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Mesoporous KIT-6 silica–polydimethylsiloxane (PDMS) mixed matrix membranes for gas separation†

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In this study, we have explored for the first time the use of the mesoporous KIT-6 silica as an additive to enhance the gas permeability and separation characteristics of PVDF supported polydimethylsiloxane (PDMS) with filler loadings varying between 0 and 25 wt%. The KIT-6 silica was synthesized by a templating method and functionalized through silanization confirmed via Fourier transform infrared spectroscopy. The SEM images of the MMMs suggested that p-KIT-6 silica particles could embed well into the PDMS matrix and the MMMs could be defect free. With an optimum loading of 2 wt%, the C_4H_{10} permeability and C_4H_{10}/N_2 ideal selectivity of the MMM were shown to increase by 464% and 248% compared with the neat polymer membrane, respectively. In addition, the optimum membrane was also evaluated for CO_2/N_2 separation, which proved that the permeability and selectivity increased simultaneously. An interface morphology has also been proposed to explain the separation phenomenon of the MMM reasonably. Taken all together, it is expected that the mesoporous KIT-6 silica would be an attractive additive to enhance the gas separation performances of polymer membranes.

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1. Introduction

Polymer membranes have been used commercially in industrially important gas separation methods like volatile organic compound (VOC) recovery.¹ Their high efficiency, easy intensification, simple operation and low costs make them economical alternatives to conventional separation processes. In order to achieve high permeability and selectivity of the membranes, many efforts were made to modify the backbones and side chains of polymers experimentally.^{2–4} However, Robeson⁵ has discovered an “upper bound trade-off” line between permeability and selectivity, which conventional polymer membrane materials cannot overcome, which was also theoretically proved by Freeman.⁶ Thus, the use of bare polymers as membranes has technical limitations.⁷

To overcome Robeson’s upper-bound, various inorganic nanoporous materials were added into the polymer to produce mixed matrix membranes (MMMs). The novel membrane approach combines the advantages of two phases: the superior gas transport properties and thermal stability of inorganic nanofillers with desirable mechanical properties, good processability and low price of polymers.^{8,9} Over the decades, the incorporation of inorganic fillers such as zeolites,^{10–12} carbon molecular sieves^{13,14} and MOFs^{15,16} into a polymer matrix has

been intensively investigated. However, the application of microporous materials is limited by the relatively small pores especially after the modification of external surfaces with silane coupling agents, which can induce pore blockage.^{17,18} This can impair the transportation of gases in the membranes and thus decrease the permeabilities reported by many researchers.^{10,11} Weak interactions from inadequate wetting between a polymer matrix and zeolite may lead to the formation of nonselective voids, resulting in Knudsen flow.¹⁹

Since the discovery of the M41S family of mesoporous silicas by Kresge *et al.*,^{20,21} they have attracted widespread interest in catalyst,²² adsorption²³ and membrane²⁴ applications because of their ordered pore structure, high surface area and convenience of surface functionalization. Compared with microporous fillers, the application of mesoporous materials may improve the filler–polymer contact more easily and result in a selective film.²⁵ Mesoporous materials have relatively large pores (2–50 nm), so the polymer chains may consequently be able to penetrate into the mesopores,²⁵ leading to the formation of intimate composites. What is more, the large pores make it easier for gases to diffuse and then improve the gas permeability. Two typical kinds of mesoporous materials, MCM-41 and MCM-48, have been used to fabricate the mixed matrix membranes and proved to improve the permeability without sacrificing the selectivity.^{26,27} In contrast to MCM-41 and MCM-48, KIT-6, another kind of mesoporous silica, has a larger pore size (~6 nm) and a three-dimensional interconnected cubic pore structure which favor the gas diffusion. The two intertwined systems of mesoporous channels in KIT-6 can also be

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connected through irregular micropores in the walls, which have been proved to have high affinity for various VOCs.²³

In this study, the KIT-6 is evaluated as an additive to enhance the gas separation performance of the polydimethylsiloxane (PDMS) polymer. PDMS was selected, not only because it is historically and still largely used in composite membranes for gas separation, but also as a rubbery polymer, it has flexible polymer chains which may result in a good interaction between inorganic fillers and the polymer because of adequate wetting. KIT-6 mesoporous silica was synthesized by a templating method and characterized by X-ray diffraction (XRD), pore size analysis, and field emission scanning microscopy (FESEM). Different loadings of silica have been added into the polymer, and the structure and properties of KIT-6/PDMS MMMs were characterized by FESEM, sorption studies and gas permeation measurements. High performances of mixed matrix membranes comprising mesoporous KIT-6 silica and a rubbery polymer for gas separation are desirable.

2. Experimental section

2.1 Synthesis and silanization of KIT-6 particles

KIT-6 mesoporous silicas were synthesized using tetraethoxysilane (TEOS) as a silica source and Pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{-EO}_{20}$) as a structure-directing agent.²⁸ In a typical synthesis, 6 g of P123 was dissolved in 217 g of distilled water and 11.8 g of HCl (35%). To this, 6 g of butanol was added under stirring at 35 °C ($\text{TEOS} : \text{P123} : \text{HCl} : \text{H}_2\text{O} : \text{BuOH} = 1 : 0.017 : 1.83 : 195 : 1.31$ in mole ratio). The mixture was left under stirring for 24 h at 35 °C, followed by a hydrothermal treatment in an autoclave at 100 °C for 24 h. The solid product obtained was filtered with a little ethanol and dried at 100 °C. The template was removed by extraction in an ethanol–HCl mixture, followed by calcination at 550 °C for 3 h to absolutely remove the P123 template. The resulting white powder is 3D cubic KIT-6 mesoporous silica.

Before functionalization, KIT-6 mesoporous silica was degassed at 150 °C for 24 h under vacuum conditions. 1 g of dried silica sample was added to 50 mL of toluene and 5 mL of phenyltriethoxysilane (PTES) followed by refluxing at 110 °C for 24 h. The obtained functionalized silica was filtered, and thoroughly washed with ethanol and dried in a vacuum at 100 °C. The functionalized sample with PTES was designated as p-KIT-6.

2.2 Pure PDMS and PDMS MMM preparation

The membrane material Momentive RTV 615 A/B was provided by Wenhao Chip Technology and contains two components: component A contains a platinum catalyst while component B contains the cross-linker. Both components are liquids and handled with standard safety measures. To get the best results for the silicone rubber material, components A and B are mixed at 9 : 1 (w/w) ratio^{29,30} in heptane solvent to make a final PDMS concentration of 40 wt%. After one hour of stirring and 30 minutes of ultrasonic treatment, an appropriate amount of the polymer solution was cast onto the PVDF membrane to form the composite membrane. The PVDF membranes were immersed in deionized water for 3 days at room temperature and then

thermally treated at 120 °C for 12 min before use. The pore size distribution of the PVDF ultrafiltration membrane is shown in Fig. S1.† The prepared membranes were placed at room temperature for 48 h and then cured for 3 h at 100 °C.

Before MMM preparation, the p-KIT-6 powder was dried at 80 °C overnight. 2 wt%, 10 wt% and 25 wt% of p-KIT-6 (with respect to PDMS content) were added to heptane, respectively and then dispersed for 30 min through stirring. Then, the PDMS components were added to the dispersion to obtain a 40 wt% polymer solution. The mixture was further stirred for 1 h and sonicated for 30 minutes prior to membrane preparation. The PDMS MMMs were prepared similarly to that of the pure PDMS membrane. The membranes were about 25–100 µm thick.

2.3 Physico-chemical characterization

Fourier Transform Infrared (FT-IR) spectra of the KIT-6 particles before and after silanization were measured on a Bruker Tensor 27 spectrometer in the range of 600–4000 cm^{-1} .

Thermogravimetric analysis (TGA) of modified KIT-6 and mixed matrix membranes (0 wt%, 2 wt%, 10 wt% and 25 wt%) was performed on a TG/DTA analyzer (Setaram, Labsys). The heating rate was 10 °C min^{-1} from 30 to 900 °C under an air flow of 60 mL min^{-1} .

The glass transition temperature (T_g) of the membranes was measured on a SEIKO DSC 6220. Around 10 mg of each sample was placed in an aluminum pan and the measurements were carried out from –160 °C to –50 °C at a 10 °C min^{-1} ramping rate under a N_2 atmosphere.

The textural properties of KIT-6 and p-KIT-6 were measured with a Micromeritics ASAP 2020 gas sorption analyzer at liquid nitrogen temperature (77 K). The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The total pore volume was estimated from the amount adsorbed at a relative pressure of about 0.99. The mesopore pore size distribution (PSD) was calculated by analyzing the adsorption branch of the N_2 sorption isotherm using the Barrett–Joyner–Halenda (BJH) method.

The XRD patterns of KIT-6 and p-KIT-6 mesoporous silicas were recorded on a Siemens D5005 diffractometer with Cu K α radiation ($\lambda = 0.1541$ nm) at 40 kV and 40 mA.

Membrane and p-KIT-6 morphologies were inspected using Field Emission Scanning Electron Microscopy (FE-SEM, SU-8020, Japan) and High Resolution-TEM images were collected on a JEM 2010 at 200 kV.

The densities of the samples were determined using the True Density Analyzer (TD-2200, Builder, China) at 35 ± 0.1 °C. A weighed sample was placed in the sample cell and degassed by pumping at a steady speed. An average of 10 measurements per sample was used to calculate the average density.

Sorption studies were conducted by using an Intelligent Gravimetric Analyzer (model IGA-002, Hiden Isochema, UK) with a sensitivity of 0.1 µg. The apparatus has an ultrahigh vacuum system with a fully computerized microbalance allowing adsorption isotherms to be determined by the approach of monitoring equilibrium in real time using a computer

algorithm.³¹ For each measurement, the samples were degassed at 100 °C for 5 h at $P \leq 10^{-6}$ mbar.

2.4 Steady-state gas permeability and selectivity measurements

A custom-built membrane module was used to conduct all gas permeation experiments based on the constant pressure method (Fig. S3†). The permeation cell consisted of two compartments separated by a membrane. O-rings provided a pressure-tight seal between the mixed membrane and the cell. A porous support was placed to protect the membrane against high feed pressure and ensure the uniformity of air flow. The membrane had an effective area of approximately 0.0072 m².

The gas temperature was set at 35 °C using a temperature control system model, which was controlled to ± 0.2 °C with on-off controllers. The permeate flow rates were measured using a bubble flow meter (BFM). Under steady-state conditions, gas permeability can be estimated using the following equation:³²

$$P = \frac{NI}{(p_f - p_p)A} \quad (1)$$

where P is the permeability in Barrer (1 Barrer = 10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg), N the permeate flow in cm³ s⁻¹, l the membrane thickness in cm, A the membrane area in cm² and p_f and p_p are, respectively, the feed and permeate pressure in cmHg.

The ideal selectivity $\alpha_{A/B}$ is the ratio of the permeability coefficients of the pure components A and B, while D_A , S_A and D_B , S_B are the solubility and diffusivity coefficients of the individual components.

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \quad (2)$$

3. Results and discussion

3.1 Characterization of KIT-6 and p-KIT-6 particles

3.1.1 XRD. During the silanization process, organic functional groups could be covalently attached to the silanol groups (Si-OH) on the external and inner pore surface in the presence of a non-polar solvent. The XRD analysis was employed to determine the crystalline structure of KIT-6 and p-KIT-6 particles and the results are illustrated in Fig. 1. The XRD patterns represent three reflections, which can be assigned to the (211), (220) and (332) planes of a 3D cubic structure (*Ia3d*).³³ After modification of the surface, though the peak intensities of p-KIT-6 show slight changes compared with those of KIT-6, the peak positions of both samples remain virtually constant, which is evidence for the maintenance of the structural characteristics of the original silicas.

The particle size distribution of p-KIT-6 is shown in Fig. S2.† The results indicate particle sizes ranging from 1 to 50 μ m with an average size of 10 μ m.

3.1.2 N₂ adsorption-desorption. N₂ adsorption-desorption isotherms and the corresponding pore size distributions of

Fig. 1 XRD patterns of mesoporous KIT-6 and p-KIT-6 silica.

KIT-6 and p-KIT-6 are shown in Fig. 2. It is apparent that all of the isotherms are of type IV (IUPAC classification),³⁴ with a sharp capillary condensation step at high relative pressures and an H1 hysteresis loop, indicative of large channel-like pores in a narrow range of sizes.³⁵ Despite the decrease in the adsorbed amount of nitrogen, the shape of the hysteresis loop for p-KIT-6 remains the same as that of KIT-6, implying that the functionalization does not change the pore shapes of the silicas. The surface areas of both types were calculated by the BET method and the results showed that the surface area of p-KIT-6, 742 m² g⁻¹, is slightly smaller than that of non-modified KIT-6 (793 m² g⁻¹), which are listed in Table S1.† It can also be observed from Fig. 2 that both samples exhibit a major peak centered at around 6.5 nm, and the average pore diameter of KIT-6 is 4.9 nm and that of p-KIT-6 is 4.8 nm, which is calculated by the BJH method.

3.1.3 FT-IR. It is generally recognized that silanes can be used to modify the inorganic porous material surface to improve the compatibility with the polymer, which is quite

Fig. 2 Nitrogen adsorption-desorption isotherms and BJH pore size distributions of KIT-6 and p-KIT-6 silica.

important for mixed matrix membranes.^{10,19} The FT-IR spectra measurements prove the successful covalent grafting of the organic groups onto the silica wall. The FT-IR spectra patterns of KIT-6 and p-KIT-6 are shown in Fig. 3. In comparison to the original silica, some new peaks were detected in the functionalized material. The peaks at 3078 cm^{-1} and 3053 cm^{-1} are attributed to the C-H stretching vibrations of the phenyl groups,²⁸ and the peaks at 740 and 700 cm^{-1} are assigned to the distinctive signals of benzene. In addition, the peaks at 2980 cm^{-1} , 2938 cm^{-1} and 2908 cm^{-1} are identified as the C-H stretching vibrations of methyl and methylene groups,³⁶ and the peak at 1431 is assigned to the C-H deformation vibration of the remaining Si-O-CH-,³⁷ which has not reacted with the hydroxyl groups through condensation. It should be noticed that the intensities of the peaks at about 3748 cm^{-1} , which is ascribed to free Si-OH groups,³⁸ decrease significantly after functionalization. All these results indicate the occurrence of the condensation reaction between Si-OH groups and organosilanes during the functionalization process.

3.1.4 SEM and TEM. Fig. 4 shows the SEM and TEM images of p-KIT-6. The cubic mesostructure (*Ia3d*) is confirmed by the TEM image of Fig. 4b, recorded along $[100]$ and $[111]$, respectively.²³ The TEM results combined with nitrogen adsorption, XRD and FT-IR results confirm that the long-range ordered arrangement of the mesoporous channels is well retained after silane groups are covalently anchored onto the silica surface.

3.2 Membrane characterization

3.2.1 TGA. The TGA curves of the PDMS membrane and the MMMs are shown in Fig. 5. It can be observed that in the whole temperature range, the p-KIT-6 silica has a weight loss of only 0.87% , exhibiting a high thermal stability. As for the membranes, the weight loss starts at about $350\text{ }^{\circ}\text{C}$, which is consistent with the results from previous reports.²⁹ The thermal degradation was ascribed to the loss of methyl groups in the Si-O backbone.³⁹ The onset degradation temperatures of

Fig. 4 FE-SEM image and HR-TEM image of p-KIT-6 silica.

MMMs are all higher than that of the pure membrane (from Table S2†), and the accumulated weight loss of the membranes decreases with the increasing loading of the p-KIT-6, which is attributed to the high thermal stability of the filler. This result indicates that the addition of the p-KIT-6 has increased the thermal stability of the MMMs.

3.2.2 SEM analysis. To investigate the dispersion of the mesoporous p-KIT-6 silica within the polymer, cross-sectional micrographs of the 0, 2, 10, and 25 wt% MMMs (Fig. 4 in the ESI†) were examined by SEM. Fig. S4a† shows a smooth surface without any cracks or plastic deformation, which is characteristic of dense pure polymer membranes. For the 2 wt% MMM, the filler distribution is apparently homogeneous. However, for the 10 wt% and 25 wt% MMMs, the p-KIT-6 particles were agglomerated in the PDMS matrix and some of them did not embed in the polymer phase, resulting in some voids in the membrane. Also from the cross-sectional images, it can be observed that all of the PDMS polymer layers were deposited on the surface of the PVDF supports with no gaps between them. A higher magnification image of the 2 wt% MMM is shown in Fig. 6, where the particle seems to be completely enfolded by the matrix. No micron-sized non-selective voids are observed, which suggests that the contact between the polymer and p-KIT-6 particles is excellent. The good adhesion between the inorganic and organic phases may be probably due to the optimized

Fig. 3 FT-IR spectra patterns of the KIT-6 and p-KIT-6 silica.

Fig. 5 TGA of pure PDMS (0 wt%), pure p-KIT-6 (100 wt%) and MMMs at different p-KIT-6 loadings.

Fig. 6 (a) Surface FE-SEM image of 2 wt% p-KIT-6/PDMS MMM and (b) details of one of the particles in (a).

mixing protocol for membrane preparation. Also, as p-KIT-6 has mesoporous pores of 6.5 nm and the cross-sectional areas per chain⁴⁰ for synthetic polymers are around 1 nm² or less, the polymer chains around the particles may be able to penetrate into the pores, which could also lead to intimate contact.^{25,41,42} Homogeneous distribution of p-KIT-6 and the absence of non-selective voids are essential for high performance gas separation membranes.⁴¹

3.2.3 Gas separation measurements. Since the addition of microporous fillers such as zeolites usually decreases the gas permeability of MMMs,^{10–12} the mesoporous phase used here with around 6 nm pores may favor gas diffusivity. So with this premise, it is not surprising that both N₂ and C₄H₁₀ permeabilities continuously increase with the p-KIT-6 mass fraction in MMMs (Fig. 7 and 8). The errors of gas separation measurements are shown as Y error bars in Fig. 7 and 8. This increase in permeability has been attributed to the three-dimensional mesopores of the filled p-KIT-6 and the disruption of polymer chain packing and linking due to the presence of silica filler,⁴³ leading probably to an increase in polymer free volume. Because of different polymer processing and membrane materials, our N₂ permeability value for the pure PDMS membrane is higher than those previously reported by other research groups.⁴⁴ Unlike permeabilities, C₄H₁₀/N₂ selectivity has an optimum of 7.8 (that of the neat polymer being 2.24) at 2 wt% p-KIT-6 content as shown in Fig. 9. At higher p-KIT-6 loadings, bypassing channels might connect surrounding voids existing between silica particles, as the 25 wt% p-KIT-6/PDMS MMM SEM image in Fig. S4d† suggests. It can be seen that for 25 wt%

MMM, the selectivity is even lower than that of the pure membrane. The poor separation performance of the MMMs with high filler loadings might be attributed to the relatively big size of the silica particles. With an optimum loading of 2 wt%, the C₄H₁₀ permeability and C₄H₁₀/N₂ ideal selectivity of the MMM were shown to increase by 464% and 248% compared with the neat polymer membrane, respectively. Note that the improvement achieved in the present study is superior to others (increase in selectivity by 36.3%, and in permeability by 41.7%,⁴⁵ and 44% and 11%, respectively³⁹ for propylene/nitrogen separation).

It is also worth noting that in this study a lower percentage of filler is used than in other studies^{25,27,46} related to mesoporous molecular sieve fillers with loadings in the 10–40 wt% range. The low filler percentage implies lower cost of inorganic materials.

In order to further prove the good performance of the p-KIT-6/MMMs, the pure PDMS membrane and the optimum loading 2 wt% p-KIT-6/PDMS membrane were also tested for the CO₂/N₂ separation. As shown in Fig. 10, the CO₂ permeability for 2 wt% p-KIT-6/PDMS MMM increases by 119% compared to that of the pure PDMS membrane (from 5.5×10^3 to 12×10^3 Barrer), and the CO₂/N₂ selectivity increases by 35% (from 1.42 to 1.92). Similar to C₄H₁₀, CO₂ has a higher solubility coefficient in PDMS than that of N₂ ($4.0\text{--}6.0$ vs. 0.2×10^{-2} cm³ (STP) cm⁻³ cmHg⁻¹).² In consequence, the addition of an optimum loading of mesoporous p-KIT-6 silica gives rise to an obvious improvement in terms of both the condensable gas permeabilities and the selectivities over nitrogen.

3.2.4 Sorption measurements. The differences in permeabilities of the pure membrane and 2 wt% MMM can be better understood by analyzing the contributions of diffusivity and solubility coefficients to the overall permeability. In order to evaluate the solubility from permeation data, gravimetric sorption isotherms were measured. It should be noted that the isotherms for N₂ cannot be obtained because there is no interaction between the membranes and N₂. The adsorption isotherms of N₂ from IGA showed that the total weights decreased with pressure, which was due to the buoyancy effect. The diffusivity and solubility coefficients for the tested gases are listed in Table 1. It can be observed that after the incorporation

Fig. 7 Absolute (a) and normalized (b) C₄H₁₀ permeability (relative to pure PDMS) of MMMs with various loadings of p-KIT-6 at 0.5 bar at 35 °C.

Fig. 8 Absolute (a) and normalized (b) N_2 permeability (relative to pure PDMS) of MMMs with various loadings of p-KIT-6 at 0.5 bar at 35 °C.

Fig. 9 Ideal C_4H_{10}/N_2 selectivity of MMMs with various loadings of p-KIT-6 at 0.5 bar at 35 °C.

Fig. 10 CO_2 permeability and CO_2/N_2 selectivity for 0 and 2 wt.% p-KIT-6/PDMS MMM at 0.5 bar at 35 °C.

of p-KIT-6 silica into the polymer, the diffusivity coefficients increase dramatically, but the solubility coefficients decrease. This may be accounted for by the polymer blockage of the silica pores. Although polymer molecules cannot fully penetrate into

the mesoporous silica channels, it is possible for them to block the pore entrances. It should be noted that the increase of diffusivity for C_4H_{10} is higher than that of CO_2 whose solubility coefficient in PDMS is lower than that of the former. Therefore, the increase in permeabilities of C_4H_{10} and CO_2 in p-KIT-6/PDMS MMM can be attributed to the increase in diffusivity which is due to the abundant three-dimensional mesopores of the filled p-KIT-6 and the extent of the increase is related to the properties of the gases themselves.

3.2.5 Interface morphology hypothesis. The transport properties of organic/inorganic MMMs are strongly dependent on the nanoscale morphology of the membranes. The morphology of the interface is a critical determinant of the overall transport properties. According to the conclusions drawn above and the four possible basic morphologies raised by others,⁴⁷ an interface morphology between the silica and the polymer has been proposed to explain this phenomenon. As shown in Fig. 11, partial pores of modified KIT-6 have been blocked, and the deeper the color, the more rigid the polymer chains. This can be proved by the DSC data (T_g , -152 °C for pure PDMS and -147 °C for the 2 wt.% p-KIT-6/PDMS membrane), because it is widely accepted that MMMs with polymer chain rigidification have a higher T_g than the original polymer membranes.⁴⁷ Therefore, because C_4H_{10} has condensability, which means that more C_4H_{10} can be adsorbed into the polymer matrix causing increased chain mobility and plasticization,⁴¹ the gas molecules can dissolve the polymer chains, and enter into the pores of p-KIT-6, which is the same for CO_2 . Once gases enter the pores, the diffusion rates increase dramatically. But for nitrogen, it is noncondensable, it is very hard for it to pass through the rigidified polymer phase, and it prefers to diffuse around the particles, which leads to slow diffusion. The results of the O_2/N_2 separation experiment also can further prove the validity of the proposal. The ideal selectivity of O_2/N_2 is almost the same for the pure membrane and 2 wt.% MMM, because the solubility coefficients of O_2 and N_2 are nearly the same.² Visually, the condensable gas has the “key” to enter into the pores which can enhance its diffusivity greatly. This is why the incorporation of p-KIT-6 can increase the C_4H_{10} permeability and C_4H_{10}/N_2 selectivity simultaneously.

Table 1 Solubility (*S*) and Diffusivity (*D*) of C₄H₁₀ and CO₂ in pure PDMS and 2 wt% p-KIT-6/PDMS MMM

Membrane	C ₄ H ₁₀		CO ₂	
	<i>S</i> (10 ⁻³ cm ³ (STP)/cm ³ cmHg)	<i>D</i> (10 ⁻⁵ cm ² s ⁻¹)	<i>S</i> (10 ⁻³ cm ³ (STP)/cm ³ cmHg)	<i>D</i> (10 ⁻⁵ cm ² s ⁻¹)
PDMS	49.58	1.76	18.16	3.04
2 wt% p-KIT-6/PDMS	33.97	14.5	15.34	7.88

Fig. 11 Simple illustration of (a) C₄H₁₀ and (b) N₂ diffuse pathways through 2 wt% MMM.

4. Conclusion

Mixed matrix membranes were prepared using a three-dimensional mesoporous KIT-6 silica modified through silanization and PDMS as the polymer matrix. Among the MMMs with different loadings (0–25 wt%) of p-KIT-6, an optimum C₄H₁₀ permeability–C₄H₁₀/N₂ selectivity binomial was obtained at 2 wt%, which is lower than those reported in the literature. SEM images of the 2 wt% MMM suggest that p-KIT-6 silica particles adhered well to PDMS and were defect free. Furthermore, the improvement in terms of permselectivity and the permeability of the selective gas with the optimum loading was also reproduced with the CO₂/N₂ mixture. These dramatic increases in gas permeability resulted from the increases in diffusivity due to the abundant three-dimensional mesopores of p-KIT-6. The sorption data of the p-KIT-6, pure membrane and 2 wt% MMM indicated that the polymer chains may block the pore entrances. C₄H₁₀, the condensable gas, could dissolve the rigidified polymer chains at the pore entrance and enter the channels of the fillers, rendering it with a much faster diffusion rate than N₂, which could barely enter the pores. The fact that very low filler loading can enhance the gas permeability and selectivity simultaneously makes mesoporous KIT-6 silica an attractive additive in condensable/permanent gas pair separation of MMMs.

Abbreviations

<i>A</i>	Area (cm ²)
<i>D</i>	Diffusivity coefficient (cm ² s ⁻¹)
<i>L</i>	Membrane thickness (cm)
<i>N</i>	Permeate flow (cm ³ s ⁻¹)
<i>P</i>	Permeability (Barrer)
<i>p_f</i>	Feed pressure (cmHg)
<i>p_p</i>	Permeate pressure (cmHg)
<i>S</i>	Solubility coefficient (cm ³ (STP)/cm ³ cmHg)
<i>T</i>	Temperature (°C)
<i>W</i>	Weight fraction (%)
<i>α</i>	Ideal selectivity
<i>ρ</i>	Density (kg m ⁻³)
<i>φ</i>	Volume fraction (%)

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