Synthesis of a mordenite/ZSM-5/chabazite hydrophilic membrane on a tubular support. Application to the separation of a water–propanol mixture

Miguel A. Salomón, Joaquín Coronas, Miguel Menéndez and Jesús Santamaría*

Department of Chemical and Environmental Engineering, University of Zaragoza, 50009, Zaragoza, Spain

A selectivity of 71 is achieved in the separation of a gas phase water–propanol mixture, using a mordenite/ZSM-5/chabazite membrane that is hydrothermally synthesized onto the inner surface of a porous α-alumina tubular support.

In recent years, the synthesis of zeolite membranes on porous inorganic substrates (disks or tubes) has received much attention. To prepare such a membrane, the crystals must form a continuous, defect-free two-dimensional layer, so that only transport through the zeolite pores takes place. Several methods have been proposed for the preparation of zeolite membranes. For ZSM-5 membranes, it was demonstrated that permeation and separation properties depend strongly on the preparation procedure used.[1] The most usual liquid-phase preparation method involves immersing the porous support into the zeolite precursor gel. With this method MFI-type zeolite,[1,2] zeolite A[3] and zeolite Y[4] tubular or flat membranes have been prepared. It is noticed that, although tubular supports are more interesting from an industrial point of view, there are still very few examples of zeolite membranes synthesized on them. This is due to the development of mechanical tensions during the drying/calcination steps, that often result in the formation of defects such as cracks and pinholes. The vapour phase method has been used to prepare ZSM-5 and ZSM-35,[5] ferrierite[6] and mordenite[7] flat membranes, where vapors containing amines and water were employed to zeolitize silica and/or alumina layers previously deposited onto the support.

Most of these zeolite membranes have been used for separations of organic–organic,[1] water–organic[3,4,8] and permanent gas–organic[2] mixtures. When there are significant differences in polarity between the components of a mixture (*e.g.* water–alcohol mixtures), the organophilic or hydrophilic character of the zeolite can play an important role. For instance, water permeated faster than ethanol through membranes of zeolites A and Y (both of them hydrophilic),[3,4] while through silicalite membranes the permeation of ethanol was faster.[8] Here we present the synthesis and some permeation properties of a mordenite/ZSM-5/chabazite membrane on a tubular α-alumina support. To our knowledge this is the first report on the preparation of such a tubular membrane. The constituting zeolites differ in their physical properties: ZSM-5 is a high-silica zeolite (Si/Al ratios between 2.5 and 100), with a structure consisting of straight channels of 0.54×0.56 nm, intersecting with sinusoidal channels of 0.53×0.55 nm; with mordenite, the Si/Al ratio is around 5, and there are large channels of 0.67×0.7 nm, and small channels of 0.26×0.57 nm; finally, chabazite is a smaller pore size zeolite (its larger channels are 0.38×0.38 nm), but in this case the Al content is higher, with a Si/Al ratio between 1.6 and 3. Since the hydrophilicity of a zeolite increases with its Al content, it can be expected that the presence of mordenite and chabazite increase the selectivity for the separation of water, with respect to what could be achieved on a pure ZSM-5 membrane.

The synthesis method employed 0.65 mm id asymmetric porous α-alumina microfiltration tubes with a 200 nm pore diameter separation layer (US Filter, SCT). An aluminosilicate gel was prepared using Aerosil 300 (Degussa) and sodium aluminate (Carlo Erba) as silica and alumina sources, respectively, tetraethylammonium hydroxide (TEAOH) solution 35 mass% in water (Aldrich) as template, NaOH and distilled water. A gel was prepared with a molar composition 80 $SiO_2 : 2080\ H_2O : 32\ NaOH : 40\ TEAOH : 1\ Na_2Al_2O_4$. The starting solution consisted of Aerosil 300 and approximately two thirds of the above amount of deionized water. This solution was kept under vigorous stirring for 5 h. Then, a solution containing the other substances was added, one fifth every 30 min, to the first solution. The resulting gel was aged under stirring for 3 days. The gel was cloudy but not thick, and had a pH of *ca.* 12.1. The gel was not completely stable, and two different phases appeared a few hours after stirring was stopped. Before synthesis, the outer surface of the dry alumina tube was wrapped with Teflon tape to avoid penetration of the gel from this side, and the tube was then immersed in the synthesis gel filling a Teflon-lined autoclave. The tube was fixed axially, and the autoclave was placed horizontally in a convection stove at 443 K for 21–23 h. The synthesis was repeated four times, with the tube–autoclave ensemble rotated 90° in each step. After the last synthesis, the tube was tested for permeability to N_2, at room temp. and pressure differences of up to 3 bar. Strict impermeability was required, which sometimes required a fifth synthesis. Finally, to remove the template, the membrane was calcined, at 753 K for 8 h using 1 K min^{-1} heating and cooling rates. The composition of the gel used for the synthesis is optimized to obtain mordenite. However, during the synthesis of the membrane on an Al_2O_3 support, it can be expected that part of the support is dissolved and incorporated into the synthesis gel, and thus other compositions such as ZSM-5 and chabazite are possible.

The zeolite mass gain and the N_2 permeance were measured for several membranes, samples M1–M3 (Table 1) to characterize initially the membrane and assess the reproducibility of the synthesis method. After the hydrothermal synthesis, crystals not attached to the support were recovered from the autoclave. These crystals which should have a composition similar to the material deposited as a continuous layer on the alumina support, were characterized by XRD analysis (Rigaku/Max System, Cu-Kα radiation, graphite monochromator). XRD patterns of the composite membrane and of zeolite crystals prepared by homogeneous synthesis (*i.e.* in the absence of a porous alumina support) using the same gel were also obtained. Fig. 1(*a*) shows the XRD pattern of zeolite crystals prepared by homogeneous synthesis. By comparison with XRD data in the literature[9] it can be seen that the pattern is practically coincident with that of a pure mordenite zeolite. On the other hand, Fig. 1(*b*) indicates that the XRD pattern of the crystals collected in the remaining liquid after the synthesis of the membrane in the presence of α-Al_2O_3 contains a significant amount of other zeolites (ZSM-5 and chabazite), in addition to mordenite. Finally, the pattern shown in Fig. 1(*c*) corresponds to composite membrane M3 (see Table 1), and is a combination of α-alumina (marked with an asterisk), and the ZSM-5, chabazite and mordenite crystals already shown in Fig. 1(*b*). The zeolite peaks in the XRD diagram corresponding to the composite membrane are smaller than those shown in Fig. 1(*b*), because the zeolite contributed only 7% to the total membrane mass, the rest being α-Al_2O_3. A closer examination of the XRD pattern of the composite

Table 1 Some characteristics of the composite zeolite membranes

Membrane	Mass gain/ mg zeolite (g support)$^{-1}$	N_2 single gas permeance/ mol (s m^2 Pa)$^{-1}$	Water–propanol–air mixture[a]		
			H_2O permeance/ mol (s m^2 Pa)$^{-1}$	Water/ propanol selectivity	Water/O_2 selectivity
M1	67	3.0×10^{-7}	2.0×10^{-7}	50	5.3
M2	79	2.5×10^{-7}	2.7×10^{-7}	71	10
M3	69	Not measured	2.8×10^{-7}	16	13

[a] Partial pressure (kPa): water = 2.4; propanol = 0.36.

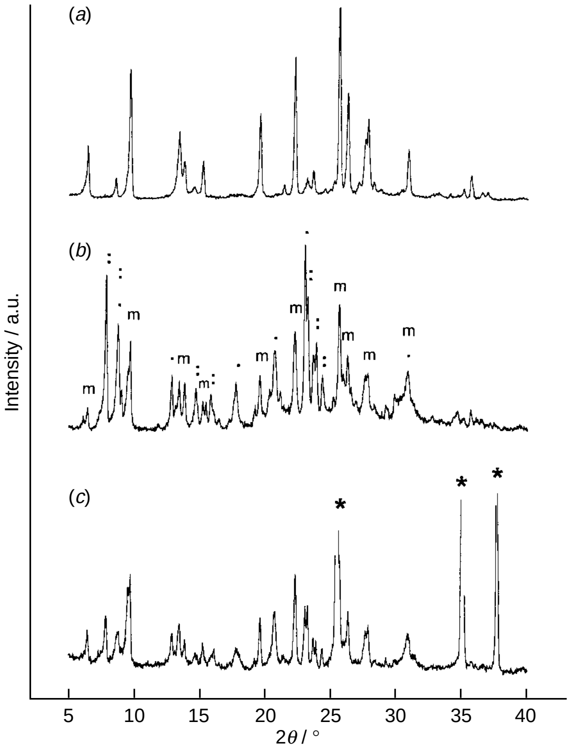

Fig. 1 X-Ray diffraction patterns of (*a*) mordenite powder; (*b*) powder collected in the remaining liquid after the synthesis of the composite zeolite membrane, ● = chabazite, ●● = silicalite, m = mordenite; (*c*) composite zeolite membrane, * = Al_2O_3 support. For clarity, zeolite peaks have not been marked.

membrane shows some additional interesting features: first, the orientation of the zeolite crystals does not change from Fig. 1(*a*) to Fig. 1(*b*) and (*c*). Second, a comparison of the intensities of the main characteristic bands in the XRD diagram gives a rough estimation of the relative proportions of the different zeolites as mordenite : ZSM-5 : chabazite = 2 : 1 : 1, *i.e.* mordenite is the preponderant species, but there are very significant amounts of ZSM-5 and chabazite.

SEM (JEOL JSM-6400) observations of cross-sections of the composite membranes (not shown) indicated that the zeolite crystals formed a continuous layer 10 μm thick, on top of the inner surface of the alumina support. Further SEM observations showed that zeolite crystals also dispersed among the large α-alumina particles of the support, indicating that the hydrothermal synthesis took place not only on the support but also inside its pores. The thickness of the mordenite layer estimated by SEM agrees well with the Si/Al profile across the membrane measured by EPMA (not shown). The Si/Al ratio in the zeolite film was lower than in the gel, as noted in other case of hydrothermal synthesis of zeolite membranes on alumina supports.[1] This indicates that a part of the alumina support was leached during the synthesis procedure, being incorporated into the composite membrane, and is consistent with the appearance of high alumina zeolites such as chabazite. The preparation procedure (in which the tube was placed horizontally and rotated 90° after every synthesis) was successful in dealing with the instability of the synthesis gel, and allowed deep penetration of the gel into the alumina support, as the 67–79 mg mass gain per g of support indicates (Table 1).

In the water–propanol separation experiments, the membrane was sealed with silicon O-rings in a stainless steel module. A gaseous mixture containing a predetermined proportion of water and propanol was obtained by mixing two air streams after passing them through two saturator trains containing liquid water and propanol respectively. This mixture was fed into the tube side of the membrane, and permeated through the membrane wall. The shell side was swept with a N_2 stream. Both the air and the N_2 streams were mass-flow controlled at approximately 34 cm^3(STP) min^{-1}. The total pressure (*ca.* 1 atm) and the pressure differential between both sides of the membrane (close to zero) were accurately maintained by means of an automated control system. When the steady state was reached, as indicated by GC analysis of both exit streams (usually after keeping the membrane under the mixture stream for around 2 h), the separation selectivities were calculated as the ratios of permeances for water and propanol, using the log(mean partial pressure) difference in the calculations. Table 1 shows the results of the water–propanol separation experiments performed with membranes M1–M3. The highest water–propanol selectivity was 71 at room temp. for membrane M2. The high selectivity of the composite membrane in the water–propanol separation may be attributed to the selective sorption of water in this hydrophilic membrane.

Footnote and References

* E-mail: iqcatal@posta.unizar.es; Fax: +34 76 762142

1 J. Coronas, J. L. Falconer and R. Noble, *AIChE J.*, 1997, **43**, 1797.
2 M. D. Jia, B. Chen, R. D. Noble and J. L. Falconer, *J. Membr. Sci.*, 1994, **90**, 1.
3 H. Kita, K. Horii, Y. Ohtoshi and K. Okamoto, *J. Mater. Sci. Lett.*, 1995, **14**, 206.
4 H. Kita, T. Inoue, H. Asamura, K. Tanaka and K. Okamoto, *Chem. Commun.*, 1997, 45.
5 J. Dong, T. Dou, X. Zhao and L. Gao, *J. Chem. Soc., Chem. Commun.*, 1992, 1056.
6 N. Nishiyama, K. Ueyama and M. Matsukata, *Stud. Surf. Sci. Catal.*, 1997, **105**, 2195.
7 N. Nishiyama, K. Ueyama and M. Matsukata, *Microporous Mater.*, 1996, **7**, 299.
8 Q. Liu, R. D. Noble, J. L. Falconer and H. H. Funke, *J. Membr. Sci.*, 1996, **117**, 163.
9 D. W. Breck, *Zeolite Molecular Sieves*, Krieger Publishing Company, Malabar, 1984.

Received in Bath, UK, 22nd October 1997; 7/07626F