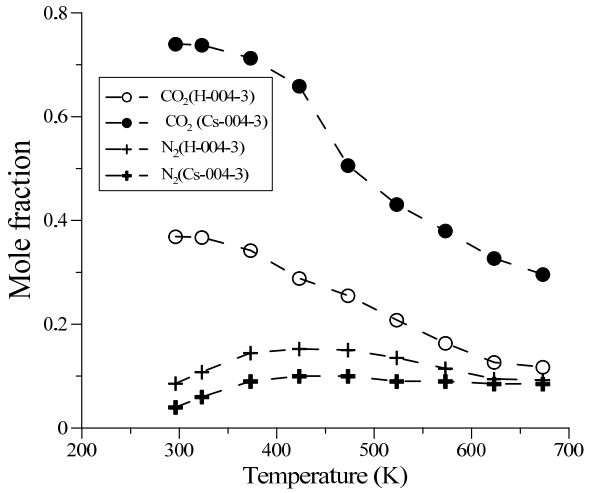

Fig. 12 Evolution of mole fraction percentage of CO_2 as a function of the temperature for samples H-004-3 and Cs-004-3 in the separation of an equimolar CO_2/N_2 mixture

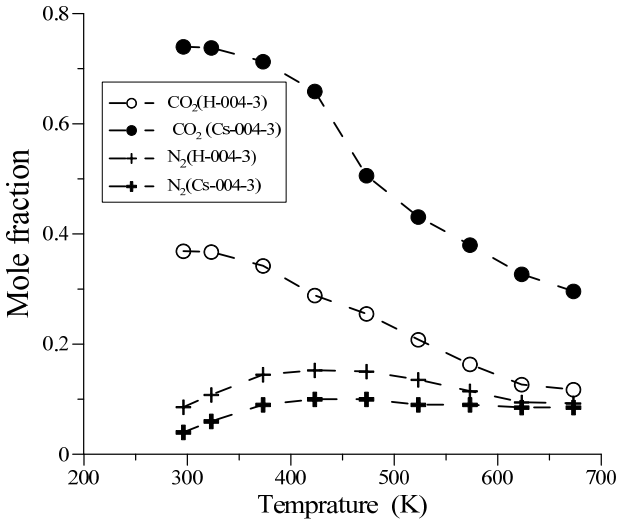

Fig. 13 Evolution of mole fraction percentage of CO2 as a function of the temperature for samples H-004-3 and Cs-004-3 in the separation of an equimolar CO_2/N_2 mixture

IV. Conclusion

In this paper zeolite hollow fibers membrane (0.2μm) were synthesized via pore-plugging via pore-plugging hydrothermal synthesis following the protocol described in a series of previous studies [21]-[30]. The hollow fibers of α–alumina were used as supports. Introduction of exchanged ion of Cs+ cations into ZSM5-type zeolites was presented by two ion-exchange methods (Impregnation and injection) used.

Using injection method for 24 hours and compared with Impregnation affected the gas permeation and gas separation performance, 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 permanant circulation of ion-exchane inside tubular module and olso the substituted cations.

The results of gas mixture permeation through a H-ZSM-5 hollow fibre membrane was 1.1-0.13 for CO_2-N_2, respectively, and through a Cs-ZSM-5 was significantly affected. The CO_2/N_2 separation factor of ion-exchanged hollow fibre membrane for an equimolar mixture of CO_2 and N_2 increased and was in the range of 18.

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