High separation selectivity with imperfect zeolite membranes

Elena Piera, Joaquin Coronas, Miguel Menéndez and Jesús Santamaría*

Department of Chemical and Environmental Engineering, University of Zaragoza, 50009, Zaragoza, Spain. E-mail: iqcatal@posta.unizar.es

Received (in Cambridge, UK) 16th April 1999, Accepted 8th June 1999

In spite of the presence of inter-crystalline defects, high selectivities can be obtained in the separation of gas phase mixtures with zeolite membranes.

The development and application of zeolite membranes constitutes a swiftly expanding area where the data published over a period of a few months often suffice to change the prevailing view on the status of development (population of defects, crystal orientation, *etc.*) of a specific family of zeolite membranes, or on the transport mechanism for a given separation. A well known example of the rapidly changing concepts in the field refers to the misnaming of zeolite membranes as molecular-sieving membranes. Nowadays there are numerous examples (see refs. *e.g.* 1–3) of 'reverse selectivity' membranes, *i.e.* membranes where the largest molecule is selectively separated because of preferential adsorption that leads to pore blockage.

Another widely used presumption in this area establishes that, if a high separation selectivity (a two to three-digit figure is often considered as sufficiently high) is observed, then one can claim that a 'defect-free' or 'almost defect-free' membrane has been obtained. This article deals with this perception by demonstrating that defective membranes are nevertheless capable of high separation selectivities, if tested under a suitable set of operating conditions.

The work was carried out using silicalite membranes, which are probably the most widely studied zeolite membranes. They were prepared by *in situ* hydrothermal synthesis onto stainless steel supports having 1 μm diameter pores. In order to confine the permeation area, the ends of the stainless steel porous supports (11 mm i.d., 16 mm o.d.) were soldered to non-permeable tubes of the same material and diameter.

The membranes were prepared by hydrothermal synthesis according to the directions in ref. 1, except that Aerosil 300 was used instead of Aerosil 130. The molar composition of the gel was: 21 SiO_2: 788 H_2O: 3, NaOH: 1 TPABr, (TPABr = tetrapropylammonium bromide). The gel was cloudy and thin, with a pH of 11.0. The support tube was wet with water, and then one end of the wet tube was wrapped with Teflon tape, plugged with a Teflon cap and filled with the synthesis gel. The other end was also wrapped with tape and plugged with another Teflon cap. The tube was placed vertically in a Teflon-lined autoclave, and the autoclave in a convection stove at 443 K for 8–15 h. XRD measurements (not shown) carried out on membranes synthesized using this procedure indicated that pure silicate was formed on the stainless steel support.

The separation measurements were performed with the membrane placed in a stainless steel separation module where it was sealed with silicone o-rings. The gaseous feed stream containing the desired partial pressure of TIPB (1,2,4,5-tetraisopropylbenzene) or water and He was obtained by mixing in variable proportions two mass-flow controlled streams of He, one of which [82 cm^3(STP) min^{-1}] had been bubbled through TIPB or water saturators. The gas mixture was fed into the tube (retentate) side of the membrane, and allowed to permeate through the membrane wall. The permeate side was swept with 83 cm^3(STP) min^{-1} of carrier gas (N_2). Retentate and permeate sides were usually at atmospheric pressure.

Before running an experiment the membranes were heated to 753 K at a rate of 1 K min^{-1}, and then calcined at this temperature for 8 h, in order to remove any adsorbed species. The separation selectivities given below were calculated as the ratios of permeances, using the log (mean partial pressure) difference in the calculations. The composition of the feed stream was accurately determined by feeding it directly into the sampling loop of the on-line gas chromatography. Similarly, when steady state was reached, which often meant keeping the membrane under continuous flow for *ca.* 2 h, samples at the exit of both the permeate and retentate sides were analyzed by on-line gas chromatography.

A first series of experiments was carried out to verify the presence of inter-crystalline defects on the membrane, and to evaluate their contribution to the total permeation flux. To this end, a He steam was saturated with TIPB at a temperature of 373 K (in order to have a sufficiently high vapour pressure of TIPB), and then fed to the retentate side of the membrane. The permeation of TIPB was measured as a function of temperature and then compared to that of He when the same experiment was carried out without TIPB. Since TIPB has a kinetic diameter of 0.87 nm, higher than the average channel diameter of silicalite (0.55 nm), the TIPB flux observed can be ascribed to permeation through inter-crystalline defects.

The results of TIPB permeation experiments are shown in Fig. 1. It is interesting that at the lowest temperature tested for permeation of TIPB/He mixtures, the permeation of He is almost completley blocked by TIPB (giving a TIPB/He selectivity over 800). This is probably due to capillary condensation of TIPB in the intercrystalline voids, blocking the access of He to the zeolite membrane. For increasingly higher temperatures the access to zeolite pores was progressively freed, and the He permeance increased. It must be noted, however, that the TIPB permeance was little affected, which again agrees with the assumption that TIPB does not use the zeolite pore network, but the inter-crystalline defects. Since a relatively high permeance of TIPB [(1.5–3.2) $\times 10^{-8}$ mol m^{-2} s^{-1} Pa^{-1}] was observed throughout the temperature interval tested, it can be concluded that the silicalite membrane has a very significant concentration of inter-crystalline defects.

A more meaningful comparison can be established between water (kinetic diameter 0.265 nm) and He (kinetic diameter 0.26 nm) both of which are able to transit easily through the zeolite

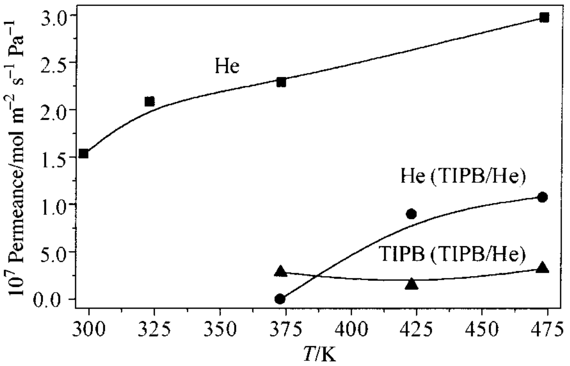

Fig. 1 He single gas permeance and He and TIPB permeances in the TIPB/He mixture as a function of temperature; partial pressure of TIPB in the feed = 1.1 kPa.

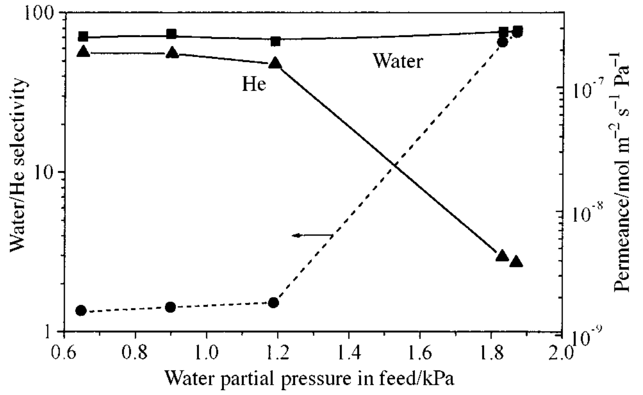

Fig. 2 He and water permeances and water/He separation selectivity in the water/He mixture as a function of the water partial pressure in the feed; temperature = 297 K.

pore network. Besides, since silicalite is an organophilic zeolite a significant interaction with water (preferential adsorption) is not expected. The experiments carried out with water–He mixtures are in general agreement with these assumptions (Fig. 2). A nearly constant value (1.3–1.5) to the water/He selectivity is obtained at water partial pressures in the feed of 1.1 kPa and lower. In spite of this low value of selectivity, it can be said that the membrane shows some water/He selectivity (about four times the Knudsen value of 0.47). This could be the result of blocking of the zeolite pores by water, which is the only condensable component present in the feed.

However, as the water partial pressure in the feed was increased to 1.9 kPa, a dramatic change takes place: the He flux is reduced by two orders of magnitude and the water/He selectivity increases markedly. This is due to blocking of most of the non-zeolite pores (*i.e.* inter-crystalline defects) by capillary condensation of water. The size of these defects can be approximately estimated by the Kelvin equation as 2.5–3 nm, much larger than the zeolite pores. In spite of these defects, a water/He selectivity of 74 is obtained at a water partial pressure in the feed of 1.9 kPa (Fig. 2).

Financial support from DGICYT (QUI97-1085), DGA (P94/97) and Fundación Repsol is gratefully acknowledged.

Notes and references

1 M. D. Jia, B. Chen, R. D. Noble and J. L. Falconer, *J. Membr. Sci.*, 1994, **90**, 1.

2 A. Giroir-Fendler, J. Peureux, H. Mozzanega and J. A. Dalmon, *Stud. Surf. Sci. Catal.*, 1996, **111**, 127.

3 E. Piera, A. Giroir-Fendler, H. Moueddeb, J. A. Dalmon, J. Coronas, M. Menéndez and J. Santamaria, *J. Membr. Sci.*, 1998, **142**, 97.

Communication 9/03036K