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# Covalent Attachment of Monochlorosilanes to Mesoporous Silica Membranes using Supercritical Fluid Deposition

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**Abstract:** We have prepared and characterized organically-modified mesoporous silica membranes using supercritical $CO_2$ fluid deposition. Supercritical $CO_2$ fluid deposition has the potential to increase both diffusion and concentration of the reactants at the reaction site, a particular advantage when the reaction site is inside a small pore, where access can be limited. The unmodified mesoporous silica membranes were prepared by surfactant-templated synthesis on α-alumina disk-shaped supports. These mesoporous silica supports had a mean pore diameter of 5 nm. The alkyl modification of the silica membranes was achieved by the covalent attachment of octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in supercritical-$CO_2$. Successful attachment was confirmed through infrared spectroscopic identification of the removal of the band due to isolated silanols accompanied by the appearance of bands due to methyl and methylene groups. We also directly measured a ~90% reduction in permeance of light gases through the modified membrane. The synthesis process did not degrade the support membrane, was relatively efficient, and was free of organic solvents required for traditional synthesis. The dominant transport mode in the membranes was Knudsen flow.

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Ideal separation factors for methane and propane over nitrogen were not increased relative to the bare support, indicating that neither the surface flow was enhanced nor the size selectivity improved for the membrane system studied. Supercritical $CO_2$ fluid deposition was demonstrated as an effective technique for the reaction of the functionalized silanes on the surface of the silica membrane.

**Keywords:** inorganic, membrane, organic, supercritical

## INTRODUCTION

Porous silica membranes have been studied quite extensively as an inorganic membrane (1). More recent efforts have been focused on surfactant-templated mesoporous silica membranes (2), following the work demonstrated on bulk powders (3,4) and thin films on non-porous supports (5,6). These mesoporous silica membranes provide an ideal support for surface functionalization of an organic terminal group because of the well-known reaction chemistry with functionalized-silanes and the potential for pore size control using specific surfactant templates and various length organosilanes (7,8). The resulting post-modification membrane is a hybrid organic/inorganic membrane that may have potential in a wide variety of applications where the combination of thermal stability with facilitated transport is required.

In order to create a hybrid organic/inorganic membrane, a functional chloro- or amino-silane is typically reacted with the surface hydroxyls (7–18). Using a monochlorinated or monoalkoxyl silane, covalent attachment to the hydroxylated surface results in a single monolayer of silane. Using di-or tri-chlorinated or alkoxy silanes, multi-layer functional groups are typically deposited as a result of silane polymerization with the multiple hydrolysable sites. The surface reaction described above is usually facilitated in solution, using a solvent such as toluene, and done under reflux over several hours to ensure diffusion of the reactant to the reaction site. The reaction of chlorosilanes requires the presence of water or an amine to catalyze the surface attachment to silica. Water also leads to polymerization of the silane in the porous structure and is the main factor for lack of reproducibility in silanation reaction chemistry (7). If the silane is volatile, synthesis from the vapor phase is appropriate and can decrease the inherent mass transport resistance in the liquid-based synthesis. An alternative synthesis route for surface functionalization is supercritical fluid deposition where a supercritical fluid is used as a solvent for the silane reactant (19).

In supercritical fluid deposition, supercritical $CO_2$ (sc–$CO_2$) is typically used, providing several advantages over traditional liquid phase processing (20). These advantages include a higher diffusivity of the silane, approximately an order of magnitude higher in sc–$CO_2$ vs. organic solvents (21), and an environmentally benign solvent, avoiding large amounts of organic solvents like toluene. Sc–CO2 is also a drying agent for silica (22) and this leads to a reduction in surface water and minimizes the level of polymerization on the silica surface (23). Advantages over vapor phase processing include greatly increasing the bulk concentration of the silane at the reaction site through solubility and the application to non-volatile silanes. Several groups have reported increased reaction kinetics of silanes on silica surfaces when using sc–$CO_2$ as a processing solvent. Cao, et al. (24) reported increased reaction rates of monochloro-, dichloro-, trichloro-, and dimethylamino-silanes on single crystal silicon and porous silica supports. Efimenko, et al. (21) reported increased reaction rates for semifluorinated and hydrocarbon chlorosilane precursors on single crystal silicon surfaces. Zemanian, et al. (25) reported increased deposition rates and increased surface coverage for silanes on mesoporous silica powder. Supercritical fluid processing is considered an alternative synthesis method that has application for modifying porous membranes.

In this paper, we present results for the supercritical fluid modification of mesoporous silica membranes with methyl and octadecyl terminal groups. We demonstrate the effectiveness of this synthesis method through reacting octadecyldimethylchlorosilane (ODMCS) using triethylamine (TEA) as a catalyst in sc–$CO_2$. Single gas permeation measurements were used to quantify permeance, provide ideal separation factors, and estimate pore size reduction after modification. The permeance of light gases was described with Knudsen and viscous flow. Diffuse reflectance infrared spectroscopy (DRIFT) was used to qualitatively monitor and correlate the extent of reaction with the physical properties of the membrane.

## EXPERIMENTAL

### Membrane Synthesis

Silica membranes were synthesized using a tetraethylorthosilicate (TEOS) silica sol templated with Pluronic P123 ($EO_{20}PO_{70}EO_{20}$,MW = 5800, BASF), a non-ionic block copolymer (26). The template/silica volume fraction ($V_{TS} = V_{template}/(V_{template} + V_{SiO2})$ was 33%. For a typical synthesis of a thin mesoporous silica film a mixture of 5.4 mL $H_2O$, 5.4 mL diluted HCl (pH = 2.0), 15.2 mL EtOH, 11.1 mL TEOS was stirred vigorously for 20 minutes. Then a mixture of P123 and EtOH was added to the solution and mixed until the P123 was dissolved, solutions were allowed to age at room temperature for 10 minutes in a sealed container to prevent evaporation of EtOH. An alumina support disk (HiTK, Germany) was dipped into the solution, using a dipping machine, at a rate of approximately 2 cm/s. After dip-coating the macroporous support, the surfactant was then removed by sintering at a temperature of 400°C. Repeated dip/fire cycles were used to ensure complete coverage of the support and minimize defects. The membranes were determined to have a mean pore size of ~5 nm by adsorption branch porosimetry (26). The membranes prepared on porous supports did not have long-range pore ordering determined by a lack of diffraction peaks in the X-ray pattern.

## Supercritical Fluid Modification

The supercritical $CO_2$ fluid deposition (SCFD) reactor system (Fig. 1) used for the silane modification experiments is described in detail elsewhere (19). The system is based on an atomic layer deposition system described elsewhere (8). The system consists of a modified HPLC pump capable of pressurizing liquid $CO_2$, delivered from a siphon tank, into the supercritical phase. Supercritical $CO_2$ was delivered to one of two 100 cc heated delivery vessels where a reactant was dissolved. The reactants were then delivered to a 100 cc heated reactor vessel containing the mesoporous silica membrane to be modified. The pressure in the system was maintained by the pump and a back pressure regulator capable of purging the vessels with a sc–$CO_2$ flow rate as low as 0.5 mL $\mathrm{min}^{-1}$.

Modification of the mesoporous silica membrane used sc–$CO_2$ as the solvent for a two step, amine-catalyzed silane attachment to surface hydroxyls (27). Triethylamine (TEA) was used as the catalyst. With the surface hydroxyls exposed to a nucleophilic attack, octadecyldimethylchlorosilane (ODMCS) was introduced to the reaction vessel resulting in a surface functionalized with an organosilane. The mesoporous silica membrane was pressurized to 200 atm at 50°C in the reaction chamber. The silica membrane support was then flushed with $CO_2$ under these conditions for two hours. A 10 cc vessel containing 200 μL of triethylamine (TEA) was exposed to $CO_2$ at 250 atm dissolving the TEA. At a rate of 3.5 ml $\mathrm{min}^{-1}$, $CO_2$ was then flowed through the reactor to remove adsorbed water from the silica (22). The TEA was then delivered to the reaction vessel by the 50 atm pressure gradient for 10 minutes. After the TEA exposure, the reaction vessel was closed off from the TEA delivery vessel.

Octadecyldimethylchlorosilane (ODCMS) was then delivered to the mesoporous silica membrane in the same fashion and exposed for 5 minutes. This was repeated for one additional cycle.

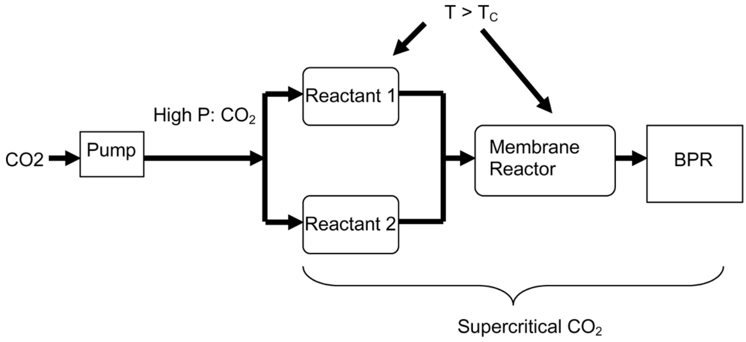


***Figure 1.*** Supercritical fluid deposition reactor.

## Gas Permeation Experiments

Single gas measurements were carried out using He, $N_2$, $CH_4$, Ar, and $CH_3CH_2CH_3$. The membrane was sealed using viton o-rings in a stainless steel device. The membrane was purged overnight at 100°C under flowing, dry He. A pressure drop was maintained across the membrane using mass flow controllers (MKS Instruments) and a differential Baratron gauge (MKS Instruments). The flow through the membrane was measured using a soap film flow meter.

## Surface Chemistry Characterization

All IR spectra were recorded on ABB FTLA 2000 spectrometers. The membranes were analyzed with DRIFT using a Praying Mantis diffuse reflectance apparatus from Harrick Scientific. KBr powder was used to record the reference for the DRIFT spectra. All spectra were recorded at $4\,\text{cm}^{-1}$ resolution using 100 scans requiring approximately 2 minutes collection time.

## RESULTS AND DISCUSSION

Supercritical fluid deposition was successful in attaching octadecyl groups onto a mesoporous silica membrane surface. While kinetic studies were not performed to quantify the surface reaction rates, the time of overall reaction was relatively short, ~15 minutes, and could be considerably shorter if the synthesis were optimized. This is consistent with similar reactions on porous silica supports or single crystal silicon surfaces reported in the literature (20,21),(25).

Infrared spectroscopy (DRIFT) was used to confirm the presence of methyl and methylene groups attached to the silica membrane surface with ODCMS in supercritical $CO_2$ as shown in Fig. 2. Figure 2a shows the infrared spectrum of a mesoporous silica membrane prior to supercritical fluid deposition of ODCMS. The large broad band centered $\sim$3300 $cm^{-1}$ is the OH stretching mode of hydrogen bonded silanols and adsorbed water. The presence of adsorbed water is confirmed by the appearance of water bending mode at 1632 $cm^{-1}$. The isolated hydroxyl band, the reaction sites for covalent silane attachment, is shown at 3747 $cm^{-1}$. The smaller bands at 1973 and 1862 $cm^{-1}$ are combination and overtone modes attributed to bulk silica. Figure 2b shows the infrared spectra of the ODMCS modified silica membrane. The presence of ODMCS on the surface is confirmed by three bands: 2955 $cm^{-1}$ due to methyl groups, and 2925 $cm^{-1}$ and 2854 $cm^{-1}$ due to methylene groups. Figure 2c is a difference spectrum derived from 2b and 2a showing negative (downward) bands where the surface bonds were removed. The surface hydroxyls were removed during covalent attachment of ODMCS as well as surface water due to the hydrophobic nature of the silane modified surface. The spectral evidence from Figs. 2b and 2c

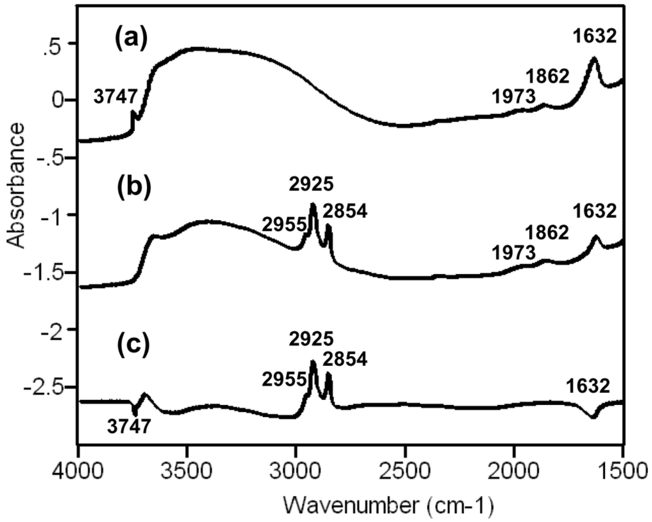


*Figure 2.* DRIFT spectra of (a) an unmodified mesoporous silica membrane, (b) a ODCMS-modified mesoporous silica membrane and (c) the difference spectrum of the unmodified and modified membrane.

confirms the covalent attachment of ODMCS to the mesoporous silica membrane. In this case, the reaction was complete as evidenced by the complete removal of the band at 3747 cm$^{-1}$. Infrared spectroscopy was also used to qualitatively correlate the membrane surface structure to membrane properties described later in this section.

The permeance for several light gases is shown as a function of pressure drop at 150°C for a ODMCS-modified mesoporous silica membrane in Fig. 3. External error analysis performed on the permeance measurements showed a 1–2% relative error in the permeance values. The overall magnitude of the permeance for these gases is consistent with values observed for mesoporous silica membranes reported in the literature (28).

A simple analysis of the permeance data (for the modified membrane) suggests that transport occurs by a combination of Knudsen diffusion and viscous flow. Although mesoporous membranes are ideally governed by Knudsen transport, the presence of a small amount of defects can give rise to a viscous flow contribution. The contribution from surface diffusion appears to be negligible. The Knudsen diffusivity ($D_k$) is given by (29):

$$D_k = 97r\sqrt{\frac{T}{M}}\,(\mathrm{m}^2 \cdot \mathrm{s}^{-1}) \tag{1}$$

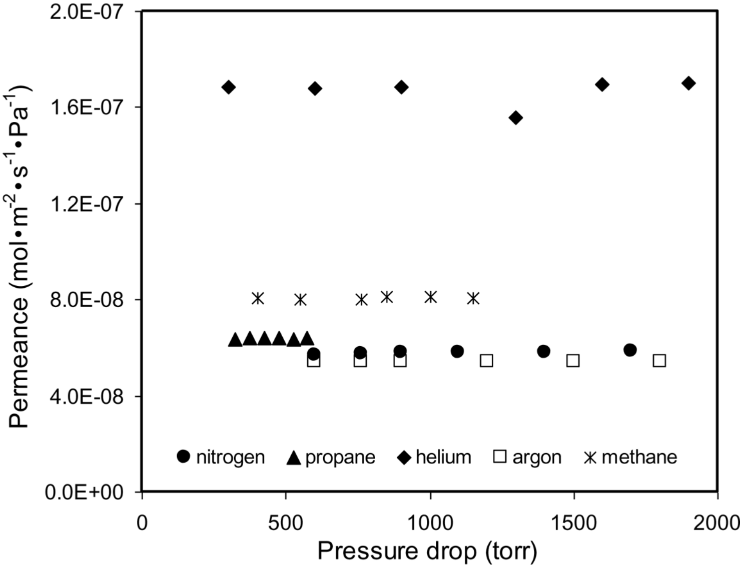


*Figure 3.* Permeance vs. pressure drop for light gases through a ODCMS-modified silica membrane.

Where r is the mean pore diameter (m), $T$ is the absolute temperature, and $M$ is the molecular weight. The corresponding Knudsen contribution to the permeance ($F_k$) is given by:

$$F_k = D_k\left(\frac{\varepsilon}{z\tau}\right)\left(\frac{1}{RT}\right) = 97\left(\frac{r\varepsilon}{z\tau}\right)\frac{1}{R\sqrt{TM}}(\mathrm{mol}\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}\cdot\mathrm{Pa}^{-1}) \tag{2}$$

where z is the membrane thickness, $\varepsilon$ is the porosity, $\tau$ is the tortuosity, and R is the gas constant ($\mathrm{J}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$ or $\mathrm{m}^3\cdot\mathrm{Pa}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1}$). The contribution to the permeance from viscous flow (Poiseuille flow) is given by: (29)

$$F_v = \frac{\varepsilon}{\tau}\frac{\overline{P}r^2}{8\mu z}\frac{1}{RT}(\mathrm{mol}\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}\cdot\mathrm{Pa}^{-1}) \tag{3}$$

where $\overline{P}$ is the average pressure and μ is the viscosity which, according to kinetic theory, is given approximately by:

$$\mu = 2.67\times 10^{-6}\frac{\sqrt{TM}}{\sigma^2}(\mathrm{Pa}\cdot\mathrm{s}) \tag{4}$$

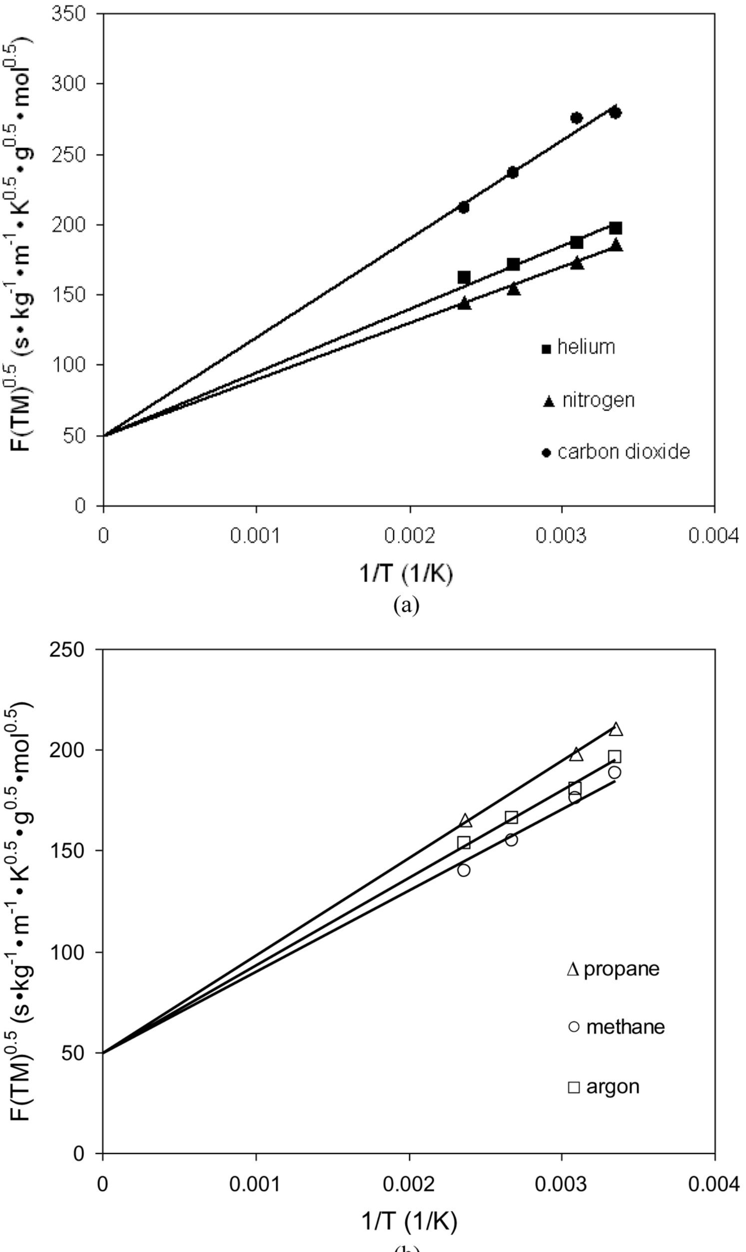
where $\sigma$ (Å) is the hard sphere molecular diameter. Assuming that the contribution from Knudsen diffusion and viscous flow are additive and that the same tortuosity factor applies to both mechanisms it follows that the total permeance is given by:

$$F = F_k + F_v = \frac{97}{R}\left(\frac{r\varepsilon}{z\tau}\right)\left(\frac{1}{\sqrt{TM}}\right) + \frac{4.68\times 10^4}{z\tau}\left(\frac{\overline{P}r^2\sigma^2\varepsilon}{R}\right)\left(\frac{1}{\sqrt{TM}}\right)\left(\frac{1}{T}\right) \tag{5}$$

This equation has the form:

$$F\sqrt{TM} = A + \frac{B}{T} \tag{6}$$

where $A = \frac{97r\varepsilon}{Rz\tau}$ and $B = \frac{4.68\times 10^4\overline{P}r^2\sigma^2\varepsilon}{z\tau R}$. The constant $A$ is the same for all species while $B$ increases with the size of the diffusing molecule. The permeance data for the modified membrane are shown, plotted in the form suggested by Eq. (6), in Fig. 4. For clarity, the plot of the six gas species, helium, nitrogen, argon, methane, propane, and carbon dioxide, is broken up into two figures, Figs. 4a and 4b. In conformity with this simple model the individual plots of $F\sqrt{TM}$ vs. $1/T$ were all approximately linear with similar intercepts and different slopes. In the combined plot,



(a)

(b)

***Figure 4a and 4b.*** $F\sqrt{TM}$ vs. $1/T$ fitted to a common intercept for light gases for ODCMS-modified membranes showing the contribution of Knudsen and viscous flow to the permeance.

shown in Fig. 4, the lines for the individual gases have been constrained to pass through the mean intercept (49.5) corresponding to the parameter A which depends only on the porosity, tortuosity, and the pore size of the membrane. It is clear that the model provides a reasonably good approximation of the experimental data although the data show some deviation at higher temperatures. In the present study it was found that the behavior of the potentially absorbable species such as $CO_2$ and $C_3H_8$ was essentially similar to the behavior of He, which is not significantly adsorbed and which therefore cannot have a surface flow contribution. Since the model for combined Knudsen plus viscous flow correlates the data for all species, including He very well, it seems reasonable to conclude that the surface flow is not significant for these systems. A more detailed analysis of these data will be presented in a forthcoming publication.

Table 1 shows a comparison of the experimental permeance ratios ($F_i/F_j$) with the ideal (Knudsen) separation factors (defined by $\alpha_{ij} = \sqrt{M_j/M_i}$) for $He/N_2$, $CH_4/N_2$ and $N_2/CH_3CH_2CH_3$ in the unmodified and ODMCS-modified membranes. The contribution from the viscous flow becomes relatively less important at higher temperatures so, at 150°C we see approximate conformity with the ideal Knudsen separation factors, especially for $He/N_2$ and $CH_4/N_2$. The separation factors for $N_2/CH_3CH_2CH_3$ are fairly similar in the modified and unmodified membranes suggesting that there is no significant contribution from surface diffusion, even in the alkyl-modified membranes.

In our work, we observed no appreciable difference in ideal nitrogen/propane separation factors for unmodified and ODCMS-modified mesoporous silica membranes. Similar results were observed from Ford (13) and Way (10). Ford's group attempted to attach the monochlorsilane ODCMS onto γ-alumina mesoporous membranes. Monochlorosilane attachment was not detectable by XPS resulting in similar separation properties to the bare mesoporous support. Way's group also compared trichloro and monochlorsilane reactions; however, they used a Vycor silica support with a mean pore diameter of 4 nm. Monochlorosilane

**Table 1.** Ideal separation factors for unmodified and modified silica membranes at 150°C

| | $He/N_2$ | $CH_4/N_2$ | $N_2/CH_3CH_2CH_3$ |
|---|---|---|---|
| Knudsen (ideal) | 2.65 | 1.32 | 1.25 |
| Pre-modified silica | 2.2 | 1.51 | 0.75 |
| ODCMS-modified | 2.87 | 1.39 | 0.9 |

attachment was successful using ODCMS. No discernable difference was measured between ideal separation factors for both the modified and unmodified membranes for n-butane and nitrogen. Permselectivity measurements revealed no change from the bare mesoporous support.

Figure 5 shows the permeance values for light gases taken at 150°C for both the unmodified and modified membrane plotted against the kinetic diameter showing the reduction in permeance values for these gases after modification. For this membrane, the reduction in permeance was approximately an order of magnitude. Individual membranes were synthesized in triplicate. Since there is some absolute permeance variability in the supports used for modification, the absolute permeance values were not used as a measure of repeatability. Rather, the reduction in permeance values for light gases after $C_{18}$ functionalization was used to assess repeatability. We did observe some variability in the percent reduction in permeance for the ODMCS membranes. Data for the $N_2$ permeance change for three ODMCS-modified membranes are shown in Table 2 along with the corresponding ratio of the integrated methyl and methylene bands at 2955 $cm^{-1}$, 2925 $cm^{-1}$ and 2854 $cm^{-1}$ to the bulk silica band at 1632 $cm^{-1}$. For two ODMCS-modified membranes we observed 93 and 91 percent reduction in nitrogen permeance attributed to the presence of ODMCS in the pores of the membrane. These samples had similar ratios of methyl and methylene bands to bulk silica bands indicating a similar surface concentration of $C_{18}$ groups on the surface.

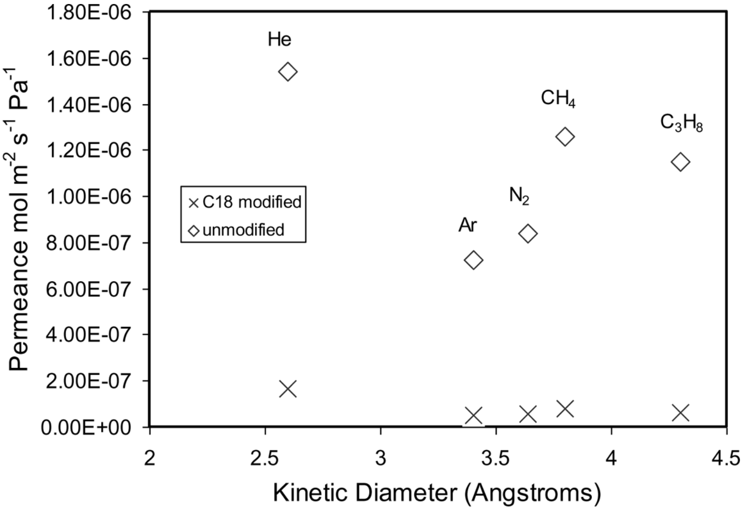


***Figure 5.*** Permeance of several light gases taken at 150°C for both unmodified and ODCMS-modified mesoporous silica membranes.

The sample with less nitrogen permeance reduction (79%) had a correspondingly lower concentration of $C_{18}$ on the surface as shown in the IR ratio in Table 2. Here, Infrared spectroscopy provided a useful tool to correlate surface coverage to membrane properties.

The Knudsen contribution to the permeance is directly proportional to the mean pore radius while the viscous contribution depends on the square of the radius. The substantial difference in the permeance between the modified and unmodified membranes therefore provides direct evidence of a pore size reduction. At the higher temperatures the contribution of viscous flow becomes less significant so one may consider the ratio of the slopes of permeance, $F$, vs. $\sqrt{1/TM}$ for the modified and unmodified membranes (see Fig. 6) as an approximate measure of the pore size reduction. Using $N_2$ permeance data, the pore diameter of the modified membrane is estimated to be ~1 nm (unmodified membrane pore diameter of 5 nm measured using adsorption branch porosimetry (26)).

Pore size reduction has also been estimated using geometrical calculations assuming uniform cylindrical pores and maximizing surface coverage of the silane (30). From these calculations it was determined that a critical pore diameter exists where steric hindrance begins to occur reducing the ability of the silane to saturate the surface hydroxyl groups. Assuming a saturated surface density of functional groups as 2.3 groups per $nm^2$ (30), the critical pore diameter within which a $C_{18}$ functional group (ODMCS length ~2.45 nm) can saturate the silica surface is 10.8 nm. Since our diameter is well below that value, steric hindrance is clearly a factor affecting surface coverage. In order to maximize surface attachment density, and one that correlates more closely with our observed IR data (lack of reactive OH groups after attachment), the alkyl chains must conform in a liquid-like manner as opposed to a brush-like configuration. Again, using simple geometric arguments, Fadeev and

**Table 2.** Correlation of IR data to $N_2$ permeance reduction for ODMCS-modified membranes

| Membrane | $N_2$ permeance of support ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$) | $N_2$ permeance of ODMCS-modified membrance ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$) | $N_2$ permeance reduction (%) | Ratio of integrated CH-stretching modes to bulk Si–O modes |
|---|---|---|---|---|
| 17 | $8.4 \cdot 10^{-7}$ | $5.7 \cdot 10^{-8}$ | 93 | 14.5 |
| 29 | $6.26 \cdot 10^{-7}$ | $1.33 \cdot 10^{-7}$ | 79 | 11.9 |
| 30 | $7.9 \cdot 10^{-7}$ | $7.2 \cdot 10^{-8}$ | 91 | 14.0 |

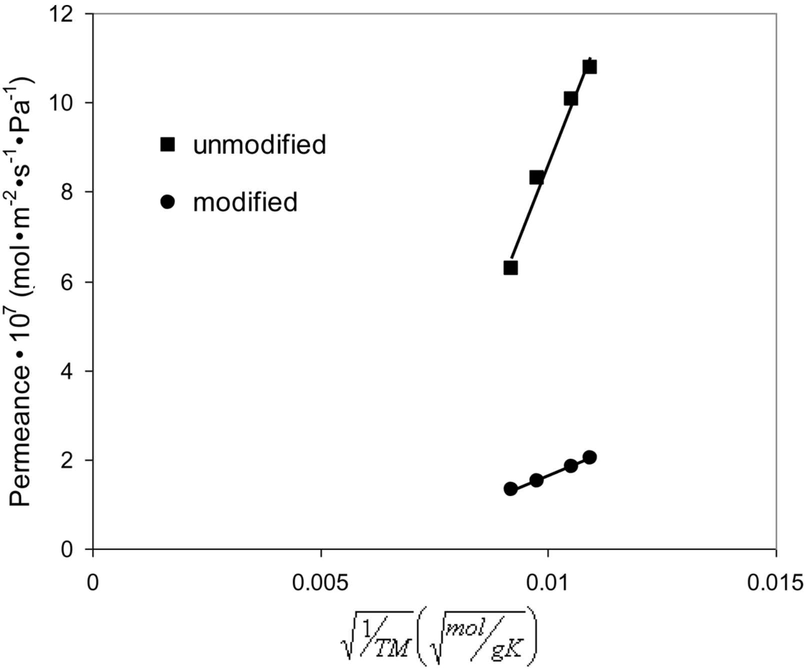


*Figure 6.* Permeance of $N_2$ for both unmodified and ODCMS-modified mesoporous silica membranes fitted to the inverse square root of the product of temperature and molecular weight used to estimate pore size reduction after surface treatment.

Staroverov (30) predicted that to maximize surface coverage, the resulting layer thickness for $C_{18}$ would correspond to ~1 nm. Using this thickness, the resulting pore diameter reduction would be from 5 to ~3 nm. Our estimation from the permeance reduction is below the final pore size estimated using geometry and steric hindrance calculations. Both methods for estimating pore size reduction are based on ideal conditions. From our data it is clear that there is a viscous flow contribution to the permeance values. The unmodified membranes were determined to have a permeance of 8–10% through pores of diameters between 15 and 40 nm corroborating the results of our permeance model.

## CONCLUSION

In conclusion, we have demonstrated that the supercritical fluid deposition of methyl and octadecyl monochlorosilanes within the pores of a mesoporous silica membrane using supercritical $CO_2$ is an effective and efficient method of preparation. The silane precursors we used resulted in covalent attachment to surface hydroxyl groups within the mesoporous membrane, in contrast to a polymerized silane layer normally found when using trichlorosilanes. The presence of methyl and methylene IR bands along with a reduction in permeance of light gases confirmed successful silane attachment and pore reduction. The permeance of light gases could be described by a combination of Knudsen diffusion and viscous flow. No appreciable change in ideal separation of hydrocarbons over nitrogen was measured as a result of surface functionalization.

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