Microporous Membranes for Gas Separation

A study towards preparation and
characterization of different sol-gel
derived membrane materials

Martin Wolf

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MICROPOROUS MEMBRANES FOR GAS SEPARATION

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A STUDY TOWARDS PREPARATION AND CHARACTERIZATION OF DIFFERENT
SOL-GEL DERIVED MEMBRANE MATERIALS

DISSERTATION

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the degree of doctor at the University of Twente,
on the authority of the rector magnificus,

Prof. Dr. H. Brinksma,

on account of the decision of the graduation committee,

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Contents

1. Introduction	1
1.1 Inorganic membranes for gas separation	2
1.1.1 <i>Inorganic membrane materials</i>	3
1.1.2 <i>Gas separation mechanisms</i>	10
1.2 Sol-gel process	13
1.2.1 <i>Colloidal route</i>	14
1.2.2 <i>Polymeric route</i>	15
1.2.3 <i>Sol-gel membrane fabrication</i>	16
1.3 Description of the project	17
1.3.1 <i>Pre-combustion process</i>	17
1.3.2 <i>Post-combustion process</i>	18
1.3.3 <i>Oxyfuel combustion process</i>	19
1.4 Scope of the thesis	20
References	21
 2. Thermal stability and gas separation performance of hybrid inorganic-organic silica membranes	 27
Abstract	
2.1 Introduction	29
2.2 Experimental	30
2.2.1 <i>Sol synthesis</i>	30
2.2.2 <i>Gel and membrane preparation</i>	31
2.2.3 <i>Sol and gel characterization</i>	31
2.2.4 <i>Membrane characterization</i>	32
2.3 Results	33
2.3.1 <i>Sol characterization</i>	33
2.3.2 <i>Characterization of gels</i>	34
2.3.3 <i>Membrane performance and morphology characterization</i>	39
2.4 Discussion	45
2.4.1 <i>Thermal analysis of hybrid silica gels</i>	45

2.4.2	<i>Single gas permeance</i>	47
2.5	Conclusions	50
	Appendix I	52
	References	54
3.	Metal oxide doping of hybrid inorganic-organic silica membranes	57
	Abstract	
3.1	Introduction	58
3.2	Experimental	59
3.2.1	<i>Sol synthesis</i>	59
3.2.2	<i>Gel and membrane preparation</i>	61
3.2.3	<i>Sol and gel characterization</i>	61
3.2.4	<i>Membrane characterization</i>	61
3.3	Results	62
3.3.1	<i>Sol characterization</i>	62
3.3.2	<i>Characterization of gels</i>	63
3.3.3	<i>Membrane characterization</i>	65
3.4	Discussion	68
3.5	Conclusions	69
	References	70
4.	Influence of acid catalyst and acid concentration used in sol-gel processing on the microstructure of TEOS derived powders	73
	Abstract	
4.1	Introduction	74
4.2	Experimental	76
4.2.1	<i>Sol, gel, powder and membrane preparation</i>	76
4.2.2	<i>Sol, gel and powder characterization</i>	78
4.2.3	<i>Membrane characterization</i>	78
4.3	Results	79
4.3.1	<i>Sol characterization</i>	79
4.3.2	<i>Characterization of gels and powders</i>	80
4.3.3	<i>Membrane characterization</i>	85

4.4 Discussion	87
4.4.1 <i>TEOS sol particle size</i>	87
4.4.2 <i>Gel and powder characteristics</i>	87
4.4.3 <i>Membrane preparation and performance</i>	91
4.5 Conclusions	92
Appendix I	93
References	95
5. Fabrication of gas-tight ultrathin films of Ta₂O₅ by a sol-gel method	97
Abstract	
5.1 Introduction	98
5.2 Experimental	98
5.2.1 <i>Sol-gel processing</i>	98
5.2.2 <i>Characterization</i>	99
5.3 Results and discussion	100
5.4 Conclusions	105
References	106
6. Recommendations and Outlook	109
Summary	117
Samenvatting	119
Zusammenfassung	121
Acknowledgements	123

Chapter 1

Introduction

1.1 Inorganic membranes for gas separation

Gas permeation membranes are selective barriers between two phases with a higher permeation for one gas than for the other, see **Figure 1**. Gas transport through the membranes can be facilitated via different mechanisms, depending on the physical and chemical properties of the membrane and its interaction with the permeating gas, as discussed in Section 1.1.2.

Figure 1: Schematics of a membrane for gas separation [1].

The fast growth of earths' population carries along a growing demand for energy, water, food and many other resources. In some of these fields membranes play an important role. Examples include CO₂ separation for fossil and biomass power plants (**Figure 2**), industry and in purification of natural gas, H₂ separation for fuel cells, and O₂ separation from air. Due to their higher chemical and thermal stability, inorganic membranes are preferred over polymeric membranes, especially in more demanding high temperature applications.

Figure 2: (a) Coal-fired power plant Niederaußem, Germany [2], (b) farm-scale biogas plant [3].

1.1.1 Inorganic membrane materials

Inorganic membrane materials for gas separation can be categorized into 5 classes, namely *metallic*, *dense mixed conducting*, *zeolite*, *silica* and *hybrid inorganic-organic silica membranes*.

Metallic membranes have drawn a great deal of attention, mostly due to their commercial availability. These membranes exist in a variety of compositions and can be made into large-scale continuous films for membrane module assemblies [4]. So far the most effective metallic membranes available are primarily palladium (Pd)-based alloys exhibiting high permselectivity towards hydrogen and in general a good mechanical stability [5-10].

Figure 3: Different Ag-doped Pd-membrane geometries [11].

Originally used in the form of relatively thick dense metal membranes, the self-supporting membranes (50–100 μm) are considered unattractive because of their high costs, low permeance and low chemical stability [4]. Instead, a variety of techniques (e.g., chemical vapor deposition (CVD), sputtering, electroless plating, and spray pyrolysis) have been applied to yield thin Pd-based membranes, deposited onto porous ceramic or metal substrates [12–15]. Defect-free metal membranes are 100% selective towards hydrogen. Permselectivities over 10.000 have been reported for H_2/N_2 separation, with H_2 -fluxes as high as $1 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, [16]. One of the main problems, for membranes consisting of pure Pd, that remains is hydrogen embrittlement [17]. To overcome the problem, Pd is usually alloyed with other metals, such as Ag, Cu, and Ru [18]. Alloying Pd with Ag increases solubility of hydrogen, but decreases its diffusivity. In general, membranes from Pd alloys exhibit a better stability, lower material costs, higher hydrogen flux and better mechanical properties than pure Pd membranes [4].

Dense mixed conducting membranes form the second class of inorganic membranes. These are permeable to oxygen or hydrogen, and are commonly referred to as oxygen transport

membranes (OTM) and hydrogen transport membranes (HTM), respectively. Their selectivities are 100%, provided that they are fabricated dense, free of cracks and connected-through porosity. Transport is facilitated by joint diffusion of ions, either oxide ions or protons, and electrons, which process is known as ambipolar diffusion.

(a) Examples of materials used for fabrication of OTM's include fluorite oxide doped with mixed valent cations (e.g., Tb-doped CeO_2) or acceptor-doped perovskites (e.g., $\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$). The oxides contain high concentrations of mobile oxygen vacancies. [19]. The oxygen flux may be partly rate limited by the rate of the oxygen surface exchange reaction at both gas/solid interfaces. High operating temperatures, usually above 800 °C, are required for the OTM's to obtain sufficiently high oxygen fluxes [19]. Development of membranes operating in the intermediate range 600–800 °C is considered to be one of the major challenges in the field.

Three methods are commonly employed for synthesis of OTM materials [20]. The most conventional one is via solid state reaction of mixed oxides, carbonates, hydroxides or salts at elevated temperatures [21]. The second method, often used for synthesis of fluorite-oxides, is via co-precipitation [22-27]. The desired cations are dissolved in aqueous solution, which is mixed with a second solution acting as precipitation agent. The third method is the sol-gel method, following either the alkoxide [20,28], alkoxide-salt [20] or the EDTA/citrate complexation route [29-31]. All of these routes involve successive hydrolysis and condensation reactions, taking place at low temperature and, in general, yield a highly pure and homogeneous sol-phase. Dense materials can be acquired already at distinctly lower sintering temperatures as compared to the more conventional synthesis methods [20].

Promising applications for OTM membranes include oxygen production by separation from air, partial oxidation of natural gas to syngas, and processes which require either highly oxygen-enriched or pure oxygen streams, such as in oxyfuel power plant operation (see also **1.3.3**) [32-35].

(b) HTM's are mostly prepared from perovskite-type proton conductors, e.g. Y-doped SrCeO_3 [36-40]. Recently, rare-earth tungstates, exhibiting ordered defective fluorite or disordered pyrochlore structures [41-43], have been identified for use in high-temperature H_2

separation at 900-1100 °C [44-46]. The materials are synthesized by methods similar to those used for the preparation of OTM's [47-53]. HTM's are targeted for application in pre-combustion power plants, because of the high process temperatures [54-55]. Another potential application is their integration in catalytic membrane reactors for, e.g., non-oxidative coupling of methane and aromatization [46,56].

Zeolite membranes represent the third class of inorganic membranes. Zeolite materials combine small pore sizes with inherent mechanical, thermal, and chemical stability of their structure. The latter is essential for long-term operation [57]. The pores are uniform, and, hence, the performance of the zeolite membranes, intrinsically determined by the crystal structure [57-58]. The membranes can separate gases based upon size, shape or affinity [58-59].

If the well-defined zeolitic pore-network is intact, *molecular sieving* (see also **1.1.2**) is the mechanism of separation. Otherwise, *viscous flow* through the intercrystalline 'grain boundaries' may become predominant. The optimum membrane thickness is always a compromise between the separation performance and the trans-membrane flux, and is often tailored to the specific needs of the targeted application [57].

Zeolites are fabricated via the so-called one-step method or via secondary growth (seeding technique) [60]. In the former case, zeolite crystals are grown within the pores of a macroporous support, which results in a robust, defect-free membrane (e.g., MFI's [64-71]). However, the permeance of the membranes obtained in this way is usually lower than that found for membranes prepared via secondary growth [61]. In the latter method, crystal seeds are deposited on a suitable support surface, followed by their growth initiated through an appropriate hydrothermal treatment [60]. Inherent advantage is the high flux exhibited by the membranes prepared following this route. A disadvantage, however, may be the higher risk of obtaining defects and non-zeolitic pores at the grain boundaries.

Figure 4: Scanning electron micrograph of a thin, freestanding MFI-zeolite membrane [62].

The zeolite structure consists of AO_2 units with a tetrahedral coordination of the A atoms (e.g., Si, Al, B, Ge). The net overall charge of the framework is negative (except for neutral silica zeolite frameworks) and is charge compensated by either organic or inorganic cations. The first zeolite membrane was reported in 1987 [63]. Ever since, significant progress has been made. The number of zeolites utilized in membranes has increased, while membrane preparation has improved significantly. Today, more than 14 zeolite structures, including MFI [64-71], LTA [72-74], MOR [75-77], and FAU [78-81], have been employed as H_2 selective separation membranes [57]. Regrettably, none of them has demonstrated industrially viable permselectivities for H_2/CO_2 and H_2/N_2 separation.

Silica and *hybrid inorganic-organic silica membranes* represent, respectively, the fourth and fifth class of inorganic membranes. The membranes are usually asymmetric, consisting of a macroporous support, one or more mesoporous intermediate layers, and a permselective microporous top layer (see **Figure 5**). The pores in the microporous top layer are usually smaller than 2 nm. For gas separation, these need to be less than 0.7 nm.

Figure 5: Schematic build-up of a multilayered membrane with a microporous separation layer.

Microporous *silica membranes* exhibit mechanical, thermal and chemical properties like zeolites. Contrary to the crystalline zeolite membranes, these membranes consist of amorphous silica. Synthesis is primarily accomplished by sol-gel methods and chemical vapor deposition (CVD). Sol-gel methods enable fabrication of membranes with high selectivity and permeability. Membranes prepared by CVD show enhanced selectivity, albeit at the expense of permeability relative to the values found for membranes prepared by sol-gel methods. [57]. A general scheme for the fabrication of sol-gel derived membranes is shown in **Figure 6**. The sol-gel technique is discussed in section 1.2. A discussion of CVD methods is considered beyond the scope of this thesis. For a thorough discussion of these methods, the reader is referred to Ref [57, 82-83].

Figure 6: Colloidal and polymeric sol-gel processing routes for the preparation of porous inorganic membrane [107].

Sol-gel derived silica membranes exhibit high permeances for gases such as He, H₂, H₂O relative to gases with a larger kinetic diameter, e.g., CO₂, N₂, and CH₄. Selectivities for H₂/CO₂, H₂/N₂, H₂/CH₄ and CO₂/CH₄ can be as high as 98, >170, >5000 and >100, respectively [84]. Although silica membranes show a high thermal and chemical stability, they lose their excellent performance characteristics at elevated temperatures in the presence of steam due to degradation of the silica network associated with disruption of the Si-O-Si bonds [4, 85-87], and which process is accompanied with densification and formation of nano- and micro-sized defects. Microporous membranes prepared from zirconia or titania do not exhibit the tight network properties similar to amorphous silica that lead to high selectivities. The reported values for microporous zirconia or titania membranes are much lower than those reported for microporous silica [88-90]. Modification of the silica network by doping with metal oxides, e.g., NiO, CoO, MgO, Al₂O₃, ZrO₂, TiO₂, Fe₂O₃, Nb₂O₅, and others, has been attempted, but none of these studies was successful or convincingly demonstrated stabilization of the silica network under humid conditions [57]. Neither modification of the silica network by incorporation of, for example, alkyl- or fluorinated alkyl groups, aiming to hydrophobicity of the silica network significantly improves hydrothermal stability of microporous silica [85,91].

Microporous *hybrid inorganic-organic silica membranes* prepared from bis-silyl bridged silsesquioxane precursors (**Figure 7**) have been intensively investigated in the last few years. These show excellent performance in pervaporation, separating water from alcohols such as n-butanol, propanol and ethanol, up to temperatures of ~150 °C [93-95]. Since 2010, the hybrid silica membranes are commercially available [92].

Figure 7: 1,2-Bis(triethoxysilyl)methane (BTESM) and 1,2-Bis(triethoxysilyl)ethane (BTESE)

Similarly to silica membranes, the hybrid silica membranes are prepared via sol-gel methods. The organic bridging entity can be varied, which has a big influence on both synthesis

parameters as well as on material and membrane properties [96]. More details about the synthesis of these membranes is described in **Chapter 2** of this PhD thesis.

Besides their hydrothermal stability in pervaporation experiments, the hybrid silica membranes have a high resistance towards chemical attack by nitric or acetic acid [93-94]. The remarkable stability of the hybrid silica membrane is rooted in the improved connectivity of the silica network relative to that of pure silica, enhancing toughness and resistance towards nano- and micro-crack formation [95-97]. Application of the hybrid membranes in gas separation has also been investigated; the selectivities towards H_2/CO_2 and H_2/CH_4 separation are, however, far too poor to consider their commercial application [95-98]. Most recently, doping of the hybrid silica matrix with metal or transition metal oxides has been adopted as a strategy to improve performance of the hybrid membranes in gas separation. In particular, doping with acidic oxides such as niobia (Nb_2O_5) appears to be a promising route to obtain high H_2/CO_2 permselectivities [99-100].

1.1.2 Gas separation mechanisms

There are four main gas transport mechanisms, namely, viscous flow, Knudsen diffusion, surface diffusion and molecular sieving. Material and microstructure determine the predominant mechanism.

In the case of *viscous flow*, the mean free path of the gas molecules is small compared to the radius of the pore. The overall gas transport is determined mainly by collisions between the gas molecules, and, hence, viscous flow is non-selective. For porous membranes with pores in excess of 50 nm, viscous flow is the predominant transport mechanism [101].

Knudsen diffusion, surface diffusion and molecular sieving mechanisms are displayed in **Figure 8**. These are the three most important transport mechanisms for achieving gas separation [102-103]. *Knudsen diffusion* occurs when the mean free path is relatively long compared to the actual pore radius, and, hence, the molecules collide frequently with the pore wall. The gas selectivity is based on the differences in the mean free path of the involved gas molecules, which in turn is related to the differences in their molecular weight (**Table 1**). Knudsen diffusion is predominant for pores that range in diameter between 2 and 50 nm.

Figure 8: Schematic representation of Knudsen diffusion, surface diffusion and molecular sieving.

For *surface diffusion* the gas molecules adsorb onto the pore surfaces and move then along the pore walls governed by a decreasing surface gradient from one site to the next [57,121].

When the pore size is in the range of the kinetic diameter of the gas molecules, i.e., below 2 nm, gases having a smaller kinetic diameter will diffuse at a much faster rate than larger ones [102]. This is referred to as *molecular sieving*. Ideally, for a binary gas mixture, the membrane should exhibit a pore size distribution, which is both narrow and located between the kinetic diameters of the involved gas molecules (**Figure 9**). This is further detailed below.

Table 1: Kinetic diameter and molecular weight of several gases.

Molecule	Kinetic diameter (nm)	Molecular weight (Da)
He	0.26	4
H ₂	0.289	2
CO ₂	0.33	44
N ₂	0.364	28
CH ₄	0.38	16
SF ₆	0.55	146

The separation factor or selectivity is one of the most important intrinsic properties of a membrane as it describes the ability to separate one component from another. The selectivity for a binary system can be defined in terms of input and output concentrations [101]:

$$\alpha_{A/B,BINARY} = \frac{y_A / y_B}{x_A / x_B} \quad \text{Equation 1}$$

where x_A and x_B represent the feed concentrations of A and B, respectively, and y_A and y_B the corresponding concentrations in the permeate stream. The permeance itself represents the volume of a specific gas or liquid passing through the membrane per unit area, time and pressure. The ideal selectivity $\alpha_{A/B}$ (also referred to as permselectivity [104]) is defined by the ratio of the permeances of the individual components [103]:

$$\alpha_{A/B,IDEAL} = \frac{P_A}{P_B} \quad \text{Equation 2}$$

In the case of Knudsen gas transport, the selectivity for a binary gas mixture is given by the square root of the inverse ratio of the molecular weights of both gas molecules:

$$\alpha_{A/B,KNUD} = \sqrt{\frac{Mw_B}{Mw_A}} \quad \text{Equation 3}$$

In the case of molecular sieving, a high selectivity for one of the components is obtained only if the membrane exhibits a well-defined and narrow pore size distribution. **Figure 9** displays three examples of pore size distributions [105]. Consider a binary gas mixture consisting of hydrogen and nitrogen. The kinetic diameters of these gases are 0.289 and 0.364 nm, respectively. In the case of distribution I, the pore sizes are smaller than the kinetic diameters of both gases. This results in no gas transport across the membrane. In the case of distribution III, the pore sizes are larger than the kinetic diameters of both gases. No separation is achieved, unless transport occurs in the Knudsen flow regime. The optimum situation is distribution II, where the pore size distribution is in between the kinetic diameters of both gases. Separation is also achieved in the case of distribution II'.

Figure 9: The pore size distribution determines whether separation of gases H_2 and N_2 with different kinetic diameters can be achieved [105].

1.2 Sol-Gel Process

As mentioned in **1.1.1**, the sol-gel technique is commonly used for the preparation of micro- and meso-porous ceramic layers, which includes silica and hybrid silica membranes. Adequate control of the reaction parameters such as pH, time, temperature, mixing, and use of template molecules enable tailoring of the pore size, pore shape, and porosity [106]. The sol-gel technique can be divided in two routes, the colloidal suspension route and the polymeric sol-gel route. Both methods employ the use of a metal oxide precursor $M(OR)_x$, where M is the metal, and OR (OC_nH_{2n+1}) the alkoxy-group. A commonly used precursor for silica is tetraethylorthosilane $Si(OC_2H_5)_4$ (TEOS). The alkoxide precursor is hydrolyzed, which is followed by condensation with other monomers and oligomers via formation of oxygen-bridges to organic-inorganic polymers or polymeric clusters. The degree of hydrolysis strongly depends on the amount of water, the presence of a catalyst (and/or modifier), resulting in either partial or complete substitution of the alkoxy-groups by hydroxyl-groups. The hydrolysis and condensation reactions are displayed in **Figure 10**.

Figure 10: Hydrolysis and condensation reactions in sol-gel synthesis [108].

1.2.1 Colloidal suspension route

In this route, the alkoxide and salt precursors are polymerized using an over-stoichiometric amount of water to yield complexly branched structures. Because of the high amount of water, the precursors tend to be fully hydrolyzed. Subsequent condensation leads to the formation of three-dimensional particles (**Figure 11**). The latter consists of a rather compact core, surrounded by unreacted OH-groups. These hydroxyl groups inhibit the particles from agglomeration [101]. The particle sizes are typically in the range 10-180 nm. The colloidal route is usually catalyzed by a base (**Figure 12**), and is ideally suited for the synthesis of crystalline, mesoporous materials, e.g., γ -alumina.

Figure 11: (a) Polymeric and (b) colloidal sol-gel particles.

Figure 12: Schematic reaction mechanism of the base catalyzed sol-gel reaction [108].

1.2.2 Polymeric route

Contrary to the colloidal suspension route, the precursor molecules are dissolved in organic media, usually alcohol. Water is added in a sub-stoichiometric or stoichiometric amount to replace only a part of the alkoxy-groups by hydroxyl-groups. This, results in partial condensation, and subsequent condensation leads to the formation of linear or randomly branched polymers (**Figure 11**). The polymeric route is generally catalyzed by acids [106, 108] (**Figure 13**).

Figure 13: Schematic reaction mechanism of the acid catalyzed sol-gel reaction [108].

Within the polymeric sol-gel route the reactivity of the metal alkoxide precursor plays an important role. Depending on the electronegativity of the metal ion, its redox properties and preferred coordination, its reactivity is either slow or fast. When the electrophilic strength of the central metal atom is low, the kinetics of nucleophilic substitution like the hydrolysis reaction is strongly favored. A nucleophilic substitution is also favored when the central transition metal has an unsaturated coordination. These properties render most of the metal alkoxide precursors hydrophilic, often hygroscopic. For this reason, humidity of the solvent must be minimal to prevent premature hydrolysis of the precursor [108-109].

Other reaction parameters can be varied to control kinetics of the sol-gel reaction. Lower concentrations of water usually lead to slower hydrolysis rates, but if too low no reaction at all might occur. Also, by mere dilution of the solution, the kinetics will become slower. By changing

the pH of the solution, the reaction kinetics can be influenced, noting that the hydrolysis reaction is either acid or base catalyzed. Chemically modification of the precursor is another option to tailor the reaction kinetics. The –OR ligands can be partially or completely substituted by more electronegative groups [108-110]. The reactivity of the precursor molecule can be lowered by complexation with ligands such as acetylacetonate and alcohol amines, but also with chlorides, alcohols, acids and bases [28,106]. There are numerous parameters involved in the sol-gel reaction that influence textural and structural properties of the synthesized materials. For a more extensive discussion, the reader is referred to the cited literature.

1.2.3 Sol-gel membrane fabrication

Membrane fabrication via the sol-gel route is a multi-step process, and is briefly depicted in **Figure 6**. The first step is the synthesis of the sol as detailed in **1.2.1** and **1.2.2**. The second step involves the coating, e.g., spin-coating or dip-coating, where the sol is applied to the substrate, followed by drying of the layer until all solvent is evaporated, and a gel has been formed. Important parameters that influence coating are pore size and roughness of the substrate, and particle size and viscosity of the sol. The drying process depends on the nature of the precursor solvent. The sols via the polymeric route are usually prepared using an alcohol as solvent, and the gelation process is comparatively fast. Colloidal sols with their much higher water content need longer drying times. Sometimes drying needs be carried out at controlled humidity and temperature to avoid cracking [119].

The drying step is followed by firing the membrane at temperatures above 300 °C. The aim of firing is two-fold: to obtain a certain texture and morphology, and to consolidate the structure [106]. Another objective of firing is to burn off organic residues, originating from the solvent, precursor and possible additives, but also to remove water, which can block the pores and inhibit permeation. Depending on the substrate and intended application of the membrane, the coating step can consist of multiple cycles with intermediate calcination steps.

1.3 Description of the project

The work presented in this thesis has been carried out in the Inorganic Membrane group of the University of Twente (The Netherlands). The group participates within the Institute for Nanotechnology (MESA+). The work has been conducted within the framework of the multi-partner MEM-BRAIN alliance funded by the Helmholtz Association (Germany), and the follow-up Portfolio project funded by the Forschungszentrum Jülich GmbH (Germany). Major mission of both projects is the development of gas separation membranes for zero-emission fossil power plants. Some details of both projects are given below. A more detailed discussion is provided elsewhere [111].

Reduction or elimination of CO₂ emissions from power plants fuelled by coal or gas, are subject of many research and development activities. Power plants account for more than 40% of the global anthropogenic CO₂ emissions, and therefore are the main focus of CO₂ capture and storage technologies (CCS). Three core CO₂ capture technologies are pre-combustion (**Figure 14**), post-combustion (**Figure 15**) and oxyfuel combustion (**Figure 16**) capture [111-116]. Simulation studies have shown that integration of membrane-based separations can both increase efficiency and reduce costs, while yielding concentrated CO₂ streams for sequestration [120].

1.3.1 Pre-combustion process

The membrane target in pre-combustion carbon capture is the separation of hydrogen (H₂) from carbon dioxide (CO₂). This separation step is preceded by the gasification of the fossil fuel (coal, natural gas or oil) by oxygen, which is provided by an air separation unit (ASU), operating at high pressures (60 bar) and high temperatures (400-600 °C) [116]. In this part of the process, syngas is produced which primarily consists of H₂ and CO. The CO is reacted with steam in a water-gas shift (WGS) reactor to H₂ and CO₂. The CO₂ content in the effluent stream is between 15 and 40 vol% [116-117]. After the shift reaction, the gas primarily consists of H₂ and CO₂. The H₂ is then separated from CO₂, and can be used as an energy-rich fuel for further combustion, while CO₂ is transported to the storage site.

For this H₂/CO₂-separation process, characterized by its intermediate to high temperatures and high pressures, the use of microporous ceramic membranes is considered. Modified silica (SiO₂), zirconia (ZrO₂) and zirconia-titania (ZrO₂-TiO₂) have been proposed as suitable membrane materials. The lack of stability of these materials in humid environments

[111] has initiated research towards membranes derived from tantalum, niobium and hybrid inorganic-organic silica. The latter type of membranes were investigated within this PhD work.

Figure 14: Schematic overview of the pre-combustion process.

1.3.2 Post-combustion process

In the post-combustion process, the CO₂ is separated from the flue gas after combustion of the fossil fuel. Here, the fuel is combusted together with air, which process is used to produce electricity via a steam turbine. The flue gas contains CO₂, typically in the range from a few to 15 vol%. Two other components are nitrogen and water vapor [114,116]. The separation is usually carried out at atmospheric pressure and temperatures between 80 and 160 °C.

In view of the moderate temperatures and pressures, mainly CO₂-selective polymeric membranes are considered for separating out the CO₂ from the flue gas. Some additional requirements for the membranes are that these should be non-abrasive, and exhibit low swelling and low flue-ash cake build-up. Also microporous ceramic membrane may be considered for separation.

Figure 15: Schematic overview of the post-combustion process.

1.3.3 Oxyfuel combustion process

In this process, the fuel is burned using a mixture of pure oxygen and recycled CO_2 to yield exhaust gases containing more than 75 % CO_2 [118]. The concentration of CO_2 in the flue gas can be increased by condensation of water. The oxygen for the burning of the fuel is provided by an ASU. The recycling and mixing of CO_2 to the oxygen is necessary to maintain the temperature in the combustion chamber for all construction materials at an acceptable level [116]. Important cost aspect for the oxyfuel process is the separation of O_2 from air in the ASU.

The heart of the oxyfuel combustion process is the ASU, where the O_2/N_2 -separation is accomplished. Conventionally, this is achieved by cryogenic air separation, but this may also be accomplished by the use of mixed ionic-electronic conducting (MIEC) ceramic membranes. These materials allow 100 % selective oxygen permeation. One drawback is their high operation temperature, which is in the range of 800-1000 °C.

Figure 16: Schematic overview of the oxyfuel combustion process.

1.4 Scope of this thesis

The key objectives of the research described in this thesis are the preparation and performance characterization of sol-gel derived microporous ceramic membranes. Main focus is their potential integration in the pre-combustion process for the separation of H_2 from CO_2 out of the H_2 -rich gas stream after the water-gas-shift reaction; a minor focus is on the performance of the membranes for H_2/N_2 , H_2/CH_4 , H_2/C_2H_6 , and CO_2/CH_4 separation.

Chapter 2 investigates the effect of the organic bridging group in hybrid inorganic-organic silica on the properties and performance of membranes derived from these materials. 1,2-Bis(triethoxysilyl)methane (BTESM), 1,2-Bis(triethoxysilyl)ethane (BTESE) and Bis(triethoxysilyl)ethylene (BTESY) are used as precursors to prepare sols, gels and subsequently, membranes. The stability of the materials in different calcination atmospheres and temperatures is studied, additionally to their effects on the hybrid silica membranes.

Chapter 3 describes the effect of metal oxide doping on the properties and performance of BTESE-derived membranes. Alumina (Al_2O_3), silica (SiO_2) and germania (GeO_2) are employed as dopants.

Chapter 4 systematically investigates the effect of employing different acids, and acid concentrations, during sol synthesis. Main focus of the work is on the sulfuric acid-assisted synthesis preparation of silica, which includes characterization of the performance of membranes prepared via this synthesis route.

Chapter 5 describes the preparation of thin films of tantalum oxide (Ta_2O_5) by sol-gel processing.

Chapter 6 summarizes main conclusions drawn from this work and finally provides some recommendations for further research.

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Chapter 2

Thermal stability and gas separation performance of hybrid inorganic-organic silica membranes

Abstract

The thermal stability of hybrid inorganic-organic silica gels, derived from 1,2-bis(triethoxysilyl)-precursors with either bridging methane, ethane, or ethylene (BTESM, BTESE, and BTESY, respectively) was assessed up to 600 °C under both air and inert atmosphere, using combined thermogravimetry, temperature-programmed decomposition and Fourier-transform infrared spectroscopy. Decomposition of the organic moiety in the hybrid silicas is initiated by heating in inert atmospheres at a temperature above 550, 480 and 480 °C, respectively, in the order as given above. These temperatures are about 200 °C higher than the corresponding onset temperatures for decomposition found when heated in air. Calcination experiments indicate that the decomposition is kinetically very sluggish. Data of infrared spectroscopy show that the organic moiety may persist even after several hours of calcination of the hybrid silica above the onset temperature for decomposition, irrespective of the calcination atmosphere.

Asymmetric membranes were prepared by dip-coating hybrid silica sols (only BTESM and BTESE) onto alumina-based porous supports, followed by calcination under nitrogen or air in the temperature range 400 - 600 °C. Single gas (H₂, CO₂, N₂, CH₄, SF₆) permeance measurements were carried out for characterization. These confirmed formation of defect-free membrane top-layers, given that the permeance for SF₆ (with kinetic diameter of 5.5 Å) was found below the limit of detection. Selectivities close to the corresponding theoretical Knudsen values are calculated for pairs of the other gases when the membranes are calcined under nitrogen. Surprisingly high selectivities are found when BTESE membranes are calcined under air. For the membrane calcined at 450 °C, selectivities at 200 °C as high as 46 and 203 are calculated for H₂/N₂ and H₂/CH₄ separation, increasing to values of 53 and 336, respectively, at 100 °C. More research is required to elucidate the origin of the enhanced selectivity of BTESE membranes after air calcination at 450 °C, and to which extent the observations can be accounted for by partial decomposition of the ethane-bridging group in BTESE.

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2.1 Introduction

Hydrogen permselective membranes can be integrated in a water-gas-shift (WGS) reactor for pre-combustion carbon capture for the separation of H_2 from CO_2 [1-2]. Taking into account the elevated temperature at which the WGS reaction occurs, typically 400-600 °C, their robust character makes inorganic membranes preferred over polymeric membranes. Microporous silica membranes have been investigated intensively because of their high fluxes and selectivities [3-4]. However, application of these membranes is constrained by their limited hydrothermal stability [5-8]. Humidity is found to rupture the siloxane (-Si-O-Si-) bonds, causing a collapse of the amorphous silica network and concomitant loss of separation performance [7-8]. Several attempts have been undertaken to improve the hydrothermal stability of silica, e.g., by methylation [8-9], doping with metal ions [10-14] and pore carbonization [15]. Zirconia, titania and composites thereof have been explored as membrane for gas separation; however, none of these showed the targeted membrane performance [6, 16-18].

More recently, the use of hybrid inorganic-organic silica has been proposed as an alternative membrane material [19-20]. By using bridged silsesquioxane precursors (e.g., shown in **Figure 1**) during sol-gel synthesis, the Si-O-Si bonds in the silica skeleton are partially replaced by Si-C-Si or Si-C-C-Si bonds. The hybrid silica membranes outperform those prepared from pure silica in long-term pervaporation tests under humid conditions [21-24], which includes their long-term stability at low pH values [9-12]. Their performance in gas separation thus far, however, is too poor to consider them as candidates for integration in a WGS reactor [6, 23, 25-28].

In the present study, we have investigated the influence of atmosphere and temperature of calcination on the stability and single gas permeance of selected hybrid silica membranes.

Figure 1: Structural formulas of 1,2-bis(triethoxysilyl)-based precursors with bridging methane, ethane and ethylene, respectively, as employed in this study.

2.2 Experimental

2.2.1 Sol synthesis

1,2-Bis(triethoxysilyl)ethane (BTESE, 97% pure, ABCR) was dissolved in absolute ethanol (dried, Emsure[®], Merck). The solution was placed into an ice bath to prevent premature hydrolysis. A known volume 1 M HNO₃ was dropped into the solution, and the solution heated under reflux for 90 min at 60 °C. Then, a similar volume of 1 M HNO₃ was added, and the refluxing continued for an additional 90 min. Subsequently, the obtained sol was cooled down to room temperature. The same procedure was employed to prepare sols from 1,2-bis(triethoxysilyl)methane (BTESM, 97% pure, ABCR). 1,2-Bis(triethoxysilyl)ethylene (BTESY, 95% pure, 80% trans-isomer, ABCR) was dissolved in absolute ethanol (dried, Emsure[®], Merck), and the obtained solution placed in an ice bath. Contrary to the above procedure, after the addition of 1 M HNO₃, the solution was stirred under cooling with ice for 40 min. The calculated molar ratios used in the sol synthesis were BTESE : ethanol : H₂O : HNO₃ of 1 : 6.54 : 4.38 : 0.082, and similarly for BTESM and BTESY. The corresponding sols were diluted with ethanol 6, 6 and 9 times, respectively, prior to further use.

2.2.2 Gel and membrane preparation

Dried gels were obtained by drying the sols in a Petri dish for 8-16 h in a fume hood. Calcined powders were obtained by calcining dried gels at temperatures between 400 and 600 °C for 3 h in either nitrogen or air with constant heating/cooling rates of 0.5 °C min⁻¹. For the preparation of membranes a home-made support, comprising a macroporous α -alumina layer with a mesoporous γ -alumina layer [29], was coated with the hybrid silica sol under clean room conditions in a flow hood (Interflow). After dip-coating (substrate speed 10 mm s⁻¹, dip-time 5 s) the membranes were calcined at temperatures between 400 and 600 °C under flowing nitrogen or air for 3 h, using constant heating/cooling rates of 0.5 °C min⁻¹.

2.2.3 Sol and gel characterization

Particle size distributions of the hybrid silica sols were obtained by dynamic light scattering (Zetasizer NanoZS, Malvern Instruments). Measurements were performed on 1.0 – 1.5 ml of the sol contained in a disposable sizing cuvette (Type DTS0012). The particle size was measured immediately after synthesis. To verify whether particle growth would occur over time, the sols were stored both at room temperature and in a freezer at -28 °C, and measured again after several months of storage.

Thermogravimetric analysis (STA 449 F3, Netzsch) was conducted on powders of dried gels. After prior evacuation of the sample chamber, the samples were heated from room temperature to 800 °C at a heating rate of 5.0 °C min⁻¹ under flowing nitrogen (50 ml min⁻¹) or synthetic air (100 ml min⁻¹). Temperature-programmed decomposition measurements were carried out in a home-built setup. A small amount of the sample was loaded between two quartz wool plugs in the center of a tubular quartz micro-reactor with inner diameter of 2 mm, and subsequently heated under a continuous flow (50 ml min⁻¹) of air or argon to 800 °C at a heating rate of 5 °C min⁻¹. The effluent gas was analyzed on line by a mass spectrometer (Omni Star™ TM GSD 301 Pfeiffer Vacuum). Signals at m/z 28, 44, 16, 28, 30, 46, 2 and 18 amu were recorded for detection of CO, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₂H₅OH, H₂, and H₂O, respectively.

Fourier-transform infrared spectroscopy (FT-IR) spectra of dried BTESE and BTESM gels were recorded on a Bruker Tensor 27 equipped with a sapphire crystal. Measurements

were conducted in the attenuated total reflectance mode. A baseline correction was applied to the spectra.

Gas sorption measurements were conducted on dried hybrid silica gels, calcined at 400-600 °C, using N₂ (Micromeritics Tristar) or CO₂ (Quantachrome Autosorb AS-1) as adsorbates. N₂ adsorption/desorption isotherms were measured at -196 °C after degassing the samples at 200 °C under vacuum with N₂ as refill gas. CO₂ sorption measurements were conducted at 0 °C after degassing at 300 °C under vacuum with helium as refill gas.

2.2.4 Membrane characterization

Single-gas (He, H₂, CO₂, N₂, CH₄, SF₆) permeation measurements were performed at 200 °C in the dead-end mode without backpressure and a transmembrane pressure difference between 1.8 – 2.5 bar (**Figure 2**). The membranes were sealed in a stainless steel module with Viton® O-rings with the separation layer exposed to the feed side. Prior to the measurements, the membranes were dried overnight at 200 °C under flowing helium. The gas permeance was calculated by dividing the flux by the transmembrane pressure difference.

Figure 2: Schematics of the experimental set-up used for gas permeation measurements.

The static water contact angle on the membrane surface was measured using a contact angle analyzer (OCA 20, Dataphysics Instruments). The microstructure of the membranes was

investigated by transmission electron microscopy (TEM), using a Tecnai G2 F20 (FEI) instrument operated at an acceleration voltage of 200 kV. The specimens were produced by means of a focused-ion beam process (Helios Nanolab 400s, FEI) with subsequent argon-ion milling.

2.3 Results

2.3.1 Sol characterization

Figure 3a shows the particle size distribution of the different hybrid silica sols as measured immediately after their synthesis, whilst **Figure 3b** shows the effect of storage temperature and duration on the corresponding distribution (for the BTESM sol).

As can be seen from **Figure 3a**, all obtained sols exhibit a unimodal particle size in the range of 1-20 nm. **Figure 3b** shows that the particle growth at room temperature is more pronounced than in the freezer at -28 °C. The average particle size shifts from a maxima value of 2.3 nm measured immediately after synthesis to 4.2 nm after one month of storage at room temperature, and to 2.7 nm after storage of five months at -28 °C. Similar observations (not shown here) were made for BTESE. For BTESY, a pronounced particle growth to an average size of 19 ± 1 nm was observed after three days of storage at room temperature (not shown).

Figure 3: (a) Particle size distributions of hybrid silica sols, and (b) effect of storage temperature and duration on the particle size distribution of the BTESM sol.

2.3.2 Characterization of gels

Figures 4, 5 and 6 show data of thermal analysis of the dried gels of BTESM, BTESE and BTESY. These are combined plots of the data of thermogravimetry (TGA) and temperature-programmed decomposition (TPD), the latter showing evolved hydrogen and carbon-containing gases during heating under air or inert atmosphere. Plots of all gases quantified during heating under air are provided in the appendix of this chapter.

All three compositions exhibit profound weight losses below ~ 300 °C. Above 300 °C, the heating atmosphere becomes distinctive to the weight losses observed for the different hybrid silica materials. The weight losses recorded for the dried BTESM gel (**Figure 4**) under both air and inert atmosphere extend up to 800 °C, corresponding to the maximum temperature of the measurements. The weight loss under air is more pronounced as that observed under inert atmosphere. At temperatures above ~ 600 °C, H_2 and some CH_4 are released upon heating under inert atmosphere. Any release of CO, CO_2 , C_2H_2 , C_2H_4 , C_2H_6 , and C_2H_5OH could not be quantified. Upon heating under air, a release of carbon-containing gases CO, CO_2 and CH_4 occurs at an onset temperature of ~ 400 °C. Some hydrogen is released as H_2 , but most of it in the form of H_2O (see **Figure A.1**)

Figure 4: TGA and TPD data recorded upon heating of a dried BTESM gel under (a) inert atmosphere (nitrogen or argon) and (b) air. Heating rates are 5 °C/min. Carbon-containing gases include in (a) CH_4 , and in (b) CO, CO_2 and CH_4 .

TGA and TPD-data for the dried BTESE gel recorded under air and inert atmosphere are illustrated in **Figure 5**. Under inert atmosphere, the weight loss between 300 and 800 °C occurs gradually with an enhanced weight loss at an onset temperature of ~ 500 °C. Data of TPD shows

that this enhanced weight loss is accompanied by releases of H_2 and carbon-containing gases CH_4 , C_2H_2 , and C_2H_4 . Under air, the weight loss strongly accelerates around 300 °C and continues up to 800 °C. Over the whole temperature range, the weight loss is accompanied by strong releases of carbon-containing gases CH_4 , CO and CO_2 . Hydrogen is predominantly released in the form of H_2O (see **Figure A.2**).

Figure 5: TGA and TPD data recorded upon heating of a dried BTESE gel under (a) inert atmosphere (nitrogen or argon) and (b) air. Heating rates are 5 °C/min. Carbon-containing gases include in (a) CH_4 , C_2H_2 , and C_2H_4 , and in (b) CH_4 , CO and CO_2 .

TGA and TPD data recorded for the dried BTESY gel are shown in **Figure 6**. Under inert atmosphere, several weight losses are observed between 200 and 500 °C. Although CH_4 and H_2 gases are evolved above ~500 °C, no significant weight loss occurs. Under air, a gradual weight loss occurs above ~200 °C, and is concurrent with releases of carbon-containing gases CO , CO_2 and methane. Hydrogen is predominantly released in the form of H_2O (See **Figure A.3**).

Figure 6: TGA and TPD data recorded upon heating of a dried BTESY gel under (a) inert atmosphere (nitrogen or argon) and (b) air. Heating rates are 5 °C/min. Carbon-containing gases include in (a) CH₄, and in (b) CH₄, CO and CO₂.

Figure 7 shows FT-IR spectra of BTESM and BTESE gels calcined under different conditions (temperature and annealing atmosphere). Both spectra show a broad peak at 960-1220 cm⁻¹ that is predominantly caused by the asymmetric stretching vibration of the Si-O-Si inorganic backbone. The Si-O-C asymmetric stretching vibration cannot be identified because it overlaps with the Si-O-Si asymmetric stretching band [30]. The peak at 700-860 cm⁻¹, which may be due to Si-C stretching vibrations and rocking vibrations of the methyl groups in Si-CH₃, is a better indication of the presence of covalently bound carbon in the network, although the peak may overlap with symmetric Si-O-Si stretching vibrations at lower wavenumbers [30].

The FT-IR spectra of BTESM and BTESE gels show a small peak, at 1360 and 1400 cm⁻¹, respectively, designated by I in **Figures 7a and b**. These peaks can be assigned to C-H₂ bending vibrations [30]. In both spectra, a small peak is also apparent at 1275 cm⁻¹, designated by II. This peak is characteristic for the vibration of Si-C bonds [32,34].

Figure 7: FT-IR spectra of calcined gels of (a) BTESM and (b) BTESE. The sample labels include the temperature and atmosphere of calcination. Also shown for comparison is the spectrum for a pure silica gel after calcination, at 450°C, under air.

Figure 8 shows CO₂-sorption isotherms from measurements on calcined BTESM and BTESE gels. When calcined under nitrogen, CO₂ sorption on both BTESM and BTESE gels decreases with increasing temperature of calcination, while the opposite trend is found for samples calcined under air. **Table 1** lists characteristic micropore volumes, surface areas and adsorption energies evaluated from the data given in **Figure 8** using the Dubinin-Radushkevich equation [33]. Both micropore volume and surface area decrease with increasing temperature of calcination when calcination is performed under nitrogen, but are found to decrease when calcination is performed under air. For the BTESY gel, calcined at either 400 °C or 500 °C in N₂ and air, no significant CO₂ adsorption was observed. Significant nitrogen sorption was not found onto any of the samples.

Figure 8: CO₂-sorption isotherms at 0 °C for calcined gels of (a) BTESM, (b) BTESE, (c) BTESM and (d) BTESE. The sample labels include the temperature and atmosphere of calcination.

Table 1: Micropore volume, surface area and adsorption energy of BTESM and BTESE gels. Data evaluated from CO₂ adsorption isotherms (Fig. 8) using the Dubinin-Radushkevich equation. Values in parentheses are standard deviations (in units of the least significant digit) from regression analysis of experimental data. The sample label includes the temperature and atmosphere of calcination.

Material	Micropore volume (cc/g)	Surface area (m ² /g)	Adsorption energy (kJ/mol)
BTESM-400-N ₂	0.101(2)	302(6)	19.7(4)
BTESM-500-N ₂	0.092(2)	275(5)	16.7(3)
BTESM-600-N ₂	0.023(1)	68(1)	17.3(4)
BTESM-400-Air	0.113(2)	338(7)	18.0(4)
BTESM-450-Air	0.169(3)	506(10)	18.2(4)
BTESE-400-N ₂	0.114(2)	341(7)	16.2(3)
BTESE-500-N ₂	0.087(2)	262(5)	17.4(4)
BTESE-400-Air	0.079(2)	236(4)	15.0(3)
BTESE-450-Air	0.084(2)	251(5)	16.6(3)

2.3.3 Membrane performance and morphology characterization

Supported hybrid silica membranes were prepared by dip-coating onto a macroporous α -Al₂O₃ support disc using a γ -Al₂O₃ intermediate layer, following standard procedures developed earlier in our laboratory (see also experimental section) [29]. Optical microscopy and SEM analysis of the membranes showed formation of a smooth and crack-free morphology at all applied calcination temperatures. **Figures 9 and 10** show typical TEM images of membrane cross sections, revealing formation of an amorphous layer of the hybrid silica, which thickness may be well below 100 nm.

Figure 9: Cross-sectional TEM image of a BTESM membrane calcined for 3h, at 400°C, under nitrogen. The cover layers (Au, Pt) were deposited in an initial step in order to protect the hybrid silica toplayer during sectioning with the FIB.

Figure 10: Cross-sectional TEM image of a BTESE membrane calcined for 3h, at 450°C, under air. The cover layers (Au, Pt) were deposited in an initial step in order to protect the hybrid silica toplayer during sectioning with the FIB.

Data of static contact angle measurements for the three different membranes investigated in this work is given in **Figure 11**. For all membranes, calcined at different temperatures under nitrogen, the contact angle is found to be smaller than 90°. Those measured for BTESM tend to be slightly smaller than for BTESE and BTESY membranes. No clear trend is seen with increasing the calcination temperature of the membranes. **Figure 12** additionally compares data of contact angle measurements of BTESE membranes calcined under either nitrogen or air, with that measured for a silica membrane calcined under air. Note the similar contact angles measured for the BTESE membranes after calcination, at 450 °C, under different atmospheres, and the fact that these are significantly larger than the value measured for the pure silica membranes calcined, at 400 °C, under air.

Figure 11: Water contact angles measured for BTESM, BTESE and BTESY membranes. The sample labels include the temperature and atmosphere of calcination.

Figure 12: Water contact angles measured for BTESE and silica membranes. The sample labels include the temperature and atmosphere of calcination.

Figures 13 and **14** show data from single-gas permeance measurements of the hybrid silica membranes obtained after calcination under different conditions. The corresponding conditions are shown in the sample labels. Except for the BTESY membranes, the permeance of SF₆ is found below the detection limit ($\sim 1 \times 10^{10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) of the experimental apparatus. The overall trend seen from both figures is that the permeance decreases with increasing kinetic diameter of the gas molecule, and with increasing calcination temperature. Note from **Figure 14** the lowering in the permeance of gases with a comparatively high kinetic diameter found for the BTESE membrane after calcination at 450 °C in air. **Figure 15** additionally shows gas permeance data for the latter membrane recorded at different temperatures.

Figure 13: Single gas permeances of hybrid silica membranes investigated in this work obtained after calcination, under nitrogen, at (a) 300-400 °C, and (b) 500 °C. Data were recorded, at 200 °C, and at a pressure differential of 2 bar across the membrane. Besides the atmosphere, the sample labels show the temperature of calcination. Also shown in (a) are data from literature (open symbols).

Figure 14: Single gas permeances of BTESM and BTESE membranes obtained after calcination, at 400-450 °C, under air. Data were recorded, at 200 °C, and at a pressure differential of 2 bar across the membrane. Besides the atmosphere, the sample labels show the temperature of calcination.

Figure 15: Single gas permeance of a BTESE membrane obtained after calcination, at 450 °C, under air. Data were recorded at the temperatures indicated, maintaining a pressure differential of 2 bar across the membrane.

2.4 Discussion

2.4.1 Thermal analysis of hybrid silica gels

The thermal stability of gels based on BTESM, BTESE, and BTESY in different atmospheres has been assessed by TGA/TPD measurements. Corresponding data are given in **Figures 4, 5 and 6**. These clearly indicate that thermal decomposition of the hybrid silica is influenced by the nature of the organic moiety, and by the calcination atmosphere.

Under nitrogen, the onset temperatures of decomposition of BTESM, BTESE and BTESY gels are 550, 480 and 480 °C, respectively. The decomposition is accompanied by weight losses. These are found most significant for the BTESE gel, where (in addition to H₂) CH₄, C₂H₄ and C₂H₂ are found to be the major gases released upon decomposition. In the case of BTESM and BTESY, only CH₄ is expelled as carbon-containing gas. The higher onset temperature of decomposition is found for the BTESM gel, and suggests that, under non-oxidative conditions, scission of carbon-carbon bonds, rather than the bond between silicon and carbon, initiates decomposition of BTESE and BTESY gels. The concurrent release of H₂ (dehydrogenation) suggests formation of carbonaceous species. The latter is also evident from the higher overall weight loss observed when the hybrid silica gel is heated under air relative to that when heated under nitrogen.

In addition, the onset temperature of decomposition is lowered when calcination of the hybrid silica is performed under air rather than nitrogen. In the order as given above, the onset temperatures are lowered to 400, 250 and 200 °C, respectively. The weight losses associated with decomposition, however, extend up to very high temperatures of ~800 °C. Similar observations have been reported by others [23,26,35], and are taken as evidence that the associated kinetics of thermal cracking of the organic moiety in the hybrid silica matrix is very slow. Some weight losses are noted below the actual onset temperature of decomposition. Since these take place without accompanying release of carbon-containing gases, they are explained by the removal of chemisorbed water and/or condensation of vicinal Si-OH groups.

As was discussed in the previous section (see Section 2.3.2), the major characteristic peaks of polysiloxane structures can be identified in the FT-IR spectra recorded for calcined BTESM and BTESE hybrid silica gels (**Figure 7**). Peaks denoted by I and II in **Figure 7** are taken as evidence for the presence of the organic moieties in both materials, which is further justified by the absence of these peaks in the FT-IR spectrum recorded for pure silica. Note from **Figure**

7 that both peaks I and II are preserved even after calcination of the gels for 3 h at 500 °C, irrespective of the calcination atmosphere. When heated under air, the latter temperature is distinctly above the decomposition temperatures of both gels, confirming that the decomposition of the organic moiety in both hybrid silicas is kinetically very sluggish.

In an exploratory study of the decomposition of BTESE gel under inert atmosphere using TPD, the temperature was incremented stepwise, with intervals of 25 °C up to 600 °C and at heating rate of 5 °C min⁻¹. At each interval temperature the sample was equilibrated for 1h. The results obtained are displayed in **Figure 16**. It can be seen that the material evolves hydrogen and carbon-containing gases (CH₄, C₂H₂, C₂H₄, and C₂H₆) up to the highest temperature covered with this experiment. In essence, the data confirm the slow decomposition kinetics of the organic moiety in this material.

Further to the thermal stability and kinetics of decomposition of the hybrid silicas, water contact angle measurements were performed on membranes calcined under various conditions. Values in the range 67-81° are obtained for the hybrid silicas containing a C₂-bridging group (BTESE, BTESY) after their calcination for 3h, at 400-500 °C, under nitrogen. These values are slightly larger than those measured for BTESM membranes, calcined under similar conditions, showing values in the range 51-60° (**Figure 11**). The fact that the extent of hydrophobicity is retained after the calcination under the above specified conditions merely validates the conclusions from the data of TGA/TPD and FTIR about the thermal stability and slow kinetics of decomposition of the organic moiety in the hybrid silicas. Surprisingly, however, the value of the contact angle observed for the BTESE membrane is retained when calcination is performed for 3h, at 450 °C, under air (**Figure 12**). Note the temperature of calcination is 200 °C above the onset temperature of decomposition under air as determined by TGA/TPD measurements. A contact angle of value 82±4° is measured for the BTESE membrane after calcination in air, whilst 32±4° is measured for a pure silica membrane (**Figure 12**). Assuming partial decomposition to have occurred, the observations may be accounted for by the presence of a retained fraction of the organic moiety in BTESE after the calcination procedure, which conclusion is in line with the observations from FT-IR.

Figure 16: TPD data for a dried gel of BTESE recorded under argon atmosphere using a stepwise heating scheme. The curves are shifted to each other for clarity.

2.4.2 Single gas permeance

Supported hybrid silica membranes were prepared by dip-coating onto home-made alumina-based multilayers supports. In general, a narrow and unimodal particle size distribution of the applied coating sol is considered a prerequisite for depositing defect-free membrane layers. The sols prepared in this study (see **Figure 3**) do comply with this requirement. The homogeneous appearance of the membranes as observed by optical and electron microscopy essentially confirms appropriateness of the dip-coating procedure. For a detailed description of the employed dip-coating procedure, see Ref. [36].

The data from sorption measurements on BTESE- and BTESM-based gels (**Figure 8** and **Table 1**) indicate that the materials retain their microporous characteristics even after calcination in the range 400-600 °C, albeit that significant densification occurs at the highest temperatures. It may be anticipated that densification of the hybrid silica matrix lowers the pore size, and is beneficial to obtaining permselectivity. In order to study the effect of calcination temperature on the single gas permeance, the hybrid membranes were calcined at different temperatures up to a maximum temperature of 600 °C in this study. Corresponding data from gas permeance measurements are shown in **Figures 13** and **14**.

The dependence of the permeance on the kinetic diameter of the permeating gas molecule, seen in both figures and which is observed for all membrane compositions and calcination temperatures, is indicative of separation by a molecular sieving mechanism. The permeance of SF₆ for all membranes (except for BTESY-500-N₂) is found below the detection limit. This essentially corroborates that the effective pore diameter of the membranes is less than the kinetic diameter of SF₆ (5.5 Å), and that the membranes are free of defects and/or pinholes.

Table 2: Permselectivities of different gas pairs for BTESM, BTESE and BTESY membranes calcined for 3h, at different temperatures, either under nitrogen or air atmosphere. Values were calculated from data of single gas permeance measurements, at 200 °C (see Figures 13 and 14). Knudsen selectivities are given in parentheses.

	H ₂ /CO ₂ (4.7)	H ₂ /N ₂ (3.7)	H ₂ /CH ₄ (2.8)	H ₂ /SF ₆ (8.6)	CO ₂ /CH ₄ (1.7)
<i>BTESM</i>					
400 °C N ₂	3.4	8.9	8.7	> 3000	2.6
500 °C N ₂	4.7	5.4	5.1	> 3000	1.1
600 °C N ₂	6.1	10.7	16.4	> 3000	2.7
400 °C Air	3.6	8.2	8.6	> 3000	2.4
450 °C Air	4.1	8.8	8.4	> 3000	2.0
<i>BTESE</i>					
400 °C N ₂	3.8	8	6	> 3000	1.5
500 °C N ₂	5.6	8.9	12	> 3000	2.2
400 °C Air	3.9	9.4	11.2	> 3000	2.9
450 °C Air	7.6	46	209	> 3000	28
<i>BTESY</i>					
400 °C N ₂	3.2	4.3	5.4	240	1.7
500 °C N ₂	3.9	4.7	6.3	1500	1.6

The ratio of single-gas permeances is referred to as the ideal selectivity. Calculated values for different binary gas pairs are listed in **Table 2**. These were calculated from data of single gas permeance measurements, at 200 °C, as shown in **Figures 13 and 14**. The high selectivities (> 3000) obtained for the H₂/SF₆ pair; in essence, confirm the molecular sieving

character and the defect-free state of the membranes, as was already discussed above. The general trend emerging from the data presented in **Table 2** is that the selectivity tends to increase with increasing membrane calcination temperature. The selectivities obtained for the membranes, in particularly those calcined under nitrogen, are poor and only slightly above the corresponding Knudsen values.

Surprising high selectivities are obtained for the BTESE membrane calcined for 3h, at 450 °C, under air. Values of 46 and 203 are calculated for the H₂/N₂ and H₂/CH₄ selectivities, respectively, to be compared with 64 and 561 measured at similar conditions for state-of-the-art silica membranes (calcined at 400 °C) by de Vos and Verweij [3]. Even higher values are obtained from data of measurements carried out at lower temperatures (**See Table 3**). The H₂/N₂ and H₂/CH₄ selectivities increase towards 53 and 336, respectively, as calculated from the data of gas permeance measurements carried out at 100 °C (**Figure 15**). Concurrently, the CO₂/CH₄ selectivity increases from 28, at 200 °C, to a value of 90, at 100 °C. The latter selectivity would facilitate use of the membranes for, e.g., upgrading of biogas and natural gas [1,37]. Note further from the data in **Table 3** that the selectivity enhancement is obtained upon increasing the temperature of calcination from 400 to 450 °C. It thus seems likely that the observations are induced by further thermal decomposition of the hybrid silica, and concomitant densification of the microporous microstructure upon increasing the temperature of calcination. As discussed in the introduction, the use of microporous membranes prepared from pure silica is severely constrained by its limited hydrothermal stability. To which extent the current BTESE membranes are stable in humid environments at elevated temperatures awaits further research. As detailed knowledge is lacking, more research is also required to understand the complex thermal decomposition behaviour of the organic moieties in the hybrid silicas.

Table 3: Permselectivities of different gas pairs for BTESE membranes calcined for 3h, at 450 °C, under air. Values were calculated from data of single gas permeance measurements at temperatures indicated (see Figure 15). Knudsen selectivities are given in parentheses.

	H ₂ /CO ₂ (4.7)	H ₂ /N ₂ (3.7)	H ₂ /CH ₄ (2.8)	H ₂ /SF ₆ (8.6)	CO ₂ /CH ₄ (1.7)
200 °C	7.6	46	209	> 3000	28
100 °C	3.6	53	336	> 3000	90
30 °C	2.5	65	190	> 3000	77

2.5 Conclusions

BTESM, BTESE, and BTESY are low-end members of bridged silsesquioxane precursors commonly employed for sol-gel processing, via the polymeric route, for the preparation of (micro-)porous ceramics. Because of the proven stability of microporous membranes derived from BTESE and BTESM under humid conditions, i.e., in pervaporation [21], the hybrid silicas hold a particular promise for gas separation at elevated temperatures, e.g., in a water-gas-shift reactor with integrated hydrogen separation, provided that their permselectivities can be improved. The aim of this research was two-fold: first, to evaluate the thermal stability of the hybrid silicas, and second, to study the effect of calcination temperature and atmosphere on the permselectivity.

Using combined TG, TPD and FT-IR on dried gels of BTESM, BTESE, and BTESY it was demonstrated that thermal decomposition of the organic moiety occurs in inert atmospheres at a temperature above 550, 480 and 480 °C, respectively, in the order as given. These temperatures are about 200 °C higher than the corresponding onset temperatures for decomposition upon heating under oxidizing (air) conditions. Decomposition appears to be kinetically very sluggish. Data of infrared spectroscopy indicate that the organic moiety may persist even after several hours of calcination of the hybrid silica above the onset temperature for decomposition, irrespective of the calcination atmosphere.

Asymmetric membranes were obtained by dip-coating the hybrid silica sols prepared from BTESM and BTESE onto alumina-based porous supports, followed by calcination under nitrogen or air in the temperature range 400-600 °C. Single-gas permeance measurements indicated formation of defect-free membrane top-layers. The permeance for SF₆ (with kinetic diameter of 5.5 Å) was found well below the limit of detection, whilst typical values of 5×10^{-6} mol m⁻² s⁻¹ Pa are found for the H₂ permeance. The calculated permselectivities for different binary pairs of gases H₂, CO₂, N₂, CH₄ are close to the corresponding theoretical Knudsen values when the membranes are calcined under nitrogen. Surprisingly high selectivities are found when BTESE membranes are calcined under air. For a membrane, calcined at 450 °C, selectivities as high as 46 and 203 are calculated for H₂/N₂ and H₂/CH₄ separation when the gas permeance measurements are conducted at 200 °C. Even higher permselectivities are obtained when the measurements carried out at lower temperatures. At 100 °C, the H₂/N₂ and H₂/CH₄ selectivities increase towards 53 and 336, respectively. The selectivity enhancement is observed upon increasing the temperature of calcination of the BTESE membrane, in air, from

400 to 450 °C. The latter temperature is about 200 °C above the onset temperature of thermal decomposition of the ethane-bridging group in BTESE. At first glance, the observations can be accounted for by densification of the microporous microstructure of the hybrid silica upon increasing the temperature of calcination. Data from TGA/TPD, FT-IR and contact angle measurements provide evidence that despite the high temperature of calcination, only partial decomposition of the organic moiety in BTESE has occurred. The extent to which partial decomposition contributes to the observed high selectivity and the membrane shows stability in humid environments is a matter of ongoing research.

Appendix I Chapter 2

Figure A1: Evolved gases recorded during temperature-programmed decomposition (TPD) of dried BTESM gel under air at a heating rate of 5 °C/min.

Figure A2: Evolved gases recorded during temperature-programmed decomposition (TPD) of dried BTESE gel under air at a heating rate of 5 °C/min.

Figure A3: Evolved gases recorded during temperature-programmed decomposition (TPD) of dried BTESY gel under air at a heating rate of 5 °C/min.

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Chapter 3

Metal-oxide doping of hybrid inorganic-organic silica membranes

Abstract

A screening study is performed to investigate the influence of metal-oxide doping on the single-gas permeance of hybrid bis(triethoxysilyl)ethane (BTESE) membranes. Alumina, silica, and germania were respectively used as dopants, at doping levels in the range 4 - 16 mol%. Continuous and defect-free membranes were fabricated via dip-coating of co-polymerized BTESE sols onto multilayered alumina supports, and subsequent firing under nitrogen at 400 °C. Out of the three dopants, doping of BTESE with germania was found to be the most successful. H_2/N_2 and H_2/CH_4 permselectivities, at 200°C, are found to increase from 8.0 and 5.9, respectively, for pure BTESE to values of 25.3 and 32.5, respectively, for 16 mol% Ge-doped BTESE membranes.

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3.1 Introduction

Inorganic membranes for gas separation, e.g., hydrogen separation from steam-reforming streams [1], hydrogen purification and carbon dioxide removal from natural gas [2], have raised much interest over the past two decades. Amorphous microporous silica membranes meet many criteria needed (high fluxes and high permselectivities at elevated temperatures, ease of fabrication, low cost of production and scalability [2-7]) for application, but their structural instability under humid conditions restricts application to dry environments. Water disrupts the silica network [8-12], inducing densification [8,9], and growth of pore size, resulting in a loss of membrane permselectivity [13].

Different routes have been employed to improve the hydrothermal stability of silica membranes. These are: increasing the hydrophobicity of silica matrix, e.g., by methylation [14,15], post-carbonization of the membranes [16], doping of the silica matrix with metal oxides, e.g., NiO, CoO, Al₂O₃, MgO, ZrO₂, TiO₂, Fe₂O₃, Nb₂O₅ [9,17-22], and finally, using alkane-bridged silsesquioxanes as alternative precursor for tetraethylorthosilane (TEOS) so as to produce a hybrid organosilica membrane [23-27]. However, none of these attempts has been fully satisfying so far.

The hybrid organosilica membranes show excellent performance stability during dewatering of lower alcohols by pervaporation, as demonstrated in several studies of membranes derived from 1,2-bis(triethoxysilyl)ethane (BTESE) [23,25,33]. However, the permselectivities of BTESE membranes measured in gas separation are poor [6, 23, 25-28, 35], though calcination of the membranes under air at temperatures high enough to induce partial decomposition of the ethane bridge group was found to give remarkably high permselectivities for H₂/N₂ and H₂/CH₄ separation [35]. Recently, Qi et al. [28, 29] reported high H₂/CO₂ permselectivities and high hydrothermal stability for niobia-doped BTESE membranes. Attempts in our laboratory to verify the results obtained by Qi et al. are ongoing, with the note that thus far no consistent and reproducible results could be obtained following the procedure as described by the cited authors. This might indicate that sol-gel processing as a method to prepare the hybrid silica membranes may be quite sensitive to the applied process parameters.

Aim of the present study is to investigate the influence of metal-oxide doping on single gas permeance of BTESE membranes. Alumina (Al₂O₃), silica (SiO₂), and germania (GeO₂) are used as dopants, and the extent of doping is varied to estimate the influence on sol characteristics (particle size, gas adsorption), and gas permeance behavior of the membranes derived from the corresponding sols.

3.2 Experimental

3.2.1 Sol synthesis

3.2.1.1 Pure BTESE synthesis

1,2-Bis(triethoxysilyl)ethane (BTESE, 97% pure, ABCR) was dissolved in absolute ethanol (dried, Emsure®, Merck). To prevent premature hydrolysis, the obtained solution was immediately placed into an ice bath, followed by the drop-wise addition of 1 M nitric acid. After an additional 5 min in the ice bath, the mixture was refluxed at 60 °C for 90 min, and an equal amount of 1 M nitric acid was added. The refluxing was continued for 90 min, after which the sol was allowed to cool to room temperature. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ of 1 : 6.54 : 4.38 : 0.082 was diluted 6 times with ethanol prior to further use.

3.2.1.2 Al-doped BTESE synthesis

a) 4 mol% Al-doped BTESE

Absolute ethanol was placed into an ice bath. Under continuous stirring 1 M nitric acid and, subsequently, BTESE were added dropwise. After an additional 5 min in the ice bath, the mixture was refluxed at 60 °C for 45 min. Next, aluminium nitrate (Al(NO₃)₃, Aldrich) was added to the mixture and the refluxing continued at the same temperature for another 45 min. Hereafter, the sol was allowed to cool to room temperature. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ : Al(NO₃)₃ of 1 : 6.35 : 4.1 : 0.052 : 0.04 was diluted 9 times with ethanol prior to further use.

b) 8 mol% Al₂O₃-doped BTESE

Aluminium nitrate was dissolved in absolute ethanol, and the mixture placed in an ice bath. Under continuous stirring 1 M nitric acid and, subsequently, BTESE were added dropwise. After an additional 5 min in the ice bath, the mixture was refluxed at 60 °C for 90 min. Hereafter, the sol was allowed to cool to room temperature. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ : Al(NO₃)₃ of 1 : 6.35 : 3.7 : 0.044 : 0.08, was diluted 9 times with ethanol prior to further use.

3.2.1.3 Si-doped BTESE synthesis

a) 4 mol% Si-doped BTESE

Absolute ethanol was placed into an ice bath, and 1 M nitric acid was added dropwise. Next, BTESE and TEOS (tetra-ethyl-ortho-silane, Aldrich, 98%) were added dropwise to the mixture under continuous stirring. After an additional 5 min in the ice bath, the mixture was refluxed at 60 °C for 120 min. Hereafter, the sol was allowed to cool to room temperature. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ : TEOS of 1 : 7.63 : 4.26 : 0.053 : 0.04 was diluted 7 times with ethanol prior to further use.

b) 8 mol% Si-doped BTESE

Absolute ethanol was placed into an ice bath, and nitric acid (1 M) was added dropwise. Next, BTESE and TEOS were added dropwise to the mixture under continuous stirring. The mixture was refluxed at 60 °C for 120 min, after which the sol was allowed to cool to room temperature. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ : TEOS of 1 : 7.63 : 4.26 : 0.053 : 0.08 was diluted 7 times with ethanol prior to further use.

3.2.1.4 Ge-doped BTESE synthesis

a) 8 mol% Ge-doped BTESE

BTESE was dissolved together with germanium ethoxide (Ge(OEt)₄, Aldrich, 98%) in absolute ethanol. To prevent premature hydrolysis, the obtained solution was immediately placed into an ice bath, followed by the drop-wise addition of 0.705 M nitric acid. After an additional 5 min in the ice bath, the mixture was refluxed at 60 °C for 30 min. Next, the mixture cooled to 25 °C, and stirred for another 30 min. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ : Ge(OEt)₄ of 1 : 14.15 : 5.38 : 0.072 : 0.08 was diluted 6 times with ethanol prior to further use.

b) 16 mol% Ge-doped BTESE

BTESE was dissolved together with germanium ethoxide in absolute ethanol. To prevent premature hydrolysis, the obtained solution was immediately placed into an ice bath, followed by the drop-wise addition of 0.705 M nitric acid. After an additional 5 min in the ice bath, the mixture was stirred at 25 °C for 60 min. The obtained sol with a molar ratio of BTESE : ethanol : H₂O : HNO₃ : Ge(OEt)₄ of 1 : 14.15 : 5.38 : 0.072 : 0.16 was diluted 6 times with ethanol prior to further use.

3.2.2 Gel and membrane preparation

Dried gels were obtained by drying the sols in a Petri dish for 8-16 h in a fume hood. Calcined powder was obtained by calcining dried gels at temperatures at 400°C for 3 h under nitrogen using constant heating/cooling rates of 0.5 °C min⁻¹. For the preparation of membranes a home-made support, comprising a macroporous α -alumina layer with a mesoporous γ -alumina layer, was coated with the hybrid sol under clean room conditions in a flow-cupboard (Interflow). After dip-coating (substrate speed 10 mm s⁻¹, dip-time 5 s) the membranes were calcined at 400 °C in nitrogen atmosphere for 3 h using constant heating/cooling rates of 0.5 °C min⁻¹.

3.2.3 Sol and gel characterization

Particle size distributions of the hybrid silica sols were obtained by dynamic light scattering (Zetasizer NanoZS, Malvern Instruments). Measurements were performed on a small amount of sample (1.0 – 1.5 ml) in a disposable sizing cuvette (Type DTS0012). The particle size was measured immediately after synthesis.

Thermogravimetric analysis (STA 449 F3, Netzsch) was conducted on dried gels. After evacuation of the sample chamber, the samples were heated from room temperature to 1000 °C at a constant heating rate of 5.0 °C min⁻¹ under flowing nitrogen (50 ml min⁻¹) or synthetic air (100 ml min⁻¹). Sorption measurements (Quantachrome Autosorb AS-1) were performed on calcined powders using CO₂ as adsorbate. The measurements were carried out at 0 °C after degassing at 300 °C for 2-12 h under vacuum with helium as refill gas.

3.2.4 Membrane characterization

Single-gas (He, H₂, CO₂, N₂, CH₄, SF₆) permeation measurements were performed at 200 °C in the dead-end mode without backpressure and a transmembrane pressure difference between 1.8 – 3.0 bar. The membranes were sealed in a stainless steel module with Viton® O-rings with the separation layer exposed to the feed side. Prior to the measurements, the membranes were dried overnight at 200 °C under flowing helium. Permeances were calculated by dividing the flux by the transmembrane pressure difference. Ideal permselectivities were calculated as the ratio of the permeance of two gases.

The microstructure of the membranes was investigated by transmission electron microscopy (TEM), using a Tecnai G2 F20 (FEI) instrument operated at an acceleration voltage

of 200 kV. The specimens were produced by means of a focused-ion beam process (Helios Nanolab 400s, FEI) with subsequent argon-ion milling.

3.3 Results

3.3.1 Sol characterization

The particle size of all sols ranged from 1 to 20 nm (**Figure 1**). The maxima particle size values are 2.7 nm for pure BTESE, 3.1 nm for 4 mol% Al- and 8 mol% Al-doped BTESE, respectively, 2.7 nm and 3.1 nm for 4 mol% Si- and 8 mol% Si-doped BTESE, respectively, and 4.8 nm and 3.6 nm for 8 mol% Ge- and 16 mol% Ge-doped BTESE, respectively.

Figure 1: Particle size distributions of (a) Al-doped, (b) Si-doped and (c) Ge-doped BTESE sols, as measured by dynamic light scattering. Data obtained for pure BTESE is shown in all three figures.

3.3.2 Characterization of gels

Data of TGA of the different gels recorded under nitrogen is shown in **Figure 2**. The weight at 150 °C, after the loss of water and ethanol, was set to 100% to enable comparison between the data for the different gels on a 'dried' basis.

Figure 2: TGA data of (a) Al-doped, (b) Si-doped, and (c) Ge-doped BTESE-gels. Data recorded under nitrogen with a constant heating rate of 5 °C/min. The weight at 150 °C was set to 100%. Data obtained for pure (undoped) BTESE is shown in all three figures.

For the pure BTESE gel, a gradual weight loss is observed extending over the entire range of temperature of the experiment. An enhanced weight loss occurs around 575 °C. Similar thermal behavior is observed for the doped BTESE gels, albeit that the weight losses around 575 °C are notably less pronounced for the Al-doped BTESE gels (**Figure 2a**) compared with those of pure BTESE, and the Si- and Ge-doped BTESE gels (**Figure 2b and c**). Further note that the overall weight loss for the Al-doped BTESE gels is larger than for pure BTESE. All samples were rendered black after the thermal analysis.

CO₂ sorption isotherms of the gels after calcination under nitrogen at 400 °C are shown in **Fig. 3**. Physical parameters estimated using the Dubinin-Radushkevich model [34] are given in **Table 1**. Excluding the data obtained for 16 mol% Ge-doped BTESE, the surface areas are in the range 233-341 m²/g. For the gel derived from 16 mol% Ge-doped BTESE, however, a distinctly lower surface area of 120 m²/g is measured. For the latter gel also comparatively low values are found for the micropore volume and the activation energy of CO₂ sorption, as can be judged from the data listed in Table 1.

Figure 3: CO₂-sorption isotherms at 0 °C of (a) Al-doped, (b) Si-doped, and (c) Ge-doped BTESE gels after calcination under nitrogen at 400 °C. Data obtained for pure (undoped) BTESE is shown in all three figures.

Table 1: Micropore volume, surface area and adsorption energy for pure (undoped) and doped BTESE gels. Data evaluated from CO₂ adsorption isotherms (Fig. 3). Values in parentheses are standard deviations (in units of the least significant digit) from regression analysis of the experimental data.

Dopant concentration (mol%)	Micropore volume (cc/g)	Surface area (m²/g)	Adsorption energy (kJ/mol)
- (undoped)	0.114(2)	341(9)	16.2(3)
4 mol% Al ₂ O ₃	0.078(1)	233(5)	16.1(3)
8 mol% Al ₂ O ₃	0.107(2)	320(6)	17.4(3)
4 mol% SiO ₂	0.096(2)	287(6)	16.5(3)
8 mol% SiO ₂	0.090(2)	269(5)	16.5(3)
8 mol% GeO ₂	0.104(2)	313(6)	17.2(3)
16 mol% GeO ₂	0.040(1)	120(2)	14.9(3)

3.3.3 Membrane characterization

Optical microscopy and SEM analysis of the alumina-supported doped BTESE membranes in all cases showed formation of a smooth and crack-free layer. TEM analysis of the membranes revealed a 140-150 nm thick amorphous hybrid inorganic-organic silica layer. A typical cross-sectional TEM image of a supported membrane is shown in **Figure 4**.

Figure 4: TEM pictures of the cross-section of an alumina-supported 16 mol% Ge-doped BTESE membrane after calcination at 400 °C under nitrogen.

Figure 5 shows data of single-gas permeance measurements of pure and doped BTESE membranes prepared in this study. The calculated ideal selectivities for different gas pairs calculated from these data are listed in **Table 2**.

Figure 5: Single gas permeances (a) Al-doped, (b) Si-doped, and (c) Ge-doped BTESE membranes. Data were recorded at 200 °C, and at a pressure differential of 2 bar across the membrane. Data obtained for pure (undoped) BTESE is shown in all three figures.

Table 2: Permselectivities of different gas pairs for pure (undoped) and doped BTESE membranes. Values were calculated from data of single gas permeance measurements (Fig. 5). Knudsen selectivities are given in parentheses.

Dopant concentration	H ₂ /CO ₂ (4.7)	H ₂ /N ₂ (3.7)	H ₂ /CH ₄ (2.8)	H ₂ /SF ₆ (8.6)	CO ₂ /CH ₄ (1.7)
- (undoped)	3.8	8.0	5.9	> 3000	1.5
4 mol% Al ₂ O ₃	3.6	7.4	8.2	> 3000	2.3
8 mol% Al ₂ O ₃	3.6	7.6	11.1	> 3000	3.1
4 mol% SiO ₂	3.7	5.3	7.1	> 3000	1.9
8 mol% SiO ₂	3.7	6.9	9.6	> 3000	2.6
8 mol% GeO ₂	4.4	12.8	14.9	> 3000	3.4
16 mol% GeO ₂	5.3	25.3	32.5	> 3000	6.2

3.4 Discussion

The particle size distributions of the doped BTESE sols prepared in this study are all observed in the targeted range of 1 to 20 nm, which is considered to be suitable for further processing of the polymeric sols to produce microporous membranes [27]. The parameters used in the sol preparation, such as pH of the solution, reflux temperature and time, were optimized by trial and error, starting from the procedure previously developed to prepare stable sols from the parent BTESE precursor [35].

Data of thermogravimetry of the dried gels prepared from the sols recorded under nitrogen (**Figure 2**) indicate that within the range of the applied dopant concentrations, the onset temperature of decomposition of BTESE, estimated to approximately 550 °C, is not significantly affected by doping of the hybrid silica network. From the present investigations it is not clear whether in accord with the definition of Zachariasen [36] the dopant oxides enter the network as *network formers* or *network modifiers*. The absence of a significant weight loss at this temperature in the Al-doped BTESE gels (**Figure 2a**) could be interpreted to reflect stabilisation of the BTESE hybrid network by the alumina doping. However, more research is needed to verify such a conclusion. The higher overall weight loss noted for the Al-doped BTESE gels relative to pure BTESE may be attributed to thermal decomposition of (alumina) nitrate used in preparation of the corresponding sols.

Sorption measurements of the gels calcined at 400 °C under nitrogen (**Figure 3**) indicate that only in the case of the gel derived from 16 mol% Ge-doped BTESE significant densification of the microstructure has occurred relative to that observed for pure BTESE. In all cases, Type I adsorption isotherms are observed for both undoped and doped hybrid silica's, confirming formation of a microporous network.

The recipes developed in this study to prepare doped BTESE sols are considered appropriate for the production of membranes. Optical microscopy, SEM and TEM analyses showed formation of an amorphous, continuous and defect-free membrane after deposition of the individual sols on alumina supports, and subsequent firing at 400 °C under nitrogen. The low permeance of SF₆ (below the detection limit of 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹) observed for all of the membranes prepared in this study not only confirms the absence of undesired pin holes or defects, but also that the effective pore diameter of the membranes is below that of the kinetic diameter of SF₆ (5.5 Å). **Table 2** lists ideal permselectivities of different gas pairs calculated from data of single-gas permeance measurements (**Figure 5**). High H₂/SF₆ permselectivities

(> 3000) are calculated for all of the membranes. Permselectivities for the other gas pairs are, however, only slightly above their corresponding Knudsen values. The single exception in this regard concerns membranes prepared from 16 mol% Ge-doped BTESE, for which notably higher permselectivities are calculated for H₂/N₂ and H₂/CH₄ pairs relative to corresponding values calculated for pure BTESE membranes. The H₂/N₂ and H₂/CH₄ permselectivities increase from 8 and 6 for the latter membranes to 25 and 33, respectively, for membranes prepared from 16 mol% Ge-doped BTESE. These values ought to be compared with H₂/N₂ and H₂/CH₄ permselectivities 64 and 561 calculated from single-gas permeance data of state-of-the-art silica membranes (calcined at 400 °C) [4]. The observations bring us to the conclusion that among the dopants considered in this study, germania is the most promising to improve the permselectivity of BTESE membranes. In this study, the maximum germania dopant concentration was 16 mol%. An obvious consideration is to further increase this concentration. However, due to time limitations no further studies were conducted. In a follow-up study, also the effect of germania doping on the hydrothermal stability of the obtained hybrid silica membranes is deemed necessary.

3.5 Conclusions

The influence of metal-oxide doping on the single-gas permeance of BTESE membranes was explored through the use of alumina, silica, and germania as dopants in the range of 4 - 16 mol%. Polymeric sol solutions with particle sizes in the range 1 - 20 nm were prepared using, in addition to 1,2-bis(triethoxysilyl)ethane (BTESE), either aluminium nitrate, germanium ethoxide or tetraethylorthosilane (TEOS) as co-precursor. As for pure (undoped) BTESE [35], continuous and defect-free metal-oxide-doped BTESE membranes could be fabricated via dip-coating of the co-polymerized BTESE onto multilayered alumina supports, and subsequent firing under nitrogen at 400 °C. The best performance in this study is found for Ge-doped BTESE membranes. H₂/N₂ and H₂/CH₄ permselectivities (calculated from data of single-gas permeance measurements at 200 °C) are found to increase from 8.0 and 5.9, respectively, for pure BTESE to values of 25 and 33, respectively, for 16 mol% Ge-doped BTESE membranes. Emphasis is drawn towards further optimization of the dopant concentration, and towards investigation of the hydrothermal stability of the metal-oxide-doped hybrid silica membranes.

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Chapter 4

Influence of acid catalyst and acid concentration used in sol-gel processing on the microstructure of TEOS derived powders

Abstract

The influence of the amount and type of acid in the acid-catalyzed sol-gel processing of tetraethylorthosilicate (TEOS) on the microstructure of silica powders derived from the corresponding sols has been investigated. By replacing the HNO_3 acid catalyst in a home-developed recipe for the synthesis of a TEOS sol, by either HCl , H_3PO_3 , H_3PO_4 , H_2SO_4 , or acetic acid, it is found that the type of acid and its concentration used in hydrolysis and condensation of TEOS greatly affects the apparent particle size in the sol, and modality of the associated distribution. However, no immediate correlation is found between these characteristics and the type and extent of porosity obtained after calcination of the gel powders at either 400 or 600 °C. Data of thermogravimetry and nitrogen sorption measurements on these powders reveal that the release of volatile components, among which those formed by thermal decomposition of the conjugate base ions (of the applied acid catalyst), and sintering during calcination largely determine the emerging microstructure, i.e., pore size and porosity, of the obtained silica powders. Results from initial experiments where selected sols prepared using different acids are used for the preparation of ceramic membranes, and corresponding data of single gas permeance are presented.

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4.1 Introduction

Gas separation membranes have become widely used for a variety of industrial gas separations over the past two decades. For high temperature applications, inorganic (e.g., metallic, ceramic and zeolite) membranes are preferred over polymeric membranes [1-3]. For obtaining a high flux and a high selectivity, the supported, microporous functional layer needs to be ultrathin with a narrow pore size distribution. A membrane material meeting these qualifications is microporous silica. The pore size of microporous silica can be tuned by controlling the catalyst during sol-gel processing. Using acid-catalyzed sol-gel processing of tetra-ethyl-ortho-silicate (TEOS), microporous silica membranes have been prepared with a pore size between 0.3 - 0.5 nm, reaching permselectivities, at 200 °C, of about 70 and over 130 for H₂/CO₂ and H₂/N₂, respectively [4]. Though the thermal stability of microporous silica is known to be high, the material suffers from a poor structural stability in humid environments. Water disrupts the silica network, inducing densification and concomitant pore growth, which results in a gradual loss of membrane permselectivity when exposed to humid process streams [2, 5-7]. Despite this serious drawback, microporous silica membranes offer great potential for, e.g., hydrogen separation from dry process streams [8].

The sol-gel method permits synthesis at low temperatures, and is commonly used for the fabrication of silica ceramics [10]. In addition to annealing atmosphere, temperature and curing time, a number of reaction parameters influences pore size, pore shape and porosity, and, ultimately, the performance of the membranes. Relevant reaction parameters include nature of the metal oxide precursor [11-13], solvent [18, 22-23], precursor/solvent ratio [15-18], temperature [14-16], precursor/water ratio [15-17], and pH maintained during synthesis [9, 16, 19-21].

Typical steps in the sol-gel polymerization of tetraethylorthosilicate TEOS molecules involve hydrolysis and condensation reactions. Acid-catalysed hydrolysis, i.e., at low pH levels, leads to sols containing weakly-branched polymers (low fractal dimension) and to ceramics with smaller pores, while base-catalysed hydrolysis, i.e., at high pH levels, leads to sols with highly branched polymers or clusters, and to ceramics with larger pores [30, 39]. The former is commonly employed for the preparation of gas separation membranes, which require pore sizes in the range of the kinetic diameter of gas molecules. Cihlář [20] focused on the kinetics of hydrolysis and condensation of TEOS. The rate of hydrolysis was found to depend on pH, showing a minimum at pH 7.0, while no effect of the type of acid catalyst was found. The rate of

condensation of the hydrolysis products of TEOS was found at a minimum at a pH of about 2.0, and markedly enhanced by HF and H₃PO₄. Karmakar et al. [21, 34] observed that any acid-water mixture in the pH range 1.35-2.25 leads to the formation of silica microspheres, irrespective of the type of acid, weak or strong, organic or inorganic. Though different acids have been employed in sol-gel synthesis of silica, using TEOS (see **Table 1**), the role of the acid catalyst, especially that of the conjugate bases, e.g., Cl⁻, NO₃⁻, SO₄²⁻, HPO₃²⁻, PO₄³⁻, and CH₃COO⁻, on the emerging microstructure of silica ceramics after firing at elevated temperature remains obscure. The aim of the present study is to identify such a possible role, as it might be anticipated that it will influence the performance of silica when used as a gas separation membrane.

Table 1: Molar ratios of TEOS, EtOH, water and acid used in sol-gel preparation of silica.

TEOS/EtOH/Water/Acid	Acid	Ref.
1/ 3.80/6.24/variable	HNO ₃ , HCl, H ₂ SO ₄ , acetic acid (CH ₃ COOH), H ₃ PO ₃ , H ₃ PO ₄	This study
1/3.8/5.1/0.06	HCl	[29]
1/3.0/1.0/0.0007	HCl	[30]
1/3.8/1.1/0.00005	HCl	[31]
1/3.8/5.0/0.004	HCl	[31]
1/3.8/6.4/0.085	HNO ₃	[32]
1/0.0/4.0/4.0	Pentanoic (CH ₃ CH ₂ CH ₂ CH ₂ COOH), butanoic (CH ₃ CH ₂ CH ₂ COOH), propanoic (CH ₃ CH ₂ COOH), and acetic (CH ₃ COOH) acid	[21]
1/0.0/1.5/0.0012	Formic acid (HCOOH), HNO ₃ , HCl, H ₂ SO ₄	[21]
1/1.0/2.01/0.005	HNO ₃ , HCl, H ₂ SO ₄ , HF, p-toluene-sulphonic acid (PTSA), H ₃ PO ₄ , HClO ₄ , Cl ₃ CCOOH, (COOH) ₂ , ClCH ₂ COOH, CH ₃ COOH, HCOOH	[20]

4.2 Experimental

4.2.1 Sol, gel, powder and membrane preparation

Sols were produced by mixing 21 ml tetraethylorthosilicate (TEOS, Aldrich 98%) with 21 ml ethanol (Merck, p.a., 99%) in an N₂-glove box to avoid any premature hydrolysis. The obtained TEOS/ethanol mixture was placed in an ice bath, and a known volume of an acid/water mixture was added drop-wise to the solution under vigorous stirring. The total amount of water added to the TEOS/ethanol mixture was kept constant. The amount of water added to a given acid with known molarity in order to prepare different acid/water mixtures are listed in **Table 2**. Following a standard recipe developed in our laboratory for the synthesis of a silica sol from TEOS, the amount of water (3 ml) added to 8 ml 1.0M HNO₃ was used as reference in order to obtain a molar TEOS/EtOH/H₂O/HNO₃ ratio of 1/3.80/6.24/0.084.

Table 2: Volumes of acid and water used to prepare acid/water mixtures used in the preparation of silica sols. Also specified is the molar TEOS/EtOH/H₂O/acid ratio in the reaction mixture.

Type of acid, and	Acid	Water	TEOS/EtOH/H ₂ O/acid ratio*
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molarity (mol/l)		volume (ml)	volume (ml)	(-)
HNO ₃	0.5	8.00	2.83	1/3.80/6.24/0.042
HNO ₃	1.0	8.00	3.00	1/3.80/6.24/0.084**
HNO ₃	2.0	8.00	3.33	1/3.80/6.24/0.168
HCl	1.0	8.00	2.91	1/3.80/6.24/0.084
H ₂ SO ₄	0.5	8.00	2.88	1/3.80/6.24/0.042
H ₂ SO ₄	1.0	8.00	3.09	1/3.80/6.24/0.084
H ₂ SO ₄	1.5	8.00	3.31	1/3.80/6.24/0.126
H ₂ SO ₄	2.0	8.00	3.52	1/3.80/6.24/0.168
H ₂ SO ₄	2.5	8.00	3.73	1/3.80/6.24/0.21
H ₂ SO ₄	3.0	8.00	3.95	1/3.80/6.24/0.25
H ₃ PO ₄	1.0	8.00	3.13	1/3.80/6.24/0.084
H ₃ PO ₄	2.0	8.00	3.60	1/3.80/6.24/0.168
H ₃ PO ₃	1.0	8.00	3.06	1/3.80/6.24/0.084
H ₃ PO ₃	2.0	8.00	3.46	1/3.80/6.24/0.168
CH ₃ COOH	1.0	8.00	3.13	1/3.80/6.24/0.084

* Calculation based upon added volumes and corresponding densities.

** Standard recipe for the preparation of silica sols from TEOS used in the authors' laboratory.

The obtained mixture was stirred for 5 min, and subsequently refluxed for 3 h at 60 °C in a water bath under continuous stirring. After refluxing, the flask was placed in an ice bath again. The mixture was diluted 19 times with ethanol to yield the final sol. For obtaining a dried gel, the diluted mixture was poured into a Petri dish and dried overnight under ambient conditions in a laminar-flow cupboard. The gel was calcined either at 400 or 600 °C for 3 h in air in a chamber furnace (Carbolite), using heating/cooling rates of 0.5 °C min⁻¹, to obtain a ceramic powder. Membranes were fabricated by dipcoating (substrate speed 10 mm s⁻¹, dip-time 5 s) the sol onto a homemade multi-layered alumina-based support, comprising a macroporous α -alumina layer with a mesoporous γ -alumina layer, under clean room conditions in a flow-cupboard. After dip-coating, the membranes were calcined either at 400 °C or 600 °C for 3 h in air in a chamber furnace (Carbolite), using heating/cooling rates of 0.5 °C min⁻¹. Membranes were fabricated from the sols prepared by using HNO₃ or H₂SO₄ as acid catalyst.

4.2.2 Sol, gel and powder characterization

Particle size distributions of the silica sols were obtained by dynamic light scattering (DLS; Zetasizer NanoZS, Malvern Instruments). Measurements were performed on a small amount of the sol (1.0 – 1.5 ml) in a disposable sizing cuvette (Type DTS0012) immediately after synthesis. Thermogravimetric analysis (TGA) was conducted on dried TEOS gels using a thermal analyzer (Netzsch, STA 449 F3) from room temperature to 800 °C at a constant heating rate of 5.0 °C min⁻¹ under flowing N₂/O₂ atmosphere (80%/20%). Sorption measurements (Micromeritics Tristar) were performed on calcined powders with N₂ as adsorptive gas. The N₂ adsorption isotherm was measured gravimetrically at -196 °C after degassing in vacuum at 200 °C for 3-20 h. Wavelength dispersive X-ray fluorescence (Philips Analytical PW 1480 WDXRF spectrometer) measurements on dried TEOS gels and calcined powders were performed at an X-ray energy of 50 kV with a current of 50 mA.

4.2.3 Membrane characterization

Single gas (He, H₂, CO₂, N₂, CH₄, SF₆) permeation measurements were carried out, at 200 °C, in the dead-end mode without backpressure at a pressure difference of 1.8 – 2.5 bar. The membranes were sealed in a stainless steel module with Viton® O-rings with the separation layer exposed to the feed side. Prior to the measurements, the membranes were dried overnight at 200 °C under flowing helium. The gas permeance was calculated by dividing the flux by the transmembrane pressure difference.

The microstructure of the membranes was investigated by means of transmission electron microscopy (TEM), using a FEI Tecnai G2 F20 instrument operated at an acceleration voltage of 200 kV. The specimens were produced by means of a focused-ion beam process (FIB, FEI Helios Nanolab 400s) with subsequent argon-ion milling.

4.3 Results

4.3.1 Sol characterization

The particle size distributions of silica sols prepared by using different acids at various concentrations are shown in **Figure 1**. Corresponding data obtained using 1.0 M acid is

displayed in **Figure 1a**. As can be seen from this figure, the average particle size for the sols prepared using 1.0 M HCl, 1.0 M H₂SO₄ and 1.0 M HNO₃ is in the range 2-3 nm. The average particle size increases to 6.5 nm if during synthesis 1.0 M H₃PO₃ is used, while the largest average particle size of ~170 nm is obtained for the sol prepared using 1.0 M acetic acid. Contrary to the other acids, a bimodal distribution is found with a particle size in the range 2-30 nm in the case of 1.0 M H₃PO₄. **Figure 1b** shows that the average particle size increases from 4.8 nm for the sol prepared by using 0.5 M HNO₃ to 6.5 nm for the sol prepared by using 2.0 M HNO₃. **Figures 1c** indicates that the size distribution becomes bimodal in case the concentration of H₃PO₃ is doubled from 1.0 M to 2.0 M, while **Figure 1d** shows that for H₂SO₄ the particle size distribution shifts to higher values with increase of acid concentration. At 2.5 M H₂SO₄, the size distribution exhibits a maximum at ~14 nm, tailing to values of ~100 nm. Multimodality is found for the sol prepared by using 3.0 M H₂SO₄.

Figure 1: Particle size distributions of silica sols obtained by using different acid catalysts. The labelling denotes the type of acid catalyst and molarity used in preparation of the corresponding sol (see Table 2).

4.3.2 Characterization of gels and powders

Figure 2 shows data of thermogravimetry of the TEOS gels prepared by using different acids. In the range from room temperature to about 150 °C significant, merely irreproducible weight losses (up to 30-40%) occur due to water and/or solvent evaporation. To enable a better comparison of the data obtained for the different gels, **Figure 2** shows the weight loss relative to the weight of the 'dried' gel at 150 °C. For all gels there is a gradual weight loss, extending up to the maximum temperature of 650 °C of the measurements. The smallest weight loss of about 4% is observed for the gel prepared by using 1.0M H_3PO_3 , while the largest weight loss of about 14% is observed if 1.0 M H_2SO_4 is used. **Figure 2b** shows no remarkable trend in the weight losses of the gels obtained by using HNO_3 in the range 0.5 M – 2.0 M. Neither significant changes are observed in the data observed for the gels prepared by using either H_3PO_3 or H_3PO_4 , when in the preparation of these the concentration of the acid is increased from 1.0 M to 2.0 M, as is shown in **Figure 2c**. On the contrary, the weight loss increases pronouncedly upon increasing the concentration of H_2SO_4 in the range 0.5 M – 3.0 M, as is shown in **Figure 2d**. Note from this figure that for these gels the weight loss is most pronounced in the temperature region 200-300°C.

Figure 2: TGA data of 'dried' TEOS gels prepared by using different acid catalysts. Data recorded under synthetic air. Weight losses are represented relative to the weight of the 'dried' gel at 150 °C. The labelling denotes the type of acid catalyst and molarity used in preparation of the corresponding sol (see Table 2).

Tables 3 and 4 show microstructural data extracted from nitrogen-sorption isotherms of the different gel powders after calcination under nitrogen at 400 °C and 600 °C, respectively. Data were analyzed using the Brunauer-Emmet-Teller (BET) method [38]. The micropore fraction was evaluated as the quotient between micropore area and total BET surface area. Note that for selected sols, prepared using different acids, the measured micropore area is either below the limit of detection ($1 < \text{m}^2/\text{g}$) or beyond the range of nitrogen adsorption. A graphical

overview of BET surface area of the different gel powders is presented in **Figure 3**.

Table 3: Structural data from nitrogen sorption isotherms of silica powders prepared by using different acid catalysts. Sorption data were acquired after calcination of the powders at 400 °C. Values in parentheses are standard deviations (in units of the least significant digit) from regression analysis of the experimental data.

Silica powder - prepared by using*	BET surface area (m ² /g)	Micropore area (m ² /g)	External surface area (m ² /g)	Micropore fraction (%)	Micropore volume (cm ³ /g)
0.5 M HNO ₃	< 1	< 1	< 1	-	-
1.0 M HNO ₃	264(5)	264(5)	< 1	100(2)	0.215(4)
2.0 M HNO ₃	426(9)	419(21)	7(4)	98(2)	0.194(4)
1.0 M HCl	273(5)	-	-	-	-
0.5 M H ₂ SO ₄	366(7)	362(7)	4(2)	99(2)	0.167(3)
1.0 M H ₂ SO ₄	427(9)	418(8)	9(5)	98(2)	0.193(4)
1.5 M H ₂ SO ₄	485(10)	477(11)	8(4)	98(2)	0.218(4)
2.0 M H ₂ SO ₄	631(13)	616(12)	15(7)	98(2)	0.279(6)
2.5 M H ₂ SO ₄	654(13)	626(13)	15(7)	96(2)	0.303(6)
3.0 M H ₂ SO ₄	738(15)	639(13)	99(5)	86(2) **	0.410(8)
1.0 M H ₃ PO ₄	< 1	< 1	< 1	-	-
2.0 M H ₃ PO ₄	309(6)	78(2)	231(12)	25(1) **	0.044(1)
1.0 M H ₃ PO ₃	< 1	< 1	< 1	-	-
2.0 M H ₃ PO ₃	330(7)	57(1)	273(14)	17**(3)	0.0260(0.0005)

* Labelling denotes acid catalyst and molarity used in preparation of the corresponding sol (see also Table 2).

** Sample is partially mesoporous.

Table 4: Structural data from nitrogen sorption isotherms of silica powders prepared by using different acid catalysts. Sorption data were acquired after calcination of the powders at 600 °C. Values in parentheses are standard deviations (in units of the least significant digit) from regression analysis of the experimental data.

Silica powder	BET	Micropore	External	Micropore	Micropore
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- prepared by using*	surface area (m ² /g)	area (m ² /g)	surface area (m ² /g)	fraction (%)	volume (cm ³ /g)
0.5 M HNO ₃	< 1	< 1	< 1	-	-
1.0 M HNO ₃	< 1	< 1	< 1	-	-
2.0 M HNO ₃	282(6)	282(6)	< 1	100(2)	0.130(3)
1.0 M HCl	177(4)	176(4)	1.00(0.02)	99(2)	0.081(2)
0.5 M H ₂ SO ₄	288(6)	288(6)	< 1	100(2)	0.133(3)
1.0 M H ₂ SO ₄	392(8)	388(8)	4.0(1)	99(2)	0.179(4)
1.5 M H ₂ SO ₄	461(9)	452(9)	9.0(2)	98(2)	0.209(4)
2.0 M H ₂ SO ₄	580(12)	568(11)	12(2)	98(2)	0.255(5)
2.5 M H ₂ SO ₄	586(12)	567(11)	19(4)	96(2)	0.266(5)
3.0 M H ₂ SO ₄	722(14)	637(13)	85(2)	88(2) *	0.393(8)
1.0 M H ₃ PO ₄	< 1	< 1	< 1	-	-
2.0 M H ₃ PO ₄	227(5)	8.0(2)	219(4)	4.0(1) **	0.0060(1)
1.0 M H ₃ PO ₃	< 1	< 1	< 1	-	-
2.0 M H ₃ PO ₃	261(5)	115(2)	145(3)	44(1) **	0.064(1)

* Labelling denotes acid catalyst and molarity used in preparation of the corresponding sol (see also Table 2).

** Sample is partially mesoporous.

Figure 3: BET specific surface area of silica powders calcined at 400 °C or 600 °C. The labelling denotes the type of acid and molarity used in preparation of the corresponding sol (see Table 2).

A qualitative elemental analysis of the silica gels prepared by using different acid catalysts and of the powders obtained after calcination was carried out by means of wavelength-dispersive X-ray fluorescence (WDXRF) spectroscopy. The method was used to detect the characteristic element in the acid used in preparation of the gel, after drying and after calcination of the gel either at 400 °C or 600 °C. Corresponding results are given in **Appendix I**, and are summarized in **Table 5**. It should be noted that WDXRF spectrometer used in this study is not suitable for the detection of nitrogen.

Table 5: Elemental analysis of silica gels and powders by WDXRF. A positive sign indicates that the element could be detected, whereas a negative sign indicates that its concentration was found below the detection limit (1 mg/g sample).

Acid catalyst*	Element	After drying	After calcination at 400 °C	After calcination at 600 °C
HNO ₃	N	n/a	n/a	n/a
HCl	Cl	+	-	-
H ₂ SO ₄	S	+	+	-
H ₃ PO ₃	P	+	+	+
H ₃ PO ₄	P	+	+	+

* Acid catalyst used in preparation of the sol (see also Table 2).

4.3.3 Membrane characterization

Optical microscopy and SEM analysis of the silica membranes prepared in this work revealed formation of a smooth and crack-free morphology in all cases. TEM analysis showed an amorphous silica layer, whose thickness varied between 80-150 nm. A typical cross-sectional high-resolution TEM image of a supported membrane is given in **Figure 4**.

Figure 4: Typical cross-sectional TEM image of a silica membrane.

Figure 5 shows data of single-gas permeance measurements of the membranes. Permselectivities for different gas pairs calculated from these data are listed in **Table 6**.

Figure 5: Single-gas permeances for selected silica membranes. The labelling denotes the type of acid and molarity used in preparation of the corresponding sol (see Table 2), and the temperature of calcination.

Table 6: Permselectivities of different gas pairs. Values were calculated from data of single-gas permeance measurements, at 200 °C (Figure 5). Knudsen selectivities are given in parentheses.

Membrane*	H ₂ /CO ₂ (4.7)	H ₂ /N ₂ (3.7)	H ₂ /CH ₄ (2.8)	CO ₂ /CH ₄ (1.7)
1.0 M H ₂ SO ₄ -400°C	10	68	131	13
2.0 M H ₂ SO ₄ -400°C	7.4	69	394	53
1.0 M HNO ₃ -400°C	9.1	89	> 3000	119
1.0 M H ₂ SO ₄ -600°C	> 750	> 750	> 750	-
2.0 M H ₂ SO ₄ -600°C	10	93	85	8.5
1.0 M HNO ₃ -600°C	35	114	> 3000	128

* Labelling denotes the type of acid and molarity used in preparation of the corresponding sol (see Table 2), and the temperature of calcination.

4.4 Discussion

4.4.1 TEOS sol particle size

Figure 1 shows the effect of acid catalyst and molarity used in the preparation of TEOS sols on particle size and particle size distribution. Though it is apparent from these results that both have a significant influence on sol characteristics, it is likely that it is the effective pH of the reaction solution that controls particle growth. Cihlář [20] argued that the rates of hydrolysis and poly-condensation of TEOS depends on pH and not on the nature of the acid, not taking weaker acids with reactive anions into account. Bernards et al. [40] showed that if HF ($pK_a = 3.17$) is used in TEOS-ethanol-water based sols the gelation proceeds rapidly at low acid concentrations as a function of influence of the F⁻ ions on the condensation reactions, at high HF concentrations the gelation is mainly enhanced by the proton concentration. Roughly speaking, the smallest particle size and most narrow particle size distribution in the present study are found when strong acids (HCl ($pK_a = -6$), H₂SO₄ ($pK_{a,1} = -4$), HNO₃ ($pK_a = -2$)) with molarity 1.0 M are used in the preparation of the sol. When either the molarity is increased or weaker acids (H₃PO₃ ($pK_{a,1} = 2.0$), H₃PO₄ ($pK_{a,1} = 2.0$), CH₃COOH ($pK_a = 4.75$)) are used the particle size increases and/or a multimodal particle size distribution is found. The TEOS/EtOH/H₂O ratio was kept constant during preparation of the sols (see **Table 2**). From literature it is known that besides pH the number of equivalents of H₂O in the reaction solution, and the TEOS to solvent ratio influence the rates of acid-catalysed hydrolysis and condensation, and consequently the gelation time [24]. However, a detailed study on these issues was considered beyond the scope of the present work.

4.4.2 Gel and powder characteristics

The relative weight loss of dried TEOS gels as measured by TGA (**Figure 2**) is due in part by the evaporation of adsorbed H₂O and/or solvent molecules, which includes species formed upon polycondensation and further polymerization of the silica network at more elevated temperatures. Superimposed on the latter weight loss is that associated with the burning out of molecules like NO and/or NO₂, and SO₂ and/or SO₃, formed by thermal decomposition of the conjugate bases NO₃⁻ and SO₄²⁻, using HNO₃ and H₂SO₄ as acid catalyst, respectively. In general, the relative weight loss is found to increase with the molarity of the acid catalyst used in synthesis of the TEOS gel. **Figure 6** shows that the relative weight loss, at 650 °C, observed for

powders prepared by using H_2SO_4 increases almost linearly with the acid concentration used during gel synthesis.

Figure 6: Relative weight loss at 650 °C observed for TEOS gels prepared by using H_2SO_4 as catalyst as a function of acid concentration. Data taken from Fig. 2d.

Chlorine could not be detected by means of WDXRF after calcination at 400 °C of gel powders prepared by using HCl . Neither sulphur could be detected after calcination at 600 °C of the powder prepared by using H_2SO_4 . Corresponding data from WDXRF analyses of dried TEOS gels and powders obtained after calcination at 400 °C and 600 °C are shown in **Table 5**. It is recalled that the WDXRF spectrometer used in the present study was not suitable for the detection of nitrogen. It is, however, likely that at temperatures of 400 °C, and above, thermal decomposition of NO_3^- has occurred [41]. Phosphorous could be detected in powders prepared by using H_3PO_3 or H_3PO_4 even after calcination of the powders at 600 °C. Noting that phosphorous pentoxide (P_2O_5) is a known glass network former, a likely explanation is that the oxide may have become incorporated into the silica host network during synthesis and/or calcination.

Figure 7: BET values measured at 400 and 600 °C observed for TEOS gels prepared by using H₂SO₄ as catalyst as a function of acid molarity. Data taken from Table 3.

Due to densification of the microstructure, the BET surface area of the powder expectedly decreases upon increasing the calcination temperature from 400 to 600 °C. As can be judged from the data presented in **Tables 3 and 4**, and **Figure 3**, this is observed for all powders investigated by nitrogen sorption experiments, irrespective of the type of acid catalyst used in sol preparation. The results from nitrogen sorption further demonstrate that the use of strong acids (HNO₃, HCl, H₂SO₄) in the sol preparation render the powders essentially microporous, whilst micropore volume and corresponding area notably increase with the applied molarity of the acid used in preparation. For powders prepared at low acid molarity, e.g., 0.5 M HNO₃, the BET surface area was found below the detection limit (1 m²/g). The absence of N₂ adsorption in systems with a narrow microporosity (size < 0.7 nm), however, can in part be explained by kinetic restrictions at the low temperature (77 K) of the sorption measurements [19]. Gel powders prepared by using 2.0 M H₃PO₃ and 2.0 M H₃PO₄ appeared to be predominantly mesoporous, with micropore fractions of 25 and 17 % after calcination at 400 °C, and 4% and 44% after calcination at 600 °C, respectively. By comparison of the data obtained from particle size distribution (**Fig. 1**) and corresponding sorption measurements for sols and powders prepared by using H₃PO₃, H₃PO₄, or H₂SO₄ as acid catalyst (**Tables 3 and 4**),

no correlation is found between sol particle size and micro/mesoporosity of the powder obtained after calcination. Note that powders obtained via 3.0 M H_2SO_4 catalyst are largely microporous in character, in spite of the fact that a trimodal particle size distribution is found in the sol, showing maxima at 44, 531 and 4800 nm (**Figure 1d**).

The widest range in acid molarity in this study was used in syntheses of sols and corresponding powders using H_2SO_4 as acid catalyst, which facilitates a more detailed analysis on the effect of acid catalyst on powder characteristics. The relative weight loss at 650 °C measured by TGA (**Figure 6**) is found to increase almost linearly with the molarity of H_2SO_4 used in synthesis of the sol, while WDXRF indicates that no sulphur can be detected in the powder obtained after calcination under synthetic air at 650 °C. Complete desulphurization thus have occurred during calcination, at which sulphur is burned out most likely in the form of gaseous SO_2 and, to some extent since the heating is performed under synth. air, as SO_3 . Higher amounts of gases will be released if a higher molarity of H_2SO_4 is used in sol synthesis. This forms a plausible explanation for the higher levels observed for the BET surface area, micropore area and volume of powders with increase of acid molarity used in sol synthesis. The observations converge to the general conclusion that, in addition to sintering phenomena at elevated temperature, the escape of volatile components from the gel during heating, which comprises dehydration of adsorbed and structural water, and the burning out of solvent molecules and conjugate base groups, has a great impact on the microstructure of the silica powder obtained after the calcination treatment. An exception to this rule is formed when H_3PO_3 and H_3PO_4 are used as acid catalysts in sol synthesis. While the use of 1.0 M acid solutions leads to non-detectable nitrogen sorption of powders derived from these sols, the use of 2.0 M acid solutions leads to a powder microstructure with a large degree of mesoporosity (**Tables 3 and 4**). A tentative explanation that may account for the latter observation is the implementation of P_2O_5 in the silica network obtained upon calcination. Finally, it is to be expected that also thermokinetic effects, e.g., heating ramp rate, will be of influence to the microstructure, which, however, requires further detailed study.

4.4.3 Membrane preparation and performance

Initial aim of this study was to study the influence of the type and concentration of the acid catalyst on the microstructure of both powders and membranes derived from TEOS sols. Due to time considerations, however, membranes were fabricated only from sols obtained using either 1.0 M or 2.0 M H_2SO_4 as acid catalyst. These were prepared by dip-coating the sol onto homemade multi-layered alumina-based supports as described in the experimental section. SEM and TEM analyses of the membranes after calcination at either 400 °C or 600 °C confirmed formation of a homogenous, amorphous functional layer with a thickness in the range 80-150 nm (**Figure 4**).

Figure 5 compares data of single-gas permeance measurements with those from membranes prepared from a 'standard' TEOS sol (using 1.0 M HNO_3 as catalyst), and calcined at similar temperatures. Compared to the 'standard' silica membrane, the H_2 flux has dropped a factor 2-4 by replacement of 1.0 M HNO_3 in synthesis of the silica sol by either 1.0 M or 2.0 M H_2SO_4 . The observed trend is irrespective of the calcination temperature of the membranes. There is no clear-cut correlation between the micropore volume of powders and single gas permeance of membranes calcined at similar temperatures. However, a definite conclusion awaits data from measurements on an extended number of powders and membranes.

Most surprisingly, high permselectivities towards H_2/CO_2 , H_2/N_2 and H_2/CH_4 are found for the membrane prepared via the sol obtained using 1.0 M H_2SO_4 , and subsequently calcined at 600 °C (**Table 6**). Gas permeances of CO_2 , N_2 and CH_4 for this membrane are found below the detection limit of the permeation set-up (**Figure 5**). Data from sorption measurements on powders prepared from the sol obtained by using 1.0 M H_2SO_4 (**Tables 3 and 4**), however, provide no immediate clue for the observed behaviour. It is recalled that complete desulphurization occurs when these powders are calcined at 600 °C, which is not the case when the powders are calcined at 400 °C. Whether the difference in calcination temperature together with the extent to which desulphurization occurs is linked to the observations from gas permeance measurements is still not fully clarified.

4.5 Conclusions

The results of this work indicate that the amount and type of acid greatly affects the particle size and distribution in the TEOS sol. Using either HNO_3 , HCl , H_3PO_3 , H_3PO_4 , H_2SO_4 , or acetic acid as acid catalyst, however, no immediate correlation is found between these characteristics and the type, and extent of porosity of powders obtained from the corresponding sols after calcination at either 400 or 600 °C. Data of thermogravimetry and nitrogen sorption measurements reveal that the release of volatile components, among which those formed by thermal decomposition of the conjugate base ions, and sintering during calcination largely determine the microstructure of the powders, i.e., pore size and porosity. Results from initial experiments where selected sols prepared using different acids are used for the fabrication of ceramic membranes are presented. The limited number of experiments, however, does not allow us to draw any conclusion with regard the role of the amount and type of acid on gas permeance and selectivity of the membranes. High permselectivities towards H_2/CO_2 , H_2/N_2 and H_2/CH_4 are found for the membrane prepared from the sol obtained using 1.0 M H_2SO_4 , after calcination at 600 °C. It is, however, imaginable that the densification process of silica with increasing temperature, is more pronounced than the desulphurization, producing more 'pores'. Looking at the single gas permeation data of the membranes prepared from the sol catalysed by 2.0 M H_2SO_4 , it seems that the higher amount of sulphate in the membranes' structure reduces the densification effect. Further research will be essential to draw more definitive conclusions.

Appendix I Chapter 4

Figure A1: Selected WDXRF-spectra of silica gels prepared by using different acid catalysts, and of corresponding powders obtained after calcination. Acid catalyst HCl: (a) dried gel, and (b) powder obtained after calcination at 400 °C; acid catalyst H₂SO₄: powder obtained after calcination at (c) 400 °C, and (d) 600 °C; acid catalyst H₃PO₃: powder obtained after calcination at (e) 400 °C, and (f) 600 °C; acid catalyst H₃PO₄: powder obtained after calcination at (g) 400 °C, and (h) 600 °C.

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Chapter 5

Fabrication of gas-tight ultrathin films of Ta₂O₅ by a sol-gel method

Abstract

Tantalum oxide (Ta₂O₅) is widely known for its high chemical, thermal and hydrothermal stability. In this study, a sol-gel method has been developed to produce homogenous, i.e., defect and pin-hole free, ultrathin films of Ta₂O₅. These were casted onto a porous substrate by means of dip-coating, and subsequently fired at 400 °C. Despite their small thickness of only 30-40 nm, the films were found to be virtually impervious to gases.

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5.1 Introduction

The chemical inertness of tantalum pentoxide (Ta_2O_5) [1], combined with several distinct physical properties, enables its potential use in, for example, corrosion protection coatings for biomedical implants [2], surgical instruments [3] and evanescent optical sensors with high surface sensitivity [4]. Ta_2O_5 is also used as catalyst for the photolysis of water to yield hydrogen [5]. Furthermore, it exhibits a high refractive index, and therefore holds promise for use as anti-reflective coating for lenses and solar panels [6]. As a piezoelectric material, it can be applied in surface acoustic wave devices such as band-pass filters [7], and various types of mechanical sensors [8]. Because of its high dielectric constant and compatibility with silicon, thin films of Ta_2O_5 are used in transistors [9,10], ion-sensors [11], and storage capacitors for dynamic random-access memory (DRAM) [12-14]. Recently, thin sheets of tantalum have been applied as dielectric spacers between metal electrodes for fabricating negative refractive index materials, also known as metamaterials [15,16]. All of these promises have resulted in an increased interest in the growth of Ta_2O_5 -films.

In this study, a sol-gel method has been developed for the fabrication of continuous thin films of Ta_2O_5 . Though the initial aim of the work was for use as membranes in size selective gas separation, during testing the thin films were found to be gas tight. The latter opens perspectives for the films towards a variety of other practical applications.

5.2 Experimental

5.2.1 Sol-gel processing

Tantalum(V)ethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$, 99% pure, ABCR) was dissolved together with diethanolamine (DEA, 99.5% pure, Fluka) in absolute ethanol (dried, Emsure®, Merck) under dry nitrogen to prevent premature hydrolysis. After adding deionized water, the solution was stirred for 30 min at room temperature. The solution had a final molar ratio of $\text{Ta}(\text{OC}_2\text{H}_5)_5$: ethanol : H_2O : DEA of 1 : 210 : 22 : 4. If not applied immediately after synthesis the sol was stored at -28 °C.

Dried tantalum powders were obtained by drying the sols in Petri dishes overnight. Calcined powders were obtained via thermal treatment for 3h in air at temperatures between 300-700 °C using constant heating/cooling rates of 1.0 °C min⁻¹. Tantalum thin films were prepared by dip-coating (substrate speed 10 mm s⁻¹, dip-time 5 s) the sol onto homemade α -

alumina supported mesoporous γ -alumina supports [17] under cleanroom class 1000 and flow cupboard class 100 conditions. The thin films were then thermally treated at 400 °C in air atmosphere using constant heating/cooling rates of 1.0 °C min⁻¹. The coating step was repeated once, to end with two coated layers of tantala.

5.2.2 Characterization

Particle size distributions of the tantala sols were measured by dynamic light scattering (DLS), using a Zetasizer NanoZS (Malvern Instruments). Measurements were performed using 1.0 – 1.5 ml of the sol in a disposable sizing cuvette (Type DTS0012, Malvern Instruments). Dried powders were analyzed using combined thermogravimetry - differential scanning calorimetry (TG-DSC). Measurements were carried out on an STA 449 F3 Jupiter® (Netzsch) instrument in synthetic air (50 ml min⁻¹) with nitrogen as protective gas (20 ml min⁻¹). Brunauer-Emmet-Teller (BET) surface area measurements of calcined tantala powders were made by nitrogen sorption, at 77 K (TriStar 3000, Micromeritics). Before the measurements, the powders were degassed at 200 °C under vacuum for 2.5-24 h. X-ray powder diffraction data were recorded at room temperature using a Philips Pananalitical pw 1830 diffractometer. Single gas permeation measurements were conducted in the dead-end mode, using H₂, CO₂, N₂, CH₄ and SF₆ as test gases. The membranes were sealed in a home-made stainless steel module with Viton® O-rings with the top layer exposed to the feed side. The pressure difference across the coated thin film was between 1.8 – 3.0 bar. The permeate side of the membrane was kept at atmospheric pressure. Before the measurements, the membranes were dried at 200°C for at least 5h under flowing helium. The microstructure of the powders and membranes was investigated by means of transmission electron microscopy (TEM), using a Tecnai G² F20 (FEI) instrument operated at an acceleration voltage of 200 kV. The membrane specimens were produced by means of a focused-ion beam process (Helios Nanolab 400s, FEI) with subsequent argon-ion milling.

5.3 Results and discussion

In general, sols can be stabilized via two routes. Firstly, the particles in the sols can be stabilized electrostatically by preparation via an acid-base-catalyzed sol-gel route. Secondly, the sol particles can be stabilized by the use of chelating/complexing agents to avoid fast condensation and rapid particle growth [18]. In this study, the latter method was employed, utilizing diethanolamine (DEA) as sol-stabilizer. **Figure 1** shows particle size distributions of the tantala sol. Immediately after synthesis the size of the sol particles is in the range of 2.7-21 nm, with a maxima size at 4.8 nm. Particle growth was experienced to be very fast. As seen from **Figure 1**, within 24h at room temperature the particles grew to a maxima size of 11.8 nm.

Figure 1: Particle size distributions of the tantala sol after synthesis and after 24h of storage at room temperature.

Shown in **Figure 2** are data of thermal analysis of a dried tantala gel. Several weight losses are observed. A continuous weight loss is observed up to 280 °C, which can be assigned to the evaporation of residual water and ethanol. This is followed by distinct weight losses between 310-380 °C and 450-520 °C, which are accompanied by pronounced exothermic effects at approximately ~340 and ~480 °C. The peak at ~340 °C may be ascribed to evaporation and/or decomposition of DEA. The peak at ~480 °C is very broad, which suggests

a slow kinetic process. A possible explanation may be the crystallization of amorphous Ta_2O_5 into the low-temperature orthorhombic structure of $\beta\text{-Ta}_2\text{O}_5$ [19]. Ling et al. [20] observed crystallization of tantalum from its amorphous form to be a nucleation and growth process and, hence, to be rather slow. Tantalum is highly acidic, especially in its hydrated form [21]. Another contribution to the weight loss at $\sim 480^\circ\text{C}$ may arise from the evaporation of strongly bound water. The small exothermic peak at 725°C may be linked to either crystallization or another structural rearrangement of the material. The small weight loss may be due to associated oxygen release.

Figure 2: TGA/DSC data of tantalum powder recorded under flowing synthetic air at a heating rate of 5°C min^{-1}

No nitrogen sorption was found for the powders obtained from calcination at $300\text{--}500^\circ\text{C}$, which suggests that the material is either dense or microporous with pores smaller than the kinetic diameter of nitrogen. Samples calcined at 600 and 700°C showed a BET surface area of $8.8\text{ m}^2\text{ g}^{-1}$ and $26.9\text{ m}^2\text{ g}^{-1}$, respectively. The observed type II isotherms (see **Figure 3**) are characteristic for mesoporous materials, and the type of hysteresis indicates the presence of bottlenecked pores [22].

Figure 3: Nitrogen sorption isotherms of tantalum powder calcined at (a) 600 °C and (b) 700 °C for 3h.

Results of X-ray diffraction and TEM analysis on tantalum powders calcined at different temperatures are shown in **Figures 4** and **5**, respectively. The observations from TEM show that the material after calcination at 300 and 400 °C is highly amorphous, which for the powder calcined at 400 °C is confirmed by the data from X-ray diffraction. The very broad non-Bragg reflection observed at 14-30° in the diffraction pattern of the sample calcined at 500 °C suggests that nanocrystals (<10 nm) are embedded in an amorphous matrix. This is confirmed by the corresponding TEM image in **Figure 5c**. The X-ray diffraction pattern of the sample calcined at 600 °C shows clear evidence of crystalline Ta₂O₅. Diffraction peaks at 2θ values 22.9, 28.4, 36.9 and 55.7° can be assigned to orthorhombic β-Ta₂O₅ [23,24], which is the low-temperature form of Ta₂O₅.

Figure 4: X-Ray diffraction patterns of tantalum powders calcined at different temperatures for 3h.

Figure 5: TEM pictures of tantalum powders calcined at (a) 300, (b) 400 and (c) 500 °C for 3h. Amorphous and crystalline regions are indicated.

Sol-gel deposition of thin films of tantalum on glass supports has been reported previously by several authors [25-28]. In the cited studies, the thickness ranged from 75 to 327 nm. In the present study, continuous thin films of Ta_2O_5 of thickness of only 30-40 nm were coated on mesoporous γ -alumina layers (supported by α -alumina). These showed good adhesion to the γ -alumina interlayers. Despite the small thickness of the films (see **Fig. 6**), a hydrogen permeance was measured, at 200 °C, of only $5.24 \times 10^{-10} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$. This value is extremely low, slightly above the detection limit of the apparatus used ($\sim 1 \times 10^{-10} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$), and

more than 3 orders of magnitude lower than found for microporous silica membranes [29]. The permeances of the gases with larger kinetic diameters, i.e., CO₂, N₂, CH₄ and SF₆, were found to be at, or below, the detection limit, which confirms that the films obtained in this work are defect and pin-hole free.

Figure 6: TEM cross-sectional images of the tantalum thin film, calcined at 400 °C in air. Also visible are the α -alumina support and γ -alumina interlayer.

5.4 Conclusions

Continuous ultrathin films of tantalum, with a thickness of 30-40 nm, were coated on porous supported γ -alumina layers by a sol-gel method. Evaluation by permeance testing, at 200 °C, showed that the deposited thin films are virtually impervious to gases. Only for hydrogen, having the smallest kinetic diameter in the present study, the measured permeance was found to be slightly above the detection limit. The imperviousness of the tantalum thin films to gases may open perspectives towards a number of practical applications.

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Chapter 6

Recommendations and outlook

In the preceding 4 chapters of this thesis different approaches have been described and discussed that were intended to reach the objectives of this study. The objective, *the preparation and performance characterization of sol-gel derived microporous ceramic membranes* was met. Membranes from tantalum, silica and (doped) hybrid inorganic-organic silica have been successfully prepared and characterized. However, the membranes have not met the key objective, which is *good performance for H₂/CO₂ separation for the potential integration in the pre-combustion process*, not taking the hydrothermally unstable silica membranes into account. Nonetheless, the secondary objectives, *good/improved performance of the membranes for H₂/N₂, H₂/CH₄, H₂/C₂H₆, and CO₂/CH₄ separation*, have been met to some extent. In following part of this chapter the main conclusions from chapter 2-5 are summarized and recommendations will be given, including some preliminary results on the one or the other matter.

The following conclusions were drawn from the investigations regarding the stability of hybrid inorganic-organic silica (BTESM, BTESE), as are presented in **Chapter 2**.

The decomposition in inert atmosphere occurs at 550 and 480 °C (BTESM, BTESE), about 200 °C lower in air. The decomposition of BTESE under nitrogen is kinetically sluggish, meaning that the decomposition is occurring over a broad temperature range (300 – 800 °C). Membranes prepared from these two precursors and calcined in air and nitrogen at temperatures between 400 and 600 °C, are ‘impermeable’ for SF₆, but show Knudsen type of transport behavior for other gases (H₂, CO₂, N₂, CH₄). An exception is a BTESE membrane calcined in air at 450 °C, which is already in the decomposition region of the material. This particular membrane shows good molecular sieving properties.

More research needs to be done to clarify the above findings. Especially studying the materials’ and membranes’ decomposition and calcination behavior in different conditions has raised numerous questions and ideas to follow. Possible investigations include, the calcination in different atmospheres, including non-oxidative, hydrogen and methane-containing atmospheres, to suppress the decomposition of the organic linker at higher temperatures. The

use of H_2 and CH_4 , is proposed because these are the main gases released from the hybrid silica material during decomposition and following Le Chateliers principle, the presence of these gases should suppress the release of H_2 or CH_4 respectively. The calcination time at the final temperature has a considerable influence on the properties of the prepared membranes, especially, if the temperature is already within the decomposition range. Calcination for 1h at 500 °C will result in a different membrane performance than 3h at the same temperature. It has also become evident that the decomposition mechanism should be analyzed in more detail and the use of simpler systems (including pure silica membranes) might reveal some parts of the decomposition mechanism. This could be achieved like described in Chapter 2, with TGA and TPD, but easier would be a combined TGA-MS or TGA-GC system. All possible decomposition gases should be recorded in order to learn more about the mechanisms of decomposition and potentially about ideal calcination temperatures and calcination times at the optimal temperature. Another additional point of interest is the drying (gelation) time and environment. These are expected to have a more or less significant influence on the membranes' performance after calcination. Rapid thermal processing, has recently become very interesting, here the focus is on shortening the calcination times to a minimum without losing characteristics of the prepared membranes. This would result in a higher production rate and hence lower membrane costs.

As indicated by Kanezashi et al. [1], a very important point for gas separation is to extend the range of measurement gases to be able to determine the pore size of the membranes more exactly. This is especially useful if a membrane exhibits no permeance for SF_6 , but a rather high permeance for methane. Therefore, gases with kinetic diameters between those of CH_4 (3.84 nm) and SF_6 (5.5 nm) should be measured. Possible examples include ethane (4.4 nm), propane (4.8 nm) and *iso*-butane (5.0 nm). The membrane performance as a function of temperature should also be measured; this, in combination with gas permeation measurements of gases with larger kinetic diameters than methane, could reveal new fields of application, e.g. separation of air from higher hydrocarbons from exhaust streams at (petro-) chemical production sites or the purification of gases for high quality pure gases.

Some preliminary results, following some of the above mentioned recommendations, are shown in **Figures 1** and **2**, and **Tables 1** and **2**. The membranes are denoted as follows: first

mentioned is the material (BTESM or BTESE), second the calcination temperature and atmosphere, the calcination time (if not stated – 3h), and followed finally by the temperature of measurement (e.g., @200 °C).

Figure 1: Single gas permeation measurement results for BTESM-derived membranes. Membranes were calcined in air and nitrogen at 400 and 450 °C for 3h.

For BTESM-derived membranes, calcined at 400 °C in air, a selectivity of 76 for H₂/C₂H₆ can be achieved when the measurements are conducted at 50 °C. At 200 °C, the selectivity is found close to the corresponding Knudsen value. An explanation for this behavior is to be found in whether the transport through the membrane is only governed by molecular sieving or partially thermally activated. Looking at permeances of the different gases through BTESM-derived membranes it becomes obvious that the thermal activation plays an important role for the bigger gases, methane and ethane. Some of the membranes were calcined at 450 °C (within initiation region of decomposition) in air to test whether there is an influence of the calcination temperature on their performance. Apparently, no significant influence could be detected. That may be an indication that the decomposition of BTESM has preceded too far, leaving some intermediate ‘free carbon’ or other structures behind, and with that larger pores and/or different affinities towards gases.

Table 1: Permselectivities of BTESM-derived membranes calcined either in air or nitrogen, at 400 and 450 °C for 3h. The membranes were measured at 50 and 200 °C.

	H_2/CO_2 (4.7)	H_2/N_2 (3.7)	H_2/CH_4 (2.8)	$\text{H}_2/\text{C}_2\text{H}_6$ (3.9)	CO_2/CH_4 (1.7)
BTESM-400- N_2 @200 °C	3.4	8.9	8.7	-	2.6
BTESM-400- Air @200 °C	3.6	8.2	8.4	14	2.3
BTESM-400- Air @50 °C	2	-	21	76	10
BTESM-450- Air @200 °C	4.1	8.8	8.4	14	2
BTESM-450- Air @50 °C	-	-	10.5	12.5	-

Figure 2: Single gas permeation measurement results for BTESE-derived membranes calcined in nitrogen at 500 °C. To compare the influence of calcination time the membranes were kept at 500 °C for 1h and 3h.

With the BTESE-derived membrane the time of calcination under nitrogen was changed from 3h to 1h with good results. The H_2/N_2 and H_2/CH_4 selectivities increased by a factor of 1.5, while the H_2 permeance increased by a factor of 1.3. Concerning the hydrogen/ethane

selectivity, a remarkable value of 122 is reached when the measurements are carried out at 50 °C. This clearly demonstrates the potential of hybrid silica membranes, and that there is more research and development necessary to fully understand this type of materials.

Table 2: Permselectivities of BTESE-derived membranes calcined in nitrogen at 500 °C for 3h and 1h and measured at 50 and 200 °C.

	H₂/CO₂ (4.7)	H₂/N₂ (3.7)	H₂/CH₄ (2.8)	H₂/C₂H₆ (3.9)	CO₂/CH₄ (1.7)
BTESE-500-N ₂ - 3h @200 °C	5.6	8.9	12	-	2.2
BTESE-500-N ₂ - 1h @200 °C	3.7	15	18	51	4.7
BTESE-500-N ₂ - 1h @50 °C	1.7	13	24	122	13.5

In **Chapter 3** the doping of hybrid silica membranes with minor amounts (4 - 16 mol%) of other metal oxides is described. As already briefly mentioned in Chapter 3, the amount of doping should be at least 10 mol% to achieve a noticeable effect on separation performance. Here, the most promising dopant was germania (16 mol%). Doping with larger amounts of GeO₂, e.g. 25 and 33 mol%, seems to be worthwhile testing and should be investigated.

Strongly recommended is the use of other promising dopants, which are also known for their hydrothermal stability and network forming or modifying properties in order to modify the membrane characteristics, e.g. surface properties, as has been shown already [2]. The best doping candidates are zirconia, tantala and phosphorous oxide. ZrO₂ is an intermediate oxide widely used in glass industry, known to increase chemical resistance of glass. Mesoporous zirconia as well as silica-zirconia membranes have already shown high thermal, chemical and hydrothermal stabilities [3-5], which would be beneficial for ZrO₂ doped hybrid silica membranes under pre-combustion conditions. Tantalum oxide would be a suitable candidate, as probably the most stable (chemically, hydrothermally) metal oxide, only vulnerable to HF and very strong bases. Judging from Chapter 5, tantala doping of hybrid silica membranes would also lead to a densification of the pore network which would be beneficial for better molecular sieving properties. Phosphorous oxide (P₂O₅) is a well suited dopant increasing the

chemical stability of silica materials. It is also known to increase hydrothermal stability of borosilicate, lime- and lime-soda glass [6,7].

Post-calcination treatments/modifications, like grafting, impregnation or plasma treatment, could also play an important role for these membranes. This could promote the affinity of the membranes towards certain gases and therefore improve the selectivities. One possibility could be the impregnation with $\text{Sr}(\text{NO}_3)_3$ to increase the affinity towards CO_2 , that would not improve H_2/CO_2 separation, but could be an interesting option towards effective CO_2/CH_4 separation for upgrading natural gas and biogas.

In **Chapter 4**, the influence of different acid catalysts on silica sol-gel derived materials and membranes is studied. It is found that with a higher concentration of sulfuric acid as catalyst the BET surface area of silica powders rise. In case of phosphorous containing acid the main porosity changes from microporous to mesoporous with increasing acidity. These and other findings open many possibilities for further research.

One interesting point for more fundamental research would be to explore the effects of sulfuric acid on the TEOS sol, but particularly its effects on the membrane properties in the range where desulphurization has not occurred yet, approximately between 400-450 °C. As the powders obtained from the sols catalyzed by H_2SO_4 exhibit large surface areas, these might be good substrates for catalysts or even act as good catalysts by themselves. Phosphates/phosphites from H_3PO_4 , H_3PO_3 or other phosphor sources as dopants in the silica membranes should be investigated on potential better hydrothermal stability, as compared to the 'pure' silica membranes, followed by doping with higher amounts of ' PO_x ' and optionally with a metal counter ion (e.g. Ca, Mg), resulting in a double doping. The use of oxalic acid in the sol synthesis and its effect on material and membranes is an interesting point of research. As strong organic acid ($\text{pK}_{a1} = 1.25$), its use should result in more stable sols as compared to acetic acid, additionally oxalic acid works also as chelating agent.

Research on the application of tantala as a working (gas separation) membrane is still in its infancy and especially more time is necessary on sol development. But also the development of micro- and mesoporous membranes should be in focus; this could be achieved by an adaption of the sol-recipe stated in **Chapter 5**. By the introduction of pore formers into

the Ta₂O₅-matrix the pores could be tuned to the wished size, leading to nano-, ultra- and microfiltration membranes.

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Summary

The development of novel hydrothermally stable, microporous membranes for pre-combustion fossil fuel power plants, with CO₂ capture, in particular for H₂/CO₂-separation, is discussed in this thesis.

Chapter 1 provides a general overview of inorganic membranes for gas separation, discussing amongst others different classes and types of materials, different transport mechanisms, and fabrication of supported membranes, and gives a detailed description of the preparation of materials via sol-gel methods. This chapter concludes with the aims of the work described in this thesis.

In **Chapter 2**, the thermal stability of hybrid silica materials, namely 1,2-bis(triethoxysilyl)methane (BTESM), 1,2-bis(triethoxysilyl)ethane (BTESE) and 1,2-bis(triethoxysilyl)ethylene (BTESY), is investigated in different atmospheres and at different temperatures. Data of temperature-programmed decomposition (TPD) measurements suggest that BTESE and BTESY are stable under nitrogen up to 480 °C, and BTESM even up to 550 °C. Membranes of the materials are fabricated via sol-gel deposition onto an alumina-based multilayer support, calcined at 400-600 °C under nitrogen, and investigated by single-gas permeation measurements. Hydrogen permeances of $7 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and single-gas permeation selectivities of up to 6 for H₂/CO₂, 11 for H₂/N₂, 16 for H₂/CH₄, and >3000 for H₂/SF₆ are measured. Furthermore, the effect of calcination temperature on the performance of BTESM and BTESE membranes is studied. Although the thermal decomposition of BTESE starts already around 300 °C, the highest permselectivities are found for membranes calcined at 450 °C. Selectivities found for H₂/CO₂, H₂/N₂, H₂/CH₄ and H₂/SF₆ are 7.6, 46, 209 and >3000, respectively.

Chapter 3 describes the effect of doping of BTESE with alumina, silica or germania on gas separation. The most promising membrane, containing 16 mol% GeO₂-doping, shows single gas permeation selectivities of 25 and 33 for H₂/N₂ and H₂/CH₄, respectively.

In **Chapter 4**, the effect of different acids (HCl, HNO₃, H₂SO₄, H₃PO₃, H₃PO₄, acetic acid) on silica sols, gels, and powders is investigated. It is found that the type of acid and its concentration used in hydrolysis and condensation of TEOS greatly affects the apparent particle size in the obtained sol, and modality of the associated particle size distribution. Data of thermogravimetry and nitrogen sorption measurements reveal that the release of volatile components, among which those formed during thermal decomposition of the conjugate base ions (of the applied acid catalyst), and sintering during calcination largely determine the emerging microstructure, i.e., pore size and porosity, of the obtained silica powders.

Chapter 5 describes an attempt to fabricate amorphous microporous membranes from tantala. The original target is, however, not achieved. Amorphous thin films of tantala are successfully coated onto porous alumina-based multilayer supports, but found to be almost impermeable to gases.

Finally, **Chapter 6** provides some suggestions and ideas for future research, and some preliminary results of investigations.

Samenvatting

De ontwikkeling van nieuwe hydrothermaal stabiele, microporeuze sol-gel-membranen voor pre-combustion fossiele energiecentrales met CO₂ afvang, met name voor H₂/CO₂-scheiding, wordt in dit proefschrift besproken.

Hoofdstuk 1 geeft een algemene inleiding over anorganische membranen voor gasscheiding, en bespreekt onder andere verschillende klassen en typen van materialen, verschillende transportmechanismes, de fabricage van gedragen membranen, en geeft een gedetailleerde beschrijving van de bereiding van materialen via sol-gel methoden. Dit hoofdstuk eindigt met de doelstellingen van het onderzoek beschreven in dit proefschrift.

In **Hoofdstuk 2** wordt de thermische stabiliteit van hybride silicamaterialen, te weten BTESM (1,2-bis(triethoxysilyl)methaan), BTESE (1,2-bis(triethoxysilyl)ethaan) en BTESY (1,2-bis(triethoxysilyl)etheen), onderzocht in verschillende atmosferen en bij verschillende temperaturen. Gegevens verkregen via temperatuur-geprogrammeerde decompositie (TPD) geven aan dat BTESE en BTESY stabiel zijn onder stikstof tot 480 °C, en BTESM zelfs tot 550 °C. De membranen van deze materialen worden bereid via sol-gel-depositie op een meerlagige aluminiumoxide drager, gecalcineerd bij 400-600 °C onder stikstof, en onderzocht met behulp van permeatiemetingen op basis van enkelvoudige gassen. Waterstofpermeaties van 7×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ en selectiviteiten van 6 voor H₂/CO₂, 11 voor H₂/N₂, 16 voor H₂/CH₄, en >3000 voor H₂/SF₆ worden gemeten. Tevens wordt de invloed van de calcinatietemperatuur op de membraaneigenschappen van BTESM en BTESE onderzocht. Ofschoon thermische ontleding van BTESE al optreedt bij 300 °C, worden de hoogste selectiviteiten gevonden voor membranen die bij 450 °C gecalcineerd zijn. Gevonden selectiviteiten voor H₂/CO₂, H₂/N₂, H₂/CH₄ en H₂/SF₆ bedragen, respectievelijk, 7.6, 46, 209 en >3000.

Hoofdstuk 3 beschrijft de invloed van dotering van BTESE met alumina, silica of germania op gasscheiding. Het meest belovende membraan, met een dotering van 16 mol% GeO₂, toont selectiviteiten van 25 en 33 voor, respectievelijk, H₂/N₂ en H₂/CH₄.

De invloed van verschillende zuren (HCl, HNO₃, H₂SO₄, H₃PO₃, H₃PO₄, azijnzuur) op de eigenschappen van silicasolen, -gels, en -poeders wordt in **Hoofdstuk 4** besproken. Gevonden wordt dat het type zuur en de concentratie die gebruikt worden tijdens de hydrolyse en condensatie van TEOS (tetraethylorthosilaan) een grote invloed hebben op de schijnbare deeltjesgrootte in de verkregen sol en de modaliteit van de bijbehorende deeltjesgrootteverdeling. Gegevens verkregen met behulp van thermogravimetrie en stikstofsorptiemetingen laten zien dat het vrijkomen van vluchtige bestanddelen, onder andere die die vrijkomen tijdens thermische ontleding van de geconjugeerde base (van de gebruikte zure katalysator), en sinteren tijdens de temperatuurbehandeling bepalend zijn voor de microstructuur, d.w.z. de poriegrootte en porositeit, van de verkregen silicapoeders.

Hoofdstuk 5 beschrijft een poging om amorfe microporeuze membranen van tantala te bereiden. Het oorspronkelijke doel wordt echter niet bereikt. Dunne amorfe lagen van Ta₂O₅ worden succesvol gecoat op poreuze alumina-dragers, maar vertonen nagenoeg geen gaspermeatie.

Hoofdstuk 6 geeft tenslotte een aantal suggesties en ideeën voor toekomstig onderzoek, en enkele resultaten van voorlopig onderzoek.

Zusammenfassung

Die Entwicklung von neuen hydrothermal stabilen mikroporösen Sol-Gel-Membranen für fossile Kraftwerke (pre-combustion), im Speziellen für die H_2/CO_2 -Trennung, wird in dieser Studie besprochen.

Kapitel 1 stellt eine allgemeine Einleitung über anorganische Membranen in der Gastrennung, inklusive Materialien, Herstellung und Transportmechanismen, dar und enthält zudem eine kurze Projektbeschreibung.

In **Kapitel 2** wird erläutert, wie drei hybride Silicamaterialien, BTESE (1,2-Bis(triethoxysilyl)methan), BTESM (1,2-Bis(triethoxysilyl)ethan) und BTESY (1,2-Bis(triethoxysilyl)ethen) auf ihre thermische Stabilität in verschiedenen Atmosphären und bei verschiedenen Temperaturen hin untersucht werden. Temperatur-programmierte Zersetzungsmessungen (TPD) suggerieren hierbei, dass BTESE und BTESY in Stickstoffatmosphäre bis 480 °C stabil sind, BTESM sogar bis 550 °C. Die Membranen dieser Materialien wurden über eine Sol-Gel-Synthese hergestellt und auf mehrschichtige Aluminiumoxid-Träger beschichtet, anschließend in Stickstoff zwischen 400-600 °C kalziniert und hauptsächlich durch Einzelgasmessungen analysiert. Dabei wurden Wasserstoffpermeanzen von $7 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ und Selektivitäten von 6 für H_2/CO_2 , 11 für H_2/N_2 , 16 für H_2/CH_4 und >3000 für H_2/SF_6 erreicht. Des Weiteren wurde der Effekt von Luft während der Kalzinierung bei verschiedenen Temperaturen auf die Membranleistung von BTESM und BTESE untersucht. Obwohl die thermische Zersetzung von BTESE bereits bei 300 °C beginnt, wurden die höchsten Permselectivitäten für Membranen gefunden, die bei 450 °C in Luft kalziniert wurden. Die Selektivitäten für die Gaspaare H_2/CO_2 , H_2/N_2 , H_2/CH_4 und H_2/SF_6 betragen unter diesen Bedingungen 7,6, 46, 209 und >3000.

Kapitel 3 beschreibt den Dotierungseffekt von kleinen Mengen Alumina, Silica und Germania auf BTESE-Membranen in der Gastrennung. Die vielversprechendste Membran wurde mit 16 mol% GeO_2 -Dotierung synthetisiert und resultierte in Selektivitäten für H_2/N_2 und H_2/CH_4 von 25 bzw. 33.

Der Effekt von sechs verschiedenen Säuren (HCl, HNO₃, H₂SO₄, H₃PO₃, H₃PO₄, Essigsäure) auf die Silica-Sole, -Gele, -Pulver und -Membranen wird in **Kapitel 4** beschrieben. Die Art der Säure und ihre Konzentration, die in der Hydrolyse und Kondensation von TEOS (Tetraethylorthosilan) verwendet werden, beeinflussen die augenscheinliche Teilchengröße im Sol und die modale Verteilung der dazugehörenden Teilchengrößenverteilung. Die erhobenen Daten der thermogravimetrischen Messungen und Stickstoffsorptionsmessungen an diesen Pulvern zeigen, dass die Freisetzung von flüchtigen Bestandteilen, darunter die, die durch thermische Zersetzung der konjugierten Anionen (der verwendeten Säurekatalysatoren) während der Kalzinierung und durch Kalzinierung selbst entstehen - entscheidend die sich entwickelnde Mikrostruktur bestimmen, u.a. Porengröße und Porosität der Silicapulver. Die besten Membranen wurden durch die Verwendung von 1.0 M H₂SO₄ während der Solsynthese hergestellt und waren nur für Helium und Wasserstoff permeabel.

Kapitel 5 beschreibt den Versuch amorphe mikroporöse Membranen aus Tantal, dem wahrscheinlich stabilsten existierenden Metalloxid, herzustellen. Dieses ursprüngliche Ziel wurde in unseren Versuchen nicht erreicht, nichtsdestotrotz ist es gelungen, amorphe Dünnschichten aus Ta₂O₅ auf poröse Aluminaträger abzuscheiden, welche nahezu gasdicht waren.

Schließlich liefert **Kapitel 6** einige Vorschläge und Ideen für zukünftige Forschungsansätze und dazu schon einige Resultate aus durchgeführten Vorversuchen.

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After four years of work and life in Enschede (followed by almost 3 years of fuss, causing much unrest (thanks)) in the Netherlands it is time to say a few words (or a little bit more) about my time here.

When I moved to Enschede I was still a real student, enjoying life to the fullest and not taking too many responsibilities. But life can change a lot, for some persons at least, during such a period of time. Speaking for me, I believe, my life got turned upside down, twirled around and so on. I got together and moved together with my Twents girlfriend and later-to-be wife. We became parents of two beautiful daughters. I also got into contact with my two brothers, after about 30 years. That was it in the short and simple version. My personal and professional responsibilities have grown massively.

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I hope I didn't forget anyone, if so, please forgive me and feel thanked by reading this sentence☺.

I'll finish with a quote of Georg Christof Lichtenberg (Mathematician, Physicist and Author, 1742-1799): "Die Leute, die niemals Zeit haben, tun am wenigsten."

My final sentence here will be written in Swabian, my home dialect.

Den glombada Gruaschd dohanna guat auf'd Reuh z'griaga hätt' mr schiergar da letschda Nerv koscht.