ELSEVIER

Catalysis Today 56 (2000) 221–227

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Mordenite and ZSM-5 hydrophilic tubular membranes for the separation of gas phase mixtures

M.P. Bernal, E. Piera, J. Coronas, M. Menéndez *, J. Santamaría

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

Abstract

Water was selectively separated from water/He, water/HC and water/HC/He mixtures (HC being methane, propane or *n*-butane) using mordenite/ZSM-5/chabazite and ZSM-5 membranes. The membranes were prepared on both alumina and stainless steel tubular porous supports by in situ liquid phase hydrothermal synthesis. Water permeated faster because its preferential adsorption on the pores of the hydrophilic zeolite membranes; furthermore, capillary condensation in microporous defects between zeolite crystals is also possible under the experimental conditions used. The influence of the nature of the hydrocarbon in the mixtures and of the operating conditions (temperature and feed composition) on the separation performance of the zeolite membranes was analyzed. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite membranes; Hydrocarbon permeance; Water separation

1. Introduction

The separation stages downstream from a chemical reactor often determine the commercial viability of new processes. A renewed interest is being focused onto the use of microporous membranes, and among these, of zeolitic membranes for selective separation of specific components from the product stream in industrial reactors. In general, zeolite membranes have been used for gas phase separations or for pervaporation applications. Examples include separations of non-adsorbing compounds (e.g., [1,2]), organic/organic (e.g., [3,4]), permanent gas/vapor (e.g., [5,6]) and water or polar molecules/organic (e.g., [7,8]) mixtures. Although several mechanisms can operate in the separation of mixtures using porous membranes (Knudsen diffusion, surface diffusion, capillary condensation and shape selectivity–molecular sieving), the majority of the separations reported using zeolite membranes can be explained in terms of surface diffusion and sometimes capillary condensation. Shape selectivity and molecular sieving are mainly invoked to justify the separation of permanent gas mixtures with significant differences in their molecular size, or of mixtures at moderate-high temperatures where the extent of adsorption is reduced.

In this work, mordenite/ZSM-5/chabazite and pure ZSM-5 membranes were prepared by liquid phase hydrothermal synthesis onto alumina and stainless steel tubular supports, and separation experiments in the gas phase were carried out using binary water/He and water/HC and ternary water/HC/He mixtures, HC being methane, propane or *n*-butane. For comparison purposes, the single gas permeance of He and the different hydrocarbons as a function of temperature was also measured.

* Corresponding author. Fax: +34-976-762142.
E-mail address: qtmiguel@posta.unizar.es (M. Menéndez).

0920-5861/00/$ – see front matter
PII: S0920-5861(99)00279-5

2. Experimental system

Pure ZSM-5 and composite mordenite/ZSM-5/chabazite (termed MOR in the remainder of this work) membranes were prepared by in situ hydrothermal synthesis onto γ-alumina (Inocermic^{TM}) and stainless steel (Mott^{TM}) supports, with 60 and 500 nm pore diameters, respectively. In order to confine the permeation zone, the tubular alumina supports (7 mm i.d. and 10 mm o.d.) were subject to enameling at both ends, while non-porous stainless steel tubular sections were soldered at the end of the stainless steel porous supports (6.4 mm i.d. and 9.5 mm o.d.); in both cases the permeation zone was approximately 5 cm-long.

The ZSM-5 and MOR membranes were prepared as described in [3] and [9], respectively. Between 4 and 5 synthesis were needed in order to obtain an impermeable membrane. Then, the template was removed by calcination at 753 K for 8 h, with a heating rate of 1 K/min.

To carry out the separation measurements, the membrane was placed in a stainless steel separation module, where it was sealed with silicone o-rings. The gaseous feed stream was obtained by bubbling a mass-flow controlled (Brooks 5850) gas stream with the desired gas phase components through a water saturator. The partial pressure of water was around 4.0 kPa, and in the case of the ternary mixture the hydrocarbon/He molar ratio was 2. The gas mixture was fed into the tube (retentate) side of the membrane, and allowed to permeate through the membrane wall. The other side (permeate) was swept with an inert carrier gas (N_2). Retentate and permeate sides were usually at atmospheric pressure (101 kPa). When steady state was reached, which often meant keeping the membrane under continuous flow for around 2 or 3 h, samples at the exit of both the tube and shell (i.e., permeate and retentate) sides were analyzed by on-line gas chromatography (Shimadzu, GC-8A).

A temperature programmed permeation (TPP) device using a TCD cell was employed to obtain single gas permeances of He and hydrocarbons as a function of temperature. Basically, the TPP unit (which is described with more detail elsewhere [10]) consists of a membrane module, similar to that just described, inside an electrical furnace. A mass-flow controlled stream of the testing compound was fed at a pressure of 50 kPa g accurately maintained by means of a back pressure regulator at the exit of the retentate side, while the permeate pressure was close to atmospheric pressure. The data generated by the TCD cell were acquired by a personal computer (also used to control the temperature ramp), and the appropriate calibration were used to calculate continuously the permeation flux as a function of temperature.

In order to remove any adsorbed species, before running temperature programmed permeation or separation experiments, the membrane was heated up to 753 K at a rate of 1 K/min, and then calcined at this temperature for at least 4 h. The separation selectivities given below were calculated as the ratios of permeances, using the log-mean partial pressure difference in the calculations. The concentration of the feed was accurately measured by sending a bypass stream directly to the GC. Mass balance closures for each of the species in the feed were in the $100 \pm 5\%$ interval for the experiments reported in this work.

3. Results and discussion

Table 1 lists some important characteristics of the membranes used in this work. In general, the ideal selectivity values reported for MFI tubular membranes prepared on stainless steel supports tend to be lower than those of membranes prepared on alumina supports [11,12], which agrees with the data in Table 1. In the case of membrane MOR, the N_2/*n*-butane ideal

Table 1
Properties of MOR and ZSM5 membranes

Membrane	Support	Permeance $\times 10^{-7}$ [mol/(m^2 s Pa)]		N_2/*n*-butane (Ideal selectivity)
		He (304 K)	N_2 (298 K)	
ZSM5	Stainless steel	2.0	2.0	3.7
MOR	γ-Alumina	1.8	1.8	~1

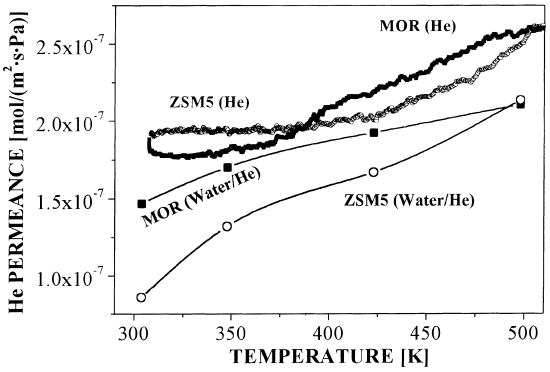

Fig. 1. He single gas permeances and He permeances in the water/He binary mixture as a function of temperature for membranes ZSM5 and MOR; the water and He partial pressures in the feed were 4 and 101 kPa, respectively.

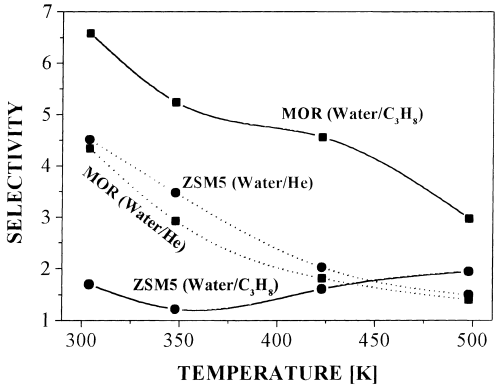

Fig. 2. Water/He and water/propane selectivities in the water/He and water/propane binary mixtures as a function of temperature for membranes ZSM5 and MOR; the partial pressures of water and the other component (propane or He) in the feed were 4 and 101 kPa, respectively.

selectivity close to 1 does not give any indication of its possible performance in the separation of mixtures. However, because of its hydrophilic character a water/propanol separation selectivity as high as 149 has been reported for this membrane [8]. As will be shown below, both ZSM5 and MOR membranes can separate water/He and water/hydrocarbons mixtures, i.e., vapor/non-condensable and polar/non-polar mixtures.

3.1. Comparison of membranes ZSM5 and MOR

Fig. 1 shows the He permeance for membranes ZSM5 and MOR as single gas and in mixtures. It can be seen that there is little change in the single gas permeance of He up to 380 and 350 K for membranes ZSM5 and MOR, respectively. Testing at lower temperatures would have probably increased the permeation, thereby producing a minimum in the permeation curves, as reported by Bakker et al. [1] for He through a flat silicalite membrane supported on stainless steel. The minimum stems from the fact that with increasing temperature the amount adsorbed in the zeolite pores decreases. After the low-temperature plateau, for both membranes, an activated diffusion mechanism governe the permeation, and the permeance increases. The existence of activated diffusion suggests that most of the transport takes place through zeolitic pores. This is also in good agreement with previous reports on He permeation through silicalite [13] and mordenite [14] flat membranes. Note that for both membranes in the temperature range tested, the permeance values of He (a non-adsorbable gas under these experimental conditions) are very similar, i.e., a similar resistance to permeation is obtained in spite of the evident differences between the MOR and ZSM5 membranes.

In the experiments carried out with water/He mixtures the water and He partial pressures in the feed were 4 and 101 kPa, respectively. Since membranes ZSM5 and MOR are hydrophilic, water adsorbs preferentially on the zeolite pores blocking the pass of He through the membranes. This leads to a lower permeance of He in the mixture, compared to the single gas permeance. On the other hand, as discussed elsewhere [8], the MOR membrane has a lower Si/Al ratio, and thus is more hydrophilic than the ZSM-5 membrane. Fig. 2 shows that the water/He separation selectivities are very close for both membranes ZSM5 and MOR; since the absolute value of He permeance was higher in the MOR membrane during the separation of binary mixtures, this indicates that water permeated faster in the more hydrophilic membrane MOR. Actually, water permeances at 303 K in the water/He mixture are 3.9×10^{-7} and 6.4×10^{-7} mol/(m^2 s Pa) for ZSM5 and MOR, respectively. Figs. 1 and 2 also indicate that at the highest temperature tested, when the water adsorption in the zeolite pores becomes negligible, water permeated at almost the same rate through both membranes.

Fig. 3 shows the permeance of propane as a single gas and in binary mixtures for both membranes. The shape of the curve for the permeance of propane as

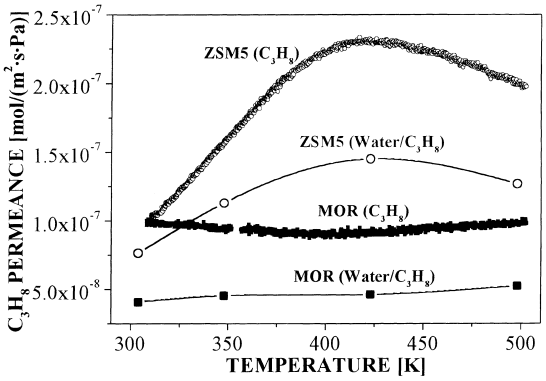

Fig. 3. Propane single gas permeances and propane permeances in the water/propane binary mixture as a function of temperature for membranes ZSM5 and MOR; the water and propane partial pressures in the feed were 4 and 101 kPa, respectively.

a single gas is exactly what could be expected for a ZSM-5 membrane, and can be explained by taking into account equilibrium adsorption and activated surface diffusion [1,13]. With increasing temperature, the propane diffusivity through the micropores of the zeolite increases but the amount adsorbed decreases. For membrane MOR, a less organophilic material, propane was only weakly adsorbed, and a minimum is observed. Again, a significant reduction of the propane permeance can be observed in mixtures with water, and this reduction is greater for the more hydrophilic MOR membrane. It is interesting to note that even at the highest temperature tested (498 K), the propane permeance did not reach its single gas value. This is in contrast with the behavior for the water/He mixture, i.e., at 498 K water was able to significantly block the passage of propane but it was less efficient at blocking He (see Fig. 1). This could be explained as the interaction between two type of channels: hydrophilic zeolitic pores, and microdefects between zeolite crystallites. Propane permeates largely through zeolite pores, where it is blocked by adsorbed water even at high temperatures; on the other hand, He permeates significantly via microdefects, and a substantial reduction of its permeance can only be obtained at low temperature by the capillary condensation of water. Because adsorption decreases with temperature, the water/propane selectivity for membrane MOR shows a steep decrease as temperature is increased, while the value stays around 1.5–2 (i.e., close to the Knudsen value) for ZSM5.

The comparison between the results obtained with ternary water/propane/He mixtures with those of binary water/He and water/propane mixtures are given in Table 2. For both membranes it seems clear that propane competes with water for the same pores: the water permeance through membrane ZSM5 was reduced by two thirds when He was replaced by propane in the binary mixture; this reduction was of 50% for the more hydrophilic MOR. Also, the water/He selectivity was reduced from 4.3–4.5 in the binary mixture to 2.9–3.0 in the ternary, i.e., water permeance was decreased by the presence of propane in the ternary mixture, while He transport was less affected. In contrast, the addition of He to the binary water/propane mixture did not change significantly the water permeance or the water/propane selectivity. All of these results are consistent with the assumption that water and propane permeate mainly through zeolite pores, while He does so through inter-crystalline defects.

3.2. Permeation of water/light hydrocarbons mixtures through membrane ZSM5

It is interesting to compare the behavior of the less hydrophilic membrane tested (ZSM5) when water

Table 2
Separation of mixtures using ZSM5 and MOR membranes at temperature 304 K

Feed [kPa]			Membrane					
			ZSM5			MOR		
Water	C_3H_8	He	Water permeance $\times 10^{-7}$ [mol/(m^2 s Pa)]	$S_{W/He}$	$S_{W/C3}$	Water permeance $\times 10^{-7}$ [mol/(m^2 s Pa)]	$S_{W/He}$	$S_{W/C3}$
4.0	–	101	3.9	4.5	4.5	6.4	4.3	–
4.0	101	–	1.3	–	1.7	2.7	–	6.6
2.7	67	36	1.2	2.9	1.1	–	–	–
4.0	65	36	–	–	–	3.5	3.0	6.9

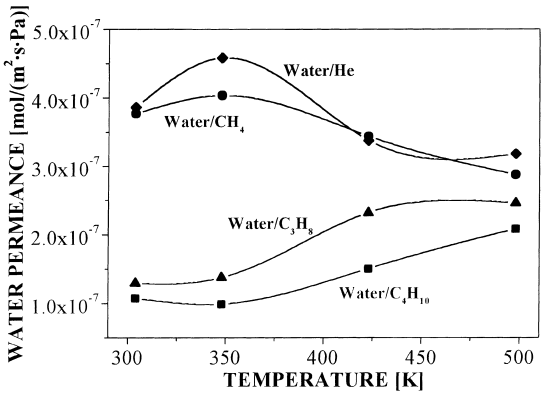

Fig. 4. Water permeances in binary mixtures of water with He, methane, propane and *n*-butane as a function of temperature for membrane ZSM5; the partial pressures for water and the other component (He or hydrocarbon) in the feed were 4 and 101 kPa, respectively.

and different hydrocarbons compete for the same zeolite pores. Fig. 4 shows the water permeance through membrane ZSM5 as a function of temperature for different binary mixtures. Since the adsorption of He on the ZSM-5 zeolite can be neglected under the conditions employed, the water permeance in the water/He mixture can be taken as a measurement of the single component permeance for water. When methane is used, instead of He in the binary mixture, the water permeance is somewhat reduced. However, methane is a small hydrocarbon that adsorbs weakly on the ZSM-5 pores, which explains the small magnitude of the water permeance reduction. As the length of the hydrocarbon increases, its adsorption becomes stronger, and the competition causes a stronger reduction in water permeance.

The water permeance in mixtures with He and methane decreased for increasing temperatures (Fig. 4), which agrees well with a transport mechanism based on surface diffusion and capillary condensation. On the other hand, the adsorption enthalpy ($-\Delta H$) measured for silicalite (with the same MFI structure that ZSM-5 but without aluminum) is considerably higher for propane (38.2 kJ/mol) and *n*-butane (45.9 kJ/mol) that for methane (22.6 kJ/mol) [13]. When propane and *n*-butane were used in binary mixtures with water, not only the reduction in the water permeance was higher than in the case of methane, but also the opposite trend with temperature was observed. As temperature increased from 304 to 498 K, the hydrocarbon adsorption decreases faster than that of water, and, since water competes for the same pores with propane and *n*-butane, the water permeance increased. At an even higher temperature, the different water permeances converged to an unique value for all the mixtures studied in this work.

In Fig. 5, the permeances of methane, propane and *n*-butane as single gases and in binary mixtures with water are plotted as a function of temperature for membrane ZSM5. Note that the conditions for the mixtures are the same as in Fig. 4, and that the single gas permeance of methane has been multiplied by a factor of 0.5. The behavior observed for the single gas permeances of methane, propane and *n*-butane as a function of temperature is the same found by Bakker et al. for silicalite [1,13]: initially, the permeance goes through a maximum with increasing temperature (which Bakker et al. [1,13] found at 243, 358 and 418 K for methane, propane and *n*-butane, respectively), and, if the temperature is further increased, a minimum is observed in the permeance. As said above, the combination of activated diffusion and adsorption explains these maxima and minima. The sequence in the maxima found in this work is methane (the lowest temperature used was already above the maximum) < propane (418 K) < *n*-butane (454 K). For all the hydrocarbons tested, the single gas permeance was higher than that in binary mixtures with water, due to the preferential water adsorption in the zeolite pores.

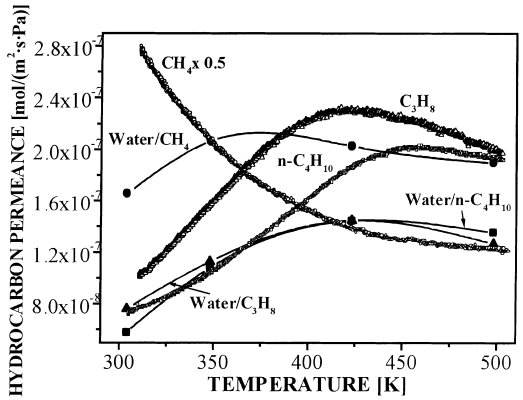

Fig. 5. Hydrocarbon (methane, propane and *n*-butane) permeances as single gases and in their binary mixtures with water as a function of temperature for membrane ZSM5; the water and hydrocarbon partial pressures in the feed were 4 and 101 kPa, respectively.

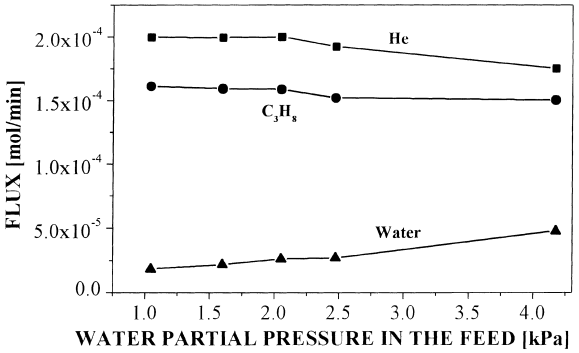

Fig. 6. Water, propane and He permeances through membrane MOR in a ternary mixture, as a function of the water partial pressure in the feed at temperature 304 K.

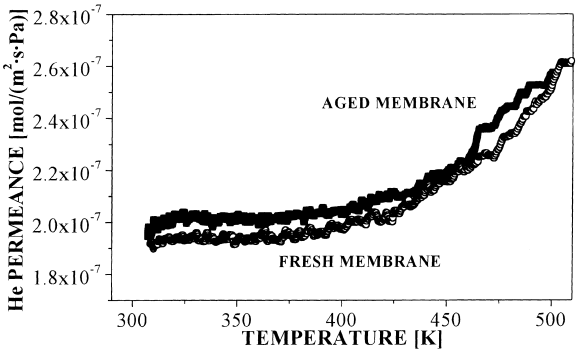

Fig. 7. He single gas permeance through the fresh and aged membrane ZSM5 as a function of temperature.

3.3. Influence of the water partial pressure

The data plotted in Fig. 6 were obtained at 304 K using membrane MOR and increasing the partial pressure of water in the feed from 1.1 to 4.2 kPa, with propane and He partial pressures in the feed were in the 60–66 and 33–36 kPa ranges, respectively. As shown in Fig. 6, as the partial pressure of water in the feed increased, so did the water flux, as a consequence of the higher water concentration in the membrane pores; at the same time, the He and propane molar fluxes decreased. The water/He or water/hydrocarbon selectivities reported above have modest values, under 10: the maximum water partial pressure used in this work is rather small (4.0 kPa), sufficient to obtain water/hydrocarbon selectivity, but not high enough to produce a total blockage, (of zeolite pores and of inter-crystalline microdefects) which requires the use of higher partial pressures of water [15].

3.4. Stability of membrane ZSM5

Finally, Fig. 7 compares the He permeance (single gas) as a function of temperature for fresh and aged ZSM5 membranes (ZSM-5 on stainless steel). The fresh membrane corresponds to the "as synthesized" membrane, before running any experiments, while the aged membrane was calcined four times at 753 K for at least 4 h and kept under 4 kPa of steam for around 60 h. It can be concluded that the membrane shows good stability, as indicated by the proximity between the permeation curves in Fig. 7.

4. Conclusions

Water can be separated with some selectivity from water/He, water/methane, water/propane and water/*n*-butane and water/propane/He mixtures through ZSM-5 and mordenite/ZSM-5/chabazite membranes. This is due to preferential adsorption and capillary condensation of water both in the membrane pores and in inter-crystalline voids. Water and the hydrocarbons compete for the same zeolite pores. The fastest permeating compound (and therefore the separation selectivity) is determined by the nature of the membrane (hydrophilicity) and of the hydrocarbon (adsorption strength), as well as by the operating conditions (temperature and concentration of adsorbing species). In general, with increasing temperature, the preferential adsorption and capillary condensation of water vanishes, and the selectivity decreases. The maximum water/He and water/propane selectivities reported in this work are 4.5 and 11 for ZSM-5 and mordenite/ZSM-5/chabazite membranes, respectively.

Acknowledgements

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

References

[1] W.J.W. Bakker, F. Kapteijn, J. Poppe, J.A. Moulijn, J. Membrane Sci. 117 (1996) 57.

[2] K. Aoki, K. Kusakabe, S. Morooka, J. Membrane Sci. 141 (1998) 197.
[3] J. Coronas, J.L. Falconer, R.D. Noble, AIChE J. 43 (1997) 1797.
[4] A. Giroir-Fendler, J. Peureux, H. Mozzanega, J.A. Dalmon, Stud. Surf. Sci. Catal. 111 (1996) 127.
[5] E. Piera, A. Giroir-Fendler, H. Moueddeb, J.A. Dalmon, J. Coronas, M. Menéndez, J. Santamaría, J. Membrane Sci. 142 (1998) 97.
[6] M.D. Jia, B. Chen, R.D. Noble, J.L. Falconer, J. Membrane Sci. 90 (1994) 1.
[7] H. Kita, K. Horii, Y. Ohtoshi, K. Okamoto, J. Mater. Sci. Lett. 14 (1995) 206.
[8] E. Piera, M.A. Salomón, J. Coronas, M. Menéndez, J. Santamaría, J. Membrane Sci. 149 (1998) 99.
[9] M.A. Salomón, J. Coronas, M. Menéndez, J. Santamaría, Chem. Commun. (1998) 125.
[10] E. Piera, M.P. Bernal, M.A. Salomón, J. Coronas, M. Menéndez, J. Santamaría, Stud. Surf. Sci. Catal. 125 (1999) 189.
[11] J.F. Smetana, J.L. Falconer, R.D. Noble, J. Membrane Sci. 114 (1996) 127.
[12] J. Coronas, J.L. Falconer, R.D. Noble, Ind. Eng. Chem. Res. 37 (1998) 166.
[13] W.J.W. Bakker, L.J.P. van den Broeke, F. Kapteijn, J.A. Moulijn, AIChE J. 43 (1997) 2203.
[14] N. Nishiyama, K. Ueyama, M. Matsukata, AIChE J. 43 (1997) 2724.
[15] R. Espinoza, J. Santamaría, M. Menéndez, J. Coronas, S. Irusta, Rep. South Africa Patt. Appl. Ner 985093 (1998).