Synthesis of Gas and Vapor Molecular Sieving Silica Membranes and Analysis of Pore Size and Connectivity

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Pervaporation and gas permeation properties of microporous silica membranes made by a sol–gel method are discussed. Defect free molecular sieving membranes are prepared by a dip coating process. The molecular sieving performance was measured and controlled based on gas permeation behavior of the membranes. The apparent activation energy for helium permeation and He/N$_2$ perm-selectivity values were used as the parameters for optimization of the membrane performance. The membranes with very high activation energy for He diffusion were used for pervaporation studies with a methanol/MTBE mixture at 323 K. Separation factor values as high as 260 were measured at a total liquid flux of 0.3 kg/m^2 hr. Sorption studies performed on corresponding silica gels revealed a separation mechanism based on diffusion of vapor molecules. Permeation of the vapor molecules through the micropores followed an activated diffusion mechanism. The gas permeation data could provide an understanding of the pore size distribution of the membrane, and the vapor sorption and diffusion data on the size and connectivity of the membrane pores.

Introduction

The pore size and morphology of adsorbents, thin films, and membranes have very important influence in deciding their final properties and engineering applications. A class of them, amorphous silica membranes with nanometric pore sizes has recently created intense interest because of their ability to separate gas molecules. Highly selective silica membranes with reasonably high fluxes could be made by sol–gel dip coating processes. The porosity of sol–gel silica membranes to a great extent depends on the reaction chemistry of silica sols. Yet, because of the absence of defect free molecular sieving membranes, permeation and sorption data through the Å order pores are scarce and hence the pore size and morphology of these films is not clearly understood. In this paper we have reported the processing of defect free molecular sieving membranes and the characterization of their porous structure based on molecular diffusion data. The reported results show the engineering applicability of these membranes as well as addressing the fundamental theory behind characterization of ultramicropores.

Synthesis composition of the reactants is an important factor in deciding the structure of the final membranes made by sol–gel strategies.[1] The synthesis parameters can influence the fractal behavior of the polymers and hence will affect the packing behavior.[2] Short-branched linear polymers are the best for making silica microporous membranes with molecular sieving capability. Under controlled sol–gel synthesis conditions we have processed molecular sieving silica membranes. Gas permeation,

sorption, pervaporation, and vapor sorption measurements were performed on such membranes and/or membrane materials.

Experimental Techniques

Polymeric silica sols were prepared by the acid-catalyzed hydrolysis and condensation of tetra-ethyl-ortho-silicate (Wako Pure Chemical Ind.) in an ethanol medium. Calculated quantities of ethanol and TEOS were first mixed. Dilute HNO$_3$ was then added slowly into the mixture while stirring. The mixture was kept at room temperature for about 30 min. Slow heating was done to raise the temperature of the mixture to 80 °C. Synthesis time was normally 3 h. The synthesis mixtures were made of 1:5 R_w/R_a, with R_w ranging from 4.5 to 8.7 and R_a ranging from 0.12 to 0.33, molar ratios of TEOS/ethanol/water/HNO$_3$. After synthesis the mixture was cooled to room temperature and diluted to 0.1 molar (Si) with ethanol. Dipping was immediately performed.

Flat supports of alpha alumina (12.5 cm^2 area) were pressed, sintered, and polished. These substrates were then dipped into a boehmite sol. Dipping time was 10 s. The synthesis of the boehmite sol and the procedure of dipping is described elsewhere.[3] On calcination at 600 °C boehmite transformed into gamma alumina.

These membranes were dipped in silica sol for 10 s. Drying was performed in a controlled humidity oven at 40 °C and 60%RH. Calcination was performed in air. Samples were heated at 25 °C/hr to 400 °C and soaked 3 h at that temperature. Unsupported membranes (gel) made from the dip solutions were treated in the same way. These gels were mostly used for adsorption studies.

Single gas permeation was carried out on a pressure controlled dead end setup. Gas at constant pressure was introduced in the feed side. Pressure increase in the downstream side was measured. For measuring helium permeation a pressure gauge (MKS, Barotron, USA) of 0–760 Torr range was used. For measuring permeation of other gases a pressure gauge with a 0–10 Torr range was used in the downstream side. The measured membrane area was 2 cm^2.

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Pervaporation experiments were performed by circulating the mixed liquid feed of methanol (MeOH; Dojindo, Japan, 99.0% pure, water content < 0.05%) and methyl tertiary butyl ether (MTBE; Wako Pure Chemical Industries, Japan. 99.8% pure, water content <0.1%) through the membrane with a gear pump. The measured membrane area was 6 cm². The permeate was collected (cold trap) and analyzed by gas chromatography. The use of cold traps at the permeate side ensured very low permeate side pressures. In other words the pressure gradient across the membrane could be approximated to the feed vapor pressure and hence the measured separation factor ($\beta_{i/j} = (c^p_i/c^p_j)/(c^f_i/c^f_j)$: where $\beta_{i/j}$ represents the measured separation factor of components i and j. The superscripts "p" and "f" of the concentration values represented by "c" refers to permeate and feed side of the membrane) can be directly correlated to the membrane selectivity and to the relative volatility of the mixture.[4]

We have employed the UNIQUAC model for calculating the individual vapor pressure values of the components in the mixture. Wagner's equation was used for calculating the single component vapor pressure values.[5] The calculations showed that the feed mixture relative volatility is very small particularly around the mixture compositions containing 10 wt % MeOH.[6] Hence under the present experimental conditions the measured PV selectivity more or less represented the separation ability of the membrane material.

N_2 adsorption was performed on continuous flow equipment (Omnisorp 100 CX) at a nitrogen flow rate of 0.1 mL/min. Unsupported silica gels, prepared under the same conditions as those of the membranes that are used for the gas separation and PV study, were used for the sorption measurements. In one case a thicker sol–gel layer deposited over the substrate was peeled off and used for the N_2 adsorption study. Vapor sorption measurements on silica gels were performed on a gravimetric sorption setup (Nekken, Japan). MeOH or MTBE vapor maintained at the required pressure (by controlling the temperature of the bath) was introduced into the sample chamber and the time to equilibrium adsorption was measured. Since complete outgassing was difficult once adsorption was performed, individual vapors were adsorbed on separate silica gel samples, but from the same lot. The porosity of the membrane was calculated from the equilibrium sorption isotherm and the diffusion coefficient D was calculated from the sorption kinetic data.[7–9] A simplified equation usually used for calculating the value of D at short sorption times was employed. where M_t is the mass of

$$D = ((M_t \times l/M_f)^2 \times 3.14/4)/t$$

adsorbate at time t and M_f is the equilibrium mass of adsorbate.

The thickness of the unsupported gel (21) was measured using a screw gauge with micrometer accuracy. The thickness of the supported membrane was measured as 60 nm by FESEM.

The synthesis compositions of the silica sols along with measured microporosity values of the calcined gels are shown in Table 1.

Results

Figure 1 shows the changes in apparent activation energy (E_{act}) for helium (He) permeation through silica membranes with changes in microporosity. The increase in porosity was brought about by changes in synthesis (increased amount of catalyst) or by aging the sol. Both

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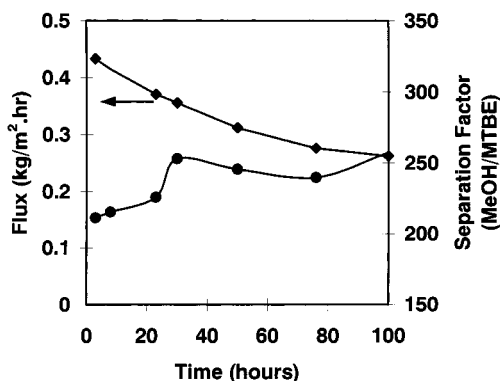(5) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987.
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Table 1. Synthesis Compositions and Room Temperature Aging Time of Silica Sols and Microporosity Values of Corresponding Calcined Gels[a]

sample	molar ratio (to TEOS)		aging time (h)	porosity
	H₂O	HNO₃		
silica A	6.8	0.122	0	0.245
silica B	6.8	0.122	24	0.26
silica C	8.7	0.157	0	0.33
silica D	4.5	0.327	0	0.362

[a] All the sols were made by refluxing the mixture at 80 °C for 3 h.
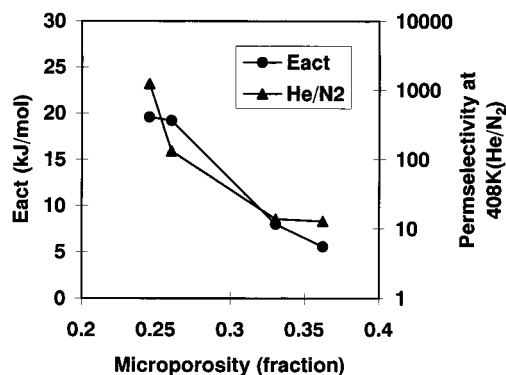
Figure 1. Helium permeation behavior of microporous silica membranes listed in Table 1. The apparent activation energy values were measured in the temperature range of 303–373 K and the He/N₂ perm-selectivity values were measured at 408 K.
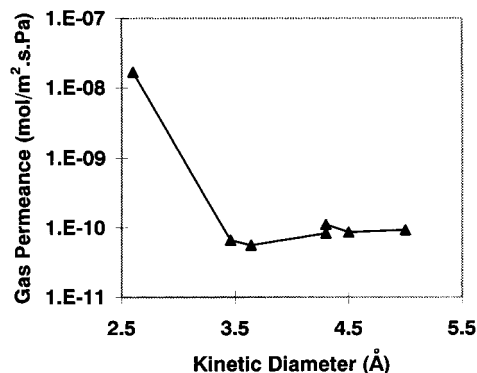
Figure 2. Dependence of gas permeation to kinetic diameter of the permeating molecules. Tested molecules were He (2.6 Å), O₂ (3.46 Å), N₂ (3.64 Å), C₃H₈ (4.3 Å), n-C₄H₁₀ (4.3 Å), C₃H₆ (4.5 Å), and i-C₄H₁₀ (5 Å).

of these will result in increased fractality of the constituent polymers of the membrane, hence increasing the porosity of the dried gel. The apparent activation energy for helium transport, however, decreased with an increase in porosity of the membrane. He/N₂ perm-selectivity (ratio of single gas permeation values) values showed a similar behavior as shown in Figure 1. These tendencies show that weak reaction conditions (like silica A in Table 1) are the best for synthesis of membranes with molecular sieving capability. A He/N₂ perm-selectivity value as high as 1230 was measured at 408 K for the silica A membrane as shown in Figure 1. The details of the gas permeation behavior of the silica A membrane is shown in Figure 2. Apart from helium all tested gas molecules (O₂, N₂, C₃H₈, n-C₄H₁₀, C₃H₆, and i-C₄H₁₀) showed very low permeance values. The molecular sieving capability of the membrane, for sizes above 3 Å, is clear from the figure. The very low permeance values of bigger molecules show that the membranes are defect free (or insignificant).
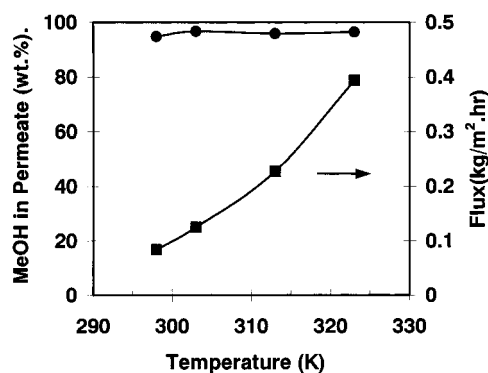
Figure 3. Time dependency of MeOH/MTBE pervaporation flux through silica membrane. Membrane was silica A type. Temperature was 323 K. Feed composition was 10:90 wt % MeOH/MTBE.

Figure 4. Temperature dependency of MeOH/MTBE pervaporation through silica membrane. Membrane was silica A type. Feed composition was 10:90 wt % MeOH/MTBE.

Figure 2 shows that the hydrocarbons showed higher permeation values than their nonadsorbing counterparts (applicable to molecules of size above 3 Å). Yet, under the conditions of the gas permeation study none of these adsorbing hydrocarbon molecules were tested at temperatures low to enough to have micropore filling be the transport mechanism. In the case of bigger pore sized membranes such capillary condensation of one of the diffusing species is found to limit the sorption and diffusion of the other diffusing species.

Pervaporation studies of MeOH and MTBE vapor molecules offered the opportunity to understand the transport properties of adsorbing molecules through silica membranes. Silica A type membranes (see Table 1 and Figure 1), which showed the best separation performance for He from bigger gas molecules, exhibited the best PV separation performance and hence such membranes were used for further PV study. Yet, it should be remembered that the performance of these types of membranes might not be the best with respect to PV separation of MeOH/MTBE. Membranes, made from silica particles, with bigger pores may be the best in this regard. Such membranes are reportedly capable of separating adsorbing molecules making use of their differences in sorption properties in the membrane material.[10]

Figure 3 shows the PV performance of the silica A type membrane. A mixture of 10 wt. % MeOH and 90 wt. % MTBE solution was used as the feed. From the figure, the flux through the membrane is time dependent. There is some change in the separation factor with time. But compared to the change in the flux this change in separation factor is negligible. It should be noted that the change of separation factor from 210 to 260 was made by a permeate concentration variation of 96.35 to 96.6% methanol. Evidently such a narrow change in permeate composition will not make a 50% change in flux. This increase in permeate concentration of MeOH can be attributed to another fact. The feed stream contains traces of water in the beginning. For a 2 L feed tank the water content can be as high 1−1.5 g. This water will be selectively removed in the beginning because of the larger permeation of water through the membrane. The decrease in concentration of water will increase the effective methanol content in the permeate mixture and hence the separation factor increases in the beginning. This drainage should account for the drop in permeation to some extent, but again this could not account for the whole change in
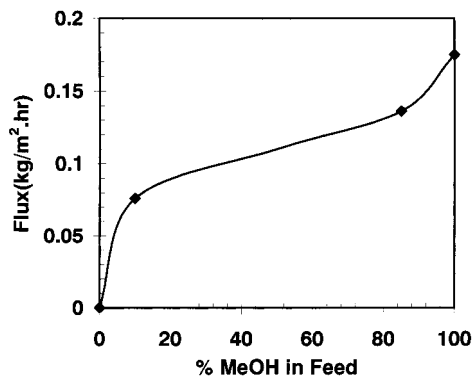
Figure 5. Feed composition dependency (MeOH: MTBE) of MeOH flux through silica A type membrane. The membrane used was similar to that used for plotting Figures 3 and 4.

flux. Treating the membrane close to the calcination temperature could regenerate the flux values. 80−90% regeneration can be done by mere vacuuming. Flux reductions due to pore clogging effects were occasionally reported in the case of silica membranes.[10,11] Asaeda et al., have indicated the possible methoxilation of unhydrolyzed sites in the silica pores as the reason for flux reduction while doing methanol PV.[10] In the present case the mechanism of flux reduction is not completely clear. Some more results are reported later on based on sorption measurements.

Figure 4 shows the temperature dependency of permeation. All the data were taken from averaging the first 30 h of measurement and hence the relative effect of flux decrease is assumed insignificant. As can be verified from Figure 4 the flux increases by about 4 times with an increase in temperature of about 25 K. The *activation energy for diffusion* was calculated as 17.8 kJ/mol for MeOH and 21.3 kJ/mol for MTBE molecules. Figure 5 shows the composition dependence of methanol flux through a silica A type membrane (similar to that used for plotting Figures 3 and 4 but not the same membrane).

The sorption isotherms of methanol and MTBE in the silica gel shown in Figure 6 are surprisingly similar. The sorption isotherms were not completely reversible. In the case of MeOH, 97% and in the case of MTBE, 96% of the sorbed volume could be desorbed by mere vacuuming. In the case of MeOH there was also decay in diffusivity between the first and second measurements performed on the same sample. Apparently these results from sorption and diffusion measurements agree with the flux

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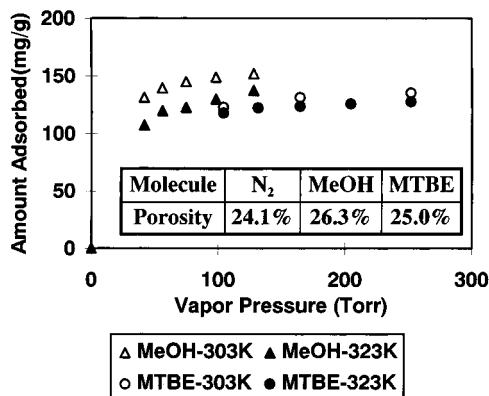
Figure 6. Sorption isotherms of MeOH and MTBE on silica gel. Gels flakes of about 250 μm were used for the gravimetric adsorption study. Equilibrium sorption values are shown. The inset table shows the porosity of silica gels calculated from equilibrium adsorption volumes of the gas and vapor molecules. Skeletal density of silica was taken as 2.2 g/cm^3.
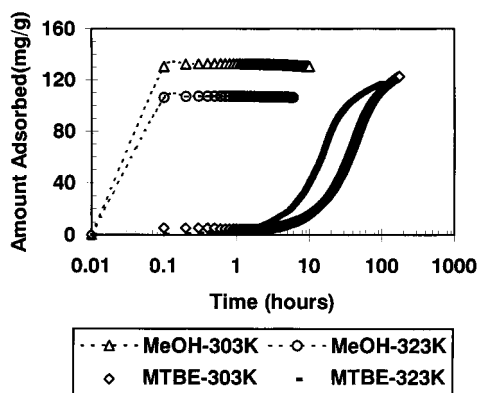
Figure 7. Kinetics of methanol and MTBE sorption in silica gel. Gels flakes of about 250 μm were used for the gravimetric adsorption study.

reduction reported earlier. But the exact mechanism of flux reduction is yet to be understood.

Figure 6 shows the amount of vapor molecules adsorbed on silica gels at 303 and 323 K. The amount adsorbed at 303 K was used for calculating the porosity of the gel assuming the density of the condensate similar to the liquid density at the same temperature. It is shown in the inset table in Figure 6, that the calculated porosity from MeOH, MTBE, and N$_2$ (adsorbed at liquid N$_2$ temperatures) sorption results are more or less similar. Previous adsorption studies with Argon gas molecules, however, gave a slightly higher porosity value of 28% for the silica gel. Considering the present evidence it can only be suggested that the majority micropore volume in silica seems to be accessible to bigger molecules such as MTBE.

Gas permeation results shown in Figure 2 clearly indicated that the membranes have molecular sieving capability to all gas molecules larger than 3 Å (e.g., N$_2$, O$_2$). This seems to contradict the present sorption results where MTBE was shown to be able to condense in the silica pores. However Figure 7 explains the cause of these contradictions. It is shown that the kinetics of sorption is entirely different for the two vapor molecules. Whereas methanol condenses in the pore and reaches equilibrium adsorption values in a matter of seconds, MTBE took as much as 100 hours to reach (almost) equilibrium. The diffusion coefficient values are obviously 2 orders of magnitude different between the molecules as in Table 2.

The diffusion coefficient values calculated from the sorption kinetic data are listed in Table 2. (In the case of

Table 2. Diffusion Coefficients of MeOH and MTBE[a]

temperature K	MeOH cm^2/sec	MTBE cm^2/sec	diffusivity ratio MeOH/MTBE
323	7.56×10^{-7}	1.55×10^{-9}	487.74
303	3.40×10^{-7}	7.39×10^{-10}	460.08

[a] The values were calculated from sorption kinetic data.

MeOH the data shown in Figure 7 was insufficient for calculating the diffusivity values because of the absence of data in the initial part of sorption curve. So sorption data from a separate measurement in which data were collected in every 36 s interval compared to the 360 s interval shown in Figure 7 was used for calculating the diffusivity of MeOH.) The thickness values of the gel pieces used for sorption studies were taken as 250 μm (from micrometer measurements) for calculating the diffusion coefficients. Table 2 shows a large difference between the calculated diffusion coefficients of MeOH and MTBE. (Methanol diffusivity at 303K may be slightly higher than this reported value. There was some experimental error involved in that case. However, MeOH diffusivity at 323K is an accurate estimate.) The diffusivity ratio is about 500, whereas the measured separation factor was only about 250.

The very low permeation values measured for N$_2$ or O$_2$ probably represents such low diffusion coefficients of the corresponding molecules in silica pores. Hence the molecular sieving concept should be valid in these types of membranes in a practical sense. Apparently molecular-sieving does not mean a 100% size cutoff as in the case of micro-filtration; it only indicates a significant fall in diffusion coefficient as the size of the diffusing species approaches the size of the pore. Our experiments have revealed that He (2.6 Å), H$_2$ (2.89 Å), and CH$_3$OH (Lennard-Jones diameter: 3.6 Å) molecules are able to diffuse through the membrane pores with significant diffusivity values. Molecules such as N$_2$ (3.64 Å) and MTBE (minimum center to center distance between two boundary atoms is 4.4 Å, volume 119 Å^3), however, showed very low diffusivity values. Based on their diffusivity calculations of a number of molecules in ZSM-5 and zeolite 5A Xiao and Wei[12] stated that such drastic reduction in diffusivity represents a change from Knudsen diffusion to configurational diffusion. In zeolitic pores this changeover generally happens when the ratio of the diffusing molecule to that of the pore size approaches a value of about 0.75–0.95 depending on the zeolite material. Though the permeation properties of silica point to a similar conclusion to some extent, the activated diffusion visible for the small molecules (He and MeOH) in the case of silica membranes is different from the reported model calculations. Though an exact comparison of silica pores with that of zeolite is impossible due to the former material's hydrophilic nature and random pore structure, it can safely be assumed that the present results indicate an active pore size capable of sieving gas and vapor molecules based on differences in diffusivity.

Discussion

It is noteworthy that the ratio of diffusivity values of MeOH and MTBE is somewhat similar to the measured separation factor of the membrane (Table 2). This similarity and the similarity of adsorbed volumes (Figure 6) indicate a separation mechanism based on the diffusivity difference. It should be noted that the pore sizes of these membranes are extremely small and hence only single

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file diffusion is expected through the pores of the membrane. Under single file transport conditions one would expect a decrease in the diffusivity of the fastest moving molecule in the presence of slow moving molecules inside the same pore. In other words the ratio of diffusivity values between the diffusing species will tend to fall. Under mixture PV conditions the expected separation factor values may not be realized. High separation factors are possible only if the condensation or competitive sorption of one of the molecules excludes the other from the membrane pores. However, preliminary mixture adsorption studies did not reveal any such competitive adsorption effect that could grant a separation factor around 250. Sorption selectivity values of 6.6, 1.3, and 1.2 were measured at MeOH feed concentrations of 8, 53, and 87% by wt. in the mixture.

The major obstacle in concluding a separation mechanism based on single file diffusion (SFD) was the assumption of a nonintersecting pore geometry, with specific diffusion channels. However this may not be the case for silica membranes. The gelation of the polymers follows a percolation mechanism.[13] The membrane pore structure is, hence, interconnected. Van den Broeke and Krishna have detailed the effect of multicomponent transport in connected pores with the help of Maxwell–Stefan formulations.[14–16] According to their calculations, the diffusivity of the fast moving component does not suffer from retardation when the surface occupancies of both molecules are similar.

In the present experiments a sorption ratio of approximately 1 was observed under ideal conditions and a sorption ratio of 6.6 was observed for the 8 wt. % MeOH mixture sorption. The results indicate a molar composition of 35–65% MeOH in the pores of the membrane for 10 wt. % MeOH in the feed. Under such conditions the single file diffusion model predicts no drastic deviation of apparent diffusivity even at high occupancy of the pores by the sorbed molecules. Further, the significant drop in permeance value as evidenced from Figure 5 for compositions that contain small amounts of MTBE could be explained

by the SFD model. The said model predicts a drop in diffusivity of the fast diffusing molecule for low occupancy of the diffusing component.

The sorption experiments performed with MeOH and MTBE as shown in Figure 6 have revealed that the membrane material has a porosity and pore size distribution fully accessible to a variety of molecular sizes. Analysis of sorption kinetics, however, revealed extremely low diffusivity during the pore filling by the larger MTBE molecules. It can be therefore safely assumed that bigger gas molecules such as N_2 or isobutane also permeate through the membrane with low diffusivity. The extremely low diffusivity values involved, however, limit the permeance and hence high perm-selectivity for He or H_2 against these gases has been observed.[17] Hence for all practical separation purposes the size of these silica membrane pores can be considered to be between the molecular sizes of He (2.6 Å) and N_2 (3.64 Å) molecules.

The preceding discussion clearly shows that defect free sol–gel silica membranes with an active pore size of about 3 Å could be designed by proper sol–gel strategies.

Conclusion

Sol–gel silica membranes capable of separating MeOH/MTBE with separation factor values as high as 260 had been prepared. The membranes also showed a significant perm-selectivity value of 1230 for He/N_2 at 408 K.

The diffusion of vapor molecules in the silica pores was activated.

The diffusivity value of MeOH calculated from the sorption data on the silica membrane material is about 500 times greater than that of the MTBE molecule.

The separation of MeOH from MTBE is realized on account of the low diffusivity of MTBE in the ultramicropores of the silica membrane.

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