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Hydrophobic modification of γ-alumina membranes with organochlorosilanes

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Abstract

Mesoporous γ-alumina membranes were chemically modified with several organochlorosilanes. XPS with depth profiling and permporometry experiments were used to study the local organosilane concentrations and their effect on the pore structure. It was found that the penetration of long chain chlorosilanes into the mesopores was sterically hindered and that grafting was not as effective as for short chain organosilanes. Membranes modified with monofunctional organosilanes showed a smaller Kelvin radius than unmodified γ-alumina membranes as observed by permporometry, indicating that methyl groups resided inside the pores. For membranes modified with di- and trifunctional organosilanes larger Kelvin radii were observed, indicating that polymerized silane networks block the smaller pores, thereby decreasing the overall permeability of the membrane. The permeability of hydrophilic and hydrophobic solvents was affected by the hydrophobic modification of the surface and the internal pore walls depending on the nature of the chlorosilane used for grafting.

Keywords: Membrane; Organosilanes; Hydrophobicity; Alumina; Permeability

1. Introduction

Conventional ceramic microporous and mesoporous membranes are hydrophilic by nature. The hydroxyl groups present in the structure and on the pore surface are the main source of hydrophilicity as they promote the adsorption of water. This may lead to pore blocking at ambient conditions and will in any case have a major effect on the separation properties of the membranes and the operating conditions under which they can be applied. The replacement of hydroxyl groups by hydrolytically stable groups with a hydrophobic character such as $Si{-}CH_3$ groups inhibits the adsorption of water. Two general strategies can be pursued to bring about a hydrophobic modification of hydrophilic ceramic membranes. The first strategy is to make a hydrophobic layer by in situ hydrolysis and condensation of alkoxide precursors with hydrophobic side groups, such as organosilanes or bridged silsesquioxanes [1]. De Vos and Verweij [2] prepared hydrophobic silica layers using a combination of tetraethoxysilane and methyltriethoxysilane as the hydrophobation agent, which resulted in a microporous silica membrane with methyl groups incorporated in the silica structure. As a result the surface and microstructural properties of the microporous silica membranes changed significantly. Water adsorption was much less compared to standard silica membranes. The methylated silica membranes showed very high fluxes for gasses of small molecular size (H_2, He, CO_2, O_2, N_2, and CH_4) and a good permselectivity (20–50) for these gasses with respect to SF_6 and larger alkanes like C_3H_8 and n-C_4H_{10}.

The second strategy, which is also employed in the present paper, is to post-modify a mesoporous inorganic membrane by grafting the internal pore surface with organosilanes. This

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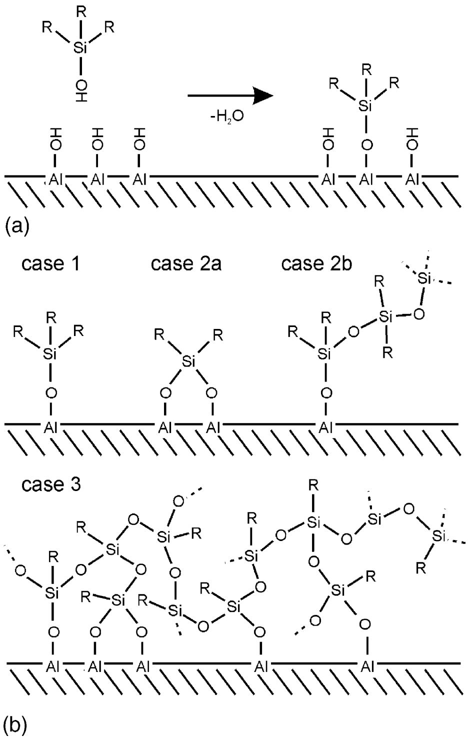

Fig. 1. (a) Schematic diagram showing monolayer deposition of a monofunctional hydrophobing agent. (b) Surface structures of organosilanes grafted on hydroxyl-terminated surfaces. Case 1: monofunctional precursor anchoring to a hydroxyl site. Case 2a: difunctional precursor anchoring to two hydroxyl sites. Case 2b: difunctional precursor forming a polymerized chain. Case 3: trifunctional precursor forming a polymerized layer on a hydroxyl-terminated surface.

process is illustrated in Fig. 1. A hydrolysable group of the organosilane undergoes coupling with the hydroxyl groups of the mesoporous layer, forming a chemically bound monolayer initially, which imparts the desired hydrophobicity. Organosilanes with two or more hydrolysable groups can undergo further coupling with other organosilanes, forming a polymeric layer. Picard et al. [3] reported the hydrophobic features of a mesoporous zirconia membrane grafted with fluorinated silanes. The membrane was impregnated by solutions of $C_6F_{13}C_2H_4Si(OMe)_3$ and $C_8F_{17}C_2H_4Si(OEt)_3$. Liquid permeation studies on the zirconia membranes showed a decrease in liquid permeability for the grafted membranes as compared to the ungrafted one. It was concluded that the grafting time is important to increase the hydrophobicity of the samples, while the differences in length of the hydrophobic tails had no influence.

Work on grafting γ-alumina membranes with Me_3SiCl, $MeSi(OMe)_3$, and $Me_2Si(OEt)_2$ organosilanes was reported by Alami Younssi et al. [4]. The surface properties of γ-alumina membranes were modified in order to change the selectivity of the membranes towards chemical solutes of different polarities. Infra-red (IR) characterization of the membranes showed that the grafting depended on the nature of the silanes used and was achieved most effectively with multifunctional silanes. The N_2 adsorption and desorption isotherms showed a decrease in specific area and microporous volume for the membrane grafted with $Me_2Si(OEt)_2$ or $MeSi(OEt)_3$, indicating that the pore wall had been covered by grafted moieties. Modification of the surface properties of the membrane was confirmed by pervaporation tests on different binary mixtures of solvents. Both solvent fluxes and membrane selectivity depended on grafting conditions. Dafinov et al. [5] modified γ-alumina membranes by alcohol chemisorption. The layer of chemisorbed alcohols was found to be stable up to 200 °C, and imparted hydrophobic characteristics to the membrane, as was seen by a decrease in water permeability. Castro et al. [6] studied the permeability of polyvinylpyrrolidone-modified porous silica membranes. Hydraulic permeability measurements showed that the permeability was determined by the configuration of terminally anchored polymer chains. Due to the affinity of the polymer for water, the hydrophilic PVP brush layer expanded, preferentially allowing the passage of water over oil. Caro et al. [7] reported silylating the γ-alumina surface with octadecyltrichlorosilane. Van Gestel et al. [8] reported the effect of surface modification of γ-Al_2O_3/TiO_2 multilayer membranes for applications involving non-polar organic solvents. The effect of silane treatment ($(CH_3)_2SiCl_2$, $C_8H_{17}CH_3SiCl_2$) on the properties was found to depend on the pore size of the membrane (microporous, microporous–mesoporous, mesoporous) and on the silane reagent used. For microporous membranes it was shown that silane coupling reactions took place in pores situated at the outer membrane surface, while reactions at the internal membrane surface in the microporous structure were sterically hindered. Liquid permeability tests with hexane and water on mesoporous membranes indicated that silanes could be successfully introduced in the pore structure of the membrane. The degree of hydrophilic/hydrophobic modification, characterized by the permeability ratio of water/hexane was found to improve with increasing calcination temperature and increasing alkyl chain length, due to the formation of larger mesopores in the membrane structure and a more hydrophobic environment in the modified pores, respectively.

In the present paper a series of monofunctional, difunctional, and trifunctional organochlorosilanes with organic groups of different sizes are used to study the influence of the nature and size of the modifying agent on the extent of grafting. The effect on surface and pore modification is studied in detail by diffuse reflectance IR measurement, X-ray photoelectron spectroscopy (XPS) with depth profiling, and permporometry measurements. Solvent permeation experiments are used to study the selectivity of the grafted membranes towards liquids differing in polarity.

The work gives an insight into the phenomenon of grafting occurring in the membrane surface and inside the pores, as seen by the characterization techniques. The effect of the number of functional groups of the precursor in forming a polymerized layer, and the consequent chemical modification of the membrane is discussed.

2. Experimental

2.1. Membrane preparation

The γ-alumina membrane consists of a macroporous α-alumina support and a thin mesoporous γ-alumina layer. The α-alumina supports were made by colloidal filtration of well-dispersed 0.4 μm α-alumina particles (AKP-30, Sumitomo). The dispersion was stabilized by peptizing with nitric acid. After drying at room temperature, the filter compact was sintered at 1100 °C. Flat discs of 39 mm diameter and 2.0 mm thickness with a specific surface area of ∼15 m^2/g were obtained after machining and polishing. The porosity of these supports is ∼35%, and the pore diameter is 80–120 nm. Mesoporous γ-alumina membranes of ∼0.5 μm thickness were prepared by dip coating the above mentioned porous α-alumina supports in a boehmite sol, followed by drying and calcination at 600 °C for 3 h. After calcination, the γ-alumina layers have a specific surface area of ∼250 m^2/g. For further details, the reader is referred to reference [9].

Triphenylchlorosilane ($Si(C_6H_5)_3Cl$, 96% purity), *t*-butyldimethylchlorosilane (t-$C_4H_9(CH_3)_2SiCl$, 97% purity), trimethylchlorosilane ($(CH_3)_3SiCl$, 99% purity), dimethyldichlorosilane ($(CH_3)_2SiCl_2$, 99% purity) and trichloromethylsilane ($(CH_3)SiCl_3$, 97% purity) were obtained from Aldrich. The stacked γ/α-alumina membranes were hydrophobically modified by immersing them for periods of 2–12 h in 2–5 wt.% solutions of the above-mentioned precursors. Triphenylchlorosilane and *t*-butyldimethylchlorosilane systems were refluxed at 50 °C for 5 h, as it enhances the dissolution of the precursors. It was found that the long chain chlorosilanes (*t*-butyldimethylchlorosilane, triphenylchlorosilane) as well as the multifunctional chlorosilanes are more soluble in toluene than in water or alcohols. The solvent used to dissolve a particular organosilane was selected on the basis of organosilane solubility and γ-alumina grafting efficiency. The organosilanes *t*-butyldimethylchlorosilane, triphenylchlorosilane, dichlorodimethylsilane, and trichloromethylsilane were therefore dissolved in water-saturated toluene, while trimethylchlorosilane was dissolved in ethanol with 5-wt.% water. After removal from the solution the membranes were rinsed five times with ethanol to remove any unreacted chemicals. The grafted membranes were calcined at 200 °C for 1 h in pure N_2 atmosphere with heating/cooling rates of 0.5 °C/min.

For comparison, some γ-alumina powders were prepared by treating them with the respective precursor solutions in a similar manner as the membranes.

2.2. Membrane characterization

Permporometry [10] was employed to determine the pore size distribution in the mesoporous membrane layers. Permporometry is based on the controlled blocking of pores by capillary condensation of a vapour phase and simultaneous measurement of the diffusional flux of a non-condensable gas through the remaining open pores. The condensable vapour chosen here was cyclohexane (the temperature of cyclohexane should be about 70 °C), as it has a high evaporation rate and is inert to the membranes to be characterized, while oxygen was used as the non-condensable gas. When cyclohexane is brought in contact with a porous medium, several mechanisms of physisorption occur on the inner surface of the pores as the relative vapour pressure increases from zero to unity. First, a monomolecular layer is formed on the inner surface of the pores. As the relative vapour pressure increases further, a multi-molecular layer starts to form. This adsorptive layer of vapour phase on the inner surface of the pores is called the t-layer. When the relative vapour pressure rises further, capillary condensation occurs on the inner surface of the pores according to Kelvin equation.

$$\ln P_{\mathrm{rel}} = -\frac{\gamma_{\mathrm{s}} V_{\mathrm{mol}}}{RT}\left(\frac{1}{r_{\mathrm{K},1}} + \frac{1}{r_{\mathrm{K},2}}\right)\cos\theta \qquad (1)$$

P_{rel} is the relative vapour pressure of the condensable vapour, γ_{s} the surface tension of the liquid–vapour interface (N/m), V_{mol} the molar volume of the condensable vapour (m^3/mol), R the gas constant (J/mol K), T the temperature (K), θ the contact angle which the liquid makes with the pore wall, and $r_{\mathrm{K},1}$ and $r_{\mathrm{K},2}$ the Kelvin radii (m), which are the radii of curvature of the vapour–liquid interface under consideration. When it is assumed that the condensable vapour wets the membrane material completely, then $\theta = 0$. Assuming that the pores are cylindrical, $r_{\mathrm{K},1}$ and $r_{\mathrm{K},2}$ are equal to the Kelvin radius r_{K} of the cylinder, and Eq. (1) transforms into

$$\ln P_{\mathrm{rel}} = -\frac{2\gamma_{\mathrm{s}} V_{\mathrm{mol}}}{RTr_{\mathrm{K}}} \qquad (2)$$

The desorption process is used for measurement of the pore size distribution. As the relative vapour pressure decreases, the larger pores are opened first. The t-layer remains after all pores are opened, and desorbs subsequently. For a cylindrical pore, the relation between the real pore radius (r_{p}) and the Kelvin radius (r_{K}) is

$$r_{\mathrm{p}} = r_{\mathrm{K}} + t \qquad (3)$$

where t is the thickness of the t-layer formed on the inner surface of the pores.

XPS was carried out on supported γ-alumina membranes with a PHI Quantera Scanning ESCA microprobe with an analysis depth of (5–75) × 10^{-10} m (5–75 Å) and a spatial resolution <10 μm. The Si 2p, Al 2p, and O 1s energy bands were analyzed and depth profiles of the concentrations of Si, Al, and O inside the membrane were obtained by sputtering with Ar^+ at a sputter rate of 24 nm/min (3 keV, 2 mm × 2 mm Ar^+).

Diffuse reflectance infra-red Fourier transform spectroscopy (DRIFTS) experiments were carried out using a BIORAD FTS-45A infrared spectrometer, with a SPECAC “The Selector” P/N 19900 series DRIFTS. The IR spectra were processed with WIN-IR (a BIORAD software program).

The chemical stability of grafted organosilanes on γ-alumina was determined by soaking grafted γ-alumina powder in water for 4 h at room temperature. The powders were then heated in N_2 at 200 °C for 1 h with a heating and cooling rate of 0.5 °C/min to remove residual water. The organosilane concentrations on freshly grafted powders and soaked powders were compared by DRIFTS experiments.

2.3. Solvent permeation experiments

Steady state liquid flux measurements were carried out using water, isopropanol, 2-butanol, and toluene in a dead-end nanofiltration cell on grafted γ-alumina membranes. The volume of the cell is 700 ml and the operating pressure range was kept at 2–14 bar [11]. The stirring speed in the cell was kept constant at 209.44×10^{-1} rad/s (200 rpm). Subsequent liquid permeation experiments on the same membrane were carried out in a sequence that started with the most hydrophobic (toluene) and ended with the most hydrophilic (water) solvent. Prior to the experiments, the membranes were left overnight in isopropanol to leach out any condensed water from the membrane mesopores [12].

3. Results and discussion

Diffuse reflectance IR spectra of grafted γ-alumina powders were recorded. For the membranes, the surface concentration of the grafted silanes was too low to be detected by DRIFTS. Characteristic peaks associated with the organic side groups of the trichloromethylsilane on γ-alumina powders were observed, as seen from Fig. 2. The characteristic peaks can be attributed to various methyl vibrations. The peak at 2970 cm^{-1} is due to $-CH_3$ asymmetric stretching and the 1267 cm^{-1} peak corresponds to $-CH_3$ deformation. The 850 cm^{-1} peak can be attributed to the $-CH_3$ rocking mode, and the 800 cm^{-1} peak is typical for the Si–C stretching mode [13]. The Si–O–Si appears at 1130–1000 cm^{-1} [14–16]. This indicates that a polymerized layer of methylated silanes has formed. In the case of the difunctional precursor $Si(Me)_2Cl_2$ the Si–O–Si peak was not observed, which may possibly indicate that both hydrolysable chlorine groups are utilized in forming bonds with the hydroxyls of the γ-alumina surface. For the monofunctional precursors triphenylchlorosilane, *t*-butyldimethylchlorosilane, and trimethylchlorosilane, the characteristic methyl, butyl and phenyl peaks were not detected. As the signal comes from one single monolayer in this case (see below), the concentrations may have been too low to be detected by the instrument.

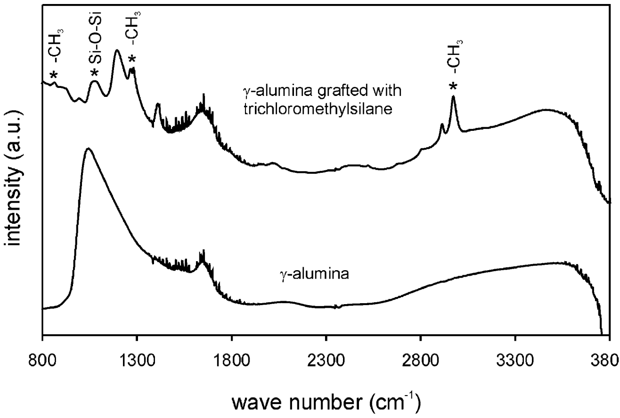

Fig. 2. DRIFTS spectra of γ-alumina powder grafted with trichloromethylsilane.

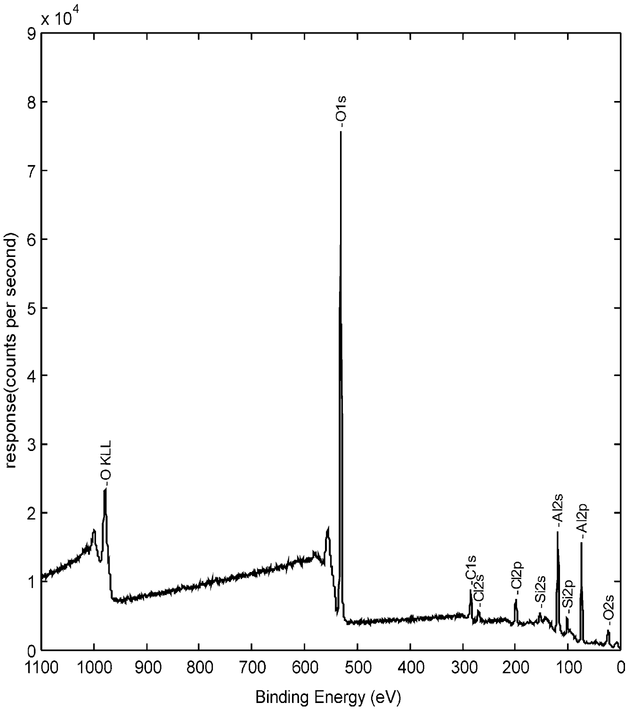

Fig. 3. XPS results of a γ-alumina membrane grafted with trimethylchlorosilane.

Compositional information on the Al and Si atomic concentrations as a function of depth was obtained by XPS. Fig. 3 shows an XPS spectrum of the surface of a γ-alumina membrane grafted with chlorotrimethylsilane. The XPS data clearly show the presence of Si on the surface, indicating that grafting of the hydrophobic precursor was successful (case 1 in Fig. 1b). A trace of Cl can also be observed, indicating that not all Cl had been washed out. In the case of silanes with large organic side groups (phenyl, butyl) silicon was only observed on the outer surface of the membrane, while silanols with one to three methyl groups were grafted both on the internal mesopore surface and on the external surface of the membrane. Probably, chlorosilanes with long chain hydrocarbon end groups (alkyl and aryl) cannot enter the 4.5–7 nm diameter mesopores easily due to steric hindrance and that grafting was therefore not as effective as for precursors with methyl end groups [8].

In the XPS depth profiles shown in Fig. 4, three regions can be distinguished: (i) the outer surface layer, with high concentrations of Si, (ii) the γ-alumina layer, until 300–400 nm

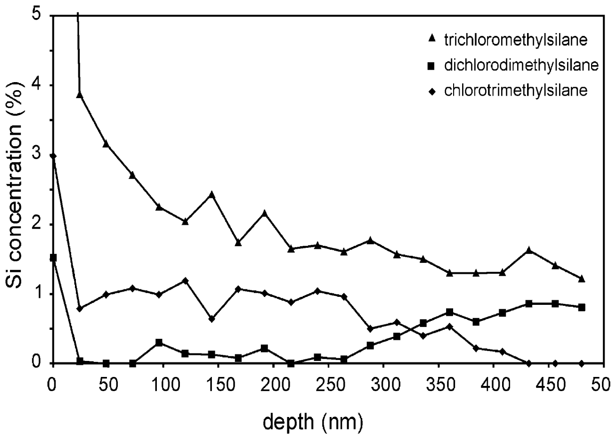

Fig. 4. XPS depth profile showing Si atomic concentration as function of depth inside the membrane.

Table 1
Silicon concentration (per unit true surface area) on the outer γ-alumina surface and inside the mesopores as calculated from XPS depth profiles

Precursor	Surface concentration (μmol/m^2)	Mesopore surface concentration (μmol/m^2)
Trimethylchlorosilane	7.3	2.0
Trichloromethylsilane	51	2.9
Dichlorodimethylsilane	3.7	0.52
Triphenylchlorosilane	0	0
t-Butyldimethylchlorosilane	0.025	0

depth, and (iii) the α-alumina support at 400 nm depth and more. Different behavior is seen for different hydrophobing agents: while the monofunctional trimethylsilane precursor reached a ~1 at.% Si concentration inside the γ-alumina pores, the concentration of the difunctional dimethylsilane remained much lower in the γ-alumina layer. There are two possible reasons to explain this phenomenon. First of all, it may be related to the fixed number of hydroxyl groups that are present on the inner pore surface of γ-alumina. While the monofunctional trimethylsilane precursor requires one OH group for covalent attachment to the alumina surface, the difunctional precursor may bond with two active OH sites (case 2a in Fig. 1b). As the total number of OH sites is limited, this would effectively result in lower Si concentrations for the grafted difunctional precursor when all hydroxyl groups would have been consumed. Secondly, the difunctional silane could also partially polymerize into linear chains inside the mesopores (case 2b in Fig. 1b), which could block pores and hinder diffusion of similar precursors into the mesopores, leading to lower Si levels inside the γ-alumina layer. A third possible explanation is that DDMS is very reactive towards itself, giving PDMS chains that are washed out, leaving hardly any DDMS inside the γ-alumina layer. A very high concentration of silicon, up to 20 at.% at the surface, was observed in the system that had been treated with trichloromethylsilane. This is most likely due to the formation of a polymerized multilayer of organosilane being formed on the surface, which was observed directly by DRIFTS in the form of a Si–O–Si peak. In this case, after the condensation with the hydroxyls of the γ-alumina layer has taken place, there will still be one or two hydrolysable groups available for further coupling with other precursor molecules (case 3 in Fig. 1b). Hence, for this precursor the silane concentration reached relatively high values in both the γ- and α-alumina layers.

Silicon was hardly detected in the α-alumina support layer that had been treated with the trimethylsilane compound, while a relatively high concentration was present in the support layer that had been treated with the dimethylsilane precursor. This suggests that the dimethylsilane precursor is grafted predominantly in the form of linear chains (case 2b in Fig. 1b) in the α-alumina layer. As the pore size of the α-alumina support is much larger than that of γ-alumina, pore blocking as a result of grafting will most likely not occur in the α-alumina support. In the α-alumina region, the Si concentration of the trimethylsilane precursor is very low, whereas the dimethylsilane precursor gives much higher values. This can be explained by taking into consideration that α-alumina has a very low specific surface area of ~15 m^2/g whereas the γ-alumina has a higher specific surface area of ~250 m^2/g. The number of OH groups on an alumina surface is limited to ~5 nm^{-2} so that even when all available sites in the α-alumina support are grafted with a trimethylsilane molecule, the Si atomic concentration will still be low. As the possibility of linear polymerization without pore blocking exists for the difunctional precursor, a higher concentration is realized in the α-alumina support.

The molar concentration of Si per unit real surface area for mono-, di- and trifunctional precursors at the outer membrane surface and inside the γ-alumina mesopores as determined by XPS are listed in Table 1. The very high concentration of Si for the trichloromethylsilane precursor on the outer surface indicates the presence of polymerized silane network, which confirms the DRIFTS results.

Fig. 5 shows the desorption curve of the permporometry process for di- and trichloromethylsilane grafted γ-alumina

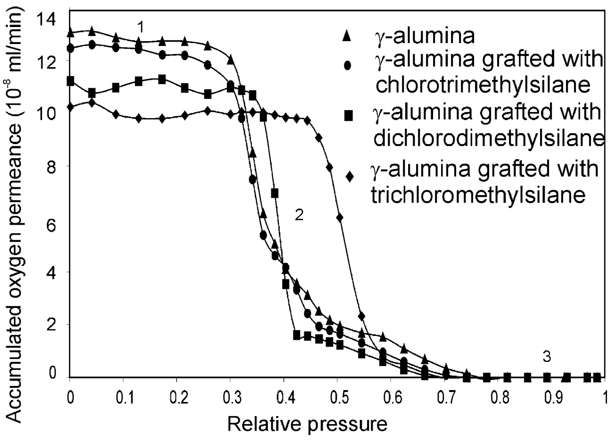

Fig. 5. Accumulated oxygen permeation vs. relative cyclohexane vapour pressure curve at 20 °C, for γ-alumina membrane grafted with di- and trichloromethylsilane.

membranes, and an unmodified membrane. The figure shows the oxygen flux through open pores versus the relative vapour pressure of cyclohexane. At relative vapour pressures close to unity (region 3 in Fig. 5) all pores are blocked. The accumulated oxygen permeation can be larger than zero only if there are some very large pores or cracks in the membrane, which is not the case here, indicating that we obtained defect-free membranes. Region 2 is the capillary condensation regime, where the Kelvin pore size distribution is calculated from the change of the oxygen permeation flux with changing pore radius. In region 1 all pores are open and only t-layer desorption is assumed to occur. The onset of capillary condensation for the membranes grafted with dichlorodimethylsilane occurred at a lower cyclohexane pressure than in the trichloromethylsilane-grafted membrane, which indicates that its Kelvin radii are smaller. Furthermore, the oxygen flux in region 1 and at zero cyclohexane pressure decreases in the order γ-alumina > trimethylsilane modified > dimethylsilane modified > methylsilane. This suggests that partial pore blocking for diffusing O_2 species due to grafting occurs in the modified membranes, and that the level of pore blocking increases in the same order. Though the organosilane surface concentration of the trimethylsilane modified sample is higher than that of the dimethylsilane modified sample, the polymerized layer fragments of the latter one appear to offer a greater resistance to the passage of oxygen than the trimethylsilane monolayer.

Fig. 6 shows the pore size distributions of the tri-, di- and monomethylchlorosilane-modified membrane, and an unmodified γ-alumina membrane as calculated from the data of Fig. 5. It is seen that grafting with chlorotrimethylsilane leads to a decrease in the pore size, indicating that the hydrophobic precursor has penetrated into the pores and formed a monolayer. The Kelvin radius decreases from 2.3 nm for the ungrafted γ-alumina membrane to 2.0 nm for the grafted one. In contrast, the pore size distribution of the dichlorodimethylsilane-modified membrane shows an average Kelvin radius of 2.5 nm, while the trichloromethylsilane-modified membrane has an average Kelvin radius of 3.4 nm. The larger pore sizes in these latter cases may be explained by assuming that the smallest pores may become blocked with polymeric organosilane networks. As a result, oxygen can diffuse only through the remaining open larger pores.

Under the assumption that all pores are cylindrical in shape, the t-layer was estimated from total the decrease in oxygen flux in region 1 of Fig. 5 [17]. Estimates of the t-layer thicknesses indicated a thickness of ∼0.5 nm for the ungrafted and chlorotrimethylsilane grafted membranes, a thickness of ∼0.8 nm for the dichlorodimethylsilane grafted membrane, and ∼1.5 nm for the trichloromethylsilane grafted membrane. Although a thickness of ∼0.5 nm for the t-layer thickness is physically reasonable, the latter two values are not. This indicates that the assumption of t-layer adsorption on cylindrical pore walls does not hold in these cases. It is most likely that the dicholorodimethylsilane and trichloromethylsilane-grafted membranes have seemingly thicker t-layers because of the polymerized silane chains or 3D network inside the pores, which facilitate the physisorption of cyclohexane by van der Waals interactions. In such cases t-layer adsorption may occur not only on the pore walls but also by association with the silane network, which effectively results in higher levels of cyclohexane adsorption than would be expected on the basis of adsorption on the pore walls only.

Liquid permeation experiments were carried out on the grafted γ-alumina membranes with water, isopropanol and toluene. Liquid fluxes were measured as function of the applied pressure. Fig. 7 shows a representative example of these results. In all cases the volumetric flux j varied linearly with the pressure applied over the membrane Δp, and the permeability constants k_m were determined from Darcy's law:

$$j = -\left(\frac{k_m}{\eta}\right)\Delta p, \qquad (4)$$

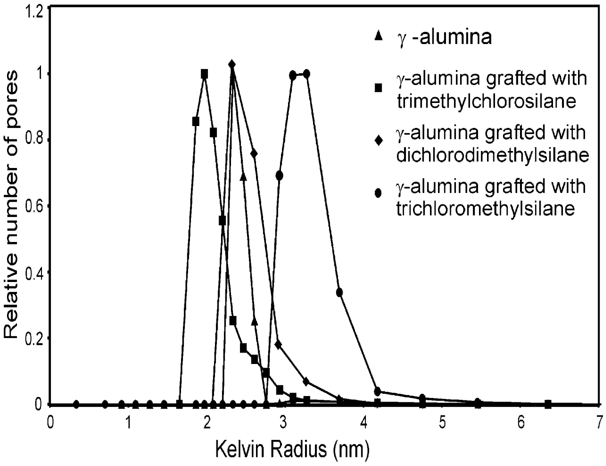

Fig. 6. Normalized pore size distribution of γ-alumina membranes grafted with mono-, di- and trichlorosilanes by permporometry at 20 °C.

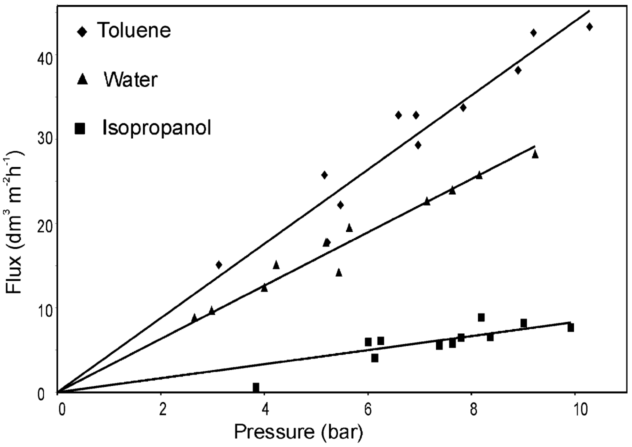

Fig. 7. Flux vs. pressure for different solvents on a γ-alumina membrane grafted with trimethylchlorosilane.

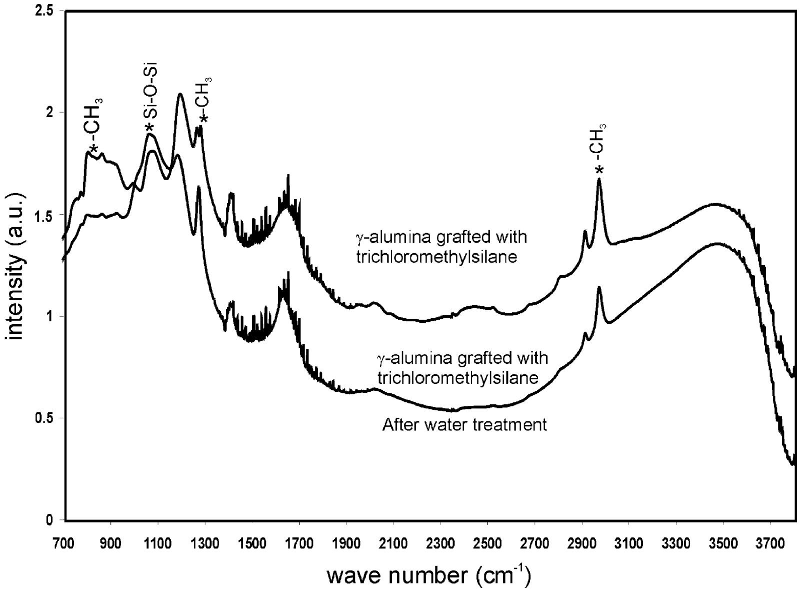

Fig. 8. DRIFTS spectra for γ-alumina powders grafted with trichloromethylsilane, before and after treatment with water.

where η is the solvent viscosity. The permeability coefficients, k_m, are listed in Table 2. Very low permeabilities were observed for the membrane grafted with trichloromethylsilane. Most likely this is due to the polymerized layer of organosilane present on the surface and inside the γ-alumina pores, which will provide an extra initial barrier for the solvents to pass through. The more hydrophobic character of this membrane in comparison with the other ones is indicated by its higher toluene/water permeability ratio. The other membranes show much higher permeabilities than the trichloromethylsilane-modified membrane, and they were all roughly in the same range. Because permeability differences up to 35–40% for a specific solvent are often observed even between similar membranes from the same batch of material [2], no definite conclusions can be drawn from the observed differences, and it is therefore preferred to compare results for various solvents on a particular membrane [18]. In general, the toluene/water permeability ratio appears to increase slightly upon grafting, but remains below unity, which indicates a low level of hydrophobic modification.

Hence, among all precursors only the trichloromethylsilane precursor imparted a predominantly hydrophobic character, since only this membrane has a larger permeability coefficient for toluene than for water. However, the liquid permeability of this membrane was very low in comparison with the results obtained on the other membranes. It appears that two effects are operating: (1) porosity reduction of the γ-alumina layer due to the presence of organosilane groups, leading to a decreased permeability, and (2) chemical modification of the outer membrane surface and the internal pores, offering a hydrophobic environment inside the pores. As the results of this study show, the permeation of solvents is influenced by the combination of these two effects, so that and a higher degree of modification also leads to a lower permeability. These results are in accordance with previous work by Picard et al. [3] on zirconia membranes grafted with fluorinated silanes. The results of Alami Younssi et al. [4], who concluded that the extent of grafting depends on the nature of the silanes used, and that hydrophobic modification is achieved most effectively with multifunctional silanes, are also confirmed by the findings of this paper.

Table 2
Permeability constants k_m (10^{-14} m) for different solvents through α-alumina supported γ-alumina membranes grafted with various precursors

Precursor	Toluene	Isopropanol	Water
None	0.62	0.67	1.03
Trimethylchlorosilane	0.68	0.53	0.78
Dichlorodimethylsilane	1.63	1.55	1.57
Trichloromethylsilane	0.048	0.041	0.044

Regarding the stability of the grafted layer, the DRIFTS results in Fig. 8 show the characteristic peaks of the trichloromethylsilane grafted powders, before and after treatment with water. As can be seen from the results the trichloromethylsilane precursor binds strongly to the γ-alumina surface and is able to resist the effect of extended exposure to an aqueous medium.

4. Conclusions

Varying degrees of hydrophobic modification of γ-alumina membranes were achieved by the use of different precursors. The degree of hydrophobation varied depending on the side chain lengths and also on the functionality of the precursors. The triphenyl and *t*-butyldimethylsilane precursors are bulky and steric hindrance dominated the efficiency of the grafting process. Monofunctional trimethylchlorosilanes were effectively chemisorbed inside the pores, but the extent of modification was not sufficient to impart a predominant hydrophobic environment for hydrophobic solvents. The trichloromethylsilane-modified γ-alumina membrane had a predominantly hydrophobic character, as concluded from liquid permeation experiments, due to a polymerized organosilane network that was present on the outer surface and inside the γ-alumina mesopores. The surface concentration on the membrane and also the extent to which the hydrophobic moiety enters the pores determines the permeability towards solvents and gases.

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