Research Article

Gas permeability of polydimethylsiloxane membranes filled with clinoptilolite in different cationic forms

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Abstract: Zeolite-polymer mixed matrix membranes were prepared by filling polydimethylsiloxane (PDMS) with clinoptilolite in various cationic forms of K, Mg, H, and Na. The membranes were characterized by scanning electron microscopy as well as measurements of O_2, N_2, and CO_2 gas permeabilities. The results indicated the presence of an optimum zeolite loading in the mixed matrix membranes maximizing permeability. The type of the cationic form of clinoptilolite used affected the permeabilities and ideal selectivities of the zeolite-polymer mixed matrix membranes investigated to some degree and some improvements were obtained when compared to the ideal selectivities of the original polymeric membranes.

Key words: Clinoptilolite, PDMS mixed matrix membrane, gas separation

1. Introduction

Polymeric membranes have received significant attention in separation applications. A noteworthy problem of using these materials in industry is the tradeoff between permeability and selectivity. Mixed matrix membranes have been proposed to improve the separation performances of purely polymeric membranes. The distribution of additional porous or nonporous materials in the polymer matrix leads to the preparation of mixed matrix membranes. Among porous materials, zeolites and carbon molecular sieves have been used most commonly as fillers of polymeric membranes. Metal organic frameworks, zeolitic imidazolate frameworks, carbon nanotubes, activated carbon, and ordered mesoporous silica may be mentioned among other materials investigated for the same purpose.[1] Carbon molecular sieves may be preferred for the separation of gas molecules with similar size since they may have adsorption properties superior for certain gases.[2] Separation by activated carbon depends on the slower permeation of the less adsorbable component.[2] On the other hand, an advantage of utilizing ordered mesoporous silica is the better wetting and dispersion of the particles in the mixed matrix membranes.[3] However, the penetration of the polymer chains into the large pores of the mesoporous materials may lead to the blocking of inner pores while providing high membrane integrity. Carbon nanotubes, metal organic frameworks, and zeolitic imidazolate frameworks are relatively new materials tested for their suitability as fillers in mixed matrix membranes. Although carbon nanotubes may be potentially useful,[4] their high cost and possibly harmful health effects due to their fast migration seem to be drawbacks. Metal organic frameworks and the closely related zeolitic imidazolate frameworks are currently popular research subjects for membranes as well as other applications. The high surface area, controlled porosity, affinity for specific gases, and flexible

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chemical composition of these materials render them suitable as fillers in mixed matrix membranes. Although enhancements have been observed in the permeabilities, significant improvements have not been reported yet for the selectivities of their mixed matrix membranes.[5] Additional research is required to prove their usefulness. Lack of sufficient stability under certain conditions may be an additional concern for the successful use of metal organic framework fillers.

The size and shape selectivity originating from the narrow pore size distribution of zeolites necessitates considering these materials as suitable alternatives of fillers in mixed matrix membranes. Unfortunately, the preparation of pure zeolitic membranes is limited by high cost and difficulties in forming continuous and defect-free membranes. Thus, their inclusion in composite materials such as zeolite-polymer mixed matrix membranes is significant. The advantage of including zeolite in the polymeric matrix mainly lies in the combination of the high selectivity of the zeolite with the high integrity and processability of the polymer. Different zeolite-polymer mixed matrix membranes have been investigated.[6] Zeolites silicalite/ZSM-5, X/Y, and A have been commonly tested as fillers in polymeric membranes for the separation of gas mixtures, consisting of CO_2, O_2, N_2, and H_2 or the separation of CH_4 from inorganic gases.[7−9] The pervaporation of alcohol/water mixtures has also been studied.

Clinoptilolite is the most common zeolite occurring in nature. Its aluminosilicate framework, which is denoted by HEU, contains a two-dimensional channel system. It may be used in different applications, mostly based on its ion-exchange properties. The applications include purification of water, nuclear waste management, agriculture, horticulture, and reduction of the concentration of heavy metals and hazardous substances in plants and environmental matrices.[10] The effective pore size of the zeolite excludes molecules larger than about 0.4 nm.[11] This value may vary to some extent when an ion-exchange procedure is applied. The pore size of clinoptilolite is reduced to below 4 Å after ion-exchange with Na and K. The extent of this reduction is more significant for the use of the latter ion. When clinoptilolite is ion-exchanged with Mg and H, its pore size increases, approaching about 4.5 Å. Clinoptilolite has also been investigated for its use in membranes. Membranes generated from natural clinoptilolite-rich rock showed promising water desalination and deoiling performance.[12] They were also utilized in the pervaporative desalination of water samples with varying salinity levels, including synthetic seawater.[13] Additionally, clinoptilolite-filled sodium alginate membranes were prepared with a solution-casting method. The separation properties of these materials were characterized by pervaporation of ethanol-water mixtures.[14] Another example is the obtaining of ceramic multilayer microfiltration membranes on a porous support by dip-coating of the natural zeolite.[15] Natural dense clinoptilolite membranes modified by cation exchange were tested for their H_2 and CO_2 separation properties.[16] It was observed that H_2 and CO_2 permeances through the membranes were very sensitive to the type, size, and charge of the cations. The inclusion of clinoptilolite in zeolite-polymer mixed matrix membranes has been limited to a few studies to date. Clinoptilolite-filled poly(vinylalcohol) membranes containing different amounts of zeolite have been prepared and tested in the pervaporation separation of aqueous-organic mixtures.[17,18]

It may be interesting to investigate further the suitability of using clinoptilolite as fillers in polymeric membranes. This zeolite has some advantages economically, as a material rather commonly found in nature. Furthermore, it possesses a number of ions, which may affect adsorption/separation properties. In this study, the effects of utilizing various cationic forms of clinoptilolite as fillers in polydimethylsiloxane (PDMS) membranes were investigated. PDMS was selected as the polymer since its mixed matrix membranes with zeolites may be prepared without any surface modification of the zeolite and there are no adhesion problems, as observed in previous studies performed by using ZSM-5, silicalite, and NaA-filled PDMS membranes.[19,20] Accordingly,

the natural zeolite was ion-exchanged to obtain its forms rich in Na, K, Mg, and H. The zeolite-polymer mixed matrix membranes were prepared by a casting-evaporation process. The characterizations of the membranes were performed by the measurements of the O_2, N_2, and CO_2 gas permeabilities as well as scanning electron microscopy (SEM).

2. Results and discussion

The zeolite-filled PDMS membranes were examined by SEM to determine if the zeolite particles were dispersed homogeneously and if there were any defects or flaws in the membrane. Figures 1a and 1b and Figures 1c and 1d show the SEM pictures of the unfilled polymer and the Na-clinoptilolite-PDMS mixed matrix membrane (with 30% zeolite loading), respectively, at two different magnifications. SEM investigations showed that homogeneous dispersion of the zeolite crystals in PDMS was obtained for all the membranes used and the zeolite particles were completely covered by the polymer without any nonselective voids at zeolite/polymer interfaces, which is usually the case with rubbery polymers. In the pure PDMS membrane, small particles of fumed silica (<1 μm) exist inherently (as also seen from Figure 1b). The larger clinoptilolite particles of about 10 μm may be observed in Figure 1d.

(a)

(b)

(c)

(d)
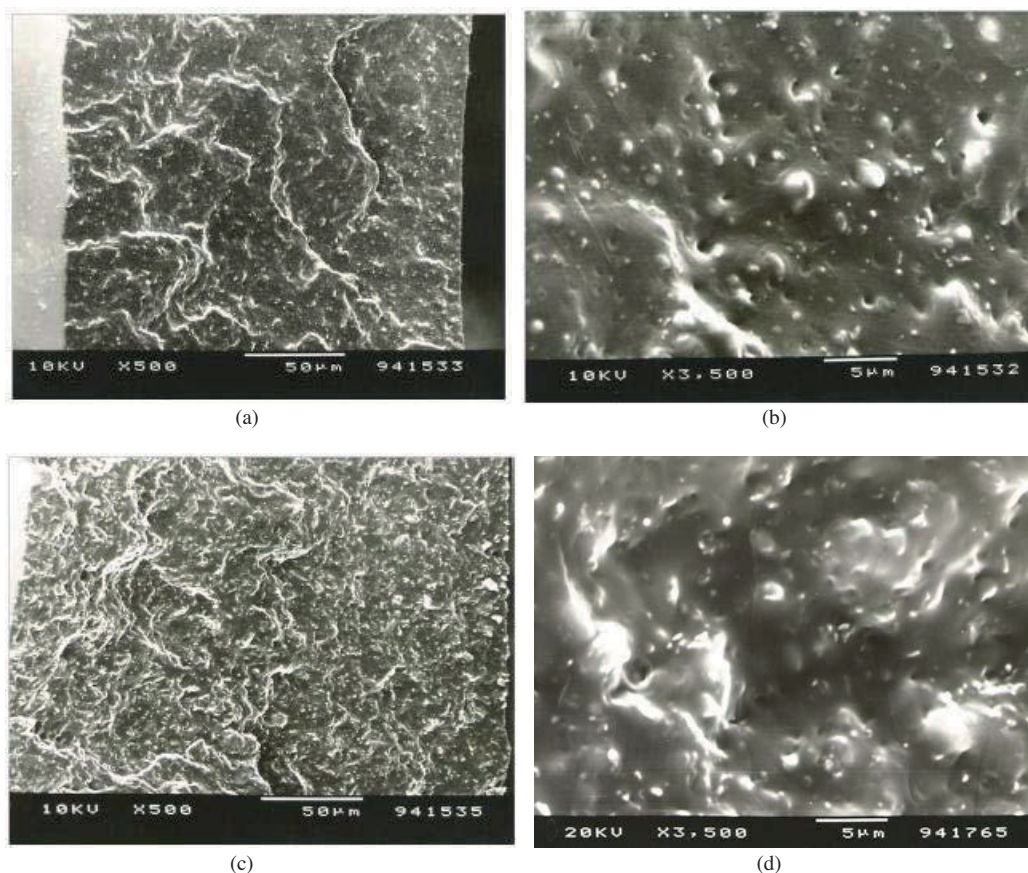
Figure 1. SEM pictures of the cross-sections of unfilled PDMS (a) at $500\times$ and (b) $3500\times$ magnifications, and of Na-clinoptilolite-PDMS membrane (30 wt.%) (c) at $500\times$ and (d) at $3500\times$ magnifications.

The variation of the permeability values of O_2 in PDMS membranes filled with Na-, K-, Mg-, and H-clinoptilolite with respect to the zeolite loading (wt.%) are shown in Figure 2. The permeability of the unfilled

polymeric membrane may also be seen from the figure. It may be observed that the highest permeabilities were obtained at the zeolite loading of 20% for all the mixed matrix membranes investigated. The O_2 permeabilities at this loading were higher to some degree than that of pure PDMS for all the cationic forms of clinoptilolite. The difference was more obvious for the clinoptilolites in K and Mg forms. However, at the higher zeolite loadings, the permeabilities were reduced to mostly below the polymer permeability. At the zeolite loading of 30%, Mg-clinoptilolite provided the highest permeability value. Na-clinoptilolite exhibited the lowest permeabilities in all cases. The presence of an optimum zeolite content maximizing the permeabilities of the mixed matrix membranes may be related to the presence of an interphase between the zeolite and polymer, as mentioned in previous studies.[19,21] An additional phase, the interphase, was assumed to surround the zeolite particles in the polymer environment in those studies. It was proposed that the permeabilities of molecules in the interphase might be different from the permeabilities in both the zeolite and polymer and the thickness of this additional phase could also have an impact on the permeabilities of the zeolite-polymer mixed matrix membranes. The type of gas, amount of zeolite loading, and zeolite particle size used were other significant parameters in determining the permeabilities. It may be hypothesized that the interphase permeability was higher than those of the zeolites and polymer used in this study. Thus, it is possible that at the relatively low zeolite loading utilized for the mixed matrix membranes, the effective permeability exceeded that of the pure polymer. It is also quite likely that at the relatively higher zeolite loadings, agglomeration of the zeolite particles might occur. In such cases, the total amount of interphase surrounding the zeolite particles in the membrane may be expected not to increase as much as the increase made in the amount of zeolite, due to the enhancement of the zeolite particle size in effect. Consequently, as the zeolite loading was increased above 20% in this study, the favorable effect of interphase permeability might have lost its significance and the effective permeability decreased to below the polymer permeability, due to the fact that zeolites generally have relatively low permeabilities. In other words, the permeability of the zeolite became the limiting factor in determining the permeabilities of the mixed matrix membranes at the higher zeolite loadings.
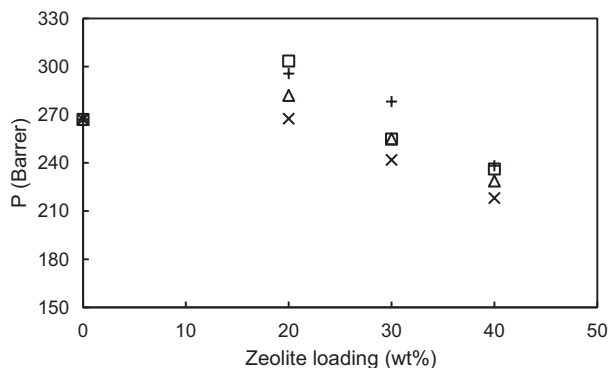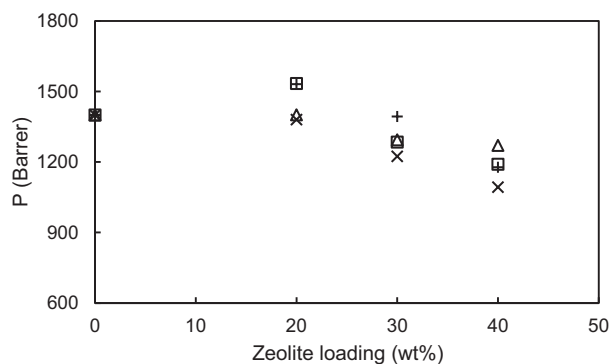

Figure 2. Variation of O_2 permeability in PDMS membranes filled with ($\times$) Na-, ($\square$) K-, (+) Mg-, and ($\triangle$) H-clinoptilolite with respect to zeolite loading (wt.%).

Figures 3 and 4 represent the permeability values of N_2 and CO_2, respectively, in the different types of clinoptilolite-PDMS membranes mentioned above. For N_2 permeabilities, values noticeably higher than that of pure polymer could be again obtained at the zeolite loading of 20% for K-clinoptilolite and Mg-clinoptilolite mixed matrix membranes. The permeabilities decreased with increasing zeolite loading. The behaviors of the membranes were generally similar to the cases where O_2 was used. For CO_2, the general trend of the variation of permeabilities with zeolite loading was also similar to those obtained for O_2 and N_2, especially at 20% and

30% loadings. However, at 40% loading, the H-clinoptilolite filled membrane was observed to provide the highest permeability among the mixed matrix membranes. The permeability at this zeolite loading was only slightly below the value obtained at 30% loading for the same membrane. This may be related to the observations made previously that CO_2 adsorption on H-clinoptilolite exhibits the lowest characteristic adsorption energy among clinoptilolite samples with different ionic forms.[22] H-clinoptilolite also has a relatively open channel structure and CO_2 is the gas molecule that has the smallest kinetic diameter among those used in this study. Thus, the adsorption of CO_2 on the inner and outer surfaces of H-clinoptilolite may be expected to be relatively weak, though still superior compared to the polymer, while its diffusion in the channels may be faster than other gas molecules. A similar behavior may be absent for the membranes filled with other ionic forms of clinoptilolite.
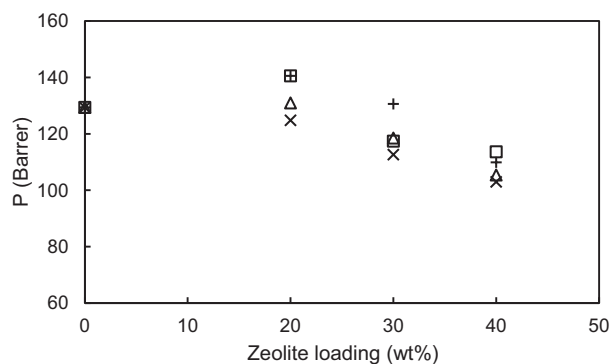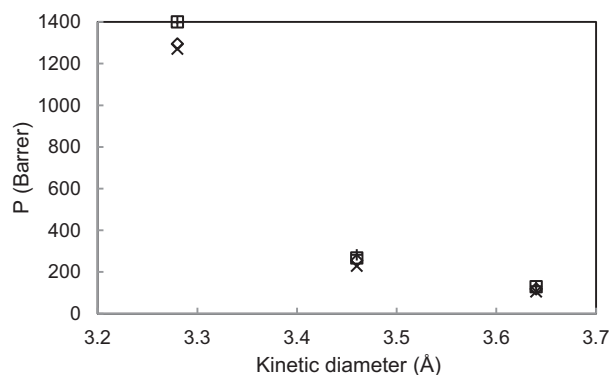

Figure 3. Variation of N_2 permeability in PDMS membranes filled with ($\times$) Na-, ($\square$) K-, ($+$) Mg-, and ($\triangle$) H-clinoptilolite with respect to zeolite loading (wt.%).

Figure 4. Variation of CO_2 permeability in PDMS membranes filled with ($\times$) Na-, ($\square$) K-, ($+$) Mg-, and ($\triangle$) H-clinoptilolite with respect to zeolite loading (wt.%).

The permeability values increased with the decreasing size of the gas molecules used. Figure 5 represents the variation of permeability with respect to the kinetic diameters of the O_2, N_2, and CO_2 molecules in H-clinoptilolite-PDMS mixed matrix membranes at different zeolite loadings. It may be observed that the permeability of the smallest molecule investigated, CO_2, was higher than those of O_2 and N_2. The magnitude of the difference between the permeabilities of CO_2 and O_2 was much larger than the difference between the permeabilities of O_2 and N_2. As also mentioned before, increasing the zeolite loading above 20% generally resulted in some decrease in the permeability values of all the gases tested in this study.

Figure 6, Figure 7, and Figure 8 respectively show the variations of O_2/N_2, CO_2/N_2, and CO_2/O_2 ideal selectivities of the mixed matrix membranes, filled by various forms of clinoptilolite, with zeolite loading. The results indicated that the O_2/N_2 ideal selectivity, depicted in Figure 6, increased in moderate amounts when compared to the performance of the purely polymeric membrane for all the mixed matrix membranes and zeolite loadings investigated. For the CO_2/N_2 and CO_2/O_2 selectivities, enhancements worth mentioning occurred at the zeolite loading of 40% for the H-clinoptilolite filled mixed matrix membrane. As may be seen from Figure 7, the CO_2/N_2 ideal selectivity increased by about 11% compared to the polymer for the H-clinoptilolite filled membrane with the relatively high zeolite loading of 40%. A similar behavior was observed for the CO_2/O_2 ideal selectivity of the same mixed matrix membrane, as depicted in Figure 8, where the enhancement amounted to about 6%. The CO_2/O_2 selectivity decreased slightly for all the other mixed matrix membranes with respect to the polymer and also zeolite loading. The improvements in the CO_2/N_2 and CO_2/O_2 selectivities obtained by using H-clinoptilolite-PDMS mixed matrix membranes at 40% zeolite loading might be related to the less significant diffusion limitations for the smaller CO_2 molecule in H-clinoptilolite with respect to the O_2 and N_2

Figure 5. Variation of permeability with respect to kinetic diameters of O_2 (3.46 Å), N_2 (3.64 Å), and CO_2 (3.28 Å) molecules in H-clinoptilolite-PDMS mixed matrix membranes at zeolite loadings of ($\square$) 0%, (+) 20%, ($\diamondsuit$) 30%, and ($\times$) 40%.
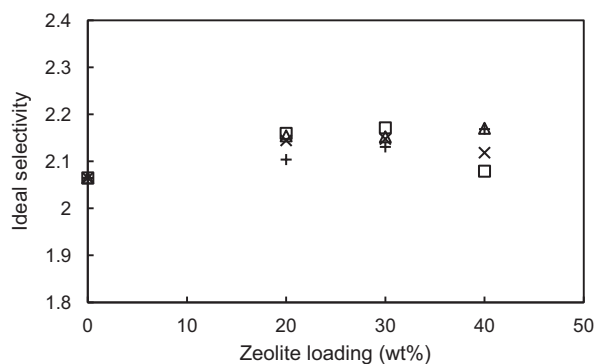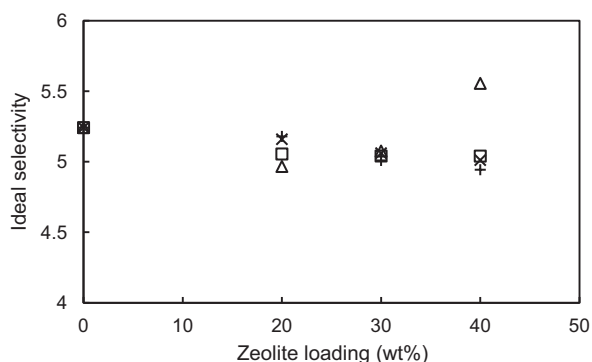
Figure 6. Variation of O_2/N_2 ideal selectivities of PDMS membranes filled with ($\times$) Na-, ($\square$) K-, (+) Mg-, and ($\triangle$) H-clinoptilolite with respect to zeolite loading (wt.%).

gases in the same material. Diffusion limitations of the zeolites might generally be expected to become dominant at relatively high zeolite loadings, thus leading to lower permeabilities, especially for the larger molecules.
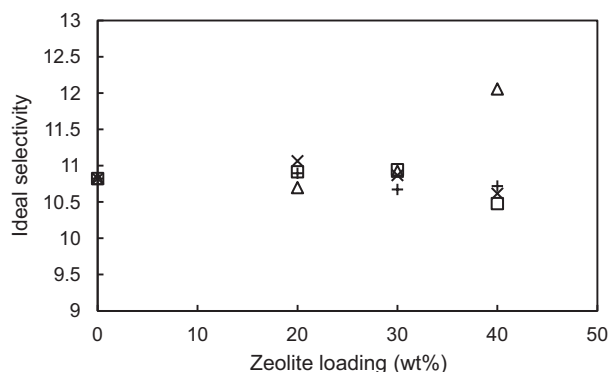
Figure 7. Variation of CO_2/N_2 ideal selectivities of PDMS membranes filled with ($\times$) Na-, ($\square$) K-, (+) Mg-, and ($\triangle$) H-clinoptilolite with respect to zeolite loading (wt.%).

Figure 8. Variation of CO_2/O_2 ideal selectivities of PDMS membranes filled with ($\times$) Na-, ($\square$) K-, (+) Mg-, and ($\triangle$) H-clinoptilolite with respect to zeolite loading (wt.%).

The differences in the pore sizes of clinoptilolite in different ionic forms did not significantly affect the permeability and selectivity values of the zeolite-filled mixed matrix membranes. In general, Na-clinoptilolite-filled mixed matrix membranes resulted in somewhat lower permeability values in accordance with its relatively small pore size; however, a similar behavior was not apparent for the membranes filled with K-clinoptilolite, which also has reduced pore size. The kinetic diameters of all the gas molecules used in this study were generally smaller than or close to the sizes of the pores of clinoptilolite in Na, K, Mg, and H forms. Thus, the existence of generally similar diffusion limitations for different ionic forms of clinoptilolite investigated, originating from the two-dimensional channel structure of this zeolite, as well as special interactions between gas molecules and different ionic forms of the zeolite, might have more profound effects on the permeabilities and selectivities of the mixed matrix membranes.

According to the results obtained, the permeability values of O_2, N_2, and CO_2 in the clinoptilolite-filled PDMS membranes were generally lower than those measured previously for PDMS membranes filled with ZSM-5 and silicalite.[19,20] The permeabilities of silicalite were highest. For zeolite NaA-filled PDMS membranes, the permeability of O_2 was higher while that of CO_2 was lower than those in clinoptilolite-filled PDMS membranes.[20] N_2 permeability was similar for both materials. The ideal selectivities of O_2/N_2, CO_2/O_2, and CO_2/N_2 for the clinoptilolite-filled PDMS membranes were generally slightly lower than or equal to those measured for PDMS membranes filled with ZSM-5, silicalite, and zeolite NaA. An interesting observation was the relatively high CO_2/N_2 and CO_2/O_2 ideal selectivities obtained for H-clinoptilolite-filled PDMS membranes at the relatively high zeolite loading when compared to the membranes filled with ZSM-5, silicalite, and NaA zeolites.

In conclusion, PDMS membranes filled with different ionic forms of clinoptilolite exhibited higher O_2, N_2, and CO_2 permeabilities compared to the pure polymer at the relatively low investigated zeolite loading of 20%. This behavior was more obvious for the membranes using clinoptilolite in K and Mg forms. However, the permeability decreased with increasing zeolite loading, pointing to an optimum value for the loading. Moderate improvements were observed in the O_2/N_2 ideal selectivities of PDMS membranes when they were filled with different ionic forms of clinoptilolite at various zeolite loadings. An interesting observation was the increase, compared to the pure polymeric membrane, for CO_2/N_2 and CO_2/O_2 selectivities in H-clinoptilolite-filled membranes at the relatively high zeolite loading of 40%. This seemed to originate from less significant diffusion limitations for the smaller CO_2 gas molecule compared to O_2 and N_2 in H-clinoptilolite. An additional phase, the interphase, previously hypothesized to exist between the zeolite and polymer phases in mixed matrix membranes, might have affected the permeability and thus selectivity values obtained for the clinoptilolite-PDMS mixed matrix membranes. The relatively large particle sizes of clinoptilolite used in this study might have reduced the extent of these effects, since the number of zeolite-polymer interfaces should be expected to decrease with increasing zeolite particle size.[19]

The results obtained in this study indicate that the ionic form of clinoptilolite used in zeolite-polymer mixed matrix membranes might affect the permeabilities and ideal selectivities of the membranes to some degree. It is possible that utilizing polymers other than PDMS, with a suitable ionic form of clinoptilolite in the zeolite-polymer mixed matrix membrane, may lead to more significant and commercially valuable improvements in the O_2/N_2, CO_2/N_2, and CO_2/O_2 ideal selectivities.

3. Experimental

Natural zeolite in different ionic forms was used as the adsorptive filler in the experiments carried out. The origin of the mineral was a clinoptilolite-rich rock from a deposit near Bigadiç, Turkey. The chemical composition of the clinoptilolite-rich rock mainly consisted of (in wt.%) 66.17 SiO_2: 9.72 Al_2O_3: 14.47 H_2O: 0.134 Na_2O: 1.50 K_2O: 2.51 CaO: 0.61 MgO: 3.19 Fe_2O_3, as reported before.[23] The mineralogical composition of the material was about 85% clinoptilolite while the remaining part included especially quartz and feldspar. After being crushed, the clinoptilolite samples were washed for 24 h with hot distilled water in a Soxhlet apparatus in order to remove the soluble impurities. A Szegvari-01.HD type attrition mill was then used for grinding the clinoptilolite samples with a rate of 450 rpm for 1.5 h to reduce the particle size from $\sim$90 μm to about 10 μm.

Since clinoptilolite has a polycationic structure, different cations such as K, Ca, Mg, and Na have to be eliminated in order to obtain clinoptilolite rich in a specific cation form. The samples were repeatedly ion-exchanged by using 1 M aqueous solutions of NaCl, KCl, $MgCl_2$, and NH_4Cl (Merck) to obtain clinoptilolite

rich in Na, K, Mg, and H forms, respectively. For this purpose, 4 g of the ground samples and 200 mL of 1 M aqueous salt solution were stirred in a hot water bath equipped with a magnetic stirrer for 5 h at 80 °C. After filtration, the samples were washed to remove Cl ions and were dried. This ion-exchanging procedure was repeated five times.

The samples were then activated at 400 °C for 6 h. The activation of all the samples was carried out using a heating rate of 2 °C/min. The membranes were prepared from polydimethylsiloxane (PDMS), a rubbery polymer. The zeolite loading was varied between 20% and 40%. The PDMS components, RTV664A/B, were kindly supplied by General Electric Company. The zeolite-filled PDMS membranes were prepared by first dispersing the zeolite particles in the polymer solution, followed by a casting-evaporation process.[24] Iso-octane was used as a solvent. Evaporation was carried out at 50 °C in vacuum overnight. The thickness of the membranes prepared varied between 400 and 600 μm. Unfilled membranes were also prepared for comparison by employing the above procedures, omitting the zeolite addition step.

The permeabilities of the membranes were measured in a gas permeability system based on a constant volume/variable pressure technique.[25] Feed pressure was at 4 atm and all measurements were carried out at 28 °C to determine the permeation rates of O_2, N_2, and CO_2 gases. The measurement system was described previously in detail.[19] Ideal selectivities were determined by calculating the ratios of the pure gas permeabilities. The permeabilities reported in this study for the clinoptilolite-PDMS mixed matrix membranes represent average values since repeated experiments were performed for all the cases investigated. The repeatability experiments were performed by employing different films in each case. The variation between the permeability values measured in the repeated experiments was within $\pm 1\%$. This amount of variation did not seem to lead to any change in the meaning of the results obtained in this study. SEM (JEOL JSM-T330) was used to investigate the morphology of the membranes and the quality of dispersion of the zeolite particles within the membranes.

References

1. Bastani, D.; Esmaeili, N.; Asadollahi, M. *J. Ind. Eng. Chem.* **2013**, *19*, 375-393.

2. Goh, P. S.; Ismail, A. F.; Sanip, S. M.; Ng, B. C.; Aziz, M. *Sep. Purif. Technol.* **2011**, *81*, 243-264.

3. Zhang, Y.; Balkus, K. J. Jr; Musselman, I. H.; Ferraris, J. P. *J. Membrane Sci.* **2008**, *325*, 28-39.

4. Kim, S.; Chen, L.; Johnson, J. K.; Marand, E. *J. Membrane Sci.* **2007**, *294*, 147-158.

5. Perez, E. V.; Balkus, K. J. Jr; Ferraris, J. P.; Musselman, I. H. *J. Membrane Sci.* **2009**, *328*, 165-173.

6. Duval, J. M.; Kemperman, A. J. B.; Folkers, B.; Mulder, M. H. V.; Desgrandchamps, G.; Smolders, C. A. *J. Appl. Polym. Sci.* **1994**, *54*, 409-418.

7. Jia, M.; Peinemann, K. V.; Behling, R. D. *J. Membrane Sci.* **1991**, *57*, 289-292.

8. Adams, R. T.; Lee, J. S.; Bae, T. H.; Ward, J. K.; Johnson, J. R.; Jones, C. W.; Nair, S.; Koros, W. J. *J. Membrane Sci.* **2011**, *367*, 197-203.

9. Chandak, M. V.; Lin, Y. S.; Ji, W.; Higgins, R. J. *J. Membrane Sci.* **1997**, *133*, 231-243.

10. Misaelides, P. *Micropor. Mesopor. Mat.* **2011**, *144*, 15-18.

11. Farjoo, A.; Sawada, J. A.; Kuznicki, S. M. *Chem. Eng. Sci.* **2015**, *138*, 685-688.

12. Adamaref, S.; An, W.; Jarligo, M. O.; Kuznicki, T.; Kuznicki, S. M. *Water Sci. Technol.* **2014**, *70*, 1412-1418.

13. Swenson, P.; Tanchuk, B.; Gupta, A.; An, W.; Kuznicki, S. M. *Desalination* **2012**, *285*, 68-72.

14. Nigiz, F. U.; Dogan, H.; Hilmioglu, N. D. *Desalination* **2012**, *300*, 24-31.

15. Hristov, P.; Yoleva, A.; Djambazov, S.; Chukovska, I.; Dimitrov, D. *J. Univ. Chem. Technol. Metall.* **2012**, *47*, 476-480.

16. An, W.; Swenson, P.; Gupta, A.; Wu, L.; Kuznicki, T. M.; Kuznicki, S. M. *J. Membrane Sci.* **2013**, *433*, 25-31.

17. Sait, Y.; Arcevik, E.; Ekinci, B. *Can. J. Chem. Eng.* **2014**, *92*, 503-510.

18. Ravindra, S.; Rajinikanth, V.; Mulaba-Bafubiandi, A. F.; Vallabhapurapu, V. S.; Vijaya, S. *Desalin. Water Treat.* **2016**, *57*, 4920-4934.

19. Tantekin-Ersolmaz, B.; Atalay-Oral, C.; Tatlier, M.; Erdem-Senatalar, A.; Schoeman, B.; Sterte, J. *J. Membrane Sci.* **2003**, *175*, 285-288.

20. Atalay, Ç. MSc, İstanbul Technical University, İstanbul, Turkey, 1994.

21. Erdem-Senatalar, A.; Tatlier, M.; Tantekin-Ersolmaz, B. *Chem. Eng. Commun.* **2003**, *190*, 677-692.

22. Sirkecioglu, A.; Erdem-Senatalar, A. *Clay. Clay Miner.* **1996**, *44*, 686-692.

23. Sirkecioglu, A. PhD, İstanbul Technical University, İstanbul, Turkey, 1994.

24. Mulder, M. *Basic Principles of Membrane Technology*; Kluwer: Dordrecht, the Netherlands, 1991.

25. Pye, G.; Hoehn, H. H.; Panar, M. *J. Appl. Polym. Sci.* **1976**, *20*, 1921-1931.