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Mechanical and pore characteristics of zeolite composite membranes

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All-inorganic membranes containing zeolite materials are produced by using fibrous sepiolite as a binder. The mechanical resistance of the resulting membranes decreases with the sepiolite clay content. However, at high zeolite concentrations, non-shape-selective pinholes are greatly reduced while the zeolite micropores are always accessible to diffusing molecules.

Introduction

Zeolites are subnanostructural materials which have important industrial applications in catalysis, separation and ion-exchange processes.[1,2] Their application prospects in other fields such as in photochemistry and electrochemistry seem very promising. Many attempts to prepare zeolite membranes, as zeolite films noncomposited[3] or deposited on various supports,[4–7] or zeolite materials embedded in polymer matrices,[8–11] have been made with some promising results. However, the need for all-inorganic membranes with pores <0.8 nm, capable of achieving a size-based separation with good selectivity,[12] has not, as yet, been fully satisfied. This is mainly due to the difficulty to prepare zeolite membranes having pore volume and surface area which are close to those of the zeolite materials. It is not easy to produce zeolite membranes which do not contain non-zeolitic connecting-through mesopores or macropores (pinholes). To be usable in separation processes, the amount of pinholes should be lower than a few percent.

Therefore, the main objective of this work was to develop a procedure for the preparation of composite zeolite membranes. The two characteristics which were particularly studied because of their importance in the industrial applications were the mechanical resistance and the microporosity. Two series of preliminary tests aiming at showing the influence of the zeolite component were performed: vapor-phase separation of hydrocarbon mixture and ion-exchange of Ca^{2+} ions in aqueous solution. The composite zeolite membranes were obtained by slow evaporation of gels containing mixtures of zeolite and sepiolite. Sepiolite is a fibrous magnesium silicate, which is formed from talc-like ribbons, the average fibre length of the mineral varying between 0.2 and 2.0 μm, and sometimes longer.[13,14] The main interest in using sepiolite as a binder is its fibrous texture which can create a network stronger than that given by a simple colloidal or polymeric gel system.[15]

Experimental

Preparation of sepiolite particles

30 g of sepiolite mineral purchased from Source Clay Minerals Repository (University of Missouri, Columbia, USA) were crushed and sieved (mesh size 12 or 1.7 mm aperture). The material was then placed in a beaker containing 4 l of an aqueous solution of 1 M NaCl. This suspension was gently stirred for 16 h, its pH being continuously adjusted to *ca.* 4 by using 0.1 M HCl. The beaker contents were allowed to settle for 24 h; then, the supernatant was discarded and replaced by 4 l of deionized water. After moderate stirring for 1 h, the suspension was allowed to settle and the supernatant was removed. The operation was repeated several times until the liquid did not contain any Cl^- ions. The 'purified' suspension was stirred for 5 min and then allowed to settle for 4 h. The portion of the suspension 15 cm above the sediment was carefully withdrawn and the operation was repeated several times: these lighter suspension portions contained small sepiolite particles which were subsequently separated from the water by centrifugation and finally dried in the rotavapor.

Preparation of Na-X/sepiolite and Na-ZSM5/sepiolite membranes

Accurately measured amounts of sepiolite and Na-X zeolite (powder, U.O.P.) with a total weight of *ca.* 1 g were placed in a beaker containing 30 ml of distilled water and the suspension was stirred with a magnetic bar for *ca.* 24 h until it became homogeneous. The suspension was poured into a 9 cm diameter Petri dish and allowed to dry at ambient temperature for *ca.* 48 h. Finally, the resulting membranes were dried at 120 °C overnight and activated at higher temperatures overnight. The thickness of the membranes ranged from 0.15 to 0.30 mm (measured by a micrometer).

The Na-ZSM5/sepiolite membrane was prepared from a mixture of 60 wt% Na-ZSM5 (powder, Uetikon Chemie) and 40 wt% sepiolite, using the procedure described above.

Characterization of the membranes

(a) Mechanical resistance. An 'I' shaped band was cut from the membrane. The length, the width of the ends and the width of the middle zone of the band were: 12, 2 and 1 cm, respectively. The band was vertically set, one end being fixed to a rigid support and the other end sustaining a small basket. The latter was filled with weights to determine the mass that led to rupture of the membrane.

Table 1 reports the composition, the final activation temperature, the thickness, the tensile force of rupture and the

Table 1 Mechanical resistances of the Na-X/sepiolite and Na-ZSM5/sepiolite composite membranes

Membrane	Composition (wt%)		Activation temp./°C	Thickness/mm	Tensile force/N m^{-1}	Rupture pressure, P_r/bar
	Zeol[a]	Sep[b]				
(Sep)1	0	100	220	0.18	147	8.2
(Sep)2	0	100	550	0.13	99	7.6
X(10/90)1	10	90	220	0.18	146	8.1
X(10/90)2	10	90	550	0.22	173	7.8
X(20/80)1	20	80	220	0.17	122	7.2
X(20/80)2	20	80	550	0.17	117	6.9
X(30/70)1	30	70	220	0.29	156	5.4
X(30/70)2	30	70	550	0.29	146	5.0
X(40/60)1	40	60	220	0.29	154	5.3
X(40/60)2	40	60	550	0.29	119	4.1
X(60/40)1	60	40	220	0.26	90	3.5
X(60/40)2	60	40	550	0.25	83	3.3
X(70/30)1	70	30	220	0.30	80	2.6
X(70/30)2	70	30	550	0.30	75	2.5
X(80/20)1	80	20	220	0.28	71	2.5
X(80/20)2	80	20	550	0.25	<50	<2.0
X(85/15)1	85	15	220	0.23	<50	<2.0
X(85/15)2	85	15	550	0.23	<50	<2.0
Na-X(1)[c]	100	0				
(Na-Z/Sep)1[d]	60	40	220	0.25	88	3.5
(Na-Z/Sep)2[d]	60	40	550	0.32	124	3.9
Na-ZSM5 (powder)[c]	100	0				

[a]Zeol = zeolite. [b]Sep = sepiolite. [c]No membrane formed. [d]Composition = 60 wt% Na-ZSM5 and 40 wt% sepiolite.

pressure of rupture (P_r) of the composite membranes under investigation.

(b) BET surface area and pore size distribution. The BET surface area and the pore size distribution of the membranes (mesopore and macropore region) were determined by adsorption–desorption of nitrogen (at liquid nitrogen temperature, 77 K), using a Micromeretics Model ASAP 2000 instrument and the BJH (Barrett–Joyner–Halenda[16]) data interpretation method. The micropore size distribution was studied by adsorption of argon (at liquid argon temperature, 87 K), using a Micromeretics Model 2000 M and the data interpretation method of Horvath and Kawazoe.[17]

Table 2 reports the BET surface areas and the pore size distributions of the various membranes studied. It is worth noting that the microporosity data of the pure zeolites, Na-X and Na-ZSM5, were used to correct the observed microporosity data of the membranes, in order to calculate the percentage of the non-zeolitic transecting pores (terminology used in ref. 10, meaning also connecting-through pores or pinholes) of the membranes (nz-TP). The surface area of the non-micropores of the pure zeolite particles corresponded to the areas of the pore openings of the zeolite micropores: this therefore could not be accounted as transecting pores which existed in the composite membranes. Indeed, the parent Na-X particles had an apparent microporosity of 94% (Table 2); since there were no transecting pores >2 nm in these zeolite particles, the nz-TP value was 0. The percentage of non-zeolitic transecting pores of the composite membranes were calculated by using eqn. (1)

$$\text{nz-TP}(\%) = 100 - (100/\text{MP}_z)X \qquad (1)$$

where MP_z and X were the microporosity of the parent zeolite particles and the zeolite content (in %) of the membrane, respectively.

The percentage of the non-zeolitic transecting microporosity of the membrane was given by eqn. (2)

$$\text{nz-TMP}(\%) = \text{MP}_m - (\text{MP}_z X/100) \qquad (2)$$

where MP_m was the microporosity of the membrane.

Finally, the percentage of the non-zeolitic transecting larger pores of the membrane was given by eqn. (3)

$$\text{nz-TLP } (\%) = \text{nz-TP} - \text{nz-TMP} \qquad (3)$$

(c) Scanning electron microscopy (SEM). SEM images were obtained using a Hitachi Model S-20 instrument.

(d) Ion-exchange properties. A 25 mm diameter membrane, cut from the original membrane using a home-made cutter, was placed in a membrane holder (filter holder, Nuclepore®, made of plastic, membrane size: 25 mm) whose entrance was connected to a syringe containing an aqueous solution of $CaCl_2$ (80 ppm). This syringe was moved by a device (infusion pump) which allowed the continuous delivery of the solution at various rates. The other side of the membrane holder was connected to a liquid fraction collector. The solution was pumped through the membrane and the liquid was collected as 5 ml fractions which were analyzed for their Ca^{2+} ion content by atomic absorption. The results reported were average values of Ca^{2+} ions removal (expressed in percent) determined in the first four liquid fractions collected (*i.e.* for a total volume of 20 ml), regardless of the flow-rate of the solution through the membrane.

The cation-exchange capacities of the two components of the composite membranes are 0.1–0.5 mequiv. g^{-1} for sepiolite[13] and *ca.* 5.0 mequiv. g^{-1} for Na-X zeolite.[18]

(e) Vapor-phase separation of hydrocarbons having different molecular sizes.

It is known that the pore sizes of Na-X and ZSM-5 are 0.74 and 0.54 nm, respectively,[19] so that the rate of diffusion of (vaporized) *n*-pentane (kinetic diameter = 0.43 nm) through the zeolite micropores must be faster than that of neohexane (2,2-dimethylbutane, kinetic diameter = 0.62 nm). The two factors which have most influence on the diffusion of a hydrocarbon molecule through zeolite micropores are: the size of the diffusing molecule (also called size effect) and the non-collision-type interactions between the molecule and the zeolite pore wall. Since the latter effect is negligible with saturated hydrocarbons, the former effect results in slower diffusion for the bulkier neohexane. Such diffusion delay becomes more

Table 2 BET surface areas and microporosities of the membranes studied (see Table 1)

	BET surface area/$m^2\ g^{-1}$			
Membrane	Total	Micropores	Microporosity (%)	nz-TP (%) (nz-TMP/nz-TLP)
(Sep)1	147	9	6	100(6/94)
(Sep)2	141	1	1	100(1/99)
(Sep)3[a]	136	6	4	100 (4/96)
X(10/90)1	189	67	35	89 (26/63)
X(10/90)2	178	65	37	89 (28/61)
X(20/80)1	233	119	51	79 (32/47)
X(20/80)2	257	137	53	79 (34/45)
X(30/70)1	307	192	63	68 (35/33)
X(30/70)2	295	186	63	68 (35/33)
X(40/60)1	347	250	72	57 (34/23)
X(40/60)2	329	232	71	57 (33/24)
X(60/40)1	445	367	83	36 (27/9)
X(60/40)2	442	363	82	36 (26/10)
X(60/40)3[a]	220	168	76	36 (20/16)
X(70/30)1	464	401	86	26 (20/9)
X(70/30)2	491	424	86	26 (20/9)
X(80/20)1	544	484	89	15 (14/1)
X(80/20)2	530	476	90	15 (14/1)
X(85/15)1	558	499	89	10 (9/1)
X(85/15)2	558	508	91	10 (10/1)
Na-X (powder, 550 °C)	558	526	94	0
Na-X (powder, 700 °C)	544	512	94	0
(Na-Z/Sep)1	273	149	55	22 (9/13)
(Na-Z/Sep)2	270	155	57	22 (11/11)
Na-ZSM5 (powder, 550 °C)	332	254	77	0

[a] Activated at 700 °C.

important with a narrower pore-sized zeolite (ZSM-5) compared with Na-X). With zeolite materials in small crystallite forms (powders), the easiest way to verify the size effect is to prepare short gas chromatographic (GC) columns packed with the zeolite powder or the reference solid particles, and by using nitrogen as carrier gas, to measure the retention times (rt) of hydrocarbons of a mixture (*n*-pentane–neohexane). The R_{rt} ratio is determined as the ratio of the retention time of neohexane to that of *n*-pentane.

The following sequence of R_{rt} was experimentally found for the various packing materials investigated: pure sepiolite < Na-X < ZSM-5 (I) and corresponds to that of the size effect of the porous materials used.

However, with zeolite crystallites embedded in composite membranes, direct measurement of the retention times using the normal GC technique was not possible. Thus, a special method was devised to obtain similar information about the size effect. These tests were carried out with a special membrane holder made of Teflon, capable of withstanding temperatures of >200 °C (Filter holder, Nuclepore®, for 25 mm diameter membranes). The experimental set-up was similar to that described for the ion-exchange studies, however with the entrance of the holder connected to a vaporizer-gas mixer chamber (Vap-gasMix) heated at a temperature >80 °C in order to vaporize the mixture of *n*-pentane and neohexane. This mixture was prepared by mixing *n*-pentane (*ca.* 50 wt%, bp = 36.1 °C) with neohexane (*ca.* 50 wt%, bp = 49.7 °C). 5 ml of such a liquid mixture was rapidly injected in the Vap-gasMix, which was immediately vaporized and mixed with nitrogen (flow rate = 5 ml min^{-1}) used as carrier gas. The gaseous stream that passed through the membrane was sampled at the outlet of the holder at regular time intervals and analyzed by means of a gas chromatograph (Hewlett-Packard 5890 instrument, FID, equipped with a PONA capillary column, 50 m long). To assess the effect of gas sweeping (stripping) of the mixture through the whole system, the pure sepiolite membrane containing only transecting large pores was used as a reference. The area ratio (*R*) of the GC peaks (neohexane/*n*-pentane) was proportional to the ratio of concentrations of the respective hydrocarbons. Since the elution of the gaseous hydrocarbons through the membrane was rapid, the first sampling and injection into the GC (after 5 min) corresponded to almost 60% of hydrocarbons already eluted. By using the *R* values, it would be possible to study the diffusion delay of the bulkier neohexane with respect to *n*-pentane. Higher *R* values would be associated with higher size effects as currently found with the normal method based on the GC column technique.

Two composite membranes were studied in this work owing to their good mechanical resistance which allowed an easy handling during the tests. These membranes contained 60 wt% Na-X and Na-ZSM-5, respectively, the balance being sepiolite. Both materials were activated at 550 °C.

Results and discussion

As expected, it was not possible to prepare self-bonded membranes by using particles of pure Na-X or Na-ZSM5 zeolite. Moreover, the non-fibrous boehmite material provided Na-X zeolite–boehmite composite membranes with much less mechanical resistance (*e.g.* much lower pressure of rupture) than that obtained with the corresponding Na-X zeolite–sepiolite composites.[20] Since membranes made of pure sepiolite showed the maximum mechanical resistance among the composite membranes studied and such resistance decreased with decreasing content of sepiolite (Table 1), the mechanical properties of the composite zeolite–sepiolite membrane were believed to be mainly associated with the fibrous texture of the sepiolite (average length = 7 µm, Fig. 1). These fibers form a network in which the smaller zeolite particles (average diameter for Na-X = 2–3 µm) were embedded (Fig. 2). Unfortunately, the presence of too many zeolite particles might result in some large pinholes as shown in Fig. 2 [X (60/40)2 composite membrane].

The pressure of rupture of the Na-X zeolite containing membranes decreased with increasing activation temperature, owing probably to some thermal expansion/contraction of the sepiolite network occurring during the activation, as observed in some zeolite supported membranes.[21] There was an opposite trend with the membranes fabricated from the silica-richer

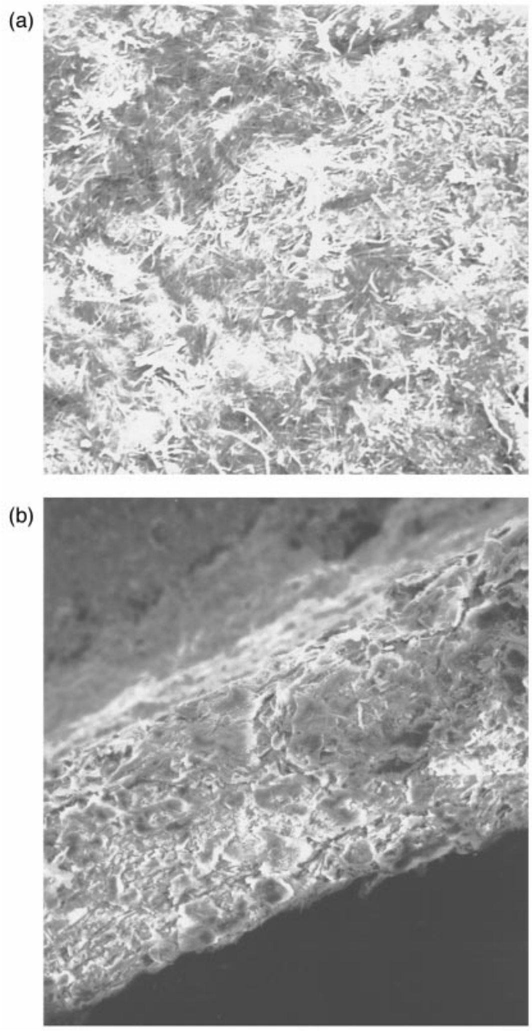

Fig. 1 Scanning electron micrograph of the pure sepiolite membrane (Sep) 2. (a) Front view (magnification = 2000); (b) cross-sectional view (magnification = 200).

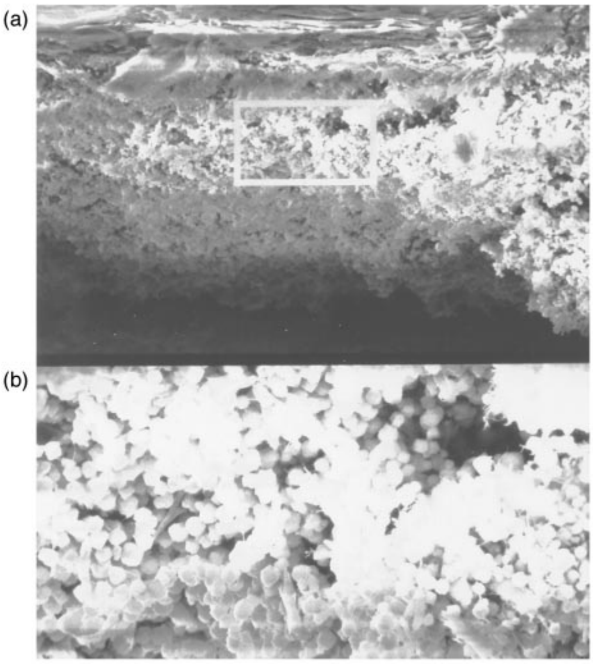

Fig. 2 Scanning electron micrograph of the Na-X zeolite containing composite membrane, X(60/40)2. Cross-sectional views: (a) magnification = 200; (b) magnification = 1000.

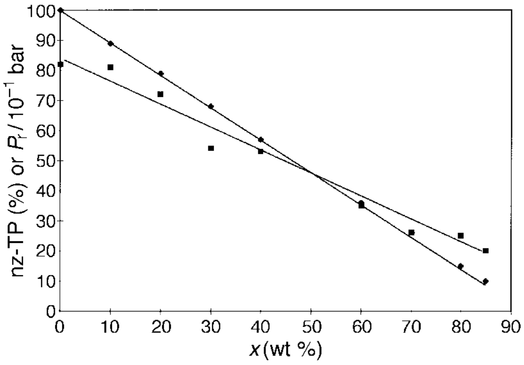

Fig. 3 Non-zeolitic transecting pores (nz-TP, in %, (◆)) and pressure of rupture ($P_r/10^{-1}$ bar, (■)) *vs.* Na-X zeolite content (x in wt%) of the composite membranes.

ZSM-5 zeolite (Table 1): this might suggest that the smaller submicron-sized particles of Na-ZSM-5 zeolite resulted in a better embedment in the sepiolite fibrous network, thus enabling the overall membrane structure to resist better the effect of high activation temperature. Nevertheless, composite Na-X/sepiolite membranes, although less resistant than the pure sepiolite membrane, were at least as resistant as the composite membranes comprising a MFI zeolite grown on porous ceramic supports.[21,22] Thus, they can be used in applications that do not require too high pressures.

Fig. 3 shows that the percentage of the transecting pores (nz-TP) of the NaX containing membranes decreased with increasing concentration of the zeolite material (ZC). It is possible in principle to reduce further the percentage of these non-zeolitic and transecting pores (<10%, Table 2), however, the resulting composite membranes would be much more fragile (low P_r values, Table 1 and Fig. 3). On the other hand, the sepiolite itself produced, in the process of membrane formation, some new micropores in addition to its large pores (nz-TMP, Table 2). Unfortunately, these transecting micropores (nz-TMP, Table 2) were not shape selectivity promoting pores. In fact, pure sepiolite membrane showed a micropore size distribution [Fig. 4(a)] much broader than for pure Na-X zeolite [Fig. 5(a)]. The composite membrane [x(60/40)2] also contained some non-shape-selective micropores [Fig. 6(a)]. Let us consider the composite membrane containing the highest amount of Na-X zeolite [X(85/15)1]; this membrane had a very low percentage of large pinholes (nz-TLP = 1%) and a significant amount of non-zeolite micropores (nz-TMP = 9%), slightly higher than that of the pure sepiolite membrane, (Sep)1. This means that these non-selective micropores were not only created by the sepiolite itself but also by the external surfaces of the zeolite particles which were not tightly bound to the sepiolite fibers. Therefore, in any applications which require perfectly gastight and shape-selective membranes, these non-zeolitic micropores must be eliminated.

The accessibility to the micropores of the zeolite particles

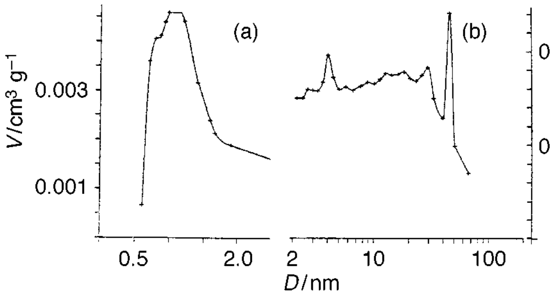

Fig. 4 Pore size distribution curves of the pure sepiolite membrane, *i.e.* pore volume (V/cm^3 g^{-1}) *vs.* diameter (D/nm): (a) micropore region; (b) mesopore and macropore region.

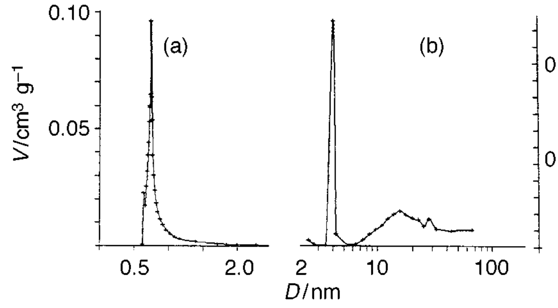

Fig. 5 Pore size distribution curves of the Na-X parent zeolite in powder form (see Fig. 4): (a) micropore region; (b) mesopore and macropore region.

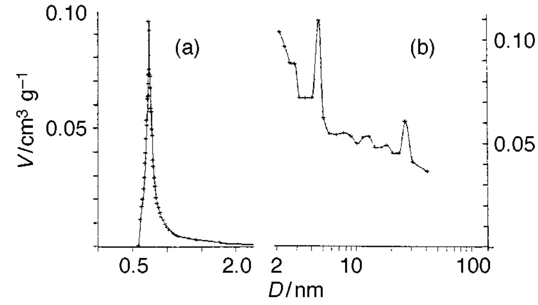

Fig. 6 Pore size distribution curves of the composite membrane X(60/40)2 (see Fig. 4): (a) micropore region; (b) mesopore and macropore region.

embedded in the composite membrane was already demonstrated through the adsorption of nitrogen (BET method) and argon under static conditions. However, under dynamic conditions (working conditions for the membranes), the free diffusion of the various species through these zeolite pores had to be also clearly shown. To investigate this, two preliminary series of tests were carried out in liquid (ion-exchange with Ca^{2+} ions) and vapor phases (separation of hydrocarbons).

Table 3 reports the ion-exchange data obtained with sepiolite and composite Na-X/Sepiolite membranes, *i.e.* (Sep)3 and X(60/40)3, respectively. It is well known that any liquid phase operation with microporous zeolite materials is seriously affected by the low diffusion rates of the liquids through the micropores. Therefore, if an aqueous solution of Ca^{2+} ions was forced to pass through the composite membrane, it would at first find its way through the non-zeolitic transecting large pores (nz-TLP, Table 2). This diffusion through preferential pathways involves cation-exchange sites of the sepiolite located in the large pinholes. At lower flow-rates, the ion-exchange sites of the sepiolite located in the non-shape-selective micropores, as well as some zeolite micropores, are more accessible, thus increasing the overall ion-exchange properties (Table 3). The effect of the microporous zeolite component in the removal of Ca^{2+} ions was evidenced by the difference Δ, as reported in Table 3.

Table 3 Ion-exchange with Ca^{2+} ions of the pure sepiolite (Sep)3 and X(60/40)3 membranes

Flow-rate of solution/ml min^{-1}	(Sep)3	X(60/40)3	Δ[a]
2.5	7.6	17.0	9.4
1.6	10.7	18.0	7.3
1.2	13.8	25.3	11.5
0.5	19.0	30.3	11.3
0.22	23.6	31.2	7.6
0.14	24.0	31.6	7.6

[a] Difference(%) in Ca^{2+} ion removal.

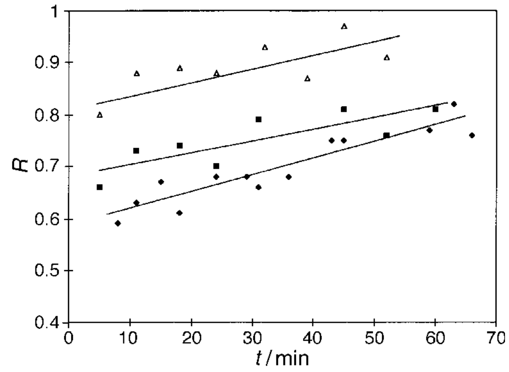

Fig. 7 *R* ratio value *vs.* time (*t*/min): (◆) pure sepiolite membrane [(Sep)2]; (■) Na-X zeolite containing membrane [X(60/40)2]; (▲) Na-ZSM5 containing membrane (Na-Z/Sep)2].

Hydrocarbon separation tests showed that when the *R* ratio (indicative of the diffusion delay, see Experimental section) was plotted *vs.* time, different curves were obtained with different membrane compositions (Fig. 7). Although the membranes containing Na-X and Na-ZSM5 zeolites had some non-zeolitic transecting large pores (Table 2), the relatively fast diffusion of gaseous molecules through the zeolite micropores prevented their absolute requirement for preferential diffusion pathways. All the *R* values obtained with the [X(60/40)2] membrane containing the large-micropore-sized Na-X zeolite were higher than those obtained with the pure sepiolite membrane [(Sep)2]. This is evidence that although the size of the Na-X micropores was much larger than those of the diffusing molecules (see Experimental section), there were some significant size effects between the walls of the zeolite pores and the diffusing molecules. Since these interactions were more important with the bulkier molecule, *i.e.* neohexane, there was some delay in diffusion through the membrane of neohexane, thus resulting in higher *R* values. The values of *R* obtained with the membrane containing Na-ZSM5 zeolite were higher than those obtained with the Na-X containing membrane. This means that in the smaller micropores of the Na-ZSM5 the size effect was more important, thus resulting in a more important delay in the diffusion of the neohexane. Thus, the following sequence of *R* values was obtained with the membranes: pure sepiolite < Na-X < Na-ZSM-5 (II).

This sequence which was also that of the size effect of the composite membrane is identical to sequence I obtained by the GC column technique using powders of the same porous materials alone (see Experimental section). However, in order to allow the quantitative assessment of the membrane efficiency for selective gas separation, an analytical method using a membrane loaded device connected to a gas chromatograph is under development. With such a set-up, more meaningful values of the retention time ratios determined for vaporized hydrocarbon mixtures can be directly related to the zeolite pore size.

Conclusion

All-inorganic membranes containing zeolite materials are produced by using fibrous sepiolite as a binder. The mechanical resistance of the resulting membranes decreases with the sepiolite clay content. However, at high zeolite concentrations, non-molecular-shape selective pinholes are greatly reduced while the zeolite micropores are always accessible to diffusing molecules. Such accessibility was evidenced by the adsorption/desorption of nitrogen and argon, the cation-exchange with Ca^{2+} ions in aqueous solutions and the vapor-phase separation of hydrocarbons using a mixture of *n*-pentane and neohexane. The results of this work have allowed us to prepare composite membranes in which the transecting large pores and the non-shape selective micropores created by the sepiolite are almost completely eliminated. The use of the multilayer preparation technique (to increase the mechanical resistance) and the introduction of an inorganic cement (to eliminate mostly the non-zeolitic micropores) result in stronger and more selective membranes.[23]

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