GAS PERMEATION
THROUGH SOL-GEL DERIVED
ALUMINA AND SILICA BASED MEMBRANES

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my mother,
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my brother,
BERTAN TOPUZ
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ABSTRACT

GAS PERMEATION THROUGH SOL-GEL DERIVED ALUMINA AND SILICA BASED MEMBRANES

The scope of this thesis is to design defect-free microporous and mesoporous ceramic membranes having micro-engineered pore network that would contribute to the enhancement of pore control abilities as well as the thermal stability.

In this study, mono-dispersed silica sols having well-defined silica spheres ranging in size from 5 to 700 nm were prepared through sol-gel methods and thin membrane layers were consolidated on either γ-alumina support or unsupported form. The packing of 5 nm silica spheres resulted in micropores of 0.87 nm in 400 °C treated membranes with the porosity of 0.32 which are in well agreement with the porosity level of random loose packing. Silica spheres with varying concentration and size were incorporated into polymeric network to complement the percolative structure of sphere packing with interpenetrated polymeric silica network in order to design well-defined thermally stable transport pathway. Low shrinkage value was obtained for sphere incorporated system providing the high thermal stability by affecting the thermally induced microcrack formation as well as the structural relaxation during consolidation. The resulting hybrid structure enabled the detailed transport properties that support to be able to control the pore structure but N₂/CO₂ separation properties are needed to be improved.

Stable polymeric alumina sols having particle sizes smaller than 2 nm could be obtained when the hydrolysis conditions were accurately controlled. The mixture of prepared polymeric silica and alumina sols in mullite compositions (3:2) provided to the crystallization of mullite with homogeneously mixed stable oxide network upon heat treatment at 775 °C.
ÖZET

SOL-JEL YÖNTEMİYLE HAZIRLANAN ALUMİNA VE SİLİKA BAZLI SERAMİK MEMBRANLARDA GAZ GEÇİRGENLİĞİ

Bu tez tasarlanabilen gözenek ağına sahip, membranların gaz ayırma yeteneğiyle ilgili gözenek yapısının kontrol edilmesi ve yüksek ısısal kararlığının sağlanmasına yönelik, kusursuz, mikro ve mezo gözenekli seramik membran geliştirmeyi kapsamaktadır.

Bu çalışmada, çapları 5 ile 700 nm arasında olan, tekil boyut dağılımı silika küreleri, sol-jel yöntemi kullanılarak hazırlıdı ve ince bir katman olarak daha iri gözenek yapısına sahip alumina destek üzerine ya da desteksiz olarak paketlenmiştir. 5 nm çaplı silika kürelerinin 400 °C de ısıt işlem görmesi sonucu gözenek çapı 0.87 nm ve gözenek miktarı 0.32 olan gözenek yapısı elde edilmiştir ve gözenek miktarı rastgele siki paketlenme seviyesiyle uyumludur. Membran gözenek yapısı ve parçacık paketlenme davranışını kontrol edebilmek amacıyla farklı boyut ve konsantrasyonlarda silika küreleri polimerik silika sol içerisinde paketlenmiştir. Polimerik ve kolloidal sistemin birlikte paketlenmesi sonucu ısıt işlem sonrasında düşük boyutsal değişimin gözenmesi ısısal kararlığının arttığını göstermiştir. Tasarlanabilen hibrid mikro yapının gaz geçirgenlik davranışlarına dayanarak gözenek yapısının kontrol edilebiliğini ancak N₂/CO₂ seçici geçirgenliğinin iyileştirilmesi gerektiğine gerekliği sonucuna varılmıştır.

Parçacık boyutu 2 nm’nin altında olan kararlı polimerik alumina solları hidroliz koşullarının siki kontrol edilmesi sonucu hazırlanmıştır. Kararlı, polimerik yapılar sahip silika ve alumina sollarının mullit kompozisyonunda (3:2) karışımı, 775 °C’dede ısıt işlem uygulanmasıyla yaklaşık 30 nm kristal boyutunda mullit kristalleşmesine neden olmuştur.
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CHAPTER 1

INTRODUCTION

A membrane can be described as a semipermeable barrier which allows preferential passage of one or more selected species of a gaseous and/or liquid mixture under a certain driving force. Preferential mass transport of one particular species can be made possible through the movement of different species to a different extent (Hsieh, 1996). Despite excluding the main function of a membrane, IUPAC defined a membrane as “a structure, having lateral diameter much greater than its thickness, through which mass transfer occurs under a variety of driving forces” (Koros et al., 1996). Ceramic membranes having greater thermal-mechanical-chemical stability and high gas flux compared to polymeric membranes have became extremely important for gas separation processes in which the species with different chemical structure are transported based on their molecular sizes. Therefore, the preparation of thermally stable ceramic membranes with controlled structural and surface properties makes them very attractive for many membrane-based separations which are introduced in recent years as a promising unit operation.

Inorganic membranes may be either dense or porous. The ion-conducting perovskite and palladium membranes are examples of dense membranes. Porous membranes can be classified into macroporous (d_p > 50 nm), mesoporous (2 nm < d_p < 50 nm) and microporous (d_p < 2 nm). Inorganic microporous membranes have a narrow pore size distribution, and the pore diameter is typically smaller than 1 nm to influence the movement of various species to different extent. The developed surface area is high but the permeability is low (Ayral et al., 2008). Thus, in order to get high gas permeation rate the thickness of membranes should be thin enough. Because of low mechanical strength of such thin layer, these considerations led to the concept of asymmetrical structure having several layers with gradually decreasing pore size and thickness onto porous support. In this way, the pore size of asymmetric composite membranes shows a gradient structure from porous supports to the separation layer, so as to minimize the resistance to permeation across a membrane. The selective (mass transport) properties of these membranes are determined by the layers with the smallest
pores and the main transport resistance is in the microporous top layer and therefore, this layer should be very thin to have high fluxes. In general, the thin layers can be achieved by dip-coating onto a multi-layered porous supporting structure, usually consisting of a $\gamma$-Al$_2$O$_3$ layer on top of an $\alpha$-Al$_2$O$_3$ layer, as seen in Figure 1.1. The $\gamma$-layer supplies a smooth surface with sufficiently small pores to enable formation of the thin microporous silica layer from sol particles by preventing penetration into the support. Table 1.1 summarizes the layer properties of porous multilayered ceramic membranes.

![Figure 1.1. SEM micrograph of the supported silica membranes](Source: Ayral et al., 2008).

<table>
<thead>
<tr>
<th>Layer</th>
<th>Top (separative)</th>
<th>Intermediate</th>
<th>Support</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>SiO$_2$</td>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>$\alpha$-Al$_2$O$_3$</td>
</tr>
<tr>
<td>Thickness</td>
<td>30-200 nm</td>
<td>$10^3$-$4\times10^3$ nm</td>
<td>$2\times10^6$ nm</td>
</tr>
<tr>
<td>Pore Diameter</td>
<td>0.3-0.8 nm</td>
<td>2-5 nm</td>
<td>80-120 nm</td>
</tr>
</tbody>
</table>

The quality and appropriateness of membranes for a certain application are generally determined in terms of two key properties; permeability and permselectivity of desired molecules. These properties are determined by the microstructure of the membrane, expressed in terms of pore size, porosity and surface area, which in turn is controlled by the synthesis conditions. Thus, pore size and morphology of the
membrane have very important influence in deciding their final properties and desired application. Moreover, it is important to understand the relationship between the synthesis conditions and resulting structures to prepare a membrane with the required properties. In this respect, sol-gel processes attract most attention due to their excellent processibility, homogeneity and their potential towards close control of pore microstructure (Brinker et al., 1994). The use of silica polymeric sols can make the design of the pore networks possible for gas separation problems. Highly selective microporous silica membranes with high fluxes could be prepared by sol-gel dip coating processes (de Vos and Verweij, 1998). The structure of the thin silica layer mainly depends on the size and shape of the silicalite polymers and their packing behavior during drying and calcination. Short branched linear polymers are best for making silica microporous membranes having sufficiently small pore size and these membranes can be considered as molecular sieves since they sieve out large molecules from mixtures (Nair et al., 2000). Synthesis of silica polymers by the sol-gel process involves the hydrolysis and condensation reactions of starting metal alkoxides (Nair et al., 1997). The relative reaction rates of the hydrolysis and condensation reactions depend on the sol-gel synthesis parameters that influence the fractal behaviour of silica polymers including, the composition of reactants, aging of the sol, the reaction time and temperature. Optimization of these parameters is important to obtain membranes with minimum defect and hence high selectivity.

Several reviews on inorganic membranes are available some of which are dedicated to the synthesis and applications of microporous silica membranes (de Lange et al., 1995a; 1995b; 1995c; Burggraaf and Cot, 1996; Benes et al., 2000; Meinema et al., 2005). The main current developments deal with gas separations, in particular hydrogen separation. The thermal stability of silica membranes compared to organic and hybrid membranes and their interconnected microporosity enable to reach high permeability and selectivity (Brinker et al., 1993). H₂ permeance of the order of 10⁻⁶ mol/m²sPa with H₂/N₂ selectivity up to 100 has been reported (Meinema et al., 2005). de Lange et al., (1995b) investigated a microporous sol–gel modified ceramic membrane in the permeation and separation of H₂, CO₂, O₂, N₂, CH₄ and iso-butane. They stated gas permeation rates of 20*10⁻⁷ mol/m²sPa for H₂ at 200 °C, the separation factors were 30 for H₂/CH₄ and 200 for H₂/iso-butane. Improvements in the synthesis of supported silica membranes have resulted in very defect free layers (de Vos and Verweij, 1998). These silica membranes show high fluxes for small molecules like H₂,
O$_2$ and CO$_2$ and high selectivities for these molecules with respect to larger gas molecules due to the small pore size of the membranes. The high fluxes and selectivities of these membranes offer large number of applications including natural gas purification, selective CO$_2$ removal and H$_2$ purification. A specific application is their potential use in high temperature membrane reactor for selective removal of H$_2$ in order to increase the thermodynamically limited conversion. The other potential applications are pervaporation and nanofiltration of organic mixtures.

In order to get efficient gas separation, three keys to membrane production are (i) avoidance of cracks, pinholes and other defects that reduce the selectivity, (ii) precise pore size control and (iii) maximisation of porosity and minimisation of the membrane thickness to maximise flux (Brinker et al., 1994). Amorphous silica with pores smaller than 1 nm is suitable as a material for highly selective membranes. However, diffusion through such narrow pores is usually slow. In order to improve both the permeance and the selectivity of silica membranes, a number of studies have been reported on attempts to control the pore structure. Chemical vapor deposition (CVD), which is one of the methods used for preparation of such membranes, provides pore properties that are appropriate for gas separation. The modification of mesoporous membranes by a chemical vapor deposition technique results in very high separation factors. Specifically, Lee et al., (2004) prepared a CVD-modified silica membrane, of which the H$_2$/CO$_2$ selectivity was as high as 1000, and the H$_2$ permeation was $10^{-7}$ mol/m$^2$sPa at 600 $^\circ$C. Advances in the development of highly selective sol-gel derived membranes described by Brinker et al., (1993) have led to narrow pore size distribution in the microporous range. Detailed analysis of gas transport through sol-gel derived microporous silica membranes (on mesoporous alumina) showed that separation factors for H$_2$/CH$_4$ and H$_2$/isobutene of 30 and 200 at 200 $^\circ$C could be obtained. The activation parameters of the activated transport have been analyzed and the calculated activated energies for micropore diffusion suggested that the pores are smaller than zeolites 4Å (de Lange et al., 1995b).

The nature of the pore structure is one of the most important factors along with molecular properties and the interaction with the pore walls of gaseous species during their transport through porous membranes. Separation is achieved because the membrane has the ability to transport one type of the species from the mixture more readily than other species. This transport may occur through various transport mechanisms (Karger and Ruthven, 1992). The driving force for mass transport can be a
gradient in the pressure, electrical potential, concentration, temperature or chemical potential. The separation performance of a membrane is determined by its resistance for mass transport of a certain species. In general, for membrane processes, high flux of the species of interest should have been acquired while low fluxes for other species. The dominant transport mechanisms can differ from layer to layer and which transport mechanisms are dominant in each of the supporting layers is mainly determined by the ratio of the mean free path of the molecules and pore size of these layers. When the mean free path of the gas molecules is much larger than the pore size, \(\lambda \gg d_p\) collisions of molecules with the pore walls are predominant and the mass transport takes place by the selective Knudsen diffusion. If the pore radius is much larger than the mean free path of the molecules and a pressure difference over the membrane exists the mass transport takes place by non-selective viscous flow. On the other hand, pore size of the silica layer is comparable to kinetic diameters of the molecules and thus the principle of the mean free path is no longer valid. Activated process based on the micropore diffusion is dominant transport behaviour in which driving force is described in terms of chemical potential that is coupled with partial pressure via adsorption isotherms. The ratio of pore diameter to molecular size become important accordingly molecule-pore wall interactions when the pore diameter is not larger than approximately three times the molecular diameter (Burggraaf, 1999).

1.1. Thermal Stability of Ceramic Membranes

High permeability and the permselectivity are the main requirements for large-scale implementation of inorganic membranes as well as the membrane reliability and the thermal/chemical stability at extreme conditions. Thermal stability of membranes can be defined as having almost constant structural properties especially phase and pore structure upon heat treatment. Three key factors that determine the thermal stability of porous membranes are; (1) sinter activity of membrane materials, (2) phase transformation, and (3) membrane support (Buekenhoudt, 2008).

According to Brinker and Scherer (1990), sintering is a process in which the densification is driven by interfacial energy. Material moves by viscous flow or diffusion from places with high energy to the place low energy in order to eliminate
porosity and thereby reduce the solid-vapor interfacial area. Sintering might be accomplished by a variety of mechanisms, including viscous flow, surface/lattice/grain boundary diffusion, vapour transport, or liquid phase depending on material being sintering and sintering conditions. Viscous flow is the dominating transport for amorphous material sintering while the crystalline materials sinter by solid state diffusion. The factors that control the rate of viscous sintering are the surface tension, viscosity and the particle size (Scherer, 1997).

During heat treatment, material movement results in the formation of necks between the contacting particles of dried membrane layers. Continued heating leads to grain boundary diffusion and hence neck broadening that increases the pore size and decreases the porosity also develop shrinkage. Finally, bulk diffusion occurs and the porous membranes are completely densified. The sinter activity of the membrane material should be as low as possible in order to obtain thermally stable porous ceramic membranes.

During the heating and cooling process, stress develops due to a thermal expansion mismatch between support and top layer, and shrinkage leading to microstructural changes and layer cracking.

Phase transformation temperatures mainly determine the stability of membranes since exceeding this temperature leads to significant structural changes that are often accompanied by the generation of cracks on the membrane surface due to changes in the lattice volume. The phase transformation rate is proportional to the number of nucleation sites on the grain boundary and activation energy for nucleation. In theory, at high temperatures the pore structure of porous ceramics does not remain constant due to sintering and/or phase transformation of the ceramic materials (Kingery et al., 1976). Several studies considered thermal and hydrothermal stability of alumina unsupported membranes (Lin et al., 1991; Chang et al., 1994; Lafarga et al., 1998; Nijmeijer et al., 2001). They reported that $\gamma$-Al$_2$O$_3$ transformed to $\alpha$-Al$_2$O$_3$ at temperatures above 900 °C. Similarly, metastable tetragonal zirconia and anatase titania transformed to the stable monoclinic zirconia and rutile at temperatures above 700 °C and 450 °C, respectively. Sharp decrease in surface area and increase in pore size are the consecutive results of the phase transformation for all mesoporous membranes. Thermal crystallization to amorphous silica to cristobalite occurs in the temperature range of 900-1400 °C with significant enlargement of pore sizes (Ayral et al., 2008). Considering the sintering properties, alumina and silica membranes are the most thermally stable (de
Lange et al., 1995d; Lin et al., 1991), whereas anatase titania and zirconia are known for their limited thermal stability caused by the relatively low phase transformation temperature (Chang et al., 1994).

The pore structure of membranes can change upon heat treatment below the phase transformation temperature due to the sintering. In this case, the sintering rate is proportional to the specific surface energy of the crystallites. The sintering results in a decrease in surface area and increase in pore size of the membranes. Despite that the crystallization does not occur at low temperature (Iler, 1979) for the amorphous silica, microporous amorphous silica shows partial densification already during heat treatment leading to the formation of microcracks. Thus, the thermal stability of microporous silica limited by viscous sintering that occurs at around 800 °C as shown in Figure 1.2. There is considerable evidence that difference in microstructure is responsible for different densification behaviour.

![Figure 1.2](image_url)  
Figure 1.2. Percent linear shrinkage for silica xerogels prepared by two-step acid-catalysed hydrolysisis of TEOS (A), two-step acid-base catalysed TEOS (B), destabilization of a particulate sol prepared from Aerosil (C) (Source: Ayral et al., 2008).

The improvement of the thermal stability of membranes can be achieved by reducing the specific surface energy and the number of nucleation sites, or increasing the activation energy for sintering and phase transformation (Lin et al., 1994). In conclusion, although several studies have been reported to stabilize pore network of the membranes, the microcrack formation on the membrane surface is still limiting issue in the development of microporous silica membranes.
1.2. Scope of Thesis

The scope of this thesis is to design *defect-free* microporous and mesoporous ceramic membranes having micro-engineered pore network that would contribute to the enhancement of pore control abilities as well as the thermal stability.

The key is to improve the separation abilities in terms of permeability and permselectivity of membranes is the close control of pore structures of the selective membrane layer without cracks and pinholes. Permeability measurements of different gases through well-defined porous membrane make clear identification of gas transport mechanisms through these controlled pore-networks. Being able to know the structure of pore network of the membrane that control the gas permeation can reveal more information on how gas transport mechanisms are changing with respect to change in pore network structures. Therefore, this study concentrates on to improve the separation abilities of alumina and silica membranes having controlled pore network with high thermal stability on top of a supporting structure and the objective of research was focused on four main areas;

1. Design and synthesis of intermediate mesoporous alumina layers and thinner defect-free microporous silica membrane layers with a controlled structure to increase permeance and selectivity.
2. Understanding of the sol-gel process parameters (polymeric/particulate) to close control of the membrane micro-structures.
3. Establish an understanding of the relationship between membrane microstructure and densification behaviour to stabilize membrane pore network to enhance the thermal stability.
4. Analysis of transport mechanisms through well-defined pore structures including macro/meso and micropores.
CHAPTER 2

INORGANIC GAS SEPARATION MEMBRANES

The main criterion for the production of ceramic membranes is to obtain defect-free (no pinholes and cracks) supported films with homogeneous thickness and narrow pore size distribution. Sol-gel process is one of the most appropriate methods for the preparation of porous inorganic membranes with a wide range of pore size and the porosity. Membrane preparation by this process includes stable sol preparation (colloidal/polymeric), layer application (dip coating/spin coating), drying and heat treatment. Although each step may be critical for the success of the membrane synthesis, the final membrane properties are mainly determined by the structure and size of the sol (Brinker and Scherer, 1990). The drying and heat treatment condition are particularly critical in order to avoid cracking of the membrane as well as the formation of the final microstructure of the membrane. The quality of the support beneath the separation layer is also important for the quality of the membrane itself. The high quality supports should be smooth, have homogeneous surface characteristics and have a relatively narrow pore size distribution. Therefore, large number of parameters has significant importance in the fabrication of a membrane, i.e., sol concentration and viscosity, deposition rate/type, type of support, heat treatment temperature/time and heating/cooling rates. Because of the complicated process for membrane preparation, the development of ceramic membrane is still carried out extensively (Burggraaf and Cot, 1996).

2.1. Sol-gel Routes

In sol-gel process inorganic or metal organic precursors are hydrolysed while simultaneously a condensation or polymerization reaction occurs with formation of colloids or clusters. Sol-gel chemistry is the process in which a sol\(^1\) agglomerates to form a gel\(^2\). This process is driven by the van der Waals attractive forces or by bond

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\(^1\) Sol is defined as dispersions of solid particles having at least one dimension in the range of 1-100 nm in liquid media.

\(^2\) Gel is defined as a 3-dimensional network of the dispersed solid particles in a liquid medium.
formation between unreacted groups. The unique property of sol-gel process is the ability to all the way from the molecular precursor to the product, allow a better control of the whole process and synthesis of tailor made structures. Table 2.1 illustrates commonly accepted rules of thumb used as starting point in sol-gel chemistry and material development based on relative hydrolysis and condensation rates.

Table 2.1. Expected product of sol-gel process

<table>
<thead>
<tr>
<th>Hydrolysis rate</th>
<th>Condensation rate</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
<td>Slow</td>
<td>Colloids/sols</td>
</tr>
<tr>
<td>Fast</td>
<td>Slow</td>
<td>Polymeric sols/gels</td>
</tr>
<tr>
<td>Fast</td>
<td>Fast</td>
<td>Colloidal gels or precipitate</td>
</tr>
<tr>
<td>Slow</td>
<td>Fast</td>
<td>Controlled precipitation</td>
</tr>
</tbody>
</table>

The ability to close control the hydrolysis and condensation reactions through sol-gel interrelated parameters makes it possible to tailor the membrane microstructure. If the stoichiometry of water to alkoxide ratio is changed, this leads to change in sol concentration and pH affecting the sol reaction conditions. These interrelated parameters are type of precursor, hydrolysis ratio, catalyst type/amount, and type of solvent.

2.1.1. Precursors

In order to gain control over the hydrolysis-condensation process, the precursor reactivity comes from the nature of metal or metalloid during the process has to be decreased. Electronegativity or degree of unsaturation in a metal or metalloid alkoxide leads to different reactivities in these materials. As the orbital size increases, the valance electrons become less tightly bounded, which results in a lower electronegativity and ionization potential and higher reactivity. Another property of the metal alkoxide that has to be taken into account is its molecular structure. The full coordination of many metals often can not be satisfied in metal alkoxides M(OR)n. This is due to the fact that the oxidation state Z of the metal is lower than its usual coordination number N which
defines the degree of unsaturation. Higher degree of unsaturation results in higher reactivity. It is a well-known fact that the hydrolysis rate of a metal alkoxide decreases with increasing size of the alkyl group (e.g. ethoxide >propoxide >butoxide). This is a consequence of the positive partial charge of the metal atom, which decreases with alkyl chain length. On the other hand, steric hindrance effects also have to be taken into account, as it has been shown that the hydrolysis rate decreases in the order tertiary > secondary > normal.

2.1.2. Hydrolysis Ratio

The hydrolysis ratio is expressed by the molar ratio of water to metal alkoxide. The stoichiometrically needed number of molecules of water per molecule of silica for complete hydrolysis is two. Increasing the water content above the stoichiometric value favors the condensation reaction through oxolation and results in particulate sol. However, at hydrolysis ratio lower that stoichiometrically value, the so-called polymeric sol may occur as a result of the dominant hydrolysis reaction.

2.1.3. Catalyst Type/Amount

Catalyst type and pH of the reaction determine the resulting morphology and growth model in sol-gel chemistry. Slow hydrolysis and fast condensation rates lead to the formation of colloidal structures that is characteristics of base catalyzed system. Fast hydrolysis, and slow condensation rates characterize an acid catalyzed system, which produces linear like polymeric clusters. The associated elemental units either particulate or polymeric cluster allow to define the membrane pore structure. Accessible micropores could be obtained by packing of polymeric clusters while the packing of colloidal particles enables to the formation of mesoporous structures. Several models have been proposed for growth of particles/species depends on reactivity (probability of elemental species to aggregate) and diffusion of elemental units (effect of dilution, viscosity and temperature. Base catalysed system is described by a Monomer-Cluster growth model while the formation of polymeric species caused by acid catalysis described by Cluster-Cluster growth (Ayral et al., 2008). These models have variations in their structures as shown in Figure 2.1 depending on condensation reaction.
limitations like Reaction Limited, Ballistic or a Diffusion Limited process. Therefore, catalyst and pH actually control the final xerogel properties by influencing microstructure of the gel.

<table>
<thead>
<tr>
<th>Reaction-Limited</th>
<th>Ballistic</th>
<th>Diffusion-Limited</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eden</td>
<td>Vold</td>
<td>Witten-Sander</td>
</tr>
<tr>
<td>Monomer-Cluster</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RLCA</td>
<td>Sutherland</td>
<td>DLCA</td>
</tr>
<tr>
<td>Cluster-Cluster</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.1. Simulated structures resulting from the various kinetic growth model (Source: Brinker and Scherer, 1990).

### 2.1.4. Solvent Type

Metal alkoxides are often dissolved in organic solvents to homogenize the reaction mixture before hydrolysis is occured. The most often used solvents are parent alcohols, which have the same number of carbon atoms in the alkyl group as in the alkoxy group of the metal alkoxide (for example, ethanol is the most suitable solvent for a metal ethoxide). As a general rule, dilution should lead to higher alkoxide association, and the formation of oligomers rather than monomers. However, solvents are often not chemically inert toward metal alkoxides and the metal alkoxide reactivity can be easily modified by changing the solvent. Solvent type and concentration have significant effect on gelation kinetics and sol-gel reaction mechanisms. Variations in gelation times can be attributed to the formation of stable reaction intermediates through hydrogen bonding and electrostatic interactions. Solvent size, and its polar-protic, nonpolar-aprotic and polar-aprotic nature determine how they will affect the final microstructure by altering hydrolysis and condensation reactions. Polar protic solvents give rise to faster gelation times but polar aprotic solvents cause a reduction in gelation time.
because of strong electrostatic interaction with the nucleophile. Since the nonpolar-aprotic solvent do not contribute to the stabilization of reaction intermediates, gelation times are longer. Moreover, solvent also affects the size and shape of the particles because of the change in the behaviour of reaction intermediates.

2.2. Sol $\rightarrow$ Gel $\rightarrow$ Film Transformation

During sol-gel processing of inorganic membranes, sols and gels evolve in a different way depending on precursors used. Two main structures of gel layers occur depending on the method used for membrane processing (colloidal or polymeric) including; (1) physical (colloidal) gels in which steric or electrolytic effects in the sol dominate gel formation. The main characteristic of this type of gel is the way in which individual particles can be arranged during the process. These gels are concerned with aqueous media, (2) polymeric gels in which the relative rates and extends of reactions are critical for gel formation. In this case organic media are preferred.

The final porous microstructure in membranes is established during drying that accompanies process of film formation by dip or spin coating. In dipping process, a porous support is brought into contact with the dip solution for a few seconds, resulting in film formation. The dip coating parameters, such as sol viscosity and dipping time as well as the withdrawal speed play a significant role in determining the thickness of the wet cake and consequently, the thickness of the final ceramic membrane (Brinker et al, 1992; Gu and Meng, 1999). Figure 2.2 shows the steady state film deposition profile during dip coating a porous support with sequential stages of structural development. The entrained sol concentrates by gravitational draining and evaporation accompanied by flow into or out of porous support. Increasing sol concentration due to the continued condensation reactions leads to aggregation and gelation. At the final stage of the deposition, the gel film is collapsed by capillary pressure that establishes the final pore size because of drying. It is also very crucial because cracks tend to form during drying and this usually necessitates very slow controlled drying rates and processes. The extent of shrinkage of the solid network at the critical point has a determining role on the final pore volume-size distribution in the dried gel. This in turn depends on a balance between the capillary pressures that tries to collapse the gel and stiffness of the gel that is controlled by the condensation reaction. There is little time for network formation...
during film deposition and the structure of the film is largely controlled by the structure of the clusters in the sol (Brinker et al., 1994).

Spin-coating differs from dip coating in that the depositing film is thinned by centrifugal draining and evaporation. Because of the balance between the centrifugal force and the friction force, liquid film tends to become uniform in thickness. Spin-coating process can be divided into four stages; deposition, spin-up, spin-off and evaporation as shown in Figure 2.3. An excess of liquid is dispensed on the surface during the deposition stage. Centrifugal forces cause the liquid to flow radially outward in the spin-up stage. In the spin-off stage excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin-off slows down, because the thinner the film, the greater resistance to flow and because the concentration of the non-volatile components increases that results in an increase in viscosity. In the final stage, evaporation takes over as the primary mechanism of thinning (Brinker et al., 1992). The thickness of membranes utilized by spin coating is expected to depend on spinning speed \( w \) as \( t = w^b \), with the value of the \( b \), known as the spin parameter and of around 0.5 for Newtonian fluids. Increasing \( b \) values gives rise to decrease in interparticle distance between particles indicating the non-Newtonian
character. Therefore, higher spinning rate, the thinner membrane layer attained at constant spinning time and which consequently increases the membrane flux.

![Diagram](image)

**Figure 2.3. The spin-coating process.**

Drying accompanies both the dip and spin-coating process and largely establishes the shape of the liquid profile. The increase in concentration leads to the formation of a gel-like structure. Further evaporation gives rise to capillary tension in the liquid and that tension is balanced by compressive stresses on the solid phase causing it to contract. Drying process has two successive stages; constant rate period (CRP) and falling rate period (FRP) (Scherer, 1992). The initial period of drying is called the constant rate period due to the constant evaporation of the liquid. During the constant rate period, the loss of pore fluid is accommodated by shrinkage of the gel surface. In other words, the volume shrinkage will be equal to the volume of the pore fluid lost by evaporation. The driving force for this shrinkage is the capillary tension $P$ developed in the liquid, which can be correlated to the pore radius through the Kelvin equation:

$$ P = \frac{2\gamma_{LV} \cos\theta}{r_p} $$

where; $\gamma_{LV}$ is liquid-vapor interfacial energy, $\theta$ is contact angle and $r_p$ is pore radius. This tension in the liquid causes the gel network to contract. Further shrinkage and condensation as the reactive terminal hydroxyl species are brought into closer contact continue up to the critical point. At this point shrinkage stops and tension is maximised. Contracting network is stiff and resists to further compaction. Further evaporation of the pore fluid causes the meniscus to go into gel interior, which is the beginning of the
second stage of drying, the falling rate period, which can also be divided into two stages (Scherer, 1992). In the first falling rate period, the pores begin to empty due to the highest capillary pressure and the liquid flows to the surface where evaporation takes place. Second falling rate period is reached when the pores have substantially emptied and surface films along the pores can not be sustained. The remaining liquid can escape only by evaporation from the pores and diffusion of vapour to the surface without further dimensional changes.

As the film dries, it shrinks in volume. Because of the presence of the rigid support, the reduction in volume is accommodated completely by a reduction in thickness. When the film has solidified and stresses can no longer be relieved by flow, tensile stresses develop in the plane of the substrate that nearly equals to stress in fluid;

\[
\sigma \left[ \frac{E}{(1-\nu)^3} \right] = \left( f_s - f_r \right)
\]

where \( E \) is Young’s modulus, \( \nu \) is Poissons ratio, \( f_s \) is the volume fraction solvent at the solidification point, and \( f_r \) is the volume fraction of residual solvent in the dry film. Although, large stress occurs in the film, it is commonly observed that cracking of films does not occur if the film thickness is below a certain critical thickness (Brinker et al., 1992).

The final stage in membrane preparation is heat treatment, which gives the microstructural, mechanical and chemical integrity to the system. During calcination physically adsorbed water (or any other solvent), residual organics and nitrates will be removed. In the initial stage of sintering, a “physical reaction” takes place on the contact points between primary particles, which results in the formation of necks between the particles. Continued heating leads to neck broadening and increase of shrinkage and consequently, densification. The change of porous structure is particularly profound around the phase transition temperature. During the heating and cooling processes, stress develops due to a thermal expansion mismatch between support and top layer and, this may lead to microstructural changes and layer cracking if it is not carefully controlled.

Compared to polymeric sol-gel routes, sol-gel processing of particles provides a sharper pore size distribution in its final products (Chu et al., 1997). In colloidal system composed of condensed particles, the pore structure is determined by the size and the
packing property of the particles. In this case, if the particles are uniform in the colloidal sol, the pore size in the resulting membrane can be expected to be narrowly distributed but the porosity is independent of the particle size as opposed to polymeric structure. For example an ordered close-packed arrangement of monosized spheres gives rise to a porosity of 26% having two types of pores with a radius equal to 0.225R (tetrahedral sites) and 0.414R (octahedral sites) (Ayral et al., 2008). Table 2.2 summarizes important characteristics of pore structures designed by the different degrees of monosize sphere packing (Rouquerol et al., 1999).

Table 2.2. Important characteristics of some monosize sphere packing
(Source: Rouquerol et al., 1999).

<table>
<thead>
<tr>
<th>Packing Type</th>
<th>CN</th>
<th>Porosity %</th>
<th>R of sphere inscribed in cavities</th>
<th>R of sphere inscribed in throats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexagonal close-packed</td>
<td>12</td>
<td>25.95</td>
<td>0.2247R-octahedral</td>
<td>0.1547R</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>10</td>
<td>30.19</td>
<td>0.4142R-tetrahedral</td>
<td>0.1547R</td>
</tr>
<tr>
<td>Body centered cubical</td>
<td>8</td>
<td>31.98</td>
<td>0.2910R</td>
<td>0.2649R</td>
</tr>
<tr>
<td>Orthorhombic (primitive hexagonal)</td>
<td>8</td>
<td>39.54</td>
<td>0.5275R</td>
<td>0.4142R</td>
</tr>
<tr>
<td>Cubic</td>
<td>6</td>
<td>47.64</td>
<td>0.732R</td>
<td>0.4142R</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>4</td>
<td>66.00</td>
<td>1.00R</td>
<td>0.732R</td>
</tr>
</tbody>
</table>

2.3. Sol-Gel Processing of Alumina Membranes

Microporous inorganic membranes are generally coated as a thin film on a sol-gel derived mesoporous ceramic layer. The advantages of using this intermediate layer are twofold. Firstly, this layer will avoid penetration of the microporous layer into the support that results in the decrease in the effective thickness of the separation layer. Thickness of the microporous layer is important in terms of increasing the flux of the membranes. Secondly, the mesoporous surface is very smooth relative to the macroporous layer, and this ensures the formation of thin, uniform microporous layer. Sol-gel derived $\gamma$-$\text{Al}_2\text{O}_3$, $\text{TiO}_2$, and $\text{ZrO}_2$ porous membranes are the commonly used
crystalline mesoporous layer in which the intercrystalline space gives rise to mesoporous structure.

Sol-gel processing starting from metal alkoxides involves hydrolysis and condensation reactions playing important roles in determining the pore structure of the membrane that mainly controlled by the size and the packing properties of the particles. Aluminum alkoxides such as, aluminum sec-butoxide and aluminum iso-propoxide are easily hydrolysed with water to form hydroxides. The initial hydrolysis reaction of aluminum alkoxide and further hydrolysis and condensation reactions can be written as follows:

\[
\text{Al(OR)}_3 + \text{H}_2\text{O} \rightarrow \text{Al(OR)}_2(\text{OH}) + \text{ROH} \quad (2.3)
\]

\[
2\text{Al(OR)}_2(\text{OH}) + \text{H}_2\text{O} \rightarrow (\text{RO}) (\text{HO}) \text{Al-O-Al (OH) (OR)} + 2 \text{ROH} \quad (2.4)
\]

The average number of OR groups per Al atom will decrease as the reactions proceed which depends on the hydrolysis temperature and the composition of the sol. Hydrolysis of aluminum alkoxide in excess water (molar ratio of water/alkoxide= 70) at 80-100 °C results in the precipitation of fibrillar boehmite (\(\gamma\)-AlOOH) into regular rectangular plates with dimensions of 20 nm x 40 nm x 5 nm that can be peptized to a clear sol with the addition of at least 0.07 mol HNO\(_3\) per mole of alkoxide followed by heating above 80 °C for several hours. Heating above 80 °C promote the boehmite formation but at lower temperature bayerite [beta Al(OH)\(_3\)] is formed which does not form a stable sol (Yoldas, 1975). The common method to obtain boehmite sols defined by Yoldas can be summarized as hydrolysis of the alkoxide to precipitate a hydroxide, peptization of the precipitated hydroxide by addition of the acid and gel formation by evaporation of the solvent. Peptization refers to acid treatment to break up agglomerates by partial dissolution and charge stabilization of the particles.

Mesoporous \(\gamma\)-Al\(_2\)O\(_3\) membrane can be prepared by dipping a porous support into a stable colloidal boehmite sol with defined concentration followed by drying and heat treatment at certain conditions and exhibits pore diameters of 3-10 nm with a narrow pore size distribution (Anderson et al., 1988.; Leenaars et al., 1984). Figure 2.4 shows a schematic representation of \(\gamma\)-alumina membranes (Leenaars et al., 1984), indicating that plate-shaped particles (boehmite and \(\gamma\)-alumina after heat treatment) are packed to form slit-shape pores, in which distance between the slits is approximately
several nm which gives rise to relatively high surface area. Thus, eventual alumina membrane microstructure can be influenced by the size and the shape of the boehmite crystallites in the sol as well as the deposition conditions upon film formation (Kuzniatsova, et al., 2008).

Figure 2.4. Pore structure of γ-alumina membranes proposed by Leenaars and Burggraaf (Source: Leenaars et al., 1984).

The pore structure of γ-Al₂O₃, TiO₂, and ZrO₂ porous membranes are compared in Table 2.3. Because of the particle size of the corresponding sols is in usually nanometer size range with a uniform particle size distribution, the pore size distributions of these membranes are rather narrow. The effects of sol-gel processing parameters like the acid type/amount, water amount utilized during sol preparation, hydrolysis temperature, dipping and addition of PVA for defect free membranes, heat treatment conditions on the microstructure of the alumina membrane have been the subject of a considerable number of studies (Yoldas, 1975; Leenaars et al., 1984; Okubo et al., 1990; Larbot et al., 1994, Huang et al., 1997).

Table 2.3. Pore structure of γ-Al₂O₃, TiO₂, and ZrO₂ membranes that heat treated at 450 °C for 3 h (Source: Chang et al., 1994).

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Average Pore Size (nm)</th>
<th>Pore Volume (mL/g)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>2.8</td>
<td>0.33</td>
<td>373</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.4</td>
<td>0.21</td>
<td>147</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>3.8</td>
<td>0.11</td>
<td>57.2</td>
</tr>
</tbody>
</table>

Gas transport mechanisms through alumina membranes were further understood and improved by impregnation of magnesium in the late 1980’s. The dominant transport mechanism through these membranes was found as Knudsen diffusion for non-
adsorbing gases while surface diffusion of CO\textsubscript{2} in \(\gamma\text{-Al}_{2}\text{O}_{3}\) membranes was reported (Keizer et al., 1988; Okubo et al., 1990; Li et al., 2005).

Impregnation of Pd into \(\gamma\text{-Al}_{2}\text{O}_{3}\) membrane has been studied by Chen et al., (2003) in order to enhance the H\textsubscript{2}/N\textsubscript{2} selectivity. In the first place, \(\gamma\text{-Al}_{2}\text{O}_{3}\) membrane has been prepared by applying heat treatment at 500 °C for 34 h dip-coated boehmite sol that was synthesized by the hydrolysis of aluminium tri-sec-butoxide with the alkoxide:water:HNO\textsubscript{3} molar ratios of 1:100:0.07. The wet-impregnation was followed by immersing the membrane into PdCl\textsubscript{2} solution with different concentrations for 10 minutes. Subsequently, the membrane was dried and heat treated under air atmosphere at 500 °C for 4 h. Lastly, Pd/\(\gamma\text{-Al}_{2}\text{O}_{3}\) composite membrane was obtained after reducing in a ratio 1:9 of H\textsubscript{2}/Ar stream at 350 °C for 90 min. It was found that the optimum concentration of PdCl\textsubscript{2} solution was about 1.2 %wt and maximum adsorption on membrane surface was observed at pH 1.5. The Pd cluster size was independent of metal loading and estimated from the result of the x-ray absorption fine structure spectroscopy as 3.3 nm. The authors suggest that the growth of Pd clusters hindered by the pore of the \(\gamma\text{-Al}_{2}\text{O}_{3}\) membrane. The permeation results show that the permeation of H\textsubscript{2} was enhanced by the surface diffusion on Pd clusters while pore blocking causes the decrease in N\textsubscript{2} permeance. Therefore, the selectivity of H\textsubscript{2}/N\textsubscript{2} has been improved to 20 at 342 K that is higher than the theoretical Knudsen selectivity (3.74).

The H\textsubscript{2} permeation through \(\gamma\text{-Al}_{2}\text{O}_{3}\) membranes had been improved by the addition of Ni due to high hydrogen adsorption capacity (Yu et al., 2008). Ni/\(\gamma\text{-Al}_{2}\text{O}_{3}\) membranes were prepared by soaking and reduction of nickel nitrate on gamma layer. The average pore size had been decreased from 4.4 to 3.7 nm indicating the penetration of Ni particles into the inner pores. The uniform Ni deposition on surface has caused the high H\textsubscript{2}/N\textsubscript{2} permselectivity (5.2) at 450 °C exceeding the theoretical Knudsen selectivity (3.74) due to the contribution of surface diffusion.

Kuzniatsova et al., (2008) compared the microstructural integrity of alumina membranes derived from unpurified and purified boehmite sols. Different techniques have been employed for purification of sols including high speed centrifugation and ultrasound-assisted screening. Membranes prepared from purified sols appear to be much less prone to interfacial micro-cracking and have a much more homogeneous structure. Application of the purified membrane precursor sols results in membranes in
which connected pore defects (pinholes) are no longer detectable for a membrane thickness of larger than 500 nm.

Ultra-thin silica layer (20-30 nm) had been deposited by CVD on alumina graded structures derived from size controlled boehmite sols in the study of Gu and Oyama (2007). The size of the boehmite crystals was in the 30-950 nm range had been controlled by changing peptization conditions in which acetic acid, nitric acid and hydrochloric acid were utilized with a molar ratio of $\text{H}^+$/alkoxide in the range of 0.03-0.25. Acetic acid was found to be more effective in terms of sol stability in the desired size range. About 1 $\mu$m in thickness alumina membranes with a graded structure was obtained through the application of dilute boehmite sols in order to get superior properties for hydrogen permeation.

A new route for the preparation of boehmite sol from an aqueous solution of aluminium chloride has been explored by Li et al., (2005). They reported that preparing alumina membranes by using inorganic salts rather than expensive alkoxide precursors is a valuable contribution in the field of alumina membrane applications. A transparent, stable boehmite sol has been prepared by the addition of anionic exchange resin in starting solution to offer $\text{OH}^-$ and simultaneously remove $\text{Cl}^-$ ion. Defect free, 7 $\mu$m in thickness alumina membranes with 3.7 nm pore diameter have been synthesized on the inner surface of $\alpha$-$\text{Al}_2\text{O}_3$ hollow fiber.

Several studies considered thermal and hydrothermal stability of alumina unsupported membranes (Lin et al., 1991; Chang et al., 1994; Lafarga et al., 1998; Nijmeijer et al., 2001). They reported that $\gamma$-$\text{Al}_2\text{O}_3$ transformed to $\alpha$-$\text{Al}_2\text{O}_3$ at a temperature above 900 °C. Similarly, metastable tetragonal zirconia and anatase titania transformed to the stable monoclinic zirconia and rutile titania at temperatures above 700 °C and 450 °C, respectively. Sharp decreases in the surface areas and increases in the pore sizes are the consecutive results of the phase transformations for all mesoporous membranes. Considering the sintering and phase transformation, the alumina membrane is the most thermally stable one while the titania is the least stable. Chang et al., (1994) concluded that the pore growth rate of alumina, titania and zirconia membranes were enhanced in the presence of steam at high temperature due to the reduction in the activation energy for phase transformation. On the other hand, the hydrothermal stability of alumina membranes has been characterized by $\text{H}_2$ permeation in the study of Zahir et al., (2005). Supported membrane characterization is more
reliable than those of unsupported membrane under practical conditions. Composite alumina membranes with improved hydrothermal stability have been prepared by the sol-gel method using \( \text{La}_2\text{O}_3 \) and \( \text{Ga}_2\text{O}_3 \) doped boehmite sol. It has been reported that \( \text{La}_2\text{O}_3 \) doped \( \text{Ga}_2\text{O}_3-\gamma\text{Al}_2\text{O}_3 \) membrane could withstand during prolonged exposure to high temperature in the presence of steam due to the unchanged pore diameter and surface morphology as well as the presence of acid-base and or neutral sites. The influence of double dopant (\( \text{Ga}^{3+}-\text{La}^{3+} \)) as well as the influence of \( \text{Ga}^{3+} \) alone over hydrothermal/thermal stability of mesoporous alumina membranes has been investigated by Zahir et al., (2006). Pore structure stabilization after hydrothermal treatment at 500 °C has been provided by the doping of combined 6 mol% \( \text{La}_2\text{O}_3 \) as well as 30 mol% \( \text{Ga}_2\text{O}_3 \) to \( \gamma\text{Al}_2\text{O}_3 \). They have observed Knudsen diffusion behaviour through composite membranes after hydrothermal treatment as was expected based on crack-free membrane layer. Although \( \text{La}^{3+} \) doping on gamma alumina layer suppressed the pore growth, the adherence of gamma to alpha alumina layer has been supplied by phosphate bonding which resulted in highly steam stable membrane support combination (Nijmeijer et al., 2001). The stability of \( \gamma \)-alumina membranes with \( \text{La}^{3+} \) addition in the presence of alkaline compounds (Li, Na) which are known to cause membrane degradation at high temperatures has been investigated for membrane application by Lafarga et al., (1998). Doping with Lanthanum was effective to retard the phase transformation which resulted in some crack formation on the surface but did not slow down the degradation process (loss of surface area, increase in pore diameter) caused by sintering. Moreover, Gestel et al., (2002) stated that the addition of alumina phase as a dopant to the titania lead to the collapse of pore structure of alumina/titania composite membrane due to the dissolution of alumina phase in harsh environment (pH<3 and pH>9).

The membrane and internal pore surface properties are modified in order to replace the surface hydroxyl groups which make the ceramic membranes hydrophilic by nature with hydrolytically stable groups with hydrophobic character, such as Si-CH\(_3\). These hydroxyl groups are the most active sites for interaction with water molecules and promote water adsorption, this may cause to pore blocking at ambient conditions which affects the separation properties of the membranes. Work on chemical modification of mesoporous \( \gamma \)-alumina with (monofuctional, difunctional and trifunctional) organochlorosilanes in liquid media was reported by Sah et al. (2004). They stated that the degree of hydrophobicity varies depending on chain lengths and
also functionality of the precursors on the basis of the results from the diffuse reflectance IR, XPS and permoporometry measurements. The main conclusion that was drawn from liquid permeation experiments was that trichloromethylsilane imparted a predominantly hydrophobic character due to the polymerized organosilane network inside the γ-alumina mesopores as well as on the surface of the membrane. The structural changes of γ-alumina induced by modifications with organochlorosilane were also characterized by sorption techniques and SEM in the study of Castricum et al., (2005). It was concluded that multifunctional organosilanes are more reactive but lead to pore blocking due to the polymerization reaction while the monofunctional precursor gave the best results for alumina membranes with 4 nm pore diameters preserving an open structure and leading to a homogeneous modification.

Another approach to modify the mesoporous alumina membrane with the aim of narrowing its pore size in order to increase the permselectivities has been reported by Lin et al., (1999). They reported the deposition of CuCl on the disk-shaped and tubular γ-Al₂O₃ membranes in order to prepare membrane having high selectivity of ethylene over ethane. Reservoir method was applied for coating of CuCl in the 4 nm pore of γ-Al₂O₃ top layer. In that method, the precursor solution was soaked in both the support and the top layer and in the course of drying from the top-layer, macroporous layer acts as a continuous reservoir that supplies an impregnation solution results in high loading of active species in the thin layer. It was reported that 10-fold reduction in gas permeances but no further improvement of ideal separation factor for ethylene over ethane. For the gas mixture experiments, rather than pure gas permeances, only 10 % increase in selectivity has been reported according to unmodified membranes. On the other hand, that improvement has been attributed to the contribution of the surface flow of ethylene, but not the reduction in pore size due to the modification. Therefore, pore modification may not lead to separation properties that microporous membranes have due to the only slight improvements of gas selectivities with reduction in gas permeances.

Mesoporous γ-Al₂O₃ membranes have little interest for gas separation beyond their role in intermediate bridging of macro and microporous layers, but they offer interesting advantages for water purification. Supported γ-Al₂O₃ membranes have high fluxes and their selectivities rest upon the presence of space charge in the pore, induced
by the adsorption of ions on the mesopore surface (Verweij, 2003). The improvements on intermediate layer processing may include;

1. The preparation of polymeric alumina sol by using sol-gel parameters may result in the increase in the particle homogeneity and decrease in particle size of the boehmite sol which will enable to thinner and finer layers and thus increases the permeability of intermediate layer.

2. For meso and microporous layers prepared by a sol-gel processing, control and architecture of desired pore morphology on a nano-scale can be achieved by the use of surfactants. For gas separation applications, the surfactant templated silica layer applied as an intermediate layer does not itself significantly influence gas transport, while it provides a smooth defect free surface for an amorphous gas selective silica layer and helps to avoid infiltration of the amorphous material into the membrane support thus results in improved gas separation performance of amorphous silica membranes (Tsai et al., 2000). Pore accessibility and connectivity through transport direction are the requirements of the membrane applications and such systems and especially cubic structures with controllable pore size may improve the performance of the membranes (Brinker et al., 1999).

2.4. Sol-Gel Processing of Silica Membranes

A convenient method to prepare defect-free microporous silica membranes starts from silicon alkoxides, Si(OR)₄, as silica precursors. The general starting precursors are tetraethoxysilane Si(OC₂H₅)₄ and tetramethoxysilane Si(OCH₃)₄, diluted in ethanol or methanol, respectively. The formation of the oxide network results from the polymerization of the molecular precursor. Depending on the reaction conditions, polymer-like silica species or colloidal silica particles would form prior to gelation. The packing of these elemental units leads to the formation of either polymeric or particulate silica membranes. Thus, the morphology formed during the condensation of the sol has a direct relationship to resulted membrane pore structure.
2.4.1. Sol-Gel Chemistry of Silica

The addition or release of water molecule initiates the hydrolysis and subsequent condensation reactions resulting in the formation of sol particles. Hydrolysis and condensation reactions occur simultaneously, but one reaction can be favoured depending on the reaction conditions. The sol to gel transition to form siloxane bridges (≡Si-O-Si≡) for a silicon alkoxide shown in Figure 2.5 can be divided into three reversible reactions. The first reaction step involves the reversible hydrolysis and esterification of the alkoxide and the rate of hydrolysis and condensation are a function of the variables. After hydrolysis of the alkoxide, two reversible condensation reactions may occur; the first condensation reaction forms an alcohol and the second condensation reaction forms water. Complete hydrolysis of the alkoxide is not necessary for the occurrence of condensation reactions. The reverse reactions of condensation are known as alcoholysis and hydrolysis.

*Hydrolysis and Esterification*

\[
\text{RO-Si-OR} + \text{OH} \rightarrow \text{RO-Si-OH} + \text{ROH}
\]

*Alcohol Condensation and Alcoholysis*

\[
\text{RO-Si-OR} + \text{HO-Si-OR} \leftrightarrow \text{RO-Si-O-Si-OR} + \text{ROH}
\]

*Water Condensation and Hydrolysis*

\[
\text{RO-Si-OH} + \text{HO-Si-OR} \leftrightarrow \text{RO-Si-O-Si-OR} + \text{H}_{2}\text{O}
\]

Figure 2.5. Hydrolysis and condensation for silicon alkoxides (Source: Brinker and Scherer, 1990).

The hydrolysis and condensation reactions are catalyzed in acidic and basic media. The formation of reactive Si-OH group through base catalysed hydrolysis reaction is proposed by three step SN2 mechanism as summarized in Figure 2.6. The first step is a nucleophilic addition of a hydroxide anion to the positively charged Si
atom. This leads to a transition state, where the coordination number of Si has been increased by one. The second step involves a charge transfer within the intermediate state leading to release of an alkoxide anion, which in its turn reacts with water regenerating the hydroxide catalyst.

![Figure 2.6. The hydrolysis of silicon alkoxide resulted from S_N2 mechanism.](image)

Addition of acids leads at the first step to the protonation of an oxygen atom in the alkoxide ligand, leading to the formation of the reactive cationic species as indicated in Figure 2.7. This step is rate-determining, which results in an S_N1-type mechanism. The cation thus formed is attacked by a water molecule, which leads again to the formation of a Si–OH bond, release of an alcohol molecule (better leaving group) and regeneration of a proton catalyst (Kessler et al., 2006).

![Figure 2.7. The hydrolysis of silicon alkoxide resulted from S_N1 mechanism.](image)

After the initial hydrolysis, the product can react further either via another hydrolysis reaction or a condensation reaction. In order to get less branched oligomers, the hydrolysis should be followed by a condensation reaction. Condensation is a complex process and, depending on the experimental conditions, three competitive mechanisms have to be considered: alcoxolation, oxolation and olation (Brinker and Scherer, 1990). Alcoxolation is a reaction by which a bridging oxo group is formed through elimination of an alcohol molecule. The mechanism is basically the same as for hydrolysis with Si replacing H in the entering group. Oxolation follows the same mechanism as alcoxolation, but a water molecule is the leaving group. Olation can
occur when full coordination of Si is not achieved. In this case, bridging hydroxo groups can be formed through elimination of a solvent molecule. The latter can be either H₂O or ROH depending on the water concentration in the medium. All these reactions are catalyzed by protons, i.e. acidic medium, and are slowed down in the presence of bases (Kessler et al., 2006).

It has been shown that the catalyst controls the silica gel microstructure. As shown in Figure 2.8, acid catalysed system has more linear polymeric species that is the requirement of microporous silica membranes due to provided efficient interpenetration. The formation of dense silica colloidal particles is favored by base catalysis as shown in Figure 2.8.b and the resulted pore structure is expected to be mesoporous. Therefore, Figure 2.8 and Table 2.4 obviously indicate that the synthesis conditions are significantly important when designing a pore structure of the membrane.

![Figure 2.8. Schematic representation of gel densification for (a) acid and (b) base catalyzed system (Source: Scherer, 1988).](image)

**Table 2.4. Influence of hydrolysis conditions on the porous structure of polymeric silica gels derived from TEOS (Source: Brinker and Scherer, 1990).**

<table>
<thead>
<tr>
<th>Hydrolysis</th>
<th>Porosity (%)</th>
<th>Pore diameter (nm)</th>
<th>Surface area (m²g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-step acid catalyzed</td>
<td>54</td>
<td>1-5</td>
<td>740</td>
</tr>
<tr>
<td>Two-step acid-base catalyzed</td>
<td>67</td>
<td>1-10</td>
<td>910</td>
</tr>
<tr>
<td>One-step base catalyzed</td>
<td>70</td>
<td>1-20</td>
<td>515</td>
</tr>
</tbody>
</table>
The other important parameter is the aging of the sol which affects the polymerization process before deposition of the sol. Differences in the aging time give rise to important differences for the pore structure of the resulting membrane layer as shown in Table 2.5 (Klotz et al., 1999), due to a continuously growing fractal structure of the elemental unit in polymeric sol (Brinker et al., 1994). Structural factors like steric effect, alkyl group and alkoxide have also significant effect on microstructure. Brinker and Scherer provide an excellent review detailing many of these variables in their book titled Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Brinker and Scherer, 1990).

Table 2.5. Effects of polymeric silica sol aging on the porous texture of the resulting layers (Source: Klotz et al., 1999).

<table>
<thead>
<tr>
<th>Aging before deposition (t/tg)</th>
<th>Porosity (%)</th>
<th>Pore diameter (nm)</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.15</td>
<td>-</td>
<td>&lt;0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>0.15</td>
<td>16</td>
<td>3.0</td>
<td>146</td>
</tr>
<tr>
<td>0.33</td>
<td>24</td>
<td>3.2</td>
<td>220</td>
</tr>
<tr>
<td>0.66</td>
<td>33</td>
<td>3.8</td>
<td>263</td>
</tr>
<tr>
<td>1</td>
<td>52</td>
<td>6.0</td>
<td>245</td>
</tr>
</tbody>
</table>

The method to prepare monodisperse silica sols, which was developed by Stober et al., (1968), uses the sol-gel process. In Stober process, well defined silica spheres ranging in size from 10 to 2000 nm are created by the ammonia catalyzed hydrolysis and condensation of silicon alkoxides in low molecular weight alcohol solvents in the presence of H₂O (van Blaaderen et al., 1992; Green et al., 2003). During the hydrolysis reaction, the ethoxy group of TEOS reacts with the water molecule to form intermediate [Si(OCH₂)₄₋ₓ(OH)ₓ] with hydroxyl group substituting ethoxy groups. The overall reaction for conversion of TEOS into SiO₂ is expressed as follows:

\[
\text{Si(OCH₂)₄ + 2H₂O} \rightarrow \text{SiO₂ + 4C₂H₅OH}
\]  

The size of silica particles from the Stober process is mainly controlled by the relative contribution from nucleation and growth. The necessary supersaturation for the formation of particles is provided by the hydrolysis and condensation reactions. In general, parameters, which affect the rate of preceding reactions, would in turn affect
the rate of generation of supersaturation and hence the number of nuclei formed. These parameters include reactant concentration, type of reactant, reaction temperature, concentration of catalyst (NH₃), concentration of water, as well as the choice of cosolvents. As the reactions proceed, the intermediate [Si(OC₂H₅)₄₋ₓ(OH)ₓ] concentration increases rapidly to generate supersaturation and eventually reaching a critical value of supersaturation and nucleation occurs as shown in Figure 2.9. The growth of these nuclei causes the concentration to fall below the nucleation concentration, after which no more particles are created. The particles continue to grow at the expense of remaining supersaturation until all intermediates are consumed (Beattie, 1989).

![Figure 2.9. Nucleation and growth process for the formation of silica colloids](Source: Beattie, 1989).

Although monodispersed silica spheres are formed under base catalysed system, at sufficiently high water content, one can expect that acid sols to have mainly particulate character (Meixner and Dyer 1999, Colomer and Anderson, 2001). High water to alkoxide ratio promotes rapid completion of hydrolysis reaction relative to condensation reactions. Fast hydrolysis, slow condensation and low solubility results in formation of small particles. In particulate sol-gel route, the pH of the colloidal sol influences the packing properties of the particles as well as the hydrolysis and condensation reactions. Under the condition of high pH, the growth of the necks, which connect adjacent particles, stiffens the pore network and creates a more porous structure. Conversely, under low pH conditions, a collapse of network is favoured and a
more densely packed structure is obtained (Chu et al., 1997). The effect of sol-gel synthesis parameters on the particulate route derived microporous silica pore structure was investigated by Meixner and Dyer (1999). They reported that xerogels with the smallest micropores were prepared at pH~3 with water to alkoxide ratio of 83. Porosity of dried xerogel corresponding to these conditions was reported as 0.3 which was consistent with nearly close packing of the sol particles. On the other hand, porosity as 0.5 was reported for the xerogel derived from sol having pH of 5 indicating a less tightly packed structure. In contrast to polymeric gel, weak dependence of xerogel microstructure on aging of the sols was attributed to a balance between growth and dissolution of the colloidal particles.

2.4.2. Microporous Silica Membranes

Because of the pore size scale in the microporous membranes, polymeric route can be advantageous in terms of resulted small particles. Generally more or less linear polymers are the best for processing microporous membranes. Nair et al., (1997), reported that under controlled conditions, variety of polymeric silica structures that were appropriate for microporous membranes could be obtained by sol-gel reactions of TEOS. The pore structure of a polymeric sol derived silica membrane depend on the structure of the inorganic polymer clusters in the sol and how these polymeric clusters are packed during film formation. The membrane microstructure in turn will affect the gas permeation properties of the membranes. Low branched silica species that occur polymerization reaction can interpenetrate during the gel collapse in which removal of solvent leading to microporous materials due to the highly compacted structures. On the other hand, highly branched clusters are not able to interpenetrate due to steric hindrance. In this case porosity will remain between collapsed clusters leading to mesoporous structures. The degree of branching is characterized by the fractal dimension which also controls the porosity of the membranes. As the fractal dimension increases, the porosity of the membranes increases when complete interpenetration is avoided. On the other hand, low porosity with the smallest pore size has been resulted when the interpenetration is large (Maene et al., 1998; Nair et al., 1998). It was reported that the interdependency of synthesis composition, fractal diameter and porosity. It could be concluded that increase in acid concentration increases the fractal dimension
indicating more branched structures and the degree of porosity increase is proportional to fractal dimension of the sol.

Nair et al., (2000) compared the changes in microporosity values of the unsupported membranes to the gas permeation behavior of the supported membranes made from similar silica sols. They concluded that the increase in porosity of gel increases the permeation of helium gas molecules through the membrane. On the other hand, this increase in permeation may not necessarily reflect an increase in He/N₂ selectivity. The selectivity in fact decreases with increase in porosity as well as the same in the case for the activation energy for helium permeation through the membrane. Nair et al., (2000) showed that molecular sieving membranes could be prepared and the membrane gave He/N₂ ideal selectivity values as high as 1230 at 408 K by properly controlling the reactant conditions.

A standard silica membrane as prepared by de Lange (de Lange et al., 1995a) consisted of a die-pressed α-alumina support, fired at 1360 °C with a pore diameter of 160 nm on which a γ-alumina membrane was coated with a boehmite sol. The coated γ-alumina layer was calcined at 600 °C, had a thickness of 7 μm with a pore diameter of ~5 nm. On top of this mesoporous membrane, a silica top-layer was coated with a polymeric silica sol. The standard reaction mixture had a final molar TEOS/ethanol/water/acid ratio of 1/3.8/6.4/0.085. The silica layer was fired at 400 °C and had a bi-modal pore size distribution having a maximum at an effective pore diameter of 0.5 nm and a very weak second maximum at about 0.75 nm. Some defects were however present in the microporous silica layer resulting in relatively low permselectivities. For example, the H₂/CO₂ permselectivity was only 5, which is very close to the ideal Knudsen selectivity of 4.7 and H₂/CH₄ permselectivity was about 40 with a H₂ permeance in the range of 10⁻⁶ mol/m²sPa. On the other hand, in the study of de Lange et al., (1995b) the comparison of the pore size distribution measured on non-supported membranes by N₂ adsorption with supported ones that were estimated from gas permeation has indicated that the average pore diameter of supported silica membranes were slightly smaller than about 0.4 nm. Extensive research has been progressed to deal with molecular sieving silica membranes including,

1. Pore size reduction and increasing flux (da Costa et al., 2002; de Vos and Verweij, 1998; Tsai et al., 2000).
2. Hydrophobicity to increase the stability in aqueous solutions or wet steams since the weak stability of microporous silica membrane limits its use in specific applications (de Vos et al., 1999).

da Costa et al., (2002) were able to produce membranes by two step acid catalysed hydrolysis process with a H$_2$/CO$_2$ permselectivity of 31 where de Vos and Verweij reported values of 18-130. In the two-step method, hydrolysis and condensation of TEOS were conducted first with smaller amount of water and acid at 60 °C for 3 h. Additional water and acid were added to the system at room temperature. Based on the permselectivity and the mobility energy results, da Costa et al., (2002) suggested that two step acid sol-gel process leads to smaller pore size than the single step as a result of the formation of more weakly branched structures. They also concluded that although the permeance of He for membranes both single and two step catalyzed are very similar, two step catalyzed membranes have higher permselectivities for gases with kinetic diameter smaller than 3 Å such as He and H$_2$ and lower permselectivities for gases with kinetic diameter higher than 3.4 Å like CO$_2$, CH$_4$. Therefore, the two-step sol-gel approach appears to provide a greater pore size tailorability allowing superior gas separation performance over single step sol-gel method. de Vos and Verweij (1998), showed the influence of particle contamination on the integrity of silica membrane layers by performing the synthesis of the membranes under clean-room conditions and they were able to produce 30 nm thick silica membranes. Furthermore, the firing temperature of the silica layer was increased to 600 °C, which resulted in a decrease of the hydroxyl group concentration on the pore-surface in the silica layer and a significant decrease in the CO$_2$ permeance. Therefore, the H$_2$/CO$_2$ permselectivity improved by more than a factor 10, while the hydrogen permeance remained high (4.7-17.7*10$^{-7}$ mol/m$^2$sPa). Thin microporous silica membranes have been prepared on the outer surface of the hollow fibre ceramic support to increase the membrane surface area to module volume ratio and decrease the support resistance to the overall mass transport resistance (Peters et al., 2005). They have found high He permeance with an Arrhenius type temperature dependency (1.1-2.9*10$^{-6}$ mol/m$^2$sPa) while for N$_2$ decrease in permeance with temperature and high He/N$_2$ permselectivity (100-1000).

Microporous amorphous silica membranes can also be prepared by using particulate sol containing small silica and mixed-oxide particles. Porous membranes with different pore size can be obtained by packing of silica particles of different sizes. Microporous silica membranes for CO$_2$/N$_2$ gas separation and understanding of gas
permeation mechanisms in micropores have been prepared by colloidal silica sols with particle size ranging from 80 nm to some tens of nanometers in the study of Yoshioka et al., (2001). The mean particle diameters of colloidal silica sol were controlled by the TEOS concentration in aqueous initial solution and decrease with increasing water to TEOS molar ratio in the sol. In order to prevent penetration of sol into the substrate pores, the hot coating method which allow instant gelation on the substrate was applied by heating the $\alpha$-Al$_2$O$_3$ support at 180-190 $^\circ$C before coating. They have concluded that the pore sizes of the membranes are smaller than 5 Å on basis of the relation between the permeance and the kinetic diameter of permeating gas molecules. The permeation ratio (CO$_2$/N$_2$) had been reported as 17.2 with the value of CO$_2$ permeance as $8.65\times10^{-7}$ mol/m$^2$sPa. They suggested that the precise control of pore size and the pore surface modification leading to high interaction with CO$_2$ molecules are needed for improving separation factor of CO$_2$/N$_2$. The use of porous silica membranes derived from colloidal silica particles ranging from 25 nm to less than 10 nm for the separation of organic-inorganic gas mixtures have been reported by Asaeda and Yamasaki (2001). They prepared silica membranes of high flux with high He and H$_2$ selectivity in the temperature range of 50-300 $^\circ$C. The pore diameter of the membrane about 1 μm in thickness were determined by gas permeation method to be less than 0.4 nm. They stated that in order to eliminate the interaction between the pore walls and gas molecules, the permeances calculated at high temperature should be used for the estimation of pore size distribution of the membranes. The H$_2$ permeance was reported as $1.3\times10^{-6}$ mol/m$^2$sPa with permeance ratios were 150 for H$_2$/CH$_4$, 1100 for H$_2$/C$_2$H$_6$ and 6300 H$_2$/C$_3$H$_8$ at 300 $^\circ$C. It was reported that although the permeance of hydrogen is slightly dependent on temperature, the temperature dependency of CO$_2$ permeation is as large as observed for ethane and butane. The largest separation factor (110) for CO$_2$/CH$_4$ was obtained at low temperatures due to the larger adsorption on the silica surface. They also reported that, gas permeation characteristics of silica membrane in humid gases changed due to the pore blocking and the increase in the membrane thickness.

Amorphous silica is not stable in aqueous solutions, especially in neutral and alkaline pHs, but has a great advantage in terms of pore-size controllability. Therefore, the incorporation of zirconia into colloidal silica membranes have been investigated to improve the stability against water, separation performance of the aqueous solutions of organic solvent by pervaporation (Asaeda et al., 2002), H$_2$ separation performance in
hydrothermal conditions (Yoshida et al., 2001) and for nanofiltration experiments in non-aqueous solutions (Tsuru et al., 2001a). Colloidal silica-zirconia sols with different ZrO₂ content have been prepared by boiling of polymeric sol that could be prepared by hydrolysis and condensation reactions of TEOS and zirconium propoxide or zirconium butoxide after addition of large amount of water and hydrochloric acid in order to control concentration and keep the pH less than 2. The average particle size was controlled by the conditions at boiling steps. Hot coating was applied (at 180-190 °C) before the heat treatment at 500-570 °C for 10 min. The pore size of membranes prepared from 0.6 wt% sol was reported as 0.6 nm. The XRD patterns show that the amorphous homogeneous composite structure without silica-rich phases has been obtained by applying quick drying at 180 °C while drying at room temperature resulted in some crystal structure of ZrO₂. Yoshida et al., (2001) reported that silica–zirconia network was densified with zirconia content that indicated by the increase in activation energy of He and H₂ permeances. They also stated that the steam firing method leads to the increase in the hydrothermal stability of membranes.

The Ni doped silica membranes were synthesized to improve the stability of the membranes against water and water vapor in the study of Kanezashi and Asaeda (2006). The preparation of homogeneous structures with well dispersed NiO in silica network is extremely important because the segregation of metal oxides leads to structural heterogeneity and causes the instability towards water. The colloidal silica sols of various molar ratios (Si/Ni=4/1, 3/1, 2/1, 1/1) were prepared by hydrolysis and condensation reactions of TEOS in ethanol with specific amount of Ni(NO)₃.6H₂O and excess water. Diluted silica sol were applied on the silica-zirconia intermediate layer by the hot coating method and then heat treated at 550-650 °C in steamed atmosphere for 30-60 min. After keeping the membranes in humid air (80 °C, 60 % RH) for a few days, the heat treatment was repeated at similar conditions. The hydrothermal stability test were performed by observing the gas permeance changes after leaving the membrane in stream of N₂-H₂O gas mixtures at 500 °C for specified time intervals. Although the permeances of He and H₂ for the fresh membranes showed the characteristics of slightly activated permeation, the N₂ permeation have behaved like a Knudsen permeation mechanism indicating the N₂ permeation through a pinhole that was left in the membrane. They concluded that hydrothermal treatment before exposed to H₂ is quite effective to prevent the further densification of Ni-doped amorphous silica networks due to reduction by H₂ and sintering in steam since, the dispersed Ni or NiO might show
very little mobility through completely densified silica networks after hydrothermal treatments. It was reported that the Ni-doped (Si/Ni=2) membrane show relatively high permeances of He and H₂ with selectivity 950 (He/N₂) and 370 (H₂/N₂) at the beginning of hydrothermal stability test and in the first 100 h, the permeances of He and H₂ decrease slightly and reach a steady state value with larger selectivities of 1450 (He/N₂) and 400 (H₂/N₂). The maximum permeance ratio of H₂/H₂O was reported as 37 for the membranes having the highest Ni content (Si/Ni=1) because of its less hydrophilicity than silica networks. The other study that conducted by Kanezashi et al. (2005) includes the application of these Ni-doped (Si/Ni=1) silica membranes for separation of He from organic gas mixtures. They suggested that inorganic membranes prepared by the sol-gel method would have two types of pores as shown in Figure 2.10. One is an inter-particle pore formed by colloidal packing and the firing processes and the other is a network pore formed by polymer chains within a colloidal particle. Small gas molecules such as He, H₂ can permeate through both types of pores while the Knudsen diffusion dominated permeation of N₂ or CH₄ occurs through the inter particle pores. Activated diffusion is controlled by only intra particle pores associated from silica network structure.

![Figure 2.10. Schematic pore structure of silica membranes](Source: Kanezashi et al., 2005).

It was reported that the permeance mechanism of small molecules like He and H₂ which can mainly permeate through not only interparticle pores but network pores as well is activated diffusion but slightly larger molecules (N₂, CH₄ and SF₆) can permeate only through the inter particle pores by Knudsen diffusion mechanism. The Ni-doped
silica membranes have showed high He permeance with high selectivity of 600 (He/CH₄) at 300 °C and after 4 days in humid air, the He permeability decreased slightly causes the increase in selectivity of 800 (He/CH₄) because of large decrease in CH₄ permeance. The activation energy of He permeance did not show significant variation after the membrane left in humid air suggesting that well-dispersed NiO through silica structure can prevent the densification of network pores through which only He and H₂ can permeate. The permeabilities of He and CH₄ decreased drastically in moist permeation conditions at temperature below around 150 °C because of adsorbed water molecules in pores.

The hydrothermal stability of microporous silica membranes had been improved by incorporation of Nb⁵⁺ ions into silica matrix causing the formation of hydrothermally stable Nb-O-Si bonds (Boffa et al., 2008). Hydrothermal exposure leads to collapse of pore networks resulting in dense layer with some microcracks. The hydrothermal instability of microporous silica membranes is generally ascribed by the surface hydroxyl groups that are subject to recondensation. The H₂ permeances of the pure silica top layer and Nb⁵⁺ doped silica layer were found as 1.6*10⁻⁶ mol Pa⁻¹m⁻²s⁻¹ and 3.8*10⁻⁸ mol Pa⁻¹m⁻²s⁻¹, respectively. Differences in permeance values were ascribed by dense membrane layer caused by incorporation of unreacted species and clusters due to lower hydrolysis and acid ratios at which niobia-silica sol was synthesised. After hydrothermal treatment at 200 °C, the H₂ permeance of the niobia silica layer had decreased by 32% while those through pure silica layer reduced by 73%. They have concluded that high hydrothermal stability for niobia-silica layer was caused by the slow kinetics of densification due to the stabilization of microporous network upon addition of Nb⁵⁺ ions.

Hydrostable and highly selective silica membranes have been synthesized by incorporating the cobalt molecule within the silica matrix (Uhlmann et al., 2009). The formed crystalline Co₃O₄ phase was subsequently reduced at high temperature in rich hydrogen atmosphere resulting in the formation of highly selective silica membrane with helium permeation close to 1.0*10⁻⁷ mol/m²sPa and He/N₂ selectivities of 1100. The membranes exposed to water vapour underwent the slight collapse of the smaller pores leading a smaller pore size with higher selectivities due to the additional structural integrity provided by the crystalline cobalt phase.

The mechanically and structurally stable microporous silica membrane have been prepared by sol-gel process by incorporating boron in the silica network (Barboiu
et al., 2009). The degree of crosslinking has reduced by the addition of Ba$_2$O$_3$ that cause the BO$_3$ formation during drying. The low degree of crosslinking allows the formation of thin silica layer with microporosity and low defect density because of flexibility of layer. The mechanical properties of boron doped layer has been found as those of the intermediate gamma layer that might avoid the crack formation during the thermal treatment. The He permeances of the 10%-B$_2$O$_3$ containing silica membranes were found as $1.0 \times 10^{-10}$ kmol Pa$^{-1}$ m$^{-2}$ s$^{-1}$ at 300 °C with He/CO$_2$ selectivities of 55.

2.4.3. Template Based Approach for Silica Membranes

Incorporation of organic template agents into a gel structure can also be advantageously applied to design the porous structure. These template agents can be organic groups chemically linked to the gel network, isolated molecules trapped in the sol-gel matrix or self-assembled systems participating in the formation of structured gels. The controlled porosity of the membranes is acquired by the uniform elimination of these templates via heat or wet chemical treatment without collapse of the solid matrix. Therefore, the pore structure of sol-gel derived membranes can be tailored easily because of the choice of removable units depends on the required pore size and shape. The nature of the interaction between the template and the matrix can be classified as covalent or non-covalent bonding. In surfactant templated silica, template-matrix interaction is via non-covalent bonding mechanisms and pore structure is established prior to drying and heat treatment while the pore structure of porous silica templated by organic ligands covalently bonded to siloxane network is strongly affected upon drying and template removal (Raman et al., 1996). A general template approach can be summarized as the organization of primary structural units around a molecular template and solidified to form a matrix.

Silica based surfactant templated membranes can exhibit improved structural stability and well controlled pore size with high surface area and they can be prepared by using evaporation induced self-assembly and hydrothermal treatment on a variety of non-porous and porous support. Self assembly is spontaneous organization of materials through non covalent interactions and uses the asymmetric molecules that are going to organize into well-defined supramolecular assemblies including amphiphilic surfactant
molecules or polymers. There is a direct relation of the surfactant array size and shape to the final pore size and geometry in the mesophases in contrast to organic molecules in zeolites. In aqueous solution above the critical micelle concentration (cmc), surfactants assemble into micelles, spherical or cylindrical structures that maintain the hydrophilic parts of the surfactant in contact with water. Further increases in surfactant concentration result in the self-organization of micelles into periodic hexagonal, cubic, or lamellar mesophases as shown in Figure 2.11. These surfactant liquid crystal structures serve as an organic template for the polymerization of silicates that is the route of the synthesis of the new family of ordered mesoporous molecular sieves designated as M41S including members having uniform pore structures of hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50).

![Figure 2.11. Schematic phase diagram for CTABr in H₂O](Source: Raman et al., 1996).

Recently, there has been increasing interest in the synthesis of inorganic membranes based on ordered mesoporous silica with uniform pore network. These membranes are highly promising because of high fluxes expected for large molecules. Membrane with cubic phases in which pores are connected in three dimensional networks is more attractive than the other phases because of pore accessibility from the membrane surfaces which decrease diffusion limitations (Brinker et al., 1999, Lu et al., 1997).
Ayral et al., (1995) described the role of amphiphilic systems in the preparation of silica membranes exhibiting ordered microporosity. Surfactant molecules and related self-assembled systems have been used as template agents during sol-gel processing of these membranes. The effect of ionic and non-ionic surfactant molecules on gel formation has also been investigated. The role of surfactant molecules have been identified by either as being modify the sol to gel transition with a template effect or they can participate in the formation of gels through a self organization process leading to an organized gel structures. Silica membranes with tailor-made microporosity and pore diameters of between 1 and 2 nm were obtained. They have found that the pore diameter tends to increase with surfactant chain length and the surface area and the pore volume is strongly affected by the concentration of surfactant.

MCM-48 membranes with a 3-D pore structure have been synthesized on porous alumina support under hydrothermal conditions at 363 K for 96 h by Nishiyama et al., (2001). Heat treatment was applied at 773 K for 4 h and surfactant to alkoxide molar ratio of 0.59 was fixed in order to get MCM-48 phases while that of 0.05 was for MCM-41. Although about 10% contraction of structure was reported after calcination, the characteristic XRD peak intensity remained constant indicating high thermal stability up to 773 K. A composite layer of MCM-48/alumina has been obtained due to grow of MCM-48 inside the pores of alumina. The permeation of H₂, N₂, CH₄, O₂ and CO₂ through calcined membranes was independent of transmembrane pressure indicating that the Knudsen diffusion governed permeance without large pinholes.

Gas transport properties of hydrothermally synthesized and dip-coated cubic mesoporous silica membranes deposited on macroporous alumina have been compared by McCool et al., (2003). It was reported that the permeation characteristics of both membranes are governed by Knudsen diffusion with no net contribution by viscous flow. The high permeation rates have been attributed to highly porous mesoporous silica layer with an interconnected pore network. The dip-coated membranes prepared in that study has exhibited gas permeation rates three times larger than the hydrothermally deposited membranes due to the distinct 2 µm in thickness silica layer. On the other hand, hydrothermally synthesized membrane was 7 µm in thickness with significant penetration into the support.

Sol-gel dip coating suggest an alternative route for the formation of thin film with mesoporous phases (Brinker et al., 1999). In traditional method that gives rise to granular textures leading to inhomogeneous film formation in which pores are oriented
parallel to the substrate in the course of time consuming batch process, the initial surfactant concentration is higher than critical micelle concentration (cmc). On the other hand, in evaporation induced self assembly process begins with a homogeneous solution with an initial surfactant concentration smaller than the cmc. Surfactant enrichment by solvent evaporation to exceed cmc and therefore develop mesophases only during the few seconds of highly ordered film deposition with controlled pore structure. By varying initial surfactant concentration, it is possible to tailor the film morphology.

Hexagonal silica layer were prepared from silicon alkoxide (TEOS) and ionic surfactant (alkyltrimethylammoniumbromides) in the study of Klotz et al., (2001). The use of surfactant diluted sols has enabled to produce crack-free silica layers exhibiting a well ordered hexagonal mesoporosity with cylindrical pores of about 2.1 nm. Moreover, the effect of nanoparticle seeding to increase pore accessibility on gas permeation has been investigated. It was found that seeding promotes heterogeneous nucleation of the templating mesophase by creating additional interfaces inside the hybrid gelling solution and destroys the preferential orientation of the 2-D structure parallel to the substrate. Although the porosity of the layers was remained unchanged, the permeability was strongly increased by the seeding of the layers with silica nanoparticles which favors the random orientation of the ordered structures in the layer. Additionally, the measured permeabilities were analyzed using Knudsen model of gas transport in mesoporous materials to determine the tortuosity of the layer. High tortuosity factor has been explained by the contribution of microporosity of the silica walls which reflects a lack of connectivity between the cylindrical mesopores of the ordered structures.

The surfactant templated silica layer has been utilized as an intermediate layer between the supporting mesoporous $\gamma$-Al$_2$O$_3$ and the amorphous silica layer for gas separation application in the study of Zivkovic et al., (2004). They reported that the application of that layer shows significant improved values for both hydrogen flux and selectivity as in the study of Tsai et al., (2000) in which that increase was attributed to the prevention of penetration of standard microporous silica into the $\gamma$-Al$_2$O$_3$ layer.

Mesoporous silica membrane with structure directing triblock copolymers (non-ionic-Pluronic P123) have been synthesized via dip-coating evaporation induced self assembly under various surfactant-silica volume percent to produce variety of mesostructures in the study of Higgins et al., (2006). Highly reproducible continuous membranes with minimum defect have been produced by applying 3 dipping into 33% vol surfactant concentration. The order of helium and nitrogen permeation was $10^{-6}$
mol/m²sPa and transport through membranes with 10 μm in thickness governed by Knudsen diffusion and the reported selectivity of He/N₂ was 2.46 that approach to ideal Knudsen selectivity (2.65). The pore size distribution that was derived from permoporometry measurement indicated that pore diameter was 5 nm and 10% microporosity while 2% microporosity and higher pore diameter have been determined from N₂ adsorption-desorption for the powder sample. Different pore size distributions have been attributed to the rapid drying during membrane formation, because of the thin layer. That phenomenon occurs when the polyethylene oxide (PEO) chains are rapidly forming into micelles and the drying process occurs faster than the surfactant can assemble, leaving coiled chains extending out of the micelle. These chains lead to interconnected microporous channels between continuous mesopores. These microporous channels will lead to a percentage of active micropores by contributing to the bulk flow.

Alumina-cubic mesostructured silica hybrid membranes have been synthesized using evaporative induced self assembly process based on dip coating of an Anapore 200 nm (formed by electrochemical etching) membrane into solution including Brij-56 (non-ionic)/TEOS/HCl/H₂O. After 15 min dip-coating and 15 min drying at 45 °C, ethanol extraction was applied for 48 h to remove surfactant. The effective pore size of the membranes were tuned based on the number of dipping cycles. It was reported that there is a significant increase in the He/N₂ permselectivities of three-time dip-coated membrane possessing comparable selectivities with 10 nm Membralox membrane and those of at theoretical Knudsen limit indicating that absence of defects and the selectivity of 4 times dipped membrane (2.7) was higher than the 5 nm commercial membranes (2.29). They concluded that silica deposited in the Anapore membrane possesses uniform pores approximately 5 nm in diameter based on the XRD, SEM and TEM results consistent with the permeation studies.

The second template approach is organic templating of amorphous microporous silica systems in which templates are introduced as ligands covalently bonded to silica precursors. In sol-gel processing, the small pore size and narrow pore size distribution are achieved at the expense of pore volume because of the collapse of the network. The organic template approach in which molecules or ligands are incorporated in a dense inorganic matrix and subsequently removed to create pores can overcome that limitation to pore volume. The covalently bonded organic ligand is usually non-hydrolysable and imparts organic character to inorganic siloxane network. In that system, porosity can be
controlled by the organic ligand volume, independently of the pore size, while the pore size depends on the template size and shape (Raman et al., 1996). Following criteria defined by Lu et al., (1999) should be satisfied for the successful implementation of the templating approach illustrated in Figure 2.12.

1. The organic ligands must be uniformly incorporated in the inorganic matrix without aggregation or phase separation to avoid creation of pores larger than the size of the individual ligands.

2. The synthesis and processing conditions should result in a dense embedding matrix so that the pores are created only by template removal.

3. Template removal should be achieved without matrix collapse so that the pores created preserve the original size and shape of the template.

Figure 2.12. Schematic illustration of the organic template approach (Source: Lu et al., 1999).

Raman and Brinker (1995) prepared microporous silica membranes exhibiting high CO₂ permeances and moderate CO₂/CH₄ selectivities (above Knudsen values and about 12) using methyl ligands as templates by copolymerizing methyltrimethoxysilane (MTES) with tetraethyl orthosilicate (TEOS). During the heat treatment the methyl ligands pyrolyse, creating a continuous network of micropores. Gas permeation measurements show a large decrease with increasing heat treatment temperatures in the region of 400 to 500 °C indicating that the densification of the membranes. However, as prepared hybrid MTES/TEOS materials are porous before removing the methyl ligands, probably because of ligand aggregation (phase separation) or unfavorable
silica/ligand/solvent interactions. Different ligand (methacryloxypropyl) have been used by Lu et al., (1999) as templates that show better silica/ligand/solvent interactions to prepare highly dense hybrid materials before the calcination process to obtain microporous silica with controlled pore structure after removal of the templates. It has been found that the final porosity of the microporous silica is due both to the primary pores (those present in the hybrid material prior to template removal) and the secondary pores (those created by pyrolytic removal of organic templates). On the other hand, it was reported that, the primary pores decrease as the mole fraction of ligands increases because of the enhanced densification of hybrid materials during drying. Gas permeation experiments indicate that the secondary pores are approximately 0.5 nm in diameter with a close correspondence of the template ligand size.

Defect-free silica based inorganic-organic hybrid membranes 2 μm in thickness have been synthesised onto α-Al₂O₃ support by using sol-gel processing of tetraethoxysilane (TEOS) and phenyltrimethoxysilane (PTMOS) in the study of Zhang et al., (2000). It has been reported that the introduction of phenyl group improves the selectivity of O₂/N₂ and CO₂/N₂ because of the affinity of gas molecules to the surface but densifies the membrane structure resulting in the decrease in permeability. The gas transport through the hybrid membrane has been defined as the surface diffusion at low trans-membrane pressure and Knudsen diffusion at high pressure.

Sol-gel derived microporous aminosilicate membrane has been developed by Xomeritakis et al., (2005) for enhanced CO₂ separation due to preferential adsorption of CO₂ in the membrane pore wall and simultaneous blocking of permeation of other gases like O₂, N₂ and CH₄. Amine functional group was randomly dispersed in amorphous silica matrix of pore size in the range of 4-5 Å in order to improve CO₂ selectivity. The pore size of the membranes with incorporated amine group was larger than the pure silica ones due to the less interpenetration of silica clusters contained in the silica sol. On the other hand, it has been revealed that the prolonged aging time causes the decrease in both pore size and the porosity of membranes as a result of densification of inorganic silica framework and considerable increase of selectivity at the expense of CO₂ permeance was observed. They concluded that new membrane appears to separate CO₂ from N₂ based on combination of molecular sieving and preferential CO₂ adsorption/pore blocking mechanism.
CHAPTER 3

GAS TRANSPORT MECHANISMS THROUGH POROUS MEMBRANES

The medium in which gas permeates through can be categorized as being porous or dense. Gas permeation through a dense medium is dependent on the gas solubility and diffusivity in the medium, and the nature of the medium. The Solution-Diffusion model is used to model gas permeation in dense (organic) materials. On the other hand, beyond taking into account the stable and rigid pore structure for inorganic porous membranes, transport resistance due to the interactions between the pore walls and the membrane materials have a significant importance. Besides these interactions, also interactions between the gas molecules influence the overall separation behaviour.

An overview of the transport mechanisms in porous membranes is given in Table 3.1 (Burggraaf and Cot, 1996). Viscous flow and molecular diffusion are non-selective but they have significant effects to total flow resistance in the macroporous supporting layer. Knudsen diffusion, viscous flow and surface diffusion are the dominant transport mechanisms through the mesoporous separation layers. Because of the spatial restrictions such as the pore walls and pore openings inside the micro-porous material, of a scale comparable to the dimensions of the gas molecule, the potential energy of molecule is not independent of position which can lead to the distinct differences in potential energy barriers and transport rate. As a result the transport of the species is not gas-like and the concepts of gas transport in macro and mesoporous media can no longer be used to describe transport in micro-porous materials. Since complicated mass transport and separation characteristics of microporous inorganic membranes, only a limited description is available (Yoshioka et al., 2001). Consequently, understanding of gas permeation mechanisms through the membranes can improve the gas separation processes for specific applications.
Table 3.1. Transport regime in porous structure
(Source: Burggraaf and Cot, 1996).

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<thead>
<tr>
<th>Transport Type</th>
<th>Pore Diameter</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscous flow</td>
<td>&gt;20 nm</td>
<td>-</td>
</tr>
<tr>
<td>Molecular diffusion</td>
<td>&gt;10 nm</td>
<td>-</td>
</tr>
<tr>
<td>Knudsen diffusion</td>
<td>2-100 nm</td>
<td>$1/\sqrt{M}$</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Capillary condensation</td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>Micropore (configurational) diffusion</td>
<td>&lt;1.5 nm</td>
<td>++</td>
</tr>
</tbody>
</table>

In membrane applications especially for gas separations, permeance and permeability are usually used as measures of gas transport rate. The permeance, $F$, (mol/m$^2$/s/ Pa) is defined as the flux per unit pressure difference between the two sides of the membrane. The permeability coefficient, $P$, (mol/ms/ Pa) is obtained by multiplication of the permeance by the unit thickness of the separation layer. During permeation of a gas through a microporous membrane three major steps occur each representing a flow resistance (Burggraaf, 1999):

1. Mass transfer (diffusion) from the bulk gas phase through a stagnant gas film which is adjacent to the membrane surface. This step is sensitive to flow conditions but is important only for gas mixtures at not too low pressures. It might play a role, however, in diffusion experiments of single gases with the Wicke-Callenbach method.

2. Mass transfer across the surface. Gas molecules have to change from a gaseous state to a state within the porous (solid) material. This happens by a sorption process at the pore entrance and a desorption process at the pore exit. These surface processes consume a part of the driving force (pressure gradient or better chemical potential gradient) and so represent a flow resistance.

3. Diffusion through the bulk of the microporous material.

In conclusion, sorption and diffusion are two major processes that play important roles in the overall gas transport since each step can contribute to the total permeation rate and the variables including temperature and pressure affect the significance of these
processes. While sorption describes the interactions between gas molecules and the membrane surface, diffusion describes the rate of gas passage through the membrane.

For supported membranes, although the selective properties of the multi-layered porous membrane are mainly determined by the thin microporous layer, transport through the support and intermediate layer can become important and to obtain the real flow resistance of the separation layer corrections for the support resistance must be applied.

### 3.1. Knudsen Diffusion and Viscous Flow

Gas permeation through porous membranes is controlled by the ratio of the mean free path length of the gas molecule, $\lambda$, to the pore diameter, $d_p$. The mean path length of a gas molecule diffusing through a porous medium is defined by Equation 3.1 (Bhave, 1991). In Equation 3.1, $\eta$ is the viscosity of the gas, $M$ is the molecular weight of the gas molecule, $P_m$ is the mean pressure, $R$ is the universal gas constant, and $T$ is the temperature.

$$\lambda = \frac{16\eta}{5\pi P_m \left( \frac{\pi RT}{2M} \right)^{1/2}} \quad (3.1)$$

Both Knudsen diffusion and viscous flow are governed by the ratio $\lambda/d_p$, where Knudsen diffusion is characterized by $\lambda/d_p>>1$ and this implies that a gas molecule collides more often with a pore wall than another gas molecule. During these collisions with the pore walls, the gas molecule is momentarily adsorbed to its surface before being randomly reflected of the pore wall. The consequence of these adsorptions is independent movement of the gas molecules. Therefore, Knudsen diffusion is a selective transport mechanism and gas separation occurs because of the differences in the mean molecular velocity $u = \sqrt{8RT/\pi M}$ of the gas. This equation also shows that $u$ is inversely related to $M$, thus gas separation is dependent on the differences in $M$. The decrease of the flux with increasing temperature is due to the inverse proportionality of temperature and concentration of ideal gas, while the molecular velocity increases with the square root of the temperature and the well known formula for diffusive flow of molecules in a long capillary,
\[ J_{Kn} = -D_{Kn} \left( \frac{dc}{dz} \right) \]  
(3.2)

where \( c \) is ideal gas concentration and the Knudsen diffusivity depends on the mean molecular velocity and the structural parameters\(^3\) is defined by Equation 3.3,

\[ D_{Kn} = \frac{4}{3} K_0 u \]  
(3.3)

and the structural factor \( K_0 \) for the cylindrical pores equals;

\[ K_0 = \frac{1}{4} \frac{\varepsilon}{\tau} d_p \]  
(3.4)

where \( \varepsilon \) is the porosity, \( d_p \) is pore diameter and \( \tau \) is the tortuosity. Taking this effect into account and inserting into Equation 3.2 with pressure dependency of ideal gas concentration, the expression for the Knudsen flow in a porous membrane is obtained:

\[ J_{Kn} = -\varepsilon^* \frac{d_p}{\tau^* l} \left( \frac{8}{9 \pi MRT} \right)^{1/2} \frac{dP}{dz} \]  
(3.5)

After integration of Equation 3.5 over the membrane thickness (\( l \)), the permeance is defined to be;

\[ F_{Kn} = -\frac{J_{Kn}}{\Delta P} = \varepsilon^* \frac{d_p}{\tau^* l} \left( \frac{8}{9 \pi MRT} \right)^{1/2} \]  
(3.6)

Gas selectivity is defined as the ratio of gas fluxes, and the gas selectivity for Knudsen diffusion which is equal to the inverse square root of the ratio of the molecular weight of the gases as seen in Equation 3.7. It is shown that for gases which are similar in molecular weight, Knudsen flow is ineffective. This is an idealized separation factor

---

\(^3\) The presence of the porous medium is accounted for by introducing two structure parameters \( K_0 \) and \( B_0 \), which can also be expressed in terms of a average pore size and the ratio of the porosity and tortuosity.
because concentration gradients at a pore entrance, membrane defects, and surface flow, cause real separations to be smaller than this idealized separation factor.

\[ \alpha = \frac{F_1}{F_2} = \left( \frac{M_2}{M_1} \right)^{0.5} \]  

(3.7)

When the mean free path of the molecules is much smaller than the pore size of the membranes (\( \lambda \ll d_p \)), the intermolecular collisions are dominant which is the case of viscous flow. In this regime, velocity of gases is moved slowly by momentum transport under pressure or concentration gradient. At low Reynolds numbers non selective viscous transport of a Newtonian fluid through a porous medium can be described by Darcy’s law;

\[ J_v = -\frac{B_o}{\eta} \frac{P}{RT} \left( \frac{dp}{dz} \right) \]  

(3.8)

where \( \eta \) is the viscosity (Pa.s) and \( B_o \) which includes the effect of real pore structure can be expressed by assuming cylindrical pores and no slip condition at the pore wall as;

\[ B_o = \frac{\varepsilon d_p^2}{\tau \cdot 32} \]  

(3.9)

Introducing this factor into the molar flux equation (Eqn 3.8), leads to;

\[ J_v = -\frac{\varepsilon}{32 \cdot \eta \cdot \tau} \frac{d_p^2}{RT} \frac{p}{dz} \left( \frac{dp}{dz} \right) \]  

(3.10)

Integration of Equation 3.10 over the thickness (\( l \)) of the membrane gives the permeance;

\[ F_v = \frac{J_v}{\Delta p} = \frac{\varepsilon d_p^2}{32 \cdot \eta \cdot \tau \cdot l \cdot RT} \frac{1}{P_m} \]  

(3.11)
where the $P_m$ is the mean pressure across the membrane. In contrast to Knudsen flow, the gases viscous flow permeance is linearly proportional to the mean pressure. In terms of temperature dependence, it decreases with temperature since the gaseous viscosity is proportional to the square root of temperature and therefore the dependence of permeance on temperature is $T^{-3/2}$.

The Knudsen and Viscous flow can occur simultaneously. In pure gas permeation, it is not necessarily that molecules can only see the pore wall or only see each other when the mean free path of the gases is comparable with the pore diameter and both mechanisms can be considered to be additive;

$$J = -\frac{1}{RT} \left( D_{Kn} + \frac{B_m}{\eta} P_m \right) \frac{dP}{dz}$$  \hspace{1cm} (3.12)

Under such conditions, for the defect free membranes, transition flow occurs by the combined effects of both Knudsen and Viscous flow. On the other hand, for mesoporous membranes which are definitely in the Knudsen regime, the increase in permeance with pressure is an indication of the viscous flow and this in turn means that there are defects in the membrane while the positive intercept of permeance is governed by the Knudsen flow.

The influence of silica particle size on permeation behaviour of stainless steel supported silica membranes has been investigated by Park et al., (2008). Silica membranes were prepared by DRFF (drying-freezing-fast drying) and SRFF (soaking-rolling-freezing-fast drying) methods using colloidal silica sols to determine the transition region between viscous flow and Knudsen diffusion. Viscous flow dominated permeation behaviour for the membranes prepared with 300 and 500 nm colloidal sols even though crack-free membrane layer formed, due to the large interstitial voids among the particles. The use of smaller particles (< 100 nm) has not resulted in uniform membrane layer due to loss of particles through the large macropores of the stainless steel support and showed the viscous flow transport properties. They concluded that 100 nm particle sizes is the most suitable particle size for the modification of stainless steel support. Crack free membrane layer had been obtained with the H$_2$/N$_2$ permselectivity (3.4-3.7) that approached the theoretical Knudsen selectivity.
Surface Diffusion

For sufficiently low temperature and/or high pressure, adsorption of molecules onto the surface of the pore walls can occur. When the adsorbed molecules are mobile, surface diffusion can take place. The extent of surface diffusion is determined by the amount of molecules adsorbed and their mobility. Gas molecules with a high adsorption capacity preferentially adsorb on the surface of the membrane pores, limiting the diffusion of the less adsorbing species in the pores. Thus, the permeation results in the presence of adsorbing gases show a higher permeance than the weakly adsorbing gas molecules by the surface diffusion mechanisms. Many descriptions of surface diffusion have been proposed. Generally, the main mechanism of the surface flow can be divided into three groups; (1) hydrodynamic model, (2) the random walk model, (3) the hopping model. An extensive review is presented by Bhave (1991) and Choi et al., (2001). For relatively low concentration, the surface diffusion flux can be described by the two-dimensional Fick law;

\[ J_s = -\rho(1-\varepsilon) \frac{\varepsilon}{\tau} D_s \frac{dq}{dz} \]  

(3.13)

where, \( \rho(1-\varepsilon) \) is the density of the porous material, \( \tau \) is the tortuosity, \( D_s \) is the surface diffusion coefficient and \( dq/dz \) is the surface concentration gradient. It is generally accepted that the surface diffusion coefficient has an Arrhenius type of relation with the activation energy for surface flow. Because the diffusion process is assumed to occur by jumping motions from one site to another, the activation energy for diffusion is related to the heat of adsorption. This suggests that (i) strongly adsorbed molecules are less mobile than weakly adsorbed molecules and (ii) the total flux will decrease as the temperature is increased since the increased diffusivity is overruled by the decrease in surface concentration (de Lange et al., 1995b). Surface diffusion permeance exhibits an increase in pressure as in the case of viscous flow as a result of increase in surface loading. It is generally accepted that, surface flux makes an additional contribution to the gas phase transport and its contribution to the total flux increases strongly with decreasing pore size due to the increase in surface area.
At low temperatures and high pressures additional transport mechanisms are
multi-layer diffusion and capillary condensation. The permeability of strongly adsorbing
gases can be improved by a factor of 6 compared with Knudsen permeability, yielding
permeabilities of $3.2 \times 10^{-5}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at relative pressures of 0.4 to 0.8 as has been
shown by Uhlhorn et al., (1992) for $\gamma$-Al$_2$O$_3$ membrane. A maximum permeability
occurs at the point where pore blocking takes place (capillary condensation).

The influence of adsorption on the permeation properties of gas molecules
having different adsorption capacity for $\gamma$-Al$_2$O$_3$ membranes with pore diameter size of
4.6 nm has been studied by Lee et al., (2004). It was found that the order of adsorption
calculated based on the adsorption measurement was as C$_2$H$_6$>CO$_2$>CH$_4$>N$_2$~H$_2$. They
reported that the adsorption of a strongly adsorbing gas inhibits the diffusion and
transport of weakly adsorbing gases and this leads to a higher separation factor due to
the contribution of the surface diffusion mechanism as the additional transport
mechanism to the Knudsen diffusion. The separation factor of C$_2$H$_6$/N$_2$ was calculated
as 2.8 at 320 K for binary gas mixture. Although pressure independence of permeance
has been analysed for weakly adsorbing gases, the permeance of strongly gas species
(C$_2$H$_6$, CO$_2$) has increased with pressure which also implies an additional transport
mechanism, surface diffusion mechanism.

**Gas Transport Through Microporous Membranes**

Microporous membranes consist of zeolites, carbon and amorphous silica with
connected pores of sub-nanometer dimension acting as an adsorption site for small
molecules. Figure 3.1 shows the separation and transport of small molecules by
selective sorption and transport through supported microporous amorphous silica
membrane containing nearly linear silica polymers (chains). The size and the adsorption
characteristics of the micropores lead to selectivities many orders of magnitude more
than Knudsen combined with reasonably high fluxes. Application examples are isomer
separation like p-xylene from o-xylene, separation of H$_2$ or CO$_2$ from bigger molecules
and H$_2$O from reaction mixtures (Verweij, 1998).
Developments in microporous membranes can be expected with more comprehensive syntheses of the porous architecture to control the pore size uniformly based on a better understanding of the basic transport phenomena.

Gas transport through microporous or dense materials such as zeolites or bulk solid oxides requires adsorption of molecules before the subsequent diffusion process. Therefore, transport through the microporous membranes are complex and several situations have been observed (Burggraaf, 1999);

1. For a particular gas the flux may increase with temperature at a given pressure and with a particular membrane, while decrease is observed for membranes with different pore size.
2. For some gases maxima in the flux as a function of temperature at a given pressure are observed, the temperature of this maxima being a function of the pressure.
3. The flux can increase linearly with feed pressure (permeance is constant), may increase strongly non-linearly, and show saturation behaviour depending on the temperature and on the particular gas-membrane combinations.
4. Usually at high temperature and for a given membrane the permeance decreases with increasing effective molecular diameter while for some conditions this trend is reversed.
5. The flux (permeance) might be very sensitive for small changes in the permeance pressure and the type of support.

Figure 3.1. Schematic morphology of an amorphous silica membrane on top a mesoporous layer (Source: Verweij, 1998).
Description of permeation and separation as a function of relevant parameters covering all these phenomena through well defined microporous structures rather than zeolites will be of important step for the predictive gas transport model availability.

Diffusion of molecules through a porous membrane can proceed in different ways depending on the nature of the interaction between the diffusing gas molecules and the membrane. Various gas diffusion processes were discussed in terms of the associated energy potential wells developed inside the pores of membrane as shown in Figure 3.2 (de Lange, 1995b). The shapes of these energy potential wells depend mainly on the distance between the pore walls and the diffusing gas molecules. Therefore, the ratio of the molecular size of the diffusing gas and the pore diameter plays a major role in determining which diffusion mechanism may apply. These diffusion mechanisms have been theoretically reviewed by Burggraaf and his group (Burggraaf and Cot, 1996; Burggraaf, 1999; de Lange et al., 1995b).

![Figure 3.2](source: de Lange, 1995b)

**Figure 3.2.** Relation between pore size and adsorption potential for the different pore size regimes related with molecular size (Source: de Lange, 1995b).

Gas diffusion mechanisms through the microporous membranes were modelled as an activated process based on the micropore diffusion (Xiao and Wei, 1992; de Lange et al., 1995b). For microporous membranes with a pore diameter smaller than 2 nm, two diffusion mechanisms can be observed. The first mechanism occurs when there are pores larger than about 1 nm. In this case the pore diameter is of the same order of the mean free path of the molecules as in Knudsen diffusion. This type of mass transport...
is referred to as gas transitional (GT) diffusion. In this model, total process of moving between sorption sites involves activated sub-step and Knudsen diffusion. Because the molecules move by GT diffusion and another part by surface diffusion, this process is called surface diffusion enhanced micropore permeation (SEMP) by de Lange et al., (1995b) and is represented by the region c1 in Figure 3.2. In SEMP model a certain fraction of the gas molecules move through the gas phase in the pore, while the remainder resides on the pore walls. The GT diffusivity is given by (Xiao and Wei, 1992);

\[
D = g_d d_p \sqrt{\frac{8RT}{\pi M}} \exp\left(\frac{-E_A}{RT}\right)
\]

(3.14)

where \(g_d\) is geometrical factor (the probability that the gas molecules jumps in the desired direction) and \(E_A\) is activation energy for diffusion. For the GT model, if pore size becomes much larger than the molecular size, the activation energy approaches zero and the molecule-framework interaction might diminish as in the case of Knudsen diffusion. Table 3.2 shows the kinetic diameters and structures of some permeating species with molecular masses.

<table>
<thead>
<tr>
<th></th>
<th>CO\textsubscript{2}</th>
<th>N\textsubscript{2}</th>
<th>O\textsubscript{2}</th>
<th>CH\textsubscript{4}</th>
<th>H\textsubscript{2}</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter (Å)</td>
<td>3.30</td>
<td>3.64</td>
<td>3.46</td>
<td>3.82</td>
<td>2.92</td>
<td>2.60</td>
</tr>
<tr>
<td>Molecular Weight (g mol\textsuperscript{-1})</td>
<td>44.02</td>
<td>28.02</td>
<td>15.99</td>
<td>16.03</td>
<td>2.02</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Table 3.2. A Comparison of physical properties of selected gases (Source: Moon et al., 2006).

For pores smaller than about 1 nm mass transport takes place by diffusion in an adsorbed layer due to the strong interaction between the molecules and the pore wall. This mechanism is referred to as micropore diffusion (configurational diffusion) and show strong similarities to the solid state diffusion. In this case, pore diameter over the molecular diameter is close to one (Figure 3.2, regions b\textsubscript{1} and a). The molecules are excluded from the micropore, because of the dominant repulsive forces in the potential...
field. Micropore diffusion coefficient, $D_{MP}$, can be described using a jump model (Xiao and Wei, 1992);

$$D_{MP} = g_d v \lambda^2 \exp\left(\frac{-E_{MP}}{RT}\right)$$  \hspace{1cm} (3.15)

in which $v$ is jump frequency (1/s); and $\lambda$ is the distance between adjacent adsorption sites (m) and $E_{MP}$ is activation energy for micropore diffusion.

Xiao and Wei (1992) assumed that the value of activation energy was equal to the difference between the potential in a channel pore and intersection (cage) pore. They calculated the activation energy for non-polar gas species from the zeolites (ZSM-5 and zeolite A) by using Lennard-Jones potential as the gas-zeolite framework interaction. It has been concluded that the transition from GT diffusion to configurational one was dependent on the properties of gas molecules and pore structures. If the pore structure and physical properties of diffusing gas are known, the activation energy and the diffusion coefficient can be evaluated in this model.

de Lange et al., (1995b) considered that the activation energy of permeation through the membranes could be described as the difference between the isosteric heat of adsorption and the activation energy for the intra-crystalline micropore diffusion. In that study, the isosteric heat of adsorption was calculated by using Clausius-Clapeyron equation from some adsorption isotherms under different temperatures. The main assumption for the calculation of the permeation through the supported membranes was equal pore characteristics for the supported and unsupported membranes. They calculated that based on the calculated activation energy, through sol-gel derived silica membranes have smaller pores than the zeolites 4 Å, since the activation energy is lower for larger pores than for small pores (de Lange, 1995b).

Shelekhin et al., (1995) have proposed that the activated permeation behaviours of nitrogen and carbon dioxide for Vycor glass membrane with pore diameter approximately 1.5 nm and tortuosity factor 5.9 can be treated as the summation of the activated diffusion in gas phase and in the adsorbed phase. Therefore, the total gas concentration $C_T$ was determined by the summation of gas phase and the adsorbed phase concentrations. The tortuous diffusion path was created by the interconnected pore necks to the large pores with a smaller diameter in the range 0.5-0.6 nm. The difference in size between these connections and the pores creates an activation barrier for gas
diffusion. They calculated activation energy by considering only fraction of gas molecules in the gas phase via Lennard-Jones potential with an assumption that the perimeter of the pore neck consists of eight oxygen atoms. The size of the interconnected pore opening has been calculated by using dependencies of the activation energy versus kinetic diameter in various zeolites as a set of rulers.

It has also been demonstrated that for gas transport through microporous silica membranes, diffusion through intra and inter-particle pores is possible (Yoshioka et al., 2001). The fact that there are two types of pores in the silica layer may be a result of the sol-gel preparation technique. It has been proposed by Yoshioka et al., (2001) the silica layer might consist of colloidal sol particles with intra-particle pores and somewhat larger inter-particle pores between the sol particles.

Mass transport through inorganic membranes has attracted considerable attention. However, for different silica membranes two different behaviours for the fluxes of gases have been observed. For the first type of silica membranes the permeance decreases significantly with an increase in the size, i.e. the kinetic diameter, of the permeating molecules (de Vos and Verweij, 1998; Lu et al., 1999; Tsai et al., 2000). For the silica membranes treated at 400 °C used by de Vos and Verweij (1998) at 473 K the permeance dropped from about $2\times10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for hydrogen to about $5\times10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for methane. Furthermore, only a weak dependence on the temperature was observed. Between 300 and 473 K a slight increase in the permeance of hydrogen was observed, while for the permeance of carbon dioxide a small decreasing behavior was obtained. The pore size of the silica top layer is smaller than 0.5 nm. The heat of adsorption of carbon dioxide is equal to 24 kJ/mol, and for hydrogen the activation energy for diffusion was found to be equal to 14 kJ/mol. Lu et al. (1999) reported results for the permeance of helium, nitrogen and sulphur hexafluoride. Between 323 and 473 K the permeance of helium was about 5 times higher than the permeance of nitrogen and about 2000 times higher than the permeance of sulphur hexafluoride. For the three gases the permeance was more or less independent of the temperature. These studies (de Vos and Verweij, 1998; Lu et al., 1999; Tsai et al., 2000) included permeation behavior through silica membranes obtained by different synthesis and calcinations procedures. By increasing the calcination temperature from 673 to 873 K the permeance through the membranes of de Vos and Verweij (1998) drops by one order of magnitude. They estimated pore diameter value between the sizes of molecules N$_2$ (3.64 Å) and CH$_4$ (3.8 Å) for membranes
treated at 600 °C and pore size value between 3.8 and 5.5 Å for 400 °C treated membranes based on the gas permeation data. Two different membranes have been prepared, one with pore sizes of about 0.3 to 0.4 nm (Tsai et al., 2000) and one with pores clearly larger than 0.5 nm (Lu et al., 1999). The smaller pore size has a significant influence on the permeance. The ratio between the permeance of helium and nitrogen goes from about 5 to about 300 by decreasing the pore size. For the second type of behaviour, there is only a weak effect of the size of the molecules on the flux. There seems to be only an effect of the kinetic diameter for helium, for all the other gases about the same permeance is observed. Nair et al., (2000) studied the mass transport of a number of gases, including helium, nitrogen and normal- and i-butane, through membranes prepared by different aging times and by using different compositions for the silica sols. At 408 K the permeance of helium is about 1*10^-8 mol/m²sPa and the permeance for the other gases is more than a factor of 100 lower. It is found that membranes have molecular sieving capability to the gases with kinetic diameters above 3 Å and low permeance values (about 10^-10 mol/m²sPa) for the bigger molecules indicate that the membranes are defect-free. According to them the bigger molecules like N₂ may be permeating through the secondary inter-aggregate pores and the high permselectivity values between He and N₂ show that only a negligible portion of the cumulative pore volume belongs to the secondary pores. The excellent properties of sol-gel derived molecular sieving silica membranes in terms of permeation of small molecules with high selectivity as illustrated Table 3.3 making them very attractive for gas separation applications.
Table 3.3. Summary of reported gas permeation through sol-gel derived silica membranes (10⁻⁸ mol/m²sPa) and permselectivities.

<table>
<thead>
<tr>
<th>P_{H₂} (A) (E_{act} – kJ/mol)</th>
<th>P_{He} (B) (E_{act} – kJ/mol)</th>
<th>P_{N₂} (C) (E_{act} – kJ/mol)</th>
<th>P_{CO₂} (D) (E_{act} – kJ/mol)</th>
<th>P_{CH₄} (E) (E_{act} – kJ/mol)</th>
<th>Selectivity</th>
<th>Temp. (°C)</th>
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<tr>
<td>60</td>
<td>23</td>
<td>A/D (2.6)</td>
<td>25</td>
<td>de Lange et al., (1995 a-b-c)</td>
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<td>200</td>
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<tr>
<td></td>
<td>1000</td>
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(cont. on next page)

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4 Tubular type module assembled with 10 pieces of silica membranes with total surface area 7.9x10⁻³m²
5 Surface modification with ethanol solution of TEOS (4:1 molar ratio) has been applied to methacryloxypropyltrimethoxysilane templated silica membrane treated at 600 °C
6 Templated silica membrane treated at 600 °C with a molar sol composition TEOS:Octyltriethoxysilane:EtOH:H₂O = 0.9:0.1:1:9:0.2
Table 3.3 (cont). Summary of reported gas permeation through sol-gel derived silica membranes ($10^{-8}$ mol/m²sPa) and permselectivities.

<table>
<thead>
<tr>
<th>P$_{H_2}$ (A)</th>
<th>P$_{He}$ (B)</th>
<th>P$_{N_2}$ (C)</th>
<th>P$_{CO_2}$ (D)</th>
<th>P$_{CH_4}$ (E)</th>
<th>Selectivity</th>
<th>Temp. (°C)</th>
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<td>(E$_{act}$ –)</td>
<td>(E$_{act}$ –)</td>
<td>(E$_{act}$ –)</td>
<td>(E$_{act}$ –)</td>
<td>(E$_{act}$ –)</td>
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<td>kJ/mol</td>
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<td>9.65</td>
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<td>Lee et al., (2004)$^{10}$</td>
<td></td>
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<td>(1000)</td>
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<td>Kanezashi et al., (2006)$^{11}$</td>
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</tbody>
</table>

$^7$ The microporous silica membranes were prepared on outer surface of hallow fiber ceramic substrates.
$^8$ Heat treatment temperature was 350 °C and molar sol composition TEOS:EtOH:H$_2$O:HCl = 1:20:2:0.01
$^9$ 600 °C 3-layer membrane with molar composition MOTMS (methacryloxypropyltrimethoxysilane):TEOS:EtOH:H$_2$O:HCl = 0.1:0.9:9:1:0.2
$^{10}$ CVD-silica
$^{11}$ Ni-doped silica
CHAPTER 4

CHARACTERIZATION OF CERAMIC MEMBRANES

4.1. Sol Characterization

In the preparation of membranes, the size of sol particles must be controlled carefully in order to be able to deposit layers with high uniformity and suitable thickness. A certain diameter of the sol particles is needed for specific application and should also take into account to prevent penetration of the sol into the large pores of the underlying support. Small Angle X-ray Scattering (SAXS) is widely used technique to gain better understanding of the formation and aggregation mechanisms of polymeric species while the Dynamic Light Scattering (DLS) is used to determine the particle size in nanometer range.

4.1.1. Small Angle X-ray Scattering (SAXS)

SAXS is a well-established scattering technique that operates at small angles in the vicinity of the primary beam and extending to less than 2 degrees for standard wavelengths. The scattering features at these angles correspond to structures ranging from tens to thousands of angstroms. It has proven to be a useful tool to monitor the sol-gel process, especially because of the property of polymeric species in the sol to be fractal objects. SAXS allows estimation of the effective particle size in sol, expressed as the gyration radius \( R_g \), and permits measurement of the fractal dimension \( D_f \). Polymeric systems in contrast to colloidal system grown by a random process are fractal-like objects and can be represented by a mass fractal dimension \( D_f \) that relates mass \( (M) \) and size \( (R_g) \) by \( M \sim R_g^{D_f} \). As the fractal dimension decreases the structure will look sparser, giving essentially a linear configuration when \( D_f = 1 \). In the case of polymeric sols, the fractal dimension of the species can be correlated with their ability to
interpenetrate and form a microporous structure. The tendency of fractal system to interpenetrate, which is inversely related to the mean number of intersections $M_{1,2}$ of two mass fractal objects of size $R$ and mass fractal dimension $D_f$ is defined as:

$$M_{1,2} = R^{(D_f+D_f-3)}$$ \hspace{1cm} (4.1)

When the fractal dimension is higher than 1.5, highly branched polymers are present, the fractal objects become dense, and their ability to interpenetrate decreases (Nair et al., 1997). Therefore, the fractal dimension is crucial parameters in terms of extent of polymer interpenetration which in turn affects the pore structures by changing sol species as a mutually transparent ($D_f<1.5$) or mutually opaque ($D_f>1.5$). Brinker et al. (1995) suggested that ultramicroporous silica membrane could be obtained by employing mutually transparent polymeric sol where condensation reaction is minimized.

In SAXS measurement the scattered intensity ($I$) is determined as a function of the scattering vector $q$[nm$^{-1}$] which is related to the scattering angle $\theta$ as follows;

$$q = \left(\frac{2\pi}{\lambda}\right) \sin(2\theta)$$ \hspace{1cm} (4.2)

where $\lambda$ is the wave length (nm) of radiation used and $2\theta$ is the scattering angle. The dimension of $D_f$ can be drawn from the plot of log($I$) vs log($q$) consisting of two scattering regimes: the Guinier and the Porod regions (Green et al., 2003). The Guinier region occurs at low $q$ ($R_g<<q^{-1}$) and allows the calculation of the particle size through the radius of gyration,

$$I_q = I_o \exp\left(-q^2 \frac{R_g}{3}\right)$$ \hspace{1cm} (4.3)

In Porod region, at high $q$ values, the scattering intensity has a power function of $q$ between the two limiting values of 2.09 nm$^{-1}$ and 0.55 nm$^{-1}$,

$$I_q = q^{-D_f}$$ \hspace{1cm} (4.4)
4.1.2. Dynamic Light Scattering

Dynamic light scattering (DLS) is a well established technique for measuring particle sizes in the $10^{-9}$-$10^{-6}$ m range. In contrast to SAXS, which probes the differences in electron density, DLS detects the differences between the refractive indices of the fluid and the particle. DLS measurements determine the velocity at which particles within a solvent diffuse due to Brownian motion. The Brownian motion is the random movement of particles due to the bombardment by the solvent molecules that surround them. This random motion causes the intensity of light scattered from the particles to form a moving pattern. This is done by monitoring the fluctuations of intensity of the scattered light beam over time. The scattered intensity varies constantly depending on particle size due to phase addition of the moving particles. The parameter calculated by DLS is defined as the translational diffusion coefficient used for the calculation of particle size. The Brownian diffusion velocity is inversely proportional to particle size, and is expressed as hydrodynamic radius $R_H$ according to the Einstein equation:

$$R_H = \frac{kT}{3\pi\eta D}$$  \hspace{1cm} (4.5)

where $k$ is Boltzmann constant, $\eta$ is solvent viscosity and $D$ is translational diffusion coefficient of particles.

4.2. Membrane Characterization

Evaluation of supported membrane microstructure and determination of change in structure upon certain application is still challenge. N$_2$ adsorption/desorption at 77 K as an intrusive method is well adapted to determine the pore structure of bulk materials. Although, a large number of studies describe the some characterization techniques for inorganic membranes, they have some limitations that cause some uncertainty (Burggraaf and Cot, 1996). Difficulties arose from the microporosity, as well as the lack of efficient methodology for the determination of inorganic membrane properties.
The development of standard characterization methods aimed by IUPAC in the project: “Standardisation of methods for the characterisation of inorganic membranes” (International Union of Pure and Applied Chemistry, 2009). The characterization techniques that have been generally employed for the evaluation of structural/thermal/chemical characteristics of inorganic membranes are described in this section.

4.2.1. Pore Structure Characterization

For the inorganic porous membranes, the gas transport rate properties including permeability and the selectivity are mainly determined by the pore structure of the membranes (porosity, pore size/connectivity/shape, surface area) which is consecutively affected by the synthesis conditions. Therefore, better understanding of the membrane microstructure and their effects on gas transport mechanisms has significant importance for the development of new and more complex inorganic membranes. Characterization of membranes in terms of pore structure is essential to decide specific application, controlling synthesis parameters and understanding of transport mechanisms.

Parameters that affect the transport rate are porosity, interconnectivity, pore size, pore size distribution, pore shape, and the particle size and shape are also important indirectly that influence the pore size distribution and the pore shape. According to IUPAC pores can be created by several routes but three of them are the most important in membrane structures. In a first case, pores are an inherent feature of particular crystalline structures, (zeolites and some clay minerals). Such intra-crystalline pores are generally of molecular dimensions, and form highly regular networks. A second class of them is formed by loose packing and subsequent consolidation of small particles as for instance in some inorganic gels and in ceramics. These processes are constitutive, in that the final structure depends mainly on the original arrangement of the primary particles and on their size. A third route is described as subtractive, in that certain elements of an original structure are selectively removed to create pores (Rouquerol et al., 1994). The pores can be classified based on their availability to an external-fluid as shown in Figure 4.1. Closed and dead ends pore do not contribute to the permeation rate except adsorbing gases for the dead end pores. Pore shape may be cylindrical (either open (c) or dead end (f)), ink-bottle shape (b), funnel shaped (d) or slit shaped.
Figure 4.1. Schematic picture of pore types in porous solids (Source: Rouquerol et al., 1994).

Figure 4.2 shows a list of static and dynamic characterization methods and the corresponding characteristic parameters which can be obtained. Each characteristic technique yields experimental parameters which are related to the pore structure of the membrane and these parameters are generally used to define porous properties on the basis of an assumed model pore structure which simply describes the pores as cylindrical, slit or spherical shapes.

Figure 4.2. Methodology for membrane characterization with methods and related parameters (Source: Julbe and Ramsay, 1996).
Static characterization techniques leading to morphology related parameters while the dynamic one leading to permeation and morphology (only active pores) related parameters. Dynamic methods which consist of rejection measurements, liquid displacement and fluid flow measurements (liquid, gas, permoporometry) are based on membrane permeation characteristics and are used to assess membrane performance. In addition, static methods provide details of porous microstructure directly. These include; (1) stereology (microscopic techniques such as SEM, TEM, AFM), (2) Intrusive methods (mercury porosimetry, physisorption of gases, calorimetric methods and NMR analysis), (3) non-intrusive methods (x-rays, ion-beam analysis, wave propagation). It is not possible to distinguish between the active and passive pores by using gas adsorption or mercury porosimetry in the evaluation of pore size and size distribution. However, in many applications, especially in gas separation, only the active pores are important as well as the narrow pore size distribution is essential. The detailed information about these techniques has been reviewed by several authors (Nakao, 1994, Ramsay, 1999).

Because of the different size and shapes of pores in the same material and connections between pores that may vary in size, and shape, pore constrictions, interconnectivity, the related tortuosity which affect the flow resistance as being decreases effective diffusivity is introduced to describe the complexity of the pore structure as a correction factor. For straight perpendicular pores with constant pore diameter, tortuosity is equal to unity while more complex structures the tortuosity is usually higher.

4.2.1.1. Gas Sorption

In most ceramic membranes, pores are voids between packed particles and the pore shapes are usually highly irregular and variable, and they contain pore constrictions. Gas (N₂) adsorption method is one of the most important and extensively used techniques for characterizing the porous structure of inorganic membranes. Nitrogen sorption detects all accessible pores of a membrane, both the interconnected and dead-end pores. In a typical measurement, the volume/weight of the nitrogen sorbed on a solid at different relative pressure and constant temperature is resulted in a sorption isotherm. It is possible to determine the pore size/distribution, surface area and porosity
of meso and microporous materials from the sorption isotherm. It is based on the principle that inside a small pore a gas can condense to a liquid at a relative pressure lower than unity; this introduces capillary condensation theory. At a certain minimum pressure, the smallest pores are filled with liquid nitrogen. As the pressure is increased further, larger pores are filled, and near the saturation pressure, all the pores are filled. The total pore volume is determined by the quantity of gas adsorbed near the saturation pressure. Desorption occurs when the pressure is decreased from the saturation pressure. Many mesoporous systems exhibit distinct adsorption-desorption behaviours, which lead to a characteristic hysteresis loop. The curve shape is linked to different geometrical factors that rule the adsorption and desorption processes. The reason for this hysteresis is that capillary condensation occurs differently in adsorption and desorption. The physisorption isotherms are grouped into the six basic types as shown in Figure 4.3. The reversible Type I isotherm is concave to the p/p$_0$ and given by microporous solids having relatively small external surface (e.g. activated carbons, molecular sieve zeolites and certain porous oxides). The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent. This isotherm represents unrestricted monolayer-multilayer adsorption. The reversible Type III isotherm is convex to the p/p$_0$ axis over its entire range. In such cases, the adsorbate-adsorbent interactions play an important role. Characteristic features of the Type IV isotherm are its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limited uptake over high p/p$_0$. Type V isotherm is uncommon, it is related to Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents. Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non porous surface. The stepwise height represents monolayer capacity for each adsorbed layer and in the simplest case remains constant for two or three adsorbed layers.
A number of several models have been applied for different regions of isotherm to determine the surface area, micro/mesopore size and distributions in addition to pore volumes. In microporous systems, various methods have been developed for the determination of micropore volume and pore size distribution, but the validity of pore sizes is often complicated. MP, Dubinin-Radushkevich, Dubinin-Ashtakhov and Horvath-Kawazoe methods are the evaluated mathematical models for pore size distribution determination.

In principle, a $t$-plot can be used to assess the micropore capacity provided that the standard multilayer thickness curve has been determined on a non-porous reference material with BET equation C constants similar (similar surface structure) to those of the microporous. Monolayer adsorption could occur on the micropore walls in the same manner as on the open surface and on the walls of mesopores. Therefore, the $t$-method did not allow for the special nature of micropore filling and a $t$-plot can provide a means of assessing the micropore volume and the external surface area. The standard $t$-curve is expressed by the empirical de Boer equation assuming the total surface area of a porous solid is directly proportional to the slope of the initial linear section of a $t$-plot. The experimental isotherm is transformed into a $t$-plot by replotting the amount adsorbed against $t$, the standard multilayer thickness on the reference non-porous material at the corresponding $p/p^o$. Thickness $t$, is determined at any point on the isotherm by multiplying the fraction of monolayer capacity ($V_a/V_m$) at that point by the fraction of
the monolayer. If the thickness of nitrogen monolayer $t_m$ is taken to be 3.54 Å, the thickness of any adsorbed layer is,

$$t = 3.54 \left( \frac{V_a}{V_m} \right) \text{ Å}$$

(4.6)

where, $V_a$ and $V_m$ are adsorbed amount and monolayer capacity, respectively. The most serious limitation of the $t$-method is that it is necessarily dependent on the BET evaluation of the monolayer capacity of the reference material, since $t$ is derived from $V_a/V_m$ and this presents a special problem if the C value is relatively low.

In the MP (micropore) method tangents to the $t$-plot were taken to represent the surface areas of different groups of micropores. The pore volume distribution was then determined for a given pore shape (e.g. parallel-sided slits).

The Horvath–Kawazoe (HK) method was developed to determine the effective slit or cylindrical pore diameters of microporous solids (solids with pore diameters smaller than 20 Å). The HK method is based on the general idea that the relative pressure required for the filling of micropores of a given size and shape is directly related to the adsorbent-adsorbate interaction energy. It is assumed that the entropy contribution to the free energy of adsorption is small in comparison with the large change of internal energy, which is itself largely dependent on the depth of the potential energy well (Rouquerol et al., 1999). The method is based on the 10:4 potential functions of Lennard-Jones. Using Lennard-Jones functions and Gibbs free energy of adsorption, Horwath-Kawazoe derived an expression that correlates the effective pore diameter of a micropore to the adsorption isotherm (Webb and Orr, 1997);

$$RT \ln \left( \frac{p}{p^o} \right) = K \left[ \frac{N_A A_d + N_A A_d}{\sigma(l-d)} \right] \left\{ \frac{\sigma^4}{3(l-d)^{\frac{1}{3}}} - \frac{\sigma^{10}}{9\left(l-d\right)^{\frac{2}{3}}} - \frac{\sigma^4}{3\left(d\right)^{\frac{1}{3}}} + \frac{\sigma^{10}}{9\left(d\right)^{\frac{2}{3}}} \right\}$$

(4.7)

where; $RT\ln(p/p^o)$ is the free energy change, $K$ is Avagadro’s number, $N_A$ the number of atoms per unit area of adsorbent, $N_A$ the number of the molecules per unit area of adsorbate, $A_d$ and $A_d$ are constants in Lennard-Jones potential for adsorbent and
adsorbate, $\sigma$ is the distance between a gas atom and the nuclei of the surface at zero interaction energy, $l$ is the distance between nucleus of two layers (slit with) and $d$ is the diameter of the adsorbate molecule. The term of $(N_{\alpha}A_{\alpha} + N_{\beta}A_{\beta})$ is defined as the interaction parameter.

BJH (Barrett, Joyner and Halenda) method uses the Kelvin Equation for calculating the pore size distribution. This method involves an imaginary emptying of condensed adsorptive in the pores in a stepwise manner as relative pressure decreasing. Mesopore size distributions are obtained from BJH fits of the $N_2$ desorption isotherms between $p/p^* = 0.35$ and 0.9. This method is based on Kelvin’s equation, stating that condensation occurs in pores with radius $r_m$ at a relative pressure $p/p^*$, which for cylindrical pores is represented by;

$$\ln \frac{p^*}{p^0} = -\frac{2\gamma V_m \cos \theta}{R T r_m}$$

where; $p^*$ is the critical condensation pressure, $\gamma$ is the liquid surface tension of the liquid-vapor interface, $V_m$ is the molar volume of condensable vapour, $\theta$ is the contact angle between the solid and the condensed phase, $r_m$ the mean radius of the curvature of liquid meniscus.

On the other hand, the interpretation of structural characterization results based on assumptions about pore geometry and complexity of gas/solid interfaces leading to uncertainty. Although assessment of the mesoporosity has been clearly defined, interpreting of adsorption data based on equations is of uncertain validity for micropores and small mesopores because of strong adsorbate-adsorbent and adsorbate-adsorbate interactions (Burggraaf, 1999). In addition, due to the small dimensions of the membrane layers, properties of the membrane layer like porosity and the sorption behaviour are not measured by standard macroscopic techniques, such as volumetric and gravimetric sorption measurements. Measuring the properties of unsupported membranes can avoid that problem. However, the microstructure of the supported and non-supported membrane that is used for the gas adsorption measurement to determine the pore size distribution may differ from each other. Because of the relatively thick layer of the non-supported one, longer drying time causes further condensation of the polymeric sol which leads to probably more open structure (de Lange et al., 1995b).
porosity of the membranes depends on the relative rates of condensation and evaporation.

4.2.1.2. Permporometry

Permporometry is a method that enables to determine the size distribution of the active pores of the supported membranes with pore diameters ranging from about 1.5 nm to 0.1 μm. It is based on the controlled blocking of the pores by capillary condensation of condensable vapour and simultaneous measurement of the non-condensable gas permeability through the remaining open pores as a function of the vapour pressure of condensable gas in the feed stream. It is based on Kelvin equation (Eqn. 4.8) in which vapour condenses at a vapour pressure lower than the saturated vapour pressure in a smaller pore (Cao et al., 1992). The common condensable gases are water, cyclohexane, carbon tetrachloride and alcohols. The applicability of Kelvin equation is the limitation of this method to evaluate the pore size smaller than 2 nm that the range of gas separation porous membranes. The physical properties needed to calculate the Kelvin diameter are the contact angle, $\theta$ and the surface tension, $\gamma$. The common assumption of permporometry characterization is complete wetting, $\theta=0$, irrespective of the types of vapors and the surface tension used for calculation is based on those measured in a bulk solution. The relationship between the real pore width ($d_p$) and the Kelvin radius ($r_K$) is given as:

$$d_p = 2(r_K + t)$$  \hspace{1cm} (4.9)

where $t$ is the thickness of the “t-layer” formed on the inner surface of the pores, which is usually 0.3-0.5 nm.

In the study of Tsuru et al., (2001b), silica-zirconia composite membranes with different pore diameter especially in nano-order range have been characterized by permporometry as called nanopermporometry. They claimed that the properties of the vapours (size and polarity) play an extremely important role in measuring the pore size distribution of silica-based membranes by nanopermporometry. The water vapour can be considered as an appropriate vapour due to the small size as compared to alcohols. Since, before the capillary condensation, adsorption of vapours on the pore wall causes
the increase in film thickness and pore size needs to be correlated with this thickness. However, in the case of water vapour, the thickness of adsorbed layer is very small due to the smallest molecular size. Although, amount of adsorption of non-polar and hydrophobic molecules like hexane and carbon tetrachloride is small, pore plugging is inevitable because of the high molecular size of these molecules.

Wormeester et al., (2004) had studied CO₂ sorption of supported thin microporous silica layer by spectroscopic ellipsometry as a new technique for characterizing membrane layers. Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. In this technique relevant data can be obtained by measuring only tan(ψ)¹² as a function of wavelength and using only this ellipsometric angle in a fit of an optical model of the sample. The angle is connected to the refractive indices and thickness of the membrane layers. The refractive index of each layer mainly depend on the wavelength of the light used, the optical properties of material the layer consists of, their porosity and the amount of gas adsorbed by the material. They have found that the thickness and porosity of the amorphous silica layer are 73 nm and 15-25%, respectively. On the other hand, in the calculation of porosity, the use of the quartz dielectric function was crude approximation due to the –OH groups in the sol-gel derived silica layer. Values obtained for the porosity of unsupported silica membranes by de Lange et al., (1995b) from N₂ adsorption measurements were found in the 35-40% range. Denser structure of the thin silica layer was in agreement with the Brinker and Scherer (1990) due to rapid drying of the film in which only little aging can occur. The heat of adsorption value was reported as 27 kJ/mol which, slightly higher than that found by de Vos and Verweij (1998) and de Lange et al. (1995b), who studied the CO₂ sorption of unsupported silica membranes that were prepared in a similar manner to this study. The higher value of heat of adsorption has been attributed to the pores in the thin silica layer are smaller than those in the unsupported silica membranes. In microporous materials, overlapping of neighboring pore walls potential can cause to enhanced sorption, depending on the ratio of the size of the pore to the size of the adsorbed molecules.

The other new technique for the characterization of the porosity of thin films has been proposed by Klotz et al., (2006). The adsorption-desorption of vapour were coupled to the measurement of the thickness and electron density of films by X-ray

¹² ψ: real angles of which the tangents is the ratio of the magnitudes of the total reflection coefficients.
reflectometry. In that study, the variation of electron density by vapor adsorption and capillary condensation have enabled to determine the amount of adsorbed vapor as a function of the solvent relative pressure and therefore the adsorption-desorption isotherms have been obtained. Data have been analyzed by converting the electron density to mass density and modeled with the assumptions of BET theory. One example that characterized in the study is sol-gel derived silica membrane which has been prepared by dip coating from a silica sol containing 15 nm particles. They reported that water condensation occurs in two different pore diameters which were centered at 4.5 nm and 15 nm and calculated surface area is 52 m$^2$/g.

### 4.2.2. Chemical /Thermal and Microstructural Characterization

Vibrational spectroscopy or as commonly known infra red spectroscopy (IR) gives information about the chemical composition of the materials, and in many cases can give information about the chain structure, degree of branching, stereoregularity, geometric isomerism, conformation, crystallinity and type of group present in the material. In IR spectroscopy IR radiation is passed through to a sample and certain frequencies are absorbed by the molecule that causes to vibrational changes in the molecule. There may be many IR bonds observed. Since each molecule has individual sets of energy levels, the absorption spectrum is characteristic of the functional groups that are in the molecule. IR spectroscopy could be useful for obtaining valuable information on the quality and relative quantity of the inorganic phases of materials.

Thermal stability of ceramic membrane is investigated by Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA). The decrease in the weight of a sample is followed as the temperature is slowly increased up to specific temperature in TGA. The information can be valuable in the determination of the optimum heat treatment temperature.

Scanning Electron Microscopy (SEM), Transition Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) are generally used to describe the surface and cross-sectional morphology of membranes providing information about particle size and shape, surface roughness, layer continuity and thickness of membranes. SEM is based on the principle that an image is formed when the electrons it emits interact with the atoms of the specimen. Interpretation of results from SEM is also subjective and
difficult to some extent especially for microporous materials. TEM provides higher resolution micrograph due to the higher accelerating voltage then SEM. Therefore, it can be used to characterize membrane layers with pores in the ultrafiltration and the upper end of gas separation range. The main common drawback of scanning and transition electron microscope is that sample preparation is required, which can influence the pore structure. AFM offers subnanometer or atomic resolution with little sample preparation requirement. The basic principle involved is to utilize a cantilever with a spring constant weaker than the equivalent spring between atoms.
5.1. Sol Preparation

Alumina and silica sols were prepared by controlled hydrolysis and condensation reactions of Aluminum-isopropoxide/Aluminum-trisecbutoxide and Tetraethyl-orthosilicate (TEOS), respectively. The specifications of chemicals utilized for preparation of sols and membranes are given in Table 5.1.

Table 5.1. Specifications of materials used for sol and membrane preparation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum-isopropoxide</td>
<td>$(\text{CH}_3\text{CHO})_3\text{Al}$ 98%, $M=204.2$, $d=1.035$ g/cm$^3$ (Aldrich)</td>
</tr>
<tr>
<td>Aluminum-trisecbutoxide</td>
<td>$\text{Al}[\text{OCH}\text{(CH}_3\text{C}_2\text{H}_3)]_3$ 97%, $M=246.33$, $d=0.96$ g/cm$^3$ (Merck)</td>
</tr>
<tr>
<td>TEOS Si(OC$_2$H$_5$)$_4$</td>
<td>98%, $M=208.3$, $d=0.934$ g/cm$^3$ (Aldrich)</td>
</tr>
<tr>
<td>Ethylalcohol C$_2$H$_5$OH</td>
<td>99.8%, $M=46.07$, $d=0.79$ g/cm$^3$ (Riedel)</td>
</tr>
<tr>
<td>1-Butanol C$_4$H$_9$OH</td>
<td>$M=74.12$ (Merck)</td>
</tr>
<tr>
<td>Ethylene-glycol</td>
<td>$\text{HOCH}_2\text{CH}_2\text{OH}$ 99.5%, $M=62.07$, $d=1.11$ g/cm$^3$ (Riedel)</td>
</tr>
<tr>
<td>Nitric Acid HNO$_3$</td>
<td>65 %, $M=63.01$, $d=1.41$ g/cm$^3$ (Merck)</td>
</tr>
<tr>
<td>Ammonium-hydroxide</td>
<td>$\text{NH}_3\text{OH}$ 28-30 % $\text{NH}_3$, $M=35.05$, $d=0.9$ g/cm$^3$ (Aldrich)</td>
</tr>
<tr>
<td>Acetyl-acetone C$_5$H$_8$O$_2$</td>
<td>99.5%, $M=100.12$, $d=0.972$ g/cm$^3$ (Fluka)</td>
</tr>
<tr>
<td>Ethyl-acetoacetate C$<em>5$H$</em>{10}$O$_3$</td>
<td>99 %, $M=130.14$, $d=1.028$ g/cm$^3$ (Fluka)</td>
</tr>
<tr>
<td>Alumina Powder $\alpha$-Al$_2$O$_3$</td>
<td>99.99%, BET = 12.3 m$^2$/g- Sumitomo (AKP-50)</td>
</tr>
<tr>
<td>Zirconia Powder</td>
<td>TOSOH TZ-3Y, BET = 16 m$^2$/g.</td>
</tr>
</tbody>
</table>
5.1.1. Monodisperse Sphere Preparation

Monodisperse silica sphere sols with sizes in the 5-500 nm range were prepared by Stober process by changing the sol parameters including, (1) catalyst to alkoxide molar ratio, (2) water to alkoxide molar ratio, (3) reaction temperature, (4) aging time/temperature and were used to prepare membranes with controlled pore networks.

Tetraethyl-orthosilicate, in ethyl alcohol (0.28 M) was hydrolyzed by the addition of an NH₄OH-ethylalcohol solution with a molar TEOS:NH₃:H₂O:EtOH ratio of 1:4.3:12.18:51.96 for the precipitation of 310 nm spheres as described by the method of Stober et al., (1968). Synthesis of monodisperse silica spheres was completed by stirring overnight at room temperature in a glove box provided dry N₂ atmosphere to prevent pre-hydrolysis of TEOS. The NH₄OH ratio was changed from 2.6 M to 0.02 M to observe the effects of catalyst amount on size of the spheres. The powder was recovered by centrifuging the precipitate solution and drying at 373 K. Before centrifuging, a sample was taken and diluted about 10 times for size analysis (ZetaSizer 3000HS). The nature of ordering from fracture surface of compact and the size of the spheres were examined by using SEM (Philips XL 30S, SFEG).

5.1.2. Acid Catalysed Silica Sol Preparation

Polymeric silica sols were prepared by acid catalysed hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol. Predetermined water and acid were added drop-wise to TEOS/ethanol mixture with constant stirring. During the addition of the acid-water mixture, the reaction mixture was placed in an ice bath to avoid partial hydrolysis as suggested by de Vos and Verweij (1998). After the addition was completed, the reaction mixture was heated to 60 °C for 3h under constant stirring in glove box. The standard silica sol molar ratios TEOS:HNO₃:H₂O:EtOH were 1:0.085:6.4:3.8. The ethylene glycol (EG) derived polymeric silica sols were prepared by the same procedure as the standard silica sol with molar ratios TEOS:HNO₃:H₂O:EG of 1:0.085:6.4:3.8 at 40 °C for 3h. The synthesis temperature and HNO₃ to TEOS molar ratio were varied in order to investigate the change in membrane pore structure. Codes of sols and synthesis parameters are given in Table 5.2.
Table 5.2. Synthesis parameters of polymeric silica sols.

<table>
<thead>
<tr>
<th>Codes</th>
<th>Temperature (°C)</th>
<th>[HNO₃]/[TEOS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-std</td>
<td>60</td>
<td>0.085</td>
</tr>
<tr>
<td>SiEg-A</td>
<td>40</td>
<td>0.05</td>
</tr>
<tr>
<td>SiEg-B</td>
<td>40</td>
<td>0.085</td>
</tr>
<tr>
<td>SiEg-C</td>
<td>50</td>
<td>0.085</td>
</tr>
<tr>
<td>SiEg-D</td>
<td>60</td>
<td>0.085</td>
</tr>
</tbody>
</table>

5.1.3. Base Catalysed Silica Sol Preparation

Colloidal silica sols, in contrast to polymeric counterpart, were synthesised in excess of water having final molar TEOS:NH₃:H₂O:EtOH ratios of 1:0.086:53.6:40 at 50 °C. The use of NH₃ as the base catalyst promoting the formation of colloids and its concentration was varied in order to control the particle size and pore size of the membranes. The pH of the prepared sol was varied in the 9.5 to 2 range to observe the change in packing behaviour of sol particles and the resulting pore structure.

5.1.4. Alumina Sol Preparation

Colloidal boehmite sol was prepared by the hydrolysis of aluminium isopropoxide at a temperature of 90 °C for 3 hours. The water to Al³⁺ molar ratio was 100. The hydroxide precipitate was peptised with appropriate amounts of nitric acid ([HNO₃/Al³⁺]=0.25) to form a stable colloidal suspension and was kept at about 90 °C under vigorous stirring as described by Yoldas (1975). Particle size of sols was controlled by employing HNO₃ to Al³⁺ molar ratio in the range of 0.1-0.25. In addition, polymeric alumina sol in alcoholic medium in which water content smaller than the theoretical ratio for complete hydrolysis and condensation reactions were prepared by controlling the rate of hydrolysis reactions. Predetermined amount of acetyl-acetone (AA) and ethyl-acetoacetate (EAA) as chelating agents were used to slow down the hydrolysis of aluminium-alkoxide in alcoholic medium in order to get stable alumina sols. In polymeric route, Al-trisec butoxide (AISB) was used and sol had final molar
ratios as $\text{AlSB}:\text{HNO}_3:\text{AA}:\text{H}_2\text{O}:1$-Butanol;$1.0:0.35:0.2:1.0:18.0$. The effects of the utilized catalyst amount, solvent type, chelating agent type and concentration, and the hydrolysis ratio (mole ratio of $\text{H}_2\text{O}$ to $\text{Al}^{3+}$) on sol characteristics were evaluated. The compositions and the codes of the polymeric alumina sols are given in Table 5.3.

### Table 5.3. Synthesis parameters employed for polymeric alumina sols.

<table>
<thead>
<tr>
<th>Codes</th>
<th>AA/$\text{Al}^{3+}$</th>
<th>EAA/$\text{Al}^{3+}$</th>
<th>$\text{H}^+$/Al$^{3+}$</th>
<th>$\text{H}_2\text{O}$/Al$^{3+}$</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>p01</td>
<td>0.4</td>
<td>0.15</td>
<td>1</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p02</td>
<td>0.4</td>
<td>0.35</td>
<td>1</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p03</td>
<td>0.3</td>
<td>0.35</td>
<td>1</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p04</td>
<td>0.2</td>
<td>0.35</td>
<td>1</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p1</td>
<td>0.3</td>
<td>1.2</td>
<td>1.6</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p2</td>
<td>0.2</td>
<td>1.2</td>
<td>1.6</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p3</td>
<td>0.2</td>
<td>1.5</td>
<td>2</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p4</td>
<td>0.1</td>
<td>1.5</td>
<td>2</td>
<td>Clear gel</td>
<td></td>
</tr>
<tr>
<td>p5$^{13}$</td>
<td>0.3</td>
<td>1.5</td>
<td>2</td>
<td>Clear gel</td>
<td></td>
</tr>
<tr>
<td>p6$^{14}$</td>
<td>0.2</td>
<td>1.5</td>
<td>2</td>
<td>Clear gel</td>
<td></td>
</tr>
<tr>
<td>p7</td>
<td>0.2</td>
<td>1.5</td>
<td>2</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p8</td>
<td>0.15</td>
<td>1.5</td>
<td>2</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p9</td>
<td>0.1</td>
<td>1</td>
<td>2</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p10</td>
<td>0.1</td>
<td>0.5</td>
<td>2</td>
<td>Clear gel</td>
<td></td>
</tr>
<tr>
<td>p11</td>
<td>0.15</td>
<td>0.3</td>
<td>2</td>
<td>Clear gel</td>
<td></td>
</tr>
<tr>
<td>p12</td>
<td>0.3</td>
<td>0.3</td>
<td>1</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p13</td>
<td>0.3</td>
<td>0.5</td>
<td>1</td>
<td>Stable sol</td>
<td></td>
</tr>
<tr>
<td>p14</td>
<td>0.3</td>
<td>0.5</td>
<td>1.5</td>
<td>Stable sol</td>
<td></td>
</tr>
</tbody>
</table>

The controlled hydrolysis of AlSB in butanol led to the formation of clear gel or stable sol depending on $\text{H}^+$/Al$^{3+}$, hydrolysis ratio as well as the chelating agents (EAA or AA) contents. Figure 5.1 shows the pseudo-phase diagram of EAA derived polymeric alumina sol indicating the influence of sol-gel parameters on sol stability.

---

$^{13}$ Al-isopropoxide and isopropyl alcohol were used

$^{14}$ Isopropyl alcohol was used
Figure 5.1. The influence of sol-gel parameters on polymeric alumina sol stability.

Although the use of particulate boehmite sol for the preparation of mesoporous alumina membranes is well-documented, almost little is known about the structure of polymeric sol as well as the preparation of polymeric alumina membrane. Consequently, polymeric alumina sol can be utilised for membrane formation and the gas permeation properties as well as the pore structures would also be compared with alumina membranes prepared by the colloidal sol-gel route.

The stable polymeric alumina sol (p9) was also mixed with polymeric silica sol (Si-Std) in Al₂O₃:SiO₂ ratio of 3:2 (mullite composition) in order to investigate the mullite crystallization upon heat treatment. Due to its high thermal stability, the development of mullite membrane having microporous network might has particular importance.

5.2. Membrane Formation

Thin membrane layers with precisely controlled uniform structures were designed by packing of spheres having different sizes on porous zirconia and α-alumina support surfaces with a γ-Al₂O₃ intermediate layer. The influence of pH of the sol, sol concentration, dipping time, withdrawal speed and heat treatment temperature on membrane structure and permeation properties were investigated. Additionally, monodisperse silica spheres in different diameters with appropriate surface properties were added to polymeric silica sol in order to improve the consolidation conditions of membranes in terms of cracking occurrence and thermal stability. The volume fraction of spheres was varied from 5% to 74% for 5 nm, 90 nm, 140 nm, 220 nm and 310 nm
spheres. The membranes were coded according to volume ratio and sphere size as sp(vol%)-Dnm shown in Figure 5.2.

![Particulate sols](image)

**Figure 5.2.** Preparation of polymeric/particulate hybrid sols.

Mesoporous alumina intermediate layers were deposited by dip coating (Nima Technology) onto slip cast zirconia and α-alumina supports (disc-shaped, diameter 40 mm and 2 mm in thickness). In order to control the membrane thickness dipping time and withdrawal speed were varied from 5 s to 20 s and 50 mm/min to 200 mm/min, respectively. All alumina membranes were dried for 3 h at 40 °C at a relative humidity of 60%, and subsequently heat treated at 500 °C with heating and cooling rate of 2 °C/min. The coating, drying and heat treatment steps were repeated in order to repair any defects on the first membrane layer. The multilayer γ-alumina with graded structures was obtained by four times dipping-drying-heat treatment steps using the diluted (0.15 M) dipping solution having different particle sizes. The coating, drying and heat treatment steps were repeated in order to repair any defects on the first membrane layer. Polymeric alumina membranes have been prepared by dip coating of mesoporous alumina layer into polymeric alumina sols (p9 and p14) with 100 mm/min withdrawal rate for 5 s.

Particulate silica top layers were applied on mesoporous γ-alumina layer by dip coating technique with withdrawing speed 100 mm/min and dipping time 5 s. The influence of sol concentration, sol particle size and sol pH on membrane performance were investigated. Drying was applied at 40 °C at a relative humidity of 60% for 3 h and heat treatment was applied in the 50-400 °C range for 3 hr with heating and cooling rate of 2 °C/min. Control of pore network has been obtained by adding monodisperse silica spheres into the polymeric sol at the sol stage. The volume fraction of spheres was changed from 5% to 74%. Before incorporation of spheres into the polymeric silica sol,
the spheres were dispersed in an appropriate solvent either ethanol or ethylene glycol according to utilized solvent in polymeric sol. Both dip coating and spin coating were performed in order to form silica membrane layer having spheres. Spinning rate and time were varied from 1000 to 3500 rpm, and 30 to 60 s, respectively while the time of dipping changed in 5 to 10s range at constant withdrawal rate of 200 mm/min (SCS G3P-8 Spin Coat, Cooksan Electronics Equipment). Drops (1 mL) of sol containing different concentrations of solvents and silica particles were spread onto gamma layer on membrane support. The drop was allowed to uniformly cover the substrate for 30 s at 200 rpm before the spin-coating process started.

Unsupported membranes were prepared for characterization experiments by drying and subsequent heat treatment of sol in petri dish under the same conditions as used to prepare supported membranes. The unsupported membranes were also consolidated by uniaxial pressing under a pressure of 30 MPa for dilatometer analysis.

5.3. Gas Permeation

Gas permeation analysis of pure gases including N2, O2 and CO2 was conducted on pressure controlled dead-end mode membrane test system to;
(1) control the quality of membrane layer in terms of the formation of defects and pinholes before the heat treatments,
(2) determine the pure gas permeation properties and relate these to the investigation of the separation properties of the membranes.

Prior to the permeance measurements the membranes were dried for several hours at 100 °C to remove adsorbed water from the pores. The disk shaped membranes were placed in permeance cell with the top layer at the feed side. The permeate side of the membrane was maintained at atmospheric pressure while four different pressures (2-3.5 atm) were applied on the feed side. The temperature of permeation cell was varied from 25 °C to 120 °C, in order to determine the apparent activation energies of permeance of gases through the membrane. A schematic representation of the permeance set-up is given in Figure 5.3.
In the dead-end mode, the feeding pressure $p_H$ is constant at all time while the pressure in the second expansion chamber $p_L$ changes from an initial condition close to zero pressure to a final condition. Pressures from both feed and permeate transducers were recorded to calculate the pure gas permeances. The permeance of gases ($P/l$) may be defined as an activated transport normalised pressure flux (mol m$^{-2}$s$^{-1}$Pa$^{-1}$) as follows (da Costa et al., 2002):

$$\frac{P}{l} = \frac{D_o K_o}{l} \exp\left(\frac{E_m - Q_{st}}{RT}\right)$$  \hspace{1cm} (5.1)$$

$$\ln\left(\frac{p_H - p_o}{p_H - p(t)}\right) = \frac{P}{l} A R T \frac{1}{V} t$$  \hspace{1cm} (5.2)$$

where $p_o$ is the initial permeate pressure and generally is equal to zero, $l$ is the membrane thickness, $p_H$ refers to the high or feed pressure in the retentate side while $p(t)$ is permeate side pressure at time $t$. $D_o$ and $K_o$ are temperature independent proportionality constant for diffusivity ($D$) and Henry’s constant ($K$) equations, respectively, $E_m$ is the mobility energy or the activation energy for diffusion (J/mol), $Q_{st}$ is the isosteric heat of adsorption (J/mol), $R$ is the gas constant (J/molK) and $T$ is the absolute temperature (K). Using equation 5.2, the slope of the natural logarithm of the pressure versus time plots yield the normalised pressure flux or permeance ($P/l$) as an
effective membrane area \((A=12.5 \text{ cm}^2)\), permeate volume \((V=80 \text{ cm}^3)\), \(R\), and \(T\) are known constants.

### 5.4. Membrane Characterization

Dynamic light scattering (DLS) was used to determine the particle size distribution in the sol and the surface charges of spheres were also analyzed by ZetaSizer 3000 HS, Malvern. \(^{27}\text{Al MAS NMR was employed with a 7-mm MAS (Magic angle spinning) probe to determine the species distribution of polymeric alumina sol (Bruker Superconducting FT.NMR Spectrometer, Avance 300MHz WB). The spinning rate of 5000 Hz was applied. The surface area, pore volume and the pore size distribution of unsupported membranes were obtained from N\(_2\) sorption isotherm (Micromeritics, ASAP 2010). The micropore volume and size were determined under the assumption of Horvath-Kawazoe method while Barreth-Joyner-Hallender method was applied for the calculation of mesopore size and volume. The pore size and pore size distribution of \(\alpha\)-Al\(_2\)O\(_3\) support was determined by using mercury intrusion data (Quantachrome Corporation, Poremaster 60). Microstructural characterization of supported membranes was performed by scanning electron microscopy (Philips XL 30S, SFEG) and atomic force microscopy (AFM, Digital Instruments-MMSPM, Nanoscope IV). FTIR spectroscopy (FTIR-8400S, Schimadzu Co.) was carried out to determine the molecular functional groups while X-ray diffraction (Philips X’pert Pro) with CuK\(_\alpha\) was employed for phase structure characterization of unsupported polymeric alumina and mullite membranes within the \(2\theta\) range of 5-80°. TGA (TGA-51/51H, Shimadzu) was used to perform the thermal behaviour analysis in which the samples were heated at a rate of 10 °C per minute to 1000 °C. The densification behaviour of alumina and silica unsupported membranes was investigated by dilatometer measurement (Linseis, L76/150B) with a heating rate of 5 °C/min up to 1300 °C.
CHAPTER 6

RESULTS AND DISCUSSION

6.1. Silica Sphere Preparation

The size of the silica spheres was controlled by changing the NH₃ to alkoxide molar ratio in the range of 4.3 to 1.5 at constant water to alkoxide molar ratio of 14. The reactions were conducted at total TEOS molarities of 0.28. Decreasing the ratio of [NH₃]/[TEOS] causes the decrease in sphere diameter as shown in Figure 6.1. Although spherical particles with narrow particle size distributions were obtained over the range of catalyst concentration utilized in preparation, monodispersity was not completely achieved and bimodal size distribution was obtained for the precipitation carried out with the smallest [NH₃]/[TEOS] ratio (Figure 6.1.d).

Figure 6.1. SEM micrographs of monodispersed silica spheres synthesized at NH₃ to alkoxide molar ratios (a) 4.3, (b) 3.6, (c) 2.65 and (d) 1.5.
The effects of catalyst amount on sphere size is also observed in Figure 6.2 which shows very sharp particle size distributions for each molar ratio of NH$_3$. The size of spheres was found to be greatly influenced by NH$_3$ concentration. It is reported that increasing the initial NH$_3$ molar ratio increases the sphere size (Bogush et al., 1988; Lee et al., 1997). The diameter of monodispersed silica spheres is mainly affected by the relative contribution of nucleation and growth processes. Hydrolysis and condensation reactions provide precursor species and the necessary supersaturation for the formation of particles. The increase in ammonia concentration leads to an increase in both hydrolysis and condensation reactions. Intermediate concentration will be increased rapidly due to high hydrolysis rate while the consumption rate also fast through the condensation reaction after reaching the supersaturation and this might shorten the nucleation period that causes the decrease in the total number of nuclei formed and the final sphere size will be relatively larger. In the concentration range studied, this behaviour is consistent with the aggregation model in which the number of particles completes to increase before nucleation is completely over due to the high aggregation rate inducing the larger sphere size (Lee et al., 1997).

Figure 6.2. Particle size distributions of spheres: 260 nm-[NH$_3$/[TEOS]= 4.3, 220 nm [NH$_3$/[TEOS]= 3.6, 110 nm-[NH$_3$/[TEOS]= 2.65.

As the water concentrations have been increased to water to alkoxide molar ratio (hydrolysis ratio) of 21, the sphere size was not significantly affected by decreasing in catalyst amount as compared to low water concentration. The decrease in sphere size with ammonia concentration is shown in Figure 6.3. On the other hand, when the water concentration is high the maximum sphere size without deterioration of monodispersity could be obtained that might be a competition between the nucleation and growth rate in
agreement with the model of Lee et al., (1997). Sphere size also has been controlled by decreasing the total molar concentration of TEOS leading to decrease in size as revealed from SEM micrograph shown in Figure 6.3.d. Although the hydrolysis reaction is expected to be function of both OH\(^{-}\) and TEOS concentration, at high concentration of monomer favour the formation of precipitate that retards both hydrolysis and condensation reactions causing the decrease in primary particle size (Aelion et al., 1950; Lindberg et al., 1997). Since the small particles are less stable, aggregation between small particles causes the increase in particle size.

Figure 6.3. Effect of molar compositions on sphere sizes at constant hydrolysis ratio of 21 and \([\text{NH}_3]/[\text{TEOS}]: (a) 4.3, (b) 3.6, (c) 2.5 \text{ and } (d) 4.3; [\text{TEOS}]=0.14\text{M.}\)

The kinetic evolution of particle size as a function of time for 260 nm spheres is shown in Figure 6.4 indicating that almost constant sphere size was obtained within two hours and further progress of reaction to 24 hours seemed to be ineffective for the growth of particles. The mean particle diameter of 160 nm was detected after 10 min of reaction in an early stage of synthesis. The substantial decrease in growth rate after two hours might be due to the reduced primary particles suggesting the hydrolysis reaction controlled nucleation and the growth model with aggregation of primary particles (Lee et al., 1997; Pontoni et al., 2002).
Figure 6.4. Time dependency of growth process for 260 nm spheres (Inset: early stage growth).

The inset in Figure 6.4 shows a power law dependency of initial stage growth indicating that the diffusion limited growth. Indeed, for the reaction limited growth, linear dependency of time would be observed since power law can be applied at the end of the growth during Ostwald ripening (Nozawa et al., 2005). Figure 6.5 also shows the time dependence of sphere diameter for 520 nm spheres. The inset of the figures indicates that growth regime corresponds to $t^{1/2}$ behaviour approaching the diffusive type of growth. Depending on the degree of supersaturation, a power law of either 1/2 or 1/3 would be expected during the early stage of nucleation. Diffusive type of growth has also been reported by Oskam et al., (2002) for the ZnO and TiO$_2$ nanoparticles coarsening.

Figure 6.5. Time dependency of growth process for 520 nm spheres (Inset: early stage growth).
Figure 6.6. Evolution of growth of 520 nm in size spheres with time (a) Particle size distributions (b) SEM micrograph (20000X) at t= 370 min.

Figure 6.6 shows the particle size distributions of sol in the course of growth process with time of particles with time and SEM micrograph of spheres corresponding end of the process. The sharp particle size distributions during the progress of growth might provide important information about the mechanisms and indicate the continuous nucleation might nevertheless been achieved inconsistent to monomer addition model for this conditions. As stated by LaMer model, when all nuclei are created during the same short nucleation period, silica spheres with narrow and even monodispersed size distribution could be obtained as shown in Figure 6.7.a for 310 nm spheres. The mean sphere size was estimated from the SEM micrograph as 310 nm with ±8 nm deviation from the mean value and this result was also verified by the very sharp peak located at abut 300 nm given in Figure 6.7.b.
Figure 6.7. Monodisperse 310 nm in size silica spheres (a) particle size distribution, (b) SEM micrograph (20000X).

SEM micrographs of the fracture surface of a 310 nm centrifuged ordered sphere compact is given in Figure 6.8 which shows that order is long range and spheres are close packed in a hexagonal arrangement with some local defects which may have been produced during sample preparation for the SEM analysis. Ordered spheres in dried states reflected brilliant colours due to Bragg diffractions of visible light. This is also clear evidence of long range ordering of spheres as shown in SEM micrographs. The range of colours depends on the size of the spheres that determines the lattice parameter and the refraction at the surface. It is well known that in any opal displaying colours, the spheres are remarkably uniform in size and they may, therefore pack regularly and regions over which the colour is the same have the same orientation of the lattice voids. Light scattering from voids due to irregular packing results in homogeneously milky colour for the opal (Sanders, 1964). The ordered structure develops when the repulsive barrier is sufficient to allow the particles to arrange the dense packing whereas disordered structures result from high attraction potential in the sol. Therefore, the structure depends on the size distribution of particles as well as the strength of the attractive forces between them. Green bodies prepared by sedimentation from mixed well-dispersed stable sols having different sizes also shown in Figure 6.8.e-f. Small spheres readily fill the channels between the interstices and some interstitial regions have hexagonal ordered small spheres as illustrated Figure 6.8.f. These locally
disordered regions might be attributed to polydispersity in size distributions as well as the difference in sedimentation rates of different sizes. Therefore, ordering for binary system depends on also the volume fractions of two sizes and the diameter ratios of the small to large spheres (Wang and Möhwald, 2004).

Figure 6.8. SEM micrographs of top and fracture surfaces of dried compact of spheres.

Figure 6.9 shows the change in zeta potential of 310 nm and 100 nm in diameter spheres with pH. The change in particle size seems to be ineffective on zeta potential and isoelectric point (IEP) was determined as about pH of 3.4. The effect of basic medium is reflected in the high zeta potential values where the surface charge is high enough for the sol to remain stable, and may cause a long range ordering of spheres due to the stability of sol. Sacks and Tseng (1984b) reported that the zeta potential values for 500 nm silica spheres vary in 5-(-70) range over the pH range ~3-10. As observed
in Figure 6.9, higher absolute zeta potential values at pH 10 indicated that better dispersion due to the repulsive electrostatic forces between particles.

![Graph showing the relationship between zeta potential and pH](image)

Figure 6.9. The relationship between zeta potential and pH ($\times$, $\triangle$).

### 6.1.1. Thermal/Densification Behaviour of Silica Spheres

Figure 6.10 shows the percent weight losses and shrinkage curve for 310 nm spheres with increasing temperature. The total weight loss of spheres is about 10% while the total dimensional shrinkage is 28% upon heat treatment to 1300 °C. Up to about 150 °C, considerable weight loss is observed that can be attributed to the evaporation of water and ethanol. Between 150-400 °C mostly removal of organics and further polymerization of the silica network take place. Above 400 °C small weight loss is related to the removal of surface OH groups. As compared to acid catalysed systems consisting of linear, slightly cross linked polymeric species, base catalysed reactions lead to granular texture with insignificant amount of chemically bound alkoxy group which resulted in less weight loss. Brinker and Scherer (1990) identified three characteristic temperature ranges for multicomponent borosilicate gel. Range I (25-150 °C), weight loss with negligible shrinkage, range II (150-525 °C), considerable weight loss and shrinkage, and range III (525-700 °C) large shrinkage with small weight loss. These regions are also significant for 310 nm silica spheres with shift in ranges to

\[\Delta\] zeta potential in ethanol
higher temperatures indicating the stability of microstructure as shown in Figure 6.10 due to the structural differences in both systems. In region I where weight losses occurred from desorption of physically bound water and alcohol, the predominant shrinkage resulted from increased capillary stress caused by solvent removal. In region II, weight loss occurred from loss of water produced by polycondensation and from the oxidation of organic residues. Shrinkage in this range resulted from skeletal densification which occur by two mechanisms: by polycondensation reactions with formation of additional $\equiv\text{Si-O-Si}\equiv$ linkages and loss of water, and by structural relaxation which occurs by atomic movements in the network without expulsion of water. Finally, in range III, rapid shrinkage occurs by a viscous sintering in which tiny pores collapse, although hydroxyl condensation and structural relaxation also contribute to the observed shrinkage (James, 1988).

In particulate structure, OH exists primarily on the surface of silica particles rather than internal hydroxyl groups and no significant shrinkage was observed until 1000 °C consistent with the sintering behaviour of 310 nm spheres shown in Figure 6.11.

![Figure 6.10. TGA and shrinkage curves of 310 nm spheres.](image)

It is proposed that alkoxide derived xerogels to glass transformation occurs by reducing their free volume (structural relaxation) and surface area (viscous sintering). Because colloidal particles are composed of fully crosslinked anhydrous core, they undergo little additional of polymerization and contain low levels of free volume. Thus, there can be no additional densification other than viscous sintering.

The increase in particle size from 50 to 500 nm shifted the densification temperature $\sim$1120 °C to 1240 °C as shown in Figure 6.11 indicating the decrease in densification rate. High temperatures are required to densify particulate systems by
viscous sintering (Brinker et al., 1982). For viscous flow, water is known as a modifier that reduces the activation energy. As the particle size is reduced, the number of hydroxyl groups increases, and the distribution of hydroxyl groups becomes more uniform and there can be no distinction between surface and interior. Therefore additional shrinkage resulted from polymerization and/or continued crosslinking (Brinker and Scherer, 1985). The peaks located in 1060-1120 °C temperature range that significantly appear for smaller sphere as shown in Figure 6.11.b might be related with the shrinkage from structural relaxation and followed by shrinkage controlled by viscous sintering at high temperature. For larger diameter sintering controlled by viscous flow became dominant indicated by significant peak at 1178-1238 °C temperature range with small contribution of structural relaxation. For sufficiently larger spheres (500 nm) there could be no densification without viscous flow because of anhydrous oxide cores which controls the densification for only 50 nm size spheres.

Sacks and Tseng (1984b) also reported that shrinkage rate is dependent on the scale of the microstructure but also viscosity of the material. Brinker et al., (1982) reported that microstructure has significant effect on gel densification and sintering models show an inverse dependence of shrinkage rate on particle size or pore size. On the other hand, particle size controlled shrinkage rate may caused by ordered structure at which pore structure is uniquely defined. For disordered system does not necessarily enhance the densification rate by reducing particle size.

![Figure 6.11. Sphere size effect on (a) linear shrinkage, (b) shrinkage rate values.](image-url)
The microstructural change of 50 and 310 nm size spheres with heat treatment temperature in 900-1200 °C range has been evaluated by using SEM micrograph as shown in Figure 6.12. Although, at 900 °C, there is no evidence for the onset of sintering for 310 nm spheres, 50 nm spheres begin to become sinter active and at high temperatures greater regions are sintered that causes the collapse of the structures at 1100 °C. However, the temperature of 1100 °C is solely required for the onset temperature of 310 nm spheres for sintering.

Figure 6.12. SEM micrographs of 50 and 310 nm spheres treated from top the bottom row wrt. 900, 1000, 1100 and 1200 °C. The heat treatment time was 5 min.
XRD patterns of the 310 nm sized spheres treated in the range of 900-1200 °C are given in Figure 6.13. The amorphous state of spheres has been conserved up to 1200°C at which cristobalite crystals begin to nucleate and complete transformation to cristobalite phase has been revealed by increasing heat treatment temperature to 1300 °C shown in Figure 6.14.

Figure 6.13. XRD patterns of 310 nm sized spheres treated at different temperatures (●; cristobalite; JCPDS, file 76-0941).

Figure 6.14. XRD pattern of 310 nm sized sphere treated at 1300 °C (JCPDS, file 76-0941).
On the other hand, more closely packed structures consolidated by cold isostatic press (CIP) had lower crystallization temperature to cristobalite probably due to the either increased nucleation or growth rate (Sacks and Tseng, 1984b). As compared to powdered samples, the enhanced phase transformation caused by powder compaction of two sized spheres has been revealed from the XRD patterns given in Figure 6.15. Since high isostatic pressure offers the nearly close packing structure in the green compacts, the maximum relative density of the green compacts reached about 55% of theoretical values that might reduce the diffusion path length for crystallization. The surface micrographs of sphere compacts in green state are given in Figure 6.16 indicating the closely packed hexagonal planes with some defects corresponding to vacancies, dislocations or grain boundaries in atomic structures. This closely ordered planes promoted by CIP have probably been introduced from colloid state of highly stable suspension.

Figure 6.15. XRD patterns of 50 and 310 nm sphere compacts consolidated by CIP.

Figure 6.16. SEM micrographs of ordered sphere compact consolidated by CIP; (a) 5000X, (b) 25000X.
The mechanism of sintering for amorphous material is viscous flow (Brinker and Scherer, 1990). Theoretical model based on the Frenkel approach describe the early stage sintering behaviour of spherical, monodispersed particles, enabling to calculate the shrinkage rate of two equal particles whose centers approximate each other. The energy gained by the decrease of surface area during densification is equal to energy dissipated for viscous flow. Frenkel’s model is valid roughly within the first 10 % of linear shrinkage in which there is considerable neck growth but insignificant densification (Scherer, 1997). In Frenkel theorem by assuming similar particle array behaviour, corrected neck growth expressions between two spherical particles have been generalized to describe linear rate of shrinkage of an array of particles at one line,

\[ \frac{L}{L_o} = 1 - \frac{3\gamma t}{8\eta R} \]  

(6.1)

Where \( L_o \) is initial length, \( \gamma \) is the surface energy, (0.3 J/m²), \( R \) is the particle radius, \( \eta \) is the viscosity and \( t \) is time. Equation 6.1 is valid if there is linear relationship between \((L/L_o)\) and time and slope can be used for the calculation of viscosity. Figure 6.17 shows the linear relationship between dimensional changes over the time of 45 min for spheres sintered at different temperature. The viscosities were calculated for 1000, 1050 and 1100 °C treated samples, as 1.53*10^{11} Pa.s, 1.2*10^{11} Pa.s, and 0.64*10^{11} Pa.s, respectively.

Figure 6.17. Dimensional changes with time during sintering of 310 nm spheres.
Figure 6.18 shows the predicted and measured values of spheres treated at different temperatures. As the time increased the predicted value approached more significantly to the experimental values for all samples. Indeed, this model predicts the shrinkage rate by neglecting particle rearrangement during the densification. The nonuniformity of packing may be the cause of the insignificantly large shrinkage values as compared to predicted value.

Figure 6.18. Predicted and measured dimensional changes of samples sintered at different temperatures.

Another model that uses the Frenkel’s energy balance approach, developed by Mackenzie and Shuttleworth (MS) elucidated the rate of densification of viscous body containing closed spherical pores. It was provided that theoretical relationship between the relative density and reduced times, $K(t-t_0)$, in which $t_0$ is fictitious time when the relative density is zero and $K$ is given by (Sacks and Tseng 1984b),

$$K = \frac{m^{1/3}}{\eta} \quad (6.2)$$

where $n$ is the number of pores per unit volume and can be expressed by,

$$n = \frac{P}{4\pi R^3 / 3} \quad (6.3)$$
where $P$ is the number of pores per particle and it was estimated as 1 for uniform microstructure (Sacks and Tseng, 1984b). Experimental values were fitted to the MS model by plotting reduced times versus sintering times corresponding to the experimentally measured densities as shown in Figure 6.19.a. The $K$ value was calculated from the slope of the plots. The theoretical curve is shown in Figure 6.19.b as dashed line and the complete agreement between experimental values and theoretical curves was found for each temperature.

![Figure 6.19. Plot of reduced times (MS model) vs experimental sintering times for 310 nm spheres.](image)

The viscosities were calculated for 1000, 1050 and 1100 °C treated samples, as $15.2*10^{11}$ Pa.s, $8.34*10^{11}$ Pa.s, and $1.6*10^{11}$ Pa.s, respectively. These values are higher than the viscosities calculated from Frenkel’s model. The assumption of constant viscosity in the course of initial stage of sintering might be ineffective for describing the densification behaviour because of surface hydroxyl groups. Figure 6.20 indicates the temperature-viscosity relationship with the varying OH⁻ contents. It can be observed that when silica contains more hydroxyl it becomes less viscous because of the creation of non-bridging bonds as silanol (Si-OH) groups that replace siloxane (Si-O-Si) bonds (Brinker and Scherer, 1985). The solid points represent the viscosities of 310 nm spheres calculated from Frenkel and MS model. Significantly lower viscosities as compared to those for reported Brinker and Scherer (1992) might be due to high content of OH⁻ for the sol-gel derived 310 nm silica spheres.
The viscosity values for both models are plotted in Figure 6.21 according to an equation of Arrhenius type,

$$\eta = \eta_0 \exp\left(\frac{Q}{RT}\right)$$

(6.4)

where $Q$ is the activation energy and the $\eta_0$ is preexponential constant. The calculated activation energies for Frenkel and MS models are 125 kJ/mol and 335 kJ/mol, respectively. However, calculated values are substantially lower than the reported value of Sacks and Tseng (1984b). They calculated activation energy of 506 kJ/mol for 500 nm spheres by using MS and Scherer model. Brinker and Scherer (1984) stated that activation energy decreases as the hydroxyl content increases. The calculated substantially low activation energy probably related to the significant amount of silanol groups which was also indicated by lower viscosity.
6.2. Polymeric/Particulate Silica Membrane Preparation

6.2.1. Sol Characterization

All sol-gel parameters were adjusted to obtain stable particulate silica sols with minimum particle size. Colloidal sols in contrast to polymeric sols are expected to be formed when hydrolysis ratio above the stoichiometrically required value for full hydrolysis of the alkoxides. However, while this ratio was kept constant at 53.6, the molar ratio of ammonia was changed from 0.085 to 0.045 to obtain spheres in 5 to 10 nm size. Figure 6.22 shows the effect of catalyst concentration on particle size and particle size distribution. The substantial decrease in ammonia ratio caused the inverse effect on sphere size because of low degree of hydrolysis reaction and particles begin to behave as polymeric structures. It is expected that nucleation and growth is the dominant growth mechanism under base catalysed conditions at high values of pH, so that depolymerization is favoured and hydrolysis is complete (Brinker, 1988). On the other hand, decrease in ammonia ratio might cause decrease in depolymerization rate. Under this conditions formed particles become more stable therefore aggregation is not necessarily occurs.
Figure 6.22. Particle size distribution in the sols having different catalyst concentration.

The surface morphology analysis of membrane, corresponding to silica sol prepared at ammonia to TEOS molar ratio of 0.085 in which the smallest particle size of 5 nm conducted by AFM is shown in Figure 6.23. Figure 6.23.a is the phase image of the surface with scan size 750 nm x 750 nm while Figure 6.23.b is the surface height image showing a three dimensional view of the surface. The clusters of silica particles are clearly visible in this image as those also shown in SEM micrograph of top surface of the un-calcined membrane (Figure 6.24). The silica grains packed uniformly having an approximate size range of 5-10 nm without any cracks on membrane surface. An estimated grain size from AFM studies is nearly close to the particle size of sol determined by light scattering experiments.

Figure 6.23. AFM picture of un-calcined silica membrane on ZrO₂ support; (a) phase image, (b) height image.
Figure 6.24. SEM micrograph of the top surface of silica membrane treated at 40 °C.

Synthesis temperature has significant effect on both size and size distribution of the sol as shown in Figure 6.25. Elevated temperature led to large particle size and gave a much broader distribution as compared to 50 °C. The increase in particle size with increasing temperature may be caused by the increase in the rates both hydrolysis and condensation reactions. Intermediate concentration will be increased rapidly due to high hydrolysis rate while the consumption rate also fast through the condensation reaction after reaching the supersaturation leading to the short nucleation period. Consequently, the total number of nuclei formed decreases and the final sphere size will be relatively larger for high temperature.

Figure 6.25 Temperature effect on particle size distribution of silica sol (NH₃/TEOS= 0.085).
The stability of the sol derived from particulate route was studied by pursuing the change in particle size with aging time as shown in Figure 6.26. An insignificant increase in particle size was observed during the first 20 days aging but upon further aging caused solely about two times increase in particle size. In contrast to polymeric sol, the weak dependence of particle size on sol aging may be caused by a balance between growth and dissolution of the colloidal particles after particle formation and initial growth (Meixner and Dyer, 1999). As indicated in Figures 6.22, 6.25 and 6.26, the precise control of sphere size through the well-known sol-gel parameters in wide range with narrow particle size distribution can make it possible to design of the pore network for specific applications.

![Figure 6.26. Effect of aging on particle size corresponding to sol synthesized at \([ \text{NH}_3]/[\text{Alkoxide}] = 0.045] suggested that un-aged, 3 day aged, 20 day aged, and 60 day aged distributions.

The variation of particle size in wide range (five to several nanometers) with process parameters is also shown in Figure 6.27. Although both decrease in molar concentration of ammonia and water caused decrease in sphere size, decreasing with catalyst amount has more prominent for those having high ammonia content. Significant decrease in ammonia ratio to decrease hydrolysis rate with high water content caused the formation of very small spheres in 5 to 10 nm. The effects of parameters on hydrolysis and condensation reactions as well as their interactions should be considered simultaneously to give insight on control of sphere size. This figure obviously indicates that the precise control of sphere size can be provided by changing the water and ammonia concentration. The significant implication of this would be the ability of controlling sphere size in wide range for different applications.
6.2.2. Pore Structure Characterization

In Figure 6.28, the N\textsubscript{2} physical sorption isotherms of unsupported silica membranes treated at 400 °C are presented. From the figure it is clear that the change in sol pH having 5 nm particles caused significant change in pore structure of the membrane. The shape of isotherms as well as the amount of adsorbed volume drastically changed upon the change in surface charge of particles that mainly affects the packing properties of gels. The physisorption isotherm of particulate silica membrane is of Type IV with H2 hysteresis loop except the unsupported membranes prepared by the sol having pH of 2.7 and 3.5. A H2 hysteresis loop is characteristic for a mesoporous material consisting of spherical particles with “ink-bottle” type pore shape. On the other hand, the occurrence of substantial amount of adsorption at low relative pressure indicates the presence of additional microporosity with pores in the sub-nanometer range. The narrowing of hysteresis loop for the membrane corresponding sol pH of 1.9 may result from the increase in connectivity and the decrease in tortuosity, since the hysteresis I caused by network percolation effect (Rouquerol et al., 1999). A change of isotherm to Type I for membranes derived from sol having pH of 2.7 and 3.5 is the evidence of the increased level of microporosity.
The sorption data are examined quantitatively in Table 6.1. The change in porosity with pH of the sol indicates that the change in packing behaviour of particles during the consolidation. The porosity was calculated from the BJH cumulative pore volume for Type IV isotherms while the H-K pore volumes were used for Type I isotherm. Combining corresponding pore volume with skeletal density of SiO$_2$ of 2.08 g/cm$^3$ gave rise to a porosity of 0.32 for the unsupported membrane derived from sol having pH of 2.7. Close packing of uniform spherical particles in face-centered cubic or hexagonal close-packed structures results in the porosity of 0.26. Random close packing of particles having distribution of sizes typically yields the porosity of 0.36 (Torquato et al., 2000). Since the close packing of silica spheres of diameter 5 nm is expected to yield interstitial micropores about 0.8 nm in diameter, the nitrogen adsorption data are consistent with membranes formed by close packing of the particles in the silica sol for the pH 2.7. Therefore, the pore size distribution shown in Figure 6.29 is in agreement with the porosity level of random loose packing.
Figure 6.28. Sorption isotherms of membranes treated at 400 °C corresponding to particulate sol: (a) pH = 1.9, (b) pH = 2.3, (c) pH = 2.7, (d) pH = 3.5, (e) pH = 6.6, (f) pH = 9.4.
Type I isotherm at pH 2.7 and 3.5 could be the result of the stability of sol before the deposition which would lead to nearly close packed particles. It was reported that the point of zero charge of Si-OH containing species is between pH 1.5 and 4.5 depending on condensation rate (Schubert and Husing, 2000). Stability is at a maximum at the point of zero charge (pzc), in contrast to other metal oxides, because the polymerization characteristics of gel (Iler, 1979). On the either side of pzc, gelation is faster because acid or base catalysis accelerates the condensation rate of Si-OH groups between particles. At pH smaller and larger than pzc, the surface charge is too small to provide efficient repulsion between particles.

Table 6.1. Pore structure properties of 400 °C treated unsupported silica membrane with respect to sol pH.

<table>
<thead>
<tr>
<th>Sol pH</th>
<th>Surface Area (m²/g)</th>
<th>Porosity</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET</td>
<td>Langmuir</td>
<td>H.K.</td>
</tr>
<tr>
<td>1.9</td>
<td>623.1</td>
<td></td>
<td>0.49</td>
</tr>
<tr>
<td>2.1</td>
<td>666.2</td>
<td></td>
<td>0.43</td>
</tr>
<tr>
<td>2.3</td>
<td>729.2</td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>2.7</td>
<td>594.2</td>
<td>854.7</td>
<td>0.32</td>
</tr>
<tr>
<td>3.5</td>
<td>638.3</td>
<td>921.5</td>
<td>0.34</td>
</tr>
<tr>
<td>6.6</td>
<td>620.7</td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>9.5</td>
<td>664.9</td>
<td></td>
<td>0.56</td>
</tr>
</tbody>
</table>

The pore size distributions, calculated with the Horvath-Kawazoe method are given in Figure 6.29. As indicated in this figure, pore size distribution of unsupported membrane derived from polymeric sol is quite narrow with a maximum at D_{eff} ~6 Å. The distribution in pore size of the particulate silica membrane is much broader but has a maximum at approximately same pore diameter.
Figure 6.29. H-K Pore size distribution of 400°C treated silica unsupported membrane corresponding to (a) 5 nm-particulate sol pH of 2.7, (b) polymeric sol.

The substantial increase in porosity for pH value greater or less than 2.7 indicates that loosely packed silica particles with larger pores. It appears that the change in pH of the particulate silica sol make it possible to design the pore network for desired application. The effects of pH on packing of particles other than hydrolysis and condensation reactions have been related to the dependence of solubility on sol pH by Brinker and Scherer (1990). As indicated in Figure 6.30, under the condition of high solubility (high pH), more porous structure is obtained due to the growth of neck that results in stiffening of the network and may resist shrinkage by capillary forces during drying. On the other hand, at low pH necking is retarded because of low dissolution-reprecipitation rate leading the collapse of the pore network and more dense structure is obtained.

Figure 6.30. Schematic representation of particulate silica gel aged under conditions of (a) high, (b) low solubility (Source: Brinker and Scherer, 1990).
The combined effect of both systems namely particulate and polymeric can provide the thermal stability with controlled pore structures which in turn affect the gas transport properties. The superior properties of both systems make it possible to design the membrane pore structures in microporous range with high porosity. The close control of sol-gel process with a better understanding of the species/particles/microstructure relations would make to design the membrane with predefined membrane pore network possible with required separation abilities. A fractal dimension <1.5 allows interpenetration of polymer chains upon drying, resulting in a fully well-packed microporous material. Thus, smaller pore size and porosities are realized (Nair et al., 1996). Colloids with a fractal dimension higher than 1.5 would rather result in relatively large pores on the order of the colloid size with narrow size distribution due to the sphere packing. The control of microstructure of membrane by managing the packing efficiency of polymeric species and colloids as well as their extents of collapse upon drying simultaneously can provide a porous network with a percolative structure in microporous range.

The mixture of polymeric silica sol and particulate silica sol (pH of 3) having particles 30 nm in size was utilized for the formation of membranes. Figure 6.31 obviously indicates that the packing of 65 vol% 30 nm spheres in polymeric silica sol affects the pore network significantly with improved properties. Although small increase in H-K pore size (Figure 6.32) was observed, the porosity and the surface area of the unsupported membrane increase considerably. This result indicated the presence of the ability to design controllable microporous membrane structures with high surface area and total porosity through hybrid sol-gel processing. The differences in pore structure properties are summarized in Table 6.2.
Figure 6.31. Effect of 30 nm sphere addition in polymeric network on N₂ sorption isotherms of 400 °C treated membranes.

Figure 6.32. H-K pore size distributions of 400 °C treated polymeric and particulate/polymeric membranes.

Table 6.2. Effect of the combined use of both particulate and polymeric systems on the pore structures.

<table>
<thead>
<tr>
<th>H-K Pore Diameter (nm)</th>
<th>Langmuir S.A. (m²/gr)</th>
<th>BET S.A. (m²/gr)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Std</td>
<td>0.61</td>
<td>487</td>
<td>328</td>
</tr>
<tr>
<td>Sp65-30nm</td>
<td>0.69</td>
<td>1025</td>
<td>683</td>
</tr>
</tbody>
</table>
The change in membrane pore structure upon the addition of 5 nm spheres with different concentrations is given in Figure 6.33 showing N₂ adsorption-desorption isotherms. Decrease in volume content of colloidal particles caused an increase in adsorbed amount indicating more porous structure. Although microporous structure having Type I isotherm was preserved upon the addition of colloidal particles, packing of 5 nm spheres in polymeric network resulted in a denser structure as compared to pure polymeric network. The porosity has a tendency to decrease with increasing sphere content as indicated Table 6.3. On the other hand, the packing of 25 vol% spheres resulted in more open structure with high surface area suggesting that more stiffen pore network by the incorporation of spheres. The resulted relatively high porosity might also be related to the level of interpenetration of polymeric species due to the incorporation of small spheres into microporous network without increasing the pore size to the mesoporous range. The incorporation of high volume content of small spheres into the microporous network may be the cause of relatively dense layer due to the collapse of pore network by decreasing interaction between polymeric species and the colloidal spheres.

Figure 6.33. Effect of 5 nm sphere addition in polymeric network on N₂ sorption isotherms of 400 °C treated membranes.
Table 6.3. Effect of sphere concentration on pore structure of particulate/polymeric systems.

<table>
<thead>
<tr>
<th></th>
<th>H-K Pore Diameter (nm)</th>
<th>Langmuir S.A. (m²/gr)</th>
<th>BET S.A. (m²/gr)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Std</td>
<td>0.61</td>
<td>487</td>
<td>328</td>
<td>26</td>
</tr>
<tr>
<td>Sp25-5nm</td>
<td>0.69</td>
<td>549</td>
<td>371</td>
<td>29</td>
</tr>
<tr>
<td>Sp45-5nm</td>
<td>0.76</td>
<td>449</td>
<td>300</td>
<td>25</td>
</tr>
<tr>
<td>Sp74-5nm</td>
<td>0.73</td>
<td>380</td>
<td>249</td>
<td>22</td>
</tr>
</tbody>
</table>

Sol dilution has significant effect on the formation of aggregates which in turn affect the development of membrane microstructure as suggested by Nair et al., (1996). Figure 6.34 shows that N₂ sorption isotherms of 400 °C treated 74 vol% 5 nm spheres loaded membranes. Sol dilution resulted in more open structure for the same sphere concentration indicated that the presence of percolative threshold that caused by volume restrictions to ordering for membranes derived from concentrated sol.

Figure 6.34. Effect of dilution on N₂ sorption isotherms of 400 °C treated sp74-5nm membranes.
Ethylene glycol (EG) was used as a solvent instead of ethanol for the preparation of stable polymeric silica sols to slow down the evaporation rate of the solvents in mixed sols. Low vapour pressure of EG gives rise to long time to evaporate allowing the spheres to order by shearing during spin coating and also increases the drying periods. Two important characteristics of solvents are; (1) polarity, which largely determines the solvating ability for polar or non-polar species, and (2) the availability of labile protons that, determines whether anions or cations are solvated more strongly and whether or not the solvent can participate in dissociative reactions (reverse of condensation reactions). Because, hydrolysis is hydroxyl and hydronium ion catalyzed, solvent molecules which hydrogen bond to hydroxyl ions or hydronium ions reduce the catalytic activity under basic and acidic conditions, respectively. Therefore, aprotic solvents, which do not hydrogen bond to hydroxyl group, have the effect of making hydroxyl ions more nucleophilic, whereas protic solvents make hydronium ions more electrophilic (Brinker, 1988). Although ethanol and ethylene glycol are polar protic solvents and can act as donors or acceptors in hydrogen bonding, ethylene glycol has a larger dipole moment and is therefore expected to hydrogen bond more strongly to protons and hydroxyls under acidic and basic conditions, respectively. In addition the viscosity of EG is approximately seventeen times greater than ethanol at 25 °C. These combined effects may cause a reduction in the hydrolysis rate.

FTIR analyses were performed to provide structural and chemical information on the ethylene glycol derived polymeric silica gelation process as well as information about structural changes occurring as a result of the heat treatment of gels. The peaks in the range of 400 and 1400 cm\(^{-1}\) observed in Figure 6.35 were characterized as the silanol and silicon alkoxide groups. The band at about 925 is attributed to the stretching mode of –Si-OH for the uncalcined sample which disappear for the calcined sample (Figure 6.32) indicating that the transformation of silanols to siloxane by polycondensation reaction and as also evidenced by the silicon oxide band at 1092 cm\(^{-1}\) with a shoulder at 1200 cm\(^{-1}\). According to James (1988), the peak shift indicates the strengthening of the xerogel network upon shrinkage by producing new bonds. The band appears at 460 cm\(^{-1}\) characterized as the vibrational modes of tetrahedral SiO\(_4\). The symmetric Si-O-Si stretching and vibrational modes of ring structures characterized by the band at 800 cm\(^{-1}\). The band at 3490 cm\(^{-1}\) is assigned to the stretching and deformation modes of hydroxyl groups and band at 1650 cm\(^{-1}\) is attributed to the deformation vibrations of the H–O–H bond, which indicates the presence of water.
incorporated in the silica matrix. Uncalcined sample also show a band at 1385 cm\(^{-1}\) associated with NH\(_3\) and alcohol (da Costa et al., 2002, James 1988).

![FTIR spectrum of un-calcined EG derived polymeric unsupported silica membranes, SiEg-0.085-40 °C (Inset: zoomed in 2800-3000 cm\(^{-1}\) range).](image)

Figure 6.35. FTIR spectrum of un-calcined EG derived polymeric unsupported silica membranes, SiEg-0.085-40 °C (Inset: zoomed in 2800-3000 cm\(^{-1}\) range).

The bands located at 2975 and 2930 cm\(^{-1}\) are characteristics of stretching vibrations of C-H bonds of the organic groups indicating the –CH\(_2\)-CH\(_2\) groups in uncalcined EG derived unsupported silica membranes. The spectrum of ethanol standart silica unsupported membranes is completely featureless in this range (Topuz, 2002). Castricum et al., (2008) reported that both methyl and –CH\(_2\)-CH\(_2\) groups are persist in the organically linked (copolymerization of methyl-triethoxysilane and bridged bis-silyl precursor) unsupported film after heat treated at 300 °C.

The effect of sol synthesis temperature on FTIR spectra of calcined EG derived polymeric unsupported silica membranes is given in Figure 6.36. However, the spectra of membranes derived from polymeric sols synthesized at 40 and 50 °C are very similar in shape. The vibrations of the SiO\(_4^{4-}\) tetrahedron are visible at 820 and 1094 cm\(^{-1}\) in the case of 40 °C while those at 815 and 1095 cm\(^{-1}\) for the sol synthesis temperature of 50 °C.
Figure 6.36. The effect of sol synthesis temperature on FTIR spectra of 400 °C treated EG derived polymeric unsupported silica membranes.

The isotherms of ethylene-glycol (EG) derived polymeric silica sols are given in Figure 6.37. They all are Type I isotherms which are the characteristics of microporous materials. Increase in temperature and molar ratio of catalyst to alkoxide causes increase in volume of adsorbed nitrogen indicating more porous structure. Increase in synthesis temperature yielded more porous structures resulted from the formation of highly branched polymeric species. According to Nair et al., (1996) the porosity of the resulting structures increases linearly with increasing molar ratio of acid to alkoxide. The increase in H⁺ concentration lead to increase in condensation rates which in turn yield polymers having a higher degree of branching. Elfering et al., (1996) claimed that porosities above 26% can be acquired with acid to alkoxide molar ratio above 0.15 for the ethanol based polymeric silica systems. As compared to ethanol based systems, EG derived polymeric silica sol resulted in more porous structures with small increase in pore sizes. These sols yielded microporous structures having very high porosity and surface areas. The assumption for designing these pore structures would be that the partially reacted species as a result of low hydrolysis rate within the synthesis time. These partially reacted species continued to polymerize during the drying and resulting in a more open structures. Stefanescu et al., (2007) claimed that EG condenses either at one-end (≡Si-O-CH₂-CH₂-OH) or two-end (≡Si-O-CH₂-CH₂-O-Si≡) to create hybrid organic-inorganic hybrid matrix.

In general, however, a reduction of pore size in microporous ceramic membranes is achieved at the expense of porosity or pore volume and, thus, good separation properties are coupled with a low gas flux. It has remained a great challenge
to synthesize ceramic membranes having micropores with a uniform or very narrow pore size distribution and with a large pore volume. Table 6.4 compares the pore structure characteristics of EG derived unsupported silica membranes with standard polymeric silica membranes.

![Graph](image)

Figure 6.37. Effect of process parameters on the adsorption isotherms of EG derived polymeric silica sols.

The addition of 30 vol% 310 nm spheres in EG derived sol synthesized at 40 °C having 0.085 HNO₃/alkoxide ratio causes a decrease in the adsorbed volume of N₂ on 400 °C treated unsupported membrane which is an indication of decrease in the porosity of film as shown in Figure 6.38. Although the pore size of membrane remained constant with the addition of spheres, the porosity level and surface area has decreased as shown in Table 6.4. This may indicate that the packing of monodispersed spheres in polymeric sol yielded more resistive pore network of membrane without changing the pore size.

Table 6.4. Pore structure properties of 400 °C treated EG derived silica membranes.

<table>
<thead>
<tr>
<th></th>
<th>H-K Pore Diameter (nm)</th>
<th>Langmuir S.A. (m²/gr)</th>
<th>Porosity (%)</th>
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<td>487</td>
<td>25</td>
</tr>
<tr>
<td>SiEg-0.05 40 °C</td>
<td>0.85</td>
<td>761</td>
<td>34</td>
</tr>
<tr>
<td>SiEg-0.085 40 °C</td>
<td>0.70</td>
<td>718</td>
<td>33</td>
</tr>
<tr>
<td>SiEg-0.085 50 °C</td>
<td>0.68</td>
<td>890</td>
<td>38</td>
</tr>
<tr>
<td>SiEg-0.085 60 °C</td>
<td>0.77</td>
<td>1085</td>
<td>41</td>
</tr>
<tr>
<td>Sp30-310 in SiEg-0.085 40 °C</td>
<td>0.70</td>
<td>608</td>
<td>30</td>
</tr>
</tbody>
</table>
6.2.3. Thermal/Densification Behaviour of Unsupported Silica Membranes

Figure 6.39 shows the percent weight losses with increasing temperature and the difference in densification behaviour of polymeric and colloidal silica unsupported membranes. The total weight loss of spheres is about 10% while the polymeric silica has 15% weight loss upon heat treatment to 1000 °C. Up to about 150 °C, considerable weight loss is observed that can be attributed to the evaporation of water and ethanol. Between 150-400 °C mostly removal of organics and further polymerization of the silica network take place. Above 400 °C small weight loss is related to the removal of surface OH groups. Base catalysed reactions result in granular texture and retaining less organic material as compared to acid catalysed systems consisting of linear, slightly cross linked polymeric clusters. The large weight loss may be caused by the presence of significant number of chemically bound alkoxy groups because of re-esterification reaction during the drying albeit complete hydrolysis. James (1988) reported that polymeric structures show enhanced densification at lower temperatures due to the removal of alkyl groups by condensation. Because of the less hydrolysed species formed for the acid catalysed polymeric system, Brinker et al., (1982) reported that...
both structural relaxation and micropore collapse combined with additional cross-linking are expected to produce dense structure at low temperatures.

Figure 6.39. Thermal/densification behaviour of polymeric and colloidal silica; (a) TGA, (b) Shrinkage curves.

Figure 6.39.b clearly shows that acid catalysed polymeric species has a significantly higher dimensional shrinkage than their base catalysed spheres up to 1200 °C. Clear conclusion can be drawn from TGA and dilatometry results that the gel to glass transformation is a direct consequence of the initial sol-gel chemistry. Differences in the rates of hydrolysis relative to the rates of condensation during gelation resulted in very different structures. The differences in crosslinking behaviour of two system results in differences in densification behaviour. In a review paper by James (1988), it was reported that a temperature of approximately 1050 °C was required to densify the base catalysed systems while a temperature of 700 °C was needed for polymeric gel. It was suggested that in polymeric systems, the gel to glass transition took place as a result of the combination of silanol (=Si-OH) groups on the surface of the pores, releasing H₂O and forming Si-O-Si bonds. On the other hand, sintering by viscous flow was assumed for the base catalysed systems due to high water content of gel. It was also suggested that only viscous flow dominating sintering caused by the vaporization of water from the surfaces of the particles on heating.

The change in thermal behaviour of EG derived silica unsupported membrane upon addition of monodispersed silica spheres is shown in Figure 6.40. The total weight loss of SiEg up to 500 °C is about 30% while Si-std has about 14 %. The addition of 30% vol of sphere into SiEg causes only 2% wt difference on the total weight loss.
However, this difference may be attributed to slow heating rate of TGA experiment for sphere mixed membrane. The TGA pattern of EG derived silica unsupported membranes reveals that weight losses occurring in four temperature intervals. A sharp weight loss occurred in the temperature interval 80-200 °C indicating the loss of water, evaporation of EG that is free in the pores or hydrogen bonded to silanol groups, followed by slower weight losses due to the progress of polycondensation reactions between silanol groups or between silanol and OH-C₂H₄-OH in the interval 200-280 °C. An abrupt weight loss between 280 and 300 °C may corresponds to the removal of organics formed by chemically interacted EG with silanol groups which entrapped in pore network. The weight loss due to the combustion of carbon and progress of condensation reaction with the elimination of OH⁻ occurs between 280-500 °C. Further small weight loss beyond 500 °C presumably caused by the removal of OH groups from the surface.

![TGA curves of EG derived polymeric unsupported silica membranes.](image)

Figure 6.40. TGA curves of EG derived polymeric unsupported silica membranes.

Linear shrinkage change and shrinkage rate curves with respect to particle size of based catalysed sol are shown in Figure 6.41. Sintering rate is roughly proportional to the inverse of the particle size. Although, the increase in particle size up to 25 nm causes decrease in linear shrinkage at 1000 °C, 50 nm spheres have relatively large shrinkage caused by most likely poor packing of spheres as compared to small sphere size. In principle, particle size is controlling parameter for unically defined pore structures as being in the ordered compact of monosized spheres. The randomly packed
particles other than the closed-packed may suffer rotation or rearrangements that allow the pores to grow rather than to shrink. The average number of nearest particle contacts per particle tends to decrease as the ordering decreases, hence pore curvature has decreased resulting in the driving force for the sintering (Sacks and Tseng, 1984b).

![Graph showing the effect of particle size on densification behaviour of spheres.](image)

Figure 6.41. Effect of particle size on densification behaviour of spheres.

The decrease in densification rate upon addition of 5 nm spheres with different concentration into the polymeric network is shown in Figure 6.42. The samples were also consolidated by cold isostatic press (CIP) at pressure of 200 MPa before dilatometer measurements. All samples had about 65% green densities. Almost constant shrinkage values were obtained up to 1000 °C for sphere incorporated structure but between 1000 and 1200 °C the packing of 25 vol% of spheres resulted in lowest densification rate. Since the viscous sintering is dominant mechanism for the base catalysed system, high amount of spheres in polymeric network might increase the contribution of viscous sintering resulted in high shrinkage value in 1200-1300 °C temperature range.
Figure 6.42. Effect of 5 nm sphere addition on densification behaviour of unsupported polymeric/particulate silica membranes.

The selective thin membrane layers have been consolidated on alumina support with gamma layers upon heat treatment 400 °C for 2 hours for the microstructural integrity. The microstructural changes during heat treatment because of removal of solvent and/or organics also partial densification of solid network as well as the heating stress lead to volume shrinkage that might cause microcrack formation and/or layer delamination. Thus, the control of consolidation step has great importance to avoid cracking on membrane surface. The dilatometer measurements were also performed for both particulate and polymeric unsupported consolidated form as well as the polymeric/particulate system to 400 °C for 2 hours to understand the structural development during consolidation. On the other hand, this result may give the first insight whether incorporating the spheres into polymeric structure would be stabilized the membrane network since, the selective thin membrane layer on support could behave differently. As shown in Figure 6.43, the consolidated samples undergo severe shrinkage upon heat treatment that might result in microcracking. The packing of pure 5 nm spheres gave enhanced stability because of high degree of crosslinking as compared to acid catalysed polymeric system. On the other hand, the incorporation of this more highly crosslinked spheres into the polymeric network prevented sharp increase in shrinkage value due to the structural relaxation and continuing crosslinking of polymeric structure. Although the packing of 74 vol% of spheres provided enhanced stability up to 300 °C, at the end of the 2 hours, sp25 had the lowest shrinkage value.
This might be related to the stiffening of pore network as confirmed by high level of porosity from the N₂ adsorption-desorption analysis.

![Graph showing shrinkage vs temperature for different materials: 5 nm, Si-std, sp25-5nm, sp45-5nm, sp74-5nm.](image)

Figure 6.43. Effect of 5 nm sphere addition on linear shrinkage values of unsupported polymeric/particulate silica membranes treated at 400 °C.

The packing of large spheres with low concentration also stabilized the pore network up to 400 °C as compared to pure polymeric silica network as shown in Figure 6.44. The significant enhancement on densification behaviour upon the addition of 10 vol% 220 nm spheres might be caused by decrease in structural free energy of polymeric/particulate system which in turn decreases shrinkage resulted from structural relaxation.

![Graph showing shrinkage vs temperature for different materials: sp10-220nm, sp5-220nm, Si-std.](image)

Figure 6.44. Effect of 220 nm sphere addition on linear shrinkage values of unsupported polymeric/particulate silica membranes.
6.3. Polymeric/Colloidal Alumina Membrane Preparation

Alumina sols were prepared both using the colloidal and polymeric sol-gel techniques. Particulate sols are expected to be resulted in mesoporous membrane with pore size in the 2-5 nm range changing with sol particle size and heat treatment temperature. The optimal $[\text{H}^+]/[\text{Al}^{3+}]$ and $[\text{H}_2\text{O}]/[\text{Al}^{3+}]$ ratios were found to be 0.25 and 100, respectively, since these led to the smallest particle size in sols (number based particle size 13 nm) and membrane had a sharp pore size distribution at about 2.8 nm (BJH-desorption) upon heat treatment temperature to 500 °C (Topuz and Çiftçioğlu, 2004). The size, shape and agglomerates of boehmite crystallites in addition to deposition conditions determine the membrane microstructure. Smooth surface, small and uniform pore sizes, as well as the small thickness with continuous structure are the key properties of intermediate layer for thin defect-free silica membrane application. The use of graded structures for the intermediate layers by applying size-controlled boehmite sols to improve the permeation properties has been reported by Gu and Oyama (2007). The schematic representation of graded structure with better filling of voids to avoid infiltration and defects is shown in Figure 6.45.

![Schematic of supports formed from (a) small sol particles, (b) large sol particles, (c) graded sol particles (Gu and Oyama, 2007).](image_url)

The supports were coated successively with boehmite sols of decreasing particle size to form a graded three layer alumina layers. The change in particle size with molar ratio of $\text{H}^+$ to $\text{Al}^{3+}$ is shown in Figure 6.46. Boehmite sols having molar ratio of $\text{H}^+$ to $\text{Al}^{3+}$ in 0.1-0.25 range were utilized for membrane coating.
Figure 6.46. Effects of acid content on particle size of boehmite sols.

The uniformity of the membrane layer can be controlled by the dipping conditions including dipping time and withdrawal speed as well as the concentration and the pH of sol. As prepared boehmite sol pH was kept at about 3.7 since the infiltrated layer could be formed from acidic sols (pH<3.4) after coating (Burggraaf and Cot, 1996). The thickness of one layer coated mesoporous alumina layer could be easily varied by changing dipping time and withdrawal speed as shown in Figure 6.47.

Figure 6.47. SEM micrographs of cross-sections of 500 °C treated colloidal γ-Al₂O₃ layer.

(cont. on next page)
Maximum layer thickness of 1μm was obtained when withdrawal speed and dipping time were 200 mm/min and 20 s, respectively while the decrease in speed to 100 mm/min and time to 10 s yielded a layer thickness of 500 nm. Highly uniform, homogeneous alumina layers were acquired on zirconia support not including for the conditions of 100 mm/min withdrawal speed and dipping time of 10 s which resulted in on the other hand, infiltrated layer of about 3.5 μm with about 250 nm layer thickness. Layer deposition by dip coating process includes dipping of dry substrates into the sol and subsequent withdrawal to form more or less dense layer with well defined thickness (Gu and Meng, 1999). During film formation two mechanisms are preceded, namely slip casting and film coating. Dipping time has a strong influence on the film thickness as well as the porosity and pore size of the substrate in the course of slip casting, because the capillary suction caused by the porous substrate drives the particles/polymers to concentrate on the surface if the particles would not enter the
support pores. During the film coating mechanism an adhering layer is formed on slip cast layer due to the drag force exerted by the substrate during withdrawal from the dispersion medium. The thickness of the adhered layer increases with the withdrawal speed and dispersion viscosity. The SEM micrographs shown in Figure 6.47 is a clear indication of consecutive formation of these two mechanisms since layer thickness changed with both the dipping time and the withdrawal speed. Meanwhile, the layer thickness should be as small as possible to increase the flux without any defects on the membrane surface. Therefore, the intermediate layer thickness was controlled as about 1μm after two times coating of 0.2 M boehmite sol.

Figure 6.48 shows the IR absorption spectra of uncalcined and 500 °C treated unsupported polymeric alumina membranes in which acetyl-acetone was used as a chelating agent. The absorption peaks at 3448, 3430, 1597 and 1651 cm\(^{-1}\) correspond to stretching and bending modes of adsorbed water. The Al-O-H bending mode is expected in the region of 900-1100 cm\(^{-1}\). For the uncalcined sample it is observed at 1076 cm\(^{-1}\) and at 1072 cm\(^{-1}\) for the heat treated one. The 1379 peak due to C-H bond is observed (Jing et al., 2007). The octahedral coordination is characterized by the Al-O stretching and bending modes of in the 500-750 cm\(^{-1}\)and 330-450 cm\(^{-1}\) region, respectively while a tetrahedral coordination of is expected to give stretching modes in the narrow range 750-850 cm\(^{-1}\) and the bending modes between 240 and 320 cm\(^{-1}\) (Priya et al., 1997). In the uncalcined sample spectrum broad band with peaks at 598, 660, and 688 cm\(^{-1}\) is observed. These are assigned to the stretching mode of AlO\(_6\) while the band observed at 425 cm\(^{-1}\) is characterized as the bending mode of AlO\(_6\). This result is consistent with the presence of only octahedral Al species for stable boehmite sol resulted from high temperature hydrolysis in large excess of water. The two peaks located at 1532 an 1605 cm\(^{-1}\) are associated with the formation of chelating complex between acetyl acetone and Al\(^{3+}\) atom in alkoxide molecule (Jing et al., 2007). Due to the formation of such chelated complex (aluminium acetyl acetone) in organic medium retards the hydrolysis and condensation reaction rates in order to control the condensation pathway of the evolving polymer.
FTIR spectra of unsupported polymeric alumina membranes in which ethyl-acetoacetate was used as a chelating agent are shown in Figure 6.49. All samples, had an intense and wide absorption band at about 3500 cm$^{-1}$, which resulted from the hydroxyls on the $\gamma$-AlO(OH) surface. The bands within the 2975-2950 cm$^{-1}$ range are the characteristic peak of $\text{–CH}_3$ stretching. The bands 1419, 1384, 1356, 1311 and 592 cm$^{-1}$ correspond to C–H bonds, 1192, 1184, and 796 cm$^{-1}$ bands due to C–O bonds, 1022 and 993 cm$^{-1}$ bands attributed to C–C bonds were observed (Jung, 2001). Ethyl-acetoacetate has the ketonic and enolic structure forms. In the IR spectrum of EAcAc, there are two characteristic peaks at 1720 cm$^{-1}$ and 1650 cm$^{-1}$ which can be assigned to the C-O stretching vibrations of the ketonic and enolic forms, respectively (Jing et al., 2007). Although, bands at located at 1720 cm$^{-1}$ and 1650 cm$^{-1}$ are too week, the strong peaks especially for p12 and p13, at 1620 and 1540 cm$^{-1}$ indicates that the formed chelate complex with aluminium sec-butoxide. All samples exhibit a band located at 1070 cm$^{-1}$ with a shoulder at 1180 cm$^{-1}$ which are attributed to the symmetrical and unsymmetrical Al-OH bending modes. However, these bands are less significant for the sample of p8. The peak at located at 1060 cm$^{-1}$ observed only p8 is characterized by Al-O-C stretching vibration indicated that uncompleted hydrolysis. The stretching Al-O modes of octahedral species (AlO$_6$) are found below 900 cm$^{-1}$ (835, 792, and 636 cm$^{-1}$) as well as the bending modes at 420 cm$^{-1}$. 

![FTIR spectra of (a) un-calcined and (b) 500 °C treated polymeric unsupported alumina membranes.](image-url)
The effects of process parameters on the formation of the polymeric alumina sol also investigated by the $^{27}$Al MAS-NMR spectra given in Figure 6.50 through 6.53. $^{27}$Al NMR provides information for distinguishing between 4-,5-, and 6-coordinate Al species in solution and in the solid state. In $^{27}$Al NMR data, characteristic chemical shifts for oxygen coordination by Al are the following; octahedral from -30 to 15 ppm, pentacoordinated 25 to 40 ppm and tetrahedral 40 to 80 ppm (Hernandez and Pierre, 2001). In boehmite the oxygens are arranged in octahedral coordination around Al and are organized in parallel layers linked by hydrogen bonds. As well as the octahedrally coordinated Al, boehmite to $\gamma$-Al$_2$O$_3$ conversion results in the portion of the Al to coordinate tetrahedral position (Brinker and Scherer, 1990). The spectrum is formed by one intense peak at -7.5 ppm as well as two components at 55, and -78 ppm for the sample p9. Zero ppm for $^{27}$Al-NMR resonance assigned to octahedrally coordinated Al species in polycrystalline boehmte. This resonance shifted to -7.5, -4, -6.2 ppm for the samples p9, p12, and p14, respectively as shown in Table 6.5. Shifting in chemical shifts is most likely the result of an interaction between the chelating agent and aluminium. $^{27}$Al-NMR resonance at 63.5 ppm attributed to the single tetrahedrally coordinated aluminium (Brinker and Scherer, 1990). The ill-defined chemical shift at about 60 ppm for uncalcined samples indicated that the tetrahedrally coordinated Al atom in the cationic species Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_7$ (Al$_{13}$ ion) (Nazar and Klein, 1988).
Figure 6.50. $^{27}\text{Al}$-MAS NMR pattern of uncalcined polymeric unsupported alumina membrane (p9).

This chemical shift is less prominent for the p12 sample of which hydrolysis ratio ($\text{H}_2\text{O}/\text{Al}^{3+}$ molar ratio) is smaller than the stoichiometric ratio for complete hydrolysis indicating highly polymerized structure.

Figure 6.51. $^{27}\text{Al}$-MAS NMR pattern of uncalcined polymeric unsupported alumina membrane (p12).
Heat treatment upon 500 °C causes the increase in chemical shifts at 59, 27 ppm as well as at -5.5 ppm that assigned to 4, 5 and 6-coordinated Al atom. Chemical shifts of tetra and octahedral components indicated the transformation to $\gamma$-Al$_2$O$_3$.

Figure 6.52. $^{27}$Al-MAS NMR pattern of uncalcined polymeric unsupported alumina membrane (p14).

Figure 6.53. $^{27}$Al-MAS NMR pattern of 500 °C treated polymeric unsupported alumina membrane (p14).
Table 6.5. Influences of process parameters on the chemical shifts.

<table>
<thead>
<tr>
<th></th>
<th>Chemical Shifts (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p9</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>-7.48</td>
</tr>
<tr>
<td></td>
<td>-78</td>
</tr>
<tr>
<td>p12</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>60.6</td>
</tr>
<tr>
<td></td>
<td>-4</td>
</tr>
<tr>
<td></td>
<td>-129</td>
</tr>
<tr>
<td>p14</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>-6.2</td>
</tr>
<tr>
<td></td>
<td>-80.2</td>
</tr>
<tr>
<td>p14 (500 °C)</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>-5.5</td>
</tr>
<tr>
<td></td>
<td>-80</td>
</tr>
</tbody>
</table>

The preparation method for polymeric alumina sol synthesized was able to be optimised. It was found that stable polymeric sols could be obtained when the hydrolysis conditions were accurately controlled. As a solvent parent alcohol was used with high dilution ratios (0.5 mol Al^3+/dm^3). The acetyl-acetone (AA) to Al^3+ molar ratio was changed from 0.4 to 0.2 at the molar ASB (Aluminium-secbutoxide):butanol:water:HNO₃ ratios of 1:18:1:0.35. The hydrolysis temperature has played an important role to get clear stable sol. The temperature lower than the 80 °C resulted in un-hydrolysed species but at the same compositions the increase in temperature to about 90 °C, the yellowish stable sols were obtained. Moreover, as the AA ratio decreases to 0.2, the more bright yellow sol was obtained. Although particle size distributions of freshly prepared polymeric alumina sols were not characterized by dynamic light scattering experiments because of the limitation in size range. Minimum size that can be measured is 2 nm for ZetaSizer 3000HS. Two months aging of sol led to be able to detect the particles and particle size distributions of aged sols are given in Figure 6.54. The average particle size varied between 1 and 4 nm depending on parameters that control the hydrolysis and condensation reactions. As shown in Table 5.2., when these parameters were strictly controlled polymeric alumina sols could be prepared. Smaller chelating ratio gave rise to larger particles indicating the fast hydrolysis caused by insufficient amount of formed chelated complex. Increasing acid content led to small decrease in particle size since H⁺ favored the hydrolysis reaction by making the alkoxy ligands better leaving groups as compared to condensation reaction. Stoichiometric ratio for the complete hydrolysis of Al^3+ is 1.5. The smallest particle size was obtained as the stoichiometric ratio was utilized.
The physisorption isotherm of 500 °C treated unsupported polymeric alumina membrane changes from Type IV to Type I as the AA ratio changed from 0.4 to 0.3 as shown in Figure 6.55. The Type IV isotherm with H2 hysteresis loop is characteristics of mesoporous alumina membranes synthesised from colloidal route as shown in Figure 6.55.a (Topuz, 2002). On the other hand, for polymeric membranes a change of the isotherm towards Type I indicates that the microporous membranes can be obtained for the alumina membranes. Accordingly, as can be seen in Table 6.6 larger AA ratios gave rise to larger pore size and smaller surface area with a low porosity. It seems that a larger amount of chelating agent has negative effect on microstructure formation. Larger pore size values might be related to the polycondensation of incompletely hydrolyzed polymeric species.
Figure 6.55. Sorption isotherms of 500 °C treated alumina membrane (a) colloidal, (b) polymeric with corresponding sol molar ratio of AA to Al$^{3+}$ 0.4 and 0.3.

Decrease in pore size and increase in surface area of polymeric membrane in accordance with the colloidal ones, may result in significant improvements on membrane properties in terms of finer microstructure, layer homogeneity without cracks and defects and also stability that could affect the permeation properties of membranes significantly.

Table 6.6. Pore structure properties of 500 °C treated unsupported polymeric alumina membrane with respect to sol molar ratio of AA.

<table>
<thead>
<tr>
<th>[AA]/[Al$^{3+}$]</th>
<th>Surface Area (m$^2$/g)</th>
<th>Porosity* %</th>
<th>Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET</td>
<td>Langmuir</td>
<td>H.K.</td>
</tr>
<tr>
<td>0.4</td>
<td>132</td>
<td>180</td>
<td>23</td>
</tr>
<tr>
<td>0.3</td>
<td>382</td>
<td>544</td>
<td>37</td>
</tr>
</tbody>
</table>

* single point pore volume was used
6.3.1. Thermal/Phase Evaluation and Stability of Unsupported Alumina Membranes

The XRD patterns shown in Figure 6.56 and Figure 6.57 were obtained from the alumina unsupported membranes synthesised from polymeric sol having molar ratios \([\text{HNO}_3]/[\text{Al}^{3+}]\) and \([\text{AA}]/[\text{Al}^{3+}]\) of 0.15 and 0.4, respectively. The X-ray diffraction pattern of 200 °C treated unsupported membrane indicates that the material is purely amorphous in structure and there is no evidence for the formation of boehmite crystalline phases. On the other hand, the amorphous nature on patterns may caused by the small size of the crystals that is not appropriate for the XRD characterization. The material kept its amorphous structure until 700 °C where slight crystallization into \(\gamma\)-\(\text{Al}_2\text{O}_3\) phase occurred. Increase in phase transformation temperature from boehmite to \(\gamma\)-\(\text{Al}_2\text{O}_3\), since for colloidal sol-gel derived gamma alumina it starts to proceed at about 500 °C, may caused by the decrease in sol species sizes which in turn affects the pore size of the membranes. Furthermore, it may result in the thermal stability of alumina membranes being improved with finer structure.

![XRD patterns of polymeric alumina membrane dried at 200 °C (p01).](image)

Figure 6.56. XRD patterns of polymeric alumina membrane dried at 200 °C (p01).
Figures 6.58 through 6.62 reveal that XRD patterns of EAA derived polymeric alumina unsupported membranes treated at different temperatures. As compared to AA derived polymeric sol (Figure 6.57), transformation temperature to $\gamma$-$\text{Al}_2\text{O}_3$ phase increased to 800 °C as shown in Figure 6.62. Although, XRD patterns of 700 °C treated samples have shown completely amorphous structure, purely gamma phase was obtained at 800 °C. This can be related to the fact that the limitation of XRD experiment for the small crystalline size. Increasing crystallographic phase transformation temperature from boehmite to gamma alumina may lead to increase in thermal stability of alumina membrane since beyond this temperature structural changes may occur, often accompanied by the generation of cracks due to significant volume changes. The significant implication of this would be the ability of using the alumina membranes derived from polymeric route with high thermal stability in separation layer other than the intermediate layer for gas separation applications.
Figure 6.58. XRD patterns of 90 °C treated polymeric alumina membranes.

Figure 6.59. XRD patterns of 500 °C treated polymeric alumina membranes.
Although only (440) reflection was observed for 700 °C treated p9 sample (Figure 6.61), XRD pattern of 800 °C treated unsupported membranes shown in Figure 6.62 revealed the presence of $\gamma$-Al$_2$O$_3$ with broad reflections due to their low crystallinity. The broad diffraction lines also reveal that the crystallites are very small. However, slight difference in peak intensities and sharpness at certain $^\circ$2 theta were observed between samples, only (400) and (440) reflections were used for the determination of the crystallite size by using Scherrer’s equation. As shown in Table 6.7, almost insignificant difference in crystallite size for the samples p8 and p12, the
smallest size of 4 nm was obtained for the p13 sample of which those of having the smallest particle size of about 1.7 nm in sol state.

Figure 6.62. XRD patterns of 800 °C treated polymeric alumina membranes.

XRD patterns of the p8 heat treated between 500 and 800 °C are given in Figure 6.63. Three γ-Al₂O₃ peaks, (311), (400) and (440) (JCPDS, file 10-0425) was observed for the 800 °C treated membranes while heat treatment at below 800 °C resulted in fully amorphous structures. This might be related with finer structures having very small particle size retarding the transformation temperature to gamma phase. Alternatively, the absence of gamma peaks may indicate that the size of the gamma alumina is below the detection limit of the XRD equipment.

Figure 6.63. XRD patterns of p8 treated at different temperatures.
Table 6.7. XRD crystallite sizes of polymeric alumina membranes treated at 800 °C.

<table>
<thead>
<tr>
<th>Codes</th>
<th>Phase</th>
<th>2 theta</th>
<th>D(hkl) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p8</td>
<td>γ-Al2O3</td>
<td>45.82</td>
<td>D_{400} = 6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66.82</td>
<td>D_{440} = 6.8</td>
</tr>
<tr>
<td>p12</td>
<td>γ-Al2O3</td>
<td>37.63</td>
<td>D_{311} = 5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45.82</td>
<td>D_{400} = 8.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66.82</td>
<td>D_{440} = 6.3</td>
</tr>
<tr>
<td>p13</td>
<td>γ-Al2O3</td>
<td>45.82</td>
<td>D_{400} = 7.7</td>
</tr>
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<td></td>
<td></td>
<td>66.82</td>
<td>D_{440} = 14.9</td>
</tr>
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<td>p14</td>
<td>γ-Al2O3</td>
<td>45.82</td>
<td>D_{400} = 7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66.82</td>
<td>D_{440} = 7.8</td>
</tr>
</tbody>
</table>

The variation of the particle size of the polymeric alumina sol and the crystallite size of the 800 °C treated unsupported membranes with the acid content of the sol is given in Figure 6.64. The increase in concentration of acid caused decreases in both particle size and crystallite size up to [H⁺]/[Al³⁺] of 0.5. Almost constant crystallite size of ~7 nm was obtained with a small variation by changing process parameters upon heat treatment at 800 °C.

![Figure 6.64. Effect of process parameters on the particle size of the sols and the crystallite size of the 800 °C treated membranes.](image-url)
Boehmite transforms on heating through a series of transitional aluminas (γ-, δ-, θ-Al₂O₃) and finally thermodynamically stable α-Al₂O₃ due to the dehydration and rearrangements. A typical sequence of crystallization with approximate temperatures (°C) is the following (Tsukada et al., 1999);

$$
\begin{align*}
&\gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3 \\
&\rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \theta\text{-Al}_2\text{O}_3 \\
&\rightarrow \alpha\text{-Al}_2\text{O}_3
\end{align*}
$$

Topotactic transformation from γ- to δ-, θ-Al₂O₃ involves only small energy difference while transformation from θ- to α-Al₂O₃ requires a reconstruction of the structure through rearrangement of oxygens from cubic to hexagonal accomplished by large energy difference. Figure 6.65 shows typical TGA/DTA curves of polymeric alumina unsupported membranes. A sharp weight loss occurred in the temperature interval 80-170 °C indicating the loss of water and solvent and in 170-300 °C caused by the decomposition of organic groups, elimination of adsorbed water in the membrane pores. In Figure 6.66, slower gradual weight losses (wt. ~14%) in the interval 300-450 °C is detailed and that might correspond to boehmite decomposition into the γ-Al₂O₃ phase involving elimination of OH groups according to the reaction (Alphonse and Courty, 2005);

$$
2\text{AlOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}
$$

The weight loss beyond 600 °C was negligible. The DTA curve shown in Figure 6.65 includes the first endothermic peak at ~100 °C corresponds to the removal of physisorbed water and solvent. A distinctive exothermic peak at 165 °C and small peak at 205 °C would be attributed to the decomposition of organics. Exothermic peaks at 330 °C and 885 °C may correspond to the conversion from boehmite to amorphous gamma alumina and the crystallization of gamma phase, respectively. Crystallization of gamma phase at ~ 850 °C appear to be correlated with XRD pattern in Figure 6.63 in which pure gamma peaks were detected at temperatures ≥ 800°C. There is also no evidence of the formation of gamma phase below 800 °C due to the amorphous structure of this phase. The small crystalline size of the boehmite might cause the decrease in phase transformation temperatures. Transformation mechanisms depend on the size of the crystallites as those being nucleation controlled in large crystallites,
phase boundary controlled in medium size crystallites and diffusion controlled in small size crystallites (Tsukada et al., 1999). The conversion boehmite to gamma alumina includes dehydration that occurs slowly for the large crystallites and suppresses the transformation leading to increase in temperatures.

Figure 6.65. DTA and TGA curves of unsupported alumina membranes (p8).

Figure 6.66. TGA curves of unsupported alumina membranes (p8).
Figure 6.67 shows that the TGA curves of unsupported polymeric membranes synthesised at various process parameters. The difference in weight loss among samples might be caused by solvent evaporation during drying. The higher weight loss could be ascribed by the evaporation of encapsulated solvent for the sols having small particle sizes. The exothermic peak at around 830 °C shown in Figure 6.68 that might corresponds to the transformation to alpha phase shifted to larger temperatures (to 885 °C) upon change in process parameters. This might be related with the size of the particles since it shows correlation with the phase transformation temperatures of boehmite to gamma and transition phases to alpha phases.

Figure 6.67. TGA curves of unsupported alumina membranes.
The shrinkage and temperature dependent derivative of shrinkage \((d(\Delta L/L_0)/dT)\) curves for the p9 sample is given in Figure 6.69 indicating four major shrinkage events at 160, 290, 837 and 1100 °C. These temperatures agree well with the DTA exotherms suggesting the gamma alumina crystallization at \(~850\ °C\). Another strong peak appeared at 1100 °C might tought to be the result of the densification of alpha phase. The result indicate that \(\alpha\)-Al\(_2\)O\(_3\) transformation is occurred below this temperature which can be related to the fine network structure. The total thermal shrinkage was to be found as 42 % up to 1200 °C.
6.3.2. Structural/Thermal/Densification Evaluation of Unsupported Mullite Membranes

Mullite has gained considerable attention due to its thermal, mechanical and optical properties like low thermal expansion and thermal conductivity, good chemical, oxidation resistance and it is the only stable binary phase in the Al₂O₃–SiO₂ system (Kleebe et al., 2001). It is assumed that stable mullites exist in the range of compositions between 3Al₂O₃·2SiO₂ (3:2) and 2Al₂O₃·SiO₂ (2:1) (de Sola et al., 2007). The sol-gel processing has been used during the last decade for producing mullite with chemically homogeneous structures (Cassidy et al., 1997).

The sol-gel processing can allow mullite formation at low temperature with controlled structures and surface chemistry due to mixing of alumina and silica on a molecular scale. However, due to the difference in hydrolysis rate, Al(III) and Si(IV) alkoxides may result in some segregation preventing the formation of chemically homogeneous mullite oxide network. A variety of crystallization reactions from chemically synthesised precursors leading to the formation of mullite ceramics of high chemical purity in the temperature range of 850 °C to 1350 °C (Griggio et al., 2008; Sunderesan and Aksay, 1991).

Mullite precursors can be classified as either single phase (atomic level homogeneity) or diphasic (homogeneity in nanometer range). The chemical homogeneity of the precursors determines the temperature range where total mullitization is achieved as well as the transformation mechanisms. Single-phase precursors including chemical vapour deposition, spray pyrolysis and polymer precursor method exhibit direct mullitization from the amorphous state at temperatures as low as 950 °C, while diphasic precursors (colloidal) mullitize above 1200 °C by the reaction of transient spinel type alumina with silica. The behavior of a mullite precursor is a direct result of the starting materials and of the synthesis conditions used (Kojdecki et al., 2007.; Kansal and Laine, 1997). In monophasic mullite formation, when an amorphous precursor displays atomic-scale arrangement of -Al-O-Si- groupings very similar to that of mullite, and the crystallization of mullite occurs by a nucleation-controlled process. The reaction between alumina surface and amorphous silica matrix causes the formation of mullite at temperature in 1200-1350 °C range and can be expressed as (Sunderesan and Aksay, 1991);
The mullite formation kinetic for the diphasic systems has been determined as the nucleation and growth process in which the controlling step is diffusion of reactants to the growth interface and the rate of mullite formation is much slower than that in monophasic system (Li and Thomson, 1990). Sunderesan and Aksay, (1991) stated that after nucleation of mullite within the matrix, the subsequent growth is controlled by the dissolution of alumina but not by interdiffusion through the mullite.

The development of mullite membranes with fine microstructure is essential in terms of high thermal stability. The use of polymeric alumina sol prepared through acidic hydrolysis of alkoxide in alcoholic solvent with low water ratio made possible the preparation of stable alumina-silica sol which underwent mullite transformation upon heating. The mixed alumina-silica sols were prepared by mixing separate sols with an Al₂O₃:SiO₂ mol ratio of 1.5. The FTIR spectra of mixed sols as a function of heat treatment are given in Figure 6.70. Mullite has both AlO₄ and AlO₆ polyhedra connected to SiO₄. The characteristics peak of Al-O and Si-O bonds are in the 1200-400 cm⁻¹ (Padmaja et al., 2006).

![Figure 6.70. FTIR spectra of unsupported mixed alumina-silica membranes treated at different temperatures.](image)

The reported standard mullite IR spectra are consisting of the following: tetrahedral (SiO₄) (Si–O) vibrations at 1130 and 1170 cm⁻¹, tetrahedral (AlO₄) (Al–O) vibrations at 740 and 830 cm⁻¹, and octahedral (AlO₆) (Al–O) vibrations in the range of 530–680 cm⁻¹.
The two bands for AlO₄ and AlO₆ probably each result from Si–O–Al and Al–O–Al bonds (Kansal and Laine, 1997). The spectra shown in Figure 6.70 are zoomed in to 400-1400 cm⁻¹ range in Figure 6.71. Although a weak band at 1150 cm⁻¹ is observed for 800 °C treated sample, characteristic band of tetrahedral Si-O in SiO₂ at 1100 cm⁻¹ is found at temperatures of 600 °C and 800 °C. Heating upon 875 and 900 °C caused splitting of this peak and the spectra show a strong band at ~1110 cm⁻¹, with a weak shoulder at about 1170 cm⁻¹ which is attributed to tetrahedral (Si–O) vibrations in mullite. Although, weak absorption bonds that could be assigned to amorphous silica at 800 cm⁻¹ was detected at temperatures in the range of 600–875°C, at 900 °C this band was diminished. No well-defined bands due to AlO₄ (Al–O) vibrations are observed at 600, 800, 875 and 850 °C. At these temperatures, a broad envelope centered at 700 cm⁻¹ with weak band at 812 cm⁻¹, most likely results from mixed bands due to AlO₄ and AlO₆ (Al–O) vibrations. At only 900°C, a weak band at 820 cm⁻¹ can be assigned to AlO₄ (Al–O) vibrations in mullite. The bands at 560 cm⁻¹, 590 cm⁻¹, 528 cm⁻¹ and 670 cm⁻¹ for all samples are due to octahedral (AlO₆) (Al–O) vibrations. The band at 670 cm⁻¹ is sharper at 800 °C.

Figure 6.71. FTIR spectra of unsupported mixed alumina-silica membranes treated at different temperatures.

The mixture of aged polymeric silica (Si-std) and polymeric alumina sols (p9) in mullite compositions (3:2) led to the crystallization of mullite upon heat treatment at 875 °C as evidenced by peaks at 20 values of ~16°, 26°, 35° and 45°, etc. These peaks correspond for stoichiometric mullite, 3Al₂O₃.2SiO₂ (JCPDS, file 15-776). The
crystallite sizes of mullite unsupported membranes treated at 900 °C are tabulated in Table 6.8. XRD patterns of mixed alumina and silica and pure polymeric silica unsupported membranes are shown in Figures 6.72 and 6.73 respectively, and these figures obviously indicated that the phase pure mullite at low temperatures could be obtained by using stable polymeric alumina and silica sols. There is no indication was found for the formation of spinel phase (sharp 2θ peak at 43°) suggesting the formation of structure with a higher degree of homogeneity because of better atomic mixture (Kansal and Laine, 1997).

![XRD patterns of unsupported mullite membranes.](image)

Table 6.8. XRD crystallite sizes of unsupported mixed membranes treated at 900 °C.

<table>
<thead>
<tr>
<th>Codes</th>
<th>Phase</th>
<th>°2 theta</th>
<th>D_{hkl}</th>
<th>°2 theta</th>
<th>D_{hkl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>P9+Si-std</td>
<td>3Al₂O₃·2SiO₂</td>
<td>16.55</td>
<td>30</td>
<td>42.7</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26.25</td>
<td>23</td>
<td>47.5</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31.1</td>
<td>41</td>
<td>53.8</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>33.3</td>
<td>25</td>
<td>60.7</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39.4</td>
<td>37</td>
<td>64.7</td>
<td>25</td>
</tr>
</tbody>
</table>
The X-ray patterns indicate that the mixed material is completely amorphous until at least 875 °C while the pure silica shows distinctive cristobalite crystallization at 800 °C as shown in Figure 6.73. This might be also the indication of the homogeneously mixed oxide structure having very fine, stable microstructure could be created.

Figure 6.73. XRD patterns unsupported silica membranes treated at various temperatures.

The use of freshly prepared sols for mullite formation decreased the crystallization temperature as shown in Figure 6.74. This might be caused by the fact that the unaged sols have smaller particle size than those for aged sols. Although broad peaks have been observed at 775 °C, and 800 °C, the transformation to crystalline mullite has occurred and pattern gave rise to sharp X-ray peaks because of grain growths. At 850 °C, the strongest mullite peaks was obtained. Besides the high specific surface of nanosized boehmite species, the low transformation temperature could be attributed to the highly reactive amorphous silica deriving from polymeric sol-gel route. Kansal and Laine (1997), used the splitting of the peak at 26.15° 2θ in tetragonal mullite (on heating at temperatures >1000°C) as a means of estimating the extent of conversion of the tetragonal phase to the orthorhombic phase. No splitting has been observed for the samples treated at 1000 °C indicating only tetragonal phase. The orthorhombic mullite with a conversion of 87% has been obtained on heating to 1400 °C. The extended scale of 2θ values in 25-27° range is shown inside the Figure 6.74. It is distinguished that the mullite formed at low temperature as 775 °C, a clear splitting of peaks can be thought as a direct orthombic mullite formation.
The change in crystallite size of selected planes with heat treatment temperature is shown in Figure 6.75. The crystallite size exhibited direct relation with heat treatment temperature as a result of growth of mullite crystallites.

The corresponding dimensional change and shrinkage rate curves of unsupported mullite membrane are given in Figure 6.76. Rapid shrinkage at 150 °C may associate with the fast removal of solvent. At temperatures below 400 °C, shrinkage of sample could be ascribed to removal of organics and polymerization of inorganic networks. XRD studies of membranes prepared from aged sol closely correlate the
shrinkage at 945 °C with crystallization of mullite. It is thus likely that shrinkage due to
the growth of mullite crystals is occurred. Holding time difference for both experiments
may cause temperature difference for crystallization. The final linear shrinkage is 35%.

Figure 6.76. Shrinkage and shrinkage rate curves during heat treatment at heating rate 5
°C/min for dry-pressed sample of mullite.

The thermal behaviour mullite membrane is summarized in Figure 6.77 as TGA
and DTA curves. No mass loss was detected at ~945 °C indicating the mullite is
crystallized through atomic re-arrangements within amorphous state (Okada, 2008). The
absence of crystallization exotherm in ~900-1000 °C range could be the result of
applied high heating rate during DTA experiment.

Figure 6.77. DTA and TGA curves of unsupported mullite membrane.
6.4. Gas Permeation

In this section pure gas (N\textsubscript{2}, O\textsubscript{2} and CO\textsubscript{2}) permeation properties of three different parts of which ceramic membranes having controlled pore structure are composed of, macroporous alumina support, both polymeric and colloidal alumina intermediate layers as well as the particulate/polymeric microporous silica membranes are described. It would be aimed to establish an understanding of the relationship between the controlled membrane microstructure and the transport properties.

6.4.1. Gas Permeation through Macroporous Support

The ratio of the mean free path of the diffusing gases (λ\textsubscript{N2} = 34 nm and λ\textsubscript{CO2} = 42 nm) to the pore size of the membranes is greater than one (at 298K and 2 atm) for γ-alumina and silica membranes. Since the mean free paths of the gases are much larger than the pore size of membrane, transport through the membrane has generally been described by the Knudsen diffusion mechanism in which molecules-pore wall collisions overwhelms intermolecular collisions. For defect free mesoporous membranes which are certainly in the Knudsen region, the permeation (mol/m\textsuperscript{2}sPa) versus the pressure should give a horizontal line because Knudsen flow is pressure independent. Pressure dependency in permeance is the indication of contribution of viscous flow. However, transport mechanisms can occur simultaneously, when the mean free path of the gases is comparable with the pore diameter, Knudsen and viscous flow can be considered to be additive that can be defined as Equation 3.12.

\[
J = -\frac{1}{RT} \left( D_{Kn} + \frac{B_o}{\eta} P_m \right) \frac{dp}{dz} \tag{3.12}
\]

When this equation is valid, a plot of the permeance \( F \) versus the average pressure yields a straight line. The intercept of this line is associated with the contribution of Knudsen flow, and the slope is associated with the contribution of viscous flow. Both the slope and the intercept are influenced by the structure of the porous medium, the temperature and the gas used. An expression in the form of \( y = ax + b \) can be obtained after appropriate manipulation of Equation 3.12, in which \( a \) and \( b \) only depend on the
structure of the porous medium. The corresponding variables $y$ and $x$ are $RL(MT)^{0.5} F$ and $(M/T)^{0.5}p_{av}/\eta$, respectively. In Figure 6.78, $y$ is plotted versus $x$, for single gas permeance of different gases through an AKP-50 slip cast, 1150 °C treated $\alpha$-alumina support layer.

\[ y = 0.1082x + 0.7125 \quad R^2 = 0.9667 \]
\[ y = 0.1095x + 0.6961 \quad R^2 = 0.9609 \]
\[ y = 0.1009x + 0.6814 \quad R^2 = 0.9894 \]

Figure 6.78. Single gas permeance of various gases through $\alpha$-alumina (AKP-50).

From the figure it is clear that for all the gases considered the permeance increases linearly with average pressure. From the $a$ and $b$ values, the structure parameters $K_o$ and $B_o$ can be obtained. Assuming cylindrical pores these parameters can also be interpreted in terms of a flow average pore size $d_p$ and tortuosity $\tau$, provided the porosity is known. In Table 6.9 the values for these parameters are presented for the different gases, obtained from intercept and slope of the experimental data with the assumption of 40% porosity.
Table 6.9. Structural parameters of AKP-50 obtained from permeance measurements.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetic Diameter</td>
<td>nm</td>
<td>0.346</td>
<td>0.364</td>
<td>0.33</td>
</tr>
<tr>
<td>η</td>
<td>Pa.s</td>
<td>2.00E-05</td>
<td>1.80E-05</td>
<td>1.45E-05</td>
</tr>
<tr>
<td>M</td>
<td>kg/mol</td>
<td>0.032</td>
<td>0.028014</td>
<td>0.044</td>
</tr>
<tr>
<td>v</td>
<td>m/s</td>
<td>444.05</td>
<td>474.59</td>
<td>378.68</td>
</tr>
<tr>
<td>Slope (B₀)</td>
<td>m²/s(mol/K)⁰.⁵</td>
<td>1.10E-17</td>
<td>1.01E-17</td>
<td>1.08E-17</td>
</tr>
<tr>
<td>Intercept (Dkn*(M/T)⁰.⁵)</td>
<td>m²</td>
<td>6.96E-09</td>
<td>6.81E-09</td>
<td>7.12E-09</td>
</tr>
<tr>
<td>Dkn</td>
<td>m²/s</td>
<td>6.71E-07</td>
<td>7.03E-07</td>
<td>5.86E-07</td>
</tr>
<tr>
<td>K₀</td>
<td>m</td>
<td>1.13E-09</td>
<td>1.11E-09</td>
<td>1.16E-09</td>
</tr>
<tr>
<td>B₀/K₀ (d₀/8)</td>
<td>m</td>
<td>9.65E-09</td>
<td>9.08E-09</td>
<td>9.31E-09</td>
</tr>
<tr>
<td>d₀</td>
<td>nm</td>
<td>77.19</td>
<td>72.66</td>
<td>74.52</td>
</tr>
<tr>
<td>ε/τ (from B₀)</td>
<td>-</td>
<td>0.06</td>
<td>6.12E-02</td>
<td>6.24E-02</td>
</tr>
<tr>
<td>ε/τ (from K₀)</td>
<td>-</td>
<td>5.88E-02</td>
<td>6.12E-02</td>
<td>6.24E-02</td>
</tr>
<tr>
<td>τ</td>
<td>-</td>
<td>6.80</td>
<td>6.54</td>
<td>6.42</td>
</tr>
</tbody>
</table>

K₀ and B₀ are almost the same for all gases. Therefore, approximately same values obtained for the flow average pore size as 75±2.5 nm and the values obtained for the tortuosity are physically realistic. The increase in heat treatment temperature to 1160 °C caused insignificant variation in pore diameter (72.4 nm) obtained from N₂ permeance. The values obtained for the flow average pore size are comparable with the value of the pore size determined by Hg intrusion measurements located at 110 nm shown in Figure 6.79. In Figure 6.80, SEM micrograph of the fracture surface of the 1160 °C treated slip-cast alumina support indicated the presence of ~100 nm size particles in a uniform porous structure.

Figure 6.79. Pore size distribution of 1160 °C treated slip-cast alumina support.
In contrast to slip-cast support, the intercept and the slope are dependent on the gas molecule shown in Figure 6.81 for the dry pressed support. Therefore, calculated structural parameters and the pore diameter are very different for different gases tabulated in Table 6.10.

![Figure 6.80. SEM micrograph of 1160 °C treated slip-cast alumina support.](image)

![Figure 6.81. Single gas permeance of various gases through dry presssed α-alumina (AKP-50).](image)
Table 6.10. Structural parameters of dry-pressed AKP-50 obtained from permeance measurements, ($\varepsilon=0.40$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>$O_2$</th>
<th>$N_2$</th>
<th>$CO_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope ($B_o$)</td>
<td>m²/s(kg/molK)^0.5</td>
<td>2.55E-17</td>
<td>1.53E-17</td>
<td>2.10E-10</td>
</tr>
<tr>
<td>Intercept ($D_{kn}*(M/T)^{0.5}$)</td>
<td>m²</td>
<td>9.99E-9</td>
<td>1.062E-08</td>
<td>9.88E-9</td>
</tr>
<tr>
<td>$D_{kn}$</td>
<td>m²/s</td>
<td>9.64E-7</td>
<td>1.0956E-6</td>
<td>8.13E-7</td>
</tr>
<tr>
<td>$K_o$</td>
<td>m</td>
<td>1.63E-9</td>
<td>1.73E-9</td>
<td>1.61E-9</td>
</tr>
<tr>
<td>$d_p$ (nm)</td>
<td>-</td>
<td>125</td>
<td>70.5</td>
<td>104</td>
</tr>
<tr>
<td>$\varepsilon/\tau$ (from $K_o$)</td>
<td>-</td>
<td>5.21E-2</td>
<td>9.83E-2</td>
<td>6.19E-2</td>
</tr>
<tr>
<td>$\tau$</td>
<td>-</td>
<td>7.68</td>
<td>4.07</td>
<td>6.46</td>
</tr>
</tbody>
</table>

In Figure 6.82, the single gas permeance of $CO_2$, $N_2$ and $O_2$ through an Alcoa $\alpha$-alumina sample is presented. Even, the particle size of this sample larger than the AKP-50, the additive model was applied for the permeance values obtained from dry pressed sample.

![Figure 6.82. Single gas permeance of various gases through dry presssed $\alpha$-alumina (Alcoa).](image-url)
In Table 6.11 the values of structural parameters are presented for the different gases, obtained from intercept and slope of the experimental data. The calculated pore diameter is larger than the AKP-50 support consistent to difference in particle size of powders. Indeed, higher heat treatment temperature was applied for the alcoa supports due to the difference in sintering behaviour of two powders.

Table 6.11. Structural parameters of dry-pressed Alcoa obtained from permeance measurements, (ε=0.40).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope (B₀)</td>
<td>m²/s(kg/molK)⁰.s</td>
<td>4.26E-17</td>
<td>4.04E-17</td>
<td>4.19E-17</td>
</tr>
<tr>
<td>Intercept</td>
<td>m²</td>
<td>1.1680E-08</td>
<td>1.2000E-08</td>
<td>1.1392E-08</td>
</tr>
<tr>
<td>Dkn</td>
<td>m²/s</td>
<td>1.12742E-06</td>
<td>1.23797E-06</td>
<td>9.37759E-07</td>
</tr>
<tr>
<td>K₀</td>
<td>m</td>
<td>1.90422E-09</td>
<td>1.95639E-09</td>
<td>1.85726E-09</td>
</tr>
<tr>
<td>dp (nm)</td>
<td>nm</td>
<td>179.01</td>
<td>165.00</td>
<td>180.31</td>
</tr>
<tr>
<td>ε/τ</td>
<td>-</td>
<td>4.25E-02</td>
<td>4.74E-02</td>
<td>4.12E-02</td>
</tr>
<tr>
<td>τ</td>
<td>-</td>
<td>9.40</td>
<td>8.43</td>
<td>9.71</td>
</tr>
</tbody>
</table>

N₂ and CO₂ permeances through alumina supports are summarized in Figure 6.83. Slight pressure dependency of permeation indicated the both viscous flow and Knudsen diffusion dominate the transport through the membranes. However, variation in permeances with pressure is more significant for the alcoa support indicating the presence of larger pores. Higher permeance values were obtained for dry-pressed AKP-50 support as compared to slip-cast support. This suggests that the packing behaviour of supports affected by consolidation type. In the case of slip cast support, the colloidal state of the suspension has a direct influence of the eventual microstructure of supports. By controlling the dispersity of suspension either by sterically of statically, it can be possible to increase porosity while retaining relatively fine pores on top surfaces with more closely packed structure as revealed from the SEM micrographs of top surfaces of both supports (Figure 6.84).
6.4.2. Gas Permeation through Colloidal/Polymeric Alumina Membranes

Almost same permeance values have been obtained for two and three layer colloidal alumina membranes as shown in Figure 6.85. This is most likely the use of very dilute boehmite sol to prevent increase in thickness for decreasing flow resistance. Pressure independent permeance obtained for both membranes implies that the dominant transport mechanism is Knudsen diffusion as could be expected with a pore size in 2.5-3 nm range.
The improved permeability as well as the inverse temperature dependency on permeability and relatively high permselectivity has been obtained for the graded alumina membranes as compared to 3-layer ungraded membrane shown in Figure 6.86. Graded structure at mesoporous alumina membranes has provide superior transport properties in terms of permeability and permselectivity and also Gu and Oyama (2007) reported that this structure results in greater interactions among the particles in the region where particle size changes causing greater hydrothermal stability.

Figure 6.86. (a) Permeances through three layer alumina membranes, (b) temperature dependence of permeances through graded alumina membranes.
A characteristic feature of gas transport by the Knudsen mechanism is that permeance shows an inverse square root dependence on temperature and molecular weight of the diffusing gas molecule. Therefore, every diffusing gas should have the same value of \( \frac{P}{l} \sqrt{MT} = \left(\frac{\epsilon dp}{\tau l} \right) \left(\frac{8}{9\pi R}\right)^{0.5} \) independent of temperature if gas transport through the membrane involved only Knudsen diffusion. Gas permeance data on alumina membranes analyzed in this manner are shown in Figure 6.87. Relatively constant values of \( \frac{P}{l} \sqrt{MT} \) for O\(_2\), N\(_2\), and CO\(_2\) indicate that the transport of these gases through the alumina membrane takes place mainly by the Knudsen diffusion mechanism. However, this value gets closer for the graded structured alumina membranes indicating that more homogeneous and defect-free membrane layer.

![Figure 6.87. \( \frac{P}{l} \sqrt{MT} \) values for alumina membranes.](image)

The experimental gas permeance through the graded alumina membrane was also plotted versus the inverse square root of temperatures for different gases, and the linear regression fits are shown in Figure 6.88. The results show a good linear dependence \((0.991 < R^2 < 0.989)\) confirming that the gas transport occurred mainly by Knudsen diffusion in which the interaction of molecule-pore wall is more significant than molecule-molecule interaction.
The permeances through 2-layer polymeric alumina membrane (p9) with temperature dependence behaviour of different gases are shown in Figure 6.89. Permeance values show characteristics of Knudsen diffusion behaviour as those having inverse temperature dependence and constant values with pressure.

Knudsen plot of p9 membrane is given in Figure 6.90.c, where the dashed line was obtained by fitting the data for the simplified Knudsen diffusion permeability equation (Eqn 3.5) (Boffa et al., 2009);
\[
\frac{P}{l}_{Knudsen} = K \sqrt{\frac{1}{MRT}}
\]

(6.8)

where \( M \) is the molecular mass of the permeating species, \( T \) refers to the absolute temperature, \( R \) is the gas constant and \( K \) is constant that depends on structural parameters (pore size, porosity, tortuosity). The quite complete agreement between experimental values Knudsen diffusion equation implies that the dominant transport through the membrane is Knudsen diffusion. The constant \( K \) was determined as 4.75E-5 \( \text{kgPa}^{-1}\text{s}^{-2}\text{m}^{-1} \) by linear fitting with \( R^2 \) of 0.983. Figure 6.90.d indicates that molecular sieving effect could not be achieved as it would not be expected in Knudsen diffusion regime. The thickness of membrane was determined as about 300 nm from SEM micrograph of pulled out region on edge top surface (Figure 6.90.d). Indeed, as compared to colloidal mesoporous alumina membranes, finer structure with thin layer has been obtained by packing of polymeric boehmite species but, permeation properties has showed the Knudsen diffusion characteristics as those dominated through the most of the mesoporous membranes. Therefore, the preparation of microporous defect free alumina layer requires optimization of the dipping conditions like dipping time, withdrawal rate and sol concentration in order to obtain membranes having molecular sieving capabilities.

Comparable results have been almost found for the permeances of \( \text{N}_2, \text{O}_2 \) and \( \text{CO}_2 \) through p14 polymeric alumina membranes as shown in Figure 6.91. On the other hand, Knudsen plot showed that there is not complete agreement experimental and predicted values that might caused by the contribution of viscous flow to the total transport.
Figure 6.90. (a) SEM micrographs of top surfaces p9-membrane (50000X), (b) 100000X, (c) Knudsen plot of p9 membrane, (d) permeances as a function of kinetic diameters.

Figure 6.91. (a) Permeances through 2-layer polymeric alumina membranes (p14), (b) Knudsen plot of p14 membrane.
6.4.3. Gas Permeation through Colloidal/Polymeric Silica Membranes

The influence of parameters like pH and particle size of the particulate silica sol as a function of feed pressure on permeation properties was investigated. The change in pore structure with respect to pH of the sol was also been observed from the permeation analysis through the membranes treated at 400 °C given in Figure 6.92. The dipping time and withdrawal speed were 5 s and 200 mm/min, respectively. The membrane corresponding the sol having the particles 5 nm in size in basic medium resulted in increase in both N₂ and CO₂ permeances as a result of change in packing properties through consolidation of membrane. The change in permeance values with pressure is more significant for the membrane synthesised from basic sol as compared to that from acidic sol suggesting that the small contribution of laminar flow.

Figure 6.92. Effect of the pH of sol on permeance through colloidal silica membranes.

Figure 6.93 illustrates that permeance of gases decrease with increase in particle size of the sol. However, it is expected that the packing of smaller particles give rise to smaller pores with constant porosity that may cause decrease in permeances through the membrane. It is probable that despite the small particle size, the thermal instability causes the collapse of the pore network resulted in increase in permeances through the membranes. This is most likely due to the formation of loosely packed structure with larger pores as a result of being particles sinter active in this temperature, because of the fact that the sintering rate is roughly proportional to the inverse of the particle size. Brinker et al., (1993) have also explained the dependence of particle size on crack formation as being related to increasing volume fraction of tightly bound solvent layer
that creates tensile stress during drying with decreasing particle size based on the DLVO theory.

Figure 6.93. Effect of sol sphere size on permeance through colloidal silica membranes.

Permeability of $N_2$ was determined from 40 to 400 °C in order to investigate the thermal stability of silica membranes. The increase in $N_2$ permeation through silica membranes corresponding to 10 and 25 nm particle size of sols with heat treatment temperature is shown in Figure 6.94. Almost constant permeances at temperatures in 150 to 400 °C range may indicate the stability of pore network of the membranes in this temperature range. Contrary to the above result, increasing packed particle size from 10 nm to 25 nm yielded the increase in $N_2$ permeance from $1.5 \times 10^{-7}$ to $1.7 \times 10^{-7}$ mol/m²sPa.

Figure 6.94. Effect of heat treatment on $N_2$ permeance through silica membrane corresponding the sol (a) 10 nm in size, (b) 25 nm in size.
The stability and the ability of the control of pore network may be provided by adding monodisperse silica spheres in different diameters with appropriate surface properties into the polymeric sol at the sol stage in order to achieve a more reliable microporous silica membrane. The volume fraction and the diameter of added spheres can affect the gelation and the consolidation properties of the membranes. The size and the concentration of spheres in polymeric silica sol were varied to investigate the thermal stability of the membranes which had been heat treated in the 40-400 °C range by determining the single gas permeation behaviour as shown in Figure 6.95 and Figure 6.96. The dramatic difference in the permeance of N₂ upon the heat treatment of membranes is most likely due to the partial sintering and micro-crack formation during the consolidation. The addition of spheres in 310 nm size seems to be ineffective to improve the thermal stability of membranes. Increase (0.7 nm to 0.8 nm) in pore size has also been revealed with the addition of 310 nm silica spheres into the sol from N₂ adsorption-desorption analysis results.

The N₂ permeation through 90 nm in size silica sphere added silica membranes, in contrast to membrane having 310 nm in size spheres, remained constant when applied heat treatment temperature was in 250-400 °C as shown in Figure 6.96(a). The spheres are likely to incorporate into the gel without any destabilization through the pore network that may cause stiffening the network to prevent collapse of the membrane structure. Figure 6.96.b shows the SEM micrograph of the top surface of a 150 °C treated silica membrane derived from polymeric silica sol having 15 vol% 90 nm in size.
silica spheres. There are no apparent cracks and pinholes on membrane surface. Therefore, defect free membrane layer is accompanied by homogeneously distributed mono size silica spheres on membrane surface.

Figure 6.96. (a) Effect of 90 nm sphere addition on N₂ permeance through polymeric silica membranes, (b) SEM micrograph of top surface of 150 °C treated silica membranes having 90 nm spheres.

Figure 6.97 shows the effect of heat treatment and sphere concentration on N₂ permeance values of 220 nm loaded 1-layer silica membranes. The permeances through the membrane to different gases also are given in Figure 6.97.d. In the case of 5 vol% loaded membrane, the nitrogen permeance was the lowest value of $3.85 \times 10^{-9}$ mol/m²sPa upon heat treatment at 40 °C. The 10 vol% loaded silica membranes were prepared with same concentration but with different diluting medium. Comparison of the Figures 6.97.b and c shows that utilizing the ethylene glycol caused only small permeance decreases through the membrane. On the other hand, 10 vol% loaded membranes had almost constant nitrogen permeance values in heat treatment temperature range of 40-250 °C shown in Figure 6.97.b while abrupt decrease in nitrogen permeance was revealed for 5 vol% loaded membrane upon heat treatment temperature to 100 °C (Figure 6.97.c). Therefore, the stability of pore network has been enhanced by increasing volume fractions of sphere of 220 nm in size.
Although the nitrogen permeance value through the ethylene glycol diluted 10 vol% loaded membrane remained more or less constant up to 250 °C, the significant increase in permeance values upon heat treatment to 400 °C could not be prevented by the addition of 220 nm spheres into polymeric silica network as shown in Figure 6.98. The thermal stability of pore network up to 250 °C might be provided by the organically bounded inorganic species that suppress the stress induced cracking on membrane surface by increasing toughness of film (Castricum et al., 2008). On the other hand, as evidenced from the TGA analysis (Figure 6.40), the removal of chemically interacted organic moieties in temperature 280 and 300 °C range resulted in increase in permeance values by either formation of large pores or microcracks on surfaces.
Figure 6.98. Effects of sphere concentration on N₂ permeances through 220 nm sphere loaded 1-layer silica membranes.

The nitrogen permeance values increased from $2.8 \times 10^{-8}$ mol/m²sPa to $6.3 \times 10^{-8}$ mol/m²sPa through 140 nm loaded membranes by changing heat treatment temperature in 250-400 °C range while for the unloaded silica membranes this change was more prominent ($6.2 \times 10^{-8}$ to $1.6 \times 10^{-7}$ mol/m²sPa ) as indicated in Figure 6.99.

Figure 6.99. Effects of sphere concentration on N₂ permeances through 140 nm sphere loaded 1-layer silica membranes.
The coating of second layer caused the decrease in N\textsubscript{2} permeance values from $8.3 \times 10^{-8}$ mol/m\textsuperscript{2}sPa down to $9.7 \times 10^{-9}$ mol/m\textsuperscript{2}sPa and from $8.1 \times 10^{-8}$ mol/m\textsuperscript{2}sPa down to $3.6 \times 10^{-8}$ mol/m\textsuperscript{2}sPa through the 400 °C treated vol 5% and vol 10% sphere 220 nm loaded membranes, respectively. Difference in permeability might be related to the thickness of the membrane layer. Decrease in permeance values may caused by increasing the film thickness which increases membrane resistance. Figure 6.100 shows the effect of heat treatment temperatures through 2-layer 5 vol% and 10 vol% sphere 220 nm loaded membranes. The 5 vol% loaded 40 °C treated silica membrane had a lower permeance of $1.9 \times 10^{-9}$ mol/m\textsuperscript{2}sPa for nitrogen.

![Figure 6.100. Effect of heat treatment on N\textsubscript{2} permeances through 2-layer 220 nm sphere loaded silica membranes.](image)

In Figure 6.101, the permeance values of 400 °C treated 2-layer 220 nm sphere loaded silica membranes for different gases are shown. The 5 vol% loaded silica membrane had better performance in terms of permselectivities of gases as compared to 10 vol% loaded silica membrane.
Figure 6.101. Permeance values of different gases through 2-layer 220 nm sphere loaded silica membranes.

Figure 6.102 shows the permeance values of 400 °C treated 2-layer 140 nm sphere loaded silica membranes for different gases. Almost constant permselectivities have been obtained for both concentration of 140 nm sphere loaded membrane.

Figure 6.102. Permeance values of different gases through 2-layer 140 nm sphere loaded silica membranes.

In Figure 6.103 the temperature dependencies of the O₂, N₂ and CO₂ permeances of 2-layer (a) 5 vol%, (b) 10 vol% and (c) 10 vol% EG diluted 220 nm sphere loaded silica membranes are shown. In contrast to 5 vol% and 10 vol% loaded membranes, the N₂ permeance across the membrane prepared with ethylene glycol diluted sol increased
up to 350 °C and remained constant to 400 °C. The increase in permeability with increasing temperature leads to positive activation energy indicating the activated transport through the microporous selective layer (Benes et al., 2000). The positive activation energy might caused by either the formation of organically bounded inorganic species due to utilizing ethylene glycol as a dilution medium that prevents the formation of microcracks on membrane surface or lower drying stress caused by slow drying in the course of ethylene glycol evaporation might results in crack-free membrane surface.

Figure 6.103. Temperature dependencies of the O₂, N₂ and CO₂ permeances of 2-layer 220 nm sphere loaded silica membranes.

The activation energy for permeation (combination of heat of sorption and activation energy for mobility) can be obtained by an expression of activated diffusion mechanism (deVos and Verweij, 1998);
\[
J = J_o \exp \left( \frac{-E_a}{RT} \frac{\Delta P}{L} \right)
\]

where \( J \) is flux (mol/m²s), \( J_o \) is temperature independent coefficient, \( E_a \) is apparent activation energy (kJ/mol), \( \Delta P \) is pressure difference across the membrane, \( L \) is membrane thickness, \( T \) is absolute temperature and \( R \) is the gas constant. Figure 6.104 shows Arrhenius plots of the \( \text{N}_2 \) permeances through 2 layer 220 nm sphere loaded membranes. Apparent activation energies of -3.4 kJ/mol and 17 kJ/mol were determined for 10 vol% and 10 vol% -ethylene glycol diluted membranes, respectively for nitrogen permeance. A negative value of \( E_a \) is generally caused by strong adsorption of the molecule on the pore surface as well as the contribution of Knudsen flow due to the inverse dependence of permeance on temperature is for Knudsen diffusion. Nair et al., (1998) reported that \( \text{N}_2 \) permeation is not always activated. Although the minus activated energy for \( \text{N}_2 \) has been also reported by Richard et al. (2001), for microporous silica membrane, Benes et al., (2000) found activation energy of \(~6\) kJ/mol for 400 °C treated silica membrane. The value of 18 kJ/mol determined for EG-diluted membrane is close to those reported by Boffa et al. (2009), who found apparent activation energy for He, and \( \text{H}_2 \) of \(~19\) kJ/mol and \(~16\) kJ/mol, respectively for niobia-silica membranes.

Figure 6.104. Arrhenius plots of the \( \text{N}_2 \) permeances through sp10-220 nm membranes.

In Figure 6.105 the temperature dependencies of the of 2-layer 140 nm sphere loaded silica membranes are shown. The permeances of both \( \text{N}_2 \) and \( \text{CO}_2 \) through 5 vol% loaded membranes remained constant with increasing temperature while small decrease of \( \text{N}_2 \) and \( \text{CO}_2 \) permeances was observed for 10 vol% loaded membranes.
Figure 6.105. Temperature dependence of the O\textsubscript{2}, N\textsubscript{2} and CO\textsubscript{2} permeances 2-layer (a) sp5-140 nm, (b) sp10-140 nm silica membranes.

The change in permeation behaviour of silica membranes with volume ratio of spheres based on silica species content is shown in Figure 6.106. As it can be seen, the silica membranes loaded 50 vol\% 310 nm spheres show high permeance values for both N\textsubscript{2}, and CO\textsubscript{2}, and the decrease in spheres concentration leads to decrease in permeances. This is most likely due to the formation of cracks on membrane surface for high sphere loading because of inhomogeneous distribution of spheres. The thickness of film is of great importance for crack formation. Although, the solid concentration of sol remained constant (0.7 vol\%), high volume ratio of spheres may result in more thick film tending to the formation of cracks.
Figure 6.106. Effects of spheres loading on permeation behaviour of 400 °C treated silica membranes: (a) N₂ permeance, (b) CO₂ permeance.

The membrane structure was also designed by incorporation of 5 nm sized spheres into polymeric structure having low fractal dimension as compared to colloidal particles. The N₂ permeance through the 400 °C treated membranes having different sphere content is given Figure 6.107. The significant increase in permeance values with increasing the sphere content might be related with the formation of the open percolative pore structure because of sphere packing.

Figure 6.107. N₂ permeances through 400 °C treated silica membranes having different volume content of 5 nm spheres.
Figure 6.108 shows the SEM micrograph of top surface of silica membranes having 74 %vol 5 nm sphere incorporated membranes. There is no evidence of the formation of the cracks on the membrane surface and 5 nm spheres have distributed uniformly into the polymeric silica matrix.

![SEM micrograph of sp74-5 nm silica membrane top surface (200000X).](image)

Figure 6.108. SEM micrograph of sp74-5 nm silica membrane top surface (200000X).

Permeances of N$_2$ and CO$_2$ at different temperatures through 2-layer membranes having 5 nm spheres at various volume concentrations are given in Figure 6.109. Although inverse temperature dependencies was found for 74 and 55 vol% loaded membranes, the permeances through 5 vol% loaded membranes remained almost constant with small increase in temperature 360-385 K range indicating the activated diffusion. The arrhenius plots of permeances are given in Figure 6.110 and activation energy of N$_2$ and CO$_2$ was found as -2 kJ/mol and 2 kJ/mol respectively.
Figure 6.109. Temperature dependence of 2-layer 5 nm sphere loaded silica membranes; (a) N$_2$ and (b) CO$_2$ permeances.

![Graph showing temperature dependence of permeance for N2 and CO2 through 5 nm sphere loaded silica membranes.](image)

Figure 6.110. Arrhenius plots of the permeances (P/l) of N$_2$ and CO$_2$ through sp5-5 nm silica membranes.

The literature values in Figure 6.111 indicate either positive activation energies for CO$_2$ permeance or negative values as well as the non-activated permeance as those in the study of Uhlhorn et al., (1992). The largest negative value was reported by Boffa et al., (2009), for niobia-silica membranes having also the lowest permeance values. The value calculated for 5 vol% -5nm loaded silica membranes is comparable to those reported in literature.
Figure 6.111. Comparisons of CO₂ permeance activation energy versus CO₂ permeance values with literature values.

Pure polymeric silica sol (2.5 vol%) was applied on 65 and 74 vol% sphere loaded membranes to repair any defects on membrane surface. The constant N₂ permeance values through 65 and 74 vol% 310 nm sphere loaded membrane layers has decreased about 1.5 and 2 fold, respectively by covering surface cracks and increasing film resistance as shown in Figure 6.112.

Figure 6.112. N₂ permeances through 2 layer silica membranes with polymeric top layer (dipping time: 10 s and withdrawal rate: 100 mm/min).
Dipping time effect on permeation was investigated for 20 and 30 vol% 310 nm loaded silica membranes in which SiEg was used as polymeric species. As compared to ethanol derived polymeric silica sol, low permeance values especially for the 10 s dipped 20 vol% loaded membrane were obtained as shown in Figure 6.113. It would be caused by ordering of highly distributed spheres in ethylene glycol derived polymeric silica sol. In addition to this, the formation of covalently bounded non-hydrolysable moieties to inorganic species might enable crack free and stiffer membrane layer that leads to decrease in permeance values. Dipping of 5 s resulted in high permeances through the membranes which would be caused by any defects on membrane surface. It is also shown that the permselectivities of gases for the 10 s dipped membrane is higher than the 5 s dipped membrane suggesting the more selective membrane layer was formed on the support.

![Figure 6.113. Effects of dipping time on N₂, O₂ and CO₂ permeances through sp20-310nm membranes.](image)

Figure 6.114 also shows the permeation behaviour of vol 30% 310 nm loaded silica membranes and increasing sphere loading causes reduce in permselectivities of gases. The decrease in permeance values upon changing dipping time from 5 s to 10 s is small as compared to 20 vol% loaded silica membranes.
Figure 6.114. Effect of dipping time on N$_2$, O$_2$ and CO$_2$ permeances through sp30-310 nm membranes.

Spin coating was applied in order to improve the ordering properties of spheres as thin membrane layer on membrane support other than dip coating. Almost insignificant change in permeance values were obtained through 55 and 74 vol% loaded silica membranes as shown in Figure 6.115 indicating that the range of ordering of spheres has not changed with changing sphere content. Since, the packing behaviour of spheres would alter the permeances through the membranes due to change in pore structure of membranes.

Figure 6.115. N$_2$, O$_2$ and CO$_2$ permeances through sp55 and sp74-310nm membranes (concentration: 2 vol%, spinning rate: 2500 rpm, time: 45 s).
The lowest permeance values through the membranes were acquired for very
diluted sol concentration (0.5 vol%) as shown in Figure 6.116. Spinning rate and time
for the coating process were 1000 rpm and 45 s, respectively. Although spinning rate of
1000 rpm caused the high permeance values for sol concentration of 0.7 vol%, the
concentration decrease down to 0.5 vol% at same spinning rate resulted in a significant
decrease in permeance values. Indeed, the formation of defect-free, homogeneous, thin
membrane layer depends on such coating parameters and those combined effects could
be considered to control membrane uniformity and thickness.

Figure 6.116. Influence of dilution rate on N₂, O₂ and CO₂ permeances through sp20-
310 nm membranes: (a) 1 vol%, (b) 0.7 vol%, (c) 0.5 vol% (Spinning rate:
1000 rpm, time: 45 s).
6.5. Microstructural Characterization of Silica Membranes

SEM micrographs were employed to determine thickness, uniformity, defects and morphology of the membrane layer on α-Al₂O₃ support. Figure 6.117 shows the top and cross-sectional micrographs of 40 vol% loaded spin coated silica membrane derived ethanol based polymeric silica sol. The top silica layer had a finer structure than the gamma alumina layer because of very small species size of polymeric silica sol as shown in Figure 6.117.f. Large crack throughout the membrane surface was observed in Figure 6.117.b in addition to some microcracks created between the spheres as indicated in Figure 6.117.d. Uncovered section particularly on the edge of the membrane surface was clearly visible as shown in Figure 6.117.c. It may induced by small concavity of disk shaped support affecting the spin-off process during the coating. It was also found that the pores of the support was unclogged indicating that no infiltration of sol particles occurred during coating process. As indicated in Figure 6.117.f the thickness of silica layer is around 45 nm which is about ten fold thinner than γ-Al₂O₃ layer.

Two times ethylene glycol diluted (4 vol%) sol having 40 vol% spheres was utilized to form a thin membrane layer on gamma layer. Large agglomerates of spheres had not been broken although 2 hours ultrasound was applied on mixture sol as shown in Figure 6.118.a. These agglomerates have partially well ordered sections as shown in Figure 6.118.e while led to large defects on membrane surface. Thickness of film was estimated as approximately 1.5 μm from the pull-out piece as shown in Figure 6.118.c. Application of concentrated sol resulted in very thick membranes on which surface cracks shown in Figure 6.118.d are detectable in combination with agglomerate induced large defects. It is also shown that the spheres were no longer connected with polymeric species leading to the microstructural inhomogeneities on membrane surface as clearly seen in Figure 6.118.f. Drying conditions might affect the crack formation since drying was applied at 40 °C. However, the vapour pressure of ethylene-glycol is very high and it is most probably this temperature was being insufficient to evaporate the solvent from the membrane structure. Applied heat treatment upon 400 °C with heating rate of 1.5 °C/min has resulted in removal of entrapped solvent very quickly causing some drying stress.
Figure 6.117. SEM micrographs of sp40-310 nm spin coated silica membrane: top surfaces; (a) 1500X, (b) 3500X, (c) 6500X, (d) 12000X, fracture surfaces; support to top layer, (e) 35000X, (f) 50000X.
Figure 6.118. SEM micrographs of sp40-310 nm (EG-diluted) spin coated silica membrane: (a) 1000X, (b) 2500X, (c) 5000X, (d) 12000X (e) 20000X, (f) 50000X.
SEM micrographs of 2 layer 55 vol% loaded spin coated silica membrane are shown in Figure 6.119. The solid content of sol is reduced to 1.5 vol% to decrease the thickness of the membrane. Two fold decreases in thickness was revealed from Figure 6.119.f as compared to membranes derived from 4 vol% in solid content. Well-ordered sphere agglomerates again caused the large cracks on membrane surface shown in Figure 6.119.c. Although the permeance properties through the membrane were affected by large variations in surface properties, the uniformity of membrane without any cracks has been provided by the polymeric structure as a very thin dense layer.

Figure 6.119.SEM micrographs of 2-layer 55 vol% loaded spin coated silica membrane: (a) 1200X, (b)-(c)-(d) 5000X, (e)-(f) 12000X.
Figure 6.120 shows SEM micrographs of 2 layer 74 vol% loaded spin coated silica membrane. In contrast to 55 vol% loaded one, large cracks have not been observed but large agglomerates possibly comes from sphere stocks still exist on membrane surface. Although agglomerate consists of completely ordered domains, membrane surface covered by spheres as a monolayer involved short-range ordered region shown in Figure 6.120.b and c. It can be clearly shown that crack-free silica layer have been obtained by packing of polymeric silica species on whole surface of membrane. However, as shown in Figure 6.120.e edge of the membrane has some disordered sphere regions with polymeric species causing the formation of defects on membrane surface.

SiEg-40 °C was applied instead of standard polymeric silica sol therefore all solvent has been replaced with ethylene glycol in which silica spheres is more stable than ethanol. SEM micrographs of 2 layer vol 55% loaded spin coated silica membrane derived from SiEg-40 °C sol is shown in Figure 6.121. Sol having 4.5 vol% solid content was utilized for the first layer with 3500 rpm spinning rate for 60 s and solid content and spinning rate had been decreased to 1.2 vol% and 1500 rpm, respectively for the second layer. As compared to Figure 6.120, membrane surface was almost completely covered by spheres but some individual spheres exist on top of the membrane layer probably indicating instabilities of sol. Large sphere agglomerates seems to be broken down but large cracks between spheres and polymeric species have not been prevented as shown in Figure 6.121.f. This may caused by the applied low drying temperatures for the removal of ethylene glycol.
Figure 6.120. SEM micrographs of 2-layer sp74-310 nm spin coated membrane: (a)-(b) 3500X, (c) 6500X, (d) 15000X, (e) 35000X (f) 50000X.
Slow drying has been applied for removal of solvent to prevent the formation of these microcracks. SEM micrographs of 1-layer 65 vol% loaded spin coated silica membrane derived from SiEG-40 °C sol is shown in Figure 6.122. The more uniform layer having well-ordered regions with ~500 nm in thickness were obtained on support structure.
Spheres dispersed in ethylene glycol having 5 vol% concentration were utilized for spin coating process to form a membrane layer on 3-layered $\gamma$-Al$_2$O$_3$. The spinning rate and time were 1500 rpm and 45s, respectively. The coating area was approximately 12.5 cm$^2$ which is very large to form a well ordered uniform layer. As shown in Figure 6.123, ordering was short range but highly uniform thickness had been obtained by rapid spin coating process. Colloidal stability in ethylene glycol other than ethanol might be attributed to refractive index matching between silica colloids (1.44) and ethylene glycol (1.43) reducing the attractive van der Waals forces between spheres (Jiang and McFarland, 2004).
Standard polymeric silica sol having 6 vol% concentrations was applied on this sphere layer with 10 s dipping time and 200 mm/min withdrawal rate. Uniform polymeric silica layer could not be obtained as shown in Figure 6.124. Although polymeric layer had partially covered the spheres but voids between these spheres were infiltrated by silica species. Large cracks on membrane surface were introduced because of ordered pull out pieces from the surface that might caused by insufficient evaporation of solvent in the course of drying process.
Decrease in spinning rate would affect the formation of silica layer during the spin-coating process. Since the film thickness can be easily controlled by changing the spinning rate and time for the planar substrates. It is inversely proportional to the final spinning rate and the square root of the time (Jiang and McFarland, 2004). Silica membrane on 3-layer \( \gamma \)-Al\(_2\)O\(_3\) support shown in Figure 6.125 has been prepared by applying spinning rate of 500 rpm for 30 s. Solid content of 1.2 vol\% sol was utilized for membrane formation. Decrease in spinning rate would tend to yield a more thick film according to the model of spin-coating process which predicts the film thickness. Apparently, slow spinning yielded uniform layer with partially ordered regions but the formation of cracks could not been avoided. Furthermore, small aggregate of spheres caused large defects as shown in Figure 6.125.f.

Figure 6.124. SEM micrographs of polymeric silica membrane on spheres dispersed in ethylene glycol: (a) 3500X, (b) 10000X, (c) 15000X.
Slow spinning rate (500 rpm) has been applied for more concentrated sol (2 vol %) to the first and second layer of 74 vol% loaded silica membrane as shown in Figure 6.126 and Figure 6.127, respectively. Lack of uniformity as well as the cracks on surface has been observed. The effect of slow spinning rate on the uniformity of layer is less pronounced for the concentrated sol. This is probably the result of the increase in film thickness by the use of concentrated sol shown in Fig. 6.127.b.
Figure 6.126. SEM micrographs of 1-layer sp74-310 nm spin coated silica membrane on 3 layer $\gamma$-alumina layers: (a) 3500X, (b) 35000X.

Figure 6.127. SEM micrographs of 2-layer sp74-310 nm spin coated silica membrane on 3 layer $\gamma$-alumina layers: (a)-(b) 6500X, (c) 10000X, (d) 25000X.
Polymeric silica sol derived in ethylene glycol having 1 vol.% solid content has been applied by using dip-coating process (withdrawal rate: 200 mm/min and dipping time: 10 s) on sphere layer coated by spinning at 1500 rpm for 45 s. SEM micrographs shown in Figure 6.128 indicate that thin membrane layer has been acquired from the polymeric sol without any cracks and pinholes except the edge of the support. Template effect is indicative of any suction of sol into the sphere layer that provides connection between spheres. However, peeling of layers from support surface may result from regime of heat treatment in which 1.5 °C/min has been utilized to 400 °C. This rate might be decreased to avoid any defects caused by consolidation.

Figure 6.128. SEM micrographs of polymeric silica membrane (SiEg) on spheres dispersed in ethylene glycol: (a) 15000X, (b) 25000X.

SEM micrographs of one layer silica membrane on graded γ-Al₂O₃ layers and ungraded γ-Al₂O₃ are shown in Figure 6.129 and Figure 6.130, respectively. It is shown that although silica sol with less concentrated sphere leads to more uniform membrane layer without any defects on surface, there is not any ordering between spheres on surface. Increasing sphere concentration to 40 vol.% caused 450 nm in thickness membrane layer having more ordered regions on graded support structure as indicated Figure 6.131.
Figure 6.129. SEM micrographs of 1-layer sp20-310 nm spin coated (spinning rate:1000 rpm; spinning time:30s) silica membrane on graded $\gamma$-alumina layers: (a) 5000X, (b) 15000X.

Figure 6.130. SEM micrographs of 1-layer sp20-310 nm spin coated silica membrane on 3 layers $\gamma$-alumina: (a) 2000X, (b) 12000X.
Figure 6.131. SEM micrographs of 1-layer sp40-310 nm spin coated silica membrane on 3-layer γ-alumina layers: (a) 2000X, (b) 5000X, (c) 10000X, (d) 20000X, (e) 35000X, (f) 100000X.

The clear conclusion can be drawn for formation of thin membrane layer on porous support either by dip-coating or spin coating, several parameters like sol concentration, solvent type, drying and coating conditions, should be considered simultaneously in order to defect-free membrane layer with selective transport pathways. These parameters are needed to be optimized for defect free selective thin membrane layer.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

The research described in this thesis deals with the synthesis and structural/transport properties of alumina and silica membranes on top of a macroporous alumina substrate. Most of the currently available inorganic membranes with required separation abilities have limited reliability and thermal stability. Therefore defect-free, thermally stable ceramic membranes with controllable pore network would contribute to improve their performance. A better understanding of the ability of controlling the consolidation step through the addition of monodisperse silica spheres with appropriate surface properties into the polymeric silica sol in order to achieve thermally stable microporous silica membranes is the main purpose of this work. The relationship between synthesis conditions and properties of the resulted oxide structure could be understood through the knowledge of sol-gel chemistry of transition-metal alkoxides.

Monodispersed silica sols having well-defined silica spheres ranging in size from 5 to 700 nm were prepared by using the Stober process. The size of spheres was controlled by changing hydrolysis ratio or catalyst amount. Diffusive type of growth of spheres has been found for 520 nm spheres from the kinetic evolution of particle size. The 310 nm ordered spheres in dried states reflected brilliant colours due to Bragg diffractions of visible light. The different thermal and densification behaviour of particulate and polymeric systems has attributed to the difference in crosslinking behaviour of silica particles/species due to the difference in relative rates of hydrolysis and condensation reactions. The evaluation of densification of spheres indicated an inverse dependence of shrinkage rate on particle size because of viscous sintering. The transformation to cristobalite phase was observed at lower temperatures for consolidated samples as compared to powders treated in a loose ordered arrangement.

The activation energies for viscous sintering according to Frenkel and MS models were calculated as 125 kJ/mol and 335 kJ/mol, respectively. The calculated substantially low activation energy might be related to the significant amount of silanol groups which was also indicated by low viscosity.
The close control of sol-gel parameters provided the synthesis of stable particulate silica sols having controlled size. Variation of synthesis temperature, utilized acid and water content, sol aging led to significant differences in the sols and microstructural properties of the final microporous/mesoporous membranes. The change in porosity with pH of the sol indicated the change in packing behaviour of particles during the consolidation. It can be envisaged that smaller pore size with the increase level of microporosity is the result of the stability of sol. The close control of sol-gel process with a better understanding of the species/particles/microstructure relations would make to design the membrane with predefined membrane pore network possible with required separation abilities. Although a small increase in H-K pore size was observed, the porosity and the surface area of the unsupported membrane increase considerably upon adding 65 vol % 30 nm sphere in polymeric silica sol. The packing of 25 vol% 5 nm spheres resulted in more open structure as compared to pure polymeric network with high surface area suggesting that more stiffen pore network by the incorporation of spheres due to the level of interpenetration of polymeric species. Thus, the use of hybrid process comprising particulate and polymeric systems provided a valuable tool in the assessment of controlling the pore structure for designing microporous silica membranes.

The control of consolidation step has great importance to avoid cracking on membrane surface. The dilatometer measurements were performed for both particulate and polymeric unsupported consolidated form as well as the polymeric/particulate system to 400 °C for 2 hours to understand the structural development during membrane consolidation. Although the packing of 74 vol% of 5nm spheres provided enhanced stability up to 300 °C, at the end of the 2 hours, 25 vol% 5 nm packed structure had the lowest shrinkage value. As a consequence, formed hybrid structure that might be associated with more stiffer pore network results in high thermal stability with low shrinkage values as confirmed by high level of porosity from the N₂ adsorption-desorption analysis.

Membranes prepared from ethylene-glycol derived polymeric sol yielded microporous structures having surface area up to 1085 m²/g though variation in pore size was particularly small. The difference in pore structure can be predominantly attributed to polymerization of partially reacted species during the drying.

Depending on process conditions, aged sols with aluminium polymeric species down to ~2 nm in diameter could be prepared. The use of chelating agent caused the
decrease in hydrolysis rate providing stable polymeric alumina sols. The utilized stoichiometric hydrolysis ratio is shown the yield the smallest particle size. The coordination of Al\(^{3+}\) atom in polymeric structure was determined form \(^{27}\)Al MAS-NMR spectra. The observed dominant chemical shifts at -7.5, -4, -6.2 ppm for the samples indicating the presence of octahedrally coordinated boehmite. The transformation of boehmite to gamma alumina phase has been elucidated by increasing peak intensity at 56 ppm corresponding to tetrahedrally coordinated Al\(^{3+}\) atom for 500 °C treated membranes. The heat treated acetyl-acetone derived alumina membranes had microporosity in 34% range with H-K pore size of 0.83 nm. The sharp decrease in porosity with increasing acetyl-acetone content would be related to un-reacted chelating molecules inhibiting the formation of membrane microstructure. The phase evaluation of the polymeric alumina unsupported membranes showed that the transformation from boehmite to gamma phase commences at 800 °C with well defined (400) and (440) reflections. Heat treatment to this temperature caused almost constant crystallite sizes of 7 nm all samples while small variation in sol particle size was observed from DLS measurement.

The mixture of freshly prepared polymeric silica (Si-std) and polymeric alumina sols (p9) in mullite compositions (3:2) led to the crystallization of mullite upon heat treatment at 775 °C. Such very low transformation temperature is likely related to formed homogeneously mixed stable oxide network having very fine microstructure.

Pure gases including N\(_2\), O\(_2\) and CO\(_2\) permeation characteristics of alumina support, \(\gamma\)-alumina and silica membranes were investigated on a pressure controlled dead-end mode membrane system. The values obtained for the flow average pore size were found as comparable with the value of the pore size determined by Hg intrusion measurements located at 110 nm for the AKP-50 supports. Slight pressure dependency of permeation indicated the both viscous flow and Knudsen diffusion dominate the transport through the support. Pressure independency obtained for two and three layer colloidal alumina membranes implied that the dominant transport mechanism is Knudsen diffusion as could be expected with a pore size in 2.5-3 nm range. The almost complete agreement between experimental values and Knudsen diffusion equation implies that the dominant transport through polymeric alumina membranes with thickness of about 300 nm is Knudsen diffusion.

The \(\text{N}_2\) permeation through 400 °C treated one layer silica membrane varied in the \(1.4\times10^{-7}\) mol/m\(^2\)sPa-\(1.0\times10^{-7}\) mol/m\(^2\)sPa range by changing the sol pH from 9.4 to 3.
The change in permeance values with pressure was more significant for the membrane synthesised from basic sol as compared to that from acidic sol suggesting that the small contribution of laminar flow. The dramatic difference in the permeance of N₂ upon the heat treatment of membranes is most likely due to the partial sintering and micro-crack formation during the consolidation of 5 nm in size particles. Heat treatment upon 150 to 400 °C range resulted in constant permeances through particulate silica membranes suggesting that the stability of pore network of the membranes in this temperature range.

The size and the concentration of spheres in polymeric sol were varied and the heat treatment was applied in the 40-400 °C range to investigate the thermal stability of the membranes by determining the single gas permeation behaviour. The increase in pore size from 0.6 nm to 0.8 nm has been revealed with the addition of 310 nm silica spheres into the sol from N₂ adsorption-desorption analysis results. The N₂ permeation through 90 nm in size silica sphere added silica membranes, in contrast to membrane having 310 nm in size spheres, remained constant when applied heat treatment temperature was in 250-400 °C range. This may caused by the stiffening of pore network that preventing the collapse of the membrane structure. Although the nitrogen permeance value through the ethylene glycol diluted 10 vol% loaded membrane remained more or less constant up to 250 °C, the significant decrease in permeance values upon heat treatment to 400 °C could not been prevented by the addition of 220 nm spheres into polymeric silica network. The thermal stability of pore network up to 250 °C might be provided by the organically bounded inorganic species that suppress the stress induced cracking on membrane surface by increasing toughness of film.

The nitrogen permeance values increased from $2.8 \times 10^{-8}$ mol m²sPa to $6.3 \times 10^{-8}$ mol/m²sPa through 140 nm loaded membranes by changing heat treatment temperature in 250-400 °C range while for the unloaded silica membranes this change was more prominent ($6.2 \times 10^{-8}$ to $1.6 \times 10^{-7}$ mol/m²sPa). The coating of second layer caused the decrease in N₂ permeance values from $8.3 \times 10^{-8}$ mol/m²sPa to $9.7 \times 10^{-9}$ mol/m²sPa and from $8.1 \times 10^{-8}$ mol/m²sPa to $3.6 \times 10^{-8}$ mol/m²sPa through the 400 °C treated 5 vol% and 10 vol% sphere 220 nm loaded membranes respectively. Difference in permeability might be related to the thickness of the membrane layer. In contrast to 5 vol% and 10 vol% loaded membranes, the N₂ permeance across the membrane prepared with ethylene glycol diluted sol increased up to 350 °C and remained constant to 400 °C.
Increasing permeance values with increasing temperature indicated the activated transport through the membrane.

Establishing a direct relation between structural and transport properties of membranes is important in determining the transport mechanisms through controlled pore network. Therefore, it would be needed to elucidate the understanding of the relation between the membrane microstructure and transport properties for meso and microporous layer.

The preparation of thin microporous alumina membranes layer requires optimization of process parameters allowing close control of sol structures. The influence of such parameters on size and structure of polymeric species in alumina polymeric sols needs to be studied in more detailed. The permeation properties and structural evaluation of the membranes would be clarified extensively.
REFERENCES


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