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APPLICATION OF A SOL-GEL BASED NANOSTRUCTURED CERAMIC MEMBRANE FOR HYDROGEN SEPARATION IN CO2 CAPTURE PURPOSES

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CHEMISTRY RESEARCH AND APPLICATIONS

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PREFACE

The two most significant industrial processes for hydrogen production from fossil fuels are coal gasification and steam reforming of natural gas. A membrane process for CO_2-H_2 separation is an attractive alternative to conventional technologies such as solvent scrubbing, pressure swing adsorption, and cryogenic distillation for capturing the CO_2. The advantages of using membrane reactors, *i.e.*, the combination of a chemical reactor and membrane separation as one unit operation, are highly evident, *e.g.*, the possibility to shift the chemical equilibrium towards the product side, the improvement of hydrogen production, along with high fossil fuel conversion at milder operating conditions and thus a lower efficiency penalty and lower cost. In principle, two different types of membranes are under development, dense Pd-alloy based and porous inorganic ceramic ones. The non-metallic inorganic membranes are in principle more robust, thermally and mechanically, but suffer from the drawback that the pore size has to be tuned to the kinetic diameter of hydrogen in order to obtain sufficient selectivity, for instance by Atomic Layer Deposition (ALD). The present contribution provides a literature overview of ceramic membranes and their performance which are currently under investigation for hydrogen separation at high temperatures, as well as recent research results by the authors. The scope of materials presented here is limited to those that are primarily based on sol-gel synthesis.

Chapter 1

INTRODUCTION

The present energy system which utilizes fossil fuels like coal, oil, and natural gas has several impacts on modern society such as the degradation of the natural environment, the current consequences of global warming, the exhaustion of fossil fuels reserves, economic dependence, and political tensions in the oil-rich region - Middle East [1-3]. Therefore, it is urgent to switch to alternative sustainable energy sources. The potential of hydrogen (H_2) as an environmentally clean energy carrier in the near future, *i.e.*, the only combustion product being water, has been attracting a lot of attention of a vast number of researchers. Meanwhile, until the transition to a sustainable energy system fossil fuels will be used but in a clean carbon free way. Therefore, H_2 needs to be separated from its carbon carrier, the fuel. The carbon containing fuels are transformed into reaction mixtures via different processes such as coal (gasification, carbonization), natural gas (steam reforming, partial oxidation, autothermal reforming, plasma reforming), biomass (gasification, steam reforming, biological conversion) from which H_2 is extracted. The most common energy feedstocks and existing commercial processes are H_2 production from coal gasification and from steam reforming of natural gas (methane (CH_4) is its principal constituent) [3, 4]. Generally, the production involves two main steps. The first step is the steam reforming of the feedstocks to a syngas, mainly consisting of carbon monoxide (CO) and H_2 as shown in the following chemical reactions:

(a) Coal gasification (CG)

$$C + H_2O \underset{40\ \text{bar}}{\overset{900°C}{\rightleftarrows}} CO + H_2 \qquad \Delta H^0_{298} = 119\ \text{kJ/mol} \qquad (1)$$

(b) Steam-methane reforming (SMR)

$$CH_4 + H_2O \underset{30\ \text{bar}}{\overset{850°C}{\rightleftarrows}} CO + 3H_2 \qquad \Delta H^0_{298} = 206\ \text{kJ/mol} \qquad (2)$$

In the second step, CO in the syngas is subsequently converted to carbon dioxide (CO_2) and H_2via the water-gas-shift (WGS) reaction:

(c) Water-gas-shift (WGS)

$$CO + H_2O \underset{20\ \text{bar}}{\overset{350°C}{\rightleftarrows}} CO_2 + H_2 \qquad \Delta H^0_{298} = -\,41\ \text{kJ/mol} \qquad (3)$$

With associated CO_2 capture and storage (CCS) technology [5-7]at minimum energy penalty, H_2 produced via coal gasification and steam methane reforming can be a key factor to secure a carbon free H_2 supply and to commercial H_2-based technologies, such as fuel cells [8]. In order to be both economically competitive and environmentally sustainable, various alternative methods such as pressure-swing adsorption (PSA) [9], cryogenic distillation [10], and membrane separation [11, 12] can be used to separate H_2. Membrane separation is considered to be an energy-efficient continuous process alternative to the commercial PSA and cryogenic distillation methods, which are quite energy demanding for the separation and purification of H_2. Under normal conditions, the steam-methane reforming (SMR) is an equilibrium endothermic reaction (reaction (2)). If H_2 is removed from the reaction system by using H_2-selective membranes, the driving force of the chemical equilibrium favours the product side, which yields higher conversion of CH_4 to CO or CO_2 and H_2, at even lower reaction temperature. Membrane reactors, in which the reaction and separation happen simultaneously, can provide such opportunity for minimising the energy penalty for carbon capture. There are various types of membranes which hold the promise for separating H_2, including metal- [13, 14], polymer- [15], silica- [16-18], and zeolite-based [18-20] ones. The most investigated metallic membranes are dense palladium (Pd)-based alloys, intrinsically having 100% H_2 selectivity. However, a pure Pd membrane suffers from H_2 embrittlement due to the phase transition between the α- and β-hydride form in a H_2-containing environment and from poisoning effects of sulphur (H_2S) and CO, which lead to membrane degradation or reduced membrane performance. The chemical stability of the Pd membranes can be improved by alloying the Pd with other metals such as silver (Ag) [14]. Currently, Pd and Pd-alloy membranes are used only when ultra-pure H_2 is needed and only as a separation step. Polymeric membranes are commercially used for H_2 separation only at low temperatures (<250°C) with H_2/CO selectivity in the range 21-30 [15], and have therefore no interest to high temperature processes as SMR and WGS. In comparison to their Pd and polymeric counterparts, ceramic membranes are not adversely affected by elevated operating temperatures and have higher chemical resistance, which make them good candidates for H_2 separation in reforming processes, provided they exhibit high (hydro)thermal stability.

Many reviews have been published [11, 12, 21] recently, which have focused on particular aspects of the above mentioned membrane classes. In the present contribution, membrane materials solely related to sol-gel based production will be considered in the present discussion. Sol-gel technology has gained great interest as a suitable method for making thin porous membranes with desired properties [22], mainly due to the relative simplicity, it being a low-temperature process, and the possibility of good control over the process parameters. The following presentation focuses on the recent results of the sol-gel preparation of membranes with an emphasis on three key parameters, i.e., the choice of materials, the tailoring/design of the pore structure for improving the gas separation factor, and the characterization of membranes. A full understanding of these parameters will put us in a better position to develop sol-gel derived materials as a potential application in porous membrane based-H_2separation.

Chapter 2

CHOICE OF MATERIALS

The state-of-the-art ceramic membranes have been a subject of research for several decades and have been made from a variety of inorganic materials. Usually, a sol-gel preparation of a membrane involves first the formation of a sol, which is a suspension of solid particles in a liquid, then the deposition of the sol on the surface of a porous support where a gel layer is formed. The solvent can be removed from the gel layer by either conventional drying in order to obtain a product known as a xerogel, or drying with supercritical extraction in order to have an aerogel. Calcination of the gel at a temperature higher than the drying temperature causes further removal of the solvent and results in a porous ceramic layer. It can be a microporous (pore size $d_p < 2$ nm) or mesoporous ($2 < d_p < 50$ nm) membrane. Figure 1 shows all sequences of a conventional membrane preparation as described.

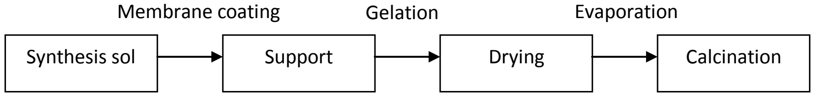


Figure 1.Sol-gel ceramic membrane preparation.

Although each step can be critical for the success of the membrane preparation, which is discussed in the excellent review of Brinker et al. [22], it is considered that the resulting membrane characteristics are mostly determined by the structure and chemistry of the sol. The formation of a sol is usually involved in the hydrolysis-condensation of metal alkoxideprecursor M-$(OR)_x$(M=Si, Ti, Zr, Al; OR=$OC_nH_{2n+1;}$ x is the valence state of the metal). The hydrolysis reaction replaces alkoxyl groups with hydroxyl groups. Subsequently, the condensation occurs through formation of an oxo-bridge (-O-) between two metal centers and the elimination of alcohol (alcoxolation) or water (oxolation).The overall hydrolysis-condensation reactions of the sol-gel routes can be presented by the following simplified ones:

Hydrolysis:

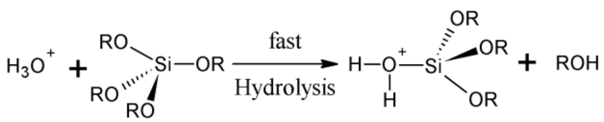
$$\text{M-(OR)}_x + \text{H}_2\text{O} \longrightarrow \text{M-(OH)(OR)}_{x-1} + \text{R-OH} \tag{4}$$

Condensation:

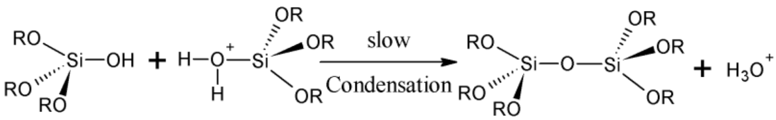
$$\text{M-(OH)(OR)}_{x-1} + \text{M-(OR)}_x \xrightarrow[\text{Alcoxolation}]{} \text{(OR)}_{x-1}\text{-M-O-M-(OR)}_{x-1} + \text{ROH} \tag{5}$$

$$\text{M-(OH)(OR)}_{x-1} + \text{M-(OH)(OR)}_{x-1} \xrightarrow[\text{Oxolation}]{} \text{(OR)}_{x-1}\text{-M-O-M-(OR)}_{x-1} + \text{H}_2\text{O} \tag{6}$$

It is well known that silicon alkoxidesSi-$(OR)_4$, such as tetraethylorthosilicate (TEOS/ $Si(OCH_2CH_3)_4$), are excellent precursors in the sol-gel process. These *precursors* can be utilized in synthesizing microporous silica via the polymeric sol-gel route under acid-catalysed conditions (HCl or HNO_3) [23-25]. During acid-catalysed hydrolysis the alkoxy OR is substituted by water according to a nucleophilic*substitution* reaction, S_N2, accompanied by inversion of the silicon tetrahedron (reaction (7a)). Condensation of the silanols is directed preferentially towards the ends of siliceous oligomers which result in the formation of an oxo-bridge (Si-O-Si) as shown in the reaction (7b) [26]:



(7a)



(7b)

Table 1. Summary of reported gas separation results of H_2 membranes

Summary of reported gas separation results of sol-gel-derived silica membranes						
T (°C)	Support	ΔP a) (Pa)	H_2permeance (mol. $m^{-2} \cdot Pa^{-1} \cdot s^{-1}$)	Gas A	Sel.* H_2/A	Ref.
300	γ-alumina	10^5	$2*10^{-7}$ - $7*10^{-7}$	CO_2	11-36	[36]
100	γ-alumina	200	$2.1*10^{-7}$	CO_2	9	[37]
200	α-alumina	$3*10^5$	$4.8 * 10^{-8}$	CO_2	16	[17]
Summary of reported gas separation results of palladium-based membranes						
200	porous glass	10^4	$2.2* 10^{-5}$ b)	N_2	7	[40]
373	α-alumina	$3*10^4$	$6.7* 10^{-6}$ b)	N_2	5000	[41]
445	α-alumina	10^5	$5* 10^{-7}$	N_2	1000	[42]

a) pressure drop across the membrane.
b) calculated from reference data.
* SelectivityH_2/gas A

Contrary to silicon alkoxides, the sol-gel chemistry of transition metal alkoxides is more complex, because transition metal precursors are highly reactive due to their low electronegativity and existence of various coordination numbers [27-31]. This in turn makes the metal ion very susceptible to nucleophilic attack, which makes it difficult to obtain a straightforward and controlled mechanism for hydrolysis-condensation reactions of these alkoxides. Dedicated chelating schemes have to be developed to prevent direct precipitation of the metal hydroxides.

In any case, both for silicon and transition metal alkoxides, it is necessary to control hydrolysis and condensation reaction rates. The fast hydrolysis and condensation rates can result in a precipitated product instead of a stable sol. By controlling a number of factors such as the nature of the alkoxy groups, solvent, molar ratio of water/alkoxide (h), pH, aging temperature and time, and drying, it is possible to influence the rate of hydrolysis and condensation reactions. The hydrolysis rate can be influenced by the nature of the alkyl group of metal alkoxides. It is decreased in the order tertiary > secondary > primary group. This is attributed to steric hindrance effects and the decreased positive partial charge of the metal ion with increased alkyl chain length. Substitution of the OR ligands by a chelating bidentate ligand such as acetylacetone (AcAcH) [32, 33] leads to the formation of a new molecular precursor which exhibits a different molecular structure. Here AcAcH acts as a bidentate, ligand on titaniumisopropoxide ($Ti(OPr^i)_4$ with Pr^i=$OCH(CH_3)_2$), i.e.,

$$Ti(OPr^i)_4 + AcAcH \longrightarrow Ti(OPr^i)_3AcAc + Pr^iOH \qquad (8)$$

These complexing ligands are much more difficult to hydrolyse than alkoxy groups. They restrain the fast hydrolysis of the precursor and consequently slow down the condensation process. Selecting an appropriate solvent such as an aprotic solvent (tetrahydrofurane, dioxane) instead of a proticsovent (H_2O, alcohols) [22] can also slow down the hydrolysis rate. In general, the solvents most often used are parent alcohols, which have the same number of carbon atoms in the alkyl group as in the alkoxy group of the precursor. The precursor can be hydrolyzed with H_2O released in-situ by the esterification reaction [34] or the oxolation reaction (reaction 6). The molar ratio of water/alkoxide (h) can control nucleation and growth of clusters in the sol. Wang et al. [35] prepared ultrafine titania particles (6nm) by carrying out hydrolysis of titanium isopropoxide with a high water/alcohol ratio (h>50). The pH is also an important parameter to prepare a sol. The peptization phenomenon with a mineral acid such as HNO_3, used to prepare a colloidal sol [27], is based on repulsive forces which prevent particle aggregation in the sol. When the pH value is decreased or increased away from the isoelectric point (IEP) of metal oxides, high repulsive forces exist in the sol stage. Near the IEP a flocculation phenomenon occurs due to absence of repulsive forces between particles, which results in precipitate formation.

Given its microporous structure and good permeability, sol-gel derived silica is one of the most studied candidates for H_2separation [17, 36, 37]. The silica synthesis from TEOS under acid catalyzed conditions results in the formation of an amorphous structure after sintering at T>400ºC, with pore sizes which can be smaller than 1nm. State-of-the-art microporous silica membranes often consist of a silica layer supported on a mesoporousγ-Al_2O_3 or α- Al_2O_3,or both, asymmetric membrane. The support provides mechanical strength to the selective silica layer, which is typically in the order of 100 nm thick. The H_2 permeance of these microporous silica membranes was reported to be in the range 10^{-8} to 10^{-7} $mol \cdot m^{-2} \cdot Pa^{-1} \cdot s^{-1}$ as shownin Table 1, with limited information on their H_2 selectivity over CO_2, though. However, the use of steam in the reforming processes has a serious impact on the resulting performance and longevity of the microporous silica membranes. The hydrophilic nature of the silica surface leads to the degradation of the silica microstructure in the presence of water vapourwhich involves the rupture and hydrolysis of siloxane bridges (Si-O-Si) at high temperature [38]. De Vos et al. [23] incorporated hydrophobic methyl groups which covalently bind to silica in the sol–gel process in order to obtain hydrophobic selective silica membranes, but only studied the sorption of water vapour of the membrane. Upon exposure to water in pervaporation experiments, this type of membrane did not perform stable at temperatures higher than 95ºC[31]. More recently, the research group of Vente at the Energy Research Centre of The Netherlands (ECN) [39]successfully developed a microporous hybrid membrane based on silica HybSi®. They introduced organic bridges to the inorganic network structure of the membrane by using 1,2-bis(triethoxysilyl)ethane $(EtO)_3Si–CH_2CH_2–Si(OEt)_3$). The role of ethyl links was suggested to provide additional shielding of the Si–O–Si bonds and reduce the number of hydrolysable groups per Si. After two years of testing at 150ºC in pervaporation, the performance of the membrane remained unaltered [39].

The hydrothermal stability of amorphous silica membranes is said to be improved by doping the starting silica sol with a second metal oxide such as Al_2O_3, TiO_2, ZrO_2, or NiO[25, 38]. For example, the alumina-doped silica membrane exhibited separation properties similar to the pure silica membranes and the hydrothermal stability was improved after doping with 3% alumina [38]. Upon exposure to 50 mol% steam/air at 600°C for 30h, the 3% alumina-doped silica had 64% reduction in the surface area and a loss of 86% micropore volume, compared to 85% and 94%, respectively, for the pure silica. It remains to be seen however if these are really doped materials or physical mixtures of the two compounds. Pure Al_2O_3, TiO_2, and ZrO_2 membranes[27-31] are considered more stable alternatives to replace silica membranes under hydrothermal conditions. However, the sol-gel chemistry of transition metal oxides is more complex than that of silica, because transition metals are highly reactive to form hydroxides and exhibit various coordination numbers. These characteristics lead to the difficult control of hydrolysis and condensation rates in the sol-gel process. Most of the reported porous membranes have pore sizes in the mesopore range [43-45]. The mesoporous membranes have lower selectivity for H_2 than the silica membranes because Knudsen diffusion is dominant. The ideal selectivity, $S_{i/j}$, of Knudsen diffusion is determined by the molecular mass M of the components i and j, which is given by:

$$S_{i/j} = \sqrt{\frac{M_j}{M_i}} \qquad (9)$$

The Knudsen selectivity of H_2 over CO_2 is about 4.69 and, therefore, insufficient for high purity H_2 separation. A high H_2 selectivity is one of the key factors for membrane performance. The presence of pinholes in the sol-gel-derived membranes may also be responsible for the relatively lower selectivity. In general, mesoporous membranes are used to provide a homogenous layer with narrower pore size distribution and sufficient smoothness suitable for the deposition of a thin microporous top layer such as silica. In order to produce a structure of defect-free layers with continuously decreasing pore sizes, it is necessary to repeat the coating and sintering steps (Figure 1) several times. This large number of processing steps is a disadvantage of such asymmetric ceramic membranes, which result in a time consuming, and expensive process, and an increase in membrane thickness, leading to a decrease in the permeability of the membrane [44]. The permeability F ($mol \cdot m^{-1} s^{-1} Pa^{-1}$) of a gas through a membrane is usually defined as:

$$F = \frac{Jl\mu}{\Delta PA} \qquad (10)$$

where J is the gas flow through the membrane ($mol \cdot s^{-1}$), l is the membrane thickness (m), μ is the pore tortuosity (dimensionless, number in between 2 and 13), ΔP is the pressure drop across the membrane (Pa), and A is the exposed area of the membrane (m^2). Due to the fact that membrane thickness and pore tortuosity can not be obtained unambiguously, the permeance P_m ($mol \cdot m^{-2} s^{-1} Pa^{-1}$) can often be used to evaluate the membrane, and is given by Eq. (11):

$$P_m = \frac{J}{\Delta P A} \tag{11}$$

Typically, the colloidal sol-gel route is used in the fabrication of mesoporous membranes which results in a wide pore size distribution, whereas uniform pore sizes with small width of the distribution are required for high performance (i.e., selectivity and flux) application of the membrane reactor. Both α- and γ-Al_2O_3 are known for exhibiting a wide pore distribution. Even the γ-Al_2O_3 has a pore size distribution centered around 6 nm and tailing up to 20 nm (see section *CHARACTERISATION OF SOL-GEL DERIVED MEMBRANES*), clearly not an ideal starting point for pore size tailoring. The mesoporous silicate molecular sieves, known as MCMs, were synthesized using the sol-gel route of silica precursors in the presence of a surfactant assembly [46]. In the evaporation-induced self-assembly (EISA) process, the arrays of self-assembled surfactant molecules are used as structural directing templates for the pore structure, around which siliceous species are polymerized. The organic surfactant is removed at the end of the synthesis by calcination in order to create pores which have the shape and size of the surfactant core filling the silica framework. These MCMs have very narrow pore size distributions that can be tuned ranging from 2 to 100 nm and low tortuosity [47]. This provides a bottom-up method for creating new porous materials and controlling their pore size through varying surfactants with different molecular sizes. Several groups have reported alternative sol-gel synthesis methods based on the surfactant assembly mechanism for the preparation of ordered mesoporousmaterials based on different metal oxides with similar MCM-like symmetries. For example, SBA-15 silica [47] exhibits a two-dimensionalhexagonal structure with a well-ordered hexagonal array and one-dimensional channel structure. The characteristics such as uniform pore size, narrow pore size distribution make MCM-like materiala suitable one for other approaches such as pore size reduction via Atomic Layer Deposition

(ALD). Figure 2 gives an illustration of two types of pore size distribution which can be obtained by sol-gel process with and without EISA.

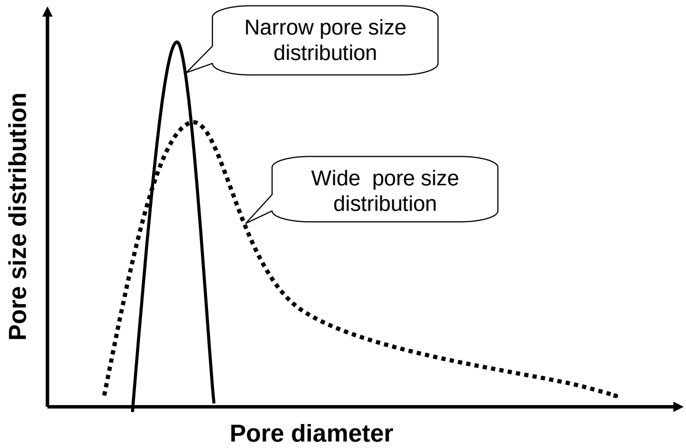


Figure 2.Schematic of pore size distribution as a function of pore size of two sol-gel derived materials, prepared with (solid line) and without the evaporation-induced self-assembly (EISA) process (dotted line).

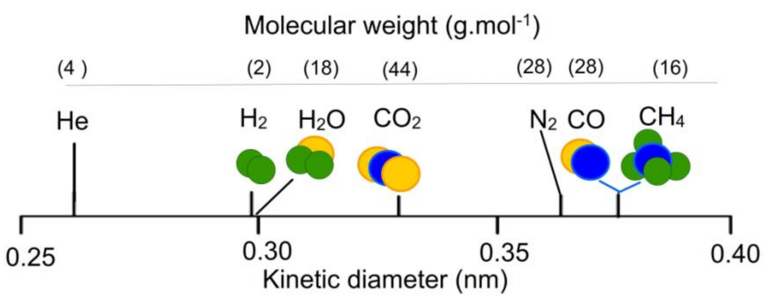


Figure 3.Selected properties of some small gases.

Chapter 3

MODIFICATION OF SOL-GEL DERIVED MEMBRANES

It must be noted that in order to enhance the selectivity of H_2 membranes, the mentioned mesoporous membranes must be modified to reduce the mesopore size to close to the size of the kinetic diameter of H_2. As shown in Figure 3 if the pore size of membrane is between the molecular sizes of H_2 and CO_2, it can result in extremely high H_2 selectivity based on the molecular sieving mechanism. However, it is a challenge to develop such a membrane because the kinetic diameter of H_2 is very close to the other gases involved in the steam-methane reforming and water gas-shift processes.

According to literature data [48], the separation of H_2 from other small molecular size gases (CO_2, CO, H_2O) relies on the competition between molecular diffusivity and/or the molecular sieving effect when the pore size is in the range of 0.5 nm. A variety of surface modification techniques has been explored to reduce the pore size in order to improve the performance of membranes, including Chemical Vapour Deposition (CVD), and Atomic Layer Deposition (ALD). CVD can graft silica on mesoporous membranes such as γ-alumina [48]. The resulting silica-alumina composite membrane exhibits a high H_2permeance in the order of 10^{-7} mol. $m^{-2} \cdot Pa^{-1} \cdot s^{-1}$ with expected higher hydrothermal stability compared with the sol-gel derived silica membranes as mentioned earlier [37]. Similar to CVD, ALD is a promising strategy to the modification of membranes. The technique is a self-limiting layer-by-layer thin film deposition method, which is based on sequential and saturating surface reactions of the alternately applied precursors. Usually, the ALD of metal oxides is comprised of sequential steps of adsorption and hydrolysis/oxidation of metal precursors such as metal halide and metalorganicprecursors. In fact, ALD has been investigated to deposit thin metal-oxide films onto complex porous substrates with a highly conformal film coverage [49-52]. The use of ALD is based on the fact that the deposition of metal-oxide films consists of two reactions in which a metal precursor first attaches to available surface sites such as surface hydroxyls, followed by a separate reaction of the metal precursor with an oxygen source such as H_2O to form a monolayer film and regenerate the surface sites. These sequential saturating reactions are referred to an ALD cycle. The review paper by Puurunen[53] described most aspects about this process with ALD of trimethylaluminum ($Al(CH_3)_3$) and H_2O as a case study. The reaction conditions lead to a self-limiting growth mechanism which is ALD's most typical characteristic. In addition, since this process uniformly deposits the film onto any exposed surface that contains active sites, including internal walls of pores as well as steps and corners, it is highly conformal with atomic precision. Conformal coatings with monolayer precision of ALD have been used to deposit metal oxide layers of Al_2O_3, TiO_2, and ZrO_2 either on the internal pore surface or on the entrance of the pores in order to reduce the initial pore sizes of the membranes. Figure 4 depicts the overall scheme of this work in our laboratory. The mesoporous membrane is prepared by a sol-gel process combined by the evaporation-induced self-assembly (EISA) process. The EISA through cooperative self-assembly of inorganic species and organic surfactant is a synthesis approach to fabricate mesostructured materials with well-defined pore structures and uniform pore sizes. This multi-layer system with the tailored top layer serves as a starting point for pore size tuning. It can be further exposed to a metal halide precursor and an oxygen source in a typical type of ALD apparatus as developed in our laboratory [54] and leads to the deposition of metal oxide layers. By adjusting the metal oxide thickness, the initial mesopore size can significantly be reduced to the desired dimension (micropores) and, therefore, improve H_2 selectivity of the membranes.

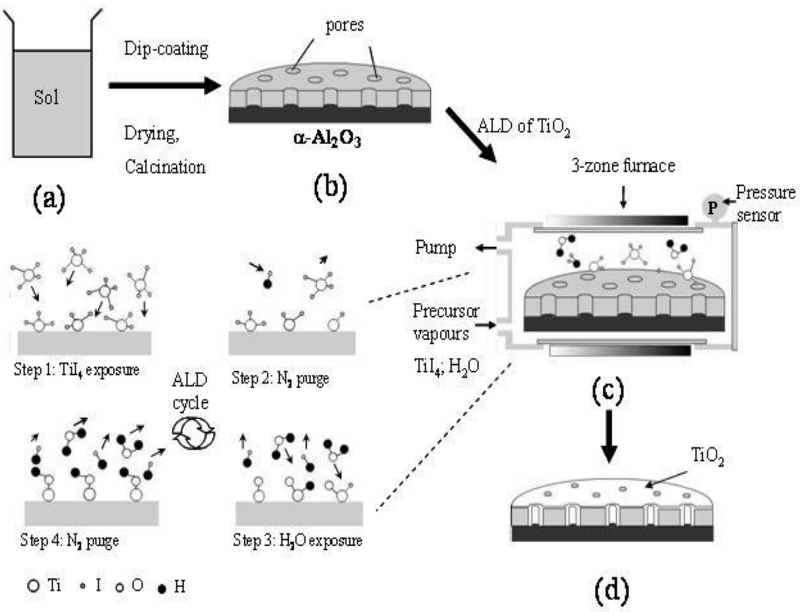


Figure 4. Schematic of the structural and chemical modification of ideal sol-gel derived membranes which includes (a) sol prepared with the evaporation-induced self-assembly (EISA) process, (b) sol-gel derived membrane, (c) atomic layer deposition (ALD) of TiO_2, (d) TiO_2 modified sol-gel membrane.

Figure 5 shows the permeance of single component gases (He, H_2, CO_2, and N_2) through the mesoporous alumina and modified alumina membranes with ALD of TiO_2 by using TiI_4 and H_2O as precursors. The alumina membrane used for this experiment is 10 nm in pore diameter, prepared by the EISA process with tri-block copolymer Pluronic© P123 ($EO_{20}PO_{70}EO_{20}$, EO=ethylene oxide, PO=propylene oxide)as template agent and aluminium tri-secbutoxide as aluminium source, which is further coated with 15 ALD cycles of TiO_2 deposition (~ 3 nm)[55]. The gas permeances decrease with increasing the molecular size of the permeating gas, which are quite different as well in both cases. The modified alumina membrane exhibits a permeance one order of magnitude smaller than that of the unmodified membrane. This result is a strong indication that the pore structure of the membrane is modified by the ALD process. The permeance of H_2 is approximately two times higher than the value of CO_2 for the mesoporous alumina. In the case of TiO_2-deposited alumina membrane, the permeance of H_2 is approximately four times higher than the value of CO_2. These results clearly show that with ALD it is possible to reduce large pore diameters of alumina and proves that the ALD technique can improve the H_2 selectivity. Knudsen diffusion takes place for micropore transport of H_2 andCO_2 in this membrane.

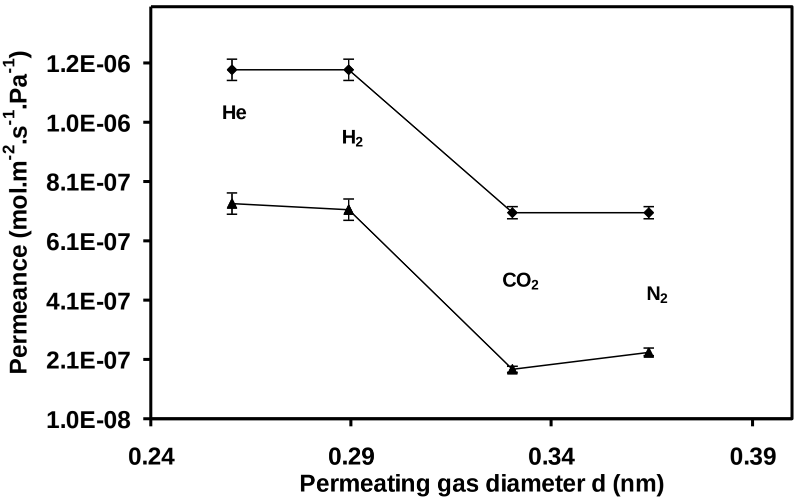


Figure 5. Relationship between permeance and the gas molecule's kinetic diameter d from single gas permeation experiments at 25 °C and a pressure drop of 10^5 Pa of bare alumina (diamond symbols) and TiO_2-deposited alumina (triangle symbols) membranes.

Chapter 4

CHARACTERISATION OF SOL-GEL DERIVED MEMBRANES

The information of the pore size distribution and of the pore volume of a sol-gelderived membrane is particularly interesting for the fundamental membrane properties, which allow for predicting membrane performance such as the selectivity, the flux, or the permeability. A variety of techniques is available with both advantages and disadvantages, and certain techniques depend strongly on the membrane material, morphology, and other specific properties. Characterization techniques can be different for “unsupported” or “supported’’ thin membrane films, depending on the state in which the membrane samples are prepared. This distinction is meaningful, because the membrane preparation can either involve the sol-gel layer without or with the meso- or macroporous support. A schematic overview of characterization techniques for sol-gel derived membranes is given in Table 2.

The conventional physisorption technique [56], employing gases like argon (Ar), nitrogen (N_2), or krypton (Kr) is predominantly used to analyze surface areas and porosities of unsupported membrane films. The characteristics of physisorption isothermscan be grouped into six types, among which type I (for micropore) and type IV (for mesopore) isothermsaccording to the IUPAC classification are of interest for this review. The specific surface area can be deduced from the isotherm data of the relative pressure between 0.05 and 0.30 using the Brunauer, Emmett, and Teller (BET) equation [57]. Figure 6 shows the N_2physisorption isotherm of an unsupported silica membrane prepared in our laboratory with TEOS ($Si(OCH_2CH_3)_4$)with a typical sol molar composition of 1(TEOS)-6.4(H_2O) –0.085(HNO_3) –3.8 (C_2H_5OH) (a). The isotherm of pure SiO_2 is type I without hysteresis, due to the absence of liquid phase formation as a result of capillary condensation but by micropore filling at low relative pressure. Figure 6 shows the N_2physisorption isotherm of an unsupported γ-Al_2O_3 membrane prepared with a typical sol molar composition of 1 (Aluminium tri-secbutoxide)-55.6 (H_2O)–0.07 (HNO_3) (c). Most of the γ-Al_2O_3 in literature is synthesized using Yoldas's recipe [27]. The N_2 isotherm is type IV with the typical hysteresis between the adsorption and desorption branches due to the capillary condensation of N_2 inside the mesopores. For the alumina/silica hybrid membrane with 36 mole % of SiO_2 (Figure 6b), the isotherm is similar to that of γ-Al_2O_3, but the volume of adsorbed N_2 is almost doubled at low relative pressures compared to that of pure γ-Al_2O_3. This result shows fingerprints of both the meso- and microporous nature of its constituents [58]. The corresponding pore size distributions of SiO_2 and Al_2O_3 are shown in Figures 7 and 8, respectively. The average pore size of the SiO_2 is in the microporous regime while the pore size of the γ-Al_2O_3centers around 6 nm in the mesoporous regime.

Table 2. Overview of some characterizations for sol-gel derived membranes

Characterization method	Determined membrane property	Membrane state during characterization
N_2physisorption	Surface area, pore size distribution	Unsupported
Permporometry	Gas flux, pore size , crack, defects	Supported
Gas permeation	Selectivity, separation	Supported
Low- and wide-angle X-ray diffractions	Composition, structure, particle size, pore size	Unsupported
SEM, TEM, AFM	Morphology	Unsupported Supported
Spectroscopic Ellipsometry (SE)	Pore size distribution, thickness	Supported

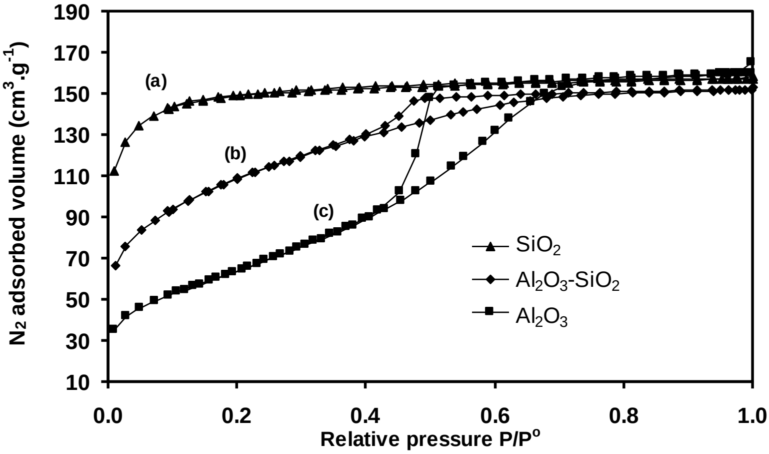


Figure 6.N_2physisorption isotherms at 77K for SiO_2(triangle symbols), alumina/silica hybrid (diamond symbols), and Al_2O_3 (rectangle symbols) calcined at 600 °C.

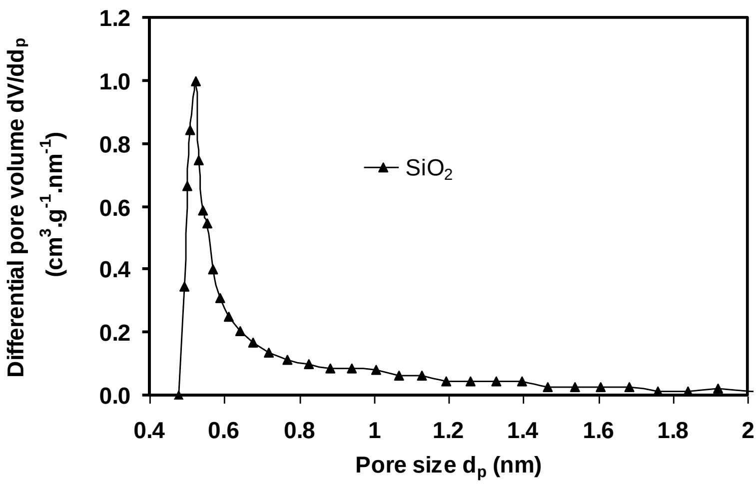


Figure 7. Pore size distribution at 77K of unsupported SiO_2calcined at 600 °C calculated using the Horvath-Kawazoe method.

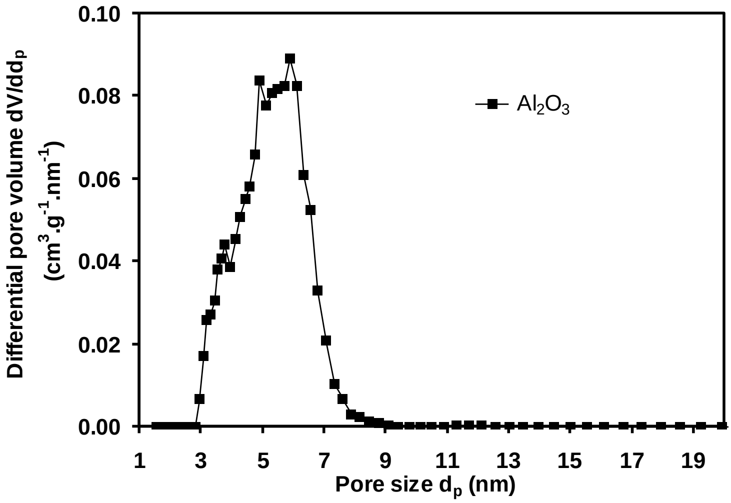


Figure 8. Pore size distribution at 77K of unsupported Al_2O_3calcined at 600°Ccalculated using the non-local density functional theory method.

In order to determine the pore size distribution of a mesoporous layer on a macroporous support, which really contributes to the permeability of a membrane, permporometry is an effective technique [59]. It is supposed that unsupported sol-gel materials have a similar structure as a processed sol-gel layer on the support, even while in reality the forces developing during the drying process of both materials are different, *i.e.*, not only evaporation and setting but evaporation, infiltration, and setting. The N_2physisorption technique is commonly used for the measurement of the pore size of unsupported membranes but cannot distinguish dead-end pores from active pores. In addition, it cannot differentiate between the thin separative (sol-gel) layer and the macroporous support. Hence, permporometry is a more adequate technique for studying the whole assembly, because active pore sizes in the separating layer on a supported membrane can be detected in-situ. In short, a condensable vapour (H_2O) and a non-condensable gas (He) are passed through the membrane. During the measurement the pores are stepwise blocked by the condensation of H_2O vapour at increasing partial water vapour pressure. The pore size in which capillary condensation of H_2O can still occur is expressed as a function of the relative H_2O pressure by the Kelvin equation [59]:

$$\ln\left(\frac{P}{P_0}\right) = \frac{-2\gamma V_M}{rRT}\cos(\theta) \tag{12}$$

where P/P_o the relative vapour pressure of the condensable gas, $\gamma$the surface tension ($N \cdot m^{-1}$), V_M the molar volume ($m^3 \cdot mol^{-1}$), R the gas constant ($J \cdot K^{-1} \cdot mol^{-1}$), Tthe absolute temperature (K), r the Kelvin radius of the pore (m), and θ is the contact angle of the liquid on the solid(rad).

For each relative pressure all pores with radius smaller than the threshold value r are blocked by the condensed H_2O vapour, the He permeation passes through the larger than r pores. At a relative pressure of 1 all pores of the membrane are filled and He transport through the membrane is not possible, provided no large defects and cracks are present. When the partial water vapour pressure is reduced, pores with larger size than r are emptied and become available for He diffusion. The Kelvin radius r of the pore does not correspond exactly to the actual pore radius. In order to obtain the real pore radius, it must be corrected by adding the thickness of one or more H_2O monolayers (t-layer) [59], which forms on the surface of the pores before capillary condensation occurs. As an example, the resulting Hepermeance – Kelvin radius r plot for a γ-Al_2O_3membrane with increasing and decreasing partial pressure of H_2O vapour is shown in Figure 9. Considering the existence of a t-layer, the pore size might be larger than 2r (~ 6 nm), which is in good agreement with that obtained by the N_2physisorption technique.

Gas permeation measurements can be used to determine the permeability of membranes (see Eq. (10) and Figure 5). This method is the main tool to evaluate the membrane performance. Comparison of the permeations of different gases (He, H_2, CO_2, N_2) can provide an estimate of the membrane pore size and the selectivity. The permselectivity of the membrane is conveniently defined as the ratio of the permeances of two different gases. For a binary gas mixture, i.e., H_2/CO_2 the separation factor α_{H_2/CO_2} is expressed as a function of their molar fractions as is given in the following equation:

$$\alpha_{H_2/CO_2} = \frac{y_{p,H_2}}{x_{r,H_2}} \frac{x_{r,CO_2}}{y_{p,CO_2}} \tag{13}$$

where y_{p,H_2}, y_{p,CO_2} are the molar fractions of H_2 ,CO_2at the permeate side and x_{r,H_2}, x_{r,CO_2} are the molar fractions of H_2, CO_2 at the retentate side.

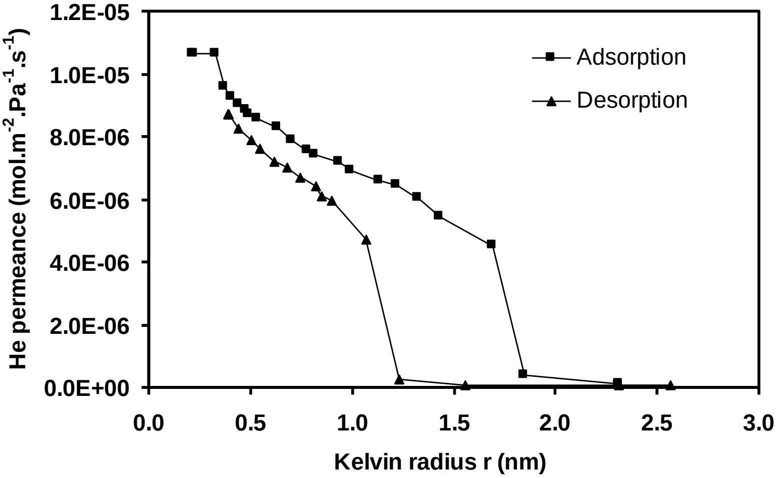


Figure 9. He permeance as a function of the Kelvin radius measured with H_2O used as a condensable gas in permporometry for a γ-Al_2O_3 membrane.

Low- and wide-angle X-ray diffraction (XRD) studies are performed to characterize the structural properties of the porous systems. The spatial resolution of low-angle XRD fits well with the dimensions of a porous system such as MCM. If there is an ordered mesoporous structure, the peaks in the low-angle range of 1-10º can be observed with the d spacing superior to 1.8 nm. Figure 10 represents the low-angle XRD diffraction pattern of mesoporous (templated) silica after calcination at 500ºC and displays one peak at 2θ=2.85º,the (1 0 0) reflection or more precisely the (1 0) reflection since a 2D array of cylinders is concerned. This result indicates good long-range hexagonal ordering with a d-spacing of 3.15 nm.

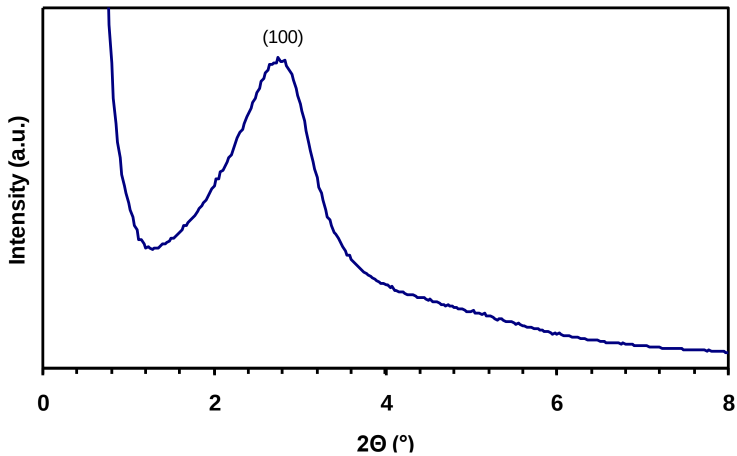


Figure 10. Low-angle XRD diffraction pattern for a templated silica sample calcined at 500ºC in air.

Wide-angle XRD is routinely used to identify crystalline phases, quantitative phase analysis, and estimate of crystallite size of sol-gel derived materials. Ceramic membranes prepared by sol–gel processing can be categorized into amorphous materials such as silica, and crystalline materials such as alumina and titania. Figure 11 shows the XRD pattern of γ-Al_2O_3, which is calcined at 600ºC in air. Depending on the calcination temperature, structural evolution in sol-gel derived materials gives other, metastable, phases of metal oxides, for example, in the case of alumina it can be summarized in the following reaction scheme:

$$(\gamma\text{-AlOOH}) \xrightarrow{500°C} \gamma\text{-}Al_2O_3 \xrightarrow{800°C} \delta\text{-}Al_2O_3 \xrightarrow{1000°C} \theta\text{-}Al_2O_3 \xrightarrow{1200°C} \alpha\text{-}Al_2O_3 \qquad (14)$$

Microscopy methods are widely used to investigate the morphology of membranes. Atomic Force Microscopy (AFM) [60] can give information about the membrane roughness, morphology, and even pore size, provided the probing tip is carefully chosen. Scanning Electron Microscopy (SEM) can only give qualitative information about the membrane morphology and an estimation of the “separative layer” thickness, because the resolution is not high enough to visualize the pores in the “separative layer” of a membrane. In addition, any asymmetry of the structure and defects (cracks, pinholes) can be observed. A ZrO_2 membrane is synthesized with an asymmetric structure as shown in Figure 12. The top ZrO_2 layer has a controlled pore size in the region of 10 nm which is responsible for the separation properties of the membrane, while the α-Al_2O_3 porous support (pore size > 100 nm) provides the mechanical strength required for the membrane to operate at high pressures.

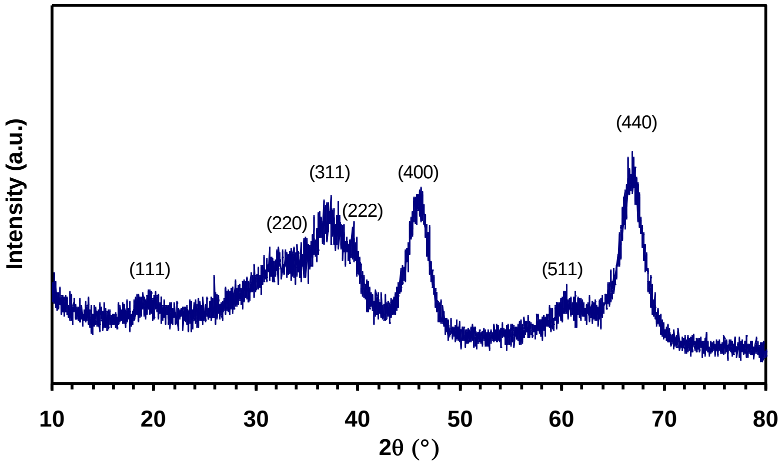


Figure 11. Wide-angle XRD pattern of γ-Al_2O_3calcined at 600ºC in air.

For Transmission Electron Microscopy (TEM) a thin slice has to be cut from the membrane which is embedded in a non-conducting resin. TEM has a very high resolution (< 1 nm), but often small cracks can be seen in the samples, caused by the cutting procedure. Also the influence of the embedding resin on the membrane structure is an issue. Figure 13 shows a TEM micrograph of a cross section of a typical γ-Al_2O_3membrane prepared as previously described. The membrane consists of a top γ-Al_2O_3layer, followed by a support with larger, coarser particles of α-Al_2O_3.

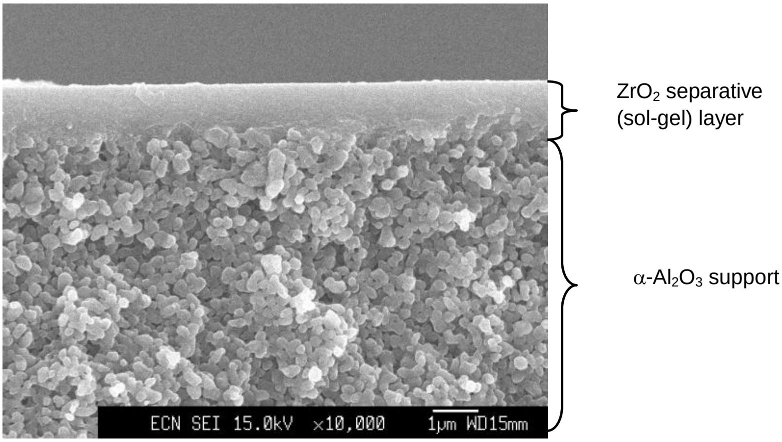


Figure 12.Scanning electronic micrograph of a cross section of a typical zirconia membrane prepared by a sol-gel synthesis method. The membrane consists of a top ZrO_2 layer (thickness of ~ 1 μm), followed by a support with larger, coarser particles of α-Al_2O_3.

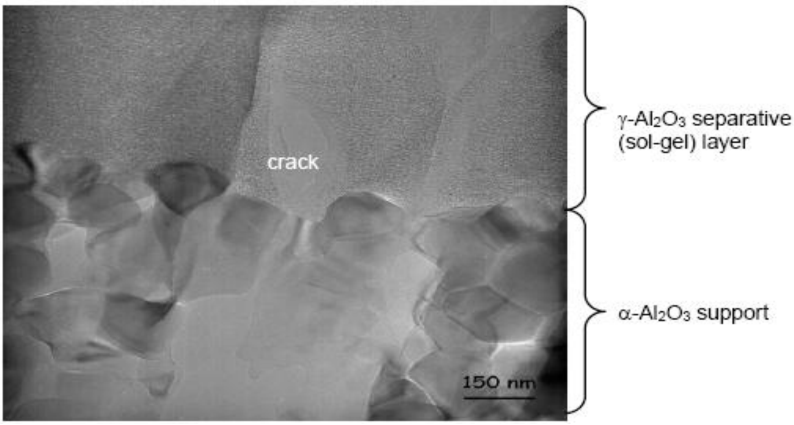


Figure 13. Transmission electronic micrograph of a cross section of a typical γ-Al_2O_3membrane prepared by a sol-gel synthesis method. The membrane consists of a top γ-Al_2O_3layer, on top of a support with larger, coarser particles of α-Al_2O_3.

An optical technique such as Spectroscopic Ellipsometry (SE) has also proven to be useful for membrane characterization. Ellipsometry measurements are routinely used to determine thickness and optical constants of dielectric and semiconductor films [61]. SE measures the change of polarization in light intensity reflected from or transmitted through a sample. The polarization change is described by an amplitude ratio, tan (Ψ), and phase difference, Δ, between light oriented in the p- and s- directions relative to the sample surface:

$$\rho = \tan(\psi) e^{i\Delta} = \frac{R_p}{R_s} \tag{15}$$

whereR_p and R_s represent the complex Fresnel coefficients for p- and s-polarizations, respectively. From the obtained ellipsometric data Ψ and Δ, the film thickness and the optical constants, e.g., the refractive index (n) and extinction coefficient (k) can be deduced from the Fresnel equations. The application of SE for studying thin film synthesis reveals a fast and reliable technique, especially in-situ during ALD where the film thickness and the growth rate per ALD cycle can be monitored [62]. Combining ES with gas adsorption (ellipsometricporosimetry) can be used for measuring porosity and pore size distribution of thin porous membranes. The method is based on the ability of the physisorption of a solvent vapor into the porous network, in the similar way of N_2physisorption. It consists in measuring the change of the optical characteristics of the porous film during solvent vapour adsorption and desorption in order to calculate porosity and pore size distribution of the film [63].

Chapter 5

MEMBRANE APPLICATION IN THE WGS REACTOR

Since the relatively low H_2 selectivity in other sol-gel derived membranes than those based on silica, there have predominantly been studies on WGS and SMR with H_2-selective microporous silica [64-66].The concept of such a membrane reactor is illustrated in Figure 14. A single step or two-step reforrning (SMR or/and WSG) takes place on the catalyst and H_2 permeates selectively through the membrane to the permeate side. In the retentate side, a stream consisting a small amount of non-recovered gases (CH_4, CO, H_2, andH_2O) and predominantly CO_2that could be sequestered to mitigate global warming effects.A sweep gas stream,i.e., H_2O can be used into the permeate side for improving the H_2 permeation driving force.

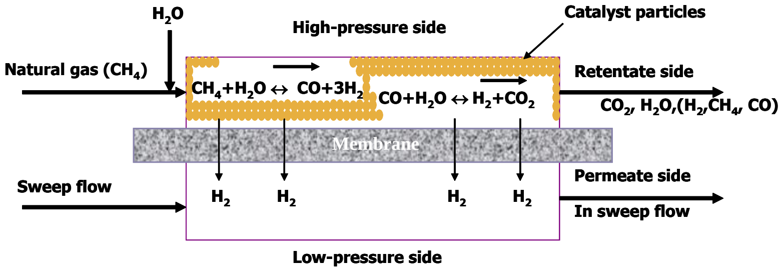


Figure 14. Membrane reactor configuration.

Giessler et al. [64] studied hydrophobic and hydrophilic silica membranes for WGS. The hydrophobic membranes presented very high hydrogen permeation fluxes at 250ºC, which reinforces the idea that higher flow rates and high conversion can be obtained with such membrane reactors as compared to a conventional reactor. At higher temperature (280ºC) another silica membrane [65] showed 95% CO conversion which was achieved at 4 bar. Silica membranes show potential benefits in WGS, though steam presence in the process is a serious issue for longevity of a membrane as previously described.

Chapter 6

OUTLOOK

This review focused on the recent progress in the research and development of sol-gel ceramic membranes for potential application in high-temperature H_2separation. The advantages of the sol-gel coating are that the sol-coating methods are simple and do not require high investment costs. The sol-gel technique can be combined with other techniques such as CVD and ALD in order to develop hybrid membranes. Amorphous microporous silica membranes prepared by the sol-gel technique or modified with CVD are the most notable of inorganic membranes with the capability of separating H_2. They exhibit very high H_2 fluxes due to their thin thickness. However, the major problem is the hydrothermal instability of these membranes. They only show excellent separation performance for H_2 in dry applications. While in steam-reforming processes hydrothermal conditions are apparent, it is necessary to choose alternative materials with higher stability. From the point of view of hydrothermal stability, non-silica materials such as Al_2O_3, TiO_2, and ZrO_2promise a high potential in H_2 separation for membrane application in steam-reforming processes. However, most of these are mesoporous membranes, but also here the selectivity of the membrane can be increased by tuning the pore size as in the silica case. Current membranes do not have high H_2 selectivity. Strategy towards the synthesis of membranes exhibiting high transport and selectivity for H_2 can be possible by combining sol-gel with templating molecules and ALD in the membrane fabrication which has proven functional in tailoring the pore size. Membrane materials with high H_2selectivitieshave been studied on the laboratory scale, which can be scaled-up for the industrial applications. Moreover, more attention to defects (pinholes), high fluxes, and reasonable H_2 selectivity will be beneficial for the successful application of ceramic membrane reactors.

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