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MICROPOROUS AND
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Chemically modified ceramic membranes[1]

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Abstract

Commercial ultrafiltration ceramic filters have been modified by chemical treatment. The γ-Al_2O_3 top layer of the asymmetric ceramic filter was modified (1) by in situ hydrolysis of tetraethylorthosilicate, giving a hydrophilic nanoporous SiO_x top layer rich in Si–OH, (2) by silylation of the γ-Al_2O_3 layer, providing an organophilic functionalization, and (3) by reaction of the γ-Al_2O_3 layer with alkyl/aryl phosphonic acids, resulting in an organophobic behaviour. By these chemical treatments both a pore narrowing and a hydrophilic/hydrophobic functionalization can be achieved. Permeation results of single gases and pervaporation data of liquid mixtures on the novel membranes are presented. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Permeation; Permselectivity; Ceramic membrane; TEOS; Silylation; Phosphorylation

1. Introduction

For more than 45 years L.V.C. Rees has been one of the most active and versatile members of the zeolite community. His research work covers several aspects of zeolite science and practice ranging from ion exchange and zeolite synthesis to single component/mixture sorption equilibria and kinetics including gas separation [1]. There are only a few areas in which L.V.C. Rees was not active. Zeolite membranes belong to these rare fields. During the last few years, the development of zeolite membranes as a pin-hole-free thin zeolite layer, low in crystal defects as diffusion barriers, strongly attached to a mesoporous support became increasingly one of the most attractive goals in zeolite research. Perfect zeolite membranes will be unbeatable in selectivity and flux. Much progress has been achieved in the last few years to solve such problems as cracks in the course of calcination, inhomogeneous, intergrown and thick layers with pin holes or problems with the attachment to the support. In the UK and in Japan the first zeolite membranes are already on the market for separation of liquids. Nevertheless, before the industrial breakthrough of zeolite membranes, ceramic membranes with amorphous metal oxide top layers will dominate the inorganic membrane market for the next few years.

Inorganic membrane science and technology based on ceramic membranes is undergoing rapid development and innovation. The state of the art is highlighted in Refs. [2–6]. Inorganic membranes exhibit remarkable advantages compared with organic membranes owing to their chemical and

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[1] Dedicated to Professor Lovat V.C. Rees in recognition and appreciation of his lifelong devotion to zeolite science and his outstanding achievements in this field.

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thermal stability. Asymmetric ceramic membranes were first commercialized in the 1980s for the micro- and ultrafiltration of liquids. The major application fields are agro-food, biotechnology, water purification and pharmaceutical industries. Ceramic membranes are used for the separation of isotopes and the removal of dust or pollen in air conditioning.

For an application in gas separation or pervaporation of liquids, pore sizes <5 nm are necessary. The usual strategy to reach this goal consists in the coating of ceramic supports with microparticles of silica, titania, zirconia, etc. prepared by the sol–gel route. In addition to Refs. [2–6], pioneering contributions on permeation and separation on microporous sol–gel modified ceramic membranes are given in Refs. [7–13]. Significant progress has been achieved by controlling both microporosity and surface polarity. The microporosity of the membrane depends on the experimental conditions of the sol–gel procedure and the drying/calcination process. The use of starting metal alcoholates which contain certain non-hydrolysable alkyl groups, such as $MetSi(OEt)_3$, is helpful in the design of the surface polarity of the membrane [14,15].

In this paper we present three simple but powerful chemical methods to modify a given ultrafiltration ceramic support to create molecular separation properties [16,17].

2. Experimental

2.1. Membrane preparation

The starting materials in all preparations were commercial asymmetric ceramic UF filters as flat sheets of the inocermic GmbH (100% subsidiary of Hermsdorfer Institut für technische Keramik e.V.—HITK). From these sheets 18 mm circular discs were cut by a laser technique. We will show in this study that these commercial substrates designed for ultra- and micro-filtration applications can be used as supports for the preparation of membranes for molecular separations of gases

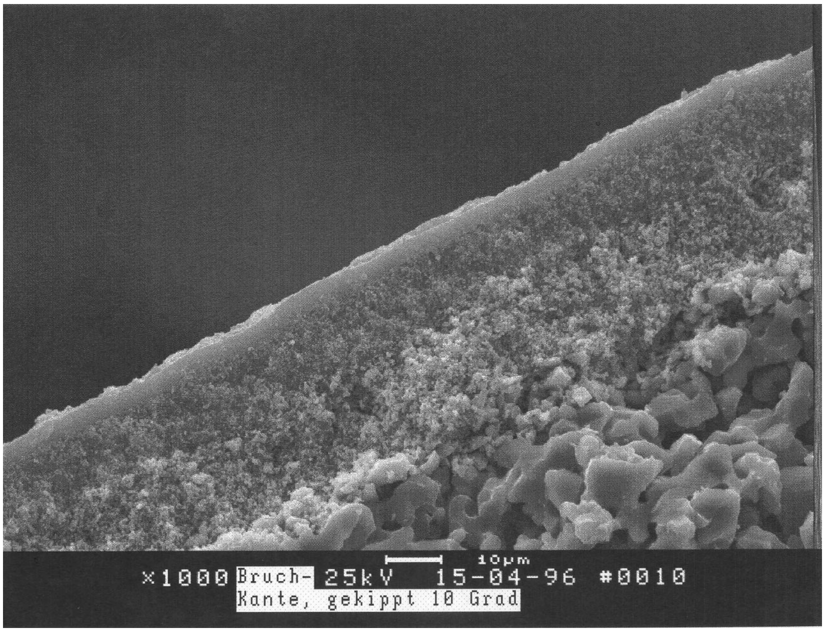

Fig. 1. Cross-section of the ultrafiltration membranes used which consist of three consecutive layers on an α-Al_2O_3 body (particle size 2–4 µm, 35% porosity). The pore radii at 50% of the pore volume (d_{50}-data) for the three layers are [18]: α-Al_2O_3 microfiltration (MF) support, $d_{50}=200$ nm, 180 µm thick; α-Al_2O_3 intermediate (IM) support, $d_{50}=60$ nm, 50 µm thick; γ-Al_2O_3 ultrafiltration (UF) top layer, $d_{50}=5$ nm, 3–4 µm thick (55% porosity).

and liquids. The cross-section of the asymmetric membrane is shown in Fig. 1.

2.2. Permeation/pervaporation experiments

The chemically modified ceramic discs were tested in a stainless steel permeation cell between 25 and 200°C. In permeation experiments the fluxes of single gases and vapours were determined. From the permeate fluxes (followed by capacitive membrane torrmeters) in units of $\mathrm{kg\,m^{-2}\,h^{-1}\,bar^{-1}}$ or $\mathrm{l(STP)\,m^{-2}\,h^{-1}\,bar^{-1}}$ the permselectivities as the ratio of the permeation fluxes of the single components have been derived. The permselectivity, defined as the ratio of the permeation of the single gases at a given membrane thickness, is not the same as the separation factor experimentally determined from gas mixtures. The permselectivity, however, is a rough estimate for the separability of a mixture if a specific interaction can be neglected, e.g. in the Knudsen region and at high temperatures (see Ref. [5] (p. 365), Ref. [3] (p. 567) and Refs. [7,19–21]). The permeation devices on-line are linked to a GC-MS (Finnigan, Magnum) or capillary GC (HP 5890) [22,23]. In the pervaporation tests, the flux was determined gravimetrically and the permeate was analysed using GC.

3. Results and discussion

3.1. Hydrophilic functionalization of γ-Al_2O_3 by an SiO_x top layer from in situ *hydrolysis of tetraethylorthosilicate (TEOS)*

3.1.1. Preparation

The Al_2O_3 support was saturated via the gas phase with water vapour (loading: 0.2 mg H_2O/cm^2 of the top layer). Then a 50% solution of TEOS in ethanol was spin coated on the support at room temperature. After drying in air, the TEOS-coated ceramic supports were heated in air at 10°C $\mathrm{min^{-1}}$ to 250°C. For selected samples this procedure has been repeated several times. Under water deficiency, the in situ hydrolysis of TEOS within the pores of the ceramics gives polymeric SiO_x species. In the initial step, $(Et\text{–}O)_4Si$ is hydrolysed to give $(Et\text{–}O)_3\text{–}Si\text{–}OH$. By intermolecular condensation (1) polymeric SiO_x species are built up and (2) by reaction with the support Si–O–Al bonds are formed [24]. The water molecules formed by this condensation can further hydrolyse Et–O–Si bonds and give additional Si–OH groups. For steric reasons, most of these Si–OH cannot react by condensation and provide the membrane the hydrophilic character.

3.1.2. Characterization

It is rather difficult to determine the thickness of the SiO_x top layer. Using X-ray photoelectron spectroscopy (XPS, excitation energy of Al K_α was 1486.6 eV, 150 W), the reduction of the Al 2p signal intensity of the ceramic support with increasing number of TEOS coatings can be taken as a rough estimate for evaluation of the thickness of the SiO_x layer. From the data in Table 1 it can be concluded that the first coating gives an SiO_x layer <6 nm. After six subsequent coatings the Al 2p signal disappears, indicating that the layer thickness is $\gg 8$ nm.

Furthermore, from the relative increase of the Si 2p signal for the species $(X\text{–}O\text{–})_2Si(\text{–}O\text{–})_2$ (X = ethyl or H) with increasing number of coatings, it can be concluded that after six coatings 2/3 of the Si in the silica network is present with two O-bondings to other Si and two non-linked terminal bondings (Si–OH or non-hydrolysed Si–O–Et). After the first coating, however, this ratio is approximately 1:1, indicating that the silica formed in the first coating has a lower degree of Si–O–Si condensation.

3.1.3. Permeation characteristics

Fig. 2 shows that the coating of the γ-Al_2O_3 top layer with SiO_x by in situ hydrolysis of TEOS gives a hydrophilic membrane with a high flux for water. After the first TEOS coating, the permeation flux of water is 28 $\mathrm{m^3(STP)\,m^{-2}\,h^{-1}\,bar^{-1}}$ which gives a permselectivity of water relative to hydrogen of 450 (Fig. 2(b)). For the untreated γ-Al_2O_3 filter a permselectivity of only 20 for water relative to hydrogen was found (Fig. 2(a)). With an increasing number of repeated coatings both the flux densities and the permselectivities for water decrease. With increasing silica coatings, the

Table 1
XPS study of an γ-Al_2O_3 ultrafiltration support after spin coating with a TEOS solution, conditioned at 250°C. Together with C and O (these data are not shown), the atom% give 100% (ESCALAB 220iXL, Fisons Instruments)

Membrane treatment	Signal intensities (at.%)		
	Al 2p	Si 2p	
		$(X^a\text{–O–})_2Si(\text{–O–})_2$	$(X\text{–O–})_3Si(\text{–O–})$
Starting ceramic	33.8	0	0
1 × TEOS coated	4.4	9.7	10.1
6 × TEOS coated	0.4	5.4	8.5

[a] X = H or ethyl.

differences in the fluxes between water and the other gases become smaller. After seven TEOS coatings water permeates 100 times faster through the membrane than hydrogen (Fig. 2(c)). This preferred water permeation is attributed to the effect of capillary condensation, as described in Refs. [3,5,25]. The onset of capillary condensation is based on an interplay of partial pressure, temperature and pore width, as well as wettability of the pore wall, in our case facilitated by the existence of Si–OH. Since a pure water steam as single component at 1 bar without carrier gas was permeated at 105°C ($p/p_{sat} = 0.84$), in the silica pore system capillary condensation can take place. For the other gases shown in Fig. 2, capillary condensation is unlikely for silica-coated ceramics at $p/p_{sat} < 0.4$ at 105°C (see Ref. [25]). In contrast to water, for these gases with an increasing number of TEOS coatings the permselectivities relative to hydrogen increase, indicating the pore narrowing of the ceramic pores and the simultaneous formation of the nanoporous silica layer on the surface of the ceramic. Fig. 2(c) shows that the order of the flux rates of the gases permeated follows the kinetic diameters [26]: ($H_2O = 0.265$ nm, $H_2 = 0.289$ nm, $CO_2 = 0.33$ nm, $O_2 = 0.346$ nm, $N_2 = 0.364$ nm, n-$C_4H_{10} = 0.43$ nm, i-$C_4H_{10} = 0.5$ nm, $SF_6 = 0.55$ nm). Methane (0.38 nm) behaves exceptionally.

The hydrophilic character of this membrane is also reflected by the pervaporation studies shown in Fig. 3. Binary mixtures of water and the corresponding organic solvent have been pervaporated on a ceramic membrane with six TEOS coatings. For mixtures of 95 vol.% water and 5 vol.% organic solvent, separation coefficients between 5 and 17 and fluxes up to 0.4 kg m^{-2} h^{-1} bar^{-1} have been measured. For binary mixtures with low water content the flux densities are less, 0.1 kg m^{-2} h^{-1} bar^{-1}, but the selectivities are up to 1000. The TEOS-modified ceramic filter can be used, therefore, for the selective removal of traces of water from solvents and for the recovery of solvents from liquid wastes. This includes the breaking of azeotropes, e.g. for the binary mixture acetonitrile–water where no acetonitrile-resistant polymer membrane is known.

3.1.4. Thermal stability

Table 2 shows the single component permeation data measured at 105°C on silica-modified membranes which were pretreated before permeation at elevated temperatures in air. With increasing pretreatment temperatures the fluxes increase and the permselectivities decrease. A membrane calcined at 400°C has higher fluxes and a modified permselectivity compared with a membrane dried at 250°C. Obviously, by condensation of Si–OH dense silica structures are formed and the nanoporous silica layer develops larger pores. Water behaves exceptionally. With increasing pretreatment temperature, the water fluxes show a maximum value at 400°C. It is not clear if the following decrease of the water fluxes for membranes pretreated at $T > 400$°C is due to the increased hydrophobicity (Si–OH dehydroxylation) or due to an

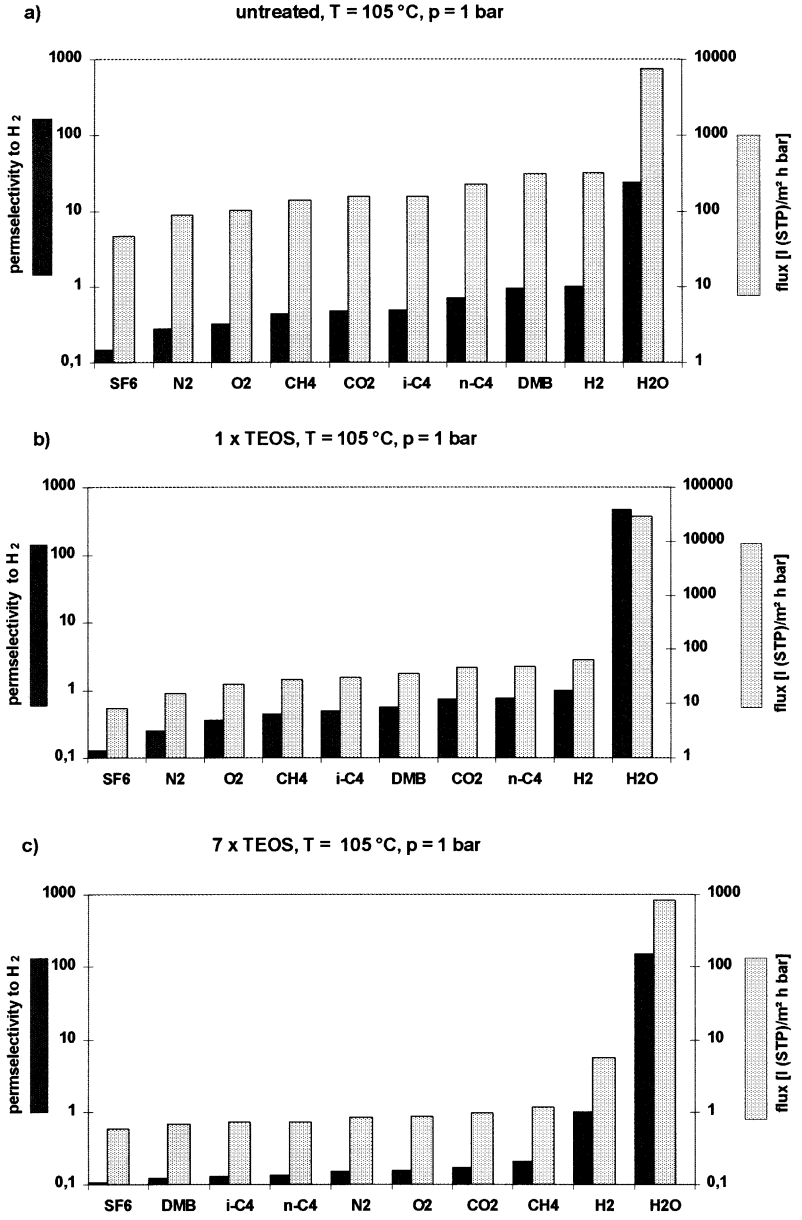

Fig. 2. Effect of repeated TEOS coatings of a UF ceramic filter with γ-Al_2O_3 top layer on the single gas permeation of different probe gases at 105°C. The permselectivities (black columns, left) are calculated from the single gas fluxes (grey columns, right). The membranes had been conditioned between the individual coatings at 250°C. DMB = dimethylbutane.

enlargement of the pores which prevents water condensation. However, a membrane treated for 0.5 h at 400°C exhibits similar permeation patterns as a membrane kept for 10 h at this temperature. This finding indicates that the membrane is quasi-stable at 400°C. Note that even for a sample treated 10 h at 550°C the H_2/n-C_4 permselectivity at 105°C is still 3.5, which is not far from the Knudsen factor of 5.4, indicating that the pores are still narrow.

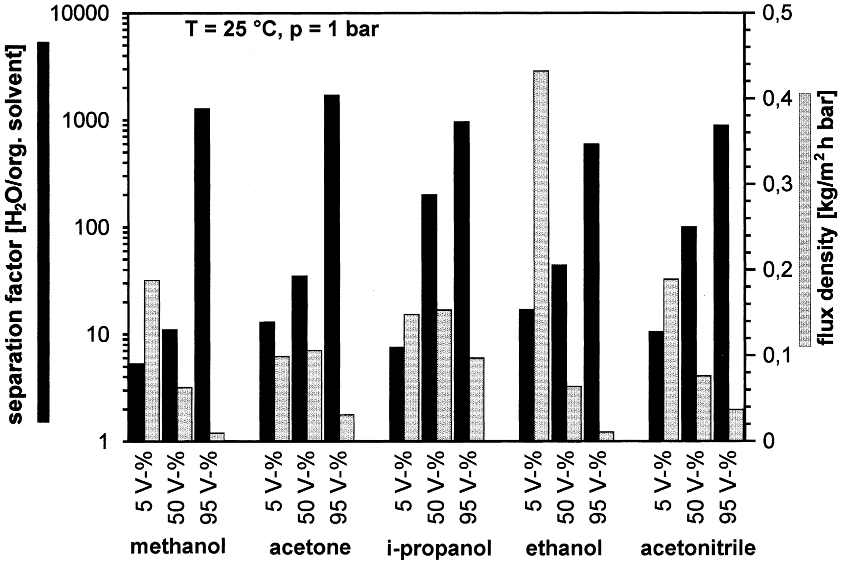

Fig. 3. Pervaporation of binary mixtures of water and an organic solvent through a UF ceramic filter with γ-Al_2O_3 top layer after six TEOS coatings. The membranes had been conditioned between the individual coatings and before the permeation measurement at 250°C. 5 vol.% means a mixture that consists of 5 vol.% of the organic solvent and 95 vol.% water. Black columns (left): separation factors; grey columns (right): total flux rate.

Table 2
Influence of the thermal pretreatment of a γ-Al_2O_3 UF ceramic filter with six TEOS coatings in air on the permeation of single gases and vapours. Permeation measurements at 105°C

Thermal pretreatment (°C)	Fluxes (l(STP) $m^{-2} h^{-1} bar^{-1}$)									
	SF_6	O_2	N_2	CO_2	CH_4	n-C_4	i-C_4	DMB[a]	H_2	H_2O
30 min										
250	0.7	1.3	1.6	1.9	1.8	1.4	1.1	1.3	9.0	870
400	290	520	560	480	750	470	470	420	1850	1530
550	310	570	610	540	880	610	610	560	2030	270
10 h										
400	270	460	490	420	650	440	450	390	1520	960
550	640	1040	1160	970	1550	1070	1050	920	3640	660

[a] 2,2-Dimethylbutane.

3.2. *Organophilic functionalization of the γ-Al_2O_3 top layer by silylation*

3.2.1. *Preparation*

First the Al_2O_3 support was saturated via the gas phase with water vapour (loading: 0.2 mg H_2O/cm^2 of the top layer). Then the water-containing support was put at 50°C for 6 h into a solution of n-hexane and the corresponding silylating agent. The silylating agent was used in a tenfold surplus. For the neutralization of the HCl formed, an equimolar amount of triethylamine was added. Oxidic surfaces become silylated by several mechanisms. In a direct way, the surface is silylated following the reaction $Al{-}OH + Cl{-}Si{-}R_3 \rightarrow Al{-}O{-}Si{-}R_3 + HCl$. Owing to the presence of traces of water in our case, in a first step $R_x{-}Si{-}Cl_{4-x}$ is hydrolysed. The resulting

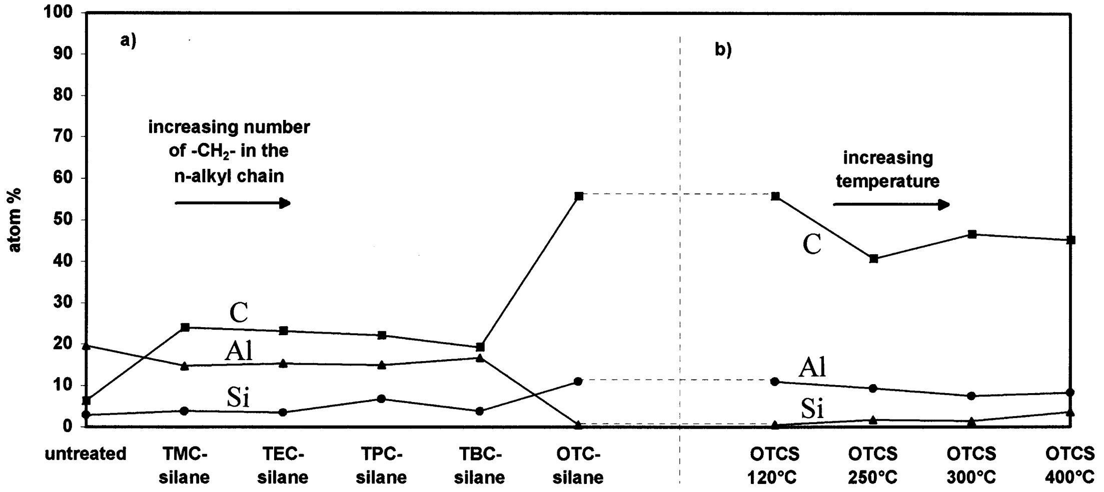

Fig. 4. XP spectra of the UF ceramic filter with γ-Al_2O_3 top layer after treatment with silylating agents (ESCALAB 22OiXL, Fisons Instruments). (a) Relative atom intensities of C, Al and Si as a result of silylation with five different silanes: TMC-, trimethylchloro-; TEC-, triethylchloro-; TPC-, tripropylchloro-; TBC-, tributylchloro-; OTC-, octadecyltrichloro-. (b) Thermal stability of the modification brought about by OTCS. Legend: ■, C 1s; ▲, Al 2p; ● Si 2p.

R_x–Si–OH_{4-x} can react with surface OH-groups of the Al_2O_3 support or can undergo intermolecular condensations to give polymeric species like –O–SiR_2–O–SiR_2–O– inside the pores of the support. Six different silylation agents have been tested with respect to their ability to alter the permeation behaviour [27]. In this paper we focus on the results obtained with octadecyltrichlorosilane (OTCS), n-$C_{18}H_{37}$–Si–Cl_3.

3.2.2. Characterization

Fig. 4 contains the results of the XPS investigation of a ceramic membrane with γ-Al_2O_3 top layer modified by treatment with different silylating agents. Fig. 4(a) shows that only for a treatment with OTCS is a drastic change of the atom composition of the γ-Al_2O_3 surface observed. Compared with the untreated γ-Al_2O_3 surface, for the OTCS-modified surface the Al 2p signal becomes practically invisible, the C 1s signal of the n-$C_{18}H_{37}$ group and the Si 2p signal are dominating. Obviously, the Al_2O_3 surface is covered by n-$C_{18}H_{37}$ groups which are believed to be oriented perpendicular to the surface. This finding is supported by the permeation results shown in Table 3. Among the silylating agents used, it is only OTCS that remarkably alters the permeation patterns of the Al_2O_3 support.

3.2.3. Permeation characteristics

Table 3 shows the effect of different silylating agents on the permeation behaviour of various gases and vapours. Treatment with the trialkylmonochlorosilanes TMC-, TEC-, TPC- and TBC-silane reduces the fluxes of the single gases in a very similar way. This finding from permeation (Table 3) is in accordance with the results of XPS, where a similar shielding of the γ-Al_2O_3 layer by the alkyl groups of these trialkylsilanes was found (Fig. 4(a)). However, a more effective shielding of the ceramic surface by the long octadecyl group is predicted by XPS (see Fig. 4(a)). This forecast from XPS is confirmed by the single gas permeation. For the OTCS-modified membrane all fluxes were found to be lower than those on the membranes modified with the four trialkylmonochlorosilanes. However, this reduction of the fluxes by the silylation did not change the hydrophobic/hydrophilic behaviour of the membrane. That is to say the fluxes of water and the hydrocarbons are reduced by the same factor: in the case of the

Table 3
Flux densities of different gases and vapours on a γ-Al_2O_3 UF ceramic filter silylated with different silylating agents: TMCS = trimethylchlorosilane, TECS = triethylchlorosilane, TPCS = tripropylchlorosilane, TBCS = tributylchlorosilane and OTCS = octadecyltrichlorosilane

Silylating agent	Fluxes of single components at 105°C (l(STP) m^{-2} h^{-1} bar^{-1})									
	SF_6	N_2	O_2	CH_4	CO_2	i-C_4	n-C_4	DMB	H_2	H_2O
Untreated	46	88	103	139	153	155	223	304	316	7440
TMCS	8	17	26	36	58	61	110	210	642	690
TECS	8	17	25	33	50	55	91	110	671	800
TPCS	5	11	15	18	31	22	39	37	48	1990
TBCS	58	110	120	160	140	140	190	820	380	2680
OTCS	0.1	0.3	0.6	0.8	2.0	—[a]	1.6	2.4	2.4	72.7
1 × TEOS[b] 250°C + OTCS	8	13	24	31	62	72	110	120	49	350

[a] Not measured.

[b] Combined treatment: first deposition of an Si–OH-rich silica layer by in situ hydrolysis of TEOS followed by a silylation using the Si–OH as anchor groups.

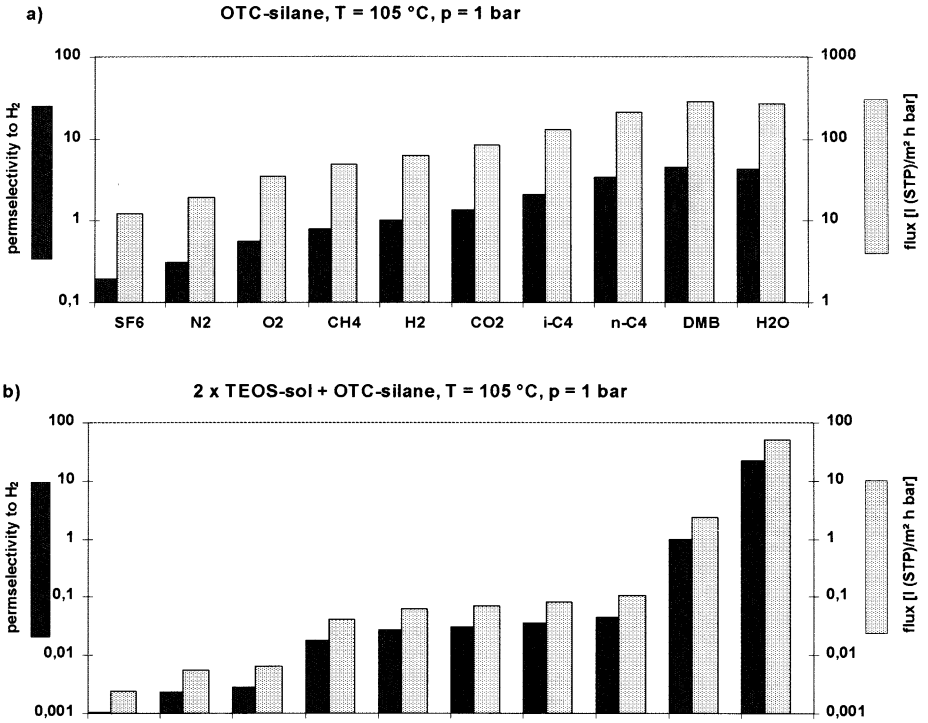

Fig. 5. Flux densities and permselectivities of the UF ceramic filter with γ-Al_2O_3 top layer after (a) a one-step treatment with OTCS and (b) two coatings with silica sol followed by a subsequent silylation by OTCS as described in Section 3.2.

OTCS-treated membrane by a factor of 100 compared with the untreated membrane.

An organophilic character of the membrane was found when the γ-Al_2O_3 top layer of the ceramic is coated before the silylation with an Si–OH-rich SiO_x layer by in situ hydrolysis of TEOS (Table 3) or alternatively two coatings with silica sol (Fig. 5(b)). The more hydroxyls as docking centres that are present at the surface, the more alkylsilane groups can be bound to the surface to modify the permeation behaviour. It can be seen from Table 3 that for the combined treatment of first a deposition of SiO_x by TEOS hydrolysis followed by silylation with OTCS the water flux is reduced by a factor of 20, but the fluxes of the butanes are reduced by only a factor of 2. Therefore, this membrane is called organophilic. Fig. 5(a) shows that the permeabilities of dimethylbutane and the i- and *n*-butane are similar to that of water. Probably, any remaining Si–OH promotes water permeation.

3.2.4. Thermal stability

The thermal stability of the silylated membranes has been studied as follows. With a heating rate of 10°C min^{-1} the membranes were heated outside the permeation cell in air to 120, 250, 300 and 400°C, and kept there for 0.5 h. Then the membranes were investigated by XPS and tested in single gas permeation. Table 4 shows the fluxes measured at 105°C on the pretreated membranes; the corresponding XPS data are given in Fig. 4(b). The fluxes in Table 4 indicate that between 120 and 250°C the fluxes of i- and *n*-butane and DMB decrease by a factor of 2.6 to 3.5. In contrast, the fluxes for water and hydrogen increase. Obviously, below 250°C the oxidative degradation of the *n*-octadecyl group starts, which leads to a reduced organophilic behaviour. Correspondingly, between 120 and 250°C the C 1s signal intensity in Fig. 4(b) decreases and the O 1s intensity increases. From long-term tests over 30 h it follows that the modification brought about by treatment with OTCS is stable up to 230°C.

3.3. Organophobic functionalization by treatment of the γ-Al_2O_3 top layer with phosphonic acid

3.3.1. Preparation and characterization

In Teflon-coated stainless steel autoclaves the UF ceramic supports with the γ-Al_2O_3 top layer reacted at 160°C with aqueous solutions of alkyl- or aryl-phosphonic acids [28]. Here we will report on the modification of the γ-Al_2O_3 top layer by phenylphosphonic acid (PPA) and *tert*-butylphosphonic acid (TBPA). The relatively strong phosphonic acids partially dissolve the γ-Al_2O_3 top layer and form the corresponding Al-salt $Al_2(R$–$PO_3)_3$.

Using X-ray diffraction, the formation of Al-phenyl- and -*tert*-butyl-phosphonates with a layer structure on the surface of the γ-Al_2O_3 top layer or in its pore system could be detected [27]. The formation of Al-alkyl- and aryl-phosphonates has been confirmed by FTIR microspectroscopy. The FTIR spectra of the phosphonylated membrane were identical with separately prepared Al-phosphonates. In XPS studies it was found that the Al 2p signal of the support is much more suppressed after a treatment with phenylphosphonic acid compared with TBPA. The relatively strong shielding of the γ-Al_2O_3 top layer by phenylphosphonates relative to *tert*-butylphosphonates is reflected by the permeation measurements.

3.3.2. Permeation characteristics

Fig. 6 shows the fluxes and permselectivities for the UF ceramic filter with a γ-Al_2O_3 top layer

Table 4
Thermal stability of the silylation of a mesoporous Al_2O_3 ceramic filter by OTCS. Pressure difference across the membrane 1 bar

Pretreatment temperature (°C) for 0.5 h	Fluxes of single components at 105°C (l(STP) m^{-2} h^{-1} bar^{-1})									
	SF_6	N_2	O_2	CH_4	CO_2	i-C_4	*n*-C_4	DMB	H_2	H_2O
120	12	19	34	49	85	130	210	280	62	270
250	9	26	47	50	110	49	87	81	140	1870
300	240	240	490	480	630	450	410	440	280	1720
400	7010	11 600	10 860	15 400	10 600	11 400	11 500	10 100	28 900	15 090

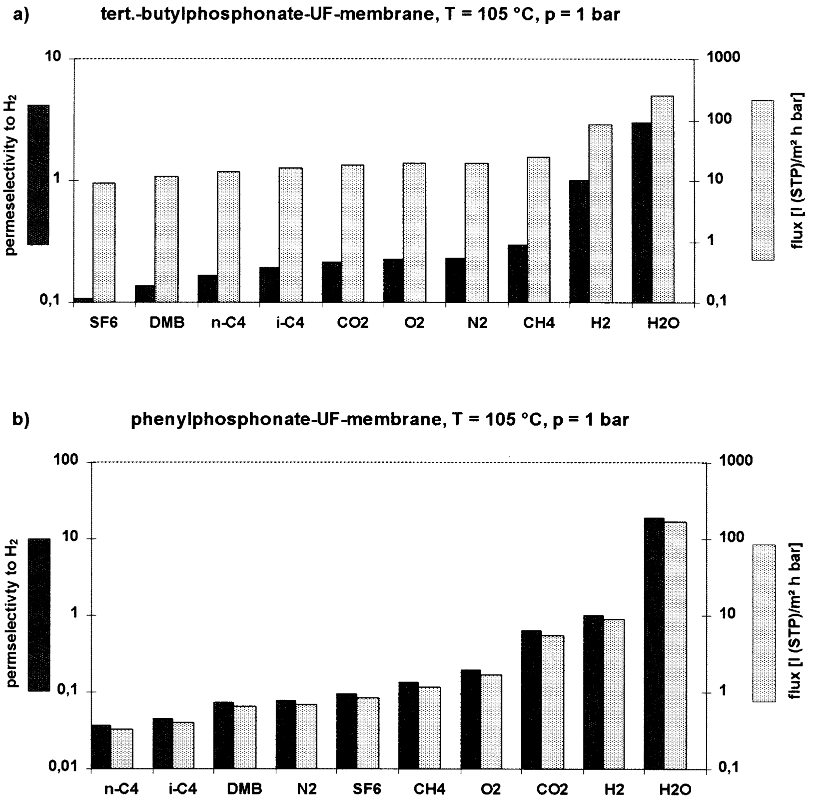

Fig. 6. Flux densities and permselectivities for ceramic UF filter with γ-Al_2O_3 top layer after treatment with phosphonic acids: (a) TBPA; (b) PPA.

treated with TBPA (Fig. 6(a)) and PPA (Fig. 6(b)). The TBPA-coated membrane exhibits for most of the probe gases permselectivities near to the Knudsen behaviour (Fig. 6(a)). After treatment with PPA, however, the fluxes became rather small, but the permselectivities are larger than the Knudsen factor (Fig. 6(b)), indicating a further pore narrowing. Owing to the reduced permeabilities for the butanes, we called this separation behaviour organophobic.

3.3.3. Thermal stability

The influence of increasing pretreatment temperatures on the flux and the permselectivity is shown in Table 5. At first sight it seems that there is a continuous damage of the membrane, the flux of hydrogen increases from 160 to 400°C by a factor of 30. Simultaneously the permselectivities for H_2/n-butane decrease from 12 to 4.5. By thermoanalysis it could be shown, however, that this effect is due to a reversible dehydration. After

Table 5
Influence of thermal treatment on the hydrogen flux and on the H_2/n-butane permselectivity of a phenylphosphonylated membrane. Measurements at 105°C

Pretreatment temperature (°C) for 0.5 h	160	200	250	300	350	400
H_2 flux (l(STP) m^{-2} h^{-1} bar^{-1})	25	41	51	110	430	790
Permselectivity H_2/n-butane	11.4	10.6	12	7.2	5.4	4.5

rehydrating the membrane, the former permeation data were obtained. Even after 45 h at 400°C, by rehydration the former permeation behaviour could be restored.

4. Conclusions

By chemical treatment of a UF ceramic filter, membranes for gas, vapour and liquid separation applications can be obtained. In all modifications, from single gas permeation measurements permselectivities were calculated which are higher than the Knudsen factor. The modified permeation behaviour is based on pore narrowing and a hydrophilic/organophilic pore wall functionalization. It is difficult to compare fluxes and selectivities with other preparations. The fluxes obtained in this paper are about 1.5 orders of magnitude less than those described in Ref. [5] (p. 419), Ref. [3] (p. 571) and Ref. [10]. Nevertheless, high selectivities seem interesting even if the fluxes are low.

The in-situ hydrolysis of TEOS by water adsorbed in the pores of the ceramic support gives a hydrophilic membrane for dehydratation purposes. The resulting silica-coated ceramics show almost constant permeation behaviour at 400°C. Promising application fields are the pervaporation of mixtures of water–organic solvents, including the breaking of azeotropes.

By silylating the γ-Al_2O_3 top layer, in a one-step preparation organophilic membranes can be prepared. The efficiency of silylation can be increased if the γ-Al_2O_3 top layer is coated with an Si–OH-rich silica film, thus providing anchor groups for the silylation. Promising results have been obtained with OTCS as silylating agent in combination with an Si–OH-rich silica layer. The silylated membranes are stable up to 230°C.

γ-Al_2O_3 can be modified in a one-step technique by phosphonylation using alkyl- or aryl-phosphonic acids. In a chemical reaction the phosphonic acid reacts with the Al of the support to give Al-phosphonates. An effective modification can be achieved if PPA is used. Owing to the relative stability of the P–C bond, the modification brought about by PPA is stable up to 400°C. Even after a thermal treatment over 45 h at 400°C, by rehydration the former permeation behaviour can be restored.

For an industrial use of ceramic membranes in gas separation further R&D is necessary to reduce the costs and to increase the specific membrane area per volume. For a 19-channel tube with 0.2 m^2 membrane area per metre of the tube length we have a packing of 220 m^2 membrane area per cubic metre. The price for such ultrafiltration module is at present about DM2500 m^{-2}. With increasing production quantities the price can be reduced [18]. Higher ratios of membrane area per volume can be obtained for ceramic hollow fibre membranes. First promising attempts are reported [29,30].

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